



**United Nations
Environment
Programme**



Distr.
GENERAL

UNEP/POPS/INC.7/INF/17
5 May 2003

ENGLISH ONLY

INTERGOVERNMENTAL NEGOTIATING COMMITTEE FOR AN
INTERNATIONAL LEGALLY BINDING INSTRUMENT
FOR IMPLEMENTING INTERNATIONAL ACTION ON
CERTAIN PERSISTENT ORGANIC POLLUTANTS

Seventh session

Geneva, 14-18 July 2003

Item 5 of the provisional agenda*

Preparations for the Conference of the Parties

COMPILATION OF VIEWS ON MEASURES TO REDUCE OR ELIMINATE RELEASES FROM
UNINTENTIONAL PRODUCTION (ARTICLE 5 AND ANNEX C) AND EVALUATION OF
CURRENT AND PROJECTED RELEASES OF CHEMICALS LISTED IN ANNEX C **

Note by the secretariat

1. As referred to in UNEP/POPS/INC.7/7, decision INC-6/4 of the Intergovernmental Negotiating Committee invited Governments and others to provide the secretariat with comments on how the “Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases” (Toolkit) can be updated and expanded before 31 December 2002.
2. In response to decision INC-6/4, as of 31 March 2003, the secretariat had received comments from: the Governments of Brunei Darussalam, Canada, Chile, Colombia, Greece (on behalf of the European Union and its member States) Mexico, Norway, Switzerland and United States of America; representatives of Governments that participated in subregional workshops in Latin America from Argentina, Brazil, Chile, Cuba, Ecuador and Paraguay, and in Asia, from Brunei Darussalam, Jordan, Lebanon, Philippines, and Viet Nam; the secretariat of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal; and Greenpeace and the World Chlorine Council. These comments have been compiled in the annex to the present note. They are issued as received by the secretariat and have not been formally edited.

* UNEP/POPS/INC.7/1.

** Stockholm Convention on Persistent Organic Pollutants, article 20; Conference of Plenipotentiaries on the Stockholm Convention, resolution 6 (in document UNEP/POPS/CONF/4, appendix I); report of the Intergovernmental Negotiating Committee at its sixth session (UNEP/POPS/INC.6/22), annex I, decision INC-6/4.

K0361470 210503

Annex

Views on how to Update and Expand the “Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases (Toolkit)” as a measure to reduce or eliminate releases from unintentional production (Article 5 and Annex C)

I. BRUNEI DARUSSALAM

24 December 2002

Mr. James B. Willis
Director
United Nations Environment Programme, Chemicals
11-13, Chemin des Anemones
CH-1219 Chatelaine, Genève
Switzerland

Fax No.: +41-22-797-3460

Subject: Request for Comments on the Standardized Toolkit for the identification and quantification of dioxin and furan releases

Dear Sir,

With reference to the above mentioned matter, we are pleased to enclose herewith our comments on the Standardized Toolkit as per requested.

Most of the comments are related to the limitations as stated on page 6 of the toolkit, i.e. little is known about process and emissions factors for processes and technologies used in less developed countries and region-specific feedstock or input materials. Therefore it will be helpful, if the following information is available

1. Estimation of the material burned in biomass burning – For the purpose of the project, estimation of the material burned in biomass burning are based on the New Zealand data which can be quite different from those found in Brunei, i.e. the amount of material found in the New Zealand forest/grassland might be very different from those in Brunei. Therefore, emission factors for the tropical type forest, if make available, should provide a better estimation for Brunei Darussalam’s emission.
2. Describe ways of how leachate or seepage from landfill and dumps can be estimated since many types of residues are dumped on the landfill which as a result has become one of the important hot spots. In addition due to the different mixtures of wastes dumped on the landfill perhaps it is necessary that samples from the leachate are collected and sent for analysis.
3. Emissions from accidental house fire cannot be estimated because of the vast variations of house material which is difficult to estimate. Perhaps the Toolkit could provide the information required for estimation.
4. Site of PCB-filled transformers and capacitors as a hot spot – it would e helpful if information such as the make, producer and date of manufacture of the transformers are made available so that comparison can be made with those available in Brunei.

Thank you for your attention and consideration.

Yours sincerely,

Roslan Haji Taja’ah
For Acting Director
Department of Environment, Parks and Recreation
Ministry of Development
Bandar Seri Begawan BB 3510
Brunei Darussalam

II. CANADA

Jan. 27, 2003

James B. Willis
Executive Secretary
Interim Secretariat for the Stockholm Convention on POPs
UNEP Chemicals
11-13 chemin des Anémones
CH-1219, Chatelaine
Geneva, Switzerland

Re: Request for Comments on the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases

Dear Mr. Willis:

Thank you for the opportunity to review and provide Canada's comments on the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, as requested in your letter of September 24, 2002. As the Focal Point for Canada to the Stockholm Convention, I am pleased to forward our response, which is attached to this letter.

Overall, Canada supports UNEP's work on the Standardized toolkit to assist countries in preparing inventories and to provide consistent estimation methods. Since Canada has developed a detailed inventory of dioxin/furan air releases, we do not foresee a need to apply the UNEP Standardized Toolkit to our country's work in this area. However, Canada views the methodologies as an important means to build capacity of certain countries to develop inventories for POPs. It is also important that guidance and requirements given in the toolkit are consistent with the requirements within the Convention.

In developing inventory methodologies, Canada supports focusing on the source categories identified in Part II and Part III of Annex C of the Convention, as they are identified as sources with the highest potential for emission.

I apologize that we were unable to provide this material by the requested Dec. 31, 2002 deadline. However, I hope and trust that our response will be useful, and look forward to further development of this important issue.

Sincerely,

**Original signed by
Greg Filyk**

Greg Filyk
Stockholm Convention on POPs
Focal Point for Canada

cc. Alain Tellier - Permanent Mission of Canada to the Office of the United Nations
Attach.

CANADA'S COMMENTS ON THE STANDARDIZED TOOLKIT FOR IDENTIFICATION AND QUANTIFICATION OF DIOXIN AND FURAN RELEASES UNDER THE STOCKHOLM CONVENTION ON POPS

Page 2, Paragraph 3, last sentence.

The statement that detailed facility process information is easily available may be misleading and could imply that the emission factors contained in the toolkit are for specific processes whereas most are applicable to sectors.

Page 12 Section 3.2.6, Hot Spots.

Recognizing that contaminated sites are not identified as a source category within Annex C to the Convention, further clarification is required on the reporting of hot spots, the inventory of contaminated sites, and reporting of releases from these sites. Canada would prefer that the toolkit indicate that releases from contaminated sites are to be reported within a country's national inventory. Canada intends to outline within our national implementation plan the groundwork for complying with Article 6.1 - the requirement for Parties to endeavour to develop appropriate strategies for identifying contaminate sites contaminated by chemicals listed in Annex A, B or C.

Page 26, Section 4.4.2 First Paragraph

The Toolkit is based on I-TEQ, not WHO TEQ and uses order of magnitude release factors. The toolkit states that since the emission factors contained in the toolkit represent order of magnitude release factors the difference between I & WHO TEQ is insignificant. This could imply over estimation. For example, some of the emission factors in the spreadsheet are 10 - 100 times the currently accepted Emissions Factors used in Canada (e.g. Residential Wood: toolkit factor – 100 ug/tonne, Environment Canada factor 0.5 ng/tonne).

WHO TEQ

Canada is concerned with the approach in the toolkit as countries will not actually be estimating their releases of the PCB congeners as included in the WHO-TEQ methods and as requested within the Convention.

Annex 9, Page 176, lists the Dioxin and Furan equivalency factors but there is no listing for the non-ortho- and mono-ortho PCBs which are included in the WHO TEQ. This creates difficulties for reporters with testing data to report. There is also no indication if there is a weighting scheme (similar to Dioxin and Furans) applied to these PCB isomers.

There appears to be no mention of other sources of information on estimation of releases (e.g. UN ECE LRTAP Protocol on POPs, US EPA, Australian NPI) who may have significant information on the estimation techniques and emission factors that reporters could use to estimate and refine their inventory.

Methodology

The methodologies given to estimate emissions are good for countries just developing inventories and begins to lead into how to enhance and refine the inventories. The techniques and stages to the inventories and examples are good for reporters to follow and will allow for checking and modification at later dates.

The descriptions of the sectors and the vectors into the environment are good and informative. The path ways into the environment seem to be described more than adequately considering that the emission factors are expressed in order of magnitude and for sectors as a whole.

III. CHILE

D. e I. N° 030028
03 ENE 2003/

SANTIAGO,

Señor
James B. Willis
Secretario Ejecutivo
Secretaría Provisional Convenio de Estocolmo
UNEP Chemicals

REF.: Observaciones al Instrumental Normalizado para la Identificación y Cuantificación de Liberaciones de Dioxinas y Furanos.

Estimado Sr. Willis,

Me dirijo a Usted en respuesta a su carta de invitación a los Gobiernos a presentar observaciones sobre el modo de actualizar y ampliar el Instrumental Normalizado para la Identificación y Cuantificación de Liberaciones de Dioxinas y Furanos (Toolkit) del PNUMA, en virtud de la decisión INC-6/4 sobre "Evaluación de las liberaciones actuales y proyectadas de productos químicos inscritos en el anexo C" (UNEP/POPS/INC.6/22).

La presente contiene el documento "Comentarios de Chile al Instrumental Normalizado para la Identificación y Cuantificación de Liberaciones de Dioxinas y Furanos", que incluye las observaciones enviadas por la Comisión Chilena del Cobre (COCHILCO), Asociación Gremial de Industriales Químicos (ASIQUM), Sociedad de Fomento Fabril (SOFOFA), Corporación Chilena de la Madera (CORMA) y Cemento Polpaico, todos miembros del Grupo de Trabajo Multisectorial Convenio de Estocolmo, coordinado por CONAMA.

Sin otro particular, saluda cordialmente a Usted,

PABLO DAUD MIRANDA
Director Ejecutivo (S)
Comisión Nacional del Medio Ambiente, CONAMA

JRS/MGB/CPC/pd

CC/
Dirección de Medio Ambiente, Ministerio de Relaciones Exteriores; Santiago, Chile

COMENTARIOS DE CHILE AL

“INSTRUMENTAL NORMALIZADO PARA IDENTIFICACION Y CUANTIFICACION DE LIBERACIONES DE DIOXINAS Y FURANOS”

1. Toolkit en general

Se rescata la importancia otorgada a las mediciones reales por sobre las estimaciones en base a factores de emisión. Por lo tanto, la aplicación en Chile de esta herramienta debiera privilegiar la información de emisiones que tenemos, en la medida que las campañas de medición hayan sido desarrolladas respetando las metodología y protocolos internacionalmente conocidos.

2. En el **Punto 4.2.2**: Subcategorías de la Producción de Metales Ferrosos y no Ferrosos, 2° párrafo (pág. 23) se dice *“En el caso de la recuperación del cobre es muy conocida la contaminación del suelo y del agua por PCDD/PCDF resultante de la incineración de cables”*.

El párrafo claramente se refiere a operaciones de reciclaje o fundición secundaria, pero sería preferible que esto quedara explícito en el texto. Además, siempre que en el texto se haga referencia a cables debe explicitarse que son aquellos revestidos o recubiertos con PVC, pues la generación de emisiones de dioxinas y furanos se produce por la presencia del plástico y no del cobre.

3. En el **Cuadro 3**: Subcategoría de la Matriz del inventario – Sector 2 (pág. 23) dice *“d Producción de cobre”*.

En este punto es necesario reiterar lo expuesto en la carta que se envió el 16 de julio pasado al Sr. James B. Willis, Director de PNUMA Productos Químicos, en el sentido que no se puede hacer una referencia de carácter general a la producción de cobre, sin distingos, ya que, la producción de cobre primario se realiza por dos métodos diferentes según se trate de minerales oxidados o sulfurados.

Los minerales oxidados se tratan por la vía hidrometalúrgica, a través de los procesos de lixiviación, extracción por solventes y electrodeposición, no alcanzándose nunca temperaturas superiores a los 50°C, lo que hace imposible la generación de dioxinas y furanos en el proceso.

Los minerales sulfurados se someten primero a una etapa de concentración a temperatura ambiente, y luego se refinan pirometalúrgicamente en las fundiciones primarias de concentrados de cobre. En las fundiciones primarias de cobre el material a fundir está compuesto básicamente por sulfuros metálicos de cobre y hierro, donde la presencia de cloro, elemento esencial para la formación de dioxinas y furanos, no es relevante. La fusión se realiza en un ambiente oxidante y a temperaturas entre 1.200 °C y 1.300 °C, por lo que cualquier dioxina que se pudiera haber formado por eventual contenido de cloro en el combustible o trazas de cloro contenido en la carga de alimentación debería descomponerse a dichas temperaturas.

Por lo anteriormente expuesto y ante la falta de evidencia científica, en el Convenio de Estocolmo se resolvió retirar a las fundiciones primarias de concentrados de cobre como fuentes prioritarias de emisiones de dioxinas y furanos.

4. En el **Punto 4.3 Etapa 3**: Acopio de Información, primer párrafo (pág. 29) dice: *“Para la evaluación es importante conocer la magnitud y escala (por ejemplo, toneladas de desechos quemados, toneladas de cobre producidas)”*

No parece conveniente que se utilice como ejemplo el cobre producido, sin distinguir su origen primario o secundario. Se sugiere utilizar otro ejemplo.

- 5. Punto 5.1:** Establecimiento de un inventario provisional (pág. 36), en el 3er. Párrafo nuevamente se habla de “*producción de cobre*” en forma genérica, al igual que en el recuadro de la misma página, no obstante que en la descripción del proceso se habla de chatarra y por lo tanto se están refiriendo a cobre secundario.

Se sugiere que todas las referencias se hagan a producción de cobre secundario, como está correctamente indicado en la fila 2d del cuadro que aparece al final de la página 36.

- 6. Punto 6.2.4:** Producción de cobre (pág. 68)

Debiera insistirse en un cambio del título de este punto, el que podría ser “producción secundaria de cobre”. Lo anterior se confirma con lo expresado en el segunda párrafo de esta página que dice “*En cuanto a las emisiones de PCDD/PCDF interesa sobre todo el procesado térmico de cobre secundario, es decir de los materiales de chatarra que contienen cobre*”.

- 7. Cuadro 23:** Factores de emisión para la industria del cobre

Se reitera el que es un error el hacer referencia a la industria del cobre. El título del cuadro debiera ser “Factores de emisión para la producción de cobre secundario”.

Teniendo en consideración el acuerdo alcanzado en el Convenio de Estocolmo, en el sentido de eliminar las fundiciones primarias de concentrados de cobre como fuentes prioritarias de emisión de dioxinas y furanos, se debiera eliminar la última fila del cuadro 23 que dice “*Cu primario – todos los tipos.....0,01*”. Tampoco se indica cual es la fuente de la que se obtuvieron los valores allí señalados.

En el 2º párrafo del punto 6.2.4.1, donde las unidades del factor de emisión están expresadas por tonelada de chatarra, todos los factores que dicen relación con procesamiento de cobre secundario debieran expresarse en estas mismas unidades.

- 8. Punto 8.1:** Compilación de todos los factores de emisión por defecto (página 173) Sector 2, Subcategoría d

Los mismos comentarios que en los puntos 5 y 6 anteriores.

- 9. Punto 6.7.1:** Fábricas de pasta y papel (página 116) Sector 2, Subcategoría d

Particular mención debe hacerse a la industria chilena de la Celulosa, la mayor parte de cuyas instalaciones datan de poco más de 10 años e incluso hay importante proyectos en actual construcción en el país así como otros cuya materialización en los próximos años ha sido anunciada por las empresas. Las plantas algo más antiguas han sido modernizadas permanentemente ajustándose sus procesos a los conceptos tecnológicos en uso.

Toda la tecnología del proceso de producción de celulosa que data de la década de los 90’ en adelante, desarrollada por los proveedores de equipamiento y sustentada en investigaciones llevadas a cabo en países con una reconocida tradición forestal como Suecia, Finlandia y otros, ha tenido en consideración la problemática de la generación involuntaria de dioxinas y furanos en los procesos de blanqueo. Esto ha generado modificaciones tecnológicas muy importantes que tienen como consecuencia reducciones tan significativas en la generación de este tipo de compuestos que sus concentraciones llegan a ser No Detectables por la instrumentación analítica disponible en dichos países. Para precisar este punto, se trata de concentraciones inferiores a órdenes de magnitud de *0,000000000000001 gramos, ó “partes por cuatrillón, ppq”*.

Adicionalmente, por tratarse de equipamiento en uso en otros sectores de la industria forestal – como también en otros sectores de la industria nacional – es del caso referirnos a las Calderas de Biomasa, a

cuyas cenizas el Toolkit asocia altas concentraciones de estos compuestos. Muchas de las unidades operadas en la industria forestal son de la tecnología conocida como de “lecho fluidizado”, de muy diferente comportamiento a las tradicionales “de parrilla”.

En referencia al Toolkit debe mencionarse que esta es una herramienta desarrollada sobre la base de datos de operación de plantas y procesos existentes a lo largo del mundo, es decir, ha tenido en cuenta tecnología de mediados del siglo pasado - en funcionamiento en países desarrollados de tradición forestal ó con una industria importante del rubro. De este modo se obtienen Factores de Emisión que, siendo representativos de una condición general, no discrimina por tipo de tecnología.

Planteadas las antedichas consideraciones, nuestra opinión es que la presunta emisión de dioxinas y furanos desde las fuentes potenciales identificadas en el Toolkit, existentes en la industria forestal chilena, no pueden ser cuantificadas usando los Factores de Emisión propuestos en dicho documento porque sus resultados no serían representativos de la realidad nacional. Esto derivaría en una importante distorsión que generaría errores de relevancia, tanto en las decisiones que eventualmente puedan sustentar como asimismo en la percepción de la ciudadanía. Todo lo anterior tiene el potencial de introducir un factor desfavorable al desarrollo de nuevas inversiones, incongruente con la realidad nacional.

DeI N° 030458 /SANTIAGO, **11 FEB 2003**

Mr.
James B. Willis
Director
UNEP Chemicals

REF.: Technical document on Dioxin
and Furan releases in Chilean primary
copper smelters.

Dear Mr. Willis,

We are complementing our communication of July 16, 2002 (DeI N° 022882), where Chile formally requested UNEP Chemicals to review the "Draft Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases, UNEP, January 2001", particularly the references to "Copper production" as main source category of Dioxin and Furan releases.

During INC 5 of the Stockholm Convention in Johannesburg, December 2000, UNEP Chemicals submitted a proposal to introduce primary and secondary copper smelters as a source category in the Annex C of the Convention. The Chilean Delegation had a long discussion with representatives from UNEP Chemicals and the European Union. Having in mind the lack of scientific evidence, the Stockholm Convention finally decided to include in the list of main source categories only secondary copper production, considering that some of the materials fed to the processes in secondary copper smelters may be possible to produce Dioxin and Furans releases.

It is important to clarify that primary copper may be produced by two different technologies, depending on the type of minerals to be treated, oxides or sulfides.

Hydrometallurgical methods are applied to treat oxidized minerals, i.e. leaching, solvent extraction and electrowinning. The temperatures of all the processes are below 50°C, making impossible the generation of Dioxin and Furans releases.

Sulfurized minerals are treated, firstly, in a concentration plant (room temperature) and then the concentrates are pyrometallurgically refined in the primary copper smelters. The concentrates to be smelted contain basically copper and iron sulfides. Chlorine, an essential element for the generation of Dioxins and Furans, normally is not present or is not relevant in the system (part per million). The smelting process is performed in an oxidizing atmosphere and the temperatures are between 1200 – 1300°C. Any Dioxins that may be formed due to the presence of chlorine in the concentrates or in the fuels will decompose at these temperatures.

Hereby, Chile is submitting for your information a Technical Paper "The Stockholm Convention, Dioxin and Furan Releases, An Analysis of the Processes in Primary Copper Concentrate Smelters in Chile", prepared by the Chilean Copper Commission based on information provided by the Chilean copper smelters. The objective of the paper is to contribute with information about the current technical status of the Chilean primary copper smelter industry, to endorse the Chilean request to eliminate in the Toolkit any reference to the copper industry or to the primary copper smelters as main sources of Dioxin and Furan releases.

Being Chile the main copper producer worldwide, we have confidence that this document will allow UNEP Chemicals to assess this issue based on technical information and therefore identify the differences between the operation of a primary and a secondary copper smelter.

Taking into account all technical arguments and considerations stated above and in the technical paper, the National Environmental Commission (Comision Nacional del Medio Ambiente, CONAMA), as Chilean Focal Point for the Stockholm Convention, on behalf of the Chilean Government kindly request UNEP Chemicals do not consider the primary copper smelters, as Dioxin and Furan emission sources and therefore any reference thereto should be eliminated unless in the future scientific evidence prove the contrary.

PABLO DAUD MIRANDA
Executive Director (S)
Comision Nacional del Medio Ambiente, CONAMA
(National Environmental Commission)

JM/RPC/CPC/ja

CC./

Ambassador Jose Manuel Ovalle Bravo, Director Medio Ambiente, Ministerio Relaciones Exteriores (Ministry of Foreign Affairs).

Mr. Patricio Cartagena Diaz, Vicepresidente Ejecutivo, Comision Chilena del Cobre, COCHILCO (Chilean Copper Commission)

**THE STOCKHOLM CONVENTION,
DIOXIN AND FURAN RELEASES,
AN ANALYSIS OF THE PROCESSES IN PRIMARY COPPER
CONCENTRATE SMELTERS IN CHILE**

**Technical Paper Prepared by the Chilean Copper Commission
based on Information Provided by Chilean Smelters**

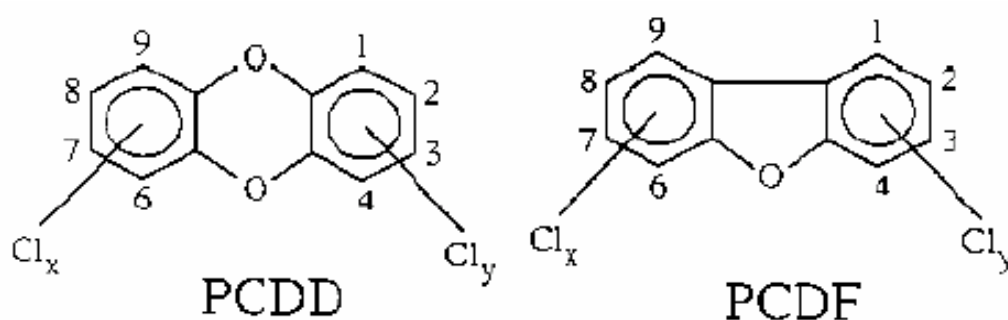
December, 2002

I. INTRODUCTION

A Structure, Composition and Characteristics of Dioxins and Furans

The term “dioxin” is frequently used to generically refer to a family of organochlorinated compounds chemically known as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

These consist of two sets of polychlorinated aromatic ethers, with similar structure and properties, grouping 210 different compounds. The basic structure of these substances is formed by two aromatic (benzene) rings bonded together by two oxygen atoms in the case of PCDDs and by a single oxygen atom and a carbon-carbon bond in the case of PCDFs. In both types of substances, benzene rings may feature varying degrees of chlorination, so that the number of chlorine atoms bonded to each PCDD or PCDF molecule may range from 1 to 8.



In addition, the various relative positions of the chlorine atoms bonded to benzene rings, even if equal in number, lead to (isomeric) compounds with different physical as well as chemical or toxicological properties.

It is worth noting that the highly toxic properties of these substances –particularly of some of them– are among their main characteristics. Furthermore, they are very difficult to biodegrade and metabolize and exhibit low chemical reactivity. They are thermally very stable and only decompose at rather high temperatures (above 750 °C in the case of 2378 – TCDD).

This high thermal stability, which is abnormally high for organic compounds, is the reason why they are difficult to destroy in combustion processes; in addition, their formation is thermodynamically enhanced in thermal processes where chlorinated compounds are present.

Their persistence in the environment extends for long periods of time, which turns them specially hazardous; however, they have shown to be relatively sensitive to ultraviolet light and sunlight and may, under proper conditions, undergo photochemical degradation reactions.

B. Origin and Sources of Dioxin Production

Unlike numerous organochlorinated compounds of industrial-use, such as pesticides, polychlorinated biphenyl (PCB) and others, dioxins are compounds that have never been produced or marketed on an industrial scale, since no practical applications thereof are known. Until now, they have only been synthesized in the laboratory, in small quantities, for analytic purposes and toxicological studies.

Dioxins are mainly unintentionally formed by-products –in trace quantities– in combustion processes and in a large variety of industrial processes, although there is also evidence of small quantities of dioxin forming in natural processes, such as volcanic eruptions or forest fires.

Annex C of the Stockholm Convention on Persistent Organic Pollutants (POPs) sets forth the following categories of sources likely to generate PCDD and PCDF releases:

Part II: Source Categories

Polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene and polychlorinated biphenyls are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions. The following industrial source categories have the potential for comparatively high formation and release of these chemicals to the environment:

- a) Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge;
- b) Cement kilns firing hazardous waste;
- c) Pulp production using elemental chlorine or chemicals generating elemental chlorine for bleaching;
- d) The following thermal processes in the metallurgical industry:
 - i) Secondary copper production;
 - ii. Sinter plants in the iron and steel industry;
 - iii. Secondary aluminum production;
 - iv. Secondary zinc production;

Part III: Source Categories

Polychlorinated dibenzo-p-dioxins and dibenzofurans, hexachlorobenzene and polychlorinated biphenyls may also be unintentionally formed and released from the following source categories, including:

- a) Open burning of waste, including burning of landfill sites;
- b) Thermal processes in the metallurgical industry not mentioned in Part II;
- c) Residential combustion sources;
- d) Fossil fuel-fired utility and industrial boilers;
- e) Firing installations for wood or other biomass fuels;
- (f) Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil;
- g) Crematoria;
- h) Motor vehicles, particularly those burning leaded gasoline;
- i) Destruction of animal carcasses;
- j) Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction);
- k) Shredder plants for the treatment of end of life vehicles;
- l) Smouldering of copper cables;
- m) Waste from oil refineries.

C. Elimination of Dioxin from Gaseous Releases

One of the main sources of PCDD and PCDF pollution are the incineration and combustion processes that release these pollutants into the environment through their gaseous releases. There are three mechanisms through which these processes may lead to dioxin formation:

- Dioxins may be present in the process feed material and are not completely destroyed during incineration or combustion at the high temperatures at which such processes take place.
- Dioxins may form by thermal decomposition and molecular rearrangement of precursor compounds. Precursor compounds are polychlorinated aromatic hydrocarbons having a structural resemblance to the PCDD/PCDF molecule. Among the identified precursors are polychlorinated biphenyls (PCBs), chlorinated phenols (CPs), and chlorinated benzenes

(CBs). The formation of PCDDs/PCDFs is believed to occur after the condensation and absorption of the precursor at the bonding sites on the surface of fly ash particles. The active sites on the surface of fly ash particles promote the chemical reactions forming PCDDs/PCDFs. It has been observed that these reactions are catalyzed by the presence of inorganic chlorides contained in the particulate. Temperatures in the range of 250-450 °C are a precondition for this reaction to occur, and both lower or higher temperatures inhibit the process. Therefore, the precursor theory focuses on the region of the combustor that is downstream and away from the high temperature zone of the furnace or combustion chamber. This is a location where gases and smoke from the combustion of organic materials have cooled during their conduction through boiler ducts, heat exchangers, air pollution control equipment or the stack.

- Dioxins are synthesized *de novo* in the so-called cool zone of the combustion process, during the processes of condensation or cooling of the resulting gaseous releases. In this case, PCDDs/PCDFs are formed from parts that bear a slight resemblance to the PCDD and PCDF molecular structure. In general, these are non-precursors and include such diverse substances as petroleum products, chlorinated plastics (PVC), non-chlorinated plastics (polystyrene), cellulose, lignin, coke, coal, particulate carbon, and hydrochloric acid gas. Formation of PCDDs/PCDFs requires the presence of a chlorine donor (a molecule that brings a chlorine atom to the pre-dioxin molecule) and the formation and chlorination of a chemical intermediary that is a precursor.

The primary distinction between these last two mechanisms is that the former requires the presence of precursor compounds in the feed material, whereas the latter begins with the combustion of diverse substances that are not defined as precursors, which eventually react to form precursors and subsequently dioxin molecules.

The formation of dioxins and furans relies more on the operating conditions under which the process takes place than on the characteristics or composition of the materials involved. These compounds are, to a large extent, formed by the incomplete combustion of residues in incineration sources, in the presence of organochlorinated compounds or organic material and chlorine donors (inorganic salts). Dioxins are formed in those regions of the incineration facility where the temperature is not excessively high, ranging between 250 - 450 °C, and with short residence times.

Given that temperature is a determining factor in dioxin and furan production, proper control of combustion conditions leads to minimizing these substance-generation risk.

A first step in preventing the generation of dioxin releases consists of strictly controlling the quality of the raw materials fed into the process. As to the conditions of the process, the so-called "primary measures" at the emission source apply, which in the case of thermal processes involving combustion are the following:

- a. Combustion temperatures over 850 °C;
- b. At least 2 seconds of residence time at that temperature;
- c. Maintaining a turbulence regime during combustion;
- d. Quick cooling of gases.

As these measures may not be sufficient to reach the emission levels required by the standards, "secondary measures" must be taken based on the treatment and purification of the gases released by the source.

These secondary measures are processes that are typically applied to eliminate:

- Suspended dust and particles
- Acid gases (HCl; HF; SO_x; NO_x; etc.)
- Heavy metals (Pb; Cd; Hg; etc.)
- Organic compounds.

II. ANALYSIS OF THE LIKELY FORMATION OF DIOXINS AND FURANS IN PRIMARY METALLURGICAL PROCESSES

Primary metallurgical processes are understood to be those aimed at obtaining metals such as copper, iron, aluminum, etc., from their original ores, whether sulfidized or oxidized, through such processes as concentration, smelting, reduction, refining, etc.

Specifically in the primary metallurgical process for obtaining copper, the basic raw material used is a "copper concentrate" together with siliceous material to form slag (fluxes).

A Copper Concentrate Smelters in Chile

There are currently seven primary copper concentrate smelters in Chile, which feature the following concentrate processing technologies:

- Flash furnace, Teniente converters and Noranda furnace for the smelting stage;
- Peirce-Smith converters for the conversion stage; and
- Slag treatment furnaces.

The country's overall copper concentrate smelting capacity is approximately 5 million tons per year.

Smelter	Capacity (Tons concentrates / year)	Technology
Chuquicamata Codelco Chile	1,620,000	1 Outokumpu Flash Furnace – 2 CT – 4 CPS – 2 HLE – 4 HR - Acid Plants – Oxygen Plants – 2 Rotary Concentrate Dryers
Potrerrillos Codelco Chile	680,000	1 CT – 3 CPS – 2 HLE – 2 HA – Acid Plant – Oxygen Plant – Fluidized bed dryer
El Teniente Codelco Chile	1,250,000	2 CT – 4 CPS – 4 HLE – 2 HA – 3 HRAF – Acid Plants – Oxygen Plants – 2 Fluidized Bed Dryers
Ventanas (Empresa Nacional de Minería)	400,000	1 CT – 3 CPS -1 HELE – 2 HR – Acid Plant – Oxygen Plant – 1 Rotary Concentrate Dryer
Paipote (Empresa Nacional de Minería)	300,000	1 CT - 2 CPS -1 HELE – 1 HR – Acid Plants – Oxygen Plant – Rotary Concentrate Dryer
Altonorte (Noranda)	400,000 (current) 820,000 (2003)	1 Noranda-type Continuous Reactor – 3 CPS – HR – Acid Plants – Oxygen Plant – Rotary Concentrate Dryer – Slag Flotation Plant
Chagres (Compañía Minera Disputada de Las Condes)	480,000	1 Outokumpu Flash Furnace – 3 CPS – 2 HLE – 2 HA – Acid Plant – Oxygen Plant – 2 Concentrate Dryers that use recovered steam.

NOTE: CT = Teniente-type converter; CPS = Peirce-Smith converter; HLE = Slag-cleaning pyrometallurgical furnace; HELE = Slag-cleaning electric furnace; HR = Refining furnace; HA = Anode furnace; HRAF = (Fire) Refining furnace

B. Basic Process in the Chilean Copper Concentrate Smelters

1. Drying

At the smelter, copper concentrates from the concentrator plant are submitted to a drying process in order to reduce the humidity content from about 8% to 0.2%. Drying takes place in either fluidized-bed, rotary dryers or steam dryers.

2. Smelting

Concentrate smelting takes place in (Flash, Teniente Converter, Noranda) smelting furnaces.

The Outokumpu-type flash smelting furnace uses oxygen-enriched air (65% – 85%) as oxidizing gas. Concentrator burners are placed on the top of the combustion tower, at one end of the furnace, and the concentrates, flux, and gases are driven down the reaction tower on the slag surface. Process gases are extracted at the opposite end of the furnace. The purpose of the top-down configuration of the burner is to cause concentrate particles to impact on the slag surface, which increases the tendency of concentrate particles to adhere to the slag surface and minimizes dust losses through the process gases. Matte temperature is approximately 1260°C and outlet gases reach temperatures of 1300 – 1350°C.

In Teniente- and Noranda-type furnaces, the process takes place through the injection of dry concentrate, fluxes and oxygen-enriched air (30%-36%) into the molten reactor bath. The process uses the heat generated by the reaction of the oxygen present in the blown-in air with the sulfur and iron of the concentrates (exothermic reactions). Such reactions occur spontaneously due to their thermodynamic nature (highly negative free energies), which makes the process an autogenous one, that is, the self-generated energy is used to smelt the solid load, reaching temperatures that range from 1200 °C to 1300°C in the reactor.

Apart from the concentrate and fluxes, other recirculation materials are occasionally loaded onto the converters, such as:

- Cold load, i.e., a mixture of materials from the cooling of the liquid material circulating in the smelting process;
- Gravel, recirculating material from the smelting works dust treatment plant, which is mixed with the concentrate;
- Internal recirculating liquids, metal from the slag-cleaning furnaces, slag from conversion and from the refining stages.
- Rejected copper.

In the smelting process, the sulfur present in the concentrate is partially oxidized forming sulfur dioxide (SO₂), while the sulfidized iron present in the mix is oxidized forming iron oxides II and III which, together with the concentrate gangue and the silica flux fed to the process form the slag.

From this stage of the process, the following is obtained:

- a copper-rich liquid phase called copper matte, whose metal content depends on the smelting furnace that has been used (flash matte: 60% - 63% Cu; white metal from the Teniente converter: 72% – 76% Cu);
- a copper-poor liquid phase called slag (5% - 8% Cu), which is sent to a cleaning process; and
- a SO₂-rich gaseous phase that is sent to the acid plant after cooling and cleaning.

3. Conversion

This stage of the process takes place in Peirce-Smith converters and basically consists of a selective oxidation at high temperature (1150 °C – 1250 °C): the iron and sulfur present in the matte or white metal from the smelting phase are eliminated by means of blowing in oxygen-enriched air, using silica as flux. This elimination takes place in two consecutive stages known as “slag blowing” and “copper blowing”. The reactions produced are spontaneous and highly exothermic, providing the heat required for the process, which makes it an autogenous process.

The products of the conversion stage are:

- blister copper (99% Cu), which passes on to the subsequent refining phase;
- converter slag, which is sent for treatment in order to retrieve the remaining copper (3% – 5%); and
- sulfur dioxide gas. A large percentage of the impurities contained in the matte or white metal –such as arsenic, bismuth, cadmium and lead– tend to vaporize, being eliminated together with the process gases.

4. Refining

The main purpose of fire-refining is to remove sulfur (on the order of 500 ppm) and oxygen (on the order of 5,000 ppm) from blister copper, so as to eliminate the formation of blisters during solidification. Traditionally this takes place in two stages:

- Oxidation: air is added to convert sulfur into SO₂, until values of 10 – 30 ppm have been reached.
- Reduction: the dissolved oxygen from the conversion and the previous oxidation stage is eliminated, until values on the order of 500 – 1000 ppm have been reached. To this end, a reducing agent (raw wood not impregnated with chemical compounds, hydrocarbons, coal) is introduced to remove the oxygen as CO and H₂O.

Furnace operating temperature during the refining stage is approximately 1200°C.

5. Anode Casting

Once the refining processes have been completed, the final product is cast at temperatures of approximately 1200 °C.

6. Slag Treatment

This stage of the process allows for the retrieving of copper content in high-grade slag (4% – 10% Cu) from the smelting and/or conversion processes. Three processes are used in Chile for slag treatment: Teniente-type furnaces, electric furnaces, and flotation.

Slag treatment in Teniente-type or electric furnaces is basically the same process and consists of reducing the magnetite (Fe₃O₄) content in the slag by means of a solid, liquid or gaseous agent so as to change its physical and chemical characteristics. Subsequent sedimentation of the mechanically trapped matte particles allows for the formation of rejected slag and a copper-rich phase. This process may occur under a discontinuous (“batch”) or semicontinuous mode.

Operation in a slag treatment furnace basically consists of four stages:

- Loading the slag onto the furnace;
- Reduction: magnetite reduction results in a decreased slag viscosity, which allows for the separation of the contained phases. The furnace is required to reach a temperature above 1200 °C for this process to take place. Because reduction reactions are endothermic, maintaining the bath temperature requires the heat generated by a burner, in the case of Teniente-type furnaces, and the heat delivered through electrodes, in the case of electric furnaces. The reducing agent is composed of carbon, hydrogen and some sulfur;
- Sedimentation: the reduced slag is left to settle so as to allow the decantation of metallic-content particles. Separation of the phases occurs due to the higher density of the metallic sulfide drops vis-à-vis the slag. To maintain the furnace temperature over 1200 °C, heat must be provided on a continuous basis. Matte sedimentation time ranges between 30 and 60 minutes and may in some cases be considerably longer.

The products obtained from sedimentation are: a low-copper content (0.7% – 1%) slag that is sent to a dump, and a high-copper content (50% – 70%) matte that is recirculated into the process, usually into Peirce-Smith converters.

7. Gas Cleaning and Treatment

The sulfur dioxide (SO₂)-rich metallurgical gases produced at the smelting and conversion stages are captured in the furnaces by means of hoods and are submitted to a process that consists of three main steps:

- Cooling and purification of the gaseous sulfur dioxide (SO₂) coming from the smelting and conversion furnaces. Cooling chambers and electrostatic precipitators are used to eliminate impurities from the gas (N₂, O₂, particulate matter, water steam, arsenic, fluorine, etc.), followed by washing towers and wet electrostatic precipitators. In the cooling chambers, gas is submitted to a quick cooling process.
- Conversion of sulfur dioxide to sulfur trioxide (SO₃). The gas is dried in the acid plant by scrubbing with dilute sulphuric acid and subsequently led to the catalytic converter.
- Absorption of SO₃ in concentrated sulfuric acid (H₂SO₄), resulting in a 98%-pure product.

All liquid effluents evacuated from the cleaning, drying and absorption systems are treated at a plant for their neutralization and the separation of their arsenic content; thus, a stable arsenic product is obtained that, once packed, goes to special dumps for final disposal.

C. Characterization of Raw Materials and Supplies

As mentioned earlier, the basic material that enters the smelting process is copper concentrate mixed with fluxes; the function of the latter is to adjust the melting points and provide the molten material with the proper fluidity to allow for the separation of the matte or white metal from the slag. The information below was provided by Chilean primary smelters based on the current feed of their productive processes.

a. Composition of Copper Concentrates Processed in Chilean Smelters

Element	Unit	Range
Cu	%	26 – 42
S	%	19 – 31
Fe	%	22 – 33
SiO₂	%	3.8 - 14
Al₂O₃	%	1 - 4
CaO	%	0.1 – 1.5
MgO	%	0.02 – 0.9
Mo	%	0.1 – 0.2
As	%	0.01 – 0.8
Au	ppm	0.1 – 1.5
Ag	ppm	32 – 186
Zn	ppm	300 – 17,000
Ni	ppm	7 – 90
Pb	ppm	50 – 3600
Cl	ppm	10 – 900
Sb	ppm	1 – 650
Co	ppm	10 – 200
Bi	ppm	1 – 135

Source: Information provided by Chilean copper concentrate smelters.

b. Flux Composition

Fluxes participating in the smelting process mainly consist of quartz, with an average SiO₂ content above 86%.

Element	Units	Range
Al ₂ O ₃	%	0.75 – 7.7
CaO	%	0.03 -2.7
SiO ₂	%	61.5 - 99
Fe	%	0.4 – 2.5

Source: Information provided by Chilean copper concentrate smelters.

In some cases, soda ash (Na₂CO₃) and calcium carbonate (CaCO₃) are also used. Characteristics of these substances are:

Component	Flux	
	Ca CO ₃	Na ₂ CO ₃
Ca CO ₃	85	-
Na ₂ CO ₃	-	99
SiO ₂	5	1
CaO	-	-
MgO	2.5	-
FeO	2.5	-
Al ₂ O ₃	5	-

Source: Information provided by Chilean copper concentrate smelters.

c. Characteristics of Fuels Used

As mentioned earlier when describing the basic processes of copper concentrate smelters in Chile, the overall balance of the reactions occurring in smelting furnaces is exothermic. Thus, the process is autogenous with regards to the load smelting. Fuels are used at the onset of the processes, where burners are required to initiate the reaction, as well as reducers during refining and smaller amounts for thermal support and homogeneous temperature profiles. Fuels used at smelting works are: Diesel Oil, Fuel Oil No. 6, Natural Gas, Petroleum Coke, Metallurgical Coke and Firewood.

Diesel Oil

Density: 0.83 – 0.87 (Kg / lt.)

Flash Point: minimum 52 °C (56 – 93 °C)

Superior Heat Value: 10,900 Kcal/Kg

Ashes: maximum 0.01% in weight

Sulfur: maximum 0.3% in weight

Vanadium: < 0.05 ppm

Nickel: < 0.04 ppm

Sodium: < 0.7 ppm

Potassium: < 0.04 ppm

Fuel Oil No. 6

Density: 0.945 (Kg / lt.)

Flash Point: minimum 60 °C (70 -128 °C)

Superior Heat Value: 10,500 Kcal/Kg

Ashes: 0.014 – 0.093 % in weight

Sulfur: maximum 5% in weight

Vanadium: 94 - 155 ppm

Nickel: 42 -70 ppm

Sodium: 10 -16 ppm
Potassium: 0.3 -1.0 ppm
Copper: 0.2 -0.8 ppm
Iron: 13 -46 ppm

Natural Gas

Superior Heat Value: 8,850 (min) – 10,200 (max) Kcal/m³
Gas Composition: Methane (95.9%) – Ethane (1.9%) – Propane (0.2%) – Butane (0.08%) – Pentane (0.02%) – Nitrogen (0.9%) – Carbon Dioxide (1%)

Petroleum Coke

Heat Value: 7,200 Kcal/Kg
Carbon: 85% minimum in weight
Sulfur: 1.2% maximum in weight
Volatile Substances: 12% maximum in weight
Ashes: 5% maximum in weight

Metallurgical Coke

Heat Value: 7,000 Kcal/Kg
Carbon: 90% minimum
Ashes: 6% maximum
Sulfur: 1% maximum
Volatile Substances: 0.9 tons/m³.

III. CONCLUSIONS

With regards to the quality of the feed and operation of primary copper concentrate smelters in Chile, it follows from the preceding exposition that:

- At present no primary copper concentrate smelter in Chile processes secondary materials (copper scrap, PVC-covered cables or other items), nor do they use other chemically-treated supplies. Feed materials used by primary copper smelters in Chile (copper concentrates, fluxes, fuels) are characterized by having minimal trace-level chlorine contents, which in practical terms makes it possible to eliminate the dioxin and furan formation risk.
- The operating conditions of primary copper concentrate smelters in Chile allows for the compliance with the three "primary preventive measures" aimed at reducing or preventing dioxin and furan formation at the emission source, i.e.:
 - *Combustion temperatures above 850 °C.* All smelting furnaces (smelting, conversion, refining, casting, etc.) operate at temperatures above 1100 °C.
 - *Residence times above 2 seconds at that temperature.* Because of furnace size, particularly smelting and conversion furnaces, residence times of materials processed in the furnaces are much longer.
 - *Sustained turbulence regime.* Injecting oxygen-enriched air directly to the molten metal phase generates turbulence in the bath.

On the other hand, at international-level there is no scientific evidence to justify the inclusion of primary copper concentrate smelters among main sources of dioxin and furan releases.

In the United States, in 1995 the National Mining Association commissioned Environmental Risk Sciences Inc. to perform a study called "Analysis of the Potential for Dioxin Emissions in the Primary Copper Smelting Industry" (cited in The Inventory of Sources of Dioxin in the United States, EPA/600/P-98/002Aa, April 1998, External Review Draft. www.epa.gov/ncea/pdfs/dioxin/dioxin.pdf). This study discussed the potential for dioxin emissions in primary copper smelters, based on the chemistry of the formation of these compounds and the

conditions under which such smelters operate. It also monitored two smelters deemed to be representative of primary copper concentrate smelters in the United States.

The main conclusions of this study were:

- *Based on the chemistry of the process and the technology of primary copper smelters, it appears that neither dioxins, dioxin contaminated materials, dioxin precursors or, in general, organic constituents are fed into the process. This was confirmed with data provided by the smelters.*
- *Only small amounts of chlorine (ppm) enter the process as constituents of the concentrates most of which is converted into HCl and volatile metallic salts or are removed in the acid plant blowdown. This is also confirmed by industry data.*
- *Based on thermodynamic calculations, copper (II) species are not expected to be formed in appreciable concentrations and, in particular, no copper chloride (II) is found among the particulate matter generated in the process.*
- *Temperatures of process gas streams and of air pollution devices are not in the range favoring the formation of copper chloride (II).*
- *Copper smelting gases contain high concentrations of SO₂, which would be expected to inhibit the formation of dioxins.*
- *Monitoring of stack emissions did not detect the presence of dioxins and furans, thus confirming the theoretical assessment.*

Given the above, it may be concluded that primary copper concentrate smelters as such entail a very low potential risk to generate dioxin and furan emissions. Despite the fact that the smelter sample used in this study only includes smelters operating in Chile, this country ranks first worldwide as copper producer, whether in mining (35%), smelting (13%), or refining (19%), for that reason its experience in this matter is worth noting.

It is not possible to express an opinion about copper smelters that are considered primary but which process secondary materials as part of their feed, because this situation does not occur in Chile. In our opinion, however, such smelters would cease to be primary smelters and would rather become secondary smelters.

Taking into account all of the above arguments, this study concludes that primary copper concentrate smelters should not be considered as dioxin and furan emission sources and that therefore any reference thereto should be eliminated unless there is evidence to the contrary.

IV. COLOMBIA

Mision Permanente de Colombia
Ante la Oficina de las Naciones Unidas
Y los Organismos Internacionales Ginebra

MPC

Ginebra, 3 de enero de 2003

Señor Willis:

Tengo el honor de dirigirme a Usted para hacerle llegar la Nota VAM/DAM/CAA 48310 de 26 de diciembre de 2002, suscrita por el Señor JAIME GIRON DUARTE, Viceministro de Asuntos Multilaterales de Colombia, con la cual remite la revisión técnica al documento "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases (Toolkit), UNEP 2001" que efectuó el Ministerio del Medio Ambiente de Colombia, el cual consta de 18 folios. Sea esta la oportunidad para expresarle mis sentimientos de consideración y aprecio.

Camilo Reyes Rodriguez
Embajador

Al Señor
James B. Willis
Director
PNUMA Productos Químicos
Ginebra

(18 paginas siguen)

GENERACIÓN DE DIOXINAS Y FURANOS Y JUSTIFICACIÓN DE FACTIBILIDAD Y VIABILIDAD DEL PNUMA-DOCUMENTO "STANDARDIZED TOOLKIT FOR IDENTIFICATION AND QUANTIFICATION OF DIOXIN AND FURAN RELEASES" PARA COLOMBIA

El presente informe es el resultado de la revisión del documento "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases"

Este informe está dividido en dos partes, en la primera muestro una visión sobre la generación y emisión de las dioxinas y los furanos, esto con la finalidad de tener sustento para comprender la segunda parte de este informe.

En la segunda parte, en el Ítem A, justifico la viabilidad y factibilidad para Colombia del documento "Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases", asimismo propongo los "Default Emission Factors" para cada planta industrial generadora de Dioxinas y furanos apropiados para Colombia. Además, debido a que en Colombia en la actualidad, no existe actividad estadística de los datos de los productos producidos o desechos alimentados o procesados anualmente para cada planta industrial (en toneladas por año), elaboré a manera de ejemplo, en un Ítem B, las calculaciones para todo Colombia de las emisiones anuales de Dioxinas y furanos en g(ITEQ)/a de las plantas cementeras (solo proceso húmedo) y de los incineradores que incineran desechos sólidos municipales, desechos hospitalarios y desechos industriales sobre todo de la industria de petróleo.

PRIMERA PARTE:

A partir de SEVESO-Incidente en Italia en el año 1976, de la fumigación con el defoliante Agente Naranja en Vietnam y de la demostración realizada en el año 1977 en Alemania acerca de la generación de Dioxinas y Furanos por parte de incineradores para desechos domésticos, todo el mundo está confrontado con el problema de las Dioxinas y los Furanos. Se trata de un grupo de compuestos orgánicos que se denominan como Dibenzo-p-Dioxina Policlorados (PCDDs) y Dibenzo-p-Furano Policlorados (PCDFs). Ellos presentan diferentes grados de toxicidad. El compuesto 2,3,7,8-Tetraclorodibenzo-p-dioxina (2,3,7,8-TCDD) se llama "Seveso Veneno" y es 10^5 veces más tóxico que el Cianuro de Potasio y 500 veces más tóxico que los PCBs.

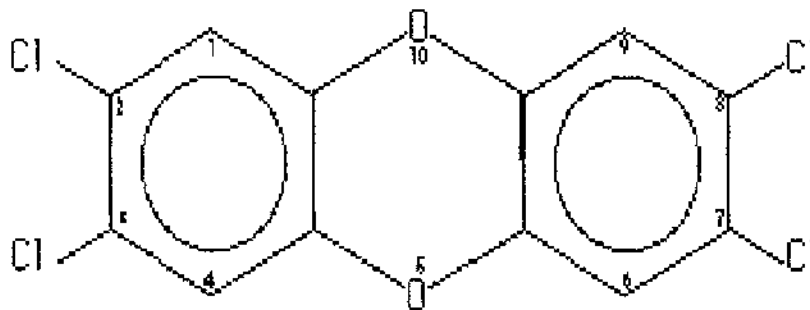
Estas sustancias son productos subsidiarios involuntarios que se producen durante la síntesis de bactericidas, funguicidas como Ácido 2,4,5-Triclorofenoxiacético (2,4,5-T), durante la descomposición pirogénica incontrolada de PCBs (por ejemplo aceite de transformadores) en la presencia de O₂ en rango de temperatura 400 – 1000° C y durante la combustión incompleta. De estas fuentes las dioxinas y furanos se propagan al medio ambiente. Estos compuestos se encuentran ubicuo en sitios alejados del lugar de origen de la generación – en aire, suelo, agua, cadena de alimentos de animales y seres humanos. Las investigaciones medicas demuestran que estos compuestos son al menos promotores de cáncer. Es así que, las Dioxinas y Furanos (PCDD / PCDF) son dos integrantes de la familia de la docena sucia de compuestos orgánicos persistentes (COPS). Con el fin de hacer un tratado global la decisión 18/32 tomada en Nairobi, Kenia en Mayo de 1995 solicitó directamente, debido a la necesidad, tomar acciones internacionales que tiendan a reducir y eliminar las emisiones de COPS. PCDD/PCDF se encuentran como productos subsidiarios involuntarios en muchos procesos, debido a que muchos materiales que tienen dioxinas y furanos son utilizados como insumos. p.ej. PCP, PCP- Na, 2,4,5,-T y PCBs (solamente furanos) etc. Como consecuencia de esto los PCDD/PCDF pueden ser transferidos al medio ambiente aunque ellos no sean formados durante el proceso. PCDD/PCDF son persistentes en el medio ambiente y la transferencia puede ser posible entre matrices diferentes, p.ej. de aire a suelo a agua. Tales transferencias son un peligro, ya que pueden hacer un aporte importante a la exposición del ser humano a estos compuestos.

¿ Que son Dioxinas y Furanos?



FORMULA ESTRUCTURAL DE LA DIOXINA

2,3,7,8-tetraclorodibenzo-p-dioxina, también llamada 2,3,7,8-TCDD



**CASI 10⁵ VECES MAS TOXICO QUE EL CIANURO DE POTASIO
500 VECES MAS TOXICO QUE LOS PCBs SON DIOXINAS Y FURANOS**

Policlorados: 75 Dioxinas y 135 Furanos
Polibromados: 75 Dioxinas y 135 Furanos
Con Mezclados en totalidad mas de 5000 Dioxinas y Furanos

FORMULA ESTRUCTURAL DEL FURANO

2,3,7,8-tetraclorodibenzo-p-furano, también llamada 2,3,7,8-TCDF

Este compuesto es semejante al 2,3,7,8-TCDD pero carece de un átomo de oxígeno y esta enlazando directamente estos dos átomos de carbón involucrados en este oxígeno.

ATOMOS DE CLORO EN MOLÉCULA	COMPUESTO	NUMERO CONGENEROS	
		DIOXINAS	FURANOS
1	Monocloro – DD (F)	2	(4)
2	Dicloro – DD (F)	10	(16)
3	Tricloro – DD (F)	14	(28)
4	Tetracloro – DD (F)	22	(38)
5	Pentacloro – DD (F)	14	(28)
6	Hexacloro – DD (F)	10	(16)
7	Heptacloro – DD (F)	2	(4)
8	Octacloro – DD (F)	1	(1)
SUMATORIA	PCDD (F)	75	(135)

Según Norma de EPA y UE se analizan solo 17 Dioxinas y Furanos (policlorados) de casi 5000 dioxinas y Furanos (policlorados/ polibromados / mezclados—Cl / Br) además con interferencia de otras sustancias semejantes. El desempeño químico analítico debe ser muy alto. Los laboratorios que realizan dichos análisis deben ser muy sofisticados. En el vector "Aire" se necesitan el límite de detección de 0.5 - 1 pg(ITEQ)/m³. Se calcula debido a diferentes toxicidades con respecto del factor de riesgo de 1 de 2,3,7,8-TetraCDDD el producto de concentración por el factor de toxicidad de cada una y al final hacer sumatoria.

Hay muchas categorías de factores de toxicología (ITEQ) a saber: EADON, EPA, BGA/UBA, NATO/CCMS-I(Internacional denominada brevemente I) y WHO-I. Común corriente se utiliza el factor de categoría NATO-CCMS-I y señala con (ITEQ).

Valores límites y toxicología de las Dioxinas y Furanos (PCDD/PCDF):

- Presión de vapor @ 298.15K <10⁻⁶ Pa
- Coeficiente de partición medio orgánico / agua > 10⁵
 Por consiguiente, la acumulación ó la absorción en materias orgánicas de sedimentos, sólidos en suspensión, cenizas volantes y tejidos grasos de organismos
- PCDD/PCDF son muy persistente en el medio ambiente
- Se encuentran en el aire en una concentración hasta de 35pg(ITEQ) /m³
- Se han encontrado PCDD/PCDF en grasa de leche materna(medido clínicamente) hasta 90pg(ITEQ)/g

- El valor límite para lugar de trabajo es de 50g(ITEQ)/m³
- Para incineradores el valor límite de emisión en países de la Comunidad Europea y en EE.UU es de 0.1ng(ITEQ)/m³

Normas técnicas y estándares ambientales:

- La Resolución No. 391 de 6 de Marzo del 2001 del DAMA y la Resolución 822/98 del Ministerio de Desarrollo establecen 10ng(ITEQ)/m³ en emisión de incineradores
- La Resolución No. 0058 de 21 de Enero del 2002 del Ministerio del Medio Ambiente establece 1ng(ITEQ)/m³ en emisión de incineradores durante los 2 primeros años de entrada en vigencia esta norma
- Límite aceptable diario a ingerir (ADI): 1pg(ITEQ)/kg peso corporal
- Inducción de Hepato-Monoxigenases
- Sarcoma de Tejidos Blandos
- Promotores de la formación de tumores
- 2,3,7,8-configuración de Dioxinas y Furanos tiene altísima afinidad e interacción a Ah-Receptores en los mamíferos en manera de hormonas esteroides
- Carcinomas y adenomas hepatocelulares
- Inducción de Etoxiresorufin-o-Detilase (EROD) y Porfirio
- Alteraciones en el sistema inmunológico y la reproducción. Particularmente la 2,3,7,8-Tetraclorodibenzo-p-dioxina (TCDD) en estudios con ratas hembras se ha identificado como potencial Hepato-Carcinogénico
- Síndrome de pérdida de peso corporal (Wasting Síndrome)
- Alteración del metabolismo (grasa corporal y colesterol)
- Permutaciones Neurológicas y Psicológicas

¿Como se producen las Dioxinas y Furanos?

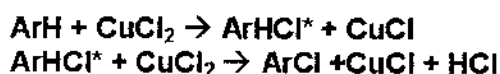
Como productos subsidiarios involuntarios

- A través de química de fuego—por encima de 200°C (descomposición pirogénica incontrolada de PCBs—p.ej. Aceite de transformadores en la presencia de O₂ en rango de temperatura 400-1000°C)
- Industria química con procesos en los que interviene el átomo de Cloro y Oxidación: PCPs, PCBs, Cloroanilina, Ácido 2,4,5-Triclorofenoxiacético (2,4,5-T), Triclorobenceno, Epiclorohidrina, Percloroetilino, Tetracloroetilino, EDC, Cloro (Cl₂) utilizando celda de mercurio y ánodos de grafito
- La combustión defectuosa e incompleta ocasionándola formación de carbono (sobre todo la estructura del carbón aromático) activo y superactivo en las cenizas volantes con contenido de Cu, Fe, Ni, Si y cloruro inorgánico y/o Cl₂ a través de DeNovo Síntesis en rango de temperatura 250-450°C
- La utilización de productos e insumos como PCPs, PCBs, PCBencenos, 2,4,5-T etc. que contienen inherentemente Dioxinas y Furanos
- En lodos de plantas de tratamiento de aguas residuales

Concentraciones de Dioxinas y Furanos generadas en el proceso de combustión dependen de:

- La zona de temperatura crítica (250°C—450/470°C)
Se han observado dos máximas de concentración para formar Dioxinas y Furanos sobre la superficie de las cenizas volantes @ 300°C y 470°C
- del tiempo de residencia de la ceniza volante en la zona de temperatura crítica
- del contenido del carbón (en la ceniza volante), Cu(II) y cloruro inorgánico y las deposiciones de cenizas en paredes de calderas

Reacción básicas de la generación de Dioxinas y Furanos son:



En donde:

Ar : Aromática

ArH: Estructura aromática del carbón

Luego resulta la descomposición catalizada por los iones de metales de la estructura macromolecular del carbón con CO₂ como producto final.

Los experimentos de agregar ¹³C y ¹³CO₂ a la ceniza volante en aire a la temperatura de 300°C produjo ¹³C-Dioxinas/Furanos.

Conclusiones de los experimentos:

El carbón residual en ceniza volante es convertido a CO₂ a través de una reacción catalizada por un metal.

Además de las dioxinas y los furanos se producen a través de este mecanismo:

Los compuestos orgánicos polihalogenados (Di-Hepta) de Bencenos.

Fenoles	Naftalines
Benzonitriles	Bifenilos
Benzofuranos	Benzofenones
Benzotiofenos	Bifenileteres
Tiofenos	Xantones

En la presencia de bromo resultan mezclas de especies de Cloro /Bromo.

HIPOTESIS DE DOS MECANISMOS GENERADORES DE DIOXINAS Y FURANOS

PRIMER MECANISMO: En partículas largas dentro de las regiones de combustión de incineradores:

Lo más probable es que en un complejo metálico activo con haluros (Cl, Br) como "Ligand" funcionando como un catalizador se efectúe una transferencia de halógeno de este complejo activo al carbón en un paso de Clorinación. por otra parte la clorinación a través de cloro elemental (Cl_2) formado por DEACON REACCION no puede ser excluida.

SEGUNDO MECANISMO:

Es responsable por la formación de dioxinas y furanos en las regiones frías hacia "DOWN STREAM" del dispositivo de combustión.

CUATRO CONDICIONES SON GENERADORAS POTENCIALES DE DIOXINAS Y FURANOS: "Pueden presentarse en forma aislada o pueden estar relacionadas entre sí":

- Procesos de alta temperatura (encima de 200°C y/o combustión incompleta)
- Carbón orgánico
- Cloro (Cl_2)
- Productos e insumos que contienen dioxinas y furanos.

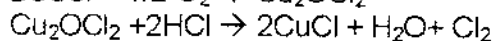
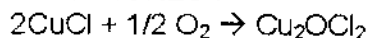
Generación de dioxinas y furanos:

- Generación directa durante la combustión a través de descomponer compuestos orgánicos clorados p. ej. PCBs.
- Reacciones homogéneas en la fase gaseosa entre los productos descompuestos orgánicos clorados que se formaron durante la combustión de la primera etapa.
- Reacciones catalíticas sobre la superficie de las partículas de ceniza volante entre los cloruros (HCl), Cloruros de Metales p. ej. (CuCl , CuCl_2) y el material orgánico quemado incompleto, sobre todo partículas de carbón activo y superactivo dependiendo de sus tamaños.

La reacción (DeNovo Síntesis) de la generación de dioxinas y furanos es óptima a la temperatura alrededor de 300°C .

Es muy probable que la ceniza volante con contenido de partículas de carbón activo y superactivo y de SiO₂ juega un papel significativo para generar las dioxinas y furanos.

ECUACIONES :



En el anterior paso intermedio de generación de dioxinas y furanos se forman sales a través de Cl₂ con ayuda de HCl según de DEACON – REACCION en donde Cu juega un papel muy importante.

La generación de dioxinas y furanos resulta a través de reacciones en la fase de gas – sólido de partículas de carbón activo y cloruro inorgánico. La reacción esta activada a partir de iones de metales sobre todo Cu. Para seguir esta reacción el oxígeno es importante.

Tomando en cuenta todo de anterior las "Fuentes de Dioxinas y Furanos en Colombia son las mismas que estan identificadas correctamente en el documento del "PNUMA : Standardized Toolkits for Identification and Quantification of Dioxin and Furan Releases" que son las siguientes:

❖ **Procesos Naturales**

- Incendios forestales
- Volcanes

❖ **Incineración de desechos**

- Desechos sólidos municipales
- Desechos peligrosos
- Desechos hospitalarios
- Desechos de trozos (fracción liviana)
(Light-Fraction Shredder Waste)
- Lodos de tratamientos de aguas residuales.
- Desechos de madera y biomasa

❖ **Producción de Metales ferrosos y no ferrosos**

- Producción de Coque
- Producción de Hierro y Acero
- Producción de Cobre
- Producción de Aluminio
- Producción de Níquel

- Producción de Plomo
- Producción de Zinc
- Producción de Magnesio
- Producción de Latón (Brass)
- Producción de los demás metales no ferrosos
- Reclamación térmica de alambre

❖ **Generación de potencia y calentamiento
(Power Generation and Heating)**

- Plantas con combustible fósiles
- Plantas con biomasa como combustible
- Combustión del gas de rellenos sanitarios y del biogas
- Calentamiento doméstico y cocción a través de biomasa
- Calentamiento doméstico con combustible fósil

❖ **Productos Minerales**

- Producción de cemento
- Producción de cal
- Producción de ladrillos
- Producción de vidrio
- Producción de cerámica
- Mezcla de asfalto

❖ **Transporte**

- Motores de cuatro ciclos (4 –stroke engines)
- Motores de dos ciclos (2 –stroke engines)
- Motores de Diesel
- Motores con combustible aceite pesado

❖ **Producción y uso de químicas y artículos a consumir**

- Pulpa y fabricas de papel
- Industria química
- Industria de petróleo
- Industria textil
- Industria de cuero

❖ **Misceláneos**

- Secado de biomasa
- Crematorios
- Procesos de ahumar
- Lavado en seco

- Fumar tabaco
- Productos comercializados (en Alemania deben contener < 2ppb de 2,3,7,8 TetraCDD ó <5 ppb de sumatoria de dioxinas y furanos)

❖ Disposición/Relleno Sanitario

- Rellenos sanitarios y vertederos de desechos
- Aguas residuales y tratamiento
- Procesos de compostaje
- Disposición no térmica de aceite usado

❖ Sitios calientes (Hot Spots)

- Sitios de producción de compuestos orgánicos clorinados
- Sitios de producción de cloro (Cl₂)
- Sitios de formulación de fenoles clorinados
- Sitios de la aplicación de fenoles clorinados
- Manufacturas de madera de construcción y sitios de tratamiento
- Transformadores con contenido de PCBs y condensadores
- Sitios de accidentes
- Dragar y espolvorear sedimentos
- Sitios de Kaolín y arcilla (Ball Clay)

MINIMIZACIÓN DE EMISIONES DE DIOXINAS Y FURANOS

- Un enfriamiento de choques de los gases de salida por debajo de 200°C reduce la generación de dioxinas y furanos.
- Las dioxinas y furanos pueden ser oxidadas a alta temperatura de (800 – 1200°C) ó en un catalizador a temperatura baja.
- Las dioxinas y furanos despues del filtro de mangas pueden ser reducidas de <0.05 ng/m³std a < 0.01 ng/m³ std a través de SCR – DENO_x catalizador de una planta de DENO_x.
- Las superficies activas de catalizadores metálicos (Cu, Fe, Ni, Si etc) en la ceniza volante generando dioxinas y furanos pueden ser bloqueadas mediante NH₃, H₂S ó Aminas.
- La ceniza volante impregnada con destructores inorgánicos no volátiles puede reducir 99.99% la concentración generada a la temperatura de 200 – 400°C por los precursores potenciales indicando que los destructores están envenenando las superficies activas de las cenizas volantes.

SEGUNDA PARTE:

ITEM. A.

Colombia no dispone de un inventario completo de emisión de fuentes susceptibles de tener presencia de Dioxinas y Furanos y el Ministerio del Medio Ambiente no tiene todavía exactamente la "Activity Statistics" del material insumo alimentada/entrada/procesada y/o el producto producido para cada uno de los procesos identificados en este "Toolkit"; por lo tanto se carece de los Factores de Emisiones experimentales y se depende, al principio, de los "Default Factores de Emisión" en ug(ITEQ)/t del material insumo ó del producto producido. Debido a que en Colombia las plantas químicas industriales no están equipadas con sistemas adecuados de control de polución de gas de salida, se toma el peor de los casos; de los factores de emisión propuestos por "Default"

Además la situación económica del país no permite equipos como SCR-DENOX que pueden reducir las concentraciones de Dioxinas y Furanos hasta 99.99% . Todavía no se toman las medidas preventivas para realizar el enfriamiento de choques "down stream" de la planta y no se inyectan los destructores como NH₃, H₂S ó Aminas encima de los sitios activos y superactivos de cenizas volantes.

En Colombia se puede ponderar la cantidad emitida anual de dioxinas y furanos por medio de la siguiente ecuación básica:

Source Strength = Default Emission Factor x Activity Rate
(Dioxin/Furan-ITEQ-
Emission per year)

La emisión de Dioxinas y Furanos anual se debe indicar en g(ITEQ)/a.
Default Emission Factor in ug(ITEQ)/toneladas (t) del material insumo alimentado/entrado/procesado ó producto producido
Activity Rate in toneladas (t) del material insumo alimentado/entrado/procesado ó producto producido anualmente (t/a)

Cuando los datos estén disponibles se multiplica la cantidad exacta del material insumo alimentado/entrado/procesado ó producto producido anualmente ("Activity Rate" en t/a) con el "Default Factor de Emisión" en ug(ITEQ)/t para cada proceso identificado en "Dioxin-/Furan-Toolkit" y con esto se logra la emisión anualmente en g(ITEQ)/a de Dioxinas y Furanos

Normalmente en Colombia se debe medir y analizar Dioxinas y Furanos en todas las fuentes generadoras señaladas en "Toolkit", esto con el fin de poder disponer de factores de Emisión propios, en ug(ITEQ)/t hallados experimentalmente en el País.

Por la solubilidad muy baja de Dioxinas y Furanos en agua (p.ej. para 2,3,7,8-TetraCDDD solo 200 ng/l) no se considera en Colombia, por ahora, el vector "Agua".

Por consiguiente se considera prioritariamente solamente los vectores "Aire" y "Suelo" y en casos específicos los vectores "Producto" y/ó "Residuos resultantes".

"Default Factores de Emisión " para Dioxinas y Furanos para categorías 1-10 viable a aplicar PARA COLOMBIA:

❖ **Main Category 1 – Incineración de desechos**

- **Desechos sólidos municipales → Aire: 3500 ug(ITEQ)/t**
Suelo: no relevante
- **Desechos peligrosos → Aire: 35000 ug(ITEQ)/t**
Suelo: no relevante
- **Desechos hospitalarios → Aire: 40000 ug(ITEQ)/t**
Suelo: no relevante
- **Desechos de trozos (fracción liviana) → Aire: 1000 ug(ITEQ)/t**
(Light Fraction Shredder Waste) Suelo: no relevante
- **Lodos de tratamiento de aguas residuales → Aire: 50 ug(ITEQ)/t**
(por ahora no actual y no aplicable) Suelo: no relevante
- **Desechos de madera y biomasa → Aire: 100 ug(ITEQ)/t**
Suelo: no relevante
- **Combustión de cadáveres de animales → Aire: 500 ug(ITEQ)/t**
Suelo: no relevante

❖ **Main Category 2 – Producción de Metales ferrosos y no ferrosos**

- **Sinterización de Mineral de Hierro → Aire: 20 ug(ITEQ)/t**
Suelo: no relevante
- **Producción de Coque → Aire: 3 ug(ITEQ)/t**
Suelo: no relevante
- **Producción de Hierro y Acero → Aire: 10 ug(ITEQ)/t**
Suelo: no relevante
- **Producción de Cobre :**
 - Sec. Cu con tecnología básica → Aire: 800 ug(ITEQ)/t
Suelo: no relevante
 - Fundición y moldear de Cu y su aleación → Aire: 0.03 ug(ITEQ)/t
Suelo: no relevante
 - Prim. Cu, todo tipos → Aire: 0.01 ug(ITEQ)/t
Suelo: no relevante
- **Producción de Aluminio → Aire: 150 ug(ITEQ)/t**
Suelo: no relevante
- **Producción de Plomo :**
 - de chatarra conteniendo

- PVC-separadores de baterías → Aire: 80 ug(ITEQ)/t
Suelo: no relevante
- de chatarra libre de PVC/Cl₂ → Aire: 8 ug(ITEQ)/t ; Suelo: no rel.
(Blast-Alto Horno con filtro de Mangas)
- de chatarra libre de PVC/Cl₂ → Aire: 0.5 ug(ITEQ)/t ; Suelo: no rel.
(No Blast-Alto Horno
pero con Scrubber)
- Producción de Zinc → Aire: 1000 ug(ITEQ)/t ; Suelo: no relevante
- Fundición de Zinc → Aire: 0.3 ug(ITEQ)/t ; Suelo: no relevante
- Producción de Latón (Brass) → Aire: 1 ug(ITEQ)/t ; Suelo: no relev.
- Producción de Magnesio → Aire: 250 ug(ITEQ)/t ; Suelo: no relev.
- Producción de los demás metales no ferrosos → Aire: 100ug(ITEQ)/t
Suelo: no relevante
- Dispositivos a hacer trizas → Aire: 0.2 ug(ITEQ)/t ; Suelo: no relev.
- Reclamación térmica de alambre :
 - Quemas abiertas → Aire: 5000 ug(ITEQ)/t ; Suelo: no relevante
 - Horno básico con Post-Quemador
y Scrubber húmido → Aire: 40 ug(ITEQ)/t ; Suelo: no relevante
- ❖ Main Category 3 – Generación de potencia y calentamiento
 - Plantas con combustible fósiles:
 - Calderas con combustible fósiles/
con coprocesamiento de desechos → Aire: 35 ug(ITEQ)/TJ
Suelo: no relevante
 - Calderas con combustible carbón → Aire: 10 ug(ITEQ)/TJ
Suelo: no relevante
 - Calderas con combustible pesado → Aire: 2.5 ug(ITEQ)/TJ
Suelo: no relevante
 - Calderas con combustible liviano → Aire: 0.5 ug(ITEQ)/TJ
/Gas Natural Suelo: no relevante
 - Plantas con biomas como combustible :
 - Calderas con combustible
biomasa mezclada → Aire: 500 ug(ITEQ)/TJ
Suelo: no relevante
 - Calderas con combustible
madera, limpia → Aire: 50 ug(ITEQ)/TJ
Suelo: no relevante
 - Combustión del gas de rellenos sanitarios
y del biogas y teas → Aire: 8 ug(ITEQ)/TJ
Suelo: no relevante
 - Calentamiento doméstico y cocción a través de biomasa:
 - Estufas con madera contaminada y biomasa
como combustible → Aire: 1500 ug(ITEQ)/TJ
Suelo: no relevante
 - Estufas con madera virgen y biomasa
como combustibles → Aire: 100 ug(ITEQ)/TJ
Suelo: no relevante

- Calentamiento doméstico con combustible fósil
 - Estufas con carbón como combustible → Aire: 70 ug(ITEQ)/t
Suelo: no relevante
 - Estufas con aceite como combustible → Aire: 10 ug(ITEQ)/t
Suelo: no relevante
 - Estufas con gas natural como combustible → Aire: 1.5 ug(ITEQ)/t
Suelo: no relevante

❖ Main Category 4 – Productos Minerales

- Producción de cemento:
 - Proceso húmedo, ESP a la temperatura >300°C
 - Aire: 5.0 ug(ITEQ)/t
 - Suelo: posible
 - Proceso húmedo, ESP/FF a la temperatura 200- 300°C
 - Aire: 0.6 ug(ITEQ)/t
 - Suelo: posible
 - Proceso húmedo, ESP/FF a la temperatura < 200°C
 - Aire: 0.15 ug(ITEQ)/t
 - Suelo: posible
- Producción de cal → Aire: 10 ug(ITEQ)/t ; Suelo: posible
- Producción de ladrillos → Aire: 0.2 ug(ITEQ)/t ; Suelo: no relev.
- Producción de vidrio → ver producción de ladrillos
- Producción de cerámica → ver producción de ladrillos
- Mezcla de asfalto → Aire: 0.07 ug(ITEQ)/t ; Suelo: posible

❖ Main Category 5 – Transporte

- Motores de cuatro ciclos (passenger cars) :
(4-stroke engines)
 - combustible con plomo → Aire: 2.2 ug(ITEQ)/t ; Suelo: no relev.
 - combustible sin plomo sin catalizador convertidor
 - Aire: 0.1 ug(ITEQ)/t ; Suelo: no relev.
 - combustible sin plomo con catalizador convertidor
 - Aire: 0.00 ug(ITEQ)/t ; Suelo: no relev.
- Motores de dos ciclos :
(2-stroke engines)
 - combustible con plomo → Aire: 3.5 ug(ITEQ)/t ; Suelo: no relev.
 - combustible sin plomo sin catalizador convertidor
 - Aire: 2.5 ug(ITEQ)/t ; Suelo: no relev.
- Motores de Diesel → Aire: 0.5 ug(ITEQ)/t ; Suelo: no relevante
- Motores con combustible aceite pesado—todo tipos
(p.ej. para barcos)
 - Aire: 4 ug(ITEQ)/t ; Suelo: no relevante

❖ Main Category 6 – Procesos de combustión incontrolados

- Quemadas de biomasa:
 - Fuegos forestales, de páramo y pastizal → Aire: 5 ug(ITEQ)/t
Suelo: 4 ug(ITEQ)/t

- Residuos agrícolas (en campo) → Aire: 30 ug(ITEQ)/t
Suelo: 10 ug(ITEQ)/t
- Quema de desechos y fuegos accidentales:
 - Fuegos de rellenos sanitarios → Aire: 1000 ug(ITEQ)/t
Suelo: posible
 - Fuegos accidentales en casas y fábricas → Aire: 400 ug(ITEQ)/t
(por evento)
Residuo: 400 ug(ITEQ)/t
 - Quemas incontroladas de desechos domésticos
→ Aire: 300 ug(ITEQ)/t
Residuo: 600 ug(ITEQ)/t
 - Fuegos accidentales en vehículos → Aire: 94 ug(ITEQ)/t
(por evento)
Residuo: 18 ug(ITEQ)/t
 - Quema abierta de madera → Aire: 60 ug(ITEQ)/t
(Construcción/Demolición) Residuo: 10 ug(ITEQ)/t
- ❖ Main Category 7 – Producción y uso de químicos y artículos
A consumir
 - Pulpa y fábricas de papel → Aire: 0.007 ug (ITEQ)/t de licor negro
Residuos: 1000 ug(ITEQ)/t
 - Nur calderas "BARK" → Aire: 0.4 ug(ITEQ)/t
Residuos: 1000 ug(ITEQ)/t
 - Kraft proceso (Cl₂), viejo → Agua: 4.5 ug(ITEQ)/t secado en aire
Residuos: 4.5 ug(ITEQ)/t secado en aire
Lodos : 100 ug(ITEQ)/t
 - Kraft proceso (ClO₂), moderno → Agua: 0.06 ug(ITEQ)/t sec. en aire
Residuos: 0.2 ug(ITEQ)/t sec. en aire
Lodos: 10 ug(ITEQ)/t
 - Productos de pulpa y papel → 0.1-10 ug(ITEQ)/t
 - Industria química:
 - PCP → Producto: 2000000 ug(ITEQ)/t
 - PCP-Na → Producto: 500 ug(ITEQ)/t
 - PCBs → Producto: 15000-1500000 ug(ITEQ)/t
(Concentración de PCDFs en nuevos PCBs)
 - 2,4,5-T → Producto: 7000 ug(ITEQ)/t
 - 2,4,6-PCPh → Producto: 700 ug(ITEQ)/t
 - Dicloroprop → Producto: 1000 ug(ITEQ)/t
 - 2,4-D → Producto: 700 ug(ITEQ)/t
 - Cloranil → Producto (p-para): 100 ug(ITEQ)/t
(Proceso de Hidroquinona)
 - Cloranil → Producto (p-para): 400000 ug(ITEQ)/t
Producto (o-orto): 60000 ug(ITEQ)/t
(Proceso viejo de Hoechst Farben)
 - CNP (tecnología vieja) → 300000 ug(ITEQ)/t
 - CNP (tecnología nueva) → 400 ug(ITEQ)/t
 - Colorantes (Dyestuffs) con base en chloranil —proceso viejo,
clase I → 1200 ug(ITEQ)/t

- Clorobencenos → no Factores de Emisión
- Producción de Cl₂ → Residuos: 30 mg(ITEQ)/kg, pero el producto (utilizando celda de Hg y ánodos de grafito) Cl₂ no contiene Dioxinas y Furanos
- EDC/VCM/PVC (tecnologías viejas) → No hay datos
- EDC/VCM y/o EDC/VCM/PVC (plantas modernas)
 - Aire: 0.95 ug(ITEQ)/t ; Productos: 0.03 ug(ITEQ)/t ; Residuos: 2 ug(ITEQ)/t
- Solo PVC (plantas modernas) → Aire: 0.0003 ug(ITEQ)/t
 - Productos: 0.1 ug(ITEQ)/t ; Residuos: 0.2 ug(ITEQ)/t
- Compuestos alifáticos clorinados → Residuos: 4000 ug(ITEQ)/t (Tri- y Percloroetilena)

- Industria de petróleo → Aire: no hay datos
- Industria textil → Aire: no hay datos ; Productos: 0.1-100 ug(ITEQ)/t
- Industria de cuero → Productos: 10-1000 ug(ITEQ)/t

❖ Main Category 8 – Misceláneos

- Secado de biomasa:
 - Madera limpia/ Forraje verde → Aire: 0.007- 0.1 ug(ITEQ)/t
 - Producto: 0.1 ug(ITEQ)/t
 - Biomasa tratada con PCP ó de otra manera → Aire: 10 ug(ITEQ)/t
 - Producto: 0.5 ug(ITEQ)/t
 - Crematorios → Aire: 90 ug(ITEQ) por cremación; Residuos: 2.5 ug(ITEQ)/t
 - Sitios de ahumar → Aire: 6 - 50 ug(ITEQ)/t ; Suelo: no relevante
 - Lavado en seco → Residuos de Destilación : 50-3000 ug(ITEQ)/t
 - Fumar Tabaco → Aire: 0.1- 0.3 pg(ITEQ) por cigarro puro ó cigarrillo

❖ Main Category 9 – Disposición/Relleno Sanitario

- Rellenos Sanitario y vertederos de desechos:
 - Desechos peligrosos → Aire : no relev. ; Agua: 200 pg (ITEQ)/l de lixiviado liberado
 - Desechos no peligrosos → Aire: no relev. ; Agua 30 pg (ITEQ)/l de lixiviado liberado
- Aguas residuales y tratamiento → (por ahora no aplicable en Colombia)
 - EN FUTURO →
 - Entradas mezcladas domésticas y industriales → (con relevancia de Cl₂)
 - Agua residual :
 - (Sin remoción de lodos): 5 pg(ITEQ)/l
 - (con remoción de lodos): 0.5 pg(ITEQ)/l
 - Lodos en ambos casos: 1000 ug(ITEQ)/t material seco
 - Aire: no relevante
 - Compostaje → Aire: no relevante ; Producto: 5-100 ug(ITEQ)/t material seco

- Vertederos en aguas abiertas (Ríos , Lagos ó Océanos) →
 - Aguas residuales contaminadas: 50 pg (ITEQ)/t
 - Aguas residuales no contaminadas: 5 pg (ITEQ)/t
 - Disposición de aceite usado –toda fracciones–
(Aceite usado/grasa de filtros de aceite de cantinas, restaurantes, empresas , de automóviles y otros motores) → Aire: 4 ug(ITEQ)/t
- ❖ **Main Category 10 – Sitios Calientes (Hot Spots)**
- Sitios de producción de compuestos orgánicos clorinados
 - Sitios de producción de cloro (Cl₂)→ Residuos: 30 mg(ITEQ)/kg (utilizando celda de Hg y ánodos de grafito)
 - Sitios de formulación de fenoles clorinados
 - Sitios de la aplicación de fenoles clorinados
 - Manufacturas de madera de construcción y sitios de tratamiento
 - Transformadores y condensadores con contenido de PCBs
 - Vertederos de Desechos /Residuos de categorías 1-9
Indicadores de vertederos con contenido de Dioxinas y Furanos consisten de la historia de vertederos de uno ó otro de desechos como los siguientes:
 - Residuos de la producción química sobre todo de clorofenoles
 - Residuos de procesos de combustión y incineración p.j. cenizas volantes
 - Equipos con contenido de PCBs (p.ej. condensadores y transformadores)
 - Lodos de fabricas de pulpas utilizando Cl₂ libre a blanquear
 - Industria de manufactura de madera de construcción aplicando PCP ó otros compuestos orgánicos clorados como preservativos
 - Cuando fueron quemados cables con recubrimiento plástico
 - Después de fuegos incidentales ó accidentales de rellenos sanitarios
 - Sitios de accidentes
 - Dragar y espolvorear sedimentos
 - Sitios de Kaolin y Arcilla (Ball Clay) →Dioxinas y Furanos son presente mucho más ante del inicio de la Cloroindustria, señalando su formación a través de actividades no antropogénicas

ITEM B

A MANERA DE EJEMPLO:

- CARACTERIZACIÓN DE LA INDUSTRIA DE CEMENTO EN COLOMBIA EN 1999:

Producción de cemento gris:	13270 kt
Producción de cemento blanco:	130 kt
Total:	13400 kt

Proceso Seco (61%):	8160 kt
<u>Proceso Húmedo (39%):</u>	<u>5240 kt</u>
<u>(Activity Rate)</u>	

Para procesos secos de fabricación de cemento, el documento "Toolkit" no tiene factores de emisión. Para procesos húmedos de fabricación de cemento con equipos de control de polución (ESP/FF) a la temperatura de 200 – 300° C el " Default Emission Factor" es: 0,6 ug(ITEQ)/t. La cantidad de dioxinas y furanos emitida anualmente por planta cementeras por procesos húmedos con base en la "Activity Rate" del año 1999 de 5240000 t según la ecuación básica:

$$\text{Source Strength (g(ITEQ)/a)} = \text{Default Emission Factor (ug(ITEQ)/t)} \times \text{Activity Rate (t/a)}$$
$$= 0.6 \times 5240000 = 3.14 \text{ g(ITEQ)/a}$$

Además, con un flujo volumétrico de gas de salida aproximado de 500 m³ por tonelada de producto producido, se alcanza un valor de emisión (aire) de 1.2 ng(ITEQ) /m³ que es alrededor de los valores límites de las Resoluciones Colombianas Nos. 391 de 6 de marzo de 2001 y 0058 de 21 de enero de 2002.

- CARACTERIZACIÓN DE LA INDUSTRIA DE INCINERADORES EN COLOMBIA:

En los 368 incineradores del país se incineran anualmente desechos hospitalarios alrededor de 30386 t/a; desechos sólidos municipales alrededor de 51100 t/a y desechos industriales (aquí de petróleo) alrededor de 10858 t/a. Utilizando los "Default Emission Factors " de la siguiente forma:

Desechos Sólidos Municipales :	3500 ug(ITEQ) /t
Desechos Hospitalarios:	40000 ug(ITEQ)/t
Desechos Industriales (de petróleo):	35000 ug(ITEQ)/t

La cantidad de dioxinas y furanos emitida anualmente por los incineradores del país es la siguiente:

Desechos Sólidos Municipales :	179 g(ITEQ) /a
Residuos Hospitalarios:	1215 g(ITEQ)/a
Residuos Industriales (de petróleo):	380 g(ITEQ)/a

Como se puede observar, en las anteriores cifras, el aporte de dioxinas y furanos que emanan los incineradores Colombianos es inmensa.

Además, con un flujo volumétrico de gas de salida aproximado de 500 m³ por tonelada de desechos alimentados / procesados, se alcanzan valores de emisión (aire), que superan drásticamente, los valores límites de las Resoluciones Colombianas Nos. 391 de 6 de marzo de 2001 y 0058 de 21 de enero de 2002.



V. GREECE ON BEHALF OF THE EUROPEAN UNION AND ITS MEMBER STATES

Comments on the adoption of the UNEP Dioxin Toolkit as a basis for guidance as required under Annex C of the Stockholm Convention

The EU considers that the UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases should provide a valuable information source. We consider that the Toolkit has the following advantages:

- Within the Toolkit, the provision of source categories and process classes for dioxins and furans covers all release sources that require evaluation under the Stockholm Convention.
- the Toolkit provides a methodology and associated emission factors for PCDD/F emissions into all media (air, water, land, products and residue). Other international methodologies that are available have been created for evaluation of impacts into single environmental media e.g. the EMEP/CORINAIR Emission Inventory Guidebook provides a guide to atmospheric inventory methodologies, while the HARP-HAZ reporting system is specific to emissions into the marine environment (and more specifically for northern European countries).

However, it does have disadvantages, some of which are already flagged in the Toolkit, and will require further examination and modification:

- The emission factors it contains are approximately 3 years old and may require updating to reflect changes in industrial technology and processes, and where applicable improvements in pollution abatement equipment.
- In the toolkit, emission factors for PCDD/Fs are based mainly on the I-TEF scheme. If these were expressed as WHO-TEQs, as required by the Convention, it could be expected that significantly higher concentration values would be derived for some source categories.
- **It would be useful if more information was available on how the emission factors were derived so that some assessment could be made of their quality. This would be helpful both to the Toolkit user and in deciding how best the Toolkit might be developed further.**
- Coverage of emission factors is incomplete. More up to date emission factors from alternative sources of inventory information such as the EMEP/CORINAIR Emission Inventory Guidebook would be valuable here (although for POPs there have been few updates due to lack of new data) and new potential sources of dioxin emissions could also be included where these have been identified since the Toolkit publication.
- Emission factors contained within the Toolkit also need further examination to ensure that they are relevant to realistic operating scenarios in both developed countries and for those with economies in transition. They are regarded by some as being somewhat conservative in nature, and as optimistic by some for some industrial sources e.g. for ferrous and non-ferrous metal production from secondary materials, and further work may be needed to get the right spread for each class. This might include a measurement programme to gather emission factors for some of the poorly understood classes - a co-ordinated programme could cover both emission factors and the controlling parameters, giving better inventory data and some

tools to reduce emissions. The recently updated EMEP/CORINAIR Guidebook will be useful in this process, as a significant institutional effort has been made by the UNECE/EMEP Task Force on Emission Inventories and Projections (TFEIP), to ensure that the given emission factors are also relevant for industry within Central and Eastern European countries.

- The Toolkit would also require expansion to cover the other pollutants that require quantification under the requirements of the Stockholm Convention, i.e. PCBs and HCB. Emission factors from other sources of existing guidance could potentially be used to complement the existing dioxin emission factors. Ideally, however, all information would be initially reviewed to ensure that it is appropriate for emissions from both developed and developing countries and up to date. The Toolkit would also require updating with additional source categories to reflect other major emission sources for these chemicals. For example, HCB can be released in the environment from pesticides in which it is present as a contaminant.

It would be helpful in terms of transparency of process for any review or modification of the Toolkit to include relevant experts from developed and developing countries as well as those who have experience in applying it. Such a process, allowing input from all parties, would help in promoting confidence in its use.

Submitted by:

Angeliki Tsatsou-Drista, Director
General Chemical State Laboratory
Division of Environment
Athens, Greece

VI. MEXICO

Misión Permanente de México

La Misión Permanente de México ante la Oficina de las Naciones Unidas y otras Organizaciones Internacionales con sede en Ginebra saluda muy atentamente a la Secretaría del Convenio de Estocolmo sobre Contaminantes Orgánicos Persistentes y tiene el honor de hacer referencia a su notificación del 24 de septiembre de 2002 relativa a la Actualización del Manual de Uso para Identificación y Cuantificación de Dioxinas y Furanos.

Sobre el particular, la Misión Permanente se permite transmitir los comentarios del Gobierno de México con información proporcionada por la Dirección General de Manejo Integral de Contaminantes, de la Secretaría de Medio Ambiente y Recursos Naturales.

La Misión Permanente de México ante la Oficina de las Naciones Unidas y otras Organizaciones Internacionales con sede en Ginebra aprovecha la oportunidad para reiterar al Secretaría del Convenio de Estocolmo sobre Contaminantes Orgánicos Persistentes las seguridades de su más alta y distinguida consideración.

Ginebra, 12 de diciembre de 2002

A la Secretaría del Convenio
de Estocolmo sobre Contaminantes
Orgánicos Persistentes
Ginebra

[una pagina sigue]

"INSTRUMENTAL NORMALIZADO PARA LA IDENTIFICACIÓN Y CUANTIFICACIÓN DE LIBERACIONES DE DIOXINAS Y FURANOS", CON BASE EN LA DECISIÓN 6/4 ADOPTADA EN EL SEXTO PERIODO DE SESIONES DEL COMITÉ INTERGUBERNAMENTAL DE NEGOCIACIÓN.

MÉXICO ESTÁ DE ACUERDO EN TÉRMINOS GENERALES CON EL DOCUMENTO EN CUESTIÓN, EN VIRTUD DE QUE EL OBJETIVO DEL INSTRUMENTAL NORMALIZADO, ES PREPARAR UNA METODOLOGÍA SENCILLA Y NORMALIZADA Y UNA BASE DE DATOS QUE PERMITA LA FORMULACIÓN DE INVENTARIOS NACIONALES DE DIBENZO-P-DIOXINAS POLICLORADAS (PCDD) Y DIBENZOFURANOS POLICLORADOS (PCDF), A PARTIR DE LOS PROCEDIMIENTOS RECOMENDADOS POR EL PNUMA QUE TIENEN COMO META LA COMPARABILIDAD INTERNACIONAL, COMO ETAPA PREVIA AL ESTABLECIMIENTO DE MEDIDAS DIRIGIDAS A CONTROLAR O REDUCIR ESAS LIBERACIONES.

SE INFORMA QUE NO OBSTANTE LO ANTERIOR, Y COMO LO RECONOCE EL DOCUMENTO DE REFERENCIA EN EL CAPÍTULO DE LIMITACIONES, ES RELATIVAMENTE POCO LO QUE SE SABE SOBRE PROCESOS Y TECNOLOGÍAS UTILIZADAS EN PAÍSES MENOS DESARROLLADOS. A PARTIR DEL INSTRUMENTAL QUE SE ANALIZA, NO ES POSIBLE INFERIR INFORMACIÓN ACERCA DEL IMPACTO DE LAS DIOXINAS Y FURANOS SOBRE SERES VIVOS EN ECOSISTEMAS ABIERTOS, YA QUE SU DESTINO VARÍA SIGNIFICATIVAMENTE ENTRE UNAS EMISIONES Y OTRAS.

POR OTRO LADO, ES MOTIVO DE PREOCUPACIÓN PARA MÉXICO LA ESCAZA DISPONIBILIDAD DE LA INFORMACIÓN EN NUESTRO PAÍS SOBRE LAS LIBERACIONES DIRECTAS, DE TRANSFERENCIA, LAS GENERADAS A PARTIR DE PRODUCTOS Y RESIDUOS, Y AQUELLAS CLASIFICADAS COMO PUNTOS CALIENTES POTENCIALES, QUE EN ALGUNOS CASOS DEPENDEN DE LOS NIVELES DE TECNOLOGÍA Y DE LOS TIPOS DE OPERACIONES Y PROCESOS APLICADOS, POR LO QUE SEGURAMENTE LA ASISTENCIA DEL PNUMA Y LA COORDINACIÓN A NIVEL NACIONAL SERÁ IMPRESCINDIBLE. SOBRE TODO SI SE CONSIDERA QUE LAS 61 ACTIVIDADES EN LAS QUE SE DEBEN APLICAR LOS FACTORES DE EMISIÓN, QUE SE DIVIDEN EN 10 CATEGORÍAS PRINCIPALES, AGRUPAN DESDE LIBERACIONES AL AGUA, ATMÓSFERA Y SUELOS, HASTA LAS LIBERACIONES PRODUCIDAS POR EL DRAGADO DE SEDIMENTOS Y DE LUGARES DONDE HAY CAOLÍN O ARCILLA PLÁSTICA.

VII. NORWAY

Interim Secretariat of the Stockholm Convention
UNEP Chemicals
11-13 Chemin des Anemones
CH – 1219 Chatelaine
Sveits
Attention: Decision 6/4

Norwegian Pollution Control Authority
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11.12.02
2002/678-5/354.3

Bjorg Fjeld

Comments on the Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases

Dear Sir or Madam,

With reference to letter from the Secretariat of 24 September 2002 inviting countries to provide comments on how the Toolkit can be updated and expanded (Decision INC 6/4) Norway would like to submit the following comments:

When developing national inventories on releases of dioxins and furans the Toolkit was one of the tools used and we found it very useful. However, when an emission factor is given we propose that also the references to the original document from which it is picked should be given together with the emission factor. Further, in the Toolkit the emission factors are linked to branches, but also linked to other codes, and we propose that the possibility to link emission factors to codes used in e.g., Crinair (SNAP-codes) or the EU-directiv on Integrated Pollution Prevention and Control (IPPC), should be looked into.

Finding the existing Toolkit as a useful and well arranged tool, we hope that the set up of the report does not change too much in the next issue.

Yours sincerely,

Signe Namdal
Head of section

Copy to: Ministry of the Environment in Norway

VIII. SWITZERLAND

CH-3003 Berne, January 13, 2002

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UNEP Chemicals
Dr Jim Willis
Geneva

by E-mail to
ssc@chemicals.unep.ch

Your reference

Your letter dated

Our reference StU / B505-0357

Subject **Comments requested by POPs INC-6**

TOOLKIT FOR IDENTIFICATION AND QUANTIFICATION OF DIOXIN AND FURAN RELEASE AS REQUESTED IN THE LETTER DATED SEPT. 24, 2002

Dear Dr Willis

In this letter please find the Swiss responses to the requests for information described in your letter of September 24, 2002, respectively.

- The toolkit is presented in an excellent, very comprehensive, and easily readable paper.
- It approaches the subject in a logical and pragmatic way.
- The lists of emission factors it contains form a very reasonable and practical basis for the establishment of internationally comparable inventories.
- Therefore, there is in our opinion no point in scrutinizing individual values or detailed assessments in these lists.
- Nevertheless, we would like to make two suggestions, whereby the first could be of specific interest to countries having started to compile pertinent data already some time ago:
 - a) It would be helpful to clearly allow for ranges in the tables in order to enable the inclusion of data established earlier on the grounds of classifications which aren't absolutely matching the proposed format or procedure, while still being more or less in line with it (having to review all the details of data collected earlier could be a tremendous work, might therefore not be done 100%, and might in the end result in the suppression of basically available information). Of course, such deviations would have to be clearly identified, which could easily be done, if the forms contained a corresponding field for comments.
 - b) It would probably be helpful for countries in development, if some of the crucial references were made available directly via UNEP's home-page.

We thank you very much for considering our proposals.

Yours sincerely,

Georg Karlaganis, Head
Substances, Soil and Biotechnology Division

IX. USA

January 2, 2003

James P. Willis
Executive Secretary
Interim Secretariat of the Stockholm Convention
on Persistent Organic Pollutants
International Environment House
11-13, chemin des Anémones
CH - 1219 Châtelaine
Geneva, Switzerland

Dear Mr. Willis:

The United States is pleased to submit the attached comments to the *Draft Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*, issued by the United Nations Environment Program in 2001. These comments are being submitted in response to the request issued in accordance with decision 6/4 of the sixth session of the Intergovernmental Negotiating Committee of the Stockholm Convention on Persistent Organic Pollutants (UNEP letter dated 24 September 2002).

We appreciate the opportunity to comment on this key document and look forward to the release of a revised draft. If you have questions or need additional information related to these comments, please contact Dale Evarts (U.S. Environmental Protection Agency, Evarts.dale@epa.gov) or John Thompson (U.S. Department of State, ThompsonJE2@state.gov).

Sincerely,

Jeffrey Lunstead
Director, Office of Environmental Policy
U.S. Department of State

Enclosure

Introduction:

The United States appreciates the extensive work by the United Nations Environmental Program (UNEP) to draft the *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases*. The *Toolkit* is a useful first step to improving the global data set on sources and emissions of dioxins and furans. It provides a basic methodology and tools for developing and industrializing countries to identify sources and characterize releases, as well as the necessary information to develop rudimentary inventories. With appropriate revisions and updates to the current draft, it can effectively serve as provisional guidance for evaluating current and projected releases of Annex C pollutants (unintentional byproducts), which is a critical step in developing action plans for addressing this category of persistent organic pollutants (POPs), as required under subparagraph (a) of Article 5 of the Stockholm Convention. The *Toolkit* also attempts to fulfill this function in a cost-effective manner, especially considering the expense and technological skill necessary to conduct source emission tests. It will lead to standardization of dioxin/furan inventories because it provides default TEQ emission factors for a number of source categories. To the extent developing countries have not tested their sources these default emission factors are useful to estimate annual dioxin releases from specific sources.

General Comments:

Transparency of Emission Factors: The *Toolkit* lacks adequate description and documentation on the derivation of the default emission factors (e.g., sources of information and selection criteria used to filter existing information). In this regard, it is not possible to understand what each emission factor for each source category is intended to represent. A user of the *Toolkit* is faced with the problem of having to match the simplistic and rather generalized emission factors with a particular source under study, and this requires careful description of each source in terms of technology, feedstocks, process flow, product produced, fuels used, and technology used for pollution control. As a suggested improvement, the *Toolkit* could further sub-classify source categories and present default emission factors on the basis of type of technology within each class and type of pollution control systems used within the class. In addition, it would be helpful if the *Toolkit* contained technical appendices that document the derivation and calculation of default emission factors for each source category reviewed in the report. This would assist the user in understanding the degree to which the emission factors can be applied to their source, and would provide a transparent resource with regard to the facilities used and the computation of the emission factor.

Uncertainty: The annual TEQ emission to air, land and water is determined by the multiplication of an emission factor by the annual activity level for a specific source class. The quality and quantity of information supporting both the estimate of the emission factor and the activity level varies greatly. In some cases only a single tested source may have been used to develop an emission factor for the entire source category, and in other cases hundreds of individual facilities within a class may have been tested.

This variability in the robustness of the data introduces uncertainty with regard to how representative an emission factor is to a particular source class. Currently the *Toolkit* is silent with respect to uncertainty, and treats all emission factors as if they were supported by the same quality of information. As a suggestion, the *Toolkit* could introduce a ranking factor scheme or scoring system that qualitatively or quantitatively reflects uncertainty. This indication of uncertainty could be presented along with the emission factor. In this way, the user would have some understanding of the robustness of the data underlying the emission factor. (The U.S. uses a ranking system for its emission factors and will be glad to provide

UNEP with additional information and assistance in developing such as system for the *Toolkit*.)

Underlying Premise of the *Toolkit*: The *Toolkit* undermines its function and purpose by asserting that all existing country-specific inventories of sources and emissions of dioxins and furans are inadequate in terms of assisting developing countries in estimating environmental releases. Furthermore, the *Toolkit* concludes that emission factors from source inventories produced by European countries, the United States, and New Zealand are not representative of sources in developing countries. This conclusion undermines the utility of the *Toolkit* itself, because the emission factors contained in the *Toolkit* are from the same sources of information reviewed in the country-specific inventory reports. As a suggestion, the *Toolkit* should emphasize that country-specific inventories can be additional sources of CDD/CDF emissions information. These inventories and databases of emission factor information should be identified and listed in the references to the report.

Dioxin/Furan Congener-specific emission factors: The emission factors are presented in values of TEQ. The *Toolkit* acknowledges that the TEQ methodology for translating mixtures of dioxins and furans to an analogous emission factor for 2,3,7,8-TCDD, is subject to change. For example, the World Health Organization (WHO) has endorsed a revision to the Toxic Equivalency Factors used to calculate TEQ from congener-specific data. This points to the need for maintaining a structure that preserves the data of emission factors on a dioxin/furan congener-specific basis. This could be accomplished in several ways. First, the *Toolkit* itself could include tables of congener-specific emission factors for each source either in the body of the report or as an appendix. As another suggestion, the *Toolkit* could model the example of the U.S. EPA and develop a rigorous database of dioxin and furan congener-specific emissions and emission factors for a variety of sources. This database could be in a spreadsheet format, and mounted on a Compact Disk, and could be released along with the *Toolkit* report.

Inclusion of hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB): Parties to the Stockholm Convention are required to “evaluate current and projected releases, including the development and maintenance of source inventories and release estimates” of sources of unintentionally produced HCB’s and PCB’s in addition to dioxins and furans. The *Toolkit* will need to expand its coverage to include unintentionally produced HCB’s and PCB’s from the source categories specified in Annex C if it is to be useful in developing inventories in accordance with the Convention. This is best done up front and as early as possible to enable countries to consider these substances along with dioxins and furans as they evaluate their various sources.

Toolkit Validation: To further the accuracy of the UNEP *Toolkit*, it is suggested that the Dioxin/Furan Standardized *Toolkit* be validated. This could be accomplished by using the dioxin/furan inventories of Thailand, which relied heavily on source testing all known source activities in the country. The validation would consist of comparing and contrasting dioxin/furan emissions using the *Toolkit* default emission factors to the inventories developed from direct test data.

Process for Updating the *Toolkit*: The *Toolkit* needs to allow for its revision at some point in the future when additional technical information (e.g., new emissions data, etc.) warrants it. To accomplish this, it is suggested that UNEP Chemicals consider creating an informal advisory committee on emission inventories. Such a committee could communicate via

email and teleconference to assist UNEP in this endeavor and would be comprised of technical experts from developed and developing countries with first-hand experience in developing national inventories of toxic chemicals. The overall benefit of such an approach is that it will enhance the standardization of the approach and broaden the technical resources underlying its effectiveness.

Detailed Comments

- Having the Executive Summary as Section 0 is somewhat awkward and is not standard practice. We recommend that it stand alone and unnumbered.
- Page 11; last ¶: "...Particulate matter from combustion and thermal industrial processes contains unburned carbon where PCDD/PCDF adsorbs onto"; delete "onto".
- Page 11; last ¶: It is not accurate to say that flyashes contain PCDDs/PCDFs in concentrated form; their concentrations are still very low in those media.
- Page 12; first line; suggest "poor process control" as being more accurate than "low process control".
- Page 12; 3rd ¶; delete "obviously" since it is not obvious.
- Page 12; 5th ¶; It must be noted that the mobility of the PCDDs/PCDFs in the residues is not well characterized. They may be present in the residue but may not ever be re-introduced into the environment.
- Page 18; Table 3; some of those sources (e.g., thermal wire reclamation and shredders) are not very well characterized. Is it therefore appropriate to list them or place an "x" under the categories?
- Page 19; another reason that fossil-fuel-fired power plants are not large emitters is that the sulfur in the fuel inhibits formation of dioxins.
- Page 26; the WHO TEQ approach also includes dioxin-like PCBs in the calculations. Clarification is needed here as to whether the dioxin-like PCBs are included or ignored in this approach in the *Toolkit*?
- Page 26; When measured emissions in ng/Nm³ are calculated, they must be corrected to a given concentration basis. The U.S. uses 7% O₂ as the basis for the correction. Canada uses 12% CO₂ and the EU may use something else. An explanation of how to correct measured concentrations to a given basis is extremely important. This might also be addressed on page 28 in the discussion of how demanding it is to obtain PCDD/F data. It should also be mentioned in the cement kiln section, where high O₂ concentrations in the bypass duct make correction to a fixed O₂ concentration less precise than correction to a fixed CO₂ concentration.
- Page 34 ¶1; 2 chamber incinerators are not typically called pyrolysis plants because the first stage is not completely oxygen-free (the definition of true pyrolysis). Rather it is an

oxygen-starved combustion where pyrolysis and combustion simultaneously occur in the first chamber.

- Page 35 ¶1 and ¶2; should be I-TEQ/Nm³ and not TEQ/Nm³. This occurs at many points within the text.
- Page 37; not all rotary kilns used for hazardous waste are slagging type. It is a design consideration that the operators use, but some are operated at lower temperatures. All have afterburners. Their afterburners usually operate at 1000 °C, not 1200 °C. The higher temperatures are typically only used with waste that contains particularly hard to destroy compounds, such as PCBs. Operating at 1000 °C is sufficient to destroy the by-products from the primary chambers for most wastes. Increasing the temperature needlessly results in dramatically increased emissions of NO_x. In addition, there has been no clear evidence that the higher halogen levels in hazardous waste result in higher dioxins than found from municipal waste combustion.

Page 38; again, not all hazardous waste incinerators produce molten slag. Some produce conventional bottom ash.

Page 42; how good are the default emission factors from shredder fluff combustion?

Page 47; how good are the default emission factors for carcass incineration?

Page 49, ¶5, needs a reference for the claim of how flame front disruptions cause more PCDD/F.

Page 59, ¶3-7, are the concentrations in units per Nm³?

Page 75; air and residue are the only considerations, but what about the proliferation of wet scrubbers on power plants. If the *Toolkit* is neglecting the scrubber effluent, it should at least be discussed why. In some countries wet flue gas desulphurization technologies might be used.

Page 75, ¶3; The last sentence is not a complete sentence. “Only if liquid or sludge waste is co-fired high concentrations of PCDD/PCDDF can be expected” is not entirely accurate either. If a liquid or sludge waste is fired, higher concentrations of PCDD/PCDF may be formed.

Page 81; section 6.3.4.2; For many of these sources such as biomass combustion, the release to water could occur if wet scrubbers are used.

Page 84, ¶1, line 3; put a comma after “afterwards”

Page 84, ¶1, put (CaSO₄) after gypsum

Page 84, ¶3, line 10; insert “gas-phase” between long and residence times

Page 85, last ¶; Parenthetical note “(here: 3 kilns, 2 rotary kilns and 1 shaft kiln in Sweden in the years between 1989 and 1993)” is confusing, plus the word “in” is missing the “i”

Page 86, section 6.4.1.5 – it might be mentioned that it is common for a certain fraction of the cement kiln dust to be recycled back into the cement kiln.

Page 95, section 6.5.4; quasi-stationary should be hyphenated

Page 95, section 6.5.4; it is likely that PCDD/F emissions from heavy fuel oil are dependent on the source of the fuel oil since different oils have different mixtures of catalytic metals present in them.

Page 99; US EPA has performed a significant amount of additional testing on uncontrolled waste burning and uses an emission factor of 76.8 ng TEQ/kg waste burned. This is somewhat less than the 300 µg/t used in the *Toolkit*. This revised number has been used in the revised US quantitative dioxin inventory. There is an additional reference for an in press article “Variables Affecting Emissions of PCDDs/PCDFs from Uncontrolled Combustion of Household Waste in Barrels,” Lemieux, P.M.; Gullett, B.K.; Lutes, C.C.; Winterrowd, C.K.; Winters, D.L.; *AWMA Journal*, in press 2002 (attached).

Page 108, ¶2; what do the units m³/t ADt mean?

Page 108, ¶5, do you mean pg/L instead of pq/L?

Page 111, “High Temperatures (>150°C)” – since elsewhere you have said that <200 °C is low temperatures, it is not consistent. Suggest changing this bullet to read “Temperatures > 150 °C”.

Page 129, section 6.7.5, ¶2; when concentrations in leather breast wallets is discussed, clarification is needed as to which compound is being talked about. Insert “of PCDD/PCDF” after concentration. It is confusing because that sentence is bracketed by 2 other sentences talking about PCP.

Page 132, section 6.8.2.2; wastewater-free wet scrubbers may not be present in the US. The scrubber blowdown may end up in the sewer system.

Page 133, section 6.8.3.4; variability in the PCDD/PCDF in the foodstuffs should not occur (e.g., in some smoked foods but not in other smoked foods) if the smoking process has anything at all to do with the presence in the foodstuffs. Rather the PCDD/PCDF is likely present in the foodstuffs themselves irregardless of the smoking process. Isn't it somewhat treating the inventory unfairly by including smoked foods but not including un-smoked foods?

Page 136, ¶1, line 9; suggest using “animal feed” instead of “feedingstuff.”

Page 139, section 6.9.2, ¶1; “Further countries like Germany and Austria with legislation in place, routinely analyze sewage sludges for PCDD/PCDF.” is somewhat awkward phrasing. Suggest revising to “Countries such as Germany and Austria, with legislation in place, routinely analyze sewage sludges for PCDD/PCDF.”

Page 142, Section 6.9.4.2 is empty.

Page 144, Section 6.10.2; “high concentrations of mercury” at the site should be a contamination concern in and of itself, worthy of evaluation, and should be mentioned (even though it is not strictly within the scope of the *Toolkit*).

Page 145-146, it is not clear whether the emission factor shown is the PCDD/PCDF emission factor in the PCB or else the TEQ of the PCBs themselves in terms of WHO98 TEFs. This section needs a bit of clarification of exactly what is in Table 70.

Page 146, section 6.10.7; the list should be bulleted. Also the (3) at the beginning of the list should be deleted.

X. WORKSHOP OF SEVEN LATIN AMERICAN COUNTRIES

Taller de Iniciación del Proyecto “Toolkit en América del Sur y Caribe”

**2–5 de diciembre de 2002
Asunción – Paraguay**

Sesión Inaugural - Lunes 5 de diciembre

Apertura

La jornada de inauguración contó con la presencia e intervención del Ministro de Agricultura y Ganadería del Paraguay Sr. Darío Baumgarten, el Director Adjunto de UNEP Chemicals Sr. John Whitelaw y el Embajador del Ecuador en Paraguay Sr. Homero Larrea Cevallos.

Las intervenciones destacaron la importancia de este proyecto, como una herramienta para avanzar en la protección de la salud pública y el medio ambiente, frente a los efectos de los contaminantes orgánicos persistentes (COPs).

El Sr. Ministro Baumgarten, destacó la diferencia entre las dioxinas y furanos, respecto del resto de los contaminantes incluidos en la lista del Convenio de Estocolmo, en cuanto a que éstas (las dioxinas y furanos) requieren de un proceso continuo de disminución o eliminación de sus emisiones, por tratarse de emisiones producidas no-intencionalmente. Asimismo, resaltó la importancia de la colaboración inter-institucional en este proceso, para el caso particular del Paraguay, entre la Secretaría del Ambiente, el Vice Ministerio de Agricultura-Dirección de Defensa Vegetal y la Dirección Nacional de Salud Ambiental (SENASA).

El Sr. John Whitelaw, destacó los objetivos y las características definidas para este Taller, enfocado específicamente a la elaboración de Inventarios de dioxinas y furanos, haciendo hincapié en la particularidad de estas sustancias, respecto de los otros COPs, en cuanto a que éstos últimos se pueden dejar de producir, sin embargo en el caso de las dioxinas y furanos, no es posible detener su producción, sino que se deben disminuir o si es posible eliminar sus liberaciones continuamente. Destaca también que en esta labor, es fundamental la participación conjunta de los distintos organismos involucrados en la elaboración de inventarios en los países.

Países presentes: Paraguay, Argentina, Chile, Brasil, Cuba, Uruguay, Ecuador.

Intervenciones - 1er día

Dra. Heidelore Fiedler, PNUMA Productos Químicos.

Destacó que los objetivos del Taller se orientan a la elaboración de Inventarios Nacionales de Dioxinas y Furanos, teniendo como directriz el Instrumental Normalizado (Toolkit) elaborado por el PNUMA. Señaló además, que el producto final de este Taller, será obtener una propuesta de Plan de Trabajo para este propósito, en cada uno de los países.

En cuanto al Proyecto de Inventario de Dioxinas y Furanos, señaló que está financiado por fondos canadienses del Banco Mundial y que es un proyecto que en la actualidad está implementado en Paraguay, Cuba y Argentina. Asimismo, agregó que se trata de un proyecto adicional a los Planes Nacionales de Implementación de los países, cuyo resultado (la realización de los inventarios de los países), se remitirá posteriormente al Comité Intergubernamental de Negociaciones o a la Conferencia de las Partes.

Sr. John Whitelaw, PNUMA Productos Químicos.

Destacó aspectos relacionados con la firma y adopción del Convenio de Estocolmo, señalando que el 22 de Mayo de 2001, 151 países firmaron este Convenio, de los cuales en la

actualidad 23 ya lo han ratificado, siendo necesaria la ratificación de al menos 50 países para que pueda entrar en vigor.

Enfatizó el hecho de que el Taller representa un paso más en la creación de capacidades nacionales para la implementación del Convenio de Estocolmo en los países de la región. Destacó además, la necesidad de que los países apliquen las mejores técnicas disponibles y las mejores prácticas ambientales para disminuir y/o eliminar las emisiones y/o liberaciones de dioxinas y furanos.

Presentaciones sobre cops no intencionales de los países participantes

Moderadores: Dra. Heidelore Fiedler PNUMA y Dr. Rodrigo Romero, Chile

Uruguay

Presenta el Inventario Nacional de Liberaciones de Dioxinas y Furanos en Uruguay. Destaca la metodología utilizada, desarrollando en detalle distintos aspectos controversiales con los cuales se enfrentaron al momento de recopilar la información y/o aplicar los factores de emisión del Instrumental Normalizado Toolkit en el país.

Asimismo, presenta las estimaciones y los resultados obtenidos para las diferentes matrices ambientales en la elaboración del inventario de emisiones de dioxinas y furanos en el Uruguay.

Dentro de las conclusiones, desglosa y analiza los resultados obtenidos para las diferentes categorías de fuentes y matrices ambientales afectadas. Asimismo, también analiza fuentes de incertidumbre, destacando que el objetivo principal de esta etapa es poder contar con una aproximación acerca de la magnitud de las emisiones y la identificación de las principales fuentes.

Finalmente describe medidas para la reducción de emisiones y menciona la posibilidad de la ejecución de un proyecto regional orientado a la validación de los factores de emisión y/o la posible afinación (mejoramiento) de resultados obtenidos.

Argentina

Presenta el inventario preliminar de dioxinas y furanos, con la identificación de las fuentes emisoras principales. Destaca la utilización de diversas fuentes de información, tales como el Inventario de emisiones de gases invernadero existente en la Argentina, estadísticas nacionales e información del Plan Nacional de Lucha contra el Fuego. Asimismo, respecto de las categorías descritas en el Toolkit, describe las principales fuentes para cada una de ellas y presenta datos de liberaciones de dioxinas y furanos en el país.

Dentro de las conclusiones destaca las fuentes principales que aportan a la emisión de dioxinas y furanos. Asimismo indica los vacíos de información existentes y finalmente entrega una lista donde identifica los actores relevantes en el tema de la elaboración del inventario, a nivel nacional.

Paraguay

Se refirió específicamente a los problemas del tratamiento de residuos patológicos de centros asistenciales públicos y privados del área metropolitana, por medio de la incineración.

Destacó dentro de las tareas urgentes de mejorar, la separación y clasificación de los residuos y el manejo adecuado de los incineradores, señalando que existe la posibilidad de implementar tecnologías alternativas como los autoclaves y sistemas de microondas para el tratamiento de los residuos. Asimismo, se refirió a la futura instalación de equipos similares de incineración, en tres sectores del país. Ciudad del Este, Encarnación y Pedro Juan Caballero.

Cuba

Destacó que aun no poseen un inventario de dioxinas y furanos. Sin embargo, considera que esto no debería representar mayores dificultades, por cuanto no cuentan con un nivel elevado de industrialización y la gestión de sustancias químicas está concentrada en agroquímicos. No obstante destaca que esta gestión en la actualidad, no está incluida dentro de las esferas

prioritarias de la Agenda Química Ambiental, puesto que el deterioro de los suelos y la salinización de aguas representan problemas de mayor envergadura.

Los principales problemas de COPs en Cuba son las existencias (almacenamientos) de plaguicidas, el uso de PCBs en equipos eléctricos y las emisiones de dioxinas y furanos. Además de algunos puntos calientes tales como la producción de cloro en celdas de mercurio. Propone una estrategia de trabajo, donde aparte de la colaboración y creación de capacidades “Norte-Sur”, también se prioricen las posibilidades de implementar y fortalecer la colaboración “Sur-Sur” en éste ámbito.

Ecuador

Describe la situación actual del Ecuador en el marco del presente proyecto, entregando además información y datos acerca de las emisiones de dioxinas y furanos en el país. Destaca que éstas son preliminares y tienen un alto grado de incertidumbre. Las emisiones caracterizadas corresponden a las categorías de incineración de desechos, generación de energía y calefacción, producción de productos minerales, transporte, procesos de combustión incontrolado, producción y uso de sustancias químicas y bienes de consumo, varios y manejo de desechos.

Concluye que en la emisión total de dioxinas y furanos, los mayores aportes se deben a la producción de productos minerales y a procesos de combustión no controlados. Asimismo, no existen factores de emisión para la producción de petróleo, que es la actividad de mayor significación económica para el país.

Destaca el interés del Gobierno actual y espera que la ratificación del Convenio de Estocolmo, al igual que el de Rotterdam, se de antes del fin de su mandato. Asimismo, señala que Ecuador es uno de los países pilotos del proyecto GEF para la Implementación del Convenio de Estocolmo, por lo cual se encuentran elaborando los términos de referencia para la realización del Inventario de dioxinas y furanos.

Chile

Se presentan tres aspectos relevantes relacionados con los COPs no-intencionales en el país. Respecto de la situación nacional, se destaca la elaboración de la norma de emisión para la incineración y coincineración de residuos, señalando que no se apoya la incineración, sino que sólo se desea establecer reglas claras para todas aquellas instalaciones que ejercen esta actividad en el país. También destaca las acumulaciones de aserrines con PCP contaminado con dioxinas en el sur del país.

Respecto de las fuentes potenciales de dioxinas y furanos se manifiesta con relación a las emisiones provenientes de la producción de cobre en el país. Destaca que Chile está elaborando un informe para remitir al PNUMA Productos Químicos, a fin de descartar las emisiones de dioxinas y furanos asignadas a las fundiciones primarias de cobre. Presenta diversos aspectos técnicos de dicho informe.

Finalmente se hizo una breve reseña acerca de aspectos técnicos relacionados con los COPs no intencionales desarrollados en el país. Se destacó la existencia de capacidad para la elaboración de inventarios de emisiones, aplicado al problema de la contaminación atmosférica de Santiago, señalando la importancia del proceso de validación de los factores de emisión utilizados, sobre la base de la experiencia desarrollada. Finalmente destacó la realización de un primer Estudio de PCBs en la atmósfera de Santiago y señaló la participación de Chile en un proyecto GEF regional sobre PTS y la ejecución de un proyecto UNEP/GEF para la elaboración de Plan Nacional de Implementación.

Brasil

Describe el estado actual del tema de las emisiones no intencionales de dioxinas y furanos en Brasil. Destacando las perspectivas y particularmente la necesidad de capacitación de personal técnico que pueda llevar a cabo la realización del Inventario de emisiones de dioxinas y furanos en el país.

PRESENTACIÓN TÉCNICA INTRODUCTORIA AL TRABAJO DEL TALLER

Dra. Heidelore Fiedler, PNUMA Productos Químicos

Se refirió al inventario de dioxinas y furanos globales y el método de establecer inventarios comparables. Señala que en 1999 el PNUMA realizó una compilación de inventarios de dioxinas y furanos concluyendo que no hay métodos armonizados y los inventarios no son fácilmente comparables. Presenta datos de emisiones a la atmósfera de diferentes países, señalando sus fuentes principales.

Con respecto al Convenio de Estocolmo presenta los requisitos del artículo 5 y el Instrumental Normalizado para la identificación y cuantificación de dioxinas y furanos aplicado en Tailandia, Uruguay, Nigeria, Filipinas, Vietnam, Brunei, Jordania, Líbano, Argentina, Cuba, Paraguay.

Respecto del Instrumental presenta sus aspectos principales tanto metodológicos como de aplicación en base a una matriz de selección con categorías y subcategorías de fuentes. Detalla los contenidos de las planillas Excel para ser utilizadas durante la elaboración de los inventarios.

PRESENTACIÓN Y DISCUSIÓN EN DETALLE SOBRE LAS CATEGORÍAS DE FUENTES

Martes 3 de diciembre - Moderador: Javier Martinez

Categoría 1. Incineración de desechos

De los países participantes Brasil utiliza la tecnología de incineración de desechos urbanos. Argentina y Brasil cuentan con incineradoras de desechos peligrosos y todos los países cuentan con incineradores de desechos hospitalarios con diferentes grados de tecnificación. En todos los casos existen registros de las condiciones y cantidades procesadas en los órganos de control públicos, por lo que la obtención de la información resulta sencilla.

Respecto a los índices para residuos hospitalarios se considera que se deberían ajustar para el tipo de residuos y las tecnologías características de esta región.

La incineración de cadáveres de animales resulta ser más difusa en cuanto a la recopilación de información.

Categoría 6. Procesos de combustión incontrolada

Respecto a los incendios forestales todos los países cuentan con estadísticas de números de incendios y superficies quemadas, en algunos casos del tipo de especies de árboles afectadas. Se plantea la inquietud en cuanto a la estimación de la biomasa quemada y a la representatividad de los índices recomendados. Se plantea la necesidad homologar los procedimientos para que todos los países hagan estimaciones comparables.

La quema de residuos agrícolas (caña de azúcar, bananos, cáscara de arroz) es práctica común en la mayoría de los países. En este caso la estimación de la biomasa quemada es difícil de contabilizar. Para esto se identifican como potenciales fuentes de información los inventarios de liberaciones de gases de efecto invernadero y datos recopilados por los ministerios de Agricultura.

En la mayoría de los países se práctica la quema a cielo abierto de residuos urbanos en los pequeños centros poblados y zonas rurales. En este caso será necesario consultar a las municipalidades y realizar estimaciones. Se plantean dudas respecto al índice recomendado. Los factores de emisión para los incendios accidentales de vehículos se deben expresar como $\mu\text{g EQT/vehículos}$, cuadro 48 página 112.

Categoría 2. Producción de metales ferrosos y no ferrosos

La producción de hierro y acero no presenta problemas debido a que se trata de industrias fáciles de identificar y recopilar la información necesaria.

Respecto a la recuperación térmica de cables, Chile solicita que se establezca que se trata de cables recubiertos con PVC.

Chile también plantea la necesidad de diferenciar dentro de la producción primaria de cobre,

aquella que no utiliza chatarra.

En general se plantea el problema de obtener información sobre pequeñas fundiciones de tipo informal que son muy comunes en el manejo de plomo y otros metales no ferrosos.

También se plantea la inconsistencia del índice recomendado para el bronce, por comparación con los del cobre.

Categoría 4. Productos minerales

En cuanto a la recopilación de datos, los hornos de cementos no representan un problema ya que es fácil obtener la información. En la mayoría de los países se incineran residuos en estos hornos.

En algunos países, la producción de ladrillos se realiza a nivel informal por lo que en tales casos resultará difícil obtener información, siendo necesaria la estimación. En el caso de la producción de cerámicas el nivel de informalidad podría ser menor.

La producción de mezclas asfálticas se podría estimar por ejemplo en base a los kilómetros de carreteras nuevas o reparadas.

Categoría 3. Generación de energía y calefacción

No se plantean problemas en este punto ya que existen datos de balances energéticos nacionales y censos de población y vivienda. Puede ser necesario recurrir a algunas estimaciones como son el consumo de leña.

Categoría 7. Producción y uso de sustancias químicas y bienes de consumo

En general se trata de actividades localizadas, por lo que en principio la recopilación de información no plantea mayores problemas.

Respecto a la fabricación de pasta y papel se sugiere plantear en forma más clara los factores de emisión para las diferentes tecnologías.

Ecuador plantea que sería conveniente contar con factores de emisión para industria del petróleo ya que esta es una actividad importante en aquel país.

Se planteó la inquietud acerca de los criterios para la elección del factor de emisión para los productos textiles.

Se solicita hacer la corrección en la página 119 del Instrumental Normalizado, 2do párrafo, donde dice “que se refiere a una pasta desecada al 90% y 900 kilos de pasta absolutamente seca” debe decir “que se refiere a una pasta desecada al 90% es decir 900 kilos de pasta absolutamente seca por tonelada”. Además en la subcategoría de pasta y papel el término “chlorine free” se considerará como blanqueo libre de cloro gaseoso (Cl₂).

Categoría 5. Transporte

No se plantearon inconvenientes para la obtención de esta información. Se indicó que se deben incluir los consumos de combustibles de los barcos de ultramar.

Se solicita hacer la corrección en la página 106, cuadro 43, No 3, donde dice “combustible con plomo con catalizador” debe decir “combustible sin plomo con catalizador”. En esta misma página (nota al pie) se debe corregir “0,000074” por “0,00074”

Se solicita también hacer la corrección en la página 108 cuadro 45 donde dice “factor de emisión µg EQT/t de combustible quemado a la atmósfera = 0,5”, debe decir, “factor de emisión µg EQT/t de combustible quemado a la atmósfera = 0,1”.

Miercoles 4 de diciembre - Continuación del análisis de categorías

Categoría 8. Varios

Respecto al desecado de biomasa los países revisarán las prácticas que utilicen el contacto directo con los gases de combustión. Esto podría ser una práctica de pequeñas producciones de yerba en Paraguay.

La información sobre crematorios sería fácil de recopilar ya que están en las órbitas de las administraciones municipales. Brasil cuenta con 13 crematorios y se encuentran bajo la ley

de residuos por lo que tienen sistemas de tratamiento para cumplir con límites máximos de emisión.

Los ahumaderos solo se utilizan a nivel de producciones de tipo artesanal por lo que se estima que la recopilación de información no será sencilla y se deberán hacer estimaciones.

Para limpieza en seco se considera que el factor más bajo es el más aplicable en la región y que la estimación de la emisión total se puede realizar en base al consumo de solventes por el sector y el índice de generación de colas de destilación.

La estimación del consumo de tabaco es sencilla pues existen estadísticas en todos los países.

Categoría 9. Manejo de desechos

Se manifiesta la necesidad de utilizar terminología más comúnmente utilizada en la región como vertederos, rellenos sanitarios, efluentes líquidos domésticos y cuerpos de agua entre otros.

Respecto al lixiviado de rellenos sanitarios se manifiesta que su estimación no es sencilla, debido a las diferentes formas tipos de vertederos y rellenos así como la forma de operación.

En relación a los efluentes líquidos domésticos, Uruguay plantea una inconsistencia en la tabla de factores de emisión (cuadro 66) ya que no cierra el balance de masa. En relación a este punto la estimación parece sencilla ya que la información estaría bastante centralizada. Se manifiesta que los factores de emisión del comportamiento están asociados a la presencia de dioxinas y furanos en la materia prima y que el aumento de la concentración por causas biogénicas no es muy importante.

En relación a los vertidos a cuerpos de agua surgen dudas del significado de este punto y su diferencia con el vertido de efluentes líquidos domésticos. En principio se acuerda que la diferencia es que el último caso corresponde a aquéllos casos que centralizan la recolección mientras que el resto corresponde a vertidos aislados.

Respecto al punto evacuación de aceites de desechos, se indica que se trata de procesos de tratamientos de aceites contaminados. No se incluye la incineración.

Como comentario general se plantea que o es conveniente realizar mucho esfuerzo en estimar las emisiones correspondientes a procesos que tienen muy poca incidencia como el caso de compostaje y cigarrillos entre otros.

Categoría 10: Puntos calientes

Brasil tiene identificado un sitio contaminado donde se producía hexa cloro ciclohexano y saben de la existencia de otros. Chile informa que cuenta con restos de aserrín contaminado y está realizando las gestiones para eliminarlos. Todos los países estiman que tienen existencia de sitios potencialmente contaminados con PCP vinculados a actividades de preservación de madera.

En relación a los PCBs los países cuentan con algo de información obtenida a través de inventarios, pero en muchos casos esa información es muy reducida. Esta actividad es contemplada en los NIP.

“ factor de emisión $\mu\text{g EQT/t}$ de combustible quemado a la atmósfera = 0,5”.

Discusión sobre los cuestionarios

Se manifiesta que los cuestionarios pueden ser demasiado detallados y extensos lo que puede implicar que los actores involucrados no los llenen. Se sugiere que cada país evalúe las posibilidades que existe de la utilización del formulario tal cual está presentado y cuando lo crea conveniente lo sustituya por otro que contenga la información básica que se requiere para poder aplicar el Toolkit.

I. Identificación de las necesidades por los países

Se elige como coordinador de esta sesión, al representante de Cuba, Sr. Mario Abó, quien da a conocer lo que se espera de este módulo del taller e invita a los representantes de las delegaciones, a identificar las necesidades específicas que se prevén para la iniciación del Inventario de dioxinas y furanos.

Se resalta que si bien se han designado tres países “piloto” (Argentina, Cuba y Paraguay) para la aplicación del instrumental normalizado “Toolkit”, todos los países deberán realizar su Plan Nacional de Implementación (NIP), y la experiencia de la aplicación de la herramienta mencionada permitirá diseñar el Plan Nacional en relación con las dioxinas y furanos.

En este contexto, los países participantes expusieron la forma de encarar dicho inventario y cómo, a su criterio, se podría facilitar la realización del mismo:

1. Chile, manifiesta que la realización se vería facilitada si se pudiera efectuar una selección previa de las categorías de mayor relevancia en la liberación de dioxinas y furanos, a efectos de no dirigir esfuerzos y recursos a categorías de poco peso, fundamentalmente en aquellas donde se cuenta con datos dispersos, de gran variabilidad y dificultad de recopilación. Asimismo, considera que será de gran utilidad la cuantificación de D&F en algunos puntos calientes, entre los que mencionan acopios de aserrín de madera potencialmente tratada con pentaclorofenol, pasivos de PCBs, etc. También, manifiesta que este país prevé iniciar el inventario a principios del próximo de año.

Se aclara que tanto este país como Ecuador fueron elegidos países Piloto en la realización del NIP; y como parte del Plan se incluye un inventario de dioxinas y furanos. El proyecto NIP para Chile se divide en siete etapas y ya se ha conformado un Comité para la realización del mismo, constituido por sectores gubernamentales, privados y no gubernamentales. Se prevé asimismo, tercerizar parte del trabajo a Consultoras contratadas a tal efecto, bajo coordinación de la CONAMA.

Asimismo destaca la necesidad de asistencia técnica para la recopilación de información de fuentes difusas que pudiesen ser significativas para la estimación del total de las emisiones. Por otra parte se mencionó algunos vacíos del Instrumental Normalizado, respecto de la descripción de algunas categorías, especialmente las de procesos metalúrgicos. Se propone desglosar aun más las subcategorías.

2. Paraguay, menciona como parte de su dificultad en la realización, la falta de una normativa nacional para el control de emisiones atmosféricas, y la falta de técnicos expertos en el tema. En este sentido, agradece toda posible colaboración del PNUMA, que pueda facilitar la realización de la normativa.

Otra de las dificultades previstas, es lograr la colaboración de todos los sectores. No se descarta en este sentido, que deba realizarse algún acuerdo ó memorandum de entendimiento entre los actores involucrados.

3. Brasil, manifiesta estar preparando su proyecto de Plan Nacional de Implementación, en el que se considera el inventario de dioxinas y furanos. En cuanto a la aplicación del Toolkit, se considera que la mayor parte de la información podrá ser suministrada por los organismos ambientales, ya que son los organismos responsables del control de las actividades potencialmente contaminantes.

Se manifiesta que Brasil cuenta con un Comité de Seguridad Química, conformado por representantes de los distintos sectores gubernamentales, privados y de la sociedad civil, que tendrá un rol importante en la realización, aunque se prevé la contratación de terceros especialistas, para el procesamiento de los datos.

4. Ecuador, considera que tendrá dificultad en la obtención de datos de fuentes difusas. Asimismo, estima que será necesario una revisión y simplificación de los cuestionarios para facilitar la recolección de información. Será necesario contar con asistencia técnica de expertos para que la recopilación y análisis de datos sea efectiva.

Asimismo, reitera la relevancia de la actividad petrolera en el país, y la importancia de contar con factores de emisión para este sector.

Se hace hincapié en la importancia de contar con determinaciones cuantitativas en la región, proponiendo la incentivación o la creación de un centro regional para la identificación de las dioxinas y furanos.

El representante de Ecuador estima que en Enero se dará comienzo al inventario, para lo cual está prevista la contratación de terceros.

Ecuador, como país piloto del NIP, ya cuenta con su proyecto aprobado, en el que se ha previsto que el mismo comité inter-institucional que trabajó hace un año en un proyecto con apoyo de UNITAR, y en el que se han incorporado nuevos actores, sea el que coordine a nivel nacional el proyecto NIP. Grupos de tareas para el desarrollo del inventario de dioxinas y furanos han sido conformados en las tres principales ciudades del país.

Actualmente se están desarrollando los términos de referencia para realizar el inventario.

A efectos de la concientización en el tema se ha programado la realización de talleres para cada una de las tres regiones en las que se ha dividido el país para este proyecto, los mismos que podrían iniciarse a fines del presente mes.

A continuación se analizan los términos para el Taller Nacional de Implementación del Toolkit. En este sentido, se realizan las siguientes consideraciones:

1. Argentina, manifiesta que dicho Taller se realizará alrededor del mes de marzo, y tendrá el propósito de concientizar a los distintos sectores y motivar la colaboración de los distintos actores.

No obstante, y dadas la experiencia del pasado en el tema del PCB, se deberá tener cuidado en la difusión del tema, de forma que no se generen recelos en los distintos sectores de la actividad industrial, que colaborarán suministrando la información pertinente.

Se menciona que es relevante la extensión de los alcances del instrumental, por ejemplo para encarar proyectos vinculados, determinación del impacto sobre la salud y el ambiente.

Argentina ya realizó un ejercicio preliminar al inventario, con mínimos recursos, lo que le permite prever ciertas categorías principales, sobre las que se trabajará preferentemente.

Si bien, Argentina deberá contar con la colaboración del Consejo Federal del Medioambiente, los Municipios, y distintos sectores, gubernamentales y no gubernamentales; la realización del mencionado ejercicio preliminar, hace prever que no sería necesario la contratación de terceros y que podrá cumplir con el término tope de referencia comprometido para la entrega del informe final.

2. Paraguay, coincide con Argentina en que es importante que el tema no caiga en sensacionalismo, y provoque recelo en los sectores privados. La necesidad de fortalecer la capacidad interna del país, el trabajo coordinado entre las instituciones para salir adelante en el tema. En este sentido, considera de gran importancia la oficina de trabajo conjunto, previsto en el proyecto del Plan Nacional de Implementación para ser presentado al GEF.

3. Cuba, manifiesta que está prevista la realización de un Taller Nacional, con el cual se garantizaría la capacitación y selección de los principales actores involucrados en la realización del inventario definitivo. Se hizo hincapié en la necesidad de asistencia técnica en las etapas iniciales de desarrollo. Se estima un plazo de tiempo de siete a ocho meses para la culminación del inventario.

Coincide con lo manifestado por otros países en cuanto a una correcta difusión del tema, y a la focalización de esfuerzos en las categorías prioritarias para el país. No se descarta, en este sentido, la adaptación de los cuestionarios para facilitar la entrega de la información.

El delegado de Cuba, y coordinador de este módulo del Taller, comenta que su país, ha presentado para su aprobación el proyecto NIP, el que actualmente, se encuentra en el proceso de revisión. El proyecto Toolkit aportará elementos para el diseño de las actividades de dioxinas y furanos comprendidas en el Plan Nacional de Implementación.

4. Chile, pone a consideración posibilidad de trabajar sólo sobre categorías prioritarias comunes. En relación con esto, otras delegaciones, como Cuba y Argentina, acotan que la priorización de categorías sea realizada por cada uno de los países, ya que de esta forma cada país podrá delinear su Plan Nacional en base a sus necesidades específicas.

Finalmente, se consideran los plazos tope para la entrega de un informe de avance, el 31 de

marzo del 2003, y el informe “final” a fines del 2003.

Argentina, comentó la ventaja de acotar el tiempo de entrega, aunque posteriormente puede darse un tiempo adicional para completar el mismo.

La delegada de **Chile** agregó que como la entrega del informe NIP tiene un término establecido, en principio no habría inconvenientes en tener el resultado del Toolkit para enero de 2004, siempre que esto se ajuste al cronograma establecido para la elaboración del NIP.

La representante de PNUMA sustancias químicas, informó que se prevé una reunión hacia la mitad del proyecto para realizar un seguimiento sobre el grado de avance del mismo. Y que el primer informe de marzo puede ser breve, con la indicación de puntos relevantes, las conclusiones del Taller de Iniciación, y la conformación del grupo de trabajo.

Asimismo, se aclararon algunos aspectos en cuanto al compromiso de los países en relación al Toolkit y al Plan Nacional de Implementación. Sin perjuicio de que los países piloto tienen un compromiso de completar el Toolkit en el plazo previsto, todos los demás países podrán incorporar este inventario como una primera etapa en el Plan Nacional de Implementación, y ajustar detalles del mismo, a lo largo de dicho Plan.

Ante consultas de un delegado sobre los términos de referencia para la realización del informe final, y el detalle de la información a aportar; se aclaró que la información que se publique, no incluirá nombres de empresas, o información que ponga en mayor evidencia a los responsables de una actividad específica. Se buscará en lo posible generalizar la información. En definitiva los detalles del informe final, se podrían decidir en el Taller Intermedio.

La reunión intermedia de grado de avance podría ser facilitada por el PNUMA alrededor del mes de octubre de 2003.

Jueves 5 de diciembre - Moderador: Carlos Martínez

Sumario

- Los países participantes se plantean de acuerdo en utilizar el Toolkit para el establecimiento de su primer inventario de emisiones de D/F.
- Asimismo, reconocen algunas lagunas o vacíos con relación a si acaso el Toolkit caracteriza correctamente algunas situaciones en los respectivos países con relación a las emisiones o liberaciones de D/F. De la misma forma, si acaso algunos de los factores de emisión son los más adecuados para aplicar debido a algunas especificidades de la región.
- Reconociendo las limitaciones asociadas a la aplicación en términos de los vacíos de información y la validez de los factores de emisión, se considera que el Instrumental Normalizado del PNUMA, constituye una buena base para el desarrollo de los trabajos orientados al conocimiento inicial de las emisiones de D y F.
- Las conclusiones y el contenido de este Taller debería considerarse como contribución de la región a la CIN, respondiendo a la decisión de CIN-6 de solicitar información a los respectivos países
- Se reconoce que el Toolkit es una herramienta importante para suministrar datos de base que serán alimentados al proyecto nacional de implementación.
- Se pretende que sea además un punto de partida para el desarrollo de proyectos futuros en los cuales se puedan realizar correlaciones con la afectación de estos contaminantes a la salud pública y el ambiente en general.

XI. WORKSHOP OF FIVE ASIAN COUNTRIES

Asia Dioxin Toolkit Project – Data Evaluation Workshop

General

The Project work plan, which was agreed upon at the Kick-off Workshop in Hanoi, Vietnam (October 1-4, 2001) includes a data evaluation workshop to discuss the draft inventories prepared by the five participating countries. This Data Evaluation Workshop was held December 17-19, 2002 at the Orchid Garden Hotel in Bandar Seri Begawan, Brunei Darussalam and was attended by experts from five Asian countries and two UNEP staff. For complete addresses of the participants, see Appendix 1, page _____. The agenda for the Workshop was as follows (for details, see Appendix 2, page _____):

- 1) Opening of the workshop
- 2) Summary of the present status of signatories/ratifications of the Stockholm Convention; decisions from the INC-6 and next steps under the Convention;
- 3) Objectives and expected outcomes of this project;
- 4) Presentation and discussions of national dioxin/furan inventories;
- 5) Lessons learnt through the application of the Toolkit and inventory making;
- 6) Finalization of the of the national inventories;
- 7) Recommendations, updating, and follow-up;
- 8) Closure of the meeting.

The workshop was opened by Hj Mohd Zakaria Hj Sarudin, Acting Director of the Department of Environment, Parks and Recreation of the Ministry of Development, Brunei Darussalam and Mr. John Whitelaw, Deputy Director, UNEP Chemicals. Hj Zakaria welcomed the participants on behalf of his Department. He highlighted the importance of this workshop in exchanging information gained during the last year, suggested that the results of this work could be adopted for wider application; and would be an important contribution to the successful implementation of the Stockholm Convention. He mentioned that Brunei Darussalam signed the Stockholm Convention on 21 May 2001 and that the country places great importance to the Dioxin Toolkit Project in laying the foundation needed for planning and development of a national implementation plan to eventually eliminate persistent organic pollutants. He informed the participants that with the assistance of UNEP Chemicals, Brunei Darussalam has formulated its national implementation plan to meet the Convention's obligations. He thanked the Brunei Consultative Committee for their valuable contribution and support in undertaking the dioxin and furan Toolkit project and UNEP Chemicals for its support throughout the project. He closed by wishing all participants a successful workshop and a pleasant and memorable stay in Brunei Darussalam. (For full text see page _____).

Mr Whitelaw thanked the Acting Director Hj Zakaria for his welcoming remarks, and welcomed participants on behalf of UNEP Chemicals. He referred to the dioxin issue as important both regionally and globally. Under the Convention, it is treated differently from the other POPs, in that the goal is continued minimization, while the goal for the other POPs is elimination. The implication is that governments have an ongoing responsibility in managing dioxins and furans. A further advantage of the Toolkit was harmonisation of inventories globally – this is important for the ongoing monitoring and evaluation of the

Convention. The first step is identifying the source, and it was in that context that UNEP Chemicals had developed the Toolkit and had sought to test it with the cooperation of the five countries participating in the project. One of the prime objectives of the project, along with the preparation of inventories for the participating countries, was the identification of regional issues and omissions. These would be addressed in the update of the Toolkit.

Ms. Heidelore Fiedler, project leader, gave a brief overview on the expected outcomes of this workshop and the project. She stressed that there are two audiences for the results:

- 1) The international community that will receive five more national inventories on releases of dioxins and furans. These five new inventories will enlarge the global database that at present has only about two dozen PCDD/PCDF inventories;
- 2) UNEP Chemicals that will obtain feedback on the applicability of the Toolkit, in order to improve and amend its methodology to better suit the needs and circumstances of developing countries.

National PCDD/PCDF Inventories

Participating countries presented their experiences and results of their national dioxin/furan release inventories. The presentations are at a draft stage presently.

Brunei Darussalam

Brunei Darussalam initiated its dioxin and furan inventory with a national workshop in January 2002, inviting all relevant departments, industry, academic and NGOs concerned. After this information and training workshop, questionnaires were designed and sent out to obtain more detailed information on certain activities realized in the country that may generate and release dioxins and furans. In some cases follow-up was needed and site visits were performed to obtain information. Information on activities was obtained for the year 2001. Brunei Darussalam screened all the sources categories listed in the Toolkit and recognized that many of the activities described therein were not practiced in the country.

- Category 1 (waste incineration) - only incineration of hospital waste is practiced; the incinerators in Brunei Darussalam are relatively small and are operated in batch-mode.
- Category 2 - (ferrous and non-ferrous metal production) charcoal production, utilizing local mangrove wood as raw material is the only activity. It was assumed that the same criteria as described in the Toolkit for the coke production would apply for charcoal production as well. This was identified though as an area for further clarification by UNEP Chemicals.
- Category 3 (generation of energy) - The production of energy is based on natural gas and Diesel fuel; whereby the natural gas fired plants emitted about 20 mg TEQ into the air. Another 0.14 mg TEQ/a is released from the diesel-fuelled plant. Cooking at home is mostly practiced utilizing a mixture of butane and propane gases; the emission factor for natural gas had been applied for this activity.
- Category 4 (...) the cement plant only grinds the clinker, which is imported from elsewhere and thus, the dioxin-generating process step takes place outside the country and the PCDD/PCDF emission is zero. The brick plants are simple ones and do not have pollution control systems.
- In Brunei Darussalam leaded gasoline is not available; and, since 1995, all newly imported 4-stroke cars are required to be equipped with catalytic converters.
- To estimate the emissions from uncontrolled burnings the experts applied conversion factors utilized in New Zealand whereby the biomass burned per hectare was 10 tons of dry mass in the case of forest fires, 20 tons/ha for bush fires, and 2.5 ton/ha for grass fires. The area in hectares that burned in the year 2001 could be estimated. From the accidental fires, 44 cases of vehicle fires occurred in 2001, which released 4.14 mg TEQ to the air

and left 0.79 mg TEQ with the residues. The releases from the 105 accidental fires in houses still need to be estimated.

- Category 7 - only the petroleum industry is present in Brunei Darussalam; however, the cracking process to break down long-chain hydrocarbons is not applied in the country. For the releases from this sub-category, the Toolkit does not provide an emission factor.
- In 2001, only six cremations were performed with a negligible emission of PCDD/PCDF. For the estimation of the release of PCDD/PCDF with dry cleaning residues it was assumed that 3 g of distillation residue is generated from the cleaning of one kg of textile.
- The leachates from landfills could not be estimated. Effluents from households were estimated utilizing average data for wastewater generation per capita (365 L per person and year). Sludge generation at wastewater treatment plants typically is at 0.4 % of raw sludge in effluent water, which contains 3 % of dry matter; 551 mg TEQ were identified in sludges from household effluents. Compost is being produced at one plant from a nursery's garden waste.
- The screening for potential hot-spots in the country only identified waste dumps and landfills as candidates. The landfills may have received ashes from the hospital waste incinerators, from industries, accidental fires, dry cleaning shops or wastewater treatment as inputs for many years. No PCB was identified at one site where transformers are stored. Although dredging of sediments is a common practice in Brunei Darussalam, the dredged sediments are thrown into the sea outside of the port.

The Brunei PCDD/PCDF inventory estimates a total of 1.4 g TEQ for the year 2001. Of these 42 % are from the medical waste incinerators and 41 % from landfilling and dumping, followed by uncontrolled burning (5.7 %) and transport (4.8 %). The major release vector is air, which accounted for 749 mg TEQ or 52.9 % of the total releases; 39.3 % were estimated to be concentrated in the residues (555 g TEQ).

For a few subcategories, no estimates could be performed especially in the category of uncontrolled burning, e.g., the amount of material burned in landfill fires, uncontrolled domestic waste burning in private gardens or roadside as well as uncontrolled fires in house, warehouses, and factories. Consequently, the inventory may underestimate the releases from these subcategories and the "total" releases from these sub-categories may be higher than the presently estimated 80.19 mg TEQ/year. A high uncertainty was identified in the estimation of the leachates from landfills and it is assumed that the actual annual releases may be higher than the present estimate of 573.8 mg TEQ per year.

In conclusion, the Brunei experts found the Toolkit very useful to estimate releases of PCDD/PCDF into the environment. The major dioxin and furan sources in the country were hospital waste incineration and residues from sewage sludge treatment plants. Both types of residues are dumped in landfills, which may constitute one of the hotspots in Brunei Darussalam. The major release vectors of PCDD/PCDF in Brunei Darussalam are releases into the air and to the landfill. All other categories and vectors together contribute to only about 20 % to the total inventory. The country identified the need to better characterize the releases from forest fires and fires in house.

Lebanon

Lebanon lies in the Middle East region and is characterized by Mediterranean mild to cool climate with wet winters and hot dry summers. The PCDD/PCDF inventory for Lebanon refers to the year 1999 when the population was 4.35 million; the major economies were trade and tourism.

- Category 1 - there were two types of medical waste incinerators in Lebanon, single chamber and double chamber incinerators; none of these had flue gas cleaning equipment installed; therefore class 1 and class 2 emission factors were applied, respectively. The

annual releases from the medical waste incinerators were estimated to be 11.6 TEQ into the air and 0.1 g TEQ with solid residues. As Lebanon is implementing legislation on segregation of wastes, it is being assumed that in the future, less medical waste will be burned in these incinerators and the releases are expected to reduce.

- Category 2 - relevant processes relate to steel, aluminum, and lead production: 75,000 tons of steel were produced in a foundry, which resulted in annual releases of 0.32 g TEQ to air and 0.015 TEQ with residues. Class 1 emission factors were applied to the secondary aluminum production as only minimal control of inputs do occur; the annual releases were 1.5 TEQ to air and 4 TEQ with residues. Approximately 4,200 tons of secondary lead was recycled from lead-acid batteries in Lebanon in 1999, which gave an estimated release of 0.064 TEQ/a into the air.
- Power plants predominantly utilized fuel oil and light oil/natural gas whereas for heating and cooking also wood was used as a low quantity. The total emissions from this category were 1.062 g TEQ in the year 1999.
- All cement plants in Lebanon are modern plants that utilize the dry process. Lime, brick, glass, ceramics, and asphalt are produced in Lebanon, which all together released not more than 0.5 g TEQ in the year 1999.
- The transport sector is the predominant energy consumption sector in Lebanon. The fleet of vehicles is relatively old and poorly maintained. For land transport, leaded gasoline was the main fuel in 1999; unleaded gasoline is gradually introduced since 1993. For the 1999 inventory, it was estimated that 2/3 of the 4-stroke engines used leaded gasoline and 33 % used unleaded fuel. The total emissions from 4-stroke cars were estimated to 2.3 g TEQ/a and the ones from the 2-stroke engines to 0.19 g TEQ/a and from Diesel cars to 0.007 g TEQ/a.
- Whereas agricultural and forest fires were a very minor contributor to the emission inventory, uncontrolled burning processes such as the burning of domestic wastes in gardens and road-site is estimated to release 12 g TEQ into the air and 25 g TEQ with residues. The open burning of wood residues is widely practiced in Lebanon and is estimated to release 4.8 g TEQ/a into the air and 0.8 g TEQ/a with residues. Recycling of used papers is practiced in Lebanon, which results in 0.7 g TEQ in the final products. Releases from textile and leather industries are very minor contributors to the inventory.
- Within category 9, about 0.9 g TEQ/a are discharged with household effluents directly into the environment and 0.78 g TEQ were present in compost.
- In Lebanon, hot-spots may have resulted from application of dioxin-contaminated pesticides such as 2,4-D. PCB-containing equipment may constitute other hot-spots. Presently about 36 tons of PCB oils (Pyralene and Askarel) were identified. The six larger landfills in Lebanon may contain PCDD/PCDF-contaminated waste and therefore constitute potential hot-spots.
- The total releases in the Lebanese inventory are estimated to be 68 g TEQ in the year 1999, of which 35 g TEQ were released to air and 30.6 g TEQ/a with residues. Within the air emissions, 17.66 g TEQ came from uncontrolled burning and 11.6 g TEQ/a from the incineration of hospital waste.

Philippines

The Philippines initiated their national dioxin and furan inventory by a national workshop, which was held in July 2001 with participation of the UNEP project manager and two international experts. The workshop was used for awareness raising, to obtain buy-in of stakeholders and to determine the dioxin and furan national action plan. The starting point for their inventory was centrally available data which were then investigated in more detail according to a shortlist of industries based on the Philippine industries/economy coding

system. The verification of the activities was accompanied by site visits. The results were extrapolated where individual plant information could not be obtained. Throughout the project close contact was maintained with UNEP Chemicals. The parameters listed in UNEP's questionnaire tables were transferred into questionnaires that were distributed to the managers of potential PCDD/PCDF sources to estimate the releases for the year 1999.

- Category 1 (waste incineration). Waste is incinerated in one hazardous waste incinerator, by some medical waste incinerators and one small facility that burns animal carcasses. The hospital waste incinerators were classified as class 1 and class 2 types and gave emissions of 38 g TEQ/a to air and 0.2 g TEQ/a with solid residues. The total category gave 38.7 g TEQ/a to air and 0.5 g TEQ/a with ashes.
- Category 2 - in the metal producing sector, the iron ore sinter plant was classified class 3 as it is well equipped with flue gas cleaning devices. The air emissions were estimated to be 1.3 g TEQ/a. Charcoal production from wood could be quantified at negligible levels. In the Philippines there were – according to MIRC-DOST – 178 foundry shops that predominantly used scrap metals such as cast iron/ mild and stainless steel, aluminum, brass and bronze as input. Most of them did not have any air pollution control systems installed. It was also found, that locally fabricated drum-type furnaces of a design not described in the Toolkit were (and are) being used. The secondary lead recycling market was identified as a major sector in the Philippines. Overall, the releases from category 2 were 8.7 g TEQ/a to air and 1.9 g TEQ/a with residues.
- Category 3 - energy production is regulated by the Department of Energy. Household and domestic cooking use a wide range of energy sources ranging from liquid petroleum gas (LPG) to biomass such as wood, rice hull, charcoal and biogas. A considerable amount of PCDD/PCDF originates from biomass fired power plants - accounting for 107 g TEQ/a in air releases - whereas the fossil fuels only contributed 1.5 g TEQ/a. Biomass cooking contributed 34 g TEQ/a to air and 6.8 g TEQ/a with residues. The fossil fuels' contribution was much lower. For biomass combustion in forests, the Philippines estimated the burnt material to be 43 tons/hectare. The Philippines also developed crop-specific conversion factors, (e.g., rice straw (25% residue from rice product), sugarcane, coconut) to provide rule-of-thumb estimations. They identified copra as a gap in the Toolkit.

The total releases along all vectors in the year 1999 in the Philippines were 530.70 g TEQ/a. Uncontrolled combustion ranked first with 187 g TEQ/a followed by power generation and cooking with 157 g TEQ/a and production of chemicals and consumer goods with 91.56 g TEQ/a. In terms of releases, emissions to air totaled 328 g TEQ/a with 35 % attributed to uncontrolled combustion of agricultural residues, 30 % were from firewood cooking, and 18 % from biomass-fired boilers. Product and land had similar contamination levels of 77.6 g TEQ/a and 46.9 g TEQ/a.

A surprising result of the inventory was that the highest emissions estimates were uncontrolled burning of agricultural residues, whereas the commonly known priority source, waste combustion, only accounted for 6.7 % of the total inventory.

Generally, the Toolkit was found to be handy for initial country-based identification of major PCDD/PCDF sources and releases. Sources could be identified, which otherwise would have been overlooked. Occasionally, the conversion of units submitted by the data providers into the units used in the Toolkit represented challenges.

The Toolkit also highlighted some interesting side aspects, such as product responsibility and life-cycle considerations. The presentation concluded with the recommendation for validation of some of the assumptions through sampling and PCDD/PCDF analysis. This inventory project is accompanied by a breast-milk study where two pooled samples of milk from Filipino mothers will be analyzed under the 3rd round of the WHO Breast Milk Study.

Results will be available in 2003.

Jordan

The dioxin and furan inventory relates to the year 2000. A national team consisting of eight experts was formed to execute this project. They were responsible for the identification of categories and sub-categories, prepared the questionnaires, followed them up, undertook site visits and drafted the preliminary inventory. There are a few subcategories left, which still need to be quantified, e.g., thermal wire reclamation, combustion of biogas/landfill gas, production of brick, glass, asphalt mixing, recycling paper, dry cleaning, open water dumping, non-thermal disposal of waste oils, and identification of potential hot-spots.

- Category 1 – waste incineration: the amount of hospital waste burned was estimated on existing beds in Jordanian hospitals multiplied with a waste generation rate of 0.5 kg per bed and day and the occupancy rate.
- Category 3: the main fuels utilized in power plants were HFO and diesel and plants were classified into classes 3 and 4;
- Category 5 – transportation: fuel consumption was derived from average annual distances traveled and average fuel consumption per distance driven. These data were centrally available from the Traffic Department.
- Category 6 - Biomass burning. It was assumed that trees and other vegetation completely burned, because fires use to occur during the dry season. Therefore, the climatic conditions are a driver towards complete burning. Landfill fires at a small site occur to reduce the volume.

The inventory so far has estimated total PCDD/PCDF releases of 70.4 g TEQ/a for the year 2000. Of these 70.9 % were caused by uncontrolled combustion processes (49.9 g TEQ/a), second were disposal operations with major releases from wastewater treatment plants either as aqueous effluents or sludges (16.3 % or 11.4 g TEQ/a). Emissions to air accounted for 53.4 g TEQ annually and releases with residues to 16.4 g TEQ/a.

Vietnam

In Vietnam, the project is coordinated by the National Environment Agency (NEA) of the Ministry of Science, Technology and Environment (MOSTE), which briefed and trained the provincial departments, scientists from the Centre for Consultation on Environmental Technology and from the Institute of Industrial Chemistry during a 2-day workshop in Hanoi in December 2001. A UNEP staff expert was present to facilitate the workshop. Within each of the 61 provinces, the regional DOSTEs (Department of Science, Technology and Environment) are responsible to collect the raw data from all dioxin-relevant activities through the respective departments of Health, Industry, Energy, etc. If possible, at the provincial level, classification of the activities, evaluation of the data will be performed resulting in a “complete” provincial inventory. The results from each province are being reported to NEA. NEA then seeks clarification of data with the DOSTEs if necessary. Field trips to evaluate data and discuss problems in implementing the inventory were performed where necessary. Site visits to industries were undertaken as well. Consultation with provinces was maintained mainly through letters throughout the project. Until mid December 22 provinces had submitted their data to NEA; the remainder were asked to complete their data collection by 31 December 2002. A national data evaluation workshop is planned for the end of January 2003.

In order to facilitate the implementation of the project, the Toolkit was translated into Vietnamese language and the questionnaires were prepared in Vietnamese as well.

Out of provinces came a commitment for annual updates of the inventory. This could result in an annual report to the INC or COP.

- Questions were raised as to the classification of the releases from medical waste incinerators. Presently, the hospital waste incinerators were put into class 1 according to the description in the Toolkit. However, it was recommended by UNEP Chemicals to apply the lower emissions factor of 3,000 µg TEQ/t of waste burned as the present class 1 and class 2 emissions emission factors are too conservative and pure estimates. In western countries, incinerators of this type had been shut down because of their suspected high dioxin emissions and without measured data. Therefore, the class 2 emission factor of 3,000 µg TEQ/t for small, simple, batch-wise operated medical waste incinerators should be applied. This assumption is based on the data obtained from the Thailand dioxin sampling project..
- Uncontrolled burning, for Viet Nam, considerably low, considering this country is an agricultural based country. After harvesting, the biomass is used as fodder for cattle, etc. or composted. Harvest residue burning is not very common in Viet Nam.

Approaches to Data Access

- Holding national workshops was found essential to understand and disseminate the Toolkit and the project.
- None of the countries reported difficulties to obtain readily available information. Also, information retrieval and channeling did not pose a major problem.
- Philippines gathered data from all the provinces and only the provinces which had relevant data the inventory was conducted. Philippines also suggested that the individual who is involved with the survey should be credible. Some companies consider the information to be confidential; therefore a trust has to be established between the companies involved and the individuals tasked to retrieve the information. Without this level of trust the validity of the information retrieved from the companies might be inaccurate to protect the companies business.
- Viet Nam was the only country that translated the Toolkit into the national language. Other countries worked from the English original.
- Two different approaches were used:
 - Vietnam realized a decentralized process whereby the provinces generated initial data. They presented their results to NEA/MOSTE and if necessary asked for assistance. In cases of doubts regarding the information reported by the provinces explanation on how the data were obtained was sought by NEA/MOSTE. Therefore all the available data was reviewed, discussed and clarified between the provincial authority and the overall leading authority.
 - The Philippines started with their own centrally available data. Decisions on which class of emission factors were to be applied were taken after consultation with relevant stakeholders such as trade associations, individual plants or other raw data providers. Relevant authorities, also at the local level, were consulted to obtain data that are related with each ministry, e.g., Department of Health for waste incinerators. A similar approach was followed by the other three countries as well.

Proposed Amendments to the Toolkit

Following the country presentations and discussions the following amendments to the Toolkit were proposed:

- In Section 6.2.2, the process to generate charcoal from wood should be added. However, presently the releases from this sub-category cannot be quantified. A conversion factor of 0.18 t/m³ of wood to produce charcoal should be applied.
- For locally manufactured furnaces in the ferrous and non-ferrous metal sectors that are not properly covered in the Toolkit, it was suggested to apply the lower emission factors for relatively well-controlled plants which utilize clean scrap/inputs and the higher

- emission factors when dirty input materials were entered into the process (Category 2).
- In Category 5 – diesel emissions: the emission factor needs to be harmonized within the Toolkit and 0.1 µg TEQ/t of diesel should be used (Note: in Table 45, a factor of 0.5 µg TEQ/t is given whereas the summarizing Table in Chapter 8.1 (page 159 – English version) gives 0.1 µg TEQ/t. In the EXCEL file, the actual calculation is being done with 0.05 µg TEQ/t).
 - Quantifying the biomass burned per hectare represents a major challenge. The numbers suggested by the different countries varied widely: e.g., for forests burned from 10 tons per hectare to 43 tons per hectare depending of the type of trees and the rate and extent of burning (note: under certain fire conditions, not all the biomass will be burned and trunks, representing a large portion of the original biomass present, can be left after the fire (Section 6.5)).
 - In many countries, types of biomass are being used for cooking, which are not defined in the Toolkit. The determination of further emission factors is desirable. For the time being, the factors displayed in Table 36 should be used, differentiating only between clean/virgin biomass and contaminated (chloro-pesticide treated biomass).
 - Concern was raised that the biomass in tropical and subtropical countries is very different from biomass in temperate countries. There is a need for additional emission factors that better reflect the vegetation in these countries and that reflect combustion conditions different from those described in the Toolkit (Section 6.6.1 through 6.6.3).
 - As a guide, it can be assumed that harvest residues of 25 % w/w are being generated from rice (in other words: 250 kg of rice straw per ton of (polished) rice produced (Section 6.6.3)).
 - Some confusion may arise in determining how to categorise landfill fires. The Toolkit differentiates between the use of the landfill gas (methane generated through decomposition of the waste) for energy, and burning of the landfill. In the first case, the burning of the landfill gas is considered to be energy production (as the gases are collected and burned in a torch or simple device and therefore will fall into Category 3.3). Landfill or waste dump burning under category 6.2.1 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). The length of the time the waste is under fire and the amount of waste that burned will determine the level of the emission.
 - There may be a need to better differentiate between landfill and dump. In the sense 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.
 - Emissions of PCDD/PCDF through discharge of wastewater may occur from the refining of petroleum (Section 6.7.3).
 - 3 g of distillation residue are being generated per kilogram of textile dry-cleaned (Section 6.7.4).
 - Copra should be added to the Toolkit as it represents an important export good for some countries. Since no measured data are available, the emission factor from biomass drying (Section 6.8.1) should be applied.
 - In Section 6.9.1, the amount of PCDD/PCDF present in landfills/waste dumps should be quantified by applying emission factors of 6 µg TEQ/t of domestic waste disposed of in countries with low use of dioxin-generating activities and 50 µg TEQ/t of domestic waste for countries with relevant PCDD/PCDF sources. In this sub-category, only the historic

load can be quantified.

Finalization of the National Inventories

The inventories need to be cleared by countries before submission to UNEP.

A common format for the inventory report is recommended, which includes among others:

Summary including aggregated data per category/sub-category (+ Summary Table)

Introduction to include country information, e.g., population, main activities, geography, relevance of the categories;

Short description how the inventory was implemented.

Countries have the option of having their inventories reported as individual self-standing documents as well as in the composite project document.

Timetable to finalize the project:

Final drafts to be received by Feb. 28, 2003 to UNEP Chemicals;

Comments back from UNEP Chemicals by March 31, 2003;

Final clearance from country by April 30, 2003

Distribution of the Inventories at INC-7, Geneva, July 14-18, 2003.

Conclusions –Experiences

Organizational Structure

Lessons learnt on how to implement the project

The Toolkit was found to be a useful in identifying sources in a country.

Releases of PCDD/PCDF could be estimated without sampling and analysis.

Good experiences with cooperation with companies;

There is not necessarily a direct correlation between size of plant and emissions - some small plants can have high emissions and large plants can have low releases;

The inventory has fostered general awareness raising on dioxin/furan issues within the countries, and has strengthened ties between government institutions and other sectors concerned. The relationship between private sector, NGOs and government improved (good cooperation and communication);

Through the Toolkit project gaps or inconsistencies in national statistics have been identified;

Follow-up activities were identified, e.g., implementation of pollution abatement strategies (also useful for other areas);

Data on dioxin emissions have been generated.

Provincial/regional vs. centrally available data.

Relevant only for large countries.

Stakeholder involvement – what were the problems? What can be done better?

In general, stakeholder buy-in was easy to obtain. There was a high level of cooperation that was facilitated through establishment of a National Committee.

In some countries, stakeholder information may be obtained easier if an institution that is not regulatory is collecting and evaluating the information.

Implementation Aspects

Use of Questionnaires

All countries used questionnaires successfully. Simplifications/modifications have been introduced occasionally;

In small countries, there was an almost 100% return; in larger countries a lower return was achieved;

The use of questionnaires facilitated the assignment of classes within the sub-categories;

Availability of the questionnaires in electronic format would be helpful.

Collection of raw data

Questionnaires used by all countries

Evaluation of information/questionnaires/ raw data and validation of data

Conversion factors had to be established to convert the units submitted by the data providers into the format required in the Toolkit;

In many cases information has to be accepted, as it cannot be verified;

Gaps in national information and record keeping have been identified;

Published data from annual reports (from agencies) present a reliable source of information; personal contacts may be used.

Updating of the inventory

Vietnam plans for annual updates of the inventory;

Updates of the inventory will become necessary when significant changes will occur in the country. Other conventions, e.g., Climate Change, may be external drivers.

Toolkit relevant aspects

Understanding and applicability

Users may need some time to become familiar with the language and the issues addressed in the Toolkit (especially when preparing the questionnaires);

Start-up workshops at regional basis and country visit by UNEP were found to be essential.

Coaching during the implementation of the project is necessary as new aspects arise in the course of the project.

Categorization of Activities

Better presentation of sub-categories is necessary for transportation sector (e.g., 4-stroke vehicles);

Burning of gas from landfills will be category 3.3 (energy production).

Amendments to the Toolkit

Data gaps identified such as biomass burning, agricultural residues, leachates from landfills, etc.;

Validation of some emission factors desirable;

The dioxins/furan content present in landfills/dumps should be included in the next version of the Toolkit (6 µg TEQ/t proposed for municipal solid waste; 50 µg TEQ/t waste for containing dioxin-contaminated wastes);

Wastes in landfills/dumps should be considered under hotspots (historic accumulation).

Follow-up

Relation of this project to the NIP. Is additional work needed for the NIP?

The Toolkit provides a basis for further steps in managing dioxin and furan emissions, including the need for future sampling and analysis, the identification of priority areas, and the development of action plans;

The dioxin/furan inventory provides an example of how to perform other inventories, e.g., for PCBs; (→ PCB Toolkit desirable);

Updating of the inventory needs to be institutionalized through the NIP.

Determination of BAT/BEP within the national action plan

Results of the Toolkit project are starting point for identification of activities that will need application of BAT/BEP;

Toolkit EXCEL sheet allows for rapid estimation of the emission reduction achieved when better techniques/practices will be used (BAT/BEP applied).

Conclusion of the Workshop

Participants asked UNEP Chemicals to take note of the issues raised and to take them into account when updating the Toolkit. Countries will reinforce that request when providing formal comment on Decision 6/4.

XII. Secretariat of the Basel Convention

Date: 31 October 2002
File ref. UNEP/Chemicals/332

Fax 022 797 34 60

Dear Mr. Willis

Subject: Request for comments on the Standardized Toolkit for Identification and Quantification of Dioxin and Furan releases

The Secretariat of the Basel Convention acknowledges receipt of your letter on the above subject dated 24 September 2002.

The Secretariat is looking forward to working jointly with the Interim Secretariat of the Stockholm Convention in experiencing and developing further the Standardized Toolkit for Identification and Quantification of Dioxins and Furans in the context of a pilot project in Ivory Coast on the Identification and Quantification of releases of dioxins in furans in a sub-saharian context, with particular focus on specific local practices.

I have taken note that a CD of the Toolkit is available in four languages and in hard copy as well upon request.

With kind regards,

Sachiko Kuwabara-Yamamoto
Executive Secretary

Mr. James B. Willis
Director
UNEP/Chemicals

XIII. GREENPEACE

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**Greenpeace Comments on UNEP Chemicals’
“Standardized Toolkit
For Identification and Quantification of Dioxin and Furan Releases”**

by Pat Costner
Senior Scientist
Greenpeace International

10 January 2003

Introduction

The draft Toolkit provides a general introduction to the process of preparing inventories of sources and releases of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and presents a list of PCDD/F sources and PCDD/F emission factors. The authors of the Toolkit acknowledge that their list of sources is not complete and that all sources are unlikely to be listed in the near future.

Nonetheless, the Toolkit offers no strategy for identifying sources of PCDD/Fs. In the absence of a complete list of PCDD/F sources, Parties can be expected to identify their PCDD/F sources only if they have a strategy for doing so.

The Toolkit presents a full complement of emission factors for only a fraction of PCDD/F sources, as evidenced in Section 8.1 “Compilation of All Default Emission Factors.” This is due in some but by no means all cases to the failure of even the industrialized countries to assess all releases from some of their most well known sources.

The Toolkit’s emission factors and monitoring data are almost entirely those for processes and activities in a few industrialized countries where PCDD/F release reduction programs in place for several decades. Indeed, the Toolkit’s emission factors are often lower than those given in the PCDD/F inventories of the industrialized regions as well as those presented in the scientific literature. Nonetheless, the Toolkit’s authors advise Parties that they need no monitoring data for any of the sources in their countries in order to estimate PCDD/F releases with sufficient accuracy to prioritize their sources.

To support the objectives of the Stockholm Convention, the Toolkit must be revised to include a coherent source identification strategy; a more comprehensive complement of default emission factors that includes those that are appropriate not only for processes and activities in industrialized countries but also for those in developing countries and countries with economies in transition; and descriptions of both regulatory and affordable analytical means for obtaining monitoring data that can be used to estimate releases and/or derive emission factors. Without these tools, Parties will waste time, effort and money in assembling inventories that do not include important PCDD/F sources and that have release estimates with little or no relationship to actual releases.

A Strategy for Identifying Sources

The Toolkit’s authors acknowledge that their list of PCDD/F sources is not comprehensive:

“There is no internationally established listing of sources (new sources are still being discovered and different sources are predominant in different countries)”;

Nonetheless, the authors also represent their list of PCDD/F sources as fully comprehensive and its emission factors as sufficiently robust and broadly applicable to enable all Parties to prepare their inventories without any sampling and analysis:

“final country inventories will clearly show that all potential sources have been addressed ...”

Some of the PCDD/F sources that are identified elsewhere but not included in the Toolkit’s list are shown in Table 1. In addition, some of the industrial chemicals and pesticides that are known or suspected to be accompanied by PCDD/F formation during their manufacture are listed in Tables 2 and 3. (Due to their sizes, Tables 2 and 3 are included at the end of this document.)

Facilities that manufacture and/or formulate the pesticides and industrial chemicals listed in Tables 2 and 3 are also potential PCDD/F sources. As illustrated in Figure 1, data from the European Union inventories show that pesticide manufacture accounts for 30 percent of total PCDD/F releases to air and land in that region.^{i,ii}

Until all PCDD/F sources have been identified and a comprehensive list is compiled, Parties need a coherent strategy for identifying PCDD/F sources. No such strategy is presented in the draft Toolkit. However, various facts that form the basis of a science-based strategy for source identification are scattered through the text of the Toolkit, as illustrated in Table 4.

At the most fundamental level, the strategy for source identification is simple: **All processes and activities in which chlorine is involved are regarded as suspected PCDD/F sources until proven otherwise, while those in which chlorine is absent are dismissed from further consideration.** This first step in the strategy for identifying PCDD/F sources is based on these scientific facts: 1) PCDD/F are composed of carbon, hydrogen, oxygen, and chlorine; and 2) PCDD/F formation occurs only when these four elements are present. Carbon, hydrogen and oxygen are commonly abundant in the materials involved in industrial processes and other human activities. This is not true for chlorine: **The availability of chlorine in any form -- elemental, organic or inorganic -- is a defining characteristic of all processes and activities that generate PCDD/Fs.** With chlorine availability as its foundation, the strategy for identifying PCDD/F sources can be further refined by 1) assessing the availability of other materials, such as metal catalysts, and conditions, such as temperatures that are conducive to PCDD/F formation; and 2) monitoring, as judiciously as possible, the gaseous emissions, aqueous discharges, solid residues and products of suspected PCDD/F sources.

The strategy of tracking the use of chlorine and chlorine-containing materials of chemical production facilities for the purpose of identifying those that are potential PCDD/F sources was followed, for example, in the preparation of Denmark's inventory of PCDD/F sources.ⁱⁱⁱ Similarly, the EU inventory notes, *"The thermal processes which involves carbon and chlorine containing materials and oxygen is suspected in general to be capable of producing dioxins and furans ..."*^{iv}

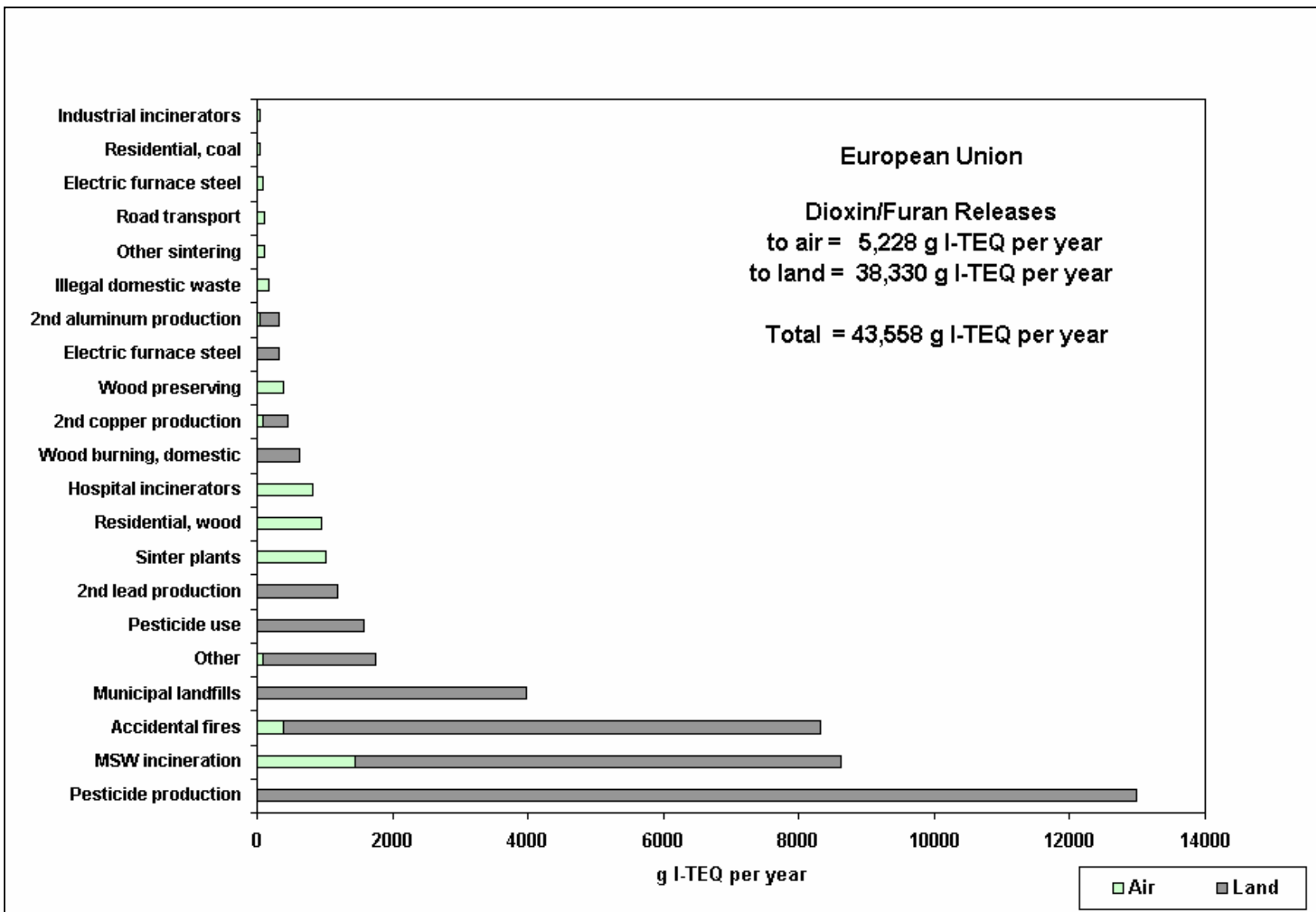


Figure 1: European Union – PCDD/F Sources and Their Estimated Releases to Air and Land

Table 1: Selection of Identified Dioxin Sources Not Included in the Toolkit’s List of Sources			
Source	Reference	Source	Reference
Tire combustion	v	Accidental fires involving stockpiles of PVC	vi
Petroleum refining catalyst regenerators ¹		Run-off from roads	vii
Tetrachlorobisphenol-A manufacture		Thermal stabilization of sewage sludge	viii
Primary aluminum production		Fireworks	ix
Primary copper production		Oil and gas exploration – well testing	x
Drum and barrel reclamation		Hog fuel boilers ²	xi
Iron chloride manufacture		Accidental fires involving stockpiles of tires	xii
Aluminum chloride manufacture		Thermal stabilization of sewage sludge	xiii
Copper chloride manufacture		Rubber manufacture, vulcanization process	xiv
Phthalocyanine dyes and pigments manufacture		Elemental chlorine manufacture, titanium electrodes ³	xv
Printing inks manufacture and/or formulation		Trichloroethylene and perchloroethylene manufacture ⁴	xvi
Carbon reactivation furnaces (industrial spent carbon and spent carbon from municipal water treatment)		Caprolactam manufacture (intermediate for manufacture of nylon)	xvii

¹ While it is acknowledged that this process has been otherwise identified as a dioxin source, it is not included in the Toolkit’s list of sources and no data are given on dioxin releases.

² While this process may be assumed to be included in the subcategory, “Biomass Power Plants”, it has been specifically identified in the scientific literature as well as in at least one national inventory as an important source due to high dioxin releases attributed to the high chlorine content of ‘hog fuel.’

³ In the text of the Toolkit, manufacture of elemental chlorine using titanium electrodes is acknowledged to be a dioxin source. However, the Toolkit’s list of sources includes only chlorine production with graphite anodes.

⁴ Manufacture of these chemicals is acknowledged as a dioxin source in the Toolkit and an emission factor is given in the text. However, these are not included in the Toolkit’s list of sources.

Alkylamine tetrachlorophenate manufacture		Titanium dioxide manufacture	xviii, xix
Candle burning			
Municipal wastewater treatment			

Chemical production	<i>“Chemical production involving elemental chlorine variously leads to wastes containing PCDD/PCDF.”⁵ ... “PCDD and PCDF can be formed in chemical processes where chlorine is involved.”</i>
Crematories	<i>“Coffins, embalming fluids, and decoration materials may contain chlorinated chemicals and plastics...”</i>
Sewage sludge incinerators	<i>“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.”⁶</i>
Biomass combustion	<i>“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.”</i>
Aluminum Production	<i>“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.”</i>
Drying aluminum turnings	<i>“Formation of PCDD/PCDF is possible as the oil-based contaminants can contain certain organic or inorganic chlorine...”</i>
Lead production	<i>“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 ... In the US PVC battery separators are effectively eliminated and it is assumed the same is true in Germany.”</i>
Thermal wire reclamation	<i>“In this process, all ingredients to form PCDD/PCDF are present: carbon (sheath), chlorine (PVC or mould resistant agents) and a catalyst (copper).”</i>
Fossil fuel power plants	<i>“The remaining organic fragments and the chlorine contained in the coal recombine in the presence of the metal-chloride catalysts to form PCDD/PCDF.”</i>
Household heating and cooking (biomass)	<i>“Thus, the differentiation is between virgin biomass and contaminated biomass such as treated and/or painted wood, straw heavily impacted by chlorinated pesticides.”</i>
Lime production	<i>“Raw materials or fuels that contain chlorides may potentially cause the formation of PCDD/PCDF in the combustion process of the lime kiln.”</i>
Transport, 4-stroke engines	<i>“Higher emissions have been associated with the use of chlorinated scavengers used in leaded gasoline.”</i>
Pulp and paper mills, elemental chlorine bleaching:	<i>“It uses chlorine (Cl₂) and hypochlorite to brighten the pulp. When elemental chlorine and hypochlorite react with the lignin, chlorinated compounds including PCDD/PCDF are formed.”</i>

⁵ While correct, this statement is also incomplete. Dioxins are formed during chemical production involving other forms of chlorine, such as hydrogen chloride, metal chlorides, organochlorines, etc., as the authors tacitly acknowledge in the second comment

⁶ Among the halogenated hydrocarbons, only the chlorinated hydrocarbons are involved in the formation of the polychlorinated dioxins and furans -- the dioxin and furans addressed by the Stockholm Convention.

Pulp and paper mills, elemental chlorine free (ECF) bleaching:	<i>“ECF bleaching is a bleaching sequence, which usually uses chlorine dioxide (ClO₂) as the main bleaching agent. Elemental chlorine (chlorine gas, Cl₂, also hypochlorite) is no longer used. ECF results in reduced levels of PCDD/PCDF.”</i>
Pulp and paper mill, totally chlorine free (TCF) bleaching	<i>“Uses no chlorinated bleaching agents to bleach the pulp; instead oxygen (O₂), peroxide (H₂O₂) or peracetic acid are used.”</i>

Table 5: Indicative List of Uses of Chlorine and Chlorine-containing Products	
Product	Uses
Elemental chlorine	<ul style="list-style-type: none"> • Industrial processes (e.g., pulp and paper bleaching) • Water and wastewater treatment • Production of hydrogen chloride
Hydrogen chloride	Many
C1 Derivatives	
Monochloromethane	Manufacture of <ul style="list-style-type: none"> • Methyl cellulose • Silicones • Tetramethyl lead
Dichloromethane	
Trichloromethane	Manufacture of HCFCs → PTFE
Tetrachloromethane	Industrial processes
Phosgene	Manufacture of <ul style="list-style-type: none"> • Diisocyanates → Polyurethanes • Polycarbonates
C2 Derivatives	
Monochloroethane	Manufacture of tetraethyl lead
1,2-Dichloroethane (EDC)	Manufacture of <ul style="list-style-type: none"> • Vinyl chloride → Polyvinyl chloride • PVDC • PVDF • Perchloroethylene → HFC • Trichloroethylene → HFC
Trichloroethylene	Manufacture of HFC
1,1,1-Trichloroethane	Manufacture of <ul style="list-style-type: none"> • HFC • HCFC
Monochloroacetic acid	Manufacture of Carboxymethyl cellulose → Foods, cosmetics
Trichloroacetic acid	Manufacture of pharmaceuticals
C3 Derivatives	
Allyl chloride	Manufacture of <ul style="list-style-type: none"> • Epichlorohydrin → Epoxy resins & Glycerols • Flocculants • Propylene oxide → Propylene glycol → Glycol ethers → Polyols → Polyurethanes
Epichlorohydrin	
C4 & Higher Derivatives	Manufacture of Chloroparaffins → Linear

	alkyl benzene
Dichlorobutene	Manufacture of Chloroprene → Polychloroprene
Aromatic Derivatives	Manufacture of <ul style="list-style-type: none"> • Pesticides, Anti-bacterials, etc. • Dyes and dyestuffs • Aramide fibers
Inorganic Derivatives	
Aluminum chlorides	
Iron chlorides	
Silicon tetrachloride	Manufacture of <ul style="list-style-type: none"> • Silicon dioxide • Silicon
Sulfur chlorides	Manufacture of <ul style="list-style-type: none"> • Pesticides, etc. • S-resins
Sodium hypochlorite	
Titanium tetrachloride	Manufacture of titanium dioxide
Phosphorus chlorides	Manufacture of pesticides, etc.

Presented in Table 5 is an indicative list of major chemical products from the use of chlorine and/or chlorine-containing materials. This information may be useful to users in identifying potential sources of PCDD/F in the industrial sector. In addition, Table 6 lists the publicly-available reports from Stanford Research Institute that provide information about production and producers of elemental chlorine and some of the more important chlorine-containing chemicals in many regions of the world. These reports can be helpful in identifying chemical production facilities that are potential PCDD/F sources.

In this regard, it would also be most useful, particularly for ranking PCDD/F sources, to revise the draft Toolkit so that primary sources – processes and activities that generate PCDD/Fs, such as chemical manufacture and waste incineration – are clearly distinguished from secondary sources – processes and activities that receive and then release PCDD/Fs into the environment, such as wastewater treatment. This important differentiation is a common practice. [See, for example, Fiedler (2002).^{xx}]

Emission Factors

As the term is used in the Toolkit, an *emission factor* is the quantity of PCDD/Fs released to air, water, land, residues, and/or products when a specified quantity of material is processed or product is produced. In discussing the Toolkit's emission factors, the authors effectively acknowledge that the emission factors in their database are not universally applicable. Indeed their descriptions suggest a near-absolute reliance on information developed in industrialized countries. For example, they say --

“The “Toolkit” has been assembled using the accumulated experience of those who have compiled inventories. ... nearly all [inventories are] from developed Northern countries. ...

Many are incomplete, out of date or lack uniform structure. ...Comparatively little is known about processes and emission factors for processes and technologies used in less developed countries and region-specific feedstocks or input materials.”

Having acknowledged the marked limitations of the Toolkit’s emission factors, particularly with respect to developing countries and countries with economies in transition, the authors nevertheless advise that

“No emission testing is necessary to apply the Toolkit and to compile an inventory.”

Reliance on default emission factors rather than monitoring data reduces the estimation of PCDD/F releases to “*a back of the envelope calculation*,” as succinctly phrased by Hori (2001).^{xxi} While this approach has an obvious appeal, its reliability in prioritizing PCDD/F sources is highly questionable.

Due to the scarcity of monitoring data, emission factors used in national inventories and those presented in the Toolkit are commonly based on a limited number of measurements from a relatively small number of sources and then assumed to be representative for all sources of the same type. This “top down” approach is likely to underestimate PCDD/F releases since it does not take into account the variability in releases from individual sources or the variability among individual sources of nominally similar types. In turn, such underestimations can result in inappropriate ranking of PCDD/F sources so that national action plans do not target the most important PCDD/F sources.

Table 6: Stanford Research Institute Reports on Production and Producers of Chlorine and Chlorinated Products^{xxii}					
Title	Year	Authors	Cost	Production	Production Locations
Chlorine/Sodium Hydroxide	Oct. 2002	Eric Linak	\$4,000		US, Canada, Mexico, Brazil, W. Europe, E. Europe, Middle East, Japan, ASEAN, China, India, Republic of Korea, Taiwan, Australia
Hydrochloric Acid	Nov 2001	Eric Linak with Yashuhiko Sakuma	\$2,500	16.6M tonnes (US, W. Europe, Japan)	US, Canada, Mexico, W. Europe, Japan
Ethylene Dichloride	Jan 2001	Aida Jebens with Katherine Shariq	\$1,500	32M tones (consumption)	North America, W. Europe, Japan, Taiwan, Republic of Korea, Other Asia, Other Regions
Vinyl Chloride Monomer (VCM)	Dec. 2000	Aida Jebens with Akihiro Kishi	\$2,000	25M tones	North America, W. Europe, Japan, Republic of Korea, Taiwan, Other Asia, Other Regions
Polyvinyl Chloride Resins	Jan 2001	Aida Jebens with Akihiro Kishi	\$2,000	25M tones	North America, Latin America, W. Europe, Japan, Republic of Korea, Other Asia, Other Regions
Chlorinated Methanes	Dec 2001	Eric Linak and Goro Toki	\$4,000	(\$1B global value)	US, Canada, Mexico, South America, W. Europe, E. Europe, Japan, China, Asia Pacific
Phosgene	July 2000	Jamie Lacson	\$1,500		US, Canada, Mexico, South America, W. Europe, Japan, Other Asia, China, Republic of Korea,
C2 Chlorinated Solvents	Jan 2002	Eric Linak and Goro Toki	\$2,500		US, Canada, Mexico, Brazil, W. Europe, E. Europe, Japan, China, Southeast Asia and Oceania
Monochloroacetic acid	Jan 2002	Jamie Lacson with Kazuo Yahi	\$1,500		US, W. Europe, E. Europe, Japan

Epichlorohydrin	Dec 2000	Elvira Greiner with Thomas Kaelin and Mashiro Yoneyama	\$1,800	640T tonnes (US, W. Europe and Japan)	US, W. Europe, E. Europe, Japan, China, Republic of Korea, Taiwan, Thailand
Chlorobenzenes	Dec 1999	Jamie Lacson with Chiara Cornetta and Masahiro Yoneyama	\$1,500	336T tonnes (US, W. Europe and Japan)	US, Canada, Mexico, Brazil, W. Europe, E. Europe,
Benzyl Chloride	July 2001	Elvira Greiner with John Bottomley and Goro Toki	\$2,000	128T tonnes (US and W. Europe)	US, Canada, Mexico, W. Europe, E. Europe, Japan, Other Asian Countries

As acknowledged by the authors, the emission factors in the Toolkit are derived almost entirely from sampling and analysis carried out in a small number of industrialized countries, primarily Western European nations and the U.S. Some argue that such default emission factors do not yield useful results even when applied to similar facilities in the same industrialized country.

For example, Webster and Connett (1998) estimated PCDD/F releases to air from US incinerators for which monitoring data were available. They compared these estimated annual air releases with estimates calculated using default emission factors. They generally found that estimates of air releases based on default emission factors were considerably smaller than those based on actual monitoring data. In fact, they found that the measurement-based estimate of annual air releases from two particular incinerators was as large or larger than 9 of 11 emission factor-based estimates for all incinerators combined.^{xxiii}

The examples presented in Table 7, some of which are discussed below, illustrate further the severe limitations of default emission factors, particularly those derived from PCDD/F-generating processes and activities in industrialized countries. Using such emission factors to estimate PCDD/F releases from processes and activities can result in gross underestimations of PCDD/F releases in any country but especially in developing countries and countries with economies in transition.

- **PVC Production:** The Toolkit's emission factors for the production chain for polyvinyl chloride – ethylene dichloride (EDC)/vinyl chloride monomer (VCM)/polyvinyl chloride (PVC) – are those put forward by the U.S. industry. However, as shown in Table 6, German emission factors for releases to water and in residues are, respectively 100 and 200 times greater than those presented in the Toolkit. PCDD/F concentrations in treated wastewater from a Russian facility also support an emission factor for releases to water that is some 100 times greater than the Toolkit emission factor. However, the Toolkit's emission factor for releases to air is similar to that reported for German facilities.^{xxiv}
- **Cement Kilns:** As shown in Table 7, the Toolkit's air emission factor for the most well controlled cement kilns is quite close to the U.S. factor for cement kilns fired with conventional fuels. However, while the Toolkit presents the same air emission factors for all cement kilns regardless of the materials used to fuel the kilns, air emission factors for U.S. cement kilns burning hazardous waste are some 77 times greater than those for cement kilns fired with conventional fuels.^{xxv} The air emission factor reported for a coal-fired cement kiln in Russia is more than 40,000 times greater than the Toolkit's highest air emission factor for cement kilns
- **Aluminum Production:** In their discussion of PCDD/F formation in aluminum production, the Toolkit's authors note that, in primary aluminum production, PCDD/F levels "*are generally thought to be low and the main interest is in the thermal processing of secondary materials,*" i.e., secondary aluminum production. With that, primary aluminum production is not listed as a PCDD/F source and no emission factors are presented for this industry. However, as shown in Table 7, monitoring data at a primary aluminum production facility in Russia resulted in high emission factors for releases to air and in residues.

Table 7: Comparison of Selected Emission Factors		
	UNEP Toolkit	Other
Emission Factor_{AIR}, □ g I-TEQ/ton		
Cement kilns, all	0.15 - 5	0.15 ⁷ OSPAR Guidance ^{xxvi}
Cement kilns, hazardous waste	No factor given	20.91 U.S. ^{xxvii}
Cement kilns, no hazardous waste	No factor given	0.27 U.S. ^{xxviii} 202231 Russia ^{xxix 8}
Municipal waste incinerator, high quality pollution control	0.5	1.5 OSPAR Guidance ^{xxx}
Aluminum Production, Primary	None or insignificant No factor given	11169 Russia ^{xxxii}
EDC/VCM/PVC “Modern plants”	0.015 ⁹	0.1 – 33 Germany ^{xxxiii}
Thermal metal reclamation	3.3	17 OSPAR Guidance ^{xxxiiii}
Emission Factor_{WATER}, □ g I-TEQ/ton		
EDC/VCM/PVC “Modern plants”	2 ^b	400 Germany ^{xxxv} 0.5 OSPAR Guidance ^{xxxvi}
Municipal waste incinerators	“minor importance” no factor given	0.09 – 1.87 □g TEQ/L OSPAR Guidance ^{xxxvii}
Hazardous waste incinerators	“not... important” no factor given	0.15 OSPAR Guidance ^{xxxviii}
Emission Factor_{RESIDUE}, □ g I-TEQ/ton		
Aluminum Production, Primary	None or insignificant No factor given	141.1 Russia ^{xxxix}

⁷ “Measurements recommended at some plants incinerating wastes”

⁸ Value confirmed by N. Klyuev via personal communication, 11 June 2002.

⁹ This value is based on data from the U.S. PVC industry, according to the Toolkit’s authors.

Pollutant Release and Transfer Registers

With Pollutant Release and Transfer Registers (PRTRs) and related mechanisms, Parties can require point sources of by-product POPs, such as manufacturing facilities, waste disposal facilities, etc., to monitor and report their releases of by-product POPs as well as intentionally produced POPs. In support of this addition to the Toolkit, the Stockholm Convention states that each Party must give sympathetic consideration to PRTRs.^{xxxix} many countries are already moving towards the use of data collected through PRTR programs for the compilation of national inventories.^{xl}

Recent developments in PRTRs include 1) a resolution promoting the development of PRTRs in countries worldwide has been passed by the Intergovernmental Forum on Chemical Safety; 2) Inter-Organization Programme for the Sound Management of Chemicals (IOMC) PRTR Coordinating Group – a coordinating mechanism among various United Nations agencies, the OECD, countries and non-governmental organizations, currently chaired by Canada; 3) Organization for Economic Cooperation and Development (OECD) has developed a guidance manual for governments, and has a Task Force on Release and Estimation Techniques that is chaired by the US; 4) European Pollutant Emission Register (EPER), a regional register among countries of the EU covering releases for approximately 50 chemicals, will be compiled every three years starting in 2003; 5) the Aarhus Convention on Access to Information, Public Participation in Decision-Making and Access to Justice in Environmental Matters, under which a PRTR working group is developing an international protocol for PRTRs which will be open to all countries for signature, not just those that have ratified the Aarhus Convention.^{xli}

Analytical Methods

Over the past decade, certain bioassay methods have found widespread use for determining the presence and levels of PCDD/Fs and similar chemicals in the full array of media: foods^{xlii}; thermally treated waste, wastewater treatment, landfill leachate treatment, commercial PCB-mixtures, the release into the environment (soil, air and water), and the final intake into wildlife and humans^{xliii}; human breast milk^{xliv,xlv}; marine mammals^{xlvi}; contaminated soils^{xlvii}; surface water^{xlviii}; industrial wastewater^{xlix}; hazardous waste combustor stack gases^l; etc.

These methods have been validated, accepted, recommended and/or relied on by scientists in academia, industry, national and international agencies. The costs of these bioassay methods are a fraction of the costs of conventional analysis by high-resolution gas chromatography/mass spectrometry. Information about these bioassay methods, including costs and availability of commercial analytical services as well as costs and availability of requisite laboratory equipment and training, can facilitate the inventorying process and conserve limited resources.

PCDD/F Releases to Land

Two EU inventories have been prepared: one that addresses releases to air^{li} and one that addresses releases to water and land.^{lii} The decision to examine releases to these three environmental sectors was undoubtedly based on the fact that these three sectors – air, water and land – taken as a whole encompass the global environment. Similarly, those reporting releases of PCDD/Fs for the U.S. Toxics Release Inventory are advised that, under U.S. law, “the disposal of toxic chemicals in on-site landfills constitutes a release to land.”^{liii} Nonetheless, the authors of the Toolkit decided that releases of PCDD/F inventories should

be configured to address “*five compartments and/or media: air, water, land, wastes (residues), and products.*”

Ancillary to this decision, the Toolkit’s authors also decreed that, for the purposes of the inventories, the environmental compartment “land” consists only of “soils”, as in surface soils. In other words, they decided that “landfills” are not a part of this or any other environmental compartment. As a consequence, according to the Toolkit, releases to landfills do not constitute releases to the environment. For example, in their discussion in Section 6.9 Disposal/Landfill of the Toolkit, the authors describe the fate of PCDD/F-contaminated residues as “containment in secure landfills, destruction (thermally or chemical decontamination) or release into the environment.” Similarly, in Section 3.2.3 Release to Land, the authors note, “Sources releasing PCDD/PCDF to land can be divided into two classes: PCDD/PCDF contaminated product “applied” to land directly or PCDD/PCDF deposited onto land via environmental processes.”

By defining surface soils as the sole components of the environmental compartment “land”, the authors of the Toolkit have created a circumstance in which, for example, they state that, for municipal solid waste incinerators, “*No release to land is expected unless untreated residue is directly placed onto or mixed with soil.*” In contrast, ashes from municipal waste incinerators accounted for approximately 20 percent of total PCDD/F releases to land in the EU based on the EU inventory.^{liv}

According to the Toolkit, even when disposed of in landfills, PCDD/F-contaminated ashes from hazardous waste incinerators, medical waste incinerators, shredder waste incinerators, medical waste incinerators, waste wood and waste biomass incinerators, etc. are not acknowledged as PCDD/F releases to land or, consequently, to the environment. Presumably, if the Toolkit were to address deepwell injection of PCDD/F-contaminated wastes, which it does not even though this method of disposal is practiced in some countries, injection of PCDD/F-contaminated wastes down deepwells would not be considered to be a release to the environment.

One Inventory for All Currently-Listed By-Product POPs

The draft Toolkit addresses two of the four currently targeted by-product POPs – PCDDs and PCDFs. However, many if not all activities and processes that have been identified as sources of PCDD/Fs are also sources of the other two by-product POPs – polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). (See, for example, the global HCB inventory by Bailey (2001)^{lv}, the European HCB inventory^{lvi}, Canada’s inventory of PCDD/Fs and HCB^{lvii}, the UK PCB inventory^{lviii}, and the U.S. inventory^{lix}). Given this circumstance, it is more efficient and cost-effective to configure the Toolkit so that users prepare a single inventory that addresses all four of the currently-listed by-products POPs, rather than following the repetitious and costly process of inventorying each by-product separately.

Detailed Comments

The following section consists of selected text excerpted from the draft Toolkit with associated comments and suggestions. This does not represent an exhaustive examination of the entire Toolkit but is a selection of illustrative examples of needed revisions, which range from modifications of fundamental concepts to more studied, consistent use of language.

Draft Toolkit Page Number	Selected excerpts from the draft Toolkit and associated comments and suggestions
1	<p>“The global convention on persistent organic pollutants (POPs) presently under negotiation, is expected to require minimization of releases of PCDD/PCDF. Therefore, dioxin sources 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.”</p> <p>Comment: This text should comply with more recent developments and more closely reflect the actual language of the Stockholm Convention.</p> <p>Suggestion: The global convention on persistent organic pollutants (POPs) require continuing minimization and, where feasible, with ultimate elimination of releases of PCDD/Fs, PCBs, and HCB. Therefore, sources of these by-product POPs must be identified and their releases quantified. The methodology used to assess sources must be consistent in order to follow or monitor dioxin releases over time and between countries.</p>
2	<p>“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, waste (residues), and products. For a comprehensive approach, all PCDD/PCDF must be considered (although it does not follow that releases to all compartments have an equal impact).”</p> <p><i>Comment: To minimize confusion, we suggest that key terms, such as “residues” are used consistently here and throughout the report, rather than interchanged. While this parenthetical phrase -- “(although it does not follow that releases to all compartments have an equal impact)” – is undoubtedly true, its insertion in this context is more diversionary than helpful. Moreover, while the desire for a “comprehensive approach” is a valid reason for addressing all PCDD/F releases, it is important that Toolkit users are reminded here that it is their obligation under the Stockholm Treaty to address all releases of PCDD/F and other by-product POPs.</i></p> <p><i>Suggestion: Information on release of PCDD/Fs is related to the following general five compartments and/or media into which PCDD/Fs are released or transferred: air, water, land, residues and products. As specified by the Stockholm Convention, all PCDD/F releases must be considered.</i></p>
2	<p>“Thus, emissions to all media where data are available can be assigned.”</p> <p>Comment: The word “emission” is specifically defined as “<i>the release of a substance from a point or diffuse source into the atmosphere</i>” in the Protocol to the Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants.^{lx} During negotiations for the Stockholm Treaty, the meaning and usage of the word “emission” and its derivatives was discussed at great length and led to the conclusion that the word “release” and its derivatives are the terms of choice to be used in the Treaty, since they most unambiguously reflect the inclusion of all releases -- emissions, discharges, depositions, etc. – of POPs. Given the basic differences between the terms “emission” and “release”, it is most important that these terms are not used interchangeably and that the term “release” and its derivatives are used in all cases except where it is intended to address solely and specifically releases to air. For the purposes of the Stockholm</p>

	<p>Convention, which the draft Toolkit is intended to serve, it is unfortunate that the term “emission factor” is used irrespective of the receiving medium (air, water, land, residues or products). Nonetheless, confusion can be minimized by using the term “release” and its derivatives and by identifying emission factors as, for example, emission factor_{WATER}, emission factor_{AIR}, etc.</p> <p><i>Suggestion: Thus, releases to all media where data are available can be assigned.</i></p>
2	<p>“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.”</p> <p>Comment: As discussed in the general comments, the Toolkit’s list of sources does not include all PCDD/F sources that have been identified in various inventories, studies, etc., and new sources are still being discovered. Given this circumstance, the above statement is not accurate. However, when the Toolkit is modified to include a strategy for identifying PCDD/F sources, a somewhat parallel statement can be made.</p> <p>Suggestion: The final country inventories will show that all sources listed in the Toolkit have been addressed, even if the activity does not exist or is insignificant in that country.</p>
6	<p><i>“Since no emissions measurement is required, this Toolkit will not produce precise results concerning national or regional releases of PCDD/PCDF. It is intended to quickly identify the major PCDD/PCDF sources and thus, provide an overview of the scale of releases. Consequently, the derived Dioxin Inventories will assist countries to direct their efforts to quantify and mitigate the problem of PCDD/PCDF releases. It will also help to indicate the relative importance of dioxins and furans for a country’s national action plan.”</i></p> <p>Comment: While the intent of the Toolkit may be as described above, this is not the reality. The Toolkit provides a list of what may be most but certainly is not all of the PCDD/F sources that have been identified in the industrialized countries. Also, as discussed earlier, the emission factors are based almost entirely on processes and activities of a few of the industrialized nations and, as such, are not necessarily applicable to similar processes and activities in other countries, especially developing countries and countries with economies in transition.</p> <p>Suggestion: In the absence of measurements of releases, the relationship between the release estimates obtained through use of this Toolkit and actual releases is unknown and unpredictable. Parties can ascertain the presence or absence in their countries of the PCDD/F sources listed in the Toolkit. To identify other sources, Parties must investigate releases from the chain of production, use and disposal of chlorine and chlorine-containing materials in their countries.</p>
7	<p>“PCDD/PCDF are formed as unintentional by-products in a wide range of processes. They are widely dispersed in the environment and may be present in manufacturing processes as raw materials or products. Consequently, releases or transfers of PCDD/PCDF can occur even where the PCDD/PCDF is not formed in the process under consideration.”</p> <p>Comment: With regard to the first sentence, it is critical that Parties are given at least the</p>

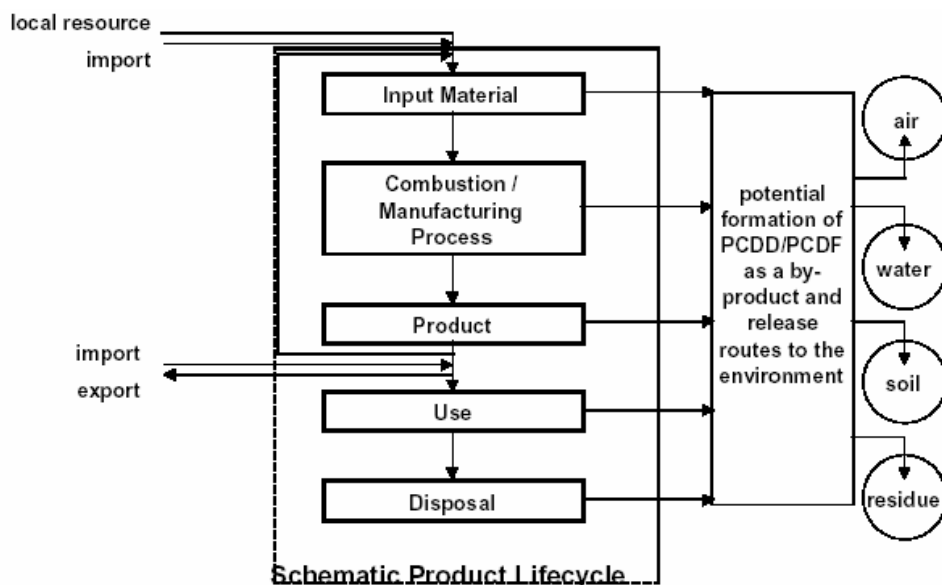
	<p>most important facts of PCDD/F formation. The latter portion of the second sentence is not accurate in that PCDD/Fs are by-products, not raw materials or products, and that the introduction of PCDD/Fs as contaminants is not limited to manufacturing processes but also occurs in activities such as washing clothes and dishes with subsequent distribution to municipal wastewater.</p> <p><i>Suggestion: PCDD/Fs are formed as unintentional by-products in certain processes and activities, all of which share one common feature: the availability of chlorine and/or chlorine-containing materials. Besides being formed as unintentional by-products of manufacturing processes, PCDD/Fs may also be introduced into processes as contaminants in the raw materials used in the processes. Consequently, releases or transfers of PCDD/Fs can occur even where the PCDD/Fs are not formed in the process under consideration.</i></p>
7	<p>“PCDD/PCDF are persistent in the environment and transfers can occur between media (e.g., run-off from soil to water). Such transfers may make an important contribution to human exposure to PCDD/PCDF but quantification of releases from these so-called reservoir sources will not be addressed in this toolkit. Releases from reservoir sources are controlled by site specific environmental factors. This Toolkit is focused on activities under direct human control.”</p> <p>...</p> <p>“Highly contaminated reservoir sites having the potential to act as a “reservoir” source are addressed in a separate category.”</p> <p><i>Comment: These statements about reservoir sources are both confused and confusing. The authors are apparently differentiating between two types of reservoir sources without having defined a “reservoir source” and without describing the characteristics that distinguish a reservoir source for which releases are not addressed from one that will be addressed. Moreover, since the overwhelming majority of PCDD/F is the product of human activities, it should go without saying that such PCDD/F is, indeed, “under direct human control.”</i></p> <p><i>Suggestion: Present a clear definition of “reservoir sources” and describe the distinguishing characteristics of both those reservoir sources that are addressed in the Toolkit and those that are not addressed. Modify the last sentence as follows: “This Toolkit is focused on activities under more immediate human control.”</i></p>
7	<p>“The Toolkit addresses direct releases and transfers of PCDD/PCDF to the following five compartments and/or media (Figure 1).</p> <ul style="list-style-type: none"> • Air • Water (fresh, ocean, estuarine; then subsequently into sediments) • Land (soil) • <i>Waste (including liquid, sludge, and solid residues, which are handled and disposed of as waste or mainly recycled)</i> • <i>Products (such as chemical formulations or consumer goods such as paper, textiles, etc.).”</i> <p>Comment: As discussed earlier, consistency in terminology is important if confusion is to be minimized. Also, with regard to the bullet point “Waste”, the meaning and purpose of the phrase “or mainly recycled” is not obvious. If the authors are suggesting that dioxin-containing wastes are mainly recycled, this is not an accurate</p>

reflection of the fate of such materials, particularly in developing countries and countries with economies in transition. In any event, if a dioxin-contaminated waste is recycled, then it ceases to be a waste and so falls outside the purview of the report. Also as discussed in the general comments, defining the environmental compartment “land” as consisting only of surface soils creates needless confusion.

Suggestion:
The Toolkit addresses direct releases and transfers of PCDD/Fs to the following five compartments and/or media (Figure 1).

- *Air*
- *Water [freshwater (surface water and groundwater), ocean, and estuarine]*
- *Land*
- Residues (including certain liquid wastes, sludge and other solid residues, that are handled and disposed of as wastes)
- Products (such as chemical formulations or consumer goods such as paper, textiles, etc.).”

8



Determination of Potential PCDD/PCDF Release Routes

Figure 1: Potential release routes of PCDD/PCDF as a by-product into the three environmental media air, water and land and/or to product and waste
 Note: reservoirs are not included in this figure but may be present in the compartment “soil”

Comment: This diagram, its title and explanation are confusing and, in certain aspects, inaccurate.

Suggestion: Delete the diagram and its appurtenances or make these corrections and additions: The arrow from the first “import” should go directly to the text box, “Input Material” rather than to the arrow from ‘local resource’; the arrows from “import” and

	<p>“export” should go directly to the “Product” box rather than the arrow leading from “Product” to “Use”; “potential formation of PCDD/PCDF as a by-product” should not be combined with “release routes to the environment” but should be a separate aspect that is associated only with those text boxes where PCDD/F formation actually may occur, e.g., “Combustion/Manufacturing Process,” “Use” and “Disposal.” I.e., PCDD/F formation should not be associated with “Input Material” or in “Product”. The receiving environmental media/compartments should be air, water, land (to be consistent with the rest of the report as well as the accompanying explanation at “Figure 1”), residues, and products. In the explanation at “Figure 1”, the word “waste” should be changed to “residues”. If, as has been suggested earlier, the term “reservoir” is clearly defined, the “Note: reservoirs are not included ...” should be deleted.</p>
8	<p>“PCDD and PCDF emissions arise from four types of sources.”</p> <p>Comment: As suggested earlier, the correct term here is “releases”.</p> <p>Suggestion: PCDD/F releases arise from four types of sources.</p>
8	<p>“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– these can generally be addressed and controlled by modifications to the process or by product substitution;”</p> <p>Comment: If measures for elimination/reduction/control of PCDD/F formation and release are to be presented in this draft report, this should be done consistently, i.e., for each category. However, according to this draft report, UNEP Chemicals is preparing a report -- UNEP (2001): Training Module for Reducing Releases of Dioxins and Furans. Report by UNEP Chemicals (<i>in preparation</i>) -- that specifically addresses such measures. Moreover, the statement made here is not demonstrably accurate. For example, PCDD/F formation during the production of ethylene dichloride via oxychlorination has been described in industry reports as unavoidable.^{lxi} In addition, the production of pulp and paper is accompanied by PCDD/F formation only when chlorine or chlorine derivatives are used in the bleaching process.^{lxii}</p> <p>Suggestion: Chemical production processes – for example, the production of chlorinated phenols, the production of chlorinated solvents via oxychlorination, the production of pulp and paper using chlorine or chlorine derivatives for bleaching – can generally be addressed by modifying the process or by product substitution.</p>
8	<p>“Thermal and combustion processes – including incineration of wastes, the combustion of solid and liquid fuels and the thermal processing of metals;”</p> <p>Comment: Thermal and combustion processes in which there is no available chlorine cannot be PCDD/F sources.</p> <p>Suggestion: Thermal and combustion processes involving chlorine and/or chlorine-containing materials – including incineration of wastes, combustion of solid and liquid fuels and the thermal processing of metals;</p>
8	<p>“Biogenic processes, which may form PCDD/PCDF from precursors – there is some evidence of this occurring in compost.”</p>

	<p>Comment: First, it is important to explain or give examples of precursors. Second, PCDD/F are also formed via phototransformation of precursors such as pentachlorophenol.^{lxiii}</p> <p>Suggestion: Biological transformation and phototransformation may form PCDD/Fs from chlorinated precursors, such as pentachlorophenol.</p>
<p>9</p>	<p>“Four conditions, present either individually or in combination, potentially cause generation of PCDD/PCDF and release to air:</p> <ul style="list-style-type: none"> • <i>High temperature (above 200 °C) processes and/or incomplete combustion;</i> • <i>Organic carbon;</i> • <i>Chlorine;</i> • <i>PCDD/PCDF containing products”</i> <p>Comment: The subject of PCDD/F formation and the conditions necessary for its occurrence is more appropriately addressed as part of the general topic of “Formation of PCDD/PCDF”, which appears in the draft Toolkit immediately before this section on “Direct Releases of PCDD/PCDF” and sub-section “Release to Air.” Moreover, it is not accurate that any of these “four conditions either individually or in combination” may cause PCDD/F formation. For example, not one of these conditions individually will lead to PCDD/F formation. Moreover, high temperature and organic carbon in combination will not lead to PCDD/F formation. “PCDD/PCDF containing products” do not “cause generation of PCDD/PCDF”, although they may cause “release to air.” Indeed, the first three “conditions” – high temperature, organic carbon, and chlorine – do not result in PCDD/F formation unless oxygen is present.</p> <p>Suggestion: Correct this text segment as indicated below and place it below the first paragraph in “3.1 Formation of PCDD/PCDF”:</p> <p>PCDD/F formation can take place only when the following four elements are available and brought into contact under appropriate conditions:</p> <ul style="list-style-type: none"> • Chlorine • Carbon • Oxygen • Hydrogen <p>PCDD/F formation is known to take place at temperatures ranging from ambient to those of high-temperature combustion. For example, PCDD/F formation has occurred during composting of materials contaminated with pentachlorophenol^{lxiv} and through photolysis at ambient temperature of pentachlorophenol-contaminated soils^{lxv}. PCDD/F formation is also known to occur as furnace gases from high-temperature incinerators cool through a temperature range of 900 to 240 °C.^{lxvi}</p>
<p>9</p>	<p>“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. A description of dioxin-preventing and dioxin-reducing techniques and technologies will be published as a Compendium to Reduce Emissions of PCDD/PCDF (UNEP 2001).”</p> <p>Comment: Again, greater consistency in terminology will minimize confusion. For</p>

	<p>example, “PCDD/PCDF”, rather than “dioxin” is the term most commonly used in the draft Toolkit. Also, to avoid confusion, the word “air” should be used in conjunction with the word “emissions”, or preferably, the term used should be “air releases”. Also, if means for reducing PCDD/F formation are to be addressed in this draft report, this should be done with greater thoroughness, accuracy and consistency.</p> <p>Suggestion: Actual PCDD/F formation and subsequent release to air will depend on process conditions and the type and mode of operation of air pollution controls. Various techniques and technologies exist whereby PCDD/F formation can be reduced and/or eliminated. For example, eliminating or reducing chlorine and chlorine-containing materials from process inputs is a recognized technique for reducing or eliminating PCDD/F formation in a variety of processes.^{lxvii, lxviii}</p>
9	<p>“PCDD/PCDF releases to water can occur with the discharge of wastewater, run-off from contaminated sites or application of dioxin-contaminated chemicals/products, e.g., direct application of pesticides, dumping of wastes, etc.”</p> <p>Comment: Another important pathway of PCDD/F releases to water is via landfill leachate.^{lxix, lxx, lxxi, lxxii}</p> <p>Suggestion: PCDD/F releases to water can occur in a variety of ways, for example, with the discharge of wastewater, run-off from contaminated sites, leaching from landfills, dumping of wastes, application of PCDD/F-contaminated chemicals and products (e.g., application of pesticides), etc.</p>
9	<p><i>“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:</i></p> <ul style="list-style-type: none"> • <i>Wastewater discharge from pulp and paper production using elemental chlorine;</i> • <i>Wastewater discharge from chemical production processes involving elemental chlorine;”</i> <p>Comment: The use of the term “elemental chlorine” in this text carries with it the implication that PCDD/F formation is an issue only when “elemental chlorine” is used. This is, of course, not the case since PCDD/F formation also takes place during pulp and paper bleaching with chlorine derivatives such as chlorine dioxide.^{lxxiii} Likewise PCDD/F are also formed and released in the wastewater discharges from industrial processes that involve not only elemental chlorine but also other inorganic and organic chlorine derivatives, e.g., scrubber water from incinerators^{lxxiv} and aluminum production involving the use of hexachloroethane.^{lxxv}</p> <p>Suggestion: 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 landfill or other repository. Examples are:</p> <ul style="list-style-type: none"> • Wastewater discharge from pulp and paper production using elemental chlorine or chlorine derivatives, such as chlorine dioxide; • Wastewater discharge from chemical production processes that involve elemental chlorine or chlorine derivatives;
10	<p><i>“Wastewater discharge from normal household operations (washing machines,</i></p>

	<p><i>dishwashers, etc.)”</i></p> <p>Comment: It seems important here to identify the actual sources of the PCDD/Fs in such household operations, such as clothing contaminated with PCDD/Fs associated with the use of pentachlorophenol as a fabric treatment or preservative and the use of detergents containing PCDD/F-contaminated dichloroisocyanurate^{lxxvi} rather than leaving the mistaken impression that such operations actually generate PCDD/Fs.</p> <p>Suggestion: Wastewater discharge from household washing machines and dishwashers in which clothing or other textiles contaminated with PCDD/Fs and/or detergents that contain PCDD/Fs are used.</p>
<p>10</p>	<p><i>“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. Examples are:</i></p> <ul style="list-style-type: none"> • PCDD/PCDF-contaminated areas such as production or handling sites of chlorophenol herbicides; • <i>Timber industry sites;</i> • Junk yards, especially when waste oils from cars are present.” <p>Comment: It is important that users know that landfills are potential sources of PCDD/F-containing leachates and that leaching occurs in landfills, regardless of their design, construction and operation^{lxxvii} and that additional mobilization occurs not only with co-disposal of organic solvents but also through the availability of humic acids, which are present in all soils.^{lxxviii} Unless it can be documented that PCDD/F is present in run-off or leachate from junk yards, this should be deleted.</p> <p>Suggestion: Leaching of PCDD/Fs occurs when rainwater migrates through landfills and similar waste repositories that contain PCDD/F-contaminated products and residues. Leaching of PCDD/Fs from landfills is enhanced by the presence of humic acids, which are present in all soils, and by co-disposal of solvents. Examples are:</p> <ul style="list-style-type: none"> • Landfills that contain PCDD/F-contaminated materials, such as incinerator ash; • <i>PCDD/F-contaminated areas such as production or handling sites of chlorophenol herbicides;</i> • Timber industry sites where pentachlorophenol or other chlorinated chemicals were used as preservatives;
<p>10</p>	<p>“Consequently, the criteria used to identify potential releases of PCDD/PCDF to water include:</p> <ol style="list-style-type: none"> <i>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;</i> <i>2. Use of PCDD/PCDF contaminated pesticides (especially PCP and 2,4,5-T) and other chemicals (especially PCB);</i> <i>3. Leachate from storage and/or disposal sites of PCDD/PCDF contaminated materials.”</i> <p>Comment: The items listed above do not constitute “criteria”; rather, they are</p>

	<p>examples. Items in this list seem to be repetitive of those in the other two lists in this section. Also, as discussed earlier, it is important to avoid the impression that only processes involving (elemental) chlorine are relevant to PCDD/F formation.</p> <p><i>Suggestion: Combine all three lists into one, avoiding repetition of individual items. Otherwise, modify the text of this portion as follows:</i></p> <p><i>Other examples of sources of potential releases of PCDD/Fs to water include:</i></p> <ol style="list-style-type: none"> 1. Wastewater discharge from processes involving chlorine and/or chlorinated materials and/or PCDD/F-contaminated products or combustion, incineration and other thermal processes where chlorine or chlorine-containing materials are involved and where wet scrubbers are used to clean flue gases; 2. Use of PCDD/F-contaminated pesticides (especially PCP and 2,4,5-T) and other chemicals (especially PCB); 3. Leachate from storage, landfills and/or disposal sites of PCDD/F-contaminated materials.”
10	<p>“3.2.3 Release to Land</p> <p>Sources releasing PCDD/PCDF to land can be divided into two classes: PCDD/PCDF</p> <p><i>contaminated product “applied” to land directly 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.</i></p> <p><i>Examples include:</i></p> <ul style="list-style-type: none"> • <i>PCDD/PCDF contaminated product or waste use, e.g. pesticides, wood preservatives;</i> • <i>Application of sewage sludge on farm land;</i> • <i>Direct disposal of PCDD/PCDF containing wastes on land.</i> <p><i>Deposition of PCDD/PCDF to land via the atmosphere is not addressed in the Toolkit.”</i></p> <p>Comment: As discussed earlier in the general comments, the decision by the Toolkit’s authors to consider the environmental compartment “<i>land</i>” to consist only of surface soils allows perhaps the largest releases of PCDD/Fs to the environment, such as deposition in landfills of PCDD/F-contaminated residues, to be ignored as such.</p> <p>Suggestion: The Toolkit should be revised so that the environmental compartment “<i>land</i>” consists, as is commonly accepted, of all land so that PCDD/F-containing materials that are sent to landfills, deepwell injection, mines, quarries, etc. do not escape consideration as environmental releases.</p>
11	<p>“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 are also contaminated with PCDD/PCDF.”</p> <p>Comment: The first sentence requires both qualification and documentation, since wastes from production of these and other organochlorines contain far higher concentrations of PCDD/Fs than the products.</p>

	<p>Suggestion: Among products, some of the highest concentrations of PCDD/Fs 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). However, far higher levels of PCDD/Fs have been found in residues from production. For example, wastes from the manufacture of vinyl chloride, the monomer of polyvinyl chloride, have been found to contain some of the highest PCDD/Fs concentrations ever reported. ^{lxxix, lxxx}</p>
<p>11</p>	<p><i>“PCDD/PCDF reduction comes from modification of the problematic step of the production process. Reduction of releases can also be accomplished by restrictions on the uses of a chemical, by substitution or bans in some cases. This type of source control 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.”</i></p> <p>Comment: This discussion should describe the possibilities for PCDD/F reduction and/or elimination more clearly. Also, the last sentence is not true in all cases, depending on the meaning given to the word “effective,” since some commonly used methods of reducing PCDD/Fs in products simply shift the PCDD/Fs from the products to a wastestream.</p> <p>Suggestion: PCDD/F elimination or reduction comes through 1) product substitution, through bans and phase-outs, so that the process that generates PCDD/Fs is no longer used; 2) modification of the process, though changing inputs and/or conditions, so that PCDD/Fs are no longer produced. Eliminating or reducing PCDD/F formation so that products contain no PCDD/Fs also reduces associated releases to the environment.</p>
<p>11</p>	<p><i>“3.2.5 Release in Residues An almost infinite number of processes can transfer PCDD/PCDF to wastes or 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:</i></p> <ul style="list-style-type: none"> • <i>Garbage, trash, and rubbish (municipal, industrial, hazardous, medical, etc.);</i> • <i>By-product waste from combustion and thermal processes (fly ash, bottom ash, soot, etc.);</i> • <i>Production residues and residual products (sludge and residues from chemical production, sewage sludge from wastewater treatment, waste pesticides, waste transformer oil, etc.).”</i> <p>Comment: Refer to earlier discussions of the need for consistency in terminology. The first sentence is simply inaccurate: the processes that transfer PCDD/Fs to residues are not infinite but are, indeed, limited to those processes that involve some form of chlorine. The meaning of the second sentence is not clear. The terms used in the bullet points are repetitious, needlessly confusing and fail to make the important distinction between primary and secondary sources of PCDD/Fs.</p> <p>Suggestion: Processes in which PCDD/Fs are formed and incorporated into process residues are those that involve chlorine and/or chlorine-containing materials. Residues that contain PCDD/Fs include, for example:</p>

	<ul style="list-style-type: none"> • Residues from incineration and other thermal processes in which materials containing some form of chlorine are burned, e.g., fly ash, bottom ash or slag, soot, etc. from incinerators, thermal power generators, etc. • Residues from the production of chlorine-containing chemicals or chemicals that are produced through the use of chlorine-containing intermediates, e.g., process sludge, heavy bottoms, distillation residues, etc.; • Discarded products, e.g., off-specification or unused pesticides, banned or discarded PCB transformer oils • Untreated wastes from households, municipalities, healthcare facilities, etc. containing discarded products that are contaminated with PCDD/Fs formed during their manufacture or transferred during their treatment with other PCDD/F-contaminated products; • Municipal wastewater treatment sludge which contain PCDD/Fs due to the use of PCDD/F-contaminated cleaning products (detergents, toilet paper, etc.), laundering of contaminated clothing and other textiles, washing of contaminated vegetables, etc.
<p>11</p>	<p><i>“Because PCDD/PCDF are persistent and widely dispersed in the environment low concentrations of PCDD/PCDF are contained in normal municipal solid waste as well as Industrial, hospital, and other solid waste streams collected during normal every day activities. These include consumer products such as plastics, paper, cloth, household chemicals and food and especially products used in industry such as solvents, oils, paints, etc.”</i></p> <p>Comment: The information in this paragraph is incorporated, in a more informative fashion, in the above-suggested text. Moreover, the information in the last sentence requires thorough documentation, since currently available data do not support the contention that all of the consumer products listed actually contain PCDD/Fs.</p> <p>Suggestion: Delete this paragraph.</p>
<p>12</p>	<p><i>“Chemical production involving elemental chlorine variously 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.”</i></p> <p>Comment: As discussed in both general comments and earlier detailed comments, PCDD/F formation is not limited to chemical production involving only elemental chlorine; it also takes place in processes involving both organic and inorganic forms of chlorine. With appropriate modification of the first sentence, the second sentence becomes superfluous and can be deleted.</p> <p>Suggestion: Chemical production involving chlorine and/or inorganic and organic forms of chlorine variously leads to wastes containing PCDD/Fs, e.g., the production of chlorine-containing industrial chemicals and pesticides,^{lxxxii} chemicals for which chlorine or chlorine-containing intermediates are used during their manufacture, such as titanium dioxide^{lxxxii}.</p>
<p>12</p>	<p>“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.</p>

	<p>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.”</p> <p>Comment: Parties to the Stockholm Convention have not yet agreed on levels of PCDD/Fs that can be regarded as insignificant, so the first sentence must be appropriately modified. Further, even though PCDD/F levels in residues, such as bottom ash from waste incinerators, may be low, the comparatively large amounts of such residues can result in their contributing substantial releases of PCDD/Fs, as illustrated in Figure 1, which is discussed in earlier general comments.</p> <p>Suggestion: PCDD/Fs may be associated predominantly with one of several residues from a process while other residues contain no or low PCDD/F levels. For example, thermal processes often concentrate PCDD/Fs in the residues from flue gas cleaning operations (fly ash) while grate ash has low concentrations of PCDD/Fs. However, for some processes, such as waste incineration, bottom ash is generated in far greater quantities and, consequently, may constitute the largest release of PCDD/Fs.”</p>
12	<p>“For example whereas contaminated wastes from the chemical industry being incinerated effectively would destroy any PCDD/PCDF present whereas dumping of a 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.”</p> <p>Comment: The destruction efficiencies achieved by modern incinerators with PCDD/Fs and other POPs has not been shown to be high. According to available data, the actual destruction efficiencies of incinerators are relatively low.^{lxxxiii} It is also worthy of note that not only “dumping”, which is a term commonly used to refer to uncontained surface disposal, but also landfills can be important reservoir sources. In addition, the second sentence raises an important issue: PCDD/F-containing wastes are necessarily POPs wastes. This means that PCDD/F-containing wastes must be managed according to the requirements of the Stockholm Convention, e.g., POPs waste are “[n]ot permitted to be subjected to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants.” This suggests that the reuse of some PCDD/F-containing residues is a contravention of this treaty.</p> <p>Suggestion: While contaminated residues from, for example, a chemical process may be effectively destroyed by an appropriate destruction technology, dumping or landfilling such residues will result in the creation of a reservoir source. Moreover, the transfer of contaminated residues for destruction or further processing can result in PCDD/F releases to air, water, land, products and other residues.</p>
12	<p>“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 are locations of no immediate or ongoing release of PCDD/PCDF. Legacy contamination from former operations has the potential to become sources in the future.”</p> <p>Comment: The use of the word “potential” with respect to “hot spots” is unnecessary. Either a “hot spot” is a “hot spot” or it is not and so is not included in the inventory. In</p>

	<p>addition, it would seem that “hot spots” are “hot spots” because they do have immediate or ongoing releases of PCDD/Fs or the strong probability for such releases. The same reasoning applies to legacy contamination.</p> <p>Suggestion: 3.2.6 Hot Spots Hot Spots are included as a category for assessment (see Section 4.1). This category differs from the other nine categories in that there is or should not be ongoing, deliberate additions to the amount of PCDD/Fs at the hot spot. Included in this category are pits, piles, ponds, landfills, etc. in which PCDD/F wastes from former as well as ongoing operations have accumulated or been deposited.</p>
12	<p>“Although the concentrations of PCDD/PCDF in these Hot Spots can be very high, present releases may be negligible or small.”</p> <p>Comment: As discussed earlier, the issues of insignificance or negligibility have yet to be resolved by the Parties to the Stockholm Convention.</p> <p>Suggestion: While the concentrations of PCDD/Fs in these Hot Spots may be very high, present releases may be relatively small, depending on the circumstances of each individual Hot Spot.</p>
15	<p>“The basic aim of the toolkit is to enable an estimate of average annual release to each vector (air, water, and land, in products and residues) for each process identified. The estimate can be calculated by this basic equation:”</p> <p><i>Comment: It is very useful to have a term, such as “vector”, as a collective term for all the five PCDD/F “sinks” and/or “carriers” identified by the Toolkit’s authors. However, it would be most helpful to introduce and explain this term as early in the report as possible.</i></p>
15	<p>“Source Strength (Dioxin emissions per year) = Emission Factor x “Activity Rate”</p> <p>Comment: This important equation should be modified to reflect the requirement that all releases are addressed. Also refer to early discussions of the need for consistency in terminology.</p> <p>Suggestion: Source Strength (PCDD/F released per year) = (Emission Factor_{AIR} x Activity Rate) + (Emission Factor_{WATER} x Activity Rate) + (Emission Factor_{LAND} x Activity Rate) + (Emission Factor_{RESIDUE} x Activity Rate) + (Emission Factor_{PRODUCT} x Activity Rate)</p>
15	<p>“The PCDD/PCDF emission per year will be calculated and presented in grams of toxic equivalents (TEQ) per year.”</p> <p>Comment: Refer to early discussions of the need for consistency in terminology.</p> <p>Suggestion: The PCDD/F releases per year will be calculated and presented in grams of toxic equivalents (TEQ) per year.”</p>

<p>15</p>	<p><i>“The annual Source Strength is calculated by multiplying the release of PCDD/PCDF (e.g. in µg I-TEQ) per unit of feed material processed or product produced (e.g. ton or liter) – referred to as the Emission Factor – with the amount of feed material processed or product produced (tons or liters per year) – referred to as the Activity Rate.”</i></p> <p>Comment: Again, it is essential that the fundamental concepts reflect the requirement that all releases are to be addressed.</p> <p>Suggestion: The annual Source Strength is determined by calculating the annual rate of release to each environmental medium or compartment and summing those releases. Each Emission Factor (Emission Factor_{AIR}, Emission Factor_{WATER}, Emission Factor_{LAND}, Emission Factor_{RESIDUE}, and Emission Factor_{PRODUCT}), expressed in µg I-TEQ per unit of feed material processed or product produced (e.g. ton or liter), is multiplied with the Activity Rate -- the amount of feed material processed or product produced (tons or liters per year). The results of these calculations are summed to yield the annual Source Strength.</p>
<p>15</p>	<p><i>“The Toolkit is designed to assemble the necessary activity data and to provide a means of classifying processes and activities into classes for which an appropriate average emission factor is provided.”</i></p> <p>Comment: This sentence is not an accurate description of the Toolkit in that the Toolkit is not “designed to assemble the necessary activity data.” Instead, it offers limited advice on possible means for obtaining such data. Also as discussed earlier, it is important to define as explicitly as possible the uncertainties of release estimates. Consequently, it is necessary to that the Toolkit presents and advises users to apply a range of emission factors.</p> <p>Suggestion: The Toolkit offers advice on assembling the necessary activity data, provides a list of source categories and sub-categories and, for each source, presents a range of emission factors for each environmental media/compartment.</p>
<p>15</p>	<p>“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.”</p> <p>Comment: Please refer to the earlier discussion of the need for a Source Identification Strategy.</p> <p>Suggestion: Insert in this section, a detailed description of the Source Identification Strategy that will enable users to identify those sources of PCDD/F and other by-product POPs that are not addressed in the Toolkit.</p>
<p>15</p>	<p><i>“In the fourth step, emissions are calculated on the basis of information obtained in the previous steps via Equation (1).”</i></p> <p>Comment: Please refer to earlier discussion about the necessity of consistent terminology.</p>

	<p>Suggestion: In the fourth step, releases are calculated on the basis of information obtained in the previous steps via Equation (1).”</p>
16	<p>“1. <i>Apply Screening Matrix to identify Main Source Categories</i> 2. <i>Check subcategories to identify existing activities and sources in the country</i> 3. <i>Gather detailed information on the processes and classify processes into similar groups by applying the Standard Questionnaire</i> 4. <i>Quantify identified sources with default/measured emission factors</i> 5. <i>Apply nation-wide to establish full inventory and report results using guidance given in the standard format</i></p> <p>Figure 2: The recommended five-step approach to establish a national PCDD/PCDF release inventory using the Toolkit”</p> <p>Comment: Please refer to the earlier discussion of the need for a Source Identification Strategy.</p> <p>Suggestion:</p> <ol style="list-style-type: none"> 1. Apply Screening Matrix to identify Main Source Categories 2. Follow Source Identification Strategy to identify any sources that are not addressed in the Main Source Categories. 3. Check subcategories and results of Source Identification Strategy to identify existing activities and sources in the country 4. Gather detailed information on the processes and classify processes into similar groups by applying the Standard Questionnaire 5. Quantify identified sources with default/measured emission factors 6. Apply nation-wide to establish full inventory and report results using guidance given in the standard format <p>Figure 2: The recommended six-step approach to establish a national PCDD/F release inventory using the Toolkit</p>
16	<p>“The emissions factors themselves will be updated, improved or amended as more information becomes available.”</p> <p>Comment: The Toolkit’s list of sources should also be updated.</p> <p>Suggestion: The Toolkit’s list of source and emission factors will be updated, improved or amended as more information becomes available.</p>
16	

Table 1: Screening Matrix – Main Source Categories

No.	Main Source Categories and Subcategories	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				

Comments: Refer to earlier discussion of the problem of defining the environmental compartment “land” as not including landfills and similar environmental repositories. This confusion is exacerbated by Main Source Category 9, which is actually entitled “Disposal/Landfill” at Section 6.9 and is described as including landfills and waste dumps; sewage and sewage treatment; composting; open water dumping (e.g., into rivers, lakes, oceans); and waste disposal (not combustion). Also, this is a list of main categories, so inclusion of the term “subcategories” in the third column is confusing. Further, while the attempt to identify “main release routes for each category” is admirable, there are far too many missing emission factors in the Toolkit’s database to support this effort. Even in those relatively few cases where all necessary emission factors are presented, the resulting prioritization of releases is potentially appropriate only for certain processes and activities in the industrialized nations. It is necessary to bear in mind that, in some developing countries and countries with economies in transition, industries are known to dump their process wastes along roadsides and discharge untreated wastes directly into waterways.

Suggestion: Delete the term “and Subcategories” in column 3. Reconfigure the main source categories into a more rational format. Delete columns 4 through 8.

16

“The Xs indicate main release routes for each category.”

Comment: Refer to discussion above.

Suggestion: Delete the four relevant columns from Table 1. In the event these columns are not deleted, modify the sentence as follows: The Xs indicate those routes of releases that are currently thought to predominate in the process and activities of industrialized countries.

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Pursuant to the earlier discussion, a new subsection should be inserted between 4.1 Step 1 and 4.1 Step 2 that describes the source identification strategy, advises users on following this strategy and on including sources so identified in the appropriate subcategories. Subsequently, the text in the remaining sections of the report must be modified to reflect

	the use of and results of the source identification strategy.
17	<p>“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.”</p> <p>Comment: Refer to earlier discussions of compartments/media, the designation of release routes and the determination of the quantity or quantities of PCDD/F that are to be regarded as significant.</p> <p>Suggestion: Delete these sentences or, alternatively, modify the text as follows: Columns identify the five compartments or media into which PCDD/Fs can be released. In this regard, the large “X” denotes the release route that is often regarded as predominant, and the small “x” denotes additional release routes that have also been identified in the industrialized countries.</p>
17	<p>“Incineration in this context means destruction 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.”</p> <p>Comment: The term “destruction” is inappropriate in this context, since all material input to waste incinerators is not necessarily destroyed.</p> <p>Suggestion: “Incineration in this context means treatment in a combustion furnace of some sort ...”</p>
18	<p>“Wastes differ in combustion characteristics and combustion equipment also typically differs for each of the waste incineration subcategories.”</p> <p>Comment: As supported by information included later in this report, there are also many variations in combustion equipment within subcategories.</p> <p>Suggestion: Wastes differ in content, e.g., presence of chlorine and metals, and combustion characteristics. Combustion equipment also typically varies both between and within the waste incineration subcategories.</p>
18	<p><i>“Main releases occur into air but residues may also contain high concentrations of PCDD/PCDF. Releases to water play only a minor role and only in cases where wet scrubbers are used for flue gas treatment and where PCDD/PCDF-laden particles are released.”</i></p> <p>Comment: The first sentence is contrary to the numerous reports and studies describing PCDD/F releases from waste incinerators, virtually all of which show that residues carry the greatest share of the total PCDD/F output from incinerators. See, for example, the inventories for the EU, the results of which have been combined and illustrated in Figure 1.^{lxxxiv, lxxxv} Among the other studies showing residues to carry the far greater share of PCDD/F output are, for example, Abad et al. (2000)^{lxxxvi}, Abad et al. (2002)^{lxxxvii}, Giugliano et al. (2002)^{lxxxviii}, and Ito and Suzuki (2002)^{lxxxix}.</p> <p>Suggestion: Main releases occur to residues while releases to air may be a much smaller fraction but vary according to the type and efficiency of air pollution control systems.</p>

	<p>Releases to water may be small, depending on whether wet scrubbers are used and scrubber water treatment and whether discharged ashes are cooled with water and any subsequent treatment of that water.</p>
18	<p>“Table 3: Subcategories of the Inventory Matrix – Sector 2”</p> <p>Comment: Several sources can be added to this subcategory.</p> <p>Suggestion: Include the following in this subcategory: titanium,^{xc} magnesium and nickel^{xc1}</p>
19	<p><i>“In large, well-controlled fossil fuel power plants, the formation of PCDD/PCDF is low since the combustion efficiency is usually fairly high 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.”</i></p> <p>Comment: Since, according to the Toolkit, there are no data describing PCDD/F levels in fossil fuel power plant residues, there is insufficient information to support the first statement above. As noted in one PCDD/F inventory, <i>“The combustion of oil and coal emits dioxin [PCDD/F] because these fuels contain both chlorine and organic precursors.”</i>^{xcii} Moreover, studies of power generating facilities, such as that by Kopponen et al. (1992), have shown that PCDD/F releases increased with increasing chlorine content in the fuel.^{xciii} Other studies, such as that by Manninen et al. (1996) have shown that “chlorine content of the fuel correlated with PCDFs and there was an inverse correlation between the S/Cl ratio and PCDFs.”^{xciv} Gullette and Raghunathan (1997) concluded that, for coal combustion processes, low or no PCDD/F formation <i>“may be due to a number of factors including lack of appropriate catalysts, lack of organic products of incomplete combustion, insufficient chlorine, and the presence of catalyst-poisoning sulfur as SO₂.”</i>^{xcv}</p> <p>Suggestion: Modify wording as follows: In large, well-controlled fossil fuel power plants, the formation of PCDD/Fs is not well documented since there are no data describing releases in residues. However, PCDD/F formation is known to vary with the chlorine content of the fuel and, based on available information, PCDD/F releases to air can be substantial.</p>
19	<p><i>“Where smaller plants or biomass are used, the fuel may be less homogeneous and burned at lower temperatures or with decreased combustion efficiency.”</i></p> <p>Comment: Again, data describing PCDD/F releases in the residues of small facilities and those burning biomass (with the exception of wood-fired power boilers) were apparently not available to the authors of the Toolkit, so the meaning of this sentence is not at all clear. If the intent is to suggest that such facilities produce PCDD/Fs at higher rates than large, fossil-fuel power boilers, there is insufficient data in the Toolkit to support this suggestion. Moreover, the data there are presented in the Toolkit show that, with the exception of biomass-fired boilers and domestic stoves burning contaminated wood, emission factors for air releases do not differ markedly. This suggests that, in general, there is insufficient evidence to support the conclusion that large fossil fuel burning power plants have markedly reduced PCDD/F generation rates. Also, as attested to by the emission factors presented in the Toolkit and documented in Costner (2001),^{xcvi} the highest PCDD/F formation occurs when the fuel burned is wood contaminated with pentachlorophenol or contains polyvinyl chloride (PVC) cladding or some other source of</p>

	<p>chlorine.</p> <p>Suggestion: Modify sentence as follows: Where smaller plants are used, the fuel may contain more chlorine and metal catalysts and such facilities may operate at lower temperatures and with poorer combustion efficiency. However, the Toolkit's emission factors are not adequate for estimating total PCDD/F releases from such facilities.</p>
19	<p><i>“The same may occur when landfill and/or biogas is used as a fuel due to the presence of unwanted and undefined additional constituents.”</i></p> <p>Comment: Again, refer to Costner (2001) for a compilation of studies that address the issue of chlorine content and PCDD/F release.</p> <p>Suggestion: Modify sentence as follows: PCDD/F formation and release may occur when landfill or biogas is used due to the presence of chlorinated species in the gases burned.</p>
20	<p><i>“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, mostly fly-ashes.”</i></p> <p>Comment: Again, the intent of these statements is not clear. As noted above, there are sufficient data presented in the Toolkit to estimate PCDD/F releases for household heating and cooking with contaminated wood/biomass, virgin wood/biomass, and coal-fired stoves but not domestic stoves fired with oil and natural gas. In those cases where sufficient data are available, contaminated wood/biomass and coal appear to be the fuels with the highest potential PCDD/F formation and releases. The last sentence is not fully supported by the release data presented in the Toolkit. See earlier discussion of the lack of sufficient data in the Toolkit. Also the chlorine content of the fuel is an important factor in PCDD/F formation [see Costner (2001)].</p> <p>Suggestion: In the cases of domestic and/or household heating/cooking, the highest potential for PCDD/F formation and release occurs during the burning of contaminated wood/biomass and coal, both of which may contain relatively high levels of chlorine. Where sufficient data are available, PCDD/F releases in residues are greatest.</p>
19	<p>“These are high-temperature processes for melting (glass, asphalt), baking (brick, ceramics), or thermally induced chemical transformation (lime, cement). In them, fuel combustion generates PCCD/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.”</p> <p>Comment: For these processes, the Toolkit presents no data that describe PCDD/F releases to land, products or, except for cement kilns and certain asphalt mixing plants, residues. In the absence of such data, it is not possible to estimate PCDD/F releases with even a minimal degree of confidence. Also in the Toolkit's emission factors, there is no distinction between cement kilns and other facilities that burn waste (e.g., tires, municipal waste, medical waste, hazardous waste, etc.) and those that do not, although important</p>

	<p>differences have been documented. For example, in the U.S. inventory, the average emission factor_{AIR} for cement kilns that burn hazardous waste were as much as 100 times higher than those for cement kilns burning conventional fuels. In addition, PCDD/F levels in the cement kiln dust of cement kilns burning hazardous waste were some 1000 times higher than that from conventionally fired cement kilns.^{xcvii} Nor does the Toolkit distinguish between such facilities that burn natural gas, oil or coal, although it is reasonable to expect emission factors to differ considerably among these conventional fuels. In the absence of emission factors for releases to land and products, the Toolkit simply does not present enough information to support the last sentence above. Moreover, it is not possible to estimate PCDD/F releases with any certainty.</p> <p>Suggestion: These are high-temperature processes for melting (glass, asphalt), baking (brick, ceramics), or thermally induced chemical transformation (lime, cement). Within these processes, combustion of fuel and/or wastes generates PCCD/Fs as unwanted byproducts when the fuel or waste contains chlorine in some form. Additional, formation of PCDD/Fs may be linked to the process raw materials used if they contain chlorine in some form. Cement and lime kilns are large volume processes, which often use various wastes as add wastes as a low/no cost fuel. There is not sufficient information to estimate total PCDD/F releases from these facilities.</p>
20	<p>“Higher emissions result from mixed wastes due to poorer combustion. Inhomogeneous and poorly mixed fuel materials, chlorinated precursors and catalytically active compounds impact the process. 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.</p> <p><i>Comment: Please refer to earlier discussions of the need for consistent terminology.</i></p> <p><i>Suggestion: Higher releases result from mixed wastes due to poorer combustion, non-homogeneous and poorly mixed fuel materials, the presence of chlorine-containing materials and metals, etc.</i></p>
20	<p>“Table 7: Subcategories of the Inventory Matrix – Sector 6 (Clean) Biomass burning Waste burning and accidental fires ”</p> <p><i>Comment: This list would be more useful if it were more specific.</i></p> <p><i>Suggestion:</i> <i>Table 7: Subcategories of the Inventory Matrix – Sector 6</i> <i>(Clean) Biomass burning</i> <i>Waste burning</i> <i>Accidental fires (buildings, vehicles, landfills, warehouses, trains, etc.)</i></p>
21	<p>“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 8).</p> <p><i>Comment: Refer again to discussions of the need for consistent terminology.</i></p>

	Suggestion: PCDD/F releases from
21	<p>“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 ‘of radicals in the reaction mixture/chemical process’ (see Section 6.7.2).</p> <p>Comment: Refer to earlier discussions of this issue.</p> <p><i>Suggestion: Indicators of high probability to form PCDD/Fs in chemical manufacturing processes are the presence of chlorine in some form and conditions such as ‘high temperature’, ‘alkaline media’, ‘the presence of UV-light as an energy source’, and/or ‘of radicals in the reaction mixture/chemical process’ (see Section 6.7.2).</i></p>
21	<p>“<i>Table 8: Subcategories of the Inventory Matrix – Sector 7</i> <i>Production and Use of Chemicals and Consumer Goods</i> <i>Pulp and paper mills</i> <i>Chemical industry</i> <i>Petroleum industry</i> <i>Textile plants</i> <i>Leather plants”</i></p> <p>Comment: This table would benefit from inclusion of more uses.</p> <p>Suggestion: Include the following in the table: Application of certain biocides (crops, textiles, buildings, etc.) Use of certain personal care products (e.g., toothpastes, etc. that contain certain bactericides)</p>
21	<p>“During production processes PCDD/PCDF releases can occur to all vectors except to land directly. 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 overall significance of contribution to the overall problem.</p> <p>Comment: The first sentence conflicts with existing evidence, e.g., the Seveso incident and similar explosions, leaks, spills, etc. Also, the second sentence would benefit from more explicit and accurate information (see earlier discussions, e.g., PCDD/F formation in bleaching occurs when any form of chlorine is used). Again, there is the issue of consistency of terminology. Also, it is disingenuous to suggest that chemical production facilities are “few”.</p> <p>Suggestion: During production processes PCDD/F releases can occur to all environmental media/compartments. The use of chlorine or chlorine derivatives for bleaching and the use of certain chlorine-containing biocides and dyestuffs, e.g., pentachlorophenol and chloranil-based dyes, have been contributors to direct releases of PCDD/Fs to water. Thus, strong emphasis should be given to detailed investigation of chemical production facilities that use or manufacture chlorine and/or chlorine-containing materials, since they are of major significance to the overall PCDD/F problem.</p>

21	<p>“Formation of PCDD/PCDF occurs mostly due to reaction of the hot gases with stray organics. In case of biomass drying and smoke-houses these compounds are mostly phenols and other hydrocarbons.”</p> <p>Comment: Again, it is important that the information presented is as unambiguous as possible.</p> <p>Suggestion: Formation of PCDD/Fs occurs due to reactions of the hot gases with sources of chlorine. In case of biomass drying and smoke-houses these chlorine sources are mostly chlorophenols and other chlorinated hydrocarbons.</p>
23	<p>“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.”</p> <p>Comment: Refer to earlier comments on the importance of consistent terminology.</p> <p>Suggestion: Within one subcategory to produce the same product, the releases of PCDD/Fs Key parameters used to distinguish processes releasing large amounts of PCDD/Fs from those releasing smaller quantities are given in Section 6.</p>
23	<p>“If no information on a certain activity is available, then the range of potential emissions should be calculated by applying the lowest and the highest emission factors.”</p> <p>Comment: Refer to earlier comments on the importance of consistent terminology.</p> <p>Suggestion: If no information on a certain activity is available, then the range of potential releases should be calculated by applying the lowest and the highest emission factors.</p>
24	<p>“Emissions from processes listed as “subcategories” above can vary by orders of magnitude depending on the process technology or operation.”</p> <p>Comment: Refer to earlier comments on the importance of consistent terminology.</p> <p>Suggestion: Releases from processes ...</p>
24	<p>“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 emissions data for every single process within a country or region and some extrapolation will be required.”</p> <p>Comment: Refer to earlier comments on the importance of consistent terminology.</p> <p>Suggestion: ... to find measured release data for every single</p>
26	<p>“In order to quantify source strength, an emission rate must be determined as an annual</p>

	<p>mass flow rate of PCDD/PCDF expressed in grams TEQ of PCDD and PCDF released per year.”</p> <p>Comment: Refer to earlier comments on the importance of consistent terminology.</p> <p>Suggestion: In order to quantify source strength, a total release rate must be determined as an annual mass flow rate ...</p>
26	<p>“Recent developments, the future POPs Convention, foresee the use of the TEFs as established by a WHO/IPCS expert group (van Leeuwen and Younes 1998).”</p> <p>Comment: This statement should be updated.</p> <p>Suggestion: Recent developments, including the POPs Convention, suggest that the TEFs as established by a WHO/IPCS expert group (van Leeuwen and Younes 1998) will be used.</p>
26	<p>“The annual releases for all vectors of a source or a source category are calculated as follows:”</p> <p>Comment: This sentence can be made considerably less confusing with slight rephrasing.</p> <p>Suggestion: The annual releases to all vectors from a source or a source category are calculated as follows:</p>
26	<p>“Source Strength (Dioxin Emissions per year) = Emission Factor x “Activity Rate” (1)”</p> <p>Comment: Please refer to the earlier discussion of this equation, which, as written, does not reflect accurately the calculation that must be carried out to determine “Source Strength”.</p> <p>Suggestion: Source Strength (PCDD/PCDF released per year) =</p> $\begin{aligned} & (\text{Emission Factor}_{\text{AIR}} \times \text{Activity Rate}) \\ & + (\text{Emission Factor}_{\text{WATER}} \times \text{Activity Rate}) \\ & + (\text{Emission Factor}_{\text{LAND}} \times \text{Activity Rate}) \\ & + (\text{Emission Factor}_{\text{RESIDUE}} \times \text{Activity Rate}) \\ & + (\text{Emission Factor}_{\text{PRODUCT}} \times \text{Activity Rate}) \end{aligned}$
26	<p>“According to equation (1), the annual Source Strength is calculated by multiplying the release of PCDD/PCDF (e.g., in $\mu\text{g I-TEQ}$) per unit of feed material processed or product produced (e.g., ton or liter) = the Emission Factor – by the amount of feed material processed or product produced (tons or liters per year) = the Activity Rate.”</p> <p>Comment: This sentence needs to capture the process whereby total releases are determined.</p> <p>Suggestion: According to equation (1), the annual Source Strength is calculated by multiplying the Activity Rate (the amount of feed material processed or product produced (tons or liters per year) by each of the Emission Factors (Emission Factor_{AIR}, Emission Factor_{WATER}, Emission Factor_{LAND}, Emission Factor_{RESIDUE}, and Emission Factor</p>

	<p>PRODUCT). Each Emission Factor is the amount of PCDD/Fs (e.g., in □g I-TEQ) that is released to one of the vectors (air, water, land, products, or residues) per unit of feed material processed or product produced (e.g., ton or liter).</p>
<p>26-27</p>	<p>“However, in some cases, e.g., within Sector 7 – Consumer Goods and Products - it may be impractical to use a default emission factor for a specific release. In such cases, default Emission 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 or residues). 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 or those mentioned in the Toolkit as the basis to calculate the emission factor (e.g., in ng I-TEQ/Nm³) by the Flux.</p> <p>Equation 2 applies:</p> <p>Source Strength (Dioxin Emissions per year) = Emission Concentration x Flux (2)</p> <p>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.</p> <p>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 calculations for consistency. Consequently, the resulting Source Strengths calculated as annual PCDD/PCDF mass flow emissions are determined by two critical factors:</p> <ol style="list-style-type: none"> 1. The annual Flux (mass or volume flow rate) or Activity Rate given either as: <ul style="list-style-type: none"> □ product produced (e.g., steel, sinter, lime, cement, etc.), or □ feed material processed (e.g., hazardous waste, sewage sludge, coal, diesel, etc.) or □ material emitted (e.g., Nm³ of flue gas, liters of wastewater, etc.) 2. The emission factor for a specific source given either as: <ul style="list-style-type: none"> □ the respective default emission factor from this Toolkit; □ actually measured real data from the respective source as a concentration (e.g., ng TEQ/Nm³, ng TEQ/liter), or □ The product of these two factors 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 emission estimate for each subcategory.” <p>Comment: Again, refer to earlier discussions of the importance of consistent terminology, especially vis-à-vis “emission” and “release”. Also the term “matrix” as it appears in the above segment is not entirely clear. Is this the same as “vector”? If so, it would be preferable to use the one term consistently. Considered as a whole, this segment is not readily understandable. In part, this can be attributed to the use of the term “Emission Concentration”, which will be interpreted by many as applying only to</p>

	<p>air releases. Also, overall, this segment does not convey the critical concept that all releases (i.e., to air, water, land, products and residues) from each source and/or source category must be determined. Rather, it is written as though only one type of release need be addressed.</p> <p>Suggestion: This segment requires thorough rethinking and rewriting if it is to explain to users the process of estimating total releases from a source or source category. Due to time constraints, we are unable to do this at this time but will be pleased to offer detailed suggestions on request.</p>
27	<p><i>“For each process within a subcategory, emissions are calculated by multiplying the activity rate for that class by the emission factor provided in the Toolkit for all release vectors, namely air, water, land, product, and residue (see Chapter 6).”</i></p> <p>Comment: Please refer to earlier discussions of the need for consistent terminology and the need to address all releases.</p> <p>Suggestion: For each process within a subcategory, total releases are calculated by multiplying the activity rate for the process by each of the vector-specific emission factors and summing the results.</p>
27	<p>“Default emission factors provided represent average PCDD/PCDF emissions for each class.”</p> <p>Comment: As discussed in earlier comments, the Toolkit should provide a range of emission factors, rather than an average, for each source or source category.</p> <p>Suggestion: “The Toolkit provides high, low and average emission factors for each source or source category where such factors are available or can be derived.</p>
27	<p><i>“4.4.5 Using Own Emission Data The Toolkit can be used where there are no measured data available or where domestic emission data and emission factors have been generated”.</i></p> <p>Comment: See earlier comments on the need for terminology that is consistent within the Toolkit as well as with the Stockholm Convention.</p> <p>Suggestion: 4.4.5 Using Own PCDD/F Release Data The Toolkit can be used where there are no measured data available or where domestic PCDD/F release data and emission factors have been generated.</p>
28	<p>“Obtaining dioxin and furan emission data is analytically challenging.”</p> <p>Comment: See earlier comments on the need for terminology that is consistent within the Toolkit as well as with the Stockholm Convention.</p> <p>Suggestion: Obtaining PCDD/F release data is analytically challenging.</p>
28	<p>“Finally, the emissions of all ten Main Source Categories are added up and the national inventory can be calculated, which represents the total estimated release from all</p>

	<p><i>identified and quantified sources in a country. This level usually represents the third and least detailed level, which is being reported.</i></p> <p><i>The emission estimates for several countries can be clustered into regional release inventories.”</i></p> <p>Comment: See earlier comments on the need for terminology that is consistent within the Toolkit as well as with the Stockholm Convention.</p> <p><i>Suggestion: Finally, the releases from all ten Main Source Categories are added up and the national inventory can be calculated, which represents the total estimated release from all identified and quantified sources in a country. This level usually represents the third and least detailed level, which is being reported.</i></p> <p>The release estimates for several countries can be clustered into regional release inventories.</p>
<p>29</p>	<p><i>“An interim inventory will contain the following information:</i></p> <ul style="list-style-type: none"> <input type="checkbox"/> <i>a listing of all process subcategories that are carried out in the country;</i> • ... • <i>the range of emission factors by process sub-category and the overall range of potential emissions (mass flow multiplied by low and high-end emission factors.”</i> <p>Comment: The first bullet point should be modified to include both sources identified via the Toolkit’s list and those identified via the Source Identification Strategy. Also see earlier comments on the need for terminology that is consistent within the Toolkit as well as with the Stockholm Convention.</p> <p>Suggestion:</p> <p>An interim inventory will contain the following information:</p> <ul style="list-style-type: none"> • a listing of all sources – those in the Toolkit as well as those identified through the Source Identification Strategy -- that are known to exist within the country. • ... • the range of emission factors by process sub-category and the overall range of potential releases (mass flow multiplied by low and high-end emission factors
<p>30</p>	<p><i>“Exerpts [sic] from Interim Inventory Report: Municipal Waste Incineration – Sector 1a.”</i></p> <p>Comment: The examples given here leave the mistaken impression that, for these and other sources, only one emission factor and so only one type of release to one environmental medium or compartment needs to be considered.</p> <p>Suggestion: Modify the information in this box so that, for each source, emission factors and release estimates to all environmental media/compartments are addressed, giving numeric values where possible as well as denoting those instances where no emission factors are available to allow the estimation of releases. Also each emission factor should be identified according to the associated environmental medium/compartment, e.g., Emission Factor_{AIR}, Emission Factor_{WATER}, etc. In addition the heading for column 5 should be modified for consistency of terminology: Potential Releases Using Default</p>

	Emission Factors. Further, the heading of column 6 should be more specific, e.g., Annual Releases to Air (or Water, Land, etc.). Also, change “Exerpts” to “Excerpts”.
31	<p>“<i>Figure 3: Example graphical presentation of an excerpt of the interim inventory</i> The bars give the lower and the upper estimate of the annual emission from the two subcategories together with the central estimate (municipal waste incineration and copper production). The points are meant to be country estimates of emissions based on measured data domestically (and do not represent the mean/median concentration or best estimate)”</p> <p>Comment: This example should be modified so that it includes estimated releases to all environmental media/compartments for each of the sources as well as denoting those potential releases for which no estimates can be made due to lack of data. Also see earlier comments on the need for consistent terminology.</p> <p>Suggestion: Modify this figure so that it includes, for each of the sources, estimated releases to each environmental medium/compartment and indicates those releases for which no estimates can be made due to lack of data. In addition, replace the words “emission” and “emissions” with “release” and “releases”.</p>
31	<p>“<i>The final country inventory of releases of PCDD/PCDF to all media will result from the application of the full Toolkit methodology.</i>”</p> <p>Comment: Based on this statement, the Toolkit gives users sufficient information to prepare complete estimates of releases to all environmental media/compartments. This is not the case, since there are many potential release routes for which no emission factors are given.</p> <p>Suggestion: Delete this sentence.</p>
31	<p>“<i>The full country inventory:</i> 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 release exists this will be identified. If a process does not exist in a country this will be clearly shown.”</p> <p>Comment: If the full country inventory does not also indicate where there are insufficient data to estimate potential releases, the protocol should be modified so that absences of appropriate emission factors and/or activity data are clearly identified.</p> <p>Suggestion: The full 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/or activity data exist so that releases can be estimated, this will be identified. Where no release exists this will also be identified. If a process does not exist in a country this will be clearly shown.</p>
33	<p>“To improve the presentation of the inventory information and to reflect the fact that more is known about releases to air than to other media it is suggested that two tables are used. The first will contain information on releases to air and the second on releases to the other media. An example of this inventory is shown in Chapter 8.3.”</p>

	<p>Comment: Preparing two inventories -- one for releases to air and one for the other environmental media/compartments – is not only unnecessary but also serves to obscure and potentially defeat the overall objective of the inventory process, which is to estimate PCDD/F releases to all environmental media/compartments. Further, the fact that more is known about releases to air than other releases is obvious when it is noted that there are no emission factors or other necessary data. Chapter 8.3 contains one-half page of text and three tables: “Table 78: 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”; “Table 79: Example table for the overview of the national releases of PCD/PCDF (output from the EXCEL sheets)”; and “Table 80: Sample format for presenting an air inventory where own measured data exists.” Compilations, such as that exemplified in Table 80, serve no useful purpose.</p> <p>Suggestion: Delete this paragraph.</p>
33	<p>“Also, as emissions 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 emissions.”</p> <p>Comment: See earlier comments on the need for terminology that is consistent within the Toolkit as well as with the Stockholm Convention.</p> <p>Suggestion: Also, as releases of ... Individual plants may have higher or lower releases.</p>
33	<p><i>“It also includes similar wastes produced during industrial, commercial or agricultural activities.”</i></p> <p>Comment: In many countries and regions, distinctions are drawn between municipal waste and wastes from industrial and agricultural activities.</p> <p>Suggestion: Delete this sentence.</p>
34	<p>“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, metals, dirt and rocks and other inert materials commonly present in consumer goods.”</p> <p>Comment: Dirt and rocks in municipal waste ordinarily come from inclusion of demolition waste, street sweepings, etc., rather than as constituents in consumer goods.</p> <p>Suggestion: 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.</p>
34	<p><i>“High emissions are associated with poor combustion (batch operation, high CO, etc.) and dust collectors operated at high temperatures. The operation of electrostatic</i></p>

	<p>precipitators (ESP) at elevated temperatures (above 200 °C) can increase releases of PCDD/F to air and in fly ash. Emissions from such plants would likely be higher than a similar plant using fabric filters or operating with an ESP at a lower temperature.”</p> <p>Comment: Refer to earlier comments on the need for terminology that is consistent within the report as well as with the Stockholm Convention. Also the contribution of chlorine and chlorine-containing materials to PCDD/F formation should be acknowledged here [see Costner (2001)^{xcviii}].</p> <p>Suggestion: High PCDD/PCDF formation is associated with poor combustion (batch operation, high CO, etc.) dust collectors operated at high temperatures, and waste composition, such as a high chlorine content and the presence of metals such as copper. ... Releases from such plants ...</p>
34	<p>“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 effluent is not adequately treated, e.g., to filter out the particles with the PCDD/PCDF adsorbed onto them. Thus, the most significant release routes are to air and residue.”</p> <p>Comment: Refer to earlier comments on the need for terminology that is consistent within the report as well as with the Stockholm Convention. The statements in this segment attest to the very important misconceptions created by defining “land” as surface soils only and excluding landfills. Also, in some European countries e.g. Germany, the Netherlands, France and Denmark about 50% of the stockpiled municipal waste incinerator bottom ash is used as secondary building material, in road construction or as raw material for the ceramic industry inter al.^{xcix, c, ci, cii, ciii, civ, cv} With regard to the second sentence, the designation of PCDD/F releases as “relevant” or not is a decision that rests with the Parties of the Stockholm Convention, not the authors of the Toolkit.</p> <p>Suggestion: MSW incinerators release PCDD/Fs into the air via stack gases. However, MSW incinerator ashes carry the largest share of the PCDD/Fs formed. The ashes are commonly sent to land (landfills) or, in some countries, used as secondary building material. Releases to water may occur 1) if wet scrubbers are used for the removal of particulate matter, in which case the amount of PCDD/Fs released to water depends on the efficacy of scrubber water treatment in which PCDD/Fs is captured in the filter cake of the treatment process; and 2) water is used to cool or “quench” incinerator ashes.</p>
34	<p>“Table 13: Emission factors for solid waste incineration”</p> <p>Comment: First, since many modern incinerators are operated in a slagging mode, the heading for column 4 should be “Bottom ash or slag.” Also, the EU inventory acknowledges the following types of incinerator residues: boiler ash, grate ash (bottom ash or slag), fly ash, sludge from the treatment of scrubber water, water used for quenching bottom ash, wash water and surface runoff and presents emission factors for bottom ashes, fly ash, and scrubber water sludge.^{cvi}</p> <p>Since the Toolkit does not include citations for its emission factors, it is not possible to determine their origins. However, they are, in many cases, very different from the emission factors in other inventories and in the scientific literature. For example, in the U.S. inventory, the seven types of incinerators, all equipped with various combinations of</p>

	<p>air pollution control devices, had emission factors_{AIR} ranging from 0.025 to 1,492 □g I-TEQ/ton,^{cvii} as compared to the Toolkit’s range of 0.5 to 350 □g I-TEQ/ton. In the EU inventory, the “typical” emission factor_{AIR} for MSW incinerators equipped with “high quality” air pollution control systems was 1.5 □g I-TEQ/ton, in comparison to the Toolkit’s 0.5 □g TEQ/ton.^{cviii} The Toolkit’s Emission Factors of 1.5 to 15 □g TEQ/ton for bottom ash of incinerators with at least some air pollution control devices are also far lower than the 12 to 72 □g TEQ/ton used in the EU inventory or, for old plants with electrostatic precipitators, 6,600 to 31,100 □g TEQ/ton.^{ciix} As another example, a recent PCDD/F mass balance study of a MSW incinerator “<i>equipped with a best available technology flue gas treatment line</i>” reported a PCDD/F release factor for slag of 7.59 □g I-TEQ/ton,^{cx} as compared to the value of 1.5 □g TEQ/ton used by the Toolkit’s authors for bottom ash.</p> <p>Suggestion: All of the emission factors presented in the Toolkit should be reassessed and adjusted so as to be more compatible with existing data. Also any emission factors presented in the Toolkit should be identified as to their sources, some rationale should be given for their selection, and some indication should be given of their uncertainty.</p>
35	<p>“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.”</p> <p>Comment: Based on the values above, the Toolkit’s authors have assumed that the incineration of one ton of waste is accompanied by the generation of 10 to 20 kg of fly ash and 100 to 250 kg of bottom ash. This is significantly different from ash generation rates reported in other sources; for example, the EU inventory notes that the incineration of one ton of waste is accompanied by the generation of 30 to 38 kg of fly ash and 300 kg of bottom ash.^{cxii} One possible result of these non-conservative assumptions by the Toolkit’s authors is substantial underestimations of PCDD/F releases in incinerator residues.</p> <p>Suggestion: Revise the values used so that the values relied on are compatible with those used elsewhere.</p>
35	<p>“Releases to air are the predominant vector for MSW combustion.”</p> <p>Comment: This statement is incorrect. Releases to residues are the predominant pathways for PCDD/F releases from MSW incinerators. Also please refer to the earlier discussions of the importance of consistency in terminology. As defined earlier by the Toolkit’s authors, “air” is a vector; “release to air” is not a vector, it is a pathway.</p> <p>Suggestion: The greatest share of PCDD/Fs formed by incinerators is released in residues, e.g., fly ash and bottom ash or slag.</p>
35	<p>“Class 2 assumes a reduction in the specific flue gas flow rate 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. 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. Also, the</p>

	<p><i>specific flue gas volume flow rate 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 will be the norm (LUA 1997, IFEU 1998)."</i></p> <p>Comment: While the results of these extrapolations are interesting, estimated releases have acceptable validity when based on the range of emission factors that are derived from measurements of some share of existing systems. It is interesting to note that, although the EU inventory is cited as one of the two sources of the information presented in the above segment, the inventory's emission factors were not used in the Toolkit. Refer also to earlier discussion on Table 13.</p> <p>Suggestion: Delete this segment.</p>
35	<p><i>"Releases to water occur only in case wet scrubbers are employed for the removal of larger quantities 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. 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. Thus, this release vector is of minor importance for this source."</i></p> <p>Comment: As described in the discussion above on Table 13, the European Inventory also identifies the following potential carriers of PCDD/Fs from incinerators: water used for quenching bottom ash, wash water and surface runoff. Also, refer again to earlier discussions on the need for consistency in terminology: a "release to water" is not a vector; water is a vector, as defined by the Toolkit's authors. It would also be helpful if the recommended default emission factors were specified more clearly than as those "supplied for residues." If the Toolkit's authors have data describing PCDD/F concentrations in scrubber water, it would be most helpful if they provided the exact data and its source.</p> <p>Suggestion: Releases to water may occur when wet scrubbers are used, when water is used for quenching bottom ash, and through wash water and surface runoff. There are no emission factors for such releases.</p>
35	<p><i>"No release to land is expected unless untreated residue is directly placed onto or mixed with soil."</i></p> <p>Comment: As discussed in the general comments as well as in several of the detailed comments, limiting the definition of "land" to include only surface soil presents an unnecessary and avoidable obstacle to understanding total PCDD/F releases.</p> <p>Suggestion: See general comments.</p>
36	<p><i>"The process has no product, thus there will be no emission factor."</i></p> <p>Comment: This statement is incorrect. See earlier comment: In some European countries e.g. Germany, the Netherlands, France and Denmark about 50% of the stockpiled</p>

	<p>municipal waste incinerator bottom ash is used as secondary building material, in road construction or as raw material for the ceramic industry inter al.^{cxii, cxiii, cxiv, cxv, cxvi, cxvii, cxviii}</p> <p>Suggestion: About 50 percent of stockpiled bottom ash is used as a secondary building material, in road construction or as raw material for the ceramic industry in Germany, The Netherlands, France and Denmark.</p>
<p>36</p>	<p><i>“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 %⁴. 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 bottom ash⁵. As fly ash is not being collected by these types of incinerators, 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.”</i></p> <p>Comments: See earlier comments on the generation of fly ash and bottom ash. In contrast to the footnote comment that bottom ash was generated at the rate of 300 kg/ton back in the 1960s and 1970s, the scientists who prepared the EU inventory regarded this as a valid ash generation rate.^{cxix} Also, in contrast to the statement that unburned carbon in ash enhances adsorption of PCDD/F, scientists have been reporting for almost twenty years that unburned carbon in fly ash enhances PCDD/F formation by serving as a source of complex carbon.^{cxx,cxxi,cxxii, cxxiii}</p> <p>The emission factors used in the Toolkit for MSW incinerator fly ash and bottom ash are based on ash generation rates and PCDD/F concentrations that are substantially lower than those that have been reported in the scientific literature and used in various inventories. This may lead to a substantial underestimation of PCDD/F releases in MSW incinerator bottom ash. For example, calculations using the data presented in the Toolkit -- a PCDD/F concentration in bottom ash of 500 ng TEQ/kg and a bottom ash generation rate of 100-200 kg ash/ton of waste burned – result in PCDD/F release in bottom ash at a rate of 50-100 □g TEQ/ton. The average of this range – 75 □g TEQ/ton – is the emission factor for bottom ash given in the Toolkit for class 1 MSWs. Using this same PCDD/F concentration given in the Toolkit, 500 ng TEQ/kg, and the bottom ash generation rate given in the European inventory, 300 kg/ton of waste burned, the emission factor for bottom ash can be calculated to be 150 □g/ton, which is two times higher than that given in the Toolkit.</p> <p>As another example, in the European inventory, the emission factor for fly ash from new MSW incinerators is given as a range, 810 to 1,800 □g I-TEQ/ton.^{cxxiv} The Toolkit’s emission factor for the most advanced incinerators is far lower, 15□g TEQ/ton. Indeed, the Toolkit’s emission factor for fly ash from MSW incinerators with the most primitive</p>

	<p>air pollution control systems, 500 □g TEQ/ton, is markedly lower than the lower end of the range given in the European inventory. As mentioned earlier, the Toolkit uses a fly ash generation rate of 10 to 20 kg/ton of waste burned, which is substantially lower than the range of 30 to 38 kg/ton reported in the European inventory.^{cxxv} Using the Toolkit's values, an advanced MSW incinerator that burned 100,000 tons per year of waste would generate 10 to 20 tons of fly ash with a PCDD/F content of 150 to 300 □g TEQ. Using the values from the European inventory, this incinerator would generate 30 to 38 tons of fly ash with a PCDD/F content of 24,300 to 68,400 □g TEQ. In summary, the estimated PCDD/F releases in fly ash from this incinerator are, when prepared according to the Toolkit, from 81 to 456 times smaller than the releases estimated using the values in the European inventory.</p> <p>For the most advanced MSW incinerator, the Toolkit assumes a PCDD/F concentration of 1,000 ng I-TEQ/kg in fly ash and 5 ng TEQ/kg in bottom ash. In contrast, a recent study of a fully modernized MSW incinerator reported 1,580 ng TEQ/kg in fly ash and 60 ng TEQ/kg in bottom ash or slag.^{cxxvi} In another study of a smaller incinerator in France that had recently been equipped to meet the EU air emission standards, the PCDD/F concentrations in fly ash were 10,700 ng TEQ/kg and, in slag, 43 ng TEQ/kg.^{cxxvii}</p> <p>Suggestion: All of the emission factors and residue generation rates presented in the Toolkit should reassessed and, where appropriate, adjusted so as to be more compatible with existing data. Also any emission factors and supporting data, such as residue generation rates, presented in the Toolkit should be identified as to their sources, some rationale should be given for their selection, and some indication should be given of their uncertainty.</p>
36	<p>“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.”</p> <p>Comment: While this information describing the hazardous contents of consumer goods is interesting, it is irrelevant in the context of a discussion of dedicated hazardous waste incinerators, which are constructed and operated for the purpose of burning large quantities of hazardous waste, the overwhelming majority of which consists of wastes from industrial processes.</p> <p>Suggestion: Hazardous waste (HW) refers to residues and wastes, which consist of or contain hazardous materials in significant quantities. [Delete remainder of paragraph.]</p>
36	<p>“Also, all somewhat exotic and rather costly technologies such as supercritical water oxidation, electric arc vitrification, etc. are included in this group.”</p> <p>Comment: While there are a number of technologies that are often categorized as</p>

	<p>incineration technologies, supercritical water oxidation is not among them. Nor can it be considered exotic, since it has been studied and in use for two decades.^{cxxviii}</p> <p>Suggestion: Delete this sentence.</p>
37	<p>“Due to the fact that in most modern facilities, the bottom ash results from molten slag, it contains no substantial amounts of PCDD/PCDF. For the older technologies, no data could be obtained.”</p> <p><i>Comment: While the PCDD/F concentration in bottom ash and/or slag from hazardous waste incinerators may be low, the question of the “substantiality” or significance of this concentration and/or the total amount of PCDD/F in the slag is a question that is to be addressed by the Parties in their continuing considerations with regard to the Stockholm Convention.</i></p> <p><i>Suggestion: “Due to the fact that in most modern facilities, the bottom ash results from molten slag, the PCDD/F concentrations are generally low in comparison to those in the fly ash.</i></p>
37	<p>“Table 14 Emission factors for hazardous waste incineration”</p> <p><i>Comment: While Table 14 presents only an emission factor for fly ash, the EU inventory noted as follows with regard to hazardous waste incinerators: “Solid wastes include bottom ash from the furnace, fly ash and residues from gas cleaning operations, and filter cakes and collected dusts from flue gas cleaning. We assume a solid waste production rate of 20% of throughput. ... Releases to water arise mainly from the use of wet scrubbers, which are common on hazardous waste incinerators. Data from one UK plant indicate that the discharge is about 6.2 m³ per tonne of waste. ... The range of levels in bottom ash and composite solid wastes is 0.1 - 34 ng ITEQ/kg. The range of levels for liquid discharges is 0.01 - 0.6 ng I-TEQ / l.”^{cxxix}</i></p> <p><i>Suggestion: Table 13 should include columns for emission factors for bottom ash/slag, scrubber water and scrubber water treatment sludge.</i></p>
37	<p>“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.”</p> <p><i>Comment: As noted above, those who prepared the European inventory assumed hazardous waste incinerators generated solid residues, including fly ash, bottom ash, etc. at the rate of 200 kg/ton of waste burned. This suggests that the Toolkit needs to provide more detailed, documented information describing the rates at which fly ash and bottom ash are generated by hazardous waste incinerators. Also, as discussed earlier, the decision as to the negligibility of PCDD/F releases lies with the Stockholm Convention, not with the authors of the Toolkit. Moreover, the information presented in the preceding comment indicates that hazardous waste incinerator residues are potentially significant in quantity and PCDD/F content.</i></p> <p>Suggestion: Either substantiate the information in these sentences or delete them.</p>

38	<p><i>“The default emission factor for class 1 was derived from a specific flue gas volume flow rate of about 17,500 Nm³/t of hazardous waste and a concentration of about 2,000 ng TEQ/Nm³. Class 2 assumes a reduction in the specific flue gas volume flow rate to 15,000 Nm³/t of hazardous waste due to better combustion controls and lower excess air. The PCDD/PCDF concentration drops to 20 ng TEQ/Nm³ 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/Nm³. Also, the specific flue gas volume flow rate is reduced to 10,000 Nm³/t HW. Class 4 represents the current state-of-the-art in HW incineration and APC technology. Thus, only 7,500 Nm³/t HW and a concentration of significantly less than 0.1 ng TEQ/Nm³ is realistic (LUA 1997, IFEU 1998, Environment Canada 1999).”</i></p> <p>Comment: The EU inventory gives the following emission factors_{AIR} for hazardous waste incinerators: 2 □g TEQ/ton, minimum; 20 □g TEQ/ton, typical; and 200□g TEQ/ton, maximum.^{cxxx} This undermines the credibility of the Toolkit’s emission factors.</p> <p>Suggestion: Delete the segment above and replace it with well-substantiated information.</p>
38	<p><i>“The maximum actual PCDD/PCDF concentration found in wet scrubber effluent was below 0.15 mg TEQ/t (LUA 1997).”</i></p> <p>Comment: The source given for this information “LUA 1997” is cited in this comments as “Quass, U., Fermann, M., 1997. Identification of Relevant Industrial Sources of Dioxins and Furans in Europe (The European Dioxin Inventory). Final Report No. 43, Essen, Germany: Landesumweltamt Nordrhein-Westfalen” and is, as the title indicates, the European Dioxin Inventory. This inventory addresses only PCDD/F releases to air and, as such, contains no information on PCDD/F concentrations in wet scrubber effluent of hazardous waste incinerators. The other European inventory, cited in these comments as “Wenborn, M., King, K., Buckley-Golder, D., Gascon, J., 1999. Releases of Dioxins and Furans to Land and Water in Europe. Final Report. Report produced for Landesumwaltamt Nordrhein-Westfalen, Germany on behalf of European Commission DG Environment. September 1999,” reported scrubber water from hazardous waste incinerators to have PCDD/F concentrations of 0.01 - 0.6 ng I-TEQ per liter.^{cxxx}</p> <p>Suggestions: Delete this segment of text and replace it with the information given in the EU inventory of PCDD/F releases to land and water.</p>
38	<p><i>“No release to land is expected unless untreated residue is directly placed onto or mixed with soil.”</i></p> <p>Comment: See earlier comments on the Toolkit’s definition of land and, consequently, the identification of releases to land.</p> <p>Suggestion: See earlier suggestions on this topic.</p>
38-39	<p><i>“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 as molten slag, no substantial contribution to the overall release of PCDD/PCDF occurs.</i></p>

	<p><i>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.”</i></p> <p>Comment: Again, defining those levels of PCDD/Fs in incinerators residues that need not be considered in estimating PCDD/F releases is a matter to be resolved jointly by the Parties. This decision does not fall within the purview of the Toolkit’s authors. See earlier comments on the role of unburned carbon on fly ash in PCDD/F formation.</p> <p>Suggestion: Delete this segment and replace it with well-substantiated data and, where appropriate, acknowledgement of the absence of data.</p>
<p>39</p>	<p>To reliably destroy viruses, bacteria, and pathogens his [sic] 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.”</p> <p>Comment: This first sentence erroneously implies that thermal treatment is the only method for reliable destruction of pathogens, such as viruses and bacteria. The second sentence erroneously implies that toxic chemicals in medical waste are the major constituents in medical waste that form PCDD/Fs.</p> <p>Suggestion: Incineration has been frequently relied on for the destruction of the pathogens, such as viruses and bacteria, in medical waste. However, a substantial fraction of medical waste commonly consists of chlorinated materials, such as polyvinyl chloride (PVC) blood bags, tubing, etc., that act as precursors for PCDD/F formation.</p>
<p>39</p>	<p>“In many countries medical waste is a waste needing special surveillance and as incineration of medical waste in small and poorly controlled incinerators was found to be a major source of PCDD/PCDF in developed countries and small plants have often been closed or upgraded for this reason.”</p> <p>Comment: This sentence appears to be missing some essential words.</p>

	Suggestion: Add the words and/or punctuation needed to make this a proper sentence.						
39	<p>“Based on these experiences, the thermal treatment medical waste constitutes an own subcategory in the Toolkit.”</p> <p>Comment: There seems to be a missing word and the word “an” appears to be a typographical error.</p> <p>Suggestion: ... the thermal treatment of medical waste constitutes its own subcategory ...</p>						
	<p><i>“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.”</i></p> <p>Comment: For medical waste incinerators, the European inventory gives a bottom ash generation rate of 150 kg/ton of waste burned; a fly ash generation rate of 80 kg/ton; and the generation of wet scrubber treatment residue at the rate of 40 kg/ton.^{cxxxii} In addition, this use of the word “vector” is incompatible with the definition given earlier in the Toolkit.</p> <p>Suggestion: The major releases of concern are air and residues.</p>						
40	<p>“Table 15: Emission factors for medical waste incineration”</p> <p>Comment: The emission factors given in this table do not correlate well with those used in the European inventory, which are shown below (grate ash is equivalent to bottom ash or slag; and dry scrubber residue, to fly ash).^{cxxxiii}</p> <p>Concentration ranges for the various solid wastes arising are as follows:</p> <table data-bbox="395 1227 1002 1326"> <tr> <td>grate ash</td> <td>15-300 ng I-TEQ/kg</td> </tr> <tr> <td>dry scrubber residue</td> <td>1800-4500 ng I-TEQ/kg</td> </tr> <tr> <td>wet scrubber residue</td> <td>680 ng I-TEQ/kg</td> </tr> </table> <p>Suggestion: Modify Table 15 to include bottom ash and scrubber water residues, and modify the emission factors to be more compatible with those used in other inventories and reported in the scientific literature.</p>	grate ash	15-300 ng I-TEQ/kg	dry scrubber residue	1800-4500 ng I-TEQ/kg	wet scrubber residue	680 ng I-TEQ/kg
grate ash	15-300 ng I-TEQ/kg						
dry scrubber residue	1800-4500 ng I-TEQ/kg						
wet scrubber residue	680 ng I-TEQ/kg						
40	<p>“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.”</p> <p>Comment: As discussed and documented in an earlier comment, the fly ash generation rate for medical waste incinerators that is used in the European inventory is 80 kg/ton, or 8 percent. This is 2.7 times higher than the Toolkit’s value. In addition, the European inventory contains the citations for the sources of the emission factors for the various outputs of medical waste incinerators.</p> <p>Suggestion: Modify this statement to comply with the available information.</p>						
40	<i>“Release to air is the predominant vector for medical waste incineration. The default</i>						

	<p><i>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. 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 in this case. Class 3 is based on European data where a concentration of 35 ng I-TEQ/Nm³ 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 was measured (LUA 1997, IFEU 1998, Environment Canada 1999).”</i></p> <p>Comment: Sufficient data are not presented to support the first statement. The air emission factors presented in Table 15 are somewhat larger than those of the European inventory.^{cxxxiv} However, in the absence of sufficient documentation for the stack gas flowrates, it is not possible to verify the air emission factors presented in the Toolkit.</p> <p>Suggestion: Delete the first sentence and provide sufficient documentation for the remaining data in this paragraph.</p>
41	<p>“Releases to water occur when wet scrubbers are employed for the removal of particulate matter. 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 are identified the water treatment should be noted.”</p> <p>Comment: Releases to water can only occur via quench water used to cool ashes. In the absence of well-documented information describing the extent to which wet scrubbers are used in the rest of the world, the second and third sentences cannot be considered as correct.</p> <p>Suggestion: Releases to water occur when wet scrubbers are employed for the removal of particulate matter and quench water is used to cool ashes. Measured concentrations of PCDD/F in these effluents are not available. Where wet scrubbers and water quenching of ashes are identified, water treatment should be noted.</p>
41	<p><i>“6.1.3.3 Release to Land</i> No release to land is expected unless untreated residue is directly placed onto or mixed with soil.”</p> <p>Comment: Refer to earlier comments on the inadvisability of the decision to exclude landfills and, consequently, incinerator ashes sent to landfills, from consideration as releases to land.</p> <p>Suggestion: Refer to earlier suggestions.</p>
41	<p><i>“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</i></p>

	<p><i>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 mg TEQ/t of waste.</i></p> <p>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 %. Classes 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.”</p> <p>Comment: As described and presented in earlier comments, data describing PCDD/F concentrations in both fly ash and bottom ash as well as the generation rates for these ashes are presented in the European inventory. The Toolkit’s values for both PCDD/F concentrations in fly ash and bottom ash and the generation rates for these two kinds of ashes are considerably lower than the values in the European inventory.^{cxxxv} Other data suggest that some of the Toolkit’s values for PCDD/F concentrations in ashes are too low. In the UNEP inventory of PCDD/F releases in Thailand, PCDD/F concentrations in bottom ash of a hospital waste incinerator were reported as 1,410 and 2,300 ng I-TEQ/kg and described as “<i>about the highest ever reported in the literature.</i>”^{cxxxvi} This is obviously not the case given the study of 18 hospital waste incinerators in Poland, eight of which had stack gas concentrations below 0.1 ng TEQ/m³, that found bottom ash to contain PCDD/F concentrations in the range of 8,000 to 45,000 ng TEQ/kg.^{cxxxvii}</p> <p>Suggestion: Delete these two paragraphs and replace with more appropriate, well-documented data.</p>
42	<p>“The default emission factors given are based on the assumption that the LFSW burned leads to about 1 % of fly ash and the PCDD/PCDF release associated with the disposal of bottom ash is negligible.”</p> <p>Comment: Assuming that this sentence is intended to mean, in part, that PCDD/F concentrations in bottom ash are negligible, please refer to earlier discussions of the purview of the Toolkit’s authors versus that of the Parties to the Stockholm Convention with regard to the negligibility or insignificance of PCDD/F concentrations in releases.</p> <p>Suggestion: Delete this sentence.</p>
42	<p>“Releases to air are the predominant vector for LWSF combustion. 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</p>

	<p>Japanese fluidized bed combustors with minimal APC equipment. An emission factor of 50 □g 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 is taken (US EPA 1999, LUA 1997, IFEU 1998, Environment Canada 1999.”</p> <p>Comment: In the absence of data describing the PCDD/F content of residues from the incineration of LWSF, this statement cannot be made. The absence of these data as well as data describing PCDD/F levels in stack gases should be openly acknowledged. Justification should be given for the selection of each of the various substitute concentrations and emission factors presented here.</p> <p>Suggestion: Replace the first sentence with the following: No information is available on releases to air from LWSF combustion. Craft and present well-documented justifications for the use of the information in the remainder of the paragraph.</p>
43	<p><i>“6.1.4.3 Release to Land</i> No release to land is expected unless untreated residue is directly placed onto or mixed with soil.”</p> <p>Comment: See previous comments on the definition of “land” and the resulting exclusion of landfills.</p>
43	<p>“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 a high combustion efficiency but also a 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).”</p> <p>Comment: The sources of these data, e.g., the rate of generation of LFSW incineration fly ash, etc., should be given. (It is not found in the sources that appear at the end of the paragraph).</p> <p>Suggestion: Either thoroughly and precisely document the information in this paragraph or delete it.</p>
43	<p>“Since PCDD/PCDF are virtually insoluble in water, they adsorb to the solids present in the wastewater. If the solids are not removed, the PCDD/PCDF will be discharged with the wastewater.”</p> <p>Comment: While this statement may be true for pure water, it is not necessarily true for municipal and industrial wastewater that commonly contains substances that are or act as</p>

	<p>surfactants, such as linear alkylbenzene sulphonates, common ingredients of detergents and cleaning agents;^{cxxxviii} humic acids, ubiquitous soil components,^{cxxxix} etc.</p> <p>Suggestion: PCDD/F are virtually insoluble in pure water. However, municipal and industrial wastewater may contain substances that are or act as surfactants, such as humic acids and linear alkylbenzene sulphonates, and increase PCDD/F solubility. However, the bulk of PCDD/Fs present will adsorb to solids present in wastewater, which can be removed by filtration or flocculation so that the PCDD/Fs are collected in the wastewater treatment sludges.</p>
43	<p><i>“The removed solids, the sludge, are either incinerated, landfilled or used as fertilizer in agriculture.”</i></p> <p><i>Comment: While information on the disposal options for this and the other wastes discussed in the Toolkit is very useful, such information should be complete and it should be provided for each of the other wastes.</i></p> <p><i>Suggestion: The removed solids, the sludge, are disposed of through various means: incineration in dedicated incinerators; co-combustion in other processes such as power plants, MSW incinerators, etc.; wet oxidation; pyrolysis; gasification; conversion to oil and/or fuel;^{cxl} and landfill.</i></p>
43	<p><i>“This subsection addresses PCDD/PCDF emissions from incineration of sewage sludge; the latter two issues are addressed in Main Source Category 9 (Section 6.9.2).”</i></p> <p>Comment: Refer to earlier comments on the need to maintain consistency of terminology.</p> <p>Suggestion: This subsection addresses PCDD/F releases from incineration of sewage sludge;</p>
43-44	<p><i>“... 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).</i></p> <p><i>Ideally 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.”</i></p> <p>Comment: Much of the information in these two paragraphs is written in a style that seems more to promote the incineration of sewage sludge rather than simply to document the pathways of release and the factors that may impact PCDD/F formation.</p> <p>Suggestion: Sewage sludge is incinerated in bubbling or circulating fluidized bed furnaces, vertical rotary stage or open-hearth-type furnaces, grate-type furnaces</p>

	<p>and muffle-type furnaces. Sewage sludge is also co-incinerated 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). The extent of PCDD/F formation depends on the composition of the sludge. Incineration of sludge with a higher content of chlorinated hydrocarbons and/or other sources of chlorine^{cxli} and carbon as well as metals such as copper can be expected to have greater PCDD/F formation, while increased sulfur content in the sludge has been associated with reduced PCDD/F formation.^{cxlii}</p>
<p>44</p>	<p>“Table 17: Emission factors for sewage sludge incineration”</p> <p>Comment: This table presents emission factors only for releases to air and releases in residues. According to a recent European Commission report on sewage sludge disposal, “incineration generates emissions to air, soil and water ...”^{cxliii}</p> <p>Suggestion: Include a column for Emission Factor_{WATER}.</p>
<p>44</p>	<p>“Releases to air are the predominant 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 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 of 0.1 ng I-TEQ/Nm³ (from Canadian, German and Swiss measurements) (LUA 1997, IFEU 1998, Environment Canada 1999).”</p> <p>Comment: As has often been the case, it is not possible to verify this information due to the marked absence of cited sources. The three classes of sludge incinerators and their respective Emission Factors_{AIR} do not coincide well with those presented by the U.S. Environmental Protection Agency: “The average TEQ emission factor based on the data for the 11 AMSA facilities and the two facilities reported in U.S. EPA (1990f) is 6.94 ng I-TEQ DF /kg of dry sludge combusted (or 7.04 ng TEQ DF -WHO98 /kg of dry sludge), assuming nondetected values are zero. Other countries have reported similar results. Bremmer et al. (1994) reported an emission rate of 5 ng ITEQ/kg for a fluidized-bed sewage sludge incinerator, equipped with a cyclone and wet scrubber, in The Netherlands. Cains and Dyke (1994) measured CDD/CDF emissions at two sewage sludge incinerators in the United Kingdom. The emission rate at an incinerator equipped with an electrostatic precipitator and wet scrubber ranged from 2.75 ng I-TEQ /kg to 28.0 ng I-TEQ /kg. The emission rate measured at a facility equipped with only an electrostatic precipitator was 43.0 ng I-TEQ /kg.”^{cxliv}</p> <p>Suggestion: Provide source citations for each value as well as each statement of fact.</p>
<p>44</p>	<p>“PCDD/PCDF concentrations in scrubber effluent from sewage sludge incinerators are not available.”</p> <p>Comment: The European inventory notes as follows: “range of values for scrubber effluent is 0.0012 - 0.0065 ng I-TEQ/l (WSL 1992b).”^{cxlv}</p>

	<p>Comment: PCDD/F concentrations in scrubber effluent from sewage sludge incinerators are reported to range from 0.0012 to 0.0065 ng I-TEQ/L.</p>
45	<p>“6.1.5.3 Release to Land No release to land is expected unless untreated residue is directly placed onto or mixed with soil.”</p> <p>Comment: See prior comments on the issue of defining “land” as surface soil only and thereby not inclusive of landfills, deepwells, etc.</p> <p>Suggestion: See suggestion in general comments.</p>
45	<p>“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 n 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.”</p> <p>Comment: See earlier comment on the classification of incinerators and the lack of documentation.</p> <p>Suggestion: Reevaluate the incinerator classes and provide more appropriate, well-documented data.</p>
45	<p>“6.1.6 Waste Wood and Waste Biomass Incineration” [including accompanying introductory text]</p> <p>Comment: First, the use of the terms “waste wood” and “waste biomass” do not convey clearly the important distinction that needs to be made between wood or biomass contaminated with pentachlorophenol, chlorine-containing paints, PVC cladding or scraps, chlorinated pesticides, etc. And wood and biomass that are simply excess materials.</p> <p>Suggestion: 6.16 Contaminated Wood/Biomass Incineration</p> <p>This subcategory address the combustion of contaminated wood/biomass in furnaces under conditions ranging from no control to highly controlled. Combustion of clean wood/biomass for generating energy is addressed in Section 6.3.2, and open burning of clean wood/biomass is addressed in Section 6.6 – Uncontrolled Combustion Processes.</p> <p>Contaminated wood/biomass may contain materials that support or contribute to PCDD/F formation, e.g., paints, coatings, pesticides, preservatives, anti-fouling agents and many other substances that contain chlorine or chlorinated chemicals as well as metals. Higher levels in the contaminated wood/biomass of chlorine-containing materials and metals, such as copper, are commonly associated with greater PCDD/F formation. While PCDD/F formation may be enhanced by poor combustion conditions, it can be reduced,</p>

	but not prevented, by good combustion in well-controlled furnaces equipped with effective, properly operated air pollution control systems. Three classes of combustion systems, together with their emissions factors for PCDD/F releases to air and residues.
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Table 2: Commercial Chemicals Known or Suspected to be Accompanied by Dioxin Formation During Their Manufacture	
Chemical	Reference
Dioxins are Known By-Products During Manufacture	
Chlorine	cxlvi
Sodium hypochlorite (bleach)	cxlvii
Ethylene dichloride (1,2-dichloroethane; vinyl chloride monomer)	cxlviii
Epichlorohydrin	cxlix
Trichloroethylene	cl
Perchloroethylene (tetrachloroethylene)	
Hexachlorobutadiene	cli
Chlorobenzenes	
Dichlorobenzene	
Trichlorobenzene	
1,2,4,5-Tetrachlorobenzene	
Pentachlorobenzene	
Hexachlorobenzene	
Chlorophenols	
2,4,5-Trichlorophenol	clii
2,4,5-Trichlorophenol, sodium salt	cliii
2,4,6-Trichlorophenol	
2,4,6-Trichlorophenol, sodium salt	cliv
2,3,4,6-Tetrachlorophenol	clv
2,3,4,6-Tetrachlorophenol, sodium salt	clvi
Pentachlorophenol	clvii
Polychlorinated biphenyls (PCBs)	clviii
4-Chlorotoluene	clix
Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione)	clx
Dioxazine dyes (Direct Blue 106, Direct Blue 108, and Violet 23)	clxi
Ni-phthalocyanine dye	clxii
Printing inks (unidentified)	clxiii
Metal Chlorides	
Aluminum chloride	clxiv
Ferric chloride	
Cuprous chloride	
Cupric chloride	
High Probability of Dioxin Formation During Manufacture	
Chlorophenols	
o-Chlorophenol	
2,3-Dichlorophenol	
2,4-Dichlorophenol	
2,5-Dichlorophenol	
2,6-Dichlorophenol	

3,4-Dichlorophenol	clxv
4-Chlororesorcinol	
4-Bromo-2,5-dichlorophenol	
2-Chloro-4-fluorophenol	
2-Chloro-4-phenylphenol	
Chlorohydroquinone	
2-Chloro-1,4-diethoxy-5-nitrobenzene	
5-Chloro-2,4-dimethoxyaniline	
3,5-Dichlorosalicylic acid	
Possible or Likely Dioxin Formation During Manufacture	
Chlorobenzenes	
o-Dichlorobenzene	clxvi
1,2,4-Trichlorobenzene	
1,2,4,5-Tetrachlorobenzene	
Hexachlorobenzene	
o-Chlorofluorobenzene	
3-Chloro-4-fluoronitrobenzene	
Chloropentafluorobenzene	
1,2-Dichloro-4-nitrobenzene	
Chlorophenols	
3-Chloro-4-fluorophenol	clxvii
4-Chloro-2-nitrophenol	
o-Benzyl-p-chlorophenol	clxviii
2,3,6-Trichlorobenzoic acid	
2,3,6-Trichlorophenylacetic acid, and sodium salt	
3,4-Dichloroaniline	clxix
3,4-Dichlorobenzaldehyde	clxx
3,4-Dichlorobenzotrichloride	
3,4-Dichlorobenzotrifluoride	
3,4-Dichlorophenylisocyanate	
Pentachlorocyclohexane	
Pentachloroaniline	
Pentabromochlorocyclohexane	
Tetrachlorophthalic anhydride	
*Phenol (from chlorobenzene)	
*1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt	
*2,5-Dihydroxybenzenesulfonic acid	
*2,5-Dihydroxybenzenesulfonic acid, potassium salt	
*2,4-Dinitrophenol	
*2,4-Dinitrophenoxyethanol	
*3,5-Dinitrosalicylic acid	
*o-Nitroanisole	
*2-Nitro-p-cresol	
*o-Nitrophenol	
*2,4,6-Trinitroresorcinol	
*Fumaric acid	
*Maleic acid	
*Maleic anhydride	
*o-Phenetidine	

*Phenyl ether	
*Phthalic anhydride	
*Picric acid	
*Sodium picrate	

*Non-chlorinated chemicals produced via routes involving chlorinated chemicals.

Table 3: Pesticides Known or Suspected to be Accompanied by PCDD/F Formation During Manufacture

Sources: 1. U.S. Environmental Protection Agency. 1998. The Inventory of Sources of Dioxin in the United States. EPA/600/P-98/002Aa, Washington, D.C., April 1998.

2. Bretthauer, E., Kraus, H., di Domenico, A. 1991. Dioxin Perspectives: A Pilot Study on International Exchange on Dioxins and Related Compounds. New York: Plenum Press.

Common Name	Pesticide	Chemical Abstract Service Number	Source
	Dichlorodifluoromethane	75-71-8	1
Bromophos	O-(4-Bromo-2,5-dichlorophenyl) O, O-dimethyl phosphorothioate	2104-96-3	1
	Dimethylamine 2,3,5-triiodobenzoate	17601-49-9	1
Neburon		555-37-3	1
Crufomate		299-86-5	1
	MCPB, 4-butyric acid [4-(2-Methyl-4-chlorophenoxy) butyric acid]	94-81-5	1
	MCPB, Na salt [Sodium 4-(2-methyl-4-chlorophenoxy) butyrate]	6062-26-6	1
	4-Chlorophenoxyacetic acid	122-88-3	1
Chloroxuron		1982-47-4	1
Dichlobenil		1194-65-6	1
Propanil	3',4'-Dichloropropionanilide	709-98-8	1
Dichlofenthion	O-(2,4-Dichlorophenyl) O, O-diethyl phosphorothioate	97-17-6	1
DDT	Dichloro diphenyl trichloroethane	50-29-3	1
Dichlone	2,3-dichloro-1,4-naphthoquinone	117-80-6	1
Ammonium chloramben	3-amino-2,5-dichlorobenzoic acid	1076-46-6	1
Sodium chloramben	3-amino-2,5-dichlorobenzoic acid	1954-81-0	1
Disul	Sodium 2-(2,4-dichlorophenoxy) ethyl sulfate	136-78-7	1
DCNA	2,6-Dichloro-4-nitroaniline	99-30-9	1
	Potassium 2-(2-methyl-4-chlorophenoxy) propionate	1929-86-8	1
MCPP, DEA Salt	Diethanolamine 2-(2-methyl-4-chlorophenoxy) propionate	1432-14-0	1
MCPP, IOE	Isooctyl 2-(2-methyl-4-chlorophenoxy) propionate	28473-03-2	1
Dicapthon	O-(2-chloro-4-nitrophenyl) O, O-dimethyl phosphorothioate	2463-84-5	1
Monuron trichloroacetate	3-(4-chlorophenyl)-1,1-dimethylurea trichloroacetate	140-41-0	1
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	330-54-1	1
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	330-55-2	1
Metobromuron	3-(p-bromophenyl)-1-methoxy-1-methylurea	3060-89-7	1
Methyl parathion	O, O-Dimethyl O-p-nitrophenyl phosphorothioate	298-00-0	1
Dichlorophene	Sodium 2,2'-methylenebis(4-chlorophenate)	97-23-4	1

Dichlorophene, sodium salt	Sodium 2,2'- methylenebis(4- chlorophenate)	10254- 48- 5	1
	1,2,4,5- Tetrachloro- 3- nitrobenzene	117- 18- 0	1
Ethyl parathion	O, O- diethyl O- p- nitrophenyl phosphorothioate	56- 38- 2	1
Carbophenothion	S-(((p- chlorophenyl) thio) methyl) O, O- diethyl phosphorodithioate	786- 19- 6	1
Ronnel	O, O- dimethyl O-(2,4,5- trichlorophenyl) phosphorothioate	229- 84- 3	1
Mitin FF	Sodium 5- chloro- 2-(4- chloro- 2-(3-(3,4- dichlorophenyl) ureido) phenoxy) benzenesulfonate	3567- 25- 7	1
	Orthodichlorobenzene	95- 50- 1	1
	Paradichlorobenzene	106- 46- 7	1
Common Name	Pesticide	CAS Number	Source
Chlorophene	2- Benzyl- 4- chlorophenol	120- 32- 1	1
	Potassium 2- benzyl- 4- chlorophenate	35471- 49- 9	1
	Sodium 2- benzyl- 4- chlorophenate	3184- 65- 4	1
	Chlorophenol	95- 57- 8	1
	2- Chloro- 4- phenylphenol	92- 04- 6	1
	Potassium 2- chloro- 4- phenylphenate	18128- 16- 0	1
	4- Chloro- 2- phenylphenol	not available	1
	4- Chloro- 2- phenylphenol, potassium salt	53404- 21	1
	6- Chloro- 2- phenylphenol	85- 97- 2	1
	6- Chloro- 2- phenylphenol, potassium salt	18128- 17- 1	1
	4- Chloro- 2- phenylphenol, sodium salt	10605- 10- 4	1
	6- Chloro- 2- phenylphenol, sodium salt	10605- 11- 5	1
	4 and 6- Chloro- 2- phenylphenol, diethanolamine salt	53537- 63- 6	1
	2- Chloro- 4- phenylphenol, sodium salt	31366- 97- 9	1
	4- Chloro- 2- cyclopentylphenol	13347- 42- 7	1
Fentichlor	2,2'- Thiobis(4- chloro- 6- methylphenol)	4418- 66- 0	1
Fentichlor	2,2'- Thiobis(4- chlorophenol)] 5	97- 24-	1
	4- Chloro- 2- cyclopentylphenol, potassium salt of	35471- 38- 6	1
	4- Chloro- 2- cyclopentylphenol, sodium salt	53404- 20- 9	1
Chlorophacinone		3691- 35- 8	1
ADBAC	Alkyl* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)	68424- 85- 1	1
ADBAC	Alkyl* dimethyl 3,4- dichlorobenzyl ammonium chloride *(61% C12, 23% C14, 11% C16, 5% C18)	not available	1
Niclosamide	2- Aminoethanol salt of 2', 5- dichloro- 4'- nitrosalicylanilide	1420- 04- 8	1
	5- Chlorosalicylanilide	4638- 48- 6	1
	2- Methyl- 4- isothiazolin- 3- one	not available	1
Tetradifon	4- chlorophenyl 2,4,5- trichlorophenyl sulfone	116- 29- 0	1

Chloranil	tetrachloro- p- benzoquinone	118- 75- 2	1
	6- Chlorothymol	89- 68- 9	1
Anilazine	2,4- Dichloro- 6-(o- chloroanilino)- s- triazine	101- 05- 3	1
Chlorothalonil	Tetrachloroisophthalonitrile	1897- 45- 6	1
Fenac, Chlorfenac	Sodium 2,3,6- Trichlorophenylacetate	2439- 00- 1	1
Chlorfenvinphos		470- 90- 6	1
	O-(2- Chloro- 1-(2,5- dichlorophenyl) vinyl) O, O- diethyl phosphorothioate	1757- 18- 2	1
PCMX	4- Chloro- 3,5- xylenol	88- 04- 0	1
Piperalin	3-(2- Methylpiperidino) propyl 3,4- dichlorobenzoate	3478- 94- 2	1
Fenamiphos		not available	1
	p- Chlorophenyl diiodomethyl sulfone	20018- 12- 6	1
Metribuzin		21087- 64- 9	1
Bifenox	methyl 5-(2,4- dichlorophenoxy)- 2- nitrobenzoate	42576- 02- 3	1
Methazole	2-(3,4- dichlorophenyl)- 4- methyl- 1,2,4- oxadiazolidine- 3,5- dione	20354- 26- 1	1
Diflubenzuron	N-(((4- chlorophenyl) amino) carbonyl)- 2,6- difluorobenzamide	35367- 38- 5	1
Oxadiazon	2-Tert- butyl- 4-(2,4- dichloro- 5- isopropoxyphenyl)- delta 2 -1,3,4- oxadiazoline- 5- one]	19666- 30- 9	1
Fenvalerate		51630- 58- 1	1
Fluvalinate	N- 2- Chloro- 4- trifluoromethyl) phenyl- DL- valine (+-)- cyano(3- phenoxy- phenyl) methyl ester	69409- 94- 5	1
Iprodione	3-(3,5- Dichlorophenyl)- N-(1- methylethyl)- 2,4- dioxo- 1- imidazolidinecarboxamide (9CA)	36734- 19- 7	1
Triadimefon	1-(4- Chlorophenoxy)- 3,3- dimethyl- 1-(1H- 1,2,4- triazol- 1- yl)- 2- butanone	43121- 43- 3	1
Common Name	Pesticide	CAS Number	Source
Diclofop - methyl	Methyl 2-(4-(2,4- dichlorophenoxy) phenoxy) propanoate	51338- 27- 3	1
Profenofos	O-(4- Bromo- 2- chlorophenyl)- O- ethyl S- propyl phosphorothioate	41198- 08- 7	1
Oxyfluorfen	2- chloro- 1-(3- ethoxy- 4- nitrophenoxy)- 4-(trifluoromethyl) benzene	42874- 03- 3	1
Imazalil	1-(2-(2,4- Dichlorophenyl)- 2-(2- propenyloxy) ethyl)- 1H- imidazole	35554- 44- 0	1
Bromothalin	N- Methyl- 2,4- dinitro- n-(2,4,6- tribromophenyl)- 6-(trifluoromethyl) benzenamine	63333- 35- 7	1
Vinclozolin	3-(3,5- Dichlorophenyl)- 5- ethenyl- 5- methyl- 2,4- oxazolinedione (9CA)	50471- 44- 8	1
Fenridazon	Potassium 1-(p- chlorophenyl)- 1,4- dihydro- 6- methyl- 4- oxo- pyridazine- 3- carboxylate	83588- 43- 6	1
Tridiphane	2-(3,5- Dichlorophenyl)- 2-(2,2,2- trichloroethyl) oxirane	58138- 08- 2	1
Paclobutrazol		76738- 62- 0	1
Linalool		78- 70- 6	1

	[a-(2- chlorophenyl)- a-(4- chlorophenyl)- 5- pyrimidinemethanol]	60168- 88- 9	1
Dicamba dimethylamine	[3,6- dichloro- o- anisic acid]	2300- 66- 5	1
Diethanolamine dicamba	[3,6- dichloro- 2- anisic acid]	25059- 78- 3	1
2,4-D	2,4- Dichlorophenoxyacetic acid	94- 75- 7	1
	Lithium 2,4- dichlorophenoxyacetate	3766- 27- 6	1
	Potassium 2,4- dichlorophenoxyacetate	14214- 89- 2	1
	Sodium 2,4- dichlorophenoxyacetate	2702- 72- 9	1
	Ammonium 2,4- dichlorophenoxyacetate	2307- 55- 3	1
	Alkanol* amine 2,4- dichlorophenoxyacetate *(salts of the ethanol and isopropanol series)	not available	1
	Alkyl* amine 2,4- dichlorophenoxyacetate *(100% C12)	2212- 54- 6	1
	Alkyl* amine 2,4- dichlorophenoxyacetate *(100% C14)	28685- 18- 9	1
	Alkyl* amine 2,4- dichlorophenoxyacetate *(as in fatty acids of tall oil)	not available	1
	Diethanolamine 2,4- dichlorophenoxyacetate	5742- 19- 8	1
	Diethylamine 2,4- dichlorophenoxyacetate	20940- 37- 8	1
	Dimethylamine 2,4- dichlorophenoxyacetate	2008- 39- 1	1
	N, N- Dimethylolyleylamine 2,4- dichlorophenoxyacetate	53535- 36- 7	1
	Ethanolamine 2,4- dichlorophenoxyacetate	3599- 58- 4	1
	Heptylamine 2,4- dichlorophenoxyacetate	37102- 63- 9	1
	Isopropanolamine 2,4- dichlorophenoxyacetate	6365- 72- 6	1
	Isopropylamine 2,4- dichlorophenoxyacetate	5742- 17- 6	1
	Morpholine 2,4- dichlorophenoxyacetate	6365- 73- 7	1
	N- Oleyl- 1,3- propylenediamine 2,4- dichlorophenoxyacetate	2212- 59- 1	1
	Octylamine 2,4- dichlorophenoxyacetate	2212- 53- 5	1
	Triethanolamine 2,4- dichlorophenoxyacetate	2569- 01- 9	1
	Triethylamine 2,4- dichlorophenoxyacetate	2646- 78- 8	1
	Triisopropanolamine 2,4- dichlorophenoxyacetate	32341- 80- 3	1
	N, N- Dimethyl oleyl- linoleyl amine 2,4- dichlorophenoxyacetate	55256- 32- 1	1
	Butoxyethoxypropyl 2,4- dichlorophenoxyacetate	1928- 57- 0	1
	Butoxyethyl 2,4- dichlorophenoxyacetate	1929- 73- 3	1
	Butoxypropyl 2,4- dichlorophenoxyacetate	1928- 45- 6	1
Common Name	Pesticide	CAS Number	Source
	Butyl 2,4- dichlorophenoxyacetate	94- 80- 4	1
	Isobutyl 2,4- dichlorophenoxyacetate	1713- 15- 1	1
	Isooctyl(2- ethylhexyl) 2,4- dichlorophenoxyacetate	1928- 43- 4	1
	Isooctyl(2- ethyl- 4- methylpentyl) 2,4- dichlorophenoxyacetate	25168- 26- 7	1
	Isooctyl(2- octyl) 2,4- dichlorophenoxyacetate	1917- 97- 1	1
	Isopropyl 2,4- dichlorophenoxyacetate	94- 11- 1	1
	Propylene glycol butyl ether 2,4- dichlorophenoxyacetate	1320- 18- 9	1
	4-(2,4- Dichlorophenoxy) butyric acid	94- 82- 6	1

	Sodium 4-(2,4- dichlorophenoxy) butyrate	10433- 59-7	1
	Dimethylamine 4-(2,4- dichlorophenoxy) butyrate	2758- 42- 1	1
	Butoxyethanol 4-(2,4- dichlorophenoxy) butyrate	32357- 46-3	1
	Butyl 4-(2,4- dichlorophenoxy) butyrate	6753- 24- 8	1
	Isooctyl 4-(2,4- dichlorophenoxy) butyrate	1320- 15- 6	1
	2-(2,4- Dichlorophenoxy) propionic acid (Dichlorprop, 2,4-DP)	120- 36- 5	1
	Dimethylamine 2-(2,4- dichlorophenoxy) propionate	53404- 32-3	1
	Butoxyethyl 2-(2,4- dichlorophenoxy) propionate	53404- 31-2	1
	Isooctyl 2-(2,4- dichlorophenoxy) propionate	28631- 35-8	1
	[2-(2- Methyl- 4- chlorophenoxy) propionic acid]	7085- 19- 0	1
MCPP, DMA	Dimethylamine 2-(2- methyl- 4- chlorophenoxy) propionate	32351- 70-5	1
Bromoxynil	3,5- Dibromo- 4- hydroxybenzonitrile	1689- 84- 5	1
Hexachlorophene	2,2'- Methylenebis(3,4,6- trichlorophenol)	70- 30- 4	1
Hexachlorophene, sodium salt	Monosodium 2,2'- methylenebis(3,4,6- trichlorophenate)	5736- 15- 2	1
Hexachlorophene, potassium salt	Potassium 2,2'- methylenebis(3,4,6- trichlorophenate)	67923- 62-0	1
Irgasan	5- Chloro- 2-(2,4- dichlorophenoxy) phenol	3380- 34- 5	1
	Tetrachlorophenols	25167- 83-3	1
	Tetrachlorophenols, sodium salt	25567- 55-9	1
	Tetrachlorophenols, alkyl* amine salt*(as in fatty acids of coconut oil)	not available	1
	Tetrachlorophenols, potassium salt	53535- 27-6	1
Bithionolate sodium	Disodium 2,2'- thiobis(4,6- dichlorophenate)	6385- 58- 6	1
Phenachlor	2,4,6- Trichlorophenol	88- 06- 2	1
	Potassium 2,4,6- trichlorophenate	2591- 21- 1	1
	2,4,6- Trichlorophenol, sodium salt	3784- 03- 0	1
Phenothiazine		92- 84- 2	1
Dacthal- DCPA	Dimethyl tetrachloroterephthalate	1861- 32- 1	1
Endosulfan	Hexachlorohexahydromethano- 2,4,3- benzodioxathiepin- 3- oxide	115- 29- 7	1
Silvex	2-(2,4,5-Trichlorophenoxy) propionic acid	93- 72- 1	1
Tetrachlorvinphos	2- Chloro- 1-(2,4,5- trichlorophenyl) vinyl dimethyl phosphate	961- 11- 5	1
Edolan	Sodium 1,4', 5'- trichloro- 2'-(2,4,5- trichlorophenoxy) methanesulfonanilide	69462- 14-2	1
2,4-DB	4-(2,4-Dichlorophenoxy)butanoic acid and its salts		2
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid, its esters and salts		2
	Dimethyl-(2,3,5,6-tetrachloro-1,4-benzodicyanate)		2
MCPA	4-Chloro-2-methylphenoxy acetic acid		2
Chloroneb	1,4-Dichloro-2,5-dimethoxybenzene		2
Erbone	2(2,4,5-Trichlorophenoxy)-ethyl-2,2,-dichloropropionate		2
Daconil	1,3-dicyano-2,4,5,6-tetrachlorobenzene		2

Please note that the following citations have not been truncated when repeated, as is the usual practice, so that readers need not spend time searching for the complete citations.

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XIV. WORLD CHLORINE COUNCIL

December 30, 2002

Interim Secretariat of the Stockholm Convention
Attention: Decision 6/4
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On behalf of the World Chlorine Council and the International Council of Chemical Associations, we appreciate the opportunity to provide comments on the Standardized Toolkit for the Identification and Quantification of Dioxin and Furan Releases.

During its sixth session held in June 2002, the Intergovernmental Negotiating Committee (INC) agreed on Decision 6/4 regarding the evaluation of current and projected releases of chemicals listed in Annex C of the Stockholm Convention on Persistent Organic Pollutants (ref.: Appendix I of UNEP/POPS/INC.6/22). The decision invited comments on how the Toolkit could be updated and expanded by December 31, 2002.

We offer the attached comments in an effort to improve the overall usefulness of the Toolkit.

If you have any questions or would like any additional information, please contact William F. Carroll at +972-404-2845 or via e-mail at william_f_carroll@oxy.com or Arseen Seys at Euro Chlor +32 2 6767251 e-mail ase@cefic.be

**World Chlorine Council & International Council of Chemical Associations
Comments on “Standardized Toolkit for the
Identification and Quantification of Dioxin and Furan Releases”**

Overall the Toolkit is a very useful approach for assisting countries in identifying potential sources of dioxin/furan releases and attempting to estimate potential releases from these sources. It organizes a diffuse set of sources and attempts to characterize them in a way that is not available elsewhere. The spreadsheet template available on the website also provides a useful mechanism for developing an “initial” inventory. The recommendations and comments outlined below are intended to help improve the overall usefulness of the Toolkit and are not meant to be critical in any way.

I. Potential modifications/expansion of the Toolkit to increase its usefulness for developing countries and economies in transition.

- There are a number of “pilot projects” in progress now in countries at various points in the spectrum of development. It will be important to assess the ease of use of the Toolkit, particularly for developing economies. Without having seen the results of these tests, it seems that the toolkit is probably most applicable to fully industrialized countries that have already characterized or partially characterized sources of dioxins and furans; e.g., those noted in UNEP Chemicals, Dioxin and Furan Inventory, May, 1999.
- The greatest need, however, is in developing countries whose knowledge about potential sources is likely to be very limited, or economies in transition whose knowledge may not be much greater.
 - An alternative approach would be to generate a tiered set of tools gauged to the broad level of industrial development. For the least developed countries, other reasonable surrogates for gross dioxin generation may be developed simply because of the impact of a few sources. As an example, open combustion for waste disposal falls into this category. In the interest of addressing some key sources in a timely fashion, these sources should be estimated, lightly cataloged and managed immediately if possible. Management should not necessarily wait for a full inventory.
 - For economies in transition (EIT), the first step can be done in retrospection if management steps have been taken for some sources. EITs should probably work to assess the portfolio of their industries that might potentially generate PCDD/F. In some cases the age or source of the technology may be useful as a surrogate if operational specifics are not known.
 - For fully developed economies, the inventory approach should be used, and there should be a good faith attempt to add value by generating and including actual measured data, where appropriate, so as to improve the toolkit database. This is a suggestion currently addressed within the toolkit.
 - Approaching it in this tiered fashion could help address egregious sources earlier at the cost of not rigorously cataloging how egregious they are. This may be a fair exchange.

II. The Toolkit should explicitly recognize the limitations and variability resulting from the use of emissions factor data.

- Emission factor data driving calculation of potential releases is, in many cases, sparse and at least in incineration cases other than BAT, can be very device-specific.

Focusing on “the numbers” will result in good precision, but low accuracy. For example, the “error bars” on the largest sources (especially open combustion) may be larger than the total magnitude of all other sources. This may be particularly true in cases where classes of sources (high-medium-low) are separated by a factor of 10 or more.

III. The Toolkit should emphasize that the implementation of BAT is the most effective means for minimizing releases of dioxins and furans and avoid any effort to promote restrictions/bans on technologies simply because they are listed as a potential source.

- The toolkit should be taken as an affirmation that the use of BAT is extremely effective in controlling emissions of byproduct POPs. The reductions in existing national inventories as a result of application of BAT show remarkable results. For example, the substantial reductions in releases of dioxins and furans that have been achieved through application of BAT as seen in the German and US inventories.
- The Toolkit should not be used as a means of defining Best Environmental Practices (BEP) beyond the application of BAT. Calls for restrictions or bans on a particular technology solely because a source is listed in the toolkit are misguided. For example, production of copper or steel should not be disallowed solely on the basis of some association with a thermal process or their listing as a potential source. Unique properties of these materials have utility to society. Techniques should be used that allow process management to minimize emissions of PCDD/F, while still allowing society to continue to benefit from such materials/technologies.

IV. Application of the Toolkit to other unintentional byproduct POPs.

- For non-PCDD/F byproduct POPs a similar toolkit could possibly be developed; however, emission factors, if sparse for dioxins and furans, could be virtually nonexistent for other byproducts – HCB and PCBs. On the other hand, a practical look at most of the Best Available Techniques suggests that Techniques which minimize PCDD/F also are useful in minimizing other byproduct POPs. Application of BAT for PCDD/F may, in itself, mitigate the need for development of similar toolkits for other byproducts.

V. Section 6.7.2.8 of the Toolkit should be revised to clarify the information on production of ethylene dichloride (EDC).

- In section 6.7.2.8--Production of EDC (a): Very little if any HCl is generated in the Direct Chlorination process. HCl is generated when EDC is cracked and recycled in the Oxychlorination process, as noted in the text.