Zero Toxics
Sources of by-product POPs and their Elimination

Darryl Luscombe and Pat Costner

Greenpeace International Toxics Campaign
May 2001

Zero Toxics

Sources of by-product POPs and their Elimination

Darryl Luscombe and Pat Costner

Greenpeace International Toxics Campaign

May 2001

Contents

List of Figures

1 Introduction

In May 2001 Governments of the world met in Stockholm, Sweden to sign the Convention on Persistent Organic Pollutants (POPs). This was an historic occasion. The Stockholm Convention on POPs is the first global agreement to eliminate some of the most insidious and damaging synthetic chemicals from the planet's biosphere.

The following information on the identification of sources of dioxins and other POPs by-products (dioxins, furans, PCBs and HCB) and their ultimate elimination, is intended to provide governments, communities and industry with practical guidance on the implementation of the provisions of the Stockholm Convention in relation to by-product POPs.

2 Background on dioxins and other by-product POPs

According to the Stockholm Convention, polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions.

While PCBs and HCB have also been deliberately produced for commercial uses, dioxins and furans have never been intentionally produced except for minute quantities for research purposes. Yet, the historical record indicates that the levels of dioxins and furans in the environment increased one hundredfold in the early half of the 20th century. [1]

The most common process, which appears to meet the criteria for the formation of dioxins and furans, is simple combustion – fire. As a result of this, some have argued that dioxins are a natural product of any combustion process and are nothing new.

So the question must be asked – what caused the massive increase in environmental levels of dioxins in the 20th century which has led the nations of the world to negotiate a legal Convention for their ultimate elimination? In 1995, U.S. Environmental Protection Agency Science Advisory Board (SAB) considered this question in its review of Anthropogenic (manmade) vs. Natural Sources of Dioxin and concluded:

> *"[T]he observation in the late 1970s that dioxins are produced by the combustion of many common materials, including municipal solid waste … led some scientists to suggest that dioxins had been with us since 'the advent of fire' and that dioxins could be produced by natural combustion (for example, by forest fires). At that time, there were some suggestions that observed levels of dioxins were primarily the result of coal combustion or perhaps of wood burned in small stoves."*
>
> *"This speculation was largely refuted by sediment core studies, both in the United States (primarily in the Great Lakes) and in Europe, which indicated that environmental dioxin levels increased significantly beginning about 1935-40.*
>
> *"Since the advent of fire clearly predated this time, it can be concluded that dioxins were largely anthropogenic and associated with events taking place around 1935-40. What were these events? Coal combustion could be ruled out because the consumption of coal in the United States was essentially*

> *constant from the turn of the century until about 1970; this record did not agree with the sediment core data."*

This statement by the SAB then suggests what has changed. The major source of dioxin in the environment is not combustion by itself. The source, rather, is the production and combustion of anthropogenic chlorine-containing materials that first began circulating in large quantities in the period following 1930.

> *"The explanation is likely to be the introduction of chlorinated organic compounds (polyvinyl chloride and chlorinated pesticides are but two examples) in the 1935-40 time-frame. Other sources such as leaded gasoline (which commonly contained ethylene dichloride and ethylene dibromide), diesel emissions, and PCBs are also possibly significant contributors.*
>
> *"Although the details of dioxin formation are not yet quantitatively understood, the introduction of these chlorinated products into wastes that were combusted appears to be the most likely cause of the increased dioxin deposition measured in sediments."*

It is undeniable that the products of the chlorine industry now pervade the world. Dioxins, furans, PCBs, HCB and hundreds of chlorinated chemicals which did not exist prior to the 20th century are now found in the soil, water and air of every place on the earth and in the tissues of virtually every human and animal.

Identifying the origins of the world-wide dioxin problem is not simply an exercise in laying blame. On the contrary, identifying the source of the problem is an essential first step in eliminating the formation and release of dioxins and other by-product POPs.

3 Stockholm Convention –The Global Goal of Elimination

For dioxins and other by-product POPs, the Stockholm Convention requires are that each Party "shall, at a minimum reduce the total releases derived from anthropogenic sources of each of the chemicals … with the goal of their continuing minimization and, where feasible, ultimate elimination."

The actions a nation chooses to follow in achieving the ultimate goal of the Stockholm Convention – elimination of by-product POPs – are critical to the success of the Convention. National Action Plans directed toward elimination would have markedly different outcomes from those focused on reduction.

For example, if dioxin elimination is the focus for national action, the economic activities, technologies, and materials that are, in effect, dioxin sources are first identified. Priority is then given to preventative measures through which these dioxin sources are either avoided, or if already present, changed or replaced with alternative activities, technologies and materials so that dioxins are neither created or released.

However, if dioxin release reduction is pursued, dioxin sources are identified and then modified so that dioxin formation and/or releases are reduced. Priority is then given to the largest of the sources that are most readily identified and measures such as pollution control systems are introduced so that dioxin releases from those specific sources are reduced, but not eliminated. In general practice this has emphasized minimising releases to air, rather than reducing the formation and total release of dioxins from a given process. Critically, this may only shift the dioxin burden from one environmental media to another (eg. from air to land through solid waste streams) leading to further environmental contamination and future release of POPs.

The choice of elimination as the primary focus for action will assist a nation in stopping the introduction of POPs-producing industries and materials, leading to genuine reductions in national and global burdens of dioxins and other by-product POPs. The choice of reduction as a primary aim on the other hand, will only encourage the further spread of those industries, which have already been identified as sources of POPs.

The desired outcome at the national, regional and global level must be programs of action that will minimise levels of dioxins and other by-product POPs in the environment, in food and in humans to the lowest possible levels as recommended by the World Health Organisation (WHO).[2] For example, dioxin levels comparable to those found in ancient human tissues,[3, 4] archived soils and vegetation,[5] etc.[6] According to the U.S. Environmental Protection Agency (USEPA), pre-industrial dioxin levels in the environment were no more than one percent of those currently existing.[7]

Greenpeace and many other NGOs are of the firm opinion that the desired outcome – dioxin and other by-product POPs levels comparable to pre-industrial levels – can be achieved only through the elimination of anthropogenic sources and that this must be the primary focus of National Action Plans on POPs.

4 Elimination

The elimination of dioxins and other by-product POPs is an iterative two-step process. The first step is *source identification* – to identify properly the source of the POP – and the second step is *source elimination* – to phase out, replace or otherwise remove the source so that the POP is no longer produced. This is true for POPs that are produced intentionally as well as by-products such as the dioxins.[*]

POPs sources fall into two general classes: primary sources — processes that produce or generate POPs; and secondary sources — products or materials in which POPs are present, or reservoirs where POPs have accumulated (e.g., soils, sewage sludge, landfills, sediments, etc.).

Figure 1 Basic Steps in Eliminating By-product POPs

(i) Identify primary sources
(ii) Prohibit or phase-out processes and/or materials that lead to the production of the by-product POP
(iii) Identify secondary sources, e.g., stocks of substances containing the by-product POP that are held by formulators, distributors and users as well as stockpiles and reservoirs of contaminated materials
(iv) Collect and properly destroy remaining stocks, stockpiles and reservoirs

In addressing sources of by-product POPs, first priority is given to primary sources so that accumulation of new stocks, stockpiles and reservoirs and additions to existing stockpiles and reservoirs will be avoided. However, the importance of identifying and destroying, by

---

[*] It is also important to note that a variety of toxic, persistent, bioaccumulative organic pollutants are being found in biota and environmental media that apparently are by-products and that display dioxinlike toxicity, e.g., the polybrominated dioxins and furans, mixed halogenated dioxins and furans, the polychlorinated azo- and azoxybenzenes, etc.

appropriate means, secondary sources must not be underestimated. For example, in many countries, releases of PCBs from stockpiles and in-use materials containing deliberately manufactured PCBs are probably the major current sources of PCBs to the environment (see Section 10).

Figure 2 Primary Dioxin Sources – Measures for Their Elimination

Primary Dioxin Sources	**Means of Elimination**	**Examples**
Processes for making chlorine-containing products, e.g., chlorinated pesticides and industrial chemicals	*Phase-out*	Ban manufacture of PCBs, PVC, PCP, HCB, 2,4-D, etc
Processes for making products that do not contain chlorine but involve the use of agents that are chlorine-based.	*Materials policies* requiring the use of chlorine-free materials in place of chlorine or chlorine-containing materials.	Bleach wood pulp using an oxygen-based, rather than chlorine-based process.
Processes that neither use nor require chlorine in any form	*Materials policies* to prevent entry of chlorine-containing materials	Remove chlorine-containing materials from materials and waste streams that may be subject to combustion

The two general policy options for eliminating primary dioxin sources are phase-outs – policies directed toward ending the application of processes that are dioxin sources, and materials policies – those directed toward replacing materials that are, in effect, dioxin sources under certain conditions.

For example, open burning of wastes is now listed by the USEPA as one of the top five sources of dioxin releases to air in the USA, and is also likely to be one of the significant sources in developing countries and countries with economies in transition. This is one of the clearest examples where materials policies are the simplest and most cost effective solutions.

A wide range of studies has demonstrated a clear correlation between burning of PVC plastics and dioxin formation (eg. open waste burning, domestic stoves, industrial furnaces, etc). By banning the use of PVC materials that may end up as wastes and be burned in this way (eg. packaging, bottles, food wraps, inks, construction materials) and requiring the substitution of non-chlorinated materials, a significant source of dioxin formation can be avoided. This would also have the benefit of reducing chlorine availability and subsequent dioxin formation in accidental fires in homes and landfills.

Of course, a ban on the open burning of wastes would be the simplest solution to the problem of dioxin formation and release from open burning. However it is realised that this may not be easily achieved in all countries in the short term, so the substitution of chlorinated materials that may end up as wastes provides an accessible solution to the problem in the short term.

A wide variety of industrial processes have been identified as having the potential to generate dioxins and other by-product POPs. A list of potential sources is shown in Figure 3, together with their primary chlorine donors.

Figure 3 Examples of Identified Dioxin Sources and their primary chlorine sources

Dioxin-generating process	Primary chlorine donor
Medical waste incineration	PVC from disposable medical devices/packaging
Ferrous metal smelting	PVC, chlorinated cutting oils, chlorinated solvents
Hazardous waste incineration	PCBs, pesticides, chemical industry wastes (eg. from chlorine/EDC/VCM and chlorinated solvent manufacture)
Secondary copper smelting	PVC-coated cables, PVC coatings, chlorinated solvents/cutting oils
Secondary lead smelting	PVC separators used in car batteries
Chemical manufacturing	Chlorine or organochlorines as a reactant
Magnesium metal production by electrolysis	Chlorine
Pulp mills	Chlorine-based bleaches
Home and building fires	PVC, pentachlorophenol, PCBs, chlorinated termiticides
Vehicle fires	PVC, chlorinated fuel additives
Vehicle fuel combustion	Chlorinated additives
Municipal waste incineration	PVC pacakaging, bottles, wraps, coatings, textiles, footware, toys, etc
Sewage sludge incineration	Pentachlorophenol and other organochlorines, such as those used in personal care products (e.g., Triclosan, etc)
Wood burning (industrial and residential)	PVC, pentachlorophenol, chemical hardeners
Cremation	PVC in coffins
Open waste burning	PVC, pesticides

5 Resource Allocation

The success of the Stockholm Convention on the issue of by-product POPs will depend primarily on the resources that national governments and funding agencies are willing to allocate to solving the problem. In each nation, existing sources of dioxin and other by-product POPs must be identified and addressed, at the same time steps must be taken to prevent the introduction of new sources. National POPs hotspots will require clean up and further releases from these cleanups must also be prevented.

Some newly industrialized countries will require ambitious programs of action simply to prevent a rapid rise in the rate at which dioxins and other by-product POPs are released into their environment, and consequently their food supplies and populations. The most important aspect of such programs must be to avoid problems before they arise.

It is not clear how, or even if, National Action Plans that focus solely on release reduction and, as yet undefined Best Available Technology (BAT) guidance, can be configured to address the overall expansion of POPs sources. This is particularly important for those newly industrialized nations and nations with economies in transition where current investment in such sources is minimal. While the release reduction approach can achieve reductions from individual point sources, these reductions will be nullified and perhaps overwhelmed at the national, regional and/or global level, if the number of such sources continues to increase.

Many industrialized countries have already heavily invested in economic activities, technologies and the production and use of materials that are, in effect, dioxin sources. In such cases, dioxin elimination may require a realistic transition period so that potential economic and social dislocations can be avoided or minimized. However, it is encouraging that a Canadian economic assessment reported "probable net benefits to society" for such a transition in that country.[8]

6 Worldwide Trends in the Chemical Industry

According to the OECD,[9] *"As the markets for chemicals mature in the industrialised world, developing countries offer the greatest growth opportunities either by exports or by investments in production facilities. Investment by chemical companies in facilities in foreign countries has been growing since the 1980s and 1990s and is expected to continue."* Also, the European Environment Agency notes that *"low value bulk chemicals"* production is being shifted from Europe *"to Asia and other areas."* [10] The OECD has predicted that in the future; *"The output in OECD countries will be primarily speciality and life science chemicals, with the non-OECD countries leading in production of high volume basic chemicals."*[9]

Such chemicals include, for example, polyvinyl chloride (PVC), and the associated production of chlorine, ethylene dichloride and vinyl chloride monomer. The production process of PVC – from chlorine to finished product – is known to produce highly dioxin-enriched wastes, while PVC products are among the world's largest single causes of dioxin formation (see appendix A).

PVC plastic, a known dioxin precursor when burned,[11] constituted about 12 percent of all plastic waste, approximately 2.1 million tonnes, in the European Union, Norway and Switzerland in 1994. With recycling rates for PVC of only 1 to 3 percent, the mass of PVC sent to incinerators and landfills[†] can only continue to escalate.[10] Trends of increasing domestic waste with rising PVC content in Europe and the Accession Countries can be expected to be mirrored in the newly industrialized nations.

To the extent that increasing waste generation with increasing PVC content occurs concurrently with increased incineration, landfilling, and open burning, a proportional rise in dioxin releases can be expected. Certainly such trends are apparent in Asia. For example, more than 22 municipal waste incinerators are expected to be constructed on the island of Taiwan by 2001.[12] In Korea, the proportion of municipal wastes treated by incineration will be increased to 20% by 2001, with approximately forty municipal waste incinerators to be in operation.[13]

The OECD also expressed concern that "*an increase in the production volumes of chemicals at factories in non-OECD countries could also lead to higher risk. As has been found with certain persistent, bioaccumulative and toxic chemicals (e.g. POPs) and other substances (e.g. NOx, SOx), once they are released from facilities during manufacturing/processing or through their final use (e.g. pesticide application), these pollutants can travel long distances before they are finally deposited on land or reach the atmosphere of local communities. If non-OECD countries do not employ the same kinds of controls on emissions and use as OECD countries, it is possible that a shift in production to these countries could lead to greater emissions and subsequently to greater concentrations of these substances in the environment in both non-OECD and OECD countries.*"[9]

[†] Higher rates of PVC disposal in landfills can be expected to lead to greater dioxin releases during landfill fires, which have been identified as a large source of dioxin releases to air in the U.S. and Sweden.

For newly industrialized countries and countries with economies in transition, National Action Plans should guide foreign investment and donor assistance toward cleaner, more sustainable development that avoids the introduction and spread of POPs producing technologies.

7 Identifying sources of by-product POPs

Primary sources of dioxin and other by-product POPs share one common feature – the availability of chlorine. These sources fall into three general classes:

1. Processes in which chlorine or a chlorine-containing material is essential. In almost all cases, these are chemical manufacturing processes. In some cases, the primary route of dioxin release to the environment is in products and materials. Most often, dioxins are concentrated in production wastes so that the wastes and/or the gaseous, liquid and solid residues from their treatment are the primary routes of dioxin release.

2. Processes in which chlorine or a material containing chlorine is used for a specific purpose that can be fulfilled by a non-chlorinated material (e.g., the use of elemental chlorine or chlorine dioxide for bleaching wood pulp); and

3. Processes in which chlorine or chlorine-containing materials are not introduced for any intended purpose but are only incidentally present (e.g., the burning of wastes, some metallurgical processes, power generation, accidental fires, etc.)

The Stockholm Convention includes two indicative lists of sources of by-product POPs (summarised in Figure 4). The sources listed in Annex C Part II are identified as those which have the potential for comparatively high formation and release of by-product POPs, while those listed in Part III are identified as being potential sources. This may be interpreted by some to mean that those listed in Part II are more significant sources than those listed under Part III.

However, this could lead to incorrect assumptions about sources in a given nation or region. It is important to note that given the variability in different industries and processes that exist within a country, and even more so between countries, that the most significant sources in a given nation may be any of the processes listed in either parts II or III, or alternatively processes which are not specifically listed in the Convention text at all.

Figure 4 Listed source categories of by-product POPs in Stockholm Convention

Annex C - Part II
Waste incinerators, including co-incinerators of municipal, hazardous or medical waste or of sewage sludge
Cement kilns firing hazardous waste
Production of pulp using elemental chlorine or chemicals generating elemental chlorine for bleaching
Secondary copper production
Sinter plants in the iron and steel industry
Secondary aluminium production
Secondary zinc production.
Annex C - Part III
Open burning of waste, including burning of landfill sites
Thermal processes in the metallurgical industry not mentioned in Part II (above)
Residential combustion sources
Fossil fuel-fired utility and industrial boilers
Firing installations for wood and other biomass fuels
Specific chemical production processes releasing unintentionally formed persistent organic pollutants, especially production of chlorophenols and chloranil
Crematoria
Motor vehicles, particularly those burning leaded gasoline
Destruction of animal carcasses
Textile and leather dyeing (with chloranil) and finishing (with alkaline extraction)
Shredder plants for the treatment of end of life vehicles
Smouldering of copper cables
Waste oil refineries

8 Inventories of by-product POPs

Each party to the Stockholm Convention is obligated to prepare: *An evaluation of current and projected releases, including the development and maintenance of source inventories and release estimates, taking into consideration the source categories identified in Annex C.* This obligation applies equally to dioxins and furans, PCBs and HCB.

8.1 Sources and Releases of Dioxins/Furans

Very few nations have inventoried their sources of dioxins/furans, and few, if any, of their inventories can be regarded as adequate. For example, UNEP described existing dioxin/furan inventories as follows:[14]

- *“The present number of … inventories is very small (15 based on national data)”;*
- *“Most data are available for countries from Western Europe and Northern America.”*
- *“[T]he coverage of sources varies from country to country.”*
- *“Almost exclusively, the existing inventories only address … emissions to air.”*
- *“[E]mission factors established in industrialized countries cannot be assumed to be representative for industries in less developed countries.”*

In addition, UNEP pointed out the need for harmonization of *“data acquisition and evaluation”* and of “*protocols for sampling stack emissions, water, soil, etc., and for analyzing these samples …”*

The most complete of the inventories are those prepared within the European Union (EU). As illustrated in Figure 5, the EU inventory underscores the magnitude and, thus, the importance of dioxin/furan releases to land, such as incinerator ash and pesticide production wastes sent to landfills.

The dioxin/furan inventories of individual member nations of the EU show striking differences in the relative contributions of major sources. For example, the largest source category in Austria is accidental fires, which contribute 30 percent of that nation’s total dioxin releases to air and land; the second largest source is pesticide production, which contributes 23 percent of total releases. In Belgium, the largest source category is municipal waste incinerators, which contribute 42 percent of total releases to air and land. In Germany, accidental fires account for 26 percent of total releases to air and land; municipal waste incinerators, 19 percent; and pesticide production, 15 percent.[15,16]

It is important to note, however, that the EU inventories do not take into account some of the major sources identified in other inventories. For example, landfill fires were not included in the EU inventories although the U.S. Environmental Protection Agency (USEPA) estimates that they may contribute as much as 20 percent of total dioxin releases to air in the U.S.[17] On the other hand, dioxin releases in incinerator ash and pesticide production wastes are not included in the U.S. inventory.

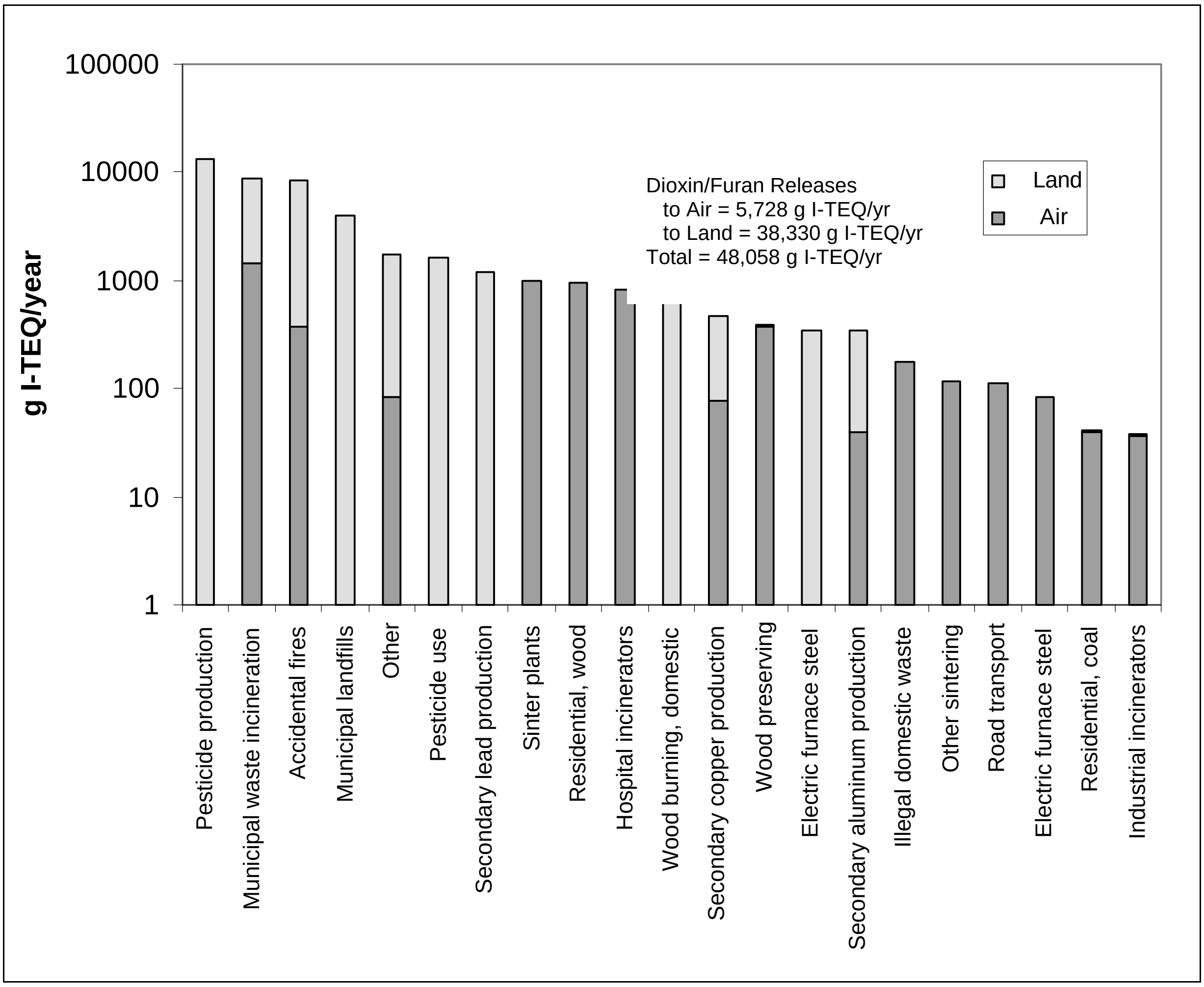

Figure 5 Dioxin releases to air and land in the European Union

The argument that existing inventories may underestimate dioxin releases is supported by studies in which estimated dioxin `fallout' – deposition of airborne dioxins to soils – has been found to exceed estimated dioxin releases to air from known sources. For example, studies by

Brzuzy and Hites (1996) and Eisenberg et al. (1998) indicate that global deposition of dioxins/furans is 6 to 60 times greater than emissions to air from major identified sources.[18,19]

Such great disparities between estimated dioxin emissions to air and deposition may be attributed to factors such as major sources that are yet unidentified, as noted by USEPA: [20]

> *"The possibility remains that truly unknown sources exist. Many of the sources, which are well accepted today, were only discovered in the past 10 years. For example, PCDD/PCDFs were found unexpectedly in the wastewater effluent from bleached pulp and paper mills in the mid 1980s. Ore sintering is now listed as one of the leading sources of PCDD/PCDF emissions in Germany, but was first reported in the early 1990s."*

Other factors that contribute to the uncertainties of estimating dioxin releases to the environment include reliance on emission factors, the paucity of data and the weakness of these data due to the limitations of methods of sampling and analysis.

- Emission Factors: Typically, existing national inventories of dioxin releases to air have used an "emission factor approach", in which emission factors are derived from a limited number of actual measurements and these factors are then assumed to be appropriate for all sources of a particular type. Since this does not take into account the enormous variability among nominally similar facilities, this approach can lead to gross underestimations of air emissions, as demonstrated by Webster and Connett (1998).[21] These researchers prepared estimates of total air emissions of dioxins for those US municipal waste incinerators for which actual measurements were available (81 of some 160 facilities) and compared these values with estimates computed by others using emission factors. Their estimates for a *fraction* of the facilities were greater than many of the emission factor-based estimates for *all* incinerators combined. Indeed, they found annual air emissions of dioxins from one single incinerator to be greater than one of the emission factor-based estimates for all incinerators combined. In general, they showed that estimated releases based on emission factors produced much smaller values than those derived from summing the emissions for measured facilities.

- Paucity and weakness of data: As described by Webster and Connett (1998), air emission data from municipal waste incinerators is most commonly obtained during "optimum" or "trial" conditions rather than during normal day to day operations. Indeed, many incinerators were tested only once, or not at all.[22] This shortcoming was further emphasized by the National Research Council in their recent evaluation of incineration: [23]

"Typically, emissions data have been collected from incineration facilities during only a small fraction of the total number of incinerator operating hours and generally do not include data during startup, shutdown, and upset conditions. Furthermore, such data are typically based on a few stack samples for each pollutant. The adequacy of such emissions data to characterize fully the contribution of incineration to ambient pollution concentrations … is uncertain. More emissions information is needed, especially for dioxins and furans … "

Single or limited numbers of measurements do not accurately represent dioxin emissions from combustion sources over an extended period of time. For example, Alcock et al. (1998) found that dioxin air emissions from a cement kiln increased by a factor of 70 times over a period of only five hours.[24] Moreover, in a recent study of a Belgian incinerator, two-week, `continuous' measurements found dioxin air emissions to be a factor of 30 to 50 times greater than emissions based on the standard 6-hour sampling period. [25] In other words, sampling stack gas measurements over a single 6-hour period greatly underestimates dioxin emissions to air.

It is also important to note that few if any existing inventories meet the obligation under Stockholm Convention to include coplanar PCBs in reporting the total TEQ values of by-product releases. This should not be interpreted to mean that this is the only requirement for reporting on PCBs. The Convention clearly requires that separate identification and measures be applied to all of the PCBs, not just those that are coplanar in nature. This is also important since a wide variety of toxic effects of PCBs appear to occur through mechanisms different from the dioxin-like toxicity of the coplanar PCBs. The significance of this requirement with respect to combustion sources is evidenced by a recent study in Korea that found that, for some MSW incinerators, coplanar PCBs might account for up to 30% of the total TEQ.[26]

Given the above list of limitations, it seems certain that current inventories greatly underestimate both air emissions and total releases of dioxins and other by-product POPs from anthropogenic sources. It seems equally certain that reliance on emission factors derived from the testing of industries and processes in OECD countries does not provide an accurate picture of dioxin and other by-product POPs releases within the OECD countries themselves, much less in developing countries and those with economies in transition,

UNEP have recently released a draft Dioxin Toolkit to enable dioxin/furan inventories to be determined under a common framework.[27] The draft toolkit consists of a background document and an electronic spreadsheet containing an extensive range of emission factors of dioxin releases from a wide range of identified dioxin sources. This will be useful for extrapolating data and gaining a rough approximation of potential dioxin releases. However, the only methodology that will provide a reasonably reliable indication of by-product POPs releases to the environment is the actual testing of the gaseous, liquid and solid outputs from individual facilities over extended periods of time and the summation of those results to provide a snapshot of total releases.

Nevertheless, the emission factors and methodologies presented in UNEP's draft Dioxin Toolkit and associated electronic spreadsheet can provide a useful, first-pass identification of sources and indication of potential releases. However, without actual testing and verification of releases, the results obtained must not be misconstrued as an accurate picture of either the major sources or the total releases for a given nation. UNEP have yet to release similar toolkits for PCBs and HCB.

9 Sources of HCB

Annex C of the Stockholm Convention provides an indicative list of potential sources of HCB(Figure 4). However, according to a recent report released by the European EMEP program,[28] the major sources of HCB production and release to the environment appears to be the production and manufacture of chlorinated chemicals.

The list of processes associated with formation and release of HCB includes; "light chlorinated hydrocarbons with short saturated chain (methyl chloride, chloroform, tetrachloromethane, 1,2-dichloroethane and other chlorinated paraffins), unsaturated chain (chlorinated methylene, vinyl chloride, trichloroethylene, epichlorohydrin etc), chlorinated aromatic compounds (different chlorobenzes, chlorinated toluenes and anilines), and chlorinated polynuclear aromatic compounds (polychlorinated biphenyls and terphenyls)."[28]

As can be seen from Figure 6, apart from the deliberate use of HCB as a product, the production and incineration of chlorinated solvents and PVC are by far the most significant identified releases of HCB to the atmosphere. [28] In the case of the Czech Republic and Slovakia it was estimated that 3-6 tonnes of HCB was released to the atmosphere in 1992, and that 80% of this was due to incineration of tetrachloroethylene (perchloroethylene), trichloroethylene and polyvinylchloride (PVC).[28]

Another potentially major source of HCB formation and release is the electrolytic production of magnesium. Chlorine-based magnesium production processes are known to generate and release relatively large quantities of organochlorines, notably dioxins/furans and HCB.[29] An indication of the estimated releases of HCB (and PCDD/Fs) from different magnesium facilities is shown in Figure 7.

The magnesium industry is growing rapidly worldwide. Annual world consumption of magnesium was 304,000 tonnes in 1995, and is expected to be 360,000 tonnes in 1999 and 500,000 tonnes in 2005. [30] If the chlorine-based processes continue to be popular, the sector is likely to be an increasingly important contributor to global emissions of PCDD/F, HCB and other organochlorine persistent organic pollutants (POPs).

Apparently other commercially important metals are produced using electrolysis of the molten chloride with graphite anodes — a guaranteed recipe for organochlorine production. In particular, the titanium and nickel industries should be investigated in this regard. Nickel production is implicated along with magnesium production in organochlorine emissions from Norsk Hydro's Porsgrunn facility.[31]

Figure 6 HCB emission factors for some identified source categories

HCB sources of emission to the atmosphere	Emission factor, µg/t
Combustion of organic fuel	
Coal	16
Wood	60
Industrial processes	
Production of chlorinated hydrocarbons:	
Tetrachloromethane	(1-20) x 10^6
Trichloroethylene	(1-6) x 10^6
Tetrachloroethylene	(3-10) x 10^6
Copper smelting	3.9 x 10^4
Secondary production of aluminium	5 x 10^6
Waste incineration	
Solid municipal	10 x 10^3
Medical	19 x 10^3
Waste water sediment	5 x 10^6
Industrial wastes:	
Tetrachloromethane	8 x 10^3
Trichloroethylene	3 x 10^3
Tetrachloroethylene	6 x 10^6
Polyvinylchloride	5 x 10^6
Motor transport *	
Leaded gasoline	0.87
Unleaded gasoline	0.024
Diesel fuel	21
Agriculture	
Used as fungicide	5 x 10^{11}

* - emission factors for motor transport is given in ng/km.

Figure 7 Summary of approximate emission factors (per kg Mg produced)

	Norsk Hydro, Porsgrunn	Norsk Hydro, Bécancour	Magnola/Noranda, Asbestos
Annual Mg production capacity	55,000 tonnes	42,000 tonnes	58,000 tonnes
PCDD/F (TEQ) generated inside the process	unknown	unknown	38,000 ng/kg
PCDD/F (TEQ) to air	100 ng/kg	6 ng/kg	2 ng/kg
PCDD/F (TEQ) to water	9,000 ng/kg	0.2 ng/kg	nil
PCDD/F (TEQ) to land	unknown	2 ng/kg	300-1,400 ng/kg
PCDD/F (TEQ) volatilised from land	unknown	unknown	30-140 ng/kg
PCDD/F (TEQ) transferred off-site	unknown	unknown	8,000-29,000 ng/kg
PCDD/F fugitive emissions	unknown	unknown	unknown
HCB generated inside the process	unknown	unknown	84,000 µg/kg
HCB to air	700-3,000 µg/kg	90-170 µg/kg	300 µg/kg
HCB to water	"mainly to water"	2-4 µg/kg	nil
HCB to land	unknown	60-120 µg/kg	800-3,000 µg/kg
HCB volatilised from land	unknown	unknown	600-2,400 µg/kg
HCB transferred off-site	unknown	unknown	27,000-29,000 µg/kg
HCB fugitive emissions	unknown	unknown	unknown

Although the level of reporting of HCB formation and releases in the chemical industry is very inconsistent around the world, the significance of the chlorine industry is further supported by data from the USA. One of the world's largest production facilities for chlorinated chemicals is the Dow Chemical plant situated in Freeport, Texas. This facility also manufactures Magnesium metal through a chlorine-based process. According to information reported to the USEPA Toxics Release Inventory for the year 1999, they generated almost 1200 tonnes of HCB wastes on site (Figure 8). However, the TRI information does not indicate whether this resulted from production of magnesium or from chlorinated solvents and intermediary production.

The authors of the EMEP report emphasised that; "It is important to include an estimate of emissions from chemical industry and different kinds of waste incineration in HCB source inventory otherwise HCB emission will be underestimated."

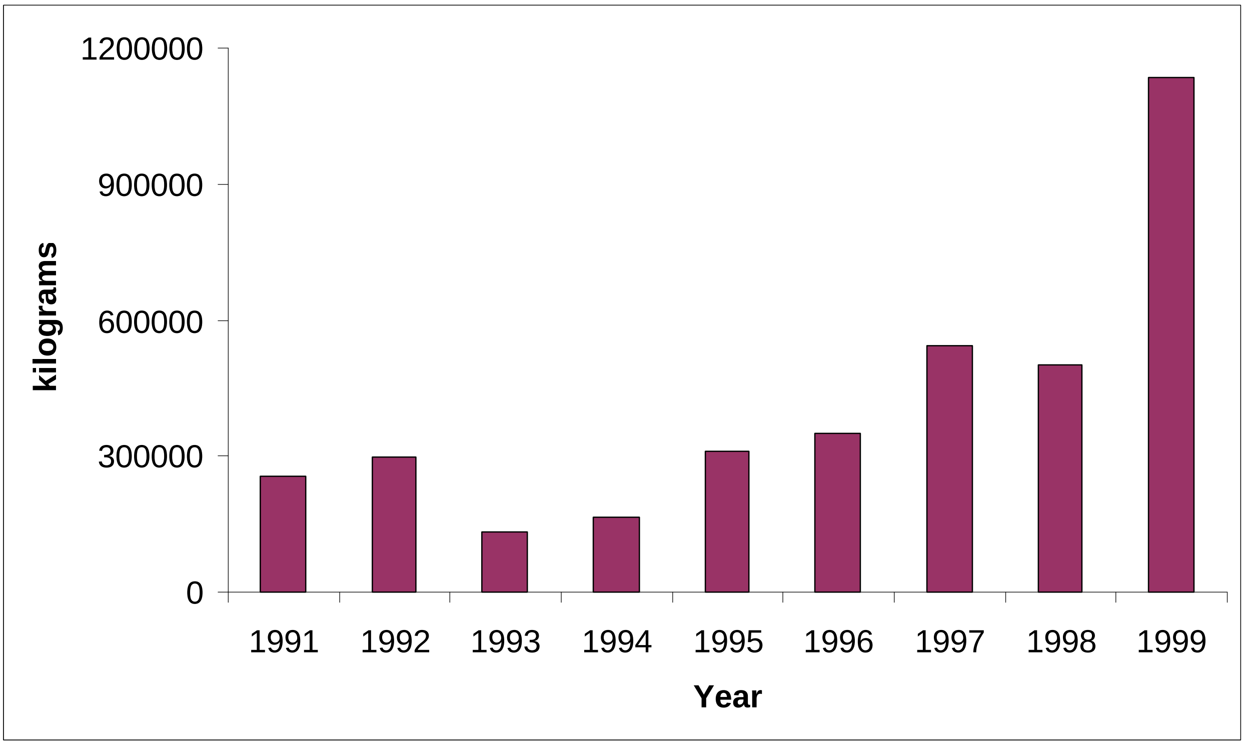

Figure 8 Total HCB wastes generated by Dow Freeport Texas USA 1991-1999 [32]

10 Sources of PCBs

Annex C of the Stockholm Convention provides an indicative list of potential sources of PCBs (Figure 4). Similarly to the situation with sources of HCB, national inventories for the release of PCBs from anthropogenic sources are far less developed than that for dioxins and furans.

The major releases of PCBs to the environment at present are almost certainly due to the ongoing use, storage and disposal of deliberately manufactured PCBs in products and equipment.[33, 34, 35] These include so called “closed systems”. (Eg. transformers, capacitors) and “open systems”, which include use of PCBs in PVC paints, PVC electrical insulation, varnishes, caulking compounds, etc.

The total intentional production of PCBs worldwide has been estimated to be 1.2 million tonnes, with up to two-thirds of that amount potentially still either in use or storage.[35] The primary efforts towards eliminating PCBs releases should most urgently be directed toward identifying and eliminating PCB stockpiles by appropriate means (see Section 11).

11 Appropriate technologies for the destruction of POPs wastes

Due to the inherent properties of POPs (i.e. the are toxic, resist natural decomposition, and accumulate in living creatures and the environment), any release of POPs into the environment is potentially harmful and therefore unacceptable.

According to the US Environment Protection Agency, chemicals with these properties *“have the potential to pose significant exposures to humans and ecosystems over a longer period of time; even small amounts of [POPs] chemicals that enter the environment can accumulate to elevated concentrations in the environment and in organisms, and therefore have a greater potential to result in adverse effects on human health and the environment.”*[36]

It is therefore vital that the search for POPs stockpiles is accompanied by a worldwide search for the most appropriate and effective means of destroying them.

Failure of traditional disposal methods: In many of the OECD nations, POPs wastes are routinely burned in incinerators costing tens if not hundreds of millions of dollars. Many nations – the USA and Canada included – also permit the burning of POPs wastes in boilers, metal furnaces, cement kilns and other systems that were not designed for this purpose. Other disposal means for POPs have included deep well injection, land spreading and burial in subterranean salt cavities.

The scientific evidence of the environmental and public health impacts of incinerators, cement kilns and similar combustion systems[37] has created strong public opposition to burning of POPs. Governments have reacted by focussing on regulations that reduce air emissions of dioxins. However, this regulatory focus on air emissions may not have reduced the levels of dioxins produced, but simply transferred the dioxin load from the air to other media (eg. solid wastes from pollution control equipment – ashes, dusts, sludges).

Of great concern is that these residues are usually buried in landfills or, worse still, used for commercial products such as agricultural fertiliser leading to soil and crop contamination. Recent studies from the EU showing that the levels of dioxins and furans in solid wastes are far higher than emissions to air tend to support this concern.[38]

Likewise, disposal in landfills, underground salt cavities and deep injection wells does not destroy POPs, but may result in wider contamination through groundwater migration and other processes. Also, such inappropriate practices may ultimately require expensive groundwater and soil remediation costing far more than properly destroying the POPs in the first place.

Non-incineration technologies: A range of POPs destruction technologies have been developed around the world over the last 20 years, which appear to overcome many of the inherent limitations of incineration and other combustion methods. These technologies generally use physical and chemical means of converting POPs waste to less harmful substances without the release of dioxins/furans and other hazardous POPs to the air, or in solid and liquid wastes. While not as widely known or promoted as incineration, some alternative technologies have demonstrated remarkably high destruction efficiencies for POPs and have a proven track record of commercial operation.

The U.S. Department of Energy have evaluated a range of non-incineration treatment technologies for the destruction of hazardous organic wastes, and note they have the potential to:[39]

- Destroy organic material without use of open-flame reactions with free gas-phase oxygen as the reaction mechanism.
- Reduce the offgas volume and associated contaminants emitted under normal operating conditions per unit mass of waste fed.
- Reduce the metals, radionuclides, and particulates suspended in the offgas exiting the process.
- Eliminate, or greatly reduce, the dioxin and furan precursors in the primary treatment process, especially in the offgas streams.
- Avoid conditions which allow free chlorine production and allow dioxin and furan precursors to form and to continue to react *de novo* with chlorine to produce dioxins and furans.

Technical Criteria for POPs Destruction Technologies: Non-incineration technologies therefore offer considerable promise as methods of disposing of POPs stockpiles in a manner which does not release or further disperse POPs into the wider environment. Greenpeace has reviewed a range of technologies for POPs stockpile destruction and in the process developed three primary technical criteria that are useful in assessing the performance of POPs destruction technologies:[40]

1. **Destruction efficiencies of effectively 100 percent for the chemicals of concern.** The determination of 100 percent destruction efficiency is necessarily based on findings of no detectable concentrations of the chemicals of concern in any and all residues, using the most sensitive analytical techniques available worldwide. Analyses of the unmodified residues must be carried out sufficiently frequently to ensure compliance with this criterion during startups, shutdowns and routine operations.

2. **Complete containment of all residues** for screening and, if necessary, reprocessing to ensure that no residues contain detectable levels of chemicals of concern or other harmful constituents, such as newly formed persistent organic pollutants or other hazardous substances.

3. **No uncontrolled releases to air, water or land**.

Greenpeace also considers that community-based public participation must be an integral part of the entire process of assessing any POPs disposal project – starting with stockpile evaluation, site and technology selection and continuing through operation, monitoring and compliance.

Further Information: Details of particular non-incineration technologies is provided in the 1998 Greenpeace Report [40] and examples of commercially available technologies are included in Appendix B.

12 Recommendations on unintentional POPs elimination

Greenpeace urges Governments to:

1. Earliest possible ratification and in the meantime, start immediate implementation of the Stockholm Convention on POPs;
2. Implement elimination as the primary goal for National and Regional Action Plans for by-product POPs;
3. Avoiding the introduction or expansion of processes or industries that are known to produce by-product POPs (eg. chlorine/chlorinated solvents and intermediates/PVC manufacture; incineration of municipal, hazardous and medical wastes);
4. Phasing out processes and industries that are known to produce by-product POPs, or requiring the substitution of chlorinated materials and processes by non-chlorine containing alternatives, where available;
5. Introducing purchasing and development policies for the substitution of chlorinated products and materials (e.g., PVC) by non-chlorinated alternatives
6. Institute a just transition strategy for effected workers and communities where industries or processes are required to change or be phased out;
7. Further development of national or regional inventories of by-product POPs that include both their potential sources of formation and their releases to air, water and land, and where feasible to the largest extent possible based on measurement and quantification of releases to air, water and land.
8. Exclusive use of methods of disposing of POPs wastes which do not themselves generate or release POPs in the process, i.e. non incineration destruction technologies.

13 Appendix A - The special case of PVC and dioxins

The world's total production of chlorine in 1995 was 38.6 million metric tonnes.[41] The production of PVC plastic has been estimated to account for more than 30% of the total chlorine usage in the world, and also more than 60% of the total organochlorine production.[42] As such, PVC is the single most significant use of chlorine today. It is also the most available and significant source of chlorine for the formation of dioxins and potentially other by-product POPs.

PVC involves the formation and release of dioxins during its production and manufacture, use and ultimate disposal. Figure 3 provides a list of processes for which PVC is, or has been implicated as, the most significant chlorine source in known dioxin producing processes and provides an overview of the potential for dioxin formation during the life-cycle of PVC.

Industry sources have described dioxin formation as unavoidable during the process of PVC manufacture.[43] Dioxins have been found in the major PVC precursor, ethylene dichloride (EDC)[44] and are found in EDC/vinyl chloride monomer (VCM) production wastes at very high levels. [45] Dioxins have also been detected in some samples of PVC at low levels.[46,47] Moreover, one of the congeners of dioxin has been identified as a "marker" for those who work in EDC/VCM production.[48]

Making the very conservative assumption that all EDC/VCM facilities in the world are designed, equipped and operated like those in Germany (including German-standard high temperature incinerators for waste treatment), dioxin releases from global production of PVC can be calculated to range from 3 to 30 grams TEQ per year released to air; 3 to 993 grams TEQ per year released to water; and 12,040 grams TEQ per year released in catalyst residues.[‡]

In reality these estimates probably underestimate global dioxin formation during the manufacture of PVC precursor compounds. In China, for example, over 200 chlor-alkali plants still use graphite electrodes in the production of chlorine gas[49] and these facilities can be anticipated to produce significantly more dioxins than this estimate.

The US EPA noted in 1997, *"[t]he chlorinated precursors [of dioxins] include … polyvinyl chloride (PVC)."*[50] This means that wherever PVC is subjected to certain conditions, such as those during combustion (e.g., waste incinerators, open burning of household and construction waste, landfill fires, and accidental fires involving vehicles, homes and buildings, PVC stockpiles, etc.), dioxins will be formed. In such circumstances, PVC is, in effect, the dioxin source.

Open burning is so common as to be accepted practice in many regions of the world. In some of these same regions, plastics (particularly PVC) are an increasingly large share of domestic waste. For example because of increased use of drinking water and milk packaged in disposable plastic containers, domestic waste in Abu Dhabi, U.A.E. and in Qatar contains 12-15 percent plastics. This can be compared to the 2-3 percent of plastics in domestic waste in the U.S. and U.K. [51] According to USEPA estimates, about 21 million people in the U.S. are burning about 8 million metric tons of household waste in piles or barrels in their backyards each year.[52] A recent USEPA study indicates that PVC materials are the major effective source of the dioxins released into the air during open burning of household waste.[53]

[‡] These calculations are based on emission factors presented in the 1997 European Dioxin Inventory [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.]

Accidental fires involving stockpiles of PVC have been documented to release substantial quantities of dioxins to the air in Canada, Germany and other countries.[54, 55] For example, Canadian officials estimated that about 13 grams TEQ of dioxins were released to the air during a 1997 warehouse fire in which between 200 to 400 tonnes of PVC were burned.[56]

In municipal and medical wastes PVC contributes the majority of the chlorine available for dioxin formation. In Denmark municipal solid waste is estimated to contain approximately 0.6-0.7 percent PVC, which contributes about 67 percent of total chlorine input to incinerators in that country.[57] In other countries, the PVC content of municipal waste may be considerably higher. For example, municipal solid waste in Japan is reported to contain an average of 12.2 percent PVC, with a maximum of 25.3 percent.[58]

PVC is the primary source of the chlorine necessary for dioxin formation in the materials burned in municipal and medical waste incinerators, trash fires, landfill fires, some secondary metal smelters, accidental fires, vehicle fires, etc. Under these conditions, PVC can be considered the single largest contributor to the global dioxin burden.[59]

Dioxins are created when …

- Pure PVC resin is brought to a high temperature or burned alone.[60, 61, 62]
- PVC products, such as vinyl gloves and other medical devices, are burned.[63, 64]
- PVC is burned in open fires with wood[65] and vegetation.[66]
- PVC-coated cables are burned.[61]
- Household wastes containing PVC are burned in open barrels.[67]
- PVC is burned in accidental fires, such as those involving homes, businesses and industrial facilities.[61, 68, 69, 70]

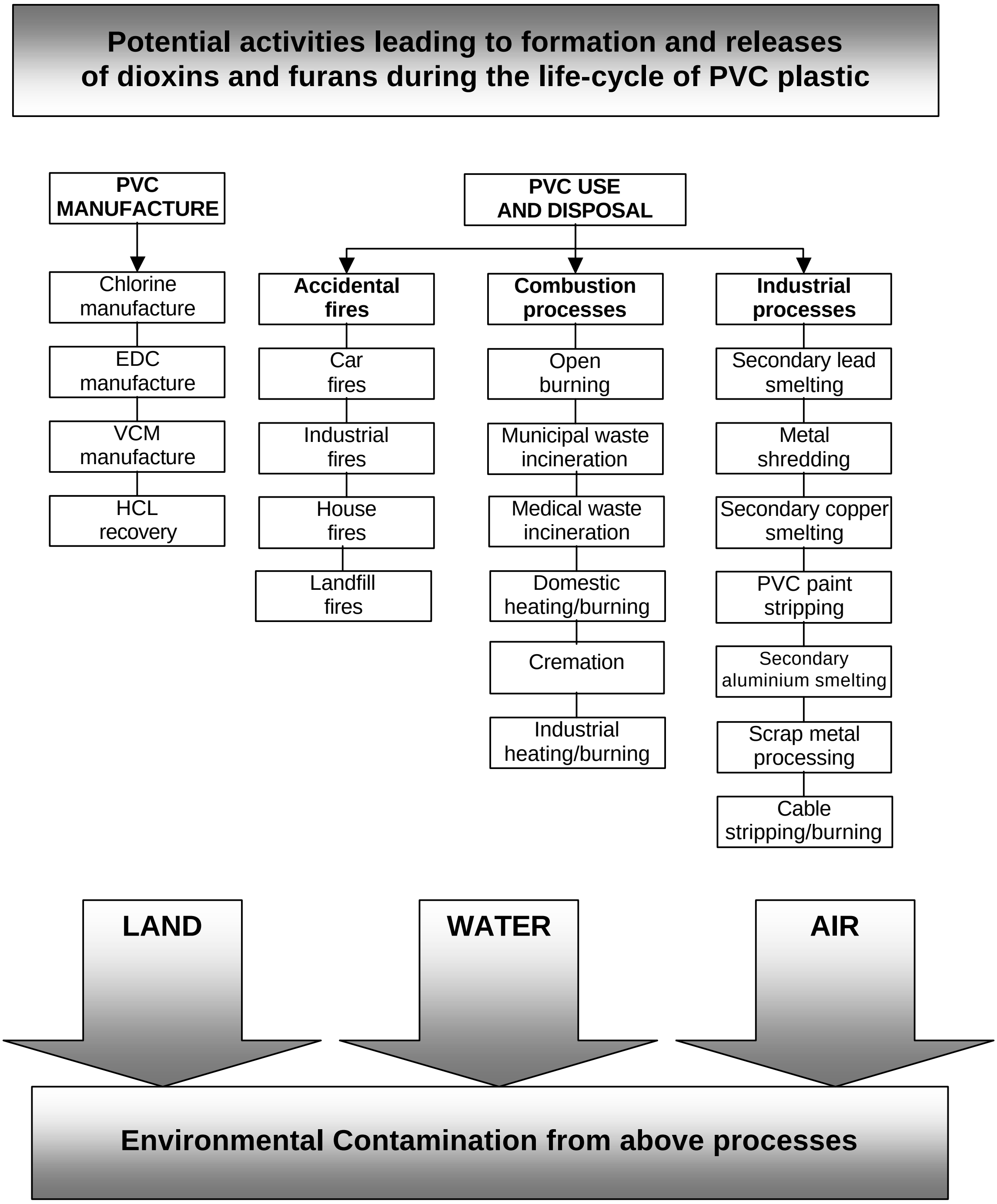

Figure 9 Potential for Dioxin formation during PVC life cycle

14 Appendix B - Examples Of Commercial Scale Pops Stockpile Destruction Technologies

Gas-phase chemical reduction (GPCR).
Process: Hydrogen reacts with chlorinated organic compounds, such as PCBs, at high temperatures, yielding primarily methane and hydrogen chloride.
Efficiency: Demonstrated high destruction efficiencies for PCBs, dioxins/furans, HCB, DDT.
Applicability: All POPs – including PCB transformers, capacitors, and oils. Capable of treating high strength POPs wastes and some experience in mixed pesticides.
Emissions: All emissions and residues can be captured for assay and reprocessing if needed.
Modular/transportable: Yes.
Concerns: Use of hydrogen gas, although company has good environmental/regulatory track record.
Licensing: Commercially licensed in Australia for POPs wastes. Recently licensed in Japan for PCBs and dioxin wastes. Has been licensed and used for full-scale remediation project in Canada and pilot scale remediation in USA. Is currently under assessment for US Army Chemical Weapons demilitarization program.
Vendor: ELI Ecologic International, 143 Dennis St., Rockwood, Ontario, Canada N0B 2K0
Phone: (519) 856-9591, Fax: (519) 856-9235
Website: www.eco-logic-intl.com

Base catalyzed dechlorination (BCD):
Process: A non-conventional heterogeneous catalytic hydrogenation process which reacts organochlorines with an alkali metal hydroxide, a hydrogen donor and a proprietary catalyst to produce salts, water and carbonaceous residue.
Efficiency: High destruction efficiencies have been demonstrated for DDT, PCBs and dioxins/furans.
Applicability: DDT, PCBs, dioxins/furans. Limited to approximately 30% strength PCBs.
Emissions: Solid residues are captured for assay and reprocessing if needed.
Concerns: Potential for emissions through pressure relief valve – although may be captured by pollution control system and is capable of operating in an essentially closed-loop mode.
Modular/transportable: Yes.
Licensing: Commercially licensed in USA, Australia, Mexico, Japan and Spain.
Vendor: BCD Group Inc., Cincinnati, OH 45208, USA, kornel_a@bcdinternational.com
Website: www.bcdinternational.com

Solvated electron process (SET):
Process: Free electrons in an anhydrous ammonia solution convert contaminants to smaller hydrocarbons and salts. eg. PCBs are reduced to petroleum hydrocarbons, sodium chloride, and sodium amide.
Efficiency: High destruction efficiencies have been reported for DDT, dioxins/furans and PCBs.
Applicability: All POPs – including PCB transformers, capacitors, and oils.
Emissions: All emissions and residues may be captured for assay and reprocessing if needed.
Concerns: Use of anhydrous ammonia and liquid sodium, potential for overpressurisation, products for some POPs may be toxic. Limited experience at commercial scale.
Modular/transportable: Yes.
Licensing: Commercially licensed for PCB wastes in USA and currently being assessed for US Army chemical demilitarization program.
Vendor: Commodore Applied Technologies Inc., 150 East 58th Street, New York, NY 10155, USA
Phone (212) 308-5800, Fax (212) 753-0731
Website: www.commodore.com

NB. Greenpeace does not support or endorse any particular technology or company. The above information is provided to assist governments and the community in the evaluation of available options for the destruction of POPs wastes and stockpiles.

References

---

[1] U.S. Environmental Protection Agency. 1994. Estimating Exposure to Dioxin-Like Compounds. Volume II: Properties, Sources, Occurrence and Background Exposures." Review Draft. EPA/600/6- 88/005Cb. Washington, D.C. June 1994.

[2] World Health Organization, 1998. Assessment of the health risks of dioxins: re-evaluation of the Tolerable Daily Intake (TDI). Executive Summary. Final Draft. WHO Consultation of May 25-29, 1998, Geneva. WHO European Centre for Environment and Health, International Programme on Chemical Safety. December.

[3] Schecter A., Dekin A, Weerasinghe N., Arghestani S, Gross M., 1988. Sources of dioxins in the environment: a study of PCDDs and PCDFs in ancient, frozen Eskimo tissue. Chemosphere 17:627-631.

[4] Ligon, W., Dorn, S., May, R., Allison, M., 1989. Chlorodibenzofuran and Chlorodibenzo-p-dioxin Levels in Chilean Mummies Dated to About 2800 Years Before the Present. Environ. Sci. Technol. 23:1286-1290.

[5] Kjeller, L., Jones, K., Johnston, A., Rappe., C. 1991. Increases in the Polychlorinated Dibenzo-p-dioxin and- furan Content of Soils and Vegetation Since the 1840s. Environ. Sci. Technol.25:1619-27.

[6] Alcock, R., Jones, K.. 1996. Dioxins in the environment: a review of trend data. Environ. Sci. Technol. 30: 3133-3143.

[7] U.S. Environmental Protection Agency. 1994. Estimating Exposure to Dioxin-Like Compounds. Volume II: Properties, Sources, Occurrence and Background Exposures." Review Draft. EPA/600/6- 88/005Cb. Washington, D.C. June 1994.

[8] Harris, J., 1999. The economic importance of chlor-alkali industry products, and alternatives to those products, to the Canadian economy. Chemosphere 38: 2533-2548.

[9] Environmental Outlook for the Chemicals Industry, OECD Environment Directorate, Environment, Health and Safety Division, Paris, France, 2001 (http://www.oecd.org/ehs)

10 European Environment Agency, 1999. Environment in the European Union at the turn of the century. Environmental assessment report No. 2. ISBN 92-9157-202-0. Copenhagen.

[11] U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Office of Air And Radiation, 1997. Locating and Estimating Air Emissions from Sources of Dioxins and Furans, EPA-454/R-97-003, Research Triangle Park, North Carolina, May 1997.

[12] Wang, K.-S., Chiang, K.-Y., Lin, S.-M., Tsai, C.-C., Sun, C.-J. 1999. Effects of chlorides on emissions of toxic compounds in waste incineration: Study on partitioning characteristics of heavy metals. Chemosphere 38: 1833-1849.

[13] Oh, J.-E., Lee, K,-T., Lee, J.-W, Chang, Y.-S. 1999. The evaluation of PCDD/Fs from various Korean incinerators. Chemosphere 38:9:2097-2108.

[14] United Nations Environment Programme, 1999. Dioxin and Furan Inventories, National and Regional Emissions of PCDD/PCDF. UNEP Chemicals: Geneva, Switzerland.

[15] Quass, U., and Fermann, M. 1997. Identification of Relevant Industrial Sources of Dioxins and Furans in Europe (The European Dioxin Inventory), Final Report, No. 43. Landesumweltamt Nordrhein-Westfalen: Essen, Germany.

[16] 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..

[17] U.S. Environmental Protection Agency, 2000. "Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. Part I: Estimating Exposure to Dioxin-Like Compounds, Volume 2: Sources of Dioxin- Like Compounds in the United States," and in "Part III: Integrated Summary and Risk Characterization for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds": Final Draft. EPA/600/P- 00/001Bb, September 2000.

[18] Brzuzy, L., Hites, R. 1996. Global mass balance for polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ. Sci. Technol. 30: 1797-1804.

[19] Eisenberg, J., Bennett, D., McKone, T. 1998. Chemical dynamics of persistent organic pollutants: A sensitivity analysis relating soil concentration levels to atmospheric emissions. Environ. Sci. Technol. 32: 115-123.

[20] USEPA (1998), *The inventory of sources of dioxin in the United States* (External Review Draft), United States Environment protection Agency, EPA/600/P-98/002Aa, April 1998

[21] Webster T. and Connett P., 1998. Dioxin emission inventories and trends: the importance of large point sources. Chemosphere 37 (9-12): 2105-2118.

[22] Webster T. and Connett P., 1998. Dioxin emission inventories and trends: the importance of large point sources. Chemosphere 37 (9-12): 2105-2118.

[23] National Research Council, 2000. Waste Incineration & Public Health. ISBN 0-309-06371-X, Washington, D.C.: National Academy Press.

[24] Alcock R., Gemmill R. and Jones K. (1998). An updated UK PCDD/F atmospheric emission inventory based on a recent emissions measurement programme. Organohalogen Compounds 36: 105-108.

[25] De Fre R. and Wevers M. (1998). Underestimation in dioxin inventories. Organohalogen Compounds 36: 17-20.

[26] Yoon-Seok Chang, Saet-Byul Kong and Michael Ikonomon, PCB Contributions to the Total TEQ Released from Korean Municipal and Industrial Waste incinerators, Chemosphere, **39**, 2629-2640, 1999.

[27] Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases - Draft, UNEP Chemicals, Geneva, Switzerland, January 2001. (http://www.chem.unep.ch/pops)

---

[28] Vulykh N., Putilina V. [2000] Technical Note "Hexachlorobenzene. Properties, emissions and content in the environment.", 6/2000. Meteorological Synthesizing Centre-East (Moscow, Russia) as an international centre of Co-operative Programme for Monitoring and Evaluation of Long Range Transmission of Air Pollutants in Europe (EMEP)

[29] There are three likely principal sources of the organochlorines: (i) conversion of MgO/MgCO3 to MgCl2 by heating with coke in a pure Cl2 atmosphere; (ii) purification of molten MgCl2 by transformation of residual MgO using gaseous HCl, mixed with graphite blades (a step called "chloridation* " in the Magnola process); and (iii) electrolysis of molten MgCl2 using anodes and bipolar electrodes made from graphite. Note that sources (i) and (ii) are not necessarily present in a given facility, while (iii) is common to all chlorine-based processes. (see next reference for further information).

[30] Projet d'usine de production de magnésium par Métallurgie Magnola inc., à Asbestos. Rapport d'enquête et d'audience publique. Bureau d'audiences publiques sur l'environnement, Québec, Québec, 1998. ISBN 2-550-32604-0.

[31] M. Oehme, S. Manø and B. Bjerke. Formation of Polychlorinated Dibenzofurans and Dibenzo-p-dioxins by Production Processes for Magnesium and Refined Nickel, page 1382. *Chemosphere* **18**, 1379-1389. Pergamon, Great Britain, 1989.

[32] US Environment protection Agency, Toxics Release Inventory 1999 Data Release, http://www.epa.gov/tri

[33] UK National Atmospheric Emissions Inventory, 1999, http://www.aeat.co.uk/netcen/airqual/naei/annreport/annrep98/naei98.html

[34] Detzel A., Patyk A, Fehrenbach H.,Franke B., Gingrich J., Lell M., and Vogt R, Investigation of emissions and abatement measures for persistent organic pollutants in the Federal Republic of Germany. Report UBA-FB 98-115/e. Federal Environment Agency (Umweltbundesamt), Germany 1998.

[35] Holoubek I., Polychlorinated Biphenyls (PCBs) World-Wide Contaminated Sites, TOCOEN REPORT No. 173, RECETOX - TOCOEN & Associates , Brno, Czech Republic May 2000

[36] Federal Register, 40 CFR Part 372, Vol. 64, No. 209, Friday, October 29, **1999**,

[37] Allsopp, M., Costner, P., Johnston, P., 2001. Incineration and Human Health: State of Knowledge of the Impacts of Waste Incinerators on Human Health, Amsterdam: Greenpeace International.

[38] Releases of Dioxins and Furans to Land and Water in Europe, Final Report produced for Landesumweltamt Nordrhein-Westfalen, Germany on behalf of European Commission DG Environment, September **1999**

[39] W. E. Schwinkendorf, B. C. Musgrave, R. N. Drake, **1997**. Evaluation of Alternative Nonflame Technologies for Destruction of Hazardous Organic Waste, Report INEL/EXT-97-00123, Idaho National Engineering Laboratory, Mixed Waste Focus Area, Lockheed Martin Idaho Technologies Company, Idaho Falls, Idaho, April **1997**

[40] Costner, P., Luscombe, D., and Simpson, M., Technical Criteria for the destruction of POPs Stockpiles, Greenpeace International, **1998**. Available at http://www.who.int/ifcs/isg3/d98-17b.htm

[41] Industry and Trade Summary: The Chloralkali Chemicals, USITC Publication 3158, U.S. International Trade Commission, Washington, DC, March 1999

[42] René Kleijn, Ester van der Voet, Chlorine in Western Europe, Materials Accounting as a Tool for Decision Making in Environmental Policy, Case Study Report 3, Report ENV4_CT96_0230, EC ENVIRONMENTAL RESEARCH PROGRAMME, April 1998

[43] ICI Chemicals & Polymers Ltd, 1994. Report to the Chief Inspector HMIP Authorisation AK6039, ICI Chemicals & Polymers Ltd., Safety & Environment Department, The Heath, Runcorn, April 27, 1994.

[44] Bretthauer E., Kraus H., de Dominico A., (eds.), Dioxin Perspectives: A Pilot Study on International Information Exchange on Dioxins and related compounds. Plenum Press, New York, 1991.

[45] Costner, P. 1995. PVC: A Primary Contributor to the U.S. Dioxin Burden. Washington, D.C. Greenpeace.

[46] Swedish Environmental Protection Agency, 1993. Swedish Dioxin Survey, an open database (11 Dec. 1993).

[47] Ministry of Agriculture, Fisheries and Food, Food Safety Directorate (UK), 1995. Dioxins in PVC food packaging. Food Surveillance Information Sheet 59, London.

[48] Hansson, M., Barregard, L., Sallsten, G., Svensson, B.-G., Rappe, C. 1997. Polychlorinated dibenzo-p-dioxin and dibenzofuran levels and patterns in polyvinylchloride and chloralkali industry workers. Int. Arch. Occup. Environ. Health 70:51-56.

[49] XU Ying, ZHANG Qinghua, WU Wenzhong & LI Wen, Chinese Science Bulletin, Vol. 45 No. 16, 1471-1475, 2000

[50] U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Office of Air And Radiation, 1997. Locating and Estimating Air Emissions from Sources of Dioxins and Furans, EPA-454/R-97-003, Research Triangle Park, North Carolina, May 1997.

[51] Qdais, H., Hamoda, M., Newham, J. 1997. Analysis of residential solid waste at generation sites. Waste Manage. & Res. 15: 395-406.

[52] 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.

[53] Lemieux, P.M. Evaluation of emissions from the open burning of household waste in barrels. Vol. 1. Technical Report. EPA-600/R-97-134a. Nov. 1997.

[54] Socha, A., Abernethy, S., Birmingham, B., McLaughlin, D., Spry, D., Dobroff, F., Cornaccio, L. 1997. Plastimet Inc. Fire, Hamilton, Ontario, July 9-12, 1997. ISBN 0-7778-6833-4. Ontario Ministry of Environment and Energy, October 1997.

[55] Meharg, A., Shorek, R., French, M., and Osborn, D. 1997. Dioxin and furan residues in wood mice (*Apodemus sylvaticus*) following a large scale polyvinyl chloride (PVC) fire. *Environmental Pollution*. 97:213-220.

---

[56] Socha, A., Abernethy, S., Birmingham, B., McLaughlin, D., Spry, D., Dobroff, F., Cornaccio, L. 1997. Plastimet Inc. Fire, Hamilton, Ontario, July 9-12, 1997. ISBN 0-7778-6833-4. Ontario Ministry of Environment and Energy, October 1997.

[57] Moller, S., Larsen, J., Jelnes, J.E., Faergemann, H., Ottosen, L.M., Knudsen, F.E. "Environmental Aspects of PVC." Environmental Project No. 313. Denmark: Ministry of the Environment, Danish Environmental Protection Agency, 1995.

[58] Muto, H., Saito, K., Shinada, M., Takizawa, Y. 1991. Concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans from chemical manufacturers and waste disposal facilities. Environ. Research 54: 170-182.

[59] Costner P., Dioxin Elimination – A Global Imperative, Greenpeace International, The Netherlands, March 2000.

[60] Blankenship, A., Chang, D., Jones, A., Kelly, P., Kennedy, I., Matsumura, F., Pasek, R., and Yang, G.. 1994. Toxic combustion by-Products from the incineration of chlorinated hydrocarbons and plastics. *Chemosphere* 28:183-196.

[61] Christmann, W., Kasiske, D., Kloppel, K., Partscht, H., and Rotard, W. 1989. Combustion of polyvinylchloride - an important source for the formation of PCDD/PCDF. *Chemosphere* 19:387-392.

[62] McNeill, I., Memetea, L., Mohammed, M., Fernandes, A., Ambidge, P. 1998. Polychlorinated dibenzodioxins and dibenzofurans in PVC pyrolysis. Polymer Degradation and Stability: 62: 145-155.

[63] Hassel, G., Rizeq, R., Barton, R., and McGrath, T. 1992. Emissions assessments from incineration of large volume parenteral plastic containers. *Proceedings of the 1992 Incineration Conference: Thermal Treatment of Radioactive, Hazardous Chemical, Mixed and Medical Wastes*, Albuquerque, New Mexico, May 11-15, 1992, pp. 483-488.

[64] Yasuhara, A., and Ito, H. 1991. Combustion products of poly(vinyl chloride). *J. Environ. Chem*. 1:525- 528.

[65] Merk, M., Schramm, K.-W., Lenoir, D., Henkelmann, B., and Kettrup, A. 1995. Determination of the PCDD/F concentration in the fumes from a PVC fire. *Organohalogen Compounds* 23:491-494.

[66] Liberti, A., Gorett, G., and Russo, M. 1983. PCDD and PCDF formation in the combustion of vegetable wastes. *Chemosphere* 12:661-663.

[67] Lemieux, P., 1997. Evaluation of Emissions from the Open Burning of Household Waste in Barrels. Volume 1. Technical Report. EPA-600/R-97-134a, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, November 1997.

[68] Thiessen, J., Funke, W., Balfanz, ì E., and Konig, J. 1989. Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials. *Chemosphere* 19:423-428.

[69] Marklund, S., Andersson, R., Tysklind, M., and Rappe, C. 1989. Emissions of PCDDs and PCDFs from a PVC-fire in Holmsund, Sweden. *Chemosphere* 18: 1031-1038.

[70] Meharg, A., Shore, R., French, M., and Osborn, D. 1997. Dioxin and furan residues in wood mice (*Apodemus sylvaticus*) following a large scale polyvinyl chloride (PVC) fire. *Environmental Pollution* 97:213-220.