# SUBSTANCE AND PERCEPTIONS OF ENVIRONMENTAL IMPACTS OF DIOXIN EMISSIONS

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# Substance and Perceptions of Environmental Impacts of Dioxin Emissions (Panagiotis Deriziotis)

## EXECUTIVE SUMMARY

The emission of dioxins is perceived widely as a major environmental impact of combustion processes. This paper reports the results of an extensive study of published data on a) the physical and chemical properties of dioxins and their environmental transport mechanisms; b) the measured impacts of dioxin emissions on the environment and on public health.; c) the rate of formation of dioxins from all U.S. and international sources; d) how the contribution of Waste-to-Energy (WTE) plants has changed with time; and e) the pre-MACT and post-MACT performance of individual Waste-to-Energy (WTE) plants in the U.S.

Although dioxins are considered to be some of the most dangerous man-made substance, there is no conclusive evidence associating present background levels with carcinogenic, reproductive, developmental or immunologic effects. Even in the Seveso accidental release, no association between dioxin and adverse health effects on humans was observed. Unfortunately, there have been very few public health studies to document the exact composition and levels of dioxin among the studied populations. For that reason results are not comparable and therefore unreliable.

Because of the unique environmental properties of dioxins and furans, such as resistance to photolytic, biological and chemical degradation, low water and high lipid solubility and tendency for bioaccumulation, they are categorized as Persistent Organic Pollutants (POPs). Dioxins can move long distances in the atmosphere before deposition, may persist in the environment for long periods of years and may bio-concentrate by factors of up to 70,000 fold. Their physical and chemical properties of high persistence and semi-volatility, coupled with other unique characteristics, have resulted in their being widely distributed through the global environment, even in regions where they have never been used. Further research is necessary in order to comprehend the various transfer processes by which dioxins move between the atmospheric, aquatic, terrestrial and biological environments, and the degradation processes and rates in each medium. Currently, few parameters are regularly monitored on a global scale and sampling procedures are not standardized and not frequent enough resulting to inconclusive results in most human health studies.

The study has shown that during the last decades dioxin emissions have decreased significantly. This decrease is the result of an international effort to curb emissions from concentrated sources such as waste-to-energy (WTE) facilities, cement kilns and the pulp and paper industry. Emissions data from around the world presented in this study indicate a sharp reduction in dioxin emissions on air mainly from concentrated (industrial) sources. For most countries, the reduction is in the range of 80-90+%. The lower quantity of dioxins emitted on air have resulted in a significant reduction in human intake of PCDD/F compounds in the past few years. Since emissions from industrial sources have been successfully controlled in most of the developed nations, future regulation should take account of multiple small sources but with high overall emission rates. Emissions from MSW combustion which were historically the biggest source have now become a minor contributor. The most important global contributor to the dioxin inventory has become the

residential combustion of wood in stoves, boilers etc, and the uncontrolled combustion of residential and agricultural refuse ("backyard barrel burning"). "Backyard barrel burning" at present constitutes over 50% of the U.S. dioxin emissions Residential combustion is still common in developing countries and in rural areas in many developed countries. In the U.S., Canada, the United Kingdom, and the European Union combustion of wood, fuels and waste domestically will became the most important source for dioxins.

Nevertheless, because of the extremely high toxic potency of dioxins, it is very important to keep dioxin emission at a minimum by focusing on additional measures aimed at reducing human exposure to high levels of dioxins in the short to medium term and to maintaining exposure at safe levels in the long term. Additionally, measures should be taken in order to minimize the levels of dioxin precursors in the waste stream by phasing out the production and use of substances such as PCPs and PCBs.

***A pdf file of this thesis is available at www.columbia.edu/cu/wtert.***

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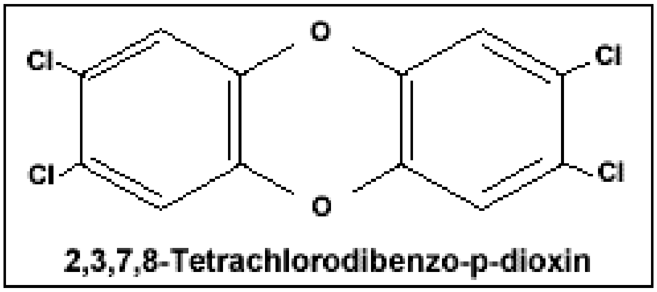
## 1. Behavior of Dioxins and Furans in the Environment

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) collectively known as dioxins, are undesirable by-products of all combustion processes and of many chemical and industrial processes. The term "dioxin like compounds" comprises 210 congeners that are detectable in trace amounts in almost all environmental compartments. PCDD/PCDFs are planar, tricyclic ethers that contain up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9 [*Fiedler et al. 2000*]. Among these, 75 congeners are polychlorinated dibenzo-*p*-dioxins (PCDD) called "dioxins", and 135 are polychlorinated dibenzofurans (PCDF), also called "furans" (Figure 1).


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

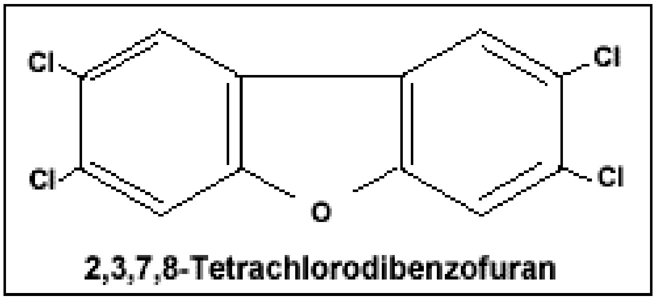

2,3,7,8-Tetrachlorodibenzofuran

Figure 1. Typical molecular structures of dioxins (above) and furans (below)

Dioxins were first discovered in a German laboratory in 1872. Historically, dioxins were released in the environment mainly from the production and use of chlorinated organic chemicals and pesticides and the incineration of various materials. Other important historical contributors were the pulp and paper industry (solely in the aquatic environment) and metal smelting. Following the accidental release of the very toxic 2,3,7,8 TCDD congener at Seveso, Italy in 1976 and the identification of dioxins in emissions from a municipal waste incineration in the Netherlands, the dioxin pollution issue was addressed intensely, both in Europe and the U.S. Interestingly, Eskenazi et al suggested that although residents of the area near Seveso were exposed to considerable levels of TCDD, it is likely that the overall total dioxin levels of these residents resulted also from substantial background exposure to dioxins, furans, and PCBs that were probably unrelated to the explosion[*Eskenazi et al 2004*].

### 1.1 Physical and Chemical Properties - Environmental Transport

Dioxins are characterized by high melting points (>593°K), low vapor pressure (<$10^{-6}$ Pa at atmospheric pressure), low water solubility and high lipophilicity. Therefore, accumulation occurs in organic matter, primarily in fatty tissues of organisms. Sediments are an important, and likely final, environmental sink for all PCDD/PCDFs releases. Dioxins have been found at significant levels in aquatic environments, bound to solid particles, soil colloids and organic matter. Due to their high physical, chemical and biological stability, dioxins degrade very slowly by means of photolysis, volatilization and biodegradation. PCDD/PCDFs are not expected to leach when deposited to soil, but mobilization can occur in the presence of lipophilic solvents (leaching into deeper layers of soils and/or groundwater) or in cases of erosion. However, *Fiedler (1995)* suggested that PCDD/PCDF transport due to soil erosion and run-off does not play a major role in environmental contamination and human exposure.

### 1.2 Atmospheric Environment

PCDD/PCDFs enter the atmosphere in the form of vapor and/or bound to particulate matter emitted from high temperature sources. The vapor to particle ratio is controlled by the vapor pressure and the suspended particle concentration [*European Commission 1999*]. *Bobet et al (1990)* and *Eitzer et al (1989)* concluded that the least chlorinated compounds tend to be in the vapor phase, usually at higher ambient temperatures. In contrast to dioxins in the aquatic environment, vapor emissions are easily degraded by direct sunlight photolysis and reaction with hydroxyl radicals. When PCDD/PCDFs are released in the form of particulate matter, they are physically removed from air by wet or dry deposition. Dry deposition occurs when PCDD/PCDFs are accumulated directly on surfaces, but as equilibrium conditions, such as temperature and concentrations, change upward, dioxin fluxes from ground sources are possible [*European Commission 1999*].

Wet deposition is the most important atmospheric mechanism for dioxin removal and can occur in-cloud or below-cloud. Below cloud removal occurs when dioxin emitted from stationary sources are directly mixed in the lower levels of the atmosphere. At greater distances, mixing takes place at higher altitudes and therefore the in-cloud mechanism dominates [*Koester et al, 1992*]. The removal mechanism of the vapor phase of semi-volatile compounds such as dioxins by rain is different from the removal mechanism of PCDD/PCDFs bound to particles, where removal of dioxins by rain falling is permanent. In the case of vapor phase dioxins, because of their low water solubility, dilution in the droplets is very low and reaches equilibrium after only one meter of fall. Therefore, the deposition of insoluble gases in rain depends on the concentration near the ground surface [*European Commission 1999*].

After deposition, there is the possibility of a small amount of dioxin that is bound to small soil or dust particles from the ground to become re-suspended in air. Re-suspension poses the threat of inhalation and an increase of the contaminated area. Another secondary transfer mechanism is termed the “rain splash”, the effect of soil and water mixtures deposited on low leafy plants and vegetables after a heavy rainfall. These amounts of contaminated soil can enter into the food chain, and consequently to the human organism, by poorly washed vegetable consumption, directly, or by meat and dairy products, indirectly.

Photolysis is considered to be the most important degradation mechanism of gas phase dioxins in the atmosphere; however, laboratory evidence [*Kwok et al 1995*] indicates that when dioxins are associated with particles, photodegradation is reduced to insignificant levels and, therefore, is too slow to provide considerable protection to the environment. *Orth et al (1989)* suggested that photolysis rates are higher for the less chlorinated compounds and *Pennise et al (1996)* reported the same behavior for dioxins bound to particles. The half-life of the tetra-chlorinated compound TCDD was found to range between 0.4 to 17 hours, depending on light intensity, and for the octa-chlorinated compound OCDD between 6.8 and 62 hours.

Hydroxylation is also more common to the less chlorinated compounds, and it takes place mainly in the troposphere where the OH radical and ozone ($O_3$) are commonly found. *Kwok et al (1995)* measured the average atmospheric residence time for PCDDs to be one day and for PCDFs 3.7 days.

### 1.3 Aquatic Environment

After PCDD/PCDFs are deposited from the atmosphere to water bodies, the contaminants follow four principal routes: a) Re-volatilization and return to the atmosphere, b) adsorption on sediments, c) bioaccumulation, and d) degradation by photolysis or biochemical reactions.

Re-volatilization rates are miniscule under common conditions since most of the PCDD/PCDFs dissolved in the water bodies bind strongly to dissolved or particulate organic matter. A small proportion, less than 1% of the PCDD/PCDFs concentrations in water, are in the form of colloidal and dissolved phases [*Gschwend et al, 1985; Servos et al, 1992*]. In general, the fate and residence time of PCDD/PCDFs in water are closely related to the fate and residence time of organic particles.

*Eadie et al (1987)* suggested that PCDD/PCDFs bound to particulates have shorter residence times in water bodies because of the rate of sediment deposition, in contrast to the larger hydraulic flushing times that define the removal of dissolved PCDD/PCDFs.; their measurements in the Great Lakes area indicated that dissolved phase PCDD/PCDFs have a 100-year residence time. When deposited in turbulent shallow waters, dioxins can be remobilized by physical or biological forces, but when particles are deposited in large depths where turbulence is minimal, they become incorporated into the sediment and thus immobilized.

PCDD/PCDFs are considered very stable when incorporated into sediments and *Hashimoto et al (1990)* detected low levels of dioxins in 8000-year-old marine sediments while *Juttner et al (1997)* detected comparable levels in lake sediments that dated back to the 17th century. The slow degradation of organic carbon under anaerobic conditions also results in dioxin immobilization

Photo-degradation in aquatic environment occurs as a result of direct sunlight and therefore bottom water or sediments are less sensitive than surface water or near-surface sediments. Dioxin half-life under these conditions has been estimated up to 550 days for sediments [*EPA, Technical Factsheet on Dioxin*; *Ward et al, 1979*], 1 to 225 days in the winter and 0.4 to 68 days in the summer for surface waters [*Atkinson et al, 1991*]. However, the longevity of dioxins increases significantly as water depth and sediment depth increase.

Biodegradation has a minor impact on dioxin destruction because of their high resistance to microbial activity. The half-life of dioxin in lake sediments under biodegradation has been estimated to be in excess of 1.5 years [*EPA, Technical Factsheet on Dioxin*].

Volatilization also contributes in the removal of dioxins from water, but when the effects of adsorption to sediment are considered, the volatilization model predicts a very long half-life of over 50 years. [*EPA, Technical Factsheet on Dioxin*]

An important pathway of human exposure to PCDD/PCDFs is regarded to be the consumption of fish and seafood. Bioaccumulation in such organisms takes place predominantly by the ingestion of sediments and to a lesser degree by the direct uptake of dioxins from water through the gill membranes. For this reason, *Weiden et al (1990)* suggested that dioxin concentrations in these organisms is directly related to sediment concentrations

### 1.4 Terrestrial Environment

After deposition on soil from the atmosphere, dioxins are bound into sediments as they are adsorbed to organic carbon or other particles. As a rule, the amount of dioxins detected below 8 cm from the surface has been approximately 1/10 or less than that detected in soils at levels above 8 cm [*EPA, Technical Factsheet on Dioxin*]; also the higher chlorinated compounds are more persistent.

The most important degradation processes for dioxin depositions in terrestrial soil sediments are photolysis and volatilization. The persistence half-life of TCDD on top soil surfaces may vary from less than one to three years  but half-lives in soil interiors may be as long as 12 years [*EPA, Technical Factsheet on Dioxin*].

Photolysis converts highly toxic chlorinated compounds to less toxic equivalents by removing one or more chlorine atoms; however, it only occurs on soil deposited dioxin degradation under special conditions [*Moore et al, 1984*], such as dissolution in a light-transmitting film, presence of ultraviolet light and organic hydrogen.

## 2. Toxic Equivalent Factors

Dioxins are usually emitted in the form of a mixture containing several of the different congeners. Therefore, for simplification purposes, it is common practice to estimate the total toxicity of the gas mixture based on the comparative toxicity of each congener with respect to the most toxic isomer; 2,3,7,8-TCDD. Since 2,3,7,8-TCDD is the most toxic, it is assigned a toxic equivalent factor of 1.0 (TEF). All other congeners are assigned lower TEFs comparable to their relative toxicity. The toxicity varies significantly among the different PCDDs and PCDFs. *Kuehl et al. (1986)*, *van den Berg et al.(*1994), and *Ryan et al.* (1990) studied various animal and human populations exposed to complex mixture of dioxins. They concluded that although nearly all of the 210 PCDD/F isomers could be detected in the environment, only seventeen 2,3,7,8-substituted congeners that were minor components of all mixtures they examined were preferentially retained and bioaccumulated. After these studies, it is generally acknowledged that only 17 out of the 210 dioxin congeners are toxic.

The congener toxic equivalent factors (TEFs) are defined on the basis that all congener modes of action and the responses elicited in biological systems parallel those of the 2,3,7,8-positional PCDD. Although the events associated with dioxin toxicity are not yet fully understood, it has been widely agreed that dioxins bind to protein receptor complexes (Ah Receptors) that "in turn induce a cascade of biochemical changes at the cellular level" [*Smith 2001*]. US EPA research notes the "role of the AhR in mediating the biologic and toxic responses induced by 2,3,7,8-TCDD and related PCDDs and PCDFs" [*US EPA Reassessment PART II, CH9*]. Human response to alterations at the Ah receptor structure and function, is believed to vary and thus individual sensitivity to dioxin toxicity differs from one person to another [*Smith 2001*].

Total toxicity is expressed by multiplying the concentrations of the dioxin congeners present in a mixture, usually in grams per unit volume, by their respective TEFs. The result is called toxic equivalent (TEQs) or usually "grams TEQ".

The TEQ of the mixture is obtained by summing all individual TEQs, with units identical to that in which the concentrations of the individual congeners are expressed (usually "grams per unit volume").

$$TEQ = \sum\left[(PCDD_A) \times TEF_A\right] + \sum\left[(PCDF_A) \times TEF_A\right]$$

Several toxicity rating methods have been developed on a national and international basis, such as NORDIC, USEPA - NATO/CCMS, FRG UBA, WHO-TEQ and EADON. Because of the lack of common methodology and extensive data, the toxicity factors assigned to various congeners vary considerably from one model to another. The first scheme to be widely adopted was that of NATO/CCMS (1991). *Ahlborg et al.*, under the umbrella of WHO-ECEH (European Centre for Environment and Health) and IPCS (International Programme on Chemical Safety), further refined the model for assessing the relative potencies and to determine widely acceptable TEFs for PCDDs, PCDFs and dioxin-like PCBs. The TEF factors calculated by this method are also known as I-TEFs. Finally, *Van den Berg et al* in 1998 revised the WHO-ECEH TEF scheme and included values for all PCDDs, PCDFs and coplanar congeners of PCBs [*Table 1*]. This scheme was adopted by the World Health Organization and therefore the TEF values are also known as WHO-TEFs.

Nevertheless, many national and international agencies, such as USEPA, still use the WHO-ECEH method for calculating TEQ using I-TEFs.

The 1998 revision established alternative definitions for - relative potency factors (REPs) that are experiment specific. REPs are "experimental endpoints for which a numerical value of the relative potency (of a congener, as) compared to TCDD had been generated from a single laboratory examining a single endpoint" while TEFs "would be restricted to describe an order-of-magnitude consensus estimate of the toxicity of a compound relative to the toxicity of TCDD that is derived using careful scientific judgment of all available data".

On a practical basis, the use of TEQs can be justified, but there are several problems regarding the scientific foundations of the model. *Smith and al* (2001) note that very few data may be available for estimating the TEF for a congener, and, from what data are available, there may be a wide range of relative potency estimates derived from the published studies. An additional problem can be the pharmacokinetic differences between other congeners and 2,3,7,8-TCDD. *Smith et al* express the concern that differences in absorption and metabolism may change the relative potencies of these chemicals. *Ritter et al* in a report prepared for UNEP Chemicals stated that TEFs "…do not necessarily represent actual toxicity with respect to all endpoints. Rather, they tend to overestimate the toxicity of mixtures."

In order to account for the latest scientific information, *van den Berg et al* (1998) suggested that "the TEQ scheme should be re-evaluated every 5 years and that TEFs and their application to risk assessment be re-analyzed".

## 2.1 Total PCCD/F to I-TEQ ratio calculation.

*Shin et al* (1999) reported that the mass ratio of total PCCD/F to I-TEQ components can range from 12 [*Shin et al. 1999*] to over 100 in the emissions from different municipal waste incinerators. However, *Fiedler et al* (2000) studied the distribution of congeners in a large number of samples from various sources and found it to be relatively constant, thus, they concluded that it was not possible to differentiate between emissions from municipal solid waste and hazardous waste incinerators. The same authors found that $Cl_8DD$ was the most abundant congener in most samples while the highest contribution (more than 30%) to the toxic equivalent (I-TEQ) was attributable to the compound 2,3,4,7,8 PeCDF. The analysis of the USEPA data resulted in an average total PCCD/F to I-TEQ ratio of 52.94 [*Table 2.2*]. The final ratio is the arithmetic average obtained by analyzing results from dioxin testings at multiple WTE facilities. The U.S. EPA has estimated that the total dioxin emissions (in grams) from large waste-to-energy plants (in grams) should be divided by the factor of 50 in order to obtain grams of TEQ emissions (50 grams of total dioxins = 1 gram TEQ).

**Table 2.1: Toxic equivalent factors (TEFs)** Ahlborg (1994); Van den Berg (1998)

| Congener | I-TEFs | WHO TEFs revised |
|---|---|---|
| 2,3,7,8-TCDD | 1 | 1 |
| 1,2,3,7,8-PeCDD | 0.5 | 1 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 |
| OCDD | 0.001 | 0.0001 |
| 2,3,7,8-TCDF | 0.1 | 0.1 |
| 2,3,4,7,8-PeCDF | 0.5 | 0.5 |
| 1,2,3,7,8-PeCDF | 0.05 | 0.05 |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 |
| OCDF | 0.001 | 0.0001 |
| 3,4,4_,5-TrCB | – | 0.0001 |
| 3,3_,4,4_-TrCB | – | 0.0001 |
| 3,3_,4,4_5-PeCB | – | 0.1 |
| 3,3_,4,4_,5,5_-HxCB | – | 0.01 |
| 2,3,3_,4,4_-PeCB | 0.0001 |  |
| 2,3,4,4_,5_-PeCB | – | 0.0005 |
| 2,3_,4,4_5-PeCB | – | 0.0001 |
| 2_,3,4,4_,5-PeCB | – | 0.0001 |
| 2,3,3_,4,4_,5-HxCB | – | 0.0005 |
| 2,3,3_,4,4_,5_-HxCB | – | 0.0005 |
| 2,3_,4,4_,5,5_-HxCB | – | 0.00001 |
| 2,3,3_,4,4_,5,5_-HpCB | – | 0.0001 |

**Table 2.2: TEQ calculations** (data provided by Walt Stevenson of USEPA)

| Name of Waste-to-Energy Unit | Total | TEQ | Conversion Factor | Recalculated TEQ |
|---|---|---|---|---|
| | | | | |
| Huntsville Refuse-Fired Steam Fac. | 3 | 0.08 | 37.50 | 0.08 |
| Commerce Refuse-to-Energy Fac. | 10 | NA | | 0.19 |
| Long Beach (SERRF) | 4 | NA | | 0.08 |
| Stanislaus (Modesto) | 32 | NA | | 0.60 |
| | 9 | NA | | 0.17 |
| Bristol RRF | 75 | 1.67 | 44.91 | 1.67 |
| | 8 | 0.14 | 57.14 | 0.14 |
| Mid-Connecticut Project | 1 | NA | | 0.02 |
| Wallingford RRF | 178 | NA | | 3.36 |
| | 50 | NA | | 0.94 |
| | 47 | NA | | 0.89 |
| Dade Co. RRF | 449 | NA | | 8.48 |
| Hillsborough Co. RRF | 178 | NA | | 3.36 |
| McKay Bay REF | 8533 | 265 | 32.20 | 265.00 |
| | 893 | 21 | 42.52 | 21.00 |
| | 2160 | 49 | 44.08 | 49.00 |
| Pasco Co. Solid Waste RRF | 11 | 0.19 | 57.89 | 0.19 |
| Wheelabrator Pinellas RRF | 3400 | 71.8 | 47.35 | 71.80 |
| Honolulu Resource Recovery Venture | 10 | NA | | 0.19 |
| | 3 | NA | | 0.06 |
| Waipahu Incinerator | 5690 | NA | | 107.47 |
| Northwest WTE | 65 | NA | | 1.23 |
| Indianapolis RRF | 12 | 0.12 | 100.00 | 0.12 |
| | 1 | 0.01 | 100.00 | 0.01 |
| Haverhill Lawrence RDF | 136 | NA | | 2.57 |
| North Andover RESCO | 53 | NA | | 1.00 |
| SEMASS RRF | 9 | NA | | 0.17 |
| | 12 | NA | | 0.23 |
| Wheelabrator Millbury | 59 | NA | | 1.11 |
| Hartford Co. WTE Fac. | 300 | 5.58 | 53.76 | 5.58 |
| Pulaski | 3313 | 37 | 89.54 | 37.00 |

| Table 2.2: TEQ calculations (cont.) | | | | |
|---|---|---|---|---|
| | 3313 | 37 | 89.54 | 37.00 |
| | 5894 | 85.2 | 69.18 | 85.20 |
| | 5894 | 85.2 | 69.18 | 85.20 |
| | 9045 | 104 | 86.97 | 104.00 |
| Southwest RRF (RESCO) | 142 | 3.41 | 41.64 | 3.41 |
| | 102 | 2.38 | 42.86 | 2.38 |
| | 199 | NA | | 3.76 |
| Greater Portland Region RRF | 173 | NA | | 3.27 |
| Maine Energy Recovery (Biddeford) | 4 | NA | | 0.08 |
| Penobscot Energy Recovery Comp. | 2 | NA | | 0.04 |
| Central Wayne Co. Sanitation Auth. | 383 | 12.2 | 31.39 | 12.20 |
| Clinton Township | 3254 | 55.8 | 58.32 | 55.80 |
| Greater Detroit RRF | 2851 | NA | | 53.85 |
| | 2 | NA | | 0.04 |
| Kent Co. WTE Fac. | 5 | 0.09 | 55.56 | 0.09 |
| | 12 | 0.31 | 38.71 | 0.31 |
| Hennepin Energy Recovery Facility | 1 | 0.03 | 33.33 | 0.03 |
| | 2 | 0.02 | 100.00 | 0.04 |
| Olmstead WTE Facility | 219 | NA | | 4.14 |
| Perham Renewable RF | 35 | NA | | 0.66 |
| Polk Co. Solid Waste Resource Recovery | 269 | 8.99 | 29.92 | 8.99 |
| Pope-Douglas Solid Waste | 446 | 7.44 | 59.95 | 7.44 |
| Ramsey-Washington | 31 | NA | | 0.59 |
| Red Wing Solid Waste Boiler Facility | 489 | 13.3 | 36.77 | 13.30 |
| Western Lake Superior Sanit. Distr.(Duluth) | 16 | NA | | 0.30 |
| Wilmarth Plant (Mankato) | 2 | NA | | 0.04 |
| UniversityCity RRF | 579 | NA | | 10.94 |
| SES Claremont RRF | 38 | NA | | 0.72 |
| | 32 | NA | | 0.60 |
| Camden RRF | 75 | NA | | 1.42 |
| Warren Energy RF | 8 | 0.18 | 44.44 | 0.18 |
| Adirondack RRF | 28 | NA | | 0.53 |
| | 40 | NA | | 0.76 |
| Babylon RRF | 1 | NA | | 0.02 |

**Table 2.2: TEQ calculations (cont.)**

| | | | | |
|---|---|---|---|---|
| Babylon RRF | 1 | NA | | 0.02 |
| Dutchess Co. RRF | 5 | NA | | 0.09 |
| | 18 | NA | | 0.34 |
| Hempstead | 1 | 0.01 | 100.00 | 0.01 |
| Huntington RRF | 12 | 0.34 | 35.29 | 0.34 |
| | 7 | 0.17 | 41.18 | 0.17 |
| | 7 | 0.18 | 38.89 | 0.18 |
| Long Beach RRF | 709 | 13.7 | 51.75 | 13.70 |
| Mac Arthur WTE | 4 | NA | | 0.08 |
| | 1 | NA | | 0.02 |
| Niagara Falls RDF WTE | 1217 | NA | | 22.99 |
| Oneida Co. ERF | 462 | NA | | 8.73 |
| Oswego Co. WTE | 386 | NA | | 7.29 |
| Westchester RESCO | 183 | NA | | 3.46 |
| Akron Recycle Energy System | 370 | NA | | 6.99 |
| | 370 | NA | | 6.99 |
| City of Columbus SW Reduction Fac. | 12998 | NA | | 245.50 |
| Montgomery Co. North RRF | 5500 | NA | | 103.88 |
| | 5500 | NA | | 103.88 |
| | 8097 | 148 | 54.71 | 148.00 |
| Montgomery Co. South RRF | 5500 | NA | | 103.88 |
| | 5500 | NA | | 103.88 |
| | 5500 | NA | | 103.88 |
| Walter B. Hall RRF | 34 | NA | | 0.64 |
| | 49 | NA | | 0.93 |
| Marion Co. WTE | 1 | NA | | 0.02 |
| | 4 | NA | | 0.08 |
| Delaware Co. RRF | 2 | NA | | 0.04 |
| | 4 | NA | | 0.08 |
| | 10 | NA | | 0.19 |
| | 11 | NA | | 0.21 |
| | 4 | NA | | 0.08 |
| | 10 | NA | | 0.19 |
| Harrisburg WTE | 1156 | 27.4 | 42.19 | 27.40 |

**Table 2.2: TEQ calculations (cont.)**

| | | | | |
|---|---|---|---|---|
| Lancaster Co. RRF | 114 | 2.38 | 47.90 | 2.38 |
| | 61 | 1.47 | 41.50 | 1.47 |
| | 49 | 1.3 | 37.69 | 1.30 |
| York Co. RR Center | 5 | NA | | 0.09 |
| | 8 | NA | | 0.15 |
| | 8 | NA | | 0.15 |
| Foster Wheeler Charleston RR | 44 | NA | | 0.83 |
| Nashville Thermal Transfer Corp. | 143 | NA | | 2.70 |
| Alexandria/Arlington RRF | 14 | NA | | 0.26 |
| | 18 | NA | | 0.34 |
| Hampton (NASA) Refuse-fired Steam Gen. | 102 | 2.52 | 40.48 | 2.52 |
| Harrisonburg RRF | 8459 | 115 | 73.56 | 115.00 |
| I-95 Energy RRF (Fairfax) | 9 | 0.23 | 39.13 | 0.23 |
| | 6 | 0.17 | 35.29 | 0.17 |
| | 8 | 0.2 | 40.00 | 0.20 |
| | 7 | 0.15 | 46.67 | 0.15 |
| Norfolk Navy Yard | 21129 | 429 | 49.25 | 429.00 |
| | 32237 | 595 | 54.18 | 595.00 |
| | 42955 | 1500 | 28.64 | 1500.00 |
| | 26360 | 800 | 32.95 | 800.00 |
| La Crosse Co. | 63 | NA | | 1.19 |
| St. Croix Co. WTE Fac. | 8 | NA | | 0.15 |
| | | | | |
| | | **Average Factor** | **52.94** | |

## 3. Dioxin Effects on Human Health

Polychlorinated dibenzo-dioxins, dibenzo-furans and related components are of the most rigorously studied substances in modern epidemiology and toxicology. As noted in Section 2, of the 210 compounds only the 17 that have chlorine atoms at the positions 2, 3, 7, an 8 are considered toxic. The 2,3,7,8-TCDD, also known just as TCDD is considered to be the most toxic man-made substance. Their toxicity has been proven by numerous animal studies. The lethal dose of 2,3,7,8-TCDD, however, varies more than 5000-fold between the most sensitive, and the least sensitive species [*Fiedler et al. 2000*]; this has induced a great deal of uncertainty in the scientific and medical community about assessing health risks for the general public.

The chemical, biological, and physical resistance of the dioxins, and thus their tendency to accumulate in the environment and in organisms, has caused national and international authorities to issue strict regulations. These were based on laboratory animal studies, the results of which were then extrapolated to low doses for human use, by applying different mathematical models. The diversity and ambiguity of the outcomes can be illustrated by the different Tolerable Daily Intake (TDI) levels that have been imposed by various national agencies: The European Commission's (EU) Health and Consumer Protection Directorate (2001) has suggested a TDI level of 2 picograms TEQ per kilogram of body weight per day (1 pigocram= $10^{-12}$gram); the Ministerial Council on Dioxin Policy of Japan (1999), a TDI level of 4 pg TEQ/kg of body weight/day; Health Canada (1996) a TDI level of 10 pg TEQ/kg of body weight/day; the US Agency for Toxic Substances & Disease Registry (2000) a TDI level of 1 pg TEQ/kg of body weight/day; and the World Health Organization (1998) a TDI level between 1 to 4 pg TEQ/kg of body weight/day (Figure 3.1).

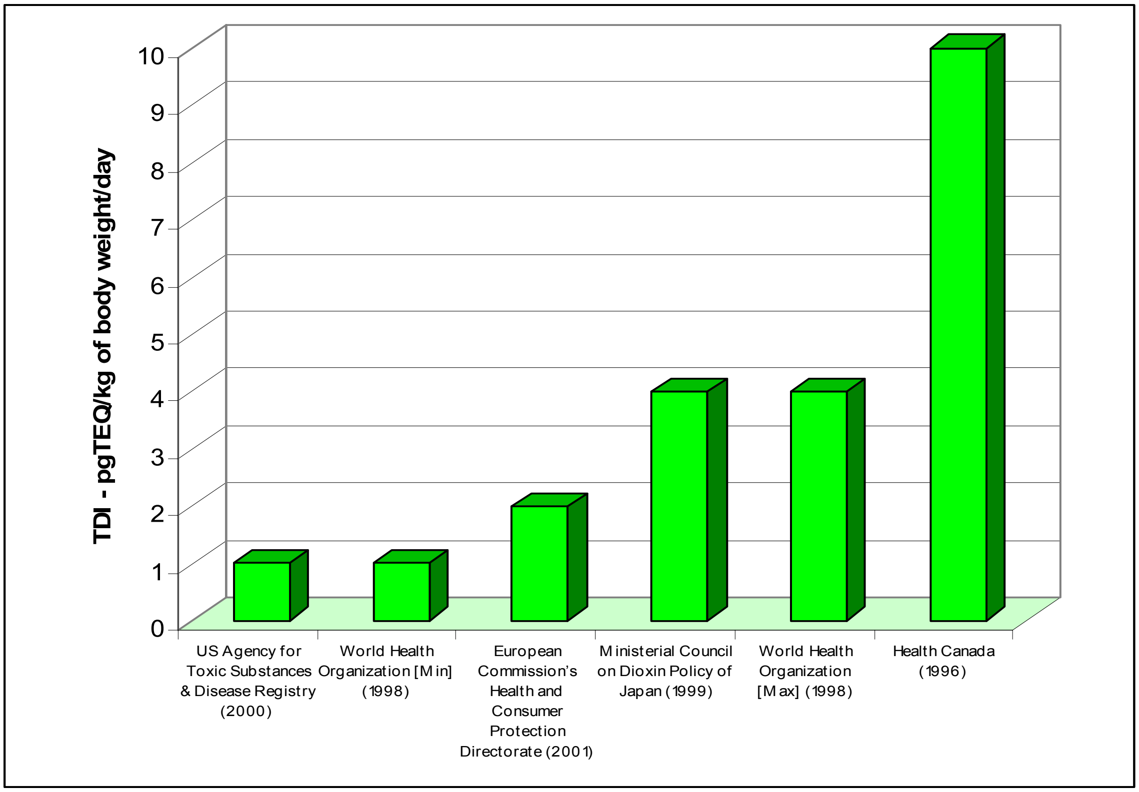


Figure 3.1. Allowable Tolerable Daily Intake (TDI)
set by various agencies including WHO min and max suggestions.

This section presents a summary of recent and earlier studies of dioxin effects on human health in an effort to estimate and understand the risk magnitude posed by dioxin emissions for the general population.

### 3.1. Pathways for Human Exposure

Oral exposure is considered the most important pathway, accounting for about 90% of the total human exposure to dioxins [*WHO 1999*]. The World Health Organization has assessed that the current average daily intake is approximately 2 to 6 pg TEQ/kg of body weight/day [*WHO 1998*], which is in the range of the new suggested TDI limit of WHO of 1 to 4 pg TEQ. The WHO experts in order to minimize the possibility of subtle effects occurring in the general population in developed countries at current background levels recommended that "every effort should be made to reduce exposure to the lowest possible level".

It has been estimated that background exposure for industrialized countries such as The Netherlands is 1 pg TEQ/kg of body weight/day for adults and 2.4 pgTEQ/kg of body weight/day for children [*Liem et al., 1991; Van Cleuvenbergen et al., 1993*]; and Germany about 1 pg TEQ/kg of body weight/day for adults [*UNEP 1999*]. The US EPA has estimated the median background exposure in a range between 0.5 and 1.0 pg TEQ/kg of body weight/day [*US EPA 2000*].

**Inhalation:** Inhalation of dioxins is considered a small exposure pathway mainly because of the low concentration of dioxins in the air and the absence of any accumulating mechanism. Dioxins are usually bound to particulate matter and human absorption depends on the particle size [*US EPA 1994*].

**Dermal Absorption**: Dermal absorption does not contribute significantly to human exposure. Results of animal studies "suggest slow dermal absorption of these compounds, which is likely to be dependent on the vehicle or adsorbent containing the compounds and the duration of the contact" [*US EPA 1994*].

**Ingestion:** Due to their lipophilic nature, dioxins are concentrated in foods that contain animal fat such as beef, pork, poultry, fish, dairy products and eggs. Ingestion of such foods is the primary pathway of exposure for the general public. Ingestion of contaminated matter has as a consequence the absorption of 30% to nearly 100% of the contained dioxins [*Pohl H., 1995; US EPA 1994*]. Food from animals raised near dioxin sources is likely to have contamination levels orders of magnitude higher than background levels. Farm animals consume soil, up to 7% of their ingested diet per day, thus transferring ground contamination to the food chain. Various studies conclude that populations living in areas with high dioxin concentration are not affected, if they do not consume locally produced foods [*Nouwen et al. 2001; US EPA 1994*]

**Retention – Half Life**: Dioxin like compounds accumulate in human fat tissue and due to their high stability are inadequately metabolized and thus stored for prolonged periods of time. Dioxin half-life in the human body has been calculated to be 6 to 12 years [*Wolfe WH, et al. 1995*; *Michalek JE, et al. 1992*].The level of dioxin contamination that signifies a considerable human risk will vary greatly depending on the different exposure pathways.

### 3.2. Human Health Studies

Dioxin contamination is usually associated with carcinogenic, reproductive, developmental and immunologic effects, although no sufficient evidence has been presented to establish a direct link. The Institute of Medicine [*IOM 1996*], in a study concerning "agent orange", a chemical that was used for defoliation during the Vietnam war, concluded that there is adequate evidence that links dioxin with increased risk of chloracne, Hodgkin's disease, Non- Hodgkin's lymphoma, and soft tissue sarcoma. Chloracne is one of the first symptoms of dioxin exposure and was the only one that was reported after the Seveso accident in 1976 where residents of the surrounding area were exposed to the highest levels of TCDD known to humans. It is interest to note that chloracne symptoms did not appear to all persons exposed to similar levels of dioxin.

Other studies reported additional associations with an increased risk of severe skin lesions (hyperpigmentation), altered liver function and lipid metabolism, general weakness associated with drastic weight loss, changes in activity of various liver enzymes, depression of the immune system, and endocrine and nervous system abnormalities [*UNEP 1999*]. Other signs of dioxin exposure include thymic atrophy, hypertrophy/hyperplasia of hepatic, gastrointestinal, urogenital and cutaneous epithelia, atrophy of the gonads, subcutaneous oedema and systemic hemorrhage. [*Fiedler et al. 2000*].

### 3.3 Carcinogenic Effects

Important epidemiological studies for the evaluation of the carcinogenic effects of dioxins have been conducted in several countries. Studies after the Seveso accident in 1976 did not report higher rates of cancer occurrence in the region of the accident [*Bertazzi P. et al. 1989*]. Also, after evaluating four cohort studies of herbicide producers (one each in the United States and the Netherlands, two in Germany) the International Agency for Research on Cancer (IARC) concluded that there is limited evidence in humans for the carcinogenicity of TCDD and that there was inadequate evidence in humans for the carcinogenicity of other dioxins than TCDD. [*IARC 1997*].

Studies on rats exposed at levels 100 to 1000 times higher than present background levels reported observation of different types of carcinomas [*Fiedler et al. 2000*]; US EPA currently accepts a casual relationship between TCDD exposure and cancer risk [*US EPA 2000*]. Studies for the effects of polychlorinated dibenzo-dioxins and furans on human health in Yusho, Japan and Yucheng, Taiwan were contradicting: In Japan, liver cancer mortality was increased three fold but in Taiwan no excess of mortality was observed [*Rogan WJ et al. 1988*]

### 3.4 Effects on Reproduction

Most of the studies in human population were unable to detect any increase in specific birth defects. Some studies reported alterations in hormone levels and sperm characteristics. An ongoing study, the Seveso Women's Health Study (SWHS) is the first to examine the reproductive health of a human population exposed to TCDD including endometriosis, menstrual cycle characteristics, and birth outcomes of pregnancies conceived after 1976 [*Eskenazi et al., 2000*]. Animal studies indicated teratogenic effects and several structural and reproductive defects after exposure in high doses of dioxins [*Peterson RJ et al. 1993; Murray FJ et al. 1979*]. Moreover, birth outcomes associated with maternal TCDD exposure in animal studies include increased fetal mortality [*Nau et al. 1986; Roman et al. 1995; Allen et al.1979; McNulty et al., 1984; Bjerke et al. 1994*], increased fetal resorptions [*Allen et al.1979*], decreased litter size [*Murray et al., 1979*], and reduced body weight of offspring [*Roman et al., 1995; Bjerke et al., 1994; Murray et al., 1979 Courtney 1976*].

### 3.5 Genetic Effects

Animal studies produced contradictory results regarding genetic alterations such as DNA damage, gene mutations, sister chromatid exchange and cell transformation, while human studies concluded that effects of dioxins on genetic material are not observed. Additional experimental data indicate that TCDD and other congeners are not direct-acting enotoxic agents [*Fiedler et al. 2000*].

### 3.6 General Remarks

Although dioxins can be extremely toxic in very low doses, each species exhibit varying levels of sensibility to them. For humans the most important pathway for dioxin exposure is through oral exposure, mainly through the food chain. Human response to dioxin action on a molecular level is believed to vary and thus sensitivity to dioxin toxicity differs considerably between individuals.

Because of the dioxin potency even in trace amounts the exact concentrations of dioxins that can increase health risks have not been defined yet. Consequently, most of the health studies conducted on humans were not able to establish with certainty evidence associating present background levels of dioxins with carcinogenic, reproductive, developmental or immunologic effects.

Nevertheless, further research must be done in order to identify if there is a threshold level for dioxin action on humans and the possible risk, if any, of widespread, low-level dioxin contamination of the environment.

## 4. The Stockholm Convention on Persistent Organic Pollutants

Because of their unique properties, such as resistance to photolytic, biological and chemical degradation, low water and high lipid solubility and tendency for bioaccumulation, dioxins and furans are categorized as Persistent Organic Pollutants (POPs). POPs can move long distances in the atmosphere before deposition occurs. Some compounds may persist in the environment for periods of years and may bioconcentrate by factors of up to 70,000 fold. POPs physical and chemical properties of high persistence and semi-volatility, coupled with other unique characteristics, have resulted in their being widely distributed through the global environment, even in regions where they have never been used [*Juttner et al, 1997; Gaus et al, 2001*].

The POP group consists of two subgroups including both the polycyclic aromatic hydrocarbons and some halogenated hydrocarbons. In addition to dioxins and furans, the POP group includes many organochlorine insecticides such as dieldrin, DDT, toxaphene, chlordane, hexachlorobenzene, aldrin, endrin, heptachlor, toxaphene, mirex and several industrial chemical products or by-products including polychlorinated biphenyls (PCBs). The chlorinated compounds are generally the most persistent of all the halogenated hydrocarbons.

In 1979, the international community concerned by the risks posed by extensive POP use urged for the formation of a working group on Long-range Transboundary Air Pollution. The group [IPEN 2001] consisted of the United Nations Environment Program (UNEP), International Programme on Chemical Safety (IPCS), International Labor Organization (ILO), World Health Organization (WHO) and the Intergovernmental Forum on Chemical Safety (IFCS). The group evaluated information on POPs, analyzed their pathways and origins, and reviewed their transport and global deposition. Additionally, it examined sources, risks and benefits, production and use while evaluating the availability, costs and efficacy of substitutes. Finally, the group evaluated strategies and suitable policies for phasing out the use of several POP congeners taking into consideration the special needs of developing countries.

Following the guidelines set by Agenda 21, adopted during the United Nations Conference on Environment and Development held in Rio in 1992, in May 1995, the United Nations Environment Program Governing Council released its first POP assessment. The decision was based on Agenda's 21 Chapters 17, 19 and the precautionary principle of the Rio Declaration on Environment and Development. Chapter 17 referred to the Protection of the Oceans and set as a priority the reduction and elimination of emissions and discharges of organohalogens and other persistent organic pollutants while Chapter 19 was concerned with the environmentally sound management of toxic chemicals.

In 1998, UNEP requested that the intergovernmental negotiating committee commence work on the development of internationally accepted science based criteria for POPs.

In June 1998, the first intergovernmental negotiating committee (INC1) was held in Montreal. INC2 was held in Nairobi in January 1999, INC3 in Geneva, September 1999 and

INC4 in Bonn, March 2000. The final negotiation session was held in Johannesburg,, South Africa in December 2000. The Stockholm Convention on the Persistent Organic Pollutants held on May 2001 is the legal instrument with the objective to eventually eliminate twelve of the most common persistent organic pollutants; PCBs, DDT, hexachlorobenzene, dioxin and furans, dieldrin, aldrin, endrin, chlordane, heptachlor, toxaphene,  and mirex.

Although the Stockholm Convention has been signed by 151 countries (in 2004) it is not as yet in force because only 46 countries (out of the needed 50) have ratified the treaty. Ratification is left upon the legislative branches of each government and often enough political and economic interests obstruct the legislative procedure.

The final text [IPEN September 2001] included the following guidelines:

- The Precautionary principle is the guiding principle and it is implemented throughout the Convention,
- Funding commitments to enable full participation of all countries,
- Elimination of intentionally produced POPs,
- Ultimate elimination of the POPs by-products where feasible,
- Environmentally sound management and disposal of POP wastes including stockpiles, products, articles in use, and materials contaminated with POPs.
- Strict limitations and bans on trade except for the purpose of environmentally sound disposal or in other very limited circumstances.
- Limited and transparent exemptions.

The projected minimization of the trade and use of POPs should result in a sharp decrease in the levels of PCDD/F precursors in the solid waste stream, as discussed in detail at the following section. .

## 5. Sources of Dioxins

Dioxins can be produced by natural processes such as biological transformation of inorganic chlorine to complex chlorinated organic compounds and large-scale events, such as forest fires and volcano eruptions.

*Juttner et al* (1997) identified considerable amounts of PCDD/F in the sediments of four remotely situated lakes in Germany where atmospheric deposition had been the only possible input. In one lake, dioxins were found in sediment layers that corresponded to a period before the beginning of production of chlorophenols in the 1920s. *Gaus et al* (2001) analyzed estuary sediment cores from Queensland in Australia and detected PCDD/F isomer patterns and congener profiles in sediments deposited during the last 350 years that were almost identical and correlated well to the characteristic profiles observed in surface sediments and soils from the entire Queensland coastline. However, in both studies, a sharp increase in PCDD/F sediment concentrations was notable during the years of industrial revolution, peaking in the decades of 1970s and 1980s.

Man-made dioxins are mainly produced as unintentional products of many industrial processes such as municipal and hazardous waste incineration, metal smelting, pulp bleaching, cement kiln calcining, iron ore sintering, and coal/oil fired power production. Throughout the industrial era, the largest quantities of dioxins were emitted by trash burning in all forms. Municipal waste incineration, uncontrolled "backyard" trash burning, and unintentional landfill fires emitted in the distant past nearly 85% of all anthropogenic dioxins.

### 5.1 Dioxin Formation in Thermal Processes.

The contributing factors to PCDD/F emissions from combustion processes can be divided into four categories; dioxins present in the incoming fuel feed, dioxins produced from chlorinated precursors, dioxins formed via de novo synthesis, and post-incinerator dioxin formation.

#### 5.1.1 PCDD/F present in the incoming fuel feed

The feed to the combustion chamber can contain actual PCDD/F. The level of concentration of such chemicals in the fuel mix may affect the final amount of dioxins emitted. Dioxin and dioxin like compounds are widely used in many commercial products, such as wood preservatives and pesticides. In Germany, the dioxin content in MSW was measured at about 50 ng I-TEQ/kg waste [*UNEP 1999*].

#### 5.1.2 PCDD/F produced from chlorinated precursors

*McKay* (2002) classified PCDD/F precursors into three main classes of precursors: chlorinated phenols, chlorinated benzenes, and PCBs. These products constitute a large amount of the organic chlorine found in the feed of municipal waste incinerators. PCDD formation from the combustion of chlorinated phenols has been tested more extensively since they are widely used as wood preserves, herbicides, and sap stain control products. Chlorobenzenes are used in solvents, dyes, pharmaceuticals and rubber production. Until 1975, PCBs were used as dielectric fluids in transformers and capacitors, hydraulic fluids, plasticizers, and dyes. Less potent precursors include aliphatic chlorinated compounds and inorganic chlorinated compounds.

### 5.1.3 PCDD/F formed via de novo synthesis

Dioxins can form from the pyrolysis of chemically unrelated compounds such as polyvinyl chloride (PVC) or other chlorocarbons, and/or the burning of non-chlorinated organic matter such as polystyrene, cellulose, lignin, coal, and particulate carbon in the presence of chlorine-donors.

*Wikström et al* (1996) studied the formation of dioxin-like compounds in thermal processes in the presence of varying levels of chlorine in the feed. They noted that chlorine level in the feed above 1% resulted in increasing PCDD/F formation. Additionally, the results indicated that combustion of organic and inorganic substances containing chlorine compounds or even inorganic chlorides, such as sodium chloride have the same potency in generating dioxins. Therefore, the widespread notion that the elimination of PVC products will contribute to a considerable reduction of PCDD/PCDF emissions from MSW incineration was contested by these authors.

*Rigo et al* (1995) after numerous field samplings of flue gases from MSW incinerators concluded that, in actual practice, there is no consistent observable relationship between chlorine in the waste feed and PCDD/F concentrations in the combustion gases of incinerators, most probably because the effect of the fluctuations of the combustion conditions such as particulate carry-over, temperature etc.

Dioxins tend to form both at low and high temperatures. At temperatures between 200 and 400°C, in combustion gas exhaust streams, highly chlorinated dibenzo-p-dioxin and dibenzofuran are formed from phenol and benzene prior to particle collection equipment. Chlorination at lower temperatures on particle surfaces is a potential source of chlorinated dibenzofuran (CDF). [*Ryu et al*, 2002]

At high temperatures, between 500 and 800°C, mainly the less chlorinated dibenzofuran congeners are formed. *Wikstrom et al* (2000) speculated that chlorination can occur on metals, in particular, copper (II) chloride (CuCl2) by the Deacon reaction. Hydrogen chloride is converted catalytically to $Cl_2$, which then can lead to gas-phase DF chlorination:

$$4\ HCl + O2 \rightarrow 2\ Cl_2 + 2\ H_2O$$

*Stieglitz et al* (1990) proposed the formation of chlorinated dibenzofurans by the chlorination of aromatic molecules with conversion of $CuCl_2$ to CuCl:

$$ArH + CuCl_2 \rightarrow ArHCl + CuCl$$

$$ArHCl + CuCl_2 \rightarrow ArCl + CuCl + HCl$$

The reported most successful method of controlling dioxins is by achieving high efficiency combustion (REF). The combustion environment can be affected by several factors such as combustion temperature, flue gas residence time, supplemental fuel, fuel processing, and oxygen availability. An environment of high temperatures, high turbulence, and long residence times minimizes dioxin emissions. Temperatures greater than 900 °C destroy all PCDDs and pyrolysis at 700 °C results in 99% destruction of PCBs and no PCDF formation (REF).. However, maintaining a constant high temperature is difficult because of the nature of the combustible material in waste-to-energy combustion chambers, i.e. high moisture, low heating values and poor mixing during combustion. High residence times in the range of two seconds can overcome this problem and decrease the formation of products of incomplete combustion, such as PCDD/Fs. [*Sakurai et al 1998*].

Despite the fact that WTE units are usually fired with high excess air, large areas of the waste may have poor air/fuel mixing due to the size of the combustible pieces. Some processing of the waste before combustion and/or addition of auxiliary fuel such as natural gas or oil can improve the conditions by lowering the moisture levels and increasing the combustion temperature.

### 5.1.4 Post-incinerator dioxin formation

Dioxins may form on particles carried in the flue gas during cooling by means of gas-solid phase reactions in the 300°C range. Additionally, dioxin formation in post-incinerator conditions can also be attributed to particulate carbon when catalyzed by copper (II) chloride in the 300-400°C temperature range.

Dioxin formation at post-incineration conditions may be reduced by means of high burn-out and low residual organic carbon, and low residence time for particulates in the low-temperature zone (300–400°C).

## 5.2 Advances in Pollution Control Equipment

During the past fifteen years, widespread public concern towards the effects of dioxins on human health resulted in the imposition of strict environmental regulations. In the United States, the waste incineration industry was the largest contributor to the dioxin inventory. In the 1990s this industry spent an estimated $1 billion in pollution control equipment in order to comply with the U.S. EPA Maximum Available Control Technology (MACT) standards. During the same period, similar regulations were implemented around the world resulting to the reduction on dioxin emissions from controlled waste incineration and WTE facilities to insignificant levels. In the United States, the reduction of air emissions from municipal waste incineration decreased from 8877 g TEQ to 1250 g TEQ, i.e., 86% reduction, over the period 1987 – 1995. Preliminary data for 2003 indicate a further reduction to 12 g TEQ or a 99.86% total reduction. These impressive results underline the success of the federal regulations in implementing technological innovation.

Air pollution control devices (APCD) that are used for capturing pollutants from WTE facilities include, lime in dry scrubbers, activated carbon injection, and fabric filters. Fabric Filters, when combined with dry scrubbing (DS) and activated carbon injection (ACI), they are considered to be the most efficient control equipment for dioxins, volatile metals and particulate matter. The DS/ACI/FFs combination have achieved greater than 99 percent reduction and control of dioxin emissions in the U.S.

Fabric Filters consist of an array of cylindrical bags (about 6 to 8 inches in diameter and 5 to 6 feet long) of tightly woven material. Depending on the gas temperature, wool, fiberglass or synthetic materials can be used. The combustion gases are forced through the fabric, thus removing fine particles and the dioxins and volatile metals associated with them. After a certain point of dust deposition, the pressure drop through the bag system increases to the point that it activates a cleaning function, using reverse air flow, bag shaking or pulse jet flow.

Electrostatic Precipitators (ESP) are gradually phased out as the main pollution control device in new WTE facilities since the temperature range of ESP efficient operation is between 250 to 350°C, range where dioxin reformation may occur resulting in a net increase of dioxin emissions. [USEPA, 1994]. ESPs are using a strong electric field to charge dust particles in the combustion gases and then collect them in oppositely charged collection plates and are currently included as complementary to FFs air control equipment in newer facilities.

### 5.3 Good Operating and Management Practices

In addition to the types of Air Pollution Control Devices (APCDs) used in a WTE, Good Operating and Management Practices play an equally important role in emissions minimization. Good combustion and gas control practice prevents excessive emissions of pollutants, irrespective of the design of a particular facility [Ruth 1998]. The continuous monitoring of crucial operating factors is very important for high efficiency combustion. With regard to dioxin emissions, the most common combustion parameters monitored at modern WTE facilities are carbon monoxide concentration, air flows and temperatures, pressure drops, and oxygen and pH levels in the flue gas. The UNEP Guidelines on Best Available Technology (BAT) for Municipal Waste Incineration recommend that CO concentration represents the best surrogate for monitoring potential POP formation and should be kept below 50 ppm by volume in the stack flue gases for PCDD/PCDFs minimization. Additionally, UNEP guidelines recommend good management of the feed rate to the furnace, constant monitoring of combustion temperature, and good mixing of fuel and air, in order to minimize the existence of long-lived, fuel rich pockets of combustion products. The recommended residence time of waste in the combustion chamber is 2 seconds. Temperatures at or above 1,000°C are required for complete combustion in most technologies. [UNEP 2003].

Finally, one of the most vital factors for good operation of WTE facilities is the regular training of the personnel and more importantly the ability of the plant operator that oversees combustion. Usually the highest emission levels of PCDD/PCDFs at a WTE facility occur during Cold Starts and Shutdowns. These events are generally characterized by poor combustion, and consequently high POP formation. Modern WTEs are equipped with large gas or oil burners that are used to heat the furnace, or maintain temperature, during start ups and turndowns of the furnace.

#### 5.3.1 Non-controlled sources of dioxins

While the WTE plant operators are trained professionals and the pollution control equipment in waste incineration and WTE facilities is thoroughly tested and inspected on a yearly basis, unregulated wood and waste burning in landfills and backyards continue to produce considerable amounts of dioxins. A similar trend has been observed worldwide where waste incineration and WTE facilities no longer represent a major dioxin source and strict regulations have minimized dioxin emissions from other industrial processes. *Hiester et al* (1997) has identified a sharp decrease of PCDD/PCDF in the ambient air of four industrial cities in Germany (North Rhine-Westphalia) The decrease was caused mainly by three factors: The phase out of halogenated compounds in gasoline, the ban of polychlorinated phenols in 1989, and finally the imposition of a national emission standard of 0.1 ng I-TEQ/m3 for waste-to-energy facilities. In order to comply with the strict regulations, 10 of 26 waste incinerators in that geographic area were upgraded and two were shut down.

*Vartiainen et al* (1997) studied lake sediment cores in subarctic Finland and concluded that there has been a partly quantifiable increase of the anthropogenic dioxins in remote arctic areas during the nineteenth and twentieth centuries. However, their research indicated a clear decrease in organic contaminants in sediments that corresponded to the period 1988-1992 (Figure 5.1).

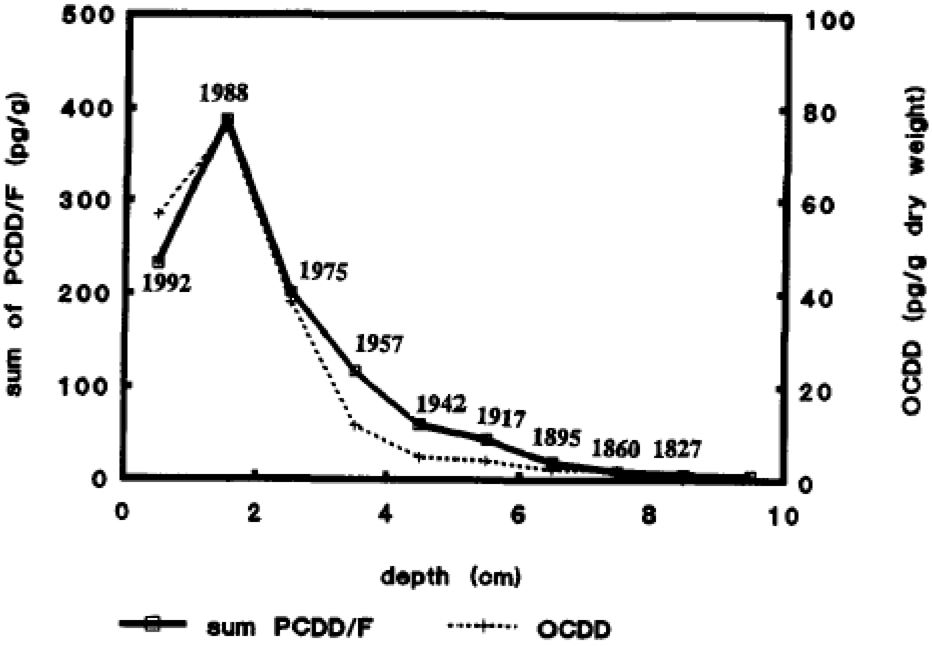


Figure 5.1. Change in dioxin concentrations in subarctic Finland.

Source: Vartiainen et al (1997)

### 5.4 Dioxin emissions in the United States

As noted earlier, the United States has been following the global trend in curbing WTE emissions and, in the nineties, the USEPA put into effect a set of regulations (referred to as Maximum Achievable Control Technology - MACT) designed to reduce dioxin and other emsiions from various combustion processes. As a result, emissions from domestic combustion of wood, fuel and waste (also called "backyard barrel burning") now constitutes over 55% of the total US inventory, as compared to only 4% in the year 1987. Figure 5.4 below illustrate this trend graphically.

#### 5.4.1. Decreased dioxin emissions in the U.S.

MACT regulations were put into effect in 2002 and require facilities to restrict emissions to levels consistent with the best performing plants resulting in less dioxin into the air or water. USEPA data for the period 1987 – 2004 (Tables 5.1 and 5.2) indicate that, there has been a significant decrease in the dioxins emitted by controlled industrial activities. WTE facilities have achieved the highest reductions reaching 99.86%. The bar chart of Figure 5.2 compares the pre-MACT and post-MACT emissions of thirty five largest WTE plants, reported here as nanograms of TEQ emissions per cubic meter of flue gas. It can be seen that most plants are now below the European standard, established in 1998, of 0.1 ng/m3. Also, on the basis that, on the average, U.S. WTEs emit about 5,000 cubic meters (dry, NTP conditions) per ton of MSW combusted, the dioxin emissions amount to less than 0.5 TEQ grams per million tons of MSW. For the U.S. 35 largest facilities that already have implemented MACT and represent about 25 million tons of MSW per year, the total dioxin emissions are less than 12 TEQ grams per year (Figure 5.3). These dioxin emissions are below the E.U. standard of 0.1 ng TEQ per standatd cubic meter of stack gas (diagonal line in Figure 5.3).

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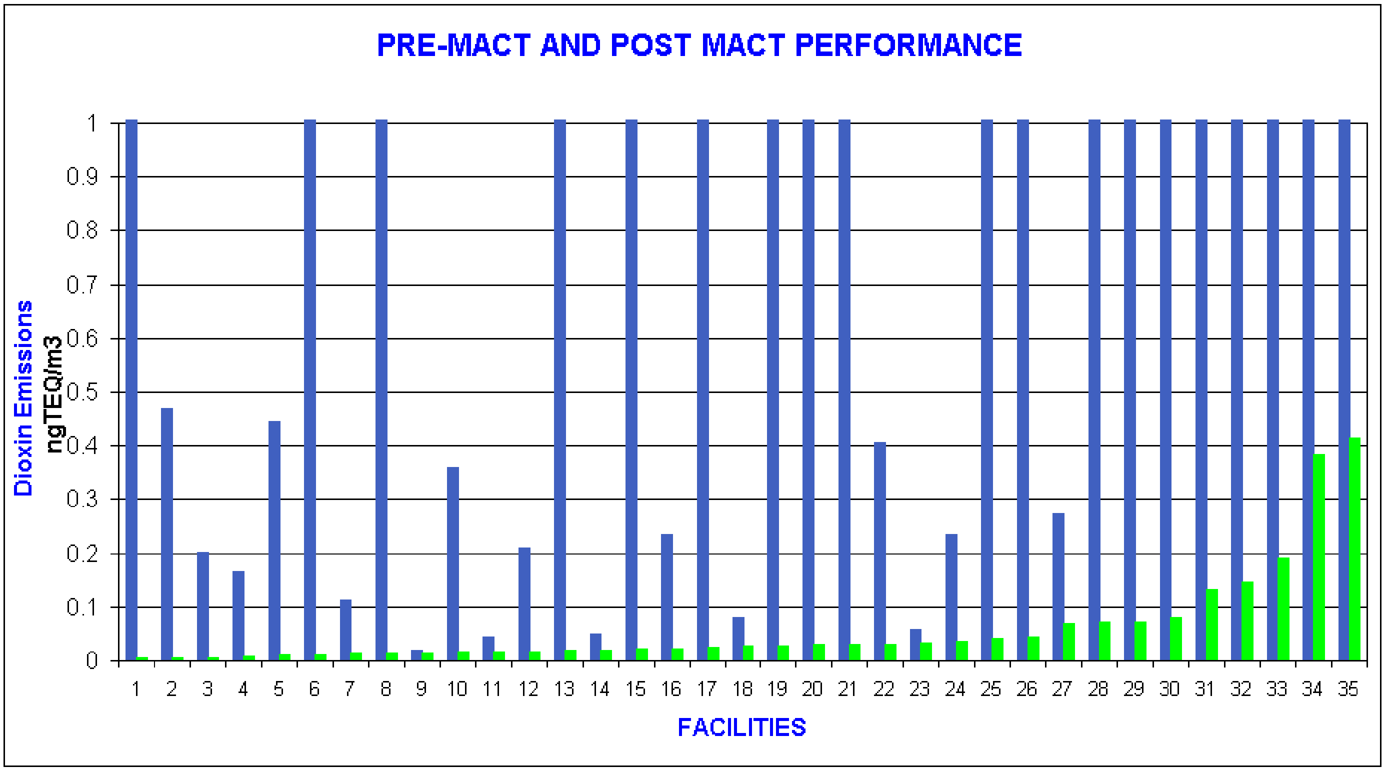

Figure 5.2. Dioxin Emission from Large WTE facilities in the United States (ngTEQ/dscm); dark lines indicate emissions prior to implementation of MACT regulations; each number refers to a particular U.S. WTE facility.

Source: USEPA (2002)

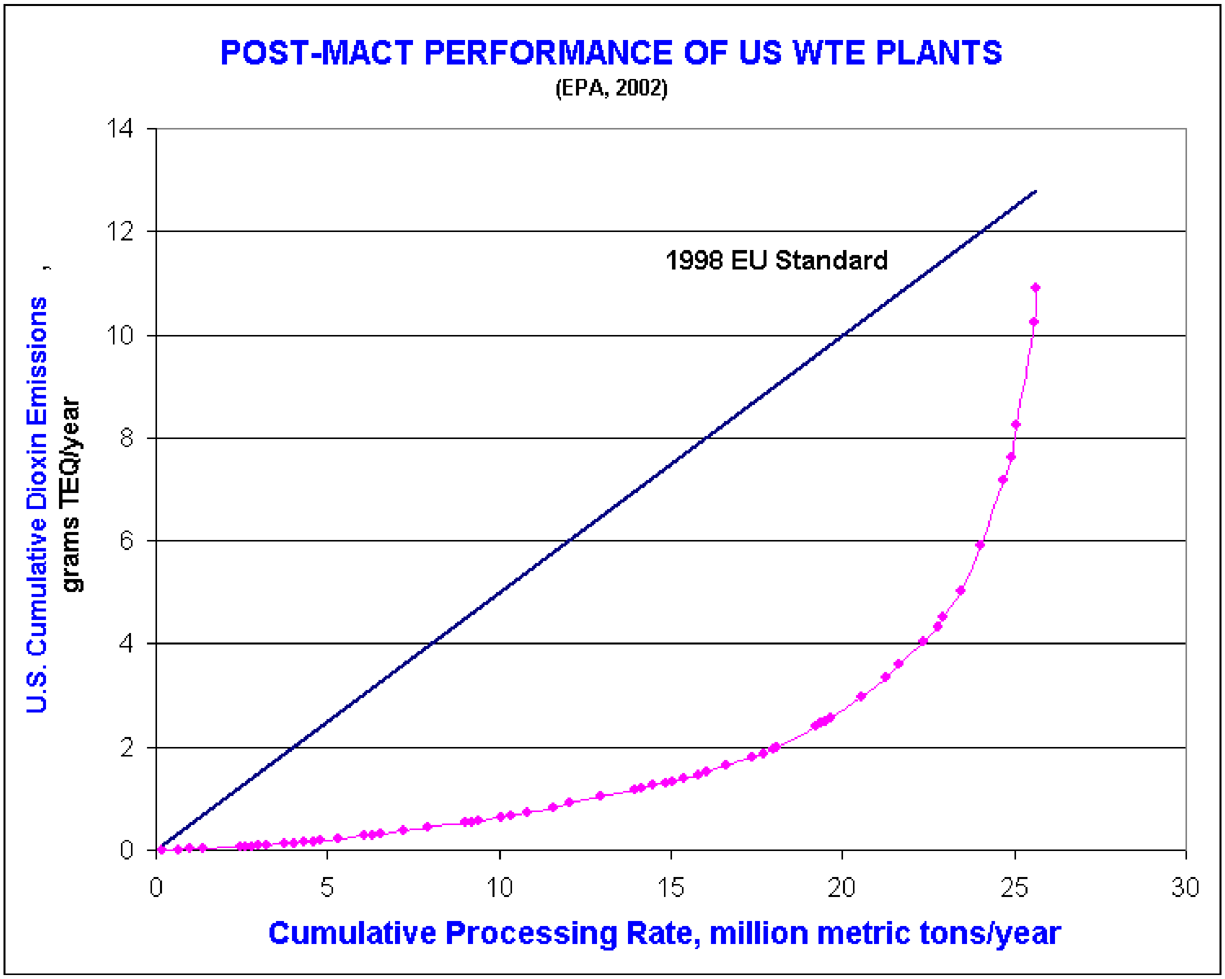

Figure 5.3. Cumulative dioxin emissions (in grams TEQ) of U.S. WTE plants in 2000 (EPA data, 9); each dot represents a WTE plant

Table 5.1 is based on EPA published data of TEQ emissions from all measured sources of dioxins. It should be noted that dispersed or unknown sources of emissions, such as forest fires, landfill emissions and flaring of methane emissions from landfills and oil/gas production and refining are not included. Table 5.1 shows that the U.S. waste-to-energy has moved from being the major source of dioxins in 1987 (8,877 TEQ grams or 63% of total dioxin sources measured), to being a minor source in 2002 (12 grams or 1.08% of U.S. total). Figure 5.4 below illustrate this trend graphically. By 2002, the predominant sources were backyard barrel burning and residential wood burning.

Table 5.1. Inventory of Dioxin Emission in the U.S. from all Sources (grams TEQ)

USEPA (2002)

| **Sources** | **1987** | **% of total** | **1995** | **% of total** | **2002/4 estimate** | **% of total** | **% reduction between 1987-2002** |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| MSW | 8,877 | 63.66% | 1,250 | 38.52% | 12 | 1.09% | 99.86% |
| Medical Waste | 2,590 | 18.57% | 488 | 15.04% | 7 | 0.64% | 99.73% |
| Sewage Sludge | 6 | 0.04% | 14 | 0.43% | 14 | 1.27% | -133.33% |
| Hazardous Waste | 5 | 0.04% | 5 | 0.15% | 3 | 0.27% | 40.00% |
| Total Incineration | 11,478 | 82.31% | 1,757 | 54.14% | 36 | 3.28% | 99.69% |
| Backyard barrel burning | 604 | 4.33% | 628 | 19.35% | 628 | 57.14% | -3.97% |
| Metal smelting | 955 | 6.85% | 301 | 9.28% | 35 | 3.18% | 96.34% |
| Cement kilns | 131 | 0.94% | 173 | 5.33% | 25 | 2.27% | 80.92% |
| Land applied sewage sludge | 76 | 0.54% | 76 | 2.34% | 76 | 6.92% | 0.00% |
| Pulp & paper | 372 | 2.67% | 23 | 0.71% | 15 | 1.36% | 95.97% |
| Coal fired utilities | 50 | 0.36% | 60 | 1.85% | 60 | 5.46% | -20.00% |
| Industrial wood burning | 26 | 0.19% | 27 | 0.83% | 27 | 2.46% | -3.85% |
| Residential wood burning | 89 | 0.64% | 62 | 1.91% | 62 | 5.64% | 30.34% |
| Diesel trucks | 27 | 0.19% | 35 | 1.08% | 35 | 3.18% | -29.63% |
| Other | 137 | 0.98% | 103 | 3.17% | 100 | 9.10% | 27.01% |
| Total | 13,945 | 100.00% | 3,245 | 100.00% | 1,099 | 100.00% | 92.12% |

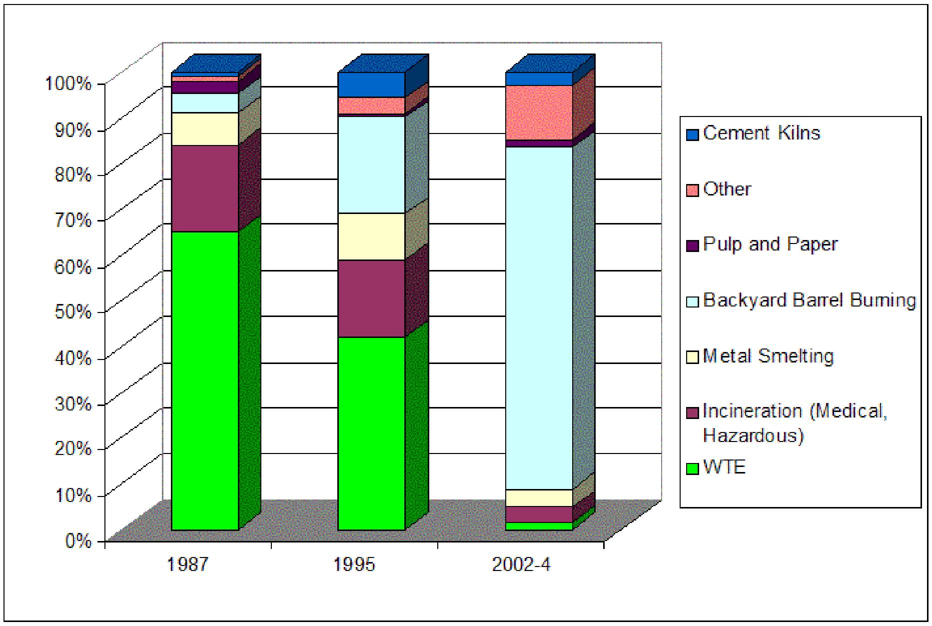

Figure 5.4. Change in Dioxin Sources in the U.S., 1987-2002 (USEPA 2002)

### 5.5 Global Emission Trends

Emissions data from around the world are presented in the following Tables 5.1-5.6 They indicate a sharp reduction in dioxin emissions on air. For most countries, the reduction is in the range of 80-90+%. The lower quantity of dioxins emitted on air have resulted in a significant reduction in human intake of PCDD/F compounds in the past few years a fact that is "evidenced by a marked decrease in dioxin levels in human milk, as found in an exposure study conducted by the WHO European Centre for Environment and Health, with the highest rates of decrease being observed in areas which had the highest initial concentrations." [*WHO 1998*] Because of the successful implementation of advanced pollution control technologies in order for the industry to comply with strict state and federal regulations, emissions from MSW combustion which were historically the biggest source have now become a minor contributor. The most important contributor to the dioxin inventory has become the residential combustion of wood in stoves, boilers etc, and the uncontrolled combustion of residential and agricultural refuse, also referred as "backyard barrel burning". Residential combustion is still common in developing countries and in rural areas in many developed countries. The control of emissions form such activities is challenging and most of the models predict only a slight decrease for the forthcoming years. In Canada, the United Kingdom, and the European Union combustion of wood, fuels and waste domestically will became the most important source for dioxins.

Table 5.3 Dioxin Emission Inventory in the Netherlands (gr TEQ) (RIVM/TNO, 1991-2000)

| **Sources** | **1991** | **2000** | % Reduction between 1991-2000 |
|---|---|---|---|
| Incineration of municipal waste: | 382.0 | 3.0 | 99.21% |
| Sintering processes: | 26.0 | 3.0 | 88.46% |
| Use of PCP in the past: | 25.0 | 20.0 | 20.00% |
| Incineration of chemical waste: | 16.0 | 1.7 | 89.38% |
| Incineration of wood: | 12.0 | 9.0 | 25.00% |
| Traffic: | 7.0 | 2.6 | 62.86% |
| Metal industry: | 4.0 | 4.0 | 0.00% |
| Burning coal and brown-coal: | 3.7 | 3.7 | 0.00% |
| High temperature processes (e.g. glass): | 2.7 | 2.7 | 0.00% |
| Incineration of hospital waste: | 2.1 | 0.0 | 100.00% |
| burn-off of cables and motors: | 1.5 | 1.5 | 0.00% |
| Burning waste oil: | 1.0 | 1.0 | 0.00% |
| Chemical production processes including chlorine- and PVC-industry: | 0.5 | 0.5 | 0.00% |
| Incineration of bio-gas and sludge: | 0.3 | 1.5 | -400.00% |
| Asphalt mixing: | 0.3 | 0.3 | 0.00% |
| Crematoria: | 0.2 | 0.2 | 0.00% |
|  |  |  |  |
| Total: | 484.0 | 54.7 | 88.70% |

Table 5.4 Dioxin Emission Inventory in Canada (gr TEQ)

(Environment Canada, 1999)

| **Dioxin emissions in Canada** | 1990 | 1997 | 1999 Estimate | % Reduction from 1990-1997 |
|---|---|---|---|---|
| Municipal Waste Incineration | 204 | 152 | 82.2 | 59.71% |
| Wood Combustion (residential) | 35.7 | 35.7 | 35.7 | 0.00% |
| Iron Manufacturing: Sintering Plants | 42.9 | 42.9 | 23.5 | 45.22% |
| Pulp & Paper: Boilers Burning Salt Laden Wood | 10.5 | 10.5 | 10.5 | 0.00% |
| Steel Man.: Electric Arc Furnaces | 9.1 | 10.2 | 10.2 | -12.09% |
| Fuel Combustion Diesel (Traffic) | 8.7 | 8.7 | 8.7 | 0.00% |
| Oil Combustion (residential) | 7 | 7 | 7 | 0.00% |
| Electric Power Generation | 3.4 | 4.6 | 4.6 | -35.29% |
| Wood waste combustion (saw mills and P&P mills) | 4.4 | 4.4 | 4.4 | 0.00% |
| Cement Kilns | 2.6 | 2.8 | 2.8 | -7.69% |
| Hospital Incinerators | 8.3 | 2.5 | 2.5 | 69.88% |
| Chemical Production (air releases) | 2.2 | 2 | 0.3 | 86.36% |
| In-service Utility Poles | 1.9 | 1.9 | 1.9 | 0.00% |
| Wood Preserving Plants | 1.8 | 1.8 | 1.8 | 0.00% |
| Hazardous Waste Incinerators | 2.1 | 1.3 | 0.8 | 61.90% |
| Pulp & Paper: Kraft Liquour Boilers | 0.7 | 0.7 | 0.7 | 0.00% |
| Federal Incinerators | 1.3 | 0.6 | 0.6 | 53.85% |
| Steel Foundries EAF | 0.4 | 0.5 | 0.5 | -25.00% |
| Sewage Sludge Incinerators | 0.3 | 0.3 | 0.3 | 0.00% |
| Base Metals Smelting | 0.1 | 0.1 | 0.1 | 0.00% |
| Secondary Lead Smelters | 0.1 | 0.1 | 0.1 | 0.00% |
| Biomedical Waste Incineration | 4.9 | 0 | 0 | 100.00% |
| Petroleum refineries (to follow) | | | | |
| Total | 353 | 290 | 199 | 43.63% |

Table 5.5 Dioxin Emission Inventory in the UK (gr TEQ)

Source: *Douben* (1997)

| **Sources** | **1995** | **2000 estimate** | **% Reduction, 1995-2000** |
|---|---|---|---|
| MSW combustion: | 580 | 15 | 97.41% |
| Clinical waste combustion: | 88 | 5 | 94.32% |
| Industrial coal combustion: | 67 | 67 | 0.00% |
| Sinter plants: | 54 | 47 | 12.96% |
| Traffic: | 45 | 45 | 0.00% |
| Iron and steel: | 41 | 14 | 65.85% |
| Non-ferrous metals: | 35 | 10 | 71.43% |
| Crematoria: | 35 | 35 | 0.00% |
| Domestic coal combustion: | 34 | 34 | 0.00% |
| Domestic wood combustion: | 18 | 18 | 0.00% |
| Natural fires: | 12 | 12 | 0.00% |
| Cement manufacturing: | 11 | 11 | 0.00% |
| Straw combustion: | 10 | 10 | 0.00% |
| Chemical waste combustion: | 8.7 | 0.3 | 96.55% |
| Sewage sludge combustion: | 6 | 0.9 | 85.00% |
| Landfill gas combustion: | 5.5 | 5.5 | 0.00% |
| Industrial wood combustion: | 2.9 | 2.9 | 0.00% |
| Waste oil combustion: | 2.4 | 2.4 | 0.00% |
| Lime manufacture: | 2.2 | 2.2 | 0.00% |
| Coke production: | 2 | 2 | 0.00% |
| Tires combustion: | 1.7 | 1.7 | 0.00% |
| Asphalt mixing: | 1.6 | 1.6 | 0.00% |
| PCP in timber processes: | 0.8 | 0.8 | 0.00% |
| Pesticide production : | 0.3 | 0.3 | 0.00% |
| Ceramic production : | 0.06 | 0.06 | 0.00% |
| Halogenated chemicals: | 0.02 | 0.02 | 0.00% |
| Glass manufacturing: | 0.01 | 0.01 | 0.00% |
| Carbon regeneration: | 0.006 | 0.006 | 0.00% |
| **Total:** | **1100** | **350** | **68.18%** |

Table 5.6 Dioxin Emission Inventory in the EU (g TEQ)

*(Quaß et al (2004)*

| **Sources** | **1995** | **Est'd min. 2005** | **Estd max. 2005** | **% reduction, 1995-2005** | **1995 distribution of dioxin sources** | **2005 est'd distribution of dioxin sources** |
|---|---|---|---|---|---|---|
| Power plants (Fossil fuels) | 666 | 50 | 67 | 92.49% | 4.86% | 2.55% |
| Res. combustion: boilers, stoves, .fireplaces - Wood | 989 | 523 | 969 | 47.12% | 7.22% | 26.63% |
| Residential boilers, stoves, fireplaces (coal-lignite)- | 900 | 82 | 337 | 90.89% | 6.57% | 4.18% |
| Industral boilers, turbines | 238 | 39 | 78 | 83.61% | 1.74% | 1.99% |
| Sinter plants | 1650 | 387 | 470 | 76.55% | 12.05% | 19.70% |
| Secondary zinc production | 450 | 20 | 20 | 95.56% | 3.29% | 1.02% |
| Secondary copper production | 29 | 15 | 17 | 48.28% | 0.21% | 0.76% |
| Secondary aluminum production | 65 | 21 | 60 | 67.69% | 0.47% | 1.07% |
| Cement | 21 | 14 | 50 | 33.33% | 0.15% | 0.71% |
| Other: metal reclamation from cables | 750 | 40 | 50 | 94.67% | 5.48% | 2.04% |
| Electric furnace steel plant | 120 | 141 | 172 | -17.50% | 0.88% | 7.18% |
| Other: non-ferrous metal foundries | 50 | 38 | 72 | 24.00% | 0.37% | 1.93% |
| Sintering and drossing facilties | 200 | 1 | 1 | 99.50% | 1.46% | 0.05% |
| Preservation of wood | 390 | 118 | 310 | 69.74% | 2.85% | 6.01% |
| Road transport | 262 | 41 | 60 | 84.35% | 1.91% | 2.09% |
| Incin. of MSW (Legal combustion) | 4000 | 178 | 232 | 95.55% | 29.22% | 9.06% |
| Domestic combustion of wastes | 200 | 116 | 187 | 42.00% | 1.46% | 5.91% |
| Incin. of Industrial (hazardous) wastes ( | 300 | 16 | 45 | 94.67% | 2.19% | 0.81% |
| Inc. of hospital wastes | 2000 | 51 | 161 | 97.45% | 14.61% | 2.60% |
| Crematories | 28 | 13 | 22 | 53.57% | 0.20% | 0.66% |
| Fires | 382 | 60 | 371 | 84.29% | 2.79% | 3.05% |
| Total | 13690 | 1964 | 3751 | 85.65% | 100.00% | 100.00% |

Table 5.7. Dioxin Emissions inventory in Taiwan (gr TEQ)
(Chen 2004)

| **Sources** | **2001** |
|---|---|
| Waste incinerators | |
| Municipal (21,900 t/d) | 5.56 |
| Industrial | 2.40 |
| Medical | 0.39 |
| Small size (281.6 t/d) | 14.73 |
| Hazardous | 0.58 |
| Power plants (coal) | 5.01 |
| Industrial oil combustion | 5.02 |
| Cement kilns | 10.30 |
| Asphalt mixing plants | 0.27 |
| Vehicle fuel combustion | 0.15 |
| Cigarette smoking | 0.03 |
| Electric arc furnaces | 10.26 |
| Secondary aluminum smelting | 6.53 |
| Secondary copper smelting | 39.36 |
| Bleached pulp/paper mills | 0.21 |

## 6. Conclusions

Although dioxins are considered to be some of the most dangerous man-made substances, there is no conclusive evidence associating present background levels with carcinogenic, reproductive, developmental or immunologic effects. Even in the Seveso accidental release, no association between dioxin and adverse health effects on humans was observed. Unfortunately, there have been very few public health studies to document the exact composition and levels of dioxin among the studied populations and therefore the results are not conclusive. However, there is strong evidence of severe health impacts in animal studies where the subjects were exposed to very high doses of dioxins. Therefore, further research must be done in order to identify the possibility of a threshold level mechanism of PCDD/F action for humans. Effects reported by various studies include chloracne, hyperpigmentation, altered liver function and lipid metabolism, general weakness associated with drastic weight loss, changes in activity of various liver enzymes, depression of the immune system, and endocrine and nervous system abnormalities. It is believed that human response to dioxin action on a molecular level varies and thus sensitivity to dioxin toxicity differs considerably between individuals.

Because of the unique environmental properties of dioxins and furans, such as resistance to photolytic, biological and chemical degradation, low water and high lipid solubility and tendency for bioaccumulation, they are categorized as Persistent Organic Pollutants (POPs). Dioxins can move long distances in the atmosphere before deposition, may persist in the environment for long periods of years and may bioconcentrate by factors of up to 70,000 fold. Their physical and chemical properties of high persistence and semi-volatility, coupled with other unique characteristics, have resulted in their being widely distributed through the global environment, even in regions where they have never been used. From a regulatory perspective, it is very important to focus on measures aimed at reducing human exposure to high levels of dioxins in the short to medium term and to maintaining exposure at safe levels in the long term. Emissions data from around the world presented in this study indicate a sharp reduction in dioxin emissions on air mainly from concentrated (industrial) sources. For most countries, the reduction is in the range of 80-90+%. The lower quantity of dioxins emitted on air have resulted in a significant reduction in human intake of PCDD/F compounds in the past few years. Since emissions from concentrated (industrial) sources have been successfully controlled in most of the developed nations, future regulation should take account of multiple small sources but with high overall emission rates. Emissions from MSW combustion which were historically the biggest source have now become a minor contributor; from 8,877 gTEQ in 1987 to only 12 gTEQ in 2004. The most important global contributor to the dioxin inventory has become the residential combustion of wood in stoves, boilers etc, and the uncontrolled combustion of residential and agricultural refuse ("backyard barrel burning"). "Backyard barrel burning" at present constitutes over 50% of the U.S. dioxin emissions Residential combustion is still common in developing countries and in rural areas in many developed countries. The control of emissions form such activities is challenging and most of the models predict only a slight decrease for the forthcoming years. In Canada, the United Kingdom, and the European Union combustion of wood, fuels and waste domestically will became the most important source for dioxins. Additionally, measures should be taken in order to minimize the levels of dioxin precursors in the waste stream by phasing out the production and use of substances such as PCPs and PCBs.

Because of the extremely high toxic potency of dioxins, the environment must be effectively monitored for even very low quantities. Regular analytical testing should be done on humans residing in areas of high risk and background levels should be established. Additionally, concentrations in ambient air, water, soil and foodstuffs must be monitored in order to identify possible routes to contamination. Further research is also needed in order to comprehend the various transfer processes by which dioxins move between the atmospheric, aquatic, terrestrial and biological environments, and the degradation processes and rates taking place in each medium. Currently, few parameters are regularly monitored on a global scale - only human breast milk is monitored by the WHO - and sampling procedures are not standardized and not frequent enough resulting to inconclusive results in most human health studies.

Finally, in areas with high risk of contamination, a system of public information should be put into place that would report on the concentration of dioxins in the region. Such a system would provide the information necessary for local population to reduce their exposure to dioxins by recommending different levels of consumption for locally produced foods. Since the most important pathway for human exposure to dioxins is dietary, diversification of food supply in highly contaminated areas can dramatically reduce the exposure of local population.

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