

# Sources and pathways of dioxins to humans – Diminished contribution of modern WTE facilities

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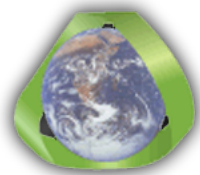
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## EXECUTIVE SUMMARY

The objective of this thesis was to examine the major sources of dioxins, globally, and the contribution of the waste-to-energy (WTE) industry in the last quarter of a century since the toxic effects of dioxins were first recognized. In the early nineties, environmental agencies in the U.S., Europe and Japan established the very stringent emission standard of 0.1 nanograms TEQ dioxins per standard cubic meter of stack gas (ng TEQ/dscm). This standard motivated innovation in the industry and major changes of the Air Pollution Control (APC) systems of WTE facilities.

The first half of this study is a literature review on the composition, deposition, accumulation, and degradation of dioxins that are toxic to humans (i.e. PCDD/Fs and dioxin-like-PCBs). In order to understand the threat of human exposure to dioxins, it is necessary to identify the sources of dioxin releases and how they are transported to biota and humans. For example, 90 to 98 percent of human exposure to dioxins is due to the consumption of food, where 50 to 70 percent of food exposure is directly linked to dioxin-like PCBs. In developed nations there are no current sources of dioxin-like PCBs. Therefore, at least one half of all observed dietary exposure to dioxins is derived almost entirely from releases of old PCBs stored in environmental reservoirs.

This study includes emission data from 40 WTE facilities in the U.S., 123 in France and 35 in the Republic of Korea, along with estimates of total national dioxin releases from all types of incinerators and other industrial sources of dioxins. For countries where modern APCs have been implemented, on average an estimated 0.04 to 0.11 grams TEQ of dioxins are released per million tons of MSW incinerated. The Republic of Korea in 2010 is reported to incinerate the highest percent of MSW at 55%, while France and the U.S. incinerated 41% in 2010 and 7% in 2012, respectively. Also presented in this report is the emissions data for 19 WTE facilities in China where, in 2009, 15% of the MSW was incinerated. This study shows that in the last twenty years, through the use of modern APC systems, dioxin emissions from WTE facilities in the U.S. have decreased by a factor of 3,000. New modern APCs have proven effective in removing dioxins from WTE emissions and therefore eliminating WTE as a major dioxin source contributor worldwide.

Despite the enormous advancements made by the global WTE industry in reducing dioxin concentrations in emissions, new WTE facilities are still opposed by some environmental organizations. In most cases, such opposition is due to misinformation from outdated facilities where APCs are not being used. The achievements that the WTE industry has made in the last 30 years with respect to the near elimination of dioxins needs to be recognized globally by both the general public and environmental agencies. Also, the global WTE industry must promote best practice in new WTE plants in the developing world, not only to eliminate negative environmental impacts, but to also strengthen the reputation of the WTE as a truly sustainable waste management practice.

## ACKNOWLEDGMENTS

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# 1 INTRODUCTION TO DIOXINS

## 1.1 Terminology: ‘Dioxins’ and ‘Dioxin-like compounds’

The terms ‘dioxins’ and ‘dioxin-like compounds’ are used in literature when referring to a large family of chemical compounds that are found in trace amounts in nearly all realms of the environment. ‘Dioxins’ include a wide range of halogenated aromatic compounds such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, also represented as “PCDD” and “PCDF” respectively; the term ‘dioxins’ is inclusive of both dioxins and furans and both are formed as a result of incomplete combustion of hydrocarbons in the presence of chlorine. They have high melting points and are stable to acids and bases, which makes them very persistence in the environment.

## 1.2 Chemical Structure

There are a total of 210 congeners of dioxins, consisting of two benzene rings joined by a single or double oxygen atom. Each of these dioxin congeners has a unique molecular structure whose hydrogen atoms may be replaced by up to eight chlorine atoms. The double oxygen atom configuration is distinct of a dioxin and the single oxygen atom and carbon bond configuration is distinct of a furan (Figure 1). Seventy-five of the 210 congeners have a dioxin (PCDD) chemical structure and the remaining 135 congeners have a chemical structured related to furans (PCDF). Out of these 210 congeners only seventeen 2,3,7,8-substituted congeners pose a potential threat to environmental and human health, therefore being noted as toxic (Van den Berg et al., 1998).

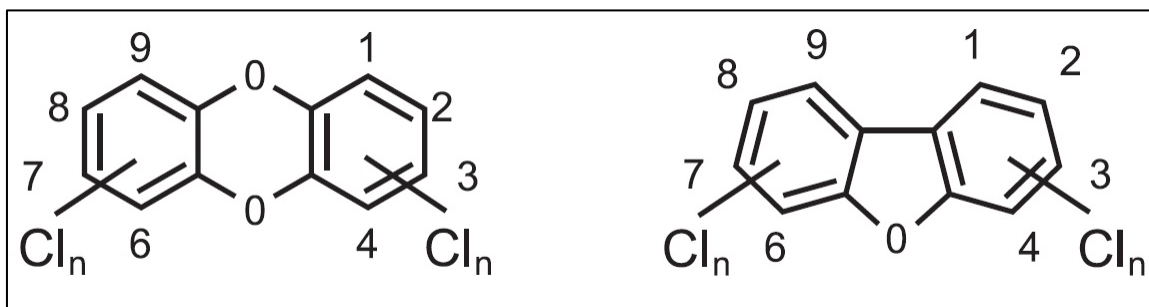
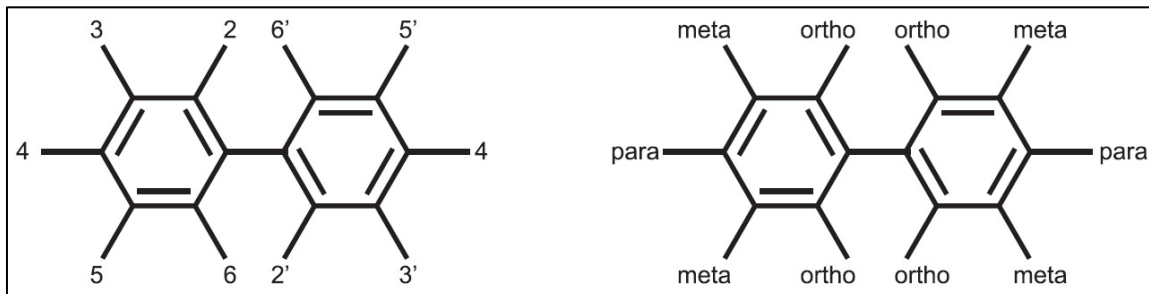


Figure 1 Dioxin and Furan Molecular Structure (Sigma-Aldrich, 2007)

Similar in chemical structure, physical-chemical properties and toxic health effects, certain polychlorinated biphenyls (PCBs) are found to exist together in the environment with dioxins. PCDDs, PCDFs and certain dioxin-like PCBs are collectively referred to in the literature as ‘dioxin-like compounds.’ The toxicity of these compounds has been studied and reported on thoroughly (ATSDR, 2012; King, 1999; Stockholm Convention, 2011; U.S. EPA, 2006; Van den Berg et al., 1998). There are a total of twelve toxic dioxin-like PCBs that have been identified by the World Health Organization (WHO) in parallel with PCDD/Fs (Van den Berg et al., 1998). Similar to dioxins, dioxin-like PCB’s are aromatic compounds whose skeletal structure also consists of two benzene rings. In the case of PCBs, these rings are connected by a single carbon bond; creating what is known as a biphenyl molecule (Figure 2). Polychlorinated biphenyl (PCB) compounds

are formed in such a way that the hydrogen atoms on the molecular structure can be replaced by up to ten chlorine atoms. Of the 12 known dioxin-like PCBs, there are four non-ortho dioxin-like PCBs and eight mono-ortho dioxin-like PCBs that all share a similar planar arrangement (Sigma-Aldrich, 2007; Stockholm Convention, 2011).



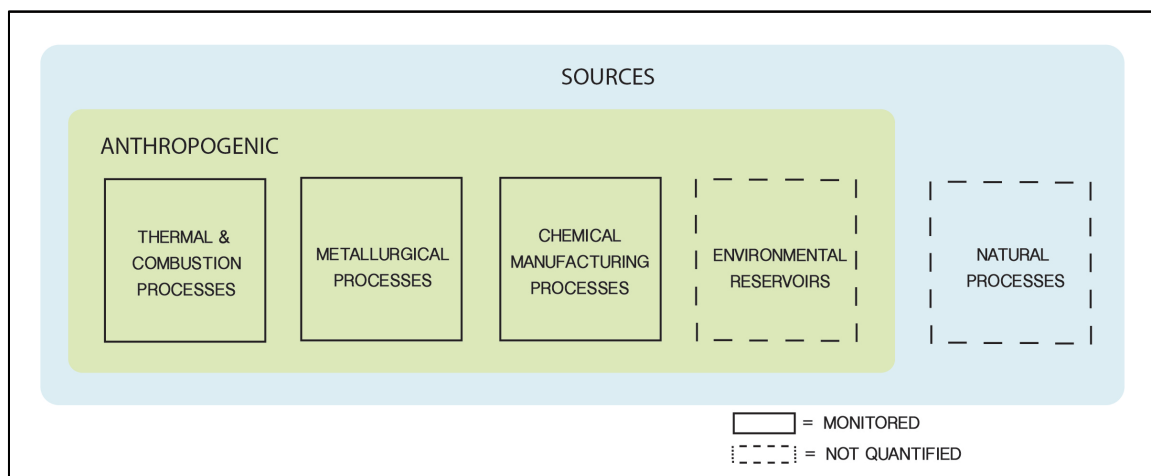
**Figure 2 Biphenyl structure of PCBs (Sigma-Aldrich, 2007)**

For the remainder of this report, the term “dioxins” will be used in reference to dioxins, furans and dioxin-like PCBs. In certain cases where data is presented for either dioxin/furans or dioxin-like PCBs specifically, it will be annotated as PCDD/Fs or DL-PCBs respectively.

## 2 SOURCES

Dioxins are the byproducts of both anthropogenic activity and natural processes. However, comparison of tissue levels in present day adults as compared to tissues in a frozen ancient Eskimo from North America, as well as levels in stillborn infants at present time, indicates an anthropogenic origin of almost all dioxins in the environment (Schechter et al., 1994). Several national and international agencies have provided detailed inventory reporting on dioxin sources around the globe. The following five source classifiers were determined to be most inclusive: Thermal and combustion processes, metallurgical processes, chemical manufacturing processes, environmental reservoirs and lastly, natural processes. It is shown in Figure 3 that all but natural processes are anthropogenic by origin. The solid line in Figure 3 delineates the more commonly monitored sources while the dotted line represents sources that are not typically quantified in current inventory reporting. Examples of actual anthropogenic sources of dioxins include but are not limited to: municipal waste combustion, secondary copper smelting, backyard barrel burning, cement kilns, municipal wastewater treatment sludge, coal fired utility boilers, automobiles using leaded gasoline, backyard barrel burning, diesel heavy-duty trucks, industrial wood combustion, and sintering plants.

The development of the five source classifiers listed above is based on a similar format that the U.S. E.P.A. presented in their 2006-inventory report. The detailed breakdowns of dioxin source categories by the U.S. E.P.A. and by the Stockholm Convention are included in Appendix A of this report.



**Figure 3 The Five Source Classifiers**

### 2.1 Monitored Inventory Sources

As it has been illustrated above, the most common sources included in dioxin inventory reporting are anthropogenic. The U.S. E.P.A. reported in the year 2000 that backyard barrel burning of refuse was the number one contributor in the U.S., releasing 35.1 percent of total dioxins recorded. Table 1 shows the top four monitored sources of dioxin releases as accounted for in the year 2000 from the U.S. E.P.A. inventory report. The Stockholm Convention reported that inventory data from 68 countries between 1999 and 2012 indicated that open burning of biomass waste was the number one contributor, releasing 48 percent of total dioxins recorded. Table 2 displays the top four monitored sources of dioxin releases as determined in this global sample. More discussion on the definition and significance of open burning of biomass waste is included in Appendix A.

**Table 1 Top four sources of dioxin releases in the U.S., 2000 (U.S. EPA, 2006)**

	Source	Percent of Total
1	Backyard barrel burning of refuse.	35.1%
2	Medical waste/pathological incineration.	26.6%
3	Municipal wastewater treatment sludge, land application and incineration.	6.3%
4	Municipal waste combustion.	5.9%

Note: Percentages based on releases calculated using WHO toxic equivalent factors.

**Table 2 Top four sources of dioxin releases in 68 countries, 1999-2012 (Fiedler et al., 2012)**

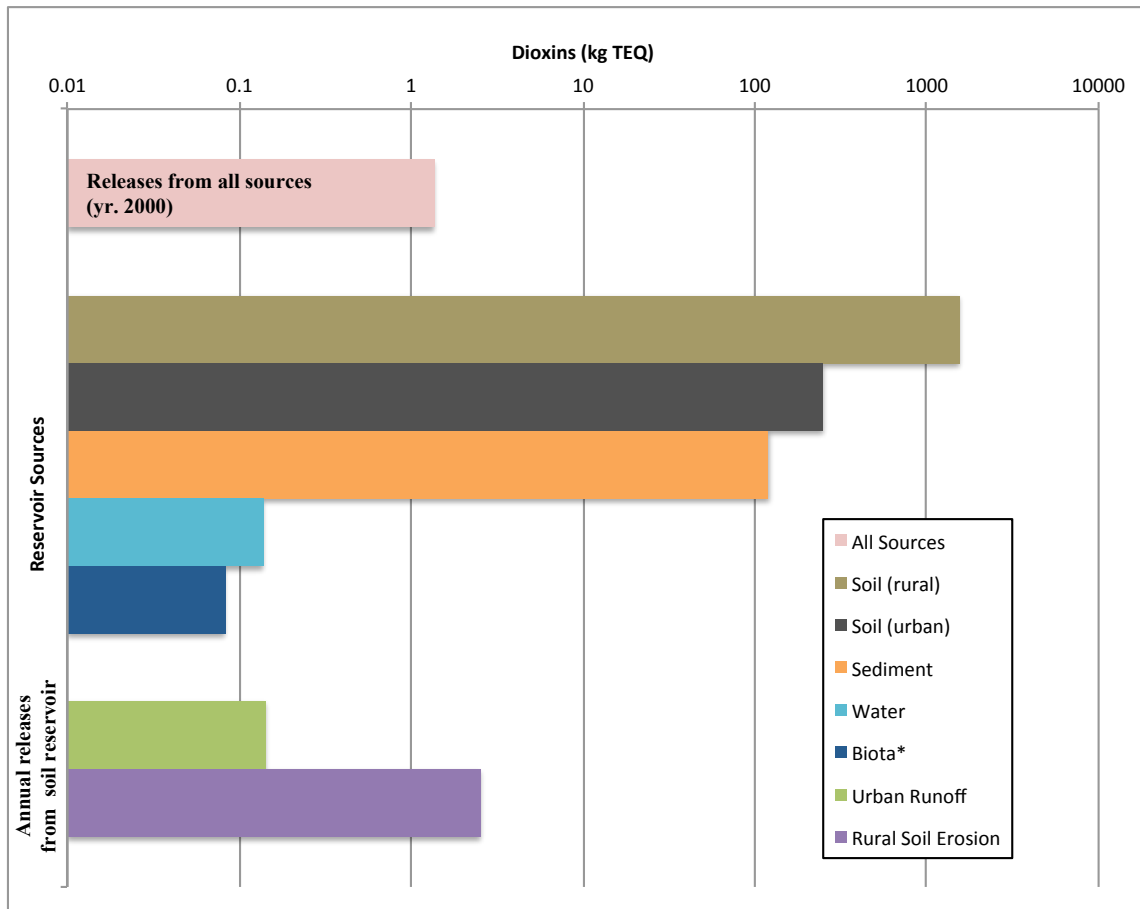
	Source	Percent of Total
1	Open burning of biomass waste	48%
2	Incineration of waste	12%
3	Power generation	10%
4	Heating and cooking	9%

Note: Percentages based on releases given in g TEQ with no indication if TEQ is calculated with WHO or International toxic equivalent factors.

It is important to note that data in Table 1 and Table 2 was provided by two separate monitoring agencies with independent protocols for dioxin inventory assessment. For example, sources that are assessed in the Stockholm Convention toolkit may or may not be deemed quantifiable by the U.S. E.P.A. standards. Furthermore, the results in these tables represent two different time trials. For example, results in Table 2 are based on 68 country-specific inventory assessments, compiled over a 13-year period, whereas the results presented in Table 1 were conducted for a single year. Of course, as will be discussed later, in the intervening 14-year period there have been further reductions in the industrial emissions of dioxins.

## 2.2 Environmental Reservoirs

The fourth of the anthropogenic source classifiers is environmental reservoirs and, as presented in Figure 3, cannot be quantified by contemporary dioxin reporting standards. There is however widespread acknowledgement of existing environmental reservoirs such as contaminated soils in historic industrial dumpsites, which are commonly overlooked as significant contributors of dioxin releases (Weber et al., 2008). The challenge of quantifying environmental reservoir sources is due to the complexity, in which dioxins are deposited, re-deposited, sequestered, and or transferred between environmental media (i.e. air, soil, water, sediments, and biota). In literature, the movement of dioxins between media is commonly termed *depositional flux*. More information will be provided in subsequent sections of this thesis with regards to the deposition of dioxins to varying environmental media as well as depositional flux. Each type of media in which dioxins are accumulated and able to be released back into the environment is considered an environmental reservoir source (i.e. soils, sediments, water, biota and some anthropogenic materials). The U.S. E.P.A. inventory report on dioxins states that it is reasonable to consider environmental reservoirs as significant contributors to human exposure, although concludes that the ability to make accurate quantitative estimates from these sources is limited at present (2006). This U.S. E.P.A. report has however calculated “preliminary” estimates of dioxin releases from environmental reservoir sources (Figure 4). It is seen that soil and sediments are two to three orders of magnitude greater than dioxins releases from all inventory sources. In Figure 4, urban runoff and rural soil erosion annual estimates are two examples of dioxin releases from an environmental reservoir such as soil. Further discussion on environmental reservoirs and their role in human exposure is discussed in section 5.2 - “Main Pathways for Human Exposure.” Environmental reservoirs have been linked as the origin of dioxin-like PCBs and therefore anywhere from one-third to one-half of human dietary exposure of dioxins is said to be from environmental reservoirs (Alcock et al., 1998; U.S. EPA, 2006; Weber et al., 2008).



**Figure 4 Levels of dioxins from environmental reservoirs in U.S. as compared to all sources (U.S. EPA, 2006)**

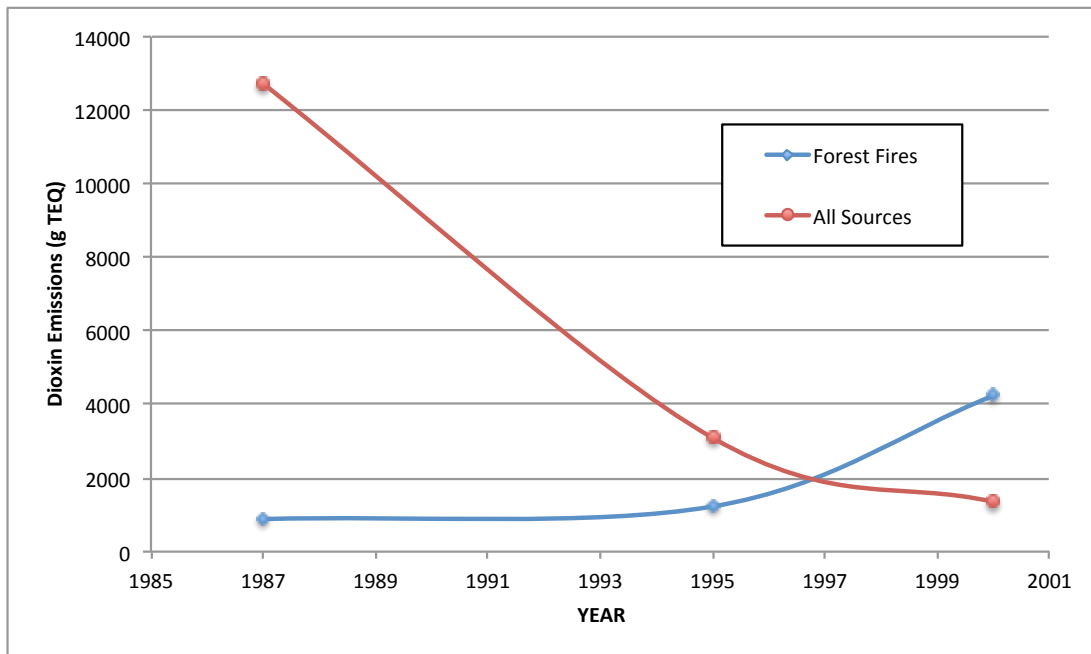
Note: Dioxin releases reflect levels of PCDD/Fs. Kg TEQ were calculated with International toxic equivalent factors.

\*There is no available data in the U.S. for quantifying dioxins in biota. The value presented in this figure is from a U.K. study cited in U.S. E.P.A. report for humans and vegetation only and is intended to place perspective on the potential magnitude of this reservoir source.

### 2.3 Natural Processes

The discovery of small levels of dioxins in ancient human remains carbon dated before the age of industrialization, suggests that dioxins are not solely a product of human activity but have for sometime existed in nature as the byproduct of natural processes (Schechter et al., 1994). The most widely recognized and studied natural source of dioxins is wildfires. One report from the American Chemistry Council concluded that dioxin emissions from forest fires alone are comparable to current levels of anthropogenic sources (ACC, In Press). Similarly, the U.S. E.P.A has estimated dioxin releases from wildfires in 2000 to be greater than releases from all monitored sources (Figure 5). In both of these accounts, results were based on the use of an emission factor for wildfires that was determined to be highly variable geographically (Gullett et al., 2003). For this reason alone, the U.S. E.P.A. report concludes that their estimated dioxin releases from wildfires are non-representative and have low confidence rating; further concluding that such estimates should only be used as a preliminary indication of the potential magnitude of dioxin releases from wildfires (2006). Figure 5 not only shows the increasing

significance of wildfires as a major source of dioxin emissions, it highlights an increasing frequency of wildfires. A recent report has concluded that the increase in wildfires in the U.S. is strongly associated with recorded increases in spring and summer temperatures (Westerling et al., 2006). With predicted increases in temperatures from global warming, wildfires will most likely continue to increase in frequency therefore resulting in a growing significance of dioxin releases from wildfires.



**Figure 5 Dioxin emission estimates from forest fires in the U.S. versus all sources (U.S. EPA, 2006)**

Note: Dioxin emissions reflect levels of PCDD/Fs. Grams TEQ were calculated with International toxic equivalent factors.

In addition to forest fires, the U.S. E.P.A. acknowledges recent studies suggesting other natural processes as sources of dioxins such as: volcanic eruptions, certain microorganism activity, and isolated soils such as ball clay. However for each of these potential sources, the U.S. E.P.A. concludes that there is an insignificant amount of data available to quantify such as major contributors to the national dioxin inventory list (2006). The Stockholm Convention acknowledges biogenic processes as those pertaining to the natural transformation of manufactured chemicals to dioxins via microorganisms that exist in the environment. The Stockholm Convention has however determined that these manufactured chemicals, which are seen as precursors to dioxin formation, have decreased dramatically in the past decade. (Stockholm Convention, 2013)

## 2.4 Other Estimated Sources

The U.S. E.P.A. has identified a number of “minimally controlled combustion sources” that have been determined to be preliminary (like wildfires and reservoir source estimates) and are therefore not included in all monitored sources (2006). In Table 3, estimated sources of minimally controlled combustion sources are presented as a percentage of all monitored sources. Second to wildfires, emissions from landfill fires

and land clearing debris burning are seen as potential major contributors. It is interesting to note that apart from wildfires, all estimated sources in Table 3 are anthropogenic.

**Table 3 Estimated minimally controlled combustion sources (U.S. EPA, 2006)**

	Percent of Total
All Monitored Sources	100%
<b>Estimated Sources</b>	
Wild fires	314%
Landfill fires	83%
Land clearing debris burning	39%
Accidental fires, structural and vehicles	3%
Combustion of landfill gas in flares	2%
Residential yard waste burning	1%

Note: Percentages based on releases calculated using International toxic equivalent factors.

### 3 DIOXINS AS PERSISTENT ORGANIC POLLUTANTS (POPS)

Dioxins belong to the group of compounds known as Persistent Organic Pollutants (POPs). POPs are considered persistent in the environment because of their long half-lives in soils, sediments, water, air and biota. Persistence is considered to be an important property of chemical compounds because it defines its ability to be transported over long distances. POPs prove to threaten the environment more than most chemical compounds known to man given their ability to bioaccumulate in nature, to cause significant adverse effects to wildlife and humans, and to undergo long-range atmospheric or oceanic transport. For these reasons the Stockholm Convention, a global treaty, was formed in 2004 and through international collaboration it is intended to protect human and environmental health by monitoring and reducing POPs globally. There are thousands of POP compounds determined by the Stockholm Convention that are arranged into groups or “families.” The most notable families of POP compounds are those related to dioxins.

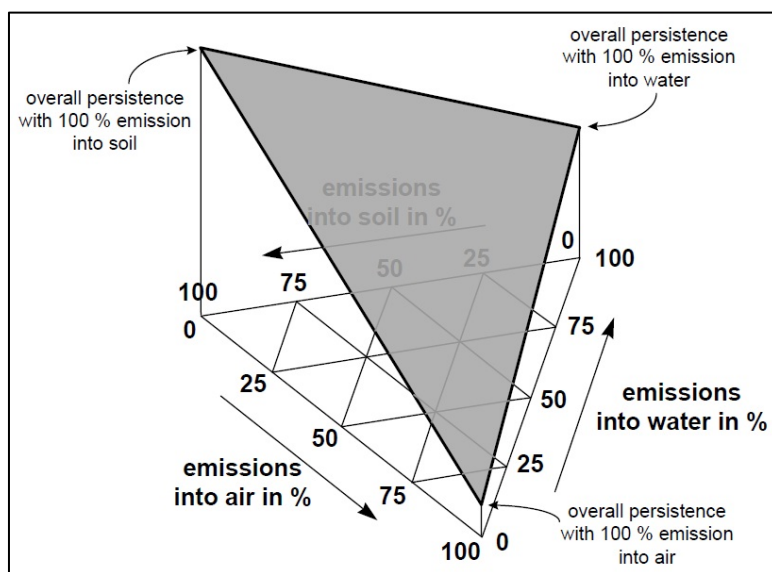
#### 3.1 Persistence Value Assessment

Persistence is a result of a compounds long half-life due to its hydrophobic and lipophilic properties. While in nature, POPs deposited in water systems tend to separate and bind onto organic matter in soils in order to avoid an aqueous phase. Similarly POPs in animals will separate and bind into lipids of organisms where they become stored in fatty tissue rather than stay deposited in the aqueous environment of a cell (Jones et al., 1999). Their hydrophobic and lipophilic properties are exactly what cause POPs to accumulate over time in biota as well as in the organics of soils and sediments. Persistence is inevitably governed by the rate at which a chemical compound is removed from the environment by biological and chemical degradation processes, such as photolysis, hydrolysis, atmospheric oxidation and biodegradation. This degradation rate is determined by a combination of substance-specific properties and environmental conditions, which make it extremely difficult to calculate an actual persistence value. A number of studies have however developed models to evaluate and quantify compounds



based on their persistence. One such study created an integrated criterion model to predict a time value (i.e. persistence) in which a compound persists in the environment (Wania, 1998). Figure 6 is a general representation of how the media onto which a compound is deposited affects the persistence value. Deposition onto soil is seen as resulting in the highest persistence value. When a compound is deposited over multiple medias the overall persistence value is additive, shown by the grey area in Figure 6. Unlike Wania et al.'s criterion modeling approach, the "persistence workgroup" at the Society of Environmental Toxicology and Chemistry (SETAC) Pellston workshop addressed persistence evaluation based on an assortment of supporting information (Boethling et al., 2009). This workgroup concluded that persistence evaluation should include a weight-of-evidence assessment identifying a compound's transformation products, non-extractable residues as well as treatment of uncertainty and conflicting data.

The development of persistence values has proven useful for directing national and international regulatory policy framework because it outlines which POPs pose the greatest threat to the environment within a designated timeline. There is however a general understanding that persistence evaluation is over simplistic when used for predicting the countless variations in outcomes that a chemical compound can travel, deposit and finally degrade in the environment. For this reason, persistence values are not commonly used in research as a means for reporting and tracking organic pollutant activity.



**Figure 6 Visual representation of overall persistence value of an organic pollutant (Wania, 1998)**

Table 4 presents calculated persistence values for varying persistent organic pollutants based on the previously noted integrated criterion model developed by Wania et al. Each column of persistence values represent independent "levels" in which the model is run. Each level is based on a myriad of assumptions relevant to the deposition pathway of each POP. In Table 4, dioxin congeners 2,3,7,8-TCDD and 2,3,7,8-TCDF are said to

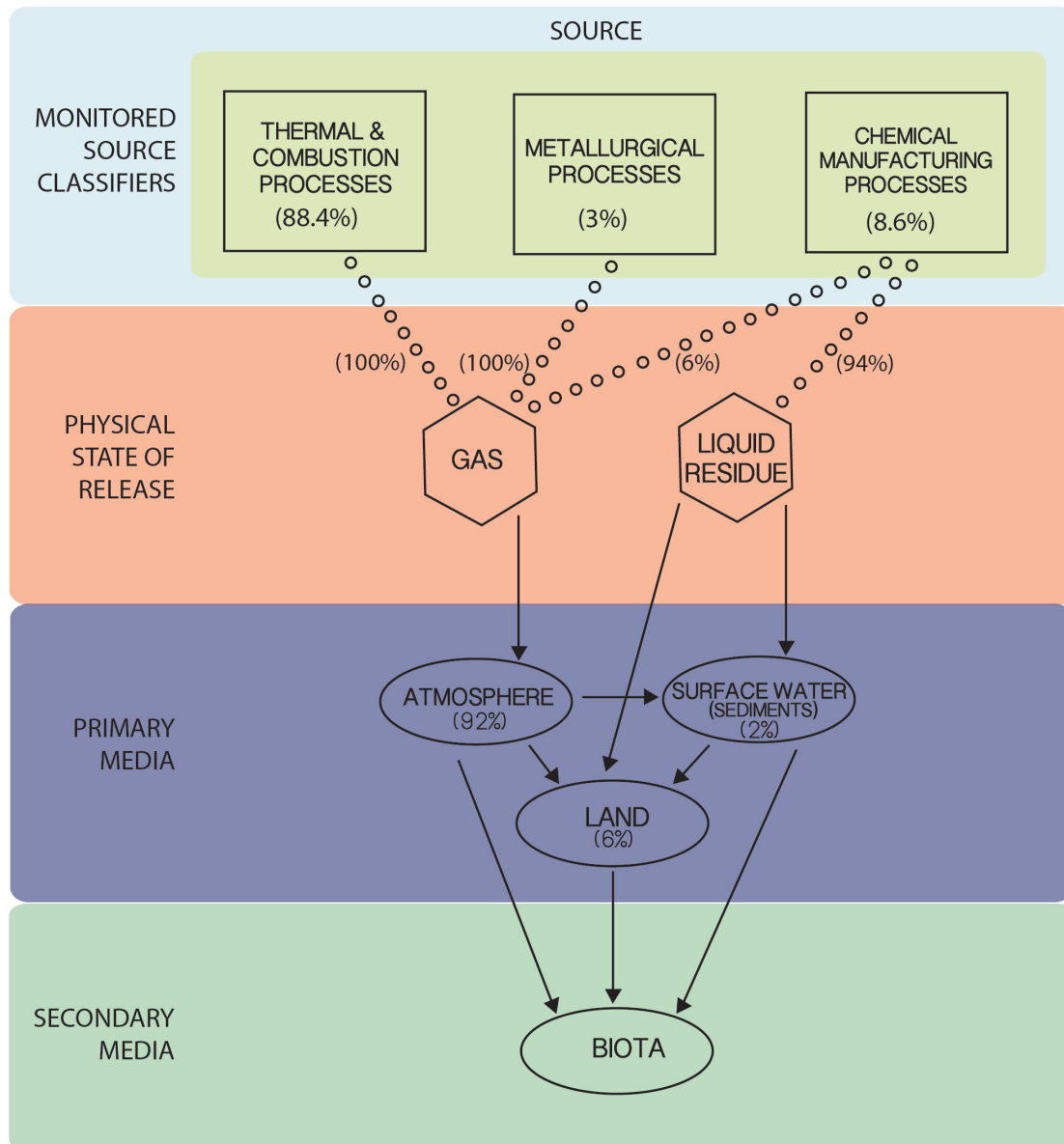
have overall persistence values that are an order of magnitude different between levels. Other POPs show noticeably large variability in persistence values, which is indicative of the large range of uncertainty in deposition pathways for these POPs. For those POPs in Table 4 with relatively small differences of persistence values between levels, it can be implied that these compounds are not very dependent on deposition pathways when determining the length of time they will persist in the environment.

**Table 4 Persistence values for varying POPs (Wania, 1998)**

POP Name	Overall Persistence Value			
	Level III		Level II	
	days	years	days	years
Aldrin	10	0	0.3	0
Chlordane	944	2.6	400	1.1
DDT	926	2.5	281	0.8
Dieldrin	916	2.5	79	0.2
Heptachlor	77	0.2	4	0
HCB	1775	4.9	1133	3.1
Mirex	1961	5.4	15	0
Toxaphene	2759	7.6	440	1.2
Dioxin (2,3,7,8-TCDD)	369	1	83	0.2
Furan (2,3,7,8-TCDF)	359	1	70	0.2

## 4 LIFE CYCLE OVERVIEW

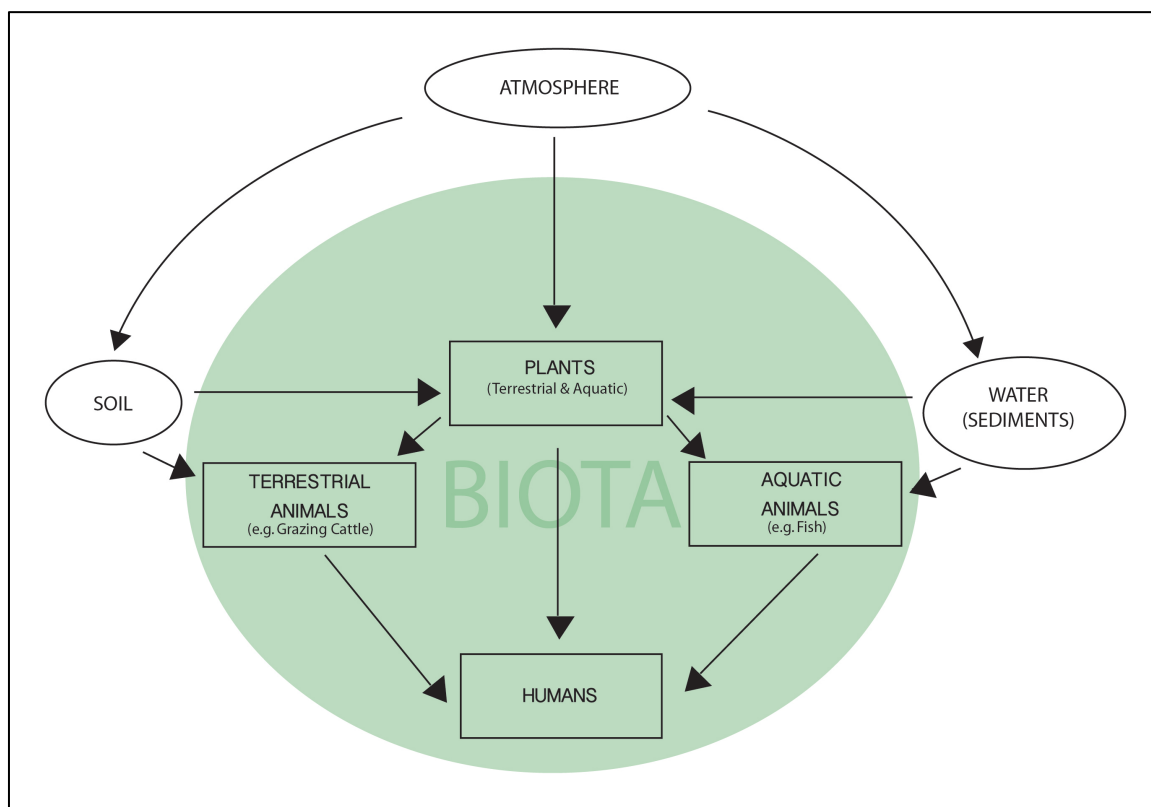
This section will provide a general overview of the lifecycle of dioxins as they are released into the environment, deposit, accumulate and degrade over time. Dioxins are released from their sources in either the form of a gaseous state or in the form of a liquid residue where they then deposit onto environmental media. In a gaseous state dioxins are deposited into the atmosphere, and as a liquid residue they are deposited into water or onto land. From any of these three primary media, dioxins may then be re-deposited onto biota. Dioxins may accumulate and degrade in any of these four environmental media. Figure 7 shows the major deposition pathways of dioxins from a gaseous state or liquid residue once they are released from monitored anthropogenic sources. The percent values presented in Figure 7 were obtained from the U.S. E.P.A., which reported that in the year 2000, 88.4%, 8.6% and 3% of all monitored sources in the U.S were associated to thermal and combustion processes, chemical manufacturing processes and metallurgical processes respectively. All dioxins produced from thermal and combustion processes as well as metallurgical processes are released in a gaseous state. Whereas 6% of dioxins from chemical manufacturing processes are released in a gaseous state and the remaining 94% are released as a liquid residue. In total, 92% of all dioxins released were said to deposit into the atmosphere, 6% and 2% deposited into surface waters and onto land respectively (U.S. EPA, 2006).



**Figure 7 Deposition pathway (quantified) from monitored anthropogenic sources**

#### 4.1 Deposition

It is the physical state of release and chemical properties such as their hydrophobic and lipophilic characteristics that dictate the deposition pathway of dioxins. For example, dioxins in a gaseous state released into the atmosphere will bind to vapor or air particles and tend to deposit onto soil, surface waters or plants. Dioxins in liquid residues tend to be deposited by human means, such as in the spreading of contaminated sewage sludge onto land or dumping into surface waters. Major deposition pathways shown in Figure 7 highlight how biota is impacted from all primary environmental media. Although the atmosphere is the largest reservoir of dioxin releases, it is important to understand how dioxins move from the atmosphere into biota. The most common depositional pathways between the atmosphere and biota are shown in Figure 8, highlighting the strong potential



**Figure 8 Most common depositional and transfer pathways leading to human exposure**

for transfer to humans. It is interesting to note that 95 percent of aerially deposited contaminants are said to ultimately deposit onto terrestrial environments, highlighting the importance of the atmosphere to soil pathway as a precursor to human exposure (Fries, 1995).

Given the large percentage of dioxin releases in the atmosphere, long-range atmospheric transport has been an important focus of research. The majority of persistent compounds, including dioxins, are said to have a strong potential for long-range transboundary atmospheric transport; that is to say dioxins are not only dispersed on a continental scale, but a considerable number are dispersed on a hemispheric to global scale (Van Pul et al., 1998; Wania et al., 1996). Dioxins are also noted for having a natural inclination to enter the gas phase under low vapor pressures and environmental temperatures, allowing them to re-volatilize after being deposited. A cycle of deposition and re-volatilization can occur many times throughout the molecule lifetime of persistent organic pollutants, bringing them over far distances over long periods of time (Jones et al., 1999). In *Tracking Distribution of Persistent Organic Pollutants*, Wania et al. use the term “grasshopper effect” to explain this phenomena of the pollutants migration, coordinated with seasonal temperature fluctuations (1996).

### 4.1.1 Depositional Flux and Mass Balance

It is important to note that Figure 7 does not accurately reflect the true multidirectional movement (i.e. depositional flux) of dioxins between environmental media that is presented in Figure 9. Once dioxin-like compounds are released from the “Source” they are deposited into air or water (note single direction arrows) and then able to travel between media (note two direction arrows). As it has been previously mentioned in the case of environmental reservoirs, the complexity associated with depositional flux makes tracking, monitoring and quantifying dioxins in media very difficult. A number of studies have attempted to estimate existing dioxin levels in the environment using a mass balance equation and tracking the deposition of dioxins from atmospheric sources. These studies however, have inevitably concluded that a mass balance equation could not be used to accurately predict dioxin levels for specific geographic locations (Baker et al., 2000; Brzuzy et al., 1995; Schröder et al., 1997). Another study developed a global mass balance model, by using five global climate zones in order to achieve a global estimate of dioxin releases (Brzuzy et al., 1996).

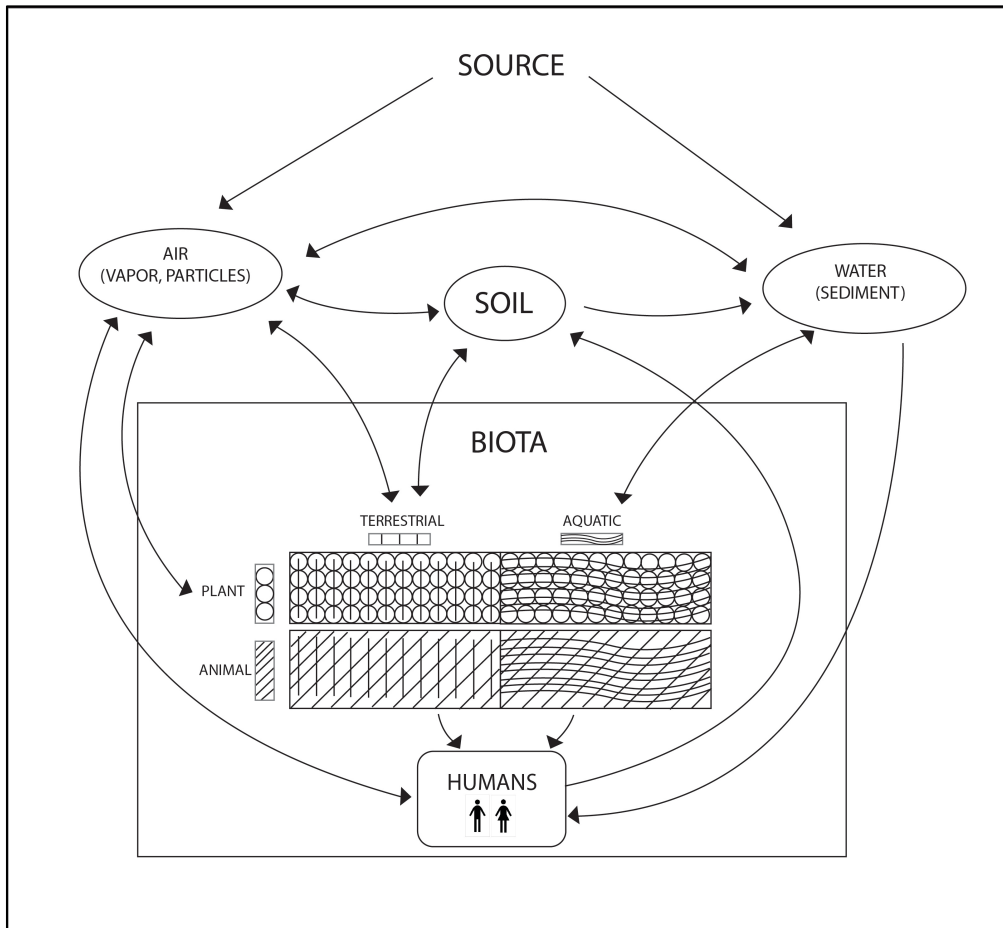


Figure 9 Inter-media depositional flux of dioxins

### 4.2 Accumulation

Dioxins are deposited onto soils in the form of liquid residues, particle-bound gases or via transmission from sediments in adjacent water bodies. They are known to have a

relatively large dry and wet deposition to particles in soils because of their large binding affinity at the soil organic fraction (Van Pul et al., 1998). Compared to other media, dioxins degrade in soil at a relatively slow rate allowing them to accumulate over time. Given their physical chemical properties, movement of dioxins in the gas or liquid phase under typical soil conditions is very limited. Studies have shown that for a given rate of atmospheric deposition onto soil, 80% of dioxins will be retained in the top 15 cm of the soil (Brzuzy et al., 1995). The capacity of soil to retain these compounds is however highly dependent on the amount of dioxins deposited and the amount of organic carbon in the soil. It is presented in certain case studies of highly contaminated sites (e.g. landfills) dioxins were revealed to have leached into groundwater (Weber et al., 2008).

Dioxins found in water bodies are most often the result of discharges of anthropogenic waste, atmospheric deposition or wastewater runoff from urban areas. Once in water, dioxins will settle and bind with sediments as well as accumulate in aquatic biota. Dioxins enter sediments in water bodies because they are hydrophobic and will naturally attach to organic matter in sediments rather than stay suspended in a liquid state. When bound to sediments, dioxins tend to be sequestered for long periods of time. For this reason, accumulation levels of dioxins in sediments have been used throughout literature as a means to monitor anthropogenic activity over time (Frignani et al., 2001). Not all dioxins in sediments are however sequestered, a strong correlation was found between dioxins accumulated in sediments and levels of these compounds in aquatic biota such as fish (Kuehl et al., 1987). The ingestion of contaminated sediments and the consumption of contaminated foods in the aquatic food chain have proven to be the major pathways in which fish uptake dioxins (Fletcher et al., 1993; Van der Oost et al., 2003).

#### **4.2.1 Bioaccumulation**

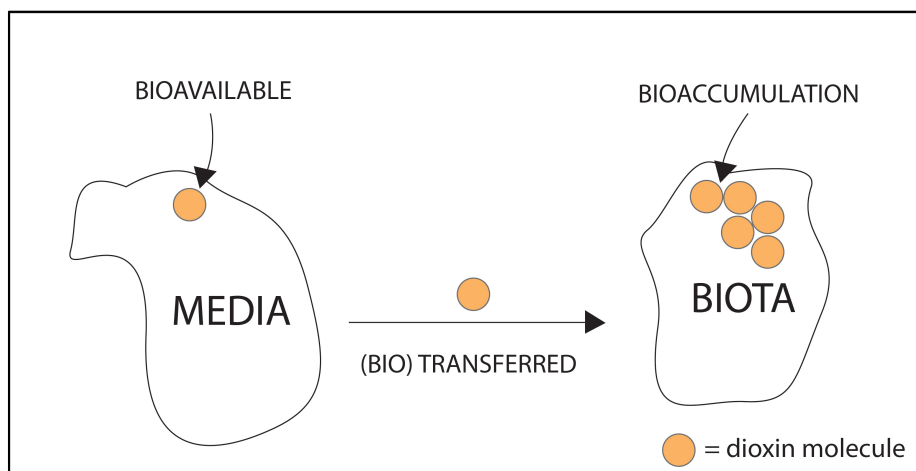
Bioaccumulation is a term used to define the accumulated concentration of dioxins within biota. Both plants and animals are susceptible to bioaccumulate dioxins during their lifetime. Bioaccumulation in both cases is a result of uptake (i.e. biotransfer) rates of dioxins from media. In principle, plants are able to uptake dioxins through a number of processes: adsorption to root surfaces, root uptake and transport to the shoot, adsorption of volatilized dioxins, contamination of foliage and fruits by soil particles and or deposition of airborne dioxins. Field studies have however proven that in outdoor conditions, atmospheric deposition is the main pathway for transmission of dioxins into plants (Huelster et al., 1994) (Müller et al., 1993). The air-to-leaf transfer process is however reversible, therefore dioxin concentrations in plants are determined by nearby air concentrations (U.S. EPA, 2006). Interestingly, air-to-leaf transfer of dioxins is closely linked to soil concentrations near plants (Bacci et al., 1992). This is most likely due to the re-volatilization of dioxins from soils to air (Van Pul et al., 1998). It is this air-to-leaf process that transfers dioxins into plants and allows for bioaccumulation to occur. Bioaccumulation of dioxins in plants allows for the biotransfer of these compounds into the food chain, attaching to fatty tissues in animals and bioaccumulating at greater concentrations than in plants.

Bioaccumulation of dioxins in animals is not as strongly correlated with nearby concentrations of dioxins in media, as is the case with plants. Terrestrial plant-eating

animals such as grazing ruminants will bioaccumulate dioxins based on local vegetation concentrations. On the other hand, in an aquatic environment certain migratory species of fish can be considered to prey on smaller fish or plankton in local or even far off areas of water bodies during their lifespan. In the case of humans, bioaccumulation is also not limited to local food concentrations of dioxins. Modern day humans in developed countries are often exposed to pollutants in foods that are harvested, hunted or manufactured and ultimately imported from around the globe. Globalization has in many ways re-defined the food chain and has certainly played a critical role in more widespread human exposure to dioxins.

#### 4.2.2 Bioavailability

Bioavailability of dioxins is a term used to define the available concentration of compounds in the environment that can be biologically transferred to plants and animals. In all environmental media dioxins are considered to be bioavailable. It is the bioavailability of dioxins in media that allow for these compounds to be transferred into biota and then bioaccumulated throughout the food chain. This relationship between bioavailability and bioaccumulation is best illustrated in Figure 10.



**Figure 10 Illustration of bioavailability and bioaccumulation of dioxins on media**

#### 4.3 Degradation

Once a chemical compound is deposited in the environment its movement and accumulation are determined by the process and rate in which it degrades. Degradation is when a chemical compound reacts and its structure deteriorates until it is inert. The quicker a compound degrades the less likely it is to accumulate in the environment. The degradation rates of chemical compounds are referred to as degradation half-lives, which are estimates based on their chemical structure and reaction to the media structure (i.e. soil, sediments, water, air and biota) in which they exist. Each chemical compound reacts uniquely to the media it comes into contact with. The study of the degradation of POPs is important because it provides a basis for removing these toxic pollutants from the environment. The degradation processes most known to remove dioxins from the environment include: biodegradation, hydrolysis, atmospheric oxidation and photolysis

(Boethling et al., 2009). For any of these biological or chemical processes, the actual rates in which compounds degrade are determined by a combination of substance-specific characteristics and environmental conditions. There is not one specific degradation rate for all dioxins, nor is there a specific degradation rate for individual media. Each dioxin congener reacts uniquely to each media it is in contact with under specific environmental conditions.

#### 4.3.1 Half-Lives

Degradation half-lives of dioxins in the atmosphere, water, soil and sediments are the primary focus of research simply because understanding the persistency of these compounds in these media dictate the potential for transmission to biota, such as humans. Degradation half-life values for two dioxin congeners (i.e. 2,3,7,8 TCDD and 2,3,7,8 TCDF) in the atmosphere, water, and soil are presented in Table 5, highlighting discrepancies in estimated values between two different studies. Degradation half-life values in Study One for water and soils are an order of magnitude smaller than those estimated in Study Two. One explanation for these differences is that Study One is reflective of environmental conditions at 25 degrees Celsius, whereas Study Two reflects conditions at 7 degrees Celsius. Degradation half-life values in all media are dependent on temperature to a certain extent. Variability in Table 5 is also reflective of the unknown assumptions in degradation processes that were used for calculating degradation half-life values in both Study One and Two.

**In soils:** Dioxins in soil degrade via biodegradation, photodegradation, and or atmospheric oxidation. Depending on which of these degradation processes were chosen to calculate the degradation half-life values, estimates can vary greatly. Variability in degradation half-lives for soil may also be due to the difference in soil types analyzed for each Study. Soil type and relative desorption rates are known to affect degradation half-lives of dioxins (Adriaens et al., 1995). For example, Study One soils may have been analyzed in sandy silt where dioxins are more available to aerobic microbial activity supportive of biodegradation whereas in Study Two soil conditions may have been clayey, sequestering residual concentration of dioxins from means of biodegradation.

**In water:** Dioxins in water may be degraded from hydrolysis, although this process is known to be extremely slow and therefore is most often neglected. Considering that photodegradation rates of dioxins in water are not strongly correlated with temperature, then the question arises to what depth of the water column do the degradation half-life value represent in Table 5? Photodegradation can occur at any water depth where light is present, although most UV light is known to be absorbed in the top two meters. Dioxins may also degrade in water through biodegradation, which is dependent on the concentrations of inorganic and organic nutrients, presence of particulate matter, temperature, oxygen concentration, redox potential, adaptation of the microbial population and also on the concentration of dioxins present (Sinkkonen et al., 2000). This complexity in environmental factors associated with biodegradation as well as the question of assumed water depth for allowing photodegradation are reason enough to explain the variability in degradation half-life values estimated for water in Table 5.



**In air:** Even though the degradation half-life values for air, as presented in Table 5 are relatively similar and of the same order of magnitude, research indicates that these values are similarly dependent on environmental conditions such as in water and soil. The dominant degradation processes that degrade dioxins in the lower region of the atmosphere (i.e. troposphere) are photolysis and reactions with OH (hydroxyl) radicals (Sinkkonen et al., 2000). Reactiveness with OH radicals increases as temperature increases, therefore degradation half-life decreases as temperature increases. Dioxins in the vapor phase are known to be removed quicker than those adsorbed onto particles in the atmosphere (Atkinson, 1991).

**In humans:** Just as it is difficult to accurately estimate the degradation half-lives for dioxins in nature, the same is true for determining degradation half-lives of these compounds within humans. Physical variables such as age and sex, as well as individual health variables including body fat and smoking habits can affect degradation of dioxins in human bodies. A comprehensive report compared data from more than 30 studies on congener-specific degradation half-lives based on human health variables (Milbrath et al., 2009).

**Table 5 Estimated Degradation Half-lives, hrs. (<sup>1</sup>Mackay et al. (1997); <sup>2</sup>Sinkkonen et al. (2000))**

	Air	Water	Soil
<b>Study One<sup>1</sup></b>	@ 25 degrees C		
Dioxin (2,3,7,8-TCDD)	170	550	17000
Furan (2,3,7,8-TCDF)	170	550	17000
<b>Study Two<sup>2</sup></b>	@ 7 degrees C		
Dioxin (2,3,7,8-TCDD)	200	4000	900,000
Furan (2,3,7,8-TCDF)	320	6400	550,000

#### 4.3.2 Steady-State Releases

If atmospheric releases of persistent compounds are relatively constant over a sufficiently long period of time, increases in environmental concentrations due to these steady-state emissions are eventually balanced by increases in losses. Losses are assumed to be from intra-media degradation at varying stages of deposition in air, water and or soil. Losses are however not limited to just degradation processes. Concentrations in soil for example can decrease due to leaching, volatilization, etc.; where soils are exposed to continual accumulation of dioxins, topsoil concentrations will increase until the only mass flux route is through re-volatilization to the atmosphere (Jones et al., 1999). From the point at which steady-state emissions are first introduced to an environment, concentrations eventually plateau also resulting in an overall decrease in bioavailability. This is shown in Figure 11, where the percent of bioavailability for POPs in soil is “squeezed” in between increasing “non-bioavailable” concentrations and increasing environmental losses.

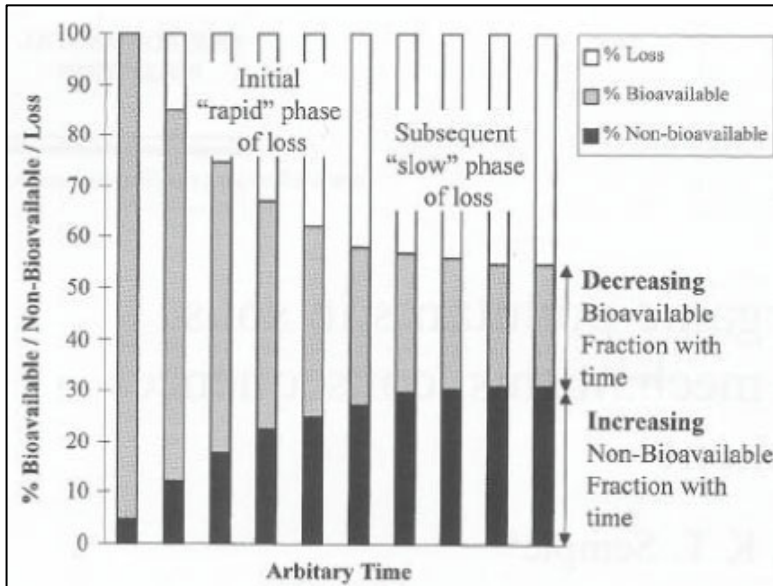


Figure 11 Changes in bioavailability as function of soil contact time (Reid et al., 2000)

If steady-state emissions were to drop suddenly to near zero, the rate of reduction would in most cases be exponential (Van de Meent et al., 2000). This concept is illustrated in Figure 12. Figure 13 is a further iteration of Figure 12, where four compounds are presented; three of which have specific half-life values and the fourth which is classified as non-biodegradable. Each compound is assumed to be immobile in soil and emitted at the same rate of 10kg/d for 100 days, at which point emissions are halted. The results presented in Figure 13 illustrate that as the half-life for a given compound reaches the total time in which it is released, reductions become somewhat linear. It is shown that for a half-life 10 percent or less than the time it is released into the environment (in this case 10 days or less), reduction remains exponential.

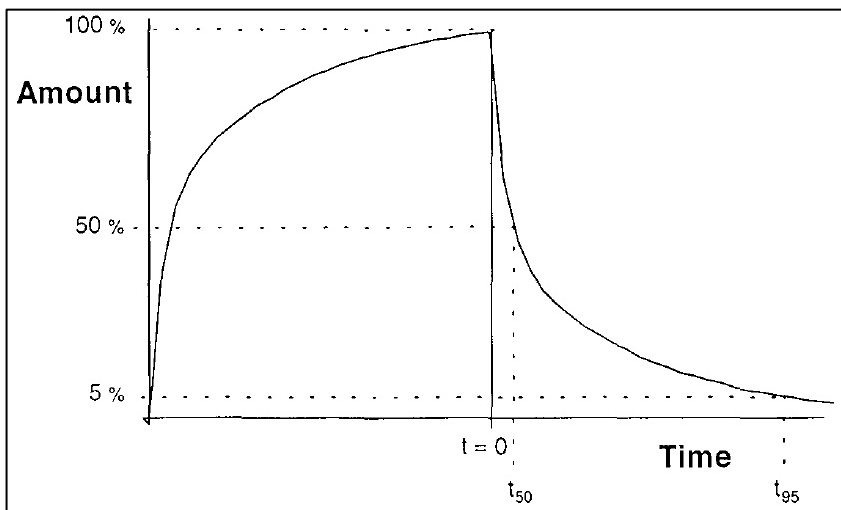


Figure 12 Reduction of Steady-State Emissions in the Environment (Van de Meent et al., 2000)

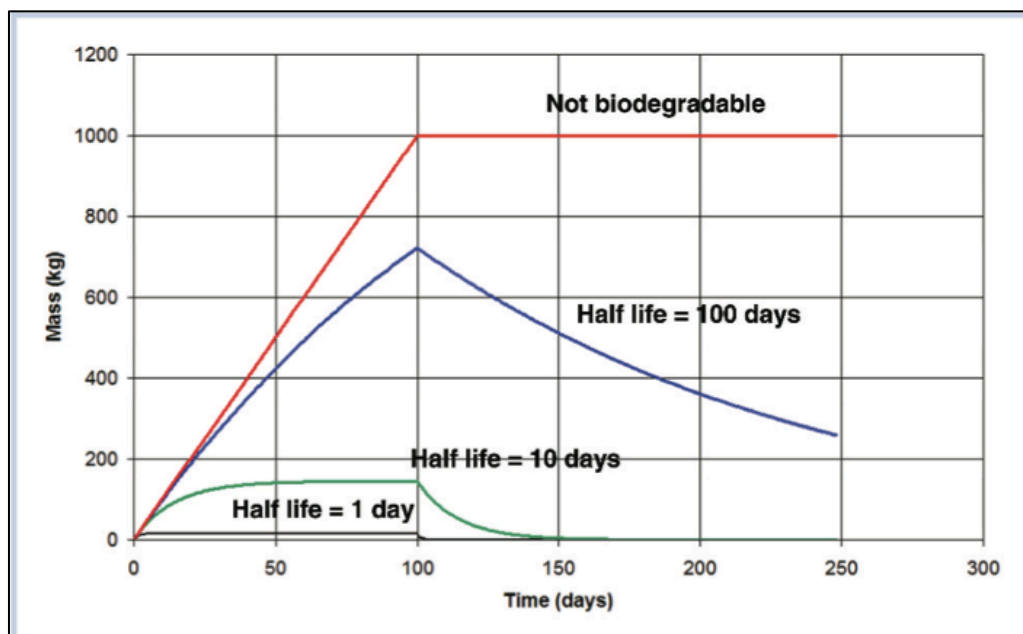


Figure 13 Environmental accumulation and reduction due to half-life values (Boethling et al., 2009)

## 5 TOXICITY & HUMAN EXPOSURE

Environmental media such as soil, air, water, and plants provides a relatively safe medium in which a dioxin molecule can react and degrade. It is their resistance to react on these media, which eventually allow organic pollutants to enter humans. The toxic effect of a dioxin molecule is realized when it reacts with a biomolecule, most notably in vertebrates in the food chain and humans. The ultimate goal is obviously to remove unnecessary, potentially toxic chemicals from the environment although Wania et al. points out that toxicity is inherently related to reactivity and a chemical that does not react at all is unlikely to show any biological effects (1998). As interesting as this notion may seem, science has however shown that dioxins will undoubtedly react when accumulated in humans. This section will discuss how the toxicity of these compounds are assessed in inventory reporting as well as discuss activity within the food chain, such as bioaccumulation and bioavailability, that often leads to human exposure.

### 5.1 Measuring Toxicity

As it was mentioned in the introduction of this report, of the hundreds of congeners associated with dioxins, there are seventeen 2,3,7,8-substituted PCDD/F congeners and twelve dioxin-like PCB congeners considered as toxic to human and environmental health. What makes these PCDD, PCDF and dioxin-like PCB congeners toxic is their high affinity to the Ah-receptor, which is a cytosolic receptor protein present in most vertebrate tissues. Once bound with any one of these 29 toxic congeners, the Ah-receptor releases biochemical and toxic responses. Toxic congeners are each given a Toxic Equivalent Factor (TEF). The TEF for any given congener is measured in comparison to the 2,3,7,8-TCDD congener. The 2,3,7,8-TCDD congener is the most thoroughly studied

congener because it is the most toxic of all congeners; therefore, it has been assigned the toxicity value of TEF=1. The TEF of the other 28 toxic congeners are assigned in terms of their relative toxicities in relation to 2,3,7,8-TCDD, as determined *in vitro* and *in vivo* studies.

The total toxicity of a sample is calculated by multiplying the concentrations of congeners present by their respective TEF. This in turn yields the total Toxic Equivalent value (TEQ), expressed in grams TEQ, which represents the total 2,3,7,8-TCDD-like activity of the mixture. In 1990, the International Toxic Equivalent Factor (I-TEF) for the calculation of International Toxic Equivalents (I-TEQ) was published as an attempt to create a new method to facilitate concise communication among scientists and regulatory agencies internationally (Kutz et al., 1990). Since the early 1990's, the World Health Organization (WHO) has organized expert meetings with the objective to harmonize the TEFs for dioxins on the international sphere. There is some discrepancy between International TEF and WHO TEF values, primarily being that I-TEF is outdated and does not include TEF values for dioxin-like PCBs. International TEF values are presented in Table 6.

**Table 6 International Toxic Equivalent Factors (Kutz et al., 1990)**

International TEF Values	
Compound	TEF
Chlorinated dibenzo-p-dioxins	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001
Chlorinated dibenzofurans	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.001

The most current WHO TEF values (Table 7) were published in: *The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxin and Dioxin-like Compounds* (Van den Berg et al., 2006). The U.S. Environmental Protection Agency in a recent 2010 report has adopted these same WHO TEF values (U.S. EPA, 2010).

**Table 7 WHO Toxic Equivalent Factors (Van den Berg et al., 2006)**

WHO 2005 TEF Values	
Compound	TEF
Chlorinated dibenzo-p-dioxins	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
Chlorinated dibenzofurans	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003
Non-ortho-substituted PCBs	
3,3',4,4'-tetraCB (PCB 77)	0.0001
3,4,4',5-tetraCB (PCB 81)	0.0003
3,3',4,4',5-pentaCB (PCB 126)	0.1
3,3',4,4',5,5'-hexaCB (PCB 169)	0.03
Mono-ortho-substituted PCBs	
2,3,3',4,4'-pentaCB (PCB 105)	0.00003
2,3,4,4',5-pentaCB (PCB 114)	0.00003
2,3',4,4',5-pentaCB (PCB 118)	0.00003
2',3,4,4',5-pentaCB (PCB 123)	0.00003
2,3,3',4,4',5-hexaCB (PCB 156)	0.00003
2,3,3',4,4',5'-hexaCB (PCB 157)	0.00003
2,3',4,4',5,5'-hexaCB (PCB 167)	0.00003
2,3,3',4,4',5,5'-heptaCB (PCB 189)	0.00003

## 5.2 Main Pathways for Human Exposure

Dioxins bioaccumulate in aquatic and terrestrial organisms that are common in the human food chain. Once entering the biota sphere, dioxins will move up the food chain and concentrate in animals, specifically vertebrates, where they will biomagnify because of their strong resistance to metabolism. Top predators, such as humans, will be subject to these now readily bioavailable dioxins in the food chain. A study that analyzed the food chain, water consumption, and ambient air inhalation, concluded that the ingestion of food accounts for 98% of human exposure (Travis et al., 1987). Results from this study are summarized in Table 8. These results are consistent with other literature, which indicate that 90 to 98% of daily human exposure of dioxins is from food consumption (ATSDR, 2012; King, 1999). The percentages in Figure 8 that are related to food types are however oversimplified because they only consider four food types, i.e. vegetable, meat, milk and fish. The following section of this report will provide more detailed estimates of dietary exposure levels relative to varying food groups.

Exposure through respiration is in most cases considered to be negligible unless air concentrations are exceedingly high. For example, one study concluded that for a person breathing ambient air near an incinerator, dioxin exposure from respiration is 200 times less than the exposure from ingesting milk from a cow grazing near the same incinerator (Connett et al., 1987). Exposure in this case is equal to eight months of breathing or consuming one liter of milk. Similarly, for high-fat dairy products, the ingestion of one-quarter pound of butter would be equivalent to about 1.5 years of breathing (Connett et al., 1987).

**Table 8 Predicted Average Daily Intake of TCDD by Humans (Travis et al., 1987)**

Source	Daily Intake (ng/day)	Percent of the Total Daily Intake
Air	0.001	2%
Water	6.5E-06	<0.01%
Food (Total)	0.046	98%
Vegetables	0.005	11%
Milk	0.013	27%
Meat	0.023	50%
Fish	0.005	10%

Table 9 shows a detailed breakdown of dietary intake of dioxins divided into 19 food groups in the year 2001. Values in Table 9 are the mean upper bound dietary exposure levels for an average adult in the U.K. organized into dioxins (PCDD/Fs) and dioxin-like PCBs. The total dietary exposure from all food groups in 1982, 1992, 1997 and 2001 is presented in Table 10. A more comprehensive table of dietary exposure from all food groups for 1982, 1992, 1997 and 2001 is included in Appendix A. It is interesting to note that in Table 10, as total dietary exposure decreases from 1982 to 2001, the percent of dioxin-like PCBs to total dioxin-like compounds of dietary exposure increases from 40 percent to 56 percent respectively.

In more developed countries, current sources of newly formed PCBs are considered to be nearly non-existent. For this reason alone, all observed dietary exposure to dioxin-like PCB congeners is derived almost entirely from releases of old PCBs stored in environmental reservoirs. It has been reported that the significance of dioxin-like PCBs in terms of human body burden is anywhere from 50 to 70% of the total toxic dioxin-like compound ( $\Sigma$ TEQ) exposed to humans (Alcock et al., 1998; Weber et al., 2008). Thus, at least one half of the overall risk to the general population from dioxins comes from environmental reservoirs. These results are consistent to the U.S. E.P.A.'s more recent study, attributing about one third of human exposure to dioxins consequence of dioxin-like PCBs and their respective environmental reservoirs (2006).

**Table 9 Average Upper bound dietary intake of dioxins by food group for U.K. adult, 2001 (F.S.A., 2003)**

Food Group	2001		
	Mean intake (pg TEQ/kg bodyweight/day)		
	Dioxins	PCBs	Total
Carcass meat	0.07	0.06	0.12
Offals	0.09	0.02	0.11
Meat products	0.04	0.05	0.09
Poultry	0.02	0.04	0.06
Fish	0.07	0.20	0.30
Oils and fats	0.01	0.02	0.03
Potatoes	0.02	0.01	0.02
Milk	0.03	0.03	0.06
Dairy products	0.12	0.10	0.22
Eggs	0.01	0.01	0.02
Misc. cereals	0.02	0.02	0.04
Bread	0.01	0.01	0.02
Nuts	0.01	0.01	0.01
Sugar and preserves	0.02	0.01	0.03
Fruit products	0.01	0.01	0.01
Green vegetables	0.01	0.01	0.01
Other vegetables	0.01	0.01	0.01
Canned vegetables	0.01	0.01	0.01
Fresh fruit	0.01	0.01	0.01
<b>Total</b>	<b>0.4</b>	<b>0.5</b>	<b>0.9</b>

NOTE: Total refers to the dietary intake by a consumer consuming one or any combination of the foods containing dioxins and PCBs. These values are derived from a distribution of the consumers' consumption patterns with regards to the individual foods. The combined dietary intakes of dioxins and PCBs were calculated from the combined concentrations. Therefore Total dietary intake of dioxins and PCBs represents the average consumer for all foods combined and is not equal to the sum of the intakes from the individual foods.

**Table 10 Average dietary intake of dioxins for U.K. adult, 1982-2001 (F.S.A., 2003; M.A.F.F., 1997)**

Year	Total mean intake from all food groups (pg TEQ/kg bodyweight/day)		
	Dioxins	PCBs	Total
1982	4.1	2.7	<b>6.8</b>
1992	1.5	0.9	<b>2.4</b>
1997	0.9	0.9	<b>1.8</b>
2001	0.4	0.5	<b>0.9</b>

### 5.3 Quantifying Human Exposure

Given this clear link between diet and human exposure it is important to bring into perspective: (1) estimated intake levels in which humans are being exposed to dioxins in the food chain and (2) identify allowable levels of dietary human exposure without toxic effects. These levels are summarized in Table 11, where tolerable intake levels are compared with estimated intake levels of dioxins in different regions, for both daily and monthly time frames.

**Table 11 Tolerable vs. estimated intake levels of dioxins**

DAILY	Tolerable Intake level	Units	PCDD/Fs	DL-PCBs	Year Reported	Region	Source
	1 - 4	pg I-TEQ/kg bw/day	x	x	1998	-	WHO (1998)
0.7	pg TCDD/kg bw/day	x	x	2012	-	U.S. EPA (2012)	
DAILY	Estimated Intake Levels	Units			Year Reported		Source
	0.93 - 3.0	pg TEQ/kg bw/day	x		1999	E.U.	King (1999)
	0.9	pg TEQ/kg bw/day	x	x	2001	U.K.	F.S.A. (2003)
	1.45 - 2.79	pg TEQ/kg bw/day	x	x	2000-2002	Japan	Nakatani (2011)
	2 - 6	pg TEQ/kg bw/day	x		1998	Global	WHO (1998)
Month	Tolerable Intake level	Units			Year Reported		Source
	70	pg TEQ/kg bw/month	x	x	2002	-	JECFA (2002)
	Estimated Intake Levels	Units			Year Reported		Source
	9.6 - 26.8	pg WHO-TEQ/kg bw/month	x		2001 - 2004	U.S.A.	U.S. FDA (2004)

### 5.3.1 Tolerable Intake Levels

In 1998, the World Health Organization (WHO) issued a re-assessment of its Tolerable Daily Intake (TDI) verifying its original tolerance range of 1-4 pg I-TEQ/kg bw/day for all dioxin-like compounds (1998). This re-assessment report emphasized that the TDI represents a tolerable daily intake for long-term time exposure and that occasional short-term spikes above the TDI do not result in any negative health consequences provided that the averaged intake over long periods is not exceeded. In many industrialized countries the average total TEQ exposure is likely to be within the range of or higher than the TDI, between 2 - 6 TEQ pg/kg bw/day, indicating that a large portion of the population is at risk of dietary dioxin exposure above the WHO TDI limit (WHO, 1998). WHO acknowledges that health effects experienced by those exceeding WHO TDI limits are considered to be subtle and not overtly adverse (1998). Following this report in 2001, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) performed an updated comprehensive risk assessment of all dioxin-like compounds. It determined that in order to assess long or even short-term risks to health from dioxins, total or average intake should be assessed over a period of at least one month (JECFA, 2002). The TDI is now expressed in terms of the PTMI or Provisional Tolerable Monthly Intake is 70-pg/kg bw/month and is considered to be the amount of dioxins that can be ingested over a lifetime without detectable health effects.

In 2012, the U.S. E.P.A. established an oral reference dose (RfD) for 2,3,7,8-TCDD of 0.7 pg TCDD/kg bw/day. This RfD, like the WHO TDI, is an allowable daily oral exposure limit to dioxins where no toxic effects are expected over a lifetime. This recently published RfD has gained attention for not only being less than the WHO TDI, it is considered a “strict” new regulatory requirement by industry and furthermore has been noted as confusing U.S. consumers who are known to be exposed to doses higher than the RfD in their typical diet.



### 5.3.2 Estimated Intake Levels

In all countries where data is available, decreases in dietary exposure have been reported similar to those presented previously in Table 10 for U.K. adults. The *Compilation of EU Dioxin Exposure and Health Data* reported in 1999 that Germany for example, between the years of 1989 and 1995, reported a 45% decrease in human exposure via the food chain. All reports presented in Table 11 for estimated intake levels, except for the U.S. F.D.A. study, were conducted before the WHO PTMI limit established in 2002 and are therefore presented in daily levels. The U.S. F.D.A. data presented in Table 11 was obtained from a total diet study where varying ages and sexes were studied. This data is included in Appendix A. It is important to pay close attention to data in Table 11 with respect to which reports have reported dietary exposure of dioxins from PCDD/Fs, dioxin-like PCBs (DL-PCBS) or both. Estimates not including dioxin-like PCBs can be considered as underestimates because of the high percentage of dietary exposure previously discussed as being associated with dioxin-like PCBs.

## 6 DIOXINS IN WASTE-TO-ENERGY (WTE) EMISSIONS

In the early nineties, environmental agencies in the U.S., Europe and Japan established the very stringent WTE emission standard of 0.1 nanograms TEQ dioxins per standard cubic meter of stack gas (ng TEQ/dscm). This standard encouraged innovation in the WTE industry such as the modification of Air Pollution Controls (APCs). With the use of APCs, dioxin emissions from WTE incinerators in the U.S. alone have decreased by a factor of 3000 (Figure 14). New modern APCs have proven effective in removing dioxins from WTE emissions and therefore eliminating WTE as a major dioxin source contributor worldwide. Continued analysis of samples from human tissue and sediments have reflected these recent reductions of dioxins in industrial regions where modern emission controls have been implemented (M.A.F.F., 1997).

To better highlight the decrease in dioxins throughout the WTE industry worldwide, emission data from 40 WTE facilities in the U.S., 123 in France and 35 in the Republic of Korea are presented in the following sections, along with estimates of total national dioxin releases from all incinerated waste in these countries. Also presented is the emissions data for China, demonstrating the potential that a developing country with an exceedingly high industrial growth rate has for achieving dioxin releases below the E.U. standard. Average dioxin emissions in stack gas (ng TEQ/dscm) as well as dioxins emitted (g TEQ) for these countries are presented in Table 12. In Appendix B the calculation of estimated total dioxin emissions are explained and the WTE dioxin emission data for each of these four countries is provided.

**Table 12 Dioxin releases from WTE emissions in U.S., France, the Republic of Korea and China**

Country	Year Sampled	Facilities Sampled	Average Dioxins in Stack Gas (ng TEQ/dscm)		MSW Combusted (million tons)	Dioxins Emitted (grams TEQ)
			Cumulative	Weighted		
USA	2012	40	0.032	0.027	16.0	1.97
France	2008	123	0.013	0.023	13.8	0.79
Korea	2010	35	0.0069	0.0065	3.9	0.11
China	2006	19	0.37	0.35	1.9 <sup>a</sup>	2.9

NOTE: MSW combusted given in metric tons. Calculation of dioxins emitted (g TEQ) shown in Appendix B using weighted average of dioxins in stack gas.

a. - Based on daily capacity of facility operating 24 hours a day for 300 days of the year

## 6.1 USA

The adverse health effects of dioxins were not recognized until the late eighties, by which time the total U.S. dioxin emissions were estimated at 13,965 grams TEQ in 1987. The major source of dioxins at that time was municipal waste combustion (incineration of refuse) estimated to account for 7,858.8 g TEQ or 63.8% of total TEQ recorded in this year (U.S. EPA, 2006). As a result of retrofitting U.S. WTE plants in the period 1990-2000 with sophisticated APCs, levels of dioxins in WTE emissions dropped precipitously, Figure 14. As it was previously mentioned in Table 1, in 2000 the U.S. E.P.A. reported that waste incineration accounted for only 5.9% of total dioxin releases from all sources. Table 13 shows that the U.S. EPA recorded a total reduction of 99.03% of dioxin emissions from municipal waste combustion nationwide between 1989 and year 2000 levels (2006). A further reduction of 95.72% of dioxins in WTE emissions has been estimated between 2000 and 2012. This is an overall reduction of 99.96% between 1989 and 2012.

**Table 13 Decrease in U.S. WTE dioxin emissions**

Inventory Year	WTE Dioxins Emitted (g i-TEQ)	Cumulative % Reduction	% Reduction from 1987
1987 <sup>1</sup>	7858.8	-	-
1995 <sup>1</sup>	1101.3	85.99%	85.99%
2000 <sup>1</sup>	76.3	93.07%	99.03%
2012 <sup>2</sup>	3.27	95.72%	99.96%

1 - U.S. EPA Reported Dioxin Emissions from Municipal Waste Combustion; (U.S. EPA, 2006)

2 - Based on emission data from 40 WTE facilities operated by Covanta. (Van Brunt, 2013)

The 2012 estimate of 3.27 g TEQ is based on the incineration of 26.5 million metric tons of MSW and an average dioxin concentration in stack gas emissions of 0.027 ng TEQ/dscm. The average emission value is based on a sample study of 40 WTE facilities in 2012. Emissions data for this 2012 sample study is presented in Figure 15, where 16 million metric tons of MSW were incinerated and a total of 1.97 g TEQ of dioxins released. Dioxin concentrations in emissions for these facilities ranged from 0.0005 to

0.2204 ng TEQ/dscm; the average weighted value was 0.027 ng TEQ/dscm. As it is shown in Figure 15, the average dioxin concentration in emissions is below the national and E.U. emission standard of 0.1 ng TEQ/dscm while only two facilities are operating above this standard. The volume of MSW incinerated in 2012 is based on reported U.S. E.P.A. estimates (2014). Both emission data from the 40 sampled WTE facilities and MSW disposition data is included in Appendix B.

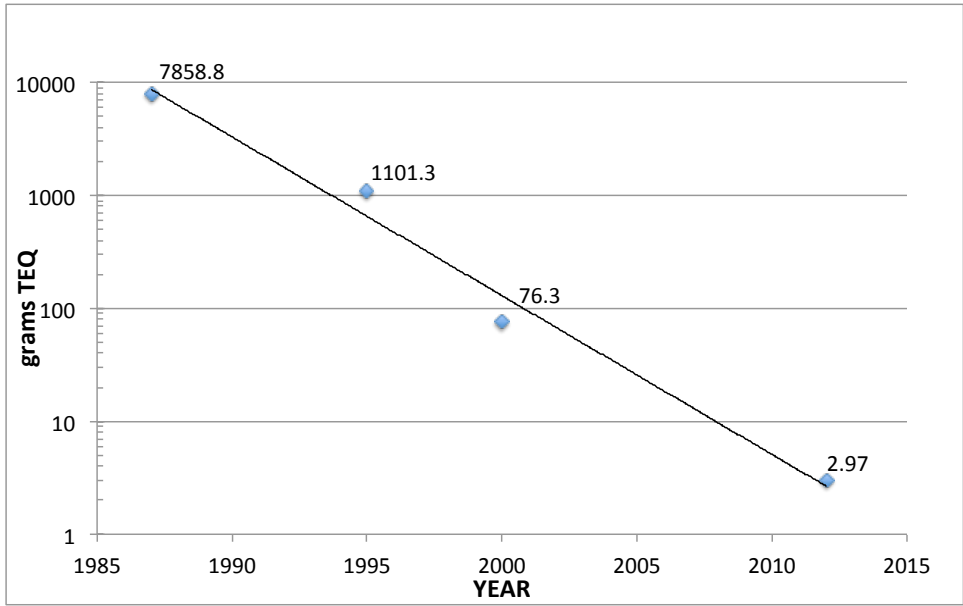
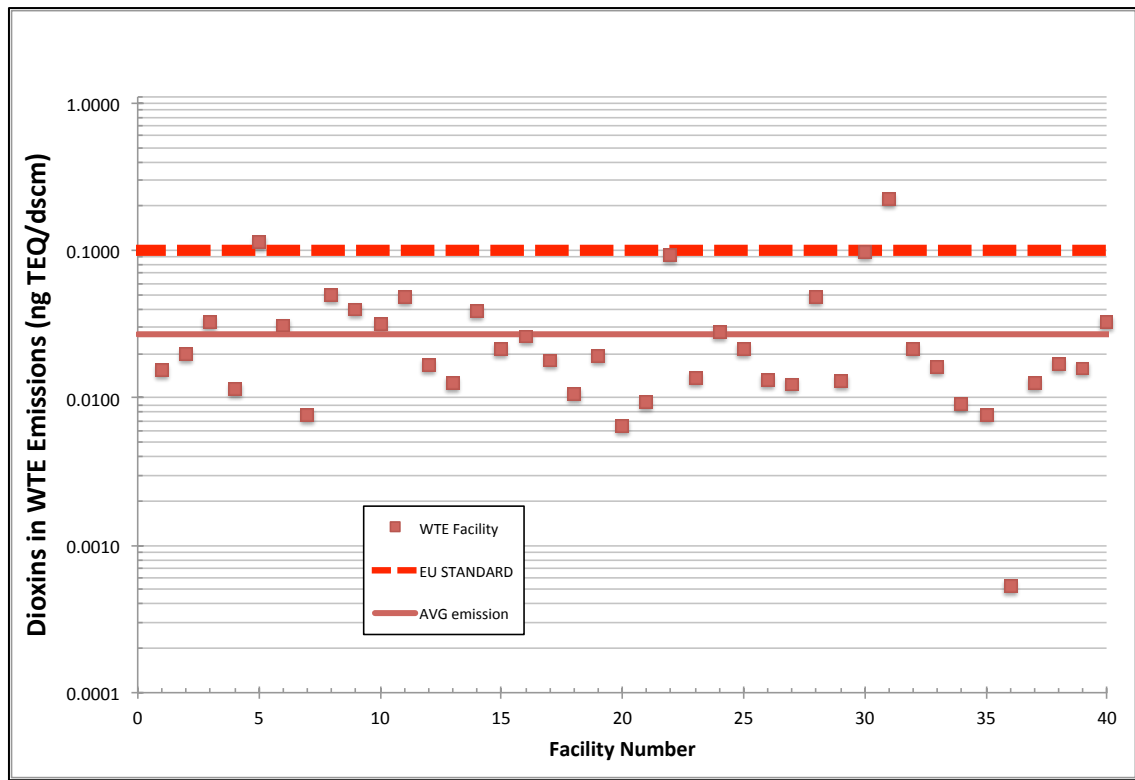


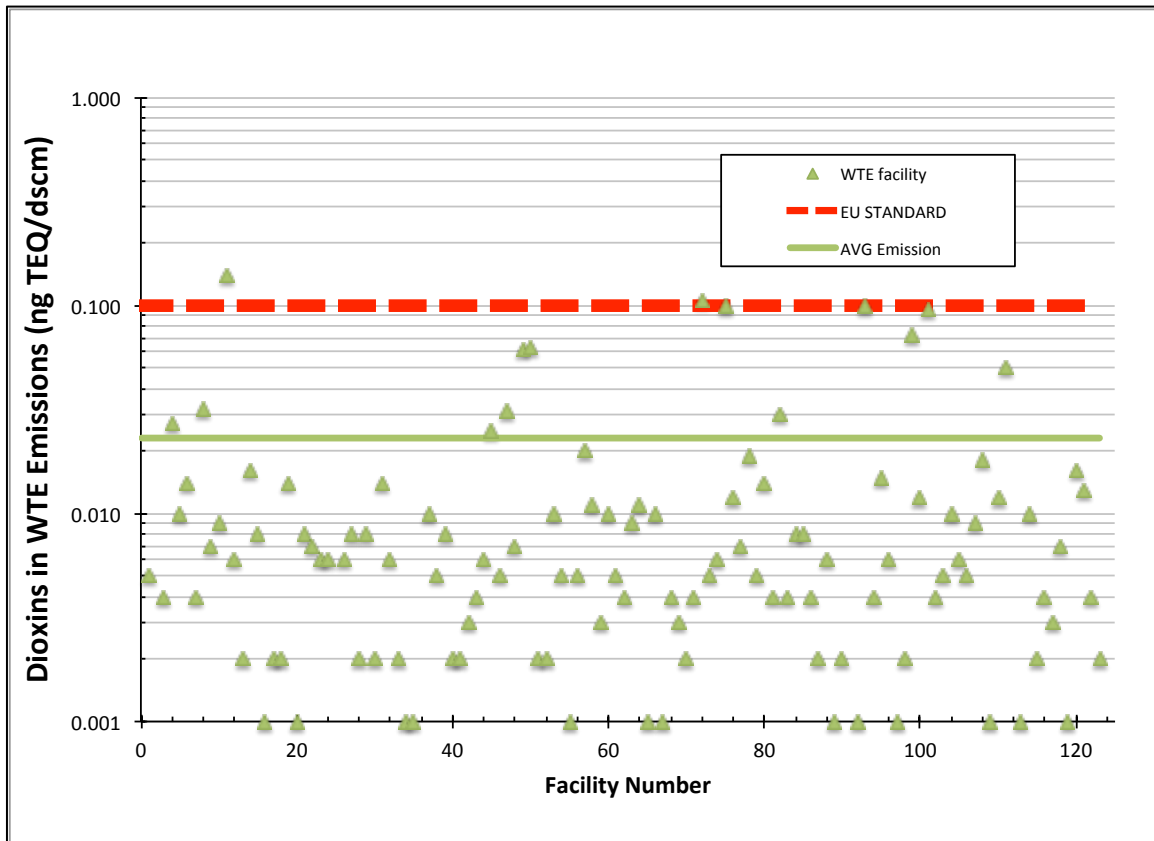
Figure 14 Reduction of dioxins in WTE emissions, U.S. (semi-logarithmic plot)



**Figure 15 Dioxin in WTE emissions from 40 WTE facilities in the U.S., 2012 (semi-logarithmic plot)**

### 6.2 France

The Earth Engineering Center conducted a detailed emissions study of 123 WTE facilities in France (Benhamou, 2010). Within these facilities, 13.8 million tons of MSW was incinerated in 2008 and 0.79 grams TEQ of dioxins were emitted. Dioxin concentrations in emissions from these facilities ranged from 0.0 to 0.14 ng TEQ/dscm; the weighted average was 0.023 ng TEQ/dscm. Figure 16 shows that the average concentration of dioxins being emitted from these WTE facilities is well below the E.U. emission standard, while only two facilities are operating above this standard. Both emission data from these 123 sampled WTE facilities and MSW disposition data are included in Appendix B.



**Figure 16 Dioxin in WTE emissions from 123 WTE facilities in France, 2008 (semi-logarithmic plot)**

### 6.3 The Republic of Korea

An Earth Engineering Center study tracked dioxin concentrations in the emissions from 35 WTE facilities in the Republic of Korea (Seo, 2014). Within these facilities, 3.9 million tons of MSW were incinerated in 2010 and 0.11 grams TEQ of dioxins were emitted. Dioxin concentrations in emissions from these facilities ranged from 0.0 to 0.0065 ng TEQ/dscm; the weighted average was 0.023 ng TEQ/dscm. Figure 17 shows

that the average concentration of dioxins being emitted from these WTE facilities is well below the E.U. emission standard and no facilities are operating above this standard. Both emission data from these 35 sampled WTE facilities and MSW disposition data are included in Appendix B. Dioxin emissions from the Republic of Korea WTE facilities are distinctly less than those recorded from WTE facilities in France and the U.S.

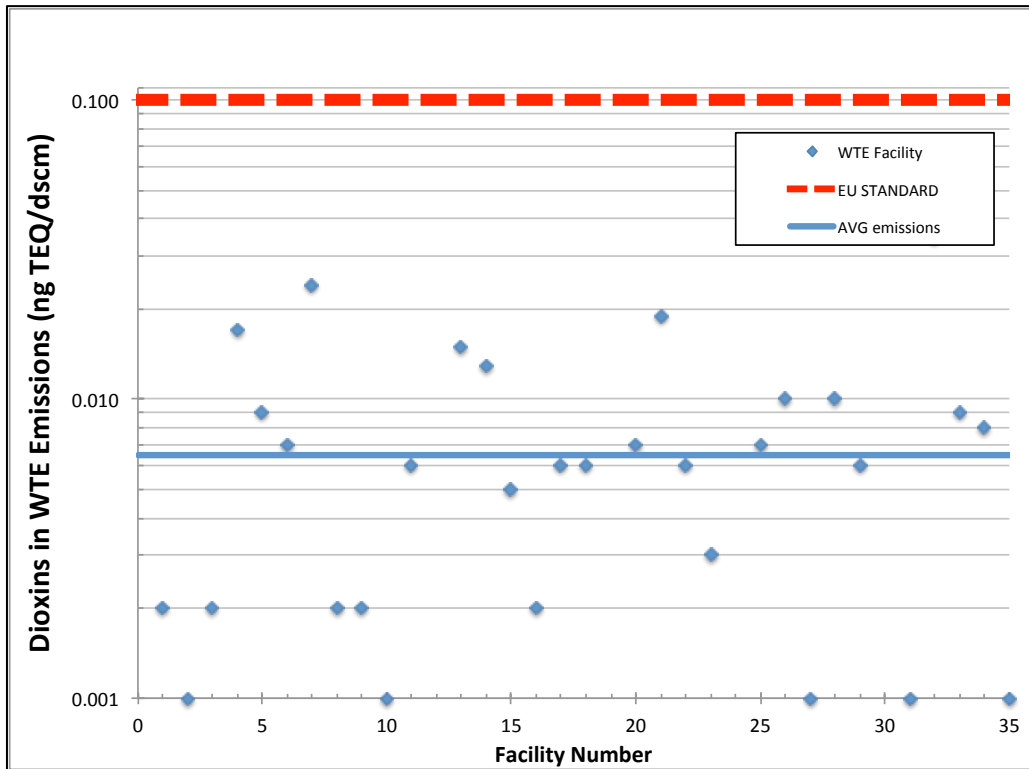


Figure 17 Dioxins in WTE emissions from 35 WTE facilities in Korea, 2010 (semi-logarithmic plot)

#### 6.4 China

In an Earth Engineering Center report issued in 2010, the majority of emissions from a sample of 19 operating WTE facilities were emitting dioxin levels above the E.U. standard (Zhang et al.). Within these facilities, 1.9 million tons of MSW were incinerated in 2006 and 2.9 grams TEQ were emitted. Dioxin concentrations in emissions from these facilities ranged from 0.03 to 2.14 ng TEQ/dscm; the weighted average was 0.35 ng TEQ/dscm. Figure 18 shows that the average concentration of dioxins being emitted from these WTE facilities is below the national China emission standard of 1.0 ng TEQ/dscm, yet above the E.U. standard. Both emission data from these 19 sampled WTE facilities and MSW disposition data are included in Appendix B.

There are currently very few available studies revealing the releases of dioxins in China, including WTE-specific emissions data. It was predicted that China’s rapid development and modernization would have resulted in an additional 100 WTE facilities to their already existing 70 plants by 2012 (Yuwen Ni, 2009). With growing public awareness

and concern of dioxin emissions, it can be expected that China's regulatory standards will soon follow suit to that of the E.U. and other developed nations. The data presented in Figure 18 shows very promising potential for China as well as other developing nations with respect to reducing dioxins in WTE emissions. It is said that China has already implemented modern technology (i.e. APCs) on a number of their WTE facilities (Zhang et al., 2010). Once China's national standards are reduced a reduction of dioxin concentrations in WTE emissions similar in that of the U.S., France, and Korea can be expected. The Earth Engineering Center at Columbia University is currently in the process of collecting up-to-date data from China WTE facilities.

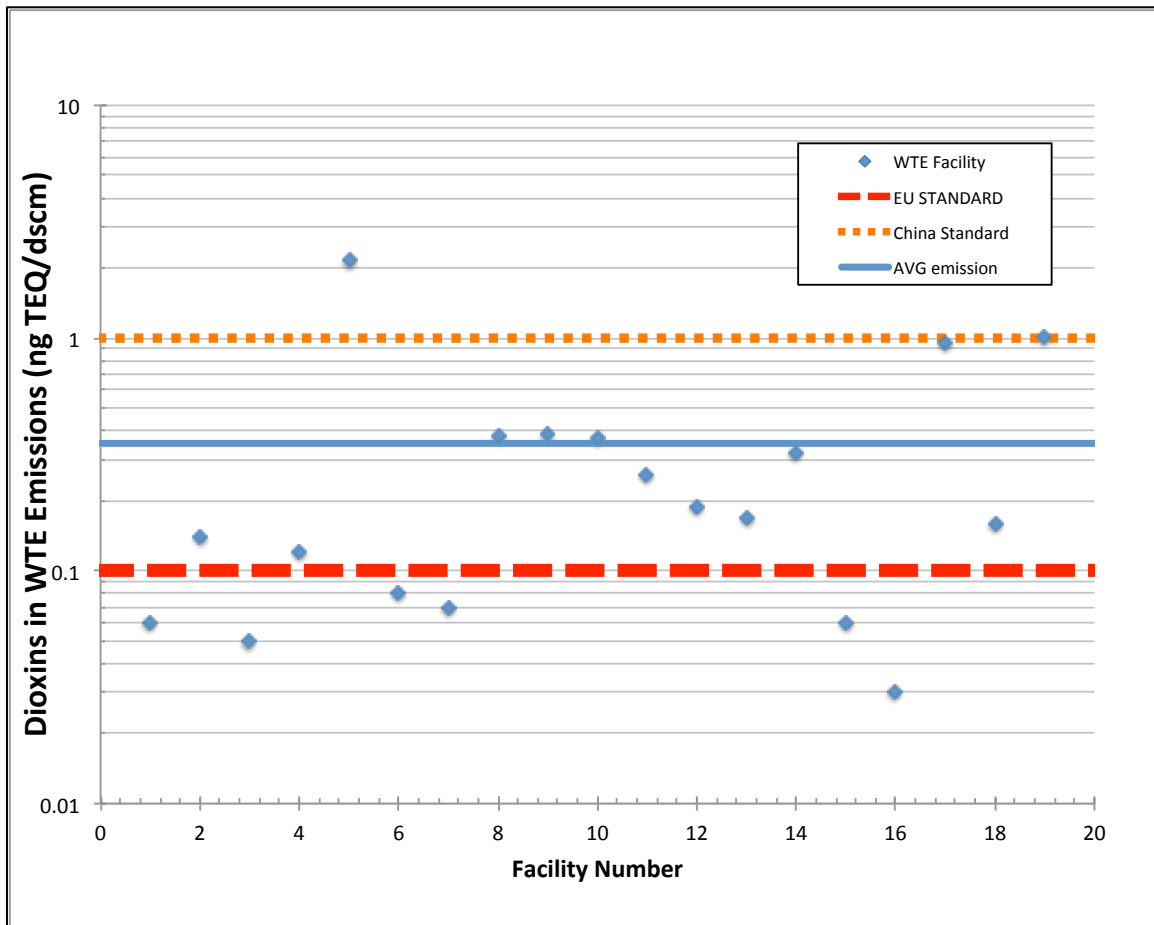


Figure 18 Dioxins in WTE emissions from 19 WTE facilities in China, 2006 (semi-logarithmic plot)

### 6.5 Total Dioxins/TEQ Ratio for Modern WTE Facilities

In order to determine the TEQ of dioxins formed during the incineration of MSW, a conventional conversion factor of 50 grams of total dioxins was considered to equal 1 gram TEQ (Deriziotis, 2004). However, the recently presented emission data from 40 WTE plants in the U.S. has shown that an actual ratio of total to toxic (TEQ) dioxins is 80 to 1. This ratio is considered to be a more accurate and up-to-date estimate based on currently operating modern WTE facilities.

In Appendix B, data used to calculate this ratio (TEQ and actual measured levels of total dioxins) from forty U.S. WTE facilities is included in tabular format. In order to derive an accurate conversion factor, two calculations were performed: one considering all data points and a second disregarding two outlying data points, see Table 14. Figure 19 shows all data points of actual total/TEQ ratio plotted, highlighting the selected mean value for all points that disregards the two outliers.

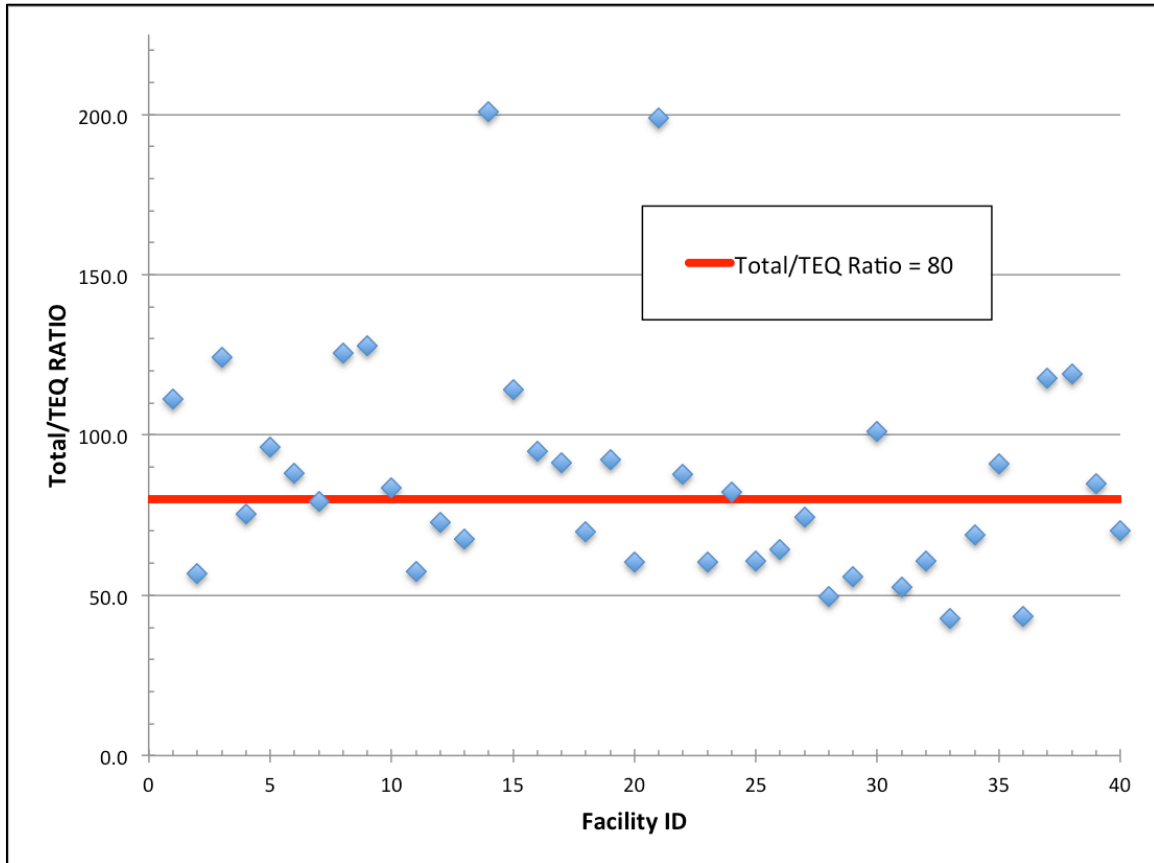


Figure 19 All data points of total dioxins/TEQ ratio

Table 14 Calculated total dioxins/TEQ ratio values

	Mean	Mean w/o Outliers
Total/TEQ RATIO	<b>86.90</b>	<b>80.95</b>

### 6.6 Composition of WTE Emissions (PCDD/Fs and Dioxin-like PCBs)

As it has been noted previously, dioxin-like PCBs from current sources are nearly non-existent which is consistent with levels of dioxin-like PCBs in WTE emissions from modern facilities. Table 15 shows the composition of WTE emissions from a facility in Kyoto, Japan reported in a 2001 study. This facility is said to have APCs such as a bag filter and slaked lime spray for waste gas purification. Total TEQ composition in Table

15 is broken into PCDD/F and dioxin-like PCB contributions. Dioxin-like PCBs are shown to represent a very small fraction (8%) of total TEQ in emissions (Sakai et al., 2001). Of this small percentage, it was found that less than 10% of total TEQ deposited is attributed to dioxin-like PCBs (Ogura et al., 2001). Total PCDD/F releases presented in Table 15 are consistent with Stockholm Convention estimates of average releases of PCDD/Fs from the incineration of municipal solid waste which are 0.02 ng I-TEQ/Nm<sup>3</sup> (Stockholm Convention, 2008). Given what was previously stated about the large percentage (50-70%) of human exposure associated with dioxin-like PCBs, WTE emissions are not strong contributors to human exposure.

**Table 15 PCDD/Fs and Dioxin-like PCBs in Emission Gas from modern WTE facility (480 ton/day capacity) in Kyoto, Japan, 2000 (Sakai et al., 2001)**

Stack Gas Composition		
Oxygen	10 %	
Wet gas vol	45600 Nm <sup>3</sup> /h	
Dry gas vol	36500 Nm <sup>3</sup> /h	
Particulate matter	0.0015 g/Nm <sup>3</sup>	
HCl	10 ppm	
CO	2 ppm	
	(ng TEQ/Nm <sup>3</sup> )	% Total
ΣDioxin-like PCBs	0.0031	8%
ΣPCDD/Fs	0.036	92%
Total	0.0391	

## 7 CONCLUSIONS

The study included emission data from 40 WTE facilities in the U.S., 123 in France and 35 in the Republic of Korea, along with estimates of total national dioxin releases from all other type of incinerators and other industrial sources of dioxins. For countries where modern APCs have been implemented, on average an estimated 0.04 to 0.11 grams TEQ of dioxins are released per million tons of MSW incinerated. The Republic of Korea in 2010 is reported to incinerate the highest percent of MSW at 55%, while France and the U.S. incinerated 41% in 2010 and 7% in 2012, respectively. Also presented in this report is the emissions data for 19 WTE facilities in China where, in 2009, 15% of the MSW was incinerated.

Table 16 shows national estimations of total dioxins (g TEQ) emitted from the incinerations of MSW in each of these countries. The national estimates presented in Table 16 are based on waste disposition data for the indicated years and can be found in Appendix B. The decreasing global trend in dioxin levels in WTE emissions indicates that by using weighted averages with more current waste disposition data, as in the case of France and China, total dioxin estimates are considered to be conservative at the least. For countries with modern APCs (i.e. U.S., France and the Republic of Korea), it is estimated that on average 0.04 to 0.11 grams TEQ of dioxins are released per million tons of MSW combusted. In Table 16 the Republic of Korea is shown to combust the highest



percent of MSW at 55%, while France, U.S. and China combust 41%, 16% and 15% respectively. Box-and-whisker plots in Figure 20 and Figure 21 also highlight the large range of emission data sampled in these four countries.

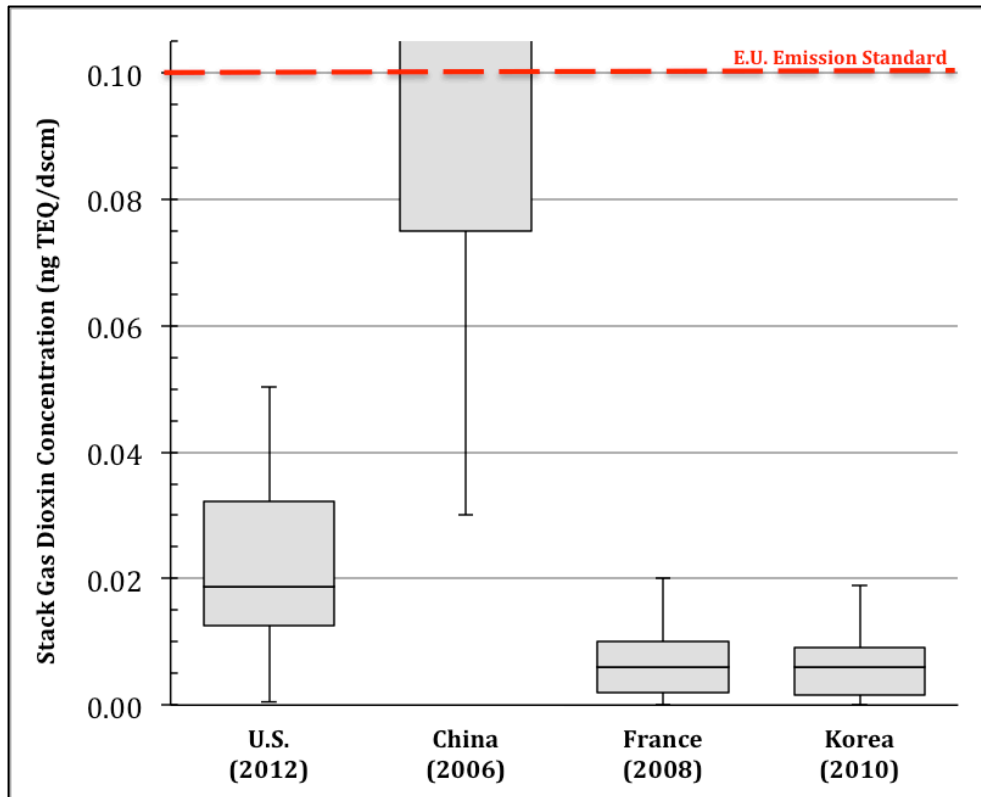
**Table 16 Estimated total dioxins (g TEQ) emitted for varying countries**

Country	Year	Weighted Average Dioxin Emissions (ng TEQ/dscm)	Total MSW Collected* (millions tons)	MSW Combusted (millions tons)	Estimated Total Dioxin Emitted (grams TEQ)	g TEQ/million tons MSW combusted	% MSW combusted
USA	2012	0.027	164	26.6	3.28	0.12	16%
France	2010	0.023 <sup>b</sup>	33.7	13.8	1.43	0.10	41%
Korea	2010	0.007	7.1	3.9	0.11	0.03	55%
China	2009	0.348 <sup>c</sup>	157	23.5	36.61	1.56	15%

a – Total MSW collected does not include waste that is composted, recycled or otherwise used for energy production (e.g. anaerobic digestion with methane capture)

b – 2008 France dioxin emission data used for estimate, Table 12

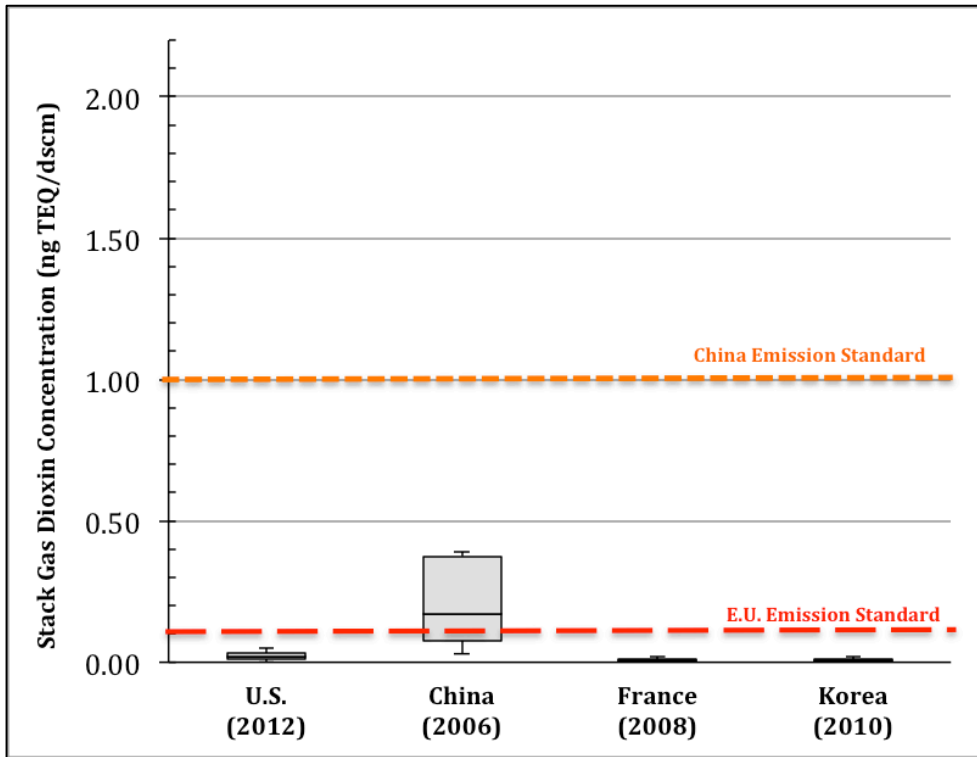
c - 2006 China dioxin emission data used for estimate, Table 12



**Figure 20 Concentrations of dioxins in WTE emissions from varying countries**

Despite the enormous advancements made by the global WTE industry in reducing dioxin concentrations in emissions over the last twenty years, new WTE facilities are still opposed by some environmental organizations. In most cases, these environmental organizations are misinformed of the new advancements made in the reduction of dioxins from emissions with APCs in modern facilities. However, as it was illustrated in China there are some outdated facilities that do in fact pose a risk to public health and the global community. WTE facilities not operating under the industries best practices are not only

causing negative environmental impacts but inevitably tarnish the industry’s reputation as a whole.



**Figure 21 Concentrations of dioxins in WTE emissions from varying countries (Extended View)**

This study showed that through the use of modern APC systems, dioxin emissions from WTE facilities in the U.S. alone have decreased by a factor of 3,000. New modern APCs have proven effective in removing dioxins from WTE emissions and therefore eliminating WTE as a major dioxin source contributor worldwide. The global WTE industry must encourage best practice standards over international borders. One of these initiatives is the Global Waste-to-Energy Research and Technology (WTERT) Council (GWC) that promotes best practices and research collaborations for sustainable waste management, globally. The Stockholm Convention is a global treaty that encourages monitoring and tracking of POPs such as dioxins. In the 2008 report, *Guidelines on best available techniques and provisional guidance on best environmental practices*, the Stockholm Convention offers expertise on reducing dioxins from waste incineration (Stockholm Convention, 2008).

The achievements that the WTE industry has made in the last 25 years on reducing and practically eliminating dioxin emissions needs to be recognized globally by both the general public and government agencies.

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## APPENDIX A – ADDITIONAL DATA AND NOTES

**Table A 1 Average dietary intake of dioxins by food group for U.K. adult, 1982- 2001 (F.S.A., 2003; M.A.F.F., 1997)**

Food Group	1982			1992			1997			2001		
	Mean intake (pg TEQ/kg bodyweight/day)			Mean intake (pg TEQ/kg bodyweight/day)			Mean intake (pg TEQ/kg bodyweight/day)			Mean intake (pg TEQ/kg bodyweight/day)		
	Dioxins	PCBs	Total	Dioxins	PCBs	Total	Dioxins	PCBs	Total	Dioxins	PCBs	Total
Carcass meat	0.5	0.34	0.84	0.13	0.12	0.26	0.1	0.1	0.2	0.07	0.06	0.12
Offals	0.45	0.08	0.53	0.17	0.05	0.22	0.1	0.04	0.1	0.09	0.02	0.11
Meat products	0.37	0.19	0.56	0.08	0.08	0.16	0.1	0.09	0.2	0.04	0.05	0.09
Poultry	0.3	0.14	0.44	0.08	0.04	0.12	0.06	0.08	0.1	0.02	0.04	0.06
Fish	0.25	0.53	0.77	0.12	0.24	0.37	0.1	0.3	0.4	0.07	0.20	0.30
Oils and fats	0.3	0.32	0.62	0.05	0.07	0.12	0.06	0.05	0.1	0.01	0.02	0.03
Potatoes	0.07	0.04	0.1	0.07	0.04	0.1	0.04	0.02	0.08	0.02	0.01	0.02
Milk	0.62	0.37	1.0	0.23	0.15	0.38	0.07	0.1	0.2	0.03	0.03	0.06
Dairy products	1.2	0.58	1.7	0.15	0.12	0.27	0.2	0.2	0.4	0.12	0.10	0.22
Eggs	0.43	0.13	0.56	0.08	0.05	0.13	0.03	0.03	0.06	0.01	0.01	0.02
Misc. cereals	0.27	0.27	0.55	0.35	0.05	0.41	0.07	0.07	0.1	0.02	0.02	0.04
Bread	0.05	0.04	0.09	0.05	0.03	0.08	0.03	0.02	0.05	0.01	0.01	0.02
Nuts	0.02	< 0.01	0.01	0.02	< 0.01	0.01	0.04	0.01	0.05	0.01	0.01	0.01
Sugar and preserves	0.02	0.01	0.03	0.02	0.01	0.03	0.06	0.02	0.08	0.02	0.01	0.03
Fruit products	0.03	0.02	0.06	0.03	0.02	0.06	0.01	<0.1	0.02	0.01	0.01	0.01
Green vegetables	0.03	0.01	0.04	0.03	0.01	0.04	<0.1	<0.01	<0.1	0.01	0.01	0.01
Other vegetables	0.03	0.02	0.06	0.03	0.02	0.06	0.01	<0.1	0.02	0.01	0.01	0.01
Canned vegetables	0.02	0.01	0.04	0.02	0.01	0.04	<0.1	<0.1	0.01	0.01	0.01	0.01
Fresh fruit	0.03	0.02	0.06	0.03	0.02	0.06	0.02	0.01	0.03	0.01	0.01	0.01
<b>Total</b>	<b>4.1</b>	<b>2.7</b>	<b>6.8</b>	<b>1.5</b>	<b>0.9</b>	<b>2.4</b>	<b>0.9</b>	<b>0.9</b>	<b>1.8</b>	<b>0.4</b>	<b>0.5</b>	<b>0.9</b>

\*Data from 1982 and 1992 available in M.A.F.F. (1997); Data from 1997 and 2001 available in F.S.A. (2003)

NOTE: Totals refer to the dietary intake by a consumer consuming one or any combination of the foods containing dioxins and PCBs. These values are derived from a distribution of the consumers' consumption patterns with regards to the individual foods. The combined dietary intakes of dioxins and PCBs were calculated from the combined concentrations. Therefore Total dietary intake of dioxins and PCBs represents the average consumer for all foods combined and is not equal to the sum of the intakes from the individual foods.

**Table A 2 Dietary PCDD/PCDF Exposure Estimates for varying age-sex groups (U.S. FDA, 2004)**

Age-Sex Group	PCDD/PCDF Exposure Estimate (pg WHO-TEQ/kg bw/month)			
	ND=0	ND=LOD/2	ND=LOD	
All Groups	9.6	18.2	26.8	
Infants 6-11 mo.	12.8	31.6	50.4	
Children 2 yrs	23.5	39.6	55.8	
Children 6 yrs	18.5	31.5	44.6	
Children 10 yrs	13.1	23.2	33.3	
14-16 yrs	Girls	7.8	15.5	23.2
	Boys	10.7	20	29.3
25-30 yrs	Women	6.6	13.6	20.7
	Men	8.4	16.3	24.2
40-45 yrs	Women	6.6	13.3	20
	Men	7.9	14.9	22
60-65 yrs	Women	5.7	11.3	16.9
	Men	7.4	12.8	18.5
>70 yrs	Women	5.6	11.1	16.5
	Men	7.1	13	18.8

NOTE: PCDD/F concentrations based on assumed relationship of: ND=Non-detects & LOD=Limit of Detect

**Sources per U.S. E.P.A. (2006):**

- (1) Combustion sources
- (2) Metals smelting, refining and processing
- (3) Chemical manufacturing
- (4) Natural sources and processes
- (5) Environmental reservoirs

The U.S. E.P.A.'s 2006 inventory report, has organized the major identified sources of dioxins into five broad categories. Within each of these source categories, more descriptive sub-categories are provided with quantitative release estimates.

**Sources per Stockholm Convention (2013):**

- (1) Waste incineration
- (2) Ferrous and non-ferrous metal production
- (3) Heat and power generation
- (4) Production of mineral products
- (5) Transport
- (6) Open burning processes
- (7) Production and use of chemicals and consumer goods
- (8) Miscellaneous
- (9) Disposal and landfill
- (10) Contaminated sites and hotspots

The Stockholm Convention's "toolkit" lists 80 sources of dioxin compounds divided into 10 "source group" categories.

**Open burning of biomass waste:**

The combustion of any household waste (plastics, paper, textiles, etc.) and or agricultural organic waste (leaves, wood chips, corn stalks, etc.) where emissions are released directly into ambient air without passing through a stack, duct or chimney is considered "open burning of biomass waste." In order to properly quantify the TEQ impact that varying biomass types in an open burn can contribute to an overall release analysis, Emission Factors (EFs) have been determined (Black et al., 2012). Emission factors for dioxins released from open burning of MSW have been determined through waste composition characterizations studies and field burning tests (Zhang et al., 2011). EFs for open burns of domestic waste are said to be 10 times greater than pre-harvest sugarcane burns, 40 times greater than forest fires and 80 times greater than EFs for municipal solid waste incinerators using best available technologies (Fiedler, 2010).

Figure A 1 is an excerpt from the Stockholm Convention Toolkit, which shows EFs for incineration of MSW. Low technology combustion with no air pollution control systems is said to have an EF 7,000 times greater than modern WTE facilities known to use high technology combustion processes with sophisticated APCS (Stockholm Convention, 2013). Releases associated with open burning are greatest in regions where there is a lack of centralized waste management practices and backyard barrel burning or open burning is the preferred solution for waste reduction. Although, as it is categorized in Figure A 1, even in cases where centralized waste management exists if a country is

operating a MSW incinerator without modern controls, the impact of the emissions can be comparable to an open burn.

Classes and emission factors for sub-category 1a – municipal solid waste incineration									
Cat.	Sub-cat.	Cl.		Emission factors (g TEQ/t of waste burned)					
				Air	Water	Land	Product	Residue	
								Fly ash	Bottom ash
1	a	<i>Municipal solid waste incineration</i>							
		1	Low technol. comb., no APCS	3500	NA	NA	NA	0	75
		2	Controlled comb., minimal APCS	350	NA	NA	NA	500	15
		3	Controlled comb., good APCS	30	ND	NA	NA	200	7
		4	High tech. combustion, sophisticated APCS	0.5	ND	NA	NA	15	1.5

NA = Not applicable (does not apply).  
 ND = Not determined (no quantitative information available).

**Figure A 1 Stockholm Convention excerpt from “toolkit” for MSW incineration (Stockholm Convention, 2013)**

## APPENDIX B – EMISSIONS & MSW DISPOSITION DATA

Dioxins emitted in grams TEQ are based on the following calculation, with special attention given to tons. For U.S. WTE emissions a C value for short tons was used, whereas for Korea, China and France a C value for metric tons was used.

$V$  = Volume MSW combusted (tons)

$p$  = Dioxins measured in stack gas (ng TEQ/dscm)

$C$  = Combustion factor, stack gas produced per ton of MSW combusted (dscm/ton)

$D$  = Dioxins emitted (g TEQ)

$$D = V * p * F$$

C is has been determined as such:

For use with MSW being measured as:	EPA (dscm7/ton)
Short ton	4075
Metric ton	4483

Per a U.S. E.P.A. report (40CFR60 Appendix A, Method 19, Table 19-2) C is calculated using the following assumed values:

HHV	5,000	Btu / lb
F-Factor	14,389	dscf @ 7% O <sub>2</sub> /MMBTU

### USA WTE Data

**Table A 3 Waste disposition in U.S.A., 2012 (U.S. EPA, 2014)**

Treatment Method	MSW Managed (million tons)	Percent Total
Recycled	59.4	26%
Composted	19.4	8%
WTE incineration	26.5	12%
Landfilled	122.7	54%
<b>TOTAL</b>	<b>228</b>	<b>100%</b>

**Table A 4 Emission data for WTE facilities in USA, 2012 (Van Brunt, 2013)**

WTE Facility #	MSW Combusted* (tons)	Avg. Dioxin iTEQ (ng / dscm)	Weighted Avg. Calc. (ng-ton/dscm)
1	n/a	0.0153	11,626
2	n/a	0.0197	15,588
3	n/a	0.0322	5,425
4	n/a	0.0114	6,877
5	n/a	0.1133	15,705
6	n/a	0.0311	31,609
7	n/a	0.0077	2,434
8	n/a	0.0503	28,841
9	n/a	0.0396	5,542
10	n/a	0.0321	38,594
11	n/a	0.0480	7,720
12	n/a	0.0166	17,972
13	n/a	0.0126	6,920
14	n/a	0.0385	7,087
15	n/a	0.0214	6,835
16	n/a	0.0262	4,469
17	n/a	0.0178	7,856
18	n/a	0.0107	3,612
19	n/a	0.0195	3,911
20	n/a	0.0064	1,615
21	n/a	0.0092	4,357
22	n/a	0.0939	38,096
23	n/a	0.0135	7,350
24	n/a	0.0284	23,784
25	n/a	0.0214	3,720
26	n/a	0.0134	3,186
27	n/a	0.0122	3,903
28	n/a	0.0481	47,431
29	n/a	0.0130	4,389
30	n/a	0.0986	42,269
31	n/a	0.2204	19,453
32	n/a	0.0212	5,495
33	n/a	0.0164	3,081
34	n/a	0.0091	1,697
35	n/a	0.0077	1,947
36	n/a	0.0005	160
37	n/a	0.0126	4,904
38	n/a	0.0169	6,035
<b>39</b>	<b>n/a</b>	<b>0.0153</b>	<b>14,352</b>
<b>TOTAL</b>	17,650,932	1.275	484,333
	<b>Mean</b>	<b>0.032</b>	
	<b>Weighted Avg.</b>	<b>0.027</b>	

**Table A 5 Emission Data for Total/TEQ Ratio (Van Brunt, 2013)**

WTE Facility #	Avg. Dioxin Concentration (ng/dscm)	Avg. Dioxin iTEQ (ng / dscm)	Actual Total/TEQ RATIO
1	1.7	0.0153	111.1
2	1.1	0.0197	56.8
3	4.0	0.0322	124.2
4	0.9	0.0114	75.5
5	10.9	0.1133	96.2
6	2.7	0.0311	88.0
7	0.6	0.0077	79.3
8	6.3	0.0503	125.6
9	5.1	0.0396	128.0
10	2.7	0.0321	83.4
11	2.8	0.0480	57.5
12	1.2	0.0166	72.8
13	0.9	0.0126	67.4
14	7.7	0.0385	200.8
15	2.4	0.0214	114.2
16	2.5	0.0262	94.8
17	1.6	0.0178	91.4
18	0.7	0.0107	69.8
19	1.8	0.0195	92.3
20	0.4	0.0064	60.3
21	1.8	0.0092	199.0
22	8.2	0.0939	87.7
23	0.8	0.0135	60.5
24	2.3	0.0284	82.1
25	1.3	0.0214	60.7
26	0.9	0.0134	64.4
27	0.9	0.0122	74.3
28	2.4	0.0481	49.7
29	0.7	0.0130	55.7
30	10.0	0.0986	101.1
31	11.6	0.2204	52.6
32	1.3	0.0212	60.6
33	0.7	0.0164	42.9
34	0.6	0.0091	68.8
35	0.7	0.0077	90.9
36	0.0	0.0005	43.5
37	1.5	0.0126	117.9
38	2.0	0.0169	119.1
39	1.4	0.0159	84.7
40	2.3	0.0323	70.2

### France WTE Data

Table A 6 Emission data for WTE facilities in France, 2008 (Benhamou, 2010)

WTE Facility #	Facility Capacity (tons)	MSW Combusted at 91% capacity (tons)	Avg. Dioxin iTEQ (ng / dscm)	Weighted Avg. Calc. (ng-ton/dscm)
1	118,000	107,851	0.005	539
2	33,000	30,162	0.000	0
3	128,000	116,991	0.004	468
4	150,000	137,099	0.027	3,702
5	87,000	79,517	0.010	795
6	307,000	280,595	0.014	3,928
7	99,000	90,485	0.004	362
8	142,000	129,787	0.032	4,153
9	71,000	64,893	0.007	454
10	98,000	89,571	0.009	806
11	126,000	115,163	0.140	16,123
12	59,000	53,925	0.006	324
13	55,000	50,269	0.002	101
14	180,000	164,518	0.016	2,632
15	260,000	237,638	0.008	1,901
16	42,000	38,388	0.001	38
17	20,000	18,280	0.002	37
18	26,000	23,764	0.002	48
19	87,000	79,517	0.014	1,113
20	142,000	129,787	0.001	130
21	32,000	29,248	0.008	234
22	83,000	75,861	0.007	531
23	126,000	115,163	0.006	691
24	171,000	156,292	0.006	938
25	32,000	29,248	0.000	0
26	118,000	107,851	0.006	647
27	158,000	144,411	0.008	1,155
28	126,000	115,163	0.002	230
29	166,000	151,722	0.008	1,214
30	114,000	104,195	0.002	208
31	118,000	107,851	0.014	1,510
32	27,000	24,678	0.006	148
33	79,000	72,205	0.002	144
34	59,130	54,044	0.001	54
35	22,000	20,108	0.001	20
36	39,000	35,646	0.000	0
37	95,000	86,829	0.010	868
38	61,495	56,206	0.005	281
39	29,000	26,506	0.008	212
40	181,000	165,432	0.002	331
41	88,000	80,431	0.002	161
42	173,448	158,530	0.003	476
43	88,000	80,431	0.004	322
44	79,000	72,205	0.006	433
45	195,000	178,228	0.025	4,456
46	79,000	72,205	0.005	361
47	343,000	313,499	0.031	9,718
48	95,000	86,829	0.007	608
49	481,000	439,630	0.062	27,257
50	788,000	720,225	0.063	45,374
51	63,000	57,581	0.002	115
52	158,000	144,411	0.002	289



53	158,000	144,411	0.010	1,444
54	47,000	42,958	0.005	215
55	99,000	90,485	0.001	90
56	229,000	209,304	0.005	1,047
57	118,000	107,851	0.020	2,157
58	39,000	35,646	0.011	392
59	126,000	115,163	0.003	345
60	189,000	172,744	0.010	1,727
61	284,000	259,573	0.005	1,298
62	95,000	86,829	0.004	347
63	110,000	100,539	0.009	905
64	87,000	79,517	0.011	875
65	87,000	79,517	0.001	80
66	126,000	115,163	0.010	1,152
67	24,000	21,936	0.001	22
68	126,000	115,163	0.004	461
69	22,000	20,108	0.003	60
70	39,000	35,646	0.002	71
71	25,000	22,850	0.004	91
72	142,000	129,787	0.106	13,757
73	63,000	57,581	0.005	288
74	16,000	14,624	0.006	88
75	166,000	151,722	0.099	15,021
76	126,000	115,163	0.012	1,382
77	130,000	118,819	0.007	832
78	89,000	81,345	0.019	1,546
79	47,000	42,958	0.005	215
80	426,000	389,360	0.014	5,451
81	110,000	100,539	0.004	402
82	106,000	96,883	0.030	2,906
83	28,000	25,592	0.004	102
84	87,000	79,517	0.008	636
85	26,000	23,764	0.008	190
86	33,000	30,162	0.004	121
87	55,000	50,269	0.002	101
88	63,000	57,581	0.006	345
89	39,000	35,646	0.001	36
90	22,000	20,108	0.002	40
91	32,000	29,248	0.000	0
92	55,000	50,269	0.001	50
93	102,000	93,227	0.099	9,229
94	126,000	115,163	0.004	461
95	102,000	93,227	0.015	1,398
96	142,000	129,787	0.006	779
97	39,000	35,646	0.001	36
98	42,000	38,388	0.002	77
99	343,000	313,499	0.072	22,572
100	134,028	122,500	0.012	1,470
101	662,000	605,062	0.095	57,481
102	126,000	115,163	0.004	461
103	110,000	100,539	0.005	503
104	158,000	144,411	0.010	1,444
105	24,000	21,936	0.006	132
106	44,000	40,216	0.005	201
107	79,000	72,205	0.009	650
108	356,000	325,381	0.018	5,857
109	79,000	72,205	0.001	72

110	126,000	115,163	0.012	1,382
111	275,000	251,347	0.050	12,567
112	39,000	35,646	0.000	0
113	11,826	10,809	0.001	11
114	300,000	274,197	0.010	2,742
115	315,000	287,907	0.002	576
116	32,000	29,248	0.004	117
117	130,000	118,819	0.003	356
118	126,000	115,163	0.007	806
119	18,000	16,452	0.001	16
120	221,000	201,992	0.016	3,232
121	87,000	79,517	0.013	1,034
122	110,000	100,539	0.004	402
123	32,000	29,248	0.002	58
<b>TOTAL</b>	<b>15,078,927</b>	<b>13,782,000</b>	<b>1.569</b>	<b>319051</b>
		<b>Mean</b>	<b>0.013</b>	
		<b>Weighted Avg.</b>	<b>0.023</b>	

**Table A 7 Waste disposition in France, 2010 (ADEME, 2012)**

<b>Treatment method</b>	<b>MSW managed (million tons)</b>	<b>Percent Total</b>
Recycling (Tri)Tri	8.30	17%
Composting	6.23	13%
Anaerobic Digestion w/ methane recovery	0.47	1%
Incineration with energy recovery (WTE)	13.8	28%
Incineration with no energy recovery	0.36	1%
Landfilling	19.6	40%
<b>Total</b>	<b>48.7</b>	<b>100%</b>
Ash maturation	2.22	5%

## Republic of Korea WTE Data

**Table A 8 Emission data for WTE facilities in Korea, 2010 (Seo, 2014)**

WTE Facility #	MSW Combusted (tons)	Avg. Dioxin iTEQ (ng / dscm)	Weighted Avg. Calc. (ng-ton/dscm)
1	89858	0.002	179.7
2	67524	0.001	67.5
3	78413	0.002	156.8
4	76972	0.017	1308.5
5	67775	0.009	610.0
6	67037	0.007	469.3
7	44847	0.024	1076.3
8	61373	0.002	122.7
9	54734	0.002	109.5
10	53244	0.001	53.2
11	50719	0.006	304.3
12	51306	0.000	0.0
13	50091	0.015	751.4
14	51221	0.013	665.9
15	46145	0.005	230.7
16	41885	0.002	83.8
17	42650	0.006	255.9
18	38530	0.006	231.2
19	72903	0.000	0.0
20	22647	0.007	158.5
21	35806	0.019	680.3
22	32213	0.006	193.3
23	58080	0.003	174.2
24	54815	0.000	0.0
25	51609	0.007	361.3
26	24532	0.010	245.3
27	23449	0.001	23.4
28	46779	0.010	467.8
29	23251	0.006	139.5
30	45554	0.000	0.0
31	19947	0.001	19.9
32	31686	0.035	1109.0
33	23869	0.009	214.8
34	11430	0.008	91.4
35	12258	0.001	12.3
<b>TOTAL</b>	1625152	0.243	10567.9
	<b>Mean</b>	0.0069	
	<b>Weighted Avg.</b>	0.0065	

**Table A 9 Waste disposition in Korea, 2010 (Changkook Ryu, 2012)**

Treatment Method	Managed (million tons)	Percent Total
Recycled	10.9	61%
Incinerated	3.9	22%
Landfilled	3.2	18%
<b>Total</b>	<b>17.9</b>	<b>100%</b>

## China WTE Data

The data for this analysis was collected from a 2009 report by Yuwen et al. although it is unclear the exact date in which the actual emission data was collected from the 19 WTE facilities. Given varying context clues in the Yuwen et al. report and for the purpose of this study, it is assumed that these emissions data were collected in 2006.

**Table A 10 Emission data for WTE facilities in China, 2006 (Zhang et al., 2010)**

WTE Facility #	MSW Combusted* (tons)	Avg. Dioxin iTEQ (ng / dscm)	Weighted Avg. Calc. (ng-ton/dscm)
1	67500	0.06	4050
2	115500	0.14	16170
3	150000	0.05	7500
4	60000	0.12	7200
5	45000	2.14	96300
6	67500	0.08	5400
7	150000	0.07	10500
8	115500	0.38	43890
9	115500	0.39	45045
10	75000	0.37	27750
11	150000	0.26	39000
12	115500	0.19	21945
13	115500	0.17	19635
14	67500	0.32	21600
15	49500	0.06	2970
16	60000	0.03	1800
17	150000	0.96	144000
18	75000	0.16	12000
19	120000	1.01	121200
<b>TOTAL</b>	1864500	6.96	647955
	<b>Mean</b>	<b>0.366</b>	
	<b>Weighted Avg.</b>	<b>0.348</b>	

**Table A 11 Waste disposition in China, 2009 (Dong, 2011)**

Treatment Method	MSW Managed (million tons)	Percent Total
Landfilled	124.03	79%
Composting	3.14	2%
Incinerated	28.26	18%
Other	1.57	1%
<b>Total</b>	<b>157</b>	<b>100%</b>