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AN ESTIMATION OF DIOXIN EMISSIONS IN THE UNITED STATES

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Total annual US air emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans (PCDD/Fs) from all known sources are estimated to be about 400 kilograms as of 1989, almost entirely from combustion sources. Municipal solid waste incineration is the largest known source of PCDD/Fs, as of 1989. The next largest sources include hospital waste incineration, forest and agricultural fires, and residential wood burning. Anthropogenic emissions of PCDD/Fs are estimated to be an order of magnitude greater than emissions of PCDD/Fs from forest fires. Dioxin emissions are shown to generally increase with the chlorine content of the combusted material, in the absence of effective pollution control systems. Dioxin emissions from 1940 and 1970 are also estimated. The estimates are verified through analysis of the concentrations of dioxin in soil, air, and sediments.

KEY WORDS: Dioxin, furan, PCDD, PCDF, sources, emission inventory, mass balance, dioxin budget, chlorine

1. INTRODUCTION

Chlorinated dioxins and furans, a group of more- and less-toxic chlorinated compounds, are emitted from virtually all combustion processes, and are by-products of some chemical and industrial processes.[1] Increases in cancer incidence have been found among dioxin-exposed workers.[2,3,4] and effects on reproductive and immune systems of animals have broadened the concern beyond cancer. Controversy remains, however, as to what effects might be expected at the current exposures of the general population.

Public concern about dioxin is high, and fear of dioxin exposure has been focused on emissions from municipal and hazardous waste incinerators, which are known to have a potential for high dioxin emissions. But are these the main sources of dioxin? Are there additional, undiscovered sources of dioxin?

Previous studies, for Canada, the United States, Sweden, and Great Britain, have estimated dioxin emissions, and the latter three tried to verify the emission estimates by comparison with dioxin concentrations in the environment. They all found that the estimated emissions from known dioxin sources were about an order of magnitude less than that expected based on the amount of dioxin found in the environment.[5–8] Much more data is now available, and we have collected a more complete database than has been used in previous studies of dioxin emissions.

Using these data, we have made a new evaluation of dioxin emissions in the United States. We consider the following source categories: consumer waste combustion, industrial waste combustion, biomass and fossil fuel combustion, and emissions from dioxin-contaminated chemical products. Based on data from these sources, total current dioxin emissions are estimated for the United States. This emissions database is also used to examine the effect of chlorine concentration on dioxin emissions from combustion processes.

To verify the estimate of total emissions, data on soil, sediment core, and air concentrations of dioxin are compared to those expected from the emission estimates. Because dioxin can have an environmental life-time of a decade or more in some situations, the history of US dioxin emissions is estimated. The historical emissions estimate also provides insight into the causes of changing dioxin emissions, and on preindustrial emissions of dioxin.

The data on environmental dioxin concentrations in air, soil and sediments are mutually constraining, in that air concentrations provide information on current emissions, soil concentrations provide information, as a function of the dioxin life-time, on total past emissions, and sediment cores provide information on the quantity emitted in each year of the time reflected in the core. Taken together, the estimates of emissions and loadings are consistent, within the error limits of the data, and do not support the hypothesis of major unknown dioxin sources.

A recent US EPA study arrived at conclusions that are largely consistent with this analysis, although the details of the ranking of source categories differ somewhat.[9] Moreover, although the EPA study evaluates emissions with a "toxic equivalent" weighting (TEQ), the total emission estimates are also consistent.

Not addressed here are dioxin emissions to water. Dioxins are emitted from pulp mills using chlorine bleach, and a number of other chemical processes. This represents an essentially separate pathway of dioxin emission and potential exposure than emissions to air and soil. Although in local ecosystems emissions to water can be significant, preliminary estimates indicate that total US direct emissions to water are much less than emissions to air and soil.

The definition used to quantify dioxin is total tetra- through octa- chlorinated dioxins and furans, abbreviated PCDD/F. This is the unit used in the US Clean Air Act for dioxin emissions from municipal waste incinerators. Emissions and emission factors are also given in terms of the I-TEF toxicity-weighted average.[10]

2. SUMMARY OF TOTAL ESTIMATED EMISSIONS

Dioxin emissions from combustion processes, responsible for the bulk of known dioxin emissions, can be highly variable, depending on the completeness of combustion, the combustion system and air pollution control equipment, and the material being burned. While temperatures, oxygen levels, and residence times in a well-operated combustion system are sufficient to destroy PCDD/Fs and their precursors, high emissions can result from poor combustion conditions such as pockets of gas with insufficient oxygen, or of low temperature pathways that allow some of the gases to escape complete combustion, and conditions that allow for the formation of dioxin in the post-combustion zone.

Nevertheless, the data presented in section 4 will show that dioxin emission factors from combustion of similar fuels, with broadly similar combustion systems and pollution control devices, typically vary by less than an order of magnitude. This holds true, for example, for hospital waste incinerators, sewage sludge incinerators, and industrial wood boilers. Thus, for most processes, dioxin emissions can be categorized by the combustion activity. Exceptions are the incineration of municipal and hazardous waste, for which different types of combustion systems can have dioxin emission factors that differ by more than an order of magnitude. Fortunately, the relatively large database on these systems allows these distinctions to be taken into account.

Table 1 Order of Magnitude Annual Emissions of Dioxin in the US (1989)
Asterisks indicate estimates based on emissions from similar sources

Emission Source (Numbers indicate number of facilities tested)	*Chlorine Content (ppm)*	*Emission Factor (µg/kg feed)*		*Material Consumed (kg /y)*	*PCDD/F Emissions (kg/y)*	
		Total	*TEQ*		*Total*	*TEQ*
Consumer Waste						
MSW Incinerators (18)	4,000	10	0.16	2×10^{10}	200	3
Hospital Incinerators (6)	10,000	20	0.35	2×10^{9}	40	0.7
Apartment Incinerators*	7,000	60	1	1×10^{9}	60	1
Open Garbage Burning*	7,000	60	1	$\sim 2 \times 10^{8}$	10	0.2
Sewage Sludge Incinerators (3)	1,600	1	0.02	3×10^{9}	4	0.07
Industrial Waste						
Hazardous Waste Incineration (35)	80,000	3	0.06	4×10^{9}	10	0.2
Copper Recycling (2)		20	0.3	7×10^{8}	10	0.2
Steel Recycling (9)		0.1	0.004	3×10^{10}	3	0.1
Steel Drum Reconditioning Furnaces (3)		30/drum	0.5/drum	4×10^{6} drum/y	0.1	0.002
Used Motor Oil Burners (2)		0.04	0.001	3×10^{9}	0.1	0.003
Bleached Pulp Production (3)	5,000	0.01	0.0002	3×10^{10}	0.4	0.007
Tire Fires (Uncontrolled)*		0.09	0.004	3×10^{8}	0.03	0.001
Carbon Regeneration (1)		0.06	0.001	5×10^{7}	0.003	0.00005
Tire Incineration (Controlled) (1)		0.009	0.0004	3×10^{8}	0.003	0.0001
Biomass Combustion, etc.						
Forest and Agricultural Burning*	~ 1,000	0.4	0.004	8×10^{10}	30	0.3
Residential Wood Burning (3)	~ 100	0.4	0.004	5×10^{10}	20	0.2
Industrial Wood Combustion (4)	100–1,000	0.05	0.001	6×10^{10}	3	0.06
Structural Fires*	1,000	0.4	0.004	5×10^{9}	2	0.02
PCP-Treated Wood Combustion (1)	10,000	8	0.1	$\sim 1 \times 10^{8}$	1	0.02
PCB Fires*	500,000	1000	20	7×10^{5}	0.7	0.01
Cigarettes (1)	700	0.1	0.002	5×10^{8}	0.05	0.0008
Fossil Fuels						
Oil Combustion (except gasoline)*	~ 10	0.003	0.00005	5×10^{11}	1	0.01
Leaded Gasoline (5)	60	0.03	0.0005	3×10^{10}	1	0.02
Unleaded Gasoline (3)	10	0.003	0.00005	3×10^{11}	0.8	0.01
Coal Combustion (1)	200	0.001	0.00002	6×10^{11}	0.6	0.01
Dioxin-Contaminated Chemicals						
PCP Wood Preservative (to Air) (1)		2×10^{6}	2×10^{4}		10	0.1
2,4-D Herbicide (to Soil) (1)		200	0.2	$2\text{-}3 \times 10^{7}$	5	0.005
Tetrachloroethylene (to Air) (4)		10	0.1	3×10^{8}	3	0.03
Total				2×10^{12}	400	6.3

The results of our emission estimates are shown by category in Table 1, which lists the emission factor, quantity of the material burned annually, and its chlorine concentration. Table 1 also includes non-combustion sources which result in the widespread dispersal of PCDD/Fs, that is, air emissions and pesticides. The numbers in parentheses refer to the number of facilities tested. Estimates that are based on indirect evidence, such as measurements from combustion of similar types of materials, are marked with an asterisk. By adding the estimated emissions from all sources, total annual emissions of dioxin in the United States are estimated to be about 400 kilograms as of 1989.

Table 1 shows that all combustion processes emit some dioxin, but that average emission factors vary by orders of magnitude. For example, the combustion of a kilogram of municipal waste is estimated to release an average of about 10 μg of dioxins (as of 1989) whereas the combustion of a kilogram of firewood is estimated to release only about 0.4 μg of dioxins.

Table 2 shows the estimated emissions of PCDD/Fs in rank order. Municipal waste incineration is by far the largest source, although environmental regulations on municipal waste incinerators can be expected to reduce total PCDD/F emissions by nearly a factor of ten over the next several years. The next largest sources are estimated to be hospital waste incineration, forest and agricultural fires, residential wood burning, use of PCP wood preservative, copper recycling, open garbage burning, apartment incinerators, and hazardous waste incineration.

Table 2 PCDD/F Emissions from Known Sources (1989)

PCDD/F Source	*PCDD/F Emissions (kg/y)*
Municipal Waste Incineration	200
Hospital Incinerators	40
Forest and Agricultural Fires	30
Residential Wood Burning	20
Copper Recycling	10
Open Garbage Burning	10
Apartment Incinerators	4–30
PCP Wood Preservative	10
Hazardous Waste Incineration	10
2,4-D Herbicide	5
Sewage Sludge Incineration	4
Industrial Wood Combustion	3
Oil Combustion (all)	3
Tetrachloroethylene	3
Steel Recycling	3
Structural Fires	2
Coal Combustion	0.7
Pulp Production	0.4
PCB Fires	0.7
Steel Drum Reconditioning	0.1
Wire Burning	0.09
Cigarettes	0.05
Tire Fires	0.03
Carbon Regeneration	0.003
Tire Incineration	0.003
Total	~ 400

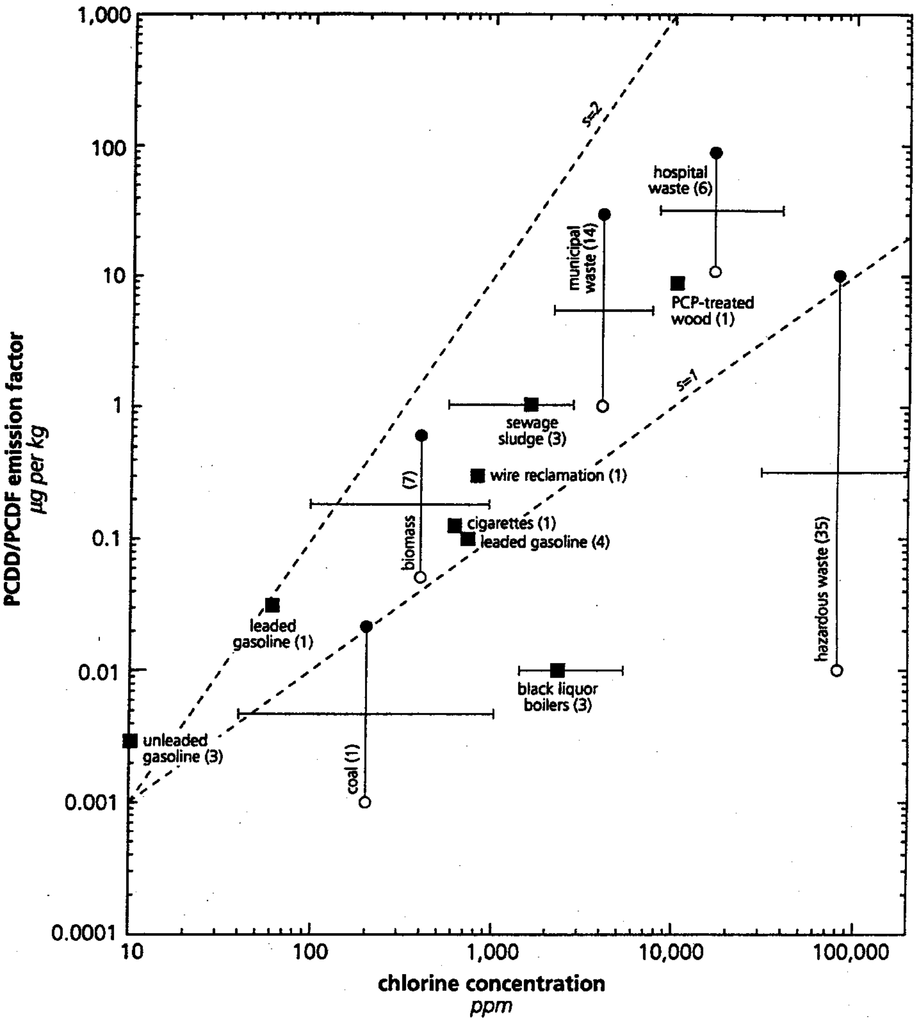

Figure 1 Average PCDD/PCDF emission factors for combustion processes, versus the average chlorine concentration of the combusted material (1989). Where information is available, poorly controlled combustion is indicated by a black dot, and well controlled combustion is indicated by a white dot. In all other cases, the black square indicates the average emission factor. The lines s = 1 and s = 2 have slopes of 1 and 2 respectively.

3. RELATIONSHIP OF DIOXIN EMISSIONS FROM COMBUSTION TO CHLORINE CONTENT

The details of the dioxin emission estimates will be given in section 4, but to show that the data from the different combustion source categories present a coherent and consistent picture of dioxin emissions, we begin with Figure 1, in which the average dioxin emission factor for each source category is plotted against the chlorine content of the combusted material. The table shows that average dioxin emissions of combustion source categories tend to increase with the average chlorine content.

While a dependence on chlorine content might seem to be a foregone conclusion, there has in fact been doubt on this point since limited data, on test-burns at municipal waste incinerators, for example, have shown no correlation. There are, of course, many variables besides chlorine content, especially the operating conditions of the combustion system, and the application of pollution control technology. Figure 1 shows that favorable operating conditions (open symbols) can lower emissions by as much as two orders of magnitude. But under poorly controlled conditions (closed symbols), there is a clear dependence on chlorine content. Moreover, the relationship is more than proportional since the slope of the log-log plot is somewhere between one and two. Since dioxin molecules contain more than one chlorine atom, a higher order dependence is not unexpected.

The data in Figure 1 are too coarse grained to evaluate differences due to the chemical form of chlorine in the combusted material. In hospital waste, a large fraction of the chlorine may be in the form of polyvinyl chloride, and in transformer fires the chlorine is in the form of polychlorinated biphenyls (PCBs), while in municipal waste a significant fraction of the chlorine may be in the form of sodium chloride, as well as PVC plastics. The figure indicates that, by and large, dioxin emissions are roughly independent of the original form of the chlorine in the combusted material. According to the current understanding of dioxin formation, HCl is the chlorine source for dioxin formation in catalyzed reactions on fly ash, with a maximum at temperatures of about 400°C.[11-15] The HCl is formed during combustion as part of the breakdown process of chlorine-containing molecules. Thus the amount of HCl formed might not depend strongly on the type of chlorine compound, although the degree of conversion of chloride salts to HCl is uncertain.

The relationship between chlorine content and dioxin emissions, demonstrated in Figure 1, provides a means to estimate how dioxin emissions are related to the presence of anthropogenic chlorinated compounds in materials that are burned. With municipal and hospital waste combustion being the largest dioxin sources that are affected by anthropogenic chlorinated organic materials (see Table 2), the relationship of total dioxin emissions to anthropogenic chlorinated compounds will depend primarily on how the emission factors for municipal and hospital waste combustion would change in the absence of chlorinated organic compounds. The next largest dioxin sources, forest and agricultural fires, and residential wood burning, are independent of the production of chlorinated organics, while the next largest sources, PCP production and dioxin emissions from copper recycling (attributed to the presence of chlorinated organics mixed in with the copper scrap), would be negligible in the absence of chlorinated organics.

4. DIOXIN EMISSION SOURCES

4.1 Consumer Waste Incineration

Municipal waste incineration: In 1989, about 20 million tons of municipal solid waste (MSW), 15% of the total, were incinerated in the US.[16]

The design of a municipal waste incinerator can significantly affect its dioxin emissions. The main types of incinerators are listed in Table 3, along with the amount of

Table 3 PCDD/F Emissions from Municipal Waste Incinerators, 1989[18,20]

Combustor Type (number of facilities tested)	*Emission Rate, ng/dscm @ 7% O_2*	*Emission Factor µg/kg*	*MSW Combusted 10^9 kg/yr*	*PCDD/F Emissions kg/yr*
Mass Burn Refractory-Wall				
Traveling Grate, hot ESP (1)	6000	35	1.0	35
Rocking Grate, no ESP (0*)	4000	23	1.2	28
Grate/Rotary Kiln, hot ESP (0)	6000	35	1.2	42
Mass Burn Waterwall				
Large (5)	500	2.9	7.0	20
Mid-size (5)	200	1.2	5.3	6
Small (1)	2000	11.7	0.5	6
Refuse-Derived Fuel				
Large, hot ESP (1)	3000	17.5	2.7	42
Small, cool ESP (1)	2000	11.7	2.3	27
Modular Starved Air				
Hot ESP (1)	600	3.5	0.5	2
Reciprocating Grate, no ESP (2)	400	2.3	0.6	1
Modular Excess Air (1)	200	1.2	0.5	1
Rotary Waterwall (0)	2000	11.7	0.3	4
Totals		11	22	190

* 0 means engineering estimate (see text).

municipal waste burned annually in these incinerators, and the EPA-estimated dioxin emission factor. Note that a number of the emission factors are based not on measured emissions, but are estimates based on the combustion technology and pollution control equipment. Note that while Table 3 presents an estimate of total emissions from municipal waste incinerators as of 1989, measured emissions at modern and well-operated incinerators are lower than this overall average.[17]

For example, the baseline emission rate of the mass burn refractory wall incinerators, most of which are about twenty years old, is assumed to be 4000 ng/dscm (dscm = dry standard cubic meter). Because the traveling grate and grate/rotary kiln varieties are typically equipped with electrostatic precipitators operating at 500°F or higher (hot ESP), which has been shown to increase dioxin emissions by roughly 50%, these two varieties were estimated by the EPA to have a dioxin emission factor 50% higher than the baseline emissions of a refractory-wall combustion system. The "hot ESP" also explains the difference between the estimated emission rates of the large and small refuse-derived fuel incinerators, and between the modular starved air incinerators with and without a reciprocating grate.

The average emission factor, weighted for the amount of waste combusted at each type of facility, is, to one significant figure, 10 µg/kg. Total emissions of PCDD/F are estimated to be about 200 kg/yr. The EPA also estimates that by 1997, the amount of MSW incinerated will increase by about 40%, but that implementation of new regulations will result in a total emission of about 16 kilograms per year.[19]

The emission factors given in Table 3 are not the highest that have been measured for the combustion of municipal solid waste. The Hampton municipal waste incinerator, a mass-burn waterwall incinerator equipped with an electrostatic precipitator, had an emission factor of as high as 60 μg/kg in several tests during the early 1980s.[20] These high emissions have been attributed to poor design and combustion conditions. This emission rate is likely to be representative of emissions from the open burning of garbage, or from incinerators operating in the 1970s, when incineration technology was less developed.

The chlorine content of municipal waste has been measured to be 2500 ppm (dry basis) in Pittsfield, Massachusetts, 4500 ppm in Baltimore, Maryland, and 8900 ppm in Brooklyn, New York.[21,22] For Figure 1, the average chlorine content is taken to be about 4000 ppm.

Hospital Incinerators: Due to the intensive use of disposable plastics, hospital waste has a higher chlorine concentration than MSW. Hospital incinerators are smaller and less regulated than municipal waste incinerators, and thus may be less well operated than typical municipal waste incinerators. Based on emissions from six hospital waste incinerators, as shown in Table 4, their dioxin emission factor is estimated to be 20 μg/kg, twice that for municipal waste incineration. (Emissions of 85 μg/kg or higher have been reported at other hospital waste incinerators.[23]) Also shown in Table 4 is the chlorine emitted as HCl from each incinerator, which gives a lower bound for the chlorine concentration of the original waste. At two facilities, dioxin emissions at the inlet to the pollution control equipment were measured; these values are shown to indicate the effectiveness of the pollution control equipment in reducing dioxin emissions.

The EPA estimates that about 2 million tons of waste are burned annually in medical waste incinerators (personal communication, R. Copeland, US EPA, 1992), so the total annual PCDD/F emissions can be estimated to be 40 kilograms. California has recently passed legislation to reduce dioxin emissions from medical waste incinerators. If adopted nationally, such regulations could reduce emissions by a factor of 10 or more.[30]

Sewage sludge incinerators, apartment building incinerators, and the open burning of garbage all make lesser contributions to total national dioxin emissions; they are discussed in Appendix A, and results are included in Tables 1 and 2.

Table 4 Dioxin Emissions from Hospital Incinerators

Facility	*Cl in HCl (as ppm of combusted mass)*	*PCDD/F Emission Factor (± range) (μg/kg)*	
St. Agnes[24]	7,000	14	± 3
Cedars Sinai[25]	9,000	5.7	(7.6 μg/kg at fabric filter inlet)
Sutter General[26]	9,000	44	± 3
St. Bernardines[27]	40,000	6.7	± 4
USC[28]	5,000	53	± 25
Kaiser[29]	5,000	6.4	± 1.5 (16 ± 8 μg/kg at scrubber inlet)

Table 5 Hazardous Waste Incineration, 1989

Incinerator Type	*Combustion/yr (10^6 tons)*[31,32,33]	*Average Emission Factor (µg/kg)*	*Median Emission Factor (µg/kg)*
Dedicated Hazardous Waste Incinerators (General)	1.4	1	0.2
Dedicated Hazardous Waste Incinerators (Soil)	0.2	0.5	0.009
Cement Kilns Burning Hazardous Wastes	0.9	3	0.7
Boilers and Furnaces Burning Hazardous Wastes	1.1	8	0.1
Net	3.6	3.6	0.2

4.2 Industrial Waste Processing and Incineration

Hazardous waste incineration: Dioxin emissions from hazardous waste incineration are of particular interest, since fear of these emissions is one of the factors in public opposition to incinerators. As of 1989, about 1.6 million tons of hazardous waste was burned at commercial and private hazardous waste incinerators in the US, and about 2 million tons at cement and aggregate kilns, boilers and other furnaces (Table 5).

Dioxin emissions from dedicated hazardous waste incinerators, cement kilns burning hazardous wastes, and boilers and industrial furnaces burning hazardous wastes, are shown in Tables 6, 7, and 8, and summarized in Table 5. Although the constituents and form of hazardous waste can vary widely, Tables 6, 7, and 8 show that for most trial burns, chlorine content is typically 1 to 10 percent. For dedicated hazardous waste incinerators, the dioxin emission factors shown in Table 6 range from 0.01 to 6.8 µg/kg, more than two orders of magnitude. The average is 1 µg/kg, and the median is 0.2 µg/kg. For soil incineration, the emission factors are lower, probably because the soils' concentrations of combustible materials were low. For soil incineration, the average emission factor is 0.5 µg/kg, and the median is 0.009 µg/kg.

For cement kilns burning hazardous wastes, shown in Table 7, the dioxin emission factors range from 0.04 to 10 µg/kg, again a range of more than two orders of magnitude. The average is 3 µg/kg, and the median is about 0.7 µg/kg. Table 7 also shows two measurements of emissions from cement kilns when hazardous wastes were not being combusted, resulting in emissions of 0.01 µg/kg and 0.4 µg/kg, respectively.

For other types of boilers and industrial furnaces burning hazardous wastes, there is very little data available. The data in Table 8 range over three orders of magnitude, from 0.01 µg/kg to 40 µg/kg of hazardous waste. The average is 8 µg/kg (determined entirely by the highest measurement) and the median is 0.1 µg/kg. In Table 8, emissions are shown as emissions per kilogram of hazardous waste, as for the preceding tables, and also as emissions per kilogram of total feed material, from which it can be seen that the emissions are correlated with, but as much as two orders of magnitude higher than, the emissions expected from the base feed material alone.

Although it may be a substantial overestimate, total dioxin emissions from hazardous waste combustion will be estimated using the average emission factor from each subcategory. This results in an overall emission estimate, to one significant figure, of 10 kg annually.

Table 6 Dioxin Emissions from Dedicated Hazardous Waste Incinerators[34]
In addition to total PCDD/F emission factors, TEF emission factors are shown in those cases for which sufficient data was available. The ranges given for the average TEF emission factor are based on the average of the listed TEF emission factors, and on the average of the conversion factor between total PCDD/F and TEF for the listed TEF emission factors.

Incinerator Type (Pollution Control Systems)	*Combustion Test Conditions*	*Feed Chlorine (%)*	*PCDD/F Emission Factor (µg/kg)*	
			Total	*TEF*
Rotary Kiln				
A (FF, WS, ESP)		20	6.8	0.2
B[35] (WS)	1) PCBs fed to 2ndary combustor	15	2.2	
	2) PCBs fed to kiln	11	0.01	
C (ESP, PBS)	1) High chlorine	4	1.3	
	2) Low chlorine	1	0.2	
D(ESP, PBS)	1) Initial Trial Burn	14	1.2	0.01
	2) Activated carbon system added	20	0.2	0.002
E (SD, FF, WS, IWS)		12	0.51	
F (VS)	1) Normal operation (2 chambers)	6	0.05	0.001
	2) Primary combustion chamber only	6	0.09	0.003
Other				
Rotary Hearth (Q, C/A, VS)		3	0.01	0.00008
Fluidized Bed (VS, IWS)		30	0.02	
Submerged Quench[36] (VS, PBS)		6	0.02	0.0001
Average			1	0.01–0.03
Median			0.1	~ 0.01
Soil Incineration				
Circulating Bed[37] (C, Q, FF)		0.02	0.002	0.00003
Infrared[38] (VS, PBS)		0.5	0.007	0.0003
Infrared[39] (Scrubber)	1) High solid feed rate	0.5	2	
	2) Feed rate lowered by 10%	1.6	0.01	
Average			0.5	0.0002–0.01
Median			0.009	~ 0.0003

VS = venturi scrubber; WS = wet scrubber; PBS = packed bed scrubber; FF = fabric filter; ESP = electrostatic precipitator; IWS = ionizing wet scrubber; Q = quench; C/A = condenser/absorber; C = cyclone.
C and F: Data for anonymous facilities provided by the Coalition for Responsible Waste Incineration.
D: Data provided by A. Sigg, Von Roll, Inc.

Table 7 Dioxin Emissions from Cement Kilns Co-Fired with Hazardous Wastes

Kiln	*Combustion Test Conditions*	*Feed Chlorine Content (%)*	*PCDD/F Emission Factor µg/kg hazardous waste*	
			Total	*TEF*
Wet Process with ESP				
A	1) good combustion conditions[40]	8	0.4	0.008
	2) poor combustion conditions[41]		~ 10	
B[42,41]	1) no haz. waste (coal only), 1990		~ 0.01	
	2) liquid haz. waste, 1990		~ 0.06	
	3) liquid and solid haz. waste, 1990		~ 0.01	
	4) liquid and solid haz. waste, 1992	5	0.2	0.003
C1[43]		4.5	3	0.06
C2[43]		3	10	0.2
D[44]		4	1.7	0.02
E[45]		0.8	2	
F[46]		3	0.2	0.008
H1[47]		2	3	
H2[47]		2	7	
Dry Process w/Fabric Filter				
I[48]		3	4	
J[49,50]	1) haz. waste, 1992	3	0.2	
	2) no haz. waste (coke only), 1985	0.05	0.4	
	3) haz. waste, 1985	0.5	0.04	
K[51]	1) maximum feed rate	2	1.4	0.02
	2) less than maximum feed rate	2	0.3	0.001
Average		1	0.009–0.04	
Median		0.1	~ 0.01	

Dioxin has also been measured in the emissions from several recycling and waste processing industries: copper recycling, steel drum reclamation, carbon regeneration, used motor oil burning, steel recycling, tire incineration, and from black liquor boilers at pulp mills. The feedstocks for each of these industries may contain chlorine-rich residues such as PVC plastic coating on wires, or residual contents in steel drums, or chlorinated compounds absorbed by activated carbon systems. Details are given in Appendix B, and results are shown in Table 1.

Table 8 PCDD/F Emissions From Industrial Boilers Burning Hazardous Wastes[52]

Boiler Type and Primary Fuel	*Expected Primary Fuel Dioxin Emission Factor (Table 1), μg/kg*	*Waste Chlorine %*	*Fuel/ Waste Ratio*	*Measured Dioxin Emission Factor*	
				μg/kg of haz. waste	*μg/kg of total feed*
Watertube Stoker Wood chips	0.05	0.3	60/40	40	10
Converted Stoker #6 Fuel Oil	0.003	10 (TCE)	80/20	0.6	0.1
		10 (Bis)	80/20	0.04	0.02
Packed Watertube #6 Fuel Oil	0.003	4	75/25	0.01	0.004
Tangentially Fired Watertube Pulverized Coal	0.001	6	97/3	0.1	0.006

TCE = trichloroethylene; Bis = Bis(2-chloroethyl)ether. Emission factors calculated based on the assumption that 10^3 lbs steam/hr corresponds to an energy use of about 2000 MJ/hr.

4.3 *Biomass Combustion*

Dioxins have consistently been found in the emissions from industrial wood boilers and incinerators, and in residential fireplace soot. Other biomass combustion, including structural fires, agricultural burning, and forest fires can also be expected to produce dioxins.

Dioxin emissions from wood and other biomass combustion are shown in Table 9, based on the dry weight of the wood. These are divided into controlled combustion with pollution control equipment, which will be taken to be representative of industrial biomass combustion, and uncontrolled combustion, which will be taken to be representative of residential wood burning and forest fires.

The average emission factor from controlled biomass combustion is 0.05 μg/kg. 60 million dry tons of wood are burned annually as paper or wood in the industrial sector, as of 1989.[53,54] Thus annual PCDD/F emissions from industrial wood burning would be about 3 kg.

For uncontrolled biomass combustion, such as for residential wood burning, agricultural burning, or forest fires, the average dioxin emission factor from Table 9 is 0.4 μg/kg. Further evidence is available from measurements of dioxin in the particulates from wood-burning residential chimneys, which yield an average of 2×10^{-5} μg PCDD per kg of chimney particulates (furans were not measured).[61] Based on a comparison of annual forest biomass combustion with annual particulate emissions from forest fires, particulate matter accounts for on the order of 1% of the mass of the original wood,[62] so the emission factor would be about 0.2 μg PCDD per kilogram of wood. If furans had been included, the overall emission factor would have been higher; half or more of the PCDD/F emissions in Table 9 were furans.

With 50 million tons of wood fuel (dry weight basis) used in the residential sector in 1989,[54] 20 kg of PCDD/F are estimated to be emitted annually from residential wood combustion.

Table 9 PCDD/F Emissions from Biomass Combustion

	PCDD/F Emission Factor		
Facility	*Total, µg/kg (± range)*	*TEQ, ng/kg*	*Notes*
With Pollution Control			
Wood-Fueled Incinerator			600 ppm Cl in feed
Pollution Control Outlet	0.06 (± 0.07)	1.6	Scrubber, Multiclone, ESP[55]
Wood-Fueled Incinerator			
Pollution Control Outlet	0.02 (±0.007)	1	ESP[56]
Wood-Fueled Incinerator	0.06 (± 0.05)	0.8	Multiclone[57]
Wood-Fueled Incinerator			
Pollution Control Outlet	0.06 (± 0.05)	0.7	Multiclone, ESP[58]
Poor Pollution Control			
Wood-Fueled Incinerator			
Pollution Control Inlet	0.9 (± 0.7)	8	600 ppm Cl in feed[55]
Residential Boilers	0.016 (± 0.015)	0.3	Various Combustion Conditions[59]
Domestic Furnace	0.3	4	Straw; poor combustion conditions[60]
Cigarettes	0.3	4	See Appendix C

60 million tons are estimated to burn annually in forest wildfires and managed burns.[63] And open agricultural burning is estimated to consume 20 million tons, as of 1990 (personal communication, P. Carlson, Pechan and Associates). The total annual emission of PCDD/Fs from these sources is therefore estimated to be about 30 kilograms. Thus, forest and agricultural fires are estimated to be the largest source of "natural" dioxins, accounting for about 8% of the total dioxin emissions shown in Tables 1 and 2.

Emissions from structural fires, PCP wood combustion, cigarette smoking and PCB fires are all estimated to be relatively small, and are discussed in Appendix C.

4.4 *Fossil Fuel Combustion*

Detection of dioxin emissions from fossil fuel combustion is difficult, because the emission factors are quite low, below the detection limits of many experiments. However, because of the large amount of fossil fuel combustion, it is worth examining these sources in some detail.

Gasoline Combustion: Among the fossil fuels, gasoline combustion has most often been suggested as a potentially significant source of dioxin emissions.[64,65] While unleaded gasoline may contain some trace quantities of chlorine (on the order of 10 ppm), leaded gasoline typically includes the additives dichloroethane or dibromoethane with a chlorine to lead weight ratio of about 1 to 3.[66] Leaded gasoline can contain up to 700 ppm chlorine (Table 10), with less chlorine in lower-lead gasolines. Thus combustion of leaded gasoline can be expected to produce more dioxin than combustion of unleaded gasoline, and gasoline with higher lead concentrations can be expected to produce more dioxin than low-lead gasolines.

Table 10 PCDD/F Emissions from Gasoline Combustion

Gasoline Type, Number of Cars Tested[67,68]	*Gasoline Chlorine (ppm)*	*PCDD/F Emission Factor μg/kg*
High-Leaded Gasoline, 4 cars*	700	0.1
Low-Leaded Gasoline, 1 car	63	0.03
Unleaded Gasoline, 1 car	14	0.003
Unleaded Gasoline, 2 cars	~ 10	< 0.005

*Assumes a fuel consumption of 11 km/l.

Based on the data in Table 10, the emission factor for unleaded gasoline combustion is estimated to be 0.003 μg/kg. For cars burning leaded gasoline, the dioxin emission factors appear to be higher for cars burning higher-lead (and higher-chlorine) gasoline. Because leaded gasoline in the United States has a relatively low lead concentration (0.1 g/gal), and a low chlorine concentration (10–30 ppm), the dioxin emission factor for US leaded gasoline combustion is taken to be 0.03 μg/kg, corresponding to the emission factor from the one car tested using low-lead gasoline. Note that this emission factor is an order of magnitude higher than that for cars burning unleaded gasoline.

In 1989, 9.8 billion gallons (29 billion kg) of leaded gasoline were used in the United States; 110 billion gallons (320 billion kg) of unleaded gasoline were used.[69] Total dioxin emissions are estimated to be on the order of 1 kilogram per year from cars using leaded gasoline, and on the order of 0.8 kilograms per year from cars burning unleaded gasoline.

The changes in the lead content of US gasoline over the past several decades may also have changed the average dioxin emission from US gasoline combustion. By 1989, the use of leaded gasoline in the United States had been reduced by about a factor of ten from its peak in the 1970s; it will be completely phased out by 1996. In addition, the lead (and chlorine) concentrations in leaded gasoline had been reduced by a factor of five. So during the 1970s, dioxin emissions from US gasoline combustion may have been at least 10 times greater than current emissions.

Combustion of diesel fuel has also been suggested as a potential source of dioxin emissions.[70] There has been only one direct measurement study of dioxin emissions from diesel fuel vehicles, which found the average emissions of a diesel car, bus, and truck to be 0.2 μg/kg.[71] However, these measurements were below the limit of resolution of the experimental technique, and the researchers characterized the results as inconclusive. Nevertheless, if those measurements had been representative of dioxin emissions from the combustion of diesel fuel, annual emissions from this source category would be about 16 kg PCDD/F, based on 1989 US diesel fuel consumption of 8×10^{10} kg/yr.[72]

For non-transportation oil combustion, PCDD/Fs have not, to our knowledge, been detected in air emissions, although trace quantities have been found in soot.[73] In the absence of better data, the emissions factor for the combustion of unleaded gasoline will be used for all oil combustion except for leaded gasoline. Excepting gasoline, the US consumes about 450 billion kg of oil annually. Thus, annual PCDD/F emissions from non-gasoline oil combustion would be about 1 kilogram.

Coal Combustion: The average chlorine concentration in US coal is about 200 ppm, ranging from 20 to 8000 ppm, and coal combustion can be expected to produce some dioxin.[74,75] Based on dioxin emissions measurements from one coal-fired utility boiler with an electrostatic precipitator, and on measurements of dioxin in coal soot, the emissions factor for coal combustion will be estimated to be 0.001 μg/kg (0.00002 ug/kg TEQ).[76] Measurements at other coal-fired utility boilers with electrostatic precipitators have reported that the dioxin emission factor was below the detection limit of 0.01 μg/kg, further evidence that the estimated emission factor is of the correct order of magnitude.[77] It should be noted that this is the lowest emission factor for any dioxin combustion source shown in Table 1.

About 660 billion kg of coal were burned in the U.S. in 1989,[78] so estimated dioxin emissions are on the order of 0.7 kilograms.

This estimate can be corroborated by measurements of the dioxin content of particulate emissions from coal combustion. Measurements of coal soot from four domestic chimneys found PCDD/Fs ranging from 0.25 to 5.3 μg/kg of soot, with an average of 2 μg/kg soot.[79] Because dioxins are believed to be formed on and associated with particulate matter, we will assume that dioxin emissions from coal combustion are roughly proportional to the particulate emissions. The validity of this assumption would depend on the distribution of particulate sizes, as well as exhaust gas temperatures and other combustion conditions.[80] In the US in 1989, 0.5 billion kg of particulate matter was released from coal combustion.[81] Assuming that coal soot and the emitted particulates have about the same dioxin concentrations, total emissions from coal would be about 1 kilogram, which is consistent with the estimate above.

This method can also be used to estimate the dioxin emission factor for coal combustion in the absence of pollution control devices. In 1970 in the US, 0.009 kg of particulates were emitted per kilogram of combusted coal, an order of magnitude more than the current particulate emission factor for coal.[78,81] From this, the dioxin emission factor for uncontrolled coal combustion can be estimated to be about 0.02 µg PCDD/F per kilogram of coal.

4.5 *Dioxin Contamination in Chemical Products*

Production of some chlorinated chemicals results in the production of small quantities of dioxins as contaminants. Chlorophenols, which include the herbicides 2,4,5-T and 2,4-D, as well as the wood preservative penta-chlorophenol (PCP), are similar in structure to dioxin, and are especially prone to dioxin contamination. Dioxins have also been found in other chlorinated chemicals, including polychlorinated biphenyls (PCBs).

In the course of their use, herbicides are widely dispersed in soils. Because we want to verify the dioxin emissions estimates with data on dioxin levels in soil, the amount of dioxins dispersed with pesticides is estimated here, in addition to the air emission estimates.

PCP: Pentachlorophenols, now used primarily to preserve utility poles, currently account for almost all chlorophenol production in the United States. PCP manufactured in the United States currently contains about 2000 ppm (corresponding to an "emission factor" of 2,000,000 μg/kg) of PCDD/F. Unlike PCDD/F emissions from combustion, which typically have a fairly even distribution of dioxins and furans with different numbers of chlorine atoms, most of the dioxins in PCP are octa-chlorinated dioxins and furans, which are thought to be less toxic than 2,3,7,8-tetra-chlorinated dioxins and furans.[82,83]

Table 11 Dioxins from PCP

Year	*Production of PCP (tons/yr)*[84,85]	*PCP Emissions (tons/yr)*		*PCDD/F Emissions (kg/yr)*	
		To Soil	*To Air*	*To Soil*	*To Air*
1960	17,800	500	70	1000	200
1965	19,800	600	80	1000	200
1970	21,400	600	90	1000	200
1973	21,100	600	80	1000	200
1977	20,000	600	80	1000	200
1982	23,000	600	90	1000	200
1987	11,000	0	6	0	10

Until the mid-1980s, PCP was used as a home-and-garden herbicide.[85] A mass-balance study of PCP use and emissions concluded that the herbicide and home-and-garden uses accounted for almost all of the emissions of PCPs to air and dispersed in soils, even though these uses accounted for only about 4% of total PCP manufacture.[86] When these uses were phased out, emissions of PCP to air and soils decreased by more than an order of magnitude (Table 11). The estimated air emissions of PCP as of 1987 are based entirely on air emissions from PCP manufacturing and application sites, as reported to the US EPA Toxic Release Inventory.[87] It is not known if these are evaporative or particulate emissions; PCDD/F emissions from these sites are assumed to correspond to the PCDD/F content of PCP. Since 1987, PCP is estimated to be among the largest sources of dioxins, amounting to about 10 kg, or about nearly 3% of total dioxin air emissions in the US; before the 1980s it is estimated to have been the largest single source.

2,4,5-T: 2,4,5-T, a trichlorophenol, was used as a herbicide in the US from the mid-1940s until it was banned in 1984, although most uses were banned in 1976.[88] In most studies, only the 2,3,7,8-TCDD content of 2,4,5-T was measured. The 2,3,7,8-TCDD content is estimated to have averaged about 5 ppm.[89] The available data indicates that the ratio of TCDD to PCDD/Fs is similar to that of other dioxin sources, typically about 1:15,[91,80] so the average PCDD/F concentration can be estimated to be about 80 ppm (an "emission factor" of 80,000 μg/kg). 2,4,5-T, in combination with another herbicide, 2,4-D (a dichlorophenol), was called Agent Orange, and was used as a defoliant during the Vietnam war. An estimated 1200 kg of PCDD/F were in the Agent Orange used in Vietnam between 1965 and 1971.[92] Table 12 shows the estimated history of 2,4,5-T use in the US through 1980, and resulting emissions of PCDD/F.

Details of dioxin contamination in hexachlorophene, 2,4-D, PCBs, and tetrachloroethylene are discussed in Appendix D.

5. HISTORY OF DIOXIN EMISSIONS

Based on the emission factors discussed in the previous sections and historical data on combustion of various materials, past dioxin emissions can be estimated for about 1970, when dioxin emission sources had not yet been controlled, and for about 1940, when

Table 12 PCDD/F Dispersion to Soil from 2,4,5-T

Year	*Estimated US Use*[90] *1000 kgyr*	*PCDD/F kg/yr*
1951	1100	90
1955	1300	100
1960	2900	200
1965	2800	200
1970	3200	300
1975	3200	300
1978	3200	300
1980	~ 0	~ 0

Table 13 Annual Combustion, 10 million tons (10^{10} kg)

Source	*1940*	*1970*	*1989*
Municipal Waste Combustion[93,62]	1.5	2	2
Agricultural Burning[63]	2	2	2
Forest Fires[94,95]	20	6	6
Residential and Industrial Wood Combustion[96]	9	9	10
Coal Combustion[95,78]	40	40	60
Gasoline Combustion[97]	10	27	34

there was little manufacture or use of chlorinated compounds. Chlorine production in the United States, currently about 11 million tons, was only 22 thousand tons in 1909, and only about 600,000 tons in 1940. According to the Chlorine Institute, Washington, DC, more than half of chlorine is used to produce chlorinated organic chemicals, with vinyl chloride alone accounting for 24% of the total.

Estimation of Historical Combustion Rates: Table 13 shows estimates of the major combustion sources – wood, municipal waste, forest fires, agricultural waste, and gasoline – for 1940, 1970 and 1989. Note the striking reduction in forest fire combustion since 1940, due to fire control programs. Reliable historical data is not available for agricultural burning, so these were assumed to remain constant.

Estimation of Emission Factors: The estimated dioxin emission factors for 1940, 1970, and 1989 are given in Table 14. For 1940 and 1970, the emission factors for industrial wood combustion and for coal combustion are those for poorly controlled wood and coal combustion, as discussed separately. The emission factors for gasoline combustion are based on the amount of lead (and chlorine) used in the gasoline for each year, as discussed separately.

Table 14 Dioxin Emission Factors, μg PCDD/F per kg feed

Source	*1940*	*1970*	*1989*
Municipal Waste Combustion	0.4–4	30–60	10
Agricultural Burning	0.4	0.4	0.4
Forest Fires	0.4	0.4	0.4
Residential Wood Combustion	0.4	0.4	0.4
Industrial Wood Combustion	0.4	0.4	0.06
Coal Combustion	0.02	0.02	0.001
Gasoline Combustion	0.003	0.1	0.006

Table 15 Chlorine Content of Biomass

Material	*Chlorine Concentration (ppm dry weight)*
Woody Biomass	
Wood samples, 11 types[61]	14–84
Pine Firewood[99]	49
Oak Firewood	125
Birch Trunk[100]	200
Legume Trunk	200
Wood Waste[55]	600
Milkweed Branches	1200
Leafy Biomass	
Tobacco[101]	700
Birch Leaves	1000
Legume Leaves	1200
Corn Plants[102]	1430
Land Plants[103]	2000
Biomass in Baltimore, MD Garbage[22]	3500
Biomass in Brooklyn, NY Garbage	7800
Milkweed Leaves	15500

The 1970 emission factor for municipal waste combustion is taken to be 30 to 60 μg/kg; 30 μg/kg being the emission factor given in Table 3 for 1970s-style mass-burn, refractory wall incinerators, and 60 μg/kg being the highest emission factor measured for municipal waste combustion. If PCDD/F emissions depend on the content of chlorinated organics, this may be an overestimate, since use of polyvinyl chloride (PVC) plastic, a major source of free chlorine in municipal waste, was about a factor of three less in 1970 than in 1989.[98]

To estimate the 1940 MSW combustion emission factor, both poor combustion conditions and the virtual absence of chlorinated organics, such as PVC plastics, must be considered. The emission factor for uncontrolled wood combustion, 0.4 μg/kg, provides a lower bound. However, as shown in Table 15, food wastes have more chlorine than wood, and even though much of this excess chlorine may be present as sodium chloride, the emission factor might be estimated to be as much as an order of magnitude higher, 4 μg/kg.

Table 16 Estimated Annual Dioxin Emissions to Air and Soil, 1940 to 1989, kg

Source	*1940*	*1970*	*1989*
Municipal Waste Combustion	6–60	600–1200	200
Agricultural Burning	8	8	8
Forest Fires	80	20	20
Residential and Industrial Wood Combustion	40	40	20
Coal Combustion	8	8	0.6
Gasoline Combustion	0.3	30	2
Chemicals to Air	0	200	20
Other	0	100	100
Total to Air	**140–200**	**1000–1600**	**400**
Pesticides to Soil	0	1000	0
Total to Air and Soil	**140–200**	**2000–2600**	**400**

An alternative approach would be to assume that the emission factor for municipal waste incineration was the same in 1970 as in 1940, under the assumption that the waste content is not a controlling factor and that the technology used in 1940 was unlikely to have been characterized by lower dioxin emissions. In this case, however, dioxin emissions in 1940 would have been about the same as in 1970 which, as will be discussed in section 6, is inconsistent with the currently available data. As new data and analyses become available, however, this possibility should be re-examined.

Estimation of Dioxin Emissions: Based on Tables 13 and 14, the estimated dioxin emissions for 1940, 1970 and 1989 are given in Table 16, including dispersion of PCDD/F with pesticides.

Overall, Table 16 shows that in 1970, dioxin emissions to air are estimated to have been three to four times that in 1989, due to higher emissions from municipal waste incineration and dioxin from chemical products. And when dioxin in pesticides is included, 1970 dioxin air and soil emissions are a factor of 5 to 6 times the 1989 estimate. The 1940 air emissions of dioxin are highly uncertain, but are estimated to be about a factor of five less than 1970 air emissions.

6. VERIFICATION OF EMISSIONS ESTIMATES

Three measures of the environmental dioxin loading will be examined here: dioxin in air, dioxin in soil, and dioxin in sediments.

6.1 Dioxin in Air

Measurements of dioxin deposition can be used as a basis for verification of dioxin emission estimates.[7,8] For the early 1980s, annual dioxin emissions are estimated to be between 400 kg and 1600 kg (Table 16). The resulting US average deposition flux would be about 4–16 pg/cm^2/yr, assuming all PCDD/Fs were deposited on US soil. In the United

Table 17 PCDD/F Concentrations in Air

Location	*Data collection period*	*PCDD/F (pg/m³)*
Trout Lake, WI[109]	Four 2-week samples	0.4
Bloomington, IN	"	2
Indianapolis, IN	"	5.6
Niagra Falls, NY[107]	3-year average of 12-day intervals	4
Bridgeport, CT[110]	48 1–3 day samples	7
Columbus, OH[111]	1 3-day sample	2
Waldo, OH	1 1-week sample	3.5
Los Angeles, CA[112]	1 2-day sample	4
Average ± Standard. Deviation		4±2

States, dioxin deposition has been reported only in four locations: Indianapolis (wet plus dry deposition of 54 pg/cm²/yr as of 1991) and Bloomington (37 pg/cm²/yr as of 1988), Indiana;[104] Siskiwit Lake, a lake on an island in Lake Superior (23 pg/cm²/yr in 1982);[105,106] and Green Lake, near Syracuse (50 pg/cm²/yr for 1979–1984).[107] Of all of these locations, Siskiwit Lake is the only one far from a city. In Bloomington, Indiana, large amounts of PCBs were used in the manufacture of capacitors and transformers, and their disposal led to severe contamination of six sites around the city.[108] Since PCBs have been associated with PCDFs, Bloomington may not be representative of the US average deposition of PCDD/Fs. But even the deposition to Siskiwit Lake is greater than the estimated average deposition of 4–16 pg/cm²/yr. Calculations such as these are the basis of statements that major emission sources remain to be discovered.

However, deposition of dioxin can be expected to be strongly influenced by local sources, and the Great Lakes region may well receive greater than average deposition of dioxins. A reliable estimate of dioxin emissions cannot be made from the few existing deposition measurements.

Table 17 shows measurements of dioxin in air, all from the late 1980s. Although these measurements include big cities, such as Los Angeles, and rural areas, such as Waldo, Ohio and Trout Lake, Wisconsin, most of the measurements are within an order of magnitude of each other.

A precise model of expected dioxin air concentrations would require information on the geographical distribution of emission sources. However, data on national emissions and urban air concentrations for a number of pollutants, given in Table 18, shows that air concentrations are, within an order of magnitude, proportional to national emissions for a number of pollutants.

Based in this proportionality factor, for the estimated annual dioxin emission of about 400 kg, dioxin levels in urban air can be expected to be 0.4 – 8 pg/m³. This is in good agreement with the measured levels given in Table 17, and indicates that the estimated dioxin emission of 400 kg is of the correct order of magnitude.

Table 18 Relationship of Emissions to Pollutant Air Concentrations

Pollutant	*Year*	*US Emissions Total,[81] g/y*	*Typical Urban Air, μg/m³ *,[113]*	*Emissions:Urban Air Ratio, 10^{17} m³/yr*
TSP (Particulates)	1988	7×10^{12}	50	1.4
	1979	9×10^{12}	63	1.4
NOx	1988	2×10^{13}	56	3.6
	1979	2.2×10^{13}	60	3.7
Lead	1988	7×10^{9}	0.1	0.7
	1985	21×10^{9}	0.3	0.7
Benzene[114,115]		3×10^{11}	6	0.5
SO_2	1988	2.1×10^{13}	22	9.5
	1979	2.4×10^{13}	32	7.5

* Average of the mostly urban National Air Monitoring Stations (NAMS), except for lead, which is reported as the maximum quarterly average. Benzene data is based on a 39-city study.

6.2 Dioxin in Sediments

A third indicator of environmental dioxin is lake sediments, which collect atmospheric deposition of dioxin. Many lakes also receive dioxin from wastewater, or drainage from the surrounding watershed. But Siskiwit Lake, located on an island in northern Lake Superior, has a water level higher than Lake Superior, and virtually no anthropogenic inputs in its drainage basin, so only atmospheric inputs are believed to contribute the the PCDD/Fs in the sediments.

Figure 2 shows a plot of the measured dioxin in a sediment core from Siskiwit Lake.[105] The sediments were dated by the ^{137}Cs method, which uses the known deposition of ^{137}Cs from atmospheric nuclear tests to determine the sedimentation rate, as well as by counting of annual layers. The figure shows that the ratios of deposition for 1940, 1970 and 1983, assuming no degradation of dioxin in sediments, were about 1:10:7. Sediments from other American and European lakes (including Lakes Huron, Erie, and Michigan), as well as archived soil samples from Britain show a similar pattern.[116] For example, in Green Lake, near Syracuse, New York, the PCDD/F deposition ratio for 1920:1970:1980 was about 1:10:10.[107] In Switzerland, Lake Lugano, Lake Baldegg, and Lake Zurich all showed a similar pattern, with deposition reaching a maximum in 1965 in Lake Zurich and in 1975 in Lake Baldegg, and with Lake Lugano showing a continuing increase.[117] However, in absolute amount, the annual sedimentation of dioxin in all of these other lakes was up to two orders of magnitude greater than in Lake Siskiwit, indicating that these lakes were either receiving non-atmospheric inputs or significant deposition from local sources.

The estimated past dioxin air emissions, given in Table 16 for or the years 1940, 1970, and 1989, is 1: (5–11) : (2–3). While there is no sediment data available which includes sediments as recent as 1989, the overall pattern is a good match to the observed pattern in sediments.

The relationship of the observed deposition pattern to the actual deposition pattern depends on the rate at which dioxin degrades in sediments. If the degradation mechanism

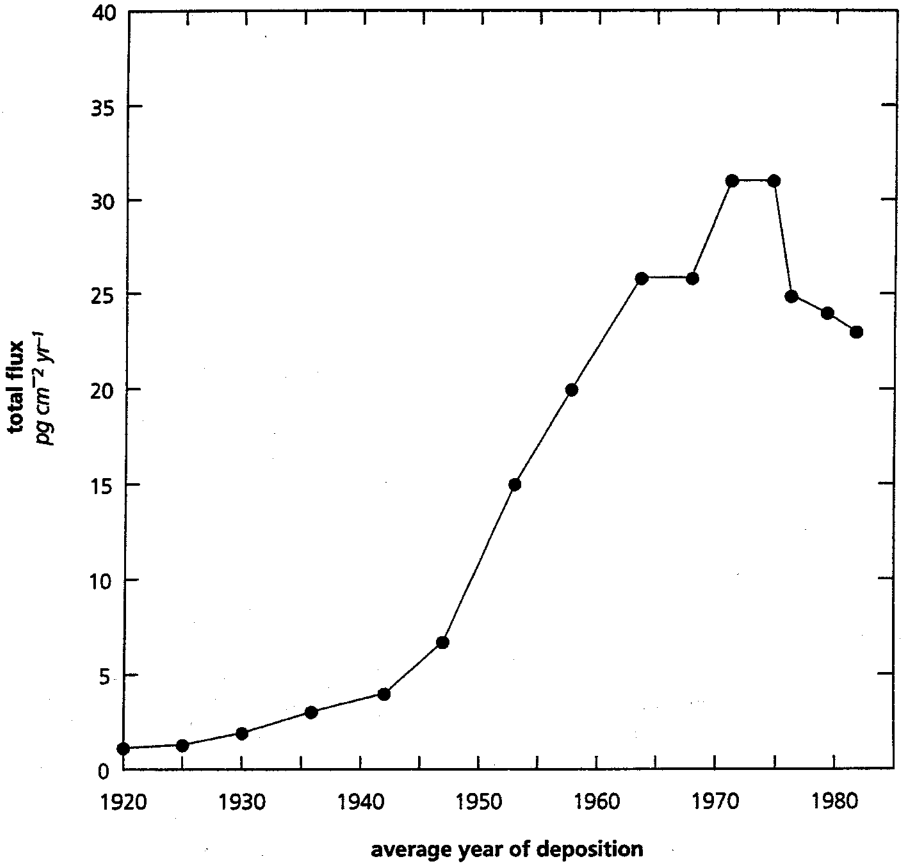

Figure 2 Flux of PCDD and PCDF to Siskiwit Lake. From Czuczwa and Hites, Ref. 105.

affected different dioxin cogeners (dioxin and furans with different numbers of chlorine atoms) differently, then the variation in the cogeners distribution in sediments of different ages should indicate the degradation rate, assuming that the distribution of cogeners as deposited did not change in time). In sediment cores from Lake Erie, covering the time from 1950 to the early 1980s, which had a high sedimentation rate and thus a high resolution for analysis of the distribution of dioxin cogeners, the distribution of cogeners has been found to remain approximately constant in time, indicating a half-life of longer than twenty years.[105]

6.3 *Dioxin in Soil*

Table 19 shows measured dioxin concentrations in soil. While there is considerable variation between samples, industrial sites appear to have the highest average

Table 19 Average Dioxin Soil Concentrations

Location	*Type*	*# Sites*	*Sample Depth, cm*	*PCDD/F Concentration, pg/cm³* average ± st. dev.	*median*
Ontario & US Midwest[118]	Rural	30	—	100 ± 150	50
Minnesota[119]	Natural Areas	3	2.5	300 ± 200	—
Britain[120]	Background	77	5	700 ± 700	500
Elk River, MN[121]	Semi-rural	4	2.5	3600 ± 2500	—
Ontario & US Midwest	Urban	47	—	3000 ± 5000	500
Ontario & US Midwest	Industrial	20	—	12,000 ± 15,000	4000

concentrations, followed by urban sites, and rural sites have the lowest average dioxin concentrations (with the exception of the four sites in Elk River, MN). The measurements from rural Ontario and the US midwest are probably the most representative of US average concentrations, because the sampling sites were far from industrial sources, and samples were taken from a relatively large number of locations.

The lifetime of dioxin in soil is not well known. 2,3,7,8-TCDD is the only PCDD/F whose environmental fate has been studied extensively, with a half-life usually estimated to be about 10 years; there is some evidence that the higher chlorinated dioxins have a longer half-life.[122,123,124,125,116] Dioxin formation during composting has also been reported, but data are not yet sufficient for a quantitative analysis of the net contribution from this source.[126]

To roughly estimate the amount of dioxin expected in soil, it will be assumed that all dioxins emitted in the US are deposited, uniformly, on the US.

Assuming that dioxin in soil degrades exponentially with time, the concentration of dioxin in soil can be expressed as

$$C = \sum \frac{E_n}{V} \exp(-n \ln 2/\tau)$$

where τ is the half-life, n is the number of years since deposition of the dioxin, E_n is the annual emissions, and V is the volume of soil.

Dioxin binds strongly to soil, so the movement of dioxin in soil will be assumed to be determined by soil mixing or erosion.[80] For an unplowed, low erosion soil, the mixing depth will be on the order of 1–10 cm. But the minimum effective mixing depth is given by the depth of the sample, usually about 2.5 cm, as shown in Table 19. The soil volume, V, is then given by the area of the US, 9×10^{16} cm², multiplied by this soil mixing depth, resulting in a soil volume of about 2×10^{17} cm³.

For the historical dioxin emissions estimated in Table 16, soil dioxin concentrations would be about 50 pg/cm³ for a half-life of 10 years, and about 100 pg/cm³ for a half-life of 20 years. Although these should be over-estimates, since they assume no degradation of dioxin in the air prior to deposition, where it may have a shorter half-life, they appear to be roughly consistent with the median and average values for rural sites in the US midwest and Ontario, given in Table 19.

7. DISCUSSION AND CONCLUSIONS

The measured concentrations of PCDD/Fs in air, soil, and sediments appear to be in reasonable agreement with estimated 1989 dioxin emissions of 400 kg/yr, and with the estimated past dioxin emissions.

Several previous studies have come to the opposite conclusion. Travis and Hattemer-Frey, in their study of 2,3,7,8-TCDD in the US, concluded that annual emissions from MSW incinerators, automobiles, residential wood combustion, and hospital waste incinerators accounted for less than 10% of their estimate of TCDD input to the environment.[6] Rappe concluded that known emissions in Sweden are 10–20 times less than measured aerial deposition.[7] Harrad and Jones, in their study of dioxin in Britain, estimated emissions that were about an order of magnitude less than their estimate of deposition fluxes.[8]

It is difficult to compare the results of these studies in detail. Travis and Hattemer-Frey's analysis was of 2,3,7,8-TCDD, not PCDD/F, and focused on food chain transport rather than environmental emissions and environmental levels, although it appears that their estimate of soil dioxin concentrations is higher than that used here. Rappe's analysis was for Sweden, and thus emissions and deposition cannot be directly compared with US data. Harrad and Jones' analysis, although for Britain, differs from ours primarily in using higher deposition rates than reported here, and in using lower emissions from MSW incinerators.

Although the estimates made here are consistent with the available data, 1970 and 1989 emissions could have been as much as a factor of four greater than those estimated here (see Tables 17 and 18) and still be consistent with air, soil, and sediment data.

If emissions were greater, what might be the source? Overall, because most dioxin sources are small contributors to the total dioxin emissions, they would have to emit over an order of magnitude more than is estimated here, in order to significantly affect the total estimate. Only for the largest sources, municipal waste incineration and total biomass combustion, could a plausible change in the emission factors significantly affect the total emission estimate.

For municipal waste incineration, emissions may indeed have been underestimated. Although the emission data indicates that highest emissions were only a factor of six greater than the estimated average, and thus it is unlikely that the true average emission factor is a factor of six greater than estimated, it is plausible that the emission factor might have been underestimated by a factor of three or four. This would increase the estimate of total national emissions by 50%.

Biomass combustion, including forest fires, might also have a higher average emission factor, since most of the data used in this estimate was for wood, a low chlorine source of biomass. However, the emissions from biomass combustion are limited by the historical sediment record. If, for example, the emission factor were a factor of ten higher than estimated here (higher, in fact, than any measured emissions from biomass combustion) then the estimated emissions would have been the same in 1940 and in 1970 (see Table 16), which is not consistent with the sediment record. Even a factor of five increase in the emission factor would be difficult to reconcile with the sediment record, and, with such an increase, total 1989 emissions could have been at most 50% higher.

There could be some unknown source of dioxin, such as a chemical process, especially because emissions from such sources have not been measured well. But, in order to make a significant contribution to total national emissions, this new source would have to have a dioxin contamination, or emission factor, at least an order of magnitude greater than other chlorinated chemicals such as 2,4-D and tetrachloroethylene, and it would have to be used in large quantities.

Further data on dioxin emissions from the combustion of various types of biomass, with chlorine in varying concentrations and chemical forms, and under poor combustion conditions, would help to reduce the uncertainty in this analysis. In addition, data on the sources of chlorine in municipal waste would provide a basis for measures to reduce the dioxin-forming potential of MSW.

These estimates of emission factors provide a basis for estimating the sources of human exposure to dioxin. These are unlikely to be proportional to the contribution of each source category to total emissions, since different source categories, such as municipal waste incinerators and forest fires, have significantly different geographic distributions, which may significantly influence their contribution to dioxin in the human food chain.

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APPENDIX A. CONSUMER WASTE INCINERATION

Sewage Sludge Incineration: About 1×10^{-3} dry kg of sludge is produced per gallon of wastewater[127], and as of 1988, the total US wastewater flow is on the order of 84,000 million gallons per day.[128] About 10% of the total, or 3×10^9 dry kg/yr of US sludge is incinerated. Emissions of PCDD/Fs at the outlet of three sewage sludge incinerators, all equipped with scrubbers, shown in Table A.1, averaged 1.2 μg/kg sludge, for a total of 4 kg/yr.

Table A.1 PCDD/F Emissions from Sewage Sludge Incinerators[129,130,131]

Sludge Incinerator Identification	*Sludge Cl (ppm)*	*PCDD/F Emission Factor (μg/kg)*
SS – A	2870	0.3
SS – B	590	0.9
SS – C	1453	2.4

Apartment Incinerators: There is no direct data on dioxin emissions from waste incinerators in apartment buildings. Because conditions in these incinerators are much less well controlled than in MSW incinerators, their emission factor could be similar to the worst of MSW incinerators, about 60 μg/kg.

The total amount of waste burned in US apartment incinerators is not reported. As of 1989, 4×10^8 kg of municipal waste (dry basis) were estimated to be burned in apartment incinerators annually in New York City alone.[132] 2.4×10^7 kg are estimated to be burned annually in New Jersey, as of the early 1990s (personal communication, I. Atai, New Jersey Department of Environmental Protection and Energy). Assuming that on the order of 10^9 kg is incinerated nationally in apartment buildings, total dioxin emissions would be on the order of 60 kg.

Open Garbage Burning: There is no good estimate of the amount of household garbage burned in the open. This category would include both backyard trash burning, and the burning of paper and other trash in fireplaces. While only a small fraction of household garbage is disposed of in this way, the emission factor may be on the order of 60 μg/kg, comparable to the worst municipal waste incinerators. If 0.1% of US municipal waste were burned in the open, then annual emissions would be about 10 kg/yr.

APPENDIX B. INDUSTRIAL WASTE PROCESSING AND INCINERATION

Copper Recycling: The source of chlorine in secondary metal processing facilities is thought to be PVC (polyvinyl chloride) plastic from the coating on copper wires, telephone residues, etc. 39 μg/kg of PCDD/Fs were measured in emissions from a smelter processing copper scrap.[133] Emissions were controlled by an after-burner and a fabric filter system. This plant, the AMAX copper smelter in Carteret, New Jersey, was closed down after being fined by environmental authorities for a variety of pollution violations, and thus the dioxin emissions from this plant may not be representative of other secondary copper smelters.[134]

Further information on dioxin emissions from recycling of plastic-contaminated copper comes from data on wire reclamation incinerators. A wire reclamation incinerator, used for recovery of copper from coated copper wire and equipped with an afterburner, emitted 0.29 mg/kg of wire.[135] The feed chlorine concentration was about 800 ppm.

Most wire burning is illegal, so it is not known how much wire is burned annually. Estimates from industry experts range from 8.5×10^7 kg for legally burned wire to 3×10^9 kg total, with 3×10^8 considered a conservative estimate. As of 1989, there were five secondary copper smelters operating in the US, with a capacity of about 4×10^8 kg of copper.[136] Thus total annual combustion of copper scrap will be estimated to be about 7×10^8 kg.

The average of the two emissions factors, 20 μg/kg, implies total annual emissions from copper recycling on the order of 10 kg PCDD/Fs.

Steel Drum Reconditioning Furnaces: Drum and barrel reconditioning furnaces recondition steel drums by combusting the residual drum contents in a furnace. About 45 million steel drums are reconditioned in the US each year, at about 150 facilities. Most of these facilities do not burn the drums, but wash them. About 25 of these facilities have reconditioning furnaces, and it can be estimated that roughly 4 million drums per year are processed in drum reconditioning furnaces (personal communication, P. Rankin, Association of Container Reconditioners, 1992).

One steel drum reconditioning furnace, equipped with an afterburner, was found to emit 1.3 μg/drum of PCDD and PCDF, and 32 ng/dscm @ 3% O_2.[137] When corrected to 3%O_2, two other furnaces emitted an average of 1948 ng/dscm and 134 ng/dscm, respectively.[138] Although this study did not report the rate per drum, this can be estimated, by comparison with the conversion factor from the previous study, to be 80 μg/drum and 5 μg/drum, respectively. Average dioxin emissions from three facilities were 30 ± 40 μg/drum. Assuming that the dioxin measurements are typical of drum reconditioner emissions, total emissions of PCDD and PCDF from such furnaces can be estimated to be on the order of 0.1 kg per year.

The drum reconditioning industry has put in place an aggressive campaign to convince drum emptiers to fully empty all containers of their content before sending them to a reclaimer. This should help to reduce dioxin emissions.[139]

Steel Recycling: Dioxin emissions from electric arc furnaces processing scrap steel are thought to result from chlorine-containing cutting fluids, as well as chlorine-containing plastics. Dioxin emissions from 9 electric arc furnace steel recycling plants, equipped with a variety of pollution control devices, have been measured in Sweden to be about 4 ± 3 μg of TCDD equivalent (Eadon) per ton of steel produced.[140,141] This would correspond to on the order of 100 μg of PCDD/F per ton.[10] In the US, 33 million tons of steel are produced annually from steel scrap in electric arc furnaces, as of 1990.[142] On this basis, PCDD/F emissions from steel recycling would be about 3 kg annually.

Carbon Regeneration Furnaces: Carbon regeneration furnaces reactivate spent carbon filters from industrial or municipal water treatment facilities; the spent carbon may contain adsorbed chlorinated compounds. The single tested facility, equipped with an after-burner, a spray cooler, and a baghouse, had emissions of PCDD/Fs of 0.057 μg/kg of regenerated carbon.[143] About 5 × 10^7 kg of carbon are regenerated annually in the US (personal communication, C. McGinty, Calgon Corp., and C. Spannard, National Environmental and Technical Applications Corp.,1992). From this, the total amount of PCDD/Fs released can be estimated to be about 0.003 kg per year.

Used Motor Oil Burners: Due to the likely presence of chlorine-containing corrosion inhibitors in waste motor oil, dioxins can be emitted from the burning of used motor oil. Two facilities that burn waste motor oil were tested for PCDD/F emissions; they emitted 0.016 μg/kg oil (0.0004 μg/kg oil TEF) and 0.065 μg/kg oil (0.0015 μg/kg oil TEF), for an average of 0.04 μg/kg oil (0.001 μg/kg oil TEF). One of these facilities had a fabric filter, and the other had a wet scrubber, and the PCDD/F levels in front of these pollution control devices were one to two orders of magnitude higher than those at the outlet of the pollution control devices.[138] The amount of waste oil burned annually in the US is estimated to be about 3 billion kg, which is about 60% of the total generation of used motor oil.[144] Assuming that the tested facilities were representative, annual PCDD/F emissions from waste oil burning would be about 0.1 kg/yr.

Tire Burning (Controlled and Uncontrolled): About 26 million tires are incinerated annually in the US.[145] With the average tire weighing 11 kg, this comes to a total of 2.9 × 10^8 kg of incinerated tires.[146] PCDD/F emissions from a tire incineration facility equipped with a scrubber and fabric filter were measured to be 0.009 μg/kg (0.0004 μg/kg TEQ).[147] Before passing through the pollution control equipment, PCDD/F emissions were 0.09 μg/kg. If emissions from this plant are representative, then emissions from controlled tire burning can be estimated to be about 0.003 kg annually.

In addition to controlled tire incineration, there are about 90 fires per year in the piles of two to three billion tires that are in thousands of dumps around the country; most of these fires are deliberately set.[148] Based on the size of typical fires, it can be estimated that on the order of 25 million tires burn annually in these fires. Assuming that PCDD/F emission factors are about the same as the emissions prior to pollution control at the tire incinerator, total emissions from uncontrolled tire burning would be about 0.03 kg annually.

Black Liquor Boilers at Pulp Mills: Another source of dioxins is the production of chlorine-bleached paper. Much of this dioxin ends up in wastewater, sludge, or in the paper itself. However, there are also air emissions, from black liquor boilers at pulp mills. Black liquor boilers burn concentrated spent liquor from the pulping process and recover inorganic chemicals used to produce pulp from wood chips. When chlorine is used to bleach the pulp, the black liquor may contain several thousand parts per million of chlorine. Despite this high chlorine content, black liquor boilers have been found to have quite a low rate of dioxin emissions, estimated to be 0.01 μg/kg, based on emissions measurements at three facilities.

The total annual U.S. production of bleached pulp is about 2.4 × 10^{10} kg.[149] Typically between 1.3 and 1.55 kg of black liquor is burned per kilogram of pulp produced.[53] Thus roughly 3.4 × 10^{10} kg of black liquor are burned in the U.S. annually. Emissions of dioxins from the outlet of three black liquor boilers, shown in the table below, averaged 0.013 μg PCDD /F per kg black liquor. Therefore total annual emissions would be about 0.4 kg PCDD /F from black liquor boilers.

Table B.1 PCDD/F Emissions from Black Liquor Boilers

Black Liquor Boiler Idenification	*Black Liquor Chlorine Content (ppm)*	*PCDD/F Emission Factor(μg/kg)*
BLB-C[150]	3000	0.03
BLB-B[151]	5000	0.006
BLB-A[152]	1400	0.004

Dioxins have also been found in emissions from magnesium and nickel refineries and from petroleum refineries, although the data are insufficient for a quantitative estimate.[153,154]

APPENDIX C. BIOMASS COMBUSTION AND RELATED SOURCES

Structural Fires: The emission factor appropriate for burning buildings is difficult to estimate. Wood is the most common combustible material in structures, but the presence of chlorine-rich plastics and other synthetic materials might result in higher emission factors. Here, emissions from structural fires are evaluated with the biomass emission factor, with combustion of PCBs and PCP-treated wood considered separately.

The EPA estimates that an average of 6.8 tons of material are burned per structural fire (personal communication, M.A. Stewart, US EPA, 1992). In 1989 688,000 structural fires were reported in the U.S. (and the number of reported fires has decreased by one third since 1980).[78] Thus it can be estimated that about 5×10^9 kilograms of material are burned annually in structural fires. If the PCDD/F emission factor is similar to that of poorly controlled wood combustion, annual emissions would be about 2 kg.

Cigarette Smoking: PCDD/F emissions from cigarette smoking were measured to be about 120 pg/cigarette.[155] The average cigarette weighs about 0.8 grams[156], so the emission factor is about 0.1 ug/kg. 680 billion cigarettes were sold in the US in 1989.[78] Thus total PCDD/F emissions from cigarette smoking can be estimated to be about 0.05 kg/yr.

Combustion of PCP-Treated Wood: As discussed in the section on non-combustion emissions from pentachlorophenol (PCP), PCP contains about 0.2% PCDD/F by weight. An industrial incinerator burning PCP-treated wood emitted 8 μg PCDD/F per kg of wood. (These wastes included PVC plastic-coated wooden window frame pieces, and wood treated with pentachlorophenols. The composite fuel contained nearly 10,000 ppm chlorine. This incinerator apparently had no pollution control devices[157]). The wood contained 1% chlorine. The amount of PCP-treated wood burned annually is not known, but if we assumed as an upper limit that 10% of annual PCP production is burned, then, since about 1.1×10^7 kg of PCP are used annually in the US (Table 11) annual emissions from PCP combustion would be on the order of 1 kg.

PCB Fires: The combustion of polychlorinated biphenyls (PCBs) during structural fires can result in significant dioxin emissions. US manufacture of PCBs was banned in 1976, but before this, three quarters of PCBs were used as dielectrics in transformers and capacitors, and many of these still remain in service. Because of the risk of dioxin and PCB emissions, PCB transformer fires must be reported to the National Response Center; about one such fire is reported annually.

Although there is no data on air emissions from uncontrolled PCB fires, the soot from these fires contains about 100 times the level of PCDD/Fs that is found in the fly ash of municipal solid waste incinerators.[64] If the air emission factor for PCB fires is also 100 times greater than emissions from municipal waste incineration, then the average emission rate would be about 1000 μg/kg of PCB.

Each transformer contains about 1 ton of PCBs.[158] A typical fire has been estimated to include about 10 transformers.[159] On this basis, annual air emissions of PCDD/F from PCB transformer fires would be about 0.01 kg, although the accuracy of this estimate is low.

In addition to large transformers, household appliances such as refrigerators and air conditioners built before the early 1980s may contain PCBs. As of 1987, it was estimated that 74,000 tons of PCBs were still in use in the US.[160] No estimate is available of the amount of PCBs burned in structural fires annually through the combustion of household appliances. There are about 80 million housing structures, and 4 million commercial structures in the US.[78] Based on the data in the structural fires section, it can be estimated that there is a fire in about 1% of US buildings each year. If roughly the same fraction of PCBs were burned, then the annual total PCDD/F emissions would be about 0.7 g.

APPENDIX D: DIOXIN CONTAMINATION IN CHEMICAL PRODUCTS

Hexachlorophene: Hexachlorophene is a bactericide made from trichlorophenol, with uses including the consumer products pHisoderm and pHisohex. It was hexachlorophene wastes that led to the contamination of Times Beach and other areas of Missouri with several hundred kg of PCDD/F. Most uses of hexachlorophene were banned in 1972.[88] No data is available on the quantities of hexachlorophene produced or the fraction emitted to air or soil.

2,4-D: Low levels of PCDD/Fs have been found in some samples of 2,4-D, which has become the most extensively used herbicide in the world. As of 1989, 20–30 million kg were used annually in the US.[161] PCDD/F levels have been measured to be about 0.2 ppm (200 μg/kg) or less.[162] On this basis, about 5 kg of PCDD/F are contained in the 2,4-D used annually in the US.

PCBs: Polychlorinated biphenyls (PCBs) have been found to contain from 1 to 10 ppm (1,000–10,000 μg/kg) PCDD/Fs.[83] Their manufacture was banned in the US in 1976.[163] US production of PCBs by Monsanto, the major US manufacturer, are shown in the following table, using a standard assumption that 0.1% escaped during production processes.[90] Emissions from PCB fires were estimated in an earlier section.

Table D.1 Dioxin Emissions from PCB Production

Year	*PCB Production 1000 ton/yr*	*PCDD/F Emissions kg/yr*
1957	~ 14	0.1
1960	17	0.2
1965	27	0.3
1970	39	0.4
1974	18	0.2
1977	0	0

About 5000 kg of PCBs are estimated to have been spilled annually during transportation, which would have included 0.005 to 0.05 kg of PCDD/F.[164]

Other: Other chlorinated organics have also been suspected of dioxin contamination.[165,83] However, the known sources all amount to low levels of dioxins compared to even the current emissions from PCP. Tetrachloroethylene, for example, is a heavily used chemical (300,000 tons per year in the US), 90% of which is emitted to the air.[165] Of four samples of tetrachloroethylene, one contained 0.047 ppm PCDD/F (all OCDD), and the others contained none, with detection limits of 0.005 or 0.01 ppm.[166] Assuming that the average PCDD/F content of tetrachloroethylene is on the order of 0.01 ppm, then annual release is about 3 kg, and perhaps 0.003 kg TEF.

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