Incineration and Dioxins
Review of Formation Processes

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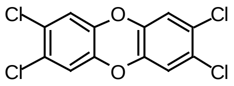
Incineration and Dioxins:
Review of Formation Processes

This review of scientific literature on dioxin and furan formation has been derived from a study conducted on behalf of Environment Australia by Environmental and Safety Services.

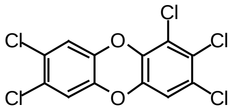
The review investigates the possible relationship between chlorine input to incinerators and presence of dioxins and furans in stack gases emitted from incinerators. It also provides an overview of dioxins and furans, their toxicity, pathways to their formation from combustion processes, sources and rates of emissions from such processes, and long-term trends in emissions from these processes.

1 Description of Dioxins and Furans

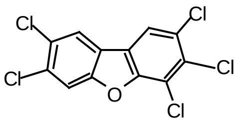
The polychlorinated dibenzo-para-dioxins (***PCDD***) and polychlorinated dibenzofurans (***PCDF***) are chlorinated, planar, aromatic compounds containing two benzene rings. The terms PCDD/F and dioxins carry the same meaning and are used interchangeably in the literature. The structures of the most toxic forms of dioxin and furan molecules are shown in Figure 1. A dioxin molecule is bonded by two oxygen atoms, and a furan molecule by a single oxygen atom and a direct bond. Under standard atmospheric conditions, all dioxins are solid and are characterised by low vapour pressure and limited solubility in water.



2,3,7,8,-TCDD



1,2,3,7,8,-pentaCDD



2,3,4,7,8,-pentaCDF

Figure 1. Most toxic isomers of dioxins and furans.

There are 75 different forms of PCDD and 135 different forms of PCDF that are distinguished by the position and number of chlorine atoms attached to the two benzene rings. These different forms of dioxins are called ***congeners*** and their number is listed in Table 1. Dioxins and furans with the same number of chlorine atoms constitute a ***homologue group*** of ***isomers***. Table 1 shows that there are 16 homologues groups, 8 for PCDD and 8 for PCDF. For example, there are 22 different isomers of dioxins and 38 of furans belonging to the same tetrachlorinated homologue groups.

For toxicity purposes, only the homologues with four or more chlorine atoms are considered and these are called tetra (TCDD, TCDF or D4, F4), penta (PCDD, PCDF or D5, F5), hexa (HxCDD, HxCDF or D6, F6), hepta (HpCDD, HpCDF or D7, F7) and octa (OCDD, OCDF or D8, F8). It is these 10 PCDD/F homologues that are normally quoted in the literature. Note the overlapping terminology as the penta homologues have the same abbreviation (PCDD, PCDF) as all 210 dioxins and furans (PCDD/F).

Table 1. Number of various isomers of dioxins (Rappe, 1996).

Number of chlorine atoms	Number of PCDD isomers	Number of PCDF isomers
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
Total	**75**	**135**

Those PCDD/F that have four chlorine atoms substituted in positions 2, 3, 7, and 8 are considered to be the most toxic. Their toxicity depends on the location and the number of additional chlorine atoms attached to the benzene rings. The 17 most toxic PCDD/F isomers, belong to the 2, 3, 7, 8-subsituted group. For comparison, the LD 50/30 values of some toxic (2, 3, 7, 8-substituted) and non-toxic dioxins are listed in Table 2 (*Steel Times*, 1995). LD 50/30 represents a lethal dose of a chemical to 50% of test animals after 30 days. In general, the more chlorine atoms a PCDD/F molecule has, the less toxic it becomes.

Table 2. Toxicity of chlorinated PCDD in Guinea pigs (*Steel Times*, 1995); the more toxic compounds have smaller LD 50/30 number.

Position of chlorine atoms	Guinea pigs
2,8	>300,000
2,3,7	30,000
2,3,7,8	2
1,2,3,7,8	3.1
1,2,4,7,8	1,125
1,2,3,4,7,8	72.5
1,2,3,6,7,8	70-100
1,2,3,7,8,9	60-100

Since the toxicity of a dioxin congener depends on the level of chlorination and location of chlorine atoms on the benzene rings, three toxicity equivalence schemes, called Eadon, Nordic and ***ITEQ*** (***i***nternational ***t***oxic ***eq***uivalent, also denoted as NATO or CCMS for NATO Committee on the Challenges of Modern Society, 1988) have been developed. Within each scheme, 2, 3, 7, 8-substituted PCDD/F have weighting or conversion factors, as illustrated in Table 3. These factors are applied to calculate the equivalent concentration of a dioxin congener. Note a small difference between NATO and Nordic schemes, which differ only in the weighting factor assigned to 1, 2, 3, 7, 8 PCDF. Recent studies indicate good correspondence between the chemical concentration of PCDD/F, expressed in equivalent concentration, and the biological potency of PCDD/F (eg Kopponen et al 1994, Clemons et al 1997).

The ITEQs are calculated as follows. If, for example, the concentration of 2, 3, 4, 7, 8 PCDF is 0.1μg/m^3, its ITEQ value is (0.1x0.5) 0.05μg/m^3, where the factor 0.5 was extracted from Table 3. Similarly, the concentration of other dioxins needs to be weighted according to the conversion factors listed in Table 3. The sum of the converted concentrations is then reported as an ITEQ value.

In the dioxin literature, the ITEQ concentration is the one most often quoted, followed by the total PCDD/F concentration, and the Nordic-equivalence concentration. As a rule of thumb, ITEQ values are smaller by about 50 times than PCDD/F concentration values. So, one can divide PCDD/F concentration by 50 to obtain a very approximate but fast estimation of ITEQ concentration, if the latter values are not available.

Table 3. The weighting factors used in Eadon, Nordic and ITEQ equivalency schemes.

Homologue group	Toxic isomer	Eadon	Nordic	ITEQ
TCDD	2,3,7,8	1	1	1
PCDD	1,2,3,7,8	1	0.5	0.5
HxCDD	1,2,3,4,7,8	0.03	0.1	0.1
	1,2,3,6,7,8	0.03	0.1	0.1
	1,2,3,7,8,9	0.03	0.1	0.1
HpCDD	1,2,3,4,6,7,8	-	0.01	0.01
OCDD	1,2,3,4,6,7,8,9	-	0.001	0.001
TCDF	2,3,7,8	0.33	0.1	0.1
PCDF	1,2,3,7,8	0.33	0.01	0.05
	2,3,4,7,8	0.33	0.5	0.5
HxCDF	1,2,3,4,7,8	0.01	0.1	0.1
	1,2,3,6,7,8	0.01	0.1	0.1
	1,2,3,7,8,9	0.01	0.1	0.1
	2,3,4,6,7,8	0.01	0.1	0.1
HpCDF	1,2,3,4,6,7,8		0.01	0.01
	1,2,3,4,7,8,9		0.01	0.01
OCDF	1,2,3,4,6,7,8,9		0.001	0.001

It is generally accepted that the mole fractions of dioxin congeners and tetra to octa homologues are specific to a dioxin formation process. The relative concentration of homologues and congeners, usually plotted as a histogram, is called the ***dioxin signature*** or ***dioxin fingerprint***. The complete signature contains 10 homologues, up to 17 toxic congeners (as listed in Table 3), and the relative ratio of the sum of congeners to the total PCDD/F. Usually, only a subset of the 17 congeners is included in the signature and even then some of the congeners may be lumped into one number, eg all hexachlorinated congeners are reported together as one item in the signature.

Rigo et al (1995) assembled signatures of dioxin formation for a range of industrial processes and these signatures are reproduced here in Figure 2. The figure contains the relative mole fractions of 2, 3, 7, 8 congener to homologue (9 bars) and the mole fraction of homologue to the total PCDD/F (10 bars). The example of TCDD ("A" bar in Figure 2) can be used to illustrate how the signature was obtained. The amount of 2, 3, 7, 8 TCDD (in moles) was divided by the total amount of all 22 homologues of TCDD, to obtain a ratio which was then multiplied by 100% and plotted in Figure 2. Similarly, the amount of all 22 tetrachlorinated dioxins was divided by the total amount of PCDD/F in moles, multiplied by 100%, and plotted as "I" bar in Figure 2.

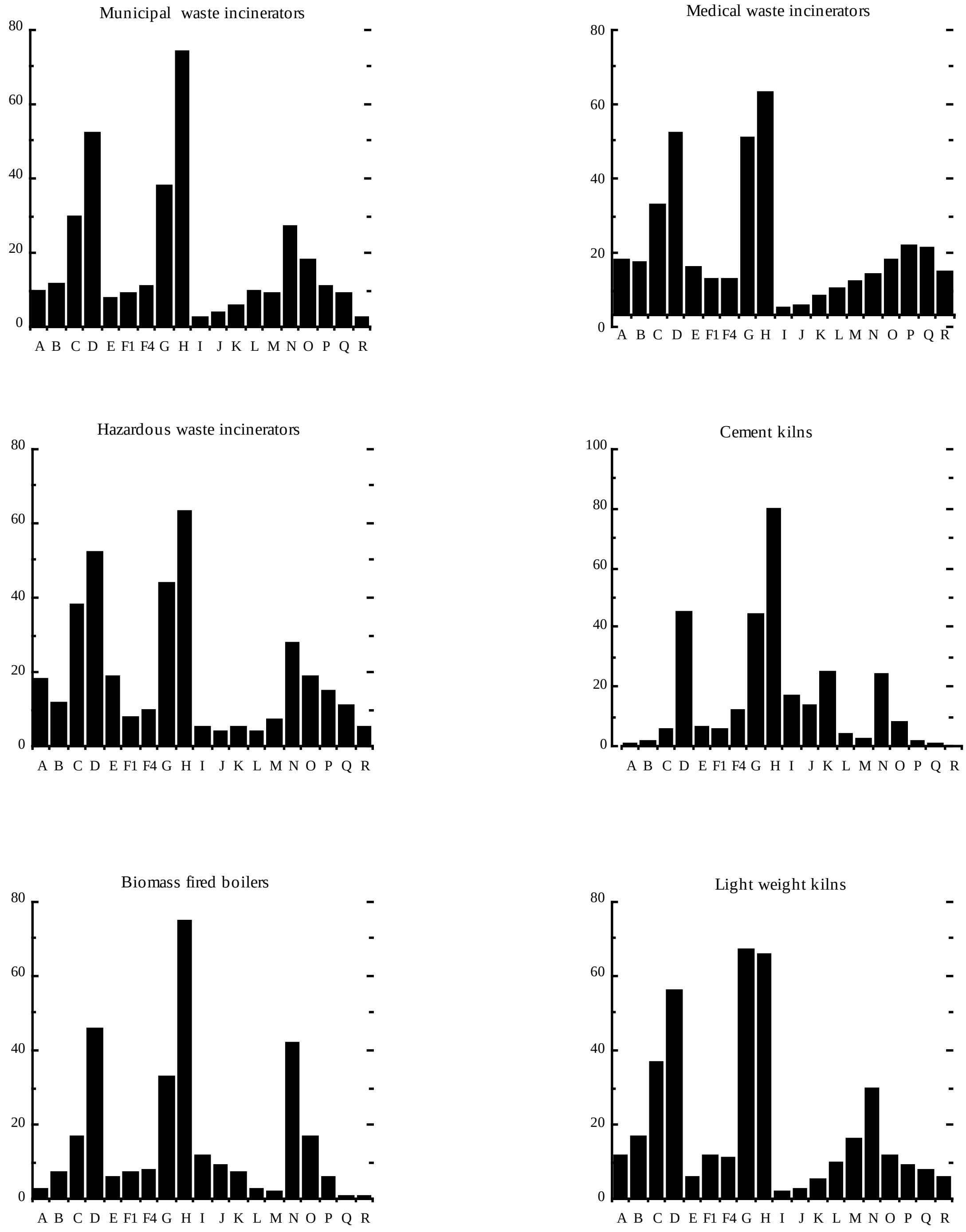


Figure 2. Dioxin signatures describing formation of dioxins in combustion processes.

A good example of different dioxin signatures is observed in stack gas emissions from boilers used in the pulp and paper industry (Luthe et al, 1997). Two types of boilers are employed, recovery boilers that burn the so-called black liquor solids containing chlorine from the Kraft process, and power boilers that burn wood waste that often contains chlorine salts, especially in coastal areas. Emissions from recovery boilers tend to contain mostly dioxins, whereas emissions from power boilers show approximately equal concentrations of dioxins and furans.

Another excellent example illustrating the utility of dioxin fingerprint for the identification of the PCDD/F source comes from the province of British Columbia in Canada. Kraft pulp mills operating there employed a bleaching technology, which used chlorine gas. This led to the formation of dioxins, and their subsequent emission in discharge water. The dioxin signature from Kraft pulp mills was dominated by three tetrachlorinated isomers. The problem was recognised and the chlorine gas was replaced by chlorine dioxide or nonchlorinated reagents (Rappe 1996), resulting in dioxin-free paper bleaching. However, the routine testing of the sediment in the vicinity of effluent discharge points from the pulping mills soon disclosed evidence of new dioxin deposition, which had a different signature (dominated by hexachlorinated dioxins laid over a typical pulp-bleaching fingerprint) from that generated by gaseous-chlorine bleaching.

It was speculated that the dioxin source was located in the paper plant but the source would have to be different from the bleaching process. Careful investigation soon revealed that on occasions the mills accepted wood chips that might have been obtained from lumber contaminated with polychlorinated phenols (***PCP***). In the lumber industry, PCP were applied to prevent staining of undried wood with sap. The testing program that followed narrowed down the source of dioxin to polychlorinated phenoxyphenols, an impurity which was originally present in PCP used to treat the wood (Luther et al, 1993). At the same time, a similar investigation using the analysis of dioxin fingerprint concluded that the recycled dioxin-contaminated corrugated containers caused the dioxin emission problems from other Canadian pulp mills (Berry et al, 1993).

2 Technical Details of Incinerators

This section describes the operation of incinerators, reviews their construction details including unit operations[1], and introduces the technical nomenclature normally used in characterising the incinerators. In general, large-scale incineration units are classified as municipal waste combustors (***MWC***), medical waste incinerators (***MWI***), hazardous waste incinerators (***HWI***), boilers and industrial furnaces (***BIF***), cement kilns (***CK***) and biomass combustors (***BC***). Here, the focus is on municipal waste combustors, since they are considered to be the most important source of dioxin from combustion processes; other types are described in detail by Rigo et al (1995).

Modern municipal waste combustors are designed to burn either the entire waste stream (mass burn systems) or refuse-derived fuel (***RDF*** systems), that is only the combustible fraction of the municipal solid waste. Recent mass burn systems, such as those built in Ireland or Portugal (Foster Wheeler Corp, 1997), incorporate furnaces, which are exclusively equipped with mechanical grates that aid the flow of refuse through a furnace, with ash being discharged at the furnace's end. Older mass-burn installations often used rotary kilns or hearths, but those were plagued by low combustion efficiencies and large emission rates of pollutants. On the other hand,

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[1] Unit operations denote individual steps in industrial processing operations, such as scrubbers, dust collectors, and furnaces.

RDF facilities use fluidised-bed technology to capitalise on technical advantages of this technology, such as low emission rates of gaseous pollutants and complete combustion of organic materials. Fluidised-bed furnaces contain a combustion chamber with a bed of sand, which is fluidised by a stream of air forcing its way through the bed.

Figure 3 illustrates a schematic diagram of a typical fluidised-bed facility burning RDF. The RDF fuel is delivered to the fluidised bed by a waste feeder. However, before feeding to the furnace, the municipal solid waste undergoes presorting to remove metals, glass and masonry. This is a very important step that results in decreased emission of heavy metals from incinerators, promotes recycling, limits emission of other pollutants (such as CO and unburned organic volatiles) due to the more homogenous nature of the fuel, and reduces production of ash (typically only 5% of the weight of the feed stream) because of a more complete combustion. Size of particles in the waste stream is reduced by a series of operations that include mills (hammer and flail mills) and shredders (rotary shredders and ring grinders).

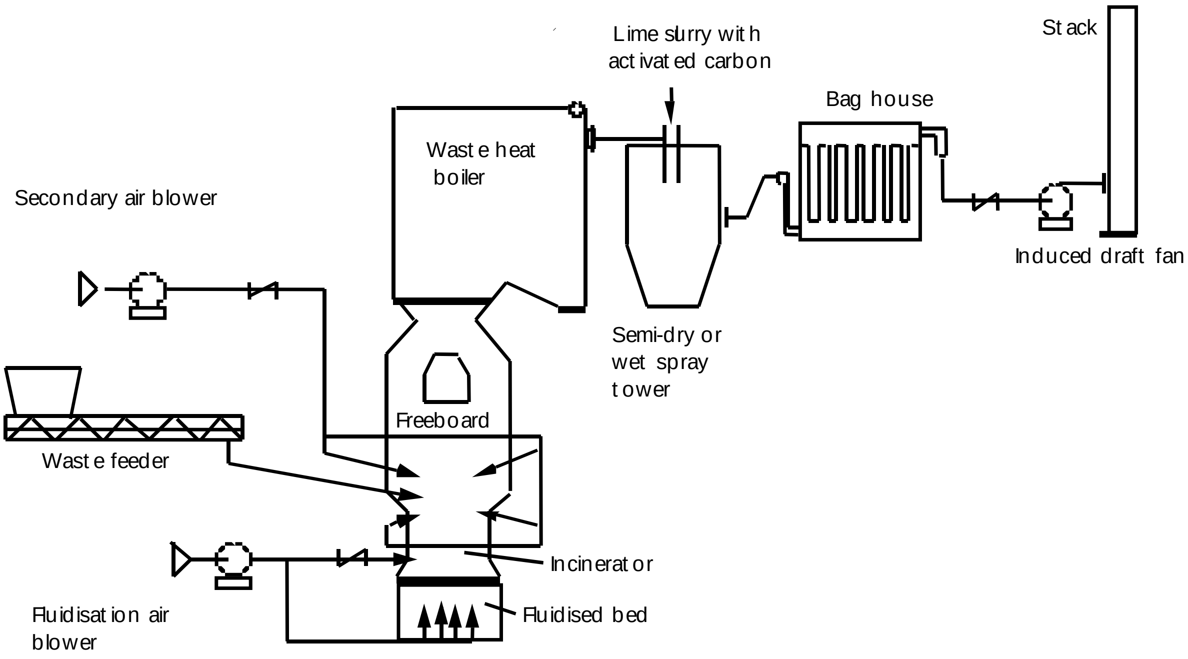

Figure 3. Municipal waste combustor that uses revolving fluidised-bed furnace. Unit operations downstream of the fluidised bed, such as scrubbers and bag house, are common to other MWC, including mechanical grate furnaces for mass burning and circulating fluidised-bed incinerators for combustion of RDF.

Two types of fluidised beds are presently in use. In the revolving or twin interchanging fluidised bed, the fluidisation air is introduced into the bed through a triangular distributor creating intense vortex and leading to substantial combustion turbulence (Saito et al, 1988). For combustion in the revolving fluidised-bed furnace, the RDF requires minimal feed preparation and the furnace has excellent combustion and emission characteristics. However, the revolving fluidised beds have low capacity of around 150 tons/day (Ishikawa et al, 1997) and are unsuitable for large facilities processing more than 1000 ton/day of RDF.

More common in large-scale installations are circulating fluidised-bed furnaces, as illustrated in Figure 4. Circulating fluidised beds operate at higher fluidising velocities, allowing partially combusted material to leave the bed and be separated from the stream of combustion gases by a large cyclone. The collected solid materials are then returned (circulated) to the fluidised bed. These characteristics allow feeding of RDF that can be irregular in shape, since uncombusted material is returned to the fluidised bed by a cyclone, in effect providing long residence time and turbulence for complete combustion of fuel particles. Other advantages of this configuration include low NOx formation rates (so a need to inject urea or ammonia to control NOx is often avoided) and stable operation due to a large thermal mass circulating between the furnace and a cyclone.

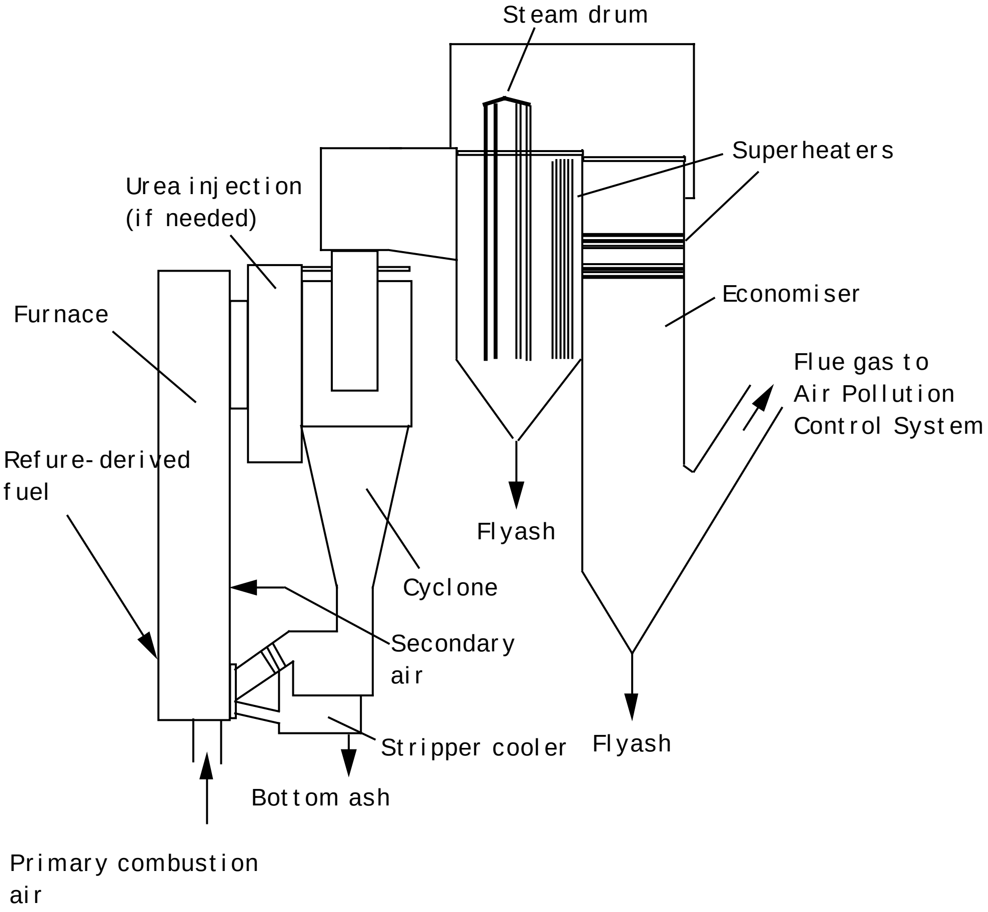

Figure 4. Details of the circulating fluidised-bed MWC constructed recently in Robbins IL, USA for firing refuse-derived fuel (Foster Wheeler Corp, 1997). Unit operations in the air pollution control system are not shown in the figure.

Recovery of heat generated in the furnace takes place downstream from the cyclone in superheaters, which are marked as waste heat boiler in Figure 3. Energy recovery from MSW and production of electric power by turbines running on superheated steam constitute an important contribution of MWC to recycling. Note that the combustion gases leaving the hot combustion zone of the furnace need to be cooled rapidly to low temperature in the post-combustion zone, to minimise the production of dioxins, which form in the temperature window of 200 to about 450^{o}C.

After boiler banks, the gases are diverted to air pollution control system (***APC***). The role of APC is to remove pollutants from the gas stream before the combustion gases are released from the stack. APC technologies are constantly evolving to satisfy emission control requirements imposed by environmental regulations, but usually typical APCs contain 4 to 5 stages, that are designed to remove PCDD/F, heavy metals such as mercury, particulates and acid gases such as HCl as well as to control the emissions of SOx and NOx.

In the first stage, the combustion gases are cooled in a spray tower that may operate with water or with hydrated lime slurry, to provide scrubbing of acid gases from the flue-gas stream. In a spray tower, liquids are atomised at the top of the tower and the droplets travel downward by gravity, evaporate and react with (absorb) acid gases. If lime slurry is completely evaporated, the tower is operated in semi-dry mode with solid particles collecting at the bottom of the tower and smaller ones being carried away by the gas flow to the bag house, where they are removed from the gas by fabric filters. The gases are cooled to about 130^{o}C in the scrubbers before entering fabric filter in the bag house. Small quantities of activated carbon can be mixed with lime slurry to absorb mercury and PCDD/F and limit their emissions.

Fabric filters that operate at low temperatures have now replaced electrostatic precipitators (EPS) in recently constructed MWC. Fabric filters possess very high collection efficiency, due to the enhancement in trapping of small particulates by the cake of collected dust. If lime slurry or other liquid and solid chemicals are injected into the combustion gases before the bag house, fabric filters provide yet another opportunity for acid gases to react with alkaline particles when the gases pass through the filter cake.

It should be noted that electrostatic precipitators have been implicated in the formation of PCDD/F. For example, Ruuskanen et al (1994) reported that octachloro congeners might be formed by electrical processes in the electrostatic precipitators (ESP). According to their measurements, the octachloro furans and dioxins increased by 700 and 400% respectively, when the flue gases were passing through the ESP.

Figure 4 also indicates discharge points for ash removal from the process. The part of ash that is carried by the flow of combustion gases is called fly ash. It accumulates on heat exchangers in waste heat boilers, at the bottom of flue-gas scrubbers and on fabric filters. Fly ash participates as a catalyst in the dioxin-formation process, and may itself contain large quantities of PCDD/F on the surface and in the pores. On the other hand, bottom ash is collected directly from the furnace, as illustrated in Figure 4.

From the review of the current technology for controlling the emission of air pollutants, one must conclude that the amount of PCDD/F leaving incinerators with the stack gases depends strongly on the efficiency of APC systems and the combustion conditions. Any attempt to relate the amount of dioxin in stack gases with the amount of chlorine introduced into the furnace with waste stream, in large scale facilities, is unlikely to yield statistically significant correlations even if they exist, because of the number of variables involved in the operating of a typical incineration installation. From this standpoint in practical systems, it appears that the emission of PCDD/F depends mainly on the combustion conditions and efficiency of APC systems rather than on the amount of chlorine in the waste stream. If MWC are designed, constructed and operated according to the most recent technological advances, their emissions fall substantially below the present-day limits. As an example, Table 4 illustrates emissions of various pollutants from the Robbins Resource Recovery Facility near Chicago that operates two recirculating fluidised-bed furnaces.

Table 4. Comparison of compliance stack test results to Illinois Environmental Protection Agency emission permit limits for the Robbins Resource Recovery Facility (Foster Wheeler Corp, 1997); burning 100% RDF, all values are at 7% O2 dry and NOx are without the injection of urea.

Pollutants	**Units**	**Boiler A**	**Boiler B**	**Permit**
Particulate	$g/m^{3(*)}$	0.053	0.198	0.35
SO_2	ppm	1.0	0.5	30
HCl	ppm	4.6	6.2	25
CO	ppm	4.4	2.2	100
Nox	ppm	73.1	90.4	130
VOC	ppm	1.5	0.6	10
Total PCDD/F	$ng/m^{3(*)}$	2.1	4.9	30
Arsenic	$\mu g/m^{3(*)}$	0.2	0.2	10
Cadmium	$\mu g/m^{3(*)}$	<det limit	0.3	40
Chromium	$\mu g/m^{3(*)}$	4.8	5.6	120
Lead	$\mu g/m^{3(*)}$	3.6	30.9	490
Mercury	$\mu g/m^{3(*)}$	15.8	2.9	80
Nickel	$\mu g/m^{3(*)}$	3.1	3.1	100

* denotes dry standard cubic meter

Note: Both Rigo et al (1995) and Costner (1997) refer to controllable and uncontrollable concentration of hydrogen chloride. The term uncontrollable concentration relates to the levels of HCl in the combustion air after the furnace, but before the scrubber, whereas controllable HCl concentration refers to loading of hydrogen chloride in the exhaust gases after the gases pass through the air-control system.

3 Pathways of PCDD/F Formation in Combustion Processes

There is considerable scientific coverage of issues related to PCDD/F, and several review articles have been compiled (eg Boening 1998, Dyke et al, 1997). A cursory examination of the literature quickly reveals information on issues related to the analysis, sources, and health aspects of PCDD/F. In spite of the extensive literature available, many fundamental issues related to PCDD/F remain uncertain or at least are the subject of considerable debate.

It is now believed that the kinetic reactions responsible for formation of dioxins never proceed to completion. These reactions do not even achieve their maximum or equilibrium conversion that can be calculated from thermodynamic considerations[2]. This means that, in spite of over-abundance of Cl and other elements that constitute building blocks for PCDD/F (carbon, hydrogen, and oxygen), most of the available material is not converted to dioxins.

Thermochemical kinetic analysis, combined with thermodynamic properties, has been used to examine important pathways to *gas phase* formation of PCDD/F (Bozzelli et al 1991, Ritter & Bozzelli 1994); see Figure 5. These analyses of various reaction pathways led to the suggestion that formation of chlorinated PCDD/F involve unimolecular HCl elimination or loss of Cl, which occurs following hydroxy radical addition. Equilibrium constants for these reactions have been calculated, and strongly favour formation of the PCDD/F products. The addition reactions of OH resulting in PCDD/F formation compete with addition of OH radical at fused ring sites, which are responsible for ring cleavage and destruction of species.

While an understanding of gas phase formation of PCDD/F is very important, the surface catalysed formation of these species is generally believed to be the major contributor to PCDD/F from incineration processes. Two different catalytic processes, the *precursor route*, which involves the surface-catalysed reaction of compounds such as chlorobenzenes and chlorophenols, and the *de novo* route, in which carbon, oxygen, hydrogen and chlorine combine and react to (eventually) form PCDD/F, have been proposed. The relative importance of the gas-phase (or *pyrosynthetic*), precursor and de novo PCDD/F formation pathways remains the subject of debate, although it is generally accepted that the precursor route is the primary mechanism for PCDD/F formation at higher temperatures, followed by de novo synthesis at lower temperatures, while the gas phase route is the least significant reaction pathway (Konduri & Altwicker 1994). The role and importance of *uncatalysed surface reactions* are not well established.

PCDD/F are emitted from high-temperature combustion processes, such as hazardous waste incinerators, municipal waste incinerators and biofuel boilers, although dioxins themselves may not necessarily be formed at high temperature. Both the quantity of PCDD/F emitted and the homologue distribution spectra are important. These emission characteristics of PCDD/F are a complex function of many operational parameters such as operation of the furnace or air-pollution control system, and these dependencies obscure or complicate the disclosure of any mechanistic pathways responsible for PCDD/F formation.

In the following discussion, the mechanistic pathways to PCDD/F formation, including gas-phase reactions, uncatalysed surfaced reactions, catalytic precursor and de novo mechanisms, are reviewed. This review is based on the present

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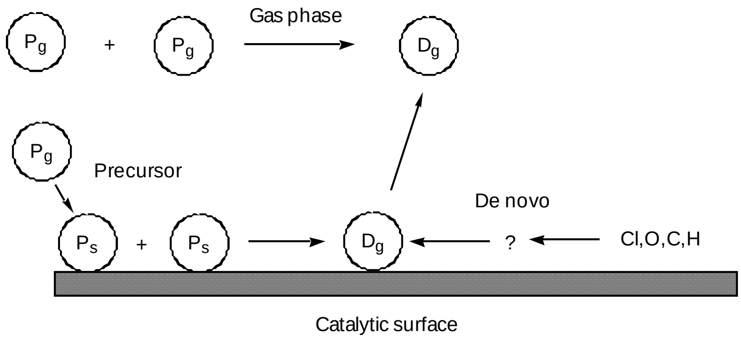
[2] This is done by minimising the Gibbs free energy of the reacting system against composition at given temperature and pressure, subject to the constraints of constant elemental abundances. If such calculations are carried out for the formation of dioxins, one observes that the predicted distribution of isomers does not correspond to that observed in the experiments (eg Addink et al 1998). This leads to the conclusion that the distribution of PCDD/F does not attain its equilibrium value, suggesting that the formation of PCDD/F is controlled by chemical-kinetic mechanisms rather than by equilibrium thermodynamics.

understanding of these pathways, as extracted from the literature, giving special attention to PCDD/F formation from large-scale combustion facilities.

Figure 5. Schematic diagram of chemical reactions leading to the formation of dioxin in combustion processes; P and D denote precursor and dioxin molecules, respectively, and superscripts s and g stand for surface-bound and gaseous species.



3.1 Reactions in the gas phase

Ritter and Bozzelli (1994) modelled the formation of PCDD/F and related reaction intermediates via the reaction of precursors including addition of hydroxyl radicals. Specifically, these authors studied the gas-phase conversion of polychlorinated biphenyls, chlorinated biphenyl ethers and chlorinated dibenzo furans to 2,3,7,8 TCDD. The major finding from this work and from others that followed (eg Bozzelli & Chiang 1996) was to conceptualise the conversion of precursor species to PCDD/F from short-chain chlorinated hydrocarbons, in the gas phase. For example, a kinetic scheme was developed to explain mechanistically the formation of polychlorinated benzene from relatively simple short-chained chlorinated hydrocarbons, subsequently leading to formation of PCDD/F (Bozzelli & Chiang 1996), as shown schematically in Figure 6.

Theoretical investigations of the mechanism and relative importance of gas-phase reaction pathways to PCDD/F formation generally support the experimental findings. The gas-phase formation mechanism contributes less than 10% of the total PCDD/F measured, although some authors have placed the gas-phase contribution as high as 50% (eg Tuppurainen et al 1998). However, it should be stressed that significant rates of PCDD/F formation are observed or predicted only at temperatures greater than 600°C, much higher than the "temperature window" for catalytic PCDD/F formation (Konduri & Altwicker 1994).

These conclusions are further supported by the work of Hinton and Lane (1991b), who examined the synthesis of PCDD, in a tubular reactor operated at 300°C, from pentachlorophenol over PCDD extracted fly ashes collected in several US incinerators. The ash acted as a catalyst in producing dioxins. However, when the same reactor was operated with no fly ash, the analysis showed no formation of PCDD. This observation signifies that reaction in the gas phase lead to negligible rates of formation of PCDD in the same temperature range that promotes catalytic reactions. Thus for practical purposes, contribution to the total dioxin formation from the gas phase reaction is usually neglected.

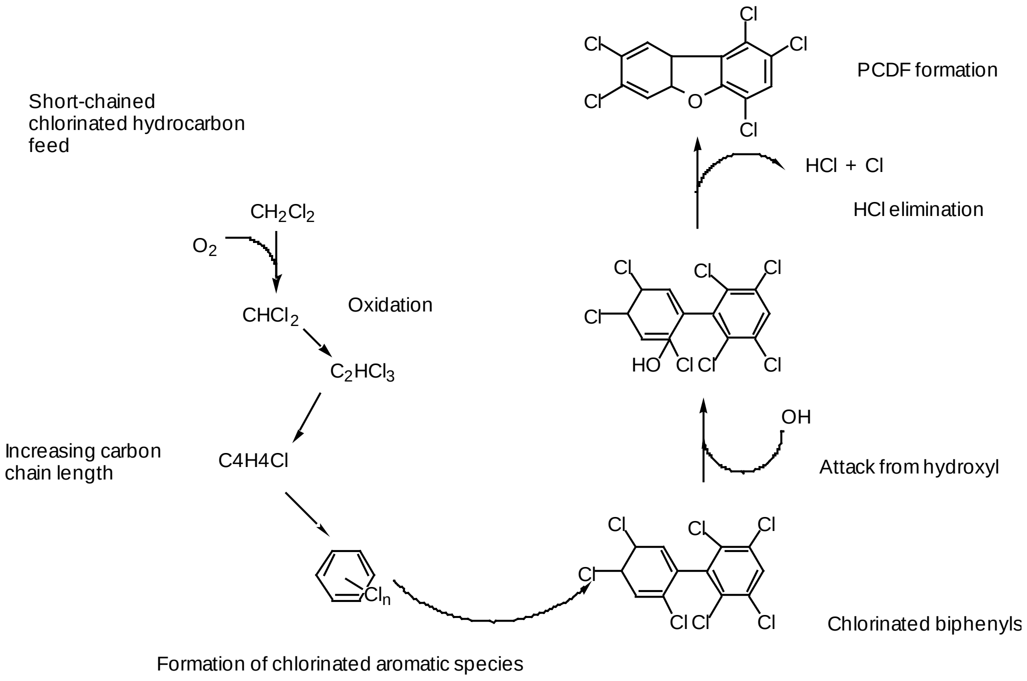


Figure 6. Details of possible homogenous pathways for PCDD/F formation.

3.2 Non-catalytic reactions on fly ash

It has been argued (Konduri & Altwicker 1994) that a surface can influence PCDD/F formation but act non-catalytically if the reaction sequence is insensitive to the nature of the surface. Konduri & Altwicker postulated that the surface acts primarily as an adsorption site for PCDD/F precursors, and is then able to concentrate reactive species for subsequent reaction. Differentiation of the catalytic and non-catalytic role of surfaces during PCDD/F formation is difficult to establish and the role of non-catalytic surface processes is not well described in the literature. It is clear, however, that surface-catalysed reactions play a dominating role in determining both the quantity and distribution of PCDD/F isomers in many combustion processes.

3.3 Fly-ash catalysed precursor pathway

It has been suggested that PCDD/F may form from precursor molecules, such as chlorophenol, chlorinated benzenes or chlorinated biphenylenes. This process has been studied extensively, and many authors claim it is the principal route for PCDD/F formation, for example Tuppurainen et al (1998). The precursors, which are products of incomplete combustion, are produced at high temperatures (>400°C, most effectively around 750°C) and later react further in the lower temperature region of the combustor (Froese & Hutzinger 1996).

The precursor molecules are believed to react catalytically with elements in the fly ash to produce PCDD/F, where the yield of PCDD/F is dependent on the feed concentration of precursor and reaction temperature (Milligan & Altwicker 1996a&b). Milligan & Altwicker studied the reaction of tetrachlorophenol on fly ash as a function of gas phase precursor concentration, reaction time and temperature. Interestingly, they only detected PCDD, while PCDF levels were beyond the detection limits of their analysis. They found that while the yield of PCDD increased with increasing precursor concentration, the effect of temperature was not so straightforward.

One of the most important categories of precursor compounds leading to PCDD/F formation is chlorophenols. These are monocyclic compounds containing one or more Cl atoms bound to a phenolic backbone structure. Mechanistically, Tuppurainen et al (1998) has proposed different reaction schemes for PCDD and PCDF formation. These authors have suggested that PCDD formation proceeds via the surface-catalysed coupling of chlorinated phenolate anions, followed by oxidative ring closing. The role of the catalyst is to serve as electron transfer oxidants, which leads to the coupling of two aromatic rings. Dioxin formation is observed following HCl and Cl elimination reactions. The process is illustrated in Figure 7, where in this example 2,4,6-trichlorophenol reacts to form 1,3,7,9-TCDD or 1,3,6,8-TCDD. It has been noted that more alkaline ash effectively adsorbs PCPs on its surface, promoting the formation of PCDD (Ruuskanen et al 1994).

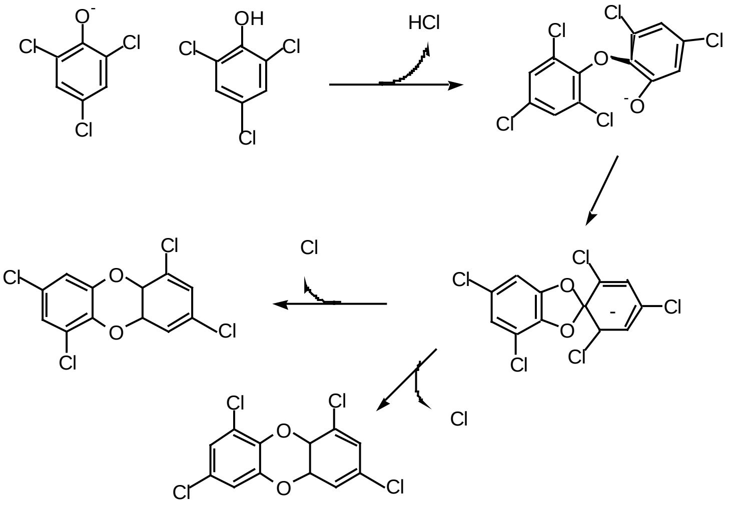


Figure 7. Mechanistic view of the formation of PCDD in the fly-ash catalysed precursor pathway.

Furthermore, these authors argue that reactions illustrated in Figure 7 cannot be used to rationalise PCDF formation, but rather precursors such as chlorobenzene and phenoxyphenols are involved with PCDF formation. Their proposed mechanism for PCDF involves a Pschorr-type ring closure catalysed by various metal species and is believed to be of particular importance during municipal waste incineration, especially where Cu and Fe metals may be present. This mechanism is illustrated in Figure 8.

The so-called Ullmann reactions (I and II) have also been proposed to facilitate condensation reactions leading to the formation of chlorinated biphenyls (Ullmann I) or chlorinated diphenyl ethers (Ullmann II), which can readily decompose to produce PCDF. The fly ash is then believed to be catalysing electrophilic chlorination, where a number of catalytic species have been investigated and shown to promote the reaction. The catalytic activity of fly ash for PCDD/F formation is well established. However, as shown by Hinton and Lane (1991), the chemical composition of fly ash often varies considerably between facilities. Table 5 lists the effect of various elements, especially metals, on the formation of dioxins via the precursor pathway.

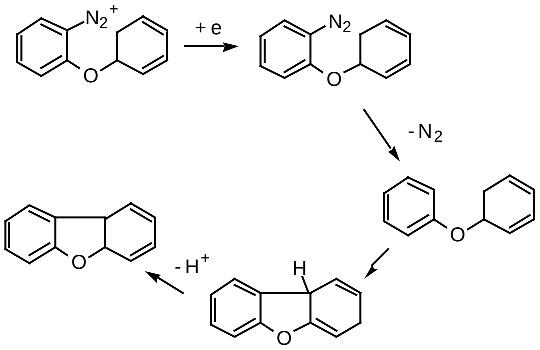


Figure 8. Mechanistic view of the formation of PCDF in the fly-ash catalysed precursor pathway.

Table 5. Examples of the effect of various elements in waste stream and in fly ash on PCDD/F formation in precursor reactions.[3]

Element	Effect	Reference
Aluminum	negative	Hinton & Lane (1991b)
Carbon[1]	no effect	Hinton & Lane (1991b)
Chlorine[1]	no effect	Hinton & Lane (1991b)
Copper	strongly positive	Hinton & Lane (1991b)
Potassium	positive or negative[2]	Hinton & Lane (1991b)
Sodium	positive or negative[2]	Hinton & Lane (1991b)
Sulfur	positive	Hinton & Lane (1991b)
Zinc	positive	Hinton & Lane (1991b)
Surface area, size distributions, etc	no effect	Hinton & Lane (1991b)

[1] From bulk analysis of the fly ash samples, after the samples were extracted with toluene.
[2] Depends on statistical analysis (Pearson's coefficients or multivariate) of the experimental data.

3.4 Fly-ash catalysed de novo pathway

If the fly ash from a municipal solid waste incinerator is exhaustively extracted from its carbon content, a very small amount of carbon remains within the ash matrix. This remaining carbon is intimately bound with catalytic sites within porous fly ash particles. If air, partially depleted of its oxygen and containing no chlorine, is then flowed through or above the fly ash bed, the unextracted carbon matrix reacts with oxygen breaking off complete aromatic rings. At the same time, it is believed that chlorine is transferred from the metal chloride ligands on the ash surface to aromatic carbon rings. This mechanism of formation of PCDD/F, illustrated in Figure 9, is called a de novo mechanism and was first observed and described by Stieglitz and Vogg (1987). Table 6 lists the effect of various elements, especially metals, on the formation of dioxins via the de novo pathway.

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[3] Catalytic reactions that produce dioxins, in both precursor and de novo mechanisms, occur on surfaces. Thus the rate of dioxin generation is related to the surface concentration of catalytically active sites (eg copper on the surface of fly ash particles). Unfortunately, in practice it is not possible to link the rates of dioxin formation with the presence of catalytic sites on fly ash. This is because the analytical techniques used to measure the surface concentration of elements, such as the x-ray photoelectron spectroscopy (XPS), are not sensitive enough. For this reason, researchers often correlate the production of dioxins with bulk rather then surface composition of fly ash, since the bulk composition of fly ash can be easily determined by standard techniques of analytical chemistry.

It is also possible for HCl in the combustion gases to serve as a source of chlorine, in addition to the metal chloride ligands. This is because HCl reacts with oxygen on copper catalysts to form chlorine (Deacon process), according to the following reaction:

$$2HCl + O_2 \rightarrow Cl_2 + H_2O \text{ (Deacon process).}$$

It is chlorine (rather than HCl) that enters into the substitution reactions to chlorinate the condensed aromatic structure of the embedded native carbon. Experimental evidence tends to support the importance of the Deacon process in dioxin formation. For example, Ruuskanen et al (1994) found a good correlation between HCl in flue gases and PCDF content of fly ash. Incidentally, higher concentrations of HCl also increase formation of chlorinated phenols, enhancing production of dioxins by the precursor route (Kanters et al 1996).

With reference to Figure 9, the oxygen from air diffuses into pores of fly ash particles where it reacts with the imbedded native carbon. The native carbon is the intimate contact with catalytic sites that contain chlorine. Although the detailed mechanism of the reactions between oxygen, carbon and chloride salts is not yet well understood, it is known that the oxidation reactions are catalysed by metals in conjunction with Cl transfer. A part of the PCDD/F formed diffuses to the gas phase, with the rest remaining in the fly ash. This is why fly ash often contains large amounts of PCDD/F. There are several important implications of this mechanism for the incineration of the municipal solid waste:

- Yields of PCDD/F depend on the reaction temperature. It has been observed that the maximum yield displays a peak around 325^{o}C (Milligan and Altwicker, 1995). This means that PCDD/F are produced, via this mechanism, in the colder sections of the process, including for example electrostatic precipitators, but not in a furnace itself.

- The mechanism relies on the presence of carbon matrix imbedded in the porous structure of fly ash particles. A more complete combustion in the furnace limits the amount of carbon available for the de novo synthesis, in the post combustion zone.

- The rates of formation of PCDD/F are defined by the activity of fly ash and by the morphology of carbon generated in the combustion process. The concentration of chlorine in the combustion gases is not important, as the chlorine in the de novo synthesis comes from metal chlorides on the pore surfaces of fly ash. This signifies no relationship between the amount of chlorine present in the waste stream and the amount of PCDD/F produced by the de novo synthesis.

- The de novo mechanism leads preferentially to the formation of PCDF in addition to PCDD, in contrast to most of the known precursor routes that generate PCDD. This is an important observation, which demonstrates that in practical systems whose PCDD/F signatures contain large amounts of furans, the de novo synthesis *may be* important.

- It has been shown experimentally that neither CO nor CO_2 from the combustion gases participates in the formation of PCDD/F, by the de novo route (Milligan and Altwicker, 1995). This is a significant observation indicating again that de novo synthesis involves reactions among materials present in the fly ash with oxygen diffusing from the air.

- The formation of PCDD/F by the de novo route is minimised in systems burning uniform fuel at higher temperatures, at longer residence times and at low chlorine-to-sulfur ratios. For example, in the pulp and paper industry in Canada (Luthe et al, 1997), waste is combusted at 950-1150°C for 8 s at very low chlorine-to-sulphur ratios in recovery boilers and at 740-1000°C for 3 s in power boilers. This leads to extremely small production of PCDD/F in recovery boilers (up to 5.2 pg ITEQ/m^3) in comparison to recovery boilers (up to 3 ng ITEQ/m^3).

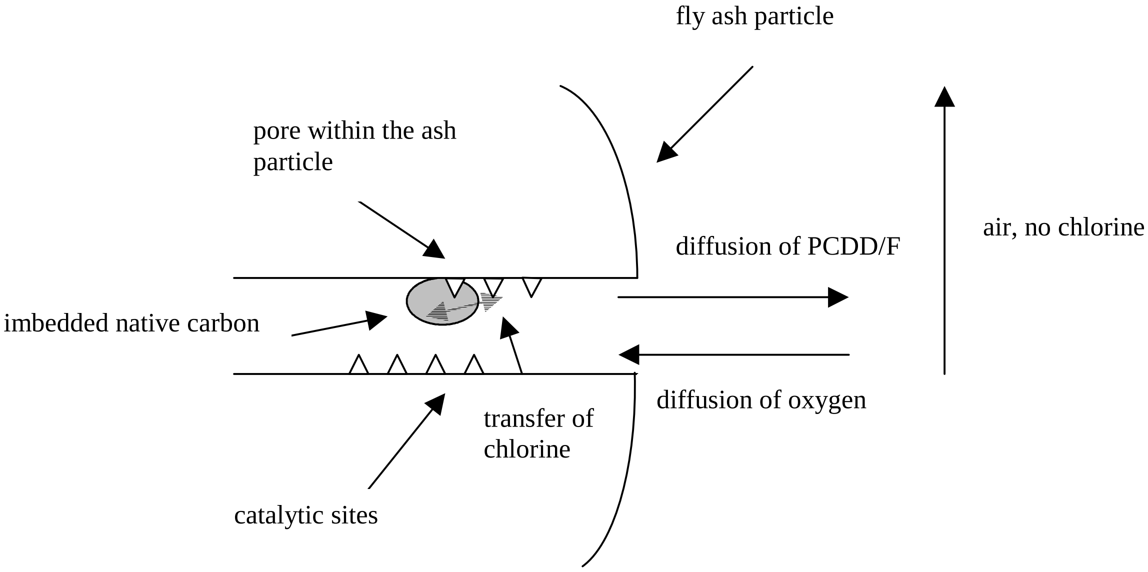

Figure 9. Mechanistic view of the de novo mechanism of dioxin formation.

Table 6. Examples of the effect of various elements in waste stream and in fly ash on PCDD/F formation in de novo reactions. Observe that fly ashes that are catalytically active in the formation of PCDD/F by de novo route are also active in the precursor route (Hinton and Lane 1991a&b).

Element	Effect	Reference
Aluminium	Negative	Hinton & Lane, 1991a
Carbon[1]	No effect	Hinton & Lane (1991b)
Chlorine[1]	Positive	Hinton & Lane, 1991a
Copper	Strongly positive	Hinton & Lane, 1991a
Potassium	Positive	Hinton & Lane, 1991a
Silicon	Negative	Hinton & Lane, 1991a
Sodium	Positive	Hinton & Lane, 1991a
Sulfur (low Cl/S)	Strongly negative	Luthe et al, 1997
Sulfur (as SO_2)	Insignificant	Ruuskanen et al, 1994
Sulfur[1]	Positive	Hinton & Lane, 1991a
Tin	Positive	Ruuskanen et al, 1994
Zinc	Positive	Hinton & Lane, 1991a
Surface area	No effect	Hinton & Lane, 1991a

[1] In the fly ash.

3.5 Relative rates of formation of PCDD/F in the incineration processes

Although it is now acknowledged that gas phase and non-catalytic reactions provide no significant contribution to the total formation of PCDD/F in the incineration processes, it is still being argued which of the catalytic processes (de novo or precursor pathway) predominates. Recently, Huang and Buekens (1994) and Altwicker (1996) observed that if the laboratory results were extrapolated to typical incinerator conditions by taking into account the concentrations of the precursors in the incinerator product gas streams, then the ratio of PCDD/F formation rates via the precursor and de novo pathways would vary between 0.03 and 211. This would indicate that both the de novo and precursor mechanisms operate in typical incineration processes.

The relative importance of each pathway depends on the operating conditions, especially the temperature history of the combustion gases. It has been argued, for example by Altwicker & Milligan (1993), that at higher processing temperatures the precursor-type reactions predominate over the de novo pathway. On the other hand, at low temperatures, the de novo-type reactions become faster than the precursor route. These conclusions are supported by other investigators (eg Takacs et al 1993) who measured the abundances of PCDD and PCDF at various points in an incineration process. Low and high ratios of PCDD/PCDF point to precursor and de novo-type reactions, respectively. Takacs et al's data suggest that dioxins and furans are formed in different regions in incinerators. These data show that as the temperature decreases to around 300°C, the PCDF formation rate subsides and the PCDD formation rate markedly increases. Clearly, this points to a changing mechanism in dioxin formation and demonstrates that both de novo and precursor-type reactions are important.

4 Role of Chlorine in Formation of PCDD/F

There is a considerable evidence that production of dioxin in large scale incineration processes is strongly linked to furnace types, their operating conditions, and the type and efficiency of air-pollution control systems. High temperatures and long residence time in the furnace (leading to complete combustion, optimised in fluidised-bed furnaces), fast cooling of combustion products (minimising the amount of time the flue gases spent in 200-450°C temperature window), and use of scrubbers rather than electrostatic precipitators (these are often operated above 200°C) result in very low emissions of PCDD/F. If an incineration process uses a new technology and is operated within its design specifications, regardless of chlorine input, PCDD/F emissions can be controlled below the present emission limits set up by environmental authorities around the world. In other words, whether an incineration process accepts feed with small (say below 1%) or large concentration (say above 80%) of chlorine, this concentration cannot be related to the emissions of PCDD/F, because of various operations within incinerator plants, specifically designed to minimise dioxin emissions.

4.1 Role of chlorine in precursor reactions

Almost all organic and part of inorganic chlorine is released during combustion of municipal solid waste to form HCl. Combustion of typical MSW results in emission of around 2.8 g HCl/kg wet MSW (Kanters et al 1996). During combustion, HCl participates in reactions with products of incomplete combustion to form chlorinated phenols and benzenes, whose generation precede the production of dioxins. These precursor reactions occur below 850°C, but most effectively around 750°C (Section 2.3.3). A relationship between HCl concentration and chlorophenol formation is shown in Figure 10a. Within the experimental scatter, which is illustrated in Figure 10a by vertical lines, an increase in HCl results in a higher generation of chlorinated phenols, but only at low concentrations of HCl. At higher concentrations of HCl, there appears to be no increase in precursor formation.

Once generated, chlorinated phenols and benzenes undergo a range of catalytic condensation and dechlorination reactions as shown in Figures 7 and 8. These reactions occur in colder regions of incineration plants, normally between 200 and

450^{o}C with a peak around 300^{o}C. The formation of dioxins depends strongly on the concentration of the precursor molecules, as illustrated in Figure 10b for the formation of PCDD (Milligan & Altwicker 1996a). It is clear from the work of Milligan & Altwicker (1996a) that neither chlorine nor hydrogen chloride needs to be present for these reactions to take place. This point is further supported by results of other researchers. For example, Hinton and Lane (1991b) reacted pentachlorophenol over PCDD extracted fly ash. The chlorine was present in the fly ash in the form of metal salts (eg KCl, NaCl). The study demonstrated that the formation of dioxins was related to the catalytic activity of fly ash and not to its chlorine content. This means that if PCDD/F are formed via the precursor pathways, their formation is related to the catalytic nature of various fly ashes, concentration of precursors and to the incinerator operating conditions, but not directly to the concentration of chlorine in the incinerator feedstock.

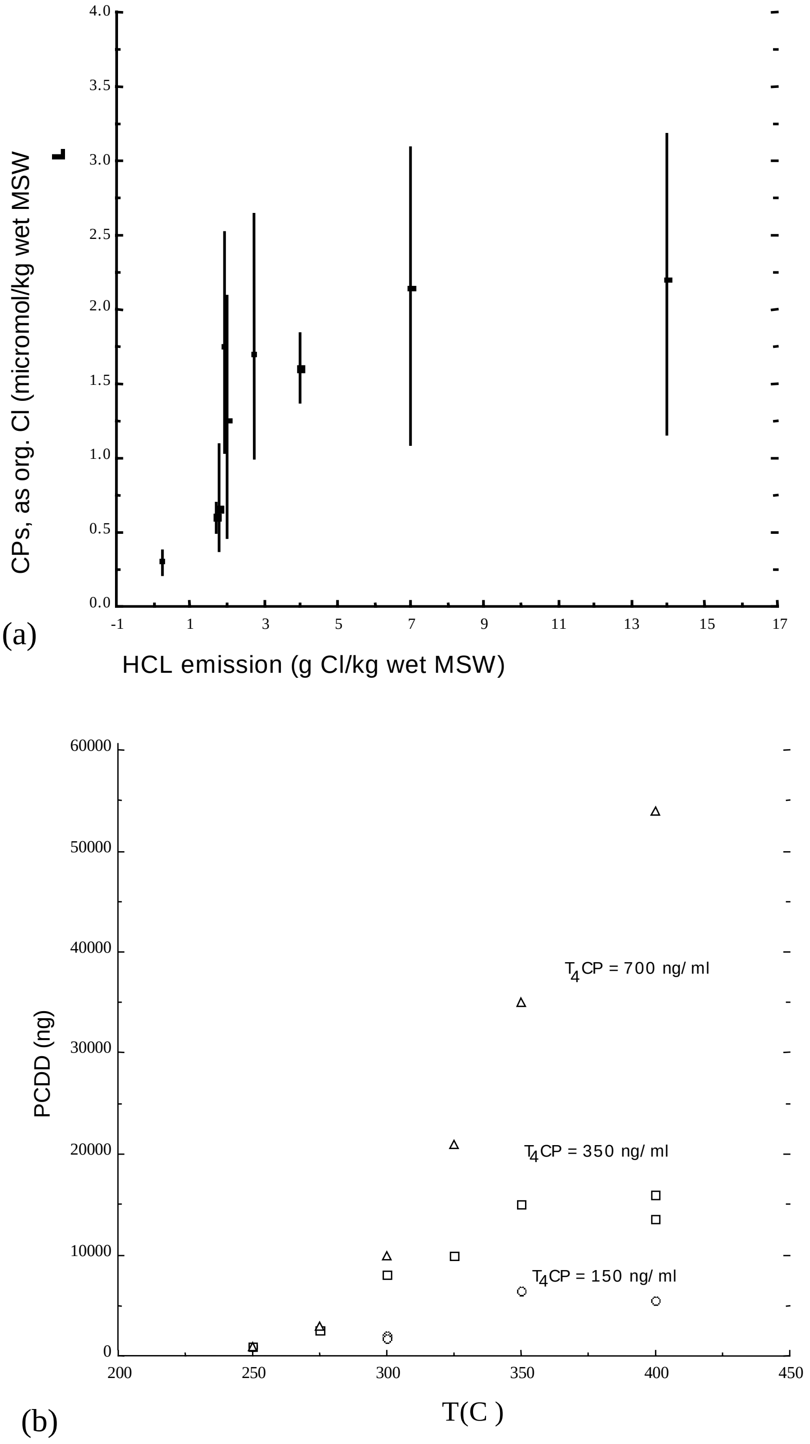

Figure 10. Illustration showing an indirect relationship between Cl in the feedstock and dioxin formation via the precursor pathway: (a) a relationship between HCl and chlorinated phenols (Kanters et al, 1996), (b) a relationship between tetrachlorinated phenol and PCDD formation (Milligan & Altwicker, 1996a).

4.2 Role of chlorine in de novo synthesis

There are a large number of papers in the literature which demonstrate a relationship between Cl in the feed and PCDD/F formation, via the de novo pathway. It would appear, however, that these studies are carried out outside optimal combustion conditions and involve a very small amount of chlorine. For example,

- Sonnenberg & Nichols (1995) showed a strong correlation between Cl and dioxin formation at low chlorine concentrations. In their study, they included up to 0.1% of chlorine in the feed; 1% of bleach plant concentrate was added to black liquor feed stock, the bleach plant solids contained 10.3% of organic and inorganic chlorine in the solids, and liquor had about 65% of solids. The temperature in the experiments was only 800°C and cooling down was not controlled, pointing to non-optimal combustion. Small-scale studies were plagued by high emissions of chlorine, generated on fused-quartz reactor, leading to small-scale emissions being 10 times higher than in a pilot plant.

- Thuß et al (1997) combusted, at low temperature, lignite briquettes containing 0.03 and 0.2% of chlorine salts. They observed substantial increase in the emission of PCDD/F and change in dioxin signature for briquettes containing the higher concentration of chlorine salts.

- Raghunathan & Gullett (1996) injected unextracted incinerator ash into the *postcombustion* zone of an experimental furnace reactor. This means that the embedded carbon material in the fly ash was not destroyed in the hot zone. Raghunathan & Gullett introduced HCl into the apparatus to simulate operation of MWI plants. HCl reacted with oxygen via the Deacon process to form chlorine, which then enhanced the production of PCDD/F by the novo route, chlorinating aromatic carbon structures of the carbon embedded in fly ash. An increase in HCl concentration correlated with an increase in PCDD/F emissions.

On the other hand, when investigations were performed for uniform fuel, burned at high temperature under turbulent conditions at long residence times, no relationships were reported between chlorine in the feed and PCDD/F in the exhaust gases. For example,

- Luthe et al (1997) observed very low emissions of PCDD/F from recovery boilers processing less than 0.5% chlorine in the feed and operating at optimum combustion conditions.

A question arises as to whether a correlation can be expected between PCDD/F in *fly ash* and chlorine input. It appears from the available information that the difference in dioxin signatures and in total concentration of PCDD/F in fly ash can be attributed mostly to furnace type rather than to fuel composition (Kopponen et al 1994). In brief, fluidised-bed combustion technologies produce ash with low PCDD/F concentration (eg Kopponen et al 1994, Foster Wheeler Corp, 1997), and those using grate furnaces are likely to show substantially higher concentration of dioxin in fly ash.

Finally, on some occasions, the reported positive dependence of dioxin emissions on chlorine input to an incineration process or on the amount of chlorine on the fly ash particles may be an artefact, related to a statistical methodology adopted in data analysis. For example, the Pearson correlation test between two variables does not account for possible confounding effects, for example for chlorine being associated with metals, such as potassium and sodium, which themselves may act as catalysts. This means that a positive correlation diagnosed by the Pearson correlation test should always be verified with partial correlation coefficients or multiple regression analysis followed by the analysis of variance (ANOVA), as the two increases (chlorine and dioxin) may have a common cause. From this perspective, a positive correlation between chlorine on fly ash and dioxin output, as reported by Hinton and Lane (1991a), comes only from the calculations of the Pearson correlation coefficient, and does seem to be supported by the multiple regression analysis.[4]

5 Dioxin Flows in Municipal Waste Incinerators

This section carries out an analysis of the balance of dioxin flows, including dioxin destruction and its re-formation in combustion and post-combustion zones of an incineration process. The analysis is based on examples drawn from the operation of old and new municipal waste incinerators. On average, the pre-1990 MWC units emitted 2.3 times as much ITEQ dioxins as they took in with the waste stream. On the other hand, the newly constructed and modernised units, operating within the emission limits, are net sinks of dioxins. Approximate but conservative analysis shows that the ratio of dioxins carried with output and input streams from modern MWC units is one to six. This section demonstrates that, for *older* MWC, it is indeed correct to say that only 12% of the total dioxin output is emitted with the stack gases, with the remainder contained in fly ash, filter cake, bottom ash, and scrubber and slag water (Ruchel et al, 1996). However, this conclusion cannot be extended to new and modernised MWC installations.

Figure 11 illustrates the average magnitude of ITEQ dioxin flows in older type of German municipal incinerators obtained from pre-1990 built installations (Johnke & Stelzner, 1992). The data came from 11 plants with 15 incineration units and their underlying numerical values are listed in Table 7. Note that the incinerator data included in Johnke and Stelzner's paper have only historical significance, since they cover the facilities that did not have to comply, when the study was conducted, with the dioxin emission limitation of 0.1μg ITEQ/m^3 of exhaust gases now enforced in Germany. Similar results can be extracted from other European studies, such as Lahl et al (1991) indicating the general nature of Johnke and Stelzner's data.

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[4] By the same token, analysis based on the Pearson correlation coefficients rather than on partial correlation coefficients or on multiple regression analysis (Ruchel, 1996) must be viewed with some caution, as this approach does not eliminate the confounding effects of other factors.

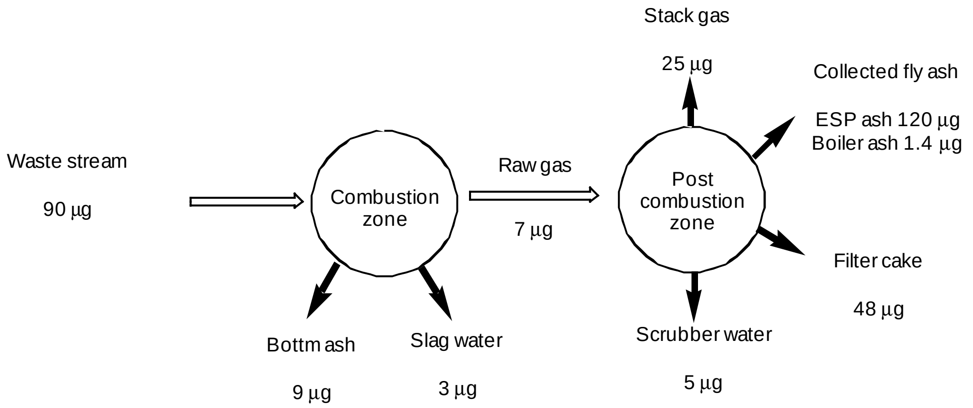

Figure 11. Average dioxins flows in old-type mass burn MWC (Johnke & Stelzner, 1992), all numbers are expressed per tonne of waste in ITEQ.

Table 7. Balance of dioxin flows in terms of ITEQ load per tonne of waste burned in pre-1990 type of municipal incinerators (Johnke & Stelzner, 1992). Geometric mean values used in plotting Figure 11 are given in column four of the table.

Output	**Mass/volume flow per tonne of waste**	**µg ITEQ/tonne waste**	
		range	**average**
Slag* (bottom ash)	300kg	3 – 42	**9**
Water from slag removal	350L	0.4 – 35	**3**
Boiler ash	7kg	0.7 – 6	**1.4**
ESP ash	30kg	30 – 840	**120**
ESP ash**	60kg	60 – 240	**120**
Scrub water	750L	0.8 – 80	**5**
Filter cake	8kg dry matter	15 – 250	**48**
Clean gas	5000m^{-3}	1.0 – 300	**25**
Input		6.5 – 180	**90*** **

* Levels below the detection limit are considered to be at the detection limit.

** ESP ash plus reaction products from dry or semi-dry flue gas treatment.

*** This number was extracted from Huang & Buekens (1995).

It is clear from Figure 11 that a relatively large amount of ITEQ dioxin (90µg ITEQ/tonne) actually enters the incineration process. The input waste also includes dioxin precursors such as polychlorinated benzenes and chlorophenols (Lahl et al, 1991). Most of the dioxin and its precursors are destroyed in the incinerator's combustion zone (furnace) and a balance around the furnace shows that only 21% of dioxin leaves the combustion zone with the raw gas, bottom ash and slag water. This is a very important observation, which demonstrates that the combustion process itself can lead to a net destruction of dioxin. The raw gas leaving the furnace carries a relatively low concentration of dioxin in spite of its high ash content (around 9g/m^3). At this stage, the fly ash is essentially free of dioxins before entering the post-combustion zone. Note, however, that the products of incomplete combustion in the primary zone are transported to the post-combustion zone as a raw gas and on surfaces of fly-ash particles.

Many studies have now confirmed (eg Fangmark et al, 1993) that dioxins are re-formed in the low-temperature post combustion zone, if the gases (including fly ash) are allowed a sufficient residence time of more than 1.6s in that zone. However, this can only happen if combustion is not complete in the furnace and the products of incomplete combustion enter the post-combustion zone. From a practical standpoint, two phenomena have been found to be critically important in reducing the formation of dioxins in MWC. Firstly, the burning in the combustion zone must be complete, as much as practicable. This is accomplished by operating the furnace at temperatures around 1000^{o}C, ensuring high turbulence during combustion by adjusting geometry and air injection in the furnace, and by allowing the waste to spend at least 2s in the hot zone (Rappe, 1996). Secondly, very fast cooling of the raw gas must be realised in the post-combustion zone to limit the re-formation of dioxin from polyaromatic carbon chains and gaseous precursors. Under the conditions of efficient combustion and for typical chlorine loads in the waste stream, reduction of chlorine concentration in the waste does not lead to decreased formation rates of dioxins in MWC installations.

A dioxin balance around the post-combustion zone in Figure 11 demonstrates 192.4μg ITEQ/tonne of net dioxin formation in that zone. Only 25μg ITEQ leaves with the stack gases to pollute the air and the rest contributes to the land and water contamination. This is because the fly ash collects in electrostatic precipitators (120μg) and on the boiler walls (1.4μg) and is subsequently disposed of in landfills. It is interesting to observe that the concentration of dioxin in ESP ash (4ng ITEQ/g ash) is about 20 times higher than in boiler ash (0.2ng ITEQ/g ash). The boiler is located just outside the combustion zone and the residence time for the ash collecting on the boiler walls is too short for significant formation of dioxins. The contaminated water (5μg) and the filter cake (48μg) are generated in wet scrubbers which are positioned after ESP units in MWC air purification trains and are used to control the emission of acidic gases, such as HCl and SO_2.

Again, it should be stressed that the information presented so far in this section relates to the historical data on the older pre-1990 incinerators. These incinerators polluted air, land and water with the dioxin emissions distributed among air, land and water according to the approximate ratio of 3.1:22.3:1. Unfortunately, not enough data (especially for dioxin concentration in fly and bottom ash and in slag water) are available to conduct accurately a similar analysis for new and modernised MWC units. New incinerators are based on efficient high-temperature burning of waste, its long residence time in the furnace and improved turbulence in the combustion zone. These new incinerators also ensure short residence time of fly ash and efficient quenching in the post-combustion zone, followed by dry flue-gas cleaning devices with the injection of lime, charcoal, and even bicarbonate before a fabric filter. These technologies are able to bring the concentration of dioxins to 0.1ng ITEQ/m^3 threshold in the stack gases and to avoid altogether the emission of contaminated filter water (Rappe, 1996; Eduljee & Dyke, 1996).

With these technological measures in mind and using the projected values published by Lahl et al (1991), which assume a thermal treatment of fly ash, Figure 12 illustrates approximately the proportion of dioxin in various waste streams in a modern MWC installation. It is clear from Figure 12 that a new or modernised incinerator acts as a sink for dioxins, providing for their net destruction. Even if no improvement in the dioxin concentration in the bottom ash and in the slag water is (conservatively) assumed, modern MWC units would discharge 13.6 and consume 90 μg ITEQ/tonne of waste.

This fundamental change in dioxin handling in MWC units (from net production to net destruction) has occurred over the last ten years, and was made possible by: (i) a better understanding of the formation mechanisms of dioxins in combustion processes, which led to improved set of operating parameters, and (ii) the advances in the development of air purification devices and the introduction of new air purification technologies. From this perspective, the emission of dioxin from incinerators depends mainly on the operating conditions in combustion and post-combustion zones and the quality of the air-purification systems installed in the commercial incinerators. It is also interesting to observe that the composting process that is now being used more frequently to treat green waste merely transfers dioxins from the waste stream to the treated compost, because of low processing temperatures. This means that compost produced in these facilities may contain high concentration of PCDD/F, if contaminated green waste enters the composting facilities
(Malloy et al 1993). The data obtained from long-term field experiments on PCDD/F persistence in sludge-amended soil support these findings, pointing to long half-lives for disappearance of dioxin in the soil (McLachlan et al 1996).

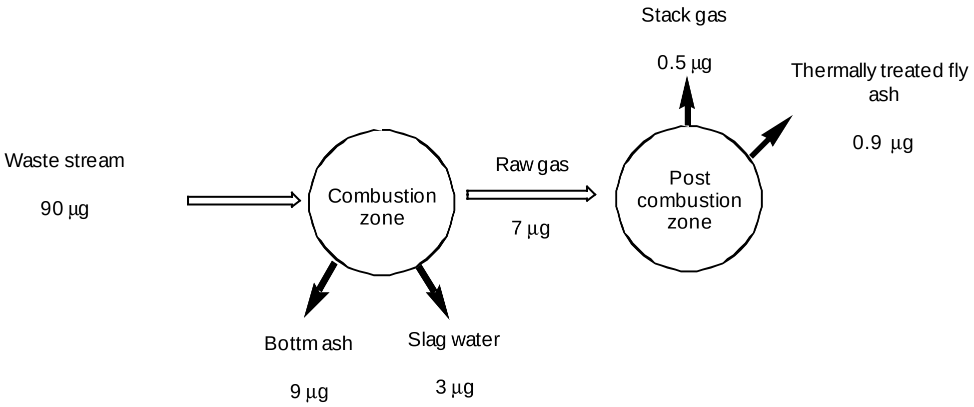

Figure 12. Balance of dioxin flows around the post-combustion zone of a modern MWC. All flows are expressed per tonne of waste in ITEQ (estimated from Lahl et al, 1991).

6 Emission of Dioxins from Combustion Processes

Several countries, including the Netherlands (Bremmer et al 1993, Wormgoor 1994), Sweden (Björndal 1996), the United Kingdom (ERM 1995) and the United States (Thomas & Spiro 1995), have carried out an inventory of their dioxin sources. Global production rates of PCDD/F based on average emissions have also been surveyed (Brzuzy & Hites 1996a). From these studies, it is immediately obvious that a number of industrial sources of dioxins need to be researched, and there are many unanswered questions, which remain to be addressed. For example, the global mass balance of dioxin formation and deposition, carried out by Brzuzy & Hites, indicates that atmospheric deposition rates of dioxin (around 13,100 kg/year) greatly exceed the known emission rates into the atmosphere (around 3000 kg/year). In agreement with these findings, the new US EPA inventory of dioxins (Hileman 1998) shows that in the US the dioxin deposition rates are much higher than the emission rates. From this standpoint, the aim here is to describe the present understanding of dioxin emission from combustion processes in general, and from municipal waste incineration in particular.

Table 8 illustrates the sources of dioxins in the USA (Hileman 1998). The dioxins generated in backyard trash burning, inadvertent landfill fires and iron ore sintering are based on the order of magnitude estimate. Clearly, more precise assessment of these dioxin sources would require further research. Table 8 demonstrates that the municipal waste incineration accounts for about 25% of known anthropogenic dioxin emission, and this number tends to decrease as new incinerators are put on stream and the old ones are shut down. A similar conclusion has been reached by Rappe (Fiedler & Van den Berg 1996) who wrote that “all European inventories claim that with modern technology the incineration of municipal solid wastes is no longer a major source of PCDD/PCDF to the atmosphere”.

Table 8. Estimates of anthropogenic sources of dioxins in the US, in g of TEQ per year.

Source	g of TEQ per year
Municipal waste incineration	1,100
Backyard trash burning	1,000*
Inadvertent landfill fires	1,000*
Secondary copper smelting	541
Medical waste incineration	447
Forest, brush and straw fires	208
Cement kilns	171
Iron ore sintering	100*

* Order of magnitude estimate.

There have been several suggestions about natural production of PCDD/F (eg Gribble 1994), but in spite of some research in that area, this remains mostly an unresolved issue. From the perspective of this report, the key issue is whether the PCDD/F observed in the deposition rates but not accounted for in the anthropogenic sources can come from natural sources.

Another important issue is an apparent mismatch between dioxin signatures of known PCDD/F anthropogenic sources and *global* deposition fingerprints[5], at some distance away from dioxin sources. The global deposition patterns are dominated by octachlorinated dioxins (OCDD, eg Bonn 1998) whereas the known man-made sources contain mostly lower-chlorinated dioxins and furans, with the exception of OCDD formed from pentachlorophenol. Possible explanations for observed deposition signatures have been suggested in the literature (eg Brubaker & Hites 1997, Trapp & Matthies 1997). Highly chlorinated PCDD/F characterised by low

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[5] The emission of PCDD/F from anthropogenic sources leads to very localised deposition of dioxin patterns that correspond to the source signature, and to global deposition pattern that reflect source signatures modified by atmospheric processes.

vapour pressure tend to accumulate on particles in the atmosphere and are removed from the atmosphere when these particles settle on the soil surface. On the other hand, lower chlorinated dioxins react with hydroxyl radicals (OH), which are produced by photolysis of H_2O_2 and by photolysis of O_3 in the presence of H_2O. From a practical perspective, this means that emission of PCDD/F from incineration processes leads to global low-level contamination, although deposition signatures do no longer correspond to the source signatures.

7 Long-Term Trends in Dioxin Emission from Combustion Processes

A large number of studies have shown decreasing concentration of dioxins in atmosphere (eg Coleman et al 1997) and their reduced deposition rates (eg Bruzy & Hites 1995, Jüttner et al 1997) in recent years. A very comprehensive review of pre-1996 literature has been conducted by Alcock & Jones (1996) and included dioxins present in the environment (that is in air, sediments, vegetation and soil), sewage sludge, milk, livestock tissue, as well as in human wildlife tissue. *The compilation of data presented by Alcock and Jones (1996) covers international sources.*

No research facility exists in Australia to study dioxins and so very little data are available in the open literature. Most of the Australian studies have been carried out by commercial organisations that have been able to support high costs of analyses carried out by foreign laboratories. Ruchel et al (1996) gave an overview of dioxin emissions in NSW indicating that BHP operations in Newcastle and Port Kembla are major dioxin sources in this country. However, at present, it is unclear whether other sources, such as bushfires, contribute to the observed deposition rates. The analysis of the emission from the Australian pulp and paper industry (Nelson 1994) confirmed that new pulp bleaching technologies effectively eliminated formation of dioxins. This is consistent with similar studies conducted in Canada (MacDonald et al 1998).

Alcock & Jones's review paper is based on more than 90 reference publications. Figure 13 provides an example of the changes in the concentration of PCDD/F and ITEQ dioxins in herbage collected in Park Grass experiment at Rothamsted Experimental Station near London. A sharp increase after 1950 followed by a rapid decrease in 1980s and 1990s is evident in the figure. Note that there is a possibility of contamination of the samples with modern air, since the vegetation was dried before storage. This may explain rather high values of total and ITEQ dioxins in the data derived from herbage collected prior to 1940.

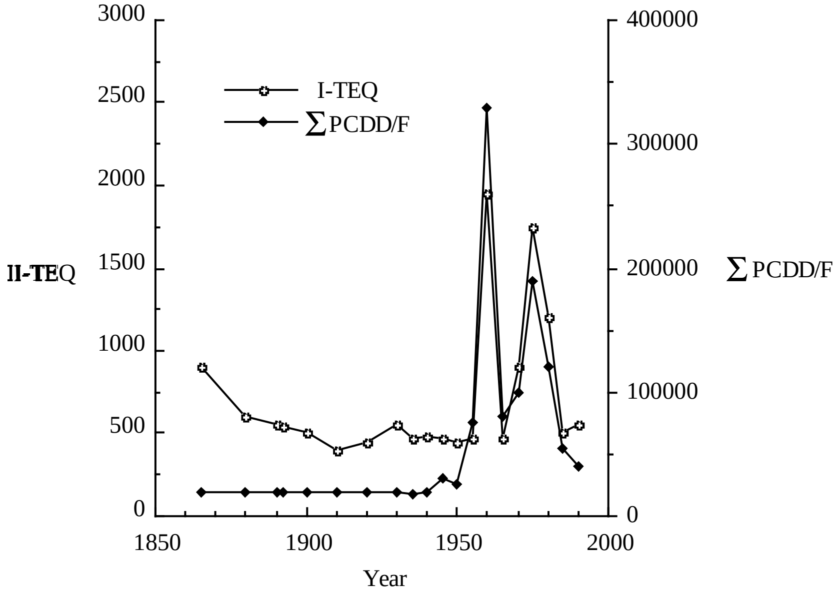

Figure 13. Trends in total and ITEQ dioxins in ng/kg in archived Park Grass vegetation (Kjeller et al, 1993).

In general, the trend data (eg Alcock & Jones, 1996) support a conclusion that rates of dioxin emission and deposition are linked to a few specific chemical and industrial processes rather than to the additional production of chlorine and the increasing use of PVC. As the concentration of PCDD/F in a wide range of environments continues to decrease, the production of chlorine and PVC increase (Alcock & Jones, 1996; Fiedler & Van den Berg, 1996). The observed decline is a direct result of the following technological changes and phase-out of certain chemicals:

1. The implementation of the phase-out of pentachlorophenol (PCP), which is considered the most potent precursor of dioxins and which itself contains dioxin impurities. The production of PCP started in the 1940s, peaked by the 1970s and stopped by the 1980s (Alcock & Jones, 1996). PCP had several applications such as treating timber, and being an ingredient for certain dyes and pigments. Because of these applications PCDD/F, originating from PCP, were observed to be present in efflux from paper mills (Luthe et al, 1993) that processed treated wood, in sewage sludges that might have contained dyes and pigments and in combustion of PCP-containing wood (Alcock & Jones, 1996).

2. Processing changes implemented in new incinerators burning municipal and medical waste and shut-down of old and polluting facilities. The new technologies that led to the dramatic decrease in dioxin emissions included fluidised-bed furnaces with long residence time, fast cooling of the combustion products, injection of lime and activated carbon and replacement of electrostatic precipitators with baghouses that are operated at lower temperatures than electrostatic precipitators. The data from monitoring the environment around new MSW combustors normally show no negative impact of these facilities on the environment. For example, a biomonitoring study carried out around a new MSW combustor in West Palm Beach (Florida, USA) found TCDD/F at pre-operational levels during the first five years of the combustor operation (Rumbold et al, 1997).

3. Replacement of bleaching of paper pulp with chlorine by bleaching with ClO_2, in the operation of paper mills. Figure 14 demonstrates a dramatic impact this new technology had on the deposition rates of dioxins, downstream from a pulp mill, in Kamloops Lake, in the province of British Columbia, Canada (MacDonald et al 1998).

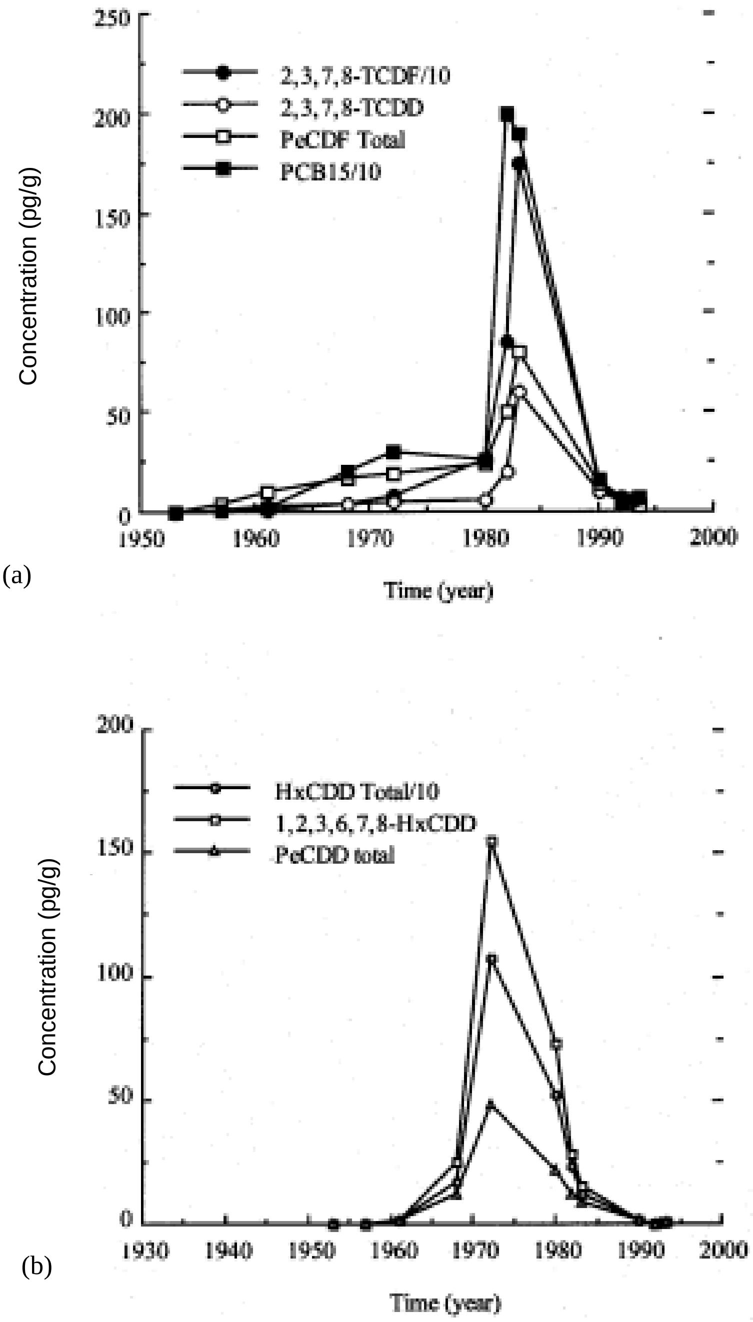

Figure 14. Reconstructed historical trends in the deposition of (I) PCDD/F formed in the bleaching of pulp with chlorine and (II) PCDD/F from processing wood chips contaminated with PCP. Arrows along the time scale refer to the following mill history: 1965 mill opens, 1972 major expansion, mill A goes to 10% ClO_2, 1988 mill B goes to 30% ClO_2, 1989 mill A goes to 30% ClO_2, 1991 mills A and B go to 60% ClO_2, 1992 mill A goes to 100% ClO_2, 1993 mill B goes to 100% ClO_2 (MacDonald et al 1998).

4. A drop in consumption of leaded petrol, due to a phase-out of leaded petrol in some countries, led to the decrease in dioxin formation in motor vehicles. In the past, lead was found to catalyse the formation of PCDD/F and especially the penta congeners (Manninen et al 1996).

5. The changes that have taken place in the use of fossil fuels, and especially in the use of coal for heating homes. This is because of the practice of burning domestic refuse with coal, under less than optimal combustion conditions. In the UK alone, the demand for house coal has decreased more than 13 fold, in the last 40 years (Alcock & Jones 1996).

6. Further minimisation of dioxin formation has been realised by closure of some open burn sites and metal recovery facilities that operated copper and alumina smelting plants. This has occurred because of air pollution regulations in some jurisdictions (eg in California, see Harnly et al 1995). However, it appears that regulations that govern open burns and incineration of copper and alumina scraps are not sufficiently widespread to have a substantial impact on dioxin emission from these sources. For example, it has been reported that in the US, meat and dairy products have very high level of dioxins, although most food production takes place away from industrial centres (Hileman, 1998). This observation may point to refuse burning as a possible cause.

If these declining trends in PCDD/F emissions are to be sustained in the long term, then open refuse burning should become controlled and new technologies should be developed for secondary copper smelting and iron ore sintering (Jager, 1993; Bröker et al, 1993). Additional research is also needed to provide more accurate figures of dioxin emissions from landfill and forest (bush) fires, to support or refute the present estimates and to guide in managing and controlling these hazards.

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