INVESTIGATION OF INFLUENCING FACTORS ON DIOXINS FORMATION FROM COMBUSTION OF PEAT IN MALAYSIA IN THE PRESENCE OF DIFFERENT PRECURSORS AND CATALYSTS

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by

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Khairulmazidah Mohamed
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LIST OF SYMBOLS

ºC	Degree Celsius
R	Correlation coefficient
%	Percentage
mg	Milligram
kg	Kilogram
ng	Nanogram
pg	Picogram
g	Gram
km	Kilometre
m	Meter
cm	Centimetre
mm	millimetre
m^3	Cubic metre
Nm^3	Normal cubic meter
h	Hour
min	Minute
ppt	Parts per trillion
m/z	Mass-to-charge ratio
mL	Millilitre
cm^{-1}	Per centimetre
%T	Percent transmittance
ID	Internal diameter
µm	Micrometre
df	Film thickness

µg	Microgram
L	Litre
rpm	Revolutions per minute
µl	Microlitre
psi	Pounds per square inch
mBar	Millibar Pressure Unit
cm^3	Cubic centimetre
p	Probability value
Mt	Megatonnes
dw	Dry weight
Al	Aluminium
C	Carbon
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
H	Hydrogen
K	Potassium
Mg	Magnesium
Mn	Manganese
N	Nitrogen
Na	Sodium
Ni	Nickel
O	Oxygen

Pb	Lead
S	Sulphur
Ti	Titanium
Zn	Zinc
As	Arsenic

LIST OF ABBREVIATIONS

AhR	Aryl hydrocarbon Receptor
APCI-MS/MS	Atmospheric-pressure chemical ionisation tandem mass spectrometry
ASE	Accelerated Solvent Extraction
ATR	Attenuated total reflectance
CA	Cellulose acetate
CBs	Chlorinated benzenes
CH_4	Methane
CI	Chemical ionisation
CO	Carbon monoxide
CO_2	Carbon dioxide
CPh	Chlorophenol
CRM	Certified reference material
$CuCl_2$	Copper chloride
CV	Coefficient of variation
DCBz	Dichlorobenzene
DCPh	Dichlorophenol
DDT	Dichloro diphenyl trichloroethane
DE	Diatomaceous earth
dl-PCBs	dioxin-like Polychlorinated biphenyls
ECEHWHO	European Centre of Environmental Health of the World Health Organisation
EI	Electron ionisation
ELISA	Enzyme-linked immunosorbent assay
ENSO	El Niño-Southern Oscillation
FMS	Fluid Management System
FTIR	Fourier Transform Infrared
GC	Gas chromatography
GC-MS	Gas chromatography mass spectrometry
GFED	Global Fire Emission Database
GM	Gravimetric method
GPS	Global Positioning System
HA	Total humic acid

HCBz	Hexachlorobenzene
HCN	Hydrogen cyanide
HOCs	Hydrophobic organic compounds
HpCDD	Heptachlorodibenzo-p-dioxin
HpCDF	Heptachlorodibenzofuran
HRMS	High-resolution mass spectrometry
HSK	Hutan Simpanan Kekal
HxCDD	Hexachlorodibenzo-p-dioxin
HxCDF	Hexachlorodibenzofuran
IARC	International Agency for Research on Cancer
IC	Ion chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IPCS	International Programme on Chemical Safety
JBPM	Jabatan Bomba dan Penyelamat Malaysia
LLE	Liquid-Liquid Extraction
LOD	Limit of detection
LOQ	Limit of quantification
MCBz	Monochlorobenzene
MS/MS	Tandem mass spectrometry
MSWI	Municipal solid waste incinerator
NATO	North Atlantic Treaty Organisation
NH_3	Ammonia
OCDD	Octachlorodibenzo-p-dioxin
OCDF	Octachlorodibenzofuran
PAHs	Polycyclic aromatic hydrocarbons
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and Polychlorinated dibenzofurans
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PCPh	Pentachlorophenol
PeCBz	Pentachlorobenzene
PeCDD	Pentachlorodibenzo-p-dioxin
PeCDF	Pentachlorodibenzofuran

PFE	Pressurised Fluid Extraction
PLE	Pressurised liquid extraction
PM	Particulate matters
POPs	Persistent organic pollutants
PUF	Polyurethane foam
RSD	Relative standard deviation
SE	Soxhlet Extraction
SFE	Supercritical Fluid Extraction
SIM	Selection of ion monitoring
SPE	Solid-Phase Extraction
SVOC	Semi-volatile organic compound
TCBz	Trichlorobenzene
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TCPh	Trichlorophenol
TeCBz	Tetrachlorobenzene
TeCPh	Tetrachlorophenol
TEFs	Toxic equivalency factors
TEQ	Toxic Equivalency
TiO2	Titanium dioxide
TOF	Time-of-flight
US EPA	United States Environmental Protection Agency
V_2O_5	Vanadium pentoxide
WHO	World Health Organisation
WO_3	Tungsten trioxide

LIST OF APPENDICES

PENYIASATAN KE ATAS FAKTOR YANG MEMPENGARUHI PEMBENTUKAN DIOKSIN DARIPADA PEMBAKARAN TANAH GAMBUT DI MALAYSIA DENGAN KEHADIRAN SEBATIAN PENDAHULU DAN MANGKIN YANG BERBEZA

ABSTRAK

Poliklorin dibenzo-p-dioksin (PCDDs) dan poliklorin dibenzofuran (PCDFs), secara kolektif dirujuk sebagai dioksin, adalah sebatian toksik yang terhasil secara tidak sengaja semasa bahan organik terbakar. Walaupun pelepasan dioksin dari industri telah menurun dengan ketara sejak tahun 2000, pelepasan dioksin daripada kebakaran hutan, pembakaran domestik dan sumber kenderaan masih membimbangkan. Kebakaran gambut yang kerap berlaku di Asia Tenggara berkemungkinan telah menyumbang kepada tahap dioksin di dalam alam sekitar. Gambut mempunyai jumlah bahan organik yang tinggi dan berkemungkinan juga mengandungi sebatian pendahulu dan pemangkin yang menjadi prospek bagi pembentukan dioksin apabila terbakar. Kajian ini bertujuan untuk menentukan sifat fiziko-kimia, sebatian pendahulu, pemangkin, dan profil kongener dioksin gambut tropika Semenanjung Malaysia pada kedalaman yang berbeza dan seterusnya menentukan profil kongener pelepasan yang terhasil daripada pembakaran sampel gambut terpilih. Tiga puluh lapan sampel tanah gambut telah dikumpulkan dari sepuluh kawasan tanah gambut di Semenanjung Malaysia daripada permukaan tanah sehingga kedalaman 200 cm. Sampel-sampel ini telah dianalisa secara komprehensif untuk pelbagai parameter, termasuklah pH, kandungan lembapan, kandungan bahan organik, komposisi unsur, pencirian FTIR, fenol, klorofenol, klorobenzena, asid humik, anion dan PCDD/F yang sedia ada di dalam sampel. Dua belas sampel kemudiannya dipilih untuk eksperimen pembakaran di dalam makmal menggunakan reaktor yang diubah suai. Pelepasan yang terhasil dianalisis bagi menentukan kandungan dioksin menggunakan GC-HRMS. Kepekatan PCDD/F di dalam gambut mentah secara konsisten berkurangan dengan kedalaman, di mana lapisan permukaan mengandungi sehingga 10 kali ganda lebih tinggi kepekatan berbanding lapisan yang lebih dalam (antara 0.8257 hingga 10.8584 WHO_{2022} TEQ ng/kg), menunjukkan bahawa pemendapan atmosfera adalah sumber pencemaran utama. Eksperimen pembakaran mendedahkan bahawa pelepasan PCDD/F selalunya melebihi kepekatan gambut mentah, sehingga hampir 8 kali ganda, dengan dioksin rendah klorin – terutamanya 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD dan beberapa congener lain– menunjukkan peningkatan ketara semasa proses transformasi. Faktor yang mempengaruhi pembentukan dioksin termasuk kandungan lembapan (korelasi negatif), kandungan nitrogen (pengaruh positif pada congener tertentu), dan kandungan logam (kuprum dan kalsium sebagai pemangkin, aluminium sebagai perencat). Anehnya, kandungan klorin menunjukkan kesan minimum terhadap pelepasan. Hasil dapatan kajian ini mencadangkan bahawa laluan pendahulu adalah laluan utama bagi pembentukan PCDD/F semasa pembakaran, berdasarkan nisbah PCDD/PCDF >1 dalam data pelepasan. Tahap dioksin berklorin yang lebih rendah dalam pelepasan yang ketara, menunjukkan potensi bahaya yang berkaitan dengan kebakaran gambut, terutamanya bagi individu yang terlibat dalam usaha memadam kebakaran. Kajian ini menyumbang kepada pemahaman tentang pembentukan dan pelepasan dioksin daripada kebakaran gambut tropika, menunjukkan kepentingan untuk pengurusan alam sekitar dan strategi kesihatan awam yang lebih baik di kawasan yang terdedah kepada kejadian begini.

INVESTIGATION OF INFLUENCING FACTORS ON DIOXINS FORMATION FROM COMBUSTION OF PEAT IN MALAYSIA IN THE PRESENCE OF DIFFERENT PRECURSORS AND CATALYSTS

ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively referred to as dioxins, are toxic compounds generated as unintentional byproducts of organic material combustion. While industrial emissions have significantly decreased since 2000, contributions from forest fires, domestic combustion, and vehicular sources remain concerning. Frequent peat fires in Southeast Asia may have leadingly contributed to the dioxins level in the environment. Peat, having high amount of organic material and possible precursor and catalysts for dioxins formation, is highly susceptible to dioxin production during combustion. This study aims to determine the physico-chemical properties, precursor compounds, catalysts, and congener profiles of dioxins of Peninsular Malaysian tropical peats at different depths and eventually determine the congener of emissions resulting from the combustion of selected peat samples. Thirty-eight raw peat samples were collected from ten peatland areas in Peninsular Malaysia at depths ranging from surface level to 200 cm. These samples underwent comprehensive analysis for various parameters, including pH, water content, organic matter content, elemental composition, FTIR characterisation, phenols, chlorophenols, chlorobenzenes, humic acid, anions, and existing PCDD/Fs in the samples. Twelve samples were subsequently selected for laboratory combustion experiments using a modified reactor, with resultant emissions analysed for dioxins by GC-HRMS. PCDD/F concentrations in raw peat consistently decrease with depth, with surface layers containing up to 10 times higher concentrations than deeper layers (ranging from 0.8257 to 10.8584 WHO$_{2022}$ TEQ ng/kg), suggesting atmospheric deposition as the primary contamination source. Combustion experiments revealed that PCDD/F emissions frequently exceeded raw peat concentrations by up to 8-fold, with lower-chlorinated dioxins – particularly 1,2,3,7,8-PeCDD, 2,3,7,8-TCDD and a few other congeners– showing notable increases during the transformation process. Factors influencing PCDD/F formation included water content (negative correlation), nitrogen content (positive influence on certain congeners), and metal content (copper and calcium as catalysts, aluminium as an inhibitor). Surprisingly, chlorine content demonstrated minimal impact on emissions. The study suggests a predominantly precursor pathway for PCDD/F formation during combustion, based on the PCDDs/PCDFs ratio >1 in emissions data. The markedly elevated levels of lower chlorinated dioxins in emissions, underscore the potential hazards associated with peat fires, particularly for individuals engaged in fire suppression efforts. This study contributes to the understanding of dioxin formation and emission from tropical peat fires, providing valuable insights for environmental management and public health strategies in regions prone to such events.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Dioxins, a term collectively include a group of chemical compounds namely polychorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofurans (PCDFs) are among the most toxic chemicals known to science. These chemical compounds are also grouped as persistent organic pollutants (POPs) along with several other pollutants. Dioxins are toxic, hydrophobic in nature, bioaccumulate in living biota and persistent to the environment (Halse et al., 2011; Vallack et al., 1998). Dioxins are formed unintentionally by industrial, non-industrial and natural processes, which is often associated to emissions from combustion (Pereira, 2004). Among the various sources of dioxin emissions, the burning of tropical peatlands has emerged as a major contributor, particularly in regions such as Southeast Asia, where peat fires are a recurring issue (Samin et al., 2025). These fires, often purposefully set for land-clearing activities or occurring naturally during prolonged dry periods, may release substantial quantities of dioxins into the atmosphere, posing severe environmental and public health risks (Samin et al., 2025). Exposure of dioxins may result in many adverse health effects in human, such as impairment of the immune system, nervous system, endocrine system, reproductive functions and causes cancers (Jang & Kwon, 2003; Ghorai & Kaur, 2022; Kimura, 2025).

Major forest types in Malaysia are lowland dipterocarp forest, hill dipterocarp forest, upper hill dipterocarp forest, oak-laurel forest, montane ericaceous forest, peat swamp forest and mangrove forest (Omar, 2025). Peat swamp forests are waterlogged forests growing on a layer of dead leaves and plant material up to 20 metres thick (Melling et al., 2006). They comprise an ancient and unique ecosystem characterised by waterlogging, with low nutrients and dissolved oxygen levels in acidic water regimes. Their continued survival depends on a naturally high-water level that prevents the soil from drying out to expose combustible peat matter (Huat et al., 2014).

Peat forms when plant material, usually in marshy areas, is inhibited from decaying fully by the acidic conditions and a lack of microbial activity. For example, peat formation can occur along the inland edge of mangroves where fine sediments and organic material become trapped in the mangrove roots (Osland et al., 2020). Peat is mostly soil with more than 75% organic matter that is composed largely of vegetation including trees, grasses, mosses, fungi and various organic remains including those of insects and animals (Huat et al., 2014). Peat formation occurs when the rate of accumulation of organic material exceeds the rate of decomposition.

Tropical peat swamp forest represents a unique ecosystem characterized by partially decomposed organic matter accumulated over thousands of years, creating a carbon-rich and highly combustible fuel source, when the water table is drained for agricultural activity or during long drought season. When these peatlands catch fire, the smouldering combustion process and temperature, coupled with the presence of chlorine in precursor compounds and specific catalysts, creates favourable conditions for the formation and release of dioxins (Ramadhan et al., 2017; Palamba & Werdhani, 2023). However, the exact mechanisms governing the formation and abundance of dioxins during tropical peat burns are not fully understood, hindering efforts to mitigate their emissions effectively.

While dioxin emissions from various combustion sources have been extensively studied, the specific formation mechanisms and emission characteristics of PCDD/Fs from tropical peat combustion remain largely unexplored. This study represents the first comprehensive investigation to systematically characterise the physico-chemical properties of Malaysian tropical peat in relation to dioxin precursor compounds, catalysts and their subsequent formation pathways during combustion. The novelty lies in establishing direct correlations between peat matrix composition, precursor compounds and catalysts concentrations, and resultant dioxin congener profiles, thereby elucidating the possible formation pathway specific to tropical peat ecosystems.

1.2 Problem Statement

PCDDs and PCDFs are classified under the Stockholm Convention as unintentional by-products of persistent organic pollutants (POPs) and are recognised as environmental contaminants found in nearly all compartments of the global ecosystem (Samin et al., 2023). Tetrachlorodibenzo-p-dioxin (TCDD), the most toxic dioxin, possesses an estimated half-life of 3-10 years in humans and is considered "the most toxic man-made chemical," leading to adverse health effects such as increased cancer incidence, immune system dysfunction, reproductive complications, endocrine disruption, neurological impairment, liver damage, dermatological conditions including chloracne, and cardiovascular disease (Chen et al., 2003; Aylward et al., 2005; Diliberto, 2001; Jang & Kwon, 2003; Ghorai & Kaur, 2022; Kimura, 2025).

The occupational exposure of firefighters to dioxins by inhalation during firefighting operations is alarming, since heightened levels of dioxins are seen in the air during firefighting operation and accumulate in the blood lipids of firefighters (Samin etal., 2025; Shaw et al., 2013; Hsu et al., 2011). Recent research indicate that firefighters demonstrate bioaccumulation of dioxins correlated with tenure, increased genetic vulnerability, genotoxic effects, and cytogenetic damage due to occupational exposure to hazardous combustion byproducts (Kriyt et al., 2020; Kriyt et al., 2022).

Malaysian tropical peat fires provide unique challenges that substantially elevate dangers for firefighters. The fires may last for days to months, leading to prolonged firefighting efforts that lengthen occupational exposure times (Smith et al., 2018; Wah et al., 2024). Tropical peatland fires mostly smoulder with limited flames, characterised by low-temperature combustion that facilitates dioxin generation and results in persistent subsurface burning that is difficult to detect and extinguish (Huang & Rein, 2019; Qin et al., 2022; Sofan et al., 2022). Malaysian peatlands, covering about 2.5 million hectares, often experience fire incidents during dry seasons and as a result of anthropogenic activity (Miettinen et al., 2017; Page et al., 2009). The smouldering properties of tropical peat fires provide conditions for incomplete combustion, facilitating dioxin generation, and these fires intensify regional haze events affecting neighbouring countries in Southeast Asia (Page et al., 2018; Kuwata, 2024).

Notwithstanding the recognised severity of dioxin formation during peat combustion and the documented health risks for firefighters, notable gaps in research remain about the specific physico-chemical factors that govern dioxin development pathways in Malaysian tropical peat systems. The present comprehension of the influence of diverse precursors in Malaysian peat on dioxin production pathways is lacking (Wang et al., 2024). The catalytic effect of transition metals, such as copper, iron, and zinc, present in Malaysian peat, has not been well investigated regarding their contribution to dioxin formation processes (Mohamed et al., 2020). A comprehensive analysis of the specific physico-chemical features of Malaysian peat, including changes in chemical compositions with depth, as well as their interaction with smouldering combustion temperature, is essential for understanding dioxin generation pathways.

An investigation into the physico-chemical factors affecting dioxin formation from peat combustion in Malaysia, taking into account various precursors and catalysts, is crucial to address knowledge gaps and provide a scientific foundation for protecting firefighter health and environment quality. This research will improve understanding of the mechanisms governing dioxin generation in tropical peat systems, aiding in the development of prediction models for emission assessment and enlightening evidence-based risk management methods for firefighting operations.

1.3 Hypothesis

Peat soil may contain many organic chlorine compounds such as chlorophenols and chlorobenzenes that occur or produced naturally, from pesticides introduced into the environment or as a result of microbial activity during decomposition or humification. Humic substances will also be formed during this humification process. Phenols, chlorophenols, chlorobenzenes and humic substances are considered as precursors to dioxins formation during peat combustion. Peat soil itself may also contain varying amounts of dioxins at different depths due to distribution by long range atmospheric transfer. Dioxins production may increase with increasing content of organic chlorine in peat soil when burned. Trace metals such as copper, iron and zinc are considered as catalysts to dioxin formation while aluminium is considered as retardant to dioxins formation. When tropical peat is burned, the emissions are expected to release a much higher concentration of dioxins compared to the original amount present in the peat soil.

1.4 Objectives of Research

1.4.1 General Aims of Study

The general aim of this research is to investigate the factors affecting dioxins formation from peat combustion with the presence of different precursors and catalysts in the raw peat.

1.4.2 Objectives

The specific aims of this study include;

1. To characterise the physico-chemical properties of Malaysian tropical peats through comprehensive analysis including: pH; water content, organic matter content, and ash content; elemental composition analysis of carbon (C), hydrogen (H), and nitrogen (N) content using CHN Analyser, and functional group identification using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy.

2. To determine concentrations of dioxin precursor compounds and catalysts in peat samples, specifically: phenol and fifteen chlorinated organic compounds using Gas Chromatography-Mass Spectrometry (GC-MS); total humic acid using UV-Visible Spectrophotometry; fifteen metallic elements using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES); and four major anions using Ion Chromatography (IC).

3. To determine PCDD/F congener profiles in depth-stratified raw peat samples and selected combustion emissions using Gas Chromatography-High Resolution Mass Spectrometry (GC-HRMS) analysis targeting the seventeen

2,3,7,8-substituted toxic congeners including 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and related homologue groups.

4. To correlate the amount of PCDD/Fs in burning peat emissions to the amount of influencing factors present in the raw peat samples and determine the possible PCDD/Fs formation pathway.

1.5 Significance of study

Tropical peatlands are essential ecosystems that store vast amounts of carbon and play a vital role in regulating the global climate. However, these peatlands are increasingly threatened by fires, which can release not only greenhouse gases but also toxic pollutants like dioxins. Tropical regions, particularly Southeast Asia, have experienced widespread peat fires in recent years, leading to severe air pollution and haze episodes. Understanding the factors that influence dioxin formation from these fires can aid in developing region-specific mitigation strategies and policy interventions. Studying dioxins formation from peat burns also can help develop strategies for better management and conservation of these ecosystems. This research can also provide insights into elements or compounds that promote or inhibit dioxin formation. This knowledge can instruct preventive measures and fire management practices to reduce exposure to dioxin emissions.

Furthermore, this research can contribute to establishing baseline data on dioxin levels from peat burns, which can be used for ongoing monitoring and assessing the effectiveness of any mitigation strategies implemented, enabling more effective risk assessment and management of potential exposure to these toxic pollutants. By elucidating these factors, the research may provide insights into controlling or minimizing dioxin formation during peat burning, which could enlighten policies, practices, and technologies for sustainable peatland management and fire prevention

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Peatlands are commonly involved in fires in North America and Southeast Asia (van der Werf et al. 2017), contributing to greenhouse gas emissions and haze episodes. According to a study by Sahani et al. (2014), constant exposure to haze can have immediate or long-term effects on mortality, with respiratory-associated death increasing by 19–66%. Firefighters, being the first responders to wildland or peat fires, are extremely vulnerable to developing diseases associated with smoke emissions from fire. Studies by Adetona et al. (2013) and Navarro et al. (2019) implied that firefighters have an increased risk of developing cancer due to their work. This could be related to their exposure to dioxins and other emissions during firefighting duties. The most potent dioxin congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), is classified as a Class 1 carcinogen, a known human carcinogen (IARC 1997). Since peat originates mainly from plant parts such as roots, leaves, and stems, including other small insects and animals, it is a large composition of organic materials such as carbohydrates and lignins, among others. These compounds are mainly precursors or can be converted to precursors for dioxins formation when burned. In the last 30 years or so, many tropical peatlands have been converted to agricultural farms where herbicides are used. This increases the risk of dioxins formation if these sites are burned.

To date, there are only a handful of studies on dioxins in peat. Dopico and Gomez (2015) reviewed global sources and data on dioxins. Another review by Pereira (2004) examined the main sources of dioxin and its possible formation pathways. Zhang et al. (2016) extensively studied dioxins from biomass combustion, including peat. A review on dioxin emissions from smouldering peat fires and their contribution to regional haze episodes was published by Hu et al. (2018). Nevertheless, there is currently no available data on emissions of dioxins from tropical peat.

2.2 Dioxins

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are listed as persistent organic pollutants (POPs) in the Stockholm Convention on Persistent Organic Pollutants. The Convention initially identified 12 POPs, known as the "dirty dozen," for global elimination or restriction. These include pesticides (e.g., DDT, aldrin, and dieldrin), industrial chemicals (e.g., PCBs, hexachlorobenzene), and unintentionally produced POPs like dioxins and furans. Dioxins and furans collectively are commonly known as dioxins or PCDD/Fs.

Dioxins and furans have triple-ring structures consisting of two benzene rings connected by an oxygenated ring in the middle. Figure 2.1 illustrates the basic structure of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF). Each position numbered 1 to 4 and 6 to 9 is substitutable with chlorine atoms. PCDD/Fs are a group of organic chemicals characterised by properties of semi-volatile organic compounds, bioaccumulative and therefore bio magnify in nature, persistent to the environment, and subject to long-range atmospheric transport (Halse et al., 2011; Vallack et al., 1998).

Dioxins and furans are considered unwanted byproducts of incomplete combustion, mainly influenced by anthropogenic activities. Some authors have claimed, however, that dioxins could also be formed by biogenic activity (Hoekstra et al., 1999; Silk et al., 1997), but these are only pertinent to lower chlorinated PCDD/Fs. Another author (Prange, 2003) offers an initial indication of biogenic formation of higher chlorinated PCDDs; the study nevertheless lacked sufficient evidence to ascertain whether such processes are responsible for the PCDD formation. There are in total 210 congeners of PCDD/Fs: 75 PCDDs and 135 PCDFs. Of these, 17 congeners are considered the most toxic, with chlorine present at 2, 3, 7, and 8 positions. 2,3,7,8-TCDD is found to be most toxic, followed by 1,2,3,7,8-PCDD and 2,3,4,7,8-PCDF (Environment Australia, 1999). The terms dioxins and PCDD/Fs, which refer to both PCDDs and PCDFs collectively, will be used interchangeably throughout this thesis.

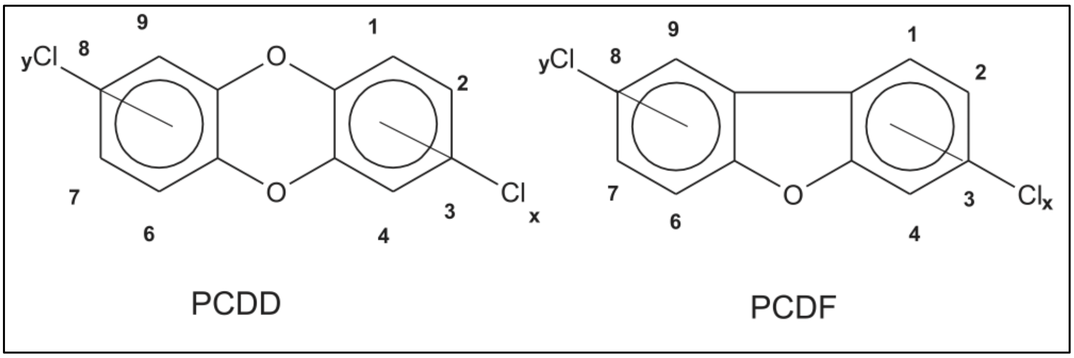

Figure 2.1 Basic structure of PCDD and PCDF (Source: Pereira, 2004).

2.2.1 Dioxins Sources

Dioxins are generated through many combustion processes. In nature, for example, they are a result of volcanic eruptions and forest fires and are even produced by some fungi (de Jong et al., 1994). Incomplete combustion, like in wood stoves or badly managed waste incineration, can also emit significant quantities of dioxins (Eurochlor, 2016). A study by Dopico and Gomez (2015) that reviewed the global dioxins trend observed that dioxins emission in general has decreased globally from its peak in the 1970’s to the 1980’s. The Dioxin Emission Inventory 2000 by the Japanese Ministry of Environment reported that the amount of emitted dioxins declined year by year. The emission for year 2000 was recorded as 2,198–2,218 g-TEQ, almost a 70% decline from 1997 (7,343–7,597 g-TEQ).

In 2002 estimates, major industrial emission sources in Europe that amounted to approximately 62% of all total dioxin air emissions were derived from municipal waste incinerators, iron ore sinter plants, hospital waste incinerators, and facilities of the non-ferrous metal industry. The remaining 38% were predominantly from non-industrial sources, i.e., domestic heating facilities (particularly wood combustion), accidental fires, and road traffic (Quass & Fermann, 1997).

The United States Environmental Protection Agency (US EPA), on the other hand, estimated that the sum of all 'uncontrolled combustion' (natural or due to 'unintentional' human activity) was by far the largest source of dioxins (about 57%) for the year 2000 (EPA, 2006). Bawden et al. (2004) reported that uncontrolled combustion (e.g., biomass burning, waste burning, and accidental fires) contributed to nearly 70% of total dioxins emissions to the air and over 80% of total emissions to land in Australia.

Table 2.1 Comparison of year 1985 maximum dioxins emission estimates with year 2000 emission and 2005 estimates of PCDD/Fs emissions in Europe.

Sources (g I-TEQ/year)	**1985 upper estimate (g I-TEQ/year)[a,b]**	**2000 actual data (g I-TEQ/year)[b]**	**Reduction (%)**	**2005 estimates (g I-TEQ/year)[a]**
Industrial sources Secondary Copper Production, Cement, Cable smelting, Non-Ferrous Metal foundries, Secondary Aluminum Production, Combustion in industry, Power plants, Electric Furnace Steel plant, Industrial Waste, Sintering of special materials and drossing facilities, Secondary zinc production, Hospital Waste, Sinter plants and Municipal Solid Waste Incinerator.	10539	1619-2461	77-85	1011-1495
Non-industrial sources Domestic solid fuel combustion, Preservation of wood, Road transport, Illegal incineration of Domestic or municipal wastes, Incineration of corpses and Accidental fires	3151	846-2144	32-73	952-2257
Total of sources considered	**13690**	**2465-4605**	**66-82**	**1963-3752**

[a](Quass et al., 2004)
[b](Quass et al., 2000)

The results from the European inventory of dioxins (expressed in g I-TEQ/year) (Quass et al., 2000, 2004) in Table 2.1 shows that dioxins from non-industrial sources are more significant compared to emissions from industrial sources, where improved technology and processes in incinerators or boilers have remarkably reduced the amount of dioxins produced. Thus, the non-industrial sector is expected to be the main producer of dioxins from sources such as forest and peat fires.

A recent study on the emission inventory of 17 PCDD/F congeners (Song et al., 2023) using 8 source sectors globally revealed that between 2002 and 2018, the emissions of PCDD/Fs dropped by 25.7% (12.5 kg TEQ), primarily in upper- and lower-middle-income countries. The major producer of PCDD/Fs was identified as coming from these sectors: open-burning processes > waste incineration > ferrous and nonferrous metal production sectors > heat and power generation (Figure 2.2). They also emphasised that the significant emissions of PCDD/Fs were primarily contributed by regions in East and South Asia, Southeast Asia, and certain regions of Sub-Saharan Africa. The decrease in dioxin emissions over the last few decades came to a halt in the early 2010s, which was caused by the growing significance of emissions resulting from wildfires in the overall emission levels (Song et al., 2023). Recent data has shown that the main dioxins source in the environment is indeed the non-industrial sector, predominantly due to open burning, particularly from wildfires.

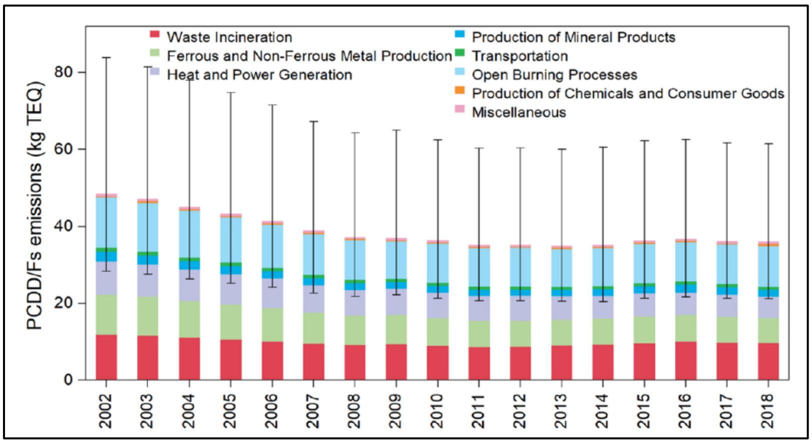

Figure 2.2 Total emissions and source profiles of global PCDD/Fs from 2002 to 2018. The whisker caps in the figure represent the 95% confidence intervals for total emissions (Souce: Song et al., 2023).

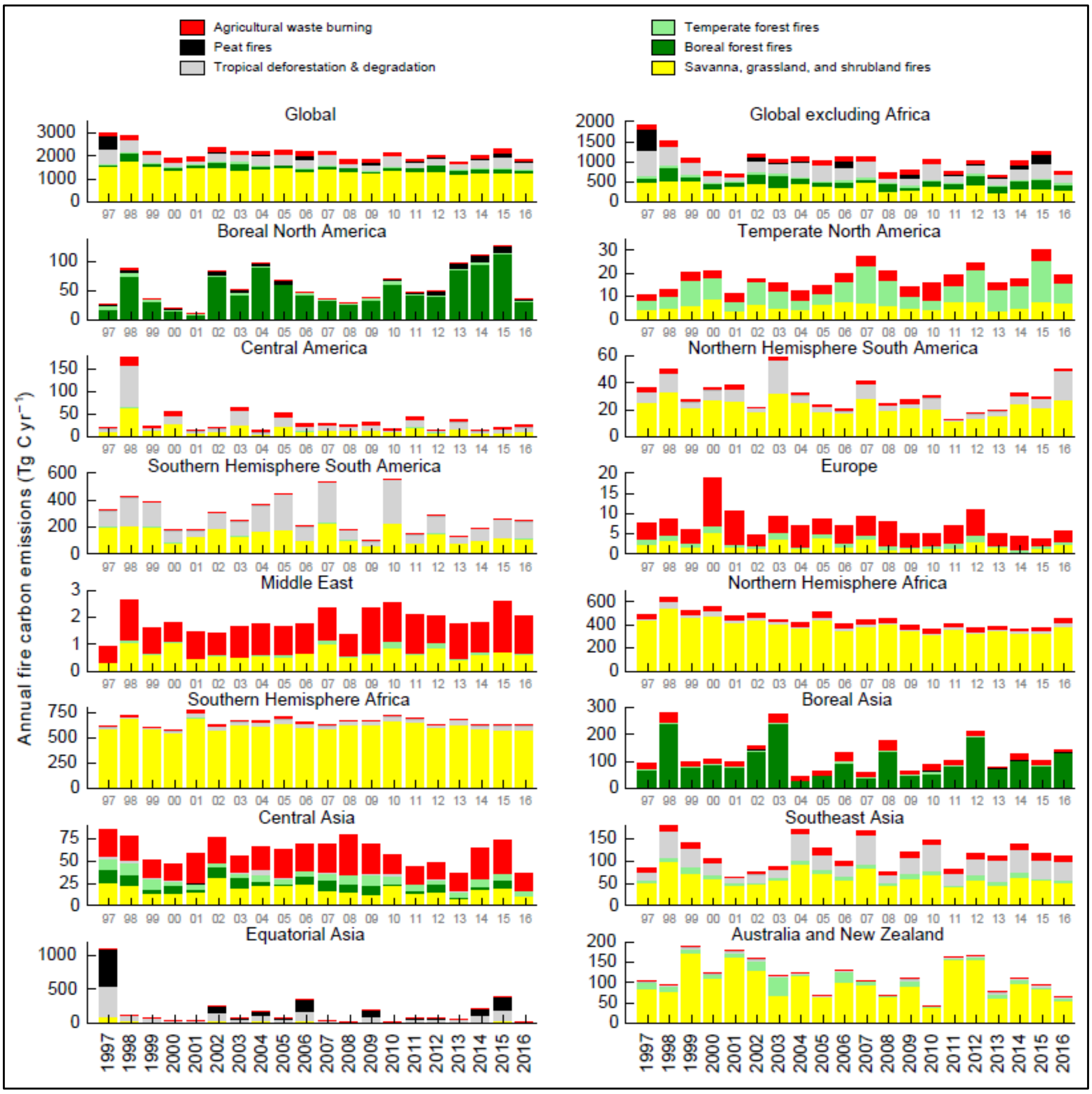

Figure 2.3 Annual emissions from different types of fire across the world. Black bars represent those from peat fires (Source: Van Der Werf et al., 2017).

Van Der Werf et al. (2017) have reported annual carbon emissions from fires, stretching data from 1997 to 2016. The black colour in this bar chart graph report (Figure 2.3) represents global peat fires. Boreal North America and Equatorial Asia are the major contributors to the global peat fire carbon emissions. Peat fire emissions peaked globally in 1997, mainly driven by extreme fire events in Equatorial Asia, which includes Malaysia. Every 3 to 5 years, the pattern of peat fires in Equatorial Asia peaks. More recent data derived from the Global Fire Emission Database (GFED) (Data - Global Fire Emissions Database (GFED), n.d.) and converted to a similar bar graph for Global and Equatorial Asia is shown in Figure 2.4. The year 2015 saw the highest carbon emissions from peat fires from 2002 to 2020. The data presented in this publication and database regarding carbon emissions indicates the potential for dioxin emissions when peatland ecosystems are subjected to combustion. However, it is important to note that all fire classifications delineated in this report carry the potential for dioxin emissions.

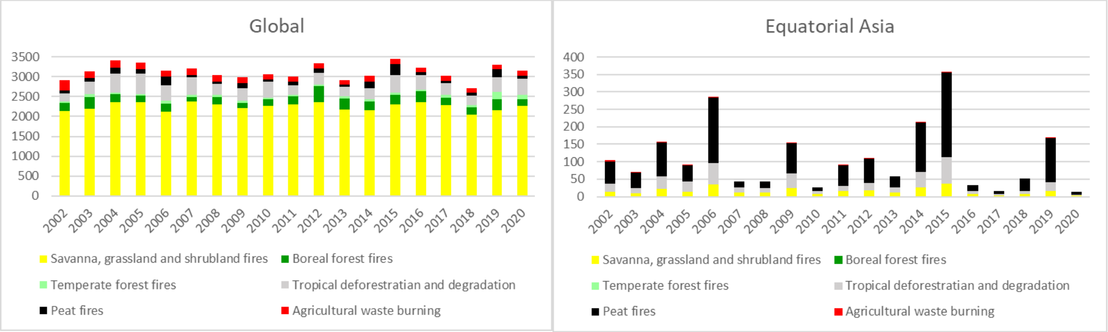

Figure 2.4 Annual fire carbon emissions (Tg C yr^{-1}) derived from recent GFED (Source: Data - Global Fire Emissions Database (GFED), n.d.).

2.2.2 Dioxins Formation

Formation mechanisms of dioxins in combustion conditions have remained hypothetical due to the complexity of their reactions. There are two temperature windows where dioxins can form: the "homogeneous" pathway between 500 and 800°C and the "heterogeneous" pathway at 200 to 400°C (Stanmore, 2004). Homogeneous reactions, the result of pyrolytic restructuring of chlorinated precursors, such as chlorophenols and chlorobenzenes in the gas phase, are not as widely studied as heterogeneous mechanisms. Heterogeneous formation is a catalytic reaction that occurs in the ash or soot particles in the combustion system (Stanmore, 2004). Two types of heterogenous pathways have been proposed.

The first is the *de novo* synthesis, which assumes heterogeneous catalytic assemblage of chlorinated dioxin arrangements from a carbon, oxygen, and chlorine source that maximises at a temperature frame of 300–325°C in the post-combustion zones (Altwicker, 1991, 1996; Huang and Buekens, 1996). The second suggested reaction for the formation of PCDD/Fs is the precursor reaction, referring to a multi-step mechanism in the hotter and cooler part of post-combustion zones (200 to 450°C), peaking at 300°C, including aromatisation of aliphatic compounds and chlorination by molecular chlorine produced from an equilibrium of hydrogen chloride (HCl) and oxygen (Altwicker, 1996; Fängmark et al., 1994). The aromatisation (transformation of a non-aromatic ring into a stable, aromatic ring system) occurs in the high temperature range with chlorination in the lower temperature range (Environment Australia, 1999). The catalytic reaction of chlorinated aromatic precursors on fly ash in the post-combustion zone was observed, although key questions on the formation of dioxins remain unanswered. Gas-phase coupling reactions of chlorinated precursors such as chlorophenols and chlorobenzenes, followed by the adsorption on the organic particular phase, occur as precursor pathways. Other than chlorophenols and chlorobenzenes, which may come from pesticides or herbicides introduced into the environment, humic acid may also be the possible precursor for dioxins formation (Pereira, 2004).

Many factors have been considered on dioxins formations in studies. Copper and iron have a major catalytic effect on dioxin formation, with the former being 20 times more effective than the latter (Environment Australia, 1999). These include types of reactors for combustion, oxygen capacity, types and amounts of fuel, temperature, amount of chlorine present, and the presence of metal species, among others. These factors influence the dioxins yield. According to Gullett et al. (2000), general requisite conditions for PCDD/Fs formation are: (1) incomplete combustion of organic fuel; (2) presence of trace metals and surfaces to act as catalysts; (3) a temperature/time history providing at least 1 s below 600°C; and (4) a source of chlorine (Cl).

2.2.3 Precursor Compounds for Dioxins Formation

Chlorophenols and chlorobenzenes have been studied for several decades and have been named as the main precursors for dioxins formation via the precursor pathway. Several studies have highlighted the significance of chlorobenzenes, chlorophenols, and halogenated phenols in the formation of dioxins (Long et al., 2011; Lomnicki & Dellinger, 2003; Zheng et al., 2018; Xu et al., 2010). These precursor compounds undergo reactions, including catalytic and gas-phase processes, leading to the generation of dioxins (Long et al., 2011; Lomnicki & Dellinger, 2003; Zheng et al., 2018; Xu et al., 2010).

The mechanisms of dioxin formation from precursor compounds have been extensively studied. Research has identified different pathways for dioxin formation, including high-temperature synthesis, catalytic synthesis, and *de novo* synthesis (Wielgosiński et al., 2016; Huang & Gu, 2019; Thompson et al., 2003). High-temperature synthesis typically occurs between 500-700°C and involves chlorinated aromatic precursors (Wielgosiński et al., 2016). Catalytic synthesis, on the other hand, can occur from both chlorinated and non-chlorinated precursors, with reactions taking place at temperatures ranging from 300-500°C (Wielgosiński et al. 2016). *De novo* synthesis, a crucial mechanism, involves the formation of dioxins outside the combustion zone from molecular carbon at lower temperatures, typically between 200-400°C (Wielgosiński et al., 2016; Huang & Gu, 2019).

Furthermore, the role of specific compounds like chlorophenols in dioxins formation has been emphasised in various studies (Xu et al., 2010; Zhang et al., 2010; Qu et al., 2009). Chlorophenols, structurally similar to dioxins, are considered significant precursors that can readily form dioxins during thermal processes (Xu et al., 2010; Zhang et al., 2010; Qu et al., 2009). Additionally, the formation of dioxins from chlorophenol precursors has been investigated in gas-phase reactions, highlighting the importance of understanding the chemical pathways involved (Zhang et al., 2010; Qu et al., 2009).

In addition to chlorophenols and chlorobenzenes, there are several other possible precursor compounds for dioxin formation. These compounds include PAHs, oxygenated compounds structurally similar to dioxins, chlorinated aliphatic compounds, polychlorinated biphenyls (PCBs), phenoxy herbicides, chlorinated catalysts, halogenated biphenyl ethers, pesticides, and humic acid (Kirkok et al., 2020; Zubair & Adrees, 2019; Okamoto & Tomonari, 1999; Holt et al., 2008; Pereira, 2004). These compounds have been identified as potential precursors that can initiate reactions leading to the formation of dioxins (Kirkok et al., 2020; Zubair & Adrees, 2019; Okamoto & Tomonari, 1999; Holt et al., 2008). Additionally, the decomposition of endosulfan has been shown to produce precursors involving all chlorinated benzenes and chlorinated phenols, contributing to the formation of dioxins (Dharmarathne et al., 2016).

Furthermore, the presence of sodium chloride and poly(vinyl chloride) has been associated with the formation of dioxins from precursors via organic chemical reactions, such as the condensation reaction of chlorophenols and the cyclisation reaction of PCBs

(Yasuhara et al., 2001). This suggests that compounds containing chlorine, such as chlorinated aliphatic, can serve as precursors for dioxin formation under specific conditions.

Studies have also explored the impact of different environmental conditions on dioxin formation. For instance, in the context of municipal solid waste incineration, the presence of chlorine and oxygen can influence the formation of chlorinated phenoxy radicals, which are primary precursors for dioxins via radical-chain reactions (Bei et al., 2022, Liu et al., 2022). Although peat possesses elevated levels of phenolic compounds that might potentially act as precursors for chlorinated phenoxy radicals upon combustion (Walpen et al., 2018), direct experimental data supporting this route in peat systems remains scarce. Nonetheless, considering the coexistence of phenolic compounds and chlorine sources in peat, along with laboratory evidence indicating dioxin formation from phenol-HCl reactions at combustion temperatures, the generation of chlorinated phenoxy radicals and subsequent dioxin production during peat combustion is a plausible mechanism (Xu et al., 2024).

The formation of dioxins during combustion processes is not solely dependent on the availability of precursor compounds, but is considerably influenced by the presence of catalytic materials that facilitate or modify reaction pathways. These catalytic processes play a critical role in determining both the rate and extent of dioxin formation, as well as the specific congener profiles that emerge during thermal decomposition. In the context of peat combustion, understanding the role of potential catalysts becomes particularly important given the complex matrix of organic and inorganic compounds present in peat substrates that may serve catalytic functions.

2.2.4 Catalysts for Dioxins Formation

Catalysts play a crucial role in the formation of dioxins, influencing the pathways and mechanisms involved in their synthesis. Various studies have identified different catalysts responsible for dioxin formation, shedding light on the complex interactions that lead to the generation of these toxic compounds.

Copper chloride ($CuCl_2$) has been highlighted as a significant catalyst in the *de novo* synthesis of dioxins (Fujimori et al., 2008; Takaoka et al., 2005). Studies have observed the presence of $CuCl_2$ during dioxin formation processes, emphasising its role in catalysing the generation of PCDD/Fs (Fujimori et al., 2008; Takaoka et al., 2005). Additionally, manganese (Mn), magnesium (Mg), and nickel (Ni) have been suggested as potential catalysts for dioxin formation, indicating a broader range of elements that can influence the synthesis of dioxins (Mohamed et al., 2020).

Furthermore, the presence of organic chloride compounds, such as tetrachloroethylene, in combination with catalysts like iron (III), tin (II), and copper (II), has been shown to promote the formation of particle-bound dioxins in combustion experiments (Yasuhara et al., 2001). This highlights the synergistic effect of specific compounds and catalysts in facilitating dioxin formation under certain conditions.

Transition metals like copper have been found to play a dual role as both catalysts and chlorinating agents in the formation of dioxins during processes such as sintering (Zhou et al., 2022; Tsubouchi et al., 2006). These metallic chlorides efficiently catalyse the synthesis of dioxins, with unburned carbon serving as a significant carbon source for the organic chlorides involved in dioxin formation (Tsubouchi et al., 2006).

Moreover, studies have explored the use of catalysts such as vanadium pentoxide (V_2O_5), tungsten trioxide (WO_3), and titanium dioxide (TiO_2) for the reduction of dioxins in flue gas emissions, highlighting the potential of specific catalysts in mitigating dioxin pollution (Verma et al., 2022). Additionally, the catalytic conversions of low-chlorinated dioxins and polychlorinated benzenes using V_2O_5/TiO_2 catalysts have been investigated, demonstrating the influence of catalysts on the transformation of these compounds (Lee & Jurng, 2007).

Apart from metal catalysts, fly ash, a byproduct of combustion processes, has been investigated for its potential role as a catalyst in dioxin formation. Several studies have explored the relationship between fly ash and dioxin synthesis, shedding light on the complex interactions that occur during waste incineration and thermal processes.

Research by Liu et al. (2013) and Wang et al. (2016) has highlighted the presence of carbon constituents in fly ash, such as unburned carbon and powder activated carbon, which are major sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). These carbon constituents in fly ash have been implicated in catalysing the formation of dioxins, indicating a potential catalytic role of fly ash in dioxin synthesis (Liu et al., 2013; Wang et al., 2016).

Furthermore, studies by Chang et al. (2009) and Takaoka et al. (2005) have investigated the effect of fly ash on the catalytic removal of gaseous dioxins over V_2O_5-WO_3 catalysts in sinter plants. The presence of carbon, chloride, and metallic catalysts like copper and iron in fly ash has been shown to be essential for *de novo* synthesis of dioxins, suggesting a catalytic influence of fly ash in dioxin formation (Chang et al., 2009; Takaoka et al., 2005).

Moreover, research by Chin et al. (2012) and Fujimori et al. (2008) has indicated that fly ash can serve as a reaction surface for the formation of dioxins. The entrained fine fly ash particles collected by air pollution control devices have been shown to facilitate surface-mediated formation of dibenzo-p-dioxins and dibenzofurans, emphasising the catalytic potential of fly ash in dioxin synthesis (Chin et al., 2012; Fujimori et al., 2008).

Additionally, studies by Cieplik et al. (2006) and Gao et al. (2016) have investigated the formation of dioxins from combustion micropollutants over municipal solid waste incinerator (MSWI) fly ash and the thermal degradation of PCDD/Fs in MSWI fly ash. These studies have demonstrated the catalytic properties of fly ash in the formation and degradation of dioxins, highlighting the importance of understanding the role of fly ash in dioxin-related processes (Cieplik et al., 2006; Gao et al., 2016).

2.2.5 Toxicity of Dioxins

The toxicity of dioxins is determined by toxic equivalency factors (TEFs), which compare the potency of different dioxin-like compounds to the most toxic form, 2,3,7,8-TCDD (Bhavsar et al., 2008). These TEFs are crucial in assessing the overall toxic impact of dioxins and related compounds (Van den Berg et al., 2006). The aryl hydrocarbon receptor (AhR) plays a central role in mediating the toxic effects of dioxins (Cespedes et al., 2010; Moffat et al., 2010). Studies have shown that the majority of the toxic effects of dioxins are mediated by the AhR, a ligand-dependent transcription factor (Moffat et al., 2010). Dioxins exert their toxicity through dysregulation of gene expression mediated by the AhR (Okey, 2007).

The toxic equivalency approach is used to convert concentrations of various dioxin-like compounds into a single concentration equivalent to TCDD, facilitating risk assessment and regulatory decisions (Bhavsar et al., 2008). This approach is essential in evaluating the health risks posed by dioxins and related compounds in various matrices (Çolakoğlu et al., 2020).

In the last decades, several different TEF schemes have been developed for PCDDs, PCDFs, and dl-PCBs. Recognising the need for a harmonised approach in setting internationally agreed upon TEFs, the North Atlantic Treaty Organisation (NATO) first came out with a pilot study to achieve international consensus on methods to assess the toxicological significance of mixtures of PCDDs and PCDFs in 1990 and derived the I-TEF method (Kutz et al., 1990). Prior to the development of the I-TEF method, at least ten slightly different TEF schemes had been used throughout the world. The European Centre of Environmental Health of the World Health Organisation (ECEHWHO) and the International Programme on Chemical Safety (IPCS) then initiated a program to derive TEFs for these compounds for assessing the impact of these compounds on human and environmental health (Van den Berg et al., 1998). This follows renewed TEF by World Health Organisation (WHO) in 2005 and more recently in 2022 (Van den Berg et al., 2006; DeVito et al., 2024). Table 2.2 shows the assigned TEF values based on discussions by experts in this field at their respective times. While I-TEFs are still used by researchers today as this method is claimed to be more suitable for environmental samples, WHO TEFs are more popular among food or human samples as they are more focused on assessing human health.

Table 2.2 The evolution of TEFs based on discussions and new evidence from 1990 to 2024.

Dioxin Congeners	**I-TEF** (Kutz et al., 1990)	**1998 WHO-TEF** (Van den Berg et al., 1998)	**2005 WHO-TEF** (Van den Berg et al., 2006)	**2022 WHO-TEFs** (DeVito et al., 2024)
Dioxins				
2,3,7,8-TCDD	1	1	1	1
1,2,3,7,8-PeCDD	0.5	1	1	0.4
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.09
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.07
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.05
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.05
OCDD	0.001	0.0001	0.0003	0.001
Furans				
TCDF	0.1	0.1	0.1	0.07
1,2,3,7,8-PeCDF	0.05	0.05	0.03	0.01
2,3,4,7,8-PeCDF	0.5	0.5	0.3	0.1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1	0.3
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.09
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.2
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.02
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.1
OCDF	0.001	0.0001	0.0003	0.002