Dioxins in peat and its formation: An overview
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Abstract: Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans collectively named dioxins, have long been investigated in numerous ways in their formation and presence in diverse types of matrices, e.g., air, soil, food, milk, and tissue, and their effects on human health among others. In the 1970s and 1980s, dioxins and other hazardous pollutants were found to be excessive in the environment prompting a global concern on its restriction and elimination. By year 2000, curbed industrial releases had remarkably lowered dioxin emission. However, dioxin emission continued to be a hazard from non-industrial sources such as forest fires, domestic combustion, and vehicles. In South East Asia, frequent peat fires may have leadingly contributed to the dioxins level in the environment. The objective of this review is to compile related data on dioxins in peats and to theorize the possible source and their formation.

Subjects: Environmental Studies; Environmental Issues; Environmental Change & Pollution

Keywords: Dioxins; PCDD/Fs; Peat; Emissions

1. Introduction
Peatland commonly involved in fires in North America and South East Asia (Van der Werf et al., 2017) contribute to greenhouse gas emissions and haze episodes. A study by Sahani et al. (2014) in Malaysia reported that constant exposure to haze can result in immediate or prolonged effects on mortality with increased respiratory-associated death by 19–66%. Firefighters being the first responder of wildland or peat fires are extremely vulnerable to developing diseases associated

ABOUT THE AUTHOR
The authors are researching on dioxins in several sample matrices, currently on tropical peat. This is a fundamental research looking at the possible formation pathway(s) of dioxins and its relation to precursors and catalysts compounds in the sample matrix. The outcome of this research will expand to studying the effects of firefighters involved in peat fire operations. If dioxins are produced in peat fires, firefighting activities could pose higher cancer risk for firefighters.

PUBLIC INTEREST STATEMENT
Dioxins are naturally produced mainly during combustion. It is one of the initial “dirty dozen” persistent organic pollutants (POPs) bearing the most toxic chemical compound and is cancer-causing. Materials having high organic matter may produce more dioxins when it burns. An example is peat soil which has at least 70% of organic matter. Peat fires commonly occur in the South East Asian region during seasons of droughts and anthropogenic activities. Studies have shown that peat fire produces dioxins. Smoldering peat is also found to have the most ideal temperature range for dioxin formation. The pathway on how dioxins are produced is still unclear. This review article is a summation of dioxin sources and formation and the correlated information suggest the probability of dioxins production during peat combustion based on the physico-chemical properties of peat soil.
with smoke emissions from fire. Studies by Adetona et al. (2013) and Navarro et al. (2019) implied that firefighters have increased risk of developing cancer due to their work. This could be related to their exposures to dioxins and other emissions during firefighting duties. The most potent dioxin congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), is classified as Class 1 carcinogen, a known human carcinogen (IARC (International Agency for Research on Cancer), 1997). Since peat originates mainly from plant parts such as roots, leaves, and stem including other small insects and animals, it is a large composition of organic materials such as carbohydrates and lignins among others (Hayes et al., 2015). These compounds are mainly precursors or, can be converted to precursors for dioxin 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 risks of dioxin formation if the sites are burned.

To date, there is only a handful of studies on dioxins in peat. Dopico and Gomez (2015) reviewed the global sources and data of dioxins. Another review by Pereira (2004) examined the main sources of dioxin and its possible formation pathways. Zhang et al. (2016) studied dioxins from biomass combustion extensively which also briefly included peat. A review on dioxin emissions from smoldering peat fires and their contribution to regional haze episodes was published by Hu et al. (2018). However, data on tropical peat dioxin emissions remain scant to date. The objective of this review is to assemble data on dioxins and other pollutants or precursor compounds in peat and their emission including from related biomass combustion. The correlated data will be used to theorize the possible formation pathways of dioxins from peat combustion. It is also an effort to heighten awareness of the emission of dioxins, particularly from tropical peat fire.

1.1. Dioxins
Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are listed as POPs in the Stockholm Convention on Persistent Organic Pollutants. Their compounds have tripling of benzene rings interconnected by an oxygenated ring in the middle. Figure 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 are substitutable with chlorine atoms. PCDD/Fs are a group of organic chemicals characterized by properties of semi-volatile organic compounds, bio-accumulative 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 as 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 study, (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 as most toxic with chlorine present at 2, 3, 7, and 8 positions. 2,3,7,8-TCDD is found to be most toxic.

Figure 1. Basic structure of PCDD and PCDF.
followed by 1,2,3,7,8-PCDD and 2,3,4,7,8-PCDF (WHO, 2000). Dioxins and furans collectively are
commonly known as dioxins or PCDD/Fs which is the subject in this review. Toxicity of dioxins is
expressed as Toxic Equivalents (TEQ). Individual dioxins congener has its own Toxic Equivalency
Factor (TEF). TEFs are estimations of the toxicity of dioxins comparative to the toxicity of
2,3,7,8-TCDD, which is assigned as TEF of 1.

1.1.1. Dioxin sources
Dioxins are generated through many combustion processes. In nature for example, they are
a result of volcanic eruptions, 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 Belarus researcher believed that the main
contribution to dioxin emissions was firewood and peat combustion through incomplete combus-
tion of organic carbon in the presence of chlorine (Kakareka, 2002). A study by Dopico and Gomez
(2015) that reviewed global dioxins trend observed that dioxins emission in general has decreased
globally from its peak in the 1970’s to 1980’s. This decrease is observed in literatures until 2010s.
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 I-TEQ, almost a 70% decline from 1997 (7,343–7,597 g I-TEQ).

In 2002, 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 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 (Environmental Protection Agency)
U.S., 2006). Bawden et al. (2004) reported that uncontrolled combustion (e.g., biomass burning,
except burning and accidental fires) contributed to nearly 70% of total dioxin emissions to air and
over 80% of total emissions to land in Australia.

The results from the European inventory of dioxins (expressed in g I-TEQ/year) (Quass et al.,
2000, 2004) in Table 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 domestic or
municipal wastes, forest and peat fires.

Dioxin 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:
“homogeneous” pathway between 500 and 800°C and “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 gas phase, is not as widely studied as
heterogeneous mechanism. Heterogeneous formation is a catalytic reaction, which 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 chlori-
nated dioxin arrangements from a carbon, oxygen, and chlorine source that maximizes at
a temperature frame of 300–325°C in the post-combustion zones (Altwicker, 1991, 1996; Huang &
Buekens, 1996). The second suggested reaction for the formation of PCDD/Fs is 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 aromatization of aliphatic compounds and chlorination by molecular chlorine produced from an equilibrium of HCl and oxygen (Altwicker, 1996; Fängmark et al., 1994). The aromatization occurs at high-temperature range with chlorination at lower temperature range (Environment Australia, 1999). 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, chlorobenzenes, followed by the adsorption on the organic particular phase occur as precursor pathway. 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 dioxin 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

| 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,   | 10,539                                | 1619-2461                        | 77-85         | 1011-1495       |
| Secondary Aluminum Production, Combustion in industry, Power plants, Electric       |                                       |                                  |               |                 |
| Furnace Steel plant, Industrial Waste, Sintering of special materials and            |                                       |                                  |               |                 |
| dressing facilities, Secondary zinc production, Hospital Waste, Sinter plants and    |                                       |                                  |               |                 |
| Municipal Solid Waste Incinerator.                                                   |                                       |                                  |               |                 |
| Non-industrial sources                                                               | 3151                                  | 846-2144                         | 32-73         | 952-2257        |
| Domestic solid fuel combustion, Preservation of wood, Road transport, Illegal       |                                       |                                  |               |                 |
| incineration of Domestic or municipal wastes, Incineration of corpses and Accidental|                                       |                                  |               |                 |
| fires                                                                                |                                       |                                  |               |                 |
| Total of sources considered                                                          | 13,690                                | 2465-4605                        | 66-82         | 1963-3752       |

a(Quass et al., 2004)
b(Quass et al., 2000)
These include types of reactor for combustion, oxygen capacity, types and amount of fuel, temperature, amount of chlorine present and the presence of metal species among others. These factors influence the dioxins yield.

1.2. Peatland coverage
Peat formation occurs when the rate of accumulation of organic material exceeds the rate of decomposition (Leete, 2006). According to the most recent estimates of global peatland by J. Xu et al. (2018), 2.85% of the world’s land area is covered by peatland. Russia has the largest peatland area covering 1.366 million km² of the country’s land followed by Canada, having 1.132 million km² of peatland. In terms of peatland coverage percentage, Ireland and Finland have the most peatland coverage where 24.06% and 23.67%, respectively. In Asian countries, Indonesia and China have the largest peatland area (148,331 km² and 136,963 km², respectively). In terms of percentage, Indonesia and Malaysia have the highest percentage of peatland area (8.19% and 6.82%, respectively). Table 2 lists the peatland coverage in area and percentage areal coverage based on countries and continents.

1.3. Physico-chemical characteristics of peat in relation to dioxins formation
Peat is a type of organic soil that contains large amounts of organic matter. The source is peatland areas where water is retained by organic matter failing to decompose. Peat soil is normally dark brown to black in color, compressible, and has a distinct odor. According to Veloo et al. (2014), tropical peat deposit differs from temperate peat as it has logs and wood.

The physical and chemical characteristics of peat in different parts of the world are diverse depending on the vegetation and plants in the immediate vicinity where they are formed. Differences in peat characteristics are also affected by the nature of mineral soil and bedrock underlying and adjoining the peatland. The substances in peat can be transported by wind and water, while its chemical characteristics may also be influenced of temperature (Ting, 2015). In tropical countries like Malaysia and Indonesia, peat is generally termed as either basin or valley

| Table 2. Global breakdown of peatland areal coverage |
|-----------------|----------------|----------------|----------------|
|                 | Country         | Land area (km²) (Worldatlas, 2018) | Peatland area (km²) (J. Xu et al., 2018) | Percentage (%) |
| North America   | Canada          | 9,084,977 | 1,132,614 | 12.47 |
|                 | United States   | 9,161,923 | 197,841 | 2.16  |
|                 | Others          | 6,462,100 | 8866 | 0.14  |
|                 | Total           | 24,709,000 | 1,339,321 | 5.42  |
| Asia            | Asian Russia    | 9,784,930 | 1,180,358 | 12.06 |
|                 | Indonesia      | 1,811,569 | 148,331 | 8.19  |
|                 | China           | 9,326,410 | 136,963 | 1.47  |
|                 | Malaysia        | 328,657 | 22,398 | 0.58  |
|                 | Others          | 23,327,434 | 135,132 | 5.36  |
|                 | Total           | 44,579,000 | 1,623,182 | 3.64  |
| Europe          | European Russia | 6,592,812 | 185,809 | 2.82  |
|                 | Finland         | 303,815 | 71,911 | 23.67 |
|                 | Sweden          | 410,335 | 60,819 | 14.82 |
|                 | United Kingdom  | 241,930 | 22,052 | 9.12  |
|                 | Ireland         | 68,883 | 16,575 | 24.06 |
|                 | Others          | 2,562,225 | 171,171 | 6.68  |
|                 | Total           | 10,180,000 | 528,337 | 5.19  |
| South America   | Total           | 17,840,000 | 485,832 | 2.72  |
| Africa          | Total           | 30,370,000 | 187,061 | 0.62  |
| Oceania         | Total           | 7,692,024 | 68,636 | 0.89  |
| Global          | Total           | 148,647,000 | 4,232,369 | 2.85  |
peat. Basin peat is usually found on the inward edge of mangrove swamps along a coastal plain. Peat is generally classified as ombrogenous or rain-fed peat and is poor in nutrients. Rainfall and surface topography control the overall hydrological characteristics of peat land. Peat is formed in anaerobic condition where dioxin formation is favorable via combustion.

Analysis of peat properties involving peat from different parts of the world have been done by several authors including Feustel and Byers (1930) and Delicato (1996). According to studies by Andriessen (1988), Charman (2001), and Bragazza et al. (2007), peat chemical composition and characteristics are predominantly influenced by the parent vegetation, degree of decomposition and original chemical environment. A study on peat pyrolysis (Cunico, 2015) derived a formula of peat, i.e. CH_{1.34}O_{0.50}S_{0.001}N_{0.022}, with comparison to approximate coal formula (CH_{0.81}O_{0.08}S_{0.02}N_{0.01}) provided by Boroujeni (2008) and municipal solid waste formula (CH_{2.62}O_{1.48}S_{0.13}N_{0.06}) calculated from Malaysian household waste (Ministry of Housing and Local Government Malaysia, 2013). Peat contains carbon, hydrogen, oxygen, and very little of sulfur and nitrogen, in which its chemical structure formula can be simplified to approximately C_{6}H_{10}O_{2}~C_{6}H_{2}(H_{2}O)_{3}, by omitting both the sulfur and nitrogen contents.

Major organic materials in peat are derived mainly from vegetative matter, and to a lesser extent, from microbial sources consisting of bitumens, carbohydrates, lignin, and lignin-like materials, and humic substances. Bitumen components can be resins, waxes, and asphalts that increase correspondingly with the state of decomposition (Boron et al., 1987). The humic substances in peat, humic acids and fluvic acid, formed through decomposition processes are the potential precursor compounds to form dioxins when burned.

The inorganic part of peat composition may also vary considerably from region to region. This inorganic content is greatly influenced by local water table and the state of decomposition of peat. The closer the peatland is to the water table the higher its inorganic content. In a state of decomposition, the more advanced the humification, the more inorganic content is in it. Some of the inorganic materials in peat include iron (Fe), zinc (Zn), copper (Cu), and lead (Pb). Elements present in peat from some countries are shown in Table 3.

A few trace metal catalysts of dioxin formation, which includes Cu is the most potent catalyst for dioxin formation. Other metals e.g., Fe and Zn in several studies have been correlated with increased dioxin formation (Gullett et al., 1992; W.S. Hinton & Lane, 1991a, Hinton &

### Table 3: Average concentrations of major and trace elements (mg/kg) in peat

| Element | Russia | United Kingdom | Estonia | Norway | Australia | Latvia |
|---------|--------|----------------|---------|--------|-----------|--------|
| Cu      | 26.3   | 54.8           | 102.1   | 3.6    | 4.2       | 4.26   |
| Pb      | 15     | 358            | 200.0   | 15.05  | 28.6      | 2.90   |
| Zn      | 59.6   | 56.2           | 446.5   | 15.95  | 11.3      | 3.88   |
| Fe      | 1783.3 | 3.52           | 1155    | 928.5  | 1686      | 217.5  |
| Cd      | -      | 2.09           | 17.4    | 0.72   | 2.7       | 0.03   |
| Mn      | 68.6   | 25.4           | 146.5   | 3.95   | -         | 3.61   |
| Ni      | -      | 10.9           | 46.6    | 2.0    | -         | 0.76   |
| Cr      | -      | 15.9           | -       | 0.85   | -         | 1.77   |
| Ca      | -      | 80.8           | -       | -      | -         | 575    |
| Mg      | -      | 246            | -       | -      | -         | 188    |
| Co      | -      | -              | 1.11    | -      | -         | 0.05   |

*Markert and Wtorova (1992), Jennifer and Hao (1993), Orru and Orru (2006), Bragazza et al. (2007), and Simon and Thomas (2003) * Teirumnieka et al. (2010)
Lane, 1991; Stieglitz et al., 1990). Some studies have indicated that manganese (Mn), magnesium (Mg) and nickel (Ni) may also serve as catalysts for dioxin formation. Table 3 shows that peats do contain these metal catalysts for dioxins formation, an indication of potential dioxins being produced when peat burns.

Peatlands are susceptible to outbreaks of fire during seasons of drought. The high organic content in peat, high surface area (porosity) and heat from high temperature produced by the sun easily stimulate peat fires. Peat fire can also happen due to anthropogenic or agricultural (land-clearing) activities. Peat burns by smoldering fire on the surface and underground layer of peats. The burning may last several days or even months, with peak temperature window ranging between 450 and 700°C (Rein, 2015), where dioxins may form through the “homogeneous” or “heterogeneous” pathway.

According to Tfaily et al. (2014), peat can be categorized into three layers based on its decomposition stage. The first layer is called acrotelm that consists of living vegetation, roots and newly formed litter. The second layer is mesotelm, the transition zone between oxic acrotelm and anoxic catotelm. The deepest layer of peatland is catotelm. Based on Fourier Transform Infrared (FTIR) spectra, catotelm decreases in amount of aliphatic molecules with depth and is also reduced in organic acid components. With depth, copious amount of aromatic compounds are evident in FTIR spectra, signifying humification, and accumulation of lignin-like aromatic residue. These findings are vital when considering the route of dioxin formation.

1.4. Dioxins, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in peat soil
In 1997, 2006 and 2015, peat fires in South East Asian countries resulted in severe haze episodes in the region. Tiny particulate matter (PM) in the smoke from the fire and haze also contain toxic gases such as carbon monoxide and nitrogen oxides and organic pollutants such as dioxins, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) among others. These organic pollutants are subject to long-range atmospheric transfer and deposition, thus leading to their presence around the world, even in the Arctic (Hung et al., 2002). Peat smoke and its danger to health was reviewed by Hinwood and Rodriguez (2005). Dioxins were listed as a group of the many compounds in peat smoke that is adverse to health. Peat fire emissions such as PAHs have been studied by several authors (George et al., 2016; Kunii et al., 2002; Muraleedharan et al., 2000) including other toxic gases (Othman & Latif, 2013) on peat soil in temperate and tropical regions. Peat soil itself may also contain pollutants such as PCBs and PAHs as reported by Berset et al. (2001). According to Pereira’s report (2004), PCBs may also be the precursors for dioxin formation where oxygen is present. Iino et al. (1999) reported that PAHs may also be the precursors for dioxin formation, especially perylene.

Detection of dioxins in raw peat soils was encountered by several researchers with different perspectives in their research (Bergknut et al., 2010; Black et al., 2016; Silk et al., 1997). Table 4 illustrates the total PCDD/F WHO-TEQ in their samples. Bergknut et al. (2010), explored how atmospherically derived soil pollution is affected by environmental processes involving remote wetlands and forested areas. Measurements of dioxins, PCBs, and hexachlorobenzene in forest soil and three peat samples collected from an oligotrophic mire at various depths (5–10 cm, 225–275 cm, and 325–375 cm) were performed at a remote boreal catchment in northern Sweden. Hydrophobic organic compounds (HOCs) in peat were concluded as evenly distributed throughout the body of the mire while levels of dioxins in the forest soil increased with the rising amount of organic matter.

Another study involved peat samples from Kelly’s bogs in New Brunswick, Canada. These were analyzed for dioxins and other organochlorine compounds (Silk et al., 1997). Seven depths of peat samples were collected (surface, 0–1 m, 1–2 m, 2–3 m, 3–4 m, 5–6 m and 6 m). The result for each congener revealed a range of concentration up to 70 pg/g dry weight, with surface peat containing
Table 4. Total PCDD/Fs, PCBs and PAHs in raw temperate peat samples

| Sample                        | PCDD/Fs (pg WHO-TEQ g$^{-1}$) | PCBs (pg g$^{-1}$) | PAHs (pg g$^{-1}$) | Reference                        |
|-------------------------------|--------------------------------|--------------------|-------------------|----------------------------------|
| Raw temperate peat (Canada)   | 2.10–7.28                       | -                  | -                 | Silk et al. (1997)               |
| (n = 7)                       |                                |                    |                   |                                  |
| Raw temperate peat (Sweden)   | 0.73–6.43                       | 900–1200           | -                 | Bergknut et al. (2010)           |
| (n = 9)                       |                                |                    |                   |                                  |
| Raw temperate peat (USA)      | 0.25–0.64                       | -                  | 0.08–0.15         | Black et al. (2016)              |
| (n = 2)                       |                                |                    |                   |                                  |
| Raw temperate peat (Switzerland) | 1170–18,940                   | -                  | 0.125–2.853       | Berset et al. (2001)             |
| (n = 7)                       |                                |                    |                   |                                  |
| Raw temperate peat (Finland)  | -                              | 42,000–350,000     | -                 | Himberg and Pakarinen (1994)    |
| (n = 14)                      |                                |                    |                   |                                  |
| Raw temperate peat (UK)       | -                              | -                  | 0.101–1.112       | Vane et al. (2013)               |
| (n = 3)                       |                                |                    |                   |                                  |
| Raw temperate peat (UK)       | -                              | 4.6–36.8           | 1.25–25.88        | Sanders et al. (1995)            |
| (n = 20)                      |                                |                    |                   |                                  |

one of the highest total concentration of PCDD/Fs. Since the concentration of each congener in Silk et al. (1997) study are only illustrated in bar chart, the best estimate made for surface peat total PCDD/Fs in the study is 5.6 pg WHO-TEQ/g.

Raw peat from North Carolina was also analyzed (Black et al., 2016) for dioxin comparisons and dioxin emissions with one depth collected for the analysis (surface to 20–25 cm) from two different locations. The total PCDD/Fs concentrations for samples from two different locations were 7.4 and 8.7 pg/g, respectively, and expressed in pg WHO-TEQ/g (Table 4). For dioxin emissions, the authors reported that total PCDD/Fs emissions were 3 to 11 times higher than the raw peat content after 7 h of burning. It was also observed that more dioxins were produced in the first 3 hours of burning compared to the next 4 hours, having 1 to 6 times more dioxins in the former combustion.

“-” means data were not measured

Besides dioxin test, peat samples were also subjected to PCBs and PAHs investigation to study their toxicity, persistency, and suitability of peat core to date the compounds of interest in their studies. As stated, PCBs and PAHs may also be precursor materials for dioxin formation. Table 4 shows the total PCDD/Fs WHO-TEQ, PCBs and PAHs for raw temperate peat samples in previous-reported studies, raising questions on the origin of the pollutants in the peat samples since the analyzed samples were all raw temperate peat.

The presence of varied amounts of dioxins among the samples was noted even though all were raw temperate peat. Dioxins in peat from Canada and the United States of America (USA) were vastly different even though they were from the same continent (approximately 1500 km apart). This is maybe due to the history of the site, sampling and average temperature differences. While dioxins in the Swedish peat was reported to be largely varied in range. The disproportion in the Swedish samples was not determined by the depth of peat samples as sample M1 (center of the mire) has the highest concentration of dioxins at 5–10 cm depth while sample M3 (west of the mire) has the highest concentration of dioxins at 325–375 cm depth. It is unclear what causes these variations. Canadian peat sample in the above-mentioned study also shows variation in dioxins concentration regardless of its depth. The authors concluded that some organochlorine compounds including some PCDD/Fs are biogenic in origin, given that these compounds existed even before industrialized era. Black et al.
did not make any conclusion on the origin of dioxin, as the source was not the objective of the research. The conclusion made by Silk et al. (1997) was based on the timeframe of industrialized era, while Bergknut et al. (2010) concluded that this was attributed to vertical transport, degradation, and/or shifting sources over time. Another oblivious likelihood on the origin of dioxins is possibly fire that may have occurred in the area in the past. This would have somewhat affected the concentration of dioxins in the area since dioxins are mainly produced during combustion. The amount of organic matter and the phase of peat decomposition could also affect the amount of dioxins in the studied samples. Although peatland could be additional source of POPs in some regions of the world but so far it is not major source of dioxins in environment, and it would be more important locally.

1.5. Sources of dioxins in related samples

Peat is considered as part of biomass since it consists mostly of organic matter. Dioxins in other type of biomasses, such as vegetation, soil and ash or sediment are also included in this review for comparison. Table 5 depicts an extensive range and volume of dioxins at varied locations and types of soils involved.

According to Martinez et al. (2000) total PCDD/Fs are more prevalent in burned soil samples compared to unburned soil. Vegetation samples are inconsistent that total PCDD/Fs are somewhat lower in burned vegetation compared to its unburned companion. There is a different homolog pattern in the burned samples with higher proportions of TCDDs, TCDFs, PeCDFs and HxCDFs compared to the unburned samples. The authors concluded however that the formation of significant quantities of PCDD/Fs in forest fires could not be assumed. The type of soil in the study was also not specified; however, soil samples were collected along with vegetation on top soil.

Concentrations of PCDD/Fs in a study by Gabos et al. (2001) was very low leading to the hypothesis that the contributing source of PCDD/Fs is atmospheric deposition rather than influence of forest fires. Nevertheless, the samples used in the study were collected from river bottom and the time frame between forest fire and sample collection was not specified making it difficult to correlate the data. Results in a study by Kim et al. (2003) indicated a decreasing trend of PCDD/Fs content with time. Total PCDD/Fs of ash sample from the study was higher than its corresponding soil sample. The presented data suggested that PCDD/Fs were formed during forest fires and subsequently introduced into the soil. The type of soil in the study was however not specified.

Eighteen soil samples collected from electronic wastes disposal area were analyzed and the results showed that the mean value of PCDD/Fs to be quite high (20 pg I-TEQ/g, a range of 5.7 to 57 pg I-TEQ/g), compared with 0.82 and 2.9 pg I-TEQ/g for background areas. Since the soil samples were from electronic wastes disposal areas, PCDD/Fs contamination were presumed to have derived from open thermal disposal of electronic wastes (P. Xu et al., 2013). Results of Huyen et al. (2015) indicate that dioxin concentrations were observed to decrease with depth. 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (TCDD) was the dominant congener in the soil sample. The type of soil samples in this study contains a very small amount of organic matter. Another study (Dang et al., 2015), which utilized the same sample as Huyen et al. (2015) found that dioxins increased with a surge in total organic carbon.

Al-Wabel et al. (2016) asserts that the highest concentration of PCDD/Fs in their study came from cement factory soil, followed by oil refinery station soil. It is suggested that the PCDD/Fs came from the industrial process as the maximum WHO-TEQ value from background site soil was only 1.24 pg WHO-TEQ/g dw compared to industrial areas soil which had maximum WHO-TEQ values of 1.73 to 3.98 pg WHO-TEQ/g dw. Results from Hsu et al. (2018) revealed that the average total PCDD/Fs for contaminated sites and background sites was 14.0 ± 19 pg WHO-TEQ/g and 6.25 ± 17.5 pg WHO-TEQ /g, respectively, hence the suggestion that dioxins are produced by industrial process.

Humus topsoil in Pandelova et al.’s (2018) study presented generally higher PCDD/Fs content compared to mineral topsoil. We did some analyses on the available data provided by the author
and found that there is a significant correlation between total organic carbon and PCDD/Fs WHO-TEQ. Pandelova et al. (2018) also suggested that the PCDD/Fs load in German forests was predominantly a result of atmospheric fluxes and this proposition is supported by the congener pattern found in their samples. A study by Le et al. (2019) show that surface soil (0–10 cm) was highly contaminated with PCDD/Fs. The sediment samples also show high PCDD/Fs WHO-TEQ values while core soil samples presented decreasing trend as the depth increased in all sampling sites.

Reviewed articles have suggested a vast array of probable dioxins sources that include atmospheric deposition, industrial process, herbicide contamination, and forest fires. The positive relationship of dioxins with organic matter and the diminishing trend of dioxin concentration with the depth of sampling sites are also reported.
2. Conclusions

It is seen in this review on the origin of dioxins found in peat, biomass and other related materials. There are varying claims that the dioxins compounds are produced by microbial activity, atmospheric decomposition, and combustion of organic materials. Since peat and biomass contain high amount of organic materials, it is probable that both will produce high amount of PCDD/Fs when burned, especially in an incomplete combustion condition with the presence of catalytic components. These organic matters and compounds (e.g., phenols, benzenes, and humic substances) could also be the potential precursor materials for the formation of dioxins, which could be the main pathway of dioxin formation from peat combustion. Studies have also shown that dioxins are undoubtedly produced when peat is burned. Further investigation on dioxin formation from peat combustion, particularly on tropical peat must be further examined.

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