Mixed halogenated dioxins and furans: a technical background document

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What are mixed halogenated dioxins/furans?

Polychlorinated dibenzo-p-dioxins/furans (PCDDs/Fs), commonly known as chlorinated dioxins and furans, have long been recognized as toxicologically significant environmental contaminants. However, PCDD/Fs are members of a larger group of closely related compounds known as polyhalogenated dibenzo-p-dioxins and furans, or halogenated dioxins and furans. This group includes three main subgroups;

- polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs)
- polybrominated dibenzo-p-dioxins/furans (PBDD/Fs)
- mixed polybrominated/polychlorinated dibenzo-p-dioxins/furans (PXDD/Fs)[1]

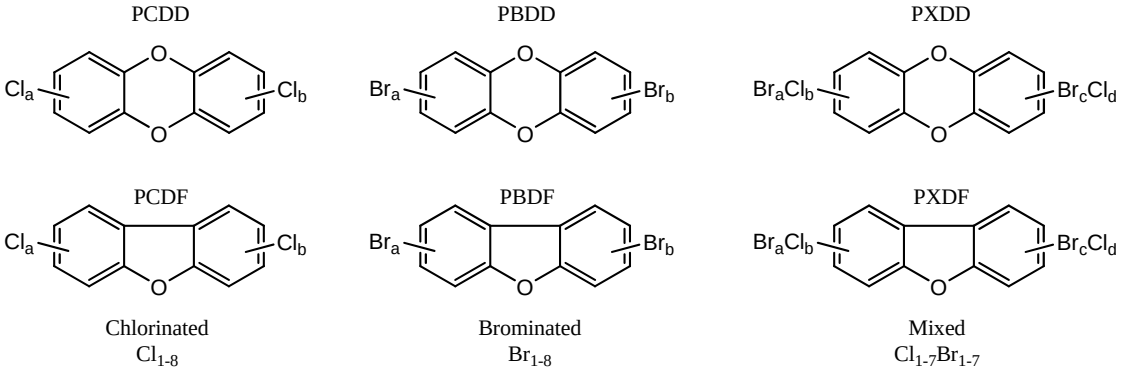

Figure 1. Three main subgroups of halogenated dioxins and furans; chlorinated (PCDD/Fs), brominated (PBDD/Fs) and mixed brominated-chlorinated (PXDD/Fs)

The individual chemicals within each group, known as congeners, have different numbers and positions of halogen (chlorine or bromine) atoms. For either the chlorinated group (PCDD/Fs) or brominated group (PBDD/Fs), there are 75 possible dioxin congeners and 135 furan congeners, making 210 in total. The toxicity of the individual congeners is largely dependant on the number and positions of the chlorine or bromine atoms. Those

[1] Mixed halogenated dioxins/furans (PXDD/Fs) refers to those compounds with both chlorine and bromine substitution of the dioxin/furan skeletal structure

congeners with chlorine or bromine atoms in the 2, 3, 7, and 8 positions have been found to be the most toxic. For each of the PCDD/Fs and PBDD/Fs groups there are 17 possible 2,3,7,8-congeners. In contrast, the mixed dioxins/furans (PXDD/Fs) is a far larger group, with 4600 possible congeners, including approximately one thousand 2,3,7,8-substituted congeners.

Chlorinated dioxins/furans are subject to the international Stockholm Convention on Persistent Organic Pollutants and as such listed under the European Directive 850/2004 (EC 2004). However, neither brominated nor mixed congeners are currently covered by the convention despite their very similar properties

Toxicity

Compared to their chlorinated analogues, little research has been carried out to investigate the toxicity of mixed dioxins/furans, despite data first emerging over 20 years ago which suggested that mixed dioxins/furans have equivalent toxicity to chlorinated dioxins/furans (Behnisch et al. 2001, Hornung et al., 1996, Mason et al. 1987, Weber & Greim 1997, WHO 1998). This is due, in part, to the far greater number of 2,3,7,8-substituted congeners for mixed halogenated congeners compared to chlorinated congeners. More recently, bioassay studies have provided further evidence that mixed dioxins/furans (2,3,7,8-substituted congeners) have equivalent, or in some cases higher, biological activity compared to their chlorinated analogues (Behnisch et al. 2003, Olsman et al. 2007, Samara et al. 2009). However, the testing of mixed congeners remains limited to only a few compounds, a very small fraction of all possible 2,3,7,8-substituted mixed dioxins/furans.

Toxic equivalency factors (TEFs)

Toxic equivalency factors (TEFs) are used to provide a measure of the toxicity of dioxins and related compounds relative to that of the most toxic chlorinated compound (2,3,7,8-TCDD). TEFs have been determined for all 17 of the 2,3,7,8-substituted chlorinated dioxin/furans (PCDD/Fs), on the basis of data from multiple *in vivo* and *in vitro* studies that take into account processes such as uptake, tissue distribution, metabolism, receptor binding, and activation (Van den Berg et al. 2006).

At present, no brominated (PBDD/Fs) or mixed (PXDD/Fs) congeners have been assigned a TEF value. For many compounds, particularly the mixed congeners, this is largely due to insufficient environmental and toxicological data available. The World Health Organization (WHO), through the International Programme on Chemical Safety (IPCS), has recently reevaluated TEF values. As part of this process it has been concluded that mixed halogenated dioxins/furans should definitely be considered for inclusion in the TEF scheme if they are detected in humans and their food (Van den Berg et al. 2006).

Where mixtures of dioxins and related compounds are present, a toxic equivalent (TEQ) value is used to represent the total dioxin related toxicity. This is a summed value based upon the TEFs and amounts of individual compounds present. As there are currently no

TEFs for brominated (PBDD/Fs) and mixed (PXDD/Fs) congeners, these compounds are not be considered in the calculation of a TEQ, and this will commonly result in an underestimation of the TEQ.

Formation

Mixed dioxins/furans can be formed under the same conditions as the formation of chlorinated dioxins, that is combustion or exposure to high temperatures in the presence of oxygen, though in the presence of both bromine and chlorine sources (Weber & Kuch 2003). As a result, mixed dioxins/furans, in addition to their chlorinated analogues, have been detected in fly ash and/or flue gas from municipal waste incinerators (Weber & Kuch 2003, WHO 1998).

Studies have demonstrated that organochlorine and organobromine compounds can act as sources of halogens for the formation of mixed dioxins/furans under thermal condition. These include organobromine compounds used as brominated flame retardants (BFRs), as well as relatively simple organic compounds such as chlorinated phenols and brominated phenols (Weber & Kuch 2003, Evans & Dellinger 2005). One study that investigated the co-combustion of a number of different BFRs with municipal solid waste (MSW) found no differences in the formation of mixed dioxins/furans between different BFRs, suggesting that all types of BFRs can act as sources of bromine for the formation of mixed dioxins/furans under such conditions (Söderström & Marklund 2000).

There is some evidence to indicate that inorganic halogenated substances can also act as the source of halogen in the formation of halogenated dioxins/furans, particularly for chlorine, though these are generally less important precursors than organohalogen compounds (WHO 1989). Though far less studied than chlorinated or brominated dioxins, there is evidence for the formation of mixed dioxin/furans through this route (Weber et al. 2002).

Though usually detected in significantly lower quantities than their chlorinated analogues, under certain conditions mixed dioxins/furans can constitute the majority of all halogenated dioxins/furans formed (Söderström & Marklund 2002). The formation of mixed dioxins/furans at lower temperatures, more typical of open burning situations than incineration, generally favours the formation of congeners with higher bromine:chlorine ratios (Weber et al. 2002, Söderström & Marklund 2004). This is in contrast to some studies of mixed dioxin formation within incinerators where only monobrominated mixed congeners were detected (WHO 1998).

Currently, electrical and electronic equipment (EEE) commonly contains both chlorinated materials and brominated materials, including the chlorinated plastic polyvinyl chloride (PVC) and a wide range of brominated flame retardant compounds. Furthermore, at end of life, significant quantities of electronic waste are recycled and disposed of using sub-standard waste management practices, including open burning. Therefore, for as long as EEE containing such materials continues to enter the waste stream, it will continue to act as a potential source for the formation of mixed dioxins. In fact, a recent study found that soil from sites where different types of waste EEE is treated by open burning contained

extremely high levels of halogenated dioxins/furans, with mixed congeners being predominant, present at far higher concentrations than their chlorinated analogues (Yu et al. 2008).

Halogenated substances used in EEE are predominantly either chlorinated substances or brominated substances, and not mixed chlorinated/brominated substances (i.e. a single substances containing both chlorine and bromine). The formation of mixed halogenated dioxins/furans from waste EEE in significant quantities indicates that their formation involves multiple precursor halogenated substances, not single precursor substances (see Figure 2). Any investigation into halogenated dioxin/furan formation from a single substance would, therefore, be unable to assess adequately the potential for formation of all halogenated dioxins/furans (including mixed congeners) in situations in which both bromine and chlorine precursors are commonly present, such as in many waste disposal and recovery situations.

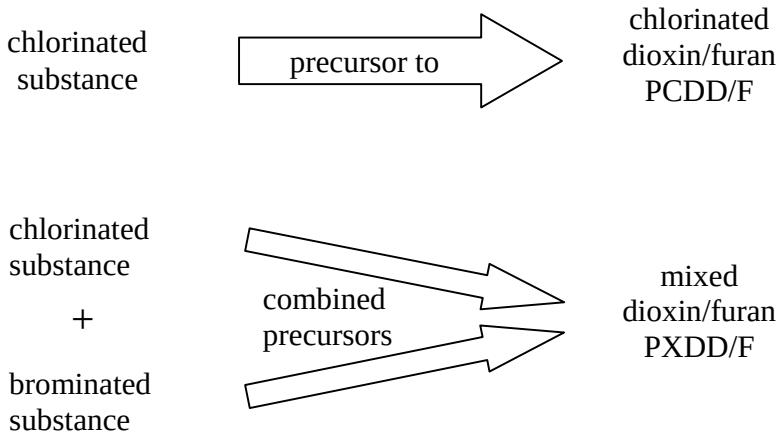

Figure 2. Formation of mixed dioxins/furans from multiple precursor substances

Presence in the environment

A review of brominated dioxin/furans including mixed dioxin/furans published by the World Health Organisation (WHO) in 1998 reported at the time, on the basis of limited data, that mixed dioxins/furans can be detected in the environment and biota, though commonly at significantly lower concentrations than those of the chlorinated analogues (WHO 1998).

More recent studies have also detected mixed dioxins/furans in the environment, in the atmosphere in Japan (Hayakawa et al. 2002), for example. In this case, although levels were significantly lower than those of chlorinated congeners, they were of a similar magnitude to brominated congeners. Subsequent studies have also detected mixed dioxins/furans in various environmental media including rain water, soil, river sediments and marine sediments (Hayakawa et al. 2002, Ohta et al. 2002, Terauchi et al. 2009).

Human exposure

Very few studies have been carried out to investigate human exposure to mixed dioxins/furans. There are as yet no reports of mixed dioxins/furans being detected in humans. In the early 1990s, analyses of human milk from Sweden (Wiberg et al. 1992) and Germany (Dawidowsky 1993 in WHO 1998) did not identify mixed dioxins/furans at detectable levels. More recently, as part of the WHO-coordinated surveys of human milk, mixed dioxins/furans (tetra- and penta-substituted congeners) were found to be below detectable levels in pooled human milk samples from 17 countries (Kotz et al. 2005), and also in a subsequent study of a single pooled sample of human milk collected from 197 Belgium women in 2006 (Colles et al. 2008). Though limited, these studies suggest that levels of mixed dioxins are currently significantly lower than those of their chlorinated or brominated analogues for the general human population in many countries. Although there may be higher levels of human exposure to mixed dioxins in areas where significant point sources of these congeners exist, data from such locations are not currently available.

Summary

Mixed halogenated dioxins/furans are a group of compounds that are closely related to their far more well known chlorinated analogues, both in terms of their mode of formation and their potential toxicity. Extensive research of the properties and distribution of chlorinated dioxins/furans, including human exposure monitoring programmes, has resulted in their recognition as persistent organic pollutants of global concern and their inclusion on the list of compounds regulated under the international Stockholm Convention. However, mixed dioxins/furans have been far less studied, and are currently not subject to any specific monitoring requirements or regulatory controls.

The very limited data available indicate that averaged exposure levels to mixed dioxins/furans for the general populations of some countries are currently significantly lower than their chlorinated analogues. However, no such data exist for human exposure levels to mixed dioxins/furans in those countries or areas in which significant point sources are likely to exist.

Despite these current data gaps, the known hazardous properties of their closely related chlorinated analogues indicate that precautionary controls are required to address the formation and release of mixed halogenated dioxins/furans. Such measures can only be adequately achieved through control of the manufacture and use of halogenated substances which can act as precursors to mixed dioxins/furans throughout their lifecycle, particularly during disposal. As this paper has demonstrated, the mode of formation of mixed dioxins/furans necessitates regulation of the group of halogenated precursor substances, rather than using a substance by substance approach.

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