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Environmental concentrations and toxicology of 2,4,6-tribromophenol (TBP)☆

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ABSTRACT

2,4,6-Tribromophenol is the most widely produced brominated phenol. In the present review, we summarize studies dealing with this substance from an environmental point of view. We cover concentrations in the abiotic and biotic environment including humans, toxicokinetics as well as toxicodynamics, and show gaps of the current knowledge about this chemical.

2,4,6-Tribomophenol occurs as an intermediate during the synthesis of brominated flame retardants and it similarly represents a degradation product of these substances. Moreover, it is used as a pesticide but also occurs as a natural product of some aquatic organisms. Due to its many sources, 2,4,6-tribromophenol is ubiquitously found in the environment. Nevertheless, not much is known about its toxicokinetics and toxicodynamics. It is also unclear which role the structural isomer 2,4,5-tribromophenol and several degradation products such as 2,4-dibromophenol play in the environment. Due to new flame retardants that enter the market and can degrade to 2,4,6-tribromophenol, this compound will remain relevant in future years – not only in aquatic matrices, but also in house dust and foodstuff, which are an important exposure route for humans.

1. Introduction

Among the brominated phenols 2,4,6-tribromophenol (TBP; CAS No. 118-79-6; Fig. 1) is the most widely produced substance (WHO, 2005). It is typically produced in closed reactors by a non-aqueous process and discharged as a melt. This melt is then cooled and pelleted for easy handling (WHO, 2005). In addition to its industrial production, it is also known to be a naturally occurring molecule in different marine organisms, which produce it as a defense against predators and biofouling (Sheikh and Djerassi, 1975; Whitfield et al., 1999). However, in environmental research mainly anthropogenically produced and emitted TBP is studied, which derives as an intermediate during the synthesis of flame retardants (FR) (Ballesteros-Gómez et al., 2014; Ren et al., 2017) or is used as a fungicide and wood preservative (Nichkova et al., 2008; Offret et al., 2016; Savory et al., 1970). Its production volume was estimated in 2001 to account for 9100 t per year worldwide (OECD, 2004). In 2012, health concerns have led to an evaluation of TBP under REACH (European Regulation (EC) No 1907/2006; REACH, 2006). This ECHA (European Chemicals Agency) report focused on several endpoints, but contains no conclusion due to the limited amount of available studies (ECHA, 2016). With the current review, we summarize recent publications concerning the environmental presence and toxicology of TBP. An updated knowledge on TBP is particularly important as TBP has been identified as a possible degradation product of both legacy (Barontini et al., 2004a, 2004b) and novel FRs (Koch et al., 2016) and might therefore still be emitted to the environment via new routes – even if the aggregated tonnage of anthropogenically produced TBP in the European Union decreased from 10,000–100,000 t to 1–10 t between 2012 and 2016 (REACH, 2006). Additionally, it was recently stated that TBP concentrations determined in the field pose an ecotoxicological risk to the environment (Xiong et al., 2016).

2. Environmental concentrations and behavior

TBP ends up in the environment through different routes (Fig. 2). On the one hand, it can enter the environment unintentionally as a degradation product of brominated flame retardants

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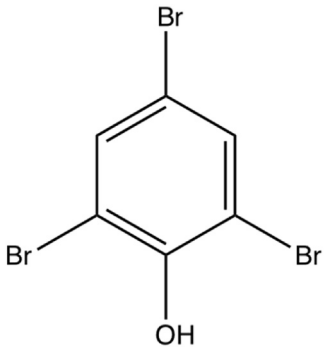

Fig. 1. Chemical structure of 2,4,6-tribromophenol (TBP).

(BFR) (WHO, 2005) or as an intermediate (Bergman, 1990) during the synthesis of these compounds (Ren et al., 2017). On the other hand, TBP is intentionally used as a pesticide and wood conservative in South America (WHO, 2005) due to its known biocidal effects (Nichkova et al., 2008; Offret et al., 2016). Additionally, TBP and other bromophenols are responsible for some of the typical flavors in marine seafood (Boyle et al., 1992). Therefore, TBP can also be part of the manufactured feed for cultivated shrimp that would otherwise not have access to this substance through their diet (Whitfield et al., 1997a) and can thus be considered as an indirect food additive. However, TBP is not only a molecule produced by humans, but appears naturally in several organisms as part of a defense mechanism against biofouling as well (Whitfield et al., 1999).

Despite a dispute about the role of TBP as an additive FR itself (Lee et al., 2016; Liu et al., 2011; Ríos et al., 2003), a clear focus is on its role as an intermediate (WHO, 1997) during the synthesis of other FRs like tetrabromobisphenol A (TBBPA) (Ren et al., 2017) or 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) (Ballesteros-Gómez et al., 2014). In the 1980s, TBP was also detected in emissions from waste incinerators (Öberg et al., 1987) and in automotive emissions from leaded gasoline (Buser, 1986; Muller and Buser, 1986). Bromophenols were also shown to arise from the degradation of other environmental contaminants (Bergman, 1990) such as brominated benzenes and polybrominated diphenyl ethers (PBDE) (Wan et al., 2009). Particularly TBP was identified as a degradation product of BFRs such as TBBPA (Barontini et al., 2004a, 2004b; Eriksson et al., 2004) and possibly the new PolyFR (Koch et al., 2016), which is now commercially being used as a substitute for hexabromocyclododecane (HBCD) in polystyrene foam. Additionally, the structural isomer of 2,4,6-TBP – namely 2,4,5-TBP (Fig. 3) – is often found exclusively as a degradation product of other FRs following biodegradation (Chen et al., 2006; Eriksson et al., 2004; Krieger et al., 2017, 2016; Stapleton et al., 2009; Zheng et al., 2015).

In addition to these unintended sources, 2,4,6-TBP is utilized as a fungicide and wood preservative as well due to its known biocidal effects (WHO, 2005) that are used by different marine organisms (Nichkova et al., 2008; Offret et al., 2016; Ríos et al., 2003; Savory et al., 1970). Since its detection in the marine environment in the 1970s (Sheikh and Djerassi, 1975), TBP was found in a huge variety of marine organisms similar to at least 50 other brominated phenols (Gribble, 2000). It was for instance detected in marine algae (e.g. *Ulva lacuta*; Flodin et al., 1999; Flodin and Whitfield, 1999a), sponges (Whitfield et al., 1997) (e.g. *Phorbas glaberrimus*; Vetter and Janussen, 2005), phoronids (e.g. *Phoronopsis viridis*; Sheikh and

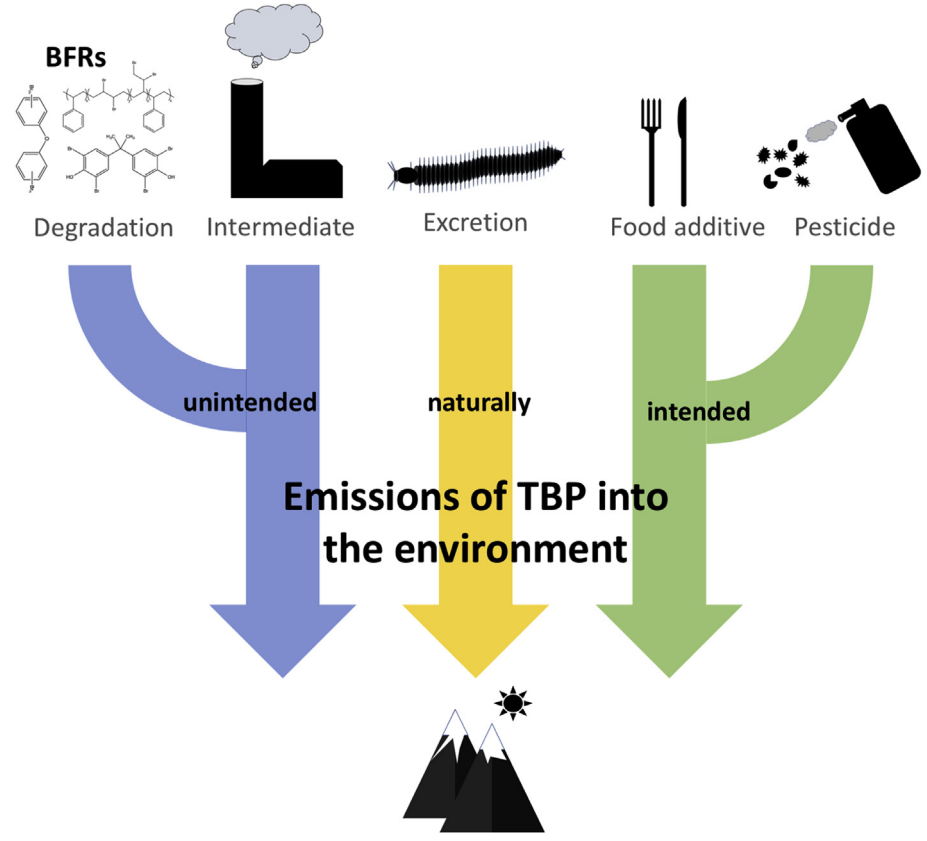

Fig. 2. TBP enters the environment either intentionally or unintentionally due to human activity and from natural sources.