



Review

Halogenated polycyclic aromatic hydrocarbons in the environment

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HIGHLIGHTS

- ▶ Reported occurrences of HPAHs in various environment media were reviewed.
- ▶ Emission sources and possible formation mechanisms of HPAHs were discussed.
- ▶ Toxic equivalents of HPAHs in environmental compartments were estimated.
- ▶ Environmental behaviors of highly substituted HPAHs need further study.

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ABSTRACT

Halogenated polycyclic aromatic hydrocarbons (HPAHs) have been reported to occur in air, sediment, fly ash, and biota samples. This review summarized current existing data on the environmental occurrence, behavior, physicochemical properties, emission sources, and toxic equivalents of HPAHs. Firstly, the physicochemical properties of HPAHs were summarized. Then, an overview of environmental occurrence of HPAHs in ambient matrices including biological samples was reviewed. Meanwhile, the emission sources and possible formation mechanisms of HPAHs were discussed. Apart from that, the aryl hydrocarbon receptor (AhR)-mediated activities were summarized, which indicated that the position and number of halogen atoms on the parent PAHs molecule were important determinant factors affecting the AhR-mediated activity of individual HPAHs congeners. Finally, some research recommendations on HPAHs were given.

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1. Introduction

Halogenated polycyclic aromatic hydrocarbons (HPAHs) are a class of compounds with one or more halogen substituent attached to the aromatic rings of corresponding parent polycyclic aromatic hydrocarbons (PPAHs) (Fu et al., 1999), including chlorinated polycyclic aromatic hydrocarbons (CIPAHs) and brominated polycyclic aromatic hydrocarbons (BrPAHs). As the simplest kind of CIPAHs, polychlorinated naphthalenes with four to eight chlorines attached to naphthalene have been comparatively well investigated (Ohura, 2007). Polychlorinated naphthalenes are persistent, bioaccumulative, and toxic contaminants (Omura et al., 2000), which have been reported to occur in a wide variety of environmental and biological matrices (Blankenship et al., 2000; Kannan et al., 2000; Krauss and Wilcke, 2003; Herbert et al., 2005; Wang et al., 2006; Pan et al., 2007; Horii et al., 2008; Schiavone et al., 2010; Bidleman et al., 2010). In comparison, little information about HPAHs with 3–5 aromatic rings in the environments is available, especially for BrPAHs (Horii et al., 2008; Ohura et al., 2009). A possible reason is that purified individual analytical standards for the larger HPAHs are not readily available commercially (Ohura, 2007; Horii et al., 2008). Some researchers use self-synthesized reference substances to conduct their studies on HPAHs (Ohura, 2007). To date, HPAHs have been detected in fly ash and bottom ash (Horii et al., 2008), urban air (Haglund et al., 1987; Ohura et al., 2009), automobile exhaust (Haglund et al., 1987), surface sediment (Sun et al., 2011), and snow samples (Haglund et al., 1987). Interestingly, CIPAHs were also found in tap water (Shiraishi et al., 1985), kraft pulp mill products and discharges (Koistinen et al., 1994a,b), electronic shredder waste, and various environmental media around of electronic waste (e-waste) recycling sites (Ma et al., 2009). Recently,

the atmospheric occurrences of CIPAHs and BrPAHs with 3–5 aromatic rings were studied (Ohura et al., 2004, 2005, 2007, 2008a,b, 2009; Kitazawa et al., 2006). These published reports provide sufficient data to review environmental behaviors of HPAHs. To our knowledge, there was only one mini-review about CIPAHs published in 2007, but no review of BrPAHs in the environment has been published so far. In this context, this review will summarize the environmental concentrations of HPAHs (with 3–5 aromatic rings) in various matrices and discuss their possible sources (Fig. 1). At the same time, toxic equivalents (TEQs) of these contaminants are studied as well. In addition, we also attempted to bring forward some recommendations for further studies.

2. Physicochemical properties

2.1. Vapor pressure, solubility, and partition coefficients

The formula, molecular weight, and abbreviation of HPAHs and corresponding PPAHs are shown in Table 1. Until now, few experimental data on the physicochemical properties of HPAHs was available, except a recently survey on the vapor pressure of 12 individual HPAHs using the Knudsen effusion method (Fu and Suuberg, 2012). According to this study (Fu and Suuberg, 2012), the di-substitution of halogen atoms further decrease the vapor pressure of HPAHs compared to single halogenation's. For instance, the vapor pressures of di-chloro substituted PAHs are approximately an order of magnitude lower than that of mono-chloro substituted analogs at room temperature. Similarly, the vapor pressures of di-bromo substituted PAHs are approximately two orders of magnitude lower than that of mono-brominated analogs. Besides, Gonzales (2011) estimated these physicochemical

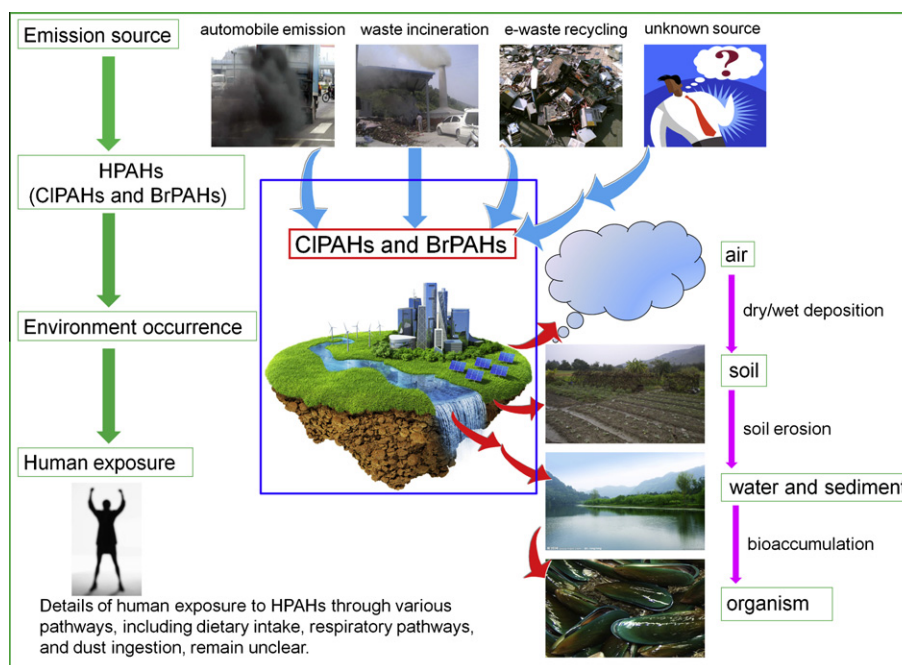


Fig. 1. Conceptual model of halogenated polycyclic aromatic hydrocarbons (HPAHs) in the environment.

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