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Are styrene oligomers in coastal sediments of an industrial area aryl hydrocarbon-receptor agonists?☆

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A B S T R A C T

Effect-directed analysis (EDA) was performed to identify the major aryl hydrocarbon receptor (AhR) agonists in sediments collected from a highly industrialized area (Lake Shihwa, Korea). Great AhR-mediated potencies were found in fractions containing aromatic compounds with log K_{ow} values of 5–8, and relatively great concentrations of styrene oligomers (SOs) and polycyclic aromatic hydrocarbons (PAHs) were detected in those fractions. Until now, there was little information on occurrences and toxic relative potencies (RePs) of SOs in coastal environments. In the present study; i) distributions and compositions, ii) AhR binding affinities, and iii) contributions of SOs to total AhR-mediated potencies were determined in coastal sediments. Elevated concentrations of 10 SOs were detected in sediments of inland creeks ranging from 61 to 740 ng g^{-1} dry mass (dm), while lesser concentrations were found in inner (mean = 33 ng g^{-1} dm) and outer regions (mean = 25 ng g^{-1} dm) of the lake. Concentrations of PAHs in sediments were comparable to those of SOs. 2,4-diphenyl-1-butene (SD3) was the predominant SO analogue in sediments. SOs and PAHs were accumulated in sediments near sources, and could not be transported to remote regions due to their hydrophobicity. RePs of 3 SOs could be derived, which were 1000- to 10,000-fold less than that of one representative potent AhR active PAH, benzo[*a*]pyrene. Although concentrations of SOs in sediments were comparable to those of PAHs, the collective contribution of SOs to total AhR-mediated potencies were rather small (<1%), primarily due to their smaller RePs. Overall, the present study provides information on distributions and AhR binding affinities for SOs as baseline data for degradation products of polystyrene plastic in the coastal environment.

1. Introduction

Effect-directed analysis (EDA) has been increasingly recognized as a powerful ecotoxicological tool for identification of key toxicant(s) in complex mixtures of crude oils and in environmental matrices, such as sediments, soils, and biota (Brack, 2003; Hong et al., 2015, 2016a; Simon et al., 2015). EDA is initially conducted by biological analyses such as *in vitro* and/or *in vivo* bioassays on environmental samples. If a significant biological response is observed in raw materials, the sample is subject to fractionation to reduce complexity and separate chemicals from the original mixture (Brack, 2003; Hecker and Hollert, 2009). Biological effects of given fractions are measured by the same testing methods to identify fraction(s) with measurable toxic potencies. Complexities of samples can be reduced though rigorous fractionation, then major toxicants are isolated and finally identified by use of instrumental quantification (Hong et al., 2016a). Several studies have successfully identified key toxicants in environmental and/or

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biological samples by use of EDA in recent years (Legler et al., 2011; Simon et al., 2011, 2013; Vrabie et al., 2012; Yue et al., 2015).

Lake Shihwa is an artificial lake which has been isolated from the sea by construction of a dike in 1994. The original purpose of the lake was to supply freshwater for use in industry and agriculture (Khim and Hong, 2014; Lee et al., 2014) (Fig. 1). However, Lake Shihwa environments had deteriorated due to inadequate wastewater treatment facilities and runoff of contaminants from surrounding industrial complexes and densely populated cities (Lee et al., 2014). Consequently, the Korean government abandoned its original plan of a freshwater lake and constructed a water gate in 1999 enabling circulation of seawater. Also, more recently the government constructed the Lake Shihwa Tidal Power Station (TPS) in 2011 as part of developmental policy (Lee et al., 2014). Although the water quality has been improving in the vicinity of the gate and TPS, various organic pollutants have been found in sediments of inland creeks and the Lake Shihwa. Thus, the opening of the gate to the sea has not fully resolved the issue of pollution (Khim et al., 1999; Hong et al., 2010; Khim and Hong, 2014; Lee et al., 2014).

In the present study, EDA combining the *in vitro* H4IIE-*luc*, transactivation bioassay with gas chromatography-mass selective detector (GC-MSD) analysis was performed to identify major AhR agonists in sediments collected from the Lake Shihwa. Results of EDA indicated that the greatest AhR-mediated potencies were found in fractions F2.6 to F2.8, which contained aromatic compounds with log K_{ow} values between 5 and 8, such as polycyclic aromatic hydrocarbons (PAHs) and styrene oligomers (SOs) (details in Results and discussion).

PAHs are widely distributed in sediments, with comparatively greater concentrations in industrial area than in rural areas and are well-known aryl hydrocarbon receptor (AhR) agonists (Hong et al., 2012a). SOs, including styrene dimers (SDs) and styrene trimers (STs) are known to originate from polystyrene plastic materials (Ohyama et al., 2001; Yanagiba et al., 2008; Kwon et al., 2014, 2015). Various SOs analogues are known to be derived from degradation of polystyrene, particularly during thermal decomposition at temperatures of 240–300 °C (Kitamura et al., 2003; Kwon et al., 2014). Polystyrene has been widely utilized for food containers (Ohyama et al., 2001), and SOs are known to migrate from polystyrene containers into foods (Hirano et al., 2001). Thus, studies on toxic effects of SOs have been concentrated in the fields of Food Chemistry and Health Sciences. However, there was little information on occurrences of SOs in coastal environments and their potential toxic effects on wildlife.

Synthetic polymers used in plastics have been thought to be chemically stable and resistant to biodegradable in aquatic environments (Carpenter and Smith, 1972; Lucas et al., 2008; Andrady, 2011; Kwon et al., 2015). Few studies have reported distributions of only a few SOs in selected areas (Kwon et al., 2015). In addition, there was no information on the physico-chemical properties of SOs. SOs have been reported to cause adverse or toxic effects on cells and organisms, such as endocrine-disrupting effects (Hirano et al., 2001; Date et al., 2002; Kitamura et al., 2003), genotoxicity (Nakai et al., 2014), proliferative activity (Ohyama et al., 2001), thyrogenic activity (Yanagiba et al., 2008), and inhibition of reproduction of daphnids (Tatarazako et al., 2002). STs have three aromatic rings, in structures similar to AhR-active compounds (Yanagiba et al., 2008), however, no experimental evidence has been documented for their AhR-binding potencies.

Specific objectives of the present study were to: i) screen and identify the major AhR-mediated potencies and agonists in sediments of inland creek flowing into Lake Shihwa by use of EDA; ii) investigate distributions and compositions of SOs in coastal sediments, iii) determine relative potency values (RePs) for AhR-mediated activities for 10 SOs, and iv) assess and compare relative contributions of SOs and PAHs to overall induced AhR-mediated potencies in sediments. To the best of our knowledge, this is the first report describing occurrences of SOs in sediments

Fig. 1. Map showing the sampling sites of surface sediments from inland creeks and inner and outer regions of the Lake Shihwa.