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Quantitative determination of ultra-trace carbazoles in sediments in the coastal environment

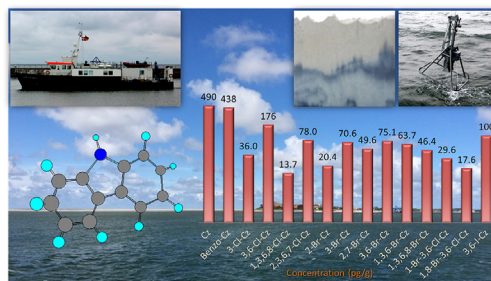
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HIGHLIGHTS

- Carbazole and its derivatives were analyzed using an ultra-trace targeted method.
- ASE with in-cell cleanup and GC–MS/MS provided sensitive quantification.
- Carbazoles are ubiquitous in coastal environment without contamination history.
- Brominated carbazoles are more abundant in marine than riverine sediment.
- Transformation into persistent carbazoles is likely to occur.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbazole and some of its derivatives may possess dioxin-like toxicity and could be persistent in the environment, but information on their distribution and environmental fate is limited. This study developed and validated an ultra-trace targeted-analysis method for the determination of carbazole, 1,2-benzocarbazole, and 13 halogenated carbazoles in sediments from the river, coast, and North Sea. An 8-g sediment sample was extracted using accelerated solvent extraction combined with in-cell cleanup and analyzed using gas chromatography-tandem mass spectrometry. The method was sensitive and reliable with method detection limits ranging from 4.54 to 52.9 pg/g, and most of the quantification biases and relative standard deviations were <20 and <15%, respectively. Carbazole and 1,2-benzocarbazole were the predominant substances in the sediments (median 565 and 369 pg/g, respectively) followed by 3,6-dichlorocarbazole (median 196 pg/g). The detection frequencies of carbazole, benzo-, 3-chloro-, and 3,6-dichlorocarbazole were >75%, while those of 3,6-dibromo-, 1-bromo-3,6-dichloro-, and 1,8-dibromo-3,6-dichlorocarbazole were approximately 50%. Brominated carbazoles occurred more frequently in marine than river-influenced sediments, which could indicate halogenation after discharge into the river. This is the first study regarding these substances in coastal environments without apparent contamination history. The ubiquity and bioaccumulative potential of these substances needs to be considered.

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1. Introduction

Carbazoles are heteroaromatic compounds and have been recently regarded as potentially persistent, bioaccumulative, and toxic substances (PBT), as defined by the European Commission (Fig. 1) (Mumbo et al., 2015). Carbazole possesses moderate aqueous solubility (1.2 mg/L), a $\log K_{ow} < 4$, and a field half-life shorter than one year (Blum et al., 2011; Harman et al., 2008; Hellou et al., 1999; Johansen et al., 1997), indicating its possibly low hydrophobicity and persistency. However, animal studies demonstrated that carbazole is difficult to be metabolized in fish and the comparison to dibenzofuran and fluorene has suggested that it is eliminated more slowly than those two compounds (Hellou et al., 1999; Willis and Oris, 2014). Zhao et al. (2015) have demonstrated that carbazole and its derivatives in coking wastewater were strongly positively correlated with the estrogenic potency. The half-maximal effective concentrations (EC_{50}) of carbazole tested using different bioassays in *Vibrio fischeri* and *Daphnia* were reported as 11.57 and 3.4 mg/L, respectively (Blum et al., 2011; Hartnik et al., 2007). Willis and Oris (2014) reported an LC_{50} of 150 $\mu\text{g/L}$, a bioconcentration factor of 3,218, and an additive lethal effect with co-existing aromatic compounds in zebrafish. However, there is very limited knowledge regarding the toxicity and environmental fate of halogenated carbazole compounds to date, in addition to the *in situ* bioconcentration and bioaccumulation. Halogenated carbazoles with molecular weights ranging from 200 to 500 Da, low aqueous solubilities, and $\log K_{ow}$ ranging from approximately 4 to 7 (Table 1) are difficult to degrade in the environment and may possess dioxin-like toxicity (Troebbs et al., 2011; Zhu and Hites, 2005). This was recently confirmed by Mumbo et al., who showed the strong ethoxyresorufin-O-deethylase reaction for cytochrome P4501A1 activity and suggested that these compounds be included in the list of potential persistent organic pollutants (POPs) (Mumbo et al., 2015).

Despite some minor natural formation in marine systems (Parette et al., 2015), the occurrence of carbazoles in water bodies have been attributed mainly to anthropogenic sources. This is

evidenced by the correlation between the environmental levels and human activities, such as an increase after thriving manufacturing and a decrease after improvement of wastewater treatment (Guo et al., 2014; Heim et al., 2004; Zhu and Hites, 2005). In addition, before large-scale industrial activities contributed to the presence of carbazoles, non- or very low-detectable concentrations were found in whale oil and sediment (Teuten and Reddy, 2007; Zhu and Hites, 2005).

Carbazole and 1,2-benzocarbazole are major carbon-catalysis products of biphenyls that co-exist with other aromatic compounds in fossil fuels, such as crude oil and coal tar from natural reactions in sediments (Asif et al., 2010; Bennett and Olsen, 2007; da Silva et al., 2014). Along with other heterocyclic compounds, these compounds have been found at and near fossil fuel contaminated sites at concentrations ranging from low ng/g to several $\mu\text{g/g}$ and spread widely with contaminated groundwater (Bennett et al., 2004; Blum et al., 2011; Heim et al., 2004; Johansen et al., 1997; Mundt and Hollender, 2005; Ololade, 2010; Schlanges et al., 2008; Seo et al., 2009). In addition to fossil fuel contamination, incineration-treated hazardous wastes containing diphenylamine and 2-nitrodiphenylamine could be another source (Altarawneh and Dlugogorski, 2015).

Industrial waste and effluent discharges are the major sources of halogenated carbazoles in the environment. Halogenation of carbazole into stable bromo- or chloro-derivatives was easily completed in the laboratory and is very likely to occur under industrial conditions, especially at the 1-, 3-, 6-, and 8- positions (Altarawneh and Dlugogorski, 2015; Gong et al., 2012). The incorporation of chlorine, bromine, and iodine into halogenated indigo dyes also leads to formation of impurities, including 3,6-dichloro-, 1,3,6,8-tetrachloro-, 1,3,6,8-tetrabromo-, and 1,8-dibromo-3,6-dichlorocarbazole, as well as iodocarbazoles (Parette et al., 2015). A positive correlation between the U.S. annual tetrabromoindigo production and the concentrations of 1,3,6,8-tetrabromocarbazole in dated sediments has been confirmed (Parette et al., 2014). Other sources of halogenated carbazoles include 3,6-dichlorocarbazole from the use of *p*-chloroaniline herbicides and

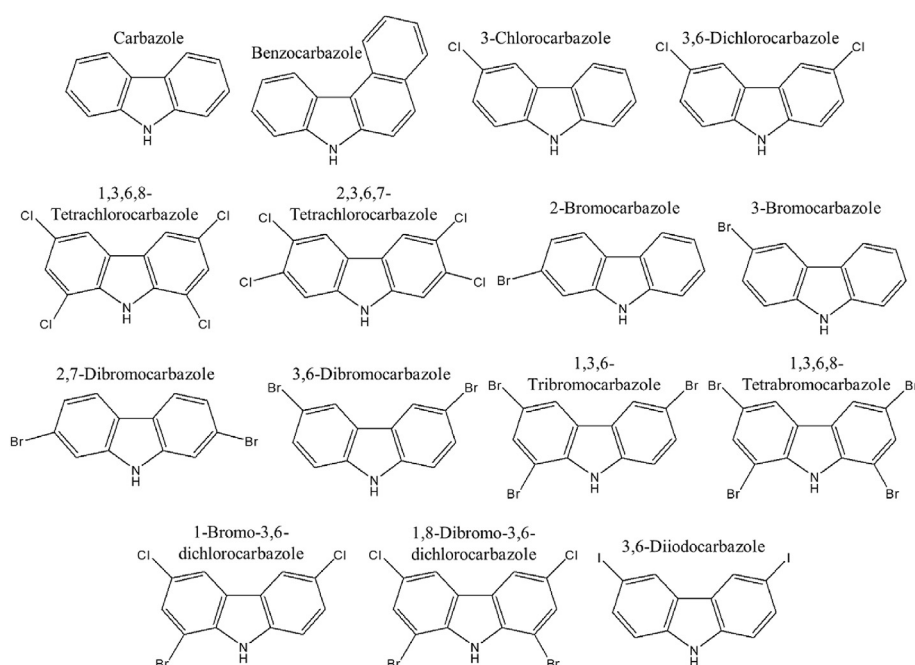


Fig. 1. The chemical structures of the carbazoles.

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