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Multi-residue determination of polyhalogenated carbazoles in aquatic sediments

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ABSTRACT

Recent studies have discovered a number of polyhalogenated carbazoles (PHCZs) in aquatic sediments and soil. These substances are attracting emerging concern due to their environmental presence, persistence, and potential dioxin-like activities. In response to the increasing interests in these chemicals, the present study aimed to develop an efficient and sensitive analytical methodology for quantitative determination of environmentally relevant PHCZs in aquatic sediments. The developed method employed time- and solvent-saving extraction and cleanup procedures and utilized gas chromatogram–mass spectrometry (GC–MS) for separation and determination of PHCZ analytes. PHCZs substituted with bromine atom(s) (except for 3-bromocarbazole) or a combination of bromine and chlorine atoms were analyzed by GC–MS in the electron-capture negative ionization (ECNI) mode, whereas congeners substituted with chlorine atoms as well as 3-bromocarbazole were analyzed in electron impact (EI) ionization mode. The developed method demonstrated negligible matrix effects, satisfactory and stable recoveries, and low method limits of quantification (0.11–0.53 ng/g dry weight (dw)) of target analytes. Using this method, we successfully determined a number of PHCZs in surface sediments from the Saginaw River system (Michigan, USA) and the Saginaw Bay of Lake Huron, with the summed concentrations of PHCZ congeners ranging up to 46.3 ng/g dw. Given that further investigations are needed to better elucidate the sources, environmental behavior, fate, and toxicity of PHCZs, highly sensitive and efficient analytical methodologies would be essentially needed to fill in these knowledge gaps.

1. Introduction

The greatest proportion of organic nitrogen in petroleum is found in the form of the nonbasic pyrrolic ring systems such as carbazole and its derivatives [1]. Carbazole and derivatives (e.g., alkylated and benzo[a]carbazole) are also abundant in source rocks and sediments, although the compositions vary with facies and maturation [2]. Recently, a number of polyhalogenated carbazoles (PHCZs) were discovered in environmental matrixes and subject to increasing reports in soil and aquatic sediments. For example, 3-chlorocarbazole (3-CCZ) and 3,6-dichlorocarbazole (36-CCZ) were found in soils from Germany and Greece [3,4]. 1,3,6,8-Tetrachlorocarbazole (1368-CCZ) and 1,3,6,8-tetrabromocarbazole (1368-BCZ) were found in sediments from the Buffalo River, New York (USA) and Lake Michigan (USA), respectively [5,6]. Carbazoles substituted with a combination of chlorine and bromine atoms (e.g., 1,8-dibromo-3,6-dichlorocarbazole or 18-B-36-CCZ) were also found in sediments from Southern Ontario, Canada, and the Laurentian Great Lakes of North America [7,8]. The latter study identified a number of PHCZs with various combinations of halogen (bromine, chlorine, and iodine) substitutions, including Br_2-, Br_3-, Br_4-, Br_3Cl-, Br_3ClI-, Br_4Cl-, Br_4I-, and Br_5-carbazole [8]. Recently, about 1600 bromine-containing compounds were identified in sediments from Lake Michigan [9], and PHCZs were found among those with the greatest peak intensities [10].

In addition to the discovery of PHCZs in environmental matrixes, studies also revealed toxicological potentials of carbazole and a few halogenated carbazoles. Treatment of adult male mice resulted in

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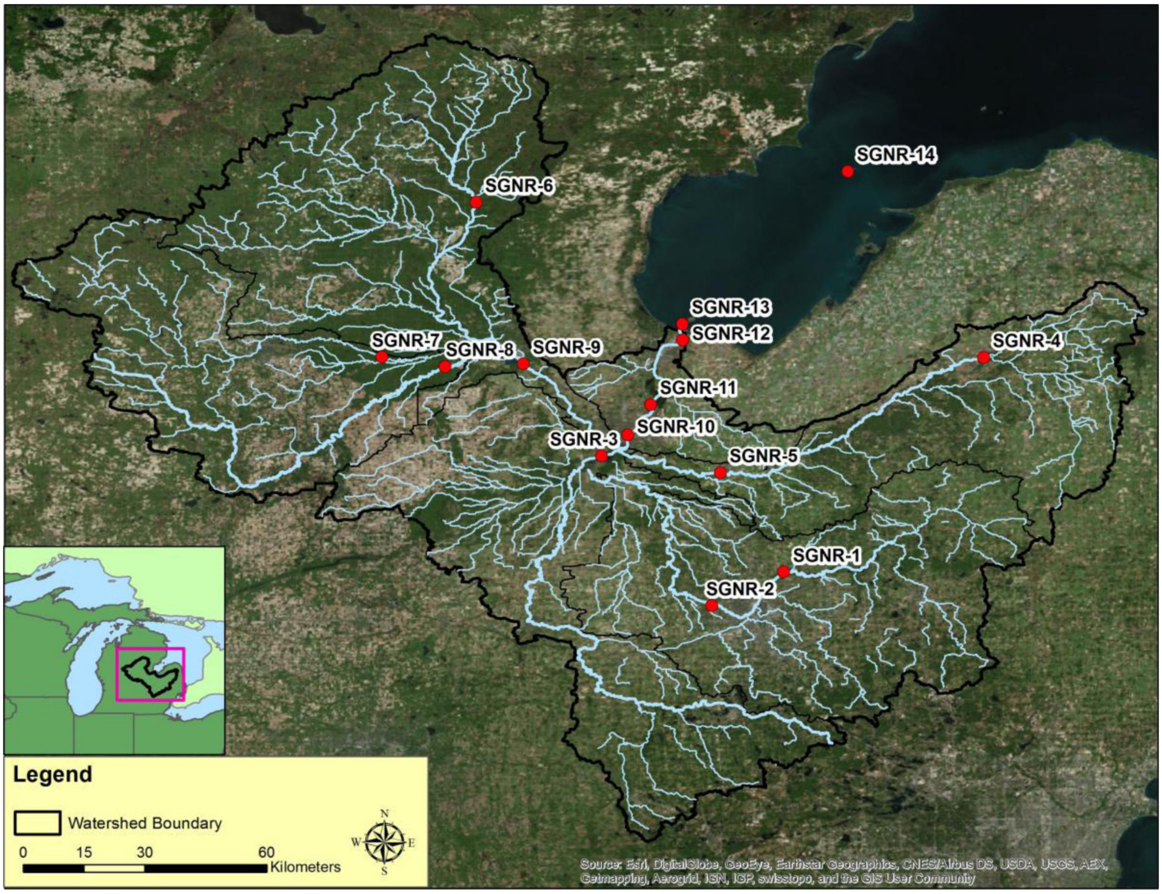

Fig. 1. Sampling sites of surface sediments in the Saginaw River system (Michigan, USA) and the Saginaw Bay of Lake Huron.

the induction of dominant lethal mutation and abnormal sperm heads [11]. Dioxin-like toxicity was reported for carbazole and a variety of PHCZs [3,12–14]. Riddle et al. investigated the induction of cytochrome P450 1A1 (CYP1A1) and CYP1B1 gene expression in aryl hydrocarbon (Ah)-responsive MDA-MB-468 breast cancer cells by PHCZs [14]. The results clearly suggest that PHCZs act through the Ah receptor [14]. For PHCZs with a 1,3,6,8 substitution pattern, their relative effect potencies (REPs) compared to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) ranged from 0.00031 to 0.00066 for CYP1A1 induction and from 0.0058 to 0.0097 for CYP1B1 induction [14]. These estimated REPs overlap with the toxic equivalency factor (TEF) for higher chlorinated dibenzofurans, dibenzo-*p*-dioxins, and some coplanar PCBs [14,15]. A TEF of 0.0016 was also reported for 18-B-36-CCZ [13], which ranges between that of 1,2,3,4,6,7,8- heptachlorodibenzodixoin (0.001) and 3,3′,4,4′,5-PentaCB (0.005) for fish [15].

Given the increasing reports of these chemicals in the environment and their potential persistent, bioaccumulative, and toxic characteristics, PHCZs have attracted mounting environmental concerns [16]. Although a couple most recent studies have determined PHCZs in sediments, both of them were subject to qualitative or semi-quantitative measurement due to lack of reference standards for most PHCZs [7,8]. To date there is a lack of analytical methodology studies addressing the quantitative determination of these compounds with detailed quality assurance and control procedures. Very recently, reference standards of a suite of environmentally relevant PHCZs were commercially available due to increasing interests in these emerging contaminants. Therefore, the main goal of this study was to develop a highly efficient and sensitive analytical method, as well as an efficient extraction and cleanup procedure, for a broad suite of PHCZs of known or expected environmental relevance. The developed method was then applied to investigate these emerging contaminants in sediments from the Saginaw River system (Michigan, USA) and the Saginaw Bay of Lake Huron.

2. Materials and methods

2.1. Chemicals and reagents

The reference standards of 3-CCZ, 36-CCZ, 1368-CCZ, 2,3,6,7-tetrachlorocarbazole (2367-CCZ), 1,3,6-tribromocarbazole (136-BCZ), 1-bromo-3,6-dichlorocarbazole (1-B-36-CCZ), and 18-B-36-CCZ were purchased from Wellington Laboratories (Guelph, ON, Canada). The standards of 3-bromocarbazole (3-BCZ), 2,7-dibromocarbazole (27-BCZ), and 3,6-dibromocarbazole (36-BCZ) were purchased from Sigma–Aldrich (St. Louis, Missouri). The reference standards of carbazole and 1368-BCZ were purchased from AccuStandard (New Haven, CT) and Florida Center for Heterocyclic Compounds of the University of Florida (Gainesville, FL), respectively. Surrogate standards 4′-fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE69), 4′-Fluoro-2,3,3′,4,5,6-hexabromodiphenyl ether (F-BDE160) and 2,2′,3,4,4′,5,6,6′-octachorobiphenyl (PCB-204), as well as internal standards 3′-Fluoro-2,2′,4,4′,5,6′-hexabromodiphenyl ether (F-BDE154) and decachlorodiphenyl ether (DCDE), were purchased from AccuStandard (New Haven, CT). Diatomaceous earth (DE) and sodium sulfate (10–60 mesh) were purchased from Fisher Scientific (Hanover Park, IL) and treated in a muffle furnace at 600 °C overnight (>12 h) prior to use. Copper (50 mesh, granular, reagent grade) and high-performance liquid chromatography