Introduction
A group of polyhalogenated carbazoles (PHCs) were discovered in the sediment of the Great Lakes (Guo et al., Environ. Sci. Technol., 2014, 48, 12807-12813), with a general molecular formula C_{n}H_{n}ClBrI. However, their sources remain unknown. The objectives of this study were to reveal their spatial and temporal trends in sediments of Lake Michigan (LM), Lake Superior (LS) and Lake Huron (LH).

Methods
Sampling. A total of 6 sediment cores plus 112 core tops (CT) were collected across the Great Lakes (LM, LS, LH). Samples were frozen and kept at −20°C until analysis. All samples were characterized for various physicochemical properties, and the geochemistry of sedimentation was determined for the 6 coring sites based on the activities of multiple radionuclides measured by gamma spectroscopy.

Extraction and Cleanup. The samples were freeze-dried, spiked with analytical standards (F-BDE99), and extracted by accelerated solvent extraction (ASE) with 1:1 hexane:acetone (v/v). Then, the extracts were thawed and cleaned column packed with silica gel and alumina. The elution solvents were hexane (F-1), 4:1 hexane:methyl chloride (F-2) and methyl chloride (F-3).

Identification. Accurate masses of unknown compounds were determined using gas chromatography (GC)-coupled with high-resolution mass spectrometry (HRMS). Mass spectra were also obtained from GC-electron ionization (EI) and GC-electron capture negative ionization (ECNI) low-resolution MS (LRMS). A total of 15 previously unknown compounds (UNCs) were identified as PHCs (Figure 2), in addition to 3,6-dibromocarbazole (3,6-DiBC) and 1,3,6,8-tetrabromo carbazole (1,3,6,8-TBrC).

Quantification. All 17 PHCs were analyzed using GC-ECNI-MS (Figure 3). The selected area monitoring (SAM) of bromine ions (m/z 79 and 81). Concentrations of 3,6-DiBC and 1,3,6,8-TBrC were determined by the internal standard method with injection standard decaclorobiphenyl (I). UNCs-1, UNCs-3, UNCs-5 and UNCs-6 were semi-quantified using the calibration curve of 3,6-DiBC because of the nearness in GC retention times. The calibration curve of 3,6,8-TBrC was used to semi-quantify other UNCs including all tribromocarbazoles, one of which (UNC-3) match with the impurity in the chemical standard of 1,3,6,8-TBrC. UNCs-3 was later confirmed as 1,3,6-tribromocarbazole.

Results and Discussion

Concentrations of PHCs ranged widely and were generally 1-3 orders of magnitude higher than PBDEs. UNCs-7 and 1,3,6,8-TBrC were comparable to RDE209 (Figure 3).

Lake Michigan had much higher concentrations than Lakes Superior and Huron (Figure 4). In Lake Michigan, most PHCs were detected more than 50% of the surface samples, and the highest concentrations were found in the center of southern and northern basins. PHCs are more abundant in the northwest of Lake Superior and northeast of Lake Huron.

Temporal trends differed among PHCs (Figure 5). 3,6-DiBC and UNCs-6 and 7 tend to have higher levels in recent deposit years. UNCs-12 and UNCs-14 have peaks either in 1900s or 1990s. Higher level PHCs were found in the deeper sediments from sites H048, M018 and M041.

Preliminary load estimates of total PHCs in Lake Michigan are in the order of 1100 tonnes with current annual load 0.7 tonnes/year. In comparison, the load of total PBDEs is estimated to be 41 tonnes with annual load 0.5 tonnes/year in Lake Michigan. Total PHC loads in Lake Superior and Huron were about 300 and 100 tonnes, respectively. The sources of PHCs remain unclear.

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