Occurrence of Halogenated Flame Retardants in Sediment off an Urbanized Coastal Zone: Association with Urbanization and Industrialization

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ABSTRACT: To examine the impacts of urbanization and industrialization on the coastal environment, sediment samples were collected from an urbanized coastal zone (i.e., Daya Bay and Hong Kong waters of South China) and analyzed for 20 polybrominated diphenyl ethers (PBDEs) and 10 alternative halogenated flame retardants (AHFRs). The sum concentration of PBDEs was in the range of 1.7–55 (mean: 17) ng g⁻¹, suggesting a moderate pollution level compared to the global range. The higher fractions of AHFRs (i.e., TBB+TBPH, BTBPE and DBDPE) than those of legacy PBDEs (i.e., penta-BDE, octa-BDE and deca-BDE) corresponded with the phasing out of PBDEs and increasing demand for AHFRs. Heavy contamination occurred at the estuary of Dan’ao River flowing through the Daya Bay Economic Zone, home to a variety of petrochemicals and electronics manufacturing facilities. The concentrations of HFRs in surface sediments of Hong Kong were the highest in Victoria Harbor, which receives around 1.4 million tons of primarily treated sewage daily, and a good relationship ($r^2 = 0.80; p < 0.0001$) between the HFR concentration and population density in each council district was observed, highlighting the effect of urbanization. Moreover, the AHFR concentrations were significantly correlated ($r^2 > 0.73; p < 0.05$) with the production volume of electronic devices, production value of electronic industries and population size, demonstrating the importance of industrializing and urbanizing processes in dictating the historical input patterns of AHFRs.

INTRODUCTION

Polyhalogenated diphenyl ethers (PBDEs), acting as flame retardants, have been routinely added to daily household items. Due to their ubiquity, persistence, and toxicity, PBDEs have been gradually banned in many countries.1 In response to the increasing regulation and phase-out of the PBDEs products, alternative halogenated flame retardants (AHFRs) have been introduced to replace the PBDEs products. By 2004, there were more than 75 different AHFRs available commercially, typified by tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) with the highest production volumes.2 The commercial product Firemaster 550 which is a mixture of 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-tetrabromophthalate (TBPH) in a ratio of 4:1, 1,2-bis(tetromophenoxy)-ethane (BTBPE) and 1,2-bis(2,3,4,5,6-pentabromophenyl)ethane (DBDPE) have been produced as the replacements of PBDE technical mixtures penta-BDE, octa-BDE, and deca-BDE, respectively. The global market demand for these emerging chemicals has rapidly increased in recent years,2,3 resulting in the widespread occurrence of AHFR residues in sediment,4 air,5,6 sludge,7 and organisms.8,9

The economic development patterns in China have continuously evolved in recent decades.10 Since the establishment of Special Economic Zones in 1978, China’s coastal zones have become the primary sites for industrial production, due to their convenience for shipping traffics and favorable pollutant-dissipating conditions. One prime example is the Daya Bay
Economic Zone of Huizhou (Figure 1), which was established in 1993 and has gradually developed into an integrated industrial park housing manufacture (dominated by petrochemical and electronic industries), tourism, mariculture, and shipping/offload activity. However, Hong Kong is a highly urbanized region, with a population of 7.1 million residing on an area of 1104 km². The population has increased by one million per decade since the 1960s. The dominant industry has also shifted from manufacture to services since the 1980s, with many factories and plants having been relocated to places with lower rental rates and cheaper labor cost, especially the adjacent Pearl River Delta region. The different economic and industrial development patterns in Huizhou and Hong Kong have presented a unique opportunity for cross-examining the impacts of industrialization and urbanization on the environmental quality of coastal zones. It was hypothesized that the usage patterns of legacy HFRs represented by PBDEs and AHFRs as described above would provide a set of useful tools for such an examination.

In the present study, sediment samples were collected from an urbanized coastal zone, Daya Bay and Hong Kong of China (Figure 1) and analyzed for PBDEs and AHFRs. The levels of sediment HFRs were compared with those in other parts of the world to establish the magnitude of sediment contamination by HFRs in the study regions. The compositional profiles of PBDEs and AHFRs were examined in association with the usage patterns of HFRs. Finally, sediment HFR concentrations were correlated with population data (size and density), production volume of electronic devices, and production value of electronics industries. These assessment results should be valuable for developing effective control measures to minimize potential adverse impact of anthropogenic activities on the coastal ecosystem and human health.

### MATERIALS AND METHODS

**Materials.** Target analytes include PBDEs (i.e., BDE-15, -17, -47, -71, -85, -99, -100, -126, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207, -208, and -209) and AHFRs, i.e., TBB, TBPH, BTBPE, DBDPE, TBBPA, HBCD, bis-(hexachlorocyclopentadienyl)cyclooctane (DP), tris(2,3-dibromopropyl) phosphate (TDBPP), pentabromochlorocyclohexane (PBCCH), and hexachlorocyclopentadienyltribromocyclooctane (HCBCO). All the analytes were purchased from AccuStandard (New Haven, CT), and the related information about AHFRs is presented in the Supporting Information (SI) Table S1. BDE-51, BDE-115, 13C-BDE-138, 13C-BDE-209, and (α, β, γ)-HBCD-d18 were used as surrogate standards, and BDE-69, 13C-BDE-139, 13C-PCB-208, 13C-TBBPA, and 13C-(α, β, γ)-HBCD were used as internal standards. Among them, 13C-TBBPA was purchased from Cambridge Isotope Laboratories (Andover, MA), (α, β, γ)-HBCD-d18 from Wellington Laboratories (Guelph, Ontario, Canada) and other standards from AccuStandard (New Haven, CT). Hexane of HPLC grade was acquired from SK Chemical (Ulsan, Korea), whereas dichloromethane (DCM) and acetone were obtained locally and further purified by double distillation before use. Laboratory glassware was cleaned with chromic acid mixture and oven-dried at 450 °C for 4 h prior to use.
Sample Collection. Daya Bay (Figure 1) is a semiclosed shallow bay, receiving water from only several small brooks. The largest among these brooks is Dan’ao River, which flows through the center of Huizhou and the Daya Bay Economic Zone. Hong Kong is situated to the west of Daya Bay and is highly urbanized but unevenly populated spatially, with much higher population densities along the shores of the Victoria Harbour on Hong Kong Island and Kowloon, as compared with the less densely populated New Territories and outlaying islands. The sampling sites in Hong Kong corresponded to the Environmental Protection Department (EPD)’s regular sediment monitoring stations, with the site names being recorded for simplicity. A total of 18 and 35 surface sediments were collected in May 21–23 and June 5–8, 2012 in Daya Bay and Hong Kong waters, respectively (Figure 1), with detailed longitude and latitude data listed in SI Table S3, using a stainless steel Van Veen grab sampler. The top 5 cm of the sediment was taken with a stainless steel scoop, packed with aluminum foil and stored in Ziplock bag. In addition, two sediment cores (64 and 84 cm) were collected in Daya Bay using a gravity corer with an inner diameter of 5 cm and length of 100 cm, and the sediment cores were placed on a self-designed extrusion machine and sliced at 2 cm intervals onboard with a stainless steel saw, which was cleaned after each cut. All samples (53 surface sediments and 74 sediment core slices) were preserved immediately with ice, transported to the laboratory, and frozen at −20 °C until analysis.

Sample Extraction. Before extraction, each sample was freeze-dried, ground, and sieved with a 80-mesh screen to remove large particles and shells. Approximately 15 g of sample was wrapped with clean filter paper, and Soxhlet-extracted for 48 h with 200 mL of a mixture of hexane/DCM/acetone (1:1:1 in volume). Before extraction, the surrogate standards and copper sheets (for removal of element sulfur) were added into the solvent. The column was eluted with 20 mL of hexane and then another 50 mL of the mixture of DCM and hexane (4:6 in volume). The eluent was further concentrated to approximately 1 mL with a Zymark TurboVap II (Hopkinton, MA). The extracts were further purified through a 10 mm i.d. glass column packed with 2 cm anhydrous sodium sulfate, 6 cm 44% sulfuric acid silica gel, 2 cm neutral silica gel, 5 cm 33% alkaline silica gel, 2 cm neutral silica gel and 6 cm neutral alumina from top to bottom. The column was eluted with 20 mL of hexane and then another 50 mL of the mixture of DCM and hexane (4:6 in volume). The eluent was further concentrated to approximately 1 mL with a Zymark TurboVap II (Hopkinton, MA), and further to 100 μL under a gentle stream of N2. The internal standards were spiked prior to instrumental analysis. An aliquot of each sample was acidified with 1 M hydrochloric acid (to remove inorganic carbon), washed with purified water (to remove chlorine ion), dried to constant weight, and homogenized before the determination of total organic carbon (TOC) by an Elementar Vario EL III (Shimadzu, Japan). Acetanilide standards were analyzed with each set of 20 field samples to ensure the relative deviation less than 5%.

Instrumental Analysis. Quantification of all target analytes except for TBBPA and HBCD was performed with an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometer (Palo Alto, CA) in the electron capture negative ionization mode. A 15 m × 0.25 mm × 0.1 μm DB-5 HT capillary column (J&W Scientific, Folsom, CA) was used for chromatographic separation. Column temperature was programmed from 110 °C (held for 5 min) to 200 °C at 4 °C min⁻¹ (held for 4 min), raised to 260 °C at a rate of 10 °C min⁻¹ (held for 1 min), and then increased to 300 °C at a rate of 15 °C min⁻¹ (held for 20 min). The mass spectrometer was operated in the selective ion monitoring mode with the temperatures of transfer line, ion source, and quadrupole held at 290 °C, 200 and 150 °C, respectively. Helium was used as the carrier gas at a rate of 1.5 mL min⁻¹, and the injection volume was 1 μL. The ion fragments m/z 79 and 81 were monitored for PBDEs, m/z 488.6 and 486.6 for BDE-209, and those for other HFRs are listed in SI Table S1. PBCCH and BDE-15 to BDE-71 were quantified with BDE-69 as the internal standard; HCBDCO, TBB, TDBPP and BDE-99 to BDE-154 with 13C-PCB-208; and BTBPE, DP, TBPB, DBDPE, and BDE-183 to BDE-209 with 13C-BDE-139. The chromatograms of a standard mixture of halogenated flame retardants, a sediment sample and a solvent blank, as well as the retention times of all analytes, are presented in SI Figure S1.

Concentrations of TBBPA and HBCD were determined with an Agilent liquid chromatograph 1200 system equipped with an Agilent 6410 triple quadrupole mass spectrometer with electrospray ionization in the negative mode. Prior to analyses, the solvent was exchanged to methanol, and the internal standards 13C-TBBPA and 13C-(α, β, γ)-HBCD were spiked. A Zorbax Eclipse plus C18 column (100 × 2.1 mm; particle size 1.8 μm) fitted with an Eclipse Plus C18 Guard column (12.5 × 2.1 mm with a film thickness of 5 μm) was used for chromatographic separation. The mobile phase was a mixture of purified water and methanol (5:95 in volume) at a flow rate of 0.15 mL min⁻¹. The injection volume was 10 μL. The ion fragments were monitored at the ([M−H]⁻) transition of m/z 640.7 → 79, 652.7 → 79 and 658.7 → 79 for HBCD, 13C-HBCD, and HBCD-d16, respectively; and m/z 542.7 → 79 and 554.7 → 79 for TBBPA and 13C-TBBPA, respectively. The concentrations of TBBPA and HBCD were determined by an internal calibration method with 13C-TBBPA and 13C-(α, β, γ)-HBCD as the internal standards.

Quality Assurance and Quality Control. A procedural blank, a solvent spiking blank, a matrix spiking blank and sample duplicate were processed for each batch of 15 field samples. In procedural blank samples, the most detectable components were BDE-183, −207 and −209, and their concentrations were 0.00033–0.0012 (mean: 0.00076), 0.0025–0.029 (mean: 0.013), and 0.018–0.12 (mean: 0.069) ng g⁻¹, respectively. These concentrations were subtracted from the measured analyte concentrations in the field samples of the same batch. Other components were undetectable or the concentrations were too low to be noticed. Recovery data are presented in SI Table S2. The average recoveries of the target analytes in spiked blank samples were 51−96% with an average relative standard deviation of 12%. All relative standard deviations between duplicate samples were less than 20% for all target analytes. The average recoveries of the surrogate standards, BDE-51, BDE-115, 13C-BDE-138, 13C-BDE-209, and HBCD-d16 in field samples were 90 ± 15%, 86 ± 14%, 82 ± 9%, 89 ± 17%, and 81 ± 14%, respectively. In the present study, the reported concentrations were corrected for these surrogate standard recoveries.

Sedimentation Rate (k). The two sediment cores (D13 and D16) were dated with the profiles of excess 210Pb activity (SI Figure S2), which were determined from the measured alpha activity of 210Po with an α spectrometer (Ortec Plus, UISA). Excess 210Pb activity was obtained by subtracting the background 210Pb activity supported by 226Ra from the total 210Pb activity. 210Pb has a decay constant of 0.03114 yr⁻¹.
Therefore, the averaged sedimentation rates in these two cores, calculated with a constant initial \(^{210}\)Pb concentration model,\(^{13}\) were 0.52 and 0.48 cm yr\(^{-1}\), respectively. The 64 cm core at D13 and the 84 cm core at D16 represented approximately 119 and 170 years of sedimentation records, respectively. It should be noted that the linear sediment rates used in the present study were calculated on the assumption of constant sediment density. In fact, mass based sediment rate (g cm\(^{-2}\) yr\(^{-1}\)) would be a better alternative.

## RESULTS AND DISCUSSION

### Comparison of Worldwide Halogenated Flame Retardant Levels

Detailed dry weight based concentration data for the surface sediments from the present study are presented in SI Table S3, while a summary of the results from the previous and present studies is in SI Table S4, where \(\Sigma\text{BDE}\) refers to the sum of BDE-15, -17, -47, -71, -85, -99, -100, -126, -153, -154, -181, -183, -190, -196, -203, -204, -206, -207, and -208. The concentrations of \(\Sigma\text{BDE}\) in surface sediment of Daya Bay and Hong Kong were in the ranges of 0.09−2.6 (mean: 0.77) and 0.06−1.88 (mean: 0.53) ng g\(^{-1}\), respectively. These values were close to previously reported concentrations in other coastal sediments off China (0−5.5 ng g\(^{-1}\))\(^{14}\) and the Great Lakes of North America (0.04−6.3 ng g\(^{-1}\))\(^{15}\), but lower than those within the Pearl River Delta (PRD) region (0.04−95 ng g\(^{-1}\))\(^{16}\). The concentrations of BDE-209 were 1.9−50 (mean: 18) ng g\(^{-1}\) in Daya Bay and 1.5−53 (mean: 16) ng g\(^{-1}\) in Hong Kong, generally lower than those found in other regions, e.g., 21−242 ng g\(^{-1}\) in the Great Lakes\(^{15}\) and 240−1650 ng g\(^{-1}\) in Scheldt Estuary of The Netherlands\(^{9}\), and much lower than those (0−7300 ng g\(^{-1}\)) within the PRD region.\(^{17}\) Overall, the levels of sediment contamination by PBDEs in the two sampling regions of the present study were moderate as compared to the global range.

Ten AHFRs were detected in the surface sediments, with mean concentrations decreasing in the order of DBDPE > HBCD > TBPPA > BTPBPE \(\approx\) DP > PBCCH > TBB \(\approx\) TBPB > HCDBCO > TDBPP (SI Figure S3). Obviously, DBDPE was the most abundant, highlighting its predominance in Chinese marketplace as the second most-used additive HFR.\(^{18}\) In fact, this chemical has been frequently detected in sediments around the world (SI Table S4).\(^{19−22}\) Another ubiquitous HFR is HBCD, and its concentrations in the present study ranged from 1.6 to 30 ng g\(^{-1}\). Although TBPPB is the most produced chemical among all HFRs in Asia,\(^{2}\) its concentration (0.23−9.0 ng g\(^{-1}\)) ranked third and was similar to those found in Western Scheldt and Dutch rivers,\(^{23}\) but substantially lower than those in Dongjiang River\(^{20}\) and English Lakes (SI Table S4).\(^{24}\) In addition, the concentrations of BTBPE (0.10−6.2 ng g\(^{-1}\)) were low, comparable to those previously reported for the PRD region, Western Scheldt, and the Great Lakes,\(^{4,19,22}\) although it was supposedly a substitute for octa-BDE. To date, sediment data of DP outside China have been reported only for the Great Lakes (5−586 ng g\(^{-1}\))\(^{6,25}\), which were much greater than the values (0.15−4.2 ng g\(^{-1}\)) in the present study. Conversely, our data were similar to those from Songhua River, Yellow Sea and Jing-Hang Grand Canal of China,\(^{26−28}\) suggesting that sediment DP contamination has remained light in China.

Other little-known AHFRs, i.e., PBCCH, HCDBCO, and TDBPP, were all detected in surface sediments with the concentrations of 0−2.4, 0−0.49, and 0−0.20 ng g\(^{-1}\), respectively, which were generally lower than those found in previous studies (SI Table S4). In the present study, only PBCCH-D was reported although commercial PBCCH mixture contains four isomers (PBCCH-A, B, C, and D), due to matrix interferences with instrumental analysis. In addition, we detected TBB and TBPB in the concentration ranges of 0.044−0.80 and 0.047−0.74 ng g\(^{-1}\), which is the first report on the occurrence of TBB and TBPB in sediment. Because there is limited data on the occurrence of AHFRs in the world’s sediments, presently it is impossible to place a global perspective on the sediment data acquired in the present study.

### Spatial Distribution of Halogenated Flame Retardant Related to Urbanization and Industrialization.

In Daya Bay (Figure 1 and SI Figures S4 and S5), HFR concentrations were higher in the western region (D1−D7, D12 and D13) than in the eastern region (D14−D16). The highest concentration was observed at Site D1, which is located at the mouth of Dan’ao River, the largest estuary within Daya Bay. This river flows through a heavily urbanized and industrialized city, Huizhou, and the Daya Bay Economic Zone, thus receiving great amounts of industrial wastewater from the thriving electronics/electrical manufacturing activities. In addition, domestic sewage discharge and surface runoff are also eminent sources of HFRs\(^{29−31}\) which may also explain the relatively higher concentrations at sites D2, D3, and D4 near D1 (Figure 1). Sites D5 and D6 near Aotou Port, a large town alongside Daya Bay (Figure 1), also contained high levels of sediment HFRs, probably associated with local surface runoff and municipal waste discharge; an important oil terminal at Site D6 also have frequent shipping activities, including vessel refueling, ship repair and freight/offload activities, which are the potential sources of HFRs. Site D7 located at Yaling Bay, a densely populated area with intensive agricultural and aquaculture activities, receives surface runoff inputs and fish feed residue. However, the north and east regions are sparsely populated and away from point sources; hence the low levels of HFRs may have been largely contributed from atmospheric deposition, and transported with water current or postdepositional particle movement from heavily contaminated areas.

Sediment HFRs in Hong Kong waters (Figure 1 and SI Figures S4 and S6) were the highest in Victoria Harbour (H13−H17 and H23; Figure 1), which receives approximately 1.4 million tons of sewage daily, 75% of the sewage are currently treated by the chemically enhanced primary treatment and the rests received preliminary treatment only.\(^{32}\) The harbor is impacted by other forms of human activities, e.g., there were 190 859 vessel arrivals with 26 million passengers for the marine ferry terminals in 2012. It is also home to the third largest container port in the world, with a total throughput of 23.1 million 20-ft units in 2012.\(^{33}\) Concentrations of HFRs in the western waters, especially Deep Bay (H1−H4; Figure 1), were lower than those in Victoria Harbour, but were in general higher than those in other areas. Deep Bay is shallow (2.9 m water depth on average), poorly flushed with tides, and polluted by the discharge of poultry and animal wastes from the Shenzhen River at the border of Hong Kong and Shenzhen, and from San Pui River in the New Territories of Hong Kong.\(^{12,34}\) In contrast, HFR concentrations in Tolo Harbour (H28−H31; Figure 1), another land-locked harbor with a bottleneck shape and slow water exchange (16−42 d per cycle\(^{11}\)), were much lower. Although Tolo Harbour was grossly polluted from the 1970s to early 1990s by large amounts of sewage effluent discharged as a result of rapid population growth during the development of a new town in Shatin,\(^{35}\) the diversion of sewage effluent through underground tunnels to
Victoria Harbour since 1997 has resulted in a great improvement in water quality. The eastern and southern sites contained relatively lower concentrations of HFRs, apparently because their adjacent areas are less populated and lower urbanized and there are relatively limited marine traffics in these areas.

Contrast to the previous perception that contaminants discharged from mainland China greatly impacted the waters of Hong Kong, there was no significant difference ($p = 0.23$) in the HFR concentration ranges between Hong Kong and Daya Bay, highlighted by low HFR levels in eastern Hong Kong adjacent to Daya Bay. In fact, the distribution patterns of HFRs in Hong Kong are self-consistent, with an excellent correlation (SI Table S5 and Figure 2) between the population densities and HFR concentrations for the relevant coastal council districts. In addition, the correlation between TOC contents (SI Table S3) and HFR concentrations for all samples was poor ($r^2 < 0.1$), suggesting a minor role of TOC-rich suspended particulates in shaping the current distribution patterns of sediment HFRs in the study regions. In other words, this may also indicate the dominance of local sources contributing to the occurrence of HFRs in sediments.

Usage Patterns of HFRs as Reflected in Compositions of PBDEs and AHFRs in Surface Sediments. The compositional patterns of PBDEs (SI Figure S7) were similar to those obtained in previous studies, i.e., BDE-209 being the most predominant constituent, accounting for more than 90% of the total abundance. In addition, BDE-206, -207, and -208, probable degradation products of BDE-209, were also abundant. BDE-47 and BDE-99 constituted a large proportion of low halogenated BDEs, and a strong correlation ($r^2 = 0.90; p < 0.0001$) (SI Figure S8a) was found between the two congeners because of their similar source from penta-BDE technical mixture. BDE-183 also accounted for a considerable portion of the low halogenated BDEs, maybe because it is the major constituent in octa-BDE commercial products. A significant correlation ($r^2 = 0.65; p < 0.0001$) was found between the concentrations of 2BDE and BDE-209 (SI Figure S8b), suggesting that low halogenated flame retardants were largely released from e-waste trade or the degradation of high halogenated flame retardants, considering that only BDE-209 has been used in China.

Among all HFRs, BDE-209, DBDPE and HBCD were the most detectable components, and they collectively accounted for 86% and 84% of the total abundances in Daya Bay and Hong Kong, respectively (Figure 3). It is interesting to note that DBDPE was the most abundant component in sediment of Hong Kong, while BDE-209 was the predominant component in Daya Bay (Figure 3). This compositional difference in HFRs may be a testament of shorter life cycles of electronic products in Hong Kong than in mainland China, as newer products should contain more AHFRs than PBDEs. The relative abundances of TBBPA were only 4.2% and 5.7% in Daya Bay and Hong Kong, respectively, which may be attributed to degradation, methylation and/or sequestration. Moreover, TBBPA is often used as reactive flame retardant and prone to debromination in anaerobic environments. The relative abundances of TBB and TBPH were also quite small (<1%), probably because the commercial product Firemaster 550 containing these chemicals was only introduced in 2003. A positive correlation ($r^2 = 0.53; p < 0.0001$) (SI Figure S9)
between the two substances was somewhat indicative of a common source for them, although their concentration ratios (0.35–3.2) were smaller than that (4) in Firemaster 550.8 Finally, the relative abundances of TDBPP were the smallest at 0.11% and 0.13% in Daya Bay and Hong Kong, respectively, reflecting its limited usage due to carcinogenicity and mutagenicity concerns.49 It should be noted that the difference in the physicochemical properties of HFRs is also an important reason for the different compositions, because there are numerous property-dependent partitioning and transformation processes from the sources (consumer products containing HFRs) to the sediments (in this case).

The concentrations of three types of AHFRs (i.e., TBB +TBPH, BTBPE and DBDPE) and legacy HFRs (i.e., penta-BDE, octa-BDE and deca-BDE) were significantly correlated with each other (p < 0.05; SI Figure S10), with the correlation between DBDPE and BDE-209 being the strongest. Similar results were also obtained with indoor dust samples.50 These findings suggested that legacy and AHFRs may be concurrently used in electronic products. In addition, the fractions of [TBB +TBPH] in [TBB+TBPH+penta-BDE], BTBPE in [BTBPE +octa-BDE] and DBDPE in [DBDPE+deca-BDE] generally represent the relative consumptions of legacy and alternative HFRs.21 In the present study, the average fractions of [TBB +TBPH] and BTBPE for all sampling sites in both regions were 0.66 ± 0.16 and 0.88 ± 0.11, respectively, significantly greater than 0.5 (p < 0.0001), indicative of increased use of AHFRs following the restrictions on use of PBDEs. Particularly, octa-BDE seemed to have been replaced by BTBPE at the fastest pace. Moreover, there was no significant difference in the fractions of [TBB+TBPH] and BTBPE between the two regions (p = 0.67 and 0.31, respectively). However, the average fraction of DBDPE for Hong Kong sites was 0.60 ± 0.16, significantly greater than 0.5 (p < 0.0001); while that for Daya Bay sites was 0.38 ± 0.14, significantly less than 0.5 (p = 0.036), further corroborating the above-mentioned notion that the life cycles of electronic products have been generally shorter in Hong Kong than in mainland China.43

Sediment Records of Halogenated Flame Retardants Related to Industrializing Process. To reconstruct the sedimentation histories of HFRs, two sediment cores were collected from two locations with relatively stable depositional conditions. Site D13 was at the downstream of Dan’ao Estuary and Aotou Port, and Site D16 on the eastern side of Daya Bay (Figure 1). The counterclockwise gyre flow within the bay can have significant dilution effects at D16. Thus, Core D13 was expected to contain higher concentrations of HFRs than Core D16. As shown in Figure 4, the concentrations of ΣBDE in both cores increased rapidly before −20 cm and leveled off afterward, a combined result of the phase-out of penta- and octa-BDE technical mixtures in 2004,51 the continuous emissions of BDE residues from e-waste recycling activities, and the uses of PBDE-containing consumer products. Because penta-BDE and octa-BDE had been produced and used since the 1970s,5,52 the occurrence of detectable BDE in deep sediment core (before 1970) can be attributed to the combined effect of bioturbation and downward leaching. Conversely, deca-BDE (mainly containing BDE-209) has been greatly used as a substitute; therefore, its concentrations increased dramatically from −30 to −15 cm for core D13 and from −45 to −25 cm for core D16, and then fluctuated with a zigzag pattern until the present time (Figure 4). Afterward, use of AHFRs was initiated, resulting in a rapid rise of HFR concentrations after −10 and −20 cm for core D13 and D16, respectively. Notably, the detectable “background” levels of AHFRs in early years may have stemmed from bioturbation and downward leaching, or other unknown causes.

In addition, the fractions of [TBB+TBPH] and BTBPE with their BDE counterparts dramatically increased toward the surface sediment layer (SI Figure S11), consistent with increasing usage of these AHFRs following the phase-out of penta-BDE and octa-BDE technical products. However, the fraction of DBDPE decreased initially and then increased, reflecting large amounts of BDE-209 used initially and subsequently increasing usage of DBDPE along with the gradual restriction of deca-BDE technical product. The increasing trends in the fractions of AHFRs in the present

![Figure 4. Vertical concentration profiles of ΣBDE, BDE-209, and alternative HFRs (AHFRs) in sediment cores collected from (a) D13 and (b) D16 of Daya Bay. ΣBDE is the same as that in Figure 3, and ΣAHFR is the sum of AHFRs.](image-url)
study were consistent with the accumulation profiles in marine mammals between 2003 and 2012, both providing evidence for the temporal shift from PBDEs to their corresponding alternative products.53

The rapid increase of AHFR concentrations from 1990 to present days was in agreement with the fast development of electronic industry in Daya Bay Economic Zone (Figure 5). The concentrations of AHFR were well correlated with the production volume of electronic devices from 1996 to 2012 (Figure 5a) and with the production value of electronic industries from 2002 to 2012 (Figure 5b), with \( r^2 > 0.73 \) within the 95% confident interval. These significant correlations were consistent with industrialization trends, confirming the key role of industrializing process in the historical HFR input patterns, as well as the important contributions of electronic manufacture to HFR emissions. In addition, the AHFR concentrations were also significantly correlated with the population size for a long period of time (1990–2012) (Figure 5c), further corroborating a close link between local anthropogenic activities and pollution intensities. Therefore, the rapid industrializing process and increasing urbanization, in conjunction with the gradual replacement of legacy PBDEs with AHFRs, will continue to drive up the environmental levels of AHFRs in the future.

Doubling time (\( t_2 \)) for individual HFR and socioeconomic index (SI Table S6) was calculated with the data points of the vertical profiles (Figure 5 and SI Figure S12). Results indicated that the \( t_2 \) values (18–107 yrs) for AHFRs in sediment were all substantially greater than those for the production volume (5.2 yrs) of electronic devices and for the production value (4.2 yrs) of electronic industries. The substantial longer \( t_2 \) values for HFRs may be ascribed to the moderate pollution by HFRs in the study region and the losses of AHFRs from various environmental processes (e.g., phase partitioning, transfer, and degradation) upon discharge into the environment. Herein, isomeric changes of DP (syn- and anti-isomers) (SI Figure S13) and HBCD (\( \alpha \), \( \beta \), and \( \gamma \)-isomers) with time (SI Figure S14) can provide examples of how fate processes may modify the contaminant trends and impact the observed doubling times. In surface sediment, the fraction of syn-DP (\( f_{syn-DP} \)) was in the range of 21–46% (mean: 30%), close to that (25–35%) in commercial mixtures.26,52,54,55 However, \( f_{syn-DP} \) decreased with increasing depth in both sediment cores, suggesting the likelihood of stereoselectivity in the persistency or bioavailability of two isomers.52,55 In addition, the fraction of \( \gamma \)-HBCD (\( f_{\gamma-HBCD} \)) in surface sediment was in the range of 52–94% (mean: 79%), similar to that (80%) in technical mixtures.56 In both sediment cores, \( f_{\gamma-HBCD} \) slightly decreased with increasing sediment depth, indicating the biodegradation of \( \gamma \)-HBCD to other isomers or biodegradation.57,58 Overall, \( f_{syn-DP} \) and \( f_{\gamma-HBCD} \) provide evidence for the degradation and/or conversion of HFRs in sediment, but more work is needed to clarify the specific migration and transformation processes of AHFRs over time.
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 41121063 and 21277144), the Natural Science Foundation of Guangdong Province (No. S201202010176), and the Collaborative Research Fund (No. HKU/CRF/12G) from the Research Grants Council of the Hong Kong SAR Government. The authors are grateful to Cheng-Zhou Wu, Yao Yao, Wen Huang, You-Da Huang, Xue-Ping Liu, and Xiao-Yi Yi for sample collection, and Chun-Li Huang and Ping Ma for laboratory support. The authors are also indebted to Wei-Fang Chen of Xiamen University for dating the sedimentation cores. This is a contribution No. IS-1928 from GIGCAS.

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