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Elevated levels of perfluoroalkyl substances in estuarine sediments of Charleston, SC

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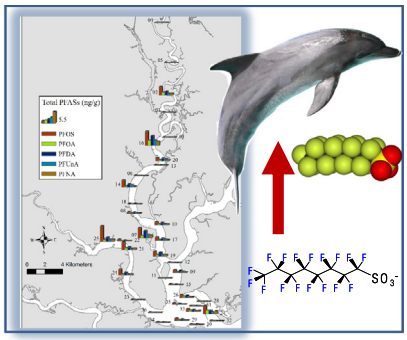
HIGHLIGHTS

- PFAS sediment levels in Charleston SC are higher than any other urban U.S. area
- Among 36 sites, 52% exceeded median global PFOS sediment concentration
- Multiple PFAS "hot spots" found spatially with likely point/non-point sources
- Occurrence and distribution of detected PFAS indicate continuing inputs
- High PFAS in dolphins served as good sentinel to further examine environmental inputs

GRAPHICAL ABSTRACT



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ABSTRACT

Urban areas are sources of perfluoroalkyl substances (PFASs) in the environment, although little is known about specific point sources and distribution of PFASs. Sentinel species, like bottlenose dolphins, are important indicators of environmental perturbations. The high PFAS levels found in dolphins inhabiting Charleston, South Carolina prompted investigation of these chemicals in this area. This study provides further evidence on the extent of contamination and potential sources of PFASs. In this study, concentrations of 11 PFASs measured in estuarine sediments collected in 2012 from the Charleston Harbor and the Ashley and Cooper Rivers (n = 36) in South Carolina revealed higher levels than those reported in any other U.S. urban areas. Detectable levels were found in all sample locations with mean total PFAS concentrations of 3.79 ng g^{-1} (range 0.22 to 19.2 ng g^{-1} d.w.). Dominant compounds were perfluorooctane sulfonate (PFOS) (mean 1.52 ng g^{-1}; range 0.09–7.37 ng g^{-1} d.w.), followed by perfluorodecanoate (PFDA) (mean 0.83 ng g^{-1}; range 0.06–4.76 ng g^{-1} d.w.) and perfluorooctanoate (PFOA) (mean 0.42 ng g^{-1}; range 0.02–2.52 ng g^{-1} d.w.). PFOS levels in sediments at 19 of 36 sites (representing 52% of the study area) exceeded the published global median PFOS sediment concentration of 0.54 ng g^{-1}.

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1. Introduction

Perfluoroalkyl substances (PFASs) have been in production for more than 60 years and used in various applications, including stain-resistant coatings for textiles and packaging, non-stick cookware, refrigerants,

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paints, fire-fighting foam, adhesives, waxes, and polishes (Kissa, 2001; Prevedouros et al., 2006). Due to its widespread use, environmental persistence, and bioaccumulation, PFASs can be detected ubiquitously in environmental matrices. Their presence in the environment results from release through direct sources, such as the manufacture and use of PFAS-containing products, as well as indirect sources (Gebbink et al., 2015; Buck et al., 2011; Butt et al., 2010). The global use of PFASs has resulted in the occurrence of these substances in air (Domingo et al., 2012), aquatic systems (Li et al., 2011), wildlife species (Ahrens and Bundschuh, 2014; Houde et al., 2011) and humans (Calafat et al., 2007).

Of the 30 PFAS homologues that have been studied to date, perfluorooctane sulfonate or sulfonic acid as in nomenclature by Buck et al., 2011 (PFOS) and perfluorooctanoic acid (PFOA) are the two most commonly detected in environmental and biological samples (Houde et al., 2011; Kumar, 2005). PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) have been included as persistent organic pollutants (POPs) in the Stockholm Convention (2009). Several PFASs bioaccumulate in marine food webs resulting in high concentrations in top trophic-level species such as marine mammals (Houde et al., 2011). Some of the highest PFASs found globally in marine mammals are in bottlenose dolphins inhabiting Charleston, South Carolina (Houde et al., 2005; Fair et al., 2012). Levels of PFASs measured in the plasma of resident Charleston dolphins are on the same order of magnitude to that of occupationally exposed humans, with higher body burdens of specific PFASs in dolphins inhabiting areas with greater developed land use (Adams et al., 2008). These high PFAS levels in dolphins are a concern and a recent study has shown that these pollutants affect immune responses (Fair et al., 2013). Habitat and diet are prominent factors that influence PFAS concentrations in marine mammals and their food webs (Houde et al., 2011; Moon et al., 2010). A dolphin food web study reported that mean sediment PFAS concentrations in 2004 from Charleston, South Carolina (2.2 ng g^{-1} w.w.) were much higher than those in Sarasota Bay, Florida (0.6 ng g^{-1} w.w) (Houde et al., 2006). Dolphins have been recognized as environmental sentinels (Bossart, 2011) and as such, the Charleston dolphins with their high PFAS levels are serving as sentinels prompting a comprehensive survey of PFASs in their environment.

A number of reviews of the toxic effects of PFASs have been published (Lau et al., 2007; Olsen et al., 2009; Kannan, 2011; Stahl et al., 2011; DeWitt et al., 2012). Toxicological studies of mammalian species with PFOS and PFOA have suggested that peroxisome proliferation (Lau et al., 2007; Kennedy et al., 2004), hepatotoxicity (3M, 2002), neurotoxicity (Harada et al., 2006), immunotoxicity (DeWitt et al., 2012), lipid metabolism (Wang et al., 2014), and developmental toxicity (Fuentes et al., 2007) may be associated with exposure to these chemicals.

Concentrations of PFASs in surface water and biota have been reported worldwide and the spatial distribution of these chemicals generally relates to urbanization (Kim and Kannan, 2007; Gewurtz et al., 2013). The detection of PFOS and PFOA in surface waters varies widely over several orders of magnitude (Wei et al., 2007; Loos et al., 2008; Jin et al., 2009; Quinete et al., 2009). Environmental studies worldwide have focused more attention on quantities of PFASs in biota and water and less on sediments and their partitioning behavior and fate (Nakata et al., 2006; Zareitalabad et al., 2013). Sediments are an important sink and reservoir of POPs and have a large impact on their distribution, transport, and fate in the aquatic environment (Nakata et al., 2006). The accumulation of potentially toxic chemicals such as PFAS in the sediments of lakes, rivers, harbors, and oceans continue to present significant risks to the health of aquatic environments as well as human populations. Data on biota monitoring reviewed by Houde et al. (2011) showed that high concentrations of PFASs continue to be detected in invertebrates, fish, reptiles, and marine mammals worldwide. There have been recent efforts to limit the production and emission of these chemicals and long-term monitoring is necessary to ascertain whether mitigation measures have resulted in reduction of some PFASs (Lindstrom et al., 2011).

Urban areas are recognized sources of perfluorinated compounds to the environment (Kim and Kannan, 2007). Charleston, SC is an urban area currently experiencing rapid growth as the 9th fastest growing metropolitan area in 2013 (U.S. Census, 2012). Monitoring surveys in Charleston Harbor during 1993–1994 demonstrated that sediments and fish were contaminated by mixtures of metals and organic compounds (Long et al., 1998). However, the status of contaminants such as PFASs is largely unknown, other than a preliminary study conducted in 2004 investigating PFASs in the dolphin food web (Houde et al., 2006). The aim of this study was to conduct a quantitative assessment of PFASs in sediment to identify spatial differences in contamination within the Charleston Harbor and facilitate a comparison with national and global sediment levels.

2. Methods

2.1. Sediment sampling

Using a stratified, random sampling design, surficial sediments were collected from 36 sites around the Charleston Harbor and its tributaries, the Ashley and Cooper Rivers in November 2012 (Fig. 1). The general sampling areas were subdivided into four sub-regions: Upper Cooper River, Lower Cooper River, Ashley River, and Charleston Harbor. Sample collection was done using a Young (modified vanVeen) grab sampler. Prior to each deployment, the grab sampler was rinsed with acetone followed by ambient water. The top 2–4 cm of sediment within the grab sampler was collected and homogenized with a clean scoop on site. Samples were stored on ice in the field and then transferred to −20 °C followed by shipment on dry ice to the laboratory for analysis.

2.2. PFAS analysis — chemicals and standards

The PFASs investigated in this study are listed in the supplementary information (Supplementary Table S1). Each was classified into two sub-groups; the perfluoroalkyl sulfonates (PFSAs) and the perfluoroalkyl carboxylates (PFCAs). PFOA and potassium salt of PFOS were purchased from TCI (Portland, OR) and Wellington Laboratories (Guelph, ON, Canada). Potassium salts of perfluorobutanesulfonate (PFBS) and perfluorohexanesulfonate (PFHxS) were provided by the 3M Company (St. Paul, MN) and Wellington Laboratories (Guelph, ON, Canada). Perfluorodecanesulfonate (PFDS) and perfluorohexanoic acid (PFHxA) were purchased from Wellington Laboratories (Guelph, ON, Canada). Perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA) were from Fluorochem Ltd. (Glossop, Derbyshire, UK), and perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA) were from Aldrich (St. Louis, MO) and Wellington Laboratories (Guelph, ON, Canada). The isotopically labeled standards, $^{13}C_4$-PFOS and $^{13}C_4$-PFOA, $^{18}O_2$-, $^{13}C_2$-PFHxA, $^{13}C_2$-PFUnDA, and $^{13}C_2$-PFDoDA, were purchased from Wellington Laboratories (Guelph, ON, Canada). $^{13}C_2$-PFNA and $^{13}C_2$-PFDA were provided by the 3M Company (St. Paul, MN). Purities of all standards were ≥95%.

2.3. Sample extraction/instrument analysis

Due to logistical constraints, sediment samples were extracted and analyzed by two laboratories (Laboratory of Organic Analytical Chemistry, Wadsworth Center, NY State Department of Health, Albany, NY and Environment Canada, Water Science Technology Directorate, Burlington, ON). The method used by the Wadsworth Center was similar to that described previously (Nakata et al., 2006). Briefly, sediment was dried at room temperature and approximately 5 g of sediment was placed in a 50-mL polypropylene tube. $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, and $^{13}C_2$-PFDoDA (5 ng of each) were spiked as internal standards and allowed to equilibrate overnight. Ten milliliters of methanol was added and the mixture was shaken for

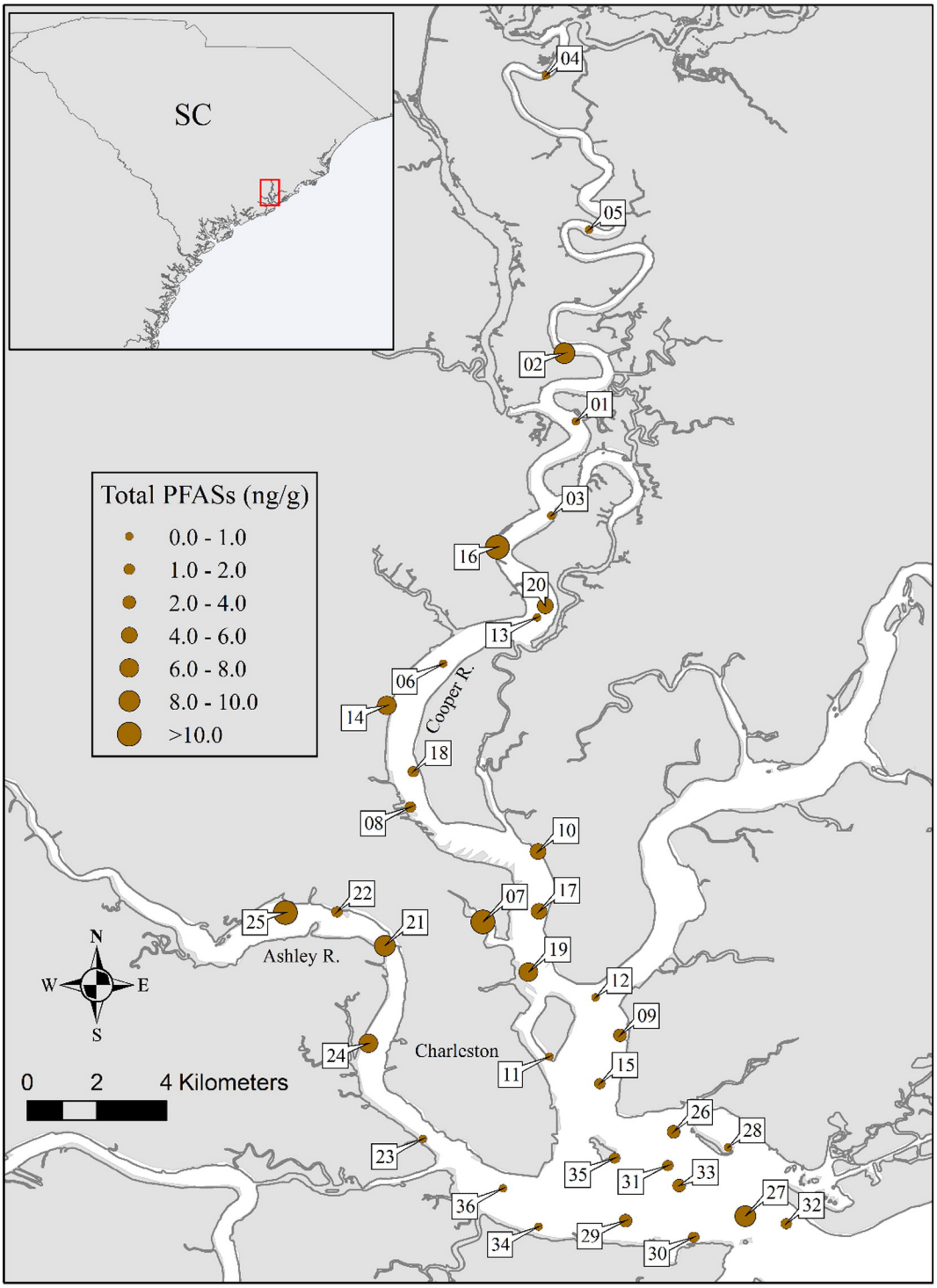

Fig. 1. Map of spatial distribution of total PFASs (ng g^{-1} d.w.) in sediment from Charleston, SC.

10 min and then sonicated using an ultrasonicator for 30 min. The extract was decanted after centrifugation at 3000 ×g for 15 min. A second extraction was performed with additional 10 mL of methanol, extracts were combined and evaporated to 1 mL with a gentle nitrogen stream and then filtered using a 0.2-μm nylon filter. An Agilent 1100 series high performance liquid chromatography (HPLC) (Agilent Technologies, Santa Clara, CA) coupled with an Applied Biosystems API 2000 electrospray triple quadruple tandem mass spectrometer (ESI–MS/MS) (AB SCIEX, Framingham, MA) with source upgrade for increased sensitivity was used to analyze PFASs in sediment samples. Ten microliters of the sample extract was injected onto a 100 × 2.1 mm Betasil® C18 column (5 μm; Thermo Electron Corporation, Bellefonte, PA) with a Javelin™ guard column (20 × 2.1 mm) connected serially. The mobile phase was 2 mM ammonium acetate/methanol delivered at a flow rate of 300 μL/min. The gradient started at 10% methanol and increased to 99% methanol in 10 min, and was held for 2 min before reverting to 10% methanol. The mass spectrometer was operated in electrospray negative ionization mode, and the target compounds were determined

by multiple reaction monitoring (MRM). Detailed compound specific MS/MS parameters and mass transitions for each of the analyte can be found in Nakata et al. (2006).

The method used by Environment Canada was based on the method by Yeung et al. (2013). Using 1 g of dried sediment, isotopically labeled surrogates in 30 μL of methanol were added for overnight sorption. A base digestion was performed by sonicating the sample with 100 mM sodium hydroxide in 2 mL of methanol. The digested sample was then extracted with two aliquots of 15 mL methanol, followed by neutralization with 100 μL of 2 M hydrochloric acid. The methanol extracts were combined and dried using nitrogen gas. The residue was reconstituted in 1 mL methanol and then subjected to carbon solid phase extraction (SPE). The extract was loaded onto a methanol-conditioned SPE cartridge and then further eluted with 3 mL of methanol. The extract was concentrated to 1 mL with nitrogen gas and then diluted in 20 mL of polished HPLC grade water. The final step of the extraction required weak anion exchange SPE clean up with basicified methanolic elution. The final extract was in 1 mL 50/50 v/v methanol water and analyzed by ultrahigh performance liquid chromatography tandem mass spectrometry (UHPLC MS/MS) using a Waters Acquity UHPLC and Xevo TQS mass spectrometer (Waters, Milford, Massachusetts, USA). Gradient elution was conducted using a methanol–water mobile phase. PFAAs were quantified by relative response to corresponding isotopically labeled surrogates. Wet weight concentrations were calculated based on percentage moisture in the samples. Performance measures were verified using method blanks, spike and recovery experiments and matrix spikes.

2.4. Quality assurance/quality control

The limits of quantification (LOQs) were generated from the two laboratories following the same criteria below. The LOQ was determined based on the linear range of the ten-point calibration curve prepared at a concentration range of 0.05–100 ng mL^{-1}. Concentrations in samples that were at least 3-fold greater than the lowest acceptable standard concentration were considered to be valid. A curve point was deemed acceptable if (1) it was back-calculated to be within 20% of the theoretical value when evaluated versus the $1/x$ weighted quadratic curve ($R^2 > 0.999$), and (2) the peak area of the standard was at least 3 times greater than that in the blank. In the present study the procedural blanks were extracted from the empty sampling devices provided by NOAA, and passed through the extraction procedure along with the samples. Procedural blanks were not detected for target compounds in the batches analyzed in Wadsworth Center, however, trace concentration of PFOA was found in the procedural blanks analyzed in Environment Canada, and the results were subtracted by the blank concentration. The reported LOQs were calculated by converting the lowest accepted concentration in the calibration curve to the concentration unit in ng g^{-1} d.w., considering the sample weight, moisture content, and dilution/concentration factors during the extraction and clean up. For each compound, the higher LOQ value reported from the two laboratories was selected for the LOQ in the whole study. The LOQs for the target analytes (ng g^{-1} d.w.) were 0.023 for PFBS, 0.022 for PFHxS, 0.022 for PFOS, 0.022 for PFDS, 0.023 for PFHxA, 0.020 for PFHpA, 0.019 for PFOA, 0.020 for PFNA, 0.019 for PFDA, 0.027 for PFUnDA, and 0.024 for PFDoDA, respectively. The PFAS concentrations were calculated using isotopic dilution internal standard method, by which means the concentrations were corrected by internal standard. The matrix spike recovery ranged from 99% to 109% for all compounds, with the exception of 65% for PFBS and PFDS. Recognizing that data sets generated from two different laboratories can introduce error into the spatial analyses of the sediment samples, we employed QA/QC procedures during the analysis of these samples. Well-defined standards and mass-labeled internal standards were used in each laboratory. Additionally, procedure blanks, duplicate samples, and spiked reference materials were run with each batch of samples. Both laboratories participate in inter-comparison studies. Duplicate samples ($n = 4$) were sent to both labs as a part of inter-laboratory comparison of PFAS concentrations. The relative standard deviation for the concentrations detected above LOQ in duplicate samples sent to two laboratories were 21% for PFHpA, 36% for PFOA, 27% for PFNA, 23% for PFDA, 12% for PFUnDA, and 11% for PFOS, respectively.

2.5. Data analysis

Sampling sites were distributed throughout each respective sampling area using a stratified, equal-probability survey design (Diaz-Ramos et al., 1996; Stevens and Olsen, 2004). Estuarine subtidal boundaries were delineated using a combination of the U.S. Fish and Wildlife Service — National Wetlands Inventory USFWS (2014) and S.C. Department of Health and Environmental Control modeled stream segments (SCDHEC, 2014) data sources. Although a stratified design was used for sampling, the analyses were conducted as if the design was unstratified, using strata to define subpopulations for analysis (Kincaid, 2012).

The use of a probabilistic sampling design allowed estimation, with known confidence, of the percent area of the surveyed region classified either according to available thresholds or in relation to distributional attributes (e.g., mean, median, percentiles). Estimates were based on procedures described in Diaz-Ramos et al. (1996) for obtaining an approximate cumulative distribution function (CDF) and implemented in the spsurvey package (Kincaid and Olsen, 2013) for R statistical software.

3. Results and discussion

3.1. Concentrations of sediment PFASs

Detectable concentrations of sediment-bound PFASs were found at each of the 36 sampling locations (Figs. 1 and 2; Supplementary Table S2). Total PFAS concentrations ranged from 0.22 ng g^{-1} d.w. to 19.21 ng g^{-1} d.w., with overall mean of 3.72 ng g^{-1} d.w. for all sites combined. Among the 11 compounds (PFBS, PFHxS, PFOS, PFDS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA) measured in Charleston sediments, dominant compounds observed were PFOS, PFDA, and PFOA with concentrations ranging from 0.09–7.37 ng g^{-1} d.w., 0.06–4.76 ng g^{-1} d.w. and 0.042–2.52 ng g^{-1} d.w., respectively for all sites. Other PFAS concentrations are listed in Supplemental Table 2. PFOS had the highest mean levels (1.52 ng g^{-1} d.w.), followed by PFDA (0.83 ng g^{-1}) and PFOA (0.42 ng g^{-1} d.w.). PFOS accounted for 19.1–51.4% of total PFASs measured in sediments (Fig. 3). Smaller contributions were observed from PFDA between 14.4 and 28.1% of the total detectable analytes, followed by PFOA (6.2–23.4%), PFUnDA (0–24.9%) and PFHpA (0–16%).

The frequency of detection of PFASs above the LOQ was as follows: 100% for PFOS, PFOA, PFDA, followed by PFNA and PFUnDA (94%), PFHpA (77%), PFDoHA (66%); PFHxA (27%), PFHxS (25%), PFBS (19%) and only 8% for PFDS. This is in contrast to a study by Long et al. (2013) in which detectable PFASs occurred only in a small minority of samples from Puget Sound, WA. In that study, only three of 13 PFASs (PFOS, PFOSA, and PFBA) were detected in sediments representing low sample detection rates (2–17%). Other studies also reported lower detection levels in sediments such as Sydney Harbor with the majority of target analytes not detected (Thompson et al., 2011) and sediment in a wastewater canal in Serbia had 9 out of 15 analytes not detected (Beskoski et al., 2013). Compared to studies with higher PFAS levels, those with lower contamination levels may also explain the lower detection frequencies in the studies cited herein.

Ecological risk to aquatic animals associated with exposure to PFAS can be estimated using water-quality criteria values (Geisy et al., 2010). While there are guidelines for assessing sediment quality for the protection of aquatic life (Canadian Council of Ministries of Environment, 1999), there are no effects-based sediment quality

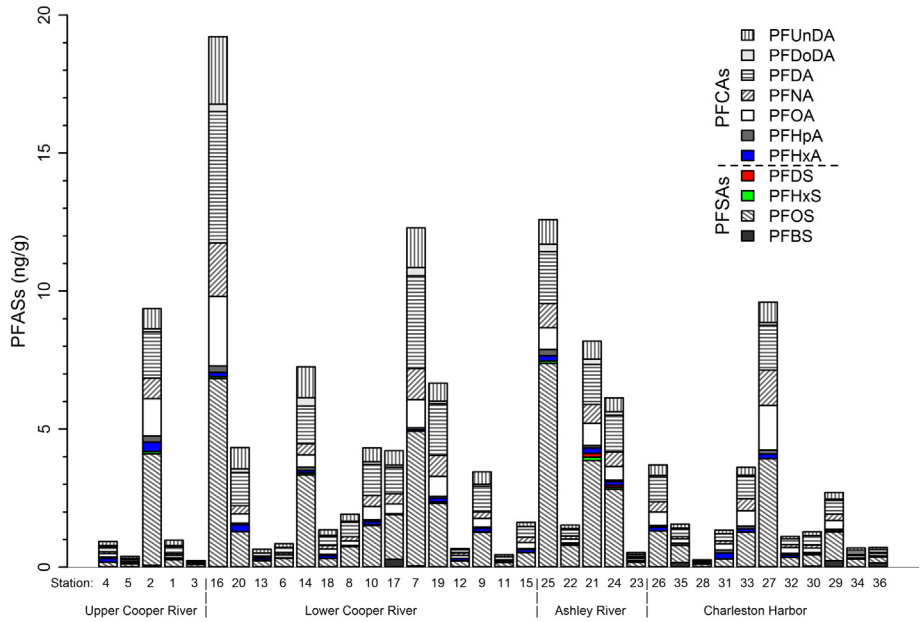

Fig. 2. PFAS concentrations (ng g^{-1} d.w.) in sediment samples from four geographical sub-regions of the Charleston Harbor Estuary.

criteria or guidelines for PFASs in sediment. Since PFASs bioaccumulate and biomagnify in aquatic food webs and can potentially pose hazards to higher tropic organisms, it is important to be able to assess risks from PFAS in sediments. As the sorption of PFASs to sediments determines their fate and distribution in the environment, Zareitalabad et al. (2013) reviewed sorption coefficients with environmental levels of these compounds and reported global median concentrations PFOS (0.54 ng g^{-1} d.w.) and PFOA (0.3 ng g^{-1} d.w.) in sediments. Some limitations noted in the above review included both the limited sediment PFAS data available and the influence of individual pollution cases by country on their distribution. We used the median PFOS and PFOA levels derived by Zareitalabad et al. (2013) to compare the observed Charleston, SC sediment PFOS and PFOA concentrations. PFOS levels in sediments at 19 of 36 sites (representing 52% of the study area) exceeded the published median PFOS sediment concentration of 0.535 ng g^{-1} d.w. Fig. 4 A–C shows the percent area per sub-region that meets or exceeds the median global levels from Zareitalabad et al. (2013) for PFOS, PFOA, and the median total PFAS level that was determined from samples in this study. The Upper Cooper River had the highest percentage area with PFOS and PFOA concentrations below the published median concentrations, followed by the Charleston Harbor and Lower Cooper River, with the Ashley River having the lowest percentage area below the median concentration. Conversely, the Ashley River had the highest percentage of samples with PFOS and PFOA concentrations that exceeded the median concentration, followed by the Lower Cooper River, Charleston Harbor and Upper Cooper River. The trend in total PFAS concentration in the sub-regions was slightly different. While the Upper Cooper River had the highest percentage area below the

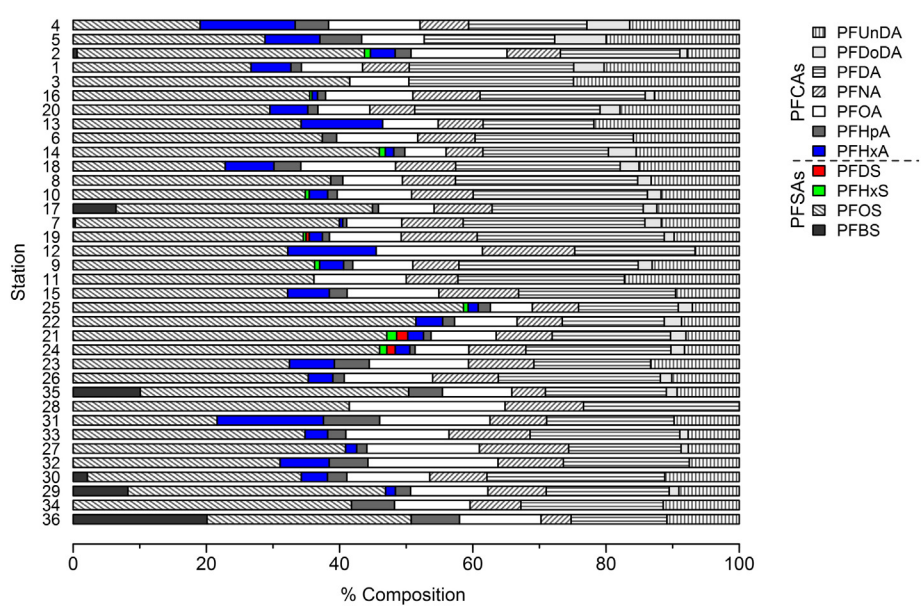

Fig. 3. Percentage contributions of PFASs in sediments from Charleston, SC.

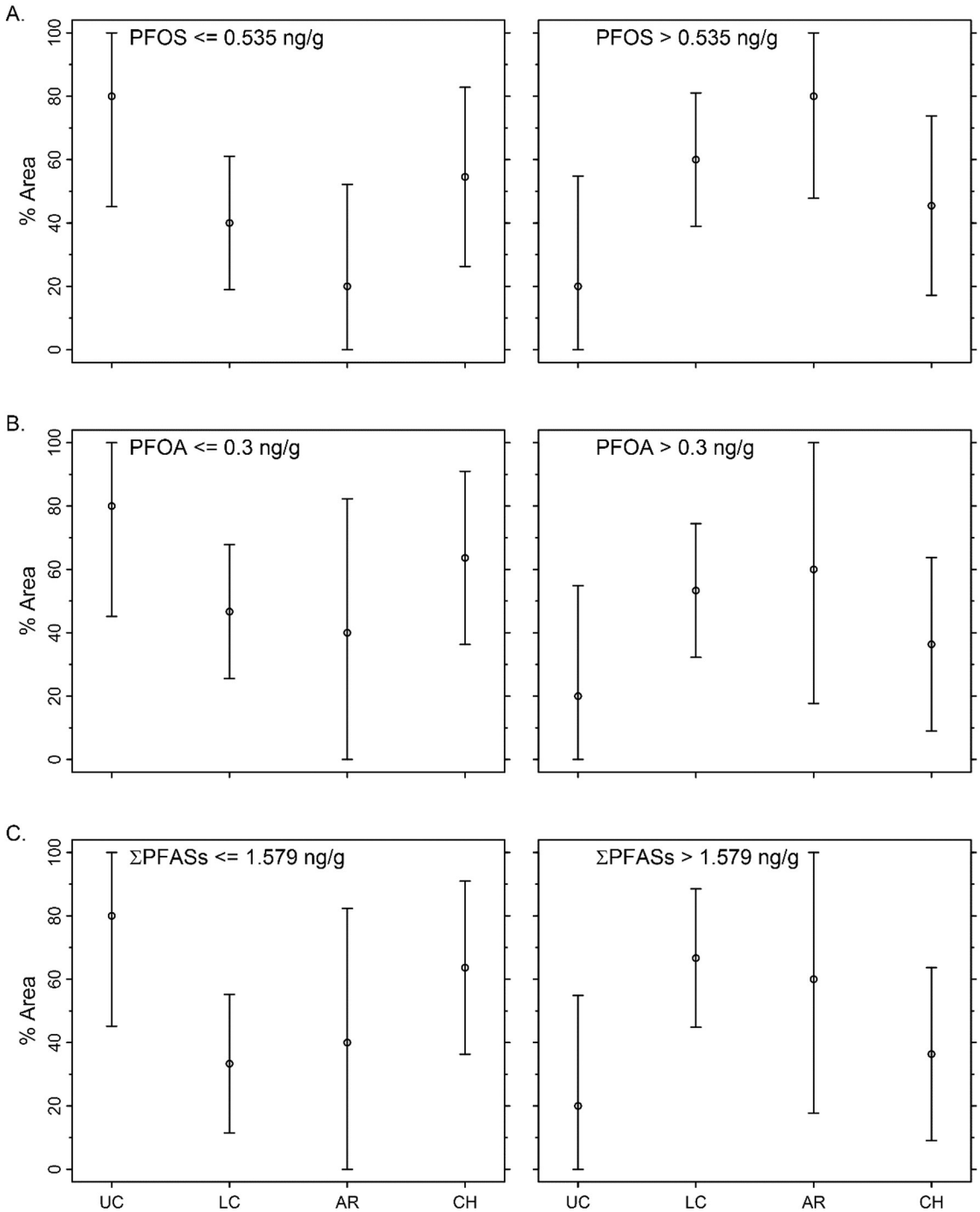

Fig. 4. Estimates (and 95% CIs) of the percent area of each sub-region classified according to the criteria shown.

median concentration (1.58 ng g^{-1}), the Lower Cooper River had the highest percentage area that exceeded the median concentration for total PFASs.

3.2. Comparisons with other published PFAS sediment results

Concentrations of PFAS in the sediments from the Charleston Harbor Estuary were comparatively higher than those in other U.S. urban areas such as Baltimore Harbor and San Francisco Bay (Higgins et al., 2005) and the Niagara River (Lucaiu et al., 2005) (Table 1). For comparative purposes, all units are presented on a dry weight basis. Relatively low sediment concentrations of PFASs were found in Baltimore's Inner Harbor (0.846 ng g^{-1} d.w. for PFOS and 0.390 ng g^{-1} d.w. for PFOA) (Higgins et al., 2005). Sediment samples analyzed for 12 PFASs from 13 locations around San Francisco Bay and Monterey Bay displayed a total range of detected concentrations of <0.12 ng g^{-1} d.w. to 3.94 ng g^{-1} d.w. for all samples and analytes (Higgins et al., 2005). Long et al. (2013) surveyed various areas throughout Puget Sound for PFASs and found concentration ranges of 0.13 ng g^{-1} to 1.50 ng g^{-1} for the 3 PFASs detected and PFOS as the predominant compounds with a maximum concentration of 1.5 ng g^{-1} d.w. Taken together, the ranges of PFOS for many of these urban areas in the USA were lower than the samples reported in this study for Charleston, SC (0.09–7.37 ng g^{-1} d.w.) (Table 1). Sediment samples from the Savannah

Table 1
Comparison of PFAS concentrations in Charleston, SC sediments (ng g^{-1} d.w.) with those reported in the literature.

Location	Year	PFOA	PFOS	ΣPFASs	Reference
USA					
Charleston, SC	2012	0.101–2.51 (0.42)	0.09–7.37 (1.52)	0.224–19.14 (3.68)[a]	Present study
Baltimore Inner Harbor, MD	2004	0.19–0.39 (0.85) (LOQ = 0.01)	n.d.–0.85 (0.39) (LOQ = 0.11)	(5.96)[b]	Higgins et al. (2005)
Savannah River, GA	2007	n.d.–0.20 (LOQ = 0.1)	0.30–0.80 (LOQ = 0.1)	–	Kumar et al. (2009)
Puget Sound, WA	2010	–	0.20–1.50 (LOQ = 0.01)	–	Long et al. (2013)
San Francisco Bay, CA	2004	n.d.–0.625 (LOQ = 0.01)	n.d.–3.07 (LOQ = 0.11)	–	Higgins et al. (2005)
Asia					
Bohai Sea	2009	n.d.–0.54 (0.30) (LOQ = 0.50)	n.d.–1.97 (1.67) (LOQ = 0.50)	n.d.–4.31 (0.62)[c]	Wang et al. (2011)
Zhujiang River, Guangzhou, China	2009	0.09–0.29 (0.20)	n.d.–3.1 (1.12) (LOQ = 0.12)	0.09–3.6 (1.25)[d]	Bao et al. (2010)
Huangpu River, Shanghai, China	2009	0.20–0.64 (0.45)	n.d.–0.46 (0.26) (LOQ = 0.12)	0.25–1.1 (0.62)[d]	Bao et al. (2010)
Taihu Lake, China	2009	<0.02–0.52 (0.16) (LOQ = 0.02)	0.06–0.31 (0.15) (LOQ = 0.02)	0.20–1.31 (0.69)[e]	Yang et al. (2011)
Europe					
Roter Main River, Germany	2006	<0.03–0.18 (0.06) (LOQ = 0.03)	0.05–0.57 (0.21)	–	Becker et al. (2008)
Orge River, France	2010	(<0.07) (LOQ = 0.07)	(4.3)	(8.4)[f]	Labadie and Chevreuil (2011)

Ranges and mean (values in parenthesis) concentrations. Sites without LOQ values were not available in the literature.
[a] Total of [PFBS] + [PFHxS] + [PFDS] + [PFOS] + [PFHxA] + [PFHpA] + [PFOA] + [PFNA] + [PFDA] + [PFDoDA] + [PFUnDA].
[b] Total of [PFHxS] + [PFOS] + [PFDS] + [FOSAA] + [N-MeFOSAA] + [N-EtFOSAA].
[c] Total of [PFBS] + [PFHxS] + [PFOS] + [PFDS] + [PFBA] + [PFHxA] + [PFHpA] + [PFOA] + [PFNA] + [PFDA] + [PFUnDA] + [PFDoDA].
[d] Total of [PFBS] + [PFOS] + [PFOA] + [PFDA] + [PFDoDA].
[e] Total of [PFBS] + [PFHxS] + [PFOS] + [PFDS] + [PFHpA] + [PFOA] + [PFNA] + [PFDA] + [PFUnDA] + [PFDoDA].
[f] Total of [PFPA] + [PFHxA] + [PFHpA] + [PFOA] + [PFNA] + [PFDA] + [PFUnDA] + [PFDoDA] + [PFTrA] + [PFTeA] + [PFBS] + [PFHxS] + [PFHpS] + [PFOS] + [PFDS].

River and the LCP Chemicals Superfund site near Savannah, GA also showed negligible PFASs, with totals ranging from 0.1–1.8 ng g^{-1} d.w. and PFOS from 0.1 to 0.8 ng g^{-1} d.w. (Kumar et al., 2009).

Many other urban areas from around the world have also reported similar low level of PFASs in sediments such as the estuarine/coastal areas of Bohai Sea with mean total PFAS of 0.62 ng g^{-1} d.w. (ranges n.d. to 4.31 ng g^{-1} d.w.) and PFOS mean of 1.67 ng g^{-1} d.w. (range <0.50 to 1.97 ng g^{-1} d.w.) (Wang et al., 2011). The Zhujiang River, China had total PFAS levels between 0.09 and 3.6 ng g^{-1} d.w. with PFOS range <0.12 to 3.1 ng g^{-1} d.w. (Bao et al., 2010), while the Huangpu River, China had total PFAS levels between 0.25 and 1.1 ng g^{-1} d.w. with PFOS range <0.12–0.46 ng.g^{-1} d.w. (Bao et al., 2010). The mean PFOS levels in Sydney Harbor, Australia were 1.5 ng g^{-1} (Thompson et al., 2011) and an urban lake, Dianchi Lake, China had total PFAS level of 0.95 ng g^{-1} d.w. and PFOS levels ranging 0.07–0.83 ng g^{-1} d.w. (Zhang et al., 2012).

Correspondingly, higher levels of PFASs have been found in several areas such as the Haihe River, China where PFOS levels ranged from 1.80 to 7.30 ng g^{-1} d.w. with a mean concentration of 5.20 ng g^{-1} d.w. (Li et al., 2011) and in the Orge River, France, where the mean PFOS level was 4.30 ng.g^{-1} d.w. (Labadie and Chevreuil, 2011). Considerably higher levels were also observed in the Huangpu River, Shanghai with mean PFOS levels of 34.60 ng g^{-1} (range: 5.20–203 ng g^{-1}) (Bao et al., 2010). Additionally, sediment samples from a wastewater canal of Pancevo (Serbia) exhibited PFOS levels up to 5.7 ng g^{-1} d.w. and total PFASs up to 6.3 ng g^{-1} (Beskoski et al., 2013). Higher levels of PFOS ranging from 0.5 to 30.1 ng g^{-1} d.w. were found in sediment cores from Lake Ontario, although this was from 1952 to 2005 (Yeung et al., 2013). Among the highest concentrations of PFASs reported are those in areas with direct industrial emissions that have impacted fresh water systems with water concentrations reaching 1000 ng L^{-1} (Lindstrom et al., 2011). Zhou et al. (2013), present a good example of this in a study where average sediment PFOS levels in the Tangxun Lake, China were measured at 74.4 ng g^{-1} d.w. This lake is located near a production base of the nearby fluorochemical industry. Due to the wide diversity of PFASs, their extreme stability and spatial heterogeneity of PFASs burdens in the environment, monitoring studies are important to define areas of concern and routes of exposure.

3.3. Spatial distribution of PFASs in sediment

In examining the occurrence and spatial distribution of PFAS in sediments within the Charleston study site we observed both differences among the patterns and multiple PFAS "hot spots" in each of the sampling sub-regions (Figs. 1, 2 and 3). The highest concentration of total PFASs was found in site 16 in the Lower Cooper River (19.2 ng g^{-1} d.w.), followed by site 25 (12.5 ng g^{-1} d.w.) in the Ashley River, site 7 (12.3 ng g^{-1} d.w.) in the Lower Cooper River, site 27 (9.6 ng g^{-1} d.w.) in the Charleston Harbor and site 2 (9.1 ng g^{-1} d.w.) in the Upper Cooper River. While all sites had detectable concentrations of PFOS, the two highest PFOS levels were from site 25 in the Ashley River (7.4 ng g^{-1} d.w.) and site 16 (6.8 ng g^{-1} d.w.) in the Lower Cooper River. Other sites with high PFOS concentrations were found in the Upper Cooper River site 2 (4.0 ng g^{-1} d.w.); Lower Cooper River site 7 (4.9 ng g^{-1} d.w.) and site 14 (3.3 ng g^{-1} d.w.); Ashley River site 21 (3.9 ng g^{-1} d.w.) and Charleston Harbor site 27 (3.9 ng g^{-1} d.w.). Site 16 is the location of the Charleston Navy Base, which operated from 1901 until its closure in 1996, and currently the Navy Nuclear Power Training Unit is approximately 1 mile upstream. These higher levels may be related with pre-2002 use of aqueous film-forming foams (AFFF) which are still used at military bases and airports throughout North America. Elevated PFOS has been documented in groundwater near Naval Air Stations (Moody et al., 2003) and the study in Puget

Sound, WA found high sediment PFOS levels associated with locations near the Puget Naval facilities (Long et al., 2013).

Only one site in Charleston Harbor, site 27 at the mouth of the harbor had elevated levels of PFASs (total 9.9 ng g^{-1} d.w.; PFOS 3.9 ng g^{-1} d.w.). This site is near a commercial anchorage for container ships entering the Port of Charleston. With the presence of PFOS in sediment taken from this area and other PFASs a reasonable assumption is that these chemicals are originating from these vessels. This assumption, however, does not take into account that other factors, including sediment composition and on-going dredging in the area, might influence the distribution these contaminants in sediments, regardless of source.

Differences existed between the composition percentages of PFOS in the Charleston, SC sediment samples. The composition percentages of PFOS ranged from 22.2 to 59%, with site 25 in the Ashley River having the highest PFOS percent composition, followed by sites 22 (53.1%) and 21 (48.2%), each in the Ashley River. Site 4 in the Upper Cooper River had the lowest percent composition of PFOS (22.2%), followed by site 18 (22.5%) in the Lower Cooper River and site 31 (25.7%) in the Charleston Harbor (Fig. 3).

Detectable concentrations of PFBS were found in 7 sediment samples (sites 2, 7, 17, 29, 30, 35, 36) ranging from 0.04 to 0.22 ng g^{-1} d.w. This observation is interesting as PFBS was the shortest chain PFAS monitored and the sediment–water distributions for PFASs tend to decrease with decreasing chain length (Lindstrom et al., 2011). While not routinely found in environmental matrices, it was among the major compounds in marine sediments from Tokyo Bay (Ahrens et al., 2009). The location of sites with detectable levels of PFBS may be related to specific point sources in Charleston and indicative of more recent emission and deposition.

The spatial differences found in PFAS concentrations in some of the samples might be due to discharge from sewage treatment plants. Twenty-four hour composite wastewater treatment plant (WWTP) effluent samples were collected in Charleston, SC in 2004 (Houde et al., 2006). Elevated levels were reported for PFOS (30 ng L^{-1}) and PFOA (59 ng L^{-1}), suggesting a possible point source of PFAS contamination to nearby receiving waters. However, the two discharge points for WWTPs in the Charleston area are in the harbor and samples with the highest PFAS sediment levels were found upstream of these locations in all but one sample (site 31). Thus, it is possible that point sources and/or stormwater runoff contribute to these higher sediment concentrations although sediment characteristics could also be an influencing factor. Storm water run-off has been established as an important contributor to environmental PFAS concentrations, especially from industrial sites (Xiao et al., 2012) although there is a lack of data on PFASs from industries that do not use these chemicals directly in production (Beskoski et al., 2013). Greater PFAS flux from stormwater runoff was suggested by Xiao et al. (2012) in that PFASs in urban environments are solubilized in rain and transported.

PFASs can be characterized as perfluorinated sulfonates and perfluorinated carboxylates based on their functional group (Kannan, 2011; Kumar, 2005). Pearson correlation analysis showed that the concentrations of PFASs were significantly correlated ($P < 0.05$) with each other (values ranging from $r = 0.41$ to 0.95). PFOS was highly correlated with PFCAs in the following order PFDA, PFOA, PFNA, PFDoDA, PFUnDA, PFHpA, and PFHxA suggestive of similar sources of contamination. PFSAs had a smaller proportion (mean 39.5%; range 22.2–59.02%) compared to PFCAs (60.5%; range 41.0–77.8% (Table 3)). Fig. 3 shows the composition of total PFCAs and total PFSAs in sediment at each study site. Total PFCAs had a greater contribution to total PFASs in each sub-region. The highest total PFCA was detected at site 16 in the Lower Cooper River (12.3 ng g^{-1} d.w.) whereas the highest total PFSA was detected at site 25 in the Ashley River (7.4 ng g^{-1} d.w.). Interestingly, site 3 in the Upper Cooper River had both the lowest total PFCA (0.13 ng g^{-1} d.w.) and PFSA (of 0.09 ng g^{-1} d.w.).

Sediments are considered as ultimate sinks and reservoirs of environmental contaminants such as PFASs (Prevedouros et al., 2006). Equilibrium parameters, such as a sediment–water partition coefficient (K_d) are necessary to predict their environmental fate (Higgins et al., 2007). PFASs with low partition coefficients predominantly exist in the dissolved phase and can be rapidly dispersed and diluted within the aquatic environment. On the other hand, PFASs with high partition coefficients associate with particulate matter and consequently become less mobile, leading to high concentrations in the sediment (Ahrens et al., 2011). Experimental data from Ahrens et al. (2011) suggest that in marine environments, where suspended solid concentrations are low, PFOA and PFOS are transported mainly in the dissolved phase rather than adsorption to suspended solids. Their studies showed that partitioning is different in each aqueous system and that PFASs can settle in marine estuaries where the sediment is typically organic-rich and muddy. As the Charleston Harbor estuarine system and its tributaries are comprised mainly of a soft silt/clay bottom (South Carolina Sea Grant Consortium, 1992) this may have an influence on the high sediment concentrations of PFASs. Although the present study did not include quantitative sediment quality analysis, descriptive data attained visually on the sediment samples indicated the vast majority contained mud (86% silt/clay composition, 8% sand, and only 6% were a sand and shell hash mixture). While sediment characteristics are a contributing factor in the accumulation of PFAS, we found that sites comprised of silt/clay had both very low as well as very high PFASs. Sites comprised of sand and/or shell hash generally had low PFAS concentrations although site 27, with sand and shell hash, at the mouth of the Harbor was among these having the highest PFAS concentrations. Thus, it is more likely that the differences in PFAS concentrations in the sediment samples are due to point and non-point sources. The results of the spatial PFAS variations in sediment samples from Charleston may reflect different inputs from the rivers, creeks and tributaries.

3.4. Inter-year trends in PFAS levels

This present study is a more comprehensive investigation of sediment samples from the Charleston area compared to a study on the dolphin food web, which included sediment samples collected during 2004 in this same area (Houde et al., 2006). We compared the sediment PFAS concentrations in the two studies to provide insight as to whether levels may be higher or lower (Table 2). The mean value reported in the 2004 study represented a total of 17 sediment samples from the same three subregions as in the present study. Since our sampling design was a stratified, random design, the exact sampling sites were not repeated for the 2012 collections. Thus, given the wide variation in PFAS concentrations in each area we used mean concentrations within sub-areas to compare the concentrations between the two sampling years. Additionally, we also included two superfund sites, which were both sampled in 2004 and 2012, as these two sites were geographically similar. Interestingly, the mean PFOS concentration at each of the superfund sites was higher in 2012 while the concentrations of all other compounds and total PFASs were lower during this time. The range of PFOS concentrations for the Cooper River and Charleston Harbor was higher in 2012, while the PFOS concentrations in the Ashley River were lower (Table 2). Similarly, this trend was noted for PFOA; while concentrations of PFUnDA were lower for all sampling locations and concentrations of PFDA slightly higher for all sampling locations. The presence of PFHxA was below detection limits in all sub-regions in 2004; however, in 2012 there were detectable levels in the Upper and Lower Cooper River and the Ashley River. Analyses for PFHpA, PFHxA, PFDS, and PFBS were not conducted in 2004. The total PFAS concentrations measured in the present study ($n = 36$) were generally slightly higher than that measured in 2004. This comparison provides insight as to the trends of PFAS sediment concentrations in Charleston, SC, however, the spatial variability and smaller sample size collected in 2004 should be considered cautiously with these comparisons. Higher concentrations of some PFAS compounds found nearly 10 years later (2004 to 2012) suggests continuing inputs into this system.

Table 2
PFAS concentration means and ranges by study sub-region (ng g^{-1} w.w.) in sediments collected in 2012 compared observed sediment PFAS concentration means and ranges (ng g^{-1} w.w.) collected in 2004 (Houde et al., 2006).

Study site	n	Year	PFBS	PFHxS	PFDS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFDoDA	PFUnDA	ΣPFAS[b]
Upper Cooper River	5	2012	**(0.01)** <0.01–0.01	**(0.03)** <0.01–0.03	<0.01	**(0.302)** 0.08–1.01	**(0.08)** <0.01–0.11	**(0.03)** 0.01–0.06	**(0.05)** 0.02–0.11	**(0.08)** <0.01–0.19	**(0.17)** 0.05–0.42	**(0.033)** <0.01–0.05	**(0.11)** 0.045–0.18	**(0.73)** 0.12–1.9
Lower Cooper River	15	2012	**(0.12)** <0.01–0.12	**(0.01)** <0.01–0.02	**(0.01)** <0.01–0.01	**(0.53)** 0.010–1.5	**(0.05)** <0.01–0.10	**(0.03)** <0.01–0.05	**(0.16)** 0.04–0.54	**(0.13)** 0.03–0.42	**(0.37)** 0.07–1.03	**(0.04)** <0.01–0.07	**(0.19)** 0.02–0.53	**(1.41)** 0.318–4.07
Ashley River	5	2012	<0.01	**(0.02)** <0.01–0.03	**(0.03)** <0.01–0.03	**(0.79)** 0.13–1.42	**(0.05)** 0.03–0.08	**(0.03)** 0.02–0.04	**(0.13)** 0.06–0.20	**(0.13)** 0.04–0.19	**(0.28)** 0.07–0.47	**(0.04)** 0.013–0.051	**(0.13)** 0.06–0.18	**(1.51)** 0.34–2.33
Charleston Harbor	11	2012	**(0.08)** <0.01–0.11	<0.01	<0.01	**(0.39)** 0.08–1.09	**(0.06)** <0.01–0.11	**(0.04)** <0.01–0.06	**(0.16)** 0.06–0.45	**(0.11)** 0.02–0.15	**(0.20)** 0.03–0.45	**(0.02)** <0.01–0.03	**(0.1)** <0.01–0.20	**(0.96)** 0.19–2.57
Koppers Superfund site	1	2012	**(0.01)** <0.01–0.01	<0.01	0.04	1.41	0.09	0.04	0.19	0.23	0.62	0.07	0.31	2.82
Macalloy Superfund site	1	2012	**(0.12)** <0.01–0.12	<0.01	<0.01	0.13	0.04	0.02	0.04	<0.01	0.03	<0.01	0.04	0.24
Previous study[a]														
Cooper River[c]	3	2004	NA	<0.02	NA	**(0.48)** 0.03–0.62	NA	NA	**(0.15)** 0.07–0.19	**(0.09)** 0.05–0.15	**(0.55)** 0.23–0.85	**(0.02)** 0.01–0.03	**(0.82)** 0.33–1.35	**(2.51)** 1.23–3.95
Ashley River	3	2004	NA	<0.02	NA	**(0.86)** 0.45–1.53	NA	NA	**(0.19)** 0.11–0.25	**(0.10)** 0.05–0.15	**(0.25)** 0.22–0.50	**(0.02)** 0.001–0.07	**(0.22)** 0.12–0.32	**(2.23)** 1.73–3.23
Charleston Harbor	3	2004	NA	<0.02	NA	**(0.09)** 0.04–0.14	NA	NA	**(0.23)** 0.13–0.40	**(0.12)** 0.01–0.23	**(0.27)** 0.07–0.52	**(0.09)** 0.01–0.16	**(0.15)** 0.01–0.30	**(1.30)** 0.85–2.09
Koppers Superfund site	1	2004	NA	<0.02	NA	1.18	NA	NA	0.91	0.80	1.24	0.014	0.56	4.68
Macalloy Superfund site	1	2004	NA	<0.02	NA	**(0.48)** 0.03–0.62	NA	NA	**(0.15)** 0.07–0.19	**(0.09)** 0.05–0.15	**(0.55)** 0.23–0.85	**(0.02)** 0.01–0.03	**(0.82)** 0.33–1.35	**(2.51)** 1.23–3.95

(NA = not analyzed).
[a] Values represent means (bold in parentheses) and ranges of observed values within the sample location (n = 3) for each range (ng g^{-1} w.w.).
[b] ΣPFAS values for 2012 were adjusted to account for compounds not analyzed in 2004.
[c] Values represent a composite of samples from the Upper and Lower Cooper River.

Table 3
Longitudinal assessment of PFSAs in sediment from geographical sub-regions in the Charleston Harbor Estuary.

Location		ΣPFSAs	ΣPFCAs	ΣPFASs
Upper Cooper River	Mean	0.97	1.30	2.28
	Min–max	0.09–4.2	0.13–4.83	0.22–9.05
	95% CI	−0.62–2.57	−0.44–3.04	−1.06–5.61
Lower Cooper River	Mean	1.73	2.82	4.55
	Min–max	0.16–6.89	0.28–12.32	0.44–19.21
	95% CI	0.74–2.73	1.17–4.46	1.92–7.17
Ashley River	Mean	3.10	2.61	5.71
	Min–max	0.24–7.37	0.35–5.12	0.58–12.49
	95% CI	0.58–5.61	0.81–4.41	1.43–9.99
Charleston Harbor	Mean	0.94	1.40	2.34
	Min–max	0.11–3.92	0.15–5.66	0.25–9.58
	95% CI	0.30–1.58	0.47–2.34	0.78–3.91

4. Conclusions

Measurement of sediment concentrations of PFASs in estuarine areas of Charleston, SC indicated that levels were elevated compared to some other urban US and global locations that have been measured to date. Among the 36 sites sampled, 52% exceeded the median global PFOS sediment concentration of 0.54 ng g^{-1} (Zareitalabad et al., 2013). Spatial distributions and differential PFAS compositions were found among the surface sediment samples with multiple 'hot spots' that are likely due to different inputs from the rivers and creeks as well as potential point sources. Occurrence and spatial distribution of detected PFAS between upstream and downstream indicate continuing input from existing sources. PFASs are not regulated under the National Pollutant Discharge Elimination System (NPDES) program or the Toxic Release Inventory, thus it is difficult to identify specific industrial or municipal users/dischargers of PFASs. While we found multiple sites in Charleston with high PFAS levels it is difficult to pinpoint specific sources because PFAS are widely used and have not been well-regulated or inventoried. As such, potential sources may include chemical companies producing industrial specialty chemical coatings, roofing and other manufacturing products using water-proofing systems, paint and other coatings as well as fabrics. The present study provides insight on sediment PFAS contamination in the Charleston estuarine system. The high PFAS levels found in dolphins in Charleston served as an alert for potential environmental concern and warrant further investigations to clarify whether environmental PFAS concentrations are sufficient to cause adverse effects to wildlife especially sensitive species in the Charleston estuarine system. The development of PFASs sediment quality values and threshold levels would assist in performing integrated exposure and risk assessments. This study provides a comprehensive baseline data on PFASs concentrations and a better understanding of the geographic distributions and extent of PFAS contamination in the estuarine area of Charleston, SC. Additional sampling efforts are necessary to fully ascertain the temporal trends related to PFAS contamination. We recommend collection of sediment cores so that deposition of PFASs might be measured chronologically. Identifying the fate and transport of PFASs in aquatic environments is important to understand hot spots in an urban estuary and support management decisions for pollution control.

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Appendix A. Supplementary data

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