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Temporal and Spatial Trends of Perfluorinated Compounds in Juvenile Loggerhead Sea Turtles (*Caretta caretta*) along the East Coast of the United States

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Perfluorinated compounds (PFCs) are globally distributed persistent environmental contaminants. This study provides temporal trends as well as large-scale spatial trends of PFC concentrations in threatened juvenile loggerhead sea turtles near or from Florida Bay (FL Bay), Cape Canaveral (FL), Charleston (SC), Core Sound (NC), and Chesapeake Bay (MD). PFCs were extracted from 163 plasma and serum samples using solid-phase extraction and quantified with LC-MS/MS. Concentrations of six compounds significantly varied by site, with MD or FL Bay turtles having the highest concentrations. Perfluorooctane sulfonate (PFOS) was the predominant PFC at all sites (range: 0.31 ng/g to 39.0 ng/g). FL Bay turtles, compared to other sites, accumulated a unique PFC pattern with a higher proportion of perfluorocarboxylates compared to PFOS. Furthermore, this study was the first to statistically correlate wildlife PFC concentrations with human population, used as a proxy for urbanization and sources of PFCs to the environment. Positive relationships were found in which human population accounted for 75 and 81% of the variance in turtle PFOS and perfluoroundecanoate (PFUnA) concentrations ($p = 0.06$ and 0.04), respectively. PFOS and perfluorononanoate (PFNA) significantly decreased from 2000−2008 in SC turtles annually by 20 and 11%, respectively ($p \leq 0.02$). Future investigations should continue temporal assessments as PFC regulations change, attempt to pinpoint specific sources and transport pathways in areas with unique PFC patterns, and assess turtle health at sites with higher PFC concentrations.

Introduction

Perfluorinated compounds (PFCs) have been manufactured for >50 years and enter the environment during manufacture and application of chemicals primarily used as repellent coatings, fire-fighting foams, and polymerization aids, or through use and disposal of products containing PFCs (*1–3*). Once PFCs or their precursors are emitted, atmospheric and water transport become important mechanisms for PFC global fate (*1, 4, 5*). Two classes of PFCs, perfluoroalkyl sulfonates (PFASs) and perfluorocarboxylates (PFCAs), are extremely stable global contaminants found in humans, wildlife, and abiotic matrices (*6, 7*). In addition, some PFCs have been shown to exhibit developmental, hepatic, immunosuppressive, and endocrine disruptive toxicity (*8*). PFCs associate with proteins found in liver and blood (*14, 15, 33*), and many are bioaccumulative and can biomagnify (*9*).

Due to the potential hazards of PFCs, many environmental samples have been analyzed for the presence of these compounds (*6*). In general, studies have shown increasing temporal trends of PFC concentrations from the 1970s to the early 2000s [6]. 3M, one of the largest former manufacturers of perfluorooctane sulfonate (PFOS)-related chemicals, completed a voluntary phase out of PFOS-related production in 2002 [2]. The European Union, Canada, and the U.S. now restrict the use of PFOS or other PFCs in certain industries, and PFOS is a candidate persistent organic pollutant (POP) under the Stockholm Convention (*10*). Due to decreased production and increased restrictions, temporal and spatial trend analyses are needed to examine changes in PFC environmental distribution. Studies have reported decreases of PFOS concentrations after 2000 in Canadian Arctic ringed seals (*11*), harbor seals from the German Bight (*12*), sea otters off the coast of California and Alaska (*13, 14*), and through human serum studies in the U.S. (*15*) and Norway (*16*). However, other studies have shown increases of some PFCs in Baikal seals (*17*) and ringed seals (*18*) from pre-2000 levels to 2005 and 2003 concentrations, respectively. Temporal resolution among these studies varies widely however, and yearly temporal monitoring studies (*15, 16*) have more statistical power to detect changes in environmental concentrations after modifications occur in production and legislation.

A previous study examined the spatial trends of PFCs in loggerhead sea turtles (*Caretta caretta*) along the U.S. East coast from northern FL to NC (*19*). Plasma PFC concentrations were significantly higher in sea turtles captured farther north, but the reason was unknown. In other studies, high levels of PFC concentrations have been cited as a consequence of close proximity to industrial or urbanized areas (*6, 20, 21*). For example, higher PFC concentrations were found in bottlenose dolphins from Charleston, SC, and Delaware Bay compared to dolphins from other sites (Bermuda, Sarasota Bay, and Indian River Lagoon, FL) (*22*). The authors suggest that Charleston and Delaware Bay are more industrial, and therefore had higher point-sources of PFCs to the environment (*22*). In addition to close proximity to urban areas, specific point-source releases of particular

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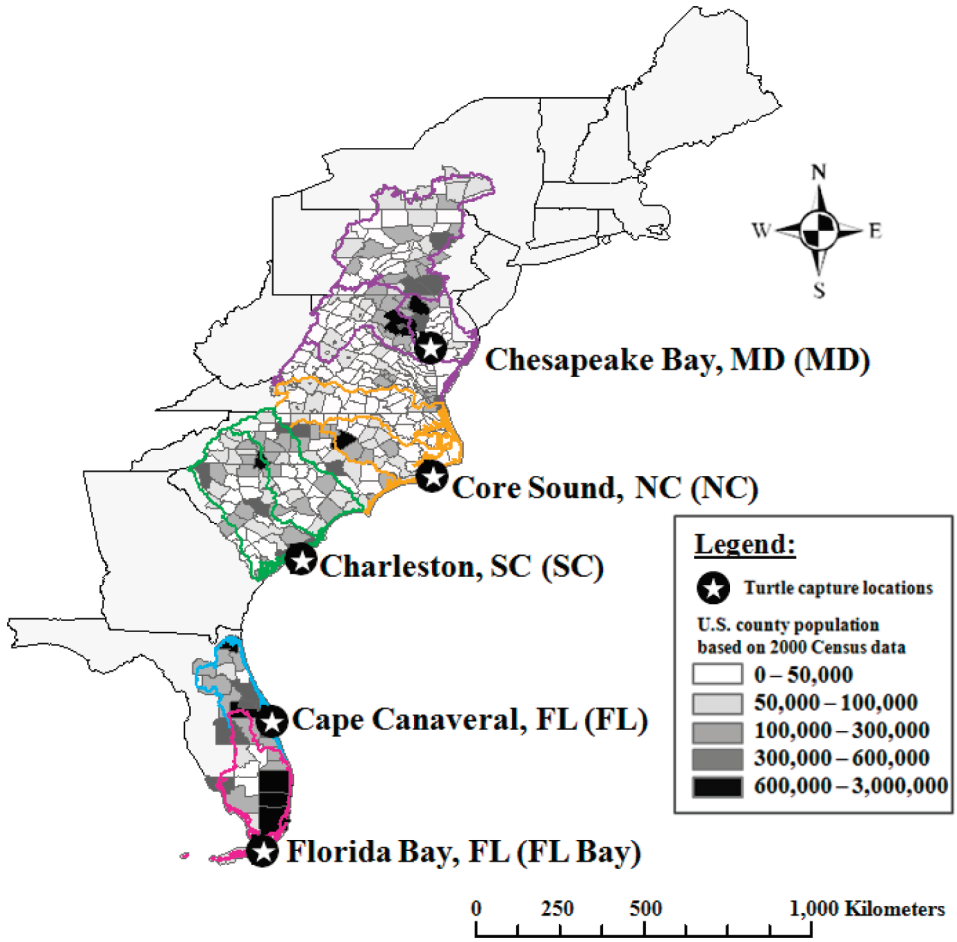

FIGURE 1. Loggerhead sea turtle capture locations along the U.S. East Coast for the spatial trend study. Site abbreviations are listed in parentheses after capture locations. To standardize location for the temporal trend study, samples came only from near Charleston, SC. Watershed areas included for each sampling location are outlined in different colors and are based on a 4-digit hydrological unit code (HUC) found within a 100 km radius of turtle capture locations. Human population of counties that were assigned to each watershed is also shown.

PFCs, such as a spill of aqueous fire-fighting foams (AFFFs) (*23*), a nearby fluoropolymer production factory (*24*), or agricultural application of sewage sludge containing high levels of PFCs (*25*) have also contributed to observed spatial differences. To date, human population, as a proxy for diffuse, nonpoint sources, has not been directly examined as an influence on spatial trends of PFC contamination.

Although there are several PFC trend studies with wild animals, juvenile loggerhead turtles have attributes that may make them a good indicator species for monitoring regional coastal PFC contamination. They are widely distributed throughout temperate and subtropical oceans, and exhibit a carnivorous diet primarily of slow moving or sessile invertebrates (*26*). Neritic juveniles exhibit summertime site fidelity (*27, 28*) during the 11+ years of this life stage (*29*), allowing them ample time to accumulate PFCs from their preferred home range. Since 1978, loggerhead sea turtles have been listed as threatened under the Endangered Species Act (*29*). Moreover, the 2008 U.S. Recovery Plan for this species identifies anthropogenic contaminants as a threat to their population survival, but indicates the great uncertainty concerning this issue (*29*). The current study contributes to this data gap by analyzing 163 juvenile loggerhead plasma or serum samples for spatial and temporal trends of 13 PFCs (see Supporting Information (SI) Table S1 for PFC names and abbreviations). A large archive of loggerhead blood samples was utilized to minimize confounding factors and allow sample selection for a nine-year temporal trend of PFCs within a tight geographic and seasonal range with yearly resolution as well as spatial analyses across five regions along the U.S. East Coast (Figure 1) that expands the previous spatial study for loggerhead turtles (*19*). Furthermore, relationships between turtle PFC concentrations and human population were assessed to begin to understand nonpoint source influences on wildlife concentrations.

Experimental Section

Loggerhead sea turtle plasma or serum samples were acquired from several long-term, in-water projects occurring along the U.S. East Coast. Site abbreviations are in parentheses here and in Figure 1. Turtles were captured using trawl nets near Charleston, South Carolina (SC) and Cape Canaveral, Florida (FL), from pound nets inside Core Sound, North Carolina (NC) and Chesapeake Bay, Maryland (MD), and by hand from research vessels within Florida Bay (FL Bay). The SC and FL turtles were captured at a mean distance of 8.4 km (range ≈ 0.8−23.6 km) from the nearest shore. Turtles were tagged, measured for straight carapace length (SCL), and sampled for blood from the dorsocervical sinus before being released on the same day. Samples were stored frozen until analysis. All samples analyzed were plasma except the MD samples that could not be identified as either serum or plasma. Differences were not expected between these two matrices since a previous study found that PFC concentrations were statistically similar between serum and plasma (*30*).

Several sample selection criteria were set to limit factors that might confound the results among years or regions which

was made possible by a large inventory of archived samples. First, adults were excluded to avoid biases from possible reproductive offloading of PFCs from adult females. Inclusion of only juveniles, based on SCL (range = 53.9−73.9 cm) (*29*), also limited the influence of bioaccumulation through age. In NC and SC, juveniles exhibit summertime site fidelity with many returning to the same site in subsequent summers (*27, 28*). Samples were selected from a limited season (late spring to early fall) to minimize samples from migratory turtles and maximize those from residents. Loggerheads included in the spatial study were collected from late April through early September in only 2005 and 2006 to minimize across-year variation. Since the spatial distribution of PFCs in loggerheads is not uniform (*19*), only turtles captured within a tight latitudinal range (32.20°N to 32.95°N) around Charleston, SC, were used for the 2000−2008 temporal study. Although samples were available from Georgia (GA) coastal waters, these were not selected for the current spatial study. This study was designed to expand the geographical range that had previously shown that turtles from GA had intermediate PFC concentrations compared to FL and NC (*19*).

PFC concentrations were measured at NIST using methods described elsewhere (*31*). Briefly, 0.5−1.0 g samples were spiked gravimetrically with internal standards (listed in SI Table S1), acidified with 50% formic acid (volume fraction), and extracted using 3 mL, 60 mg Oasis WAX solid-phase extraction columns (Waters, Milford, MA). After filtering, extracts were concentrated in volume with nitrogen and spiked with a $^{13}C_2$-PFOA recovery solution. Three nonextracted standards were prepared containing only internal and recovery standards to calculate the recovery of internal standards from the samples.

Calibration curves, ranging from 0.005 to 100 ng of each compound, were added to deionized water and extracted alongside samples. Control materials used in this study included an in-house pool of loggerhead turtle plasma (*Cc* pool) and NIST Standard Reference Material (SRM) 1957 organic contaminants in non-fortified human serum. At least three procedural blanks consisting of deionized water were extracted alongside each batch of samples. Field blanks (n = 13) were prepared by pulling deionized water through available unused blood collection supplies from multiple years and projects to assess possible contamination from sampling supplies. For most samples, field blanks were made from exact or representative lot numbers of Vacutainer tubes and syringe needles.

PFCs were quantified using an Agilent 1100 HPLC (Santa Clara, CA) coupled to an API 4000 tandem mass spectrometer (Applied Biosystems, Foster City, CA) operated in negative electrospray ionization mode as described elsewhere (*31*). PFCs were separated on a Thermo Betasil C8 column (100 mm × 2.1 mm × 5 μm, Franklin, MA) with a methanol: 20 mmol/L ammonium acetate buffer gradient. Injection volume was 20 μL. Compounds were quantified using transitions listed in SI Table S1. PFC concentrations were calculated using a relative response ratio to a structurally similar internal standard, and at least three points of the linear calibration curve that bracketed the peak area in the sample chromatograms. The reporting limit (RL) was conservatively determined as the maximum value resulting from three different calculations: (1) the ng amount of the lowest detectable calibration point divided by the extracted sample mass; (2) the mean plus three times the standard deviation of the ng amount detected in the procedural blanks all divided by the extracted sample mass; or (3) three times the mean concentration (ng/g) detected in field blanks. In other words, for each compound in each sample the RL varied and was the maximum (most conservative) value obtained from all three RL calculations described above. The term RL is used here as suggested by Helsel (*32*) instead of limit of detection (LOD) or limit of quantification (LOQ) to avoid confusion.

For PFOS, which was detected in all samples, conventional statistics were performed on log-transformed concentrations using R statistical software (R development core team, Vienna, Austria) or Statistica (StatSoft, Inc., Tulsa, OK). For all other compounds with <100% detection frequency, statistical testing was performed as suggested by Helsel (*32*) using the R "NADA" package for handling left censored data sets (those with nondetects) without the need to substitute nondetects with an arbitrary value. In NADA, Kaplan−Meier or Regression on Order (ROS) models were used to estimate central tendency and variability. A choice between the two was based on sample size and assumptions of normality. Statistical hypothesis tests were performed for only PFCs that were detected in ≥60% of samples within each data set.

A censored Kruskal−Wallis test followed by pairwise censored Wilcoxon tests were used to determine site differences in PFC concentrations after Bonferroni adjustment to the alpha value. A principle components analysis (PCA) was used to preliminarily assess site differences in PFC compositional pattern using percent of total PFC concentrations after values were mean-centered and variance-scaled to reduce loading bias. The PCA required substitution of nondetects with a value, so half the RL was used. For the temporal assessment, log−linear regressions based on annual geometric means were modeled using the Arctic Monitoring and Assessment Programme (AMAP) PIA program (*33*), and one outlier was taken out of the PFOS and PFNA models by examining internally studentized residuals (>|2.5|). Since the AMAP program requires substitution of nondetects with a value, half the RL was used and the statistical significance of the temporal regressions were confirmed with NADA's maximum likelihood regression for censored data. The possibility of turtle size confounding the spatial and temporal trends was assessed and ruled out as described in the SI.

Geographic information system (GIS) analyses were conducted with ArcGIS software and used 2000 U.S. Census data and a four-digit hydrological unit code (HUC) map from USGS, which maps watersheds. A 100 km radius from the turtle capture locations was used to define the coastal region where watershed boundaries (4-digit HUCs) were likely to provide PFC runoff into turtle habitat of that site. Human population counts were summed for counties that fell fully inside the watershed boundaries and those that had more than half of their land area inside the watershed (Figure 1). Linear regressions were performed between the mean PFC concentrations (PFNA, PFDA, PFUnA, PFTriA, PFHxS, and PFOS) measured in the turtles from each site and the human population inhabiting that site's watershed.

Results and Discussion

Two control materials (*Cc* pool and SRM 1957) were used to compare data among batches and to assess accuracy and precision. Measured concentrations in SRM 1957 were within 20%, on average, of the reference values (*31*). For the predominant compounds in *Cc* pool (PFDA, PFUnA, and PFOS), measured concentrations were within 14%, on average, of past NIST values. PFOS values differed from past NIST values for both control materials by ≤2% (mean ± standard deviation for PFOS: SRM 1957 = 20.7 ng/g ± 0.882 ng/g; *Cc* pool = 15.8 ng/g ± 1.00 ng/g), and relative standard deviations were <7%. Average percent recoveries of internal standards were >64%. Measured concentrations were not corrected for internal standard recovery because calibration solutions were run through the entire procedure so they represented both response and recovery solutions.

PFCs measured in loggerhead samples are presented by site (Table 1) and by year (SI Table S2). Few turtles contained

TABLE 1. Spatial Comparison of Perfluorinated Compounds (ng/g) in Juvenile Loggerhead Plasma/Serum[a]

	Florida Bay			Cape Canaveral, FL			Charleston, SC		
compound	mean (SD)	median	$n > RL$ ($n = 11$)	mean (SD)	median	$n > RL$ ($n = 10$)	mean (SD)	median	$n > RL$ ($n = 9$)
PFHxA	<0.279		0	<0.279		0	<0.279		0
PFHpA	<0.200		0	<0.200		0	<0.200		0
PFOA	0.641 (0.164)	0.553	4	<0.098		0	<0.098		0
PFNA	2.21 (1.07) A	1.83	11	0.141 (0.164) BC	0.057	6	0.059 (0.050) B	0.049	5
PFDA	1.04 (0.233) A	1.025	11	0.157 (0.123) B	0.118	10	0.316 (0.398) BC	0.193	9
PFUnA	1.42 (0.546) A	1.351	11	0.227 (0.111) B	0.184	5	<0.194 B		2
PFDoA	0.108 (0.077)	0.096	11	<0.089		2	<0.089		0
PFTriA	0.203 (0.089) A	0.171	11	0.389 (0.168) AB	0.421	8	0.190 (0.159) A	0.165	6
PFTA	0.063 (0.030)	0.046	3	<0.097		0	<0.097		0
PFBS	0.026 (0.025)	0.016	10	<0.117		0	<0.117		0
PFHxS	0.138 (0.051) A	0.132	11	<0.053 B		2	0.039 (0.038) B	0.024	3
PFOS	3.67 (1.03) A	3.801	11	1.44 (0.94) B	1.24	10	3.86 (2.92) AB	2.87	9
PFOSA	<0.098		1	<0.098		0	<0.098		0

	Core Sound, NC			Chesapeake Bay, MD			Overall Spatial Data set			
compound	mean (SD)	median	$n > RL$ ($n = 15$)	mean (SD)	median	$n > RL$ ($n = 14$)	mean (SD)	median	range ng/g	$n > RL$ ($n = 59$)
PFHxA	<0.315		0	<0.279		0	<0.279			0
PFHpA	<0.200		0	<0.200		0	<0.200			0
PFOA	<0.104		0	<0.326		0	<0.742		<0.076−0.993	4
PFNA	1.30 (3.63) C	0.245	10	0.974 (1.37) C	0.382	14	1.01 (2.09)	0.254	<0.034−14.37	46
PFDA	0.487 (0.601) BC	0.217	11	0.720 (0.817) AC	0.357	14	0.566 (0.599)	0.239	<0.092−3.110	55
PFUnA	0.668 (0.751) B	0.343	12	2.27 (4.20) AB	0.556	9	1.05 (2.20)	0.343	<0.063−16.04	38
PFDoA	0.186 (0.441)	0.055	8	0.240 (0.359)	0.098	7	0.156 (0.289)	0.067	<0.040−1.761	23
PFTriA	0.717 (0.484) B	0.551	11	0.789 (0.787) B	0.561	14	0.490 (0.531)	0.354	<0.100−3.278	50
PFTA	<3.97		0	<0.324		1	<0.101		<0.060−0.266	4
PFBS	0.024 (0.042)	0.006	3	<0.389		0	0.024 (0.037)	0.012	<0.010−0.195	13
PFHxS	0.135 (0.107) AB	0.109	15	0.065 (0.034) B	0.063	8	0.089 (0.076)	0.070	<0.032−0.317	39
PFOS	6.47 (7.53) A	3.134	15	9.34 (11.4) A	3.54	14	5.38 (7.22)	3.01	0.305−36.6	59
PFOSA	<0.070		0	<0.098		1	<0.098		<0.070−0.123	2

[a] No descriptive statistics were performed for compounds with ≤20% detection frequency; those are shown as <maximum reporting limit. PFOS concentrations were calculated conventionally, all other concentrations were calculated using either Kaplan-Meier or Regression on Order statistics. $n > RL$ indicates the number of samples above the reporting limit; SD is one standard deviation. Different letters after means indicate significant differences among regions (by Kruskal-Wallis multiple comparison test for PFOS ($p < 0.05$) and by censored pairwise Wilcoxon comparisons with Bonferroni adjusted alpha values for all other PFCs ($p < 0.005$).

detectable concentrations of PFOA, PFBS, and PFOSA, and no samples had detectable concentrations of PFHxA or PFHpA. Longer-chained PFCAs (PFNA, PFDA, PFUnA, and PFTriA), PFHxS, and PFOS were detected in most samples. Similar to other wildlife (*6*) and to the previous loggerhead study (*19*), PFOS was the predominant PFC in concentration, and longer-chained PFCAs (PFNA, PFDA, PFUnA, and PFTriA) were higher in concentration than shorter-chained PFCAs (*17, 22, 34*). In general, concentrations of odd-chained PFCAs were higher than the even-chained PFCA with one less carbon. Originally, this observation was noted for Canadian Arctic wildlife (*34*) and has since been seen in loggerhead turtles (*19*) and other aquatic wildlife in the southeast U.S. (*21*). PFC concentrations measured in this study can be compared to those measured previously in loggerhead turtles captured from similar locations in 2003 (*19*). Concentrations of most compounds were similar between studies except PFOS and PFOA were lower in the current study. A detailed comparison and reasons related to improvements in analytical procedures are presented in the SI.

Along the southeastern U.S. Atlantic coast, an increasing northward spatial trend of PFC concentrations was generally observed in loggerhead turtles sampled during the current study (Table 1), similar to what was previously reported (*19*). However, the expected declining trend did not continue into the southernmost region, FL Bay. Turtles from FL Bay had some of the highest PFC concentrations, some even higher than MD. Generally, FL and SC had the lowest means for most PFCs, whereas MD and FL Bay had some of the highest. For PFOS, the trend was MD > NC > SC ≈ FL Bay > FL. Significant site differences in PFOS concentrations were observed between FL and the two northernmost study regions, MD and NC ($p = 0.03$). In addition, significant site differences were seen for PFNA, PFDA, PFUnA, PFTriA, and PFHxS ($p < 0.005$). For these compounds, either MD or FL Bay had the highest concentrations, suggesting significant inputs of PFCs into these regions compared to others. FL Bay turtles had the highest concentrations of PFNA, PFDA, and PFHxS, whereas MD turtles were highest in PFUnA and PFTriA. In addition, FL Bay contained the only turtles with detectable concentrations of PFOA.

A PCA was used to investigate PFC patterns among sites (Figure 2). A distinct clustering of the PC scores for FL Bay turtles indicates a unique pattern relative to the other regions. The first two principle components (PC1 and PC2) accounted for 60% of the variance. PFOS and PFTriA contributed the greatest loading in PC1 and PC2, respectively, thus these compounds became the focus of a more thorough assessment into the spatial pattern differences. PFOS made up >60% of the total PFCs in all sites, except in FL Bay where PFCAs contribute ≈ 60% of the total (Figure 3). This difference separated FL Bay turtles from the rest on PC1. Furthermore, FL Bay turtles contained a lower proportion of PFTriA than other sites, causing moderate separation on PC2. Lower interturtle variability at FL Bay also helped emphasize their unique pattern by grouping them closer together than turtles

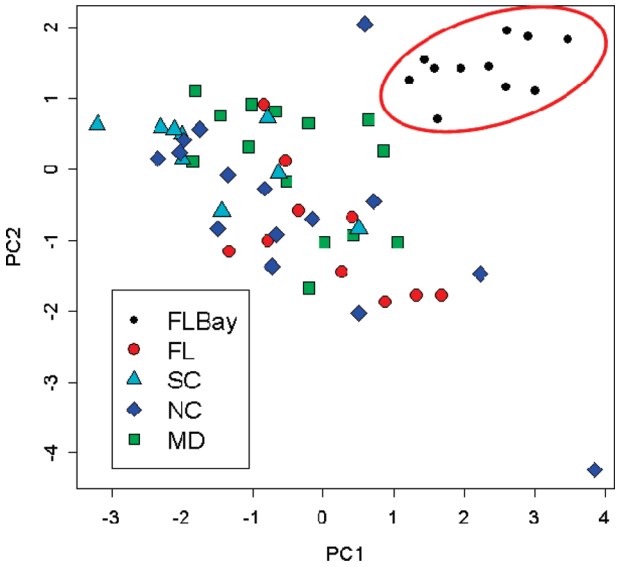

FIGURE 2. Plot of principle component scores of perfluorinated contaminant concentrations in loggerhead sea turtles plasma/serum from five sites: Florida Bay (FL Bay), Cape Canaveral (FL), Charleston (SC), Core Sound (NC), and Chesapeake Bay (MD). FL Bay samples are encircled.

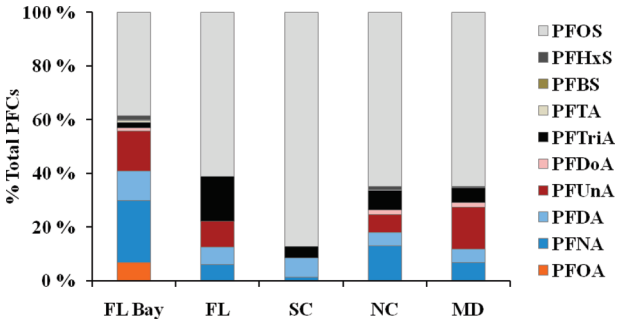

FIGURE 3. Perfluorinated compound (PFC) patterns in loggerhead sea turtle plasma/serum from five capture regions: Florida Bay (FL Bay), Cape Canaveral (FL), Charleston (SC), Core Sound (NC), and Chesapeake Bay (MD). Percent of total PFC contribution was based on means of each region from Table 1. When no mean could be calculated because samples from that region were nondetectable, that compound was considered 0% of the total PFC concentration.

from other regions. Future studies should investigate why FL Bay turtles accumulate more PFCAs, especially PFOA and PFNA. Local point sources of these particular compounds may be elevating the exposure of wildlife in FL Bay.

PFOS environmental emissions are largely driven by consumer use and disposal of stain repellent-treated carpets and waterproofed apparel compared to direct releases from chemical manufacturing (*2*). For this reason, human population would likely influence the regional PFOS environmental concentrations and serve as a proxy for the magnitude of nonpoint source releases of PFOS. In fact, several studies have associated PFC contamination with urban areas (*20, 35, 36*). A GIS spatial analysis was undertaken to assess whether human population within each watershed was related to spatial differences in the loggerhead plasma/serum PFOS and other PFC concentrations. Positive relationships were observed for PFOS ($r^2 = 0.75$, $p = 0.06$) and PFUnA ($r^2 = 0.81$; $p = 0.04$) (Figure 4). These indicate that 75 and 81% of the variance in PFOS and PFUnA concentrations, respectively, were explained by human population inside the designated watersheds. These findings suggest that nonpoint sources of PFOS and PFUnA are more important drivers to

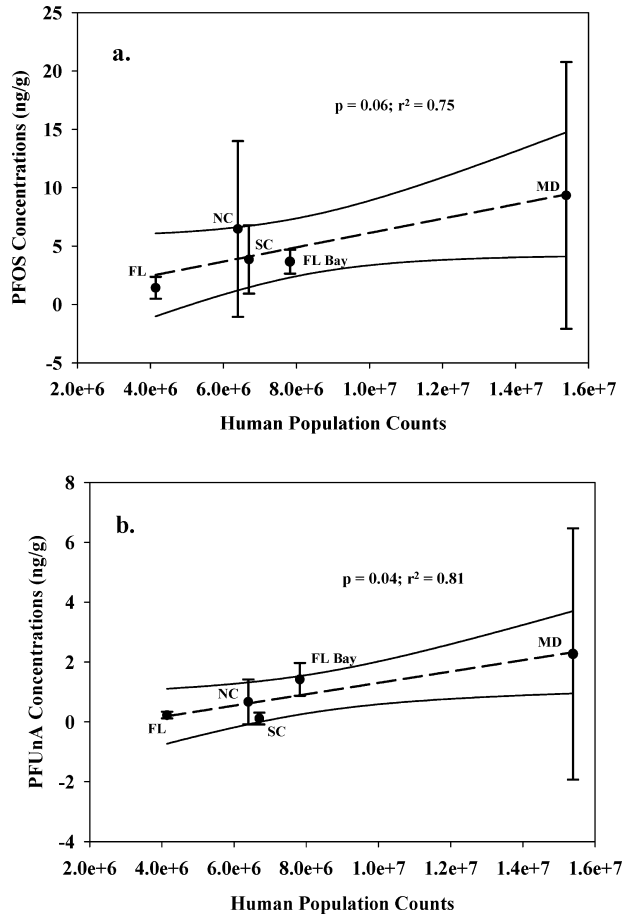

FIGURE 4. Linear regressions of (a) PFOS and (b) PFUnA concentrations as a function of human population counts. Error bars are one standard deviation, and curved 95% confidence intervals (curved solid lines) are plotted along the line of best fit (dashed line).

the exposure of nearshore, coastal wildlife compared to point sources. The relationships also indicate that humans residing in the nearby environment provide greater PFOS and PFUnA inputs to their coastal region than distant inputs from atmospheric or oceanographic transport. Interestingly, the NC site fell above the PFOS regression line (Figure 4a), suggesting a factor in addition to human population may be influencing this site. Plasma samples from people in Charlotte, NC, have consistently higher PFOS concentrations than from other U.S. cities (*15, 37*). North Carolina is also known for furniture manufacturing and has several military bases within this watershed. AFFFs used at military bases and civilian airports have been shown to contribute to PFC contamination (*23, 38*). Future studies could examine historical application of PFC-based chemicals to furniture upholstery, use of AFFFs at military bases and airports, as well as other land use sources of PFCs as part of a more comprehensive GIS investigation to explore potential reasons for observed higher concentrations in NC or any other PFC contaminated area.

Temporal trends were examined over a nine-year period in loggerheads captured near Charleston, SC (SI Table S2). A decreasing trend in concentration was significant for PFOS ($p = 0.02$, $r^2 = 0.56$) and PFNA ($p = 0.01$, $r^2 = 0.71$ from AMAP program; $p = 0.01$, likelihood $r = 0.24$ from maximum likelihood regression in NADA) (Figure 5). Other compounds did not significantly change through time. Temporal changes were most dramatic for PFOS, which decreased 20% annually, while PFNA decreased 11% annually. Decreases in PFOS concentration within the past decade coincide with the

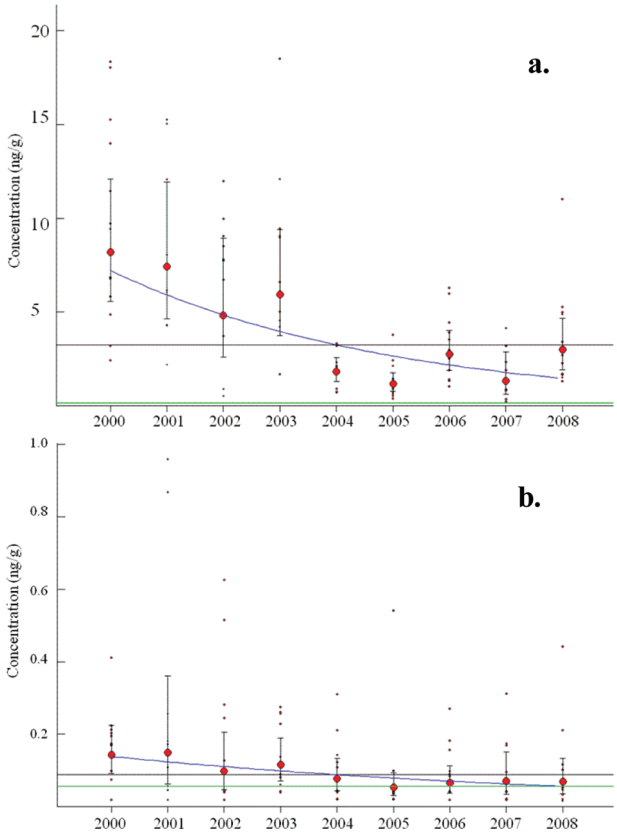

FIGURE 5. Temporal trends of a) PFOS and b) PFNA concentrations in plasma from loggerhead sea turtles from Charleston, SC, drawn with AMAP PIA program. Individual data points are black, geometric means are red, and error bars are 95% confidence intervals. The blue lines are the log linear regression, black horizontal lines indicate the overall mean, green lines are the average reporting limit.

production phase-out of perfluorooctane sulfonyl fluoride (POSF), a PFOS precursor, by its largest global manufacturer, 3M (*2*). A dramatic reduction in turtle PFOS concentration was evident starting in 2004 (Figure 5a), two years after 3M completed this phase-out. Similar decreases in PFOS have also been reported in humans from the U.S. (*15*) and Norway (*39*). PFOS in human milk samples from Sweden were stable from 1996 to 2004, but showed an apparent decrease after 2001 (*40*). PFOS also decreased in other marine wildlife since 2000 (*11–13*). In addition, PFOS and PFNA concentrations peaked in Lake Ontario lake trout in the late 1980s or early 1990s with possible declines since then (*41*). However, not all studies have shown decreases in PFCs since 2000. Some PFCs, including the longer-chained PFCAs (like PFNA, PFDA, and PFUnA), have increased in the past decade in marine mammals (*17, 18, 42*). Furthermore, PFOS concentrations measured in east Greenland polar bear livers have increased as late as 2005 (*43*). Differences in temporal resolution and collection sites among studies may reconcile differences in recent temporal trends seen in wildlife. Additionally, PFC contamination across the world reflects local sources and/or long-range transport processes of PFCs or their precursors, such as fluorotelomer alcohols (FTOHs). Southeast U.S. marine wildlife are near known PFC production sites and large human populations, so temporal trends in this region may reflect changes more rapidly than regions far removed from production, such as the Arctic. Remote regions may receive delayed temporal changes in PFCs due to long-range atmospheric and oceanic transport (*1, 2, 44*), and remote wildlife samples may reflect decreases in PFOS and other PFCs in years to come.

In summary, occurrence of PFCs in juvenile loggerheads along the U.S. East Coast agrees with reports for other aquatic wildlife, and PFOS is the predominant PFC. FL Bay is unique in PFCA contamination and had lower variability. This lower variability is likely due to a more resident population of loggerheads there, as shown by higher recapture rates in FL Bay compared to the other sites sampled in this study (B. Schroeder, unpublished data). Further investigation could examine local sources of PFOA and PFCAs to this region. MD has the highest concentrations of PFOS in loggerheads and would be a good study area for assessing PFOS health effects, which currently are unknown for sea turtles. A preliminary study observed significant correlations between plasma chemistry values and immune function with concentrations of PFOS in loggerheads from primarily Georgia and South Carolina (*45*). These correlations were consistent with known toxic end points from laboratory studies (*8*), and more pronounced effects may be expected in the more contaminated MD site. The declining PFOS temporal trend is supported by other recent time trends and is consistent with 3M's phase-out of PFOS-related products (*15*). A significant decrease in PFNA was also observed. A relationship was apparent between human population and PFOS and PFUnA concentrations, suggesting that nearby human nonpoint sources greatly influence these PFC concentrations in nearshore, coastal wildlife. Continued monitoring of PFCs and other environmental contaminants in endangered and threatened sea turtles will help determine the changing magnitude of this understudied anthropogenic threat to their populations.

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Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Supporting Information Available

Includes PFC abbreviations, internal standards and transitions used for quantification; PFC concentrations found in the 104 turtles selected for the temporal trend; a discussion ruling out turtle size as a confounding factor in the spatial and temporal trends; a discussion of differences between the PFC measurements in the current study and those in Keller et al. (*19*); correlations among individual PFCs; and a list of permits allowing the collection of loggerhead sea turtle samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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