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SURVEY OF TWO PERFLUORINATED ORGANIC COMPOUNDS (PFOA AND PFHxA) IN WATER AND BIOTA SURROUNDING A POLYFLUORINATED CHEMICAL PLANT

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ABSTRACT: Perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA) concentrations were measured in water and biota samples collected within and near a polyfluorinated chemical plant in coastal Mississippi. Effluents from the site and from the local public water treatment plant were sampled along with municipal water supplies, shallow groundwater beneath the site, nearby surface waters, and local biota. Highest concentrations were from stormwater ([PFOA] = 85–530 ng/l; PFHxA = 140–590 ng/l) and shallow groundwaters ([PFOA] = 44–1000 ng/l; PFHxA = 210–3100 ng/l) collected at the site. The local public water treatment effluent also had relatively high PFHxA concentrations (310–590 ng/l). Intermediate PFOA concentrations were measured in effluent samples (21–33 ng/l) and irrigation water from a public works facility (15–48 ng/l). Drinking water and all surface waters had low PFOA and PFHxA concentrations (PFOA = 1.1–3.0 ng/l; PFHxA < 1.4 ng/l). Tissues from local fish and blue crab had undetectable PFOA and PFHxA concentrations. Results suggest that evaporation and subsequent percolation of contaminated stormwater into the shallow aquifer is the major pathway for perfluorinated contaminants to escape from this site.

KEY WORDS: Perfluorooctanoic acid, C8, perfluorohexanoic acid, stormwater, groundwater

INTRODUCTION

Perfluorinated organic compounds (PFCs) were first manufactured in the 1940's and have been used in a variety of applications ranging from providing water and oil repellency for a multitude of surfaces (clothing, furniture, floor waxes, etc) to its use in aircraft production, electronics, personal care products, cookware and food packaging products. These compounds are of particular concern due to their ubiquity and persistence in the environment and their bioaccumulation in wildlife and humans. The average PFOA concentration in American adults' blood serum is 4 ng/ml (Calafat et al. 2007) while much higher concentrations (> 76 ng/ml) have been observed in other populations exposed to contaminated drinking waters (Bartell et al. 2010; Hoffman et al. 2011). PFCs are suspected to be carcinogenic and may also act as endocrine disruptors (White et al. 2011). In an effort to better understand the environmental and organismal impacts of such compounds, many studies have assessed contamination in water supplies (Post et al. 2009), wastewater treatment plants (Sinclair and Kannan 2006; Guo 2010), and a wide variety of environmental samples including fresh and marine waters (Kallenborn et al. 2004, Yamashita et al. 2005, Tanaka et al. 2006, Skutlarek et al. 2006, deVoogt et al. 2006, Weremiuk et al. 2006, Loos et al. 2007), stormwater (Murakami et al. 2009a, Xiao et al. 2011, Nguyen et al. 2011), groundwaters (Shultz et al. 2004, Murakami et al. 2009b) and biota ranging from small invertebrates (vanLeeuwen et al. 2006, Gulkowska et al. 2006, Nakata et al. 2006) to large mammals in a wide variety of habitats (Giesy and Kannan 2001). Few studies have examined a wide variety of sample types (municipal waters, natural waters and biota) collected within and near a single manufacturing plant.

The First Chemical Corporation (FCC) in Pascagoula,

MS uses several industrial processes to purify fluorotelomer alcohols as precursors to the manufacture of surfactants and ingredients for fire-fighting foam. This study was conducted on samples collected during 2008 and 2010, as a follow up to the 2006 Pascagoula baseline study conducted by FCC to provide a snapshot of perfluorooctanoic acid (PFOA) concentrations in local waters and biota prior to the startup of a new fluorotelomer alcohol purification operation at the site. The manufacturing of 8–2 fluorotelomer alcohol, a precursor of PFOA, is currently being phased out and being replaced by a process that exclusively produces 6–2 fluorotelomer alcohol (6–2 FTOH). Therefore, analysis of perfluorohexanoic acid (PFHxA), which is both a potential low level impurity and degradation product of 6–2 FTOH, was also conducted for samples in this study. Industrial effluents from the chemical plant are discharged to the Pascagoula Publicly-Operated Treatment Works (POTW) wastewater treatment facility which in turn discharges its treated effluent to the Pascagoula River. The objective of this study was to report concentrations of 2 PFCs within and around an operational perfluorinated chemical plant and in local municipal waters (i.e., water supply and wastewater treatment plant effluent) and biota.

MATERIALS AND METHODS

Sample Collections

To examine sources of PFOA and PFHxA, I collected samples from a variety of locations in 2008 and 2010, including the effluent from the FCC to the POTW, the POTW effluent discharged to the Pascagoula River, and solid wastewater sludge from the Pascagoula POTW. Also, stormwater and groundwater samples were collected on the chemical

FIGURE 1. Map of the study area near Pascagoula, Mississippi showing the location of the chemical plant (square symbol ■) and all sampling locations (black circles ●). Biota were sampled at the 3 estuarine sites.

plant site and municipal water samples were collected to evaluate background concentrations of the local drinking water supply and irrigation water used at the West Jackson County Landfarm which originates from the nearby City of Ocean Springs POTW. Consistent with the FCC 2006 baseline study, a variety of surface water samples were collected from locations in nearby rivers and in Mississippi Sound (Figure 1). The Pascagoula River was sampled 34 km upstream and 2 km downstream of the Pascagoula POTW discharge (Figure 1). An additional river sample was collected from the Escatawpa River before its confluence with the Pascagoula River. Estuarine samples included a site outside of Bayou Cassotte, a heavily industrialized bayou near the FCC plant; a site in Grand Bay, a nearby NOAA National Estuarine Research Reserve; and a site in Mississippi Sound near the mouth of the Pascagoula River. Hardhead Catfish (*Ariopsis felis*), Spotted Seatrout (*Cynoscion nebulosus*) and the blue crab (*Callinectes sapidus*) were collected in 2008 at the same locations as the 2006 Pascagoula baseline study. Biota sampling sites corresponded to water sampling sites (Figure 1). All samples were collected from mid-July to

early September, consistent with the 2006 baseline study methodology.

Effluent samples

FCC effluent samples were provided by FCC, as a QA/QC split from their weekly monitoring. This sample was composited from hourly sub-samples taken over a 24-hour period. Effluent samples from the Pascagoula POTW were collected on 18 August 2008 and 21 August 2010. Irrigation water samples were taken from a spigot at the West Jackson County Landfarm on 31 July 2008 and 1 September 2010. This effluent comes from the City of Ocean Springs POTW and is not connected to the Pascagoula water supply or the Pascagoula POTW.

POTW Sludge Sampling

Sludge samples were collected from the Pascagoula POTW on 18 August 2008 and 21 August 2010 from the top 5 cm of the sludge bed, placed in a clean aluminum mixing bowl, and homogenized in the field. In 2010 duplicate field samples were collected within 1 m of each other. Sample bottles were filled, placed on ice and shipped to the contract laboratory.

Water Samples

Storm-water samples were taken from a stormwater trough at the Pascagoula plant on 11 August 2008 and 12 August 2010 after rain events by submerging the sample bottle and capping while submerged to avoid sampling surface microlayer particles. Groundwater was sampled from three pre-existing shallow groundwater wells (screened from 4.3 to 4.9 m) at the FCC site on 30 July 2008 and 12 August 2010 near a new chemical process unit (Figure 2). Prior to sampling, each monitor well was purged of 3 well volumes using a peristaltic pump with aged and pre-cleaned Tygon tubing. None of the wells were pumped dry during the purging and sampling. Water from this unconfined sand aquifer is not a potable water source and is isolated from deeper aquifers by a clay confining layer. Samples were collected at monitoring wells MW-17 and MW-63 near the new chemical process unit whereas monitor well MW-28 was down gradient from the process unit (Figure 2).

Municipal drinking water samples from the Jackson County Port Authority were collected directly from taps at the chemical plant on 31 July 2008 and on 12 August 2010. Surface water samples were collected from the Pascagoula and Escatawpa Rivers, Bayou Cassotte, Grand Bay and the Mississippi Sound (Figure 1) during flood and ebb tides at approximately mid-stream and mid-depth using an aged,

pre-cleaned acrylic horizontal Beta water sampler (Wildco part number 1940-G64). All water samples were collected in pre-cleaned and pre-labeled bottles and stored on ice and cold-shipped to the contract laboratory overnight.

Biota samples

Hardhead Catfish and Spotted Seatrout were collected at the Grand Bay and Mississippi Sound stations with gill nets deployed for 2 hours on 8, 15, 20, 22, and 28 August 2008. Six fish of each species were collected, ranging in size from 23–43 cm total length (TL). The captured fish were placed in a live well, whereas by-catch species or fish not meeting the minimum size requirements were returned to the water to avoid injury. The selected fish were euthanized with MS222 and placed in Ziploc™ bags on ice until tissues were processed. Fillets and carcass (viscera, liver, and skin) were separated, sealed in Ziploc™ bags, and frozen at -20°C . Blue crabs were collected from the same sites with a baited crab trap deployed over a tidal cycle. Six legal-sized crabs (> 12.7 cm carapace width) were placed directly on ice, whereas by-catch and crabs not meeting the minimum size requirements were returned to the water as soon as possible. Soft tissues samples were separated from the crabs and placed in Ziploc™ bags and frozen (-20°C). Tissue samples were shipped on dry ice overnight to the contract laboratory.

FIGURE 2. Site map of the chemical plant showing the location of the 3 monitoring wells used to collect groundwater samples. Arrows denote the primary direction of groundwater movement based on the hydraulic gradient of the water table across the site during the Pascagoula Baseline Study

Analytical Methods

Water samples from 2008 and 2010 were analyzed by Axys Analytical Services, Ltd (Sidney, British Columbia, Canada) for PFOA and PFHxA concentrations. Since a different lab, MPI Research (formerly Exygen; State College, Pennsylvania), analyzed water samples from FCC's 2006 baseline study, duplicate water samples were collected in 2008 and sent to MPI Research to compare results from the two labs. Sample preparation, instrumental analysis and analyte quantification procedures followed Axys Method MU-060 *Analytical Procedure for the Analysis of Perfluorinated Organics Compounds in Aqueous Samples by LC-MS/MS*. Accurately weighed samples (about 500 g) were spiked with ^{13}C -labelled quantification standards, extracted and cleaned using solid phase extraction (SPE) cartridges. Target analytes were extracted in basic methanol. After being spiked with labeled recovery (internal) standards, the extract was analyzed using HPLC-MS/MS. Analyte concentrations were determined by isotope dilution/internal standard method, comparing the area of the quantification ion to that of the ^{13}C -labelled quantification standard and correcting for response factors. The limit of detection (LOD) and limit of quantification (LOQ) for both PFOA and PFHxA ranged from 0.99–1.9 for PFOA and 1.0–1.4 ng/l for PFHxA during 2008. The LOD and LOQ for PFOA and PFHxA during 2010 ranged from 1.0–2.6 ng/l.

For sludge and tissue samples, sample preparation and analyte quantification procedures followed Axys Method MLA-041: *Analytical Procedure for the Analysis of Perfluorinated Organic Compounds in Solid Samples by LC-MS/MS*. Accurately weighed samples (about 5 g dry) were spiked with ^{13}C -labelled quantification standards and extracted in acetic acid and basic methanol. The extract was purified using SPE cartridges and activated carbon. The extract was analyzed using HPLC-MS/MS with the isotope dilution/internal standard method by comparing the area of the quantification ion to that of the ^{13}C -labelled quantification standard and correcting for response factors. The LOD for this method was 1.9–2.5 ng/g.

RESULTS AND DISCUSSION

Effluents

The PFOA concentrations of effluent from the chemical plant were 38 ng/l in 2008 and 13 ng/l in 2010, similar to that measured during the 2006 baseline study (Table 1). The PFHxA concentrations were 590 ng/l in 2008 and 310 ng/l in 2010. The PFOA concentrations in the POTW effluent from 2006 to 2010 were similar to the FCC effluent (21 ng/l–33 ng/l). The PFOA concentrations of the Ocean Springs POTW effluent water used for irrigation at the Jackson County Landfarm were 11 ng/l in 2006, 48 ng/l in 2008 and 16 ng/l in 2010. The PFHxA concentrations in this irrigation water were 22 ng/l and 8 ng/l during 2008

and 2010, respectively. This irrigation water is not connected to the Pascagoula water supply or the Pascagoula POTW. These results appear to be within the normal variability of PFOA concentrations in these different effluents, which are all lower than PFOA concentrations measured in 6 U.S. city wastewater effluents (40 ng/l–2420 ng/l; 3M Environmental Laboratory 2001). The PFHxA concentrations were on the low end of measurements from 19 different wastewater treatment plants in Korea (3.4 ng/l–591 ng/l; Guo et al. 2010). Sewage treatment plants can be a source of PFOA if the influent stream contains significant concentrations of PFOA precursors (Sinclair and Kannan 2006). Guo et al. (2010) found that the concentrations of PFCs in POTW were highest in large cities of Korea, suggesting that household sewage is likely a larger source of some PFC's to the environment than industrial wastewaters, which had high concentrations but small release volumes.

Sludge samples

The PFOA concentrations in sludge samples from 2008 and 2010 were similar (32 $\mu\text{g/kg}$ and 33 $\mu\text{g/kg}$, respectively) and were lower than during the 2006 baseline study (68 $\mu\text{g/kg}$; Table 1). The PFHxA concentrations in the sludge were 6.6 $\mu\text{g/kg}$ in 2008 and 2.5 $\mu\text{g/kg}$ in 2010. The PFOA concentrations from the wastewater sludge are on the low end of the range reported in sludge from 6 U.S. cities which ranged from < 0.2 $\mu\text{g/kg}$ –244 $\mu\text{g/kg}$ (3M Environmental Laboratory 2001). Guo et al. (2010) found PFOA concentrations in wastewater sludge ranged from below detection (<4.0 $\mu\text{g/kg}$) to 24.7 $\mu\text{g/kg}$ in Korea while PFHxA concentrations were all below detection (<4 $\mu\text{g/kg}$).

Water Samples

The PFOA concentrations measured in water samples by MPI and Axys labs were very highly correlated ($y = 1.01x + 8.7$; $r^2 = 0.996$, where x and y are the PFOA concentrations from MPI and Axys, respectively), showing good agreement among these independent laboratory analyses (Table 1). The PFOA concentrations of stormwater samples collected in 2008 and 2010 were 530 ng/l and 85 ng/l, respectively, while PFHxA concentrations in stormwater in 2008 and 2010 were 590 ng/l and 140 ng/l, respectively. These stormwater concentrations were much higher than the effluent from the chemical plant, suggesting a source of PFOA within the plant grounds, such as from a leak or from released aerosols that settled onto surfaces and entrained into stormwater effluent. These measured concentrations are high relative to other studies that examined stormwater, although most other studies sampled in urbanized areas rather than from a chemical plant site. For example, stormwater from Minnesota's Twin Cities metropolitan area had a mean PFOA concentration of 9.3 ng/l (Xiao et al. 2011) while an urbanized region of Singapore had PFOA concentrations of 5 ng/l – 31 ng/l (Nguyen et al 2011), and stormwater runoff in Tokyo had PFOA concentrations ranging

TABLE 1. Perfluorooctanoic acid (PFOA) concentrations in 2006, 2008, and 2010 and perfluorohexanoic acid (PFHxA) concentrations in 2008 and 2010 for water samples collected near a chemical plant in Pascagoula, MS during this study. Number in parenthesis shows minimum limit of detection (ND) or quantification (NQ).

Sample location	2006* PFOA (ng/l)	2008a** PFOA (ng/l)	2008b PFOA (ng/l)	2010 PFOA (ng/l)	2008 PFHxA (ng/l)	2010 PFHxA (ng/l)
Effluent POTW	33	17	21	33	22	14
Effluent POTW lab dup		16				
Effluent FCC	10	40	38	13	590	310
Effluent FCC lab dup		45				
Effluent FCC - field dup	11	49				
Stormwater FCC	460	480	530	85	590	140
Stormwater FCC lab dup		500				
Stormwater FCC - field dup		700				
Irrigation water - Ocean Springs POTW	11	43	48	15	22	7.3
Irrigation water - Ocean Springs POTW - field dup				17		8.6
Pascagoula drinking water	ND (1.6)	ND	2.8	ND	1.6	ND
Pascagoula drinking water - field dup	ND (1.6)	ND	2.5	1.4	1.7	ND
Monitor well 17	44	1000	1000	280	790	520
Monitor well 28	NQ (7.8)	94	82	250	210	360
Monitor well 28 lab dup		91				
Monitor well 63	79	250	290	940	810	2900
Monitor well 63 - field dup		260		950		3100
Pascagoula River upstream high tide	NQ (7.8)	ND	2.9	1.7	3.7	ND
Pascagoula River upstream high tide - lab dup				1.5		ND
Pascagoula River upstream low tide	NQ (7.8)	ND	2.2	1.5	2.1	ND
Pascagoula River downstream high tide	NQ (13)	ND	1.8	2.1	ND	ND
Pascagoula River downstream low tide	NQ (13)	ND	2.4	2.2	1.3	ND
Escatawpa River high tide	NQ (13)	ND	1.6	1.7	2	ND
Escatawpa River low tide	NQ (13)	ND	2.6	1.7	1.5	ND
Bayou Cassotte high tide	NQ (13)	ND	1.2	2.2	ND	1.4
Bayou Cassotte low tide	NQ (13)	ND	1.7	2.1	1.5	1.6
Mississippi Sound high tide	NQ (13)	ND	2.1	1.7	1.6	ND
Mississippi Sound low tide	NQ (13)	ND	1.8	2.2	ND	ND
Grand Bay high tide	NQ (7.8)	ND	2.2	2.9	1.7	1.3
Grand Bay high tide lab dup				2.5		1.4
Grand Bay low tide	ND (1.6)	ND	3	2.7	2.8	ND
	(µg/kg)		(µg/kg)		(µg/kg)	
Sludge - Pascagoula POTW	68		32	33	6.6	2.5
Sludge - Pascagoula POTW - field dup	67			34		2.5

*Data from 2006 was provided by the First Chemical Corporation's Pascagoula Baseline study.

** Results from MPI Research Labs

from 15 ng/l to about 105 ng/l (Murakami et al. 2009a).

Groundwater collected during 2008 from monitor well MW-17 (Figure 2) contained the highest PFOA concentration (1000 ng/l) of all water samples in this study (Table 1). Groundwater from MW-63 had a lower PFOA concentration (290 ng/l) and groundwater collected down gradient of the new chemical processing unit at MW-28 had still lower PFOA concentrations among lab and field duplicates (82–94 ng/l). During the 2010 sampling, the PFOA concentration in MW-17 was 280 ng/l while MW-28 and MW-63 had PFOA concentrations of 250 and 945 (± 5 ng/l), respectively. The PFHxA concentrations in MW-17

were 790 ng/l and 520 ng/l during 2008 and 2010, respectively. The PFHxA concentrations at MW-28 and MW-63 followed the same trend as the PFOA concentrations with lower concentrations during 2008 (210 and 810 ng/l, respectively) than during 2010 (360 ng/l and 3000 $\pm$ 100 ng/l, respectively). Notably, the latter measurement was the highest PFHxA concentration observed for any water sample during the study. Published values of PFOA in shallow groundwater are sparse in the literature as most studies have justifiably focused on drinking water wells which often pump from deeper aquifers. However, groundwater from 33 m depth beneath metropolitan Tokyo had lower

PFOA concentrations (0.1 ng/l–94 ng/l; Murakami et al. 2009b) than those reported here. More extreme cases of PFC contamination have been observed in other shallow groundwaters where sources of PFCs are high. For example, extremely high PFOA concentrations were measured (up to 6.57×10^6 ng/l) in shallow groundwaters beneath US Air Force's fire training pads, where PFCs were in heavy use over long periods (Shultz et al. 2004).

The PFOA and PFHxA concentrations in drinking water supplied by the Jackson County Port Authority were some of the lowest observed in the study (<2.8 ng/l; Table 1). For comparison, PFOA concentrations in drinking water in 6 southern U.S. cities (Decatur, AL; Mobile, AL; Columbus, GA; Pensacola, FL; Cleveland, TN and Port St. Lucie, FL), was measured during 1999–2000 and found that it was only detectable (> 7.5 ng/l) in Columbus, GA where concentrations up to 27 ng/l were found (LOQ of 25 ng/l; 3M Environmental Laboratory 2001). Other studies have shown drinking water PFOA concentration in New Jersey (< 39 ng/l (Post et al. 2009) were similar to those typically measured in several Asian countries (< 0.1 –41 ng/l; Saito et al. 2004; Tanaka et al. 2006), although sporadic concentrations from some sites were as high as 456 ng/l (So et al. 2007).

All 2008 and 2010 surface water samples from the Pascagoula River, Escatawpa River, Bayou Cassotte, Grand Bay, and the Mississippi Sound had PFOA concentrations that ranged from below detection (< 1.0 ng/l) to 3.0 ng/l (Table 1). The PFHxA concentrations were also undetectable or low in all surface water samples (< 1.0 –3.7 ng/l). The surface water concentrations reported here are on the low end of those reported in other coastal and fresh waters (Kallenborn et al. 2004, Yamashita et al. 2005, Tanaka et al. 2006, Skutlarek et al. 2006, deVoogt et al. 2006, Weremiuk et al. 2006, Loos et al. 2007).

Biota

PFOA concentrations in all Hardhead Catfish, Spotted Seatrout, Eastern oyster (*Crassostera virginica*) and blue crab samples (fillets and viscera) were low in the 2006 Pascagoula baseline study (1.4–2.2 ng/g). Hardhead Catfish, Spotted Seatrout and blue crab all had undetectable concentrations of PFOA and PFHxA (< 2.5 ng/g) with the analytical limits of the analytical technique used in 2008. Oysters were not sampled during 2008. The 2006 baseline study results are on the low end of reported PFOA concentrations in fish

from other North American studies (1.0–44 ng/g; Martin et al. 2004, Furdui et al. 2007). Many studies in Europe and Asia have also reported a large percentage of undetectable concentrations in fish (57–85%; van Leeuwen et al. 2006, Gulkowska et al. 2006, Tseng et al. 2006) and crustaceans (30–100%; van Leeuwen et al. 2006, Gulkowska et al. 2006, Nakata et al. 2006).

CONCLUSION

Cumulatively, the results of this study show that stormwater and shallow groundwater near the chemical plant appear to have elevated concentrations of PFOA and PFHxA. The PFCs from the FCC facility are likely entrained into stormwater where evaporation may concentrate PFCs, which then percolate into the shallow sand aquifer, thereby resulting in the high groundwater concentrations observed in this study. Short chain PFCs ($C \leq 8$), such as PFOA and PFHxA, do not appreciably bind to sediments relative to longer chain PFCs ($C \geq 11$), and thus are usually present in their dissolved form in field and laboratory settings (Higgins and Luthy 2006, Ahrens et al. 2010, Ahrens et al. 2011). PFOA has been shown to weakly sorb to sediments while PFHxA does not bind significantly (Chen et al. 2015). Thus, percolation into ground water appears to be the major pathway for perfluorinated chemicals to escape the production site. Groundwater flow rates (v) can be estimated across the site if the hydraulic conductivity (K) and the hydraulic gradient (dh/dl) are known using Darcy's Law:

$$v = K (dh/dl).$$

Calculated geometric means for K in the area ranged from 28–51 m/d (Prudic 1991) and the hydraulic gradient across the site during the 2006 baseline study was very small ($0.25 \text{ m} / 295 \text{ m} = 8.5 \times 10^{-4}$), resulting in a groundwater velocity of 2.4–4.3 cm/d (0.9–1.6 m/yr). While groundwater seepage and tidal exchange between groundwater and surface waters are likely to occur, the slow groundwater transport rate along with the microtidal nature of the Mississippi Sound results in a slow exchange rate of the contaminant plume with Mississippi Sound surface waters. Thus, the dilution of the contaminated groundwater seeping into Mississippi Sound by surface waters likely explains the low PFOA and PFHxA concentrations in nearby estuarine waters and biota.

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