Perfluorinated carboxylates and sulfonates in sediments from Homebush Bay, Sydney, Australia

Jack Thompson[1]; Geoff Eaglesham[2]; Anthony C Roach[3]; Michael E. Bartkow[4]; Jochen F Mueller[1]

[1]The University of Queensland (EnTox) 39 Kessels Rd. Coopers Plains, QLD 4109
[2]Queensland Health and Forensic Scientific Services (QHFSS) 39 Kessels Rd. Coopers Plains, QLD 4109;
[3]Department of Environment and Climate Change, PO Box A290, Sydney South, NSW 1232;
[4]SEQWater level 3, 240 Margaret St., Brisbane QLD., 4000

Abstract

Concentrations are presented here for perfluorinated carboxylates and sulfonates in sediments collected from 5 sites around Homebush bay in Sydney Harbor, Australia. Samples were extracted following the methods of Higgins et al. (06) and analysed using LC/MS/MS. Four sulfonates and 11 carboxylates were quantified using internal standards. Detection limits ranged from 0.02 – 11.6 ng/ml based on blank contamination or standard deviation of repeated injection of the lowest standards (0.01 – 1 ng/ml). The effects of ageing were investigated by allowing some samples to equilibrate overnight after spiking with internal standards, while others were extracted immediately after. Effects of moisture content were also evaluated by comparing samples extracted after drying with those extracted moist. Equilibration overnight did not have large effects on recovery or calculated analyte concentration, but improvements to recoveries were seen working with dried instead of wet samples. Ten of the 15 analytes were detected in one or more sample. PFOS contributed the largest amount to the total PFC contamination at all sites (50 – 66%), with concentrations of 0.8 – 6.2 ng/g d.w. Concentrations of total PFCS ranged from 0.2 – 9.3 ng/g d.w and are within the higher end of other sediment data available in the literature.

Introduction

Perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs) are two groups of perfluorochemicals (PFCs) manufactured since the 1950's for use as industrial surfactants, fluoropolymer production aids, and components of fire-fighting foams, and resistant textile and paper surface treatments among other applications. Due to recent concerns regarding the persistence of these compounds and their dissemination throughout the globe, manufacturing and use has been decreased dramatically [1, 2]. Compared with other organic pollutants, estimating the partitioning of PFCs is complicated by the dual hydro- and oleo-phobicity of the fluorocarbon tail, the polarity of the head groups and their electronic charge. Soil and sediments have not typically been considered important sinks for PFCs such as PFOS and PFOA relative to water [2, 3]. Work done by Higgins and Luthy suggested that partitioning of these compounds to organic carbon is determined by the length of the fluorocarbon chain, with increasing hydrophobicity corresponding to increasing chain length and partitioning to solids [4]. Organic carbon partition co-efficients (K_{oc}) have been published for selected PFCAs and PFSAs, these Log K_{oc} values range from 2.1 (PFOA) – 3.5 (PFDS) [4]. From batch tests, these Log K_{oc} values increased by an estimated 0.5 – 0.6 log units with each additional CF_2 unit. For a given fluorinated chain length the PFSAs exhibit greater partitioning to solids than the PFCAs.

Soil and sediment concentrations have mostly been determined near point sources. Surveys of "background" soil and sediment concentrations are generally lacking from the literature. Higgins et al detected low concentrations of PFCAs and PFSAs (n.d – 2.81 ng/g, and n.d – 9.6 ng/g) in sediments collected from San Francisco Bay [5]. Similar concentrations have also been observed in Japan, in Osaka and Kyoto [6]. In contrast APFO (measured as PFO^- anion)in top soil near a fluoropolymer manufacturing plant ranged from 110 – 170 ng/g [7]. Table 3 provides a comparison of the concentrations of PFCs determined in this study with the same analytes determined in other work.

Methods & Materials

Sediment samples were collected in 2009 from 5 sites along the Parammatta River at Homebush bay in Sydney harbor. All 5 sites were within a relatively small radius (~ 5 km) and to the best of the authors knowledge, no PFCs have been, or are, manufactured in the area. Samples were extracted following slightly modified methods of Higgins

et al.[5]. A 10 µl solution containing 2.5 ng of internal standards was added to 0.5 – 2 g of sample in a 15 ml polypropylene (PP) centrifuge tube. Internal standards consisted of mass labeled PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFHxS, and PFOS (all >98%, Wellington Laboratories). As described elsewhere [5], three aqueous acidic wash fractions (8 ml 1% Acetic acid) and three methanol extraction fractions (2 ml) were introduced separately one at a time to the sample tube before each being sonicated in a warm water bath for 30 minutes, allowed to settle, and decanted to a separate 50 ml PP centrifuge tube. The combined methanol and water fractions (30 ml, 20:80 methanol water) were passed through C-18 solid phase cartridges (SPE) (Strata C18-E 55 µm, 70 Å, 500 mg/3 ml, phenomenex) to concentrate the analytes and remove interferences. The SPE's were prepared by passing 3 ml's of methanol, 1% acetic acid in milliQ water, and milliQ water through each cartridge before loading the sample under vacuum at roughly 1 drop/s. After loading, 3 ml of milliQ water was passed through each SPE as a wash fraction, before being dried by passing air through the cartridge. Samples were eluted with 3 ml of Methanol and concentrated under high purity nitrogen to 500 µl. A further 500 µl of 1% NH_4OH in MilliQ water was added to each sample, and 10 ng of 9-H ethyl perfluorononanoic acid (97%, Fluorochem) added as a recovery standard just prior to analysis.

Samples were analysed using a QTRAP 4000 (ABsystems) LC/MS/MS (Shimadzu) operating in –ve ESI mode. MS data was acquired in the scheduled multiple reaction monitoring mode (SMRM). Two transitions were monitored for all PFCs barring the two smallest PFCAs (C4 & C5) which produce only one. Details of the transitions are published elsewhere, as are details of optimized ESI/MS parameters (e.g. [8]). The mobile phase used was 90% H_2O, 10% methanol with 5 mM ammonium acetate (A) and 10% H_2O, 90% methanol with 5 mM ammonium acetate (B) using a gradient elution and a run time of approximately 15 minutes. Modification of the instrument to reduce background was not possible due to other routine commitments. Instrumental peaks were observed consistently in the PFDoDA channels and occaisionally in the PFOA and PFHpA channels. These were separated from sample peaks by use of a 'guard' column (Altima, C18, 5 µm, 4.6 mm i.d x 150 mm) installed between solvent reservoirs and injector, and avoided further by careful setup of the time windows used in the SMRM. The analytical column used was a Gemini C18 (3 µm, 110 Å , 2 mm i.d x 50 mm).

The moisture content of the sediments was estimated by weighing a subsample before and after drying overnight in a vacuum oven. These values were used to convert wet weight concentrations to estimated dry weight concentrations.

Results & Discussion

Detection limits varied with instrumental run and analytes 0.02 – 11.6 ng/ml (in vial). Blank contamination was not an issue for most analytes, the exception being PFDoDA contamination in one set of blanks which raised the reporting limit for this compound. However blanks were run with each batch of samples, and these high reporting limits affected only the wet extracted samples. Butyl and pentanoic PFCAs were also analysed for, but were impossible to quantify due to interferences and poor chromatography. PFBS, PFHxDA & PFODA (C4 PFSA, C16 & 18 PFCAs) were not found above detection limits in any sample, so these analytes are also excluded from further discussion. The same applies to PFHpA and PFTeDA (C7 & C14 PFCAs), which were detected in only 2 samples at close to detection limits.

Recoveries of internal standards were estimated by dividing peak areas with those of the recovery standard, and comparing these ratios in the samples, with the same ones in the calibration standards. These values are shown in Table 1. Recoveries were fairly poor for samples extracted moist (<10 – 40% for the most part), and particularly poor for the shorter and longer chain analytes (C6, and >C8). Drying samples before extraction improved recoveries two to three fold in some cases. The poorer efficiency when wet may be due to extractions being complicated by exchange process involving hygroscopic layers of water, but further work would be required to clarify this. When adjusted for moisture content, the analyte concentrations determined in wet samples were similar to those determined in dry samples.

The calculated concentrations are given in Table 1. These are all expressed on a dry weight basis for ease of comparison. Although individual PFCs are all fairly low in concentration, the sum values are relatively high compared to other sediment studies. Table 3 shows concentrations of the same PFCs reported in other studies, in sediments from various locations, including other urban areas such as San Francisco, USA [5] and Kyoto and Osaka,

Japan [6]. These concentrations are comparable with those obtained in this study. Of the 15 PFCs analysed for, 10 were detected in one or more sample. Four compounds contributed to roughly 90% of total PFCs detected, which were PFOS (50 – 66 % of Σ), PFDoDA (12 – 26 %) when not hidden by elevated reporting limits, PFDA (5 – 9 %), and PFUnDA (4 – 8 %). Concentrations varied between the 5 sites, which given the small distance between, could be indicative of possible point sources in the area or simply reflective of hydrological conditions. Only Brays Bay and Homebush Bay had quantifiable levels of PFDoDA, at an average of 1.06 and 0.65 ng/g d.w respectively. As a whole, a mean value for ΣPFCs for the stretch of the Paramatta River encompassing these sites is 3.5 ng/g d.w. The highest concentrations were found at Bray's Bay, with an average ΣPFCs of 9.1 ng/g and an average PFOS concentration of 5.95 ng/g. The ΣPFC concentration at this site was almost four times higher than the the second most contaminated site, Homebush Bay (average ΣPFCs of 2.8 ng/g, PFOS 1.5 ng/g). The wharf road site showed similar concentrations (average ΣPFCs of 2.1 ng/g). The Kissing Point and Meadowbank sites showed the lowest PFC levels, with averages ΣPFCs of ~ 1 ng/g. Tests of biota collected from these areas are currently underway to investigate the relationship between sediment concentrations and biota body burdens.

Table 1 Recoveries of internal standards used in PFC analysis (replicate 1/ replicate 2)

Samples equilibrated overnight following addition of internal standards (standard recovery %)								
Site	**L-PFHxA**	**L-PFOA**	**L-PFNA**	**L-PFDA**	**L-PFUnDA**	**L-PFDoDA**	**L-PFHxS**	**L-PFOS**
Brays Bay	2/29	49/35	46/34	28/24	22/15	11/8	51/36	27/23
Homebush bay	15/19	33/42	34/41	25/33	22/28	12/18	30/43	20/30
Kissing Point	7/2	30/37	33/39	24/30	21/21	12/15	26/37	19/27
Meadowbank	3/11	54/68	53/69	50/50	36/33	25/23	81/73	49/48
Wharf road	1/3	49/71	45/75	37/56	33/43	18/24	48/60	29/39
Lab blanks	1/5	3/3	4/3	4/3	2/60	1/75	2/32	3/28
Samples extracted immediately after addition of internal standards (standard recovery %)								
Brays Bay	1/4	30/69	28/69	26/61	17/55	7/46	22/63	16/51
Homebush bay	5/8	23/44	25/48	19/43	16/28	10/21	22/47	15/33
Kissing Point	24/11	47/47	44/50	40/43	26/41	17/33	45/47	28/30
Meadowbank	3/3	39/35	40/37	33/31	29/24	19/16	30/41	22/24
Wharf road	27/3	45/44	42/43	33/34	14/24	5/16	52/51	31/29
Lab blanks	1/5	9/24	9/37	6/60	6/40	2/15	13/71	8/16
Samples dried in vacuum oven before extraction immediately after spike (standard recovery %)								
Brays Bay	72/95	68/96	62/90	51/84	36/70	21/60	81/108	64/99
Homebush bay	93/82	88/78	83/71	68/58	47/41	28/21	100/82	81/69
Kissing Point	83/92	80/85	73/79	61/68	42/48	24/30	82/83	68/73
Meadowbank	87/82	85/74	77/70	65/53	46/33	32/17	98/86	79/67
Wharf road	89/106	82/97	67/82	45/60	67/33	52/15	88/107	59/76
Lab blanks	83/61	80/53	78/50	74/48	67/40	52/29	91/39	84/37

Table 2 Concentrations of PFCs in Sydney sediment (ng/g dw)

Site	PFOA	PFNA	PFDA	PFUnDA	PFTriDA	PFTeDA	PFHxS	PFOS	PFDS
Samples equilibrated overnight following addition of internal standards (ng/g d.w)									
Brays Bay	<DL	<LOR	0.89	0.37	0.21	0.09	0.15	4.63	0.18
	<DL	0.18	0.8	0.48	0.26	0.09	0.12	4.05	nd
Homebush bay	<DL	0.1	0.24	0.2	0.16	<DL	0.08	1.3	<LOR
	<DL	0.08	0.24	0.19	0.14	<DL	<LOR	1.26	0.05
Kissing Point	<DL	nd	0.22	0.13	nd	nd	<LOR	0.71	nd
	<DL	0.14	0.23	0.23	nd	nd	nd	0.65	nd
Meadowbank	<DL	<LOR	0.14	0.12	0.08	<DL	<LOR	0.76	nd
	<DL	<LOR	0.16	0.12	0.07	nd	nd	0.58	<LOR
Wharf road	<DL	<LOR	0.08	0.13	0.07	nd	<LOR	1.22	nd
	<DL	0.05	0.09	0.13	0.08	nd	<LOR	1.52	nd
lab blanks	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	0.17	nd	nd	nd
Samples extracted immediately after addition of internal standards (ng/g/ d.w)									
Brays Bay	<DL	0.4	1.2	0.54	nd	nd	<LOR	4.42	nd
	<DL	<LOR	0.77	0.39	0.18	<DL	<LOR	3.84	0.12
Homebush bay	<DL	0.17	nd	0.31	0.23	nd	nd	1.38	nd
	<DL	<LOR	0.21	0.25	0.13	nd	nd	1.29	nd
Kissing Point	<DL	0.11	0.18	0.14	nd	nd	nd	0.7	nd
	<DL	<LOR	0.17	0.14	0.18	nd	nd	0.7	nd
Meadowbank	<DL	<LOR	nd	0.18	0.2	<DL	nd	0.71	nd
	<DL	nd	0.14	0.21	0.17	<DL	nd	0.73	nd
Wharf road	<DL	0.23	0.14	0.18	nd	nd	<LOR	1.34	nd
	<DL	<LOR	0.21	0.14	<LOR	nd	<LOR	1.44	nd
lab blanks	0.25	nd	nd	nd	nd	nd	nd	nd	nd
	0.11	nd	nd	nd	nd	nd	nd	nd	nd
Samples dried in vacuum oven before extraction (immediately after spike)									
Brays Bay	0.16	0.11	0.81	0.54	0.16	<LOR	0.1	6.21	0.14
	<LOR	<LOR	0.8	0.61	0.27	<LOR	0.1	5.7	0.22
Homebush bay	<LOR	<LOR	0.18	0.17	0.07	<LOR	0.04	1.31	0.06
	0.1	<LOR	0.23	0.2	0.09	<LOR	0.05	1.64	0.07
Kissing Point	<LOR	<LOR	0.15	0.12	0.07	<LOR	0.03	0.81	0.04
	<LOR	<LOR	0.15	0.12	0.06	<LOR	0.03	0.75	0.05
Meadowbank	<LOR	<LOR	<LOR	0.1	0.08	<LOR	0.02	0.77	0.05
	<LOR	<LOR	<LOR	0.11	0.04	<LOR	0.02	0.8	0.03
Wharf road	<LOR	<LOR	0.14	0.11	0.04	<LOR	0.06	1.7	0.05
	<LOR	<LOR	0.12	0.1	0.06	<LOR	0.06	1.61	0.08
lab blanks	0.03	0.01	0.01	0.01	0.01	0.01	nd	nd	Nd
	0.03	0.01	0.02	0.01	nd	0.01	nd	nd	Nd

Note:- values in lab blanks have been turned into ng/g units by applying an 'average' sample size of 1.5 g, these are below detection limits (DL = average blank concentration + (3 x stdev)), but have been included to show the degree of contamination. PFBS, PFHxDA & PFODA were not detected and so excluded from the table, PFHpA, PFDoDA, PFTeDA were quantified in only a few samples and are also excluded from table for brevity.

Table 1 Comparison of levels of PFCs sediments from the literature (ng/g d.w).

Location	Region / Country	∑PFCs*
Brays Bay	Sydney Harbour -Australia	9.2
Homebush Bay	Sydney Harbour -Australia	2.8
Kissing Point	Sydney Harbour -Australia	1.6
Meadowbank	Sydney Harbour -Australia	1.5
Wharf Rd	Sydney Harbour -Australia	2.5
Kamo River	Kyoto, Japan	4.7
Uji River St-1	Kyoto, Japan	2.0
Uji River St-2	Kyoto, Japan	4.8
Tenjin River	Kyoto, Japan	22
Katsura river	Kyoto, Japan	4.0
Osaka river St-1	Osaka, Japan	0.0
Osaka river St-2	Osaka, Japan	6.2
Osaka river St-3	Osaka, Japan	10.5
Osaka river St-4	Osaka, Japan	0.0
Savannah River	Georgia, USA	0.1
LCP superfund site	Georgia, USA	0.0
Bolinas Lagoon	San Francisco Bay USA	0.9
Hayward Marsh	San Francisco Bay USA	2.3
Kirby Park	San Francisco Bay USA	0.2
Lagunitas Creek	San Francisco Bay USA	0.0
Palo Alto Mudflats	San Francisco Bay USA	1.6
Petaluma River	San Francisco Bay USA	1.5
Salinas River	San Francisco Bay USA	1.8
San Francisquito Creek	San Francisco Bay USA	3.6
San Lorenzo River	San Francisco Bay USA	0.0
San Pedro Creek	San Francisco Bay USA	0.5
Soquel Creek	San Francisco Bay USA	0.3
Waddell Creek	San Francisco Bay USA	0.3
Yosemite Slough	San Francisco Bay USA	0.6
WWTP 5 Outfall	San Francisco Bay USA	4.7
Baltimore Inner Harbor, MD	San Francisco Bay USA	1.9
Gwynn's Run, MD	San Francisco Bay USA	0.2
Willametee River, OR	San Francisco Bay USA	0.2

Values in table are taken from the following references in order of listing*: this study, [6], [9], [5]* values have been recalculated to ensure comparisons are made only between the same compounds as analysed in this work

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