Supplementary Materials for

Polystyrene plastic: a source and sink for polycyclic aromatic hydrocarbons in the marine environment

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Experimental

Chemicals and Reference Materials

All solvents and reagents, equal or above pesticide grade, were purchased from Fisher Scientific (Fisher Scientific, Fair Lawn, NJ, USA). Standard solutions of 18 PPAHs were purchased from ChemService (West Chester, PA, USA), standard solutions of 9 MPAHs, 18 NPAHs and 2 SPAHs were purchased from AccuStandard (New Haven, CT, USA), and neat standards of 17 OPAHs were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard solutions of 15 ClPAHs and 6 BrPAHs were synthesized by Dr. Takeshi Ohura from the University of Shizouka in Shizouka, Japan, using published procedures (Kitazawa, 2006) (Ohura, 2005) (Wang, 2012). Isotopically labeled PAHs solutions were purchased from CDN Isotopes (Point-Clare, Quebec, Canada) and Cambridge Isotopes Laboratories (Andover, MA) and included d_{10}-fluorene as an internal standard and d_{10}-phenanthrene and d_{10}-acenaphthene as surrogates for calibration standard solutions. Standards d_{10}-phenanthrene and d_{10}-acenaphthene spiked to the samples were purchased from AccuStandard as mixtures (Z-014J-0.5X).

Sample preparation

Briefly, pellets from each field-collected Nitex bag were rinsed in ultrapure water to remove sediment. In a few cases, large fouling organisms were seen attached to individual pellets; these pellets were excluded from chemical analyses. Two grams of rinsed pellets were prepared for extraction following published methods (Van et al., 2011). Virgin pellets were used as laboratory blanks and 0-month controls.

Quality Assurance and Quality Control

Glassware was cleaned and muffled at 450˚C for 6 h. Laboratory procedural blanks and a spiked matrix blank, consisting of virgin pellets, were extracted with every sequence of seven samples and run at the beginning, middle and end of the 20-sample set.. The reported concentrations of total PAHs are recovery corrected. In spiked matrix blank samples, recoveries for the 15 PPAHs detected had an average of 93.4% and range of 66.4-120.8%. For comparison with other plastic types, total PPAH concentrations measured in 0-month polystyrene pellets were subtracted from the sorbed concentrations of total PPAHs on PS samples deployed in San Diego Bay.

Table S1: GC×GC/ToF-MS optimized parameters for the analysis of PAHs in NIST SRMs.

	LC-50 × NSP-35
1D column	LC-50 (10 m × 0.15 mm × 0.10 μm)
Max Temperature	270 °C
2D column	NSP-35 (1.2 m × 0.10 mm × 0.10 μm)
Max Temperature	360 °C
Injection Volume	1 μL
Inlet Temperature	300 °C
Carrier Gas	He
Carrier Gas Flow	0.80 mL/min (constant)
1D Oven Program	90 °C (2 min), 20 °C/min to 170 °C, 2 °C/min to 270 °C (28 min)
2D Oven Program	120 °C (2 min), 20 °C/min to 200 °C, 2.5 °C/min to 325 °C (28 min)
Modulator Temp. Offset	45 °C
Modulation Time	7 s
Hot Pulse Time	1.5 s
Cold Time	2.0 s
Transfer Line Temp.	285 °C
Ion Source Temperature	250 °C
Scan Speed	151.5 spectra/second
Total run time	84 min

Table S2: List of PAHs analyzed using GC×GC/ToF-MS.

	PPAH			**SPAH**	
1	acenaphthene	ACE	46	2-nitrodibenzothiopene	2 N Dibenth
2	acenaphthylene	ACY	47	dibenzothiopene	Dibenzoth
3	anthracene	ANT		**OPAH**	
4	benz[a]anthracene	BaA	48	1,2-naphthoquinone	1,2 NAPq
5	benzo[a]pyrene	BaP	49	1,4-anthraquinone	1,4 ANTq
6	benzo[b]fluoranthene	BbF	50	1,4-naphthoquinone	1,4 NAPq
7	benzo[e]pyrene	BeP	51	2-methyl-9,10-anthraquinone	2 met ANTq
8	benzo[ghi]perylene	BghiP	52	4H-cyclopenta[def]phenanthrene-4-one	CdefPHEq
9	benzo[k]fluoranthene	BkF	53	5,12-naphthacenequinone	5,12 NAPq
10	chrysene	CHR	54	9,10-anthraquinone	9,10 ANTq
11	dibenzo[ah]anthracene	DahA	55	9,10-phenanthrenequinone	9,10 PHEq
12	fluoranthene	FLA	56	9-fluorenone	9 Fluo
13	fluorene	FLO	57	acenaphthenequinone	ACEq
14	indeno[1,2,3-cd]pyrene	IcdP	58	aceanthrenequinone	AANTq
15	naphthalene	NAP	59	benz[a]anthracene-7,12-dione	7,12 BaAq
16	phenanthrene	PHE	60	benzanthrone	Benzan
17	pyrene	PYR	61	benzo[a]fluorenone	BaFluo
18	triphenylene	TRI	62	benzo[c]phenanthrene-[1,4]-quinone	1,4 BcPHEq
	MPAH		63	benzo[cd]pyrenone	BcdPYR
19	1,3-dimethylnaphthalene	1,3 met NAP	64	phenanthrene-1,4-dione	1,4 PHEq
20	1-methylnaphthalene	1 met NAP		**BrPAH**	
21	1-methylpyrene	1 met PYR	65	1-bromopyrene	1 Br PYR
22	2,6-dimethylnaphthalene	2,6 met NAP	66	2-bromofluorene	2 Br FLO
23	2-methylanthracene	2 met ANT	67	7-bromobenz[a]anthracene	7 Br BaA
24	2-methylnaphthalene	2 met NAP	68	9,10-dibromoanthracene	9,10 Br ANT
25	3,6-dimethylphenanthrene	3,6 met PHE	69	9-bromoanthracene	9 Br ANT
26	6-methylchrysene	6 met CHR	70	9-bromophenanthrene	9 Br PHE
27	retene	RET		**ClPAH**	
	NPAH		71	1,3-dichlorofluoranthene	1,3 Cl FLA
28	1-nitronaphthalene	1 N NAP	72	1,9-dichlorophenanthrene	1,9 Cl PHE
29	1-nitropyrene	1 N PYR	73	1-chloropyrene	1 Cl PYR
30	2-nitroanthracene	2 N ANT	74	2-chloroanthracene	2 Cl ANT
31	2-nitrobiphenyl	2 N BiPhe	75	3,4-dichlorofluoranthene	3,4 CL FLA
32	2-nitrofluoranthene	2 N FLA	76	3,8-dichlorofluoranthene	3,8 Cl FLA
33	2-nitrofluorene	2 N FLO	77	3-chlorobenzanthrone	3 Cl Benzan
34	2-nitronaphthalene	2 N NAP	78	3-chlorofluoranthene	3 Cl FLA
35	2-nitropyrene	2 N PYR	79	6-chlorochrysene	6 Cl CHR
36	3-nitrobiphenyl	3 N BiPhe	80	8-chlorofluoranthene	8 Cl FLA
37	3-nitrodibenzofuran	3 N Dibenf	81	9,10-dichloroanthracene	9,10 Cl ANT
38	3-nitrofluoranthene	3 N FLA	82	9,10-dichlorophenanthrene	9,10 Cl PHE
39	3-nitrophenanthrene	3 N PHE	83	9-chloroanthracene	9 Cl ANT
40	4-nitrobiphenyl	4 N BiPhe	84	9-chlorofluorene	9 Cl FLO
41	5-nitroacenaphthalene	5 N ACE	85	9-chlorophenanthrene	9 Cl PHE
42	6-nitrochrysene	6 N CHR			
43	7-nitrobenz[a]antracene	7 N BaA			
44	9-nitroanthracene	9 N ANT			
45	9-nitrophenanthrene	9 N PHE			

Table S3a: Distribution of PAHs found in PS pellets (%) deployed for 0, 1, 3, 6, 9 and 12 months in Harbor Excursion, determined using GC×GC/ToF-MS.

				Harbor Excursion									
months	**0 (blank)**			**1**		**3**		**6**		**9**		**12**	
	n=3			**n=2**		**n=2**		**n=2**		**n=2**		**n=2**	
1,3-Dimethylnaphthalene	12.4	10.7	11.2	2.65	2.72	3.30	3.44	2.31	4.00	2.55	2.22	2.67	2.02
1-Methylphenanthrene	5.27	6.37	5.75	2.60	2.52	2.48	2.38	2.45	2.70	2.70	2.16	2.71	2.34
1-Methylpyrene	n.d.	n.d.	n.d.	1.56	2.45	2.35	3.13	2.34	2.67	2.45	2.32	2.44	2.44
2,6-Dimethylnaphthalene	4.11	4.64	4.53	0.74	1.01	0.97	1.09	0.98	1.47	0.95	0.80	1.04	0.95
2-Methylanthracene	n.d.	n.d.	n.d.	1.51	2.79	2.50	2.48	2.69	2.83	2.64	2.40	2.71	2.59
2-Methylphenanthrene	5.91	7.16	6.19	1.76	2.35	2.25	2.31	2.27	2.60	2.09	2.04	2.36	2.09
Triphenylene	n.d.	n.d.	n.d.	0.97	1.30	1.24	1.13	1.32	1.13	1.29	1.24	1.21	1.39
ΣMPAHs	**27.73**	**28.9**	**27.7**	**11.8**	**15.2**	**15.1**	**16.0**	**14.4**	**17.4**	**14.7**	**13.2**	**15.1**	**13.8**
Acenaphthene	2.17	2.62	2.70	3.44	2.02	1.95	2.20	2.19	2.37	2.13	1.81	2.31	1.91
Acenaphthylene	2.57	4.02	3.16	1.66	2.92	2.27	2.65	3.41	2.48	2.62	2.92	2.79	3.02
Anthracene	2.42	2.81	2.50	3.92	6.40	5.78	5.85	6.57	4.56	6.41	6.84	6.62	6.76
Benz[a]anthracene	n.d.	n.d.	n.d.	3.04	3.22	2.53	2.54	2.84	2.24	2.97	2.34	2.40	2.69
Benzo[a]pyrene	n.d.	n.d.	n.d.	2.13	3.24	2.72	2.86	2.56	2.42	2.32	3.16	2.40	2.49
Benzo[b]fluoranthene	n.d.	n.d.	n.d.	2.93	5.31	6.37	5.21	5.82	4.05	4.98	5.11	4.14	4.31
Benzo[e]pyrene	n.d.	n.d.	n.d.	2.22	3.81	3.29	3.44	3.77	2.60	3.07	4.30	3.10	3.10
Benzo[ghi]perylene	n.d.	n.d.	n.d.	n.d.	5.77	5.28	5.41	5.99	6.02	5.39	5.36	5.66	5.13
Benzo[k]fluoranthene	n.d.	n.d.	n.d.	1.93	3.53	4.02	3.46	3.46	2.85	3.03	2.99	2.60	2.76
Chrysene	n.d.	n.d.	n.d.	3.02	3.18	2.70	2.98	2.88	2.09	3.07	3.02	2.30	3.22
Fluoranthene	16.8	8.25	6.92	11.2	5.03	6.00	5.24	5.90	4.44	6.48	4.60	5.01	6.00
Fluorene	11.9	11.4	12.8	6.58	6.09	6.96	8.07	5.57	7.75	5.42	5.51	7.05	6.37
Indeno[1,2,3-cd]pyrene	n.d.	n.d.	n.d.	2.71	5.11	4.87	4.85	5.13	4.96	4.63	5.07	4.91	4.43
Phenanthrene	5.52	6.32	6.13	18.5	11.3	9.93	10.6	10.05	18.8	13.5	18.0	14.5	15.5
Pyrene	5.26	6.36	10.8	18.1	8.42	10.8	8.87	10.23	3.77	10.2	7.36	8.81	9.36
ΣPPAHs	**46.7**	**41.8**	**45.0**	**81.4**	**75.3**	**75.4**	**74.2**	**76.4**	**71.4**	**76.2**	**78.4**	**74.6**	**77.0**
9-Fluorenone	3.64	3.45	4.07	0.89	1.52	1.51	1.67	1.36	1.88	1.51	1.36	1.93	1.65
1,4-Naphthoquinone	20.0	23.6	21.2	4.18	6.96	6.89	7.08	6.98	8.21	6.62	6.14	7.28	6.54
ΣOPAHs	**23.7**	**27.1**	**25.3**	**5.08**	**8.49**	**8.41**	**8.75**	**8.34**	**10.1**	**8.13**	**7.50**	**9.22**	**8.19**
Dibenzothiophene	1.89	2.28	2.06	1.72	1.05	1.07	1.09	0.93	1.07	1.03	0.88	1.07	0.96
ΣSPAHs	**1.89**	**2.28**	**2.06**	**1.72**	**1.05**	**1.07**	**1.09**	**0.93**	**1.07**	**1.03**	**0.88**	**1.07**	**0.96**
Total PAHs	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

n.d.: compound not detected

Table S3b: Distribution of PAHs found in PS pellets (%) deployed for 0, 1, 3, 6, 9 and 12 months in Shelter Island, determined using GC×GC/ToF-MS.

				Shelter Island									
months	**0 (blank)**			**1**		**3**		**6**		**9**		**12**	
	n=3			**n=2**		**n=2**		**n=2**		**n=2**		**n=2**	
1,3-Dimethylnaphthalene	12.4	10.7	11.2	4.60	5.04	4.09	3.67	2.91	3.13	2.06	2.75	2.95	1.76
1-Methylphenanthrene	5.27	6.37	5.75	3.29	3.23	3.22	2.81	2.84	2.69	3.10	2.89	2.96	2.70
1-Methylpyrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-Dimethylnaphthalene	4.11	4.64	4.53	1.86	1.85	1.57	1.42	1.23	1.28	1.35	1.27	1.32	1.14
2-Methylanthracene	n.d.	n.d.	n.d.	3.44	3.28	3.35	2.87	2.96	2.90	3.23	3.24	3.29	2.95
2-Methylphenanthrene	5.91	7.16	6.20	3.47	3.26	3.39	2.87	2.76	2.84	3.09	3.00	3.06	2.73
Triphenylene	n.d.	n.d.	n.d.	1.46	1.26	1.29	1.15	1.24	1.20	1.35	1.26	1.44	1.33
ΣMPAHs	**27.7**	**28.9**	**27.7**	**18.1**	**17.9**	**16.9**	**14.8**	**13.9**	**14.0**	**14.2**	**14.4**	**15.0**	**12.6**
Acenaphthene	2.17	2.62	2.70	1.35	1.31	1.49	1.22	1.12	1.16	1.33	1.21	1.28	1.18
Acenaphthylene	2.57	4.02	3.16	2.33	2.26	2.36	2.15	2.19	2.19	3.25	2.38	2.45	2.62
Anthracene	2.42	2.81	2.50	2.52	2.47	2.63	2.83	3.04	3.05	3.87	3.02	3.69	3.56
Benz[a]anthracene	n.d.	n.d.	n.d.	1.52	1.61	1.52	1.50	1.66	1.43	1.85	1.68	1.73	1.96
Benzo[a]pyrene	n.d.	n.d.	n.d.	1.60	1.80	1.72	1.71	1.85	1.61	2.43	2.01	2.12	2.03
Benzo[b]fluoranthene	n.d.	n.d.	n.d.	3.00	3.14	3.33	3.10	3.71	3.27	3.98	4.04	3.66	4.37
Benzo[e]pyrene	n.d.	n.d.	n.d.	2.19	2.19	2.24	2.21	2.46	2.20	2.94	3.23	2.59	2.95
Benzo[ghi]perylene	n.d.	n.d.	n.d.	8.55	7.96	8.36	6.97	6.93	7.03	7.46	7.79	7.60	6.84
Benzo[k]fluoranthene	n.d.	n.d.	n.d.	2.35	2.03	2.05	2.18	2.32	2.16	2.42	2.38	2.37	2.35
Chrysene	n.d.	n.d.	n.d.	1.86	1.70	1.80	1.59	1.80	1.59	1.94	1.69	1.85	2.32
Fluoranthene	16.8	8.29	6.92	4.58	4.52	4.40	4.01	4.24	3.87	5.51	4.76	5.08	5.14
Fluorene	11.9	11.4	12.8	7.88	8.56	6.16	8.01	6.14	7.42	8.67	7.17	5.29	5.94
Indeno[1,2,3-cd]pyrene	n.d.	n.d.	n.d.	6.89	6.61	6.71	6.14	5.98	5.93	5.98	6.52	6.57	6.07
Phenanthrene	5.52	6.32	6.13	15.7	16.5	20.6	26.0	25.9	27.0	17.6	20.0	21.7	21.5
Pyrene	5.26	6.36	10.8	4.44	5.11	3.48	3.12	4.46	3.76	2.91	4.52	3.85	5.44
ΣPPAHs	**46.7**	**41.8**	**45.0**	**66.8**	**67.8**	**68.9**	**72.8**	**73.8**	**73.7**	**72.2**	**72.4**	**71.8**	**74.3**
9-Fluorenone	3.64	3.45	4.07	2.40	2.53	2.28	1.99	2.34	2.09	2.36	2.01	2.01	2.20
1,4-Naphthoquinone	20.0	23.6	21.2	11.7	10.8	11.0	9.62	9.16	9.36	10.4	10.3	10.3	10.1
ΣOPAHs	**23.7**	**27.1**	**25.3**	**14.1**	**13.4**	**13.2**	**11.6**	**11.5**	**11.4**	**12.8**	**12.3**	**12.3**	**12.3**
Dibenzothiophene	1.89	2.28	2.06	0.99	0.93	0.93	0.83	0.80	0.83	0.89	0.88	0.88	0.80
ΣSPAHs	**1.89**	**2.28**	**2.06**	**0.99**	**0.93**	**0.93**	**0.83**	**0.80**	**0.83**	**0.89**	**0.88**	**0.88**	**0.80**
Total PAHs	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**

n.d.: compound not detected

Figure S1: Map of San Diego Bay showing the two field locations: Harbor Excursion and Shelter Island. Figure generated with ArcGIS version 9.3.

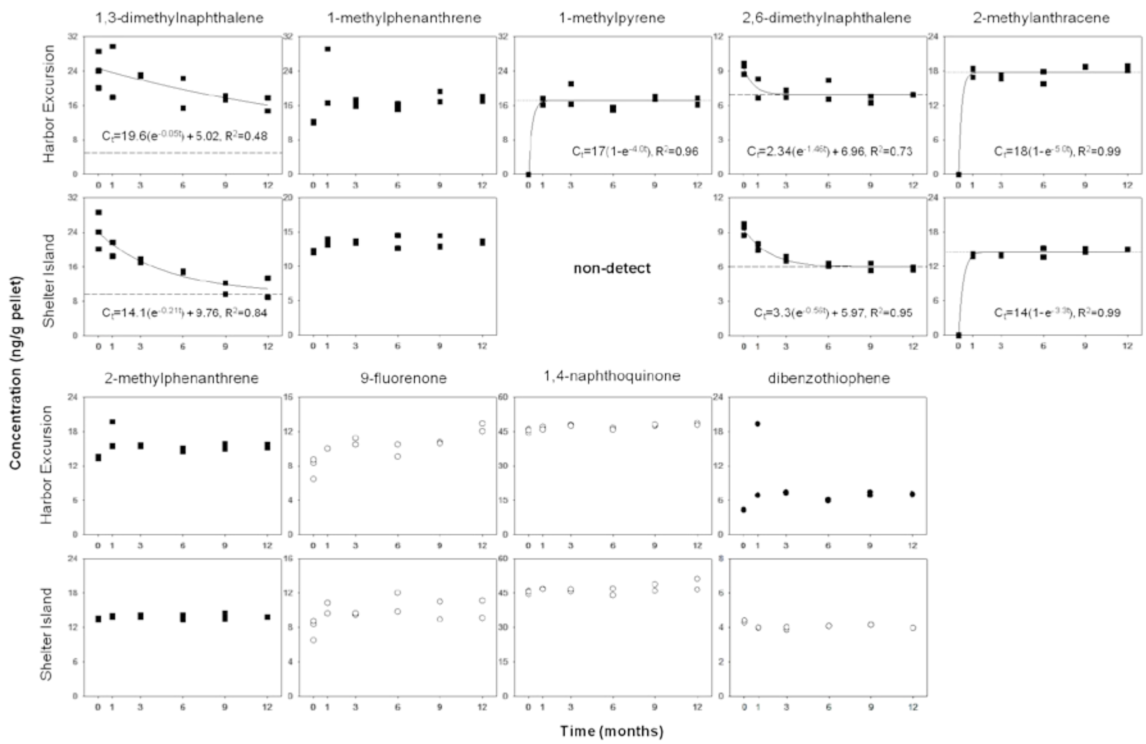

Figure S2. Concentrations of individual MPAHs, OPAHs and SPAHs (ng/g of pellets) vs. time for PS at Harbor Excursion (top row) and Shelter Island (bottom row). Please note that vertical axes differ among graphs. Data were fit to the first-order approach to equilibrium model[25] using the exponential rise to maximum equation $C_t=C_{eq}(1-e^{-kt})$ or the exponential decay model[26] using the equation $C_t=(C_0 - C_{eq})e^{-kt} + C_{eq}$, where C_t is the concentration at time t, C_{eq} is the predicted equilibrium concentration, C_0 is the initial concentration and k is the rate constant. The horizontal dotted line denotes the predicted C_{eq} for each plastic type. Where the equation and lines are missing, concentrations were non-detect or the data could not be fit to the equation.

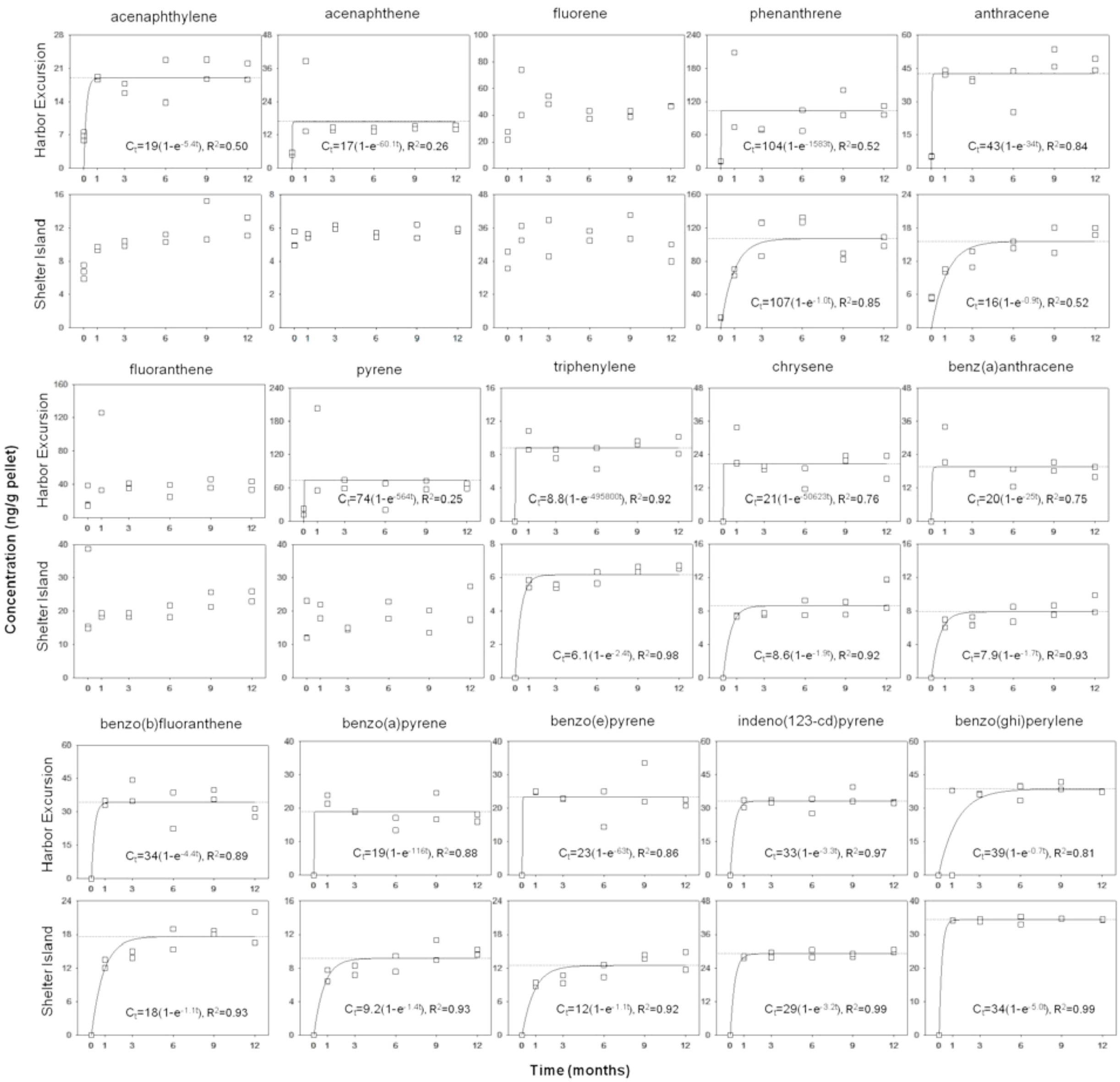

Figure S3. Concentrations of individual PPAHs (ng/g of pellets) vs. time for PS at Harbor Excursion (top rows) and Shelter Island (bottom rows). Individual congeners are ordered from smallest to greatest log K_{ow} value (hydrophobicity). Note that vertical axes differ among graphs. Data were fit to the first-order approach to equilibrium model[25] using the exponential rise to maximum equation $C_t=C_{eq}(1-e^{-kt})$, where C_t is the concentration at time t, C_{eq} is the predicted equilibrium concentration, and k is the rate constant. The horizontal dotted line denotes the predicted C_{eq} for each plastic type. Where the equation and lines are missing, data could not be fit to the equation.

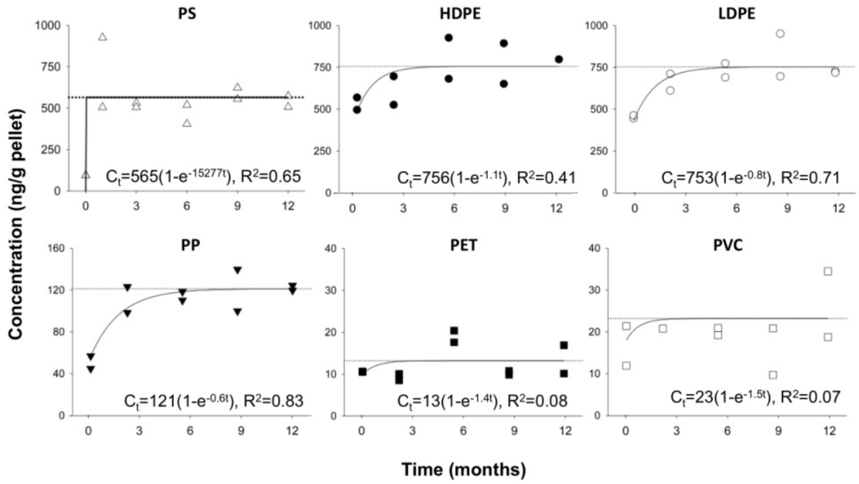

Figure S4. Concentrations of total priority PPAHs (ng/g of pellets) vs. time for each type of plastic at Harbor Excursion (PS, HDPE, LDPE-top row; PP, PET, PVC-bottom row). Please note that vertical axes differ among graphs. Data were fit to the first-order approach to equilibrium model[25] using the exponential rise to maximum equation $C_t=C_{eq}(1-e^{-kt})$, where C_t is the concentration at time t, C_{eq} is the predicted equilibrium concentration, and k is the rate constant. The horizontal dotted line denotes the predicted C_{eq} for each plastic type.