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Baseline

PAH, PCB, TPH and mercury in surface sediments of the Delaware River Estuary and Delmarva Peninsula, USA

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ABSTRACT

Surface sediment concentrations of polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB), total petroleum hydrocarbons (TPH) and mercury, were compared from two areas with contrasting land use history, the industrial Delaware Estuary and the rural Delmarva Peninsula (USA). TPH in the Delaware (38–616 mg/kg) and saturate/aromatic fractions suggested petroleum/industrial sources compared to biogenic sources in the Delmarva coastal control (< 34–159 mg/kg). Within the Delaware the Σ PAH18 ranged from 3749 to 22,324 μ g/kg with isomeric ratios indicative of petroleum combustion source/s, conversely, those in the Delmarva (5–2139 μ g/kg) also yielded relatively higher perylene that were consistent with natural background levels derived from vegetation/coal combustion source/s. Σ PCB(tri-hepta) concentrations in the Delmarva (0.6–6.5 μ g/kg) were less than the threshold effect concentration (TEC), whereas the Delaware had received much higher PCB loading (18.1–136.8 μ g/kg) as evidenced by a significantly higher amounts in some samples (> TEC).

Diffuse pollution from urban-residential run-off and industrial discharges can adversely impact river, salt-marsh and tidal-creek sediment quality (Barrett and McBrien, 2007; Fox et al., 2001; Iannuzzi et al., 1995; Long et al., 1995; Sanger et al., 2004; Vane et al., 2008; White et al., 2005). Point source pollution from shipping (e.g. fuel discharge) can also impact rivers and salt marshes (White et al., 2005). Due to their negative effect on flora and fauna, the contaminants of greatest concern in these environments are mercury (Hg), and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Bioaccumulation of contaminants in organisms that are part of a detritus-driven food web is a potential health hazard if pollutants are concentrated and subsequently consumed by humans. Once sorbed to the sediment, PAHs and PCBs also accumulate in the leaves and roots of standing and decaying salt-marsh plants (e.g. *Spartina alterniflora*), which are an important food source for the base of the detrital salt marsh food chain (Mrozek et al., 1983; Wall et al., 2001). Bioaccumulation of POPs to higher trophic levels occurs by a combination of lipid-water partitioning and dietary accumulation processes as well as other food-web specific routes (Connolly and Pedersen, 1988; Kelly et al., 2007). Also, organic pollutants at high concentrations can cause growth impairment of halophytic plants, which in turn may limit buffering of storm events and stabilisation of

coastal sediments (Mrozek et al., 1983; Watts et al., 2006). Therefore monitoring of sediment-hosted organic pollutants is important to ensure the protection of populations that consume species of fish and shell fish.

Estuary sediments and salt marshes on the east coast of the USA are potentially important sinks for POPs due to preferential adsorption of pollutants to organic matter (Fox et al., 2001; Scrimshaw and Lester, 2001). In this study we examine the sediments from an urban (the Delaware River Estuary) and rural (Delmarva Peninsula) setting to: (1) determine individual concentrations of Hg, total (non-volatile) petroleum hydrocarbons (TPH), PAHs and PCBs, (2) identify, where possible, sources of pollution and related spatial gradients of contaminants, (3) compare the contaminant concentrations to published sediment quality guideline values (SQGs) to evaluate their possible impact upon ecological habitats. This dataset provides a baseline for long-term ecosystem monitoring and assessment of the impact of future pollution events.

The study areas chosen were a ~130 km length of the Delaware Estuary (Fig. 1) and a ~100 km length of the Delmarva Peninsula, from Chincoteague to its southern most point, Kiptopeke, along the Atlantic coast (Fig. 2).

The Delaware Estuary is ~200 km long from Trenton to the eastern seaboard of the U.S.A., however, the Delaware River extends a further

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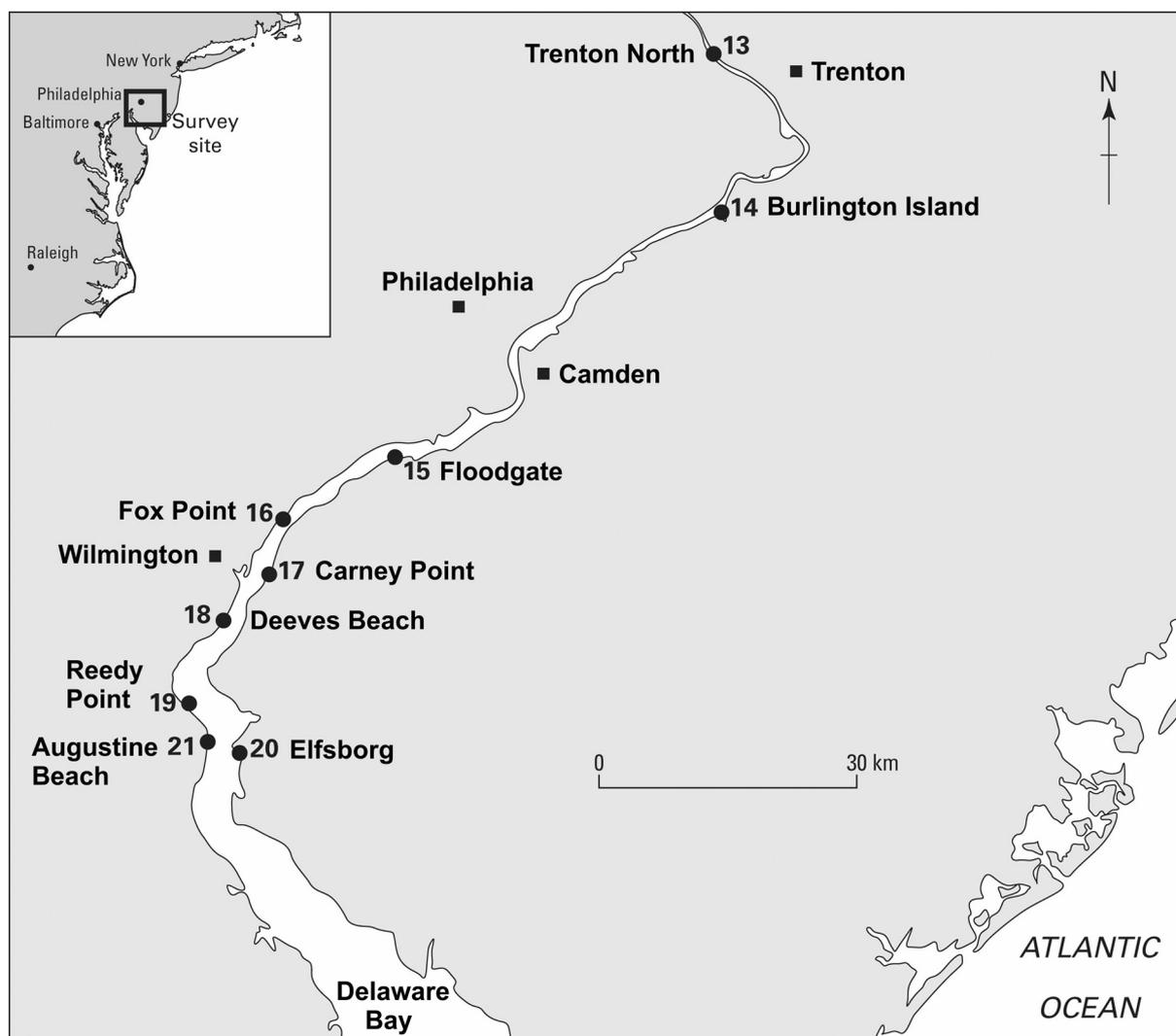


Fig. 1. Map showing locations of sample sites in of the Delaware River Estuary, USA.

474 km north from Trenton and the combined estuary-river catchment area is 36,570 km² that encompasses five U.S. states (New York, New Jersey, Pennsylvania, Maryland and Delaware). It flows into the Delaware Bay and finally into the Atlantic Ocean. The zone of this study extends from Artificial Island (80 km, from the Atlantic Ocean) to Trenton (214 km). This area includes the variable salinity transition zone (0–18 psu) from 80 to 129 km which is characterised by high turbidity and low biological productivity. Along this 130 km stretch, it flows through the heavily industrial and urbanised area of Philadelphia, PA and Wilmington, DE. The Delaware Estuary has a history of diffuse and point-source pollution (Church et al., 2006; Hall and Burton, 2005; Sutton et al., 1996; Tarr and McCurley, 1984).

The Delmarva Peninsula is located ~120 km south from the mouth of Delaware Bay. The watershed of the peninsula flows either west into the Chesapeake Bay or east towards the Atlantic Ocean via tidal creeks and salt marshes. The peninsula borders the Atlantic by a complex changing barrier of low lying islands, shallow bays, lagoons and sand banks (Kastler and Wiberg, 1996) and the land-use is predominantly rural and agricultural. Coastal regions, such as this peninsula, are currently under pressure from population growth and subsequent development (Culliton et al., 1990). Development of these watersheds, especially those surrounding tidal creek-salt marshes, can potentially increase point and nonpoint source pollution inputs into these ecosystems.

These two contrasting sites were chosen to demonstrate the

differences in mercury and organic contaminants between, an area heavily impacted by urban/industrial activity and a less impacted area in a rural environment.

Surface sediments (0–1 cm) were collected from the intertidal zone at low tide from the Delaware Estuary shore (Pennsylvania, New Jersey USA, April 2010) and salt marshes on the Delmarva Peninsula (Virginia, USA, June 2008) using a clean, stainless steel trowel (Figs. 1, 2, Table 1). Sediments were sealed in polyethylene plastic bags and transported in a cool box at ~4 °C, then immediately frozen at ~–20 °C. In the laboratory, an aliquot of each (~500 g) sediment was freeze-dried, sieved to < 2 mm and ground to a fine powder (Beriro et al., 2014).

Total organic carbon (TOC) content was determined using an Elementar VarioMax C, N analyser after acidification with HCl (50/50 v/v) to remove carbonate. The limits of quantification (LOQ) reported for a typical 300 mg sample were 0.18%.

Total (non-volatile) petroleum hydrocarbons (TPH) were determined using a thin layer chromatography - flame ionization detector (TLC-FID). 8 g of sediment was extracted using an ASE 200, Dionex accelerated solvent extraction (dichloromethane:acetone 1:1 v/v, 100 °C, 1500 p.s.i.). The resulting extract was reduced in volume/dried using a Turbovap® (dry nitrogen, 30 °C) and reconstituted in toluene (1.0 mL). A 1.2 µL aliquot of this was spotted onto silica Chromrods®. The saturated and aromatic hydrocarbons were separated by developing the rods for 21 min in *n*-hexane and then for 8 min in toluene.

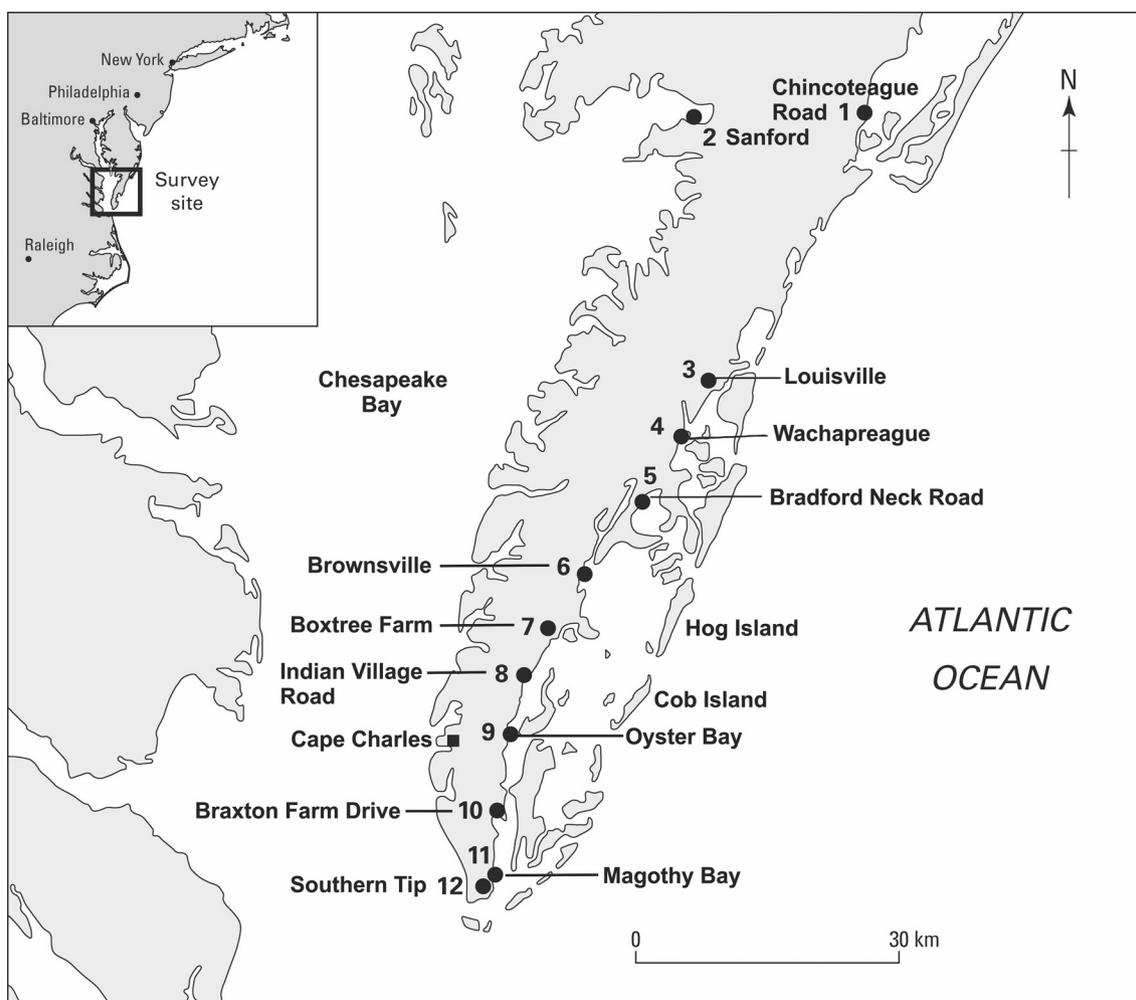


Fig. 2. Map showing locations of sample sites in of the Delmarva Peninsula, Virginia USA.

The concentration of each fraction was determined using an Iatroscan® Mk6s instrument. The limit of quantification (LOQ) for total non-volatile hydrocarbons was 3 mg/kg.

Total mercury was determined using a DMA-80 dry solid sample analyser (Milestone, c/o Analytix Ltd., South Tyneside, UK). Operated at 650 °C and calibrated at 1–20 ng (9 duplicate points) in duplicate and 30–200 ng (5 single points). Two different certified reference materials were determined in duplicate sample in every ten analyses as a quality control. Data for the lower value certified reference material (CRM) is presented in Table 1. The limit of quantification (LOQ) for Hg was 0.02 mg/kg (calculated from a blank where $n = 9$).

High pressure liquid chromatography (HPLC) was used to determine PAH concentrations in the Delmarva sediments (Vane et al., 2007, 2008) and gas chromatography mass spectrometry (GCMS) was used to measure PAHs in the Delaware sediments. For the GCMS method, 1 g sample was spiked with: naphthalene- d^8 , biphenyl- d^{10} , phenanthrene- d^{10} , pyrene- d^{10} , benzo[*a*]anthracene- d^{10} , benzo[*a*]pyrene- d^{12} and benzo[*g,h,i*]perylene- d^{12} of between 267 and 4000 $\mu\text{g}/\text{kg}$ dry/wt. and extracted using ASE (hexane/acetone 1:1 v/v, 100 °C, 2000 p.s.i.). Extracts were reduced to 0.25 mL, and transferred to a solid phase extraction (SPE) cartridge (Bond Elut, TPH, W500MG, Na₂SO₄). The first fraction was eluted with pentane (0.5 + 1 mL), the second with 6 mL hexane/iso-propanol (97:3 v/v) and reduced to 0.2–1.0 mL. Concentrations of PAH were measured using a Varian 3800 gas chromatograph (GC) fitted with a VF35ms column, 30 m, 0.25 mm i.d., 0.1 μm df (Agilent Technologies, Stockport, UK) coupled to a Varian 1200L triple quadrupole mass spectrometer operating in full scan mode

(ionization energy 70 eV, mass range 47–500 amu). Quality control was achieved by subjecting a certified reference material, NRCHS5 Harbour Sediment, (Table 2) to the above procedure. A procedural blank prepared from 1 g silica (Sigma Aldrich, UK) – a material devoid of PAH – was treated in a similar way. LOQs were determined by peak height at 5 times signal/background ratio of the procedural blank and are presented in Table 2.

PCB concentrations were determined as follows: samples (10g) were spiked with PCB 34, 62, 119, 131 and 173 (9.0–9.7 ng/g) and PCB 19 and 147 (7.9–10.1 ng/g) and extracted using ASE, reduced in volume to 3–4 mL followed by addition of concentrated H₂SO₄ (3 × 0.6 mL) and agitated. The acidic aqueous layer was immediately removed, any remaining moisture was removed by passing the organic layer through a glass Pasteur pipette containing anhydrous Na₂SO₄. The hexane extract was reduced to 0.3–0.25 mL and subjected to the same SPE method as for PAH, spiked with PCB 29 and 157 (3.1–3.3 ng/g) and reduced to 0.1–0.2 mL. Concentrations of PCB were measured using GCMS fitted with a DB1 column, 60 m, 0.25 mm i.d., 0.1 μm df (Agilent Technologies, Stockport, UK). The MS was operated in selected ion mode (m/z 71, 220, 256, 258, 290, 292, 326, 328, 360, 362, 394, 396) with a scan time of 0.5 s. Congener profile distributions for tri to heptachlorinated biphenyls were determined using 5 separate individual relative response factors for each congener group. A standard consisting of 2 × 5 individual PCBs based on first and last eluting congener was used to define the ‘retention time window’ for each group. The sum of these 5 groups is $\Sigma\text{PCB}(\text{tri-hepta})$ and $\Sigma 7\text{PCB}$ comprised congeners 28, 52, 101, 118, 153, 138, 180.

Table 1

Total organic carbon (% TOC), total Hg (mg/kg dry wt) and total (extractable, non-volatile) petroleum hydrocarbons (TPH) in sediments from the Delmarva (sites 1–12) and Delaware River Estuary (sites 13–21) study areas. Quality control reference materials were MESS-3 (a marine sediment certified reference material from the National Research Council Canada) and in-house quality control sediments. Marine/estuarine sediment quality values (SQVs) are presented where PEC is the probable effects concentration, ERM is the effects range median, TEC is the threshold effect concentration and ERL is the effects range low.

I.D.	Site name	Longitude (decimal)	Latitude (decimal)	TOC (%)	Hg (mg/kg)	TPH (mg/kg)	Aromatics (mg/kg)	Saturates (mg/kg)	Aromatics (%)	Saturates (%)
1	Chincoteague Road	37.94076	75.44227	3.41	0.09	87	11	77	13%	89%
2	Sanford	37.93858	75.67121	1.58	0.06	141	42	98	30%	70%
3	Louisville	37.65347	75.65574	3.95	0.08	77	20	56	26%	73%
4	Wachapreague	37.60106	75.69001	2.95	0.10	79	21	59	27%	75%
5	Bradford Neck Road	37.53311	75.74141	0.15	< 0.02	< 34	< 3	< 31		
6	Brownsville	37.45812	75.81896	0.73	0.02	37	< 3	37		
7	Boxtree Farm	37.39568	75.86998	1.53	0.07	51	< 3	51		
8	Indian Village Road	37.35071	75.90047	2.62	0.09	74	19	55	26%	74%
9	Oyster Bay	37.28773	75.91784	0.49	0.03	< 34	8	< 31		
10	Braxton Farm Drive	37.20486	75.93775	4.39	0.07	81	23	58	28%	72%
11	Magothy Bay	37.14027	75.94189	3.64	0.05	69	20	49	29%	71%
12	Southern Tip	37.12908	75.95486	2.36	0.06	159	72	87	45%	55%
Delmarva	Mean			2.32	0.07	86	26	63	28%	72%
Delmarva	Median			2.49	0.07	78	20	57	27%	72%
13	Trenton North	40.23822	74.80900	3.95	0.07	195	37	158	19%	81%
14	Burlington Island	40.09132	74.09132	2.08	0.04	240	75	164	31%	68%
15	Floodgate	39.83095	75.33162	5.30	0.04	242	107	135	44%	56%
16	Fox Point	39.75765	75.48870	0.33	0.06	212	66	146	31%	69%
17	Carney Point	39.71485	75.47670	6.23	0.25	543	307	236	57%	43%
18	Deeves Beach	39.65288	75.58392	9.05	0.28	616	233	383	38%	62%
19	Reedy Point	39.55940	75.56603	3.23	0.18	201	104	97	52%	48%
20	Elfsborg	39.54513	75.52980	0.05	< 0.02	38	38	< 31		
21	Augustine Beach	39.50605	75.57912	1.94	0.09	151	74	77	49%	51%
Delaware	Mean			3.57	0.13	271	116	175	40%	60%
Delaware	Median			3.23	0.08	212	75	152	41%	59%
	QC name			In-house	MESS-3	In-house	In-house	In-house		
	Assigned value			7.53	0.091	2934	761	2172		
	Uncertainty			± 0.15	± 0.01	± 587	± 152	± 434		
	Permissible max.			7.91	0.10	3668	951	2715		
	Permissible min.			7.15	0.08	2201	571	1629		
	no. of QC runs			4	2	8	8	8		
	Value obtained			7.62 [± 0.07]	0.10 [± 0.001]	3294 [± 260]	647 [± 110]	2647 [± 247]		
	PEC (MacDonald et al., 2000)				1.06					
	ERM (Long et al., 1995)				0.71					
	TEC (MacDonald et al., 2000)				0.18					
	ERL (Long et al., 1995)				0.15					

Quality control was achieved by subjecting a PCB certified reference material EC-1, PCBs in harbour sediment to the above procedure and analysing it by the same method as for the samples (Table 3). A procedural blank prepared from silica (Sigma Aldrich, UK) – a material devoid of PCBs was treated in a similar way.

Mercury is one of the most important heavy metal pollution indicator in estuarine and coastal sediments, due to its toxic effect on marine invertebrates and tendency for the methyl-Hg to bio-accumulate up trophic levels, where it can enter humans via the ingestion of fish and shellfish (Bigham et al., 2006; Boening, 2000). An upstream to downstream spatial trend of Hg was observed in the Delaware River Estuary sediments (Fig. 3). Hg concentrations upstream from Trenton North (sites 13–16) had low values of < 0.1 mg/kg. Hg concentrations were elevated (0.18–0.28 mg/kg) from Carney Point to Reedy Point (sites 17–19), but returned to lower values (< 0.1 mg/kg) downstream at Elfsborg to Augustine Beach (sites 20–21).

The Delaware sediments had higher Hg concentrations, mean 0.13 mg/kg, compared to Delmarva, mean 0.07 mg/kg (Table 1). These sediment-hosted Hg concentrations were indicative of natural background conditions and did not exceed Hg effects range median (ERM) limit of 0.71 mg/kg (Long et al., 1995), or the probable effects level (PEC) limit of 1.06 mg/kg (MacDonald et al., 2000) for marine and estuarine ecosystems, which according to these criteria, indicates that Hg may not be impacting the aquatic organisms in these regions. The

highest concentration observed at sites 17–19 (Fig. 1) are above the threshold effects concentration (TEC) and the effects range low (ERL) (Table 1); below these values, adverse effects on biota are not expected to occur.

The higher concentrations of Hg in Delaware River Estuary sediments compared to those from the Delmarva Peninsula likely reflects sedimentary input from urban and industrial areas along the Delaware River Estuary compared to the rural Delmarva watershed. A plausible cause for the elevated concentrations from Carney Point to Reedy Point (sites 17, 18, and 19) on the Delaware River Estuary is that it may come from the diffuse source of numerous heavy industry and waste processing activities (vehicle scrap yards) in the vicinity of Wilmington. A similar spatial trend was observed in the Thames River Estuary, UK where total Hg ranged from 0.01 to 12.07 mg/kg (mean = 2.10 mg/kg; n = 351) and the highest concentrations were found close to likely point sources of industrial pollution (Vane et al., 2015). Alternatively, differences in Hg concentration between the two current study regions may arise from differences in sediment characteristics and dynamics (i.e. river estuarine and coastal oceanic). Total Hg is more strongly correlated to TOC in the Delaware (R^2 0.6372) compared to the Delmarva (R^2 0.5194), suggesting that organic matter is one of the controlling factors of Hg sorption. The correlation difference between the two sites may be partly explained by a lower availability of Hg to sorb in the Delmarva sediments, but other factors such as grain size, bacteria

Table 2
PAH concentrations ($\mu\text{g}/\text{kg}$ dry wt) in the Delmarva (sites 1–12) and Delaware River (sites 13–21) study areas compared to quality control reference materials NRCHS 5 (a marine sediment certified reference material from the National Research Council Canada). Marine/estuarine sediment quality values (SQVs) are presented where PEC is the probable effects concentration, ERM is the effects range median, TEC is the threshold effect concentration, ERL is the effects range low and NOAA is the National Oceanic and Atmospheric Administration. Standard deviation is given in the parentheses, where n are the number of analyses, n.d. = not determined. < LoQ = less than limit of quantification. † value for total PAHs. Naph: naphthalene, 1-MN: 1-methylnaphthalene, 2-MN: 2-methylnaphthalene, Ace: acenaphthene, Fluor: fluorene, Phen: phenanthrene, Anth: anthracene, Fanth: fluoranthene, Pyr: pyrene, B[a]A: benzo[a]anthracene, Chrys: chrysene, TPh: triphenylene, B[b]F: benzo[b]fluoranthene, Pery: perylene, B[a]F: benzo[a]fluoranthene, B[a]P: benzo[a]pyrene, DBA: dibenz[a,h]anthracene, B[ghi]P: benzo[ghi]perylene, IP: indeno[1,2,3-cd]pyrene.

Site no.	Site name	Naph	1-MN	2-MN	Ace	Fluor	Phen	Anth	Fanth	Pyr	
1	Chincoteague Road	13	3	5	1	2	11	4	22	16	
2	Sanford	5	4	3	5	8	139	22	288	263	
3	Louisville	6	1	4	0	3	13	4	28	14	
4	Wachapreague	8	3	7	1	4	16	7	44	26	
5	Bradford Neck Road	0	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	< LoQ	
6	Brownsville	< LoQ	< LoQ	< LoQ	< LoQ	0	2	1	6	3	
7	Boxtree Farm	4	2	3	1	2	8	3	22	11	
8	Indian Village Road	11	3	7	1	3	14	4	28	12	
9	Oyster Bay	2	< LoQ	0	< LoQ	0	2	1	10	9	
10	Braxton Farm Drive	5	2	3	1	2	17	7	132	111	
11	Magothy Bay	5	1	1	0	1	8	1	12	7	
12	Southern Tip	35	40	51	3	13	123	26	250	179	
Delmarva	Mean	9	7	8	2	4	32	7	77	59	
Delmarva	Median	5	3	3	1	2	13	4	28	14	
13	Trenton North	163	57	61	63	267	578	134	912	1223	
14	Burlington Island	124	28	41	40	231	627	185	698	975	
15	Floodgate	122	39	53	86	272	428	83	440	542	
16	Fox Point	113	26	56	36	89	330	65	423	483	
17	Carney Point	175	74	89	156	305	606	242	792	1152	
18	Deeves Beach	173	111	169	321	1532	1942	728	2258	3020	
19	Reedy Point	146	48	80	43	146	202	64	219	350	
20	Elfsborg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	29	227	286	
21	Augustine Beach	119	30	53	14	191	280	75	280	365	
Delaware	Mean	142	52	75	95	379	624	178	694	933	
Delaware	Median	135	43	58	53	249	503	83	440	542	
NRCHS 5	Certificate values	250	Not listed	Not listed	230	400	5200	380	440	5800	
NRCHS 5	Value obtained (n = 27)	243	86	109	246	402	5235	366	(\pm 2600)	(\pm 1800)	
NRCHS 5	LoQ	7	(\pm 24)	(\pm 33)	(\pm 131)	(\pm 99)	(\pm 356)	(\pm 63)	(\pm 924)	(\pm 347)	
PEC (MacDonald et al., 2000)		561	6	5	4	50	5	5	4	4	
NOAA; ERM (Long et al., 1995)		2100		670	500	536	1170	845	2230	1520	
TEC (MacDonald et al., 2000)		176				540	1500	1100	5100	2600	
NOAA; ERL (Long et al., 1995)		160		70	15	77	204	57.2	423	195	
						19	240	85.3	600	665	
Site no.	B[a]A	Chrys + TPh	B[b]F	Pery	B[k]F	B[a]P	DBA	B[ghi]P	IP	Σ PAH 18	% Pery
1	7	149	2	2	0	0	< LoQ	< LoQ	0	96	2%
2	142	7	158	49	87	165	18	112	97	1714	3%
3	9	10	16	50	8	9	3	10	9	197	26%
4	18	17	30	59	18	21	3	17	17	317	19%
5	< LoQ	0	1	1	< LoQ	0	< LoQ	1	0	5	25%
6	3	3	4	9	4	3	< LoQ	3	2	42	21%
7	7	8	15	32	7	7	< LoQ	6	6	143	23%
8	10	9	16	43	9	10	1	14	7	200	21%
9	8	10	11	9	5	8	< LoQ	11	5	91	10%
10	66	86	108	41	55	56	10	36	49	789	5%
11	5	6	11	13	6	3	< LoQ	7	3	89	15%
12	112	110	255	95	126	180	45	277	219	2139	4%
Delmarva	35	34	52	34	30	39	13	45	34	485	14%
Delmarva	9	9	15	37	8	8	7	11	7	170	17%

Table 2 (continued)

Site no.	B[a]A	Chrys + TPh	B[b]F	Pery	B[k]F	B[a]P	DBA	B[ghi]P	IP	ΣPAH 18	% Pery
13	884	443	539	205	225	723	171	736	522	7907	3%
14	574	325	349	126	188	494	67	374	296	5742	2%
15	307	3910	139	297	68	222	n.d.	191	177	7374	4%
16	389	297	317	89	160	263	39	333	243	3749	2%
17	863	565	425	274	213	672	78	429	386	7495	4%
18	2945	1328	1161	612	702	2100	289	1489	1443	22,324	3%
19	242	153	174	362	76	257	31	238	199	3030	12%
20	203	211	328	161	118	430	41	188	133	n.d.	n.d.
21	228	149	133	197	59	256	n.d.	163	137	2729	7%
Delaware	737	820	396	258	201	602	102	460	243	7544	5%
Delaware	389	325	328	205	160	430	67	333	243	6558	3%
NRCHS 5	2900	2800	2000	Not listed	1000	1700	200	1300	1300		
	(± 1200)	(± 900)	(± 1000)		(± 400)	(± 800)	(± 100)	(± 300)	(± 700)		
NRCHS 5	2857	2814	2012	466	967	1696	196	1292	1245		
	(± 257)	(± 321)	(± 144)	(± 62)	(± 72)	(± 165)	(± 31)	(± 111)	(± 143)		
	1	2	2	4	2	10	4	7	4		
PEC	1050	1290				1450				22,800 [†]	
(MacDonald et al., 2000)											
NOAA; ERM	1600	2800				1600	260			44,792 [‡]	
(Long et al., 1995)											
TEC	108	166				150	33			1610 [†]	
(MacDonald et al., 2000)											
NOAA; ERL	261	384				430	63.4			4022 [‡]	
(Long et al., 1995)											

Table 3

Surface sediment PCB concentrations ($\mu\text{g}/\text{kg}$ dry wt.) from the Delmarva Peninsula, Delaware River and quality control PCB concentrations for National Water Research Institute reference material EC-1 in harbour sediment and relevant marine/estuarine sediment quality values (SQVs). Standard deviation is given in the parentheses, where n are the number of analyses, n.d. = not determined. < LoQ = less than limit of quantification. a = possible interference at m/z 258 for tri-chlorinated PCBs observed in this sample.

Site No.	Site name	PCB 028	PCB 052	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Σ PCB (ICES 7)	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	Σ PCB(tri-hepta)
1	Chincoteague Road	0.1	0.0	0.0	0.1	0.4	0.2	0.0	0.9	0.6	0.5	1.0	0.8	0.6	3.4
2	Sanford	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.5	0.3	0.2	1.1
3	Louisville	0.0	0.1	0.0	0.0	0.4	0.0	0.0	0.5	0.1	0.2	0.6	0.7	4.0	5.6
4	Wachapreague	0.2	0.1	0.0	0.2	0.4	0.0	0.2	1.2	0.3	0.9	1.3	1.0	1.4	4.8
5	Bradford Neck Road	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.1	0.1	0.6
6	Brownsville	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.3	5.3 ^a	0.1	0.7	0.0	0.4	6.5
7	Boxtree Farm	0.0	0.1	0.0	0.1	0.4	0.2	0.0	0.8	0.3	0.2	0.5	1.0	0.3	2.3
8	Indian Village Road	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.6	0.2	0.6	0.6	0.6	0.7	2.7
9	Oyster Bay	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.1	0.3	0.2	0.5	1.1
10	Braxton Farm Drive	0.1	0.1	0.2	0.0	0.7	0.3	0.2	1.5	0.3	0.7	1.2	1.3	2.7	6.1
11	Magothy Bay	0.1	0.1	0.2	0.1	0.4	0.2	0.1	1.2	0.2	0.4	0.6	1.2	2.0	4.4
12	Southern Tip	0.0	0.1	0.3	0.2	0.9	0.4	0.0	2.0	0.0	0.0	1.2	1.8	0.9	4.0
Delmarva	Mean	0.1	0.1	0.1	0.1	0.3	0.1	0.0	0.8	0.6	0.3	0.7	0.7	1.2	3.6
Delmarva	Median	0.1	0.1	0.0	0.0	0.4	0.1	0.0	0.7	0.2	0.2	0.6	0.7	0.6	3.7
13	Trenton North	0.4	0.5	1.0	0.5	0.5	0.0	0.0	2.8	11.8	4.0	18.2	18.0	7.2	59.2
14	Burlington Island	0.4	0.3	3.0	1.7	9.3	5.4	12.1	32.2	6.8	2.2	24.3	47.6	29.6	110.6
15	Floodgate	0.2	0.1	0.9	1.0	1.0	0.0	1.0	4.2	5.0	2.0	18.4	17.2	4.2	46.8
16	Fox Point	0.9	1.3	3.1	3.6	2.2	2.3	1.3	14.7	19.1	7.4	20.8	13.9	3.8	65.0
17	Carney Point	0.0	0.9	1.8	3.7	1.2	1.2	0.5	9.4	3.0	9.0	21.7	5.9	1.6	41.1
18	Deeves Beach	0.6	2.2	6.5	5.0	9.5	7.4	8.0	39.2	4.3	14.4	47.6	40.9	29.6	136.8
19	Reedy Point	0.6	0.4	0.8	1.1	1.3	0.7	0.0	4.8	4.2	1.9	8.0	3.1	0.8	18.1
20	Elfsborg	0.6	0.0	0.0	0.1	0.2	0.0	0.0	0.8	0.9	0.4	8.1	11.0	1.1	21.9
21	Augustine Beach	0.2	0.1	0.8	0.5	1.0	0.0	0.0	2.7	13.0	3.2	15.6	15.2	3.9	50.8
Delaware	Mean	0.4	0.7	2.0	1.9	2.9	1.9	2.5	12.3	10.0	4.9	20.3	21.2	9.1	61.1
Delaware	Median	0.4	0.4	1.0	1.1	1.2	0.7	0.5	4.8	6.8	3.2	18.4	17.2	3.9	50.8
EC-1, harbour sediment	Certificate values	48.7	99.4	109.4	79.8	68.2	72	44.9	522						2000
	(± 17)	(± 43.2)	(± 74.4)	(± 37.1)	(± 22.1)	(± 26.3)	(± 23.2)								(± 50)
EC-1, harbour sediment	Value obtained (n = 22)	40.0	94.6	103.2	93.2	82.3	83.8	57.4	555						1869
	(± 6.3)	(± 5.4)	(± 4.2)	(± 11.9)	(± 7.9)	(± 9.1)	(± 5.3)		(± 50)						(± 167)
	LoQ	1.4	1.3	1.2	1.1	1.1	1.2	1.5	0.0						6.4
PEC (MacDonald et al., 2000)															676
NOAA; ERM (Long et al., 1995)															180
TEC (MacDonald et al., 2000)															59.8
NOAA; ERL (Long et al., 1995)															22.7

and mineral colloids are also important in fixing Hg in the environment (Haitzer et al., 2003).

Worldwide, marine coastal and estuarine sediments have Hg background concentrations of approximately 0.02 to 0.1 mg/kg (Kannan and Falandysz, 1998; Shi et al., 2007). The low concentrations of the Delmarva are similar to those found in other salt marshes such as Barnegat Bay – Little Egg Harbour Estuary, NJ, which ranged from < 0.02 to 2.61 mg/kg, mean 0.31 mg/kg (Vane et al., 2008) and in South Carolina coastal estuaries which ranged from 0.02 to 0.13 mg/kg, mean 0.07 mg/kg (Sanger et al., 1999a). Delaware and Delmarva Hg concentrations are considerably lower than in sediments from waterways in the industrialized Passaic River (New Jersey) which ranged from 0.91 to 5.80 mg/kg, mean 2.70 mg/kg (Armstrong et al., 2005) and the Mersey Estuary, UK at a mean concentration of 0.84 mg/kg for surface sediments (Vane et al., 2009). In this current study, the Hg concentrations observed in the Delaware River Estuary are similar to those previously reported for surface sediments collected from the Mullica River which varied from 0.24–0.46 mg/kg, mean 0.32 mg/kg (Armstrong et al., 2005). The Mullica River (New Jersey, USA) was used as a reference area for regional background concentrations of metals in the absence of significant anthropogenic input; according to this criteria

total the Hg concentrations found in the Delaware Estuary (current study), are within regional background levels.

Total (extractable, non-volatile) petroleum hydrocarbon (TPH) concentrations in surface sediments are presented in Table 1. The

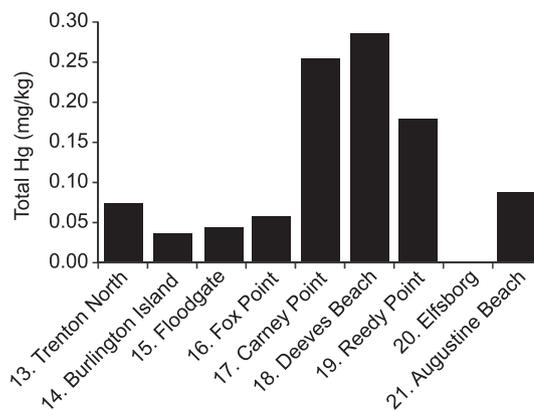


Fig. 3. Spatial distribution of Hg in surface sediments of the Delaware River.

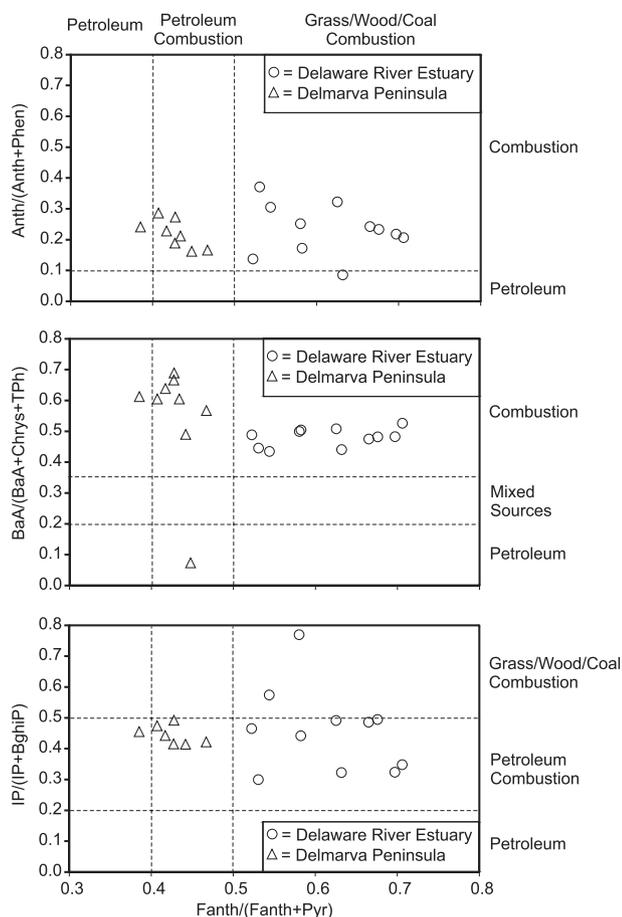


Fig. 4. PAH isomeric plot for surface sediments from the Delmarva Peninsula (circles) and Delaware River Estuary (triangles).

Delaware TPH mean was 271 mg/kg which is significantly higher than the Delmarva, where the mean was 86 mg/kg. Previous studies have found that in pristine estuarine and intertidal sediments total hydrocarbon concentrations range from about 0.5 to 10 mg/kg and can be as high as 30 mg/kg, where there is significant input from *n*-alkanes sourced from plant waxes for example (Volkman et al., 1992; Volkman and Nichols, 1991). The values of the Delaware are broadly comparable to that from a study of salt marsh surface sediments of Barnegat Bay-Little Egg Harbor Estuary, New Jersey, where mean TPH was 231 mg/kg (Vane et al., 2008).

Sediments containing total TPH > 100 mg/kg are generally considered to have received some petroleum pollution and sediments with values > 500 mg/kg are indicative of significant petroleum inputs (Volkman et al., 1992; Volkman and Nichols, 1991). Using these criteria for the Delmarva, all twelve sites had TPH values that suggested minimal levels of petroleum contamination. The low hydrocarbon values at all sites (with the exception of sites 2 and 12) probably represent background hydrocarbons derived from biological sources such as the dominant salt marsh plants, namely cord grasses (*Spartina patens* and *S. alterniflora*) and possibly other sources such as animals as well as micro and macroalgae (Volkman et al., 1992). The range of hydrocarbon concentrations encountered in the Delmarva, are consistent with biologically derived hydrocarbon source augmented by low levels anthropogenic hydrocarbon contamination. This rationale can be substantiated further because the Delmarva sediments were dominated by saturates (mean 72%), as compared to aromatic hydrocarbons (mean 28%), whereas in the Delaware the aromatics were in greater abundance (mean 40%), compared to the saturates of mean 60% (Table 1). A possible explanation for this difference is that the Delmarva has a larger input of saturates derived from the waxy cuticle of terrestrial and

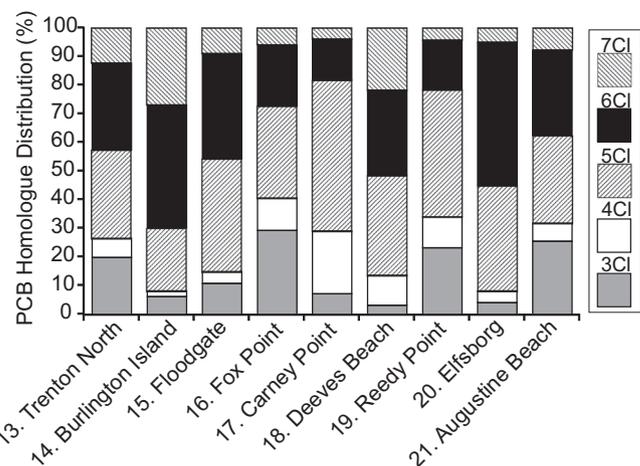


Fig. 5. Spatial variation of the relative contribution of PCB homologues for surface sediments from the Delaware River Estuary.

aquatic plants, whereas in contrast, due to the low biological productivity of the transitional zone (McLusky and Elliott, 2004) there is a lower input of these plant derived saturates and that it receives sedimentary input from urban and industrial sources containing aromatic compounds. Using the same criteria for the Delaware, seven of nine sites had TPH values that suggested only some petroleum contamination. However, for Carney Point (site 17) and Deeves Beach (site 18) the TPH (543 and 616 mg/kg respectively) suggests significant petroleum input within this 5 km stretch of the river-estuary. This is not surprising as this section is in close proximity of areas of heavy industry which may be a possible source of diffuse contamination. Possible sources could be: the Port of Delaware (shipping and fuel storage) situated on the western bank of the Delaware at the tributary of the Christina River; the DuPont Chambers Plant at Deepwater (chemical manufacturing) on the eastern bank; the Croda plant (manufacture of lubrication oils) situated on the southern side of the Delaware Memorial Bridge; and historic records of oil refinery effluent discharge into the Delaware, notably from the Motiva refinery situated 5 km north of the Chesapeake-Delaware Canal (Alexander et al., 2005; Hall and Burton, 2005; Uhler et al., 2005).

In a study of comparable rivers (that flow through eastern U.S. industrial zones) and catchments, in the Newark Bay, New Jersey area (Huntley et al., 1995) the mean sediment TPH concentrations were: Arthur Kill River, 703 mg/kg (median 205 mg/kg); Hackensack River, 119 mg/kg (median 106 mg/kg); Passaic River 1520 mg/kg (median 294 mg/kg). These concentrations are broadly comparable to those reported in the current study (Table 1).

PAHs are derived from four broad sources: biogenic, geogenic, petrogenic and pyrolytic (formed during the combustion of organic matter and fossil fuels); their environmental distribution and attenuation have been extensively documented (Boehm, 2006; Sanger et al., 1999b).

PAH concentrations in the Delaware are significantly higher than the Delmarva (Table 2). Total PAHs (Σ PAH18) in the Delaware (mean 6967 μ g/kg; median 5742 μ g/kg). Whereas in the Delmarva the mean was 485 μ g/kg and the median 170 μ g/kg. The sediment quality guidelines (SQGs) for total PAHs for the effects range median (ERM) limit is 44,792 μ g/kg (Long et al., 1995) and the probable effect concentration (PEC) limit is 22,800 μ g/kg (MacDonald et al., 2000) for marine and estuarine ecosystems. This indicates that the PAH concentrations, in both study areas, is unlikely to have no possible adverse effect on aquatic organisms in this area. In the current study, the Σ PAH18 concentrations (not total PAHs) were indicative of natural background for both the Delaware and Delmarva (Table 2). The range

and mean of values of the Delmarva are broadly comparable to those from a study of salt marsh surface sediments of Barnegat Bay-Little Egg Harbor Estuary, New Jersey, where Σ PAH18 was 37–1696 $\mu\text{g}/\text{kg}$ with a mean value of 671 $\mu\text{g}/\text{kg}$ (Vane et al., 2008). The Delmarva Σ PAH18 are also comparable with those reported for contaminants in surface sediments taken from the mudflats of the Mullica River, New Jersey, that has been relatively unaffected by industrial and urban influences (Iannuzzi et al., 2005), where Σ PAH25 concentrations were 436–1380 $\mu\text{g}/\text{kg}$ with a mean of 786 $\mu\text{g}/\text{kg}$. In the current study, the mean concentration is marginally lower (485 $\mu\text{g}/\text{kg}$) than that reported by Iannuzzi et al., 2005 and can be mitigated by the fact that we report Σ PAH18 rather than Σ PAH25.

The Σ PAH18 concentrations in the Delaware study area from Reedy Point (site 19) to Augustine Beach (site 21) were lower (2355–3030 $\mu\text{g}/\text{kg}$) than at sites further upstream from Trenton North (site 13) to Carney Point (site 17) (3749–7907 $\mu\text{g}/\text{kg}$). A possible source for these higher concentrations, in this stretch, is delivery of PAH-laden sediment from the Schuylkill River, where there is a large industrial cluster of refineries, a naval base, an international airport, and vehicle breakers yards. The PAH concentrations of the current study seems to be in agreement with previous studies that found PAH in sediment traps from both the Delaware and Schuylkill Rivers to be 5120 $\mu\text{g}/\text{kg}$ and 5150 $\mu\text{g}/\text{kg}$ respectively (Pohlman et al., 2002); they also discussed the movement sediment along the tidal incursion zone at the intersection of both rivers. The lower PAH concentration observed downstream in this study (sites 19–20) could probably be attributed to sediment dilution or mixing affect with less contaminated sediment.

The Σ PAH18 values found at sites clustered in the vicinity of the Motiva refinery and C&D Canal (sites 19–21) in the Delaware were 2355–3030 $\mu\text{g}/\text{kg}$ (Table 2) and are similar to those found by other workers in the same study area (Alexander et al., 2005) where the total PAH concentrations from two sediment cores were 3100–3200 $\mu\text{g}/\text{kg}$ at 4–6.5 cm depth, they attributed this to be consistent with historic sediment PAH inputs in such an industrial river system. Approximately 17 km north of this cluster is the PAH ‘hot-spot’ of Deeves Beach (site 18) where Σ PAH18 was 22,324 $\mu\text{g}/\text{kg}$ which also had the highest Hg concentration of all the sites at 383 mg/kg (Table 1). As explained earlier, one probable reason for these elevated PAH concentrations at this site, is that it is from the numerous heavy industrial activities in the vicinity, road run-off and the sedimentary outflow from the Christina River which sorb to the relatively high TOC (9.05%) contained in this sediment. It was found that Σ PAH18 is strongly correlated to TOC in the Delaware River Estuary sediment (R^2 0.7353) compared to the Delmarva salt marsh where no correlation was observed (R^2 0.0068), this poor correlation was also observed in the salt marshes of Barnegat Bay – Little Egg Harbor Estuary (R^2 0.22) by Vane et al. (2008).

The mean proportion of perylene to Σ PAH18 in the Delmarva sediments was 14%, this was higher than those from the Delaware at 5% (Table 2). Perylene is a diagenetic product derived from natural precursors during early diagenesis (Conde et al., 2005; Silliman et al., 1998; Venkatesan, 1988; Wilcke, 2007) and formed in situ in river sediments (Luo et al., 2008), however only trace amounts of perylene are produced during combustion (Gonzalez-Perez et al., 2004; Kakareka and Kukharchyk, 2003). Previous workers (Vane et al., 2013) have demonstrated that perylene was one of the predominant PAHs in five species of upland vegetation and had a greater relative abundance (10–18%) than is usually observed in particles/sediments (< 2%) receiving PAH of anthropogenic/pyrolytic origin. Therefore a possible explanation for the higher proportion of perylene in the Delmarva sediment is that the Peninsula is dominated by vegetation from rural, agricultural, woodland and marshland sources which are likely to contain a higher amount of perylene compared to the anthropogenic input seen in the Delaware study area.

Further evidence for identifying urban and rural PAH sources, is demonstrated in the use of isomeric ratio cross plots (Fig. 4) which were constructed based on the relative concentrations of isomeric pairs of

PAHs whose ratios have been identified as diagnostic of PAH origin (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002). The resulting three cross plots revealed that petrogenic inputs of PAHs did not predominate from the Delmarva, but in contrast in Delaware sediment, a distinct petroleum/petroleum combustion contribution was observed. The cross-plots from the Delmarva saltmarsh sediments strongly suggested PAH sources from grass-wood-coal combustion which would be expected from such a rural setting, very similar isomeric ratios has also been observed in the salt marshes of Barnegat Bay – Little Egg Harbour Estuary (Vane et al., 2008).

The only point that plot outside the purely combustion zones of the cross plots for the Delaware was from Floodgate (site 15), this was attributed to an unknown point source of triphenylene contamination; triphenylene co-elutes with chrysene during GC analysis and has a very similar mass spectrum to that of chrysene.

Polychlorinated biphenyls (PCBs) are used e.g. as dielectric and coolant fluids in electrical equipment and in heat transfer fluids. PCBs are environmentally toxic and have possible carcinogenic properties. Consequently their industrial use and production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001. Their environmental distribution and attenuation have been extensively documented (Johnson et al., 2006).

The concentrations of individual congeners (ICES 7 group) and total PCBs as well as summed tri-, tetra-, penta-, hexa-, hepta-chlorinated congeners are presented in Table 3. In this study the di-, octa-, nona-, and deca-PCBs were not determined and this has to be considered when comparing Σ PCB(tri-hepta) concentrations with other reported values where the total PCBs are calculated from the sum of a wider congener range.

PCB concentrations in the Delaware are significantly higher compared to the Delmarva. The mean concentration of Σ PCB (ICES 7) in the Delaware 12.3 $\mu\text{g}/\text{kg}$ (median 4.8 $\mu\text{g}/\text{kg}$), whereas, in the Delmarva it was 0.8 $\mu\text{g}/\text{kg}$ (median 0.7 $\mu\text{g}/\text{kg}$). The sites presenting minimum and maximum PCB concentrations are identical to those listed for PAH concentrations, demonstrating the concomitant POPs loading at each of the sites.

The sediment quality guidelines (SQGs) for total PCBs for the ERM limit is 180 $\mu\text{g}/\text{kg}$ (Long et al., 1995) and the PEC limit is 676 $\mu\text{g}/\text{kg}$ (MacDonald et al., 2000) for marine and estuarine ecosystems. This indicates that the PCBs may not be having adverse effect on aquatic organisms in both study areas. In the current study, the Σ PCB(tri-hepta) concentrations were indicative of background for both the Delaware and Delmarva (Table 3).

The Σ PCB(tri-hepta) concentrations of the Delmarva are significantly lower compared to that from a study of salt marsh surface sediments of Barnegat Bay-Little Egg Harbor Estuary, New Jersey, where it ranged from 4 to 50 $\mu\text{g}/\text{kg}$ with a mean of 21 $\mu\text{g}/\text{kg}$ (Vane et al., 2008). Higher values have been reported in surface sediments taken from the mudflats of the Mullica River, New Jersey, that has been relatively unaffected by industrial and urban influences (Iannuzzi et al., 2005) where total PCB concentrations were 25–46 $\mu\text{g}/\text{kg}$ (mean of 36 $\mu\text{g}/\text{kg}$). This can be explained by the sorption of PCBs to clay and or natural organic matter (Fox et al., 2001; Scrimshaw and Lester, 2001). Generally as %TOC of sediments increase so does its capacity for PCB sorption. In the Delmarva the mean TOC was 2.32% (Table 1), whereas in Barnegat Bay and in the Mullica River the mean TOC were approximately twice as high at 4.91% and 4.34% respectively. The low PCB concentrations reported in this study (Table 3) supports the notion that the sediments of the Delmarva are not receiving significant inputs of PCB pollution.

In the current study, the Σ PCB(tri-hepta) mean concentration in the Delaware was 61.1 $\mu\text{g}/\text{kg}$ and significantly higher than the Delmarva (Table 3), again this points to the close proximity of heavy industry in the vicinity of the Delaware which is a possible source. In a similar study of the Delaware River Estuary by other workers (Cavallo and

Fikslin, 2011), the majority of sediments (also collected in 2008) were found to contain ~0.4–150 µg/kg total PCBs (mean ~10 µg/kg, n = 51), although not directly comparable to our study (fewer homologues used), the values of Cavallo and Fikslin (2011) are broadly consistent with our study.

The PCB homologue distributions are presented (Fig. 5). They are generally centred at the tetra-, penta- and hexa-chlorinated congeners. Although homologue distributions encountered here may be from industrial formulation Aroclor 1254 (the most widely sold mixture in the USA) the proportions of tri- and hepta-chlorinated were higher than would be expected if this was the sole source. The most plausible explanation being that factors such as dechlorination, volatilization and partitioning from air to water to sediment have probably also modified the congener profiles and homologue distributions to such an extent that source apportionment is beyond the scope of this study. The Delaware River Estuary has a history of being impacted by PCB contamination (Fikslin and Greene, 1998). In 2003 a total maximum daily load (TMDL) for PCBs was issued by the Delaware River Basin Commission via the Clean Water Act to minimize PCB pollution. To assist with this management strategy, PCB congener data have been used to help establish pollution source apportionment (Du et al., 2008; Praipipat et al., 2013). These studies have demonstrated the importance of non-Aroclor PCB sources. For example, a PCB ‘fingerprint’ was observed in the vicinity of a plant near Wilmington which produces high molecular weight (nona/deca-chlorinated) congeners as a by-product in the manufacture of TiCl₄ used in pigment production. Another significant non-Aroclor signal is from the atmospheric deposition of PCB11 (a dichlorinated PCB) used in the production of diarylide yellow pigment (Praipipat et al., 2013). However in the current study the di-, octa-, nona-, and deca-PCBs were not determined and consequently we are not able to detect a non-Aroclor congener signal which would concomitantly increase the Delaware total PCB concentrations.

To conclude: The concentration of PCBs, TPH and total Hg in the majority of surface sediments were considered mainly to be within regional (i.e. industrialized and rural) background levels in both of the study areas. Concentrations are elevated throughout the Delaware River Estuary study area compared to the Delmarva Peninsula. Applying suitable SQG (PEC) values to the Delaware Estuary sediments, the PAH concentrations are unlikely for have adverse effects aquatic life and ecosystems using these habitats. Spatial trends showing elevated concentrations in the vicinity of heavy industry for Hg and TPH were only observed in the Delaware but none were seen in the rural Delmarva study area. The presence of multiple heavy industry and historic discharge into the Delaware indicates multiple diffuse sources of Hg, TPH, PAHs, and PCBs. The combined use of PAH isomeric ratios, % perylene, and saturate aromatic ratios demonstrate that the majority of hydrocarbons in the Delaware are from anthropogenic/pyrolytic/petroleum sources whereas in the Delmarva they are mainly of biogenic origin.

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