ENDOCRINE DISRUPTING POLLUTANTS IN SEDIMENTS AND OYSTER TISSUES FROM ATLANTIC COASTAL SALT MARSH ECOSYSTEM OFF SAVANNAH, GEORGIA, USA

Kenneth S. Sajwan[1], Bommanna G. Loganathan[2], Siva Pramasivam[1], Joseph P. Richardson[1] and Kurunthachalam Kannan[3]

1 Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA
2 Department of Chemistry and Center for Reservoir Research, Murray State University, Murray, KY 42071, USA
3 Wadsworth Center, New York State Department of Health and Department of Environmental Health and Toxicology, State University of New York, Albany, NY 12201, USA

Introduction

As part of assessment of environmental health of the salt marsh ecosystem around Fort Pulaski National Monument in Chatham County, Georgia, USA., several organic compound and inorganic elements were measured in water, sediment and oyster tissues collected at selected locations of this region (Figure 1). This short paper presents baseline data on selected endocrine disrupting chemical pollutants such as alkylphenols (AP) and certain PAHs in sediment and oyster tissues collected from the salt marsh ecosystem. Alkylphenols, including octyl and nonylphenols and certain polynuclear aromatic hydrocarbons (PAHs) are well known endocrine disrupting chemicals causing serious environmental and health problems[1-3]. Common household products such as heavy-duty laundry powders, liquid detergents, personal care products and household cleaners contain nonionic surfactants that breakdown in the environment to form chemicals that can mimic estrogen[1]. These surfactants are a class of chemicals known as alkylphenol polyethoxylates and they breakdown in the environment into octylphenol and nonylphenols. The high production, use and moderate persistence in sediments and documented toxicity including estrogenic effects to aquatic organisms have resulted in concern over the risk posed by this class of chemicals. PAHs are a group of common environmental contaminants. They originate from anthropogenic sources such as waste incineration, coal gasification, and accidental oil spill as well as natural processes like fossil fuel and wood combustion[4] . Because of their hydrophobicity, low water solubility and vapor pressures, PAHs tend to accumulate in sediment and other organic phases. Occurrence of PAHs in the environment is of concern due to their carcinogenic properties and ability to exert toxic effects through aryl hydrocarbon receptor (AhR) mediated mechanism, similar to those of dioxins.

Methods and Materials

Six sampling sites were chosen within/along McQueen's island within the Fort Pulaski National Monument salt marsh ecosystem (Fig. 1). Three of these sites were within Oyster Creek, two sites were along the Bull River, and one site was at the mouth of the Savannah River at the inlet opening to the Atlantic Ocean. At each site, sediment and oysters were collected during a three-day period in mid-November 2000. Thirty sediment samples (5 samples per site) and six composite samples of oyster meat from 25-36 oysters were collected from each site. The samples were analyzed for polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and alkylphenols (APs) using standard procedures[2,3]. Briefly, the samples were homogenized with anhydrous sodium sulfate salt to remove moisture and Soxhlet extracted with methylene chloride and hexane (3:1) v/v, 400 mL) for 12h. Extracts were concentrated to 10 mL by rotary evaporation and treated with acid-activated copper granules to remove sulfur. Extracts were then fractionated and purified by eluting through 10g of activated Florisil (ITC, Hunt Valley, MD, USA) packed in a glass column (i.d. 10 mm). The first fraction (F1) which was eluted with 100 mL of hexane, contained PCBs, PAHs were eluted in the second fraction (F2) using 100 mL of 20% dichloromethane in hexane (v/v), Nonylphenol, octylphenol and butylphenol were eluted in the third fraction (F3) with 10 mL of 50% dichloromethane in methanol. PCBs and PAHs were quantified using a gas chromatograph with ^{63}Ni electron capture detector and a mass spectrometer respectively. A solution containing 100 individual PCB congeners with known composition and content was used as a standard, and concentration of 100

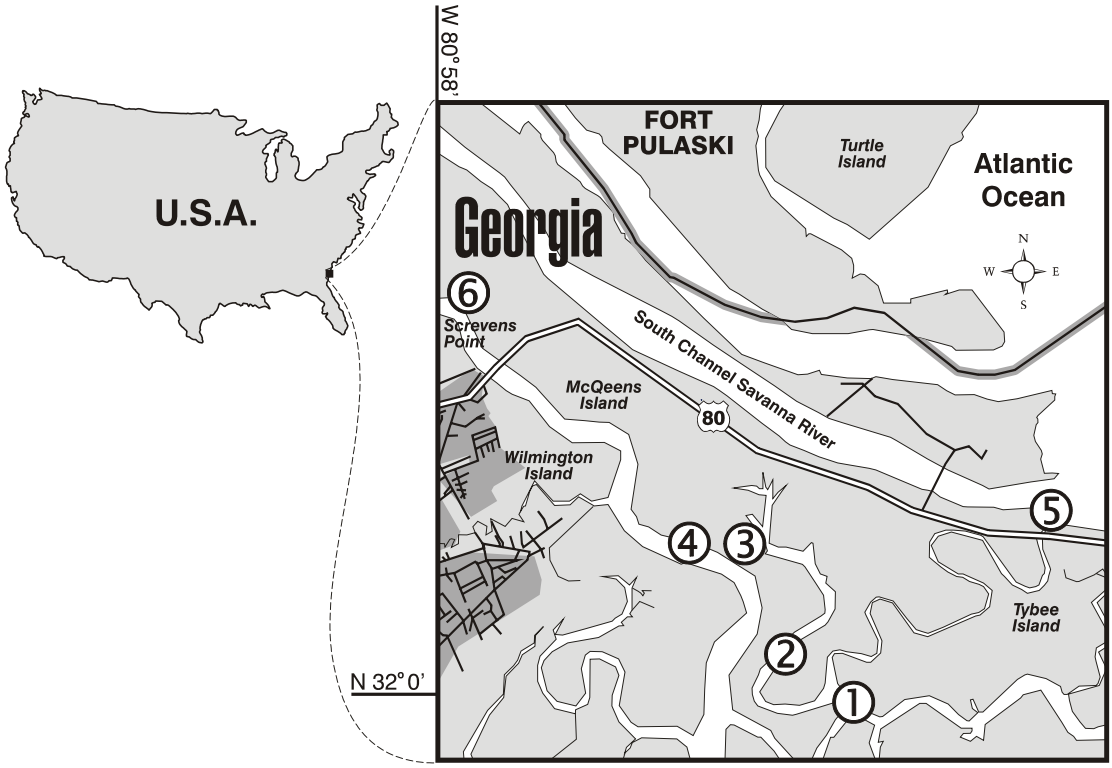

Figure 1. Map showing sediment and oyster sampling locations. Numbers 1 through 6 indicate the sampling sites.

individually resolved peaks were summed to obtain total PCB concentration. The PAH standard consisted of 16 priority pollutant PAHs as identified by the U.S. Environmental Protection Agency (EPA). The mass spectrometer was operated under selected ion monitoring (SIM) mode using the molecular ion selective for individual PAHs. Alkylphenols were quantified using a reverse-phase high performance liquid chromatograph with fluorescence detection. Fraction 3 extracts and standards were injected (10 µL) by a Perkin-Elmer Series 200 autosampler (Perkin-Elmer, Norwalk, CT, USA) on to an analytical column (Prodigy ODS, 250 X 4.6 mm; Phenomenex, Torrence, CA, USA), which ws connected to a guard column (Prodigy ODS, 30 X 4.6 mm Phenomenex) and eluted with a flow of acetonitrile (ACN) and water at a gradient from 50% ACN in water to 98% ACN in water delivered by a Perkin-Elmer Series 200 Pump for 20 min. Detection was accomplished using a Hewlett-Packard (Wilmington, DE, USA) 1046A fluorescence detector with an excitation wavelength of 229 nm and an emission wavelength of 310 nm. Further details of the fractionation procedure and instrumental analyses have been described elsewhere[3].

Results and Discussion

Total PCB concentrations in sediments and oysters collected at all six sites were below the detection limit (<10 ng g^{-1} dry wt). Similarly, butylphenol were not detected in the sediment and oyster tissues. However, several sediment and oyster tissue samples exhibited measurable concentrations of octyl and nonylphenols (Table 1a and 1b). Octyl- and nonyl phenol concentrations in sediment ranged from 2.0 to 22 ng g^{-1} g dry wt. and 2.0 to 78.1 ng g^{-1} g dry wt. respectively. Among the six sites, highest average concentration of ocytlphenol in sediment was 8.09 ng g^{-1} g dry wt. at site 3, while greatest concentration of nonylphenol recorded was 78.1 ng g^{-1} g dry wt. at site 5. The alkylphenol concentrations in sediment and oyster tissues from the Atlantic coastal salt marsh ecosystem are considered relatively low. Concentrations of PAHs in mussel tissues and sediment were shown in Table 2. The concentration of PAHs in oyster meat samples ranged from 18 to 210 ng g^{-1} g wet wt., with the highest concentration was found in oysters collected at site 2 (oyster creek).

Table 1a. Butyl-octyl and nonyl phenol concentrations (ng g^{-1} dry wt.) in sediment samples from selected locations at salt marsh ecosystem of Fort Pulaski National Monument.

Compound	Site 1 (n=5)	Site 2 (n=5)	Site 3 (n=5)	Site 4 (n=5)	Site 5 (n=5)	Site 6 (n=5)
Butylphenol	<4	<4	<4	<4	<4	<4
Octylphenol	<4	<4	8.09 (2.0-29)	5.97 (2.0-21.85)	5.97 (2.0-10.9)	5.7 (2.0-20.5)
Nonylphenol	18.53 (2.0-40.4)	11.88 (2.0-23.8)	18.16 (2.0-33.9)	14.76 (2.0-30.1)	18.67 (2.0-78.1)	18.19 (8.15-34.6

Table 1b. Butylphenol, Octylphenol and nonylphenol concentrations (ng g^{-1}wet wt.) in pooled oyster tissue samples from selected locations at salt marsh ecosystem of Fort Pulaski National Monument.

Compound	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Butylphenol	<1	<1	<1	<1	<1	<1
Octylphenol	<1	<1	7.93	<1	3.57	<1
Nonylphenol	<1	5.31	15.61	<1	10.43	<1

Table 2. Concentrations of PAHs in oyster samples collected from selected locations at salt marsh ecosystem of Fort Pulaski National Monument. Average total PAHs concentrations in sediments are shown in the last row.

Compound	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Naphthalene	0.30	<0.1	<0.1	0.40	<0.1	<0.1
Acenaphthalene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acenaphthene	0.53	0.55	<0.1	0.32	0.38	<0.1
Fluorene	<0.1	1.00	0.69	0.64	0.96	<0.1
Phenanthrene	<0.1	6.54	1.88	1.61	3.31	1.70
Anthracene	<0.1	<0.1	<0.1	<0.1	0.28	<0.1
Fluoranthene	2.16	15.40	1.33	0.30	3.72	5.34
Pyrene	10	106	7.16	0.07	5.48	32.78
Benzo[a]anthracene	0.24	<0.1	<0.1	<0.1	0.28	0.30
Chrysene	<0.1	<0.1	<0.1	<0.1	0.58	0.83
Benzo[b]fluoanthene	<0.1	<0.1	<0.1	1.36	4.38	<0.1
Benzo[k]fluoranthene	10.80	<0.1	<0.1	<0.1	3.74	<0.1
Benzo[a]pyrene	39.50	7.24	<0.1	<0.1	48.11	<0.1
Indeno(1,2,3-cd)pyrene	108.71	73.34	43.46	13.68	63.73	19.50
Dibenz(a,h)anthracene	6.38	<0.1	0.77	<0.1	3.76	<0.1
Benzo(g,h,i)perylene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sample wt.	20.02	20.63	20.69	20.62	20.14	20.19
Fat Content	1.34	1.40	1.53	1.46	1.17	NA
Total PAHs (ng/g wet wt)	178.69	209.61	55.29	18.39	138.70	60.46
Total PAHs (ng/g fat wt)	13322.88	14918.81	3620.73	1258.33	11850.41	NA
Sediments						
Total PAHs (ng/g dry wt) (n=5)	42.83	17.44	7.52	34.05	46.28	46.21

The concentrations of total PAHs in sediments were remarkably less than the suggested threshold effect concentrations (i.e. the concentration below which harmful effects are unlikely to occur) of 1,684 ng g^{-1} g dry wt. in all the locations[5]. Kannan *et al.* reported that PAHs in the upper Detroit River and Lower Rouge River sediments ranged from 18-43,810 ng g^{-1} dry wt[6]. Yamashita *et al.* reported that in surface sediments of Tokyo Bay contain 380 and 4,810 ng g^{-1} dry wt. of PAHs and nonylphenols respectively[7]. Considering the concentrations of PCBs, alkylphenols and PAHs in sediment and oyster tissues collected from salt marsh ecosystem of Fort Pulaski National Monument, negative biological effect by these compounds may be unlikely to occur. However, further studies including more number of samples, sampling sites and wide variety of persistent organic pollutant measurements are needed to confirm the observation.

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