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Concentration and Distribution of Specific Siloxanes (D5 and D6) and PAHs in the Anacostia and Potomac Rivers, USA

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Abstract: The waterways adjacent to Washington DC, USA have a history of contamination from heavy metals, nutrients, pesticides, and industrial chemicals. Among the chemicals of concern are PAHs, which are a historical contaminant but also have modern pyrogenic and petrogenic sources in the area's waterways. Another group of contaminants that are of emerging interest are siloxanes (silicones), which are widely used as lubricants, sealants, and cosmetics. Some lower-molecular-weight siloxanes are regulated by the EU in recognition of harm to aquatic life, but there are no restrictions in the United States. In fact, studies examining water pollutants do not typically test for siloxanes. Here, we present the concentrations of specific PAHs and siloxanes from surface sediments in the Potomac and Anacostia Rivers (including the Anacostia's tributaries) collected between 2018 and 2023. Both D5 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane) were found in most locations, with concentrations averaging 0.13 and 0.006 mg/g (dry mass), respectively. Pyrene, fluoranthene, bibenzyl, and phenanthrene were also found in the Anacostia and some of its tributaries, with concentrations increasing downstream. In the Potomac, concentrations were generally lower than those observed in the Anacostia. Based on ratios of pyrene to fluoranthene + pyrene, the likely source of PAHs was petrogenic.

Keywords: PAH; siloxane; freshwater contamination

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1. Introduction

The Anacostia River is a tributary of the Potomac River in Washington DC, which is one of the major rivers leading to Chesapeake Bay. The Anacostia River has historically been one of the nation's ten most contaminated rivers, as it contains metals, sewage, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAHs), and excess nutrients [1]. In fact, the EPA classified it as a "major area of concern" for the Chesapeake region. As a response, DC adopted a policy to make the Anacostia "fishable and swimmable" by 2032 [2]. Substantial progress has been made in identifying and eliminating contaminant point sources such as the combined sewage outflow (CSO) that exists in older sections of the city. Indeed, 98% of CSO is now diverted to the area's water treatment facilities rather than flowing into the area's rivers [3]. Seventy-five percent of the Anacostia's watershed is urban or impervious, and although there have been recent improvements in dealing with CSO and other point sources of pollution, the Anacostia is still struggling to recover [4]. In addition to traditional nutrients and contaminants, the river also exhibits odd inorganic geochemistry. The inorganic geochemical characteristics of the Anacostia and some other urban rivers have been characterized as experiencing "urban stream syndrome" [5–9]. The syndrome itself is described as the "alteration of the urban landscape inextricably linked to the geochemistry of the river system". PAHs have been documented in the water column [9] and sediments [10–12], but there have not been concentrations reported for specific PAH sediments in recent years, particularly in the suburban tributaries that comprise the northwest and northeast branch tributaries of the Anacostia. Additionally, there is increasing evidence of the presence of synthetic contaminants in the Anacostia, which are traditionally overlooked in the USA, such as siloxanes (silicones) [13,14]. In the EU and Canada, some siloxanes are considered emergent contaminants and regulators have limited their use in certain cases [15]. In January 2019, the European Chemicals Agency announced that octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) should all be restricted to concentrations < 0.1% in consumer products [15]. D4 and D5 are considered potentially more harmful than D6. Both D4 and D5 have been found in the Anacostia mainstem in recent years, although their concentrations were not determined [13,14]. Those papers reported the presence of siloxanes in water column samples collected in two sections of the Anacostia River and that those same siloxanes had impacts on the development of zebrafish embryos. In fact, concentrations as low as 1 nM in water have resulted in 100% mortality after 11 to 14 days post-fertilization in zebrafish (*Danio rerio*), but it is not known if there are in situ impacts on native fishes or what impacts siloxanes have for organisms living in sediments [14]. It is very likely that cyclic siloxanes bioaccumulate through ecosystems, but this has not been examined in North America. In this study, we report the first determination of D5 and D6 concentrations in sediments from the Anacostia River, its tributaries, and two locations on the Potomac River. Additionally, surface sediment concentrations of pyrene, fluoranthene, phenanthrene, and bibenzyl at the same locations are reported.

2. Materials and Methods

Site description: Three urban and four suburban sites in the Anacostia River plus two sites on the Potomac River were sampled 25 times between October 2018 and July 2023 (Figure 1). The more suburban sites were Long Branch Park (approximately 33% impervious), Still Creek (19% impervious), Paint Branch (37% impervious), and the Northeastern Branch (37% impervious). The Anacostia mainstem (and more urban) sites were the Bladensburg Marina, Kenilworth Park, and Anacostia Park Section D (the collective tidal Anacostia is 40% impervious and 70% urban) [3]. The two Potomac sites are west of the figure area. One site is Riley's Lock near Poolesville MD (29 km from the Washington DC border) and the other is Swain's Lock in Potomac MD (approximately 15 km from the Washington DC border).

Long Branch Creek (40°44′30.822″ N, 73°59′21.508″ W) runs through relatively suburban Takoma Park, Maryland. Still Creek flows through Greenbelt Park (a 445-hectare National Park in Maryland, 38°98′95.53″ N, 76°89′51.13″ W) but is surrounded by suburban development. The Northeastern Branch (39°0′15.39″ N, 76°55′59.90″ W) is due east of the University of Maryland main campus. Paint Branch (38°58′43.39″ N, 76°54′59.90″ W) is a tributary of the Northeastern Branch and flows through the University of Maryland campus. The sources of pollution in these suburban locations are street runoff, possible leaking sewage infrastructure, or lawn treatments. The Bladensburg site (38°56′11.6″ N, 76°56′28.3″ W) is directly downstream from where the northeast and northwest branches converge and is adjacent to two stormwater overflows. Kenilworth Park (38°54′33.22″ N, 76°57′18.92″ W) was previously an open burn landfill for DC trash that was shut down in 1968 and covered. It was turned into a recreational park in the 1970s. The Anacostia Park Section D is upstream and across the river from the Navy Yard, and the sample site is at a boat ramp and pier across from a marina (Seafarer's Yacht Club) and adjacent to the CSX railroad bridge (38°52′46.77″ N, 76°58′13.8″ W). Riley's Lock on the Potomac River is located between Seneca and Poolesville MD and is named for the C&O Canal lock nearby. It drains a mix of forest and agricultural land estimated to be only 2% impervious [16]. The sample site is approximately 10 m from where Seneca Creek meets with the Potomac mainstem (N 39°04.127 W 77°20.44). Swain's Lock (Lock #21), Potomac, Maryland is also adjacent to the C&O Canal (N 39°01.898 W 77°14.62). It is estimated to be approximately 7% impervious [17]. The Anacostia sites were chosen because they ranged between the most urban portions of the river (the Anacostia Water Park) and tributaries that included the smallest first-order creek (Long Branch). These locations have also been studied as part of a long-term water chemistry project examining inorganic and organic transformations in Washington DC area streams [7,8,13,14,16]. The two Potomac River sites were chosen because they represent the more rural area west of Washington DC.

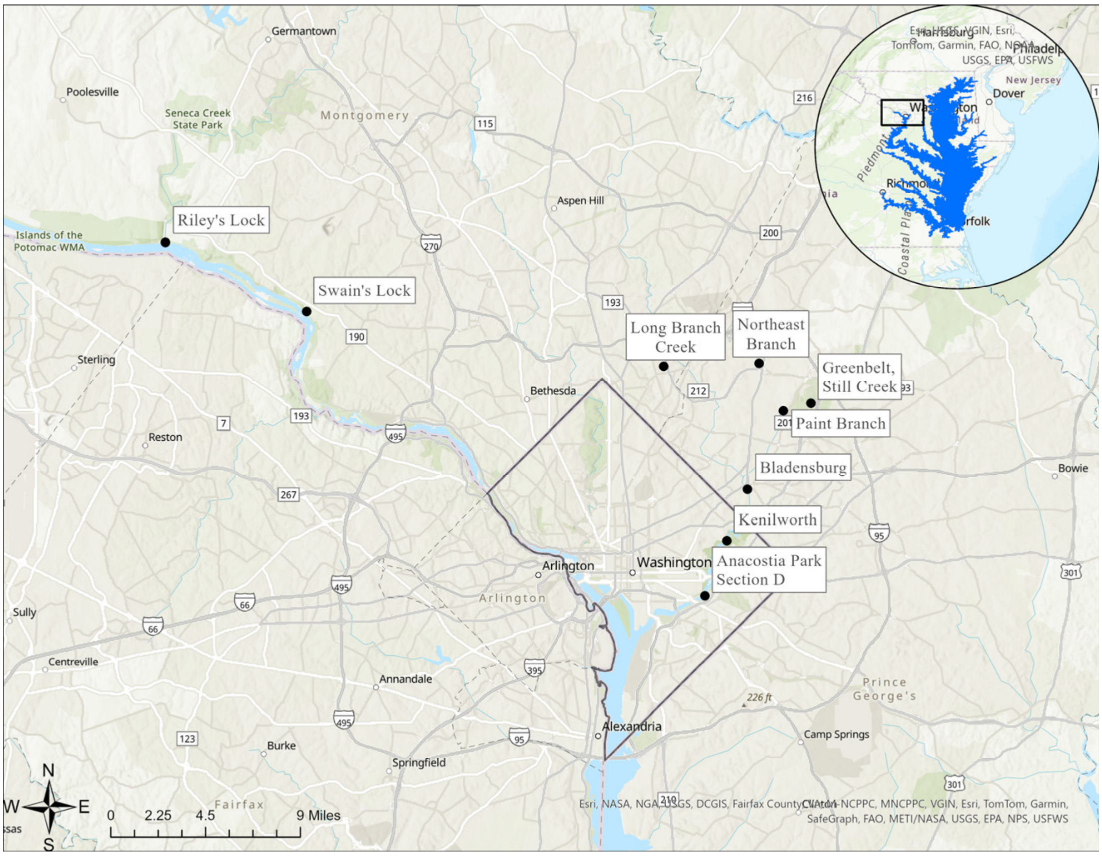


Figure 1. Sampling sites along the Potomac and Anacostia Rivers and tributaries. Long Branch Creek, Still Creek, Paint Branch, and the Northeast Branch are suburban sites, which are tributaries of the Anacostia. The three sites on the Anacostia mainstem, Bladensburg, Kenilworth, and Anacostia Park Section D, are considered more urban. The two Potomac sites are west of the Anacostia. One site is Riley's Lock near Poolesville MD (29 km from the Washington DC border) and the other is Swain's Lock in Potomac MD (approximately 15 km from the Washington DC border).

2.1. *Sediment Collection*

Surface sediments (0–2 cm depth) were collected into polyethylene whirlpaks approximately every 2 months using a small metal trowel. Approximately 100 g (wet mass) of surface sediments were collected from each location for %OM and organic geochemistry (see below). A total of 96 sediment samples were collected during 25 field days and extracted for siloxanes and PAHs.

2.2. *Laboratory Procedures*

Polycyclic Aromatic Hydrocarbon (PAH) and Siloxane Characterization: After collection, sediments were dried at 60 °C for 3 days. Samples were then sieved through a 2 mm sieve, and 30 or 40 g were weighed using a Mettler/Toledo AX26 microbalance (Langacher Greifensee 8606 Switzerland). Extraction and separation of organics was performed using standard methods [14,18,19]. Each 30 or 40 g sediment sample was Soxhlet-extracted for 16 h and saponified in 1 M KOH–ethanol for 3 h. This process allowed the separation of the saponifiable lipids (fatty acids, for example) from the non-polar hydrocarbons. See below for the methods pertaining to the polar, saponifiable lipids. In the non-polar fraction, the alkanes were separated from aromatics by charging them to an activated silica/alumina column containing 2.5 g silica (JT Baker (Radnor, PA, USA) 40–140 mesh) and 1.6 g alumina (Fisher Science (Waltham, MA, USA) 80–200 mesh) (activation was performed by heating the silica and alumina at 200 deg C for 4 h). Washing the non-saponifiable hydrocarbons through the column using hexane (one 10 mL and two 5 mL washes) yielded the alkanes. Subsequent washing with a 2:1 hexane–toluene mix yielded the PAHs. Usually, the siloxanes appeared in the hexane–toluene wash but occasionally they appeared in both washes. Amounts from a single sample were always added together to determine the concentration.

The polar, saponifiable lipids (after separation from the non-polar fraction) were neutralized with 1 M HCL and extracted with one 15 mL and two 5 mL washes of 99% pure hexane in a separatory funnel. The hexane portion was removed from the funnel, rotovaped to 1 mL, and derivatized by adding 0.5 mL of boron fluoride methanol (BF_3CH_2OH) and heating at 60 deg C for 8 min. This portion was then washed with two 5 mL portions of saturated KCl, and powdered $BaCl_2$ was added (to remove the emulsion). The hexane mix was removed and allowed to mix with Na_2SO_4 for 15 min to remove any remaining water.

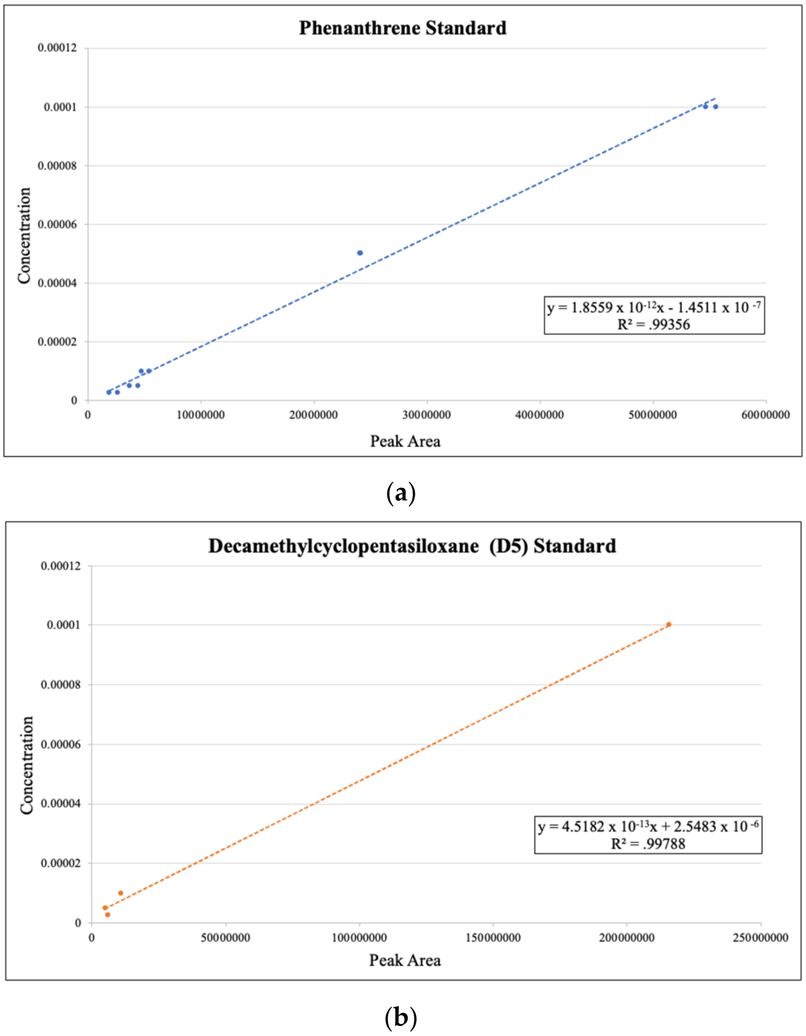
All extracted materials were rotovaped and resuspended into 1 mL in 99% pure hexane or 2:1 hexane–toluene (for PAHs). Samples were then characterized using a Thermo Trace GC/Polaris Q GC/MS containing a 30 m Restek Rxi-5 ms fused silica column to find the compounds of interest, and four- or five-point standard curves were created for all compounds at environmentally relevant concentrations (see below for more details).

Gas Chromatography Mass Spectrometry (GC/MS) Injection and Peak Analysis: After separation of non-saponifiable hydrocarbons through each respective wash, 1 μL (at room temperature) of extract was injected into a GC/MS device. The heating program used started at 50 °C, ramped at 10 °C/min to 250 °C, and held at that temperature for 2 min. After injection, there was a 4 min delay before the MS was activated to allow the solvent to pass. Between injections, the syringe was washed with hexane three times. For analyzing the saponifiable lipid fraction, a slower ramp and longer run was used. The over started at 50 °C, ramped at 8 °C/min to 250 °C, and held at that temperature for 4 min.

Blanks (1 μL 99% hexane) were run after every 10th sample injection. This was performed consistently to ensure the column was flushed of residual samples and to ensure that the system was functioning normally. Compounds in injected samples were identified by comparing the mass fragment patterns to a NIST MS Search 2.0 library both automatically via software (Thermo Xcalibur 2.2 SP1) and manually by matching at least two dominant fragment peaks, and by matching the retention times determined by pure compounds to the unknowns. Compounds of interest (PAHs and siloxanes within the scope of this project) identified with 60% or greater certainty and those of interest (PAHs and siloxanes within the scope of this project) had their peak area and height recorded for concentration determination.

2.3. Concentration Calculations

Using Standard Curves for Identified Compounds: For each compound of interest, four- or nine-point standard curves were created using peak area to produce a line of best fit. The compounds had their concentrations determined using this line. As mentioned above, this was performed for each compound that was identified with a probability of 60% or higher. Examples of two standard curves are shown in Figure 2. An internal laboratory standard (0.0001 M pyrene) injected three times showed an accuracy of ±9.6%.



(**a**)

(**b**)

Figure 2. Examples of standard curves. Concentrations are in moles. (**a**) shows phenanthrene and (**b**) shows decamethylcyclopentasiloxane (D5).

3. Results

Between 2018 and 2023, there were 25 field collection trips resulting in 96 sediment samples. The number of sediments collected from each of the nine sites were different over the 5 years because of logistical access difficulties, grant priorities, and issues with the mass of useable sediments. In some cases, there was not enough mass in the < 2 mm sediment fraction to extract enough material to yield high-confidence data. All the reported data are for 30 to 40 g dry mass < 2 mm sieved sediments. Extracts were separated into three compounds classes; aromatics, alkanes, and saponifiable hydrocarbons (siloxanes appeared in the non-saponifiable fractions). Therefore, each single sediment sample had these three compound classes examined. The total number of samples yielding positive detections from the individual sites were Bladensburg (25), Kenilworth (22), Northeast Branch (14), Long Branch (11), Still Creek (7), Riley's Lock (6), Anacostia Park (5), and Swain's Lock (4).

3.1. Siloxanes

D6 was found at six of the nine sites but not in most samples, and concentrations were very low, generally between 0.06 and 0.0003 mg/g (Table 1). There were not significant differences in D6 among the sites. D5 was found at seven of the eight sites and in much higher concentrations. A Wilcoxon multiple comparison test showed that D5 was significantly greater per gram surface sediment than D6 between 2018 and 2022. D5 was 0.130 mg/g ± 0.294 (N = 48), and D6 was 0.006 ± 0.018 mg/g (N = 12) in sediments

(Table 2). Among the seven sites where D5 was detected, the only significant difference was between Kenilworth and Long Branch ($p < 0.0001$). An example chromatogram showing D5 and D6 from the Bladensburg site on the Anacostia mainstem is shown in Figure 3a. The figure also shows one of the blanks that was injected after every 10th sample (Figure 3b).

Table 1. Mean ± standard deviations (and N) for concentrations of siloxanes from 2018–2023 ± SD and N. All sample dates combined. mg per g dry sediment. ND is "not detected".

	D5 (mg/g)	D6 (mg/g)
Anacostia Water Park	0.06 ± 0.03 (3)	ND
Kenilworth	0.23 ± 0.51 (12)	ND
Bladensburg	0.14 ± 0.23 (11)	0.0001 ± 0.001 (3)
Northeast Branch	0.11 ± 0.06 (5)	0.0166 ± 0.031 (4)
Long Branch	0.05 ± 0.12 (6)	0.0006 (1)
Still Creek	0.08 ± 0.4 (3)	0.002 (1)
Paint Branch	0.07 ± 0.05 (4)	ND
Swain's Lock (Potomac)	ND	0.029 ± 0.034 (4)
Riley's Lock (Potomac)	0.05 ± 0.02 (3)	0.0003 ± 0.00004 (2)

Table 2. Mean ± standard deviations (and N) for concentrations of siloxanes show significant differences ($p = 0.0001$).

D5	0.130 ± 0.294 (48)
D6	0.006 ± 0.017 (12)

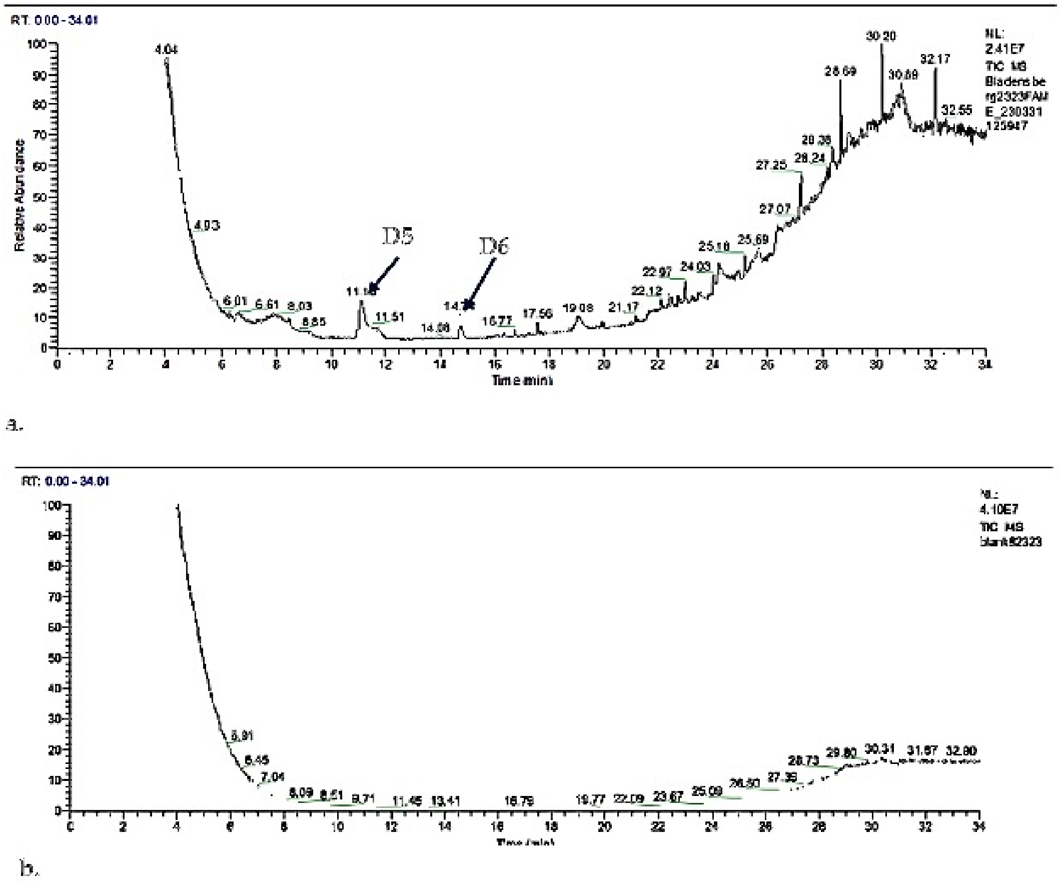


Figure 3. Chromatograms from GC/MS runs: (**a**) shows D5 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane) from the Bladensburg site on the Anacostia mainstem and (**b**) shows an example of a blank (blanks were injected after every 10th sample).

3.2. PAHs

Of the four PAHs examined, pyrene had the highest concentrations for each site where it was detected, although the concentration range among sites was substantial (Table 3). Comparing pyrene across the Anacostia sites (none was detected in the Potomac sediments) showed that Anacostia Water Park Section D had higher concentrations than any of the mainstem upstream sites or in the Anacostia's tributaries (Table 3). In Paint Branch Creek, which runs through the University of Maryland campus and supports a brown trout fishery, pyrene was not detected. Fluoranthene was also higher at Anacostia Park Section D than any of the other sites other than Kenilworth. Kenilworth fluoranthene was higher than the Northeast Branch, Bladensburg, or Still Creek. None of the Anacostia's tributaries had significant differences in fluoranthene, and mean concentrations ranged from 0.10 to 0.26 mg/g (Table 3). The four PAHs were not detected with enough certainty to report in most Potomac samples.

Table 3. Mean ± standard deviations (and N) for concentrations of PAHs from 2018–2023 ± SD and N. All sample dates combined. mg per g dry sediment.

	Pyrene (mg/g)	Fluoranthene (mg/g)	Bibenzyl (mg/g)	Phenanthrene (mg/g)
Anacostia Water Park	77.7 ± 53.7 (7)	4.42 ± 3.79 (5)	ND	ND
Kenilworth	18.0 ± 30.7 (13)	1.51 ± 2.10 (11)	0.05 (1)	ND
Bladensburg	3.3 ± 5.1 (11)	0.26 ± 0.32 (13)	0.06 ± 0.009 (2)	ND
Northeast Branch	1.5 ± 2.0 (9)	0.19 ± 0.14 (11)	0.05 ± 000 (2)	0.07 (1)
Long Branch	0.7 ± 0.5 (7)	0.24 ± 0.29 (9)	0.06 (1)	0.11 (1)
Still Creek	0.40 ± 0.24 (3)	0.11 ± 0.06 (6)	0.06 (1)	ND
Paint Branch	ND	0.10 (1)	ND	0.04 (1)
Swain's Lock	ND	ND	0.06 (1)	0.12 (1)
Riley's Lock	ND	0.70 (1)	ND	ND

4. Discussion

While there have not been studies reporting siloxanes in the Anacostia or its tributaries, previous studies have reported PAHs in filtered water and sediments [9–11,20]. Wade et al. [10] report total PAHs ranging from 4 µg/g to 33 µg/g in sediments collected from midstream (with concentrations trending higher downriver) but also observed concentrations as high as 620 µg/g in sediments near storm flow outfalls. They surmised that the observed PAHs were a mix of combustion byproducts (pyrogenic) and direct runoff/discharge of petroleum products [10]. When the fine grain fraction (<0.63 µm) adjacent to combined sewage overflows was examined, the PAH concentrations increased 500% relative to midchannel measurements [10]. They also noted that sampling near boat launches, near dock infrastructure, and adjacent marina communities, would elevate the PAH concentration (and other contaminants) because of boat engine material and chemicals to preserve pilings. This is perhaps why the concentrations of pyrene and fluoranthene are highest in this study adjacent to the boat launch at Anacostia Park Section D. We observed concentrations much higher than those reported by Wade et al. [10], even relative to the sewer overflow samples. Wade et al. [10] found mean total hydrocarbons and PAHs to be 4500 µg/g and 160 µg/g, respectively, in fine-grained sediment. We found pyrene plus fluoranthene to be more than 96 mg/g (<2 mm sediments) at the boat launch and the ratio of fluoranthene to pyrene was substantially less than one, which may indicate petrogenic (petroleum) rather than pyrogenic (combustion) sources. Yunker et al. [21] found that a fluoranthene/fluoranthene + pyrene ratio < 0.4 indicated petrogenic sources, and all sites where the two PAHs were found had ratios < 0.28. Like the data reported by Wade et al. [10], Velinsky et al. [11] reported low concentrations of PAHs for midchannel surface sediments near the Navy Yard (generally 10 µg/g). They also found that the fluoranthene to pyrene ratio was greater than one for their surface sediments, indicating pyrogenic sources. For all sediments examined in this study that had both fluoranthene and pyrene, all but one had a ratio of less than one (the one that did not was from Kenilworth marsh, which is the site of the old DC open trash burning area). The two mainstem sample locations upstream from the Anacostia Park are Kenilworth Park and Bladensburg waterfront park. Both are within 100 m of stormwater discharge areas (Bladensburg has two of them), and this could contribute to the high concentrations of fluoranthene and pyrene observed. Concentrations of pyrene and fluoranthene are four to five times higher at Kenilworth than Bladensburg, and this could be a legacy of the open burn landfill, which existed there until 1968 (when it was covered). Also, all samples were taken at the water's edge where there is potential for lower sediment flux, scouring from tidal forces, and higher flow rates characteristic of the midchannel sites previously examined. In a recent study, Davey et al. [20] reported phenanthrene, fluoranthene, and pyrene in sediments from one of the Anacostia's tributaries (Nash Run). The reported concentrations ranged from 0 to 1.25 μg/kg for phenanthrene and fluoranthene and 0 to 38.7 μg/kg for pyrene. These concentrations are higher than those reported by Wade et al. [10], and the authors suggest that the compounds might be associated with microplastics (the compounds have been shown to bind with microplastics in marine sediments [22,23]. The PAH concentrations observed by Davey et al. [20] are similar to those reported here, and the association with microplastics might be an important consideration since there may be a higher concentration of microplastics in sediments today than there was 30 years ago when the earlier studies were published [10,11].

The relative abundance of low- versus higher-molecular-weight (MW) PAHs can also indicate sources. High-MW PAHs are those with four or five benzene rings, such as fluoranthene and pyrene. Low-MW PAHs include phenanthrene and bibenzyl with two or three benzene rings. When low-MW PAHs have higher concentrations than higher-MW PAHs that could indicate oil sources. PAHs associated with combustion (pyrogenic) are usually higher MW. If that were the case, then the PAHs from this study might be pyrogenic, which is what Wade et al. [10] concluded for the PAHs in their samples. However, Velensky et al. [11] report that fluoranthene/pyrene ratios > one indicate pyrogenic sources, and we do not see that in most of our samples. Pyrene is by far the PAH with the highest concentration, and this is the case throughout all the sites where the two were found. A possible association with discarded and fragmented plastics, which may bind to PAHs like pyrene, may be suggestive, although we did not investigate that possibility. PAHs remain a persistent chemical contaminant in the rivers around Washington DC, although the sources of the chemical may shift.

Siloxanes have not been reported in North American freshwaters, although they have been reported in air samples and wastewater (see [24]). They are commonly used in sealants, lubricants, and cosmetics, as well as dry cleaning and other industrial processes. They are probably widely distributed in wastewater; however, North American municipalities typically do not test for them. Some countries in the EU do monitor them and have limited their use in cosmetic products and other processes. Concentrations of D5 and D6 in sewer sludge have ranged from 0.27 to 0.50 and 0.001 to 0.003 mg mg/g, respectively [24], which are similar to the concentrations reported here. Concentrations of D5 and D6 in Canadian wastewater reported in 2015 ranged between 7.75 and 135 μg/L and 1.53 to 26.9 μg/L, respectively [25]. Dust samples from industrial areas have higher concentrations of D5 than those reported here (0.08 mg/g) [24]. Here, we report D5 concentrations that are 100 times higher than D6, which was also what the TemaNord [25] and the Xiang et al. [24] reviews report. Although the values reported here are for surface sediments, it should be noted that D5 and D6 appear to biomagnify with a trophic magnification of between 0.1 and 0.8 [26], meaning that bottom-feeding fishes could have biomass loads greater than what we observed. A study that examined water, sediments, and fishes from the Geum River in Korea found siloxane concentrations between 114 and 190 ng/L in water and up to 294 ng/g in sediments [27]. Chen et al. [28] also report total sediment siloxane concentrations between 19.1 and 2995 (mean 455) ng/g in Masan and Haengam Bays, Korea. These concentrations are far lower than what was observed in this study and likely reflect flushing and dilution within the estuaries. The concentrations reported here are more akin to wastewater than ambient estuary environments. It should also be noted that cyclic siloxanes, which are the type reported here, are thought to be more persistent in the environment than linear ones and have been found at twice the concentration of linear siloxanes in sediments [28]. Additionally, atmospheric emissions of siloxanes result in rapid reactions with hydroxyl groups and removal, so finding high concentrations in air and water are not likely relative to sediments, where they are likely persistent [26]. It is likely that siloxanes will become more widely tested and emerge as another synthetic chemical class that should be regulated.

Taken together, siloxanes and PAHs show that anthropogenic pollution is likely to persist in urban waterways such as the Anacostia. Cleanup efforts will certainly help reduce the input of new chemical contaminants, but those that have been released during previous years could remain in sediments. Additionally, as researchers and regulators become more aware of emerging chemical environmental hazards, monitoring of persistent synthetic pollutants to establish background concentrations may be prudent.

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Data Availability Statement: Data available on AU's library repository.

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