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Sedimentary Nonylphenol Contamination in an Urbanized, Industrialized Segment of the Delaware River Estuary, USA

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Nonylphenols (NPs) are primarily used as intermediates in the manufacture of nonylphenol ethoxylates (NPEs), a major group of nonionic surfactants. Worldwide, about 500,000 tons of alkylphenol ethoxylates (which include NPEs) are produced annually for use in detergents, paints, pesticides, textile and petroleum recovery chemicals, metal working fluids, and personal care products (Naylor et al. 1992). Because of their wide spread use, especially in cleaning products and as industrial processing aids, the majority of NPEs are delivered to wastewater treatment plants (WWTPs). During anaerobic sewage digestion, NPEs are biodegraded by the hydrolytic removal of ethoxylate groups forming short-chain ethoxylates, carboxylic acid derivatives and NPs. Subsequently, wastewaters originally containing high concentrations of NPEs may potentially contain elevated concentrations of NPs upon discharge. Additionally, NPs may be formed after NPE-containing waters are discharged directly to receiving waters from run-off and equipment cleaning areas (Hale et al. 2000).

Studies reporting environmental levels of NPs are relatively limited, even in heavily urbanized and industrialized areas where concentrations would likely be detectable and potentially high. This is particularly true for the Delaware River estuary which stretches approximately 200 Km from the fall line of the Delaware River just above Trenton, NJ to the mouth of the Delaware Bay between Cape May, NJ and Cape Henlopen, DE. The most industrialized and urbanized segment of the river runs between the cities of Philadelphia, PA and Camden, NJ. In 1978, NP isomers were identified within the water column of the Delaware River with highest levels being centered around Philadelphia (0.04 to 2.00 µg/L) (Sheldon and Hites 1978). However, since this study, levels of nonylphenols in the water column, particularly those adjacent to the urbanized and industrialized regions of Philadelphia, PA, have not been reported in the literature.

Because of the relatively hydrophobic nature of NPs, with Log K_{ow} values between four and five (Ahel and Giger 1993), a significant proportion of the discharged contaminant load eventually becomes bound to suspended particles, particularly those having high organic carbon contents. Evidence demonstrating NP persistence in the environment as well as its bioaccumulation and toxicity to organisms has been

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mounting (*e.g.*, Ekelund et al. 1990, Marcomini et al. 1990). Furthermore, estrogenic and reproductive effects have been shown, particularly during the larval stages of some fishes (*e.g.*, Gimeno et al. 1997; Lye et al. 1999). These and other environmental and human health concerns have led some European countries to voluntarily ban the use of alkylphenol ethoxylates in household cleaning applications (Renner 1997). Addressing both the magnitude and spatial extent of sedimentary NP contamination is the first step is evaluating an aquatic system's potential for adverse effects, especially to benthic organisms. To our knowledge, only one published study reported measurable levels of NP species in sediments in the Delaware River (Naylor et al. 1992). Considering this relative paucity of NP data in coastal waters and specifically the Delaware River estuary, the overall objective of this research was focused on quantifying the magnitude, and to a limited degree, the spatial extent of NP contamination in portions of the urbanized/industrialized Delaware River, and one of its major tributaries, the Schuylkill River.

MATERIALS AND METHODS

It was not the intention of this study to produce a spatially explicit mapping of sedimentary NP concentrations in the industrialized/urbanized portions of the Delaware and Schuykill Rivers. Rather, for this cursory study, sites and sediment types were specifically chosen for their potential to harbor significant concentrations of NPs. Primarily fine-grained sediments were collected from near shore locations at sites having depths of 3-15 m (Figure 1). Five sediment samples were collected from the Delaware River adjacent to the Philadelphia Water Department's southeast municipal WWTP discharge site south of the Delaware's confluence with the Schuylkill River (Sites 6-10). Four sites were situated in the tidal portion (from the Fairmont Dam to the Philadelphia Naval Complex) of the Schuylkill River (Sites 1-4). The remaining site was approximately 5 Km upstream of the WWTP discharge site (Site 5). These sites were in the freshwater tidal portion of the Delaware River estuary. Using a petite Ponar grab, the top 2 cm from three separate surficial sediment collections were collected, homogenized, and sub-sampled for analyses. Sediment samples were frozen and stored at –5°C until extraction. All necessary precautions were taken to ensure no cross contamination of sediment samples.

Approximately 5 grams of thawed homogenized sediment was sub-sampled for nonylphenol analysis. Approximately 30 g of sodium sulfate (previously baked at 450°C for 4 hrs) was added to sub-samples to remove water. The mixture was placed in a Soxhlet apparatus and extracted with ~300 mL of dichloromethane (DCM) for at least 18 hrs. The solvent was then exchanged with hexane through rotoevaporation, followed by concentration under a purified stream of N_2 gas. Liquid-solid chromatography using 300 mg aminonitrile cartridges (Burdick and Jackson) was performed on the samples. The cartridges were cleaned by pre-elution with 5 mL of methanol, acetone, and hexane, respectively. The sample was then eluted with 10 mL of a 75:25 hexane:acetone mixture followed by solvent reduction using a purified stream of N_2 gas.

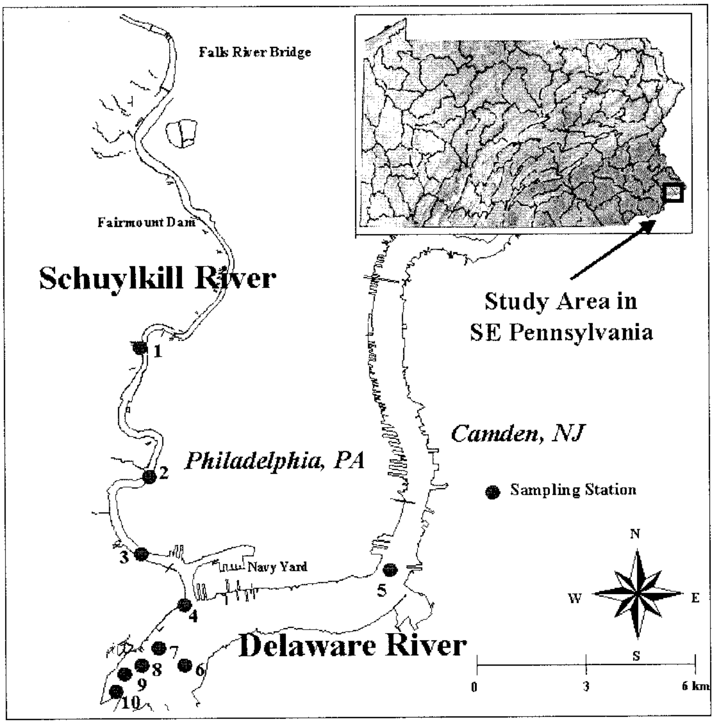

Figure 1. Sampling sites in Delaware and Schuylkill Rivers at Philadelphia, PA and Camden, NJ.

A technical mixture of nonylphenol (NP) was purchased from Sigma-Aldrich (CAS # 84852-15-3). An internal standard, 2,4,6-trimethylphenol, and a surrogate standard, 4-tert-butylphenol, were purchased from Crescent Chemical Co., Islandia, N.Y. Surrogates were added to samples prior to extraction by Soxhlet apparatus while internal standards were added to extracts prior to instrumental analysis. Nonylpyhenol was quantified using a Hewlett Packard 5890/5972A gas chromatograph-mass selective detector (GC/MSD) operated in the selective ion monitoring mode. Quantification and confirmation ions for nonylphenol were 107 and 121, respectively. Chromatographic conditions were as follows: injection port temperature was maintained at 250°C; detector temperature was maintained at 280°C and oven temperature ramp was initially held for one minute at 70°C followed by a 30°C/min ramp to 160°C and then a ramp of 5°C/min to 240°C which was held for an additional 5 min. Helium was used as the carrier gas through the GC and the flow was maintained at 1.40 ml/min through a 30 m DB-5 column. To assess analytical precision, a replicate analysis of one of the samples was performed. Three laboratory blanks were used to quantify laboratory contamination throughout the preparation of samples.

RESULTS AND DISCUSSION

In the study area, NPs were detected in all samples from all sites. Surrogate recoveries ranged from 90 – 116% (Table 1) suggesting little loss of analytes through the manipulations of sample preparation. Duplicate analysis of one sample produced a relative percent difference of 6% verifying the reproducibility of preparatory and analytical techniques employed. Laboratory blanks contained satisfactorily low masses of NPs (0.04-0.52 μg). Values reported in this study were blank corrected using the average mass obtained from three laboratory blanks.

In this study, NP concentrations ranged from 0.20 (Site 1) to 12.50 (Site 2) μg/g, expressed on a dry weight basis (Table 1). Nonylphenol concentrations were not correlated with solid content, grain size or organic carbon (OC) content (r^2= 0.05, 0.06, and 0.14, respectively). Bennett and Metcalfe (1998) observed no apparent relationship between alkylphenol concentrations and OC content. As with that study, proximity to source rather than particle characteristics such as OC content influence the NP concentration within the study area.

Table 1. Summary of NP and ancillary measurements for sediments collected from the Delaware and Schuylkill Rivers.

Site Number	Solid Content %	Grain Size % < 63μm	Organic Carbon Content %	[NP] μg/g dry wgt	Surrogate Recovery %
1	68	7	8.5	0.14	110
2	42	83	8.3	12.50	109
3	37	97	5.5	0.36	105
4	33	94	4.2	0.55	106
5	62	52	1.7	0.37	90
6	64	42	1.3	1.80	103
7	62	40	2.1	4.50	116
8	64	33	1.3	1.50	90
9	50	68	3.7	3.80	116
10	58	68	3.3	2.40	105

While there may be numerous sources of NPs in the study region, one suspected source is discharge of wastewater from the Philadelphia Water Department's southeast municipal WWTP adjacent to site 7. Another source of NPs to the tidal Delaware River may be from the Schuylkill River, the most significant tributary to the estuary in delivering fresh water, sediment and likely organic contaminants (Ashley and Velinsky, unpublished data). This approximately 15 km long tidal section of the river meanders through a heavily industrialized/urbanized segment of the city of Philadelphia (Figure 1). Though no WWTPs discharge to this segment of the river, combined sewer overflows (CSOs), stormwater run-off and industrial discharges empty into the river at numerous locations.

With the exception of site 2, sediments collected in close proximity to the WWTP discharge site (sites 6-10) had significantly greater NP concentrations than those north of the discharge site (sites 4 and 5) and in the tidal Schuylkill River (sites 1 and 3). This suggests proximity to this source is a determinant in NP contamination in this study area. However, the highest concentration observed came from a site within the tidal Schulykill River (site 2) suggesting that others sources in addition to WWTPs may be important. Previous data have shown high levels of trace metals and organic contaminants (e.g., polychlorinated biphenyls, polycyclic hydrocarbons) in the sediments from the mid to lower portions of the tidal Schuylkill River (Boyd et al. 1998). Site 2 site was adjacent to a large oil-refinery and the composite sediment sample collected from this site had an oily sheen and smelled of hydrocarbons. As part of a separate research project (Ashley and Velinsky, unpublished data), total PAH concentrations were found to be the highest at this site (28.0 μg/g dw) as compared to sites 1 and 3-5 having a range of concentrations from 3.2 to 13.4 μg/g dw. This suggests that local industrial discharge or run-off of NPE-containing wastes may be the reason for the high sedimentary concentration.

Though studies addressing the magnitude and extent of NP contamination are limited, the ranges observed in this portion of the Delaware and Schuylkill Rivers may be compared to those in the Delaware River and other regions (Table 2). With the exception of the Bennett and Metcalfe (1998) study on sediments collected from lakes, this study produced the highest measured sedimentary concentration (12.5 μg/g) of those listed. Naylor et al. (1992) surveyed 30 sites in U.S. rivers, including one from the Delaware River, for sedimentary NPs and found an average NP concentration of 0.162 μg/g. An average NP concentration of 2.8 μg/g was found in this study though our study specifically sampled sediments from industrialized and urbanized systems unlike other studies that included less impacted sites. Although site-specific NP concentrations were not reported in the Naylor et al. (1992) study, the authors stated that the Delaware River at Croydon, PA had measurable levels of all the NP species. This is the only known published reference to sedimentary concentrations in the Delaware River estuary. Hale et al. (2000) quantified NP concentrations in sediment collected from WWTPs and other suspected sources. As with our study, sites closer to WWTPs had elevated NP concentrations though other sources may be important.

Though NP concentrations may be elevated compared to other areas, it is difficult at present to assess how this would translate into risk to organisms. Unlike other organic contaminants of concern (e.g., polychlorinated biphenyls, polycyclic hydrocarbons, organochlorine pesticides), there exist no sediment quality guidelines for NP with which to assess the potential of these sediments to induce adverse effects on benthic organisms. Studies documenting NP-induced effects through exposure to contaminated sediments or porewater are also lacking. Moreover, although the total concentrations within sediments may be high, the bioavailable fraction (that which is primarily available for uptake by benthic organisms) has not been fully addressed in the literature. These and other issues must be addressed to more completely assess the potential effects from sedimentary NP contamination.

Table 2. Comparison of NP concentration ranges from sediments collected from various locations.

Location	**[NPs] (µg/g dry weight)**	**Source**
Glatt River, Switzerland	0.2 - 13.1	Ahel *et al.*, 1994
Marine Lagoon, Venice, Italy	0.005 - 0.04	Marcomini *et al.*, 1990
A Survey of 30 US Rivers	<0.003 – 3	Naylor et al., 1994
Great Lakes, US and Canada	Non-detect. – 37	Bennett and Metcalfe, 1998
Tees Estuary, United Kingdom	1.60 – 9.05	Lye et al., 1999
Tyne Estuary, United Kingdom	0.03 – 0.08	Lye et al., 1999
Virginia, USA	0.3 - 12.4	Hale et al., 2000
Schuylkill and Delaware Rivers, USA	***0.14 - 12.5***	***This Study***

This research provided the first known multi-site evaluation of NP concentrations in surficial sediments within the Delaware and Schuylkill Rivers. These data suggest that sediments within some portions of the Delaware and Schuylkill Rivers are elevated and that proximity to WWTPs is a large determinant of the magnitude and spatial extent of sedimentary NP inventories though other sources (e.g., industrial run-off and discharge) may be equally or more important.

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