

URBAN Waterways

Polycyclic Aromatic Hydrocarbons (PAHs) in Urban Waters

Purpose of this document

Recent studies by the US Geological Survey (USGS) and several universities indicate that PAHs are an important emerging contaminant in urban waterways, including the rapidly growing metro areas of North Carolina. This document offers an overview of recent studies of potential sources for PAHs in urban waterways and provides information on management strategies for reducing the risks of PAH impacts on aquatic ecosystems.

What are PAHs?

PAHs, or Polycyclic Aromatic Hydrocarbons, consist of hundreds of separate chemicals that occur together as mixtures. PAHs are naturally occurring and are concentrated by the burning of fossil fuels and the incomplete burning of carbon-containing materials (such as wood, tobacco, and coal). PAHs are a wide and varied group of compounds whose sources include tire particles, leaking motor oil, vehicle exhaust, crumbling asphalt, atmospheric deposition, coal gasification, and parking lot sealants, as well as sources inside the home (such as tobacco smoke, wood fire smoke, grilling or charring meat). PAHs are also commonly found in particulate matter of air pollution. PAHs tend to adhere to surfaces, attaching readily to sediment particles and leading to elevated concentrations in sediments. PAHs have complex chemical structures (see figure 1), so they do not break down easily and are persistent in the environment.

Why should we be concerned about PAHs?

Some PAHs are known to be toxic to aquatic animals and humans. Generally, higher molecular

weight PAHs tend to be more stable, persist in the environment longer, are less water soluble, and are more toxic. Exposure to UV light can increase toxicity of PAH compounds and increase toxicity to some aquatic species. (Garrett 2004)

Scientific studies have documented detrimental impacts from PAHs on aquatic organisms. Examples include:

- In Austin, Texas biological studies revealed a loss of species and decreased number of organisms in streams with PAHs present (Van Metre 2005)

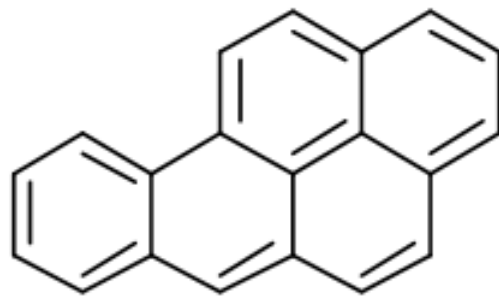


Figure 1. The chemical structure of Benzo[a]-pyrene, a carcinogenic PAH.

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- In Puget Sound, Washington's Ambient Monitoring Program (WA DFW) found PAHs were associated with:
 - Liver lesions and tumors in fish,
 - Liver problems leading to reproductive impairment,
 - Malformations in fish embryos and embryonic cardiac dysfunction,
 - Reduction in aquatic plants (eelgrass) that provide fish habitat.
- Benzo(a)pyrene was lethal to newt larvae at low levels (50 parts per billion) (Fernandez and Lharidon 1994)
- A 2006 study showed developmental delays and deformities in amphibians with exposure to coal tar pavement sealants (which contain PAHs), with larger levels of sealant causing greater developmental problems and death. (Bryer 2006)
- Brown bullhead catfish and English sole have been documented as among the more sensitive bottom-dwelling fish to the carcinogenic effects of PAHs (Garrett 2004).
- Crustaceans and fish metabolize PAH compounds more efficiently than do bivalve species such as mussels, clams, and oysters, which readily accumulate PAHs (Garrett 2004).
- Interactions between aquatic organisms and PAHs in sediment are complex, depending on many factors including—but not limited to—sensitivity of species, stage of development, bioavailability of PAHs, and exposure to sunlight (Garrett 2004).

The most significant effect of PAH toxicity to humans is cancer. Increased incidences of lung, skin, and bladder cancers are associated with occupational exposure to PAHs (USDHHS 2009). Other non-cancer effects are not well understood, though they may include adverse effects on reproduction, development,

and immunity. PAHs generally have a low degree of acute toxicity to humans, meaning harmful effects through a single or short-term exposure are minimal. Mammals absorb PAHs through inhalation, contact with skin, and ingestion (EPA Ecological Toxicity). Recent research by USGS raises concerns about exposure of children through inhalation and ingestion of house dust contaminated by PAHs that have abraded from nearby parking lots sealed with coal tar sealant (Mahler 2010). The International Agency for Research on Cancer (IARC) classifies two PAHs as probable human carcinogens and three as possible human carcinogens. The US EPA classifies seven PAHs as probable human carcinogens, while the state of California classifies 25 PAHs as carcinogenic PAHs (cPAHs). The IARC and EPA both classify benzo(a)pyrene and benz(a)anthracene as probable human carcinogens. Benzo(a)pyrene is often used as an environmental indicator for PAHs.

PAHs in streams and lakes are thought to rarely pose a human health risk via drinking water because of

their tendency to attach to particles rather than dissolve in water. USEPA has a maximum contaminant level (MCL) for PAH in drinking water of 0.2 ppb of drinking water. Human health risks from consuming fish are thought to be low because PAHs do not readily bioaccumulate within vertebrates. Bivalve mollusks readily accumulate PAHs in their tissues, however. (Garrett 2004). The U.S. Food and Drug Administration (FDA) has not established standards governing the PAH content of foodstuffs (USDHHS 2009), with the exception of issuing levels of concerns for PAHs in fish and shellfish following the Deepwater Horizon oil spill. The European Union has set a maximum allowable level of benzo(a)pyrene for bivalve mollusks on the market (EU Commission 2006).

How do PAHs get into streams, lakes, estuaries, and the ocean?

PAHs enter water bodies through atmospheric deposition and direct releases of substances through petroleum spills and use, municipal wastewater treatment plants, industrial



Figure 2. Bivalves, including oysters, readily accumulate PAHs in their tissues.

discharges, stormwater runoff, landfill leachate, and surface runoff. Many studies have been conducted recently regarding runoff sources of PAHs. Rainfall runs off parking lot and road surfaces, transporting PAHs that originate from tire particles, leaking motor oil, vehicle exhaust, crumbling asphalt, atmospheric deposition, coal gasification, and parking lot sealants. PAHs attach readily to sediment particles, leading to high concentrations in bottom sediments of water bodies. A literature review on tire wear particles in the environment indicates that the high aromatic (HA) oils generally used in tires contain PAHs. Zinc, PAHs, and a suite of other organic compounds (including phthalates, benzothiazole derivatives, phenolic derivatives, and fatty acids) found in tires are noted to likely cause toxicity in aquatic organisms. Because of this toxicity, the European Union has banned sales of tires that contain HA oils. This is estimated to reduce future PAH emissions from tires by 98 percent. (Wik & Goran 2009) It is unclear whether tire manufacturers will continue to sell tires containing HA oils in the United States.

Coal tar-based sealants

Research from the USGS in the City of Austin, Texas (Van Metre et al 2005), nine other cities (Van Metre et al 2009)), and from the University of New Hampshire (Mahler et al 2012) indicates that coal tar-based sealants (also called sealcoats) on parking lots likely contribute significant amounts of PAHs to waterways via stormwater runoff. These sealants (CTS) are made of coal tar, a product created during the coking of coal. This type of sealant and another sealant made from asphalt are used to prevent damage to asphalt surfaces. Friction from automobile tires causes the sealcoat to flake off. These flakes are then scrubbed from the surface during a rain event and into storm-drain networks, and then flow into lakes and streams. In the



Figure 3. Sealant is applied to a parking lot.

Austin study, parking lots with coal tar sealcoat yielded an average PAH concentration of 3,500 mg/kg on particles in runoff, 65 times more than from unsealed lots in simulated rain events. The average concentration of PAHs in particles washed off asphalt-based sealants was 620 mg/kg, about 10 times higher than the average concentration from the unsealed parking lots. The other sources of PAHs previously mentioned, besides sealants, can account for the PAH concentrations found washing off the unsealed parking lots (Van Metre 2005). A recent UNH study compared runoff from lots they sealed with both types of sealants to an unsealed lot. They found both types of sealcoat led to a rapid increase in PAH concentrations in the initial runoff—up to 5,000 parts per billion (ppb), compared to 10 ppb released from the unsealed lot. Concentrations decreased after several rainstorms. The PAH concentrations in the sediments immediately downstream of the coal tar sealed lot increased by nearly two orders of magnitude within the first year (14). The Pavement Coating Technology Council maintains that improper

curing of the test plots at UNH contributed to the high concentrations of PAHs found in runoff (LeHuray 2009). The results of analyzing sources of PAHs in sediment cores from 40 lakes across the U.S. has led some USGS researchers to conclude that coal tar sealcoat likely is the primary cause of upward trends in PAHs in response to urban sprawl in much of the United States. (Van Metre 2010)

Attributing sources of PAHs to land uses

Determining the sources of PAHs in streams is a complex process and is usually done by evaluating the ratios of individual compounds found in stream sediment. USGS is currently conducting research in North Carolina to examine PAH concentrations in bridge deck runoff. Research on metals and PAHs in Santa Monica, California, found that both commercial and industrial land uses and roads provided higher concentrations of both metals and PAHs than single-family residential land uses (Lau & Strenstrom 2005). A study of the relative importance of individual source areas in contributing to contaminants

in an urban watershed in Marquette, Michigan, found parking lots to be a major contributor (~64 percent) of PAH compounds (Steuer et al 1997). The USGS study of bridge decks may be the first North Carolina study evaluating land-use contributions to PAH concentrations in waterways. Future research in N.C. could seek to attribute sources of PAHs to land uses, including commercial and industrial land uses, roads, and parking lots. Estimating PAHs from various land uses could be calculated using methods used in the Marquette, Michigan, study.

At what concentration do PAHs affect in-stream aquatic organisms?

The sediment quality guideline, known as the Probable Effect Concentration (PEC), represents the concentration of a contaminant in bed sediment expected to adversely affect bottom-dwelling organisms. The PEC for PAHs is 22.8 mg/kg.

How do PAHs affect streams in North Carolina?

The North Carolina Division of Water Quality (NCDWQ) does not monitor the presence of PAHs in streams. Laboratory analysis for PAHs is much more expensive than for commonly measured pollutants like nutrients and bacteria, and North Carolina has no official standard for PAHs. Special studies do sometimes include PAH analysis, such as:

- The USGS National Water Quality Assessment found a strong correlation between PAHs and urban intensity across the country, including 30 watersheds of the Raleigh-Durham metro area. The highest concentrations of PAHs in sediments at the bottom of water bodies were found in watersheds with increasing development and motor vehicle traffic. These results



Figure 4. Burnt Mill Creek is an urban stream in NC that is impaired by PAHs.

echo studies from around the world (Garrett 2004).

- Levels of PAHs have been indicated by NCDWQ as the lead impairment of Burnt Mill Creek, an urban stream in Wilmington, N.C. A subsequent

UNC-Wilmington/NC State University research project found high levels of PAHs throughout the creek at six sites for four yearly sampling events. Zinc levels, which can be used as indicators of tire-wear particles, were



Figure 5. This bioretention cell reduced PAHs in runoff flowing through it.

low at these same sampling sites, indicating that tire-wear particles from parking lots may be ruled out as major contributors to this watershed's PAH toxicity problems. (Perrin et al 2008)

Reducing risk of PAH contamination from stormwater runoff

Use asphalt sealants or latex modified asphalt sealants if sealing an asphalt surface is necessary. Asphalt or latex modified asphalt sealants contain PAH concentrations of about 5 percent, whereas coal tar based-sealants contain between 20 to 35 percent PAHs. Homeowners should read and follow directions closely for applying and curing the sealant, or consider hiring a trained professional. Industry professionals note that coal tar-based sealants perform better than asphalt sealants at protecting parking lots from petroleum and UV degradation and wear, and they are focusing research and development on creating higher-performing asphalt sealants (WECO 2009).

A number of national home-improvement and hardware stores have discontinued coal tar-based sealants (Hogue 2007), so homeowners who purchase sealant at these stores are using asphalt or latex modified asphalt sealants. That said, coal tar-based sealants are still readily available for purchase online and through wholesale and commercial suppliers, and they are produced and used in North Carolina (WECO 2009).

Intercept and manage stormwater runoff from all parking lots and roads. PAH compounds can be removed from aquatic systems or transformed to new compounds by volatilization (of low molecular weight PAHs), photo oxidation, and biodegradation (Garrett 2004). Installing bioretention cells (also called rain gardens) to treat parking lot runoff reduces PAHs in stormwater, likely through biodegradation. An NC State study in Wilmington, N.C., found a reduction in the



Figure 6. A parking lot with interlocking pavers in Swansboro, N.C.

concentration of PAHs from parking lot runoff after treatment by a vegetated bioretention cell (Wright et al 2009). A University of Maryland study indicates that a shallow bioretention cell design is adequate for removing PAHs, with mitigation focused on the top surface layer near the inlet where sediment accumulation occurs. PAHs were found to be degraded through indirect plant processing of microbial-soil-root interactions with the rhizosphere (the area of soil 1 mm from the plant root). (Dibiasi, et al 2009). Since PAHs are often sediment-bound, stormwater practices that reduce sediment (such as bioretention, stormwater wetlands, wet ponds, swales, and filter strips) may be important for reducing PAH concentrations. Some proprietary stormwater management devices, such as inlet filtration devices, are marketed as reducing organic toxins, including PAHs. Regular maintenance of these and all stormwater management devices is integral for continued pollutant removal (see AG-588-7 for further discussion on maintenance). Proper disposal of contaminated sediment is a concern.

Recommendations for disposing of sediments from BMP maintenance are included in the NCDENR Stormwater Best Management Practice Manual.

Create parking lots with surfaces other than asphalt, such as concrete or permeable pavement. The upfront costs for installing concrete are higher than those for installing asphalt parking lots. Long-term maintenance is likely lower, however, since concrete parking lots do not require sealants and have a longer lifespan. The lighter surface of concrete also provides a benefit of reducing the urban heat island effect by absorbing less solar energy than darker surfaces (EPA 2008). Pervious pavement, including interlocking pavers and permeable concrete, are alternatives to concrete and asphalt that reduce stormwater runoff and pollution (see AG-588-14). Although pervious pavement is the most expensive of the paving options when considering only construction cost, regulatory credit from NCDENR for reducing imperviousness and attenuating peak runoff with appropriate design can offset the cost. This may allow permeable pavement to replace or reduce the size of other stormwater practices.



Figure 7. A permeable pavement lot in Wilmington, N.C.

Summary

PAHS have been identified by USGS as an important emerging contaminant in the waterways of growing metropolitan areas of the United States, including those of North Carolina. Negative impacts from PAHs in waters have been well documented in fish, amphibians, bivalves, and benthic macro-invertebrates. Human-health impacts from drinking water and short-term contact with contaminated waters are thought to be minimal, though consumption of contaminated bivalves is a concern. There are many potential sources of PAHs to urban waters, though a growing body of research has highlighted the use of coal tar based parking lot sealant as a major contributor. Strategies for reducing the risks of PAHs to aquatic ecosystems include eliminating the use of coal tar-based sealants on parking lots, intercepting and managing runoff from parking lots and roads, and creating parking lots with materials that don't require sealing such as concrete or permeable pavement.

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