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Polycyclic Aromatic Hydrocarbons in Urban Runoff – Sources, Sinks and Treatment: A Review

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Prepared for:

DuPage River Salt Creek
Workgroup, Naperville, IL

October, 2010

About the DRSCW

The East & West Branches of the DuPage River and Salt Creek are located in Northeastern Illinois, including portions of Cook, DuPage and Will Counties.

In response to concerns about the East & West Branch DuPage River TMDLs and the Salt Creek TMDL, a local group of communities, POTWs and environmental organizations have come together to better determine the stressors to the aquatic systems through a long term water quality monitoring program and develop and implement viable remediation projects.

Because of the similarities of water quality issues, development patterns and multiple agency/organizational overlap this group will address both watersheds simultaneously.

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ACKNOWLEDGEMENTS

We thank the DuPage River Salt Creek Workgroup (DRSCW) for this opportunity and for funding this review work. In particular, we wish to thank Stephen McCracken (DRSCW), Robert Swanson (DuPage Country Division of Stormwater Management) and Robert Covey (Village of Schaumburg), for their part in the initial review of this report and for their valuable comments.

And finally, we thank Illinois Institute of Technology's Galvin Library for making the review work for this report possible through vast collection of literature sources and direct technical help during the search.

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ABBREVIATIONS

ADI	Acceptable daily intake
AWQC	Ambient Water Quality Criterion (mg/L)
BAF	Bioaccumulation factor (L/kg)
BC	Black carbon
BMP	Best management practices
BW	Human body weight (kg)
CBI	Catch basin inserts
CBSF	Catch basin storm filter
CSO	Combined sewer overflow
DI	Drinking water intake (L/day)
DRSCW	DuPage River and Salt Creek Workgroup
EPA	U.S. Environmental Protection Agency
FI	Fish intake (kg/day)
gal/yd^2	Gallons per square yards
HHS	U.S. Department of Health and Human Services
HMW	Higher molecular weight
IARC	International Agency for Research on Cancer
LMW	Lower molecular weight
MCL	Maximum contaminant level
mg/L	Milligram per liter (ppm)
MGPs	Manufactured gas plants
MW	Molecular weight
ng/L	Nanogram per liter (ppt)
NPS	Nonpoint source
PAH	Polycyclic aromatic hydrocarbon
POM	Polycyclic organic matter
POP	Persistent organic pollutants

RfD	Reference dose for noncancer effects (mg/kg-day)
RSC	Relative source contribution factor to account for non-water sources of exposure
TEF	Toxic equivalency factors
TMDL	Total maximum daily load
TOC	Total organic carbon
TPAHs	Total polycyclic aromatic hydrocarbons
TSS	Total suspended soilids

EXECUTIVE SUMMARY

This document provides detailed information on Polycyclic Aromatic Hydrocarbons (PAH) in the aquatic environment, with a focus of storm runoff sources. The contents include current information on the PAHs sources, physical and chemical characteristics, biological effects and best management practices (BMP) that can be employed for treatment and controlling PAHs in urban stormwater runoff. Additionally, the document also presents material on coal tar-based sealants in comparison with asphalt-based sealants and its contribution to PAHs in urban stream runoffs.

The purpose of this report is to serve as reference for DuPage River and Salt Creek Workgroup (DRSCW).

This report includes nine chapters.

Chapter 1 presents pollution issues due to urbanization and their contribution to urban runoff water quality. This chapter also introduces Polycyclic Aromatic Hydrocarban (PAHs) and provides information on their natural & anthropogenic occurrences and presents data on aquatic loading of PAHs from these sources in urban environment.

Chapter 2 discusses the physical and chemical properties of PAHs that influence their presence in stormwater and surface water.

Chapter 3 presents regulatory issues and standard including the US EPA’s list of PAHs as priority pollutants, EPA’s drinking water limits, and section 304(a) criteria for PAHs.

Chapter 4 discusses the effects of PAHs on microorganisms, fish and other aquatic organisms, plants and humans. Data on toxicity equivalency factors (TEFs) and carcinogenicity of PAHs are also presented in this chapter.

Chapter 5 describes various PAH degradation pathways - Biotransformation and degradation by algae, bacteria, fungi and plant; and photolysis by ultraviolet radiation in sunlight.

Chapter 6 discusses PAHs loading of sediments with respect to the particle size distribution, total organic carbon (TOC) and organic matter present in urban runoff.

Chapter 7 presents a comparative study of coal tar-based sealants, an urban PAH source, with asphalt-based sealants, an alternative option, used for pavement surface finishes.

Chapter 8 presents recommendations for non-structural and structural best management practices (BMPs) to address PAHs loading and treatment of urban runoff.

Chapter 9 summarizes the report and presents the findings of this review work. This chapter also suggests future research needs.

Chapter 1

INTRODUCTION

1.1. Urbanization and its effects on urban runoff water quality

Worldwide, virtually all population growth until 2030 is expected to occur in urban areas. Urban population is expected to increase by 2.1 billion versus 2.2 billion in world population, during the same period (United Nations, 2002). The alarming rate of urbanization expected in the future and the urban growth that has already occurred in the recent decades has caused concerns amongst the environmentalist and governing bodies in regards to their impacts on environment. Increases in urban population and developments have serious consequences on the surrounding water bodies like lakes, rivers and ground water. Understanding the sources, pathways and fate of contaminants in the urban environment is essential for making informed management decisions. Urban areas are major concentrators, repositories and emitters of a myriad of chemicals because of the wide range and intensity of human activities and the characteristics of the built environment. Much of the land surface in urban areas is impervious, covered by buildings and pavement, which do not allow rain and snowmelt to soak into the ground; thus, contributing to the increase of runoff volume (Figure 1). Rainfall and snowmelt in urban areas are converted into urban runoff, which is transported by drainage channels, streams and sewers and ultimately discharged to receiving waters as urban stormwater in areas serviced by storm sewers or as combined sewer overflows (CSOs) in older areas with combined sewers. As little as 10 percent impervious cover in a watershed can result in stream degradation (Figure 2). A typical city block can generate more than 5 times more runoff than a woodland area of the same size (US EPA, 2003). Urban runoff discharges cause physical, chemical, biological and combined effects on receiving waters, either of acute or cumulative nature (Harremoes, 1988) and seriously impair beneficial water uses in many locations (House et al., 1993).

Nonpoint source (NPS) pollution is the Nation's largest source of water quality problems (US EPA, 1996). NPS pollution occurs when rainfall, snowmelt, or irrigation runs over land or through the ground, picks up pollutants and deposits them into rivers, lakes and coastal waters or introduces them into ground water. The pollution of both stormwater and CSOs greatly varies during and between rainfall events, ranging from severe (usually during early phases of runoff, also referred to as the first flush) to low, towards the end of runoff events (Marsalek et al. 1993).

Impacts on water quality are exerted by combinations of physical, chemical and microbiological factors (Marsalek et al. 2001; House et al. 1993):

- Physical factors include flow (the effects of which are flooding, erosion, habitat washout), sediment (causing habitat destruction, interference with water quality processes, impacts on aquatic life, transport of contaminants), thermal energy (causing thermal pollution, loss of cold water fisheries) and densimetric stratification (causing the impairment of mixing).

- Chemical factors include biodegradable organics in CSOs (contributing to dissolved oxygen depletion), nutrients (contributing to eutrophication), trace metals, chloride, persistent organic pollutants (POPs) like polycyclic aromatic hydrocarbons (PAHs), pesticides and hydrocarbons, often occurring in complex chemical mixtures in stormwater and CSOs (contributing to acute and chronic toxicity and genotoxicity).

- Microbiological factors include bacteria and viruses of fecal origin in stormwater and CSOs (causing beach closures and contamination of shellfish).

  A long-term demographic trend in urban population, due to overall population increase and migration from rural to urban areas, will increase demand for water services, including drinking water supply, drainage infrastructure, wastewater management and protection of receiving waters. Meeting these demands will become even more challenging; because of increased per capita resource consumption and emissions leading to higher pollution loads and more constituents in stormwater and CSOs. The relative significance of these sources is increasing with improved control of point source pollution.

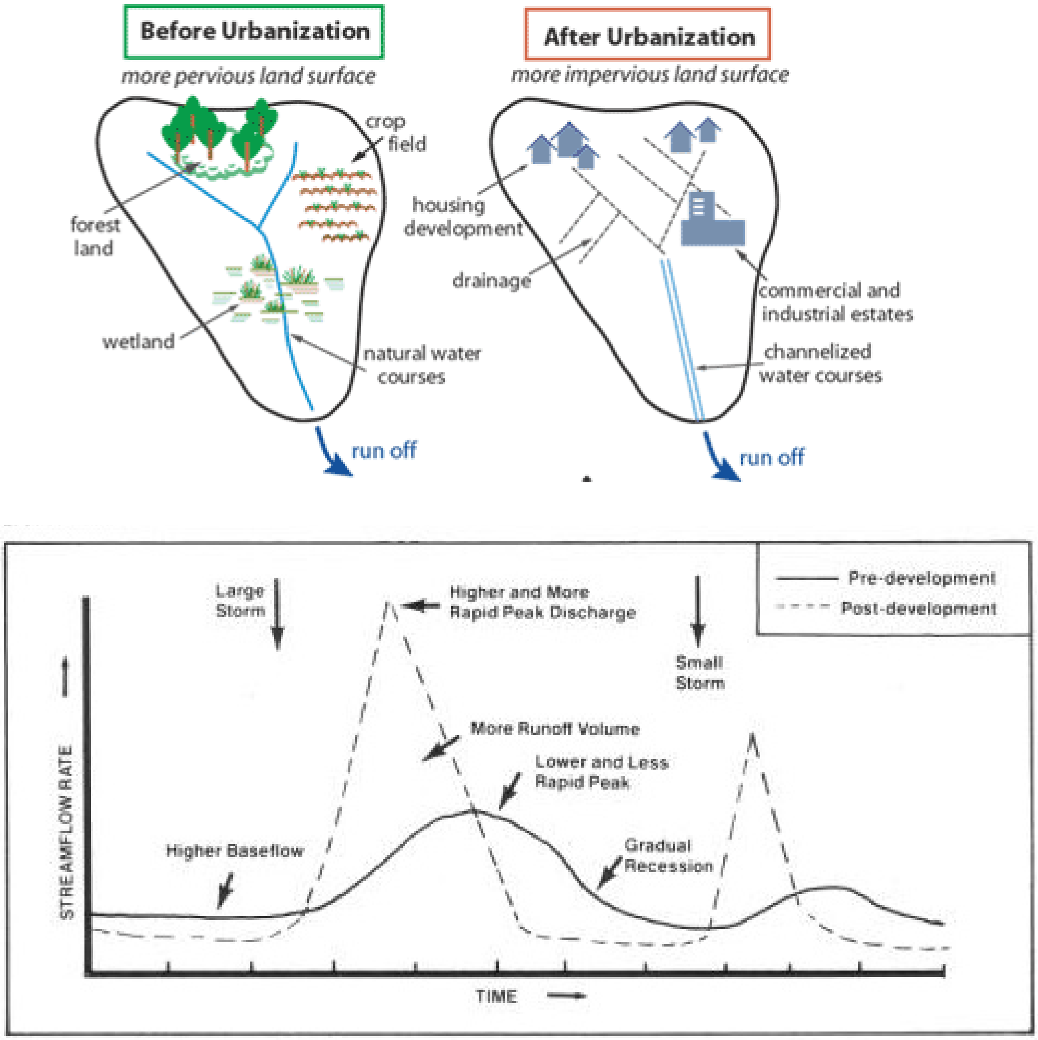

Figure 1. A typical effect of urbanization and impervious surface on runoff volume and time compared to unpaved previous surface. The increase in impervious surface area together with channelization of water courses contribute to the loss of water retention capacity (LBERI, 1994 and Schueler, T. R., 1987)

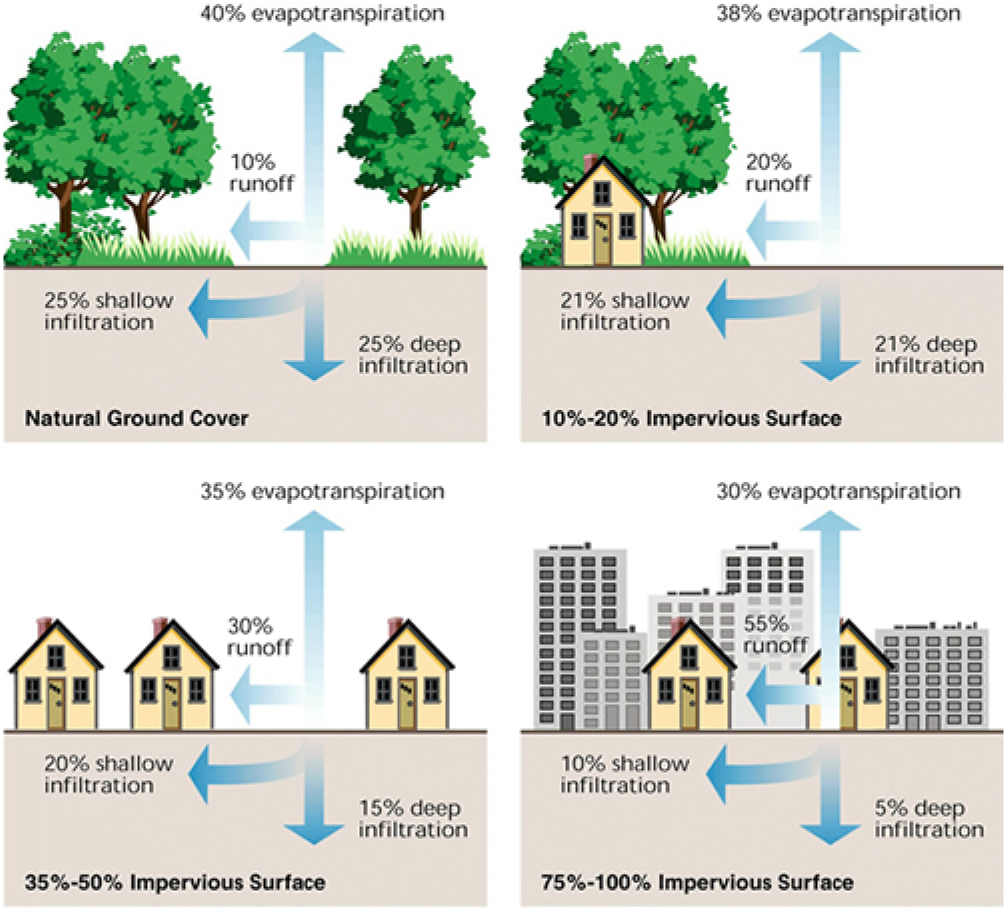

Figure 2. Relationship between impervious cover and surface runoff. Impervious cover in a watershed results in increased surface runoff. As little as 10 percent impervious cover in a watershed can result in stream degradation (EPA, 2003).

1.2. Occurrences of PAHs in urban environment

Urban runoff can contain high concentrations of chemical contaminants, including polycyclic aromatic hydrocarbons and heavy metals (US EPA, 1983). Polycyclic aromatic hydrocarbons are a group of over 100 different organic compounds. PAHs are composed of up to six benzene rings fused together such that any two adjacent benzene rings share two carbon bonds. PAHs are formed by incomplete combustion of carbon-containing materials such as fuels (e.g. gasoline, diesel), domestic matter (e.g. tobacco, residential wood or coal) and other area source matter (e.g. agricultural wastes, municipal waste). Concentrations of PAHs have been increasing in recent decades in many urban lakes and streams, particularly in areas with rapid urbanization (Van Meter et al., 2000). PAHs are regarded as persistent organic pollutants (POPs) in the environment. This persistence is increasing with ring number and condensation degree (Jones K.C., 1989). These organic contaminants show long half-lives in geological media. In aerobic sediment, for example, half lives range from 3 weeks for naphthalene up to 300 weeks for benzo[a]pyrene (Bossert I., 1984).

Occurrences of PAHs in natural media such as soil, sediment, water, air and plants are a result of both natural and anthropogenic processes (Table 1).

1.2.1. Natural Sources

In nature, PAHs may be formed three ways:

- high temperature pyrolysis (partial breakdown of complex organic molecules during combustion to lower molecular weight free radicals) of organic materials,
- low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel and
- direct biosynthesis by microbes and plants (Neff, 1979).

Fires: Forest fires, prairie fires and agricultural burning contribute the largest volumes of PAHs from a natural source to the atmosphere. The actual amount of PAHs and particulates emitted from these sources varies with the type of organic material burned, type of fire (heading fire vs. backing fire), nature of the blaze (wild vs. prescribed; flaming vs.

smouldering) and intensity of the fire. PAHs from fires tend to sorb to suspended particulates and eventually enter the terrestrial and aquatic environments as atmospheric fallout (Eisler, 1987).

In the atmosphere, PAHs may undergo photolytic and chemical (ozone) transformations. However, most of the material does not degrade quickly in the atmosphere and thus may reside in the environment for extended periods of time. During this atmospheric entrainment, winds may distribute these particle-sorbed PAHs in a global manner such that they appear even in remote areas of the Arctic or Antarctica.

Fossil fuels: PAHs occur naturally in bituminous fossil fuels, such as coal and crude oil deposits, as a result of diagenesis (i.e., the low temperature, 100-150 °C, combustion of organic material over a significant span of time). This process favors the formation of alkylated PAHs; the unsubstituted (or the parent) compounds being relatively low in abundance in these sources. It has been suggested that 70-75% of the carbon in coal is in aromatic form; the 6-membered ring aromatics are dominant with a small 5-membered ring fraction present as well (Neff, 1979). PAHs such as benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, dibenzo[c,d,m]pyrene, perylene and phenanthrene have been identified in coal samples (Woo et al., 1978). Atwater and Mavinic (1985) analyzed wastewater and sludge samples from 11 coal operations across Canada In wastewater, naphthalene and phenanthrene were detected at levels >10 μg/L, whereas anthracene, benzo[k]fluoranthene and dibenzo[a,h]anthracene levels were <10 μg/L. Naphthalene, phenanthrene, anthracene, fluorene and pyrene were usually found in sludges at μg/g levels.

Under natural conditions, fossil fuels contribute a relatively small volume of PAHs to the environment. Because most oil deposits are trapped deep beneath layers of rock, there is little chance to emit PAHs to the surface environment. There are some petroleum bodies (e.g., tar sands) which, being near the surface, are capable of contributing PAHs to both atmospheric and aquatic surroundings. These deposits are small in number and are likely to contribute little to the overall volume of PAH in the environment.

Table 1. Main sources of polycyclic aromatic hydrocarbons (PAHs)

Natural Sources	**Anthropogenic Sources**
• **Fires** - Forest fires, prairie fires and agricultural burning • **Fossil fuels** - coal and crude oil • **Other Sources** - Volcanic activity and biosynthesis by bacteria and plants	• **Aquatic discharge sources** – accidental spillage and/or leakage of PAH-containing fluids (e.g.,waste oils, gasoline, etc.), industrial and domestic wastewaters, urban runoff, discharges originating from landfills and use of creosoted pilings for docks and other shoreline structures • **Atmospheric discharge sources** – (a) **Stationary sources**: coal and gas-fired boilers; coal gasification and liquefaction plants; carbon black, coal tar pitch and asphalt production; coke-ovens; catalytic cracking towers; petroleum refineries and related activities, electrical generating plants; industrial incinerators; municipal incinerators, agricultural and refuse burning and any other industry that entails the use of wood, petroleum or coal to generate heat and power. (b) **Non-stationary (or mobile) sources**: automobiles or other vehicles which use petroleum products as a fuel.

Other Natural Sources: Volcanic activity and biosynthesis by bacteria and plants are other natural sources of PAHs. Relative to fires, these sources contribute small amounts to the environment.

Natural sources of pyrogenic PAH such as volcanic activity and forest fires do not significantly contribute to overall PAH emission (Wild S.R., 1995).

1.2.2 Anthropogenic sources

Major anthropogenic sources of PAHs in urban runoffs are deterioration of asphalt pavement surfaces and car tires (Halsall et al.,1994; Harrison et al., 1996), leading to passing the compounds to runoff waters; vehicular emissions leading to atmospheric fallout; and rain water runoff across impervious areas (such as roads, motorways, paved parking lots, sidewalks); and pervious areas (such as gardens, landscaping, grass and unpaved surfaces etc.). Incomplete combustion of organic matter at high temperature is one of the major anthropogenic sources of environmental PAHs.

The environmental sources of PAHs of pyrolitic origin are many (Neff, 1979):

- Charcoal-broiled steaks and commercially available smoked food products have been identified to contain PAHs.
- Conditions are ideal for PAH pyrosynthesis (combination of free radicals containing one or more carbons druing combustion) within a cigarette flame.
- Burning of fossil fuels is an important source of PAHs in the environment. Significant quantities of benzo[a]pyrene and other PAHs have been identified in vehicular exhaust.
- Many heat and electrical generating facilities burn fossil fuels and produce, as byproducts, liquid, solid and gaseous wastes that may be rich in PAHs.
- Catalytic breakdown of crude petroleum to produce hydrocarbon fuels and other refined products results in the production of PAHs. Many of the PAHs thus produced become concentrated in the high boiling residual oil and asphalt. Significant quantities of PAHs may also be released in flue gas.

- The production of coke involves subjecting hard coal to high temperatures (1400 °C) in a reducing atmosphere, conditions ideal for pyrosynthesis of PAHs.
- Coal tars, produced by the high temperature treatment of coal, are also known to contain a host of PAHs. These PAHs are derived either from PAHs indigenous to the coal or from pyrolysis of coal hydrocarbons.
- Incineration is a valuable means of waste disposal and waste reduction. PAHs in the stack gases, solid residues and wastewaters from municipal incinerators have been identified (Davies et al., 1976). It has also been found that PAHs released each day in solid residues were 10 times more than in the stack gases and 100 times more than in the wastewater (Davies et al., 1976).

There are many other anthropogenic sources of pyrolytic PAHs. In fact, any industrial or domestic process in which organic carbon is subjected to high temperature will result in the production of some PAHs. Treated wood has also been recognized as a source of PAHs in water and sediments.

In general, anthropogenic sources can be divided into two categories: sources that discharge directly into a body of water and sources that discharge into the atmosphere. These sources are listed in Table 1.

Atmospheric PAH sources contribute PAHs to the environment either through the formation of these compounds during industrial processing or through pyrolysis of the fuels for energy generation. These PAHs, if not degraded in the atmosphere, are sorbed onto particulates in the air and are then deposited onto bodies of water, as well as the surrounding terrestrial environment.

Non-stationary sources of PAHs usually refer to automobiles or other vehicles which use petroleum products as a fuel. Temperatures within an internal combustion engine are often sufficient enough to convert a fraction of the fuel or oil into PAHs via pyrolysis. These compounds are then emitted to the atmosphere through exhaust fumes whereupon they sorb onto particulates. Most PAHs are then photolytically degraded or are deposited onto street surfaces. Precipitation then washes these PAHs into stormwater drainage systems eventually flushing them into the aquatic environment.

1.2.3 Aquatic environmental loading

According to Eisler (1987) approximately 230,000 metric tons of PAHs are discharged to the aquatic environment per annum as a result of human activity (Table 2). Petroleum spillage and/or leakage of a major and/or a minor nature is the largest contributor to this loading and amounts to 170,000 tons (roughly 75%) of this total. The other major contributor is the atmospheric fallout from the sources listed in Table 1, adds an accumulated total of 50,000 tons to aquatic systems. The remaining mass of PAH is contributed through industrial wastewater effluents, sewage effluents and from runoff. The PAH mixtures disposed of in this manner are highly variable and complex due to the large number of sources contributing to this discharge.

In the State of Illinois, former manufactured gas plant (MGP) sites are also a contributor of PAHs into their respective environments. In the late 1800s, manufactured gas plants produced gas for lighting prior to the advent of electricity. A by-product of these former manufactured gas plants (MGPs) was coal tar, which contains PAHs. As of October, 2009, 520 former MGP sites have been identified in Illinois, including several adjacent to the Illinois River (Doyle, B.C., 2006, Figure 3). Some of these sites are being remediated but still continue to leach out PAHs in to its surrounding soil and water bodies.

PAHs in stormwater result from a variety of sources, including residential, industrial and commercial areas; streets and parking lots and atmospheric fallout (Figure 5). In general, most samples of surface water contain individual PAH at levels up to 50 ng/L, but highly polluted rivers have concentrations of up to 6,000 ng/L. The PAH levels in groundwater are within the range 0.02-1.8 ng/L and drinking-water samples contain concentrations of the same order of magnitude. Levels of individual PAH in rainwater range from 10 to 200 ng/L, whereas levels of up to 1000 ng/L have been detected in snow and fog. Studies have shown that atmospheric deposition contributes to contaminants in rainwater. There is an increase in the PAH and other contaminant flux in traffic and industrial areas compared to outer suburbs, implicating traffic as a major contributor (R. Huston et al. 2009). During storm event, runoff from roads, roof tops, sealed parking lot surfaces, gas stations and vehicle maintenance wash off particulates and sediments containing high levels of PAHs. Illegal dumping may also cause PAH contamination in stormwater.

Table 2. Main sources of PAHs in the atmospheric and aquatic environments (Eisler, 1987)

Sources	Annual Input of TPAHs
Atmosphere	
Forest and prairie fires	19,513
Agricultural burning	13,009
Refuse burning	4,769
Enclosed incineration	3,902
Heating and power	2,168
Total	43,361
Aquatic Environments	
Petroleum spillage	170,000
Atmospheric deposition	50,000
Wastewaters	4,400
Surface land runoff	2,940
Biosynthesis	2,700
Total	230,040

Figure 3. Locations of former MGPs in State of Illinois (Doyle, B.C., 2006).

Chapter 2

PAH IN URBAN RUNOFF

2.1. Physical and chemical properties of PAHs

All PAHs are solids ranging from colorless to pale yellow to golden yellow. PAHs vary in molecular weights but PAHs range in molecular weight from 128 (Naphthalene; $C_{10}H_8$) to 278.4 (Dibenz[a,h]anthracene; $C_{22}H_{14}$) (Table 3). The majority of all PAHs entering the atmosphere are deposited directly to soils, waters and vegetation (Simonich S. L., 1994). Amongst, soils, water and vegetation, PAHs primarily exists adsorbed to soil particles (Table 4) in natural environments. Higher molecular weight (HMW) PAHs (>3 aromatic rings) are relatively immobile because of their large molecular volumes. They are less water-soluble, less volatile and more lipophilic than lower molecular weight (LMW) PAHs (Wild S.R., 1995) (Table 5). Solubility characteristics of PAH vary for each PAH, but in general:

- PAH solubility in water decreases as the molecular weight increases.
- Alkyl (i.e., CH_2- group) substitution of the aromatic ring results in an overall decrease in the PAH solubility, although there are some exceptions to this rule. For example, Benz[a]anthracene is less soluble than either methyl- or ethylbenz[a] anthracene.
- Molecules with a linear arrangement tend to be less soluble than angular or perifused molecules (Polycyclic compounds in which two rings have two and only two, atoms in common are said to be "ortho-fused". Such compounds have n common faces and 2n common atoms. Polycyclic compounds in which one ring contains two and only two, atoms in common with each of two or more rings of a contiguous series of rings are said to be 'ortho- and peri-fused'. Such compounds have n common faces and fewer than 2n common atoms.). For instance, anthracene is less soluble than phenanthrene and naphthacene is less soluble than chrysene or benz[a]anthracene.

The solubility of PAHs in water is enhanced three- to four-fold by a rise in temperature from 5 to 30 °C. Dissolved and colloidal organic fractions also enhance the solubility of PAHs which are incorporated into micelles (a micelle is composed of an aggregate of surface-active molecules, or surfactants, each possessing a hydrophobic hydrocarbon chain and an ionizable hydrophilic group) (Neff, 1979).

Vapor pressure characteristics determine the persistence of PAHs in the aquatic environment. Two- to 3-ring PAHs are very volatile, while PAHs with 4 or more rings show insignificant volatilizational loss under all environmental conditions (Moore and Ramamoorthy, 1984).

Due to their hydrophobic nature, PAHs entering the aquatic environment exhibit a high affinity for suspended particulates in the water column. As PAHs tend to sorb to these particles, they are eventually settled out of the water column onto the bottom sediments. Thus, the PAH concentrations in water are usually quite low relative to the concentrations in the bottom sediments (Moore and Ramamoorthy, 1984).

Urban runoff washes off PAHs from various anthropogenic sources and facilitates their accumulation and availability in stormwater. Low solubility of PAHs and the hydrophobic sorptive capacity (K_{ow}) correspondingly high, coupled with low volatilities (Henry's Law constant) and general chemical stability mean that PAHs are environmentally persistent compounds that are strongly held to solids, both suspended particles and bottom sediment. After entering water, the physiochemical properties of PAHs make them quickly become adsorbed to organic or inorganic compounds and are mostly deposited in bottom sediments. Once adsorbed they are much more stable than pure compounds and are resistant to oxidation and nitration reactions to which they would otherwise be quite sensitive due to photochemical processes (Catoggio. J. A., 1991). Furthermore, the high partitioning to organic carbon (as reflected by high K_{ow}) is the root cause behind the high rate of bioconcentration for these compounds and the ease with which they enter the food web.

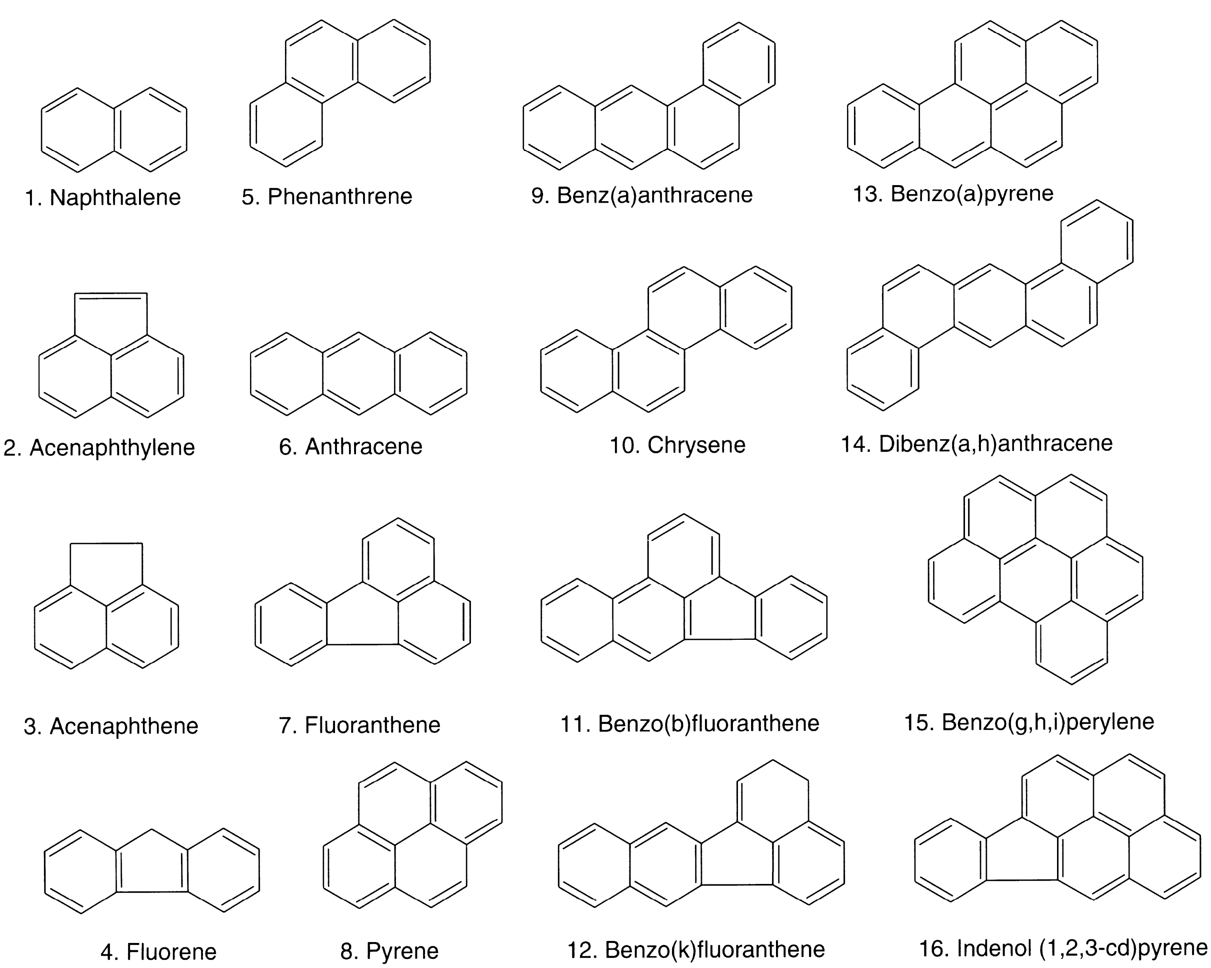

Figure 4. Structure of sixteen polycyclic aromatic hydrocarbons as US EPA and WHO priority pollutants.

Table 3. Molecular formula, molecular mass, solubility and sorption affinity (Log K_{ow}) of EPA-listed PAHs.

PAH	Molecular Formula	Relative Molecular Mass	Solubility in Water at 25°C (µg/l)	Log K_{ow} (Log K_{oc})	CAS Number
Naphthalene	$C_{10}H_8$	128.2	3.17×10^4	3.29 (2.97)	91-20-3
Acenaphthylene	$C_{12}H_8$	152.2	3.4×10^3	4.07 (3.40)	208-96-8
Acenaphthene	$C_{12}H_{10}$	154.2	3.93×10^3	3.98 (3.66)	83-32-9
Fluorene	$C_{13}H_{10}$	166.2	1.98×10^3	4.18 (3.86)	86-73-7
Phenanthrene	$C_{14}H_{10}$	178.2	1.29×10^3	4.45 (4.15)	85-01-8
Anthracene	$C_{14}H_{10}$	178.2	73	4.45 (4.15)	120-12-7
Fluoranthene	$C_{16}H_{10}$	202.3	260	4.90 (4.58)	206-44-0
Pyrene	$C_{16}H_{10}$	202.3	135	4.88 (4.58)	129-00-0
Benz[a]anthracene	$C_{18}H_{12}$	228.3	14	5.61 (5.30)	56-55-3
Chrysene	$C_{18}H_{12}$	228.3	2.0	5.16 (5.30)	218-01-9
Benzo[b]fluoranthene	$C_{20}H_{12}$	252.3	1.2	6.04 (5.74)	205-99-2
Benzo[k]fluoranthene	$C_{20}H_{12}$	252.3	0.76	6.06 (5.74)	207-08-9
Benzo[a]pyrene	$C_{20}H_{12}$	252.3	3.8	6.06 (6.74)	50-32-8
Benzo[ghi]perylene	$C_{22}H_{12}$	276.3	0.26	6.50 (6.20)	191-24-2
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.3	62	6.58 (6.20)	193-39-5
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.4	0.5 (27°C)	6.84 (6.52)	53-70-3

Table 4. Partition of PAHs in the natural environment (Wild S.R., 1995)

Element of the Environment	**Percent of Total**	
	∑PAH	**BaP**
Soil	94.4	92.9
Freshwater sediment	5.4	7.1
Water	< 0.01	< 0.01
Air	0.1	< 0.01
Vegetation	0.1	< 0.01
Biota	< 0.01	< 0.01

Table 5. Typical properties of lower (≤ 3 aromatic rings) and higher molecular weight (≥ 4 aromatic rings) PAHs.

Property	**PAHs ≤ 3 rings**	**PAHs ≥ 4 rings**
Water solubility (mg/l)	≥ 32	≤ 0.26
Volatility (Henry's constant, Atm.m^3.mol^{-1})	5.0 E-2 to 7.9E-4	3.5 E-4 to 2.2 E-6
Sorption Affinity (Log K_{ow})	3.4 to 4.18	5.2 to 7.3
Ecotoxicity	+	+/-
Carcinogenecity	-	++
Examples	Naphthalene (2-rings) Acenaphthene (3-rings) Fluorene (3-rings) Anthracene (3-rings)	Pyrene (4-rings) Chrysene (4-rings) Benzo[a]pyrene (5-rings) Benzo[ghi]perylene (6-rings)

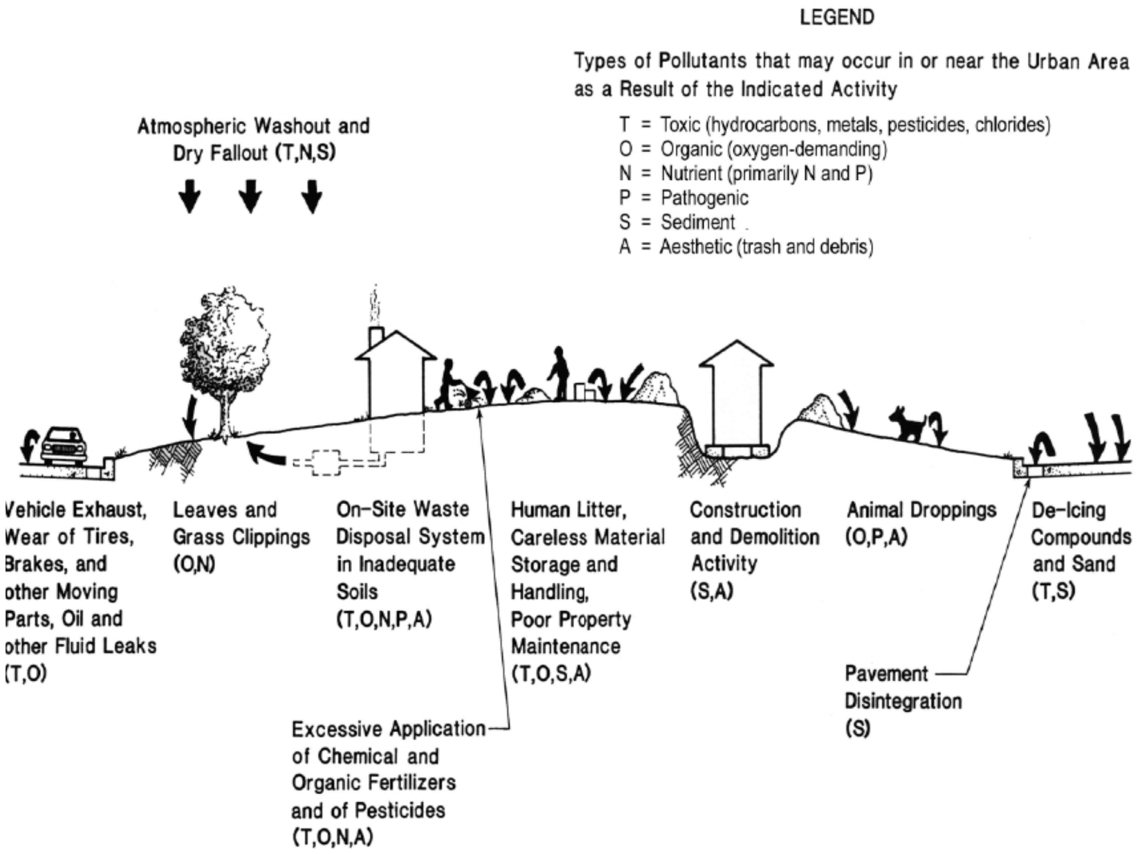

Figure 5. Typical pollutant sources in urban environment (Walesh, S. G., 1989). Hydrocarbons primarily refer to PAHs.

Chapter 3

STANDARDS & REGULATIONS

The United States Environmental Protection Agency (US EPA) and the World Health Organization have listed 16 PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo(b)fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene (BaP), Benzo[g,h,i]pyrene, Dibenzo[a,h]anthracene and Indeno[1,2,3-cd]pyrene) as priority pollutants (Figure 4). Of the listed 16 PAHs, at least 7 PAHs (Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene and Indeno[1,2,3-cd]pyrene) are commonly found in stormwater.

EPA has established ambient water quality criterion (AWQC) in terms of maximum contaminant level (MCL) for each of these pollutants in drinking water (Table 6). AWQC is calculated by EPA pursuant to Section 304(a) of the Clean Water Act:

$$AWQC = RfD * RSC * \frac{(BW)}{[DI + (FI * BAF)]}$$

Where,

AWQC = Ambient Water Quality Criterion (mg/L)
RfD = Reference dose for noncancer effects (mg/kg-day)
RSC = Relative source contribution factor to account for non-water sources of exposure
BW = Human body weight (kg)
DI = Drinking water intake (L/day)
FI = Fish intake (kg/day)
BAF = Bioaccumulation factor (L/kg)

Toxics criteria based on fish/shellfish and water consumption, for those states not complying with EPA's Clean Water Act section 303-(c)-(2)-(B), are listed in Table 7.

Table 6. EPA standards and regulations for PAHs in drinking water

MCL in Drinking Water (mg/L)	**PAHs**
0.0001	Benz(a)anthracene
0.0002	Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Chrysene
0.0003	Dibenz(a,h)anthracene
0.0004	Indenol(1,2,3-c,d)pyrene

Table 7. EPA’s Section 304(a) criteria for PAHs as priority pollutants

PAH Priority Pollutants	**Human Health for the consumption of**	
	Water + Organism (µg/L)	**Organism Only (µg/L)**
[1]Acenaphthene	670 B,U	990 B, U
Acenaphthylene		
Anthracene	8,300 B	40,000 B
Benzo(a)anthracene	0.0038 B,C	0.018 B,C
Benzo(a)pyrene (BaP)	0.0038 B,C	0.018 B,C
Benzo(b)fluoranthene	0.0038 B,C	0.018 B,C
Benzo(g,h,i)pyrene		
Benzo(k)fluoranthene	0.0038 B,C	0.018 B,C
Chrysene	0.0038 B,C	0.018 B,C
Dibenzo(a,h)anthracene	0.0038 B,C	0.018 B,C
Fluoranthene	130 B	140 B
Indeno(1,2,3-cd)pyrene	0.0038 B,C	0.018 B,C
Naphthalene		
Phenanthrene		
Pyrene	830 B	4,000 B

B This criterion has been revised to reflect The Environmental Protection Agency's q1* or RfD, as contained in the Integrated Risk Information System (IRIS) as of May 17, 2002. The fish tissue bioconcentration factor (BCF) from the 1980 Ambient Water Quality Criteria document was retained in each case.

C This criterion is based on carcinogenicity of 10-6 risk. Alternate risk levels may be obtained by moving the decimal point (e.g., for a risk level of 10-5, move the decimal point in the recommended criterion one place to the right).

U The organoleptic effect (e.g., taste and odor) criterion is more stringent than the value for priority toxic pollutants.

1 Acenaphthene’s Organoleptic Effect Criteria (µg/L) is 20.

Chapter 4

EFFECTS OF PAHs

4.1. Aquatic organisms

The carcinogenicity of certain PAHs is well established in laboratory animals. PAHs reveal their toxicity following biotransformation to toxic metabolites which can be bound covalently to cellular macromolecules such as DNA, RNA and proteins, which causes cell damage, mutagenesis, tetragenesis and cacinogenesis. After PAH exposure, there is an increase in the number of DNA adducts, as well as some inhibition in RNA and protein synthesis (Arvo T. 1995; M. Pufulete 2004). Researchers have reported increased incidences of skin, lung, bladder, liver and stomach cancers, as well as injection-site sarcomas, in animals. Studies on animals show that certain PAHs also can affect the hematopoietic (growth of blood cells) and immune systems and can produce reproductive, neurologic and developmental effects (Blanton 1986, 1988; Dasgupta and Lahiri 1992; Hahon and Booth 1986; Malmgren et al. 1952; Philips et al. 1973; Szczeklik et al. 1994; Yasuhira 1964; Zhao 1990).

PAHs are absorbed through ingestion, inhalation and dermal contact, according to animal study data. The percent absorbed varies in these studies for several reasons, including the vehicle (transport medium) in which the PAHs are found. Aquatic organisms are known to adsorb and accumulate PAHs from water. The degree of contamination is related to the extent of industrial and urban development. PAH concentrations of up to 7 mg/kg have been detected in aquatic organisms living near industrial effluents and the average levels of PAH in aquatic animals sampled at contaminated sites were 10-500 µg/kg, although levels of up to 5 mg/kg were also detected.

The average levels of PAH in aquatic animals sampled at various sites with unspecified sources of PAH were 1-100 µg/kg, but concentrations of up to 1 mg/kg were found, for example, in lobsters in Canada.

PAHs are acutely toxic to fish and *Daphnia magna* in combination with absorption of ultraviolet radiation and visible light. Metabolism and degradation alter the toxicity of PAHs. At low concentrations PAHs can stimulate the growth of microorganisms and algae. The most toxic PAH for algae is Benz [a]anthracene (four-ring) and Naphthalene (two-ring) is the least toxic. No clear difference in sensitivity was found between different taxonomic groups of invertebrates like crustaceans, insects, mollusks, polychaetes and echinoderms. Acute toxicity in fish was seen at concentrations of 110 to > 10 000 µg/liter of naphthalene, 30-4000 µg/litre of three-ring PAH (anthracene, 2.8-360 µg/litre) and 0.7-26 µg/litre for four- or five-ring PAH. Contamination of sediments with PAHs at concentrations of 250 mg/kg was associated with hepatic tumors in free-living fish. Tumors have also been induced in fish exposed in the laboratory. Exposure of fish to certain PAH can also cause physiological changes and affect their growth, reproduction, swimming performance and respiration.

The available information on the toxicity of the PAHs suggests that most are considerably less potent than Benzo(a)pyrene (B[a]P) (Table 8) (Nisbet, I.C.T et al. 1992). B[a]P is expected to bioconcentrate in aquatic organisms that cannot metabolize it. Reported Bioconcentration Factors (BCFs) include: Oysters, 3000; Rainbow trout, 920; Bluegills, 2,657; zooplankton, 1000 to 13,000. Those organisms which lack a metabolic detoxification enzyme system, tend to accumulate PAHs. The presence of humic acid in solution has been shown to decrease bioconcentration. For example, BCFs have been found to be very low (<1) for mudsuckers, sculpins and sand dabs.

4.2. Plants

Biological effects of PAHs on terrestrial vegetation have been reviewed by several groups (Santodonato. J et al., 1981), Wang and Meresz (1982), Edwards (1983) and Sims and Overcash (1983). In general, these authorities agreed on several points. First, plants and vegetables can absorb PAHs from soils through their roots and translocate them to other plant parts such as developing shoots. Uptake rates were governed in part, by PAH concentration, PAH water solubility, soil type and PAH physicochemical state (vapor or particulate). LMW PAHs were absorbed by plants more readily than HMW PAHs. Under laboratory conditions, some plants concentrated selected PAHs above that of their immediate geophysical surroundings, but this has not been conclusively demonstrated in field-grown cultivated crops or other vegetation. Second, above-ground parts of vegetables, especially the outer shell or skin, contained more PAHs than underground parts and this was attributed to airborne deposition and subsequent adsorption. Externally deposited PAHs in vegetables were difficult to remove with cold water washings; not more than 25% were removed from lettuce, kale, spinach, leeks and tomatoes using these procedures. Third, PAH-induced phytotoxic effects were rare; however, the database on this subject is small. Fourth, most higher plants can catabolize benzo(a)pyrene and possibly other PAHs, but metabolic pathways have not been clearly defined. Finally, the biomagnification potential of vegetation in terrestrial and aquatic food chains needs to be measured; this work should be conducted with a variety of PAHs in both field and laboratory experiments.

Some plants contain chemicals known to protect against PAH effects (US EPA, updated May, 2008). Certain green plants contain ellagic acid, a substance that can destroy the diol epoxide form of benzo(a)pyrene, inactivating its carcinogenic and mutagenic potential (Edwards 1983). PAHs synthesized by plants may act as plant growth hormones (Edwards 1983). Some vegetables, such as cabbage, brussel sprouts and cauliflower, contain naturally occurring antineoplastic compounds including benzyl isothiocyanate and phenethyl isothiocyanate; these compounds are known to inhibit mammary cancers, stomach tumors and pulmonary edemas induced in rats by benzo(a)pyrene and 7,12-dimethylbenz(a)anthracene (EPA 1980).

The concentrations in plants are substantially lower than in soil and the two are poorly correlated because of deposition and absorption of atmospheric PAHs. Eating of leaves by other animals including humans, does not appear to be a significant route of exposure to soil PAHs. Fruits and vegetables grown in polluted atmospheres may contain up to one hundred times higher levels of total PAHs than those grown in unpolluted environments (EPA 1980; Lee and Grant 1981). PAH concentrations for plants are generally greater on plant surfaces than internal tissues, greater in above ground plant parts than those below ground and greater in plants with broad leaves (greater surface area) than those with narrow leaves (Edwards, 1983).

4.3. Humans

The U.S. Department of Health and Human Services (HHS), International Agency for Research on Cancer (IARC) and the EPA considers several PAHs and PAH derivatives to be probable or possible human carcinogen (Table 9). Structural-activity analysis may suggest that additional PAHs are carcinogenic (Collins, J.F. et al., 1998).

As noted before, PAHs are lipid soluble and can be absorbed through the skin, respiratory tract and gastrointestinal tract in humans. PAH metabolism is complex and occurs primarily in the liver and to a lesser extent, in other tissues. Once absorbed, PAHs enter the lymph (interstitial fluid between the cells), circulate in the blood and are metabolized primarily in the liver and kidney. PAHs differ with respect to distribution patterns and lipophilic properties (Busbee et al. 1990). Because of their lipophilic nature, PAHs can accumulate in breast milk and adipose tissue. However, biliary and urinary excretion of PAHs is relatively efficient because of the wide distribution of enzymes that transform PAHs into polar metabolites. The hydroxylated metabolites of the PAHs are excreted in human urine both as free hydroxylated metabolites and as hydroxylated metabolites conjugated to glucuronic acid and sulfate (CDC, 2005).

Table 8. Toxic equivalency factors (TEFs) proposed by Nisbet, I.C.T et al. (1992)

PAH	**TEF**
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benz[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Benzo[g,h,i]perylene	0.01
Indeno[1,2,3-cd]pyrene	0.1
Dibenz[a,h]anthracene	5[a]

[a] For low-level environmental exposure

Table 9. Carcinogenic classification of PAHs by HHS, IARC and U.S. EPA.

Agency	PAH Compound(s)	Carcinogenic Classification
U.S. Department of Health and Human Services (HHS)	• Benz(a)anthracene • Benzo(b)fluoranthene • Benzo(a)pyrene • Dibenz(a,h)anthracene • Indeno(1,2,3-c,d)pyrene	Known animal carcinogens
International Agency for Research on Cancer (IARC)	• Benz(a)anthracene • Benzo(a)pyrene	Probably carcinogenic to humans
	• Benzo(a)fluoranthene • Benzo(k)fluoranthene • Ideno(1,2,3-c,d)pyrene	Possibly carcinogenic to humans
	• Anthracene • Benzo(g,h,i)perylene • Benzo(e)pyrene • Chrysene • Fluoranthene • Fluorene • Phenanthrene • Pyrene	Not classifiable as to their carcinogenicity to humans
U.S. Environmental Protection Agency (EPA)	• Benz(a)anthracene • Benzo(a)pyrene • Benzo(b)fluoranthene • Benzo(k)fluoranthene • Chrysene • Dibenz(a,h)anthracene • Indeno(1,2,3-c,d)pyrene	Probable human carcinogens
	• Acenaphthylene • Anthracene • Benzo(g,h,i)perylene • Fluoranthene • Fluorene • Phenanthrene • Pyrene	Not classifiable as to human carcinogenicity

Chapter 5

PAH DEGRADATION

5.1. Biodegradation

PAHs do not degrade easily under natural conditions. Persistence increases with increase in the molecular weight. Although PAHs may undergo adsorption, volatilization, photolysis and chemical degradation, microbial degradation is the major degradation process. The PAH-degrading microorganism could be algae, bacteria and fungi. It involves the breakdown of organic compounds through biotransformation into less complex metabolites and through mineralization into inorganic minerals, H_2O, CO_2 (aerobic) or CH_4 (anaerobic). Both bacteria and fungi have been extensively studied for their ability to degrade xenobiotic substances (chemicals found in organisms but which is not produced by them; typically pollutants) including PAHs. The extent and rate of biodegradation depends on many factors including pH, temperature, oxygen, microbial population, degree of acclimation, accessibility of nutrients, chemical structure of the compound, cellular transport properties and chemical partitioning in growth medium. Enzymes involved in the degradation of PAHs are oxygenase, dehydrogenase and lignolytic enzymes. Fungal lignolytic enzymes are lignin peroxidase, laccase and manganese peroxidase. They are extracellular and catalyze radical formations by oxidation to destabilize bonds in a molecule. The biodegradation of PAHs has been observed under both aerobic and anaerobic conditions. The microbial communities in contaminated sediments and soils exist under anaerobic conditions and biotransformation of pollutants is observed under such conditions. The anaerobic biodegradation of PAHs is a slow process and its biochemical mechanism has not yet been elucidated.

PAHs when in prolonged contact of the soil are bound to the soil particles and show reduced bioavailability towards biodegradation. This phenomenon is known as sequestration. Since the particles are inaccessible to the solution phase and are partially immobilized, they pose less risk/threat to the environment and human health and their remediation carries unnecessary economic burden with minimal health and safety benefits. The members of genus Mycobacterium have exceptionally lipophilic surfaces, which makes them suitable organisms for the uptake of bound pollutants from the soil particles and hence widely used in bioremediation of aged contaminated sites. They are also known to have good catabolic efficiency towards PAHs composed of up to five benzene rings. Figure 6 summarizes pathway for microbial catabolism of PAHs (Haritash et al., 2009).

5.2. Photolysis by Ultraviolet Radiation

Photolysis is a major degradation pathway for PAHs in the environment especially in aquatic ecosystems. Due to the chemical structure, PAHs readily absorb sunlight in visible (400–760 nm) and ultraviolet regions (280–400 nm) and are particularly sensitive to the photochemical effects of UV radiation. The phototoxic properties of PAHs are most active between 300 and 400 nm with the toxicity increasing with UV intensity in dose-dependent fashion. The mechanism of PAH phototoxicity are predominantly photodynamic (oxygen-dependant) and is described in previous studies (Arfsten et al., 1996). Growing evidence suggests that the real hazards of PAHs to aquatic life may result from their photo-induced toxicity caused by exposure to UV radiation in sunlight. However, a number of environmental conditions are required for the induction of the phototoxic effects of PAH compounds in animals and plants. The enhancement of UV carcinogenesis by PAH compounds is heavily dependent on the admission of optimal doses of UV radiation at the appropriate time. Continuous exposure to PAH compounds and direct sunlight in higher aquatic organisms may be lethal as the result of complications associated with massive tissue damage. At lower UV intensities and PAH concentrations, it is possible that PAHs may cause sublethal phototoxic damage within biological systems.

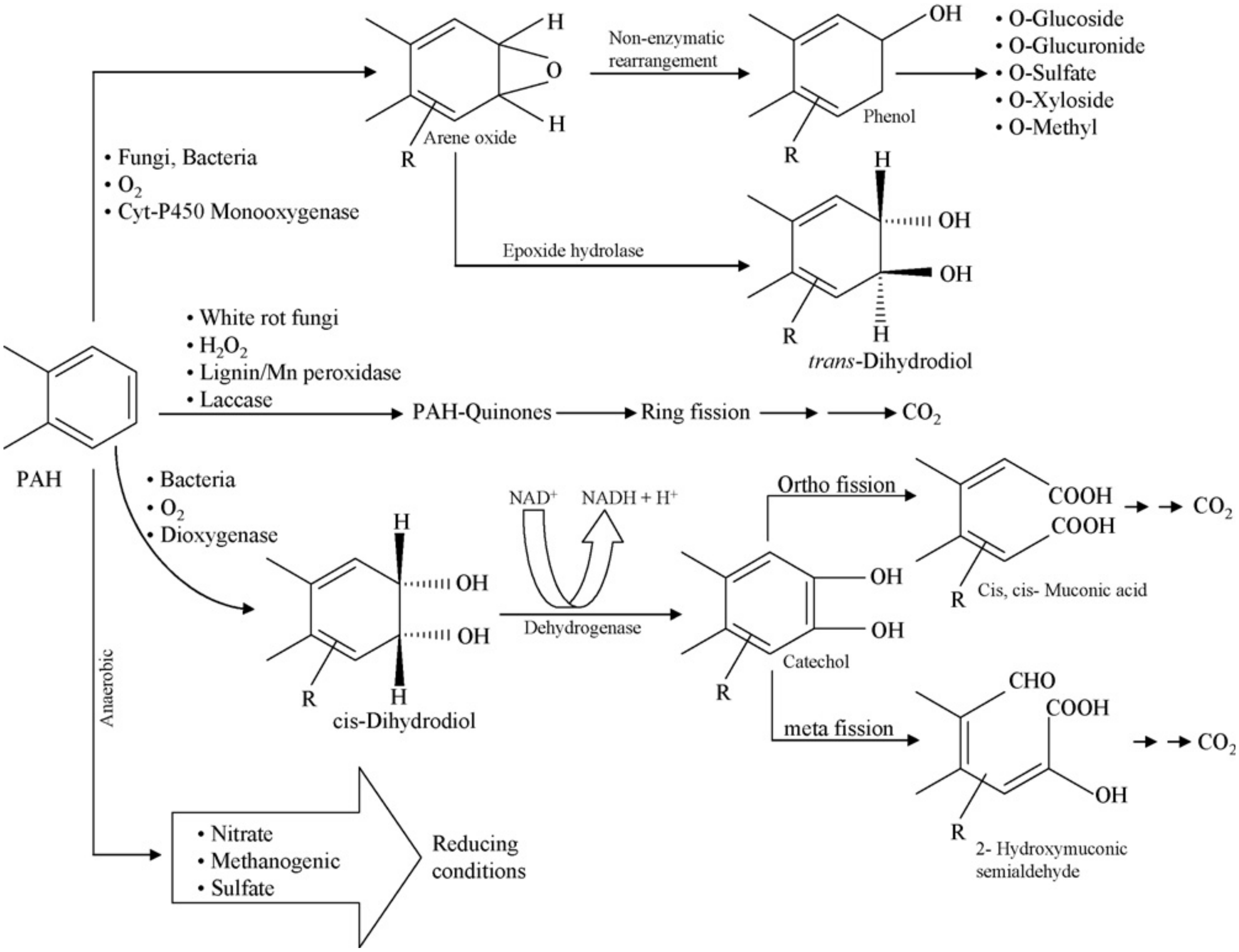

Figure 6. Proposed pathway for microbial catabolism of PAHs

Chapter 6

PAHs IN URBAN STORMWATER RUNOFF AND DISTRIBUTION IN SEDIMENT PARTICLES

During the wet weather period, the surface deposited PAHs (from vehicle exhaust emission, vehicle tires, asphalt pavement, pavement paint markings etc.) are washed off in to the stormsewer system. In general, urban runoff from highways and industrial land uses has been found to have higher PAHs than that from commercial or residential land uses (Eva Hoffman et al., 1984). Studies show single-family residential land uses have lower concentration of PAHs than other land uses (S.-L. Lau et al., 2005) The PAHs are carried off mostly at the early stages of runoff. The initial runoff volume where the pollutants concentration is high is known as the "first flush". In road and highway runoff, suspended solids (SS) are considered as one of the major pollutant since many micropollutants such as PAHs are attached to them. The intensity of rainfall is responsible for the wash load, whereas the sediment grain size transported is controlled by the amount of rainfall.

The concentration of PAHs varies largely among different soil size fractions and depends on the organic carbon content in sediments. PAHs have a high tendency to bind to natural organic matter and studies have shown positive correlation between PAH concentrations and organic carbon contents in sediments. In one of the recent studies (Helian Li et al., 2010), the highest total PAH concentration was found in the 250–500 µm size fraction. The size fractions of 125–500 µm and <50µm had higher percentages of the PAH mass. Among the 16 EPA-listed PAHs studied, Phenanthrene, Fluoranthene, Benzo[a]anthracene, Chrysene, Benzo[b&k]fluoranthene, Benzo[a]pyrene and Indeno[1,2,3-cd]pyrene were the most important contaminants in the soil. The maximal total organic carbon (TOC) content was found in the 125–250 µm size fraction. Black carbon (BC) (carbon formed by incomplete combustion of fossil fuels or biomass) was also present in the soil tested and the maximum concentration of BC was also found in the same 125–250 µm size fraction. Despite relatively low contents in soil, TOC and BC play an important role in the sequestration of PAHs. It was finally concluded in this study that the concentrations of PAH in bulk soil and different size fractions were influenced by BC content more than by TOC content, which means BC could be the dominant adsorbent of PAHs in soil samples.

Chapter 7

COMPARISON OF COAL TAR-BASED SEALANTS WITH ASPHALT-BASED SEALANTS

Coal tar sealants are used primarily as pavement surface sealants. Pavement sealants are surface finishes for parking lots, driveways and airport runways that provide a protective barrier from weather and chemicals. Apart from coal tar-based sealants, asphalt-based sealants are also commonly used and contain far less concentration of PAHs than coal tar sealants. Coal tar sealants contain over 50,000 mg/l and asphalt sealants contain only about 50 mg/l of total PAHs. However, coal tar has a great advantage over asphalt in that it has better chemical resistance than asphalt coatings. Coal tar coatings hold up better under exposures of petroleum oils and inorganic acids. Another outstanding quality of coal tar coatings is their extremely low permeability to moisture and high dielectric resistance, both of which contribute to corrosion resistance. Table 10 compares the major characteristics of both asphalt and coal tar-based sealants.

Since the sealants wear off the surface, recommendations call for reapplication every two or three years and the application rate of total coats could be as high as 0.51gal/yd^2 per application (Item P-631, Pavement Council; Federal Specification R-P-355e; ASTM D 5727, D 490, D 2939). The significance of pavement sealants as a source of PAHs in urban stream sediment is indicated by an estimated application rate of – over 600,000 gallons/year of undiluted sealant in the Austin, Texas metropolitan area and 1,400,000 gallons/year in the NY/NJ watershed region.

In 2005, the City of Austin TX and USGS released their studies on coal tar-based sealants. This study showed that one of the major sources of PAHs found in urban runoff is coal tar-based sealants. The City of Austin, demonstrating the toxicity of PAHs and their effects on aquatic and human health, triggered several municipalities (Austin, TX; Dane County, WI; Washington, DC; Circle Pines, MN; White Bear Lake MN; and Centerville, MN) to ban coal tar sealants. Also, the State of Minnesota has proposed a ban on and the Commonwealth of Massachusetts has restricted the use of coal tar sealants near wetlands. All of these areas banning coal tar sealants have recommended using asphalt-based sealants as an alternative. Table 11 names some of the available asphalt-based sealant alternatives for commercial use.

The findings of USGS and City of Austin have been challenged by several groups and there are websites dedicated to provide countering the conclusions reached in earlier studies. One such website is – www.truthaboutcoaltar.com. Major sources of PAHs in urban runoff have been attributed to automobiles (tire wear, motor oil, roadway wear, car soot and exhaust) and their increase in numbers in recent decades (Van Meter et al., 2000), rather than from coal tar sealants, which is agreeably a negligible contributor of PAHs.

In any case, PAHs in stormwater runoff, especially during the first flush from coal tar sealed surfaces, can be limited by following proper application procedures and best management practices (BMP). Pavement Coatings Technology Council (PCTC) recommends at least 48 hours cure time prior to rain. Adoption of this recommendation might decrease initial runoff load. BMPs that may limit PAHs in stormwater runoffs are discussed in the following section.

Table 10. Major characteristics of both asphalt and refined coal tar-based sealants

Test	**Refined Coal Tar Emulsion Sealer**	**Typical Asphalt Cement Emulsion Sealer**
Binder Component	Refined Coal Tar, mostly aromatic, closed ring compounds (stable)	Asphalt Cement (AC), mostly aliphatic, open chain compounds (unstable)
Origin of the binder	Coal-Decay of vegetation	Petroleum-Marine life decay
Ultraviolet Resistance	Excellent	Fair-Color Fades
Gas Resistance	Excellent-No Effect	Poor-Dissolves
Motor Oil Resistance	Excellent-No Effect	Poor-Dissolves
Kerosene Resistance	Excellent-No Effect	Poor-Dissolves
Oil, Fat, Grease	Excellent-No Effect	Poor-Dissolves
Scrub Resistance - (Durability test)	4000 cycles	2400 cycles
Water re-absorption *	1.00%	3.2%
Odor	Some - Characteristic coal tar	Milder - Asphalt odor
Photosensitive	Yes	No
Skin Irritant **	Yes	Yes
Flexibility	pass	Pass
Drying time	Pass	Pass
OSHA Emission testing ***	Pass	Pass
Environmental	Non-Hazardous, industrial waste in both Dry and Wet state	Non-Hazardous, industrial waste in both Dry and Wet state
Handling Precautions	Similar per MSDS	Similar per MSDS

**The Water re-absorption test is an indicator for durability since water attacks seal coatings causing re-emulsification, which can lead to tracking sealer into your place of business. Low numbers are better.*

***This is what causes burning to some contractors but in no way affects the consumer)*

****Both showed no detectable amounts or less than 2% of the permissible limits by OSHA of carcinogenic compounds including Benzene, CTPV's, PNAH's, or any other compounds of concern.)*

Source: Pavement Coatings Inc. (www.pavecoat.com)

Table 11. Coal tar sealants alternative products

Coal Tar Alternative Products **Commercial/Wholesale**	
Manufacturer	**Product***
Neyra www.neyra.com	• PaveShield (Asphalt-based) • Jennite Asphalt Emulsion (Asphalt-based)
Asphalt System, Inc www.asphaltsystems.biz	• GSB-88 (Gilsonite)
Seal Master www.sealmaster.net	• Master Seal Pavement Sealer (Asphalt-based) • Polymer Modified Master Seal (Asphalt-based)
Professional Coating Technology Inc. www.pctworldwide.com	• COS-50 (Asphalt-based)

*These products contain no coal tar according to the product labels. Sealant product availability is changing rapidly. There may be other sealant products available that do not contain coal tar.

Chapter 8

PAH REMEDIATION

8.1 Best management practices (BMPs)

Stormwater runoff best management practices are in general a collection of methods designed to control stormwater runoff incorporating erosion and sediment control, urban runoff and/or hydrologic/habitat modification. EPA defines stormwater BMPs as a "… technique, measure or structural control that is used for a given set of conditions to manage the quantity and improve the quality of stormwater runoff in the most cost-effective manner."

Cities and towns have come up with best management practices to control and limit PAHs in stormwater runoffs. One such example is the City of Portland, OR. BMPs recommended and listed in §303-(d) evaluations report for the City of Portland to address PAH loading are –

- Implement public information, education, involvement and stewardship activities that will raise awareness, foster community stewardship and promote pollution prevention and stormwater management.
- Operate and maintain components of the municipal separate storm sewer system to remove and prevent pollutant discharges.
- Operate and maintain components of public rights-of-way, including streets, to remove and prevent pollutants in discharges from the municipal separate storm sewer system.
- Operate and maintain other City facilities and infrastructure to remove and prevent pollutants in discharges from the municipal separate storm sewer system.
- Implement the Industrial Stormwater Management Program to control the discharge of pollutants in stormwater discharges from industrial and commercial facilities (both

existing and those undergoing changes in operations) to the municipal separate storm sewer system.

- Provide educational programs and materials and technical assistance to reduce industrial and commercial pollutant discharges to the municipal separate storm sewer system.
- Identify, investigate, control and/or eliminate illicit discharges (illicit connections, illegal dumping and spills) to the municipal separate storm sewer system. Evaluate and, if appropriate, control non-stormwater discharges to the municipal separate storm sewer system.
- Control erosion, sediment and pollutant discharges from active construction sites.
- Implement and refine stormwater management requirements for all new development and redevelopment projects to minimize pollutant discharges and erosive stormwater flows.
- Structurally modify components of the storm drainage system to reduce pollutant discharges. Implement structural improvements on existing development to reduce pollutants in discharges from the municipal separate storm sewer system.

A variety of stormwater control and treatment BMPs can be selected for a site, including structural and non-structural treatment BMPs for mitigation of polycyclic aromatic hydrocarbons in urban runoffs. Typical structural BMPs and non-structural BMPs are listed in Table 12.

Table 12. Structural & nonstructural BMPs

Best Management Practices	
Nonstructural	**Structural**
• Public outreach & education • Source controls • Planning & management of developing areas • Good housekeeping practices • Illicit discharge & detection programs	• Infiltration technologies, including bioretention • Ponds and pond/wetland combinations • Filtering systems • Vegetated swales and filter strips • Water quality inlets • Porous pavements

8.2. Recommendations for Non Structural BMPs

8.2.1 Public outreach & education

Outreach programs can be designed to reduce individual contributions to stormwater problems and improve program implementation by maintenance personnel and government officials. Training programs and educational materials for public officials, contractors and the public are also crucial to implementing effective urban runoff management programs. Contractor certification, inspector training and competent design review staff are important to the success of a stormwater management program. The State of Illinois has developed manuals and training materials to assist in implementation of urban runoff requirements and regulations (US EPA, 1993). Education programs should be implemented in homes, in residential communities and at the workplace. At a minimum, they should educate and encourage the public to participate in and support local pollution prevention programs. Such programs might include storm drain stenciling, used oil and hazardous chemical recycling, litter control, street sweeping, lawn management and landscaping, safe use and disposal of household hazardous materials and chemicals, correct operation of onsite disposal systems, including the danger of industrial wastewater discharges to septic systems, proper disposal of pet excrement and water conservation.

8.2.2. Source Control Measures

Source controls are management techniques that reduce the amount of pollutants and volumes of water entering the stormwater drainage system. Reducing the volume of pollution entering the stormwater system can often be the most effective and least expensive means of control (RDA, 2005) –

Covering - Areas that are potential sources of chronic loading or acute releases of PAH to the environment (such as oils & petrochemicals storage facilities, vehicle maintenance areas, etc.) should be covered with a permanent canopy, roof, or awning. Rainfall should not come in contact with materials and activities in these areas. Areas that are covered should be paved beneath the cover and hydraulically isolated through grading, berms, or drains to prevent uncontaminated stormwater from running onto the area and carrying pollutants away. Drainage from the hydraulically isolated area should be directed to an approved on-site industrial wastewater treatment facility, or other approved on-site temporary storage facility or containment device/structure.

Pavement – Areas used to store fuels should be paved with Portland cement concrete and the pavement should be epoxy coated. Gasoline and other materials can react with asphalt pavement, causing the release of toxic oils from the asphalt pavement. If the area is already paved with asphalt, an asphalt sealant can be applied to the pavement surface (instead of coal tar sealants).

8.2.3 Planning and management of developing areas

This BMP is aimed at reducing urban stormwater runoff and discharge of PAHs from new developments. It is applicable to all types of land use and represents one of the most effective pollution prevention practices. Land use planning and management are critical to watershed management.

Better Site Design – The use of better site design techniques is one of the few watershed management practices that seeks to simultaneously reduce pollutant loads, conserve natural areas, save money and increase property values and at the same time it collectively employs a variety of methods to accomplish three goals at every development site, to: (i) reduce the amount of impervious cover and/or directly connect impervious cover; (ii) increase natural lands set aside for conservation; and, (iii) use pervious areas for more effective stormwater treatment (Schueler T.R., 2000).

Alternative Paving – There are two categories of alternative paving: porous pavement and concrete grid or modular paving (this method of pavement is only applicable in areas where the sub-soils have adequate infiltration rates, which should be determined prior to final design.). Porous pavement is an open-graded aggregate laid on top of a permeable soil layer. Modular pavements are formed using concrete blocks with open spaces that are filled with sand and vegetation. Alternative paving is used to reduce the amount of impervious cover and to maximize infiltration of rainfall at a site. Alternative paving systems also provide passive treatment of stormwater through adsorption and biodegradation of pollutants entering these systems. The use of alternative paving materials is appropriate in low-traffic areas such as employee parking lots and emergency access roads. Modular paving is generally more expensive than porous paving; however porous paving is subject to clogging.

Green Roof – Green roofs, also known as vegetated roof covers, eco-roofs or nature roofs, are multi-beneficial structural components that help to mitigate the effects of urbanization on water quality by filtering, absorbing or detaining rainfall (GreenRoofs; Liptan and Strecker, 2003). In areas of high-density development, where pervious surfaces and open ground often make up 10% or less of total surface area capable of absorbing or diverting stormwater runoff, green roofs are one of the best ways to reduce runoff volumes via evapotranspiration losses. Green roofs utilize the biological, physical and chemical processes found in the plant and soil complex to prevent airborne and rain-entrained pollutants from entering the storm drain system and reduce the runoff volume and peak discharge rate by holding back and slowing down the water that would otherwise flow quickly into the storm drain system.

Low-Impact Development (LID) – LID practices such as bioretention facilities or rain gardens, grass swales and channels, vegetated rooftops, rain barrels, cisterns, vegetated filter strips and permeable pavements perform both runoff volume reduction and pollutant filtering functions (US EPA, 1999).

8.2.4 Housekeeping practices

Street Sweeping – Street sweepers remove debris and particulate from paved surfaces using rotating brushes, water jets and/or vacuums. They are a good method of pollution reduction for urban areas that are hard to retrofit with physical structures or biological areas. Optimal frequencies of street sweeping are usually between weekly and monthly.

Roadway & bridge maintenance – Road and street surfaces undergo breakdown due to frictional action of traffic, freeze-thaw temperatures, frost heaving, ultraviolet degradation and erosion of road subbase. This results in exposure of unstabilized subbase material to erosive forces of water and subsequent increases in suspended solids concentration as well as other constituents such as PAHs. The substantial loadings of sediments and other pollutants generated during daily roadway and bridge use and scheduled repair operations pose a threat to local water quality by contributing heavy metals, hydrocarbons, PAHs, sediment and debris to stormwater runoff (U.S. EPA, 2001).

8.2.5. Illegal dumping control

Illegal dumping controls should focus on the following program areas (U.S. EPA, 1998): (i) cleanup efforts; (ii) community outreach and involvement; (iii) targeted enforcement; and (iv) tracking and evaluation.

Stormdrain Stenciling – Dumping of waste materials into these systems (inlets, catchbasins, channels and creeks) could have severe impacts on receiving water quality. Storm drain stenciling programs that educate residents not to dump materials into storm drains or onto sidewalks, streets, parking lots and gutters is an effective means of reducing nonpoint source pollution associated with such illegal dumping. Storm drain signs and stencils use prohibitive language and/or graphic icons discouraging illegal dumping of improper materials into the urban stormwater runoff conveyance system and are typically placed directly adjacent to storm drain inlets.

Used motor oil recycling – Used motor oil is a hazardous waste as it contains high concentrations of PAHs and heavy metals picked up from the engine during use and should be disposed of at a local recycling or disposal facility. The recycling of used motor oil is a responsible alternative to improper disposal practices such as dumping oil in the sanitary sewer or storm drain system, applying oil to roads for dust control, placing used oil and filters in the trash for landfill disposal, or simply pouring used oil on the ground. Used oil can be recycled in a number of ways (US EPA, 2001).

8.3. Recommendations for Structural or Treatment BMPs

8.3.1. Filtration Control Measures

Filtration controls are either structural or non-structural (landscape based) treatment systems that are normally installed or integrated as a part of a storm drain system. They usually take up less surface area than downstream controls and can be integrated into the site design as landscaped areas. Inline controls are often located underground.

Bioretention filter – Bioretention filters utilize landscaped areas to reduce pollutants in stormwater runoff. In this system, the site is graded so that stormwater runoff is directed over a curtain drain and buffer strip to a vegetated bioretention area. The bioretention area is composed of several layers including woody and herbaceous plants, mulch, soil and a sand bed. As runoff percolates through the system, pollutants are transformed, sequestered, or filtered out by the plant and soil system. Bioretention areas are generally designed in a manner that allows water to pond on the surface for brief periods of time. Bioretention is typically used as a stormwater management BMP in road medians and parking lot islands. .

Typical maintenance for bioretention filters might include mowing grass and removing grass clippings, occasional removal of sediment especially at inlets, revegetation as necessary and the removal of debris that has blown onto the filter.

Vegetated Channels – Vegetated channels refer to ditches, grass channels, vegetated dry and wet swales. These are vegetated channels with a slope that is similar to that of a standard storm drain, but is wider and shallower to minimize velocity and maximize infiltration and adsorption of pollutants. Often vegetated channels are used in road medians like bioretention filters, but unlike bioretention, they emphasize flow along the surface rather than infiltration and subsurface flow. The actual dimensions of the swale, including depth, width and length will depend on site conditions, such a depth to shallow groundwater and volume of water conveyed in the swale system.

Sand filter – Sand filter units are located either in open units or in vaults. In a sand filter, stormwater filters through a sand layer and into an underdrain. They are convenient for urban areas because they can be located underground. However, they can only treat a relatively small area and they can require a high level of maintenance. Sand filters are usually two-chambered stormwater treatment practices; the first chamber is for settling and the second is a filter bed filled with sand or another filtering media. As stormwater flows into the first chamber, large particles settle out and the finer particles and other pollutants are removed as stormwater flows through filtering media. There are several modifications of the basic sand filter design, including the surface sand filter, underground sand filter, perimeter sand filter, organic media filter and the Multi-Chamber Treatment Train (MCTT). All of these filtering practices operate on the same basic principle. Modifications to the traditional surface sand filter were made primarily to fit sand filters into more challenging design sites (e.g., underground and perimeter filters) or to improve pollutant removal (e.g., organic media filter).

Catch Basin Inserts / Filter traps – There are a variety of commercially available catch-basin type filter traps - AquaShield insert (AquaShield Inc.), Enviro-Drain (Enviro-Drian Inc.) Fossil Filter & FloGard+Plus® (Kristar Enterprises, Inc.), HydroCartridge (Geotechnical Marine Corp.), Siltsack, Stream Guard, Ultra Urban Filter (AbTech Industries), DrainPac (PacTec Inc.), UltraDrainguard® Oil and Sediment Model (UltraTech International, Inc.), HydroKleen® (Hydro Compliance Management, Inc.), DrainPac® (United Stormwater, Inc.), etc. These systems are typically designed with baffles and/or cartridge type filters that trap sediment, oil and grease. Catch basin inserts (CBI) are a relatively new type of technology in the area of best management practices (BMP's). This technology involves the placement of devices that contain a filtering media (a sorbent or absorbing material) just under the inlet of a storm drain. Runoff flows into the inlet and through the filter where the targeted contaminants are removed. Many are designed to capture and treat the 'first flush' or rainfall events of one inch or less and are designed to bypass peak storm events in excess of the one-inch event. Since these events are the most frequent events and often generate the highest PAH loads over the course of a rainy season, catch basin inserts can be an effective means of reducing non-point source pollution. Routine cleaning, often after every storm, is critical to maintain the effectiveness of the traps. These units are designed to remove trash, sediment, oil and grease and some systems are designed specifically to remove hydrocarbons from stormwater. Performance of these systems is highly variable and generally dependent on the design of the system and maintenance frequency. Filters are not worth using and should not be used unless they can be inspected and maintained on a very frequent basis.

Centrifugal Units – There are a variety of specially designed systems for stormwater treatment that use vortex or adjustable weirs to route low flows to a water quality treatment unit to remove solids, oil and grease. Higher flows from more intense storms are restricted by low-flow orifices and directed over the adjustable weir, bypassing the water quality facility and preventing the resuspension of sediments. They can also be used in conjunction with other stormwater treatment BMPs to provide higher levels of treatment. Hydroworks Hydroguard and V2B1 Stormwater treatment systems are hydrodynamic separators designed to remove pollutants, including hydrocarbons from stormwater. These technologies have been verified by New Jersey Corporation for Advanced Technologies (NJCAT) to perform well in treating stormwater at both low and high flows. These systems are appropriate to pretreat runoff from areas with high concentration of solids and oil and grease, such as truck tire washing areas, processing plant yards and material storage areas.

Pre-Engineered Stormwater Treatment System – The Stormwater Management's StormFilter is typical of a more advanced inline treatment system that is designed to remove solids, oil, grease and soluble metals. The StormFilter uses filter cartridges housed in concrete vaults creating a self-contained stormwater filtering system that is inline with storm drains. The filter media traps particulate and adsorbs materials such as dissolved metals and hydrocarbons.

Infiltration – Infiltration can be achieved using trenches and basins. They reduce pollution loading by infiltrating stormwater into the ground. Media such as coarse gravel and sand are used to allow for rapid percolation into the soil. The life expectancy of infiltration system can be short if the permeable bed becomes clogged. Infiltration of polluted stormwater into the underlying ground water can also be a concern.

Infiltration drainfields are innovative technologies that are specially designed to promote stormwater infiltration into subsoils. These drainfields help to control runoff and prevent the contamination of local watersheds. The system is usually composed of a pretreatment structure, a manifold system and a drainfield. Runoff is first diverted into a storm sewer system that passes through a pretreatment structure such as an oil and grit separator. The oil and grit chamber effectively removes coarse sediment, oils and grease from the runoff. The stormwater runoff then continues through a manifold system into the infiltration drainfield. The manifold system consists of a perforated pipe which distributes the runoff evenly throughout the infiltration drainfield. The runoff then percolates through an underlying aggregate sand filter and filter fabric into the subsoils.

8.3.2. Detention Type Stormwater Treatment Systems

Detention type stormwater treatment systems are generally located at the outlet of the conveyance system just before stormwater runoff enters receiving waters or exits a site. Detention type controls are typically larger then filtration systems because they usually handle a larger volume of water. They typically have higher construction costs than other types of treatments, but their cost per volume of water treated and pounds of pollution removed can be competitive or less than other treatment schemes.

Dry Ponds.

Dry ponds are conventional extended ponds that are normally dry between storm events. They detain water over the course of days to allow particulates to settle out of the runoff. Pollutant removal efficiency is variable with dry ponds. Heavier pollutants that settle out of runoff can be partially removed; however, negligible removal of soluble pollutants is achieved.

Wet Ponds.

Wet ponds have a permanent pool of water for treating incoming stormwater runoff. Pollutants are removed via settling, plant uptake and bacterial decomposition. The degree of pollutant removal is a function of the pool size in relationship to the drained area. Maintenance is often low and is partially a function of aesthetic value required.

Constructed Wetlands – Wetlands operate in a similar manner to ponds and can provide very effective stormwater treatment. They are generally shallow, allowing vegetation to grow, but they are less tolerant to fluctuations in water depth. They provide more habitat value than ponds; however, they can require a lot of space.

Phytoremediation – Plants are able to degrade PAHs through their metabolic processes and the bacterial activity associated with the roots of grasses and other plants has been explored for its organic degradation potential (enhanced rhizosphere phytodegradation). Phytoremediation is an umbrella term that covers many different plant-based approaches for cleaning up contaminated environments and refers to the use of plants to degrade, sequester and stabilize organic and metal pollutants in stormwater (U.S. EPA, 1998). In simple terms, this means rendering pollutants harmless by using green plants to remove them from the environment. More recently, the bacterial activity associated with the roots of grasses and other plants has been explored for its organic degradation potential. The efficiency of phytoremediation may vary depending on the depth of soil and the type and species of pollutants in water that are most available for plant uptake (U.S. EPA, 2001).

Phytoremediation is a recent technology with immense development potential. The positive effects of plants can be both direct and indirect and include:

- increased microbial degradation in the rhizosphere, including co-metabolism,
- uptake and accumulation in roots and foliage,
- degradation in the plant,
- volatilization of the compounds and
- phyto-enzymes which degrade pollutants (Rasmussen and Olsen, 2004).

Phytoremediation can involve any of the following approaches. Phytoextraction uses the ability of plants to take up and remove contaminants from soil and water and accumulate them in plant tissues, which may then be harvested and removed from the site. The use of plants and (or) their associated microbes to volatilize contaminants (volatile organic compounds, LMW PAHs and recently, inorganics such as mercury, selenium, etc.) from soil or water is known as phytovolatilization. In this process, plants take up water containing organic contaminants and release the contaminants or the breakdown products into the air through their leaves. Although transferring contaminants to the atmosphere may not achieve the goal of complete remediation, phytovolatilization may still be desirable in that it reduces prolonged soil exposure and the associated risk of groundwater contamination; another advantage is that there is no hazardous waste generation that warrants proper disposal measures as may be the case in phytoextraction. Phytodetoxification involves the ability of plants to change the chemical species of the contaminant to a less toxic form. Phytostabilization uses plants to immobilize contaminants chemically and physically at the site, thereby preventing their movement to surrounding areas (Terry, 2001b).

Phytotransformation, also referred to as phytodegradation, is the breakdown of organic contaminants sequestered by plants via (i) metabolic processes within the plant, or (ii) the effect of compounds, such as the enzymes deoxygenase and halogenase, which are produced by the plant. The organic contaminants are degraded into simpler compounds that are integrated with plant tissue, which in turn, foster plant growth. Remediation of a site by phytotransformation is dependent on the direct uptake of contaminants from the media and accumulation in the vegetation. Certain enzymes produced by plants are able to breakdown and convert chlorinated solvents (e.g., trichloroethylene), ammunition wastes and herbicides. This technology can also be used to remove contaminants from petrochemical sites and storage areas, fuel spills, landfill leachates and agricultural chemicals. Successful implementation of this technology requires that the transformed compounds that accumulate within the plant be non toxic or significantly less toxic than the parent compounds. Phytotransformation may also be used in concert with other remediation technologies or as a polishing treatment. For example, a combination of phytoremediation using orchard grass and a soil/sand filter material can efficiently treat creosote-contaminated groundwater (Rasmussen and Olsen, 2004).

The direct uptake of chemicals into plant tissue via the root system is dependent on uptake efficiency, transpiration rate and concentration of the chemical in soil water. Uptake efficiency depends on chemical speciation, physical/chemical properties and plant characteristics, whereas transpiration rate depends on plant type, leaf area, nutrients, soil moisture, temperature, wind conditions and relative humidity. Two processes of remediation can occur after the organic compound has been translocated by the plant: (i) storage of the chemical and its fragments into the plant via lignification and (ii) complete conversion to carbon dioxide and water. These techniques have been successfully employed to treat and remove the following contaminants in the environment: aromatics (BTEX); chlorinated aliphatics (TCE); herbicides (atrazine, alachlor); hydrocarbons (TPH); nutrients (NO_3^-, NH_4^+, PO_4^{3-}) (U.S. EPA, 1998).

8.4. Summary

The above subsections 8.1 and 8.2 discussed various BMPs currently in practice that can be used for PAH control and treatment. It must be noted that the BMPs suggested here for PAHs removal are also useful methods for control and treatment of other contaminants encountered in urban runoff. Table 13 summarizes various structural best management practices that have shown better PAHs removal efficiencies than other options available (not listed). Removal efficiencies for non-structural BMPs are harder to generalize and quantify. In general any BMP structural or non-structural BMP's, performance is site-specific and also varies for different storm events due to several external or internal factors. Intensity of storm flow, load or PAHs and other pollutants, including sediments and other organic matter and condition of the treatment system itself are some of the factors influencing PAHs removal efficiency of a particular treatment system. Maintenance is an important requirement for structural BMPs performance. Typically, structural BMPs may require increased frequency of maintenance during higher flows than low flow storm events for their proper functioning. Bioretention, vegetated swales and infiltration basins are extremely effective and have up to one hundred percent PAHs removal efficiency, assuming none of the stormwater entering the treatment area remains on the surface or leaves the system. However, these BMPs have their limitations in terms of layout and land requirement in urban landscape. Other structural treatment methods discussed here are more expensive and may need a trained crew for their maintenance.

Table 13. Summary of structural stormwater treatment BMPs for PAH removal:

Structural BMPs	Source	Pollutant Removal Efficiency	Advantages & limitations
Bioretention Filters	Diblasi, C. J. et. al., 2009	PAH event mean concentration (EMC) reduction ranged from 31 to 99%.	• PAHs accumulate in surface sediment and media of the bioretention cell near the runoff entry location and PAH concentrations in the bioretention media decrease with depth. Therefore, systems that focus on PAH abatement may only require a shallow cell depth and bioretention PAH mitigation procedures should be focused on the top surface layer near the inlet where sediment accumulation occurs.
Vegetated Channels	Bryan Young C. et. al., 2009	20 to 100% mass retention of pyrene and chrysene; and 9 to 42% mass retention of benzo(a)pyrene. Mass retention was dependant on PAH properties in runoff. The overall result is a significant reduction	• Pollutant retention in vegetated filter strips is affected by physical characteristics of the filter strip, the nature of runoff flow, vegetative cover density, vegetation stalk height, flow channeling and soil factors affecting infiltration. • Median % removal of TSS is 81%

		in pollutant mass to the local watershed when embankments are greater than 30 to 45 ft in length.	• It is efficient in reduction of peak flows and increases runoff infiltration and lower capital costs. • Typically ineffective in and vulnerable to, large storms, because high-velocity flows can erode the vegetated cover.
Sand Filters	US EPA, EPA 832-F-99-007, 1999	Removal efficiency of 70% TSS and 48% TSS	• Sand filters achieve high removal rates for sediment and is frequently used to treat runoff contaminated with oil and grease from drainage areas with heavy vehicle usage. The filter media is periodically removed from the filter unit, thus also permanently removing trapped contaminants. • If they are designed with an impermeable basin liner, sand filters can also reduce the potential for groundwater contamination. • Sand filters also generally require less land than other BMPs, such as ponds or wetlands. • Not enough field data is available for sand filter’s performance in cold weather conditions.

Filter Traps / Catch Basin Inserts	Tennessee BMP Manual Stormwater Treatment; NPDES Stormwater menu of BMPs, Catch basin inserts	Average removal % is in the range of 80-99.4% of PAH in field studies.	• Does not require a supply of water (such as wet detention basins or wetlands). • Can be placed underground as part of the storm drainage system. • Suitable for smaller catchments including parking lots and roadways. • Many types of filters are suitable for larger drainage areas up to 5 or 10 acres. • Sand or cartridge media filters may be particularly suitable for industrial sites because they can be located underground and industrial facilities generally have the resources to routinely inspect and maintain the systems. • There can be marked reduction of hydrocarbon loadings from areas with high traffic/parking volumes. • The underground placement is not generally noticeable and therefore does not make this BMP aesthetically unpleasant. • Their underground placement does require

			the utilization of valuable space in highly urban areas. - This BMP can also be retrofit into most existing catch basins without additional construction.
Centrifuge Units	NJCAT, 2009	V2B1 (Model 4) – 63.8% (avg) removal efficiency at 0.8 cfs Hydroguard (Model 6) – 60.5% (avg) removal efficiency at 1.8 cfs.	- Sediment removal efficiency increases with decrease in flow rate. - Regular maintenance is very important for proper functioning of these systems. - Heavy sediment loads, depending on the current stored material loading in the system, may require a shorter maintenance interval or potentially cause the system to re-suspend captured pollutants. - If the system is not inspected and serviced regularly, then accumulation of organic matter may produce increased levels of phosphates & nitrates in the treated water.
Pre-Engineered Stormwater Treatment System	US EPA 2005	PAH removal efficiency range from 52 to 81%	- CBSF systems are flexible in terms of the flows they can treat. By varying the cartridge bay size and number of filter cartridges, the

– CatchBasin Stormfilter (CBSF)			treatment capacity of a CBSF can be modified to accommodate runoff from a range of watershed sizes. • CBSF systems treatment capabilities, both in terms of flow and sediment capacity, are limited by the number of filter cartridges incorporated into a particular unit. Each filter cartridge is designed with a flow rate of 15 gpm and a dry sediment capacity of 25 lb. • Flows exceeding the filter cartridge's flow capacity bypass the filter cartridges and discharge directly to the outlet. The four-cartridge CBSF has a maximum bypass flow rate of 1 cfs (448 gpm) and the cartridge bays can retain one cubic yard of sediment.
Infiltration Trenches, basins & drainfields	US EPA 1999, Stormwater technology fact sheet infiltration trench; US EPA 1999, Stormwater	90% sediment removal rate with infiltration trenches. 100% pollutant removal rate with infiltration basins and drainfields because none of the stormwater entering the practice remains on	• Ultra-urban areas are densely developed urban areas in which little pervious surface exists and may have limited space for infiltration trench & basins. • Two features that can restrict their use are the potential of infiltrated water to interfere

	technology fact sheet infiltration drainfields; NPDES Menu of BMPs – Infiltration basin	the surface.	with existing infrastructure and the relatively poor infiltration capacity of most urban soils. • The use of infiltration drainfields may be restricted in regions with colder climates, arid regions, regions with high wind erosion rates and areas of sole source aquifers. • High maintenance when sediment loads to the drainfield are heavy. • High costs of engineering design, excavation, fill material and pretreatment systems. • Short life span if not well maintained. • Not suitable for use in regions with clay or silty soils.

Chapter 9

CONCLUSION AND RECOMMENDATIONS

9.1. Review findings

Chemical contaminants like PAHs in urban runoffs are serious threats to human health if left uncontrolled and untreated. There are several sources of PAHs in the urban environment, both natural and anthropogenic. The effects of anthropogenic sources like vehicular emissions, asphalt pavement, roads and parking lots are more pronounced and increasing rapidly in urban areas. This report provides information on physical and chemical characteristics of PAHs for better understanding of their behavior in stormwater runoffs. Effects on various organisms have been discussed including their carcinogenic effects on humans. PAHs are biodegradable and also degraded by ultraviolet radiation. However, their degree of degradation depends on the molecular weights of the PAHs. Typically the LMW PAHs are more degradable than HMWs. PAHs concentrations vary and depend on the sediments and associated organic content in stormwater. PAHs have a tendency to bind to organic matter and their concentration in stormwater runoff has a positive correlation between PAH concentration and organic carbon content in sediments.

Coal tar-based sealants were compared with asphalt-based sealants. Clearly, coal tar sealants have high concentrations of total PAHs (50,000 mg/l) compared to the concentration in asphalt-based sealants (50 mg/l) but coal tar sealants have better durability and physical characteristics. Though coal tar sealants have high total PAHs concentrations, there are contradicting results from studies on whether they are a major source of PAHs in urban runoff when compared to other anthropogenic PAH sources. In general, PAHs concentrations in runoff from coal tar sealed surfaces can be limited by following proper application procedure and best management practices.

Finally, this report has presented information on structural and non-structural BMPs for PAH control and remediation. There were several treatment methods discussed here but selection and effectiveness of any BMP will depend on the existing site conditions including the stormwater quality and volume of flows.

9.2. Future research needs

This report can serve as reference material for future research in addressing PAH issues in urban stormwater runoffs. Future research can be focused on one or all of the below:

- Locate local stormwater runoffs containing high total PAHs concentration and identify their major source(s).
- Study effects of sediments and organic carbon in local stormwater runoffs on PAHs concentration and compare with the published results.
- Provide source control solutions (non-structural BMPs).
- Evaluate the total PAHs removal efficiency of structural stormwater BMPs for PAH removal such as filter traps/catch basin inserts and/or larger pre-engineered stormwater treatment systems such as CBSF.
- Identify native plant species that can degrade PAHs through their metabolic processes so that they may be effectively used in vegetated swales or bioretention basins for phytoremediation
- Evaluate concentration of PAHs in stormwater runoffs from coal tar sealed surfaces (parking lots, driveways etc.) and provide suitable treatment solutions.

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