Enhanced Filtration and Contaminant Degradation Opportunities Offered by Natural Drainage Systems

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1. INTRODUCTION: THE NEED FOR IMPROVED MANAGEMENT AND REMEDIATION OF URBAN RUN-OFF

Polluted run-off represents a challenge for urban water management, reclamation, and reuse. Run-off is dominated by the toxic byproducts of cars and asphalt paving, laced with contaminants washed from industrial and agricultural sites, and often flows in swift surges that overwhelm storm drains and treatment systems. Polluted waters degrade surface and subsurface water quality and, as a result, the composition of urban stormwater is a matter of concern to urban planners, ecological stewards, and public health experts alike.

In Seattle, stormwater in some suburbs is managed by Natural Drainage Systems (NDS), so named for their ability to reduce peak flow surges that overwhelm municipal infrastructure by imitating the hydrologic behavior of an undisturbed watershed[1]. In addition to improved flow control, NDS provide valuable water quality treatment benefits, notably assisting in the removal and degradation of petroleum byproducts present in stormwater.

This paper focuses on the treatment of high molecular weight (HMW) polycyclic aromatic hydrocarbons (PAH)[2], and the potential for bioswales and rain gardens to mitigate contamination in urban settings is discussed. When considering the treatment of HMW PAHs in NDS, a thorough understanding of the behavior of individual PAH compounds, the degradative mechanisms that underpin rhizo-, phyto- and microbial remediation, and risks to public health posed by the long-term accumulation of these compounds in soil it is necessary for effective implementation. Parameters pertaining to the design, use, and long-term maintenance of ecologically based systems are briefly explored, with special attention to the projects underway in Seattle. This paper follows on the work of a previous intern[3], and is designed to serve as a point of reference for planners, public officials, and ecologists interested in exploring what contribution biofiltration and phytoremediation can make to polycyclic aromatic hydrocarbon mitigation of urban run-off.

1.1 PAH Characterization: Sources and Impacts

PAHs are widely distributed in urban and, to a lesser extent, rural environments; generally speaking, high molecular weight species are more persistent in the environment and have greater associated risks as carcinogens and mutagens in humans (ATSDR; Table 1).

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[1] See Appendix B or www.seattle.gov/util/About_SPU/Drainage_&_Sewer_System/index.asp for details.

[2] See Appendix A for a listing of the 17 priority PAHs identified by the EPA and addressed here.

[3] Phytoremediation of Petroleum Hydrocarbons. Amanda Van Epps, August 2006. www.clu-in.org

Table 1:
Carcinogenicity of Selected Hydrocarbon Constituents

Chemical	Classification	Explanation
Benzene	A	Known Human Carcinogen
Benz[a]anthracene	B2	Probable Human Carcinogen
Benzo[b]fluoranthene	B2	Probable Human Carcinogen
Benzo[k]fluoranthene	B2	Probable Human Carcinogen
Benzo[a]pyrene	B2	Probable Human Carcinogen
Chrysene	B2	Probable Human Carcinogen
Dibenz[a,h]anthracene	B2	Probable Human Carcinogen
Indeno[1,2,3-c,d]pyrene	B2	Probable Human Carcinogen
Source: EPA (2006a).		

PAHs are hydrocarbon compounds with two or more benzene rings bonded together. Sixteen species of PAH are routinely identified as contaminants of concern in remediation projects. Larger numbers of rings are generally associated with lessened likelihood of successful biodegradation. The compounds are produced by a wide range of anthropogenic and natural activities; as constituents of crude oil, refined petroleum projects, incomplete combustion of coal, oil, wood and other organic matter, they are widely distributed in the environment (ATSDR 2004).

Common urban sources include wood-burning stoves, traffic emissions, and road byproducts (wearing of tires, asphalt constituents); the emission of traffic-related PAHs is highest for starting and accelerating vehicles, and lowest for vehicles at a constant speed (Joneck and Prinz, 1996; Gobel 2007). Urban sources tend to produce a preponderance of high molecular weight (four rings and higher) PAHs. While atmospheric deposition is the main mode of PAH transport, proximity to roads results in higher concentrations of PAH species and decreases with distance from roads (Dierkes 1999).

PAHs frequently adhere to carbon particles in the soil and dust or the lipophillic surfaces of vegetation, but are also carried into surface water through urban run-off. HMW PAHs have been demonstrated to suppress the germination of plants, but germination alone is not indicative of long-term success as subsequent growth may also be stunted (Smith 2006). Delicate stream and estuarine ecosystems are considered particularly vulnerable to surges of contaminated urban run-off, as they are both a common site for finfish and shellfish spawning and are also prone to erosion and siltification.

The Natural Drainage System employed in Seattle enhances urban run-off management and reuse options with bioswales and rain retention cells. Given the remediation capacities that vegetated systems have demonstrated on hazardous waste sites[4], it is appropriate to assume that

[4] http://www.clu-in.org/techfocus/default.focus/sec/Phytoremediation/cat/Overview

thoughtful choices for urban vegetation may increase the potential for PAH sequestration and degradation and thus limit the impact of PAHs on downstream water users.

1.2 PAH Behavior in the Environment

The persistence of PAHs, in particular HMW PAHs, in the environment has vexed many a diligent site manager. PAHs vary widely in molecular structure, ranging from naphthalene (two rings, C10H8) to coronene (seven rings C24H12), and are surrounded by dense clouds of **π** (Pi) electrons and thus resistant to nucleophilic attack. Certain physical properties also act against their ready microbial utilization or degradation, including their low aqueous solubility and high solid-water distribution ratios; the bioavailability of PAHs is believed to decrease almost logarithmically with increasing molecular mass (Johnson 2005).

Weathering mechanisms include volatilization, leaching into water, and microbial and microrhizal degradation (AEHS 1998b); all forms of natural attenuation favor low molecular weight (two, three ring) PAHs. PAHs with log K_{ow} values above four are not considered to be mobile within the environment, whereas those less than four (generally two and three ring PAHs) readily enter the food chain and can bioconcentrate because of the slowness of their degradation in the biota (Harvey 2002). Also, low molecular weight (LMW) PAHs tend be absorbed directly through plant cuticles, whereas HMW PAHs adhere to the surface; decaying organic matter can thus eventually provide microniches of concentrated exposure for soil microorganisms.

1.3 Overview of Current Biological PAH Remediation Strategies in Soils

Plant uptake through soil or atmospheric absorption has historically not been a successful remediation method, except insofar as root exudates and structures either change the soil composition or act as host for soil bacteria. Further research is needed to characterize the capacity of plants to accumulate HMW PAH compounds; a growing body of (primarily, though not exclusively, lab and greenhouse-based) research suggests that certain conditions may optimize plant uptake potential (Harvey 2002, Huang 2004, Parrish 2006; Appendix C). Given that phytoremediation efficacy varies greatly among plant species, depends on soil and environmental conditions, and is influenced by the physiochemical profile of the entire contamination on the site, the performance of plant-based interventions is far from guaranteed across different sites. Conventional remediation methods often use soil amendments to increase available organic carbon for sorbtion and defacto sequestration, with the assumption that bound particles no longer pose a public health hazard as they are largely inaccessible to soil microbes and humans alike[5].

2. FACTORS INFLUENCING PAH DEGRADATION IN THE ENVIRONMENT

2.1 Microbial Degradation

Several factors that influence the probability and rate of PAH degradation should be closely examined to reveal ways in which vegetation used for storm water management can be

[5] http://www.clu-in.org/download/remed/epa-542-r-07-013.pdf

engineered for optimal contaminant removal. Circumstances that increase the likelihood of successful degradation include the presence of low molecular weight PAH species, relatively recent PAH emission or deposition, moderate soil pH, the presence of appropriate PAH degrading bacteria, and plants to facilitate decomposition by virtue of large root surface area or uptake affinity. Root-microbe interactions are considered the primary process of PAH phytoremediation (Rugh 2005). Natural attenuation in vegetated settings is thought to degrade one, two, and three chain PAHs in periods ranging from16 to 126 days (Parrish 2006).

Byproducts of degradation are thought to be less toxic and may serve as an energy source for other soil organisms. Research suggests that PAHs with fewer benzene rings are more easily digested by soil microbes. Johnson (2005) suggests that "microbial degradation of PAHs and other hydrophobic substrates is believed to be limited by the amounts dissolved in the water phase, with sorbed, crystalline, and non-aqueous phase liquid dissolved PAHs being unavailable to PAH degrading organisms. Bioavailability is a dynamic process, determined by the rate of substrate mass transfer to microbial cells relative to their intrinsic catabolic activity." Put more simply, bioavailability explains the difference between the amount of PAHs that are present in soil or water and the fraction that can be ingested by (and possibly harm) microorganisms, plants, and animals. A substance that passes through the digestive process without changing is not considered bioavailable, and confers neither benefits nor problems to its host.

Degradation of PAHs serves three different functions in the microbial community: assimilative biodegradation, wherein metabolism yields carbon and energy for the degrading organism and is often accompanied by mineralization of the compound parent; intracellular detoxification, whose purpose is to make PAHs water soluble prior to excretion; and co-metabolism, wherein PAHs degrade without generation of energy and carbon for cell metabolism, although the byproducts may eventually provide fuel for another organism (Johnson 2005).

2.2 Mechanisms for Microbial Degradation

Microbial degradation is thought to be the primary mechanism for PAH degradation in soil and is dominated by members of the Sphingomonas, Burkholderia, Pseudomonas, and Mycobacterium taxonomic groups (Johnson 2005). Microbial communities that are capable of digesting specific compounds will proliferate exponentially in response to digestible contamination. However, some higher order PAHs are not accessible to microbes as food due to their absorption inside organic particles or location in small pores that are inaccessible for bacteria. In his 2005 review, Johnson notes that "biofilm formation on PAH-containing sorbents or separate phase PAHs is an efficient way of increasing the PAH flux to cells, noting that biofilm cells on the crystalline surfaces 'etched' craters (attributed to consumption-driven PAH dissolution) that may make the compound more bioavailable." The degree to which these "etches" accelerate degradation is unclear, and the addition of nitrogen and phosphorous-containing soil amendments is the best way to facilitate the growth of biofilms, given supportive pHs (Albert Venosa, personal communication).

Bacteria may also release biosurfactants – small, detergent-like molecules that solubilize the hydrophobic PAH compounds into water phase compounds that are bioavailable. Biosurfactants can act to increase the bioavailability of PAHs, but biosurfactant production is not common among PAH degraders and is not considered essential for obtaining PAHs under environmental conditions. Harvey notes that "surfactants of synthetic or biological origin have been used to enhance the apparent water solubility and bacterial degradation of organic pollutants in soils with high contents of humic substances" (Harvey 2002), but (to this author's knowledge) the surfactants are not a common amendment in most remediation processes. Bacteria that degrade alkane substances commonly produce surfactants, and may contribute to PAH degradation, although lab and field trials have not supported amending contaminated soil with surfactants for this purpose. Each organism produces different surfactants, and manufacturing the appropriate surfactant in large enough quantities to effect PAH degradation presents significant financial and technical challenges[6].

2.3 Microbial and Fungal Amendments

The presence of lower molecular weight PAHs supports microbial communities that may be needed for the metabolization of higher molecular weight PAHs, which puts older, more weathered sites at a disadvantage in the absence of amendments. Researchers have amended weathered sites with limited amounts of fresh pollutants to engender native microbial populations with limited success, while adding microbes drawn from more recently contaminated sites is controversial and has largely not proven effective outside of laboratory trials[7].

The benefits of amending soil with arbuscular and ectomycorrhizal fungi are more clear; the fungi extend the rhizospheric network with soils, increasing the range and efficacy of degradation for PAHs ranging in size from naphthalene to benzo(a)pyrene (Cerniglia 1992, Johnson 2005). Soil can be inoculated directly by mixing PAH-contaminated soil with organic matter containing mycelia of white rot fungi (Lestan and Lamar, 1996), which can possess an "extracellular oxidative enzyme system capable of degrading high molecular weight polymeric compounds and facilitating their ultimate mineralization" (Harvey 2002). Alternately, white rot fungi can be used while composting pollutant accumulating plants, again resulting in harmless byproducts.

A final method of biotransformation of PAHs occurs within the digestive tracts of nematodes and other soil fauna, where oxidation by cytochrome P-450 may produce metabolites that are more bioavailable than the host compound (Harvey 2002). While it is possible that a similar process may exist in the digestive tracts of humans, data on this subject have been limited, and ingestion of PAHs is not considered a major route of exposure or biotransformation. The bioavailability and extractability of PAHs is known to decrease with time, making it difficult to predict exposure routes through sheer soil concentration alone. The EPA recommends the use of toxicity characteristic leaching procedure (TCLP) or technical performance measures (TPM) tests to determine the bioavailability of a substance and the degree of clean-up necessary to protect surrounding organisms.[8]

2.4 The Role of Plants in Facilitating PAH Degradation

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[6] Albert Venosa, personal communication
[7] Ibid
[8] http://www.clu-in.org/products/tpm/

Plants play a structural and biochemical role in facilitating PAH degradation. Roots produce an array of nutritious exudates such as sugars, acids, and oxygen that nourish microbial, bacterial, and fungal communities. Small root hairs increase the surface area for diffusion and change the pH of the surrounding soil, which can affect the availability of contaminants in the direct vicinity of the plant roots. Qui et al (1997) suggested that organic compounds released by plant roots increase the solubility and bioavailability of PAHs, effectively facilitating microbial and bacterial degradation. Optimal plant characteristics for facilitating these soil communities include large below-ground root biomass and small above-ground biomass to increase the surface area available for degradative processes while limiting competition for nutrients that might otherwise support soil microbes and bacteria.

Grasses are a common choice based on these criteria. Plant studies have illustrated that certain types and concentrations of PAHs can prove phytotoxic but, generally speaking, the "plant toxicity of fossil fuel hydrocarbons cannot be predicted and varies widely with type and concentration of hydrocarbons, soil characteristics, and plant species" (Liste 2006). Hass et al (1990) noted that there may be a stimulation of PAH uptake in heavy metal stressed soils. A study published by Henner et al (1999) on plant growth characteristics in fresh and weathered gasworks soils found that water soluble, LMW, volatile hydrocarbons such as benzene, toluene, and xylene tend to be phytotoxic. Once removed through surface weathering or microbial degradation, plants are more likely to grow; researchers concluded that HMW PAHs did not show any phytotoxicty under the conditions studied (Henner 1999).

The author suggests that there is value in staging remedial interventions for petroleum compounds that recognize the succession of attenuation processes and give the living flora and fauna the best opportunity to thrive. This information also has the potential to inform the design of bioswales and stormwater berms, which receive direct deposits of petroleum compounds over long periods of time and have the potential to bioaccumulate particles that strongly sorb to soil. While limited information suggests that plants may uptake PAHs directly, it is generally agreed that under some circumstances they can indirectly promote phytostabilization through humification and thereby decrease the bioavailability of PAHs in soil. Parrish (2005) noted that "the presence of plant roots, in addition to the passage of time, contributes to reduction in the bioavailability of target PAHs." The strong tendency of PAHs to sorb onto soil particles means they are often too big to fit through plant cell walls, and thus plants are generally unable to uptake them. Tolerance to the pollutant

"appears to be correlated with the plant's ability to deposit large quantities of pollutant metabolites in the 'bound' residue fraction of the plant cell walls compared to the vacuole. In this regard, particular attention is paid to the activities of peroxidases, laccases, cytochrome P450, glucosyltransferases and ABC transporters. The penalty of using the cell wall as a reservoir for pollutant deposition lies, however, in the increased extent of lignification and consequently an accelerated rate of plant cell death." (Harvey 2002).

Lignification is also associated with reduced fine root hair growth, effectively limiting the surface area available for exudate production, and microbial and bacterial communities, thus suggesting that some plants have a time-limited capacity to uptake and store PAH compounds. Additionally, Parrish et al. (2006) noted that certain plants, notably C. pepo ssp. Pepo (zucchini), exude low molecular weight organic acids, possibly as a part of a nutrient acquisition strategy. The sequestering soil matrix is disrupted as a result, likely increasing the bioavailability of PAHs and potentially disrupting the phytostabilization strategy that was encouraged as a form of site management. Thus while plants foster the rhizosphere and soil dynamics that contribute to the degradation of PAHs, they have a mixed effect on rendering PAHs bioavailable by virtue of direct uptake, humification, or soil desorption.

2.5 Field Trials with Plants in PAH-Contaminated Soil

Some plants perform better than others in remediation ecologies. A 2006 study found that a combined (as opposed to single species) remediation ecosystem populated by maize, rye grass, and white clover significantly enhanced phenanthrene and pyrene dissipation (Xu 2006). In a second study using rye grass, vegetation was correlated with a broader spectrum of PAHs degraded when compared with non-vegetated (soil microbes only) plots; researchers concluded that enhancement of microbial degradation was the source of the effect (Phillips 2006). A third study using rye grass noted that, along with maize, it is least susceptible to growth suppression due to the presence of LMW, volatile, water-soluble PAHs. The researchers also confirmed results observed in other studies regarding the germination stimulation effects of benzo(a)pyrene and its degradation byproducts, suggesting that at least one HMW PAH may aid the growth of remediation ecosystems.

Plants may cause enhanced mobility and chemical extractability of initially unextractable molecules in the root zone by virtue of changes in soil pH, oxidation, compaction, or nutrient availability, as in a study by Liste, et al, which noted enhanced concentration of four and five ring PAHs around root zone of tall fescue (Liste 2000b). Other plants, such as allium porrum or common leek, have been shown to degrade five and six ring PAHs (Oleszczuk 2007). Finally, in a comparison of PAH uptake levels among zucchini, squash, and cucumber, Parrish noted that the total PAH accumulation in the zucchini was 4.04 and 5.47 times that of cucumber and squash, respectively, and that this increased accumulation was also greatest in the zucchini roots (Parrish 2006). The researchers hastened to add that, over four growth cycles, the total PAH removal by zucchini approximated 0.07 percent of the soil burden and not a viable remedy unto itself. Nonetheless, they speculate that low molecular weight acids produced by zucchini roots effectively chelate bound PAHs as part of a nutrient acquisition strategy, noting that exudate excretion increases under nutrient depleted (low phosphorous) soil conditions. For a partial listing of studies cited in this paper that explore the use of a variety of plants to uptake PAHs in soil, please see Appendix C.

2.6 A Synergistic Field Trial

Given the variable potential for PAH degradation exhibited by previously mentioned interventions, one can assume that some combination of microbial, fungal, bacterial, and plant-based remediation strategies (particularly under optimal conditions) might prove more effective than any one method alone. While field conditions are almost exclusively less than optimal, it is nonetheless worthwhile to examine promising research results in the event that field conditions can be realistically manipulated to become more productive.

Huang (2004) designed a multi-step phytoremediation process that involved volatilization (tilling soil to induce weathering through oxidation), photoxidation (weathering due to sun exposure), microbial remediation (seeding exhumed soil with rhizobacteria that are known to degrade PAHs), and phytoremediation (using tall fescue, a plant with an excellent root system and tolerance for petroleum compounds). Perhaps unsurprisingly, creosote-contaminated soil given this protocol exhibited a 95 percent reduction in total hydrocarbons and 78 percent reduction in 16 priority PAHs consisting of HMW species such as Benzo[a]pyrene, Dibenzo[a,l]pyrene, Benzo(g,h,i)perylene and lndeno(1,2,3-cd)pyrene. The authors reported that the average removal efficiency of sixteen priority PAHs by the multi-step process remediation system was twice that of land farming, 50 percent more than bioremediation alone, and 45 percent more than phytoremediation by itself (Huang 2006). The authors specifically noted the use of plant growth promoting rhizobacteria as crucial in increasing plant tolerance of PAHs and growth under stress, citing increased removal with amended soil. The significance of this lab-based finding for field trials is unclear, given concerns ranging from the contested efficacy of seeding sites with microbes from other areas to the likelihood that site managers and city stewards do not have the funding necessary for maintaining a landscaped intervention in this way. However, the degradation of complex, persistent compounds using a multi-step, carefully staged process that is realized over time is well supported and has implications for the management of contaminated sites. Urban run-off management is bound by the demands of storm surges and limited space, but remediation staging in vegetated cells can be influenced by stewarding the selection of plants, soil and fungal amendments.

3. NATURAL DRAINAGE SYSTEMS: ACHIEVEMENTS AND LIMITATIONS

Natural drainage systems rely in part on the ability of plants to filter and degrade storm water constituents, but plants are often not chosen based on any established capacity for contaminant remediation. The bioengineering industry is still young, and design strategies are pursued with much more straightforward goals: plants must be able to survive the twin assaults of water shortages and deluges, require little to no maintenance, foster native ecology and wildlife if possible, and provide an aesthetically pleasing interlude in the otherwise grey cityscape.

Despite the voluminous characterizations of stormwater – including, but not limited to, the preponderance of HMW PAHs among their lighter brethren in the complex mix of contaminants found in urban run-off – the effects of long-term exposure to these chemicals on bioswale plant growth is not well understood, and the remediation capacity of the plants in those settings is not well characterized. This is particularly true for heavy metals; because they do not degrade, are difficult for plants to uptake, can limit plant growth, and can pose a danger to public health if ingested in ambient dust, their behavior in run-off inundated swales should be characterized.

While the City of Seattle notes in its prospectus materials that the swales can help filter and degrade storm water contaminants, it does not compose its planting strategy with directed phytoremediation in mind[9]. Swales in low and high density areas feature a range of interventions to slow, filter, and clean run-off on its way to local waterways, including the introduction of curves to formerly linear streets and the installation of vegetated, depressed roadside channels and weirs to filter water (Appendix B). Over the six to seven years that its innovative natural

[9] Tracy Tackett, personal communication

drainage system has been in place, the city has not consistently monitored the soil quality to determine if in fact contaminants and sediments are accumulating at a rate that might become phytotoxic and limit swale functionality[10].

While contaminant loading levels seem unlikely to cause a problem anytime soon in suburban areas, installation in dense urban districts or abutting highways may require more vigilance. The existing literature concerning phytoremediation is likely not comprehensive enough to recommend a large number of empirically tested native plants to augment the existing landscaping palette, and so monitoring of the current installation might be the best way to reveal whether plants, microbes, and fungi have been successful in accelerating the degradation of certain species of hydrocarbons. Limited monitoring of water leaving the swale system indicates that organic pollutants, including nitrogen and phosphorous, have been removed prior to outfall into neighboring bodies of water.

As a more general issue, monitoring of bioswale performance needs to be improved to substantiate the remediation dynamics of the stormwater basins and optimize planting strategies. In Seattle, the landscaping responsibilities have been shared by residents and city gardeners, predictably leading to an uneven stewardship and performance of the swales. The occasional case of vandalism, including the intentional disruption of plants or disposal of inappropriate substances, suggests that community education and support remain very important in ensuring the continued health of the swales[11]. The city recognizes that it will need to assume full responsibility for the landscaping maintenance in the future, and will likely attempt to engage a local university or eco-stewardship organization in a plan to monitor the swale sediments and plants as they mature[12]. A mass balance test to determine contaminant loading and subsequent soil sequestration or plant uptake/metabolization, in conjunction with studies that verify improved water quality on the out-flow path, might distinguish the contribution of specific plants from natural attenuation. With continued thoughtful study and maintenance, natural drainage systems can potentially improve the function of urban utilities and health of watersheds in communities across the country.

4. CONSIDERATIONS FOR INTEGRATING PHYTO- AND BIOREMEDIATION INTO STORMWATER MANAGEMENT

While PAHs are only one of many compounds that contaminate urban run-off, they are ubiquitous (particularly in urban environments) and are worrisome insofar as they can alter the germination and growth of human, animal and plant cells. Though frequently not bioavailable due to their strong capacity for sorbtion to carbon, they can become accessible to plants, animals and soil organisms through changes in factors such as soil pH, microbe populations, and biosurfactant production. PAH degradation can be enhanced by some combination of exposure to oxygenation, sunlight, microbes, fungi, bacteria, and plants root surfaces where some combination of transformation and uptake tends to take place. Researchers suggest that a thorough characterization of the site, including native microbial and plant species, is crucial to setting appropriate expectations for designing appropriate landscape ecologies.

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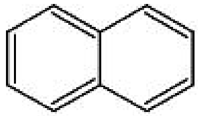
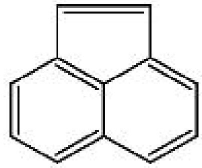
[10] Tracy Tackett and Drena Donofrio, personal communication
[11] Drena Donofrio, personal communication
[12] Tracy Tackett and Drena Donofrio, personal commuincation

Different plant species, through their root exudates, select for different rhizosphere communities; whenever possible, plants should be selected which are “known to host a degrading rhizosphere community or that have shown past phytoremediation potential for survival/tolerance at a specific site” (Kirk 2002). In summary, there appears to be the potential to increase the benefit of natural drainage systems by enhancing their capacity for contaminant filtration and degradation, with specific reference to the increased mitigation of persistent HMW PAHs. More research needs to be done on the long-term durability and remediation capacities of swales to determine appropriate planting practices, contaminant loading, and maintenance. These factors can and should inform urban watershed management decisions, as landscaped interventions have the potential to improve infrastructure, environmental quality, and public health through the mindful use of phyto- and bioremediation.

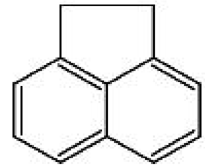
Appendix A: Priority PAH Structures



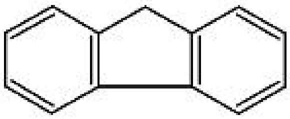
Naphthalene



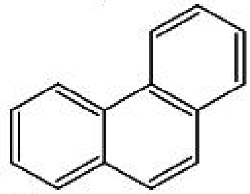
Acenaphthylene



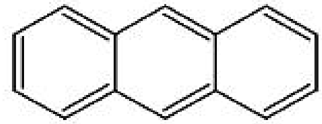
Acenaphthene



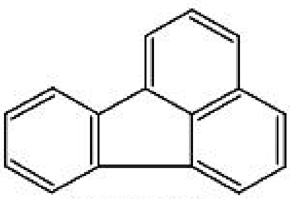
Fluorene



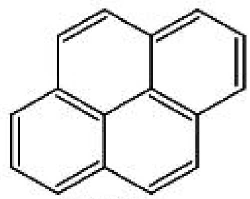
Phenanthrene



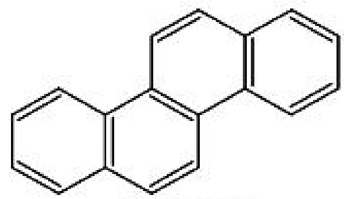
Anthracene



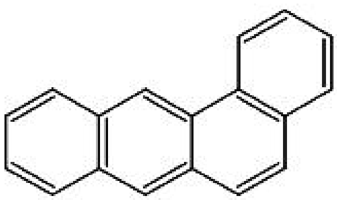
Flouranthene



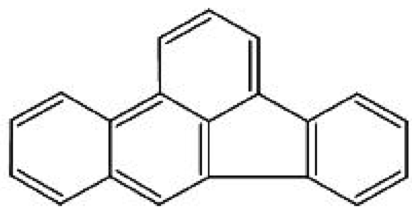
Pyrene



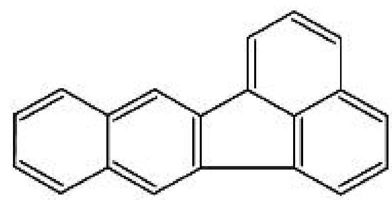
Chrysene



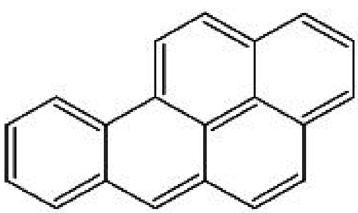
Benzo(a)anthracene



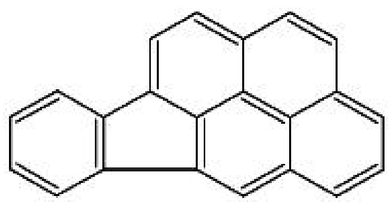
Benzo(b)fluoranthene



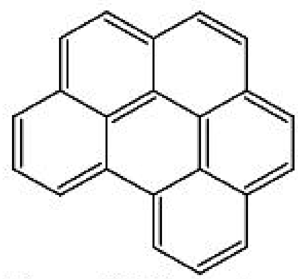
Benzo(k)fluoranthene



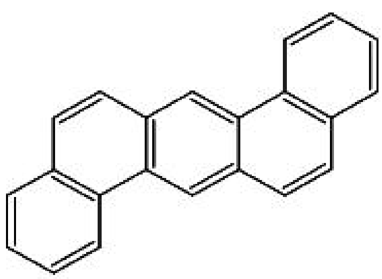
Benzo(a)pyrene



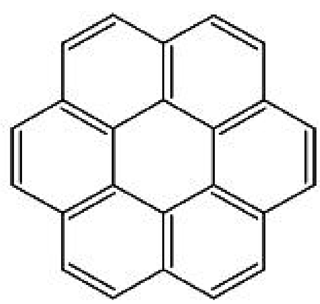
Indeno(1,2,3-cd)pyrene



Benzo(ghi)perylene



Dibenzo(ah)anthracene



Coronene

APPENDIX B:
SEATTLE NATURAL DRAINAGE SYSTEM: A CASE STUDY

The Seattle Public Utilities Department has set a new benchmark for innovation in stormwater management, and in the process has opened doors for potential collaborations between urban planners, biochemists, and landscape architects interested in remediating contaminated urban run-off.

A decade ago, nearly a third of the city functioned without storm drains, and the resulting flux of polluted urban run-off threatened nearby streams and lakes. A series of clever interventions, under the collective title of the Natural Drainage System (NDS), aims to reconfigure the streets and their margins to mimic the contours and functions of an urban watershed. A typical suburban street, previously angular and hemmed on either side by concrete margins or stretches of gravel, now curves sinuously down the block to slow traffic and the passage of water at the margins. Streets have been narrowed to reclaim the sidewalk for vegetation, thereby creating more surface area for groundwater recharge and increasing the pedestrian friendliness of the neighborhood. The swales, which range from depressed channels filled with plants for low flow zones to stepped weirs with flow gates to slow larger storm surges on hillsides, are stocked with low maintenance native plants that beautify the neighborhood environment.

The city had initially asked residents to do minimal maintenance, and this has, perhaps predictably, been a mixed success; in the future, the city intends to assume the entire responsibility for periodic watering and pruning activities, which are estimated to be far less expensive than the installation and maintenance of a conventional storm drain system. This project could not have been realized without the strong support of utilities managers and residents alike, and the resulting system sets a new benchmark for urban design that is protective of ecological resources while remaining, and even improving, the experiences of residents.

One dimension of swale functionality that has been less well explored is the degree to which swales are able not only to filter but also to degrade contaminant-laden storm surges. While the word "phytoremediation" is not used in the literature[13] the swales are said to "capture and degrade contaminants," although no ongoing monitoring is currently being done to assess their performance. Furthermore, less is known about the long-term performance of swales that are saturated with heavy metals and other toxins. While some contaminants will degrade through natural attenuation or bind to soil particles, others may remain bioavailable and gradually impair the growing environment for plants over time. It is entirely possible that the existing plant palette of native species includes plants and microbes that are absorbing or metabolizing contaminants in the soil and water. However, additional monitoring, including plant and soil samples as well as mass balance estimates, is needed to know how well the swales are functioning and what, if anything, can be done to maximize their ability to retain and degrade contaminants in run-off.

As the city adapts the NDS to more densely populated areas, the project is faced with challenges including more established urban infrastructure, higher contaminant loads, and more varied

[13] http://www.seattle.gov/util/About_SPU/Drainage_&_Sewer_System/Natural_Drainage_Systems/Natural_Drainage_Overview/index.asp

demands on the uses of public space. Accordingly, city planners hope to make use of or establish large trees for canopy rainwater interception and evapotranspiration, provide vegetated conveyance and infiltration trenches embedded within sidewalks and traffic medians, and reduce surface flow by direct infiltration through porous pavement on sidewalks and streets.

The Capitol Hill Water Quality Channel, for instance, serves one of the most densely developed commercial and residential neighborhoods of the city and helps clean water that would otherwise have gone straight to Lake Union. To achieve high volume treatment, infiltration into the soil was not part of the design or function of the swales. Instead, water is diverted from an existing storm drain into a pretreatment vault where contaminants settle out, and thereafter flows into one of four city-block length (270 feet) treatment swales that provide additional surfaces for settling. Each separate swale is capable of treating run-off from 50 acres of Capital Hill drainage. This second step takes 10 minutes and, while not as thorough as the neighborhood swales discussed above, manages to meet the Washington State Water Quality treatment standards of 80 percent removal of total suspended solids. Given the hazards to aquatic life and public watersheds posed by contaminated run-off, specialists in remediation technologies have experiences from the bench and field that can contribute to the thoughtful redesign of urban spaces. As these swales age, a better understanding of optimal remediation ecologies and sediment maintenance or replacement is crucial for keeping the swales at peak performance.

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http://www.seattle.gov/util/About_SPU/Drainage_&_Sewer_System/Natural_Drainage_Systems/Natural_Drainage_Overview/index.asp

APPENDIX C:
PLANTS STUDIED FOR PAH PHYTOREMEDIATION POTENTIAL AS REFERENCED IN THIS PAPER

Plant species	Contaminant	Location	Test Period	Effect	Reference (author, year)
Maize	Phenanthrene, Pyrene	Greenhouse	60 days	Removed 92.10% Phen., 85.36%Pyrene	Xu 2005
Ryegrass + Maize	Phenanthrene, Pyrene	Greenhouse	60 days	Removed 98.22% Phen., 95.81% Pyrene	Xu 2005
White Clover	Phenanthrene, Pyrene	Greenhouse	60 days	62.33-88.89% Pyrene removed	Xu 2005
Creeping Red Fescue	TPH	Greenhouse	135 days	TPH reduced by 50%	Phillips 2006
18 MI natives	Phenthrene	Field trial (MI)	"growing season"	PAH reduced by 25-40%	Rugh 2005
Tall Fescue (Festuca arundinacea)	Napthalene	Field Trial (CA)	1-3 years	Napathelene mineralization increased by strong increase in ndoB-positive bacteria	Siciliano 2003
Perennial Ryegrass (L. perenne)	Aged coking works soil	Greenhouse	1 year	Germination + yield unaffected by PAHs; in general, legumes fared worse than grasses in all PAH treatments	Smith 2006
Maize and Ryegrass	Aged coking works soil	Greenhouse	2 months	Relatively resistant to growth inhibition	Smith 2006
Willows (Salix viminalis L. 'Orm')	Mineral oils and PAHs	Field trial (Belgium)	1.5 years	57% mineral oil decrease, 23% PAH decrease; unplanted sediment registered 32% PAH decrease	
Tall Fescue (Festuca arundinacea)	Pyrene	Greenhouse	82 days	Rhizosphere concentration was 4-5 fold greater than surrounding soil	Liste 2000
Wheat	Pyrene	Greenhouse	82 days	Rhizosphere concentration was 4-5 fold greater than surrounding soil	Liste 2000
Perennial Ryegrass	TPH	Greenhouse	10 days	Relatively successful germination + root growth	Kirk 2002
Alfalfa (Medicago sativa L)	TPH	Greenhouse	10 days	Relatively successful germination + root growth	Kirk 2002
Ryegrass (Lolium perenne)	Weathered PAH soil	Greenhouse	18 months	Vegetation correlated with higher number of PAH species degraded between 12-18 months, although no significant difference in biodegradation rates	
Leek (Allium Porrum)	PAH contaminated soil	Greenhouse		Leek rhizosphere contained least amount of 5 and 6 ring PAHs	Oleszczuk 2007
Cucumber (Cucumis sativus)	PAH contaminated soil	Greenhouse		Cucumber rhizosphere contained least mount of 5 ring PAHs	Oleszczuk 2007
Onion (Allium Cepa)	PAH contaminated soil	Greenhouse		Reduced sum of 16 PAH compounds vs control	Oleszczuk 2007
Parsley (Petroselinium sativum)	PAH contaminated soil	Greenhouse		Reduced sum of 16 PAH compounds vs control	Oleszczuk 2007
Zucchini (Cucurbita)	PAH contaminated soil	Greenhouse		Reduced sum of 16 PAH compounds vs control	Oleszczuk 2007
Leek (Allium Porrum)	PAH contaminated soil	Greenhouse		Reduced sum of 16 PAH compounds vs control	Oleszczuk 2007
Reed (Phragmites australis)	PAH contaminated soil		2 years	Degraded PAHs in soil by 74.5%	Muratova 2003
Alfalfa (Medicago sativa L)	PAH contaminated soil		2 years	Degraded PAHs in soil by 68.7%	Muratova 2003
Hemp (Cannibus sativa L)	TPH, TPAH contaminated soil	Greenhouse	68 days	Increased PAH removal by 18-27%	Liste 2006
Mustard (Sinapis alba L)	TPH, TPAH contaminated soil	Greenhouse	68 days	Increased PAH removal by 18-27%	Liste 2006
Lupin	TPH, TPAH contaminated soil	Greenhouse	68 days	PHCs improved seed germination	Liste 2006
Oat, Mustard, Pea	TPH, TPAH contaminated soil	Greenhouse	68 days	PHCs improved shoot biomass production	Liste 2006
Mustard, Oat and Cress	TPH, TPAH contaminated soil	Greenhouse	68 days	High amounts of dioxygenase-expressing bacteria in rhizosphere	Liste 2006
Ryegrass, Corn, Oat and Pea	TPH, TPAH contaminated soil	Greenhouse	68 days	100% survival after germination	Liste 2006
Hemp, Mustard	TPH, TPAH contaminated soil	Greenhouse	68 days	TPAH concentrations dropped 17.6% and 26.9% respectively	Liste 2006
Pea, Cress, Pansy	TPH, TPAH contaminated soil	Greenhouse	68 days	Increased amounts of TPAHs after 68 days	Liste 2006

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Appendix A: PAH diagram taken from http://www.hearnas.sk/pops/pict6.JPG

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