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This Master's Project

Urban Stormwater Management: Treatment of Heavy Metals and Polycyclic Aromatic Hydrocarbons with Bioretention and Permeable Pavement Technologies

by

Viktoriya Sirova

is submitted in partial fulfillment of the requirements for the degree of:

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ABSTRACT

Urban stormwater runoff is a major non-point source of pollutants release into the environment. Pollutants of concern include sediments; heavy metals; polycyclic aromatic hydrocarbons (PAHs); petroleum hydrocarbons; and chlorinated organic compounds, such as pesticides and polychlorinated biphenyls. Conventional stormwater management practices are designed to dispose of the runoff as quickly as possible, not to treat the pollutants. Low Impact Development (LID) concept is an alternative approach to the conventional framework that attempts to recreate hydrologically functional landscape mimicking pre-development regimes. This research paper assesses the effectiveness of two LID technologies, bioretention and permeable pavements in treating PAHs and common urban runoff metals such as lead, copper and zinc. Select case studies are used to synthesize data collected in the field and in the laboratory. Both technologies appear to be effective at treating metals with the exception of copper. Bioretention removal rates for dissolved zinc and lead range from 77-99% and 7-88% respectively. Removal rates for the same constituents by permeable pavements range from 40-97% and 30-80% respectively. Removal rates for dissolved copper by bioretention and permeable pavements range from export of 26% to removal of 70% and export of 40% to removal of 90% respectively. A clear mechanism behind dissolved copper leaching has not been determined. Bioretention is consistently effective at attenuating PAHs with removal rates ranging from 90-95%. No studies were found that evaluated the ability of permeable pavements to attenuate PAHs. Leaching of nitrogen and phosphate has been reported for both technologies, which presents a concern for nutrients overload. Long-term studies of both technologies in semi-arid climates are limited and require further research to demonstrate their effectiveness. Ongoing maintenance is essential for the continued long-term performance of bioretention and permeable pavements in attenuating pollutants. Making a single statement regarding which of the two technologies is better at producing cleaner effluent is not justified, since both are effective with some exceptions. Most likely, the use of both of these control measures in the treatment train set up would produce the most beneficial results.

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LIST OF ACRONYMS

- Basin Plan SF Bay Basin Water Quality Control Plan
- **BMP** Best Management Practice
- Caltrans California Department of Transportation
- EPA United States Environmental Protection Agency
- **LID** Low Impact Development
- MS4 Municipal Separate Storm Sewer Systems
- **NPDES** National Pollution Discharge Elimination System
- PAHs- Polycyclic aromatic hydrocarbons
- **PCBs** Polychlorinated biphenyls
- SFBRWQCB San Francisco Bay Regional Water Quality Control Board
- SWRCB California State Water Resources Control Board
- TMDL Total Maximum Daily Load
- **TSS** Total Suspended Solids

I. INTRODUCTION

The phrase "urban stream syndrome" describes a phenomenon of ecological degradation of streams and other water bodies that drain urban landscapes (Walsh et al., 2005; NRC, 2008). Urban stormwater is believed to be the primary cause of degradation in receiving waters and is responsible for 15% percent of all impaired river miles (38,114 miles), 18% of all impaired lakes (948,420 acres) and 32% of all impaired estuaries (2,742 square miles) in the United States (Erickson et al., 2013; NRC, 2008). In California, urban stormwater is thought to be responsible for impairment of 10% of all rivers, 10% of all lakes/reservoirs and 17% of all estuaries (SWRCB, 2013). Urban stormwater is generally defined as water produced by precipitation events (i.e., rain or snow) and can be measured downstream in streams, ditches, pipes, or gutters after reaching the ground (NRC, 2008). To be regulated, the stormwater has to pass through engineered passageways (NRC, 2008).

Land use modifications associated with urbanization significantly alter local environments creating direct impacts on the quantity and quality of the aquatic ecosystems (Goonetilleke et al., 2005). Increases in impervious surfaces, such as roads and roofs, increases the volume of runoff that would otherwise infiltrate into soils and be lost to the atmosphere through evapotranspiration (Walsh et al., 2012). In a study of twenty-seven watersheds, Klein (1979) found a relationship between the level of watershed urbanization and stream quality. The study concluded that impairment of stream quality can be prevented in watersheds where impervious surfaces do not exceed 15% and 10% in sensitive ecosystems. Severe stream quality impairment was observed in watersheds where imperviousness reached 30%. A similar relationship between stream health and impervious cover is reported by Arnold and Gibbons (1996) as shown in Figure 1. The amount of impervious cover in the greater San Francisco Bay Area is highly variable, ranging from zero to up to 80% as illustrated in Figure 2 (NRDC and PI, 2014). Large urban cities such as San Francisco, Oakland, Richmond, San Jose, and Fremont exhibit the largest impervious cover percentages, from 40 to 80%.



Figure 1: Relationship Between Stream Health and Impervious Cover (Arnold and Gibbons, 1996). This figure demonstrates a relationship between the degree of impervious cover and the health of a stream. No impacts to stream health are observed when the impervious cover is less than ten percent. A stream becomes negatively impacted when the impervious cover reaches between ten and twenty percent. The stream becomes degraded when impervious cover reaches thirty percent.



Figure 2: San Francisco Bay Area Impervious Surface Cover (NRDC and PI, 2014). This figure illustrates a connection between urbanization and the degree of impervious cover. Large urban cities such as San Francisco, San Jose, Oakland, Fremont, Antioch, Concord, San Mateo, and Richmond show the highest level of imperviousness ranging from 40 to 80%.

The impacts of urbanization on aquatic ecosystems include biological, chemical and physical changes (Walsh et al., 2005; Klein, 1979; Walsh et al., 2012; Erickson et al., 2013; NRC, 2008). One of the most consistent and easily observed changes is a modification of the stream hydrograph (Walsh et al., 2005; Goonetilleke et al., 2005). Due to reduced infiltration capacity and the engineered efficient transport of runoff water, urban streams experience more frequent and larger flow events (Walsh et al., 2015; Goonetilleke et al., 2005). Such increased frequency of erosive forces causes channel incision, bank erosion and hydraulic disturbance to instream biota (Walsh et al., 2005; Klein, 1979). Changes to water quality can be just as significant. Urban runoff tends to be high in nutrients such as nitrogen and phosphorous and toxic substances such as metals, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides (Gilbreath and McKee, 2015; Kinsella and Crowe, 2015; Klein, 1979; Walsh et al., 2005). A study of the roadway runoff in the San Francisco Bay Area by the Bay Area Stormwater Management Agencies Association detected toxicity in over 90% of collected samples and attributed their toxicity to metallo-organic complexes and non-polar organic compounds such as pesticides and petroleum hydrocarbons (Woodward-Clyde, 1996).

Managing urban stormwater runoff efficiently and effectively is challenging for a variety of reasons. According to NRC (2008), the difficulty can be attributed to three basic features of the stormwater itself: 1) it accumulates and transports a lot of urban waste; 2) it is produced everywhere; and 3) it is produced and delivered episodically, making attenuation difficult. The conventional approach to stormwater management has been mostly about flood control and has been identified as the primary driver for the observed "urban stream syndrome" (PGC, 1999; Walsh et al., 2012). The goal of the conventional approach is to create an efficient drainage system that prevents flooding (i.e., 10 or 100 year flood), promotes drainage and conveys treated or untreated runoff directly to the receiving water bodies (EPA, 2000; PGC, 1999; Walsh et al., 2012).

The Low Impact Development (LID) approach to urban stormwater management is one alternative to the conventional framework. It is a comprehensive technology-based approach that attempts to create a hydrologically functional landscape that mimics the natural

predevelopment regimes of infiltration, evaporation, transpiration, filtration, and storage by favoring conservation and use of local natural features (PGC, 1999; Hinman, 2012). LID employs small-scale technologies, called Integrated Management Practices (IMPs) to manage and treat water at the site level (PGC, 1999; LID Center, 2015a). Currently identified IMPs include: 1) bioretention facilities; 2) green roofs; 3) permeable pavements; 4) swales; 5) infiltration trenches; 6) rain barrels and cisterns; 7) reduction and disconnection of impervious surface; 8) habitat preservation; and 9) restoration of wetland and riparian areas (LID Center, 2015b; PGC, 1999).

As part of the Clean Water Act, urban stormwater discharges in the United States are regulated as point source discharges under the National Pollution Discharge Elimination System (NPDES) permit framework (NRC, 2008). NPDES regulations for municipalities with separate storm sewer systems became effective in 1990 (NRC, 2008). In California, the State Water Resources Control Board and the nine Regional Water Quality Control Boards implement and oversee the NPDES permit program. In the San Francisco Bay Area, large municipalities (i.e., counties of Alameda, Contra Costa, San Mateo, Santa Clara and the cities of Fairfield, Suisun City and Vallejo) are covered under a single municipal regional permit (SFBRWQCB, 2015a). Smaller municipalities (i.e., counties of Marin, Solano, Napa, and Sonoma) are also covered under one single permit but with different provisions (SFBRWQCB, 2015a). Discharges associated with the California Department of Transportation (Caltrans) facilities are covered by a single statewide NPDES permit (SWRCB, 2015). Requirements to use LID stormwater controls as part of the post-construction runoff management began surfacing in NPDES permits in 2005 (SWRCB, 2012a). LID requirements are permit specific and have been evolving over the last ten years.

The main objective of this research paper is to evaluate the effectiveness of bioretention and permeable pavement technologies at treating PAHs and common heavy metals, such as copper, lead and zinc that are found in typical urban stormwater runoff. The question is whether one technology is better than the other at treating metals and PAHs. Data review of published case studies is used to synthesize existing information for both technologies. Where information does not exist, an alternative approach to closing data gaps is suggested. Technology specific

recommendations are developed based on contaminant specific treatment effectiveness, design considerations and maintenance implications. In support of the main objectives, the paper presents synopsis of the following subjects: 1) conventional stormwater management; 2) LID framework; 3) stormwater regulatory background for San Francisco Bay Estuary; 4) stormwater quality and pollution sources; and 5) stormwater toxicological potential. Where appropriate and feasible, data is compared and/or related to the San Francisco Bay water quality objectives contained in the San Francisco Basin Water Quality Control Plan (hereafter referred to the Basin Plan).

II. CONVENTIONAL STORMWATER MANAGEMENT

Generally referred to as "end of pipe control," conventional stormwater management has been implicated to be a major cause of watershed impairment (Walsh et al., 2012; Roy et al., 2008; LID Center, 2007). Flood control has been the main goal of urban stormwater control for decades (Roy et al., 2008; NRC, 2009; LeFevre et al., 2015). Most cities have a separate sewer infrastructure to contain and transport sanitary waste and stormwater runoff. The City and County of San Francisco is the only coastal city in California with a combined system (SFPUC, 2015). One major downside of a combined system is that waste overflows during large storm events, resulting in direct discharge of untreated sewage and runoff into receiving waters (Roy et al., 2008). Control and management of stormwater via curb and gutter conveyances as well as detention and retention management practices, have dominated runoff management in municipalities with separate sewer infrastructure (NRC, 2009).

The primary objective of conventional control practices is to efficiently move and direct runoff to minimize local flooding by containing and storing water for future release at a predetermined rate (EPA, 2014). Retention/detention practices include detention basins, retention basins and constructed wetlands (EPA, 2014; Fassman, 2012). All of these post construction controls require large amounts of space, making them a rarity within an urban landscape (EPA, 2014). Curbs and gutters have been used as standard elements of road construction, often conveying untreated stormwater directly into local receiving waters (EPA, 2014a). The monitoring of close to 4,000 storm events nationwide revealed that 88% of all sites

sampled did not have any post construction management controls (Maestre and Pitt, 2005). Those with controls had a combination of detention and retention basins. An evaluation of conveyance types in the same dataset revealed that curbs and gutters were used in 65% of all sites (Maestre and Pitt, 2005).

To provide a better understanding of how retention/detention controls are designed and the function they provide, a few are described here. Centralized off-site collection and treatment of stormwater is an attribute they all share. Although use of these management practices does produce some improvement in water quality, they do so at the expense of impaired local hydrological cycle. The conventional stormwater management practices described here include detention/retention basins and constructed wetlands.

Constructed Wetlands

A constructed wetland basin is a shallow retention pond built to provide flood control, flow attenuation, sedimentation, filtration, and biological uptake (Fletcher et al., 2004). Wetland basins employ wetland plant types able to withstand prolonged waterlogging conditions. Pollutant removal is achieved through sediment settling and biological uptake (EPA, 2014b). This management practice is



Figure 3: Typical Constructed Wetland Basin (SuDS, 2015). Constructed wetlands incorporate wetland plants in shallow water pools. Pollutant removal is achieved via settling and biological uptake. These systems differ fundamentally from natural wetlands and exhibit less biodiversity.

considered to be among the most effective in removing pollutants from the runoff while also providing aesthetic and habitat value (EPA, 2014b). When compared to natural wetlands, the

constructed type tends to exhibit less biodiversity (EPA, 2014b). Maintaining constructed stormwater wetlands in a semi-arid environment, like San Francisco Bay could be challenging because of substantial water loss from high evaporation rates relative to incoming water volumes (EPA 2014b). An example of a constructed wetland basin is illustrated in Figure 3.

Detention/Retention Basins

Detention/retention basins include several variations of the same management principle, which is to capture large amounts of runoff for future controlled release. A dry detention basin, sometimes referred to as a sedimentation basin, is an excavated impoundment designed to detain runoff and facilitate sedimentation thereby removing particles and particle-bound contaminants and dissolved metals (CSUS, 2015). These basins are designed primarily for flood control



Figure 4: Typical Dry Detention Basin (SSM, 2009). Dry detention basins collect runoff and slowly release it at a controlled rate. This BMP is effective at flood control but not water quality improvement. Dry detention basins stay dry between storm events.

purposes and tend to stay dry between storm events (SSM, 2009). They are not efficient at removing pollutants, especially those in the dissolved phase, and require large amounts of land (EPA, 2014; LeFevre et al., 2015). A retention basin, also referred to as a wet pond or a retention pond, is similar to a detention basin with one main exception: a retention basin permanently maintains a water level (SSM, 2009). Retention basins tend to be more effective than detention basins at removing pollutants, especially nutrients, via biological uptake (EPA, 2014c). As with constructed wetlands, maintaining permanent water levels can be challenging in semi-arid climates (EPA, 2014c). Figure 4 and Figure 5 illustrate typical examples of detention and retention basins.



Figure 5: Typical Retention Basin (SSM, 2009). Similar to dry detention basins, retention (wet) basins capture runoff for future controlled release. Wet basins are more effective at treating pollutants via biological uptake. These basins permanently maintain water level.

III. LOW IMPACT DEVELOPMENT FRAMEWORK

Because of numerous issues associated with the conventional urban stormwater management approach, a Low Impact Development (LID) concept was first introduced by the Department of Environmental Resources (DER) of Prince George's County, Maryland in the 1980s (LID Center, 2015a). Since then, numerous municipalities across the United States have turned away from the conventional land use development and redevelopment practices. Instead of a centralized downstream stormwater control, LID is a comprehensive technology-based approach that attempts to create a hydrologically functional landscape that mimics the natural predevelopment hydrological regime of infiltration, evaporation and transpiration, filtration, and storage; favoring conservation and use of local natural features (PGC, 1999; Hinman, 2012). The design techniques are based on the principle that stormwater management is not about stormwater disposal (LID Center, 2013). Instead, stormwater is managed at the site level through numerous small-scale controls (PGC, 1999). Over the last several decades, this approach has evolved and has become closely associated with the terms as "smart growth," "ecological landscape" and "green infrastructure." Some of the broad key goals and principles of the LID approach include: 1) protection of receiving waters through technological improvements; 2) development and implementation of landscape features that mimic the hydrologic cycle and protect the environmental integrity of receiving waters; 3) environmentally sensitive site planning and design; 4) economic incentives that encourage sensitive development; 5) public education and participation; 6) reduced construction and maintenance cost; and 7) regulatory flexibility that encourages innovations to promote "smart growth" principles (PGC,1999). Figure 6 provides a visual summary of the LID approach and its components. This model has been further developed, modified and scaled to fit the need by various municipalities throughout the country.

LID site management controls are a major component of the approach and serve as its building blocks. These practices include: bioretention facilities; green roofs; blue roofs; permeable pavements; wet vegetated treatment systems; dry and wet swales; infiltration trenches; rain barrels and cisterns; rain gardens; reduction and disconnection of impervious surfaces; habitat preservation; and restoration of wetland and riparian areas (EPA, 2009; PGC, 1999). They are all designed to mimic the predevelopment hydrologic cycle through strategic control of interception, infiltration, evaporation, water storage, frequency and volume of discharge, groundwater recharge, and water treatment (EPA, 2009; PGC, 1999). Most are small cost-effective technologies located at the source level (LID Center, 2013).

Site specific planning and hydrological analysis is required for the selection of the most appropriate controls (PGC, 1999). Site planning requires incorporation of concepts like site hydrology; micromanagement; source control; use of simple and non-structural techniques; and creation of a multifunctional landscape (PGC, 1999). The goal of the hydrologic analysis is to preserve pre-development regime through consideration of measures such as runoff volume, peak runoff rates, water quality management, and storm frequency and size (PGC, 1999). As the focus of this project is bioretention and permeable pavement technologies, the two are discussed here in more detail. These two technologies were chosen because of their apparent versatility, increasing popularity and direct ability to manage and treat road runoff.



Figure 6: LID Framework (modified from PGC, 1999). This framework aims to achieve the major goals of the LID approach, such as improved environmental protection with innovative technologies, environmentally sensitive site planning and design, increased public education and participation, economic incentives for sensitive development, reduced construction and maintenance costs, and regulatory flexibility that promotes smart growth principles.

IV. REGULATORY FRAMEWORK

The first time the EPA considered regulating stormwater was in 1973 (NRC, 2008). It took almost two decades however for the agency to issue final regulations (generally referred to as the Phase I program), promulgated under the Clean Water Act (NRC, 2008; SFBRWQCB, 2015a). The initial regulations (i.e., 1973 version) exempted most nonindustrial and noncommercial point source discharges, which triggered a successful lawsuit by the Natural Resources Defense Council against the EPA (NRC, 2008). The court ruled that the EPA had no authority to exempt point source discharges, and this led to revised regulations in 1980 (NRC, 2008). The newly revised regulations were challenged again in court by a variety of stakeholders over numerous issues, including the definition of stormwater (NRC, 2008). Eventually, final regulations were published in 1990 that established the stormwater regulatory process as it stands today.

In addition to regulating specific industrial sectors (i.e., recycling facilities, electric plants, construction activities, petroleum refineries, etc.), the new regulations now applied to medium and large municipalities with separate storm sewer systems (NRC, 2008). Municipalities with separate storm sewer systems are generally referred to as MS4 facilities. In order to legally discharge stormwater, each municipality or industry had to obtain a permit to discharge, known as a National Pollution Discharge Elimination System (NPDES) permit. The definition of a medium and a large municipality is based on the size of the population served. To be regulated, medium municipalities have to serve a population of 100,000 to 250,000 people (NRC, 2008). The population size of large municipalities has to be 250,000 or more (NRC, 2008). Broadly speaking, Phase I MS4 permits require the development and implementation of Stormwater Management Plans aiming to reduce discharge of pollutants to the maximum extent practices (BMPs), public education/outreach, illicit discharge detection and elimination, construction and post-construction controls, water quality monitoring, and good housekeeping practices (SWRCB, 2013).

In 1999, the EPA promulgated additional stormwater regulations (generally referred to as the Phase II program), which required small municipalities with separate storm sewers to obtain

permit coverage (NRC, 2008). Small MS4s are defined as those not covered under the medium or large MS4 permits, those located in "urbanized areas" or those designated as such by the permitting authority (NRC, 2008). The dischargers have a choice of using either a "general permit" that covers multiple facilities, or they can apply for an individual permit. In general, NPDES permit requirements for Phase II MS4, are not as elaborate as those for Phase I facilities. For example, water quality monitoring requirements are fairly limited unless required by existing Total Maximum Daily Loads (TMDLs). The permit also does not require development of comprehensive stormwater management plans unless there is a known pollutant hotspot (SWRWCB, 2013).

The EPA delegated its regulatory authority to the State of California to implement and oversee the stormwater NPDES program through the State Water Resources Control Board and the nine Regional Water Quality Control Boards. In the San Francisco Bay Area, the counties of Alameda, Contra Costa, San Mateo, and Santa Clara, and the cities of Fairfield, Suisun City and Vallejo are regulated under a single Municipal Regional Stormwater Permit (SFBRWQCB, 2015a). Smaller municipalities located in the counties of Marin, Napa, Solano and Sonoma, as well as some non-traditional facilities (i.e., universities, prisons, hospitals, military bases, parks, etc.) are regulated under the General Permit for Discharge of Storm Water from Small MS4s (SFBRWQCB, 2015a). Discharges associated with California Department of Transportation (Caltrans) facilities are covered by their own statewide general NPDES permit (SWRCB, 2015). All discharges under these general permits must address post-construction treatment controls as well as published TMDLs.

Requirements for LID stormwater controls as part of the post-construction runoff management appeared in NPDES permits beginning in 2005 when California adopted sustainability as a core value for all of the California Water Board's activities and programs (SWRCB, 2012a). Review of current and past Phase I and II MS4 permits shows that the LID requirements have evolved over time. The LID discussion that follows focuses primarily on SF Bay Area Phase I and II MS4 permits and statewide Caltrans NPDES permit for postconstruction stormwater management. The current Caltrans NPDES permit has minimal LID language written into it. The permit requires post construction stormwater controls for projects that create one acre or more of new impervious cover and for non-highway facilities that create 5,000 square feet or more (the size of a NBA basketball court is 4,700 square feet) of new impervious cover (SWRCB, 2012a). This applies to both new and redevelopment projects. The selection of post-construction BMPs is guided by stormwater treatment in the following order of preference: infiltration, harvest, reuse, evapotranspiration, capture, and treatment (SWRCB, 2012a). Where feasible, LID treatment controls may be used to treat excess runoff (i.e., runoff that was not infiltrated, harvested, re-used, etc.), otherwise conventional treatment devices are allowed (SWRCB, 2012a). The permit does require use of landscape (i.e., use of natural or man-made landscape features) and soil-based BMPs to treat storm water runoff where feasible (SWRCB, 2012a). Discharges to Areas of Special Biological Significance require Caltrans to consider use of LID controls first to determine their feasibility.

The most recent Caltrans Statewide Storm Water Management Plan was reviewed for this paper for any specific LID language but none was found (Caltrans, 2012b). However, Caltrans has recently finished a pilot study evaluating effectiveness of several bioretention cells constructed for the new span of the San Francisco-Oakland Bay Bridge (Caltrans, 2015). The results of this multi-year study are described in Section IX of this paper. To get an idea of any upcoming LID activities in the Bay Area by the Department in the 2016-2017 fiscal year, the Stormwater Management Program District 4 Work Plan was reviewed but no LID specific plans could be found (Caltrans, 2015a).

LID language in NPDES permits for Phase I and II MS4s is much more prescriptive. For example, a Phase II MS4 permit requires implementation of LID technology for regulated projects to reduce runoff, treat storm water, and provide baseline hydromodification management to the extent feasible (SWRCB, 2013). Regulated projects are those that create and/or replace 5,000 square feet or more of impervious cover. Permit includes a special exception for bioretention facilities, where in the case of demonstration of infeasibility, other types of biotreatment or media filters (i.e., tree-box type biofilters or in-vault media filters) may be allowed. This exception is applicable to projects that create or replace one acre or less of impervious area

located in a designated pedestrian-oriented commercial district; facilities that receive runoff solely from existing impervious areas, and historic sites (SWRCB, 2013). Permit does not appear to include any special water quality monitoring requirements to evaluate the effectiveness of the chosen LID controls. LID control measures are also applicable to projects that create and/or replace between 2,500 and 5,000 square feet impervious surface in order to reduce site runoff. These control measures include: 1) stream setbacks and buffers; 2) soil quality improvement and maintenance; 3) tree planting and preservation; 4) disconnection of rooftops and impervious areas; 5) porous pavement; 6) green roofs; 7) vegetated swales; and 8) rain barrels and cisterns (SWRCB, 2013). One or more of these measures is required.

A revised Municipal Regional Stormwater NPDES permit for Phase I MS4 Bay Area facilities was reissued on November 16, 2015 and appears to have the most robust LID requirements. Based on the review of the permit, the numerical sizing criteria for LID controls appears to be tied more to reducing hydrological impacts associated with the development and less with water quality improvement (at least not explicitly). LID elements apply to all regulated projects for source control, site design and onsite stormwater treatment or treatment at a joint stormwater treatment facility (SFBRWQCB, 2015b). This requirement has not changed since the last permit issuance back in 2011 (SFBRWQCB, 2011). The definition of a regulated facility is more complex in comparison to Phase II MS4 facilities. For example, the LID applicability threshold for new commercial, residential and industrial development is 10,000 square feet or more of impervious surface but 5,000 or more for parking areas, restaurants, gasoline stations, and automotive shops (SFBRWQCB, 2015b). The definition is full of nuances and the reader is encouraged to consult the actual permit language for a complete description. Exemptions from LID site controls are just as complex. For example, on site LID treatment can be substituted for a partial offsite LID treatment (SFBRWQCB, 2015b). With the Water Board's approval, LID controls can also be substituted with conventional controls in smart growth, high density or transit-oriented developments (SFBRWQCB, 2015b).

The revised Municipal Regional Stormwater NPDES permit has one major new requirement for the development of a Green Infrastructure Plan, which is to be endorsed by the manager of each municipality (SFBRWQCB, 2015b). Several non-prescriptive elements are

required to be addressed by the plan. These include: 1) prioritization and mapping of planned developments on a drainage-area specific basis; 2) impervious surfaces retrofit projections; 3) a process for tracking and mapping completed projects and making them publically available; 4) general guidelines and standard specifications for the overall streetscape; 5) requirements that regulated projects be designed to meet specific treatment and hydromodification limits (such as TMDLs and Basin Plan water quality objectives for example); 6) mechanisms for ensuring green infrastructure designs in urban planning; and 7) a work plan to complete prioritized projects. The long term goal of this new requirement is to shift from conventional stormwater management (i.e., storm drain infrastructure) to a more sustainable system that employs LID control measures to treat, harvest, and infiltrate urban runoff (SFBRWQCB, 2015b). This is a major shift in approach to management of stormwater runoff in SF Bay Area. A minor new element in comparison, but important here, is a requirement to develop and adopt design specifications for pervious pavement systems. It will be interesting to see if similar green infrastructure requirements will be included in the next Phase II MS4 permit revision due in 2018.

V. STORMWATER QUALITY & POLLUTION SOURCES

Sources of metals and PAHs within the urban environment that contribute to stormwater pollution loadings are numerous. Some sources have been studied extensively and quantified on the basis of load and source. This section focuses on major diffuse sources and does not include discussion of non-anthropogenic (i.e., naturally occurring metals in soil and release of PAHs associated with wild fires), industrial (i.e., emissions from coal burning plants) and construction related activities. Table 1 provides a summary of stormwater quality data from various published literature reviewed for this project. As evident by the data, exceedances of water quality objectives, as set in the San Francisco Bay Basin Plan, for both freshwater and marine receptors exist. Table 1: Summary of Urban Stormwater Data (μ g/L). Data in bold exceeds either marine or freshwater objectives set in the Basin Plan. Water quality objectives for metals are based on the dissolved fraction and total fraction for PAHs. Marine objectives for PAHs are set as a 24-h average. Data was compiled from the studies reviewed for this project.

Fraction	Cu	Pb	Zn	PAHs	Location/Notes	References
Total	33.5	48	187		Runoff from California highways. Data	Kayahanian et al.,
Dissolved	14.9	7.6	68.8	_	reported as mean values.	2007
Total	23	21	-	0.95 - 5.8	Concrete lined channel fed by storm drains (Ballona Creek) in Los Angeles, CA. Mean values reported.	McPherson et al., 2005; Stein et al., 2006.
Total	17.5	17	131		National data for mixed commercial use. Median values reported.	Maestre and Pitt, 2005
Dissolved	10	3.5	73			
Total		-		1.5 - 12.5	Lowe Anacostia river, MD and Washington, DC. Ranges reported.	Hwang and Foster, 2006
Total		-		1.4 - 22.6	Stormwater channel in Hayward, CA. Stormflow ranges reported.	Gilbreath and McKee, 2015
Total	46	3.5	690	2.3	Parking lot in Daly City, CA. Mean values reported for runoff prior to bioretention installation.	David et al., 2015
	3.1	8.1	81	15	Marine Objectives	s (4-day average)
	9	2.5	120	-	Freshwater Objectives	s (4-day average)

Deposition Routes

Atmospheric deposition of metals and PAHs is one of the major stormwater pollution pathways and is primarily associated traffic patterns, overall air emissions, from non-traffic related sources, and local land use practices (Gunawardena et al., 2014; Gunawardena et al., 2013; NRC, 2008). Atmospheric deposition can occur as either wet deposition during rain events or as dry deposition at other times. Condensation and sorption of pollutants to water droplets (i.e., rain) leads to wet deposition and is the primary deposition pathway for gases and aerosols (NRC, 2008). When atmospheric turbulence is not strong enough to counteract gravitational fall of particles from the air, dry deposition occurs (NRC, 2008). Atmospheric deposition source of stormwater pollution in semi-arid regions where long antecedent periods allow for a significant buildup of contaminants on impervious surfaces (Sabin et al., 2006).

Numerous studies have linked atmospheric pollutants with pollutants in urban stormwater. Sabin et al. (2006) have quantified atmospheric deposition of chromium, copper, nickel, lead and zinc to stormwater loadings in a small urban watershed in Los Angeles, California. The authors of the study concluded that: 1) urban areas exhibit higher total deposition rates than non-urban areas; 2) dry deposition (vs. wet) is a dominant pathway in a semi-arid environment; and 3) atmospheric deposition could potentially account for 57% to 100% of total metal loads in stormwater discharges.

Pollutants can also be introduced directly to stormwater as in the case of accidental or intentional spills of hazardous materials. Other direct inputs include runoff from source areas such as roofs, buildings and landscaped areas (Pitt et al., undated). Non-exhaust related automobile emissions come from particles generated from tire wear and brake pads. These particles settle on road surfaces during dry periods and get washed away with the next storm (Pitt et al., undated).

Metals

Metals in the urban environment come primarily from automobiles and structures with metallic constituents (Davis et al., 2001; Pitt et al., undated). Vehicular traffic (both highway and inner city) is thought to be a major source of metals such as zinc, cadmium, chromium, vanadium, copper, and manganese (Li et al., 2009; McKenzie et al., 2009; Kayhanian et al., 2007). Pavement itself can be a source of metals including copper, lead, zinc, and nickel (Apul et al., 2010). Galvanized roofs and drainpipes can be a major source of zinc (Li et al., 2009). Older structures that still have lead based paint on them can be a significant contributor of lead (Davis et al., 2001). Historic uses of lead in gasoline still contribute to stormwater pollution (Gunawardena et al., 2015).

Several studies have examined and characterized stormwater runoff to be related to the average daily traffic, age of pavement overlay, brake and tire wear, road build-up, roofs, and building components (Davis et al., 2001; McKenzie et al., 2009; Chang et al., 2004). Davis et al. (2001) examined and quantified source-specific contribution of common metals to stormwater

loadings. Sources they examined included dry and wet deposition; building siding and roofs; automobile brakes; tires and oil leakage. Stormwater samples from buildings' siding and automobile wheels were collected using synthetic (i.e., laboratory made) rainwater, sprayed over surfaces and collected in aluminum sheets for metals analysis. Loadings from used engine oil were assessed by combining used engine oil with synthetic rainwater at a rate of 5%. This mixture was shaken for 24 hours and chilled afterwards for oil/water separation to occur. After separation, the water phase was analyzed for metals. Loadings associated with roof runoff were determined under real rain conditions. First flush samples were collected in an open area using plastic identical plastic bags. Loadings from tires were assessed by abrading tire surfaces with a steel brush to produce tire powder. This powder was combined with synthetic rainwater (100 mg of tire powder/100 ml of synthetic rain water) and shaken for 24 hours. The mixture was then filtered through a 0.2 μm membrane prior to analysis for metals.

A summary of the estimated metal contribution by source type in urban commercial runoff is illustrated in Figure 7. Roof and buildings' siding appear to be the major sources of the metals studied. Zinc had the highest annual load of 2.16 kg/ha with all sources combined. In addition, building materials themselves were determined to be as a source of metals, as opposed to collecting atmospheric deposition.

Rooftop runoff has long been recognized as a major source of metal contamination in stormwater (Lye, 2009; Davis et al., 2001; Yaziz et al., 1989; Chang et al., 2004). According to Chang et al. (2004), there are at least two reasons why roofs serve as a source of stormwater pollution. First, construction materials themselves can act as a source and may leach into the runoff, especially in the presence of acidic rainwater. Second, roof temperatures are usually much higher than that of other surfaces, which may aid the decomposition and leaching processes. Numerous studies have focused on assessing the quality of rooftop runoff and its reuse implications. The quality of the rooftop runoff depends on roof type, age and maintenance regime, local climate, local air quality, and surrounding environment (Chang et al., 2004).



Figure 7: Estimated Source Specific Metal Contributions (Davis et al., 2001). This figure presents the estimated contribution of metals from various sources in urban commercial stormwater. Total annual metal loadings were estimated to be 0.18 kg/ha for lead, 0.243 kg/ha for copper, 0.0022 kg/ha for cadmium, and 2.16 kg/ha for zinc.

It should be noted that rain water itself can be contaminated with metals even before it reaches a rooftop. Table 2 presents stormwater metal loads from various roof types from several case studies reviewed for this project. As evident by the data presented and as concluded by others, relative to other metals, zinc is found in high concentrations in rooftop runoff due to its prevalence and the fact that it corrodes easily (Davis et al., 2001). Studies have also been conducted to demonstrate that elevated metal concentrations are in fact due to the roofing materials themselves and not to atmospheric deposition (Clark et al., 2008).

Another significant source of metals entering stormwater, especially copper, is automobile brake pads. Abrasion of brake pads results in road deposition of metals such as lead, copper and zinc (Davis et al., 2001; McKenzie et al., 2009). Composition and amount of metals in brake materials vary significantly and is often considered proprietary information by the manufacturers (Thorpe and Harrison, 2008). A few attempts have been made to analyze and estimate releases of metals into the environment from car brakes (Davis et al., 2001; McKenzie et al., 2009; Thorpe and Harrison, 2008). Table 3 summarizes brake pad metal data found in case studies reviewed for this project. Because metals concentration data is reported as a total fraction, comparison to San Francisco Bay water quality objectives is not possible. As evident by the data presented, the concentration of metals in car brake dust and brake linings is wideranging. Therefore, one would expect stormwater metal loadings from this specific source to be wide-ranging as well. In addition, copper and zinc are found in much higher concentrations than lead and cadmium.

Table 2: Metal Loading in Rooftop Runoff (\mu g/L). This table summarizes data from several case studies reviewed for this project. Comparison to San Francisco Bay water quality objectives is not possible as all reported values are expressed as a total fraction and not as a dissolved one. Relative to other metals, zinc dominated the runoff from the rooftops.

Reference	Roof Type	Lead	Copper	Zinc
	Wood Shingle	45/700 (min/max)	29/5,410 (min/max)	16,317/109,000 (min/max)
Chang et al., 2004	Composition Shingle	38/203 (min/max)	25/126 (min/max)	1,372/13,590 (min/max)
	Aluminum	37/134 (min/max)	26/248 (min/max)	3,230/16,600 (min/max)
Chang et al., 2004		49/255 (min/max)	28/224 (min/max)	11,788/212,330 (min/max)
Davis et al., 2001	Galvanized Steel	ND	_	7,600 (max)
Clark et al., 2008			1,400 (max)	14,700 (max)
	Terra Cotta	28 (x)	_	1,080 (x)
Debusk, et al., 2009	Asphalt Shingle	56 (_	2,330 (x)
	Metal With Aluminum Paint	302 (20 (12,200 (

Table 3: Metal Concentration in Brake Lining, Brake Dust, and Simulated Rainwater.

Data presented here was compiled from case studies reviewed for this project. Comparison to San Francisco Bay water quality objectives is not possible as all reported values are expressed as a total fraction. The concentration of metals in car brake dust and brake linings is wide-ranging making it safe to assume that stormwater loadings from this specific source to be wide-ranging. Copper and zinc are found in much higher concentrations than lead and cadmium.

	Mean concentration (µg/L) from brake areas using synthetic rainwater (Davis et al., 2001)	Concentration range (mg/kg) in car brake linings (Thorpe and Harrison, 2008)	Concentration range (mg/kg) in car brake dust (Thorpe and Harrison, 2008)
Copper	280	11 - 234,000	70 - 39,400
Zinc	330	25 - 188,000	120 - 27,300
Lead	11	1.3 - 119,000	4 - 1,290
Cadmium	1.9	<1-41.4	< 0.06 - 2.6

The States of California and Washington both have passed laws in 2010 (CA Senate Bill 346) severely restricting the amount of metals in brake pads. After January 1, 2014, the law bans the sale of brakes in California that contain more than a trace amount of cadmium, lead, chromium, asbestos, and mercury (DTSC, 2010). The amount of copper cannot exceed more than 5% by 2021 and should be almost zero by 2025 (DTSC, 2010). This ban came as a result of the municipalities in South San Francisco Bay not meeting Clean Water Act requirements because of high copper loadings in urban stormwater and ultimately the Bay (Copper Development Association, 2015). It was estimated that copper from brake pads in South San Francisco Bay ranged from 16% to 75% of all copper loads contributed (WCC, 1994). Table 4 illustrates the estimated total annual loads into South San Francisco Bay from brake pads.

Automobile tires are another source of metals found in urban stormwater, especially zinc (Legret and Pagotto, 1999). Abrasion of the tire treads from road friction creates particle emissions which accumulate on the ground surfaces and eventually end up in stormwater. The nature of the emissions depends on tire composition, road conditions, and vehicle operation and maintenance (Thorpe and Harrison, 2008). In addition to organic compounds (such as PAHs), metals such as zinc, copper, cadmium and lead are present in a typical passenger car tire. Similar to automobile brakes, the range of tire types and their composition vary significantly. Table 5

illustrates the range of metals found in tire treads. Releases of zinc appear to be of particular concern since concentration is highest and ranges between 0.4 and 1.5% by weight (Councell et al., 2004). In the mid-1990s for example, zinc from tire wear was identified as one of the major sources (approximately 60%) of total zinc load to South San Francisco Bay (Councell et al., 2004).

Table 4: Estimated Annual Mean Loads of Select Metals into South SF Bay from Brake Pads (modified from WCC, 1994). Concentration of metals in brake pads is wide ranging. Brake pads manufactured by General Motors have the lowest copper concentration and a relatively low zinc concentration. Brake pads were once a major source of copper loads into South San Francisco Bay.

Manufacturer Group	Copper (lbs/yr)	Zinc (lbs/yr)	Lead (lbs/yr)
Ford	290	23	4.3
General Motors	8	168	5.5
Honda	3,549	1,125	4.2
Mercedes-Benz	937	ND	ND
Toyota	435	74	2.8
Nissan	1,179	419	1.4
Volkswagen	1,319	1,311	421

Table 5: Summary of Metal Concentrations in Tire Treads (modified from Thorpe and Harrison, 2008). Concentration of metals in brake pads is wide-ranging. Compared to other metals, zinc is found in much higher concentrations. Tire wear was identified as one of the major sources of zinc in South San Francisco Bay.

Metal	Concentration Range (mg/kg)
Copper	< 1 - 490
Lead	1 – 160
Zinc	430 - 10,250
Cadmium	< 0.05 - 2.6

Polycyclic Aromatic Hydrocarbons (PAHs)

The primary sources of PAHs in urban stormwater are automobile emissions, tire wear and pavement degradation (Kose et al., 2008). By far, incomplete combustion of fossil fuels is the largest source of PAHs in the atmosphere and the road dust, especially on the West Coast of the United States where coal burning is not as prevalent (Gunawardena et al., 2012; NRC, 2008; Stein et al., 2006; Hwang and Foster, 2006). The majority of all PAHs that enter the atmosphere eventually find their way onto ground surfaces and into waterways (Prabhukumar and Pagilla, 2011).

A study by Stein et al. (2006) attempted to identify sources of PAHs in the greater Los Angeles metropolitan area by examining the relative distribution of individual PAHs in stormwater for source signatures indicative of origin (i.e., pyrogenic vs petrogenic). Petrogenic PAHs are those that form at relatively low temperatures (i.e., 100–300°C) and are mostly associated with petroleum spills in the urban environment (Boehm and Saba, 2008). Pyrogenic PAHs form at much higher temperatures (i.e., > 400°C) and are mostly associated with fuel combustion (Boehm and Saba, 2008). Most experts generally agree that the presence of low molecular weight PAHs is indicative of petrogenic sources, while the presence of high molecular weight PAHs points towards pyrogenic sources (Mitsova et al., 2011). Stein et al. (2006) study also looked at ratios of specific PAHs (i.e., Fluoranthene/Pyrene and Phenanthrene/Anthracene) to determine and confirm their origin. High molecular weight PAHs dominated the stormwater runoff in the Los Angeles study, ranging from 61 to 89% (Stein et al., 2006). Similar PAH concentrations were observed across all urban land uses, suggesting a regional source. The ratios of Fluoranthene/Pyrene and Phenanthrene/Anthracene were also indicative of the aerial deposition of combustion by-products.

Coal-tar-based pavement sealcoats are another significant source of PAHs in the urban environment. There are two main types of sealants used in the United States: coal-tar-based and asphalt-based (Watts et al., 2010; Mahler et al., 2012). These sealcoats are used as surface finishes for parking lots, airport runways, and driveways as barriers against weather and chemicals (Prabhukumar and Pagilla, 2011). Coat-tar-based sealants contain up to 50,000 mg/l

of PAHs, whereas asphalt based sealants contain less than 100 mg/l (Prabhukumar and Pagilla, 2011; Watts et al., 2010). A byproduct of coke used in the steel production industry, coal-tarbased sealants are used primarily in the Eastern United States where coke plants are more prevalent (Watts et al., 2010; Mahler et al., 2005).

Coal-tar-based sealcoats are a significant cause of high PAHs in urban lakes, streams, and sediments (Mahler et al., 2012). Because these sealants wear off rapidly over time due to abrasion forces, a reapplication every couple of years is needed to maintain their barrier effect (Prabhukumar and Pagilla, 2011; Mahler et al., 2012). Overall, annual loss of sealcoats from parking lots is about 2.4% per year and 5% from driving areas per year, with higher rates in colder climates (Mahler et al., 2012). Concentration of PAHs in runoff from surfaces sealed with coal- tar-based sealants can be 65 times higher than that of unsealed surfaces (Mahler et al., 2012). Table 6 illustrates concentrations of PAHs in various media from coal-tar-based sealcoats and asphalt sealcoats. Data is compared to San Francisco Bay water quality objectives for PAHs, which reveals exceedances.

Table 6: Concentration of PAHs in Various Mediums (modified from Mahler et al., 2012). Concentration of PAHs is reported as a sum of most common individual compounds. Across all media, concentration of PAHs from coal-tar-based products are much higher than from asphaltbased sealcoats. Values in bold indicate exceedances of San Francisco Bay water quality objectives for PAHs.

Media	Coal-Tar-Based PAH concentration	Asphalt Sealcoats PAH Concentration	Units
Sealcoat Product	66,000	50	mg/kg
Pavement Dust	685 - 4,760	<1-11	mg/kg
Runoff (particle)	3,500	54	mg/kg
Runoff (water)	52 - 71	2-5	μg/L
Soil	105	2	mg/kg
Marine Objectives	(24-hour average)	15	µg/L

Several experimental studies looked at whether coal tar-based sealcoats are a significant source of PAHs in stormwater runoff (Watts et al., 2010; Mahler et al., 2005). Over a period of

two years, Watts et al. (2010) collected stormwater runoff from two parking lots recently sealed with coal-tar-based sealants and one unsealed lot. At the end of the study, a total mass of PAHs (expressed as the sum of 16 most common compounds) exported by stormwater was calculated. The lots sealed with coal-tar-based sealants exported between 9.8 and 10.8 kg of PAHs per hectare (or 0.54 and 1.41 kg per lot). The unsealed lot exported a total of 0.34 kg of PAHs per hectare (or 1.23 per lot). The authors estimated that 15% of the total mass applied prior to the experiment was exported by stormwater. However, visual examination of the lots revealed that only 25-50% of the sealant remained, leading the authors to conclude that other mechanisms exported PAHs, such as wind and physical abrasion. The study also looked at the effect coal-tar-based sealants have on sediments. The authors found that sealant use on 4% of a paved watershed resulted in a 100-fold increase in PAHs in surface sediments near stormwater outfalls.

Coal-tar-based sealants are being used in California but the extent of the use is unknown (CTFA, 2012). The State has been contemplating a complete ban on the use of coal-tar-based sealants over the last several years, but a complete ban is yet to happen (CTFA, 2012; CTFA, 2013). On a positive note, Caltrans claims not use coal-tar-based sealants in the construction and maintenance of their facilities (CTFA, 2011).

Automobile tire wear is an additional source of PAHs in urban stormwater. PAHs are part of the aromatic oil that makes up between six to eight percent of the entire tire mass (Aatmeeyata, 2010). Concentration of PAHs in the oil can range from thirteen to over one hundred mg/kg (Aatmeeyata, 2010). It is suggested that release of PAHs from tire emissions will surpass that of exhaust emissions as engines become cleaner over time (Aatmeeyata, 2010). Average loss of tire rubber is estimated at ninety mg per kilometer, resulting in annual loss of over one million metric tons in the entire United States (Allen et al., 2006). One published study, which developed emission factors for the most common PAHs found in tires, can be used to estimate tire related emissions of PAHs (Aatmeeyata, 2010). Table 7 provides a summary of the calculated emission factors by Aatmeeyata (2010).

Using emission factors for PAHs developed by Aatmeeyata (2010) for tires, annual release of PAHs in San Francisco Bay Area from this source was calculated for this project. In

2007, almost 250,000,000 kilometers were traveled in the greater San Francisco Bay Area (MTC, 2005). Assuming loads from four wheeled small cars only, a total daily release of all four PAHs would be 0.38 kg per day or 140 kg annually. This of course is a conservative estimate since heavy-duty vehicles and large trucks are not included in this calculation.

Table 7: Emission Factors of PAHs in ng/tire/km (Aatmeeyata, 2010). Emission factors are based on the abrasion of tires from rolling friction.

Vehicle Type	Phenanthrene	Fluoranthene	Pyrene	Benzo[ghi]pyrelene
Two wheeled	22	21	105	59
Three wheeled	19	19	93	53
Small car	40	39	191	108

VI. URBAN STORMWATER TOXICITY

The study of the environmental toxicity of metals and PAHs is multifaceted and continuously evolving. In general, the effects of a contaminant on an organism can be seen as either direct or indirect. Direct effect usually happens when a chemical causes an adverse consequence on a physiological level, such as a change in cellular function, interference at nerve synapses (i.e., neurotoxicity), disruption of the endocrine system, suppression of the immune system, direct DNA damage, and macrophage disruption (Thompson et al., 2007). An indirect effect involves a change in food supply and habitat availability due to alteration in prey/competitor dynamics (Thompson et al., 2007).

Toxicological impacts of various anthropogenic contaminants on a range of San Francisco Bay Estuary species was summarized by Thompson et al. (2007). Table 8 provides a summary of select findings from this study. No claim is made here that the observed effects are solely due to urban stormwater runoff. However, it is reasonable to presume that at least some of the adverse impacts are due to urban stormwater runoff since it is considered to be a major source of pollution in San Francisco Bay Estuary (SFBRWQCB, 2015c).

Urban stormwater has been shown to produce acute toxicity and even genotoxicity (Marsalek et al., 1999). With regard to metals and PAHs, there are a few intrinsic differences that make them behave differently in the environment thereby affecting their toxicity, environmental partitioning and mode of action. Metals do not biodegrade and cannot be broken down into less harmful substances, which is generally not the case with PAHs (Luoma and Rainbow, 2008). Low molecular weight PAHs, such as those with 3 benzene rings or less, tend to break down fairly quickly in the environment and are not considered persistent (Connell, 1997). If found in a favorable environment with reduced sunlight and reduced oxygen, high molecular weight PAHs tend to be recalcitrant and are capable of bioaccumulation. Aquatic partitioning and bioaccumulation of PAHs is fairly predictable, which is not the case for metals, where water biogeochemistry, metal speciation and oxidation state are all at play (Luoma and Rainbow, 2008). Knowing or predicting site specific partitioning of both metals and PAHs is essential for developing effective treatment technologies. Metals do not tend to bioaccumulate to the same degree that PAHs do except for some organometals such as methylmercury (USGS, 1999). In addition, most organisms from bacteria to humans require metals for life sustaining purposes (Luoma and Rainbow, 2008). Antimony, arsenic, copper, cobalt, chromium, iron, manganese, molybdenum, nickel, tin, titanium, vanadium, and zinc are considered to be essential metals playing important biochemical roles in metabolic processes like protein functioning (Luoma and Rainbow, 2008). Too much or too little of any specific essential metal can cause adverse effects. In contrast, PAHs have no known essential biological roles in living organisms.

Predicting bioavailability of a specific metal in the aquatic environment is not a simple task since such variables are at play as partitioning between particulate, colloidal, and dissolved phase; dissolved organic matter; redox form; organic and inorganic ligands (Luengen, April 8, 2015). However, there is a general consensus that the dissolved fraction is the bioavailable one (Luoma and Rainbow, 2008; LeFevre et al., 2015). In terms of toxicity mechanisms, one of the major and most well-known is the "isomorphic substitution" where one metal substitutes for another changing a specific biological function within the affected organism (USGS, 1999; Luoma and Rainbow, 2008). The issue is a little more simplified with PAHs, where toxicity tends to increase with rise in molecular weight and octanol-water partition coefficient (Crosby, 1998). PAHs can produce lethal and sub lethal toxic effects at very low concentrations (i.e.,

parts per billion) and they can also be exacerbated by solar radiation (Connell, 1997; Crosby, 1998). Almost all PAHs are thought to be carcinogenic to both humans and aquatic species (Connell, 1997).

Table 8: Toxicity Effects of Select Contaminants in San Francisco Bay (modified from Thompson et al., 2007). This table provides a summary of toxicological effects caused by select pollutants. No claim is made that these effects are solely due to urban stormwater. However, it is reasonable to presume that at least some of the adverse impacts are due to urban stormwater runoff since it is considered to be a major source of pollution in San Francisco Bay Estuary.

Organism Type	Contaminant of Concern	Observed Effect
Benthic Clams (<i>Macoma balthica</i> and <i>Corbula</i> <i>amurensis</i>)	Silver	Decrease in total wastewater loadings from Palo Alto Water Quality Control Plan, lead to an 87% decrease in silver concentration in both sediments and clams located adjacent to the plant. Improvements in reproductive capabilities were observed. A similar observation was found in clams from San Pablo and Suisun Bay (<i>Corbula amurensis</i>).
White croakers (Genyonemus lineatus and Starry flounder (Platichthys stellatus)	PAHs	Livers of both species from SF Bay showed greater incidences of lesions in liver conduits (i.e., biliary epithelial cells) due to elevated concentrations of PAHs in sediments and tissue.
Benthic Clams (<i>Macoma balthica</i>) and Mussel larvae (<i>Mytilus</i> galloprovincialis)	Copper	Decrease in copper loadings from Palo Alto Water Quality Control Plan led to decrease in copper concentrations in surface sediments followed by decrease in clam's tissues. This decrease was associated with improved reproductive capabilities. Elevated copper concentration in Grizzly Bay sediments were showed to be toxic to mussel larvae.
Amphipods	PAHs	PAHs in sediments at two Central Bay sites were associated with seasonal toxicity.
Ridgeway's Rail (<i>Rallus obsoletus</i>)	Methylmercury	Elevated concentrations of methylmercury in various marshes across the Bay are believed to be responsible for reduced egg hatchability of Ridgeway's rails as well as overall poor reproductive success due to embryo hemorrhaging, deformities and embryo malposition.

Scientific studies dating back to the 1970s and 1980s were conducted to assess stormwater runoff toxicity on marine and freshwater species (Pitt et al., 1995). Pinpointing a single contaminant responsible for a toxic effect is challenging since runoff usually contains a complex mixture of chemicals (i.e., metals, pesticides, petroleum hydrocarbons, polychlorinated biphenyls, pharmaceuticals, etc.) that can modify each other's effect (Kinsella and Crowe, 2015; Kayhanian et al., 2008; Selbig et al., 2013). Factors contributing to level and magnitude of toxicity are many and include transport and fate of each contaminant, pollutants loading, antecedent period, storm intensity, storm duration, site-specific physiochemical composition of the stormwater, and ecological state and nature of the receiving water bodies (Greenstein et al., 2004; Pitt et al., 1995). Therefore, attempting to generalize stormwater toxicity would be misleading since many of the factors are intrinsically site specific.

A review of published literature on the subject of stormwater toxicity revealed that the majority of work has focused on metal toxicity. According to Makepeace et al. (1995), arsenic, beryllium, cadmium, copper, lead, nickel, and zinc are the metals of most concern when it comes to stormwater toxicity. Very few studies were found that looked specifically at toxicity of PAHs in urban stormwater. A complete synthesis of findings from the individual studies presented here is not feasible since the design and approach that each study has for assessing toxicity is intrinsically different. This also demonstrates the variation in approach to the study and evaluation of urban stormwater toxicity.

Between 2002 and 2005, Kayhanian et al. (2008) evaluated the toxicity of urbanized highway runoff in west Los Angeles, CA on three freshwater species (the fathead minnow *Pimephales promelas*, the water flea *Ceriodaphnia dubia*, and green algae *Pseudokirchneriella subcapitatum*) and two marine species (the purple sea urchin *Strongylocentrotus purpuratus* and the luminescent bacteria *Photobacrerium phosphoreum*). To assess toxicity of stormwater throughout the hydrograph, samples were collected hourly for the duration of the entire storm. Specific causes of toxicity and concentration of metals in the runoff (i.e., copper, zinc, lead, and nickel) were evaluated. EPA toxicity identification evaluation (TIE) methods were used to identify a pollutant(s) responsible for observed toxicity. Several TIE treatments were applied to stormwater: 1) addition of EDTA for divalent cationic metals; 2) addition of sodium thiosulfate for oxidizable compounds; 3) C18 solid-phase extraction for non-polar organic compounds; 4) C18, ethanol elution for confirmation of non-polar organics; 5) pH adjustment for pH-dependent toxicants; 6) aeration for volatile compounds and surfactants; 7) zeolite extraction for ammonia; and 8) EDTA to post zeolite treatment for ammonia vs. cationic metals. TIE treatments were carried out on the select stormwater samples that were toxic to fathead minnows and water fleas.
Purple sea urchin toxicity was measured as a reduction in ability to fertilize eggs. Toxicity to photoluminescent bacteria was measured as a reduction in light output. Toxicity of stormwater to water fleas was measured as a 7-day rate of survival and reproduction, and to fathead minnows as a 7-day rate of survival and growth. Green algae toxicity was measured as a 96-hour growth inhibition rate.

The results of the study led to several major conclusions. First, toxicity was observed to both freshwater and marine species. Out of the five test methods, the sea urchin fertilization test was the most sensitive. Table 9 illustrates the toxicity incidence of both grab and composite samples. Fathead minnows were more sensitive than water fleas. Green algae and

Table 9: Mean Incidence of Toxicity For 2002-2003 Storm Seasons (modified from Kayhanian et al., 2008). First flush data represents stormwater samples collected in the first 60 minutes of each storm. "N" stands for the number of samples collected in the entire storm season. Generally, first flush samples appear to be more toxic than composite samples. First flush samples were least toxic to green algae and photoluminescent bacteria.

Toxicity Test	First	Flush	Composite Samples		
	Ν	% Toxic	Ν	% Toxic	
Purple sea urchin fertilization	35	74	5	100	
Photoluminescent bacteria	35	20	5	80	
Water flea survival	34	66	2	50	
Water flea reproduction	34	83	2	0	
Fathead minnow survival	34	80	2	50	
Fathead minnow growth	20	48	2	50	
Algal growth	33	49	1	0	

luminescent bacteria showed an inconsistent response and occasional stimulation, most likely due to a high availability of nutrients. Second, a large proportion of the toxic effects were observed during the first flush (i.e., first 60 minutes of the storm) for all species tested. Third, the majority of the composite samples were found to be non-toxic to the freshwater species even with a strong "first flush" effect. Forth, zinc and copper were identified as the dominant toxicants. In addition, a large number of samples with below threshold concentrations of dissolved copper and zinc were still toxic. The researchers attributed this either to other

chemicals being responsible for observed toxicity, or to environmental parameters like pH and low hardness that can enhance toxicity of copper and zinc.

Table 10 provides a summary of dissolved metals concentrations measured in the Kayhanian et al. (2008) study compared to the water quality objectives set in the Basin Plan. A large amount of variability in the dataset appears to be intrinsic to stormwater loadings. Although a direct data comparison might not be fully accurate, it is clear that concentrations of dissolved copper and zinc are above those found in the Basin Plan and the toxicity effects demonstrated by the study are not surprising. The highest measured concentration of dissolved copper was almost 60 times higher than the lowest acute LC50 value for the water flea and 37 times higher than the lowest chronic LC50 value for the fathead minnow (Kayhanian et al., 2008). The highest measured dissolved zinc concentration was 47 times higher than the lowest acute LC50 value for the study acute for the fathead minnow (Kayhanian et al., 2008).

Selbig et al. (2013) attempted to assess the toxicity potential of stormwater transported sediments contaminated with metals and PAHs in the urban environment. The researchers looked at four different sources of stormwater sediments characterized by different particle size (i.e., silt and sand): suspended solids (particles in the stormwater were captured with filter plates), streambed sediments (collected directly from the beds of three urban streams using Teflon cores), street dirt (collected directly from the street with wet/dry vacuum), and storm sewer bedload (collected using plastic sumps). Metals evaluated by this study included aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, silver, strontium, vanadium, and zinc. Of more than one hundred PAHs found in the environment, the authors looked at most common total PAHs and the following individual PAHs: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, 3,6-demethylnaphthalene, fluoranthene, fluorene, indeno(1,2,3-CD)pyrene, 2-methylnaphthalene, naphthalene, phenanthrene, and pyrene. Toxicity was assessed by comparing sampling results with the sediment quality guidelines provided by the US EPA and the Wisconsin Department of Natural Resources.

Table 10: Dissolved Metal Concentrations at Select Sites for 2003-2005 Storms (modified from Kayhanian et al., 2008). Data in bold exceeds either marine or freshwater water quality objectives as set in the Basin Plan. Exceedances of mean values only are shown here. However, in some instances where mean values do not exceed water quality objectives, upper range values do, as in the case of lead at site 7-202. Of note are standard deviation values (shown as SD here). Standard deviation values for all metals are either larger or similar to mean values, indicating high data variability. High data variability is also supported by wide-ranging values. Sites 7-201 and 7-202 are both highly urbanized highway sites in Los Angeles, CA. First flush samples represent 5 grab samples collected in the first 60 minutes of the storm.

Site	Sample	Statistical	Di	ssolved Trace	Metals (µg/I	L)
Site	Size/Sample Туре	Value	Copper	Lead	Nickel	Zinc
		Range	8-161	0.25-1.9	0.99-35	6.8-880
	47/All grabs	Mean	38	0.86	6.8	166
7-201		SD	38	0.4	6.8	189
7-201	20/First	Range	14.3-161	0.25-1.63	4.4-35.3	6.8-880
	Flush	Mean	55	0.99	11	241
		SD	49	0.43	8.3	252
		Range	3.5-560	0.19-13	0.42-100	18-4490
	60/All Grabs	Mean	71	1.3	13	290
7 202		SD	107	1.8	19	617
7-202	25/First	Range	3.5 - 560	0.5-12.5	5.1-100	86-4490
	Flush	Mean	136	2.3	25	563
		SD	141	2.5	25	890
Marine (Objectives (4-da	(\overline{x})	3.1	8.1	8.2	81
Freshwa	ter Objectives ($(4-\operatorname{day} \overline{\mathbf{x}})$	9	2.5	52	120

With respect to metals concentration by particle size, the smaller silt particles had higher concentrations of metals across all four sources. This finding is in line with a general agreement that for the majority of metals, concentrations tend to increase as particle size decreases. There was no statistically significant difference in total PAHs between the sand and the silt bound particles across all four sources. However, the sand fraction tended to have higher concentrations of PAHs, and this goes against findings by other investigators that found patterns

similar to those of metals (Selbig et al., 2013). In general, highest concentration of metals and total PAHs were associated with suspended and storm sewer bedload. All four sources of sediments exhibited toxicity potential; the suspended load had the highest potential. Figure 8 illustrates the percentage of samples exhibiting toxicity for metals and PAHs combined. Copper, chromium, lead, and zinc consistently exceeded the set sediment quality guidelines. Higher molecular weight PAHs (i.e., pyrene, phenanthrene and fluoranthene) were more often detected than the rest. Acenapthene, chrystene, dibenzo(a,h)anthracene, fluoranthene, phenanthrene, and pyrene were responsible for the majority of exceedances over the set sediment quality guidelines.



Figure 8: Metals and PAHs Histogram Meeting or Exceeding Sediment Quality Guidelines (**Selbig et al., 2013**). This histogram represents the percentage of samples exhibiting toxicity for metals and PAHs combined. Stormwater bedload, followed by stormwater suspended load, appears to be the most toxic of all loads examined.

Table 11 compares concentrations of select metals and total high molecular weight PAHs from the Selbig et al. (2013) study to the San Francisco Bay sediment quality objectives adopted in 2008 by the California State Water Resources Control Board (SWRCB) for the enclosed bays and estuaries. High and moderate disturbance categories are based on a Chemical Score Index that uses chemical concentrations to predict the disturbance to the benthic community (SWRCB, 2009). High disturbance means that a community could exhibit a high magnitude of stress

(SWRCB, 2009). Moderate disturbance means that the community exhibits stress related to physical, chemical, natural, or anthropogenic factors (SWRCB, 2009). A comparison of this data suggests that if similar concentrations associated with the stormwater carried suspended sediments were found in the Bay Area, short term toxicological impacts due to metals and PAHs would be highly likely.

Table 11: Comparison of Select Metals and Total PAHs in Sediments. This table compares concentrations of metals and total high molecular weight (HMW) PAHs from the Selbig et al. (2013) study to the San Francisco Bay sediment quality objectives. High disturbance means that a community could exhibit a high magnitude of stress. Moderate disturbance means that the community exhibits stress related to physical, chemical, natural, or anthropogenic factors. This comparison suggests that if similar stormwater suspended sediments were found in the Bay Area, short term toxicological impacts due to metals and PAHs would be highly likely.

Disturbance Type	Total HMW PAHs in Suspended Load (silt + sand) µg/kg	Zinc in Suspended Load (silt + sand) mg/kg	Cooper in Suspended Load (silt + sand) mg/kg	Lead in Suspended Load (silt + sand) mg/kg
	194,558	2,001	388	102
High	>9,320	>629	>406	>154
Moderate	1325 to 9320	200 to 629	96.5 to 406	60.8 to 154

The effect of runoff from coal-tar-sealed pavements on genotoxicity and weakening of DNA repair pathways in rainbow trout liver cells was studied by Keinzler et al. (2015). Liver cells were exposed to unfiltered runoff at environmentally relevant dilution rates of 1% and 10% from pavements sealed with asphalt based and coal-tar sealants. The effects of exposure were evaluated at different intervals following the initial sealant application, ranging from 4 hours to 36 days. The effect of ultraviolet radiation was studied as a co-toxicant. The authors measured a significant genotoxic effect for co-exposure from a coal tar parking lot across all time intervals and dilutions except for 1% dilution at the 36-day mark. Runoff from the asphalt parking lot diluted at 10% produced a genotoxic effect at 26 hour, seven day, and 36-day marks, and at a 7-day mark only for 1% dilution. No significant genotoxicity was observed when ultraviolet radiation was removed as a co-toxicant for both types of parking lot. Impairment to the DNA

repair pathway was observed under all conditions for both lots. The impairment capacity did not diminish with time following the application of both types of sealcoats.

A different assessment approach was taken by Kinsella and Crowe (2015) that looked at the relationship between the distance of stormwater outfalls and the abundance of select taxa, the structure and taxon richness, and the size of limpets (*P. vulgata*) on the rocky shore assemblages in North County Dublin, Ireland. The authors wanted to study the long-term cumulative effect of stormwater discharges compared to the short-term effects of a single rainfall event. Three similar but geographically separate (at least 200 meters apart) sites were included in the study. All were classified as having high ecological status. Sampling took place at five different distances from each outfall at 0 meters, 10 meters, 20 meters, 60 meters, and 100 meters.

The study revealed statistically significant differences in the percent algal cover, size of *P. vulgata*, and the taxon richness between the assemblages located less than 20 meters away from the outfall and those located at 60 to 100 meters. At all three sites, the lowest percent cover for perennial and ephemeral algae was found at 10 meters. Based on other studies with similar results, the authors attributed this finding to potential metal toxicity. At all three sites, there was a significant increase in the size of *P. vulgata* as the distances away from the outfalls increased. In terms of taxa abundance, the study did not reveal any significant species-specific consistent patterns. No differences were observed in the abundance of *Nereis* worms, barnacles (*Chthamalus montaguii*), and *C. filum* algae along the sampling gradient. Certain species however, such as common mussel (*M. edulis*) and sea snails (*Littorina saxatilis*), were more abundant closer to the outfalls, while others, such as Irish moss (*Chondrus cripis*) and marine red alga (*Polysiphonia* sp.), were more abundant between 60 and 100 meters. Even though this particular study did not establish a definitive causal link between the effects of stormwater on the patterns observed, the study did document a relationship between the distance of the outfalls and the assemblage structure.

VII. BIORETENTION TECHNOLOGY OVERVIEW

Bioretention, also referred to as rain gardens, is a widely popular engineered management practice that uses depressions to collect, store, and treat stormwater through a variety of biological, physical, and chemical processes (DPLU, 2007; LeFevre et al., 2015; Liu et al., 2014). Bioretention cells are essentially surface and subsurface water treatment systems (DPLU, 2007). The goal of this technology is to discharge water of a quality and quantity similar to that of pre-development as well as to enhance biodiversity, increase real estate values and facilitate groundwater recharge (Sample and Liu, 2013; PGC, 2007; LeFevre et al., 2015). A typical bioretention cell is composed of a vegetative depression with an engineering soil media, an overflow, an underdrain and a water storage layer (Sample and Liu, 2013; LeFevre et al., 2015; Liu et al., 2014). Figure 9 illustrates a typical design of a bioretention cell.

The basic concept of bioretention is to capture and treat pollutants and sediments prior to discharge (Liu et al., 2014). Once the cell is saturated, the excess water can then be dewatered by either infiltration into the subsoil (also called an infiltration design) or by means of an underdrain (also called a filter design) or a combination of both (PGC, 2007; Liu et al., 2014). The processes that can take place within the cell are: filtration; sedimentation; adsorption; volatilization; ion exchange; decomposition; storage capacity and bioremediation (PGC, 2007; Brown et al., 2009a). Because of its flexibility in design and application, different processes can be maximized and minimized depending on site-specific needs. This stormwater management practice can be used in a variety of settings including new and existing built environments, such as commercial and residential areas, parks, parking lots, and highways (Sample and Liu, 2013). The following list summarizes some of the major processes that can be controlled and managed by a well-designed and maintained bioretention cell:

- 1. Interception capture of runoff or rainwater by plants and soil medium;
- 2. Infiltration downward migration of the runoff into the soil medium;
- 3. Settling ponding of runoff allows for suspended solids to settle down;
- 4. Evaporation shallow ponding areas allow for sunlight to transform water into vapor;
- 5. Filtration mulch and soil filter particles as water moves downwards;
- 6. Absorption mulch, soil, and plants allow for water to be absorbed;

- 7. Nutrient assimilation runoff laden with nutrients is used by biota to sustain itself;
- 8. Adsorption organic rich soils attract and immobilize contaminants; and
- Degradation/Decomposition breakdown of chemical compounds by soil fauna (PGC, 2007; Brown et al., 2009a; Sample and Liu, 2013).



Figure 9: Typical Bioretention Cell (Brown et al., 2009a). Bioretention cells function as soil and plant-based filtration systems that use physical, chemical and biological treatment processes to remove pollutants from the runoff. General system components (from top to bottom) include vegetation, shallow ponding area, engineered soil media, and underdrain. System design is flexible and can be modified to meet specific management needs.

Various types of bioretention cells have been developed to suit site-specific performance needs such as infiltration or filtration. An Infiltration/Recharge type is used where groundwater recharge is desirable and is recommended for areas where nutrient rich runoff is expected (PGC, 2007). Such design does not employ an underdrain but utilizes an in situ high porosity soil media to facilitate infiltration (PGC, 2007). Depth of the soil media should be deep enough to allow sufficient filtration (PGC, 2007). A Filtration/Partial recharge type is recommended for runoff rich in nutrients and other pollutants such as metals (PGC, 2007) An underdrain and lack of impervious liner in this type of a cell provides for a partial recharge and a controlled rate of draining (PGC, 2007). Carefully selected soil media type and/or a filter fabric allow for desired

filtration rates (PGC, 2007). An Infiltration/Filtration/Recharge type cell utilizes a fluctuating aerobic/anaerobic zone below a raised underdrain discharge pipe, which facilitates denitrification and is thus suitable at sites with high nitrogen load (PGC, 2007). A filtration type cell is suitable for runoff with known pollution problems (PGC, 2007). This type uses an impervious liner and an underdrain discharge pipe to prevent migration of contaminated runoff into the groundwater (PGC, 2007).

The type of media used in the bioretention cell is a key design factor (Liu et al., 2014). Selection of the media type is governed by the desired treatment performance, local hydrogeomorphology and prescribed infiltration rates (Liu et al., 2014; WRA, 2010). A development of regional bioretention soil guidance was commissioned by the Bay Area Stormwater Management Agencies Association in 2010 to meet 2009 (now superseded) regional NPDES requirements for the permittees to develop bioretention media specifications that achieve long term runoff infiltration rates of five to ten inches per hour (WRA, 2010; SFBRWQCB, 2015). The guidance does not address design specifications for the purposes of pollutant removal but only runoff infiltration with the numerical limits based on the actual NPDES permit requirements. The NPDES permit and the guidance that followed recommended bioretention soil to be composed of sixty to seventy percent sand and thirty to forty percent compost (WRA, 2010).

Because bioretention cells have been shown to occasionally export nutrients in excess amounts, the specifications provide for additional requirements for compost nutrient content, such as limitations for ammonium and total nitrogen but not phosphorous (Roy-Poirier et al., 2010; WRA, 2010; LeFevre et al., 2015). The permit recommended limiting compost with known high phosphorous content such as biosolids and manure to reduce possibility of nutrient export (WRA, 2010; SFBRWQCB, 2011). Content of phosphorous in the media is important since there is a leaching potential that is not desirable (Liu et al., 2014).

The depth of the media layer is also an important design consideration. In contrast to the NPDES permit recommendation (18 inches), some researchers have recommended a much deeper depth (28 – 40 inches) (Davis et al., 2009; Liu et al., 2014). Creation of an anaerobic

layer within a bioretention cell is important for denitrification process but might undermine desired infiltration rates (Roy-Poirier et al., 2010). Nutrient Numeric Endpoints have not been established for San Francisco Bay, which could be the reason why the 2009 NPDES permit did not address potential nutrient export from the bioretention cells. In addition, the permit did not require but only recommended the use of mulch (as the top layer in the cell) to prevent erosion, retain moisture and minimize the growth of weeds.

Treatment of metals in a bioretention cell is dictated by individual metal characteristics and speciation (LeFevre et al., 2015). Due to their bioavailability, removal of metals in the dissolved phase is of particular importance. For some metals (e.g., cadmium, copper and zinc), approximately half of total metal concentrations are found in the dissolved phase (LeFevre et al., 2015; Kayhanian et al., 2007). In contrast, 83% of lead was found to be particle-bound in the studies of California highway runoff (Kayhanian et al., 2007). Particle-bound metals can be easily removed via sedimentation or filtration, which bioretention cells are very effective at when designed and maintained properly (LeFevre et al., 2015). Sedimentation and physical filtration are accomplished in the top layer and the soil media (LeFevre et al., 2015; Roy-Poirier et al., 2010).

Plant uptake and sorption are believed to be the primary mechanisms for the removal of metals in the dissolved phase (LeFevre et al., 2015; Genc-Fuhrman et al., 2007). The degree of sorption depends on the sorbent used in the cell and the solution chemistry (LeFevre et al., 2015). Organic matter, with its high concentration of chemically reactive humic substances, has been shown to be very effective at removing metals (e.g., copper, lead and zinc) out of solution (LeFevre et al., 2015; Paus et al., 2014). Removal effectiveness of metals from runoff using eleven different sorbents was studied by Genc-Fuhrman et al., (2007). The study evaluated and calculated sorption constants for the following sorbents: alumina, activated bauxsol-coated sand, fly ash, bauxsol-coated sand, bark, granulated activated carbon, granulated ferric hydroxide, natural zeolite, sand, iron oxide-coated sand, and spinel. The top three effective sorbents in descending order were alumina, bauxsol-coated sand and granulated ferric hydroxide; with bark and sand being the least effective. A few studies have found mulch to be effective at sorbing and retaining dissolved metals and PAHs (Ray et al., 2006; Jang, et al., 2005). Removal of dissolved

metals from runoff via plant uptake has been shown to be somewhat limited with the highest reported rates of up to ten percent (LeFevre et al., 2015; Roy-Poirier et al., 2010; Blecken et al., 2011). However, removal efficiencies might be significantly different if the plants are selected on metal uptake capabilities and not aesthetic values (LeFevre et al., 2015).

Removal mechanisms of PAHs from stormwater with bioretention have not been studied as extensively as metals and hydrocarbons. Because most of the PAHs in stormwater are particle bound, sedimentation and filtration appear to be the dominant removal mechanisms (LeFevre et al., 2015). Analysis of core samples from bioretention cell soils revealed concentration of PAHs of an order of magnitude higher in the top ten centimeters supporting the sedimentation removal mechanism (Roy-Poirier et al., 2010). Biodegradation and sorption to organic matter within the cell could be another significant removal pathway but literature supporting this hypothesis appears to be very limited. Only one published was found that addresses the use of mulch in removing select dissolved PAHs from the stormwater (Ray et al., 2006). Sorption rates for naphthalene, benzo[a]pyrene and fluoranthene were sixty, eighty and ninety percent respectively. Desorption rates for the same suite of PAHs in the same order were five, zero, and five percent respectively.

From the perspective of how stormwater management relates to ecological protection, the prospective ability for bioretention technology to reduce the toxicity of urban stormwater prior to reaching receiving waters is notable. McIntyre et al. (2014) and McIntyre et al. (2015) studied bioretention capabilities in reducing the toxicological effects of urban stormwater on Zebrafish embryos (*Danio rerio*), Coho salmon (*Oncorhynchus kisutch*) and the Water fleas (*Ceriodaphnai dubia*). The stormwater runoff used in both studies came from a busy urban highway in Seattle, WA. Twelve bioretention cells were built using PVC columns and filled with a mix of sand (60%), compost (15%), shredded bark (15%) and the flocculation byproduct of the drinking water treatment process (10%). This soil medium was underlain with a 30 centimeters deep gravel aggregate drainage layer. Half of the cells were left unplanted and half were planted with sedge (*Carex flacca*). Each cell received 22 liters of runoff over a period of one hour, equivalent to 5 millimeters of rain over a drainage area of 4.3 square meters. Three runoff treatments were

evaluated for toxicity: untreated runoff, bioretention treatment with plants, and bioretention treatment without plants.

Untreated runoff produces several toxicological effects: acute mortality in coho salmon, water fleas, and zebrafish embryos; reproductive impairment in water fleas; and sublethal developmental effects in zebrafish embryos such as delayed hatching, reduced growth, small eyes, cardiac abnormalities, and lack of swim bladder inflation. Runoff treated with bioretention cells generally reduced or completely eliminated all adverse outcomes. Planted and unplanted bioretention cells eliminated lethal toxicity to water fleas and coho salmon. It appears that total reduction of lethal toxicity for zebrafish was not measured; however, treated runoff restored embryo development to nearly normal. Even though severe health effects in zebrafish were alleviated with the bioretention treatment, treated runoff still caused development of slightly smaller eyes and produced insignificant problems in their aortic valve. Reproductive impairments observed in water fleas under untreated conditions were reversed with bioretention. Both studies did not show any significant difference in toxicity outcomes between planted and unplanted bioretention cells. The authors attributed this finding to a relatively short time allowed for the root system to develop, eliminating any potential significant impacts.

With regard to what caused toxicity, the authors believe that PAHs are most likely responsible for the observed toxicological effects for several observations. First, despite the high concentration of dissolved metals in the runoff, no neurotoxic effects were observed in zebrafish embryos, which are usually caused by metals like copper. Second, high concentrations of dissolved organic matter (27-400 mg/L) were associated with the runoff, most likely rendering metals bioavailability via complexation. Third, metal concentration in the gills of coho salmon did not differ between the treated and untreated group. Fourth, untreated runoff samples stored for seven days eliminated acute mortality in water fleas. Such storage periods have been shown to significantly reduce concentration of PAHs in stored water samples, likely due to microbial degradation. Fifth, concentrations of PAHs (2-23 μ g/L) found in the untreated stormwater have been shown by other studies to cause cardiotoxicity, which was also observed in zebrafish embryos. These two studies are fine examples of how bioretention technology can reduce toxicity in aquatic species.

The maintenance of bioretention cells is crucial for achieving desired treatment effectiveness. Routine maintenance involves regular replacement of mulch, soil pH control, erosion repair, removal of accumulated sediments, and removal and replanting of dead plants (Sample and Liu, 2013; LID, 2007). The lack of long-term viability of this technology has been attributed to clogging of the media, which results in diminished hydraulic capacity and loss of pollutant removal ability (Paus et al., 2013). The amount of time it takes to reach sorption capacities for cadmium, copper and zinc is estimated to be 90, 21 and 36 years respectively (LeFevre et al., 2015). However, the sorption capacity is cell and media specific and should not be applied universally. Accumulation of high amounts of metals within the top layer of soil media is of a special concern, as there is a potential of creating hazardous exposure conditions to humans and wildlife. As with the sorption capacity limits, the time it will take to accumulate metals in excess of exposure guidance levels are site specific.

Because of their versatility and flexibility, the construction costs of bioretention cells can vary significantly and can be considered expensive or inexpensive depending on the design, system size, pre-existing and current site conditions and ultimate goal. For new construction projects, the cost has been estimated to be slightly higher than that of required landscaping with annual maintenance costs being five to eight percent of the construction costs (DPLU, 2007; Houle et al., 2013).

VIII. PERMEABLE PAVEMENT TECHNOLOGY

Just as the name implies, permeable pavements (or pervious pavements) represent an alternative to mainstream asphalt and concrete by allowing water to completely pass or infiltrate through while simultaneously providing a stable load-bearing surface (Hunt and Szpir, 2006; DPLU, 2007). Pervious pavements are typically designed to manage rainfall landing directly on its surface, but can also accept runoff from adjacent impervious areas if equipped with an underlying reservoir (MPCA, 2014; Caltrans, 2014).

Permeable pavements include several types: pervious concrete and asphalt, permeable interlocking concrete pavers (PICPs), plastic reinforced grass pavement, and concrete grid pavers

(Hunt and Szpir, 2006). Even though the specific design can vary, all permeable pavements have a common structure which include a surface layer, an underlying stone aggregate reservoir layer and a filter layer (DCR, 2011). An installation of a subdrain might be necessary for sites with low permeability soils (LID, 2010). A typical design is illustrated in Figure 10. The runoff is allowed to pass through the permeable surface and temporarily accumulates in the gravel storage layer (Hunt, 2006). Depending on the local geology and climate, the water then exits either through infiltration or drain pipes, or it can build up inside the pavement, which results in a runoff (Hunt, 2006).



Figure 10: Typical Permeable Pavement Design (Sample and Doumar, 2013). Permeable pavements generally consist of four major layers (Shoemaker et al., 2002). The top layer could be permeable asphalt, permeable concrete or lattice-type pavers set in a bedding material. The next layer usually consists of a stone reservoir layer providing water storage capacity. Two transition layers are usually built between the top layer and the reservoir and between the reservoir and the native subgrade soil. Coarse stones are used in the construction of the transition layers.

Permeable pavements are usually used in low traffic load areas such as residential parking pads, driveways, overflow parking areas, pedestrian traffic areas, patios, and certain highways (Sample and Doumar, 2013; Hunt, 2006). The California Department of

Transportation does not allow permeable pavements to be used in the construction of its highways, weight stations, low volume roads, and road shoulders due to perceived moderate and high risk of failure under heavy loads (Caltrans, 2014). A few benefits provided by this management practice include reduction of peak flow rates and runoff volume, groundwater recharge, filtration, infiltration, reduced pollutants load, and minimization of impervious land cover (LID, 2010; Welker et al., 2013). The design choice of using pervious concrete, asphalt, or interlocking pavers depends on various site-specific factors, which include intended use, soil properties, available space, contributing drainage area, pavement slope, depth to groundwater table, setbacks and local water quality regulations (DCR, 2011). Table 12 provides a comparative summary of properties associated with three major types of permeable pavements.

Table 12: Comparative Summary of Permeable Pavements (MPCA, 2014; DCR, 2011).This table presents a summary of various attributes for three types of permeable pavement.

Properties	Pervious Concrete	Pervious Asphalt	Interlocking Pavers		
Surface Thickness	5 to 8 inches	3 to 4 inches	3 inches but can vary		
Bedding Layer	None	1 inch	2 inches		
Reservoir Layer	ASTM No. 57 stone	ASTM No. 2 stone	4 inches of ASTM No. 57 stone		
Construction Properties	Cast in place	Cast in place	Mechanical installation of prefabricated units		
Permeability	10 feet/day	6 feet/day	2 feet/day		
Overflow	Catch basin or overflow edge	Catch basin or overflow edge	Surface, catch basin or overflow edge		
Traffic Bearing Capacity	Can handle all vehicle lo	oads with appropriate bed	ding layer and thickness.		
Construction Cost	\$2-6.5/sq.ft.	\$0.50-2/sq.ft.	\$3-10/sq.ft.		
Longevity	20-30 years	15-30 years	20-30 years		

Permeable pavements remove pollutants from stormwater primarily via sedimentation, adsorption and biodegradation (Welker et al., 2013; Brown et al., 2009; Beecham et al., 2012).

Sedimentation removes pollutants that are particle bound by trapping them within the pore spaces (Scholz and Grabowiecki, 2007; Welker et al., 2013). Trapped materials can be difficult to transport and could be locked in for the life of the pavement (Barrett, 2008). Dissolved contaminants are removed by adsorbing to soil particles already trapped within or to the pavement itself (Welker et al., 2013). Naturally occurring microbial communities within the pavement system have been shown to successfully biodegrade petroleum hydrocarbons (Scholz and Grabowiecki, 2007). Most of the published literature on the capacity of permeable pavements to remove pollutants from stormwater focuses on metals, nutrients and total suspended solids (Barrett, 2008; Pagotto et al., 2000; Brattebo and Booth, 2003; Drake et al., 2014; Legret et al., 1996). Not a single published study appears to specifically explore the capacity of permeable pavements to remove PAHs, which is a considerable data gap.

As with all management practices, there are certain limitations associated with the use of permeable pavements. Pervious pavements require ongoing maintenance to ensure continuous functionality such as vacuum sweeping or pressure washing to reduce sedimentation of the surface layer, monitoring of the storage reservoir to ensure it empties between storm events and management of the surrounding landscape to reduce system sedimentation (Pavement Interactive, 2010; Sample and Doumar, 2013; Welker et al., 2013). Completely clogged systems might require complete system replacement (Welker et al., 2013). Life cycle and structural durability is another major concern due to the intrinsic structural design to pass water and not carry heavy loads (Pavement Interactive, 2010; CSQA, 2003; Sample and Doumar, 2013). Structural durability problems can arise due to rutting and distortion under heavy loads and increased photo-oxidative degradation (Roseen et al., 2012). There are also concerns over pollutants migrating into the groundwater in unlined systems (CSQA, 2003).

Cost is an important consideration factor and can vary significantly depending on the installation type, existing site conditions, local geomorphology, local stormwater management requirements, and project size (EPA, 2009). Even though the construction costs are significantly higher when compared to conventional systems, when combined construction and drainage costs are accounted for, the cost of pervious pavements can be 25% less expensive than traditional concrete or asphalt construction (CSQA, 2003). Annual maintenance costs as a percent of initial

capital costs are calculated to be around 4%, which is one of the lowest in comparison to select conventional and other LID management practices (Houle et al., 2013).

IX. STORMWATER TREATMENT EFFECTIVENESS

In order to provide meaningful assessment of treatment effectiveness of bioretention and permeable pavements technology, a brief comparison of conventional and LID stormwater treatment technologies is necessary. Conventional BMPs included here are: detention basins; retention ponds; and wetland basins. It is important to note that most of the published studies on treatment effectiveness that are discussed here use percent removal for each contaminant as a performance metric. This approach is being increasingly criticized for many reasons, some of which are described here. First, a percent removal metric is closely related to how contaminated the influent is resulting in high removal efficiencies (Jones et al., 2008; Fassman, 2012). Even with high percent removal rates, the resulting effluent might still contain pollutants in high enough concentrations to cause adverse effects in the receiving waters (Fassman, 2012). Second, various statistical methodologies, such as mean of event percent removal, inflow median to outflow median, inflow load to outflow load, and event by event, are used to calculate percent removal prohibiting direct comparison (Jones et al., 2008). Third, even with low percent removal, discharges can still comply with numerical effluent limitations (Jones et al., 2008). Fourth, the ability of any particular BMP to treat stormwater is a combination of the BMP's design, storm characteristics and the watershed structure, none of which are incorporated in the percent removal calculations (Fassman, 2012). Fifth, percent removal often misses how much volume is, and is not, treated due to bypass mechanisms designed to effectively deal with clogging issues (Jones et al., 2008).

Jones et al. (2008) suggests several alternative assessment approaches that can be used to demonstrate effectiveness of any particular BMP: reduction in runoff volume; runoff treated vs. bypassed; statistical difference in influent and effluent quality; reduction in peak runoff rates; and distribution of achieved effluent quality. Fassman (2012), on the other hand, suggests using observed ecosystem effects as a measure in assessing performance and effectiveness. GeoSyntec et al. (2002) provides additional model based approaches. Despite the many issues associated with evaluating BMP performance using percent removal, the data presented here is based on

this approach since most published literature uses this methodology. However, in the attempt to provide some relevancy, data is compared to Basin Plan water quality objectives where possible.

Conventional vs. LID Control Measures

The assessment of performance effectiveness in removal of metals and PAHs by conventional and LID control measures focuses on the review of data submitted to the International Stormwater Database. The International Stormwater Database is a repository for hundreds of case studies (over 500) which do not appear to include any information on PAHs. The International Stormwater BMP Database began as a database project in 1996 under an agreement between the American Society of Civil Engineers and the EPA (BMP Database, 2015). By 2004, the project acquired a broader coalition support that included the Water Environment Research Foundation, U.S. Federal Highway Administration, American Public Works Association, and the Environmental and Water Resources Institute of American Society of Civil Engineers (BMP Database, 2015). The main objective of the project is to standardize BMP reporting protocols to facilitate consistent performance analysis with an overarching goal of providing scientifically sound information to improve the design, selection and performance of BMPs (BMP Database, 2015). These reporting protocols are used widely by various municipalities and special districts (BMP Database, 2015).

The database is not all-inclusive and has considerable data gaps and limitations. Most of the limitations associated with this data set appear to echo the criticism discussed earlier pertaining to the percent removal metric. In addition, when comparing different BMPs side by side, the number of case studies included in the summaries for each specific BMP might differ substantially. Noteworthy is the fact that the BMP database is not a repository for laboratory tested BMPs, but rather for field studies of permanent post-construction installations.

Table 13 and Table 14 provide a summary of metal removal efficiencies by BMP type and are based on the 2014 Statistical Summary Report prepared by GeoSyntec et al. (2014). This Statistical Summary Report was developed by GeoSyntec et al. (2014) using data from the International Stormwater Database. This category-based data summary includes several

screening approaches employed by the authors: 1) at least three case studies must exist for any particular BMP; 2) base flow samples are excluded; 3) grab samples with the exception of retention and wetland basins are excluded; 4) studies with a gross imbalance between inflow and outflow sample results are excluded; and 5) proprietary manufactured devices are not included. Data is summarized for select dissolved metals. Removal efficiency rate was calculated for this paper using influent and effluent concentrations from GeoSyntec et al. (2014) to provide an additional approach to data interpretation. The removal efficiency rates were calculated by means of the following equation: removal efficiency rate = $\left(\frac{influent-effluent}{influent}\right) * 100$.

Table 13: Dissolved Copper and Zinc Removal Efficiencies by BMP (modified from GeoSyntec et al., 2014). Values marked with a single asterisk show statistically significant increase or decrease. Values in bold indicate exceedances of either fresh or marine water quality objectives as set in the Basin Plan. EMC stands for Event Mean Concentration. Of note are the large differences in pollutant concentrations between EMC and median values. The difference is most likely due to EMC values being skewed by the first flush effect. % Δ means removal efficiency rate.

		Сорре	er (µg/I	.)		Zinc (µg/L)					
BMP Type	Numł Studies/	oer of / EMCs	Median Metals Concentration			Numl Studies	oer of / EMCs	Median Metals Concentration			
	In	In Out		Out	% Δ	In Out		In	Out	%Δ	
Bioretention	7/ 125	7/ 107	5.21	5.79	+11	6/ 126	6/112	19.7	12.2*	-38	
Permeable Pavement	7/ 351	7/206	4.9	5.05	-3	7/ 351	7/206	13.4	1.52*	-880	
Retention Pond	16/ 363	16/ 364	4.9	3.25	-34	18/ 360	18/ 346	23	14.9*	-35	
Wetland Basin	6/ 106	6/100	3.97	2.54	-36	6/106	6/100	21.8	7.64*	-285	
Detention Basin	9/ 186	9/ 196	4.79	2.86	-40	9/186 9/197 13.1 7.83 -60					
Marine Objectiv	3.1			81							
Freshwater Obj	9			120							

Because this data is presented as event mean concentrations (EMC) and median, the effect of the first flush phenomenon and its subsequent treatment is difficult to distinguish and evaluate. The EMC value represents a composite data point, proportional to the flow rate, of all samples collected throughout the storm event. It is generally agreed upon that first flush tends to

be high in pollutant loads compared to subsequent runoff (Caltrans, 2012a; Lee et al., 2004; Lee et al., 2002). Therefore, evaluating first flush removal efficiencies might be more valuable than evaluating EMCs, medians and means. Because median concentrations appear to be much lower than EMC for all metals, it is reasonable to suggest that the EMC values are skewed by the first flush phenomenon.

Table 14: Dissolved Cadmium and Lead Removal Efficiencies by BMP (modified from GeoSyntec et al., 2014). Values marked with a single asterisk show statistically significant increase or decrease. Values marked with a double asterisk indicate limited conclusions for that BMP due to a large percentage of non-detect values in the influent. Values in bold indicate exceedances of water quality objectives for either marine or freshwater objectives as set in the Basin Plan. EMC stands for Event Mean Concentration. Of note are the large differences in pollutant concentrations between EMC and median values. The difference is most likely due to EMC values being skewed by the first flush effect. % Δ means removal efficiency rate.

		Cadmiu	ım (µg	<u>/</u> L)		Lead (µg/L)					
BMP Type	Numb Studies/	er of EMCs	Median Metals Concentration			Numb Studies/	er of EMCs	Median Metals Concentration			
	In	In	Out	%Δ	In Out		In	Out	%Δ		
Bioretention	4/ 98	4/ 85	0.03	0.08*	-267	5/101	5/ 88	0.07	0.05	-28	
Permeable Pavement	4/250	4/123	0.06	0.04*	-33	4/292**	4/144	0.5	0.5	0	
Retention Pond	3/54**	3/69	0.27 0.13 -52		11/ 163 11/ 172		1	0.81	-19		
Wetland Basin	4/36	4/30	0.12	0.28*	+233	4/36	4/30	0.67	0.71	+6	
Detention Basin	8/135**	8/141	0.12	0.39	+325	8/164	8/165	0.64	0.55	-14	
Marine Object	9.3			8.1							
Freshwater O		1.1		2.5							

A comparison of San Francisco Bay four-day average water quality objectives to effluent (In) and influent (Out) EMC values indicates that regardless of stormwater control strategies and individual metals, the objectives would not be met. Once again, direct comparison should be taken with caution since the data is not Bay Area specific and the applicability of a four-day average (vs. one-hour average) might not be accurately applied here. When effluent and influent median values are compared to San Francisco Bay water quality objectives, copper shows exceedances across all control strategies. Although not significant, bioretention technology shows increased median concentrations of dissolved copper in the influent by eleven percent. This finding aligns with several bioretention studies that have found leaching of the dissolved copper out of the cell, which was attributed to the release of organic matter for which copper has very high affinity (LeFevre et al., 2015; Li et al., 2012). In comparison to detention basins, reduction of dissolved copper with permeable pavements as presented by this dataset is also insignificant (i.e., three percent).

There is not a clear pattern of metal removal efficiencies (as presented in Table 13 and Table 14) in an evaluation and comparison of bioretention and permeable pavements to conventional controls. Bioretention appears to be the most effective at removing dissolved lead against all other management strategies but not as effective at zinc removal. Detention basins appear to contribute significant amounts of cadmium to the influent but are effective at removing dissolved copper and zinc. Permeable pavements appear to be the most effective at removing dissolved zinc but marginal at reducing dissolved copper. Because there is a considerable difference in the number of LID vs. conventional case studies in this dataset (i.e., more studies exist for conventional systems), direct comparison between them might not be very accurate. However, a comparison of permeable pavements and bioretention using this data would be relevant since the number of case studies is almost equal. Metal-specific removal effectiveness for bioretention cells follows the order of cadmium > zinc > lead. As stated earlier, bioretention cells exported more copper than received. Removal effectiveness for permeable pavements, however, is not reliable due to the limited number of detections in the runoff.

To supplement the BMP Database statistical summaries, select case studies on bioretention and permeable pavements are discussed next. Careful review of individual case studies allows for better understanding of the study designs, limitations and conclusions. Bioretention case studies address both metals and PAHs. Review of case studies on permeable pavements only include metals since published literature on PAHs appears to be lacking. Even though PCBs and mercury are not the focus of this project, capabilities of treating PCBs and mercury in stormwater are addressed where data exists, since TMDLs have been established for both in the San Francisco Bay Estuary to address impairment. Bioretention case studies are

summarized first, followed by permeable pavements. Data from all bioretention case studies reviewed is summarized in Table 16. Data from all permeable pavement case studies reviewed is summarized in Table 17. Noteworthy is the fact that most published case studies assessed the total concentration of metals and PAHs and not the dissolved fraction. In addition, published literature on bioretention technology appears to be much more comprehensive and diverse than that on permeable pavements.

Bioretention Case Studies

Removal efficiencies for metals, PCBs, PAHs, and dioxins in a field constructed bioretention cell in Daly City, CA were evaluated between 2008 and 2010 (David et al., 2015). This is one of a few bioretention studies done in a semi-arid climate. The system was sized at approximately 3% (427 square meters) of the drainage area comprised of a parking lot and a recreation yard serving a local library. The effectiveness of the bioretention cell was evaluated by sampling stormwater runoff before (three storm events) and after (seven storm events) system installation, targeting peak flows and the receding stage of the storm. The overall conclusion of this study was that the system was very efficient at reducing total metals, PCBs, PAHs, and dioxins with reductions in pollutant loads similar to systems in temperate climates. Methylmercury was a significant exception to the overall outcome as the effluent concentrations actually increased after the installation (concentration of both total and dissolved mercury however decreased). The authors explained this to be a result of a defect in the system installation (i.e., missing subdrain) which created anaerobic environment within the cell, favoring production of methylmercury.

A multi-year water quality study (2009-2014) was conducted by Caltrans to assess the treatment effectiveness of six bioretention cells built as part of the new San Francisco Oakland Bay Bridge east span (Caltrans, 2014a). Bioretention cells were constructed to treat stormwater runoff from the toll plaza, the maintenance facility area and the eastbound and westbound lanes of Interstate-80 approaching the toll plaza. The following contaminants and parameters were part of the study: lead, copper, nickel, zinc, iron, mercury, methylmercury, PCBs, pH, total dissolved solids, total suspended solids, salinity, hardness, and electrical conductivity. The

original goal of the study was to assess performance of the experimental design features associated with each cell (i.e., vegetation type, ponding heights, and size of the drainage area). Water quality results from the initial phase of the project was not indicative of any cell specific design trends (i.e., no apparent differences in treatment from cell to cell) and Caltrans came up with a new objective of determining whether suspended sediment concentrations could be used to predict stormwater concentrations of total mercury and PCBs.

Table 15 provides a summary of removal efficiency ratios for dissolved metals (a more condensed summary is also included as part of Table 16). Removal efficiency rates ratios were calculated for this project using integrated (i.e., 2010 to 2014 monitoring season) average influent and effluent data from the Caltrans (2014a) report. The removal efficiency rates were calculated by means of the following equation:

removal efficiency rate = $\left(\frac{influent - effluent}{influent}\right) * 100$. As with other bioretention case studies reviewed for this project, removal rates for dissolved copper are not consistent across all six bioretention cells. Removal rates vary widely from export of 286% to 52% attenuation. The authors came up with one potential explanation for this observation, which has to do with saltwater intrusion into some of the cells. The authors attempted to correlate dissolved copper removal rates with effluent salinity. Export of dissolved copper was observed across all salinity levels but the removal only happened when salinity was below 2 g/L. The authors theorized that because removal of dissolved copper in bioretention occurs via complexation to organic matter, the presence of other cautions in salt-water (i.e., calcium and magnesium) might create competition for organic matter binding sites, resulting in export. This is the only study reviewed for this project that has brought up the issue of salinity in this context. Noteworthy is the fact that concentrations for both influent and effluent of dissolved copper were consistently above San Francisco Bay water quality objectives (Caltrans, 2014a).

Removal rates for dissolved zinc appear to be favorable and consistent across all cells with the exception of Cell No. 5 where an export of 19% was recorded. The authors did not provide an explanation for this inconsistency. Removal rates for dissolved lead were highly variable with four of the six cells actually exporting dissolved lead. This is the only study reviewed for this project that found export of dissolved lead in bioretention cells. The mechanism behind this observation is not known. All bioretention cells consistently exported dissolved nickel. This was attributed to the fact that native soils in San Francisco Bay Area are high in nickel, leading to leaching of naturally occurring nickel from the cells. With the exception of nickel and copper, concentrations of dissolved zinc and lead in influent and effluent were always below water quality objectives. Currently, Caltrans has no plans for additional water quality monitoring at the site and it is unclear whether anything will be done about copper export from some of the cells.

Table 15: Removal Efficiencies of Dissolved Metals for San Francisco Oakland Bay Bridge Bioretention Pilot Project. Removal efficiency ratios were calculated using 2010-2014 integrated average influent and effluent data from the Caltrans (2014a) report. Bioretention cell No. 6 has two flow outlets (i.e., east and west). Negative values indicate export of pollutants.

Metal	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6 East	Cell 6 West
Copper	36%	52%	36%	-10%	-286%	10%	-29%
Lead	-66%	76%	58%	-52%	-107%	-204%	-452%
Nickel	-133%	-168%	-121%	-167%	-124%	-200%	-236%
Zinc	58%	71%	75%	52%	-19%	75%	68%

Findings of bioretention studies in cold climates would also be applicable to San Francisco Bay Area since low and even freezing temperatures are a norm in inland areas during winter months. Blecken et al. (2011) evaluated the effect of cold temperatures on the performance of bioretention cells to remove total and dissolved metals in laboratory settings. The study evaluated bioretention performance at 2°C, 8°C and 20°C. With the exception of copper, the effluent concentrations of cadmium, lead and zinc were not affected by different temperatures. Cadmium and zinc removal effectiveness, for both dissolved and total concentrations, ranged from 98 to 99% across all temperatures. The removal range for total lead and copper across all temperatures was 89 to 96%. The removal rate of dissolved copper decreased with increasing temperatures as follows: 64% 2°C, 66% at 8°C and 24% at 20°C. Because copper readily complexes with dissolved organic matter, higher temperatures may increase biological activities (i.e., organic matter decomposition) within bioretention, leading to elevated leaching of dissolved copper. This line of reasoning is similar to the conclusions provided by LeFevre et al. (2015) and Li et al. (2012). Given these observations, the choice of bioretention media, specifically the type of chosen organic matter, should be carefully analyzed and considered if the removal of dissolved copper is the desired treatment outcome.

Only three published studies were found that directly or indirectly evaluate removal of PAHs from stormwater via bioretention (Diblasi et al., 2009; David et al., 2015; McIntyre et al., 2014). The results of all three are presented in Table 16. The work by Diblasi et al. (2009) is briefly summarized here since this appears to be the only study that specifically focused on the removal and fate of most common PAHs. The bioretention studied was a field constructed unlined cell with an underdrain, releasing filtered runoff directly into a local creek in College Park, MD. An event mean concentration of effluent and influent were measured for a total of five storm events and analyzed for both dissolved and total PAHs. Mean reduction of total PAHs was 90% with a range of 31 to 99%. The calculated total mean annual mass load reduction was 87%.

As expected, the authors found that PAHs removal effectiveness was closely associated with the removal of total suspended solids. High molecular weight PAHs, dissolved and particle-bound, were found to dominate the influent and effluent leading to a conclusion that low molecular weight PAHs should not present water quality concerns. The study also looked at the vertical accumulation of PAHs within filter media. The concentrations of PAHs in the top ten centimeters were an order of magnitude higher than lower layers, indicating low mobility within the cell and high sorption rates. The concentration of PAHs in the upper layer was close to ecological screening levels for the protection of soil invertebrates. This finding suggests that periodic removal of the upper media layer might be necessary for the protection of soil dwelling invertebrates. In addition, if the goal of the bioretention cell is to treat runoff contaminated with PAHs, a shallow system might be sufficiently effective because of low mobility within the cell.

Table 16: Summary of Bioretention Performance Studies: Select Metals and PAHs. Values in italic and bold represent dissolved phase. Marine water quality objective for PAHs is a 24-hour average aquatic life protection objective. Data presented here is based on the review of case studies for this paper.

	Copp (µg/I	Der		Lea (µg/]	ad L)		Zinc (µg/L			PAHs (µg/L)		References and Notes
In	Out	% removal	In	Out	% removal	In	Out	% removal	In	Out	% removal	Kererences and Notes
46	7.7	83	3.5	1.7	51	690	46	93	2.3	0.2	90	David et al. (2015). Mean values are reported and represent runoff quality before and after system installation in Daly City. CA. System size is 3% of the drainage area. Media composition(top to bottom): 5 cm gravel mulch; 34 cm soil mix composed of 84% sand, 7.5% silt, 8% clay, and 5% organics; 15 cm pea gravel. Native subgrade is high in clay-loam content. No subdrain.
13	5.9	54	5	3	31	72	17	77		-		Hunt et al. (2008). Average values are reported. System size 6% of the drainage area. Soil media depth is 1.2 meters and is composed of loamy sand. System design includes an underdrain. Predominant vegetation: <i>Iris virginica, Juncus effuses, Hibiscus Spp., Acer rubrum, Lobelia cardinalis, Chamanthium latifolium, Itea virginica.</i>
				-					2.1	0.2	90	Diblasi et al. (2009). Mean values are reported. System size is 6% of the drainage area with an underdrain. The system is located in College Park, MD
19	16	31	6	3	55	71	12	78		-		Li and Davis (2009). Median values are reported. Diblasi et al., (2009) evaluated the same cell. Media depth is 80 cm composed of 80% sand, 13% silt, 7% clay, 5.7% organic matter. Vegetation types: grasses, small trees, and shrubs.
37 10	23 15	38 -50	11	1	90	659 355	29 24	95 93		-		Trowsdale and Simcock (2011). Median values are reported. The cell treats road runoff in Auckland, New Zealand. Media composition (top to bottom): 8 cm mulch; 40 cm topsoil composed of pumice sand and fertile horticultural soils; 70 cm of well-draining subsoil; 15 cm of coarse sand. Vegetation type: <i>Apodasmia similis</i> .
102	31	70	2.8	0.3	88	887	9	99	1.6	0.1	95	McIntyre et al. (2014). Laboratory based study using highway runoff in Seattle, Washington. Average values of triplicate sample are reported. Values for vegetated cells are used. Plant of choice: <i>Carex flacca</i> . Media composition (top to bottom): 62 cm soil mix composed of 60% sand, 15% compost, 15% shredded bark, and 10% drinking water treatment residual (amorphous aluminum hydroxides) and 30 cm sandy gravel.
42 8.8	17 11	60 -26	25 0.6	3.2 0.56	87 7	151 30	22 7	85 77		-		Caltrans (2014a). Field study evaluating cells treating runoff from San Francisco Oakland Bay Bridge in California. Data reported here is an integrated average of 6 cells studied from 2010 to 2014. Data for all six cells was averaged. Media depth of all six cells is 2.5 feet. Maximum ponding depth is 6 inches in cells No. 1, 2, 4, 5, and 6 and 12 inches in cell No. 3. Vegetation type: unknown seed mix, <i>Carex praegracilis, Cyperus eragrostis, Dantonia californica, Juncus balticus, Distichlis spicata</i> .
	9			2.5	5		120			-		Freshwater Objectives (4-day $\overline{\mathbf{x}}$)
	3.1			8.1	!		81			15		Marine Objectives (4-day x̄)

Bioretention Design Considerations

As illustrated by data presented in Table 16, bioretention cells, where designed and maintained properly, can be successful in mitigating potential impacts associated with metals and PAHs in stormwater. However, a perfect bioretention design "formula" targeting specific stormwater problems does not yet exist. A few important design considerations should be assessed when considering a bioretention system as a stormwater runoff management strategy. Because bioretention is very flexible in its design, function and purpose, the treatment goal of the system should be clearly identified early on. Is the goal only to infiltrate runoff, treat it or both? The quality of the incoming runoff should be known to some extent. Is it expected to be high in sediments (if so, what size), various contaminants (if so, what kind) or both?

The review of published literature revealed consistencies as well as inconsistencies pertaining to removal efficiencies, especially for some of the metals. For example, the literature review is consistent in that bioretention cells are great at removing PAHs and most metals studied, in both dissolved and total fraction. However, copper has conflicting results and some studies find export instead of reduction, particularly in the dissolved phase. A clear definitive mechanism for copper leaching and method for reducing its export out of the system has not been found and requires further study. As of the time of this writing, the San Francisco Bay Estuary is not listed under the Clean Water Act as an impaired water body due to elevated concentrations of metals commonly associated with urban stormwater such as cadmium, copper, lead, and zinc. However, copper is a pollutant of concern in the Estuary, requiring ongoing monitoring (SFBRWQCB, 2015c). When the whole State is considered, TMDLs for metals do exist. Therefore, given the high removal rates that bioretention cells can achieve with regard to metals, this control strategy should certainly be considered for both flows attenuation and specifically for stormwater treatment.

Portions of the San Francisco Bay Estuary (almost 750 acres) are impaired due to elevated concentration of PAHs in sediments (SWRCB, 2012). To date, TMDLs for PAHs have not been developed, but are scheduled to be completed in 2019. The major sources of PAHs in the Bay include stormwater runoff, wastewater treatment plants, tributaries, atmospheric

deposition, industrial effluents, and disposal of dredged materials (Oros et al., 2007). Stormwater runoff is believed to account for over 50 % of calculated maximum annual load into the Bay of almost 11,000 kilograms (Oros et al., 2007). Therefore, use of bioretention technology could be a viable treatment mechanism for reducing loads associated with urban stormwater discharges. Assuming strategic installation of bioretention cells within the watershed, with a goal of treating a maximum annual estimated stormwater load of 5,500 kilograms, the annual maximum load could be reduced to a range of 275 to 550 kilograms using 95 and 90% removal efficiency respectively. Load reduction calculations were done using the following formula: Load Reduction = Annual Load - $\left(\frac{Removal rate* Annual Load}{100}\right)$. This calculation is an exaggeration, as it is not feasible to assume 100% treatment of all stormwater with bioretention cells across the whole San Francisco Bay Area.

Load data for a small urban watershed in South San Francisco Bay can be used to provide more realistic load reduction estimates. The annual long-term average load of total PAHs was estimated to be 5.4 kilograms for a small watershed in Hayward, California (Gilbreath and McKee, 2015). As noted earlier, using the same formula and assuming strategic installation of bioretention cells within the watershed with a goal of treating 100% of all stormwater, the annual long-term average load could be reduced to a range of 0.27 to 0.54 kilograms using 95 and 90% removal efficiency respectively.

The Bay is also impaired for elevated concentrations of PCBs in sediments. Urban stormwater runoff has been designated as the largest source of PCBs in the Bay at twenty kilograms per year (SFBRWQCB, 2008). Only two published studies appear to examine bioretention effectiveness at attenuating PCBs (David et al., 2015; Caltrans, 2014a). Mean removal rate in the David et al. (2015) study was determined to be 40%. Using available influent and effluent data from the Caltrans (2014a) study for three separate bioretention cells, removal rates for PCBs using a removal efficiency rate formula (i.e., Removal efficiency rate =

 $\left(\frac{influent-effluent}{influent}\right)$ * 100) were calculated resulting in the following rates: 26% for cell No. 1, 54% for cell No. 2 and 90% for cell No. 3. The average removal rate for all three cells is 57%. Using the same line of earlier assumptions and calculations for reducing PAHs loads,

bioretention could be capable of reducing total loads of PCBs from 20 kilograms to a range of 12 to 8.6 kilograms using 40 and 57% removal efficiency rates respectively.

Even though breakdown and attenuation of nutrient loads by bioretention is not the focus of this paper, treatment of nutrients with this management strategy is an important consideration, especially where nutrients are of concern, as is the case with the San Francisco Bay Estuary. As with copper, published literature provides variable results for treatment of orthophosphate and nitrogen species. Removal efficiencies for orthophosphate range from negative 9% (export) to 100% attenuation (LeFevre et al., 2015). Published removal rates for nitrogen species and ammonium range from negative 800% (export) to 90% attenuation and negative 100% (export) to 96% attenuation respectively (LeFevre et al., 2015). Choosing media with low organic content, using vegetation and creating anoxic conditions should aid nutrients attenuation and reduce possibility of export (Hatt et al., 2009; LeFevre et al., 2015). However, prolonged anaerobic conditions have been implicated in the production of methylmercury in a bioretention cell studied by David et al. (2015). Since the San Francisco Bay Estuary is impaired due to elevated mercury, the potential for adding the most bioavailable and toxic form of mercury into the Bay would not be a desirable outcome. In contrast, the Caltrans (2014a) study did not observe any methylation in any of the cells studied. However, given that only a few studies have examined this issue, further research is warranted. In addition, if infiltration of stormwater is a highly desirable outcome, the creation of a saturated anoxic zone might compromise high infiltration rates.

Prolonged wet and dry conditions associated with the San Francisco Bay Mediterranean climate could pose a challenge to the effectiveness of bioretention. Most research studies have focused on the treatment of individual storm events or use continuous dosing in laboratory settings ignoring the effect of intermittent drying and wetting on the pollutant removal processes within the cells (Blecken et al., 2009; Hatt et al., 2009). Drying conditions within the cell affect metal solubility making initially insoluble metals soluble, posing an export problem during the next wetting period (Blecken et al., 2009). Retention times and plant uptake rates could also be compromised from increased soil porosity and decreased plant activity (Blecken et al., 2009). Though few studies have looked specifically into this issue, existing data does warrant the

consideration of the drying and wetting cycle during the design process. Two laboratory-based studies examined the effect of wetting and drying on removal of pollutants in nonvegetative cells (Hatt et al., 2009; Lau et al., 2000; Lim et al., 2015). These studies did not observe any negative impacts associated with wetting and drying on pollutant removal capabilities. A significant increase in nitrogen was observed, however, after a re-wetting event (Hatt et al., 2009). Contrary to these findings, a study of vegetative cells found a prolonged antecedent period, causing reduced metal removal performance (Blecken et al., 2009). However, even with reduced performance, the system was able to remove seventy percent of copper and approximately ninety percent of lead and zinc (Blecken et al., 2009). To counter this effect, the authors suggested a cell design with a submerged zone that would facilitate removal of both metals and nutrients.

The choice of soil media is highly important and could be driven by desired infiltration rates as well as pollutant removal goals. If the ultimate goal is removal of pollutants, such as metals and PAHs, then the addition of organic media would facilitate a desirable outcome from increased sorption but could contribute to export of dissolved copper and nutrients. Whatever the choice of filtering media, the capacity of any media to attenuate pollutants has its limitations due to progressive loss of sorption over time (LeFevre et al., 2015). The time it takes to reach sorption capacity is cell-specific and will be affected by the incoming stormwater pollutants load and local precipitation patterns. In addition, because high molecular weight PAHs tend to be recalcitrant and metals do not break down into less toxic components, there is a potential for accumulating these to levels above regulatory thresholds (LeFevre et al., 2015). Since metals and PAHs tend to accumulate in the upper most layer of the cell, periodic testing and removal of contaminated soils might be required and may need to be included as part of the cell's operation and maintenance.

Permeable Pavements Case Studies

With respect to permeable pavements as pollution control strategies, only metals are discussed here since published literature on this topic does not appear to address PAHs. In addition, published literature on the topic appears to be somewhat dated. Two studies were reviewed, but were not considered for further evaluation because of the limited number of samples collected and/or high detection limits set for the metal analysis, which resulted in a lot

of non-detect values (Jiang et al., 2015; Beecham et al., 2012). Unlike bioretention studies, the evaluation of the effectiveness of permeable pavements is accomplished by comparing runoff from traditional paved surfaces to that of permeable pavements. This is due to the intrinsic design of infiltrating water where it falls, vs. having discrete influent and effluent points. Data from the case studies reviewed here is summarized in Table 17.

Load reductions of total and dissolved lead, copper and zinc in highway runoff was evaluated in Austin, Texas using event mean concentrations over a 32-month period (Barrett, 2008). The type of pavement evaluated was a 50-millimeter thick porous asphalt overlay, applied on top of a conventional highway surface. This design allows rainwater that falls directly onto the surface to infiltrate to the original impervious surface and remerge at the edge of the pavement. Water quality data was collected before and after installation of the porous overlay.

The overall conclusion of this study was that this nontraditional type of permeable pavement is very effective at reducing total metals but not the dissolved fraction. In fact, there was export of dissolved copper in comparison to the runoff from the traditional asphalt pavement. Reduction of dissolved zinc was low ranging from 22 to 42%. Lead in the dissolved fraction was below detection limits for both types of asphalt surfaces. This study did evaluate PAHs, but none were detected in the any of the samples above set detection limit of 5 μ g/L. Reduction in suspended solids was excellent, ranging from 87 to 93% and was most likely related to the observed attenuation of total metals. In comparison to the conventional surface, one potentially major downside with this type of pavement is the observed increased amount of runoff and very little lag time between the rainfall and the runoff peak. From the perspective of restoring the hydrologic cycle, this might not be considered a beneficial outcome.

A similar design was evaluated on a French highway by Pagotto et al. (2000). This study also found higher runoff rates from the porous overlay, which was attributed to a decrease in water splashing, causing reduced water losses due to evaporation and wind dispersion. Rates of metal removal effectiveness were similar to the Barrett (2008) experiment with some exceptions. There was no export of dissolved copper, and a much better attenuation of dissolved zinc was

demonstrated. This study also calculated the relative difference for the particulate fraction of metals resulting in a range of 74 to 83% percent.

As opposed to evaluating one single type of permeable pavement, parking stalls constructed of four different commercial variations were evaluated for infiltration capacity and infiltrate quality by Brattebo and Booth (2003). The type of pavements evaluated included: 1) virtually 100% permeable grass planted sand filled plastic grid (Grasspave^{2®}), 2) virtually 100% permeable unplanted gravel filled plastic grid (Gravelpave^{2®}), 3) concrete block lattice planted and filled with soil with 60% impervious coverage (Turfstone[®], and 4) gravel filled concrete blocks with 90% impervious surface (UNI Eco-Stone^{®).} A conventional asphalt-paved parking stall was used as a control. Prior to this experiment, the study site has been in use for six years by the employees of a public works facility. Stormwater runoff samples were collected over nine storm events and analyzed for dissolved copper, lead and zinc.

A significant reduction of dissolved copper was observed in all four types of pavements, ranging from 83 to 89%. All infiltrate copper samples for Grasspave^{2®} were below detection limits of 1 μ g/L. Removal of zinc was less but still ranged from 39 to 69%, with Grasspave^{2®} system being the least effective. The dissolved lead fraction was not detected above detection limits of 1 μ g/L in any of the samples collected. There was not an apparent difference in copper removal efficiencies among the four pavement types. It is not clear why Grasspave^{2®} was the least successful in attenuating dissolved zinc, while others showed almost identical removal rates.

This study was almost identical to the one conducted shortly after system installation six years prior (Booth and Leavitt, 1999). Curiously enough, the water quality results between the two are quite different. For example, Grasspave^{2®} was the least successful in attenuating dissolved copper. Moreover, runoff infiltrate from UNI Eco-Stone and Grasspave^{2®} had much higher dissolved copper concentrations than the runoff from the conventional asphalt. Zinc data was also inconsistent in that there was no similarity in removal rates between different types of pavements. Unfortunately, neither of the two studies really addressed the mechanisms behind

the observed removal rates. However, the 2003 study did show that the pavements were able to retain pollutant removal capacity after six years of operation.

Other types of permeable pavement such as interlocking permeable concrete pavements (AquaPave[®] and Eco-Optiloc[®]) and pervious concrete (Hydromedia[®]) were evaluated against standard asphalt by Drake et al. (2014). The water quality results are generally consistent with other reviewed case studies. Lead removal efficiency was not calculated due to initial design issues. Even though both types of pavements reduced pollutant loads, interlocking permeable concrete pavements were slightly more effective than pervious concrete. In addition, the study showed that pavements themselves are capable of introducing new materials into the stormwater such as strontium, boron, potassium, uranium, argon, molybdenum, and magnesium, which could be problematic.

Permeable Pavements Design Considerations

As illustrated by data presented in Table 17, permeable pavements are capable of mitigating stormwater impacts with respect to metals. Similar to bioretention technology, a few important design considerations should be assessed when considering permeable pavements as a stormwater management strategy. As stated earlier, data pertaining to the attenuation of PAHs does not appear in any of the studies reviewed for this project. However, given the fact that PAHs are mostly found in association with solid particles, it would follow that if permeable pavements are effective at capturing suspended solids, then attenuation of PAHs would be expected. As shown in Table 17, the range of removal rates for total suspended solids is between 80 and 90%.

One potential way of estimating removal rates of PAHs via total suspended solids could be with the use of a soil/water partition coefficient (K_d). However, because PAHs are lipophilic, they tend to adsorb to the organic content of the soil particles. Because concentrations of organic matter is highly variable and is dependent on soil type and other organic constituents found in the stormwater as suspended solids, calculating accurate removal rates for PAHs using total suspended solid data is deemed not feasible unless a site and source specific K_d are known.

Results of metal removal efficiencies, as presented here, are highly variable for both the dissolved and total fraction. This could be partly due to the fact that the data presented encompasses different permeable pavement types. Export of dissolved copper was found in two of the five studies (Legret et al., 1996; Barrett, 2008). However, two other studies demonstrated high removal rates in the range of 50 to almost 90% (Drake et al., 2014; Brattebo and Booth, 2003). There is not an apparent pattern that could provide an explanation for such a significant difference in the removal rates. Removal of total fraction was also the lowest for copper across all designs, ranging from 50 to 60%. Removal rates for total zinc and lead ranged from 60 to 80% and were somewhat consistent across all studies. Lack of significant organic matter as part of the layers within each system could be the reason why copper was not removed as efficiently as lead or zinc. None of the studies included here provided reasoning for the observed effectiveness. Additional research exploring copper attenuation appears to be warranted.

Similar to metals, nutrients removal efficiencies appear to be variable as well. Systems with aerobic conditions have been shown to nitrify ammonia to nitrate creating a positive outcome (Hunt and Collins, 2007; Drake et al., 2014). Different designs lead to variable results. For example, systems that incorporate sand media have been shown to improve total nitrogen concentrations in the effluent (Hunt and Collins, 2007). Two of the evaluated studies reported reduction rates for ammonium ranging from 74 to 87% (Pagotto et al., 2000; Drake et al., 2014). The same studies reported very different removal rates for nitrate. An export range of 50 to 140% was reported by Drake et al., (2014). Reduction of almost 70% was reported by Pagotto et al. (2000) but only 6% percent by Barrett (2008). With regard to total phosphorus, removal efficiencies are also wide ranging from 36 to 86% (Drake et al., 2014; Barrett, 2008). Areas where nutrient pollution is of concern, system design should account for a wide variability of the existing nutrient treatment data.

Table 17: Summary of Permeable Pavement Performance Studies: Select Metals and TSS. Values in italic and bold represent dissolved phase. Marine water quality objective for PAHs is a 24-hour average aquatic life protection objective. Data presented here is based on the review of case studies for this paper.

	Copp	er		Lea (µg/]	nd L)		Zinc (µg/L)			TSS (mg/L)		Deferences and Notes
In	Out	% removal	In	Out	% removal	In	Out	% removal	In	In Out % removal		Kererences and Notes
29 6	13 9	55 -33	12	1.5	88	153 32	29 20	80 37	146	16	89	Barrett (2008). Mean values (averaged over all sampled sites) are reported and represent runoff quality before and after system installation in Austin, Texas. System type is 50 mm permeable friction coarse applied on top of conventional asphalt surface. Void space.
30 19	20 16	33 15	40 3.3	8.7 2.2	78 32	228 140	77 54	66 61	46	8.7	81	Pagotto et al. (2000). Mean values are reported. System type is 30 mm think porous asphalt overlay.
8	1-1.3	83-89		-		22	7 – 13	39 - 69		-		Brattebo and Booth (2003). Mean values are reported. Ranges represent four types of pavement evaluated.
16	6-9	50-62	3.2	4-6	-	85	13 – 19	62-80	54	7-11	81-87	Drake et al. (2014). Mean values are reported. Ranges represent three types of pavement evaluated.
11	15	- 36	26	5.4	80	165	5.4	97	33	12	64	Legret et al. (1996). Mean values reported and represent two different urban catchment areas. Permeable pavement composition (top to bottom): 6 cm of porous asphalt; 20 cm of porous bitumen; 40 cm of 10/80 crushed stone; and geotextile layer. Four year study.
	9			2.5	5		120			N/A		Freshwater Objectives (4-day $\overline{\mathbf{x}}$)
	3.1			8.1	1		81			1 1 /A		Marine Objectives (4-day \overline{x})

Clogging is a major concern when it comes to maintenance and longevity of this stormwater control technology (Hunt and Collins, 2007; Barrett, 2008; Welker et al., 2013). Clogging due to sedimentation reduces infiltration capacity, leading to impaired performance. The degree of clogging will depend on site-specific conditions such as sediment load and particle size in the runoff, surrounding soil type and pavement use intensity (Hunt and Collins, 2007). Regular maintenance employing regular street sweepers, pressure washing and specialized vacuum equipment can help maintain infiltration and pollutant removal rates and significantly prolong the life of the pavement (Hunt and Collins, 2007; Barrett, 2008). Unless maintained properly, complete clogging may require replacement of the entire system (Scholz and Grabowiecki, 2007).

X. COMPARATIVE SUMMARY OF BIORETENTION AND PERMEABLE PAVEMENTS

With regard to pollutant removal capacities, both bioretention cells and permeable pavements are highly capable of attenuating metals in total and dissolved fraction. Table 18 illustrates side by side comparison of metal removal efficiencies for both technologies. Removal efficiency ranges shown are taken from Table 16 and Table 17. With the exception of copper, both technologies are comparable in their ability to attenuate dissolved zinc and lead. Published data on the removal of dissolved copper is not consistent and ranges from export to very high attenuation rates for both bioretention and permeable pavements (Trowsdale and Simcock, 2011; Barrett, 2008; Legret et al., 1996; Brattebo and Booth, 2003; Caltrans, 2014a; McIntyre et al., 2014). High removal rates for total copper fraction can be achieved by both control measures (Drake et al., 2014; Barrett, 2008; David et al., 2015; Hunt et al., 2008).

Because dissolved copper has a high affinity to organic matter, permeable pavements might not be as effective as bioretention cells in attenuating this metal because of an intrinsic relative lack of organic constituents. Most of the materials used in the construction of permeable pavements are generally chosen for load bearing and infiltration capacities. This might not be the case for interlocking pavements that use vegetation to fill the gaps. Additional research in dissolved copper control by both technologies is warranted.
Table 18: Summary of Metal Removal Efficiencies (%) by Bioretention and Permeable **Pavement.** This table summarizes data taken directly from Table 16 and Table 17. Negative values indicate pollutant export.

Pollutant		Bioretention	Permeable Pavements
Copper	Total	-40 - 83	33 - 62
	Dissolved	-26 - 70	-33 - 89
Lead	Total	31 - 90	78 - 88
	Dissolved	7 – 88	32 - 80
Zinc	Total	61 – 99	62 - 80
	Dissolved	77 – 99	37 - 97
PAHs	Total	90 - 95	-

Side by side comparison of PAHs removal rates is not possible since published data was not found for permeable pavements. This is a considerable data gap. As discussed earlier however, permeable pavements could be expected to perform well in retaining PAHs, since removal rates for total suspended solids are positive (i.e., 64 to 90%). In comparison to metals, attenuation rates for PAHs with bioretention are consistently high with a narrow range of 90 to 95%. Since portions of San Francisco Bay Estuary are impaired due to PAHs, this technology appears to be viable in treating and attenuating these pollutants.

Similar to metals, both technologies show highly variable results in treating nutrients. This is an important planning consideration especially in areas where nutrient loads are of concern. The tradeoff between desired infiltration rates and nutrients removal rates has to be balanced out for both technologies. An anaerobic zone would need to be created for denitrification to occur which can compromise infiltration rates. Even though there is only one study by David et al. (2015) that found export of methylmercury in bioretention cells due to anaerobic conditions, no such studies were found for permeable pavements.

Appropriate maintenance for both technologies is important to maintain their effectiveness. Both systems tend to clog, requiring different types of maintenance. Bioretention requires periodic landscape type maintenance (i.e., mulch replacement and vegetation tending) as well as trash removal to minimize clogging of the inlets and outlets. If the system is located in an area with known high pollutant loads, periodic assessment of the media's sorption capacity will be needed to ensure continuous pollutant attenuation. What constitutes periodic will depend on the type of media used, pollutant loads, use of vegetation or lack thereof, and storm characteristics. Permeable pavements on the other hand require vacuuming and sweeping to remove surface sediments as well as sediments trapped in the pores of the upper layer. Unless maintained properly, the system can clog to a point of no return, requiring complete replacement. Specialized cleaning vehicles equipped with both pressure washing and vacuum equipment have been developed and are being used in Europe to maintain permeable pavement functionality (Barrett, 2008). Similar to bioretention cells, the degree of clogging and the frequency of cleaning will be site specific and depend on the degree of sedimentation and associated particle size, the type of permeable pavement used and storm characteristics.

Given the variability of climate conditions within the greater San Francisco Bay Area, the effects of semi-arid and sub-freezing conditions on both technologies is in need of consideration. A few studies to date have examined the effects of prolonged wetting and drying conditions on bioretention cell functionality. So far, the results have been mixed concerning dissolved metals but generally positive otherwise. Long-term multiyear studies are lacking and are needed to generate more comprehensive and reliable data. No published studies were located that examined the pollutant removal performance of permeable pavements in semi-arid environments. Experience with pervious pavements in cold climates has been generally favorable with some indications of a winter maintenance cost benefit from reduced surface road freeze (Roseen et al., 2012).

Making a single statement in terms of which technology is better at producing cleaner effluent is not justified as both bioretention and permeable pavements, as demonstrated by the case studies reviewed here, perform very well. The choice between the two would more likely be driven by: 1) treatment goals; 2) watershed conditions; 3) site specific settings such as local runoff patters, influent pollutant loadings, local geomorphology, etc.; 4) existing infrastructure; 5) space limitations; 6) land use patterns; 7) local policies and incentives; 8) nature of the receiving waters; and 9) public involvement. Coordination between different municipalities and between projects within a single municipality would need to be aligned to ensure most effective use of these LID control measures. More likely than not, the use of both technologies in the treatment train set up would probably produce the best results.

XI. MANAGEMENT RECOMMENDATIONS

 As stated earlier, both bioretention and permeable pavements show mixed results in treating copper in the dissolved fraction (Brattebo and Booth, 2003; Legret et al., 1996; Barrett, 2008; Caltrans, 2014a; McIntyre et al., 2014; Trowsdale and Simcock, 2011). Because copper is a pollutant of concern in the San Francisco Bay Estuary, this uncertainty needs to be addressed. Further study of leaching mechanism(s) is warranted. Once there is a more robust understanding, solutions aiming to prevent leaching could be developed.

2. The research into bioretention and permeable pavements technology primarily comes from Europe, Canada, Australia, and North and Southeast United States. Very few bioretention cells have been studied in a semi-arid environment such as the one found in the San Francisco Bay Area (David et al., 2015; Caltrans, 2014a). Long-term studies on the effects of prolonged wetting and drying on pollutant treatment effectiveness for both technologies are essential to ensure long-term viability in local settings.

3. Since PCBs and methylmercury are the two major pollutants in the San Francisco Bay Estuary, evaluating both technologies for long-term treatment effectiveness targeting these two pollutants, would be crucial, especially in light of the recent Phase I MS4 NPDES requirements for Green Infrastructure Plans and PCBs and methylmercury load reduction goals. If effective, these two technologies can help accomplish both at the same time. The concerns over potential methylation inside bioretention cells should also be addressed.

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4. It appears that the Bay Area municipalities are not doing routine and consistent water quality assessment on the existing bioretention and permeable pavement facilities. Instead, the Bay Area Stormwater Management Agencies Association has modeled removal rates for metals, PCBs, and total mercury for bioretention cells only, using removal rates data from the International Stormwater BMP Database and twenty-year old stormwater quality data as influent input (GeoSyntec, 2013). Removal rates for PCBs and total mercury were modeled using removal efficiency data for total suspended solids. To determine the applicability of International Stormwater BMP Database data to local conditions, the data was compared to only one local bioretention cell monitored for four storms producing four data points. It is unclear how exactly the comparison was done, but using data from one study with four data points seems inadequate. Developing and implementing long term water quality monitoring plans for bioretention cells and permeable pavements (and other types of LID control measures for that matter) to assess treatment effectiveness, given local conditions and local maintenance regimes, is essential for assessing overall effectiveness as well as establishing long term trends. BASMAA plans to conduct additional water quality monitoring at one more site for a limited number of total and dissolved pollutants such as PCBs, mercury, copper, and PAHs (GeoSyntec, 2013). Given that one of the bioretention studies by David et al. (2015) found export of methylmercury, monitoring for methylmercury, at least initially, is important given its great environmental concerns.

5. The most recent Bay Area wide assessment and analysis of stormwater quality and toxicity is twenty years old (Woodward-Clyde, 1996). Relying on twenty-year-old data for decision-making might not be effective and realistic. Municipalities regulated under the NPDES program are required to conduct routine annual stormwater sampling. However, the sampling regimes are not comprehensive. Obtaining new and synthesizing already existing recent stormwater quality data could serve both as a baseline for future assessments and could be used to assess the effectiveness of stormwater treatment in the Bay Area over the last twenty years.

6. As stated earlier, no studies were successfully located that assessed permeable pavement capabilities at attenuating PAHs. Given that the State of California plans to complete TMDLs for PAHs by 2019 and the recent push to "green" the Bay Area's stormwater infrastructure,

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investing in this specific research topic could prove very useful in light of TMDLs attainment requirements.

XII. CONCLUSION

This research paper evaluated effectiveness of bioretention and permeable pavement technology at treating PAHs and common heavy metals found in typical stormwater. Numerous case studies were reviewed and analyzed to determine treatment effectiveness. Both technologies are effective at treating metals with the exception of dissolved copper. Data on attenuating dissolved copper fraction is not consistent and requires further study. Use of permeable pavements in attenuating PAHs is conceivable in theory but the lack of published studies on the topic is a data gap. Data on treatments of PAHs with bioretention is promising and shows consistently high removal rates. Making a single statement in terms of which technology is better at producing cleaner effluent is not justified, as both performed well with some already mentioned exceptions. Most likely, the use of both technologies in the treatment train set up would probably produce the best results.

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