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# **The Effect of Asphalt Pavement on Stormwater Contamination**

An Interactive Qualifying Project Report

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by

Andrew F. Nemeth

Devon A. Ward

Walter G. Woodington

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Approved:

Professor Paul P. Mathisen, Major Advisor

## **Executive Summary**

One of the greatest pollution problems in the world today is the threat to safe drinking water. Less than 1% of the water on earth is clean and available for potable drinking water. The sources of human drinking water are a mixture of groundwater aquifers and surface water reservoirs. It is vitally important to the sustainability and safety of society that these water sources be protected from pollutants. A significant source of pollution to drinking water supplies comes from the discharge of untreated or under treated stormwater runoff.

Stormwater runoff occurs naturally during precipitation when the ground cannot absorb all of the rainfall. However, with the increase in man-made impervious surfaces, such as roads, rooftops, and parking lots, the volume of stormwater runoff has drastically increased. As the runoff flows over the land or impervious surfaces, it accumulates debris, chemicals, sediment or other pollutants that can drastically impact water quality. One of the largest contributions of pollution to stormwater runoff is from roadways.

The rise of the automobile in the early 20th century created an unprecedented demand for an affordable, tough, and impervious pavement with which to construct better roads. This need was met with the creation of asphaltic concrete, or more commonly known as hot mix asphalt pavement. The advent of asphalt pavement allowed for the rapid expansion of human society, allowing the population to sprawl outwards from cities. As automobiles became more prevalent in society, the amount of asphalt pavement increased exponentially. Today 95% of the paved roads in America are paved with hot mix asphalt, covering more than 4 million kilometers of roadway.

There has been a great deal of scientific attention given to pollutant deposition on roadways from automobiles. Sources include vehicle exhaust, tire wear, accidents, lubricating

oils, and deicing operations. These contributing factors result in oils, heavy metals, salts, and other chemicals being put down on the road surface, which can then wash off during the first-flush period of a storm. While there is an abundance of research into this phenomenon, there is relatively little concern given to pollution coming from the roadway material itself.

Furthermore, due to the nature of the bituminous binder used in hot mix asphalt, it is known that there are harmful chemicals present in the pavement. Very little is known however, about the specific concentrations of such constituents, or the extent to which they leach out of the pavement and into stormwater runoff. This project investigates the presence and concentration of several selected petroleum hydrocarbons in runoff from asphalt pavement. Field samples taken from various local sites were collected during the first-flush period of a rainstorm, in addition to laboratory-generated runoff samples from both virgin hot mix asphalt and reclaimed asphalt pavement.

The samples generated during this project were analyzed using several methods of detection. These include fluorometry, high performance liquid chromatography (HPLC), and total petroleum hydrocarbon (TPH) analysis. In particular the high performance liquid chromatography has not commonly been used to detect petroleum hydrocarbons, but offers a fresh perspective as to the chemical makeup of samples as it offers exceptionally low detection limits.

Overall, reclaimed asphalt pavement (RAP) runoff was shown to have higher concentrations of petroleum hydrocarbons and greater complexity than virgin asphalt. Fluorescence values from the field fluorometer as well as absorbance value integrands from the HPLC and TPH concentrations done by a third party were universally higher in the RAP samples compared to the virgin asphalt samples. This shows that RAP has higher petroleum hydrocarbon

concentrations. The HPLC results show greater numbers of peaks in the RAP samples as compared to the Virgin samples showing that RAP contains a larger number of unique petroleum hydrocarbons and are therefore is more complex. From the HPLC results the most complex sample was a field sample from a high traffic road.

The most polluted laboratory sample, a shake table sample, had concentrations of petroleum hydrocarbons far beyond federal regulations. In comparison, all of the field samples and laboratory samples modeling realistic conditions were either below detection or had very low petroleum hydrocarbon concentrations. It was found that asphalt does contain carcinogenic petroleum hydrocarbons but these molecules seem to be leaching into runoff at very low concentrations. However, as usage and wear is increased, this concentration in runoff can increase as shown by the shake table samples. These carcinogenic petroleum hydrocarbons, most notably Benzo[a]pyrene, are harmful and should be investigated further.

The project also investigated the current regulations and policies in place regarding stormwater treatment and management practices. Additionally, recommendations for changing or creating policies regarding the chosen constituents and their allowable limits in the environment based on their toxicity are also presented.

Given the wide scope of the problems involving hydrocarbons and pavement, there is still much more investigation that can be done into the emerging problem of petroleum hydrocarbons leaching from asphalt pavement. One goal for this project is to raise attention to a matter that has widely been overlooked, and one that may be far greater in magnitude than has been yet realized. While the concentrations of toxic hydrocarbons entering our environment through stormwater runoff from asphalt surfaces may be relatively low, when the extent of roadways and

parking lots in the United States alone is considered, the total volume of deposited toxins may be significant.

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## **Abstract**

Polycyclic aromatic hydrocarbons (PAHs) leaching from asphalt pavement is both an ecological and human health concern. Three constituents of greatest concern were selected from scientific research for investigation. Stormwater runoff samples from field sites were collected, and laboratory samples were created from virgin and reclaimed asphalt for chemical analysis. Methods of analysis included high-performance liquid chromatography, fluorometry, and gas chromatography. These were used to determine the extent to which PAHs leach into stormwater runoff. Existing environmental policy was reviewed and new policy was proposed in light of findings.

## **1. Introduction**

### **1.1 Background**

Water is essential to the survival of every living species on earth. While water is the single most abundant resource on our planet, only about 1% of the water on earth is available for human use. Society is dependent on clean drinking water supplies. In the United States, residents and businesses obtain their drinking water by drilling wells into ground water or by pumping water from reservoirs and rivers. It is imperative that these drinking water supplies are free of contaminants and toxic pollutants that can harm human health. Unfortunately in today's rapidly developing society, potable drinking water is at constant risk of contamination from man-made constituents.

Extensive research has been devoted to finding the sources of many man-made constituents entering water supplies, and how to prevent or treat them. There are laws and policies in place that regulate and govern the usage and disposal of a large number of known harmful chemicals, however, there are newly-emerging contaminants being discovered every day in the environment and in water supplies. As these new constituents gain attention, it has become clear that there is a lack of understanding in the source of these chemicals, as well as a lack of governmental policy in place to protect water supplies and human health.

### **1.2 Problem Statement**

It is vitally important that public drinking water supplies are safe for human consumption and free of contaminants. Ground and surface water supplies are maintained by natural precipitation. When water falls to the earth in the form of rain or snow, known as stormwater, some of it runs off of the surface of the ground into stormdrains or streams, some falls into water

bodies, and some soaks directly into the ground. One of the leading causes of water supply pollution is the discharge of untreated stormwater runoff into surface waters.

Human development has caused a drastic increase in the amount of impervious surfaces in the environment. This increase in impervious surfaces, largely caused by pavement and roofs, has resulted in much higher levels of stormwater runoff entering water supplies. When stormwater flows over man-made impervious surfaces it collects pollution put down on that surface, primarily caused by other human activity. This includes automotive pollution put down on roads and parking lots such as gasoline, motor oil, and heavy metals from vehicles. While much is known about the man-made pollution put down on roads by foreign sources, the impervious surface itself has largely been overlooked as a potential source of pollutants.

Asphalt pavement covers 95% of the total paved roads in the United States (Federal Highway Administration (FHWA), 1997). With the amount of surface area of asphalt pavement in the United States alone, and the associated stormwater runoff it causes, there is an enormous potential for harmful chemicals in this runoff to become deposited in human water supplies. It is known that many of these chemicals may be attributed to distributed sources (or non-point sources) of contaminants that are deposited on the land surface, and end up being washed off by the runoff. There is also a possibility that the asphalt itself may contribute to some of these contaminant loadings. This project investigates the presence of petroleum hydrocarbons in asphalt pavement and their harmful effects on human health. The concern is that these constituents are present in asphalt pavement and are potentially leaching out of pavement materials into stormwater runoff and into local ecology and drinking water supplies.

### **1.3 Objectives & Scope**

The focus of this Interactive Qualifying Project (IQP) is on asphalt pavement and its effects on stormwater runoff quality. The goal is to determine the extent to which asphalt leaches contaminants into stormwater. The areas of research consisted of which constituents are present in asphalt runoff, which are of primary concern, and their harmful effects on ecology and human health. Additional research into current stormwater runoff management practices and their effectiveness at removing these constituents was also completed, as well as a study into the regulation and policies in place addressing these concerns.

The results of this project consist of policy update recommendations on emerging constituents with harmful effects on human life that have not yet been fully investigated or regulated. The results will reexamine current stormwater collection and treatment practices and their effectiveness at controlling and removing the constituents of potential concern.

These results are of concern to public health agencies, as well as environmental protection agencies, and organizations concerned with drinking water quality. These agencies may consist of the United States Environmental Protection Agency, The Agency for Toxic Substances and Disease Registry, and more local organizations such as the Massachusetts Water Resource Authority. Toxicologists may be particularly interested in the results of this project as it addresses the presence of a highly complex mixture of harmful petroleum hydrocarbons in asphalt pavement, an extremely large point source that has been mostly overlooked previously.

### **1.4 Approach & Methodology**

The goal of this project was met through a combination of literature research, field sample collection, laboratory asphalt production, and chemical analysis. The project began with

an investigation into the potential petroleum hydrocarbons present in asphalt pavement materials. In depth research into the harmful effects of these constituents led to a selection of three chemicals for further analysis. The current policy and regulation of the selected constituents was investigated, and used later as a framework for additional policy proposal in conjunction with the laboratory findings.

In order to explore the presence and extent of the selected constituents in asphalt pavement, field samples of roadway stormwater runoff were collected from local areas of concern. As a basis for comparison, laboratory samples of asphalt were made using fresh asphalt as well as reclaimed asphalt pavement. Experiments were then conducted on the produced asphalt samples in order to generate water samples for analysis. The experiments were designed for the comparison of concentration levels of constituents between cases designed for producing the maximum potential concentration levels, and a laboratory controlled procedure designed to simulate a realistic roadway runoff situation.

The water samples collected from the field and laboratory procedures were tested using three different methods of analysis. On campus, fluorometry analysis was performed in order to gain a baseline comparison of the level of contamination of polycyclic hydrocarbons between the samples. Further analysis was conducted using high performance liquid chromatography (HPLC) for the three constituents of main concern. HPLC was selected because it shows overall chemical complexity and allows for exceedingly low detection limits. Finally, a representative selection of the samples were sent to a third-party laboratory for analysis of total petroleum hydrocarbon (TPH) content to provide an additional layer of information regarding sample contamination.

## **1.5 Outline**

Chapter 2 of this report is the literature review, which contains background information necessary for a good understanding of stormwater, the asphalt industry, the harmful chemicals being investigated, and current policy surrounding these topics. Chapter 3 describes in detail the procedures and methodology used in the creation of this report. Chapter 4 is the results section of this report, and contains analysis of the data produced from the laboratory procedures. Finally, chapter 5 presents final conclusions and recommendations for future work on the subject matter.

## **2. Literature Review**

The following is a comprehensive review of the many facets comprising this Interactive Qualifying Project. This project focuses on the presence of petroleum hydrocarbons in asphalt pavement, and the extent to which they leach into stormwater runoff and subsequently the surrounding environment. It is important, therefore to understand the composition of hot mix asphalt, its production process, and the harmfulness of the constituents found in it. Attention must also be given to the nature of stormwater runoff, and how it is treated prior to reentering the drinking water supply.

### **2.1 Stormwater Runoff**

Ground and surface water supplies are maintained by natural precipitation. When water falls to the earth in the form of rain or snow, known as stormwater, some of it runs off of the surface of the ground into stormdrains or streams, some falls into water bodies, and some soaks directly into the ground. Water that seeps into the ground travels downward due to gravity until it reaches a depth where the soil and rock are saturated with water. Water at this level below ground is known as ground water. The New England area naturally features subsurface rock and soil that contains large quantities of ground water which can be used for drinking water.

Stormwater runoff is generated when precipitation from rain and snowmelt events flows over land or impervious surfaces and does not percolate into the ground. As the runoff flows over the land or impervious surfaces (paved streets, parking lots, and building rooftops), it accumulates debris, chemicals, sediment or other pollutants that could adversely affect water quality if the runoff is discharged untreated. The primary method to control stormwater discharges is the use of best management practices (BMPs). In addition, most stormwater



discharges are considered point sources and require coverage under a National Pollutant Discharge Elimination System permit (U.S. Environmental Protection Agency, 30 Apr. 2009).

For the past two decades the rate of land development across the country has been more than twice as high as the rate of population growth. If unchecked, the increased impervious surface (paved roadways and parking lots) associated with this development will increase stormwater volume and degrade water quality, which can harm lakes, rivers, watersheds, and local ecology. The best way to mitigate stormwater impacts from new developments is to use practices to treat, store, and infiltrate runoff onsite before it can affect water bodies downstream. Innovative site designs that reduce imperviousness and smaller-scale low impact development practices dispersed throughout a site are excellent ways to achieve the goals of reducing flows and improving water quality (U.S. Environmental Protection Agency, 24 May. 2006. Web. 14 Oct. 2009).

## **2.2 Asphalt Pavement**

### **2.2.1 Production process**

Asphaltic concrete or more commonly known as simply hot mix asphalt (HMA) contains three main materials. The first is coarse aggregate such as crushed rocks and small stones. The second is fine aggregate such as sand or the dust washed off of crushed stones. These first two are generally obtained from local sources, quarries or gravel pits, and are mineralogically similar to the rock surrounding the future roadway. The third and most important material is the binder, in this investigation, bitumen. The mixture proportion of these three main components affects roadway strength and durability. The requirements for both of these are based on location, climate, and usage of the roadway which varies city to city and state to state. While there may be

some variation in the mixture, typically the coarse aggregates and sand make up approximately 95 percent of the mix and the binder makes up the remaining five percent by mass.

Bitumen, the binder, also known simply as asphalt, is the residual portion left over from the refining process of crude petroleum. The refining process separates the bitumen from lighter oils and fuel oils which include: kerosene, diesel oil, butanes and the components to gasoline. The bitumen is composed of long chained hydrocarbons found in the crude oil, which have very high vaporization temperatures and remain after the smaller, lighter molecules have been refined away (Speight, 2006). The types and content of the long chained hydrocarbons found in bitumen varies batch by batch because the crude oil, from which bitumen is derived, varies by depth and content of the different oil fields around the world (Asphalt Institute, The, 1990). At room temperature the bitumen binder is solid because of its high viscosity and must be heated to a temperature of approximately 150°C before it becomes liquid and properly workable.

Two types of hot mix asphalt are used in the construction of roadways: virgin asphalt and reclaimed asphalt pavement. Virgin asphalt is comprised of aggregates, either recycled from other projects or freshly quarried, as well as bitumen binder directly from the refining process. Reclaimed asphalt pavement (RAP) is pavement which has been removed from the roadway and typically reprocessed. RAP contains both asphalt binder and aggregates. The RAP is generated during reconstruction and repaving when layers of the road surface are milled off or the full depth of asphalt pavement is removed. After this collection process the RAP is brought to a central facility to be processed before it can be reused as pavement. This process involves crushing, filtering and optionally mixing in an additive to change its properties such as binder, aggregate or various rejuvenating and softening compounds (ASTM, 1980).

### 2.2.2 Chemical composition

The constituents of concern in this investigation come from the materials from which the pavement is created. The aggregate is typically from local sources so it is not of human or ecological concern. However, the bitumen binder is composed of long chained hydrocarbons which could be of concern.

Virgin asphalt contains only aggregates and binder. So its constituents of concern come only from the binder. RAP however contains pollutants, deposited on the road surface during use, and possibly rejuvenating agents in addition to aggregates and binder. Thereby constituents of concern in RAP could also come from these two additional sources which are not involved in the creation of new hot mix asphalt.

Pollutants and concentrations on the road surface are linked to traffic and usage. Sources include vehicle exhaust, tire wear, accidents, lubricating oils, and deicing operations, among others (Mangiani, 2003). These will contain various sized hydrocarbons, metals, and salts. Hydrocarbons, specifically polycyclic aromatic hydrocarbons, are present in exhausts, fuels, and oils. Copper is present in brake linings, cadmium in tires, and zinc in roadway barriers and tires. Sodium, calcium, and chlorine, as salts, are found in winter time deicing compounds as well as zinc and cadmium but not to the same extent.

The rejuvenating agents added to reclaimed asphalt mixes are usually comprised of simple paraffins. These are “soft” asphalts and small, monocyclic hydrocarbons and are used to increase viscosity. These materials are typically found in most asphalt binders. The purpose of these rejuvenating agents is to restore the binder compounds which are leached out of asphalt by time and water. As these are present in virgin asphalt mix, they shall not be considered a complicating factor in the analysis.

Tests of Reclaimed Asphalt Pavement (RAP) would account for both pollutants deposited on the surface of roadways as well as any pollutants still remaining in asphalt. One such series of tests was performed in Florida. The tests were performed in leaching columns using deionized water and other leaching agents intended to mimic the most severe natural precipitation cases, such as an acid solution to mimic acid rain. These experiments concluded that the highest concentration leachate coming off of the asphalt was the polycyclic aromatic hydrocarbon (PAH) Anthracene at 2100 micro-g/L. Other important leached constituents were Benzo[a]pyrene at 0.2 micro-g/L, Pyrene at 210 micro-g/L, and Benz[a]anthracene at 4 micro-g/L (Brantley, 1999).

Polycyclic aromatic hydrocarbons found in roadway runoff and first flush stormwater collection analysis include the four constituents above as well as many others. In varying concentrations these include; Benzo(ghi)perylene, Chrysene, Coronene, Dibenz(ah)anthracene, Fluoranthene, Fluorene, Indeno(cd)pyrene, Naphtalene , Phenanthrene and Pyrene (Mangiani, 2003) (Krein, et al., 2000).

It is important to note that the polycyclic aromatic hydrocarbons listed above should not be present in the residual portions of the refining process because of their small molecular size. This means that bitumen straight out of the refinery should not contain any of these constituents. These compounds which the above tests found in runoff and in leaching column samples could either come from roadway usage or the changed chemical composition of bitumen binder due to asphalt production.

### **2.2.3 Extent of Use**

Hot mix asphalt (HMA) is a widely used paving material in the United States. There are many types of pavers besides asphalt including Portland concrete and tarmac. Asphalt paving has

been the primary paving technique in the United States since the 1970s. Since at least 1909 roads in the United States have been paved with asphalt. 95% of the estimated 4 million kilometers of paved roads in the US are currently paved with asphalt. According to the Federal Highway Administration 80% of the RAP removed each year during repaving projects in the United States is reused in roadway construction. This totals approximately 73 million tons of RAP every year (Federal Highway Administration (FHWA), 1997). Asphalt is widely used and widely recycled therefore asphalt pavement and its effects on water quality should be better understood to protect human health and the health of the ecosystems surrounding roadways.

### **2.3 Ecological and Health Concern of Constituents**

The majority of products deposited into the environment by the asphalt paving process are thought to be products of pyrolysis (a form of incineration that decomposes organic materials by heat in the presence of oxygen) of tiny branches of asphaltenes. Asphaltenes are large, bulky hydrocarbons with wildly variable and highly branched structures that make the asphalt composition resist cracking by lying between long-branch bituminous hydrocarbons. This pyrolysis generates a wide variety of hydrocarbons of variable size and stability. This report will be concerned with three products: benzo[a]pyrene, pyrene, and anthracene, due to their high toxicity and ease of detection with HPLC.

Benzo[a]pyrene, pyrene, anthracene, and other similar pyrolysis products are not water-soluble. Their only point of entry into ecological systems as well as stormwater systems is generally thought to be by sorbing from fine particulate matter in the immediate area of the location of the pyrolysis. This model is substantiated by the discovery of PAH accumulation on silty river beds and other such locations (Sutton, 2009).

The principle of biological magnification or bioaccumulation states that the concentration of substances in an ecology can increase across the higher ends of the food chain because many deleterious compounds (such as PAHs) cannot be broken down by metabolic processes. Ergo, this can unbalance entire ecologies: toxic products can affect predators higher up in the food chain (Sutton, 2009) by inducing cancer or even death. Groundwater contaminated with PAHs has the potential to affect human populations by this mechanism via accumulation of toxic products in livestock and comestible plants (Karacık).

The general heading of PAHs will be considered together because of their tendency to behave as endocrine-disruptors. This tendency is due to the fact that many hormones, cell-signalers, and steroid derivatives have similar, bulky multi-ringed structures. PAHs therefore have the potential to act as enzymatic inhibitors with the capability of disrupting a number of important biological processes, such as tumor suppression and programmed cell death.

A general concern is growing regarding the presence of benzo[a]pyrene (BaP) in groundwater. BaP is one of the only PAHs recognized by the International Agency for Research on Cancer as a definite carcinogen. BaP appears to enter the environment mainly through combustion of fuels, burning of coal, and the laying of asphalt. This contaminant has a strongly cytotoxic effect in concentrations over  $0.25 \cdot 10^{-6}$ g due to its metabolic products (Tarantini, 2009). Upon ingestion, BaP is converted to a diol epoxide by an enzyme known as cytochrome P450. This diol epoxide differs from BaP in that it features two hydroxyl groups and an epoxide oxygen (see figure 2.1). This reaction occurs in order for a cell to be able to “clean up” the compound better through metabolism; however, the production of this metabolite is actually the source of the compound’s toxic properties.

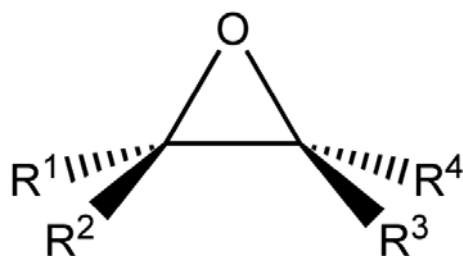


Figure 2.1 – An Epoxide

The diol epoxide metabolite has the particular capability to insert itself into a double helix and break strands of DNA by binding with guanine nucleotides, as shown below in figure 2.2. Studies of workers in tin mines and aluminum factories have revealed a relative risk of 1.8-2.7 and 2.0-6.7 for cancers of the lungs and bladder, respectively (Mastrangelo, 1996). The BaP carcinogenicity mechanism is perhaps the best understood due to its high toxicity. Several sources in scientific literature suggest that other PAHs have a similar pathology of harm (McCarty, et al., 2009). Complexing of PAHs and DNA could result in the mutation of regions of exposed DNA that are involved in the production of cellular reproduction inhibition factors or tumor inhibitors. The mutation of these inhibition factors and tumor inhibitors, such as p53, a gene classically referred to as the “guardian of the cell” which protects it from becoming cancerous, is the cause of the vast majority of cancers (Ruggeri, 1993).

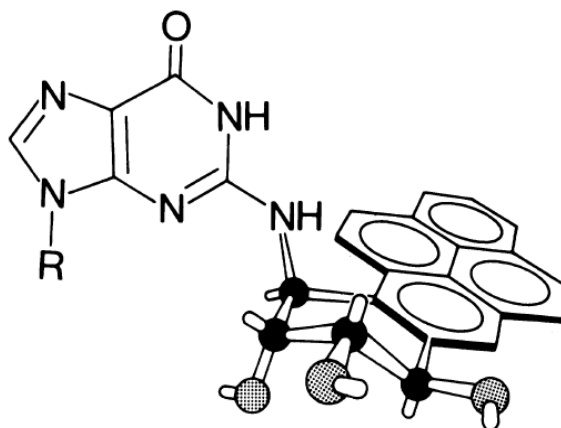


Figure 2.2 - A Benzo[a]Pyrene-diol-epoxide (right, rotated) interacting with a guanine nucleotide (planar)

The absorption of generalized benzene-soluble (that is, non-polar) material is the benchmark for maximum accumulation for PAH, as there is no specific guideline regarding those compounds. The current limit imposed by the EPA is  $0.2\text{mg}/\text{m}^3$ . This is a gaseous measure; there is no aqueous concentration limit. Constant exposure to PAH in heavy industry workers revealed a 1.2-1.4 relative risk for development of lung cancer and a 2.2 relative risk for bladder cancer, as shown in Table 3.1 below (Mastrangelo, 1996). One previously-overlooked concern is that the majority of studies of PAH take into account only single exposure to one pure compound, whereas most carcinogenesis by PAHs are likely to be caused by a prolonged exposure to a complex mixture of compounds acting in concert.



**Table 2.1 - Cancer in Asphalt Paving Industry**

Author, country, and occupation	Number of study subjects	Dates of case ascertainment	Type or site of condition	Number of deaths or cases	Risk ratio	95% CI or P value
Hansen (1989a), Denmark, mastic asphalt workers <sup>b</sup>	679	1959–1986	All cancers	74	SIR 1.95 <sup>c</sup>	1.53–2.44
			Lung cancer	27	SIR 3.44 <sup>d</sup>	2.27–5.01
			Mouth	2	SIR 11.11 <sup>d</sup>	1.35–40.14
			Oesophagus	3	SIR 6.98 <sup>d</sup>	1.44–20.39
			Rectum	7	SIR 3.18 <sup>d</sup>	1.28–6.56
Hansen (1991), Denmark, mastic asphalt workers <sup>c</sup>	679	1959–1986	All causes	148	SMR 1.57 <sup>d</sup>	1.34–1.85
			All cancers	62	SMR 2.29 <sup>d</sup>	1.75–2.93
			Lung cancer	25	SMR 2.90 <sup>d</sup>	1.88–4.29
			Non-lung cancer	37	SMR 2.00 <sup>d</sup>	1.41–2.76
			Bronchitis, emphysema, asthma	9	SMR 2.07 <sup>d</sup>	0.95–3.93
Engholm et al. (1991), Sweden, pavers <sup>f</sup>	2572	1971–1985	All causes	96	SMR 0.69	NR
			All cancers	47	SIR 0.86	NR
			Stomach cancer	5	SMR 2.01	NR
			Stomach cancer	6	SIR 2.07	NR
			Lung cancer	7	SMR 1.10	NR
			Lung cancer	8	SIR 1.24	NR
Bender et al. (1989), USA, highway maintenance workers <sup>g,h</sup>	4849	1945–1984	All causes	1530	SMR 0.9	0.86–0.96
			All cancers	274	SMR 0.83	0.73–0.94
			Lung cancer	57	SMR 0.69	0.52–0.90
			Mouth, pharyngeal cancer	2 <sup>i</sup>	SMR 11.10	1.30–40.10
			Gastrointestinal cancer	3 <sup>j</sup>	SMR 5.82	1.20–17.00
			Prostate cancer	11 <sup>k</sup>	SMR 2.98	<i>P</i> < 0.01
			Kidney, bladder, other urinary organ cancers	7 <sup>l</sup>	SMR 2.92	1.17–6.02
			Leukaemia	8 <sup>m</sup>	SMR 4.49	1.94–8.84
Partanen et al. (1997), Finland, road pavers (males only)			Lung cancer	NR	SMR 1.5	1.2–1.9
			Lung cancer	NR	SIR 1.4 <sup>n</sup>	0.9–1.9

Table from National Institute for Occupational Safety and Health (Wess)

This data demonstrates that exposure to asphalt fumes poses a serious health risk. While this project is mostly concerned with runoff from asphalt, it can be surmised that because the PAHs that result from pyrolysis are nonpolar and they run off in water, fine particulate matter has sorbed the PAHs that would be in the fumes otherwise. The compounds in the fumes are very likely the same as those found in runoff due to pyrolysis. The wide varieties of cancer caused by the fumes imply that they tend to cause cancer in all systems involved in ingesting and processing the fumes and their toxic products, especially the mouth and throat (particularly visible in Hansen and Bender's data by examining the risk ratios).

## **2.4 Stormwater Policy**

The National Pollutant Discharge Elimination System (NPDES) Stormwater Program regulates stormwater discharges from several sources. The 1972 amendments to the Federal Water Pollution Control Act (known as the Clean Water Act or CWA) provide the statutory basis for the NPDES permit program and the basic structure for regulating the discharge of pollutants from point sources to waters of the United States. Section 402 of the CWA specifically required the EPA to develop and implement the NPDES program. The CWA gives the EPA the authority to set effluent limits on an industry-wide (technology-based) basis and on a water-quality basis that ensures protection of the receiving water. The CWA requires anyone who wants to discharge pollutants to first obtain an NPDES permit, or else that discharge will be considered illegal. The CWA also allowed the EPA to authorize the NPDES Permit Program to state governments, enabling states to perform many of the permitting, administrative, and enforcement aspects of the NPDES Program. In states that have been authorized to implement CWA programs, the EPA still

retains oversight responsibilities (U.S. Environmental Protection Agency, 10 Feb. 2009. Web. 13 Oct. 2009).

Three potential sources covered by the NPDES Stormwater Program are: municipal separate storm sewer systems (MS4s), construction activities, and industrial activities. This project will be focusing mostly on MS4s, particularly paved roadway runoff. This permitting mechanism is designed to prevent stormwater runoff from washing harmful pollutants into local surface waters such as streams, rivers, lakes or coastal waters (U.S. Environmental Protection Agency, 2 Dec. 2008. Web. 14 Oct. 2009).

Polluted stormwater runoff is commonly transported through MS4s, from which it is often discharged untreated into local waterbodies. To prevent harmful pollutants from being washed or dumped into an MS4, operators must obtain a NPDES permit and develop a stormwater management program. There have been two separate phases enacted by the U.S. Environmental Protection Agency since the inception of the Clean Water Act that deal with the NPDES permitting. Phase I, issued in 1990, requires medium and large cities or certain counties with populations of 100,000 or more to obtain NPDES permit coverage for their stormwater discharges. Phase II, issued in 1999, requires regulated small MS4s in urbanized areas, as well as small MS4s outside the urbanized areas that are designated by the permitting authority, to obtain NPDES permit coverage for their stormwater discharges. Generally, Phase I MS4s are covered by individual permits and Phase II MS4s are covered by a general permit. Each regulated MS4 is required to develop and implement a stormwater management program (SWMP) to reduce the contamination of stormwater runoff and prohibit illicit discharges. An MS4 is defined as a conveyance or system of conveyances that is: owned by a state, city, town, village, or other public entity that discharges to waters of the U.S.; is designed or used to collect

or convey stormwater (including storm drains, pipes, ditches, etc.); is not a combined sewer; and is not part of a Publicly Owned Treatment Works (sewage treatment plant) (U.S. Environmental Protection Agency, 30 Apr. 2009).

The EPA outlines six minimum control measures for BMPs required for MS4s. They include public education, public involvement, illicit discharge detection and elimination, construction, post-construction, and pollution prevention (U.S. Environmental Protection Agency, 9 Jan. 2008. Web. 14 Oct. 2009). Public education is an important portion of stormwater BMPs because stormwater runoff is generated from dispersed land surfaces—pavements, yards, driveways, and roofs. Therefore, efforts to control stormwater pollution must consider individual, household, and public behaviors and activities that can generate pollution from these surfaces. These common individual behaviors have the potential to generate stormwater pollution:

- littering
- disposing of trash and recyclables
- disposing of pet-waste
- applying lawn-chemicals
- washing cars,
- changing motor-oil on impervious driveways
- household behaviors like disposing leftover paint and household chemicals

It takes individual behavior change and proper practices to control such pollution. Therefore it is important to make the public sufficiently aware and concerned about the significance of their behavior for stormwater pollution, through information and education, that

they change improper behaviors. Phase II MS4s are required to educate their community on the pollution potential of common activities, and increase awareness of the direct links between land activities, rainfall-runoff, storm drains, and their local water resources. Most importantly the requirement is to give the public clear guidance on steps and specific actions that they can take to reduce their stormwater pollution-potential (U.S. Environmental Protection Agency, 17 Sept. 2008. Web. 14 Oct. 2009).

Phase II MS4s are required to address post-construction stormwater runoff from new development and redevelopments that disturb one or more acres. This primarily includes developing strategies to implement a combination of structural and non-structural BMPs, an ordinance to address post-construction runoff, and a program to ensure adequate long-term operation and maintenance of BMPs (U.S. Environmental Protection Agency, 24 May. 2006. Web. 14 Oct. 2009).

## **2.5 Literature Review Conclusion**

The background presented above served as a basis for understanding the material addressed in this project. A broad overview of the current state of policy and concern regarding toxic petroleum hydrocarbons lead to the conclusion that more investigation was needed into the matter. Through researching the current knowledge of chemicals known to leach from asphalt pavement, the three constituents of most concern were selected for this project. The processes through which they were analyzed can be found in the methodology section of this report, which follows in chapter 3.

### **3. Methodology**

#### **3.1 Overall Methodology**

The methodology for this project consisted of several phases. The first phase was comprised of general research into current stormwater management practices, the composition and production process of hot mix asphalt, and the constituents known to be present in asphalt. Academic papers investigating both laboratory leaching column tests and field tests of asphalts were considered. From the obtained list of chemical compounds found in asphalt, further research was conducted into the harmful health effects of each chemical, and the current governmental policy and regulations regarding these constituents. This led to the selection of three constituents of most concern; pyrene, benzo(a)pyrene and anthracene. Standards for these three chemicals were then ordered to be used for future laboratory test comparison.

The second phase of the investigation consisted of stormwater sample collection and laboratory sample creation. Stormwater samples were collected from local roadways during a rainstorm, and the collection process is detailed in section 3.2. To add a level of control and sample comparison, multiple asphalt samples were created in the laboratory for testing. Two mix designs were used: one of virgin hot mix asphalt, and one using reclaimed asphalt pavement. The process followed for the creation of the asphalt samples is explained in section 3.3. Laboratory procedures were then developed to generate runoff samples from the created asphalt cylinders. These were designed to mimic stormwater runoff in both realistic and worst case scenario runoff situations. The procedures followed for generating the laboratory water samples are found in section 3.4.

The third phase of this project consisted of testing the samples. Laboratory testing was required to properly analyze the constituent content of the collected and generated samples.

Three different laboratory analysis procedures were used. The first level of testing was performed using fluorometry. Fluorometry was the most general and least precise analysis method used and served as a baseline indicator for the presence of conjugated carbon ringed molecules in the samples. The samples were then analyzed using high performance liquid chromatography (HPLC) and compared to the constituent standards to obtain a better representation of the chemical composition of the samples. To supplement the data produced through on-site analysis, a selection of samples were sent to a third-party laboratory for total petroleum hydrocarbon (TPH) testing to determine the total concentrations of petroleum hydrocarbons. A description of the procedures followed for the fluorometry and HPLC testing can be found in section 3.6.

The final phase of this project consisted of a comparison of the results obtained from the various analyses (presented in chapter 4) to current policy and governmental standards. A discussion of the findings and proposed policy change can be found in chapter 5.

## **3.2 Stormwater Runoff Sample Collection**

### **3.2.1 Collection Preparation**

A list of sites was compiled for sample collection based on a list of criteria to encompass locations of different roadway conditions with the hope of collecting stormwater samples with a high degree of content variation. The factors used for site determination included land use in the area, asphalt condition, pavement age, and traffic patterns. Additional consideration was paid to the ease of access to the site, and safety of the sample collector. Sample sites were selected in the area surrounding the WPI campus.

Table 3.1 contains the collection sites that were selected, and their associated criteria. The Grove St. and Faraday St. site was valued for its old pavement age, poor condition and industrial land use in the area. Drury St. and Park St. was selected primarily because it is a highly trafficked road. The Highland St. and Harvard St. samples were selected because the road was freshly paved.

**Table 3.1 - Sample Collection Sites & Criteria**

<b>Collection Site</b>	<b>Land Use</b>	<b>Pavement Condition</b>	<b>Pavement Age</b>	<b>Traffic Level</b>
Grove St. & Faraday	Industrial	Poor, Rutted, Broken Edges, Pot Holed	Oldest of Samples	Low
Drury St. & Park St.	Residential	Fair, Worn, Few Patches	Second Oldest of Samples	Very High
East of Highland St. & Harvard St.	Public/ Business	New	< 1 Week Old	Moderate to High
West of Highland St. & Harvard St.	Public/Business	New	< 1 Week Old	Moderate to High

Weather forecasts were monitored to anticipate a storm with significant enough rainfall for collection purposes. The ideal weather situation was determined to be a period of heavy precipitation following a lengthy dry period to maximize the concentration of deposited constituents in roadway runoff. Sample collection was performed during the first-flush period of the rainstorm, in order to collect the highest concentration of constituents. The following materials were used in the field for sample collection and storage: two sterile 40mL glass vials per site, one sterile 1 L plastic container per site, a collection scoop, a plastic funnel for transferring samples, labels, and a travel cooler for sample preservation.



### **3.2.2 Sample Collecting Procedure**

Once at the desired roadway collection field site, exact collection points were determined based on several factors. Gutters and areas of heavy sedimentation were avoided. When possible, flowing runoff was selected for collection over pooled stormwater. Additionally, longer runoff flows were desirable due to the flow passing over a larger surface area of pavement.

The collection scoop was used to capture the flowing stormwater by placing it directly in the path of flow. Care was taken to prevent any large sediment or debris from entering the sample containers. The sample was then transferred into the 40 mL vials and 1 L container from the collection scoop using the plastic funnel. This process of collection was repeated as necessary until both 40 mL vials and the 1 L container were filled with stormwater runoff. Each sample container was then labeled with the date and time of collection, as well as the site location information. The sample containers were stored in the travel cooler until returning from the field. The samples were then refrigerated to preserve them for subsequent laboratory analysis.

### **3.3 Production of asphalt samples**

Laboratory samples of virgin hot mix asphalt pavement and reclaimed asphalt pavement were created to analyze and compare the constituent content of the differently aged pavements. Virgin asphalt samples were desired for analysis because the chemical content of freshly created samples would not contain any roadway pollution put down by vehicle traffic or chemical spills that may be present in the field samples collected. Conversely, reclaimed asphalt pavement began as virgin hot mix asphalt and throughout its lifetime of use collected roadway pollution.

The increased age of the reclaimed material could also produce a different chemical content in comparison to virgin asphalt. The rejuvenation process of the reclaimed asphalt pavement can also produce different constituents in the material due to the addition of more bituminous binder, or the continuation of chemical reactions in the reheating of the material.

### **3.3.1 Pre-mix preparations**

Reclaimed Asphalt Pavement (RAP) was obtained from Aggregate Industries (AI), one of the leading companies in the construction industry. Aggregate Industries produces a wide range of construction materials including aggregates, asphalt, ready-mixed concrete, and reclaimed asphalt pavement. The RAP used in the laboratory samples created was most likely recycled from roadways in the Northeast of the United States. In order to directly compare the different contaminants leaching from the RAP and virgin asphalt samples, the mix proportions for the virgin batch were designed to match the RAP mix as closely as possible. The virgin asphalt mix design was created to match the known binder content of the selected RAP mix, which was 6% binder by mass. The aggregate gradation of the obtained RAP mix was unknown. Without this information a typical aggregate gradation was selected for the virgin asphalt mix design. Figure 3.1 shows a sample of the RAP material used, as well as the three different aggregate types selected for the virgin asphalt mix.



**Figure 3.1 - RAP & Aggregate Samples**

From left to right, AI RAP, crushed rock dust, sand, and crushed rock aggregate are depicted in the figure. Tables 3.2 and 3.3 contain the breakdown by percentage and mass of each material used in the production of these mix designs. While only 6.0 kg of each RAP and virgin material was needed for the production of the four asphalt sample cylinders, additional asphalt was produced for use in the shake table experiment which is discussed in section 3.3.1.

**Table 3.2 - Virgin Asphalt Mix Design**

<b>Material</b>	<b>% of Total mix design by mass</b>	<b>Mass</b>
Sand	42.3%	4.050 kg
Dust	18.8%	1.800 kg
Coarse Aggregate 7	32.9%	3.150 kg
PG64-28 asphalt binder	6%	0.5745 kg
<b>Total Batch size:</b>		9.5745 kg

**Table 3.3 - AI RAP Mix Design**

<b>Material</b>	<b>% Binder</b>	<b>% of Total mix design by mass</b>	<b>Mass</b>
Aggregate Industries RAP	6%	100%	9.500 kg

### **3.3.2 Batching & Mixing**

#### **3.3.2.1 Virgin Samples**

The specified mass of each selected aggregate was measured out using a laboratory scale according to the mix design proportions. The binder, measured aggregates, a 5 gallon mixing bowl, two gyratory compaction molds, and a mixing blade were heated to 150°C in the Despatch LEB Series oven. After heating, the aggregates were combined in the 5 gallon mixing bowl. The bowl was then placed on a scale and the known mass of heated binder was added. The binder material and the container in which it was heated can be seen in Figure 3.2 below.



**Figure 3.2 - PG64-28 Asphalt Binder**

The mixing bowl was placed in the mixer and the blade was attached. The materials were mixed for 5 minutes. After completion of mixing, two 3.0 kg samples were measured from the mixing bowl and placed on separate metal trays, and then were returned to the oven for 30 minutes to be reheated to 150°C. Once this temperature was reached the samples were compressed into cylinders using gyratory compaction, which is discussed in section 3.2.3.

### **3.3.2.2 AI RAP Samples**

Two 3.0 kg samples of Aggregate Industries reclaimed asphalt pavement material were measured using a laboratory scale and placed into separate metal trays. The two samples and two gyratory compaction molds were then placed in the oven and heated to 150°C. Upon reaching this temperature, the samples were ready for gyratory compaction.

### **3.3.3 Gyratory Compaction**

The 6-inch compaction molds were assembled, and a contact paper was placed in the bottom of each mold. Each 3 kg sample of asphalt was transferred into the molds, and leveled

using hand tools. A second piece of contact paper was then placed over the sample on top of the leveled surface. The compaction mold was placed into the Pine Instrument Co. 6-inch gyratory compactor, which was set to a height control of 100 mm. Each sample was then compacted. After compaction, the sample was extruded from the compactor and mold, and the temperature of each sample was recorded using a laser thermometer. This process was repeated for both the RAP and virgin mixes, as only two gyratory compactors were available. Figure 3.3 below shows the gyratory compactor with a sample cylinder extruded and cooling above the machine.



**Figure 3.3 - Pine Instrument Gyratory Compactor & Extruded Sample**

### 3.3.4 Sample Cooling & Storage

Each sample was allowed to cool for 30 minutes after being extruded from the mold while still sitting on the gyratory compactor. After cooling, the mass of each sample was measured again. Each sample was then labeled with its number, mix design, date, and mass. The samples were placed on a shelf overnight for storage. Table 3.4 contains the temperature of each sample upon extrusion, as well as the final masses of the samples after compaction.

Table 3.4 - Sample Cylinder Temperatures & Final Masses

Sample	Extruded Temperature	Mass
AI RAP cylinder 1	91°C	2.9900 kg
AI RAP cylinder 2	94°C	2.9746 kg
Virgin cylinder 1	113°C	2.9937 kg
Virgin cylinder 2	91°C	2.9855 kg

## 3.4 Laboratory Experiments on Prepared Asphalt Samples

### 3.4.1 Shake Table Procedure

This experiment was designed to produce high constituent content samples. The shake table used for this procedure was a Lab Line Instruments Orbit Shaker. A shake table is a mechanical apparatus designed to mix liquid samples at a constant rate for extended periods of time. The asphalt material in question was allowed to mix in water on the shake table for 125 hours to increase the rate of leaching of constituents from the asphalt binder.

Eight 250 ml opaque plastic Nalgene sample bottles were used for this experiment. To prepare the samples, 3 Nalgene bottles were filled with 150 g of virgin sample material each and 3 bottles were filled with 150 g of AI RAP sample material. The bottles were labeled virgin 1-3,



and AI RAP 1-3, respectively. Additionally, one sample bottle was filled with 150 g of the aggregates used in the virgin asphalt mix design, in the same proportions, to be used as a control. 150 ml of Poland Springs water was then added to each of the sample bottles, including the eighth bottle which served as a control. Poland Springs water was selected for use due to its consistent mineral content and PH level, as a better control over the variable contents of rain water.

Samples 1 and 2 of both the virgin and AI RAP samples were secured on their sides onto the shake table. The two control samples were also placed on their sides on the shake table. The third samples of both AI RAP and virgin material were secured vertically to the shake table. The shake table was then turned on and set to 100 rpm. The samples were allowed to shake for 125 hours. Figure 3.4 and Figure 3.5 below show the location of the sample bottles on the shake table and the shake table turned on and set to 100 rpm.



Figure 3.5 - Instrument Panel



Figure 3.4 - Shake Table Setup



### 3.4.2 Circulating Water Procedure

The circulating water experiment was designed to represent field conditions for stormwater flowing over the surface of asphalt pavement. The following materials and equipment were required for this experiment:

- 2 Cole Parmer Masterflex pumps
- 4 rubber intake and outflow tubes
- Glass sample bowl
- Vacuum grease
- Wooden cover
- Poland Springs water

Figure 3.6 below shows one of the Cole Parmer Masterflex pumps used in this experiment and its controller. Two pumps were used in this experiment to increase the flow rate of the water circulating around the asphalt sample cylinder, thus increasing the volume of water passing over the surface area of the sample. This was to increase the rate of constituents being released into the sample water.

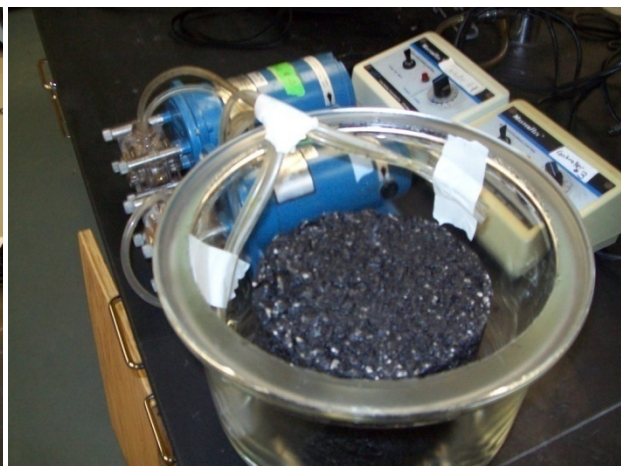


**Figure 3.6 - Cole Parmer Masterflex pump**

The rubber intake and outtake tubes were connected to each pump. The intake tubes were taped to the inside of the glass sample bowl, with the end located 1 inch below the top of the asphalt sample cylinder when placed in the bowl. The pump outflow tubes were located with their ends against the container wall at the bottom of the asphalt cylinder and were also taped in place. Figures 3.7 & 3.8 show the location of the intake and outtake tubing inside of the sample container.

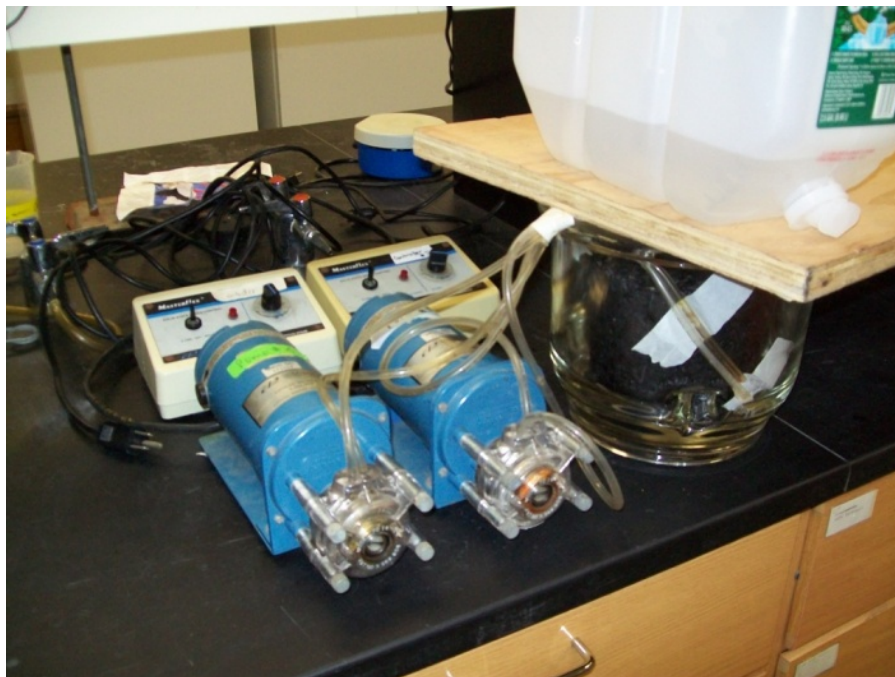


**Figures 3.8 - Outflow Tubing**



**Figure 3.7 - Pump Intake**

The glass sample bowl was selected for this experiment because the interior contained three points elevated from the bottom of the bowl which the asphalt cylinder rested on and allowed water to freely flow beneath the sample. Then 1.5 L of Poland Springs water were added to the sample container before the asphalt cylinder. This allowed the pumps to fill before the addition of the asphalt sample. The pumps were then turned on and set to the maximum output of 100 rpm and the pumps and tubing were allowed to fill. Once full, the pumps were shut off and the sample asphalt cylinder was placed in the bowl, resting on the three glass points. Vacuum grease was applied to the top lip of the sample container and the container was sealed using a piece of plywood with notches cut in it to accommodate for the intake and outtake pump tubing. The pumps were then turned on and water was circulated around the asphalt sample for 3 hours and 45 minutes. After the specified time period the pumps were turned off, the asphalt cylinder was removed, and the water was collected into 1 qt containers to be used for later laboratory analysis of its contents. Figure 3.9 depicts the entire circulating water setup.



**Figure 3.9 - Circulating Water Experiment Setup**

### **3.5 Sample Storage & Preparation for Analysis**

All samples collected from the field or produced in the lab were stored in dark, refrigerated conditions until they were analyzed. Sterile, conical test tubes were filled with 40 mL of every sample, pressure-filtered through 0.45 micron filters, to be used for HPLC analysis, which is discussed in section 3.6.3.

### **3.6 Sample Analysis Procedures**

#### **3.6.1 Constituent Selection**

Representative petroleum hydrocarbons were selected to be analyzed in order to establish a baseline measure for asphalt runoff toxicity and environmental impact. Scientific literature provided a list of materials commonly found in reclaimed asphalt pavement from which suitable candidates were drawn (Krein, et al., 2000). Desirable candidate compounds had to exhibit the following features in order to be selected for analysis: detectable concentrations via the analysis methods selected, high toxicity, a tendency to bioaccumulate, and a large base of knowledge regarding the compound in scientific literature. The following is a list of polycyclic aromatic hydrocarbons typically found in asphalt runoff (Mangiani, 2003):

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(g, h, i)perylene

- Benzo(a)pyrene
- Chrysene
- Dibenzo(a, h)anthracene
- Fluoranthene
- Fluorene
- Indeno(1,2,3,-c,d)pyrene
- Naphthalene
- Phenanthrene
- Pyrene

The constituents contained in this list were cross-referenced with chemical absorption, and the following compounds were selected for analysis because they met all of the designated criteria; anthracene, benzo[a]pyrene, and pyrene.

### **3.6.2 Fluorometer Testing Procedure**

A fluorometer is a tool which calculates the emission of fluorescence of molecules in solution. In particular, molecules that feature delocalized electrons (electrons from atoms in double bonded configuration next to single bonded atoms would be considered delocalized). This is highly useful for the purposes of this project, as petroleum hydrocarbons can feature several carbon ring systems which are highly delocalized, leading to a strong emission of fluorescent light when the molecules are “excited” by light energy. This assay therefore provided an excellent metric of sample contamination by most petroleum hydrocarbons. A 10-AU field fluorometer, shown in Figure 3.10, was used for this analysis, which provided a numeric value for total fluorescence absorbance.

The samples selected for fluorometry testing were transferred from their original containers into small, labeled glass test tubes. One test tube was used for each sample to be tested, and each test tube was filled approximately halfway. The fluorometer was turned on, and set to the crude oil setting. Before each sample was inserted into the machine, a Kim wipe was used to remove any foreign matter from the outside of the sample test tube that may disrupt the fluorescence reading. The sample receptacle cap on the fluorometer was removed, and a test tube containing a sample was inserted, and then the cap was replaced. The fluorescence value of the sample was allowed to stabilize on the fluorometer, and then the value was recorded. The sample was then removed and this process was repeated for the remaining samples.



Figure 3.10 - 10-AU Fluorometer



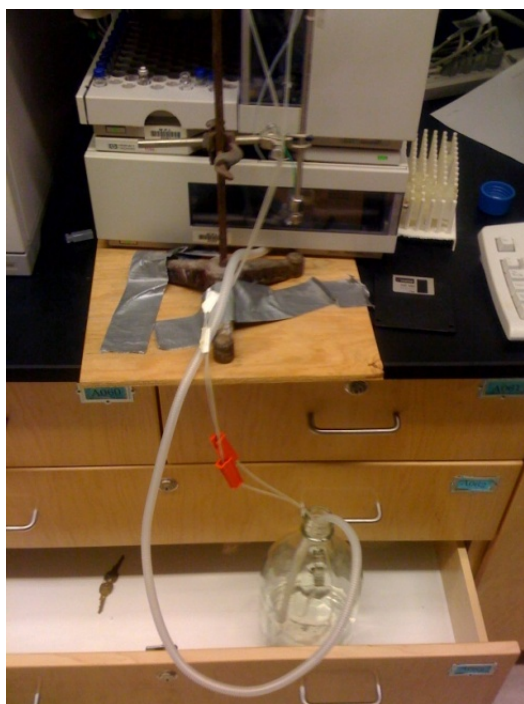
### 3.6.3 HPLC Testing Procedure

The HPLC is a high-accuracy, low-concentration-detecting chromatograph which allows for the analysis of complex mixtures via separation of chemicals along their relative polarities. At present, this analytical technique has not been commonly used in asphalt runoff analysis. The resultant spectra can be compared to spectra generated from chemically pure standards. To identify chemicals using the HPLC, it is necessary to obtain standards for the chemical in question, establish optimal conditions for analysis, and then record the retention time for the analyte. The retention times for analytes are highly specific; retention times established in disparate conditions are not comparable. A PerkinElmer HPLC machine, shown in figure 3.11, was used for this analysis.



Figure 3.11 - A PerkinElmer HPLC

The HPLC computer software was booted and all HPLC machinery was turned on, with the feed valve rotated to the closed position. Acetonitrile and deionized water were procured for use as solvents. The feed valve was opened and the flow rate was set to 3 ml/s (of 100% water) to flush out any air bubbles. The bubbles were tracked in drip feed tubes and extracted with a plastic gas syringe. Dual drip feeds were placed into a receiving jar under the HPLC with a tube-flow crimper loosened so that approximately 1 droplet of solvent would elute from the tubes per second, as shown in Figure 3.12.



**Figure 3.12 - Drip Feed Tubes & Receiving Jar**

The standard was removed from ampoule and transferred to a half-dram vial. The standard was then run through the HPLC column, shown in Figure 3.13, with progressively higher amounts of water relative to acetonitrile until a stable column pressure could be established while maintaining a quick retention-time. The HPLC's pressure was constantly monitored to prevent over-pressurization.





**Figure 3.13 - HPLC Column**

The solvent mix for all three standards was determined to be approximately a 50/50 acetonitrile/water ratio at a flow rate of 1.5 mL/s. This solvent mix was chosen because it provided decent peak separation and a stable bar pressure for a medium to fast flow rate. This yielded a retention time of 2.6 minutes for benzo[a]pyrene, 2.1 minutes for anthracene, and 1.2 minutes for pyrene. Additionally, after the standard of benzo[a]pyrene was left in a refrigerator for a time period of 3 weeks, it apparently decomposed within the sample vial, yielding a secondary peak at 3.8 minutes. This secondary peak was also considered as a B[a]P-type peak.

The samples selected for analysis were subsequently placed into labeled screw-top half-dram rubber-topped vials. The computer array for automation was set to match the ordered vials placed in the physical array, shown in Figure 3.14, with corresponding sample descriptions. The retention time for any signals was compared to the standard retention times and the acetonitrile/water mix was recorded.



Figure 3.14 - Sample Array with Robotic Arm (visible on left)

### 3.6.4 Laboratory Analysis

In order to provide an additional perspective on the data, several samples were sent to Alpha Analytical, a local environmental laboratory located in Westborough, Massachusetts. The samples were analyzed for total petroleum hydrocarbon (TPH) concentration using gas chromatography. Table 3.5 below contains the samples that were sent to Alpha Analytical for testing.

**Table 3.5 - Alpha Analytical Samples**

#	Sample
1	AI RAP (circulating water sample)
2	Virgin (circulating water sample)
3	AI RAP (shake table sample)
4	Virgin (shake table sample)
5	Grove St & Faraday St (field sample)

This concludes the methodology utilized in this project. The results of each of the laboratory analyses are presented in chapter 4. A more in-depth discussion of the data presented in the results and its implications on policy and regulation can be found in chapter 5.

## **4. Results**

This chapter contains the results of the three methods employed to test the water samples generated in this project. Section 4.1 contains the results of the fluorometry testing which was performed on every sample, and lists the results in terms of absorbance units. These numbers provide a baseline picture for the amount of hydrocarbons in the solution. Section 4.2 shows the results of the samples tested using High Performance Liquid Chromatography. The samples analyzed using HPLC were tested for the presence of anthracene, pyrene, and benzo[a]pyrene, the three constituents of greatest concern selected for this project. Section 4.3 contains the results of the Alpha Analytical total petroleum hydrocarbon testing.

### **4.1 Fluorometry Results**

Fluorescence values from the field fluorometer were universally higher in the RAP samples compared to the virgin asphalt samples. Higher values of FAu indicate larger presence of ringed carbon. The range of values for virgin shake table samples is 116 to 310 fluorescence absorbance units (FAu), while the range for RAP shake table samples is 245 to 1005 FAu. Absorbance for field samples fell in the range of 128-174. FAu. Values from the shake table were universally higher than the circulating water, and both were higher on average than the field samples. This indicates that our asphalt samples released more material than would be expected for regular runoff that has already undergone preliminary washing. This can be seen in Table 4.1.

**Table 4.1 Fluorometer Results**

Fluorometer Test Results		
Image #	Sample	Absorbance Units
Shake Table Samples		
1	Virgin 1	116
2	Virgin 2	305
3	Virgin 3 (standing)	310
4	AI RAP 1	245
5	AI RAP 2	>621.2
	AI RAP 2 – half diluted with DI water	502
6	AI RAP 3 (standing)	>621.2
	AI RAP 3 – half diluted with DI water	410
Shake Table Controls		
7	Water	7.33
8	Water & Aggregate	25.6
Circulating Water Samples		
9	Virgin 1	30.6
13	Virgin 2	33.9
11	AI RAP 1	187
10	AI RAP 2	217
Field Samples		
12	Grove St & Faraday St	159
-	Drury Ln & Park Ave	152
-	East of Highland St & Harvard St	174
-	West of Highland St & Harvard St	128
Fluorometer Controls		
B1	Deionized Water	4.31
B2	Poland Springs	10.2
	Rain Water	49.3

## 4.2 HPLC Results

To properly interpret the output generated by the HPLC software, it is vital to understand the main principle of chromatography. In all chromatography, separation of chemicals occurs through differences in an effect called partitioning. Partitioning occurs due to differences in a compound's concentration between two immiscible solvents as a result of the compound having different chemical equilibrium constants for each solvent. These differences have a net effect of changing the speed at which the compound travels through the compound. Therefore, retention times output by the HPLC are indicative of individual compounds, with minor allowance for highly similar chemicals "sticking" to one another in the column. Individual peaks that result may include several decompositions or monosubstituted variations of the main species represented by the peak.

Analysis of these results is particularly illuminating as to the nature of RAP and virgin asphalt. Comparison of these two also sheds some light on how these experimental models match up to real-world asphalt pavement. Overall, RAP runoff seems to have greater complexity than virgin asphalt. The greater complexity is evident upon examinations of Table 4.3, based mostly upon discrete signals yielded in HPLC as well as more spectroscopic absorbance from both HPLC and the fluorometer. For example, all the RAP shaker table samples run through HPLC have two discrete absorbance peaks in addition to a decent magnitude of fluorometric absorbance, whereas their virgin asphalt shaker table counterparts have one or no peaks and a correspondingly lower fluorometric absorbance. The field samples indicated that small quantities of PAHs are leaching out of pavement, as well what appears to be a large variety of heavy metals, although this conclusion is a conjecture at best.

A visual comparison between Figure 4.1 and Figure 4.2 establishes a general trend for the differences between RAP and virgin asphalt samples, namely that all of the RAP shake table samples featured multiple integration peak signals that were more intense (at 20 and 43 mAU from Figure 4.1) compared to the virgin asphalt shake table samples (at 9.5 mAU from Figure 4.2), which all had one or no peaks. Please note the difference in the value axis for the HPLC figures, as the HPLC data analysis software would not allow for a change in that axis for a print-out. The added chemical complexity between the RAP and virgin samples is likely due to a combination of the addition of materials trapped in asphalt by vehicular pollution as well as the second round of incomplete combustion which occurs during the rejuvenation process. The circulating water tests for both RAP and virgin asphalt generated no peaks, but the FAu values corroborated the notion that there was less leached material present in the virgin asphalt samples compared to the RAP samples. The integrand values for virgin shake table samples ranged from 8.17-96.50 integrated absorbance units (IAu), while the IAu for the RAP shake table samples ranged from 93 to 1191 IAu.

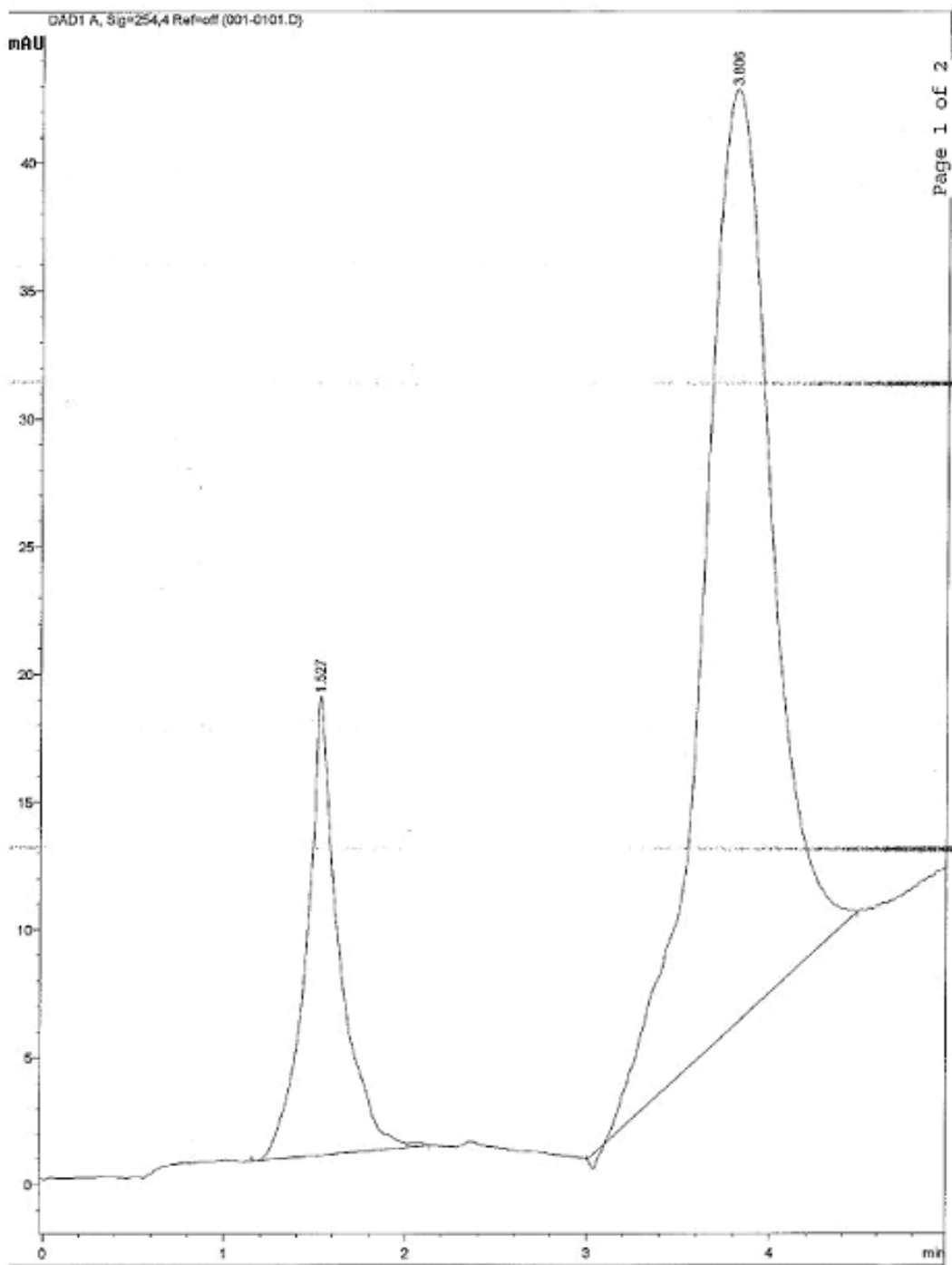


Figure 4.1 - AI RAP 2 Shake-table Sample HPLC



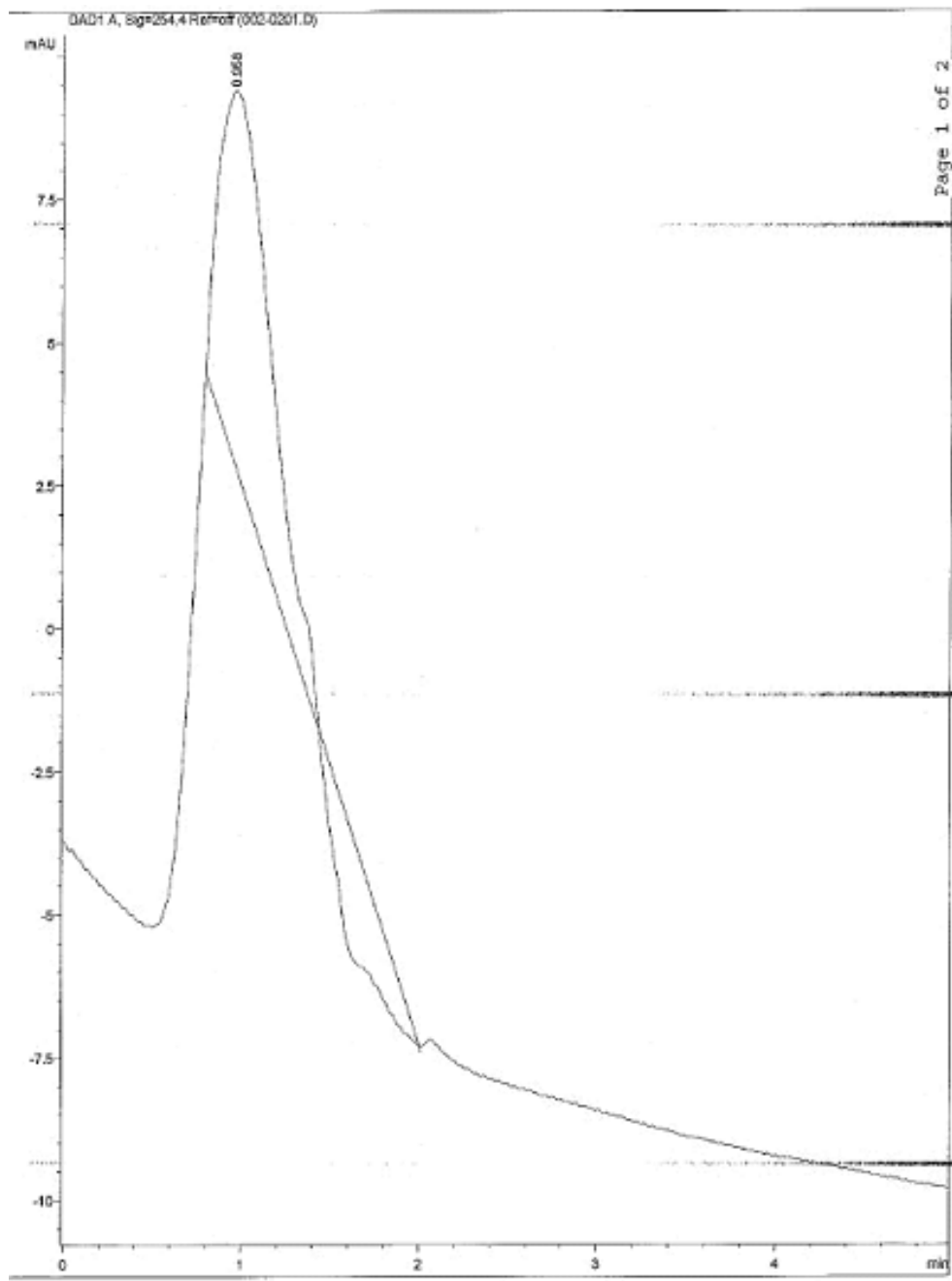


Figure 4.2 -Virgin 1 Shake-table Sample HPLC

The field samples with a decent amount of contamination (for example, Drury Lane/Park Ave, shown in Figure 5.3) tended to feature high complexity shown in the figure by multiple peaks, likely due to greater use and varied use of the pavement. The peaks in the most polluted field sample, Drury Lane and Park Ave, shows lower intensity peaks than the shake table samples, as expected, and are at 8 mAU or less as seen in Figure 4.3. Therefore, the field samples are more complex than RAP and virgin asphalt laboratory tests. This complexity could come from pavement use, which results in increased asphalt breakdown from wear such as greater rutting and cracking of asphalt, as well as additional pollution deposition from motor oils, tire wear, and vehicle exhaust.

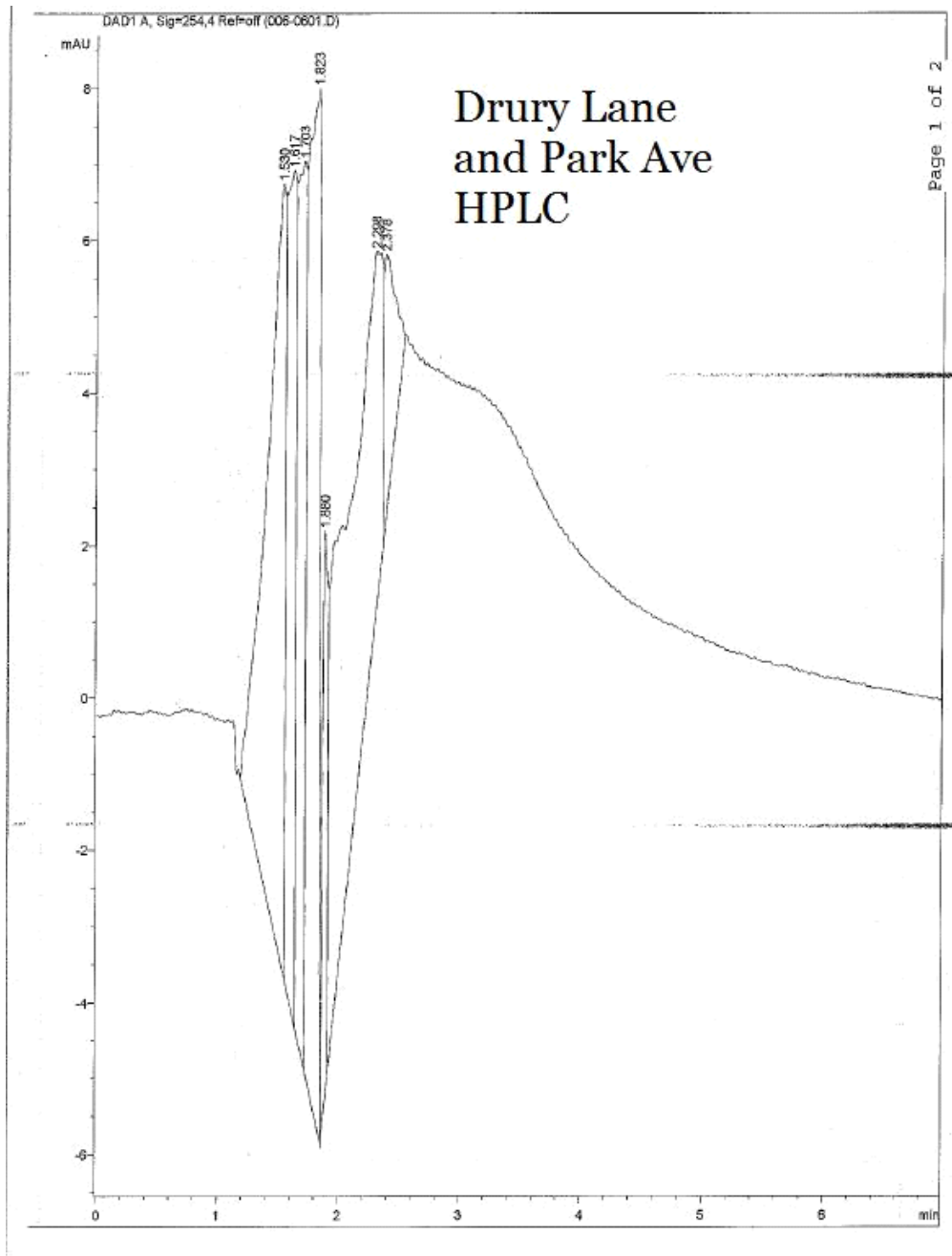


Figure 4.3 - Drury Lane and Park Avenue Sample HPLC

Table 4.2 - HPLC Results

<b>HPLC Results</b>					
	Total Integral Under 7 min.	Complexity/ Number of peaks	Anthracene-Type Peak Height	Benzo[a]pyrene-Type Peak Height	Pyrene-Type Peak Height
<b>Field Samples</b>					
Grove St. & Faraday St.	40.65	1	--	--	--
Park Ave & Drury Ln.	489.75	7	131.94	21.04	--
Highland St.& Harvard St. East	43.04	1	--	--	--
Highland St.& Harvard St. West	29.04	1	--	--	--
<b>Laboratory Samples</b>					
Virgin Shake Table 1	96.50	1	--	--	--
Virgin Shake Table 2	8.17	2	--	--	8.17
Virgin Shake Table 3	No peaks	0	--	--	--
AI RAP Shake Table 1	1190.71	2	--	964.53	--
AI RAP Shake Table 3	93.10		--	--	93.1
Shake Table Aggregate Control	No peaks		--	--	--
Shake Table Water Control	No peaks		--	--	--
AI RAP Circulating Water Cylinder 1	No peaks	0	--	--	--
AI RAP Circulating Water Cylinder 2	No peaks	0	--	--	--

### **4.3 Total Petroleum Hydrocarbons Results**

The total petroleum hydrocarbon (TPH) test only gave concentrations for the virgin and RAP shake table samples. A TPH concentration was expected for the most polluted field sample, Drury Lane and Park Ave, but came back below the detection limit. The results do however mirror the fluorometry and HPLC results that RAP samples contain more petroleum hydrocarbons than virgin asphalt samples, these concentrations were 10200 and 8340 microgram/L for RAP and virgin respectively as seen in Table 4.3.

Table 4.3 - Combined Test Results

	Fluormeter	TPH	HPLC				
	Absorbance Units	Micrograms /liter	Total Integral Under 7 min.	Complexity/ Number of peaks	Anthracene-Type Peak Height	Benzo[a]pyrene-Type Peak Height	Pyrene-Type Peak Height
<b>Field Samples</b>							
Grove St. & Faraday St.	159	BD	40.65	1	--	--	--
Park Ave & Drury Ln.	152		489.75	7	131.94	21.04	--
Highland St.& Harvard St. East	174		43.04	1	--	--	--
Highland St.& Harvard St. West	128		29.04	1	--	--	--
<b>Laboratory Samples</b>							
Virgin Shake Table 1	116	8340	96.50	1	--	--	--
Virgin Shake Table 2	305		8.17	1 (minor)	--	--	8.17
Virgin Shake Table 3	310		No peaks	0	--	--	--
AI RAP Shake Table 1	245	10200	1190.71	2	--	964.53	--
AI RAP Shake Table 2 (Projected)	1004						
AI RAP Shake Table 3 (Projected)	820		93.10	2	--	--	93.1
Shake Table Aggregate Control	25.6		No peaks		--	--	--
Shake Table Water Control	7.33		No peaks		--	--	--
Virgin Circulating Water Cylinder 1	30.6	BD					
Virgin Circulating Water Cylinder 2	33.9						
AI RAP Circulating Water Cylinder 1	187	BD	No peaks	0	--	--	--
AI RAP Circulating Water Cylinder 2	217		No peaks	0	--	--	--

#### 4.4 HPLC Based Concentration

To derive a rough approximation of concentration from HPLC results, the molar extinction coefficient of benzo[a]pyrene was calculated from the standard. This value was applied to the absorbance peak height for benzo[a]pyrene in the AI RAP shake table 2 sample (the most polluted laboratory sample, see Figure 4.1) to act as a representative figure to compare to the IAU value. The multi-ringed compounds under investigation (and produced by incomplete combustion) all have molar extinction values within the same order of magnitude, so it would be fair to use this as an overall comparison. The resultant approximation yields about 9000 microgram/L, which sits very near the TPH-derived concentration of 10200 microgram/L for the combined shaker table RAP sample. This figure is well over the EPA-established maximum contaminant level of 200 nanograms/L.

Due to the unknown composition of the field samples, concentrations cannot be derived explicitly from total integration, as overlapping peaks may obfuscate or warp results based on how the complex mixture travels through the column. The presence of heavy metals would cause complexing with the electronegative portions of monosubstituted polycyclic aromatics, thus changing the partitioning coefficient for both compounds. In effect, this renders the extinction coefficient derived from standards to be inapplicable to the field samples. In light of this however, it would be fair to say that the peaks within a few seconds of the standard peaks probably retain the identity of their ring-groups, but much more extensive work using chelating agents would be necessary to confirm this beyond a doubt.

## 4.5 PAHs from Pyrolysis

Based upon review of current scientific literature, the asphalt production process, and the experimental data, it can be concluded that the source of the majority of PAHs involved in the asphalt paving process are derived from the asphalt paving process in itself, and not from the petroleum product or aggregate which asphalt pavement is produced from. Specifically, the PAHs under review are sourced entirely from incomplete combustion (pyrolysis). High temperature (high energy) processing of the asphalt leads to the complex mixture of light hydrocarbons which this investigation has been concerned with. The nature of this incomplete combustion is highly variable based on temperature, asphalt mix, and production methods to the extent that it produces products in proportions that are essentially unpredictable. The process of incomplete combustion is essentially the decomposition of long-chain hydrocarbons and the subsequent reorganization of carbon bonds once they lose their thermal energy (see Figure 5.4).

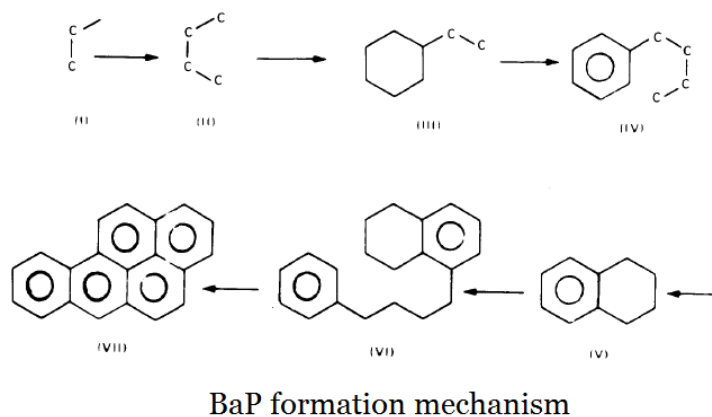


Figure 5.4 - Benzo[a]Pyrene formation. Perera, 1981.



The nature of pyrolysis makes predicting exact compositions of combusted material nearly impossible given current technology and scientific techniques. It is imperative to ecological health and human health that more attention be paid to the deposition of pyrolysis products into the environment on a large scale. A first approximation for how much B[a]P alone has been deposited into the environment given that there are roughly 4 million kilometers of asphalt paving at a conservative figure of 3.1 meters average width yields an estimation of approximately 3600 kilograms of deposited B[a]P.  $(4000000 \text{ km road}) / (100 \text{ mm per puck (millimeters)}) \times 10 \text{ pucks for width of road} \times 9000 \text{ micrograms}$ . This figure illuminates the magnitude of the problem posed by compounds leaching from asphalt pavement.

## **4.6 Policy Recommendations**

### **4.6.1 Roadway Paving Pollution Control**

One of the types of point sources covered by the NPDES Stormwater Program is construction activities. In 1990, the EPA promulgated rules establishing Phase I of the NPDES stormwater program. Phase I addresses discharges from large construction activities disturbing 5 acres or more of land. Then, on March 10, 2003, Phase II NPDES regulations came into effect that extended coverage to construction sites that disturb one to five acres in size. These construction activities include, among other things, roadway construction, which this project is concerned with.

For construction and other land disturbing activities in areas where the EPA remains the permitting authority, such as Massachusetts, operators must meet the requirements of the EPA Construction General Permit (CGP). CGP permit requirements include the submission of a Notice of Intent and the development of a stormwater pollution prevention plan (SWPPP). The

SWPPP must include a site description and measures and controls to prevent or minimize pollutants in stormwater discharges (U.S. Environmental Protection Agency, Office of Water, 2005).

While there are regulations in place for construction activities, they are primarily concerned with the associated increase in volume of runoff, as sediment runoff rates from construction sites are typically 10 to 20 times greater than those from agricultural lands, and 1,000 to 2,000 times greater than those of forest lands (U.S. Environmental Protection Agency, Office of Water, 2005).

They also address issues with runoff collecting harmful sediment and chemicals such as oil and grease, pesticides, heavy metals, and nutrients. NPDES regulations recommend several BMPs, including non-structural, planning-based BMPs, as well as structural BMPs. Structural BMP recommendations consist of stormwater retention methods such as catch basins and wet ponds which reduce the rate the runoff is released, and allows for particulates to settle out of the stormwater for pollutant removal. Also included are suggestions for vegetative BMPs that facilitate runoff percolation and maintain natural site hydrology and healthier ecologies. These BMPs consist of filter strips, artificial wetlands, and rain gardens which naturally filter many organic pollutants from stormwater runoff before it re-enters the water supply (U.S. Environmental Protection Agency, Office of Water, 2005).

All of these BMPs and regulations focus mostly on increased runoff volume associated with impervious surfaces, increased sediment washout from construction sites, and pollution from construction activities and roadway deposition. None of them however, focus on the constituents present in the roadway pavement itself. The research conducted in this project has lead to the finding that there are toxic PAHs that are present in asphalt pavement, and that they

are largely a result of the pavement creation and laying process. This leads to the assumption that the largest concentration of these harmful constituents is present immediately following the laying of asphalt pavement. Rather than relying on in-place remediation structures to handle the pollution from the roadway, a man-made first flush could be conducted on the newly paved surface immediately after finishing the site. If the associated runoff was collected separately and removed from the site for professional treatment and not allowed to enter the stormwater management system, a potentially large amount of the toxic petroleum hydrocarbons could be removed without the surrounding ecology ever being exposed. This pollution management practice could be added to the EPA's Best Management Practices list and also be made a necessary practice for all permitted roadway construction projects under NPDES regulation.

#### **4.6.2 Integrated Risk Information System**

The EPA's IRIS (Integrated Risk Information System) provides a decent review of certain chemicals deposited into the environment. However, the EPA only examines a handful of compounds per year. The process by which a compound is determined to be a mutagen or not relies primarily on prolonged single-compound exposure, usually always in laboratory mice. Additionally, the initial review process to decide whether or not to even publish an IRIS report for a single compound takes nearly two years by the EPA's own standard projections (U.S. Environmental Protection Agency, 2005), never mind propose any regulation. Even by its own admission, this process is sluggish and rife with procedural problems. In a press release from early 2009 regarding the IRIS reporting process, the organization claims the following:

“For far too long the success of EPA's IRIS program has been hampered by an assessment development process that took too long, was redundant, and was not transparent to the public. The new IRIS process

will be entirely managed by EPA. EPA will have final authority over the contents of all IRIS assessments after considering the scientific input of experts at other agencies and White House offices. The well established processes of rigorous independent external peer review and public review and comment will remain key components of the new IRIS process[...] Other highlights of the new IRIS development process include a streamlined review schedule, ensuring that the majority of assessments are posted on IRIS within two years of the start date. This will result in more human health assessments being available to EPA's programs and regions and to other users of the IRIS database. The new process will no longer provide other federal agencies the opportunity to request suspension of an assessment process to conduct research on "mission critical" chemicals." (U.S. Environmental Protection Agency, 05/21/2009)

This two-year framework is essentially a long, multistep process of literature review in which the scientific community and public are allowed to comment and submit scientific literature for review. However, introducing some more structure to this process could potentially streamline the initial phases of report-making.

A compound which is to be analyzed by IRIS program for carcinogenicity should first undergo the Ames test as a time-saving process. The Ames test is a simple, inexpensive manner of testing mutagenicity of a compound using an agar plate and a bacterial colony. The mutagen in question is placed in the center of the plate, and the amount of bacteria produced relative to the control plate gives a fairly accurate measure of mutagenic quality. Instead of taking several

years to determine that a known carcinogen is indeed carcinogenic, the Ames test should be performed first and then rigorous investigation should follow. In addition, it is highly recommended that the Ames test be performed with a mixture of PAHs to determine multi-component mutagenicity and whether those pathologies would work in concert.

This combined pathology would not be suited to the bacterial (prokaryotic) model because the organisms lack the same cellular machinery that would be affected by the PAHs. For example, benzo[a]pyrene in itself is not carcinogenic, but its metabolite is highly carcinogenic. The enzymes which metabolize the compound would have to be present to yield a positive result. Therefore, a model using yeast containing liver S9 (a complex fluid containing liver enzymes to simulate a human cell) could be used (Ames, 1973). A positive result would then proceed through an accelerated review process once mutagenicity was determined.

#### **4.6.3 Maximum Contaminant Levels**

The current regulation for individual constituents consists of enforceable concentration recommendations from the EPA, called Maximum Contaminant Levels (MCLs). Currently, if constituents are found to exceed MCLs, water suppliers must notify consumers and treat their water supply. This approach, while practical, does not address bioaccumulation of toxic materials such as those which leach into groundwater or sewer systems from asphalt pavement. An MCL for all PAHs could be established for non-potable groundwater which abuts important ecologies such as estuaries or swamps, as well as agricultural zones. This would help to protect human populations as well as ecologies. A reasonable figure for this MCL would fall at around 1 microgram/L, considerably higher than the potable water limit of 200 nanogram/L for B[a]P. No other individual PAHs have enforceable MCLs.

#### **4.6.4 Chemical Remediation Techniques**

In areas where non-potable sites of ecological concern exceed this proposed MCL, a mixture of hydrogen peroxide and ozone (peroxone) could be injected in small amounts to help oxidize PAHs to more biologically inert forms. Peroxone is also capable of oxidizing other pollutants such as methyl tertiary butyl ether (MTBE) and benzene. In areas of higher concentrations, a remediation hub could be created by the creation of a wood chip and soil compost infected with white rot fungus, which oxidizes pollutants when they are high in concentration (National Institute of Health, 1993). This fungus is capable of breaking down a large number of environmental pollutants and is otherwise biologically inert.

#### **4.7 Summary of Results**

The results confirm that RAP leaches out more material than virgin asphalt, and that pyrolysis products are generally not present in the field samples, which contain a very different variety of pollutants. The data substantiates the model of the shake table and circulating water tests simulating large and realistic wear (respectively) on asphalt paving. The data presented from the various instruments works in concert. The fluorometry data corroborates the added complexity indicated our HPLC results and adds another dimension of detail as well, as the fluorescence absorbance is sensitive almost exclusively to carbon rings. This is in contrast to the HPLC's utility for detection of a wide range of extremely low-concentration compounds in samples. The TPH results provided another dimension of detail by providing sample concentrations generated from a gas chromatograph.

## **5. Conclusions**

### **5.1 Summary of Work**

The focus of this Interactive Qualifying Project (IQP) is on asphalt pavement and its effects on stormwater runoff quality. The goal is to determine the extent to which asphalt leaches contaminants into stormwater. The areas of research consisted of which constituents are present in asphalt runoff, which are of primary concern, and their harmful effects on ecology and human health. Additional research into current stormwater runoff management practices and their effectiveness at removing these constituents was also completed, as well as a study into the regulation and policies in place addressing these concerns.

The results of this project consist of policy update recommendations on emerging constituents with harmful effects on human life that have not yet been fully investigated or regulated. The results will reexamine current stormwater collection and treatment practices and their effectiveness at controlling and removing the constituents of potential concern.

The goal of this project was met through a combination of literature research, field sample collection, laboratory asphalt production, and chemical analysis. The project began with an investigation into the potential petroleum hydrocarbons present in asphalt pavement materials. In depth research into the harmful effects of these constituents led to a selection of three chemicals for further analysis. The current policy and regulation of the selected constituents was investigated, and used later as a framework for additional policy proposal in conjunction with the laboratory findings.

In order to explore the presence and extent of the selected constituents in asphalt pavement, field samples of roadway stormwater runoff were collected from local areas of

concern. As a basis for comparison, laboratory samples of asphalt were made using fresh asphalt as well as reclaimed asphalt pavement. Experiments were then conducted on the produced asphalt samples in order to generate water samples for analysis. The experiments were designed for the comparison of concentration levels of constituents between cases designed for producing the maximum potential concentration levels, and a laboratory controlled procedure designed to simulate a realistic roadway runoff situation.

The water samples collected from the field and laboratory procedures were tested using three different methods of analysis. On campus, fluorometry analysis was performed in order to gain a baseline comparison of the level of contamination of polycyclic hydrocarbons between the samples. Further analysis was conducted using high performance liquid chromatography (HPLC) for the three constituents of main concern. HPLC was selected because it shows overall chemical complexity and allows for exceedingly low detection limits. Finally, a representative selection of the samples were sent to a third-party laboratory for analysis of total petroleum hydrocarbon (TPH) content to provide an additional layer of information regarding sample contamination.

Policy recommendations were made to fill voids discovered in the current control and monitoring of asphalt roadway runoff based on research of current policy.

## **5.2 Recommendations for Future Work**

### **5.2.1 Expanding on Current Work**

This project has drawn attention to a largely unexplored concern to public health and drinking water. Due to the limitations in the scope of this IQP, there are many more questions to be asked concerning petroleum hydrocarbons and hot mix asphalt pavement. The following contains suggestions for future expansion upon the work performed in this project, and ways to



further investigate and solve the problem of toxic petroleum hydrocarbons leaching from asphalt.

One of the difficulties encountered during the project was the inability to determine which pollutants in the field stormwater samples came from deposition on the roadways, and which leached from the asphalt itself. In continuing the work of this project, a stronger focus could be placed on how virgin asphalt pavement chemically breaks down over multiple rain events without considering the pollutants deposited on the roadway. This could be accomplished using a long-term, large-scale roadway asphaltic concrete model in laboratory conditions.

Unfortunately this was not possible due to the time and budget constraints of the project. By simulating first-flush situations and through periodic chemical analysis of the runoff collected, the rate and volume of constituents leaching from the pavement could be plotted over time. In conjunction with this test, road bearing and strength testing could also be performed, simulating traffic loads on the roadway to analyze the effect of traffic on the breakdown of the chemical compounds in the asphalt.

In order to determine which constituents come from the asphalt itself and not roadway pollution the results obtained from these procedures could be compared against the constituent analysis of field samples. In continuing the investigation of this project, more field samples should be collected from a wider variety of sites which could be categorized by pavement age, condition, land usage, and traffic patterns. This data could be used to categorize the types of pollutants found in the samples collected from each roadway location and can be used to better determine which types of contaminants come from the asphalt pavement and which come from external sources.

Estimations for concentrations and rates at which petroleum hydrocarbons leach from asphalt roadways could then be generated from these methods as well. This could be

accomplished by collecting many samples from a site during the course of a rainfall event and then comparing rain fall data to these samples and the results of their chemical analysis.

Additionally, a more varied set of asphalt samples would be beneficial for standardizing the results of laboratory analysis. Virgin asphalt samples generated from materials that came from as many different sources as possible (such as from different sets of oil barrels, for example) would better account for the variability of chemical composition in asphalts. Also, the use of RAP materials from known sites, with a known original mix design of the asphalt, remediation techniques, its age, and site conditions, would lead to a better picture of its contents and clarify the implications of its chemical analysis.

HPLC analysis may have been used to a greater extent, but time limitations and limited access to equipment did not make it possible to fully analyze each sample generated from this project. The HPLC is a very powerful tool, and could certainly be used more effectively for analysis of petroleum hydrocarbons, as its very low detection limits can give a strong picture of the chemical makeup and concentration of a sample. Additional methods of chemical analysis may be another avenue to explore if a greater budget and resources are available.

### **5.2.2 Related Future Work**

Detection of low-concentration compounds is currently a problem which the science and engineering communities solve in varied ways. A cheap, high-accuracy, low-concentration analyte detection method could be engineered via the design of a cell which secretes a detector protein which fluoresces upon metabolism of a constituent. This could be accomplished via protein engineering, by activating green fluorescent protein (GFP) once the detector protein

binds the analyte.

The chromophore of GFP fluoresces about one hundred times brighter than most PAHs at a single, fixed wavelength (Soboleski, et al., 2005). This would be highly appropriate for use in detection, as many constituents of concern (including all those that were assayed in the project) gain their mechanism of toxicity by conversion to a toxic product via protein action or by changing sensitive protein activity, such as in the case of endocrine disruptors (McCarty, et al., 2009). The utility of this would essentially be a massive signal amplification of highly specific analytes: B[a]P, anthracene, pyrene, bisphenol-A, many polychlorinated biphenyls, and several other highly significant compounds could all potentially be detected at picomolar ( $10 \times 10^{-12}$  m/L) concentrations by commonly available fluorometers.

Once organisms carrying these proteins were engineered, the cost would be minimal – all that would be required would be to maintain the health of the cell line. The process would be to simply transfer a small quantity of sample into a fixed number of cells, and then placing the sample in a fluorometer tuned to detect the specific wavelength of GFP fluorescence. Multiple detectors could even be engineered into a single cell if an additional GFP chromophore were changed to a different color (via the various fluorescent protein chromophores available from Clontech), making the process even simpler by eliminating the need for multiple cell lines for different constituents. This detection method could be used en-site for minimal cost, and individual sets of cells could be cloned with ease for re-use.

### **5.3 Conclusion**

Investigation into asphalt runoff revealed that it is a relatively unaddressed problem which is not being dealt with to full capacity for the protection of the environment as well as the

human population. In the course of the project's completion, there have been indicators from both our experimental data as well as research that PAHs in asphalt runoff originate from pyrolysis of asphaltenes during laying of asphalt, and any additional compounds, such as heavy metals and oils that are deposited onto asphalt during road use and leach into stormwater runoff. According to our fluorometry, HPLC, and TPH data, PAHs do have the capacity to leach from asphalt and into groundwater. Research indicated that PAHs may be bound to particulate matter within the asphalt and leach out over time due to surface wear and water exposure. As so little is known about asphaltenes, there is much research to be done to determine the extent and nature of this pyrolytic deposition. This research is currently greatly hindered by the extreme difficulty of isolating asphaltenes.

In reviewing current policy and regulatory procedures, several redundancies in the review process for compound legislation were identified and addressed alongside potential problems in current policy, such as PAH concentrations being measured for individual components rather than as a group. Techniques and procedures for lessening the impact of asphalt pavement upon the environment and human health were discussed in the context of harm reduction.

Carcinogenic and toxic compounds in water that are sourced from asphalt runoff are of great concern. The data and research provided points to the fact that many changes could be made to policy in order to reduce the penetration of these harmful compounds into the environment.

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