Environmental Impacts of Reclaimed Asphalt Pavement (RAP)

FINAL REPORT
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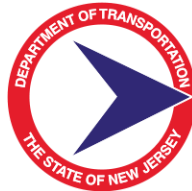
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16. Abstract:
The primary goal of this study was to investigate the environmental impacts of reclaimed asphalt pavement (RAP) while it is freshly processed (i.e., fresh HMA) and after subjecting it to accelerated weathering. Three RAP materials were obtained from 3 plants throughout New Jersey; denoted as NORTHRAP, CENTRALRAP, and SOUTHRAP. In addition, a NJ supplier provided fresh HMA loose mix samples (denoted as Fresh) which were utilized as a control. Materials from all RAP sources and HMA underwent four different types of weathering processes including: ultra violet (UV) and precipitation weathering on unbounded RAP, UV and precipitation weathering on compacted RAP, weathering by heat and moisture cycles, and groundwater flow-through leaching. Batch experiments were conducted to mimic leaching of pollutants from landfills. Among these samples, CENTRALRAP and NORTHRAP released levels of Pb greater than EPA drinking water MCL of 15 ppb, with the highest level being released by NORTHRAP, which was thus selected for further column experiments. Two-column experiments (a RAP column followed by a soil column) were conducted to investigate the release of metals and PAHs from RAP samples and the attenuation effect of soils on these potential pollutants. The results of these experiments showed that high molecular weight polycyclic aromatic hydrocarbons (PAHs) can elute from the weathered RAP materials, but none was above EPA guidelines. These released pollutants were largely attenuated in the soils. A subset of NORTHRAP leachate samples was also screened by the Microtox® Assay and tested for mortality and DNA damage in fish embryos exposed using the comet assay. Micotox® assay indicated only minimal toxicity of the RAP extract, mainly due to the extraction solution, and no toxicity in the rainwater elutriates. Similarly, embryo mortality was even more sensitive to the solution used to extract RAP, where the only significant toxicity was associated with soils in the column experiment, rather than the RAP itself. Based on the results, RAP may be used as an unbound material in all environments except those which are highly acidic (i.e., pH $\leq$ 4). These highly acidic environments include but may not be limited to: mines with sulfur-containing minerals and landfills where organic materials decompose, creating an acidic environment. Acceptable uses of unbound RAP materials may include but not be limited to: using the unbound RAP as surface materials for parking lots, farm roads, or pathways; for quarry reclamation; as non-vegetative cover underneath guiderails; and mixed with other materials for subbase or base materials; in addition to the current uses in hot mix asphalt applications. Due to the inconsistent pollutant levels found among the three RAP stockpiles evaluated in this study, it is also recommended, as a precautionary measure, to determine the releasable levels of metals and PAHs for RAP stockpiles before using RAP in highly acidic environments; by extracting leachate samples using batch experiments and measuring pollutants (PAHs and metals) levels. If the releasable levels of pollutants are below US EPA drinking water standards, unbound RAP can be used in acidic environments. If the releasable levels of metals and PAHs exceed US EPA drinking water standards, it is recommended to conduct column experiments to ensure the release of pollutants is not of environmental concern (i.e. < EPA guidelines).

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List of Acronyms

BDL	*Below Detection Limit*
COV	*Coefficient of Variation*
CUV	*Continuous Ultra-Violet*
DCM	*Dichloromethane*
DI	*Deionized Water*
EC	*European Commission*
EC50	*The Concentration at which 50 percent reduction of light is observed*
EDX	*Energy-Dispersive X-Ray Spectroscopy*
ELS	*Early Life Stage*
EPA	*Environmental Protection Agency*
ERM	*Embryo Rearing Medium*
FRCR	*Fast-Rate-Constant-Rate*
GC-MS	*Gas Chromatography-Mass Spectrometry*
HEPA	*High-Efficiency Particulate Air*
HMA	*Hot Mix Asphalt*
HPLC	*High-Pressure Liquid Chromatography*
ICP-AES	*Atomic Emission Spectrometry*
ICP-MS	*Inductively Coupled Plasma Mass Spectrometry*
LPM	*Liters Per Minute*
MCL	*Maximum Containment Level*
NAAQS	*National Ambient Air Quality Standards*
NADP	*National Atmospheric Deposition Program*
NDD	*Non-Linear Differential Dynamic Model*
NJ	*New Jersey*
NJDEP	*The New Jersey Department of Environmental Protection*
NJDO	*The New Jersey Department of Transportation*
PAHs	*Polycyclic Aromatic Hydrocarbons*
PBS	*Phosphate Buffered Saline*
PFC	*Permeable Friction Course*
PM$_{2.5}$	*Particulate Matter*
SOUTHRAP	*RAP from Source No. 3*
QUV	*Q-Lab UV Tester*
RAP	*Reclaimed Asphalt Pavement*
SEM	*Scanning Electron Microscope*
SMCL	*Secondary Maximum Containment Levels*
CENTRALRAP	*RAP from Source No. 2*
TCLP	*Toxic Characteristic Leaching Procedure*
Fresh	*Fresh "Control" RAP*
NORTHRAP	*RAP from Source No. 1*
UV	*Ultra-Violet*
VOC	*Volatile Organic Compounds*
WPO	*Weight Percentage of Oxygen*

EXECUTIVE SUMMARY

Reclaimed asphalt pavement (RAP) is obtained through milling and removal of existing pavement surfaces. RAP materials have been successfully reused and recycled into new asphalt pavements since the 1970s. Despite the benefits of recycling RAP materials, not all of it can be recycled into new asphalt pavements. Therefore, the unused RAP materials have to be either stored on site for long periods of time or disposed of in waste landfills; which is often costly. RAP materials have been used as aggregates for unbound base materials, aggregates for stabilized base materials, pothole filler materials, and roadway shoulder materials. However, New Jersey (NJ) RAP usage in these applications (i.e., in unbound engineering applications) has been restricted due to environmental concerns from the possibility of potential toxic pollutants that might leach out of it.

To address these concerns in NJ, a research study, which is documented in this report, was initiated with the goal of investigating the environmental impacts of unbound reclaimed asphalt pavement (RAP) while it is freshly processed (i.e., when it is obtained directly after mixing from the plant) and after subjecting it to an accelerated weathering process. The secondary goal was to explore potential engineering solutions to meet federal and state environmental standards or guidelines. To accomplish these goals, three RAP materials were obtained from asphalt plants in northern NJ, central NJ, and southern NJ. In addition, the plant in northern NJ provided a fresh Hot Mix Asphalt (HMA) loose mix samples to serve as a fresh asphalt sample (i.e., not aged or contaminated) for comparison. These materials are denoted thereafter as: NORTHRAP, CENTRALRAP, SOUTHRAP, and Fresh (containing 0 percent RAP).

A gradation analysis was conducted on the collected RAP materials. This analysis showed that the majority of the collected RAP samples were smaller than ½ inch and larger than Sieve No. 30. Extraction and recovery tests were also conducted to determine the binder content in each of the RAP materials. Based on these tests, the binder contents in the RAP ranged from 2.9 to 4.5 percent.

Each RAP then underwent four different types of weathering processes in an environmental chamber at Columbia University. These procedures included: (a) solar ultra-violet (UV) and precipitation weathering of unbounded RAP, which mimicked weathering of uncovered filling materials using RAP (sunlight exposure), (b) UV and precipitation weathering of compacted RAP mimicking sunlight exposure conditions, (c) weathering of unbounded RAP by heat and moisture cycles, and (d) groundwater leaching of unbounded RAP (covered filling materials). With regard to RAP extracted binders, three types of asphalt binders extracted from RAPs and an unused asphalt binder sample (i.e., binder was not mixed with aggregates before) were aged under Continuous UV and UV/Heat/Moisture. After the accelerated weathering tests, the weight percentage of oxygen (WPO) in all samples were tested using the Energy-dispersive X-ray spectroscopy (EDX). The EDX results indicated that the asphalt binder ageing rate under UV or UV/Heat/Moisture would be fast at the beginning, but after some time, it would reduce significantly.

The test results of continuous UV were then fitted by the nonlinear differential dynamic (NDD) model. The fitting results show that the continuous UV aging follows the NDD model very well with all the R^2 values being greater than 99 percent. The test results of samples after UV/Heat/Moisture aging were fitted using both the NDD model and the fast-rate–constant-rate (FRCR) model. The fitting results show that both the NDD and FRCR model can simulate the initial stage of UV/Heat/Moisture aging, however the FRCR model provides more accurate predictions on the transition and final part of the aging process. Overall, both the FRCR model and the NDD model were able to predict the UV/Heat/Moisture aging very well with the R^2 values greater than 95 percent. The fitting results also show that, after both continuous aging and UV/Heat/Moisture aging, the WPO in FRESH samples was the lowest among different binders, while the SOUTHRAP samples had the highest WPO, the WPO in NORTHRAP samples are lower than that in SOUTHRAP samples but higher than CENTRALRAP samples. This suggests that the service life of the pavement originated from the SOUTHRAP was the longest, followed by NORTHRAP, and then CENTRALRAP. In addition, the aging rates of FRESH in both continuous aging and UV/Heat/Moisture aging are higher than that in samples extracted from RAPs. Additionally, the effects of condensation and moisture on UV aging were evaluated by comparing the change in WPO caused by UV radiation during the continuous UV aging and UV/Heat/Moisture aging tests. It was found that the WPO caused by the UV radiation during the UV/Heat/Moisture aging was lower than that during the continuous UV aging, which indicates that condensation and moisture would effectively reduce the UV aging rate.

Samples of weathered and un-weathered RAP were then utilized to conduct batch experiments. The goal of these experiments was to collect leachate samples from RAP and quantify the amount of metals and polycyclic aromatic hydrocarbons (PAHs) released from the various RAP samples. The results showed that NORTHRAP released the highest levels of lead (Pb) when compared to CENTRALRAP, SOUTHRAP, and Fresh. This might be attributed to the historical usage of tetraethyl lead and/or white paint on roads in the northern NJ area (i.e., close to New York City). Lead concentrations in the leachates of NORTHRAP and its weathered products are all close to or higher than the U.S. Environmental Protection Agency (EPA) Maximum Containment Level (MCL) of Lead at 15 ppb, with 16.1 ppb in leachate from groundwater weathered NORTHRAP and 50.1 ppb from unbound UV weathered NORTHRAP samples. The chemical tests also showed that levels of other toxic chemicals (e.g., As, Ba, and U) in leachates were well below the EPA MCLs, and levels of aluminum (Al), Iron (Fe) and manganese (Mn) in leachates were higher than Secondary Maximum Containment Levels (SMCLs). The acidic solution used in batch experiments, which mimicked the leachate from landfills, leads to increased dissolution of lead (Pb), Al, Fe, and Mn at levels higher than EPA guidelines. NORTHRAP and Fresh were selected for further column elution experiments because NORTHRAP released the highest levels of lead.

A two-column serial setting (i.e., a RAP column followed by a soil column using NJ natural soil) was used to investigate the release of metals and PAHs from RAP and soil's attenuation effects on these potential pollutants. Leachate samples from the RAP

column and from the soil column were collected respectively, every hour for four days to assess the amount of toxicants leaching with time. In comparison to batch experiments, which used solutions with stronger acidity, flow-through column experiments using rainwater (pH 5.1) eluted much lower concentrations of metals. The actual concentrations of metals leached from the RAP column were only 1 to 10 percent of those after the batch experiments. All major and trace elements leaching from NORTHRAP and Fresh were below the primary MCLs established by EPA for drinking water. PAHs were released from the RAP column, but all were below EPA guidelines.

Metals and PAHs that leached out from the RAP column were contained in the column filled with NJ local soils. Levels of PAHs leached out from soils were lower than from RAP, indicating the adsorption of PAHs by soil. PAHs after soil column were at levels below either their detection limits or EPA guidelines for individual PAH compounds (e.g., 0.0001 mg/L for benz(a)anthracene).

The soil used in this study was a major source of pollutants. By comparing the leachate samples obtained after the RAP column only to those obtained after passing through both columns at various times, it was observed that the soil column was a major source for low molecular weight PAHs such as 2, 6-dimethylnaphthalene, major elements including Ca, K, Mg, and S, and some trace elements, such as Al, AS, Ba, Cu, Fe, Mo, P, Pb, U, and Zn.

Air inhalation experiments showed PM2.5 emissions from all the tested RAP samples was low. For example, NORTHRAP emitted an average of about 0.8 mg/m^3 of toluene. This level is well below the EPA guideline for short-term (6 hour) exposure to toluene of 37 mg/m^3.

The acidic solution used in EPA method 1311 for mimicking landfill leachate was found to be highly toxic in the Microtox® screening tests, obscuring any possible toxicity elicited by the RAP material itself, even after pH was neutralized. Modification of this solution to use sodium hydroxide instead of ammonium hydroxide, reduced, but did not eliminate solution toxicity. Even using the ammonium hydroxide solution, there did not appear to be appreciable toxicity associated with the various RAP samples, nor with the various methods of weathering. Weathered RAP samples eluted with artificial rainwater in the column experiments appeared to be less toxic in the Microtox® assay than the batch RAP and weathered RAP samples, however, this might be primarily due to toxicity associated with the solutions used to elute the batch samples.

Assays using the Medaka embryos also proved to be even more sensitive to the solutions used for batch elution, again compromising our attempts to determine toxicity associated with the RAP materials. In the embryos tests, although the artificial rainwater was not toxic, there was some toxicity associated with the samples run through the soil column, which in some cases also appeared to carry fungal contamination that were, in themselves, toxic to embryos.

Based on the conclusions of this study, we provide the following recommendations:
1) RAP may be used as an unbound material in all environments except those which are highly acidic (pH ≤ 4) such as, but not limited to, mines with sulfur-containing minerals or landfills where other materials may decompose creating an acidic environment.
2) Acceptable, beneficial, uses of unbound RAP materials may include, but are not limited to, using the unbound RAP as surface materials for parking lots, farm roads, or pathways; for quarry reclamation; as non-vegetative cover underneath guiderails; and mixed with other materials for subbase or base materials; in addition to the current uses in hot mix asphalt applications.
3) Due to the inconsistent pollutant levels found among the three RAP stockpiles evaluated in this study, it is also recommended, as a precautionary measure, to determine the releasable levels of metals and PAHs for RAP stockpiles before using RAP in highly acidic environments; by extracting leachate samples using batch experiments and measuring pollutants (PAHs and metals) levels.
   a. If the releasable levels of pollutants are below US EPA drinking water standards, unbound RAP can be used in all acidic environments.
   b. If the releasable levels of metals and PAHs exceed US EPA drinking water standards, it is recommended to ensure that there is a soil layer between the RAP and the groundwater aquifer. It is important to note; however, that it was beyond the scope of this study to determine the type and thickness of the soil layer that is appropriate for the use of RAP.

INTRODUCTION

Background

In the United States, the road network consists of more than 2 million miles of paved roads. Approximately 95 percent of these roads are paved with asphalt pavements; typically in the form of hot mix asphalt (HMA). The typical life expectancy for HMA pavements ranges from 12 to 15 years during which several maintenance procedures are implemented to ensure satisfactory performance of these pavements. Eventually however, roadway sections must be removed and a new pavement surface placed. During the construction of new pavement sections, reclaimed asphalt pavement (RAP) is obtained through the milling and removal of existing pavement surfaces.

RAP materials have been successfully reused and recycled into new asphalt pavements since the 1970s. In fact, asphalt pavements are considered America's most recyclable materials due to the reuse of RAP into new pavements. The main factor driving the recycling of RAP materials into new pavements is the sizeable amount of natural aggregates typically used in producing those pavements, enhancing the benefits of conserving these natural resources and reducing costs of new asphalt pavements. Despite the benefits of recycling RAP materials, not all of it can be recycled into new asphalt pavements. Therefore, the unused RAP materials have to be either stored on site for long periods of time or disposed of in waste landfills, which is often costly. RAP materials can also be used as aggregates for unbound base materials, aggregates for stabilized base materials, pothole filler materials, and roadway shoulder materials.

Despite the advantages of recycling RAP, several environmental concerns can arise due to the reuse of this material. Currently, the New Jersey Department of Environmental Protection (NJDEP) prevents the use of RAP materials as unbound base materials, stabilized base materials, shoulder materials, and in parking lots due to the potential toxic pollutants that might leach from RAP used in these applications. Concerns about pollutants leaching from RAP are associated with two groups of RAP components. First, RAP materials contain asphalt binders that are derived from various types of petroleum hydrocarbons. Second, RAP materials may also be contaminated by a variety of chemicals generated from traffic. These chemicals typically include vehicle exhaust, gasoline, lubricating oils, and metals from tires and brakes (Legret et al., 2005). Studies on pollution from pavement have generally focused on heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) and polycyclic aromatic hydrocarbons (PAHs) (Lindgren, 1996; Brantley and Townsend, 1999).

Studies conducted to date on contaminants leaching from pavement and RAP materials generally indicate that release of metal and PAH contaminants is low to non-detectable, and even when detectable, concentrations in leachate are below environmental limits or values of toxicological concern (Kriech 1990, 1991, 1992; Sadecki et al. 1996; Brandt and DeGroot 2001; Legret et al. 2005; Birgisdottir et al. 2007; Kayhanian et al. 2009). However, there are several limitations to the work published on RAP. For instance, these studies do not consider important physicochemical processes essential to the weathering and fate of materials in the environment. In these processes, most metals and all high molecular weight PAHs are typically associated with soil particles when

transported by surface water and ground water (Weissenfels et al., 1992). Therefore, a better experimental design to approximate environmental conditions would incorporate a column leaching test for soils or aquifer solids after completion of the RAP leaching experiment. This would produce a more environmentally realistic leachate from both RAP and soils. Lower molecular weight (LMW) PAHs such as naphthalene are highly soluble in water, but are also subject to biodegradation (Cerniglia, 1992; Chang et al., 2002).

Weathering processes are also important to the fate of material in RAP because they oxidize the major component of asphalt (i.e. asphaltene compounds). Although asphaltene compounds have been determined to be environmentally friendly (Schreiner, 2011), the concern remains whether the oxidization process might result in the release of toxic compounds. Structural analysis can help predict the toxicity of the compounds produced. By definition, asphaltenes are a petroleum fraction soluble in toluene and insoluble in n-heptane. They are the heaviest components in crude oil having the highest boiling points. They have a high degree of aromaticity and can contain nitrogen, oxygen, sulfur, and metal atoms. Due to their molecular complexity, high boiling points, limited solubility, and tendency to aggregate, the analysis of asphaltenes has proven to be a challenging and complicated endeavor. Nonetheless, recently developed high mass resolution Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICRMS) has provided powerful tools used in the identification of the asphaltene components (Fernandez-Lima et al., 2009; Gaspar et al., 2012).

To evaluate the potential impact of RAP leachate and components produced by weathering, it is also important to directly assess the toxicity using toxicity assays. A suite of generally accepted methods and approaches (Burton, 1992) has been in place for the past several decades. McElroy et al. (2000) assessed sediment toxicity at five sites within the Harbor Estuary and a Long Island Sound reference site using six different sediment bioassays. These bioassays are *Ampelisca abdita / Mysidopsis bahia* using an assay developed by Ho et al. (2000), two fish, embryo/larval survival tests using *Fundulus heteroclitus* and *Menidia menidia*, and two bacterial assays, Microtox™, and Mutatox™. In this case, the *Ampelisca* test was most sensitive (McElroy et al., 2000). She and others have adopted fractionation approaches to attempt to determine the causes of toxicity in soil and sediments. Using a toxicity identification evaluation or TIE approach, Ho et al. at the EPA laboratory in Narragansett found that manipulations designed to remove organic contaminants, such as treatment with C18 or powdered coconut charcoal, reduced toxicity in standard sediment toxicity tests (Ho et al., 2001Ho et al., 2001; Kuhn Hines, 1995). McElroy et al. (2000) employed a reverse TIE approach (also known as assay assisted fractionation) where chemical class specific fractions of sediment extracts were amended back onto reference sediments prior to toxicity testing, and then compared results with amended sediments to the toxicity of native sediments. Her results not only provided support for organic contaminants having a causative role in the sediment toxicity observed, but also further identified the fraction enriched in aromatic hydrocarbons as opposed to PCBs, pesticides, or other more polar or saturated contaminants, as contributing most to the toxicity observed in at least one site examined. The inclusion of toxicity assays in this project allowed for the determination

of what types of RAP leachate, if any, are toxic, and furthermore what approaches for beneficial reuse minimize toxicity.

In summary, although previous published studies indicate the toxicity of RAP leachate is minimal, further work using environmentally realistic testing scenarios is needed to provide supporting evidence justifying a wider usage of RAP. The proposed work will determine:
- Whether there is any toxicity associated with the freshly collected RAP materials;
- Whether there is any toxicity associated with aged (weathered) RAP materials;
- If toxicity is observed, the research team will determine which classes of contaminants are associated with toxicity; and finally,
- Whether there are engineering solutions that minimized potential toxicity of RAP material.

Study Objectives

The primary research goal of this study was to investigate the environmental impacts of unbound reclaimed asphalt pavement (RAP) while it is freshly processed and after subjecting it to an accelerated weathering process. The secondary goal is to explore potential uses of RAP that are currently restricted, but that can be applied while meeting environmental standards. In addition, affordable treatment methods and remedies for unbound RAP applications where adverse environmental impacts have been identified will be explored.

The specific objectives to achieve these goals are summarized below:
- Investigate levels of PAH and metals toxicity in leachate from RAP
- Examine the toxicity of oxidized organic compounds in aged RAP products after accelerated weathering.
- Explore affordable solutions to mitigate or reduce toxicity levels of RAP, if any, and recommend potential engineering applications to utilize RAP in NJ

Report Organization

This report is organized into seven chapters. In chapter one, the problem statement, objectives, and outline of the report are presented. Chapter two presents a comprehensive literature review summarizing the current state of practice for compaction quality control of unbound pavement layers. Chapter three describes RAP materials selected for this study and their sources. Chapter four provides a discussion the procedures implemented for aging (or weathering) the RAP materials. In chapter five, a detailed discussion of the batch and column experiments is presented. Chapter six the toxicity procedures and their results. In chapter seven, the conclusions, and recommendations made after conducting the experiments and analyzing the results are presented.

LITERATURE REVIEW

Introduction

In this chapter, a comprehensive discussion of relevant literature is presented. Specifically, studies pertaining to the most practical environmental and engineering laboratory tests generally utilized by researchers to obtain leachate and evaluate toxicity of Reclaimed Asphalt Pavement (RAP) are discussed. This chapter also includes a comprehensive discussion of the typical toxicants that might be found in RAP and as reported in previous research studies. In addition, findings of published studies relevant to the toxicity of RAP are presented.

Environmental Tests for RAP

Toxic Characteristic Leaching Procedure (Batch Leaching)

The Toxic Characteristic Leaching Procedures (TCLP) is a test that simulates contaminant releases that are most likely to arise when a material is left in a constructed waste facility (Ogunro 2013). The procedure involves analyzing leachate samples (a liquid that extracts any constituent of the material it passes through) to determine if the material is hazardous. It is meant to be representative of prolonged exposure in a landfill. In carrying out the procedure the EPA Method-1311 requires that a bulk material (in this study RAP) to be added to a leaching solution and then allowed to soak for a specified time period, up to a few days. This solution is either TCLP fluid or deionized water (DI). A typical soak time is 24 hours and is carried out in a covered 2.5L glass jar. The bulk material is crushed to a grain size of 19.1mm. Liquid to solid ratios (L/S) of 5, 10, 15, and 20 is used to determine any relationships that may exist. Once the liquid is separated from the material it is analyzed for contaminants.

Column Leaching Experiments

Column leaching is another common test that is used to collect leachate samples. In comparison to Batch Leaching, the liquid to solid ratio is greater in column leaching and there is characteristically more dilution in batch leaching tests (Brantley and Townsend 1999). Furthermore, the bulk material is subjected to a more realistic environmental impact when undergoing the column leaching procedure. This procedure is conducted according the EPA Method-1311 standards and can either be used with a standard TCLP fluid to simulate extreme conditions or deionized water as the leaching fluid. To perform this experiment, RAP (or bulk materials to be tested) is sampled and crushed to a minimum grain size just as the batch-leaching test. The difference is that in column experiments the sample is subjected to a continuous flow of the leaching fluid though the column with the sample inside.

In order to simulate field conditions, the column can contain layers of RAP and soil. Column leaching tests consist of many cycles over a designated period of time. Each cycle consists of running the test fluid through the sample and collecting the liquid as it exits the columns after passing through the sample. Cycles can be completed as many times as desired; however, the concentration of the contaminant tends to decrease with each additional cycle. Column leaching tests are more useful to run when field conditions involve water running through the system, which is why it is an important test to conduct (Thapalia et al 2010).

Chemical Analysis

Chemical assessment of leachate is one test that is typically used to analyze the chemical toxicity of leachate samples. After the leachate samples are collected they are typically filtered and the metals present in them is separated. The metals are typically quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is a type of mass spectrometry, which is capable of detecting metals and several non-metals at concentrations as low as one part in 1012 (parts per trillion). This is achieved by ionizing the sample with inductively coupled plasma and using a mass spectrometer to separate and quantify those ions (Zhuang 2014). This first phase of chemical analysis is typically conducted to detect metal and non-metal compounds in the leachate solution, along with their concentrations.

The second phase of the chemical toxicity analysis involves determining the PAHs and their concentrations. The EPA Method W-846 3510 standard procedure can be utilized to extract theses PAHs. The Gas Chromatography- Mass Spectrometry (GC-MS) device is typically used for determining the concentrations of PAHs within a leachate sample. In general GC-MS is an analytical method that combines the features of gas chromatography and mass spectrometry to identify different substances within a test sample. Gas chromatography separates and analyzes compounds through vaporization and mass spectrometry identifies the amount and type of chemicals present in a sample by measuring the mass-charge ratio and abundance of gas-phase ions. The GC-MS can also identify trace elements in materials that were previously thought to have disintegrated beyond identification (Moniruzzaman 2014). This analysis is especially useful for weathered RAP samples because the sample will be deteriorated.

In addition to determining the concentrations of metals and PAHs, methods for analyzing inhalable chemicals are also available. Materials that may discharge inhalable pollutants or semi-volatile pollutants can be evaluated using these methodologies. For instance, RAP used under the guiderails (in an unbound application) can tremble and shake when heavy trucks drive by; leading to the release of particulate matter and, possibly, even semi-volatile pollutants. High surface temperature in the summer may lead to the release of air pollutants as well. Breathing inhalable pollutants may cause nose, throat, and/or lung irritation and inflammation, depending on the degree of exposure.

One method for quantifying the amount of inhalable pollutants released from potentially toxic materials involves placing this material inside a box, and then shaking it for 8 hours. The cap of the box can be retrofitted with a gas inlet. The box can also be designed to include a high-efficiency particulate air (HEPA) filter and two sampling ports, one typically connected to a pump running at 1.5 LPM and the other connected to a phosphate buffered saline (PBS) solution. Fine particulate matter with aerodynamic diameter less than 2.5 um (i.e. PM2.5) can be collected using a quartz filter whereas semi-volatile pollutants (e.g., naphthalene) can be collected using polyurethane foam (PUF) placed downstream of the filter.

Microtox® Toxicity Screening

In environmental assessments of pollutants and contaminants, it is important to be able to test many samples for toxic effects in an efficient manner. Bacterial assays have been commonly employed in first pass toxicity screenings because they provide biological insight relatively easily and quickly. The cost of the test is low and is relatively easy and quick to perform. Accordingly, it is usually prescribed as the first prescreening tool in assessing chemicals hazardous nature (Johnson 2005; Wells et al. 1997; De Zwart and Sloof 1983). Due to their extremely short generation periods, bacterial assays allow scientists to measure sensitive metrics like growth or reproduction in a short period of time, allowing more samples to be processed in a shorter amount of time (Perez et al., 2012). Higher animals like invertebrates and vertebrates require longer experimental durations and incur higher husbandry costs as well, preventing more efficient data collection (Teodorovic et al., 2009).

The Microtox® assay relies on the marine bacterium Vibrio fischerii, which produces measureable light when colonies are in healthy condition. With the addition of various dilutions of a potential toxicant or environmental sample, the relative decrease in light output can be used to calculate effective concentrations, such as EC50s (the concentration where 50 percent of the test population exhibits an effect, in this case light inhibition). The Microtox® test has been shown to be quick and reproducible (Stronkhorst et al., 2003). However, like any other biological assay, use of a living organism has the risk of introducing biases and confounding factors that influence their behavior. Many researchers have found that variations in chemical properties of test samples, including things like organic matter, turbidity, and pH can influence Microtox® results. Many of these chemical parameters vary in non-linear ways with serial dilution, which can interfere with EC50 calculations (Perez et al., 2012). Suspended sediments provide another potential bias as Vibrio tends to adsorb to particle surfaces, which reduces light output without causing toxicity, resulting in overestimation of toxicity (Ringwood et al., 1997).

Furthermore, the performance of Microtox® assays are highly dependent on the test conditions, where contaminant type and matrix complexity may greatly influence toxicity determinations. Teodorovic and colleagues compared the Microtox® assay with another bacterial inhibition assay, the Pseudomonos putida growth inhibition test, and a standard Daphnia magna survival test to various heavy metals, and found that in nearly all cases, the Daphnia test is much more sensitive to heavy metals, and that even between the two bacterial tests, the P. putida tests tended to be more sensitive than Microtox® (Teodorovic et al., 2009). On the other hand, studies have shown that for many organic contaminants, Microtox® might be more sensitive than higher level organisms (Celebi et al., 2012).

Lastly, the scalability of Microtox® results to biological endpoints that are of concern to risk managers, such as invertebrate or vertebrate population health, are typically inconsistent. Similar to results obtained by our study, Microtox® assays were unable to predict toxic effects to developing vertebrates. Dieter and colleagues conducted wetland mesocosm experiments with the organophosphate insecticide phorate and used the

Microtox® assays in addition to measuring the invertebrate (Chironomus larvae and the amphipod Hyallela Azteca) and mallard duckling (Anas platyrhynchos, 21 days old) survival. The Microtox® assays showed little to no toxicity, which was not reflected in the animal survival data: both invertebrate species experienced complete mortality in all phorate treatments and duckling survival decreased by 40 to 80 percent (Dieter et al., 1994).

While the Microtox® system, as well as other bacterial assays, provide a quick assessment of biological effects, their variable sensitivity, as well as potential biases and confounding factors makes it inadvisable to apply it as the only biological test for toxicity in environmental risk assessment. It would then be recommended that Microtox® screening should take place concurrently with other biological assays, particularly with animals like Daphnia magna or early life stage fish, to corroborate and support Microtox® results as well as providing more comprehensive scope for toxicant evaluation.

To this end, a subset of samples screened by the Microtox® Assay were also evaluated for their relative ability to increase mortality in fish embryos and for their ability to cause DNA damage in embryos exposed using the comet assay. The comet assay is a widely adapted method which measures the extent of broken DNA in the nucleus using microgel electrophoresis combined with fluorescence microscopy (Olive et al. 1990).

Early life stage (ELS) toxicity testing with aquarium fish has long been a workhorse for toxicity testing. Large numbers of embryos can be obtained daily from a modest colony of breeder fish. Their small size (often ~1 mm diameter) and transparancy allows multipe endpoint to be evaluated within the same group of exposed individual ustilizing relatively small volumes (< 1 ml) of test solution per individual replicate. In addition concerns about the need to sacrifice large numbers of sentient organisms in traditional toxicity testing with rodents or adult fish has lead to popularity of ELS testing with embryos (Embry et al. 2010). In our laboratory we have used ELS fish tests to succesfully evaluate a wide range of chemicals associated with both sediment and aqueous exposures (McElroy et al. 2000, 2006, 2011; Dasgupta et al. 2014, 2015). In addition to providing data on a vertebrate model, ecologically important endpoints such as larval survival can be linked to population level effects. Assessment of DNA damage is important because it can mechanistically be linked to direct genetic damage and potential mutation risk, and has been associated with PAH exposure. Finally, *in vivo* testing with intact organisms such as fish embryos provides a more relistic toxicity assessment by testing an intact organism with it host of physiological dfense mechanisms intact. (Koshmehl et al. 2008).

Typical Toxicants Found in RAP

Heavy metals are one type of toxins that can be found in RAP. The presence of such metals can negatively affect a person's health, and furthermore, the health of animals and plants when exposure is prolonged. The most common sources of heavy metals in RAP are the vehicles that drive over pavements it is collected from. After extensive research, there are a few notable heavy metals present in RAP including: Lead, from

vehicle emissions, Cadmium, from tires, Copper, from brake linings, zinc, from roadway barriers and tires, and lastly Aluminum (Mangiani 2003).

Polycyclic Aromatic Hydrocarbons (PAHs) are another type of chemical that can be present in RAP materials. PAHs have two sources, petrogenic sources from fossil fuel and pyrogenic sources, from the incomplete burning of organic substances such as coal, oil, gas, and even grass and wood. RAP contains asphalt binders which is the heaviest product of the oil refining process. Therefore, PAHs are expected to be present in RAP. In general, low molecular weight (LMW) PAHs (e.g., naphthalene) can be harmful to the environment and human health due to the fact that LMW PAHs have high vapor pressure and thus have appreciable concentrations in air after emission. PAHs most commonly enter the body through inhalation; however, they can also be ingested (e.g., in food), and absorbed through the skin. Once they are in the body, PAHs can target organs such as the kidneys or liver, and some can be mutagenic and carcinogenic. Therefore, determining the concentrations of PAHs leaching from RAP materials is of great importance.

<u>Findings from Pertinent Research Studies</u>
A number of research studies have been conducted to quantify the amount of chemicals leaching from RAP materials. The results of these studies are presented in the following paragraphs.
In a study conducted in France, Legret et al. (2005) used RAP samples that were generated from the RN 76 highway and conducted batch and column leaching tests, followed by atomic emission spectrometry (ICP-AES) and high-pressure liquid chromatography (HPLC) chemical analysis to determine if chemical concentrations were above the European Commission (EC) minimum limits. In the batch leaching test, only zinc and mercury were detected above minimum levels for heavy metals and only phenanthrene was detected above minimum levels for PAHs. It was noted that phenanthrene is not a known carcinogen. Chemical concentrations were highest in the first stage of the column leaching tests, but drastically lowered to below detection levels. This was first noted by Brantley and Townsend (1999). Unlike Brantley and Townsend, Legret found benzo(ghi)perylene, dibenzo(ah)anthracene, indeno(123cd)pyrene, and chrysene at concentrations above their detection limit initially. This was thought to occur because of the higher levels of detection limits that were used with Brantley and Townsend's study. Lastly, it was determined that slowing down the flow rate for the column leaching test helped diffusion of zinc and copper and lead to higher levels initially, but even these levels drastically fell below detection limits with time.
Taking asphalt material from four refineries in Montana, Pribanic (1994) sought to represent a worst case scenario by using samples that had not been in service and therefore had forgone any effect from surface contamination. It is a "worst" case in the sense that any lower molecular weight components would still be expected to be present in the sample. Only batch leaching tests were performed and no leachable PAHs or metals were observed. It was concluded that the leaching of these contaminants from RAP, either from a stockpile or shoulder cover, would not be likely.

At the University of Wisconsin, Sedivy et al. (2012) collected RAP from Ohio, Wisconsin, New Jersey, California, and Colorado and performed batch leaching with TCLP fluid solution and deionized water. When considering the differences between using TCLP solution and DI water, there was clearly more heavy metals detected when using the TCLP solution. Consequently, all concentrations were found to be below the maximum contamination levels (MCL) for drinking water, except for manganese and arsenic. Considering PAH levels, there was no discernible difference between the TCLP solution and DI water. Furthermore, most PAH levels were close to or below the detection limit and well below groundwater intervention limits. It was also found that raising the L/S ratio saw a corresponding rise in PAH levels, but overall they were still below the detection and groundwater intervention limits.

In a study by Brantley and Townsend (1999), levels of lead were actually found to be above the minimum levels for groundwater guidance. These levels were found after performing column leaching tests and was thought to occur due to the lower dilution found in this leaching test as opposed to batch leaching tests that were performed. Interestingly, the levels of lead eventually went down over time with the exception of one sample. Townsend (1998) also found that lead levels were a result of vehicle emissions and traffic since the highest levels of lead were found in the oldest RAP samples.

In a Danish study conducted on four asphalt specimens, Birgisdottir et al. (2007) modeled their experiment for general road use and investigated the leaching characteristics of 16 PAHs typically found from bitumen-based asphalt. The total content of PAHs in the asphalt specimens was below the Danish soil quality criteria for three of four asphalt specimens. Calculations indicated that only a minor part of the PAHs present in the asphalt leached out during 25 years of leaching, 0.004–1.1 percent for five PAHs. Finally they concluded that concentrations of PAHs that are found above the Danish soil quality criteria near roads paved with bitumen-based asphalt in Denmark are very unlikely to occur due to leaching of PAHs from the asphalt.

Nine petroleum bitumen's covering a representative range of commercially available products and one asphalt made from one of the bitumen's were tested by Brandt et al (2001) in a static leach test. The asphalt was also subjected to a dynamic leach test. The equilibrium PAH concentrations in the leach water from bitumen's stayed well below the surface water limits that exist in several EEC-countries and were also more than an order of magnitude lower than the current EEC limits for potable water.

Taking samples received directly from the Illinois Department of Transportation, Kreich (1991) prepared the RAP for TCLP. Following the TCLP test the leachate was tested for PAH's by HPLC and metals by atomic absorption. After a thorough investigation of these samples it was ascertained that all of these samples met current guidelines for TCLP maximum concentration for the contaminants. Further, the migration of metals and organics was impaired greatly by the matrix of asphalt and aggregate. Finally the conclusion that RAP should not be a concern for clean fill was made.

In another study, Kriech (1992) prepared asphalt and concrete pavement for TCLP by following the EPA guidelines for crushing the samples. PAHs and heavy metals, including barium, cadmium, chromium, lead, silver, arsenic, selenium, and mercury were tested in the samples. The study found that both Portland Cement Concrete (PCC) and Hot Mix Asphalt (HMA) pavements each have very low level of leachable metals

and PAH materials. The relative low levels of leachable materials from both pavement types are quite similar. Also, soils from the shoulder of the road are quite similar in characteristics to the PCC and HMA pavements.

Leachate metal pollutant concentrations produced from asphalt and concrete pavement materials were measured by Kayhanian et al (2009). The results showed most of the metal pollutants were below the reporting limits. Dissolved chromium was detected in leachate from concrete (not asphalt), with strong readings in early-time leachate samples. Cr concentration decreased to below the reporting limit as time passed. The cement was found to be the source of the chromium. Samples of leachate coming from different cement distributors was taken, with Cr concentrations ranging from 124 to 641 mug/L, proving that the chromium leachate concentration can be reduced through source control. The leachability of Cr in hardened pavements was substantially reduced meaning the concentration of dissolved Cr in highway runoff was found to be lower than the Cr concentration produced from leachate of both open and dense graded concrete pavement specimens. Testing concluded that pavement materials are not the source of pollutants of concern in roadway runoff.

Environmental concerns regarding the quality of runoff water from salvaged pavement stockpiles was addressed by Sadecki et al. (1996). Three experimental stockpiles were studied consisting of: (1) coarse concrete, (2) fine concrete material, and (3) RAP. The leachate samples were examined using EPA approved methods. The pH of the leachate exceeded Minnesota standards for surface waters, as well as chromium levels. Long term concerns from stockpiles reduce to suspended and dissolved solids. Finally, PAHs were near or below the detectable limits level in the RAP that was tested.

Barrett and Shaw (2006) evaluated the storm water quality benefits of porous asphalt overlay. The project was a study of the implementation of a porous asphalt overlay and its effects on the quality of highway storm water runoff. The overlay, known as permeable friction course (PFC), was a layer of asphalt 50 mm thick applied on top of the highway to enhance safety and reduce noise. The study monitored the quality of runoff from a four-lane highway in Austin, Texas both before and after the implementation of PFC. The observed runoffs in PFC covered asphalt were much less than before it was implemented. Total suspended solids were reduced 92 percent, total lead was reduced 91 percent, total copper was reduced 47 percent, and total zinc was reduced 75 percent. PAHs were not observed above the MDL either before or after PFC implementation.

A test on asphalt millings, supply well, and storm water retention pond was conducted by S&S Environmental at NY's Prospect Park Quarry. The motivation behind the environmental testing was to determine any leaching of PAHs or heavy metals into water ways. Concentrations higher than the NJDEP Direct Contact Soil Remediation Standards were found for benzo[a]anthracene, benzo[b]fluoranthene, and benzo[a]pyrene. SPLP leachate testing did not find any elevated levels for these compounds, however, leading to the conclusion that no PAHs were leaching from the RAP stockpile. Arsenic was detected at slightly elevated levels using SPLP leachate,

however since that is the only metal that was found to be elevated, the study suggested that it was due to the initial site area. The site's storm water retention pond also passed NJDEP Groundwater Quality standards for both PAHs and heavy metals. Many metals and PAHs were found to be at levels below the MDL, indicating that the RAP at the Prospect Park stockpile is not harming the environment.

In a study on parking lot seal coats as a possible source of PAHs, Mahler et al. used two primary sealcoat materials in his study; (1) coal-tar-pitch based emulsion and (2) asphalt-based emulsion. The main difference in the two substances is that coal tar can be 50 percent or more PAHs by weight than the asphalt based emulsion. Seal coats were investigated for their PAH contribution since they are heavily used to protect the underlying asphalt pavement and enhance its appearance. Furthermore, seal coats get reapplied approximately every 2 to 3 years, so the chance that they leach PAHs into urban water bodies in the US is enhanced. The chemical analysis used was GC-MS and large differences between concentrations for the different surface types suggest that abraded sealant products are a potentially important contributor to PAH contamination in water ways. An important result was that the average yield of PAHs from sealed parking lots was 50 times greater than from unsealed. Ultimately, Mahler et al. estimated that the sum of PAHs could be reduced 5-11 percent if all lots were unsealed.

Summary of Literature Review
In summary, it is evidently clear that PAHs and heavy metals are the appropriate groups of chemicals to focus on when evaluating RAP samples. This is the case (for PAHs) because RAP contains asphalt binders that are petroleum by-products, derived from the distillation process. In addition, RAP undergoes heavy pollution while in service, as roadway pavements, and can become contaminated by vehicle exhaust, gasoline, or lubricating oils. The presented studies conducted to date have used batch and column leaching as ways to simulate leaching of these contaminants under harsh and realistic conditions. Although a variety of chemical analyses were executed, it appears that the release of the majority of metal and PAH contaminants is low to non-detectable for pavement and RAP materials.

Furthermore, even when these chemicals were detected, the concentrations in the leachate were well below environmental limits or values of toxicological concern. When chemical concentrations were above minimum guidelines during column leaching tests, this only held true for the initial stage and always drastically dropped below minimum guidelines. One thing these studies did not consider is the effect of chemicals leaching out of aged RAP. Weathering plays an important role in aging the RAP due to the effect it has on oxidizing the asphaltene compounds of asphalt. Despite all these promising results, the toxicity of RAP materials in New Jersey still requires additional evaluation. This is the case simply because RAP is highly variable and what applies to one state may not necessarily apply to another.

DESCRIPTION OF RAP MATERIALS

Introduction

The RAP materials collected for this study were obtained from three locations; covering northern, central, and southern New Jersey (NJ). A fresh asphalt mix (referred to as fresh RAP) was also obtained in order to establish a baseline for the chemical and toxicity analyses employed in this study. This chapter presents a detailed discussion of these RAP materials.

Collected RAP Materials

Three different types of RAP and one freshly mixed HMA loose mix samples were collected from various sources throughout the State of New Jersey (NJ). The collected RAP materials were obtained from northern NJ, central NJ, and southern NJ. These RAP materials are denoted as NORTHRAP, CENTRALRAP, and SOUTHRAP depending on the plant from which they were obtained. In addition, the plant in northern NJ provided a freshly produced HMA loose mix samples (denoted as Fresh) which were utilized as a control RAP mix.

<u>Gradation Analysis of Collected RAP Materials</u>

A sieve analysis was conducted to determine the gradation for each of the RAP materials collected. The sieve analysis results are presented in Figure 1 below. As can be seen from this figure, the collected RAP materials for the most part were smaller than ½ inch and larger than Sieve No. 30. Figure 1 also shows that the collected RAP materials had approximately 50 percent passing Sieve No. 4; indicating that half the materials is "sand-like" and the other half is coarse RAP aggregates.
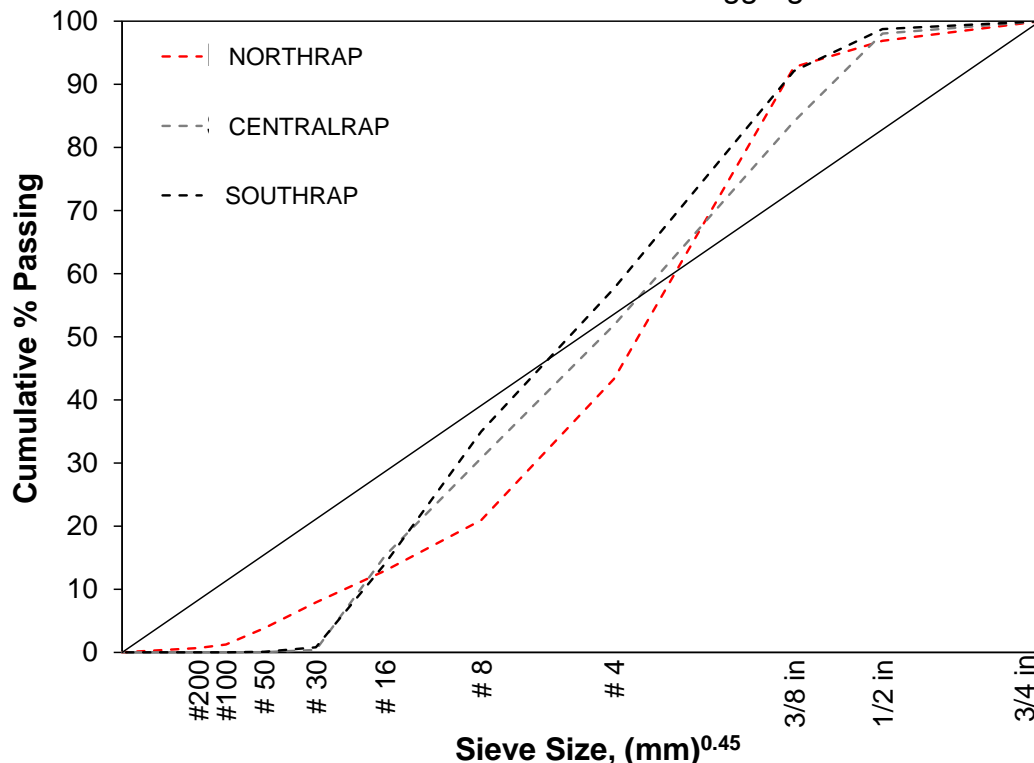
Figure 1: Gradation Curves for Collected RAP Samples.

Binder Content (Extraction & Recovery)

In addition to the gradation analysis, the binder content in each of the collected RAP samples (including the fresh HMA mix) was determined through conducting binder extraction and recovery experiments. AASHTO T 319 "Standard Method of Test for Quantitative Extraction and Recovery of Asphalt Binder from Asphalt Mixtures" procedures were employed for the purpose of extracting and recovering the binders and ultimately determining the binder content in each RAP sample. Table 1 below presents the binder content in each of the collected RAP materials and fresh HMA mix samples. As can be seen from this table, the collected materials had binder contents ranging between approximately 3 and 5 percent.

Table 1: Binder Content Results as Obtained from Binder Extraction and Recovery Experiments.

Specimen ID	Asphalt Binder Content
SOUTHRAP	2.89
CENTRALRAP	3.50
NORTHRAP	4.45
Fresh	4.17

PREPARATION AND WEATHERING OF RAP SAMPLES

Sample Preparation Procedure

RAP materials along with asphalt binders extracted and recovered from these RAP samples were prepared to facilitate conducting weathering and other toxicity testing procedures. The RAP samples (or extracted binders) preparation procedures varied according to the desired aging/testing procedure. For instance, weathering procedures were conducted on both RAP materials (in its loose form) and asphalt binder extracted from these materials. As shown in Figure 2a, the loose RAP sample was placed into specimen holders and a No. 200 sieve screen, whose open area is 46 percent of the total surface area, was used to cover the sample and prevent the loose RAP from falling down. The extracted and recovered asphalt binder samples were prepared by first extracting and recovering binders from the RAP materials. The AASHTO T319 "Standard Method of Test for Quantitative Extraction and Recovery of Asphalt Binder from Asphalt Mixtures" procedures were employed to extract and recover binder samples from the collected RAP and fresh mix samples. The extracted asphalt binder samples prepared for weathering experiments were in the form of pressed asphalt binder placed on aluminum plates. To prepare each sample for the aging test, a layer of masking tape was first applied to an aluminum plate while three 0.5" × 0.25" sections were left bare as shown in Figure 2b. A small amount of the extracted and recovered asphalt binders was then attached to the bare sections and pressure was applied until a thickness of 0.025" was reached. Thereafter, the masking tape was removed and three 0.5" × 0.25" × 0.025" asphalt binder samples were obtained on each plate, which is shown in Figure 2c. Once the samples were trimmed, masking tape was reapplied around each sample to prevent the binder from running off as a result of the elevated temperatures employed during the weathering process. The prepared samples were named based on the source where it was extracted. For instance, the SOUTHRAP binder sample is the asphalt binder sample extracted from SOUTHRAP and the FRESH- binder sample is the asphalt binder sample extracted from fresh HMA. It is important to note that additional information about sample preparation for toxicity and chemical analysis procedures are presented in the upcoming chapters.

(a)   (b)   (c)
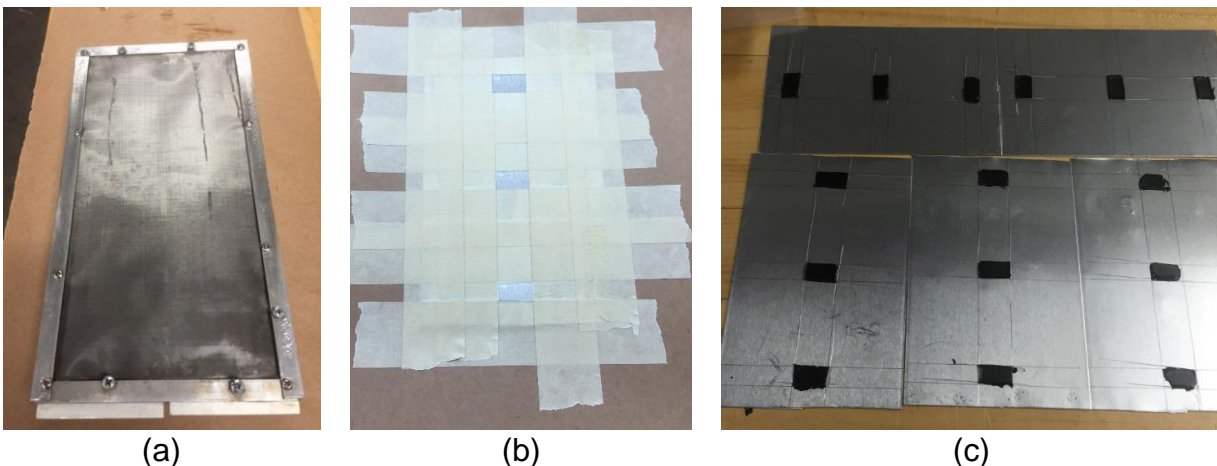
Figure 2: Preparation of Samples: (a) Loose RAP samples, (b) Taped Aluminum Plate, and (c) Asphalt Binder samples on an Aluminum Plate (Final Product).

Weathering Procedures

Both loose RAP materials and extracted RAP binder were aged as a part of this study using a QUV Machine (Q-Lab UV Tester) as shown in Figure 3. This machine can simulate long-term outdoor degradation of pavements due to aging over months or years (depending on intensity) in a few days or weeks. The QUV accomplishes this by exposing materials to alternating cycles of UV light and moisture at controlled, elevated temperatures. The effect of sunlight is simulated with fluorescent UV lamps (UVA 340 nm), whose spectral irradiance is a close match to the ultraviolet A (UVA) portion of sunlight and gives an excellent simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cut-off of 295 nm where most of the damage in durable materials occurs (QUV Accelerated Weathering Tester- Q-Lab, 2016).

Two types of aging procedures were employed in this study using the QUV machine. These included a continuous UV aging procedure and a UV/Moisture/condensation aging procedure. The cyclic exposure conditions for both test methods were based on ASTM D4799 Standard Practice for Accelerated Weathering Tests Conditions and Procedures for Bituminous Materials - Cycle D ("ASTM D4799" 2016):

- 4 hours of UV at 140°F (60℃) with a radiation intensity of 0.89 W/m^2·nm.
- 15 minutes of water spray.
- 3 hours and 45 minutes of condensation at 122°F (50℃).

(a)
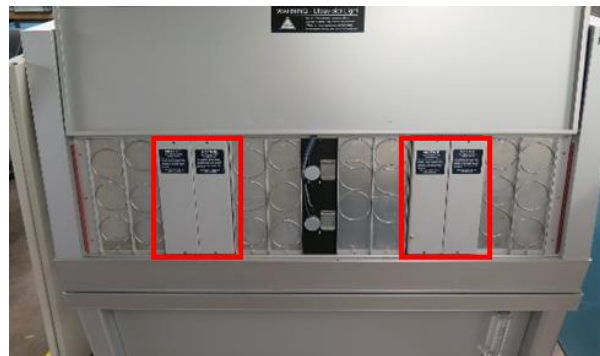
(b)

(c)

Figure 3: (a) Q-Lab UV Tester; (b) Sample Positions in QUV Machine (Highlighted).

Continuous Ultra-Violet (UV) Aging

Four samples of each of the four extracted asphalt binders were placed at the bottom of the QUV machine. Specimen holders containing loose RAP samples were placed in a vertical position near the door of the QUV machine. Both samples were weathered using continuous UV with a radiation intensity 0.89 W/m^2·nm and a temperature of 113°F (45°C) as shown in Figure 3b and 3c. In order to study the effects of UV radiation only, the water spray and condensation steps established in ASTM D4799 were omitted. In addition, lower temperatures than specified in ASTM D4799, were utilized in this study to minimize the impact of temperatures and only focus on UV effects. This was employed because UV effects are typically coupled with temperature effects at high temperatures; making it difficult to distinguish these effects. The specific temperature of 45°C was selected to conduct the continuous UV procedure based on what was recommended in the literature (i.e., according to Zeng et al. 2015). In fact, Zeng et al. (2015) reported that the influence of temperature can be ignored below 50°C. The sample conditionings were interrupted at 10, 30, 50, and 100 hours of UV when one extracted asphalt binder sample for each type was taken out for analysis and the loose RAP samples were shaken in order to make sure all loose RAP samples has similar UV exposure duration.

Ultra-Violet (UV), Moisture and Condensation Aging

In this procedure, fourteen extracted and recovered asphalt binder samples per RAP type were placed at the bottom of the QUV machine as shown in Figure 3c. The specimen holders containing loose RAP samples were placed vertically near the door of the QUV machine as shown in Figure 3b. The aging cycle was set based on ASTM D4799 - Cycle D ("ASTM D4799" 2016).

Based on Zeng et al. 2015, the temperature influence on UV aging could be ignored when the aging temperature is lower than 50°C, however when temperatures increase, some coupling effects happen. Therefore in order to minimize the temperature influence, the aging condition was modified as following:
- 4 hours of UV at 113°F (45°C) with radiation intensity 0.89 W/$m^2 \cdot nm$.]
- 15 minutes of water spray.
- 3 hours and 45 minutes of condensation at 104°F (40°C).

One asphalt binder sample for each type was removed to do further analysis and the loose RAP samples were shaken to make sure all loose RAP samples were exposed under UV for similar period at the following number of cycles: 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, 15, 18, 21, and 25.

Aging Index Evaluation

In order to study the aging process, an aging index which can represent the aging degree is essential. It is noted that most researches used carbonyl area, which represents the amount of oxygen that has reacted with carbon, as an aging index. However, oxygen will not only react with carbon but also with sulfur in asphalt binder during the aging process. Therefore, the WPO in asphalt binder is a more straightforward and accurate index to indicate the aging degree and it is used as the

aging index in this study as it can reveal the total oxygen which has reacted with asphalt.

Additionally, based on academic journals (Liu et al. 1996, Boysen and Schabron 2015), there is a relationship between the carbonyl area and WPO. Using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR FTIR), Liu et al. (Liu et al. 1996) found that the carbonyl area measured in the infrared spectrum as the absorbance peak area above the 1820 to 1650/cm is linearly related to the amount of oxygen which has reacted with asphalt. Also, Boysen and Schabron (Boysen and Schabron 2015) demonstrated that both the WPO and the carbonyl area can be related to the asphaltene determinator aging index ratio at 500 nm (500nm ADAIR) as shown in Figure 4 and Eq. (1) which is obtained by combining the equations for the linear trend lines shown in Figure 4.

$$CA(t) = 0.01257\, O(t) + 0.000446 \hspace{4cm} \text{Eq. (1)}$$

Where CA(t) is the carbonyl area at time t and O(t) is the WPO. Therefore, considering the linear relationship between the carbonyl area and WPO, the latter is found to be used as an appropriate aging index to characterize the asphalt aging process in this study.

After the accelerated aging tests, the WPO in the aged asphalt binders was measured through Energy Dispersive X-Ray Spectroscopy (EDX) using a Scanning Electron Microscope (SEM), which is shown in Figure 5a. Because the asphalt binder is nonconductive, all the aged samples were first coated using a sputter coater, as shown in Figure 5b, before the EDX analysis was performed. Using a coating time of 20 seconds, a uniform 10 nm layer of gold/palladium is obtained.

(a)   (b)
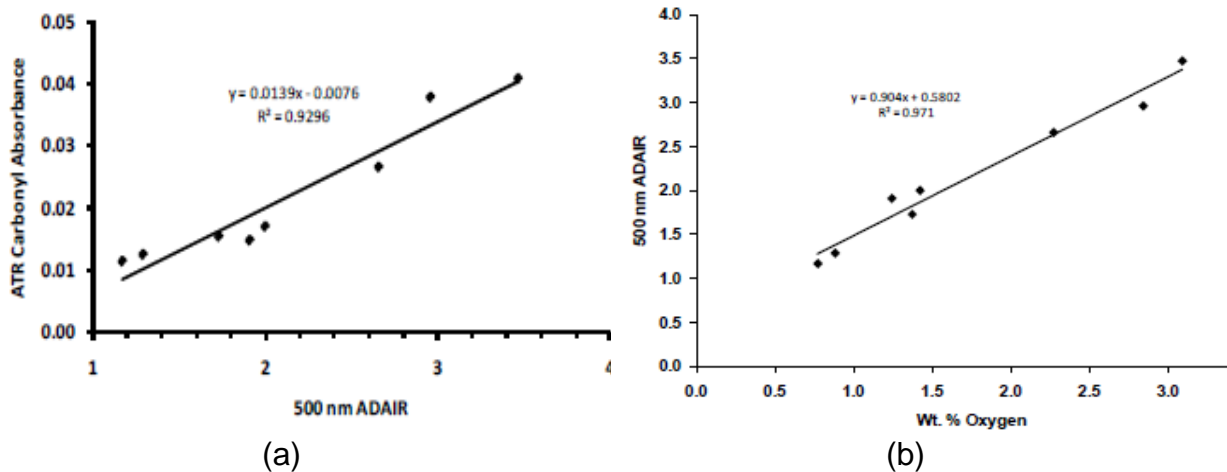
Figure 4: Relationships between WPO and Carbonyl Area (Boysen and Schabron 2015).

(a)   (b)

Figure 5: (a) Hitachi 4700 Scanning Electron Microscope (SEM) (b) Sputter Coater.

Through the EDX analysis, it was found that the primary elements in the samples were oxygen, sulfur, and carbon. Also certain amounts of gold and palladium were also presented due to the coating (denoted in Figure 6a), while nitrogen was also found in smaller quantities. Figure 6b illustrates an example of EDX results for unaged SOUTHRAP. Note that results of EDX are a spectrum of Counts vs. Energy (KeV).
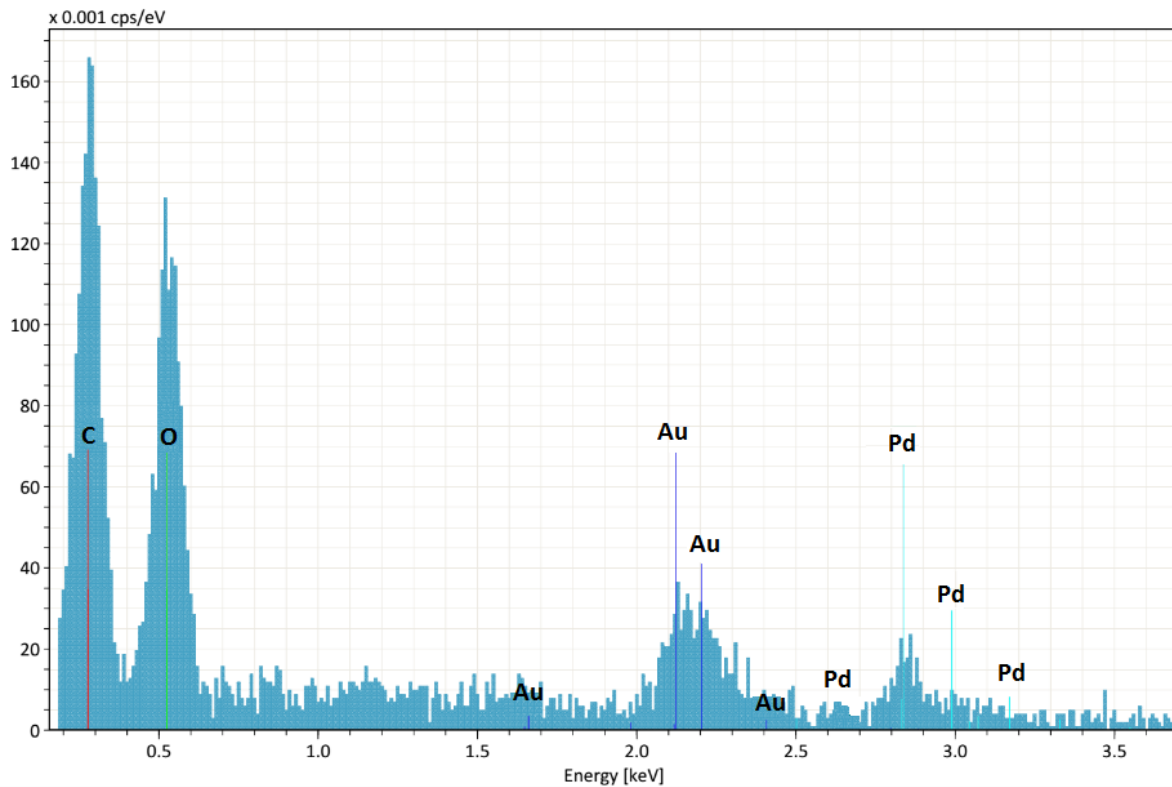
(a)
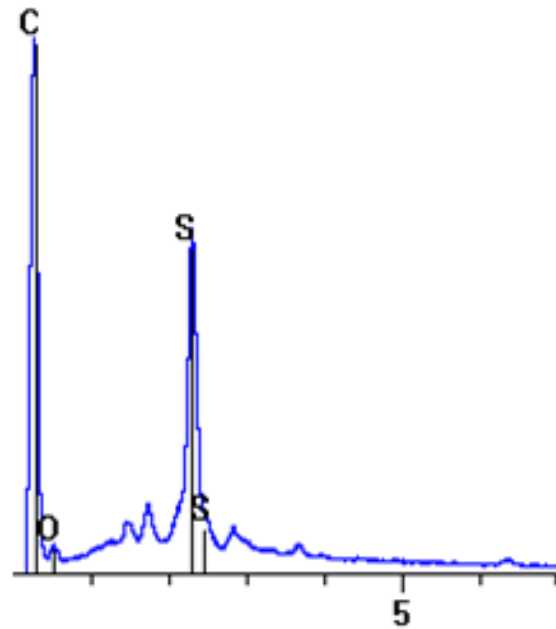
(b)

Figure 6: (a) Gold and Palladium in the Coating; (b) EDX test result for Un-Weathered SOUTHRAP with 92.17 percent Carbon, 4.8 percent Oxygen, and 3.03 percent Sulfur.

Analysis and Discussion of Weathering Results

Based on the EDX test results, the WPO in the same asphalt binder sample would vary from point to point. Therefore, an average WPO of four to six random points on the surface was determined as the overall WPO in all subsequent analyses.

Continuous Ultra-Violet (UV) Aging Results

Table 2 presents the EDX analysis results for the asphalt binder samples after continuous UV aging, this includes the WPO at individual points on each sample, along with the average and coefficient of variation (COV). The data clearly shows that the WPO in aged asphalt quickly increases initially, followed by a decreasing rate at around 30 hours of aging. These observations are consistent with the overall trend of both the FRCR and NDD models. The following part outlines the FRCR and NDD models and uses the method of least squares to the fit the models to the results of the EDX analysis.

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Table 2: WPO in Asphalt Binder Samples after Continuous UV.

RAP Material		Aging times (hours)				
		0	10	30	50	100
NORTHRAP	WPO (%)	4.54	8.86	12.84	14.68	14.81
		4.37	8.86	13.45	14.29	15.62
		4.32	8.74	13.57	14.11	15.21
		4.27	8.64	13.71	13.38	14.78
		4.56	8.76	12.98	-	14.79
		-	8.49	-	-	15.65
	Ave. (%)	4.412	8.725	13.31	14.115	15.143
	COV	0.0297	0.0162	0.0285	0.0386	0.0273
CENTRALRAP	WPO (%)	4.32	7.86	12.69	13.43	13.21
		4.11	7.95	13.02	13.6	13.97
		4.05	7.98	12.89	13.03	13.62
		3.99	7.65	13	13.76	14.34
		4.53	7.89	12.86	-	13.96
		3.9	-	-	-	13.98
	Ave. (%)	4.15	7.823	12.892	13.406	13.974
	COV	0.0563	0.02	0.0103	0.0219	0.0182
SOUTHRAP	WPO (%)	4.86	8.86	15.44	16.29	16.97
		4.75	8.74	15.56	16.23	17.17
		4.7	8.8	15.97	16.42	16.83
		4.85	8.71	15.83	16.2	16.65
		4.8	8.6	15.79	-	16.5
	Ave. (%)	4.792	8.742	15.718	16.285	16.824
	COV	0.0141	0.0112	0.0136	0.006	0.0156
FRESH	WPO (%)	3.89	7.95	10.76	12.06	12.85
		3.63	8.08	11.65	11.51	12.57
		3.28	8.23	11.99	12.16	12.41
		3.28	8.16	11.41	12.06	12.59
		3.56	8	11.57	-	13.52
	Ave. (%)	3.528	8.084	11.476	11.974	12.788
	COV	0.073	0.0141	0.0395	0.0247	0.0343

Jin (Jin 2012) proposed an asphalt oxidation kinematics model in terms of carbonyl formation, as shown in Eq. (2) to Eq. (5), based on aging data of two asphalt binders at five different temperatures and air pressures.

$$CA = CA_{tank} + M(1 - e^{-k_f t}) + k_c t \qquad \text{Eq. (2)}$$
$$k_f = A_f e^{-E_{\alpha f}/RT} \qquad \text{Eq. (3)}$$
$$k_c = A_c e^{-E_{\alpha c}/RT} \qquad \text{Eq. (4)}$$
$$M = CA_0 - CA_{tank} \qquad \text{Eq. (5)}$$

In Eq. (2) through (5), CA_{tank} is the carbonyl area of the unaged tank asphalt, CA_0 is the intercept of the constant-rate line, k_f and k_c are two reaction constants that are

temperature dependent according to the Eq. (3) and (4). M does not depend on the temperature, but on the source of the asphalt and the oxygen partial pressure. A_f and A_c are pre-exponential factors for k_c and k_f, $E_{\alpha f}$ and $E_{\alpha c}$ are the apparent activation energies for k_c and k_f, R is the idea gas constant (8.314 J/mol/K), and T is the absolute temperature (K).

Recall that there is a linear relationship between carbonyl area and WPO, therefore, Eq. (6) was proposed to have a similar correlation between the carbonyl area and the WPO to that in Eq. (1):

$$CA(t) = a \times O(t) + b \qquad \text{Eq. (6)}$$

Where a, and b are constants which correlate with the type of binder and O(t) is the WPO in the aged asphalt.

By substituting Eq. (3), (4), (5), and (6) into Eq. (2), the FRCR model proposed by Jin (2012) is rewritten in terms of WPO as:

$$\text{a} \times \text{O(t)} = \text{a} \times O(t)_{tank} + [O(t)_0 - \text{a} \times O(t)_{tank} - \text{b}]\left(1 - e^{-A_f e^{-E_{\alpha f}/RT} t}\right) + A_c e^{-E_{\alpha c}/RT} \text{ t}$$

$$\text{Eq. (7)}$$

For the FRCR model shown in Eq. (7), there are seven parameters that need to be determined using nonlinear curve fitting, however, only five different aging times were used in this continuous UV aging test. Therefore, the test results of continuous UV aging cannot be fitted by FRCR model, but can be fitted by the NDD model, where only two parameters need to be determined through curve fitting. According to the study in Li et al. (Li et al. 2009) the nonlinear differential dynamic model can be written as:

$$\text{x}(t) = (\text{L}x_0)/[1 + (L-1)e^{-rt}] \qquad \text{Eq. (8)}$$

Where $\text{x}(t)$ is the property of asphalt binder at time t, while x_0 is the value of $\text{x}(t)$ when t is equal to zero. The parameter L in this model is the ratio between the maximum and the initial values of x. In other words, it is a measurement of the maximum increase in x (This is demonstrated by substituting t = ∞ in the equation). Additionally, r is a measurement of the rate of increase in x for a given value of L. These two parameters can be used to compare the magnitude and rate of aging of different types of asphalt binder.

In order to show the variance of the EDX test results plots the test data of NORTHRAP with error bars, and includes a fitted curve using the nonlinear differential dynamic model. The test and fitted results for all types of binder samples are shown in Figure 7b. The determined constants L and r are summarized in Table 3. The R square values for all types of asphalt binder are larger than 99 percent which indicates that the continuous UV aging follows the prediction of the nonlinear differential dynamic model with very little deviation. Also from Figure 7b, FRESH samples have the lowest final WPO, while the SOUTHRAP samples have the highest final WPO, the WPO in NORTHRAP

samples are lower than that in SOUTHRAP samples but higher than NORTHRAP samples. The reason behind this phenomenon is that during the service period of asphalt pavement, the amount of aging that the asphalt binder experiences (here measured by the WPO) will increase proportionally to the service time. This explains why the FRESH binder had both a lower initial and lower final WPO than the three binders extracted from RAP. With all other variables being equal, this suggests that the service life of the pavement from which the SOUTHRAP material originated from was the longest, followed by NORTHRAP, and then CENTRALRAP.

(a)

(b)
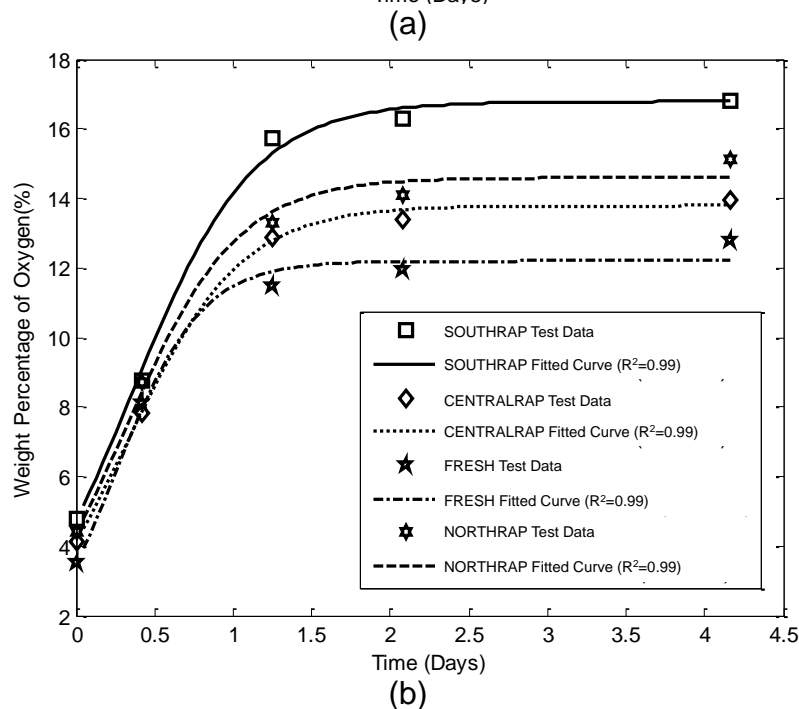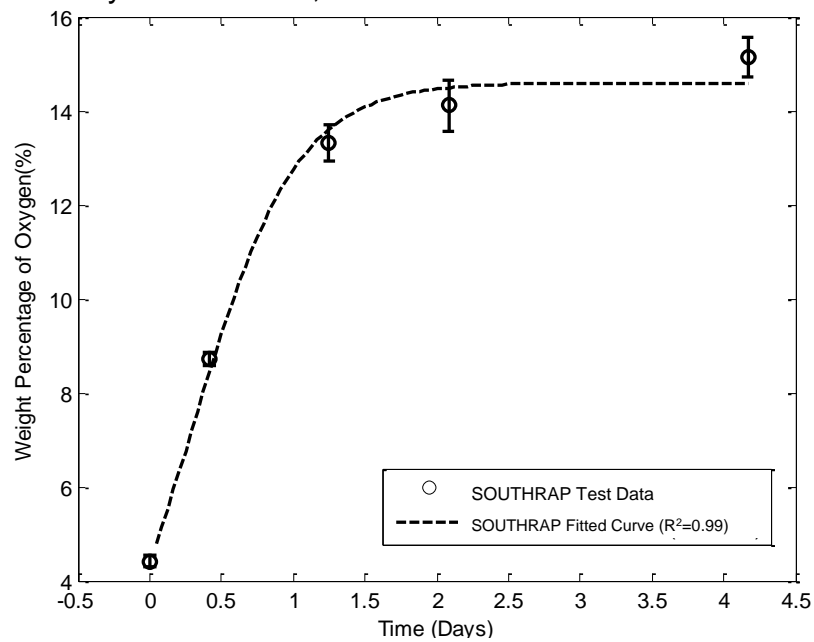
Figure 7: (a) EDX Test Results and Fitted NORTHRAP Curve with Error Bars and (b) EDX Test Results and Fitted Curves for All Extracted RAP Binders.

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Table 3: Coefficients of the NDD Model Based on Continuous UV Aging.

Binder Extracted From	L	r (days^{-1})	R^2
SOUTHRAP	3.503	2.598	0.99
CENTRALRAP	3.323	2.706	0.99
FRESH	3.458	3.655	0.99
NORTHRAP	3.308	2.767	0.99

Ultra-Violet (UV), Moisture, and Condensation Aging Results

Similar to that in the binder samples after continuous UV aging, the WPO in each sample after UV/Moisture/Condensation aging varies between different points (see the COV shown in Table 2). Therefore, four test points in each sample were chosen to be analysed and the average of these four test results were used as the WPO of this sample. The EDX test results for UV/Moisture/Condensation aging are included in Table 4 along with the COV. Similar to the result of the continuous UV aging tests, the WPO would increase fast at the beginning, however, after some time, this rate reduces significantly.

Figure 8a plots the EDX test results for all four types of asphalt binder samples and fits the data using the NDD model and the fitted results using the FRCR model are presented in Figure 8b. In both Figure 8a and Figure 8b, the FRESH samples have the lowest WPO while the SOUTHRAP have highest WPO, which is consistent with the result shown in Figure 7b for the continuous UV aging.

In order to present the variability of WPO in same asphalt binder sample and investigate which classic aging model can predict the aging under UV/moisture/condensation better, Figure 9 compares the fitted results of the two aging models for each type of asphalt binder with error bars. It indicates that both the NDD model and FRCR model are able to capture the aging process very well. This can be denoted by the fact that the R square value for all types of binder samples are greater than or equal to 95 percent as shown in Table 5. During the initial aging period both models are in close agreement with the data. However, at the transition part between the initial fast-rate aging and the later constant-rate aging, the NDD model increases at too fast a rate and overestimates the WPO. After about 8 cycles, the NDD model begins to level off and underestimates the WPO while the FRCR model continues to rise with the EDX results. Therefore, the NDD model can only be used to simulate the short term UV/moisture/condensation aging process, while the FRCR model can capture the entire UV/moisture/condensation aging process.

Table 4: WPO in Asphalt Binder Samples subjected to UV, Heat, and Moisture Aging.

RAP Material	Property	Cycle Number													
		1	2	3	4	5	6	7	9	11	13	15	18	21	25
SOUTHRAP	WPO (%)	4.6	7.9	10.1	11	12	13	13.3	14	14.6	14.6	15.5	12.3	14.9	15.6
		4.5	7.4	10.1	11	12	12.7	13.9	13.6	14.7	14.9	15.1	13.3	16.2	15.6
		4.5	7.6	10.2	11.4	12.2	11.9	13.3	13.7	14.3	14.8	14.6	14.1	15.1	15.6
		4.6	7.6	9.9	10.9	11.7	12.9	13.8	13.7	14.3	14.6	14.6	13.7	15	15.6
	Ave. (%)	4.6	7.6	10.1	11.1	12	12.6	13.6	13.7	14.5	14.7	14.9	13.3	15.3	15.6
	COV	1.5	3	1.4	2.1	1.7	3.8	2.3	1.4	1.3	0.9	2.9	6	4	0.2
CENTRALRAP	WPO (%)	5	7.7	9.1	10.1	11	11.4	11.2	11.4	12.3	12.4	12.4	13.3	12.7	12.9
		5	7.6	8.9	10.5	11.3	11.5	11.4	12.3	12	12.3	12.5	12.9	13.1	14.4
		5.4	7.7	9.3	10.5	10.6	11.1	11.7	11.6	11.8	11.9	12.4	13.1	13.1	14.1
		5.5	7.8	9.4	9.9	11.3	11.2	11.3	11.5	11.9	12.7	12.8	12.7	13.4	13.3
	Ave. (%)	5.2	7.7	9.2	10.3	11.1	11.3	11.4	11.7	12	12.3	12.5	13	13.1	13.7
	COV	4.7	1.4	2.3	3.1	2.9	1.8	2	3.6	1.6	2.7	1.6	2.1	2.2	4.9
NORTHRAP	WPO (%)	4.3	7.9	9.7	10.1	11	10.8	10.9	12.3	12.2	13..0	13.6	13.9	14.1	14.7
		4.4	7.3	9.4	9.8	10.8	11.4	11.7	11.8	12.8	13.1	13.6	14.3	14.3	14.6
		4.6	7.9	9	10.1	10.4	10.6	11.6	11.9	12.7	13.2	13.8	13.8	14.2	14.8
		4.5	7.8	8.8	10.3	10.1	11.3	11.9	12.7	13.1	13	13.3	13.9	14.1	14.6
	Ave. (%)	4.5	7.7	9.2	10.1	10.6	11	11.5	12.2	12.7	13.1	13.6	14	14.2	14.7
	COV	2.9	3.7	4.4	2.1	5.1	3.5	3.7	3.4	3	0.6	4.6	1.7	0.8	0.8
FRESH	WPO (%)	4	7.3	8.4	9.4	9.9	9.4	10.5	10.9	10.8	10.6	11	11.4	12.1	12.51
		4	7.7	8.3	9.1	9.2	10.2	10.3	10.4	10.7	10.9	10.8	11.1	12.4	12.54
		4.2	7.2	8.3	9.3	10.3	10.4	10.4	10.2	10.6	11.2	11.7	12	11.5	12.53
		3.9	7.5	8.3	9.3	9.3	10.6	10.7	11	10.9	11.3	11.1	11.1	11.9	12.53
	Ave. (%)	4	7.4	8.3	9.3	9.7	10.2	10.5	10.6	10.8	11	11.2	11.6	12	12.53
	COV	3.4	3.2	0.6	1.3	5.6	5.4	1.6	3.9	1.1	2.9	3.6	3.8	3.2	0.12
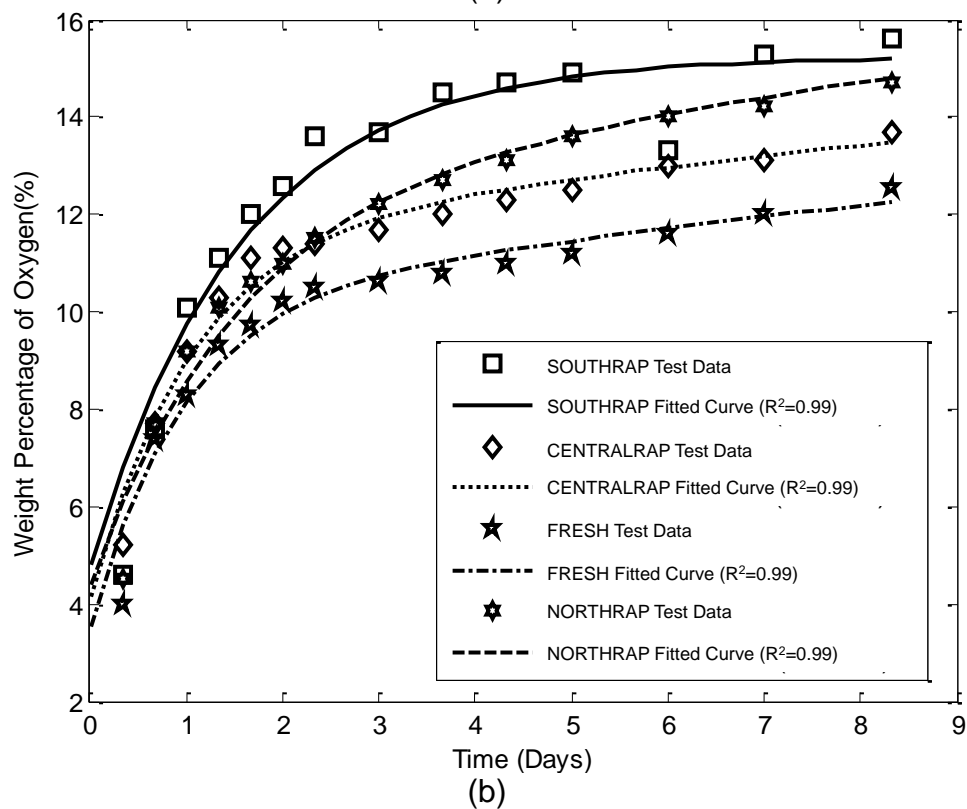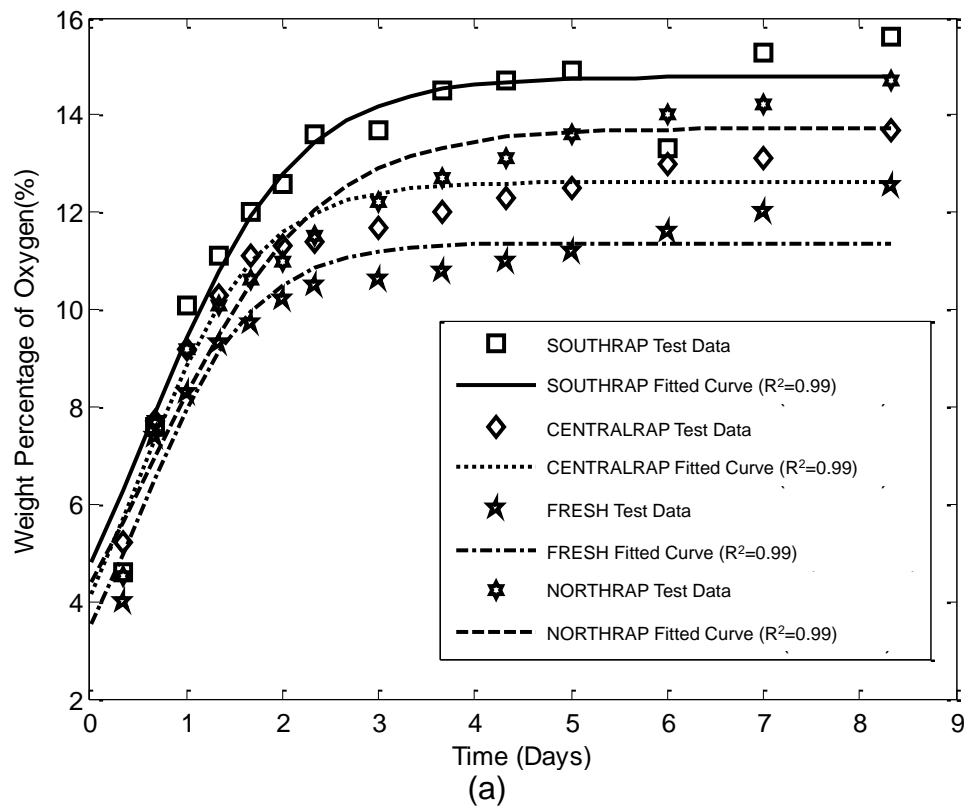
Figure 8: (a) EDX Results and Curves Fitted using NDD Model and (b) EDX Results and Curves Fitted using FRCR Model.
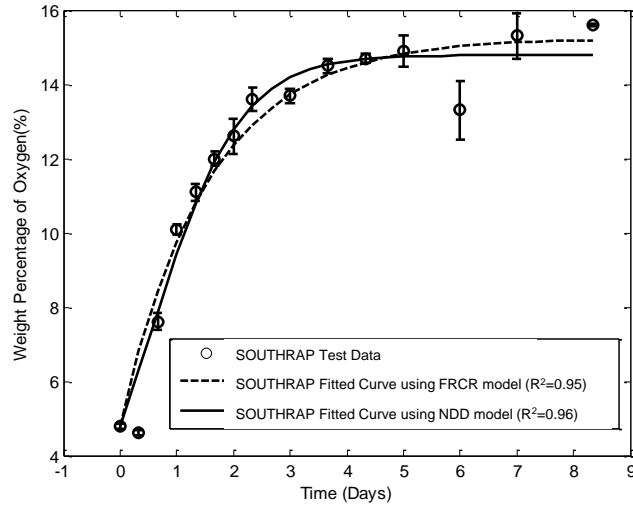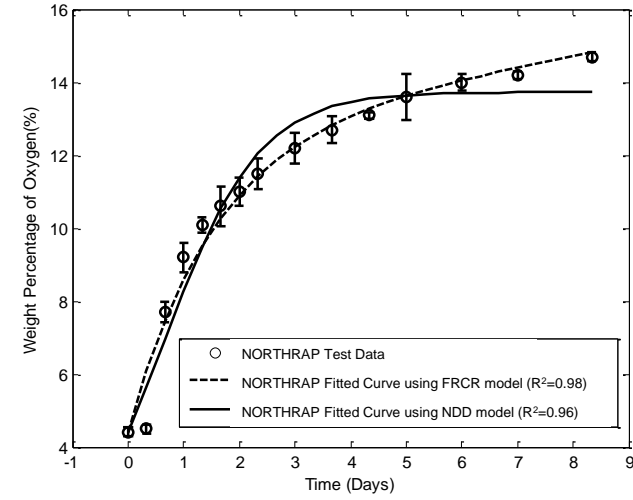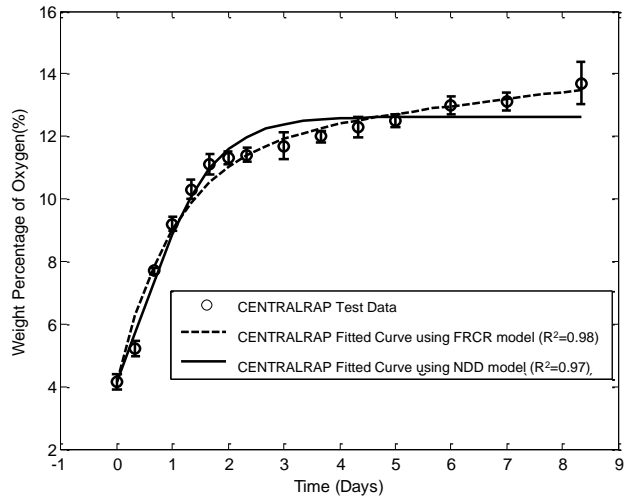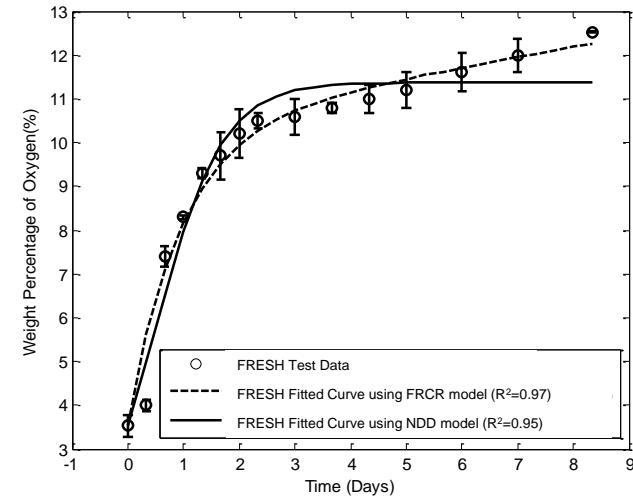
Figure 9: Comparison Between NDD Fitted Curves and FRCR Fitted Models for: (a) SOUTHRAP, (b) NORTHRAP, (c) CENTRALRAP, and (d) Fresh

The curve fitting parameters for both the NDD model and the FRCR model are summarized in Table 5. Referring to the ranges of optimized parameters presented in (Jin 2012) (A_f: $10^6 \sim 10^{10}$; $E_{\alpha f}$: $4.5 \times 10^4 \sim 7.5 \times 10^4$; A_c: $10^7 \sim 10^{11}$; $E_{\alpha c}$: $6 \times 10^4 \sim 10 \times 10^4$), and the coefficients (a = 0.01257; b = 0.000465) in Eq. (1), it is noted that the parameters fitted using FRCR in Table 5 are in the reasonable range for all types of asphalt binders, which reveals that the FRCR model can predict UV/Heat/Moisture aging very well. By comparing the values of r between Table 3 and Table 5, the r value for each type of asphalt binder in Table 5 is much smaller than the corresponding value in Table 3. Recall that r is a measurement of the rate of increase in WPO, therefore UV/Heat/Moisture aging is much slower than continuous UV aging.

Table 5: Fitted Model Parameters obtained from UV, Heat, and Moisture Aging Tests.

Fitting Model	Coefficient	CENTRALRAP	NORTHRAP	SOUTHRAP	FRESH
NDD	L	3.041	3.112	3.068	3.223
	r (days^{-1})	1.567	1.163	1.298	1.65
	R^2	0.97	0.96	0.96	0.95
FRCR	a	0.04431	0.03718	0.03831	0.03356
	b	0.0007783	0.0005748	0.0008489	0.000685
	A_c(days^{-1})	1.005×10^8	1.454×10^8	1.147×10^8	1.23×10^8
	A_f(days^{-1})	1.801×10^8	1.5×10^8	1.515×10^8	1.92×10^8
	$E_{\alpha c}$(J/mol)	6.012×10^4	6.091×10^4	9.098×10^4	6.11×10^4
	$E_{\alpha f}$(J/mol)	4.962×10^4	5.014×10^4	5.019×10^4	4.95×10^4
	$O(t)_0$	0.5201	0.4689	0.5847	0.3466
	R^2	0.98	0.98	0.95	0.97

Effect of Condensation and Moisture on UV Photo-Oxidative Aging

By comparing the increase in the WPO caused by UV radiation during the continuous UV aging tests with that in the UV/Moisture/Condensation aging tests, the effect of moisture and condensation on UV aging can be evaluated. In the continuous UV aging test, only UV was used to condition the asphalt binder. However, for the UV/Moisture/Condensation aging test, continuous UV was applied for only the first 4 hours of the aging cycle which lasted for 8 hours, then moisture was introduced by 15 minutes of water spray, which was followed by a condensation period that lasted 3 hours and 45 minutes. Therefore, the increase in the WPO caused by UV radiation during UV/Moisture/Condensation aging needs to be known. The extreme case will be considered by assuming that the asphalt binder samples were only aged during the UV radiation period. Based on this assumption, the data listed in Table 4 are the aging results of UV radiation only, and the effective aging time should be half of the time listed in Table 4.

Figure 10 presents the WPO for both continuous UV aging tests and UV/Moisture/Condensation aging tests as a function of the effective aging time (equal to the elapsed time for continuous UV and half of the elapsed time for UV/Moisture/Heat). It clearly shows that under the same time of UV radiation, the WPO in asphalt binders

after continuous UV aging tests are larger than that in binders after UV/Moisture/Condensation aging tests for all types of binder samples. In reality, the moisture and condensation during the second half of one UV/Moisture/Condensation aging cycle could also cause the increase in the WPO. Therefore, the WPO caused by UV radiation in UV/Moisture/Condensation tests should be smaller than that used in Figure 10. This indicates that the condensation and moisture in UV/Moisture/Condensation aging tests actually decreases the UV aging rate. One possible explanation is that the water vapor which is formed in the QUV during the condensation step remains during a portion of the UV step. This water vapor then absorbs some of the UV radiation, effectively reducing the intensity of the UV radiation that is incident on the surface of the asphalt binder. Based on Wu et al (Wu et al. 2009),the UV degradation rate would decrease with a reduction in the intensity of UV radiation.

Weathering Study Summary and Final Remarks
To fulfill the weathering study's objectives, four asphalt binders were extracted from RAP materials obtained from three different asphalt plants located in northern, central, and southern NJ based on AASHTO T 319. In order to study the kinematics of asphalt UV photo-oxidation and the effect of condensation and moisture on UV photo-oxidation, two kinds of UV aging tests, continuous UV aging test and UV/Heat/Moisture aging test, were conducted. The aging cycle used for the UV/Heat/Moisture aging test was based on but revised from ASDT D4799.; the aging temperature under UV radiation in ASTM D 4799 is 140℉ (60℃). However, based on academic journals presented, the temperature influence on UV aging cannot be ignored when the aging temperature is higher than 50℃, as coupling effects occur. Therefore, in order to minimize the effect of temperature in UV aging, the temperature was modified to 113℉ (45℃), subsequently the condensation temperature was reduced to 104℉ (40℃).

Although carbonyl area is widely used as an aging index in literature, it can only represent the amount of oxygen that has reacted with carbon, however, apart from this, a certain amount of oxygen will react with other elements such as sulfur during the oxidation process. Therefore, in order to investigate the total amount of oxygen involved during the aging process in a more accurate and straight forward way, WPO, which is linearly related with carbonyl area, was used as an aging index in this study. The WPO in asphalt binder samples after aging was measured using EDX, and the test results of samples after continuous UV were then fitted by the NDD model. The fitting results show that the continuous UV aging follows the NDD model extremely well with the R-square values being larger than 99 percent. The test results of samples after UV/Heat/Moisture aging were fitted using both the NDD model and the FRCR model. The fitting results indicate that both the NDD and FRCR model can accurately simulate the initial stage of UV/Heat/Moisture aging, but the FRCR model can more accurately simulate the transition and final part of the aging process (after 8 cycles). Overall, both the FRCR model and the NDD model can predict the UV/Heat/Moisture aging very well with the R square values larger than 95 percent.
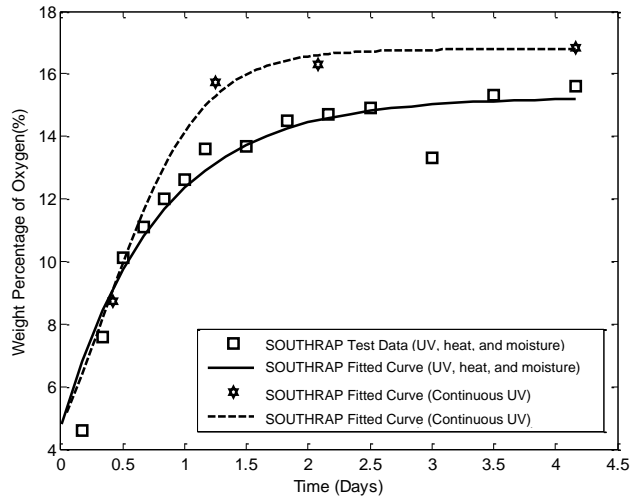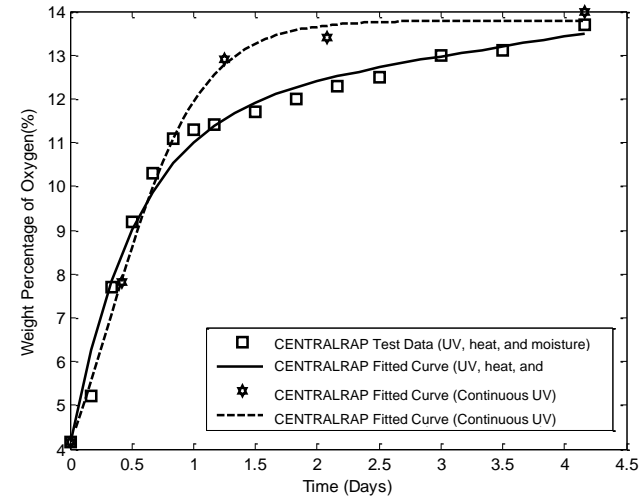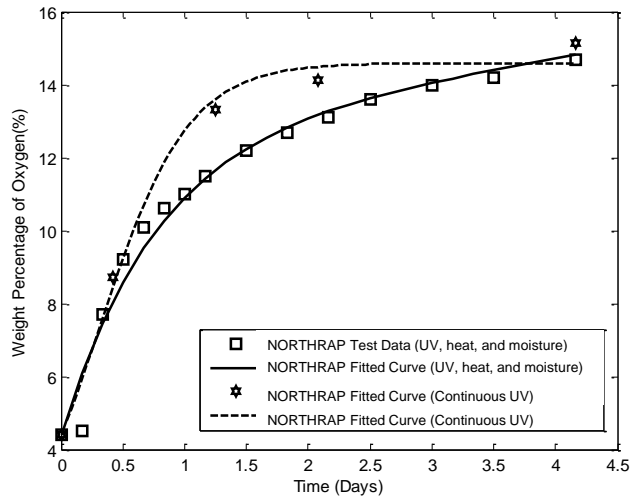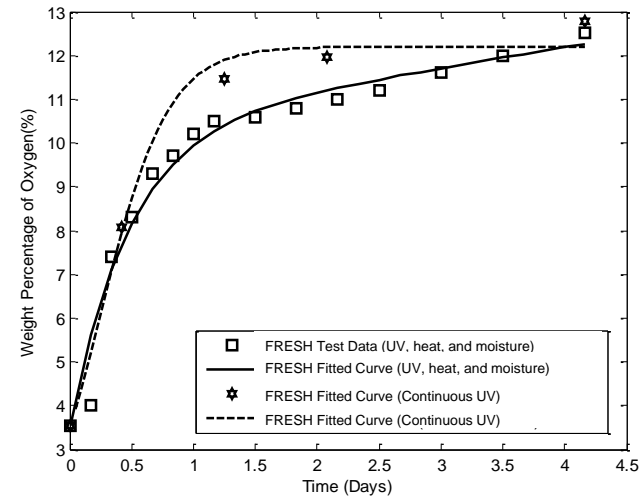
Figure 10 : Comparison of UV Aging in Continuous UV Aging and in UV, Heat, & Moisture Aging Test for: (a) SOUTHRAP, (b) NORTHRAP, (c) CENTRALRAP, and (d) Fresh

Additionally, the effects of condensation and moisture on the UV aging were evaluated by comparing the change in WPO caused by UV radiation during the continuous UV aging and UV/Heat/Moisture aging tests. It was found that the increase of weight percentage of oxygen caused by the UV radiation during the UV/Heat/Moisture aging tests was lower than that during the continuous UV aging tests, which indicated that condensation and moisture will effectively reduce the UV aging rate.

BATCH, COLUMN, AND AIR CHAMBER EXPERIMENTS TO DETERMINE POSSIBLE ELUTION AND EMISSION OF POLLUTANTS FROM RECLAIMED ASPHALT PAVEMENT (RAP)

Introduction

Reclaimed Asphalt Pavement (RAP) contains organic pollutants, such as Polycyclic Aromatic Hydrocarbons (PAHs), mainly from the binder (Fernandes *et al.*, 2009). However due to relatively low solubility and high octanol-water partition coefficient, a majority of these pollutants are tightly associated with the asphalt matrix and thus have low bioavailability (De Maagd *et al.*, 1998). This substantially decreases the impact of RAP on the environment since, in order to pose ecological threats, pollutants would have to be bioavailable. The goal of the elution and emission experiments in this study is to evaluate the amount of these pollutants that might possibly be released from RAP, including various heavy metals and PAHs. At Lamont-Doherty Earth Observatory (LDEO) of Columbia University, three types of elution and emission experiments, which are batch extraction experiments, flow-through column experiments, and closed-chamber air inhalation experiments were conducted. RAP samples were analyzed to determine the levels of metals and PAH compounds in leachate solution and the levels of Particulate Matter (PM$_{2.5}$) and Volatile Organic Compound (VOC) released from the RAP materials. Based on these results, samples were selected and sent to Dr. McElroy's laboratory at Stony Brook University for further aquatic toxicity analyses (the following chapter).

Materials and Methods
RAP Samples

RAP materials used in batch extraction, flow-through column, and closed-chamber air inhalation experiments were obtained from Dr. Yin's lab (Chapter 4). The list of un-weathered and weathered RAP samples is summarized in Table 6. See Chapter 4 for details on weathering process.

Table 6: Coding of RAP Samples (N=20) Used in Batch and Column Experiments.

Un-weathered	Unbound QUV 25 Cycles	Compacted QUV 25 Cycles	Heat & Moisture 60 cycles	Groundwater Leaching
Engineering Applications	Uncovered Fill	Guiderail Base	Guiderails Subbase	Covered Fill
NORTHRAP	NORTHRAP-uv	NORTHRAP-cuv	NORTHRAP-hm	NORTHRAP-gw
CENTRALRAP	CENTRALRAP-uv	CENTRALRAP-cuv	CENTRALRAP-hm	CENTRALRAP-gw
SOUTHRAP	SOUTHRAP-uv	SOUTHRAP-cuv	SOUTHRAP-hm	SOUTHRAP-gw
Fresh	Fresh-uv	Fresh-cuv	Fresh-hm	Fresh-gw

Note: uv- Unbound Ultra Violet aging, cuv- Compacted Ultra Violet aging, hm- Heat & Moisture aging, gw-Groundwater Leaching

Soil Sample

In the flow-through column experiments, a New Jersey (NJ) soil was used to evaluate the adsorption capability of soil particles for pollutants eluted from RAP. The soil sample

was obtained from Dr. Mehta's lab and collected from an NJDOT project on Route 35. Testing revealed that the selected soil had a specific gravity (G_{sb}) of 2.650 and a soil texture of sandy loam according to USDA classification system with 75 percent sand, 16 percent silt and 9 percent clay.

Artificial NJ Rain Water

Certain RAP applications, such as non-vegetative cover under guiderail, can be exposed to rainwater. Artificial NJ rainwater was thus used as a flow-through solution in column experiments. The 2014 annual averaged chemical composition of rainwater from three NJ monitoring sites in Atlantic, Ocean, and Mercer Counties from the National Atmospheric Deposition Program (NADP) (http://nadp.sws.uiuc.edu/data/sites/list/?net=NTN) was averaged as the chemical composition of the artificial NJ rainwater (Table 7). Chemicals including $CaCl_2$, $MgCl_2 \bullet 6H_2O$, KCl, $(NH_4)_2SO_4$, $NaNO_3$ and NaCl were dissolved into Milli-Q water (>18.1 MΩ) to make a 10,000X stock solution following the recipe in Table 7. A pre-cleaned 4L glass bottle was used to make the reaction solution by adding 0.4 mL of the stock solution into 4 liters of Milli-Q water, followed by vigorous shaking for homogenization and 2 hours of continuous air bubbling from the bottom for air saturation. The well mixed and air saturated solution has a pH ~5, which is very close to the pH range of 5.04-5.09 in the three monitored rain water samples.

Artificial NJ Groundwater

When being used as fill material, such as in mines, RAP could be exposed to groundwater. At this setting, RAP will not be exposed to sunlight or large variation of temperature. The groundwater leaching experiments attempt to mimic this weathering environment (Table 6). The chemical composition of ground water from 150 monitoring sites throughout NJ during 2004-2008 from the NJ Department of Environmental Protection Division of Water Supply and Geoscience's "New Jersey's Ambient Ground Water Quality Monitoring Network" program (http://www.nj.gov/dep/njgs/geodata/dgs05-2.htm) was averaged as the chemical composition of the artificial NJ ground water (Table 8). A stock solution (100X) of artificial NJ ground water was prepared for groundwater flow-through weathering tests conducted in Dr. Yin's laboratory using the recipe in Table 8. The stock solution has a pH of around 5.5.

Total organic DCM extraction

As aforementioned, though some PAHs exist in RAP, they are typically bound tightly inside asphalt matrices. In order to know the total amount of PAH compounds in RAP, RAP samples (both un-weathered and weathered samples in Table 6) were extracted in an ultrasonic bath for 60 minutes using the strong solvent dichloromethane (DCM) as the extraction fluid at a 10:1 liquid to solid ratio (w/w). The liquid extract was separated from the solids by filtration though a 0.7 um glass fiber filter, then underwent alumina column cleanup before GC-MS analysis.

Table 7: Chemical Compositions and the Recipe of Artificial NJ Rain Water.

Chemical	molar mass (g)	weight (g)	mmol		Na	Mg	K	Ca	NH$_4$	NO$_3$	Cl	S
CaCl2	110.98	0.206	1.86					1.86			3.71	
MgCl2.6H2O	203.30	0.678	3.33			3.33					6.67	
KCl	74.55	0.117	1.57				1.57				1.57	
(NH4)2SO4	132.14	0.797	6.03						12.06			6.
NaNO3	84.99	0.813	9.57		9.57					9.57		
NaCl	58.44	1.041	17.81		17.81						17.81	
dissolved in		100 ml MQ water		Stock solution (x10,000)	273.78	33.35	15.69	18.56	120.63	95.65	297.65	60.
				NJ artificial rain water	27.38	3.33	1.57	1.86	12.06	9.57	29.76	6.

Table 8: Chemical Composition and the Recipe for Artificial NJ Ground Water.

chemical	molar mass (g)	weight (g)	mmol		Na	K	Mg	Ca	Cl	SO$_4$	NO$_3$	
KCl	74.551	0.374	5.02			5.02			5.02			
NaNO3	84.995	1.788	21.04		21.04						21.04	2
Na2SO4	142.040	3.123	21.99		43.97					21.99		
MgCl2.6H2O	203.310	7.05	34.68				34.68		69.35			
CaCO3	100.087	6.803	67.97					67.97				6
NaHCO3	84.007	7.814	93.02		93.02							9
	morlarity (M)	volume (ml)	mmol									
HCl (1N)	1	213	213.00						213.00			
HCl –concentrated	12.18	5	60.89						60.89			
NaOH (25%)	7.94	7	55.56		55.56							
total volume	1.157 L			stock solution (x100)	184.61	4.34	29.97	58.75	301.00	19.00	18.18	15
				NJ artificial ground water	1.85	0.04	0.30	0.59	3.01	0.19	0.18	

Batch Extraction Experiments

Batch extraction has been widely used to estimate the pollutants in leachate from landfills (Legret, *et al.,* 2005). In landfills, because of the decomposition of buried organic material (Musson *et al.,* 2000), leachates tend to be acidic, leading to increased dissolution of metals. In order to compare our results with those published data, we also conducted batch extraction experiments.

Water-soluble fraction was extracted using a modified version of the Environmental Protection Agency (EPA) Method 1311. Initially, the recommended EPA method to prepare the extraction fluid, which uses ammonia hydroxide (NH_4OH) and acetic acid (CH_3COOH) to adjust fluid pH, were followed. In the first round of batch samples sent to Dr. McElroy' lab, this extraction fluid was found to be highly toxic in the Microtox® screening assay, making it impossible to determine if any additional toxicity was due to RAP materials extracted by this process. The Columbia and SUNY research teams then met and discussed the results, and came to the conclusion that NH_4OH could be a major reason leading to high toxicity in blank solution since ammonium is a paradoxical nutrient, notorious for its cytotoxic effect (Von Wiren *et al.,* 2004). After replacing NH_4OH with sodium hydroxide (NaOH), the toxicity of blank solution was substantially reduced, and testing the RAP samples was then continued (the following chapter).

The water-soluble batch extraction experiment procedure involved preparing a water-based extraction fluid consisting of acetic acid and sodium hydroxide (pH 4.93 ± 0.05) to extract RAP samples at a 20:1 liquid to solid ratio (w/w). Samples were placed on an orbital shaker (~350 RPM, Figure 11) for 18 ± 2 hours, after which the liquid extract was separated from the solids by filtration through a 0.7 um glass fiber filter. A liquid-liquid extraction was then performed on the water-based extract using dichloromethane, where 8 mL of dichloromethane was added to 50 mL of the water-based extract in a 60 mL vial. The vial is then shaken for 1-2 minutes, then set to rest to allow the organic layer to separate from the water phase. The organic phase was then pipetted into a separate container, and the liquid-liquid extraction repeated two more times. Each of the three organic portions was combined, concentrated, and dried by passing through a flash column of anhydrous sodium sulfate before analysis on GC-MS.
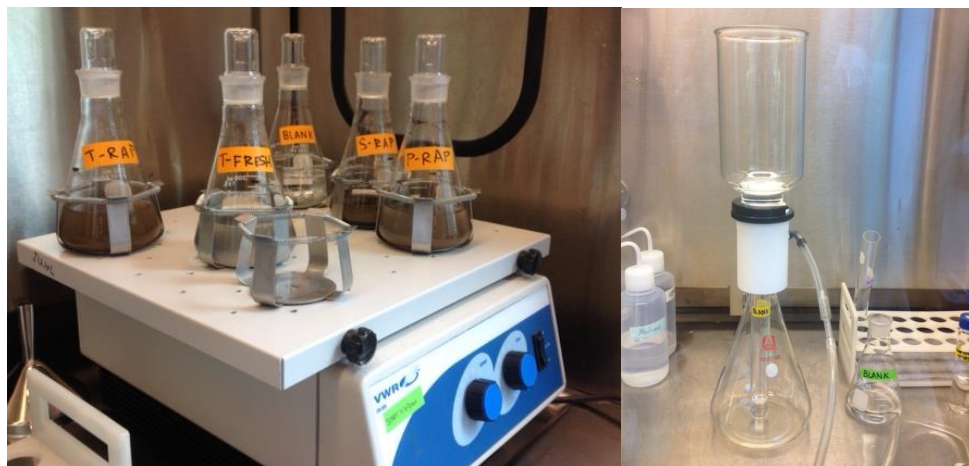
Figure 11: Laboratory Setup for Batch Extraction Experiments.

Flow-through Column Experiments

A unique two-column experiment was designed to investigate the release of metals and PAHs from RAP samples and the attenuation effect of soil on these potential pollutants before they could enter groundwater systems. The setup of the two-column experiment was shown in Figure 12. The columns were made of Teflon to minimize the possible release of metals or organic compounds from the column, and customized for this project with an inner diameter of 5.08 cm and a filling length of 26.5 cm, which made an inner volume of 537 mL for each column. All the other tubing and connection parts were made of Teflon with an exception that the Tee was made of stainless steel.

The aforementioned artificial NJ rain water was introduced by a peristaltic pump at about 2 mL/min flow rate from the bottom into the RAP-filled column first. The outflow from the RAP column was then split using a Tee, with one end connected to a fraction collector for automatically and continuously collecting solution samples after the RAP column (referred to as RAP solution hereafter) into sterile glass vials at a rate of 1 hour per sample, and the other end was driven by another peristaltic pump to flow into the soil-filled column from the bottom at a flow rate of 1 mL/min. The solution after the soil column (referred to as soil solution hereafter) was collected by another fraction collector also at a rate of 1 hour per sample.

For quality control, before running column experiments, an Equipment Blank Test of running Milli-Q water through the two columns without filling of RAP or soil in any column was conducted for baseline definition and comparison. This equipment blank test was run at 2 mL/min through RAP column (without filling of RAP) and 1 mL/min through soil column (without filling of soil) for 3 hours before 180 mL filtered water samples were collected after RAP (sample ID B-R-01) and soil (sample ID B-S-01) columns, respectively.
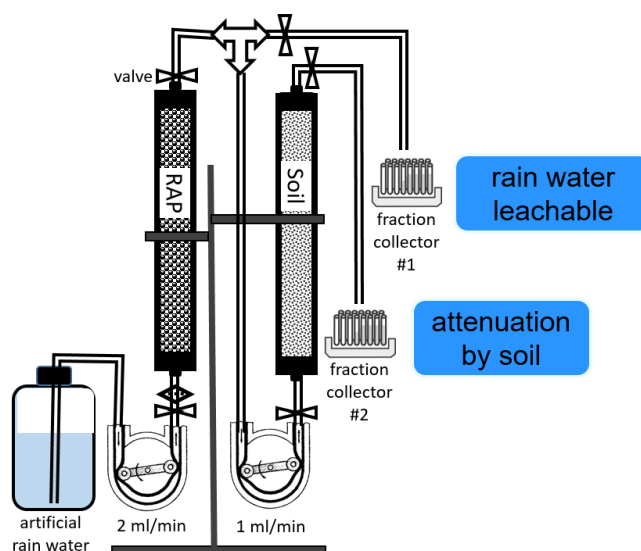
Figure 12: A Schematic Illustrating the Setup Utilized for Column Experiments.

To characterize the levels of metals and PAHs that could release from the soil sample, a Soil Blank Test was conducted by running artificial NJ rainwater through the two

columns with only the 2nd column filled with the soil sample. First set of filtered water samples S-R-02 (the second letter R refers to samples after the RAP column, hereafter) and S-S-02 (the second letter S refers to samples after the soil column, hereafter) were collected after continuous flow of 1 pore volume (PV) of the soil column. Second set of filtered water samples S-R-03 and S-S-03 were collected after continuous flow of 15.5 PVs of the soil column.

Based on baseline levels of metals and PAHs in artificial rain water and in soil leachates, samples including Fresh, NORTHRAP, Fresh-cuv, and NORTHRAP-uv were selected for flow-through column experiments (see Table 6 for details about weathering processes of these samples). The criteria for selecting Fresh are: (1) Fresh was the only pre-application sample that's not utilized on roadways hence selected for comparison with RAPs, (2) Fresh had the lowest water extractable PAH concentrations, which are about one magnitude lower than those from RAPs. The criteria for selecting unweathered NORTHRAP over other unweathered RAPs are (1) NORTHRAP sample had the highest water extractable PAH concentrations, which are approximately 2 times of those in CENTRALRAP and SOUTHRAP; (2) NORTHRAP sample had much higher extractable Pb concentration (13.5 ppb) than CENTRALRAP and SOUTHRAP. The criteria for the selection of Fresh-cuv and NORTHRAP-uv include: (1) they were selected for comparison with their un-weathered counterparts; (2) the weathering treatment Fresh-cuv showed higher concentrations of Pb, Co, Cr, Fe, K, La, and lower Cu, S, As, Se, Zn than Fresh-un and Fresh-hm; (3) the weathering treatment NORTHRAP-un showed relatively higher Pb concentration (50.1 ppb, exceeding drinking water standard of 15 ppb), than other NORTHRAP weathering treatments. Lead level in leachate from groundwater weathered NORTHRAP was 16.1 ppb. Overall, a total of 6 sets of flow-through column experiments were conducted. The experimental setup and specifications are summarized in Table 9.

Most of the column experiments were conducted at relatively constant flow rates throughout the 96 hour experiment period, an example is shown in Figure 13, which confirmed the stability of this two-column two-pump flow through system. An exception was weathered Fresh-cuv column experiment in which the soil column was clogged after 9 hours of continuous flow and resulted a reduced flow rate from 0.89 mL/min in the first 9 hours to 0.11 mL/min after 52 hours. As a consequence, multiple samples were combined together to make enough solution for one sample for this experiment.
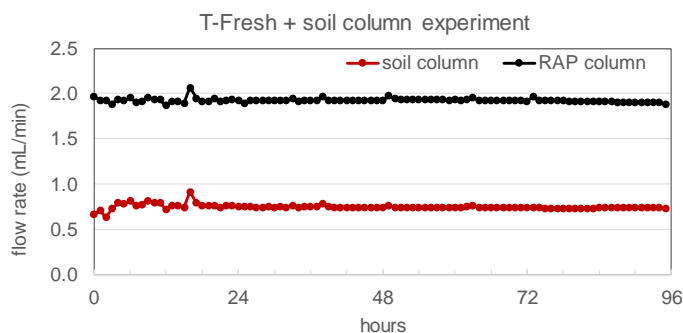
Figure 13: Flow Rate During the Fresh Column Experiment.

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Table 9: Summary of Flow-Through Column Experiment Setup.

Experiment ID	RAP Sample	Packed RAP Column				Soil	Packed Soil Column			
		RAP (g)	Water (g)	Porosity (percent)	Flow Rate (ml/min)		Soil (g)	Water (g)	Porosity (%)	Flow Rate (ml/min)
Blank	No	NA	537	NA	2.0	No	NA	537	NA	1.0
Soil blank	No	NA	537	NA	3.0	Yes	889	159	30 %	0.60
Fresh	Fresh	605	234	44	1.9	Yes	929	123	23 %	0.75
NORTHRAP	NORTHRAP	760	174	32	2.0	Yes	890	152	28 %	0.79
Weathered Fresh	Fresh-cuv	531	281	52	2.0	Yes	945	132	25 %	0.21*
Weathered NORTHRAP	NORTHRAP -uv	675	226	42	1.9	Yes	861	175	33 %	0.77

*Soil column was clogged after 9 hours.

Chamber Inhalation Experiments

Chamber inhalation experiments (Figure 14) were completed for a Field Blank treatment and three chosen RAP treatments (Fresh, NORTHRAP, NORTHRAP-uv). Approximately 1 – 1.5 kg of RAP material is placed inside a chamber, on top of a shaker table. The chamber outlet is connected to two different types of samplers, which collects samples every three hours while the chamber is agitated on the shaker table. One of these samplers consists of a 25mm Teflon filter and two polyurethane foam (PUF) filters, which are preceded by a size-selective impactor with an average particle cut-point of 2.5 µm at a sampling flow rate of 1.5 liters per minute (LPM). The fine particulate matter (PM2.5) is collected on the Teflon filter while semi-volatile chemicals are collected on the PUFs. The other sampler consists of a charcoal sorbent tube designed to collect volatile organic compounds (VOCs) from the chamber, sampled at a flow rate of 0.2 LPM. Three repetitions are collected from each of the two samplers for PM2.5 and VOC analysis for the RAP treatments and the blank treatment. The chamber is supplied with a high-purity grade of compressed air at ~ 1 atmosphere pressure through its inlet to replace the ambient air pumped out of the chamber during sampling.
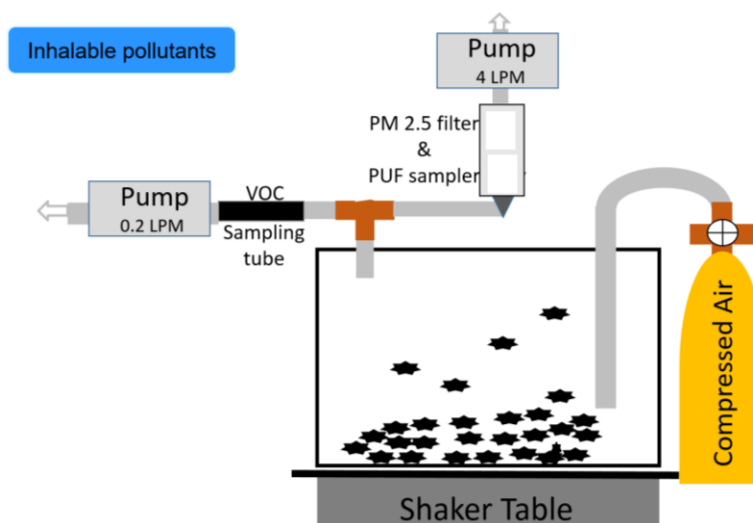
Figure 14: A Schematic Illustrating Chamber Utilized in Inhalation Experiments.

Sample Processing and Analysis

Solution samples collected from both batch and column experiments were combined from every 3 samples into one sample to obtain enough volume for PAH extraction and analysis, which reduced the number of samples from 96 to 32 in each of the four sets of RAP column experiment. Half of the 32 combined samples were analyzed for metals and PAHs, including all 8 from the first day, 4 from the second day, 2 from the third day and 2 from the fourth day. Other samples have been archived frozen at -18°C for future analysis, if needed.

Element analysis of solution samples

Combined solution samples were filtered through 0.7 µm pore space glass fiber filter and then acidified to 1 percent HNO_3 (Optima grade) for analysis of 32 elements on HR ICP-MS (Thermo Scientific Element XR) at Lamont-Doherty Earth Observatory following a modified EPA method 200.8 (Cheng et al., 2004).

PAH analysis of solution samples
Combined solution samples were filtered through 0.7 µm pore space glass fiber filter, extracted with dichloromethane, then dried with anhydrous sodium sulfate for analysis of 29 PAHs on GC-MS (Varian – now Agilent 1200L MS) at Lamont-Doherty Earth Observatory following the method in Yan et a. (2005).

PM2.5 of inhalable samples
The PM2.5 samples were collected on 25 mm diameter Teflon filters, which were gravimetrically analyzed for particle concentrations at Lamont-Doherty Earth Observatory.

VOC analysis of inhalable samples
The charcoal sorbent tubes were extracted and analyzed following NIOSH Method 1501. Briefly, the sorbent was extracted in carbon disulfide, which was then analyzed on GC-FID for a profile of 31 VOCs. VOC analysis was conducted in Galson labs.

Results and Discussion
Batch Extraction Experiments
Element analysis
Figure 15 shows element results from the batch experiments. Water soluble fraction of metals from RAP batch extraction experiments were analyzed for 32 elements, i.e., Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn. Complete analysis results are attached in the supplemental material (i.e., Final Report CD).

Overall, no elements exceed EPA drinking water Maximum Contaminant Levels (MCL), except lead (Pb) in groundwater leached NORTHRAP (16.1 ppb) and unbound QUV 25 cycles weathered NORTHRAP samples (50.1 ppb) (Figure 16). In fact, Pb in NORTHRAP and its weathered products are all close to or higher than the EPA drinking water MCL of 15 ppb, most likely from the historical usage of tetraethyl lead and white paint on the road. SMCLs are set by the EPA as guidelines for management of aesthetic considerations of water quality (https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals). SMCLs are not legally enforceable. Levels of Al, Fe and Mn are higher than SMCLs (Figure 16), possibly due to increased dissolution of minerals under acidic condition. The relatively high rock components (e.g., Al and Ca) are mainly due to the mineral dissolution by acidic leachate solution.

For un-weathered RAP samples, Fresh showed significantly lower concentrations for most of elements including Ba, Be, Ca, Cd, Co, Cs, Cu, K, Li, Mg, Mn, Mo, Ni, Pb, S, Sb, Sr, U, and Zn in comparison to other RAPs that underwent road exposure (Figure 15), indicating the source of these elements from road material, vehicle emission and dust deposition. Weathered Fresh showed consistently low levels, indicating aging did not lead to contamination.
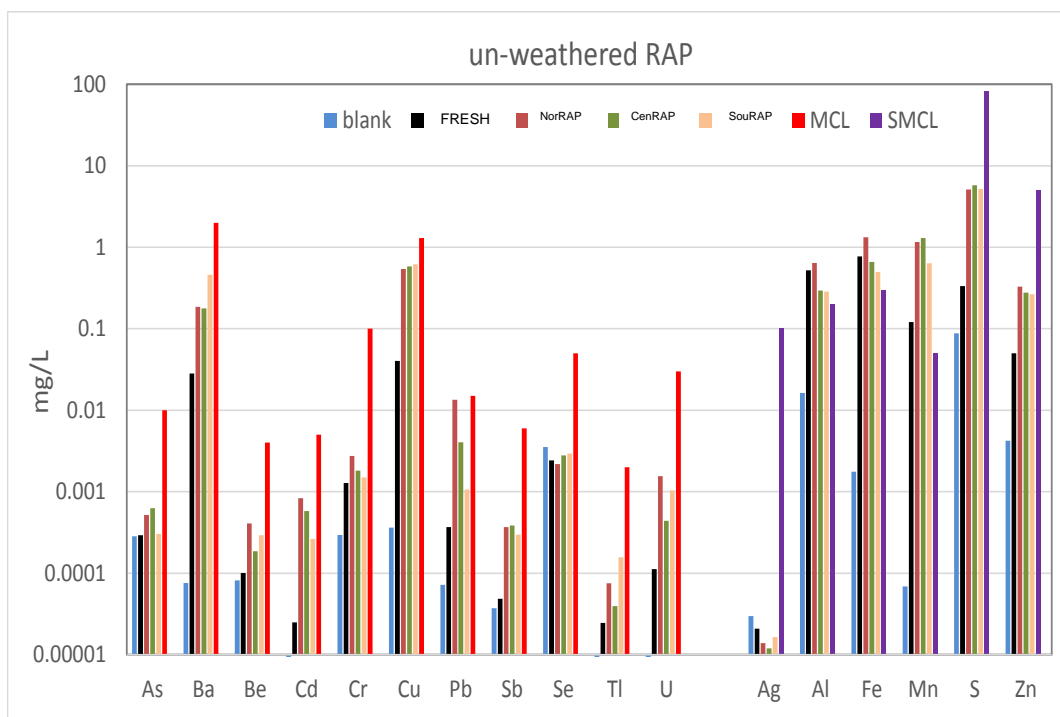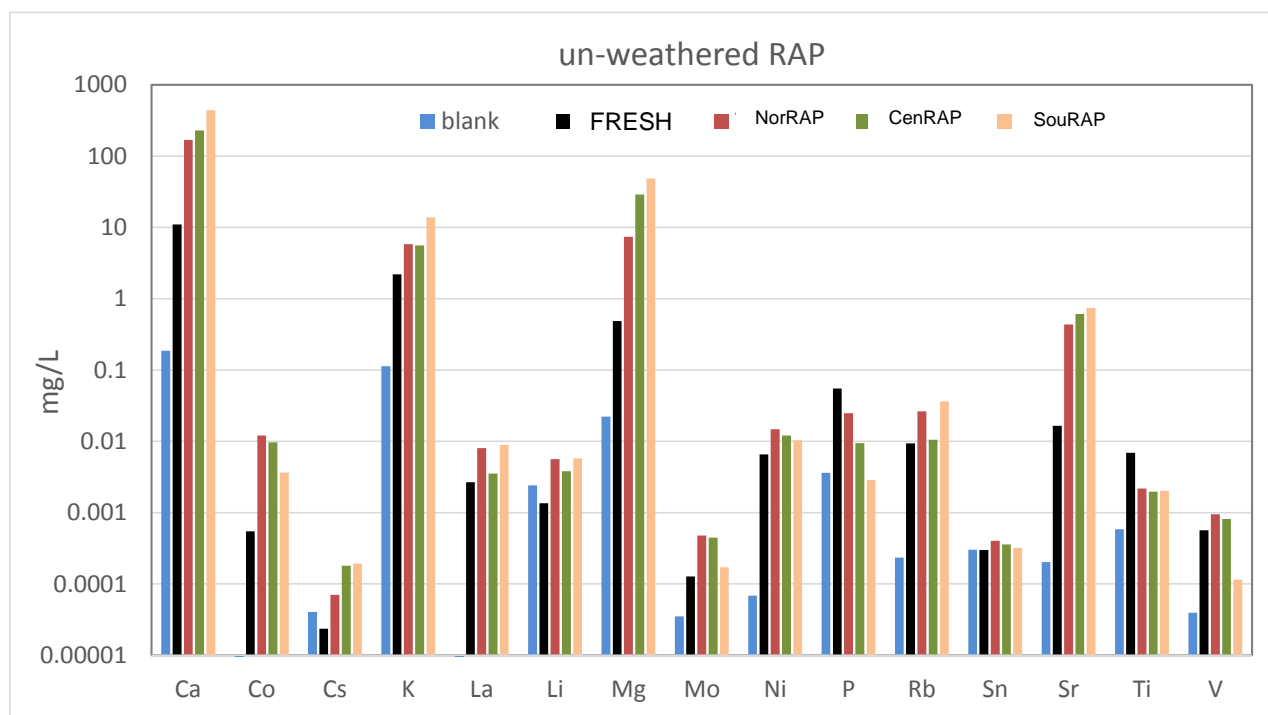
Figure 15: Water Extractable Concentrations of 32 Elements in Un-weathered RAP Samples: (a) Elements With (S)MCLs and (b) Elements Without (S)MCL).

* Blank stands for method blank concentrations.

* (S)MCL stands for EPA drinking water (secondary) Maximal Contaminant Levels.

Water-extractable levels of most elements were comparable between un-weathered RAPs and their weathered counterparts except titanium (Figure 16). For example, for Ca, Mg, Al, K, and Li, their water extractable levels in un-weathered and weathered products are almost the same, demonstrating that UV exposure and precipitation have very limited effects on these elements that are mainly from mineral aggregates (rock and sand). This was anticipated since those rocky elements would need much longer and extensive weathering to show weathering effects. Among all four RAP samples (Fresh, NORTHRAP, CENTRALRAP, and SOUTHRAP), the Ti level in un-weathered RAP was consistently and significantly higher than weathered products. This may be associated with loss of TiO_2 coating during the weathering.

Asphalt binder (from asphalt in crude oil) can contain elevated level of Ni and V and the two elements in aerosol particulate matter have been used in NYC as a source indicator of burning of bunk oil in boilers. Interestingly, their levels in fresh RAP were similar to used RAPs and the weathering process appears to have little to no effect on their water-extractable levels as well. The high insolubility of these elements in water may be the reason.

NORTHRAP showed a higher Pb level than fresh RAP and two other used RAP (Central and North RAP). In addition, its level in NORTHRAP is not affected by weathering processes.
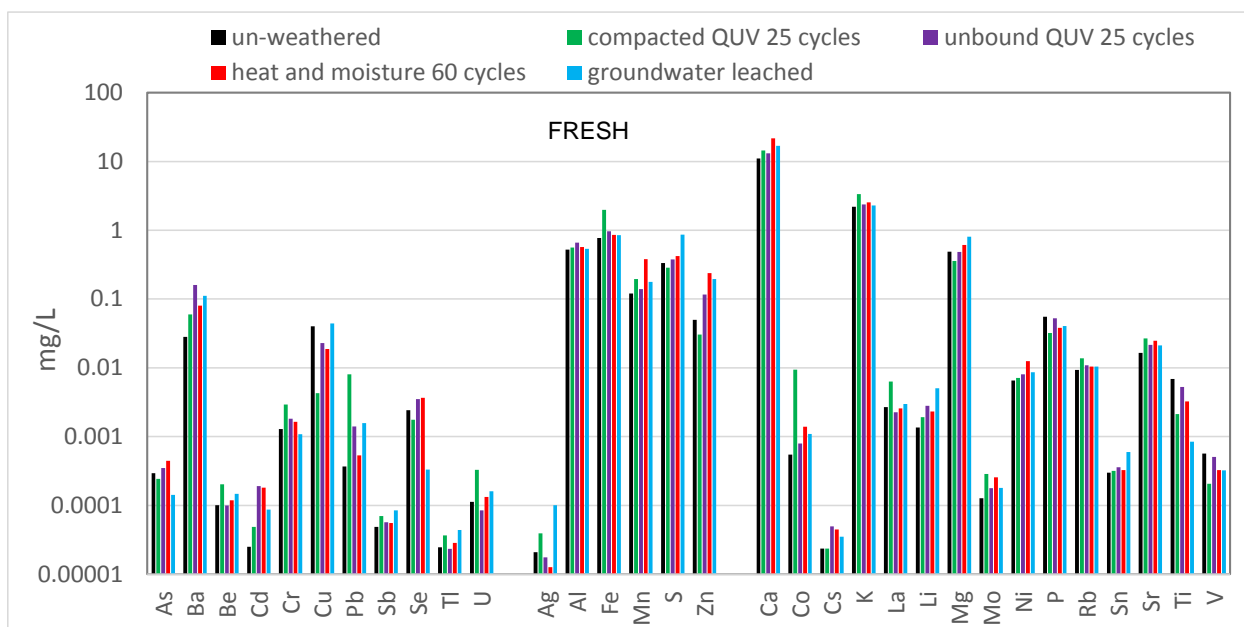
(a)
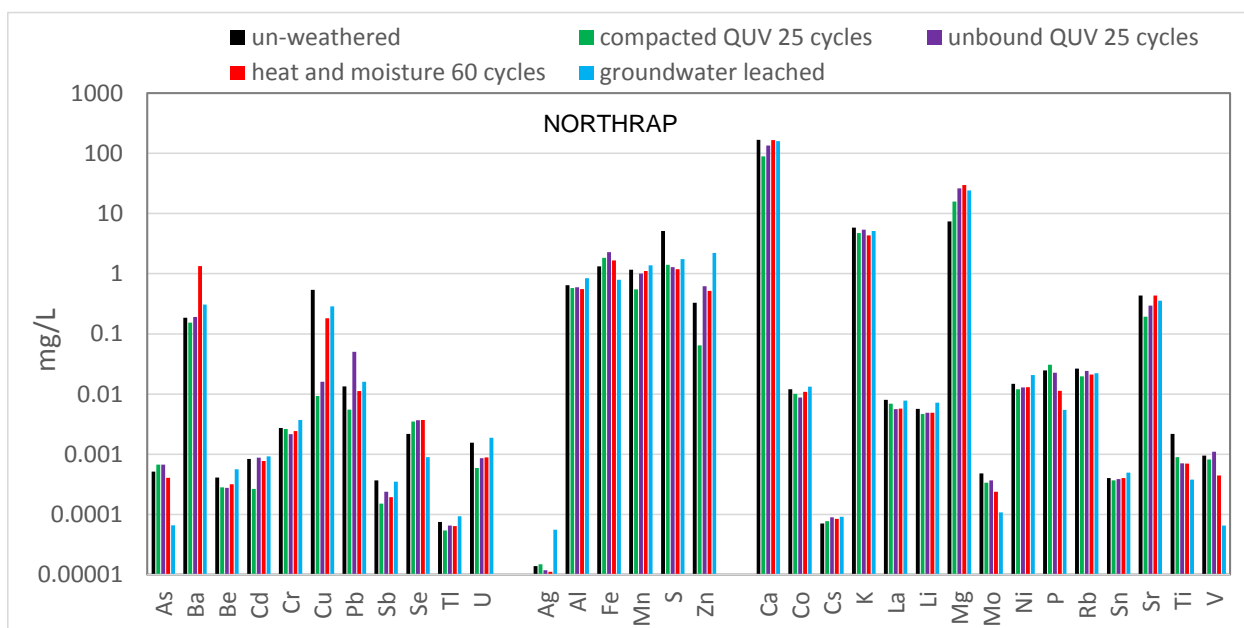
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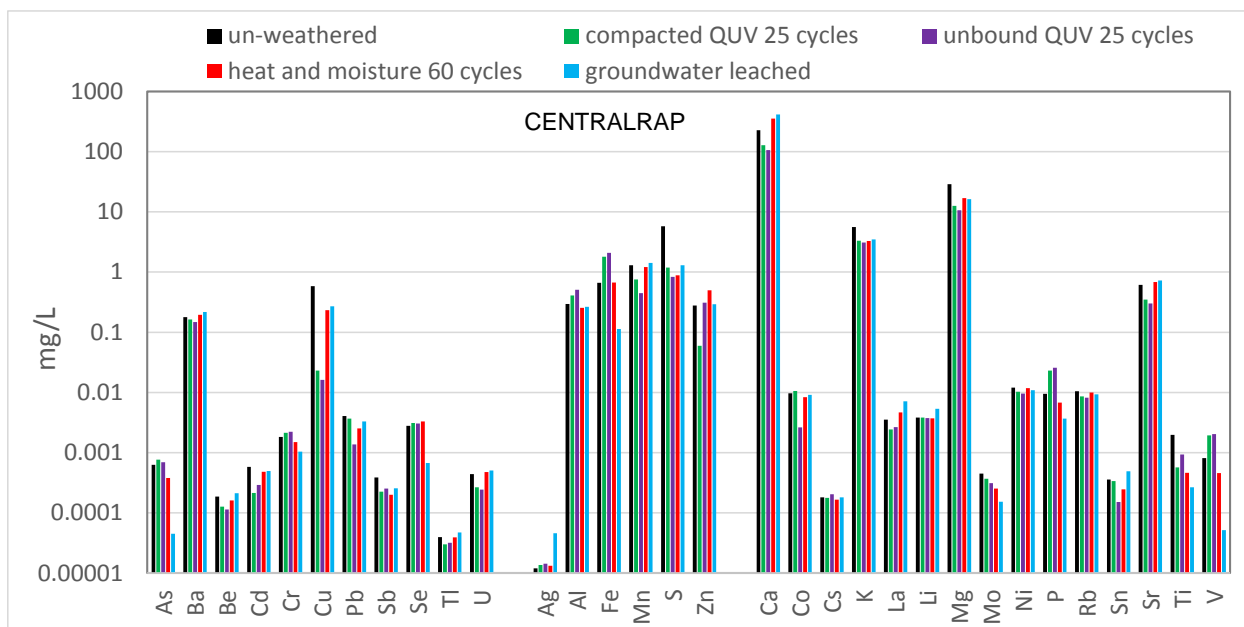
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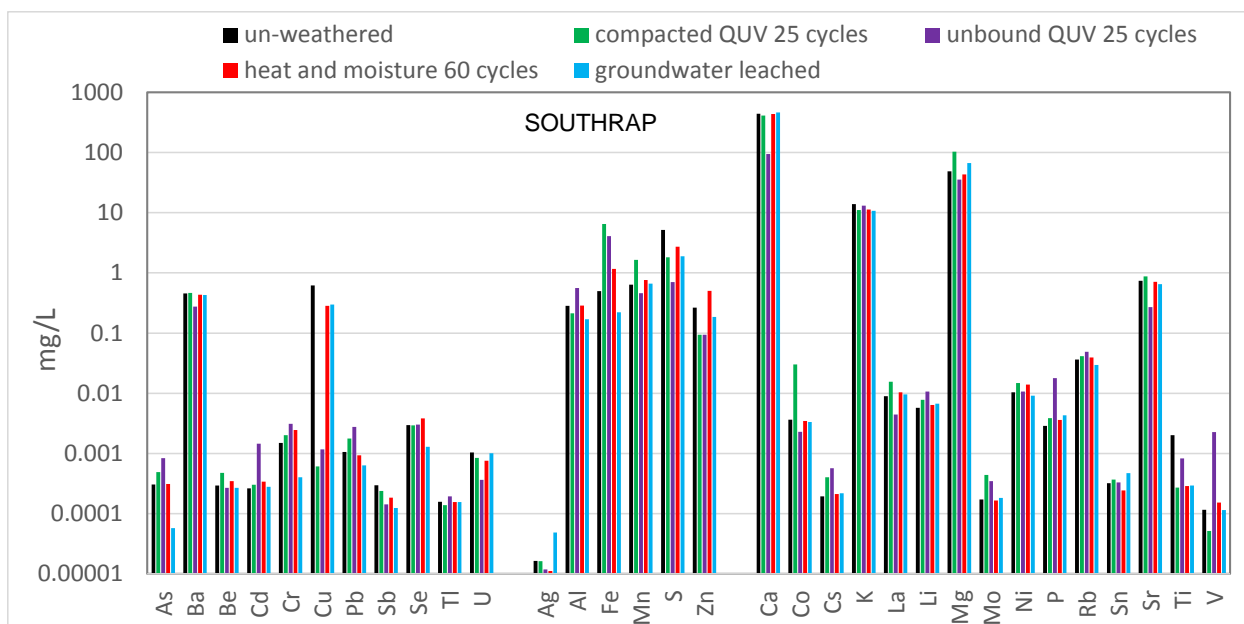
(d)

Figure 16: Water Extractable Concentrations of 32 Elements in Un-Weathered & Weathered RAP Samples: (a) Fresh, (b) NORTHRAP, (c) CENTRALRAP, and (d) SOUTHRAP.

* left: elements with MCL; middle: elements with SMCL; right: elements without (S)MCL

PAH analysis

Water soluble fraction and total organic DCM extractable fraction of PAHs from RAP batch extraction experiments were analyzed for 29 PAH compounds, including 1-methylpyrene, 4-methylpyrene, 2-methylphenanthrene, 3-methylphenanthrene, 4-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, 1,3-,2,10-,3,9-,3,10-DMP, 1,6-,2,9-DMP, 1,7-dimethylphenanthrene, 2,3-dimethylphenanthrene, 2,6-dimethylphenanthrene, 2,7-dimethylphenanthrene, 6-methylbenz[a]anthracene, acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[ghi]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, fluoranthene, fluorene, phenanthrene, and pyrene. Complete analysis results are attached in the supplemental material (i.e., Final Report CD).

Selected total organic DCM extractable PAH concentrations in various conditioned RAP samples are summarized in Table 10 and shown in Figure 17. Total organic DCM extractable PAH concentrations represent the maximal amount of organic compounds that could be released from RAPs. Many PAHs showed concentrations greater than 0.0001 mg/L, with low molecular weight PAHs, e.g. 2,6-dimethylnaphthalene, acenaphthene, fluorine, 2-methylphenanthrene, averaged at 0.004 mg/L and high molecular weight PAHs, e.g. fluoranthene, pyrene, benz[a]anthracene, chrysene, averaged at 0.035 mg/L, a ten-fold higher. Among the RAP samples, Fresh and its weathering products showed lowest concentrations for most PAHs, while NORTHRAP and its weathering products showed the highest.

Table 10: Selected Total Organic DCM Extractable PAH Concentrations (mg/L).

RAP Material	Aging Procedure	2,6-dimethyl-napthalene	Ace-naphthene	Fluorene	2-methyl-phenanthrene	Fluranthene	Pyrene	Benz[a]-anthracene	Chrysene
Fresh	Unaged	7.4E-04	2.6E-04	3.4E-04	1.4E-03	3.4E-04	1.3E-03	3.4E-03	4.3E-03
	Compacted RAP QUV 25 Cycles	2.7E-04	BDL	1.0E-04	1.2E-03	BDL	BDL	7.8E-04	2.3E-03
	RAP QUV 25 Cycles	3.4E-04	BDL	1.6E-04	1.5E-03	BDL	BDL	7.6E-04	2.8E-03
	Heat & Moisture 60 Cycles	4.6E-04	BDL	5.3E-04	2.7E-03	BDL	1.3E-03	1.2E-03	4.2E-03
	Groundwater Aging	5.9E-04	BDL	4.0E-04	2.7E-03	BDL	1.8E-03	1.2E-03	5.6E-03
NORTHRAP	Unaged	9.0E-04	4.7E-03	7.3E-03	1.5E-02	7.6E-02	7.5E-02	5.0E-02	6.6E-02
	Compacted RAP QUV 25 Cycles	1.6E-03	2.0E-03	7.5E-03	1.8E-02	8.1E-02	7.8E-02	5.1E-02	6.1E-02
	RAP QUV 25 Cycles	1.3E-03	1.6E-03	7.0E-03	2.0E-02	5.6E-02	5.5E-02	6.0E-02	6.7E-02
	Heat & Moisture 60 Cycles	9.3E-03	2.2E-02	4.6E-02	3.7E-02	1.3E-01	1.5E-01	7.0E-02	8.4E-02
	Groundwater Aging	1.3E-03	4.0E-03	7.4E-03	1.3E-02	8.5E-02	1.0E-01	7.3E-02	1.0E-01
CENTRALRAP	Unaged	BDL	1.4E-04	2.7E-04	1.0E-03	2.6E-02	3.2E-02	1.5E-02	2.3E-02
	Compacted RAP QUV 25 Cycles	2.1E-04	5.0E-04	1.2E-03	6.0E-03	4.7E-02	4.2E-02	3.0E-02	4.1E-02
	RAP QUV 25 Cycles	1.6E-04	2.1E-04	6.3E-04	3.7E-03	2.4E-02	2.5E-02	1.7E-02	2.6E-02
	Heat & Moisture 60 Cycles	BDL	1.3E-03	1.3E-03	1.4E-03	2.9E-02	6.7E-02	2.2E-02	5.2E-02
	Groundwater Aging	BDL	BDL	4.7E-04	1.6E-03	3.3E-02	6.5E-02	2.6E-02	4.5E-02
SOUTHRAP	Unaged	2.8E-03	1.0E-03	7.0E-04	5.4E-03	2.0E-03	3.3E-03	3.8E-03	1.2E-02
	Compacted RAP QUV 25 Cycles	BDL	BDL	4.9E-04	3.9E-03	1.1E-02	1.0E-02	9.1E-03	2.2E-02
	RAP QUV 25 Cycles	2.9E-04	9.1E-05	2.9E-04	3.1E-03	9.8E-04	1.7E-03	1.9E-03	8.3E-03
	Heat & Moisture 60 Cycles	BDL	BDL	4.7E-04	5.4E-03	3.1E-03	4.7E-03	3.6E-03	1.8E-02
	Groundwater Aging	9.6E-04	BDL	4.3E-04	3.6E-03	5.7E-03	1.3E-02	5.5E-03	2.5E-02

Table 11: Selected Water Soluble PAH Concentrations (mg/L).

RAP Material	Aging Procedure	2,6-dimethylnaphthalene	Acenaphthene	Fluorene	2-methylphenanthrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
Fresh	Unaged	9.3E-06	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Compacted RAP QUV 25 Cycles	BDL	BDL	2.2E-06	BDL	BDL	BDL	BDL	BDL
	RAP QUV 25 Cycles	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Heat & Moisture 60 Cycles	1.1E-05	BDL	2.3E-06	BDL	BDL	BDL	5.2E-06	BDL
	Groundwater Aging	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
NORTH RAP	Unaged	BDL	1.5E-05	9.6E-06	BDL	7.7E-06	1.4E-05	BDL	BDL
	Compacted RAP QUV 25 Cycles	BDL	1.8E-04	2.6E-04	BDL	1.2E-04	9.6E-05	BDL	BDL
	RAP QUV 25 Cycles	BDL	7.8E-05	3.6E-05	BDL	9.6E-05	7.8E-05	BDL	BDL
	Heat & Moisture 60 Cycles	1.6E-05	BDL	1.3E-05	BDL	2.0E-05	5.5E-05	7.1E-06	7.0E-06
	Groundwater Aging	BDL	BDL	1.9E-05	BDL	4.2E-05	8.8E-05	==2.7E-04==	==2.8E-04==
CENTRALRAP	Unaged	BDL	BDL	BDL	BDL	8.7E-06	2.4E-06	BDL	BDL
	Compacted RAP QUV 25 Cycles	BDL	1.2E-04	8.9E-05	BDL	8.3E-05	5.9E-05	BDL	BDL
	RAP QUV 25 Cycles	BDL	BDL	BDL	BDL	6.0E-05	5.0E-05	BDL	BDL
	Heat & Moisture 60 Cycles	BDL	BDL	7.4E-06	BDL	BDL	5.0E-05	7.2E-06	6.0E-06
	Groundwater Aging	BDL	BDL	BDL	BDL	8.6E-06	3.3E-05	2.9E-05	6.7E-05
SOUTH RAP	Unaged	2.1E-05	2.0E-05	9.5E-06	BDL	3.9E-06	BDL	BDL	BDL
	Compacted RAP QUV 25 Cycles	BDL	4.1E-05	3.6E-05	BDL	2.9E-05	BDL	7.5E-06	7.7E-06
	RAP QUV 25 Cycles	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Heat & Moisture 60 Cycles	1.9E-05	BDL	8.8E-06	BDL	BDL	BDL	BDL	BDL
	Groundwater Aging	BDL	BDL	BDL	BDL	2.9E-05	3.1E-05	7.1E-05	9.2E-05

Note: According to EPA drinking water standard and health advisories (EPA 1994, Reference: 40 CFR 141.50), maximum contaminant level in drinking water are as follows: Benz[a]-anthracene, 0.0001 mg/L; chrysene, 0.0002 mg/L.

Selected water soluble PAH concentrations in various conditioned RAP samples are summarized in Table 11 above and shown in Figure 17. Many PAHs showed concentrations lower than 0.0001 mg/L, with low molecular weight PAHs, e.g. 2,6-dimethylnaphthalene, acenaphthene, fluorene, 2-methylphenanthrene, averaged at 3.5E-5 mg/L and high molecular weight PAHs, e.g. fluoranthene, pyrene, benz[a]anthracene, chrysene, averaged at 5.5E-5 mg/L. Among the RAP samples, NORTHRAP and its weathering products showed the highest concentrations for most PAHs, while Fresh and other RAPs often had concentrations below detection. In the batch experiments, benz[a]anthracene showed a concentration in a sample from water soluble extraction higher than 0.0001 mg/L, the current EPA health advisory level for benz[a]anthracene (US Department of Health Human Services. Toxicological profile for polycyclic aromatic hydrocarbons. Agency for Toxic Substances and Disease Registry, Atlanta, Ge., USA, 1995:19.)

In comparison to total extraction by DCM, water extracted little, if any, PAHs from Fresh and reclaimed asphalts, e.g. NORTHRAP, CENTRALRAP, and SOUTHRAP (Figure 17). The water leaching process on average mobilized only less than 1 percent of PAHs from RAPs, with higher percentages up to 3.3 percent found in low molecular weight compounds than those high molecular weight PAHs (averaged 0.1 percent).
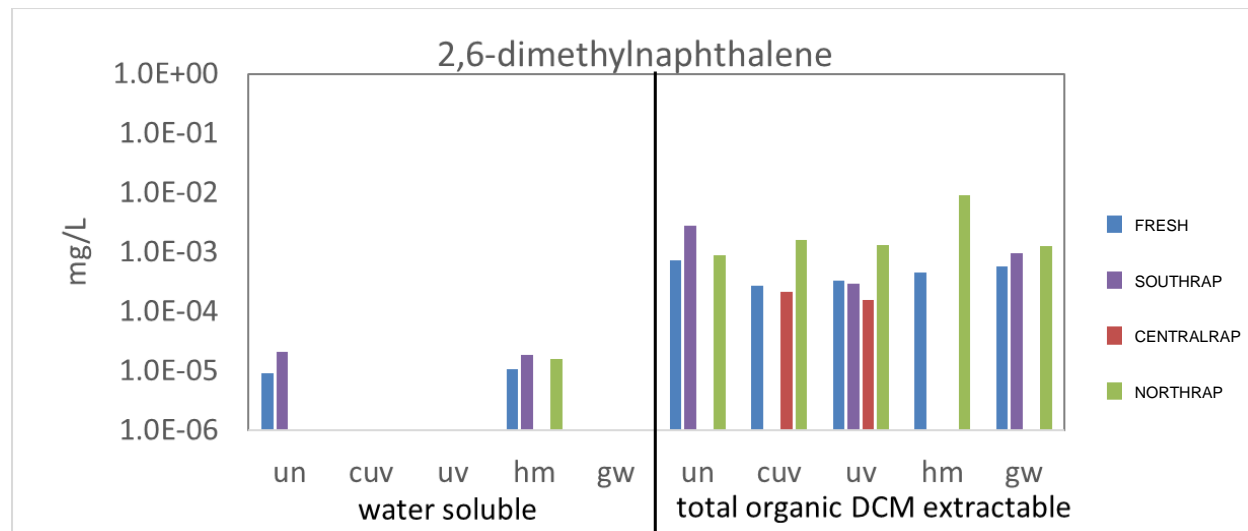
Figure 17: Selected PAH Concentrations (μg/g, in log scale) in RAP Batch Extraction Experiments.
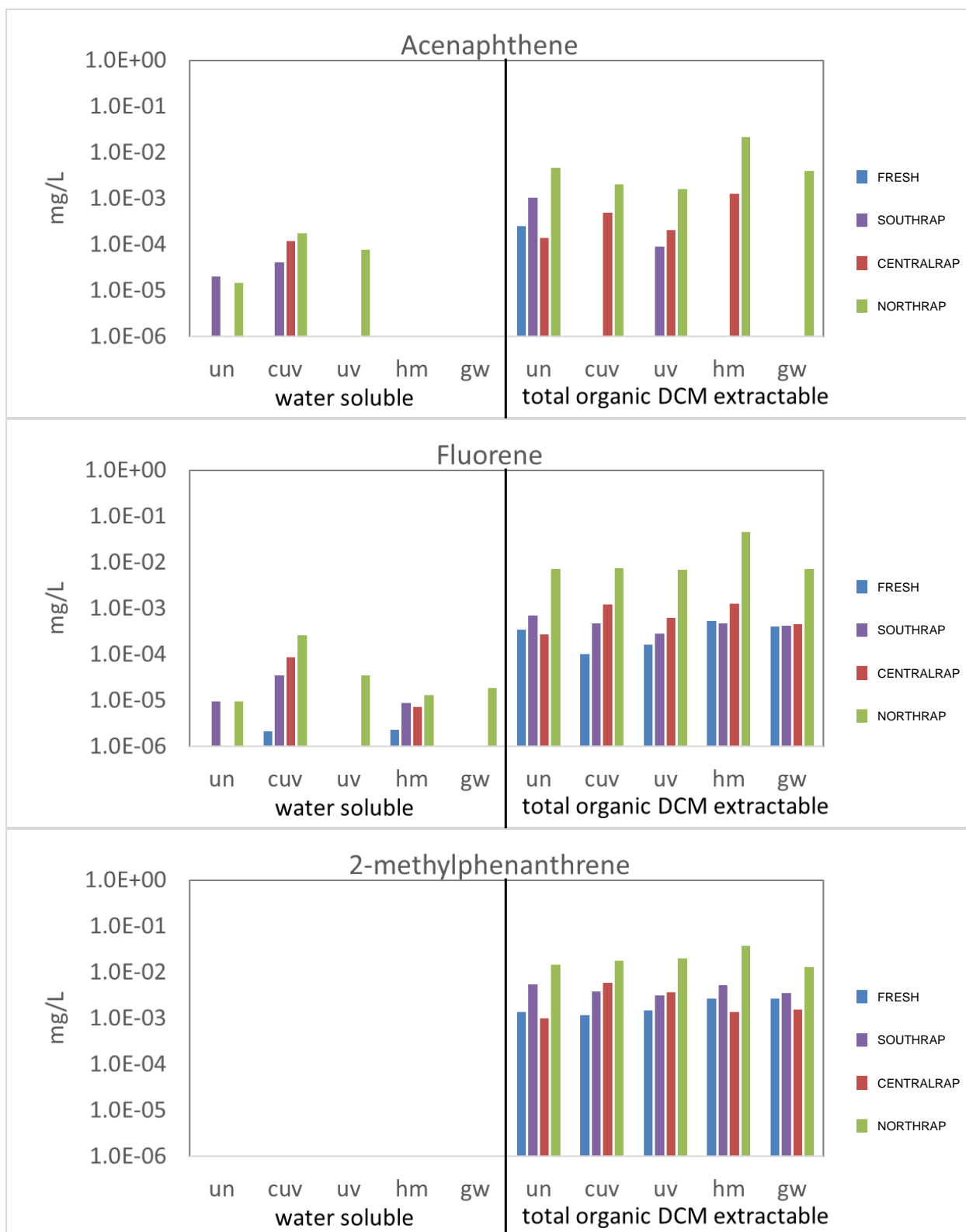
Figure 17 (_Continued_) Selected PAH Concentrations (μg/g, in log scale) in RAP Batch Extraction Experiments.

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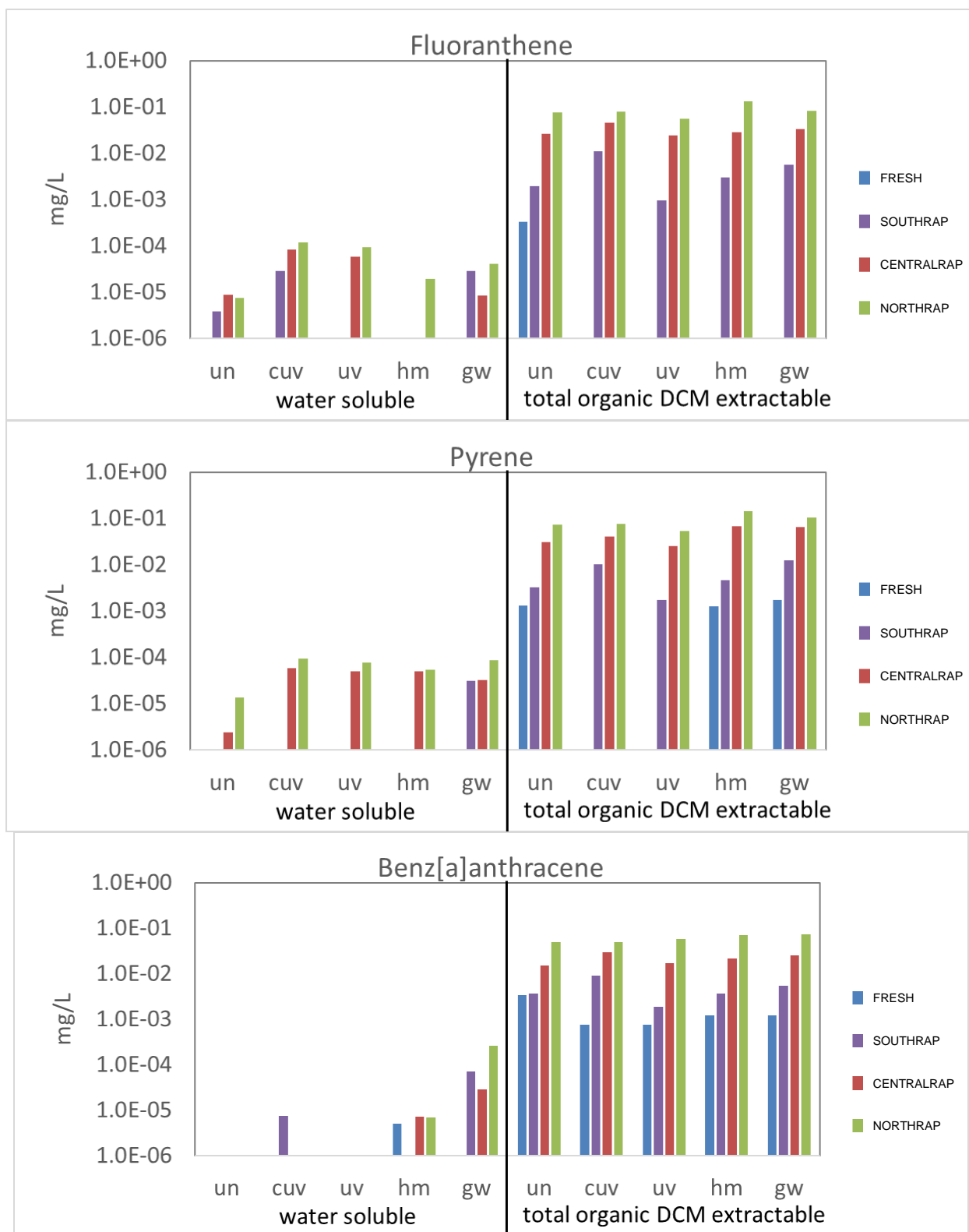
Figure 17 (_Continued_) Selected PAH Concentrations (µg/g, in log scale) in RAP Batch Extraction Experiments.
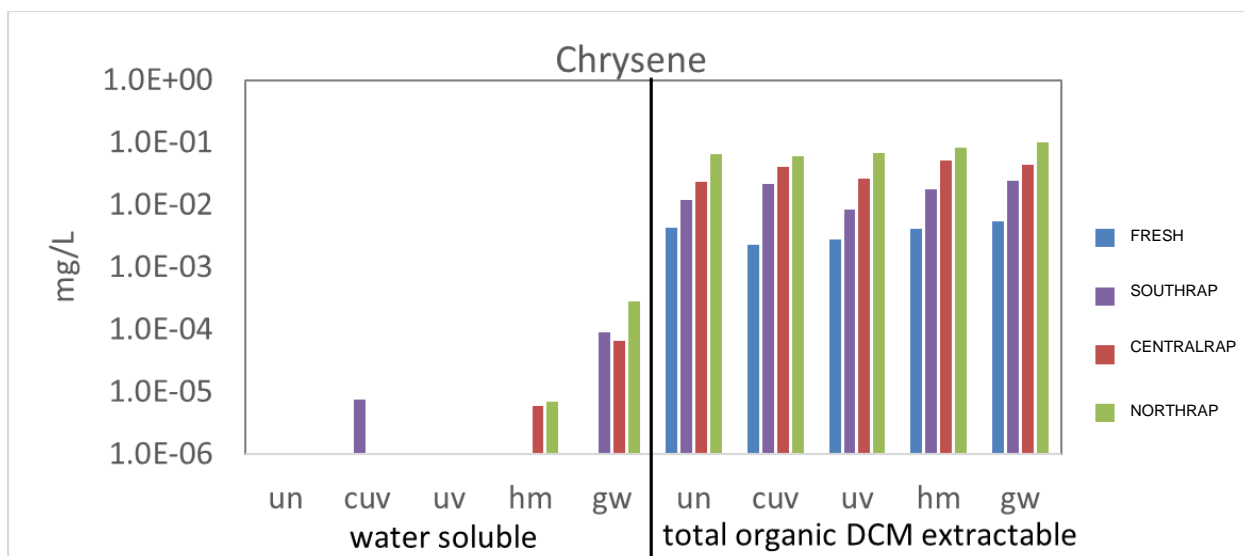
Figure 17 (_Continued_) Selected PAH Concentrations (μg/g, in log scale) in RAP Batch Extraction Experiments.

* un: un-weathered;
  cuv: compacted RAP QUV 25 cycles;
  uv: Unbound RAP QUV 25 cycles;
  hm: heat and moisture 60 cycles;
  gw: groundwater flow-through column weathering.

For both fluoranthene and pyrene, their water-extractable concentrations in weathered products were significantly higher than in un-weathered RAP (Figure 18). The higher level after weathering indicate that these HMW PAHs were more extractable, possibly due to the weaker sorption capability of weathered asphalt binder for PAH compounds than that of un-weathered RAP.

Flow-through Column Experiments
Element analysis
Water samples from all the flow-through column experiments were analyzed for 32 elements, including Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn. Complete analysis results are attached in the supplemental material.

Overall, no major or trace elements were found exceeding the US EPA's primary drinking water MCLs from RAP column, only Al and Fe from soil column exceeded the secondary MCLs in very few samples. This clearly demonstrated that compared to strong dissolution capability of the acidic batch extraction fluid, the synthetic NJ rain water used in column experiments is less capable to elute elements, including these regulated metals, such as Pb and As. For example, the Zn level in batch experiments from four RAPs was about 0.3 mg/L, while the Zn level in column experiment samples was about 0.03 mg/L. Mn also showed much lower levels (~10 percent) in column experiment samples than from batch experiment samples.

Time-series concentrations of selected elements in all 6 sets of flow-through column experiments are shown in Figure 18. Major elements including Ca, K, Mg, and S have much higher levels in soil effluents than in RAP effluents, and are leached out fast in both. Most trace elements including Al, As, Ba, Cu, Fe, Mo, P, Pb, U, and Zn showed a major source from soil, while Mn and Ni showed higher release from asphalt but were attenuated by the soil column. NORTHRAP showed elevated levels of As, Ba, Cu, Mo, and V than fresh asphalt samples, suggesting a road source. Further studies are needed to quantify the release time and rates of metals of concern from RAPs and the soil attenuation capacity, coefficient, and rate.

PAH analysis

Water samples from all 6 sets of flow-through column experiments except the Equipment Blank Test were analyzed for 29 PAH compounds, including 1-methylpyrene, 4-methylpyrene, 2-methylphenanthrene, 3-methylphenanthrene, 4-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, 1,3-,2,10-,3,9-,3,10-DMP, 1,6-,2,9-DMP, 1,7-dimethylphenanthrene, 2,3-dimethylphenanthrene, 2,6-dimethylphenanthrene, 2,7-dimethylphenanthrene, 6-methylbenz[a]anthracene, acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[ghi]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, fluoranthene, fluorene, phenanthrene, and pyrene. Complete analysis results are attached in the supplemental material. Selected PAH concentrations in flow-through column experiments using Fresh and weathered Fresh are summarized in Table 12, and those in column experiments using NORTHRAP and weathered NORTHRAP are summarized in Table 13. Selected time-series PAH concentrations in all the experiments are plotted in Figure 19.

Overall, PAHs with EPA standards were detected at concentrations less than the EPA guidelines (e.g., 0.0001 mg/L for benz[a]anthracene) (US Department of Health Human Services. Toxicological profile for polycyclic aromatic hydrocarbons. Agency for Toxic Substances and Disease Registry, Atlanta, Ge., USA, 1995:19). Low molecular weight PAH compounds including 2,6-dimethylnaphthalene, Acenaphthene, and 2-methylphenanthrene showed relatively high concentrations up to 1.4 E-4 mg/L in the solutions collected after soil column or were detected in soil solution earlier than in RAP solution (Figure 19, Table 12, and Table 13), suggesting their major sources from soil. High molecular weight compounds including Fluorene, Fluoranthene, Pyrene, Benz[a]anthracene, and Chrysene were mostly released from weathered RAPs, but their concentrations were below EPA standards. Their concentrations after the soil column were even lower or below the detection limit, due to the attenuation of these compounds by the soil column. The majority of other PAH compounds had concentrations below their detection limits (Table 12 and Table 13). Consistent with batch experiments, levels of HMW PAHs in Fresh after RAP column is much lower than NORTHRAP, possibly indicating different binder sources. Benz[a]anthracene and chrysene compounds (5 ringed PAHs) can be derived from the soil as well (Figure 19), but their levels were much lower than 0.0001 mg/L after several pore volumes of elution. These two compounds showed up once in samples collected after NORTHRAP column, but not in the samples after soil column.
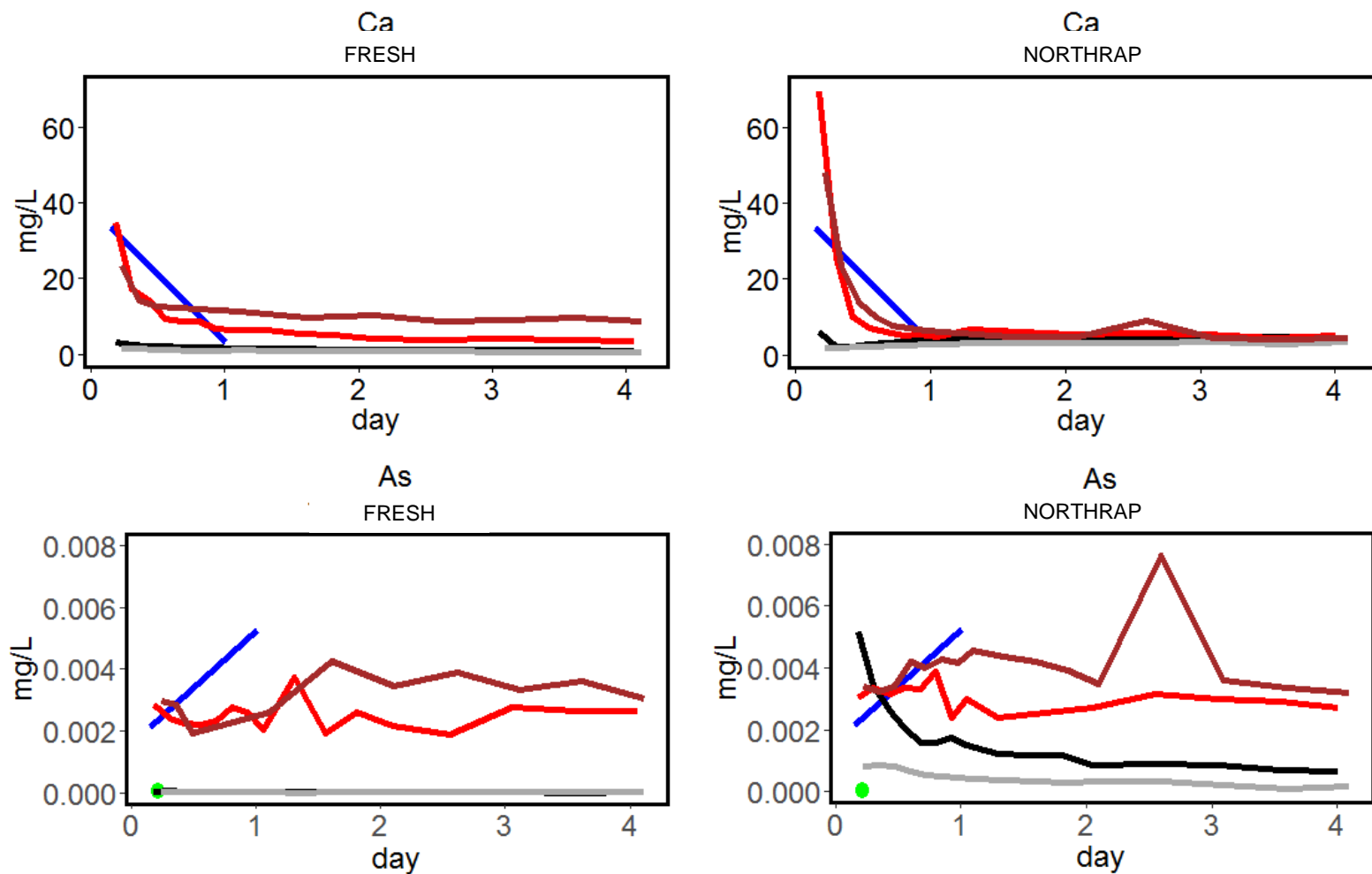
Figure 18: Time-Series Concentrations of Selected Elements in Flow-Through Column Experiments of Fresh RAP and NORTHRAP and their Weathered Counterparts.

Figure 18 (Continued): Time-Series Concentrations of Selected Elements in Flow-Through Column Experiments of Fresh RAP and NORTHRAP and their Weathered Counterparts.
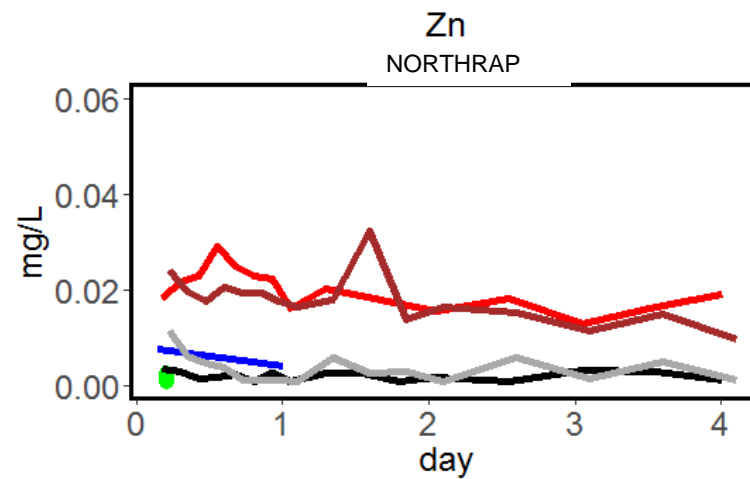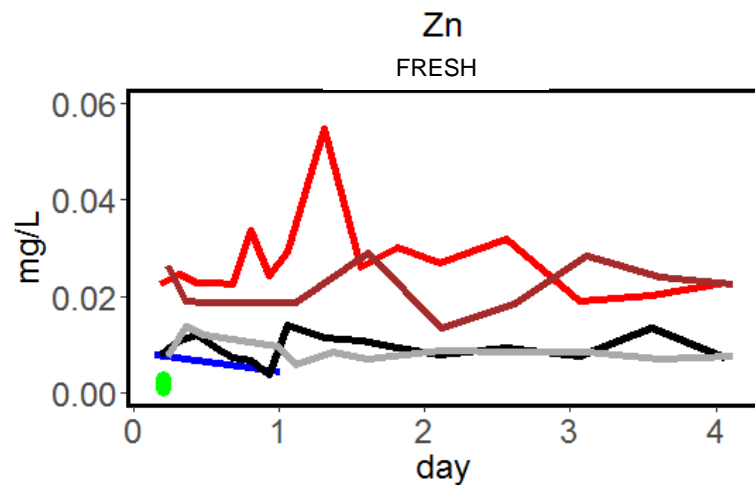
Figure 18 (Continued): Time-Series Concentrations of Selected Elements in Flow-Through Column Experiments of Fresh RAP and NORTHRAP and their Weathered Counterparts.

Table 12: Selected PAH Concentrations (mg/L) in Solution Collected after RAP Column and Soil Column in Two-Column Flow-Through Experiments Using Fresh.

Experiment Settings	Time After Starting (Hour)	2,6-di-methyl-naphthalene	Acenaphthene	Fluorene	2-methyl-phenanthrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
Soil Blank After RAP Col.	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	24	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Soil Blank After Soil Col.	2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	22	BDL	2.75E-05	4.98E-05	BDL	BDL	BDL	BDL	BDL
Fresh After RAP Col.	4	BDL	BDL	BDL	BDL	1.38E-06	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	10	BDL	BDL	BDL	BDL	BDL	1.60E-06	BDL	BDL
	16	BDL	BDL	BDL	BDL	3.49E-06	1.38E-06	BDL	BDL
	22	BDL	BDL	BDL	BDL	1.87E-06	9.35E-07	BDL	BDL
	31	BDL	BDL	BDL	BDL	2.52E-06	8.86E-07	BDL	BDL
	43	BDL	BDL	BDL	BDL	1.80E-06	1.19E-06	BDL	BDL
	61	BDL	BDL	BDL	BDL	4.01E-08	2.30E-08	BDL	BDL
	86	BDL	BDL	BDL	BDL	BDL	8.40E-07	BDL	BDL
Fresh After Soil Col.	2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	14	1.21E-05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	20	7.80E-06	BDL	BDL	BDL	BDL	BDL	5.49E-08	BDL
	29	1.73E-05	BDL	BDL	7.50E-06	BDL	BDL	BDL	BDL
	41	8.51E-06	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	59	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	83	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Table 12 (_Continued_): Selected PAH Concentrations (mg/L) in Solution Collected after RAP Column and Soil Column in Two-Column Flow-Through Experiments Using Fresh.

Experiment Settings	Time After Starting (Hour)	2,6-di-methyl-naphthalene	Acenaphthene	Fluorene	2-methyl-phenanthrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
Aged Fresh After RAP Col.	6	1.79E-05	BDL	1.11E-05	BDL	BDL	BDL	2.59E-06	BDL
	9	BDL	BDL	6.02E-06	BDL	BDL	BDL	BDL	BDL
	12	9.68E-05	BDL	1.02E-04	BDL	BDL	BDL	8.54E-06	BDL
	18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	24	BDL	BDL	BDL	BDL	BDL	BDL	4.42E-06	8.16E-06
	27	BDL	4.91E-05	3.38E-05	BDL	BDL	BDL	BDL	BDL
	33	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	45	BDL	2.17E-06	BDL	BDL	BDL	BDL	BDL	BDL
	63	BDL	BDL	2.66E-06	BDL	6.56E-06	2.35E-05	9.17E-06	3.84E-06
	75	BDL	BDL	BDL	BDL	1.16E-06	2.18E-06	BDL	2.53E-06
	87	BDL	BDL	BDL	BDL	7.56E-06	1.92E-05	6.09E-06	4.46E-06
	99	BDL	BDL	BDL	BDL	1.82E-05	3.82E-05	1.07E-05	8.79E-06
Aged Fresh After Soil Col.	3	7.04E-05	2.74E-05	BDL	2.36E-05	BDL	BDL	2.29E-06	1.25E-06
	6	BDL	2.75E-05	BDL	BDL	BDL	BDL	2.52E-06	BDL
	9	5.55E-05	2.17E-05	BDL	2.10E-05	BDL	BDL	1.95E-06	BDL
	12	4.92E-05	5.08E-06	BDL	9.60E-06	BDL	BDL	2.87E-07	BDL
	24	5.58E-05	6.35E-06	BDL	9.60E-06	BDL	BDL	BDL	BDL
	55	5.04E-05	BDL	BDL	1.22E-05	BDL	BDL	1.37E-07	BDL

Table 13: Selected PAH Concentrations (mg/L) in Solution Collected after RAP Column and Soil Column in Two-Column Flow-Through Experiments Using NORTHRAP.

Experiment Settings	Time After Starting (Hour)	2,6-di-methyl-naphthalene	Acenaphthene	Fluorene	2-methyl-phenanthrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
Soil Blank After RAP Col.	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	24	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Soil Blank After Soil Col.	2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	22	BDL	2.75E-05	4.98E-05	BDL	BDL	BDL	BDL	BDL
NORTHRAP After RAP Col.	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	22	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	31	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	43	8.66E-06	BDL	5.08E-06	BDL	BDL	1.64E-05	BDL	BDL
	61	3.41E-05	8.78E-05	2.82E-05	BDL	BDL	1.94E-05	BDL	BDL
	85	BDL	BDL	BDL	BDL	BDL	1.58E-05	BDL	BDL
NORTHRAP After Soil Col.	1	1.54E-05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	7	1.31E-05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	13	1.34E-05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	19	9.21E-06	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	28	BDL	BDL	3.70E-06	2.35E-05	BDL	BDL	BDL	BDL
	58	BDL	BDL	BDL	BDL	4.97E-06	BDL	BDL	BDL
	82	BDL	BDL	BDL	BDL	1.73E-06	2.42E-06	BDL	BDL

**Table 13 (_Continued_): Selected PAH Concentrations (mg/L) in Solution Collected after RAP Column and Soil Column in Two-Column Flow-Through Experiments Using NORTHRAP.**

Experiment Settings	Time After Starting (Hour)	2,6-di-methyl-naphthalene	Acenaphthene	Fluorene	2-methyl-phenanthrene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene
Aged NORTHRAP After RAP Col.	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	11	BDL	BDL	BDL	BDL	BDL	1.48E-05	BDL	BDL
	17	BDL	BDL	BDL	BDL	BDL	1.15E-05	BDL	BDL
	23	BDL	BDL	BDL	BDL	BDL	1.71E-05	BDL	BDL
	32	BDL	BDL	BDL	BDL	BDL	1.76E-05	BDL	BDL
	44	BDL	6.89E-06	1.62E-06	BDL	1.62E-05	1.72E-05	1.03E-06	2.51E-06
	62	6.91E-06	BDL	BDL	BDL	1.26E-05	1.43E-05	BDL	BDL
	86	BDL	BDL	5.79E-07	BDL	1.10E-05	9.46E-06	BDL	BDL
Aged NORTHRAP After Soil Col.	2	1.38E-04	5.35E-05	BDL	4.22E-05	BDL	BDL	BDL	BDL
	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	8	2.77E-05	BDL	BDL	1.61E-05	BDL	BDL	BDL	BDL
	14	4.99E-05	BDL	BDL	1.73E-05	BDL	BDL	BDL	BDL
	20	1.43E-05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	29	6.85E-06	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	41	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	59	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	83	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
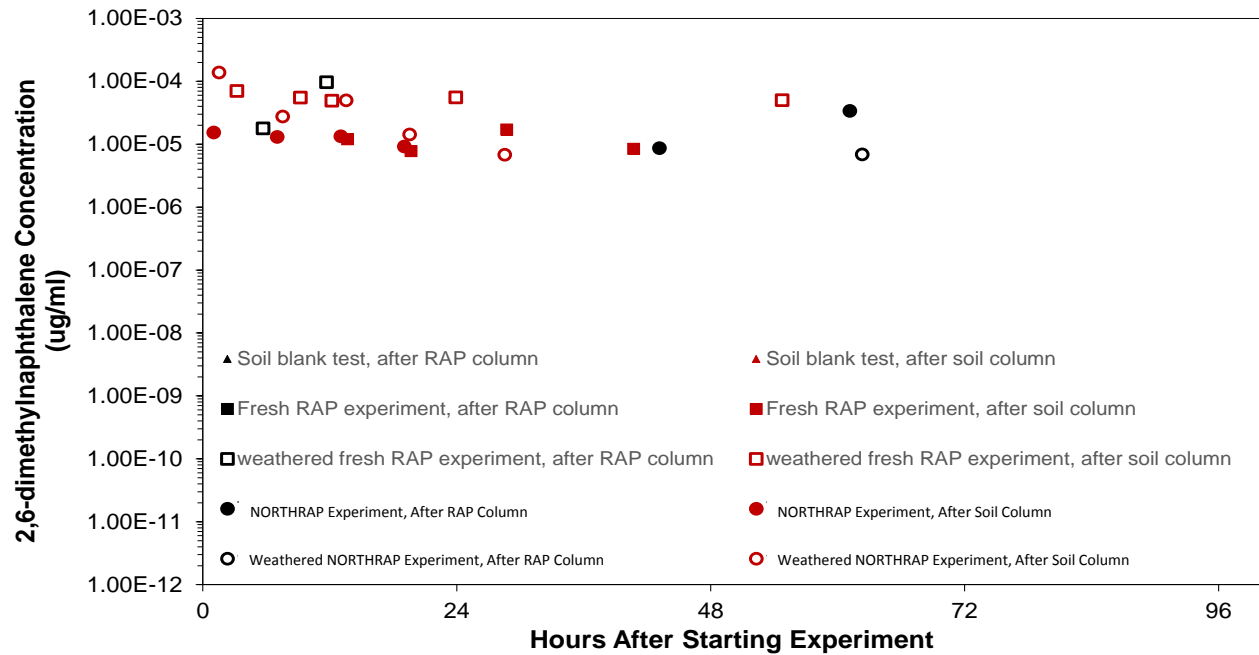
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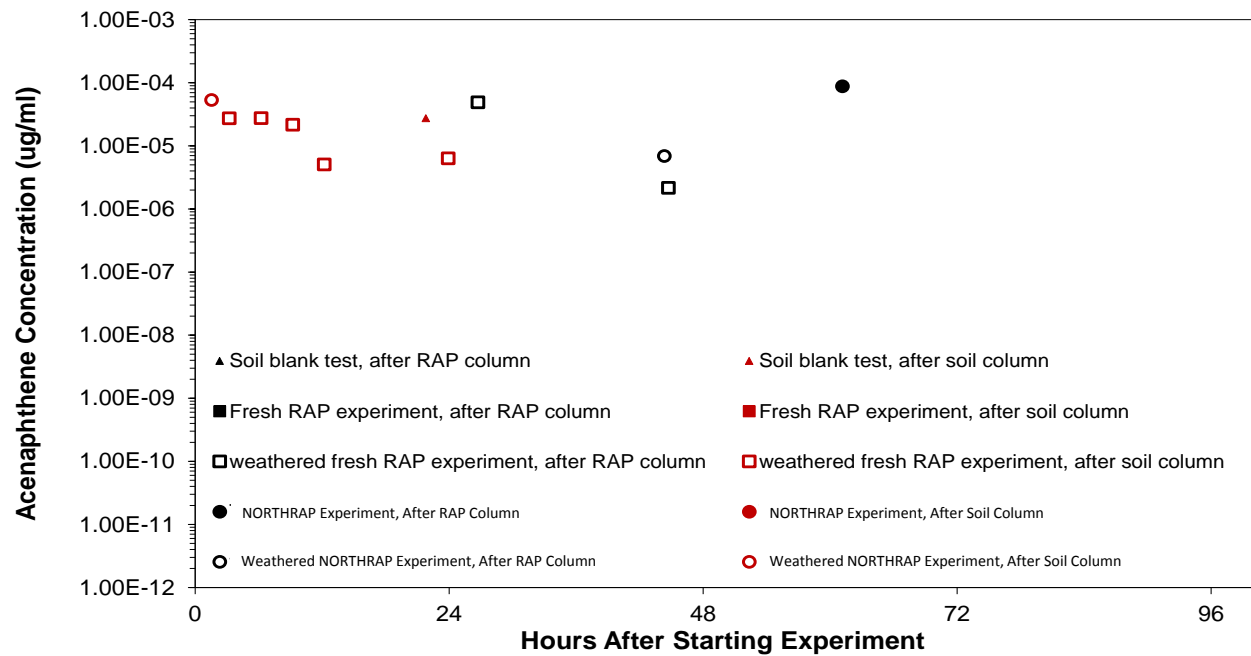
(b)

Figure 19: Time-Series PAH Concentrations in Solution Collected after RAP
Column (Black) and Soil Column (Red) in Two-Column
Flow-Through Experiments. Note: ug/ml is equivalent to mg/L.

(c)

(d)

Figure 19 (_Continued_): Time-Series PAH Concentrations in Solution Collected after RAP Column (Black) and Soil Column (Red) in Two-Column Flow-Through Experiments.

(e)

(f)

Figure 19 (_Continued_): Time-Series PAH Concentrations in Solution Collected after RAP Column (Black) and Soil Column (Red) in Two-Column Flow-Through Experiments.
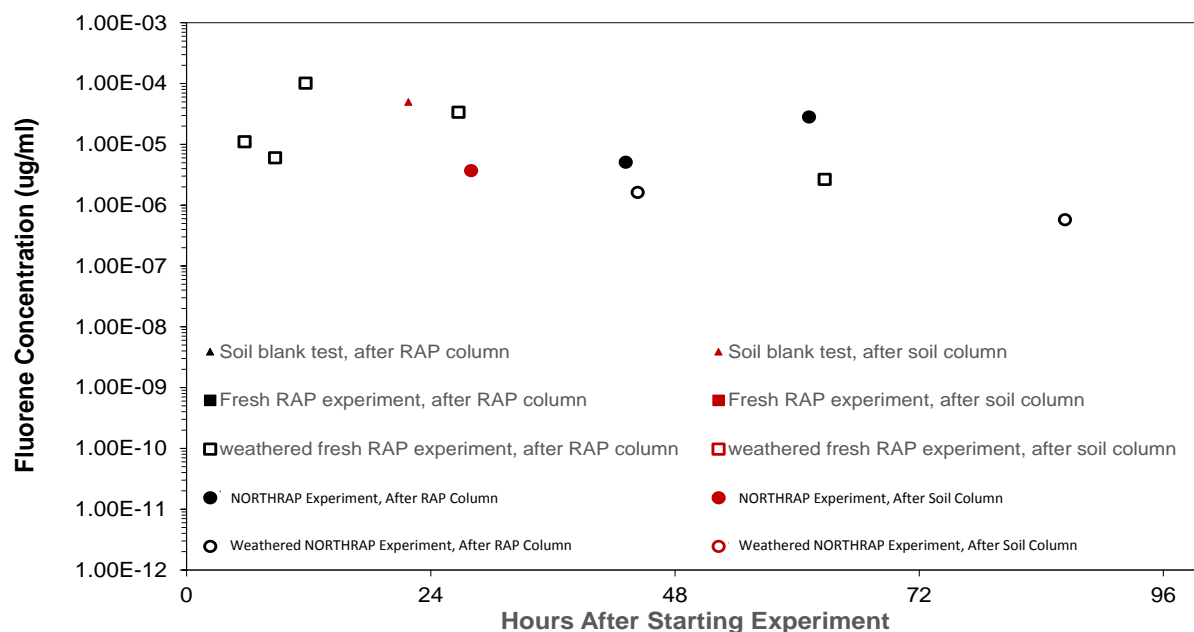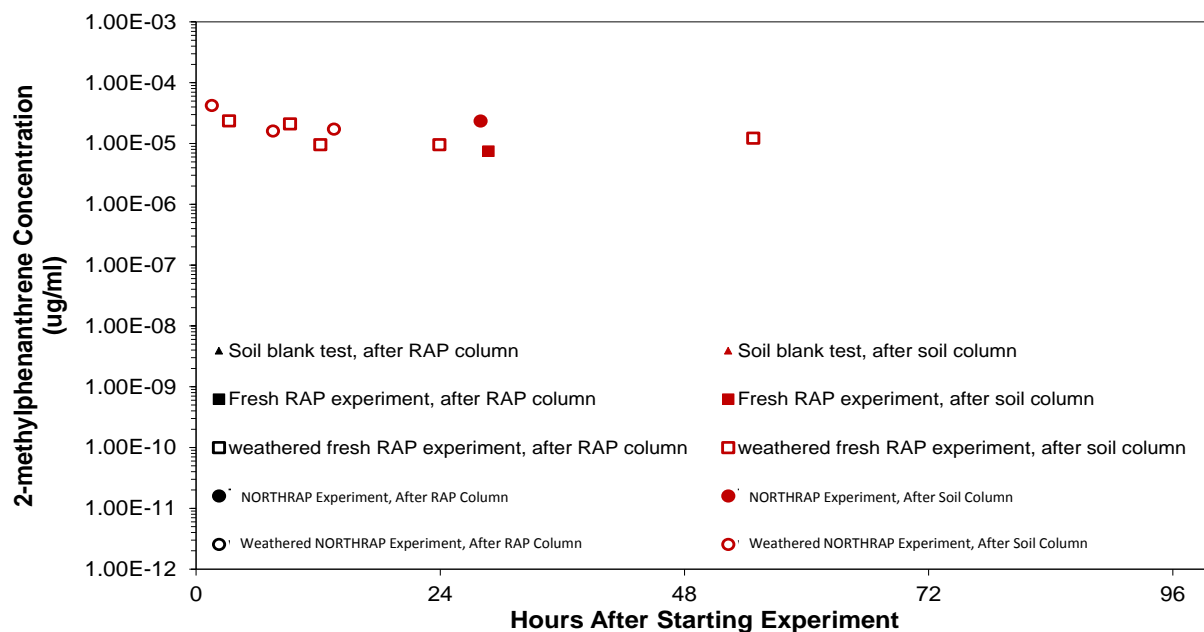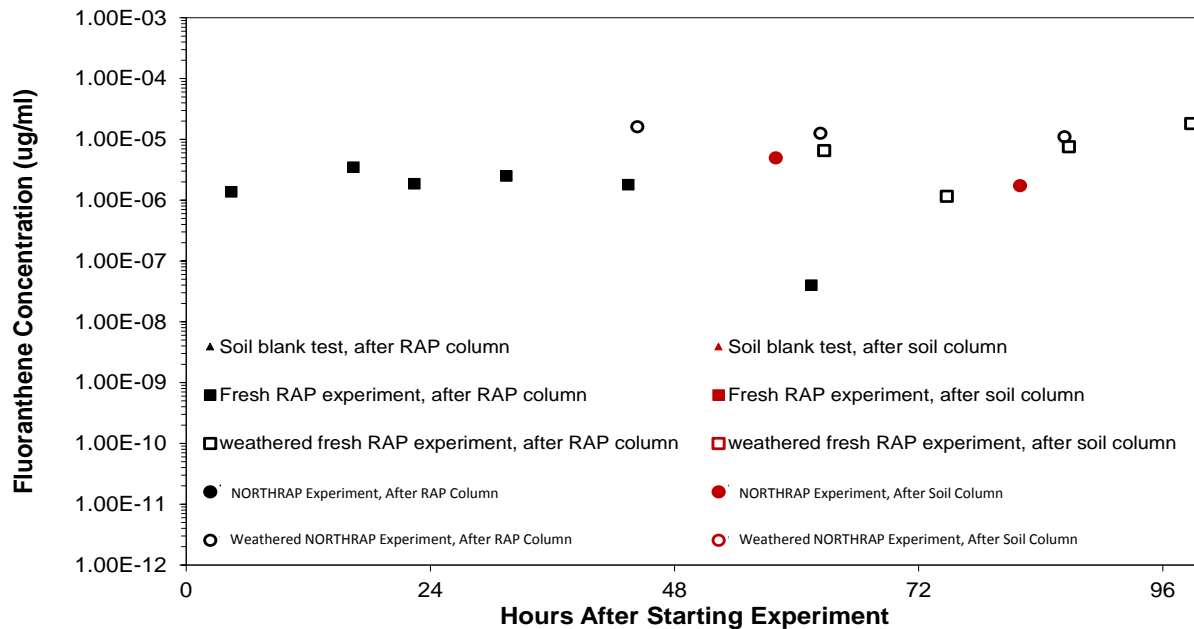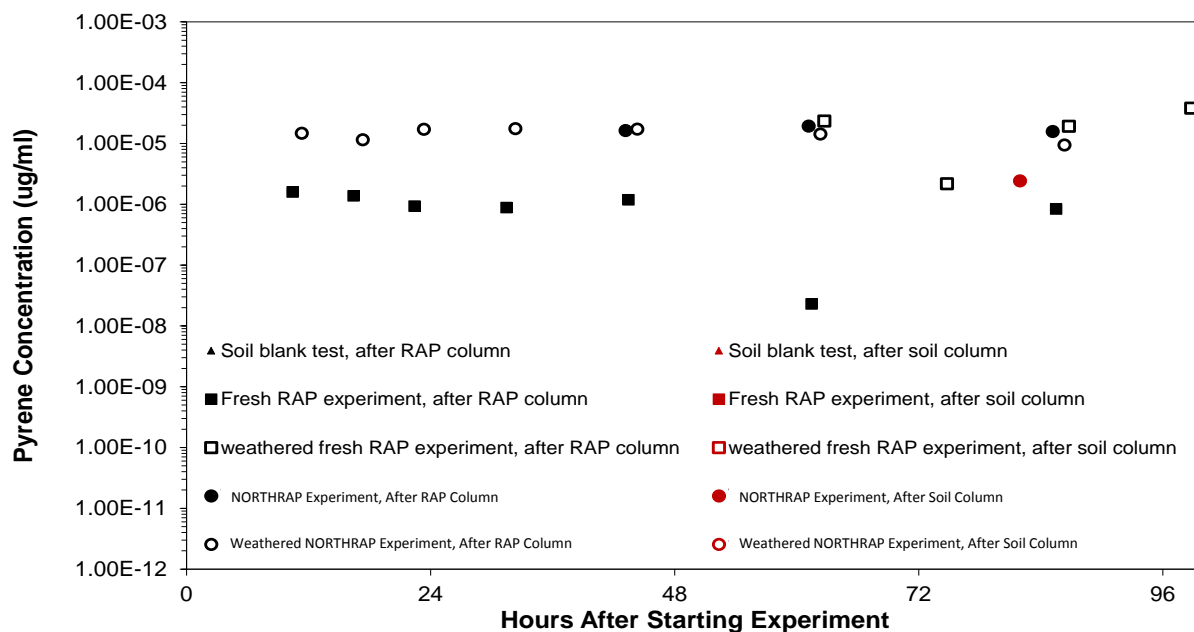
(e)

(f)
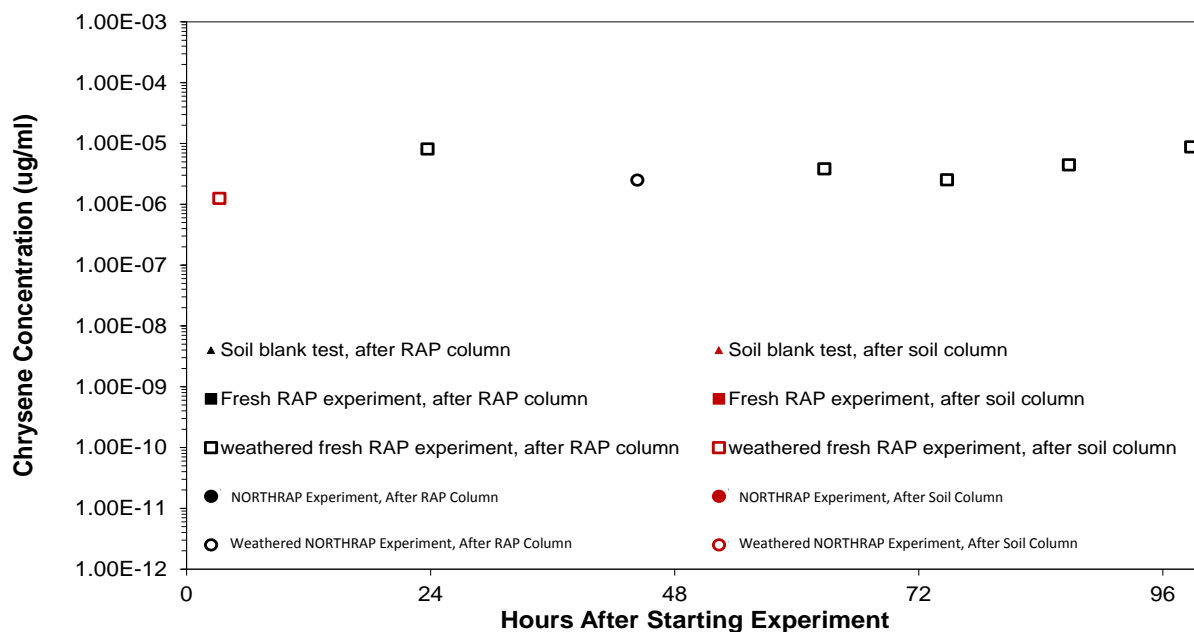
Figure 19 (_Continued_): Time-Series PAH Concentrations in Solution Collected after RAP Column (Black) and Soil Column (Red) in Two-Column Flow-Through Experiments.
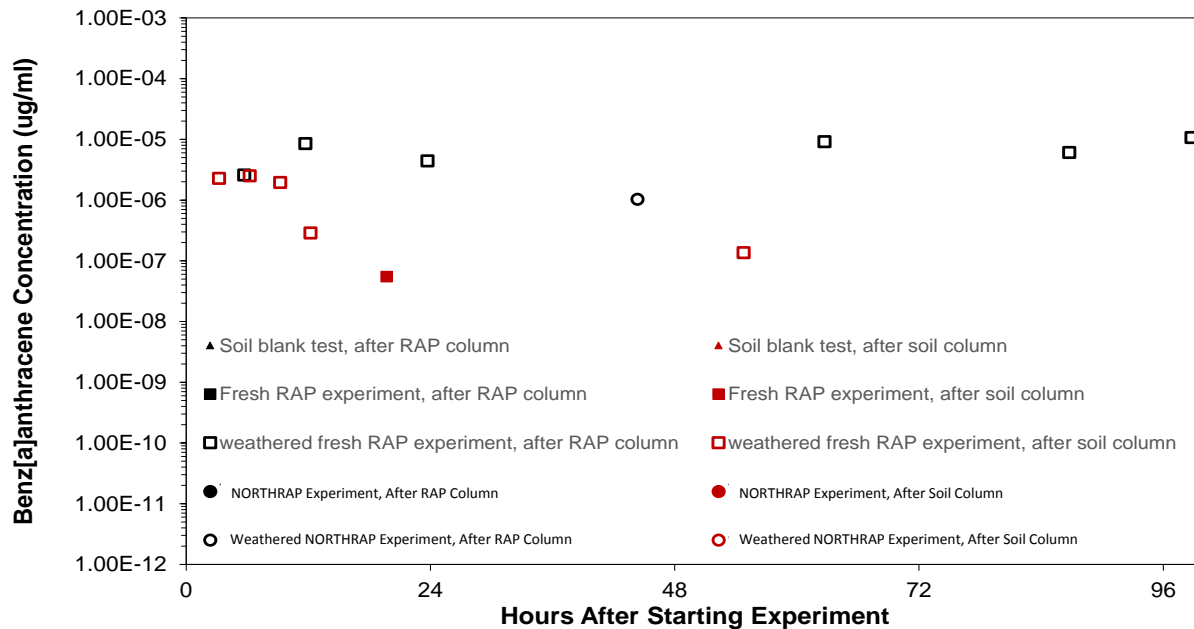
Chamber Inhalation Experiments

PM$_{2.5}$ analysis

PM$_{2.5}$ emission from the 3-hour RAP chamber experiments was low for all samples, with PM$_{2.5}$ concentrations from RAPs (Fresh averaged at 13.1 µg/m^3, NORTHRAP averaged at 10.0 µg/m^3, NORTHRAP unbound QUV 25 cycles averaged at 11.0 µg/m^3) only slightly higher than in field blank experiments (averaged at 8.0 µg/m^3) (Table 14). These PM$_{2.5}$ emission levels during 3-hour vigorous shaking are much lower than the current PM$_{2.5}$ standards established as a 24-hour standard of 35 µg/m^3 by the United States Environmental Protection Agency (USEPA) National Ambient Air Quality Standards (NAAQS) in pursuant to the Clean Air Act (USEPA).

The net particle mass weighed on each of the filters were within the margin of error of the highly-sensitive microbalance used for gravimetric analysis. In some cases, net masses were even negative, likely due to slight changes in filter mass caused by the temperature and humidity change between pre-sampling and post-sampling. The low PM2.5 emission is also partially due that RAP particles are typically more than 1 mm, much larger than 2.5 µm. Because of the low mass of PM2.5 emitted, there is no need for metal and PAH analyses for these Teflon filter samples.

Table 14: PM2.5 Concentrations in Chamber Inhalation Experiments.

Sample ID	Analysis No. 1	Analysis No. 2	Analysis No. 3	Average
Field Blank	9.3	8.8	5.9	8.0
Fresh	8.1	9.4	21.9	13.1
NORTHRAP	12.8	< LOD of 5.5	14.5	10.0
NORTHRAP unbounded QUV 25 cycles	19.8	10.3	< LOD of 5.5	11.0

VOC analysis

In chamber inhalation experiments, only NORTHRAP emits toluene at a level around 0.8 mg/m^3, but not in its weathered product (Table 15). In addition, 0.8 mg/m^3 is well below the EPA's 6-hour exposure standard of 37 mg/m^3 for general public. (https://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=512650)

The low VOC emission from RAPs is expected since asphalt is simply the residue left over from petroleum refining and almost all VOC compounds have already been released, mainly in butane or gasoline fractions. The identification of toluene in NORTHRAP indicates the contaminated road sources. Toluene was removed or decomposed during the weathering processes. The identification of both Pb and toluene in NORTHRAP demonstrated this RAP contained substantial road pollutants and should be used with caution.

Table 15: VOC Concentrations in Chamber Inhalation Experiments.

Volatile Organic Compound (VOC, mg/m³)	Field Blank	Field Blank	Field Blank	Fresh	Fresh	Fresh	NORTHRAP	NORTHRAP	NORTHRAP	QUV-NORTHRAP	QUV-NORTHRAP	QUV-NORTHRAP
Methyl Chloroform	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1,2-Trichloroethane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Dichloroethane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2-Dichloroethane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Acetone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Benzene	<0.05	<0.05	<0.05	<0.05	<0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.06
Chlorobenzene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chloroform	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cumene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cyclohexane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cyclohexanone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cyclohexene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethyl Alcohol	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethylbenezene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Isopropyl Alcohol	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
m-dichlorobenzene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methyl Ethyl Ketone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methyl Isobutyl Ketone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methyl n-Propyl Ketone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Methylene Chloride	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
n-Butyl Acetate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
n-Hexane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
n-Propyl Acetate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
o-Dichlorobenzene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2
p-Dichlorobenzene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pentane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tetrachloroethylene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tetrahydrofuran	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Toluene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**0.63**	**0.55**	**1.4**	<0.1	<0.1	<0.1
Trichloroethylene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Xylene	<0.4	<0.38	<0.4	<0.4	<0.42	<0.4	<0.42	<0.4	<0.41	<0.4	<0.39	<0.43

ANALYSIS OF THE TOXICITY OF RAP

Microtox® Toxicity Testing

Methods

The first batch of RAP samples received from Co-Investigators at Columbia included a sample of each of the batches of RAP to be tested (NORTHRAP, FRESH, CENTRALRAP, and SOUTHRAP) plus a sample of the blank solution used to elute the RAP samples. Testing for relative acute toxicity began using the Microtox® system following manufacturer instructions (Modern Water 1995). The Microtox® system uses the bioluminescent marine bacterium *Vibrio fischeri*, quantifying toxicity as attenuation of light production, allowing determination of an effective concentration resulting in 50 percent light reduction (EC50, i.e., the concentration at which a 50 percent reduction of light is observed) obtained by testing a dilution curve made from each sample. A lower EC50 indicates higher toxicity. The Microtox® system allows for a relatively high throughput of sample testing and is a commonly used method for screening aqueous samples for relative toxicity. A 100 mg/L phenol solution was prepared as a positive control. Use of this control with every assay provided effective quality control by ensuring the bacteria are active, and the analysis system responding appropriately. The acceptable range for EC50 of phenol is 13-26 mg/L (Ghosh et al. 1992). A sample response curve for phenol is presented in Figure 20. All our values were within this range, indicating our analytical protocol was acceptable.

Prior to running the assay, sample pH was adjusted in accordance with the minimum tolerable conditions required by the Microtox® system using 1 N NaOH. Table 16 lists the initial and adjusted pH of the RAP samples. Osmotic pressure was also adjusted for the Microtox® tests using a 2 percent NaCl osmotic adjustment solution (provided with the Microtox® system).

Table 16: RAP Sample pH's: Before and After 1 N NaOH Titration.

Sample	Starting pH	Titrated pH
Blank	4.603	5.975
NORTHRAP 1	4.769	6.069
FRESH 1	4.591	5.968
CENTRALRA	4.749	6.368
SOUTHRAP 1	5.183	5.968

Results

Analysis of Initial Batch Extracted RAP Samples

Range finding tests were performed on batch extracted RAP samples to identify a range of sample dilutions that would best calculate an EC50. Initial tests used a dilution range spanning 81.9 to 10 percent of sample. The batch extracted RAP samples were found to have EC50s at between 3 and 20 percent sample dilutions, so a new test range between 45 and 0.7 percent was used in subsequent EC50 determinations. All samples were run in 5 independent tests.

Table 17 illustrates the mean EC50 for each sample, as well as for phenol and ethanol (positive control and reference toxicant, respectively), and their standard error. We

adopted a p value of 0.05 indicating a 95 percent confidence as a statistically significant outcome throughout this study.
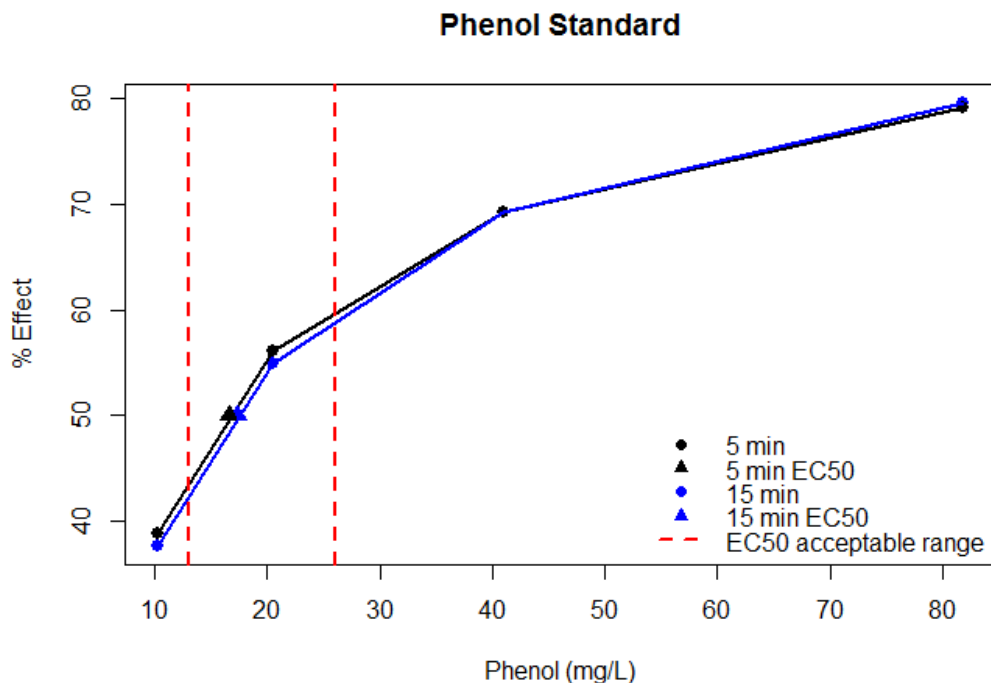
Phenol Standard

Figure 20: An Example of a Dose-Response Curve Obtained by the Microtox System.

Table 17: Mean EC50 and Standard Error of the Mean for Each Batch Extracted RAP Sample, as well as Phenol (Positive Control) and 25 percent Ethanol (Reference Chemical).

Sample	Mean	Standard Error
Phenol	21.04	1.96
25 percent	16.99	0.89
Blank	5.90	0.22
NORTHRAP	5.27	0.54
FRESH	6.97	1.06
CENTRALRAP	16.24	3.02
SOUTHRAP	6.81	0.71

To analyze whether or not RAP samples had significant toxic effects, we ran an analysis of covariance, using RAP samples as the factor and pH as the covariate. Both RAP sample treatment and pH were significant factors (RAP sample: $F_{6,27} = 4.51$, p = 0.0027; pH: $F_{1,27} = 5.62$, p = 0.025). A Tukey's multiple comparisons test was run to find individual differences between the EC50's of the samples. Phenol, ethanol, and CENTRALRAP were not significantly different from each other but had significantly higher EC50's than the other RAP samples, including the blank solution (Figure 21).

The high toxicity of the blank solution was unexpected and implies that much of the toxicity observed in our samples is a result of the extraction media used to treat the RAP samples, thus making any evaluation of the relative toxicity of the RAP samples problematic.
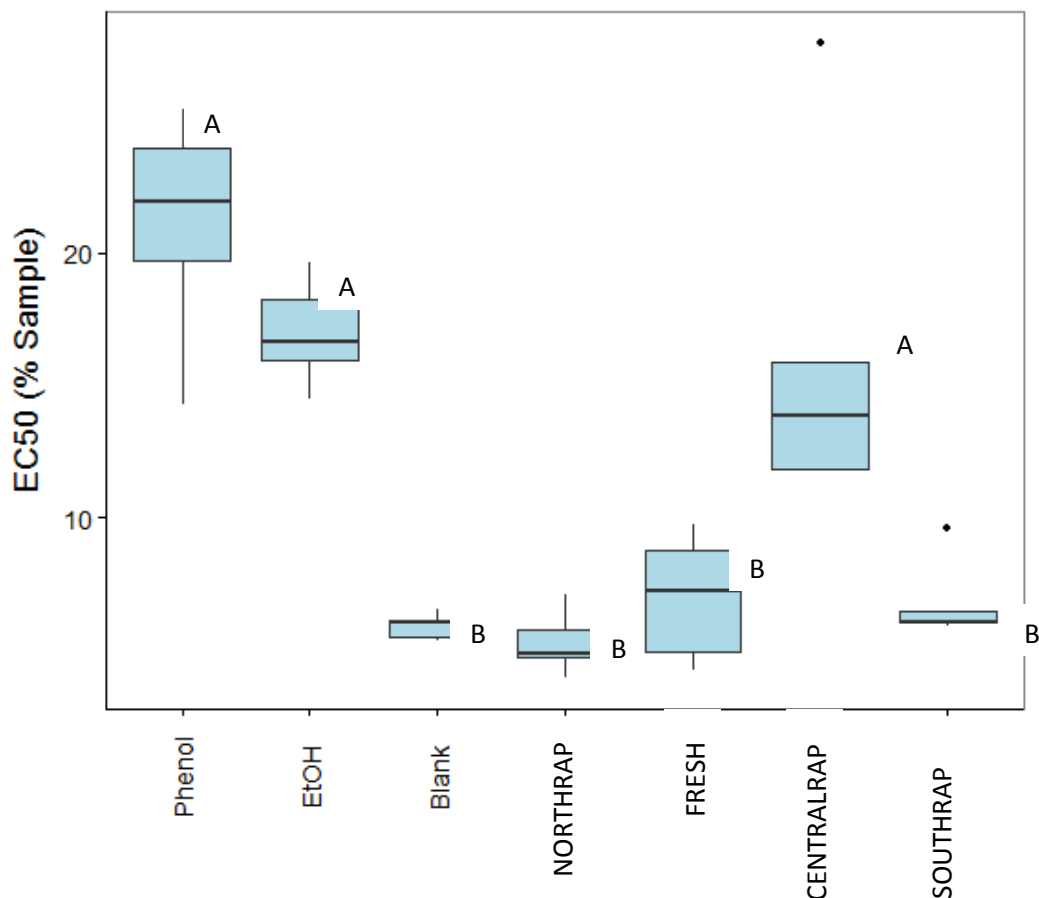
Figure 21: Boxplot of EC50 Values for all RAP Samples and Phenol (Positive Control) and 25 percent Ethanol (Reference Chemical): Different Letters Denote Significant Differences in EC50's.

Evaluation of Modified Batch Extraction Media
Discussions with Dr. Yan's team identified ammonium hydroxide from the extraction media as the likely cause of toxicity. Many studies have shown that ammonium is a toxic compound to aquatic organisms, and is often used as a biocide in invasive species and aquaculture management (Ward et al. 2013; Sink 2010). Dr. Yan's team suggested using sodium hydroxide as a substitute for ammonium hydroxide and altered their batch leachate extraction protocol. They sent us the pure extraction media as well as blank solutions (the same solution run through their extraction protocol) made with this new extraction media. Preliminary tests showed greatly reduced toxicity (increased EC50s – Table 18). While the toxic effect has been reduced, the EC50's are not significantly higher than that for phenol, the positive control and much lower than Japanese Medaka fish embryo rearing media (ERM - 17 mM NaCl, 0.40 µM KCl, 0.36 mM CaCl2, 0.66 mM

MgSO4 7H20 - which was not toxic enough to allow an EC50 calculation). Though the new extraction solution is an improvement, it is still not optimal for toxicity testing. However after consultation with Dr. Yan's team, we decided that the modified solution was the best compromise allowing them to compare their results to standard EPA methods, but still allow some assessment of toxicity.

Table 18: Mean EC50 Values and Standard Error for the New Extraction Media and Blank Extract.

Sample	Mean EC50	Standard Error (SE)
NaOH Extraction Media	28.85	3.46
NaOH Blank Extract	26.14	3.27
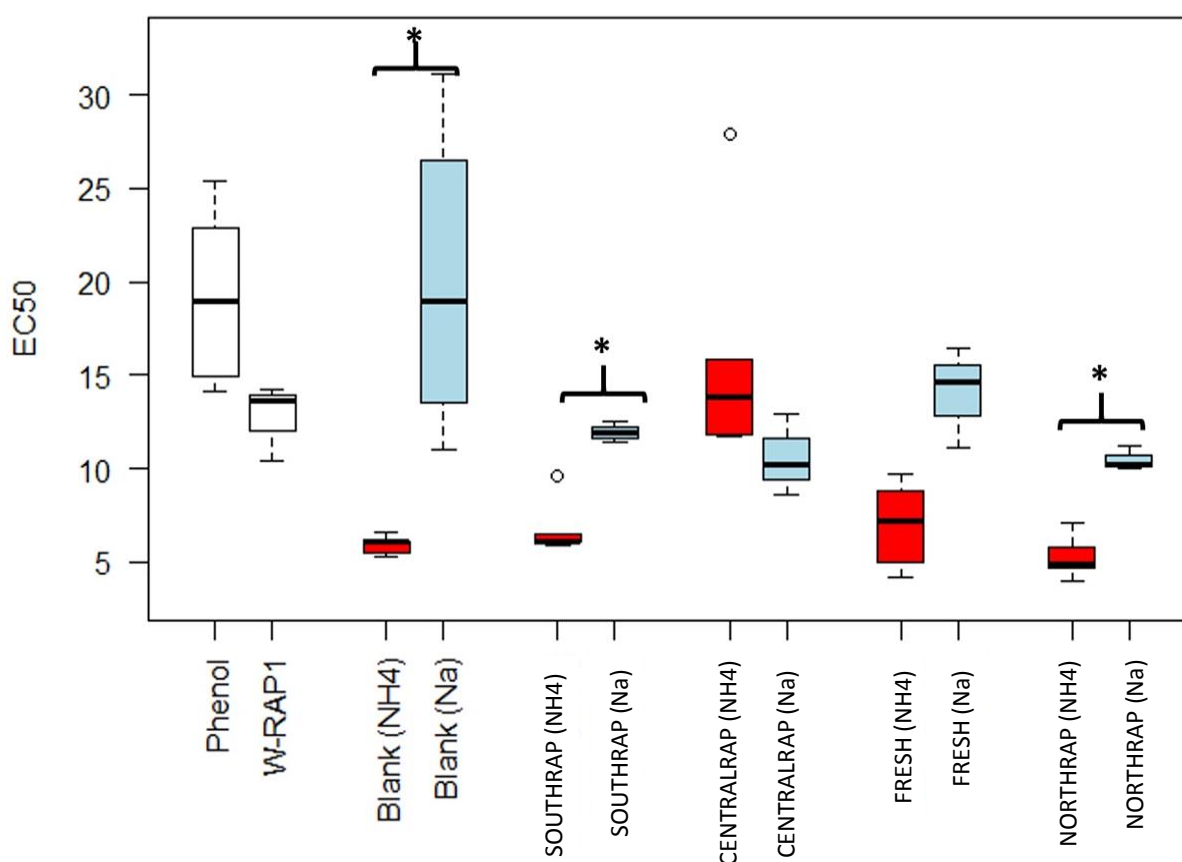
Figure 22: Box Plots of EC50s of Samples Run Previously with the Ammonium Hydroxide Blank (Red) and the Newer NaOH Blank (Blue).

As can be seen in Figure 22 above, in 3 of the 4 samples run with both extraction materials, those extracted with NaOH were significantly less toxic. The only exception being the batch CENTRALRAP sample where there appeared to be a slight enhancement of toxicity with the NaOH extraction media. None of the batch RAP samples from different sources were significantly different from each other or from the NaOH extraction media.

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Assessment of Column samples

We evaluated samples received from a variety of blanks and column samples prioritized (priority 1, 2 or 3) based on chemical analysis conducted in Dr. Yan's laboratory at Columbia University using the Microtox® assay. A description of the samples analyzed is presented in Table 19. There was insufficient light reduction produced in the assay in response to any of these samples, so EC50s could not be calculated. Thus, none of these samples were identified as toxic by the Microtox® system.

Table 19: Description of 12 Column Samples Evaluated with the Microtox® Assay: All were Extracted with Artificial Rainwater.

Sample ID	Description
Artificial Rain Water (ARW)	Extraction solution
ARM + Bromide (ARW+Br)	ARW with 10ppm bromide
B-R-01, B-S-01	Blank column run
S-R-02-1, S-R-03-1	Blank RAP column with no soil
S-S-02-1, S-S-03-1	Blank RAP column with soil
F-R-28	FRESH column eluent (Priority 1)
F-S-28	Soil column eluent following FRESH column (Priority 1)
W1-R-22	WRAP 1 column eluent (Priority 1)
W1-S-10	Soil column eluent following WRAP 1 column (Priority 1)
T-R-4	NORTHRAP column eluent (Priority 2)
T-S-4	Soil column eluent following NORTHRAP column (Priority 2)
F-R-4	FRESH column eluent (Priority 2)
F-S-4	Soil column eluent following FRESH column (Priority 2)
WT-R-4	WRAP 7 column eluent (Priority 3)
WT-S-4	Soil column eluent following RAP 7 column (Priority 3)
W1-R-4	WRAP 1 column eluent (Priority 3)
W1-S-4	Soil column eluent following WRAP 1 column (Priority 3)

The result of little to no toxicity of column samples by Microtox® tests was consistent with the chemical results; metal levels in column samples were merely about 10 percent of these in batch samples (acidic landfill leachate extraction). The NJ soil had LMW PAHs in column samples with levels up to 0.1 mg/L, but it appears that toxicity from LMW PAHs was not noticeable.

Microtox® analysis of weathered RAP samples

Sixteen weathered RAP samples were received from Dr. Yan's laboratory at Columbia University along with one blank sample using the newer NaOH based extraction media). pH was normalized using 1 N NaOH to ~6.0 as before. Phenol (100 mg/L) was also run as a positive control. The description of the samples analyzed is provided in Table 20 below.

Table 20: Description of 16 Weathered RAP Samples Evaluated with the Microtox® Assay: All were Extracted with Artificial Rainwater.

Sample ID	Description
WRAP-1	Fresh compacted RAP QUV 25 cycles
WRAP-2	Fresh Unbound RAP QUV 25 cycles
WRAP-3	NORTHRAP Compacted RAP 25 cycles
WRAP-4	CENTRALRAP Unbound RAP QUV 25 cycles
WRAP-5	CENTRALRAP Compacted RAP QUV 25 cycles
WRAP-6	SOUTHRAP Unbound RAP QUV 25 cycles
WRAP-7	NORTHRAP Unbound RAP QUV 25 cycles
WRAP-8	SOUTHRAP Compacted RAP 25 cycles QUV
WRAP-9	CENTRALRAP heat and moisture 60 cycles
WRAP-10	FRESH heat and moisture 60 cycles
WRAP-11	SOUTHRAP heat and moisture 60 cycles
WRAP-12	NORTHRAP heat and moisture 60 cycles
WRAP-13	Fresh groundwater weathering
WRAP-14	NORTHRAP groundwater weathering
WRAP-15	SOUTHRAP groundwater weathering
WRAP-16	CENTRALRAP groundwater weathering

Microtox® screening was conducted on 3 independent analyses of each sample. Data for WRAP-1 is presented in Figure 22, as the first sample was sent from Columbia along with the other samples shown in that figure. Data for WRAPs 2-16 as well as a fresh blank are shown in Figure 23. In this test, the blank extraction media (a fresh sample) was significantly less toxic than all weathered RAP samples, which reduced light in the Microtox® test to a similar extent as the fresh RAP samples and WRAP 1 sample analyzed previously (Figure 23).Looking at the same samples undergoing different treatments (e.g. comparing bound to unbound, or groundwater weathering to heat and moisture), there do not seem to be clear patterns in alteration of toxicity associated with treatment.
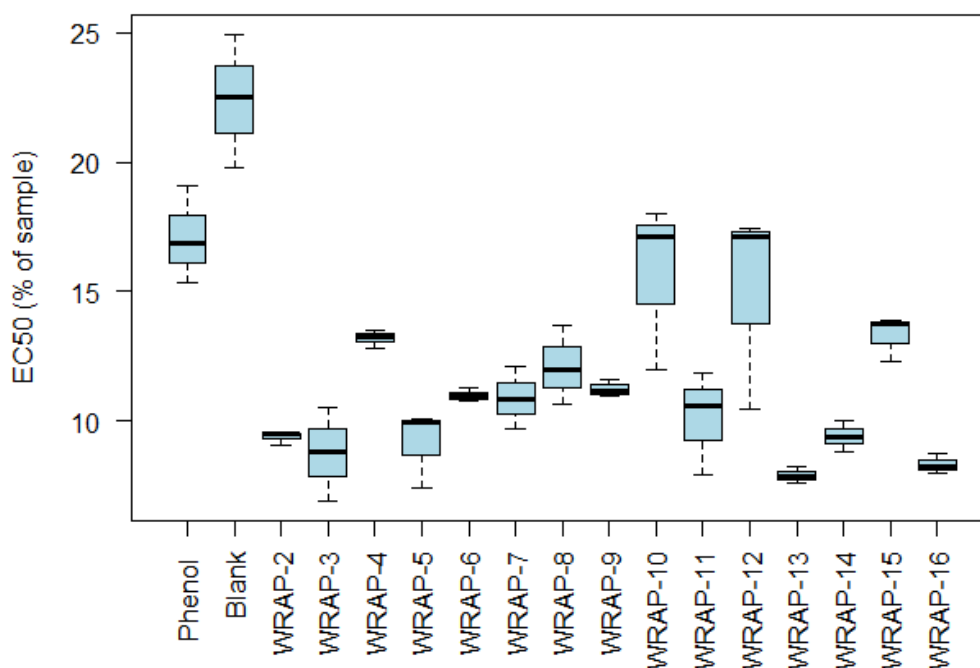
Figure 23: Microtox® EC50 (Dilution of Pure Sample at which there is a 50 percent Reduction in Light – Box Plots Showing Median, 25th and 75 percent Percentile and the Ends of the Whiskers are the 5th and 95th Percentile of the Data with 3 Independent Tests): Data for WRAP-1 is on Previous Figure.

Embryo Toxicity Tests

Once we resolved the issue with the highly toxic ammonium chloride blank, we went on to evaluate toxicity of a select number of the RAP samples to fish embryos. We conducted two types of analyses of RAP samples using embryos of the Japanese medaka Oryzias latipes. We evaluated both survival and DNA damage via the comet assays. We have used similar assays in our laboratory to investigate the toxicity of a wide range of compounds including PAHs (Dasgupta et al. 2015) and more recently the harmful algae Microcystis aeruginosa and its toxin pure microcystin (unpublished data).

One day post fertilization (dpf) embryos were exposed to a 75 percent solution of the RAP samples diluted with ERM. Any appropriate blanks derived from preparation of the RAP samples was also run, along with an ERM blank. Five replicate samples with individual embryos each exposed to 1 mL of solution in a 4 ml glass vial. Survival was monitored daily for up to 21 days. Typical hatching time for medaka is 13 days, but in our hands individuals typically hatch over a period from 12 to 18 days.

Figure 24 presents the cumulative mortality, plotted as the proportion of fish alive at any given time, from 1-21 days post fertilization for the batch RAP samples and the WRAP-1 sample. In all treatments, embryos survived until 11 days, with individuals beginning to die over the next 11 days. Statistical analysis using the Cox proportional hazard models indicated no significant differences among the samples. All embryos in the ERM control treatment survived until Day 18, so we chose this as a good benchmark against which to compare the different treatments. Average mortality (and survival) observed between

the different groups at Day 18 is shown in Table 21, with Day 18 indicated by a dotted vertical line on this and all subsequent mortality graphs. Unfortunately the extraction fluid was still toxic to embryos, again compromising our ability to evaluate additional toxicity due to RAP materials. However, based on average mortality at Day 18, apart from the Blank, which had the lowest survival, Fresh was most toxic, followed by CENTRALRAP and WRAP-1. SOUTHRAP seemed to have no toxicity associated with it (the curve for SOUTHRAP is obscured by the other treatments and is not visible in this plot, but SOUTHRAP treatment only had 1 mortality event at day 20).

Table 21: Mortality at Day 18 for First Medaka Embryos Survival Tests.

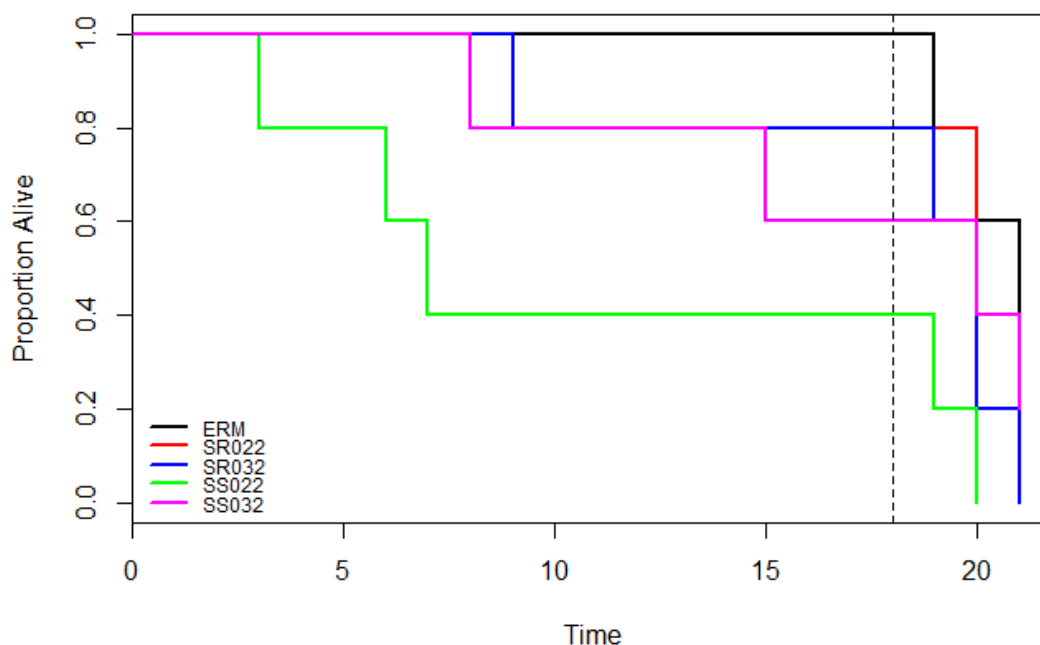| Sample	percent	percent
ERM	100	0
Blank	40	60
SOUTHRAP	100	0
CENTRALRAP	80	20
Fresh	60	40
NORTHRAP	100	0
W-RAP1	80	20
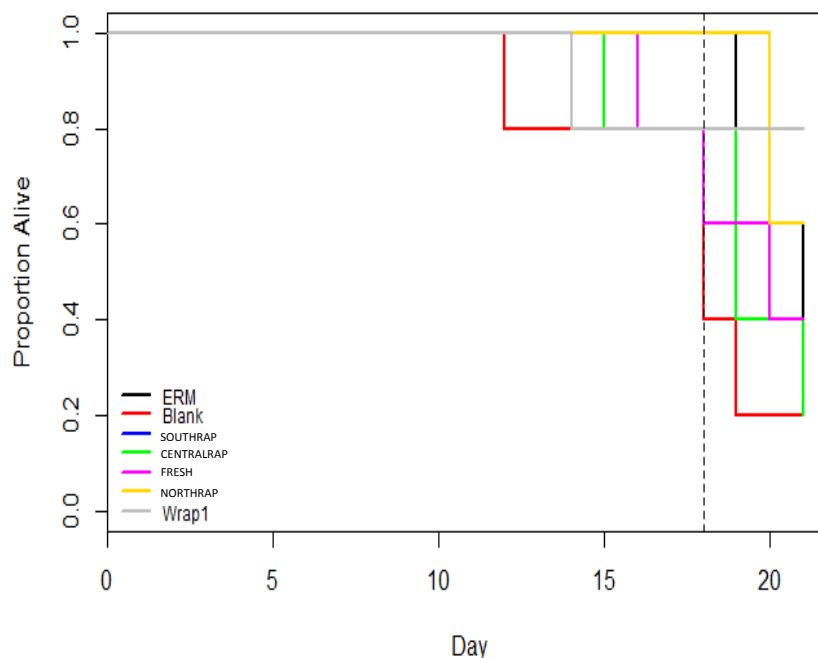
Figure 24: Cumulative Mortality of Early Life Stage (ELS) Medaka Exposed to Various RAP Samples: Dotted Line Indicates Day 18.

In the first experiment we evaluated survival of medaka embryos exposed column flow through experiment soil blank samples (S-R-02-1, S-S-02-1, S-R-03-1, S-S-03-1). In the second experiment we evaluated survival of medaka embryos exposed column flow

through experiment soil blank samples (S-R-02-2, S-S-02-2, S-R-03-2, S-S-03-2), These samples represent water collected after the RAP column (S-R) or also after then flowing through the soil column (S-S). The cumulative mortality curve for these samples tested with ERM is shown in Figure 25. In this case the Cox proportional hazard model identified samples S-S-022 (the first sample exiting from the sediment column) as having significantly higher mortality than the rest of the samples (p=0.0119). Although no statistically significant differences were detected between the other samples (p>0.05), it can be seen that the first samples appeared to be more toxic than the second samples, and that solutions exiting the RAP column were less toxic than the samples exiting the soil column, with all column samples appearing to exert greater mortality than the ERM control.

A surprising finding with the embryo column tests was that the sample showing the greatest toxicity S-S-022 also had some evidence of fungal infection. As is discussed below, soil samples seemed to be a source of infection that was also associated with toxicity in more than one experiment, complicating analysis of the results.
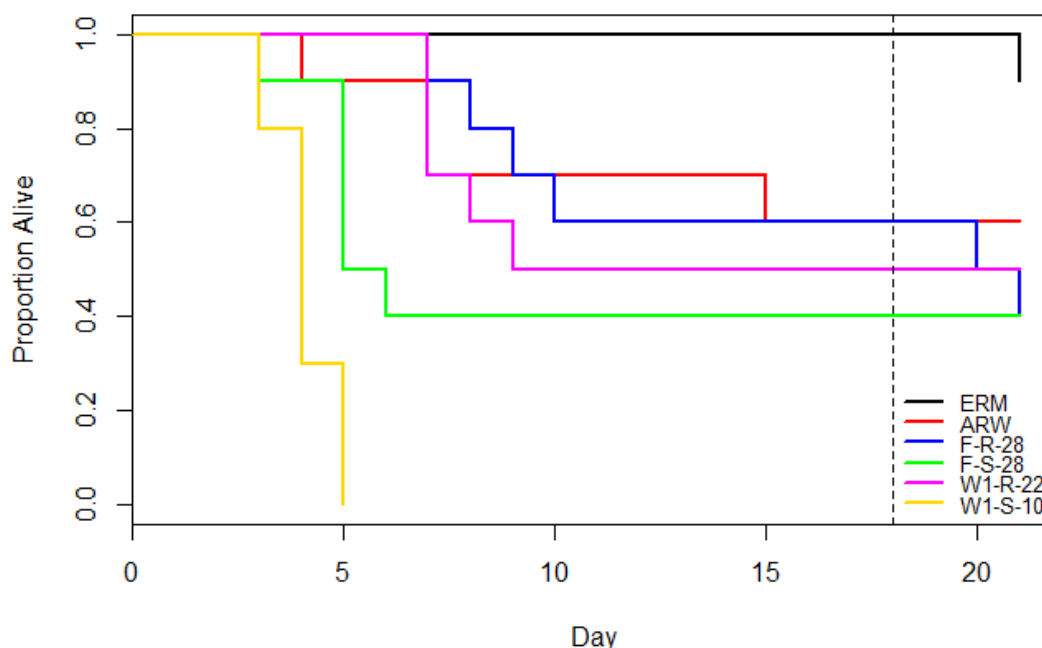

Figure 25: Cumulative Mortality of Medaka Embryos Exposed to Various Column Flow-Through Samples: Dotted Line Indicates Day 18.

Table 22: Mortality at Day 18 Among the Column Experiments Samples.

Sample	percent	percent
ERM	100	0
S-R-02-1	80	20
S-S-02-1	40	60
S-R-03-1	80	20
S-S-03-1	60	40

Further experiments with medaka embryos were guided by chemical analysis data obtained from Columbia University. Based on their recommendation we focused further work on samples from the column experiments (F-R-28, F-S-28, W1-R-22, W1-S-10 - fresh RAP and weathered fresh RAP column samples). – Figure 26), but for completeness we also evaluated select of weathered RAP samples (WRAP5, WRAP10, WRAP13 and WRAP 16 – Figure 27) and appropriate blanks (artificial rainwater (ARW) and Blank extraction solution, respectively) as well. As is indicated in Table 22, WRAP 5 and 16 were the compacted QUV weathered and groundwater weathered samples respectively for CENTRALRAP, and the WRAP 10 and 13 were the heat and moisture weathering and groundwater weathering sample samples respectively for Fresh (made from asphalt material not previously used in a roadway). The high priority samples were also all derived from Fresh material, with F-R-28 being Fresh column eluent, F-S-28 being Fresh soil column eluent, W1-R-22 being Fresh compacted QUV weathered RAP column eluent, and W1-S-10 being the Fresh compacted QUV weathered sample soil column eluent.

Survival data are shown in Figure 26 and Figure 27 with survival on Day 18 summarized in Table 23. Survival was low in all the column experiment samples (both SR and SS), with the soil column samples (F-S-28 and W1-S-10) causing a statistically significant increase in mortality relative to fish exposed to the control (ERM) media (using a Cox proportional hazards model). However, once again many of the embryos exposed to the soil columns also had evidence of fungal infection, once again compromising the results of the experiment.
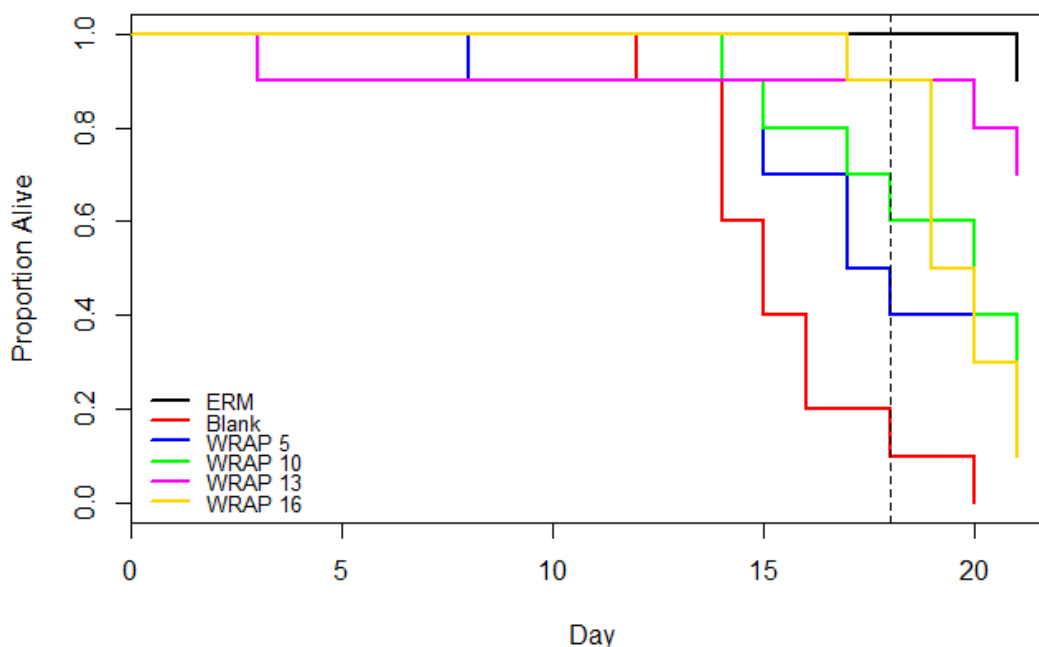

Figure 26: Cumulative Mortality of Early Life Stage (ELS) Medaka Exposed to Column Flow Through Experiment Samples: Dotted line indicates Day 18.

Fortunately, fungal infection was not evident in the embryos exposed to the weathered RAP samples. All appeared to increase mortality in the embryos, but the Cox proportional hazards model identified only WRAP 5, WRAP 10, and WRAP 16 treatments as significantly increasing mortality relative to control fish. Note even though we modified the extraction fluid used with the WRAP samples to minimize toxicity in the Microtox® test, it still elicited significant mortality in the fish embryo bioassay, once again compromising our ability to attribute mortality observed solely to the material present in the RAP or WRAP material. This result was observed in more than one independent embryo test, so we feel the finding is robust.

Both Microtox® and medaka tests indicate the weathering do not lead to changes in toxicity, which is consistent with the similar metals levels in weathered and unweathered samples.

Figure 27: Cumulative Mortality of Early Life Stage (ELS) Medaka Exposed to Select Weathered RAP Samples: Dotted Line Indicates Day 18.

Comet Assay
Our second mode of analysis in embryo tests was the comet assay which quantifies single strand breaks in DNA. Two comet assay experiments were conducted, both focusing on the high priority column RAP samples.

In the first preliminary experiment, Medaka embryos were incubated in 3 groups of 5 individuals at 75 percent sample dilutions. Samples included the 4 priority samples (W1-R-22, W1-S-10, F-R-28, F-S-28) and an ERM control. Fish were exposed for 7 days before samples were processed for the Comet assay (see Dasgupta et al., 2014 for method details). Preliminary results (Figure 28) indicated that only the W1-S-10 sample

had significantly greater DNA damage than observed in response to the ERM control. Other samples may have also caused DNA effects, but survival was not sufficiently high enough to evaluate all samples.

Table 23: Percent Mortality by 18 Days Post Fertilization

Treatment	percent	percent
ERM	100	0
ARW	60	40
F-R-28	60	40
F-S-28	40	60
W1-R-22	50	50
W1-S-10	0	100
Blank	10	90
WRAP5	40	60
WRAP10	60	40
WRAP13	90	10
WRAP16	90	10
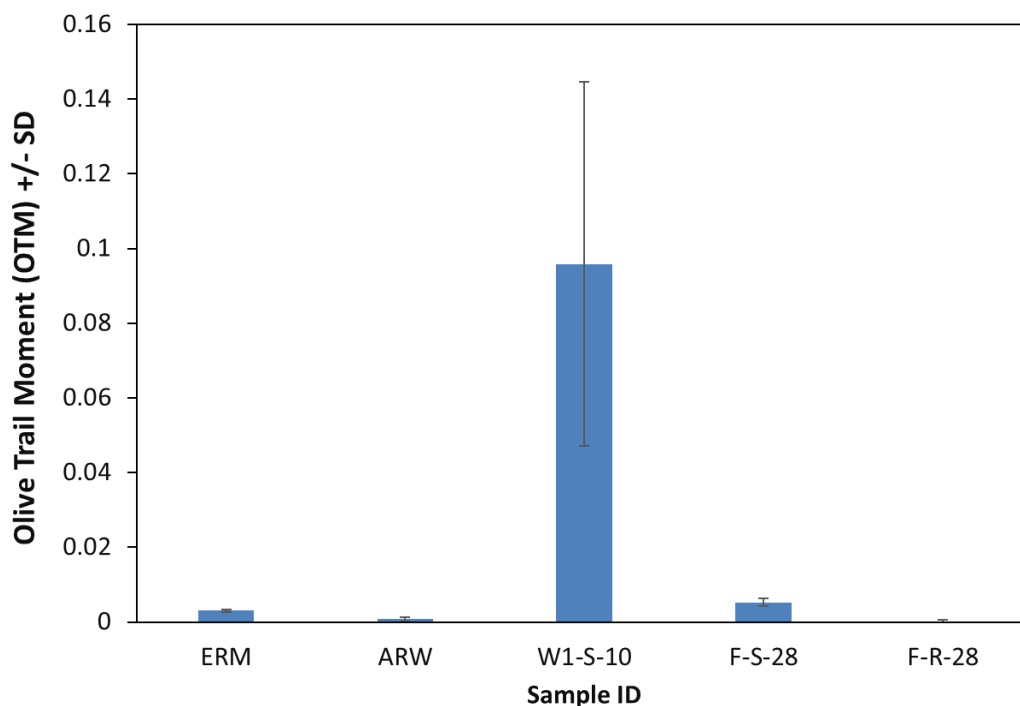
Figure 28: Olive Tail Moment (OTM) as a Measure of DNA Damage from First Comet Assay Experiment.

Based on these results and the chemistry data provided by Columbia University (Dr. Yan's Lab), we completed a second experiment comparing the W1-S-10 sample and W1-R-22, the sample collected from the RAP column prior to passing the soil control, and ARW as a vehicle control. In order to put the results from these samples in perspective, we also ran two PAHs (acenaphthene (ACENAPH) and benzo[a]pyrene

(BAP)) at a concentration of 10 µg/L. Previous work in our laboratory had demonstrated the both these PAHs can cause DNA damage in this assay (Dasgupta et al. 2015).

The results of this second experiment are presented in Figure 29. Note, based on results from the first comet assay experiment, we also modified electrophoresis conditions to improve run parameters in this second assay. This is why the magnitude of the responses is larger in Figure 29 than in Figure 28. A one-way ANOVA identified sample treatment as a significant factor in DNA damage ($F_{4,10} = 26.18$, $p=2.8 \times 10^{-6}$). Although both the RAP column and RAP sediment samples and BAP appeared to increase DNA damage, a post hoc Tukey's test run to make pairwise comparisons showed that only ACENAPH treatment was significantly different from any other treatment. These data show that RAP treatment did not lead to significant increases in DNA damage, particularly in comparison to a known mutagen such as acennaphthalene. Additionally, they show that passage through a soil column does not alter the DNA damaging potential of the sample. During the assay, survival was high (95-100 percent survival for all treatments – much higher than equivalent periods in previously run survival assays) and there were only minor instances of fungal growth in this case, so we consider the results of this experiment to be more robust.
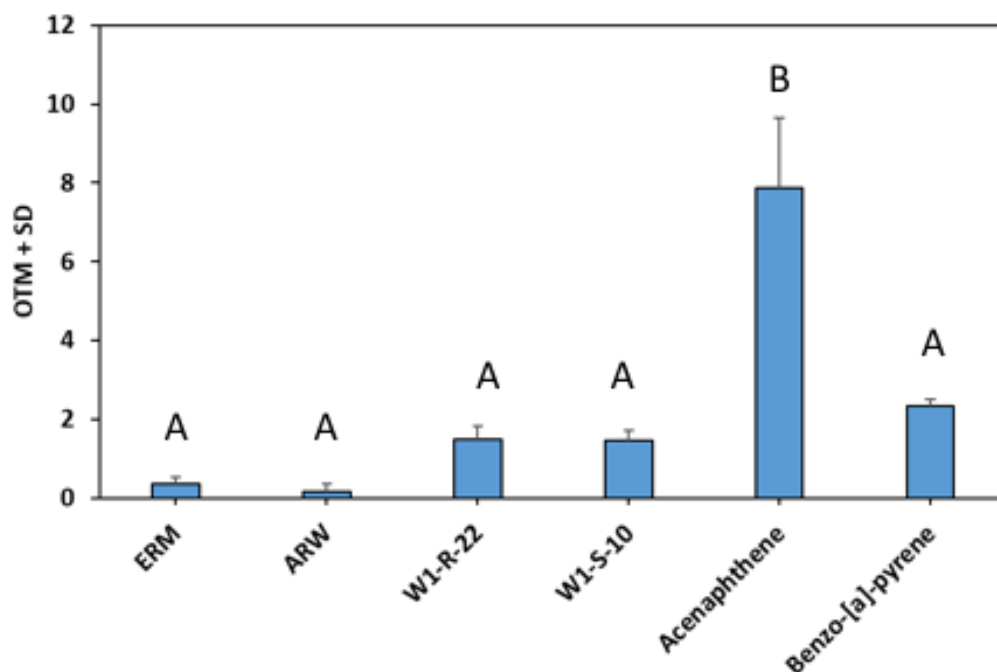
Figure 29: Olive Tail Moment (OTM) as a Measure of DNA Damage in Final Comet Assay Experiment: Different Letters Denote Significant Difference between Treatments.

Summary of Toxicity Assessment
Overall, the results of this assessment failed to quantify significant toxicity associated with aqueous solutions emanating from fresh or weathered RAP material. Of the samples analyzed, the only ones showing any indication of increased toxicity across the

different tests were the samples derived from the soil column experiments. However, results should be interpreted with caution as toxicity associated with the extraction fluid used with the batch samples, even after modification, was toxic in and of itself in both the Microtox® and embryo assays, possibly obscuring minor toxicity truly associated with the RAP materials. Although we did not detect significant toxicity, it is possible that if these examples had been extracted with a fluid without measurable toxicity, that subtle increases in toxicity due to some of the RAP materials may have been detected. A less toxic eluent solution should be found to address this problem. Furthermore, fungal contamination issues resulting from the RAP sediment column materials also appeared to influence toxicity resulting from soil column exposures. Given the scope of work in this study, it was not possible to separate these two effects. Due to the confounding effects of acidic solutions used to extract RAP material, a better approach to really assessing toxicity would be to collect natural elutrates from an in-place RAP environmental placement. This could be accomplished through analysis of test wells placed to capture ground water percolating through RAP placements. Due to the potential toxicity of road run-off materials, or other soils, care will need to be taken to obtain appropriate reference samples without RAP for comparison.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary and Conclusions

This study was initiated with the goal of investigating the environmental impacts of Reclaimed Asphalt Pavement (RAP). The RAP considered in this study included un-aged (or un-weathered) and weathered (aged) RAP materials. The study also involved exploring potential engineering solutions through which RAP materials can be used in an unbound form while also meeting federal and state environmental standards and guidelines. To fulfill these goals, three RAP materials were obtained from northern NJ, central NJ, and southern NJ, denoted as NORTHRAP, CENTRALRAP, and SOUTHRAP, respectively. In addition, the plant in northern NJ provided fresh Hot Mix Asphalt (HMA) loose mix materials (denoted as Fresh with 0 percent RAP materials), which has not been exposed to vehicle traffic or natural weathering.

The collected RAP materials underwent four different types of weathering processes in an environmental chamber; subjecting the samples to: ultra violet (UV) and precipitation weathering on bounded RAP (i.e. Superpave Gyratory compacted (SGC) RAP samples), UV and precipitation weathering on compacted RAP, weathering by heat and moisture cycles, and groundwater leaching. Batch experiments were also conducted to quantify the amount of metals and polycyclic aromatic hydrocarbons (PAHs) released from both un-weathered and their weathered counterpart RAP materials.

Based on the result of the batch experiments, additional two-column experiments were conducted on the RAP materials that had the highest lead and PAHs leaching from it (i.e., NORTHRAP) to investigate the release of metals and PAHs from RAP samples and the attenuation effect of soil on pollutants potentially eluted from the RAP materials. In addition, air inhalation experiments were conducted on NORTHRAP materials. Furthermore, the study involved a screening assessment of the toxicity of RAP materials using a Microtox® Assay, and further analysis of select materials using fish embryo tests where mortality and DNA damage using the comet assay were evaluated in embryos exposed to RAP and column experiment leachates.

Based on the tests conducted and the subsequent statistical analyses performed as part of this study, the following conclusions were drawn:

- Weathering, especially UV light, increased the oxygen levels in RAP. Weathering experiments showed that weight percentage of oxygen (WPO) is linearly related with carbonyl area (R^2 values > 0.95), and can be used as an aging index. Additionally, the effects of condensation and moisture on the UV aging were evaluated by comparing the change in WPO caused by UV radiation during the continuous UV aging and UV/Heat/Moisture aging tests. It was found that the increase of WPO caused by the UV radiation during the UV/Heat/Moisture aging tests was lower than that during the continuous UV aging tests. This indicates that condensation and moisture will effectively reduce the UV aging rate.
- Acidic leaching (e.g., in landfills where organic materials decompose creating an acidic environment) can lead to elution of lead (Pb) at a level higher than Maximum Contaminant Levels (MCLs). RAP batch extraction experiments demonstrated that levels of most metals including Arsenic (As), Barium (Ba), and Uranium (U) in

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leachate are below EPA drinking water MCL. However, the same experiments showed that lead (Pb) in NORTHRAP and its weathered products exceeded or were close to the MCL of 15 ppb. This might be attributed to the historical usage of tetraethyl lead and white paint on the road (in northern NJ close to New York City). Levels of Fe and Mn are higher than secondary MCLs; possibly due to increased dissolution of minerals under acidic condition.

- Leaching of LMW PAHs from RAP under acidic conditions (e.g., landfills) can be at a level of concern. Though the leaching processes mobilize on average less than 1 percent of these PAH compounds in the RAP materials investigated in this study. Levels of certain compounds such as benz[a]anthracene in water leachate from batch experiments were higher than their EPA guidelines.

- NJ rainwater elutes negligible metals, indicating RAP can be used as unbound aggregates in surface, base, and subbase (except landfills). Column elution experiments showed that the concentrations for major or trace elements were below the US EPA's primary drinking water standards. These results are contradictory to those obtained from the batch experiments in the case of weathered and un-weathered NORTHRAP. This is most likely due to enhanced leaching provided by the acidic solution used in the batch extraction samples, as compared to the more neutral NJ's rainwater solution used in the column experiments.

- Contaminated soil is a source for toxic elements (e.g., Pb and U) and PAHs, thus soil testing for metal and PAHs is necessary before usage. Testing of samples collected at various times during column elution experiments (i.e., time-series samples) showed that the natural NJ soil, utilized in these experiments, had significantly higher levels of Ca, K, Mg, and S (major elements) than the evaluated RAP materials. The rate at which these major elements leached out of both materials (i.e., RAP and NJ soil) was relatively fast, with the majority of the leachable part getting into solution in <1 to 2 days. In addition, tests on time-series samples collected from column elution experiments showed that NJ's natural soil was the main source for trace elements leaching out of the experiment including Al, As, Ba, Cu, Fe, Mo, P, Pb, U, and Zn. Testing results also showed that Low Molecular Weight (LMW) PAHs were originated mainly from NJ's natural soil.

- Mn and Ni can be leached out from RAP by rainwater, but attenuated by soil. From the RAP materials, these experiments showed that Mn and Ni were the main trace elements leaching out; however, these elements were attenuated by the soil columns.

- Chemical analysis of weathered RAP materials (in column elution experiments) showed that PAHs, including fluoranthene; pyrene; BaA; and chrysene, can leach out from weathered RAP. However, the concentrations of these PAHs were significantly reduced (reached baseline levels) after the soil column as they were attenuated by the soil.

- Based on air inhalation chamber experiments, it was found that RAP will not emit significant amounts of $PM_{2.5}$ and Volatile Organic Compounds (VOCs). This was expected because asphalt is the residue left over from petroleum refining process and almost all VOCs are typically collected during this process. It is noted, however, that toluene was emitted from un-weathered NORTHRAP during the air inhalation experiments. The level of toluene in the air was about 0.8 mg/m^3, well below the

EPA short-term standard, 37 mg/m^3, for general public (6 hours) (https://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=512650). The same compound was removed or decomposed during the weathering process (i.e., was not identified in weathered NORTHRAP samples). It is believed that the source of toluene in NORTHRAP is due to road pollutants during the service of RAP as a pavement.

- Microtox® screening analysis indicated that both weathered and un-weathered RAP samples were more toxic than the blank extraction material, although did not differentiate among them. However, these results must be viewed with some caution as the test appeared to be very sensitive to the acidic solution used in the RAP extractions even after readjustment of pH prior to testing. The column samples eluted with artificial rainwater were much less toxic, not even eliciting a measurable reduction in light from the bacteria in the Microtox® assay.
- Similarly, toxicity testing evaluating survival of Japanese Medaka fish embryos indicated that none of the batch samples was more toxic than the blank material used to extract them when mortality was compared. However, even the modified blank was toxic to the Medaka embryos as compared to embryo rearing medium (ERM). Analysis of weathered RAP samples indicated that some also induced toxicity in Medaka embryos. However, the most toxic treatment was the blank solution used to extract the weathered RAP.
- There was some evidence of toxicity associated with some of the column extracts, particularly those associated with the soil columns. However, some of these experiments were compromised by the appearance of a toxic fungal growth that was present in samples from the soil columns.
- Further analysis of the weathered RAP (WRAP) samples both before and after passing through the soil column indicated that both induced some level of DNA damage, but the effect was not significantly different from that observed in blank and control solutions, and was statistically smaller than that observed from a positive control, ancenaphthylene, a PAH found in the WRAP material in this sample. This test provides further evidence that these elutriates are not of toxicological concern to a sensitive aquatic life stage such as fish embryos.

Recommendations

Based on the conclusions of this study, the following recommendations are provided for consideration by the New Jersey Department of Transportation (NJDOT) and the New Jersey Department of Environmental Protection (NJDEP):

1) RAP may be used as an unbound material in all environments except those which are highly acidic (pH ≤ 4) (such as, but not limited to, mines with sulfur-containing minerals or landfills where other materials may decompose creating an acidic environment).

2) Acceptable, beneficial, uses of unbound RAP materials may include but are not limited to, using the unbound RAP as surface materials for parking lots, farm roads, or pathways; for quarry reclamation; as non-vegetative cover underneath guiderails; and mixed with other materials for subbase or base materials; in addition to the current uses in hot mix asphalt applications.

3) Due to the inconsistent pollutant levels found among the three RAP stockpiles evaluated in this study, it is also recommended, as a precautionary measure, to determine the releasable levels of metals and PAHs for RAP stockpiles before using RAP in highly acidic environments; by extracting leachate samples using batch experiments and measuring pollutants (PAHs and metals) levels.
   a. If the releasable levels of pollutants are below US EPA drinking water standards, unbound RAP can be used in acidic environments.
   b. If the releasable levels of metals and PAHs exceed US EPA drinking water standards, it is recommended to ensure that there is a soil layer between the RAP and the groundwater aquifer. It is important to note; however, that it was beyond the scope of this study to determine the type and thickness of the soil layer that is appropriate for the use of RAP.

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