Pollutant Releases during the Initial Aging of Asphaltic Pavements

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Sree Usha Veeravalli

Civil, Construction and Environmental Engineering,

University of Alabama, Tuscaloosa

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Abstract

Prior studies (such as those conducted by the USGS) have shown that PAH releases associated with coal-tar sealants applied to asphaltic pavements are significant toxicant sources to receiving water sediments. Others (such as conducted by NCHRP) have examined highway construction materials as pollutant sources. This project examined the role of freshly constructed asphaltic materials as pollutant sources during the initial exposure period, when releases of materials are expected to be most significant. With the aging of the asphalt, the pavement undergoes physical and chemical changes which are expected to affect the quality of the runoff.

Three square pavement slabs were examined during this project. Two (a hot-mix asphalt pavement and a warm-mix asphalt pavement) were freshly constructed, while the third is a two year old pavement which was freshly coated with asphalt sealant. The test slabs have a surface area of 0.25 m^2 and are 5 cm thick. They were prepared for this project by the National Center for Asphalt Technology (NCAT), at Auburn University, in Auburn, AL. The pavement slabs were set up outdoors in mostly full sun and exposed to rains. They were therefore aged under natural conditions. During the project period, a 0.5in rain (using prior collected roof runoff) was simulated on each of the pavement slabs for each controlled sampling. The resulting runoff was collected once every two weeks for a period of six months and analyzed for PAHs, heavy metals (Zn, Cd, Cr, Pb, and Cu), and nutrients (total phosphorous, total nitrogen, nitrate plus nitrite, ammonia, and COD). The samples were also tested for toxicity using the Microtox screening procedure which makes use of bioluminescent bacteria, *Vibrio Fischeri*. The presence of anionic detergents in the samples was also measured using MBAS kits.

Chapter 1: Introduction and Literature Review

1. Introduction. Asphalt is a widely used paving material, because of its ability to act as binder and hold together stone and gravel (aggregate) and due to its waterproofing properties. Its wide use is also attributed to its ability to meet the heavy traffic loads on busy roads. Asphalt is a viscoelastic material, a crude oil derivative and is obtained by controlled distillation of crude oil where the lighter fractions are separated out and the heavy bitumen residue (the asphalt) is left behind (Robinson, H.L, 2005).

1.1 Asphalt Composition. Asphalt is a high molecular weight compound with complex structure and properties. Its primary composition is hydrocarbons, with many other compounds, including calcium, iron, manganese, nitrogen, oxygen, sulfur and vanadium. The composition of asphalt varies with the source of the Crude oil (Robinson, H.L, 2005). However, most bitumen contains about:

- Carbon 82-88%
- Hydrogen 8-11%
- Sulfur 0-6%
- Oxygen 0-1.5%
- Nitrogen 0-1%

Other than the source of the crude oil, the manufacturing process and aging in service also leads to different compositions of asphalt (Shell Bitumen Handbook, 2003). .

In general, asphalt chemical composition is broadly classified in apshaltenes and maltenes, with the maltenes further divided into saturates aromatics and resins. However, the four groups are not well defined and tend to overlap (Shell Bitumen Handbook, 2003). Asphalt chemistry is approximately determined using a saturates-aromatics-resins-asphaltenes (SARA) analysis to compare composition (Robinson, H.L, 2005).

According to Mack et al., asphalt consists of five groups of compounds:

- Oily Constituents – These are primarily hydrocarbons, viscous and fluorescent in nature with a high percentage of sulfur and oxygen.
- Asphaltic Resins – These are intermediate products formed during the formation of asphaltenes from oil constituents due to oxidation with air. The molecular weight is always slightly higher than that of the oily constituents.
- Asphaltenes – These are formed when sufur or oxygen acts on asphaltic resins. They have a black or dark brown powder-like texture and tend to swell on heating. They are soluble in benzene, chloroform, carbon tetrachloride, while being insoluble in alcohol, ether and petroleum ether.
- Carbenes and Carboids – These compounds constitute only a small percentage of the asphalt. Carbenes are soluble in only carbon bisulphide, while carboids are insoluble in all solvents.
- Asphaltic acids and their Anhyrides – These are present in small amounts in petroleum derived asphalt, but are present in higher amounts in natural asphalt (12%). Asphaltic acids are brownish black in color with tar-like texture and tend to form their respective anhydrides on heating (Charles Mark, *Colloidal Chemistry of Asphalt*).

1.2 Manufacturing of Asphalt

About 1,500 sources of crude oil are available worldwide, mainly from the USA, Mexico, South America, the Caribbean, the Middle East and the old Soviet states, although all are not suitable for the production of bitumen. Based on the different crude oil sources, different physical and chemical properties are attributed to asphalt. Refining of crude oil involves heating the crude oil to a temperature of 350° to 380° in a furnace before sending the liquid and vapor components of the crude oil into a distillation tower. Once in the distillation tower, the lighter fractions of the crude oil are in the vapor phase and rise in the tower through holes in trays placed in the tower. As the lighter fractions rise, they lose their heat energy and condense when the temperature is just below its boiling point and are drawn away by pipes. The lighter fractions separating out include propane, butane, naptha, and kerosene. The heavier factions at the bottom of the column are subjected to further distillation under higher pressure to obtain short residue, which can then be used in the manufacture of different grades of bitumen. The short residue is then subjected to a blowing process where oxidation, dehydrogenation and polymerization of asphaltenes and

formation of additional asphaltenes from maltenes takes place, and bitumen suitable for road construction is formed (*Shell Bitumen Handbook*, 2003)..

1.3 Asphalt-Aggregate Interaction

Asphalt-aggregate interactions are important to ensure that thesphalt binds the aggregate to maintain the integrity of the mixture for road bed construction. The ratio of asphalt to aggregate in a mix is typically 5-6 wt% of asphalt to 94-95 wt% of aggregate. The aggregate present varies in size ranging from ¾ inch fractions to fines that are in the 200 mesh range.

Asphalt coats each of the aggregate particles and also provides cohesion between the aggregate particles to maintain the integrity of the mixture. Asphalt can also enter the pores and crevices of the aggregate. Aggregates have active sites for binding asphalt molecules at different levels. Their surface is frequently either fully charged or partially charged. Asphalt, being a mixture of hydrocarbons that is organomettalic (contains Nickel, Vanadium and Iron) and polar in nature, gets attracted to the active sites on the aggregate surface. The bonds formed may include hydrostatic, electrostatic or Vander Waal's forces. According to the SHRP report, autoradiographic experiments with labeled molecules having a similar structure as asphalt confirmed the presence of active sites on the aggregates (SHRC, 1993).

The asphalt adhering to, and between, the aggregate must remain in contact with the aggregate under all environmental condition, serving a cohesive role to maintain the integrity of the system. However, this integrity of the cohesion and adhesion of the asphalt-aggregate is damaged in the presence of moisture. In the presence of moisture, the pH of the local environment may substantially change and this pH value depends on whether the aggregates are siliceous or calcareous. The acidity and basicity of the asphaltic components can influence the effect of pH under such environmental conditions. It is recommended that asphalt with amphoteric characteristics be used, since amphoteric species can either assume an acidic or basic character and the amphoterics may bond in either acidic or basic environments (SHRP, 1993)

Moisture damage does not occur as one mechanism, a list of theories that explain the mechanisms of moisture damage are given in the following table.

Mechanisms explaining moisture damage of asphalt-aggregate interaction	
Theory	Principle
Contact Angle	When the contact angle of water is less than that of the asphalt molecules, asphalt is displaced.
Interfacial Energy or Molecular Orientation	When the surface energy of water molecule is than asphalt molecules, asphalt is displaced.
Chemical Reaction Theory	pH changes around the aggregates results in the buildup of negative charge and electrical double layer on the aggregate and asphalt layer.
Pore Pressure	Asphalt may rupture when the pore pressure of entrapped water molecules increases with the densification of the mixture with traffic.
Spontaneous Emulsification	Inverted emulsion can result in the loss of adhesion between the asphalt and aggregate.

Source: Apated from Dong-Woo Cho and Kyoungchul Kim et al., 2009.

1.4 Asphalt Aging

Peterson (1984) has listed three major factors causing hardening of asphalt in asphalt mixtures:

1) Loss of oily components by volatility or absorption.

2) Changes in composition by reaction with atmospheric oxygen.

3) Molecular structuring that produces thixotropic effects (steric hardening).

Asphalt ages (oxidizes) in the presence of air and oxidation leads to bitumen hardening and embrittlement of the pavement. This leads to asphalt failure due to adhesion failure with aggregate and cracking. However, asphalt hardening in the base layers is thought to be helpful due to improved stiffness which contributes to improved performance. The factors that contribute to the aging of the asphalt are the composition of the asphalt mixture, the binder film thickness, the air void content of the asphalt and the composition of the asphalt itself. Air voids are particularly important because in dense asphalt mixtures, air is unable to penetrate easily, and the rate of oxidation will be much slower compared to an open graded (a lower density, porous material – basically less dense due to the aggregate grading) material (Robinson, H.L, 2005).

Oxidative aging of asphalt leads to the formation of ketones, carboxylic acids and sulfoxides. According to SHRP (1993), the oxidative aging products produced were found to be uniform and dependent on the amount of sulfur present in the asphalt. The chemical composition of the asphalt and the composition of the aggregate were found to have little or no influence on the oxidative products being formed (SHRP report, 1993).

Infrared spectrometric studies on aged asphalt pavements also found that the principle components formed as a result of aging are Carbonyl groups, Sulfoxides and Sulfones. The embrittlement and increased viscosity of the pavement is a result of formation of highly polar groups and functional groups that contain Oxygen that strongly interact (Usmani M. Arthur, 1997).

1.5 Laboratory Aging of Asphalt:

Under natural conditions, short term aging occurs during the construction phase, primarily dominated by volatilization of an asphalt pavement. It begins at the mixing plant and ends when the compacted pavement has cooled. Long-term aging occurs during the service life of the pavement due to oxidation. Both factors cause an increase in viscosity of the asphalt and a consequent stiffening of the mixture.

These conditions are studied in an asphalt test laboratory by the following means,

1.5.1 Short- term aging:

- The SHRP, recommended procedure for short-term aging tests is to age a loose mixture (to simulate pre- compaction phase) in a forced-draft oven for 4 h at 135°C (275°F). The aging achieved with the extended mixing method is similar to the aging achieved using this method, however, the advantage of this approach over extended mixing is that several trays of material can be aged at the same time.
- The extended mixing test method may also be used where a modified rolling thin film oven (RTFO) is used. An attachment to the RTFO drum enables loose mixtures to be rolled, thus extending the mixing time. This method was found to produce more uniform aging in the mix than oven aging.

1.5.2 Long-term aging:

- The SHRP, recommended procedure for long-term aging tests is to precondition compacted samples for two days at 60°C (140°F). The compacted mixture specimens are then aged in a forced-draft oven for 5 days at 85°C (185°F). This procedure is best suited for dense-graded mixtures. A temperature of 100°C (212°F) for two days may also be used, however; such a high temperature may cause damage to the specimens.
- The other long-term aging test method includes triaxial cell aging and requires conditioning of the sample, followed by passing oxygen or air through the sample. A flow rate of 0.11 cubic m per h (4 cubic ft per h) is used, at a pressure of about 345 kPa (50 psi) and 85°C (185°F) temperature. The low-pressure oxidation (triaxial cell) technique is recommended for long-term aging of open-graded mixtures or dense-graded mixtures using soft grades of asphalt. A temperature of 85°C (185°F) is recommended for a period of five days.

A study conducted by the NCHRP (2001) to observe the toxicity of runoff from construction materials involved the use of a loose mixture of open graded asphalt concrete with MSWIBA (Municipal solid waste incinerated bottom ash) and was aged in a forced draft oven for 4hrs at 135°C for short term aging, and for 5 days at 85°C for long term aging, as recommended by the SHRP protocol. Long term oven aging of 5 days is representative of a sample of 10 years old. .

1.6 Summary of Asphalt Characteristics and Aging

Asphalt has a complex structure and rheological properties that gradually change with time. The effect of aging is more rapid in the presence of light and air. Oxidation on the exposed surface of the pavement causes aging and the extent of aging is proportional to the surface area exposed (the surface and voids) to the atmosphere and the rate of diffusion of air into the pavement. Therefore, during the service of the pavement, asphalt undergoes aging forming insoluble, condensation products as a result of the oxidation and the loss of volatile compounds from the pavement. As a result of these changes, the composition and the concentration of contaminants that leaches into the runoff is likely to vary with aging (Pal Zakar, 1996).

When pavements are aged under laboratory conditions, the runoff profile may vary depending on the aging method used. For instance, in the NCHRP study when leachate samples were collected at regular intervals from specimens' under-going long term aging tests, no change was observed in either the toxicity or the chemistry of the leachate during the aging process. However, when the long term aging process was modified and oxidation was provided (10 atms in a pressure aging vessel (PAV) system at 85°C for 30 days), a significant drop in the algal toxicity with time was observed (NCHRP, 2001).

Chapter 2 : Contamination of Runoff from Asphalt Surfaces

With increasing urbanization, there has been a corresponding increase in the amounts of paved areas such as parking lots, roads and other impervious surfaces which has impacted stormwater quality and quantity. Studies in the past have shown that impervious surfaces have increased pollutant loads and have degraded the stormwater runoff quality more than any other type of land cover in a watershed (Rushton T. Betty, 2001).

According to the NCHRP report, asphalt (AC) and concrete (PCC) roads, and the constituents used in their production, account for the largest volume of construction materials used in the US. Almost 90% of surfaced roads in the US are asphaltic, while 6% (2000 km^2 area) of the surfaced roads are of concrete. During wet weather conditions, the impact of these materials to surface and groundwaters is a major concern. The stormwater runoff from highways include organic toxicants, metals, nutrients and PAHs which leach into the stormwater on contact with the pavement (Azizian F. Mohammad et al., 2003).

The extensive use of additives in AC and PCC mixtures also present potential water quality problems. The additives enhance the properties of AC and PCC by increasing strength, temperature stability, durability, aging etc. The additives include organic salts, detergents, calcium chloride, carbonates, coloring agents, and ammoniacal-copper-zinc-arsenate (ACZA) (Azizian F. Mohammad et al., 2003).

In the study conducted by National Cooperative Highway Research Program in 2001 on the impact of construction materials on surface and groundwater, individual components and the aggregates of the pavements were subjected to exposure and aging tests. Testing of individual components may not result in complete insight into the impact they may have on the environment since the assemblage of all components is exposed to the environment. The NCHRP study of individual components did offer relative findings of the toxicity of the chemicals used in pavements. It was found that although the individual components of AC and PCC showed high toxicity levels, this was reduced when incorporated into the complete assemblage. The overall toxicity is much lower when field conditions are considered due to the lower leaching rates and greater dilution under rain conditions in the field.

In 2005, parking lot sealants were identified as another major source of PAHs in Austin, TX runoff. Parking lots with coal tar based sealants were found to contribute 65 times more PAH mass in the runoff compared to unsealed parking lots. The sealing layer on these parking lots tend to wear off by vehicle use, with the crumbled seal coat losses producing up to 2200 mg PAH/kg sediment of 12 PAHs, compared with 27 mg/kg from unsealed parking lots . Sealcoats are applied to asphaltic pavements because they act as a protective coating on the pavement by decreasing ultraviolet ray exposures, weathering, petrochemical losses and degradation from deicing salts (Mahler et al., 2005).

The sealant forms an inert coating on the parking lot surface where it may remain for many years until it begins to wear off, with PAH's released into the environment by the stormwater runoff. Studying the rate at which sealant-derived PAHs enter the environment could improve strategies for controlling PAHs accumulation in urban watersheds. With this aim, a photographic sealant wear study was conducted in Austin by Scoggins et al, in 2009. The rate of wear of the sealant was estimated to be about 7% per year in the drive areas. The rate of wear is dependent on the traffic, the rainfall energy and wind. Another study conducted by Mahler et al. 2005, using an artificial washoff rig with low rainfall energy on a small parking lots ($50m^2$) indicated that the sealant wears of at a rate of about 0.2% per year [16], with no traffic activity.

Two types of sealants are commonly used, coal tar based and the asphalt based, as described below:

(a) **Coal tar based sealant:** This sealant is a shiny, black emulsion applied on asphalt pavements. Its most active compounds are PAHs, containing 3.4% to 20% of PAHs by dry weight. Light rains have shown to transport significant amounts of PAHs from coal tar sealers into nearby water bodies. In a study conducted by Bryer et al. , 2006, coal tar pavement sealers appeared to affect the growth and development of amphibians, at low parts per million concentrations. Although coal tar has been identified as a toxic material, its chemistry is uncertain. However, PAHs are recognized as the most active material in coal tar mixtures. It was originally assumed that the pavement sealant would not be able to desorb the PAHs. However, frogs exposed to coal tar sealant took longer to hatch and were smaller and developmentally behind control frogs at multiple time points of exposure (Bryer J. Pamela et al., 2006).

(b) **Asphalt based sealant:** Following the Mahler et al. study in 2005, the City of Austin in 2005, also studied the direct amounts of PAHs in the sealant products, in scrapings and particulates from the parking lots and found that the profile of the PAHs in the sealant products although similar, showed that the coal tar had a significantly higher percentage of PAHs when compared to asphalt sealants (a maximum of 1,800 ppm total PAHs for asphalt-based and 50,000 ppm for coal-tar based sealants on a dry weight basis). These sealants are advertised as an environmental friendly alternative to coal tar based sealants as they contains lower amounts of PAHs (usually 0.03% to 0.66% of PAHs by dry weight) (Bryer J. Pamela et al., 2006). Other alternatives suggested by USGS in 2006 included concrete or unsealed pavements.

The results of a recent study on the PAH levels in Austin streams, conducted two years after the ban of sealants, showed that the there was no change in the level of the PAHs in the sediments. They concluded that sealants may not have been the principal source of PAHs in the sediments as concluded by the earlier studies. However, PAHs have very long half-lives during natural exposures (several years to decades, as reported by MacKay, et al. 2010) and unless physically removed or scoured, they would remain in the receiving water sediments at high levels for extended periods, even after their sources were removed.

2.1 Transport of PAHs in Runoff

Most PAHs are immobile in soil and groundwater systems. However individual PAHs have different physical and chemical properties such as water solubility, vapor pressure, Henry's Law constants, the octanol-water partitioning coefficient (K_{ow}), and the organic carbon partitioning coefficient (K_{oc}). Based on these properties, the fate and transport of PAHs in the environment can be predicted. As a group, PAHs tend to have relatively low water solubility, low vapor pressure, and low Henry's Law constants, and high K_{ow} and K_{oc} values. The K_{ow} value can provide an indication of the potential for the organic compound to partition from water into lipids and helps give a correlation for bioconcentration in aquatic organisms while the K_{oc} value indicates a compound's potential to bind to organic carbon in soils and sediments (Simon John et al., 2006). As these chemical characteristic imply, PAHs are mostly highly hydrophobic and rapidly bind to sediments in the water column and in stream sediments.

In a study conducted in Cincinnati, OH, 1996, on the sources for PAHs in street and creek sediments, vehicles, along with coke oven use, were found to be the major contributors. In another study from California, diesel vehicle emissions were found to result in ultrafine particulate PAHs discharges, and gasoline vehicle emissions were also related to high molecular weight PAHs in ultrafine particulates (Pitt et al.,2004).

In another study conducted by Krein and Schorer, 2000, the characteristics of PAHs in road runoff was investigated and they found that three-ringed PAHs were found in the fine sand fractions and the six-ringed PAHs were found in the fine-silt fractions (Pitt et al.,2004). PAHs are the most commonly detected organic toxicant in stormwater and is found in higher concentrations from areas having high vehicle use, and 68-97% of the PAHs found are particulate bound (Bathi .Jejal, 2007).

2.2 Transport of Heavy metals in Runoff

Heavy metals are usually found in high levels in stormwater from urban roadways in mostly particulate forms and to a lesser extent, in dissolved forms (Pitt et al., 2004). Since metals do not degrade naturally and also tend to associate with particulates, high receiving water sediment concentrations are common, with resulting detrimental effects to benthic organisms. A roadway runoff study from a busy highway in Cincinnati, OH, showed that Zn and Cd were also largely found in dissolved forms, while Pb was mostly associated with particulates (Sansalone and Buchberger, 1997).

On road surfaces, heavy metals are primarily found to be bound to the road surface dust or other particulates , although they primarily originate from automobile use (tire and break wear and exhaust emissions). During precipitation, the bound metals can be transported off the road surface with the dust, depending on the rainfall energy. Metals can be transported through an urban area in several ways and these are governed by the chemical nature of metals and the surrounding environment, along with wind and traffic-induced turbulence, and rain characteristics. The heavy metal fractions that are soluble tend to be more dangerous to the environment because they are more readily available to plants and animals. In a study conducted in Australia, highway exit-lanes were found to contribute higher Zn and Cu concentrations due to brake pad and tire wear during rapid deceleration. The sources of Al, Co, Fe, Mn and Ni were found to have geological origin, while Zn, Cu and Pb were enhanced due to anthropogenic use,

in a study conducted in Hawaii. Stormwater heavy metals were found to be associated with the sediment extraction method, acid-extractable, reducible, oxidizable, and residual, with Zn and Cu being acid-extractable (Pitt et al., 2004).

2.3. Toxicity of runoff samples

The NCHRP study tested the toxicity of leachate samples from highway construction materials using Selenastrum capricornutum (algae) and Daphnia magna. The alga represents plant species while the Daphnid represents animal species. These organisms were chosen based on their wide geographic availability, sensitivity, feasibility to culture in the laboratory, and availability of standardized protocols for the tests. The NCHRP research showed that construction materials, especially the additives used to incorporate special characteristics to the pavements, were found to be significantly toxic, however the toxicity was reduced when they were incorporated in the pavements. Aluminum was identified as being the key metal causing the algal toxicity. They also concluded that algal toxicity testing was more sensitive than the Daphnia and Microtox screening method for assessing metals and organic chemicals in roadway runoff.

In a toxicity study conducted in Sweden on leachates from road construction materials using Vibrio fischeri and Phaseolus aureus showed that the later were more sensitive to the leachates than the former, since the salinity of the contaminants tends to interfere with the Vibrio fischeri method. They found that in comparison to a road built with conventional method, roads built with municipal solid waste incineration ash (MSWI) released higher concentrations of Al, Cl, Cr, Cu, K, Na, NO2–N, NH4–N, total N, TOC and SO4 however, the release of of Ca, Co, Fe, Mn, Ni, NO3–N and Pb did not differ significantly between the two pavement types. From their study, they concluded that more than one kind of toxicity test may be needed since different species may respond differently to the same environmental sample (Solvita Ore et al., 2007).

The Microtox toxicity test use luminescent bacteria and measures the light intensity before and after its exposure to the sample which gives an insight into the toxicity of the contaminant with the reducing light intensity. Any component present in the sample that interferes with the respiration of the bacteria results in reduced light output. The lower the EC_{50} value, the higher the toxicity. Samples with pH ranges outside 6.3 to 7.8 may not be suitable for the Microtox procedure because samples outside this pH range may be toxic to the bacteria due to the pH and

not a chemical constituent; however, if the natural pH of a sample is outside this range, it is still toxic and the test will indicate this fact. Sample pH is therefore not adjusted since pH may be the factor causing the toxicity (Pitt et al., 2001).

Summary

From the literature review, roads are seen to be a major contributing source for stormwater pollutants, especially for PAH, heavy metals, and some nutrients. However, most of the reported studies focused on identify pollutants in roadway runoff with heavy traffic and on aged roads. Since asphalt composition evolves with time, the objectives of this research project was to study the characteristics of stormwater runoff from the surface of newly laid asphalt pavements for a period of six months under natural environmental conditions, specifically:

- To determine the changes in the concentrations of the contaminants in the stormwater runoff with the short-term aging of asphalt pavements.
- To study the toxicity characteristics of the pavement runoff with the aging of the pavement.
- To study the impact of sealed and unsealed pavements and also unconventional pavements (energy efficient warm mix pavements) on the runoff.

Chapter 3: Description of the Experimental Setup and Analyses

3.1 Experimental Set up and Sampling

Three square pavement slabs were examined during this project. Two (a hot-mix asphalt pavement and a warm-mix asphalt pavement) were freshly constructed to represent unsealed pavement types, while the third was a two year old pavement which was freshly coated with asphalt sealant. The test slabs have a surface area of 0.25 m^2 and are 5 cm thick. They were prepared for this project by the National Center for Asphalt Technology (NCAT), at Auburn University, in Auburn, AL, the preparation method used to prepare the pavement slabs is given in Appendix A. The pavement slabs were set up outdoors in mostly full sun and exposed to rains. They were therefore being aged under natural conditions. During the project period, a 0.5in rain was simulated on each of the pavement slabs and the resulting runoff was being analyzed for pollutants.

The pavements were supported by un-treated wooden boxes and placed on bricks such that they were slightly inclined to allow the sheetflow of the runoff to flow into the sample containers. All three pavements were placed adjacent to each other at about the same inclination to the ground. The water used for simulating the rainfall was from prior collected roof runoff. The roof runoff was repeatedly poured onto the pavement slabs to allow a contact time of 5 minutes and the resulting final runoff collected in the plastic containers were transferred to the sample bottles for further analysis.

The hot mix pavement and the warm mix pavement were 5 days old when the first runoff samples were collected. The 2 year old pavement was coated with driveway asphalt sealant and allowed to dry for 2 days before the first sample was collected. The collected samples were analyzed within the maximum holding time for each of the analysis. The samples were stored in appropriate containers for the different analysis as suggested by *Standard Methods for the Examination of Water and Wastewater (1992)*. The following equipment was brought to the sampling site for sample collection.

- 1 lt amber glass bottles (for PAHs analysis)

- 100 ml Nalgene bottles (for heavy metals, nutrient and detergent analyses)
- 20 ml glass vials (for Microtox analysis)
- Labels for bottles
- Marker pens
- Glass jars (for pouring the roof runoff onto the pavement)
- Trough-like plastic containers (placed near the lower edge of the slabs for collecting the runoff)
- Stop watch

Summary of sampling schedule

Date of Sample collection	Average mean temperature (°F) on day of sampling	Observations
05/30/2010 (asphalt tests started on this date)	75	The runoff was collected from only HMA and WMA pavement slabs. The third pavement was freshly sealed with asphalt driveway sealant. The runoff from the pavements looked clean, free of any sediment.
06/02/2010 (sealant tests started on this date)	87	The runoff from the pavements looked clean, free of any sediment.
06/11/2010	89	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
06/25/2010	91	The runoff from all the three

		pavements was pale yellow but relatively less pale than from the previously collected samples.
07/08/2010	82	The runoff from all the three pavements was cleaner than from the previously collected samples. It was free of soil deposits on the pavements.
07/21/2010	93	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
08/04/2010	93	The runoff from all the three pavements was cleaner than from the previously collected samples. It was free of soil deposits on the pavements.
09/14/2010	88	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
10/19/2010	77	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on the pavement.
11/18/2010	66	The runoff from all the three pavements was pale yellow, with dust and deposited soil particles on

		the pavement.

Samples that were collected after a recent wet period appeared cleaner compared to samples after a dry period.

3.2. Chemical Analysis

The following chemical analyses were performed on the samples. For each set of samples, blanks and standards were also analyzed. HACH methods were used for the nutrient analyses. A DR 2010 spectrophotometer and incubator were used to perform the nutrient analyses using the HACH methods. All the methods are USEPA approved for the measurement of the respective nutrient. All the nutrient and detergent tests were performed within 48 hrs after the collection of the samples.

pH: All the samples were measured for pH soon after they were delivered to the laboratory from the sampling site. An IQ 160 pH meter was used for measuring the pH. Before each set of measurements, the pH meter was calibrated with pH 7 and pH 4 standard solutions, provided by the manufacturer. The calibration required approximately 3 minutes after which the pH meter was used to measure the pH of the sample. Between each sample reading, the probe was rinsed with deionized water.

COD (0-150mg/L COD): COD is a measure of the organic content present in the water samples. The COD for the samples was measured within 48hrs after the sample collection. This test was performed using HACH Method 8000 which uses a strong oxidant, dichromate to measure the COD. The test method contain premeasured reagents to which the water samples are added and incubated for 2hrs, followed by cooling of vials and reading the values directly in a spectrophotometer.

Nitrate: This test was performed using the HACH AccVac Ampuls method. The principle behind the method is cadmium metal present in the ampul reagent mix reduces the nitrates present in the sample to nitrites and the nitrite reacts with sulfnilic acid to form an intermediate dizonium salt, which in turn binds to gentisic acid to form an amber colored product. It takes approximately 10 minutes to measure each sample using this method.

Ammonia-Nitrogen (0-2.5 mg/L NH_3-N): The HACH Salicylate Method determines the ammonia-nitrogen levels in the samples. The principle behind the test kit is the ammonia in the water samples combines with chlorine to form monochloramine, which then reacts with salicylate to form 5-aminosalicylate, which is then oxidized in the presence of a catalyst and a colored compound is formed in the reaction related to the ammonia concentration. This test takes approximately 45 min for a set of 3 samples.

Total Nitrogen (0-25 mg/L N): The total nitrogen in the samples was measured using the HACH Test N Tube method. The principle behind the test is that all forms of nitrogen are converted to nitrate, which then reacts with chromotropic acid in a strong acidic environment to form a yellow complex which has an absorbance at 410 nm. Sodium metabislfite is added to the samples after digestion to remove any halide interferences. This test takes approximately 1.5 hrs for a set of 3 or more samples.

Total Phosphate (0-3.5 mg/L PO_4^{3-}): For this test, PhosVer 3 with Acid Persulfate Digestion from HACH was used. The principle behind the method is that the Orthophosphate reacts with molybdate under acidic condition to produce a phosphomolybdate complex, which is then reduced by ascorbic acid to give the molybdenum blue color. This test takes approximately 1.5 hrs for a set of 3 or more samples.

Detergents (0-3ppm): The anionic detergent method from CHEMetrics was used for these tests. This kit uses the methylene blue extraction method. Anionic detergents react with methylene blue to form a blue complex which is extracted into an immiscible organic solvent. The intensity of the blue color gives an indication of the concentration of methylene blue active substances in the sample. It takes approximately 10 minutes per sample to perform the test.

Microtox: The objective of this test was to measure the reduction of light output at specific time intervals during a run where bacteria are exposed to a water sample. This reduction in light output is compared to that of a control sample to calculate relative toxicity. The Microtox Screening Procedure has a range of relative toxicities between 0 and 100% (light output reduction, as compared to control). The procedure used is given in the Appendix B (adapted from Stormwater Effect Handbook, Pitt et al., 2001).

Heavy Metals Analysis: The water samples were preserved in 2% nitric acid and sent to Stillbrooke Laboratories, in Fairfied, AL for acid digestion and ICP/MS analyses.

PAH Analysis: The water samples were collected in amber glass bottles and sent to Miles College, AL for analysis. EPA Method 625 was used after liquid-liquid extraction of the samples. A GC/MS was used for analyses.

A Kruskal-Wallis test was performed on the six groups of data of each of the pollutants analyzed to identify any significant difference that was present among the six groups. This was followed by pair-wise ANOVA and Mann-Whitney tests to detect any significant differences between the initial and final exposure periods of each of the pollutants from each of the pavement types. A One-way linear regression analysis was performed on the nutrients to identify trends in the loss of these components from the pavements.

Chapter 4: Results and Discussion

The rainfall accumulation during the project duration is as shown Fig (4.0.1). This chart also includes the 0.5 in simulated rainfall on the slabs when sampling. Most of the sample results were compared for two exposure periods: an initial phase (0-2 months aging) and the final phase (2-6 months aging). The regression equations corresponding to the trend lines on the graphs are significant based on the ANOVA analyses shown in Appendix C. If the ANOVA analysis indicated that the intercept was not significant, the regression analysis (and ANOVA) was repeated with the intercept set to zero. If the slope (trend) coefficient was not significant, then the result was a constant, and the average and COV (coefficient of variation) values are shown on the figures.

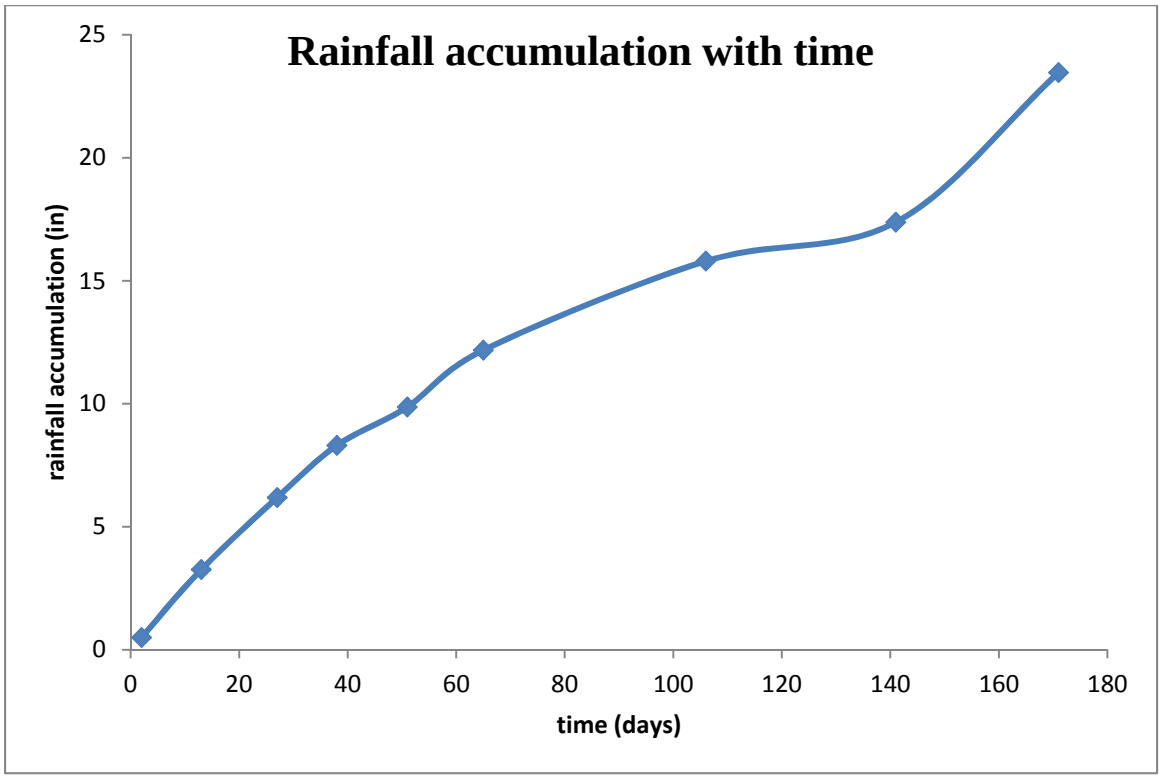


Fig (4.0.1): Rainfall accumulation during the project period.

4.1. Summary of the nutrients results

Nitrate concentrations (mg/L as N) from all the three pavements showed a weak increasing trend in concentrations with the aging of the pavements over the six months exposure duration. The highest nitrate release from the pavements was observed towards the final experimental stages, with 4 mg/L, 6 mg/L and 5 mg/L during the 5 month sampling, as can be seen in the Fig (4.1.1).

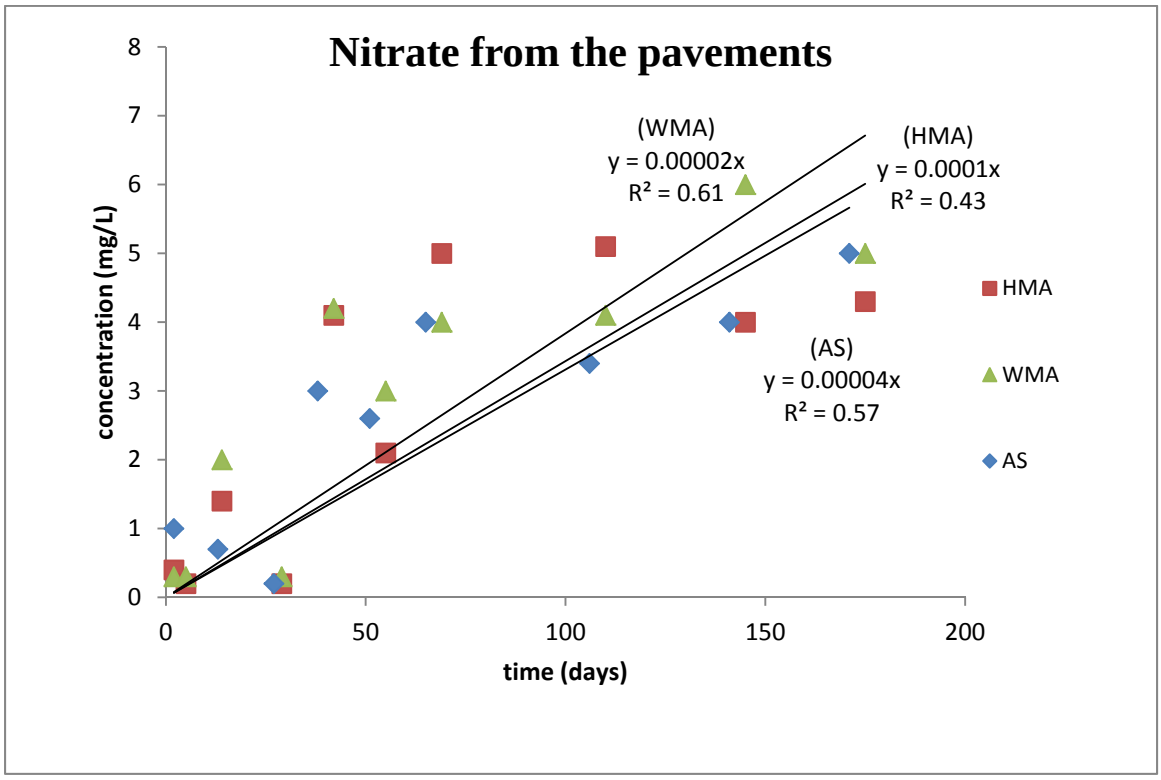


Fig (4.1.1): Nitrate loss from the pavements with the aging of the pavements

From the Kruskal-Wallis test for the six groups of data sets, a significant difference with a p-value of 0.012 was found, indicating that there is a significant difference in the medians in at least one of the leaching patterns from the pavements. The Box and Whisker plot of the nitrate loss, from the initial and the final phases is given in Fig (4.1.2). A Mann-Whitney test was performed to find if any significant difference exist between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 4.1.

Mann-Whitney test results for loss of Nitrate	
Asphaltic Sealant (AS)	0.020
Hot Mix Asphalt (HMA)	0.037

Warm Mix Asphalt (WMA)	0.060

Table 4.1: Mann-Whitney test results for loss of Nitrate

A significant difference between the loss of nitrate from the pavements comparing the initial and final phases was observed as indicated by the p-values. One-way ANOVA test results to determine differences between the initial values from all three samples and the final values from all three samples indicated they were similar, with little likely difference in behavior between the three pavement types. The test results for individual contaminants are given in Appendix D.

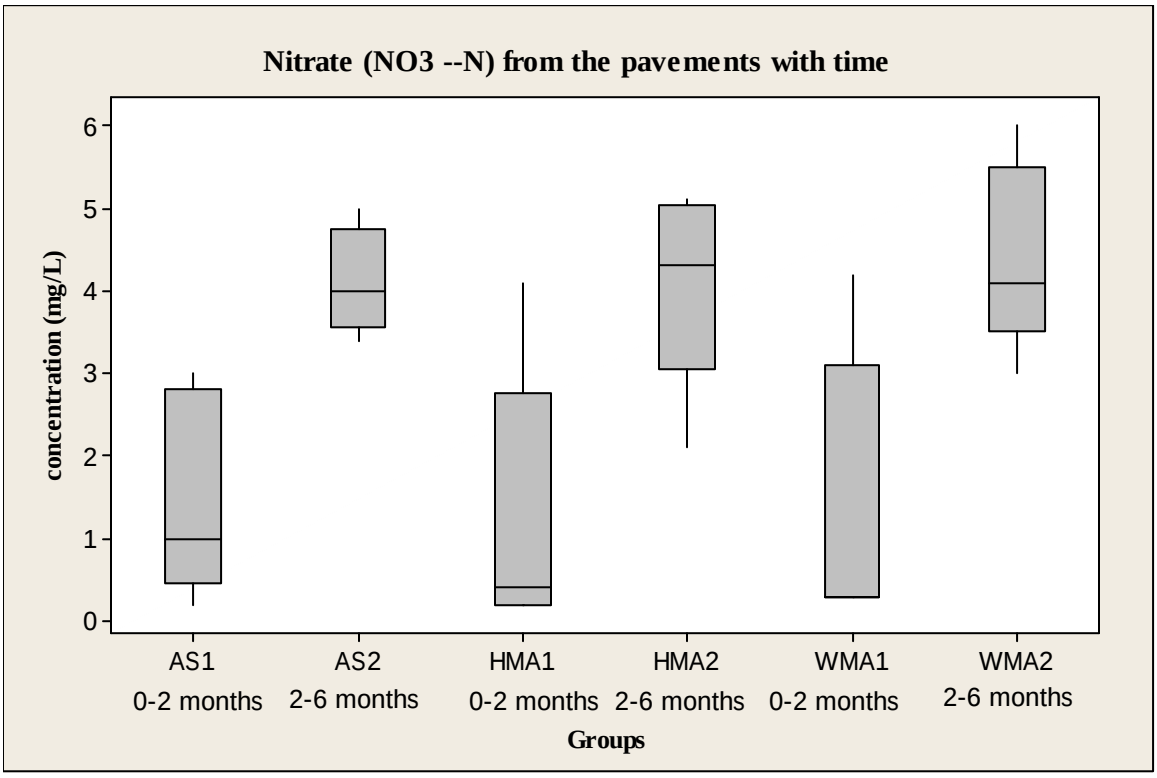


Fig (4.1.2): Nitrate loss from the pavements during the initial and final experimental stages.

Fig (4.1.3) shows the resulting total phosphorus (mg/L as P) with the aging of the pavements. The hot mix asphalt pavement and the pavement with the asphalt sealer showed significant increasing concentrations with time, while the warm mix asphalt showed a weak decreasing trend with time. ANOVA on the linear regression however showed that the trend from the warm

mix pavement was not significant. ANOVA test results on the linear regression for the individual nutrients are given in Appendix D.

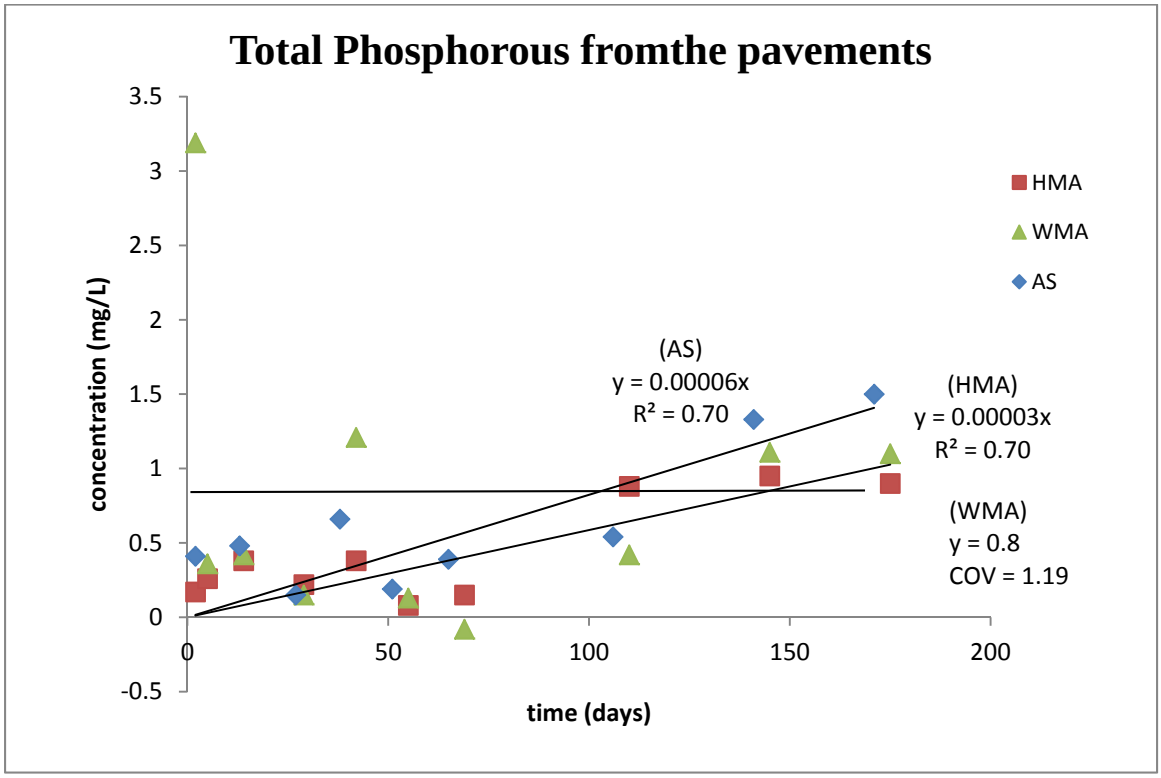


Fig (4.1.3): Total Phosphorous from the pavements with time.

From the Kruskal-Wallis test for the six groups of data sets for total phosphorous leaching into the runoff, a p-value of 0.410 was observed indicating no significant difference in the medians in

the leaching data from the pavements. A Box and Whisker plots of the total phosphorous loss, from the initial and the final phases is given in Fig (4.1.4). A Mann-Whitney test was performed to find if any significant difference exist between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 4.2. None of the three pavements indicated any significant differences in the total phosphorous concentrations between the two exposure periods, however, the Appendix D ANOVA test results comparing the differences do show an apparent change for the asphalt sealant observations (a decrease).

Mann-Whitney test results for loss of total phosphorous	
AS	0.178
HMA	0.465
WMA	0.676

Table 4.2: Mann-Whitney test results for loss of total phosphorous

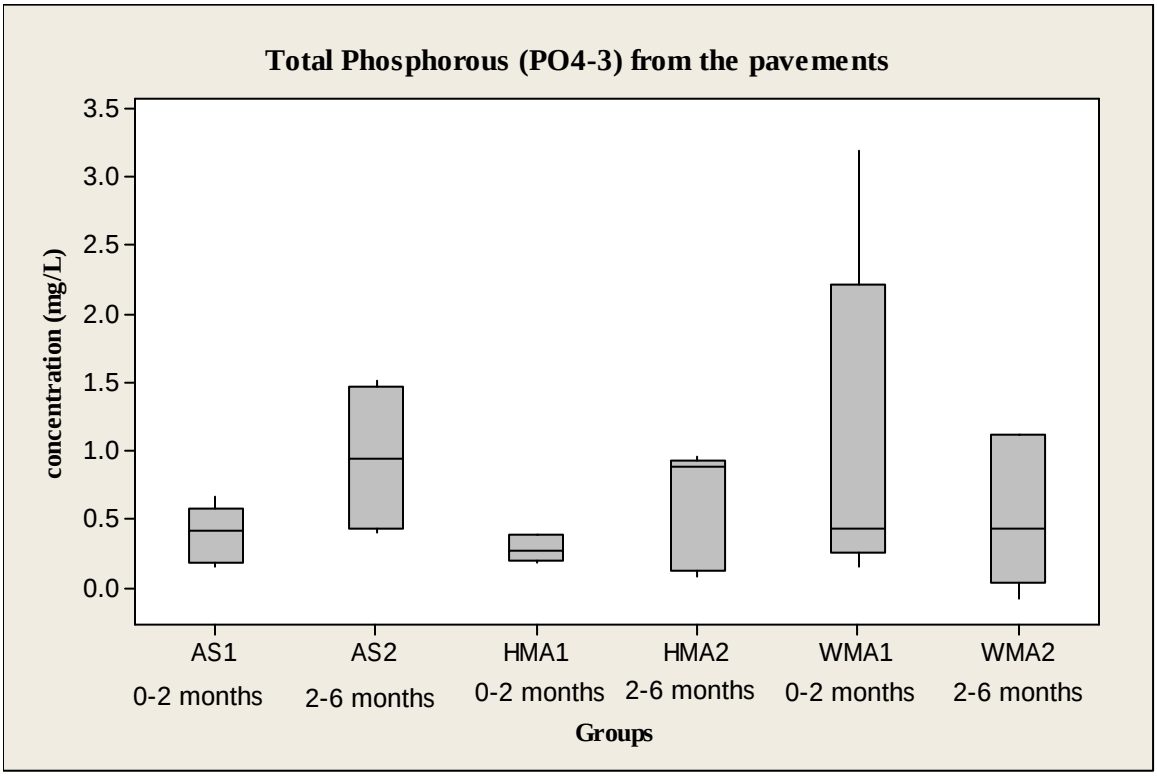


Fig (4.1.4): Loss of Total Phosphorous form the pavements during the initial and the final experimental stages.

The concentrations of ammonia, total nitrogen and COD form the pavements did not show any significant pattern in their leaching from the pavements, as can be seen in the Fig (4.1.5), Fig (4.1.6) and Fig (4.1.7). The pattern observed in the leaching of total nitrogen from the warm mix pavements and the pavement with asphalt sealer showed no significant differences from the ANOVA test performed on the linear regression equation. COD losses from the pavements with the asphalt sealer however, showed a decrease with time with an R^2 value of 0.56.

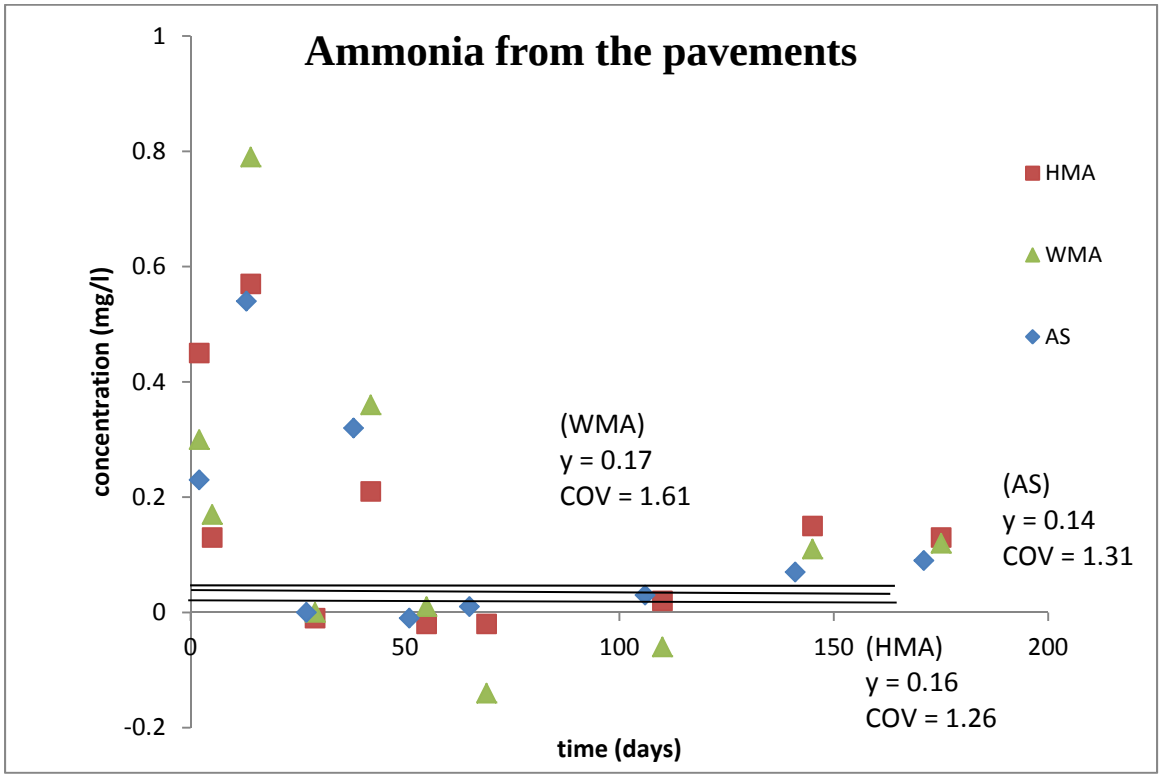


Fig (4.1.5): Ammonia from the pavements with time.

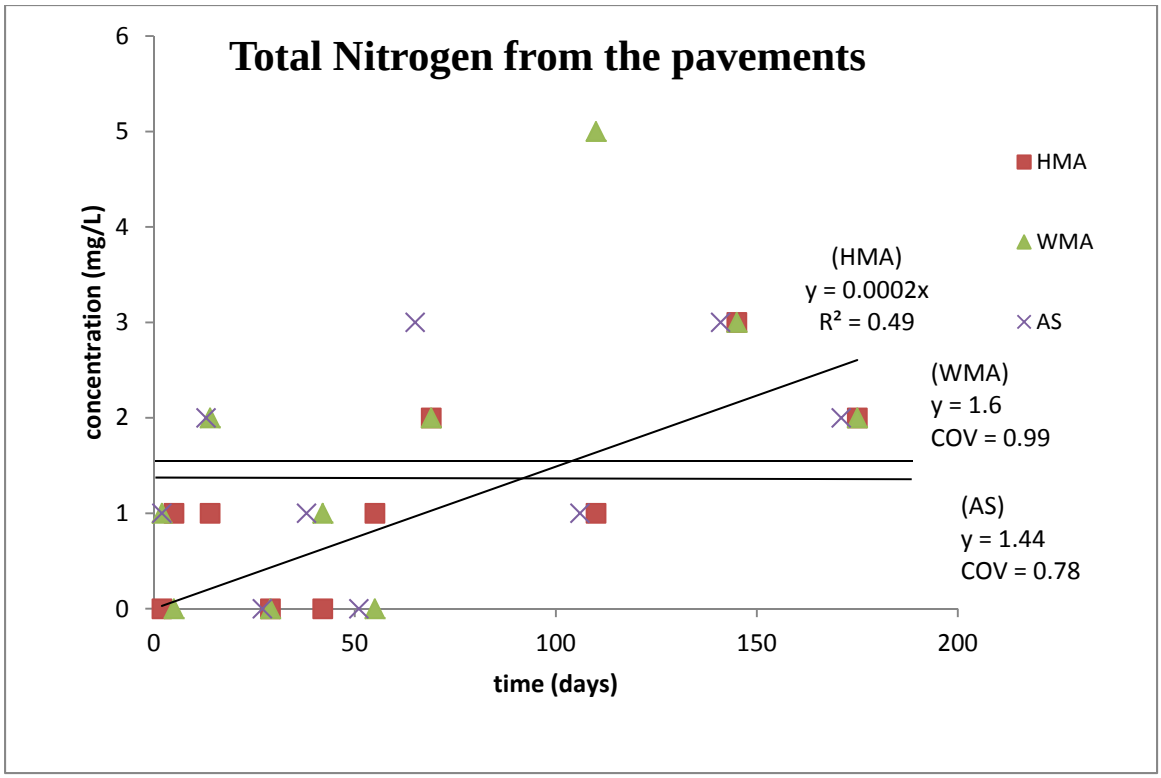


Fig (4.1.6): Total Nitrogen from the pavements with time

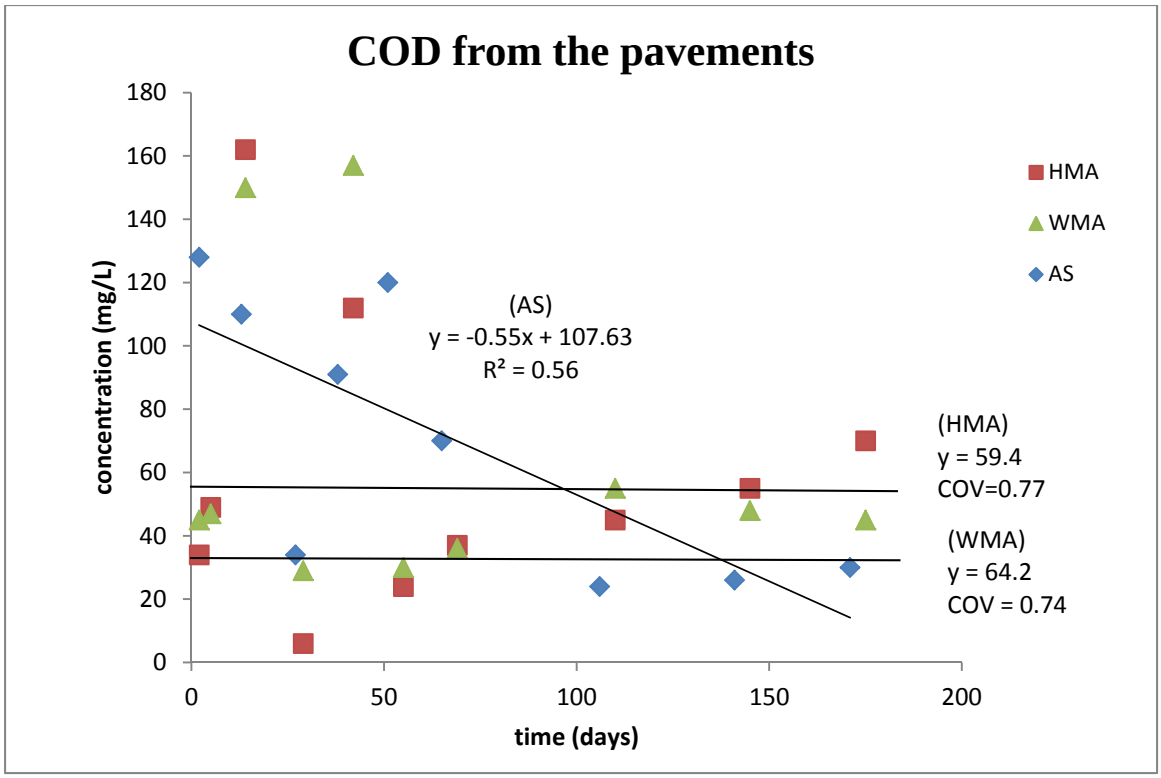


Fig (4.1.7): COD from the pavements with time.

A significant difference was observed in the leaching of total nitrogen from the pavements amongst the three pavement samples, with a p-value of 0.037, from the Kruskal-Wallis test. The ANOVA pairwise tests in Appendix C showed significant differences for the hot mix asphalt and the sealer samples, with a somewhat weaker change for the warm mix sample. Whereas, for the loss of ammonia and COD from the pavements, the six groups of data did not show any significant differences, with higher Kurskal-Wallis p-values of 0.128 and 0.312 for ammonia and COD respectively. The Box and Whisker plots of the loss of total nitrogen, ammonia and COD from the pavements in initial and the final phases is given in Fig (4.1.8), Fig (4.1.9) and Fig (4.1.10). The Mann-Whitney test was performed to find if any significant difference exist between the initial and final phases for each of the pavement types and the p-values from the test are presented in Table 4.3. From the table we can see that the nitrogen loss from the hot mix pavement shows a significant difference, similarly for COD from the pavement with the sealer,

contradicting the Kruskal-Wallis result. The short-term concentrations from all three samples are all very similar, as are the long-term concentrations for these constituents, with little apparent difference in concentration behavior for the different samples.

Mann-Whitney test results for loss of nutrients		
Total N	AS	0.086
	HMA	0.037
	WMA	0.144
Ammonia	AS	0.713
	HMA	0.060
	WMA	0.117
COD	AS	0.037
	HMA	0.835
	WMA	0.601

Table 4.3: Mann-Whitney test results for loss of nutrients

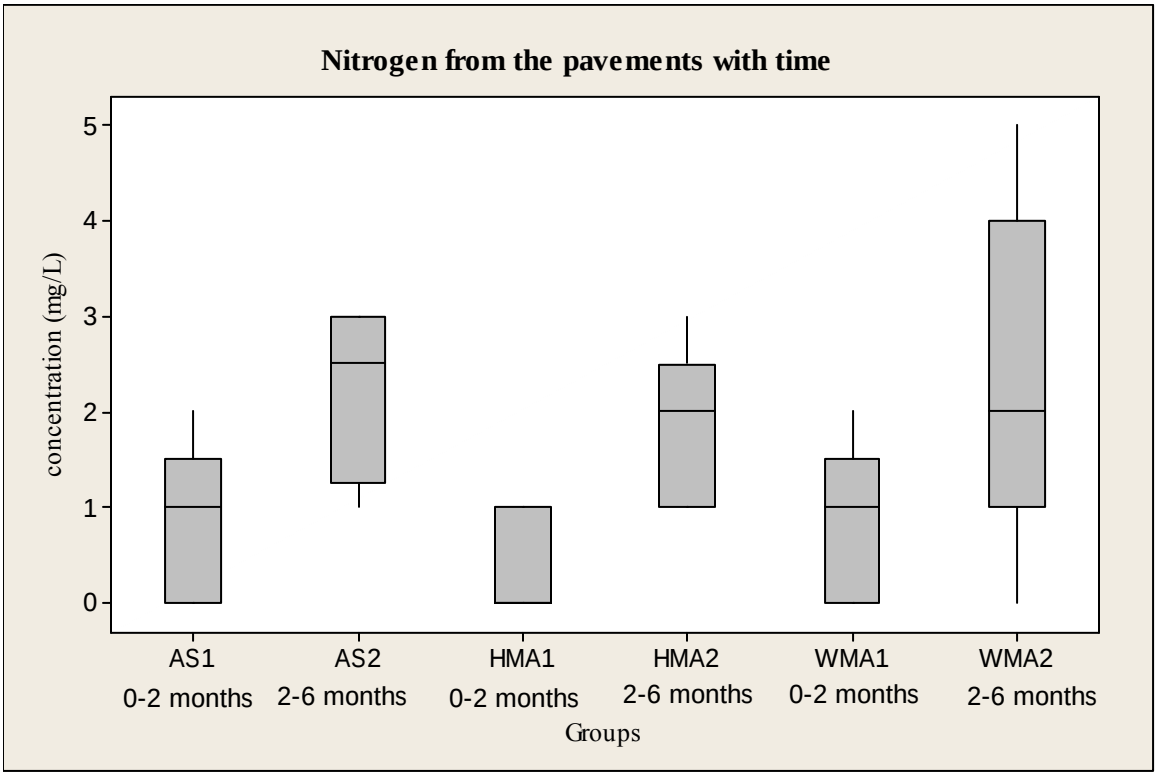


Fig (4.1.8) : Nitrogen loss from the pavements between the initial and final experimental stages.

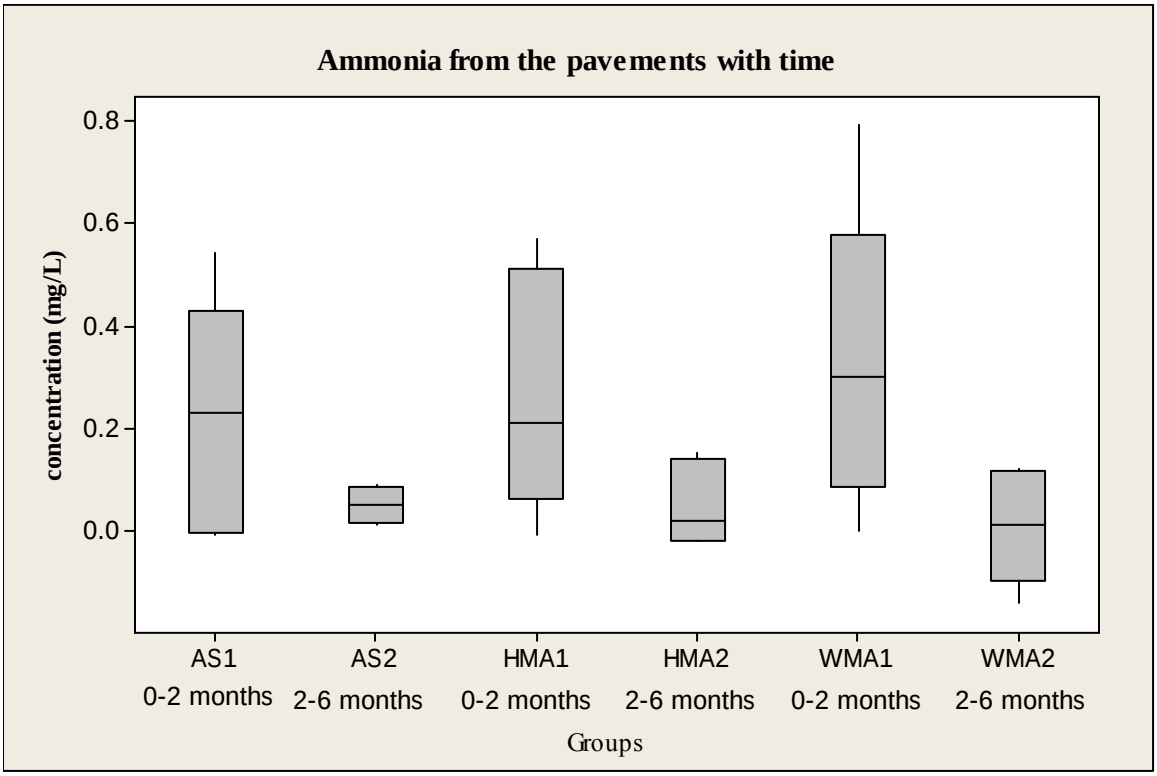


Fig (4.1.9): Ammonia loss from the pavements between the initial and final experimental stages.

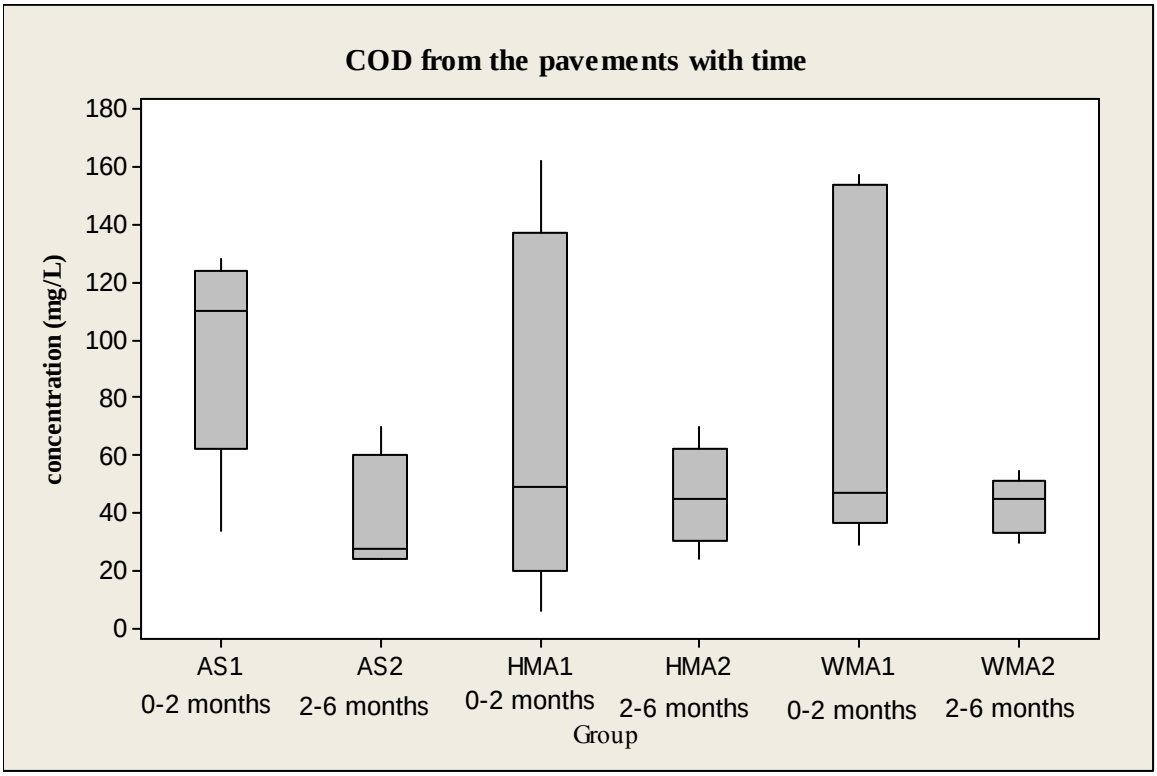


Fig (4.1.10) : COD loss from the pavements between the initial and final experimental stages.

4.2 Summary of Detergents results

The pavements showed anionic detergent concentrations between 0.25 mg/L to 1.75 mg/L during the six months of aging of the pavements; however no patterns were observed or statistically detected between the different time frames or the different samples, as shown in Fig (4.2.1) and Fig (4.2.2). The p-values from the Mann-Whitney test are presented in Table: 4.4. The pairwise ANOVA test results in Appendix C also indicate no significant differences.

Mann-Whitney test results for loss of nutrients		
Total N	AS	0.327
	HMA	1.000
	WMA	0.835

Table: 4.4: Mann-Whitney test results for loss of detergents.

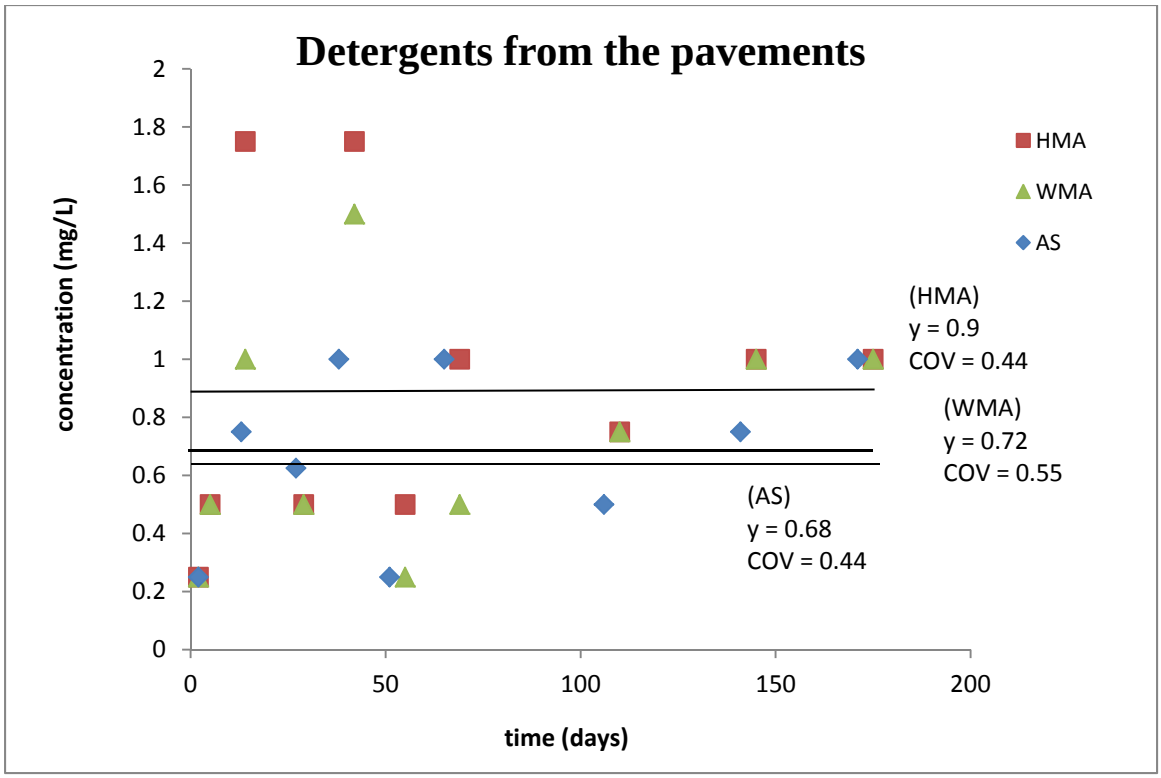


Fig (4.2.1) Detergent release from the pavements with aging.

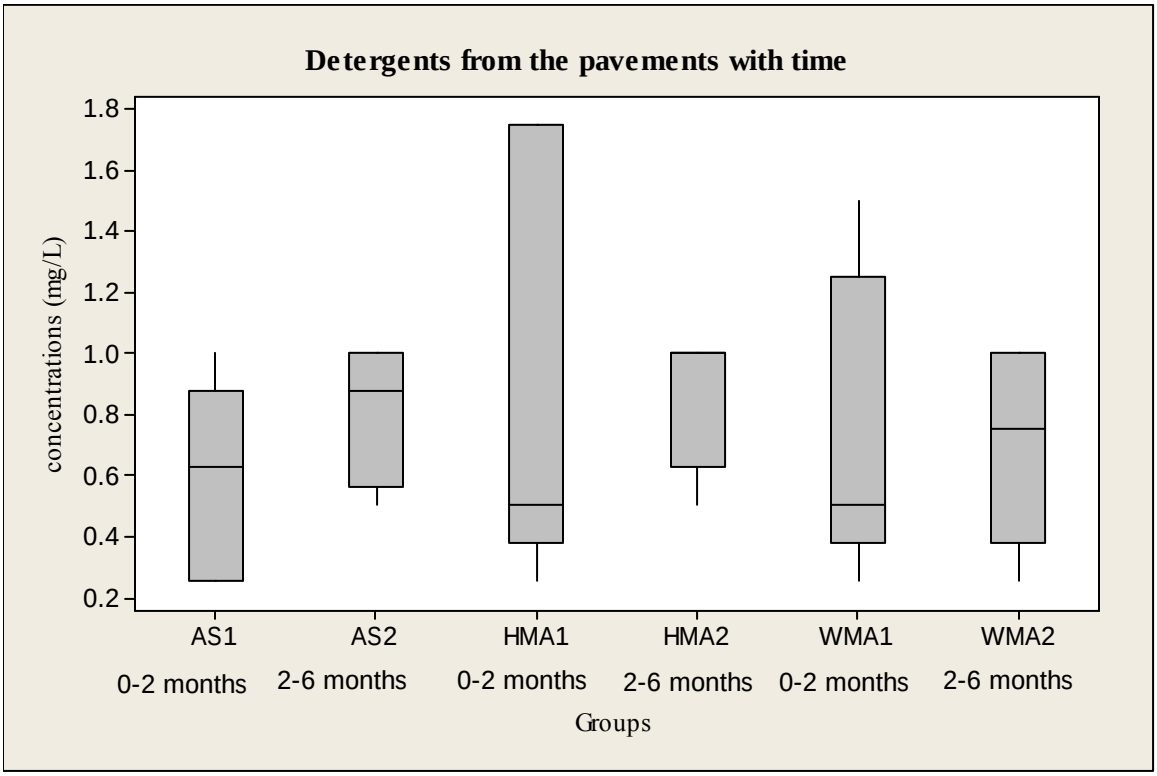


Fig (4.2.2): Detergents from the pavements during the initial and final experimental stages.

4.3.Summary of Heavy Metals

Amongst the heavy metals analyzed, cadmium and chromium were always below the detection limits for all the samples. Lead was only detected in the 2 week exposure samples from the pavements at 0.008 mg/L, 0.01 mg/L and 0.017 mg/L concentrations from the hot mix asphalt, warm mix asphalt and from the pavement with asphalt sealer respectively. The pavement with the sealer also had a lead runoff concentration of 0.006 mg/L in the 7th week of the exposure, as shown in table 4.3.1. Zinc was also below detection limits for the first sampling event, however with aging (2-6 months period) both zinc and copper showed an increasing trend from all three pavements as seen in Fig (4.3.1) and Fig (4.3.2). The leaching from all three pavements showed a similar pattern for the heavy metals examined.

Lead from the pavements

	HMA	WMA	AS
Day 14	0.008 mg/L	0.01 mg/L	0.017 mg/L
Day 51	-	-	0.006 mg/L

Table (4.3.1) : Lead from the pavements with time.

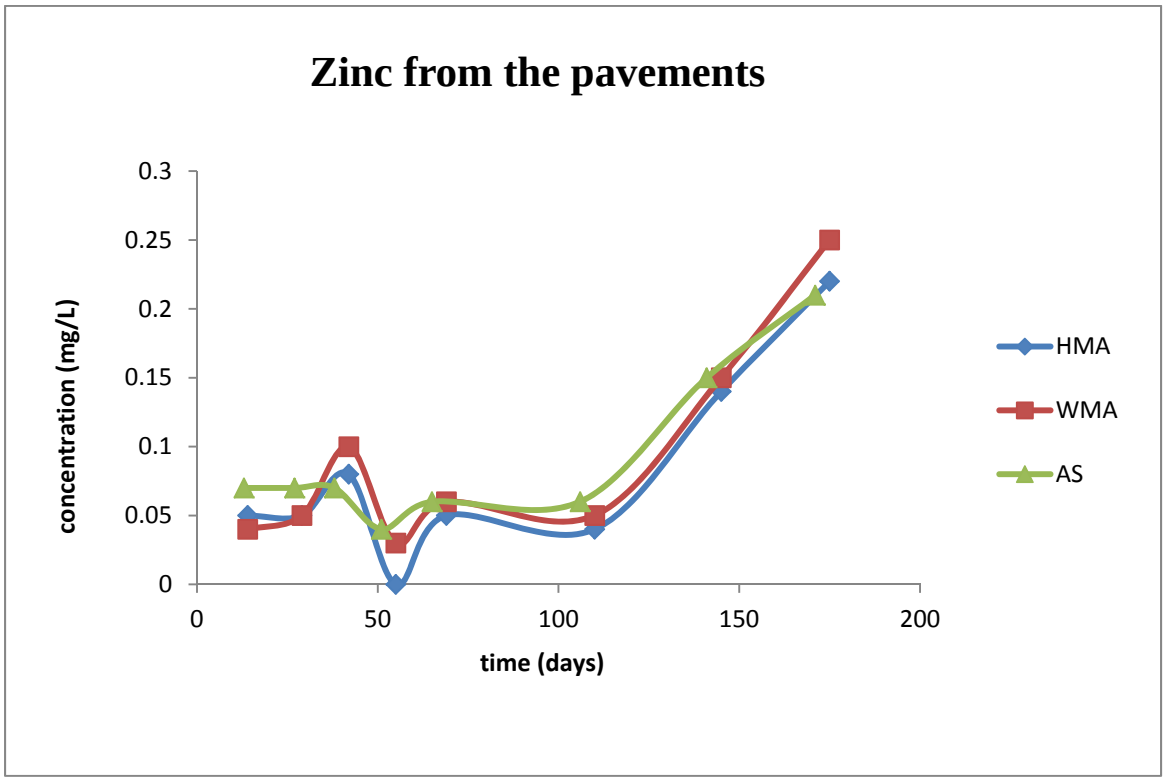


Fig (4.3.1): Zinc from the pavements with time

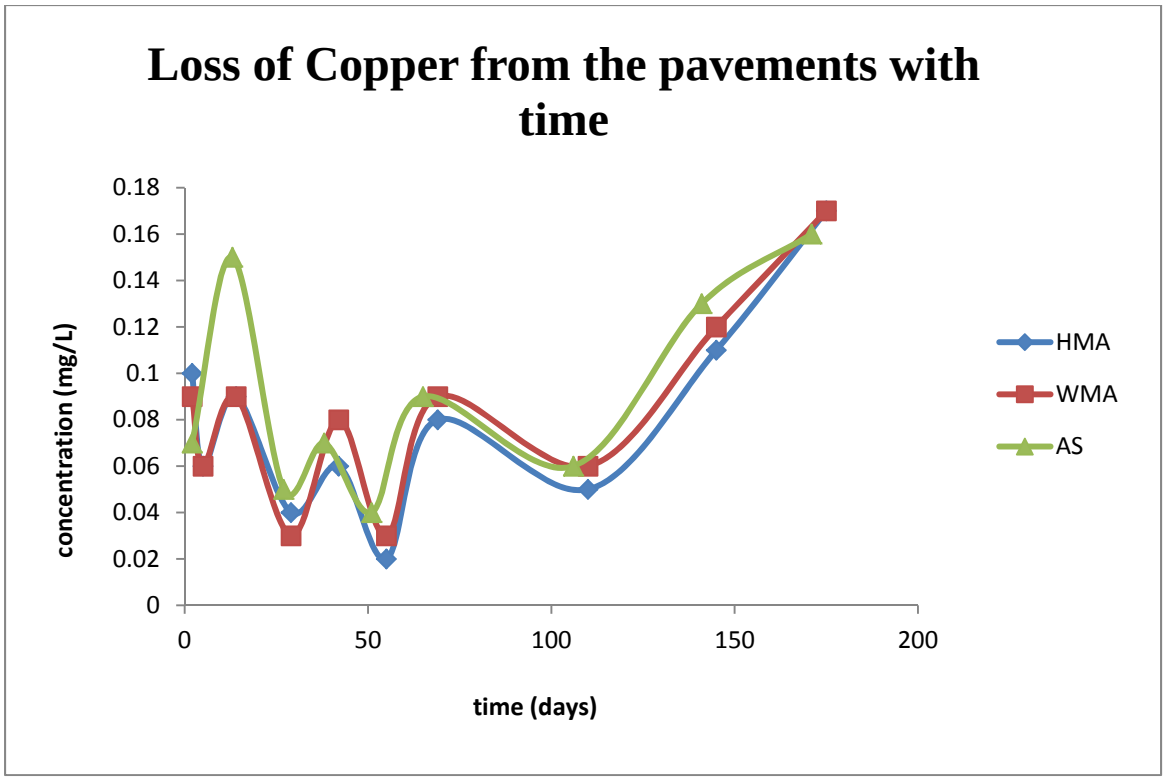


Fig (4.3.2): Copper from the pavements with time.

As seen in Fig (4.3.3) and Fig (4.3.3) the Kruskal-Wallis test results for copper and zinc showed high p-values, 0.319 and 0.764 respectively, also supported by the Mann-Whitney and pairwise ANOVA results and the box plots. However, the time series plots show apparent large increases in copper and zinc concentrations during the last few samples after the longest exposures.

Heavy metal	Pavement type	p-value
Cu	AS	0.270
	WMA	0.530
	HMA	0.835
Zn	AS	0.391
	WMA	0.175

	HMA	0.530

Table 4.4: Mann-Whitney test results for loss of heavy metals.

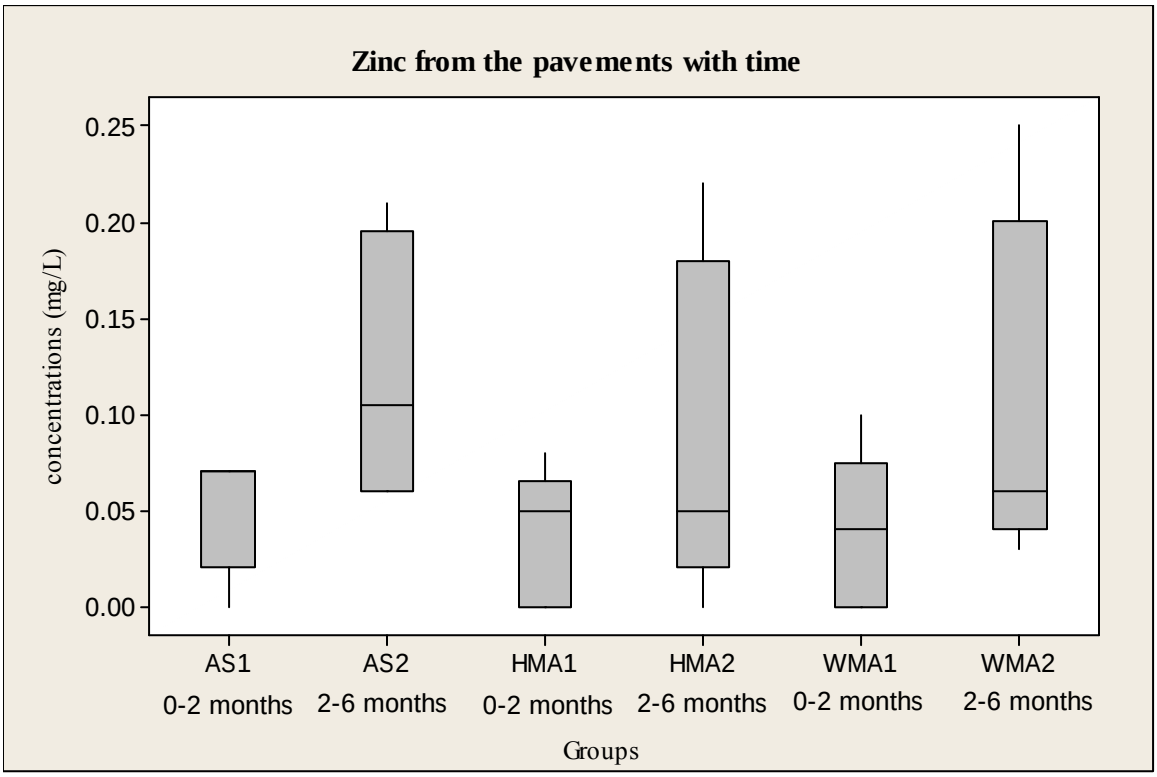


Fig (4.3.3): Zinc loss from the pavements during the initial and final experimental stages.

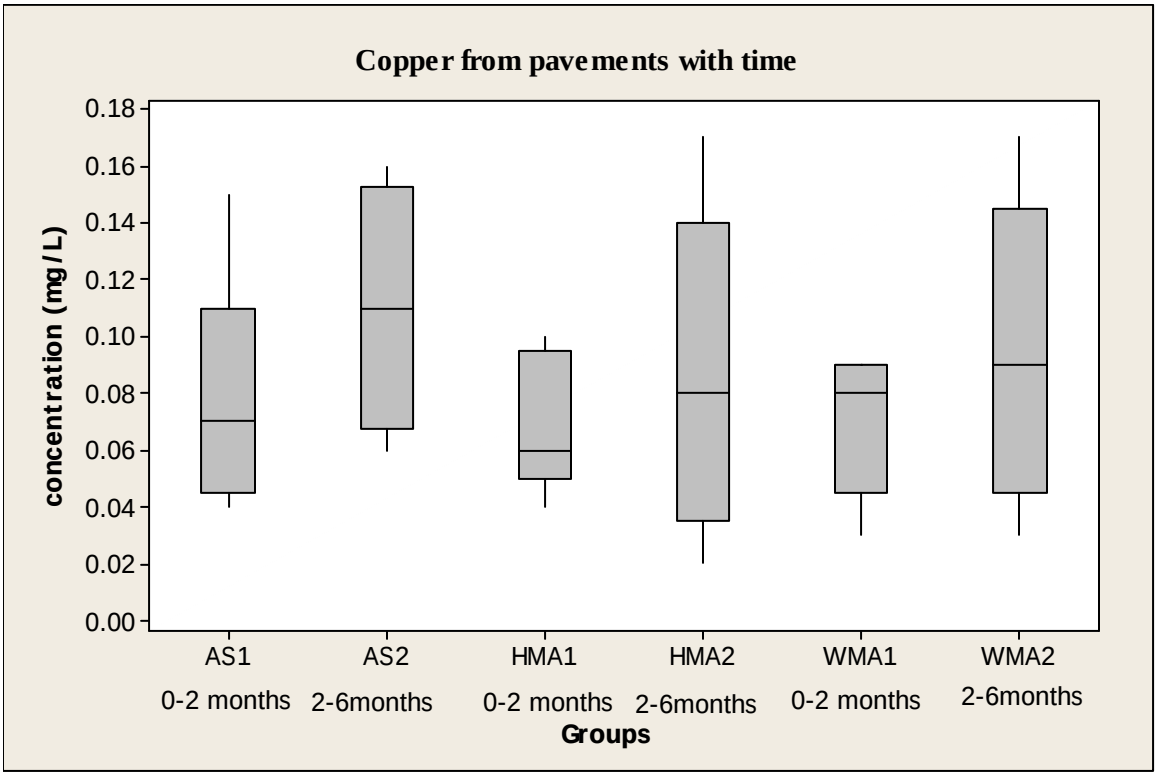


Fig (4.3.4): Copper loss from the pavements during the initial and final experimental stages.

4.4. Toxicity Tests

The pavements showed high levels of toxicity, but with no significant changes with time observed. The results for the Microtox toxicity screening test are presented below in Fig (4.4.4). Amongst the three pavements, the highest toxicities recorded occurred after at least 42 days of aging, as shown in Table 4.4.1..

	% toxicity/day recorded
HMA	63%, after 175 days of aging
WMA	94%, after 42 days of aging
AS	80%, after 106 days of aging

Table (4.4.1): Highest toxicity recorded during the six months exposure from the pavements.

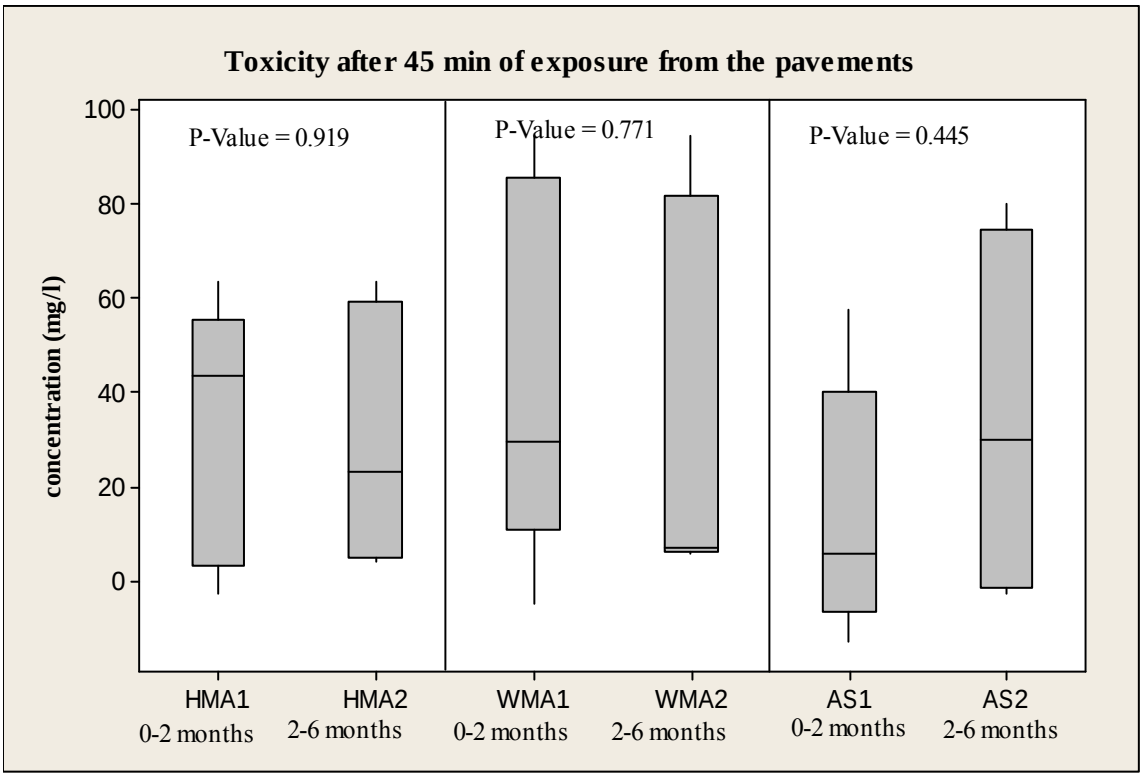


Fig (4.4.4): Toxicity after 45 min exposure of the samples from the pavements.

4.5. PAHs

A p-value of 0.10 is high-lighted as significant for the PAH concentration differences for the different exposure periods. Acenapthene, fluoranthene, pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene showed p values <0.1 based on the Kruskal-Wallis test, as seen in the box plots shown in Fig (4.5.1) to Fig (4.5.5). The Mann Whitney test was used to examine differences in each pavement type with aging (Table 4.6). From this table, acenapthene in the hot mix pavement and warm mix samples indicated significant differences with aging. Similarly, warm-mix pavement samples had significant differences in benzo(k)fluoranthene concentrations with time .

Mann-Whitney test results for PAHs with significant p-values from Kruskal-Wallis test		
Acenapthene	AS	0.38
	HMA	0.06
	WMA	0.09
Fluoranthene	AS	0.31
	HMA	0.67
	WMA	0.47
Pyrene	AS	0.31
	HMA	1.00
	WMA	0.19
Benzo(k)fluoranthene	AS	1.00
	HMA	0.67
	WMA	0.03
Benzo(ghi)perylene	AS	0.31
	HMA	0.11
	WMA	0.89

Table 4.6: Mann-Whitney test results for PAHs with significant p-values from Kruskal-Wallis test.

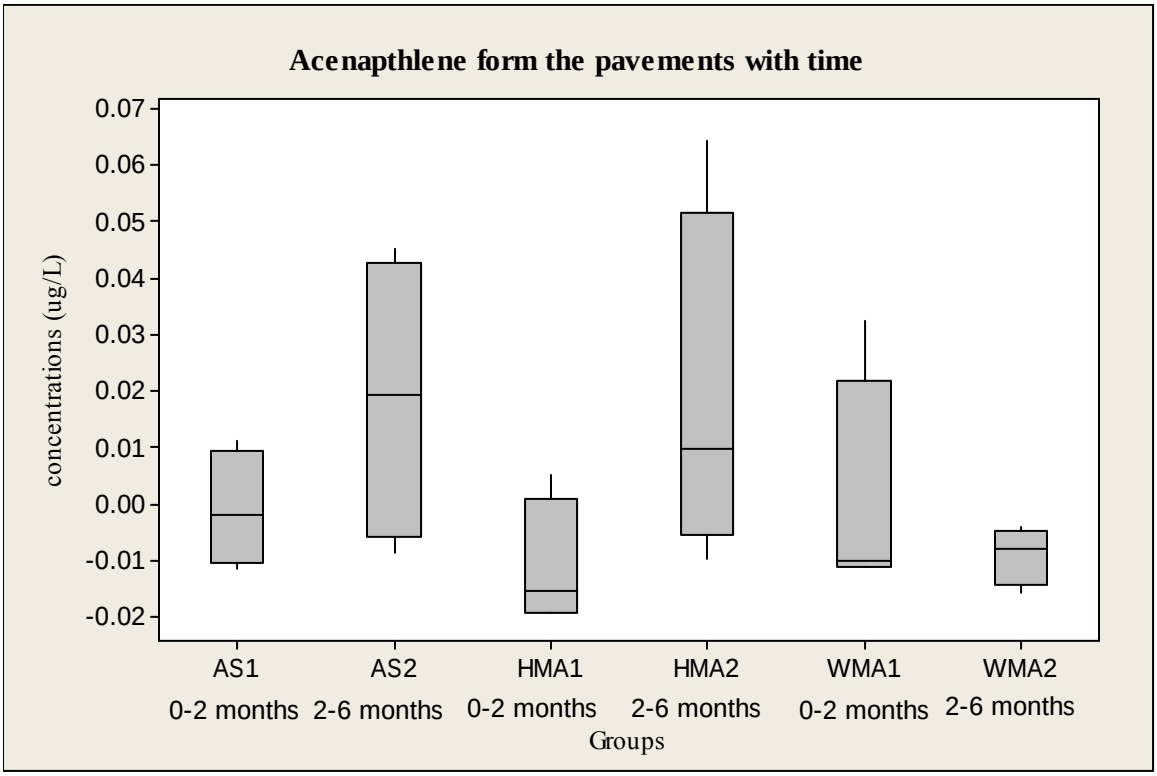


Fig (4.5.1): Acenapthlene from the pavements with aging.

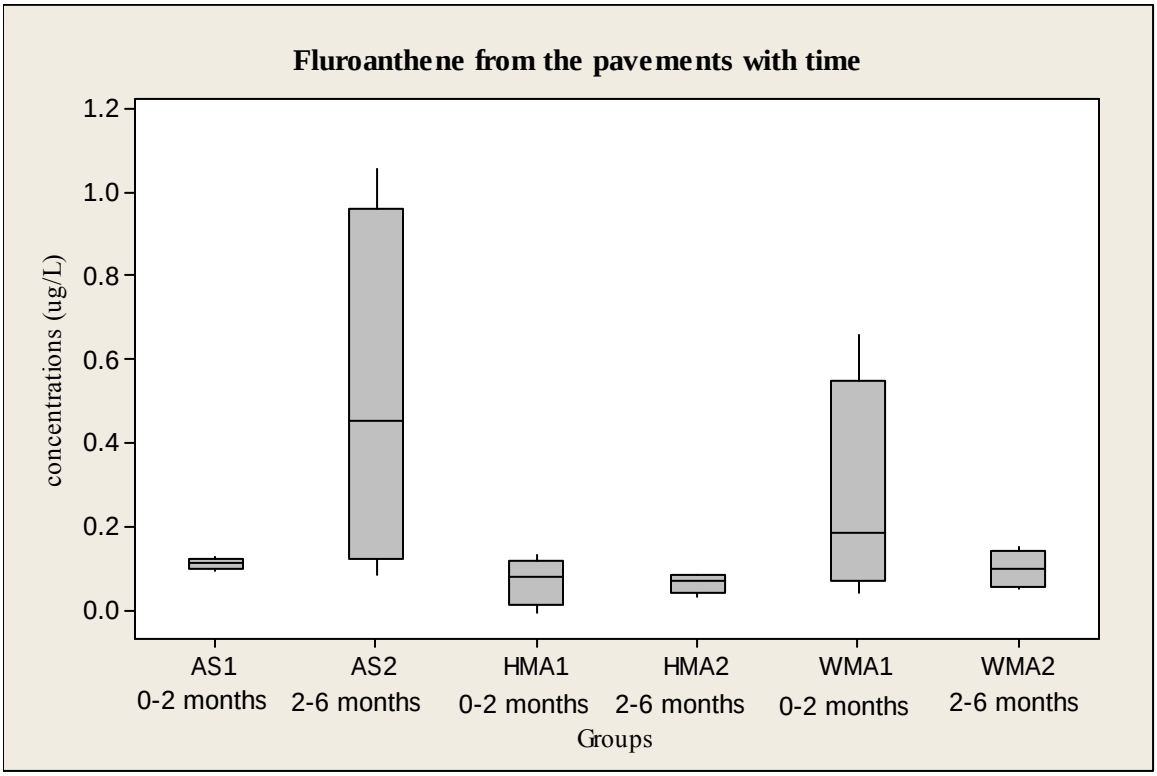


Fig (4.5.2): Fluroanthene from the pavements with aging.

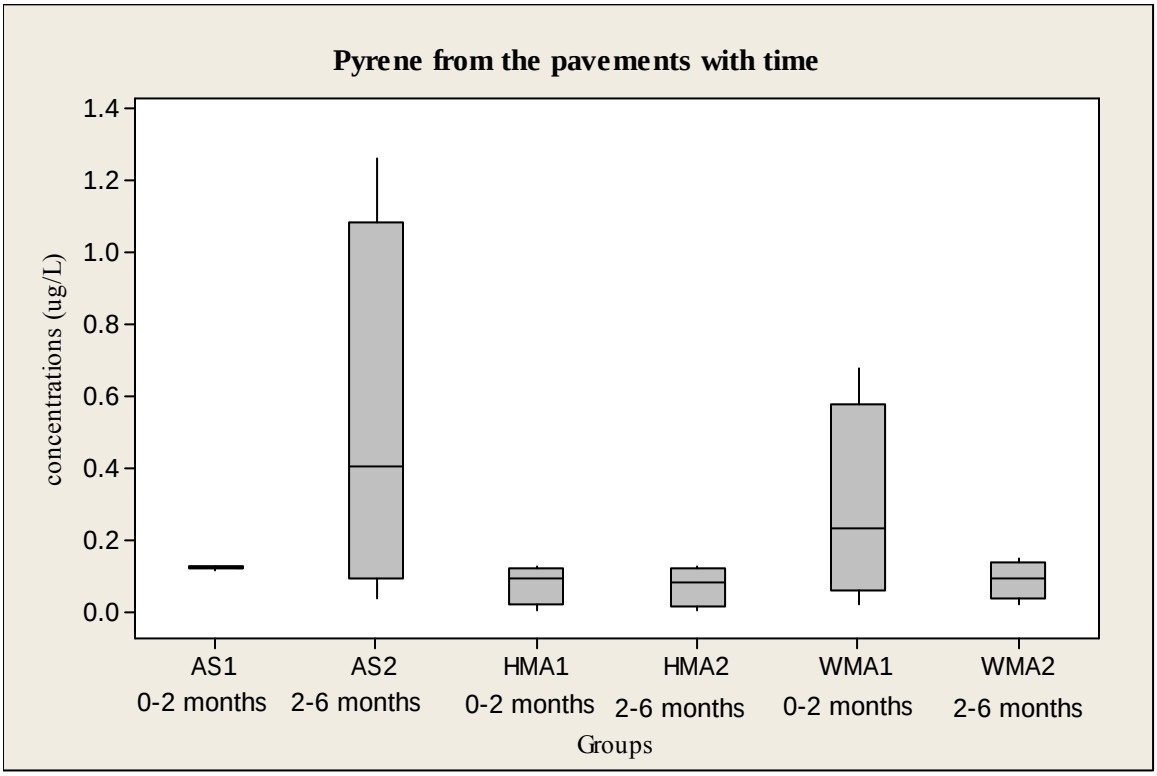


Fig (4.5.3): Pyrene from the pavements with aging

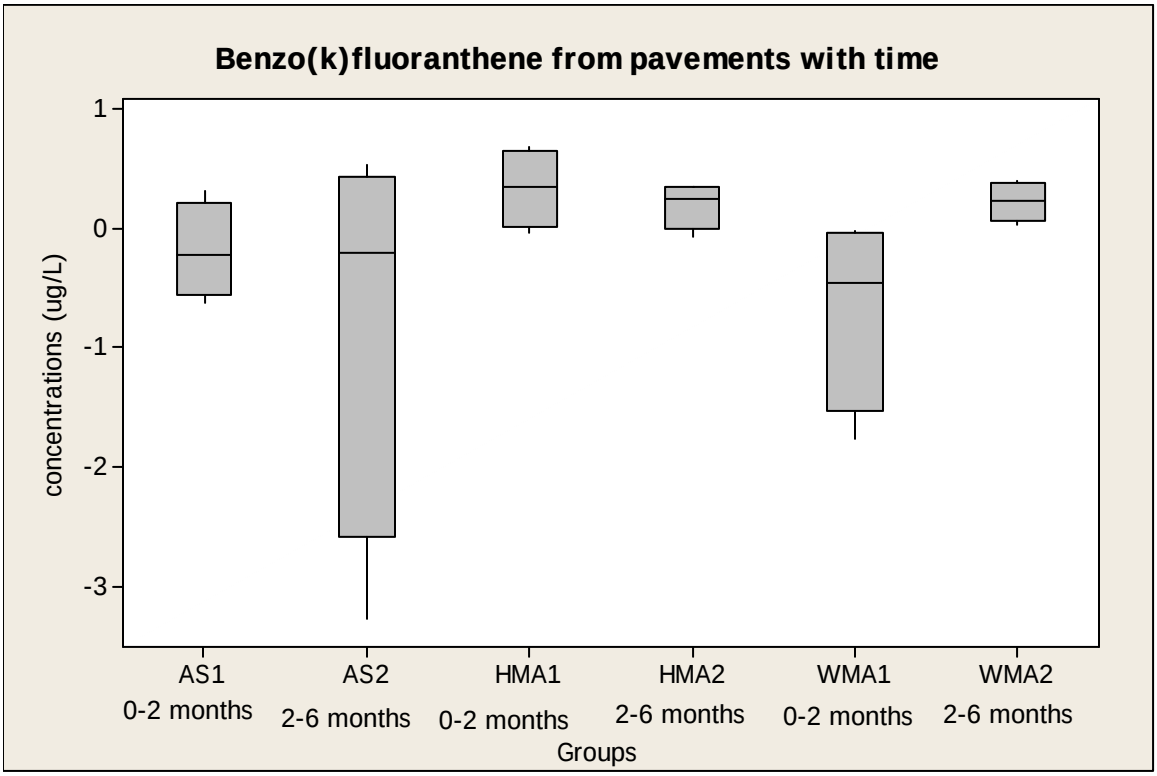


Fig (4.5.4): Benzo(k)fluoranthene from the pavements with aging.

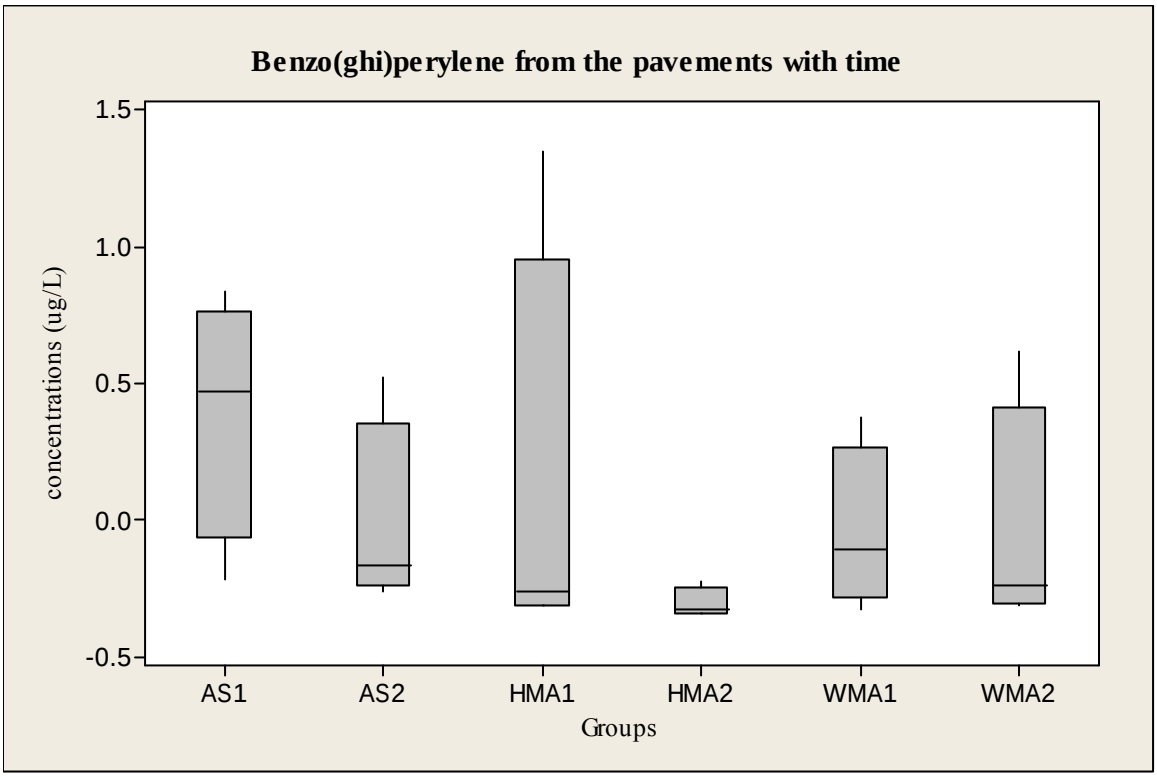


Fig (4.5.5): Benzo(ghi)perylene from the pavements with aging.

No significant differences were observed for the remainder of the PAHs analyzed based on the Kruskal-Wallis one-way ANOVA tests. The box-plot forthese are presented in Fig (4.5.6) through Fig (4.5.15). The Mann Whitney tests examined difference for each pavement type with aging, and these results are presented in Table 4.7. According to the table, napthalene is showing an apparent difference with aging for the warm mix asphalt. Similarly fluorine and anthracene from asphalt sealant runoff samples, and anthracene from both the asphalt sealer and the warm mix pavement samples indicated significant concentration differences with time.

Mann-Whitney test results for PAHs with insignificant p-values from Kruskal-Wallis test		
Napthalene	AS	0.31
	HMA	0.89
	WMA	0.11
Acenapthylene	AS	0.25
	HMA	0.31
	WMA	1.00
Fluorene	AS	0.19
	HMA	0.89
	WMA	0.89
Anthracene	AS	0.03
	HMA	1.00
	WMA	0.03
Benzo(a)anthracene	AS	0.47

	HMA	0.67
	WMA	0.31
Chrysene	AS	0.31
	HMA	1.00
	WMA	0.47
Benzo(b)fluoranthene	AS	0.47
	HMA	0.31
	WMA	0.47
Benzo(a)pyrene	AS	0.31
	HMA	0.67
	WMA	0.89
Indeno(1,2,3-cd)pyrene	AS	0.19
	HMA	0.89
	WMA	0.895
Benzo(a,h)anthracene	AS	0.895
	HMA	1.00
	WMA	0.47

Table 4.7: Mann-Whitney test results for the rest of the PAHs.

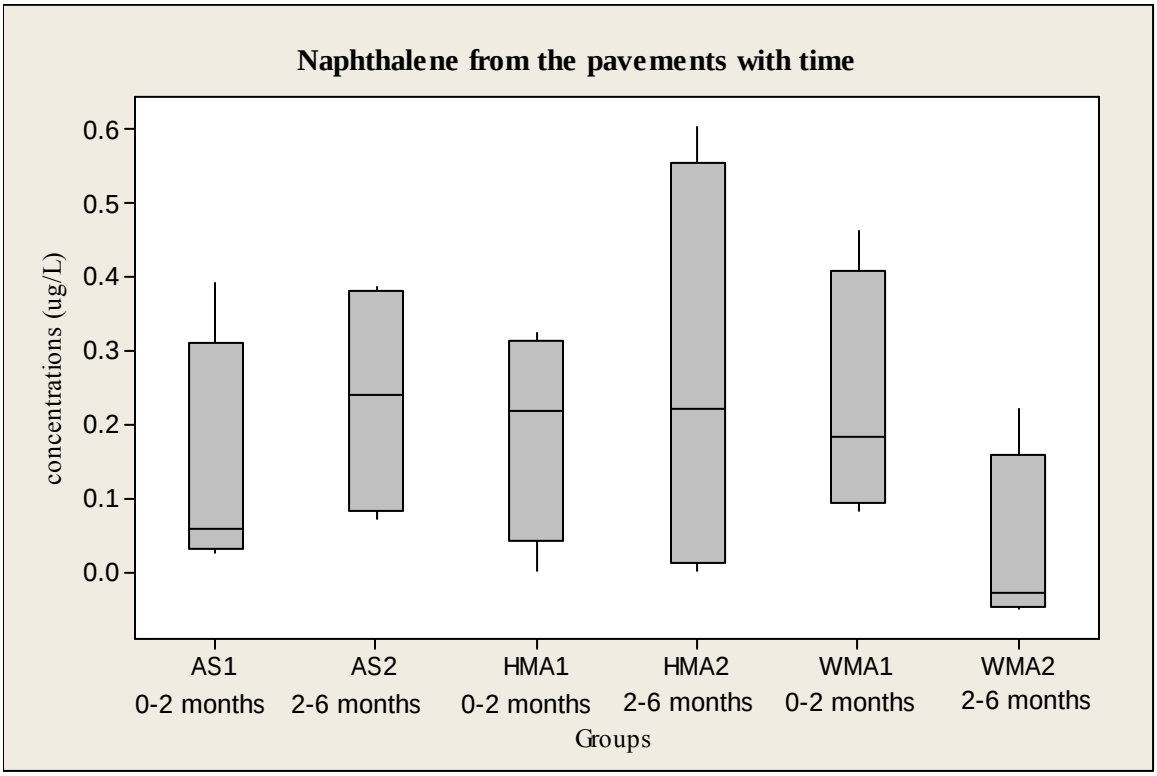


Fig (4.5.6): Naphthalene from the pavements with aging.

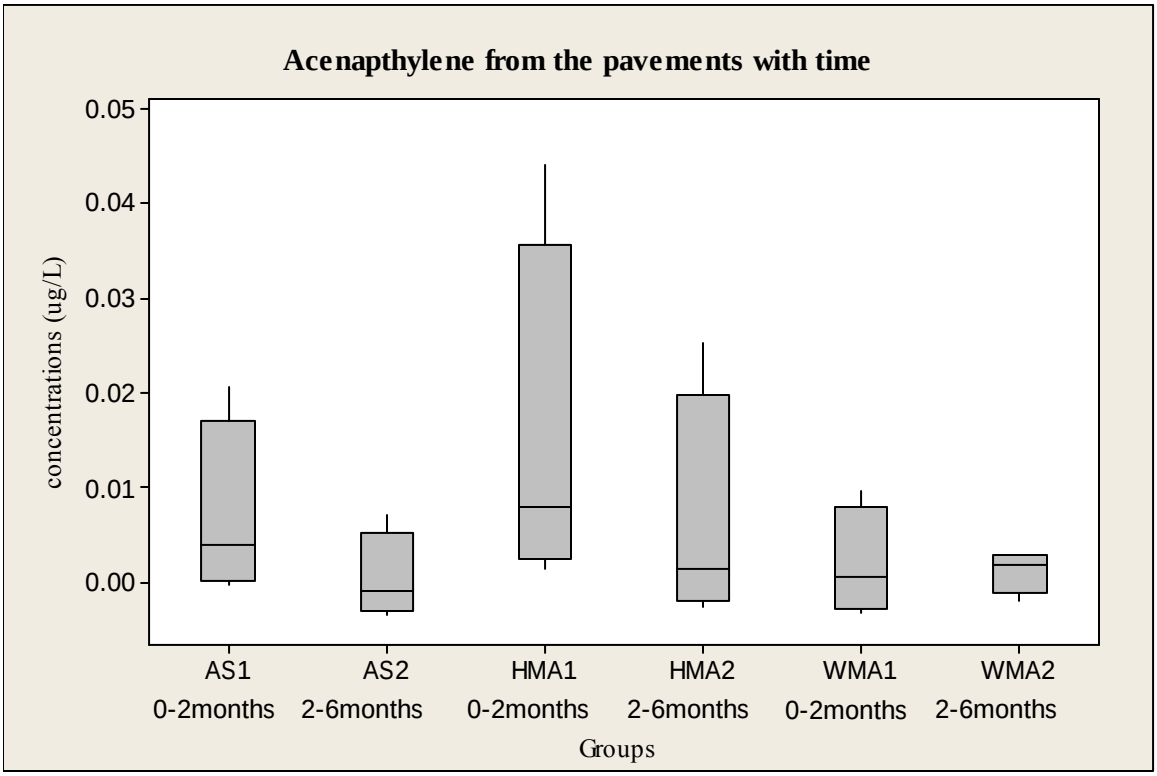


Fig (4.5.7): Acenapthylene from the pavements with aging.

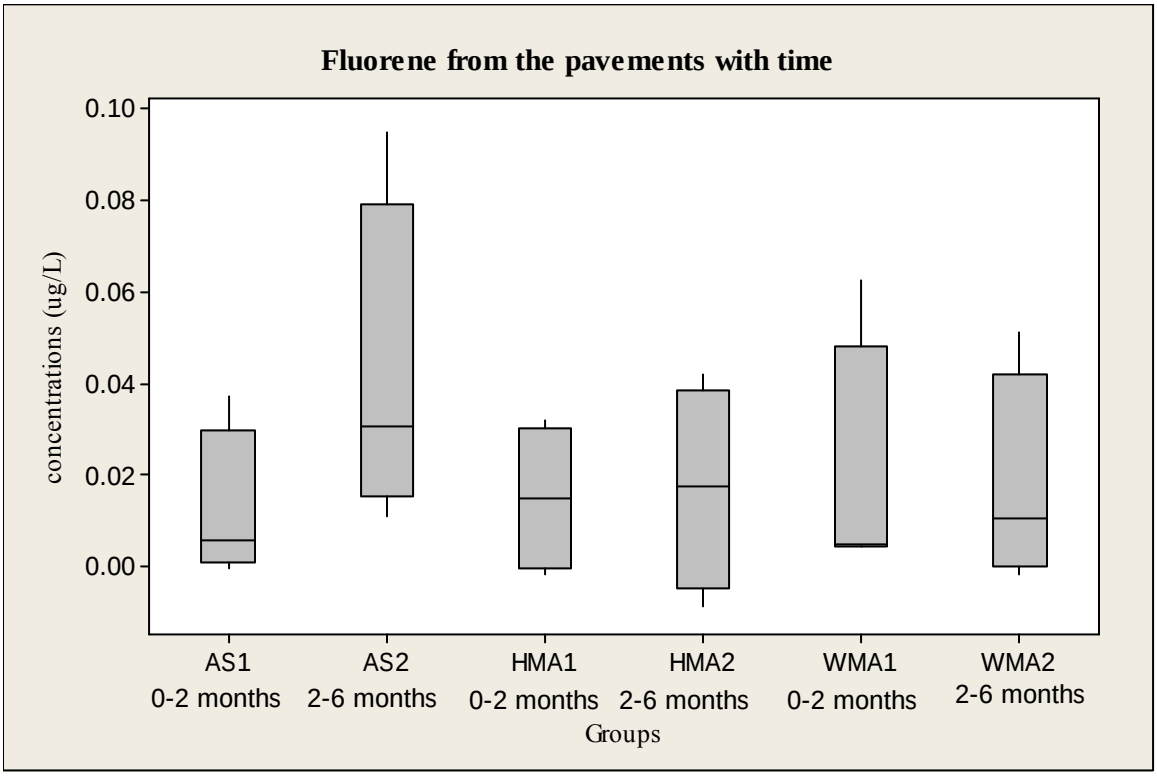


Fig (4.5.8): Fluorene from the pavements with aging.

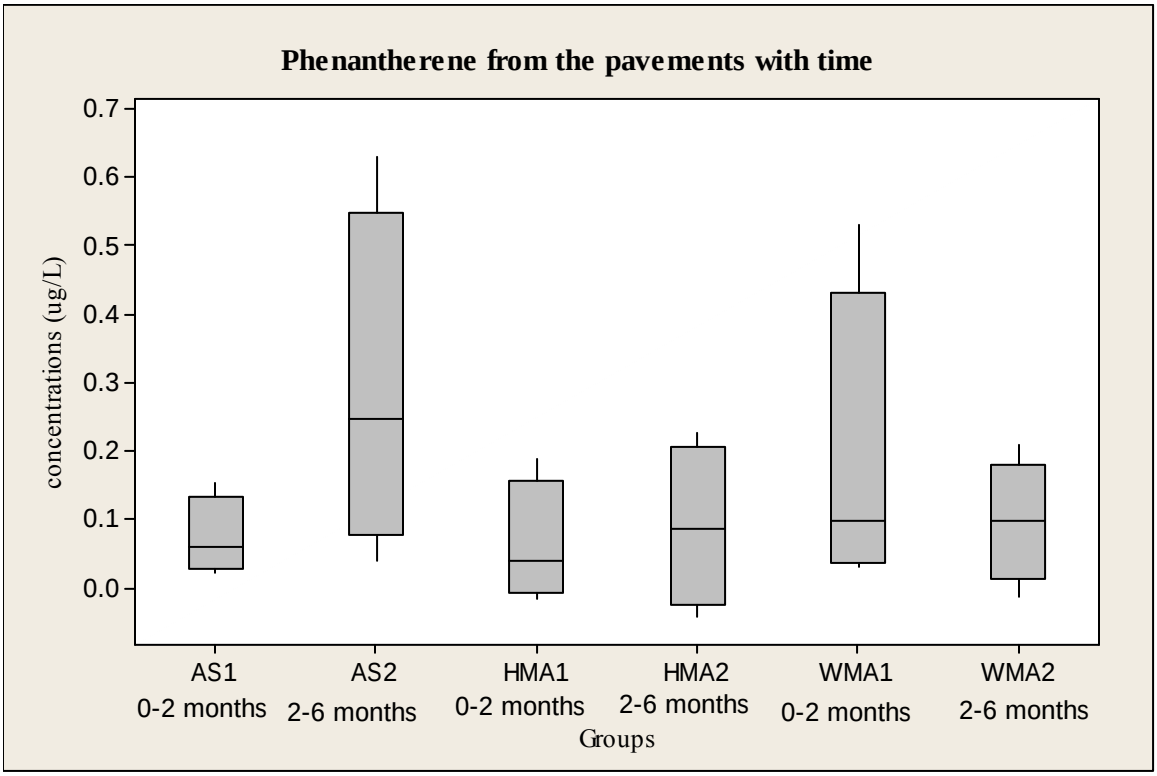


Fig (4.5.9): Phenanthrene from the pavements with aging

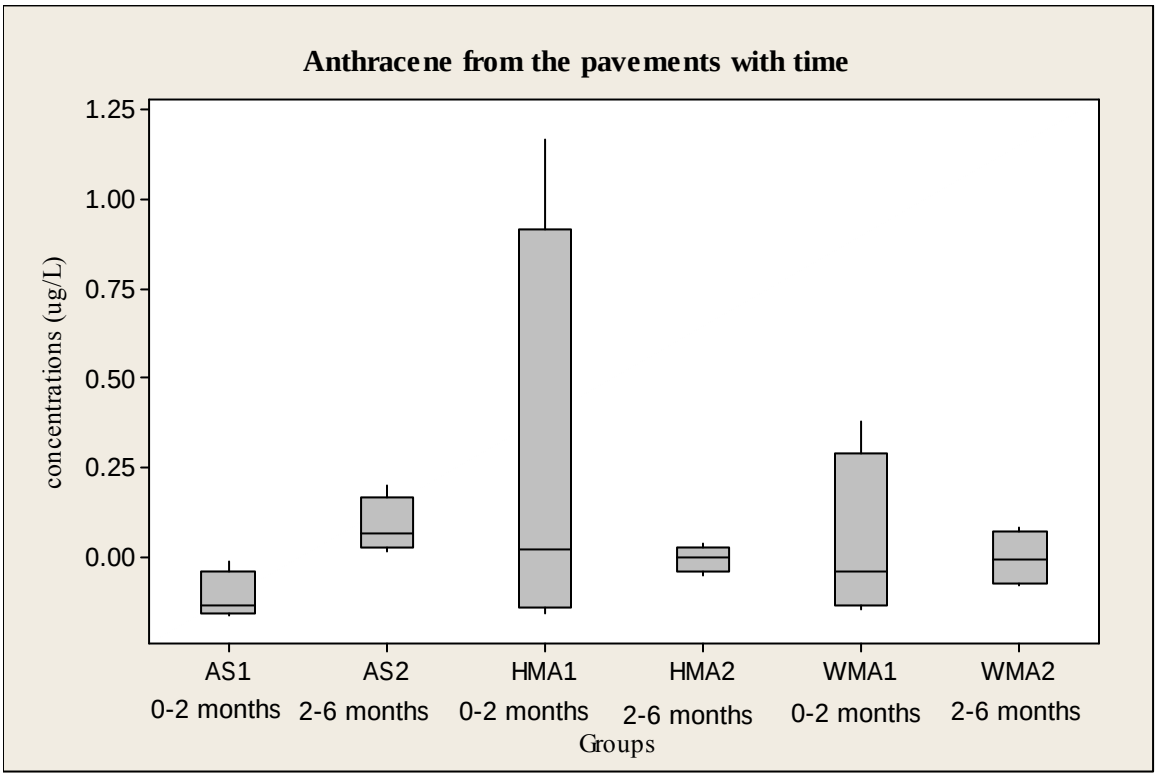


Fig (4.5.10): Anthracene from the pavements with aging.

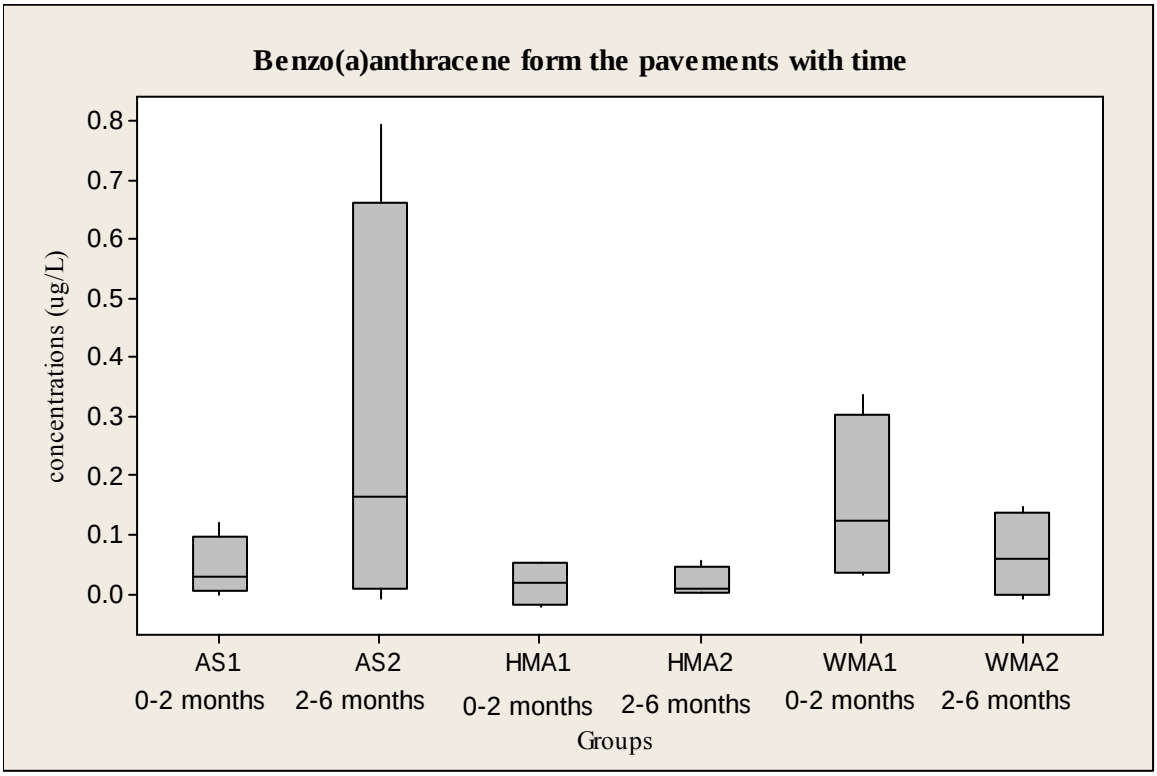


Fig (4.5.11): Benzo(a)anthracene from the pavements with aging.

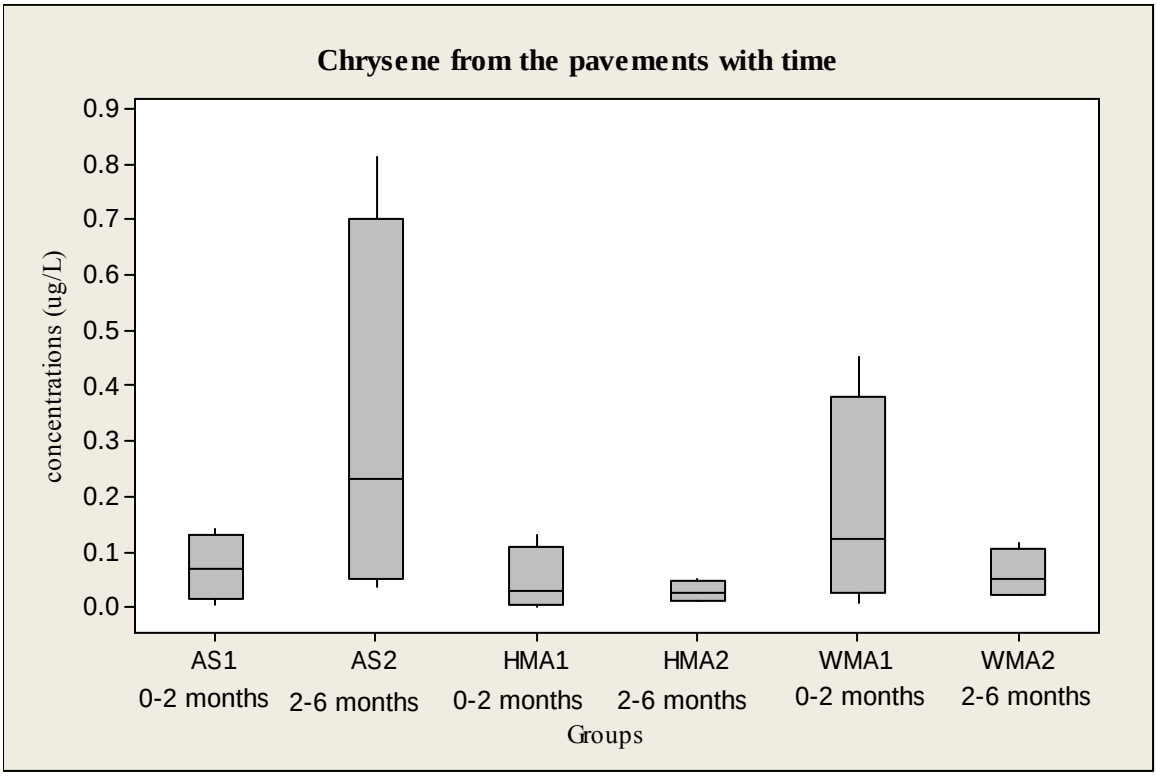


Fig (4.5.12): Chrysene from the pavements with aging.

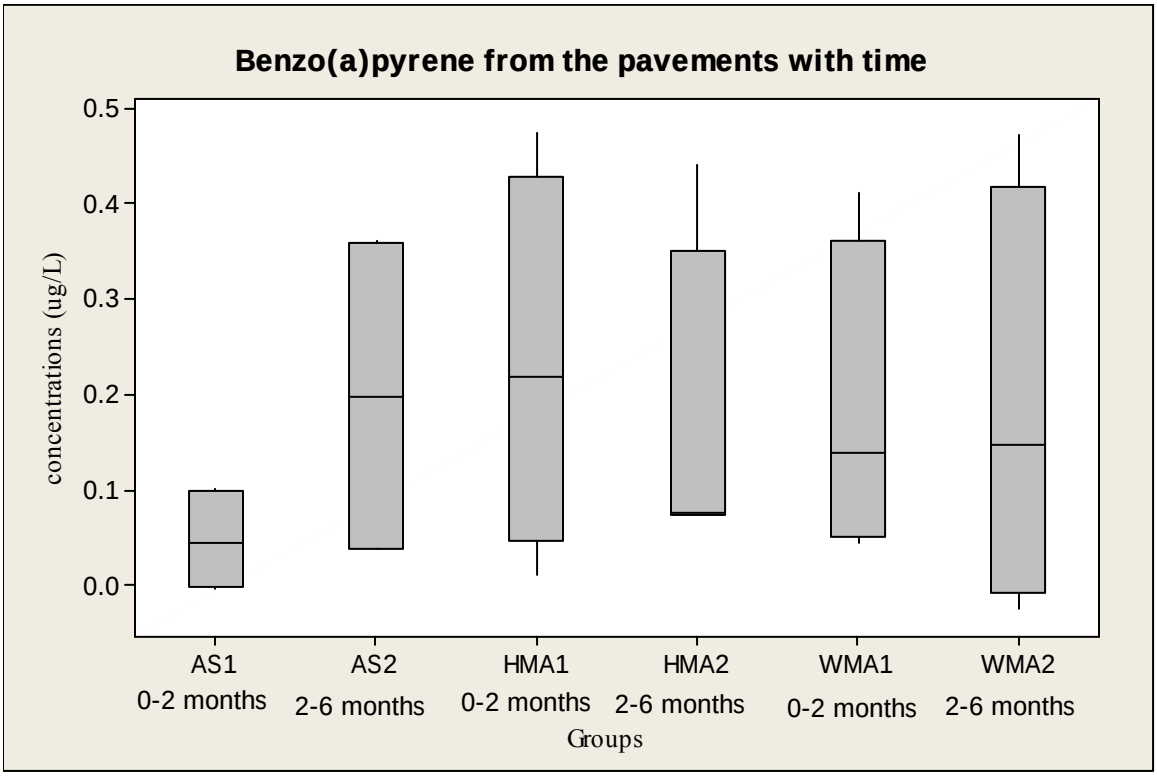


Fig (4.5.14): Benzo(a)pyrene from the pavements with aging.

Summary of Findings

The following table shows the average concentrations of the different constituents in each exposure group for the major constituents studied, along with the corresponding pairwise ANOVA p results comparing the short-term and long-term exposure results. As indicated above, many constituents did not indicate significant differences in concentration between the different pavement types or exposure periods for the limited numbers of samples obtained during the 6 month exposure period. However, nitrates, ammonia, total nitrogen, and COD all had significant differences for exposure periods for some of the samples ($p<0.05$), while total phosphorus, zinc, and naphthalene also had large (but less significant) differences.

Pairwise ANOVA test results for short-term vs. long-term runoff concentrations

		average concentrations in group						p values		
		HMA1	HMA2	WMA1	WMA2	AS1	AS2	HMA1-HMA2	WMA1-WMA2	AS1-AS2
Nitrate	mg/L as N	1.3	4.1	1.4	4.4	1.5	4.1	0.02	0.01	<0.01
Ammonia	mg/L as N	0.27	0.05	0.32	0.01	0.22	0.05	0.09	0.06	0.2
Total Nitrogen	mg/L as N	0.4	1.8	0.8	2.4	0.8	2.3	0.01	0.11	0.05
Total Phosphorus	mg/L as P	0.28	0.59	1.01	0.54	0.38	0.94	0.16	0.41	0.07
COD	mg/L	73	46	86	43	97	38	0.39	0.17	0.03
Detergents (MBAS)	mg/L	0.95	0.85	0.75	0.7	0.58	0.81	0.78	0.86	0.26
Copper	µg/L	0.07	0.086	0.07	0.094	0.076	0.11	0.58	0.4	0.28
Zinc	µg/L	0.036	0.09	0.038	0.11	0.05	0.12	0.24	0.16	0.09
Napthalene	µg/L	0.19	0.26	0.23	0.03	0.13	0.23	0.67	0.11	0.43
Phenanthrene	µg/L	0.062	0.089	0.19	0.1	0.07	0.29	0.74	0.48	0.14
Flouranthene	µg/L	0.07	0.06	0.27	0.1	0.11	0.51	0.83	0.27	0.12
Pyrene	µg/L	0.078	0.072	0.29	0.003	0.12	0.53	0.86	0.21	0.18
Benzo(a)anthracene	µg/L	0.019	0.018	0.16	0.065	0.044	0.28	1	0.31	0.25
Chrysene	µg/L	0.049	0.029	0.18	0.06	0.07	0.33	0.52	0.28	0.2

ANOVA on the linear regression for the nutrients:

	average values (mg/L)			COV values			p - values (slope term/intercept term)		
	HMA	WMA	AS	HMA	WMA	AS	HMA	WMA	AS
Nitrate	2.68	2.92	2.65	0.76	0.72	0.63	0.0001/NA	0.00002/NA	0.00004/NA
Total Phosphorous	0.44	0.80	0.63	0.78	1.19	0.76	0.00003/NA	NA/NA	0.00005/NA
Ammonia	0.16	0.17	0.14	1.26	1.61	1.31	NA/0.03	NA/0.05	NA/0.04
Total Nitrogen	1.1	1.60	1.44	0.90	0.99	0.78	0.0003/NA	0.002/NA	0.006/NA
COD	59.4	64.2	70.3	0.77	0.74	0.61	NA/0.03	NA/0.01	0.02/0.0003
Detergent	0.9	0.73	0.68	0.57	0.55	0.44	NA/0.01	NA/0.02	NA/0.01

Average and COV values for PAHs with no differences with time of exposure:

	Average (ug/L)			COV		
	HMA	WMA	AS	HMA	WMA	AS
Napthalene	2.7	1.5	2.2	0.9	1.3	0.8
Acenapthlylene	0.12	0.02	0.04	1.4	2.7	2.0
Fluorene	0.19	0.21	0.3	1.1	1.2	1.1
Phenanthrene	0.91	1.7	2.2	1.1	1.1	1.1
Benzo(a)anthracene	0.22	1.3	1.9	1.5	1.0	1.6
Chrysene	0.47	1.4	2.4	0.99	1.1	1.3
Benzo(a)pyrene	2.4	2.2	1.5	0.84	0.9	1.1

Average and COV values for metals and toxicity:

	AVERAGES (mg/L)			COV		
	HMA	WMA	AS	HMA	WMA	AS
Zinc	0.06	0.07	0.08	1.1	1.05	0.77
Copper	0.08	0.08	0.09	0.55	0.51	0.49
Toxicity (45 min exposure)	31	41	21	0.79	0.9	1.4

Chapter 5 Conclusions

The main objectives of this research were to:

- Identify any patterns of runoff concentrations of contaminants from newly prepared unsealed pavement materials and pavements with freshly laid sealant with time. To assess the differences in the release of the contaminants in the early stages to that of aged pavements.
- To compare the release of contaminants from the unsealed pavements to the sealed pavements.
- To assess the toxicity of the leachate from the pavements during the early age of the pavement when more contaminants are expected to be released.

The results from this project conclude that:

- No consistent trends were observed for all contaminants from the pavements during the first six months of aging of the pavements, but significant trends were observed for some constituents. Ten sampling times were obtained at irregular times (more frequent at the beginning and fewer near the end), for this study. Additional data observations would increase the power of the analyses allowing smaller trends to be significantly identified. The observed trends were contradictory to what was expected from the literature review, in that the runoff concentrations increased with time during the 6 month exposure period.
- Nitrate concentrations from the pavement with asphalt sealant, total nitrogen from the hot mix pavement, and COD from the pavement with sealant indicated significant concentration increases with time.
- Detergents were observed in runoff from all of the pavement samples, but with no apparent.
- Observed heavy metals in the runoff samples were zinc and copper, with apparent increasing concentration trends, especially noticeable towards the end of the experiment. Cadmium and chromium were not detected in any runoff samples, while lead was only detected in a few of the samples.

- PAHs were observed in the pavement runoff samples at very low concentrations (generally <1 ug/L). Some of the PAHs in the asphalt sealant samples indicated apparent increasing trends with aging, compared to the unsealed pavements.
- Toxicity in the runoff from all the three pavement types was high during the six months test duration. No significant trends were observed in the patterns of the toxicity from the runoff, contradictory to what was expected based on the literature. Runoff samples from the warm mix pavement showed the highest toxicity values.

These tests focused on pavement runoff characteristics during a relatively short 6 month exposure period. The majority of observed significant concentration trends with time indicated increasing concentrations. However, the literature indicates that runoff characteristics from newly laid asphalt should decrease with time. It is likely that the observed concentrations would decrease eventually with longer exposure periods.

Chapter 6:
Deepwater Horizon Oil Spill Degradation with Grand Isle, LA, Area Beach Sand

6.1. Site description

Six soil samples were collected from Gulf of Mexico and infrared scans were performed on the samples to test for presence of oil. The samples were collected in glass jars from six different locations from Grand Isle, LA. Since the beach was off limits, the pictures of the sample location sites were taken from a pier overlooking the beach as seen Image (1) to Image (7).

Image 1: Cleanup crews, view towards southwest from the pier.

Image 2: Same view as previous panned slightly right (less south, more west): showing accumulated sand piles, security fences, and hauling vehicles.

Image 3 – First available access past (southwest of) State Park boundary, looking southwest. Left-to-right, shows clean-up personnel, oily-sand pile, sand collector (that looked a lot like a street-sweeper collecting about 3 to 4 inches per sweep), sand pile, massive dump truck (and an apparent front-end loader beside a sand pile is out of view), multiple sand piles, and security-fence to the horizon. All above are from Gulf of Mexico (marine) side of the island.

Image 4 – First available access to Barataria Bay (estuarine) side of the island (was dominated by gated residential communities and fenced/guarded industrial sites, latter of which included the local FEMA HQ).

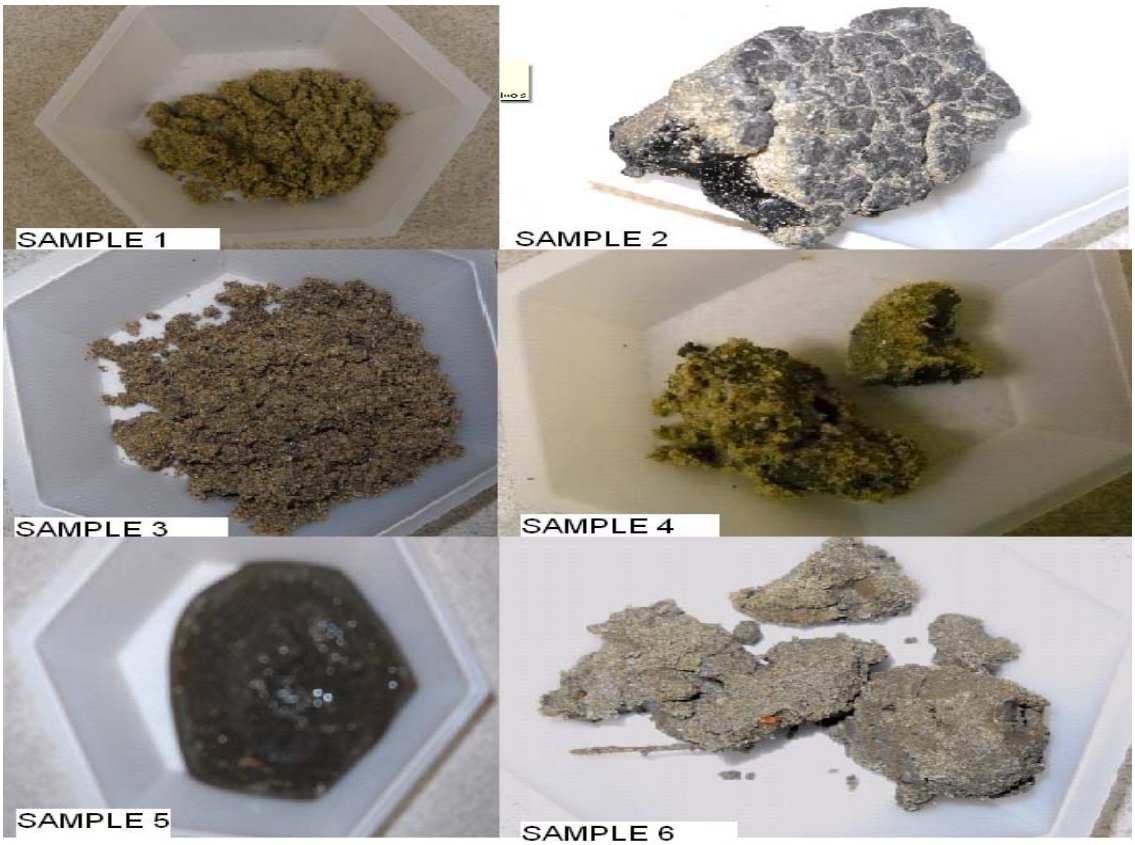
Image 5 – Site of sample 1, Apparent “tar balls” (gray in color, texture that would be best described as slick/sticky* but no sandy grit in interior) on shore of a seafood-company boat-slip (situation picture at Image 5, looking generally north, from the un-fenced side of the slip). [*slick/sticky – If you rub it back and forth between your fingers, it’s fairly frictionless. If you then try to pull your fingers apart, they really try to stick together]

Image 6 – First available access to the marine (Gulf) waterfront (terminus of security fence easily visible to the northeast from this location). Site of Sample-3, very dark gray, sprinkles appeared to be actively washing ashore in (calm) surf. Sprinkles were slick/sticky but not gritty when ground between fingers. Sample-3 included a few "brown gobs" (slick/greasy*, but with incorporated sandy texture, visually more like what was described as weathered tar balls on TV) that were intimately co-located. Sample-2 was also taken near here (directly up-gradient) above the apparent high-tide line (well dried rind, smelled distinctly of hydrocarbon when broken, but nothing but sticky inside). [*slick/greasy - little friction when rubbed (except for obvious sand), little resistance to pulling fingers apart]

Image 7 – Marine side. Denser (further from active clean-up activities and further from Macondo) wash-up of sprinkles. Material obviously washing up with every wave, and actively being disgorged from clam holes between waves. Site of Sample-5. Note that Sample-5, by necessity of location in active wave region, included a good deal of sand and seawater. Sampling location, however, allowed for exclusion of any apparent brown gobs. Sample-4 (all brown gobs) was collected about 1 meter (near the apparent high-tide line) up-gradient from this picture.

Image 8 – Not on Grand Isle, Estuarine side, but very near pass between island and mainland. Location is at boat-slip for a bait-shop/marina. Similar to Sample-1.

6.2. Sample Descriptions



Sample 1: This was loose soil, with small clayey lumps. When in contact with solvent it gave a pale yellow color to the colorless solvent.

Sample 2: This sample had asphalt-like structure and when it was cut open, it had a shiny black surface. It disintegrated rapidly when it was in contact with denatured alcohol, turpentine and toluene and turned the solvent to black color but remained unchanged in presence of acetone.

Sample 3: This was loose soil and looked similar to sample 1 but it was free of any clayey lumps. In presence of solvent, it gave the solvent a brown color.

Sample 4: This sample looked similar to sample 1 but it contained less of the loose particles and more clayey structures. It turned the solvent to brown color.

Sample 5: This sample contained water and had an oily layer on the water surface. When analyzing, the oily layer from the jar was also used. It did not affect the solvent color greatly.

Sample 6: This sample had large clay-like lumps.

6.3. Materials and Methods

Acetone, denatured alcohol, turpentine and toluene were used as solvents for the analysis. For each of the solvents used, six 60 ml Nalgene bottles were labeled and 10 grams of each sample were weighed from each of the glass jars containing each sample and was added to the bottles. Using a measuring cylinder, 30 ml of solvent was added to these bottles, the caps were closed and shaken vigorously, after which it was allowed to sit undisturbed for 30 min. Using a pasture pipette, samples (solvent with the extracted oils) from these bottles were transferred to the sampling cell of the Spectrum RX 1 FTIR and analyzed with the corresponding solvent as the background (background IR spectra was automatically subtracted).

Sampling cell description: A semi demountable liquid sampling cell having calcium fluoride salt plates was used for scanning the samples. A 0.2 mm thick Teflon^{TM} spacer was used to separate the calcium fluoride windows.

6.4. Results

6.4.1. Acetone

When using acetone as the solvent, background, sample 1 and sample 2 showed straight horizontal lines, indicating no contaminants were extracted into the solvent. Whereas sample 3, sample 4, sample 5, and sample 6 showed peaks in the regions 3500 cm-1, 3000cm-1, and 1600 cm-1, indicating the presence of contaminants that were extracted from the respective soil samples, as can be seen in the scan (2) to scan (5) in Appendix A. The area responses of the peaks varied between the samples. The scans of the solvents and the samples after solvent extraction are given Appendix F.

6.4.2. Denatured Alcohol

With denatured alcohol, all the samples showed peaks in the regions 900 cm-1, 1600 cm-1, 2100 cm-1, and 3600 cm-1, as seen in scan (7) to scan (12), indicating the presence of a similar

compound being extracted into the solvent. However, the height and width of the peaks varied greatly among the samples.

6.4.3. Turpentine

With turpentine, all the samples showed very narrow, sharp peaks in the 3000 cm-1 region, while samples 2, 3 and 6 showed a short and wide peak in the region between 3000cm-1 and 3500cm-1, indicating the presence of a similar compound being extracted into the solvent, as seen in the scans (15) to (19) in Appendix A.

6.4.5. Toluene

With toluene as the solvent, all the samples showed narrow peaks in the 3000 cm-1 region. The peaks were short for sample 5, but relatively higher for the samples 1, 2 and 3. Samples 4 and 6 could not be analyzed with this solvent because of insufficient sample. The scans can be seen in Appendix A, scan (21) to scan (24).

Table of principle peaks for the analyzed samples

Acetone

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	-	-	-
Sample 2	-	-	-
Sample 3	3500 cm-1	14.4 cm	1.9 cm
	3000 cm-1	8.5 cm	0.05 cm
	2000 cm-1	3.3 cm	1.5 cm
	1650 cm-1	13.8 cm	0.6 cm
	1250 cm-1	6.5 cm	1.3 cm

	1200 cm-1	8 cm	0.05 cm
	1125 cm-1	4.3 cm	0.6 cm
	1000 cm-1	4.4 cm	1.2 cm
Sample 4	3625 cm-1	13.5 cm	1.15 cm
	3000 cm-1	7.1 cm	0.05 cm
	1937.5 cm-1	1.8 cm	2.1 cm
	1625 cm-1	11 cm	0.5 cm
	1250 cm-1	4.1 cm	0.7 cm
	1187.5 cm-1	2.8 cm	0.7 cm
Sample 5	3500 cm-1	14.5 cm	2.3 cm
	2062.5 cm-1	6.3 cm	1.8 cm
	1625 cm-1	13.6 cm	0.7 cm
	1250 cm-1	6.1 cm	0.5 cm
	1125 cm-1	7.3 cm	0.65 cm
	937.5 cm-1	11.15 cm	1.3 cm
Sample 6	3500 cm-1	13.5 cm	2 cm
	2000 cm-1	4 cm	1.4 cm
	1625 cm-1	11 cm	0.5 cm
	1281.5 cm-1	1.4 cm	0.2 cm
	1125 cm-1	3.7 cm	1.45 cm

	1000 cm-1	5.2 cm	1.2 cm

Denatured Alcohol

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	3625 cm-1	14.1 cm	0.4 cm
	2187.5 cm-1	7.8 cm	2 cm
	1625 cm-1	14.5 cm	1.6 cm
	1281.25 cm-1	3.8 cm	<0.05 cm
	1125 cm-1	10.5 cm	0.8 cm
	984.375 cm-1	12.5 cm	0.5 cm
Sample 2	3625 cm-1	13 cm	0.4 cm
	2187.5 cm-1	6.8 cm	1.9 cm
	1625 cm-1	13.8 cm	1.9 cm
	1406.25 cm-1	7.5 cm	<0.05 cm
	1281.25 cm-1	1.5 cm	<0.05 cm
	1125 cm-1	6.3 cm	0.9 cm
	984.375 cm-1	12 cm	0.6 cm
Sample 3	3625 cm-1	13.6 cm	0.5 cm
	2187.5 cm-1	7.5 cm	1.8 cm

	1625 cm-1	14.4 cm	1.5 cm
	1406.25 cm-1	5.4 cm	<0.05 cm
	1125 cm-1	9.2 cm	0.8 cm
	984.375 cm-1	11.8 cm	0.7 cm
Sample 4	3625 cm-1	12.6 cm	0.4 cm
	3250 cm-1	1.5 cm	<0.05 cm
	2187.5 cm-1	6.4 cm	1.9 cm
	1625 cm-1	13.5 cm	1.2 cm
	1125 cm-1	6.5 cm	1 cm
	984.375 cm-1	10.2 cm	0.5 cm
Sample 5	3625 cm-1	14.5 cm	0.7 cm
	2187.5 cm-1	11.9 cm	2.1 cm
	1625 cm-1	14.5 cm	3.3 cm
	1281.25 cm-1	13.3 cm	<0.05 cm
	1125 cm-1	11.1 cm	1 cm
	984.375 cm-1	13 cm	0.5 cm
Sample 6	3625 cm-1	14.5 cm	0.5 cm
	2187.5 cm-1	11 cm	2.1 cm
	1625 cm-1	14.5 cm	2.6 cm
	1125 cm-1	12.7 cm	1 cm

	984.375 cm-1	13 cm	0.5 cm

Turpentine

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	2812.5 cm-1	4.4 cm	<0.05 cm
	1437.5 cm-1	8.5 cm	<0.05 cm
	1000 cm-1	3 cm	0.004 cm
Sample 2	3250 cm-1	1 cm	1.2 cm
	2812.5 cm-1	8.7 cm	0.05 cm
	1062.5 cm-1	2 cm	0.6 cm
Sample 4	Not analyzed	Not analyzed	Not analyzed
Sample 3	3250 cm-1	1 cm	1.1 cm
	3000 cm-1	11.5 cm	<0.05 cm
	2812.5 cm-1	2 cm	<0.05 cm
	1437.5 cm-1	5.5 cm	<0.05 cm
	1062.5 cm-1	2.3 cm	0.5 cm
	750 cm-1	5.5 cm	<0.05 cm
Sample 5	3000 cm-1	0.6 cm	<0.05 cm

	1468.75 cm-1	5 cm	<0.05 cm
	1437.5 cm-1	7.4 cm	<0.05 cm
	1000 cm-1	4.8 cm	<0.05 cm
	890.625 cm-1	6.7 cm	0.2 cm
Sample 6	3250 cm-1	2.4 cm	1.1 cm
	3000 cm-1	2.3 cm	<0.05 cm
	2875 cm-1	7 cm	<0.05 cm
	1000 cm-1	3.7 cm	0.4 cm

Toluene

Sample ID	Peaks at wavelength	Height of the peak	Width of the peak at 50% height
Sample 1	3000 cm-1	13.1 cm	<0.05 cm
	2875 cm-1	12 cm	0.3 cm
	1062.5 cm-1	5 cm	<0.05 cm
Sample 2	3000 cm-1	11.8 cm	0.1 cm
	2875 cm-1	10.8 cm	0.1 cm
	1593.75 cm-1	5.7 cm	0.1 cm
	1062.5 cm-1	7.6 cm	<0.05 cm
Sample 3	3000 cm-1	5.1 cm	0.1 cm
	2875 cm-1	10 cm	0.05 cm

Sample 4	Not analyzed	Not analyzed	Not analyzed
Sample 5	2875 cm-1	4.7 cm	0.05 cm
	1062.5 cm-1	14.5 cm	<0.05 cm
Sample 6	-	-	-

7. IR scans of crude oil samples:

After soil-sand samples from the Deepwater Horizon spill were analyzed using the IR spectroscope, crude oil sample from Fayetteville, AL mixed with sand were aged in a UV chamber and periodically sampled and analyzed to determine the degradation of the oil. Acetone was used as the solvent. The aging tests of this local crude oil sample was followed by analyzing crude oil samples from ONTA, Ontario, Canada. Six sets of crude oil samples were obtained from the company, four of the sets contained four crude oil samples and two sets contained six crude oil samples and the oils were numbered 1-4 and 1- 6 in the sets and the oils increased in viscosity, with crude oil # 1 being the least viscous to crude oil # 6 being the most viscous.

For example, Crude oil set # 5 numbered 1005, 2005, 3005, 4005, 5005 and 6005 are paraffinic (light, sweet), paraffinic-naphthenic (light-medium, sweet-sour*), naphthenic (medium, sour*), aromatic- intermediate (medium-heavy, sour*), aromatic-naphthenic (heavy, sour*), and aromatic-asphaltic (extra-heavy, sour*) oils, respectively.

These crude oil sets were collected from different parts of the world, from USA, Nigeria, Iraq and South America. The crude oil set # 1 and set # 2 are replicates, set # 3 and set # 4 are replicates and set # 5 and set # 6 are replicates. Set # 5 and set # 6 were found to be relatively more viscous than the remaining sets. Set # 6 could not be analyzed because of its high viscosity; it stained the salt plates and could not be spread easily on the salt plates.

Some of these samples (sample # 1001,1002,1003,1004, 1005) were also aged under UV, similar to the above method but without the sand.

7.1. Materials and Methods

30ml of Fayetteville crude oil was mixed with 100 gms of sand in a glass container and mixed such that all the sand particles were coated with the crude oil. The glass container had a wide mouth and was placed in a RPR 100 UV chamber. An oil-sand subsample was periodically taken from this container and analyzed using the Spectrum RX 1 FTIR, with acetone as the solvent. Five grams of the oil-sand mixture was weighed out for each subsample from the glass jar. This was then added to 30 ml of acetone in 60 ml Nalgene bottles. The Nalgene bottles were then shaken well and allowed to stand for 30min before pipetting out the oil-acetone mixture into the sampling cell of the Spectrum RX1 FTIR.

Sampling cell description: A semi demountable liquid sampling cell having calcium fluoride salt plates was used for scanning the samples. A 0.2 mm thick Teflon^{TM} spacer was used to separate the calcium fluoride windows.

7.2. Results

The initial IR scan showed wide peaks at 3600-3400 cm-1, 3000-2800 cm-1, 1700-1600 cm-1, 1500- 1350 cm-1, and 1230-1250cm-1. These peak heights and areas were reduced with time with the continued exposure to UV lights. After 5 days of aging under the UV light, the scan showed a straight line with no peaks, indicating complete degradation. The scans for this experiment covering the one day to five days exposures, are in Appendix G.

In contrast, the crude oil samples obtained from Canada that were aged under UV without the sand (due to minimal sample volumes) did not show any degradation even after three weeks of UV light exposure. The IR scans of the samples are given in Appendix H.

Wavelengths and transparencies of principle peaks for the analyzed samples

Fayetteville Crude Oil with sand at 0 hr.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil (0)	4322.9	43.54

	4249.6	49.19
	4050.4	60.53
	3610.2	80.10
	3180.5	59.57
	2887.0	0.04
	2729.8	26.3
	2656.4	39.20
	2402.9	72.40
	2195.3	79.75
	2038.3	82.05
	1940.4	82.18
	1893.2	79.70
	1741.3	70.38
	1704.6	65.76
	1605.0	38.56
	1453.0	0.04
	1374.4	0.08
Fayetteville Crude Oil sampled after 3hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil (1)	4185.8	42%

	3414.4	1.86
	3002.5	0.50
	2858.5	22.14
	2579.2	88.84
	2444.7	90.01
	2145.4	81.35
	1679.3	0.12
	1443.6	0.05
	1233.9	0.09
	1093.7	1.16
Fayetteville Crude Oil sampled after 24hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(2)	4259.0	86.60
	3595.9	17.38
	3396.4	56.69
	2911.8	3.24
	2857.7	4.80
	2729.5	83.47
	2547.5	89.87
	2391.3	90.45

	2178.5	90.40
	2042.7	86.44
	1755.0	74.36
	1698.2	30.15
	1640.9	49.56
	1376.1	43.40
	1276.2	94.55
	1147.3	89.63
Fayetteville Crude Oil sampled after 48hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(2)	4258.4	93.79
	3605.6	36.44
	3396.1	76.74
	2918.3	4.68
	2857.0	14.05
	2730.9	92.27
	2043.7	94.52
	1684.2	30.96
	1641.9	64.79
	1396.7	32.06

	1355.5	15.13
	1277.2	97.98
	1230.7	32.89
	1152.3	94.92
Fayetteville Crude Oil sampled after 72hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(3)	4261.6	95.24
	3606.8	74.01
	3387.2	92.83
	3000.6	63.32
	2928.7	2.94
	2192.4	97.73
	2043.2	96.87
	1757.6	33.08
	1640.4	91.62
	1340.3	20.03
	1282.3	99.84
	1148.9	97.53
Fayetteville Crude Oil sampled after 96 hr UV light exposure with Acetone as the solvent.		

Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(4)	3601.1	58.25
	3006.4	40.40
	2952.6	90.29
	2916.1	75.31
	1755.0	24.02
	1727.9	62.47
	1454.0	51.05
	1452.4	45.31
	1427.5	32.03
	1219.5	71.37
Fayetteville Crude Oil sampled after 120 hr UV light exposure with Acetone as the solvent.		
Sample ID	Wavelength (cm-1)	Transparency (%)
Crude Oil(5)	3595.1	79.45
	2856.9	37.61
	1752.0	22.37
	1699.4	32.34
	1427.8	32.60
	1228.7	19.42
	1090.2	46.51

Wavelength and Principle Peaks of the Crude Oil Samples from Ontario, CA.

Sample ID	Wavelength (cm-1)	Transperancy (%)
1001	4330.1	45.91
	4258.1	51.50
	4067.6	65.46
	2925.4	3.06
	2729.3	32.50
	2670.1	39.68
	2404.8	82.93
	2026.2	90.69
	1902.8	90.42
	1701.6	73.75
	1606.7	47.01
	1459.0	3.38
	1376.8	3.95
	1304.0	26.99
	1169.3	45.61
	1076.6	50.84
	1032.3	46.98

2001	4330.0	29.36
	4254.7	33.37
	3607.3	52.68
	2923.5	0.60
	2729.3	23.12
	2670.8	27.86
	2398.7	55.10
	2314.4	55.53
	1706.1	36.58
	1606.9	32.37
	1455.5	1.38
	1376.8	1.83
	1303.6	15.94
	1169.1	27.24
	1031.9	28.63
3001	4329.7	47.07
	4257.7	53.67
	4067.9	65.42
	2919.8	0.04
	2729.3	29.26

	2671.8	42.90
	2313.9	84.45
	1868.1	85.53
	1605.2	24.40
	1468.2	0.03
	1377.1	0.03
	1167.7	26.35
	1031.8	28.18
4001	4329.5	47.84
	4254.7	54.21
	4066.5	65.30
	2930.7	0.99
	2728.9	31.03
	2669.7	42.39
	2313.9	82.45
	1906.6	82.73
	1604.2	20.92
	1459.5	1.18
	1376.7	1.25
	1169.0	25.19

	1032.3	27.46
1002	4330.2	43.22
	4258.4	48.93
	4068.1	63.91
	2849.4	0.01
	2729.4	30.54
	2670.3	38.14
	2401.7	83.25
	2308.7	85.35
	2027.1	89.02
	1902.0	88.32
	1701.9	71.12
	1606.8	44.21
	1446.6	0.03
	1377.2	0.07
	1304.0	24.47
	1169.3	44.49
	1076.9	50.28
	1032.3	46.25
	965.9	35.66

	885.6	36.80
2002	4330.4	42.63
	4258.2	48.14
	2921.7	0.46
	2729.3	30.64
	2671.0	37.51
	2401.5	82.47
	2314.3	83.46
	2027.0	87.80
	1902.4	88.21
	1706.9	58.96
	1606.3	47.35
	1456.4	0.75
	1377.2	0.97
	1303.8	23.66
	1169.2	43.53
	1076.8	48.66
	1031.9	47.08
3002	4329.7	47.78
	4257.7	54.02

	4068.3	65.33
	2924.8	2.24
	2729.2	32.26
	2671.8	45.45
	2402.1	81.74
	2312.7	84.35
	2027.6	88.81
	1867.9	82.75
	1601.9	26.8
	1455.5	2.87
	1377.4	3.34
	1167.6	29.16
4002	4329.4	46.50
	4257.6	52.40
	4067.4	64.40
	2925.4	0.01
	2728.8	31.01
	2670.2	42.58
	2027.2	87.98
	1905.6	80.41

	1604.1	18.38
	1468.8	0.01
	1376.5	0.07
	1168.9	24.34
1003	4329.9	41.06
	4258.1	46.05
	4067.0	57.13
	2882.1	0.00
	2728.9	25.97
	2670.0	34.28
	1900.1	79.59
	1707.6	62.50
	1606.2	36.32
	1448.1	0.04
	1377.2	0.09
	1304.6	20.16
	1168.8	25.75
2003	4329.7	47.78
	4257.7	54.02
	4068.3	65.33

	2924.8	2.24
	2729.2	32.36
	2671.8	45.45
	2402.1	81.74
	2312.7	84.35
	2027.6	88.81
	1867.9	82.75
	1605.1	25.91
	1455.5	2.87
	1377.4	3.34
	1167.6	29.16
	1377.4	3.34
	1167.6	29.16
	1031.9	30.65
3003	4330.3	40.74
	4258.1	47.04
	4068.1	57.49
	2974.0	0.03
	2729.7	26.77
	2671.1	37.94

	2033.9	81.02
	1903.8	76.52
	1604.5	25.94
	1458.2	0.02
	1376.9	0.02
	1307.0	13.21
	1155.7	19.80
4003	4329.5	42.83
	4258.0	47.96
	4067.6	58.10
	2890.0	0.06
	2728.4	25.56
	2669.6	35.27
	1903.8	77.42
	1708.3	44.20
	1605.4	29.32
	1449.7	0.02
	1376.6	0.06
	1168.4	20.87
1004	4330	40.98

	4258.1	46.06
	4067.3	57.04
	3902.9	70.65
	3854.1	69.64
	3839.2	71.02
	3821.8	71.22
	3802.3	72.65
	3751.6	72.99
	3735.7	73.84
	3712.0	75.75
	3690.1	75.81
	3676.0	75.43
	3649.9	75.21
	3629.8	76.40
	3567.7	81.72
	2868.3	0.10
	2729.0	25.88
	2669.9	34.21
	2366.1	71.65
	1890.1	78.64

	1772.0	74.05
	1734.0	69.07
	1700.6	60.09
	1684.4	63.55
	1653.8	63.13
	1606.5	35.83
	1559.4	55.73
	1540.1	53.64
	1444.1	0.07
	1376.6	0.10
	1304.7	20.48
	1169.0	25.69
2004	4329.4	41.87
	4258.2	46.66
	4067.6	57.62
	3903.0	70.68
	3854.1	69.59
	3839.1	71.07
	3821.8	71.25
	3802.3	72.84

	3751.6	73.04
	3735.8	73.98
	3712.0	75.51
	3690.2	76.05
	3676.0	75.65
	3649.9	75.41
	3619.6	75.51
	3567.5	80.26
	2882.0	0.00
	2728.5	26.78
	2668.7	34.58
	2407.5	71.51
	1890.1	77.75
	1734.1	67.14
	1700.4	59.34
	1684.2	61.51
	1670.0	62.89
	1653.8	59.74
	1605.9	30.17
	1559.6	53.21

	1540.2	51.77
	1450.5	0.02
	1376.5	0.05
	1305.4	19.52
	1169.2	23.33
3004	4330.2	40.65
	4257.7	46.95
	4068.0	57.62
	3903.0	70.55
	2904.0	0.02
	2729.6	26.54
	2671.8	37.54
	2028.3	80.60
	1907.9	75.63
	1734.0	67.48
	1684.1	56.13
	1604.4	24.75
	1461.3	0.01
	1377.5	0.08
	1155.9	19.34

4004	4329.4	42.93
	4257.8	48.00
	4067.1	58.21
	2914.1	0.01
	2728.4	25.50
	1890.0	76.55
	1706.9	43.03
	1605.6	29.13
	1459.6	0.04
	1376.8	0.10
	1168.6	20.92
1005	4329.4	42.31
	2558.5	47.09
	3619.9	77.83
	2924.6	0.51
	2828.4	27.95
	2363.4	70.58
	1892.4	78.22
	1708.1	62.18
	1605.8	30.73

	1458.7	1.37
	1376.7	1.79
	1305.2	20.47
	1169.0	24.06
2005	4329.1	42.31
	4252.8	46.73
	2924.6	0.51
	2729.1	27.73
	2406.7	72.73
	1900.9	78.94
	1605.7	33.38
	1457.9	0.90
	1376.9	1.03
	1156.1	27.84
3005	4329.6	42.74
	4257.4	47.83
	2944.4	0.00
	2728.4	25.47
	1708.1	44.52
	1605.4	29.06

	1446.1	0.00
	1376.5	0.01
	1168.4	20.85
4005	4330.1	38.49
	4257.8	44.59
	2929.9	0.00
	2031.6	79.99
	1904.7	75.67
	1604.9	23.08
	1469.5	0.00
	1376.6	0.04
	1306.4	11.86
	1156.1	18.79
5005	4328.5	40.45
	4256.8	45.46
	3177.1	44.15
	2865.7	0.00
	2670.0	33.98
	1696.5	44.10
	1604.0	14.28

	1451.3	0.01
	1374.3	0.02
	1168.3	15.84

APPENDIX A Preparing Hot-Mix Asphalt Specimens (HMA) by Means of the Rolling Slab Compactor

1. Apparatus

1.1 Rolling Slab Compactor – A rolling compactor with a hydraulically lifted platform. The lift platform shall have a pressure gage capable of measuring pressure up to 3,000 psi. The platform shall be capable of being uniformly lifted (manually or automatically) across the bottom of the platform.

1.2 Specimen Mold – A rectangular, 2-piece, steel mold with walls at least 9 mm thick. When the mold is assembled it shall have inside dimensions of 510 mm by 507 mm. It shall have a height of 228 mm. The dimension perpendicular to the side marked "Front" is the length dimension specified in Section 3.1.

1.3 Base Insert Frame – A steel framed spacer with dimensions of 509 mm by 506 mm by 40 mm.

1.4 Thick Insert Plates – Steel plates with dimensions of 509 mm by 506 mm by 10 mm.

1.5 Thin Insert Plates – Steel plates with dimensions of 509 mm by 506 mm by 3 mm.

1.6 Vertical Kneading Plates – Steel plates that go on top of mix that are 105 mm by 10 mm by 505 mm. They are 105 mm tall when standing on their 10 mm side. There are 49 of the 10 mm kneading plates and one 3 mm thick plate.

1.7 Wax Paper – Paper coated with wax so the HMA will not stick to it.

1.8 Metal Partition – A metal partition capable of dividing the mix into four quadrants.

1.9 Mix Transfer Funnel – A metal device with a tapered end capable of transferring mix from pans into the four quadrants created by the splitter.

1.10 Thermometers – Armored, glass, or dial type thermometers with metal stems for determining the temperature of aggregates, binder, and HMA up to 204 °C and readable to 1°C.

1.11 Balance – A balance meeting the requirements of AASHTO M 231, Class G 5, for determining the mass of aggregates, binder, and HMA.

1.12 Oven – An oven thermostatically controlled to ±3°C, for heating aggregates, binder, HMA, and equipment as required. The oven shall be capable of maintaining the temperature required for mixture conditioning in accordance with AASHTO R 30.

1.13 Miscellaneous – Flat bottom scoop, large trowel, vice grips, rubber mallet, screw driver and mechanical jack.

2. Equipment Preparation

2.1 Determine the number of insert plates needed to achieve desired slab thickness. Table 1 shows plates needed to achieve different thicknesses.

Table 1: Number of base plates required to reach desired slab thickness

Slab Ht. (mm)	Frame	10 mm plates	3 mm plates
113.3	no	1	0
110.0	no	1	1
103.8	no	2	0
100.5	no	2	1
94.3	no	3	0
91.0	no	3	1
79.9	yes	0	1
73.7	yes	1	0
70.4	yes	1	1
64.2	yes	2	0
60.9	yes	2	1
54.7	yes	3	0
51.4	yes	3	1
45.2	yes	4	0
41.9	yes	4	1

2.2 Cut two pieces of wax paper, one for the top and one for the bottom, to fit in mold by using one of the insert base plates as a template.

2.3 Place assembled mold, base plates, and partition in an oven set to the desired compaction temperature a minimum of 30 minutes prior to compaction.

3. Material Preparation

3.1 Determine mass of total mix needed to achieve desired height and air voids (usually target 7%). Equation 1 shows how to calculate total mix mass.

$$m_T = (lwt)(G_{mm} * \rho_w)\left[\frac{(100 - \%V_a)}{100}\right]$$

where:

m_T = total mass of slab in g;

l = length of slab, 509.5 mm;

w = width of slab, 506.5 mm;

t = desired thickness of slab in mm;

G_{mm} = theoretical maximum specific gravity of the mix;

V_a = desired percent air voids of slab, usually 7%;

ρ_w = density of water, 0.001 g/mm^3.

3.2 Prepare four separate batches. Determine the total mass of each batch by dividing m_T by four.

3.3 Mix each batch separately and set aside.

3.4 Place all 4 pans in oven for two hours at 300°F, or the desired compaction temperature, in accordance with AASHTO R 30.

3.5 For specimens using field mix, sample according to AASHTO T 168. Reduce the mix to batch size using Method B in AASHTO T 328.

4. Procedure

4.1 When the compaction temperature of the mix is achieved, remove the heated mold and assemble it on the mechanical jack with the side marked “Front” facing the jack.

4.2 Place base frame in mold. Place base plates in mold.

4.3 On the top base plate, place a piece of pre-cut wax paper.

4.4 Place the metal partition on top of the wax paper. Pour mix from one pan into the mix transfer funnel, then into one quadrant. Pour the next into the mix transfer funnel and then into the quadrant diagonally across from the first quadrant. Repeat for the other two pans.

4.5 Carefully remove the metal partition from the mix.

4.6 Spade the mix with a large trowel until the mix is at a relatively uniform depth. Then level the mix out with the trowel, taking care not to segregate the mix. The mix should be kept in the vicinity of the quadrant in which it was poured.

4.7 Place the other piece of wax paper on top of the leveled mix.

4.8 Place 49 vertical kneading plates on the mix, taking care not to wrinkle the paper or move the mix. Put the plates in simultaneously from each side. The plates should be orientated perpendicular to the front of the compaction mold. The rubber mallet may be required to get the last plate in the mold.

4.9 Move specimen mold to the rolling compactor using the mechanical jack. Adjust the jack platform with the specimen mold until it is level with the compactor platform. Slide the mold onto the compactor’s platform with one person guiding from behind the compactor and one person pushing from the front. Do this in one uniform motion. Take care not to let the frame or bottom plate slip out of the bottom of the mold.

4.10 Once mold is set on the platform make sure the entire base of the mold is touching the platform. The rubber mallet may be needed here.

4.11 Turn hydraulic valves to the closed position and turn the roller on. Lift the mold and platform to the roller by pumping the hydraulic handle.

4.12 When the top of the kneading plates reaches the roller, stop pumping the handle and let the roller roll atop the kneading plates. Now only pump the handle when the roller is at the ends of the mold. This will pick up the other end of the mold. Slightly pump the handle each time the roller goes to the end without letting the pressure go above 1200 psi. If the pressure is increasing too rapidly, let out a small amount of pressure using the hydraulic valves. Continue gradually lifting the compaction platform until the kneading plates are level with the top of the mold.

4.13 Stop the roller and release the pressure so that the platform is lowered.

4.14 Slide specimen mold back onto the mechanical jack. One person should hold the jack against the compactor platform while the other pushes the mold from the back of the compactor at the same time.

4.15 Remove the kneading plates. A screw driver and vise grips shall be used to pull the first couple of plates out. The plates should be removed starting in the middle and working out to each side simultaneously.

4.16 Slide the mold onto a counter and let it cool in front of a fan for a minimum of one hour before removing the mold. Do not handle the slab before it reaches room temperature.

4.17 Once the slab has cooled to room temperature, flip the slab over and remove the wax paper from the bottom. The bottom of the slab is the ideal side for most testing.

4.18 The slab should be stored on a rigid plate such as a 1-inch thick piece of plywood to protect against deformation. Never stack slabs or leave on a non-flat surface.

APPENDIX B Microtox Screening Procedure

The Microtox Screening Procedure makes use of a lyophilized preparation of bioluminescent marine bacteria, Vibrio fischeri, to measure the toxicity of a sample relative to a control sample. Readings are taken four times during the 45 minute run. At each of the four reading times, the light output of each sample and each control is measured on a scale of 0 to 100 and recorded (only the first three readings are recorded by the MicrotocOmni software).

V. fisheri emits light as a byproduct of respiration and if a water sample contains one or more components that interfere with the respiration, then the bacteria's light output is reduced proportionally to the amount of interference with respiration, or toxicity. The light output reduction is proportional to the toxicity of the sample. The relative toxicity of a sample to the control can then be calculated. These relative toxicities can be compared to toxicity test results using standard reagents.

Apparatus

- Microtox Model 500 Analyzer and MicrotoxOmni software
- Eppendorf repeater 4780 pipettor (with tips) or 10 µl pipettor (with disposable tips)
- 500 µl pipettor or an adjustable 100-1000 µl pipettor (with disposable tips)
- Glass cuvettes
- Plastic weighing cups

Reagents

- Microtox bacterial reagent
- Microtox reconstitution solution
- Microtox diluent
- Reagent grade Sodium Chloride
- Hydrated Zinc Sulfate or crystalline Phenol standards

Sample preparation

Note: Microtox instrument has space in its incubator for 30 cuvettes. For a normal run, three of the cuvettes (A1, A2 and A3) are reserved for the control solution. The next three of the remaining 27 cuvettes is reserved for the 0.75 mg/l of ZnSO4.7H2O EC50 standard solution, followed by three cuvettes for 5 mg/l of Phenol EC50 standard solution. The EC50 values where the toxicities are reduced by 50% were determined during the calibration of the instrument. The remaining 23 cuvettes contain the samples to be tested.

1. Weighing cups were labels according to the samples.
2. 3 gms of Nacl was weighed into the weigh cups.
3. The sample vial was inverted several times before adding the adding sample to the weighing cups.
4. 10 ml of the sample was added to the respective weighing cup and using a separate eppendorf tip for each sample and the sample and salt were mixed using the eppendorf tip until the salt is completely dissolved.

Alternatively, your samples maybe stored in the 40 ml sample vials immediately after collection and stored for up to one week at 4°C. Do not add salt to the vials until you are ready to run the Microtox test. Fill the vial up completely so that there is no head space above the sample water. Then, when ready to run the Microtox procedure, invert the vial a few times, pour out some of the sample, and add 0.2 g of NaCl per 10 ml of sample.

Logging on to the computer program and database (optional)

1. On the computer desktop, open up the MicrotoxOmni program (icon is solid blue triangle).
2. Username: MANAGER

Password: MANAGER

Be sure to enter both in all capital letters.

3. On the next screen, choose cancel.
4. Choose “Data Capture Test” under the Options menu. This is to ensure the Analyzer and the computer is communicating with each other properly.
5. Select Acute mode and click READ.

6. If the screen says anything other than “Ready to Receive Data”, check the connections on the back of the computer.

7. Click cancel.

8. Under the Test menu or from the toolbar, choose “Run Test” and select the screen.mtt template based on the WET screening protocol.

9. Click NEXT.

10. Leave all default setting as they are unless you are specifically instructed to change them. Only the number of samples should need to be changed.

11. Click Next.

12. Enter your sample name and click OK.

13. Here you will see a display of the wells which are color-coded according to the number of controls and samples. The standards are also recognized by the program as samples. DO NOT press the space bar until you are ready to add the Microtox reagent to begin the test.

Preparation of Apparatus

1. Any cuvettes in the Incubator and REAGENT slots from earlier experiments were discarded.
2. New cuvettes were placed into the REAGENT slot and into the incubator slots (3 for controls and 6 for standards and the remaining for the samples). All the cuvettes were rinsed in 18 mega ohm water five time and air dried before use in the experiment.
3. 1 ml of the Reconstitution Solution was added to the cuvette in the REAGENT position.
4. A timer was set for 5 minutes to allow for temperature stabilization of the Reconstitution Solution.
5. Meanwhile 1 ml of Diluent was pipetted into the cuvettes in the positions A1, A2 and A3.
6. 1 ml of the standard solutions, 0.75 mg/l of Zinc Sulfate and 5mg/l of Phenol was pippetted into the cuvette in positions A4, A5, B1, B2, B3 and B4.
7. 1 ml of each of the samples (already adjusted for salinity, as specified above) were pipetted into the cuvettes in position B5 through F5 depending on the number of samples.
8. The Mictrotox Reagent bacterium was then removed from the freezer. (Must be stored prior to use in a freezer no warmer than -20°C).

9. The reagent vial was tapped gently on the countertop several times to break up the contents.
10. After the 5 minute temperature stabilization period has expired, the vial was opened.
11. The Reconstituion Solution was poured into the REAGENT slot into the reagent vial. The contents were swirled ensured its mixed (all solid reagent should go into solution).
12. The bacterium solution in the reagent vial was mixed using a 500 µl pipette, for 10 times.
13. A timer was set for 15 minutes.

Analysis of Samples

1. The reagent was then added to the controls, standards and samples, using a 10 µl repeating pipettor.
2. After the reagent is added to all the vials the solution in each of the vials was mixed 3 times, with a 500 µl pipettor, using a new pipette tip each time.
3. It takes approximately 5 min to finish with the mixing in each of the vials.
4. The cuvettes were then placed in the reading slot and the reading was noted for each of the cuvettes at the end of 5, 15, 25 and 45 minutes.
5. The values so recorded were then used to calculate the % toxicity.

APPENDIX C: ANOVA ON LINEAR REGRESSION

Nitrates

Nitrate test			
Sample #	HMA	WMA	AS
1	0.4	0.3	1
2	0.2	0.3	0.7
3	1.4	2	0.2
4	0.2	0.3	3
5	4.1	4.2	2.6
6	2.1	3	4
7	5	4	3.4
8	5.1	4.1	4
9	4	6	5
10	4.3	5	
Average	1.1	1.6	1.4
COV	0.90	0.99	0.78

HMA
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.89717637
R Square	0.80492543
Adjusted R Square	9 0.69381432
Standard Error	8 1.53650111
Observations	8 10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	87.6724788 2	87.6724 8	37.1362053 4	0.000291408
Residual	9	21.2475211 8	2.36083 6		
Total	10	108.92			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.03433558 3	0.00563437 4	6.09394 8	0.00018056 6	0.021589744	0.04708142 3

WMA
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.936536512
R Square	0.877100637
Adjusted R Square	0.765989526
Standard Error	1.305033354
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	109.3919915	109.392	64.23065	4.3106E-05
Residual	9	15.3280085	1.703112		
Total	10	124.72			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.038353549	0.004785578	8.014403	2.18E-05	0.02752782	0.04917928

AS
SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.94241757
R Square	0.888150877
Adjusted R	0.763150877

Square	
Standard Error	1.095573322
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	76.24775277	76.24775	63.52492	9.3343E-05
Residual	8	9.602247231	1.200281		
Total	9	85.85			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.033115202	0.00415485	7.970252	4.49E-05	0.0235341	0.0426963

AmmoniaAmmonia test			
Sample #	HMA	WMA	AS
1	0.45	0.3	0.23
2	0.13	0.17	0.54
3	0.57	0.79	0
4	-0.01	0	0.32
5	0.21	0.36	-0.01
6	-0.02	0.01	0.01
7	-0.02	-0.14	0.03
8	0.02	-0.06	0.07
9	0.15	0.11	0.09
10	0.13	0.12	
mean	0.161	0.166	0.142222
cov	1.259184	1.614987	1.312971

The slope terms were insignificant for the pavements.

Total Phosphate

Total Phosphate			
Sample #	HMA	WMA	AS
1	0.17	3.19	0.41
2	0.26	0.36	0.48
3	0.38	0.42	0.15

4	0.22	0.15	0.66
5	0.38	1.21	0.19
6	0.08	0.13	0.39
7	0.15	-0.08	0.54
8	0.88	0.42	1.33
9	0.95	1.11	1.5
10	0.9	1.1	
mean	0.437	0.801	0.627778
cov	0.777811	1.191262	0.75734

Both the slope and intercept terms were insignificant for WMA.

HMA

Regression Statistics	
Multiple R	0.931161
R Square	0.86706
Adjusted R Square	0.755949
Standard Error	0.208728
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2.557395	2.557395	58.69992	5.95E-05
Residual	9	0.392105	0.043567		
Total	10	2.9495			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.005864	0.000765	7.661587	3.12E-05	0.004133	0.007596

AS

Regression Statistics	
Multiple R	0.938204
R Square	0.880228
Adjusted R Square	0.755228
Standard Error	0.283156
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	4.713882	4.713882	58.79331	0.000119

Residual	8	0.641418	0.080177			
Total	9	5.3553				

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.008234	0.001074	7.66768	5.92E-05	0.005758	0.01071

Total Nitrogen

Total Nitrogen			
Sample #	HMA	WMA	AS
1	0	1	1
2	1	0	2
3	1	2	0
4	0	0	1
5	0	1	0
6	1	0	3
7	2	2	1
8	1	5	3
9	3	3	2
10	2	2	
mean	1.1	1.6	1.444444
cov	0.904026	0.986013	0.782577

HMA

Regression Statistics	
Multiple R	0.885831
R Square	0.784696
Adjusted R Square	0.673585
Standard Error	0.708785
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	16.47862	16.47862	32.80139	0.00044
Residual	9	4.521381	0.502376		
Total	10	21			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.014886	0.002599	5.72725	0.000284	0.009006	0.020765

WMA

Regression Statistics	
Multiple R	0.81775
R Square	0.668715
Adjusted R Square	0.557604
Standard Error	1.32923
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	32.09834	32.09834	18.16697	0.002753
Residual	9	15.90166	1.766851		
Total	10	48			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.020776	0.004874	4.262273	0.002104	0.009749	0.031802

AS

Regression Statistics	
Multiple R	0.797189
R Square	0.63551
Adjusted R Square	0.51051
Standard Error	1.149467
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	18.4298	18.4298	13.9485	0.007313
Residual	8	10.5702	1.321275		
Total	9	29			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	0.016281	0.004359	3.734769	0.005748	0.006228	0.026333

COD

COD			
Sample #	HMA	WMA	AS
1	34	45	128
2	49	47	110
3	162	150	34
4	6	29	91
5	112	157	120
6	24	30	70
7	37	36	24
8	45	55	26
9	55	48	30
10	70	45	
mean	59.4	64.2	70.33333
cov	0.773361	0.74444	0.612613

HMA and WMA showed insignificant values.

AS (Slope term and intercept term are significant)

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.745877
R Square	0.556333
Adjusted R Square	0.492952
Standard Error	30.68118
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	8262.657	8262.657	8.777597	0.021024
Residual	7	6589.343	941.3347		
Total	8	14852			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	107.633	16.22018	6.635744	0.000294	69.27833	145.9876
X Variable 1	-0.54674	0.18454	-2.9627	0.021024	-0.98311	-0.11037

Detergent

Detergent

Sample #	HMA	WMA	AS
1	0.25	0.25	0.25
2	0.5	0.5	0.75
3	1.75	1	0.625
4	0.5	0.5	1
5	1.75	1.5	0.25
6	0.5	0.25	1
7	1	0.5	0.5
8	0.75	0.75	0.75
9	1	1	1
10	1	1	
mean	0.9	0.725	0.680556
cov	0.573775	0.550045	0.441496

Insignificant values for slope terms for all the pavement types.

APPENDIX D: ANOVA TEST RESULTS FOR THE PAVEMENTS FOR THE INITIAL AND FINAL EXPERIMENTAL STAGES

Nitrate Test Results:

Nitrate test						
$N03^-$-N						
HMA1	HMA2	WMA1	WMA2	AS1	AS2	
0.4	2.1	0.3	3	1	4	
0.2	5	0.3	4	0.7	3.4	
1.4	5.1	2	4.1	0.2	4	
0.2	4	0.3	6	3	5	
4.1	4.3	4.2	5	2.6		

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	6.3	1.26	2.768
HMA2	5	20.5	4.1	1.465

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	20.164	1	20.164	9.527049	0.014967	5.317655
Within Groups	16.932	8	2.1165			
Total	37.096	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	7.1	1.42	2.957
WMA2	5	22.1	4.42	1.282

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	22.5	1	22.5	10.61571	0.011559	5.317655
Within Groups	16.956	8	2.1195			
Total	39.456	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	7.5	1.5	1.51
AS2	4	16.4	4.1	0.44

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	15.02222	1	15.02222	14.28744	0.006893	5.591448
Within Groups	7.36	7	1.051429			
Total	22.38222	8				

Ammonia Test results:

Ammonia					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.45	-0.02	0.3	0.01	0.23	0.01
0.13	-0.02	0.17	-0.14	0.54	0.03
0.57	0.02	0.79	-0.06	0	0.07
-0.01	0.15	0	0.11	0.32	0.09
0.21	0.13	0.36	0.12	-0.01	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	1.35	0.27	0.056
HMA2	5	0.26	0.052	0.00677

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.11881	1	0.11881	3.785566	0.087578	5.317655
Within Groups	0.25108	8	0.031385			
Total	0.36989	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	1.62	0.324	0.08693
WMA2	5	0.04	0.008	0.01237

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	0.24964	1	0.24964	5.027996	0.055225	5.317655
Within Groups	0.3972	8	0.04965			
Total	0.64684	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	1.08	0.216	0.05343
AS2	4	0.2	0.05	0.001333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.061236	1	0.061236	1.968808	0.203341	5.591448
Within Groups	0.21772	7	0.031103			
Total	0.278956	8				

Total Phosphorus test results:

PO_4^{-3}					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.17	0.08	3.19	0.13	0.41	0.39
0.26	0.15	0.36	-0.08	0.48	0.54
0.38	0.88	0.42	0.42	0.15	1.33
0.22	0.95	0.15	1.11	0.66	1.5
0.38	0.9	1.21	1.1	0.19	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	1.41	0.282	0.00902
HMA2	5	2.96	0.592	0.19087

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.24025	1	0.24025	2.403822	0.159636	5.317655
Within Groups	0.79956	8	0.099945			
Total	1.03981	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	5.33	1.066	1.57173
WMA2	5	2.68	0.536	0.30133

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.70225	1	0.70225	0.749843	0.411741	5.317655
Within Groups	7.49224	8	0.93653			
Total	8.19449	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	1.89	0.378	0.04457
AS2	4	3.76	0.94	0.3094

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.701876	1	0.701876	4.440323	0.073089	5.591448
Within Groups	1.10648	7	0.158069			
Total	1.808356	8				

Total Nitrogen (mg/l)					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0	1	1	0	1	3
1	2	0	2	2	1
1	1	2	5	0	3
0	3	0	3	1	2
0	2	1	2	0	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	2	0.4	0.3
HMA2	5	9	1.8	0.7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.9	1	4.9	9.8	0.014005	5.317655
Within Groups	4	8	0.5			
Total	8.9	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	4	0.8	0.7
WMA2	5	12	2.4	3.3

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.4	1	6.4	3.2	0.111434	5.317655
Within Groups	16	8	2			
Total	22.4	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	4	0.8	0.7
AS2	4	9	2.25	0.916667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.672222	1	4.672222	5.892893	0.045586	5.591448
Within Groups	5.55	7	0.792857			
Total	10.22222	8				

Detergent test results:

Detergent ppm					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.25	0.5	0.25	0.25	0.25	1
0.5	1	0.5	0.5	0.75	0.5
1.75	0.75	1	0.75	0.625	0.75
0.5	1	0.5	1	1	1
1.75	1	1.5	1	0.25	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	4.75	0.95	0.54375
HMA2	5	4.25	0.85	0.05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.025	1	0.025	0.084211	0.77905	5.317655
Within Groups	2.375	8	0.296875			
Total	2.4	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	3.75	0.75	0.25
WMA2	5	3.5	0.7	0.10625

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00625	1	0.00625	0.035088	0.856076	5.317655
Within Groups	1.425	8	0.178125			

Total	1.43125	9

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	2.875	0.575	0.10625
AS2	4	3.25	0.8125	0.057292

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.125347	1	0.125347	1.470041	0.264667	5.591448
Within Groups	0.596875	7	0.085268			
Total	0.722222	8				

COD Test results:

COD					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
34	24	45	30	128	70
49	37	47	36	110	24
162	45	150	55	34	26
6	55	29	48	91	30
112	70	157	45	120	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	363	72.6	4006.8
HMA2	5	231	46.2	305.7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1742.4	1	1742.4	0.80807	0.394942	5.317655
Within Groups	17250	8	2156.25			
Total	18992.4	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	428	85.6	3896.8
WMA2	5	214	42.8	97.7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4579.6	1	4579.6	2.292953	0.168424	5.317655
Within Groups	15978	8	1997.25			
Total	20557.6	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	483	96.6	1415.8
AS2	4	150	37.5	475.6667

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7761.8	1	7761.8	7.663056	0.027765	5.591448
Within Groups	7090.2	7	1012.886			
Total	14852	8				

Copper test results:

Copper					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.1	0.02	0.09	0.03	0.07	0.09
0.06	0.08	0.06	0.09	0.15	0.06
0.09	0.05	0.09	0.06	0.05	0.13
0.04	0.11	0.03	0.12	0.07	0.16
0.06	0.17	0.08	0.17	0.04	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	0.35	0.07	0.0006
HMA2	5	0.43	0.086	0.00333

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00064	1	0.00064	0.3257	0.583872	5.317655
Within Groups	0.01572	8	0.001965			
Total	0.01636	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	0.35	0.07	0.00065
WMA2	5	0.47	0.094	0.00293

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00144	1	0.00144	0.804469	0.395949	5.317655
Within Groups	0.01432	8	0.00179			
Total	0.01576	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	0.38	0.076	0.00188
AS2	4	0.44	0.11	0.001933

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.002569	1	0.002569	1.350017	0.283355	5.591448
Within Groups	0.01332	7	0.001903			
Total	0.015889	8				

Zinc test results:

Zinc					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0	0	0	0.03	0	0.06
0	0.05	0	0.06	0.07	0.06
0.05	0.04	0.04	0.05	0.07	0.15
0.05	0.14	0.05	0.15	0.07	0.21
0.08	0.22	0.1	0.25	0.04	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	5	0.18	0.036	0.00123
HMA2	5	0.45	0.09	0.0079

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00729	1	0.00729	1.596933	0.241917	5.317655
Within Groups	0.03652	8	0.004565			
Total	0.04381	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	5	0.19	0.038	0.00172
WMA2	5	0.54	0.108	0.00842

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.01225	1	0.01225	2.416174	0.158695	5.317655
Within Groups	0.04056	8	0.00507			
Total	0.05281	9				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	5	0.25	0.05	0.00095
AS2	4	0.48	0.12	0.0054

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.010889	1	0.010889	3.811111	0.091868	5.591448
Within Groups	0.02	7	0.002857			
Total	0.030889	8				

PAHs ANOVA TEST RESULTS

Napthalene:

Naphthalene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.002734	0.405772	0.083341	0.221123	0.026059	0.071191
0.277982	0.039186	0.124361	-0.02678	0.063336	0.117841
0.156745	0.605175	0.240391	-0.03046	0.051131	0.387003
0.324622	0.002083	0.463271	-0.0514	0.392536	0.363352

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.762083	0.190521	0.020679
HMA2	4	1.052216	0.263054	0.085213

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.010522	1	0.010522	0.198734	0.67138	5.987378
Within Groups	0.317675	6	0.052946			
Total	0.328197	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.911364	0.227841	0.029058
WMA2	4	0.112482	0.02812	0.016673

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.079777	1	0.079777	3.48897	0.111005	5.987378
Within Groups	0.137192	6	0.022865			
Total	0.216969	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.533062	0.133266	0.030117
AS2	4	0.939387	0.234847	0.026713

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.020637	1	0.020637	0.726291	0.42679	5.987378

Within Groups	0.170489	6	0.028415
Total	0.191127	7	

Acenapthylene:

Acenaphthylene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.001379	0.002684	-0.00328	0.002125	-0.00048	-0.00048
0.009897	7.46E-05	0.002628	0.001379	0.020522	-0.0016
0.044007	-0.00272	-0.00185	0.00287	0.001789	0.006971
0.005666	0.025238	0.009581	-0.00216	0.006039	-0.00365

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.060951	0.015238	0.00038
HMA2	4	0.025275	0.006319	0.000164

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000159	1	0.000159	0.585002	0.473358	5.987378
Within Groups	0.001632	6	0.000272			
Total	0.001791	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.007083	0.001771	3.34E-05
WMA2	4	0.004212	0.001053	4.97E-06

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.03E-06	1	1.03E-06	0.053635	0.82455	5.987378
Within Groups	0.000115	6	1.92E-05			
Total	0.000116	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.027866	0.006966	8.9E-05
AS2	4	0.00123	0.000308	2.15E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8.87E-05	1	8.87E-05	1.606072	0.252009	5.987378
Within Groups	0.000331	6	5.52E-05			
Total	0.00042	7				

Acenapthene:

Acenaphthene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.01128	0.006328	-0.00949	-0.00412	0.003343	0.035582
-0.01916	-0.00949	-0.0111	-0.00651	-0.01155	0.003343
-0.01916	0.012896	-0.01066	-0.00919	0.011284	0.045134
0.005134	0.064239	0.032299	-0.01576	-0.0071	-0.0086

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	-0.04448	-0.01112	0.000131
HMA2	4	0.07397	0.018493	0.001018

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001754	1	0.001754	3.05101	0.131286	5.987378
Within Groups	0.003449	6	0.000575			
Total	0.005203	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.001045	0.000261	0.000457
WMA2	4	-0.03558	-0.0089	2.52E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000168	1	0.000168	0.695984	0.436085	5.987378
Within Groups	0.001446	6	0.000241			
Total	0.001613	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	-0.00403	-0.00101	0.000106
AS2	4	0.075463	0.018866	0.000655

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between	0.00079	1	0.00079	2.075918	0.199716	5.987378

Groups						
Within Groups	0.002283		6	0.00038		
Total	0.003073		7			

Fluorene

HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.004046	0.028262	0.004758	0.050912	0.005043	0.032963
0.025726	0.007179	0.004786	0.005897	0.006496	0.028405
-0.00162	0.04208	0.004359	0.014872	-0.00034	0.094501
0.031966	-0.00849	0.062308	-0.00179	0.037236	0.010883

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.060114	0.015028	0.000266
HMA2	4	0.069031	0.017258	0.000501

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.94E-06	1	9.94E-06	0.025919	0.877382	5.987378
Within Groups	0.002301	6	0.000383			
Total	0.002311	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.076211	0.019053	0.000832
WMA2	4	0.069886	0.017472	0.000543

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5E-06	1	5E-06	0.00727 3	0.93481	5.987378
Within Groups	0.00412 5	6	0.00068 7			
Total	0.00413	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.04843 3	0.01210 8	0.00028 9
AS2	4	0.16675 2	0.04168 8	0.00133

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.00175	1	0.00175	2.16101 4	0.191949	5.987378
Within Groups	0.00485 9	6	0.00081			
Total	0.00660 9	7				

Phenanthrene:

Phenanthrene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.01563	0.14967	0.029239	0.207236	0.065602	0.300425
0.058835	0.024308	0.05865	0.09568	0.054213	0.190102
0.020376	0.225233	0.138342	0.099131	0.020376	0.628561
0.187513	-0.043	0.529455	-0.01353	0.154231	0.039716

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*

HMA1	4	0.251094	0.062773	0.00784
HMA2	4	0.356216	0.089054	0.014616

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.001381	1	0.001381	0.123024	0.737764	5.987378
Within Groups	0.067368	6	0.011228			
Total	0.06875	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.755686	0.188921	0.053663
WMA2	4	0.388512	0.097128	0.008125

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.016852	1	0.016852	0.545475	0.488045	5.987378
Within Groups	0.185366	6	0.030894			
Total	0.202218	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.294422	0.073606	0.003258
AS2	4	1.158804	0.289701	0.062451

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.093395	1	0.093395	2.842667	0.142768	5.987378
Within Groups	0.197127	6	0.032855			
Total	0.290522	7				

Anthracene:

Anthracene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.153922	0.036713	-0.09662	0.039194	-0.12515	0.058419
-0.1533	-0.04763	-0.14307	0.083845	-0.13749	0.080124
-0.10493	0.009426	0.01693	-0.05135	-0.15981	0.199814
1.166016	-0.0129	0.379039	-0.07988	-0.00856	0.015628

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	1.061705	0.265426	0.378664
HMA2	4	-0.01439	-0.0036	0.001273

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.144747	1	0.144747	0.761952	0.41628	5.987378
Within Groups	1.139811	6	0.189969			
Total	1.284558	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.156279	0.03907	0.055885
WMA2	4	-0.00819	-0.00205	0.005855

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.003381	1	0.003381	0.109526	0.751937	5.987378
Within Groups	0.185222	6	0.03087			
Total	0.188603	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	-0.43101	-0.10775	0.004579
AS2	4	0.353984	0.088496	0.006225

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.077027	1	0.077027	14.25851	0.009223	5.987378
Within Groups	0.032413	6	0.005402			
Total	0.10944	7				

Flouranthene

Flouranthene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.00389	0.08633	0.043963	0.151626	0.126579	0.674617
0.091738	0.06253	0.149121	0.125209	0.119589	0.235614
0.067065	0.075988	0.224822	0.07524	0.107065	1.053059
0.130816	0.032623	0.657919	0.052685	0.095801	0.086579

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.285732	0.071433	0.00321

HMA2	4	0.25747	0.064368	0.000543

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.98E-05	1	9.98E-05	0.053203	0.825244	5.987378
Within Groups	0.011259	6	0.001877			
Total	0.011359	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	1.075826	0.268956	0.072741
WMA2	4	0.40476	0.10119	0.002049

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.056291	1	0.056291	1.505317	0.26581	5.987378
Within Groups	0.224369	6	0.037395			
Total	0.28066	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.449034	0.112259	0.000186
AS2	4	2.049869	0.512467	0.192187

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.320334	1	0.320334	3.330354	0.117814	5.987378
Within Groups	0.577117	6	0.096186			
Total	0.897451	7				

Pyrene:

Pyrene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.001858	0.123943	0.022711	0.151242	0.122047	0.559204
0.127621	0.055507	0.177384	0.092284	0.125915	0.252664
0.086957	0.1029	0.286863	0.091526	0.129043	1.257592
0.098351	0.003943	0.675602	0.022332	0.117308	0.039393

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.314787	0.078697	0.002917
HMA2	4	0.286294	0.071573	0.002852

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000101	1	0.000101	0.035179	0.857404	5.987378
Within Groups	0.017308	6	0.002885			
Total	0.01741	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	1.162559	0.29064	0.077608
WMA2	4	0.357384	0.089346	0.002778

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.081038	1	0.081038	2.01623	0.205435	5.987378
Within Groups	0.241158	6	0.040193			
Total	0.322197	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.494313	0.123578	2.57E-05
AS2	4	2.108853	0.527213	0.282608

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.325843	1	0.325843	2.305762	0.179696	5.987378
Within Groups	0.8479	6	0.141317			
Total	1.173742	7				

Benzo(a)anthracene:

Benzo(a)anthracene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.00788	0.002137	0.033523	0.147045	-0.00254	0.264574
0.049282	0.056227	0.209549	0.016828	0.025242	0.066244
-0.01983	0.013489	0.041269	0.104975	0.032254	0.793456
0.052888	0.002137	0.336694	-0.00721	0.119666	-0.00788

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.074457	0.018614	0.001432
HMA2	4	0.07399	0.018497	0.000661

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.73E-08	1	2.73E-08	2.61E-05	0.99609	5.987378
Within Groups	0.006279	6	0.001047			
Total	0.006279	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.621035	0.155259	0.021227
WMA2	4	0.261636	0.065409	0.005288

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.016146	1	0.016146	1.217894	0.312057	5.987378
Within Groups	0.079544	6	0.013257			
Total	0.09569	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.174624	0.043656	0.002793
AS2	4	1.116394	0.279098	0.130813

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.110866	1	0.110866	1.659598	0.245104	5.987378
Within Groups	0.400819	6	0.066803			
Total	0.511685	7				

Chrysene:

Chrysene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.002941	0.010294	0.009804	0.116667	0.043137	0.367157
0.014706	0.05	0.166912	0.021569	0.004412	0.09951
0.130882	0.018627	0.077941	0.069608	0.142647	0.812255
0.047549	0.035294	0.452451	0.030392	0.096569	0.037255

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.196078	0.04902	0.003335
HMA2	4	0.114216	0.028554	0.000312

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000838	1	0.000838	0.459358	0.523186	5.987378
Within Groups	0.010942	6	0.001824			
Total	0.011779	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.707108	0.176777	0.037914
WMA2	4	0.238235	0.059559	0.001885

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.02748	1	0.02748	1.380934	0.28446	5.987378
Within Groups	0.119398	6	0.0199			
Total	0.146878	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.286765	0.071691	0.003665
AS2	4	1.316176	0.329044	0.124257

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.132461	1	0.132461	2.070957	0.200183	5.987378
Within Groups	0.383768	6	0.063961			
Total	0.516229	7				

Benzo(b)fluoranthene:

Benzo(b)fluoranthene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.31524	0.249048	-0.29381	-0.06286	-1.26286	-1.07952
0.262857	-0.36762	0.030714	-2.07476	0.109286	-1.45571

0.273571	-1.06762	-0.56214	-0.18667	-0.94786	-5.47714
-0.25333	0.018095	-3.27714	0.196667	-0.39619	0.599048

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	-0.03214	-0.00804	0.10241
HMA2	4	-1.1681	-0.29202	0.332065

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.161298	1	0.161298	0.742499	0.421958	5.987378
Within Groups	1.303424	6	0.217237			
Total	1.464723	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	-4.10238	-1.0256	2.311852
WMA2	4	-2.12762	-0.5319	1.083473

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between	0.487461	1	0.487461	0.287136	0.611333	5.987378

Groups			
Within Groups	10.18597	6	1.697662
Total	10.67344	7	

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	-2.49762	-0.6244	0.367542
AS2	4	-7.41333	-1.85333	6.63435

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.020531	1	3.020531	0.862776	0.388804	5.987378
Within Groups	21.00568	6	3.500946			
Total	24.02621	7				

Benzo(k)fluoranthene:

Benzo(k)fluoranthene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.04328	0.310448	-0.02985	0.161194	-0.63731	0.128358
0.669403	-0.07612	-0.7903	0.398507	0.3	-0.56716
0.129851	0.340299	-0.1209	0.014925	-0.36269	-3.2791
0.541791	0.165672	-1.77612	0.277612	-0.10299	0.529851

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	1.297761	0.32444	0.113109
HMA2	4	0.740299	0.185075	0.036137

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.038846	1	0.038846	0.520557	0.497743	5.987378
Within Groups	0.447738	6	0.074623			
Total	0.486584	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	-2.71716	-0.67929	0.649644
WMA2	4	0.852239	0.21306	0.026835

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1.59258	1	1.59258	4.708435	0.073073	5.987378
Within Groups	2.029438	6	0.33824			
Total	3.622018	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	-0.80299	-0.20075	0.15904
AS2	4	-3.18806	-0.79701	2.943496

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.711073	1	0.711073	0.458382	0.523612	5.987378
Within Groups	9.307607	6	1.551268			
Total	10.01868	7				

Indeno(1,2,3-cd)pyrene

HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.09627	-0.23186	-0.09288	-0.53695	0.024068	-0.52847
-0.08847	-0.02339	0.041186	-0.40983	0.015763	-0.02847
-0.01475	0.035932	0.17339	0.127458	-0.27915	-1.3522
-0.29797	-0.10475	-0.07085	0.188475	-0.04034	-0.14034

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	-0.49746	-0.12436	0.014744
HMA2	4	-0.32407	-0.08102	0.013439

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.003758	1	0.003758	0.266692	0.624033	5.987378
Within Groups	0.084547	6	0.014091			
Total	0.088305	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.050847	0.012712	0.01492

WMA2	4	-0.63085	-0.15771	0.136184

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.058088	1	0.058088	0.768855	0.414296	5.987378
Within Groups	0.453312	6	0.075552			
Total	0.5114	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	-0.27966	-0.06992	0.020276
AS2	4	-2.04949	-0.51237	0.35938

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.391538	1	0.391538	2.062588	0.200973	5.987378
Within Groups	1.13897	6	0.189828			
Total	1.530507	7				

Benzo(a,h)anthracene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.49933	-0.04989	-0.30157	-0.38921	-0.49933	-0.41618
-0.68494	-0.02517	-0.74225	-0.56	-0.34449	-0.41843
0.407191	-0.56674	0.761124	-0.38472	2.810562	-0.40719

-0.14876	-0.5218	-0.19596	-0.22067	-0.46112	-0.07236

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	-0.92584	-0.23146	0.230704
HMA2	4	-1.1636	-0.2909	0.086034

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.007066	1	0.007066	0.044616	0.839703	5.987378
Within Groups	0.950216	6	0.158369			
Total	0.957282	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	-0.47865	-0.11966	0.400769
WMA2	4	-1.55461	-0.38865	0.019197

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.14471	1	0.14471	0.689149	0.43823	5.987378
Within Groups	1.2599	6	0.209983			
Total	1.40461	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	1.505618	0.376404	2.637725
AS2	4	-1.31416	-0.32854	0.029192

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.993892	1	0.993892	0.745349	0.421118	5.987378
Within Groups	8.000749	6	1.333458			
Total	8.99464	7				

Benzo(ghi)perylene:

Benzo(ghi)perylene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
-0.30379	-0.22276	-0.32621	-0.27966	0.546207	-0.17621
-0.22034	-0.31931	-0.17121	-0.20724	-0.21517	-0.26414
1.349483	-0.3469	0.371897	0.615172	0.84	0.523793
-0.31414	-0.3331	-0.04	-0.31586	0.401379	-0.16241

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.511207	0.127802	0.665098
HMA2	4	-1.22207	-0.30552	0.003171

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.375531	1	0.375531	1.12389	0.329881	5.987378
Within Groups	2.004808	6	0.334135			
Total	2.380338	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	-0.16552	-0.04138	0.089594
WMA2	4	-0.18759	-0.0469	0.196855

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.09E-05	1	6.09E-05	0.000425	0.98422	5.987378
Within Groups	0.859346	6	0.143224			
Total	0.859406	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	1.572414	0.393103	0.197742
AS2	4	-0.07897	-0.01974	0.133332

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.340882	1	0.340882	2.059249	0.20129	5.987378
Within Groups	0.993221	6	0.165537			
Total	1.334103	7				

Benzo(a)pyrene:

Benzo(a)pyrene					
HMA1	HMA2	WMA1	WMA2	AS1	AS2
0.012113	0.073489	0.06855	0.254088	-0.0027	0.360614
0.152561	0.077016	0.044624	0.471372	0.00018	0.042448
0.474254	0.441743	0.41182	-0.02387	0.100709	0.352854
0.28654	0.077016	0.207527	0.038921	0.091125	0.038215

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
HMA1	4	0.925467	0.231367	0.038774
HMA2	4	0.669263	0.167316	0.033474

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.008205	1	0.008205	0.227139	0.650514	5.987378
Within Groups	0.216743	6	0.036124			
Total	0.224948	7				

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
WMA1	4	0.732522	0.183131	0.028402
WMA2	4	0.740515	0.185129	0.050582

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7.99E-06	1	7.99E-06	0.000202	0.989115	5.987378
Within Groups	0.236953	6	0.039492			

Total	0.236961	7

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
AS1	4	0.189312	0.047328	0.003165
AS2	4	0.794131	0.198533	0.033383

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.045726	1	0.045726	2.502247	0.16477	5.987378
Within Groups	0.109643	6	0.018274			
Total	0.155369	7				

APPENDIX EBonferroni test results for PAHs

			Naphthalene			
Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.00273393	0.40577163	0.08334147	0.2211229	0.026059	0.071191
2	0.277982099	0.03918633	0.124361269	-0.0267752	0.063336	0.117841
3	0.156745321	0.605174939	0.240390561	-0.0304638	0.051131	0.387003
4	0.324621644	0.002082994	0.463270952	-0.0514022	0.392536	0.363352
mean	0.190520749	0.263053973	0.227841063	0.0281204	0.133266	0.234847

stdev	0.143802187	0.291911892	0.170463019	0.1291245	0.173542	0.163441

S2p = 0.034742035 Sp = 0.1863922

Using,
tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.43221903

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.072533225	0.43221903	NO
HMA2-WMA1	0.03521291	0.43221903	NO
WMA1-WMA2	0.19972064	0.43221903	NO
WMA2-AS1	-0.105145105	0.43221903	NO
AS1-AS2	-0.101581231	0.43221903	NO
AS2-HMA1	0.04432601	0.43221903	NO

Acenaphthylene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.00137931	0.002684063	-0.003280522	0.002124884	-0.0004846	-0.00048
2	0.009897484	7.45573E-05	0.002628145	0.00137931	0.0205219	-0.0016

3	0.044007456	-0.002721342	-0.001845294	0.002870457	0.00178938	0.006971
4	0.005666356	0.025237651	0.009580615	-0.00216216	0.00603914	-0.00365
mean	0.015237651	0.006318733	0.001770736	0.001053122	0.00696645	0.000308
stdev	0.019492583	0.012804283	0.00578274	0.00222829	0.00943276	0.004632

S2p = 0.000115458 Sp = 0.010745147

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.02491659

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.008918919	0.02491659	NO
HMA2-WMA1	0.004547996	0.02491659	NO
WMA1-WMA2	0.000717614	0.02491659	NO
WMA2-AS1	-0.005913327	0.02491659	NO
AS1-AS2	0.0066589	0.02491659	NO
AS2-HMA1	-0.014930103	0.02491659	NO

Acenaphthene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.011283582	0.006328358	0.009492537	-0.0041194	0.003343	0.035582

2	-0.019164179	-0.009492537	0.011104478	-0.0065075	-0.01155	0.003343
3	-0.019164179	0.012895522	0.010656716	-0.009194	0.011284	0.045134
4	0.005134328	0.064238806	0.032298507	-0.0157612	-0.0071	-0.0086
mean	-0.011119403	0.018492537	0.000261194	-0.0088955	-0.00101	0.018866
stdev	0.011454949	0.031912272	0.021369012	0.0050246	0.010302	0.025591

S2p = 0.000398748 Sp = 0.0199687

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.046304737

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.02961194	0.046304737	NO
HMA2-WMA1	0.018231343	0.046304737	NO
WMA1-WMA2	0.009156716	0.046304737	NO
WMA2-AS1	-0.00788806	0.046304737	NO
AS1-AS2	0.019873134	0.046304737	NO
AS2-HMA1	0.029985075	0.046304737	NO

Fluorene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.004045584	0.028262108	0.004757835	0.05091168	0.005043	0.032963
2	0.025726496	0.007179487	0.004786325	0.00589744	0.006496	0.028405
3	0.001623932	0.042079772	0.004358974	0.01487179	-0.00034	0.094501
4	0.031965812	-0.008490028	0.062307692	-0.0017949	0.037236	0.010883
mean	0.01502849	0.017257835	0.019052707	0.01747151	0.012108	0.041688
stdev	0.01632225	0.022373706	0.028837317	0.02331063	0.017008	0.036473

S2p = 0.000626919 Sp = 0.02503836

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.05806068

Comparison	Mean difference	Critical Value	Significance ?
HMA1-HMA2	-0.002229345	0.05806068	NO
HMA2-WMA1	-0.001794872	0.05806068	NO
WMA1-WMA2	0.001581197	0.05806068	NO
WMA2-AS1	0.005363248	0.05806068	NO
AS1-AS2	-0.029579772	0.05806068	NO

Phenanthrene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.0156302	0.149670262	0.029238829	0.2072357	0.065602	0.300425
2	0.058835131	0.024308166	0.058650231	0.0956795	0.054213	0.190102
3	0.020375963	0.225232666	0.138342065	0.099131	0.020376	0.628561
4	0.187513097	-0.042995378	0.529454545	-0.0135347	0.154231	0.039716
mean	0.062773498	0.089053929	0.188921418	0.0971279	0.073606	0.289701
stdev	0.088544093	0.120896679	0.231653616	0.0901407	0.057079	0.249902

S2p = 0.024992319 Sp = 0.1580896

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.366589088

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.026280431	0.366589088	NO
HMA2-WMA1	-0.099867488	0.366589088	NO
WMA1-WMA2	0.091793529	0.366589088	NO
WMA2-AS1	0.023522342	0.366589088	NO
AS1-AS2	-0.216095532	0.366589088	NO
AS2-HMA1	0.226927581	0.366589088	NO
AS2-HMA1	0.026659544	0.05806068	NO

Anthracene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.153922481	0.036713178	-0.09662016	0.0391938	-0.12515	0.058419
2	0.153302326	-0.047627907	-0.14306977	0.08384496	-0.13749	0.080124
3	0.104930233	0.009426357	0.016930233	-0.0513488	-0.15981	0.199814
4	1.166015504	-0.012899225	0.37903876	-0.079876	-0.00856	0.015628
mean	0.265426357	-0.003596899	0.039069767	-0.0020465	-0.10775	0.088496
stdev	0.615356709	0.035682724	0.236400536	0.0765207	0.067668	0.078901

S2p = 0.075413678 Sp = 0.27461551

Using, $t_{v,\alpha/2k} * Sp * (1/ni + 1/nj)^{0.5}$,

t = 3.279376311

Critical value = 0.636797454

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.269023256	0.636797454	NO
HMA2-WMA1	-0.042666667	0.636797454	NO

WMA1-WMA2	0.041116279	0.636797454	NO
WMA2-AS1	0.105705426	0.636797454	NO
AS1-AS2	-0.196248062	0.636797454	NO
AS2-HMA1	-0.176930233	0.636797454	NO

Flouranthene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.00388785	0.086330218	0.043962617	0.1516262	0.126579	0.674617
2	0.091738318	0.062529595	0.149121495	0.1252087	0.119589	0.235614
3	0.067065421	0.075987539	0.22482243	0.0752399	0.107065	1.053059
4	0.130816199	0.032623053	0.657919003	0.0526854	0.095801	0.086579
mean	0.071433022	0.064367601	0.268956386	0.10119	0.112259	0.512467
stdev	0.056659735	0.023298599	0.269704975	0.0452652	0.013622	0.438391

S2p = 0.045152538 Sp = 0.2124913

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.492739456

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.007065421	0.492739456	NO
HMA2-WMA1	-0.204588785	0.492739456	NO
WMA1-WMA2	0.167766355	0.492739456	NO
WMA2-AS1	-0.011068536	0.492739456	NO
AS1-AS2	-0.400208723	0.492739456	NO
AS2-HMA1	0.441034268	0.492739456	NO

Pyrene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.00185782	0.123943128	0.0227109	0.15124171	0.122047	0.559204
2	0.127620853	0.055507109	0.177383886	0.09228436	0.125915	0.252664
3	0.086957346	0.102900474	0.286862559	0.09152607	0.129043	1.257592
4	0.098350711	0.003943128	0.675601896	0.02233175	0.117308	0.039393
mean	0.078696682	0.07157346	0.29063981	0.08934597	0.123578	0.527213
stdev	0.054013284	0.053403974	0.278581454	0.05271108	0.005065	0.531609

S2p = 0.061464801 Sp = 0.24792096

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.574896277

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.007123223	0.574896277	NO
HMA2-WMA1	-0.219066351	0.574896277	NO
WMA1-WMA2	0.201293839	0.574896277	NO
WMA2-AS1	-0.034232227	0.574896277	NO
AS1-AS2	-0.403635071	0.574896277	NO
AS2-HMA1	0.448516588	0.574896277	NO

Benzo(a)anthracene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.0078798	0.002136895	0.033522538	0.1470451	-0.00254	0.264574
2	0.049282137	0.056227045	0.209549249	0.016828	0.025242	0.066244
3	-0.019833055	0.013489149	0.041268781	0.104975	0.032254	0.793456
4	0.052888147	0.002136895	0.336694491	-0.007212	0.119666	-0.00788
mean	0.018614357	0.018497496	0.155258765	0.065409	0.043656	0.279098

stdev	0.03783891	0.025716019	0.145693519	0.0727183	0.052853	0.36168

S2p = 0.027035635 Sp = 0.1644252

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.381280457

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.000116861	0.381280457	NO
HMA2-WMA1	-0.136761269	0.381280457	NO
WMA1-WMA2	0.08984975	0.381280457	NO
WMA2-AS1	0.021752922	0.381280457	NO
AS1-AS2	-0.235442404	0.381280457	NO
AS2-HMA1	0.26048414	0.381280457	NO

Chrysene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2

1	0.002941176	0.010294118	0.00980392	0.116667	0.043137	0.367157
2	0.014705882	0.05	0.16691176	0.021569	0.004412	0.09951
3	0.130882353	0.018627451	0.07794118	0.069608	0.142647	0.812255
4	0.04754902	0.035294118	0.45245098	0.030392	0.096569	0.037255
mean	0.049019608	0.028553922	0.17677696	0.059559	0.071691	0.329044
stdev	0.057747512	0.01767597	0.19471517	0.043421	0.060541	0.352502

S2p = 0.02856153 Sp = 0.169002

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.27937631

Critical value = 0.39189254

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.020465686	0.39189254	NO
HMA2-WMA1	-0.14822304	0.39189254	NO
WMA1-WMA2	0.117218137	0.39189254	NO
WMA2-AS1	-0.01213235	0.39189254	NO
AS1-AS2	-0.25735294	0.39189254	NO
AS2-HMA1	0.28002451	0.39189254	NO

Benzo(b)fluoranthene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.315238095	0.249047619	0.293809524	-0.0628571	-1.26286	-1.07952
2	0.262857143	-0.367619048	0.030714286	-2.0747619	0.109286	-1.45571
3	0.273571429	-1.067619048	0.562142857	-0.1866667	-0.94786	-5.47714
4	-0.253333333	0.018095238	3.277142857	0.1966667	-0.39619	0.599048
mean	-0.008035714	-0.29202381	1.025595238	-0.5319048	-0.6244	-1.85333
stdev	0.320015493	0.576250735	1.520477439	1.0409002	0.606253	2.575723

S2p = 1.805281953 Sp = 1.3436078

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 3.11565081

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.283988095	3.11565081	NO
HMA2-WMA1	0.733571429	3.11565081	NO
WMA1-WMA2	-0.493690476	3.11565081	NO
WMA2-AS1	0.0925	3.11565081	NO

AS1-AS2	1.228928571	3.11565081	NO
AS2-HMA1	-1.845297619	3.11565081	NO

Benzo(k)fluoranthene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.043283582	0.310447761	-0.0298507	0.161194	-0.63731	0.128358
2	0.669402985	-0.0761194	-0.7902985	0.398507	0.3	-0.56716
3	0.129850746	0.340298507	-0.1208955	0.014925	-0.36269	-3.2791
4	0.541791045	0.165671642	-1.7761194	0.277612	-0.10299	0.529851
mean	0.324440299	0.185074627	-0.679291	0.21306	-0.20075	-0.79701
stdev	0.336316591	0.190097934	0.80600524	0.163814	0.398798	1.715662

S2p = 0.654710233 Sp = 0.809142

Using, $t_{v,\alpha/2k} * Sp * (1/ni + 1/nj)^{0.5}$,

t = 3.27937631

Critical value = 1.87629371

Comparison	Mean difference	Critical Value	Significance?

HMA1-HMA2	0.139365672	1.87629371	NO
HMA2-WMA1	0.864365672	1.87629371	NO
WMA1-WMA2	-0.89235075	1.87629371	NO
WMA2-AS1	0.41380597	1.87629371	NO
AS1-AS2	0.596268657	1.87629371	NO
AS2-HMA1	-1.12145522	1.87629371	NO

Indeno(1,2,3-cd)pyrene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.096271186	-0.231864407	0.092881356	-0.5369492	0.024068	-0.52847
2	-0.088474576	-0.023389831	0.041186441	-0.4098305	0.015763	-0.02847
3	-0.014745763	0.035932203	0.173389831	0.1274576	-0.27915	-1.3522
4	-0.297966102	-0.104745763	0.070847458	0.1884746	-0.04034	-0.14034
mean	-0.124364407	-0.081016949	0.012711864	-0.1577119	-0.06992	-0.51237
stdev	0.121423645	0.115925265	0.12214786	0.3690309	0.142394	0.599483

S2p = 0.09315715 Sp = 0.3052166

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 0.707757293

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.043347458	0.707757293	NO
HMA2-WMA1	-0.093728814	0.707757293	NO
WMA1-WMA2	0.170423729	0.707757293	NO
WMA2-AS1	-0.08779661	0.707757293	NO
AS1-AS2	0.442457627	0.707757293	NO
AS2-HMA1	-0.388008475	0.707757293	NO

Benzo(a,h)anthracene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.49932584	-0.04988764	-0.301573	-0.38921	-0.49933	-0.41618
2	-0.68494382	-0.02516854	-0.7422472	-0.56	-0.34449	-0.41843
3	0.407191011	-0.56674157	0.7611236	-0.38472	2.810562	-0.40719
4	0.148764045	-0.52179775	-0.1959551	-0.22067	-0.46112	-0.07236
mean	0.231460674	-0.29089888	-0.1196629	-0.38865	0.376404	-0.32854
stdev	0.480317055	0.293315821	0.63306341	0.138555	1.624107	0.170855

S2p = 0.567270275 Sp = 0.753173

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.27937631

Critical value = 1.74651078

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.059438202	1.74651078	NO
HMA2-WMA1	-0.17123596	1.74651078	NO
WMA1-WMA2	0.268988764	1.74651078	NO
WMA2-AS1	-0.76505618	1.74651078	NO
AS1-AS2	0.70494382	1.74651078	NO
AS2-HMA1	-0.09707865	1.74651078	NO

Benzo(ghi)perylene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	-0.303793103	-0.222758621	0.326206897	-0.2796552	0.546207	-0.17621
2	-0.220344828	-0.319310345	0.171206897	-0.2072414	-0.21517	-0.26414
3	1.349482759	-0.346896552	0.371896552	0.6151724	0.84	0.523793

4	-0.314137931	-0.333103448	-0.04	-0.3158621	0.401379	-0.16241
mean	0.127801724	-0.305517241	-0.04137931	-0.0468966	0.393103	-0.01974
stdev	0.815535678	0.056310109	0.299321898	0.4436834	0.444682	0.365147

S2p = 0.214298606 Sp = 0.462924

Using,
tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.279376311

Critical value = 1.073460158

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.433318966	1.073460158	NO
HMA2-WMA1	-0.264137931	1.073460158	NO
WMA1-WMA2	0.005517241	1.073460158	NO
WMA2-AS1	-0.44	1.073460158	NO
AS1-AS2	0.412844828	1.073460158	NO
AS2-HMA1	-0.147543103	1.073460158	NO

Benzo(a)pyrene

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.012112875	0.073488536	0.06855026	0.254088	-0.0027	0.360614
2	0.152560847	0.077015873	0.04462434	0.471372	0.00018	0.042448
3	0.474253968	0.441742504	0.41182011	-0.02387	0.100709	0.352854
4	0.286539683	0.077015873	0.20752734	0.038921	0.091125	0.038215
mean	0.231366843	0.167315697	0.18313051	0.185129	0.047328	0.198533
stdev	0.196910204	0.182958761	0.16852965	0.224905	0.056254	0.18271

S2p = 0.031296592 Sp = 0.176908

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.27937631

Critical value = 0.41022751

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.064051146	0.41022751	NO
HMA2-WMA1	-0.01581481	0.41022751	NO
WMA1-WMA2	-0.00199824	0.41022751	NO
WMA2-AS1	0.137800705	0.41022751	NO
AS1-AS2	-0.15120459	0.41022751	NO
AS2-HMA1	-0.03283422	0.41022751	NO

Bonferroni test results for Nutrients

Nitrate test

$N03^-$-N

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.4	2.1	0.3	3	1	4
2	0.2	5	0.3	4	0.7	3.4
3	1.4	5.1	2	4.1	0.2	4
4	0.2	4	0.3	6	3	5
5	4.1	4.3	4.2	5	2.6	
mean	1.26	4.1	1.42	4.42	1.5	4.1
stdev	1.663730747	1.210371844	1.719592975	1.132254	1.228821	0.663325

S2p = 1.793391304 Sp = 1.339176

Using, $t_{v,\alpha/2k} * Sp * (1/ni + 1/nj)^{0.5}$,

t = 3.559678201

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-2.84	3.014937159	NO
HMA2-WMA1	2.68	3.014937159	NO
WMA1-WMA2	-3	3.014937159	NO
WMA2-AS1	2.92	3.014937159	NO
AS1-AS2	-2.6	3.197823765	NO
AS2-HMA1	2.84	3.197823765	NO

Ammonia						
Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.45	-0.02	0.3	0.01	0.23	0.01
2	0.13	-0.02	0.17	-0.14	0.54	0.03
3	0.57	0.02	0.79	-0.06	0	0.07
4	-0.01	0.15	0	0.11	0.32	0.09
5	0.21	0.13	0.36	0.12	-0.01	
mean	0.27	0.052	0.324	0.008	0.216	0.05
stdev	0.236643191	0.08228001	0.294838939	0.111220502	0.231149	0.036515

S2p = 0.037652174 Sp = 0.194041681

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.559678201

Comparison	Mean difference	Critical Value	Significance ?
HMA1-HMA2	0.218	0.436853443	NO
HMA2-WMA1	-0.272	0.436853443	NO
WMA1-WMA2	0.316	0.436853443	NO
WMA2-AS1	-0.208	0.436853443	NO
AS1-AS2	0.166	0.463353048	NO
AS2-HMA1	-0.22	0.463353048	NO

PO_4^{-3} (mg/l)

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.17	0.08	3.19	0.13	0.41	0.39
2	0.26	0.15	0.36	-0.08	0.48	0.54

3	0.38	0.88	0.42	0.42	0.15	1.33
4	0.22	0.95	0.15	1.11	0.66	1.5
5	0.38	0.9	1.21	1.1	0.19	
mean	0.282	0.592	1.066	0.536	0.378	0.94
stdev	0.094973681	0.436886713	1.253686564	0.548935	0.211116	0.556237

S2p = 0.40862087 Sp = 0.639235

Using, $t_{v,\alpha/2k} * Sp * (1/ni+1/nj)^{0.5}$,

t = 3.559678201

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.31	1.439133247	NO
HMA2-WMA1	-0.474	1.439133247	NO
WMA1-WMA2	0.53	1.439133247	NO
WMA2-AS1	0.158	1.439133247	NO
AS1-AS2	-0.562	1.526431317	NO
AS2-HMA1	0.658	1.526431317	NO

Total Nitrogen (mg/l)

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0	1	1	0	1	3
2	1	2	0	2	2	1
3	1	1	2	5	0	3
4	0	3	0	3	1	2
5	0	2	1	2	0	
mean	0.4	1.8	0.8	2.4	0.8	2.25
stdev	0.547722558	0.836660027	0.836660027	1.81659	0.83666	0.957427

S2p = 1.110869565 Sp = 1.053978

Using, $t_{v,\alpha/2k} * Sp * (1/ni + 1/nj)^{0.5}$,

t = 3.559678201

2.372860839

2.516798985

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-1.4	2.372860839	NO
HMA2-WMA1	1	2.372860839	NO
WMA1-WMA2	-1.6	2.372860839	NO
WMA2-AS1	1.6	2.372860839	NO
AS1-AS2	-1.45	2.516798985	NO
AS2-HMA1	1.85	2.516798985	NO

	Detergent					
Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.25	0.5	0.25	0.25	0.25	1
2	0.5	1	0.5	0.5	0.75	0.5
3	1.75	0.75	1	0.75	0.625	0.75
4	0.5	1	0.5	1	1	1
5	1.75	1	1.5	1	0.25	
mean	0.95	0.85	0.75	0.7	0.575	0.8125
stdev	0.73739406	0.223606798	0.5	0.32596	0.32596	0.239357

S2p = 0.191168478 Sp = 0.437228

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t = 3.559678201

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	0.1	0.984348483	NO
HMA2-WMA1	0.1	0.984348483	NO
WMA1-WMA2	0.05	0.984348483	NO
WMA2-AS1	0.125	0.984348483	NO
AS1-AS2	-0.2375	1.044059231	NO
AS2-HMA1	-0.1375	1.044059231	NO

COD

Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	34	24	45	30	128	70

2	49	37	47	36	110	24
3	162	45	150	55	34	26
4	6	55	29	48	91	30
5	112	70	157	45	120	
mean	72.6	46.2	85.6	42.8	96.6	37.5
stdev	63.2992891	17.48427865	62.42435422	9.884331	37.62712	21.80978

S2p =	1752.965217	Sp =	41.868443

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

t =	3.559678201

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	26.4	94.25998885	NO
HMA2-WMA1	-39.4	94.25998885	NO
WMA1-WMA2	42.8	94.25998885	NO

		94.2599888	
WMA2-AS1	-53.8	5	NO
		99.9778159	
AS1-AS2	59.1	7	NO
		99.9778159	
AS2-HMA1	-35.1	7	NO

Bonferroni test results for Heavy metals

Copper						
Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2
1	0.1	0.02	0.09	0.03	0.07	0.09
2	0.06	0.08	0.06	0.09	0.15	0.06
3	0.09	0.05	0.09	0.06	0.05	0.13
4	0.04	0.11	0.03	0.12	0.07	0.16
5	0.06	0.17	0.08	0.17	0.04	
mean	0.07	0.086	0.07	0.094	0.076	0.11
stdev	0.024494897	0.05770615	0.0254951	0.054129474	0.043358967	0.043969687
	S^2p =	0.00188522	Sp =	0.04341909		

α/2k = 0.00166667

t = 3.5596782

Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

Comparison	Mean difference	Critical Value	Significance?
HMA1-HMA2	-0.016	0.0977511	NO
HMA2-WMA1	0.016	0.0977511	NO
WMA1-WMA2	-0.024	0.0977511	NO
WMA2-AS1	0.018	0.0977511	NO
AS1-AS2	-0.034	0.1036807	NO
AS2-HMA1	0.04	0.1036807	NO

	Zinc					
Groups	HMA1	HMA2	WMA1	WMA2	AS1	AS2

1	0	0	0	0.03	0	0.06
2	0	0.05	0	0.06	0.07	0.06
3	0.05	0.04	0.04	0.05	0.07	0.15
4	0.05	0.14	0.05	0.15	0.07	0.21
5	0.08	0.22	0.1	0.25	0.04	
mean	0.036	0.09	0.038	0.108	0.05	0.12
stdev	0.035071356	0.08888194	0.0414729	0.091760558	0.0308220 7	0.07348469 2

S^2p = 0.00422087 Sp = 0.06496822

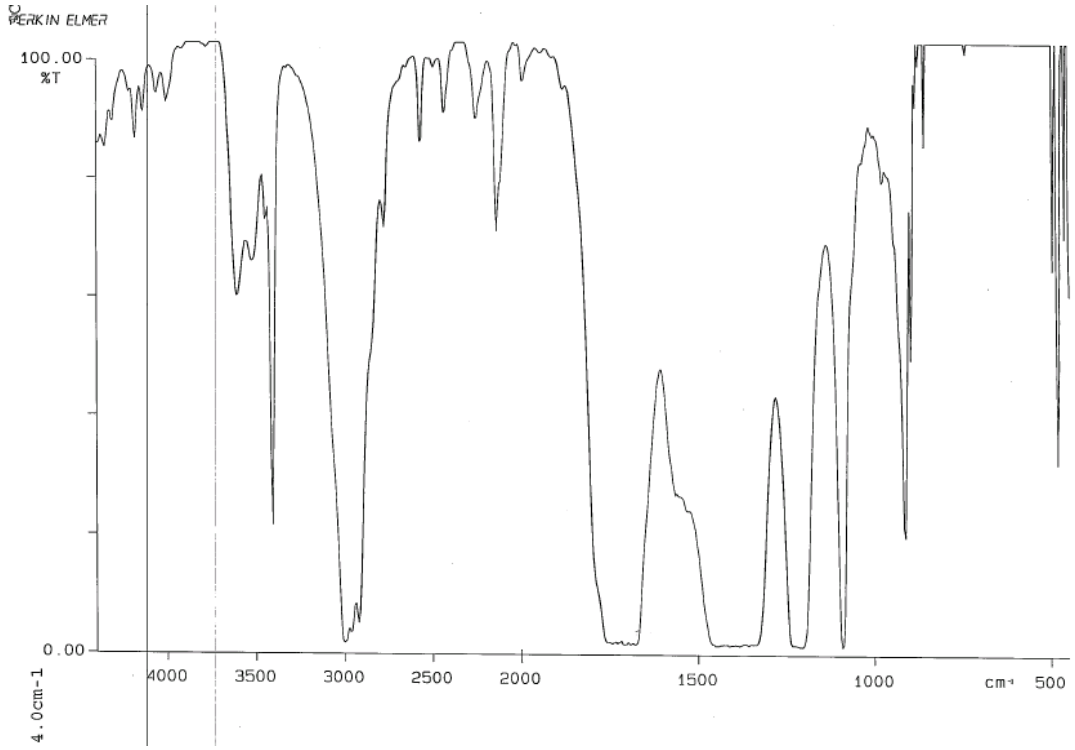
Using, tv,α/2k*Sp*(1/ni+1/nj)^0.5,

Comparison	Mean difference	Critical Value	Significance ?
HMA1-HMA2	-0.054	0.1462654	NO
HMA2-WMA1	0.052	0.1462654	NO
WMA1-WMA2	-0.07	0.1462654	NO
WMA2-AS1	0.058	0.1462654	NO

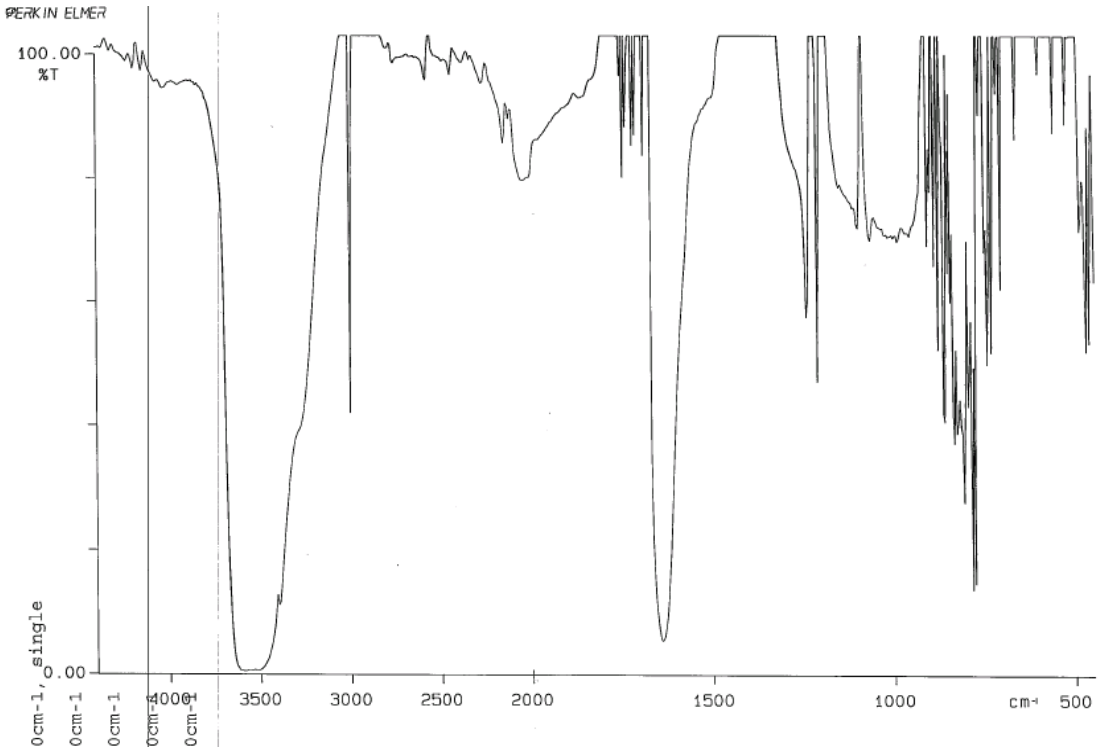
AS1-AS2	-0.07	0.1551379	NO
AS2-HMA1	0.084	0.1551379	NO

APPENDIX F

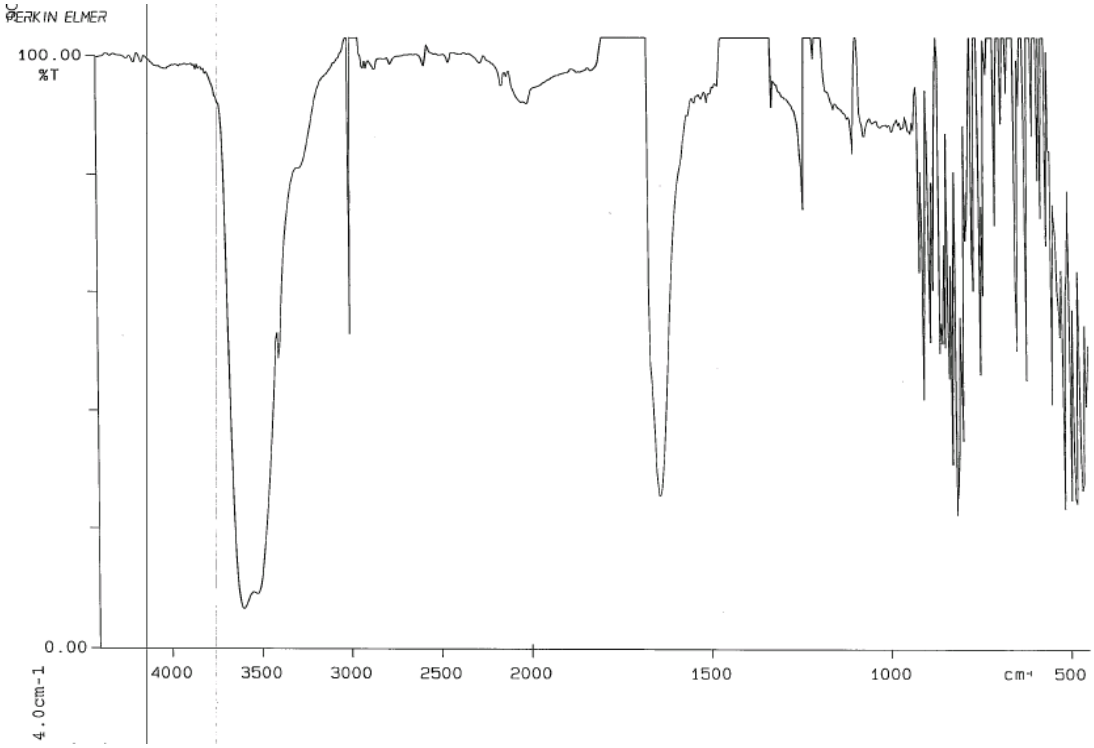
Acetone



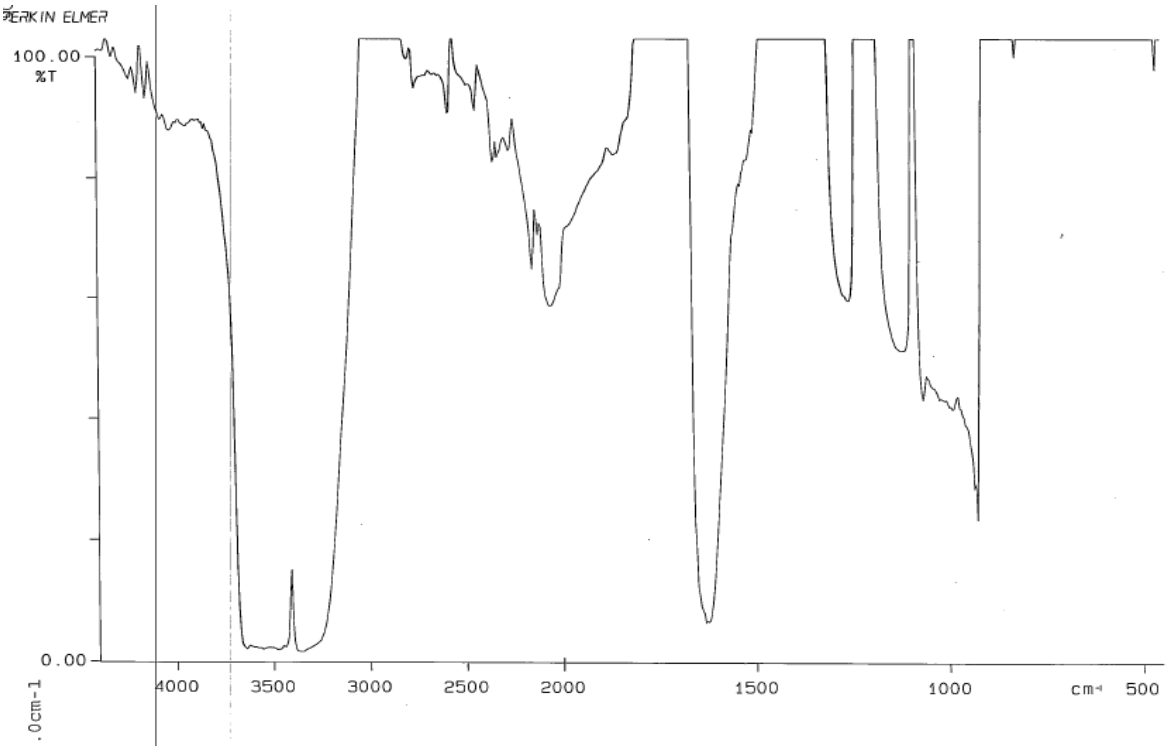
Scan 1: Scan of Acetone as the solvent



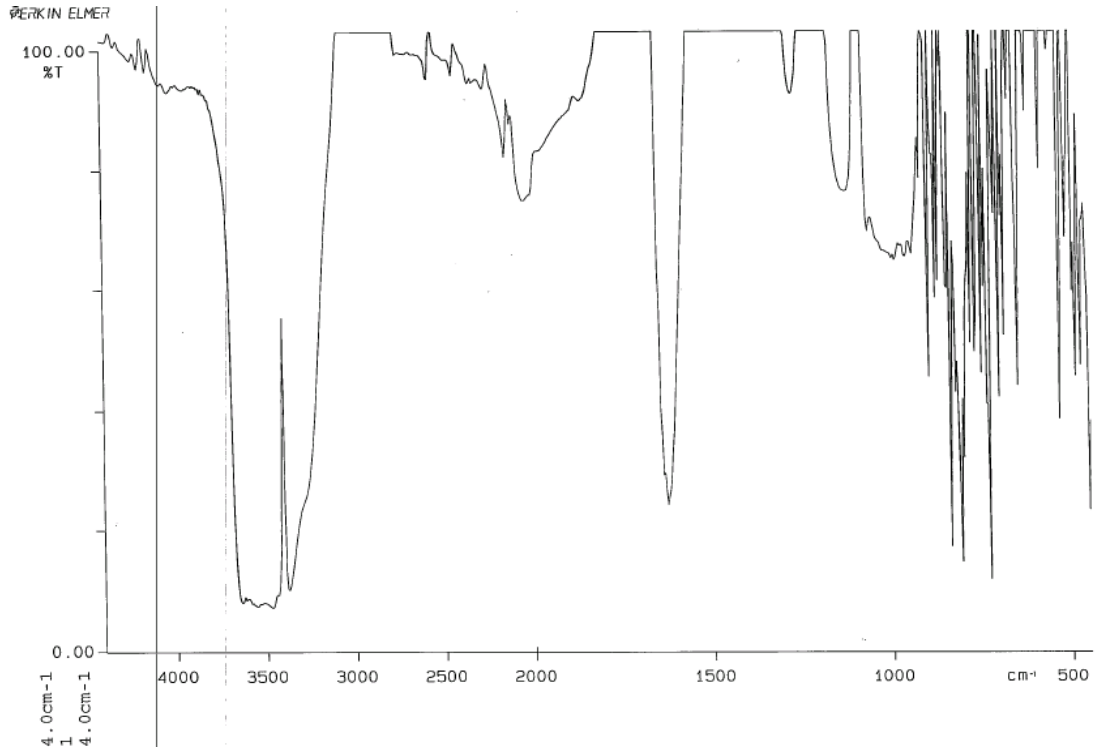
Scan 2: Scan of sample 3 after the Acetone background was subtracted.



Scan 3: Scan of sample 4 after the Acetone background was subtracted.

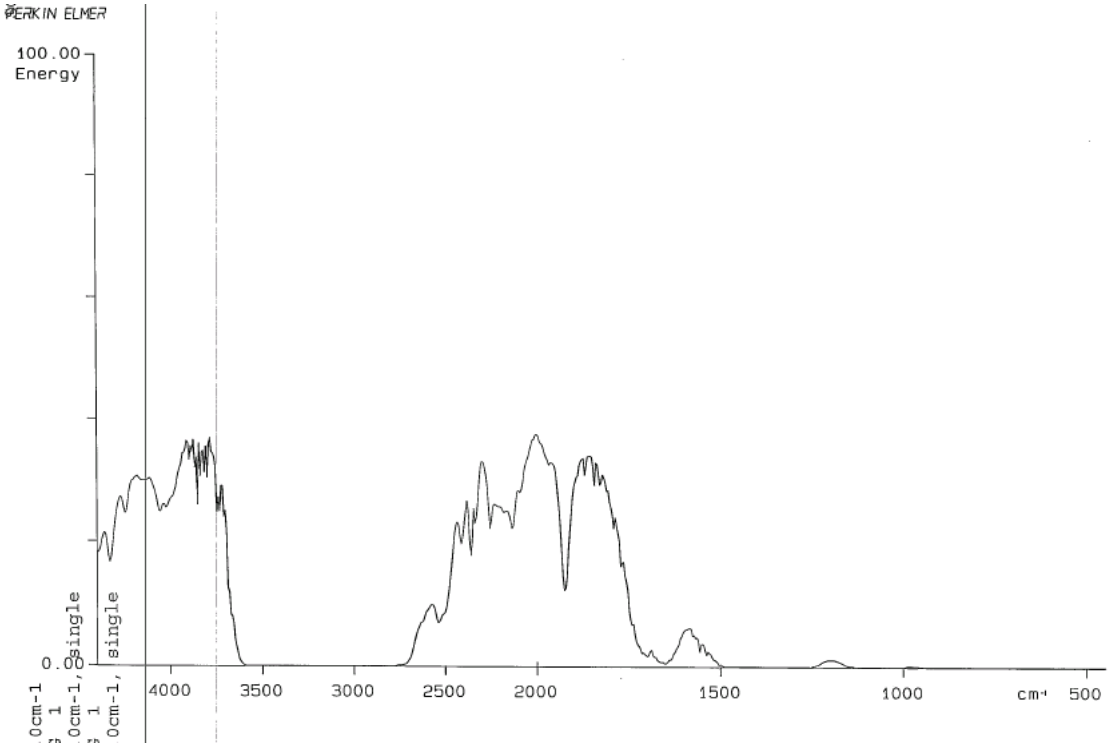


Scan 4: Scan of sample 5 after the Acetone background was subtracted.

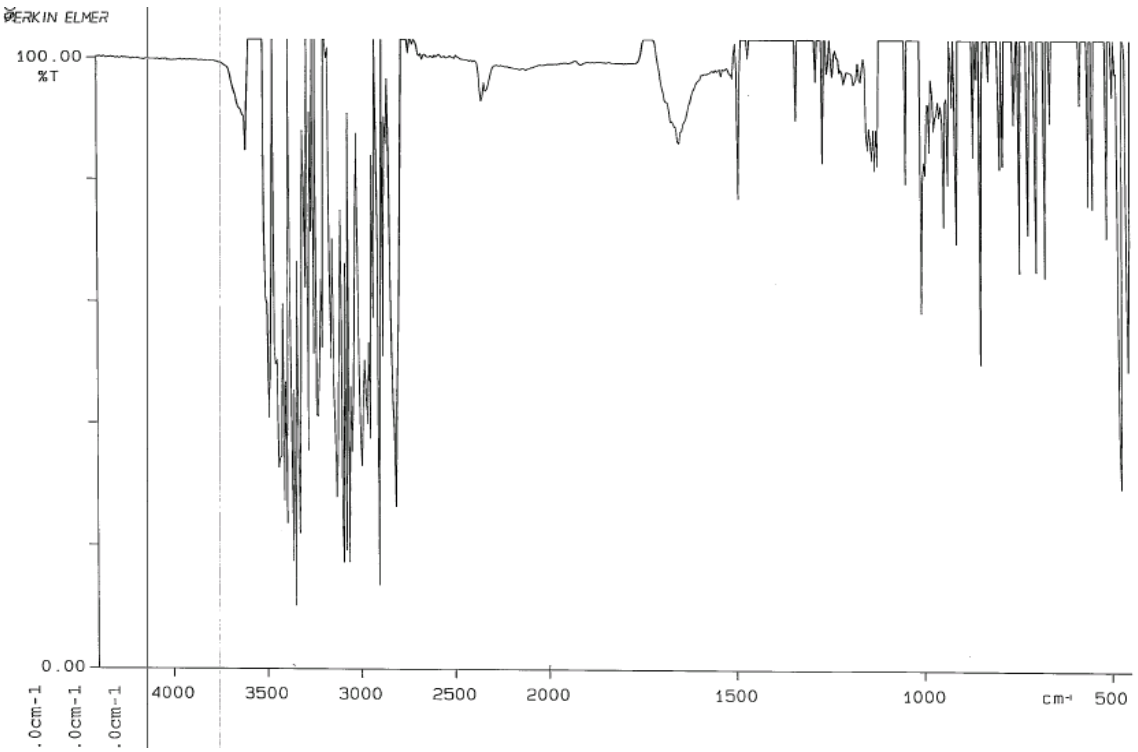


Scan 5: Scan of sample 6 after the Acetone background was subtracted.

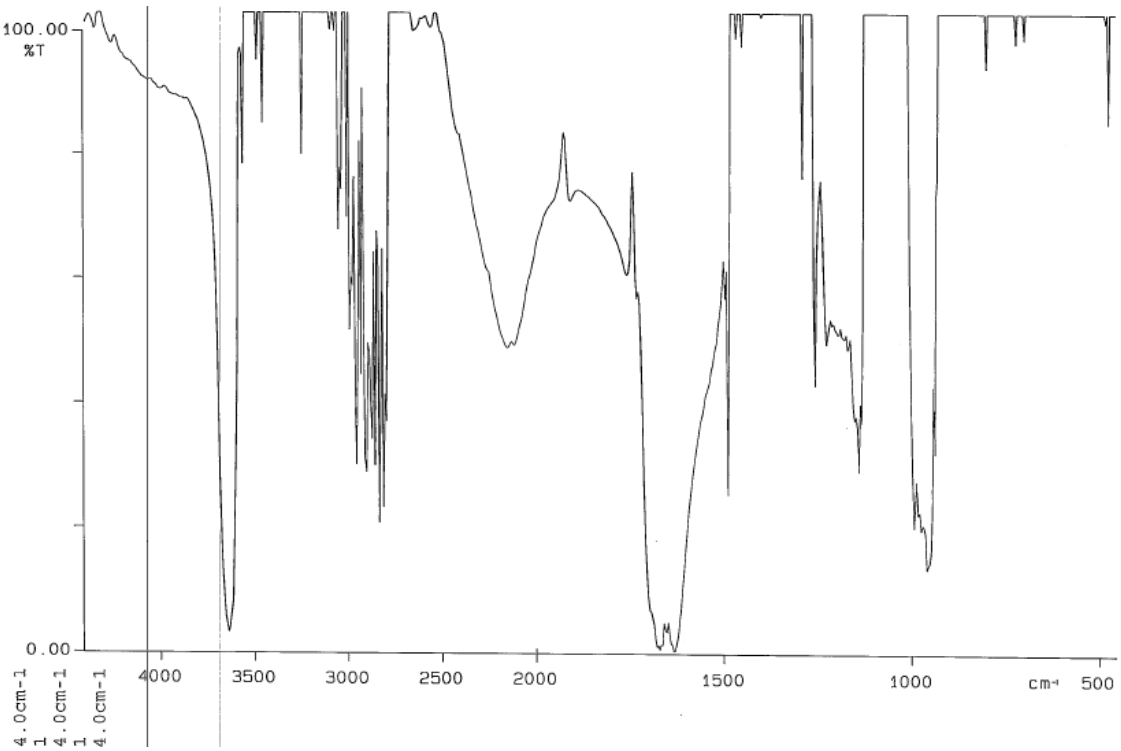
Denatured Alcohol



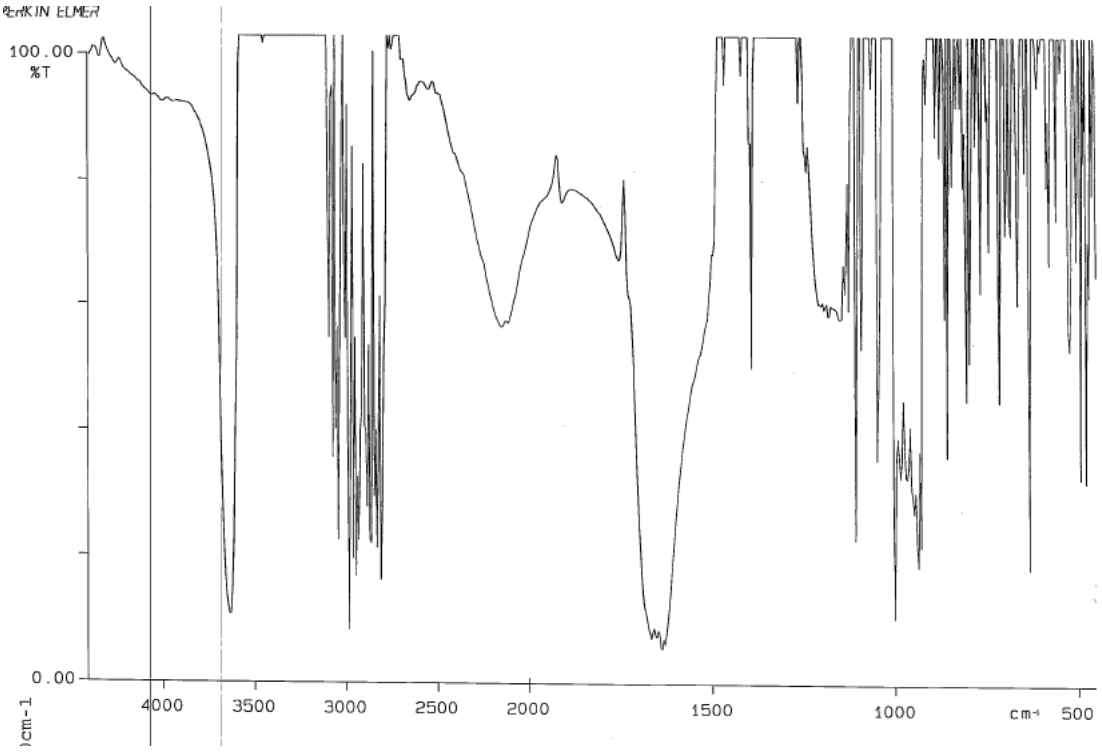
Scan 5: Denatured alcohol as the background.



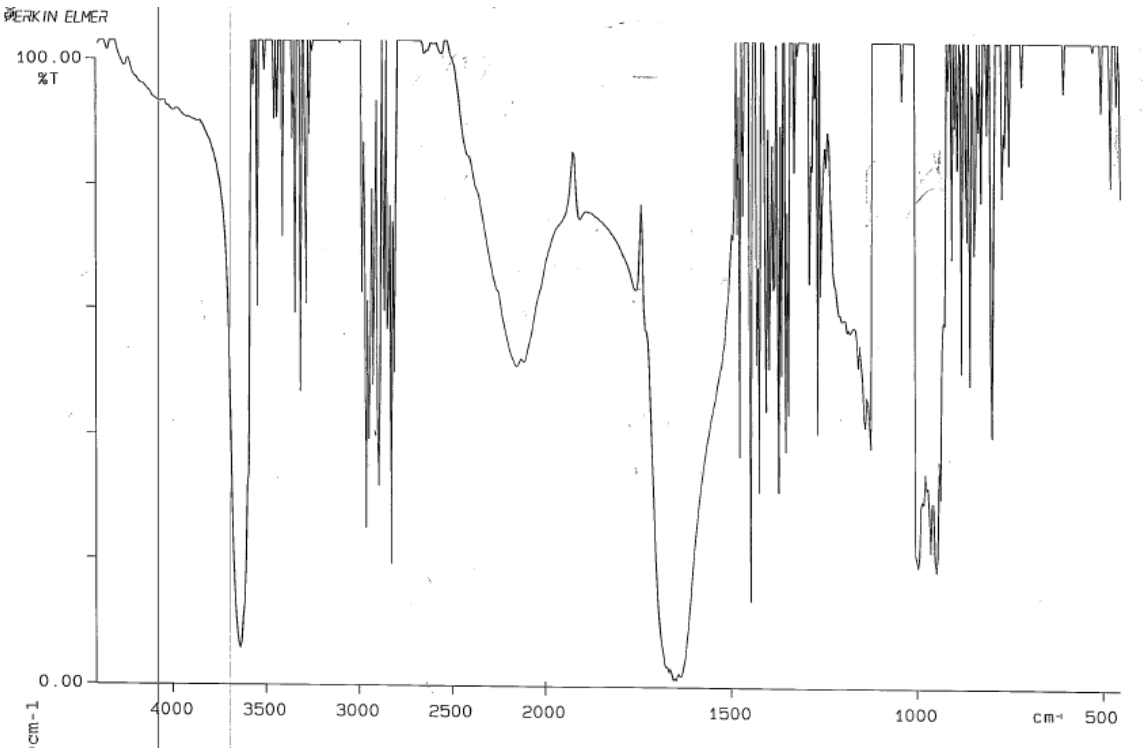
Scan 6: Denatured alcohol.



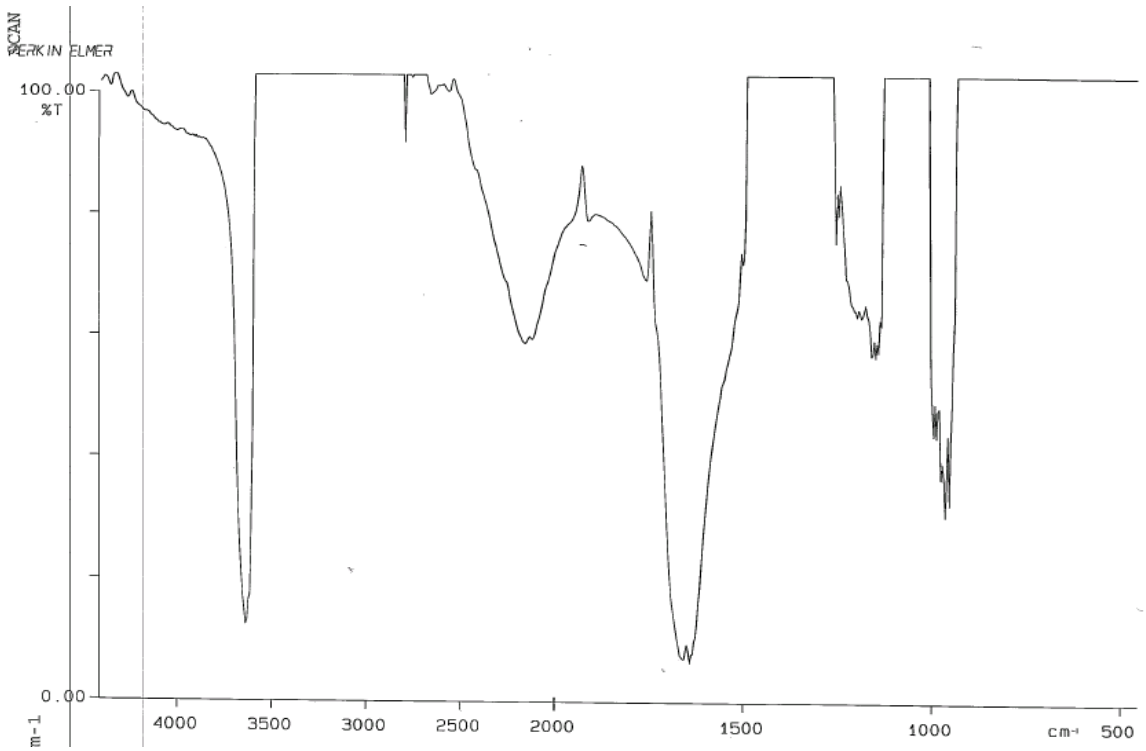
Scan 7: Scan of sample 1 after the Denatured Alcohol background was subtracted.



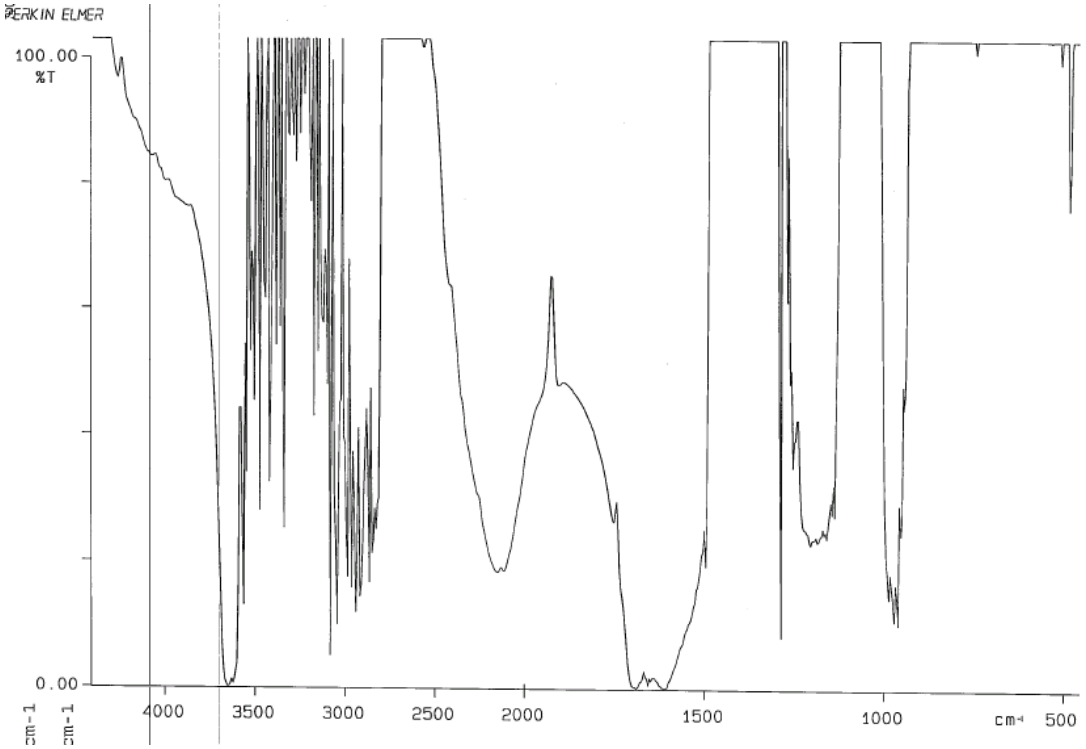
Scan 8: Scan of sample 2 after the Denatured Alcohol background was subtracted.



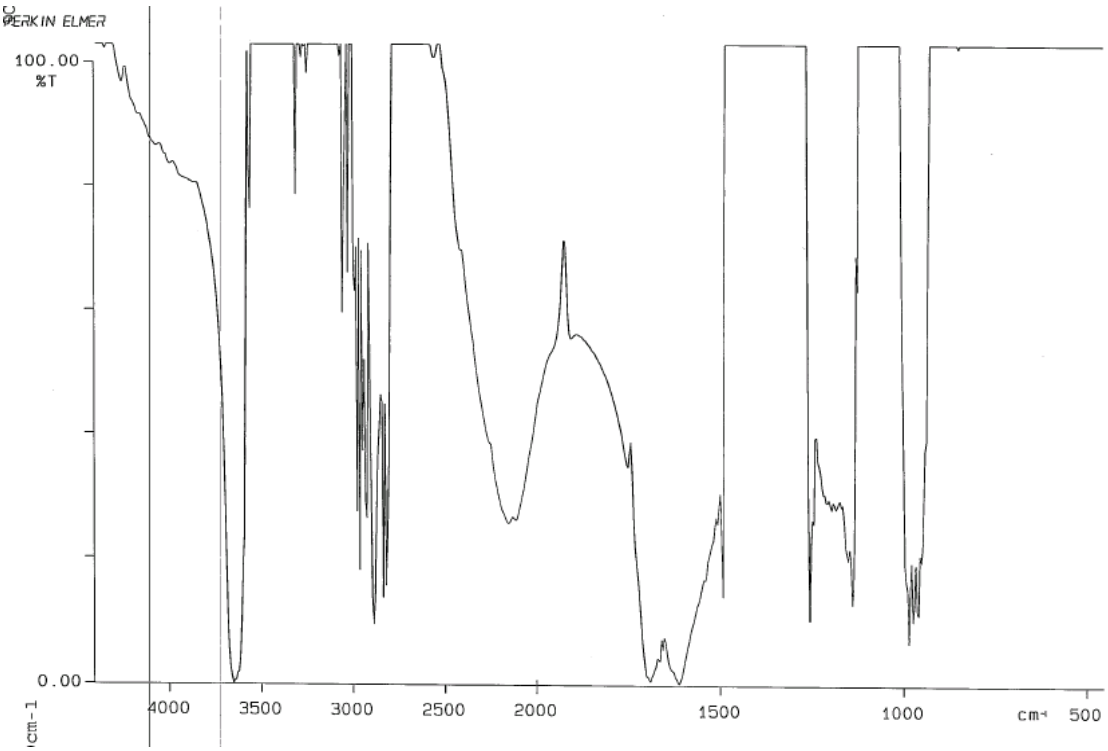
Scan 9: Scan of sample 3 after the Denatured Alcohol background was subtracted.



Scan 10: Scan of sample 4 after the Denatured Alcohol background was subtracted.

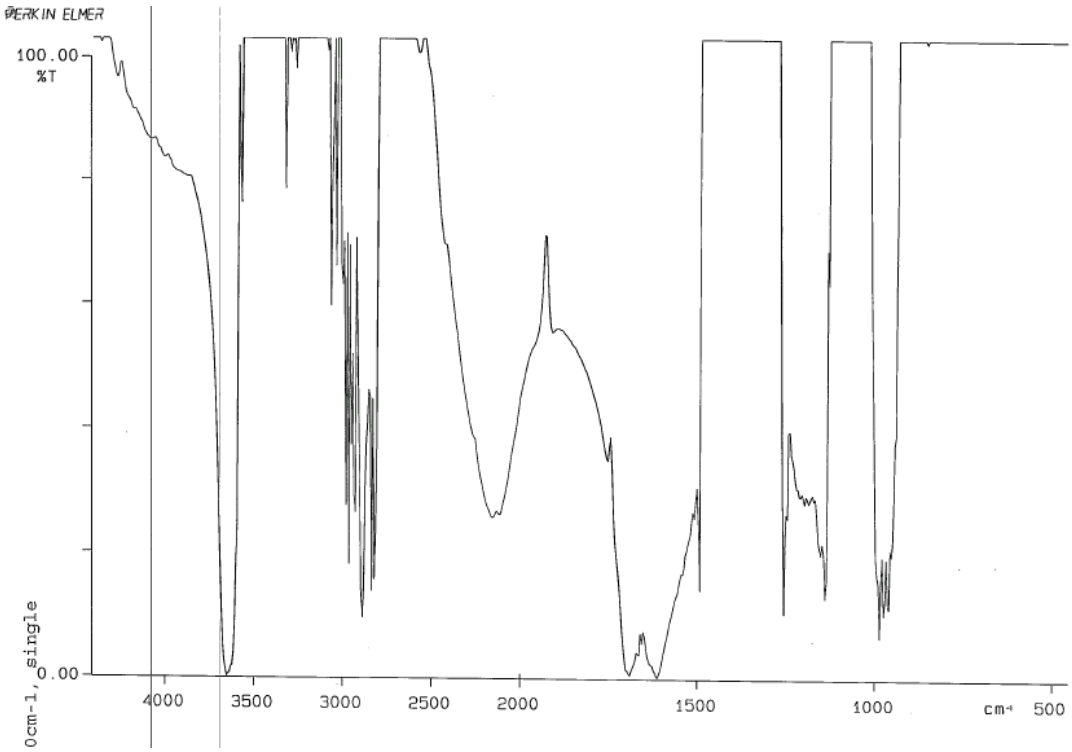


Scan 11: Scan of sample 5 after the Denatured Alcohol background was subtracted.

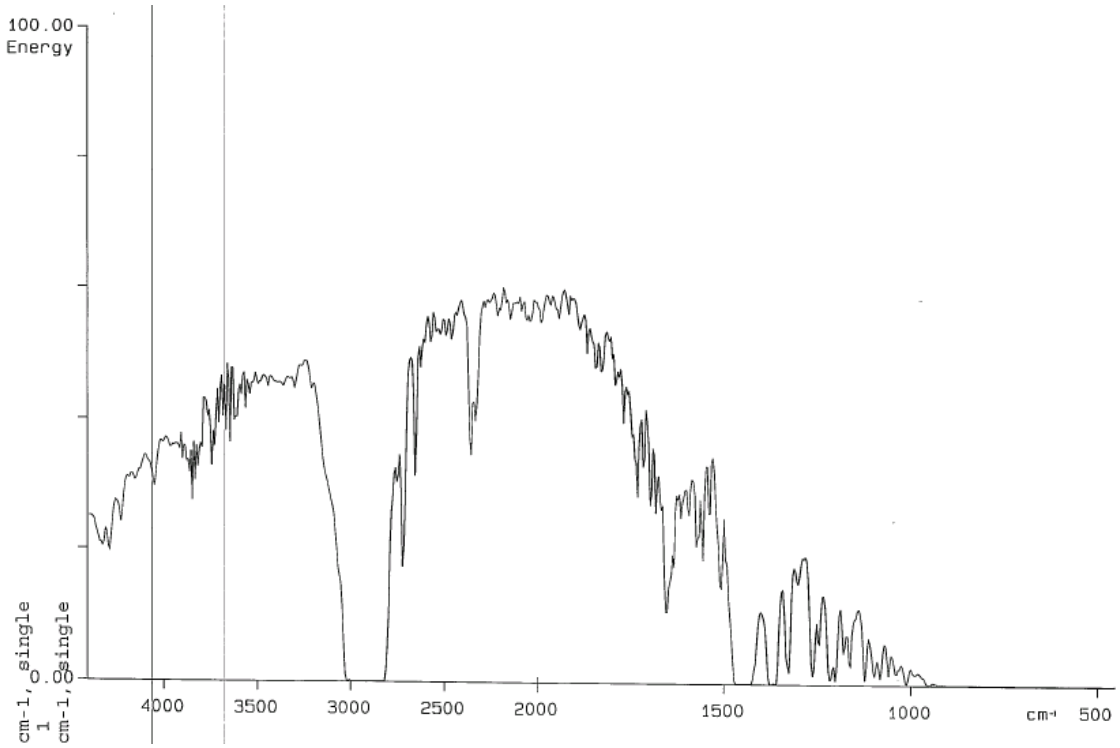


Scan 12: Scan of sample 6 after the Denatured Alcohol background was subtracted.

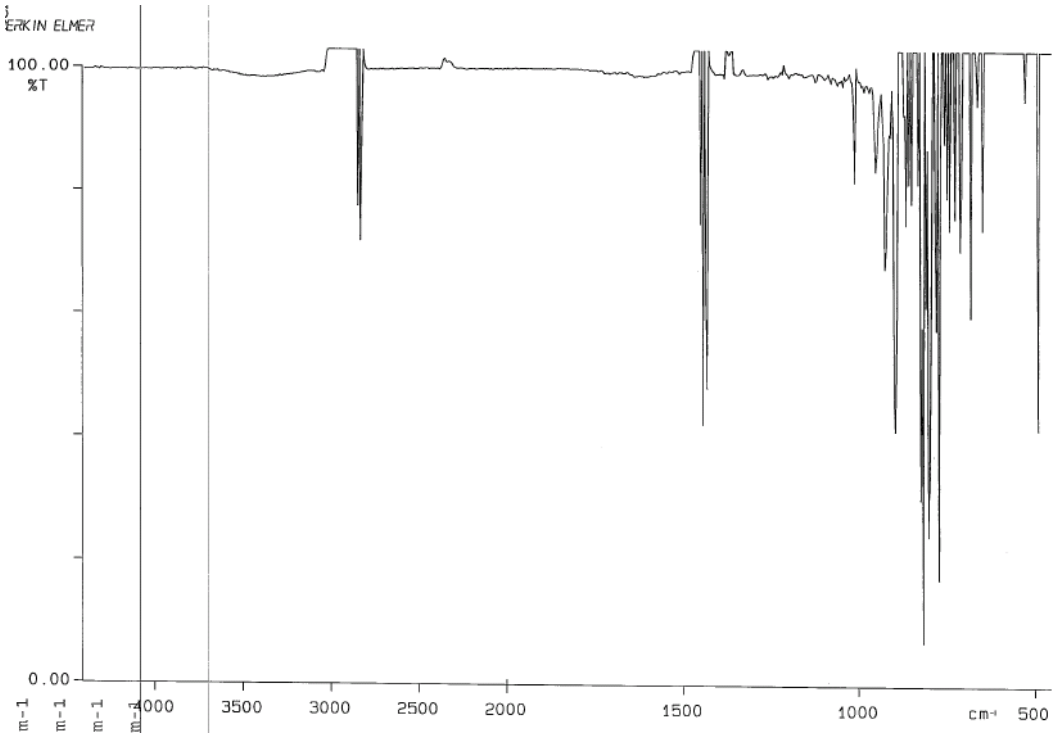
Turpentine



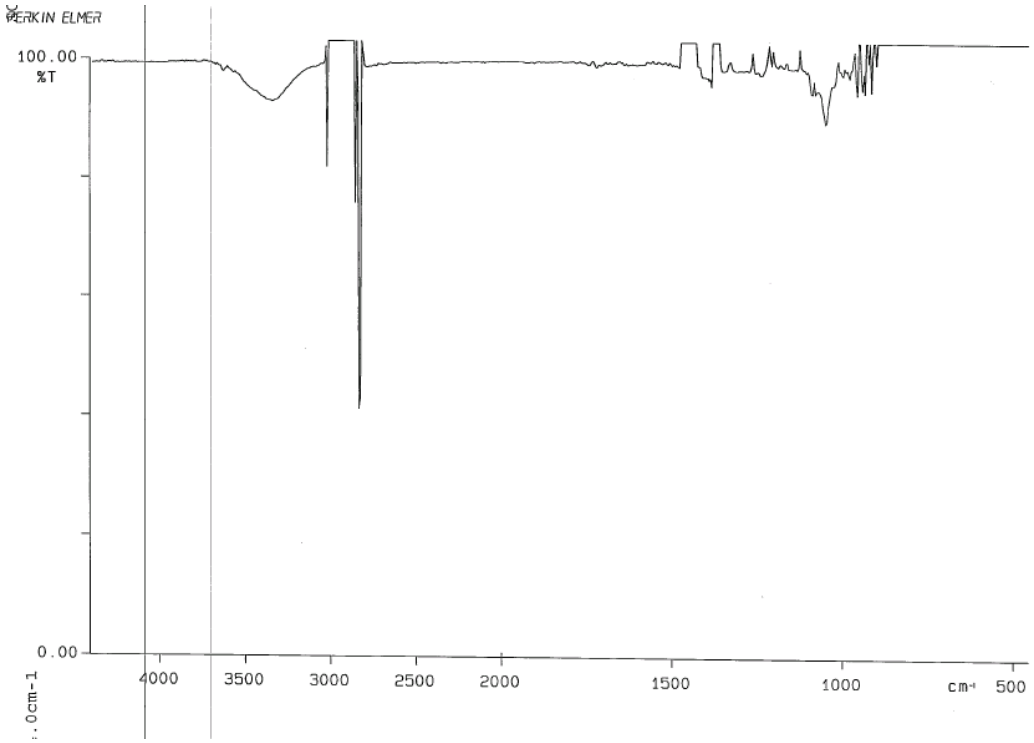
Scan 13: Turpentine with air as the background.



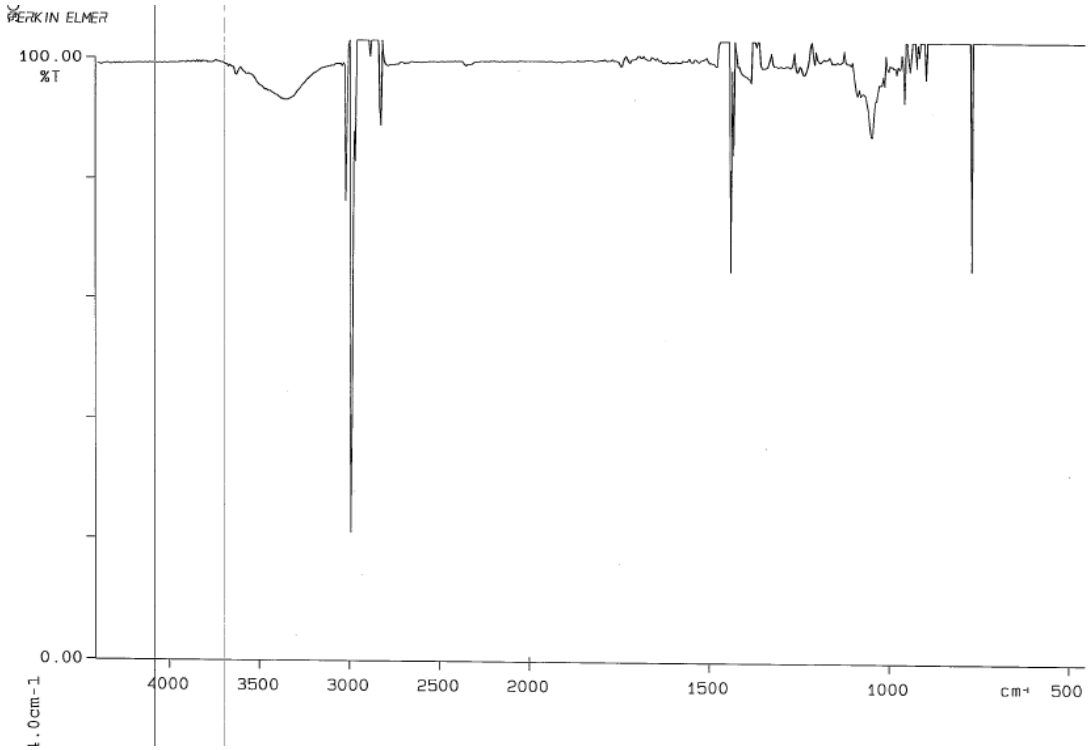
Scan 14: Turpentine as the background.



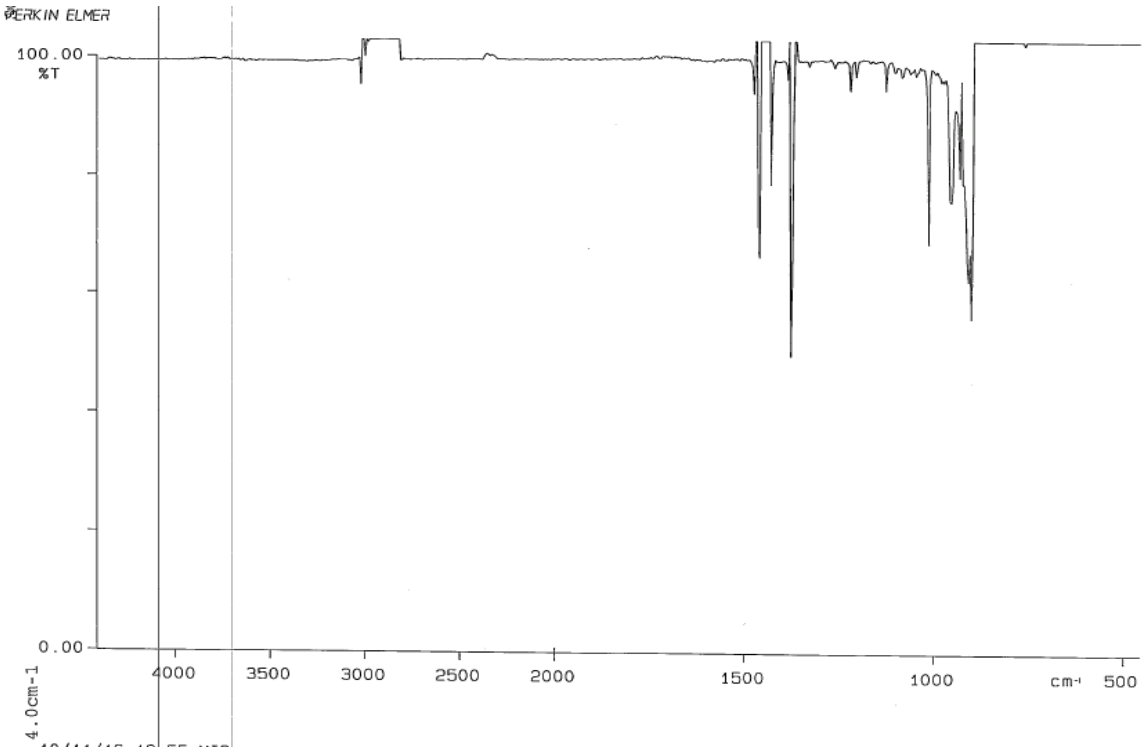
Scan 15: Scan of sample 1 after the Turpentine background was subtracted.



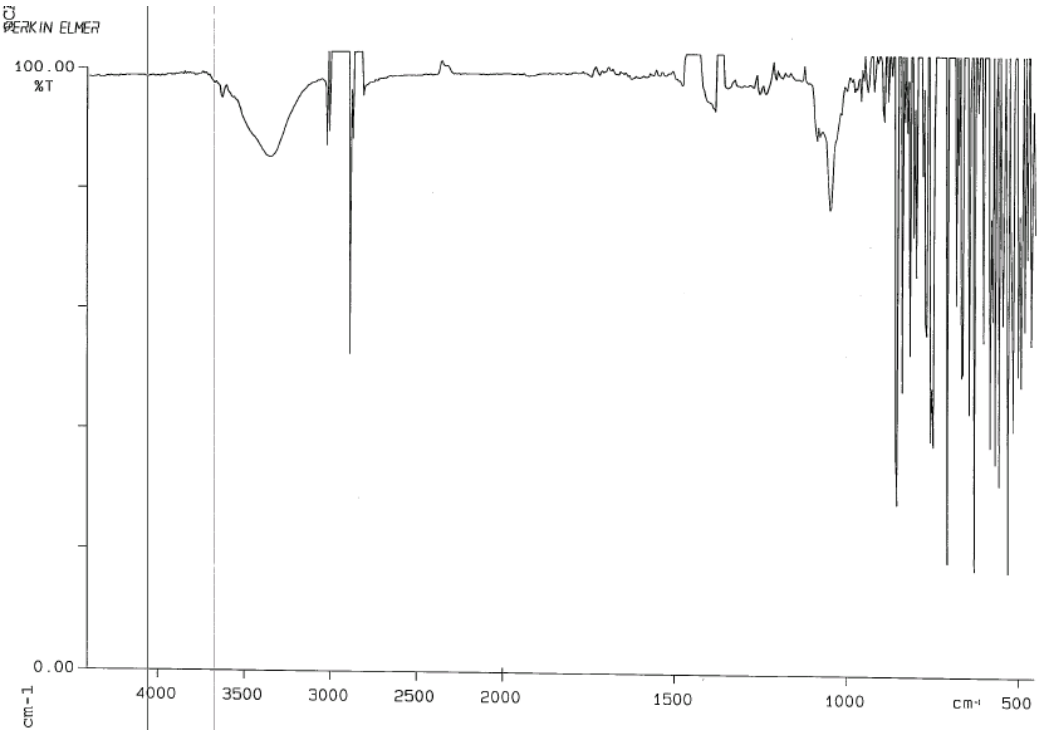
Scan 16: Scan of sample 2 after the Turpentine background was subtracted.



Scan 17: Scan of sample 3 after the Turpentine background was subtracted.

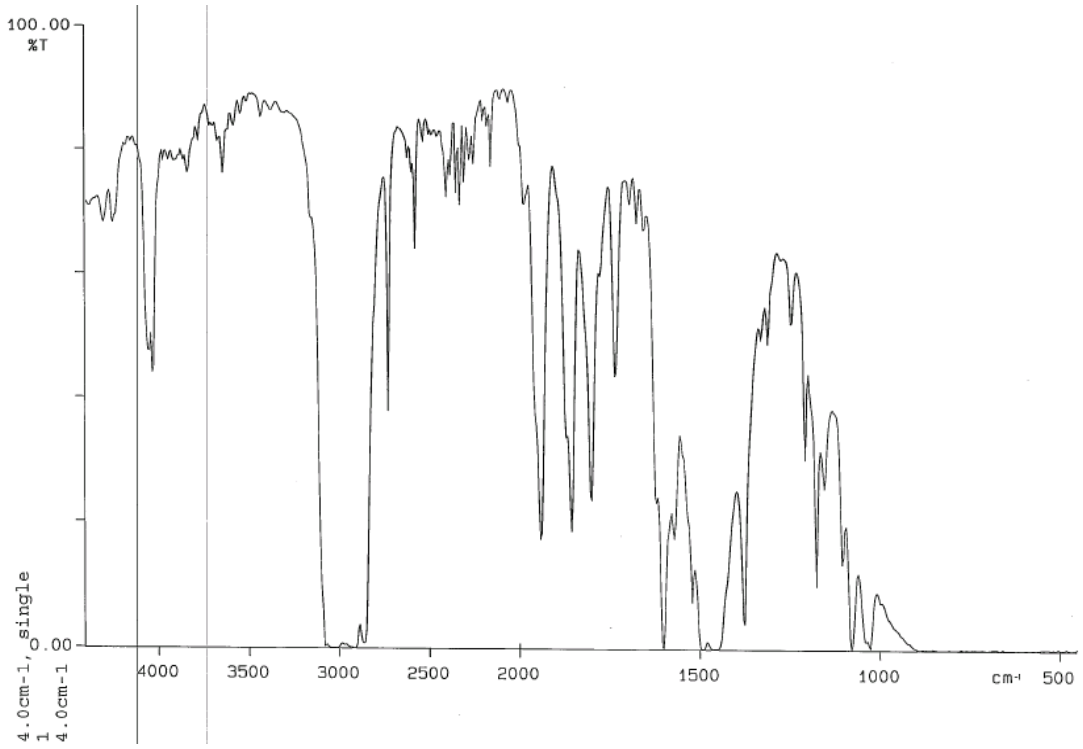


Scan 18: Scan of sample 5 after the Turpentine background was subtracted.

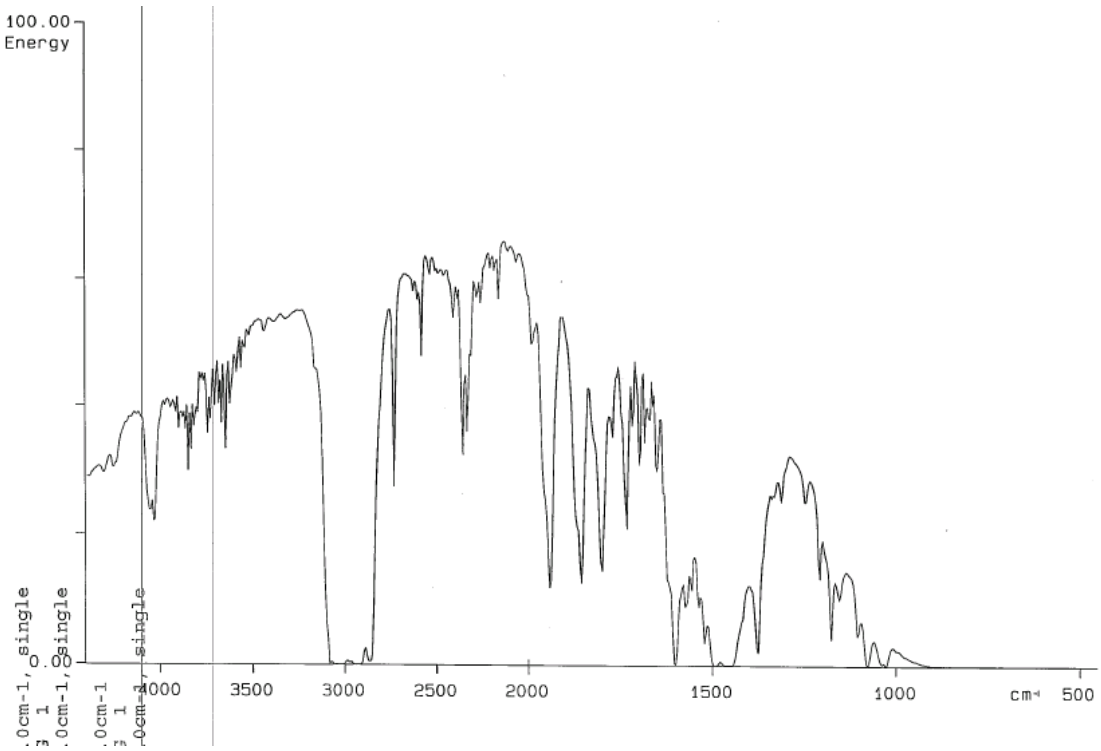


Scan 19: Scan of sample 6 after the Turpentine background was subtracted.

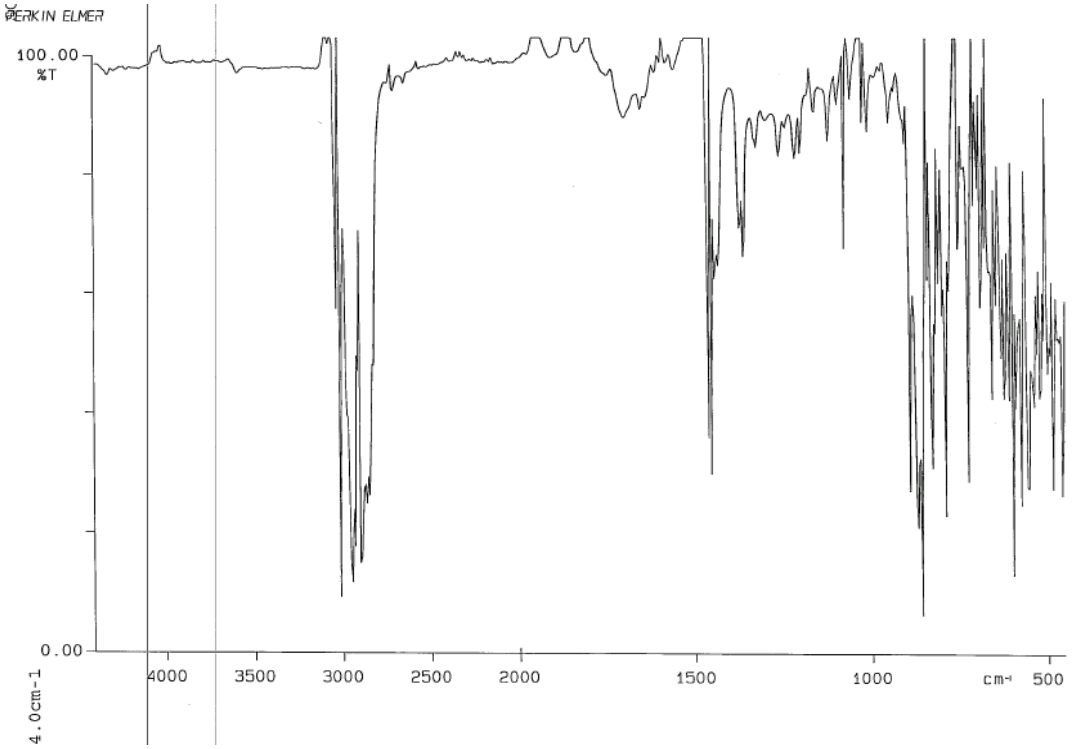
Toluene



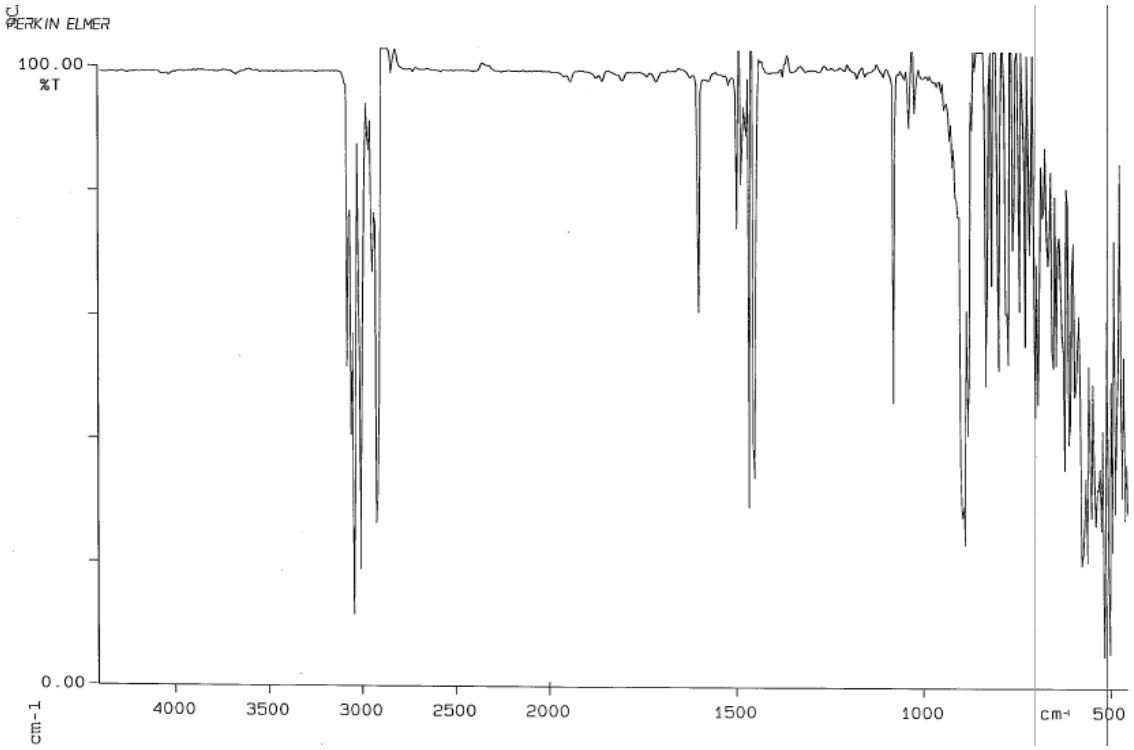
Scan 19: Toluene with air as the background.



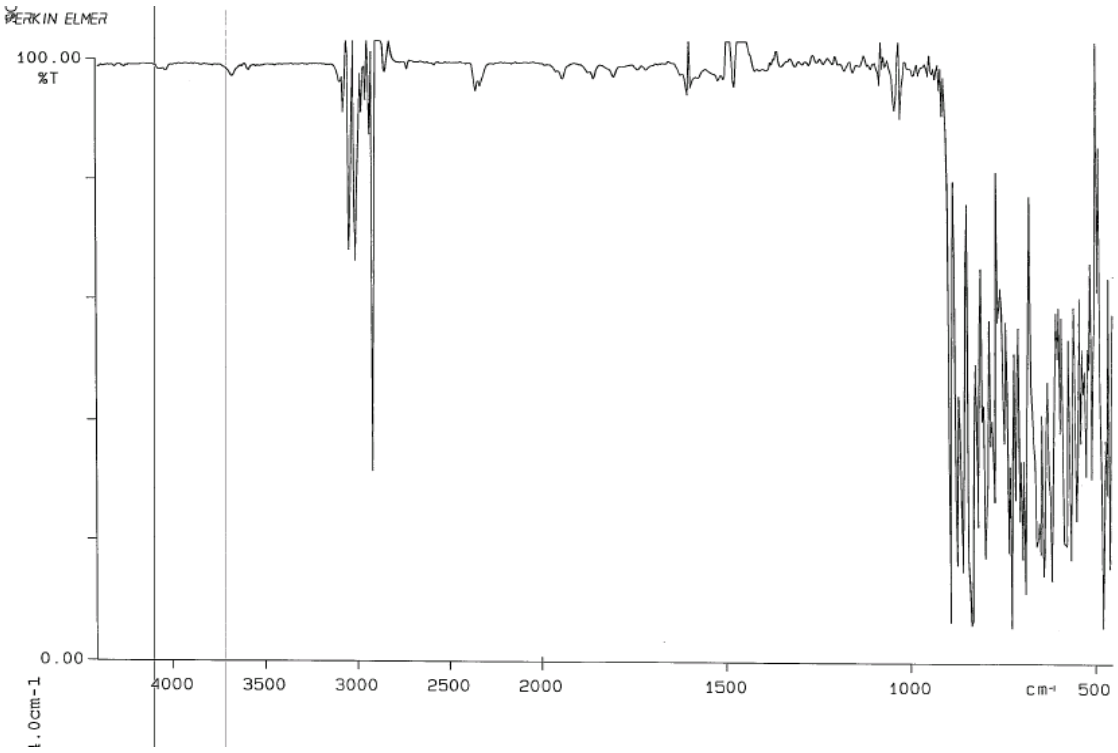
Scan 20: Toluene as the background.



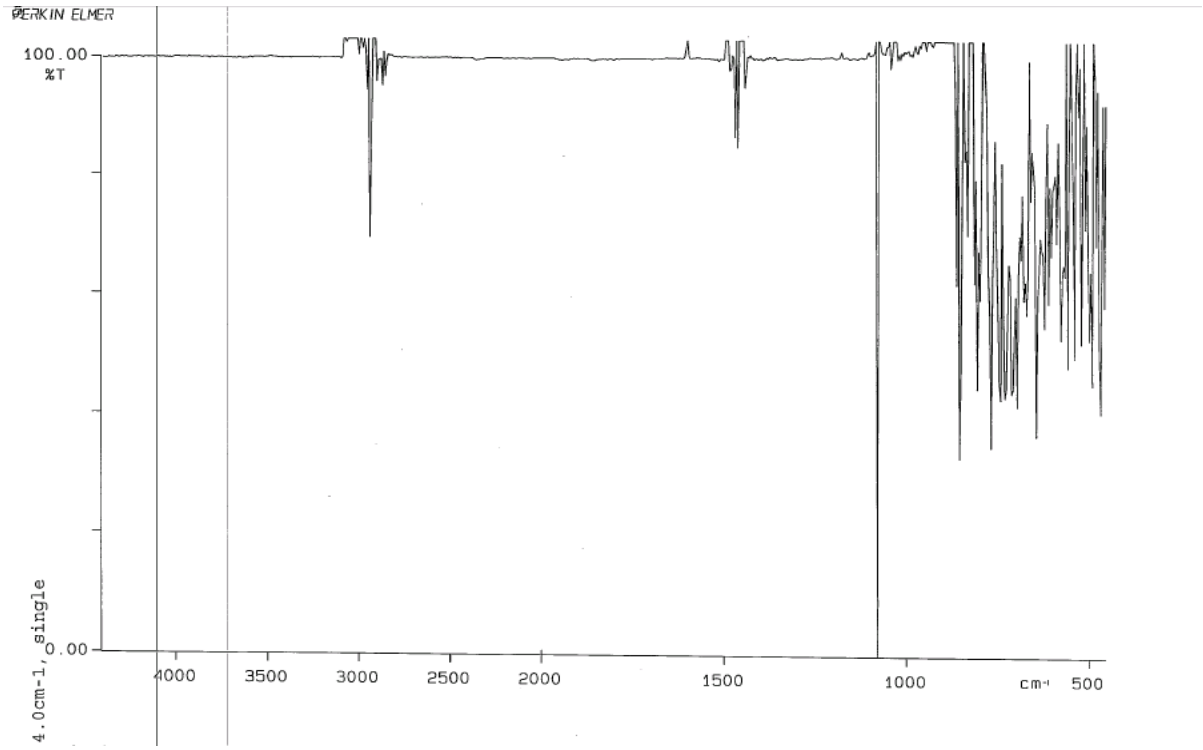
Scan 21: Scan of sample 1 after the Toluene background was subtracted.



Scan 22: Scan of sample 2 after the Toluene background was subtracted.

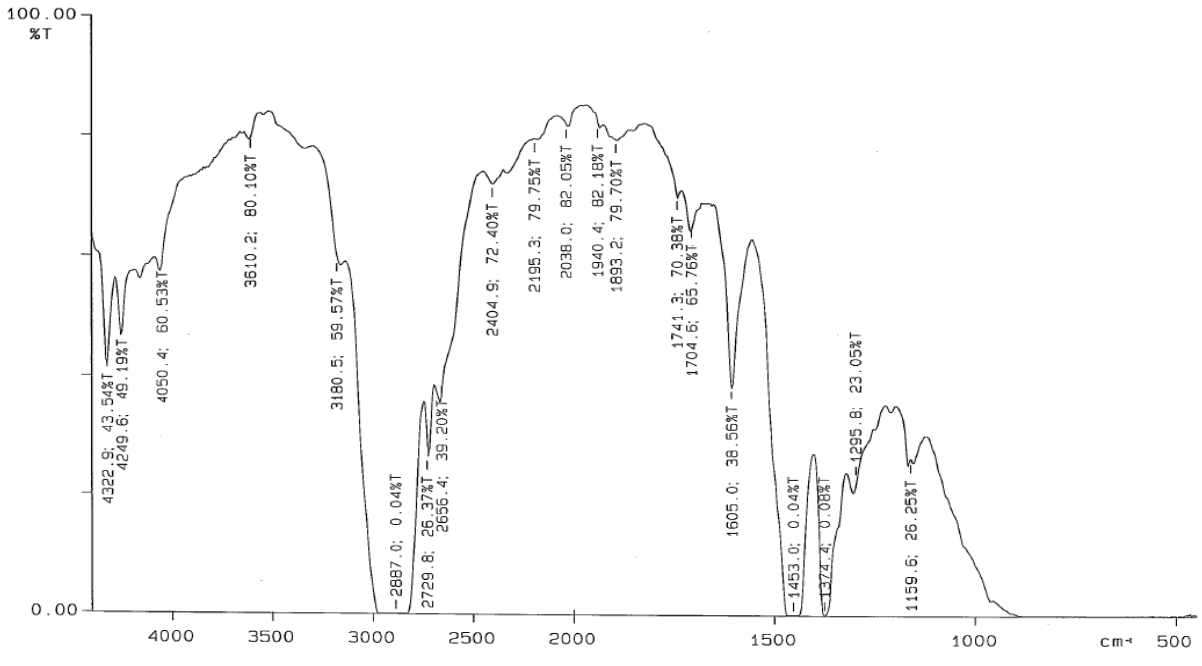


Scan 23: Scan of sample 3 after the Toluene background was subtracted.

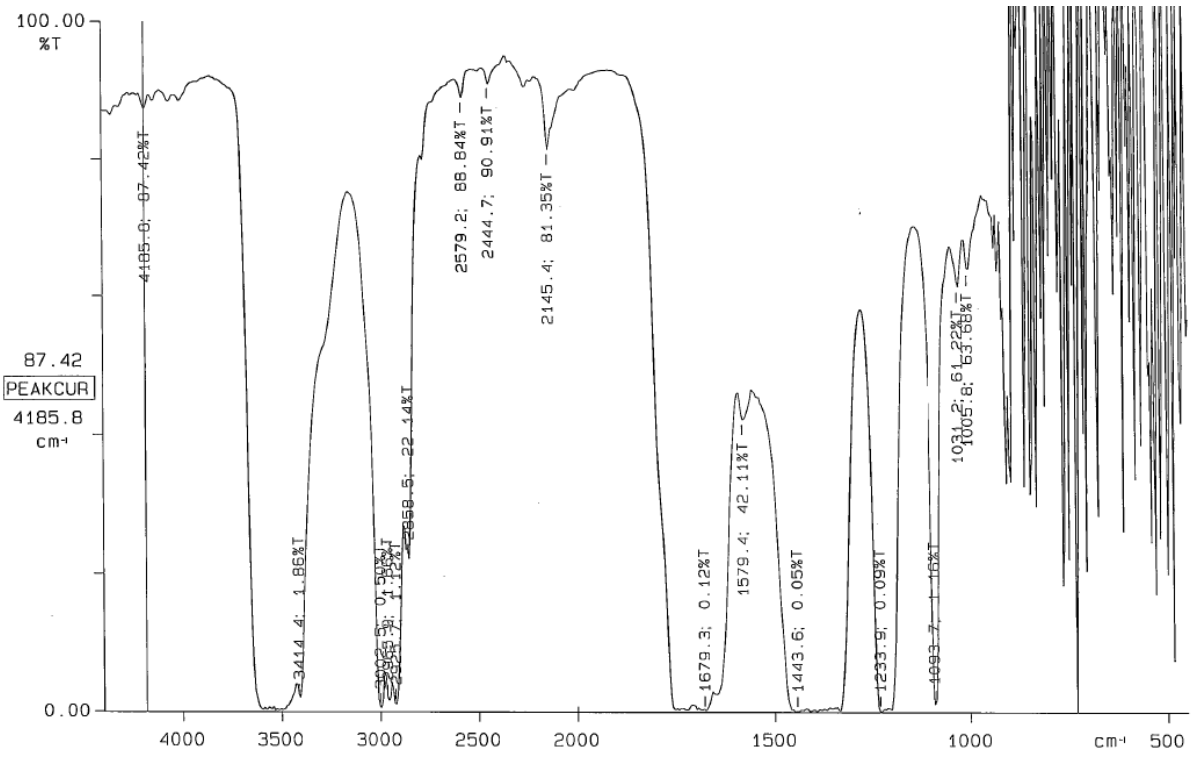


Scan 24: Scan of sample 5 after the Toluene background was subtracted.

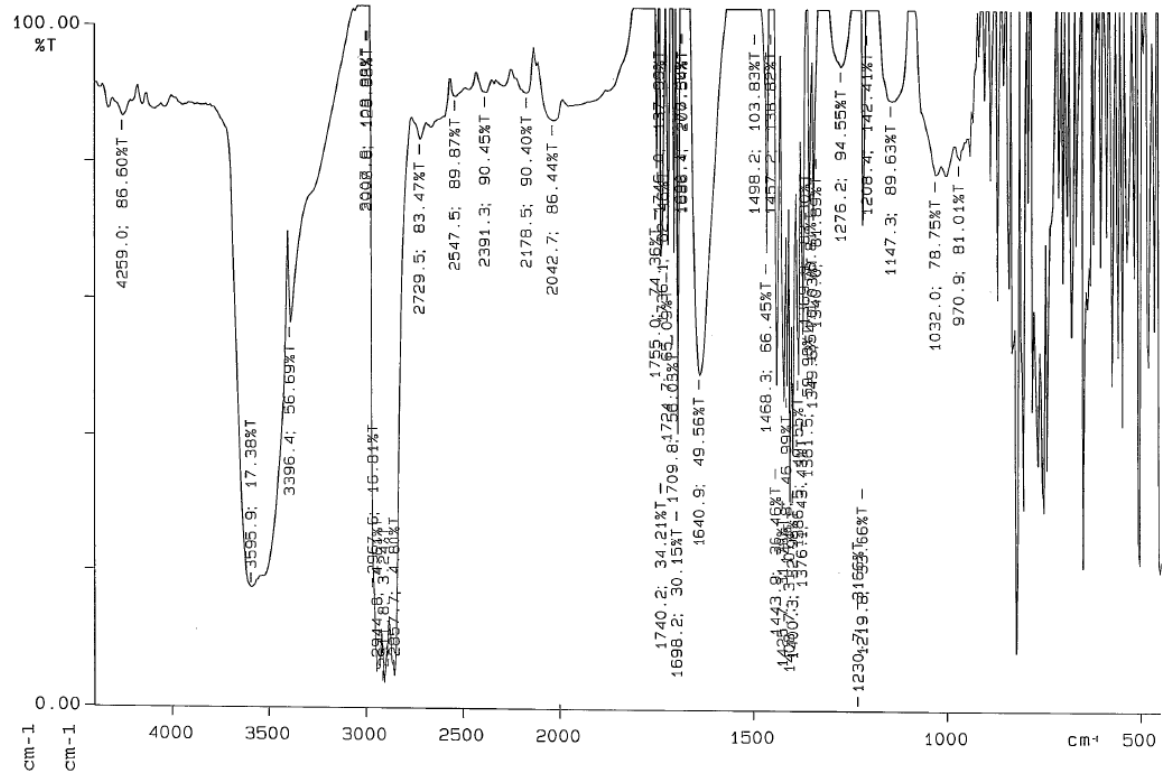
APPENDIX G



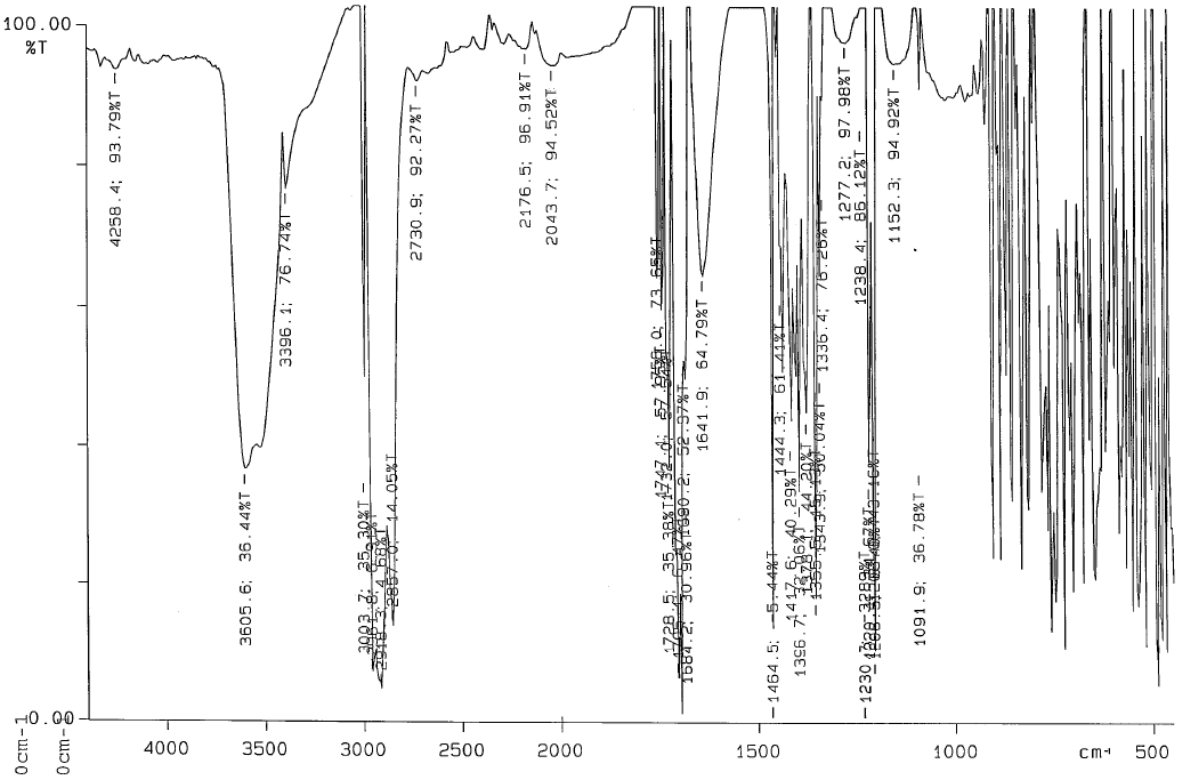
Scan 25: Crude Oil with air as the background, before aging.



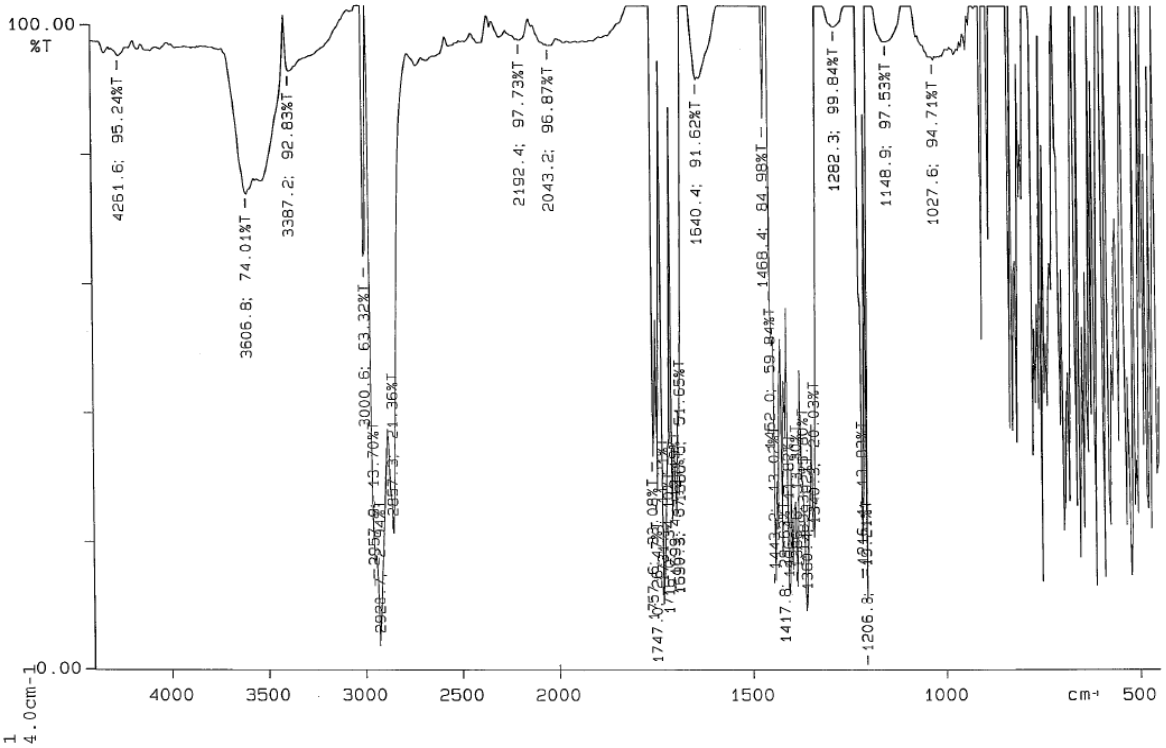
Scan 26: Crude oil sample after 24hr aging with UV radiation, with Acetone solvent.



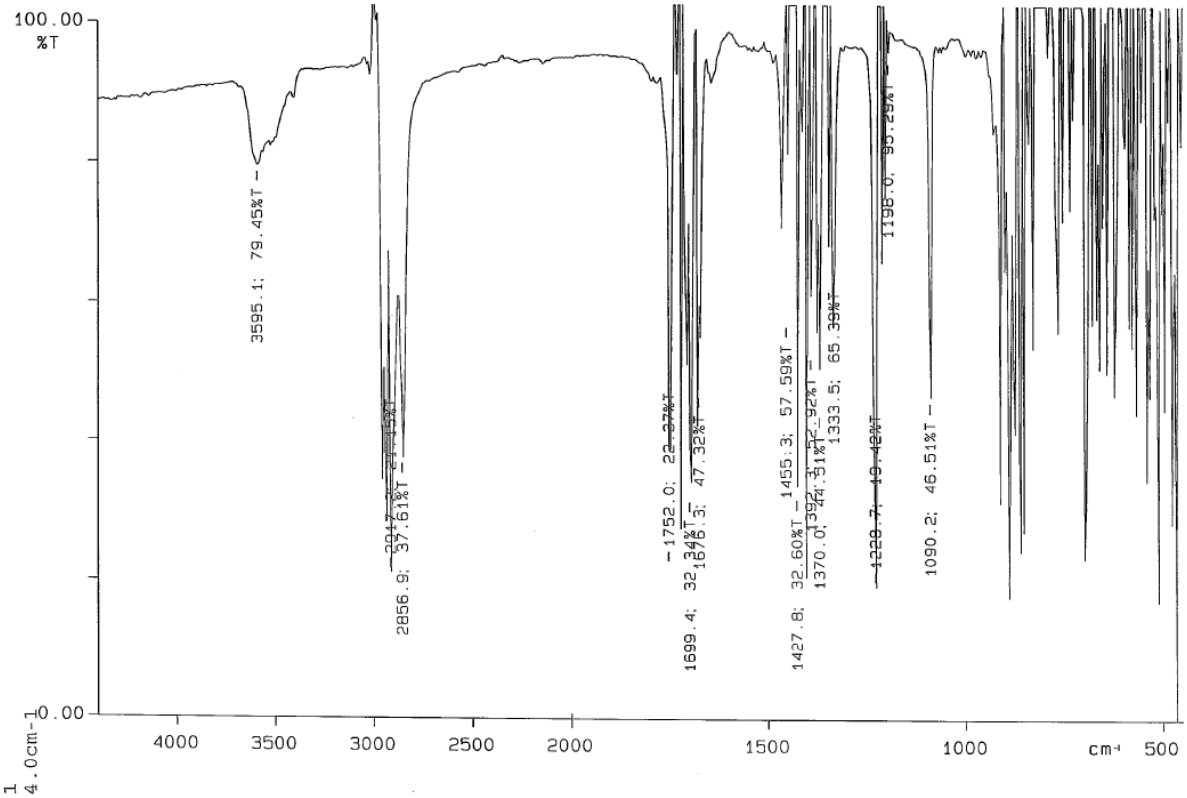
Scan27: Crude oil sample after 24hr aging with UV radiation with Acetone solvent.



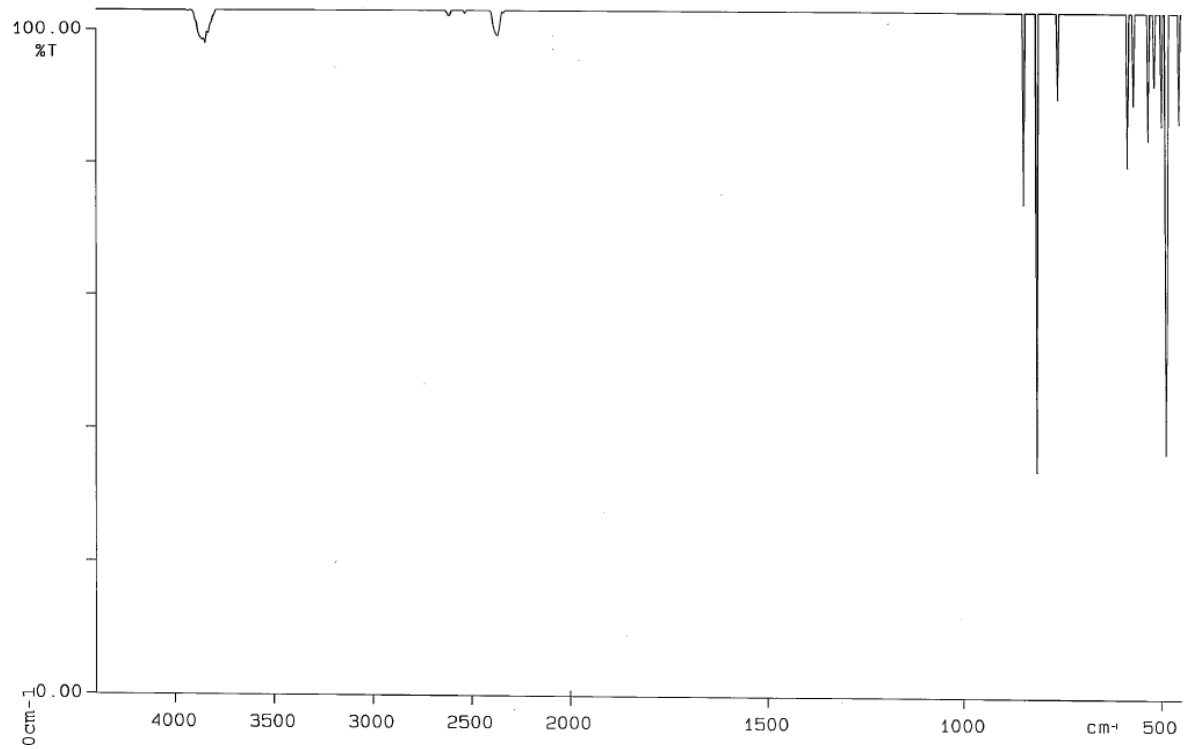
Scan 28: Crude oil sample after 48hrs of UV light exposure with Acetone.



Scan 29: Crude oil sample after 72hrs of UV light exposure with Acetone as solvent.

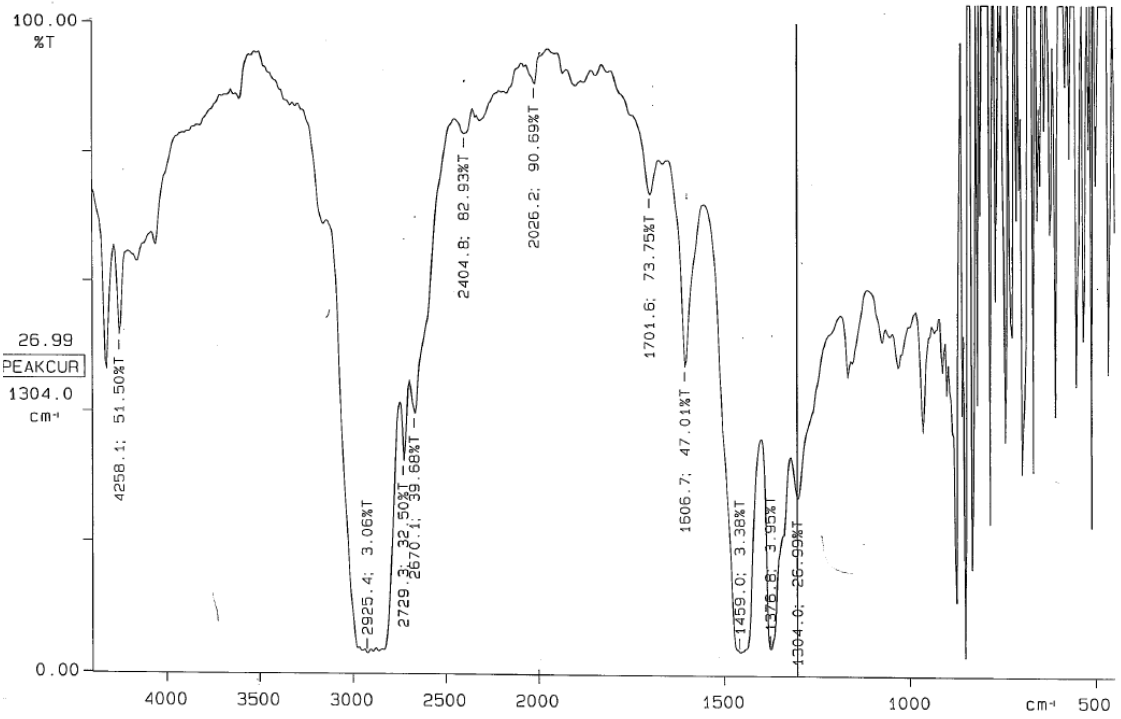


Scan 30: Crude oil sample after 120hrs of UV light exposure with Acetone as the solvent.

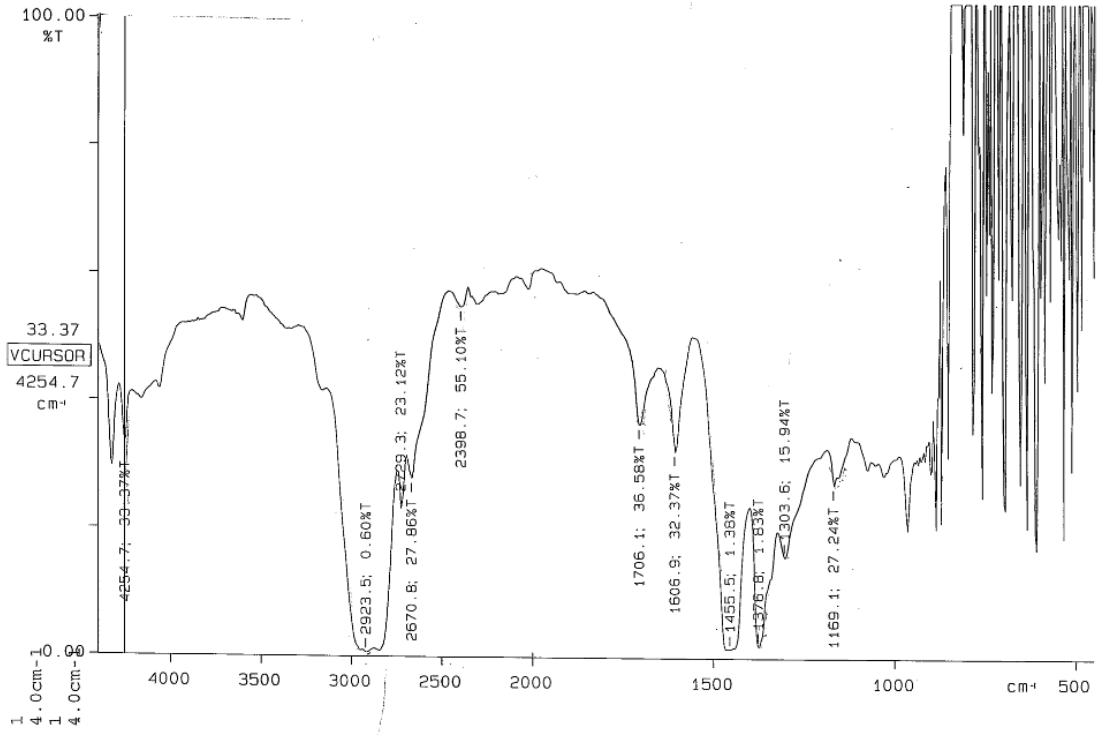


Scan 31: Crude oil sample after 124 hrs of UV light exposure with Acetone as the solvent.

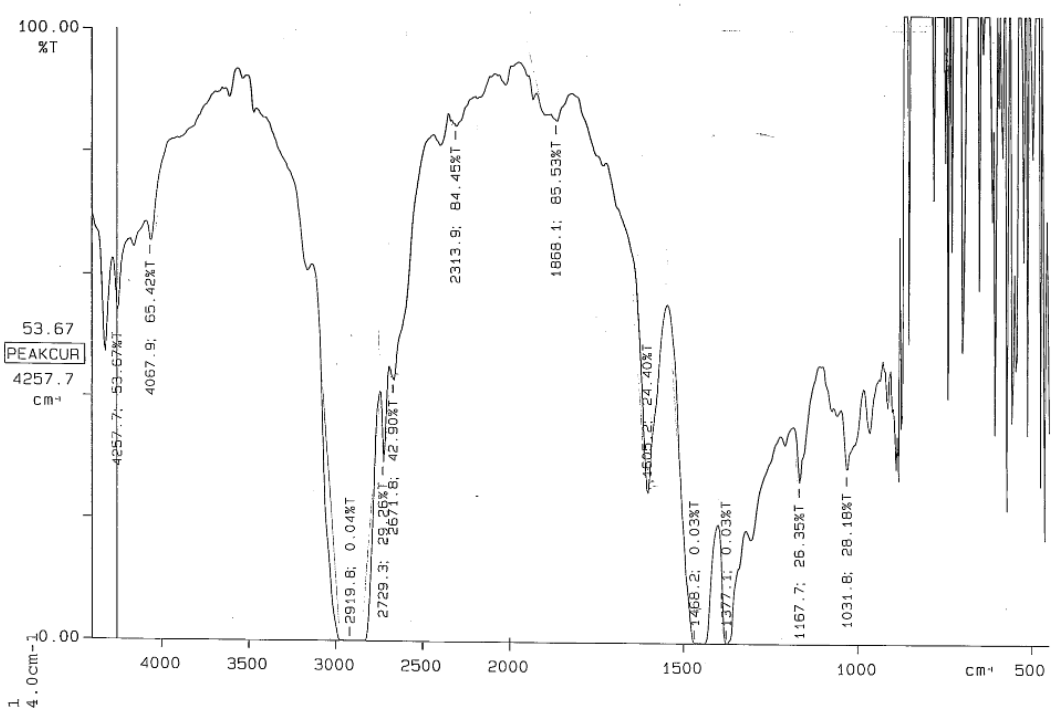
APPENDIX H



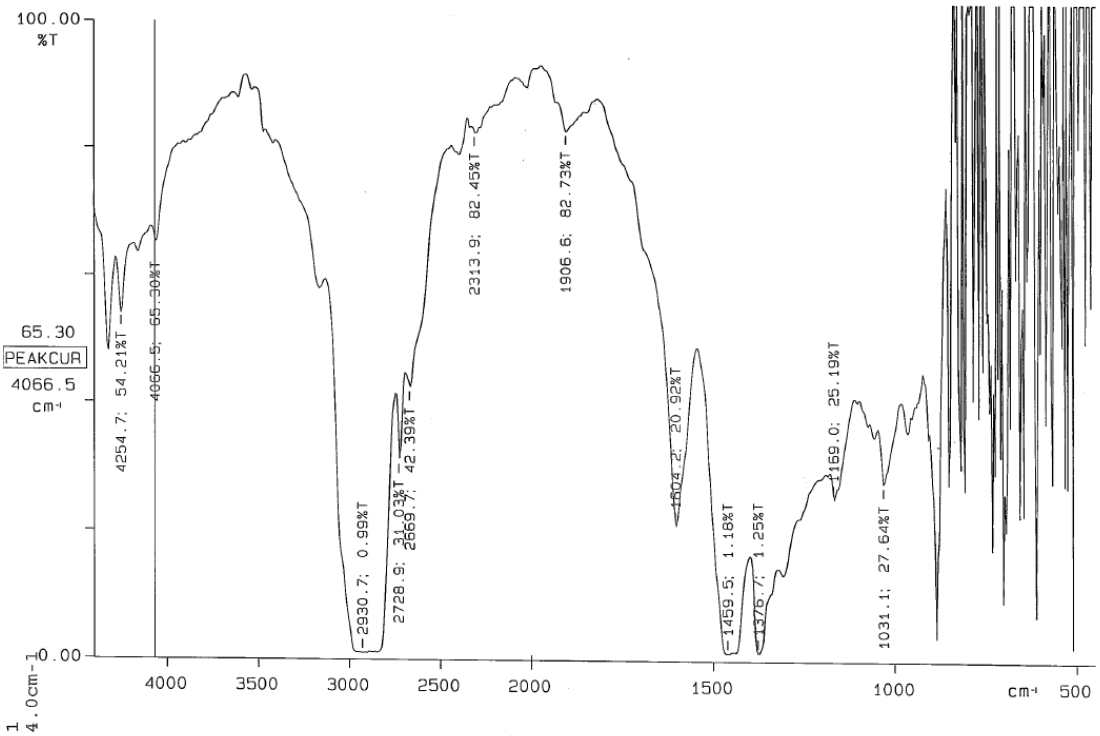
Scan 32: Crude oil sample 1001 sampled at Oxford County.



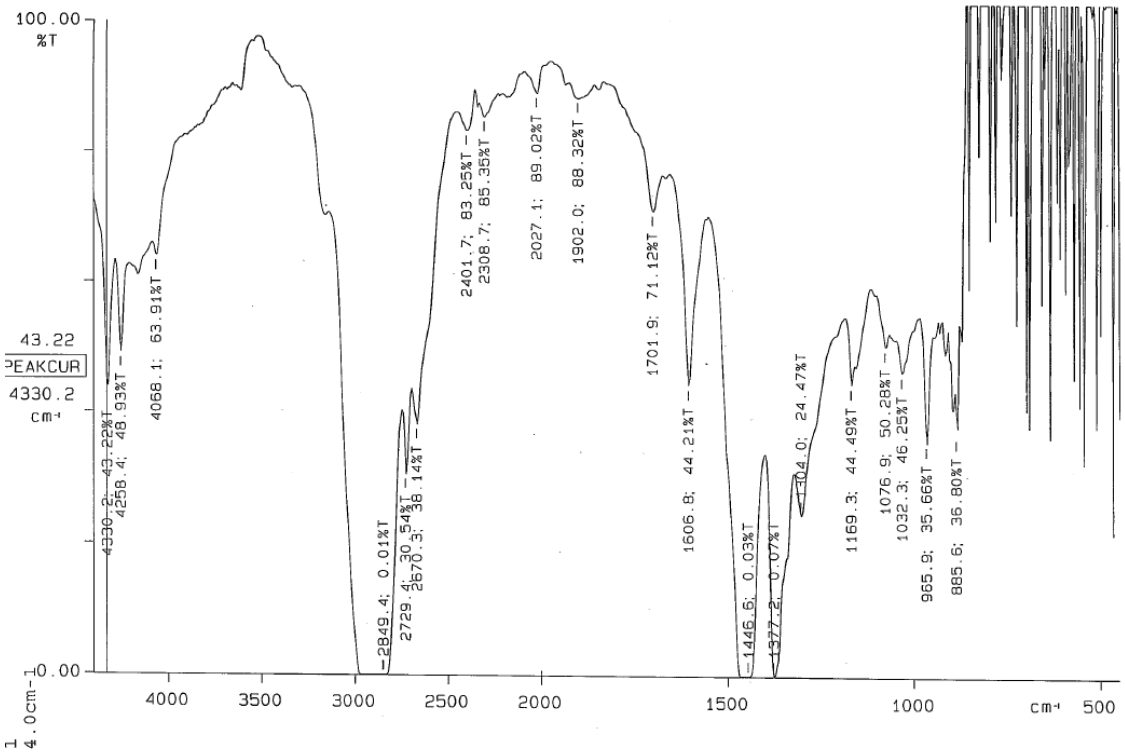
Scan 33: Crude oil sample 2001 sampled at Brount County.



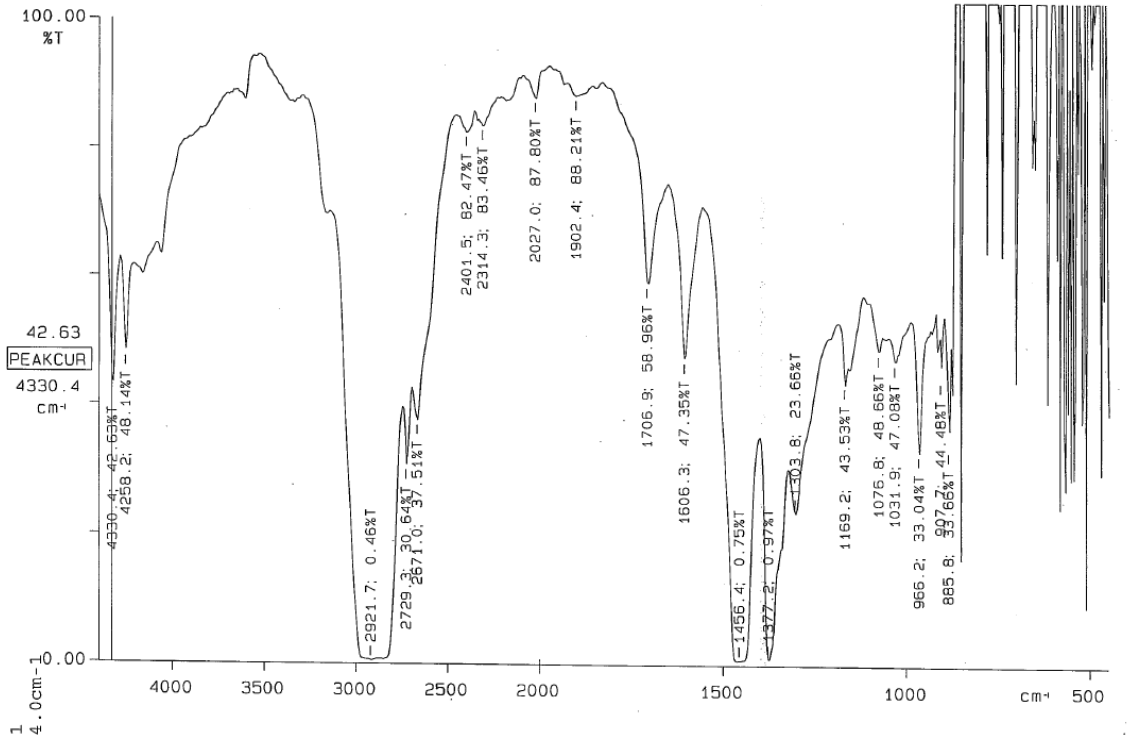
Scan 34: Crude oil sample 3001 sampled at Enniskillen well.



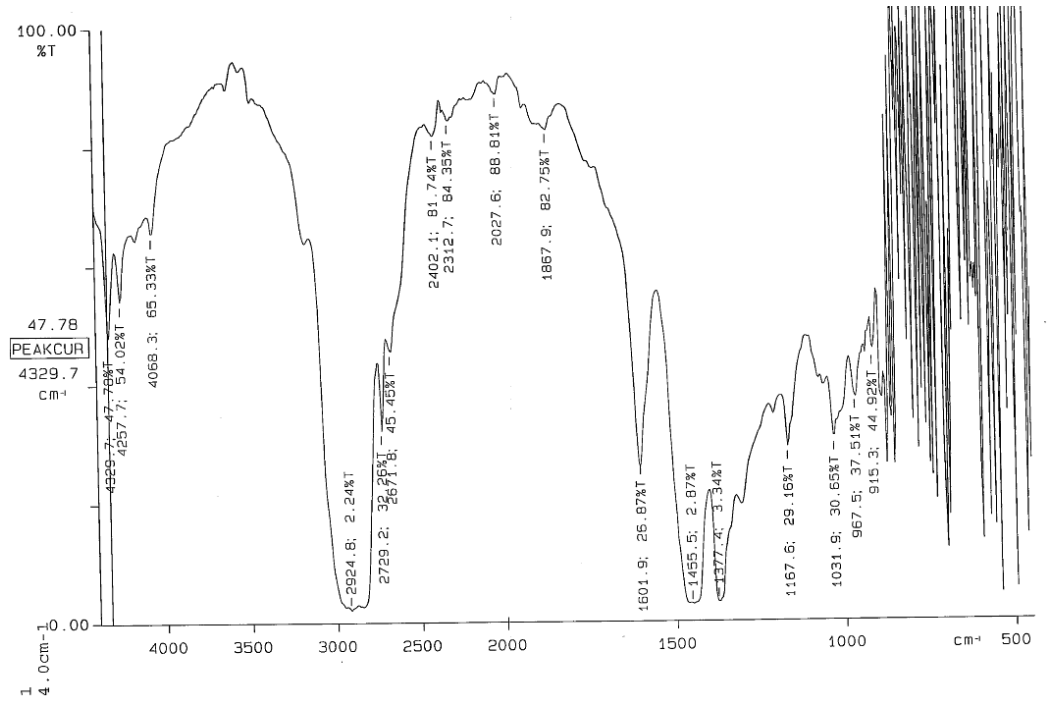
Scan 35: Crude oil sample 4001 sampled at Lambton County.



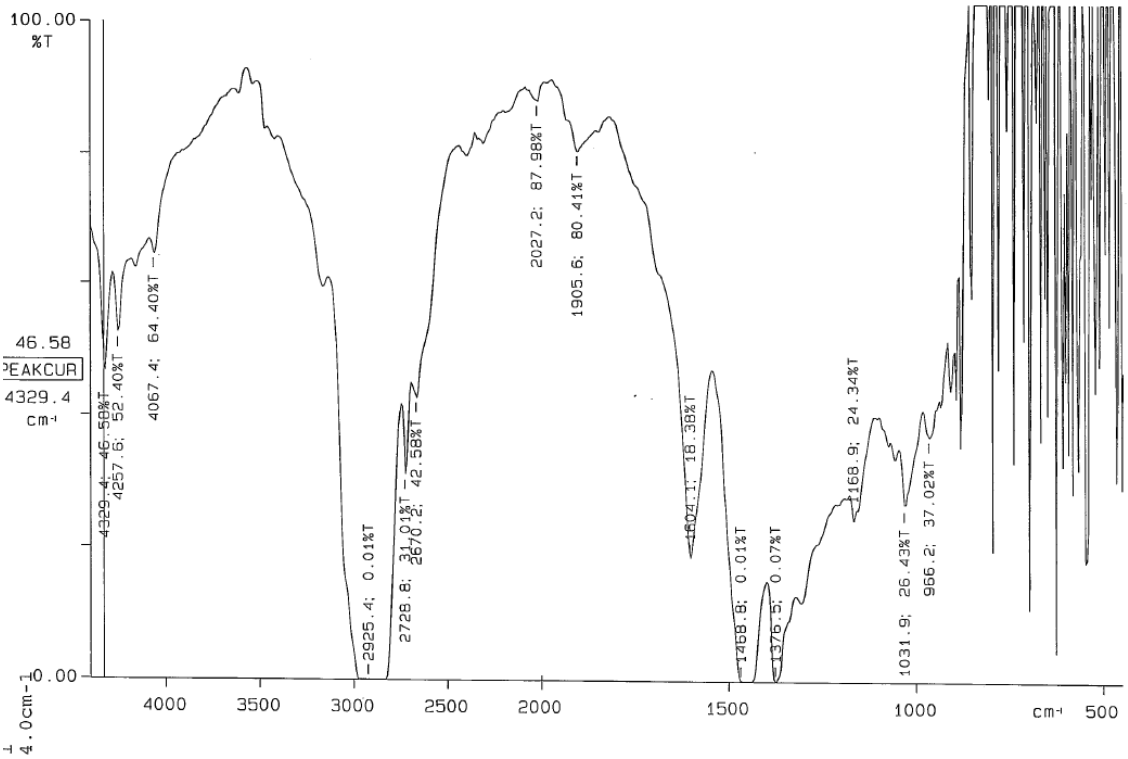
Scan 36: Crude oil sample 1002 sampled at Oxford County(replicate of 1001).



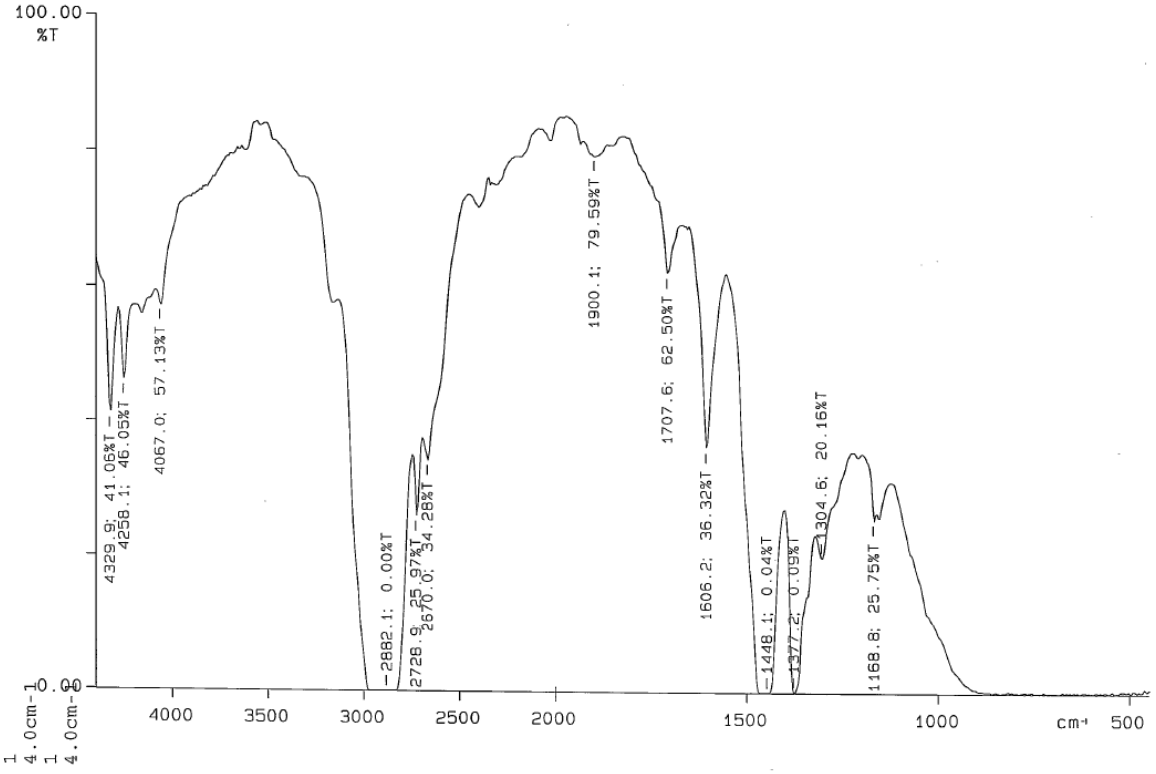
Scan 37: Crude oil sample 2002 sampled at Brount County (replicate of 2001).



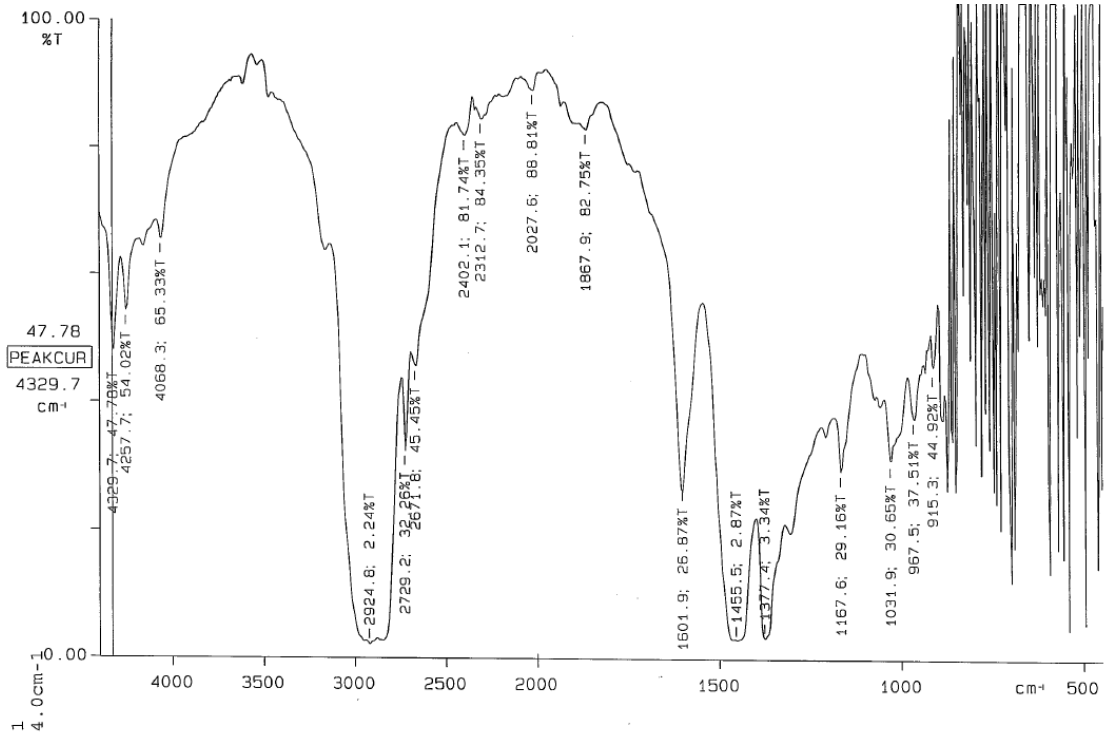
Scan 38: Crude oil sample 3002 sampled at Enniskillen well (replicate of 3001).



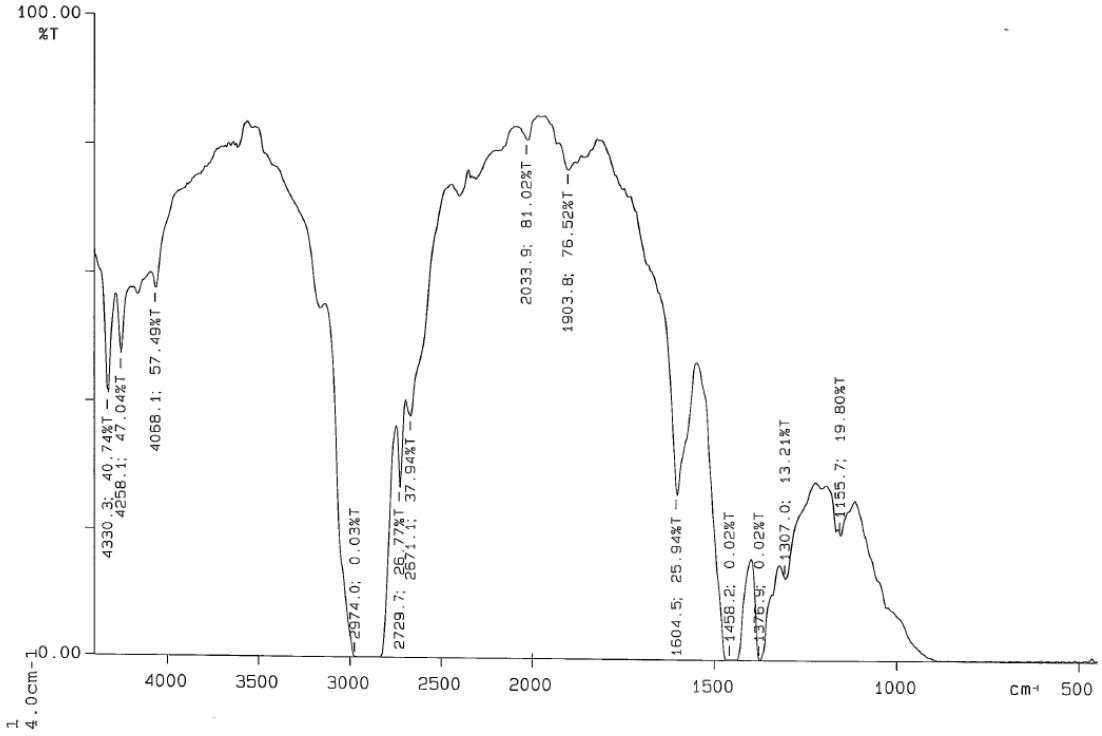
Scan 39: Crude oil sample 4002 sampled at Lambton County (replicate of 4001).



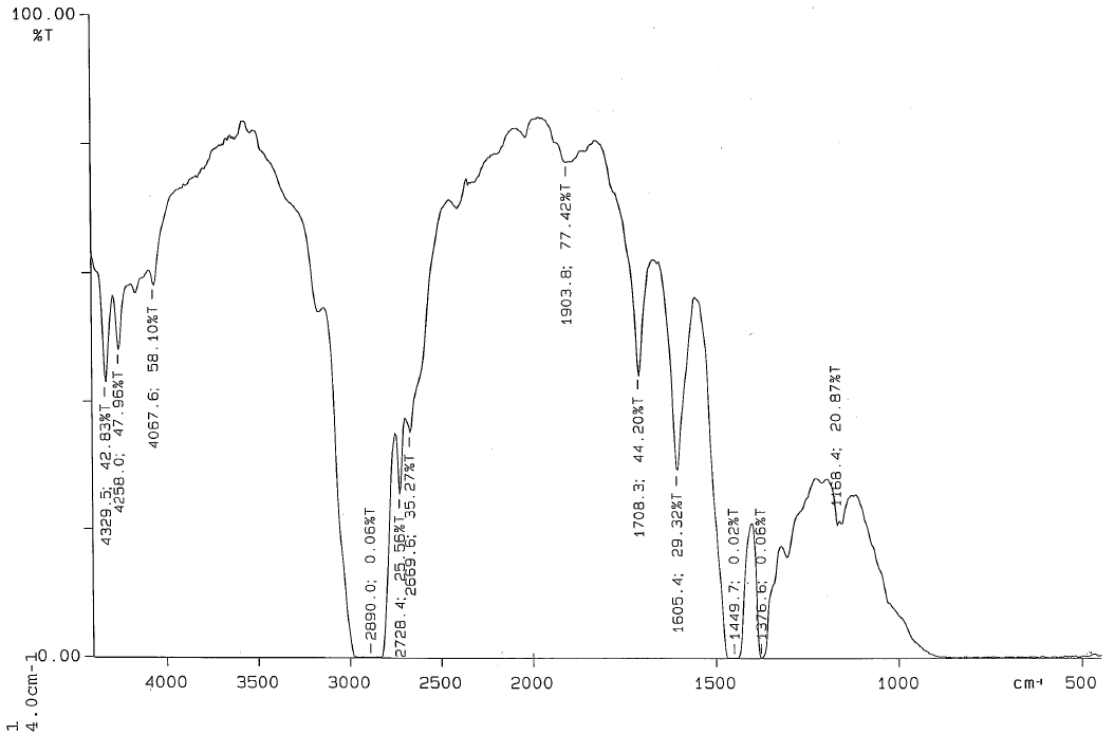
Scan 40: Crude oil sample 1003 sampled at Lousiana, USA.



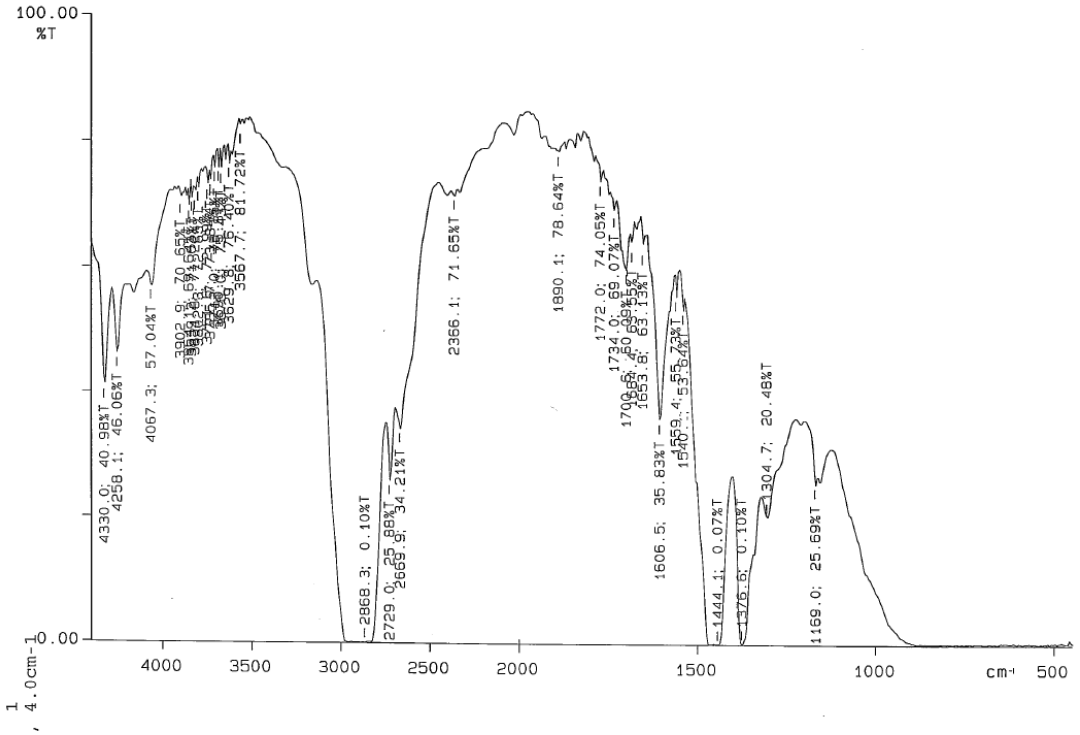
Scan 41: Crude oil sample 2003 sampled at Qua Iboe, Nigeria.



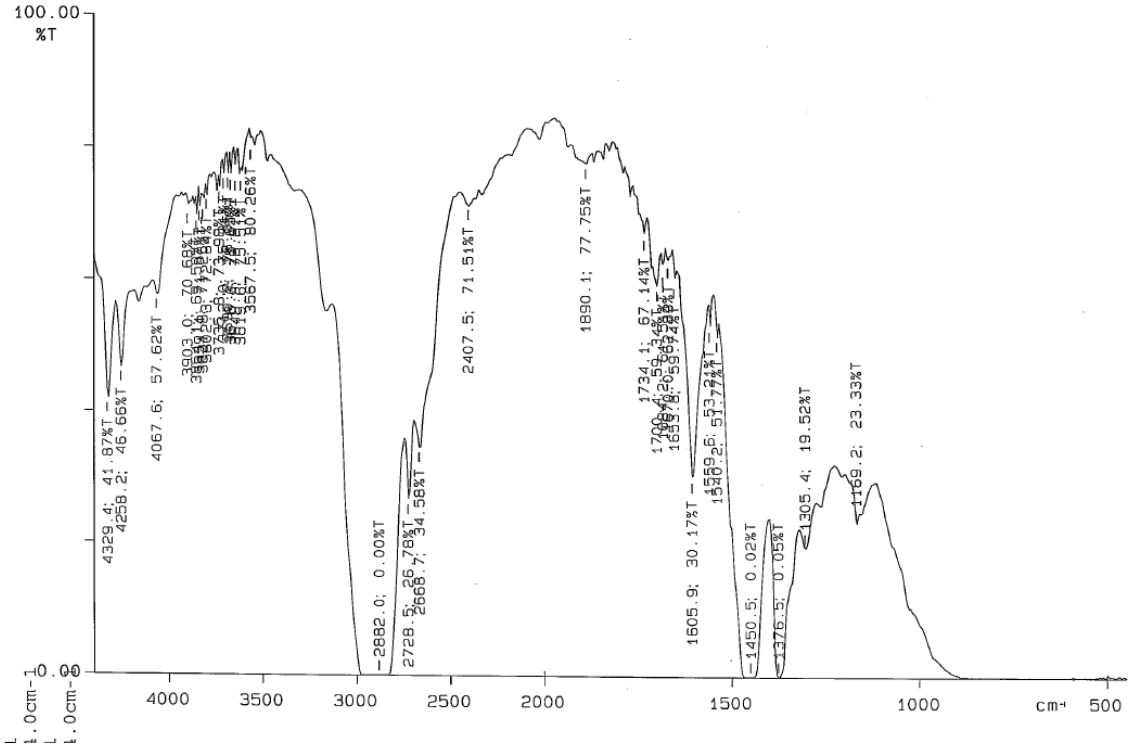
Scan 42: Crude oil sample 3003 sampled at Iraq (Basra Light).



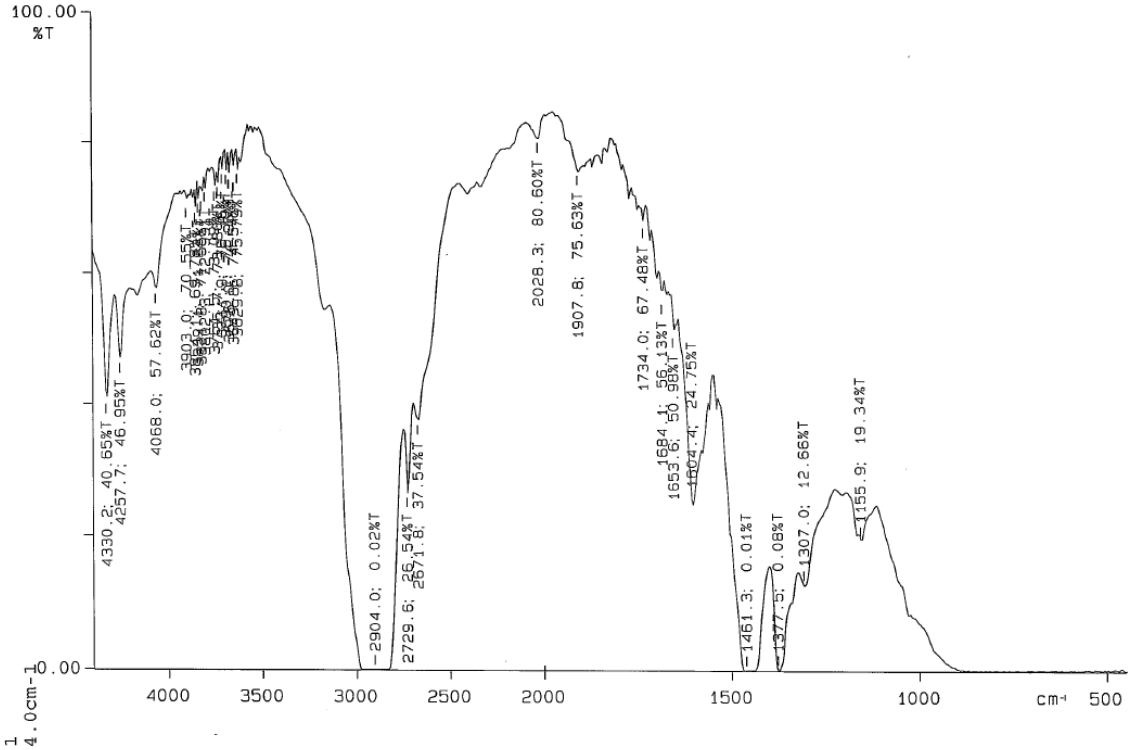
Scan 43: Crude oil sample 4003 which is a Hoops blend.



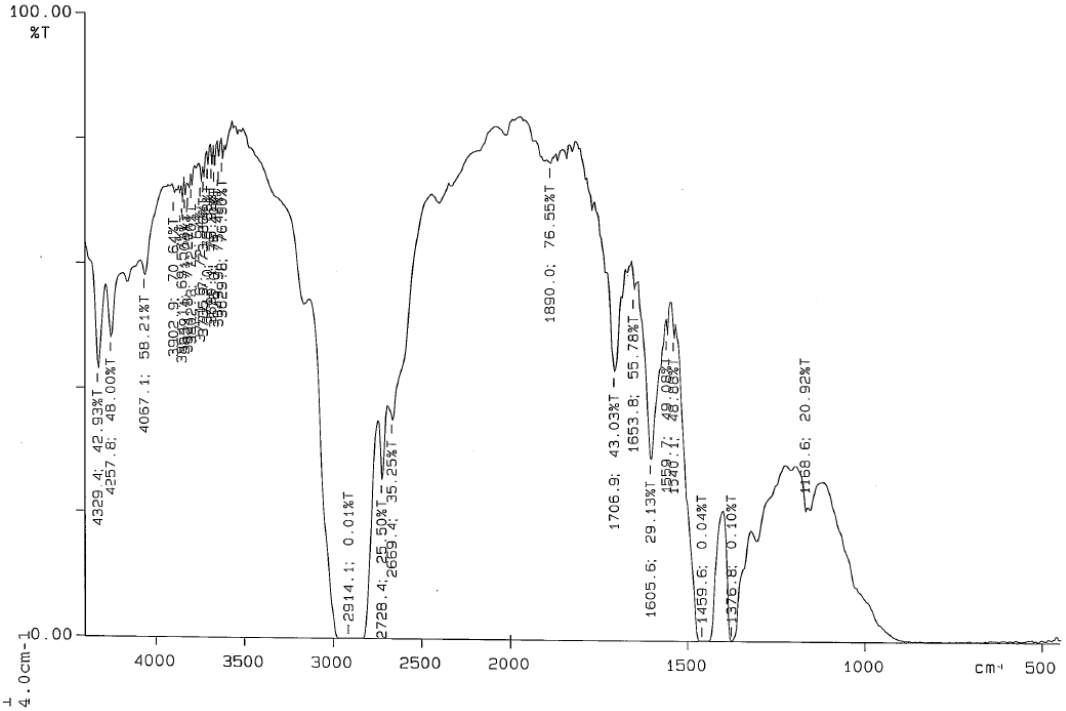
Scan 44: Crude oil sample 1004 sampled at Louisiana, USA (replicate of 1003).



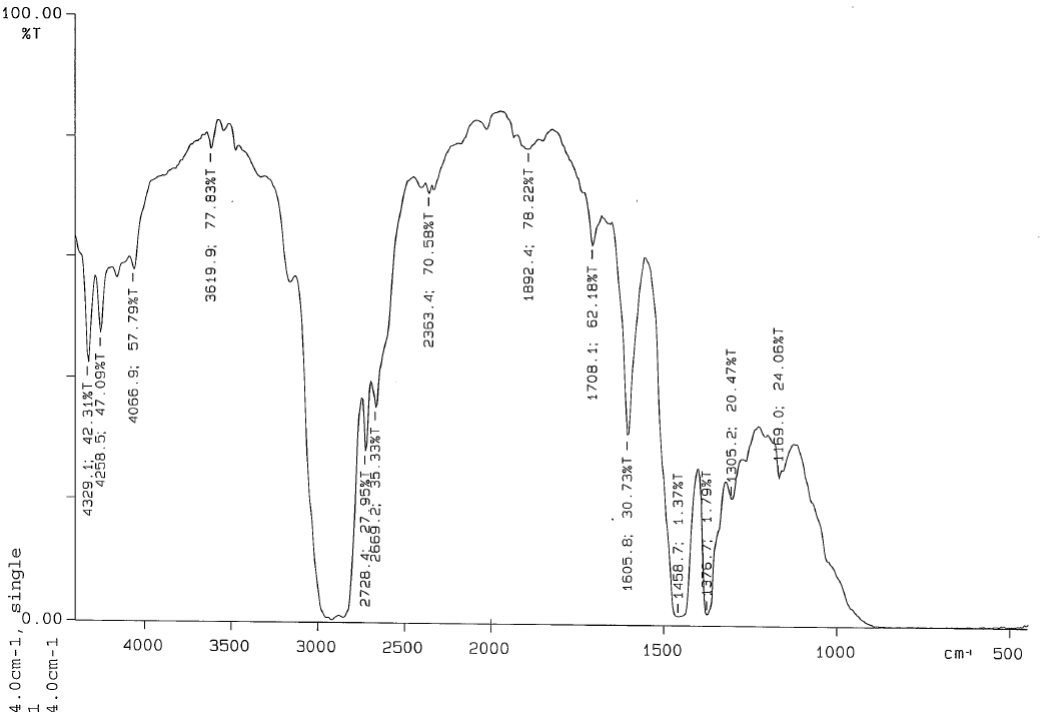
Scan 45: Crude oil sample 2004 sampled at Nigeria (replicate of 2003).



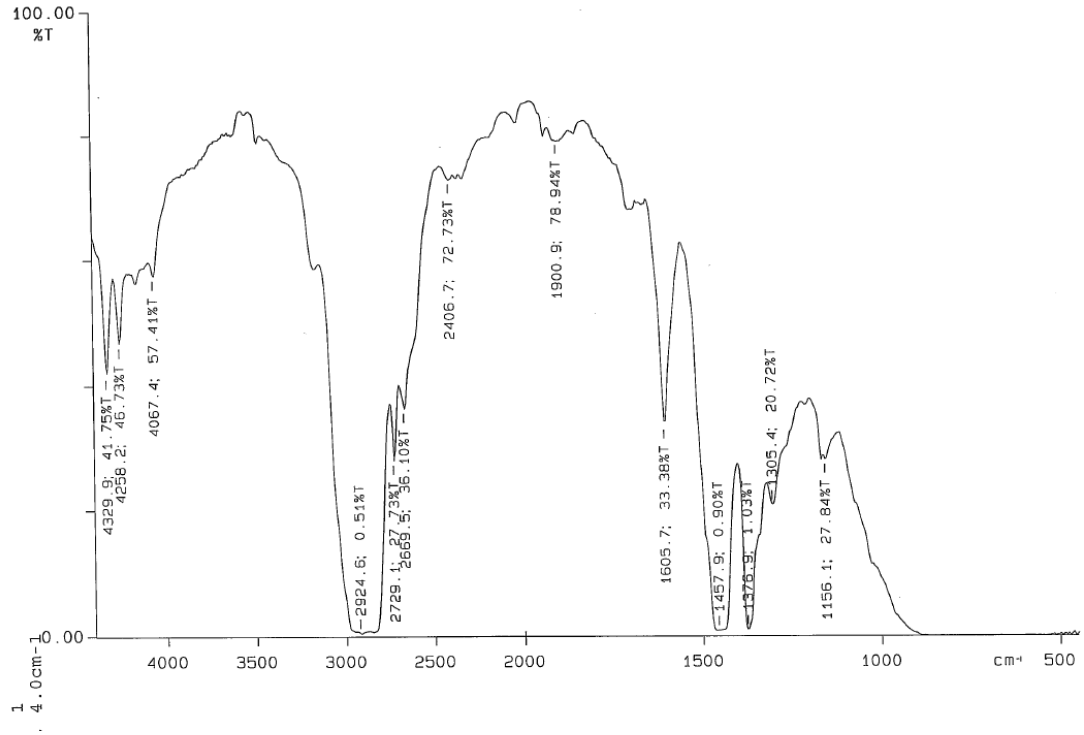
Scan 46: Crude oil sample 3004 sampled at Iraq (replicate of 3003).



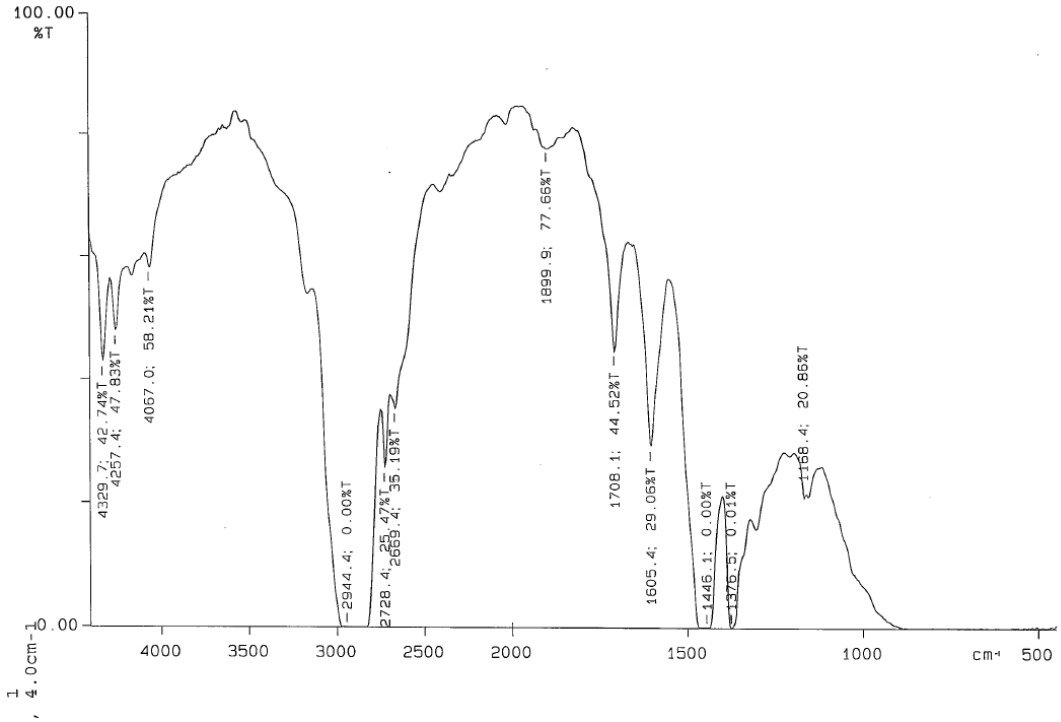
Scan 47: Crude oil sample 4004 which is a Hoops blend (replicate of 3003).



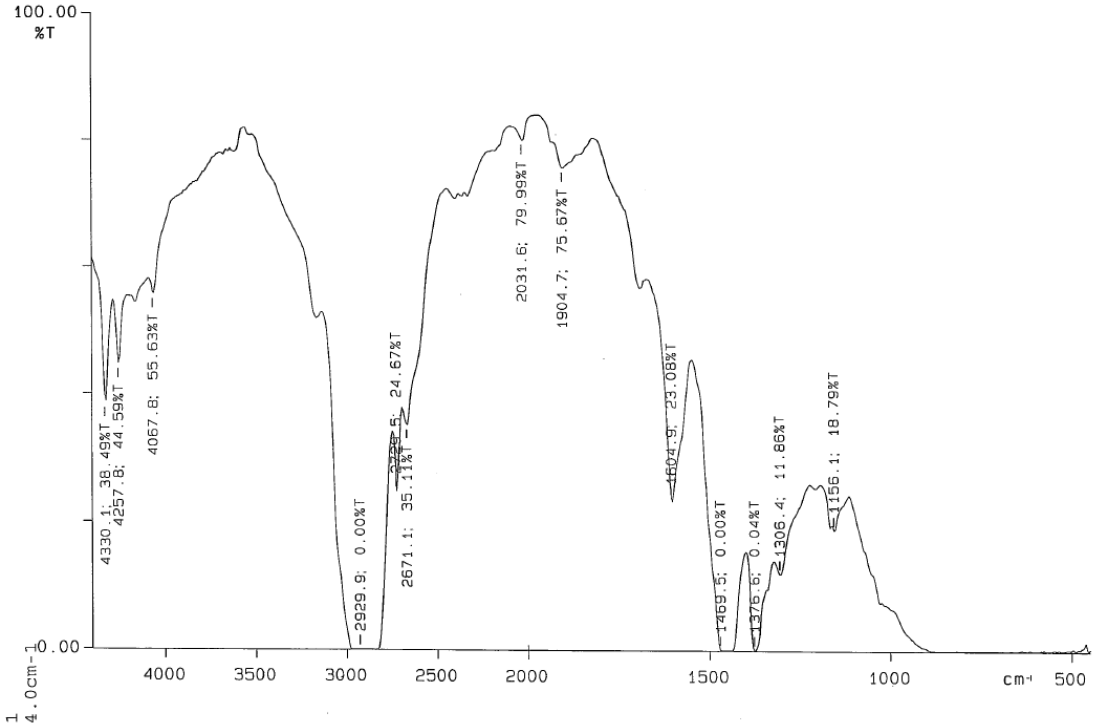
Scan 48: Crude oil sample 1005 sampled from unknown location.



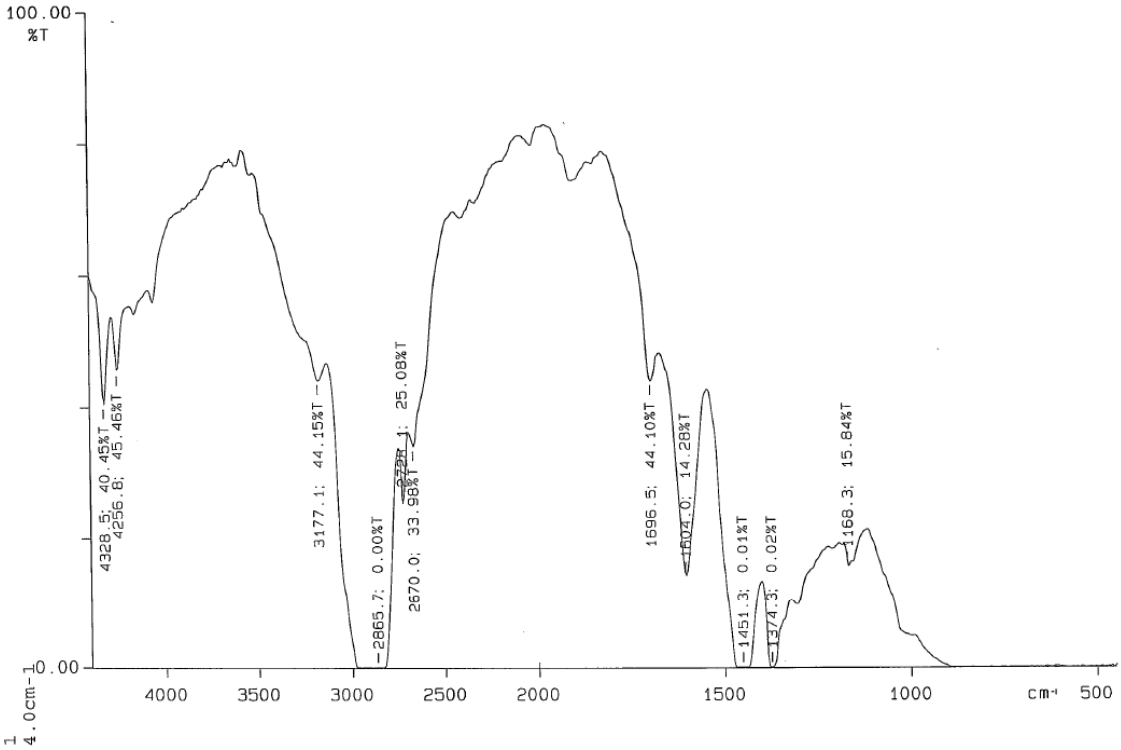
Scan 49: Crude oil sample 2005 sampled from unknown location.



Scan 50: Crude oil sample 3005 sampled from unknown location.



Scan 51: Crude oil sample 4005 sampled from unknown location.



Scan 52: Crude oil sample 5005 sampled from unknown location.

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