Pollutant Releases During the Initial Aging of Asphaltic Pavements

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Objectives

To study the runoff quality from freshly constructed asphaltic materials and during several months of exposure.

- The changes in the concentrations of the contaminants (toxicity, heavy metals, nutrients, detergents and PAHs) in the stormwater runoff concurrent with the natural aging of the asphaltic pavements were examined during a six month period.
- Concentration differences due to length of exposure (and rainfall depth) and type of asphalt were compared.

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Asphalt Characteristics and Aging

- Asphalt is a viscoelastic material, a crude oil derivative and is obtained by controlled distillation of crude oil.
- It's a high molecular weight compound with complex structure and properties and its composition varies with the source of the crude oil. However, most asphalt contain about:
  - Carbon 82-88%
  - Hydrogen 8-11%
  - Sulfur 0-6%
  - Oxygen 0-1.5%
  - Nitrogen 0-1%

The Shell Bitumen Handbook, Fifth Edition, Thomas Telford Publishing ltd, London, 2003.

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Asphalt Characteristics and Aging (cont.)

- Asphalt provides cohesion between the aggregate particles to maintain the integrity of the mixture in the road bed construction.
- Asphalt coats the aggregate particles and 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.

Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption, Strategic Highway Research Program, National Research Council, Washington DC, 1993

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Asphalt Characteristics and Aging (cont.)

- Oxidation on the exposed surface of asphaltic pavements 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.
- The effect of aging is more rapid in the presence of light and air.
- The insoluble, condensation products formed as a result of the oxidation and the loss of volatile compounds from the pavements may effect the composition and the concentration of contaminants that leaches into the runoff with aging.

Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption, Strategic Highway Research Program, National Research Council, Washington DC, 1993

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Literature Review

In the study conducted by National Cooperative Highway Research Program on the impact of construction materials (asphalt and its additives) on surface and groundwater, individual components and the aggregates of the pavements were subjected to exposure and aging tests. Their conclusions were that:

- Although some construction materials caused high toxicity levels, this was reduced or eliminated when they were incorporated into the complete pavement assemblage.
- Leachate from short term aging and long term aging did not show any significant differences.
- Leaching reduces with time and that it is a function of wet weather hours, independent of dry weather. The toxicity of the leachate was found to reduce by photolysis, volatilization and degradation.

Azizian F. Mohammad et al., "Environmental impact of highway construction and repair materials on surface and groundwater", 2003.

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Literature Review (cont.)

- In 2005, parking lot sealants were identified as a 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 tends to wear off by vehicle use, with the crumbled seal coat losses producing up to 2,200 mg PAH/kg sediment of 12 PAHs, compared with 27 mg/kg from unsealed parking lots. *Parking Lot Sealant Identified as Major Contaminant* (USGS 2005) (http://www.usgs.gov/newsroom/article.asp?ID=718).
- This lead to various bans on coal tar based sealants in different areas of the US (Austin, TX, State of Washington).
- Most PAHs have a several year half-life for degradation in streams so immediate sediment quality improvement will not occur.

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Method

- Three square pavement slabs were examined during this project.
  - A Hot-mix asphalt pavement, freshly constructed and unsealed.
  - A Warm-mix asphalt pavement, freshly constructed and unsealed.
  - A Hot-mix asphalt pavement (two years old), freshly coated with asphalt sealant (coal tar sealant was to be tested also, but was not available for purchase in Alabama).
    - "Most consumer-grade sealers are water-based emulsions containing water, clay fillers, latex, polymers, additives and either coal tar (a byproduct of baking coal to make coke) or asphalt (a byproduct of petroleum refining). Some so-called "asphalt" emulsions also contain some coal tar" (http://www.naturalhandyman.com/iip/infdrivewaysealer/infdrivewaysealer.html).

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- The standard test slabs have a surface area of 0.25 m^2 and are 5 cm thick, 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 and exposed to sun and rains, therefore being aged under natural conditions.
- A 0.5 in rain (using prior collected roof runoff) was used to obtain runoff on each of the pavement slabs.
- The resulting runoff was analyzed for contaminants and toxicity levels.

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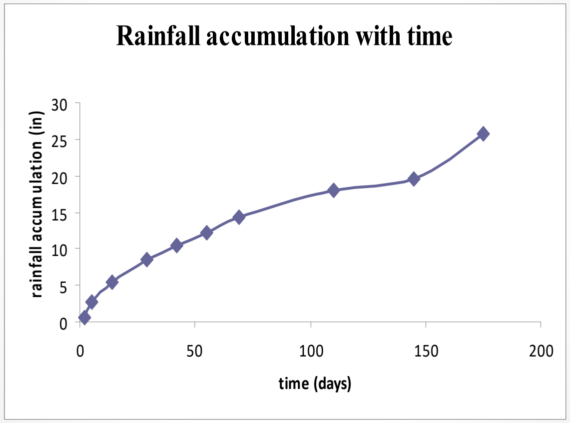
Rainfall accumulation during the project period



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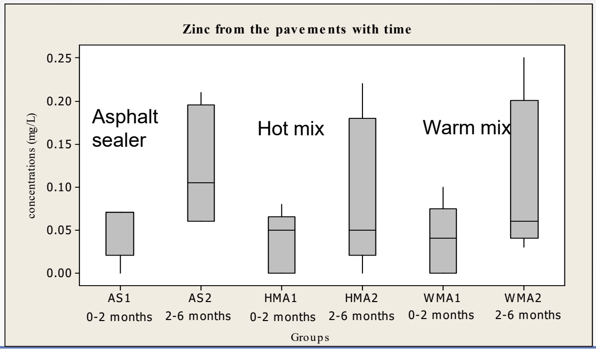
Zinc Concentrations in Pavement Runoff



- The runoff was analyzed for Pb, Cu, Cr, Zn and Cd.
- Cd and Cr always below the detection limits in all samples. Pb was detected for one sampling event.
- Zinc showed an increasing trend with the aging of the pavement from the samples, with the highest concentrations being 250 µg/L, 220 µg/L and 210 µg/L from HMA, WMA and AS respectively after the 6 month aging period.

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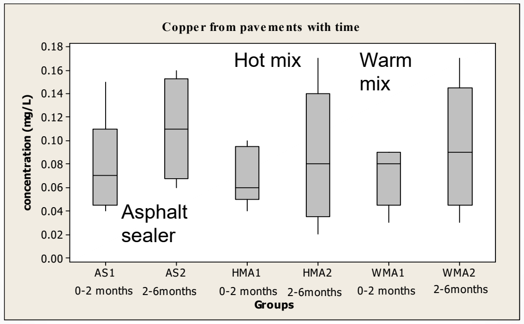
Copper Concentrations in Pavement Runoff



Cu release from the pavements showed a weak increasing trend with the highest concentrations being 170 µg/L, 170 µg/L and 160 µg/L for the final sample at the end of 6 months of aging of the pavements.

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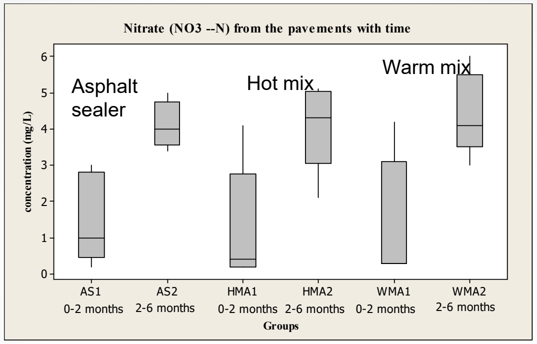
Nitrate Concentrations in Pavement Runoff



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

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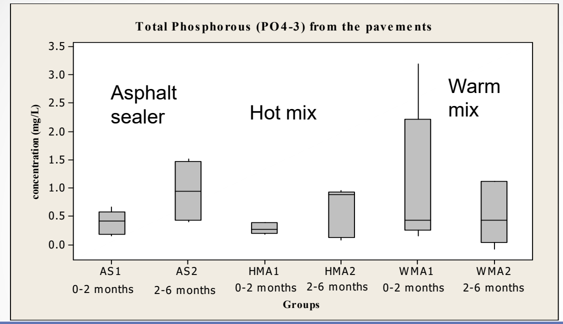
Phosphate Concentrations in Pavement Runoff



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

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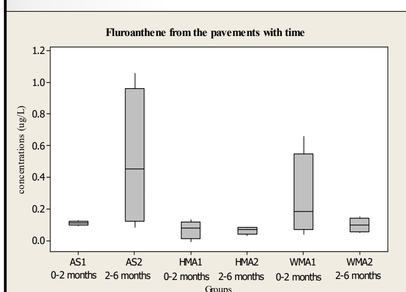
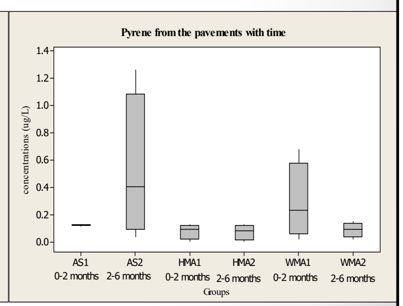
PAH Concentrations in Pavement Runoff

The Kruskal-Wallis test showed p values <0.1 for the following PAHs Acenapthene, fluoranthene, pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene indicating an apparent difference in groups.





The PAH concentrations in the pavement runoff samples were very low (most less than 1 μg/L).

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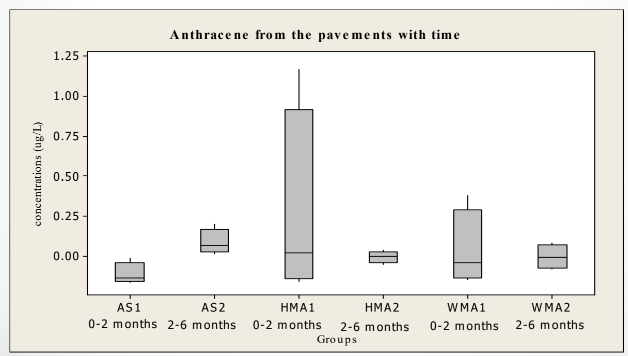
No significant differences were observed for the remainder of the PAHs analyzed based on the Kruskal-Wallis one-way ANOVA tests. However a Mann-Whitney test on the two exposure periods showed a significant difference for Anthracene.



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Conclusions

- Zn and Cu were the only heavy metals that were detected in the runoff. They both had apparent concentration **increases** with exposure time for all samples. Pb was detected at only one sampling point. (Cr, Cd were not detected in any of the pavement runoff samples).
- Nitrates also had apparent concentration **increases** with exposure time for all samples. The phosphate changes were mixed and not very apparent.
- The PAH concentrations were very low (generally <1 μg/L). The asphaltic sealed pavement sample was the only sample showing apparent PAH concentration changes (**increases**) with time.

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Conclusions (cont.)

- No obvious patterns were observed for the detergent concentrations (ranged between 0.25 to 1 mg/L).
- The apparent concentration changes observed were all increases with exposure time (most evident with the asphaltic sealer sample), while most literature indicated concentration decreases with aging. The six month test period was relatively short compared to pavement life and these results may indicate an initial increase in these contaminant releases before subsequent decreases in runoff concentrations.

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References

- *The Shell Bitumen Handbook*, Fifth Edition, Thomas Telford Publishing ltd, London, 2003.
- *Colloid Chemistry of Asphalts* by Charles Mack.
- *Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption*, Strategic Highway Research Program, National Research Council, Washington DC, 1993.
- *Selection of Laboratory Aging Procedures for Asphalt-Aggregate Mixtures*, C. A. Bell, Y. AbWahab, M. E. Cristi, D. Sosnovske, Oregon State University.
- Nelson L. Peter et al., NCHRP report 448,*Environmental impact of highway construction and repair materials on surface and ground waters: Case study: crumb rubber asphalt concrete*, 2001.
- *Parking Lot Sealant Identified as Major Contaminant*. U.S. Department of the Interior, U.S. Geological Survey. 2005.
- Pal Zakar, "Physical and Chemical Characteristics," in *Asphalt*, Chemical Publishing Company, Inc., New York, 1971.
- Usmani M. Arthur, "Oxidation of Asphalt Fractions," in *Asphalt Science and Technology*, Marcel Dekker Inc., 1997.

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