



# Molecular Composition of Complex Organic Mixtures of Potential Emerging Contaminants Generated from Coal- and Petroleum-Derived Paving Materials Revealed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry



# NATIONAL HIGH **MAGNETIC** FIELD LABORATORY




**What happens to asphalt binders and petroleum- and coal derived seal coats in the Florida sun...**

**Measured by really expensive equipment in the lab.**







# **Understanding the Impact of Sunlight on Petroleum Materials Commonly Used in Our Built Environment**





## What Happened



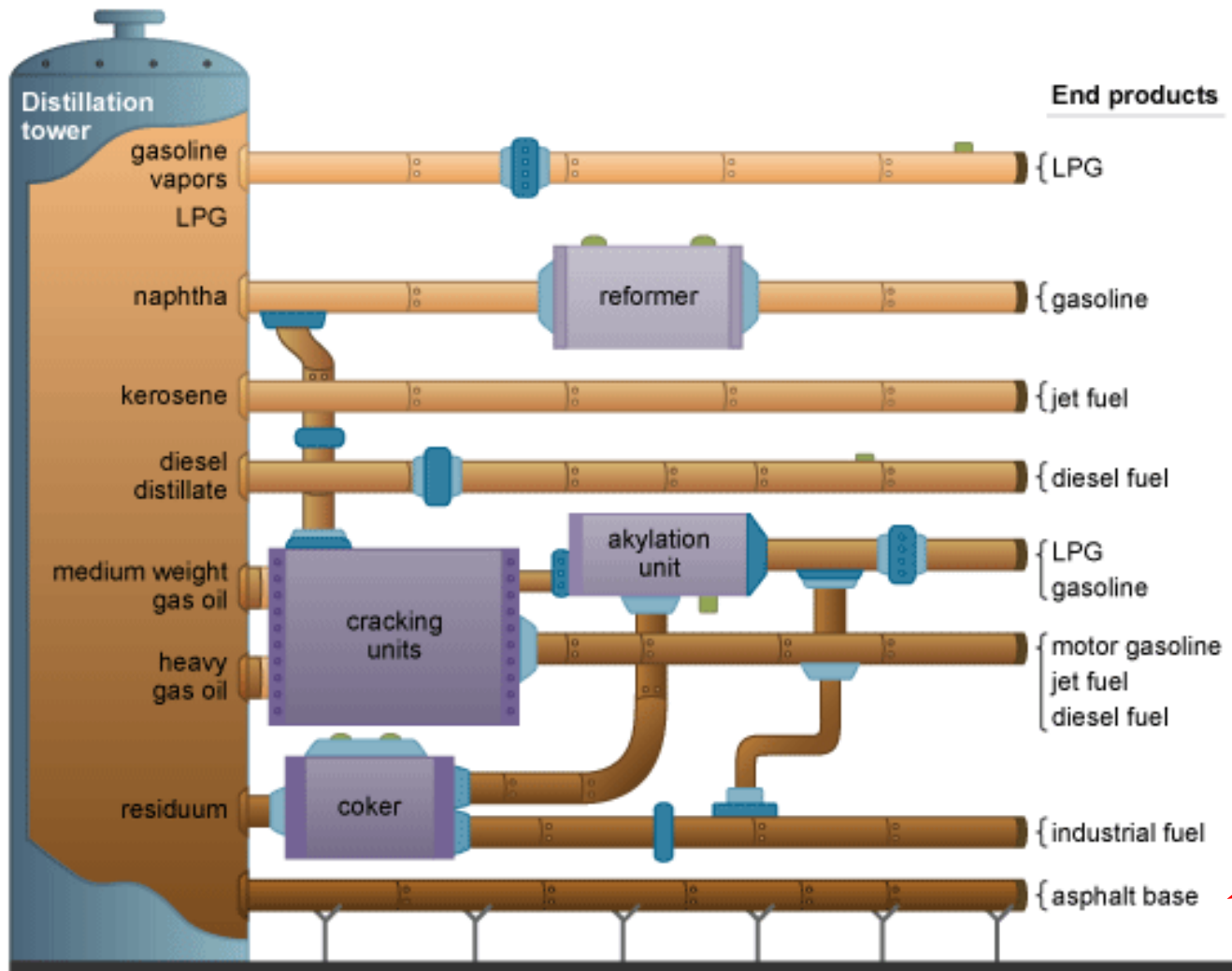
Photobleaching  
Settling  
Wear  
Embrittlement  
Migration?  
“Weathering”

?



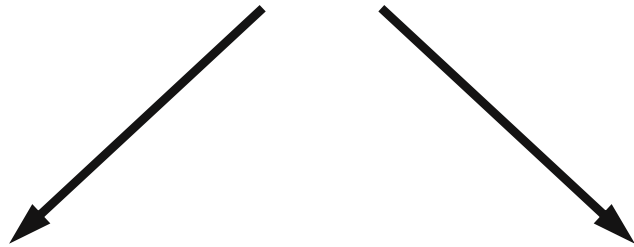


## Binder is a “Spec” product





## What is in this stuff? “Vac Bottoms”



**Maltenes**



**Waxes**

**Aromatics**

**Sulfur- and  
Nitrogen Organics**

**Asphaltenes**



**Waxes**

**Aromatics**

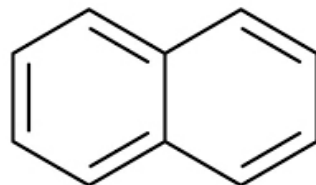
**Sulfur- and  
Nitrogen Organics**



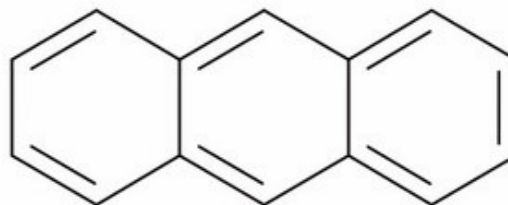
**Can kill you...**



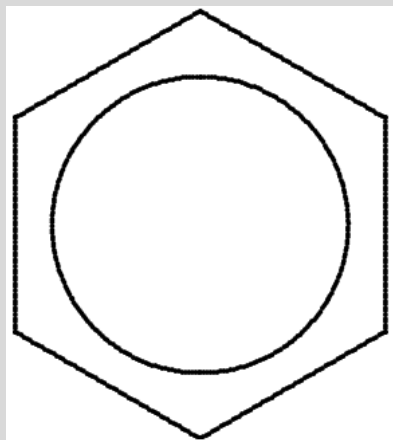
## Aromatics...



naphthalene



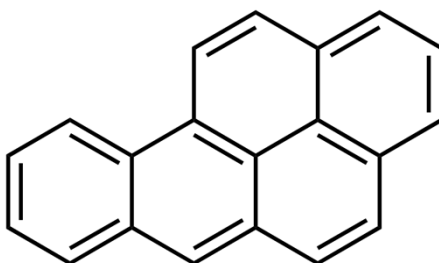
anthracene



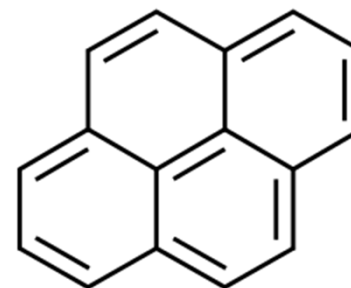
benzene ring

## PAHs

Polycyclic Aromatic Hydrocarbons



benzo[a]pyrene



pyrene

**BUT Bare PAHs are not abundant in Vac bottoms**

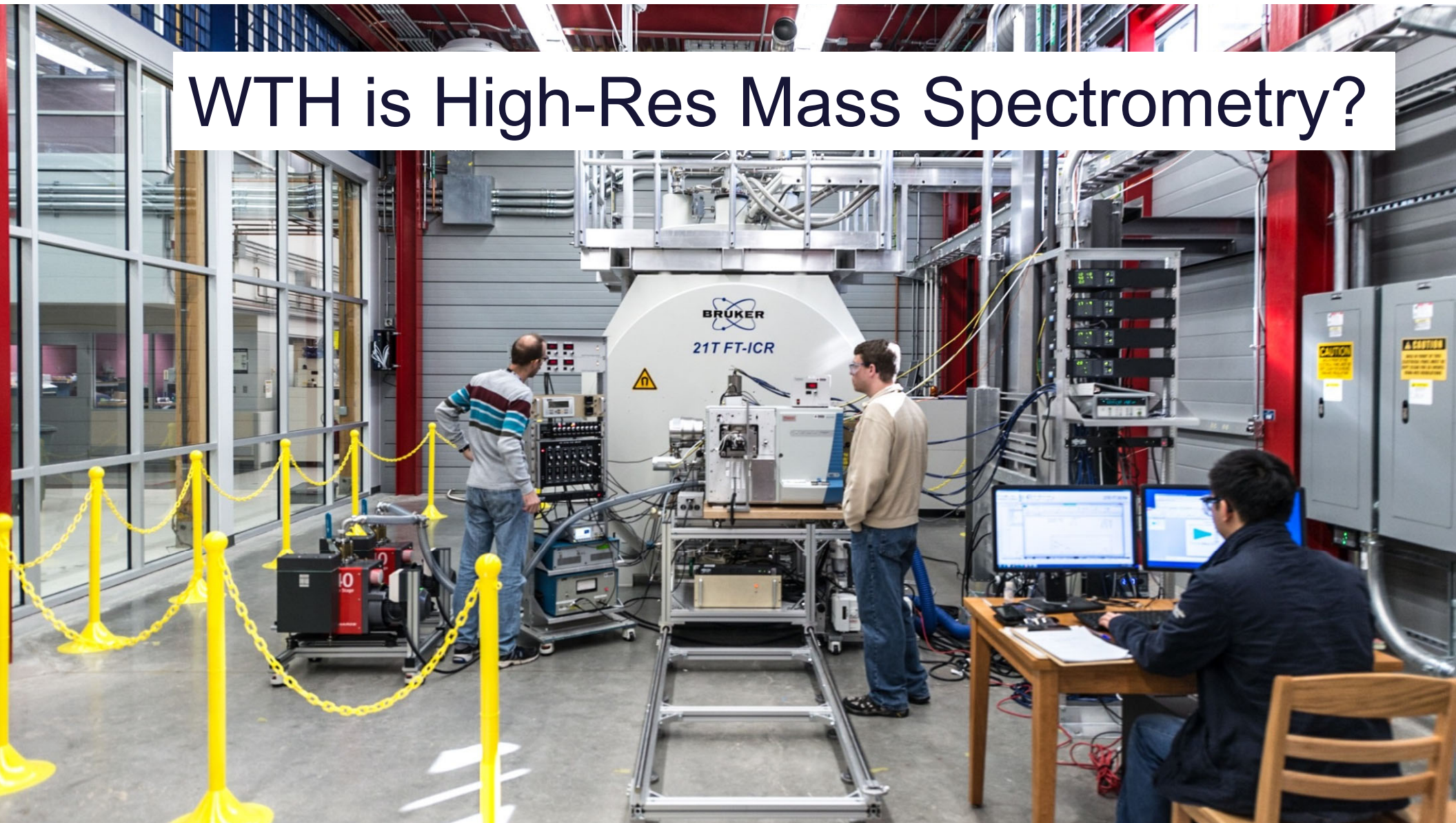


# National High Magnetic Field Laboratory





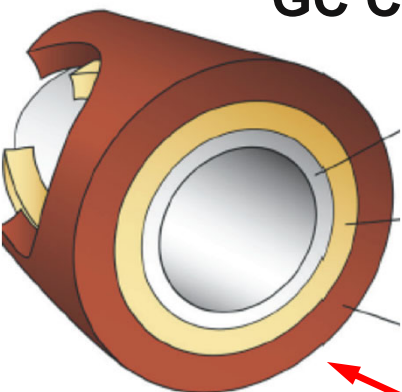
# WTH is High-Res Mass Spectrometry?



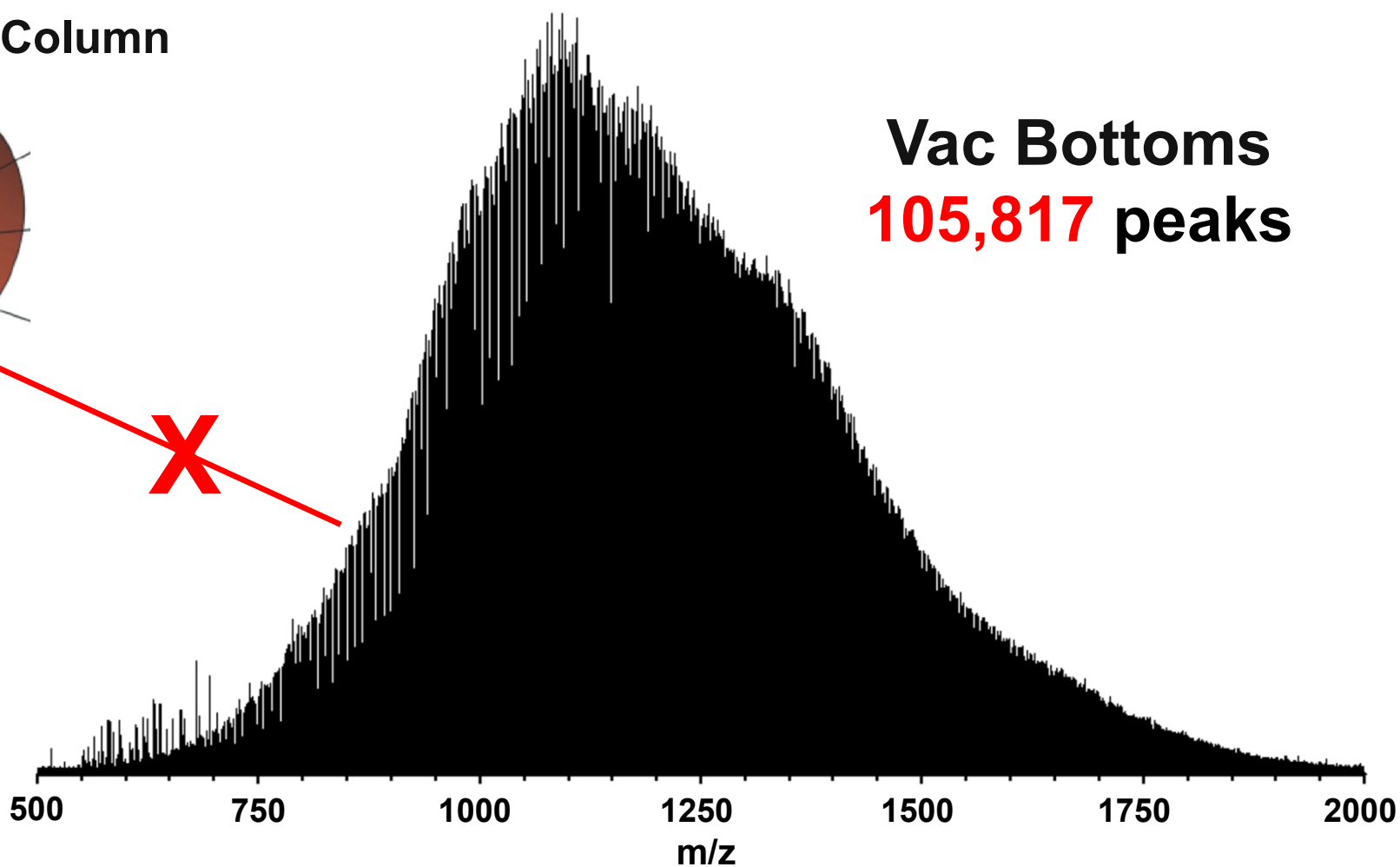


# Not all petroleum is GC amenable.

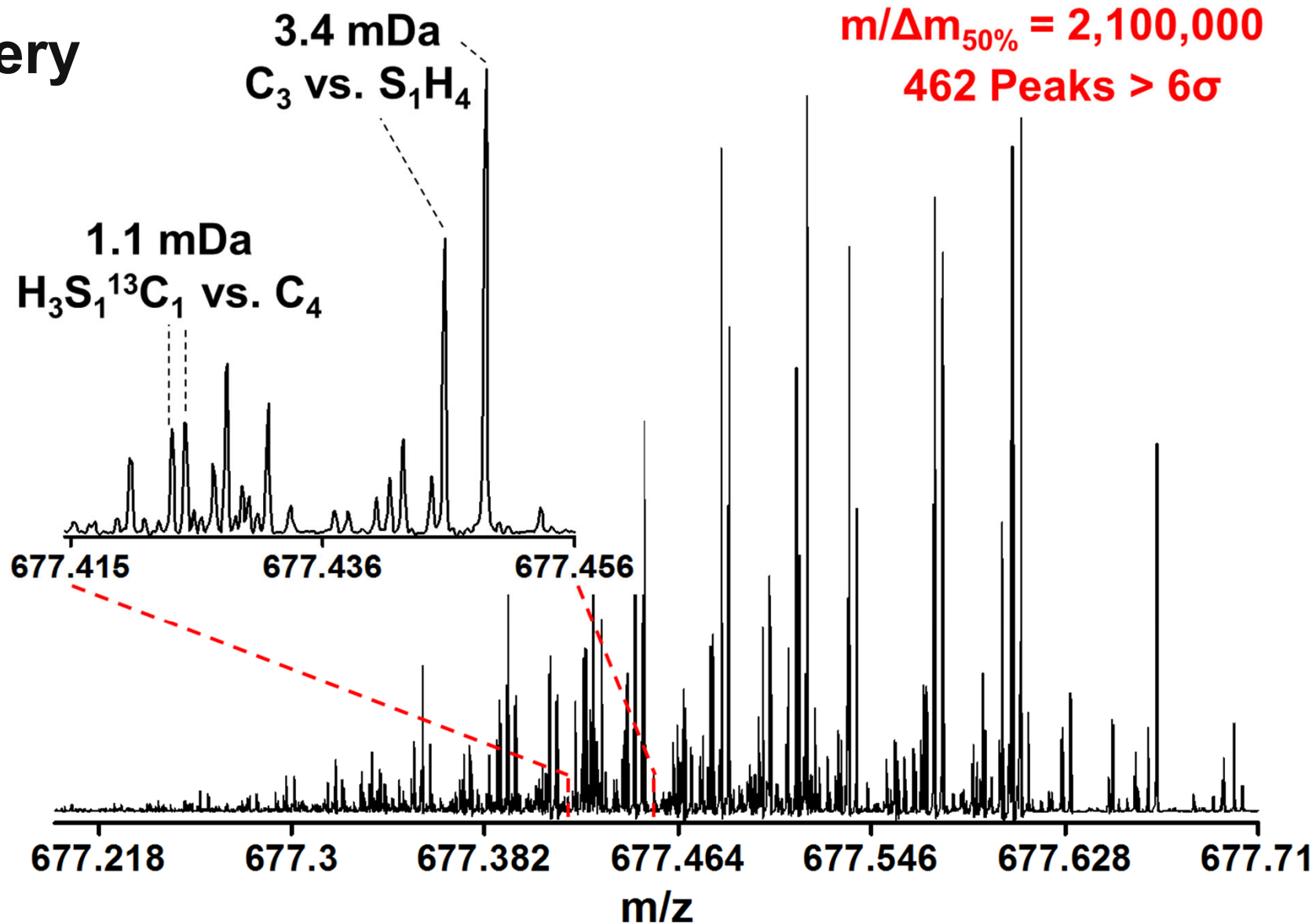
GC Column



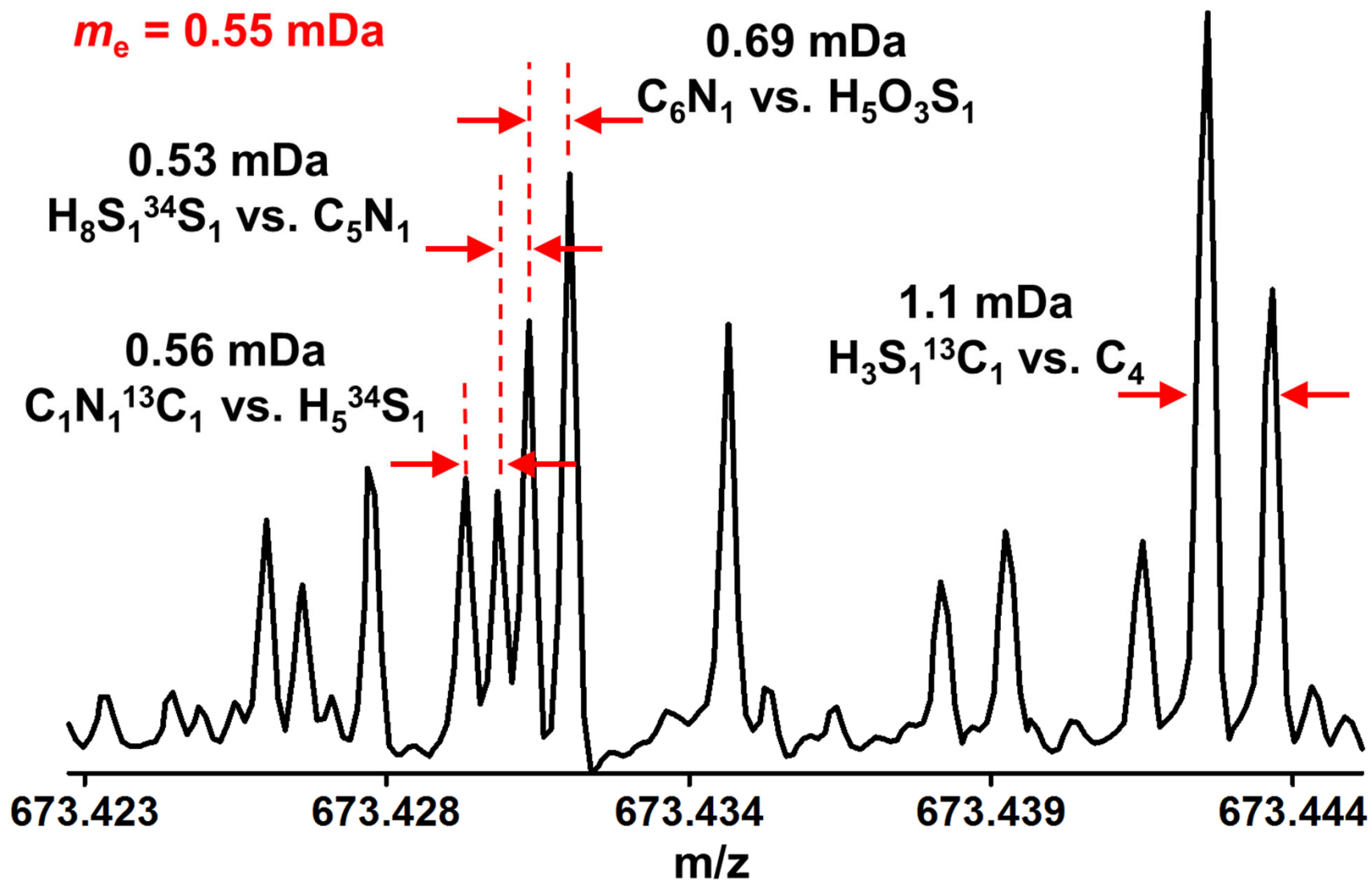
Vac Bottoms  
**105,817** peaks



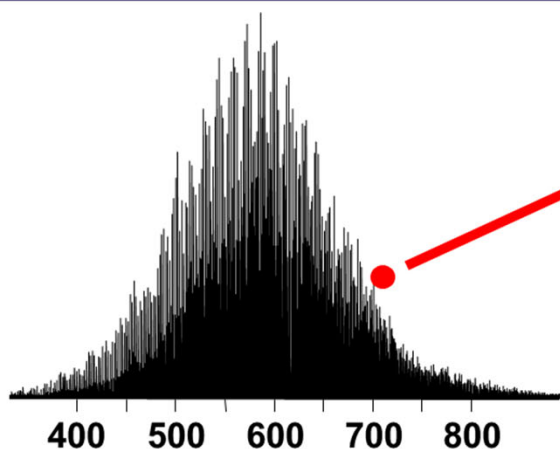
And it is Very  
Complex.







# The “Magic”: Accurate Mass = Molecular Formula



**m/z 704.53510**

50 - 200 ppb



**S<sub>1</sub> Class**

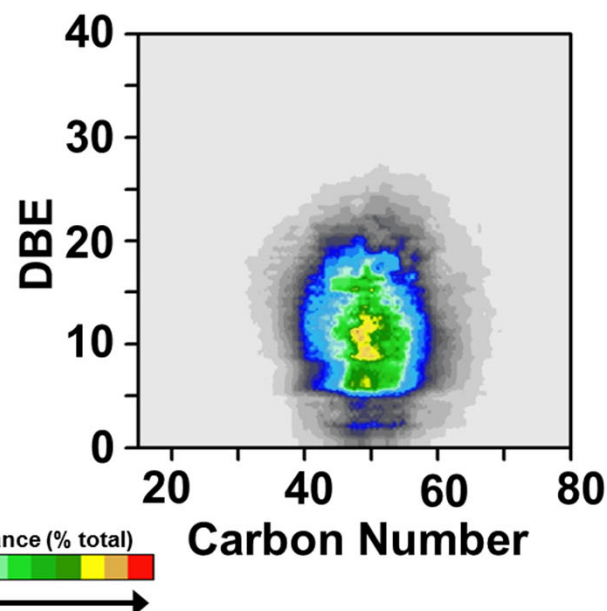
**1. Carbon Number**

**2. Aromaticity (Rings + Double Bonds)**

$$DBE = C - \frac{H}{2} + \frac{N}{2} + 1$$

McLafferty & Turecek *Int. Mass Spectra*, 1993

$$[Z = -2(DBE) + n + 2]$$







America's first asphalt road was paved in Newark, New Jersey in 1870.

The understanding of what is exactly in asphalt binder is still unknown today.

Is this legacy commitment to a product of unknown composition a good idea?

What are the possible dangers given the amounts that are used?

Admittedly an odd detour, but first, let's revisit the *Deepwater Horizon* oil spill...



**How does this form?**





**And this?**

# Sunlight is Key...

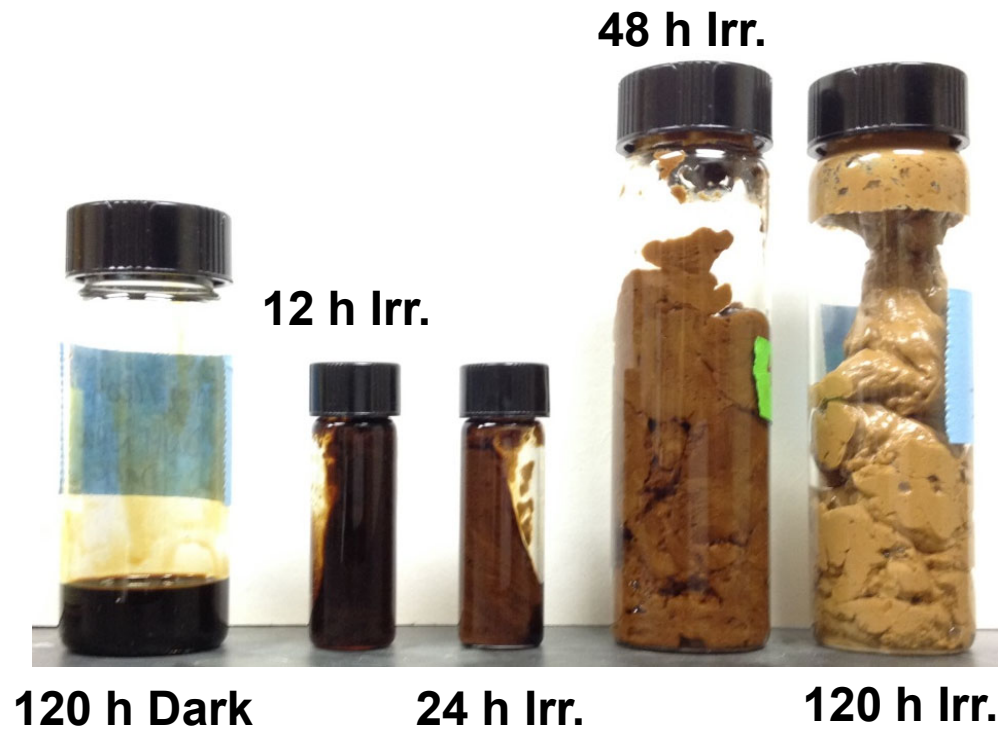
IM



Luke McKay, University of Georgia



AP Photo/Charlie Riedel



M. Tarr and P. Zito, unpublished data





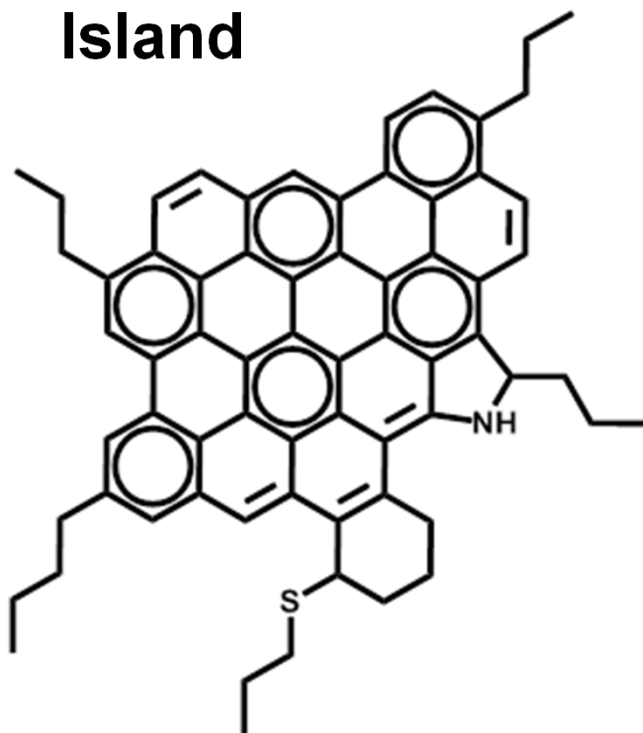
**Why does this form?**



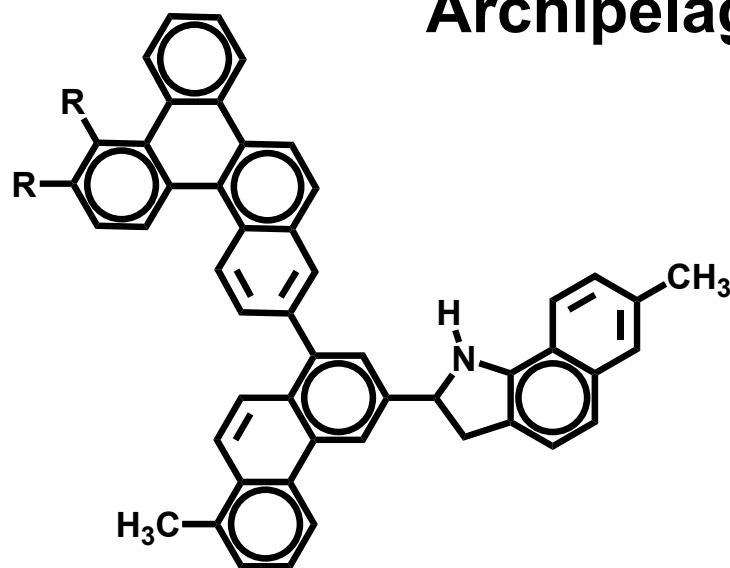
# Petroleum: The Structural Controversy

## 2 Proposed Structural Motifs

Island

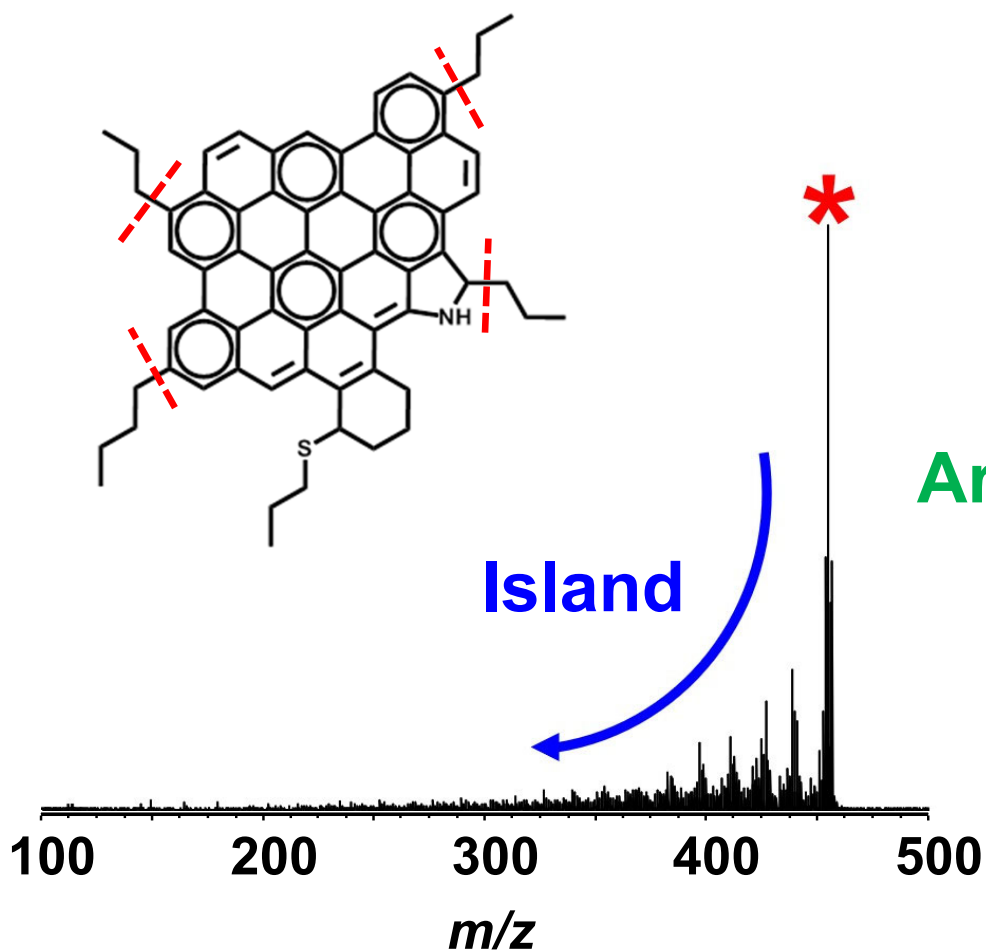


Archipelago

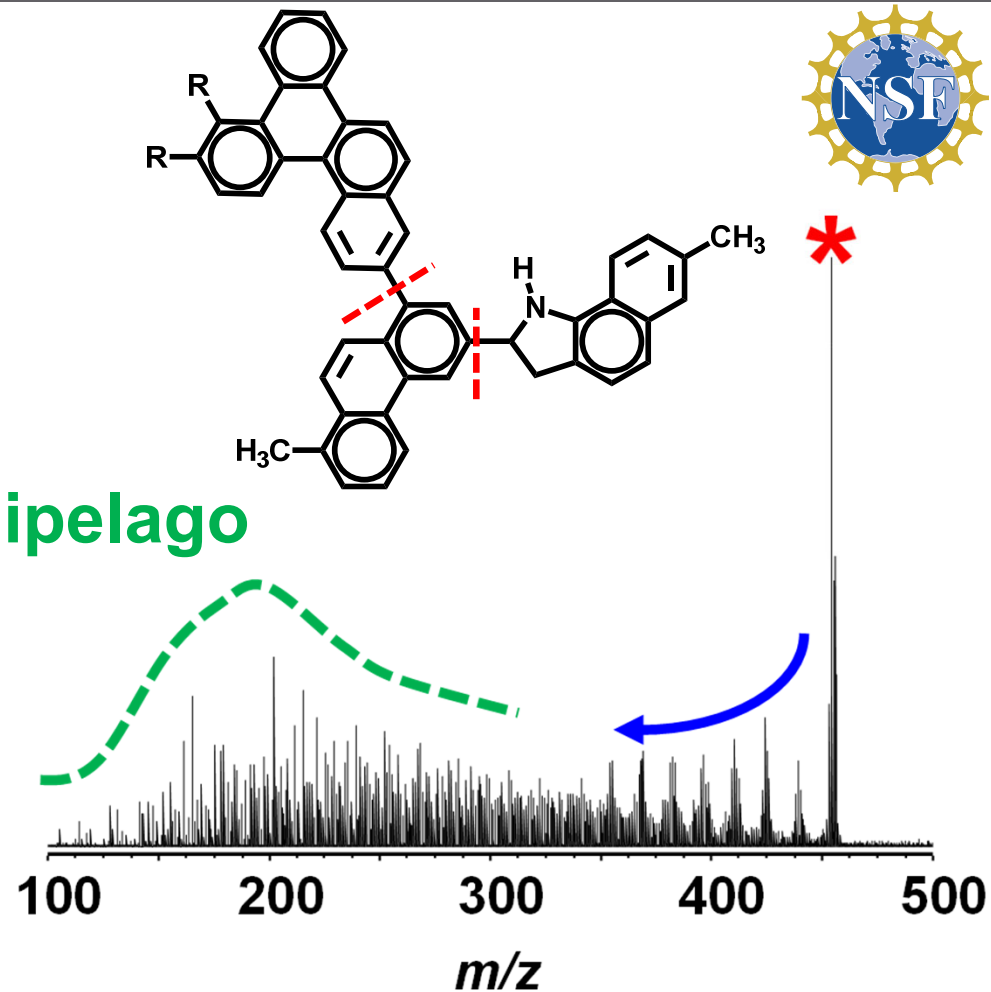


Seems trivial, but this is a big deal...

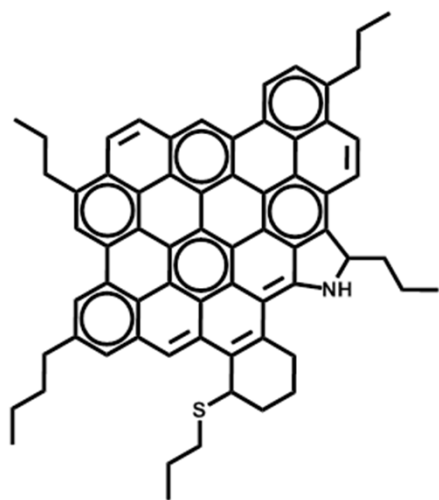
# Petroleum Structure



**Archipelago**



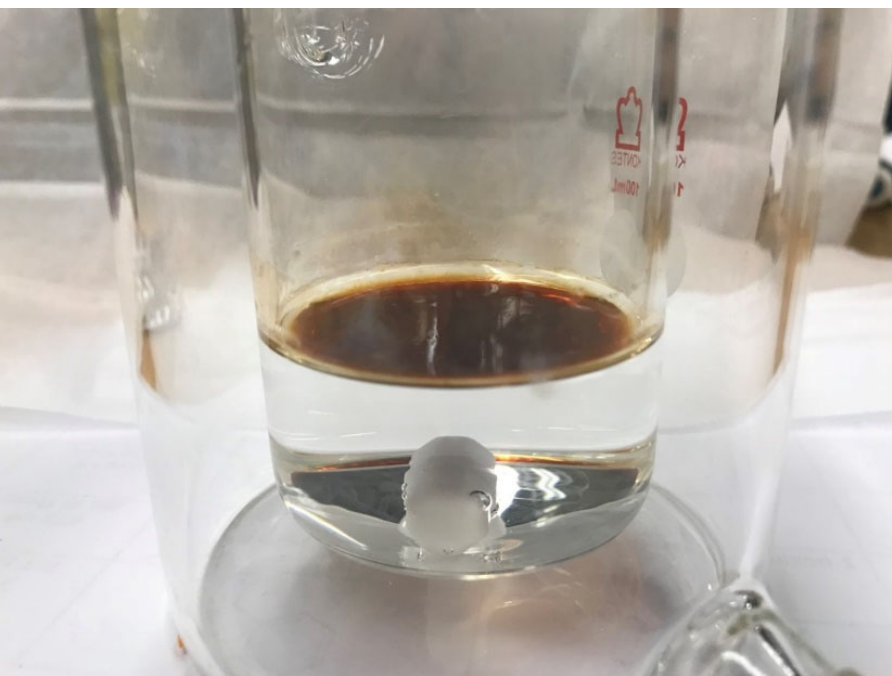




## Island Structure

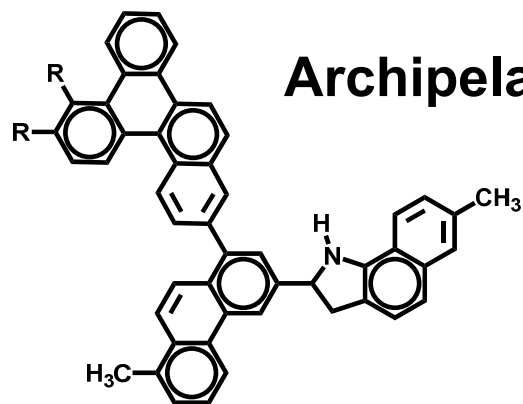


## After Sunlight





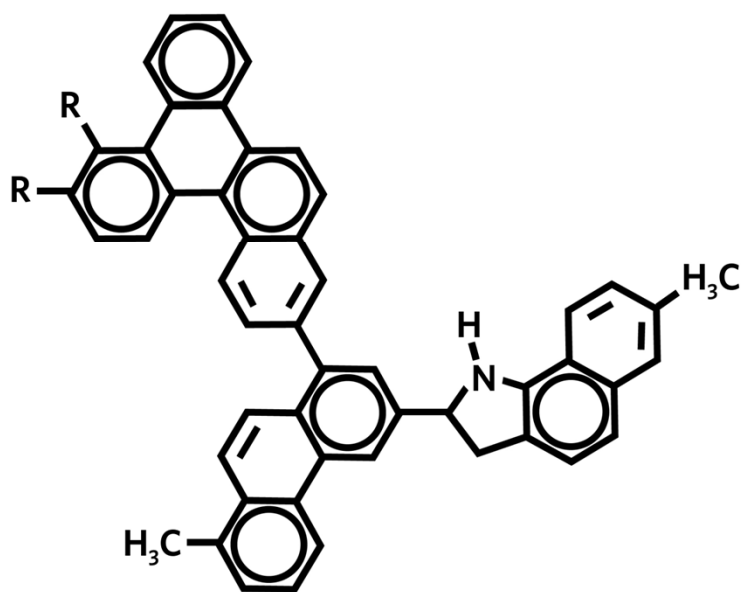




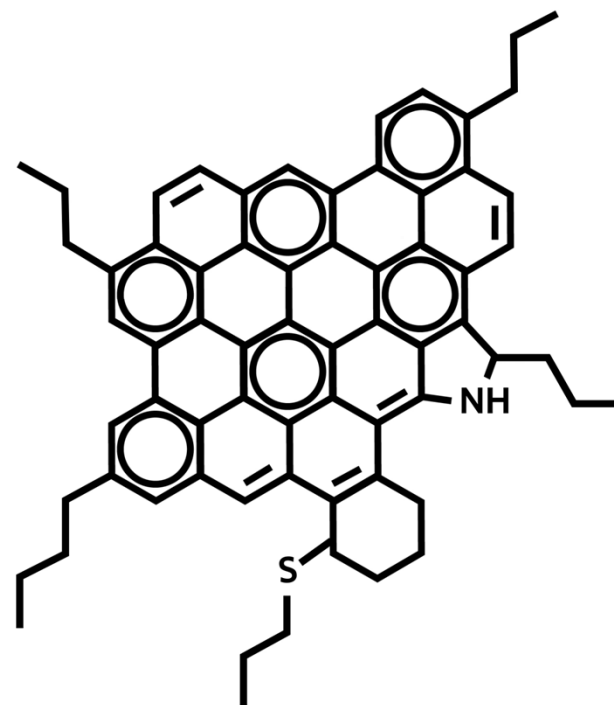
**Archipelago Structure**

**After Sunlight**





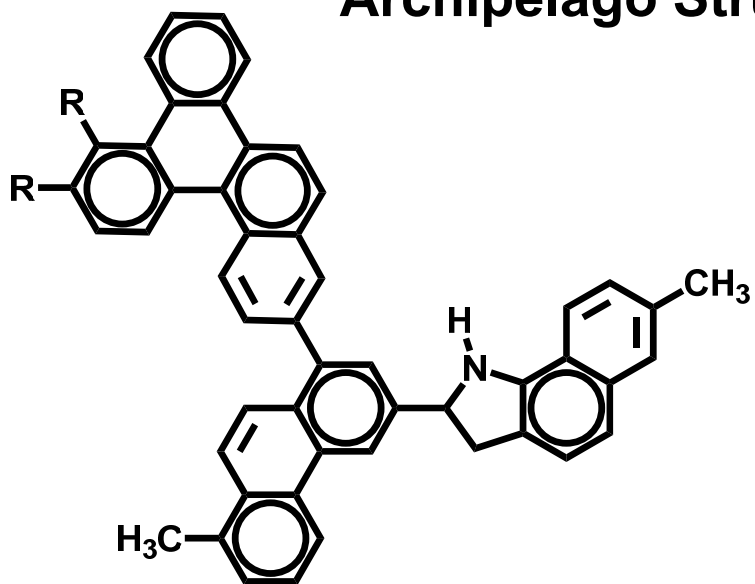
**ARCHIPELAGO MODEL**



**ISLAND MODEL**



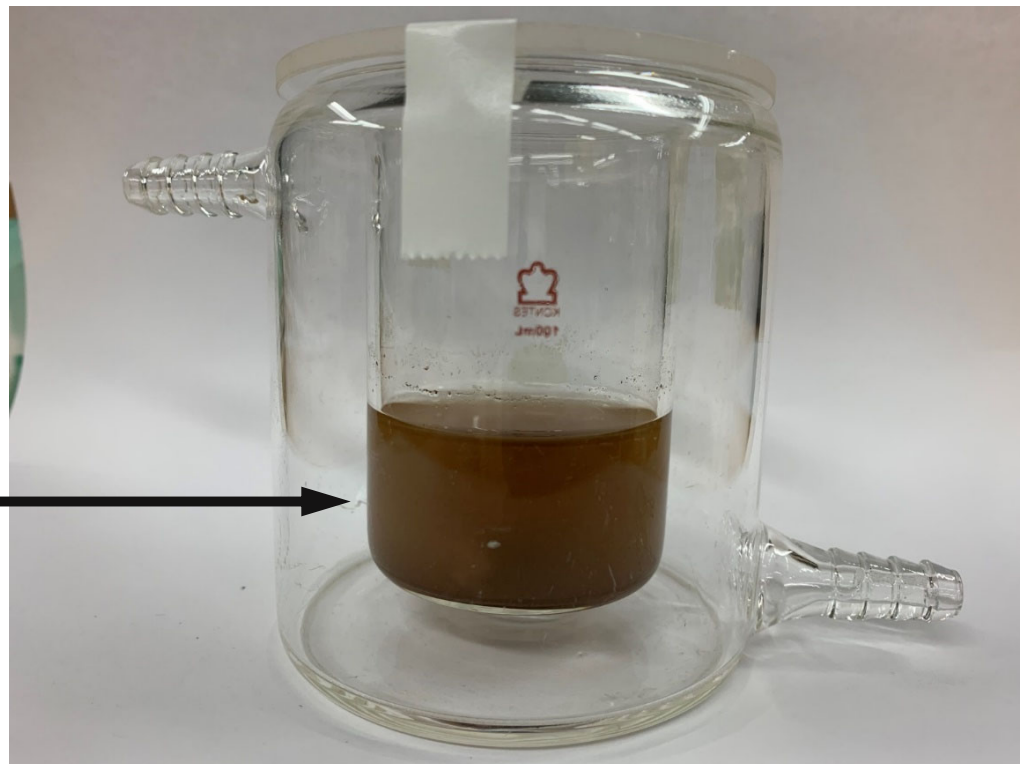
## Archipelago Structure



**Archipelago structures form  
water soluble contaminants.**

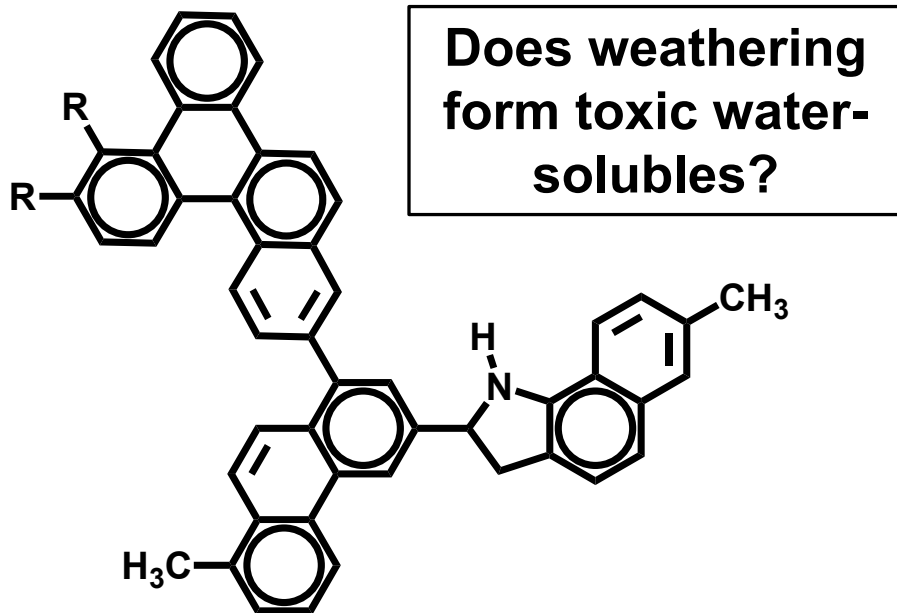
**Does this happen in asphalt?**

**After Sunlight**

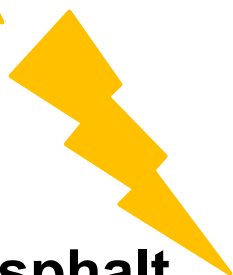


# Asphalt Binder

- High boiling-point petroleum-derived compounds
- Mixed with aggregate to pave roads
- High asphaltene content







A diagram illustrating the addition of a methyl group ( $\text{H}_3\text{C}-$ ) to a benzene ring. An arrow points from the methyl group towards a brown spot on a surface, representing the site of addition.



## - Glass ring

# Asphalt Binder in Simulated Sunlight

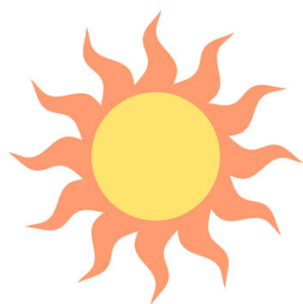


**Toxicity Unknown...**

Sample	NPOC (mg/L)
168 h Asphalt Dark Control	2.0
24 h Irradiated Asphalt	16.5
72 h Irradiated Asphalt	42.1
168 h Irradiated Asphalt	52.9

~ 26x





# Characterization of an Asphalt Binder and Photoproducts by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Reveals Abundant Water-Soluble Hydrocarbons

Sydney F. Niles, Martha L. Chacón-Patiño, Samuel P. Putnam, Ryan P. Rodgers,\* and Alan G. Marshall\*



Cite This: *Environ. Sci. Technol.* 2020, 54, 8830–8836



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Article Recommendations



Supporting Information

Then the phone call that blew us away...



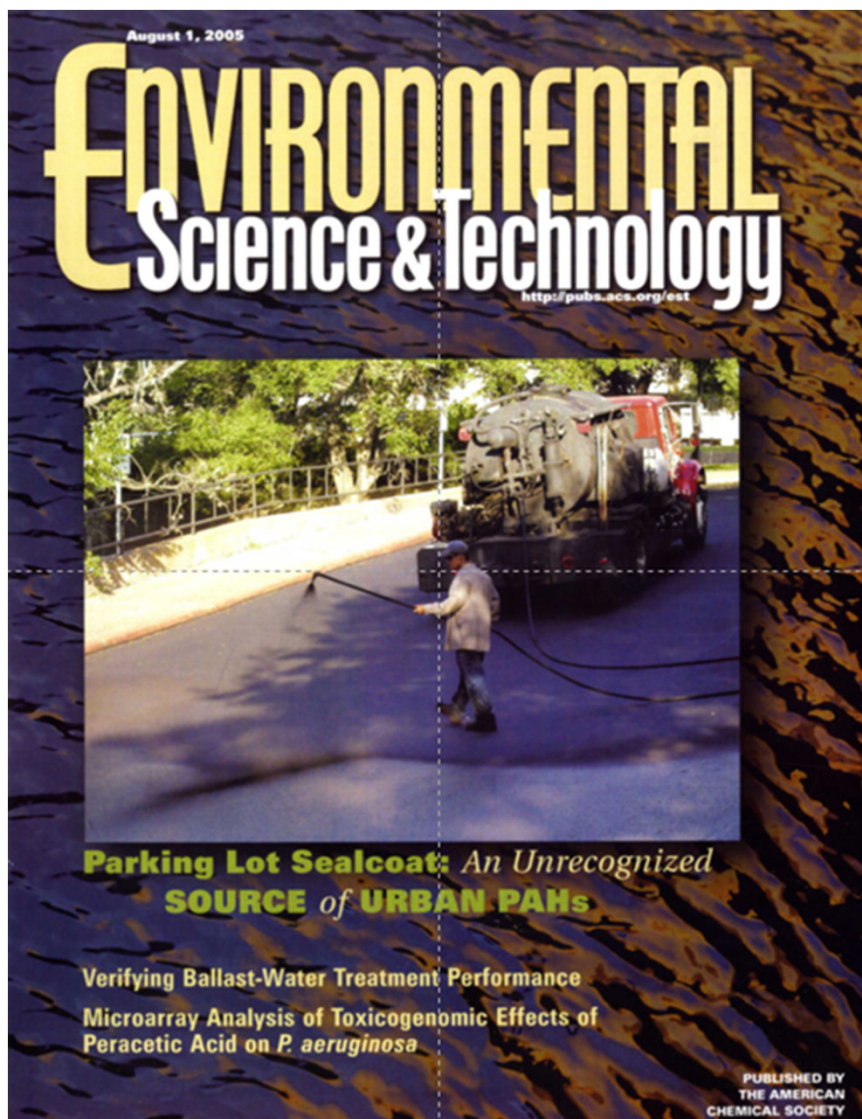
Thomas Ennis, P.E.,  
LEED AP –  
Watershed  
Protection  
Department, City of  
Austin, Texas

**Have you guys looked at coal  
derived products?**

**WHAT?**

**You're kidding right... Who the  
hell would allow that?**





We were shocked to learn that the US still allows **coal** derived materials for asphalt sealants.

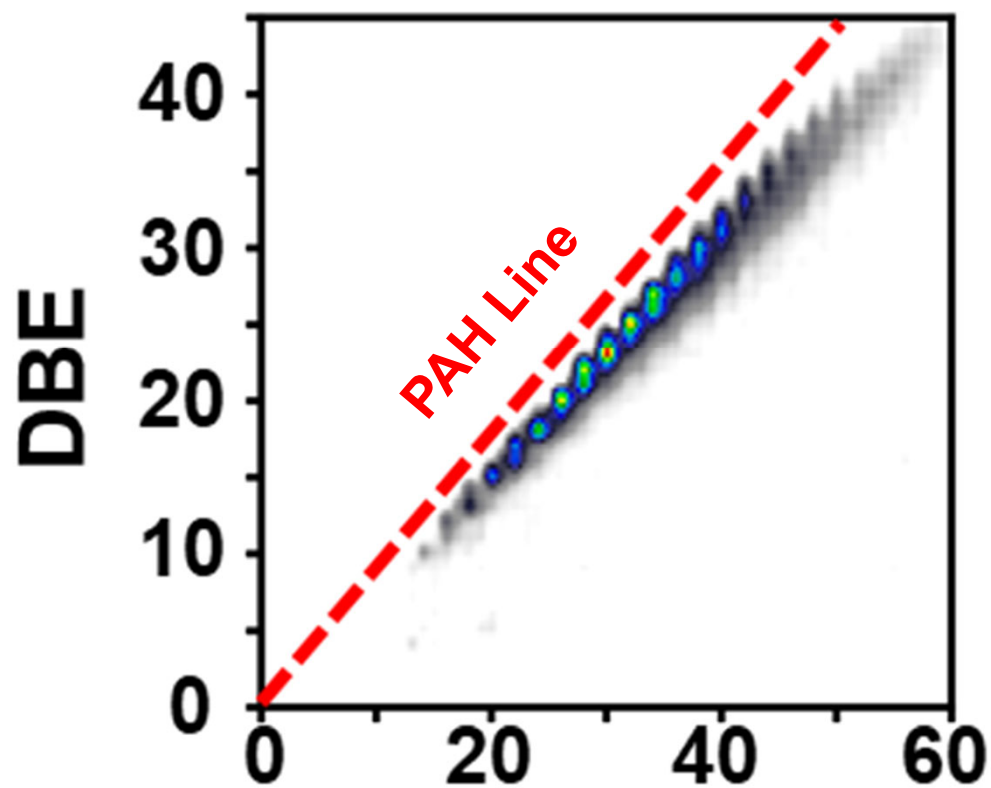
Why is this a big deal?

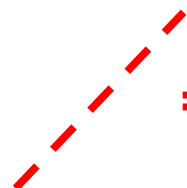
Coal tar liquids are almost entirely composed of PAHs. They are known carcinogens.

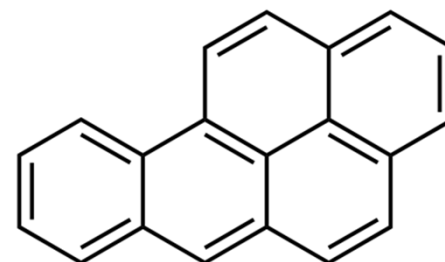
Research shifted towards coal vs. petroleum-derived products

Coal Tar sealant

HC



 = Carcinogen



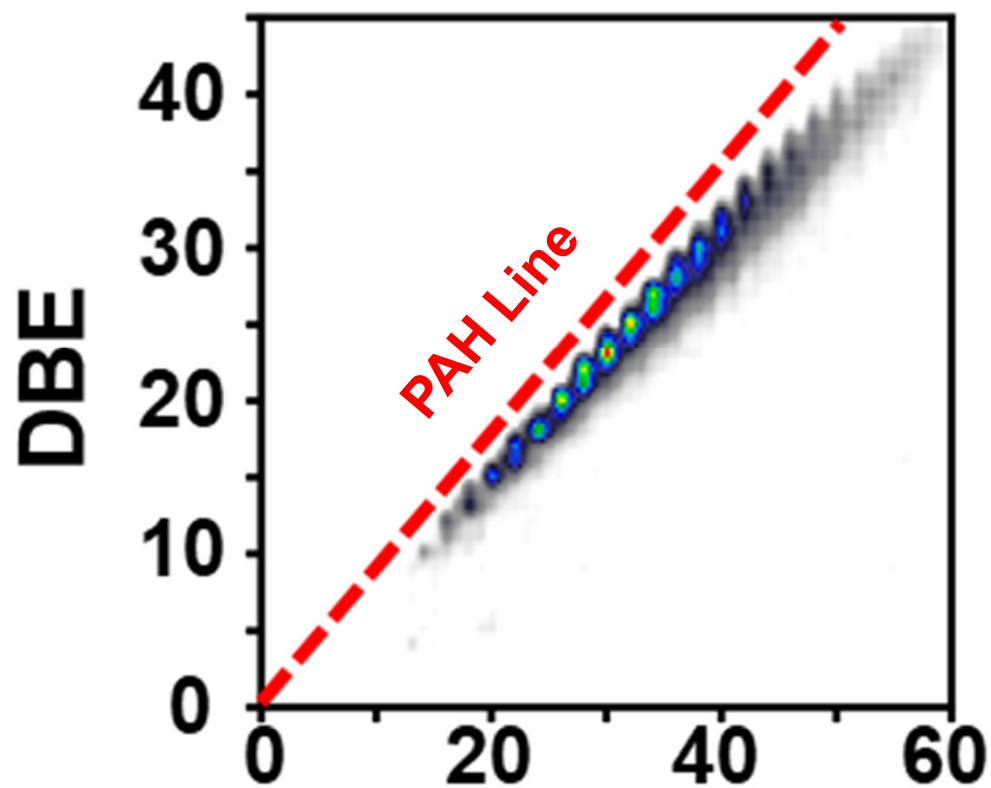
benzo[a]pyrene

Carbon Number



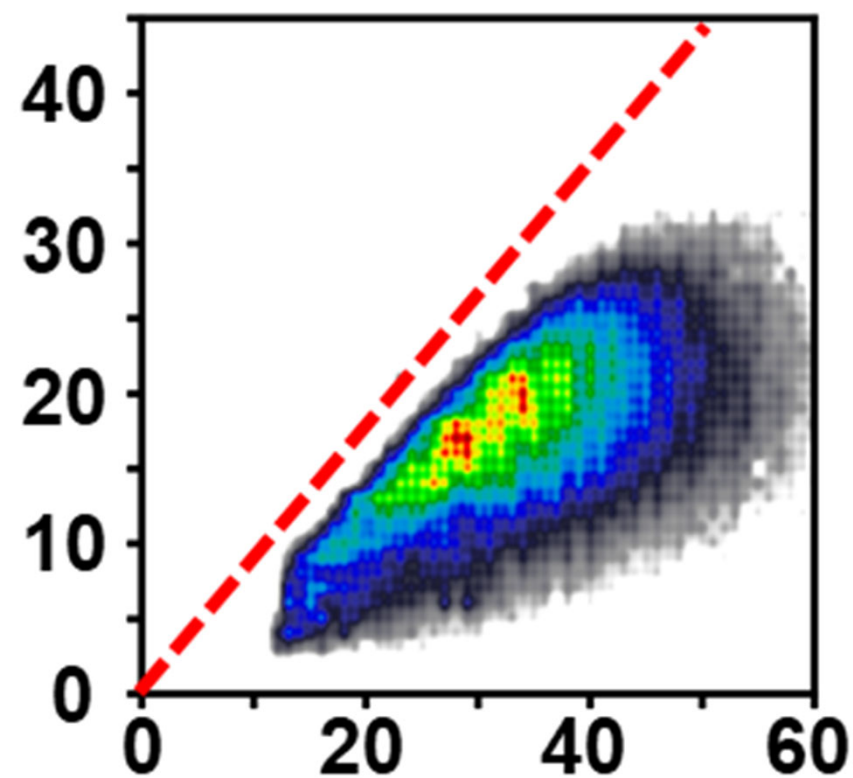
**Coal Tar sealant**

**HC**



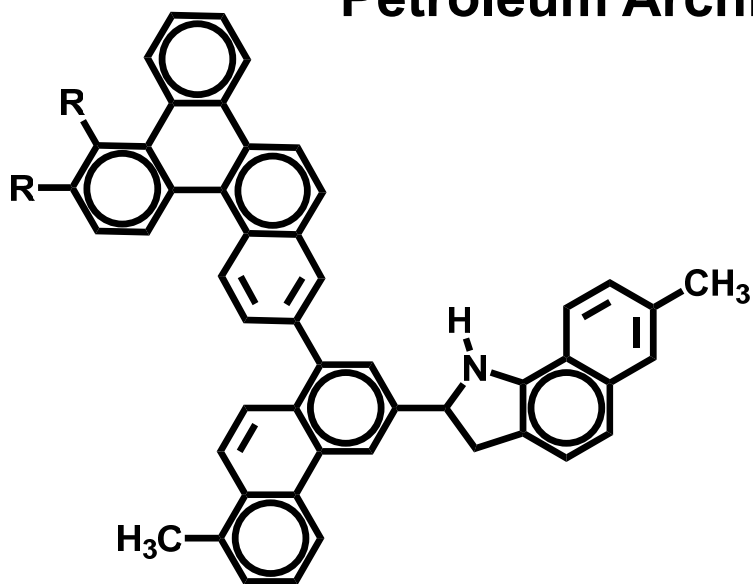
**Petroleum sealant**

**HC**



**Carbon Number**

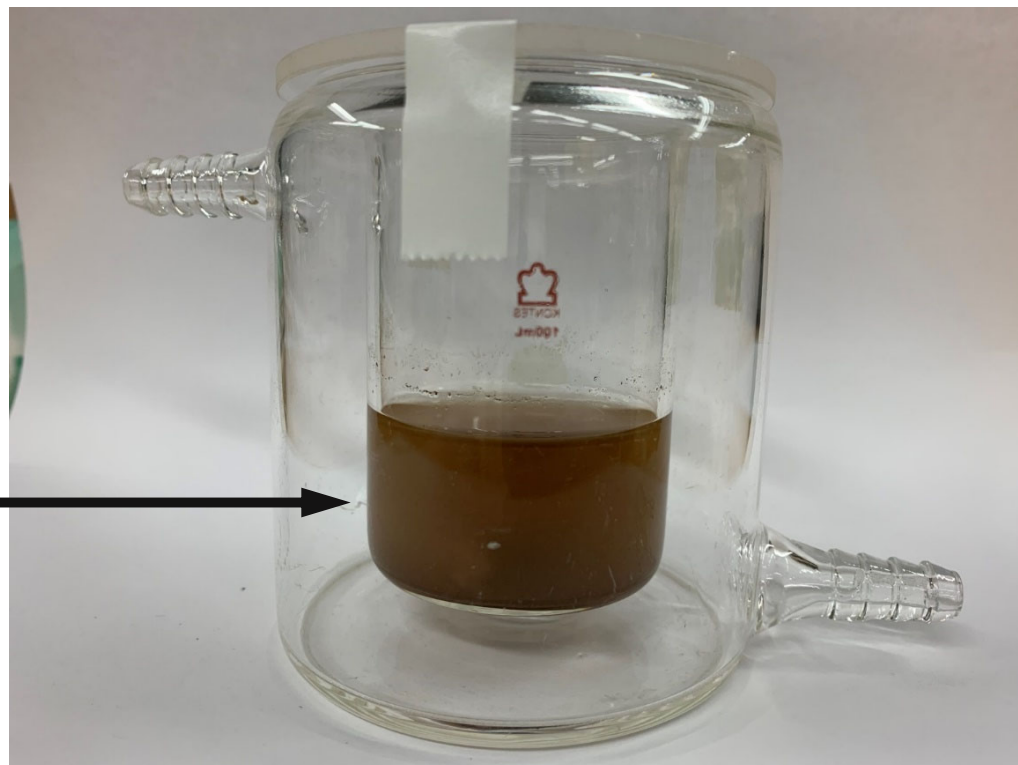
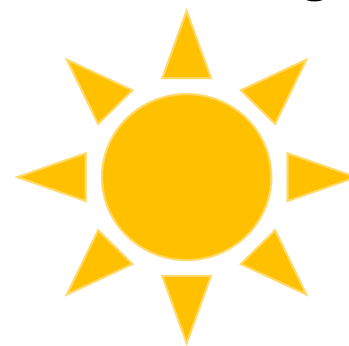
## Petroleum Archipelago Structure



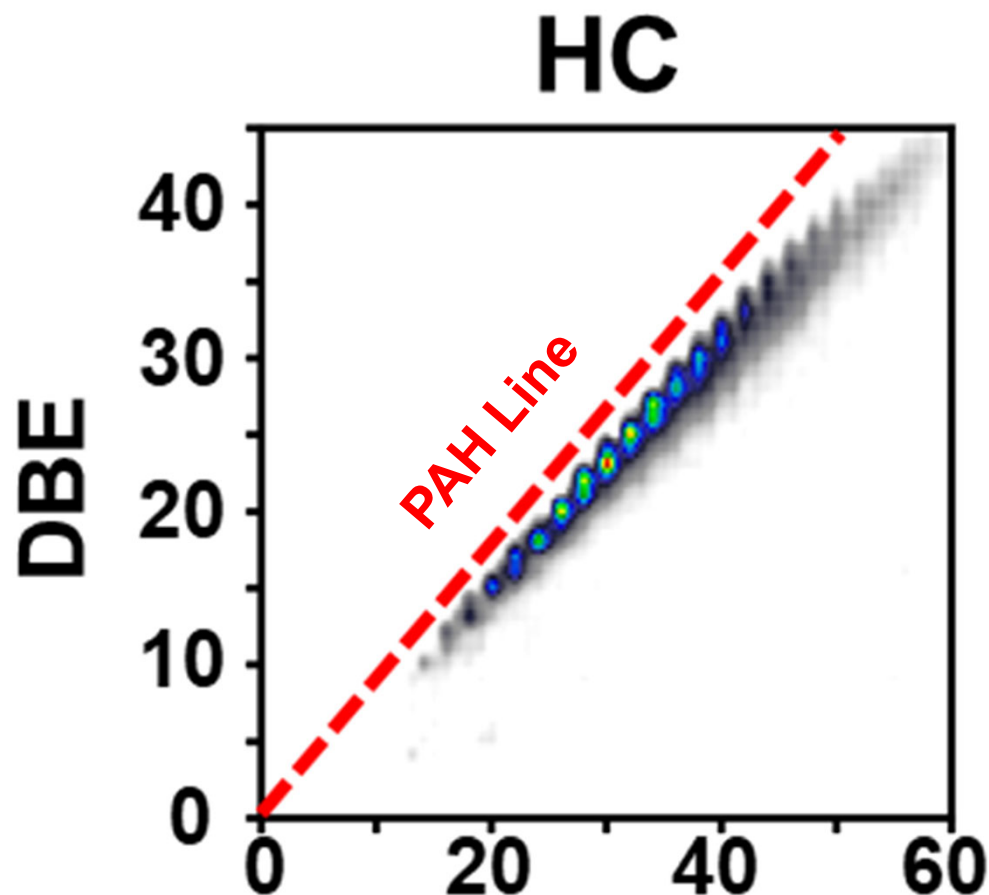
Archipelago structures form water soluble contaminants.

BUT, this is a **fraction of a fraction** in petroleum-derived materials

After Sunlight



**But Coal Tar sealant is almost entirely PAHs**



No cracking by  
sunlight required.

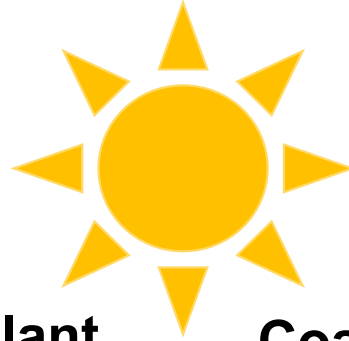
And they are known to  
be toxic.

But do they form water  
soluble species?



# Move from Asphalt Binders to Petroleum- and Coal-derived Sealants

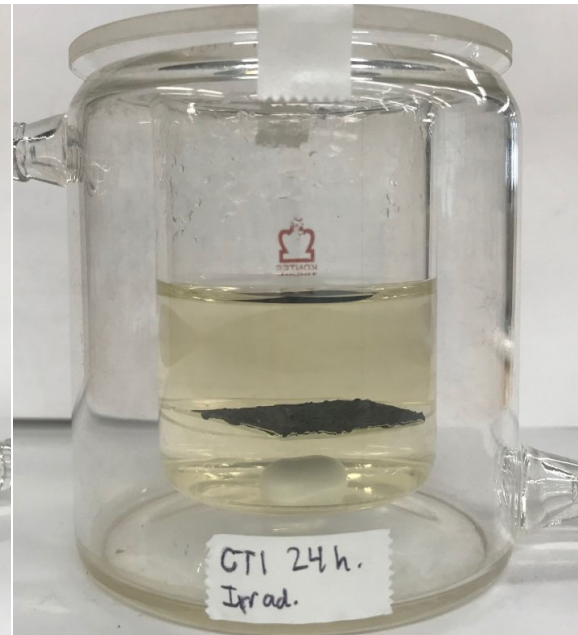
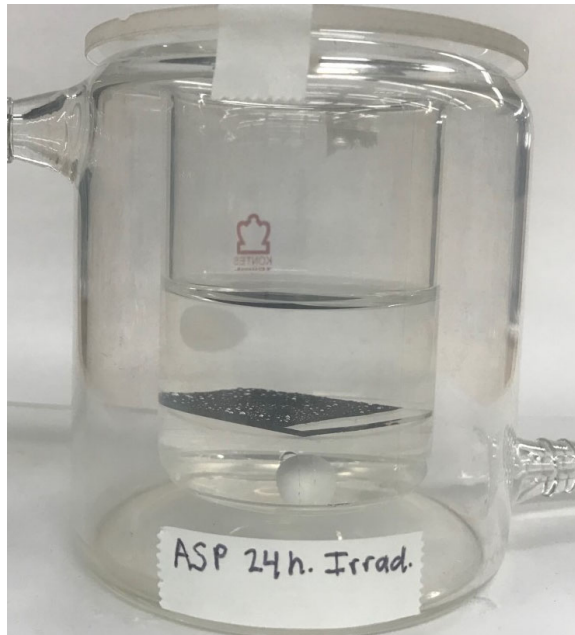
After Sunlight



Asphalt Sealant

Coal Tar Sealant

ASPHALT-BRAND-1  
NO TO VERY LOW PAHS  
<50 PPM

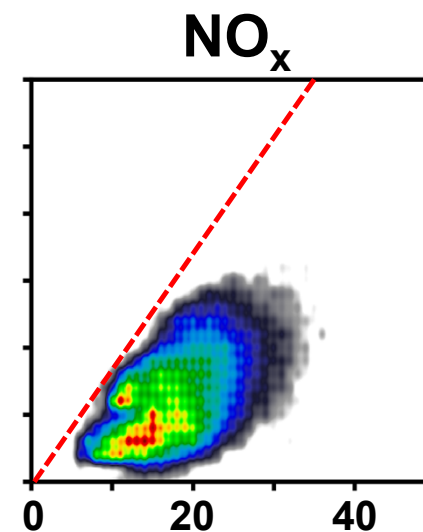
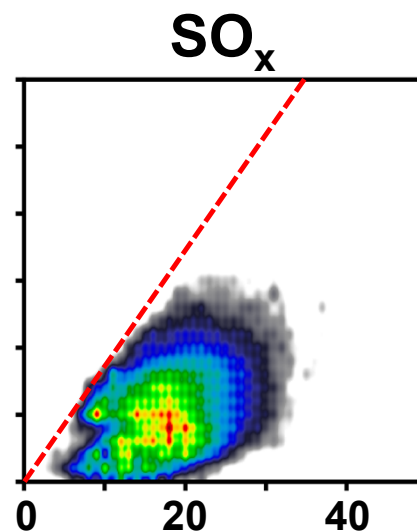
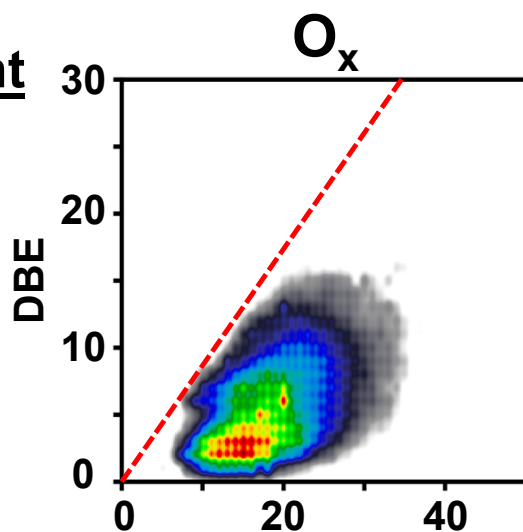


COALTAR-BRAND-1  
HIGH PAHS  
50,000 TO 75,000 PPM

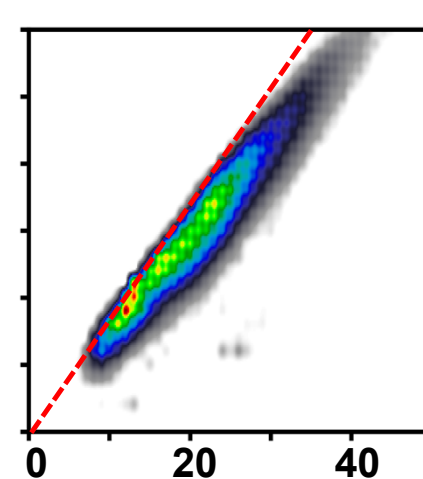
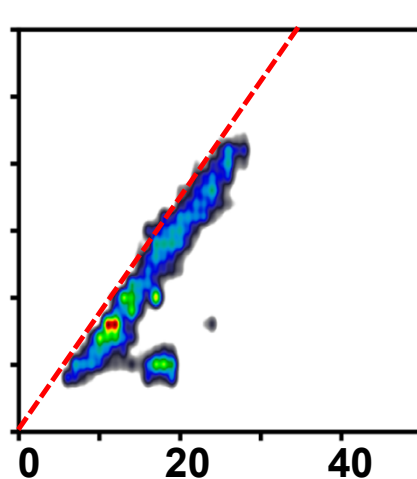
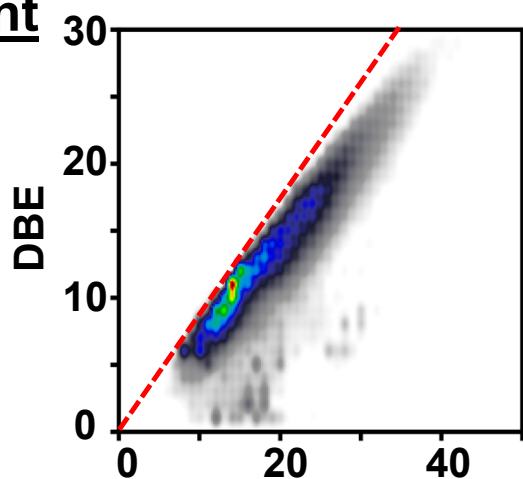
**1000X** higher  
in PAH

# Asphalt Emulsion and Coal Tar Water-Solubles

Asphalt in Sunlight



Coal Tar in Sunlight



Carbon Number



## More Problems with Coal-derived materials...



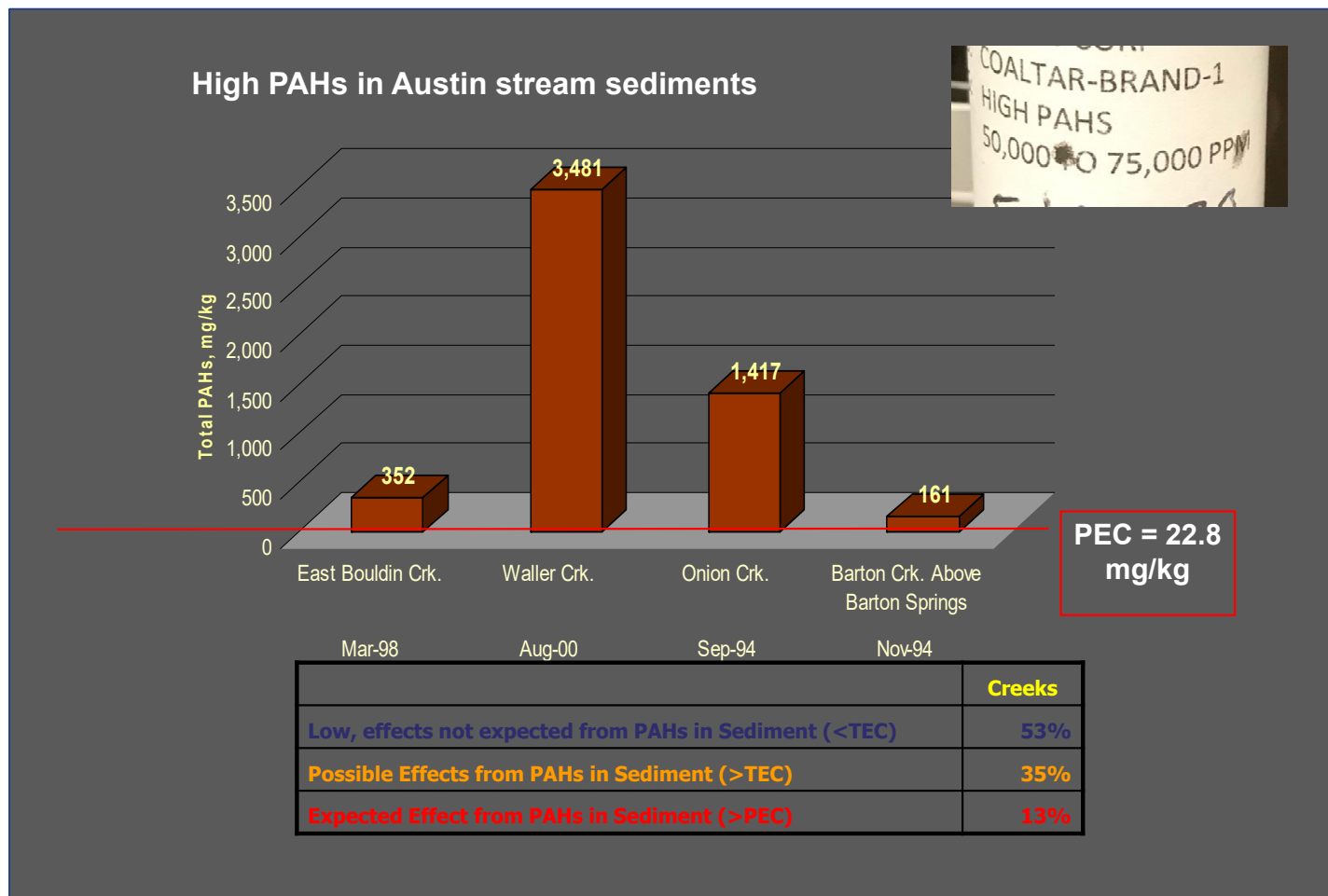
Coal Tar sealant chips as it ages. The flakes stick to dirt and transport the PAHs off site.

Now we have another problem...

Where does this material go?

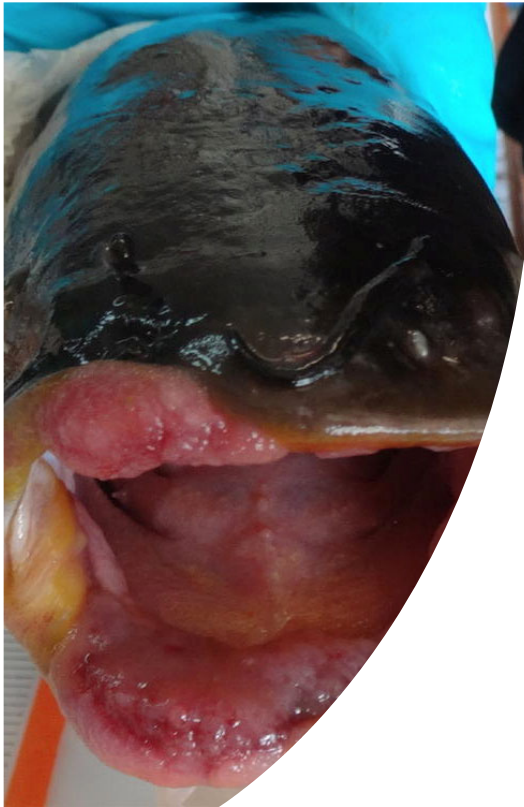


# US cities have learned this the hard way...



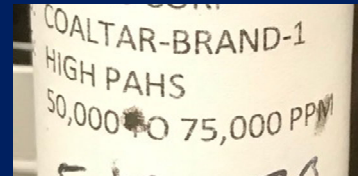
# PAHs and Environmental Health – DC Area

Varying levels of exposure to PAHs from sealants are toxic to human and aquatic health



## Aquatic Life:

- PAH Aquatic Wildlife
- Toxicity linked to increased skin and liver tumors in fish
- “Acutely toxic” to fathead minnows and water fleas
- Probable Effect Concentration (PEC) for PAHs in sediment is 22.8 mg/kg (.00228%)



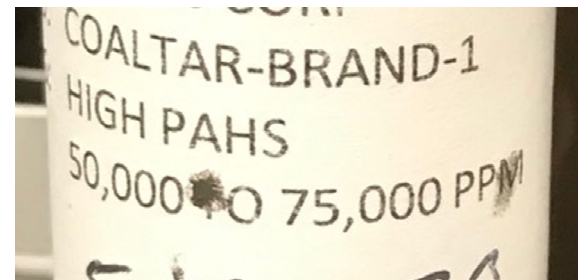


**Relatively Low**  
in PAH

But the potential health effects  
of the water-soluble  
compounds are unknown...





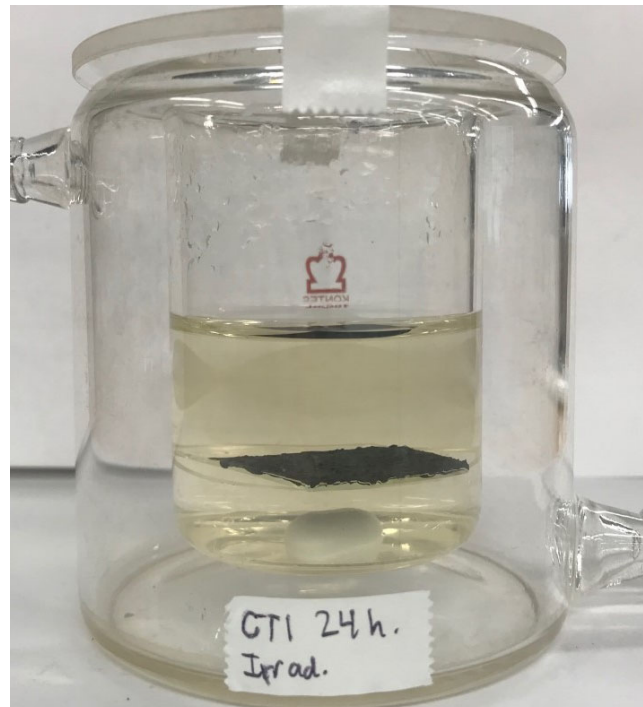


**Coal Tar Sealant**



**1000X higher  
in PAH**

The potential health effects of the water-soluble compounds are unknown... But the health effects of the coal tar "dust" is known.



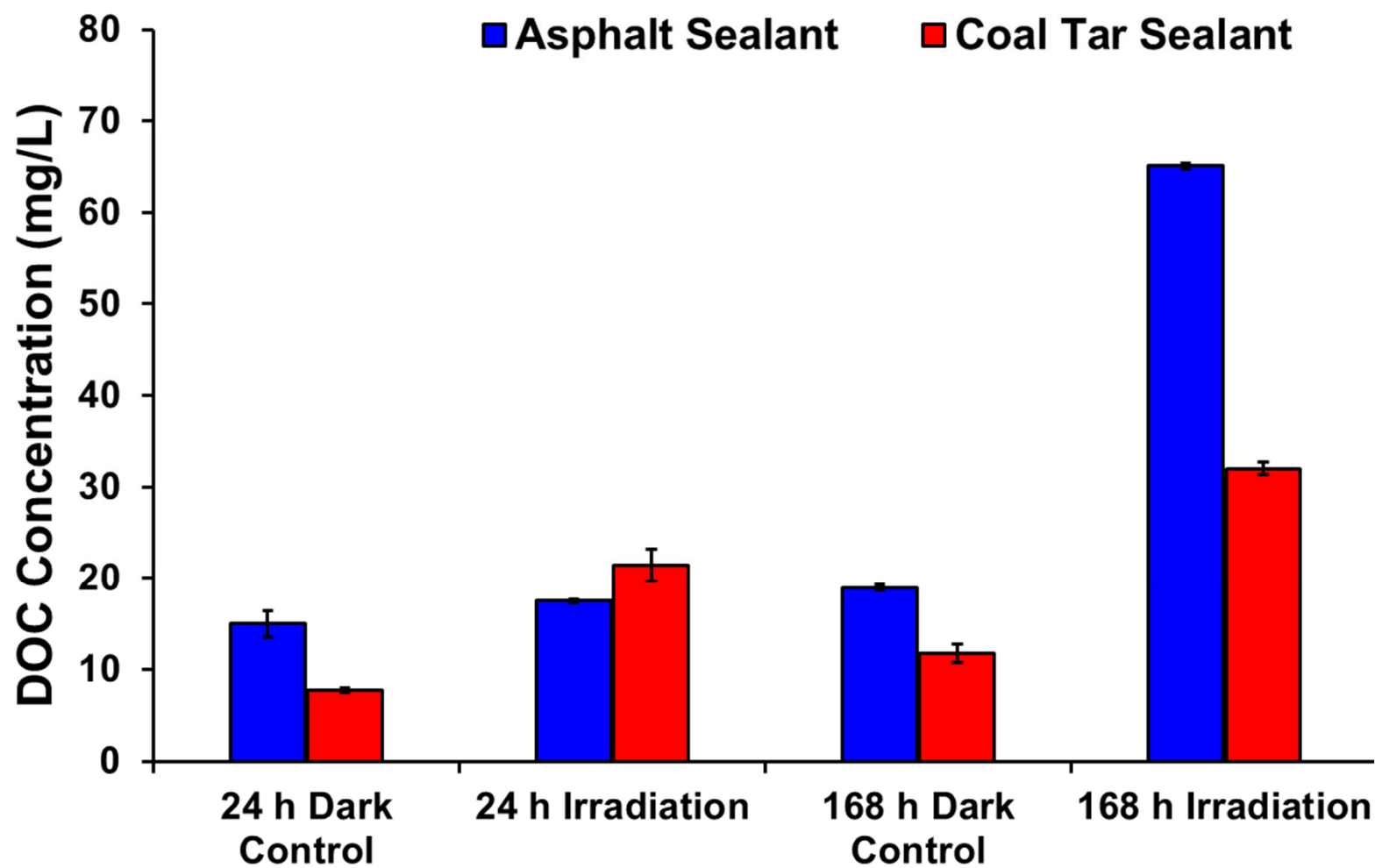
## DOC and Microtox® Bioassay Testing



**Alive**  **Dead**

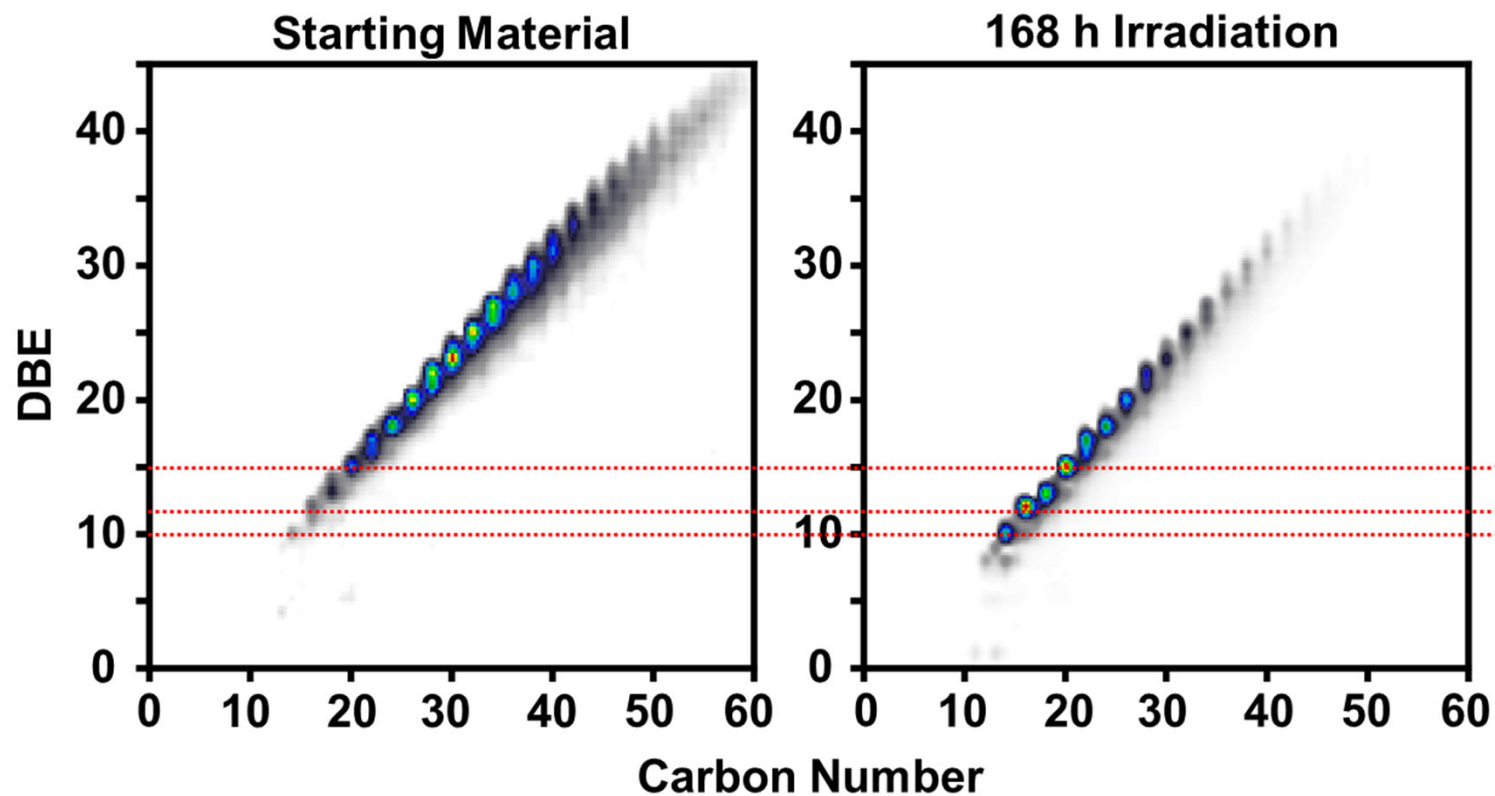
**Simply, when bacteria die, there is less light.**

## Dissolved Organic Carbon (DOC) Measurements

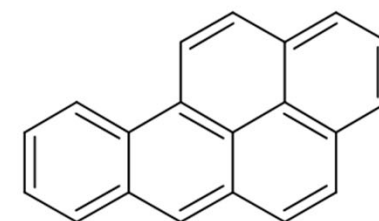




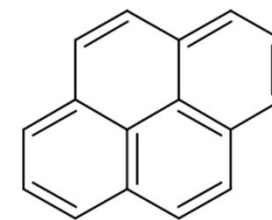
# Coal Tar Sealant – HC Class



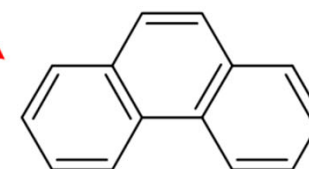
+ APPI FT-ICR MS



**Benzo(a)pyrene**  
 $C_{20}H_{12}$  DBE 15



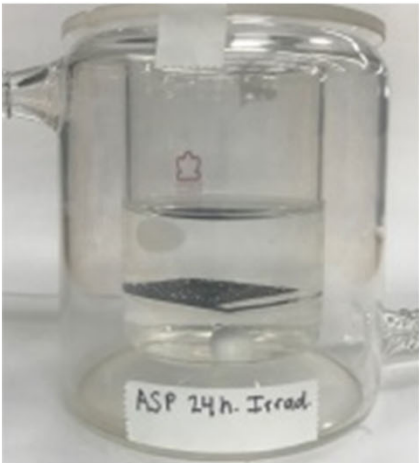
**Pyrene**  
 $C_{16}H_{10}$  DBE 12



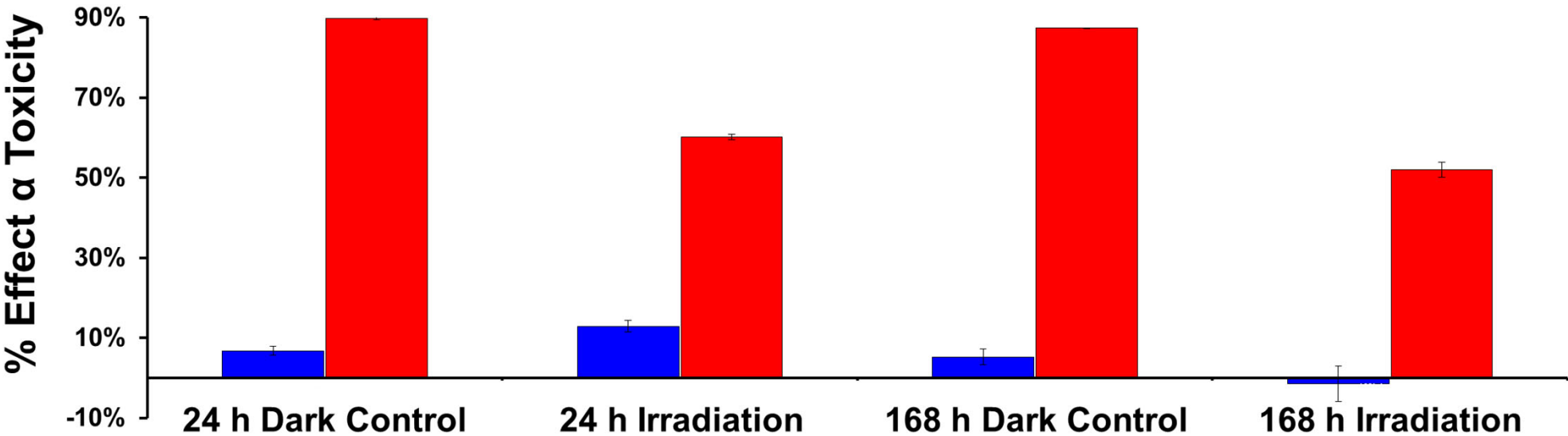
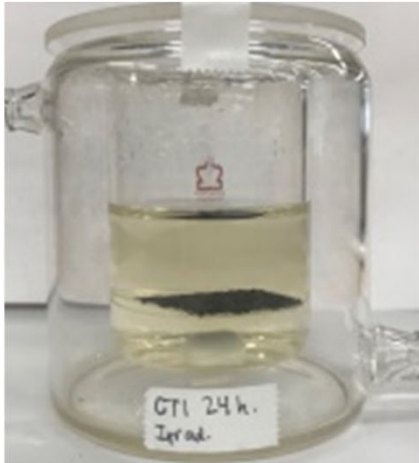
**Phenanthrene**  
 $C_{14}H_{10}$  DBE 10

Microtox<sup>®</sup> Bioassay After 15 Minutes

**Asphalt  
Sealant – 24 h  
Irradiation**

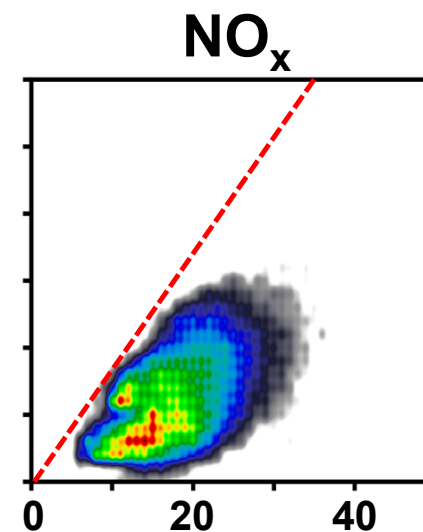
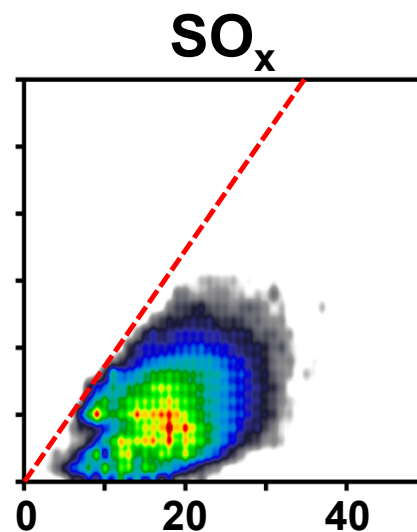
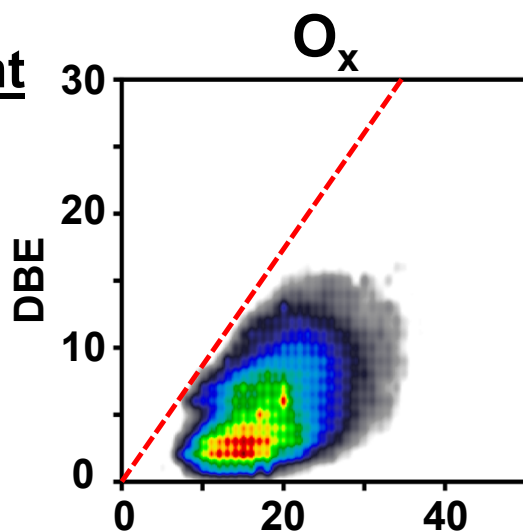


**Coal Tar  
Sealant – 24 h  
Irradiation**

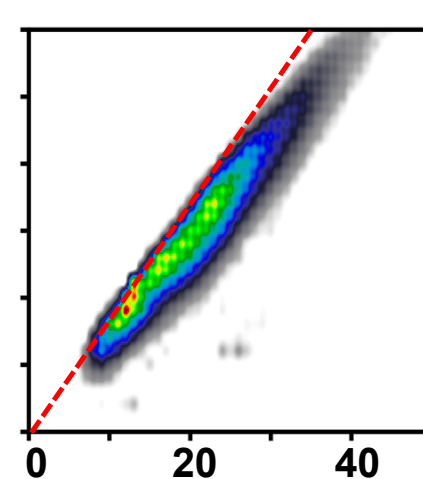
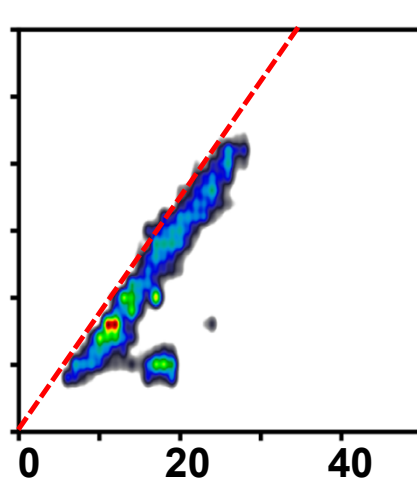
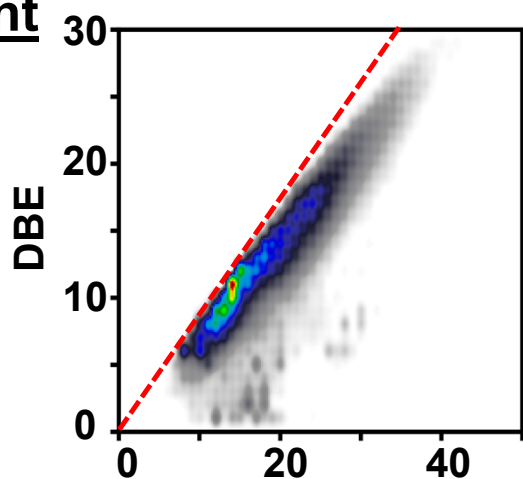


# Asphalt Emulsion and Coal Tar Water-Solubles

Asphalt in Sunlight

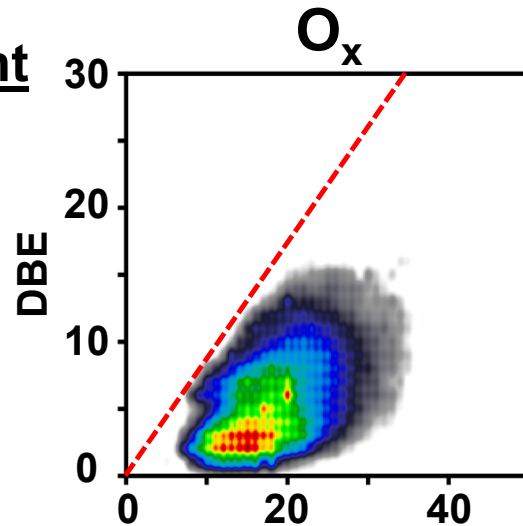


Coal Tar in Sunlight

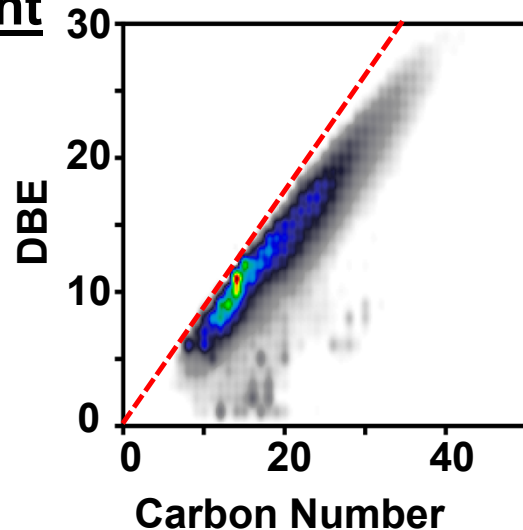




### Asphalt in Sunlight



### Coal Tar in Sunlight



Although both petroleum- and coal derived coatings produce abundant water-soluble species upon photoirradiation, the coal derived water-soluble species have notably higher toxicity. The increased toxicity is most likely due to the low degree of alkylation of the species generated by photooxidation.

Future studies will isolate these species prior to photoirradiation to determine if they account for the majority of the associated toxicity.



# Thank You!

rodgers@magnet.fsu.edu



*Science. Restoration. Partnership.*

