Forensic Analysis using UVF and USGS Laboratory Results Testing PAHs in Coal Tar Pavement Sealants

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Project Description

Environmental scientists use a variety of forensic techniques to identify the source of hydrocarbons using laboratory data. This study compares Sitelab's UVF data and laboratory GC/MS data using double ratio plots testing pavement sealants for Polycyclic Aromatic Hydrocarbons (PAHs). Ratios were then applied using data in three studies conducted by the United States Geological Survey (USGS), concerning the use of coal tar sealants and how they impact the environment.

Background

In 2022, Sitelab Corporation completed a U.S. EPA funded grant with Chesapeake Bay Trust for DOEE in Washington, DC, to create a certification program testing the PAH content in pavement sealants. Materials used to manufacture sealcoats vary; most in commercial use are made with coal tar, ethylene cracked residue (ECR) or are asphalt-based. These products are generally not used on roads.

Manufacturers who participate will know if their product meets a "Gold" 1,000 ppm (0.1%) or "Silver" 10,000 ppm (1%) regulatory limit. An ongoing list of qualified products is available on Sitelab's website informing communities who want to ban high-PAH pavement sealants.

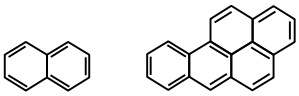
FIGURE 1

17 PAH Compounds

Compounds listed in order from C10 to C22 carbon range

1. Naphthalene
2. 2-Methylnaphthalene
3. Acenaphthylene
4. Acenaphthene
5. Fluorene
6. Phenanthrene
7. Anthracene
8. Fluoranthene
9. Pyrene
10. Benzo(a)anthracene
11. Chrysene
12. Benzo(b)fluoranthene
13. Benzo(k)fluoranthene
14. Benzo(a)pyrene
15. Indeno(1,2,3-cd)pyrene
16. Dibenz(a,h)anthracene
17. Benzo(g,h,i)perylene

PAHs are ring-shaped molecules, which increase in size with carbon weight



Naphthalene, C10
More volatile with 2 rings

Benzo(a)pyrene, C20
Less volatile with 5 rings

- Total PAH is calculated by adding the 17 compound concentrations together.
- Test Method 8270D includes the EPA's priority pollutant compounds, which are regulated and have specific toxicity limits.
- The PAH content in sealants varies depending on what type of hydrocarbons they're made with. See CAS numbers in Figure 2 below.

The Quality Assurance Protocol developed for this program requires certified laboratory analysis be performed using EPA Method 8270D by GC/MS to report 17 PAH compounds in Figure 1. Sitelab has had the opportunity to test many different brands of sealcoat products. This includes bucket brands purchased at retail stores and samples provided by manufacturers.

FIGURE 2

Types of Parking Lot Sealcoats, Total PAH Concentration Ranges and Products Available in U.S. Market

Most bucket brands sold at retail stores used on driveways are asphalt-based

1 Asphalt-Based Sealcoats
Hydrocarbons CAS# 8052-42-4

- Total PAHs = 0 ppm (ND <50)
- Number of products in market = 86
- Qualify for DOEE's Gold <1,000 ppm or Silver <10,000 ppm certification

2 ECR "Cracked Residue" Sealcoats
Hydrocarbons CAS# 64742-90-1

- Total PAHs = 20,000 to 30,000 ppm
- Number of products in market = 9
- Do not qualify, PAHs > 10,000 ppm

3 Coal Tar-Based Sealcoats
Hydrocarbons CAS# 65996-93-2

- Total PAHs = 50,000 to 180,000 ppm
- Number of products in market = 29
- Do not qualify, PAHs > 10,000 ppm

Other: Latex-Based Sealcoats, CAS# 25085-34-1 or CAS# 25067-01-0. Products made with soybean oil or acrylic latex (like paint). Number of products in market = 6.

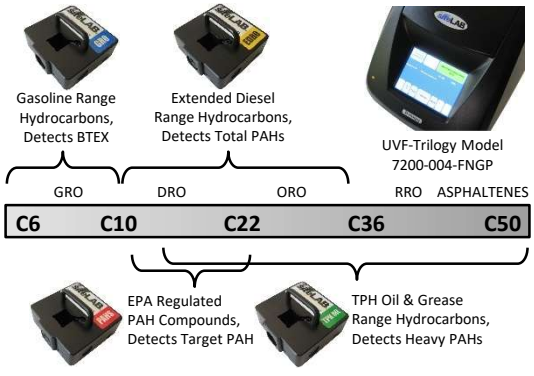
Data listed as of November 2022

PAH Screening Analysis using UVF-Trilogy Analyzer

Sealcoat samples received by Sitelab for the PAH certification program are also analyzed using Sitelab's UVF-Trilogy instrument. The analyzer uses ultraviolet fluorescence to detect petroleum contaminants in soil, sediment, water or other samples using solvent extraction. It uses snap-in UV modules fitted with LED UV lights and optical filters sensitive to different types of aromatic hydrocarbons (Figure 3). It can perform both quantitative and qualitative measurements. This includes hydrocarbon fingerprinting used to help identify the type or age of petroleum in a sample. It cannot detect one compound from another and as such, was only used for screening purposes when developing DOEE's QA protocol for the sealcoat certification program.

FIGURE 3

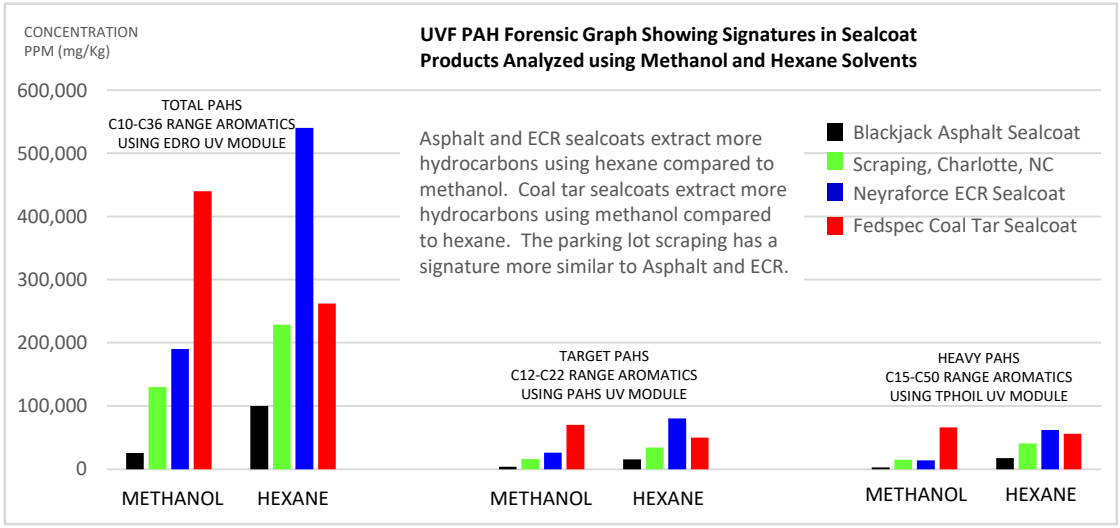
Types of Hydrocarbons Detected using UV Modules



For advanced fingerprinting applications, samples are extracted and tested using two solvents; methanol (a polar solvent) and hexane (a non-polar solvent) to compare extraction efficiency. The EDRO, PAHS and TPHOIL modules are used to test (1) Total PAHs, (2) Target PAHs and (3) Heavy PAHs. Sitelab's PAH calibration kit, CAL-060M (in methanol), is used to calibrate the analyzer for all three tests. The calibration standards contain a mixture of the same 17 PAH compounds used by certified laboratories for EPA Method 8270D analysis. Sealcoats are extracted for 24 hours, filtered and then diluted in methanol using a high precision micro-pipette. Dilutions are poured into a glass cuvette and then measured in the instrument. Readings are multiplied by the dilution factor to report the final concentration.

Figure 4 shows examples of three different types of sealcoat products plus a parking lot scraping collected by regulators in Charlotte, North Carolina, from a site sealcoated 3 months prior to sample collection. The city enforces a 1,000 ppm limit. The graph illustrates how sealcoats and the scraping fluoresce when extracted in methanol and hexane solvents.

FIGURE 4



Results in ppm (mg/Kg)

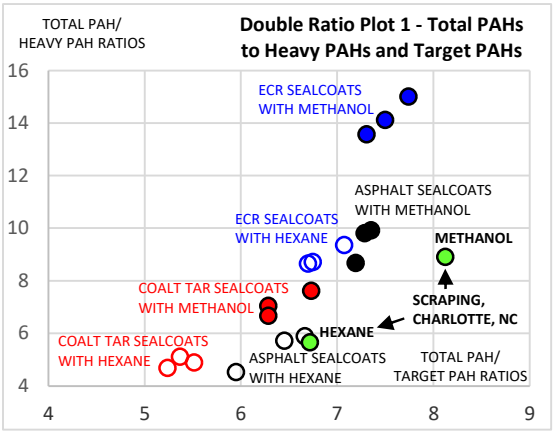
	Solvent Used	Total PAHs	Target PAHs	Heavy PAHs
Asphalt	M	22,800	3,100	2,300
	H	100,000	15,000	17,000
ECR	M	190,000	26,000	14,000
	H	540,000	80,000	62,000
Coal Tar	M	440,000	70,000	66,000
	H	262,000	50,000	56,000
Scraping	M	130,000	16,000	14,600
	H	228,460	34,000	40,380

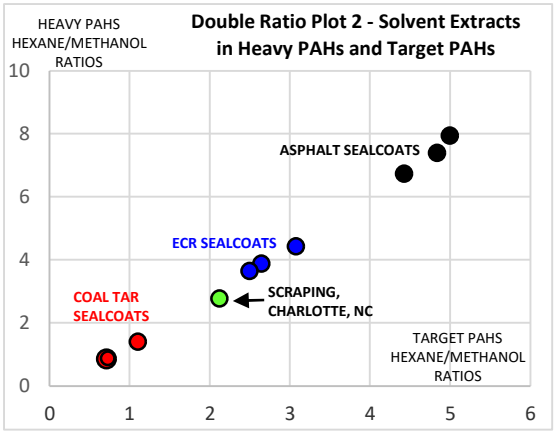
1 gram of dust and fragments is extracted with 20 mL solvent, shaken and then sit 24 hours

Double Ratio Plots using UVF Data

Figure 5 shows two ratio plots using the data in Figure 4, plus other asphalt, ECR and coal tar sealcoat brands tested in the sealcoat certification program. The signatures in Plot 1 show clear differences in sealcoat contents. This is more definitive in Plot 2, especially for the scraping sample. This sample came from a site baking in the sun all summer, so it's weathered. Fresh sealcoats tested here were dried indoors for 2 days in a controlled environment, split and then sent to the lab.

FIGURE 5





Plot 1 Ratios Exhibited

	Solvent Used	Total PAHs ÷ Target PAHs	Total PAHs ÷ Heavy PAHs
Asphalt	M	7.4	9.9
	H	6.7	5.9
ECR	M	7.3	13.6
	H	6.8	8.7
Coal Tar	M	6.3	6.7
	H	5.2	4.7
Scraping	M	8.1	8.0
	H	6.7	5.7

Plot 2 Ratios Exhibited

	H ÷ M Target PAHs	H ÷ M Heavy PAHs
Asphalt	4.8	7.4
ECR	3.1	4.4
Coal Tar	0.7	0.8
Scraping	2.1	2.8

Values calculated using Figure 4 results

Double plot ratios are calculated by dividing the PAH concentrations from one test to another. The scatter chart feature in Microsoft Excel is used to plot the data. Dots are colored showing how different types of samples fluoresce.

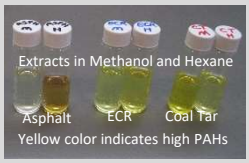
Accuracy vs. Laboratory PAH Results

Sitelab's "Target PAH" test using methanol performs best when comparing UVF results to laboratory Total PAH results. See Figure 6. The PAHS module is more selective to these compounds compared to the other modules. It does, however, detect elevated PAHs in asphalt sealcoats, ranging from 2,500 to 5,000 ppm, where the lab detects no PAHs. ECR and coal tar sealcoats are more accurate.

Sitelab's "Total PAH" test using the EDRO module always exhibits the highest concentrations and often requires more dilutions. The EDRO module detects all polyaromatics in the C10 to C36 carbon range. The test name can be misleading. The "Heavy PAH" test using the TPHOIL module detects the larger PAH molecules, including asphaltenes up to C50 carbon weight.

Some asphalt sealcoats tested in DOEE's Task 2 round contained low levels of coal tar. This was first discovered using the UVF screening analysis, where Target PAHs exceeded 5,000 ppm. New samples were received without the coal tar and Target PAH results improved.

FIGURE 6



Correlation to Lab PAH Results Testing Different Sealcoat Types

PPM (mg/Kg)	Solvent Used	Target PAHs	vs. Lab PAHs	Comment
Coal Tar	M	70,000	77,779	Good
ECR	M	26,000	25,585	Good
Asphalt	M	3,100	0, ND	High, But Normal

Lab results reported by Pace Contest and Alpha Analytical DOEE Task 1 dry sealcoat samples.

Target PAHs range from 2,500 to 5,000 ppm testing asphalt sealcoat products. This interference is normal.

Asphalt Products Contaminated with Coal Tar from Factory

PPM (mg/Kg)	Original Samples	New Samples (No Coal Tar)		Adjusted Target PAHs	Original Samples Lab PAHs	Comment
Brand 1	11,400	4,000	→	7,400	4,487	Okay, RPD 49%
Brand 2	8,400	3,700	→	4,700	3,538	Good, RPD 28%
Brand 3	5,900	3,300	→	2,600	2,387	Good, RPD 9%

3 manufacturers submitted samples of their asphalt sealcoats, but were collected in error from the same tank used for coal tars. New samples were provided and the laboratory reported no PAHs. Accuracy for the UVF results improve when subtracting out the background interference detected in the new samples without the coal tar.

As for the scraping from Charlotte, both the lab and Sitelab results were above the 1,000 ppm PAH limit. They were curious to know what type of sealcoat was applied. The property owner said their contractor used an asphalt sealcoat, but the brand used had been analyzed previously for the sealcoat certification program and the lab reported non detect.

Double Ratio Plots using Laboratory Data Performed in Sealcoat Certification Program

Normally, a larger group of alkylated PAHs using EPA Method "8270D-SIM" is performed for definitive PAH forensic analysis. However, simple diagnostic ratios exhibited from one compound to another is often the first step when lab data like this is only available. Exponent, Inc., has several good publications about this topic, where 8 compounds are used. Exponent is the same company hired to investigate Tom Brady's deflated footballs in 2016, but we won't hold that against them. Figure 7 compares different brands of sealcoats, most of which were performed by multiple laboratories. Ratios for the scraping are also shown and are closest to ECR in both plots.

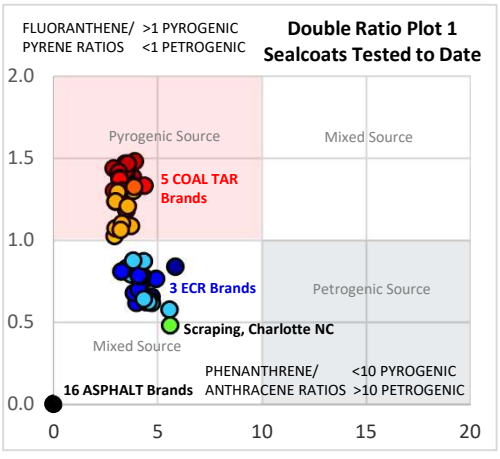
FIGURE 7

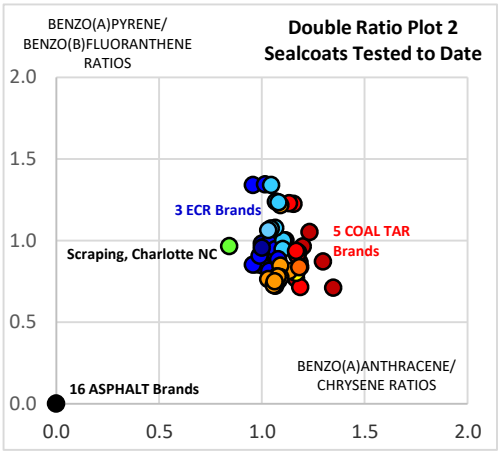
PAH Compounds Used For Ratios:

Example showing coal tar sealcoat concentrations in ppm (mg/Kg) with four ratios calculated

Naphthalene	2,600	
2-Methylnaphthalene	790	
Acenaphthylene	0	
Acenaphthene	2,300	
Fluorene	2,800	
Phenanthrene	14,000	PHEN ÷ ANTH = 3.5
Anthracene	4,000	
Fluoranthene	11,000	FLA ÷ PYR = 1.3
Pyrene	8,600	
Benzo(a)anthracene	3,400	BAA ÷ CHR = 1.2
Chrysene	2,900	
Benzo(b)fluoranthene	3,300	BAP ÷ BBF = 0.9
Benzo(k)fluoranthene	1,300	
Benzo(a)pyrene	3,000	
Indeno(1,2,3-cd)pyrene	2,400	
Dibenz(a,h)anthracene	430	
Benzo(g,h,i)perylene	1,800	

Asphalt sealcoats cannot be calculated. None of the 17 PAH compounds are detected.





Sealcoats are made with different sources of hydrocarbons. The two ratios used in Plot 1 have specific limits separating three source types. Coal tars are made from combustion and exhibit a pyrogenic source of PAHs. ECRs exhibit a mixed source; it starts as petrogenic and then undergoes a pyrogenic process when it's made. Asphalt sealcoats are petrogenic and do contain PAHs, but the lab does not detect any of these 17 compounds. As such, these samples cannot be plotted.

Double Ratio Plots using USGS Laboratory Data

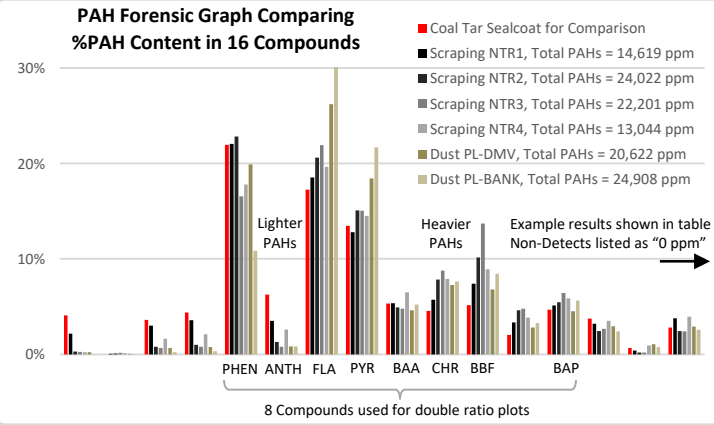
The ratios exhibited in the 8 compounds were then applied using lab data performed by USGS studies conducted from 2005 to 2017. The USGS lab did not report 2-Methylnaphthalene, but the 16 PAH compounds were reported. Samples consisted of parking lot scrapings and dust from sealed and unsealed lots, plus lake and stream sediments collected from different watersheds throughout the United States. A large number of samples were too clean, no or too few compounds were detected and could not be used here. The data is assumed to be valid. QC tests reported were within limits.

The USGS studies were performed before ECR sealcoats arrived in the market, so samples with high PAH concentrations, like these scrapings, would have derived from coal tar sealcoating. Coal tar ratios exhibited in Figure 7 are plotted in the USGS plots for comparison. ECR ratios are not plotted. Figures 8 thru 11 highlight some of their data.

USGS Milwaukee, Wisconsin Sites

Scrapings and dust samples having the highest PAH concentrations in this data set are graphed in Figure 8. This is what Sitelab typically reports when summarizing lab results for sealcoat clients. Use of double ratios digs further into the data.

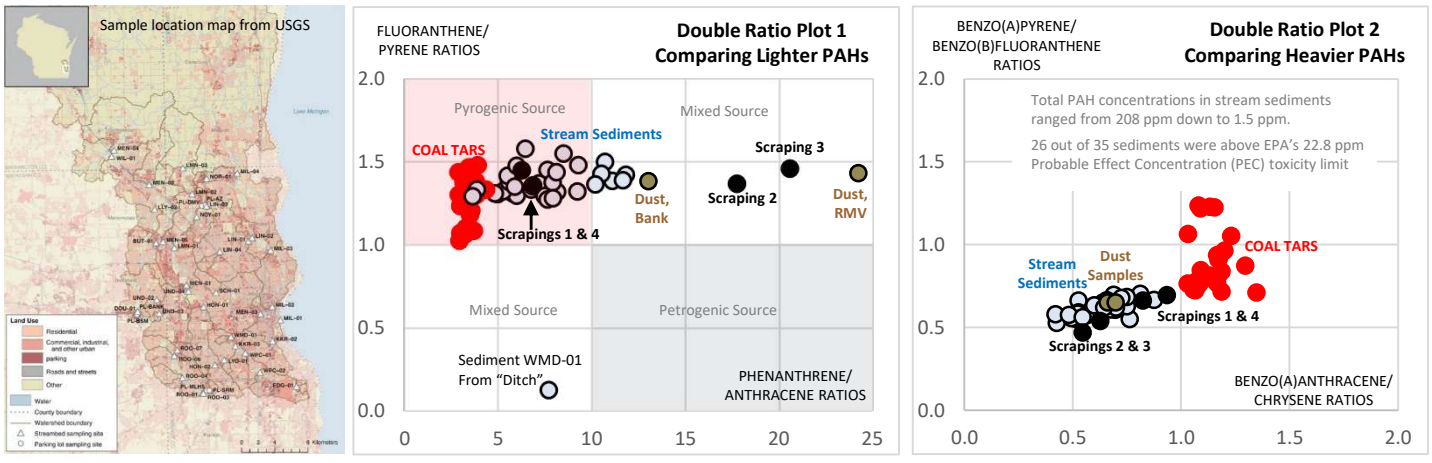
FIGURE 8



Most abundant PAHs highlighted for visual observation	Coal Tar Sealcoat for Comparison		Parking Lot Scraping NTR1		Parking Lot Scraping NTR2		Dust from Bank Parking Lot	
	PPM	%PAH	PPM	%PAH	PPM	%PAH	PPM	%PAH
Naphthalene	2,600	4%	319	2%	72	0.3%	5.2	0.0%
Acenaphthylene	0	0%	9	0.1%	24	0.1%	4.6	0.0%
Acenaphthene	2,300	4%	441	3%	189	1%	56	0.2%
Fluorene	2,800	4%	522	4%	239	1%	82	0.3%
Phenanthrene	14,000	22%	3,330	22%	5,480	23%	2,700	11%
Anthracene	4,000	6%	513	4%	309	1%	210	1%
Fluoranthene	11,000	17%	2,710	19%	4,950	21%	7,500	30%
Pyrene	8,600	13%	1,870	13%	3,620	15%	5,400	22%
Benzo(a)anthracene	3,400	5%	781	5%	1,180	5%	1,300	5%
Chrysene	2,900	4%	835	6%	1,880	8%	1,900	8%
Benzo(b)fluoranthene	3,300	5%	1,080	7%	2,440	10%	2,100	8%
Benzo(k)fluoranthene	1,300	2%	488	3%	1,110	5%	820	3%
Benzo(a)pyrene	3,000	5%	750	5%	1,310	5%	1,400	6%
Indeno(1,2,3-cd)pyrene	2,400	4%	467	3%	587	2%	600	2%
Dibenz(a,h)anthracene	430	1%	60	0.4%	44	0.2%	190	1%
Benzo(g,h,i)perylene	1,800	3%	554	4%	588	2%	640	3%
TOTAL 16 PAHS =	**63,830**		**14,619**		**24,022**		**24,908**	

Double ratio plots in Figure 9 compares scrapings and dust from the sealed parking lots in Figure 8, plus 35 stream sediments collected years later in another study, where USGS tested samples from different rivers and tributaries within Milwaukee's watershed. Two of the scrapings were very close to coal tar sealcoats. Two other scrapings and the dust samples exhibit both pyrogenic and petrogenic sources. This is likely coal tar plus motor oil, tire wear or other petroleum from the surface. Signatures in most of the sediments are close to coal tar and scrapings 1 and 4. These streams are likely contaminated by coal tar plus other combustion pollutants, like exhaust from atmospheric fallout and runoff.

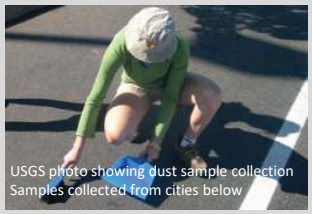
FIGURE 9



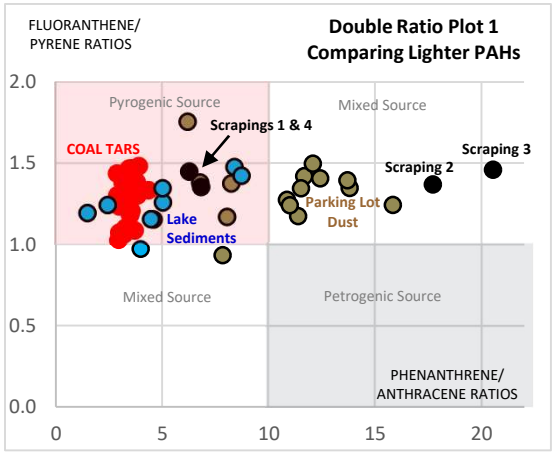
USGS Parking Lot Dust and Urban Lake Sediments in Different Cities

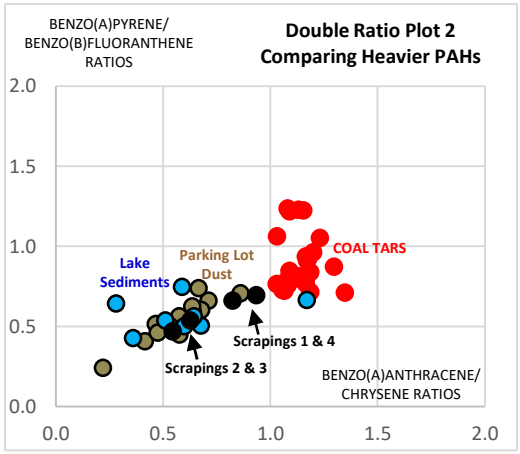
Lake sediments, dust samples having the highest PAH concentrations and several soil samples in this data set are plotted in Figure 10. Samples were collected from 7 different cities, within the watersheds of 8 different lakes. Scrapings from Milwaukee are also shown for comparison. USGS did not collect new scrapings from these sites. The highest dust sample came from Chicago, Total PAHs were 11,998 ppm, while most others were above 1,000 ppm. A number of samples collected from unsealed parking lots contained too few PAHs and were not plotted. The USGS lab was able to detect very low concentrations, with detection limits well below 1 ppm (see examples in Figure 11).

FIGURE 10



Sediment Sample Locations		16 PAHs (PPM)
Austin	Town Lake	11.8
Chicago	Lake in the Hills	19.3
Detroit	So. Commerce Lake	6.0
Washington DC	Lake Anne	20.1
Seattle	Lake Ballinger	21.9
Minneapolis	Palmer Lake	33.3
Minneapolis	Lake Harriot	41.3
New Haven	Lake Whitney	47.9
EPA's PEC Aquatic Toxicity Limit		22.8





The USGS "PAHs Underfoot" article in 2008 states "Synopsis: Extremely high PAH concentrations in pavement dust from six of nine cities indicate regional contamination from coal-tar sealcoat use and a link to lake-sediment contamination." The article features a double ratio plot used to help make their conclusion, but it includes Benzo(e)pyrene, which is not detected or reported in the sealcoat certification program. USGS did not apply the Phenanthrene/Anthracene ratio either.

Use of the two double ratio plots exhibited here helps support their case. These lakes are less contaminated than the Milwaukee sediments, but the plots are fairly similar. South Commerce Lake in suburban Detroit, which had the lowest PAH concentration at 6 ppm, was closest to coal tar in both plots compared to the other lakes. These lakes are likely impacted by other combustion sources too, so use caution when interpreting the dots. These and other USGS studies have been scrutinized by some in the sealcoat industry. Their arguments were helpful in this case evaluating the data performed here.

Comparing Contamination Levels to State Regulatory PAH Limits in Soils for Residential Use

USGS stream, lake and soil samples with the highest PAH concentrations are illustrated in Figure 11 and compared to soil clean up limits in different States. These limits vary considerably from State to State. Seven of the most toxic compounds are highlighted in gray. In this case, New York has stricter limits than it's neighbors. New York and Maine ban the use of coal tar and high-PAH pavement sealants.

Sediments shown here exceed the 22.8 ppm toxicity limit and residential soil limits. Samples with PAH concentrations below these limits would be considered safe for human exposure. Regulatory limits in water also exist and are much lower. Coal tar sealcoats, scrapings and most of the dust samples exceed these limits. These contaminants become highly diluted when mixed with sediment, soil and water.

FIGURE 11

17 PAH Compounds in ppm (mg/Kg)	Maine DEP	Mass DEP	NY DEC	Lincoln Creek Sediment, Milwaukee	Lake Whitney Sediment, New Haven	Soil near Sealed Lot, Chicago
Naphthalene	29	4	12	0.5	0.099	0
2-Methylnaphthalene	330	0.7	0.41	---	---	---
Acenaphthylene	4,900	1	100	0.216	0.513	0.292
Acenaphthene	4,900	4	98	1.2	0.13	0.58
Fluorene	3,300	1,000	100	1.5	0.255	0.66
Phenanthrene	2,500	10	100	28	3.51	21
Anthracene	25,000	1,000	100	2.4	0.696	1.35
Fluoranthene	3,300	1,000	100	50	8.75	44
Pyrene	2,500	1,000	100	36	6.95	35
Benzo(a)anthracene	16	7	1	13	3.43	11
Chrysene	1,600	70	1	20	5.06	16
Benzo(b)fluoranthene	16	7	1	19	7.98	23
Benzo(k)fluoranthene	160	70	1	8.2	2.98	8.7
Benzo(a)pyrene	1.6	2	1	12	4.03	14
Indeno(1,2,3-cd)pyrene	16	7	0.5	7	1.59	10
Dibenz(a,h)anthracene	1.6	0.7	0.33	2.2	1.68	0
Benzo(g,h,i)perylene	2,500	1,000	100	7.1	0.238	12
Compounds in red exceed limits in all 3 States			TOTAL PAHs =	208	47.9	196

Summary and Conclusions

Hydrocarbon fingerprinting is like a jig saw puzzle. You start with the edges and easy pieces first. As demonstrated here, analyzing the contents in pavement sealants has been improved graphing double ratio plots using conventional laboratory data when more advanced forensic tests are not performed. The signatures in pavement sealants vary depending on what they're made with and how old they are. Sitelab's UVF screening analysis can also be helpful by mimicking similar ratios testing samples for PAHs with methanol and hexane solvents, normally used by Sitelab for soil and water analysis.

Coal tar scrapings collected by USGS were very useful. Sitelab has limited data testing weathered coal tar samples like these. Total PAHs were lower compared to fresh coal tar concentrations, with little to no Naphthalene, the first to go since it's the most volatile and soluble compound. Over time, as the lighter PAHs diminish, the heavier PAHs become more abundant, a classic weathering pattern. It's why parking lots don't stink so bad the older they get. This was also the case with the scraping from Charlotte. It's PAH concentrations dropped too compared to fresh ECR concentrations.

Where do all the PAHs go? Into the air we breathe and wash away into the environment. Fortunately, as more bans go into effect around the country, the cleaner PAH-friendly products are becoming more popular. To meet this demand, many manufacturers who make coal tar and ECR products also make high performance asphalt-based products.

This pollutant is easily preventable. Watersheds everywhere can only benefit by eliminating these toxic chemicals. Please contact Steve Greason at sgreason@site-lab.com if you would like additional information about this project.

References Cited:

EXPONENT: "Identification and Allocation of Polycyclic Aromatic Hydrocarbons (PAHs)"
https://www.exponent.com/files/Uploads/Documents/EF%20Notes%20Vol%204.pdf

USGS: "Collection and Analysis of Samples for Polycyclic Aromatic Hydrocarbons in Dust and Other Solids Related to Sealed and Unsealed Pavement From 10 Cities Across the United States, 2005–07"
https://pubs.usgs.gov/ds/361/pdf/ds361.pdf

USGS: "Primary Sources and Toxicity of PAHs in Milwaukee-area Streambed Sediments"
https://setac.onlinelibrary.wiley.com/doi/full/10.1002/etc.3694

USGS: "PAHs Underfoot: Contaminated Dust from Coal-Tar Sealcoated Pavement is Widespread in the United States"
https://pubs.acs.org/doi/pdf/10.1021/es802119h

More Information:

See Sitelab's webpage detailing sealcoat certification program with list of qualified products and other downloads available. Chain of Custody forms and instructions are also available for submitting samples for analysis.

https://www.site-lab.com/pahs-coal-tar-sealcoats-certification.htm