Spatial Variability of PAHs in Stream Sediments in an Urban Karst Watershed

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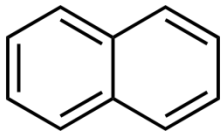
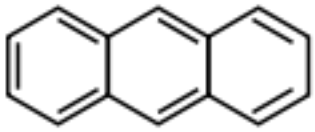
What are Polycyclic Aromatic Hydrocarbons (PAHs)?

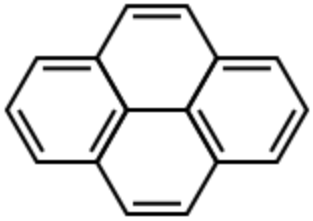
- Group of chemicals that occur naturally in crude oil, coal, and tar, and are produced by the burning of fossil fuels and biomass (wood, etc.)
- Widely distributed in the environment
- Several are toxic, carcinogenic, mutagenic, and/or teratogenic (causing birth defects) to aquatic life
- Seven are probable human carcinogens



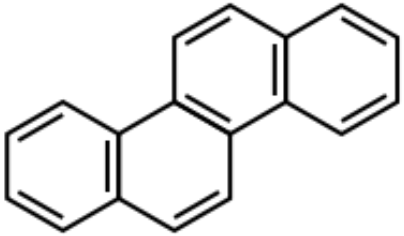
Naphthalene



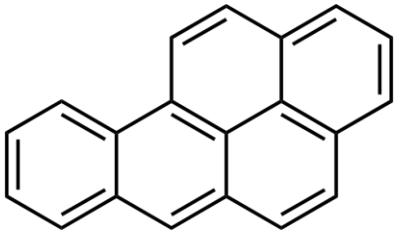
Anthracene



Pyrene



Chrysene



Benzo[*a*]pyrene

What is the problem?

- PAHs increasing in lake sediment cores from urban watersheds over the past 30-40 years.
  (Van Meter et al., 2000, 2005, & 2010)

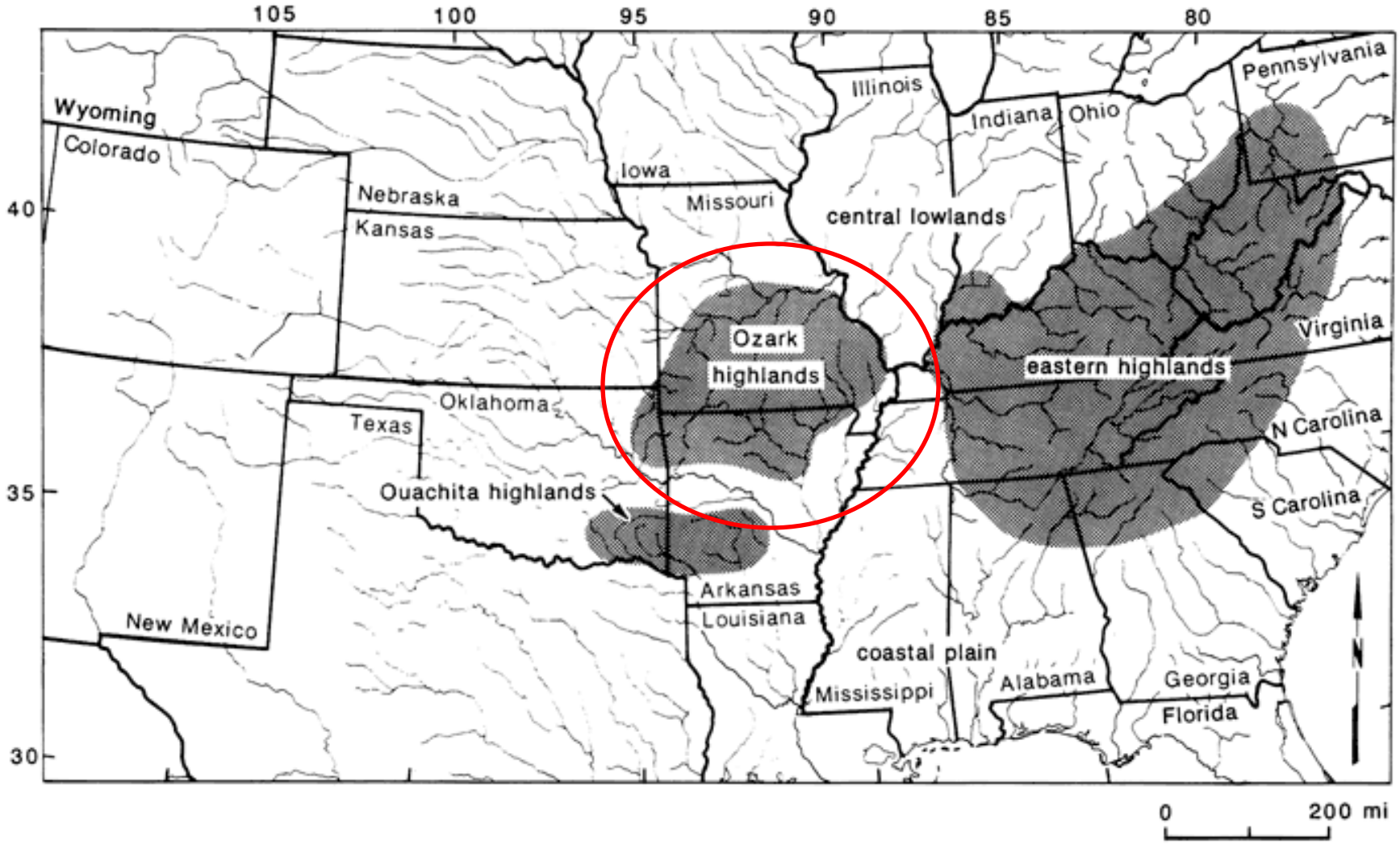
- Coal-tar based sealcoat on parking lots reported to be the primary source of PAHs to sediment contamination.
  (Mahler et al., 2005 & 2012)

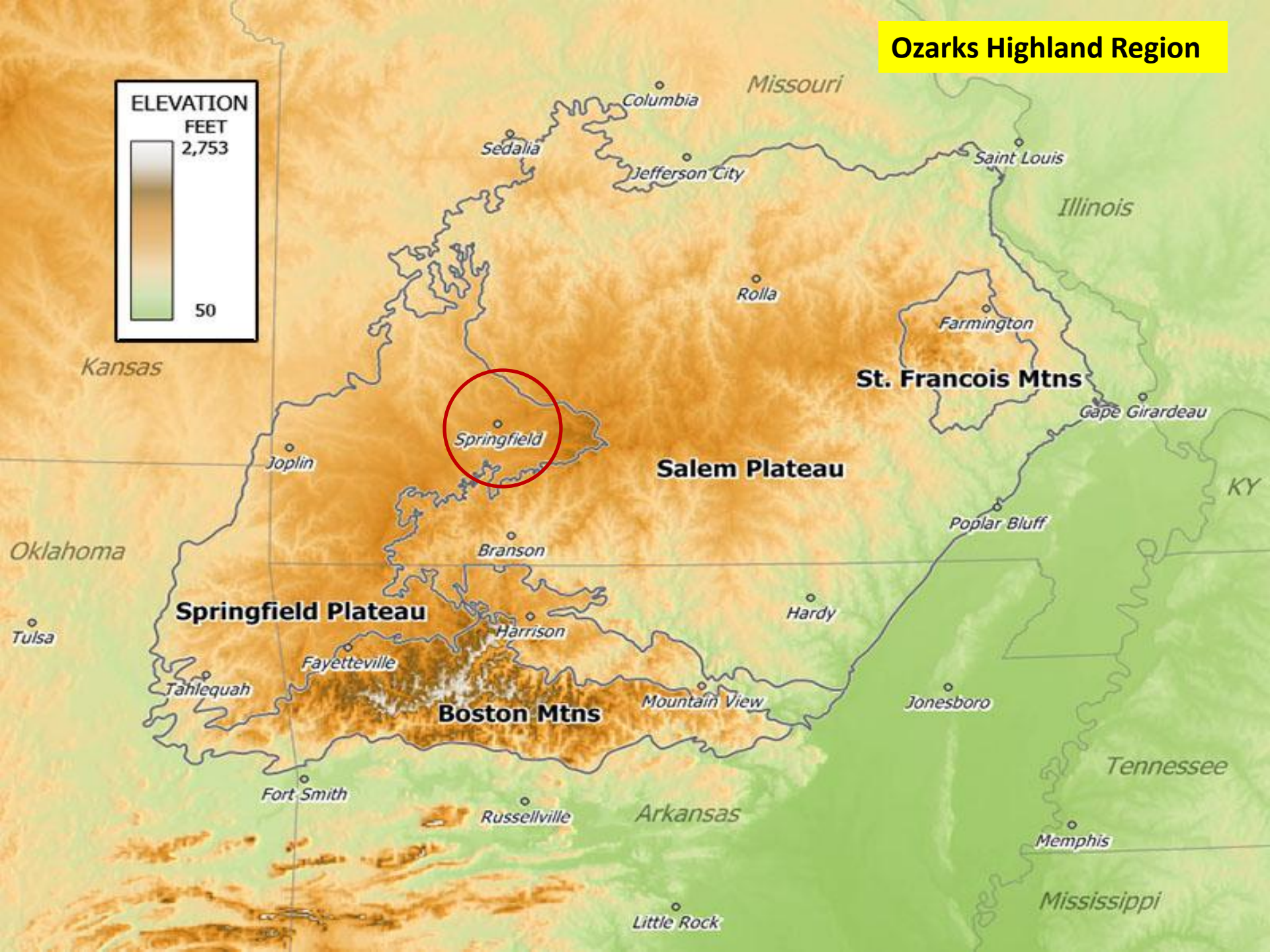
- PAH contamination of stream bed sediment has been shown to degrade macroinvertebrate communities.
  (Beasley and Kneale, 2004; Neff et al., 2005; Scoggins et al., 2007).

Questions to Address

- Are PAHs found in urban stream and pond sediments at concentrations high enough to raise environmental concerns in Springfield, Missouri?
- What degree is coal-tar sealcoat from parking lot applications the source of PAH contamination?
- Can spatial modeling be used to determine the effects of a Coal-tar sealant ban on sediment quality and toxicity to sediment-dwelling organisms?

Ozark Highlands




Ozarks Highland Region
ELEVATION
FEET
2,753
50
Missouri
Columbia
Sedalia
Jefferson City
Saint Louis
Illinois
Rolla
Farmington
St. Francois Mtns
Cape Girardeau
Kansas
Springfield
Joplin
Salem Plateau
KY
Poplar Bluff
Oklahoma
Branson
Springfield Plateau
Hardy
Tulsa
Harrison
Fayetteville
Tahlequah
Mountain View
Jonesboro
Boston Mtns
Tennessee
Fort Smith
Russellville
Arkansas
Memphis
Mississippi
Little Rock

PAHs in Urban Stream Water

Wilson, South, Pearson Creeks & Jones Branch

- Detections during Baseflow
  - Phenanthrene
  - Anthracene
  - Fluoranthene
  - Pyrene
  - Benzo[a]anthracene (WC/SC)
  - Chrysene (WC/SC)
  - Benzo[b]fluoranthene (WC/SC)

Richards, J.M., and B.T. Johnson, 2002. *Water quality, selected chemical characteristics, and toxicity of base flow and urban stormwater in the Pearson Creek and Wilson Creek Basins, Greene County, Missouri, August 1999 to August 2000*. U.S. Geological Survey Water-Resources Investigations Report 02-4124.

URS Corporation, 2010. *Sampling for consent decree waters in Missouri: Pearson Creek (& Wilson Creek), Springfield, MO*. Prepared for U.S. Environmental Protection Agency Region 7 under Task Order no. 2008-54 by URS Corporation, St. Louis, Missouri.

- Runoff Events… nonpoint source characteristics
  - Increase in detection frequency
  - Increase in concentration

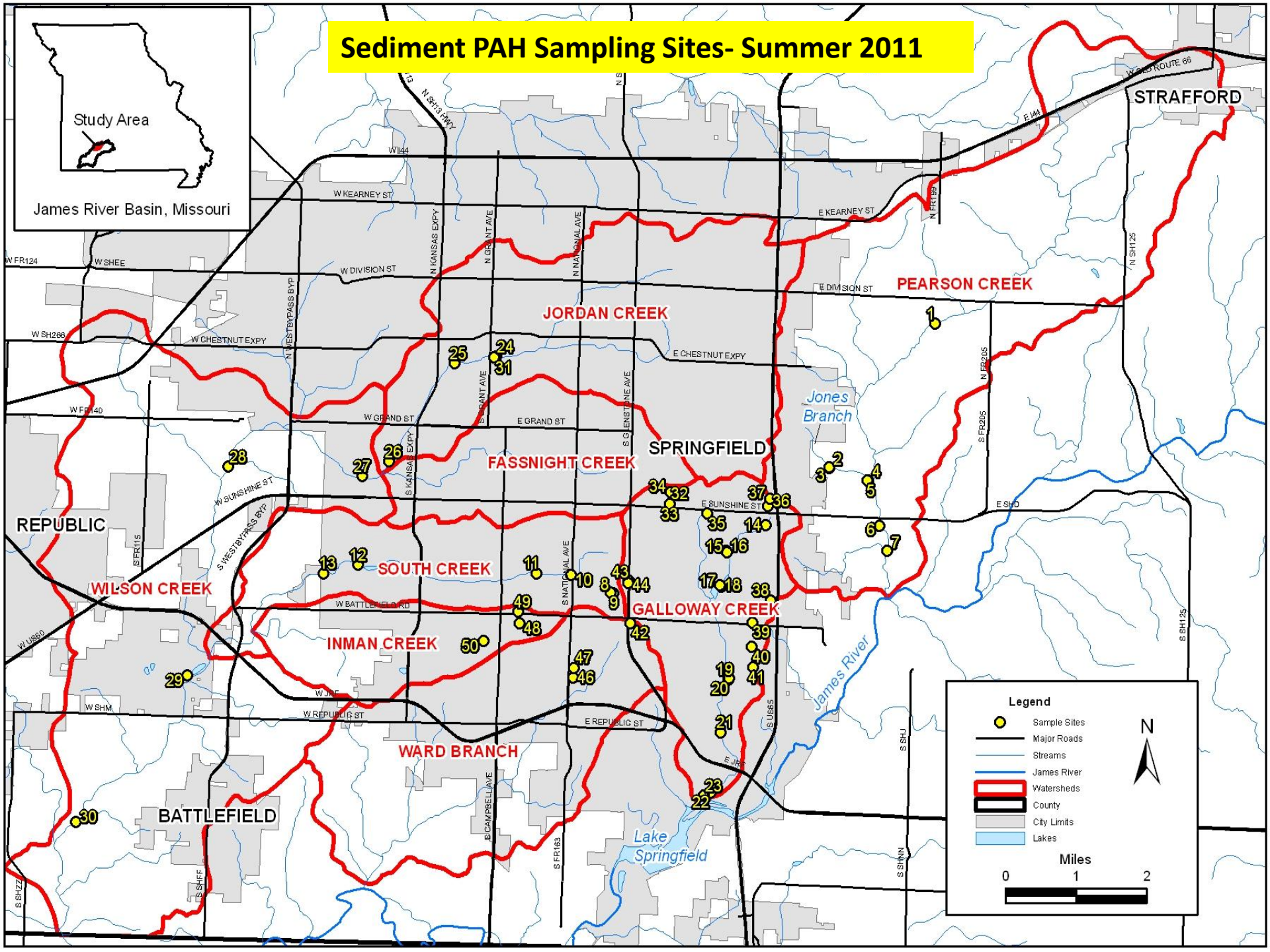
Urban Sediments

Sediment Sampling

- **Total of 58 sites sampled**
  - 50 in urban and suburban areas
  - 8 in Christian and Stone Counties (rural control)

- **Analyzed for 16 PAHs**

- **Sediment is important:**
  - **Highest concentrations of PAHs**
  - **Standard collection and analytical methods**
  - **Habitat for aquatic life**


Sediment PAH Sampling Sites- Summer 2011
Study Area
James River Basin, Missouri
STRAFFORD
PEARSON CREEK
JORDAN CREEK
SPRINGFIELD
FASSNIGHT CREEK
Jones Branch
REPUBLIC
SOUTH CREEK
WILSON CREEK
GALLOWAY CREEK
INMAN CREEK
WARD BRANCH
BATTLEFIELD
James River
Lake Springfield
W KEARNEY ST
E KEARNEY ST
W DIVISION ST
E DIVISION ST
W CHESTNUT EXPY
E CHESTNUT EXPY
W GRAND ST
E GRAND ST
W SUNSHINE ST
E SUNSHINE ST
W REPUBLIC ST
E REPUBLIC ST
N KANSAS EXPY
S KANSAS EXPY
S WESTBYPASS BYP
N NATIONAL AVE
S NATIONAL AVE
S GLENSTONE AVE
S CAMPBELL AVE
Legend
Sample Sites
Major Roads
Streams
James River
Watersheds
County
City Limits
Lakes
Miles
0
1
2
N

PAH Toxicity Guidelines

Blue= Priority Chemical & Brown= Probable Human Carcinogen

PAH Compound		CAS #	Rings	Sediment Toxcity Guidelines ug/kg	
				TEC	PEC
1) Naphthalene	Nap	91-20-3	2	176	561
2) Acenaphthylene	Any	208-96-8	3		
3) Acenaphthene	Ace	83-32-9	3		
4) Fluorene	Flu	86-73-7	3	77	536
5) Phenanthrene	Phe	85-01-8	3	204	1,170
6) Anthracene	Ant	120-12-7	3	57	845
7) Fluoranthene	Fth	206-44-0	4	423	2,230
8) Pyrene	Py	129-00-0	4	195	1,520
9) Benzo[a]anthracene	BaA	56-55-3	4	108	1,050
10) Chrysene	Chr	218-01-9	4	166	1,290
11) Benzo[b]fluoranthene	BbF	205-99-2	5		
12) Benzo[k]fluoranthene	BkF	207-08-9	5		
13) Benzo[a]pyrene	BaP	50-32-8	5	150	1,450
14) Indeno[1,2,3-cd]pyrene	InP	193-39-5	6		
15) Dibenz[a,h]anthracene	DahA	53-70-3	5	33	140
16) Benzo[g,h,i]perylene	BghiP	191-24-2	6		
Total PAHs, sum of above 16	**PAH_{16}**			**1,610**	**22,800**

Stream Biomonitoring

- Based on what organisms are present, you can get an idea of what the stream water quality is like.

- **How do macroinvertebrates indicate stream quality?**
  - They are affected by the conditions of the stream, including pollution.
  - They are fairly sedentary, and therefore cannot escape pollution events.
  - Specific species are more or less tolerant of pollution.
  - Presence or absence of certain species indicates good or poor water quality.

SEDIMENT TOXICITY CRITERIA

MacDonald D.D., C.G. Ingersoll, and T.A. Berger, 2000. *Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems*. Arch. Environ. Contam. Toxicol. 39:20-31.

- For sediment-dwelling organisms in freshwater ecosystems (e.g., macroinvertebrates).
- **Threshold effect concentration (TEC)** is the value below which harmful effects are unlikely to occur. Testing showed that 70-80% of the samples were correctly classified as "Non-toxic.“
- **Probable effects concentration (PEC)** is the value above which harmful effects are likely to occur. Testing showed that >90% of the samples were correctly classified as "toxic.“
- Reported for some PAHs and metals

Parking Lot Sampling

- Sealed lots
- Mixed sealed/unsealed lots
- Asphalt Lots-unsealed
- Concrete lots-unsealed

Sealed Lots = Coal-tar Lots

Reasons for this assumption:

- Survey by the City indicated that almost all applicators for large parking lots use coal-tar based sealants:
  - Assumption: **80 to >95% of sealed lots are coal-tar coated.**
- PAH concentrations in sediments from below and edges of sealed lots are high.
- The results of this study are in the range of coal-tar lot sediment results published in other studies.

PAHs in Coal-tar Sealants vs. Asphalt Sealants

- Coal-tar based sealcoat products contain about **1,000 times** more PAHs than sealcoat products with an asphalt base. (USGS Fact Sheet 2011-3010 reporting results from a 2005 study in Austin, TX)

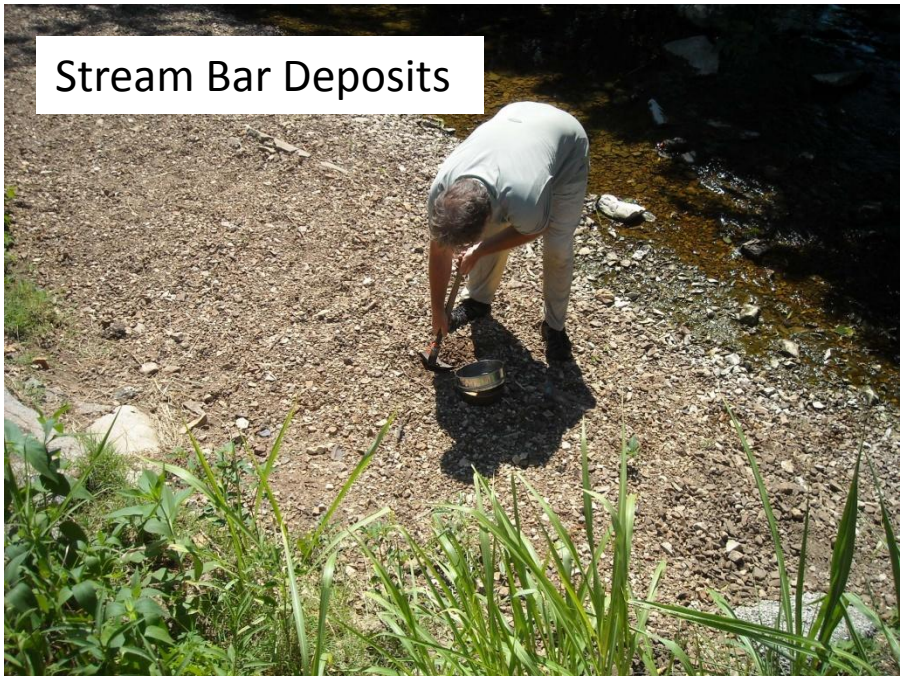
- Storm runoff from coal-tar sealed parking lots released **100 times** more PAH_{16} than asphalt sealed lots. (USEPA, 2011)

- Suspended particulates in runoff from coal-tar sealed parking lots in Austin, Texas contained on average **6 times** more PAH_{16} than asphalt sealed lots. (Mahler et al., 2005 & USGS Fact Sheet 2005-3147)


Basin Sediment


Parking Lot Sediment


Stream Bed Deposits

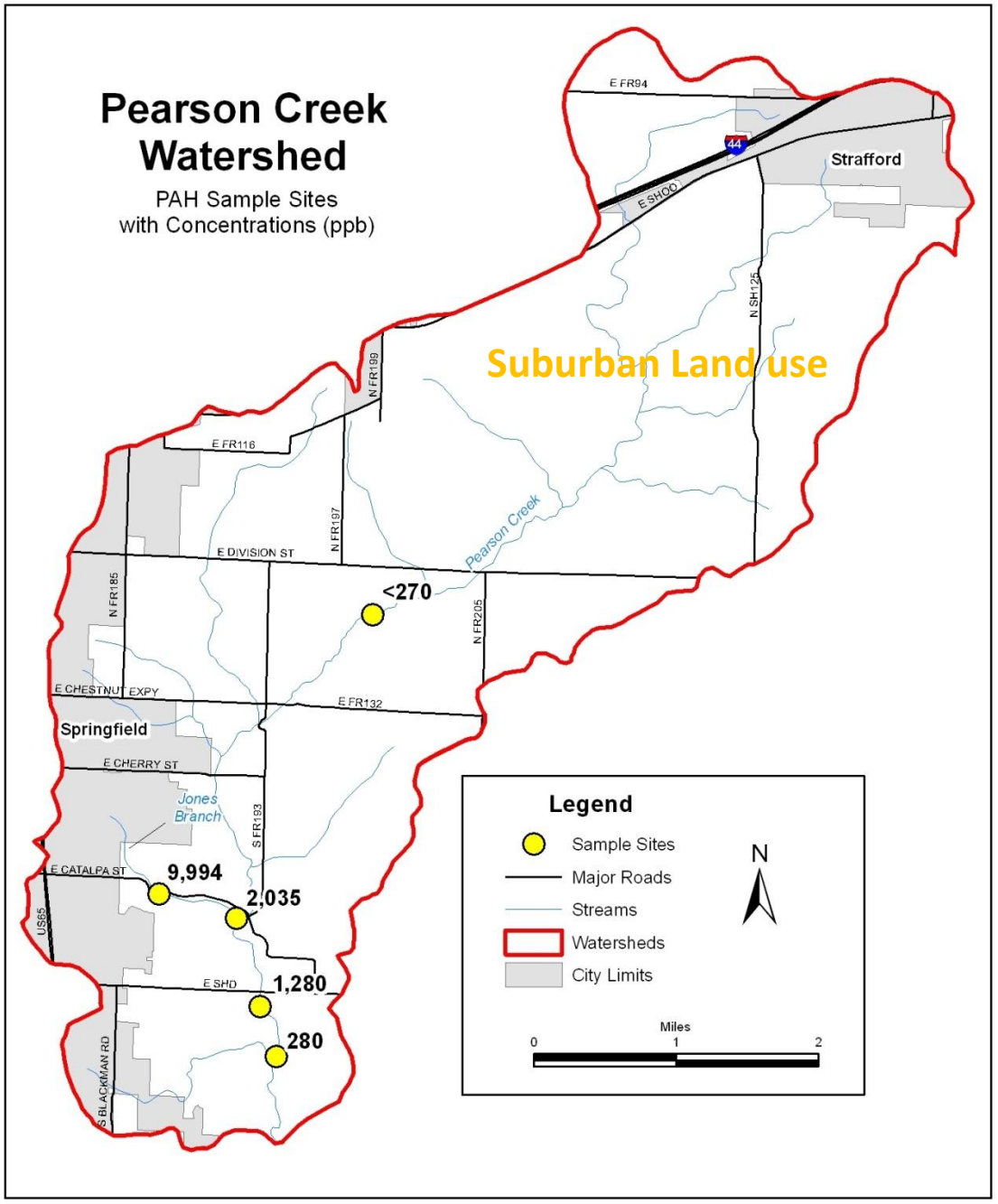

Stream Bar Deposits

Controls for PAH Supply Effects

- **Sealer type:** Compare Western US sediments with widespread asphalt-sealant use with Eastern US sediments with heavy coal-tar sealant use.
  - Lower PAHs in western streams and lakes. (Van Meter et al., 2000, 2005, & 2010)
- **Land Use:** Compare rural stream sediments to urban streams.
  - Very low PAHS found in Christian/Stone Counties streams and ponds compared to Springfield/Greene County)
- **Traffic and Roof Runoff**: Compare sealed lot sediments to unsealed lots.
  - Sealed lots have much higher PAHs)

Downstream decrease in PAH concentration away from source

1) Dilution
2) Sediment mixing
3) Deposition in ponds & stream beds
4) Storage in floodplains
5) Biologic uptake
6) Volatilization



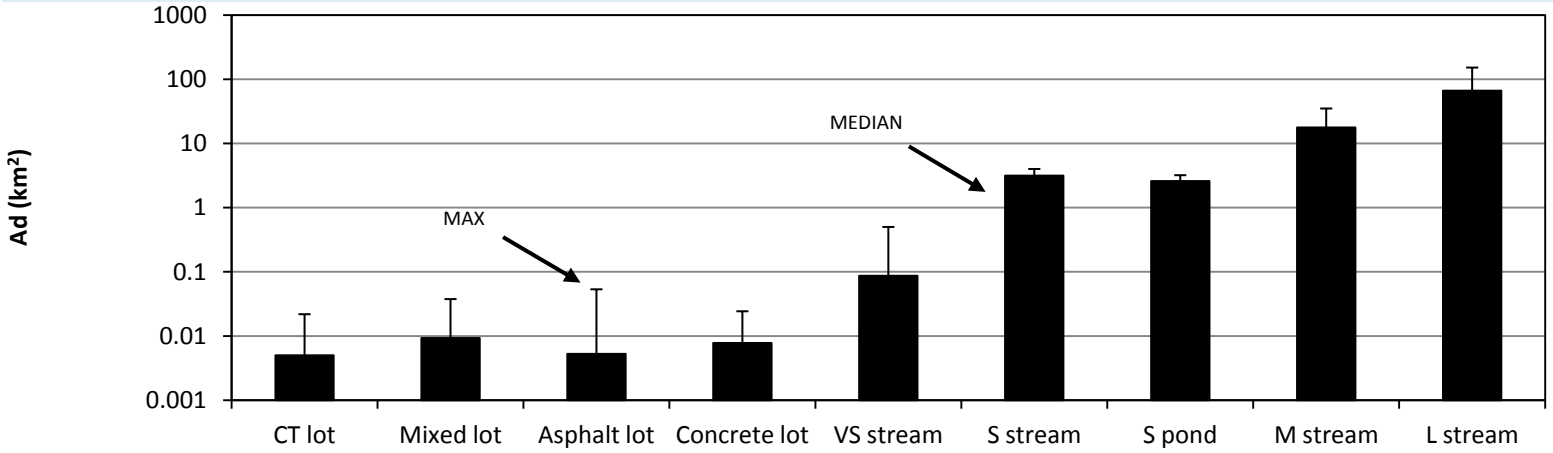
PAH_{16} Concentrations in Sediments

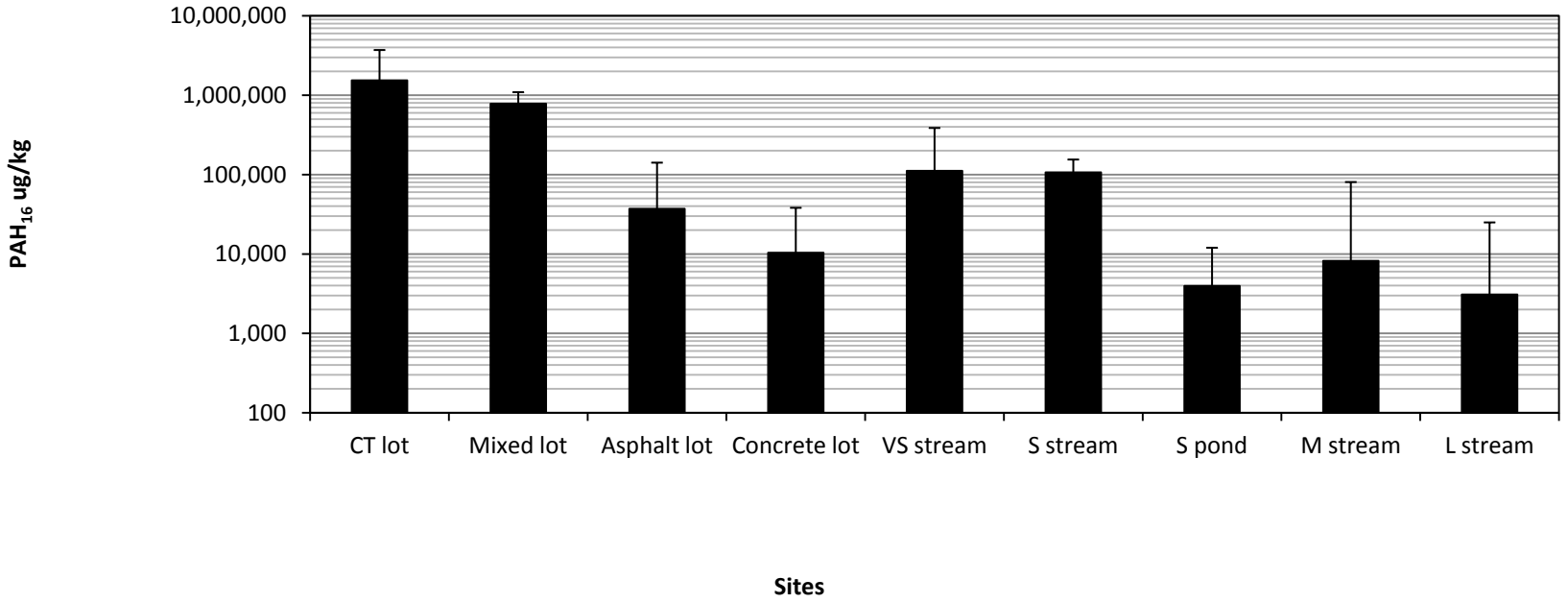
Sealed Lot Sediment PAHs: 148 times concrete lots & >5,500 times rural samples

Nontoxic= <1,610 ppb and **Toxic**= >22,800 ppb total PAHs

Sampling Location	No. of Samples	PAH_{16} geomean ug/kg	*Relative Concentration* Concrete Lot	Rural
Sealed lots	4	1,538,736	148	5,657
Mixed lots	4	782,840	76	2,878
Asphalt lots	6	37,182	4	137
Concrete lots	4	10,368	1	38
Very small streams	5	111,849		411
Small streams	2	107,021		393
Small ponds	8	3,965		15
Medium streams	8	8,189		30
Large streams	6	3,089		11
Rural streams & ponds	8	272		1

Generalized Sample Location Types





PAH Toxicity to Sediment-dwelling Organisms

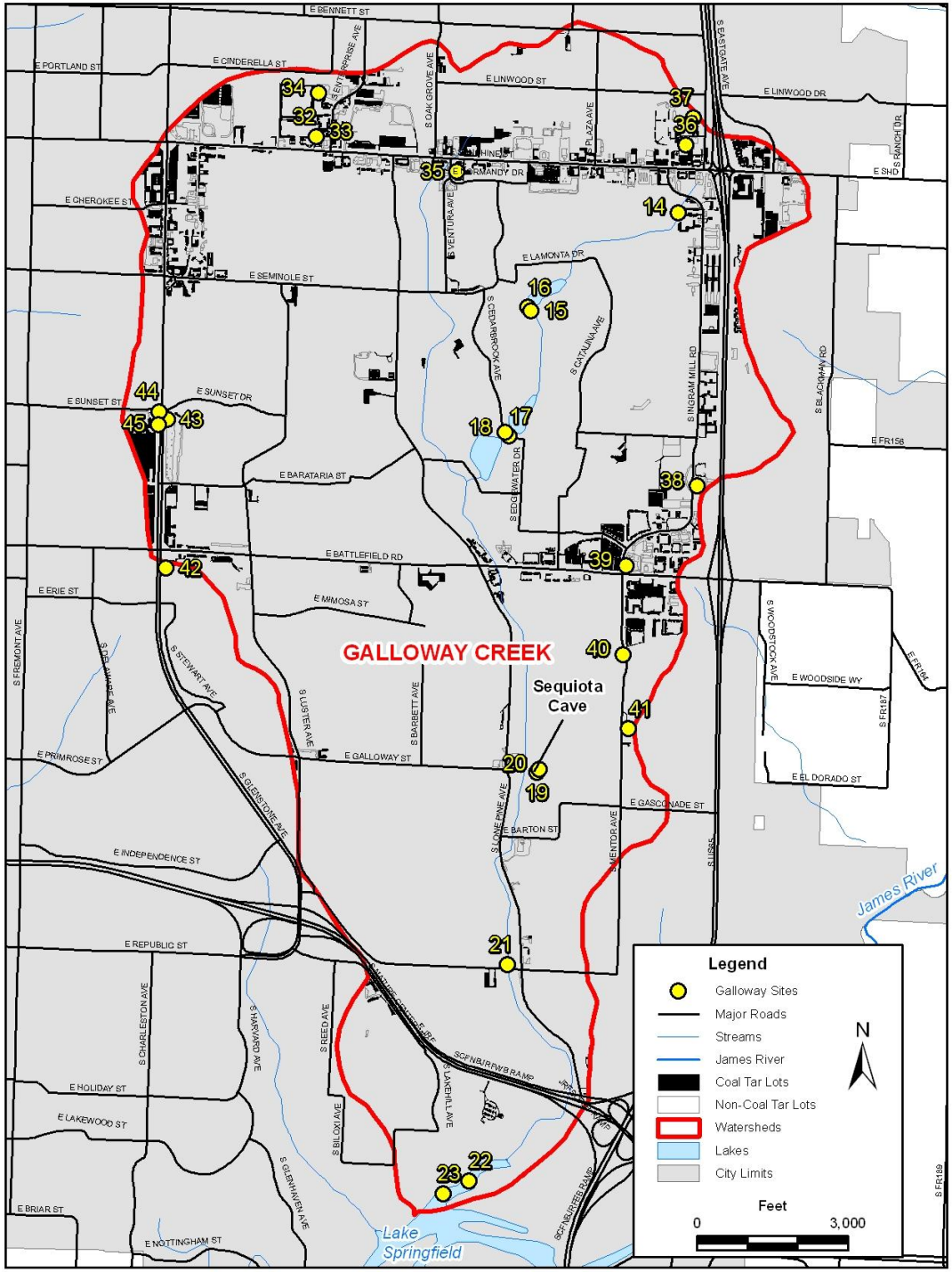
Sediment Quality Guidelines by MacDonald et al. (2000)

24 Stream and Ponds Sediment Samples		
Non-toxic	**Borderline**	**Toxic**
3 samples	**10 samples**	**11 samples**
12%	**42%**	**46%**

Galloway Creek

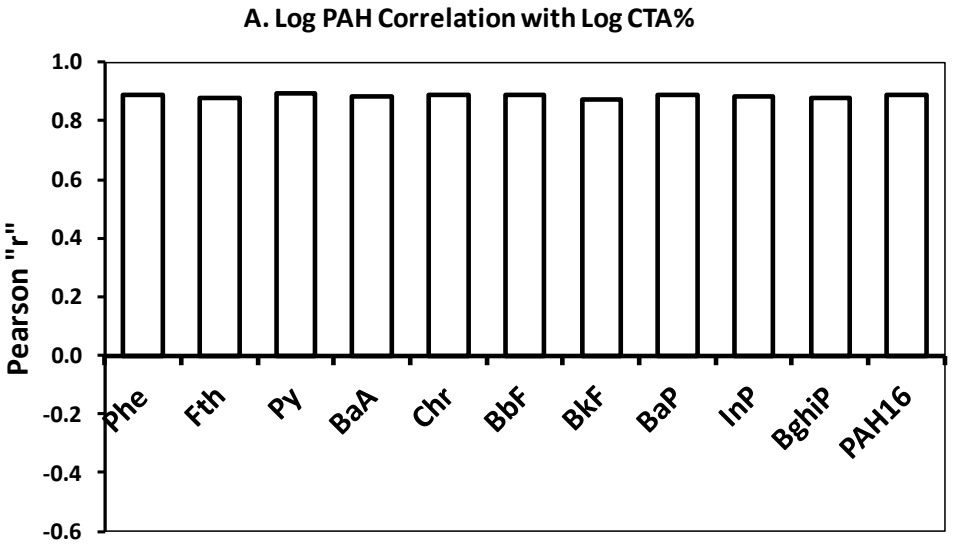
DA= 18.2 km^2

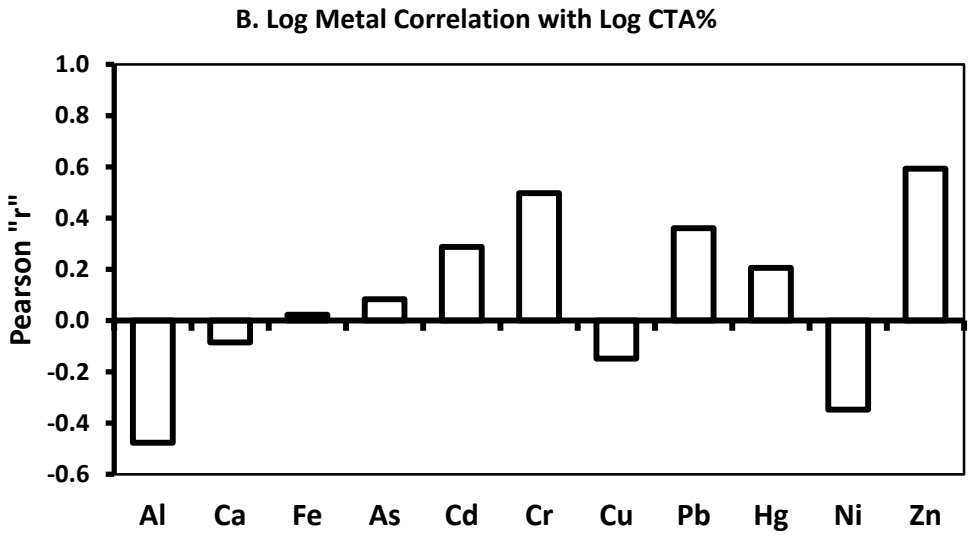
- **Total lot area**
  - 382 lots (245 sealed)
  - 1.2 km^2
  - 6.7% of drainage area
- **Lot type and % DA**
  - Sealed= 4.8%
  - Asphalt= 1.4%
  - Concrete= 0.4%
  - Mixed gravel/asphalt= 0.1%



PAH contaminants are strongly linked to Sealed Lots while metal contaminants are not

- Correlation statistics are strong for Sed PAHs (>0.8 out of 1)
- Poorly correlated with metals (-0.4 to +0.4)
- Sealed lots are a specific source of PAHs.
- Metal sources are related to broader urban area contributions.





Source to Sediment Relationships[a]

Sediment Property	Source Variables				
	Ad	*U%*	*IA%*	*TLA%*	*SLA%*
	Drainage Area	Urban %	Impervious Area	Total Lot Area %	Sealed Lot Area %
D50	-0.28	0.35	0.28	0.30	-0.14
TOC	-0.22	0.21	0.22	0.24	0.47
N	-0.14	-0.06	-0.20	-0.20	0.15
P	-0.14	-0.02	0.00	0.00	0.10
Cu	-0.10	-0.20	-0.27	-0.31	-0.15
Pb	-0.16	0.22	0.41	0.40	0.38
Hg	-0.02	0.02	0.08	0.09	0.46
Zn	-0.31	0.40	0.62	0.62	0.31
Phe	-0.28	0.38	0.42	0.44	0.71
Fth	-0.27	0.37	0.38	0.40	0.66
Chr	-0.27	0.37	0.36	0.39	0.65
BbF	-0.26	0.36	0.29	0.33	0.57
InP	-0.32	0.44	0.32	0.37	0.66
PAH16	-0.28	0.38	0.36	0.39	0.65

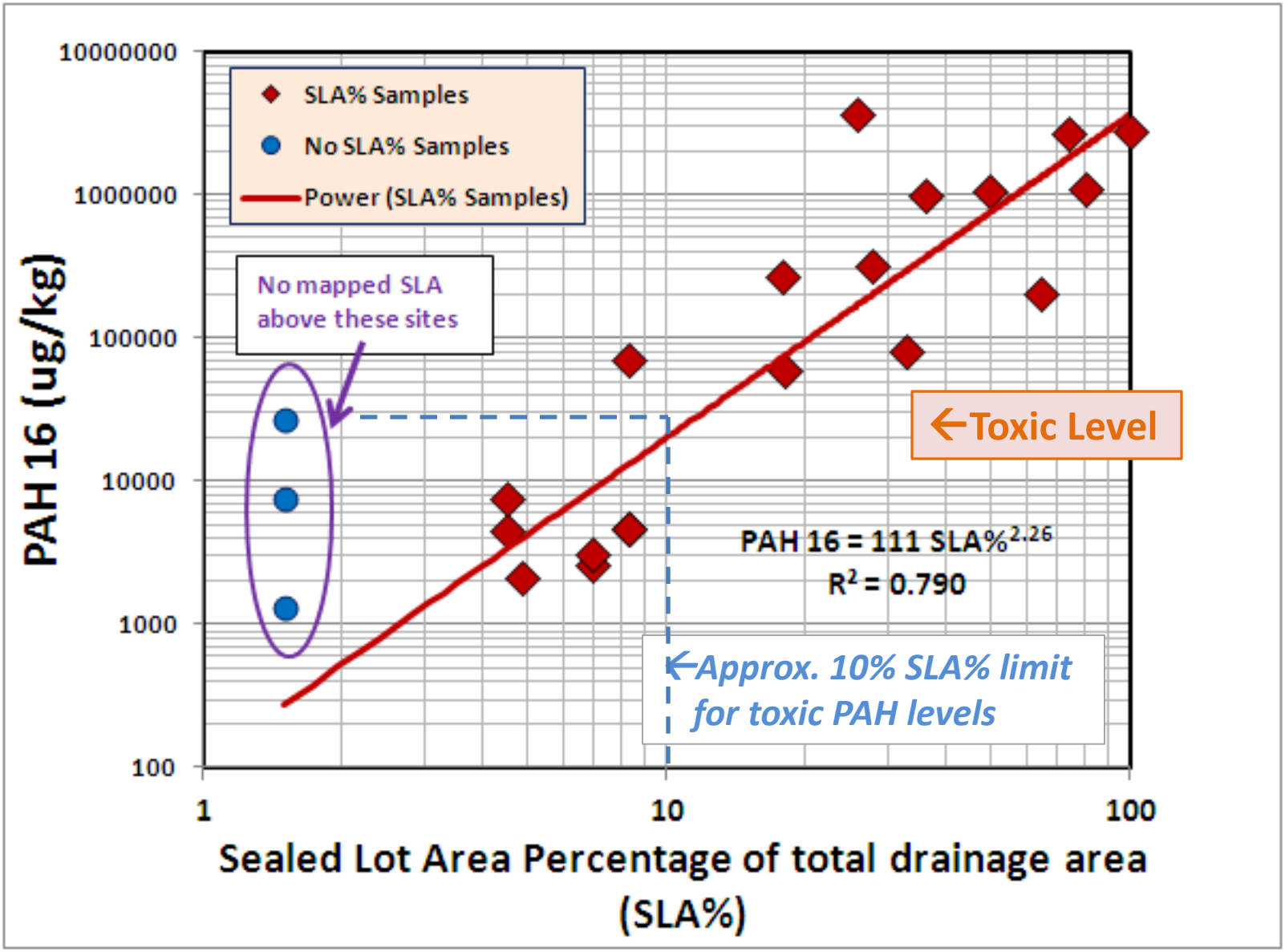
Weaker correlation of PAHs with Total Lot Area %.

Suggests distinct source of PAHs from Sealed Lots

[a] n=22; Pearson correlation analysis of arithmetic values

[b] underlined values are significant at p =0.05

More Sealed Parking Lot Area = Higher Sediment PAH Concentrations

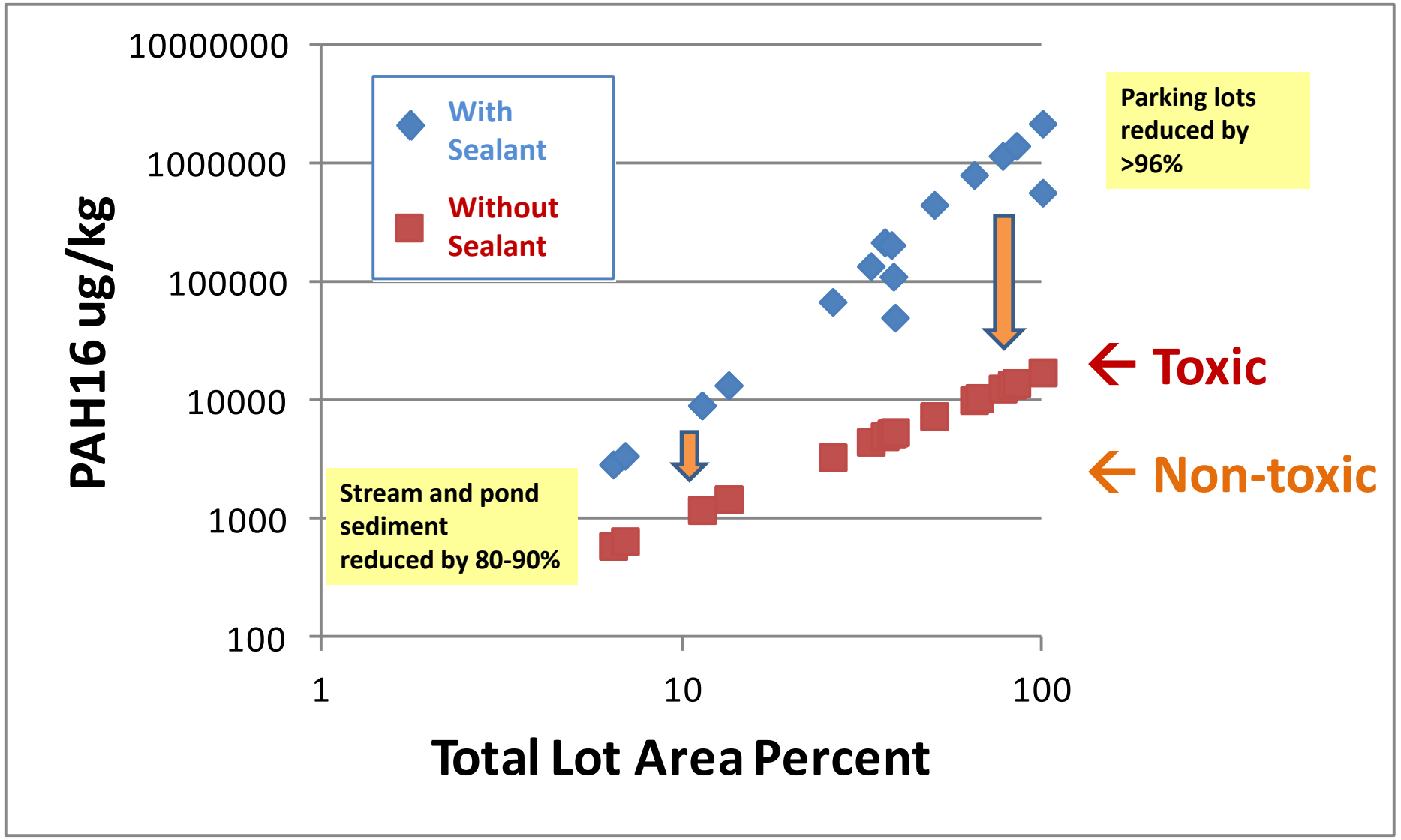


Regression Model to Quantify PAH Trends

Log PAH16 ug/kg = bo + (b1 Log SLA%) + (b2 Log TLA%) + (b3 Log OC%) + (b4 Log D50)

- **SLA%=** Sealed lot area in the drainage area above the sample point (km^2) / drainage area above the sample point (km^2) x 100
- **TLA%**= Total lot area in the drainage area above the sample point (km^2) / drainage area above the sample point (km^2) x 100
- **OC%**= Organic carbon content of the <2 mm fraction of the sediment (%)
- **$D50_{<2mm}$** = median particle size of the <2 mm fraction in microns
- **This equation explains 85% of the variability in sediment PAH16 concentrations**

Scenario Testing: PAH levels without sealant



Effect of coal tar sealant in Galloway watershed

Non-toxic	Borderline	Toxic

With Sealant

Parking Lots		**3** samples	**9** samples
Streams & Ponds		**7** samples	**3** samples

Without Sealant

Parking Lots		**12** samples	
Streams & Ponds	**7** samples	**3** samples	

Note: Use of asphalt-based sealants is expected to produce similar results to the "Without Sealant" scenario, but increase in PAH concentrations by < or = 15%.

Conclusions

1) Sealed parking lots contain PAH concentrations that are 148 times higher than concrete parking lots and 41 times higher than unsealed asphalt parking lots.

2) For stream and pond samples, **12% are non-toxic, 42% are borderline**, and **46% are toxic** to sediment dwelling organisms.

3) Sites with more sealed parking lot areas draining to them also had higher sediment PAH levels. This strong relationship indicates that parking lot sealant is a significant source of PAHs in Springfield watersheds.

4) If sealants were not used on parking lots in Springfield, PAH concentrations in urban streams and ponds would be below toxic levels.

QUESTIONS?

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- **http://oewri.missouristate.edu/**

- R.T. Pavlowsky (2013) Coal-tar pavement sealant use and polycyclic aromatic hydrocarbon contamination in urban stream sediments, *Physical Geography*, 34:4-5, 392-415

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