Polycyclic Aromatic Hydrocarbon Concentrations of Selected Southern Arkansas Streams

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of
Pollution Control and Ecology
Technical Services Division

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A survey of polycyclic aromatic hydrocarbon (PAH), also known as polynuclear aromatic hydrocarbons (PNAs), concentrations was conducted in selected southern Arkansas streams. PAHs are composed of hydrogen and carbon arranged as one or more benzene rings which may or may not have attached groups. Some PAHs are known carcinogens and have been linked to increased tumor and lesions rates and other health problems. PAHs can be transformed to intermediates which are highly toxic, mutagenic or carcinogenic to the host (Eisler 1987).

The basis of this survey was in response to a survey of the Felsenthal National Wildlife Refuge tributaries conducted by biologists from the U.S. Fish and Wildlife Service. The Arkansas Department of Pollution Control and Ecology's survey included two sites which they identified as having elevated concentrations as well as 40 additional sites. All samples were collected between April 12, and June 16, 1993 by personnel within Technical Services division.

Sample Sites

Thirty-eight sites were selected on the basis of potential influences from nearby oil fields and accessibility. Most of the sites were located at bridges on highways and county roads with some located in more remote areas. Four reference sites (39, 40, 41, 42) were established outside the areas of oil field influence to provide some indication of "naturally" occurring levels. Sample locations are described in Table 2 and plotted on county maps in Appendix A.

Methods

Samples were collected with a petite ponar dredge (6 in x 6 in x 6 in) or with an Ekman dredge (6 in x 6 in x 6 in) attached to an aluminum handle. The Ekman was used in areas where factors such as debris or bridge pilings did not allow access to the sediment from the bridge. A boat was used in areas where neither bridge sampling or wading were possible. Three to five grabs were collected along a visually established transect and composited into a stainless steel mixing pan. The composite was homogenized by stirring and forced through a 2 mm sieve (to remove debris) into another mixing pan. An aliquot of the sieved material was then taken and placed into a precleaned 500 ml glass jar with a teflon lined lid. The number of grabs was dependant on the width of the streams and the availability of sediment at the site.

Upon completion of a sample, all equipment (dredge, pans, scoops, and sieve) was cleaned and decontaminated in the field with the following procedure: 1) all visible debris was removed 2) cleaned and brushed with soapy water 3) rinsed 4) visually inspected for any remaining evidence of the sample , and finally 5) rinsed with liberal amounts of acetone. In addition to the field cleaning, all equipment would be periodically cleaned with a high pressure car wash. The high pressure wash was done at the conclusion of the day and during the day when accessible. Once again acetone would be used as a final rinse.

All samples were labeled with appropriate information in the field and any pertinent observations or deviations from the sampling plan noted in field notebooks. Sample preservation was accomplished by storage in ice chests at approximately four degrees Celsius until receipt by the laboratory where they were placed in a refrigerator.

Laboratory analyses were performed by ADPC&E personnel using method SW-846-3540A extractions with gel permeation cleanups (GPC 3640) (EPA 1986a) followed by GC/MS analysis SW-846-8270A modified with Selected Ion Monitoring (SIM) (EPA 1986b).

QA/QC measures were implemented using surrogate standards, D8 naphthalene, D10 phenanthrene, and D12 perylene. All surrogates were normally distributed with average percent recoveries of 49.69%, 87.29%, and 95.74%, and standard deviations of 15.73, 26.93, and 19.61, respectively. All recoveries fell within the 99.7% confidence limits except site 14 which had a high percent recovery of D10 Phenanthrene. All values for this site were still below the detection limit.

Results

Several sites were found to have quantifiable levels of the target compounds, and four sites were identified with total PAH concentrations above 1.0 ppm. Results of total PAHs and total carcinogenic PAHs for all sites are listed in Table 1.

Bodcau Creek NW of Stamps (site 5) had the highest levels of both total PAHs and carcinogenic PAHs with 20.326 ppm total PAHs and 10.04 ppm carcinogenic PAHs. This was the first sample site below (approximately 2 miles) a petroleum holding tank spill which had occurred within the previous few weeks. Evidence of the spill was still on site during the sampling period. Levels downstream at site 6 were slightly elevated but below the 1.0 ppm levels and were even lower near the mouth at site 7.

Cornie Bayou (site 33) had a total PAHs concentration of 1.521 ppm. Concentrations further downstream at site 34 were not indicative of polluted sediments with total PAHs of 0.048 ppm.

Black Creek (site 37) and Caney Creek (site 38) also had higher levels. Black Creek is a tributary to Caney and each was sampled just above the confluence. PAH concentrations at Black Creek was considerably higher with 12.677 ppm total PAHs and total carcinogenic PAHs of 3.77 ppm. Caney had 2.585 ppm total PAHs with 0.763 ppm being carcinogenic PAHs. No additional samples were taken on either stream.

The USFWS identified the upper site on Lapoile Creek (site 27) and Lapile Creek near Felsenthal NWR (site 30) as potential cleanup sites in a report prepared by Inmon in 1989. Inmon reported total PAH concentrations of 14.22 ppm and 7.281 ppm total carcinogenic PAHs at site 27 and 4.01 total PAHs at site 30 with 1.17 ppm being carcinogenic. Results in ADPC&E's survey were much lower with total PAHs of 0.117 ppm at site 27 and 0.109 ppm at site 30 (Table 1.).

All reference sites were below the detection limits or at levels which can be contributed to natural processes.

Discussion

PAHs found in the environment are the result of both natural occurrences and anthropogenic factors. Atmospheric deposition results from volcanic activities and forest fires. Man made sources contribute much more than natural sources ; the largest single source being the burning of wood in homes (US Department of Health & Human Services). Other sources include automobile emissions, industrial discharges, coke production in the iron and steel industry; the manufacture of carbon black, coal tar pitch and asphalt; heating and power generation, and open burning (Eisler 1987). Diet is the major source of PAHs found in humans. Cooking methods used in meat preparations can increase PAH concentrations and accumulation in fresh vegetables has been documented. Total PAH background levels for soils have been reported at 210 ppb in remote areas of Wyoming and 150 ppb in arctic soils.

PAHs can bioaccumulate in plants, aquatic organisms, and animals from intake of contaminated water, soil, and food. Extensive metabolism of the compounds by higher trophic level consumers, including humans, has been demonstrated. Therefore, food chain biomagnification does not appear to be significant (US Dept. of Health & Human Services).

PAHs can enter the aquatic environment via atmospheric deposition, domestic and industrial sewage effluent and especially from spillage of petroleum and petroleum products into water bodies (Eisler 1987). PAHs are removed from the water column by volatilization to the atmosphere, binding to sediments (especially those with a high organic component), and accumulation in biota. Biomagnification in higher organisms is not prevalent due to their ability to metabolize these compounds. Some of the PAHs with low molecular weights such as: acenaphthene, acenaphthylene, anthracene, fluorene, and phenanthrene, can undergo significant volatilization. Higher molecular weight compounds have lower solubility rates, do not readily volatilize, and are normally found sorbed to the sediments (Eisler 1987). The fate of PAHs sorbed in sediment is believed to be biodegradation and biotransformation by benthic organisms (EPA 1980). PAHs in sediments may persist indefinitely in oxygen poor basins and/or anoxic sediments (Neff 1979).

Individual PAHs vary substantially in toxicity to aquatic organisms. Toxicity will increase with increasing molecular weight. In most cases, PAH concentrations that are considered acutely toxic are several orders of magnitude higher than concentrations found in heavily polluted waters (Eisler 1987). PAHs bound to sediments (normally those with heavier molecular weights) are relatively unavailable to aquatic biota due to the low solubility and immobile nature.

In fish, PAHs absorbed and assimilated from food sources are rapidly metabolized and excreted (Neff 1979). Several studies have shown that aquatic biota (especially bottom dwelling fish) from polluted sediment areas have greater incidence of tumors and hyperplastic diseases than those from nonpolluted environments (Eisler 1987). Bauman et al noted increased incidence of liver neoplasms in brown bullheads from Cuyahoga River exposed to carcinogenic PAHs concentrations (in sediments) of 10.80 ppm. In the same study no neoplasms were observed from sites with concentrations as high as 3.60 ppm.
Other studies have noted the occurrence of increased liver tumor rates in the bullheads collected from systems with elevated levels of sediment bound PAHs.

Total carcinogenic levels (10.04 ppm) at Bodcau Creek (site 5) were near concentrations which have resulted in increased tumors and lesions in bullhead catfish. We cannot speculate on the occurrence of such negative effects in the fish population in Bodcau Creek without the collection and examination of specimens. This particular collection site was approximately 2 miles downstream of the holding tank spill noted earlier. One can only speculate on the possibility that even higher levels would have occurred in the immediate area of the spill due to the fact no sample was obtainable in the area because of depth and a debris laden channel. Minimum measures had been taken in the area to cover the spill with soil and it appeared that much of the spilled product was applied on the service road leading to the area.

Black Creek (site 37) also had considerably higher concentrations than other sites. The watershed above this site was not examined therefore we have no physical evidence to formulate an explanation of these levels. Data from other streams in the survey indicate values decrease downstream from the source. This suggests that upstream values may be even higher as there are oilfields located within the watershed approximately 4 miles above the sample site. The same scenario is possible at the Caney Creek site as it too was sampled approximately 2 miles below potential sources.

Cornie Bayou at site 33 had total PAH concentrations of 1.521 ppm with all carcinogenic PAHs below the detection limits. These lower molecular weight compounds should be short lived within the sediment component and should be readily removed from the water column.

The concentrations found at sites 27 and 30, which were previously identified as problem sites by USFWS, were well below levels which would cause concern for aquatic biota. These lower concentrations suggest that the influx of PAHs into the aquatic systems is perhaps episodic and could be the result of accidental spills or mishandling of petroleum products within the watersheds. Nonetheless, the levels which were reported by the USFWS are not acceptable within these systems and should not be dismissed until further analysis confirm these as anomalies.

Concentrations at the references sites give a good indication of levels expected in streams of this area. Champagnolle Creek (site 42) had the highest concentration at .0097 ppm total PAHs, and two sites (40 and 41) were below the detection limits. These results indicate that while low levels of PAHs are present in many systems, elevated levels found in this survey can be attributed to oilfield influences.

Conclusion

Historical management practices of oilfield runoff led to severe influxes of PAHs into the aquatic systems of this region. Current practices and regulations, although not always eliminating these influxes, are much more effective from the environmental standpoint. While it is not believed that PAHs are purposely discharged into these systems, some method of accountability for reporting and mitigation of spills should be set forth. Spills occurring throughout the watersheds of these streams should be documented to provide information pertaining to the frequency and amount of products potentially entering the stream. Three sites (5, 37, 38) within this survey should have additional data collected to determine the extent of contamination and the persistence of PAHs within these systems. Of particular concern is the Bodcau Creek site which had concentrations near levels which have been shown harmful to aquatic biota.

Table 1. Total PAHs and Total Carcinogenic PAH values in ppm. Shading indicates carcinogenic, * indicates concentrations less than the detection limit.

PARAMETER	SITE																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
NAPHTHALENE	<.005	<.006	<.004	<.005	<.009	<.011	<.005	<.006	<.005	0.0070	<.005	<.004	<.004	<.004	<.005	<.004	<.005	<.005	<.008	<.005	0.0085
ACENAPHTHYLENE	<.005	<.006	<.004	<.005	.110	<.011	<.005	<.006	<.005	<.005	<.005	<.004	<.004	<.004	<.005	<.004	<.005	<.005	<.008	<.005	<.006
ACENAPHTHENE	<.005	<.006	<.004	<.005	.041	<.011	<.005	<.006	<.005	0.019	0.005	<.004	<.004	<.004	<.005	<.004	<.005	<.005	<.008	<.005	0.0096
FLUORENE	<.005	<.006	<.004	<.005	.075	<.011	<.005	<.006	<.005	0.021	0.007	<.004	<.004	<.004	<.005	<.004	<.005	<.005	<.008	<.005	0.0089
PHENANTHRENE	<.010	<.012	<.008	<.010	1.500	<.022	<.010	<.012	<.010	0.180	0.043	<.008	<.008	<.009	0.065	0.011	<.010	<.010	0.018	<.010	0.039
ANTHRACENE	<.010	<.012	<.008	<.010	.220	<.022	<.010	<.012	<.010	<.009	<.010	<.008	<.008	<.009	0.019	<.009	<.010	<.010	<.016	<.010	<.012
FLUORANTHENE	0.014	<.012	<.008	<.010	4.600	<.022	0.014	<.012	0.021	0.150	0.120	<.008	<.008	<.009	0.260	0.014	<.010	<.010	<.016	<.010	0.050
PYRENE	0.012	<.012	<.008	<.010	3.200	<.022	<.010	<.012	0.011	0.120	0.089	<.008	<.008	<.009	0.180	0.010	<.010	<.010	<.016	<.010	0.039
BENZO(A)ANTHRACENE	0.016	<.012	<.008	<.010	1.500	<.022	<.010	<.012	<.010	0.059	0.041	<.008	<.008	<.009	0.091	0.011	<.010	<.010	<.016	0.017	<.012
CHRYSENE	0.016	0.036	<.008	<.010	3.300	<.022	<.010	<.012	0.012	0.058	0.077	<.008	<.008	<.009	0.083	<.009	<.010	0.010	<.016	0.021	0.040
BENZO(BK)FLUORANTHENE	0.035	0.021	<.008	<.010	3.700	0.042	<.010	<.012	0.019	0.110	0.083	<.008	<.008	<.009	0.120	0.013	<.010	<.010	<.016	<.010	0.026
BENZO(A)PYRENE	0.013	<.012	<.008	<.010	1.100	<.022	<.010	<.012	<.010	0.071	0.035	<.008	<.008	<.009	0.022	<.009	<.010	<.010	<.016	<.010	<.012
PERYLENE	0.028	<.012	<.008	<.010	.320	0.560	0.012	0.061	0.023	0.025	0.013	<.008	<.008	<.009	0.019	<.009	<.010	0.026	<.016	<.010	<.012
INDENO(123CD)PYRENE	0.011	<.012	<.008	<.010	.320	<.022	<.010	<.012	<.010	0.063	0.025	<.008	<.008	<.009	<.011	<.009	<.010	<.010	<.016	<.010	<.012
BENZO(GHI)PERYLENE	0.011	<.012	<.008	0.010	.220	<.022	<.010	<.012	<.010	0.044	0.014	<.008	<.008	<.009	<.011	<.009	<.010	<.010	<.016	<.010	<.012
DIBENZ(AH)ANTHRACENE	<.010	<.012	<.008	<.010	.120	<.022	<.010	<.012	<.010	<.009	0.011	<.008	<.008	<.009	<.011	<.009	<.010	<.010	<.016	<.010	<.012
Total Carcinogenic PAHs	0.091	0.0057	*	*	10.040	0.560	*	*	0.031	0.361	0.272	*	*	*	0.316	0.024	*	0.010	*	0.038	0.026
Totol PAH'S	0.156	0.057	*	0.010	20.326	0.602	0.026	0.061	0.086	0.927	0.564	*	*	*	0.859	0.059	*	0.036	0.018	0.038	0.221

1. Big Creek at Hwy 132 -Columbia Co.
2. Moccasin Bayou West of Garland City on Hwy 132 - Miller Co.
3. Beech Creek/Dry Creek West of Fouke Oil & Gas Field - Miller Co.
4. West Fork Kelly Bayou at Hwy 71 - Miller Co.
5. Bodcau Creek Northwest of Stamps - Lafayette Co.
6. Bodcau Bayou South of Stamps off Hwy 53 - Lafayette Co.
7. Bodcau Creek - Upper Lake Erling - Lafayette Co.
8. Dorcheat Bayou at Hwy 82 - Lafayette/Columbia Co. line
9. Dorcheat Bayou West of Macedonia - Columbia Co.
10. Horsehead Creek at Columbia Co. Road #11 - Columbia Co.
11. Horsehead Creek at Hwy 19 - Columbia Co.
12. Big Cornie Creek South of Village - Columbia Co.
13. Cornie Creek South of Village - Columbia Co.
14. Big Cornie Creek Southeast of Spottville - Columbia Co.
15. Big Cornie Creek at Hwy 15 - Union Co.
16. Smackover Creek West of Stephens - Ouachita Co.
17. ~~Smackover Creek East of Stephens Ouachita Co.~~
18. Smackover Creek at Hwy 7 - Union Co.
19. Smackover Creek North of Smackover - Union Co.
20. Smackover Creek south of Joyce City - Ouachita Co.
21. Camp Creek and tributary of Hwy 160 - Union Co.

Table 1 continued. Total PAHs and Total Carcinogenic PAH values in ppm. Shading indicates carcinogenic, * indicates concentrations less than the detection limit.

PARAMETER	SITE																				
	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42
NAPHTHALENE	<.005	<.007	<.005	<.005	<.006	<.004	<.005	<.005	<.013	0.014	<.005	<.012	<.006	<.005	<.004	0.140	0.021	<.007	<.006	<.006	<.005
ACENAPHTHYLENE	<.005	<.007	<.005	<.005	<.006	<.004	<.005	<.005	<.013	<.005	<.005	<.012	<.006	<.005	<.004	0.014	<.006	<.007	<.006	<.006	<.005
ACENAPHTHENE	0.0056	<.007	<.005	0.007	<.006	<.004	<.005	<.005	<.013	0.005	<.005	<.012	<.006	<.005	<.004	0.280	<.006	<.007	<.006	<.006	<.005
FLUORENE	0.0062	<.007	<.005	0.007	0.060	0.004	<.005	<.005	<.013	0.005	<.005	<.012	<.006	<.005	<.004	0.340	<.006	<.007	<.006	<.006	<.005
PHENANTHRENE	0.020	<.014	<.010	0.012	0.011	0.027	0.039	0.012	0.040	0.021	0.027	0.021	0.016	<.010	<.009	2.500	<.012	<.014	<.013	<.012	.0097
ANTHRACENE	<.010	<.014	<.010	0.009	0.058	<.008	<.010	<.010	<.026	<.010	<.009	0.040	<.013	<.010	<.009	0.390	<.012	<.014	<.013	<.012	<.009
FLUORANTHENE	<.010	<.014	0.030	0.046	0.052	0.031	0.064	0.037	<.026	0.030	0.011	0.990	<.013	0.021	<.009	2.800	0.760	<.014	<.013	<.012	<.009
PYRENE	0.043	0.020	0.085	0.042	0.023	0.025	0.055	0.034	<.026	0.026	0.072	0.120	<.013	0.019	<.009	2.000	0. 700	<.014	<.013	<.012	<.009
BENZO(A)ANTHRACENE	<.010	0.016	<.010	0.020	0.032	0.010	0.027	<.010	<.026	0.012	<.009	<.024	<.013	<.010	<.009	1.800	<.012	<.014	<.013	<.012	<.009
CHRYSENE	0.012	0.031	0.050	0.029	0.037	0.008	0.054	0.045	<.026	0.021	0.120	<.024	<.013	0.015	<.009	1.100	<.012	<.014	<.013	<.012	<.009
BENZO(BK)FLUORANTHENE	<.010	0.023	<.010	0.059	0.019	0.012	0.069	0.073	<.026	0.028	<.009	<.024	0.017	0.025	<.009	0.670	0.440	<.014	<.013	<.012	<.009
BENZO(A)PYRENE	0.014	0.018	<.010	0.013	0.040	<.008	0.023	0.019	<.026	<.010	<.009	<.024	<.013	0.017	<.009	0.200	0.280	<.014	<.013	<.012	<.009
PERYLENE	<.010	<.014	0.070	0.040	<.011	<.008	<.010	0.010	0.069	0.016	<.009	0.350	0.015	<.010	<.009	0.430	0.072	0.063	<.013	<.012	<.009
INDENO(123CD)PYRENE	<.010	<.014	<.010	<.010	<.011	<.008	0.014	<.010	<.026	<.010	<.009	<.024	<.013	<.010	<.009	<.011	<.012	0.022	<.013	<.012	<.009
BENZO(GHI)PERYLENE	<.010	<.014	<.010	<.010	<.011	<.008	<.010	<.010	<.026	<.010	0.013	<.024	<.013	<.010	<.009	0.013	0.024	<.014	<.013	<.012	<.009
DIBENZ(AH)ANTHRACENE	<.010	<.014	<.010	<.010	<.011	<.008	<.010	<.010	<.026	<.010	<.009	<.024	<.013	<.010	<.009	<.011	0.043	<.014	<.013	<.012	<.009
Total Carcenogenic PAHs	0.026	0.088	0.050	0.121	0.128	0.030	0.187	0.137	*	0.061	0.120	*	0.017	0.057	*	3.770	0.763	0.022	*	*	*
TOTAL PAH's	0.1716	0.108	0.235	0.284	0.332	0.117	0.345	0.230	0.109	0.178	0.243	1.521	0.048	0.097	*	12.677	2.585	0.085	*	*	.0097

22. Holmes Creek off Hwy 7B in Smackover - Union Co.
23. Haynes Creek at Hwy 335 - Ouachita Co.
24. Bayou de Loutre - at Hwy 167 - Union Co.
25. Bayou de Loutre off Hwy 7 - Union Co.
26. Lapile Creek - Uppermost site - Union Co.
27. Lapoile Creek - Upper Site - Union Co.
28. Lapoile Creek at Jones Lake Road - Union Co.
29. Lapile Creek of Lapile Road - Union Co.
30. Lapile Creek at edge of Felsenthal NWR - Union Co.
31. Hibank Creek off Hwy 7 - Union Co.
32. Loutre Creek off Hwy 82 Bypass - Union Co.
33. Cornie Bayou South of Wesson - Union Co.
34. Cornie Bayou East of Junction City - Union Co.
35. Three Creeks West of Three Creeks Community - Union Co.
36. Beech Creek of Spott Attwater Rd. - Union Co.
37. Black Creek East of Rosston at Hwy 4 - Nevada Co.
38. Caney Creek East of Rosston on Hwy 4 - Nevada Co.
39. Bodcaw Creek at Hwy 355 - Hempstead Co.
40. Freeo Creek South of Amy on Ouachita Co. Rd.
41. Moro Creek East of Tinsman - Calhoun Co.
42. Champagnolle Creek 6 mi. North of Hampton, 2 mi. East of 167 - Calhoun Co.

Table 2. PAH sample site locations.

1.	Big Creek	T 17 S, R 21 W, S 10
2.	Moccasin Bayou	T 16 S, R 26 W, S 13
3.	Beech Creek	T 16 S, R 27 W, S 35
4.	West Fork Kelly Bayou	T 20 S, R 27 W, S 10
5.	Bodcau Creek	T 16 S, R 23 W, S 7
6.	Bodcau Creek	T 16 S, R 23 W, S 31
7.	Bodcau Creek - Lake Erling	T 17 S, R 24 W, S 33
8.	Dorcheat Bayou	T 16 S, R 22 W, S 7
9.	Dorcheat Bayou	T 18 S, R 22 W, S 16
10.	Horsehead Creek	T 17 S, R 20 W, S 27
11.	Horsehead Creek	T 18 S, R 21 W, S 30
12.	Big Cornie Creek	T 17 S, R 19 W, S 21
13.	Cornie Creek	T 17 S, R 19 W, S 29
14.	Big Cornie Creek	T 18 S, R 18 W, S 30
15.	Big Cornie Creek	T 19 S, R 19 W, S 36
16.	Smackover Creek	T 15 S, R 19 W, S 29
17.	Smackover Creek	T 15 S, R 19 W, S 35
18.	Smackover Creek	T 15 S, R 16 W, S 32
19.	Smackover Creek	T 15 S, R 16 W, S 35
20.	Smackover Creek	T 16 S, R 15 W, S 4
21.	Camp Creek	T 16 S, R 16 W, S 5
22.	Holmes Creek	T 16 S, R 16 W, S 12
23.	Haynes Creek	T 16 S, R 15 W, S 14
24.	Bayou de Loutre	T 18 S, R 15 W, S 23
25.	Bayou de Loutre	T 19 S, R 14 W, S 6
26.	Lapile Creek	T 18 S, R 12 W, S 28
27.	Lapoile Creek	T 18 S, R 11 W, S 18
28.	Lapoile Creek	T 18 S, R 11 W, S 15
29.	Lapile Creek	T 18 S, R 11 W, S 31
30.	Lapile Creek	T 18 S, R 11 W, S 25
31.	Hibank Creek	T 18 S, R 14 W, S 32
32.	Loutre Creek	T 17 S, R 15 W, S 32
33.	Cornie Bayou	T 19 S, R 16 W, S 2
34.	Cornie Bayou	T 19 S, R 16 W, S 25
35.	Three Creeks	T 19 S, R 18 W, S 6
36.	Beech Creek	T 19 S, R 17 W, S 29
37.	Black Creek	T 13 S, R 20 W, S 30
38.	Caney Creek	T 13 S, R 20 W, S 30
39.	Bodcau Bayou	T 14 S, R 23 W, S 28
40.	Freeo Creek	T 12 S, R 16 W, S 18
41.	Moro Creek	T 12 S, R 12 W, S 34
42.	Champagnolle Creek	T 12 S, R 13 W, S 33

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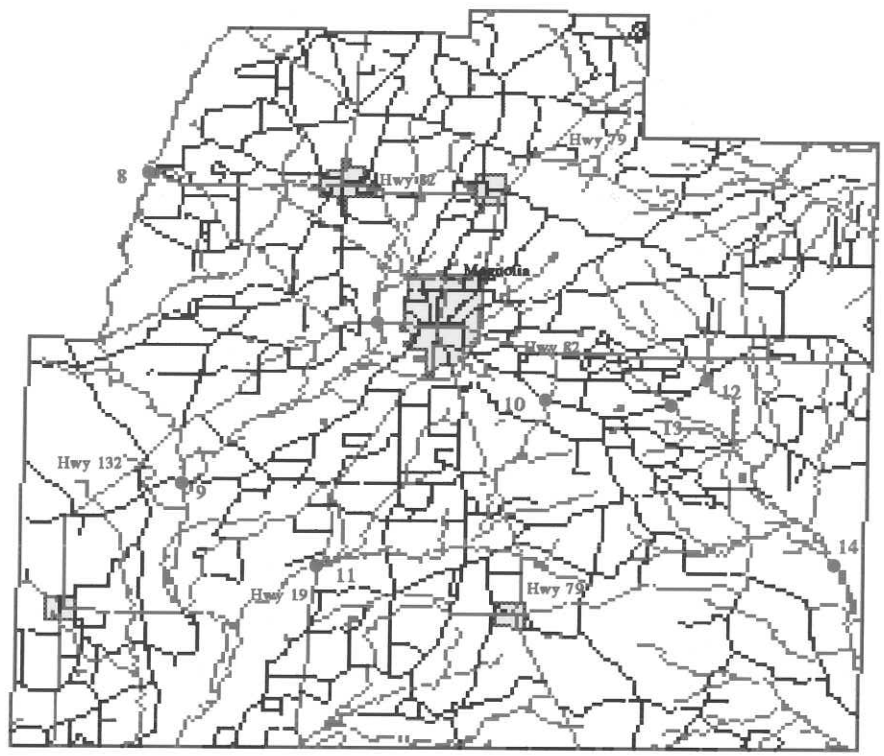
APPENDIX A

Calhoun County - PAH Survey

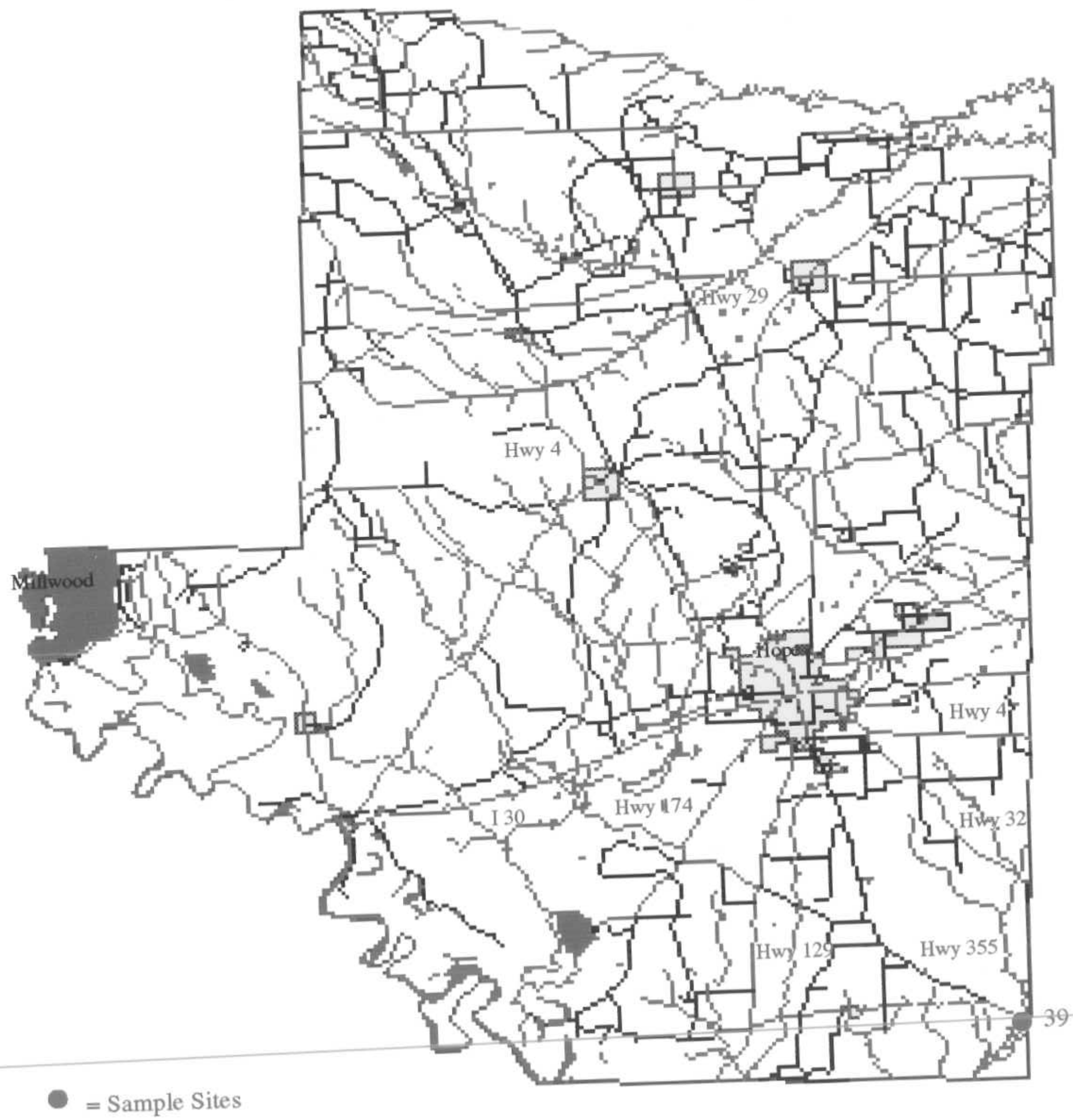
● = Sample Sites

Columbia County - PAH Survey

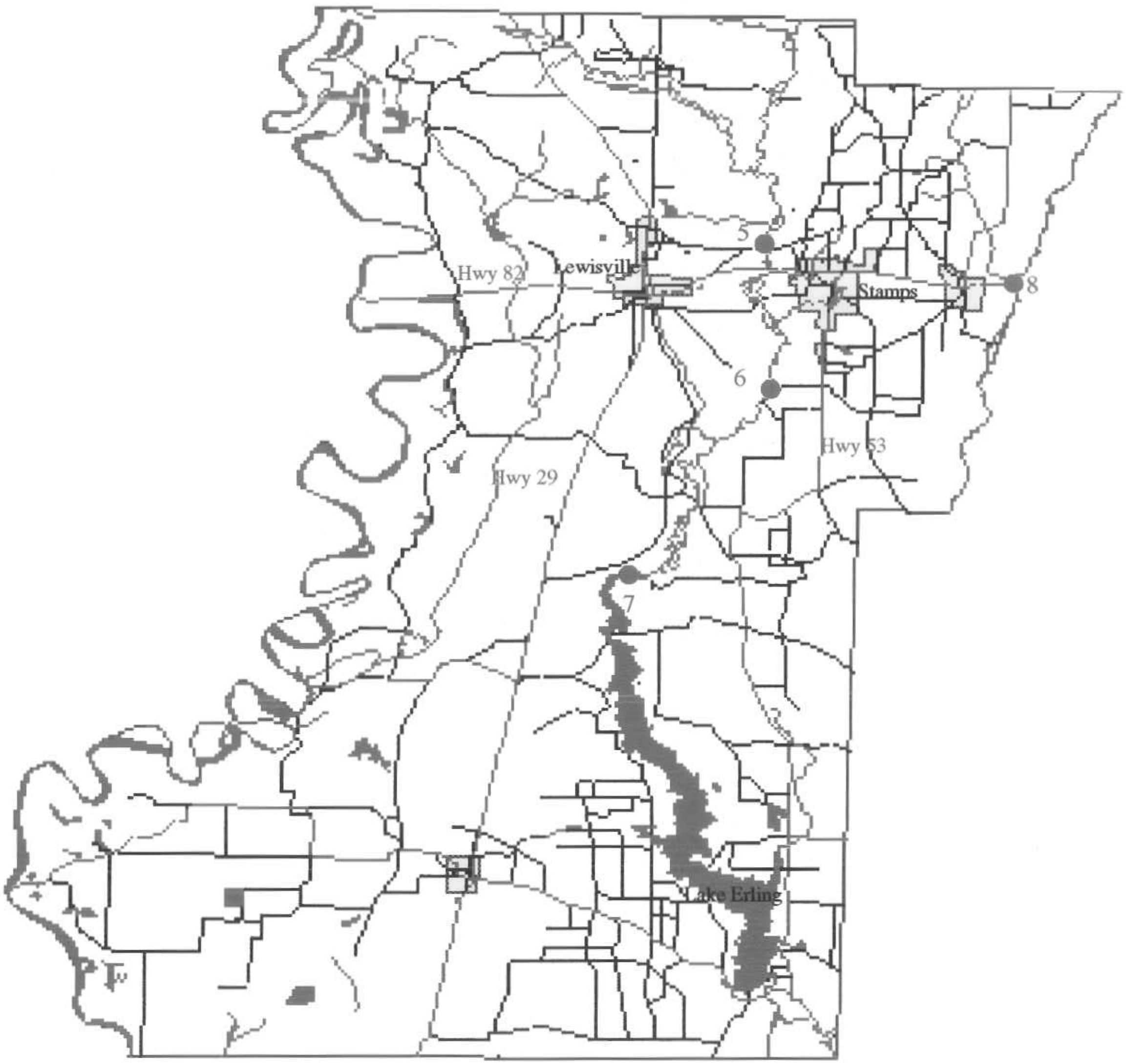


● = Sample Sites

Hempstead County - PAH Survey

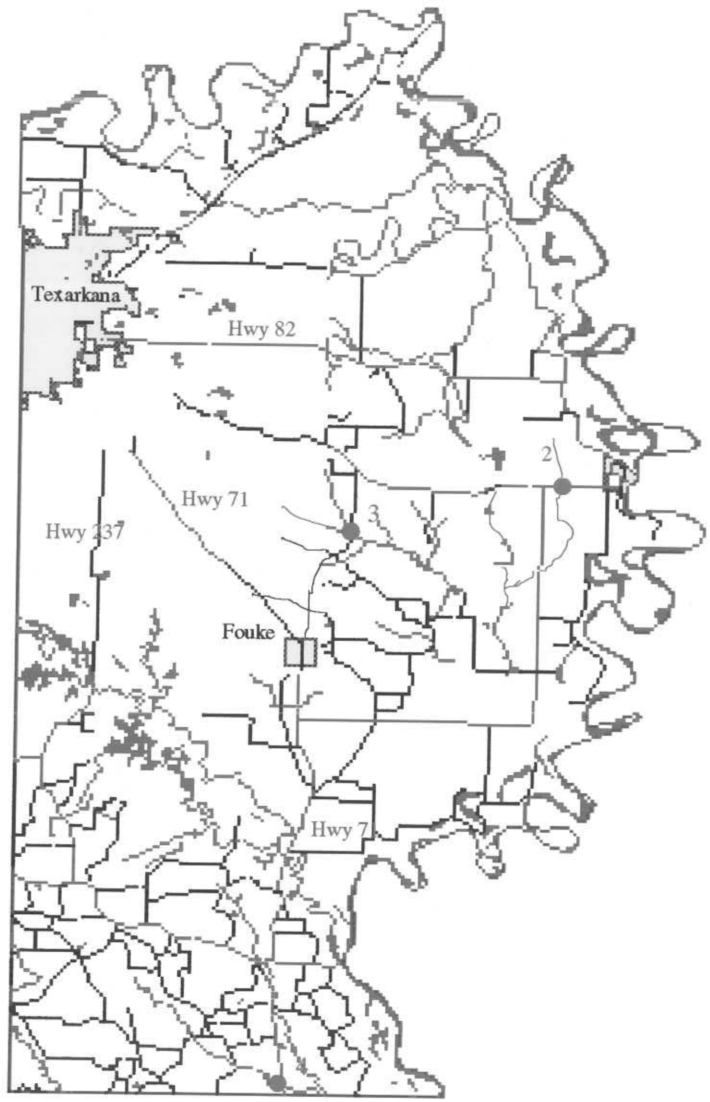


Lafayette County - PAH Survey



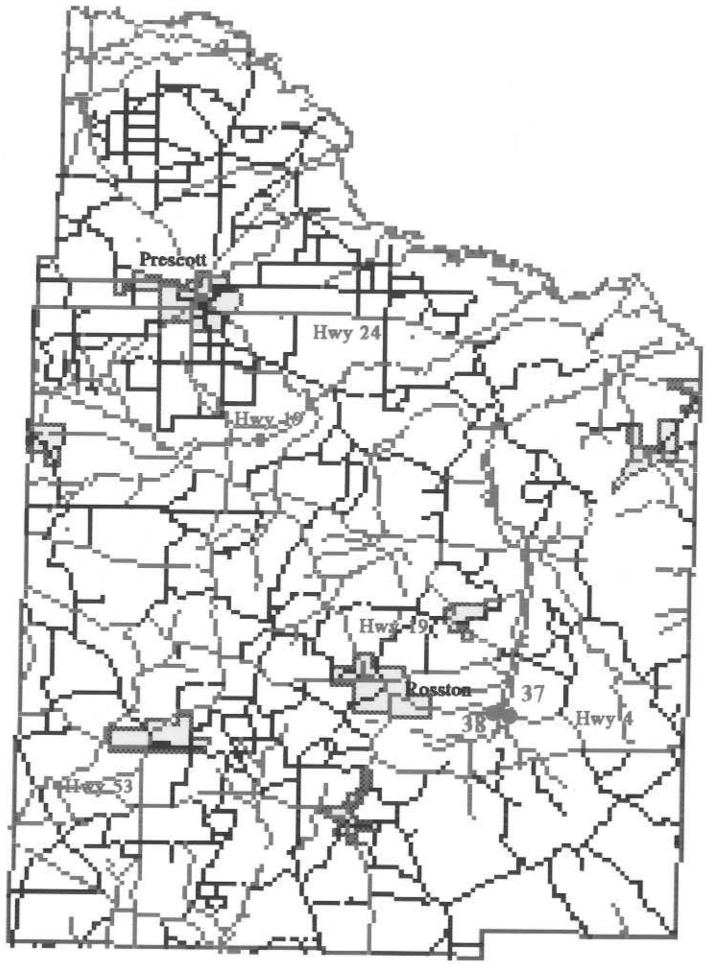
● = Sample Sites

Miller County - PAH Survey



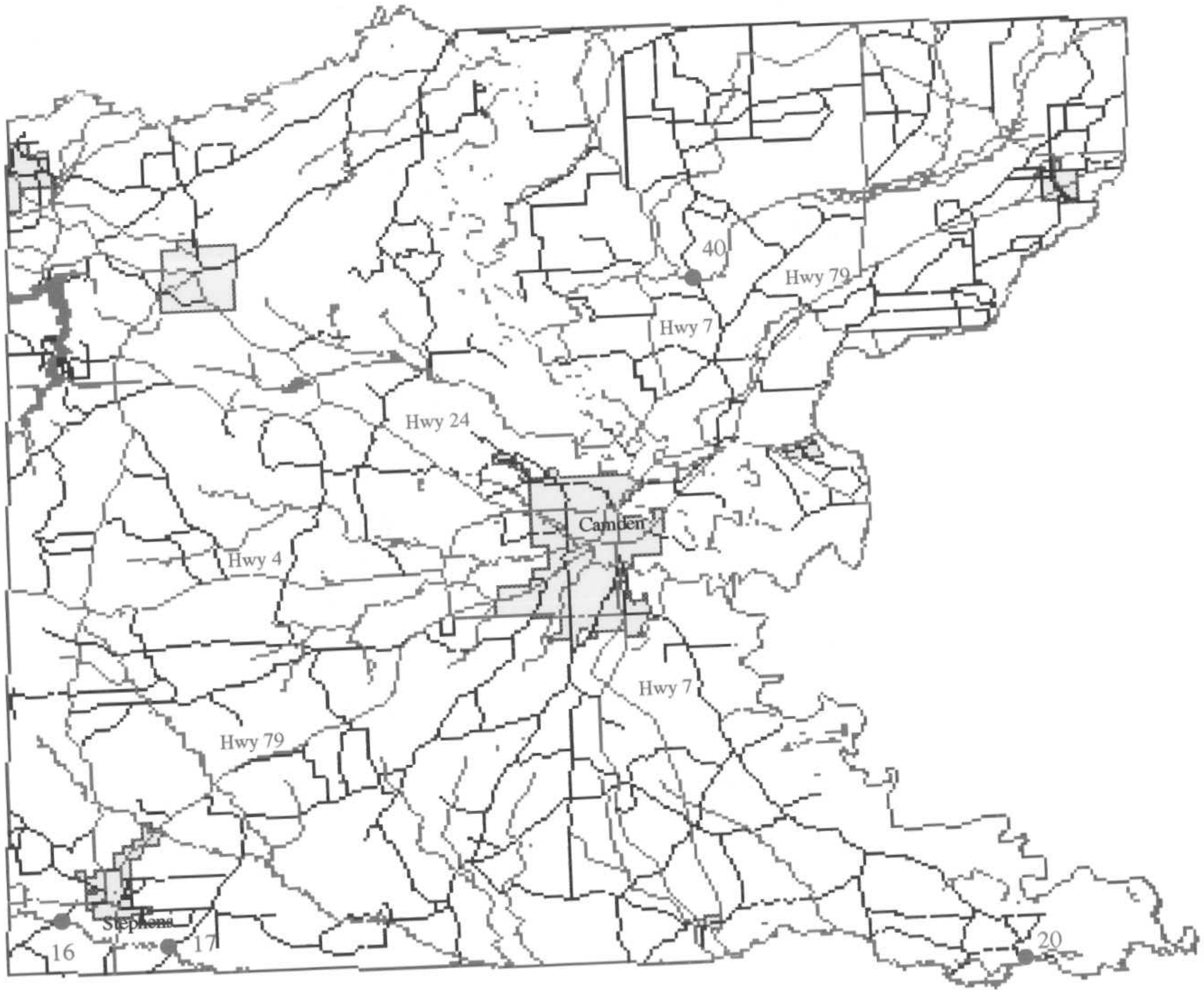
● = Sample Sites

Nevada County - PAH Survey



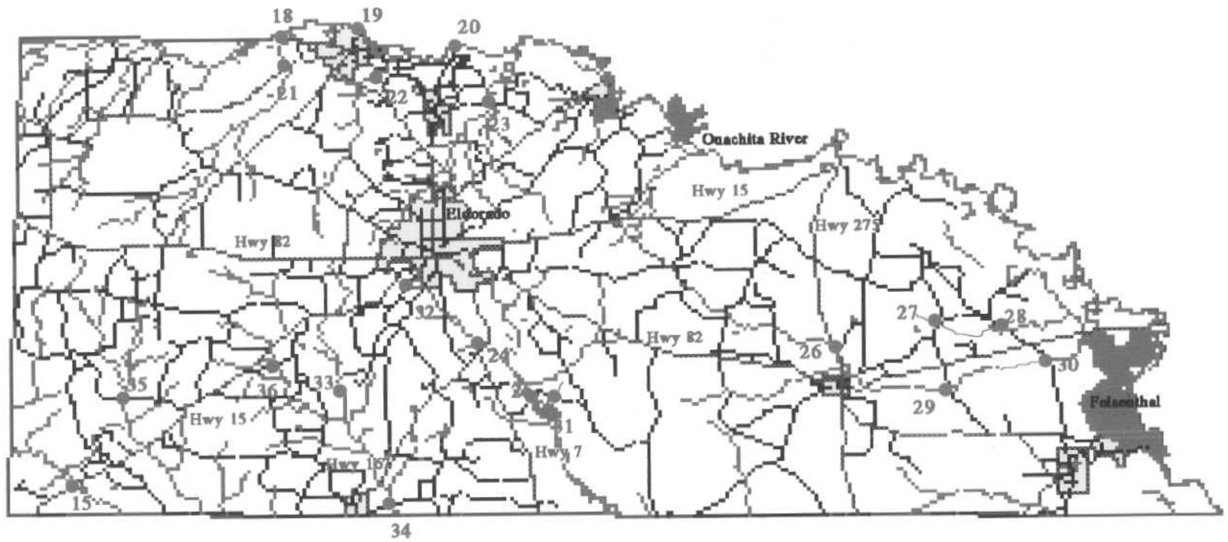
● = Sample sites

Ouachita County - PAH Survey



● = Sample Sites

Union County - PAH Survey



● = Sample Sites