

PRELIMINARY EVIDENCE FOR PHENANTHRENE, A
POLYCYCLIC AROMATIC HYDROCARBON (PAH),
IN SOME BATCHES OF PAVING MATERIALS USED
IN SAN JUAN COUNTY, WA



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Introduction

Materials commonly used to pave roads, including “chip sealers” and “fog coats”, are composed primarily of asphalt or bitumen, a mixture of heavy petroleum tars that is a byproduct of the manufacture of gasoline and other refined fuels. Although most volatile hydrocarbons generally boil off in the manufacturing process, residual amounts of highly volatile (and extremely toxic) compounds including polycyclic aromatic hydrocarbons or PAHs may remain in the tar mass until it has been spread on a road surface and exposed to weathering; or even persist in the congealed or polymerized paving material for some time after its application, sealed in by the weathering of the exposed surfaces. Larger and heavier molecules with relatively high boiling points are more likely to persist than very light ones that are volatile at room temperature. The Centers for Disease Control identify asphalt plants, asphalt road paving operations, and vehicle emissions as major sources of human exposure to PAHs (CDC 2005).

At the outset, a distinction must be drawn between petroleum-derived asphalt and coal tar based products, which include some pavement sealing products that are currently in use (Grosenheider et al. 2005). Petroleum-derived asphalts generally contain less than 5 parts per million PAH, while coal tars may contain up to ten thousand times more PAH—sometimes as much as 50 percent PAH by weight.

No two asphalts are chemically identical, moreover. The chemical composition of asphalts depends largely on the composition of the original petroleum, which differs from oilfield to oilfield and even within oilfields (Wess et al. 2004). Published data indicate a more-than-hundredfold variation in the PAH content of different asphalt products, and a range of variation in toxic metals such as cadmium, lead, vanadium and nickel from trace amounts to several parts per thousand.

The widespread use of asphalts on roads poses two distinct toxicological issues: (1) the short-term impacts of workers’ exposure to asphalt fumes during paving; and (2) the subsequent migration of asphalt components into the environment. There are limited data on the health impacts of asphalt fumes, and even less on the extent to which paving materials leach into surrounding habitats via surface water (Wess et al. 2004). Most manufacturers issue a Material Safety Data Sheet (MSDS) acknowledging that the environmental impacts of their asphalt product are unknown. OSHA nonetheless requires paving workers to wear protective gear to minimize their exposure to volatile PAHs released as asphalt is sprayed or poured onto road surfaces (OSHA 2007).

A California field study was unable to detect PAHs in road runoff at the detection level of 0.5 µg/L (0.5 parts per billion or ppb) (Cooper and Kratz 1997). A controlled laboratory leaching study found that some, but not all samples of paving asphalts leached detectable amounts of naphthalene and phenanthrene at levels below the 15 ppb drinking-water limits for these PAHs set by EPA (Kriech et al. 2002). A European study (Brandt and DeGroot 2001) likewise found that PAHs leached from some paving asphalts but at levels below the European drinking water standard of 0.1 ppb. As described below, we were unable to detect dissolved phenanthrene in road runoff at a limit of detection (LOD) of 6.7 ppb, much higher than the studies just cited.

A more recent Texas study found significant dispersal of PAHs from coal tar “seal coat” applied to parking lots—as high as 3.5 parts per thousand—in the form of asphalt abrasion particles rather than dissolved PAH (Mahler et al. 2005; also Werth et al. 2005). This suggests that gradual weathering of chip-seal surfaces may indeed contribute to the environmental burden of PAHs. Vehicles abrade road surfaces and the particles wash off roads into aquatic ecosystems where they gradual wear down, like natural mineral grains, releasing the more water-soluble PAHs over periods of months to years. The cumulative effect would be far greater than has been suggested by instantaneous measurements of PAH concentrations in road-runoff water.

Objectives

The present report is a first step in evaluating the potential adverse environmental impact of paving materials on San Juan County’s aquatic ecosystems, and focuses on the detection and measurement of a less toxic representative PAH (phenanthrene) in road runoff water and in the road-paving materials themselves.

We initially considered naphthalene as an indicator PAH. It is a smaller and more volatile molecule, once used in mothballs. Naphthalene has been reported elsewhere as a significant component of asphalt mixes. Our instrument limit of detection (LOD) for naphthalene proved to be relatively high, however, as discussed below (under Results). We were able to detect phenanthrene at concentrations nearly an order of magnitude lower, and therefore chose phenanthrene as a better representative of the larger family of PAHs found in asphalts.

Phenanthrene is a solid at room temperature, melting at 99° C, but it is moderately soluble in water (1.15 mg/L at 25°C). As such, it may be expected to persist in paving materials for some time after their application, gradually dissolving into runoff water and moving from road surfaces to nearby aquatic habitats.

Although U.S. and European environmental agencies regard all PAHs as hazards to human health, data on the specific toxicity and kinetics of phenanthrene in humans are limited (US EPA 1990 [not subsequently revised]). There is more data on the toxicity of phenanthrene in aquatic ecosystems because it is feasible to expose aquatic organisms to toxics experimentally. Phenanthrene is highly toxic and bioaccumulative in fish (Sun et

al. 2006), and extremely genotoxic to fish in the presence of nitrites (Shailaja et al. 2006), at concentrations in the part-per-billion range.

Here, we ascertain (1) whether the paving materials recently applied in San Juan County contain appreciable amounts of phenanthrene and (2) whether, and to what extent, phenanthrene in paving materials is dissolved in road runoff. This report does not include an assessment of particulate transport of phenanthrene to aquatic habitats, or our ongoing research on the metals content of asphalts in recent and current use in San Juan County.

Methods

Asphalt specimens were collected in June-August 2007 from freshly chip-sealed road surfaces on Lopez Island; and from two recently paved roads on San Juan Island.

Surface water was collected in June-August 2007 from Lopez Island and Shaw Island for evidence of PAH migration from roads to aquatic environments. The Lopez samples were taken from the west shore of Hummel Lake, less than 4 meters from edge of Center Road, one, 30 and 45 days following the re-paving and chip-sealing of that road. Shaw samples were collected from marsh, pond, creek, and bay environments on Neck Point, all within 50 meters of paved roads.

Asphalt specimens dissolved readily in hexane, but hexane is not miscible with the 30/70 H₂O/ACN (acetonitrile) mobile phase, which proved best for the determination of phenanthrene by liquid chromatography (LC). DCM (dichloromethane) accordingly was used as a substitute for hexane.

Preliminary identification of our target PAHs is based on their LC column elution times matching those of known standards. Because there is the unlikely possibility that another compound could be eluting with the same retention time, definitive identification by mass spectrometry (MS) is the generally accepted criterion. We will subject samples to MS analysis when a suitable instrument becomes available.

A more detailed description of our methods may be found in the Supplemental Materials appended to this report.

Results

Analysis of naphthalene in asphalt extracts: We initially screened DCM extracts of three Lopez asphalt specimens (COAp57, FHCSp61, FHCSp67) for both naphthalene and phenanthrene. All three were negative for naphthalene at our instrument LOD of 40 ppb, and positive for phenanthrene at our instrument LOD of 6.7 ppb, based on matching retention times with standards. We concluded that phenanthrene offers a more sensitive and reliable indicator of PAH in asphalt than naphthalene.

Analysis of phenanthrene in asphalt extracts: Table 1 list results from multiple LC analyses of a freshly applied asphalt sealer (FPL) and a relatively recently applied road

asphalt (SB). Minimum concentrations in the original specimens were back calculated from measured concentrations in extracts. Variations are due to exploration of different extraction solvents with losses observed during the filtration steps.

Table 1. Minimum concentrations of putative* phenanthrene in asphalt specimens

Sample	Type	From	Extract	Solvent	Phenanthrene
FPL	Chip sealer	Lopez	FPL p.79	DCM	25.7 ppm
			FPL p.83	DCM-ACN	95.6 ppm
SB	Road asphalt	San Juan	SB p.69	Hexane	4.0 ppm
			SB p.71	Hexane	3.7 ppm
			SB p. 75	MEOH-DCM	0.56 ppm
			SB2 p. 85	MEOH-DCM	5.9 ppm
			SB p. 87	DCM-ACN	18.5 ppm

*Identity to be confirmed by mass spectrometry.

SBP69 and SBP71 are replicate LC analyses of the same asphalt extract, offering some indication of the level of precision of our LC quantifications (about $\pm 10\%$).

Analysis of naphthalene and phenanthrene in surface water samples: None of the fresh water or marine water specimens we collected produced unambiguous peaks at the retention times for phenanthrene.

Discussion

Phenanthrene in the SB road asphalt specimens varied widely (4 ppm, 3.7 ppm, 0.56 ppm, 5.9 ppm, and 18.5 ppm). We decided to reject the two outliers of this data set due to experimental conditions described above. The estimate is therefore the average of 4, 3.7, and 5.9 = 4.5 ppm phenanthrene in the extractable tar portion of SB road asphalt. Higher results for the FPL chip sealer is consistent with known higher PAH levels in coal tar derived products.

This much phenanthrene in surface water (or drinking water) would be regarded as a serious hazard. However, as noted in our Introduction, asphalt PAHs migrate slowly into runoff water at highly diluted concentrations i.e. in the low ppb range. Since the rate of leaching (directly from the road surface, or from abrasion particles dislodged from the road surface) is almost certainly low, it will have to be measured with more sophisticated instrumentation such liquid chromatography-mass spectrometry (LC-MS).

Conclusions

Asphalt and chip seal products recently used on San Juan County roads appear to contain significant concentrations of phenanthrene, a toxic PAH (polycyclic aromatic hydrocarbon). This finding must be regarded as preliminary until it is confirmed by mass spectrometry and reproduced by other laboratories.

Phenanthrene poses a health hazard to humans and, to an even greater extent, fish and other aquatic organisms, should it migrate out of these materials. Phenanthrene undoubtedly dissolves into runoff water, but at a rate too low to measure in the present study. Any adverse environmental effects will accordingly be cumulative and long-term.

Local decision-makers should consider the following actions:

- (1) Require protective clothing and respirators for employees engaged in paving (including sealing) local roads, in accordance with OSHA standards to avoid potential liability for claims based on occupational exposure.
- (2) Require that every batch of paving material purchased by the county whether petroleum- or coal tar-derived be accompanied by a complete chemical assay of its constituents, in particular PAHs and metals. This is imperative in view of the high level of variability in composition of batches of these products.
- (3) Ensure that batch assays and manufacturer MSDS' are provided to employees and made conveniently public in advance of paving work.
- (4) Support further study of road abrasion and particulate transport of PAHs and metals into wetlands in San Juan County.

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Supplemental Materials

Analytical Methods used to Assay Naphthalene and Phenanthrene in Asphalt

Jack Bell, PhD

Liquid Chromatography (LC) System

Reservoirs: Bottle A, MilliQ purity water; Bottle B, LC-grade acetonitrile (ACN), not degassed. Pump: Dual Waters 510 pumps with solvent A on the left, solvent B on the right, operated at a speed of 1 mL/minute. Injector: Rheodyne with 1 mL loop and chart mark connection to the recorder. Column: 4mm x 250 mm, reverse phase C18 bonded to a 5-micron silica particle stationary phase except as otherwise noted. Detector: ABI 757 variable UV-Visible detector. Recorder: Kipp & Zonen flatbed, 22 cm wide recorder, run at 10 mm/minute.

Data recording

Page-numbered data are from a blue, 7 x 9 inch lab book entitled "HPLC I, Friday Harbor Labs, 2004- " by J. Bell. The last two digits of each specimen name comprise the relevant page of the lab book. Original chromatograms were scanned on an HP 7100 to jpeg files before conversion to with Photoshop Elements 3 on a Mac Mini, OS 10.4.10.

Preparation of standards

Very dilute LC standards were prepared using small quantities of stock reagents. Syringes, pipettes, solvents, and working surfaces employed in preparing standards were kept separate from field samples and the tools used to prepare them for analysis.

Naphthalene: 1 $\mu\text{L} \pm 20\%$ of a 0.01 molar (M) naphthalene/ACN standard was diluted into 10.0 mL ACN for a 10,000-fold dilution approximating 10^{-6} M naphthalene.

Phenanthrene: 5.0 mg of accurately weighed phenanthrene crystals were placed in a 20 mL glass vial with a teflon-lined cap, and diluted with 2.8 mL ACN to give a 10^{-2} M phenanthrene stock solution (0.0050 grams/178 grams/mol of phenanthrene=0.00002809, or 2.8×10^{-5} mols; 2.8×10^{-5} mols divided by 10^{-2} mole/liter = 2.8×10^{-3} liter or 2.8 mL). Take 50 μL of 10^{-2} M stock with an accurate LC syringe and add it to 5.0 mL ACN in a new vial for a 10^{-4} M phenanthrene stock. Take 50 μL of 10^{-5} M stock with an accurate LC syringe and add it to 5.0 mL ACN in a new vial for a 10^{-6} M phenanthrene stock. Take 1.0 mL of the 10^{-6} stock and add it to 9.0 mL ACN for a 10^{-7} M phenanthrene stock.

Polycyclic aromatic hydrocarbons (PAHs) are known to oxidize quickly in air and light; the rate of oxidation increases with greater dilution. To retain accuracy, our highly dilute standards must be used immediately.

Calculation of Limits of Detection (LOD)

Baseline noise is typically about 1 mm wide on the Isco and Waters chart recorders. For 99 percent confidence that an observed peak is real and not random noise, it must be at least three times baseline noise, or 3 mm high. Instrument response factor is calculated from the peak height in mm divided by the mass of analyte injected in nanograms (ng). LOD is calculated from a peak height of 3 mm divided by the response factor. In "stronger" mobile phases with higher percentages of ACN to water, compounds elute as faster, narrower, and taller peaks and thus lower LODs.

1. Naphthalene¹

LC condition 1 (Isco, 30/70 H₂O/ACN, 4 x 150 mm C18 column, 0.002 UV₂₅₄, 2006): response factor 2.8 mm/ng; LOD 1.1 ng in 10 µL standard injected on-column, or 110 ppb.

LC condition 2 (Isco, 20/80 H₂O/ACN, 4 x 150 mm C18 column, 0.002 UV₂₅₄, 2007): response factor 8.4 mm/ng (average of 8.6, 9.5, 7.1 mm/ng); LOD 0.4 ng (0.357 calc) in 10 µL of standard injected on-column, or 40 ppb.

2. Phenanthrene²

LC condition (Waters LC, 30/70 H₂O/ACN, 4 x 250 C18 column, 0.005 UV₂₅₄, with a 10⁻⁷ M standard in ACN: 8 mm peak with 0.178 ng = 45 mm/ng response factor. The LOD is 0.067 ng in 10 µL solvent injected on-column, which is 6.7 ng/mL or 6.7 ppb in the standard solution (or sample extract) injected.

Preparation of asphalt specimen extracts

COA (p. 57). A fragment of recently applied road asphalt near Hummel Lake was dissolved in 10 mL warm ACN and passed through a 0.2 µm Acrodisc syringe filter.

FHCS (p.61-61). A 43.3 mg piece of fresh chip seal road tar taken near Hummel Lake dissolved in several 1 mL portions of hexane. The combined extracts passed easily through a 0.2 µm Acrodisc syringe filter yielding 3 mL of clear brown extract, calculated to contain 14.4 mg/mL tar.

FPL (p.79). A 16.0 mg sample of fresh parking lot sealer containing no gravel easily dissolved in 5.0 mL DiChloroMethane (DCM) to give a dark, slightly cloudy solution, which easily filtered through a 0.2 µm Acrodisc syringe filter.

FPL (p.83). A 3.6 mg sample of the same parking lot sealer on the tip of a glass pipette was swirled in 100 μ L DCM to dissolve, then the extract was squirted into 5.0 mL ACN in another vial plus two 100 μ L DCM chasers (low boiling-point DCM is continually evaporating) to produce a cloudy brown solution. It easily filtered through a 0.2 μ m Acrodisc syringe filter giving a clear, pale yellow extract.

Hummel (p.85). A 29.4 mg sample of road chip seal on the tip of a glass pipette easily dissolved in \sim 200 μ L DCM, which was then squirted into 5 mL ACN to create a cloudy suspension of sticky, mostly insoluble particles of asphalt matrix with any PAHs present hopefully in solution. The suspension quickly plugged a 0.2 μ m Acrodisc PTFE syringe filter, and pre-filtering with cotton or glass fiber syringe filters did not help. About 200 μ L of clear, almost colorless filtrate was eventually collected.

SB (p. 69). A specimen of road asphalt was weighed, extracted overnight in 10 mL hexane at room temperature, and the extract filtered through a 0.2 μ m Acrodisc syringe filter. By reweighing the vial containing the residual dry gravel, it was calculated that 160 mg of tar had been extracted into the hexane. **SB (p. 71)** is a second aliquot of the same extract.

SB (p. 75). Pieces of asphalt (total 159 mg) were triturated in 5 mL of 33/67 methanol/DCM, which is partly miscible in the 30/70 H₂O/ACN mobile phase.

SB1 (p. 85) and SB2 (p.85). A single piece of asphalt weighing 469.4 mg was extracted in 5 mL of 33/67 methanol/DCM, like **SB (p. 75)**. Although 26.4 mg of the asphalt specimen dissolved, the extract was difficult to filter, and only \sim 300 μ L could be rendered sufficiently clean for LC analysis.

SB (p. 87). A 98.4 mg asphalt chunk was broken up in exactly 100 μ L DCM using a 200 μ L Dade micro-folin glass pipette and the suspension was quickly transferred to 5 mL ACN, another 50 μ L DCM rinse was added, and the extract immediately filtered easily through a 0.2 μ m Acrodisc syringe filter that had been pre-rinsed with ACN. The filtrate contained 1.8 mg of material dissolved from the original tar.

Analysis of extracts from asphalt specimens

COA (p. 57). At 0.1 sensitivity on a 4 x 250 mm C4 column there is no evidence of naphthalene in this extract at or above our LOD of 40 ppb. A small but noticeable "bump" is visible at the elution time of phenanthrene, however, and may indicate that phenanthrene is present in the extract at or above 6.7 ppb.

FHCS (p. 61). At 0.1 sensitivity on a 4 x 250 mm C4 column there is no evidence of naphthalene in this extract at or above our LOD, but a small "blip" is visible where phenanthrene would elute.

FHCS (p. 67). At 0.1 sensitivity on a 4 x 150 mm C8 column there is no evidence of naphthalene in this extract at or above our LOD, but an unambiguous peak where phenanthrene elutes.

FPL (p. 79). At 0.005 sensitivity on a 4 x 250 mm C18 column a 37-mm somewhat broadened peak appears where phenanthrene elutes. Assuming without MS confirmation that this is phenanthrene, 37 mm at the response factor reported above (45 mm/ng)=0.822 ng in the 10 μ L of extract injected on-column. The total extract (5.0 mL DCM) therefore contains 5,000 μ L x (0.822 ng/10 μ L) = 411 ng of phenanthrene, and this is from 16.0 mg of tar. To put the result in standard reporting units of ppb in tar (1 ppb = 1 ng in 1 gram of solid), 411 ng/0.016 g = 25687.5 or 25700 ppb, i.e., 25.7 ppm (*parts per million*) putative (assumed) phenanthrene. The sample (not instrument) LOD is a 3 mm peak, which by a 3/37 mm proportion x 25.7 ppm = 2.08, or a sample LOD of 2 ppm phenanthrene in tar.

FPL (p. 83). At 0.005 sensitivity on a 4 x 250 C18 column there is a well-shaped, 31-mm peak where phenanthrene elutes (Figure 1). At the response factor of 45 mm/ng, this 31 mm peak=0.688 ng in the 10 μ L of extract injected on-column. The total extract consequently contains 5000 μ L x (0.688 ng/10 μ L) = 344 ng phenanthrene, and this from the specimen of 3.6 mg tar. In standard reporting units for tar: 344 ng/0.0036 g = 95,555 ppb or 95.6 ppm phenanthrene in the tar. The sample LOD is a 3 mm peak/31 mm peak x 95.6 ppm = 9.3 ppm phenanthrene in tar.

SB (p. 69). At 0.005 sensitivity on a 4 x 150 mm C8 column there is a 29-mm peak close to the retention time for phenanthrene. We back-calculated concentration using the 45 mm/ng response factor for the 4 x 250 mm C18 column, but note that a more accurate response factor should be determined on the C8 column and mobile phase used here. At the response factor of 45mm/ng, the 29 mm peak= 0.644 ng in 10 μ L of extract injected on-column. The total extract therefore contains 10,000 μ L x (0.644 ng/10 μ L) = 644 ng, and 644 ng/0.160 g = 4,025 ppb or 4.0 ppm phenanthrene in the original tar. The sample LOD is 3/29 x 4 = 0.4 ppm phenanthrene in tar.

SB (p. 71). At 0.005 sensitivity on a 4 x 150 mm C8 column there is a 27-mm peak close to the retention time for phenanthrene. At a response factor of 45mm/ng, this 27 mm peak represents 3.7 ppm phenanthrene in the original tar, and sample LOD of 0.4 ppm phenanthrene in tar.

SB (p. 75). At 0.005 sensitivity on a 4 x 150 mm C8 column there is an 8- mm peak at the retention time for phenanthrene. At a response factor of 45mm/ng, this 8- mm peak = 0.177 ng in 10 μ L of extract injected on-column, and 5000 μ L x 0.177 ng/10 μ L = 88.5 ng in the total extract; hence there was 88.5 ng/0.159 g = 557 ppb or 0.56 ppm phenanthrene in the original tar. Precipitates in the extract may explain the lower result for SnowberryP75 in comparison with SnowberryP69 and SnowberryP71.

SB1 (p. 85) and SB2 (p. 85). At 0.005 sensitivity on a 4 x 150 mm C8 column SB1 (p. 85) gave an 18-mm peak at the retention time for phenanthrene but we concluded

that syringe contamination had contributed to peak height. SB2 (p. 85) gave a 14-mm peak which at 45 mm/ng = 0.31 ng in the 10 μ L injected on-column; 0.31 ng x 5000 μ L = 155 ng in the total extract; and 155ng/0.0264 g = 5,871 ppb or 5.9 ppm phenanthrene in the original tar.

SB (p. 87). At 0.005 sensitivity on a 4 x 150 mm C8 column, this extract produced a 3-mm peak at the retention time for phenanthrene. At a response factor of 45 mm/ng this peak = 0.0666 ng in 10 μ L of extract injected on-column; 0.0666 x 5000 μ L = 33.3 ng in the total extract; hence there was 33.3 ng /0.0018 g = 18,520 ppb or 18.5 ppm phenanthrene in the original tar—exactly at the sample LOD because the amount of tar extracted was so small.

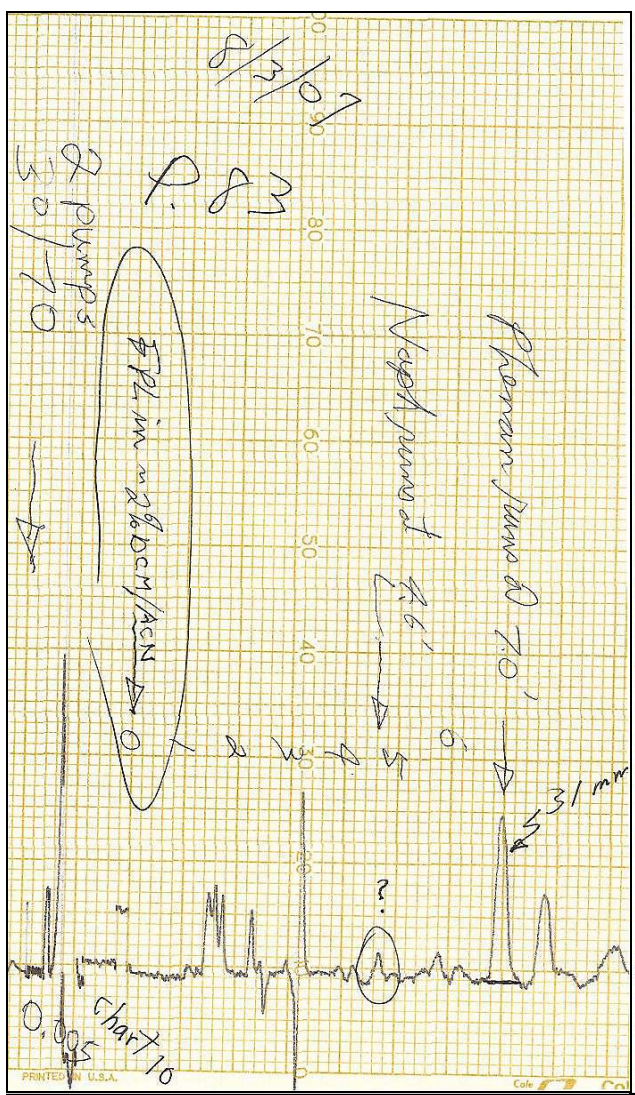


Figure 1.
LC chromatogram of extract FPL (p.83) showing a distinct 31 mm tall peak at the elution time for phenanthrene.

¹ Lab book pages 37-8, 41,44, 48-9, 61.

² Lab book page 81.