ENVIRONMENTAL EFFECTS OF SCHUYLKILL OIL SPILL II (June 1972)





U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER PROGRAM OPERATIONS
WASHINGTON, D.C. 20460

ENVIRONMENTAL EFFECTS OF SCHUYLKILL OIL SPILL II

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By
Division of Oil and Special Materials Control
Office of Water Program Operations
U.S. Environmental Protection Agency
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FOREWORD

Since 1971, the Environmental Protection Agency has supported a program for studying the effects of oil pollution under special contractual arrangements providing for a multi-disciplinary, fast response, field survey team. This study was activated under such an agreement to investigate the impact of a spill of six to eight million gallons of sludge from ruptured dikes at a waste crankcase oil re-refinery plant in the aftermath of Hurricane Agnes. The main section of this report is devoted to detailed chemical and biological data on the distribution and occurrence of hydrocarbon residues and heavy metals in the aquatic environment. In the section entitled recommendations, the report suggests use of cleanup techniques that are least damaging to vegetation, and what corrective measures can be taken to prevent erosion.

Results from this and similar studies are intended to provide a better understanding of the multiple pathways oil can follow when discharged into the aquatic ecosystem. Furthermore, such investigations will assist in the formulation of regulations, policies and procedures that are most effective in the removal of oil from water.

This report is intended for use by government, industry, and other interested parties. I want to express my sincere thanks and appreciation for all who participated in the successful completion of this project.

H. D. Van Cleave Chief, Spill Prevention & Control Branch Oil & Special Materials Control Division Office of Water Program Operations Washington, D. C. 20460

NOTICE

This report has been reviewed by the Oil and Special Materials Control Division, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The fate and effects of a spill of six to eight million gallons of waste crankcase oil rerefined sludge into the Schuylkill River, Pa., in June of 1972 have been studied. The spilled oil contained high concentrations of heavy metals and aliphatic and aromatic hydrocarbons. The spill occurred during a flood, and riverbank trees were coated with oil. Levels of lead were higher in downstream trees; however, no direct permanent effects were noted. Levels of heavy metals in river waters remained below those set by the U. S. Public Health Service for drinking water supplies; however, higher concentrations of lead and zinc were observed downstream.

Levels of lead in sediments were higher downstream. Concentrations of petroleum hydrocarbons in sediments were higher at downstream stations. Concentrations of lead in downstream benthic macrofauna were higher. Immediately downstream from the spill, there was evidence of environmental degradation not observed upstream or further downstream.

Recommendations for handling of similar spills have been formulated.

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SUMMARY

Six million gallons of rerefined waste crankcase oil sludge spilled into the Schuylkill River near Douglassville, Pennsylvania, in June of 1972. This report summarizes a study of both the immediate and the long-term effects of the spill.

The spilled oil coated and caused extensive temporary damage to vegetation along approximately 17 miles of riverbank. Most trees and herbaceous species lost their leaves, thus the aesthetic value of the riverbanks was impaired during the summer of 1972. Some oil-coated branches were killed. Some dead branches have been invaded by wood-rotting fungi that may in time damage the trees.

The spilled oil did not cause direct permanent damage to deciduous species along the riverbank; however, many ornamental evergreens have been seriously damaged and have lost their aesthetic value.

Leaves on trees in the heavily affected downstream areas had significantly higher lead levels than leaves from trees in the area immediately upstream from the spill site in the summer of 1973. However, lead levels were not higher than levels in urban trees reported in the literature.

Concentrations of the heavy metals, lead, zinc, cadmium, and copper in Schuylkill River water downstream from the spill site in July, 1972, were below permissible levels for drinking water supplies set by the U. S. Public Health Service.

Lead and zinc levels in the Schuylkill River water were higher in the downstream areas than at the immediately upstream site during early July, 1972. In mid-late July, 1972, concentrations of lead and zinc had generally decreased to background levels.

Lead levels in Schuylkill River sediments collected during November, 1972, were significantly higher in the downstream areas than immediately upstream.

Petroleum hydrocarbon concentrations in sediments collected in November, 1972, from the downstream areas were significantly higher than in sediments from the upstream station at Monocacy. Comparison of the gas chromatograms of oil in the sediments suggests that the spill was responsible in part for the high petroleum hydrocarbon concentrations at downstream stations.

Lead concentrations in Diptera larvae and Oligochaete worms collected in July, 1973, were three to seven times higher in the immediately downstream area than in the immediately upstream area.

Heavy metals concentrations in fishes collected from the Schuylkill River in July, 1972; November, 1972; January, 1973; and July, 1973, were similar at both upstream and downstream sample stations.

Aromatic and aliphatic hydrocarbon concentrations were similar in upstream and downstream fish collected in July, 1973, but are markedly higher than concentrations in fish from a pure environment.

Zooplankton samples taken on 16 July 1972 and 14 July 1973 indicated no differences in taxon diversity between upstream and downstream lengths of the river that can be attributed to the oil spill.

Macrofauna samples collected five and thirteen months after the spill (29 November 1972 and 28 July 1973) indicated no differences between upstream and downstream lengths of the river that can be attributed to the oil spill.

Chemical oxygen demand (COD) during July, 1972, was greatest in the length of the river downstream from the spill site between Douglassville Bridge and Spring City Bridge. A substantially greater amount of pheopigment level characterized Parker Ford, downstream from the spill site, on 29 July 1972. Repspiration of the biotic community at Parker Ford was marginally greater on 30 July 1972 than at the immediately upstream site. Bacteria (including hydrocarbon oxidizers) consistently reached peak levels at the Parker Ford Bridge station. Each of the above observations, taken separately, offers only weak evidence of environmental differences among upstream and downstream lengths of the river. Collectively, they present circumstantial evidence that the length of the river between Douglassville Bridge and Spring City Bridge (0.7 - 16.5 miles below the oil spill) was characterized by a degree of environmental degradation not evident immediately upstream or downstream.

Existence of numerous actual and potential sources of pollution in the Douglassville Bridge - Spring City Bridge length of the river preclude positive assignment of the oil spill as the cause of environmental

degradation. However, the oil spill could quite plausibly have resulted in both the high COD and pheopigment content that was observed in this length of the river. These conditions, in turn, could be expected to stimulate a buildup of bacterial decomposers which would cause the increased community respiration that was detected by the diurnal oxygencurve technique.

CONCLUSIONS

The rerefinery sludge temporarily damaged deciduous trees and other vegetation along the riverbanks by causing premature loss of leaves and reduction of aesthetic values during the summer of 1972. Recovery from this contamination by the summer of 1973 was evident. Evergreen trees and ornamental evergreen shrubs were permanently damaged by rerefinery sludge as evidenced by loss of needles from affected branches.

Although flood conditions on the Schuylkill had an overriding influence on many of the aquatic aspects of the study, environmental degradation due to rerefinery sludge and associated heavy metals was obvious as late as thirteen months after the spill.

Heavy metal concentrations in the river remained below those concentrations listed as prohibitory for drinking water by the U. S. Public Health Service.

Techniques used in the removal operation represented the best practice available for the problems encountered. These techniques included:

- . Oil deposited on the land areas was physically removed. Care was taken not to bury removed oil where contamination to ground water or livestock might occur.
- . Only trees, shrubs, and branches in the most heavily polluted areas were removed in order to leave a root system to prevent bank erosion.
- . "Quick-cover", fast growing grass was used to prevent erosion of river banks, following physical removal of oil.

RECOMMENDATIONS

In the event of a spill of similar material near a stream or river:

- 1. Immediately mobilize quick-response study teams to analyze the impact of the spill.
- 2. Utilize cleanup techniques that do the least harm to trees and vegetation including:
- A. Remove oil from the ground using hand implements so as not to disturb root systems and cause erosion.
- B. Remove only downed trees and heavily coated brush without unnecessarily disturbing the soil.

INTRODUCTION

On 22 June 1972 floods caused by heavy rains from Hurricane Agnes inundated oil storage lagoons on the banks of the Schuylkill River near Douglassville, Pennsylvania. The lagoons contained residue from several years of operation of a petroleum rerefining plant employing the vacuum distillation process. The plant rerefined waste crankcase oil collected from service stations and garages. A byproduct of the rerefined process was a thick, tarry residue which could not be economically reduced or used. An estimated 6 - 8 million gallons was stored in the lagoons at the time of the flood.

The flooding river swept the oil from the lagoons and carried it downstream. Because the flooded Schuylkill was far beyond its usual boundaries, the oil coated trees, homes, and riverbanks as the water receded. Riverbanks on both sides of the river were coated on the average to a distance of 50 yards inland along 17 miles of the river.

A study of the effects of the spill has been conducted during the year following the spill. The objectives of the study were to:

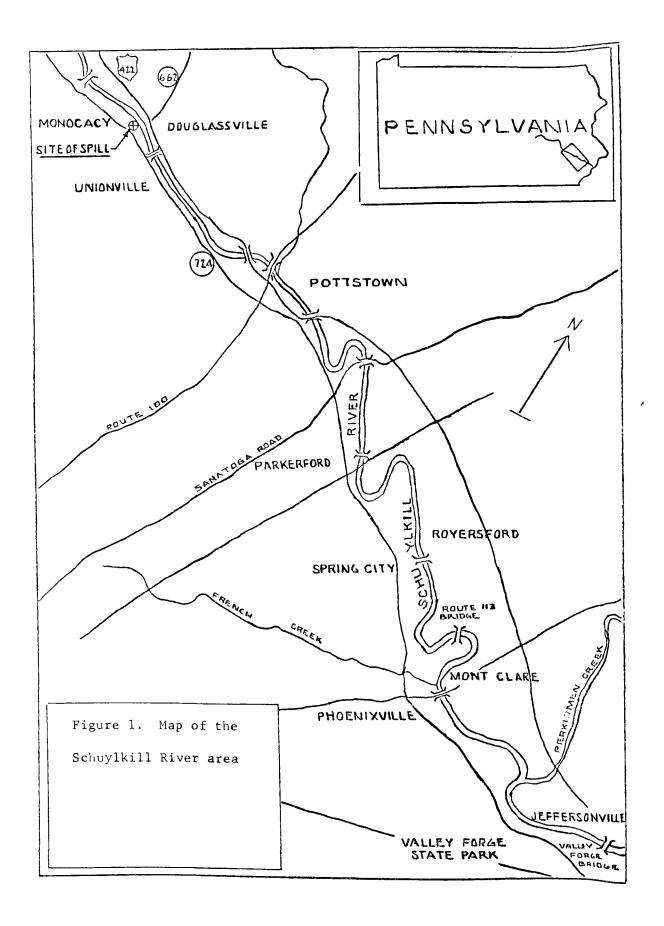
- 1. Evaluate the severity and extent of damage to vegetation along the river,
- 2. Determine the health hazard due to heavy metal contamination of drinking water supplies,
- 3. Determine the constituents of the oil and its fate and effects in the river, and
- 4. Evaluate the impact and effectiveness of shore clean-up operations and recommend procedures for handling similar spills.

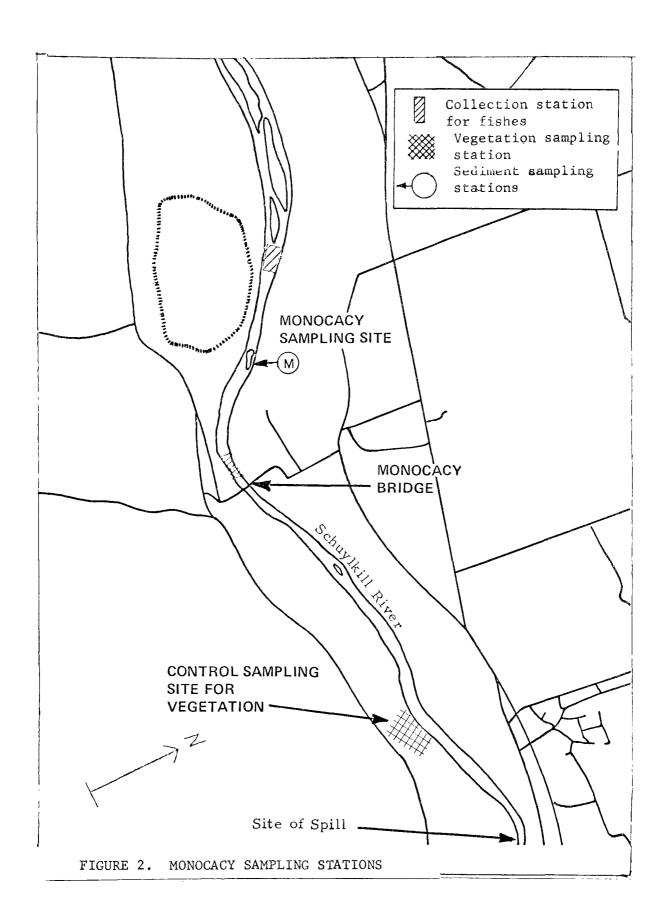
To accomplish the objectives:

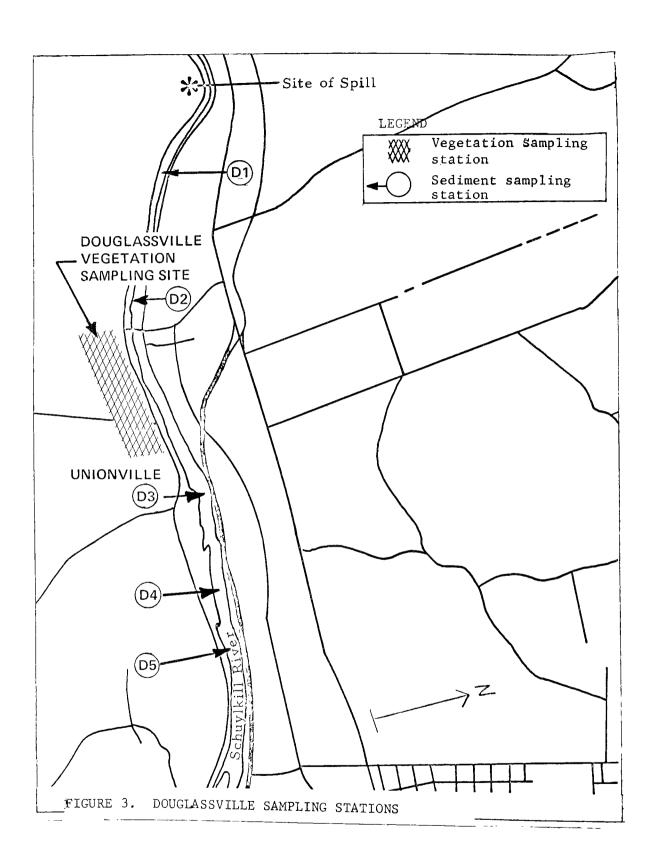
- -- The properties of the spilled crankcase oil waste were determined.
- --the recovery of trees along the banks of the Schuylkill was monitored during the summer of 1972 and during fall bud set and spring 1973 leaf formation. In the spring of 1973, the concentrations of heavy metals in tree leaves downstream from the spill were determined and compared to concentrations in leaves of trees from an upstream station.

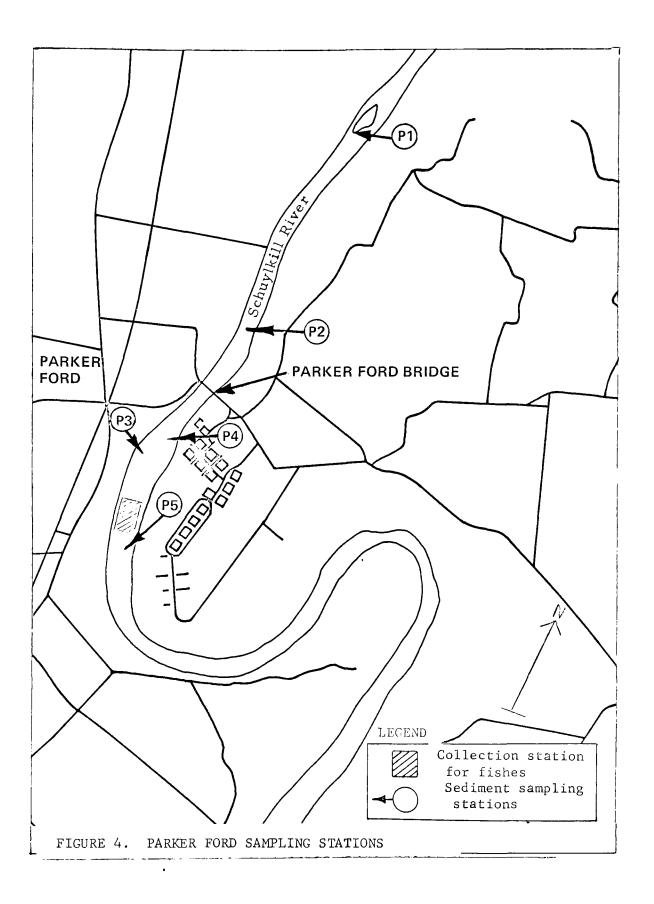
- --physical and chemical parameters of river water were monitored at upstream and downstream stations. Biochemical oxygen demand, chemical oxygen demand, alkalinity, temperature, dissolved oxygen, and hydrogen-ion concentrations were determined during the summer of 1972.
- --concentrations of lead, zinc, cadmium, and copper in the Schuylkill River water were determined on a daily basis from 3 July 1972 until 4 August 1972.
- --concentrations of the metals lead, zinc, cadmium, and copper, and of petroleum hydrocarbons were determined in Schuylkill River sediment samples collected in November, 1972.
- --concentrations of the heavy metals lead, zinc, cadmium, copper, and mercury were determined in macrofauna collected from the river in winter 1972 and summer 1973.
- --levels of polycyclic aromatic and aliphatic hydrocarbons were determined in fishes from the Schuylkill River.
- --other possible effects of the spill were monitored. Average levels of total and active chlorophyll <u>a</u> were measured in July, 1972. Zooplankton were collected at stations upstream and downstream from the spill, and major taxon diversity was determined. Benthic macrofauna were sampled upstream and downstream from the spill and ranges of abundance of the dominant macrofaunal taxons determined. The types and abundance of bacteria in Schuylkill River sediments were determined during the summer of 1972. Using diurnal curve techniques, community respiration, including that of the bottom community, was determined during July of 1972.
- --clean-up operations were monitored, and recommendations were submitted to the EPA on a day-to-day basis during July, 1972. Recommendations for the handling of similar spills are included in this report.

This report summarizes work conducted under Basic Ordering Agreement 68-01-0701, Delivery Order 1, a study of the immediate effects of the spill and work under Contract 68-01-0781, a follow-up study of the longer-term effects of the oil spill.









MATERIALS AND METHODS

1. DESCRIPTION OF SAMPLING STATIONS

A. <u>Vegetation</u>

Bark and leaf samples were collected from sampling stations on the banks of the Schuylkill River in heavily oiled areas near Unionville and Pottstown Bridge (Route 100), and from a control station on the southwest bank of the Schuylkill at Monocacy Farm, approximately 1/2 mile upstream from the site of the spill. These stations are shown on Figures 1 through 3.

B. River Water

River water samples for heavy metals and physical and chemical analyses were collected at Monocacy Bridge, Douglassville Bridge, Parker Ford Bridge, Spring City-Royersford Bridge, and Falls Bridge at Philadelphia. These bridge locations are shown on Figure 1.

C. <u>Fishes for Petroleum Hydrocarbon and Heavy Metals</u> Analyses

Fishes were collected at stations in the Monocacy area 1.3 miles upstream from the spill, Figure 2, and from the Parker Ford area, Figure 4, 11 miles below the spill.

For the analysis of fish from a clean environment, channel catfish were taken from Harrison Lake National Fish Hatchery located on Route 5 between Williamsburg and Richmond, Virginia.

D. Sediment

Sediment samples for heavy metals and hydrocarbon analyses were collected in the Monocacy area, 2.1 miles above the oil spill, in the Douglassville area 0.4 and 2.3 miles downstream from the oil spill, and in the Parker Ford area 10.6 to 12.5 miles downstream from the oil spill. Figures 2, 3, and 4 show the locations of these sample stations. The characteristics of each station are shown in Table 1.

E. Benthic Macrofauna

Benthic organisms for biological and heavy metals analyses were collected at the sediment sampling stations discussed above.

F. Zooplankton and Phytoplankton Pigment

Plankton were sampled from Monocacy Bridge and Parker Ford Bridge. Locations of these stations are shown in Figure 1.

TABLE 1 Location and Characteristics of Schuylkill River Sediment Sampling Sites

| IDENTIFICATION | DISTANCE FROM SOURCE OF SPILL (Miles) | CHARACTERISTICS |
|----------------|---------------------------------------|--|
| Monocacy | | |
| Monocacy | 2.1 above | Downstream edges of small island |
| Douglassville | | |
| DI | 0.4 below | Downstream edge of small island (1-3 ft. deep) |
| D2 | 1.0 below | Downstream edge of island (1-3 ft. deep) |
| D3 | 1.7 below | Downstream of small islands (1-3 ft. deep) |
| D4 | 2.1 below | Behind snag (1-3 ft. deep) |
| D5 | 2.3 below | Downstream of small islands |
| Parker Ford | | (1 ft. deep) |
| P1 | 10.6 below | Downstream edge of large island (2-4 ft. deep) |
| P2 | 11.4 below | Over shoal area (2 ft. deep) |
| P3 | 12.0 below | In mouth of creek (6 ft. deep) |
| P4 | 12.0 below | Over shoal area (2 ft. deep) |
| P5 | 12.5 below | Open river (5-6 ft. deep) |

2. <u>ANALYSES OF VEGETATION</u>

Ground and air surveys were made in July, 1972, to determine the extent and severity of damage to trees. Follow-up surveys were conducted in the fall of 1972 and the spring and summer of 1973. Individual specimens of various species were selected within the upstream (Figure 2) and downstream (Figure 3) sampling stations and marked with plastic tape so that their recovery could be monitored during fall bud-set and spring leaf formation. Sections of branches and bark from oil-soaked trees within the sampling stations were removed and placed in vials of fresh Formalin Acetic Acid and Alcohol (FAA) killing and preserving fluid (Sass 1958). Sections were allowed to stand in the killing and preserving fluid for three weeks to become sufficiently rigid. Freehand sectioning was used to obtain thin cross sections that were stained, mounted, and examined to determine the extent and effects of oil penetration.

3. PHYSICAL AND CHEMICAL ANALYSES OF RIVER WATER

Dissolved oxygen was determined in the field using the modified Winkler micromethod with a LaMotte dissolved oxygen kit (Model EDO, Code 7414). Hydrogen-ion concentration (pH) was measured in the field with a LaMotte electrode kit (Model HA, Code 1901).

BOD, COD, and alkalinity were determined per <u>Standard</u> <u>Methods</u>, 13th ed. Samples were collected in polyethylene containers, refrigerated, and delivered to the laboratory within four hours of collection.

4. HEAVY METAL ANALYSES

A. <u>Leaves (Dry Ash Method)</u>

Leaves from the spring 1973 growing season were taken for analysis. They were stored in clean polyethylene bags until analysis. To remove surface contamination, the leaves were washed: they were wet in a 0.1% ivory soap solution, rinsed once in tap water, and then again in distilled water. Ten to fifteen leaves from each species were composited and analyzed for lead, zinc, cadmium, and copper using a dry-ashing technique. The procedure is:

Sass, J. E. 1958. <u>Botanical Microtechnique</u>. Iowa State University Press, Ames, Iowa, 228 p.

- (1) Dry leaves for two days at 85 °C.
- (2) Grind sample to finely divided particles in a Wiley mill.
- (3) Weigh out 1 g of particles into a crucible for dry ashing at 500 $^{\circ}$ C for one hour in a muffle furnace.
- (4) Cool and dissolve ash in 5 ml of 12HCl diluted
- (5) Take the sample to dryness by evaporating HCl off on hot plate.
 - (6) Redissolve residue in 4 ml HCl diluted 19:1.
 - (7) Filter solution through filter paper.
- (8) Bring filtrate to 25 Ml in a volumetric flask with distilled water.
- (9) Set up standard curves for each element in question, and analyze samples with atomic absorption spectrophotometer (Perkin-Elmer Model 303).

B. River Water

Since the sensitivity of the atomic absorption method is limited by the instrument, organic extractions and concentrations had to be utilized for the metals cadmium and lead.

The procedure used was that of the Environmental Protection Agency as described in: Methods for Chemical Analysis of Water and Wastes (1971).

The values for copper and zinc were obtained by direct aspiration of the water since the permissible levels of these metals for water supplies were above the sensitivity of the instrument.

C. Sediments

Composite samples from ten downstream stations

U. S. Environmental Protection Agency, 1971. Laboratory Branch, Inter-Office Correspondence.

(Figures 3 and 4) and one upstream (control) station (Figure 2) were observed to determine if, and in what quantities, oil had been deposited in the river. Ten to twenty (10-20) subsamples were taken at each site with a .25 ft. Ekman dredge. Attempts were made to sample the upper 2-3 inches of sediment. Samples were stored in clean polyethylene bags.

The non-crystalline forms of lead, zinc, cadmium, copper, and mercury were analyzed using atomic absorption techniques. Since it is likely that the surface area of sediments affects the amount of oil-metals accumulated, each subsample was wet sieved (U. S. standard sieve, No. 230, 63 micron openings) to assure that each composite sample was similar in particle size distribution, thereby allowing a better comparison among locations. The sieved subsamples were than air dried and 1 g portions of each were combined to obtain the composites.

The procedure for extracting lead, zinc, cadmium, and copper is:

- (1) Place 1,000 g of samples in an acid-washed Phillips beaker.
- (2) Add 5 ml of concentrated HNO₃ (Boxes Ultrex, if possible).
- (3) Heat until solution begins to boil, being careful not to lose sample by bumping.
 - (4) Allow sample to cool. Repeat Steps 2 and 3.
 - (5) After cooling, add 10 ml of distilled water.
 - (6) Centrifuge and save supernatent liquid.
- (7) Set up standard curves for each element in question and analyze with Varian AA-5 atomic absorption spectrophotometer.

Analyses of replicate samples extracted by this method showed a precision of $\frac{1}{2}$ 8% for lead, $\frac{1}{2}$ 5% for zinc, $\frac{1}{2}$ 3% for cadmium, $\frac{1}{2}$ 7% for copper and $\frac{1}{2}$ 10% for mercury.

The method for mercury consisted of sulfuric acidpotassium permangenate oxidation and a reduction step with hydrooxylamine sulfate--stannous sulfate. The analyses were performed on a Coleman mercury analyzer which had been modified with a quartz flow cell and recorder attachment. This method has been utilized successfully on sediments elsewhere (Huggett, et al; 1971).

D. Biota

Benthic organisms and fishes were analyzed for lead, zinc, cadmium, copper, and mercury after digestion in concentrated nitric acid, as performed by Huggett, et al; (1973).

Replicate analyses of all biota were performed by atomic absorption spectrophotometry using a Varian AA-5 instrument.

5. PETROLEUM HYDROCARBON ANALYSES

A. Sediment

The composite samples, each composed of ten to twenty subsamples, from the ten downstream (Figures 3 and 4) and one upstream (Figure 2) sample sites were extracted and analyzed by flame ionization gas chromatography to obtain an estimate of oil content.

The procedure of extraction and cleanup is given in detail here, since in the problem of oil pollution gas chromatography results are comparable only if obtained in the same manner.

- (1) Place 5 g of each dried composite sample into a clean 125 ml Erlenmeyer flask.
- (2) Add 50 ml benzene-methanol azetrope (benzene 60.4%, methanol 39.6%) and 50 ml n-heptane.
- (3) Allow to stand twenty-four hours and then place in an ultrosonic bath for fifteen minutes.
- $\ensuremath{\text{(4)}}$ After settling, decant heptane/azetrope solution into glass tubes and centrifuge.

Huggett, R. J., M. E. Bender, H. D. Sloan. 1971. Mercury in sediments from three Virginia estuaries. Ches. Sc. 12:4. 280.

Huggett, R. J., M. E. Bender, H. D. Sloan. 1973. "Utilizing metal concentration relationships in the Eastern oyster (crasostrea virginica) to detect heavy metal pollution." Water Res. 7:451-460.

- (5) Transfer supernatent liquid into 300 ml roundbottom flasks and evaporate on a rotary vacuum dryer until disappearance of the azetrope fraction (bottom layer disappears when temperature of flask increases to 260 C).
- (6) Pass the partially evaporated samples through a chromatographic column consisting of activated alumina (AG-7, 100/200 mesh, 4.1% H₂O), eluted with 3 ml of heptane. Evaporate samples to 0.25 ml and inject portions into the gas chromatograph.

B. Petroleum Hydrocarbons in Fishes

The analytical procedure which was used to determine the kinds and amounts of petroleum hydrocarbons in fish is complex and time-consuming, and some of the techniques reported below were developed solely for this investigation.

The procedure reported below is that of a typical run on a fish sample of upstream white suckers taken from the Monocacy area (Figure 2), and each step was performed sequentially. Any variations in sample sizes and weights of products obtained with other fish samples (and spilled crankcase oil waste) are discussed in the Results and Discussion, page 48.

Samples were packed in dry ice and shipped in insulated chests. The samples were thawed to remove flesh for heavy metals analysis, then refrozen and kept in cold storage until analysis.

(1) General Laboratory Precautions

The following laboratory precautions were practiced to minimize error, contamination, and decomposition during the analysis of hydrocarbons:

- a. Samples were stored in either a dark cabinet or in brown bottles capped with aluminum foil liners, since ultraviolet radiation is known to decompose polycyclic aromatic hydrocarbons.
- b. The laboratory was equipped with General Electric F-40-G $_0$ yellow fluorescent lamps to minimize ultraviolet light.

- c. Observations of fluorescent zones during chromatography, using a Gelman Camag ultraviolet lamp at 350 nanometers, were held to a minimum to avoid hydrocarbon decomposition.
- d. Smoking was not permitted in the laboratory to avoid possible contamination of samples.
- e. All glassware (and grinding/blending equipment) was detergent-washed, rinsed in water followed by acetone, and dried under an infrared lamp or in the atmosphere. It was further rinsed in fractionated benzene and dried under an infrared lamp prior to use.

(2) Solvent Purification

All solvents (except where specified) were purified by fractionation of 2.5 liter batches, under nitrogen, through a 22 x 2.3 (ID) cm column packed with cut glass tubing. The all-glass apparatus was assembled using ungreased ground joints and protected from the atmosphere with a tube of anhydrous calcium sulfate. The first 250 Ml forerun and last 250 Ml pot residue of each batch were discarded. Fractionated solvents were stored in metal foil-lined capped brown bottles. Ethyl ether used in column chromatography was glass-distilled from Burdick and Jackson Laboratories, Inc.

(3) Extraction of Oils from Fish

Materials used were fractionated benzene, Fisher B-245(see previous Solvent Purification Section); anhydrous magnesium sulfate, Fisher M-65, which was Soxhlet extracted forty-eight hours with fractionated benzene before use, and dried under an infrared lamp.

Blending and extraction procedures are as follows:

- a. Grind two to three fish specimens with a standard meat grinder into a porcelain dish and mix with a spatula.
- b. Weigh, to the nearest gram, about 500 g of ground fish into a one-quart stainless steel Waring blender, and partially blend.
- c. Add 7% by weight of benzene for the purpose of aiding the grind, and blend until a "fish soup" after blending to determine the losses of volatiles.

- d. Weigh the "fish soup" after blending to determine the losses of volatiles.
- e. Weigh 250 g of "fish soup" into a beaker and immerse in ice.
- f. Add 180 g of preextracted anhydrous magnesium sulfate and stir until a solid mixture is formed.
- g. Regrind blend in a Waring blender to a powdery consistency (some lumpy material cannot be eliminated, however), to give a "fish powder".
- h. Weigh approximately 100 g of 'fish powder' sample into a Soxhlet thimble which has been previously extracted for forty-eight hours with benzene.
- i. Extract "fish powder" for twenty-four hours in refluxing benzene.
- j. Strip benzene extract of solvent at the water pump on a hot water bath using a rotary evaporator by trapping the benzene distillate in a filter flash assembly immersed in ice water, and save the fish oil residue.
- k. Repeat steps (h) and (j) with a fresh fish powder sample and combine the oils obtained in step x.

Assuming the losses in volatile material from step (d) to be the added benzene, the fraction of fish in the fish "soup" can be calculated as:

fraction of

weight original ground fish

fish in =

final weight fish soup

fish "soup"

The percent fish in the final "fish powder "is then calculated as:

% fish in

= wt. fish soup x wt. fraction fish in fish "soup" 100

wt. fish soup + wt. MgSO₄

 $\label{eq:the_samples} The \ extraction \ data \ for \ the \ samples \ processed \ are \ given \\ in \ Appendix \ V-1.$

(4) Saponification of Oil Extracts.

Materials used were 6N KOH (Fisher USP) in fractionated methanol; cyclohexane, Fisher C-556, fractionated; benzene, Fisher B-245, fractionated; sodium chloride, Fisher S-271; magnesium sulfate, Fisher M-65, preextracted forty-eight hours with fractionated benzene.

Saponification procedures are as follows:

- a. Mix extracted oil with 6N potassium hydroxide and leave at room temperature for forty-eight hours.
- b. Dilute mixture with water, transfer to a 500 ml separatory funnel, and extract twice with cyclohexane and twice with benzene. Combine extracts.

The separation of the layers in this step was difficult. The addition (and mixture) of solid sodium chloride in the separatory funnel for as long as twelve to sixteen hours helped to break the emulsions. In those cases where a clear cut separation of the layers could not be achieved, the top hydrocarbon layer was separated with a pipette so that a clear hydrocarbon extract devoid of interfacial material was obtained for the next step.

- c. Wash hydrocarbon extract with about 25% its volume of IN sulfuric acid (twice) and water (twice).
- d. Dry extract over anhydrous sulfate and filter off the magnesium sulfate using a medium-porosity sintered glass funnel (Pyrex #36060) washed with benzene.
- e. Evaporate extract leaving a viscous oil to be used for column dromatography.

The data, including volumes of 6N KOH, volumes of water and solvents used, etc., are given in Appendix V-2.

(5) Column Chromatography of Saponified Extracts.

Materials used were aluminum oxide (alumina), basic, Type E, (activity I), Brinkmann Instruments, Inc., without

further purification; anhydrous magnesium sulfate, Fisher M-65, preextracted forty-eight hours with fractionated benzene; cyclohexane, Fisher C-556, fractionated; benzene, Fisher B-245, fractionated; ethyl ether, glass distilled, Burdick and Jackson Laboratories, Inc.; chromatographic column (Fisher Porter) 5.0 cm ID fitted with a fritted disk and stopcock, A. H. Thomas catalog Nos. 2726-Q82, -R20, -R83, -S42.

Chromatographic procedures are as follows:

- a. Mix saponified extract with four times its weight of basic alumina, blanket with a little cyclohexane, and leave for forty-eight hours at room temperature.
- b. Assemble chromatographic column (5.0 or 2.0 cm inside diameter) with a fritted glas disc and stopcock at its base, and partially fill with cyclohexane. Add alumina from the top, stir in the cyclohexane, and allow to settle. Add anhydrous magnesium sulfate equal to 10 percent of the weight of alumina, stir, and allow to settle.
- c. Place slurry of alumina/sample/cyclohexane (from a) in the chromatographic column and open the stopcock to allow the cyclohexane to approach the level of the top of the sample (save eluate).
- d. Collect the following three fractions from the column:
 - -- cyclohexane fraction
 - -- benzene fraction
 - -- 90:10 benzene; ethyl ether fraction
- e. Strip cyclohexane fraction at the water pump on a hot water bath.
- f. Combine benzene and benzene-ethyl ether fraction and strip solvent at the water pump.
- g. Reserve the non-volatile hydrocarbon residues from (e) and (f) for infrared and gas chromatographic analysis.

 $\label{eq:the column chromatographic} The data for the column chromatographic step are given in Appendix V-3.$

(6) Infrared and Gas Chromatographic Analysis

Infrared spectra of all hydrocarbons were determined as smears between salt plates on a Bausch and Lomb Schimadzu Spectronic 250 infrared spectrophotometer. After analysis, the samples were reisolated from the salt plates by washing with fractionated benzene. The benzene solvent was stripped at the water pump to leave the hydrocarbons which were subsequently analyzed by gas chromatography.

Gas chromatography of the cyclohexane eluate was performed on a Varian Aerograph Model 2720 using 7' x 1/8" 1.5 percent OV-17 on Chromosorb G 100/120 DMCS for the cyclohexane fraction. All runs were programmed from 50-293°C at 8°/min using N2 carrier gas at 22 psig. Injector and detector temperatures were 216°C and 270°C, respectively.

Gas chromatography of the aromatic hydrocarbons from benzene-benzene/ethyl ether eluate was performed on the same instrument using a 7' x 1/8" 4.5 percent SE-52 on Chromosorb G 100/120 DMCS at 50-293° at 8°/min using N2 carrier gas. For gas chromatography of hydrocarbons from benzene-benzene/ether fraction obtained from the Harrison Lake fish samples and standard hydrocarbon mixture, the isothermal hold period was set at 300°C.

The benzene-eluted compounds from column chromatography of the Harrison Lake samples were each treated with a known quantity of triphenylmethane just before gas chromatography.

The infrared spectra are given in Figs. 13-23, and gas chromatograms are given in Figs. 24-41. Gas chromatograms pertaining to Harrison Lake fish are shown in Figs. 42-47.

6. BIOLOGICAL ANALYSES OF RIVER BIOTA

A. Chlorophyll a

Chlorophyll <u>a</u> samples were filtered in the field on GF/C filters and shipped in darkened ice containers to the laboratory where they were frozen and kept darkened until analysis. They were analyzed

by standard spectrophotometric techniques (Lorenzen, C.J., 1966 & 1967) that measure pigment fluorescence within two days of field collection. Since most petroleum products also emit fluorescence, tests were performed to determine if presence of oil in the river would bias chlorophyll a readings. Oil from the Berk Associates plant was added to three water samples (collected from an area not contaminated by the oil spill) at concentrations of . 4 percent and compared to three controls lacking oil. total chlorophyll a levels were similar between treated and control samples, active and dead chlorophyll a concentrations in the oiled samples averaged 64% higher (7.4 as compared to 4.5 mg/1) and 32 percent lower (10.4 as compared to 15.3 mg/l), respectively, than in the controls. Thus, spectrophotometric techniques may tend to overestimate the ratio between live and dead pigments below the oil spill. This bias is probably minimal due to the relatively low oil levels found in the river (measured in ppm) as compared to the amounts added in these tests.

B. Zooplankton

Zooplankton samples were collected with a #12-mesh metered net (2-ft diameter), preserved in 10 percent formalin, and subsampled to determine organism abundance.

C. Benthic Macrofauna

Macrofauna were collected with a .25 ft² Ekman dredge, preserved in 10 percent formalin, and washed onto a 1.mm screen prior to separation. Organisms in the more important taxons were identified down to the generic level.

D. Ba**c**teria

Sediment samples for bacteria analysis were placed in sterile petri dishes in the field and transported in ice to the laboratory where several decimal dilutions were prepared by placing 11 g of mud sample into 99 ml of sterile buffered dilution water. The mixture was

Lorenzen, C.J. 1966. "Method for the Continuous Measurement of Invivo Chlorophyll Concentration," <u>Deep Sea Research</u>, Vol. 13, pp. 223-227.

Lorenzen, C.J. 1967. "Determination of Chlorophyll Pheo-Pigments: Spectrophotometric Equations," Limnol. Oceanography, 12:343-345.

shaken twenty-five times and transferred (11 ml) to each successive 99 ml dilution bottle. Bacteriological counting procedures were as follows:

- (1) Standard plate count. Estimation of viable aerobic, mesophilic, heterotrophs was made by spreading 0.1 ml portions of diluted samples on plates of tryptone glucose extract agar using sterile glass rods. Colony counts were made after five days at 25°C.
- (2) Hydrocarbon oxidizers. Bushnell-Haas medium was prepared from ingredients and solidified with 1.5 percent agar (Oxoid brand Ion-agar No. 2). B-H medium is a mineral-salts base without carbon source and supposedly does not support bacterial growth unless a suitable carbon source is added. For counts of hydrocarbon oxidizers, spread plates of suitable dilutions were prepared on B-H agar and inverted with 0.1 ml of kerosene added to the lid. In a few instances, additional plates were prepared, and 0.1 ml of sterile dodecane was pipetted to the surface of the inoculated, non-inverted plates.
- (3) Casein hydrolyzers. Spread plates of nutrient, agar containing 10 percent (v/v) of sterile skim milk were made, and colonies showing zones of clearing (hydrolysis) were counted.
- (4) Amylolytic organisms. Nutrient agar containing 0.2 percent of soluble starch was used to prepare spread plates. After flooding with iodine solution, colonies surrounded by clear zones were counted.
- (5) Fermentative bacteria. Tubes containing 10 ml of purple broth base (BBL) plus 0.5 percent glucose were inoculated in triplicate with 1.0 ml of appropriate dilutions. These showing acid production (yellow indicator) were scored positive and used to determine mpn values from standard tables.
- (6) Sulfate reducing bacteria. From the initial 1:10 dilution of mud sample, 1.0 ml portions were transferred to 9 ml of sulfate reducer agar API (Difco) at 450°C in screwcapped tubes. Serial decimal dilutions were made in the molten agar. After twenty-one days at 25°C in an anaerobic jar, tubes showing blackening were scored positive and MPN values determined.

E. Dissolved Oxygen and Community Respiration

Oxygen measurements were taken throughout the twenty-four hour daily cycle and used to estimate gross primary productivity and community respiration according to the diurnal-curve method of Odum (1956). The single-curve modification was employed. Corrections for diffusion were obtained by assuming the coefficient of gas transfer (K) to be 2.0 g/m²/hr at 0 percent saturation (estimated from Odum's table 1). Community respiration was determined by extrapolating the diffusion-corrected hourly predawn oxygen decrease (measured in ppm) to the twenty-four hour daily cycle and multiplying by river depth. Gross primary production was calculated by measuring the area between the diffusion-corrected rate-of-change curve and a horizontal line drawn through the predawn hours and multiplying by river depth. Depth at both sampling stations was about 1 m.

F. Food Habits of Fishes

Fishes were captured by hook and line and net. Stomachs were extracted, slit along one surface to allow rapid preservation of contents, wrapped in gauze stripping, and shipped in 10 percent formalin to the laboratory.

7. OBSERVATIONS OF SHORE CLEANUP IMPACT AND EFFECTIVENESS

Cleanup operations were monitored by direct observation for the first five days and recommendations submitted on a daily basis during July, 1972. Hosing operations removed oil from sight but put it into the river where the effects where the effects may be more serious.

Booms properly and rapidly deployed in reaches of the river with currents less than 2 knots will permit containment of the oil for pickup by vacuum trucks or other oil collection systems.

Burning of oil-covered debris and recovered oil was not considered judicious since burning releases lead and other heavy metals in their most harmful vapor form.

Pools of oil along the shore line were observed requiring cleanup since several were running into the river.

Odum, H. T. 1956. "Primary Production in Flowing Waters," Limno. Ocean. 1: 102-117.

RESULTS AND DISCUSSION

1. PROPERTIES OF SPILLED CRANKCASE OIL WASTE

The spilled oil had a specific gravity of 0.97. A sample of spilled crankcase oil waste (SCOW) collected from the riverbank near Unionville in July of 1972 contained 33 percent petroleum hydrocarbon, 51 percent water, 13 percent insoluble residue, and 3 percent water soluble remainder by difference. Direct distillation of the SCOW up to 185°C yielded approximately 0.5 percent organic volatile material.

Visual inspection of the spilled oil suggested that it contained mostly tars and aliphatics. The oil sample contained 48 percent aliphatic hydrocarbons and 4.5 percent aromatic hydrocarbons.

The spilled oil contained high concentrations of the heavy metals lead, zinc, cadmium, and copper (Table 2). An analysis of oil samples from the storage pits, conducted by the Environmental Protection Agency in 1971 (Table 3), also indicated the presence of heavy metals.

2. EFFECTS OF THE OIL SPILL ON VEGETATION

A. General

A survey, taken on 1 and 2 July 1972, of oiled riverbank areas from the spill site to Valley Forge revealed that trees along both banks of the Schuylkill River were extensively coated with spilled oil (Figure 5) to a height of approximately 20 to 25 feet above the normal river level (Figure 6) with the trees in the Douglassville area most heavily coated. No variation in oil thickness at different tree heights was noted. However, the upper, uncoated foliage did not show symptoms of damage.

The riverbank tree community had sustained considerable damage by the force of the river water which pushed the trees over and, in some cases, uprooted them. This type of mechanical damage occurred all along the river and was not related to the oil-coating problem. It was observed during an air survey on 1 July that the foliage of some uprooted trees in the river was trapping and collecting the floating oil. Since the foliage would probably release oil into the river over a period of weeks, it was recommended that these oil-coated and uprooted trees by removed to a disposal site.

TABLE 2 Constituents of Spilled Crankcase Oil Waste Collected Near Douglassville Bridge in July, 1972

HEAVY METALS

| Lead | 16,300 ppm + 6% |
|---------|-------------------------|
| Zinc | 1,960 ppm ± 2% |
| Cadmium | 5.1 ppm ⁺ 6% |
| Copper | 87 ppm ⁺ 2% |
| | |

% Solids: 11.1%

HYDROCARBONS

| | Water | 51% |
|---|-------------------------|-----|
| | Hydrocarbon Oil | 33% |
| - | Insoluble Residue | 13% |
| | Water Soluble Remainder | 3% |

POLYCHLORINATED BIPHENYLS

Test: negative, sensitivity 0.5 ppm

Mean of replicate analyses.

TABLE 3 Heavy Metal Concentrations in Waste Crankcase Oil Samples Collected and Analyzed in 1971 by the U. S. Environmental Protection Agency

| Element (mg/kg of oil) | Sample 14604 | Sample 14612 | Sample 14631 | Sample 14634 |
|---------------------------|-----------------|-----------------|-----------------|-----------------|
| | | | | |
| Zinc | 1,800 | 2,100 | 165 | 350 |
| Cadmium | 10 | 9 | 5 | 16 |
| Arsenic | 50 | 45 | 25 | 80 |
| Boron | 5 | 18 | 25 | 8 |
| Phosphorous | 50 | 1,700 | 970 | 950 |
| Iron | 2,500 | 2,200 | 128 | 96 |
| Molybdenum | 20 | 18 | 10 | 30 |
| Manganese | 58 | 63 | 5 | 64 |
| Aluminum | 430 | 560 | 85 | 66 |
| Beryllium | 0.1 | 0.1 | 0.05 | 0. |
| Copper | 210 | 190 | 18 | 41 |
| Silver | 1 | 0.8 | 0.5 | 2 |
| Nickel | 10 | 8 | 5 | 16 |
| Cobalt | 10 | 0.8 | 9.9 | 31 |
| Lead | 10,000 | 19,000 | 5,200 | 6,600 |
| Chromium | 16 | 28 | 3 | 10 |
| Vanadium | 22 | 18 | 22 | 48 |
| Barium | 360 | 740 | 24 | 1,600 |
| Strontium | 64 | 2.7 | 5,8 | 3. |
| | | | | |



Figure 5 Extensively Oiled Riverbank Vegetation

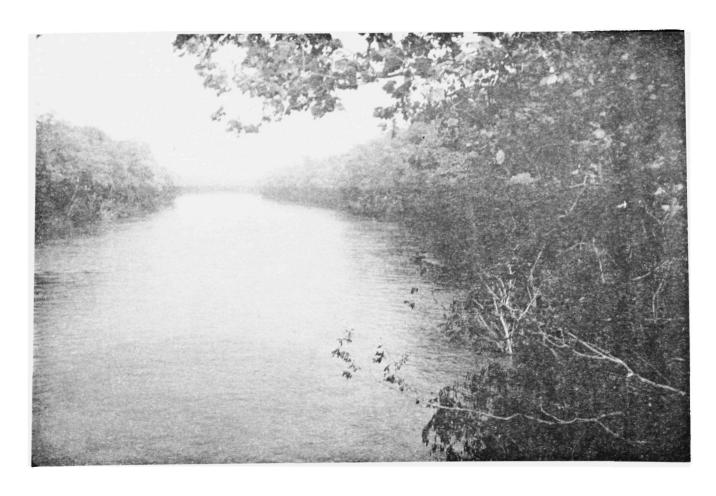


Figure 6. Oil-coated riverbank vegetation along the banks of the Schuylkill River in July, 1972

Many tree species at the Douglassville Bridge sampling station were developing new leaves from the oil-coated branches as early as 8 July 1972. This indicated that the growing points had not been killed by the oil and that biological recovery was progressing in spite of presence of oil on the soil, foliage, and trunks. Herbaceous plants on the riverbank were beginning to show signs of recovery.

A winter survey was made on 3 January 1973 of the trees along the riverbank at Douglassville Bridge, Unionville, Parker Ford, and other points to examine the terminal and lateral buds of several mixed stands of trees. Longitudinal and cross-section of buds and small twigs were made on the scene and examined for evidence of tissue necrosis. Internode lengths of the trees were also examined and compared to the previous season's growth. There was no evidence that the buds of the oil-soaked trees were dying nor was there any obvious indication of decreased growth rates. Dormant buds on the trees were plentiful and appeared to be normal. Some dead trees were still coated with oil. However, they were relatively few compared to the population of trees examined. Some trees had a few dead, oil-coated branches. It was expected that these dead branches would become infected with wood-rotting pathogenic fungi which would invade the main trunk and eventually kill the tree.

Additional checks on the recovery of the deciduous tree community were made during the spring and summer of 1973. The results of these surveys were basically the same. No unusual symptoms of permanent damage were found. During the summer survey, some dead branches were found; and there was evidence of invasion by wood-rotting fungi. In general, however, the trees and herbaceous species in affected areas showed excellent recovery.

There was one exception to the remarkable recovery of the tree community. Evergreens and other ornamental species in the yards of private residences along the river had been severely damaged. Damaged trees included conifers, such as pines, hemlocks, firs, and spruces. Other evergreen species that suffered damage were yews and junipers (Figures 7 and 8). The growing pattern of evergreens is much different than that of the deciduous trees. Deciduous trees were able to shed their damaged leaves. In contrast, conifers shed their needles very slowly and are unable to rid themselves of damaged tissue that can cause harm to affected branches. Many oil-soaked evergreens in private residences have lost their aesthetic value and are probably irreparably damaged.

Oil Level



Figure 7. Oil-coated ornamental evergreens 10 days after the oil spill



Figure 8. Oiled evergreens 1 year after the oil spill

B. Penetration of Oil Through Bark

Freehand, stained sections of oak, maple, and sycamore tree bark revealed that oil which was tenaciously attached to the outer bark did not appear to penetrate beneath the surface to any great degree (Figure 9). Penetration was probably prevented by the cork layer. Oak and maple have relatively thick cork layers compared to sycamore. However, the bark of sycamore is exfoliative and falls off in time.

C. Heavy Metals in Tree Leaves

Plants have been shown to accumulate metals from their surroundings. One potential long-term effect of this spill was viewed as the uptake of toxic concentrations of heavy metals from the oil-coated soil or through the bark. Thus, a study of heavy metal accumulation was conducted. Based on the analyses of the oil (Tables 2 and 3), the metals selected for study were lead, zinc, cadmium, and copper. The study was designed to detect trends of abnormally high accumulations of heavy metals derived from the oil which may have correlated with any observed symptoms of phytotoxicity. Sampling was concentrated on those species representative of the mixed deciduous forest along the banks of the Schuylkill.

Data from the heavy metals analysis of the leaves collected at Monocacy, Douglassville, and Parker Ford in May, 1973, is presented in Tables 4, 5, and 6.

A non-parametric sign test (Snedecor and Cochran 1967) was applied to the pooled data of seven pairs of species at Monocacy Farm and Douglassville Bridge. Lead values were significantly greater at the 95 percent confidence level in affected leaves from the Douglassville Bridge area. The levels of other metals at oiled and control stations were not significantly different.

The statistically significant difference in lead concentrations between Monocacy Farm and Douglassville Bridge is probably not important in terms of well-being of the trees. Considerably higher amounts of lead are known to occur in many plant species. Smith (1973) reported difficulty in establishing "normal" levels of lead even after sampling trees in relatively unpolluted areas and comparing values to published concentrations obtained from similar areas. He

Snedecor, G. W., and W. G. Cochran. 1967. <u>Statistical</u> methods: Iowa State University Press, Ames, Iowa. 593 p.

Smith, W. H. 1973. "Metal contamination of urban woody plants." Envir. Sci. Tech. 7:631-636.



Figure 9. Cross-section of oiled oak bank magnified 613X

TABLE 4 Heavy Metal Concentrations in Tree Leaves Collected from Monocacy Farm in May, 1973

Heavy Metal Concentration (ppm)

0.8

米

0.5

0.8

0.5

No. of Trees Species Sampled Zinc Cadmium Copper Lead Maple 12 5.0 26.0 0.4 * Oak 7 6.0 28.0 * 0.4 Oak 7 5.0 21.0 0.6 岑 Sassafras 6 3.0 29.0 *0.5

4.0

5.0

6.0

20.0

73.0

24.0

l Mean of replicate analyses for each element from the pooled sample.

8

4

3

*Less than 0.5 ppm.

Sycamore

Black Walnut

Elm

TABLE 5 Heavy Metal Concentration in Tree Leaves Collected Near the Douglassville Bridge in May, 1973

| | N. of There | Heavy Metal Concentration (ppm) | | | opm) l |
|--------------|----------------------|---------------------------------|------|---------|--------|
| Species | No. of Trees Sampled | Lead | Zinc | Cadmium | Copper |
| Maple | 12 | 11.0 | 32.0 | * | 0.4 |
| Oak | 6 | 8.0 | 32.0 | * | 0.8 |
| Oak | 1 | 9.0 | 25.0 | * | 0.8 |
| Sassafras | 3 | 4.0 | 25.0 | ж | 0.6 |
| Sycamore | 1 | 6.0 | 20.0 | * | 0.8 |
| Elm | 8 | 10.0 | 25.0 | * | 0.4 |
| Black Walnut | 7 | 8.0 | 27.0 | ҂ | 0.6 |

Mean of replicate analyses for each element from the pooled sample.

^{*}Less than 0.5 ppm.

TABLE 6 Heavy Metal Concentrations in Tree Leaves Collected Near the Pottstown Bridge in May, 1973

| | | | Heavy Metal Concentration (ppm) | | |
|----------|-----------------------------|------|---------------------------------|---------|--------|
| Species | No. of Trees <u>Sampled</u> | Lead | Zinc | Cadmium | Copper |
| Oak | 4 | 6.0 | 22.0 | * | 0.5 |
| Oak | 2 | 6.0 | 24.0 | * | 0.4 |
| Sycamore | 5 | 5.0 | 30.0 | * | 0.6 |

Mean of replicate analyses for each element from the pooled sample.

^{*}Less than 0.5 ppm.

cited literature describing lead concentrations in unpolluted environments as approximating 1 ppm. Baumhardt and Welch (1972) reported lead concentrations from 3.6 to 27.6 ppm in symptomless corn leaves. Concentrations of lead in grasses along two highways ranged from 20 to 60 ppm (Chow 1970). Warren and Delavault (in Campbell and Mergard 1972) suggested that "normal" lead concentrations be considered to be 0.1 to 2.5 ppm. On the other hand, Mortvedt et al (1972) reported apparently healthy radish plants growing at concentrations of 2.3 ppm to 12,000 ppm lead. Lead levels in trees along the Schuylkill are not abnormally higher than concentrations reported in other investigations (Chapman 1966, Gauch 1972, Lounamaa 1956, Smith 1973). Similarly, Jones's (in Montvedt et al 1972) normal range for zinc is 25 to 150 ppm with zinc toxicity not occurring below 400 ppm.

3. PHYSICAL AND CHEMICAL PARAMETERS OF SCHUYLKILL RIVER WATER

Water temperature at Monocacy and Parker Ford Bridges (Appendix I-1) ranged from 21°C to 28°C during July, 1972. Oxygen levels (Appendix I-1) varied from lows of around 4.5 to 7.0 ppm in the

Baumhardt, G. R., and L. F. Welch. 1972. "Lead Uptake and Corn Growth with Soil-Applied Lead," J. Envir. Qual. 1:92-94.

Chow, T. J. 1970. "Lead Accumulation in Roadside Soil and Grass," Nature 225:295-296.

Campbell, I. R., and E. G. Mergard. 1972. <u>Biological Aspects of Lead: An Annotated Bibliography, Part I and Part II.</u> E.P.A. Publication No. AP-104.

Mortvedt, J. J., P. M. Giordano, and W. L. Lindsay (eds). 1972. Micronutrients in Agriculture, Soil Soc. Amer., Inc., Madison, Wisconsin. 666p.

Chapman, H. D. (ed.). 1966. <u>Diagnostic Criteria for Plants</u> and Soils, Div. Agr. Sci., University of California, Berkeley. 793 p.

Gauch, H. G. 1972. <u>Inorganic Plant Nutrition</u>, Dowden, Hutchinson, and Ross, Inc., Stroudsberg, Pa. 488p.

Lounamaa, J. 1956. "Trace Elements in Plants Growing Wild on Different Rocks in Finland," Ann. Bot. Soc. Vanamo 29:1-196.

Smith, W. H. 1973. "Metal Contamination of Urban Woody Plants," Envir. Sci. Tech. 7:631-636.

early morning to 5.5 to 8.0 ppm (about 62 to 91 percent saturation at 22°C) during midday. No differences were noted between upstream and downstream stations.

Alkalinity (Appendix I-2) ranged from 50 to 84 ppm with no apparent differences among upstream and downstream stations. Normal alkalinity in fresh water rivers and streams is about 0 to 200 ppm.

Daytime hydrogen-ion concentrations in July and August, 1972, (Appendix I-3) were 7.0 to 7.8 with maximum values usually occurring at the Valley Forge Bridge station. The presence of the highest values at Valley Forge suggests a downstream increase in primary productivity that is characteristic of many streams and rivers.

Biochemical oxygen demand (BOD) measurements taken during the summer of 1972 (Appendix I-2) ranged from 0.4 to 4.2 ppm. Highest levels were usually observed in the Douglassville Bridge - Parker Ford Bridge length of the river (0.7 to 11.7 miles below the oil spill).

Chemical oxygen demand (Appendix I-2) was between 5.38 to 15.44 during July and August, 1972. Maximum COD usually occurred in the length of the river between Douglassville Bridge and Spring City Bridge stations (0.7 to 16.4 miles below the oil spill).

4. CONCENTRATIONS OF METALS IN SCHUYLKILL RIVER WATER

Lead and zinc levels were generally highest directly below the oil spill (Douglassville-Parker Ford Bridge stations) until about mid-July, 1972 (Appendix II-1). Concentrations had dropped to background levels during the remainder of July. An increase in concentration was noted in August at Parker Ford. This trend is shown for lead in Figure 10. No differences in copper or cadmium levels were noted among stations sampled (Appendix II-1).

5. HEAVY METALS IN SEDIMENTS

Sediment's in the Schuylkill River were analyzed for lead, zinc, cadmium, and copper during the summer of 1972. During November of 1972 sediments were analyzed for lead, zinc, cadmium, copper, and mercury.

Data from the summer of 1972 is presented in Appendix II-2. The summer 1972 survey was conducted to determine if there were areas of oil or metals contamination from the spill. No such areas were found. The winter 1972 sampling was concentrated in areas where sediment deposition was expected.

FIGURE 10. CONCENTRATIONS OF LEAD IN SCHUYLKILL RIVER WATER FROM JULY 3 TO AUGUST 4 1972

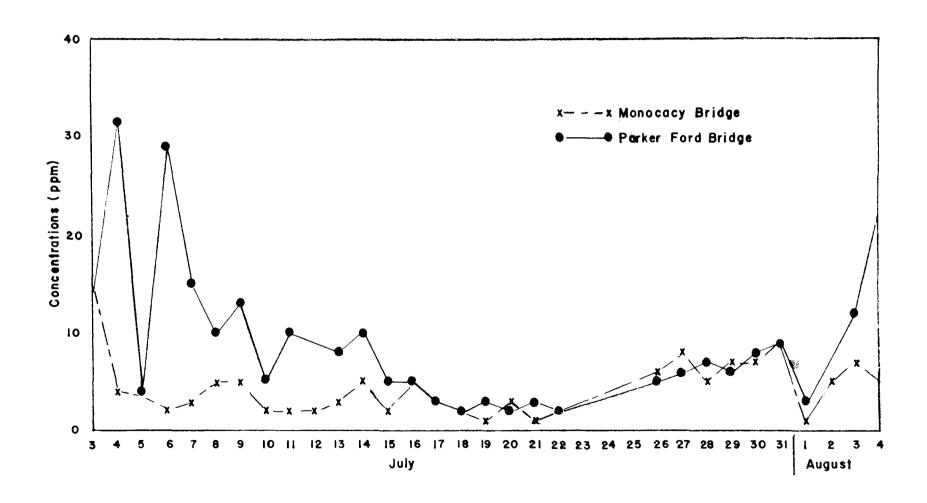
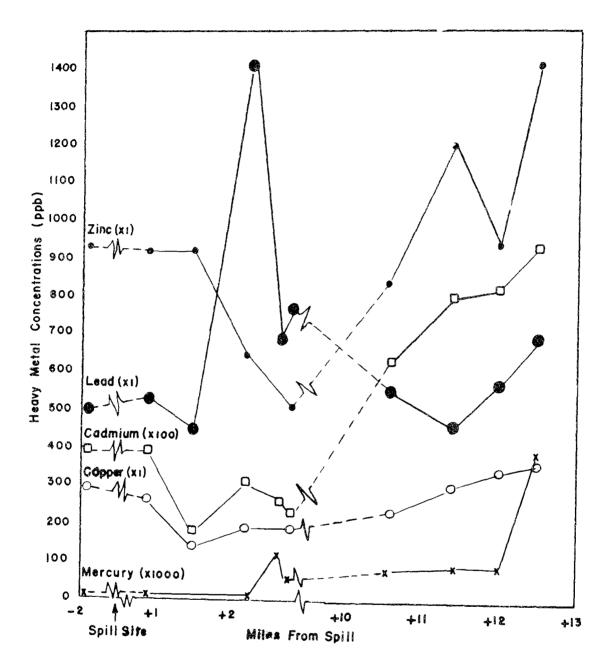


FIGURE 11. CONCENTRATIONS OF LEAD, ZING, CADMIUM,
COPPER AND MERCURY IN SCHUYLKILL RIVER
SEDIMENTS COLLECTED IN NOVEMBER 1972



¢.

Data from the winter analyses is presented in Figure 11. The existence of many possible sources of pollution in the river between Douglassville and Parker Ford preclude assignment of the spill as the cause of the increased metals levels. Data from the November, 1972, analyses are tabulated in Appendix II-3).

Concentrations of all heavy metals were analyzed by "t" tests, or modifications of this procedure (Guenther, 1964) if heterogeneity of variances existed between samples, to determine if levels below the oil spill were greater than those observed in the Monocacy area. Only lead levels were significantly higher below the spill. The calculated t value was 3.71 as compared to a tabled value of 2.05 at the .95 confidence level extrapolated to 4.5 degrees of freedom. However, the significance was due to one extremely high lead level (1,400 ppm) observed below the spill.

Table 7 compares concentrations of lead, zinc, and copper in the Schuylkill with concentrations of the same metals reported by Houser (1972) in the Potomac River.

TABLE 7 Comparison of Metals in Schuylkill River and Potomac River Sediments

| | Schuylkill Schuylkill | Potomac |
|--------------|-----------------------|---------|
| Lead (ppm) | 619.0 | 52.7 |
| Zinc (ppm) | 823.0 | 348.1 |
| Copper (ppm) | 234.1 | 70.2 |

Concentrations of these metals in the Schuylkill are significantly higher. It is realized that the Potomac is estuarine while the Schuylkill is fresh water. However, data presented by Hugget, et al (1972), for fresh water portions of the Rappahannock also suggest that

Guenther, W. C. 1964. <u>Analysis of Variance</u>, Prentiss-Hall, Inc., New Jersey. 23 p.

Huggett, R. J., M. E. Bender, H. D. Slone. 1972. Final Report to the Corps of Engineers, Norfolk Dist. Analysis of dredge spoils from the James and Elizabeth Rivers.

the Schuylkill has unusually high background levels of heavy metal pollution. Levels of zinc and copper in the Schuylkill at the control (Monocacy) site are ten times higher than in the Rappahannock.

6. PETROLEUM HYDROCARBONS IN SCHUYLKILL RIVER SEDIMENTS

Gas chromatograms of oil from sediment composites collected in November, 1972, from above and below the spill (Appendix III-1 through III-12) show very high unresolved backgrounds.

The relative amounts of petroleum hydrocarbons in the sediment composites were computed using data on instrument attenuations, volumns injected, and the areas under the chromatograms. Relative concentrations at downstream stations as compared to Monocacy (control station) are shown in Figure 12. The underlying assumption was that hydrocarbons in the unresolved backgrounds of each chromatogram were of similar nature. In general, downstream stations show a much higher concentration of petroleum hydrocarbons than the upstream control stations. Levels were especially high directly below the oil spill. However, the upstream control stations exhibited the same types of oils, although at lower concentrations, as observed at the other stations.

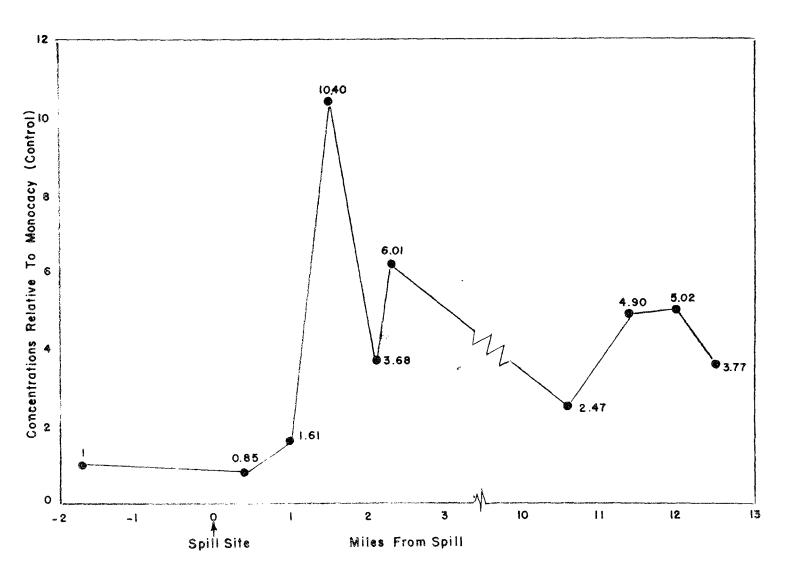
One subsample of a composite collected 1.7 miles below the spill was highly contaminated with oil, as evidenced by smell and visible sheen when mixed with water. Since the sample apparently contained the most oil, it was extracted and analyzed separately (Appendix III-5). By comparing this with the other analyses, it was noted that it contained twenty-five times as much oil as the control composite.

7. HEAVY METALS IN BENTHIC MACROFAUNA AND FISHES

Lead concentrations in mixed samples of Diptera larvae and Oligochaeta worms (mostly <u>Tubifex</u>) collected at benthos sampling station D-2-were a factor of 3-7 higher than samples taken above the oil spill (Appendix IV-1). Other metals exhibited no noticeable differences.

Levels of metals in fishes collected above and below the spill are presented in Appendices IV-2, IV-7. No significant differences due to the oil spill can be detected.

FIGURE 12. RELATIVE CONCENTRATIONS OF PETROLEUM HYDROCARBONS IN SCHUYLKILL RIVER SEDIMENTS COLLECTED IN NOVEMBER 1972



The extensive use of Diptera larvae as food by several species of fish (Appendix V 1) suggested that this food link could serve as a pathway by which metals could be accumulated in the fishes.

PETROLEUM HYDROCARBONS IN FISHES 8.

The overall sequential analytical procedure used to search for the possible presence of petroleum hydrocarbon residues in fish is given in the Materials & Methods Section, page 20, and is diagrammed below:

WHOLE FISH

- grind in meat grinder.
 blend in a Waring blender with 7.4% by weight of benzene,

"FISH SOUP"

blend in a Waring blender with approximately 70% weight percent of anhydrous magnesium

"FISH POWDER"

- 1) Soxhlet extract 24 hours with refluxing benzene,
 2) evaporate benzene,

EXTRACTED OIL (Appendix V-1, V-4)

- saponify oil in 6N methanolic KOH
- 48 hours at room temperature,
 2) dilute with water and extract with cyclohexane and then with benzene (simple extraction),
 3) wash the combined organic extracts with 1N H₂SO₄, dry, and evaporate solvent,

TOTAL HYDROCARBONS FROM SAPONIFICATION (Appendix V-2, V-4)

(Continued)

TOTAL HYDROCARBONS FROM SAPONIFICATION (Continued from previous page)

- apply to a basic alumina column for column chromatography,
- 2) elute with cyclohexane, leaving any fluorescent material on the column,
- 3) elute the fluorescent material i. with benzene followed by ii. 90/10 benzene/ethyl ether combine 1) and ii),
- evaporate solvent from the above two fractions
- A) CYCLOHEXANE-ELUTED
 ALIPHATIC HYDROCARBONS
 (VERY WEAKLY FLUORESCENT) (see Appendix V-3,
 V-5)
 - 1) infrared analysis
 - 2) flame ionization GC analysis

IRs: Figs. 14-16 GCs: Figs. 26-29

IR = Infrared spectrum

- B) BENZENE-BENZENE/
 ETHER-ELUTED AROMATIC HYDROCARBONS
 (STRONGLY FLUORESCENT)(see Appendix V-3,
 V-5)
 - 1) infrared analysis
 - 2) flame ionization GC analysis

IRs: Figs. 17-20

GCs: Figs. 30-33, 42,

46-47

GC = Gas Chromatogram

This procedure was applied to two sets of fish samples:

- 1) fish obtained from the Schuylkill River in July, 1973, in the region of the oil spill,
- 2) fish (presumably free of oil contamination) from Harrison Lake National Fish Hatchery, designated in this report as "HLFH" fish (see Subsection J, p. 86). In order to test the above analytical procedure, some "HLFH" samples were deliberately tainted with known amounts of polycyclic aromatic hydrocarbons in the initial blending step of the analysis, and finally the composite benzene-benzene/ether fraction from column chromatography was analyzed by GC.

The procedure, with some modification, was also applied to a sample of the spilled crankcase oil waste (SCOW), collected from the river in July, 1972. The GCs and IR spectra from this analysis, after column chromatography, are listed:

IR cyclohexane fraction: Fig. 13

IR benzene and benzene/ether fractions: Figs. 21-22

GC cyclohexane fraction (SCOW): Fig. 24

GC benzene/ether fraction (SCOW): Fig. 25

The above procedure was adopted because it combined the merits of published procedures and provided as much information as possible in the fewest analytical steps. These steps included:

- 1) separation of the benzene soluble oils from the fish
- 2) separation of the hydrocarbons from these extracted oils
- 3) separation of the hydrocarbons into two classes,
 - i) the saturated aliphatic hydrocarbons, and
 - ii) the polycyclic aromatic hydrocarbons

A similar type procedure was applied to the spilled crankcase oil waste (SCOW) to determine if any intelligible comparisons could be made between the hydrocarbons isolated from the fish vs. those isolated from SCOW.

The polycyclic aromatic hydrocarbons were of special interest in view of the known carcinogenic properties of some of these compounds. The notable early work of Cahnmann and Kuratsune (1957) describes the isolation and identification of these polycyclic aromatics in oysters which were taken from waters slightly contaminated by oil pollution. Their procedure involved a direct liquid-liquid extraction step on 5 kg of shucked oysters blended in methanol followed by saponification of the extract with methanolic potassium hydroxide. About

Cahnmann, H. and M. Kuratsune. 1957. "Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Water," Anal. Chem. 29:1312.

twenty-one chromatographic columns were prepared using various adsorbents to isolate the polycyclic aromatics, many of which were identified by their characteristic ultraviolet absorption spectra. A list of these polycyclic aromatics appears in Fig. 34. This procedure applied to fish in the Schuylkill River would be very time-consuming and might limit the number of fish samples which could be examined.

On the other hand, facile and rapid methods of analysis such as direct gas chromatography on oils extracted from fish (or on SCOW) would render little conclusive information due to the extreme chemical complexity of any petroleum product. The suspected waste oil is theoretically able to be comprised of multi-thousands of hydrocarbons.

However, it should be noted that the work of Zafiriou, Blumer, and Myers (1972) provided "fingerprint" gas chromatographic comparisons of spilled crude oils with crudes from the spill source and were able to correlate them in many cases.

The examination of kerosene-like materials in the Australian mullet was pursued by Connell (1971), and the procedure included extraction of fish flesh with ethyl ether followed by steam distillation to separate the steam volatile hydrocarbons. The isolated hydrocarbons were subjected to gas chromatography, and the chromatograms compared to the chromatograms from oily river sediments and commercial kerosene. Similar studies were conducted on edible shellfish by Blumer, Souza, and Sass (1970) in which shucked shellfish were extracted with refluxing methanol, and the methanol extracts (and solids precipitated) extracted with pentane. Further separations were achieved with column chromatography followed by fingerprint gas chromatography. Comparison of the chromatograms obtained with those of a No. 2 fuel oil (accidentally spilled in the area before shellfish examination) revealed similarities in some cases.

Zarifiou, O., M. Blumer, and J. Myers. 1972. <u>Correlation of Oils and Oil Products by Gas Chromatography</u>. National Technical Information Service Report PB-211-337 UNPUBLISHED MANUSCRIPT.

Connell, D. W. 1971. "Kerosene-like Tainting in the Australian Mullet," Marine Pollution Bulletin, 12 (2): 188.

Blumer, M., G. Souza, and J. Sass. 1970. "Hydrocarbon Pollution of Edible Shellfish by an Oil Spill," Biol. 5:195.

In the present study of the spill in the Schuylkill River, the material spilled might well be composed primarily of a complex mixture of hydrocarbon materials. However, the material spilled was the waste product from the rerefining of waste crankcase oil. Thus, the expected tarry and intractible residues would undoubtedly differ in composition from a crude oil or a given kerosene fraction.

A. Blending and Extraction of Fish Samples (and SCOW)

The above published procedures for extracting oils from fish (and SCOW) may not be applicable to the present problem. For example, steam distillation of ether extracts from Schuylkill River fish may separate hydrocarbons; but the suspected contaminating material (SCOW) might be composed of high molecular weight hydrocarbons of low-vapor pressure. Because of the low-steam volatility of high molecular weight hydrocarbons, separation of these materials by this technique will be incomplete.

The blending of Schuylkill River fish with magnesium sulfate and subsequent Soxhlet extraction of the fish powder with refluxing benzene is a modification of a procedure published by the Patuxent Wildlife Research Center. In this process, fowl were ground and blended with anhydrous sodium sulfate, and the resulting free-flowing powder was subsequently extracted with refluxing petroleum ether. The use of anhydrous sodium sulfate failed with Schuylkill River fish, because the refluxing benzene resulted in liberation of water from the sample which clogged the flush tube in the Soxhlet apparatus completely inhibiting the extraction process.

The use of benzene \underline{vs} . pentane or petroleum ether as an extracting solvent was preferred due to the known insolubility (or partial solubility) of some polycyclic aromatics in these solvents.

The essential data from the extraction are outlined in Appendix V-1 and the process is described on page 20. Some heat was developed in the blending process, and corrections were made for weight losses due to evaporation. Thus, the column labelled "Actual Sample Extracted" in Appendix V-1 represents a corrected value. The selection of twenty-four hours reflux time was based on weight studies of the amount of organic material extracted vs. time. These studies revealed that all the organic material was extracted in eighteen hours. The weight percent of the total oil extracted, based on weight of starting fish, varied from 2.8 to 5.9 percent. The oils extracted from HLFH fish samples on forty-eight hours benzene extraction gave variations ranging from 4.9 to 7.2 percent (Appendix V-4).

B. Saponification

The purpose of the saponification step was to further refine the fish oil obtained from the extraction step by converting the relatively non-polar materials (e.g., fat or lipid) to relatively polar materials (fatty acid salts and glycerol).

These polar and water soluble products can then be more easily separated in the next steps. The polar compounds were removed in the extraction of the water-diluted saponification mixture with hydrocarbon solvent followed by column chromatography. Other organic compounds that may be present such as aldehydes, organic acids, ketones, esters, and proteins are also sensitive to treatment with methanolic potassium hydroxide, but hydrocarbons in general are inert. A saponification step was used by Cahnmann and Kuratsune (1957) in their determination of polycyclic aromatic hydrocarbons in oysters.

The percent recoveries of oil from the saponification step varied from 17.8 percent in the downstream brown bullhead sample to 64.3 percent in the upstream crappie sample, based on the oils obtained from the original extraction (Appendix V-2).

The saponification step was the most difficult step in the analysis. Samples emulsified badly on extraction of the diluted saponification mixture with cyclohexane and benzene. The separation of layers was accomplished to some extent by the addition of solid sodium chloride. Even with the addition of salt, the clean-cut separation of layers, devoid of interfacial material, was not achieved. Sometimes the interface was not well defined. Despite these difficulties, clean organic layers containing the sought-after hydrocarbons devoid of interfacial material were separated. It is possible, however, that some of the hydrocarbon material was left behind in the interfaces.

Another difficulty was the gelation of some of the cyclohexane/benzene extracts after separation from the aqueous saponification mixture. The upstream brown bullhead extract gelled very badly after magnesium sulfate filtration. The gel completely clogged the chromatographic column in the next step of the analysis. Thus, the analysis for upstream brown bullheads had to be abandoned. During the analysis of the downstream crappies, gelation occurred before the filtration through magnesium sulfate, which increased the time required to perform the normally simple laboratory operation.

Cahnmann, H. and M. Kuratsune. 1957. "Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Water," Anal. Chem. 29:1312.

The apparent high yields of oil from the upstream crappies seemed to be largely a gel-like material, which was not revealed until the column chromatographic step. Then only plastic, brittle, gel-like materials were eluted from the column, as opposed to the oils usually observed, and these could not be analyzed.

The spilled crankcase oil waste extract was saponified to eliminate any interfering acidic substances. All saponification data are contained in Appendix V-2.

C. Column Chromatography

The purpose of this step was to separate the hydrocarbons from other polar materials and also to separate the aliphatic from the aromatic hydrocarbons for analysis by infrared and gas chromatography.

The three principal eluting solvents which were used, in sequence, were cyclohexane, benzene, and 90/10 benzene/ethyl ether. The last two eluates were combined to give a benzene-benzene/ether fraction. The principal criteria for the volumes of eluting solvents used was the observation of fluorescent material on the alumina column. Thus, the cyclohexane fraction was largely free of fluorescent material while the benzene-benzene/ether fractions were heavily fluorescent. Not all fluorescent material was eluted from the alumina column even when using a benzene/ethyl ether solvent combination.

The column chromatographic data are given in Appendix V-3. The upstream crappies, eluted only solid gels, while the chromatographic columns of the upstream brown bullhead became so badly clogged no solvent would pass through it, even under pressure. Consequently, these analyses were abandoned.

Except for the upstream brown bullheads, all column loadings were in excess of 33:1 alumina:oil sample. The lowest column loading (20:1 alumina: oil sample) was used for the badly clogging upstream brown bullhead samples.

Column chromatography data for downstream and upstream suckers are compared in Appendix V-3. Here the percent solids recovered based on starting material is 1.8 vs. 0.77 for cyclohexane eluates and 1.1 vs. 0.48 for benzene and benzene/ethyl ether eluates in downstream and upstream suckers, respectively.

D. Infrared Analysis

Infrared analyses (as smears between salt plates) were performed on all materials from column chromatography except for the upstream brown bullheads, the upstream crappies and the cyclohexane fraction from the downstream crappies. Analyses were abandoned if there was insufficient sample for a suitable spectrum. After spectral analysis, the samples were recovered by solvent washing from the salt plates and analyzed by gas chromatography.

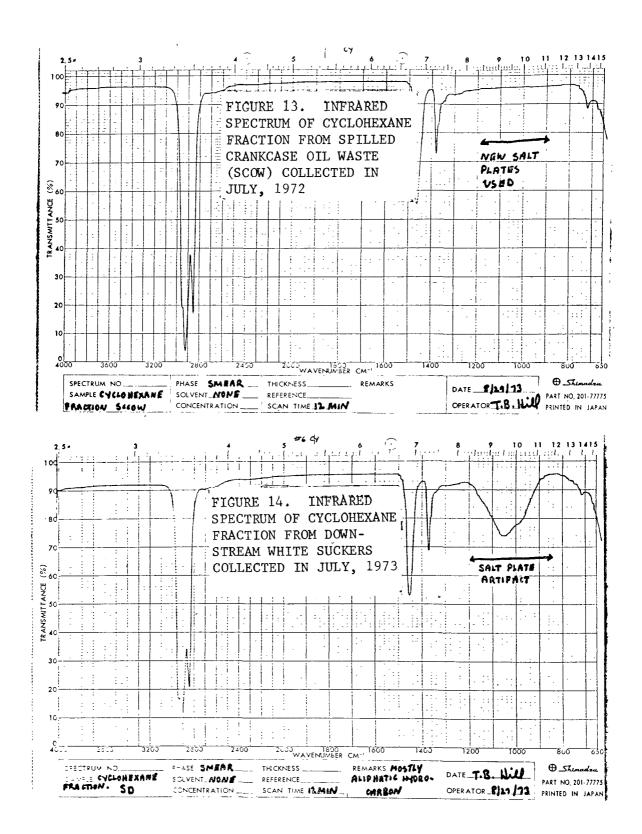
The infrared spectra of all cyclohexane fractions, Figs. 13-16, from column chromatography were essentially identical and showed the predominant presence of aliphatic hydrocarbons both in the waste oil and fish. There were some small unidentified peaks from 12.2 to 13.8 μ in the spectrum from an unusually thick sample of downstream brown bullheads.

All spectra of the benzene + benzene/ethyl ether fractions from fishes, Figs. 17-20, were essentially identical and are strongly indicative of aromatic hydrocarbons. A relatively small amount of hydrocarbon residue was recovered from the downstream crappies during the extraction, saponification, and column chromatography steps. Therefore, the infrared spectra of this sample was not as clear as the others and minor differences were not discernible.

The spectrum for the "benzene" fraction of SCOW from column chromatography is given in Fig. 21. While it was indicative of aromatic hydrocarbons, its peaks were not as well resolved as the corresponding spectra of fish, and it was not identical to the spectra of the "benzene" eluates from fish. The spectrum of the 90:10 benzene: ethyl ether fraction given in Fig. 22, showed that other material, probably having a carbonyl (> C=0) group, was eluted from SCOW. An attempt was made to further purify the benzene fraction from SCOW by rechromatography on alumina. The benzene-eluted material from rechromatography is given in Fig. 23. No further purification seemed to be achieved in this rechromatograph step, since no essential differences were observed on comparison of the spectra (Figs. 22 and 23).

E. Gas Chromatography

The purpose of gas chromatography was to separate and estimate the components in the "cyclohexane" and "benzene-benzene/ ethyl ether" fractions. These fractions were recovered from column chromatography of the SCOW and fish extracts after saponification.



The technique has developed in practice to the extent that a present-day working organic chemist cannot function without a gas chromatograph. If the peaks observed in the gas chromatogram of a complex mixture are well resolved, the analyst has an opportunity to:

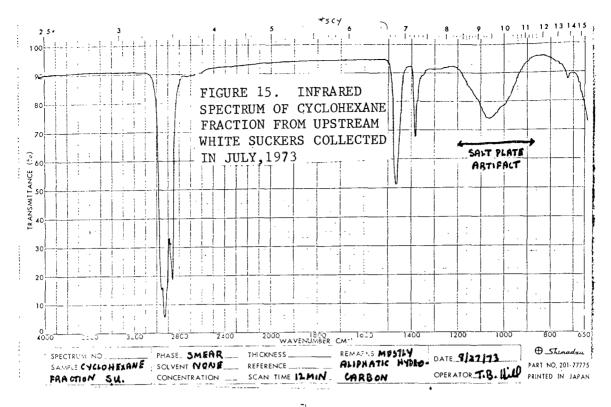
- 1) tentatively establish, but not prove, the presence of a given component by adding known compounds to the sample, rerunning the chromatogram, and observing peak height enhancement,
- 2) establish the definite absence of a given component in the original sample by the same technique as 1) and observe extra peaks in the chromatogram of the sample doped with known compounds (assuming no background) or
- 3) conclusively identify a compound from the gas chromatograph by trapping the effluent gas from each peak after the component passes the detector, thereby isolating the component to study other physical properties. This latter technique can be applied where a) the sample is not destroyed by the detector, b) relatively large amounts of samples are available, and c) a relatively large column is used.

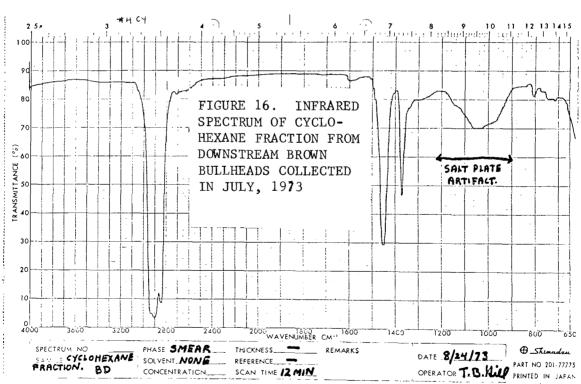
In the case of complex mixtures, the gas chromatogram may show only poorly resolved peaks against a large "background." If the chromatograms of two samples of multi-component mixtures have identical peaks of similar relative intensity, the samples are presumed to be identical. This "fingerprint" technique has been studied with some success in efforts to identify the source in crude oil spills. That success is due to the fact that different crude oils, while extremely complex in their chemical composition, show significant differences in their gas chromatograms.

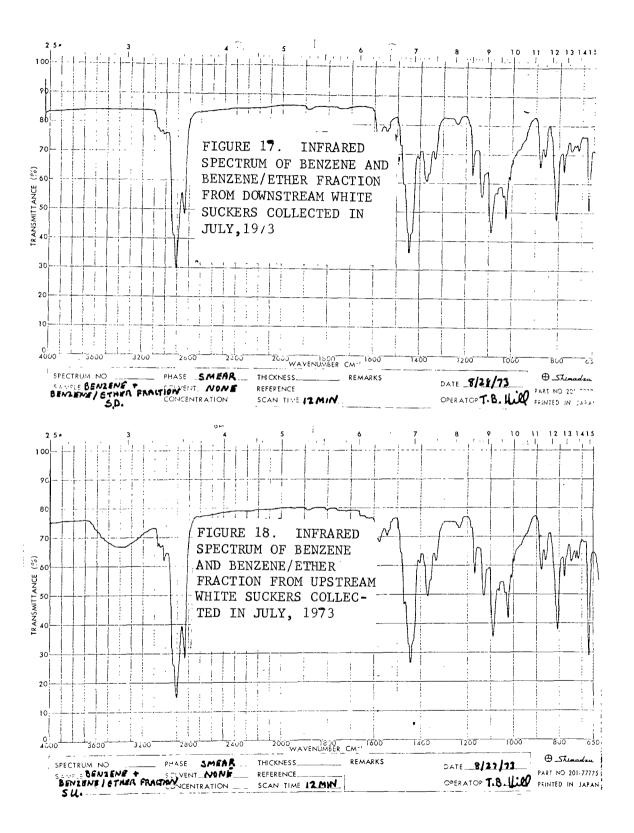
The application of fingerprint gas chromatography to identify hydrocarbons in marine life has been applied with some success by Blumer et al. (1970) and by Connell (1971). Connell obtained fingerprints on extracts of the Australian mullet and compared these to substances isolated from river sediments.

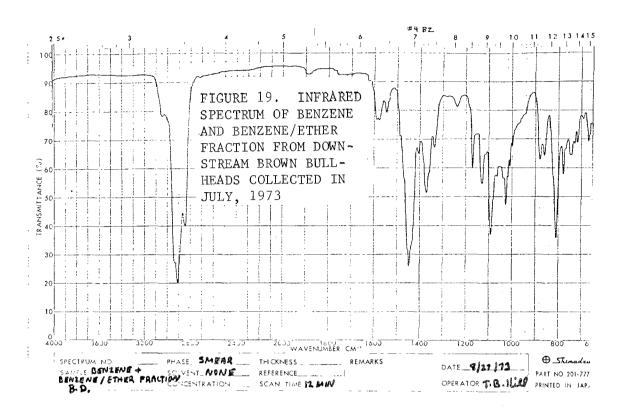
Blumer, M., G. Souza, and J. Sass. 1970. "Hydrocarbon Pollution of Edible Shellfish by an Oil Spill," <u>Biol.</u> 5:195.

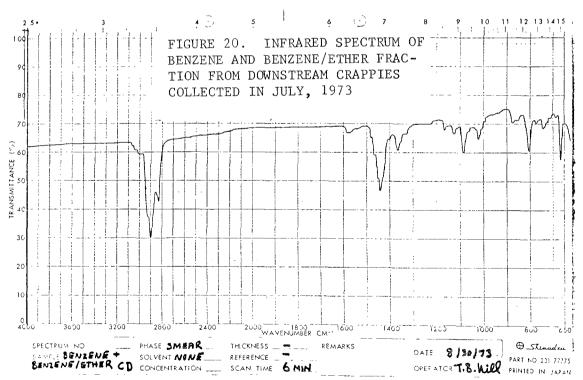
Connell, D. W. 1971. "Kerosene-like tainting in the Australian Mullet," Marine Pollution Bulletin, 12 (2): 188.

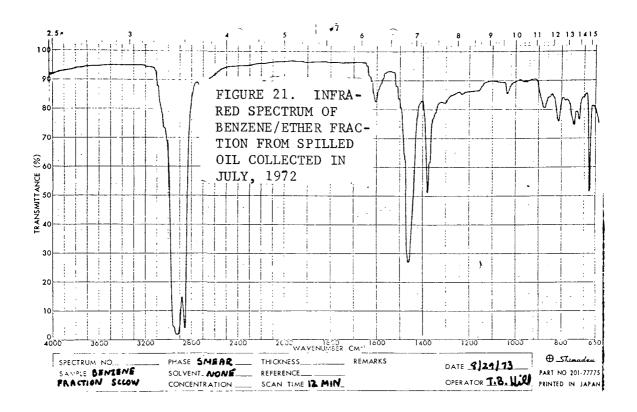


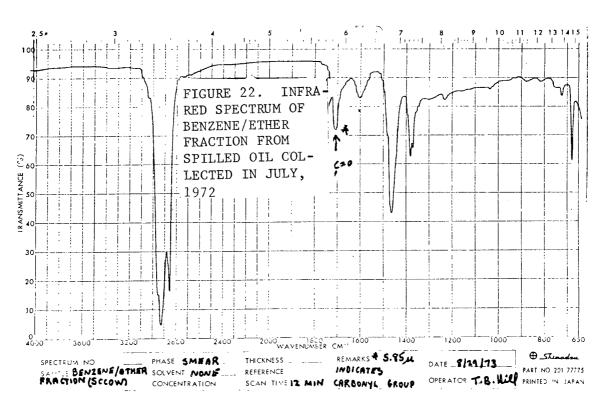


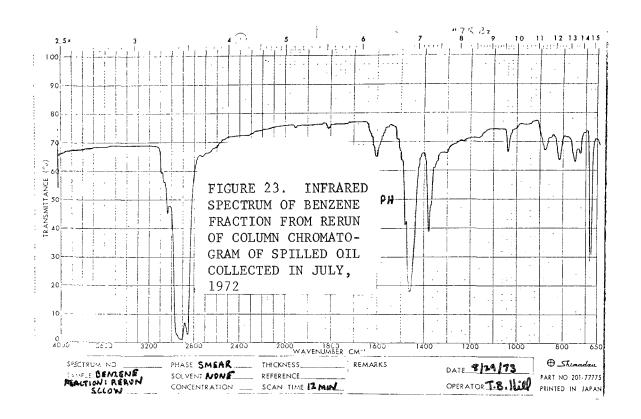












The spilled crankcase oil waste was an extremely complex mixture as indicated by the large unresolved backgrounds in the chromatograms of the waste oil (Figs. 24 and 25).

In this study two sets of gas chromatograms were determined on refined extracts from fish and waste crankcase oil.

- 1) the cyclohexane fraction from column chromatography on alumina using a 6' by 1/8" OV-17 column programmed from 50-293°C at 8°C per minute.
- 2) the benzene (actually benzene + benzene/ethyl ether) fraction from column chromatography on alumina using a 7' by 1/8" SE-52 column programmed from 50 to 293°C at 8°C per minute.

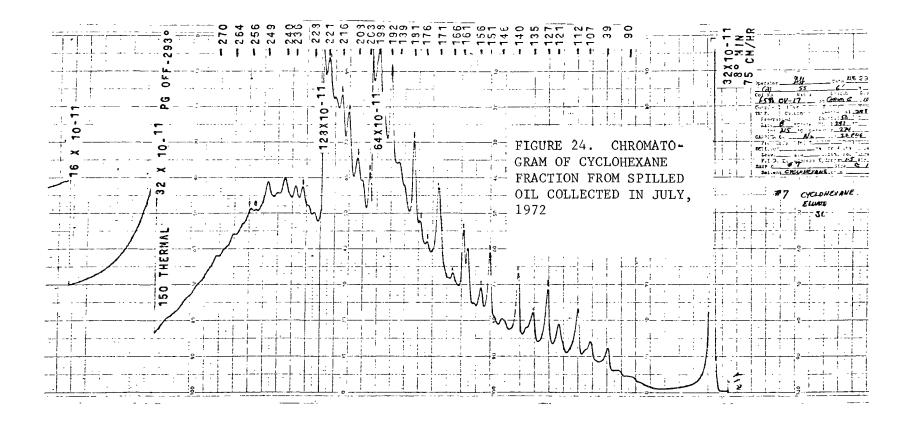
Both of these columns were methyl phenyl silicone gum rubber columns. The OV-17 column was used by the Virginia Institute of Marine Science (Gloucester Point, Virginia) for analysis of crude oils, while the SE-52 column was used specifically for the analysis of polycyclic aromatic hydrocarbons by Chatot et al. (1969).

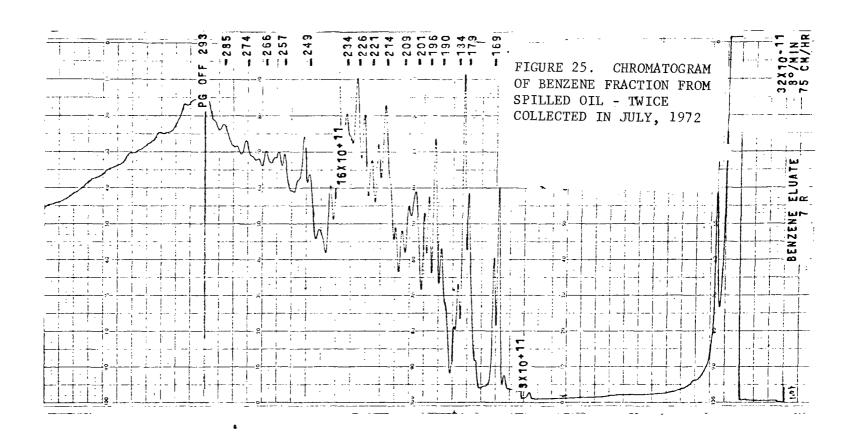
F. Cyclohexane Fractions

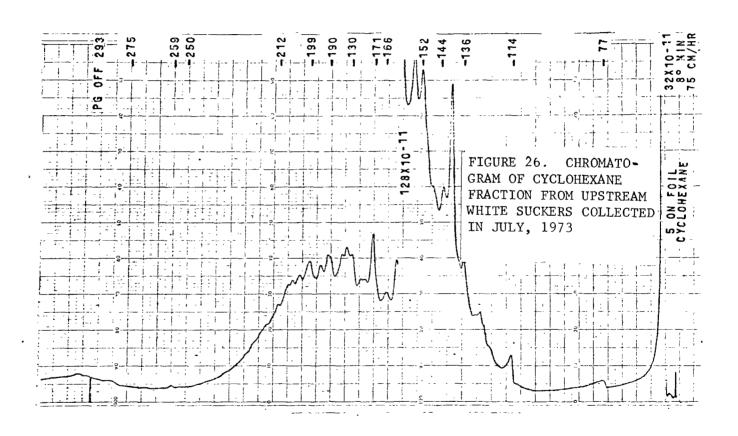
Gas chromatograms were obtained on cyclohexane fractions from column chromatography of spilled crankcase oil waste (Fig. 24), upstream white suckers (Fig. 26), downstream white suckers (Fig. 27), downstream brown bullheads (Fig. 28), and downstream crappies (Fig. 29). These samples were chromatographed by a prebaking process in which the sample was placed in a small aluminum foil cup and baked for five minutes inside the injection port of the instrument before the temperature program was started.

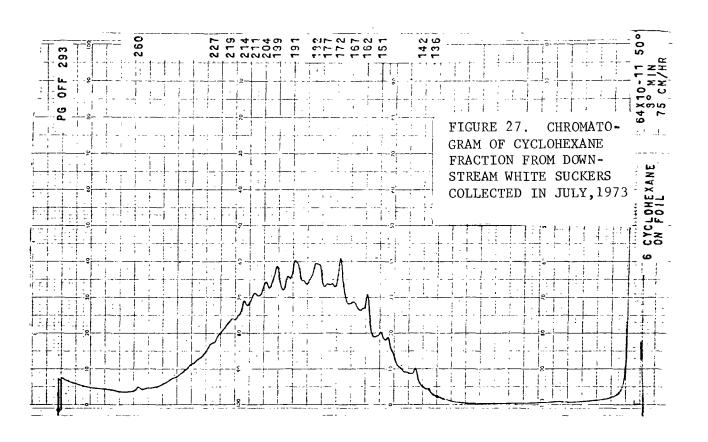
While the infrared evidence (page 55) clearly illustrated the presence of aliphatic hydrocarbons in all cyclohexane fractions of SCOW and fish, the gas chromatograms (Figs. 24, 26-29) indeed illustrated their expected complexity. All samples showed a broad, undefined background ranging from approximately 140°C to 270°C. However, no consistent fingerprint pattern was evident on comparing the relatively small peaks superimposed on the prominant background.

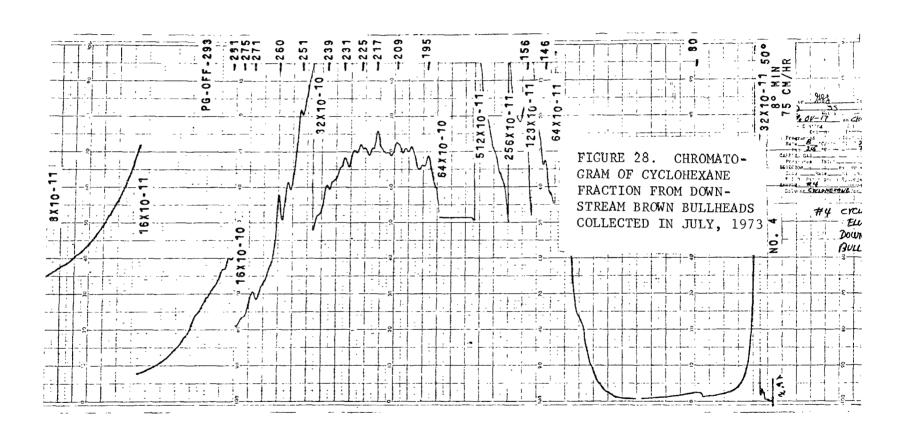
Chatot, G., Jequier, W., Jay, M., and Fontanges, R. 1969. "Study of Atmospheric Polycyclic Hydrocarbons: Problems Connected with Coupling of Thin Layer Chromatography with Gas Phase Chromatography," Journal Chromatography 45:415.

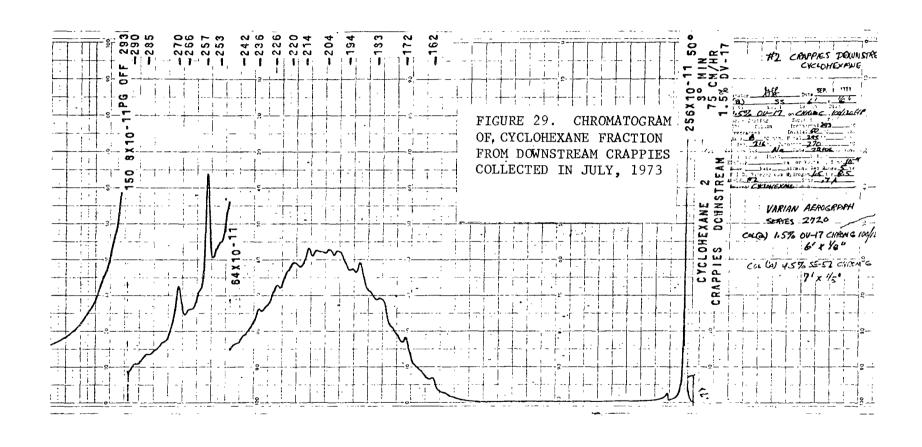












G. Benzene-Benzene/Ether Fractions

In contrast to the cyclohexane fractions, the gas chromatograms from the "benzene" fraction of fish showed very well resolved peaks with much less background. A typical example was seen in the chromatogram of the upstream suckers (Fig. 30). This chromatogram showed at least twenty-one well resolved peaks, thus offering an excellent chance for peak matching studies with authentic samples of polycyclic aromatic hydrocarbons.

A peak to peak analysis of the chromatograms from the benzene fraction of fish will not be detailed here. The chromatograms of the downstream suckers (Fig. 31), downstream brown bullheads (Fig. 32), and downstream crappies (Fig. 33) samples all showed remarkable similarity with many matching peaks. Admittedly, many of these peaks varied in intensity, but their retention times were quite reproducible.

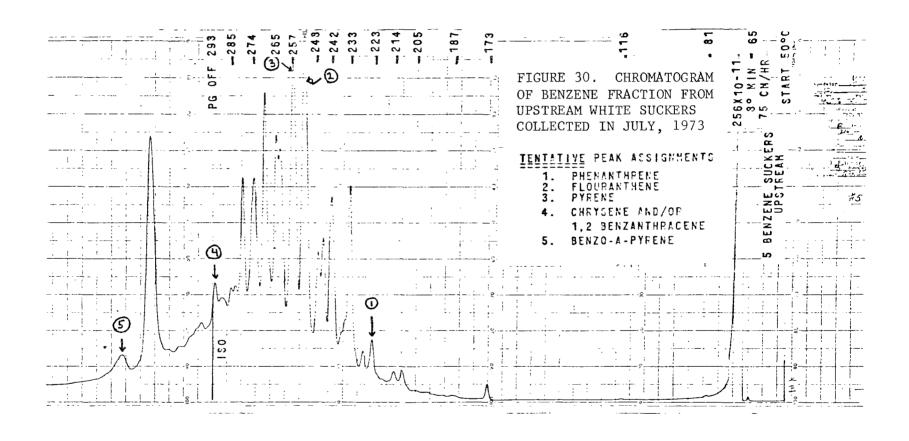
While the gas chromatogram of the benzene fraction from rechromatographed SCOW (Fig. 25) showed many well-resolved peaks, it also contained a very large undefined background. As discussed above, this was due to the complexity of the spilled material. The pattern differed from those of fish. Many peaks matched, but there were many others of questionable identity.

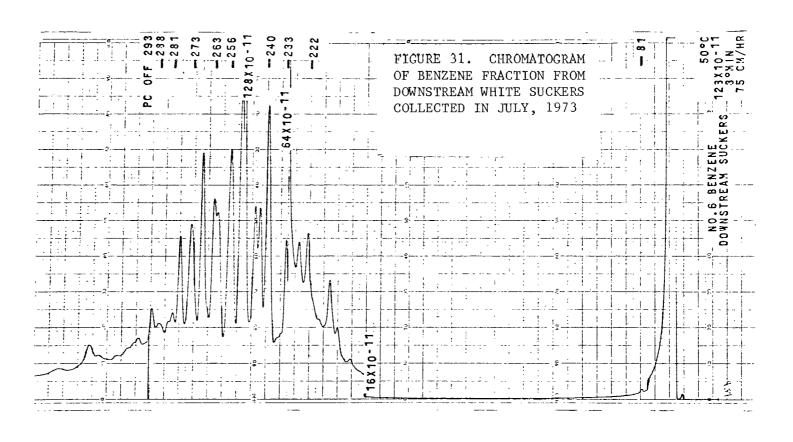
H. Peak Matching Studies by Chromatography

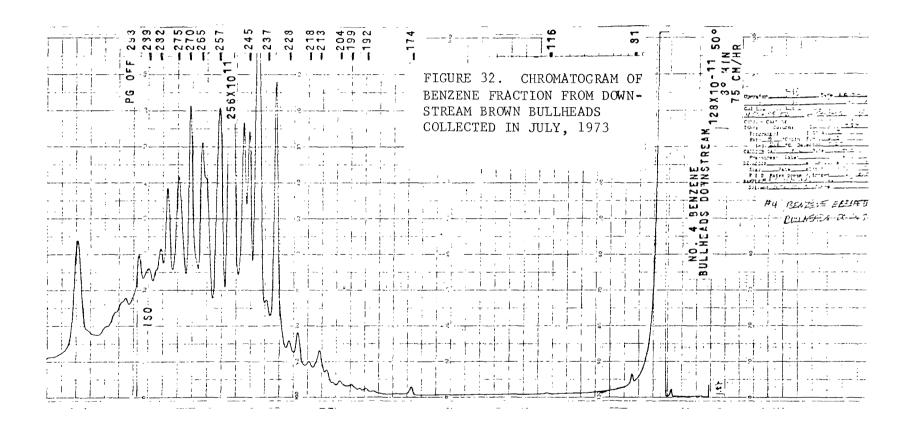
Peak matching studies of the benzene eluate from upstream white suckers (Fig. 30) were conducted. This chromatogram was compared with chromatograms of the same sample spiked with individual polycyclic aromatic hydrocarbons. A list of these aromatics, their structures and sources are given in Fig. 34. These hydrocarbons, except for phenanthrene, were found in oysters by Cahnmann and Kuratsune (1957).

The chromatogram of the mixture of these polycyclic aromatics is given in Fig. 35, which was obtained from a standard solution containing 0.116 mg/ml of each aromatic. The location of

Cahnmann, H. and M. Kuratsune. 1957. "Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Water," Anal. Chem. 29:1312.







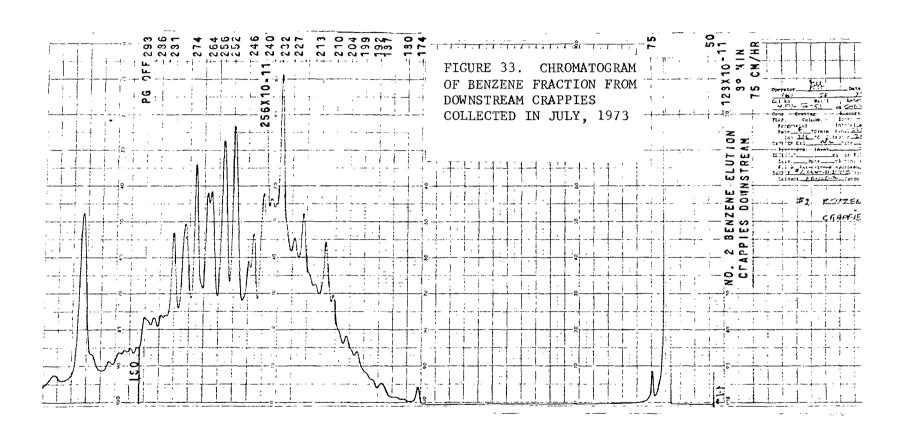


Figure 34. Standard polycyclic aromatic hydrocarbons

| Name | Chemical Structure | Supplier |
|---------------------------|--------------------|---|
| Chrysene | | Aldrich Chemical Co., 95% |
| Flouranthene | 0 0 | Aldrich Chemical Co., 99.9+% |
| Pyrene | 010 | Aldrich Chemical Co., zone refined 99.9+% |
| Phenanthrene | (0) | Purified sample prepared by author |
| Benzo (g,h,i) perylene | 1010 | Aldrich Chemical Co. |
| Benzo (a) pyrene | 01010 | Aldrich Chemical Co. |
| 1,2-Benzanthrace | ne OOO | . K & K Laboratories, Inc. |

these aromatics as specified on the chromatogram in Fig. 35 was accomplished in a separate study by spiking the mixture with individual standards.

It is to be seen from Fig. 35 that chrysene and 1,2-benzanthracene were not resolved on an SE-52 column. Furthermore, the heavy polycyclics (benzo-a-pyrene) and benzo (g,h,i) perylene did not emerge from the column until after the temperature program to 293°C was completed.

Tentative assignments of these polycyclic aromatics are given on Fig. 30 for the upstream white suckers, and the gas chromatograms, listed below, supporting these tentative assignments are given in Figs. 36-41.

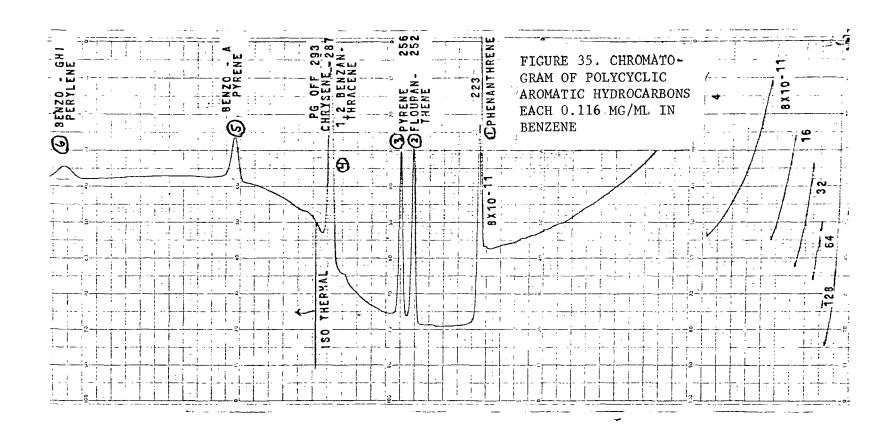
Known hydrocarbon compounds (Fig. 34) were added to samples of upstream white suckers to tentatively establish the presence of these hydrocarbons in the fish residues by peak enhancement.

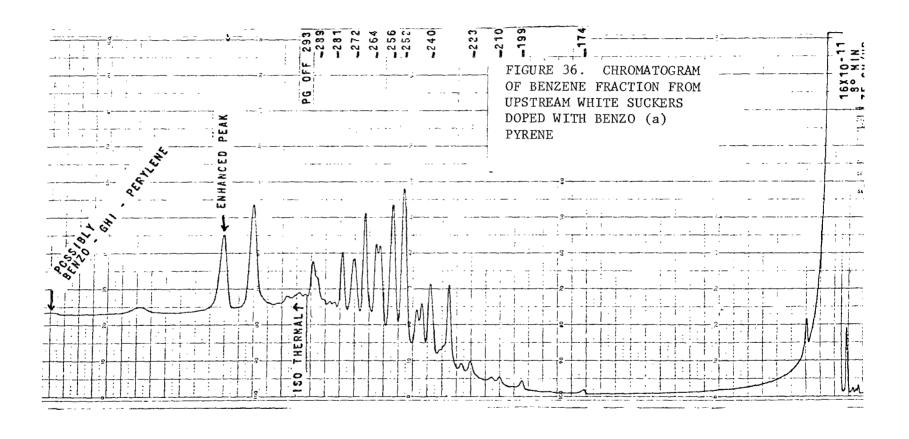
| Fig. 35 | Polycyclic aromatic hydrocarbons each 0.116 mg/ml in benzene |
|---------|--|
| Fig. 36 | Upstream white suckers + benzo (a) pyrene |
| Fig. 37 | Upstream white suckers + 1, 2-benzan-thracene |
| Fig. 38 | Upstream white suckers + chrysene |
| Fig. 39 | Upstream white suckers + fluoranthene |
| Fig. 40 | Upstream white suckers + pyrene |
| Fig. 41 | Upstream white suckers + phenanthrene |

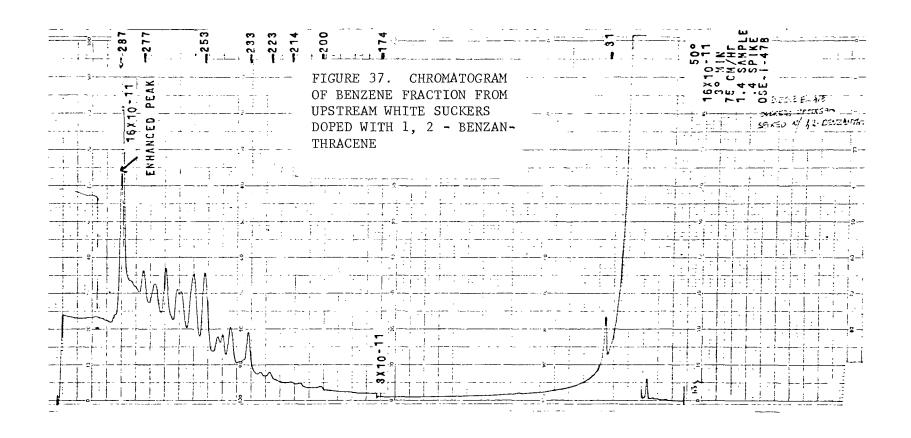
Possibly a benzo (g,h,i) perylene peak was observed in Fig. 47 at 17.5 cm from the isothermal hold period.

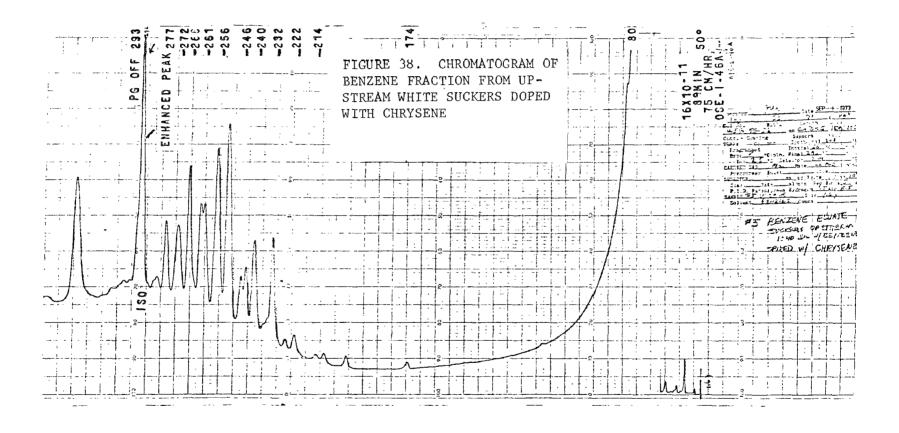
I. Kinds and Levels of Hydrocarbons in Fish

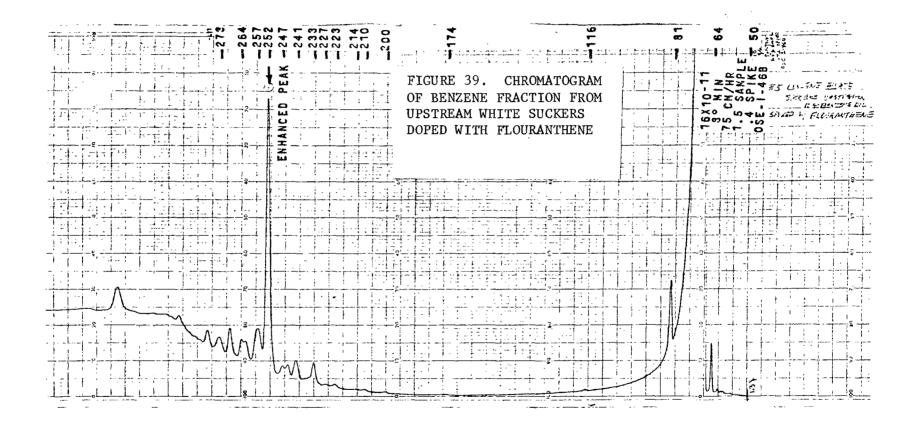
The data given to ascertain the kinds and levels of petroleum hydrocarbons in Schuylkill River fish must be treated with caution. The weights of hydrocarbons obtained from column chromatography, given in Table 8, can only be judged in the context of considerable variation in the results of the analytical process, particularly in the saponification step.

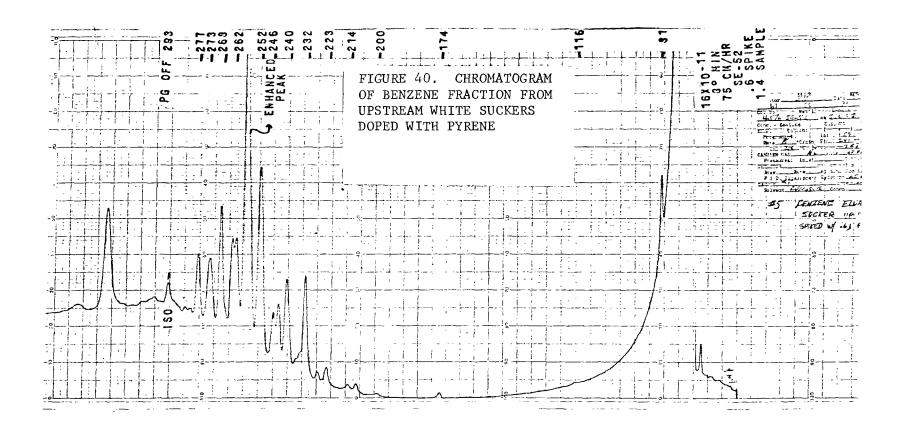












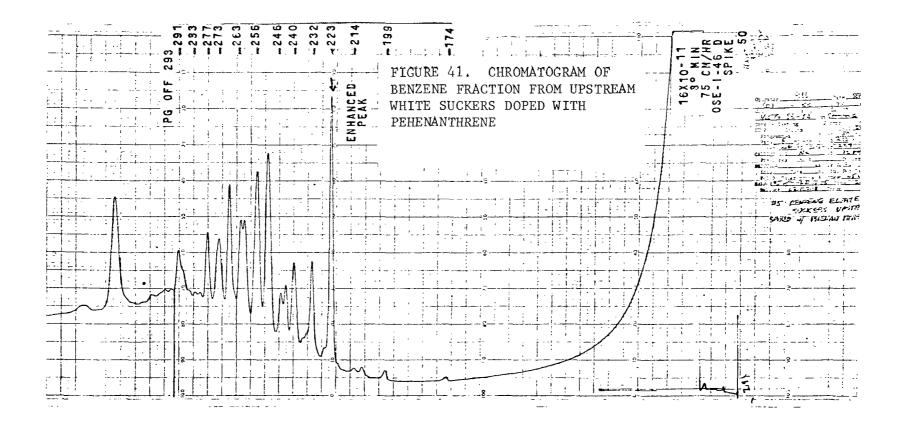


TABLE 8 Levels of Aliphatic and Aromatic Hydrocarbons in Sch ylkill River Fish Collected July, 1973

| Sample | Starting Sample (g) | Aliphatic Hydrocarbons (mg) | Aromatic Hydrocarbons (mg) | Aliphatic Hydrocarbons (ppm)+ | Aromatic Hydrocarbons (ppm)+ |
|-------------------------------|------------------------|-----------------------------------|----------------------------------|-------------------------------------|------------------------------------|
| Spilled oil (SCOW) | 93 | 575* | 90* | 481,000 | 45,300 |
| White suckers downstream | 110 | 25 | 15 | 227 | 136 |
| White suckers upstream | 113 | 24 | 15 | 212 | 133 |
| Brown bullheads downstream | 116 | 15 | 9 | 129 | 78 |
| Brown bullheads upstream | 112 | ** | ~- ** | | |
| Grappies downstream | 115 | 8 | 10 | 70 | 87 |
| Crappies upstream | 116 | *** | *** | | |

*From 1,196 g oil extract at saponification step

**Analysis abandoned due to clogged chromatographic column

***Only solid gel products on column chromatography

+Based on starting sample (fish or spilled oil)

In the analyses of the Schuylkill River fish, the infrared spectra of either the cyclohexane or the benzene-benzene/ether fractions showed qualitative reproducibility in the analyses that could be completed to this stage. All spectra indicated to a large degree the absence of absorptions corresponding to hydroxyl, primary and secondary amino, and carbonyl functional groups. This means that typical organic substances such as fats, amino acids, proteins, alcohols, carboxylic acids and esters, simple sugars and polysaccharides were largely absent in the final fractions from column chromatography.

The infrared spectra of the cyclohexane fractions of Schuylkill River fish and SCOW, along with the GC data, indicate the predominant presence of a complex mixture of saturated aliphatic hydrocarbons. The average level of aliphatics in Schuylkill River fish was 160 ppm (Table 8) vs. our average level of 13 ppm for cyclohexane eluted residues obtained from similar analytical treatment of HLFH fish (Subsection J, page 86, and Appendix V-5).

The infrared spectra of the fluorescent benzenebenzene/ether fractions indicated the possible presence of polycyclic aromatics. The weak absorptions at 3000-3100 cm⁻¹ (absent from the cyclohexane eluates) suggested carbon to hydrogen bonds of the olefinic and/or aromatic type. The absorptions at 650-1250 cm⁻¹ were characteristic of the complex absorption of polycyclic aromatics. Furthermore, the presence of saturated aliphatic structures was also indicated by the absorptions at 2800-3000 cm⁻¹, 1440 cm⁻¹ and 1380 cm⁻¹. It was not determined whether these absorptions indicated the presence of saturated aliphatic hydrocarbons, or if the saturated aliphatic radicals were bonded to other kinds of structures. Even simple methyl (-CH3) derivatives would show these absorptions. The gas chromatographic data, including the peak matching studies with polycyclic aromatics (Fig. 34) previously identified as being in oysters by Cahnmann and Kuratsune, indicated the presence of these materials in the benzene-benzene/ether fraction of Schuylkill River fish.

Cahnmann, H. and M. Kuratsune. 1957. "Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Water," Anal. Chem. 29:1312.

J. Studies of Fishes from Harrison Lake National Fish Hatchery

1. Test of Analytical Procedure for Polycyclic Aromatic Hydrocarbons

environment and to check if the polycyclic aromatics can be determined by the analytical method used, samples of channel catfish were taken from the Harrison Lake National Fish Hatchery and tainted with benzene solutions of polycyclic aromatics (Fig. 34) at the initial blending stage of the procedure. Four analyses were conducted with the added hydrocarbons at levels of zero, two, five, and ten ppm of each hydrocarbon. Two minor modifications were made in the procedure: 1) the fish powder was extracted 44-48 hours instead of 24 hours (no appreciable change in variation of oils extracted occurred, Appendix V-4), and 2) the saponification time period was reduced from 48 hours to 24 hours, which seemed to result in less troublesome gel formation.

The Harrison Lake fish are designated as "HLFH fish." The fish hatchery itself is located in Virginia at the head of Herring Creek which empties into the James River about four miles from the hatchery. The waters used by the hatchery all come from Harrison Lake which is about 190 acres in area (approximately 70 acres of open water) with no industry on its shores. Its clear waters are bordered by about 150 yards of woodland, and motorboat traffic is minimal since no public boat ramps or motorboat services are available. The traffic is basically limited to five horsepower engines which must be carried manually.

The percent yields of non-volatile residues from the extraction and saponification processes are given in Appendix V-4, and the yields of non-volatile residues from the cyclohexane and benzene/benzene-ethyl ether fractions from column chromatography are given in Appendix V-5.

2. Gas Chromatographic Studies on Benzene-Eluted Residues from Harrison Lake Fish

The residues from the benzene-benzene/ether fraction (Appendix V-5) were subjected to vapor phase chromatography

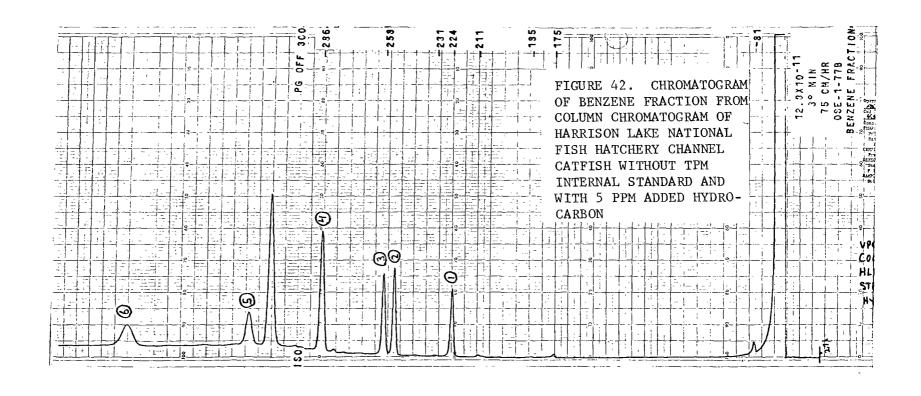
A typical chromatogram is given in Fig. 42, which was determined on fishes with 5 ppm added polycyclic aromatic hydrocarbon. Except for a large peak after the isothermal hold period, all peaks corresponded to those from the chromatogram of the standard aromatic hydrocarbon mixture (Fig. 43). Except for the addition of triphenylmethane (TPM) internal standard, the chromatogram of the benzene-benzene/ether residue from Harrison Lake fish with no added polycyclic aromatic hydrocarbons showed no peaks corresponding to these hydrocarbons (Fig. 44). All gas chromatograms of the benzene-benzene/ether fractions eluted from the Harrison Lake fish containing added polycyclic aromatic hydrocarbons showed similar patterns (Figs. 42 and 45-47).

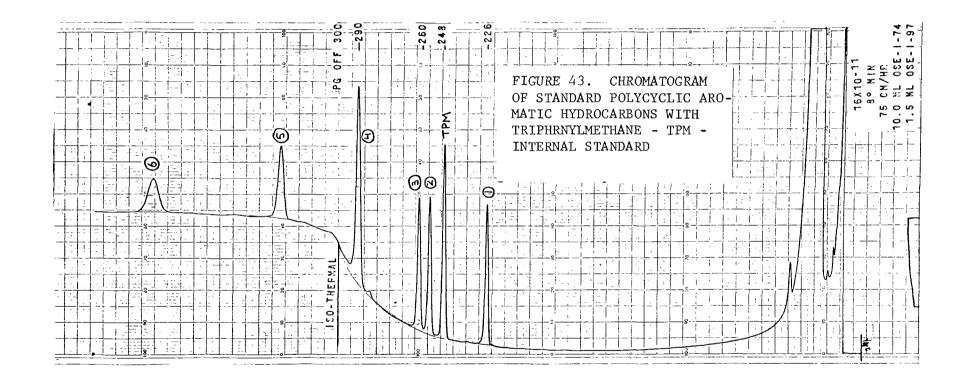
3. Percent Recoveries of Polycyclic Aromatic Hydrocarbons from HLFH Fish

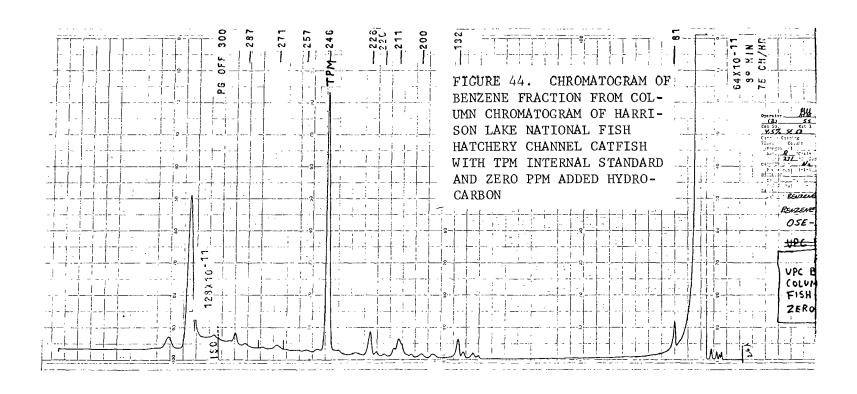
The percent recovery of polycyclic aromatic hydrocarbons from the Harrison Lake fish, which were purposely treated with known amounts of these hydrocarbons during the blending stage of the analysis, was determined. The method used involved the addition of a known quantity of an internal standard to the benzenebenzene/ether fraction from column chromatography prior to the gas chromatographic analysis.

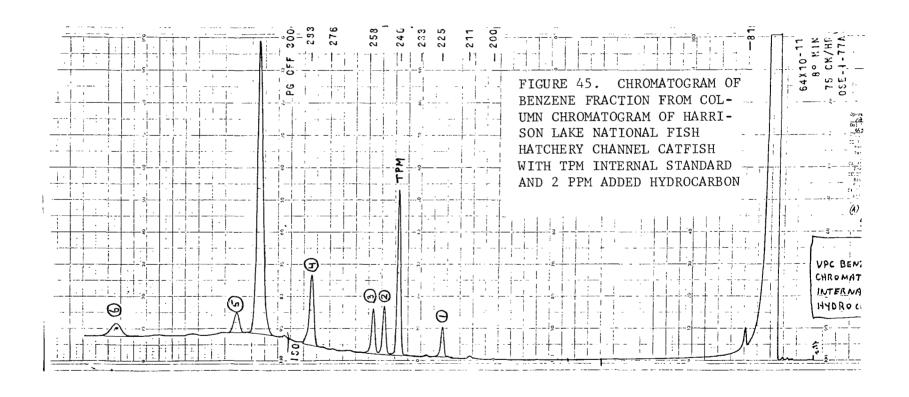
To determine weight relationships from the internal standard, a solution of known amounts of the polycyclic aromatic hydrocarbons was mixed with a known amount of triphenylmethane internal standard. The chromatogram of this mixture is given in Fig. 43. From this chromatogram the area ratio for each hydrocarbon peak vs. the peak for TPM standard was determined, and the area ratio divided by the known weight ratio for each peak was also determined. The area ratio/weight ratio listed for each hydrocarbon in the table (Appendix V-6) represented a correction factor to be applied later to the analysis of benzene-benzene/ether eluted compounds from column chromatography.

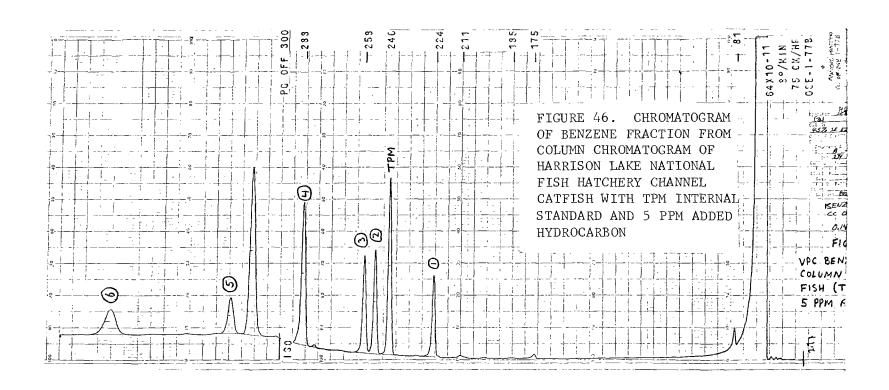
Calculations of the percent recovery of the hydrocarbons from HLFH fish are summarized in Appendices V-7 to V-9. No calculations were made on the benzene-benzene/ether eluted material from HLFH fish with zero ppm added hydrocarbons. From the calculations in Appendices V-7 to V-9, the percent recovery of hydrocarbons ranged? om 27 - 43 percent for fishes doped with 2 ppm hydrocarbon, 54 - 106 percent for fishes doped with 5 ppm hydrocarbon, and 43 - 78 percent for fishes doped with 10 ppm hydrocarbon.

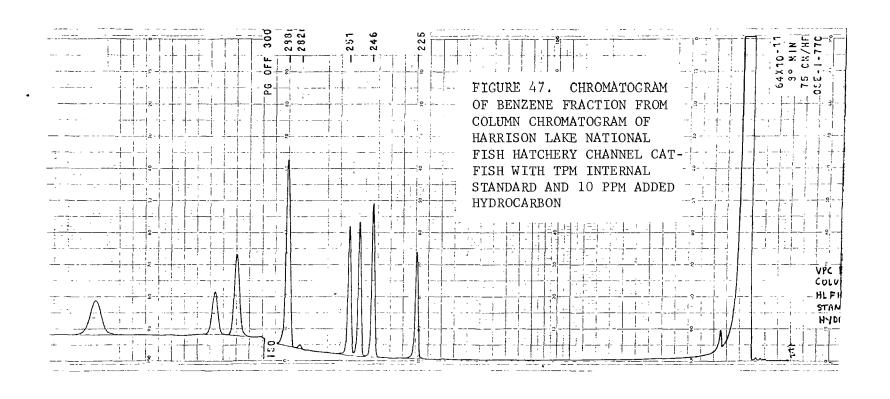












The chromatograms clearly show that the analytical procedure is useful for detecting levels of polycyclic aromatics at the one ppm concentration level.

9. OTHER EFFECTS OF THE SPILL ON RIVER BIOTA

A. General Trophic-Level Interactions Among Schuylkill River Biota

The river ecosystem is composed of four basic components: abiotic substances, producer organisms, consumer organisms, and decomposer organisms. Abiotic materials, such as water, carbon dioxide, nitrogen, and phosphorous, are assimilated by two main types of producers--phytoplankton and algae attached to substrata on the river bottom. Members of this first trophic level are, in turn, grazed upon by the major components of the second trophic level--zooplankton and bottom-dwelling types of herbivores. These organisms are then preyed upon by the secondary consumers or primary carnivores that constitute the third trophic level--small adult fishes and the young of most fish species. Tertiary consumers (secondary carnivores), which are usually large fishes, prey upon the secondary consumers. Decomposers (aquatic bacteria and fungi) break down the excretory products and dead remains of both producers and consumers into abiotic substances, thus completing the trophic cycle.

Additional trophic pathways are usually superimposed upon the basic structure described above. Some organisms (omnivores) feed upon a number of trophic levels. For example, brown bullheads captured in the Schuylkill River had been feeding on small fish, dipteran larvae, and algal mats. It has also been suggested that members of the upper-trophic levels can directly utilize certain abiotic substances. Some organisms switch trophic levels as they mature and become physically able to ingest larger food items, and other organisms utilize trophic components of other ecosystems (for example, crappies observed in this study had been feeding upon flying insects).

In many lakes and ponds, the most abundant types of producers and primary consumers are phytoplankton and zooplankton, respectively. However, in relatively shallow bodies of water, such as the Schuylkill River, the bottom community (attached algae, benthic invertebrates such as Oligochaeta and Diptera larvae and pupae, bacterial flora) plays a more dominant role.

Major food items of species of fish collected during the winter of 1972-73 and the summer of 1973 were: white suckers -- Diptera larvae and pupae; brown bullheads -- Diptera larvae and pupae, small fish; crappies -- Diptera larvae and pupae, aquatic insects; bluegills -- small fish (Appendix VI-5). The importance of planktonic and benthic life forms of Diptera to the trophic needs of these fish species is apparent. The families Psychodidae, Tendipedidae, and Ceratopogonidae were the most widely represented groups of dipterans observed in stomach contents.

Stomach contents of white suckers, brown bullheads, crappies, and bluegills gave no indication of differential food habits that could be attributed to the oil spill.

B. Chlorophyll <u>a</u>

Average levels of total and active chlorophyll <u>a</u> (Appendix VI-1) increased from Monocacy Bridge station to Valley Forge Bridge station on 16 and 29 July 1972. This tends to substantiate the hypothesis of increased downstream primary productivity as suggested by pH measurement. Average levels were higher at all stations on 29 July than on 16 July.

Comparison of the ratios between pheopigment (inactive chlorophyll <u>a</u>) and total pigments indicated a substantially greater amount of "dead" material at Parker Ford Bridge (11.7 miles below the oil spill) on 16 July than at either Monocacy Bridge or Valley Forge Bridge (Figure 48). A slightly greater amount of pheopigment was observed at Parker Ford Bridge on 29 July than at the other stations.

Duplicate pigment measurements at the same sampling station generally indicated an acceptable degree of precision in sampling and spectrophotometric methods. The reason for the large differences between duplicate samples taken on 16 July at Valley Forge Bridge is unknown.

C. Zooplankton

Zooplankton samples taken on 16 July, 19 July, 28 November, 1 December 1972, and 14 July 1973 (Appendix VI-2) were generally similar at upstream and downstream stations. Members of the groups Cladocera (water fleas), Copepoda (copepods), and Tendipedidae (midges) were dominant forms throughout much of the study.

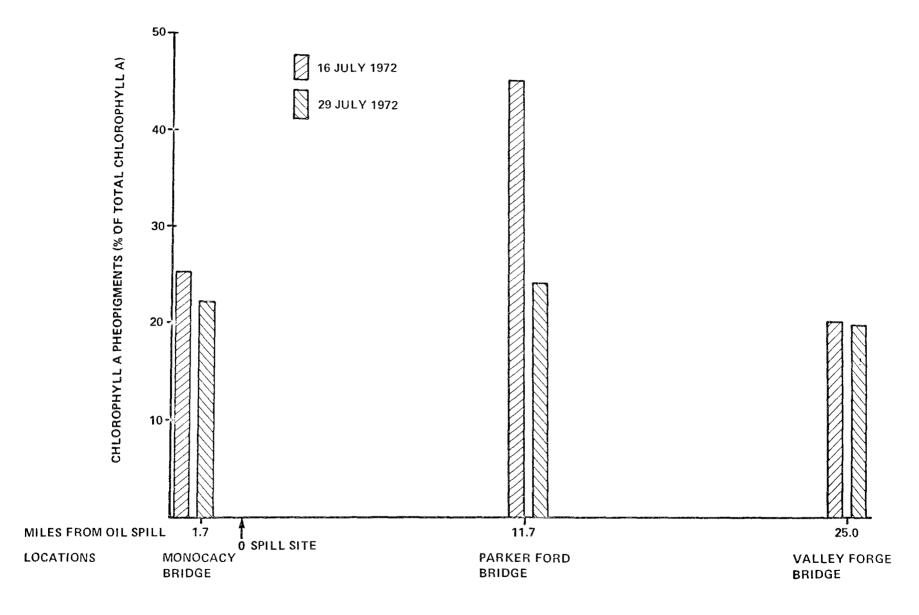


FIGURE 48 CHLOROPHYLL a PHEOPIGMENTS OF SCHUYLKILL RIVER WATER DURING JULY 1972

Ranges of abundance of these groups shortly after the oil spill (Figure 49) did not indicate differences between upstream and downstream stations that can be attributed to the oil spill. All three taxons exhibited greater abundance at Parker Ford Bridge station than at the upstream control station (Monocacy Bridge).

Major taxon diversity fluctuated between 6 and 10 during the study. Most taxons exhibited sharply reduced numbers during fall and winter. Lesser numbers of Cladocera, Copepoda, and Tendipedidae were observed in the summer of 1973 than during the summer of 1972.

D. <u>Benthic Macrofauna</u>

Larvae of the families Hydropsychidae (net-building caddis flies) and Psephenidae (water pennies) decreased in abundance in the area of the river directly below the oil spill and did not increase to their former production levels during the summer of 1972. Both groups are tolerant of rapid stream velocities and were collected in Perkiomen Creek, a small tributary emptying into the Schuylkill River between Phoenixville and Norristown, during and after the flooding caused by Tropical Storm Agnes. Therefore, it is likely that their scarcity in the Schuylkill was caused by the presence of oil rather than by the flood conditions. The food-gathering nets of many caddis fly larvae were visibly coated with oil. This may have reduced feeding efficiency. Water penny larvae breathe by ventral abdominal gills which rest directly against the rock surfaces upon which the animals attach. Any oil adhering to the rocks could conceivably have interfered with normal respiratory processes.

Quantitative sampling efforts directly after the oil spill were unsuccessful because of high-water conditions and lack of familiarity with the more suitable habitats of the river. Macrofauna samples collected on 29 November 1972 and 28 July 1973 (Appendix VI-3) exhibited no apparent variation among stations that can be attributed to the oil spill.

Ranges of abundance of the two dominant macrofaunal taxons (Figure 50) indicate that Oligochaeta (represented primarily by sludge worms of the genus <u>Tubifex</u>) were more abundant at both the Monocacy stations (above the oil spill) and the Parker Ford stations (10.6 to 12.5 miles downstream from the spill) than at the Douglassville stations (0.4 to 2.3 miles directly below the spill), and that numbers of Tendipedidae observed at the Monocacy and Douglassville stations did not differ greatly. Parker Ford stations were not

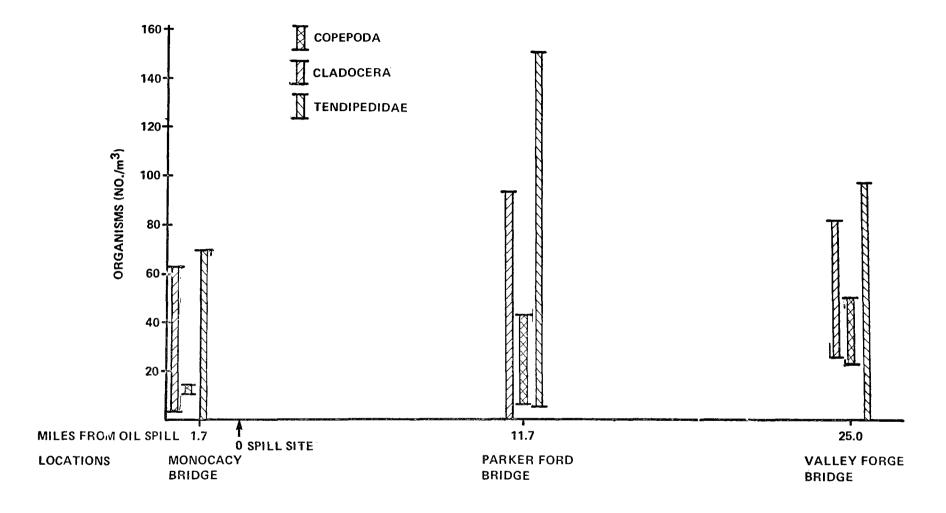


FIGURE 49 RANGES OF ABUNDANCE OF THREE DOMINANT ZOOPLANKTON TAXONS COLLECTED ON 28 JULY AND 29 NOVEMBER 1972 IN THE SCHUYLKILL RIVER

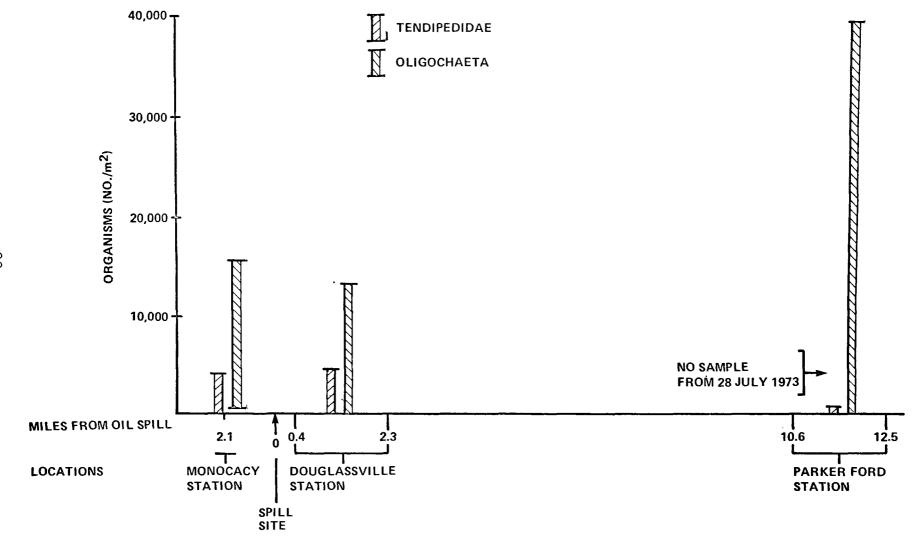


FIGURE 50. RANGES OF ABUNDANCE OF TWO DOMINANT MACROFAUNAL TAXONS COLLECTED ON 29 NOVEMBER 1972 AND 28 JULY 1973 IN THE SCHUYLKILL RIVER

sampled on 28 July 1973. Tendipedidae were commonly encountered at the other sampling stations on that date. Since both <u>Tubifex</u> and Tendipedidae are biological indicators that are resistant to most forms of pollution (Rounsefell and Everhart, 1953), the most likely result of the oil spill on the bottom community might be expected to be elevated numbers of both taxons in relation to other organisms directly below the spill at the Douglassville stations. This was not the case.

Major taxon diversity at the sampling sites ranged from 0 7 during the study (Appendix VI-3). Oligochaeta were more abundant than Tendipedidae on 29 November 1972. This relationship was reversed on 28 July 1973 presumably due, in part, to the onset of the midge reproductive season.

E. Bacteria

Bacteria counts of river sediment were taken on 17, 23, and 30 July 1972 and are shown in Appendix VI-4. On each collection date, the greatest numbers of casein splitters, glucose fermenters, and sulfate fermenters were found at the Parker Ford Bridge station. The generally low counts of glucose fermenters could indicate little recent addition of carbohydrate-like pollution to the river. Similarly, low numbers of sulfate fermenters may be due to relatively aerated conditions in the river bottom or to inactivation of the samples by air after sampling.

Contamination of the agar medium prevented estimation of the important hydrocarbon oxidizers on 17 and 23 July. However, on 30 July these bacteria were at least twice as abundant in the Parker Ford Bridge area than at the other stations.

Standard plate counts (Table 23) also revealed highest bacteria counts in the Parker Ford Bridge area on all sampling dates.

F. Community Metabolism

Suitability of oxygen data (Appendix I-1) for treatment by diurnal-curve techniques was determined. Data collected on 16 and 29 July 1972 were not usable since normal predawn decreases in

Rounsefell, G. A. and W. H. Everhart. 1953. <u>Fishery Science</u>: Its Methods and Applications. J. Wiley and Sons, London. 444p.

oxygen concentrations, from which estimates of community respiration are derived, did not occur.

Oxygen data for 30 July 1972 and diurnal-curve analysis are presented in Figures 51 and 52. Community respiration and gross primary production were slightly higher at Parker Ford Bridge than upstream at Monocacy Bridge. Community respiration at both sampling stations was relatively high as compared to several river systems described by Odum (1956, Table 2). Both P/R ratios were just over 1.0, indicating an autotropic river system in which in-situ primary production slightly exceeds community respiration.

Biochemical oxygen demand (BOD) measurements taken during the summer of 1972 (Appendix I-2) ranged from 0.4 to 4.2 ppm. Highest levels were usually observed in the Douglassville Bridge - Parker Ford Bridge length of the river (0.7 to 11.7 miles below the oil spill).

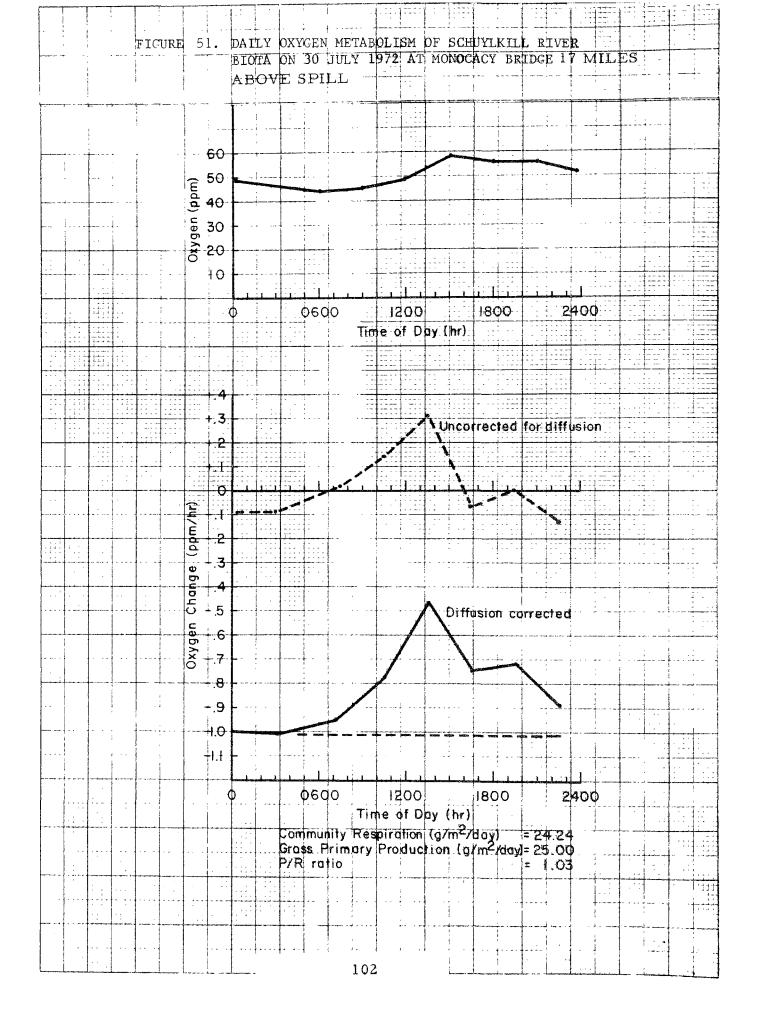
The importance of the bottom community in the Schuylkill is evidenced by comparing biochemical-oxygen-demand of the river water to estimates of community respiration obtained by the diurnal-curve techniques. BOD, which measures respiration of only the planktonic flora and fauna of the river, was only 0.4 to 4.2 ppm oxygen over a five-day period. However, total community respiration, including that of the bottom community, as determined by diurnal-curve techniques, was approximately 25 ppm oxygen during a single 24-hour cycle.

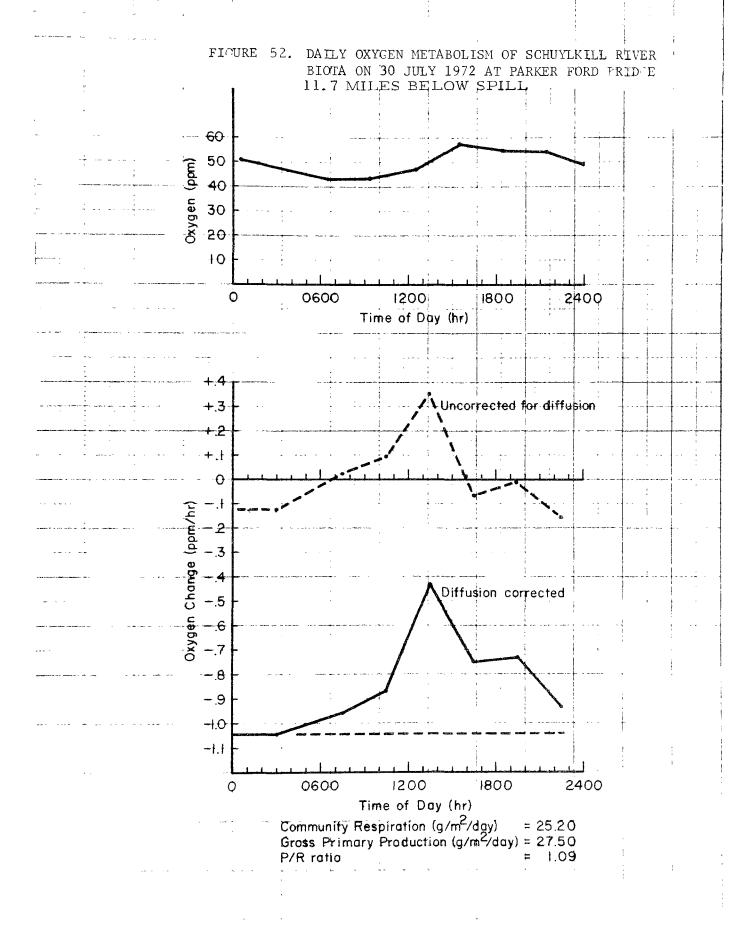
10. CLEANUP IMPACT AND EFFECTIVENESS

A. A major portion of the oil swept from the pits of Berk Associates was filtered from the rising flood waters by land vegetation or deposited on the river's banks and proximal areas. Apparently only a small amount of oil was carried directly into the river basin.

It is likely that much of the oil that was carried into the river basin combined with the heavy silt and clay load that characterized the flooding river and was rapidly carried downstream toward Delaware Bay. No large masses of oil were observed during bottom

Odum, H. T. 1956. "Primary Production in Flowing Waters," Limno. Ocean. 1:102-117.





sampling operations. Most of the silt and clay particles upon which hydrocarbon and heavy metals precipitate were washed away by the flood waters. Only a sand-pebble substratum remained. Chemical analysis of heavy metal and hydrocarbon concentrations of the bottom indicated that there was some oil contamination of the river bottom below the spill.

Cleanup of the river bottom was considered unnecessary due to the high cost. The inefficiency of the operation would have only served to redistribute much of the oil that had been deposited on the river bottom.

- B. Oil that was deposited directly on land had to be physically removed. Heavy metal constituents of the oil were likely to persist through time. Workmen had to avoid accidental oral intake of the oil (Physical contact with the metals' components is not a problem). Burning of oil will vaporize heavy metals and result in a potential hazard to workmen and to the surrounding environment. Burning should never be attempted. Vaporization of low-boiling aromatic hydrocarbon (another component of the oil) caused a noticeable "oily" smell in the affected area. Toxic materials will evaporate and be oxidized and decomposed with time. However, they are considered a health hazard to men subjected to chronic exposure through inhalation. Care was taken not to bury removed oil where contamination to ground water or livestock might occur.
- C. Oil deposited on vegetation (leaves, grasses, etc.) adhered tightly to the plants after a period of consolidation. Rainfall or falling of leaves into the river resulted in only small amounts of heavy metals and remaining hydrocarbons (most toxic hydrocarbons had already been evaporated or decomposed) going into solution. Hence, periodic precipitation and gradual fall of leaves into the river unlikely caused major human health problems. Any hosing of vegetation during a short time period or before low-boiling aromatic hydrocarbons had evaporated or decomposed would have resulted in a more acute problem of river pollution than doing nothing. Primary cleanup operations performed for the removal of vegetation resulted in the following:
- 1) Only trees, shrubs, and branches in the most heavily polluted areas were removed in order to leave a root system to prevent bank erosion.
- 2) "Quick-cover," fast-growing grass was used to prevent erosion.

3) Angled booms were placed at strategic locations along the river to collect floating leaves and oil slicks. Booms were placed in slowly moving sections of the river and kept in operation until most oil-covered leaves had dropped from the banks. Angled booms also directed floating oil to the bank at water velocities of less than 2 knots. Trucks were permanently at locations to suck leaves and oil from the junctions of the booms and riverbank.

ACKNOWLEDGEMENTS

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Mr. Charles R. Mainville was the Program Manager.

Dr. Charles R. Curtis, Associate Professor of Plant Pathology at the University of Maryland, conducted the investigations of the effects of the spill on vegetation.

Techniques for the analysis of hydrocarbons in vertebrate fishes were developed by Professor Trevor Hill of the College of William and Mary. Dr. Hill was assisted in his work by Messrs. William S. Eck, Robert Huggett, and Gerry Lasser.

Mr. Robert Huggett of the Virginia Institute of Marine Science performed the heavy metaos analyses of the oil, sediments, and organisms.

Biological analyses and water-quality investigations were performed by Dr. Curt D. Rose, Head of the Shellfish Division of the University of Maryland's Center for Environmental and Estuarine Studies. Dr. Rose was assisted by Messrs. Rodgers Huff, Joseph Ustach, Bud Millsaps, Dan Terlizzi, and Don Meritt.

Messrs. Michael Clark, Larry Kingsbury, and Roy L. Rice of OSE performed much of the field work during the program.

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GLOSSARY

Common Name Biological Name

Birch Betula sp.

Black walnut Juglans nigra L.

Bluegill Lepomis macrochirus

Brown bullheads Ictalurus nebulosus

Channel catfish <u>Ictalurus punctatus</u>

Crappies Pomoxis sp.

Elm Ulmus sp.

Golden shiver Notemigonus crysoleucas

Hickory Carya sp.

Maple <u>Acer sp.</u>

Net building caddis flies <u>Hydropsychidae</u>

Oak Quercus sp.

Sassafras Sassafras albidium

Sycamore Platanus occidentalis L.

Tree of heaven Ailanthus altissima

Tuliptree <u>Liriodendron tulipifers L</u>

Water pennies <u>Psephenidae</u>

White suckers <u>Catostomus commersoni</u>

Wild cherry Prunus sp.

APPENDIX I DATA FROM ANALYSES OF RIVER WATER

Appendix I-1. Twenty-four (24) hour temperature and dissolved oxygen

July 1972

| Above Spill | | 16 Jul <u>y 1972</u> | | Below | Below Spill | | |
|-------------|---------------|-----------------------------------|------|----------------------------|--------------------------------|--|--|
| Monocacy | | | | Parker Ford | | | |
| Time | Temp. (°C) | Dissolved O ₂ (ppm) | Time | Temp. (^O C) | Dissolved O ₂ (ppm) | | |
| 0025 | 24 | 5.2 | 0000 | 26 | 5.3 | | |
| 0630 | 24 | 5.7 | 0600 | 25 | 5.8 | | |
| 0930 | 25 | 5.9 | 0900 | 25 | 5.8 | | |
| 1230 | 27 | 6.1 | 0200 | 27 | 6.3 | | |
| 1530 | 27 | 6.2 | 1600 | 28 | 6.4 | | |
| 2020 | 25 | 6.2 | 1830 | 28 | 6.4 | | |
| | | 29 July 1 | 972 | | | | |
| Monocacy | | | | Parker 1 | Ford | | |
| Time | Temp. | Dissolved O2 (ppm) | Time | Temp. | Dissolved O ₂ | | |
| 0100 | 23 | 5.2 | 0030 | 23 | 5.7 | | |
| 0640 | 23 | 6,2 | 0625 | 23 | 7.0 | | |
| 0950 | 24 | 6.3 | 0925 | 24 | 7.1 | | |
| 1310 | 23 | 7.5 | 1245 | 24 | 7.6 | | |

8.0

7.6

Appendix I-1. (continued)

Above Spill

30 July 1972

Below Spill

| Monocac | у | | | Parker : | Ford |
|---------|---------------|--------------------------------|------|----------------------------|-----------------------------------|
| Time | Temp. (°C) | Dissolved O ₂ (ppm) | Time | Temp. (^O C) | Dissolved O ₂ (ppm) |
| 0000 | 21 | 4.9 | 0030 | 23 | 5.1 |
| 0600 | 21 | 4.4 | 0630 | 23 | 4.4 |
| 0900 | 21 | 4.5 | 0930 | 23 | 4.4 |
| 1200 | 21 | 4.9 | 1230 | 23 | 4.7 |
| 1500 | 21 | 5.8 | 1530 | 23 | 5.7 |
| 1800 | 21 | 5.6 | 1830 | 23 | 5.5 |
| 2100 | 21 | 5.6 | 2130 | 23 | 5.5 |
| 2400 | 21 | 5.2 | 2430 | 23 | 5.0 |

Appendix I-2. Biochemical oxygen demand, chemical oxygen demand, and M.O. alkalinity of Schuylkill River water above and below spill site in July 1972

| Station | BOD (ppm-5 day) 3 July 1972 | COD (ppm) | M.O. Alkalinity (ppm CaCO3) |
|--------------------|-----------------------------|-----------|--------------------------------|
| Above Spill | | | |
| Monocacy | 1.1 | 6.71 | 50 |
| Below Spill | | | |
| Douglassville Br. | 0.9 | 7.38 | 54 |
| Parker Ford Br. | 1.5 | 9.40 | 53 |
| Spring City Br. | 1.5 | 15.44 | 56 |
| Rt. 113 Br. | 1.3 | 10.07 | 52 |
| Valley Forge Br. | 1.4 | 15.10 | 52 |
| Falls Br. (Phila.) | 1.3 | 10.74 | 55 |
| | | | |
| | 11 July 1972 | | |
| Above Spill | | | |
| Monocacy | 1.0 | 5.59 | con last |
| Below Spill | | | |
| Douglassville Br. | 0.9 | 5,38 | en un |
| Parter Ford Br. | 0.4 | 10.40 | |
| Valley Forge Br. | 0.8 | 4.97 | ca so |

| | 18 July 197 2 | | |
|-------------------|----------------------|-------|------------|
| Above Spill | | | |
| Monocacy Br. | 0.6 | 9.27 | 70 |
| Below Spill | | | |
| Douglassville Br. | 0.9 | 10.50 | 68 |
| Parter Ford Br. | 0.7 | 16.10 | 72 |
| Valley Forge Br. | 0.5 | 9.67 | 67 |
| | 25 July 1972 | | |
| Above Spill | | | |
| Monocacy Br. | 1.8 | 7.56 | 73 |
| Below Spill | | | |
| Douglassville Br. | 2.7 | 11.10 | 8 2 |
| Parkerford Br. | 1.8 | 7.96 | 84 |
| Valley Forge Br. | 1.6 | 11.10 | 76 |
| 1 | 1 August 1972 | | |
| Above Spill | | | |
| Monocacy Br. | 1.9 | 8.97 | 68 |
| Below Spill | | | |
| Douglassville Br. | 4.2 | 11.30 | 78 |
| Parkerford Br. | 1.7 | 6.24 | 76 |
| Valley Forge Br. | 1.3 | 6.63 | 78 |

Appendix I=3. Hydrogen-ion concentration in Schuylkill River water 12 July - 5 August 1972

| Date | | Stations | | |
|-----------------|-------------------------|---------------|----------------------------|--------------|
| | Above Spill Monocacy | Douglassville | Below Spill Parker Ford | Valley Forge |
| July 12 | 7.4 | 7.4 | 7.4 | 7.5 |
| July 13 | 7.4 | 7.3 | 7.4 | 7.7 |
| July 14 | 7.2 | 7.2 | 7 .2 | 7.3 |
| July 15 | 7.4 | 7.4 | 7.4 | 7.4 |
| July 16 | Bub Oto | 7.5 | 7.4 | 7.7 |
| July 1 7 | 7.0 | 7.0 | 7.0 | 7.3 |
| July 18 | 7.1 | 7.1 | 7.0 | 7.2 |
| July 19 | 7.2 | 7.2 | 7.0 | 7.2 |
| July 20 | 7.2 | 7.1 | 7.2 | 7.2 |
| July 21 | 7.1 | 7.2 | 7.1 | 7.1 |
| July 22 | 7.2 | 7 .2 | 7.2 | 7.2 |
| July 23 | 7.2 | 7.2 | 7.2 | 7.3 |
| July 24 | 7.3 | 7.3 | 7.4 | 7.8 |
| July 25 | 7.2 | 7.2 | 7.2 | 7.6 |
| July 2 6 | 7.2 | 7.2 | 7.2 | 7.2 |
| July 27 | 7 .2 | 7.2 | 7.2 | 7.3 |
| July 28 | 7.2 | 7.2 | 7 .2 | 7.2 |
| July 29 | 7.2 | 7.2 | 7 .2 | 7.6 |
| July 30 | 7.2 | 7.2 | 7 .2 | 7.8 |
| July 31 | 7 .2 | 7.2 | 7.2 | 7.6 |

Appendix I-3. (continued)

| Date | | Stations | | |
|----------|----------|---------------|-------------|--------------|
| | Monocacy | Douglassville | Parker Ford | Valley Forge |
| August 1 | 7.2 | 7.2 | 7.2 | 7.4 |
| August 2 | 7.3 | 7 .2 | 7.2 | 7.4 |
| August 3 | 7.2 | 7.1 | 7.2 | 7.3 |
| August 4 | 7.1 | | 7.2 | 7.3 |
| August 5 | 7.2 | | 7.5 | |

 $^{^{1}}_{\mbox{\sc All}}$ readings were taken during the day and, therefore, represent maximum daily values.

APPENDIX II DATA FROM HEAVY METALS ANALYSES OF RIVER WATER AND SEDIMENTS

Appendix II-1. Concentrations of lead, zinc, cadmium, and copper in Schuylkill River water 3 July - 4 August 1972

| STATION | HEA | HEAVY METAL CONCENTRATION (ppm) | | | |
|----------------------------|-------|---------------------------------|---------|--------|--|
| | Lead | Zinc | Cadmium | Copper | |
| 3 July | | | | | |
| Monocacy Farm Bridge | 0.015 | 0.01 | 0.002 | 0.05 | |
| Douglassville Bridge | 0.014 | 0.025 | 0.002 | 0.05 | |
| Parker Ford Bridge | 0.014 | 0.01 | 0.002 | 0.05 | |
| Spring City/Royersford Br. | 0.011 | 0.03 | 0.002 | 0.05 | |
| Route 113 Bridge | 0.039 | 0.070 | 0.002 | 0.05 | |
| Valley Forge Bridge | 0.033 | 0.03 | 0.002 | 0.05 | |
| Falls Bridge | 0.018 | 0.025 | 0.002 | 0.05 | |
| 4 July | | | | | |
| Monocacy Farm | 0.004 | 0.01 | 0.002 | 0.05 | |
| Douglassville Bridge | 0.038 | 0.05 | 0.002 | 0.05 | |
| Parker Ford Br., Sample 1 | 0.023 | 0.04 | 0.002 | 0.05 | |
| Parker Ford Br., Sample 2 | 0.040 | 0.02 | 0.002 | 0.05 | |
| Spring City/Royersford Br. | 0.003 | 0.01 | 0.002 | 0.05 | |
| Route 113 Bridge | 0.024 | 0.04 | 0.002 | 0.05 | |
| Valley Forge Bridge | 0.010 | 0.02 | 0.002 | 0.05 | |
| Falls Bridge | 0.009 | 0.01 | 0.002 | 0.05 | |
| 5 July | | | | | |
| Monocacy Farm, Sample 1 | 0.004 | 0.03 | 0.002 | 0.05 | |
| Monocacy Farm, Sample 2 | 0.003 | 0.03 | 0.002 | 0.05 | |
| Douglassville Bridge | 0.086 | 0.05 | 0.002 | 0.05 | |

| STATION | HEAVY METAL CONCENTRATION (ppm) | | | |
|----------------------------|---------------------------------|------|---------|--------|
| | Lead | Zinc | Cadmium | Copper |
| 5 July (contd) | | | | |
| Parker Ford Bridge | 0.004 | lost | 0.002 | 0.05 |
| Route 113 Bridge | 0.046 | 0.04 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.016 | 0.01 | 0.002 | 0.05 |
| Falls Bridge | 0.011 | 0.01 | 0.002 | 0.05 |
| 6 July | | | | |
| Monocacy Farm, Sample 1 | 0.002 | 0.02 | 0.002 | 0.05 |
| Monocacy Farm, Sample 2 | 0.002 | 0.02 | 0.002 | 0.05 |
| Douglassville Bridge | 0.040 | 0.01 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.029 | 0.03 | 0.002 | 0.05 |
| Spring City/Royersford Br. | 0.011 | 0.04 | 0.002 | 0.05 |
| Route 113 Bridge | 0.005 | 0.02 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.016 | 0.04 | 0.002 | 0.05 |
| Falls Bridge | 0.012 | 0.01 | 0.002 | 0.05 |
| 7 July | | | | |
| Monocacy Farm, Sample 1 | 0.004 | 0.05 | 0.002 | 0.05 |
| Monocacy Farm, Sample 2 | 0.002 | 0.02 | 0.002 | 0.05 |
| Douglassville Bridge | 0.041 | 0.06 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.015 | 0.07 | 0.002 | 0.05 |
| Spring City/Royersford Br. | 0.019 | 0.08 | 0.002 | 0.05 |
| Route 113 Bridge | 0.018 | 0.05 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.019 | 0.01 | 0.002 | 0.05 |
| Falls Bridge | 0.015 | 0.04 | 0.002 | 0.05 |

| STATION | <u>HEA (</u> | Y-METAL CO | NCENTRATION | (ppm) |
|-------------------------|--------------|------------|-------------|--------|
| 8 July | Lead | Zinc | Cadmium | Copper |
| Monocacy Farm, Sample 1 | 0.006 | 0.04 | 0.002 | 0.05 |
| Monocacy Farm, Sample 2 | 0.004 | 0.02 | 0.002 | 0.05 |
| Douglassville Bridge | 0.018 | 0.05 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.010 | 0.03 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.028 | 0.07 | 0.002 | 0.05 |
| 9 July | | | | |
| Monocacy Farm | 0.005 | 0.010 | 0.002 | 0.05 |
| Douglassville Bridge | 0.015 | 0.06 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.013 | 0.06 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.015 | 0.01 | 0.002 | 0.05 |
| 10 July | | | | |
| Monocacy Farm | 0.002 | 0.010 | 0.002 | 0.05 |
| Douglassville Bridge | 0.008 | 0.037 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.005 | 0.010 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.006 | 0.012 | 0.002 | 0.05 |
| 11 July | | | | |
| Monocacy Farm | 0.002 | 0.018 | 0.002 | 0.05 |
| Douglassville Bridge | 0.010 | 0.031 | 0.002 | 0.05 |
| Parker Ford Bridge | 0.010 | 0.018 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.014 | 0.010 | 0.002 | 0.05 |
| 12 July | | | | |
| Monocacy Farm | 0.002 | 0.010 | 0.002 | 0.05 |
| Douglassville Bridge | 0.006 | 0.031 | 0.002 | 0.05 |

| STATION | HE/ | AVY METAL C | ONCENTRATION | N (ppm) |
|----------------------|-------|-------------|--------------|---------|
| | Lead | Zinc | Cadmium | Copper |
| 12 July (contd) | | | | |
| Parker Ford Bridge | 0.017 | 0.018 | 0.002 | 0.05 |
| Valley Forge Bridge | 0.016 | 0.010 | 0.002 | 0.05 |
| 13 July | | | | |
| Monocacy Farm | 0.003 | 0.004 | 0.001 | 0.03 |
| Douglassville Bridge | 0.006 | 0.016 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.008 | 0.029 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.006 | 0.004 | 0.001 | 0.03 |
| 14 July | | | | |
| Monocacy Farm | 0.005 | 0.009 | 0.001 | 0.03 |
| Douglassville Bridge | 0.013 | 0.026 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.010 | 0.016 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.011 | 0.009 | 0.001 | 0.03 |
| 15 July | , | | | |
| Monocacy Bridge | 0.002 | 0.015 | 0.001 | 0.03 |
| Douglassville Bridge | 0.007 | 0.029 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.005 | 0.015 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.002 | 0.011 | 0.001 | 0.03 |
| lo July | | | | |
| Monocacy Bridge | 0.005 | 0.011 | 0.001 | 0.03 |
| Douglassville Bridge | 0.003 | 0.009 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.005 | 0.015 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.006 | 0.018 | 0.001 | 0.03 |

| STATION | HEA | HEAVY METAL CONCENTRATION (ppm) | | | | |
|----------------------|-------|---------------------------------|---------|--------|--|--|
| 17 July | Lead | Zinc | Cadmium | Copper | | |
| Monocacy Bridge | 0.003 | 0.007 | 0.001 | 0.03 | | |
| Douglassville Bridge | 0.003 | 0.007 | 0.001 | 0.03 | | |
| Parker Ford Bridge | 0.003 | 0.007 | 0.001 | 0.03 | | |
| Valley Forge Bridge | 0.003 | 0.009 | 0.001 | 0.03 | | |
| 18 July | | | | | | |
| Monocacy Bridge | 0.002 | 0.013 | 0.001 | 0.03 | | |
| Douglassville Bridge | 0.016 | 0.012 | 0.001 | 0.03 | | |
| Parker Ford Bridge | 0.002 | 0.014 | 0.001 | 0.03 | | |
| Valley Forge Bridge | 0.003 | 0.014 | 0.001 | 0.03 | | |
| 19 July | | | | | | |
| Monocacy Bridge | 0.001 | 0.013 | 0.001 | 0.03 | | |
| Douglassville Bridge | 0.003 | 0.011 | 0.001 | 0.03 | | |
| Parker Ford Bridge | 0.003 | 0.013 | 0.001 | 0.03 | | |
| Valley Forge Bridge | 0.002 | 0.012 | 0.001 | 0.03 | | |
| 20 July | | | | | | |
| Monocacy Bridge | 0.003 | 0.013 | 0.001 | 0.03 | | |
| Douglassville Bridge | 0.003 | 0.012 | 0.001 | 0.03 | | |
| Parker Ford Bridge | 0.002 | 0.013 | 0.001 | 0.03 | | |
| Valley Forge Bridge | 0.002 | 0.011 | 0.001 | 0.03 | | |
| 21 July | | | | | | |
| Monocacy Bridge | 0.001 | 0.012 | 0.001 | 0.03 | | |
| Douglassville Bridge | 0.002 | 0.014 | 0.001 | 0.03 | | |
| Parker Ford Bridge | 0.003 | 0.013 | 0.001 | 0.03 | | |
| Valley Forge Bridge | 0.003 | 0.012 | 0.001 | 0.03 | | |
| | | | | | | |

| STATION | HEAVY METAL CONCENTRATION (ppm) | | | |
|--------------------------|---------------------------------|-------|---------|--------|
| 22 July | Lead | Zinc | Cadmium | Copper |
| Monocacy Bridge | 0.002 | 0.011 | 0.001 | 0.03 |
| Douglassville B ridge | 0.002 | 0.013 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.002 | 0.014 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.002 | 0.013 | 0.001 | 0.03 |
| 23, 24, 25 July | | | | |
| Samples lost in shipment | | | | |
| 26 July | | | | |
| Monocacy Bridge | 0.006 | 0.005 | 0.001 | 0.03 |
| Douglassville Bridge | 0.009 | 0.007 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.005 | 0.005 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.008 | 0.005 | 0.001 | 0.03 |
| 27 July | | | | |
| Monocacy Bridge | 0.008 | 0.004 | 0.001 | 0.03 |
| Douglassville Bridge | 0.006 | 0.004 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.006 | 0.005 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.007 | 0.009 | 0.001 | 0.03 |
| 28 July | | | | |
| Monocacy Bridge | 0.005 | 0.003 | 0.001 | 0.03 |
| Douglassville Bridge | 0.006 | 0.002 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.007 | 0.009 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.007 | 0.011 | 0.001 | 0.03 |

| STATION | HEAVY METAL CONCENTRATION (ppm) | | | | |
|----------------------|---------------------------------|-------|---------|--------|--|
| 29 July | Lead | Zinc | Cadmium | Copper | |
| Monocacy Bridge | 0.007 | 0.007 | 0.001 | 0.03 | |
| Douglassville Bridge | 0.006 | 0.007 | 0.001 | 0.03 | |
| Parker Ford Bridge | 0.006 | 0.009 | 0.001 | 0.03 | |
| Valley Forge Bridge | 0.034 | 0.008 | 0.001 | 0.03 | |
| 30 July | | | | | |
| Monocacy Bridge | 0.007 | 0.008 | 0.001 | 0.03 | |
| Douglassville Bridge | 0.006 | 0.008 | 0.001 | 0.03 | |
| Parker Ford Bridge | 0.008 | 0.007 | 0.001 | 0.03 | |
| Valley Forge Bridge | 0.008 | 0.004 | 0.001 | 0.03 | |
| 31 July | | | | | |
| Monocacy Bridge | 0.009 | 0.009 | 0.001 | 0.03 | |
| Douglassville Bridge | 0.006 | 0.005 | 0.001 | 0.03 | |
| Parker Ford Bridge | 0.009 | 0.007 | 0.001 | 0.03 | |
| Valley Forge Bridge | 0.009 | 0.017 | 0.001 | 0.03 | |
| 1 August | | | | | |
| Monocacy Bridge | 0.001 | 0.013 | 0.001 | 0.03 | |
| Douglassville Bridge | 0.001 | 0.012 | 0.001 | 0.03 | |
| Parker Ford Bridge | 0.003 | 0.012 | 0.011 | 0.03 | |
| Valley Forge Bridge | 0.001 | 0.012 | 0.001 | 0.03 | |
| 2 August | | | | | |
| Monocacy Bridge | 0.005 | 0.007 | 0.001 | 0.03 | |
| Douglassville Bridge | 0.005 | 0.009 | 0.001 | 0.03 | |
| Parker Ford Bridge | 0.007 | 0.012 | 0.003 | 0.03 | |
| Valley Forge Bridge | 0.006 | 0.007 | 0.001 | 0.03 | |

| STATION | <u>HEAV</u> | Y METAL CO | NCENTRATION | (ppm) |
|----------------------|-------------|------------|----------------|--------|
| | Lead | Zinc | Cadmium | Copper |
| 3 August | | | | |
| Monocacy Bridge | 0.007 | 0.015 | 0.001 | 0.03 |
| Douglassville Bridge | 0.007 | 0.015 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.012 | 0.012 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.012 | 0.009 | 0.001 | 0.03 |
| 4 August | | | | |
| Monocacy Bridge | 0.005 | 0.009 | 0.001 | 0.03 |
| Douglassville Bridge | 0.007 | 0.009 | 0 .0 01 | 0.03 |
| Parker Ford Bridge | 0.022 | 0.006 | 0.001 | 0.03 |
| Valley Forge Bridge | 0.012 | 0.012 | 0.001 | 0.03 |
| 5 August | | | | |
| Monocacy Bridge | 0.006 | 0.012 | 0.001 | 0.03 |
| Parker Ford Bridge | 0.007 | 0.009 | 0.001 | 0.03 |

Appendix II-2. Concentrations of lead, zinc, cadmium, and copper in Schuylkill River bottom samples collected in July, 1972

| STATION | Loi | Lead | Zinc | Cadmium | Copper |
|-------------------------|-----|-------|------|---------|------------------------|
| 1 July | | | | | |
| 12.4 miles below spill | | 32.5. | 259 | 0.2 | 45.1 |
| 12.4 miles below spill | | 154.0 | 218 | 0.2 | 32.6 |
| 11.72 miles below spill | | 14.2 | 426 | 0.4 | 30.0 |
| 11.72 miles below spill | | 16.9 | 353 | 0.4 | 47.5 |
| 2 July | | | | | |
| 2.35 miles below spill | | 61.7 | 133 | 0.2 | 4 94 . 0 |
| 2.35 miles below spill | | 3.7 | 70 | 0.2 | 25.0 |
| 3.75 miles below spill | | 1.3 | 51 | 0.2 | 22.7 |
| 5.75 miles below spill | | 17.5 | 169 | 0.2 | 31.4 |
| 6.75 miles below spill | | 19.7 | 161 | 0.2 | 35.8 |
| 6.75 miles below spill | | 16.9 | 177 | 0.2 | 35.1 |
| 8.75 miles below spill | | 11.9 | 119 | 0.2 | 38.1 |
| 8.75 miles below spill | | 28.8 | 158 | 0.2 | 36.4 |
| 10.7 miles below spill | | 171.0 | 225 | 0.2 | 33.3 |
| 19.90 miles below spill | | 38.5 | 235 | 0.2 | 27.3 |
| 19.90 miles below spill | | 37.6 | 300 | 0.2 | 32.0 |
| 22.25 miles below spill | | 44.1 | 309 | 0.2 | 40.5 |
| 22.25 miles below spill | | 26.2 | 233 | 0.2 | 29.1 |
| 4 July | | | | | |
| Parker Ford Bridge | | 5.1 | 135 | 0.2 | 34.9 |
| Parker Ford Bridge | | 9.3 | 230 | 0.2 | 23.7 |
| Route 113 Bridge | | 22.1 | 274 | 0.2 | 28.6 |

| STATION | <u>Loi</u> | Lead | Zinc | Cadmium | Copper |
|----------------------|------------|--------|------|---------|--------|
| 5 July | | | | | |
| Route 113 Bridge | | 161.0 | 310 | 0.2 | 33.5 |
| 9 July | | | | | |
| Monocacy | | 395.0 | 416 | 1.3 | 145.0 |
| Douglassville Bridge | | 14.1 | 101 | 0.2 | 22.5 |
| Parker Ford Bridge | | 13.5 | 192 | 0.2 | 38.4 |
| Valley Forge Bridge | | 9.2 | 38 | 0.2 | 11.9 |
| ll July | | | | | |
| Monocacy Farm | 16.70% | 304 | 373 | 1.7 | 161 |
| Douglassville Bridge | 10.08% | 372 | 312 | 2.1 | 113 |
| Valley Forge Bridge | 12.42% | 124 | 162 | 1.5 | 42.7 |
| 15 July | | | | | |
| Douglassville Bridge | 9.90% | 32.1 | 62,1 | 1.2 | 25.9 |
| Parker Ford Bridge | 26.31% | 2210.0 | 656 | 2.6 | 193 |
| Valley Forge Bridge | 5.71% | 39.2 | 144 | 3.1 | 22.0 |

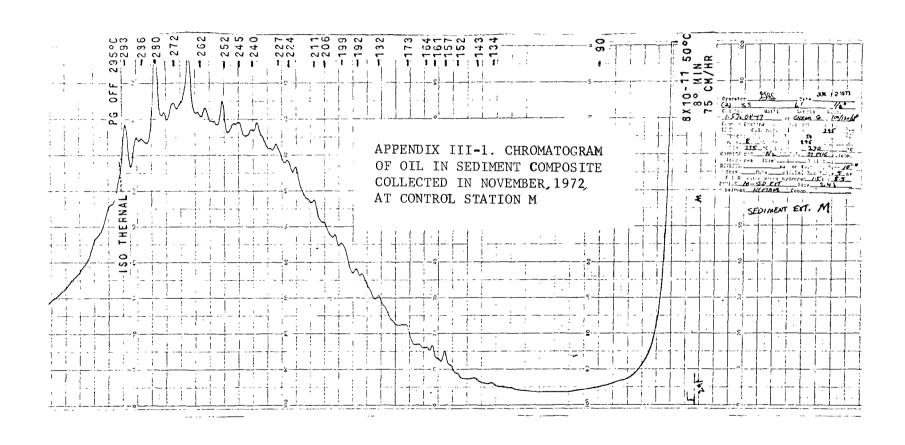
Appendix II-3. Concentrations of lead, zinc, cadmium, copper and mercury in Schuylkill River bottom sediments collected in November, 1972

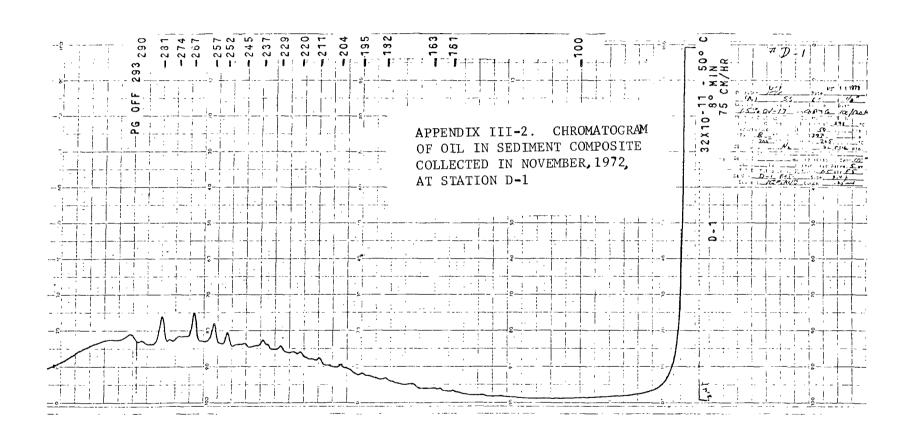
| Sample Station | <u>Lead</u> | Zinc | ppm D Cadmium | ry Weight ¹ <u>Copper</u> | Mercury |
|--------------------|-------------|------|------------------|---|---------|
| Monocacy* | 500 | 930 | 3.9 | 290 | 0.013 |
| Monocacy - 1 | 426 | 820 | 3.9 | 240 | 0.010 |
| Monocacy - 2 | 445 | 640 | 2.8 | 277 | 0.021 |
| Monocacy - 3 | 413 | 576 | 2.5 | 248 | 0.008 |
| Monocacy - 4 | 435 | 602 | 2.2 | 242 | 0.016 |
| Monocacy - 5 | 458 | 698 | 2.9 | 266 | 0.027 |
| Douglassville - 1* | 530 | 920 | 3.9 | 260 | 0.009 |
| Douglassville - 2* | 450 | 920 | 1.8 | 140 | 0.295 |
| Douglassville - 3* | 1400 | 650 | 3.1 | 190 | 0.016 |
| Douglassville - 4* | 690 | 700 | 2.6 | 240 | 0.115 |
| Douglassville - 5* | 780 | 510 | 2.3 | 190 | 0.045 |
| Parker Ford - 1* | 550 | 840 | 6.3 | 240 | 0.081 |
| Parker Ford - 2* | 46 0 | 1200 | 8.0 | 310 | 0.090 |
| Parker Ford - 3* | 70 | 130 | 0.2 | 51 | 0.130 |
| Parker Ford - 4* | 570 | 940 | 8.2 | 350 | 0.087 |
| Parker Ford - 5* | 690 | 1420 | 9.3 | 370 | 0.490 |

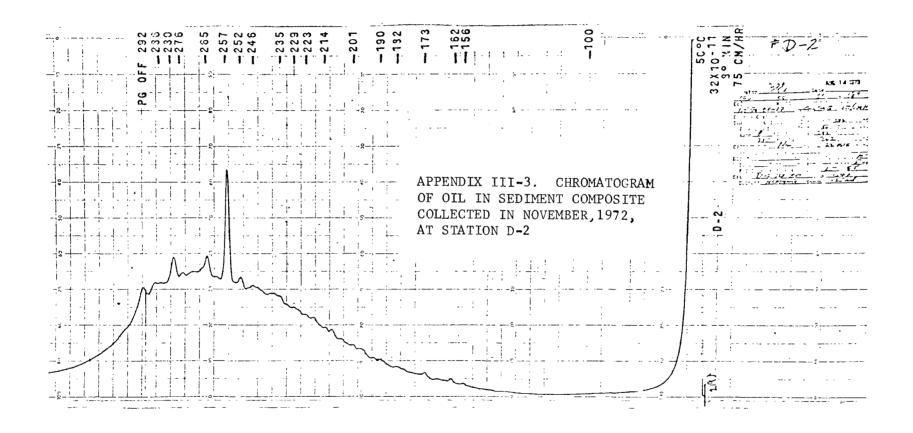
^{*} Composite

l Mean of replicate analyses

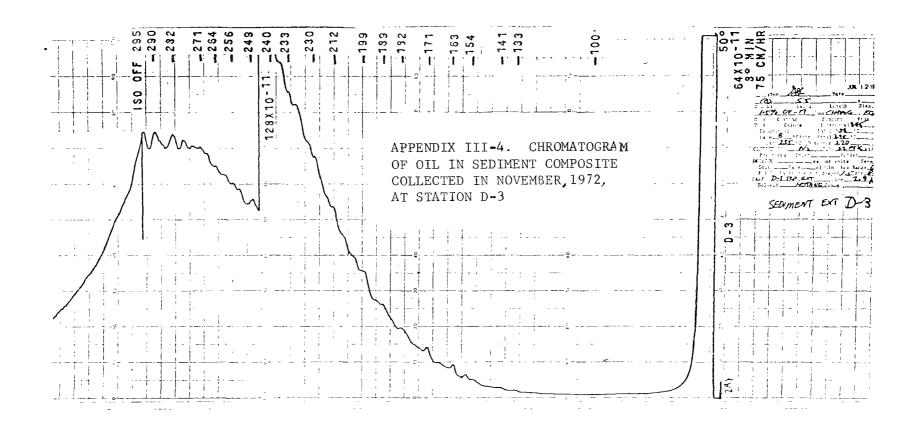
APPENDIX III DATA FROM HYDROCARBON ANALYSES OF SEDIMENTS

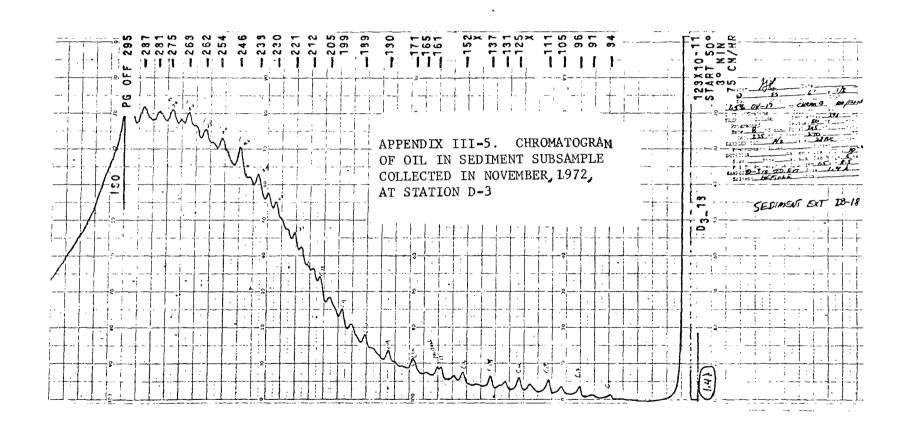


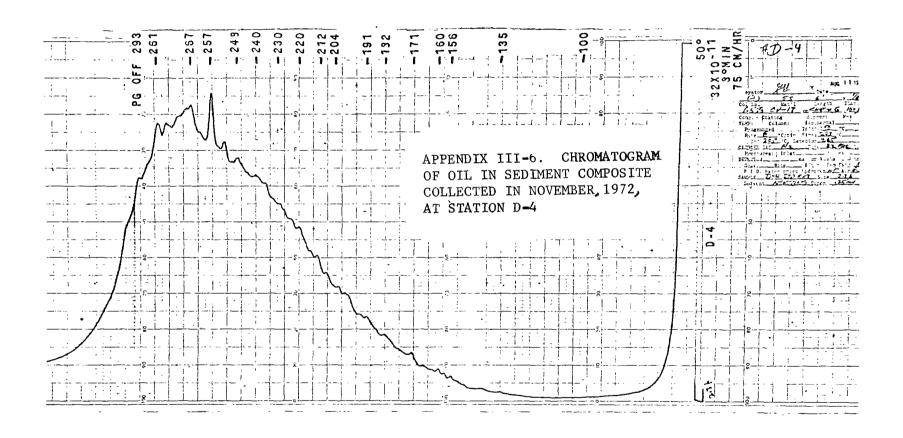


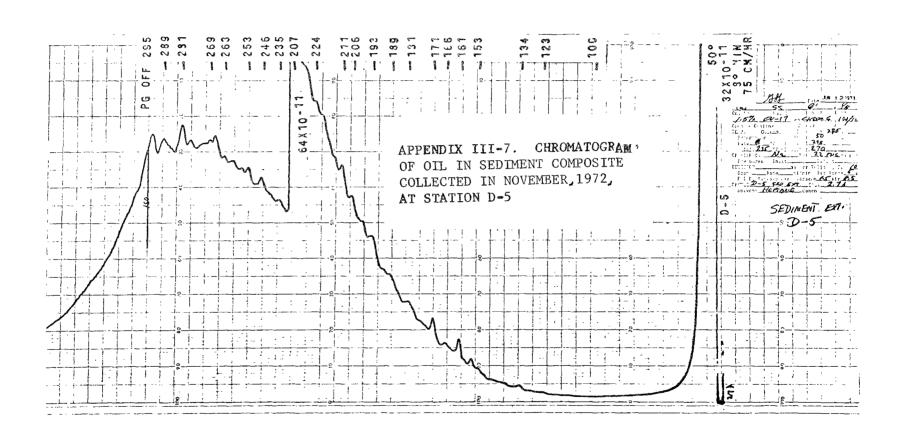


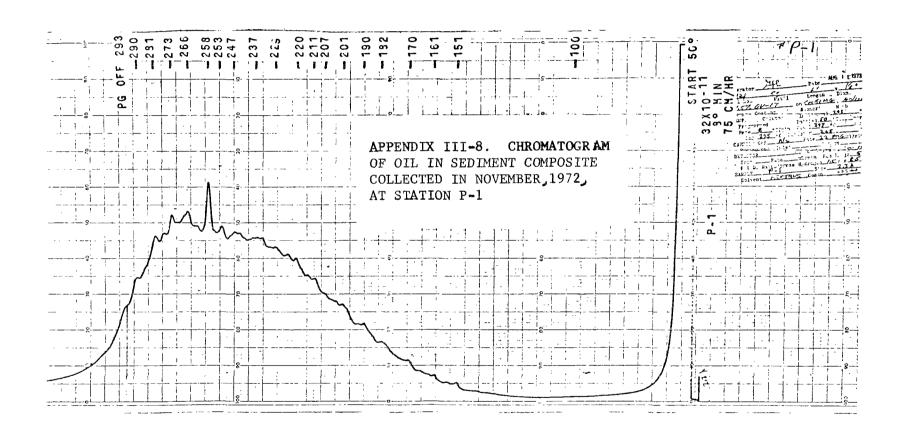
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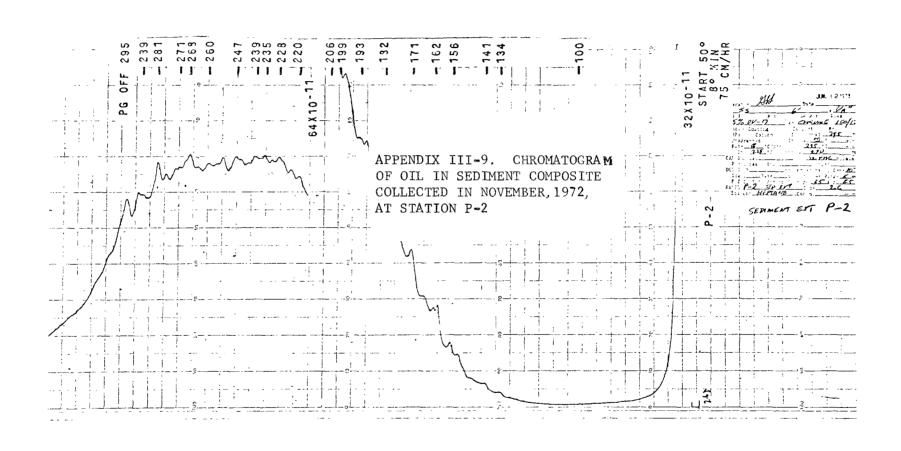


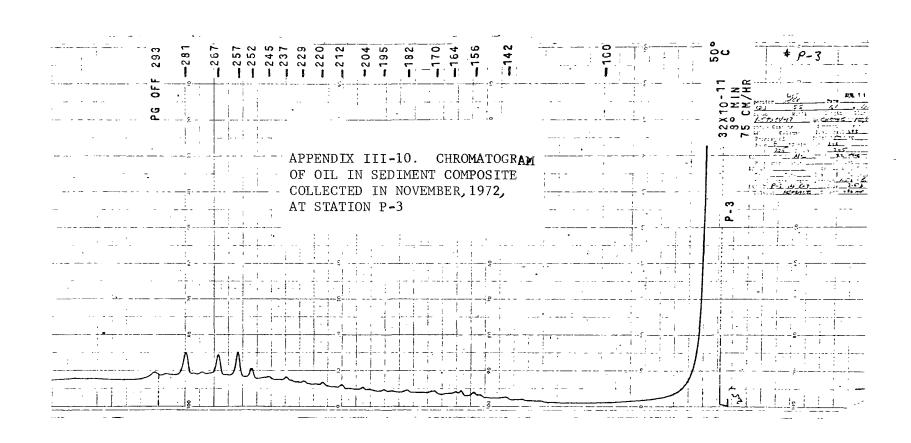


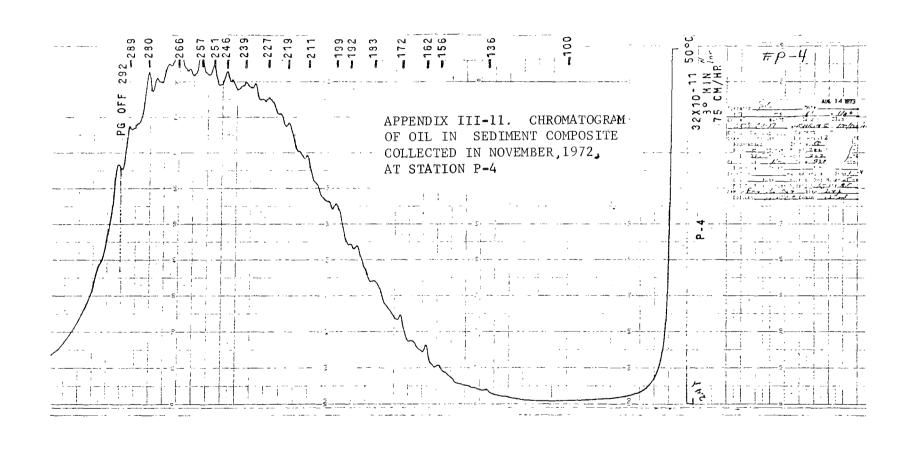


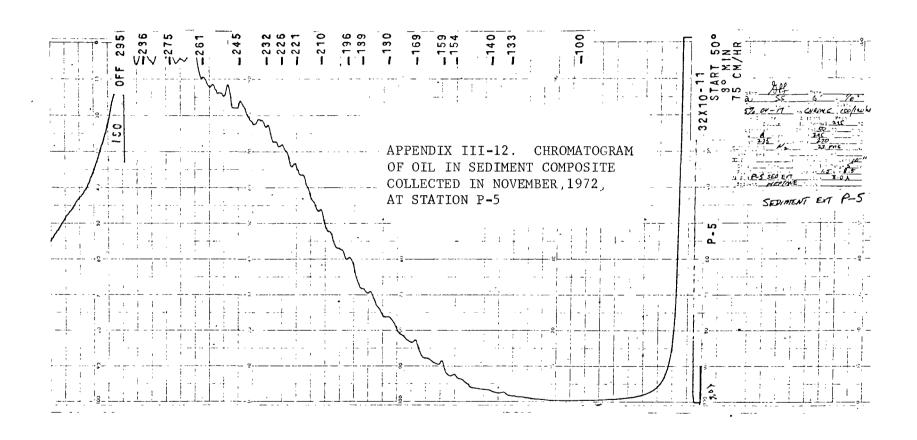












APPENDIX IV DATA FROM HEAVY METALS ANALYSES OF RIVER BIOTA

Appendix IV-1. Concentrations of lead, zinc, cadmium, and copper in benthic macrofauna collected in July, 1973

| Sample | ppm (whole body, wet weight) | | | | | | | |
|----------------------|------------------------------|----------------------|-------------------|----------------------|---------|--|--|--|
| | Lead | Zinc | Cadmium | Copper | Mercury | | | |
| M(a) | 49.3 | 102.0 | 0.1 | 29.7 | * | | | |
| M(b) | 51.1 | 107.0 | 0.1 | 31.5 | * | | | |
| M(c) | 51.4 | 99.5 | 0.1 | 35.0 | * | | | |
| M(d) M(e) M(f) | 79.1 10.9 49.3 | 99.4 43.3 68.7 | 0.1 0.1 0.1 | 73.9 71.1 21.8 | * * | | | |
| D2(a) | 143.0 | 65.4 | 0.1 | 19.9 | * | | | |
| D2(b) | 362.0 | 68.9 | 0.1 | 9.1 | * | | | |
| D2(c) | 16.9 | 31.0 | 0.1 | 19.8 | * | | | |
| D 3 | 24.2 | 38.6 | 0.1 | 7.0 | * | | | |
| D3 | 49.8 | 33.1 | 0.1 | 23.2 | * | | | |

^{*}Not abundant enough for mercury analysis.

Appendix IV-2. Concentrations of lead, zinc, cadmium, copper, and mercury in white suckers collected in November, 1972, January and July, 1973

| Sample | Organ | ppm (wet weight) | | | | |
|-------------------------------|----------------|------------------|------|--------------|----------------|--------------|
| Monocacy | | Lead | Zinc | Cadmium | Copper | Mercury |
| Nov. 1972 Fish 1 Fish 2 | Liver Liver | • | 21.8 | | 3. 24 3. 83 | |
| July 1973 Fish 1 Fish 2 | Flesh Flesh | <0.4 <0.4 | | - | 0.05 0.05 | 0.18 0.14 |
| Parkerford | | | | | | |
| Jan. 1973 Fish 1 Fish 2 | Flesh Flesh | ∠0.4 ∠0.4 | | | 0.60 0.33 | 0.12 0.09 |
| July 1973 Fish 1 Fish 2 | Flesh Flesh | 0.7 0.5 | | <0.1 <0.1 | 0.10 0.13 | 0.13 0.16 |

Appendix IV-3. Concentrations of lead, zinc, cadmium, copper, and mercury in brown bullheads collected in November, 1972, January and July, 1973

| Sample | Organ | | ppr | n (wet weigh | nt) | |
|---|----------------------------------|---------------------------|----------------------------|--------------------------|----------------------------|------------------|
| Monocacy | | Lead | Zinc | Cadmium | Copper | Mercury |
| Nov. 1972 Fish 1 Fish 2 | Liver Liver | 0.4 0.4 | 21.7 22.0 | 0.7 0.1 | 6.3 45.9 | |
| July 1973 Fish 1 Fish 2 Fish 1 | Flesh Flesh Liver | 0.4 0.7 0.4 | 2.1 2.5 22.0 | 0.1 0.1 0.5 | 0.05 0.20 0.05 | 0.18 0.19 |
| Parkerford | | | | | | |
| Jan. 1973 Fish 1 Fish 2 | Liver Liver | 0.4 | 23.9 21.9 | 4.1 0.2 | 12.6 87.3 | |
| July 1973 Fish 1 Fish 2 Fish 1 Fish 2 | Flesh Flesh Liver Liver | 0.4 0.4 64.2 1.4 | 2.7 3.2 31.0 20.0 | 0.1 0.1 1.3 0.5 | 0.05 0.11 53 0.05 | 0.07 0.05 |

Appendix IV-4. Concentrations of lead, zinc, cadmium, copper, and mercury in crappies collected in November, 1972, and July, 1973

| Sample | Organ | ppm (wet weight) | | | | |
|-------------------------------|----------------|------------------|----------------------|------------|--------------|--------------|
| Monocacy | | Lead | Zinc | Cadmium | Copper | Mercury |
| Nov. 1972 Fish 1 Fish 2 | Liver Liver | 0.4 0.4 | 1 7.4 17.1 | 0.1 0.1 | 9.48 1.84 | |
| July 1973 Fish 1 Fish 2 | Flesh Flesh | 0.4 0.4 | 3.8 4.1 | 0.1 0.1 | 0.05 0.05 | 0.09 0.11 |
| Parkerford | | | | | | |
| July 1973 Fish 1 Fish 2 | Flesh Flesh | 0.4 0.4 | 3.0 11.1 | 0.1 0.1 | 0.05 0.05 | 0.11 0.08 |

Appendix IV-5. Concentrations of lead, zinc, cadmium, copper, and mercury in bluegills collected in November, 1972, and January, 1973

| Sample | Organ | ppm (wet weight) | | | | | |
|-------------------------------|----------------|------------------|--------------|------------|--------------|--------------|--|
| Monocacy | | Lead | Zinc | Cadmium | Copper | Mercury | |
| Nov. 1972 Fish 1 Fish 2 | Flesh Flesh | 0.4 0.4 | 10.4 15.6 | 0.1 0.4 | 1.79 7.65 | 0.10 0.07 | |
| Parkerford | | | | | | | |
| Jan. 1973 Fish 1 Fish 2 | Liver Liver | 0.4 0.4 | 15.8 19.4 | 0.4 0.4 | 0.77 1.35 | | |

Appendix TV-6. Concentrations of lead, zinc, cadmium, and copper in Schuylkill River fishes collected 19 and 22 July, 1972

| | Sample | | Met | al Con | centration | ppm |
|-------------------------------|--|----------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | | | Lead | Zinc | Cadmium | Copper |
| Monocacy 19 & 22 July | Brown bullhead Brown bullhead Bluegill Shiner | Flesh Flesh Flesh Flesh | 1.3 2.0 2.3 2.6 | 1.0 1.0 3.0 7.9 | 0.1 0.1 0.1 0.1 | 0.5 0.3 0.4 0.4 |
| Parkerford 19 & 22 July | Bluegill Composite 3 Samples 8.0, 7.2, 7.8 cm | Flesh | 4.4 | 3.4 | 0.1 | 0.6 |

Appendix IV-7. Concentrations of lead, zinc, cadmium, and mercury in Schuylkill River fishes collected 23 and 29 July, 1972

| Sample | | Organ | | Metal Con | centratio | n ppm |
|-------------------------------|---|-------------------------|-------------------|----------------------|----------------|-------------------------|
| | | | Lead | Cadmium | Copper | Mercury |
| Monocacy 23 & 29 July | Bluegill Brown bullhead Brown bullhead (Composite) | Flesh Flesh Flesh | 0.9 0.3 0.2 | 0.38 0.10 0.07 | 0.5 | 0.741 0.776 0.162 |
| Parkerford 23 & 29 July | Bluegill Bluegill (Comp.) Bluegill (Comp.) | Flesh Flesh Flesh | 0.5 1.0 1.0 | 0.06 0.10 0.08 | 0.6 0.1 | 0.330 0.104 0.241 |

APPENDIX V HYDROCARBON IN FISHES

Appendix V-1. Extraction Data

| Sample description | Sample/ MgSO ₄ extracted (g) | Wt. sample extracted (g) | Extraction time (hr) | Wt. oil product (g) | % Oil (based on sample*) |
|--------------------------------------|---|--------------------------------|----------------------|------------------------|--------------------------------|
| Spilled Crankcase Oil Waste (SCOW | | 93 | 48 | 39.5 | 42.6 |
| White suckers (downstream) | 201 | 110 | 24 | 3.37 | 3.06 |
| White suckers (upstream) | 206 | 113 | 24 | 6.65 | 5.88 |
| Brown bullheads (downstream) | 200 | 116 | 24 | 3.21 | 2.77 |
| Brown bullheads (upstream) | 201 | 112 | 24 | 5.32 | 4.75 |
| Crappies (downstream) | 201 | 115 | 24 | 4.68 | 4.07 |
| Crappies (upstream) | 200 | 116 | 24 | 5.44 | 4.61 |

^{*} Original fish or SCOW

Appendix V-2 Saponification Data

| | Oil from extraction (g) | 6N KOH (ml) | H ₂ O added (ml) | Solvent (ml)* | Oil product (g) | % oil prod.** |
|--------------------------------------|-------------------------|----------------|--------------------------------|---------------|--------------------|---------------|
| Spilled Crankcase Oil Waste (SCOW | | 30 | 30 | 30 | 0.94 | 78.4 |
| White suckers (downstream) | 3.37 | 84 | 168 | 68 | 1.38 | 41.0 |
| White suckers (upstream) | 6.65 | 166 | 398 | 142 | 3.11 | 46.8 |
| Brown bullheads (downstream) | 3.21 | 80 | 160 | 64 | 0.57 | 17.8 |
| Brown bullheads (upstream) | 5.32 | 133 | 266 | 106 | 3.27 | 61.6 |
| Crappies (downstream) | 4.68 | 117 | 234 | 94 | 1.70 | 36.3 |
| Crappies (upstream) | 5.44 | 136 | 272 | 108 | 3.50 | 64.3 |

^{*} Volume used in separatory funnel extraction, 2X with cyclohexane followed by 2X with benzene.

^{**} Based on oil sample from first column

Appendix V-3. Column Chromatographic Data (Cyclohexane Elutions)

| | Spilled Crankcase Oil Waste | White suckers (downstream) | White suckers (upstream) | Brown bullheads (downstream) |
|---|-----------------------------------|----------------------------------|--------------------------|------------------------------------|
| Sample (g) | 0.94 | 1.38 | 3.11 | 0.57 |
| Alumina (g) | 47 | 124 | 124 | 23 |
| MgSO ₄ (g) | 4.7 | 12.4 | 12.4 | 2.3 |
| Column diameter (cm) | 2.0 | 5.0 | 5.0 | 2.0 |
| Volume cyclo- hexane solvent (ml) | 450 | 550 | 550 | 300 |
| Aliphatic hydrocarbons (mg) | 575 | 25 | 24 | 15 |
| Aliphatic hydrocarbons (% based on above sample) | 61 | 1.8 | 0.8 | 2.6 |

Appendix V-3 (Cont.) Column Chromatographic Data (Cyclohexane Elutions)

| | Brown bullheads (upstream) | Crappies (downstream) | Crappies (upstream) |
|---|----------------------------|-----------------------|------------------------|
| Sample (g) | 3.27 | 1.70 | 3.50 |
| Alumina (g) | 66 | 116 | 116 |
| MgSO ₄ (g) | 6.6 | 11.6 | 11.6 |
| Column diameter (cm) | 2.0 | 5.0 | 5.0 |
| Volume cyclo- hexane solvent (ml) | * | 600 | 600 |
| Aliphatic hydrocarbons (mg) | * | 8 | 307** |
| Aliphatic hydrocarbons (% based on above sample) | * | . 5 | 8.8** |

^{*} Column clogged with gel, analysis abandoned

^{**} Solid gel eluted

Appendix V-3 (Cont.) Column Chromatographic Data (Benzene-Benzene/Ether Elutions)

| | Spilled Crankcase Oil Waste | White suckers (downstream) | White suckers (upstream) | Brown bullheads (downstream) |
|--|-----------------------------------|----------------------------------|--------------------------------|------------------------------------|
| Sample (g) | 0.94 | 1.38 | 3.11 | 0.57 |
| Alumina (g) | 47 | 124 | 124 | 23 |
| MgSO ₄ (g) | 4.7 | 12.4 | 12.4 | 2.3 |
| Column diameter (cm) | 2.0 | 5.0 | 5.0 | 2.0 |
| Volume benzene solvent (ml | 200 | 400 | 250 | 300 |
| Volume benzene/ ether* solvent (ml) | 200 | 150 | 150 | 200 |
| Aromatic hydrocarbons (mg) ** | 107 | 15 | 15 | 9 |
| Aromatic hydrocarbons (% based on above sample) | 11.4 | 1.1 | .5 | 1.6 |

^{*} 90/10 v/v benzene/ether

^{**} From combining benzene-benzene/ether fractions

Appendix V-3 (Cont.) Column Chromatographic Data (Benzene-Benzene/Ether Elutions)

| | Brown bullheads (upstream) | Crappies (downstream) | Crappies (upstream) |
|--|----------------------------------|-----------------------|---------------------|
| Sample (g) | 3.27 | 1.70 | 3.50 |
| Alumina (g) | 66 | 116 | 116 |
| MgSO4(g) | 6.6 | 11.6 | 11.6 |
| Column diameter (cm) | 2.0 | 5.0 | 5.0 |
| Volume benzene solvent (ml) | *** | 350 | 500 |
| Volume benzene/ ether* solvent (ml) | *** | 150 | 200 |
| Aromatic hydrocarbons (mg)** | *** | 10 | 214+ |
| Aromatic hydrocarbons (% based on above sample) | *** | 0.6 | 6.1 |

^{* 90/10} v/v benzene/ether

^{**} From combining benzene-benzene/ether fractions

^{***} Column clogged with gel during cyclohexane elutions

⁺ Solid gel eluted

Appendix V-4. Extraction and Saponification Results From Harrison Lake National Fish Hatchery Fish

| | (1) | (2) | (3) | (4) | (5) | (6) |
|--------|----------------------------------|-----------------------------|---|----------------------------|--------------------------------------|--|
| Sample | HLFH* fish ex- tracted (g) | ppm added hydrocarbon | Percent oil from extraction based on (1) ** | Oil saponi- fied (g) | Oil obtained from saponification (g) | Percent oil from saponification based on (4) |
| HLFH-1 | 246 | 0 | 5.3 | 4.89 | . 44 | 8.9 |
| HLFH-2 | 254 | 2 | 7.2 | 8.00 | .38 | 4.7 |
| HLFH-3 | 226 | 5 | 5.9 | 8.00 | . 44 | 5.6 |
| HLFH-4 | 80 | 10 | 4.9 | 3.96 | .29 | 7.2 |

^{*} HLFH: Harrison Lake National Fish Hatchery

^{**} Extractions conducted on fish/MgSO $_4$ mixtures 44-48 hrs. in refluxing benzene

Appendix V-5. Column Chromatographic Data Harrison Lake National Fish
Hatchery (HLFH) Fish

| Sample | Oil from saponification for chromatography (g) | Added Hydro- carbon (ppm) | Non-volatile residue from cyclohexane elution (mg)* | Non-volatile residue from benzene elution (mg)** | Residue from cyclohex- ane elution (ppm) | Residue from benzene elution (ppm) |
|--------|--|------------------------------------|---|--|--|--|
| HLFH-1 | . 44 | 0 | 1 | 3 | 11 | 33 |
| HLFH-2 | .38 | 2 | 2 | 4 | 13 | 40 |
| HLFH-3 | . 44 | 5 | 2 | 6 | 12 | 45 |
| HLFH-4 | .29 | 10 | 1 | 5 | 17 | 66 |

^{*} Column eluted with cyclohexane (425 ml)

^{**} Column eluted with 650 ml benzene + 350 ml 90/10 benzene/ethyl ether (v/v)

Appendix V-6 Peak Area and Weight Correlations of Polycyclic Aromatic Hydrocarbons Compared to Triphenylmethane Internal Standard

Chromatograph sample: 1) 10.0 ml standard hydrocarbon (HC) mixture (1.16 mg each hydrocarbon)+

2) 1.50 ml (1.63 mg) triphenylmethane (TPM) in benzene

Chromatogram: Fig. 55

| Peak number | Aromatic hydrocarbon | Peak area** X10 ⁻² (mm ⁻²) | Area HC÷ area TPM | Wt HC: wt TPM | Area ratio HC/TPM: wt ratio HC/TPM*** |
|----------------|--------------------------------|--|----------------------|------------------|---------------------------------------|
| 1 | Phenathrene | 3.3 | .72 | .71 | 1.0 |
| 2 | Fluoranthene | 3.4 | .74 | .71 | 1.0 |
| 3 | Pyrene | 3.3 | .72 | .71 | Ć |
| 4 | Chrysene/1,2 benzanthracene | 6.3 | 1.4 | 1.4 | 1.0 |
| 5 | Benzo (a) pyrene | e 3.0 | .65 | .71 | .92 |
| 6 | Benzo (ghi) berylene | 2.5 | .54 | .71 | .76 |
| TPM | TPM | 4.6 | | | |

^{**} Height (mm) x width at 1/2 peak height (mm)

^{***} Values used as correction factors in Appendix V-7, -8, -9

Appendix V-7. Percent Recovery of Polycyclic Aromatic Hydrocarbons from Harrison Lake

National Fish Hatchery Fish (2 ppm Added Hydrocarbon)

Chromatograph sample: 1) Benzene eluate from column chromatography (4.4 mg. solids) +

2) 0.70 ml. benzene solvent +

3) 0.30 ml.(0.33 mg) triphenylmethane (TPM) in benzene

Chromatogram:

Fig. 58

| Hydrocarbon (HC) | Area HC ÷ area TPM | Corr.* factor | Wt. HC : wt. TPM | HC (mg) | Theor** HC (mg) | Percent HC recovery |
|--------------------------------|-----------------------|------------------|------------------|---------|--------------------|---------------------|
| Phenanthrene | .18 | 1.0 | .18 | .059 | .22 | 27 |
| Fluoranthene | .31 | 1.0 | .31 | .10 | .22 | 45 |
| Pyrene | .28 | 1.0 | .28 | .092 | .22 | 42 |
| Chrysene/1,2 benzanthracene | . 59 | 1.0 | .59 | .19 | . 44 | 43 |
| Benzo (a) pyrene | .21 | .92 | .23 | .075 | .22 | 34 |
| Benzo (ghi) perylene | .26 | .76 | .34 | .11 | .22 | 50 |

^{*} See last column, Appendix V-6

^{**} Based on known quantities (2 ppm) of each added hydrocarbon to ground fish before blending, and subsequently processed (extraction - saponification - column chromatography)

Appendix V-8. Percent Recovery of Polycyclic Aromatic Hydrocarbons from Harrison Lake National Fish Hatchery Fish (5 ppm Added Hydrocarbon)

Chromatograph sample: 1) Benzene eluate from column chromatography (6.1 mg solids) +

2) 1.00 ml benzene solvent +

3) 0.80 ml (0.87 mg) triphenylmethane (TPM) in benzene

Chromatogram: Fig. 59

| Hydrocarbon (HC) | Area HC ÷ area TPM | Corr* factor | Wt HC ÷ wt TPM | HC (mg) | Theor** wt HC (mg) | Percent HC recovery |
|--------------------------------|-----------------------|-----------------|-------------------|---------|--------------------|---------------------|
| Phenanthrene | .42 | 1.0 | .42 | .37 | .68 | 54 |
| Fluoranthene | .60 | 1.0 | .60 | .52 | .68 | 76 |
| Pyrene | .58 | 1.0 | .58 | .50 | .68 | 74 |
| Chrysene/1,2 benzanthracene | 1.0 | 1.0 | 1.0 | .87 | 1.4 | 62 |
| Benzo (a) pyrene | .42 | .92 | .46 | .40 | .68 | 59 |
| Benzo (ghi) perylene | .63 | .76 | .83 | .72 | .68 | 106 |

* See last column, Appendix V-6

** Based on known quantities (5 ppm) of each added hydrocarbon to ground fish before blending, and subsequently processed (extraction - saponification - column chromatography)

Appendix V-9. Percent Recovery of Polycyclic Aromatic Hydrocarbons from Harrison Lake National Fish Hatchery Fish (10 ppm Added Hydrocarbon)

Chromatograph sample: 1) Benzene eluate from column chromatography (5.3 mg solids) +

2) 0.90 ml benzene solvent +

3) 0.60 ml (0.65 mg) triphenylmethane (TPM) in benzene

Chromatogram: Fig. 60

| Hydrocarbon (HC) | Area HC ÷ area TPM | Corr* factor | Wt HC ÷ wt TPM | Wt HC (mg) | Theor** wt HC (mg) | Percent HC recovery |
|--------------------------------|-----------------------|-----------------|-------------------|---------------|--------------------|---------------------|
| Phenanthrene | .65 | 1.0 | .65 | .42 | .80 | 53 |
| Fluoranthene | .86 | 1.0 | .86 | .56 | .80 | 70 |
| Pyrene | .89 | 1.0 | .89 | .58 | .80 | 73 |
| Chrysene/1,2 benzanthracene | 1.5 | 1.0 | 1.5 | .98 | 1.6 | 61 |
| Benzo (a) pyrene | .49 | .92 | .53 | .34 | .80 | 43 |
| Benzo (ghi) perylene | .73 | .76 | .96 | .62 | .80 | 78 |

^{*} See last column, Appendix V-6.

^{**} Based on known quantities (10 ppm) of each added hydrocarbon to ground fish before blending, and subsequently processed (extraction - saponification - column chromatography)

APPENDIX VI DATA FROM BIOLOGICAL ANALYSES

Appendix VI-1. Chlorophyll-a content of Schuylkill River water above and below the oil spill site in July, 1972

| Chlorophyll A (micr | ograms/liter) |
|---------------------|---------------|
|---------------------|---------------|

| Date | Station ¹ | Total | Active | Pheopigment (Dead) |
|--------------|----------------------|--------------|---------------|--------------------|
| 16 July 1972 | ABOVE SPILL | | | |
| | Monocacy Bridge | 3.78 3.41 | 2.78 2.63 | 1.00 0.78 |
| | Average | 3.60 | 2.71 | 0.89 |
| | BELOW SPILL | | | |
| | Parker Ford Bridge | | 6.72 4.39 | 1.76 7.31 |
| | Average | 10.09 | 5.56 | 4.54 |
| | Valley Forge Bridge | | 6.27 11.39 | 1.39 2.80 |
| | Average | 10.93 | 8.83 | 2.10 |
| 29 July 1972 | ABOVE SPILL | | | |
| | Monocacy Bridge | 6.15 | 4.80 | 1.35 |
| | Average | 6.15 | 4.80 | 1.35 |
| | BELOW SPILL | | | |
| | Parker Ford Bridge | | 8.13 7.73 | 2.33 2.73 |
| | Average | 10.46 | 7. 93 | 2.53 |

| | | <u>Ch</u> | lorophyll | A (micrograms/liter) |
|--------------|---------------------|-----------|-----------|----------------------|
| Date | Station 1 | Total | Active | Pheopigment (Dead) |
| 29 July 1972 | | | | |
| - | BELOW SPILL | | | |
| | Valley Forge Bridge | 14.19 | 10.58 | 3.61 |
| | | 11.45 | 9.24 | 2.21 |
| | Average | 12.82 | 9, 91 | 2, 41 |

Duplicate samples were usually taken at each station.

mollusk) larvae

Appendix VI-2. Zooplankton abundance in Schuylkill River water above and below the oil spill in July, November, and December, 1972, and July, 1973

| | 16 | July 1972 | | 29 | July 1972 | |
|-----------------------------|----------------|-------------|--------------|-------------|-------------|--------------|
| | Above Spill | Belov | w Spill | Above Spill | Below | Spill |
| STATION: | Monocacy | Parker Ford | Valley Forge | Monocacy | Parker Ford | Valley Forge |
| Taxons | | | | | | |
| Peritricha | | | | | 100+ | 100+ |
| Protozoa | p. 100 | | 100+ | | | |
| Coelenterata | ~ ~ | | | | | 18 |
| Nemertina (ribbon worms) | 4 | | | | | |
| Rotifera | | | | 3 | | 12 |
| Nematoda (round worms) | | 1 | | 3 | | 3 |
| Nematomorpha (hair worms) | | | | | | |
| Bryzoa (moss animals) | | | 100+ | | 100+ | 100+ |
| Pelecypoda (biv | alve 2 | | | | | |

| | 16 July 1972 Above Spill Below Spill | | | | 29 July 1972 Above Spill Below Spill | | |
|-----------------------------|---------------------------------------|-------------|----|----|--------------------------------------|----|--|
| STATION: | | Parker Ford | | | Parker Ford | | |
| Taxons | | | | | | | |
| Oligochaeta (segmented w | orms) | | 2 | 13 | 30 | 6 | |
| Tardigrada (water bears) | | | | | | | |
| Cladocera (water fleas) | 61 | 92 | 80 | 3 | | 24 | |
| Ostracoda | 9 | | | 5 | | | |
| Copepoda | 13 | 41 | 48 | 10 | 5 | 21 | |
| Amphipoda | 1 | | | | | | |
| Hydracarina (water mites) | 9 | 6 | | | | | |
| Hemiptera (true bugs) | 1 | | | | | | |
| Odonata (dragand damsel f | | 1 | | | 100+ | | |
| Trichoptera fly) larvae | (caddis 1 | 3 | 5 | | | | |

| | 16 July 1972 | | | | 29 July 1972 | | |
|----------------------------------|--------------------|-----------------------|------------------------|--------------------|-----------------------|------------------------|--|
| | Above Spill | Belov | w Spill | Above Spill | v Spill | | |
| STATION: | Monocacy Bridge | Parker Ford Bridge | Valley Forge Bridge | Monocacy Bridge | Parker Ford Bridge | Valley Forge Bridge | |
| Taxons | | | | | | | |
| Ephemeroptera (May fly) larva | | | | | | | |
| Tendipedidae (midge) larvae | | 4 | | 68 | 149 | 95 | |
| Culicidae (mosquito) larv | ae | | | 5 | | 3 | |
| Coleoptera (beetles) | 3 | | | 10 | | | |
| Unidentified | 8 | 15 | 1 | 5 | 5 | 12 | |
| Major taxon diversity | 10 | 7 | 7 | 9 | 6 | 10 | |

| | 28 Nove | mber 1972 | 1 December 1972 | | 14 Jul | y 1973 |
|-----------------------------|---------------|--------------------------|-----------------|---------------|-------------|-------------|
| | Above Spill | Below Spill | Above Spill | Below Spill | Above Spill | Below Spill |
| STATION: | Monocacy | Parker Ford ¹ | Monocacy | Parker Ford | Monocacy | Parker Ford |
| Taxons | | | | | | |
| Peritricha | | 2 | | 3 | | 1 |
| Protozoa | 1 | | 2 | | 4 | 4 |
| Coelenterata | < 1 | | | | | |
| Nemertina (ribbon worm | 6 s) | ۷ 1 | 7 | < 1 | 11 | 1 |
| Rotifera | 7 | ∠ 1 | .11 | <1 | | |
| Nematoda (round worms |) | <1 | | < 1 | | |
| Nematomorph (hair worms) | a <1 | | 9 | | | |
| Bryzoa (moss animal | < 1 | <1 | 7 | < 1 | | |

| | 28 November 1972 | | 1 Decemb | per 1972 | 14 July 1973 | | |
|----------------------------------|------------------|-------------|-------------|---------------|--------------|-------------|--|
| | Above Spill | Below Spill | Above Spill | Below Spill | Above Spill | Below Spill | |
| STATION: | Monocacy | Parker Ford | Monocacy | Parker Ford | Monocacy | Parker Ford | |
| Taxons | | | | | | | |
| Pelecypoda (bi mollusk) larva | | | | < 1 | | | |
| Oligochaeta (segmented wo | 2 rms) | 4 | 13 | 1 | 4 | 3 | |
| Tardigrada (water bears) | | | | | 2 | | |
| Cladocera (water fleas) | 5 | 5 | 7 | < 1 | 7 | 5 | |
| Ostracoda | | | | | | | |
| Copepoda | 1 | | 9 | | 4 | | |
| Amphipoda | | | | | | | |
| Hydracarina (water mites) | | | | | | 1 | |
| Hemiptera (true bugs) | | < 1 | | | 2 | 1 | |

| | 28 Nove | mber 1972 | 1 Decemb | er 1972 | 14 July 1973 | | |
|-----------------------------|--------------|------------------|-------------|-------------|--------------|-------------|--|
| | Above Spill | Below Spill | Above Spill | Below Spill | Above Spill | Below Spill | |
| STATION: | Monocacy | Parker Ford | Monocacy | Parker Ford | Monocacy | Parker Ford | |
| Taxons | | | | | | | |
| Odonata (dra and damsel | - | | | ₩ | | 1 | |
| Trichoptera fly) larvae | (caddis | | | | | | |
| Ephemeropt (May fly) lan | | , | 9 | < 1 | 83 | 4 6 | |
| Tendipedida (midge) larv | | | | | | | |
| Culicidae (mosquito) l | arvae | | | | | 1 | |
| Coleoptera (beetles) | | | | | | | |
| Unidentified | | | | | - | | |
| Major taxon diversity | 9 | 9 | 9 | 9 . | 8 | 10 | |
| 10:1 4==104 | a wana ahaan | rad in this same | 1. | | | | |

Oil droplets were observed in this sample

Appendix VI-3. Benthic macrofauna abundance in Schuylkill River sediments in November, 1972, and July, 1973

| STATION: Above Spill | Monocacy (Re | | Monocacy (Repl | | Monocacy (Repli | |
|---|--------------------------|---------------|--------------------------|---------|--------------------------|-------------|
| Taxons | Organisms/m ² | Type 1,2 | Organisms/m ² | Type | Organisms/m ² | Туре |
| Nematoda | 86 | | 43 | | | |
| (round worms) | 60 | | 43 | | | |
| Gastropoda (snails) | | | | | 43 | (4) |
| Pelecypoda (bivalve mollusks) | 86 | (1) | 43 | (1) | 43 | (1) |
| Oligochaeta (segmented worms) | 15,566 | (1)+ (2)+ (5) | 7,912 | (1) (2) | 5,461 | (1)+(2)+(5) |
| Hirudinea (leeches) | | | | | 43 | ,(1) |
| Odonata (dragon- damsel fly) larvae | | | | | | |
| Tendipedidae (midge) larvae and pupae | 129 | | | | 86 | |
| Ceratopogonidae (biting midge) larvae and pupae | | | | | | |
| Other Diptera larvae and pupae | 215 | (1) | | | | |
| Fish larvae | | | | | | |
| Major taxon diversity | 5 | | 3 | | 5 | |
| | | | | | | |

29 November 1972

| STATION: Below Spill | Parker For Organisms/m ² | <u>d 1</u> Type | Parker Ford Organisms/m ² | <u>2</u> Type | Parker For Organisms/m ² | d 3 Type |
|---|--|--------------------|---|------------------|--|--------------------|
| Taxons | OI gamismis/in | Type | Organisms/m | 1 y p c | Olganisms, iii | 1,00 |
| Nematoda (round worms) | | | | | | |
| Gastropoda (snails) | 301 | (1)(2)(4) | | | | |
| Pelecypoda (bivalve mollusks) | 172 | (1) | | | | |
| Oligochaeta (segmented worms) | 3,314 | (1)+(2)+ (3)(4) | No | | 11,621 | (1)+(2)+ (4)(6) |
| Hirudinea (leeches) | | | Organisms | | | |
| Odonata (dragon- damsel fly) larvae | | | | | | |
| Tendipedidae (midge) larvae and pupae | 43 | | | | 301 | |
| Ceratopogonidae (biting midge) larvae and pup | | | | | 43 | |
| Other Diptera larvae and pupae | 43 | (1) | | | | |
| Fish larvae | | | | | | |
| Major taxon diversity | 5 | | 0 | | 3 | |

29 November 1972

| STATION: Below Spill | Douglassville | | Parker F | | Parker Fo | |
|---|--------------------------|------|------------|-----------------------|-------------|---------------------|
| Taxons | Organisms/m ² | Type | Organisms/ | m ² Type | Organisms/r | n ² Type |
| Taxons | | | | | | |
| Nematoda | | | 129 | | 86 | |
| (round worms) | | | | | | |
| Gastropoda (snails) | | | 301 | (1)+(3)(4) | 43 | (2) |
| Pelecypoda (bivalve mollusks) | | | 43 | (2) | | |
| Oligochaeta (segmented worms) | 43 | (1) | 29,123 | (1)+(2)+ (3)(4)(5) | 6,327 | (1)+(4) |
| Hirudinea (leeches) | | | | | | |
| Odonata (dragon- damsel fly) larvae | | | | | 43 | |
| Tendipedidae (midge) larvae and pupae | | | 129 | | 2 58 | |
| Ceratopogonidae (biting midge) larvae and pupae | | | 129 | | | |
| Other Diptera larvae and pupae | 43 | (1) | 301 | (1) | 86 | (1) |
| Fish larvae | | | | | | |
| Major taxon diversity | 2 | | 7 | | 6 | |

29 November 1972

| STATION: Below Spill | Douglassville Organisms/m ² | Type | Douglassvill Organisms/m ² | | Douglassville Organisms/m ² | |
|---|---|--------------------|--|---|---|--------------------|
| Taxons | | -71 | | - , | - 0 | 71 |
| Nematoda (round worms) | | | | | /"· | |
| Gastropoda (snails) | | | | | 43 | (1) . |
| Pelecypoda (bivalve mollusks) | | | | | | |
| Oligochaeta (segmented worms) | 12,986 | (1)+(2)+ (3)(4) | 989 | (1)+(2)+ (3)(4) | 1,851 | (1)+(2)+ (3)(4) |
| Hirudinea (leeches) | 43 | | | | | |
| Odonata (dragon- damsel fly) larvae | | | | | | |
| Tendipedidae (midge) larvae and pupae | | | | | 129 | |
| Ceratopogonidae (biting midge) larvae and pupae | ı | | | | | |
| Other Diptera larvae and pupae | | | | | 43 | (1) |
| Fish larvae | | | | | 43 | |
| Major taxon diversity | 2 | | 1 | | 5 | |

29 November 1972

| STATION: Below Spill | Douglassville | |
|---|--------------------------|--------------------|
| Taxons | Organisms/m ² | Type |
| Nematoda (round worms) | 43 | |
| Gastropoda (snails) | | |
| Pelecypoda (bivalve mollusks) | | |
| Oligochaeta (segmented worms) | 4,433 | (1)+(2)+ (3)(4) |
| Hirudinea (leeches) | 43 | (1) |
| Odonata (dragon- damsel fly) larvae | | |
| Tendipedidae (midge) larvae and pupae | 129 | |
| Ceratopogonidae (biting midge) larvae and pupae | | |
| Other Diptera larvae and pupae | | |
| Fish larvae | | |
| Major taxon diversity | 5 | |

28 July 1973

| STATION: Above Spill | Monocacy (Repli | | Monocacy (Replicate 2) | | Monocacy (Replicate 3) | |
|---|--------------------------|-----------------|--------------------------|--------------------|--------------------------|-----------------|
| | Organisms/m ² | Type | Organisms/m ² | Type | Organisms/m ² | Type |
| Taxons | | | | | | |
| Nematoda (round worms) | | | 43 | | | |
| Gastropoda (snails) | | | | | | |
| Pelecypoda (bivalve mollusks) | | | | | | |
| Oligochaeta (segmented worms) | 688 | (1)+(2)+ (3) | 301 | (1)+(2)+ (3)(6) | 1,419 | (1)+(2)+ (3) |
| Hirudinea (leeches) | | | | | | |
| Odonata (dragon- damsel fly) larvae | | | | | | |
| Tendipedidae (midge) larvae and pupae | 1,290 | | 4,601 | | 1,643 | |
| Ceratopogonidae (biting midge) larvae and pupae | | | , | | | |
| Other Diptera larvae and pupae | | | | | | |
| Fish larvae | | | | | | |
| Major taxon diversity | 2 | | 3 | | 2 | |

28 July 1973

| STATION: Above Spill | Monocacy (Replicate 4) | | Monocacy (Replicate 5) | | |
|---|--------------------------|-----------------|--------------------------|-----------------|--|
| | Organisms/m ² | Туре | Organisms/m ² | Type | |
| Taxons | | | | | |
| Nematoda (round worms) | | | 86 | | |
| Gastropoda (snails) | | | | | |
| Pelecypoda (bivalve mollusks) | | | | | |
| Oligochaeta (segmented worms) | 1,634 | (1)+(2)+ (3) | 2,838 | (1)+(2)+ (3) | |
| Hirudinea (leeches) | | | | | |
| Odonata (dragon- damsel fly) larvae | | | | | |
| Tendipedidae (midge) larvae and pupae | 3,096 | | 1,032 | | |
| Ceratopogonidae (biting midge) larvae and pupae | | | | | |
| Other Diptera larvae and pupae | | | | | |
| Fish larvae | | | | | |
| Major taxon diversity | 2 | | 2 | | |

28 July 1973

| STATION: Below Spill | Douglassville Br. (I | Replicate 1) | Douglassville Br. | |
|---|--------------------------|--------------------|--------------------------|-----------------|
| | Organisms/m ² | Type | Organisms/m ² | Type |
| Taxons | | | | |
| Nematoda (round worms) | | | 86 | |
| Gastropoda (snails) | | | | |
| Pelecypoda (bivalve mollusks) | | | | |
| Oligochaeta (segmented worms) | 5 ,24 6 | (1)+(2)+ (3)(4) | 2,666 | (1)+(2)+ (3) |
| Hirudinea (leeches) | | | | |
| Odonata (dragon- damsel fly) larvae | | | | |
| Tendipedidae (midge) larvae and pupae | 1,677 | | 4,472 | |
| Ceratopogonidae (biting midge) larvae and pupae | | | | |
| Other Diptera larvae and pupae | | | | |
| Fish larvae | | | | |
| Major taxon diversity | 2 | | 3 | |

28 July 1973

| STATION: Below Spill | Douglassville Organisms/m ² | <u>2</u> Type | Douglassvill Organisms/m ² | le 4 Type |
|---|---|------------------|--|----------------------|
| Taxons | | | | |
| Nematoda (round worms) | | | | |
| Gastropoda (snails) | | | | |
| Pelecypoda (bivalve mollusks) | | | | |
| Oligochaeta (segmented worms) | | | 7,482 | (1)+(2) - (3)+(4) |
| Hirudinea (leeches) | | | | |
| Odonata (dragon- damsel fly) larvae | | | | |
| Tendipedidae (midge) larvae and pupae | 3,870 | | 1,030 | |
| Ceratopogonidae (biting midge) larvae and pupae | | | 86 | |
| Other Diptera larvae and pupae | | | | |
| Fish larvae | | | | |
| Major taxon diversity | 1 | | 3 | |

Type of macrofauna present is described by the following codes:

Gastropoda: (1) Ferissia; (2) Physa; (3) Lymnaea; (4) Gyranlus(?)

Pelecypoda: (1) Pisiclium; (2) Musculium

Oligochaeta: (1) <u>Tubifex</u>; (2) <u>Limnodriluso</u>; (3) <u>Peloscolex</u>;

(4) Nais; (5) Lumbriculidae; (6) Enchytraeidae

Hirudinea: (1) Glossiphoniidae

Other Diptera larvae

and pupae: (1) Psychodidae

²Abundance within taxons is indicated by "+" signs.

Appendix VI-4. Counts of bacteria in Schuylkill River sediment (organisms/g of sediment) above and below oil spill in July, 1972

| STATION: | Hydrocarbon Oxidizers | Casein Splitters | Starch Splitters | Glucose Fermenters (MPN) | Sulfate Fermenters (MPN) |
|------------------|--------------------------|---------------------|---------------------|--------------------------------|--------------------------------|
| | | 17 | July 1972 | | |
| ABOVE SPILL | | | | | |
| Monocacy | No results. | 4.5×10^6 | 6.8×10^6 | 2.4×10^5 | 1.5×10^2 |
| BELOW SPILL | Agar was | | | | |
| Parker Ford Br. | contaminated. | 1.0×10^{7} | 4.2×10^{7} | 4.6×10^6 | 2.4×10^3 |
| Valley Forge Br. | | 3.9×10^6 | 1.3×10^6 | 9.6×10^{5} | 3.0×10^{1} |
| | | 23 | July 1972 | | |
| ABOVE SPILL | | | | | |
| Monocacy | No results. | 6.0×10^5 | 3.5×10^5 | 1.5×10^5 | 9.0×10^{1} |
| BELOW SPILL | Agar was | | | | |
| Parker Ford Br. | contaminated. | 2.8×10^6 | 5.6×10^6 | 1.5×10^6 | 4.6×10^3 |
| Valley Forge Br. | | no sample | no sample | no sample | no sample |
| | | 30 | July 1972 | | |
| ABOVE SPILL | | | , | | |
| Monocacy | 5.0×10^5 | 2.9×10^6 | 3.1×10^6 | 4.6×10^{5} | 4.3×10^2 |
| BELOW SPILL | | | | | |
| Parker Ford Br. | 1.0×10^6 | 9.7×10^6 | 9.0×10^6 | 4.6×10^5 | 2.4×10^3 |
| Valley Forge Br. | 2.4×10^{5} | 8.0×10^5 | 3.9×10^6 | 1.5×10^{5} | 9.0×10^{1} |

Winter 1972-73

| Species | Above S | Spill <u>F</u> | Below | w Spill | | |
|----------------|-------------|--------------------------------|--------|---------------------|--|--|
| White sucker | No. of Stom | achs Contents No. c | of Sto | machs Contents | | |
| | 6 | 100 ⁺ Diptera pupae | 1 | 100 + Diptera pupae | | |
| | 8 | Empty | 4 | Empty | | |
| Brown bullhead | 1 | l unidentified fish | 1 | l Diptera larvae | | |
| | 4 | Empty | | vertebrate hair | | |
| | | | | mud | | |
| | | | 1 | 3 Diptera larvae | | |
| | | | | 2 Diptera pupae | | |
| | | | | Mud | | |
| | | | 3 | Empty | | |
| Crappie | None ca | aptured | 3 | 1 unidentified fish | | |
| | | | 2 | Empty | | |
| Bluegill | 2 | 1 unidentified fish | No | one captured | | |
| | 1 | l unidentified fish | | | | |
| | | l water boatman (Coroxidae) | | | | |
| | 2 | Empty | | | | |

Summer 1973

| Species | Al | pove Spill | Bel | Below Spill | | |
|----------------|-------------|---|-------------|-----------------------|-------------------|--|
| | No. of Ston | nachs Contents | No. of Stor | nachs Contents | <u>.</u> | |
| White sucker | 1 | unidentified orga | anic 1 | Gravel | | |
| | 1 | Gravel | 4 | Empty | | |
| | 3 | Empty | | | | |
| Brown bullhead | 1 | 45 Diptera larva | .e 2 | Fish so | ales | |
| | 1 | 100 Diptera larva | e 1 | Fish bo | nes | |
| | 4 | Empty | | Mud | | |
| | | | 1 | Fish ske | eleton | |
| | | | | Algae m | ıat | |
| | | | 1 | unidenti fish (13r | | |
| | | | 1 | Empty | | |
| Crappie | 1 | ll Diptera larvae | 2 | Fish sc | ales | |
| | 1 | 25 Diptera larva unidentified o material | | insect a fish sca | appendage .les | |
| | 1 | l Diptera larvae insect appendag unidentified org material | ge l | Insect a Empty | ppendage | |
| | 1 | δ Diptera pupae 4 Diptera larva insect append | е | | | |
| | 3 | Fish remains | | | | |
| | 1 | Empty | | | | |

Note: Most Diptera larvae observed in fish stomachs were members of the family Psychodidae. Diptera pupae were not further identified. It is probable that many were members of the families Tendipedidae and Ceratopogonidae.