# THE SCHUYLKILL RIVER, 1973

Some Interesting Biological Affects Of The Oil Spill During Hurricane Agnes

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Region III

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#### INTRODUCTION

The oil spill of the Berks Oil Company in 1972 raised a serious question in relation to the heavy metal effects on the biclogy in the Schuylkill River. Seven to ten million gallons of sludge were lost, containing 17,000 to 50,000 ppm of lead, as well high amounts of copper, zinc and cadmium. A smaller spill of the same material had occurred in 1970. During the fall of 1972, winter, and early spring of 1973, preliminary studies were inconclusive in regards to the effects of the oil spill and suggested other metals problems in the Schuylkill River masking the effects of the oil spill.

The state of Pennsylvania proposed a comprehensive biological study of the Schuylkill River in the summer of 1973. Region III of the U.S. Environmental Protection Agency suggested that such a study might be utilized to evaluate the heavy metals problems on the Schuylkill River and better define possible oil spill effects. As a result, a cooperative special metals study was conducted on the Schuylkill River in conjunction with the comprehensive study. The Pennsylvania Department of Environmental Resources, Pennsylvania Fish Commission, and U.S. Environmental Protection Agency were involved.



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### DESCRIPTION OF AREA

The Schuylkill River flows in a southeasterly direction one hundred and thirty-one miles to its confluence with the Delaware River'in Philadelphia, draining 1,912 square miles. It begins in the southern coal fields of the Anthracite Basin where coals, sandstones, shales predominate. The River continues to pass through such rock types as sandstones, shales, red beds, limestone and metamorphic rock, ending in sand and gravel deposits at its mouth.

Nine dams cross the mainstem of the Schuylkill River which has an average flow of 2,945 cfs at Philadelphia.

The River has numerous bedrock outcrops and tends to flow relatively fast through the better portion of its course. Four (4) basic types of habitat are found on the River: 1) fast flow over shallow, course gravel and sand beds; 2) fast flow over bedrock outcrops; 3) deep pools with high silt accumulations and occasional bedrock outcrops; 4) shallow pools with sand, some silt accumulations and bedrock outcrops.

Between Reading and Philadelphia, the Schuylkill River flows through heavily industrialized areas, marginal forest land, marginal farm land, and distinctly urban areas. Throughout this stretch of the River, some signs of pollution are consistently found with many areas having major pollution problems.

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#### METHODS

## Field Procedures

Bottom sediments, benthic macroinvertebrates, and fishes were collected at selected sampling stations on the Schuylkill River and several of its major tributaries (Figure 1).

Grab samples of bottom sediments were collected directly in Whirl-Pak plastic bags at shallow water stations by wading. Bottom sediments from deep water areas were brought to the surface by means of a biological dredge. Samples were stored in Whirl-Pak plastic bags and placed in dry ice for shipment to the EPA laboratory in Charlottesville, Virginia.

Fishes were collected by electrofishing methods. The gills, viscera, and fillets of large specimens were placed in separate collection bags. All samples were stored in Whirl-Pak bags and kept in dry ice for shipment to the EPA laboratory in Charlottesville, Virginia.

### Laboratory Procedures

#### Bottom Sediments

Bottom sediments were analyzed following a modified procedure of the method by the Great Lakes Region Committee on Analytical Methods (1).

A 2.5 gm. well mixed bottom sediment sample was placed in a 250 ml beaker. Ten milliliters of conc.  $HNO_3$  acid and 0.5 ml of  $H_2O_2$  (30%) were added and the sample was evaporated to dryness.

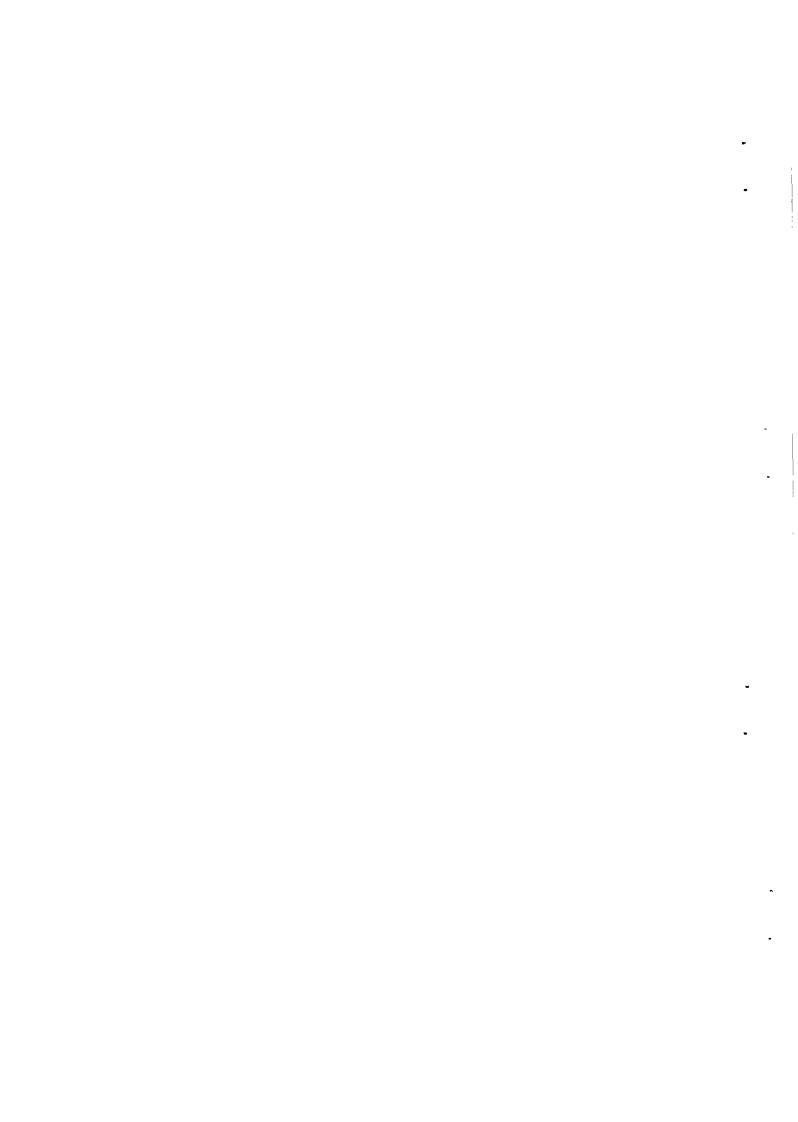
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The sample was then ashed at 400°-425°C for 1-hour in a muffle furnace and allowed to cool. To this sample was added 25 ml of acid mixture (200 ml of ccnc. HNO3, 50 ml conc. HC1 and 750 ml of redistilled water), 20 ml of 10% NH4 C1 and 1 ml of Ca (NO3)2. 4H20 (11.8 g/100 ml). The sample was heated gently for 15 minutes and allowed to cool for five minutes or longer. The sample was then transferred to a centrifuge for 10 minutes at 20,000 rpm. The supernatant was transferred to a 250 ml volumetric flask. The residue in the centrifuge tube was rinsed twice with redistilled water. The washings were added to the supernatant, diluted to volume, and then subjected to analysis by atomic absorption spectrophotometry using a Perkin-Elmer Model 305B.

## Benthic Macroinvertebrates

After low temperature ashing the samples and bringing them to a given volume with HNO3, a micro-pipette is used to transfer a 5 ul aliquot of the sample to the graphite furnace which has previously been set for a three temperature program. The program is then initiated and in sequence the furnace heats to a drying, ashing and then atomizing temperature. The drying and ashing times and temperatures are determined by the solution being analyzed and the atomization time and temperature by the metal for which one is analyzing.

The instrument used was a Varian AAS with a graphite rod furnace.



### Fishes

Tissue samples or whole fish approximately 100 gm in wet weight (2gm dry) were dried overnight at 100°C in a weighed glazed porcelain dish and the sample dry weight determined. The samples were then transferred to a muffle furnace preheated to 200°C. The temperature of the furnace was raised at 50°C intervals over two (2) hours to a final temperature of 500°C and ashed overnight. The ash was dissolved in 5 ml conc. HNO3 and evaporated to dryness. The resulting residue was dissolved in 5 ml HNO4 and 20 ml of deionized water with warming. If needed, samples were filtered and brought to a final volume of 100 ml. The concentration of each element was determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 305B.

### Sampling

A total of 17 sampling stations were established in the Schuylkill River Basin, ll stations on the main stem and 6 stations on selected tributaries (Figure 1). Only the ll main stem stations are considered in this paper. Of these stations, 8 on the main stem had the complete compliment of metals analysis on sediment, benthos, and fish. At station SCH019 only sediments were analyzed. Benthos samples were not collected at stations SCH039 and 006.

Based on the data obtained from the oil spill analyses and state industrial waste reports, the metals selected for analysis included lead, zinc, cadmium, copper, nickel, chromium, antimony, and mercury.

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#### RESULTS AND DISCUSSION

#### Metals

At this point, it seems appropriate to discuss briefly the natural occurrence and toxicity of each of the metals analyzed in this study. The metals are grouped according to apparent relationships found in this study. This grouping will be used throughout the discussion in this text.

### Zinc and Cadmium

Zinc occurs abundantly in rocks and ores. In zinc mining areas, zinc has been found in natural waters in concentrations as high as 50 mg/l and in effluents from metal plating works it may occur in significant concentrations. Zinc is highly toxic to fish and benthic macroinvertebrates especially in soft waters. Its toxicity varies with species and physical-chemical characteristics on the water.

Cadmium occurs naturally with zinc. It is used in metalurgy, electroplating, and chemical industries. Most of the quantitative data on toxicity of cadmium to aquatic life indicates that it is moderately toxic but acts snyergistically with other substances to increase its toxicity.

### Lead and Antimony

Lead can be found in small concentrations in natural waters, but most is introduced from various industrial and mining effluents. Lead is quite toxic to aquatic life with fish apparently being most sensitive.

Antimony is used for alloys and other metalurgical purposes.
Antimony is toxic to aquatic life.

### Chromium and Nickel

Elemental nickel seldom occurs in nature, although many nickel salts are highly soluble in water. Most occurs as a result of waste from metal plating operations. Nickel appears to be less toxic to fish and benthic macroinvertebrates than copper, zinc, or iron. Toxicity of nickel towards aquatic life varies with species, pH, and its synergism to other metals.

Hexavalent chromium salts which are extremely toxic to aquatic life are used extensively in metal pickling and plating operations. The toxicity of chromium salts towards aquatic life varies widely with the species, temperature, pH and hardness of the water. Fish are relatively tolerant of chromium salts, but lower forms of aquatic life are extremely sensitive.

#### Copper

"Copper and copper salts occur in natural surface waters only in trace amounts up to about 0.05 mg/l so that their presence is generally the result of pollution" (2). Toxicity of copper to aquatic life varies with the species and with the physical-chemical characteristics of the water such as its temperature, turbidity,



and hardness. The toxicity of copper salts is less in hard water than in soft water.

## Mercury

Mercuric salts occur in nature chiefly as the sulfide and are used industrially. Mercuric ions are considered to be highly toxic to aquatic life.

## **Sediments**

Sediment samples were collected at each of the selected stations. Grab samples designed to show significant qualitative differences between stations were collected and seem sufficient for the purposes of the report. They were not intended as samples in the geologic sense, but rather approximates of industrial pollutants as well as geologic deposition.

More impressive data could have been developed with more refined sampling procedure and sieving procedure in the laboratory analysis. Metals tend to be found in the sediment fraction less than 16 microns, according to deGroot (3). In future studies utilization of the above observation will enable the production of uniform reproducable results for sediment data. Percentage silt and clay composition on the main stem is shown in Figure (2). Zinc tends to follow closely to the silt and clay configuration (Figure 3).



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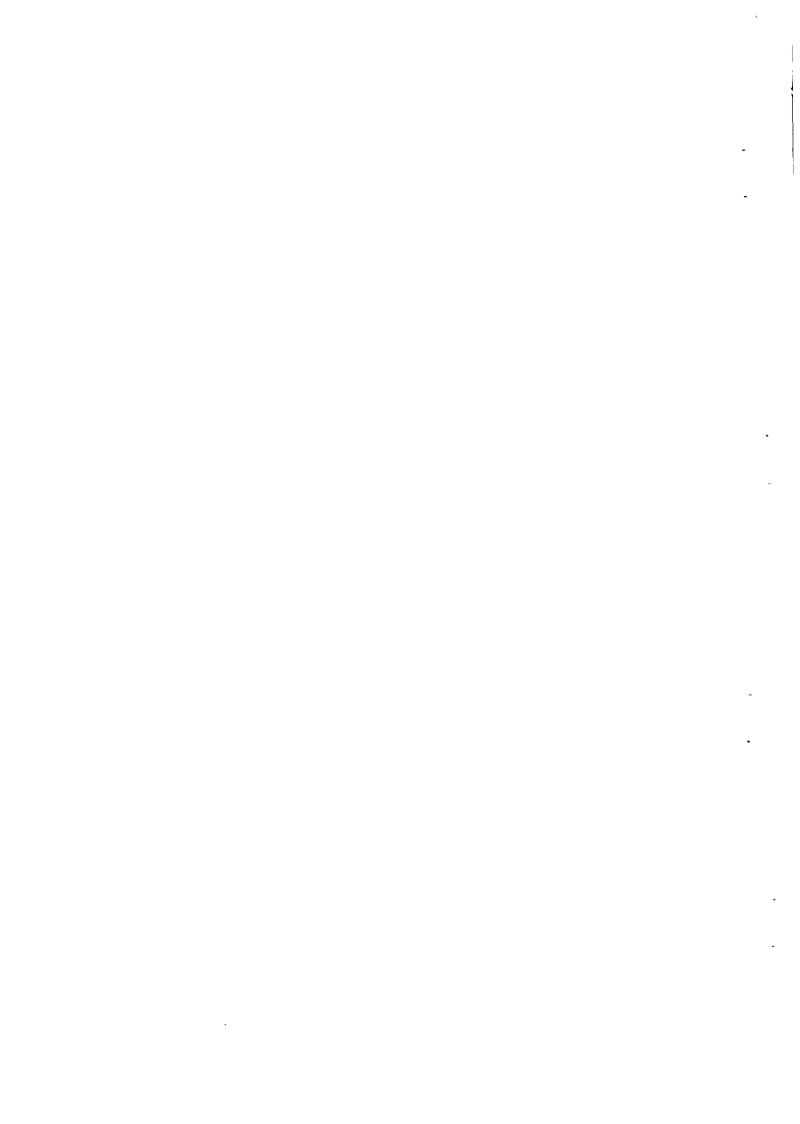
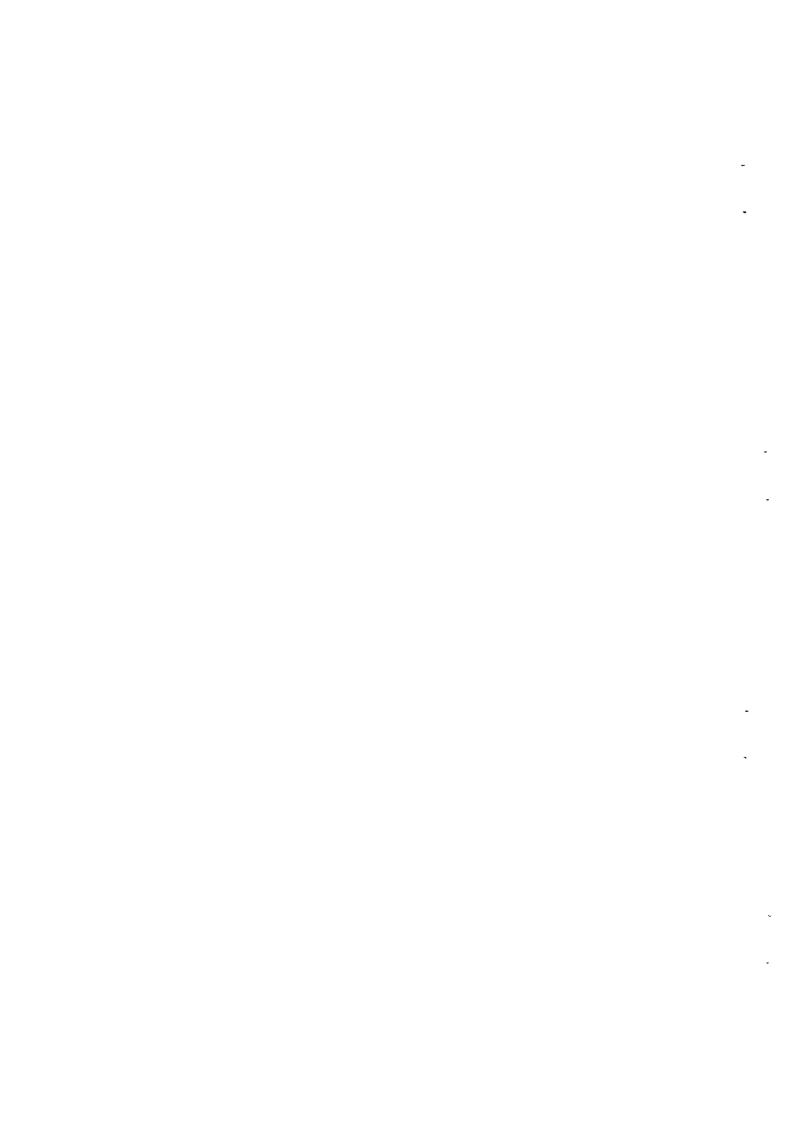


Table 1: Percent composition of sediments (sand, silt, clay), Schuvlkill River, July 9-25, 1973. Tributaries in downstream order are added for comparison.

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| STAT.       | SAND               | SILT                            | CLAY                               |
| SCH<br>114  | 92.3               | 5.4                             | 0.5                                |
| SCH<br>1.09 | 98.1               | 0.5                             | .03                                |
| SCH<br>090  | 98.3               | 0.7                             | 0.3                                |
| sсн<br>087  | 96.4               | 1.8                             | 0.4                                |
| SCH<br>077  | 98.5               | 0.1                             | 0.2                                |
| TRIB.       | 99.4               | 0.2                             | 0.2                                |
| SCH<br>061  | 94.6               | 3.0                             | 0.5                                |
| TRIB.       | 97.4               | 1.2                             | 0.2                                |
| SCH<br>049  | 99.4               | 0.2                             | 0.3                                |
| SCH<br>039  | 88.3               | 5.9                             | 0.7                                |
| TRIB.       | 91.8               | 5.4                             | 1.0                                |
| SCH<br>024  | 93.3               | 3.5                             | 0.6                                |
| SCH<br>019  | 98.8               | 0                               | 0.1                                |
| SCH<br>_006 | 37.4               | 49.6                            | 13.5                               |
| TRIB.       | 95.3               | 0.4                             | 0.1                                |
| TRIB.       | 97.5               | 1.4                             | ·.<br>0.3                          |
| TRIB.       | 90 5               | 0                               | 0                                  |



3 Figure 18: Zinc concentrations (mg/gm) in sediment and benthic macroinvertebrates, Schuylkill River, July 9-25, 1973 SCH 900 SCH 019 ° 6€0 SCH 049 ② Zn SEDIMENT (Dry Weight)
 △ Zn BENTHOS (Wet Weight) RIVER MILES .09 SCH 061 SCH SCH SCH 090 087 077 80 100 SCH 109 SCH 114 120 420 -360 m3/3m nZ 300 240 120 9



Dr. Robert C. Smith of the Pennsylvania Geologic Survey and Dr. David Poche, currently with the Virginia Department of Highways, assisted in providing a descriptive evaluation of the sediment samples in relation to the metals concentrations found. Percentage composition of the sediments at the various stations is shown in Table I. Dr. Poche states: "Heavy metals absorb to the surfaces of most of the smaller particles (silt and clay), particularly clays where unbalanced charges are present at the surface. It is my opinion that sediment at station SCH006 had the best potential for heavy metal absorption followed by stations SCH039, SCH114 respectively". Dr. Smith tends to corroborate the above statement in his discussion of the data.

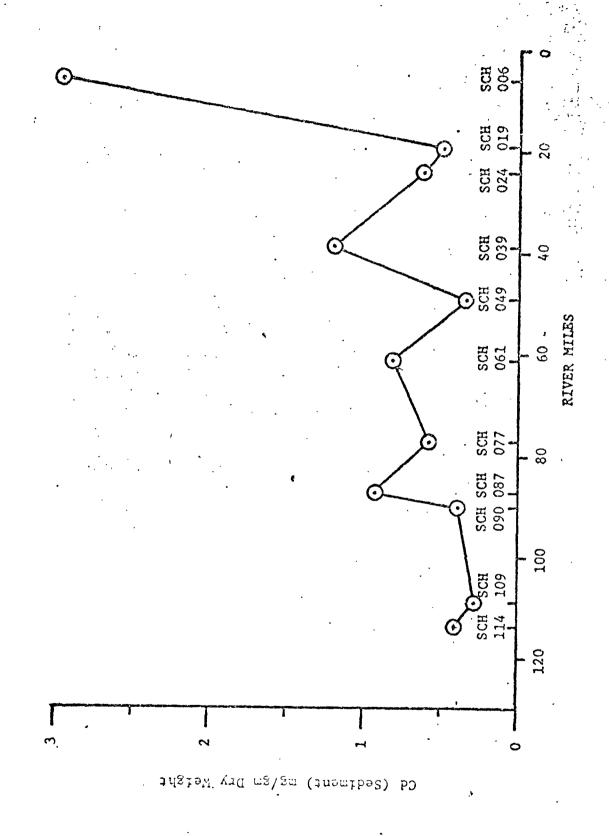
### Zinc and Cadmium

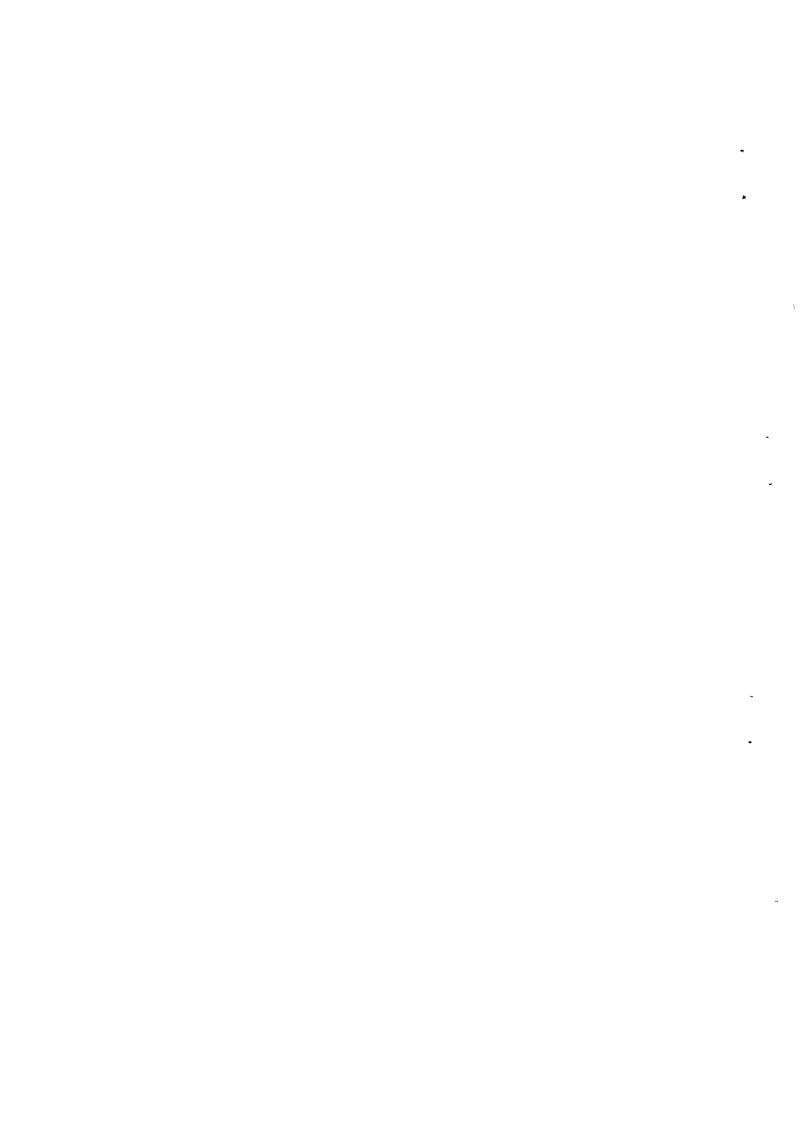
According to Dr. Smith, zinc ore deposits are found in the coal regions encompassing the upper portions of the Schuylkill Basin, thus, zinc concentrations throughout the Schuylkill River System tends to be rather high. There seems to be a natural tendency for zinc concentrations to progressively increase in the sediment as the Schuylkill drainage flows towards its mouth (Figure 3). When allowances are made for differences in silt and clay composition at sampling sites, the tendency still holds true. It is difficult to separate the effects of industrial sources from the natural concentrations.

Cadmium concentrations closely follows the zinc concentrations in the sediments (Figure 4). Dr. Smith points out that cadmium



Cadmium concentrations (mg/gm) in sediments, Schuylkill River, July 9-25, 1973 Figure 19;





is associated with zinc in natural sources and anything over 0.9 mg/l may be considered anomalous.

Another observation supporting the natural relationship is the close' correlations of the concentrations to the percent silt and clay (Figure 2). This correlation also helps account for the high concentrations at Station SCH006. Industrial and sewerage effluents also contribute to the problem at Station SCH006 which is tidally affected. Tidal action could contribute to increased metals by causing incomplete, selective flushing.

## Lead and Antimony

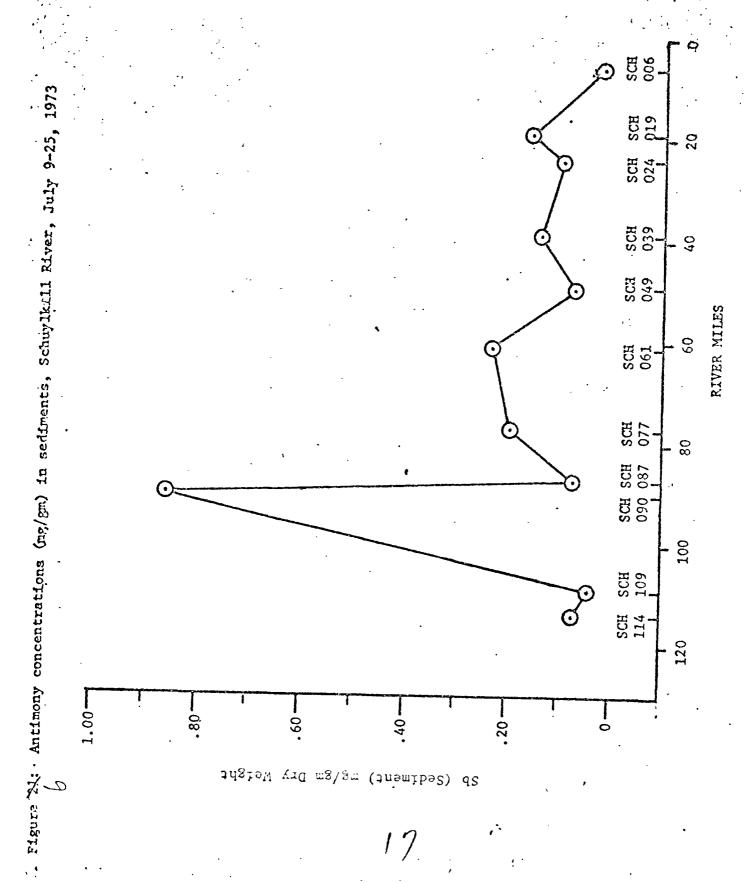
According to Dr. Smith, the samples collected at SCH090 and SCH077 suggest pollution. He states that in central Pennsylvania, values of over 70 ppm of lead are anomalous and while no data exists for southeast Pennsylvania, the geologic structure should generally contain less than 100 ppm of lead. Station SCH090 had the highest lead concentration in the sediment, other significant peaks are at SCH077, SCH039 and SCH006 (Figure 5).

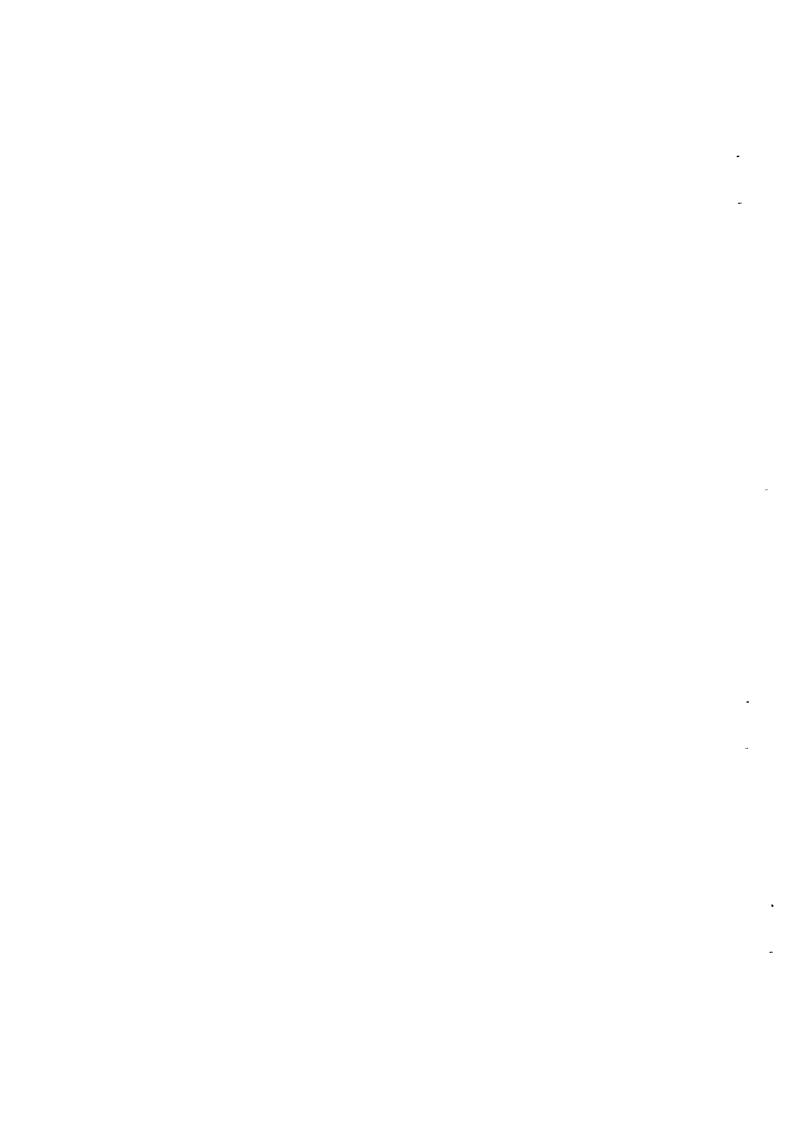
Antimony also had its highest concentration at SCH090 (Berne) (Figure 6). A second peak spread from station SCH077 to SCH061, with peaks at SCH039 and SCH019, except for stations SCH019 and SCH006, the changes in antimony concentration correlate closely with the two battery operations near SCH090 (Berne) and SCH077 (downstream of Bernhart Creek). These plants, Browns Battery Breaking and General Battery Corporation respectively, tend to use both lead and antimony in their operations.



5 lead concentrations (mg/gm) in sediments and benthic macroinvertebrates, Schuylkill River July 9-25, 1973 O Pb SEDIMENT (Dry Weight) A Pb BENTHOS (Wet Weight) SCH 019 SCH SCH 039 024 40 SCH SCHO RIVER MILES 09 SCH SCH SCH 090 087 077 80 100 SCH SCH 114 , 109 120 1 007 320 -80 240 160 mg/gm dq 16







The high concentrations of lead and antimony at station SCH039 are probably related to the Berks Associates oil spill of 1972.

The sludge involved in that spill had an average concentration of 20,000 ppm lead. While antimony was not analyzed for in the sludge at the time of the spill, one of the major sources of lead in that sludge, from reclaimed motor oil, would be Babbit metal. Babitt metal contains a combination of lead and antimony.

The differences in relationship between lead and antimony at stations SCH019 and SCH006 is likely due to a difference in the sources of the two metals in the Norristown-Philadelphia area.

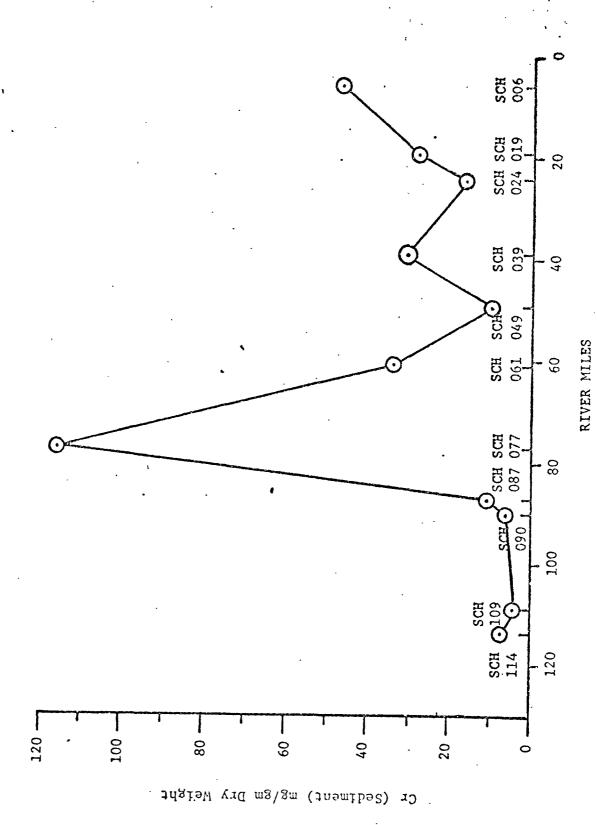
# Chromium and Nickel

There is a natural relationship between nickel and chromium according to Smith. However, nickel and chromium often occur together in industrial use as well. Thus, in this data the close correlation of chromium and nickel doesn't necessarily imply a natural relationship.

In the headwaters from SCH114 through SCH087 (opposite Maiden Creek) total chromium concentrations were low (10 microgram/gram or less), increasing to 116 micrograms per gram at station SCH077 (downstream from Bernhart Creek in Reading (Figure 7). The General Battery Corporation on Bernhart Creek manifests itself through a marked increase in chromium concentration in the sediment with a tendency towards oscillation. A significant peaking tendency







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is noted between SCH024 (Norristown) and SCH006 (Philadelphia). This is probably the result of a massive influx of domestic and industrial waste in this area and accompanying tidal influences at station SCH006.

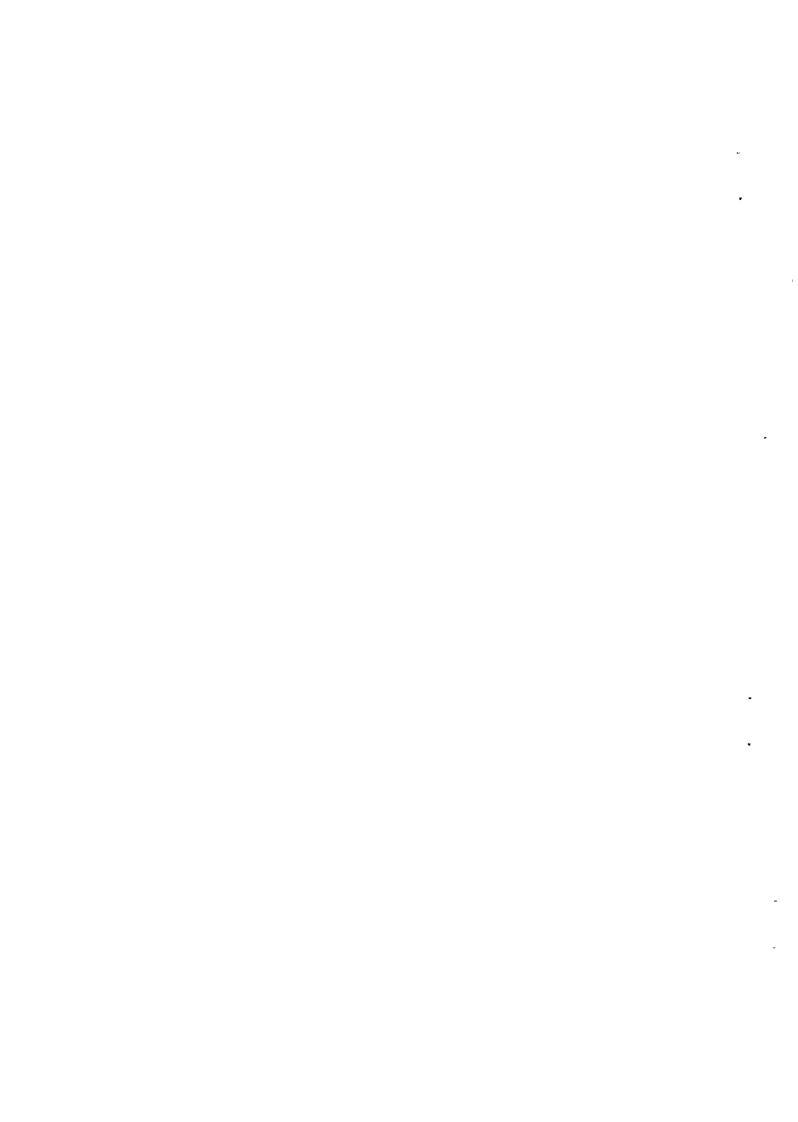
The nickel concentrations are low upstream of Reading, increasing to a high of 138 micrograms per gram at station SCH077, thus paralleling chromium concentrations (Figure 8). Oscillations downstream of station SCH077 also parallel chromium. However, at station SCH039 nickel peaks much higher than chromium. This downstream station appears to show the effects of the oil spill, since nickel would be higher than chromium in relative concentrations in the oil sludge.

### Copper

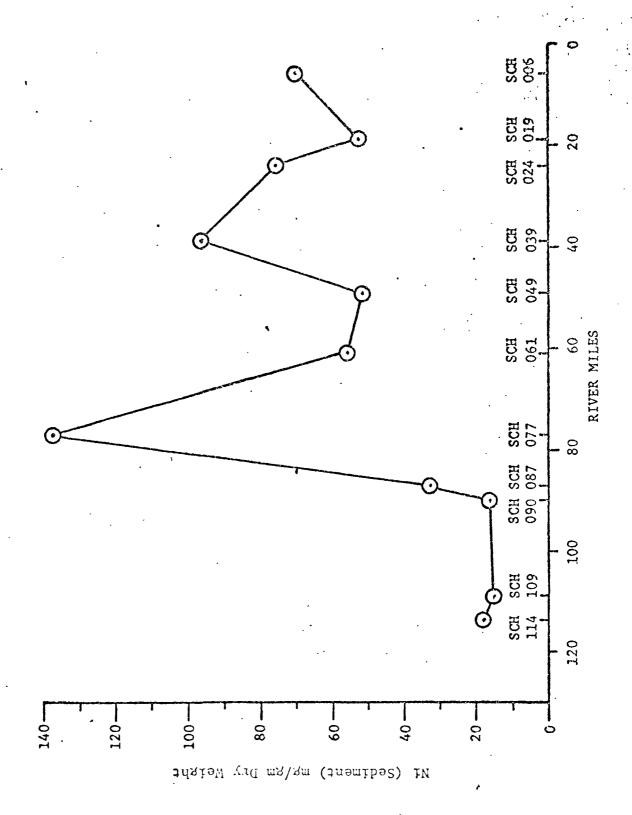
Downstream to Berne, Pennsylvania (SCH090) copper concentrations ranged between 23 and 35 micrograms per gram.

Station SCH087 opposite the mouth of Maiden Creek showed the highest concentration of copper (Figure 9). This area is composed of ordovician stonehenge limestone, a common host for mineralization. In addition, copper sulfate has commonly been used in this area to control algae, causing anomalous copper concentrations in many tributary streams in the area.

Copper concentrations increased in the sediments downstream from SCH077 (Reading) and peaked at SCH049 (Pottstown). The large iron-copper ore deposits on Fritz Island at Reading and anomalous









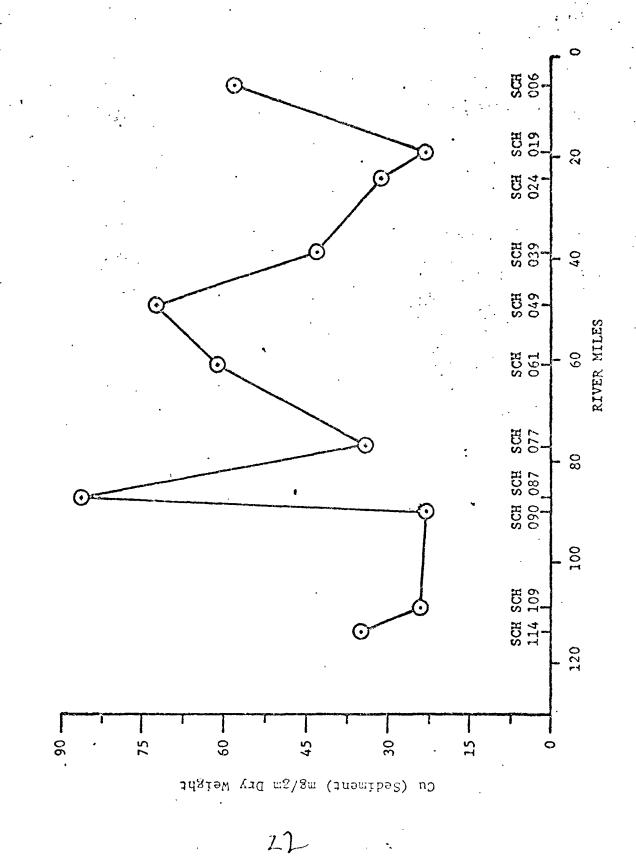


Figure 24: Copper concentrations (mg/gm) in sediments, Schuylkill River, July 9-25, 1973

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concentrations on several tributaries above Pottstown are likely sources. It seems unlikely, in view of the other data, that the oil spill was significantly contributing to high concentrations in this area.

From station SCH049 to station SCH019 (Norristown), the concentrations decline steadily. The sharp rise in copper concentrations at station SCH006 is due to the tidal conditions and wastewater problems discussed above for this area.

# Mercury

The concentration of mercury at each station is shown in Figure 10. Dr. Smith states that all mercury concentrations found are all within the range of background concentrations. Only station SCH006 exceeds 1 microgram/gram and the concentration tends to follow the silt and clay fraction of the sediment (Figure 2).

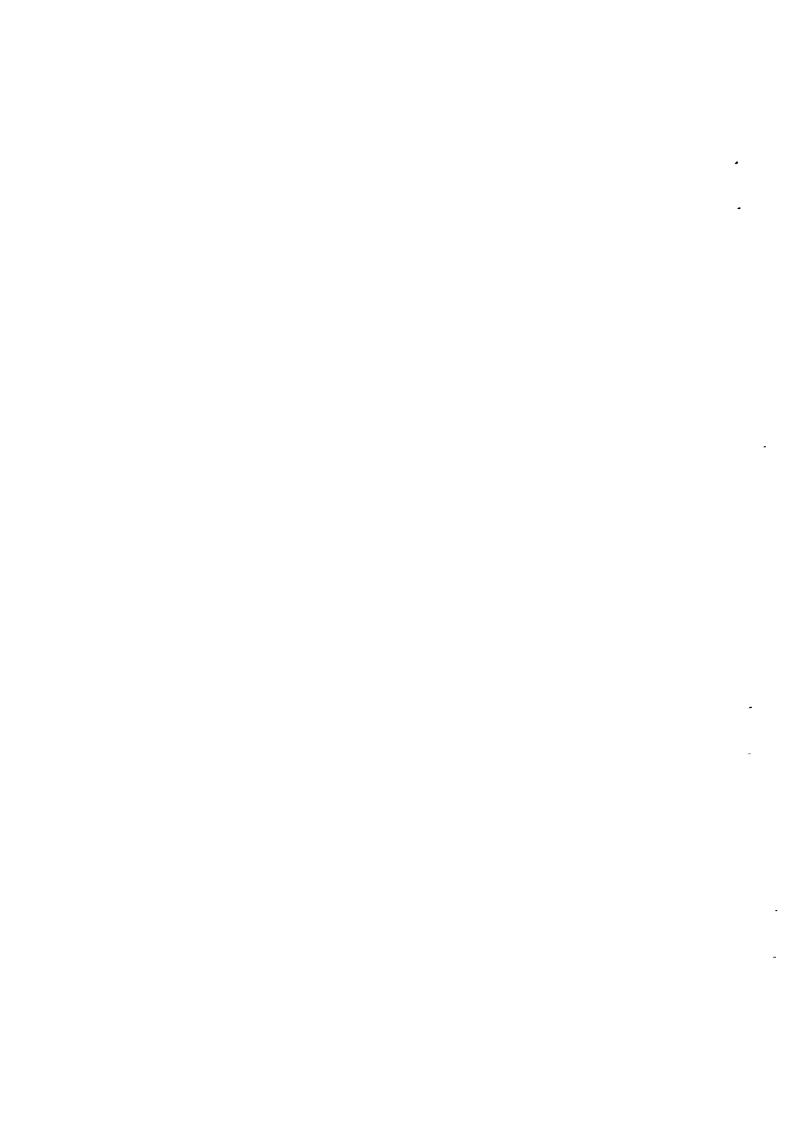
One interesting observation is that there is a somewhat anomalous rise in concentration between stations SCH087 and SCH049. This area encompassed the battery operations at Berne and Munlenberg Township.

see 23A)

FISH

### Zinc and Cadmium

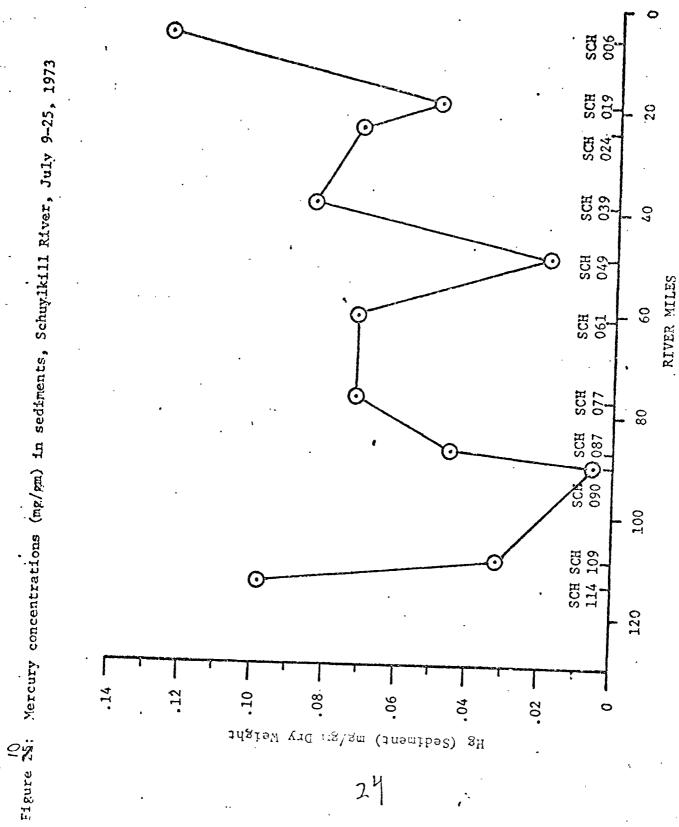
Zinc and cadmium for pumpkinseed and <u>Lepomis</u> correspond closely in uptake within the main stem, with the exception of stations



#### RENTHOS

Benthos metals were only run for zinc and lead due to equipment difficulties. Zinc uptake in benthos (Figure 3) tends to follow the sediment concentrations quite closely except at stations SCHO49 and SCHO24 (Figure 3). SCHO49 is immediately below the spill site. High uptake here could be explained by the increased availability of biologically active species of zinc, i.e. organically bound. Lead (Figure 5) also follows the sediment concentrations closely. There is an apparent lag, probably due to the natural conversion of lead to biological assimilable form, between sediment concentration and benthos concentration. Unfortunately, benthos samples could not be obtained at the critical stations SCHO39 and SCHO19 to confirm the trends in benthos metal sediment metal relationships suggested by upstream stations.





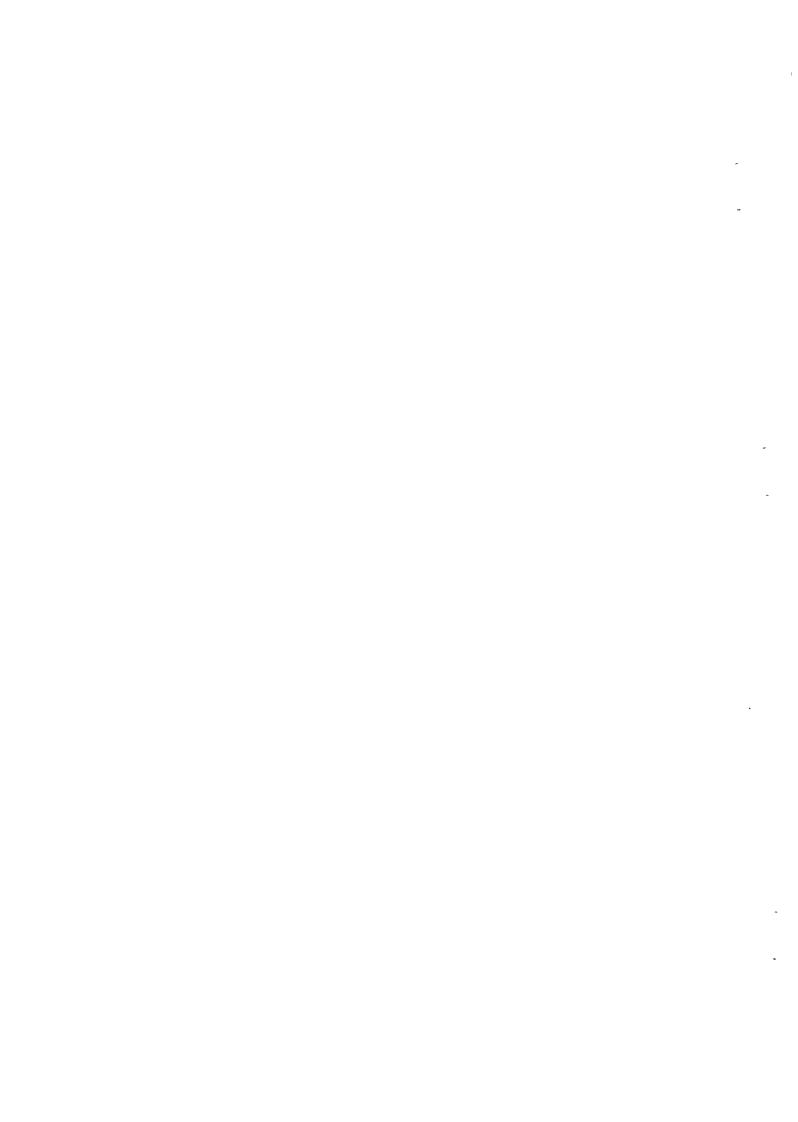


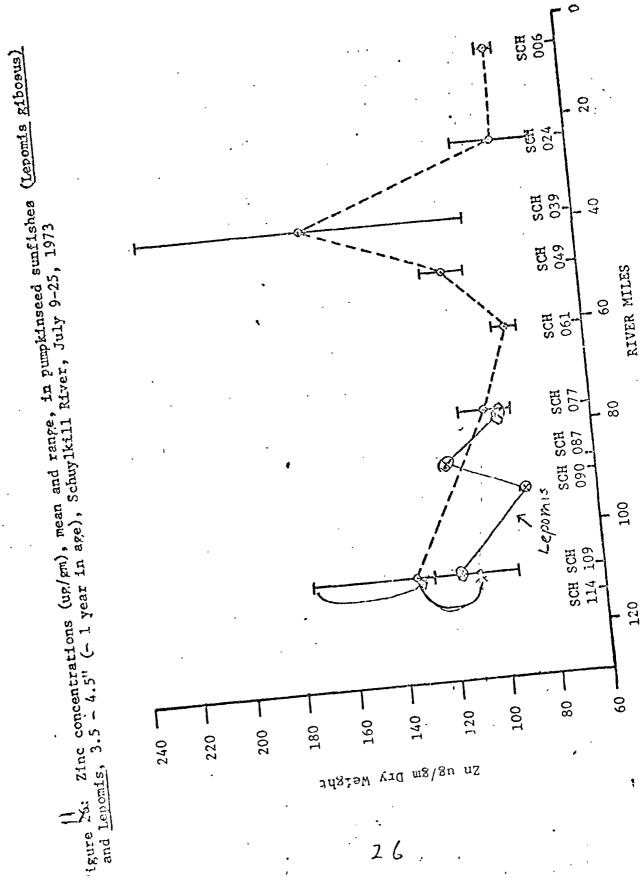
SCH061 and SCH024 (Figures 11 and 12). The reason for these occurrences is not apparent with available data.

One should note the upsurge of concentration in pumpkinseeds for both cadmium and zinc below station SCH061 which may be attributed to the oil spills. The lead, chromium, cadmium, zinc, nickel, and copper, found in such high concentrations in the spilled sludge, is likely to have been an organically bound form more amendable to biological absorption. This would account for a higher concentration of zinc and cadmium in the fish in relation to the sediment concentration at this location.

Zinc concentrations in pumpkinseeds and Lepomis dropped significantly after a peak at SCH039, when compared to an increase in concentrations in the sediment. This corresponds with the findings for the benthos discussed above. The concentration of zinc remains stable at a 100 micrograms per gram in the whole fish for the Lepomis in the two downstream stations. Considering the fact that both the zinc concentrations in the sediment and the percent of silt and clay are high at station SCH006, one would expect a large increase in the fish. However, this is not the case. Since this is a tidal area with many and varied sources of pollution utilizing zinc, unknown tidal action and type of zinc in the sediment may be influencing factors.

Cadmium has a rise at SCH061 which corresponds to the rise of cadmium in the sediment. Zinc, which has a corresponding rise in





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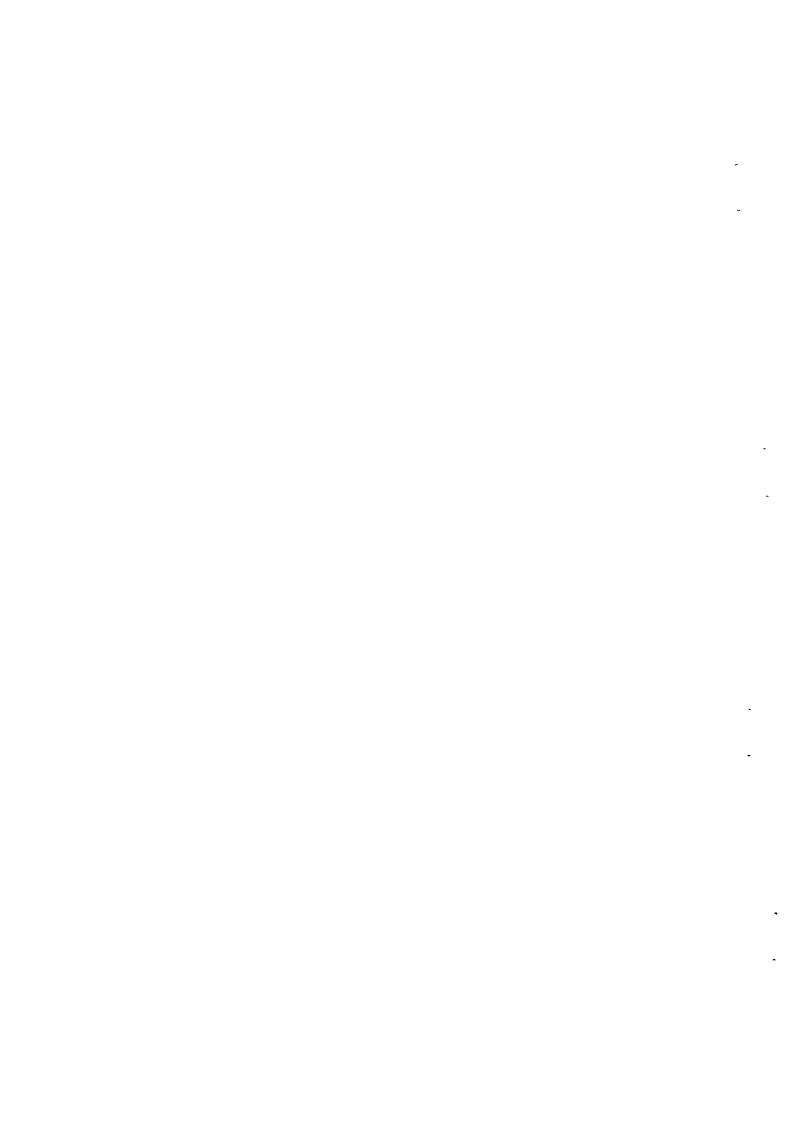
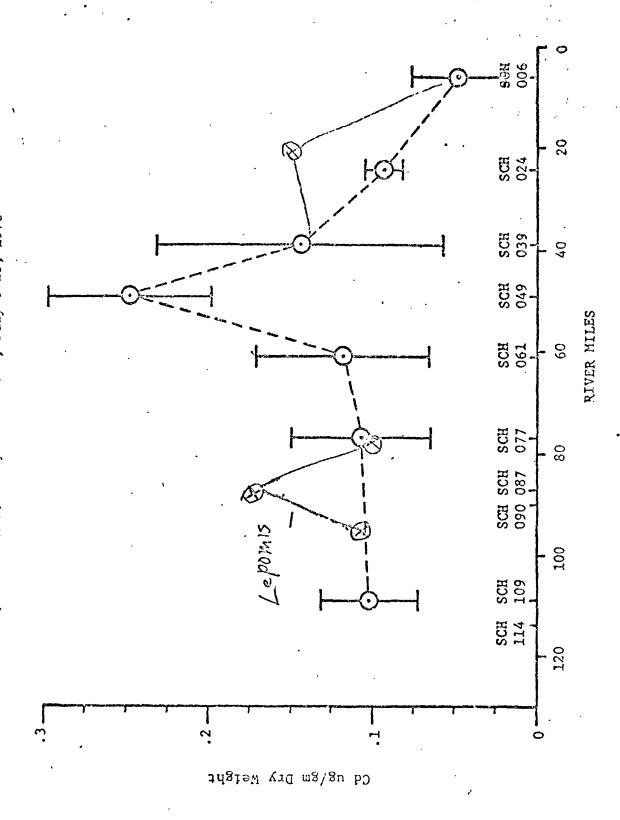


Figure 24: Cadmium concentrations (ug/gm), mean and range, in pumpkinseed sunfishes (Leponis gibbosus) and Lelonis, 3.5 - 4.5" (- 1 year in age), Schuylkill River, July 9-25, 1973



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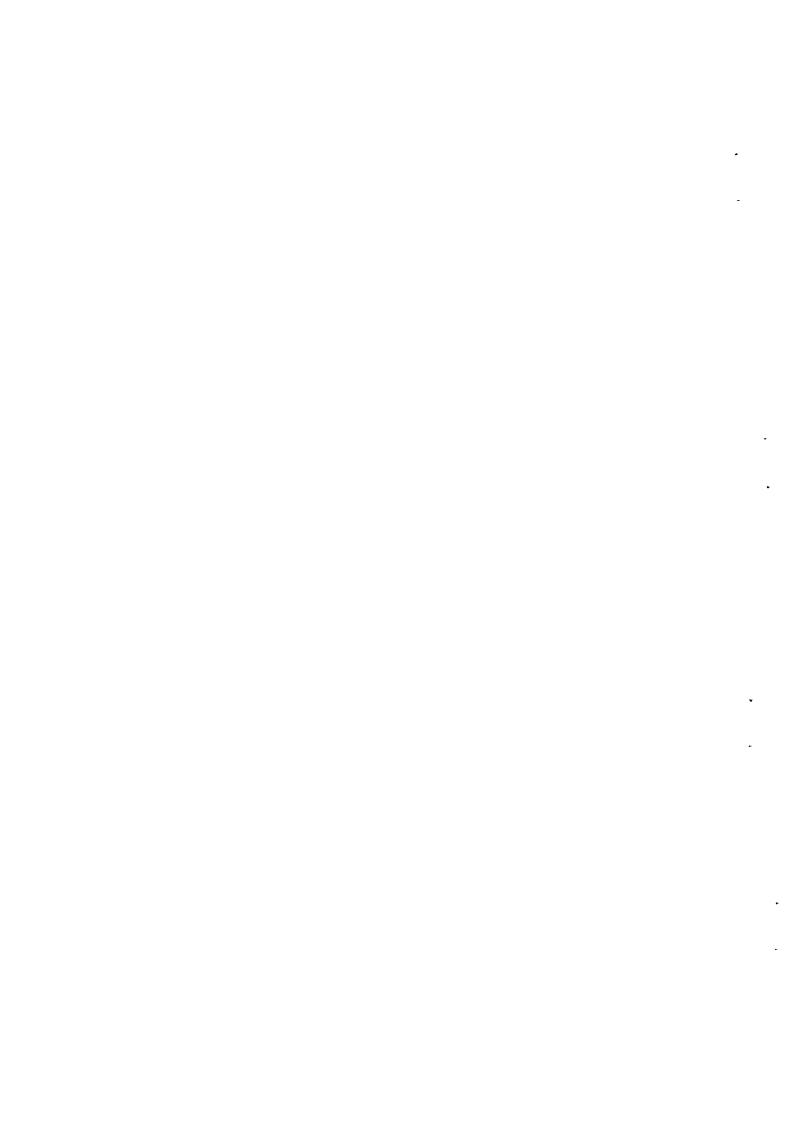


sediment, shows a drop at this site for both pumpkinseed and genus Lepomis data. The benthos data for zinc at this station shows only a moderate tendency to increase with the corresponding increase in sediment. The present data provides no insight into this difference in behavior between zinc and cadmium.

At station SCH024 the decrease in cadmium in pumpkinseeds corresponds to the decrease in cadmium found in the sediment. However, the <u>Lepomis</u> data shows an increase in cadmium at this station. A larger proportion of bluegills were collected here than at other stations and appear to have contributed to this increase in average concentration.

Station SCH006 shows the same decrease in cadmium concentration in the pumpkinseed and <u>Lepomis</u> data compared to increases in the sediment which is found for zinc. This association phenomenon likely occurs for the same reason as for zinc.

It should be noted that the pumpkinseed <u>Lepomis gibbosus</u> and the genus <u>Lepomis</u> are discussed and graphed together. This is done for all metals. The member species and the genus tend to coincide quite nicely in relation to metals uptake with some exceptions. Utilizing the genus enables the inclusion of data bracketing the very important source of heavy metals at Berne (SCH090) which is missed with the pumpkinseed data.

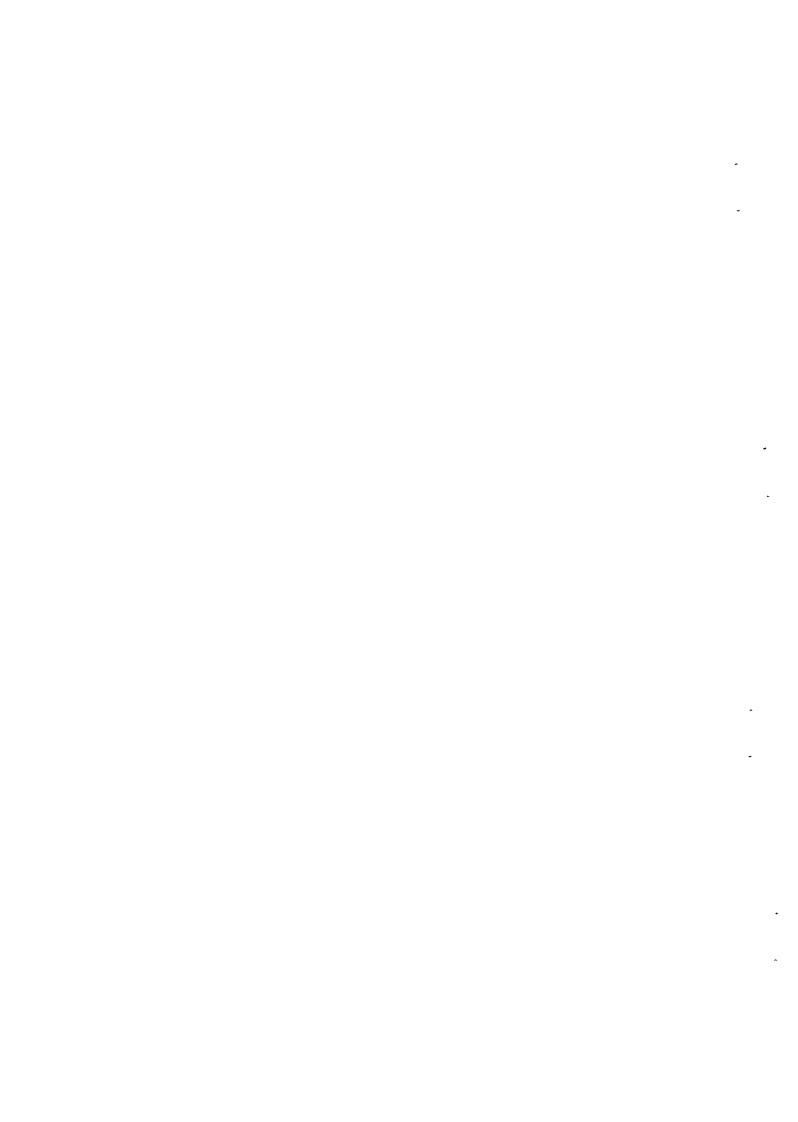


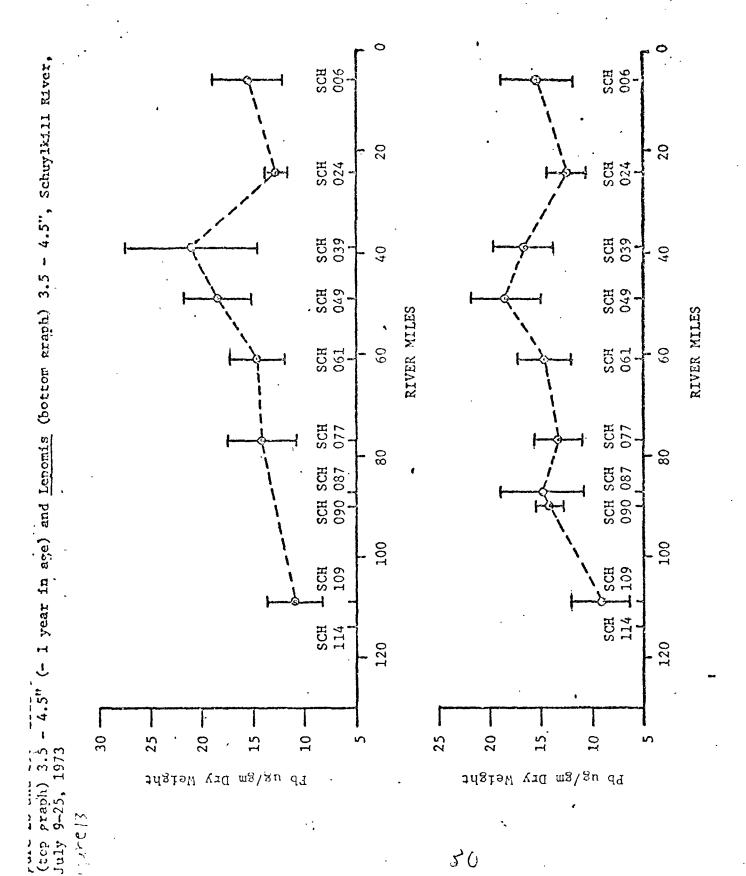
#### LEAD AND ANTIMONY

#### Lead

Background lead for <u>Lepomis</u> and pumpkinseed is about 10 ppm dry weight for whole fish on the Schuylkill River main stem (Figure 13). Between stations SCH090 and SCH087 concentrations increase to about 15 ppm which corresponds with the high lead concentration in the sediments (385 ppm) at station SCH090. From that point on the lead concentrations remained high, greater than 13 ppm, the entire length of the Schuylkill. This increases to approximately 18 ppm between stations SCH049 and SCH039 which corresponds to the two oil spills in Berks County just below station SCH061. It is interesting to note that sediment concentrations of lead here are lower than upstream polluted sites even though lead concentration in fish is higher. The explanation stated for zinc and cadmium applies.

Antimony values in fish all fell below 0.05 to 0.005 ppm for both whole fish and fillets. This would suggest minimal uptake of antimony by fish life. However, the maximum concentration of antimony in the sediment is only 0.8 ppm and uptake may be occurring without being within the detection limits of current methodology. It seems likely that antimony is not as biologically active as mercury tends to be and thus requires higher quantities in the sediment before showing uptake in the biosphere.







# Chromium and Nickel

Again there is a rise in the content of the pumpkinseed and genus Lepomis which corresponds with increases in levels of chromium and nickel in the sediment at stations SCH077 and SCH039 (Figure 14). For nickel these increases are quite distinct at stations SCH061 and SCH039 (Figure 15). For chromium the two distinct peaks are not found, but rather a steady rise in concentration in fish from section SCH039. The reason for this difference in uptake pattern is not readily explained by the data available, unless a different uptake pattern exists for the two metals.

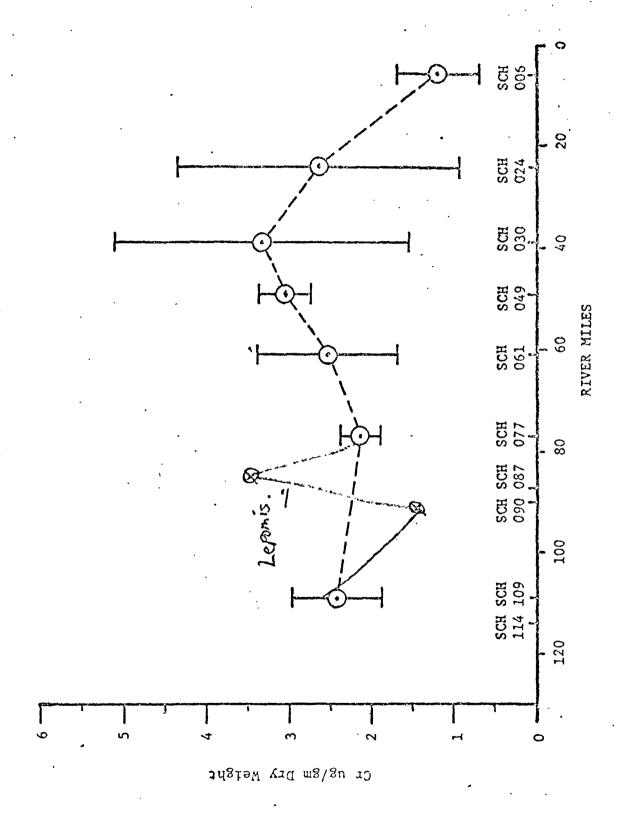
The highest concentration in the sediments is found at station SCH077, but as in the other metals, the highest concentration in fish is between stations SCH049 and SCH039 downstream of the oil spills.

## Copper

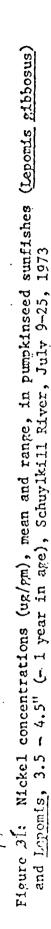
Copper does not follow other metals in pattern of uptake by pumpkinseeds (Figure 16). Rather the distribution of copper in the pumpkinseed and <u>Lepomis</u> emphasizes the presence of anomalous copper concentrations in the tributaries between Reading, station SCH077 and station SCH061 as well as the presence of a copper deposit below Reading. The tendency of pumpkinseeds to migrate in and out of tributary mouths is emphasized by the high concentration in them at station SCH061. In this area, according

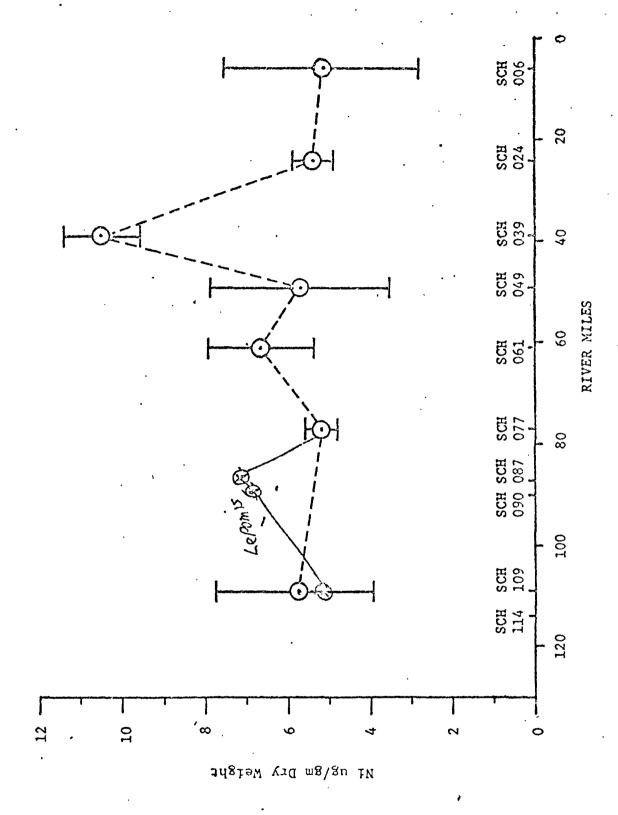


[4] Figure 36: Chromium concentrations (ug/gm), mean and range, in pumpkinseed sunfishes (Lepomis gibbosus) and Lepomis, 3.5 - 4.5" (-1 year in age), Schuylkill River, July 9-25, 1973





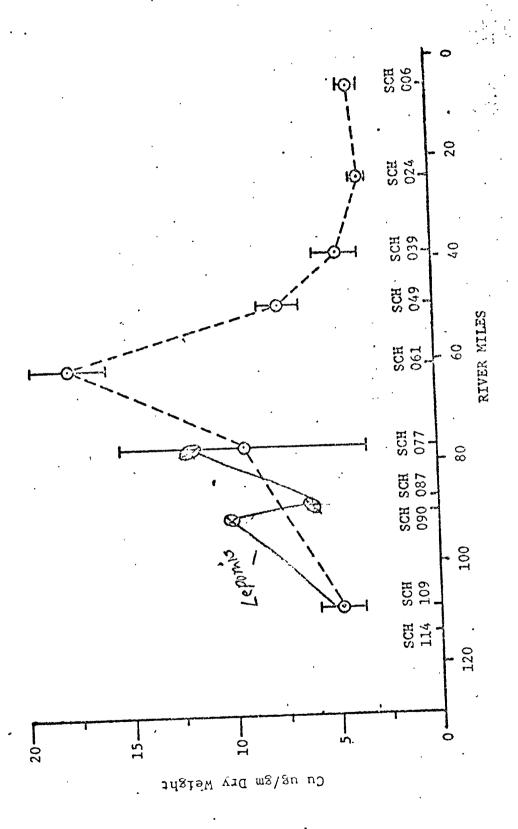




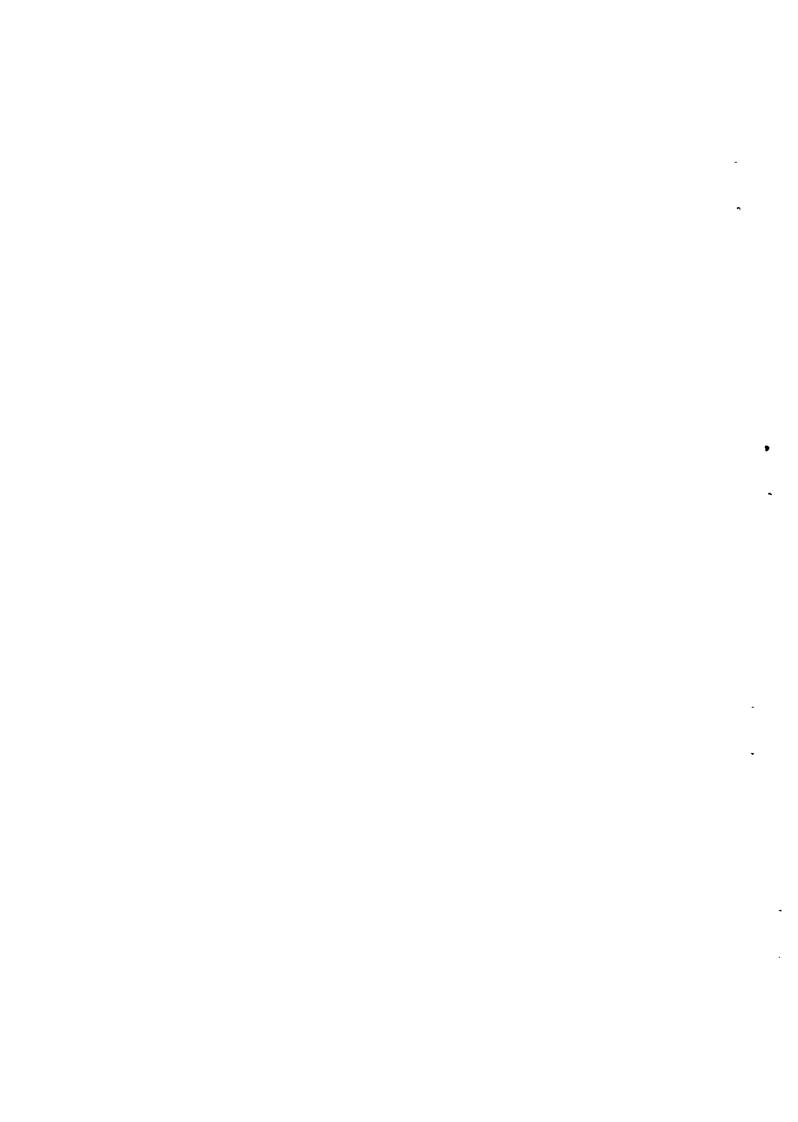
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Igure 22: Copper concentrations (ug/gm), mean and range, in pumpkinseed sunfishes (Lepómis gibbosus) and Lepomis, 3.5 - 4.5" (- 1 year in age), Schuylkill River, July 9-25, 1973



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to geologic information, it seems likely they are exposed to larger amounts of copper in the tributaries than the main stem. It is also possible the copper from the high concentration areas upstream is converted to a form more readily available to the biomass in the vicinity of station SCHO61.

The genus <u>Lepomis</u> data shows a rise at SCH090 (Figure 16). However, the highest concentration in the sediment is at SCH087. The difference is not easily explained based on this data, but is likely due to a change in the species of copper affecting uptake.

As with zinc and other materials mentioned previously, copper uptake at station SCH006 drops, even with a rise in the sediment concentration. This phenomena seems consistent for several metals. The explanation is presented in the zinc discussion for this phenomena.

#### Mercury

Since mercury showed only background concentrations, it was not analyzed in the fish.

#### ENVIRONMENTAL CONSIDERATIONS

The sediment concentrations in the Schuylkill River were considerably higher for several metals than the metals found in the sediments of Shenandoah River (Table 2). The major exception is zinc. A major problem with zinc in the Shenandoah was the



Table 2: Shenandoah River fish kill related to zinc: concentrations in the sediments, August, 1969, (ug/g dry weight)

| C of adjustment and properties of the annual | AR SPREMENT & MARKET AND THE THE SPRESS AND THE | METALS |      |       |  |  |  |
|--|---|--------|------|-------|--|--|--|
| CONTROL<br>AREA                              | Zn  | Cr     | Pb   | Cu    |  |  |  |
| 1  | 84.4  | 14.9   | 4.47 | 14.6  |  |  |  |
| 2  | 45 <b>.</b> 5                                   | 14.3   | 2.01 | 11.8  |  |  |  |
| 3  | 71.3  | 32.2   | 2.82 | 15.1  |  |  |  |
| Avg.   | 67.07   | 20.47  | 3.10 | 13.83 |  |  |  |

|                  |       | METALS |      |       |  |  |  |
|------------------|-------|--------|------|-------|--|--|--|
| AFFECTED<br>AREA | Zn    | Cr     | Рb   | Cu    |  |  |  |
| 1                | 643   | 30.6   | 5.35 | 32.80 |  |  |  |
| 2                | 1073  | 67.4   | 5.97 | 33.2  |  |  |  |
| 3                | 166   | 9.9    | 2.50 | 3.92  |  |  |  |
| 4                | 247   | 10.5   | 1.99 | 9.16  |  |  |  |
| 5                | 1.220 | 40.1   | 6.28 | 32.10 |  |  |  |
| Ava.             | (69.8 | 31.7   | 3.68 | 22.24 |  |  |  |



reason for that investigation. In the control area of the Shenandoah, zinc never exceeded 90 ppm, copper never exceeded 16, lead never exceeded 5 ppm. In the polluted area, copper reached a high of 32 ppm, zinc 1220 ppm, lead 6 ppm.

The Schuylkill, on the other hand, had a high of 378 ppm lead in one polluted area and 55 ppm in unaffected areas; zinc never exceeded 220 ppm anywhere in the basin; copper reached a high of 72 ppm in an area where known deposits of ore as well as pollution sources existed. Rolfe (5) also found a similar distribution of lead related to mine and smelter sources. Mathis and Cummings (6) in their study on the industrialized Illinois River showed significantly lower metals in the sediments than those found in the Schuylkill. In their study, lead never exceeded 140 ppm with a mean of 28 ppm; zinc had a mean of 81 ppm and a maximum of 339 ppm; copper had a mean of 19 ppm and a maximum of 82 ppm.

Wisconsin (7) conducted a survey of toxic metals at selected points in the state. They found large increases of metals in sludges of treatment plants which had metals sources emptying into them. However, they did not measure any concentrations in the sediments of the streams. They did, however, find low concentrations in the effluents. The water chemistry of the Schuylkill River found low concentrations in the water



and effluents as compared to the sediments. This points up the fact that metals tend to be associated and concentrated in the sediments or solid materials rather than remain free in the water.

Concentrations of heavy metals in the sediments are highly significant from the biological point of view. Microbial action on heavy metals in the sediments could provide a mechanism for uptake into the aquatic biosphere. This has been sufficiently demonstrated for mercury. Tornabene and Edwards (8) found certain soil microbial systems are capable of extracting substantial quantities of inorganic lead and theorized such systems may be of importance in the transfer through the food chain. The implications of these findings is of special importance in the Schuylkill study where a serious heavy metals problem exists, as indicated in the above comparisons. It is of particularly large importance when it is noted that the major metal problem in the Schuylkill River is lead.

Little is known about the effect of oil in these systems. However, Jobsen et al (9) found that some of the same microbial systems; i.e., Micrococcus, active in lead extraction, are also highly active in the natural breakdown of some oil fractions. No direct connection is demonstrated between these two phenomena; however, the higher lead uptakes by fish, compared to lead available in the sediment below the oil spill, suggests one might exist.

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When the metals concentrations in the fish of the Schuylkill River are compared to concentrations found in other river systems, they are considerably higher. Average zinc concentrations for whole Lepomis range between 80 ppm and 140 ppm dry weight throughout the main stem. The highest whole fish dry weight average concentrations of lead range between 16 ppm and 21 ppm for the genus Lepomis. The highest average concentration of lead in the Lepomis fillets was 14.7 ppm dry weight or approximately 4 ppm wet weight. For whole fish Lepomis the highest average copper readings ranged between 16 and 20 ppm dry weight.

Data from the State of Virginia on whole fish and fillets are in dry weight and are directly comparable to the Schuylkill River data. Tables 3, 4, and 5 show the metals concentrations for fish in the Shenandoah, James, and Roanoke Rivers. Fish in the Shenandoah River generally had less than 6 ppm lead in whole fish and less than 2 ppm in the flesh, while copper is less than 10 ppm whole fish and 4 ppm in the flesh. Zinc was over 100 ppm for the whole fish. For Lepomis in the James River, lead concentrations were generally less than 2 ppm and never more than 7 ppm, while copper averaged around 5 ppm not exceeding 10 ppm, and zinc averaged around 100 ppm never exceeding 150 ppm.

The Roanoke River data is only for fillets or striped bass and are not quite comparable to any species collected in the Schuylkill River. However, the concentrations of lead did not exceed 0.18 ppm. Copper did not exceed 3.0 ppm and zinc remained



Table 3: Shenandeah River fish kill related to zinc: metals concentrations in fishes, August, 1969,  $(v_1/g)$  dry weight)

|          |              |                       | op. V.   |          |          |          |          |
|----------|--------------|-----------------------|----------|----------|----------|----------|----------|
| <b>=</b> | weight (lbs) | STANDARD LENGTH (INS) | Cr (ppm) | (mdd) uz | Pb (ppm) | (mdd) no | нг (ррш) |
|          | . 2.6        | 27.5                  | 0.55     | 18.5     | 0.18     | 2.22     | 10.      |
| Ţ        | 2.6          | 18.5                  | 0.38     | 18.8     | 0.13     | 2.50     | 0.44     |
|          | 3.3          | 21.5                  | 0.47     | 19.8     | 0.12     | 1.87     | 0.01     |
| - }      | 13.8         | 31.5                  | 0.22     | 24.4     | 0.11     | 2.89     | 0.17     |
| 1        | 8.7          | 28.                   | 0.18     | 24.5     | 0.09     | 2.18     | 0.25     |
| ı        | 6.5          | 25.5                  | 0.14     | 16.5     | 0.07     | 1.98     | 0.14     |
| 1        | 6.9          | 27.0                  | 0.21     | 15.7     | 0.10     | 2.17     | 0.10     |
|          | 7.8          | - 0°-26               | 0.55     | 9.02     | 0.00     | 2.22     | E CO     |

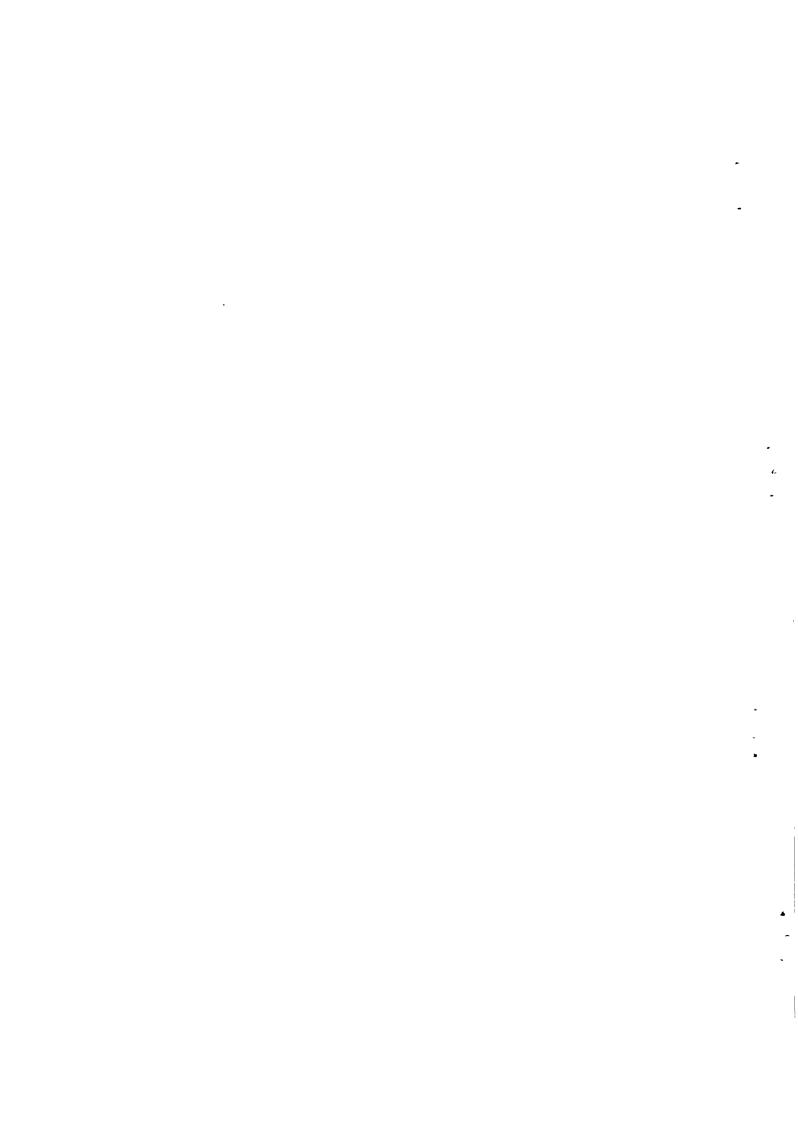


Table 4: Surmary of selected, average data on the concentrations of metals in the fish for the James River Basin, May-June, 1971

| CAN DANN PROMOTER TO A STREET TO A STREET ST | and the second | META | ALS  | CONTRACTOR OF THE STATE OF THE |
|--|----------------|------|------|---|
|  | Zn             | Cr   | Pb   | Cu  |
| <u>Lepomis</u> flesh  Control Area   | 38.6           | 0.44 | 1.13 | 2.8   |
| Lepomis flesh Affected Area  | 47.9           | 0.51 | 0.95 | 3.6   |
| Catfish flesh Control Area   | 41.0           | 0.1  | 0.1  | 3.5   |
| Catfish whole  | 253.11         | 1.19 | 2.50 | 7.71  |

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Table 5: Metals analysis of edible neat in striped bass, Roanoke River at Brookneal, June 1, 1972

| CLFAN AREA |             | METALS |      |      | Control of the same of the sam |      |
|------------|-------------|--------|------|------|--|------|
| STATION    | FISH        | Zn     | Cr   | Pb   | Cd   | Cu   |
| 6В         | Purpkinseed | 33.38  | 1.85 | 0.30 | 0.59   | 3.04 |
| 6в         | Leponis     | 85.44  | 1.34 | 0.81 | 0.43   | 3.06 |
| 6в         | Bullhead    | 58.83  | 2.29 | 0.78 | 0.37   | 4.68 |

| CONTRACTOR AND ADDRESS OF THE PARTY OF THE P | editi i pito en bresime a billionica i incidere citarione. | CAMPAGAN S 27850 L PRICERARANES GOMES AND SECURE SEC | CONTRACTOR SECURITIES | WAY AVE ET SPREED LOSING | THE THORSE OF STREET OF STREET | THE PERSON NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT OF THE PERSON NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TRANSPORT |
|--|--|--|---|--------------------------|--------------------------------|--|
| . CLEAN AREA   |  |  | METALS  |                          |                                |  |
| STATION  | FISH   | Zn   | Cr  | Pb                       | Cď                             | Cu   |
| 6A   | Pumpkinseed  | 57.53  | 1.37  | 0.34                     | 0.18                           | 2.32   |
| 6A   | Lepomis  | 66.80  | 1.38  | 0.28                     | 0.30                           | 3.16   |

| 1 | TELY CLEAN  |        |      | TALS | TOTAL STATE OF THE |      |
|---|-------------|--------|------|------|--------------------|------|
| 5 | Pumpkinseed | 101.22 | 1.60 | 0.15 | 0.38               | 2.92 |
|   |             |        |      |      |                    |      |

| ORGANICAI | LY POLLUTED | METALS |      |      | T TEMPERATURE TO CONTRACTOR |      |
|-----------|-------------|--------|------|------|-----------------------------|------|
| 4         | Shiner      | 80.6   | 1.29 | 2.57 | 0.96                        | 6.18 |
| 4         | Eullhoad    | 92.57  | 3.75 | 3.35 | 0.37                        | 9.09 |
|           |             |        |      |      |                             |      |

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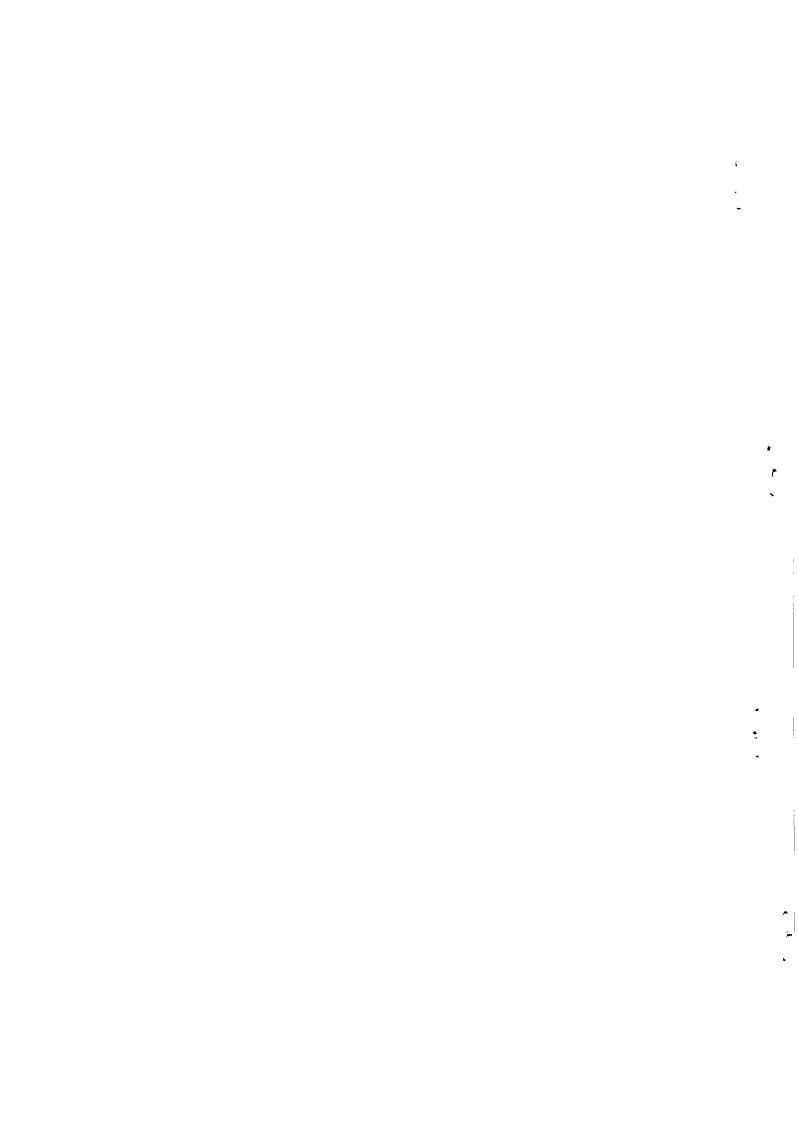
under 30 ppm for fish ranging between 18 and 30 inches. Carp, approximately the same size, in the lower Schuylkill River, had 2.0 ppm lead, less than 5 ppm copper and less than 70 ppm zinc.

The Shenandoah is a natural hard water river and the James in its upper reaches is a moderately hard water river. The Roanoke is a moderately hard water river with several areas of known organic pollution problems. The Schuylkill is a moderately hard water river due to both the presence of limestone deposits and the effects of coal mining operations. The major difference between the rivers from the water quality standpoint is the amount of pollution sources and kinds of pollution found in the various basins. Strictly speaking, metal concentrations of fish and sediments cannot be compared between rivers systems. However, looking at the other river systems does provide baseline information on what normal expectations would be under a variety of conditions.

Mathis and Cummings found significantly lower concentrations for similar species of fish in the Illinois River. Only muscle tissue was analyzed in this study on a wet weight basis. For carp they found a mean of 0.56 ppm and a range from 0.15 ppm to 2.13 ppm for lead; a mean of 0.24 and a range from 0.12 to 0.14 for copper; a mean of 10.2 and a range from 4.1 to 16.1 ppm for zinc; a mean of 0.19 and a range from 0.04 to 0.28 for nickel.

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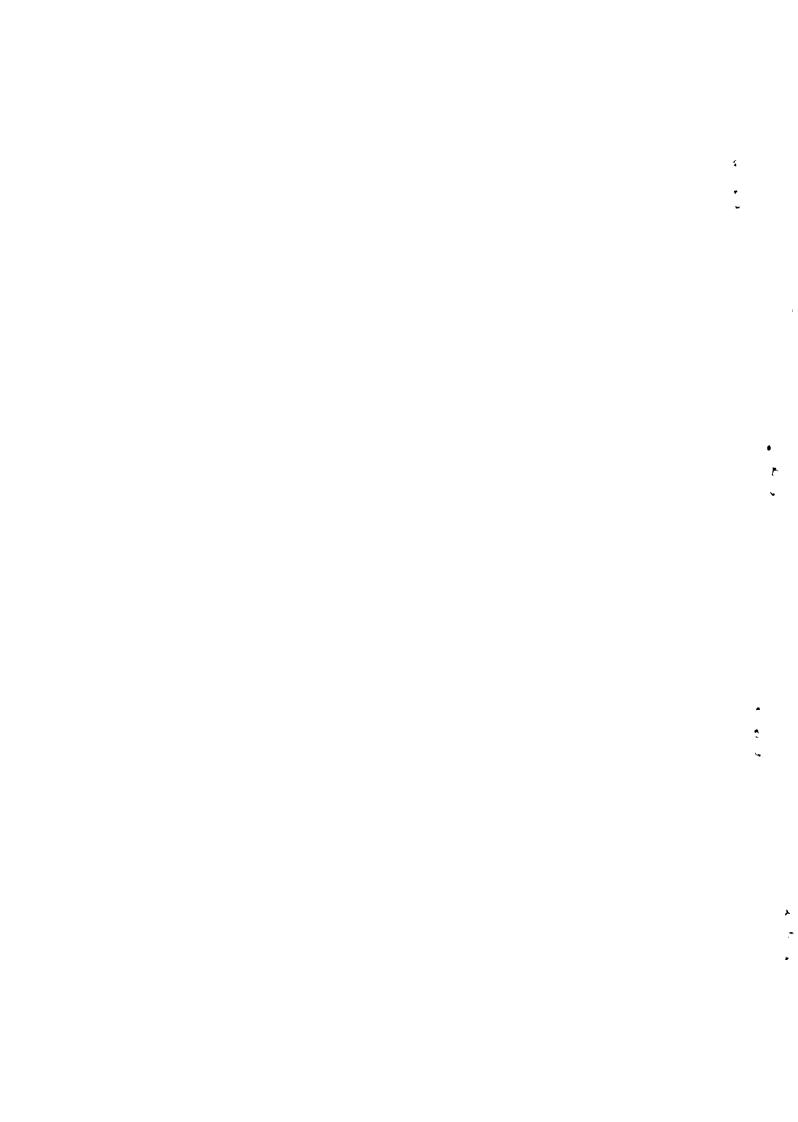
All carp collected in the Schuylkill River were below the first source of metals and were over a range of stations showing varying degrees of effects from heavy metals. The results of fillet analysis showed them to have a mean of 4.53 ppm dry weight (approximately 1.51 ppm wet weight), and a dry weight range from 1.78 ppm to 15.7 ppm for lead. For copper they had a mean of 3.10 ppm and a range from 1.42 ppm to 6.85 ppm. zinc they had a mean of 73.09 ppm and a range from 27.6 ppm to 145.7 ppm; for nickel they had a mean of 3.13 ppm and a range from 0.54 ppm to 6.44 ppm. While this is significantly higher than the concentrations in the Mathis and Cummings study, it should be noted that the carp seems to have the least potential for uptake of the omnivorous fish samples in the Schuylkill River study. In the Mathis and Cummings study of the Illinois River, omnivorous fish showed a mean of 0.64 ppm wet weight for lead and 5.02 ppm wet weight for zinc; carnivorous fish showed a mean of 0.57 ppm wet weight for lead and 3.49 ppm wet weight for' In the Schuylkill River the upstream stations affected by mine drainage had a mean of 47.66 zinc and 7.25 ppm dry weight for lead in the omnivorous fishes. The stations downstream of the metal sources had a mean of 8.48 ppm for lead and 66.77 ppm for zinc (dry weight) in omnivorous fish. Upstream carnivorous fish had a dry weight mean of 7.64 ppm for lead and 47.68 ppm for zinc. The fish downstream from the metal sources showed a mean of 12.18 for lead and 72.54 for zinc.



The above analysis as applied to the Schuylkill River has serious weaknesses. The size class and species composition of the stations varies widely for the two categories used. This is particularly true of the omnivorous classifications since the upstream stations have a composition of smaller fish with higher uptake rates.

In the Wisconsin study the highest lead concentration found was 4.31 ppm wet weight and the highest zinc concentration was 18.3 ppm wet weight. Most of the concentrations for lead were less than 1.0 ppm wet weight and for zinc less than 10 ppm. It is obvious that the mining and metal industries on the Schuylkill River have had a severe impact on the distribution of metals and fish flesh and biota. The evidence points to the sediments as the vehicle facilitating uptake in the biosphere. It seems likely that the species of metal and the kind of material with which it is associated has a significant effect on the route of uptake.

Rolfe and Jennett found that large quantities of heavy metals moved through the aquatic system in association with suspended matter. They also found fish near lead sources and higher levels than unexposed fish, which supports the findings of this study. This study suggests that a highly organic matrix such as oils may greatly facilitate uptake of metals. In a heavily loaded system such as the Schuylkill River, with a highly toxic metal such as lead, it seems reasonable to suspect that

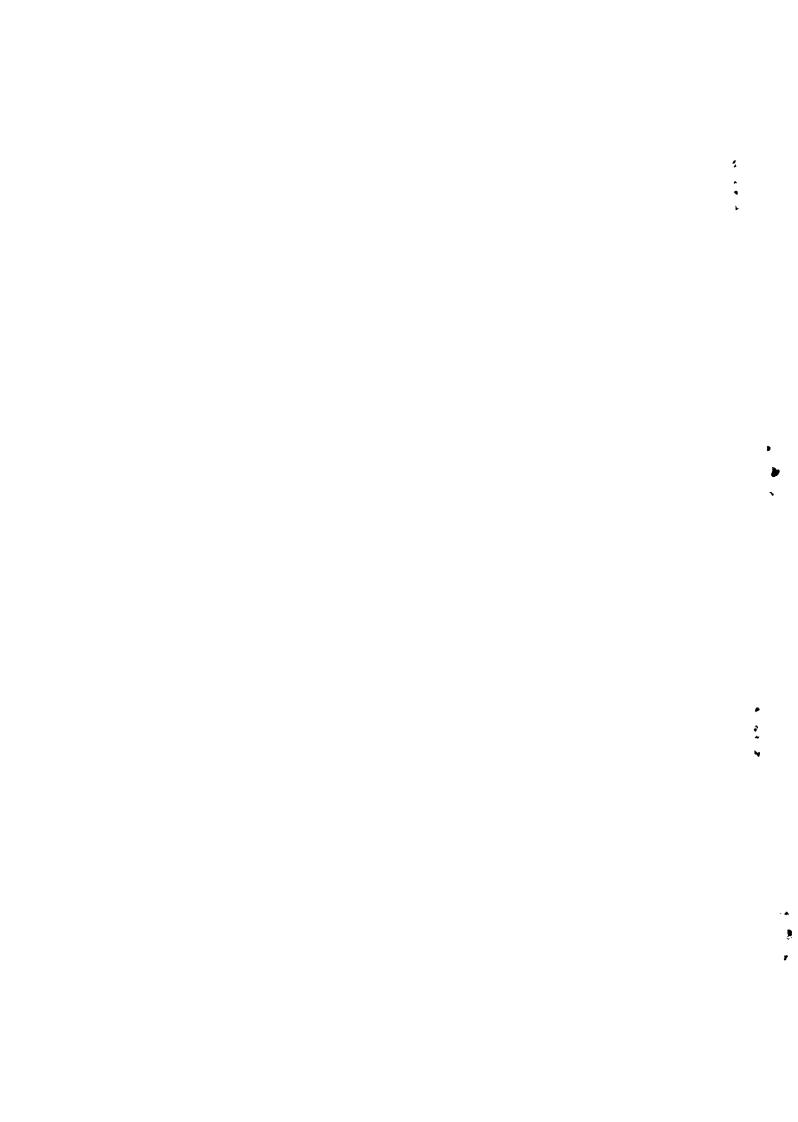


health hazard situations could develop under the proper conditions.

## Hazardous Aspects

The high concentrations of metals, particularly lead, in the sediment and fish requires the acknowledgement of health hazard aspects of the problem. Lead and fish flesh approach the environmental alert levels (3 to 5 ppm or micrograms per gram wet weight) proposed, but not accepted, in the 1971 Shellfish Sanitation Workshop. (10)

Hardy, et al. (11) and Browder et al. (12) found a maximum amount of lead that could be safely consumed in food is 400 to 500 micrograms per day or about 5 micrograms per kilogram body weight. Hardy also notes that protein tends to minimize toxicity of lead. However, Trieff (personal communications) considers the toxic level to be 100 to 300 micrograms per day absorbed lead. Taking Trieff's calculations and applying them to a 100 gram portion of fish flesh per day with the average concentration of 4.06 micrograms per gram, the absorbed lead would be 20 to 40 micrograms per day. A 200 gram sample would double the amount of absorbed lead. He points out that 100 to 300 micrograms per day figure is for absorbed lead from all sources including food Thus, other known sources of lead absorption could consumption. significantly reduce the amount of lead in food which could be safely consumed.



The Wisconsin study states that the Canadian Food and Drug Directoriate has set a 10 ppm standard for lead in marine and fresh water animal products. Dr. Sandi of the Directoriate was contacted and he confirmed that 10 ppm is the current regulation. However, he stated that the regulation is "quite unrealistic" and is currently being revised to a lower level.

California Water Quality Criteria states that total lead consumption in excess of 0.6 mg per day may cause dangerous accumulations of lead and that daily ingestion of 0.1 mg per day of lead over a period of years has resulted in lead poisoning.

The data from this study clearly indicates the levels of lead in fish flesh are sufficient for environmental concern in some areas of the Schuylkill River. However, insufficient data exists to clearly define a health hazard. A distinct health hazard does not appear to exist at this time.

The data suggests significant effect of the oil spill in regard to lead concentration in fish.

