PHASE II FINAL REPORT
REMEDIAL INVESTIGATION

TASK 7 HAZARD ASSESSMENT

ALLIED CHEMICAL/
IRONTON COKE SITE
IRONTON, OHIO

ALLIED CORPORATION
MORRISTOWN,
NEW JERSEY

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1.0 EXECUTIVE SUMMARY

This analysis was undertaken to estimate the human health risk from exposure to potentially toxic chemicals found at the Ironton Coke Plant Site. The analysis was done by studying each chemical individually, because detailed toxicological data are not available for mixtures found at the Site. Since the route of human exposure to these chemicals would be primarily *via* drinking water, the analysis focuses on: identification of chemicals potentially found in drinking water and of their sources; reported health effects of exposure to these chemicals at various levels; and estimates of potential health risk based on the best available data. Chemical concentration data for the water supply and its sources were provided by IT Corporation. Data from the Dayton Malleable well system were not included in this assessment, however, additional analysis using this information will be provided if desired.

The compounds of most concern in assessing health risk from exposure *via* drinking wate were identified as: cyanide; benzene and its congeners; heavy metals; and polynuclear aromatic hydrocarbons (PAHs). Cyanide levels predicted for the drinking water sources result in a daily intake less than that determined acceptable by the EPA, so they are no considered a significant health risk. Benzene was not detected in water samples above t detection limit of the analytical method. Using the detection limit as a worst-case scenario, the estimated increased leukemia rate associated with exposure to benzene wo contribute little to the overall estimated rate for the U.S. A comparison of the metals found at the Ironton Coke Plant Site with their acceptable drinking water levels, as established by EPA and WHO, indicates no health hazard. The health risk associated PAH exposure is uncertain, primarily because of the insensitive method of detection compared to the biological potency. The risk appears minimal, but it can not be quantified, despite use of the best available EPA approved techniques.

Though the primary concern is exposure *via* drinking water, a large volume of poten toxic waste is located at the Ironton Coke Plant Site. The present physical state of t waste products has reduced their toxicity, and the health risk associated with exposi these wastes at the present site is less than that associated with their relocation.

2.0 INTRODUCTION TO HEALTH RISK ANALYSIS

2.1 STATEMENT OF THE PROBLEM

The Ironton Coke Plant Site, like most other Superfund sites, handled a broad mixture of potentially toxic chemicals. The Site is composed of several sources of contamination which are not uniformly distributed. To complete Phase II of the remedial analysis of the Ironton Coke Plant Site, an environmental and human health risk analysis of the Site has been developed and is presented here.

2.2 TOXICOLOGICAL PRINCIPLES UTILIZED

Historically, toxicologists have attempted to reduce the variables in their experiments by studying pure compounds and not mixtures. Experiments have rarely been conducted on mixtures of two compounds, and most of these studies have been conducted with the pric knowledge that the two chemicals are likely to interact with each other through some common pathway of metabolism. Few experiments have attempted to measure the toxici of mixtures of more than two compounds, since the experiment becomes unwieldy. Consequently, very little is known about the toxicity of complex mixtures such as those present at the Ironton Coke Plant Site. Fortunately, much of the toxicity of the mixtur can be explained by an examination of the chemicals constituting the mixture on a chemical-by-chemical basis. This analysis undertakes such an approach. The literatur the compounds known to be present at the Ironton Coke Plant Site indicates that interactions between the chemicals are not likely to produce potentiation or antagonis The environmental and health risks were determined for the Site as a whole using the loading assumptions calculated by IT for the receptor water supplies, Ice Creek, the O River, and Coal Grove Municipal Water Field.

2.3 OBJECTIVE OF THE ANALYSIS

The primary objective of this analysis is to estimate the human health risks from dr water obtained near the Ironton Coke Plant Site. Because the Site is now inactive, from the manufacturing process is not available to disperse wastes into the air. In addition, because of the physical state of the wastes, contaminants are not easily transported by air from the Site to distant places of habitation or to areas of food production. As detailed below, the most hazardous materials present at the Site a likely to be bioconcentrated or reach humans through food chains. Physical conta

wastes is also limited, since the Site is secured. These considerations place drinking
:er as the primary vehicle for human exposures.

e environmental risk analysis focuses on Ice Creek and the Site's impact on the biota of
: Creek. The lack of effects of the Site on the Ice Creek biota is used to support the
nclusions of the human health risk analysis. A brief discussion of the potential health
fects of ingestion of Ice Creek fish is also provided.

3.0 IDENTIFICATION OF COMPOSITE LIST CHEMICALS AND THEIR SITES

The composite lists of chemicals for the different areas of the Ironton Coke Plant Site are based on water solubility, chemical analyses reported in both Phase I and Phase II investigations, as well as on data obtained prior to the Site Remedial Investigation/Feasibility Study. Five parameters were selected by D'Appolonia as indicators of tar and coke plant-related contaminants, based on their prevalence in process and waste materials, their water solubility, and their recurrence in historical Site groundwater quality data (D'Appolonia, 1984). Ammonia, chloride, and cyanide were selected as indicators of inorganic compounds; phenolics as an indicator of acid extractable organic compounds; benzene as an indicator of volatile organic compounds; and naphthalene as an indicator of base neutral compounds. While these indicator parameters were useful in identifying different classes of compounds, a more complete analysis of specific compounds within these classes is necessary for evaluating health risks. Of the coal tar chemicals and wastes, the compounds of most concern in estimatir health risks are benzene and its congeners, polynuclear aromatic hydrocarbons (PAHs), heavy metals, and cyanide. These compounds were selected because of their known or potential carcinogenicity and acute/chronic toxicity. The composite lists contain those chemicals within these groups that were detected in soil, sediment, or water samples ar include those chemicals that were present, but below the methods detection limit (BMI

3.1 LAGOON AREA

In the early 1970s, a series of lagoons were constructed on the east side of the Ironto Coke Plant Site for treatment of coke plant process wastewater. These wastes includ process wastewater, coke and coal fines, tar decanter sludge, boiler ash, quench wate plant storm water runoff. Process and storm water were discharged to lagoons 1, 2, 4, and tar decanter sludge was deposited in lagoon 5 (solid waste lagoon). Lagoons and 4 are separated and enclosed by a series of dikes. However, because of numerc changes in the waste process streams between 1970 and 1973, all of the lagoons rec portions of all the process streams over their history. Chemical analyses performec show that essentially the same contaminants are present in lagoons 1, 2, 3, and 4, a concentrations may vary. Lagoon 5 is unique in that it is a solid waste landfill ar received waste material which was subsequently covered with fill.

iminary analyses of the chemicals reported by IT to be present in the lagoons suggest t only lagoon 5 is of sufficiently different composition to consider it as an ependent mixture of materials. While heterogeneities clearly exist in the lagoons for cific chemicals, a composite analysis is acceptable for health risk analysis because all the reported chemicals occur to some extent throughout the lagoons. IT also proposes consider the lagoons as a single source for hydrogeological purposes. These factors mbine to justify the selection of a single composite listing for all of the lagoon samples. ecause IT has reported a range of concentrations present in lagoon samples, such a range f exposure concentrations is also presented in these analyses.

Throughout the history of the plant, ammonia, phenolics, and cyanide-containing wastes have been deposited in the area currently occupied by the coke plant lagoon system. Based on cyanide, naphthalene, phenolic compounds, and arsenic content, the ammonia still lime sludge deposited in lagoons 1 and 3 is a listed hazardous waste. The tar decanter sludge deposited in lagoon 5 is also a listed hazardous waste based on phenol and naphthalene contents (D'Appolonia, 1984).

A composite list of chemicals for the lagoon area is shown in Table 3.1. This list contains only those chemicals detected in water or solid samples from lagoons 1, 2, 3, 4, or 5. Because lagoon 5 (tar pit) contains tar decanter sludge wastes and other solid wastes, it is the major source of organic chemicals in the lagoon area.

ICE CREEK

Ice Creek is a backwater of the Ohio River in the area along the outer lagoon embankment. From approximately 1920 through the late 1960s, the coke plant discharged wastewater and solid wastes directly into Ice Creek. Many of the compounds associated with these discharges were found in samples of the Creek borings in Phase II studies. In 1961, the Greenup lock and dam was completed, raising the Ohio River elevation and creating a broad backwater condition of sluggish shallow water in Ice Creek. After construction of a lagoon system (prior to December 1979), Ice Creek received: the overflow from lagoon 1 (wastes contained phenolics, ammonia, and cyanide), overflow from the "ash pit", and overflow from the No. 2 quench station settling basin. Discharge from the main sewer was also diverted into Ice Creek. This stream was composed of most of the plant cooling water and the major part of the Armco gas cooler water, and it contained cyanide, phenolics, and ammonia.

TABLE 3.1

COMPOSITE LIST OF CHEMICALS IN LAGOON SEDIMENTS

Compound	CAS No.	Range of Reported Values (mg/kg)
BENZENE and CONGENERS		
Benzene	71-43-2	<0.01 - 940
Styrene	100-42-5	<0.01 - 4.9
Toluene	108-88-3	<0.01 - 260
o-Xylene	95-47-6	<0.01 - 1.3
POLYCYCLIC AROMATIC HYDROCARBONS		
Acenaphthene	83-32-9	<1 - 850
Acenaphthylene	208-96-8	<1 - 2500
Anthracene	120-12-7	<1 - 13000
Benzo(a)anthracene	56-55-3	<1 - <7300
Benzo(a)pyrene	50-32-8	<1 - 8800
3,4-Benzofluoranthene	205-99-2	<1 - <4000
Benzo(g,h,i)perylene	191-24-2	<1 - 2000
Benzo(k)fluoranthene	207-08-9	<1 - <4000
Chrysene	218-01-9	<1 - <7300
Dibenzo(a,h)anthracene	53-70-3	<1 - 600
Fluoranthene	206-44-0	<1 - 6700
Fluorene	86-73-7	<1 - 3900
Indeno(1,2,3-c,d)pyrene	193-39-5	<1 - 1300
2-Methylnaphthalene	91-57-6	<1 - 3300
Naphthalene	91-20-3	<1 - 32000
Phenanthrene	85-01-8	<1 - 13000
Pyrene	129-00-0	<1 - 3500
Dibenzofuran	132-64-9	<1 - 3400
4-Methylphenol	106-44-5	<1 - 200
LOW MOLECULAR WEIGHT COMPOUNDS		
Cyanide	57-12-5	76 - 3300
Ammonia	7664-4-41-7	20 - 190
METALS		
Arsenic	7440-38-2	4.1 - 56
Barium	7440-39-3	1.2 - 430
Chromium	7440-47-3	12 - 76
Cadmium	7440-43-9	<0.04 - 16
Lead	7439-92-1	0.32 - 19
Mercury	7439-97-6	0.15 - 6.6
Selenium	7782-49-2	<0.1 - 8.4
Silver	7440-22-4	1.1 - 68
Vanadium	7440-62-2	<0.01 - 39

December 1970, the No. 2 quench station and the main sewer discharges were combined to form a single stream to Ice Creek. The chemical composition of the main sewer stream did not change significantly with the addition of the quench water. In May 1971, lagoon 3 was constructed to receive wastes from the ash pit. Lagoon 3 was also constructed and received wastes from lagoons 1 and 2. At this time, both the main sewer and lagoon 3 were discharged into Ice Creek. During December 1971, lagoon 4 was added to the system to receive the main sewer discharge. Discharge to Ice Creek during this time was only from lagoon 3. Early in July 1972, a fixed ammonia recovery system was activated, resulting in a decrease in the ammonia concentration in lagoon 1 effluent. Lagoons 1 and 2 were drained in September 1972 to facilitate construction of the lagoon walls. During this time the main sewer was discharged directly into Ice Creek. By February 1973, all lagoons had been returned to service, and the contaminant concentrations in lagoon 3 effluent into Ice Creek decreased.

In January 1976, a leak was observed at the base of the outer dike of lagoon 4. When tested in March 1976, and again in May 1976, no evidence of leakage into Ice Creek was found. However, percolation of water at the base of the lagoon walls along the bank of Ice Creek was evident and most easily observed when the creek level was low (D'Appolonia, 1984).

The lagoon wastewater treatment system was shut down in 1982. When the lagoon system was in operation, it efficiently removed most contaminants from the waste streams before discharge into Ice Creek. Cyanide and phenol were 98% and 96% removed, respectively, however only 36.4% of the ammonia was removed (D'Appolonia, 1984).

Ice Creek water and sediment samples were analyzed to determine the impact of past coke plant operations. These samples were analyzed for ammonia, chloride, cyanide, phenolics, sulfate, naphthalene, and benzene. Acid-extractable and base-neutral organics were also analyzed in Ice Creek sediments (see Addendum). Table 3.2 lists compounds detected in Ice Creek sediment. Materials listed at below method detection limits are included.

Chloroform was detected at several borings, however, the absence of chlorinated organic compounds at the Site suggests an off-site source. This same rationalization holds for phthalate compounds found in various samples in Ice Creek.

TABLE 3.2

COMPOSITE LIST OF CHEMICALS IN ICE CREEK SEDIMENTS

Compound	CAS No.	Range of Reported Values (mg/kg)
BENZENE and CONGENERS		
Ethylbenzene	100-41-4	<0.001 - 0.0013
Toluene	108-88-3	<0.001 - 0.0058
POLYCYCLIC AROMATIC HYDROCARBONS		
Acenaphthene	83-32-9	<0.33 - 154
Anthracene	120-12-7	<0.33 - 9.26
Benzo(a)anthracene	56-55-3	<0.33 - 57.7
Benzo(a)pyrene	50-32-8	<0.33 - 49.9
Benzo(b)fluoranthene	205-99-2	<0.33 - 44.7
Benzo(g,h,i)perylene	191-24-2	<0.33 - 39.0
Benzo(k)fluoranthene	207-08-9	<0.33 - 43.6
Chrysene	218-01-9	<0.33 - 44.2
Dibenzo(a,h)anthracene	53-70-3	<0.33 - 57.1
Fluorene	86-73-7	<0.33 - 9.66
Indeno(1,2,3-c,d)pyrene	193-39-5	<0.33 - 31.9
Naphthalene	91-20-3	<0.33 - 92.5
Phenanthrene	85-01-8	<0.33 - 38.7
Pyrene	129-00-0	<0.33 - 43.5
LOW MOLECULAR WEIGHT COMPOUNDS		
Cyanide	57-12-5	<0.5 - 110
Ammonia	7664-41-7	<1.0 - 770
METALS		
Arsenic	7440-38-2	0.0087 - 49
Cadmium	7440-43-9	0.00028 - 0.37
Chromium	7440-47-3	0.025- 48
Iron	7439-89-6	0.23- 24000
Manganese	7439-96-5	0.4 - 360
Lead	7439-92-1	0.018- 3.4

COAL GROVE MUNICIPAL WELLS

.e Coal Grove municipal water wells are located south of the Ironton Coke Plant Site. ıe wells are bound on one side by the Ohio River and are separated from the Ironton)ke Plant Site on another side by Ice Creek. Computer simulations (IT, 1985) indicated .at approximately 30% of the water pumped at Coal Grove is derived from Ice Creek :7%) and groundwater underflow from the Site (3%). The flow balance indicates that pproximately 41% of the water pumped at Coal Grove is derived from southeast of the vell fields, and 29% is from the Ohio River. Chemical constituents are thought to nigrate from the Site to the Coal Grove wells primarily *via* discharge to Ice Creek surface vater and by mass transport in groundwater flowing beneath Ice Creek (IT, 1985).

Results of mass loading calculations for the Coal Grove wells indicate that leakage from Ice_ .eek and groundwater underflow from the Ironton Coke Plant Site may contribute up to 40 mg/L chloride and 0.2 mg/L ammonia to water pumped at the Coal Grove well field. The mass loadings of chloride and ammonia are likely to be a result of leakage from Ice Creek, with contributions both from the Site and from sewage discharges. The composite list of chemicals found in solid samples and a list of metals detected in the groundwater near the Coal Grove municipal wells are shown in Table 3.3. Volatile organic priority and nonpriority compounds were not detected in water samples obtained from the Coal Grove municipal wells or from areas around the Coal Grove municipal wells.

3 4 GOLDCAMP DUMP

_.e Goldcamp dump is located adjacent to the tar plant on the northwest side of the Ironton Site and was used for disposal of tar plant process chemical wastes from 1945 to 1977. During this time, the dump received wastes from: the tar plant (wastes included anthracene residue, anthracene salts, phthalic anhydride residue, and miscellaneous coal tar processing wastes), foundry sand from the Dayton Malleable Iron Co. (wastes thought to contain heavy metals, phenolics, and oils), and wastes disposed by the Goldcamp Gravel Company. The distillation bottoms from the production of phthalic anhydride from naphthalene are a listed hazardous waste based on phthalic anhydride and 1,4-naphthoquinone content.

TABLE 3.3

COMPOSITE LIST OF CHEMICALS AROUND COAL GROVE WELLS

BENZENE and CONGENERS Compound	CAS No.	Range of Reported Values (mg/kg)
Benzene	71-43-2	nd - <0.01
o-Xylene	95-47-6	nd - <0.01
LOW MOLECULAR WEIGHT COMPOUNDS		
Ammonia	766-4-41-7	<0.05 - 2.2
Cyanide	57-12-5	nd - <0.02
Methylene chloride	75-09-2	nd - <0.01
METALS - Coal Grove Groundwater		Range of Reported Values (mg/L)
Aluminum	7429-90-5	0.03 - 0.57
Antimony	7440-36-0	0.002 - <0.01
Arsenic	7440-38-2	nd - 0.001
Barium	7440-39-3	0.05 - 0.38
Berylium	7440-41-7	nd - 0.01
Boron	7440-42-8	<0.1 - 0.68
Cadmium	7440-43-9	0.001 - 0.008
Chromium	7440-47-3	0.005 - 0.076
Cobalt	7440-48-4	0.06 - 0.15
Copper	7440-50-8	0.02 - 0.08
Iron	7439-89-6	0.02 - 1.3
Lead	7439-92-1	0.02 - 0.98
Manganese	7439-96-5	0.16 - 2.2
Mercury	7439-97-6	0.0002 - 0.0014
Nickel	7440-02-0	0.01 - 0.19
Selenium	7782-49-2	0.001 - 0.002
Silver	7440-22-4	0.001 - 0.009
Thallium	7440-28-0	0.001 - 0.01
Tin	7440-31-5	0.2 - 0.4
Vanadium	7440-62-2	0.1 - 0.17
Zinc	7440-66-6	0.06 - 1.2

he use of the Goldcamp dump for disposal of chemical wastes was discontinued by .llied in 1977. Before closure of the dump, standing water and tar oil residues were emoved from the pond for treatment and recycling, respectively. Drums containing vastes were removed from the Site, or they were punctured and their contents stabilized with soil before sealing the dump. All drums deposited in the dump contained waste materials similar to the bulk contents of the dump.

A groundwater survey by Geraghty and Miller, Inc. (G & M) in 1978 showed that the groundwater was more than ten feet below the bottom of the dump and that the groundwater beneath the dump was contaminated. However, because the major source for the contamination was stated to be off-site, G & M recommended that the dump be covered. After removing standing water, the dump was covered with a medium-plastic cl. The filling operation began in November 1979 and was completed in August 1980 (D'Appolonia, 1984).

The tar plant wastes deposited in the Goldcamp dump were estimated to include: 5081-5531 tons of anthracene, 6104 tons of carbazole, 9959-10,359 tons of phenanthrene, 595 tons of naphthalene, 1786 tons of acenaphthylene, 3869 tons of fluorene, 3888 tons of phthalic anhydride, and 216 tons of fumaric acid (D'Appolonia, 1984). A complete analysis of solid wastes in the Goldcamp dump site for specific volatile priority and nonpriority pollutants was not reported, however, data were obtained for these compounds from borings and monitoring wells along the perimeter of the dump. A composite list of chemicals in these aqueous samples is shown in Table 3.4.

TABLE 3.4

COMPOSITE LIST OF GROUNDWATER CHEMICALS AROUND GOLDCAMP DUMP

Compound	CAS No.	Range of Reported Values (mg/L)
BENZENE and CONGENERS		
Benzene	71-43-2	0.068 - 18.0
Ethylbenzene	100-41-4	0.0052 - 1.9
Styrene	100-42-5	0.14 - 1.0
Toluene	100-88-3	0.0021 - 3.5
o-Xylene	95-47-6	0.21 - 3.2
POLYCYCLIC AROMATIC HYDROCARBONS		
Acenaphthene	83-32-9	<0.01 - 10.0
Acenaphthylene	208-96-8	nd - 0.35
Anthracene	120-12-7	<0.01 - ≤16
Benzo(a)anthracene	56-55-3	<0.01 - ≤6.7
Benzo(a)pyrene	50-32-8	0.61 - 5.6
3,4-Benzo(b)fluoranthene	205-99-2	≤0.13 - ≤3.6
Benzo(ghi)perylene	191-24-2	0.035 - 0.74
Benzo(k)fluoranthene	207-08-9	≤0.13 - ≤3.6
Chrysene	218-01-9	<0.01 - ≤6.7
Dibenzo(a,h)anthracene	53-70-3	nd - 0.22
Fluoranthene	206-44-0	<0.01 - 14
Fluorene	86-73-7	<0.01 - 7.2
Indeno(1,2,3-cd)pyrene	193-39-5	nd - 0.89
Naphthalene	91-20-3	0.026 - 13
2-Methylnaphthalene	91-57-6	0.18 - 5.8
Phenanthrene	85-01-8	<0.01 - ≤16
Pyrene	129-00-0	<0.01 - 9.8
LOW MOLECULAR WEIGHT COMPOUNDS		
Cyanide	57-12-5	<0.5 - 110 mg/kg
Ammonia	7664-41-7	<1.0 - 770 mg/kg
METALS		Range of Report Values (mg/L)
Aluminum	7429-90-5	0.2 - 0.4
Arsenic	7440-36-0	0.012 - 0.059
Barium	7440-39-3	0.21 - 1.8
Cadmium	7440-43-9	nd - 0.001
Chromium	7440-47-3	nd - 0.001
Copper	7440-50-8	nd - 0.01
Iron	7439-89-6	0.06 - 48.0
Manganese	7439-96-5	3 - 24
Mercury	7439-97-6	nd - 0.0003
Nickel	7440-02-0	0.04 - 0.08
Selenium	7782-49-2	nd - 0.001
Vanadium	7440-62-2	0.1 - 0.31
Zinc	7440-66-6	0.01 - 0.55

4.0 COMPREHENSIVE LITERATURE SURVEY OF COMPOSITE LIST

4.1 CYANIDE

Cyanides have historically been a major concern, because they are known to be highly toxic and often lethal. However, at the present time cyanides do not constitute an important or widespread environmental health problem. Previous examples of human cyanide poisoning and adverse environmental effects have involved occupational exposures or relatively localized sources of pollution. Cyanides are uncommon in U.S. water supplies and in the atmosphere.

Use of cyanide in the U.S. is increasing, and therefore, general environmental monitoring throughout the U.S. is indicated. However, certain properties of cyanide indicate that it will probably remain only a potential pollutant or one of secondary concern nationally. Cyanide has a low degree of persistence in the environment, and it is not accumulated or stored in any mammalian species that has been studied. In addition, a sizeable body of evidence suggests that cyanide has an unusually low degree of chronic toxicity. It does not appear to be mutagenic, teratogenic, or carcinogenic (U.S.E.P.A., 1980b).

Despite its widespread use, cyanide is relatively uncommon in most U.S. water supplies. survey of U.S. water supply systems in 1970 revealed no cyanide concentrations above th mandatory limit (McCabe *et al.*, 1970). In 2595 water samples, the highest cyanide concentration was 8.0 ppb (Towill *et al.*, 1978). These low levels are probably due, in pa to the high volatility of undissociated hydrogen cyanide which would be the predomina form in all but highly alkaline waters. In addition, cyanide ion would have a tendenc be "fixed" in the form of insoluble or undissociable complexes by trace metals. These undissociable cyanide complexes are considered to be biologically inactive in terms of toxicity. However, some cyanide complexes, such as nitroprusside, are readily dissocia and elicit toxic responses directly attributable to the release of cyanide *in vivo* (U.S.E. 1980b).

Cyanide generally exists in water as hydrocyanic acid (HCN), the cyanide ion, simpl cyanides, metallocyanide complexes, or simple chain and complex ring organic comp Salts such as sodium cyanide or potassium cyanide are extremely soluble in water, a resulting cyanide ions readily hydrolyze to form HCN, depending upon water tempe

pH. The cyanide ion readily combines with various heavy metal ions to form allocyanide complex ions which have a highly variable stability.

.1 Exposure from Drinking Water

anide is an uncommon pollutant in U.S. water supplies, and documented examples of vels in excess of the 1962 U.S. Public Health Service limits (U.S.P.H.S., 1962) are tremely rare. No human cases of illness or death due to cyanide in water supplies are iown. Pulse discharges of industrial wastes could result in high localized concentrations hich have escaped detection, but general recognition of the high toxicity of cyanide has iade its removal standard practice in most industries (Reed *et al.*, 1971). Fortunately, nown methods for cyanide removal are effective and relatively economical (Lawes, 1972; Vats~, 1973).

4.1.2 Dermal Exposure

Hydrogen cyanide (HCN), in either liquid or gaseous form, may be absorbed through the skin (Drinker, 1932; Potter, 1950; Tovo, 1955; Walton and Witherspoon, 1926). Absorption is probably increased if the skin is cut, abraded, or moist. Many accidents involving skin contamination also involve inhalation exposure; the contribution due to skin absorption in these cases is difficult to assess. Potter (1950) described a case in which liquid HCN ran over the bare hand of a worker wearing a fresh air respirator. Cyanide inhalation was prevented, but the worker collapsed into deep unconsciousness within five minutes, suggesting significant percutaneous absorption.

4.1.3 Inhalation Exposure

Hydrogen cyanide gas is rapidly absorbed through the lungs (Gettler and St. George, 1934). In humans, inhalation of 270 ppm HCN gas causes immediate death, while 135 ppm is lethal after 30 minutes (Dudley *et al.*, 1942). Inhalation of cyanide salt dusts is also toxic, because of the ability of cyanide to dissolve on contact with moist mucous membranes and be absorbed into the bloodstream (Davison, 1969; Knowles and Bain, 1968).

4.1.4 Metabolism

Inorganic cyanides are rapidly absorbed from the stomach and duodenum, and distributed to all organs and tissues *via* the blood. Concentrations in red blood cells are usually greater than that in the plasma by a factor of 2 to 3, presumably due to binding of

cyanide by methemoglobin (U.S.E.P.A., 1980b). Cyanide may also accumulate in other cells in the body because of binding to metalloproteins or enzymes (Smith *et al.*, 1977).

The major pathway for the metabolic detoxication of cyanide involves conversion to thiocyanate *via* the enzyme rhodanese (de Duve *et al.*, 1955), which is found in highest concentrations in the liver. Alternative minor pathways for metabolism of cyanide include nonenzymatic conjugation with cysteine (Wood and Cooley, 1956), binding by hydroxocobalamin (Brink *et al.*, 1950), or excretion unchanged as HCN *via* the lungs (Friedberg and Schwarzkopf, 1969). In rats, 80% of sodium cyanide ingested over 8 days was excreted as thiocyanate in the urine (Wood and Cooley, 1956). Cyanide does not appear to accumulate significantly in any body compartment with repeated doses or chronic exposures (U.S.E.P.A., 1980b).

4.1.5 Health Effects

The mean lethal ingested dose of cyanide in humans ranges from 1 to 3 mg/kg (U.S.E.P.A., 1980b). In nonfatal poisonings, recovery is generally rapid and complete. Despite the high lethality of large single doses of cyanide, repeated sublethal doses do not result in cumulative adverse effects. Cyanide has a high acute toxicity, but an unusually low degree of subacute or chronic toxicity (Hayes, 1967).

The toxic effects of cyanide are directly or indirectly due to inhibition of cytochrome c oxidase (Gosselin *et al.*, 1976), leading to impairment of both oxidative metabolism and oxidative phosphorylation. The result of this inhibition by cyanide is to block the utilization of oxygen by aerobic cells-a condition termed histotoxic hypoxia. Because of their high rates of oxidative metabolism, the brain and heart are the most profoundly affected tissues. Cyanide poisoning in man is characterized by flushing of the skin due to high concentrations of oxyhemoglobin in the venous blood, metabolic acidosis, and stimulation of carotid body chemoreceptors causing a marked augmentation of respirati Stimulation of chemoreceptors also causes a transient increase in blood pressure and bradycardia, followed by a fall in blood pressure to potentially fatal hypotensive level (Heymans and Neil, 1958). Another prominent effect of cyanide is on the brain stem nuclei responsible for the control of breathing, resulting in fatal arrest.

The U.S. Public Health Service (PHS) Drinking Water Standards of 1962 established 0. CN^-/L as an acceptable criterion for water supplies. In addition to defining the 0.2 n

:erion for cyanide, the PHS set forth an "objective" to achieve concentrations below 0.1 CN^-/L in water "because proper treatment will reduce cyanide levels to 0.1 mg/L or s" (U.S.P.H.S., 1962). The criterion of 0.2 mg CN^-/L (200 ug/L) allows for safety factors nging from 41 to 2100, and the data since 1962 suggest that 0.2 mg CN^-/L is a safe iterion for humans (U.S.E.P.A., 1980b).

2 BENZENE AND ITS CONGENERS

enzene is produced as a by-product of coal tar distillation, coal processing, and coal oking. It has widespread use in the chemical and drug industries as a solvent, as a onstituent of motor fuels, and as a starting material in the synthesis of many aromatic :ompounds. The major use of benzene is as an intermediate in the production of styrene, :yc! :xane, detergents, and pesticides.

Compared with the other aromatic hydrocarbons, benzene is relatively soluble in water (0.8 ppm by weight at 20°C) (N.A.S., 1977). In the National Organic Monitoring Survey, conducted from March 1976 through January 1977, benzene analyses were performed on three samplings from community water supplies. These samples were selected to be representative of various types of sources and treatment processes. The number of positive benzene analyses per number of cities sampled were 0/111, 7/113 and 4/16 (U.S.E.P.A., 1978). In four of ten water supplies surveyed by the U.S.E.P.A. (1975a,b), benzene was detected at levels between 0.1 - 0.3 ug/L. The highest concentration of benzene reported in finished water was 10 ug/L (N.A.S., 1982).

4.2.1 Exposure Routes

Because of its high volatility, the most common route of industrial exposure to benzene is by inhalation. In most studies with laboratory animals, benzene was administered as a vapor. In other studies, benzene was usually injected subcutaneously, either in pure form or mixed with a carrier. The oral route of exposure is the least investigated, and therefore limited information is available concerning the toxicity of ingested benzene (U.S.E.P.A., 1980b).

Wolf *et al.* (1956) administered 132 feedings of benzene to rats at doses of 1, 10, 50, and 100 mg/kg over 187 days. No effect was observed at the 1 mg/kg level; slight leukopenia was observed after the 10 mg/kg dose; and leukopenia and anemia were observed after the higher doses. In a later study, ingestion of liquid benzene by humans was reported to

cause local irritation of mucous membranes, followed by systemic toxicity after absorption (Gerarde, 1960). Gerarde also reported that ingestion of about 15 mL of benzene has been known to cause collapse, bronchitis, and pneumonia in humans.

4.2.2 Metabolism

The metabolism of benzene has been extensively reviewed by the U.S.E.P.A. (1979a), Rusch *et al.* (1977), Snyder and Kocsis (1975), and Snyder *et al.* (1977). Since Parke and Williams (1954) suggested that a metabolite of benzene is responsible for benzene toxicity, a considerable amount of evidence has been accumulated to support this hypothesis (Nomiyama, 1964; Andrews *et al.*, 1977; Drew and Fouts, 1974; Ikeda, 1964). Although additional data are needed to prove this hypothesis, metabolism of benzene is widely accepted as a prerequisite to its toxicity. Metabolism of benzene is similar in animals and humans (Laskin and Goldstein, 1977).

Benzene is metabolized by cytochrome P-450 monooxygenases to form the highly reactive metabolite benzene oxide. This oxide can then undergo one of several reactions which determines its toxicity. The oxide can spontaneously rearrange to form phenol, undergo enzymatic hydration followed by dehydrogenation to catechol, react enzymatically to form a glutathione conjugate, or bind covalently with cellular macromolecules. Sulfate and glucuronide conjugates are also formed (N.A.S., 1982). The specific benzene metabolites that induce leukemia and other toxicities have not yet been identified. Likely candidates include benzene oxide, catechol, and hydroquinone or the corresponding semiquinones (U.S.E.P.A., 1979b).

Regardless of the route of administration, benzene is eliminated rapidly by expiration and excretion in the urine (N.A.S., 1980). Benzene appears to be distributed in the tissues according to their fat content. Metabolites are thought to be important in the development of hematotoxicity, in part because of the effects of altered liver metabolism on leukopenia and other hematopoietic responses (N.A.S., 1980). However, the metabolic fate of benzene in the bone marrow has not been established (Snyder and Kocsis, 1975).

4.2.3 Health Effects

The toxicity of benzene has been reviewed in a number of reports (N.A.S., 1976, 1977, 1980; Snyder and Kocsis, 1975; U.S.E.P.A., 1979a). Benzene exposure is strongly implic

in several pathological conditions that may be of concern to public health at environmental exposure levels.

In humans, the toxicity to the hematopoietic system after chronic exposure is well documented. Reported effects include myelocytic anemia, thrombocytopenia, or leukopenia (occurring either independently or in cases of pancytopenia), and leukemia, particularly acute myelogenous and monocytic leukemia (N.A.S., 1980). Whether benzene causes leukemia as part of its hematotoxic effects, as a consequence of damage to immunological components of the marrow, or whether the leukemic effects are unrelated to the other hematotoxic effects is not known (Laskin and Goldstein, 1977). Humans that develop benzene-induced hematotoxic effects have a greatly increased probability of developing leukemia and aplastic anemia. These data suggest that benzene is a leukemogen in humans (N.A.S., 1980).

Carcinogencity studies by Maltoni and Scarnato (1979) and Snyder *et al.* (1980) demonstrated a positive tumorigenic effect of benzene in rodents. Toxic effects of benzene on bone marrow cells of laboratory animals include changes in chromosome number and chromosome breakage similar to that observed in humans. In tests for mutagenicity, benzene was uniformly negative in the Ames test (Lyon, 1975). Some studies have reported teratogenic effects (Watanabe and Yoshiba, 1970; Gofmekler, 1968). An analysis of the quantitative leukemia risk from benzene exposure is presented in Chapter 7.

4.3 METALS

The metals found in the Ironton Coke Plant Site are listed in Table 4.1. Certain of these metals are essential for life, while others are not. Some metals have no known biologic function and are not associated with serious toxic hazard. The metals which are essential nutrients may exert toxic action if the homeostatic mechanism maintaining them within physiologic limits is unbalanced.

The setting of safe levels of metal exposure must take into consideration various routes of exposure. For example, skin absorption of alkyl lead and thallium compounds can lead to intoxication by these metals. The potential for bioconcentration of metals released to the environment must be considered. Concentrations of aluminum, vanadium, chromium, tin, lead, and cadmium in the lung increase until about age 40.

The toxicity of metals does not occur from interaction of biologic systems with the elemental form. Metals occur as discrete compounds, and their ability to cross biologic membranes varies with the compound constituency. Soluble metal salts dissociate readily in the aqueous environment of biologic membranes, thereby facilitating their transport as metal ions. Insoluble metal salts are relatively poorly absorbed, and anything affecting the solubility of metals can affect their intestinal absorption. Foods have a high capacity for binding metal which results in reduced metal absorption in the gut. Thus, absorption of metals is much greater when ingestion occurs during a period of fasting than during a postprandial period.

Metals may exist in the environment as alkyl compounds (metal bound to carbon). Such alkyl compounds remain intact in the biologic environment, because they are lipid soluble and cross the biologic membrane unaltered. Methyl mercury and tetraethyl lead are such alkyl compounds. Their toxicological properties are quite different from the inorganic forms of these metals. Most toxicologically important metals bind strongly to tissues and, therefore, are only slowly excreted. Consequently, with continuing intake they tend to accumulate to a high degree.

Drinking water criteria and standards for the metals found at the Ironton Coke Plant Site are listed below in Table 4.1. Because some metals in food and drinking water have a low toxicity, the establishing of nationwide limits for them is unnecessary. Thus, the United States Environmental Protection Agency National Interim Primary Drinking Water Standards and WHO European standards do not include all metals.

Some apparent elevations in the Coal Grove well water supplies were found. Chromium concentrations were below the established limit with one exception (0.076 mg/L) which approximated the limit (0.05 mg/L). The elevated level of iron in the Coal Grove wells (0.02-1.3 mg/L) is not expected to produce any untoward effects, assuming normal physiological function of the consuming population. The elevation in lead (0.98 mg/L) that occurred was present only once in one well (CG-3) as tested in May 1984. The surrounding wells had nontoxic lead levels, and the CG-3 well tested normally in June of 1984. This single aberration in lead content of CG-3 should be resolved by further testing. The manganese elevations (0.16-2.2 mg/L) in the Coal Grove wells are expected to result in only undersirable taste and color of the water from these wells and should not present a health hazard. Chronic toxicity from elevated manganese levels in drinking

TABLE 4.1

DRINKING WATER CRITERIA AND STANDARDS FOR METALS

	Standard (mg/L)	Reference
tal	35[a]	N.A.S., 1977
uminum	0.145	U.S.E.P.A., 1980a
timony	0.05	Code of Federal Regulations, 1984[e]
senic	1.0	Code of Federal Regulations, 1984[e]
rium	0.011	U.S.E.P.A., 1980d
eryllium	5.0[b]	U.S.P.H.S., 1970
oron	0.01	Code of Federal Regulations, 1984[e]
admium	0.05	N.A.S., 1977
hromium	0.632	U.S.E.P.A., 1980d
obalt	1[c]	N.A.S., 1977
opper	0.3[d]	U.S.P.H.S., 1970
on	0.05	Code of Federal Regulations, 1984[e]
ead	0.05	U.S.E.P.A., 1980d
Man ese	0.002	Code of Federal Regulations, 1984[e]
Mercury	0.632	U.S.E.P.A., 1980e
Nickel	0.01	Code of Federal Regulations, 1984[e]
Selenium	0.05	Code of Federal Regulations, 1984[e]
Silver	0.013	U.S.E.P.A., 1980f
Thallium	None	N.A.S., 1977
Tin	None	N.A.S., 1977
Vanadium	5	U.S.E.P.A., 1980g
Zinc		

a 24 hr Suggested No Adverse Response Level (SNARL)

b Mandatory upper limit

c Secondary interim standard

d Desirable upper limit

e Summary drawn from various United States Environmental Protection Agency criteria documents

water has never been reported. In conclusion, a comparison of the standards from Table 4.1 with the levels of metals found in the Coal Grove Municipal Well groundwater (Table 3.3) indicates that the levels reported are nontoxic and present no hazard to the surrounding population.

4.4 POLYNUCLEAR AROMATIC HYDROCARBONS (PAHS)

PAHs are a major component of environmental pollutants (Shabad, 1967; Hangebrauck *et al.*, 1964; Committee on Biological Effects of Atmospheric Pollutants, 1972). Many of the current combustion processes and certain industrial processes (e.g., power production, coal carbonization, and petroleum refining) have led to the widespread presence of PAHs in industrial and ambient atmospheres (Sawicki *et al.*, 1962). Human exposure to PAHs occurs primarily through the smoking of tobacco, inhalation of polluted air, and ingestion of food and water contaminated by combustion effluents (IARC, 1983). The following section lists PAHs and their toxicities relevant to the surroundings of the Ironton Coke Plant.

4.4.1 PAHs and Their Relevant Toxicities

4.4.1.1 Benz[a]anthracene

The available data on reproductive toxicity and teratogenicity are inadequate for evaluation. Benz[a]anthracene was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (McCann *et al.*, 1975) and was mutagenic to *Drosophila melanogaster* (Fahmy and Fahmy, 1973); it was also mutagenic to mammalian cells *in vitro* in the presence of an exogenous metabolic system (Slaga *et al.*, 1978). This compound was positive in one study of sister chromatid exchange (Pal, 1981). It induced unscheduled DNA synthesis in cultured mammalian cells and morphological transformation (Probst *et al.*, 1981). In one *in vivo* study, it induced sister chromatid exchange in hamsters (Roszinsky-Kocher *et al.*, 1979); reports for *in vivo* studies on the induction of chromosomal aberrations were conflicting (Sugiyama, 1973; Peter *et al.*, 1979). Sufficien evidence is available to indicate that benz[a]anthracene is active in short-term tests. Benz[a]anthracene is also carcinogenic to mice by skin painting (Bingham and Falk, 196 oral administration (Klein, 1963), and subcutaneous administration (Steiner and Edgcon 1952).

4.4.1.2 Benzo[b]fluoranthene

No data on the teratogenicity of benzo[b]fluoranthene are available. This compound is mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (Mossanda *et al.*, 1979). In one available study, it was reported to induce sister chromatid exchange but not chromosomal aberrations in bone-marrow cells of hamsters treated *in vivo* (Roszinsky-Kocher *et al.*, 1979). Inadequate evidence is available to indicate that benzo[b]fluoranthene is active in short-term tests. Sufficient evidence is available to indicate that benzo[b]fluoranthene given by skin (Wynder and Hoffman, 1959) or subcutaneous (Lacassagne *et al.*, 1963) administration to mice is carcinogenic.

4.4.1.3 Benzo[k]fluoranthene

Benzo[k]fluoranthene was tested for carcinogenicity in females of two strains of mice by skin application and produced a few skin tumors (Wynder and Hoffman, 1959). It was also tested in a mouse-skin initiation-promotion assay and was active as an initiator (LaVoie *et al.*, 1982). In one experiment involving subcutaneous injection of benzo[k]fluoranthene to mice, it produced sarcomas of the lung in rats in a dose-related manner following its direct injection into pulmonary tissue (Lacassagne *et al.*, 1963). No data on the teratogenicity of this compound are available. Benzo[k]fluoranthene was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (LaVoie *et al.*, 1980). Inadequate evidence is available to indicate that benzo[k]fluoranthene is active in short-term tests. Sufficient evidence is available to indicate that benzo[k]fluoranthene is carcinogenic to experimental animals (LaVoie *et al.*, 1982; Lacassagne *et al.*, 1963).

4.4.1.4 Benzo[a]pyrene

The LD_{50} (i.p.) for benzo[a]pyrene (BaP) in the mouse is 250 mg/kg body weight (Salamone, 1981). BaP is embryotoxic and teratogenic in mice; the inducibility of aryl hydrocarbon hydroxylase activity in dams and fetuses is an important factor in determining these effects (Shum *et al.*, 1979). A reduction in fertility in both male and female offspring was observed in mice following exposure to BaP *in utero* (MacKenzie and Angevine, 1981). BaP undergoes metabolism to reactive electrophiles capable of binding covalently to DNA (Lutz, 1979). It was active in assays for bacterial DNA repair, bacteriophage induction, and bacterial mutation; mutation in *Drosophila melanogaster*; DNA binding, DNA repair, sister chromatid exchange, chromosomal aberrations, point mutation, and transformation in mammalian cells in culture; and tests in mammals *in vivo*.

including DNA binding, sister chromatid exchange, chromosomal aberration, sperm abnormality, and the somatic specific locus test (Hollstein *et al.*, 1979; de Serres and Ashby, 1981). Sufficient evidence is available to indicate that BaP is active in short-term tests and that BaP is carcinogenic to experimental animals; it produces tumors after oral administration to mice (Neal and Rigdon, 1967), rats (Gibel, 1964), and hamsters (Dontenwill and Mohr, 1962) and after skin application to mice (Wynder *et al.*, 1957; Poel, 1963), rats (Nakano, 1937), and rabbits (Wynder *et al.*, 1957). Lung tumors were produced after exposure of rats (Laskin *et al.*, 1970) and hamsters (Mohr, 1971) to BaP by inhalation. Subcutaneous carcinogenicity of BaP has been shown in mice (Shubik and Hartwell, 1957) and rats (Oberling *et al.*, 1939). Intraperitoneal injection of BaP also produced tumors in rats and mice (Payne, 1958).

4.4.1.5 Chrysene

The LD_{50} (i.p.) for chrysene is >320 mg/kg body weight for the mouse (Simmon *et al.*, 1979). Chrysene was tested for carcinogenicity in several studies by skin application to mice and produced skin tumors (Barry *et al.*, 1935; Schurch and Winterstein, 1935; Riegel *et al.*, 1951); in one study, an enhancing effect was observed when chrysene was tested simultaneously with n-dodecane (Bingham and Falk, 1969). Chrysene was also tested in the mouse-skin initiation-promotion assay and was active as an initiator (Van Duuren *et al.*, 1966). Local tumors were observed following its subcutaneous injection in mice (Steiner, 1955). Perinatal administration of chrysene to mice by subcutaneous or intraperitoneal injection increased the incidences of liver tumors (Grover *et al.*, 1975). No relevant data on the teratogenicity of this chemical are available. Chrysene was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (McCann *et al.*, 1975). Chrysene did not induce mitotic recombination in yeast, unscheduled DNA synthesis in primary rat hepatocytes (Tong *et al.*, 1981), or mutations in Chinese hamster V79 cells (Huberman and Sachs, 1976). However, in one study each in mice and hamsters, it induced sister chromatid exchange and chromosomal aberrations, respectively (Roszinsky-Kocher *et al.*, 1979; Basler *et al.*, 1977). Chrysene was positive in one of two reported studies of morphological transformation in mammalian cells (Pienta *et al.*, 1977; Marquardt *et al.*, 1972). Limited evidence is available to indicate that chrysene is active in short-term tests and that chrysene is carcinogenic to experimental animals (Barry *et al.*, 1935; Steiner, 1955; Grover *et al.*, 1975).

4.4.1.6 Dibenz[a,h]anthracene

Dibenz[a,h]anthracene is embryotoxic to rats when given at high doses (Wolfe and Bryan, 1939). The available data on teratogenicity are inadequate for evaluation. Dibenz[a,h]anthracene was positive in differential survival assays using DNA-repair-proficient/-deficient strains of bacteria (Ichinotsubo *et al.*, 1977) and was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (McCann *et al.*, 1975). In cultured mammalian cells, dibenz[a,h]anthracene was mutagenic (Huberman and Sachs, 1976) and induced unscheduled DNA synthesis in the presence of an exogenous metabolic system (Lake *et al.*, 1978). It was positive in assays for morphological transformation (DiPaolo *et al.*, 1969). In the one available study, it induced sister chromatid exchange but not chromosomal aberrations *in vivo* (Roszinsky-Kocher *et al.*, 1979). Sufficient evidence is available to indicate that dibenz[a,h]anthracene is active in short-term tests and that dibenz[a,h]anthracene is carcinogenic to mice when given orally (Snell and Stewart, 1962), by skin application (Van Duuren *et al.*, 1967), and by intramuscular injection (Bryan and Shimkin, 1943).

4.4.1.7 Indeno[1,2,3-cd]pyrene

Indeno[1,2,3-cd]pyrene was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (LaVoie *et al.*, 1979). Inadequate evidence is available to indicate that indeno[1,2,3-cd]pyrene is active in short-term tests. Sufficient evidence is available to indicate that indeno[1,2,3-cd]pyrene is carcinogenic in mice by skin application (Hoffman and Wynder, 1966) and subcutaneous administration (Lascassagne *et al.*, 1963).

4.4.1.8 Benzo[ghi]perylene

Benzo[ghi]perylene was tested for carcinogenicity in two studies by skin application to female mice, and no carcinogenic effect was observed (Lijinsky and Saffiotti, 1965; Hoffman and Wynder, 1966). It was tested in three studies in the mouse-skin initiation-promotion assay, also with negative results (Hoffman and Wynder, 1966). In two studies using mice, subcutaneous injection caused no observable tumor at the injection site (Muller, 1968). The results of a test using intrapulmonary injection in rats are inadequate for evaluation, although some pulmonary tumors occurred. When benzo[ghi]perylene was administered simultaneously with benzo[a]pyrene to the skin of mice, an increased number of skin tumors was observed over that with benzo[a]pyrene alone (Deutsch-Wenzel *et al.*, 1983). No data on teratogenicity of this compound are available. Benzo[ghi]perylene was

mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (Andrews *et al.*, 1978). It was negative in one study of morphological transformation in mammalian cells (Quarles *et al.*, 1979). Inadequate evidence is available to indicate that benzo[ghi]perylene is active in short-term tests. The available data are inadequate to permit an evaluation of the carcinogenicity of benzo[ghi]perylene to experimental animals (IARC, 1983).

4.4.1.9 Fluorene

Fluorene was tested for carcinogenicity in mice by skin application (Kennaway, 1924) and by subcutaneous administration (Shear, 1938) and in female rats by oral administration in the diet (Morris *et al.*, 1960). The studies were considered inadequate for evaluation. No data are available on the teratogenicity of fluorene. Fluorene was not mutagenic to *Salmonella typhimurium* (McCann *et al.*, 1975). In the one available study, it did not induce unscheduled DNA synthesis in primary rat hepatocyte cultures (Probst *et al.*, 1981). Inadequate evidence is available to indicate that fluorene is active in short-term tests. The available data are inadequate to permit an evaluation of the carcinogenicity of fluorene to experimental animals (IARC, 1983).

4.4.1.10 Phenanthrene

The LD_{50} for the mouse (i.p.) is 700 mg/kg body weight (Simmon *et al.*, 1979). Phenanthrene was tested for carcinogenicity in two fragmentary studies in mice by skin painting, and no skin tumor was reported (Kennaway, 1924; Salaman and Roe, 1956). In the six studies in which phenanthrene was tested in the mouse-skin initiation-promotion assay, it was active as an initiator in one study (Salaman and Roe, 1956), inactive as a initiator in four others (Scribner, 1973; LaVoie *et al.*, 1981; Roe and Grant, 1964; Roe, 1962), and inactive as a promoter in one study (Wood *et al.*, 1979). Phenanthrene administered by intraperitoneal or subcutaneous injection to neonatal mice did not increase the incidence of tumors over that in controls (Grant and Roe, 1963). Experiments involving a single oral administration to rats and a single subcutaneous injection to mice were inadequate for evaluation. No data on the teratogenicity of this compound are available. Phenanthrene has generally been reported to be non-mutagenic to *Salmonella typhimurium* in the presence of a high concentration of an exogenous metabolic system (Oesch *et al.*, 1981). It gave negative results in an assay for differential survival using DNA-repair-proficient/-deficient strains of *Bacillus subtilis* (McCarroll *et al.*, 1981). It did not induce DNA repair (Lake *et al.*, 1978), chromosomal aberrations, or sister chromatid

exchange in cultured mammalian cells (Popescu *et al.*, 1977). It did induce mutation in one experiment in human cells in culture in the presence of an exogenous metabolic system (Barfknecht *et al.*, 1981), and it induced sister chromatid exchange in Chinese hamster bone-marrow cells *in vivo* (Bayer, 1978). The compound failed to induce morphological transformation (Quarles *et al.*, 1979). The available data are inadequate to permit an evaluation of the carcinogenicity of phenanthrene to experimental animals (IARC, 1983).

4.4.1.11 Anthracene

The LD_{50} for the mouse (i.p.) is greater than 430 mg/kg body weight (Salamone, 1981). Anthracene was tested for carcinogenicity in mice by skin application in several studies (Kennaway, 1924; Pollia, 1939; Wynder and Hoffman, 1959) and in the mouse-skin intiation-promotion assay in two studies (Salaman and Roe, 1956; Scribner and Suss, 1978). The results were not indicative of a carcinogenic effect or of initiating activity. It was tested in rats by oral (Schmahl, 1955), subcutaneous (Boyland and Burrows, 1935), intraperitoneal (Schmahl, 1955), and intrapulmonary administration (Stanton *et al.*, 1972); and in rabbits by implantation into the brain or eyes (Russell, 1947). The studies involving oral or intrapulmonary administration produced no evidence of carcinogenicity. The studies in rats by subcutaneous or intraperitoneal administration and in rabbits by implantation into the brain or eyes were inadequate for evaluation. When anthracene was administered by skin application to mice with exposure to ultraviolet radiation, contradictory results were obtained (Forbes *et al.*, 1976). No data on the teratogenicity of this compound are available. Anthracene was negative in an assay for differential survival using DNA repair-proficient/-deficient strains of *Bacillus subtilis* (Rosenkranz and Poirier, 1979). It induced neither mutations in bacteria (McCarroll *et al.*, 1981) or yeast (Simmon, 1979) nor unscheduled DNA synthesis of mutations in cultured mammalian cells (Williams, 1977). No cytogenetic effect in mammalian cells was observed *in vitro* or *in vivo*, and assays for morphological transformation were negative (DiPaolo *et al.*, 1973). No evidence is available to indicate that anthracene is active in short-term tests. The available data provide no evidence that anthracene is carcinogenic to experimental animals (IARC, 1983).

4.4.1.12 Fluoranthene

The LD_{50} for the rat (oral) is 2000 mg/kg body weight (Smyth *et al.*, 1962). Fluoranthene was tested for carcinogenicity by skin application to mice in two studies, and no

tumorigenic effect was observed (Wynder and Hoffman, 1959; Hoffman *et al.*, 1972). It was also tested in the mouse-skin initiation-promotion assay and was inactive as an initiator (Hoffman *et al.*, 1972). A study in mice by subcutaneous administration was considered inadequate for evaluation (Shear, 1938). When fluoranthene was administered to mice by skin application with benzo[a]pyrene (BaP), an excess of skin tumors was produced over that induced by the same dose of BaP alone (Van Duuren and Goldschmidt, 1976). No data are available on the teratogenicity of fluoranthene. Fluoranthene was mutagenic to *Salmonella typhimurium* (Hermann *et al.*, 1980) and to cultured human lymphoblastoid cells (Thilly *et al.*, 1980) in the presence of an exogenous metabolic system. Limited evidence is available to indicate that fluoranthene is active in short-term tests. The available data provide no evidence that fluoranthene *per se* is carcinogenic to experimental animals (IARC, 1983).

4.4.1.13 Pyrene

The LD_{50} for 7 days was 514 mg/kg body weight in mice injected intraperitoneally (Salamone, 1981). Pyrene was tested for carcinogenicity in several experiments by skin application to mice, and no skin tumor was observed (Badger *et al.*, 1940; Roe and Grant, 1964; Horton and Christian, 1974). It was also tested in several studies in the mouse-skin initiation-promotion assay, with inconclusive results (Salaman and Roe, 1956; Scribner and Suss, 1978). When tested on mice skin simultaneously with BaP, it enhanced the carcinogenic effects of BaP (Van Duuren and Goldschmidt, 1976). A study in mice by subcutaneous injection was inadequate for evaluation of carcinogenicity (Shear and Leiter, 1941). Intratracheal administration of pyrene to hamsters attached to haematite did not produce tumors (Sellakumar and Shubik, 1974). No data on the teratogenicity of this compound are available. Pyrene has been tested extensively in both *in vitro* and *in vivo* short-term tests. It was negative in assays for differential survival in DNA-repair-proficient/-deficient strains of bacteria (Ashby and Kilbey, 1981) and was mutagenic in some assays in *Salmonella typhimurium* in the presence of an exogenous metabolic system (Bridges *et al.*, 1981). Tests for genetic activity in yeast were negative (de Serres and Hoffman, 1981). It was not mutagenic to *Drosophila melanogaster* (Valencia and Houtchens, 1981). It did induce mutations (Jotz and Mitchel, 1981) and unscheduled DNA synthesis (Lake *et al.*, 1978) in some *in vitro* assays in mammalian cells. Pyrene did not induce morphological transformation (DiPaolo *et al.*, 1969). In tests in mammals *in vivo*, it did not induce sister chromatid exchange or micronuclei (Paika *et al.*, 1981). Limited evidence is available to indicate that pyrene is active in short-term tests. The available

data provide no evidence that pyrene *per se* is carcinogenic to experimental animals (IARC, 1983).

4.4.1.14 Naphthalene

Naphthalene is the most abundant single constituent of coal tar. Exposure to vapor or dust of naphthalene can produce corneal ulceration and cartaract formation in humans. The most significant reaction in naphthalene intoxication is a hemolytic crisis. The OSHA 8-hr. time weighted average for industrial exposure is 10 ppm (Athreya *et al.*, 1961). Inhalation of naphthalene by mice caused damage of nonciliated bronchiolar epithelial (Clara) cells. Irritation of the bladder and acute renal failure may occur with naphthalene exposure. Subcutaneous exposure of rats to naphthalene produces neoplasms (N.I.O.S.H.,1976). The minimum toxic dose known to affect reproduction of rats by subcutaneous exposure is 5925 mg/kg body weight. Oral toxicities in children (LD_{LO}, 100 mg/kg), rats (LD_{50}, 1250 mg/kg), mice (LD_{50}, 580 mg/kg), dogs (LD_{LO}, 400 mg/kg), rabbits (LD_{LO}, 3000 mg/kg), and guinea pigs (LD_{LO}, 1200 mg/kg) have been established (N.I.O.S.H., 1976). Subcutaneous exposure of rats to 3500 mg/kg was shown to be tumorigenic (N.I.O.S.H., 1976).

4.4.1.15 Acenaphthene

Acenaphthene is known to be irritating to skin and mucus membranes (N.I.O.S.H., 1976). Neoplasms have been caused experimentally by acenaphthene exposure. Acenaphthene was positive in cultured mouse fibroblast mutagenicity tests at 1 mg/L (N.I.O.S.H., 1976).

4.4.1.16 Acenaphthylene

Acenaphthylene is positive in microsomal mutagenic assays with *Salmonella typhimurium* at 1 mmol/L concentration (N.I.O.S.H., 1976).

4.4.1.17 2-Methylnaphthalene

2-Methylnaphthalene has an oral rat LD_{50} of 1630 mg/kg and an intraperitoneal mouse LD_{50} of 1000 mg/kg (N.I.O.S.H., 1976).

4.4.2 Metabolism of PAHs

In mammals, an enzyme system variously known as cytochrome P-450 dependent mixed function oxidase, mixed-function oxidase (MFO), or aryl hydrocarbon hydroxylase

initiates the metabolism of various lipophilic organic compounds including xenobiotics such as PAHs. The primary function of this enzyme system is to render poorly water-soluble lypophilic materials more water soluble and, therefore, more available for excretion. While this system sucessfully detoxifies many xenobiotics, some PAHs are transformed to intermediates which are highly toxic, mutagenic, or carcinogenic to the host. Oxidative metabolism of PAHs in this system proceeds via highly electrophilic intermediate arene oxides, some of which combine covalently to cellular macromolecules such as DNA, RNA, and protein. Rendering lipid soluble xenobiotics like PAHs more water soluble is accomplished by enzymic reactions of two types--phase I reactions involving oxidation, reduction, and hydrolysis; and phase II reactions consisting of conjugation or synthesis (Neal, 1980).

The cytochrome P-450-containing monooxygenases are the most important enzymes involved in phase I reactions. They serve to introduce oxygen atoms into many foreign compounds. This enzyme system is localized in the endoplasmic reticulum and has been found in the hepatic endoplasmic reticulum of every animal species examined so far. The cytochrome P-450-containing monooxygenases can catalyze several reactions, but aromatic hydroxylation is most important in the consideration of PAH metabolism. Aromatic hydroxylation involves the addition of oxygen across a double bond and results in the formation of an unstable epoxide which may enzymatically be converted to the corresponding *trans* dihydrodiol by epoxide hydrase (Phase I). Other subsequent steps in enzymatic biotransformation of PAHs are the formation of glutathione conjugates by glutathione S-transferase and the conversion of phenols to sulfates by sulfokinases (Phase II) (Neff, 1979).

Nonenzymatic pathways of epoxides include reaction with glutathione, solvolysis to yield diols, and isomerization to form phenols. Epoxide hydrase can direct PAH metabolism in the direction of water soluble compounds which are excreted or in the direction of active carcinogen formation. The 7,8-epoxide of benzo[a]pyrene reacts with epoxide hydrase; then its glutathione conjugate is formed, allowing it to be excreted normally. However, the diol-epoxide is also a substrate of epoxide hydrase and can be converted to an active carcinogen. The reaction which takes precedence is thought to depend upon the concentration of initial substrate and the activity of the MFO system (Bentley *et al.*, 1977). A great many endogenous and exogenous factors influence the MFO system activity. Each species seems to respond differently to these factors, as indicated by the difference in

activity across species. Intraspecific differences (probably genetic) also exist. Endogenous factors which cause these differences may include age, sex, nutritional status, and period of molt cycle in invertebrates. PAH metabolism may be affected exogenously by temperature, season, salinity, and current and previous history of exposure to potential inducers or inhibitors of different components of the microsomal PAH-metabolizing system (Neff, 1979).

4.4.3 Distribution of PAHs in the Aquatic Environment

One important factor in the metabolism of PAHs is their solubility in water. Solubilities of PAHs are quite low in general and decrease as the aromaticity increases. Apparent solubility of PAHs may be facilitated by dissolved or colloidal organic matter in natural and wastewaters. PAHs may increase solubility by incorporation into micelles. Natural waters which contain substances such as humic acids, fulvic acids, and other degradative products of biological materials may act as PAH solubilizers (Neff, 1979). In the study of the absorption of anthracene from solution by organic particles, a constant fraction (0.45) of the anthracene was found to be adsorbed over a wide range (0.02 to 31 ug anthracene/L). This study concluded that a significant fraction (0.15-0.65) of anthracene would be associated with detrital and living organic matter in natural waters containing moderate levels of suspended organic solids. Thus, the role of suspended mineral particulate material is far less significant in adsorption of PAHs than is the role of organic matter in natural waters (Herbes, 1977). An exchange equilibrium probably exists between adsorbed and soluble PAHs, but the particulate form is favored. Rivers near industrialization have been shown to have higher levels of PAHs than rivers remote from human activity which are relatively uncontaminated (Lewis, 1975).

The concentration of PAHs in sediments and the overlying water column are vastly different. Because of the favorable partition coefficient and greater persistence of sedimentary PAHs compared to those in solution, PAH concentrations in sediments are 1000-fold greater than those in the overlying water. Thus, sediment PAH concentrations can serve as useful indices of the PAH concentrations in the overlying water column (Neff, 1979).

4.4.4 Degradation of PAHs in the Aquatic Environment

PAHs are also degraded in the aquatic environment. The rate of loss of PAHs from aquatic systems is a function of evaporation, photochemical oxidation, microbial

degradation, and sedimentation. Using an enclosed water system, Lee *et al.* (1978) showed that approximately 40% of the benzo[a]pyrene (BaP) introduced into the system was recovered in bottom sediments, thereby suggesting that more than 50% of the BaP was photooxidized. In an oil treated system BaP and benz[a]anthracene (BaA) were not degraded by bacteria, but naphthalene and methylnaphthalene were. Naphthalenes were rapidly accumulated by phytoplankton which subsequently sank to the bottom. The higher molecular weight PAHs became associated primarily with colloidal and detrital material which sank more slowly. Only naphthalene and methylnaphthalene were lost by evaporation. Zooplankton accumulated anthracene, fluoranthene, BaP, and BaA.

5.0 BIOAVAILABILITY OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAHS)

5.1 TOXICOLOGY OF PAHS

5.1.1 Sources of PAHs in the Aquatic Environment

Many industrial activities, *inter alia* coke production, result in the production of polynuclear aromatic hydrocarbons (PAHs). For example, in 1972, 87 x 10^6 tons of bituminous coal were processed to 60 x 10^6 tons of coke. Coke is produced by exposing coal to high temperatures (140° C) in a reducing atmosphere. These are ideal conditions for the synthesis of PAHs. PAHs represent as much as 5% of the particulate emissions from coke production (Guerin, 1977). While leaching of PAHs from soil contaminated by the particulate matter of industrial emissions is a source of PAHs in streams, rivers, and oceans, the main source of PAHs in soil is vehicular exhaust (Blumer *et al.*, 1977). Localized elevated concentrations of PAHs have also been shown to arise from creosoted pilings used for docks and other shoreline structures. Creosote may contain as much as 93 g PAH/kg, and 22 mg/kg may be BaP. The PAHs derived from the creosoted pilings can be expected to decrease nearly logarithmically with distance from the source and, thus, create only localized areas of increased PAH concentration (Zitko, 1975).

5.1.2 Rates and Routes of PAH Entry into the Aquatic Environment

Biosynthesis of PAHs also occurs and may represent a significant localized source of these compounds (e.g., in anoxic sediments rich in plankton lipids). The biosynthetically produced PAHs are of a simpler structure than those produced by heating in a reducing milieu (Youngblood and Blumer, 1975). The alga *Chlorella* has a biosynthetic rate of 67 ug/kg dry algal biomass per day, and 0.617 ug/kg of this is BaP. The annual productions of PAHs by marine phytoplankton has been estimated at 2.7 x 10^3 metric tons/yr, while BaP is 25 metric tons/yr (Koons and Monaghan, 1976). Biosynthesis of PAHs does not, however, represent a significant proportion of the total global burden. PAHs in the aqueous phase are quite persistent, because they are less sensitive to photooxidation than airborne PAHs. In fact, when PAHs are incorporated into the anoxic sediments, they may persist for long, even geological, times. When PAHs enter aquatic systems, they become adsorbed to organic and inorganic particulate matter. Particulate PAHs are deposited in bottom sediments. Leaching or biological activity in the sediment may return a small fraction of sediment PAHs to the water column. PAHs are accumulated by aquatic biota. Relative concentrations of PAHs in aquatic ecosystems are generally highest in the sediments, intermediate in aquatic biota, and lowest in the water column. PAHs may be

removed from the aquatic environment by volatilization of PAHs from the water surface, photooxidation, chemical oxidation, microbial metabolism, and metabolism by higher metazoans (Neff, 1979).

5.1.3 Water Quality Criteria for PAHs

The quantitative risk relationship between PAHs and lifetime cancer risk has been estimated (U.S.E.P.A., 1980c). Numerous studies of workers exposed to coal gas, coal tars, and coke oven emissions, all of which have large amounts of PAHs, have demonstrated a positive association between the exposures and lung cancer. Several PAHs are well-known animal carcinogens; others are not carcinogenic alone, but they enhance or inhibit the response of the carcinogenic PAH. Most of the information about the combined carcinogenic effects of several PAHs come from skin painting and subcutaneous injection experiments in mice, whereas oral administration, intratracheal instillation, and inhalation have been shown to induce carcinogenic responses to single compounds. The mutagenicity of PAHs in the *Salmonella typhimurium* assay correlates well with their carcinogenicity in animal systems. PAH compounds have damaged chromosomes in cytogenetic tests, have induced mutations in mammalian cell culture systems, and have induced DNA repair systhesis in human fibroblast cultures (U.S.E.P.A., 1980c).

The water quality criterion for carcinogenic PAH compounds is based on the assumption that each compound has a potency equal to BaP and that the carcinogenic effect of the compounds is proportional to the sum of their concentrations. The water quality criterion for BaP is based on an experiment reported by Neal and Rigdon (1967), in which BaP at doses ranging between 1 and 250 ppm in the diet was fed to mice for approximately 110 days. Stomach tumors, which were mostly squamous cell papillomas, but some carcinomas, appeared with an incidence statistically higher than controls at several doses. The carcinogenic potency factor for humans is 11.53 $(mg/kg/day)^{-1}$. The calculated lifetime risk for 10^{-6} is 28 ng/L. While it is recognized that numerous carcinogenic PAHs other than BaP are found in water, there is probably little need to derive criteria for all PAHs, since efforts to reduce BaP levels to within acceptable limits will result in the reduction of all PAHs (U.S.E.P.A., 1980c).

5.2 UPTAKE OF PAHS FROM FOOD AND WATER

Many of the compounds found in the analysis of the Ironton Coke Plant Site and surroundings are fat soluble xenobiotics. The intestinal mucosa is the main area of contact for ingested fat-soluble xenobiotics. Enzymes secreted into the intestinal lumen or residing microorganisms may alter ingested chemicals before absorption occurs. The micellarization of dietary fats and fat-soluble vitamins and subsequent absorption provide a model for uptake of fat-soluble environmental agents (Akesson *et al.*, 1983).

There is evidence that lypophilic xenobiotics are absorbed in a fashion similar to trace nutrient lipids and fat-soluble vitamins which are dependent on normal processes of fat digestion (Hollander, 1981). Micelle formation encapsulates trace lipids and xenobiotics in their hydrophobic interiors and provides a vehicle for carrying these lipophilic substances through the aqueous milieu of the lumen to the absorbing villous cell membrane. Following break-up of the micelles in the unstirred water layer, the lypophilic xenobiotics are partitioned from the aqueous phase to the lipid phase of the villous cell plasma membrane. Micelles do not penetrate the brush border membrane, so the lipid soluble material must be taken up as simple molecules. The maximum rate of uptake would occur when the monomer solution at the interface is saturating. Thus, the micelle serves to increase the concentration of lipid near the membrane and, thereby, increase the driving force for membrane transport (Hoffman, 1970).

Once inside the cell the resulting triacylglycerols, phospholipids, cholesterol esters, PAHs, and intestinally derived apoproteins form chylomicrons. Chylomicrons are exported through the basolateral membrane by a process of reverse pinocytosis and arrive in the systemic circulation *via* the lymphatic system. This means that the hydrocarbons bypass the liver initially and go directly to other tissues as lipoprotein metabolism proceeds, and low density lipoproteins are bound by the various organ receptors (Riley and Glickman, 1979). The partition of xenobiotics between organic solvents and water has been demonstrated to be closely related to the actual appearance of the same chemicals in the lymph, blood, and tissues. The potential absorption of chemicals can, thus, be implied from their partition characteristics. The PAHs (e.g., BaP) have low solubilities in water. Oral administration of PAHs to experimental animals indicates that they are rapidly absorbed and eliminated through biliary excretion in the feces and urine. Biological half-lives may be considerable, and PAHs may persist in the adrenals, ovaries, and body fat, even after 8 days. Oral administration of PAHs to rodents has been shown to induce

leukemias, stomach tumors, hepatomas, pulmonary adenomas, and mammary gland tumors. The partition of 7,12-dimethylbenzanthracene, 3-methylcholanthrene, and BaP between an emulsified oil phase and a mixed micellar solution has been quantitated. At the critical micellar concentration of sodium taurocholate, these hydrocarbons partitioned nearly identically from the lipid phase into the micellar system (Laher and Barrowman, 1983).

In conclusion, fat soluble environmental hydrocarbons are of public health concern because of their toxic or carcinogenic properties. The relatively harmless paraffins, the PAHs, the polychlorinated polycyclics, and the aromatic acid esters, are some of the hydrocarbon groups that are influenced by intestinal absorptive processes. While some esters may undergo luminal lipolysis, most of these environmental agents undergo little luminal transformation and are subject to micellarization. Thus, these compounds are absorbed *via* the pathways normally involved in the uptake of fat-soluble vitamins. The appearance of fat-soluble micronutrients parallels their solubility in organic solvents. The relative absorption of foreign hydrocarbons has been deduced from their partition between organic solvents and aqueous buffers. The result of micellarization is to increase the concentration gradient many fold and favor the passive absorption of lipophilic compounds. Evidence of specific membrane receptors or carrier proteins in the absorption process of lipophilic compounds is not available. Based on studies of the absorption of natural fats and fat-soluble vitamins, inferrences about the digestion and absorption of various fat-soluble environmental agents can be made. A complete understanding of the mechanism involved would necessitate detailed biochemical studies with the individual agents.

5.3 INHALATION HAZARDS OF PAHS

Non-occupational respiratory exposure to PAHs is mainly from tobacco smoke and urban air. Cigarette, cigar, pipe, and marijuana smoke, as well as the side stream smoke from these products, contain many PAHs. Urban air pollution is from vehicle exhausts and combustion products. Exhaust gases from internal combustion engines can contribute 80% of the total PAHs in the air in some cities. Urban atmosphere PAH pollution varies with time of day, degree of coal-fired stoves in use, and degree of photochemical decomposition (IARC, 1983). The importance of PAHs as carcinogens derived from the organic particulate matter of emissions from gasoline and diesel engines has been demonstrated by mouse skin or rat lung bioassays (Kotin *et al.*, 1954). Aircraft engines have also been shown to release 2-10 mg PAHs/min, and at high speeds the BaP emission

increases drastically. As a result of the introduction of emission control devices in Canada, France, Sweden, United Kingdom, and the USA, around 1970, release of organic particulate matter from gasoline engines has been diminished drastically (IARC, 1983).

Absorption of PAHs across the pulmonary endothelium has been studied following inhalation of pure aerosols and after intratracheal administration of PAHs adsorbed on particles of various sizes. Clearance of PAHs has not been differentiated between systemic absorption and mucociliary clearance in these studies. Mucociliary clearance can result in high gastrointestinal levels and subsequent absorption. BaP has been shown to clear the rat biphasically--first a rapid phase with a two-hour half-life and then a slower phase with approximately a two-day half-life (Mitchell, 1982). Deposition and clearance rates of PAHs in the lung are dependent upon the particle size to which the PAH is attached (Henry and Kaufman, 1973). Significant levels of pyrene have been detected in the liver, kidney, and muscle of rats following inhalation (Mitchell and Tu, 1979).

5.4 EFFECT OF PHYSICAL STATE ON ABSORPTION

5.4.1 Accumulation and Release of PAHs by Aquatic Organisms

In assessing toxicity of PAHs, their accumulation and release must be considered. The high hydrophobicity and lipophilicity of PAHs account for the capability of freshwater and marine organisms to take up PAHs in low concentrations from the ambient medium, food, or sediments. The intrinsic lipid/water partition coefficient accounts for the ready transferrance of PAHs from the aqueous phase into the lipophilic compartment, such as biological membranes, macromolecules, and depot lipid stores (Leo *et al.*, 1971). Naphthalene is the most water soluble of the PAHs and is, therefore, most bioavailable. BaP has a very low aqueous solubility. Reported BaP solubilities range from 0.01 ug/L (Andelman and Snodgrass, 1974) to 12 ug/L (Wilk and Schwab, 1968). Most BaP in aquatic systems is in a colloidal or particulate form, which decreases its bioavailability. Thus, BaP does not readily partition back into the aqueous phase, even when the concentration of BaP in the medium is low (Neff, 1979). When aquatic animals are exposed to PAHs, the octanol/water partition coefficient usually has a good correlation with its accumulation factor (concentration in tissue/concentration in water). Therefore, bioaccumulation factors increase as molecular weight of the PAH increases. Scaccini-Cicatelli (1966) found that the freshwater oligochaete *Tubifex* sp. was able to accumulate as much as 88.2 ug BaP/kg tissue during exposure for 11 days to a concentration of 100 ug BaP/L freshwater. When the shrimp *Penaeus-duerarum* was exposed to 5 ppb

chrysene, it accumulated 1.8 ug chrysene/g tissue in the cephalothorax (Miller *et al.*, 1978). *R. cuneata* accumulated up to 7.2 ppm BaP during a 24-hr exposure to 0.03 ppm ^{14}C-BaP (Neff and Anderson, 1975). Mummichogs (*Fundulus heteroclitus*) accumulated naphthalene in the spleen 34-105 times the exposure concentration (Statham *et al.*, 1976). When the freshwater crustacean *Daphnia pulex* was exposed to an aqueous concentration of 0.02 ug ^{14}C-anthracene/L, it rapidly accumulated 760 times the aqueous concentration. After return to fresh water, 30-35% of the accumulated anthracene was released in 5-10 min. Anthracene metabolites accounted for only 6% of the product excreted, even after 48 hr., at which time only 8% of the original remained in the crustacean. Thus, most of the excreted anthracene was excreted unmetabolized (Herbes and Risi, 1978). When the sheep's head minnow *Cyprinodon variegatis* was exposed for 4 hr. to 1 ppm naphthalene and 1-methylnaphthalene, it accumulated 60 ppm naphthalene and 210 ppm 1-methylnaphthalene. Nearly 90% of that accumulated was released after 29 hr. in hydrocarbon-free sea water (Anderson *et al.*, 1974). The half-life of BaP in mussels is approximately 16 days (Stich, and Acton, 1976). The half-lives of anthracene, fluoranthene, BaA, and BaP ranged from 2 to 18 days in molluscs (Lee *et al.*, 1978).

To assess the potential for biomagnification of PAHs in aquatic food chains, the ability of aquatic animals to accumulate PAHs from food sources must be ascertained. When the marine copepod *Calanus* was fed ^{14}C-naphthalene contaminated dead copepod nauplii (*Elminuis* sp.) or living algae (*Biddulphia*), ^{14}C-naphthalene was taken up, and the uptake was much more efficient than from solution. After 24 hr., 94% of the radioactivity in the copepods was unmetabolized ^{14}C-naphthalene. The amount of ^{14}C-naphthalene present in solution must exceed the amount in food alone by 2000- to 4000-fold to give the same increase in hydrocarbon level in copepods (Corner *et al.*, 1976). Approximately 60% of naphthalene ingested was assimilated by copepods. Of the assimilated naphthalene, about one-half (53.7%) was retained in the tissues; the other half was released as naphthalene or its metabolites (Harris *et al.*, 1977). Dixit and Anderson (1977) administered ^{14}C-naphthalene to the Gulf killifish *Fundulus similis* and found 12% to be assimilated. After 8 hr., 79% of the radioactivity recovered was present in the gall bladder. Thus, PAHs appear to be transported to the liver, where they are rapidly metabolized and excreted in the bile. Similarly, 48 hr. after ^{14}C-BaP contaminated squid were fed to young cod (*Gadus morrhua*), 83.5% of the radioactivity was still present in the stomach, and 12% was still present in the intestinal contents. After 72 hr., the bile fluid contained 12.5% of the total recovered ^{14}C activity (Corner *et al.*, 1976). In herring (*Clupea harengus*), 80% of the recovered radioactivity remained in the BaP unmetabolized lipid fraction of the stomach

43-hr after ingestion of ^{14}C-BaP-contaminated squid. The largest fraction of the remaining activity was in the lipid fraction of the intestine (10.3%), and the residual fraction (unextractable BaP metabolites) was in the stomach, pyloric caecae, and intestine (4.9%). Most of the activity recovered in bile was water soluble, indicating polar metabolites (Whittle *et al.*, 1977). The authors concluded that retention of BaP in the stomach implies strong adsorption or binding to the stomach wall. This binding prevents subsequent absorption and assimilation of ingested BaP. Although the digestive tract of fish represents the major site of both uptake and excretion of orally administered PAHs, the fact that more than 98% of the radioactivity recovered from fish 43 hr. after feeding was in the digestive tract strongly suggests very little assimilation of ingested BaP; and the small amount of BaP that was assimilated was rapidly metabolized and excreted *via* the gall bladder into the intestine.

Lu *et al.* (1977) conducted freshwater model ecosystem studies to evaluate bioaccumulation and food-chain biomagnification potential of BaP. At 2 ppb, ^{14}C-BaP was added to the model ecosystem and allowed to pass through a freshwater food chain of plankton, filamentous green algae (*Oedogonium cardiacum*), water fleas (*Daphnia magna*), mosquito larvae (*Culex pipiens*), snails (*Physa*, sp.), and mosquito fish (*Gambusia affinis*) for three days. BaP was accumulated and retained by all organisms in the model ecosystem. Bioaccumulation factors ([BaP]tissues/[BaP] water) ranged from 930 in fish to 134,248 in *Daphnia*. The authors reasoned that since the fish bioaccumulated substantial amounts of BaP in this study but not when exposed to BaP in water alone, food chain biomagnification of BaP was demonstrated. However, based on observations of BaP assimilated by fish from food, the *Gambusia* accumulation of BaP was due to unassimilated BaP in the digestive tract and not to actual biomagnification of BaP.

The limited data available indicate large differences between species in ability to absorb and assimilate PAHs from food. Polycheate worms have a limited ability to do so, while in fish, adsorption of PAHs from the gut is limited and variable depending upon species of fish, the PAH, and possibly the food matrix in which the PAH is administered. Crustaceans, on the other hand, apparently readily assimilate PAHs from contaminated food. In all cases which demonstrated assimilation of ingested PAHs, metabolism and excretion of PAHs were rapid. Thus, the potential for food chain biomagnification of PAHs seems to be limited. For biomagnification to occur, the material must be readily

absorbed from food, and once assimlated, it must be relatively resistant to metabolism or excretion (Neff, 1979).

5.4.2 Biological Effects of PAHs in the Aquatic Environment

It is estimated that as much as 50% BaP and other high molecular weight PAHs entering the water column are eventually deposited in bottom sediments. The rich bacterial and fungal flora at the water-sediment interface readily degrades PAHs. If PAHs are buried in anoxic sediments, they are extremely resistant to degradation and persist indefinitely. Aquatic organisms are able to accumulate PAHs from water, food, and sediment. In most cases, accumulation from water is more efficient than from food or sediment. Sediment-adsorbed PAHs have only a very limited bioavailability to aquatic organisms. Most aquatic animals have the ability to degrade PAHs to more polar metabolites and excrete them rapidly. Even species lacking PAH-metabolizing abilities are able to release accumulated PAHs rapidly when they are returned to a PAH-free environment. PAHs are acutely toxic to aquatic animals at concentrations of about 0.2-10 ppm. Deleterious sublethal responses in aquatic organisms are sometimes observed at concentrations in the 5-100 ppb PAH range.

Macek *et al.* (1979) have determined that biomagnification of chemical residues in aquatic food chains is not a significant phenomenon. The movement of chemicals through the food chain is small compared to the amount of bioconcentration. Furthermore, when biomagnification does occur, it is less than the error associated with the estimation of the chemical residues due to bioconcentration alone. The rate of depuration of chemical residues from biological systems correlates with the ability of chemicals to move through the food chain. While the evidence for biomagnification of DDT in the food chain has suggested to many that most chemicals can biomagnify, a comparison of DDT depuration rates with those of other chemicals indicates the uniqueness of this pesticide. DDT has a depuration $t_{1/2}$ in rainbow trout of greater than 160 days (Macek *et al.*, 1970), while the $t_{1/2}$ for depuration of BaP in mussels is 18 days (Lee *et al.*, 1978); the $t_{1/2}$ for depuration of naphthalene and 1-methylnaphthalene in the sheep's head minnow is less than 10 hr.; the $t_{1/2}$ for depuration of BaP in three species of marine fish is less than 8 hr. (Lee *et al.*, 1972); and the $t_{1/2}$ for depuration of BaP in mosquito fish is such that it excretes BaP and its metabolites almost as quickly as it is taken up (Lu *et al.*, 1977). In all cases where assimilation of ingested PAHs was demonstrated, metabolism and execretion of PAHs were

rapid compared to biomagnified compounds such as DDT. Thus, the potential for food chain biomagnification of PAHs seems to be limited.

5.5 THE PHYSICAL STATE OF PAHS IN THE LAGOONS AND ICE CREEK

Any remarks regarding the state and toxicity of PAHs in the Lagoons and Ice Creek around the Ironton Coke Plant must be tempered with the knowledge that human toxicity will vary widely. While the mechanism for lipid soluble PAH intestinal adsorption is known, genetic variations are expected. Ground water PAHs may also contribute to the total PAHs found in rivers, streams, and drinking water sources. Based on previous findings (*supra vide*), the large difference in PAHs found in Ice Creek water samples and Ice Creek sediment samples is expected. PAHs entering the water column of Ice Creek bind to organic matter and detritus, whereupon the complex precipitates and, to a large extent, remains buried in the bottom sediment. Here an anoxic state obtains and little degradation occurs.

The Ice Creek water column *per se* and the fish living in this water showed no detectable PAHs. While fish would be expected to bioaccumulate PAHs, their ability to biomagnify these xenobiotics is quite variable based on the tendency of PAHs to stay in the digestive tract for extended periods and the ability of fish to excrete the absorbed PAHs in the bile. The low concentrations of PAHs in these samples did not produce any detectable PAH biomagnification, even among the "rough" fish such as carp and catfish known to be sediment feeders. Since PAHs may be acutely toxic to aquatic animals at the level of 0.2-10 ppm and the minimum detectable level of these assays ranged from 0.810 to 0.980 ppm, these fish analyses have some limitations in evaluating aquatic life toxicity.

The water in the Coal Grove wells tested below the level of detection (1 ppb) for each PAH. The PAHs which derive from the Lagoons or Ice Creek sources are actively bound to organic and detrital matter (*supra vide*), thus preventing migration of these compounds, except by surface water movement. Hamaker (1975) has pointed out that leaching behavior of chemicals through soil depends upon soil adsorption, hydrodynamic dispersion and diffusion, adsorption dynamics, and evapo-transpiration and that little, if any, of even quite mobile chemicals is leached to sufficient depth to enter the ground water. Unless the distant Coal Grove wells are affected by surface waters which would derive from the Lagoons or Ice Creek, there is no reason to expect PAH entry into these wells. Again, this assessment of PAH toxicity in these wells is limited by the sensitivity of the

assay procedure. While the detection limit for water samples is less than 1 ppb, the EPA ambient drinking water criterion is 0.028 ppb.

6.0 QUANTITATIVE CANCER RISK ESTIMATES

Both benzene and benzo[a]pyrene are known carcinogens present at the Ironton Coke Plant Site. A sufficiently high concentration of either of these chemicals reaching the wells of Coal Grove would pose a serious health hazard for residents.

Assays for both substances were performed using the gas chromatograph/mass spectrophotometric (GC/MS) method, and in each case the substance was not found in either Coal Grove well water or in Ice Creek and its groundwater. Either substance may still be present at levels below the detection limit of the assay used, one part per billion (ppb) in each case.

Quantification of the increased risk to the population at large of contracting cancer due to the presence of low concentrations of carcinogenic substances in the air or water supply is difficult. The expected hazard is so small (perhaps an increased cancer probability of from one in a million to one in ten thousand or so) that animal exposure experiments would require tens of thousands of animals to measure the risk at such low dose levels. Instead of exposing so many animals to these low levels, often a modest number of animals are exposed to much higher dose levels in an attempt to make quantitative inference about the carcinogenic potency of these substances. Unfortunately, no generally accepted basis exists for extrapolation of these high-dose experiments to predict low-dose adverse health effects.

Nevertheless, it is generally agreed that low-dose risk decreases at least linearly (*i.e.*, that lessening the concentration by half decreases the risk by at least half, and possibly more), and hence that it is conservative to estimate low-dose risk by linear extrapolation from higher-dose experimental data. This is the method used below and currently by the United States Environmental Protection Agency (EPA).

6.1 BENZENE

Benzene was not detected in the Coal Grove wells or in the groundwater of Ice Creek which feeds the Coal Grove drinking water, using a GC/MS assay with a detection limit of one ppb. Since leakage from Ice Creek constitutes 27% of the Coal Grove drinking

water and groundwater seepage another 3%, this leads to an upper bound for the daily quantity of benzene ingested by a human drinking two liters of water each day of:

$$(30\%) \times (2.0\ \text{L } H_2O/\text{day}) \times (1000\ \text{g } H_2O/\text{L } H_2O) \times (10^{-9}\ \text{g } C_6H_6/\text{g } H_2O) = 0.60\ \text{ug } C_6H_6/\text{day}$$

The EPA has judged the primary cancer risk attributable to inhaled vapors of benzene to be an increased incidence of leukemia, with a potency factor of 22.3×10^{-6}/ppm, *i.e.*, an expected increase of 22.3 cases of leukemia per 100,000 population exposed to a lifetime average of 1.0 ppm benzene in the atmosphere (U.S.E.P.A., 1979b). Assuming retention of 60% (Eutermoser *et al.*), the daily intake for a 70 kg human breathing 20 m^3 of air/day containing an average of 1.0 ppm benzene (3.3 mg/m^3 air) would be:

$$(60\%) \times (3.3\ \text{mg } C_6H_6/m^3\ \text{air}) \times (20.0\ m^3\ \text{air/day}) = 39.60\ \text{mg } C_6H_6/\text{day}$$

Under the EPA's policy of applying linear, nonthreshold models in all low-dose carcinogenesis extrapolation (see, *e.g.*, U.S.E.P.A., 1984), the increased risk of leukemia upon drinking two liters per day of Coal Grove water is less than:

$$(0.60\ \text{ug } C_6H_6/\text{day}) \times (22.3 \times 10^{-5}/\text{ppm } C_6H_6) / (39.60\ \text{mg } C_6H_6/\text{day /ppm } C_6H_6) = 3.38 \times 10^{-9},$$

i.e., 0.00034 cases of leukemia per 100,000 population lifetimes. For comparison, the incidence of leukemia in the US is about 6-9 cases per 100,000 population; we conclude that no significant increased risk of cancer exists due to the presence of benzene in the water at concentrations near the detection limit of 1.0 ppb. Lower levels represent even less risk.

6.2 BENZO(A)PYRENE

Benzo[a]pyrene (BaP) also was undetectable in the Coal Grove wells or in the groundwater of Ice Creek which feeds the Coal Grove drinking water, using a GC/MS assay with a detection limit of one ppb. This leads to a range of possible values for the concentration of BaP in the Coal Grove water supply of:

$$(30\%) \quad x \ (0 - 10^{-9} \text{ g BaP/g } H_2O)$$
$$x \ (1000 \text{ g } H_2O/\text{L } H_2O)$$
$$= 0.00 - 0.30 \text{ ug BaP/L } H_2O$$

The estimated carcinogenic potency for BaP in drinking water is $35.71 \times 10^{-5}/(ug/L)$ (*i.e.*, 1 cancer incidence per 100,000 population with an ambient concentration of 1/35.71 = 0.028 ug/L; see U.S.E.P.A., 1980c). Using a linear nonthreshold extrapolation to low-dose, the increased risk of cancer due to this exposure is:

$$(0.00 - 0.30 \text{ ug BaP/L } H_2O) \quad x \ (35.71 \times 10^{-5}/(ug/L))$$
$$= 0.00 - 10.71 \times 10^{-5},$$

i.e., 0 to 11 additional cases of cancer per 100,000 population lifetimes. This wide range of possible cancer risks is due to the relatively high detection limit of the BaP assay; the EPA recommended limit on ambient levels of BaP in drinking water is 28 parts per trillion (ppt), while the assay found no BaP present with a detection limit of 1000 ppt. In "relatively clean" water, BaP and other PAHs are "extremely insoluble", with a reported solubility as low as 10 ng/L (N.A.S., 1982; Andelman and Snodgrass, 1974); at this concentration, the cancer risk would be:

$$(10.0 \times 10^{-3} \text{ ug/L } H_2O) \quad x \ (35.71 \times 10^{-5}/(ug/L))$$
$$= 3.57 \times 10^{-6},$$

i.e., 0.357 additional cancer cases per 100,000 population. Others have reported higher solubilities for BaP in clean water, however, and the apparent solubility is known to be higher still in water containing detergents or particulate matter.

6.3 CONCLUSION

It is reasonably certain that the "worst case" concentration of benzene likely at the Coal Grove water supply is not a significant human cancer risk. Insufficient data now exist regarding BaP as a surrogate for PAHs from the site. It is unlikely that a cancer risk exists for the PAHs transported from the Site to drinking water, due to their low solubility and affinity for particulate matter. Present state-of-the-art techniques cannot detect levels of PAHs which may pose human cancer risks. Even though appropriately conducted, the present PAH analyses do not provide adequate data to judge quantitatively the potential human cancer risk.

7.0 AQUATIC HAZARD ASSESSMENT

A general design for aquatic ecological studies in the lagoons on the site and in Ice Creek was developed to assist in the conduct of an aquatic hazard assessment for the Allied Chemical/Ironton Coke Site. Allied used the general study design as the basis for a contract with Battelle Columbus Laboratories (Battelle) to conduct these studies. Battelle conducted the survey in September, 1984. The purpose of the survey was to assess the impacts of waste materials from the Allied Chemical/Ironton Coke Site on aquatic biota of Ice Creek.

In developing the aquatic hazard assessment which follows, the Site was visited on July 24, 1984; a review was made of the Initial Site Assessment and Remedial Investigation of Allied Chemical/Ironton, Coke Site, Ironton, Ohio, Phase I Report prepared by D'Appolonia, the Remedial Investigation Allied Chemical/Ironton Coke Site, Ironton, Ohio, Phase II Report prepared by IT Corporation, and Battelle's report Aquatic Ecological Studies at Allied Chemical's Ironton, Ohio, Coke Site Report. The site visit provided a perspective on the nature, size, and location of the Site relative to Ice Creek and the Ohio River. The Site Assessment and Remedial Investigation reports provided useful qualitative and quantitative information regarding the types of chemicals associated with the Site, as well as, a spatial perspective. The results of the Battelle field studies provided data for assessing the impact of the Site on chemical, physical, and biological water quality in Ice Creek.

The approach used in assessing the impact of the site on the Creek ecosystem basically relies on an asssessment of the biology of Ice Creek. The organisms in Ice Creek are useful monitors of their environment. Presence, absence, and abundance of aquatic organisms are indicators of water quality. Aquatic organisms, particularly the benthic macroinvertebrate fauna which are relatively sessile, integrate the totality of stress impinging upon them from natural and man-made causes. Fish, while not as reliable monitors as benthic macroinvertebrates due to their mobility, can provide useful information on water quality. The results of chemical analyses of water, sediments and biota were utilized in the aquatic hazard assessment. Chemical data developed by Battelle during their ecological survey of Ice Creek were used to determine the probable environmental exposure levels of chemicals in Ice Creek potentially emanating from the site. In addition, chemical data contained in IT's remedial investigation reports on Ice

TABLE 7.3

BASIC DESIGN OF BATTELLE'S IMPACT ASSESSMENT STUDIES ON ICE CREEK AND LAGOONS

Parameters	Sampling Location								
	IC1	IC2	IC3	IC4	IC5	IC6	OR2	LG4	LG3
	IC9		IC7			IC8			
WATER									
Metals	/	/	/	/	/	/	/	/	/
Cyanide	/	/	/	/	/	/			
Acid and base							/	/	/
Neutral priority pollutants	/	/	/	/	/	/	/	/	/
Benzene	/	/	/	/	/	/	/	/	/
Dissolved oxygen	/	/	/	/	/	/	/	/	/
PH	/	/	/	/	/	/	/	/	/
Temperature	/	/	/	/	/	/	/	/	/
Conductivity	/	/	/	/	/	/	/	/	/
Alkalinity	/	/	/	/	/	/	/	/	/
Hardness	/	/	/	/	/	/	/	/	/
Chloride	/	/	/	/	/	/	/	/	/
Sulfate	/	/	/	/	/	/	/	/	/
SEDIMENTS									
Metals	/	/	/	/	/	/	/	/	/
Acid and base							/	/	/
Neutral priority pollutants	/	/	/	/	/	/	/	/	/
BIOLOGICAL								/	/
Phytoplankton								/	/
Zooplankton								/	/
Macrophytes								/	/
Macroinvertebrates	/	/	/	/	/	/	/	/	/
Fish	/	/	/	/	/	/	/	/	/
BIOCONCENTRATION									
Fish tissue	/	/	/	/	/	/	/		

Creek sediments were used to gain further insight into potential environmental exposure levels of chemicals in the Ice Creek ecosystem.

The sections of this chapter which follow contain an explanation of the rationale and conclusions regarding the extent of aquatic resource damage to Ice Creek attributable to waste materials associated with the site. Battelle's report (see Addendum) should be examined for the detailed results supporting the conclusions, as should IT's Remedial Investigation Phase II Report. An attempt has been made to place some perspective on the bioavailability of the chemicals associated with the waste site.

7.1 OVERVIEW OF BATTELLE'S ECOLOGICAL SURVEY

In September, 1984 Battelle conducted intensive water quality studies on lagoons located on the Ironton Coke Site and in Ice Creek, a tributary of the Ohio River passing along the East boundary of the Site. Table 7.3 summarizes the parameters assessed at sampling stations in Ice Creek and in the lagoons. The location of the sampling stations are shown in Figure 1 of the Battelle report (see Addendum).. Reference should be made to Battelle's report for specific information on methodology and sample location descriptions, etc. The lagoons are located adjacent to Ice Creek and are on the Site in intimate contact with materials associated with the Site. Water in the lagoons comes from surface runoff from the Site and groundwater. The bottoms of the lagoons are located in the water table. Studies of the chemistry and biology of the lagoons were conducted, since exposures to chemicals associated with the Site probably represent a worst case scenario. Studies conducted, in Ice Creek were designed to assess the impact of the Site on the aquatic resources in Ice Creek.

7.2 RESOURCE DAMAGE ASSESSMENT

7.2.1 Ice Creek

Based on the results of Battelle's ecological survey in Ice Creek, the following conclusions can be reached:

(1) Ice Creek currently has a depauperate benthic macroinvertebrate community upstream, adjacent to and downstream of the Allied/Ironton Coke Site.

Battelle collected quantitative and qualitative samples of the macroinvertebrate community in Ice Creek, all of which demonstrated the presence of a depauperate

TABLE 7.3

BASIC DESIGN OF BATTELLE'S IMPACT ASSESSMENT STUDIES ON ICE CREEK AND LAGOONS

Parameters	Sampling Location								
	IC1	IC2	IC3	IC4	IC5	IC6	OR2	LG4	LG3
	IC9		IC7			IC8			
WATER									
Metals	/	/	/	/	/	/	/	/	/
Cyanide	/	/	/	/	/	/	/	/	/
Acid and base Neutral priority pollutants	/	/	/	/	/	/	/	/	/
Benzene	/	/	/	/	/	/	/	/	/
Dissolved oxygen	/	/	/	/	/	/	/	/	/
PH	/	/	/	/	/	/	/	/	/
Temperature	/	/	/	/	/	/	/	/	/
Conductivity	/	/	/	/	/	/	/	/	/
Alkalinity	/	/	/	/	/	/	/	/	/
Hardness	/	/	/	/	/	/	/	/	/
Chloride	/	/	/	/	/	/	/	/	/
Sulfate	/	/	/	/	/	/	/	/	/
SEDIMENTS									
Metals	/	/	/	/	/	/	/	/	/
Acid and base Neutral priority pollutants	/	/	/	/	/	/	/	/	/
BIOLOGICAL									
Phytoplankton								/	/
Zooplankton								/	/
Macrophytes								/	/
Macroinvertebrates	/	/	/	/	/	/	/	/	
Fish	/	/	/	/	/	/	/	/	/
BIOCONCENTRATION									
Fish tissue	/	/	/	/	/	/	/		

community. The macroinvertebrate community can be characterized as low in diversity, density, and species abundance. The largest number of macroinvertebrate taxa collected was 15 at Sampling Station OR2. Sampling Station IC2, upstream of the Site, had only two taxa present in the quantitative samples. The dominant types of organisms found in Ice Creek, particularly in the backwater portion, were diptera and aquatic annelids which are considered pollution tolerant. A variety of factors probably contribute to the depauperate fauna found in Ice Creek. Battelle observed that the predominant substrate at the two upstream Stations IC1 and IC2 was sand. Sand is an unstable substrate and typically does not support a productive benthic fauna. Considerable trash and debris were also observed in these reaches of Ice Creek. The silt substrate present in the slough areas (Stations IC6, IC4, and IC3) also does not typically support a highly diverse benthic community. Battelle observed an increase in density of Tubifex and Branchiura downstream of a sewage outfall at Station IC6. These organisms are known to tolerate low dissolved oxygen and high organic loadings. The results of chemical analyses of Ice Creek sediments by Battelle and by IT have shown the presence of polynuclear aromatic hydrocarbons (PAHs) at some of the sampling stations. These and other factors may interact to cause the depauperate macroinvertebrate fauna found in Ice Creek. Based on the results of Battelle's benthic macroinvertebrate survey, it is not possible to specifically identify impacts attributable to the Allied Chemical/Ironton Coke Site. The substrata and backwater conditions of Ice Creek in general do not support a highly diverse benthic macroinvertebrate fauna. The data do clearly demonstrate that some macroinvertebrates are successfully living and reproducing in Ice Creek. It is of interest that while the benthic community present can be characterized as being pollution tolerant, that some taxa considered to be sensitive indicators of water quality, namely the amphipod Hyalella and several species of freshwater mussels (Corbicula, Sphaerium, and Potamilus), are also present. Potamilus ohioensis is considered an endangered species in Ohio.

(2) Ice Creek supports a diverse fish fauna.

In contrast to the depauperate macroinvertebrate community the fish community in Ice Creek is very diverse and plentiful. Battelle collected twenty-seven (27) fish species. The gizzard shad, emerald shiner, and bluegill sunfish were the most abundant species. The centrarchidae was the most abundant family. Game fish found in Ice Creek included largemouth bass, crappie, channel catfish, and flathead catfish. A variety of sunfish species were found in Ice Creek. Battelle analyzed the game fish for condition factors

and reported that all species were in the normal ranges reported in the literature. Fish appeared to be robust and healthy with no disease or abnormalities.

The backwater area of Ice creek appears to serve as a refuge for fish. It is likely that many of the fish found in the area move in and out of Ice Creek from the Ohio River. However, it is highly probable that many of the more territorial species (i.e., the sunfish) are permanent residents of Ice Creek. Backwater areas and small tributaries frequently serve as important habitats for fish associated with large rivers like the Ohio. It appears that Ice Creek is serving such a function.

The diversity and density of fish found in Ice Creek may in part also explain the rather depauperate benthic macroinvertebrate fauna found in Ice Creek., It is possible that predation by fish on the benthic macroinvertebrates in Ice Creek keep the standing crop low.

(3) Water quality in Ice Creek appears to be acceptable to aquatic life.

Battelle took water samples at the locations coinciding with their ecological sampling stations and analyzed for routine water quality parameters and priority pollutants. The results of these analyses showed Ice Creek water contains no adverse levels for any of the parameters. For those compounds or ions for which Water Quality Criteria have been established, none were in concentrations exceeding the criteria. Total ammonia was fairly high (1.6 to 6.4 mg/L) at Stations IC4, IC6, and IC3. The sources for the elevated ammonia may have been the sewage outfall upstream of Station IC6 and the storm water/sewer at IC3 as reported by Battelle, or ammonia leaching from the Allied Chemical/Ironton Coke Site as indicated by IT in its Remedial Investigation Report, or from all sources. Considering the pH (7.0-7.6) and temperature of Ice Creek, it is not likely that the ammonia was causing toxicity problems in Ice Creek since it would be mostly in the relatively nontoxic ionized form. The chemical analyses of Ice Creek conducted by Battelle provide results which are compatible with the biological data. Ice Creek has a diverse fish community and a viable, if not depauperate, benthic macroinvertebrate fauna.

(4) Sediments in Ice Creek contain chemicals associated with the Allied Chemical/Ironton Coke Site.

The results of chemical analyses of surface sediments collected by Battelle show the presence of the following PAHs.

Anthracene	Dibenzo(a,h)anthracene
Benzo(a)anthracene	Fluoranthene
Benzo(a)pyrene	Fluorene
Benzo(b)fluoranthene	Indeno(1,2,3-cd)pyrene
Benzo(ghi)perylene	Naphthalene
Benzo(k)fluoranthene	Phenanthrene
Chrysene	Pyrene

The PAHs present at Station IC3 and OR2 are similar to those found in sediment samples from the lagoons, indicating the site as the source of PAHs in sediments in Ice Creek. The PAH present in highest concentration in IC3 surface sediments is benzo(a)anthracene (approximately 100 mg/kg). Most of the other PAHs are present in the 5-50 mg/kg range of concentrations.

IT, as part of its remedial investigation, made 19 borings at 12 locations in Ice Creek for sediment testing. Chemical analyses of these borings showed chemical constituents associated with past coke plant operations present in the bed sediments at several locations in Ice Creek. Tar-like compounds, oily sheens, and tar-like odors were reported by IT at various depths in Ice Creek sediments at a number of sampling stations indicating the presence of materials associated with the Site. The absence of PAHs in surface waters of Ice Creek indicates that while present in the sediments they are not mobilized. This is further supported by the results of IT's sediment leach tests, which did not detect mobility of the constitutents from the sediments.

(5) Fish in Ice Creek do not appear to be bioconcentrating chemicals to unacceptable levels.

Samples of fish tissues were analyzed by Battelle for metals and organic priority pollutants. Results showed no differences in metal concentrations in fish tissues upstream and downstream of the site. Of the metals analyzed zinc was present in the highest concentration (approximately 250 mg/kg). It was also the highest metal in Ice Creek sediment samples upstream and downstream of the Site. The only organic priority pollutants detected in fish samples were bis(2-ethylhexyl)phthalate at Stations IC1, IC5,

IC4, and IC6; di-n-butyl-phthalate at Stations IC1, IC2, IC5, IC4, and IC6; and phenol at IC6 and IC4. Phthalates are known to be fairly ubiquitous in the aquatic environment, due to their widespread use as plasticizers. Their presence in the fish tissues may also be attributable to the plastic bags used by Battelle to contain fish samples or some other undefined environmental source. Phenolic compounds are known to be associated with the Site. Phenol was present in concentrations ranging from 2.3 to 15.9 mg/kg. Phenol has been reported to cause off flavors in fish flesh. Whether or not fish in Ice Creek are tainted is not known. The absence of other neutral organic PAHs found in the Site and in Ice Creek sediment in the tissues of fish is probably attributable to their great affinity to sorb tightly to sediments.

(6) Neutral organic chemicals associated with the Site are not bioavailable to be toxic or to bioaccumulate.

Aquatic organisms in Ice Creek adjacent to Allied Chemical/Ironton, Ohio Coke site can be potentially exposed to chemicals via several routes:

- Seepage of contaminated groundwaters;
- Surface water runoff from the site;
- Dissolution of chemicals from contaminated sediments into Ice Creek Waters;
- Direct contact with contaminated sediments; and
- Ingestion of contaminated sediments and/or organisms.

For a chemical to cause an adverse impact (i.e., be lethal, suppress reproduction or growth, etc.), it must be bioavailable. The results of the Battelle field monitoring studies in Ice Creek indicate that chemicals which originated from Allied Chemicals's Coke Site have limited bioavailability. Samples of water and fish from sampling locations in Ice Creek upstream, adjacent to, and downstream of the Coke Site, failed to detect the presence of acid and base/neutral priority pollutants and metals directly attributable to the Site. Yet, some priority pollutants attributable to coke site were present in the sediments in Ice Creek. These chemicals do not appear to be sufficiently bioavailable to adversely affect fish by accumulating in their tissues; nor were they sufficiently bioavailable to significantly impact on the benthic macroinvertebrate community in Ice Creek.

The results of the Lagoon studies conducted by Battelle on lagoon 3 and 4 at the coke plant Site provide further evidence that PAHs associated with the Site are basically not bioavailable to cause adverse impacts on aquatic life. The lagoons collect surface runoff from the Site, as well as groundwater percolating through the Site. Waters in the lagoon are in intimate contact with sediments contaminated with a variety of chemicals. Yet, zooplankton and phytoplankton were present, indicating that chemicals associated with the Site were either relatively nontoxic or were tightly bound to soils and sediments limiting their bioavailability. Mature and immature (i.e., nauplii) life history stages of a copepod were present, indicating reproduction was not being totally eliminated. While the ponds had limited and certainly not "normal" phytoplankton and zooplankton communities by comparison to those found in ponds and lakes, they do support aquatic life even under a probable worst case exposure scenario.

A number of factors probably attribute to the limited bioavailability of chemicals from the coke site to aquatic life in Ice Creek. First, chemicals being released from the soils and sediments are diluted, thus decreasing their concentrations. Secondly, many of the chemicals associated with the Site (i.e., some neutral organics and some metals) will be sorbed to suspended and sedimented solids thereby removing them from the water column. Many of the chemicals will be biodegraded by microorganisms in the water and sediment. The biodegradability of many of the aromatic hydrocarbons reported from the site are relatively rapid. Some of the chemicals will be oxidized, others will undergo chemical hydrolysis reactions. Metals will be precipitated and may become associated with a variety of ligands. The importance of each of these removal processes for chemicals from the coke site is basically unknown. Yet, the Battelle field monitoring data clearly indicate that processes are at work to remove the chemicals from the water column and, thus, reduce their bioavailability to water column associated aquatic life. The field survey data for Ice Creek indicate that sediment associated chemicals are probably also not bioavailable to cause significant adverse impacts on the number and diversity of benthic organisms which live on or in the sediments.

The results of the Ice Creek survey clearly demonstrate that chemicals from the coke site are not adversely impacting the diversity or density of fish present in Ice Creek. The overall impact of chemicals from the coke plant site on the aquatic ecology of Ice Creek is negligible, due in part to the limited bioavailability of the chemicals associated with the site.

(7) The Allied Chemical/Ironton Coke Site is currently having a negligible impact on aquatic resources in Ice Creek.

Ice Creek, by its physical nature, is not and will not be a high quality aquatic resource. It does not support a highly diverse benthic macroinvertebrate fauna. The nature of its substrate (i.e., silt) adjacent to the Ironton Coke site and long term, low level stress contribute to its condition. Chemicals from the coke site may contribute marginally to the multitude of stresses on this aquatic system. However, it will be very difficult to separate their impacts from the myriad of other stresses on this ecosystem. A high quality aquatic system supports highly diverse and productive communities of aquatic organism at all trophic levels. If all stressers were eliminated from Ice Creek (i.e., natural and man made), Ice Creek at its best would not be considered a high quality aquatic ecosystem.

It is concluded that very little to no improvement in the value of aquatic life in Ice Creek will be gained by "cleaning up" the Ironton coke site. Chemicals at the site appear at the present time not to be bioavailable. It is doubtful whether an improvement in the aquatic resource could be detected following cleanup of the site. Remedial cleanup of Ice Creek sediments is not recommended. Attempts to remove the sediments containing chemicals from Ice Creek would cause orders of magnitude more harm to aquatic life than leaving them in place. The aquatic resources of Ice Creek are what they are, due primarily to the physical nature of the system rather than to the chemical nature of the environment.

7.2.2 LAGOON STUDIES

The results of Battelle's studies in Lagoon 3 and 4 located on the Site demonstrate that some aquatic organisms can live and reproduce in water which was in intimate contact with the materials in the Site. Both Lagoons 3 and 4 had limited phytoplankton and zooplankton communities. Four genera of zooplankton were present. Protozoa, copepods, and rotifers were collected. Nauplii of a copepod were present. Fish were not present in the lagoons. Chemical analyses of lagoon water showed higher levels of metals, pH, ammonia, conductivity, and hardness than Ice Creek. Acid and base neutral priority pollutants were not detected in water samples from Lagoons 3 or 4. However, sediments from Lagoons 3 and 4 sediments had relatively high concentrations of PAHs. The results of the lagoon studies show that materials in the site are not acutely toxic nor chronically toxic to all forms of aquatic life. The results circumstantially imply a lack of bioavailability of the sediment associated PAHs.

8.0 INTERPRETIVE SUMMARY

The Ironton Coke Plant Site contains a myriad of chemicals, some of which are potentially toxic to humans. A complete evaluation of the toxicity of the mixture of chemicals present at the Site is not possible, because data on the toxicity of the mixture itself are not available. Nonetheless, a fairly detailed estimate of the human health effects can be provided by examining the chemicals on an individual basis and estimating the human health effect from the amount of the chemical likely to leave the Ironton Coke Plant Site and to reach human populations.

The potential exposure of humans to Ironton Coke Plant Site chemicals could occur by a variety of means. Waste materials can be entrained in the air as dust and transported to urban areas where inhalation could occur. Because no significant active manufacturing or disposal is occurring at the Site now, no mechanism exists to disperse the coarse material of the Site in particles small enough to be entrained in the air or to be of respirable size (<10 um diameter particles, but mostly <1 um diameter for respirable dusts). Direct volatilization is also minimal, given the tarry nature of the Site in the Lagoon areas and the soil covering the Goldcamp Dump Site. Thus, direct inhalation of Ironton Coke Plant Site chemicals was not considered. Long distance transport and deposition on food plants grown at places removed from the Site will also not be considered for the same reasons. Since the Ironton Coke Plant Site is secured, no direct contact or cultivation of food plants on the Site is likely for the general population. These potential routes of human exposure were, therefore, also not considered in this analysis.

Ice Creek contains both sediments associated with the Site and groundwater infiltrating from the Site (IT, 1985). The Coal Grove Municipal Water Field draws on water from Ice Creek, the Ohio River, and the Lagoon area (IT, 1985). Thus, humans are potentially exposed mainly *via* drinking water drawn from the Coal Grove Municipal Water Field and the Ohio River. Some ingestion of fish caught in Ice Creek or the Ohio River could also serve as a potential means of exposure, but exposure *via* drinking water would predominate.

Amcast (Dayton Malleable, Inc.) production wells were not considered as potential source receptors in this risk analysis. Subsequent to this effort, however, the Ohio EPA

indicated a need to include data from these sites in an assessment of health risk. Should an evaluation of data from this area be required to complete the overall analysis presented here, further assessment of risk can be provided when such data become available.

This analysis focuses, therefore, on the human health risk through ingestion of drinking water as potentially contaminated by the Ironton Coke Plant Site. Three drinking water sources have been considered as delineated in the IT final report (IT, 1985): the Ohio River, Ice Creek, and the Coal Grove Municipal Water Field. A second part of the analysis addresses the public health risk from the sources themselves. Further analysis of the impact of the Site on Ice Creek as an aquatic resource is also provided.

8.1 POTENTIAL SOURCE AREAS

An inventory of the potential sources and the chemical content of the sources is given in the IT report and is summarized in Chapter 3. The chemicals are of a diverse nature and of widely different physico-chemical properties. To estimate the contribution from different sources, IT chose to model the transport of surrogate compounds (Table H.9, H.10, and H.11; IT, 1985). Since none of the inorganic compounds were found in groundwater, Ice Creek, or Coal Grove Municipal Water Field samples at levels exceeding the EPA Interim Ambient Drinking Water Standards (Tables E.7, D.3, and E.11, respectively), IT did not model their transport. Because of analytical limitations, modeling data form the base for this analysis.

8.2 BIOLOGICAL AVAILABILITY OF LAGOON AND ICE CREEK CHEMICALS

Chemical analyses of Ice Creek and Lagoon sediments present concentrations of several chemicals of particular concern to human health. These chemicals and their toxicity are summarized in Chapters 3 and 4. Accurate chemical analyses, such as those reported in Phase I and II studies, require vigorous extraction with organic solvents or digestion in acids in order to recover completely any chemical which might be present. These vigorous conditions do not apply to biological exposure to these materials. The detection of a chemical in Lagoon or Ice Creek sediments does not necessarily mean that the chemical is available for biological uptake.

The description of the physical state of the Lagoon materials, for example, given in the Phase I and II reports and a physical inspection of these materials *in situ* suggest that the

materials are mixed with tarry substances, are a part of coal fines, or are residues from retorts, coke production, or solid by-products of process streams. For a substance to exert its toxicity on humans or other organisms, the substance must enter the cell. Chemicals enter cells either as soluble materials or as solids. Solids are inactive until they are dissolved by cellular fluids to soluble forms. Hydrophobic substances such as PAHs or heavy metal oxides are not active until solubilized and translocated intracellularly.

In the present case, Ironton Coke Plant Site chemicals are poorly soluble. The Ironton Coke Plant Site chemicals are found in neither water samples from Ice Creek nor the Coal Grove Municipal Water Field (IT, 1985). Fish flesh also did not contain the constituent Site chemicals (Chapter 7). Leaching of Site chemicals from borings was not detectable (IT, 1985), and Site chemicals were not available to the fish or other biota of Ice Creek. Battelle (see Addendum) reported aquatic biota present in the surface water overlying the Lagoons, indicating that the concentrations of these chemicals must be at least below the toxic dose for the species found living and reproducing in the Lagoons. Invertebrates have been used as bioassays for trace toxicants such as pesticides and are often sensitive to toxicants present at ppm ranges. In addition, a large concentration difference exists between the Lagoon materials themselves and the groundwater underlying the Lagoons. These data suggest that the chemicals present in the Lagoons are not readily dissolved in water.

As discussed in Chapter 5, the PAH content of the Lagoon material is of particular concern. These materials are similar in nature to those found in Ice Creek. While fish and other vertebrates do not bioaccumulate PAHs to detectable levels, absorption of PAHs from the sediments or water should have been detected in the biopsy samples of fish. These data further support the hypothesis that Lagoon materials are not readily available.

It should be kept in mind, however, that interpretation of the bioavailability of Lagoon materials is restricted by chemical detection limits for the particular chemicals and samples. Site chemicals could be present at lower concentrations than the detection limits for the methods used. Since the methods used were state-of-the-art, this data deficiency is the minimum currently possible.

8.3 HUMAN HEALTH RISKS FROM SITE CHEMICALS IN DRINKING WATER SOURCES

As pointed out above, the detection limit of the chemical method used for a particular Site chemical restricts interpretation of the health risk associated with that chemical. The dispersion modeling of the Ironton Site by IT (1985) provides an estimate of the chemicals and levels likely to occur in the three possible drinking water sources studied: the Ohio River, Ice Creek, and Coal Grove Municipal Water Field. In all three cases, the contribution of the Site to the chemical was calculated to be less than the detection limit of the chemical method. The health risk analysis has two possible bounds. The upper bound is the detection limit of the chemical method; the lower bound is the model prediction for the chemical concentration in the receptor drinking water. The health risk of each chemical or major class of chemicals is summarized using the model predictions for drinking water source receptor loading as the lower bound and the chemical detection limit as the upper bound.

8.3.1 Estimated Health Risk for Cyanide and Mobile Inorganic Compounds

Ammonia and chloride ion are present in all drinking water sources. The estimated contributions of the Ironton Coke Plant Site to the Ohio River, Ice Creek, and Coal Grove Municipal Water Field are estimated by IT to range from 1.2×10^{-4} to 37 mg/L for chloride and 2.4×10^{-6} to 0.6 mg/L for ammonia (Tables H.9, H.10, and H.11; IT, 1985). Although no drinking water standards are established for these compounds, existing toxicological data indicate these added levels are not biologically significant.

Chemical methods used did not differentiate between the various chemical forms of cyanide compounds. The cyanide potentially present in drinking water is assumed to be primarily present as a soluble cyanide salt such as sodium or potassium cyanide, and the toxicity is assumed to be due to the cyanide content alone.

Systemic toxicity is the major health risk associated with the ingestion of cyanide compounds. No mutagenic, teratogenic, or carcinogenic effects have been reported for cyanide itself. The most significant adverse health effect of cyanide is inhibition of oxidative metabolism and oxidative phosphorylation, resulting in a loss of oxygen utilization by the tissues. Respiratory arrest and death can result in acute poisoning. Chronic effects of cyanide have not been reported.

On the basis of Table H.9 (IT, 1985), the predicted cyanide loading of Ice Creek will result in 0.0005-0.0046 mg/L, with a representative value of 0.0015 mg/L. Cyanide loading for the Coal Grove Municipal Water Field is predicted to result in 0.0024-0.037 mg/L, with a representative value of 0.015 mg/L, while the estimated mass loading for the Ohio River is predicted to result in much lower concentrations of 6.4×10^{-8} to 3.2×10^{-7} mg/L (Table H.10; IT, 1985).

The EPA ambient water quality criterion for cyanide is 0.2 mg/L with an acceptable daily intake of 4.2 mg (U.S.E.P.A., 1980b). The predicted cyanide concentration in all three drinking water sources is roughly one tenth the ambient water quality criterion and would result in a daily intake of about 0.03 mg or about 0.7% of the acceptable daily intake. No interactions with other Ironton Coke Plant Site chemicals are likely to increase the sensitivity of individuals drinking the Coal Grove Municipal Water Field water to cyanide or conversely. Thus, the predicted cyanide levels in all three drinking water sources does not constitute a significant human health risk.

8.3.2 Estimated Health Risk from Phenol and Its Conseners

Phenol and its homologs (primarily cresols and xylenols) are by-products of the coking process and are typically found in tar acids. Phenol is the name given for a group of phenolic compounds, defined as hydroxy derivatives of benzene and its condensed nuclei. Phenol is the most water soluble of these compounds (66 g/L) and is used as a model compound.

Phenols were detected at relatively high concentrations at various sampling points at the Ironton Coke Plant Site, but were not detected in Coal Grove groundwater (IT, 1985). The estimated loading of phenols for the Coal Grove Municipal Water Field from the Site is 0.0034-0.027 mg/L with a representative value of 0.0043 mg/L. The potential mass loading of phenolics for the Ohio River is 1.5×10^{-8} - 7.3×10^{-8} mg/L (IT, 1985). The USEPA ambient water criterion for phenol is 3.5 mg/L (U.S.E.P.A., 1980h).

The estimated mass loading of phenolics into the Ohio River from the Site (IT, 1985) would be insignificant, based on the above water quality criterion. The estimated representative mass loading of phenol into the Coal Grove Water Field (4.3 ug/L) is well below the suggested USEPA criterion of 3.5 mg/L. Phenolics were not detected in the Coal Grove municipal well groundwater (IT, 1985). The phenols could have been

absorbed, biodegraded, or lost through reactions before reaching the Coal Grove Water Field.

8.3.3 Estimated Health Risk from Benzene and Its Congeners

The process at the Ironton Coke Plant Site produced benzene and a series of benzene congeners, including toluene, ethylbenzene, and xylene, as major components. Of these compounds, benzene is of most concern to public health. Toluene, ethylbenzene, and xylene are not metabolized as readily to reactive arene oxides and are not carcinogenic. Benzene is metabolized to a reactive metabolite, which is thought to initiate leukemia in humans (U.S.E.P.A., 1978; N.A.S., 1982).

The mass loading of benzene from the Site to Ice Creek is estimated to result in 0.00001-0.0001 mg/L with a representative value of 0.00004 mg/L (Table H.9; IT, 1985). Concentrations calculated for the Ohio River are lower at 3.6×10^{-9} - 1.8×10^{-8} mg/L with a representative value of 5.2×10^{-9} mg/L (Table H.10; IT, 1985). The estimated benzene concentration in the Coal Grove Municipal Water Field is <0.0003 mg/L (Table H.11; IT, 1985).

No benzene could be detected in the samples from these drinking water sources, nor at the groundwater monitoring site, C-13. The detection limit of the chemical method was estimated to be 1 ppb. Benzene could have been present below this level and undetected in the samples. Following the assumptions in Chapter 6, a lifetime exposure to drinking water containing no more than 1 ppb of benzene is estimated to result in an increased leukemia rate of 11.27×10^{-9} or 0.001 cases per 100,000 population lifetimes. At the estimated benzene loading for the Coal Grove Municipal Water Field, drinking water contaminated with <0.0003 mg/L benzene would be expected to result in 3.38×10^{-9} excess leukemia or 0.0003 cases per 100,000 population lifetimes. Compared to the estimated U.S. leukemia rate of 6-9 cases per 100,000, these estimates suggest that the risk of excess leukemia due to benzene contamination of the Coal Grove Municipal Water Field is not significant and is unlikely to contribute to the overall leukemia rate.

8.3.4 Estimated Health Risk from Polynuclear Aromatic Hydrocarbons (PAHs)

The Ironton Site contains a number of PAHs, some of which are suspected human carcinogens. A wide variety of organ systems are affected by these compounds. Of the PAHs present, benzo(a)pyrene (BaP) is best studied and is present in largest amounts. BaP

can be considered a surrogate for the PAHs present at the Ironton Site. Chemical detection methods of BaP are relatively insensitive compared to its biological potency as a carcinogen. For example, the detection limit for BaP, if present, would represent a tumor risk of 10.71 per 100,000 population lifetimes. Detection of BaP in more complex matrices, such as the fish flesh samples, is poorer than in water. Failure to detect BaP by the best methods approved by EPA does not provide absolute assurance that BaP and other PAHs are not present. The ubiquitous nature of PAHs suggests that they will be present in virtually every environmental sample.

In the present case, PAHs were detected in measurable concentrations in the Lagoon and Ice Creek sediments, but not in fish or water samples. The results are not unexpected, given the very low solubility of BaP and other PAHs in water. BaP and other PAHs also have a high affinity for organic material, and often a concentration difference of 1,000 exists between the BaP content of sediments and the water column overlying the sediments. Fortunately, while fish and other vertebrates accumulate BaP, bioaccumulation through the food chain does not occur due to the rapid metabolism of BaP. Bioaccumulation through the food chain to humans eating fish caught in Ice Creek is not likely.

IT has not provided estimates of the mass loading of Ice Creek or Coal Grove Municipal Water Field for naphthalene or other PAHs, and these compounds were not detected in water samples. Because of their high affinity for sediments, movement of PAHs from the Lagoons to the Coal Grove Municipal Water Field is not likely to occur. Sediment particles containing sorbed PAHs are not likely to pass through the aquifer and into the Coal Grove Municipal Water Field and then into the water distribution system.

Humans exposures to BaP also occur through media other than drinking water (e.g., smoked, roasted or charcoal-broiled food; vegetables; vegetable fats and oils; and air pollutants, including cigarette smoke). The amount of carcinogenic PAHs consumed by man in drinking water has been estimated to be only about 0.1% of the amount accumulated from food. Andelman and Suess (1970) made calculations based on four samples of drinking water and showed annual human consumption of PAHs to be about 9, 22, and 70 ug for the populations served by these water supplies. The 1970 World Health Organization European Standards for Drinking Water (WHO, 1970) recommended that the concentration of total PAHs in drinking water not exceed 0.2 ug/L. Based on a

daily consumption of 2.5 liters for human consumption of drinking water, this concentraton of PAHs would result in the ingestion of 182.5 ug PAH per year. By comparison, smoke from 100 cigarettes (five packs) contains about 264 ug total PAHs and 2.4 ug BaP.

A major uncertainty in this analysis is the insensitivity of the methods of detection compared to the biological potency of the PAHs. Before a better estimate of the associated health risk can be made, more sensitive methods are needed to determine more precisely the actual concentrations likely to be present in Coal Grove Municipal Water. Since the best available EPA approved techniques were used, and since their detection limit are close to those of state-of-the-art (as yet, unapproved) methods, the data deficiency is not likely to be eliminated in the foreseeable future.

At present, a quantitative health risk for PAHs can not be provided, even though the risk appears to be minimal.

8.3.5 Estimated Health Risk from Heavy Metals

None of the water samples presented heavy metal concentrations above the National Interim Primary Drinking Water Standards. Therefore, the human health risk for ingesting this group of compounds is judged to be acceptable.

8.4 HUMAN HEALTH RISK FROM SOURCES

The Phase I and II studies indicate the presence of a large volume of potentially toxic wastes at the Ironton Coke Plant Site. The present physical state of the wastes, particularly those located in the Lagoons and Ice Creek, has reduced their toxicity through low solubility in water and decreased biological availability. The tarry nature of the wastes has tended to produce aggregates of low vapor pressure and has not produced materials likely to be entrained in the air and transported long distances. While certainly not pristine, the Ironton Coke Plant Site is less hazardous to humans and the environment in its present state than if the wastes were excavated in an attempt to move them to some other site. Such operations would result in entrainment of potentially toxic wastes in both air and water and would most likely result in a wide dispersion. The biological availability of the material could also be increased in the process. Containment at the present Site, therefore, is a lower human health risk than relocation.

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Report

AQUATIC ECOLOGICAL STUDIES AT ALLIED CHEMICAL
IRONTON, OHIO, COKE SITE

to

ALLIED CHEMICAL CORPORATION
MORRISTOWN, NEW JERSEY

February 12, 1985

FINAL REPORT

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INTRODUCTION

Industrial development of Allied Chemical's site at Ironton, Ohio, began in the early 1900's with the construction of a coke plant. A tar plant was built adjacent to the coke plant in 1946. Wastes from the coke plant consisted of coke quench waters, coke fines, tar sludges, losses of coal tar oil, and weak ammonia liquer. These wastes and losses were discharged from the plant to an area adjacent to Ice Creek, a tributary of the Ohio River which formed the eastern boundary of the plant site. In the 1970's, Ice Creek was relocated to accommodate construction of a series of lagoons to treat plant waste waters. Dikes were built using site materials including soils and solid wastes from historical operations at the site. Waste constituents which were placed in the lagoons included cyanides, phenolics, chlorides, ammonia, metals, naphthalene, and benzene. The coke plant ceased operations in 1982.

The site has been designated by the U.S. Environmental Protection Agency as a Superfund hazardous waste site and included in the National Priorities List. By agreement with the U.S. EPA and the Ohio EPA, Allied Chemical is conducting a Remedial Investigation/Feasibility Study to determine mitigation alternatives at the site. A Phase I initial site assessment and remedial investigation of the Ironton site has been conducted by D'Appolonia Waste Management Services, Pittsburgh, Pennsylvania (1984). D'Appolonia (IT Corporation) has performed a hydrologic investigation of Ice Creek which included determination of the stream channel profile, stage/flow velocities, discharge and surface water and sediment quality.

Battelle Columbus Laboratories, under contract to Allied Chemical Corporation, has conducted aquatic ecological surveys designed to assess the impacts of the waste materials from site operations on the aquatic biota of Ice Creek. These studies included investigations of the on-site waste lagoons. These studies, their results, and concluding observations on the ecological quality of Ice Creek in relation to Allied Chemical's Ironton coke site are the subject of the following research report.

METHODS

This section presents descriptions of the sampling station locations, the rationale for their selection, and the procedures used to collect and analyze samples and data. All samples were collected during a one-week field survey conducted September 24-28, 1984, at Allied Chemical's Ironton, Ohio, coke site.

Sampling Station Locations

In general, sampling station locations in Ice Creek were the same as those surveyed by IT Corporation in their Phase I investigations (1984). These same sites were chosen in order to expand the existing data base for these sites and to allow comparison and correlation of data. Two additional stations were added to the IT Corporation sites in Ice Creek, one to serve

as a reference site (IC 1) and another to identify effects of what appeared from field observations to be an untreated sewage outfall (IC 6). In total, there were seven locations sampled in Ice Creek. For the lagoon studies, transects in each of the four lagoons were sampled. Locations of all Ice Creek and lagoon sampling stations are shown in Figure 1. Descriptions of these stations are presented in Table 1.

Water Sample Collection

Results of analysis of water samples performed during Phase I investigations (D'Appolonia, 1984) served as a screening for the list of compounds and priority pollutants analyzed during this survey. The final list included acid and base/neutral priority pollutants, cyanide, benzene, chloride, sulfate, and metals (arsenic, selenium, zinc, lead, mercury, and cadmium), and general water quality parameters.

Metals and Cyanide

Water samples were collected at IC 1, IC 6, OR 2, and Lagoons 3 and 4 (Lagoons 1 and 2 were dry). At each station, the water samples were collected prior to the acquisition of sediment and biological samples. The samples were taken mid-channel whenever possible. Water samples were collected by holding the sampling bottle subsurface to the flow of the stream in order to minimize contamination by material in the surface flow. Samples for metals analysis were collected in one-liter Nalgene bottles which had been acid rinsed and air dried. The samples were adjusted to pH 2-3 by the addition of 8M HNO_3. Samples for cyanide analysis were collected in 500 ml Nalgene bottles which had been acid-rinsed, rinsed with reverse osmosis water, and air dried. These samples were adjusted to pH 11-12 with 1N sodium hydroxide. The water samples were stored at 4°C prior to analysis.

Organic Priority Pollutants

Water samples for the analysis of acid and base/neutral priority pollutants as well as benzene, sulfate, and chloride were collected at the

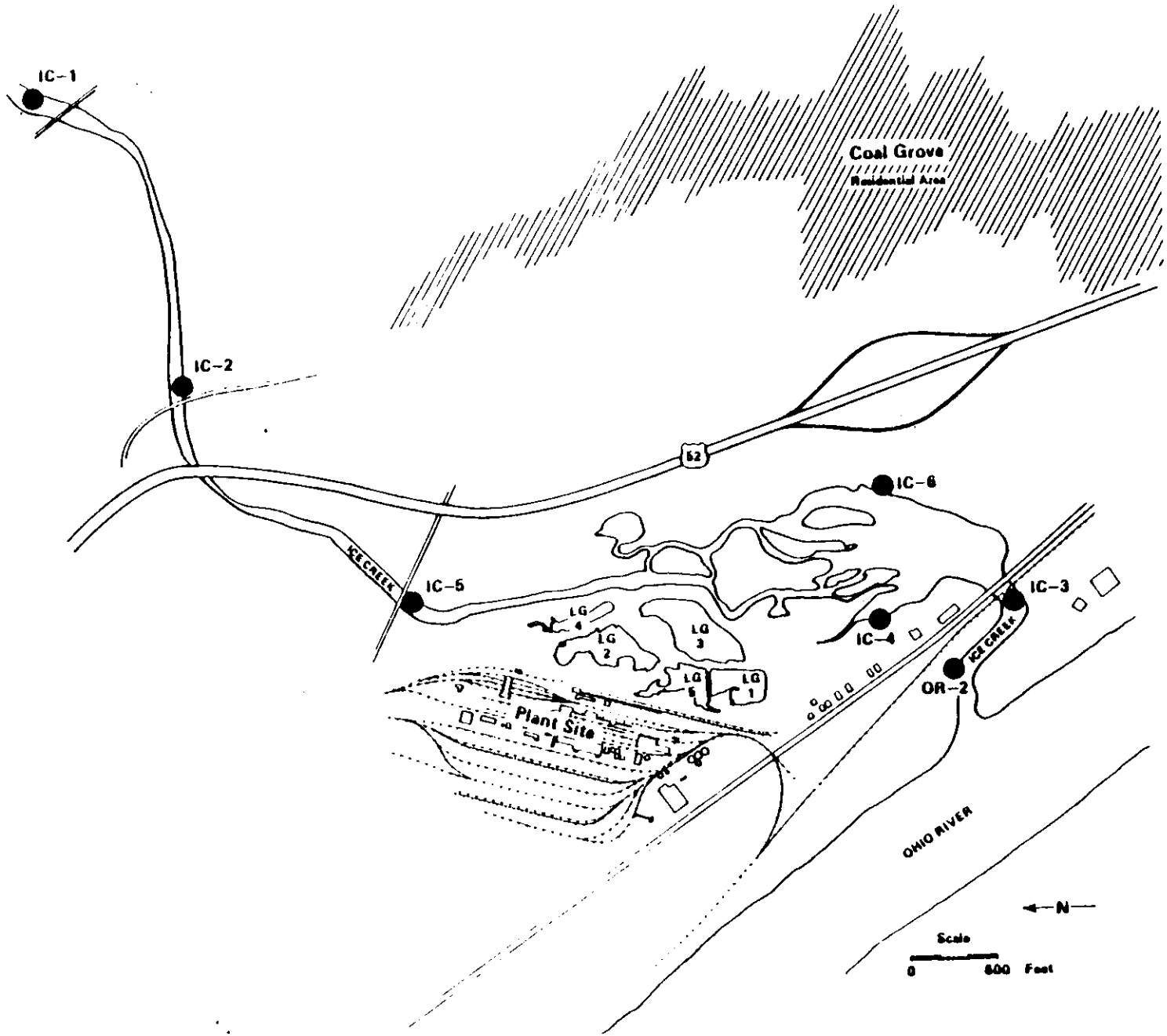

FIGURE 1. LOCATION OF SAMPLING STATIONS AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE

TABLE 1. DESCRIPTIONS OF SAMPLING STATIONS AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE

Station Code	Description
LG 1	Lagoon 1, located in the southwest quadrant of the plant lagoon area; lagoon was dry; steep sides covered with grasses; sediments composed of muck and fine black silty clay.
LG 2	Lagoon 2, located in the northwest quadrant of the plant lagoon area; predominantly dry with a temporary pool in the southeastern section of the lagoon; 15 feet wide by 75 feet long; two feet deep; steep, grass covered banks; oil/tar odor in sediments; black oily muck.
LG 3	Lagoon 3, located in southeast corner of the plant lagoon area; water in southern portion of lagoon, northern half dry; 50 feet wide (E-W); 80 feet long (N-S); 3 feet deep in center; steep, 10 to 12-foot banks with some vegetation; powdery, black coal/coke fines surrounding lagoon; cattails around 60 percent of perimeter; minor colonization of shallow areas with new growth; water dark green in color; sediments composed of shiny, black muck, oily residues; tar odor prevalent.
LG 4	Lagoon 4, located in the northeast quadrant of site; water in southern portion of lagoon only; 30 feet wide (E-W); 60 feet long (N-S); 1 foot deep around edges; soft, grass and weed covered banks approximately 10-12 feet high; very soft coke fines surrounding the lagoon; water with a black cast; fine sand bottom with oily tar; some organic muck; tar odor.
IC 1	Ice Creek 1; reference station approximately 500 yards upstream of cement plant and 200 feet downstream from wooden farm bridge; 20 feet wide, 3 inches-3 feet deep in riffles and pools; steep, wooded, trash-littered banks; 80 percent canopy; no emergent vegetation; sand with some silt/detritus cover; raw sewage odor in places, low flow; red flags tied to trees on shores; new station.
IC 2	Ice Creek 2; 25 feet upstream of the Lorain Street Bridge; immediately downstream of the cement plant; 40 feet side; 2-3 feet deep; sand bar on east bank halfway through channel; steep, wooded banks; sand with some detritus; low flow; red flagging on trees on shore; corresponds to IT Corporation's station IC 2.

TABLE 1. (CONTINUED)

Station Code	Description
IC 5	Ice Creek 5; approximately 100 feet downstream of the Cemetary Street Bridge; 70 feet wide; 3-4 feet deep; water green/brown in color, domestic garbage in stream and on banks; raw sewage odor; 4 to 6-foot wooded banks; fallen logs in stream; fine sand, black muck, detritus; low flow, red flags on trees on shore; corresponds to IT Corporation's station IC 5.
IC 6	Ice Creek 6; east side of slough area, transect from mid-channel island to east bank across slough area from Allied Corporation Lagoon 3; 60 feet wide; 6 inches deep; downstream of an apparently untreated domestic sewage outfall; blue-green sewage effluent concentrated along shoreline; strong anaerobic sewage odor; black organic muck; low flow; new station.
IC 4	Ice Creek 4; west side of slough area, 350 yards downstream of Lagoon 3 outfall; creek 100 yards wide; sampling station 100 feet wide from shore to mid-channel island; 10-12 inches deep; station designed to incorporate former outfall flows; steep, wooded bank; extensive garbage in stream and on bank; odor ranged from anaerobic to tar/petroleum in sediments; sediment ranged from black silt with muck and detritus to black muck with coke fines covered with black oily slick; low to no flow; red flagging tied to in-stream truck axle; corresponds to IT Corporation's station IC 4.
IC 3	Ice Creek 3; immediately (<25 feet) below Third Street Bridge, railroad trestle overhead; 120 feet wide; maximum depth of 10 feet; very steep (25 feet) wooded banks; sewage-storm sewer outfall under bridge; oil and tar on water surface; naphthalene/organic chemical odor in air upstream of bridge and in sediments; sediments composed of soft, brown muck, silt, some detritus; low flow; red flagging on trees on both banks; corresponds to IT Corporation's station IC 3.
OR 2	Ohio River 2; at bend, approximately 100 yards upstream in Ice Creek from its confluence with the Ohio River; 100 feet wide; maximum depth of 8 feet; steep, forested, garbage-strewn banks; brown muck on bottom with some detritus near shore; low flow; red flagging on both banks; corresponds to IT Corporation's station OR 2.

same sampling sites and in the same manner as those for metals and cyanide analyses. The water samples were collected in duplicate at all sites. The samples were collected in 2-L glass jars with Teflon-lined lids. The jars had been hexane rinsed and dried in an oven at 100°C. The samples were kept at 4°C until analysis. One set of the samples along with random duplicates for quality control were sent to Environmental Testing and Certification (ETC) for organic analysis. The other set of samples was analyzed by BCL for benzene, chloride, and sulfate. A field blank, spike, and three random duplicates were taken for quality control.

General Water Quality Parameters

Dissolved oxygen, pH, temperature, conductivity, alkalinity, and hardness measurements of the water samples were performed on the same day of sampling for each site.

Sediment Sample Collection

Sediment samples were analyzed for arsenic, selenium, zinc, lead, mercury, and cadmium and organic priority pollutants.

Metals

Sediment samples were collected for metals analysis at Lagoons 1-4, IC 1-6, and OR 2. The sediments were sampled immediately subsequent to the collection of the water samples.

Three sediment samples were collected along a representative transect the length or width of the sampling site using a petite ponar grab. The three samples were then composited by manual mixing. Aliquots of the sediments were transferred to 1-L Nalgene bottles which had been acid rinsed and air dried. The sediment samples were stored at 4°C prior to analysis.

Organic Priority Pollutants

Sediment samples for the analysis of acid and base/neutral priority pollutants were collected at Lagoons 1-4, IC 1-6, and OR 2. The samples were collected at the same time as the samples for metals analysis.

Samples were collected in 1-liter glass jars with teflon-lined lids. The jars had been rinsed in hexane and oven-dried at 100°C. Random duplicate sediment samples were collected for quality control. All samples were stored at 4°C and sent to ETC for analysis.

Tissue Sample Collection

One means of assessing the impact of the coke site materials on aquatic biota was to analyze for possible bioaccumulation of compounds in fish tissue.

Efforts were made to collect fish at Lagoons 3 and 4, IC 1-6, and OR 2. The fish samples were collected subsequent to the collection of water, sediment, and invertebrate samples at each site. Fish were collected utilizing minnow buckets in the lagoons and electroshocking and seining in the creek.

Whenever possible, sport fish specimens of such size as to be potentially edible by humans were taken for tissue analysis. For these specimens (i.e. large catfish and bass), the whole edible portion (including skin) was taken for analysis. When sufficient sport fish were not found at a station, the dominant species was taken. For these samples, whole, gutted specimens (greater than 7 cm) were used. The digestive tract and its contents were removed to avoid contamination of tissue with sediment. For the smaller fish (i.e. bluegills and carp), several specimens had to be composited to provide sufficient sample volume for analysis. An attempt was made to collect three specimens each of three species per station. In order to have at least one tissue sample type consistent for all stations for comparative purposes, juvenile and young-of-the-year bluegills were taken at all locations and small (less than 6 cm) gizzard shad at most locations. Because these small fish are eaten whole by larger fish, their gut contents also would be ingested and would provide a source for bioaccumulation of sediment materials. Therefore, the small fish were composited whole.

All fish samples were homogenized. Each sample was divided into two aliquots. One aliquot was placed in a 1-liter glass, hexane-rinsed, oven-dried jar for priority pollutant analysis. The other aliquot was placed in an acid-rinsed 25 ml Nalgene bottle for metals analysis. Random duplicates were processed for quality control. All samples were held at 4°C prior to analysis. The samples for priority pollutant analyses were sent to ETC; samples for metals analyses were sent to Battelle.

Biological Sample Collection

Biological communities in Ice Creek and Lagoons 3 and 4 were surveyed in order to detect ecological impacts attributable to the coke site's former operations. Sampling locations were chosen upstream and downstream of the site in an attempt to isolate effects due solely to previous discharges and/or current leaching from the lagoon area. Other sampling stations were located in Ice Creek to identify other sources of potential contamination (i.e. a cement plant, raw sewage inputs, a drain from a tank truck terminal) and to define the reference system upon which to determine the nature and extent of impacts of the coke site.

Phytoplankton, zooplankton, aquatic macrophytic plants, fish, and benthic invertebrates were sampled in the two lagoons. Fish and invertebrates also were collected at seven stations in Ice Creek.

Phytoplankton and Zooplankton

Phytoplankton and zooplankton were sampled at Lagoons 3 and 4. For each sample, five liters of water drawn from the middle of each lagoon were poured through a plankton net. The plankton were rinsed into a 250 ml Nalgene bottle. The two samples for each lagoon were preserved with 1 ml of a 30-percent formaldehyde solution. All samples were taken to BCL for identification and quantification. Plants and organisms were identified to the lowest practicable taxon (usually genus) using appropriate taxonomic keys (Edmonson, 1959; Prescott, 1975; Smith, 1950).

Aquatic Macrophytic Plants

Emergent aquatic plants were collected from accessible shoreline areas of the lagoons. Visual estimates of percent composition were made. The plants were placed in a polyethylene bag and kept at 4°C. The plants were then identified to the lowest practicable taxon (genus) using appropriate taxonomic keys (Edmonson, 1959).

Benthic Macroinvertebrates

Benthos samples were collected at Lagoons 3 and 4 and each of the Ice Creek stations. Five grab samples were taken from representative habitat types at each station with a petite ponar grab. In addition to this quantitative sampling, qualitative collections were made either by hand, using a 40-mesh U.S. Standard soil sieve, or by using a D-frame bottom net. All benthic organisms were separated from debris in the field using U.S. Standard 40-mesh sieves. Organisms were placed in 25-ml sample bottles and preserved with 2 ml of 100 percent isopropyl alcohol. Substrate types were described on a data sheet for each sample. All samples were taken to BCL for enumeration and identification. Organisms were identified to genus using appropriate keys (Brigham et al., 1982; Edmonson, 1959; Merritt and Cummins, 1978; Pennak, 1953; Hilsenoff, 1975; Usinger, 1971). Shannon-Weaver and Brillouin's diversity indices were calculated for the quantitative data.

Fish

Fish were sampled in Lagoons 3 and 4 using minnôw buckets which were allowed to remain for 24 hours. Collection of fish in Ice Creek at stations IC 2-6 and OR 2 was carried out using an electroshocker. Fish were sampled at IC 1 with a 6 x 8-foot seine with a ¼-inch mesh. A 30-minute sampling effort was conducted at each station to allow comparison of catches between stations. Stations IC 3 and OR 2 were located less than one-quarter mile apart in Ice Creek (see Figure 1). This section of stream was sampled as one zone (OR 2) and the data combined. Because the proximity of the two stations and the mobility of fish, no difference in the fish communities

at the two stations would be expected. Fish specimens were identified in the field, numbers and species recorded, adults measured, and returned to the stream. Representative individuals of each species at each station were preserved for reference and to verify taxonomy. These samples were preserved in 50 percent isopropyl alcohol and were taken to BCL for identification. Specimens were identified using Trautman (1957).

Specimens taken for tissue analyses were identified, enumerated, weighed and sized, placed in plastic bags and held on ice until further processing in the field laboratory.

General observations of fish health and condition were made at the time of collection and during laboratory processing. Condition factors were calculated for the major species (i.e. sport fish and dominant species) using methods described by Carlander (1969), Bennett (1970), and Nielson and Johnson (1983).

Analytical Methodology

The analytical methods used to quantitatively determine Zn, Cd, Pb, As, Hg, Se, CN, Cl, SO_4, benzene, and the acid and base/neutral priority pollutants in the environmental samples collected in the vicinity of the Ironton coke site are summarized in Table 2. Additional information for certain of these determinations is presented in the following paragraphs. Quality control/quality assurance procedures implemented in performing these analyses are described in Appendix I.

Cyanide (CN)

The distillates were found to be free of sulfide interference. The CN concentrations were determined using a HNU Systems CN electrode (ISE-30.13) in conjunction with an Orion digital analyzer (601A).

Chloride (Cl) and Sulfate (SO_4)

A Vydac anion column (302 IC 4.6) was used with a Varian 5020 HPLC equipped with a Varian conductivity detector. Samples were prefiltered through

TABLE 2. ANALYTICAL METHODS

Parameter	Method	Reference
Zinc (Zn)	Flame, atomic absorption, EPA Method 289.1	US EPA, 1979
Cadmium (Cd)	Graphite furnace, atomic absorption, EPA Method 213.2	US EPA, 1979
Lead (Pb)	Graphite furnace, atomic absorption, EPA Method 239.2	US EPA, 1979
Arsenic (As)	Graphite furnace, atomic absorption, EPA Method 206.2	US EPA, 1979
Selenium (Se)	Graphite furnace, atomic absorbtion, fish and sediment EPA Method 270.2* Gaseous hydride, atomic absorption, water EPA Method 270.3	US EPA, 1979 US EPA, 1979
Mercury (Hg)	Cold vapor, atomic absorption, EPA Method 245.1*	US EPA, 1979
Cyanide (CN)	Distillation, CN electrode, Method 412 E	APHA, et al., 1980
Chloride (Cl)	Reverse phase high pressure liquid chromatography, anion column	Fritz, 1982
Sulfate (SO_4)	Reverse phase high pressure liquid chromatography, anion column	Fritz, 1982
Benzene	Solvent extraction, gas chromatography	Mieure, 1980 Otson, 1979 US EPA, 1982
Acid and Base/ Neutral Priority Pollutants	Solvent extraction, gas chromatography/mass spectrometry, EPA Method 625**	US EPA 1979

*Stilson Laboratories

**ETC Corporation

0.22 µm Millipore filters. The mobile phase was 0.002 M phthalic acid (pH to 5.4 with sodium borate). Sample size was 100µl.

Benzene

One liter samples were extracted with 10 ml of hexane at 4°C for 24 hours (magnetic stirring). The hexane was removed and analyzed for benzene using a Varian GC 3700 equipped with FID detector. The column employed was a 5 percent SP-1200/1.75 percent Bentone 34 on 100/120 Supelcoport, 6' x 1/8" SS. A calibration curve was prepared by extracting one liter samples of Barnstead water spiked with 2, 4, and 10 ug of benzene and analyzing the hexane extract in a manner identical to that used for the environmental samples.

Metals

All samples were digested for total metal content. Water samples were digested as received. A representative subsample of wet sediment was taken from each sample and air dried. Approximately one gram (accurately weighed) of the dry sediment was then digested.

Tissue samples were received as homogenates. The entire tissue sample from each site was placed into the digestion beaker, weighed, dried (40°C) and then reweighed prior to digestion. A nitric acid digestion (EPA, 1979) modified with sulfuric acid for tissue analysis (Kramer, 1983; Boush, 1983) was employed.

Acid, Base/Neutral Priority Pollutants

The methods employed in the GC/MS analysis for priority pollutants are established EPA methods. Rigid compliance with the instrument parameters and performance criteria of the published methods was achieved. In some cases, the precise amounts of sample used and the sample handling procedures vary with the complexity of the sample matrix. Qualitative identification of the priority pollutants was performed using the relative retention time, the relative abundance of three characteristic ions and the abundance ratio

The entire mass spectrum was reviewed to confirm each identification. Quantitative analysis of detected compounds was performed by using a response factor generated by a major characteristic ion of the specific compound and an internal standard.

Water. For the analysis of the acid and base/neutral priority pollutants in an aqueous liquid matrix, EPA Method 625 (Federal Register, December 3, 1979; page 69540) was used. Approximately one liter of sample was adjusted to a pH greater than 11 and extracted with methylene chloride. The pH of the sample was adjusted to a value less than 2 and extracted with an aliquot of fresh methylene chloride. A separatory funnel or continuous extractor was used to perform the extractions. The two extracts were dried and concentrated to a 1 ml final volume. Each extract was injected into a GC/MS instrument specifically configured for the correct fraction.

Sediment. EPA Method 625 (Federal Register, December 3, 1979; page 69540) also was used for the analysis of the acid and base/neutral priority pollutants in a soil matrix. A 30 gm semi-wet soil sample was Soxhlet extracted with a 1:1 mixture of acetone and hexane. The acetone was thermally stripped. The remaining hexane extract was diluted to 200 ml with methylene chloride and twice extracted with an aqueous NaOH solution followed by an extraction with deionized water. The methylene chloride extract was dried and concentrated to a 1 ml final volume. This concentrate was injected into a GC/MS instrument configured for the analysis of base/neutral priority pollutant compounds. The remaining aqueous extracts were combined and the pH adjusted to a value less than 2. The aqueous phase was serially extracted with 3 aliquots of methylene chloride. The methylene chloride extracts were dried and concentrated to a 1 ml final volume. The concentrate was injected into a GC/MS instrument configured for the analysis of acid extractable priority pollutant compounds.

Fish Tissue. For the analysis of the acid base/neutral priority pollutants in a fish matrix, a 20 gm semi-wet sample was Soxhlet extracted with a 1:1 mixture of acetone and hexane. The acetone was thermally stripped. The remaining hexane extract was diluted to 200 ml with methylene chloride and twice extracted with an aqueous NaOH solution followed by an extraction with deionized water. The methylene chloride extract was dried and concentrated to a 1 ml final volume. This concentrate was injected into

a GC/MS instrument configured for the analysis of base/neutral priority pollutant compounds. The remaining aqueous extracts were combined and the pH adjusted to a value less than 2. The aqueous phase was serially extracted with 3 aliquots of methylene chloride. The methylene chloride extracts were dried and concentrated to a 1 ml final volume. The concentrate was injected into a GC/MS instrument configured for the analysis of acid extractable priority pollutant compounds.

RESULTS AND DISCUSSION

The following sections present the results of analyses of samples collected in the vicinity of the Ironton, Ohio, coke site during the September 24-28, 1984, survey.

Chemical Analyses

Results of chemical analyses of environmental concentrations of compounds or elements of concern are presented for water and sediment samples. Whenever possible, results are compared to existing environmental guidelines or criteria. Results of tissue analyses are presented in a later section dealing with the results of the biological surveys.

Water

Field measurements of physical water quality parameters generally showed no unusual values for any of the parameters measured (Table 3). Ammonia and specific conductance were an order of magnitude higher in Lagoon 3 than at any other station sampled. Ammonia is elevated over background in Ice Creek waters and exceeds criteria at stations IC 4, IC 6, IC 3, and OR 2. The likely source of the increase is from the domestic sewage outfall immediately upstream of IC 6. Some of the ammonia may be coming from the lagoons, but the highest in-stream levels are immediately below the sewage outfall (IC 6). Further augmentation occurs in the storm water/sewage outfall under the Third Street Bridge at IC 3.

TABLE 3. PHYSICAL WATER QUALITY PARAMETERS MEASURED AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE, SEPTEMBER 24-27, 1984

Station	Dissolved Oxygen (mg/l)	pH	Temperature (°C)	Specific Conductance (μmhos/cm)	Alkalinity (mg/l $CaCO_3$)	Total Hardness (mg/l $CaCO_3$)	Ammonia (mg/l NH_3-N)
LG 3	9.1	8.6	20.3	1193	40	544	12.5 (0.18)[b]
LG 4	9.3	8.3	21.0	741	52	336	0.86 (0.18)
IC 1	8.8	7.3	19.0	548	108	252	0.003 (1.6)
IC 2	8.9	7.6	19.1	562	116	224	0.04 (1.6)
IC 5	6.7	7.3	19.6	650	116	288	0.101 (1.6)
IC 6	3.6	7.4	18.9	618	160	236	3.10 (1.6)
IC 4	9.8	7.3	25.4	502	88	180	1.6 (1.1)
IC 3	9.4	7.0	25.2	438	52	168	6.4 (3.5)
OR 2	8.8	7.2	25.6	411	172	124	5.5 (3.5)
Aquatic Life Criteria[a]	---	6.5-9.0	---	---	> 20	---	0.020[c]

(a) Source: EPA, 1976 and 1980.

(b) Approximate criterion at pH and temperature of sample, total ammonia.

(c) As un-ionized ammonia.

Chemical analyses for the priority pollutants and other parameters measured indicate that no environmentally adverse level for any of these parameters was found (Tables 4 and 5). For those compounds or ions for which Water Quality Criteria have been established (EPA, 1976), none was found in concentrations exceeding the criterion level. In fact, most of these parameters were either below-detection-limit or in concentrations well below the maximum permissible values. In general, the lagoon waters had slightly higher arsenic and SO_4 (Cl in Lagoon 3) levels than did the waters of Ice Creek. This might be expected considering the history of the lagoons. The higher levels of arsenic in Lagoons 3 and 4 and at the Third Street Bridge suggests possible contamination of Ice Creek at this point from the lagoons and/or the sewage outfalls. There are no other significant, discernable differences between lagoon and Ice Creek waters.

Sediments

No firmly established sediment quality criteria exist; therefore, it is difficult to discuss the environmental significance of the values obtained for metal levels in the sediments taken from Ice Creek and the lagoons. Arbitrarily, two comparisons have been made: (1) the data from this study were contrasted with the EPA Region V guidelines for pollutional classification of sediments (JRB Associates, 1984) and (2) the results of this study were compared with values listed as average abundances of trace elements in sediments (Brooks, 1977). The following table summarizes the metal concentrations from these sources that are pertinent to this study.

TABLE 6. SEDIMENT CONCENTRATIONS OF TRACE ELEMENTS (µg/g)

	EPA Region V Guidelines[a]	Average Abundance in Sediments
Arsenic	3	6.6
Cadmium	6	0.5
Lead	40	20
Mercury	1	0.04
Selenium	--	0.6
Zinc	90	80

(a) Level is regarded as cut-off between non-polluted and moderately polluted sediment.

TABLE 4. RESULTS OF CHEMICAL ANALYSES OF WATER SAMPLES COLLECTED IN ICE CREEK AND LAGOONS 3 AND 4 AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE, SEPTEMBER 24-26, 1984

Station	Zinc ug/L	Cadmium ug/L	Lead ug/L	Arsenic ug/L	Mercury[a] ug/L	Selenium ug/L	Cyanide mg/L	Benzene ug/L	Chloride mg/L	Sulfate mg/L
LG 3	75	< 0.8	6.9	5.4	< 1.0	6.0	< 0.10	< 0.10	118.6	424.2
LG 4	77	1.8	7.5	5.0	< 1.0	0.6	< 0.10	< 0.10	15.1	319.2
IC 1	48	1.3	11.4	< 2.0	< 1.0	< 0.5	< 0.10	< 0.10	27.6	152.2
IC 2	26	0.8	9.4	< 2.0	< 1.0	< 0.5	< 0.10	< 0.10	27.3	151.4
IC 5	22	< 0.8	11.6	< 2.0	< 1.0	< 0.5	< 0.10	< 0.10	32.0	193.1
IC 6	87	< 0.8	8.0	3.1	< 1.0	< 0.5	< 0.10	< 0.10	69.0	106.7
IC 4	56	< 0.8	6.7	< 2.0	< 1.0	< 0.5	< 0.10	< 0.10	36.3	78.2
IC 3	34	< 0.8	4.5	4.0	< 1.0	< 0.5	< 0.10	< 0.10	32.1	78.4
OR 2	36	< 0.8	6.9	3.6	< 1.0	< 0.5	< 0.10	< 0.10	100.5	76.6
Aquatic Life Criteria[b]	180-570[c]	0.4-12.0[c]	74-400[c]	440	0.0017	260	0.052	---	---	---

(a) Stilson Laboratories, Columbus, Ohio.

(b) Source: EPA, 1976 and 1980.

(c) For hardness range of 50-200 mg/l.

ETC ENVIRONMENTAL TESTING and CERTIFICATION

TABLE 5. DATA MANAGEMENT SUMMARY REPORT, WATER SAMPLES

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Chain of Custody Data Required for ETC Data Management Summary Report

See Below	BATTELLE COLUMBUS LABS	BATCOLUM	See Below	
ETC Sample No.	Company	Facility	Sample Point	Date

Parameters	Units	Sample Points, Sampling Dates, and ETC Sample No.'s							
		LG3 840929 F6769	LG4 840929 F6770	IC1 840929 F6771	IC2 840929 F6772	IC3 840929 F6773	IC4 840929 F6774	IC5 840929 F6775	IC6 840929 F6776
PP Base/Neutral Compounds									
bis(2-Ethylhexyl)phthalate	ug/l	ND	ND	ND	ND	ND	ND	ND	ND
Pyrene	ug/l	ND	ND	ND	ND	ND	ND	ND	ND

Footnotes: BMDL=Below Method Detection Limit ND=Parameter not detected '-'=Parameter not tested

TABLE 5. (CONTINUED)
WATER SAMPLES

Chain of Custody Data Required for ETC Data Management Summary Report

See Below	BATTELLE COLUMBUS LABS	BATCOLUM	See Below	
ETC Sample No.	Company	Facility	Sample Point	Date

Parameters	Units	Sample Points, Sampling Dates, and ETC Sample No.'s							
		IC7 840929 F6777	IC8 840929 F6778	IC9 840929 F6779	IC10 840929 F6780	IC11 840929 F6781	OR2 840929 F6782		
PP Base/Neutral Compounds									
bis(2-Ethylhexyl)phthalate	ug/l	ND	ND	ND	17	ND	ND		
Pyrene	ug/l	ND	ND	ND	22	ND	ND		

Footnotes: BMDL=Below Method Detection Limit ND=Parameter not detected '-'=Parameter not tested

02

Levels of arsenic are all essentially below background at all sites and exceed the Region V guidelines slightly in only two sites in Ice Creek and in Lagoons 3 and 4 (Table 7). Cadmium is below Region V guidelines at all stations and only slightly above the literature background level at most of the sites. Lead is well below both Region V and background figures. Mercury is below the EPA guidelines except for Lagoons 2 and 3 (detection limits prevent comparison with the low background figure reported in Table 6). Zinc is two-to-three times higher than both EPA guidelines and background values at nearly all sites. Since no guideline is given for selenium and the analytical detection limit was high, it is impossible to comment on this element. Thus, the sediments are relatively non-polluted with trace metals with the possible exception of moderate pollution by mercury in Lagoons 2 and 3. The high zinc levels found at all sites probably reflect local geoabundance of this element.

Acidic and Base/Neutral Priority Pollutants. As mentioned with the metals, no firmly established sediment quality criteria exist for the organic priority pollutants. It is more difficult to discuss the environmental impact of the levels of the organic compounds detected in this study than for the metals, since little or no sediment background data exist. Organic carbon content of the sediments as well as sediment-water distribution coefficients for these compounds are not known. Therefore, only general statements about the concentrations detected may be made.

No acidic compounds were detected; all sediments apparently are non-polluted with these materials. There are high concentrations of a number of PAH's (polynuclear aromatic hydrocarbons) in both lagoon and Ice Creek sediment samples (Table 8). Lagoon 4 clearly is the most polluted station sampled with reference to the PAH's. The high levels of PAH's in the sediments of the Third Street Bridge station immediately below the lagoon sites probably reflects contamination of Ice Creek, at this point at least, from materials (PAH's) in the lagoons. Levels found at OR 2 are reduced by at least ar order of magnitude, or to below method detection levels.

TABLE 7. RESULTS OF CHEMICAL ANALYSES OF SEDIMENT SAMPLES COLLECTED IN ICE CREEK AND LAGOONS 3 AND 4 AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE, SEPTEMBER 24-26, 1984[a]

Station	Zinc ug/g	Cadmium ug/g	Lead ug/g	Arsenic ug/g	Selenium[b] mg/g	Mercury[b] ug/g
LG1 B	145.5	1.1	3.8	2.6	< 0.2	< 0.2
LG2 B	243.1	1.4	16.6	< 2.0	< 0.2	1.0
LG3 B	339.8	1.2	14.2	4.3	< 0.2	2.8
LG4 B	215.5	1.4	16.6	4.0	< 0.2	0.5
IC1 B	17.8	< 0.4	3.4	3.4	< 0.2	< 0.2
IC2 B	34.1	0.4	3.4	3.6	< 0.2	< 0.2
IC5 B	274.8	0.5	3.6	< 2.0	< 0.2	< 0.2
IC6 B	231.7	0.6	9.7	< 2.0	< 0.2	< 0.2
IC4 8A	99.4	0.5	8.6	1.8	< 0.2	< 0.2
IC4 8B	189.5	0.5	5.6	2.4	< 0.2	< 0.2
IC3 B	215.6	0.8	15.4	6.8	< 0.2	< 0.2
OR2 B	300.6	0.9	13.8	2.1	< 0.2	< 0.2

(a) All values reported for dry weight.

(b) Stilson Laboratories, Columbus, Ohio.

ETC ENVIRONMENTAL TESTING and CERTIFICATION

TABLE 8. DATA MANAGEMENT SUMMARY REPORT, SEDIMENT SAMPLES

Chain of Custody Data Required for ETC Data Management Summary Report

See Below ETC Sample No. | BATTELLE COLUMBUS LABS (Company) | BATCOLUM (Facility) | See Below Sample Point | See Below Date

Parameters	Units	Sample Points, Sampling Dates, and ETC Sample No's							
		LG1 840929 F6783	LG2 840929 F6784	LG3 840929 F6785	LG4 840929 F6786	IC1 840929 F6787	IC2 840929 F6788	IC3 840929 F6789	IC4 840929 F6790
PP Base/Neutral Compounds									
Acenaphthene	ug/kg	BMDL	BMDL	4010	BMDL	ND	ND	15400	ND
Anthracene	ug/kg	4050	BMDL	6010	21100	BMDL	ND	9260	BMDL
Benzo(a)anthracene	ug/kg	66900	16700	ND	198000	592	ND	104000	3360
Benzo(a)pyrene	ug/kg	57500	8130	9940	90800	BMDL	ND	49900	ND
Benzo(b)fluoroanthene	ug/kg	59300	10100	15500	90100	BMDL	ND	44700	ND
Benzo(ghi)perylene	ug/kg	84300	9280	13400	82200	ND	ND	39000	ND
Benzo(k)fluoranthene	ug/kg	39000	4300	7510	60800	BMDL	ND	43600	BMDL
bis(2-Ethylhexyl)phthalate	ug/kg	ND	ND	BMDL	ND	400	ND	BMDL	ND
Chrysene	ug/kg	37200	8700	13100	90300	BMDL	ND	44200	BMDL
Dibenzo(a,h)anthracene	ug/kg	19300	ND	BMDL	BMDL	ND	ND	14400	ND
Fluoranthene	ug/kg	32300	13800	31200	340000	559	ND	57100	3650
Fluorene	ug/kg	3690	3770	11200	BMDL	ND	ND	9660	ND
Indeno(1,2,3-c,d)pyrene	ug/kg	59200	5350	7570	54300	BMDL	ND	31900	ND
Naphthalene	ug/kg	42700	29600	52600	44200	BMDL	ND	92500	BMDL
Phenanthrene	ug/kg	18200	12600	22100	83400	436	ND	38700	BMDL
Pyrene	ug/kg	24500	12000	25100	100000			43500	BMDL

Footnotes: BMDL = Below Method Detection Limit ND = Parameter not detected --- = Parameter not tested

TABLE B. (CONTINUED),
SEDIMENT SAMPLES

Chain of Custody Data Required for ETC Data Management Summary Report

See Below	BATTELLE COLUMBUS LABS	BATCOLUM	See Below
ETC Sample No.	Company	Facility	Sample Point Date

Parameters	Units	Sample Points, Sampling Dates, and ETC Sample No's							
		IC5 840929 F6791	IC6 840929 F6792	IC7 840929 F6793	IC8 840929 F6794	IC9 840929 F6795	OR2 840929 F6796		
PP Base/Neutral Compounds									
Acenaphthene	ug/kg	ND	BMDL	10500	BMDL	BMDL	BMDL		
Anthracene	ug/kg	ND	BMDL	5730	BMDL	ND	BMDL		
Benzo(a)anthracene	ug/kg	ND	ND	57700	BMDL	ND	11600		
Benzo(a)pyrene	ug/kg	ND	ND	23900	ND	ND	4020		
Benzo(b)fluoroanthene	ug/kg	ND	ND	22100	ND	ND	5860		
Benzo(ghi)perylene	ug/kg	ND	ND	18100	ND	ND	3850		
Benzo(k)fluoranthene	ug/kg	ND	ND	20700	ND	ND	BMDL		
bis(2-Ethylhexyl)phthalate	ug/kg	ND	ND	ND	BMDL	ND	ND		
Chrysene	ug/kg	ND	ND	25600	BMDL	ND	6000		
Dibenzo(a,h)anthracene	ug/kg	ND	ND	5300	ND	ND	ND		
Fluoranthene	ug/kg	BMDL	BMDL	37800	3340	ND	8750		
Fluorene	ug/kg	ND	ND	6460	ND	ND	BMDL		
Indeno(1,2,3-c,d)pyrene	ug/kg	ND	ND	13800	ND	ND	BMDL		
Naphthalene	ug/kg	ND	ND	72000	ND	BMDL	BMDL		
Phenanthrene	ug/kg	BMDL	BMDL	26000	BMDL	BMDL	5650		
Pyrene	ug/kg	BMDL	BMDL	28400	BMDL	BMDL	7010		

Footnotes: BMDL=Below Method Detection Limit ND=Parameter not detected "-"=Parameter not tested

Biological Surveys

Biological surveys of existing aquatic communities were conducted in Lagoons 3 and 4 and at seven stations in Ice Creek. Lagoons 1 and 2 are normally dry and do not retain sufficient runoff to support an aquatic community.

Lagoons

Plankton. Water quality in both Lagoons 3 and 4 was apparently sufficient to support both plant and animal life in the water column. The compositions of the phytoplankton (floating algae) communities in both lagoons was similar (Table 9). The dominant species in both cases was the blue-green algae, Anabaena. Growth of the species in Lagoon 3 was particularly abundant, approaching a "bloom" condition. Water in this lagoon was green in color at the time of the survey (see Table 1). Density of cells per milliliter in Lagoon 3 was approximately 80 times greater than in Lagoon 4. Lagoon 3 is apparently receiving enrichment input which is not simultaneously available to Lagoon 4.

Both lagoons also supported limited zooplankton communities (Table 10). A total of four genera were found in Lagoon 3; a total of five in Lagoon 4. The most abundant organism in Lagoon 3 was a ciliated protozoan, Bursaria. Also dominant in Lagoon 3 was an immature stage of copepod, probably Cyclops. Rotifers were the dominant organisms in Lagoon 4 with Pleurotrocha being the most abundant. There was a relatively large number of copepod nauplii in this lagoon, also. Density of organisms was about three times greater in Lagoon 4 than in Lagoon 3. Water quality is suitable for reproduction of copepods, evidenced by nauplii, in both lagoons.

Emergent Aquatic Vegetation. Shorelines of both Lagoons 3 and 4 supported stands of cattail, Typha latifolia. In Lagoon 3, approximately 60 percent of the shoreline was colonized by cattail in stands extending 1-3 feet from shoreline, representing about 17 percent occupancy of the pond. Stands in Lagoon 4 were much sparser, covering no more than 10 percent of the perimeter, or about 3 percent occupancy of Lagoon 4. In both ponds, minor colonization of shoreline by beak rush, Rynchospora, was noted; less

TABLE 9. PHOTOPLANKTON COLLECTED IN LAGOONS 3 AND 4 AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE, SEPTEMBER 24, 1984

	LG 3 Number/Field										Cells/l	LG 4 Number/Field										Cells/l
	1	2	3	4	5	6	7	8	9	10		1	2	3	4	5	6	7	8	9	10	
CHLOROPHYTA																						
Chlorogonium						2	1	1	1		1.46×10^3	*									1	1.67×10^3
Pediastrum	1		1														1		6			
Rhizoclonium	18	8	5	8	23	13	4	9	15	4	2.23×10^3	*										2.08×10^2
Spirogyra							1				4.16×10^2	1										
Ulothrix				1																		
CYANOPHYTA																						
Anabaena	24	18	60	1700	1400	2500	2700	1900	1600	1800	3.70×10^6	*	18	22	30		23	10	19	12	16	3.12×10^4
Lyngbya	*														1				1			4.16×10^2
Microchaete											2.08×10^2		12					6	4	1	7	6.25×10^3
Nostoc	1										3.30×10^3											
Spirulina		4	1	1	1	1	2	2	1	3												
CHRYSOPHYTA															1		1					4.16×10^2
Diploneis											2.08×10^2						2			1		6.25×10^2
Fragilaria			1							1	2.08×10^2		1	1		2		1				1.04×10^3
Gomphonema	2		1								6.25×10^2					4						8.30×10^2
Melosira																				1	1	1.25×10^3
Oscillatoria	2	2		1	2	1	3		3		2.91×10^3	1	3									
EUGLENOPHYTA																						
Euglena	1										2.08×10^2								1		1	4.16×10^2
Number of Genera	7	4	6	5	4	5	6	4	5	4		3	4	2	3	2	4	4	4	4	5	

*Identified in sample but not seen in count.

TABLE 10. ZOOPLANKTON COLLECTED IN LAGOONS 3 AND 4 AT ALLIED CHEMICAL'S IRONTON, OHIO, COKE SITE, SEPTEMBER 24, 1984

	LG 3				LG 4			
	Count/Strip			Organisms/L	Count/Strip			Organisms/L
	1	2	3		1	2	3	
CLADOCERA	*				*			
Daphnia								
Moina					*			
COPEPODA	3	3	1	14	1			2
Cyclops	1	1		4	3	4	9	32
--copepodite	7	2	8	34	23	36	26	170
--nauplii					3	7	6	32
ROTIFERA					1		1	4
Pleurotrocha								
Polyarthra								
Keratella	1		2	6				
Asplanchna								
CILIOPHORA	6	7	10	46				
Bursaria					4	3	4	
Number of Genera	3	2	3					

*Identified in sample but not seen in the strip counts.

than 5 percent shoreline (or less than 1 percent occupancy) in Lagoon 3 and only occasional growth, less than one percent (less than 1 percent occupancy) in Lagoon 4. Banks of both lagoons were vegetated with predominant growths of smartweed, Polygonum; however, in neither lagoon was this plant found rooted under water.

In neither of the lagoons was there any other macrophytic growth. Observed growth was in areas of pond shorelines where substrates had begun to stabilize.

Benthic Macroinvertebrates. Compositions of benthic fauna in the lagoons were dissimilar at the time of the surveys (Table 11). Lagoon 3 supported an abundant population of tubificids (aquatic earthworms), a species indicative and tolerant of organic pollution. The other organisms present in Lagoon 3 were chironomid (midge) larvae, which are also tolerant of organic pollution and low oxygen concentration.

In Lagoon 4, the most abundant organisms were snails, Physa (Table 11). However, all snails found in this lagoon were dead when collected. Other organisms in Lagoon 4 were beetles (Coleoptera) and dragonfly nymphs (Libellulidae). Both of these types of organisms were associated with the shoreline vegetation.

Because of the inaccessibility of Lagoon 4, all sampling was conducted along the shoreline. Samples from Lagoon 3, however, were collected from a boat which permitted sampling of all available habitat types in the lagoon. Differences in species composition of the two lagoons can be attributed as much to physical habitat differences (i.e. shoreline versus mid-lagoon transect) as to any real difference in habitat quality (i.e. water or substrate quality).

Species diversities in both lagoons were very low, in a range indicative of polluted conditions (Wihlm, 1970). Lagoon 4 sediments contained higher levels of both PAH's and metals than the sediments of Lagoon 3, but Lagoon 4 had slightly higher species diversities. Because of the sampling methods used in Lagoon 4, it was not possible to correlate observed species diversities with sediment concentrations. Also, because of the small sample size and the very low diversities observed, the difference between diversities in the two lagoons may not be significant.

TABLE 11. NUMBERS AND GENERA OF BENTHIC MACROINVERTEBRATES COLLECTED IN ALLIED CHEMICAL'S LAGOONS 3 AND 4, SEPTEMBER 24, 1984

		Lagoons									
		LG-3					LG-4				
		1	2	3	4	5	1	2	3	4	5
DIPTERA											
Chironomidae –	Parachironomus			2	N						
	Tanypus			15	O	35					
	Psectrotanypus			2							
					O						
					R						
ODONATA					G						
Libelluidae –	Plathemis				A			1		1	2
					N						
					I					1	
COLEOPTERA					S						1
Haliplidae –	Peltodytes				M			10			
Dytiscidae –	Laccophilus				S						
OLIGOCHAETE											
Tubificidae –	Tubifex	58	867	27		46					1
HIRUDIREA											
Piscicolidae –	Illinobdella						1	47*	36*	27*	19*	6*
GASTROPODA								1*	1*	1*	1*	
Physidae –	Physa											
Lymnaeidae –	Lymnaea											
Number of Genera/Replicate		1	1	4	0	3	2	4	2	4	4
Number of Genera/Site				5					6		
Number of Individuals Repl/Site		58	867	46	0	82	48	48	28	22	10
				1053					156		
Brilliouin's Diversity Index				H = 0.008 decits					H = 0.225 decits		
Shannon Weaver Index				H = 0.098/J = 0.032					H = 0.245/J = 0.112		

*Dead when collected.

Fish. All attempts to collect fish in the lagoons were unsuccessful. This is unfortunate because analysis of fish tissue samples from specimens collected in the lagoons would provide information on the uptake of lagoon compounds in species exposed to "worst-case" contaminated sediments. During the survey, no signs of fish activity in the lagoons were observed. However, since the source of water in both lagoons is surface runoff of rain water, there is no source of fish life to either lagoon. Receding flood waters from the Ohio River could leave river fishes stranded in the ponds but, because of the high banks of the lagoons, even this source is not likely. Therefore, no conclusion on the quality of the lagoon water suitability for the support fish fauna can be made. No fish life was observed in the lagoons, but it is not reasonable to expect fish life where there is no source for recruitment.

It can be stated, however, that the lagoons are suitable for turtles, as many were observed during the survey. The lagoons also receive use by ducks and other waterfowl.

Ice Creek

Benthic macroinvertebrate (aquatic insects associated with substrates) and fish communities were surveyed in Ice Creek at seven sampling locations. Stations were located to detect effects from various sources of possible contamination, including the Ironton coke site, as well as to establish a baseline or reference condition with which to evaluate impacts.

Benthic Macroinvertebrates. Species composition was similar for all Ice Creek stations downstream of the Cemetery Street Bridge (IC 5). The dominant organisms were tubificid worms (Table 12). The densest population was found at the slough area station IC 6, immediately downstream of an apparently untreated sewage outfall on the east shore. The genera found, Tubifex and Branchiura, are particularly tolerant of low dissolved oxygen concentrations and organic pollution. Other numerous organisms at these stations were midge larvae, which also are tolerant of low dissolved oxygen concentrations. Organisms with greater oxygen requirements (i.e. damselfly nymphs--Coenagrionidae, water bugs--Hebridae) were found in shoreline, qualitative samples (Table 13).

TABLE 12. NUMBERS AND GENERA OF BENTHIC MACROINVERTEBRATES COLLECTED IN PETIT PONAR GRAB SAMPLES IN ICE CREEK, IRONTON, OHIO SEPTEMBER 24-27, 1984

		Ice Creek Stations																																
		IC-1					IC-2			IC-5					IC-6					IC-4					IC-3					OR-2				
		1	2	3	4	5	1	2	3	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
DIPTERA																																		
Chironomidae –	Chironomus				N				N	2	3	1	4	4		11	16	14	4	1	1	5						1				1		
	Cryptochironomus	1			O			1	O																			1			1	1	2	
	Polypedilum			1																														
	Tanytarsus				O	1			O																									
	Tanypus				R				R								1	2	5		2	1		1	1		2			1	1	1		
	Psectrotanypus				G				G			1		2					1	1	4	5	2				2				6	5	4	1
	Procladius				A				A		1			5							1										1	1		1
Chaoboridae –	Chaoborus				N				N																							1		
					I				I																									
EPHEMEROPTERA					S				S																									
Baetiscidae –	Baetisca			4	M				M																									
Ceanidae –	Caenis			1																														
Ephemeridae –	Hexagenia				S		1		S			1																						
ODONATA																																		
Gomphidae –	Progomphus		4																															
Coenagrionidae –	Argia																					1												
Libellulidae –	Dythemis																													2				
COLEOPTERA																																		
Elmidae –	Dubiraphia										1																			1				
OLIGOCHAETE																																		
Tubificidae –	Tubifex									9	14	1		7	38	83	68	27	22	8	24	25	9			24	25	21	1		44	69	57	6
	Branchiura									3	1	1					15	32	12	10	8	3	2	7				3				4		14
Lumbriculidae –	Lumbriculus																													2				
Naididae –	Dero																															1		
HIRUDINEA																																		
Piscicolidae –	Illinobdella																						1											
AMPHIPODA																																		
Gammaridae –	Gammarus																							1						9	2			
GASTROPODA																																		
Physidae –	Physa																							1*										

		Ice Creek Stations																																				
		IC-1					IC-2			IC-5					IC-6							4			IC-3					OR-2								
		1	2	3	4	5	1	2	3	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
PELECYPODA																																						
Corbiculidae –	Corbicula												1																									
Sphaeridae –	Sphaerium									2	1	1																										
Unionidae –	Potamilus																1																					
Number of Genera/Replicate		1	3	1		1	1	1		4	7	6	2	4	1	2	5	4	5	4	6	6	4	3	4	1	3	3	2	6	6	9	4	5				
Number of Genera/Site				6				2				9					6					9					6					15						
Number of Individuals Repl/Site		1	9	1		1	1	1		16	21	6	5	18	38	94	101	75	44	20	40	40	14	9	4	24	29	23	4	16	55	84	64	23				
				12				2				66					352					123					84					242						
Brillioun's Diversity Index		H = 0.493 decits					H = 0.15 decits			H = 0.618 decits					H = 0.399 decits					H = 0.538 decits				H = 0.290 decits					H = 0.465 decits								
Shannon Weaver Index		H = 0.678/ J = 0.628					H = 0.301/ J = 1.0			H = 0.69/ J = 0.379					H = 0.411/J = 0.161					H = 0.580/ J = 0.278				H = 0.342/ J = 0.177					H = 0.501/ J = 0.214								

*Dead when collected.

TABLE 13. NUMBERS AND GENERA OF MACROINVERTEBRATES COLLECTED IN QUALITATIVE SAMPLES IN ICE CREEK, IRONTON, OHIO, SEPTEMBER 25-27, 1984

		IC 1	IC 2	IC 5	IC 6	IC 4	IC 3	OR 2
DIPTERA					NO SAMPLE	NO SAMPLE	1	
Chironomidae	- Chironomus						1	
	- Parachironomus						2	
	- Tanypus							
EPHEMEROPTERA			1					
Heptageniidae	- Stenacron		2					
	- Stenonema		1					
Leptophlebiidae	- Paraleptophlebia		2					
Baetidae	- Baetis							
ODONATA		1						
Gomphidae	- Gomphus	6						6
	- Progomphus		1				13	
Coenagrionidae	- Argia			1			1	
	- Enallagma							1
Libellulidae	- Sympetrum							
Cordulidae	- Epicordulia						3	
COLEOPTERA			1					
Haliplidae	- Peltodytes							
HEMIPTERA			1					
Gerridae	- Metrobates		1				4	2
Salididae	- Pentacora				1			
Hebridae	- Merragata				1			
Belostomatidae	- Belostoma							
OLIGOCHAETE							4	
Tubificidae	- Branchiura							4
TURBELLARIA								
Planaridae	- Dugesia							
DECAPODA			1					
Astacidae	- Orconectes							

TABLE 13. (CONTINUED)

	IC 1	IC 2	IC 5	IC 6	IC 4	IC 3	OR 2
AMPHIPODA							
Gammaridae - *Gammarus*						4	22
Talitridae - *Hyalella*						13	
GASTROPODA							
Physidae - *Physa*		1	1*			1*	
Lymnaidae - *Lymnaea*			1				
PELECYPODA							
Sphaeridae - *Sphaerium*							1
Number of Genera	3	9	5			11	6
Number of Individuals	8	11	5			47	36

*Dead when collected.

The unionid bivalve found at station IC 6, Potamilis ohioensis, is listed as endangered in Ohio (Stansbury, November 2, 1984; personal communication). This species is abundant in the Ohio River (which, in the Ironton area, is predominantly in Kentucky), but is at the edge of its range in the Ohio streams. The specimen found was approximately two years old and was collected immediately downstream of an apparently untreated sewage outfall near the east shore of the slough area. The freshwater drum, or sheepshead (Aplodinotus gruenniens), is the host fish for this bivalve. (Juvenile drum were found at IC 6.) Water and sediment quality in the area of the sewage effluent and/or the slough are apparently suitable for this endangered species.

Stream habitat at the upstream reference station, IC 1, was notably different than at the downstream stations (see Table 1). Riffle substrates were covered with leaf litter; pool substrates were predominantly sand. Four of the five replicate grab samples contained only one or no organisms (Table 12). The most numerous organism in grab and qualitative samples was the dragonfly nymph Progomphus. A total of eight different genera were collected from this site.

At the Lorain Street Bridge station, IC 2, only two organisms, one midge larvae and one mayfly nymph, were collected in grab samples Qualitative sampling of shoreline habitats produced individuals representin nine other genera for a total of 11 from this site.

Numbers of specimens per unit effort at these two upstream site were the lowest of all the Ice Creek stations (Tables 12 and 13). Substrate in this section of the stream contained predominantly sand, which is n a suitable medium for most aquatic invertebrates. Substrate type at stati IC 5 downstream of the Cemetery Road Bridge was more typical of the re of the creek than the two upstream stations (see Table 1).

There was no statistically significant ($p > 0.6$) difference species diversities calculated for the Ice Creek station quantitat invertebrate data. A simple Kruskal-Wallis test (Hollander and Wolfe, 19 was performed for each of the indices calculated. Stations were grou for upstream (IC 1, IC 2, IC 5), slough (IC 4, IC 6), and downstream 3, OR 2) areas. Calculations were performed both including and exclu IC 1 and IC 2 data to test for substrate differences. The Shannon-We

indices were evaluated both including the IC 2 value and excluding it as outlier. [This value is an anomaly in that it is the highest index but corresponds to a station with the lowest diversity (Table 12)]. There was a significant difference in diversity of the various stream sections for any of the tests performed. Shannon-Weaver diversities for all stations fall within the range of those typical or characteristic of polluted waters (Wilhm, 1970).

There is a significant ($p < 0.05$) difference in numbers of organisms per unit effort between stations when all data are considered. Tolerant organisms were more abundant in the muck substrates than in sand. However, when the calculation is corrected for substrate differences (i.e. IC 1 and IC 2 data are not considered), there is no difference among numbers found at the three stream areas.

Total numbers of genera found in upstream (IC 1, IC 2, and IC 5) and downstream (IC 3 and OR 2) quantitative and qualitative (Tables 12 and 13) samples were similar. No qualitative samples were taken in the slough area (IC 6 and IC 4) because shorelines were inaccessible by boat or on foot. However, numbers of genera in quantitative samples (Table 12) were similar to upstream and downstream samples.

Species diversity at station IC 3, where substrates showed high levels of PAH's, was similar to that found for Lagoon 4. (Again, comparison of species diversities from Lagoon 4 is tenuous because of the different sampling methods used for Ice Creek.) Diversity at the mouth station, OR 2, where sediment contamination was reduced but still detected was similar to the control, or background, station IC 1. In any case, as was previously discussed, there were no significant differences in the benthic community parameters measured for any of the stations. Contamination of sediments by lagoon compounds at IC 3 and OR 2 does not appear to be impacting the benthic macroinvertebrate communities in Ice Creek. Similarly, no impact from the elevated ammonia levels found in water samples from downstream stations is apparent in the benthic communities.

Fish. A total of 27 fish species (and one amphibian) was collected from Ice Creek (Table 14). Emerald shiner, green sunfish, bluegill, longear sunfish, and largemouth bass were found at all sampling stations. Emerald shiners, bluegill, and gizzard shad were the most numerous species. Stations had an average number of 13 species (range, 10-16) with no significant

TABLE 14. NUMBERS AND SPECIES OF FISHES COLLECTED IN ICE CREEK IRONTON, OHIO, SEPTEMBER 24-27, 1984

		IC 1	IC 2	IC 5	IC 6	IC 4	OR 2(a
Cyprinidae	Carp (Cyprinus carpio)				2	4	
	Silverjaw Minnow (Ericymba buccata)	26					
	Emerald Shiner (Notropis antherinoides)	30	62	290	23	16	45
	Steelcolor Shiner (Notropis whipplei)	1					
	Bluntnose Minnow (Pimephales notatus)	27	38	25		6	18
Percidae	Fantail Darter (Etheostoma flabellare)	2					
	Johnny Darter (Etheostoma nigrum)	11	1				1
	Yellow Perch (Perca flavescens)		2				
Centrarchidae	Northern Rock Bass (Ambloplites rupestris)			3	1	4	7
	Warmouth Sunfish (Chaenobryttus gulosus)	1		12	1	10	1
	Green Sunfish (Lepomis cyanellus)	4	34	31	45	110	112
	Bluegill (Lepomis macrochirus)	52	13	10	7	15	24
	Longear Sunfish (Lepomis megalotis)	6	15		5	26	10
	Longear Sunfish x Bluegill Hybrid	1			2	34	24
	Longear Sunfish x Green Sunfish Hybrid	1	1	1	1	2	3
	Green Sunfish x Bluegill Hybrid				13	34	9
	Northern Largemouth Black Bass (Micropterus salmoides)	6	7	7		1	4
	White Crappie (Pomoxis annularis)					1	
	Black Crappie (Pomoxis nigromaculatus)		9			2	
	Pumpkinseed Sunfish (Lepomis gibbosus)				21	2	
Catostomidae	Quillback Carpsucker (Carpiodes cyprinus)		11				
	Creek Chubsucker (Erimyzon oblongus)						

TABLE 14. (CONTINUED)

		IC 1	IC 2	IC 5	IC 6	IC 4	OR 2(a
Clupeidae	Gizzard Shad (Dorosoma cepedianum)		115	15	80	100	31
	Skipjack Herring (Pomolobus chrysochloris)				2		
Sciaenidae	Freshwater Drum (Aplodinotus grunniens)				7		1
Ictaluridae	Channel Catfish (Ictalurus punctatus)				1		
	Flathead Catfish (Pilodictis olivaris)			1			
Amphibia	Central Mudpuppy (Necturus maculosus)						
Total Number of Species		13	12	10	15	16	1
Total Number of Individuals		168	308	395	211	367	29

(a) Because of proximity of stations, the stream segment between IC 3 and OR 2 was sampled as one location and the data combined.

difference in the number of species found at any sampling location. (Stations IC 3 and OR 2 were sampled as one zone because the distance between stations was small.)

The downstream and slough area stations generally produced larger specimens and species characteristic of those found in large rivers, such as channel and flathead catfishes, skipjack herring, drum, quillback carpsucker. Upstream stations had larger numbers of young-of-the-year shad, minnows and shiners.

Specimens appeared robust, well formed, free from external parasites, in good color and health in gross observations of fresh specimens. Only one specimen showed signs of fin rot; one other had a deformed pectoral fin.

Condition factors were calculated for all sport fish and dominant species (Table 15). Mean values were compared to ranges published (Carlander, 1969; Bennett, 1970) for Ohio and/or Midwest fishes. Weight and length data used in calculations of condition factors are presented in Appendix II.

Bluegill adults fell within the normal range of plumpness at all stations except IC 5. This is the furthest upstream station where adult bluegill were found. Largemouth bass adults were well within the normal range at all stations as were the crappie, carp, gizzard shad, flathead catfish, and channel catfish. The condition factors indicated that the fish were of normal "plumpness" throughout the stream.

Results of chemical analyses of fish tissue samples showed no difference in levels of metals in samples upstream and downstream of the coke site (Table 16). Highest levels of most metals were found in the clam tissue at IC 6. This organism, a filter feeder, is a particularly good bioaccumulator. Concentrations in the clam tissue (dry weight) were generally 2-5 times higher than in the sediments at IC 6. Levels of metals in fish tissue were lower than sediment concentrations of those metals in the same locations (see Table 7). Levels found in whole fish (i.e. juvenile bluegill and shad) were similar to sediment concentrations which is likely a result of sediment in the digestive tracts of these specimens.

Levels of organic priority pollutant compounds identified in fish tissue samples also are presented in Table 16. With the exception of the samples from IC 6 and IC 4, the acidic compound, phenol, was found only in trace levels or not detected in fish tissue. The source of this contamin

TABLE 15. CONDITION FACTORS CALCULATED FOR FISH COLLECTED IN ICE CREEK

Station	Species	Condition Factor	Range	Normal Range
IC 2	Largemouth Bass	5.2	---	4.6-5.5
IC 5	Bluegill	5.8	5.6 - 6.0	7.1-8.0
IC 4	Bluegill	7.1	6.4 - 8.2	7.1-8.0
	Crappie	5.0	---	4.6-5.5
	Carp	1.5	1.49- 1.51	1.2-2.9
IC 6	Bluegill	7.0	6.0 - 7.7	7.1-8.0
	Largemouth Bass	5.0	---	4.6-5.5
	Flathead Catfish	1.0	---	0.9-1.1
	Gizzard Shad	1.6	1.2 - 2.0	0.9-2.2
OR 2	Bluegill	7.7	5.7 -11.0	7.1-8.0
	Largemouth Bass	5.4	4.7 - 6.0	4.6-5.5
	Channel Catfish	0.98	---	0.8-1.2

TABLE 16. RESULTS OF CHEMICAL ANALYSES OF FISH TISSUE SAMPLES COLLECTED IN ICE CREEK, IRONTON, OHIO, SEPTEMBER 27, 1984

Station	Sample Type	Zinc Weight Dry µg/g	Zinc Weight Wet µg/g	Cadmium Weight Dry µg/g	Cadmium Weight Wet µg/g	Lead Weight Dry µg/g	Lead Weight Wet µg/g	Arsenic Weight Dry µg/g	Arsenic Weight Wet µg/g	Selenium(a) Weight Wet mg/g	Mercury(a) Weight Wet µg/g	Phenol µg/kg	bis (2 ethylhexyl) phthalate µg/kg	Di-n-butyl phthalate µg/kg
IC1 1	Bluegill, juveniles, composite--49	178.9	25.8	1.1	0.15	11.1	1.59	<1.1	<0.15	<0.1	<0.05	BMDL(b)	2380	6620
IC2 1	Bluegill, juveniles, composite--12	253.5	17.3	2.8	0.19	31.2	2.13	4.3	0.30	<0.1	<0.05	ND(c)	ND	BMDL
IC2 2A	Shad, juveniles, composite--115	149.0	22.5	0.9	0.14	7.3	1.10	1.6	0.23	<0.1	<0.05	ND	ND	ND
IC2 2B	Duplicate	134.4	20.4	0.9	0.14	4.0	0.61	1.9	0.28	<0.1	<0.05	ND	ND	ND
IC2 3	Bass--22 cm, 150 g	82.8	12.8	0.7	0.11	2.3	0.35	1.4	0.22	<0.1	<0.05	BMDL	ND	2560
IC5 1	Bluegill, juveniles, composite	258.8	31.8	<0.8	<0.10	3.3	0.41	3.8	0.47	<0.1	<0.05	BMDL	4980	1370
IC5 2	Bluegill, composite--2	254.7	35.3	<0.3	<0.04	1.2	0.16	1.0	0.14	<0.1	<0.05	BMDL	1780	3660
IC5 3	Shad, juveniles, composite--15	256.1	29.5	1.1	0.13	1.9	0.22	1.8	0.21	<0.1	<0.05	ND	7540	6800
IC6 1	Bluegill, juveniles, composite--41	255.6	25.5	<0.5	<0.05	5.2	0.23	<1.5	<0.12	<0.1	<0.05	BMDL	17400	3340
IC6 2A	Catfish--54 cm, 1605 g	85.1	16.7	<0.2	<0.04	2.4	0.19	<0.7	<0.11	<0.1	<0.05	ND	ND	ND
IC6 2B	Duplicate	91.0	17.8	<0.2	<0.03	0.9	0.11	<0.5	<0.07	<0.1	<0.05	ND	ND	BMDL
IC6 3	Shad, juveniles, composite--80	147.5	21.4	0.6	0.08	0.6	0.18	1.8	0.26	<0.1	<0.05	ND	ND	BMDL
IC6 5	Bass--24 cm, 190 g	51.1	7.6	<0.2	<0.03	1.2	0.46	1.0	0.14	<0.1	<0.05	ND	ND	BMDL
IC6 6	Bluegill, composite--3	131.7	18.6	0.2	0.03	3.1	0.25	<0.6	<0.07	<0.1	<0.05	15900	BMDL	ND
IC6 7	Carp--14 cm, 42 g	326.3	37.2	<0.6	<0.07	1.8	0.61	<2.0	<0.18	<0.1	<0.05	ND	BMDL	ND
IC6	Clam--1	1193.3	35.4	<1.9	<0.06	5.3	0.47	<6.0	<0.14	<0.1	<0.05			

TABLE 16. (CONTINUED)

Station	Sample Type	Zinc Weight Dry ug/g	Zinc Weight Wet ug/g	Cadmium Weight Dry ug/g	Cadmium Weight Wet ug/g	Lead Weight Dry ug/g	Lead Weight Wet ug/g	Arsenic Weight Dry ug/g	Arsenic Weight Wet ug/g	Selenium(a) Weight Wet mg/g	Mercury(a) Weight Wet ug/g	Phenol µg/kg	bis (2 ethylhexyl) phthalate µg/kg	Di-n-butyl phthalate µg/kg
IC4 1	Bluegill, juveniles, composite--103	177.0	22.9	<0.2	<0.02	0.8	0.10	2.1	0.25	<0.1	<0.05	BMDL	ND	ND
IC4 2	Crappie--17 cm, 68 g	111.0	16.7	0.4	0.07	1.0	0.14	1.8	0.27	<0.1	<0.05	2260	ND	2080
IC4 3	Bluegill, composite--6	139.5	21.9	0.6	0.10	0.6	0.10	1.2	0.18	<0.1	<0.05	ND	BMDL	1350
IC4 4	Shad, juveniles, composite--100	98.2	15.8	0.9	0.14	1.9	0.31	0.9	0.14	<0.1	<0.05	ND	1990	BMDL
IC4 5	Carp, composite--2	188.5	24.3	0.6	0.08	2.9	0.37	1.9	0.24	<0.1	<0.05	BMDL	ND	ND
OR2 1	Bluegill, juveniles, composite--104	240.1	34.0	0.3	0.05	3.4	0.48	2.7	0.38	<0.1	<0.05	ND	ND	ND
OR2 2	Bluegill, composite--4	184.3	26.1	<0.3	<0.05	4.1	0.58	2.6	0.37	<0.1	<0.05	ND	ND	ND
OR2 3	Bluegill--14 cm, 44 g	171.3	23.0	<0.6	<0.08	6.6	0.89	<1.8	<0.19	<0.1	<0.05	ND	BMDL	ND
OR2 4	Catfish--56 cm, 1713 g	22.9	16.7	0.5	0.11	2.4	0.52	1.6	0.34	<0.1	<0.05	ND	ND	ND
OR2 6	Bass--31 cm, 364 g	78.9	8.4	0.2	0.04	2.0	0.40	1.3	0.26	<0.1	<0.05	ND	ND	ND
OR2 7	Bass--30 cm, 383 g	56.0	10.7	<0.2	<0.05	2.3	0.54	1.4	0.27	<0.1	<0.05	ND	BMDL	ND
OR2 8	Bass--28 cm, 362 g	82.7	14.6	<0.1	<0.02	2.2	0.38	0.6	0.11	<0.1	<0.05	ND	ND	ND

(a) Stilson Laboratories, Columbus, Ohio.

(b) BMDL--Below Methal Detection Limit.

(c) ND--Parameter Not Detected.

is unclear as phenol was not detected in either water or sediment samples. However, it is not likely associated with former operations of the coke site. Phenol is a highly-soluable, biodegradable compound which does not linger in the environment.

Two phthalate esters were detected in fish tissues from both upstream and downstream locations. One compound, bis (2 ethylhexyl) phthalate was detected only in bluegill and shad specimens. When both species are considered, no difference between upstream to downstream concentrations is seen. However, the concentration of this compound in bluegills was 6 times higher in the downstream sample (IC 6) than the upstream samples. This compound was not detected in water samples and found in only one sediment sample IC 1, the furthest upstream station. The other phthalate, D-n-butyle phthalate, was detected only in fish tissue, not in water or sediment. The fish tissues which contained this substance were from a variety of species. No difference in concentration was found either between species or within species groups. Again, neither of these compounds was specifically associated with former operations at the coke site. Phthalate esters are ubiquitous in their environmental distribution.

Although elevated levels of PAH's were found at stations IC 3 and OR 2, no accumulation of these compounds was detected in any fish tissue sample. There also were no discernible effects on fish populations in Ice Creek which may be associated with the contaminated sediments. Similarly, no effect on fish populations from elevated ammonia concentrations in water samples was detected.

CONCLUSIONS

Results of the September 24-28, 1984, aquatic surveys at Allied Chemical's Ironton, Ohio, coke site support the following general conclusions:

- Water quality in Lagoons 3 and 4 is currently suitable to support limited planktonic plant and animal communities. Lagoon 3 receives enrichment from a source not simultaneously available to Lagoon 4, evidenced by a blue-green algae bloom.

- Sediments in Lagoon 3 supported a benthic community indicative of organic pollution. Inaccessibility of Lagoon 4 prohibited comparable sampling methods which precludes any conclusion on sediment quality for Lagoon 4.

- Surface water currently is unaffected by the coke site, with the possible exception of elevated ammonia concentrations. Nutrient enrichment and reduction in dissolved oxygen concentration can be directly attributed to currently active domestic sewage discharges to Ice Creek in the vicinity of the plant site.

- There is no discernible difference in benthic macroinvertebrate populations at any station either upstream or downstream of the plant site. Current baseline for these populations is indicative of a polluted condition the entire length of stream sampled.

- There is no measurable difference in fish populations among the upstream and downstream stations sampled during this survey. The community found in the slough area and at the mouth of Ice Creek consists of species commonly found in large river systems, reflecting the influence of the Ohio River on this stream section.

- Levels of certain PAH's in sediments at the Third Street Bridge station in Ice Creek downstream from Lagoon 3 reflect the former discharge of these compounds from the lagoon area. Levels of these same compounds are reduced by at least an order of magnitude or to below method detection limits at the mouth station of Ice Creek.

- Levels of three priority organic pollutants were found in fish tissues. However, the source of these contaminants is unclear as the compounds in fish tissues were not detected in either the water or the sediment samples from the lagoon area.

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APPENDIX I

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES (QA/QC)

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES (QA/QC)

Used by Battelle Columbus Laboratories in Analysis of Metals, Cyanide, Chloride, Sulfate, and Benzene

These chemcial analyses were conducted under a QA/QC program developed from recommendations of the United States EPA (EPA, 1979) and the American Chemical Society (ACS,1983). The significant features of this program which pertain to this project are as follows:

Verification and Validation. Well documented and well defined protocols were used.

Precision and Accuracy. Replicates were performed on two fish tissue samples, one sediment sample, and one water sample. Recoveries (spikes) were conducted with the same number and types of samples. Precision and accuracy data from this analysis are presented in Tables I-1 and I-2.

Sampling. Samples were appropriately preserved in the field according to EPA procedures and were checked upon arrival at the laboratory.

Blanks. Appropriate blanks were prepared and all values corrected for blanks.

Measurements. Measurements were performed with properly tested and documented procedures.

Calibration and Standardization. At least three different concentrations of calibration standards were measured. No data were reported beyond range of calibration of the methodology. Spike and analyte concentrations were made as close as practical. Recoveries of the spike sample were determined in the same matrix as the sample. Analytical values were reported as measured (uncorrected for recovery but corrected for blanks) with full and complete supporting data.

Documentation and Reporting. Samples were logged from collection to laboratory through analysis to final results (chain of custody) Methodologies, quality assurance, and quality control procedures were documented.

Data. All samples were coded upon receipt. Initial weights, extraction volumes, final volumes, and volumes analyzed were recorded. Instrument conditions and calibrations, sample calculations, and concentrations of samples (analyte value determined) were recorded.

ABLE I-1. PRECISION DATA FOR DUPLICATE SAMPLES, MEAN, STANDARD DEVIATION(a,b)

	SAMPLE TYPE		
	Water	Sediment	Fish Tissue
Zn	47.6 ± 36.2	114.5 ± 63.7	23.4 ± 1.3
Cd	1.3 ± 0.71	0.51 ± 0.01	0.10 ± 0.01
Pb	11.4 ± 0.8	7.1 ± 0.2	0.60 ± 0.2
	DBDL(b)	2.1 ± 0.4	0.20 ± 0.04
Se	DBDL	DBDL(c)	DBDL(c)
Cn	DBDL	---	---
Cl	26.6 ± 1.0	---	---
SO_4	152 ± 1.0	---	---
Benzene	DBDL	---	---

(a) Water, ug/L for Zn, Cd, Pb, As, Hg, and benzene; mg/L for Se, Cl, SO_4, and Cn.
Sediment, ug/g, dry weight.
Fish Tissue, ug/g, dry weight.

(b) Duplicates below detection level.

(c) Stilson Laboratories, Columbus, Ohio.

TABLE I-2. ACCURACY DATA FOR SPIKED SAMPLES, RECOVERY, PERCENT

	SAMPLE TYPE		
	Water	Sediment	Fish Tissue
Zn	62	31	75
Cd	90	72	87
Pb	143	58	78
As	68	78	52
Hg	SBDL[a]	SBDL	SBDL
Se	93	SBDL	SBDL
CN	81	---	---
Cl	101	---	---
SO_4	99	---	----

(a) Spikes below detection level.

Used by ETC (Environmental Testing and Certification) in Analysis of Acid and Base/Neutral Priority Pollutants

ETC bases its quality assurance protocols on the following government guidelines:

- "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, March 1979;
- National Enforcement Investigation Center Policies, and Procedures manual; EPA-330/9/79/001-R, October 1979;
- The Recommended Guidelines for EPA Methods 624 and 625. (Federal Register, December 3, 1979, pp. 69532-69559);
- "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples," EPA 600/8-80-038, June 1980; and
- "Determination of 2,3,4,8-TCDD in Soil and Sediment," EPA, Region VII, Kansas City, September 1983.

However, protocols have been modified to provide a higher level of QA/QC than the guidelines require. For example, a higher than required number of quality control samples are analyzed, and special attention is paid to the certification of the "reference standard" compounds used in analysis. Key QA/QC elements for the methods used are listed below.

Analysis of Organic Compounds Extracted in Acid or Base/Neutral Solutions by Gas Chromatography/Mass Spectrometry

- Each batch of 20 samples consists of 16 customer samples (at a maximum), one blank sample, one spiked blank (for water matrices), one sample spiked with the priority pollutant standard mixture, and a duplicate customer sample. This amounts to a 20 percent quality control factor.

- Three surrogate compounds are added to each sample in the batch for Base/Neutral analysis.

- Two surrogate compounds are added to each sample in the batch for Acid analysis.

- A blind quality control sample is introduced to the laboratory for analysis on a weekly basis.

- Each GC/MS is checked and returned, if necessary, at the beginning of each day to ensure that its performance on decafluorotriphenylphosphine (DFTPP) meets the EPA criteria.

- A calibration curve for quantitation is prepared using a mixture of standards composed of either the Organic Acid or Base/Neutral Extractable Compounds at a minimum of three concentrations and using 2,2-difluorobiphenyl as an internal standard.

Chain-of-Custody

The chain-of-custody procedure is part of the quality assurance protocol. ETC's chain-of-custody record fully complies with the legal requirements of federal, state, and local government agencies and of the courts of law. For this project, the record covers:

- Incoming shipping manifests;
- Storing each labeled sample bottle in a secured area;
- Disposition of each sample to an analyst or technician; and
- The use of the sample in each bottle in a testing procedure appropriate to the intended purpose of the sample.

The record shows for each link in this process:

- The person with custody; and
- The time and date each person accepted or relinquished custody.

Recovery and Precision Data on Spiked and Split Samples Submitted to ETC

Spiked Water Sample

A spiked water sample was prepared at Battelle Labs and submitted to ETC along with all other samples.

Parameter	Spike, ug/L	Reported Concentration ug/L	Percent Recovery
Naphthalene	16	ND	< 56
Butylphthalate	10	BMDL	< 90
Hexylphthalate	20	17	85
Pyrene	19	22	116

Duplicate Samples

Sediment samples taken at IC 1, IC 3, and IC 6 were split (IC 9, IC 7, IC 8, respectively) and submitted to ETC for precision data. Several parameters detected in the sample have been contrasted with surrogate duplicate data supplied by ETC to provide precision information.

Parameter	IC 3, IC 7 Values, ug/kg	Relative Standard Deviation, Percent: Mean	IC 3, IC 7	ETC Surrogates	EPA[a]
Chrysene	44,200; 25,600	34,900	37	50	28
Fluoranthene	57,100; 37,800	47,400	21	83	26
Pyrene	43,500; 28,400	36,000	29	14	23

(a) EPA-600/4-82-057

Water samples from the same locations as the sediment samples were taken for duplicate analyses. No organic priority pollutant compounds were found in any water sample (except the spike). Therefore, no precision calculation is possible. Similarly, no organic priority pollutants were found in IC 1 or IC 6 sediment samples or duplicates.

APPENDIX II

FISH LENGTH AND WEIGHT DATA AND CONDITION FACTORS

FISH LENGTH AND WEIGHT DATA AND CONDITION FACTORS

Fish	Length (mm)	Weight (g)	K*	$\bar{K}$	C**	$\bar{C}$
Bluegill (Adults)						
OR 2	110	20.8	1.56		5.7	
	140	44.4	1.62		5.9	
	100	30.2	3.02		11.0	
	110	34.4	2.58		9.45	
	130	39.6	1.80	2.12	6.6	7.73 (7.1-8.0 Normal Range
IC 4	130	40.0	1.80		6.6	
	90	16.4	2.25		8.2	
	110	24.9	1.87		6.8	
	110	27.9	2.1		7.7	
	110	23.4	1.76		6.4	
	90	14.3	1.96	1.96	7.2	7.1
IC 5	90	11.2	1.54		5.6	
	100	16.4	1.64	1.59	5.9	5.8
IC 6	130	43.2	1.97		7.2	
	120	36.4	2.11		7.7	
	110	21.9	1.64	1.91	6.0	6.9
Bluegill (Juveniles)						
	44	0.9	1.05			
	36	0.6	1.29			
	34	0.9	2.3			
	57	3.3	1.78			
	50	2.4	1.92			
	55	3.2	1.92			
	45	1.8	1.97			
	55	3.5	2.1			
	45	1.3	1.43			
	45	2.2	2.4	1.82		
Largemouth Bass						
OR 2	305	364.2	1.28		4.68	
	295	383.0	1.49		5.5	
	280	361.5	1.65	1.47	6.0	
	220	150*	1.41		5.2	
	240	190*	1.37		5.0	5. (4.6-5 Avera Plumpn

Fish	Length (mm)	Weight (g)	K*	$\bar{K}$	C**	$\bar{C}$
Crappie						
IC 4	170	67.5	1.37		5.0	
Carp						
IC 4	160	60.9	1.49			
	100	15.1	1.51	1.5		
					(Normal Range 1.23-2.92)	
Gizzard Shad	95	10.5	1.22			
	55	2.2	1.32			
	65	4.1	1.49			
	80	6.9	1.35			
	65	4.6	1.67			
	80	7.7	1.50			
	75	6.9	1.64			
	70	5.7	1.66			
	70	5.7	1.66			
	65	5.5	2.00	1.55		
					(Normal Range 0.91-2.2)	
Flathead Catfish						
IC 6	540	1605.4	1.02			
					(Normal Range 0.95-1.12)	
Channel Catfish						
OR 2	560	1713.1	0.975			
					(Normal Range 0.75-1.2)	

K* Calculated according to the method in Carlander, 1969.

$$K = \frac{w(10^5)}{L^3}$$

where w = weight in grams
L = length in millimeters

C** Calculated according to method in Bennett, 1970.

$$C = \frac{10{,}000 \text{ (weight in pounds)}}{\text{length}^3 \text{ in inches}}$$