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**Ground water transport of polycyclic aromatic hydrocarbons  
in association with humic substances in the Pinal Creek basin,  
Globe, Arizona**

Wallin, Robert Walter, M.S.

The University of Arizona, 1991

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GROUND WATER TRANSPORT OF POLYCYCLIC AROMATIC  
HYDROCARBONS IN ASSOCIATION WITH HUMIC  
SUBSTANCES IN THE PINAL CREEK BASIN,  
GLOBE, ARIZONA

by

Robert Walter Wallin, M.S.

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A Thesis Submitted to the Faculty of the  
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES  
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For the Degree of

MASTER OF SCIENCE  
WITH A MAJOR IN HYDROLOGY

In the Graduate College  
THE UNIVERSITY OF ARIZONA

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## APPROVAL BY THE THESIS DIRECTOR

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**ABSTRACT**

Polycyclic aromatic hydrocarbons (PAH) are present in groundwater in the Pinal Creek basin near Globe, Arizona. The maximum concentration of quantified PAH in samples from monitoring wells was 35 micrograms per liter. PAH contamination was found in a plume about 11 kilometers long. The source is probably in an area of active mining operations several kilometers upstream from the sample wells. Concentrations of quantified PAH in the aquifer decrease significantly as the pH rises above 4. Concentrations of dissolved organic carbon (DOC) decrease in the same area. The fractions of the DOC that decrease are predominantly dissolved humic substances (DHS). Analyses of the data indicate that partitioning of PAH onto DHS could be taking place and the removal of PAH could be controlled by the adsorption of DHS onto metal hydroxides.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Mining activities have been occurring in the Pinal Creek basin near Globe, Arizona, for more than 100 years. More than \$1 billion worth of metals were taken from the Globe/Miami district by 1953. Copper mining began in 1872 and copper has been the most important commodity mined in the area (CAAG, 1983). Currently, there are two active mining operations in the area: operations of the Pinto Valley Copper Division of Magma Copper Corporation and the Cyprus Miami Mining Corporation. Both Companies operate large pit mines as well as leaching, milling, and concentrating operations. CAAG (1983) summarizes the history of the mining district.

Groundwater quality in the Pinal Creek basin has been shown to be degrading for at least 50 years (Envirologic Systems, 1983). Process solutions from acidic mining and milling activities have seeped into groundwater along Miami Wash and Pinal Creek, and there is now a plume extending downgradient the full extent of the aquifer for a distance of 17 km. (Eychaner and Stollenwerk, 1985). Total dissolved solids at the Pringle Well Field near the outflow of the aquifer were reported as 800 mg/l in 1942, 1,800 mg/l by 1963, and 2,900 mg/l by 1983 (Envirologic Systems, 1983). In significant stretches of the aquifer, groundwater contains

elevated concentrations of dissolved metals and sulfate and low pH. Levels of contamination in the aquifer have been monitored by the U.S. Geological Survey since 1984. A sample from well 051, the most contaminated well in the study area (See Figure 2.1) near Miami Wash was reported to have a pH of 3.6, 3,000 mg/l iron, 150 mg/l copper, 73 mg/l manganese, 10,800 mg/l sulfate, and 16,400 mg/l total dissolved solids in 1985 (Eychaner and Stollenwerk, 1985).

Elevated levels of dissolved organic carbon (DOC) above that which would normally be observed in natural aquifers have been detected, and associated with the inorganic contamination. The maximum DOC is 4.2 mg/l or as high as 8 times background of 0.5 mg/l (Reese, 1989). Because of the small amount of vegetation in the streambed and the low fraction of organic carbon ( $f_{oc}$ ) in the aquifer, contributions from mining activity in the area are suspected to account for most of the organic material. A major historical source for contamination entering the groundwater has been identified as an unlined lake retained behind waste and tailings piles. This lake, known as Webster Lake, was used to contain waste solutions from mining processes (Eychaner, 1989). The pH of the lake was measured at 2.7 in 1986. The U.S. Environmental Protection Agency ordered the lake drained in 1987 and, by 1988, most of the contents of the lake had been spread on inactive tailings piles to evaporate (Eychaner, 1989).

An analysis of a component of the DOC from the most contaminated well was made by Reese (1989) using gas chromatography mass spectrometry (GC/MS). Polycyclic aromatic hydrocarbons (PAH) were detected in the 1-10 ppb range in a well in the upgradient portion of the study area (Reese, 1989). Sixteen PAH are on the EPA Priority Pollutant List (U.S. E.P.A., 1979). Some PAH are considered to be carcinogenic, and an upper limit of 28 mg/l for total PAH has been recommended (Minnesota Department of Health, 1978). The detection of PAH in the aquifer was unexpected and is cause for concern. Pinal Creek discharges into the Salt River just above Roosevelt Lake. Roosevelt Lake is a major water source for the Phoenix metropolitan area.

### 1.2 Purpose and Scope

This study involves the characterization of PAH present in the Miami Wash-Pinal Creek aquifer system. Ground water samples for the purpose of this study were collected in four sampling trips between March 1989 and May 1990. A total of twenty-five wells have been sampled. PAH were detected in 14 wells and the distribution of concentrations defines a plume of PAH extending the entire length of the study area.

The objectives of this research are as follows:

- (1) To identify and quantify polycyclic aromatic hydrocarbons (PAH) and any other micropollutants

extractable with the same procedures, present in the aquifer;

(2) To determine the distribution, partitioning, and relevant transport mechanisms of PAH in the aquifer; and

(3) To determine, if possible, the probable chemical source of PAH contamination and its pathway into the aquifer.

Samples were collected in the field from monitoring wells constructed by the U.S. Geological Survey. The PAH were extracted from the samples by a solid phase extraction process using cartridges containing C-18 bonded porous silica then eluted with solvent. The resulting eluate was then analyzed by GC/MS to identify and quantify PAH contained in the samples. Distribution and fate was analyzed by a study of the characteristics of the aquifer matrix and other dissolved constituents in relation to the chemical properties of PAH. Possible sources were investigated by examining processes used in the mining operations in the Globe/Miami area as well as other local industries and waste sources. The determination of a definite source of contamination was not possible because of a lack of specific information about practices in the area and the lack of data from a wider area of study.

## CHAPTER 2

### DESCRIPTION OF FIELD SITE

#### 2.1 Hydrogeologic Setting

The Globe area consists of block-faulted mountains and valleys ranging from 670 to 2,400 m in elevation. A north-south trending fault system is downthrown to the east about 450 m (Peterson, 1962). Figure 2.1 shows the location of geologic cross sections and the major fault, the Miami Fault, through the area. Figure 2.2 shows geologic cross sections through the Pinal Creek basin.

West of the fault zone are granite porphyry ore bodies formed by hydrothermal leaching of metals into the granite. The disseminated ore minerals are primarily sulfides and are enriched in quartz-filled veins. Oxidized layers overlying the ore bodies are enriched in oxide minerals. Associated metamorphic rocks and other intrusives are also present. Mining operations are situated at about 1100 m. The area along Pinal Creek has been mined since 1903 (Peterson, 1962).

The Miami Wash - Pinal Creek drainage flows northward just east of the fault system. The aquifer is bounded to the east by a mineralized complex and to the north by welded tuff and granite. The aquifer consists of two units, a lower conglomerate or basin fill, the Gila Conglomerate, and an upper unit of unconsolidated alluvium present along the valley floors and arroyos.

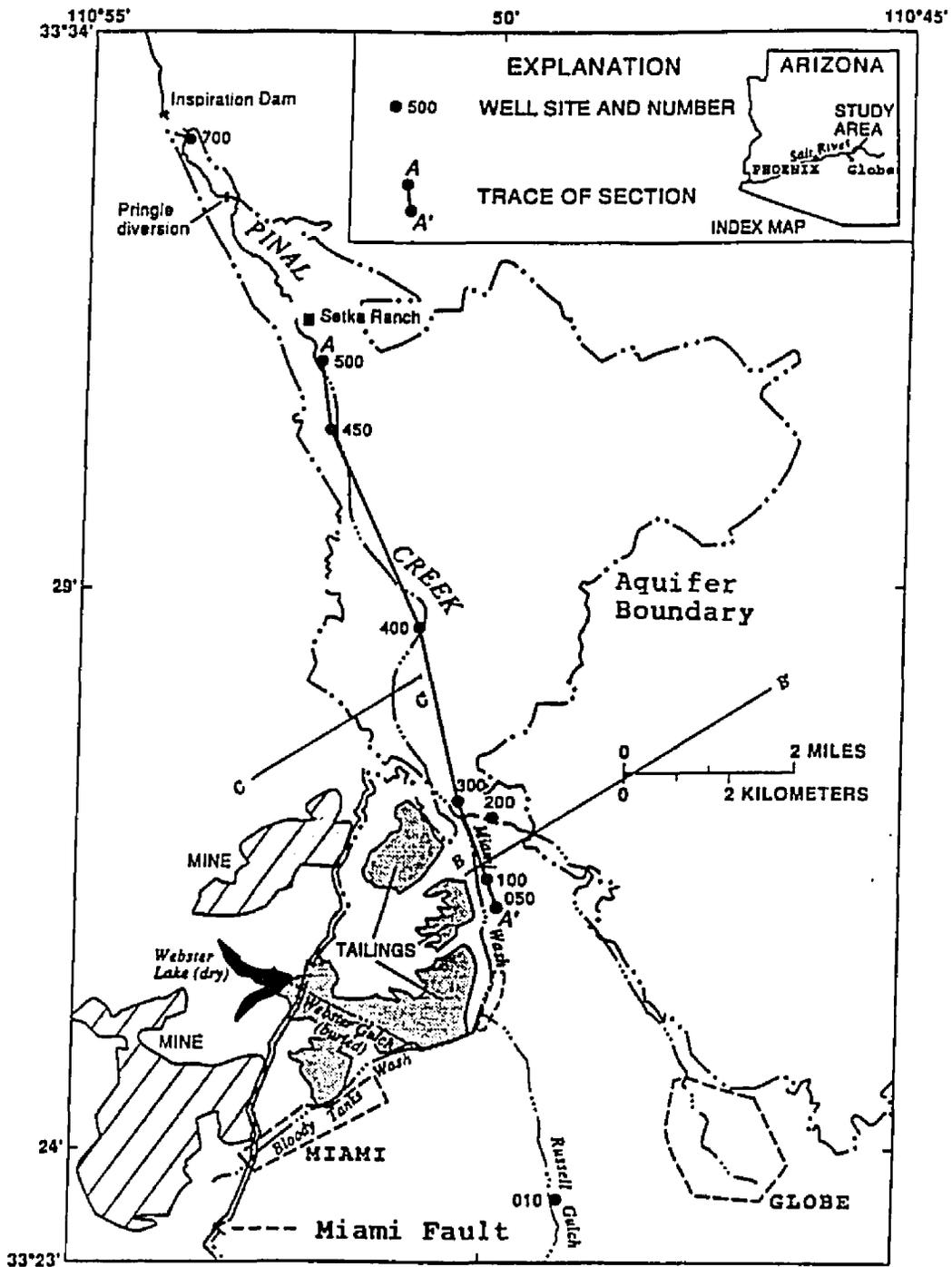
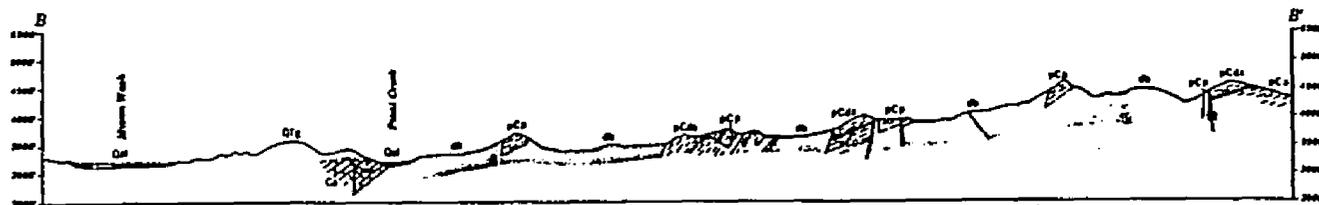
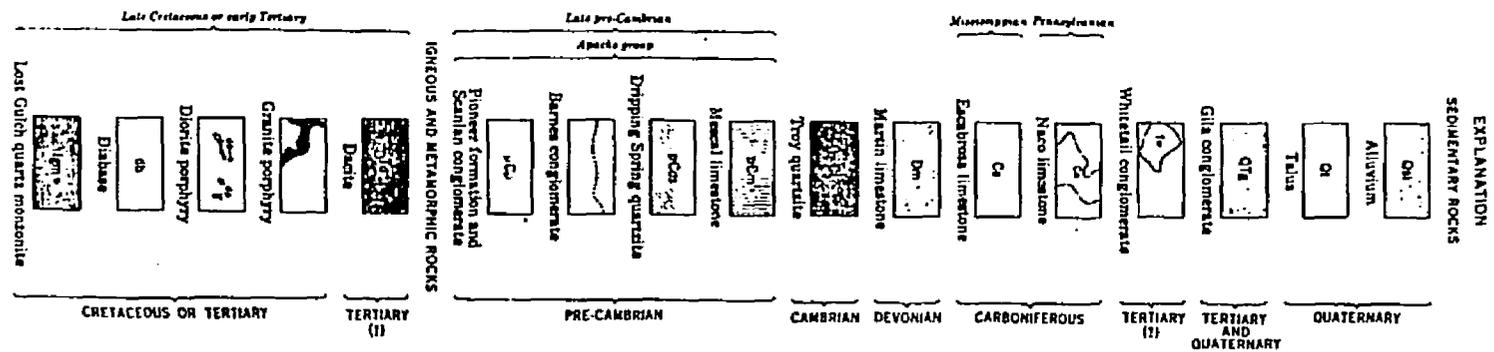
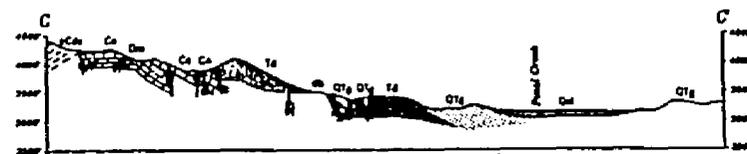


Figure 2.1 - Area of study (after Wallin et al., 1991)



SECTION ALONG LINE B-B'



SECTION ALONG LINE C-C'

0 3000 6000 Feet

GEOLOGIC STRUCTURE SECTIONS

Figure 2.2 - Geologic sections through the Pinal Creek basin  
(after Peterson, 1962)

The Gila Conglomerate includes deposits of Pliocene and early Pleistocene age and is described by Peterson (1962) as a bouldery conglomerate of local origin interbedded with layers of slightly coherent sand, tuff, and sheets of basalt. The Gila Conglomerate overlies older formations on an erosional surface of great relief characterized by pronounced angular unconformities. The Gila Conglomerate features deposits typical of coalescing alluvial fans ranging from 100 to 1,200 m thick and 2 to 9 km wide (Eychaner, 1988). The deposits range from unsorted and unconsolidated rubble containing angular blocks up to 15 m in diameter to well stratified deposits of firmly cemented sand, silt, and gravel containing well-rounded pebbles and cobbles. Calcite content of the conglomerate is about 1.5 percent (Eychaner, 1988).

The alluvium unit is composed mainly of reworked detritus of the Gila Conglomerate and material derived from older rocks. Materials range from clay to boulders with a large amount of fragments, cobbles, and pebbles of granite, schist, and granite porphyry. The deposits range up to 50 m in thickness and 300 to 800 m in width. Fine sand to coarse gravel is the predominant size range with much brown clay and coarser materials present in lenses (Peterson, 1962).

Although the conglomerate and alluvium are considered to be a single aquifer, their hydraulic conductivities vary greatly. In the alluvium, the hydraulic conductivity is on

the order of 200 m/d; in the conglomerate, it is on the order of 0.03 m/d, but may be much larger in discontinuous zones of coarser or less indurated material (Eychaner, 1988). Peterson (1962) reports well yields ranging from a few hundred liters per day to 600 liters per minute. Two major faults and many minor faults perpendicular to the direction of flow offset the conglomerate in the high conductivity zones and impede flow (Eychaner, 1988).

Average precipitation over the basin ranges from 340 mm/yr to 780 mm/yr and is about 450 mm/yr near the mines. Precipitation occurs as heavy but brief thunderstorms in the summer or storms lasting up to several days in the winter. Snow commonly accumulates above 2,000 m. in winter. Most of the recharge to the aquifer takes place during the winter and spring. Temperatures in the area range from -15 to 45°C. Groundwater temperatures in the wells sampled range from 17 to 19°C (Eychaner, 1988).

The water table in the area where the alluvium is present ranges from 1 to 20 m below the surface but varies with seasonal cycles. Head in observation wells also varies with depth of well, with the lowest head being near the contact between the conglomerate and the alluvium (Eychaner, 1988). Stream flow in Miami Wash and Pinal Creek is ephemeral until a point approximately 10 km downstream from the intersection of these two drainages, at which point flow becomes perennial.

Impermeable rocks truncate the aquifer just before the stream gaging station, approximately 16 km downstream from the intersection of Miami Wash and Pinal Creek. The discharge at the gaging station ranged from 0.2 to 0.4 m<sup>3</sup>/sec during 1980-86 (Eychaner, 1988). The specific discharge of groundwater in the alluvium is estimated to be 1.6 m/d (600 m/yr) based on measurements of total aquifer discharge, the groundwater gradient, and the average hydraulic conductivity (Eychaner, 1988). The specific discharge in the conglomerate is estimated to be  $2.4 \times 10^{-4}$  m/d (.09 m/yr) but may be larger in zones of discontinuous material. Most of the flow moves from the conglomerate to the alluvium except during times of prolonged recharge (Eychaner and Stollenwerk, 1985). Figure 2.1 shows the area of study along with locations of monitoring wells discussed in section 4.1. Figure 2.3 shows a longitudinal section of the aquifer, also with well locations. Well location numbers ending in zero refer to sites of nested wells rather than a specific well. Well location numbers ending in one through 6 refer to specific wells.

## 2.2 Mining Activity in the Globe-Miami Area

The Globe-Miami mining district has been active since 1872 with over 200 mines in the area. Copper has been mined from granite porphyry deposits adjacent to the aquifer since 1903. Since 1931, most of the major mining activity has been within



four miles of the town of Miami which is located along Bloody Tanks Wash, at the headwaters of Miami Wash. Figure 2.4 illustrates mining activities in the Miami area in 1982. Large mining complexes include the Inspiration, Miami, Copper Cities, and Bluebird, the largest of which is Inspiration. Facilities include the Inspiration, Miami, and Bluebird leaching plants, and the International Smelter (Figure 2.4). Many large tailings and waste piles are present in the area and at least four large tailings ponds lie near the concentrator plants (CAAG, 1983).

Copper ore in the Globe-Miami area is present as both copper oxide and copper sulfide minerals. Leaching has been a common technique for removing copper from low-grade oxide or oxide/sulfide ore. High-grade copper ores can be smelted directly, but ores with 2% or less copper are usually leached. The ore is soaked in sulfuric acid, creating a copper sulfate solution. Four methods of leaching used in the Globe-Miami area are dump leaching, vat leaching, in-situ leaching, and heap leaching (CAAG, 1983).

Solvent extraction is a concentrating process that uses a solution of chemical reagents and solvents with a copper sulfate solution obtained from leaching. Copper ions complex with chelating agents and settle out. Oxine (8-hydroxyquinoline) is a commonly used chelating agent. This compound contains two aromatic rings with a nitrogen atom substituted

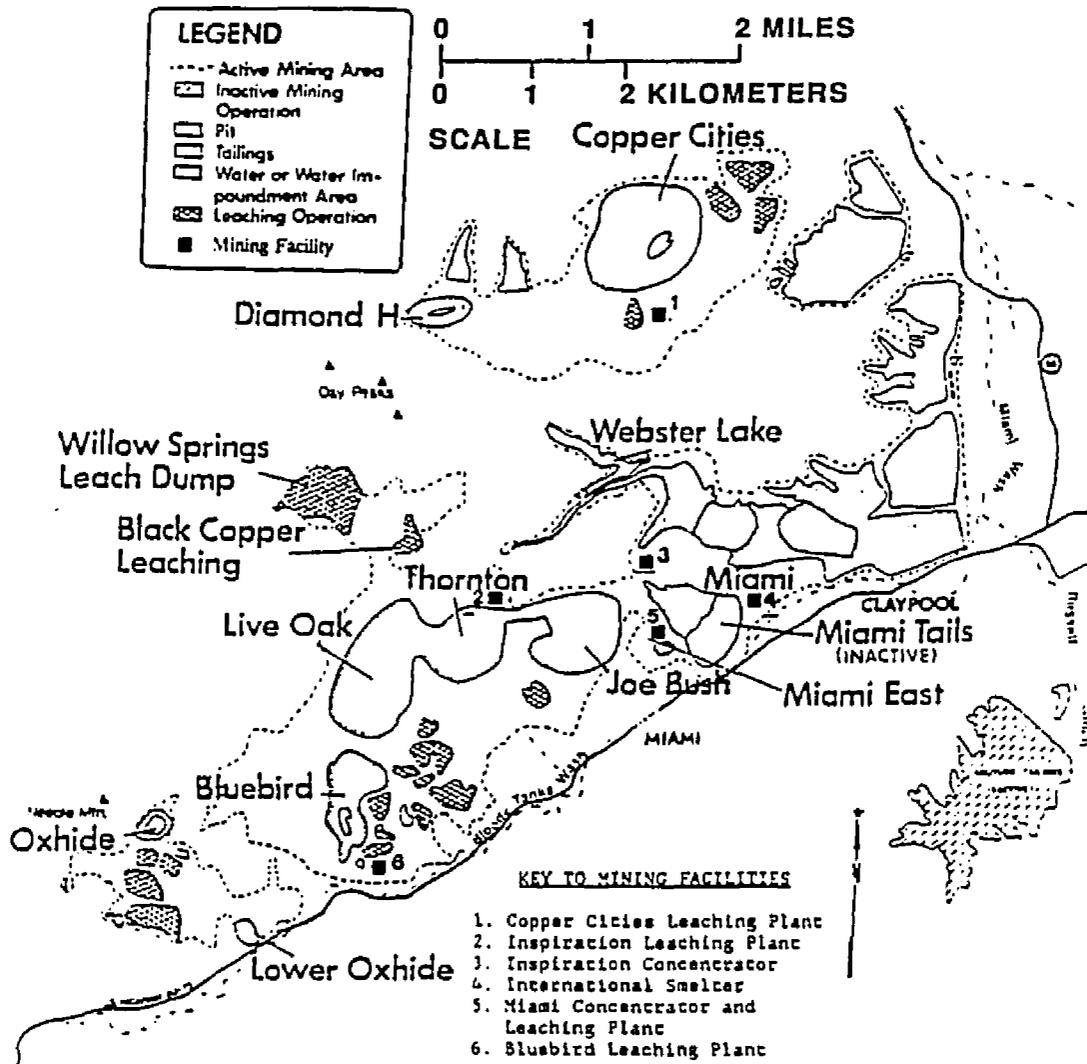


Figure 2.4 - Mining activities in the Miami area as of 1982 (after CAAG, 1983)

into one ring and a hydroxyl group attached to the other ring. The copper is bound between two oxine atoms (CAAG, 1983). This process enriches the copper in solution from 3 to 50 grams/liter. The copper solution is then placed in an electrowinning tank where a current is passed through lead anodes. The copper is then plated onto a copper starter sheet. The finished copper cathode is more than 99.9% pure (CAAG, 1983). Leaching produces waste solutions high in organics, sulfates, and dissolved metals and low in pH (Eychaner, 1988).

The predominant method of concentrating copper sulfide ore is through the froth flotation process which became widely used in the Globe-Miami area after 1915. Froth flotation is the method by which copper minerals selectively attach to air bubbles rising through an aqueous solution called a slurry (CAAG, 1983). The process begins by mixing the ore with a small quantity of a light oil as a lubricant while it is being ground. The mixture is then put into a water bath mixed with a small amount of sulfuric acid and sodium cyanide to keep other minerals from rising. Between 0.2 and 0.4 kg of cyanide is added for each ton of ore. Air is bubbled through the slurry, and copper, along with other desirable minerals, collects in a froth at the surface (Albert, 1984).

Froth flotation is done in a series of large tanks which hold the copper ore slurry. The froth is separated from the

slurry and sent on for further processing. The slurry remaining after the copper minerals have been removed is then searched for other minerals in another floatation process. Eventually, the slurry is thickened and pumped into tailings ponds (Albert, 1984). Tailings solutions that result from the processing of sulfide ores may produce seepage water high in sulfate, metals, particularly iron, and low in pH both from the sulfuric acid solutions and because of the oxidation of remaining sulfide minerals, especially pyrite in situ in the tailings pile (Eychaner, 1988).

Webster Lake, located approximately 8 km upgradient from the intersection of Miami Wash and Pinal Creek, was a collection area for waste water from mining processes from 1946 to 1986. The lake was dammed up behind piles of waste and tailings. The lake was unlined and was recorded to have a pH as low as 0.7 in 1983 (Envirologic Systems, 1983). In 1986, the lake had a volume of  $5.5 \times 10^6$  m<sup>3</sup> and a surface pH of 2.7 (Eychaner, 1988). In late 1986, the process of draining the lake was begun even though significant quantities of water were already leaking into the aquifer. Water was pumped from the lake and sprayed on the tailings piles where it evaporated (Reese, 1989). The Webster Lake area is now considered to have been a major source of contamination in the Miami Wash - Pinal Creek Basin (Envirologic Systems, 1983; Eychaner and Stollenwerk, 1987).

### 2.3 Inorganic Groundwater Contamination

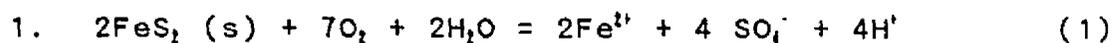
The groundwater in the Pinal Creek basin has been of low quality for at least the past 50 years as a result of seepage of waste solutions from mining processes. A plume of groundwater with total dissolved solids as high as 16,400 mg/l and pH as low as 3.5 were defined in the Miami Wash - Pinal Creek drainage basin (Eychaner and Stollenwerk, 1985). A study done by Envirologic Systems, Inc. for the Central Arizona Association of Governments (CAAG) defined the portion of the plume upgradient from monitoring wells installed by the USGS (Envirologic Systems, 1983). Contour mapping of the concentrations of sulfate, iron, and other metals shows that the plume extends up Miami Wash and then up into Bloody Tanks Wash about 1.5 to 2.5 km. From this point, upgradient, sulfate and iron rapidly decrease in concentrations. This means that the most likely source of contamination is the area of intensive mining and ore processing near the town of Miami. Contaminated groundwater probably flowed into Bloody Tanks Wash from Webster Gulch which is now filled with tailings and waste ponds (Envirologic Systems, 1983). Webster Gulch is the site of the former Webster Lake.

The entire downgradient extent of the aquifer along Pinal Creek is affected; however, the lateral extent of the contamination is limited as well as the extent of the contamination from the alluvium into the conglomerate.

Contamination in the conglomerate appears to be limited to the top 25 meters. Groundwater discharging from the aquifer into Pinal Creek still reflects contamination, containing high concentrations of sulfate and manganese (Eychaner and Stollenwerk, 1985).

Acid water in mining areas can be produced by direct introduction of waste sulfuric acids used in ore processing into ponds and soils. This introduction can be either a result of the flushing of residual reagents into ponds or from accidental leaks and spills. Another common source of acid water in most mining areas is from the oxidation of pyrite and other metal sulfides.

The rate of oxidation of pyrite is insignificant without catalysis by bacteria, *Thiobacillus* and *Ferrobacillus* being the most widely distributed. The oxidation reaction can proceed by numerous processes such as:

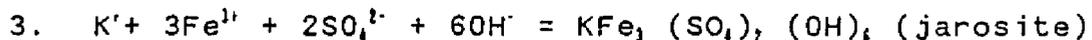
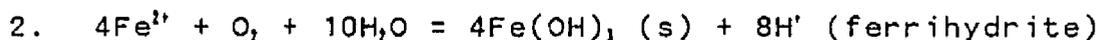


all of which generate acidic solutions (Hiskey and Schlitt, 1982).

The solubility of many of the metals in the contaminated waters is controlled by pH. The mobilization of metals is potentially of greater environmental concern than the acid. High concentrations of metals can be a hazard to humans, fish

and livestock (EPA, 1976). The solubilities of several metals increase considerably below pH 5. Each metal becomes soluble in a different narrow pH range.

The presence of oxygen may cause metal oxides to precipitate from solution. Iron hydroxide minerals are formed by reactions such as: (Hiskey and Schlitt, 1982; Nordstrom and Munoz, 1986)



The above reactions are highly dependant on the pH of the water. The solubility of aluminum is also controlled by the precipitation of aluminum hydroxides.

Acid waters may be neutralized by numerous reactions with mineral species present in the aquifer. For example, carbonate minerals such as calcite ( $\text{CaCO}_3$ ) when present in sufficient quantities, will effectively neutralize the acid solutions. Contaminated waters already containing high sulfate concentration may precipitate secondary minerals such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), but solubility is such that total dissolved solids will still remain high (Eychaner, 1988). Other carbonates such as dolomite or rhodochrosite ( $\text{MnCO}_3$ ) and silicate minerals such as feldspar, etc., also provide additional acid neutralizing capacity.

An acid front has been identified in the aquifer and is defined as the point at which pH is less than 5 and iron concentration is greater than 1 mg/l. This front advances in the aquifer as reactive acid neutralizing minerals are consumed. The location of this front moves more slowly than the velocity of the bulk groundwater and may be slower by as much as a factor of 10. In the Pinal Creek basin, the acid front has been moving at a rate of 0.2 to 0.3 km/yr for the past several decades (Eychaner, 1988).

All available calcite in the aquifer has been consumed along a flow path below Webster Lake for at least 15 km. Water in the aquifer 6 km from the former location at Webster Lake has pH 3.6 and dissolved solids over 10,000 mg/l. The pH increases slowly to 4.5 at a point 15 km from the lake. The pH then increases rapidly over the next 2 km to 6.1 at well site 500 (Fig. 2.1). Dissolved solids concentration at the gaging station was 800 mg/l in 1942, 2,700 mg/l in 1980, and 3,200 mg/l in 1987. Sulfate was about 60 percent of the dissolved load in 1987 (Eychaner, 1988).

Virtually all of the dissolved oxygen in the contaminated groundwater has been depleted and is typically only 0.5 mg/l. However, at downgradient locations, in contaminated water that has been neutralized by the presence of calcite, the amount of dissolved oxygen is much less. At well sites 501 and 503, the

recorded level was below the detection limit of 0.1 mg/l in June 1988 (Reese, 1989).

Geochemical modeling of the system in the Pinal Creek Basin was done by Stollenwerk and Eychaner (1989) with the PHREEQE computer model using analyses from about 200 groundwater samples. Their modeling indicated that at pH values less than 4.9, solubility of aluminum may be controlled by aluminum sulfate ( $\text{Al(OH)SO}_4$ ) and kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). At pH values above 4.7, microcrystalline gibbsite ( $\text{Al(OH)}_3$ ) should control solubility. Physical evidence from the alluvium and chemical data from the ground water tends to indicate that the solubility of iron is controlled by the precipitation of amorphous ferric hydroxide ( $\text{Fe(OH)}_3$ ) at all pH values (Stollenwerk and Eychaner, 1989). Additional statistical work with the model as well as additional physical evidence is needed to better characterize the solid phases forming in the aquifer.

#### 2.4 Organic Ground Water Contamination

A study by Reese (1989) analyzed the composition of DOC found in samples of ground and surface water of the Pinal Creek basin. His extraction procedure separated the DOC into different fractions based on their hydrophobic and hydrophilic character as well as their acid, base, or neutral character. The distribution of DOC demonstrates a correlation with the

distribution of inorganic contamination (Reese, 1989). Values assumed to be representative of background DOC range from 0.3 to 0.5 mg/l from wells deep in the conglomerate; however, DOC values in the upgradient part of the plume reach as high as 4.2 mg/l. Loss of organic matter from the system correlated with changes in pH. Loss of DOC may be the result of pH-controlled sorption (Reese, 1989). Average DOC values agreed well with TOC values determined by the USGS. These results indicate that the amount of particulate organic matter in the groundwater samples is negligible (Reese and Bassett, 1990).

Reese (1989) found that although the hydrophobic acid fraction generally follows the distribution of the DOC values, the concentration of hydrophobic acid as a percent of DOC decreases with depth from 25% to 20%. This indicates that recharge water coming into the aquifer has a higher hydrophobic acid content than the most contaminated part of the plume (Reese, 1989).

Some hydrophilic acids may also be present in the DOC. Hydrophilic acids in ground waters can be present up to 50 percent of DOC (Thurman, 1985). Reese (1989) found the entire hydrophilic fraction of the DOC in the Pinal Creek basin to be approximately 48%. As much as 25% of the hydrophobic acid fraction was lost from solution after accounting for dilution, and as much as 47% of the hydrophilic fraction was lost from

solution after accounting for dilution. Portions of the hydrophobic acid and hydrophilic fractions totaling 28% of DOC are thus being lost from solution as the pH rises above 4 (Reese, 1989) [See section 3.9 for a further discussion of humic substances in groundwater].

## CHAPTER 3

## PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS

3.1 General Properties

PAH are compounds composed of two or more aromatic (benzene) rings. Of primary environmental concern are compounds ranging in molecular weight from naphthalene ( $C_{10}H_8$ , MW 128.16) to coronene ( $C_{24}H_{12}$ , MW 300.36), encompassing an extremely large number of compounds varying in position and number of aromatic rings and in number, chemistry, and position of substituent groups on the basic ring system (Neff, 1979). Naphthalene consists of two fused aromatic rings. Two rings are said to be fused if a pair of carbon atoms are shared. Many configurations are possible. The concern regarding the presence of PAH in the environment is that several of the PAH produced by humans and released into the environment have been shown to be carcinogenic to mammals. Table 3.1 gives the name, structure, and other properties of the 16 PAH on the Environmental Protection Agency Priority Pollutant List (U.S.E.P.A., 1979).

PAH are typically produced by the pyrolysis of organic materials at high temperature ( $>700^{\circ}C$ ). Complex mixtures of PAH, however, have been found in fossil fuels such as coal and crude petroleum, leading to the conclusion that, given enough time, PAH can be produced by pyrolysis of organic materials at low temperature,  $100-150^{\circ}C$  (Blumer, 1976). In

	Molecular Structure	Molecular Formula	Molecular Weight	Aqueous Solubility (ppm, 25 °C)	Melting Point (°C at 766 mm)	Boiling Point (°C at 760 mm)	logK <sub>ow</sub> (unitless)	log K <sub>oc</sub> (unitless)
Naphthalene		C <sub>10</sub> H <sub>8</sub>	128	31.7	80	218	3.29	2.97
Acenaphthylene		C <sub>12</sub> H <sub>8</sub>	152	3.93	92	265-275	3.72	3.40
Acenaphthene		C <sub>12</sub> H <sub>10</sub>	154	3.42	96	279	3.98	3.66
Fluorene		C <sub>13</sub> H <sub>10</sub>	166	1.69	116-117	293-295	4.18	3.86
Anthracene		C <sub>14</sub> H <sub>10</sub>	178	.045	216	227	4.45	4.15 (53 mm)
Phenanthrene		C <sub>14</sub> H <sub>10</sub>	178	1.00	101	210-215	4.45	4.15 (12 mm)
Fluoranthene		C <sub>16</sub> H <sub>10</sub>	202	.26	111	217	4.90	4.58 (30 mm)
Pyrene		C <sub>16</sub> H <sub>10</sub>	202	.13	150	393	4.90	4.60
Benzo(a)anthracene		C <sub>18</sub> H <sub>12</sub>	228	.0057 20. °C	155-157	ND	5.61	5.30
Chrysene		C <sub>18</sub> H <sub>12</sub>	228	.0018	256	448	5.61	5.30

Table 3.1 Properties of 16 PAH from EPA Priority Pollutant List  
(Source: EPA, 1982)

	Molecular Structure	Molecular Formula	Molecular Weight	Aqueous Solubility (ppm, 25 °C)	Melting Point (°C at 766 mm)	Boiling Point (°C at 760 mm)	logK <sub>ow</sub> (unitless)	log K <sub>oc</sub> (unitless)
Benzo(b) fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	.014	167-168	ND	6.06	5.74
Benzo(k) fluoranthene		C <sub>20</sub> H <sub>12</sub>	252	.0043	217	ND	6.06	5.74
Benzo(a) pyrene		C <sub>20</sub> H <sub>12</sub>	252	.0038	179	ND	6.06	5.74
Dibenzo(a,h) anthracene		C <sub>22</sub> H <sub>14</sub>	278	.0005	270	ND	6.84	6.52
Benzo(g,h,i) perylene		C <sub>22</sub> H <sub>12</sub>	276	.00026	222	ND	6.51	6.20
Indeno(1,2,3-cd) pyrene		C <sub>22</sub> H <sub>12</sub>	276	.00053	164	ND	6.51	6.20

TABLE 3.1 (continued)

addition, trace amounts of PAH synthesized by bacteria, fungi, and plants are ubiquitous in the environment. Industrial activities resulting in the increased environmental load of these compounds include preparation of acetylene from natural gas, pyrolysis of kerosene to form benzene, toluene, and other organic solvents, pyrolysis of wood to form charcoal, wood tars, and carbon blacks, manufacture of electrolytic aluminum using graphite electrodes, coke production, gas production from petroleum, coal gasification, production of synthetic alcohol, and oil refinery operations (Andelman and Snodgrass, 1972). Coal tar distillation plants as well as creosote production and wood-preserving plants are also sources of PAH contamination (Hult, 1984; Mattraw and Franks, 1986). Incineration of wastes, forest and grass fires, power generation from fossil fuels, and combustion of fuels in internal combustion engines also produce PAH. These PAH may reach the aquatic environment in sewage effluents, surface runoff, deposition of airborne particulates, and spillage of petroleum products (Neff, 1979).

### 3.2 Solubility

Aqueous solubility is a fundamental parameter in determining the extent and rate of PAH dissolution and their persistence in the environment. The solubilities of PAH are quite low, reflecting their hydrophobic character. Published

solubilities of PAH in water vary considerably owing to differences in experimental procedures. Despite the variability, some definite trends emerge. Solubility tends to decrease as the number of aromatic rings increases. Naphthalene has a solubility of around 30 ppm, while PAH with five rings have solubilities in the 0.5-5.0 ppb range. PAH with alkyl substituent groups have lower solubilities than unalkylated parent compounds, and solubilities decrease with increased degree of alkylation. Linear PAH tend to be much less soluble than angular isomers. For example, anthracene is less soluble than phenanthrene and naphthalene is less soluble than chrysene or benzo(a)anthracene (Neff, 1979).

PAH are slightly less soluble in seawater than in freshwater due to the "salting-out effect", where a solute dissolves less well in water that is bonded to ions (Snoeyink and Jenkins, 1980). Temperature strongly effects the solubility of PAH. In some cases, but not all, the presence of one or two PAH in solution affects the solubility of an additional PAH in the solution. This is known as the cosolvency effect. Eganhouse and Calder (1976) demonstrated that the solubility of naphthalene was unaffected by the presence of other PAH, while both naphthalene and phenanthrene enhanced the solubility of acenaphthene. The presence of surfactants in the solution can also increase the solubility of PAH. Humic acids, fulvic acids, and other degradation

products of biological materials in natural waters may also act as PAH solubilizers (Boehm and Quinn, 1973)(see section 3.9 for a further discussion of solubility enhancement of PAH by humic substances). PAH can also be solubilized by incorporation into micelles (Neff, 1979).

### 3.3 Adsorption

PAH readily sorb onto organic surfaces in water. Smith et al. (1978) indicated that most PAH accumulate in the sediment and biota portion of the aquatic environment and that adsorption is the dominant transport process for PAH. Smith et al. (1978) also reported partition coefficients of 150,000 for benzo(a)pyrene and 21,000 for benzo(a)anthracene between water and sediment containing 5 percent organic carbon, indicating that sorption onto sediments is strongly correlated to sediment organic carbon content. Southworth (1977) found a partition coefficient of approximately 25,000 for the sorption of anthracene on suspended organic particulates using autoclaved yeast cells. In contrast, sorption onto inorganic particulates was less with an approximate partition coefficient of 1600. These data indicate that sorption onto suspended organic particulates can be a significant transport process.[see section 3.9 for a discussion of adsorption onto dissolved humic substances.]

### 3.4 Biodegradation

Bacteria and fungi demonstrate a great diversity in their ability to use PAH as a sole carbon source. PAH and related compounds have been trace elements in the biosphere for billions of years (Neff, 1979) and many microbes have evolved the capacity to metabolize them. Some organisms such as Pseudomonas can use simple PAH such as naphthalene and oxidize them completely. The carbon is used as a source of carbon for increase in biomass. Most organisms require an alternative growth substrate as a carbon source and then only partially metabolize the PAH. This process is called co-oxidation or co-metabolism (Gibson, 1977). PAH are then transformed into various oxygenated metabolites. Higher molecular weight PAH generally require co-oxidation.

Naphthalene, containing only two rings, is probably the most easily biodegraded PAH. Lee and Ryan (1976) measured microbial degradation rates for naphthalene in river water as high as 4 µg/liter/day. Vennberg (1977) observed that 50 percent of naphthalene in a test flask had been converted to CO<sub>2</sub> by microbes after one day. Herbes and Schwall (1978) determined microbial degradation half-times for naphthalene, anthracene, benzo(a)anthracene, and benzo(a)pyrene in pristine and petroleum-contaminated sediments. Half-times ranged from 5 hours for naphthalene to 21,000 hours for benzo(a)pyrene in petroleum-contaminated sediment. Degradation rates were

10-400 times slower in pristine sediments, demonstrating the importance of microbial accumulation and adaptation as well as availability of a cosubstrate.

Napthalene can be metabolized by Cunninghamella and Pseudomonas bacteria (Gibson, 1978; Davies and Evans, 1964). Anthracene and phenanthrene can be metabolized by Pseudomonas (Evans et al., 1965). Lorbacher et al. (1971) reported that soil microbes degrade 3,4-benzopyrene, anthracene, and phenanthrene, and the rate of degradation is greatest when the microbes have been acclimated to the compounds. Soil systems are known to provide much better conditions for biodegradation than surface water systems (EPA, 1979).

Figures 3.1 and 3.2 show the proposed metabolic pathways and products for the degradation of naphthalene by Pseudomonas and Cunninghamella bacteria respectively. Figures 3.3 and 3.4 show the proposed metabolic pathways and products for the degradation of anthracene and phenanthrene by Pseudomonas. Adsorption of PAH onto organic aquifer material decreases their availability to microbial degradation (Novak, 1990).

### 3.5 Photolysis

Most PAH adsorb solar radiation strongly at wavelengths above 300 nm and undergo direct photolysis or photooxidation (Radding et al., 1976). This process can be an important fate process in the surface water environment, especially for PAH

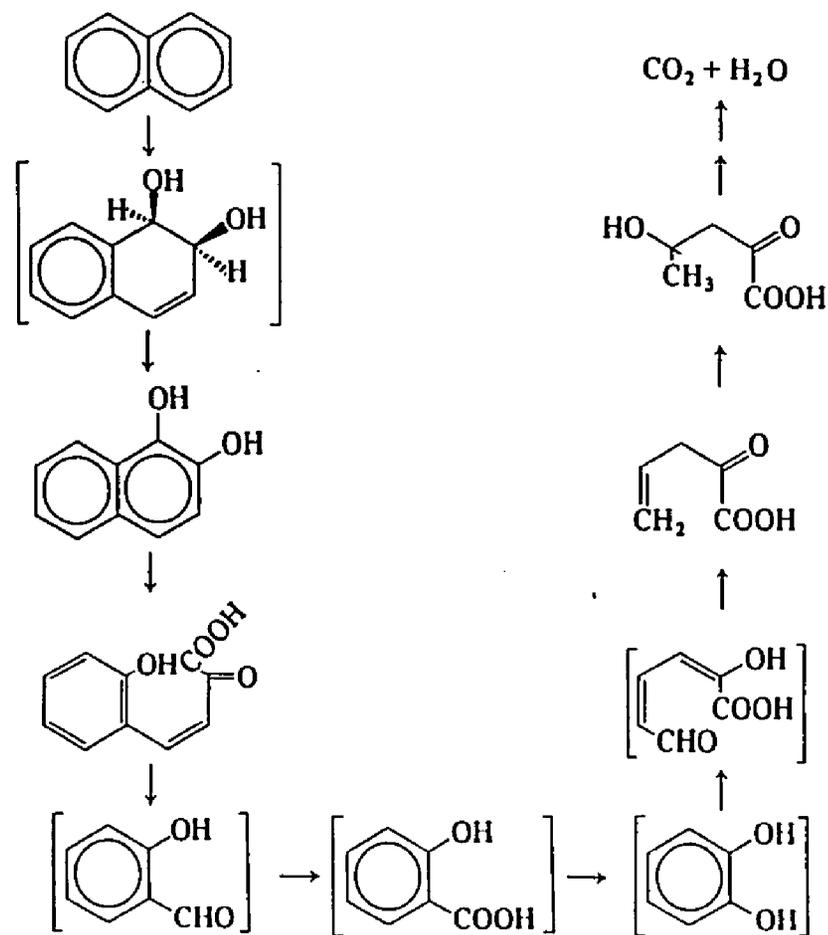


Figure 3.1 - Proposed metabolic pathway for the degradation of naphthalene by *Pseudomonas* (after Davies and Evans, 1964)

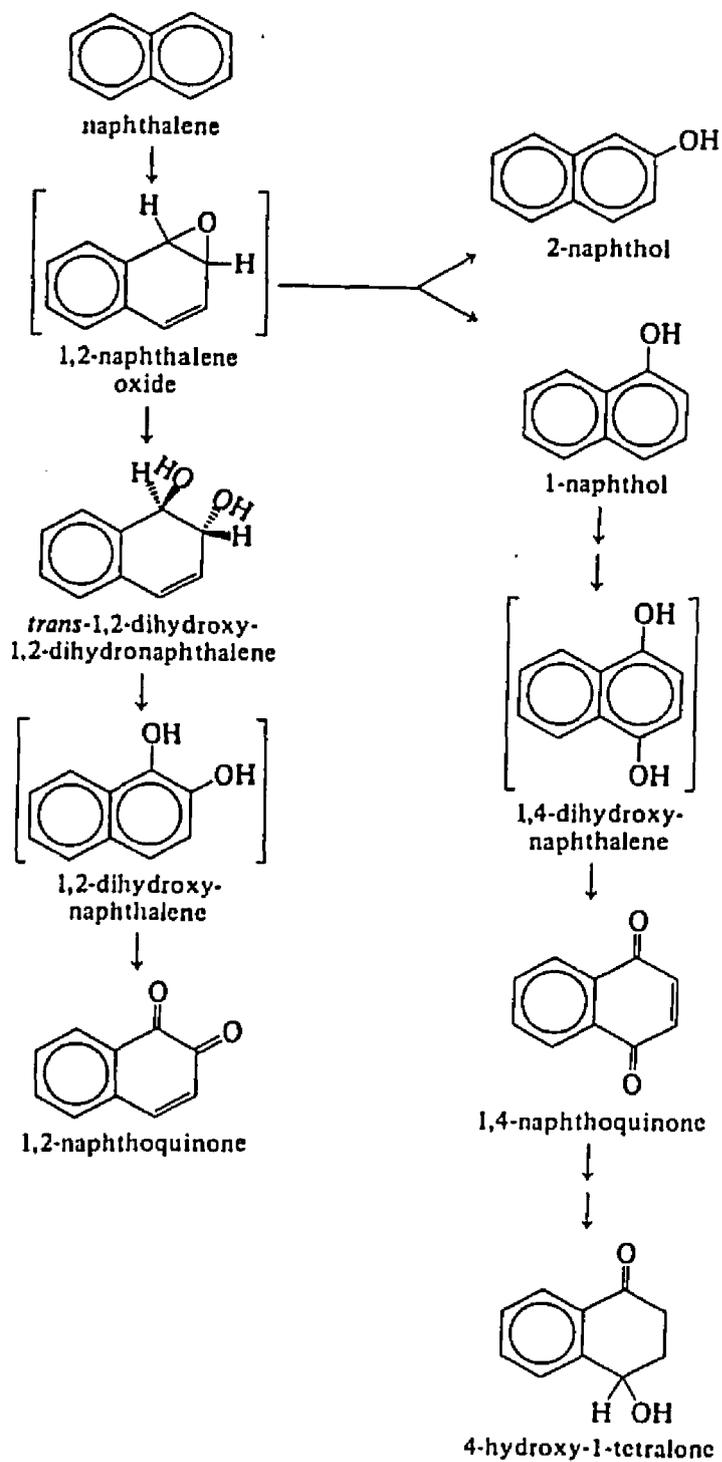


Figure 3.2 - Proposed metabolic pathway for the degradation of naphthalene by *Cunninghamella* (after Gibson, 1978)

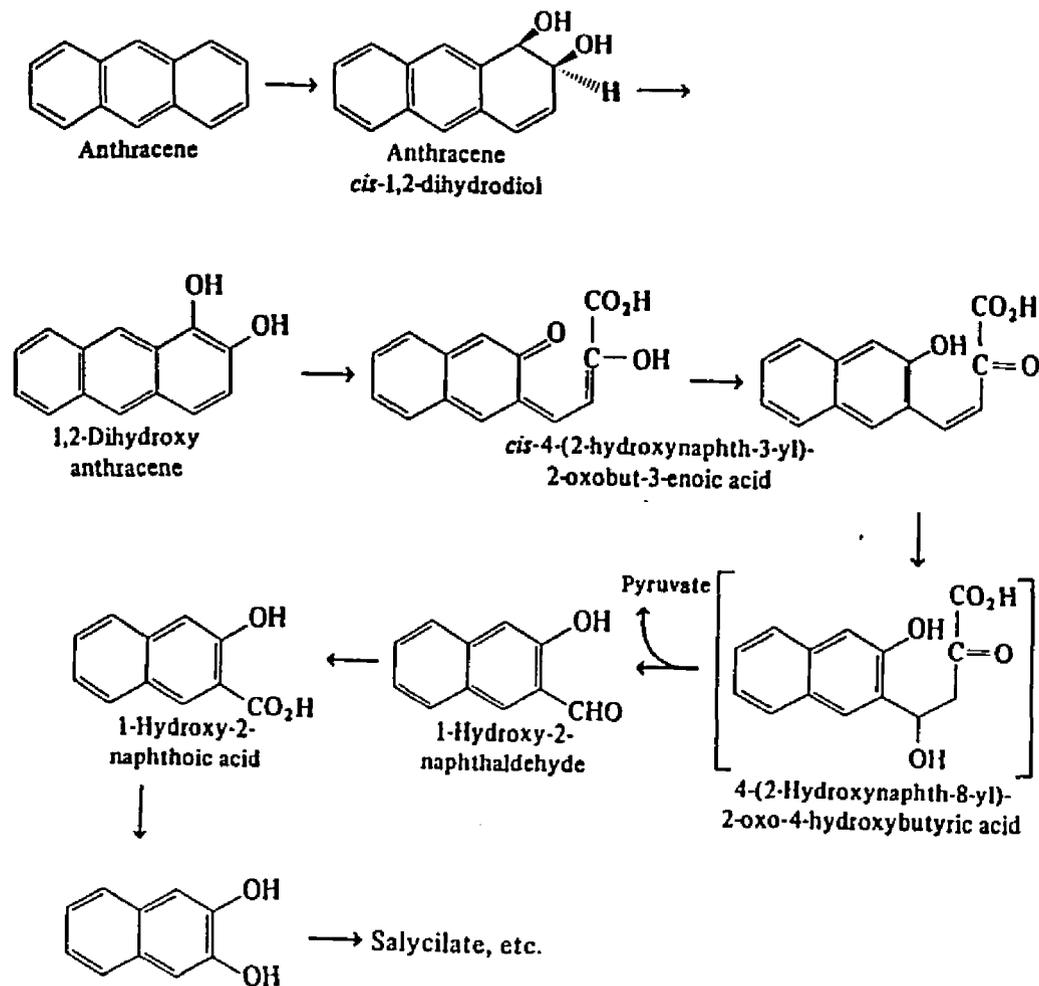


Figure 3.3 - Proposed metabolic pathway for the degradation of anthracene by *Pseudomonas* (after Evans et al., 1965)

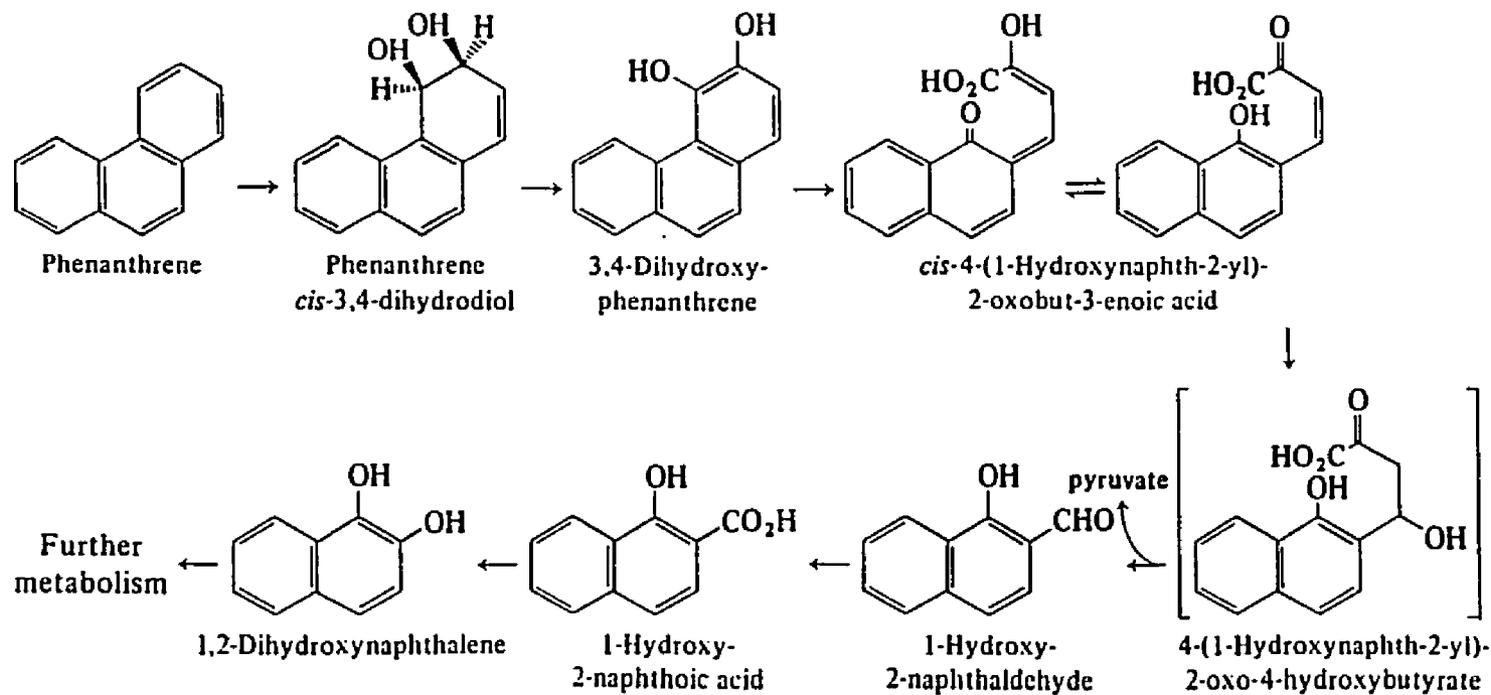


Figure 3.4 - Proposed metabolic pathway for the degradation of phenanthrene by *Pseudomonas* (after Evans et al., 1965)

with relatively high solubilities such as naphthalene. Stevens and Algar (1968) concluded that singlet oxygen radical ( $^1O_2$ ) is the primary oxidant. Smith et al. (1978) reported half-lives of 1.2 hours for benzo(a)pyrene and 1 to 2 hours for benzo(a)anthracene for midday photolysis in water. Southworth (1977) reported that anthracene in distilled water exhibited a half-life of 35 minutes in summer solar conditions and 4.8 hours under average conditions at 35°N latitude.

### 3.6 Oxidation

Chlorine and ozone are both used as disinfecting agents in drinking water. They are strong oxidants and react chemically with PAH to form quinones. Perry and Harrison (1977) studied the removal of eight PAH from water by chlorination. Concentrations of PAH ranged from 30-860 mg/l, free chlorine was 2.2 mg/l, pH 6.8, and temperature 20°C. Twenty-five percent of fluorene was degraded after 25 minutes and 50% of pyrene was degraded after 20 minutes. The rate of degradation was increased by both decreased pH and increased temperature.

Radding et al. (1976) reported half-lives of several PAH (pyrene, benzo(a)pyrene, benzo(a)anthracene) with ozone in water to be approximately one minute. Oxidation by chlorine and ozone may be a significant fate process when those oxidants are available in sufficient quantity.

### 3.7 Volatilization

Southworth (1979) reported volatilization rates of PAH containing 2 to 5 rings. He reported that, in general, volatilization rate decreases as vapor pressure decreases, and that both properties are inversely proportional to the number of aromatic rings. Southworth (1979) also reported that volatilization rate is highly dependent upon the mixing rates within the water and air column. Lee (1975) reported a 50% loss of naphthalene from a marine environment contaminated as a result of an oil spill. The rate of loss is dependant on wave action, wind speed, and water and air temperature.

Smith et al. (1978) reported that when benzo(a)pyrene and benzo(a)anthracene are sorbed onto sediments, evaporation from the solid phase is presumed not to be an important transport process for PAH (EPA, 1979).

### 3.8 Hydrolysis

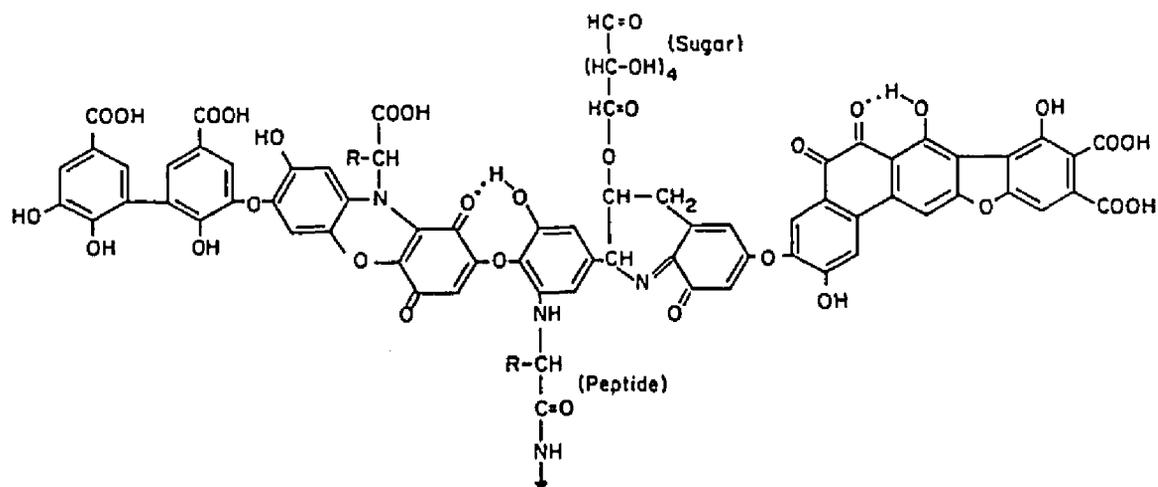
Radding et al. (1976) stated that PAH do not contain functional groups amenable to hydrolysis. Therefore, hydrolysis cannot be considered to be a significant fate process.

### 3.9 Solubility Enhancement of Micropollutants by Humic Substances

Dissolved humic substances (DHS) are hydrophobic acids that include humic and fulvic acids. Generally, the fulvic acids are low in molecular weight, from 500 to 2000, and contain numerous carboxyl and hydroxyl functional groups. Humic acids are higher than 2000 in molecular weight and often colloidal in size, with fewer carboxylic acid functional groups. Humic acids will precipitate out of solution below pH1, while fulvic acids will remain in solution. In uncontaminated ground waters, fulvic acids are typically about 20% of DOC, and humic acids are about 10% of DOC (Thurman, 1985). Figure 2.4 shows hypothetical structures of humic and fulvic acids according to Stevenson (1982) and Buffle (1977).

Another important constituent of DOC is the hydrophilic acid fraction. Leenheer (1981) has characterized this fraction as containing simple organic acids, such as volatile fatty acids and hydroxy acids, as well as complex polyelectrolytic acids that contain many hydroxyl and carboxyl functional groups. In natural ground waters, this fraction may be present up to 50% (Thurman, 1985).

There is evidence that DHS can enhance the solubility of organic micropollutants in ground water. DHS can act as chelating agents for organic compounds, greatly increasing



Proposed structure of humic acid (after Stevenson, 1982)

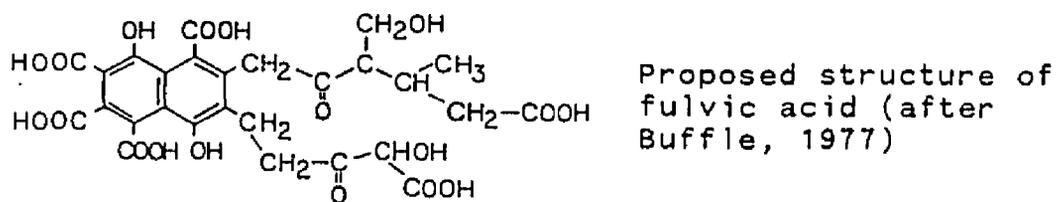


Figure 3.5 - Hypothetical structures for humic and fulvic acids

their solubility and effecting their mobilization and transport (Carlberg and Martinsen, 1982). Hydrogen bonding appears to play a major role in the complexation of organic material to DHS. Reaction rates between DHS and polycyclic aromatic hydrocarbons were found to be quite large and equilibria reached quickly (Carlberg and Martinsen, 1982). Partitioning of organic micropollutants into the structure of the humic molecule is probably a more important process than hydrogen bonding, since the hydrophilic functional groups of humic molecules would be more effectively associated with water. Humic substances are high molecular weight molecules containing nonpolar organic portions where partition interaction is likely to take place (Chiou et al., 1986).

At low DHS concentrations, partition coefficients for binding of fluoranthene, phenanthrene, and triphenylene onto DHS was determined to be approximately equal to the octanol-water partition coefficients ( $K_{ow}$ ) (Landrum et al., 1984). Another study also found partitioning of organic micropollutants to soil derived humic acids to be proportionate with  $K_{ow}$ , however, degree of solubility enhancement was found to be dependant on DHS molecular size and polarity (Chiou et al., 1987). The binding of pyrene to DHS was found to be modified by the degree of aromaticity in the DHS (Gauthier et al., 1987). Because of the different binding properties of different DHS and because DHS represent

a mixture whose composition is not consistent from one location to another, precise quantification of solubility enhancement is difficult. Hydrophilic acids as well as humic and fulvic acids can act as chelating agents for micropollutants and enhance their solubility.

In the pH range of 4 to 6, the surfaces of iron and aluminum hydroxides have a positive charge (Thurman, 1985). DHS have numerous carboxyl groups that contribute to their hydrophilic character and dissociate between pH 2 and 6. DHS containing carboxyl groups become increasingly more negatively charged below pH 6 and would be sorbed onto metal hydroxides. Metal hydroxides of Fe and Al would be positively charged in this pH range (Thurman, 1985). Oxide surfaces become hydroxylated when exposed to aqueous solutions, and the surface hydroxyl groups can be exchanged for acid functional groups (Tipping, 1990). For large organic acid molecules with more than one functional group, more than one reaction can take place per molecule. These reactions are highly dependent on pH (Tipping, 1990). Organic micropollutants adsorbed onto DHS would be sorbed out of solution onto the oxide surface as well. The absorption of organic micropollutants onto DHS can also highly reduce their availability to microorganisms for degradation (Novak, 1990).

## CHAPTER 4

## FIELD AND LABORATORY TECHNIQUES

4.1 Installation of Monitoring Wells

Monitoring wells were installed at the site by the U.S. Geologic Survey. The first 24 wells were drilled from 1984-87 (Eychaner et al., 1989). Subsequently, other wells were drilled to provide a greater sampling range. There were 31 wells at 9 different locations as of May, 1990 (Figure 2.1).

Two wells at site 700, the furthest downstream, were installed in May 1990. Depths of wells range from 10 to 68 meters and are screened at the bottom 0.9 meters. Water levels range from between 1 and 20 meters below land surface, with the lowest head near the contact between the alluvium and the conglomerate (Eychaner, 1989).

Drilling was done with a conventional rotary drill rig and bentonite mud. Wells were installed with 102 mm (4 inch) PVC casing. Sections of casing were solvent-welded with screen and well cap at the bottom. The 0.9-meter screens contain 0.6 mm slots and 340 cm<sup>2</sup> total open area. The area surrounding the screen was packed with washed pea gravel from an uncontaminated area. A one meter cap of bentonite pellets was placed above the gravel in the area between the casing and the wall of the drill hole to seal off flow from above. Drilling mud was removed from the screen area by high pressure air jetting. Initial samples were not collected until a month

after drilling to allow effected water to move away from the well area (Eychaner and Stollenwerk, 1985).

#### 4.2 Collection of Samples in the Field

Water samples were collected from monitoring wells using stainless steel submersible pumps. Three different sizes were employed depending on the depth of the well. Water was pumped to the surface through PVC riser pipe and silicone tubing. Thus, samples came in contact with only stainless steel PVC and silicon tubing. Contamination from the substances did not appear to be a factor in the analysis. Pumping rates were generally about 4 to 10 gal/min.

The samples were collected in 1 liter (later 500 ml) amber glass bottles with Teflon caps that had been previously cleaned, rinsed with methylene chloride and baked to remove all possible residue from the factory or storage. After collection, the sample bottles were sealed with electrical tape and stored in ice chests until they could be removed to a refrigerator in the laboratory and stored at 4°C. U.S. Geologic Survey personnel collected data on temperature, pH, specific conductance, dissolved oxygen, alkalinity, and total and ferrous iron in the field. Samples were not filtered or acidified.

### 4.3 Laboratory Techniques

#### 4.3.1 Column Extraction Procedures

PAH were isolated from the samples collected in the field by using a sorbent extraction process with a bonded silica solid-phase. Pre-packed cartridges were purchased from Analytichem International. Each polyethylene cartridge was filled with 150 mg of octadecyl (C-18) resin bonded to 40 um silica particles.

Bonded silica is formed by the reaction of an organosilane molecule with a substrate of activated silica. The functional group of the organosilane attaches to the substrate through a silyl ether linkage. A surface is then created, of which the principal properties are due to the functional group with minimal interactions from the silica substrate (Van Horne, 1985).

The sorbent product is stable within a pH range of approximately 2 to 7.5. Above pH 7.5, the substrate is susceptible to dissolution. Below pH 2.0, the functional groups on the surface begin to cleave, changing the sorptive properties in a non-reproducible manner (Van Horne, 1985). Bonded silica sorbents are rigid and do not shrink or swell in different solvents. Therefore, bonded silicas equilibrate rapidly to new solvent conditions allowing extraction procedures involving many different solvent changes, as

required in the procedures used in this study (Van Horne, 1985).

Particle sizes range from 15-100 microns with a mean particle size of 40 microns. Particle shape is irregular rather than spherical. The porosity of the sorbent described here is 60 Angstroms, suitable for compounds with molecular weight up to approximately 15,000. Larger molecules are exposed to too little surface area and pass through without being retained. Wide pore sorbents as high as 4,000 Angstroms are used for extraction of higher molecular weight molecules (Van Horne, 1985).

A sorbent will not retain isolates until they have been solvated. An effective solvent must interact with both the silanols on the silica surface and the carbon atoms of the bonded functional groups. The solvating solvent should be miscible with the solvent used to prepare the sorbent to receive the sample. Once solvated, the sorbent should not be allowed to desolvate by excessive drying. (Van Horne, 1985).

The extraction procedure used in this study is based on a method developed by Greg Junk and John Richard at the Ames Laboratory (U.S. Department of Energy), Iowa State University, Ames, Iowa. A wide range of sample size, flow rate, cartridge size, and volume of eluting solvent was used to determine best conditions for optimum recovery. Optimum procedures were determined to be 100 ml of sample, 100 mg cartridges, and

eluting solvent volume of 0.1 ml. The ratio of 100 ml of sample to 0.1 ml of eluting volume effectively concentrates the isolate in solution by 1,000 to 1. Results determined that flow rate did not have to be closely controlled. Recoveries for spiked samples ranged from 80% for indene to 97% for phenanthrene (Junk and Richard, 1988a).

In this study, 150-mg cartridges were used because of their ready availability in the laboratory used for these experiments. The difference of 50 mg of sorbent in the cartridges from the amount used in the study cited above was considered not to be significant (Junk, 1990). Solvation of the sorbent was achieved by washing the sorbent with 3 ml of the eluting solvent (benzene) in order to elute any interfering hydrophobic neutral compounds that may be on the sorbent from the manufacturing process. This step was followed by one column volume of methanol (4 ml), and then 10 ml of de-ionized (D.I.) water was added to prepare the sorbent to receive the sample (Junk and Richard, 1988b).

The laboratory setup for extraction of a sample is shown in Figure 4.1. A glass funnel was fit into the top of the cartridge as a sample reservoir, and 1/8" I.D. tygon tubing was used to connect the bottom of the cartridge to a vacuum flask. A vacuum pump was used to draw the sample through the cartridge with the pump at its highest setting. Three different pumps were used, depending on their availability on

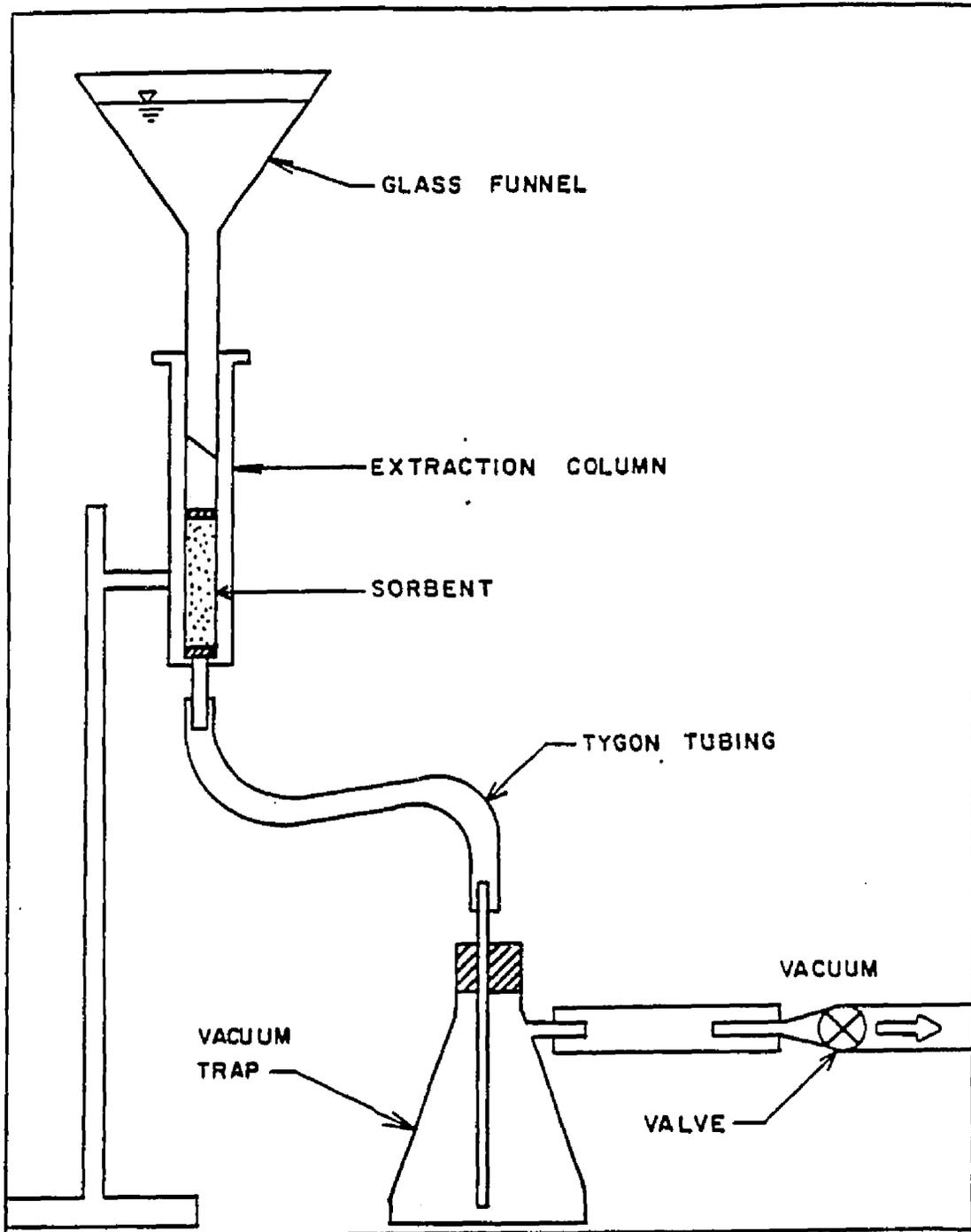


Figure 4.1 - Diagram of experimental setup for column extraction (after Reese, 1989)

the day of the experiments. Flow rates ranged from 5 to 20 ml/min. All glassware was cleaned with detergent and rinsed thoroughly in tap water, rinsed thoroughly in D.I. water, rinsed with methanol, and then baked in a laboratory oven at 300°C to remove any organic residue. D.I. water was obtained from a milli-Q system using ion-exchange, reverse osmosis, and a final carbon filter for purification. (See Appendix A for detailed description of extraction procedures. Appendix B contains dates for collection, extraction, and GC/MS analysis of samples.)

#### 4.3.2 GC/MS Analysis

Gas chromatography is an instrumental method of analysis involving the vaporization of a liquid sample and separation of the gaseous components so that they can be identified and measured. Each component has a retention time in the chromatographic column based on its structure and molecular weight. A typical chromatogram is shown in Figure 4.2. The concentration of the compound in the sample is proportional to the area under the peak (Sawyer and McCarty, 1978).

A mass spectrometer is a commonly used detector which can give positive identification and quantification for many organic compounds. Each organic molecule has its own pattern of fragmentation called a spectrum. The spectrum of an unknown can be compared to a library of known compounds for

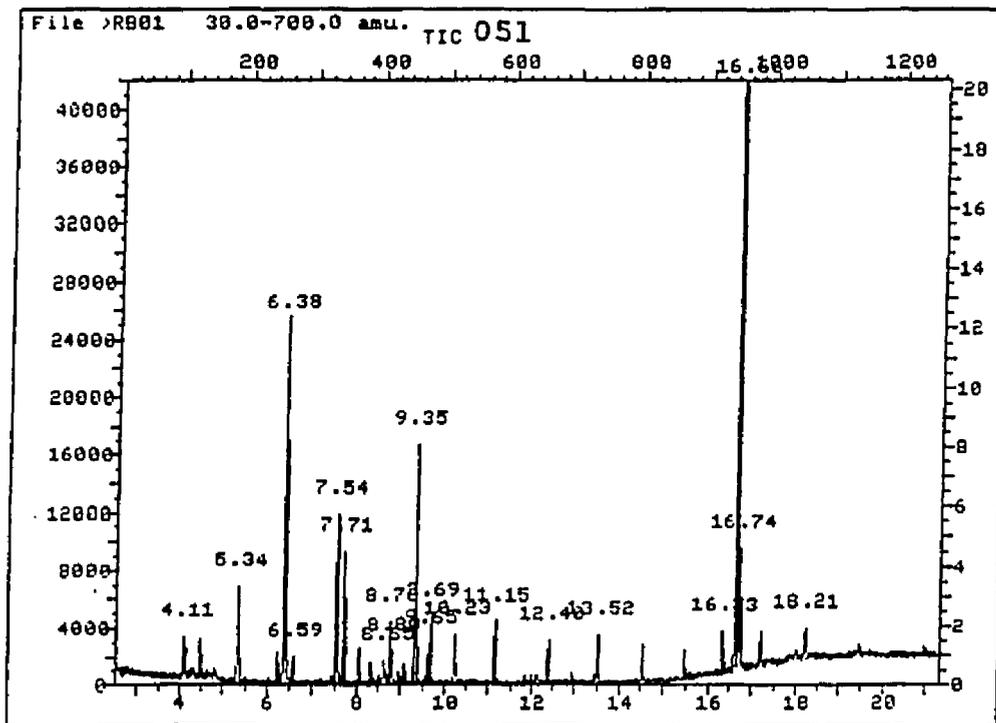


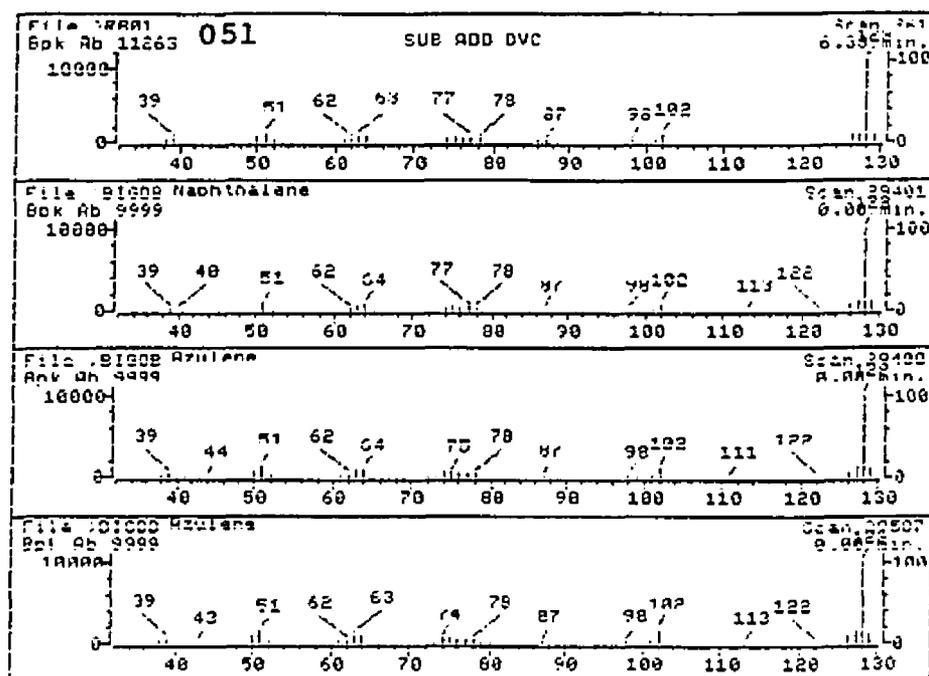
Figure 4.2 - Chromatogram of sample 051 showing large phthalate peak at retention time 16.66 minutes

identification (Sawyer and McCarty, 1978). An unknown spectrum is compared to three known spectra in Figure 4.3.

GC/MS analysis for this study was performed at the Mass Spectrometry Facility, Department of Chemistry, at the University of Arizona. The system consists of a Hewlett-Packard model 5890 gas chromatograph, a model 5970 mass spectrometer, and an RTE-6/VM computerized data system and library. The GC uses a Hewlett-Packard Ultra 2 chromatographic column. A fused silica capillary column uses a cross linked 5% phenyl methyl silicone stationary phase, 0.33  $\mu\text{m}$  film thickness, 0.20 mm internal diameter, and 25 m length. The capillary column has the greatest separation efficiency for the compounds under investigation in this study. The GC oven was held at 50°C for two minutes and increased at a rate of 15°C per minute up to 300°C. Starting at a low temperature allows the recondensing of the PAH into a narrow band at the front of the column. The different PAH are eluted separately as narrow peaks for greater resolution and sensitivity. The analyzer temperature was also held at 300°C.

#### 4.3.3 Interferences

Analysis of a blank and of standards consistently revealed the presence of interfering compounds derived from the solid-phase extraction cartridges. These extraneous compounds



1. Naphthalene	128 C10H8
2. Azulene	128 C10H8
3. Azulene	128 C10H8
4. Naphthalene	128 C10H8
5. Naphthalene	128 C10H8

Sample file: 051 Spectrum #: 261  
Search speed: 3 Tilting option: N No. of ion ranges searched: 36

	Prob.	CAS #	CON #	ROOT	K	DK	#FLG	TILT	%	CON	C_I	R_IV
1.	97*	91203	29401	*BIGDB	85	0	0	0	86	1	72	97
2.	93*	275514	29400	*BIGDB	77	15	1	0	72	0	68	69
3.	92*	275514	29587	*BIGDB	82	16	0	0	52	23	57	94
4.	92*	91203	29588	*BIGDB	64	18	0	0	91	12	64	92
5.	86*	91203	29590	*BIGDB	60	25	0	0	86	8	59	74

Figure 4.3 - Spectrum of unknown compound compared with 3 known spectra and probabilities of identification

were of two classes: phthalates and silanes. The most prominent was bis (2-ethylhexyl) phthalate, a plasticizer, sometimes comprising as much as 83% of the total mass of compounds coming through the GC. The intensity of this large peak was much greater than even the largest of the chromatograms of the PAH, although its retention time exceeded those of the PAH and masking was not a problem. Other phthalates, siloxanes, and silanols of various molecular weights and retention times, were also detected as interferences.

An analysis of interferences in solid-phase extraction using C-18 bonded porous silica cartridges was done at the Ames Laboratory, Iowa State University (Junk et al., 1988). The researchers identified four different siloxane/silanol compounds that were apparently leached off of the bonded porous silica. Three different phthalates were identified, including bis (2-ethylhexyl) phthalate, which was apparently leached from the polyethylene housing of the cartridge, the polyethylene frit holding the sorbent, as well as the C-18 porous bonded silica itself. Junk et al. (1988) reported that alkylphthalates were found in concentrations well above background levels. A technical consultant for the manufacturer of the cartridge, Analytichem International (Carpenter, 1990), suggested preceeding the benzene conditioning step in the extraction process with two

additional conditioning steps, 10 ml of methylene chloride, followed by 10 ml of acetone. Trials with this suggested procedure in the lab showed no significant decrease in the amount of interference. Junk et al. (1988) also reported naphthalene, acenaphthene, and biphenyl to be present in extracts of cartridge components soaked with ethyl acetate. Many of the interferences could be eliminated with the use of glass cartridges, although interferences from the sorbent itself would still be present.

#### 4.3.4 Experimental Error

The percent recoveries from standards mixed at 10 ug/l from a laboratory standard provided by CHEM SERVICE (see Section 4 for a discussion of laboratory procedures) are listed in Table 4.1. All standards were run with exactly the same procedure in the lab. Variations in recoveries can be explained by several factors.

Although 100 ul of benzene was added to the extraction cartridge for elution of PAH, the full 100 ul was never recovered. Varying amounts of additional benzene needed to be added in order to acquire a minimum amount of organic phase in the chromatographic cartridge for analysis by GC/MS. This may indicate that, despite following a careful conditioning procedure for the cartridge, the surface of the sorbent was

## Standards

	1	2	3	4	5	6	mean	SD
naphthalene	94.3	106.9	122.2	129.4	95.5	83.0	105.2	17.9
acenaphthylene	93.5	115.9	119.0	147.2	93.6	78.9	108.0	24.5
acenaphthene	98.4	132.1	121.0	149.3	106.5	91.4	116.5	21.6
fluorene	93.5	126.7	120.5	124.9	94.4	75.8	106.0	20.8
phenanthrene	88.4	116.1	110.5	102.1	84.1	63.6	94.1	19.6
anthracene	63.3	88.8	103.2	27.3	61.2	57.8	66.9	26.5
fluoranthene	89.8	139.1	110.8	51.5	84.7	80.4	92.7	29.7
pyrene	91.8	156.1	102.5	50.4	93.7	88.1	97.1	34.1

Table 4.1 Percent recoveries from six standards for individual PAH.

not thoroughly wetted, resulting in incomplete adsorption. This might explain some low recoveries.

Because 100 ul of organic phase was not present in the chromatographic vial after elution, the amount present needed to be precisely measured. This measurement was complicated by the fact that the inner volume of the vial was conically shaped and that the organic phase was floating on top of a water phase. Curved surfaces between phases also complicated measurements. A separate vial was carefully filled with 20 ul at a time and marked off as a measuring device for comparison. Estimates using this method of measurement may be off by as much as 20 ul.

If the caps of chromatographic vials are accidentally left loose, evaporation of the solvent may occur, artificially concentrating the dissolved PAH. This process could explain unusually high recoveries over 100%.

Generally, recoveries from the standards fell within a narrow range. Standard 4 had some unusually high recoveries and some that were unusually low. Others showed a pattern of being either uniformly high or low, which is what would be expected. The mean recovery for each compound, along with the standard deviation, is listed in Table 4.1. Average recoveries for the eight PAH quantified in Table 4.1 range from 66.9% to 116.5%. Standard deviations range from 17.6% to 34.1%. Detection limits in the GS/MS for the PAH detected are

in the 0.1-0.5 mg/l range or approximately in the 0.1-0.5 ug/l range when concentrated 1,000 to 1 by the solid-phase extraction process.

CHAPTER 5  
DISTRIBUTION AND FATE OF PAH IN THE AQUIFER

5.1 Discussion of the Data

Results of the analysis of groundwater samples collected from the Globe site are presented in Table 5.1. Of 25 wells sampled, 14 contained detectable PAH. Well site 050 was the most contaminated site, and well 051 had the highest measured concentration. Wells 053, 101, and 302 were the next most contaminated. This trend in the concentrations of PAH defines a plume, the axis of which is situated in the upper part of the conglomerate in the upgradient portion of the sample area and in the lower part of the alluvium in the downgradient portion of the sample area. This trend is coincident with the trends in high concentrations of DOC and low pH.

Naphthalene is the PAH present in the highest measureable concentrations, followed by acenaphthene, and fluorene. Quantifiable amounts of phenanthrene, acenaphthylene, and anthracene are also present in the most contaminated wells. These six PAH were quantified by the GC/MS by comparison to a known standard containing the 16 PAH on the Environmental Protection Agency Priority Pollutant List. Six other PAH were detected but not quantifiable. Probabilities of identification were calculated based on the percent matching of peaks from a spectrum of the unknown compound to a spectrum of a known compound.

[Concentrations, in micrograms per liter. X, indicates detected but not quantified;  
Dashes indicate analyzed for but not detected]

Compound	Molecular weight	Well number and date sampled													
		051 5/80	052 5/90	053 5/89	101 5/90	102 5/89	103 3/89	104 6/88	105 3/89	301 5/90	302 2/90	304 5/90	402 5/89	501 3/89	506 3/89
Naphthalene	(128)	16.21	1.35	8.32	7.27	1.78	0.43	--	--	--	3.11	--	--	--	--
Acenaphthene	(154)	12.09	.80	5.42	4.17	1.26	.35	--	--	--	2.03	1.63	--	--	--
Fluorene	(166)	3.62	1.81	.90	--	--	--	--	--	--	1.53	--	--	--	--
Phenanthrene	(178)	1.07	--	.60	--	--	--	--	--	--	--	--	--	--	--
Acenaphthylene	(152)	.62	--	.31	.26	--	--	--	--	--	--	--	--	--	--
Anthracene	(178)	1.06	--	--	--	--	--	--	--	--	--	--	--	--	--
Methylnaphthalene	(142)	X	X	X	X	X	<sup>1</sup> X	--	--	X	X	<sup>1</sup> X	--	--	--
Dimethylsaphthalene	(156)	X	X	X	X	X	--	--	--	X	X	<sup>1</sup> X	--	--	--
Dimethylisopropyl- naphthalene <sup>2</sup>	(188)	--	--	--	X	--	--	--	--	--	--	--	X	X	X
Methylbiphenyl <sup>3</sup>	(168)	<sup>1</sup> X	--	--	X	--	X	<sup>1</sup> X	<sup>1</sup> X	--	--	--	--	--	--
Dibenzofuran	(168)	X	<sup>1</sup> X	--	--	--	--	--	--	--	--	--	--	--	--
Isobenzofurandione	(148)	--	<sup>1</sup> X	--	X	--	X	<sup>1</sup> X	--	--	--	--	--	--	--

<sup>1</sup>Probability of identification less than 50 percent.

<sup>2</sup>Identified as dimethylisopropyl-naphthalene or ethylphenoxybenzene.

<sup>3</sup>Identified as methylbiphenyl, propenyl-naphthalene, or methylenebisbenzene.

Table 5.1 Concentrations of polycyclic aromatic hydrocarbons,  
Pinal Creek basin, Globe, Arizona, 1989-1990

An unknown compound of molecular weight 198 was identified as being either dimethylisopropylnaphthalene or ethylphenoxybenzene. Both compounds were identified at similar probabilities. The unknown could have a higher probability of being either compound at any specific location. Another unknown compound of molecular weight 168 and formula  $C_{11}H_{12}$  was identified as either methylbiphenyl, propenyl-naphthalene, or methylenebisbenzene. All three compounds were identified at similar probabilities.

Besides naphthalene and acenaphthene, the next most commonly detected compounds were methylnaphthalene and dimethylnaphthalene. Methylnaphthalene has eight isomers; of these, 1-methylnaphthalene and 2-methylnaphthalene were the only isomers identified, with 1-methylnaphthalene being more common. Dimethylnaphthalene has 28 isomers; of these, only the 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, 2,7-, and 2,8-isomers were detected at varying probabilities. 1,4-dimethylnaphthalene was the most commonly identified at the highest probability. Dimethylisopropylnaphthalene is detected the furthest downgradient, at well sites 400 and 500. However, it was also detected upgradient in well 101, one of the most contaminated wells. Why dimethylisopropylnaphthalene is the only contaminant detected downgradient is not clear. Others may be present, but below detection limits. Methylbiphenyl, dibenzofuran, and isobenzofurandione are only

detected at well sites 050 and 100 in the most upgradient part of the sample area.

All U.S. Geological Survey well sites were sampled except the newest site, 700, which is situated at a downgradient location not considered to be contaminated by PAH. At well sites 050 and 200, wells 054 and 202 are now dry and were not sampled. At well site 100, well 106 was abandoned when the casing was crushed during grouting. It was not sampled. Well 504 is the deepest well in the sample area, and it is situated deep in the conglomerate. It is considered to be uncontaminated and was not sampled.

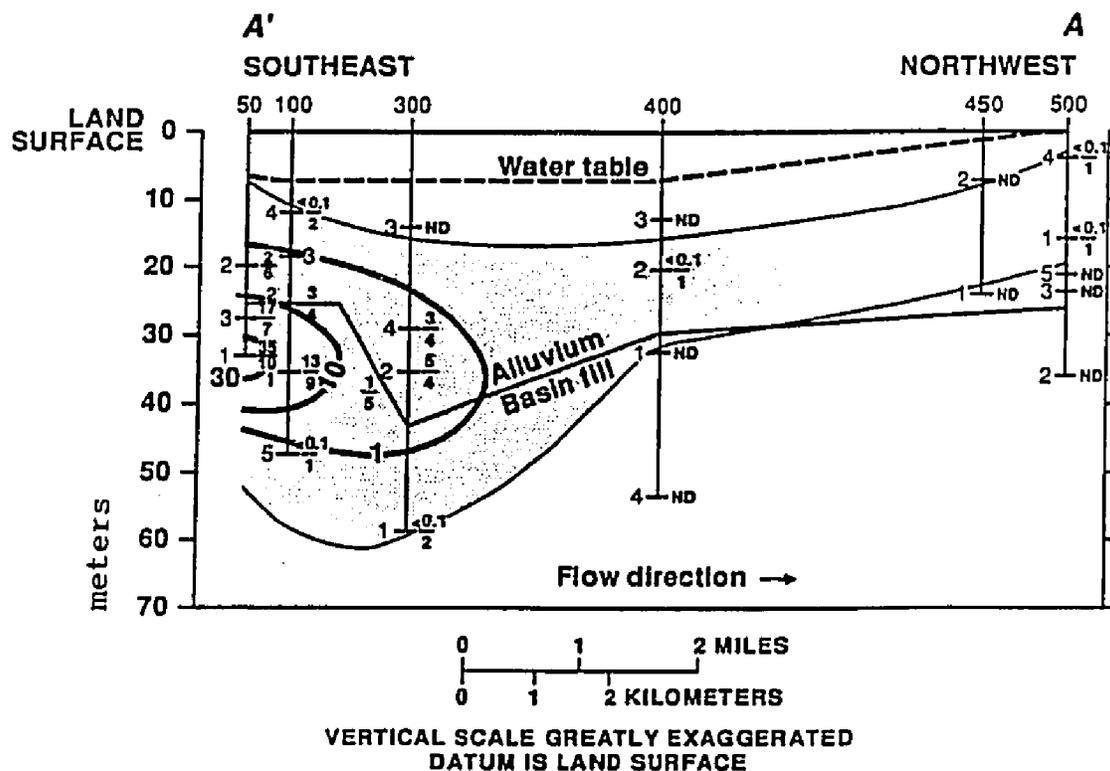
The dates when each sample was taken in the field, extracted in the laboratory, and analyzed on the GC/MS are given in Appendix B. In some cases, holding times exceed those recommended by the Environmental Protection Agency. Samples collected in the field were stored in a refrigerator in the laboratory at 4°C. Positive analysis of samples exceeding holding times indicated little or no loss of PAH from aqueous solution while stored in sample bottles. PAH have very low volatility and, therefore, would be expected to remain in solution. Some loss of PAH from the solvent phase after extraction was suspected. In some cases, samples were recollected and/or re-extracted for analysis on the GC/MS.

A sample collected 2 years earlier from Webster Lake by the U.S. Geological Survey before the lake was drained was

also extracted and analyzed. It had been stored for almost two years in a plastic bottle; results were negative. Any PAH present might have sorbed out of solution onto the plastic and may not have been detected. Well 010 was also sampled and analyzed. This well is located in Russell Gulch, upstream from its intersection with Miami Wash in an area considered to be uncontaminated. This well was used to measure background levels. No PAH were detected. A sample of road asphalt, from a pile in a highway department maintenance yard located near well site 050, was stored in distilled water in a sample bottle in the lab for a month and analyzed for PAH in order to determine if leaching from asphalt piles was a possible source of contamination to the aquifer. No PAH were detected.

### 5.2 Distribution of PAH

A cross-section showing the distribution of PAH in the aquifer is shown in Figure 5.1. The highest values occur in the upper part of the conglomerate upgradient and in the lower part of the alluvium downgradient. Data are given for total measurable PAH. Appendix C contains concentration data for DOC, pH, and total measurable PAH in the Pinal Creek Basin for the wells sampled in this study. The outer contour line represents the limit of all PAH detected in the system. The detection limit for PAH in this study is considered to be < 0.1 ug/l. Upgradient sampling is limited by access and thus



### EXPLANATION

- AREA OF IDENTIFIED POLYCYCLIC AROMATIC HYDROCARBON COMPOUNDS
- 100 WELL LOCATION—Number, 100, is well site; number, 2, is well screen location and sequence number. Number, 1, is total concentration of polycyclic aromatic hydrocarbons, in micrograms per liter; number, 5, is number of polycyclic aromatic hydrocarbon compounds detected; ND, no polycyclic aromatic hydrocarbons detected
- 10- LINE OF EQUAL CONCENTRATION OF THE SIX QUANTIFIED CYCLIC AROMATIC HYDROCARBONS, IN MICROGRAMS PER LITER—Interval variable

Figure 5.1 - Generalized hydrogeologic section showing distribution of PAH in the aquifer, Pinal Creek basin, Globe, Arizona, 1989-90 (after Wallin et al., 1991)

the upgradient extent of the plume is not known. Wells labeled ND were sampled and analyzed but no PAH were detected.

The trend of PAH in the aquifer is consistent with the distribution of DOC as determined by Reese (1989) and the distribution of inorganic constituents as determined by Eychaner (1988). The coincidence of PAH concentrations with those of the DOC and inorganic constituents suggests the same source for all contaminants.

### 5.3 Transport Processes

#### 5.3.1 Solubility

PAH are neutral substances with no ionizable functional groups unless oxidized through biodegradation (see Section 5.3.3); therefore their solubility is not affected by pH. In addition, none of the measurable PAH in the aquifer approach their maximum aqueous solubility.

The fraction of DOC in the aquifer that is hydrophobic acids (humic substances) is about 20% (Reese, 1989). Humic substances contain ionizable functional groups, particularly carboxylic acid groups, which can dissociate and increase their solubility. Most carboxylic acid groups have a  $pK_a$  between 3 and 6 (Drever, 1988). As carboxyl groups dissociate above pH 3 to 6, humic acids become increasingly negatively charged. The fraction of DOC that is hydrophobic neutral in character is about 30% (Reese, 1989). The solubility of these

compounds is less affected by pH because of the absence of significant numbers of dissociated functional groups. The fraction of DOC that is hydrophilic in character is almost 50%. These substances are very highly soluble in water. Most of the DOC in the aquifer is highly soluble, therefore there is no evidence that any of these compounds are in any way limited by solubility.

### 5.3.2 Adsorption

The fraction by weight of organic carbon in the aquifer matrix is extremely low (Reese, 1989). The alluvium is primarily sands and gravels with little natural organic material; therefore, adsorption by partitioning of PAH onto naturally occurring particulate or adsorbed organic material is probably not an important process. There is some evidence demonstrating that PAH will adsorb onto dissolved humic substances. In a study in Norway (Gjessing and Berglind, 1981), PAH added to natural waters containing humic substances were only 46-76% extractable by XAD-2 ion exchange recovery and only 2-7% extractable with cyclohexane. Dissolved organic carbon concentrations were from 5 to 14 mg/l. These results suggest that the mobility of PAH can be increased by the presence of humic substances. (See Section 3.9 for a discussion of solubility enhancement of PAH by humic substances).

Although PAH have in general no ionizable functional groups and, therefore, cannot be ionically or electrostaticly adsorbed onto charged mineral surfaces; humic substances contain many such ionizable groups. Sands and gravels are primarily silicate minerals. The isoelectric point for silica is pH 2, becoming negatively charged above pH 2 (Thurman, 1985). Because carboxylic acid groups on humic substances have a  $pK_a$  of 2 to 6 and become negatively charged above pH 2 to 6, adsorption of humic substances onto silica does not take place. Iron and aluminum minerals, however, are also important in the aquifer at the Globe site. The isoelectric point of aluminum hydroxide is pH 5.0, and the isoelectric point of iron hydroxide is pH 7.8. Below these pHs, their surfaces are positively charged. In the upgradient portion of the aquifer, where the pH is low, iron and aluminum are still in solution. As the pH increases above pH 4 aluminum hydroxide  $Al(OH)_3$ , and iron hydroxide  $Fe(OH)_3$ , begin to precipitate out of solution.

Reese (1989) noticed a significant drop in the levels of DOC in the aquifer where the pH exceeded 4. This observation suggests that the humic substances fraction of DOC may be adsorbing out of solution onto aluminum and iron hydroxide precipitates. Figure 5.2 shows a plot of total measurable PAH versus DOC, demonstrating a strong correlation between total PAH and DOC in the aquifer. Results of DOC analysis for well

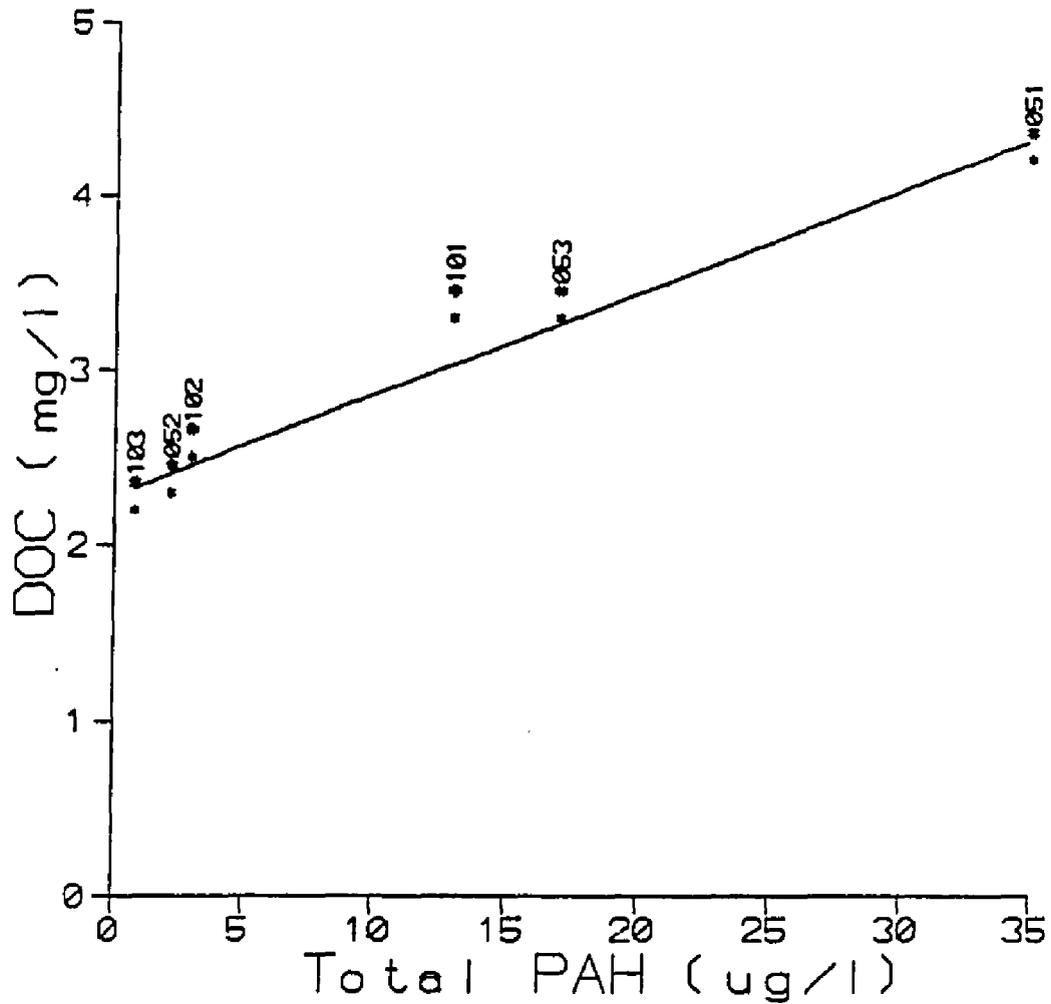


Figure 5.2 - Plot of total measurable PAH versus DOC for wells from Pinal Creek basin. Line represents best fit to data. Correlation coefficient,  $r = .9808$ .

302 were anomalously low and were not included in the plot. Data for the plot appear in Appendix C. The correlation coefficient for the best fit linear approximation is .9808. No measureable PAH were detected in the aquifer where the pH exceeded 4. This drop in the amount of PAH coincides precisely with the drop in levels of DOC. An explanation for this observation could be that PAH are adsorbing onto humic substances in the aquifer and are being transported by them. As humic substances are adsorbed out of solution onto aluminum and iron hydroxides where the pH rises above 4, PAH are also taken out of solution. Thus, concentrations of both DOC and PAH are limited by pH; this phenomenon could explain why DOC, pH, and PAH concentrations are all moving simultaneously through the aquifer.

### 5.3.3 Biodegradation

The primary pathway of biodegradation of PAH is oxidation (Neff, 1979). Because microbial oxidation requires dissolved oxygen, it will be limited at the very low levels of oxygen present in the Globe area aquifer. Biodegradation by sulfate-reducing bacteria would produce H<sub>2</sub>S gas however none has been detected. Furthermore, no oxidized PAH as possible degradation products were detected.

Lower weight PAH can be completely metabolized by some strains of bacteria; however, in most cases, metabolism

requires a cosubstrate (Neff, 1979). The generally low level of DOC in the aquifer may mean that the system is limited in its ability to provide a cosubstrate. Humic substances are highly refractory to biodegradation and would not provide necessary nutrients. In addition, low pH is toxic to many organisms. Biodegradation of PAH is probably not an important process in this system.

#### 5.3.4 Advection/Dispersion

In sand and gravel aquifers, the dominant factor in the transport of a dissolved contaminant is advection (Mackay et al., 1985). Advection is the process by which solutes are transported by the bulk motion of flowing groundwater. The hydraulic gradient describes the magnitude of the driving force. Eychaner (1988) estimated the hydraulic conductivity of the alluvium at 200 m/d and the hydraulic gradient at 0.008. The specific discharge or Darcy velocity can then be estimated at 1.6 m/d or 600 m/yr. Typical velocities in sand and gravel aquifers range from 1 to 1,000 m/yr, although, under most natural gradient conditions, the range is between 10 to 100 m/yr (Mackay et al., 1985). Velocities in the conglomerate have been estimated to be much lower, only 0.09 m/yr (Eychaner, 1988).

Dissolved substances spread as they move with the groundwater. This process is called dispersion. Dispersion

results in the dilution of solute pulses and the attenuation of concentration peaks. Dispersion may result in the arrival of detectable solute concentrations at a given location significantly before the arrival based solely on advective velocities (Mackay et al., 1985).

Infiltration along the flow path of the aquifer will affect the degree of dilution predicted solely on advection and dispersion. Reese (1989) noted that some but not all of the fractions of DOC in the aquifer deviated from a dilution line based on chloride concentrations, indicating more than one possible source of infiltration of water along the flow path (Section 2.4). Therefore, advection and dispersion are not the only mechanisms effecting dilution in this system. However, after accounting for dilution, 28 percent of the DOC is still being lost from solution during transport through the study area (Reese, 1989). This loss is probably due to adsorption of portions of the DOC onto metal hydroxides (Section 5.3.2).

## CHAPTER 6

## CHEMICAL SOURCES OF PAH CONTAMINATION

6.1 PAH in Coal and Coal Tar

Coal consists mainly of macromolecular organic matter of a complex nature. Coal is known to be predominantly an aromatic material, and 70 to 75% of the carbon in bituminous coal is in aromatic form. Six-ring PAH predominate; however, five-ring PAH are also present. A large variety of complex PAH and heteroaromatic compounds form when coal is pyrolyzed (Neff, 1979).

When coal is heated to 1,000°C in the absence of air, coal molecules break down, and a mixture of volatile products, called coal tar, distills off. The principle commercial products made from coal tar in the United States are wood-preserving oils (creosote), road tars, industrial pitches, and pitch coke. Wood-preserving oils are distilled from the tar, whereas road tar, pitches, and pitch coke are residuals from the distillation process. Percentages of primary products are road tar (28%), pitch (26%), and creosote (22%) (Lowry, 1963).

On a worldwide basis, the wood-preserving industry uses more pesticides than any other industry. The major chemicals used are creosote, pentachlorophenol, and CCA (copper, chrome, and arsenate). Wood-preserving operations in the United States reportedly use 454,000 metric tons of creosote annually

(Matraw and Franks, 1986). Creosote is a complex mixture of chemical constituents, composed of approximately 85% PAH, 10% phenolic compounds, and 5% N-, S-, and O- heterocyclics. Of the 150 to 200 chemicals in creosote, only a small portion are present in amounts of 1% or greater. Table 6.1 lists the principle components of coal tar creosote. Creosote-related compounds enter the environment at treatment sites from leaking tanks, drippings from treated lumber, spills, leachate from unlined holding ponds, and improper disposal (Mueller et al., 1989).

Coal tar derivatives from a coal tar distillation and wood-treatment plant at St. Louis Park, Minnesota, contaminated ground water in the area of the plant down to a depth of 900 feet and minimum distance of 4,000 feet to the southeast. Coal tar related fluids contaminated the surficial glacial drift aquifer upon which the plant site is located. A differential attenuation of phenolic compounds seems to be due primarily to bacterial degradation of phenols to carbon dioxide, methane, and probably volatile fatty acids. The pH ranged from 6.9 to 7.5 and dissolved oxygen content was less than 0.1 mg/l. Little or no adsorption of contaminants was observed (Hult, 1984). Concentrations of PAH in the most contaminated well at the St. Louis Park site are listed in table 6.2.

<u>Compound</u>	<u>Percent</u>	<u>Percent at Pinal Creek</u>
Naphthalene	33.4	49.3
Acenaphthene	4.3	35.6
Fluorene	4.9	10.1
Phenanthrene	12.2	2.1
Acenaphthylene	3.1	1.5
Anthracene	3.4	1.4
Methylnaphthalene	7.6	X
Dimethylnaphthalene	3.4	X
Carbazol and related non- basic nitrogen - containing compounds	7.0	-
Phenol	2.1	-
Phenol homologs (largely cresols and xylenols)	4.6	-
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and aeridine)	<u>7.0</u>	<u>-</u>
	100.0	100.0

X indicates detected but not quantified  
- indicates not detected

TABLE 6.1 Constituents of Coal-Tar Creosote  
(Source: Lowry, 1963)

<u>Compound</u>	<u>Concentration mg/kg (ppm)</u>	<u>%</u>	<u>Percent at Pinal Creek</u>
Naphthalene	310	32.0	49.3
Methylnaphthalene	88	9.1	X
Dimethylnaphthalene	8	0.8	X
Acenaphthylene	72	7.4	1.5
Dibenzofuran	40	4.1	X
Fluorene	48	4.9	10.1
Anthracene	68	7.0	1.4
Phenanthrene	156	16.1	2.1
Fluoranthene	84	8.7	-
Pyrene	60	6.2	-
Carbazol	<u>24</u>	<u>2.5</u>	<u>-</u>
	970	100.0	64.4

X indicates detected but not quantified  
 - indicates not detected

TABLE 6.2 Concentrations of PAH from most contaminated well, St. Louis Park, Minn.  
 (Source: Ehrlich et al, 1982)

Another site contaminated by creosote, and very similar to the St. Louis Park site, is located at Pensacola, Florida. The former site of a wood treatment plant is contaminated with creosote and pentachlorophenol. Sorption did not seem to be a major transport mechanism. Phenols seemed to be undergoing anaerobic biodegradation as evidenced by high levels of methane. The pH in the area ranged between 5.2 and 6.4. Dissolved oxygen content at both sites was less than 0.1 mg/l (Goerlitz et al, 1985).

Residual coal tar deposits at a former coal gasification plant at Wallingford, Connecticut, were found to have contaminated ground water in the underlying aquifer. The aquifer under the site is a series of silt, sand, and gravel layers of glaciofluvial origin. Coal tar constituents were detected in both shallow and deep wells. Ten PAH were detected. Phenols were only detected in small quantities downgradient, suggesting that the more soluble phenols had been leached out. (Quinn et al., 1985).

There are several similarities between the sites mentioned above and the Globe site. The particular suite of PAH found at the Globe site is very similar in the specific PAH present and the relative concentrations of PAH found at the other sites. The absence of phenolic compounds at the Globe site may be accounted for by anaerobic biodegradation. Dissolved oxygen content is low in the upgradient portion of the sample

area and may also be low in the unsampled area below Webster Lake. Although the area below Webster Lake may have a low pH, it may not be low enough to inhibit anaerobic biological activity. Sand and gravel aquifers at all locations provided very limited adsorption. Creosote may have been used at the mine site for the treatment of mine timbers, railroad ties, and telephone and electrical poles. Accidental leaks and spills into Webster Lake could have provided a pathway for the introduction of PAH from coal-tar creosote into the aquifer.

Coal tar is also used as a coating for water storage tanks and distribution pipes. In one study, water samples were exposed to test panel surfaces coated with commercial coal tar, and samples of water were also collected from a 12,000-gallon storage tank. The study concluded that the leachate from tanks and pipes was not a significant source of PAH in the environment (Alben, 1980).

### 6.2 PAH in Petroleum and Petroleum Products

Crude petroleum and most refined petroleum products are complex mixtures of many organic compounds. Hydrocarbons represent about 75% of the weight of oil, with the rest being sulfur, oxygen, and nitrogen containing organic compounds (Speers and Whitehead, 1969). Gilchrist et al. (1972) analyzed 11 different samples of crude oil for PAH content. Total PAH varied from 1.9 to 19.5% with an average of 10.7%.

Different boiling fractions of petroleum contain different percentages of PAH, with the higher boiling fraction containing more PAH. The gasoline fraction commonly contains no PAH; kerosene may contain up to 3%. Fuel oils can contain up to 10% PAH, and lubrication oils can contain up to 15%. Higher boiling fractions of petroleum, such as bitumen and asphalt, contain PAH and other very large organic molecules (Speight, 1980). Concentrations of PAH in two crude oils and two distillate fuel oils, established by the American Petroleum Institute as reference oils, are given in Table 6.3.

Fuel oils and lubricating oils are used in the mining industry for operating power plants and machinery. Fuel oil is also used in ore processing as a collector reagent in the froth floatation method of ore concentration (see Section 6.3). PAH from fuel oils and lubricating oils could enter the environment in the area of mining operations from leaks and spills and from froth floatation residues discharged into tailings ponds. Fuel oils are higher in the proportion of the alkylhomologs of two-ring, three-ring, and four-ring PAH than the parent PAH (Neff, 1979). This trend was not observed in the PAH detected at the Globe site.

<u>Compound</u>	Concentration in mg/kg (ppm)			
	<u>South Louisiana Crude</u>	<u>Kuwait Crude</u>	<u>No. 2 Fuel Oil</u>	<u>Bunker L Residual Oil</u>
Naphthalene	400	400	4,000	1,000
Methylnaphthalenes	1,700	1,200	27,100	7,500
Dimethylnaphthalenes	3,600	2,000	31,100	12,300
Trimenthylnaphthalenes	2,400	1,900	18,400	8,800
Fluorene	200	100	3,600	2,400
Phenanthrene	70	26	429	482
Methylphenanthrene	255	89	7,850	871
Fluoranthrene	5	3	37	240
Pyrene	4	5	41	23
Benzo(a) anthracene	2	2	1	90
Chrysene	18	7	2	196
Triphenylene	10	3	1	31
Benzo(a)pyrene	1	3	1	44
Benzo(c)pyrene	3	1	21	10
Perylene	35	<1	-	22

TABLE 6.3 Concentrations of PAH in two crude oils and two distillate fuel oils, used as API reference oils (Source: Neff, 1979)

### 6.3 PAH in Reagents Used in Copper Mineral Processing

Most of the organic reagents used in the processing of copper ore are those used in the froth floatation method of concentration. Collectors and frothers are all organic compounds. Two common aromatic frothers are pine oil (terpineol) and cresylic acid (xylenol) (Albert, 1984). These are monoaromatic compounds and would not account for the presence of PAH in the system, although cresylic acid was identified as a contaminant at the Globe site (Reese, 1989). Fuel oil is used as a collector, particularly for the separation of molybdenum from copper sulfides. Fuel oil is refined from crude petroleum and can contain up to 10% PAH (see Section 6.2). No data were available as to whether fuel oil was used as a collector at the mining operations in the Globe area.

### 6.4 PAH in Runoff and Sewage Effluent

Domestic and urban wastewaters include raw sewage and storm sewer runoff which may contain PAH. PAH in road runoff arises from wear and leaching of asphalt road surfaces, wear of tires containing carbon black, motor oil spills, and condensation from vehicular exhaust (Neff, 1979). Household sewage contains PAH from cooking and washing activities and from human waste (Andelman and Suess, 1970).

Much of the PAH entering the environment from runoff is from non-point sources. Extensive asphalt paving is not present in the mining area and, therefore, is not a major source of PAH. Municipal effluent from Globe is discharged into Pinal Creek upstream from its intersection with Miami Wash. No PAH were detected at well site 200 and DOC measurements at well site 200 were low (see Appendix C). These data indicate the sources of PAH and elevated DOC are probably not up Pinal Creek from its intersection with Miami Wash in the direction of Globe. Effluent from the town of Miami is sprayed on tailings piles for evaporation. Population in Globe and Miami is low; thus, large amounts of contamination from effluent would not be expected (Reese, 1989).

Industries which contribute a large amount of PAH to urban wastewater and runoff, such as oil refineries, chemical plants, plastics and dyestuffs manufacturers, and industries using high-temperature electrodes (Neff, 1979) are absent in the Globe-Miami area. Septic systems at housing projects and trailer parks in the area would probably not contribute significant PAH.

## CHAPTER 7

### CONCLUSIONS

#### 7.1 Characterization of Contamination

Results presented in this thesis demonstrate the presence of PAH contamination in the Miami Wash-Pinal Creek aquifer. The concentrations detected at different well locations describe a plume, the axis of which is situated in the upper part of the conglomerate in the upgradient portion of the study area and in the lower part of the alluvium in the downgradient portion of the study area. High levels of PAH contamination are associated not only with high levels of dissolved organic carbon but with low pH as well.

Of 25 wells sampled, 14 contained detectable PAH (see Table 5.1). Well site 050 was the most contaminated site in the most upgradient portion of the study area. Well 051, at a depth of 33.5 m, is the most contaminated well. This well also contains the highest levels of DOC (Appendix C) and inorganic contamination (Eychaner, 1989). Well site 050 is 6 km downgradient from one probable source of contamination, an unlined lake that contained waste process solutions. The lake was drained in 1988. A lack of data from the unsampled region upgradient of the study area makes a precise determination of the upgradient extent of the plume impossible at the present time.

Total measurable PAH in the most contaminated well, 051, is approximately 35 ug/l. This level exceeds the standards recommended by the Minnesota Department of Health (1978) by three orders of magnitude. Concentrations of PAH upgradient of well site 050 may exceed this.

### 7.2 Transport and Fate

The aquifer in the Miami Wash-Pinal Creek basin is composed of sands and gravels. Very little vegetation exists along the stream channel, and the fraction of organic carbon in the aquifer material is negligible, therefore hydrophobic partitioning of PAH onto organic carbon material in the aquifer is not considered to be taking place. PAH do not contain ionizable functional groups; therefore, electrostatic adsorption of PAH onto charged inorganic surfaces does not appear to be a significant process either.

PAH are very refractory to biodegradation. When biodegradation does occur, oxidation is the primary process. Amounts of dissolved oxygen are low in the study area, and oxidized degradation products of PAH have not been detected. Microorganisms that degrade PAH with four or more rings require another source of carbon as a cosubstrate for metabolism. Even the higher than background levels of DOC in the aquifer represent a carbon-limited system. Low pH may also be a factor limiting biodegradation. Biodegradation is

not considered to be an important process for PAH in this system.

Comparisons of the distribution of PAH with the distributions of DOC and pH tend to indicate a relationship between PAH, DOC, and pH. Research has indicated that PAH may be sorbed onto or partitioned into humic substances in groundwater systems and transported by them. Humic substances do contain ionizable functional groups, (such as carboxyl, hydroxyl, and amine groups) which may provide a mechanism for sorption onto inorganic material, particularly metal hydroxides. A zone of water in which the low pH has been neutralized by carbonate sediments extends out in front of the zone of inorganic contamination in the aquifer. This zone contains iron and aluminum hydroxides that have precipitated out of solution. DOC concentrations are dramatically lower in this area (Reese, 1989), and the probable cause is absorption of DOC molecules onto metal hydroxides. If significant amounts of PAH are sorbed onto DOC molecules, then pH could indirectly be a limiting factor in the transport of PAH in this system.

### 7.3 Possible Sources of Contamination

Coal and products derived from coal contain a high percentage of PAH. Wood-preserving oils distilled from coal and coal tar are known as creosote. Creosote represents one

of the most widely used insecticides. Creosote is composed of approximately 85% PAH, 10% phenolic compounds, and 5% N-, S-, and O- heterocyclic compounds.

Contamination by creosote has been investigated at two former sites of creosote-producing and wood-preservation plants by the U.S. Geological Survey. The specific PAH present and their relative abundances at these two sites closely match the trend of PAH contamination observed at the Globe site. A large mining operation uses mine timbers, railroad ties, and telephone and electrical poles. It is possible that these may have been treated at the site, although data needed to determine this are not available. Other possible sources of creosote or coal tar in the Globe-Miami area, such as former sites of coal tar distillation plants, wood-preserving plants, or coal gasification operations, are not known to exist. The absence of phenolic compounds in the study area may be explained by possible anaerobic biodegradation of phenolic compounds upgradient from the study area.

Crude petroleum contains approximately 10% PAH. Higher boiling fractions of petroleum contain increasingly more PAH. Gasoline commonly contains no PAH, kerosene may contain up to 3%, fuel oils up to 10%, lubricating oils up to 15%, and asphalt can contain even higher percentages (Speight, 1980). Fuel oils and lubricating oils have probably been used all

over the Globe-Miami area as well as at mining operations for operating power plants and machinery. Fuel oil is also used as a collector reagent in the froth floatation process of ore concentration. Unused reagents can be discharged into waste containment ponds. Petroleum products contain a higher proportion of alkylhomologs of PAH than the parent PAH. This trend was not observed in the PAH detected at the Globe site.

Runoff from road surfaces contains PAH leached from asphalt, oil spills, and condensation from vehicular exhaust. The amount of paving in the Globe-Miami area is not extensive because of the small size of the community. Mining areas are generally unpaved. Domestic and urban sewage effluent contain PAH (Andelman and Suess, 1970), but are not considered to be a significant source of contamination in the area. Because no PAH were detected at well site 200, the source of contamination appears to be coming down Miami Wash. Of all the sources of chemical contamination listed above, contamination from coal tar and creosote-derived compounds best fits the trends observed at the Globe site.

#### 7.4 Additional Work

To more fully determine the upgradient extent of the contamination plume and its probable physical source, data need to be obtained from the region upgradient to the study area. The Inspiration Consolidated Copper Company has

expressed an interest in this being done, and these data may be available in the future. More information is needed on mining operations and ore processing in the Globe area in order to determine possible chemical sources. This may be difficult if formal records do not exist.

Total PAH in the aquifer only account for a very small portion of the total dissolved organic carbon. A complete analysis of other organic compounds in the system, particularly the lighter weight hydrocarbons, could help more closely fingerprint a chemical source for the contamination.

A further investigation into the possible adsorption of PAH onto humic substances in the aquifer could help to confirm this mechanism as an important transport process for PAH. A further investigation, including physical evidence, of the minerals that control the solubility of iron and aluminum at the Globe site, would help determine adsorption processes involving humic substances and inorganic mineral surfaces.

**APPENDIX A**  
**PROCEDURE FOR EXTRACTION, ELUTION, AND**  
**CONCENTRATION OF A SAMPLE**

APPENDIX A  
PROCEDURE FOR EXTRACTION, ELUTION, AND  
CONCENTRATION OF A SAMPLE

The following procedure was used in this study for extraction, elution, and concentration of a sample:

(1) Cartridge conditioning: The following solvents were passed through the cartridge in order to solvate the sorbent. During this procedure, solvents were kept in 50-ml glass bottles with Teflon septa in order to limit their contact with the air and with each other. Aliquots of solvent were introduced into the cartridge, before placement of the funnel reservoir, by use of graduated glass syringes with metal tips and needles. Use of syringes with 2-inch needles allowed the solvent to be applied directly onto the sorbent with minimum contact with the walls of the cartridge. The vacuum pump was used during this step of the procedure to draw the solvents through the cartridge. All procedures were performed under a hood.

- (a) 3 ml benzene
- (b) 4 ml methanol
- (c) 10 ml D.I. water

Each additional solvent should immediately follow the previous solvent to prevent drying. A total of 42 extractions were performed in the lab.

- (2) Sample pass: 100 ml of sample was pre-measured into a 100-ml volumetric flask. After the cartridge was conditioned by the above procedure, the funnel reservoir was placed in the cartridge, and the sample was introduced immediately after the conditioning step so that no room air was drawn through the cartridge. After all the sample had been drawn through the cartridge, room air was drawn through the cartridge for 30 seconds to remove water. Longer drying times may cause loss of sorbate due to evaporation (Junk and Richard, 1988b).
- (3) Elution: After drying, the vacuum pump was detached from the cartridge, and a 0.1-ml microvial was placed underneath. Next, 250  $\mu$ l of benzene was introduced into the cartridge using a 100- $\mu$ l syringe with a metal needle. 150  $\mu$ l of benzene will adsorb onto the partially dried 150 mg of sorbent, and 100  $\mu$ l of benzene will then act to desorb the target compounds, pass through the column, and collect in the microvial (Junk, 1990). Flow through the cartridge was induced by forcing air through the top with a 60 ml plastic syringe. Despite introducing 250  $\mu$ l of benzene into

the cartridge, 100  $\mu$ l did not always collect in the microvial. An additional 50 to 100  $\mu$ l was added and forced through the cartridge using the 60-ml syringe in an effort to collect a minimum of 50  $\mu$ l of benzene in the microvial. Because the cartridges had only been partially dried, water was also eluted with the benzene, so that two phases were present in the microvial. Centrifugation was necessary to create 2 distinct phases with an interface that was either flat or regularly curved. This was necessary to measure the amount of benzene phase present in the microvial. Because benzene has a very low solubility in water, the assumption was made that all of the target compounds were dissolved in the benzene phase. Later, GC/MS analysis of the water phase from 2 samples indicated no target compounds present.

**APPENDIX B**  
**DATES FOR COLLECTION, EXTRACTION, AND**  
**GC/MS ANALYSIS OF SAMPLES**

Sample location	Collection Date	Extraction Date	GC/MS Analysis Date	Positive Results
010	3/9/89	12/6/89	7/5/90	No
051	5/21/90	9/12/90	9/25/90	Yes
052	5/21/90	9/12/90	9/25/90	Yes
053	5/22/89	12/6/89	1/11/90	Yes
054	Not collected			
101	5/22/90	9/12/90	9/25/90	Yes
102	5/23/89	12/6/89	1/11/90	Yes
103	3/7/89	12/7/89	1/11/90	Yes
104	6/14/88	12/7/89	1/11/90	Yes
105	3/7/89	12/7/89	1/11/90	Yes
201	3/8/89	12/6/89	1/11/90	No
202	Not collected			
301	5/22/90	9/13/90	9/24/90	Yes
302	2/14/90	2/15/90	3/29/90	Yes
303	6/16/88	12/7/89	1/11/90	No
304	5/22/90	9/13/90	9/25/90	Yes
401	5/24/90	9/13/90	9/24/90	No
402	5/25/89	12/6/89	12/18/89	Yes
403	5/25/89	12/7/89	5/2/90	No
404	5/24/90	9/13/90	9/24/90	No
451	5/24/90	9/13/90	9/25/90	No
452	5/24/90	9/12/90	9/25/90	No

APPENDIX B Dates for collection, extraction, and GC/MS analysis of samples

Sample Location	Collection Date	Extraction Date	GC/MS Analysis Date	Positive Results
501	3/8/89	12/6/89	5/3/90	Yes
502	5/23/90	9/12/90	9/25/90	No
503	3/8/89	12/6/89	5/2/90	No
504	Not collected			
505	3/8/89	12/6/89	5/3/90	No
506	3/8/89	12/6/89	5/3/90	Yes
<sup>1</sup> Webster Lake	2/1/88	12/7/89	1/11/89	No

<sup>1</sup> - Collected by Ron Reese

<sup>2</sup> - Collected by Jim Eychaner

APPENDIX B (continued)

**APPENDIX C**

**Concentrations of DOC, pH, and total measurable PAH,  
Pinal Creek Basin, Globe, Arizona, 1989-90**

APPENDIX C. Concentrations of DOC, pH, and total measurable PAH, Pinal Creek Basin, Globe, Arizona, 1989-90

Well locations	<sup>1</sup> DOC (mg/l) 8/87-6/88	<sup>2</sup> pH 5/89	total measured PAH (µg/l)
010	1.1	6.91	<0.1
051	4.2	3.65	35
052	2.3	3.82 <sup>3</sup>	2.2
053	3.3	3.64	17
054	1.9	3.83	--
101	3.3	3.69	13
102	2.5	3.68	3.0
103	2.2	3.73	.78
104	1.4	4.01	<0.1
105	1.6	6.51	<0.1
201	0.7	7.06	<0.1
202	0.7	--	--
301	0.7	6.71 <sup>1</sup>	<0.1
302	1.1	3.90 <sup>3</sup>	5.1
303	1.3	4.19	<0.1
304	--	4.00 <sup>3</sup>	3.2
401	0.5	4.60	<0.1
402	1.8	4.07	<0.1
403	1.2	4.63	<0.1
404	0.3	7.41	<0.1
451	--	4.26	<0.1
452	--	5.40	<0.1
501	1.1	5.92	<0.1
502	0.1	7.34	<0.1
503	1.1	5.82	<0.1
504	0.5	7.59	--
505	--	6.11	<0.1
506	1.8	5.96	<0.1

<sup>1</sup>Data from Reese (1989)      <sup>2</sup>Brown (1990)  
<sup>3</sup>Data from Eychaner et al (1989)

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