HAZARDOUS ORGANIC WASTES FROM NATURAL GAS PRODUCTION,

PROCESSING AND DISTRIBUTION: ENVIRONMENTAL FATES

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ABSTRACT

Hydrocarbons and polycyclic aromatic hydrocarbons are generated as waste fluids and solids throughout all aspects of natural gas production, processing, and distribution. Wastes have often been and continue to be disposed in earthen unlined waste pits sometimes near vulnerable aquifers. Wastes move from pits through soils with no apparent abatement to depths greater than roughly 2 meters. As expected, groundwater contamination does occur in river flood plains where depth to groundwater can be less than 2 meters. Contamination of groundwater and nearby soils with hydrocarbons from an unlined pit was documented in the Duncan Oil Field west of Farmington, NM. Plumes for volatile compounds including benzene, toluene, and xylenes in the water and polycyclic aromatic hydrocarbons in the soil were clearly evident downgradient from the earthen pit at distances up to 50 meters. Waste pits containing produced water and hydrostatic discharge water were found to contain large amounts of polycyclic aromatic hydrocarbons which are phototoxic to fish. Legal or illegal discharges of natural gas wastes to surface waters should be reconsidered using not only salt and heavy metal contamination but also using toxicity and mutagenicity of aromatic hydrocarbons.

Keywords: Hydrocarbons, natural gas, groundwater contamination

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INTRODUCTION

Origins of Petroleum and Natural Gas

The origins and mechanisms for the formation of petroleum are not completely known (Katz, et. al. 1959, Harder and Backhurst 1981, Newman, et. al. 1985, Meyer 1983) although in the most accepted theory, primary source materials were marine plants and animals (Katz, et. al. 1959, Harber and Backhurst 1981, Newman, et. al. 1985, Meyer 1983). When these organisms died, the remains settled to the sea bottom and were embedded in layers of the sediment. The marine sediments accumulated a large quantity of organic matter over geologic ages. Formation of petroleum is thought to have occurred through transformation of this deposited organic matter by heat and pressure, bacteria, or by other processes (Meinschein and Yen Huang 1981).

Natural gas is believed to have an origin that is common to petroleum. Natural gas is often associated with crude oil (petroleum) especially at deep wells where earth temperature is higher, about 2.75° C/100m below the surface (Harder 1982). In addition, oil and gas reservoirs (Hubbert 1954) are generally found in combination with water, usually saline, in which gas will almost always rise to the top with oil underneath, and salt water remaining at the bottom due to the relative specific gravity. However, more than 70% of the United States domestic gross production of natural gas originates from wells with natural gas alone (Oppenheimer 1980, Gas Facts 1976). Most oil and gas occurs in reservoirs from 500 to 25,000 ft. below the surface of earth under high pressure (about 0.44 psi per foot of depth) (Harder 1982).

Occurrence and Use of Natural Gas

While natural gas was first used by Chinese in ancient times for making salt from brine, the first gas company was chartered in London in 1812 (Harder 1982). The earliest reported discovery of natural gas in the United States

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occurred about 1820 in Pennsylvania at a salt works during drilling operations for salt water. However, first productive use of natural gas was at Fredonia, New York, in 1821 where gas was consumed for house lighting. Currently, the United States (with over 30% of the annual world total production of 55.066 trillion cu ft of natural gas) is the second largest gas producer after the Soviet Union (Oil and Gas J. 1984). In addition, the United States has the third largest natural gas reservoirs after the Soviet Union and Iran. Major natural gas fields as well as petroleum deposits are shown in Figure 1 (Kraft 1984). The majority of the United States gas is produced in the Southwestern states and off the coasts of Texas and Louisiana, as shown in Figure 1 (Cuff and Young 1984).

Natural gas is the most consumed source of energy in the United States next to liquid petroleum, and is used in four sectors of energy consumption. These are industrial, commercial, residential, and production of other forms of energy such as electricity (Darmstader 1983). Although a slight decline in U.S. gas consumption is expected through year 2000, natural gas will continue to be an important source of energy as shown in Table 1 (Oil and Gas J. 1985).

Composition and Properties of Natural Gas

Natural gas is not a pure substance but is comprised largely of methane (59-90 + mole % ratio), ethane, propane, butane, pentane, and hexane. Additionally, a few nonhydrocarbon gases such as hydrogen sulfide, carbon dioxide, nitrogen, helium, and water vapor, and a mixture of higher molecular weight hydrocarbons (C_{7+}) are present in natural gas.

Unrefined natural gas with a relatively large concentration of C_3+ hydrocarbons is called a wet gas while gas with low concentrations of these components is called dry gas. Natural gas with relatively high acid gas (H_2S, CO_2) content (usually greater than 10%) is termed sour gas in contrast to sweet gas with low H_2 and CO_2 content. Approximately 2-5% of natural gas

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Table 1. U.S. energy demand. (Reprinted from Oil and Gas Journal, Jan. 28, 1985, p. 89).

U.S. energy demand

| | 1983 | 1984 | % change 1984/83 | 1985 | % change 1985/84 | % share of market 1985 |
	-Trillion BTU-		--Trillion BTU--			
Oil	30,076	31,290	+ 4.0	31,580	+ 0.9	41.7
Natuaral Gas	17,535	18,450	+ 5.2	18,910	+ 2.5	24.9
Coal	15,860	17,090	+ 7.8	17,630	+ 3.2	23.3
Hydro & Geothermal	4,015	3,995	- 0.5	3,900	- 2.4	5.1
Nuclear	3,235	3,610	+11.6	3,800	+ 5.3	5.0
Total	70,721	74,435	+ 5.3	75,820	+ 1.9	100.0

Source: 1983 DOE; and 1985 OGJ estimates

Table 2. Characteristics of methane.

Characteristics	English	Metric
Molecular weight	16.04	16.04
Boiling point at 1.0 atm	-263.2°F	-164.0°C
Melting point at 1.0 atm	-296.5°F	-182.5°C
Specific heat C_p at	0.528 Btu/lb·F 59°F, 1 atm	0.528 kcal/kg ·C 15°C, 1 atm
C_p/C_v	1.31	1.31
Critical Temperature	-116.5°F	-82.5°C
Critical pressure	45.8 atm	45.8 atm
Density of gas at	0.0448 lb/ft^3 32°F, 1 atm	0.718 kg/m^3 0°C, 1 atm
Density of gas at boiling point	0.1124 lb/ft	1.8004 kg/m^3
Density of liquid at boiling point	26.47 lb/ft^3	424 kg/m^3
Heat of Vaporization at boiling point	248.4 Btu/lb	577,600 J/kg
Higher heating value	23,890 Btu/lb	55.55 x 10^6 J/kg
at	978 Btu/ft^3 77°F, 1 atm	36.43 x 10^6 J/m^3 25°C, 1 atm

Source: Harden 1982

Oil and Natural Gas—United States
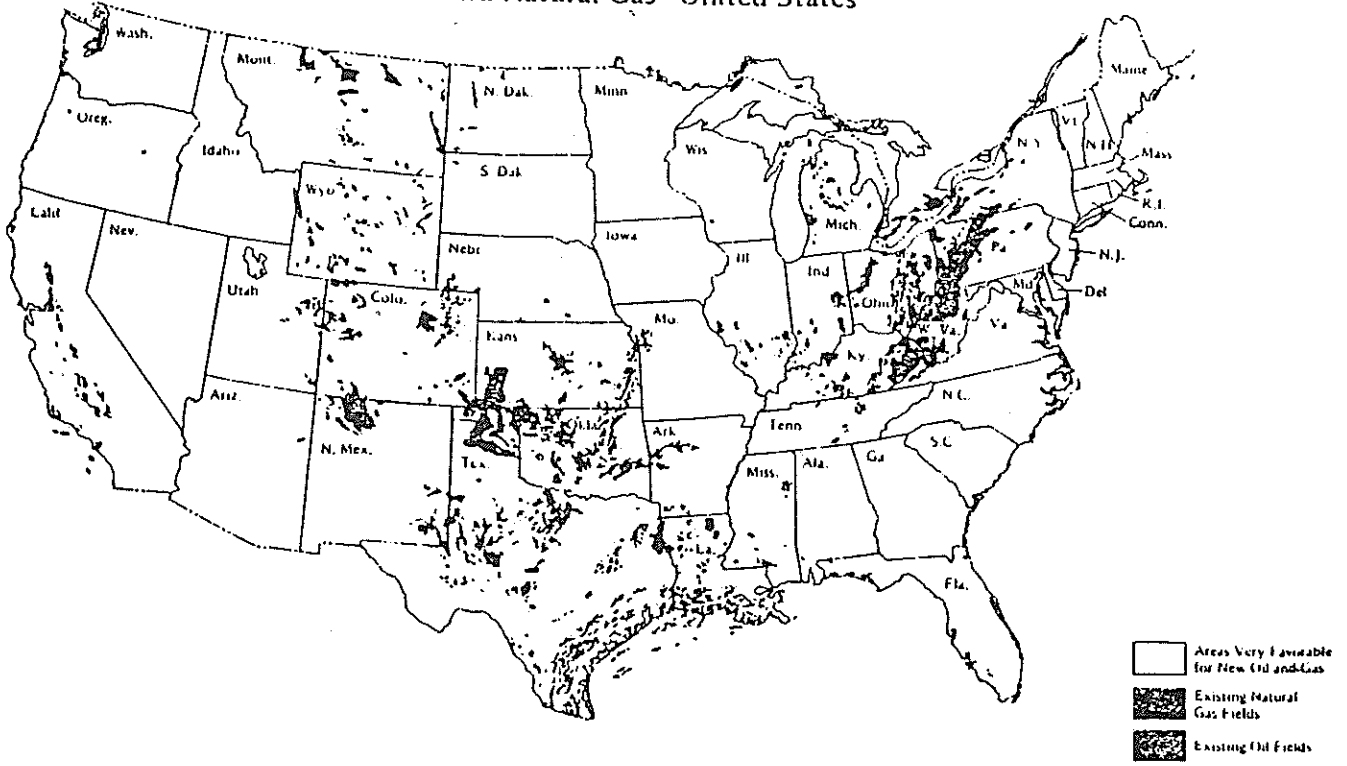
Figure 1. Oil and and natural gas-reserves in the United States.

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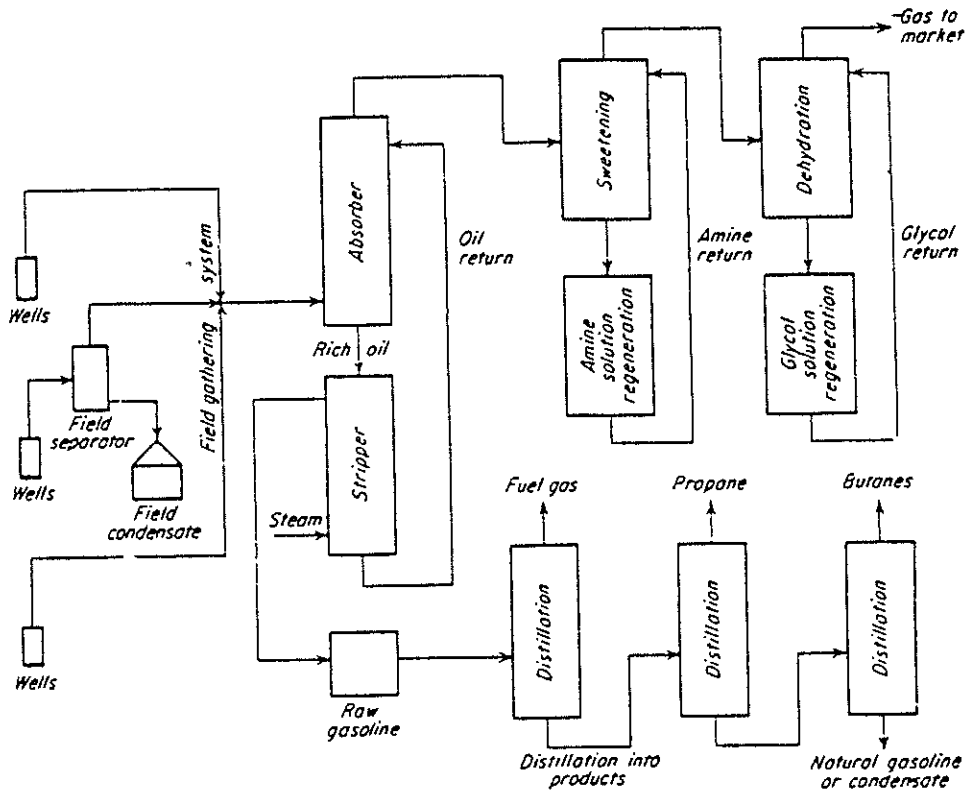
Figure 2. Simplified flow diagram for gas processing.

in the United States is classified as sour (Wade 1979). Since the principle

constituent of natural gas is methane, a list of common properties for methane

is given in Table 1. However, due to the presence of other hydrocarbons in

natural gas, properties will be slightly different for natural gas.

Different Forms of Natural Gas

Both propane and butane can be removed from crude oil or raw natural gas

and are recovered conveniently as liquids. These liquids are called liquified

petroleum gas (LPG) and are usually sold in steel cylinders as an alternative

energy form to natural gas, particularly where natural gas pipelines are not

available. Heavier aliphatic hydrocarbons such as C_5, C_6, C_7 and others in an

unrefined natural gas can also be removed and condensed into a liquid termed

"condensate" or "natural gasoline". Condensate and LPG together are referred

to as natural gas liquids (NGL), which is an important petrochemical feedstock

as well as fuel (Greek 1984). Natural gas, when liquified for storage or

shipment in tankers, is called liquified natural gas (LNG). The major

composition of LNG is methane (greater than 80 mole %), a mixture of C_2-C_5 and

higher hydrocarbons, and nitrogen. A relatively new form for natural gas, LNG

was nonexistent prior to 1964. However, use has increased rapidly due to

certain attractive features including low volume and transportation (ship or

rail and storage) that is more economical than for natural gas. Moreover, LNG

transportation is not limited to land areas only as is the case with

gas-carried by pipelines. Another form of natural gas which is gaining

increasing attention in recent years, due in part to supply shortages of

conventional natural gas, sometimes referred to as nonconventional, synthetic,

or supplemental natural gas, (all abbreviated as SNG). Substituted natural

gas is a methane-rich gas derived from coal seams, coal gasification crude

oil, western tight sands (gas-bearing tight sands in United States West),

Devonian Shale (shales deposited during Paleozoic Devonian Period), urban

wastes and animal residues, geopressured zones and gas hydrates (ice-like crystals of water containing gas in their void volumes), and other carbon containing compounds. Substituted natural gas is currently providing about 7% of the total United States gas supply with an estimated increase to 40 to 60% by year 2000.

Technology of Natural Gas Production, Processing, and Distribution

A large volume of wastes throughout natural gas production, processing, and distribution is generated (Section 1-6). Therefore, a brief description for this technology as shown in Figure 2 is presented below. Natural gas is often associated with oil and/or water under high pressure and it is usually separated from these phases at the wellhead. Furthermore, valuable fractions used as fuel or petrochemical feedstock can be stripped from raw natural gas and used elsewhere. These fractions include natural gasoline (C_5+ hydrocarbons), LPG, naptha (a petroleum fraction boiling between 80 and 180°C), kerosene (a petroleum fraction in the boiling range 150-250°C) (Cottrell and Southwook 1977), and isobutane. The majority of the water is separated physically from oil and the gas in the field (phase, or oil/water) separator unit. This water is called brine or produced water: the heavier hydrocarbons (C_5+) and the remaining water vapor are stripped from the gas by a sudden pressure drop (Joule-Thomson expansion) and are isolated individually in the phase separator. The gas, with condensate and water removed, may still contain light hydrocarbons, some condensate, impurities such as H_2S, CO_2, mercaptans, disulfides, and some water. Both light and heavy hydrocarbons are recovered from the gas for use of such components as heating fuels and/or petrochemical feedstock or removed to reduce disruptions in gas flow from condensation in gas pipelines, particularly in winter. In addition, other impurities, specifically water and acid gases, must be removed to prevent

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pipeline freeze-ups and corrosion of the operational equipment. These processes are accomplished also in the field and later at processing plants.

Oil Absorption — Oil absorption is a process in which a lean oil containing little or no extractable hydrocarbon, is used to remove hydrocarbon products from natural gas (Petroleum Extension Service, 1974). Absorption is more efficient for larger hydrocarbon, (gasoline and condensate) than lighter hydrocarbons. In addition, cooling systems are used in modern processing plants to enhance the absorption process. Trapped hydrocarbons are subsequently recovered from the oil and are separated into individual components using a fractionation distillation. Furthermore, the rich oil contains some dissolved methane which is removed in the demethanizer unit.

Acid Gas Removal — Sour natural gas containing CO_2, H_2S and other gases must be purified using sweetening processes, for which thirty available variations exist (Rissenfled and Kohl). However, these generally can be categorized in three classes (Rissenfled and Kohl; Goar and Arrington, 1979): A) absorption into liquid, B) absorption of acid gases on a solid and C) chemical conversion of acidic gases to other compounds. Amine and carbonate processes, physical adsorption methods, and solid bed sweetening are some common terms for sweetening of natural gas. Alkanolamines are usually used in amine processes and include monoethanol-amine (MEA), diethanolamine (DEA), and triethanolamines (TEA). The typical reactions of MEA with H_2S and CO_2 are given as follows (1974):

$$2RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S$$
$$(RNH_3)_2S + H_2S \rightleftharpoons 2(RNH_3)HS$$
$$2RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3$$
$$(RNH_3)_3 + CO_2 + H_2O \rightleftharpoons 2RNH_3HCO_3$$
$$\text{where } R \rightleftharpoons C_2H_4OH$$

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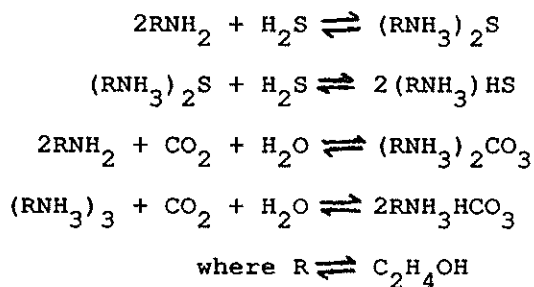
The following overall reactions are representative of carbonate processes (Maddox 1974).

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$$
$$K_2CO_3 + H_2S \rightleftharpoons KHS + KHCO_3$$
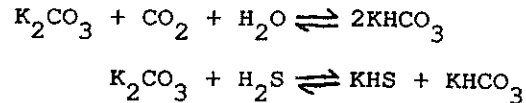
Additionally, removal of acid gases by water is a very common example of physical adsorption while the iron oxide process with the following reactions is a typical example of solid bed sweetening.

$$Fe_2O_3 + 6H_2S \rightleftharpoons 2Fe_2S_3 + 6H_2O$$
$$2Fe_2S_3 + 3O_2 \rightleftharpoons 2Fe_2O_3 + 6S$$
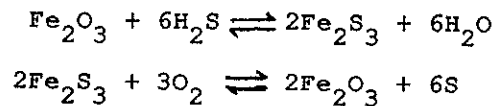
Dehydration - Removal of water from natural gas aids prevention of pipeline freeze-ups and can be accomplished through the use of solid absorbants, liquids, and occasionally a gas. The most common liquid dehydrators are ethylene glycol (EG) and triethylene glycol (TEG). High affinity for water, low cost, stability toward gas components, noncorrosiveness, and low solubility for natural gas and hydrocarbon liquids are among some advantageous properties of EG and TEG. Another alternative for lowering the water content of the gas is in the expansion- refrigeration systems where water condensation occurs due to low temperature and a sudden reduction in pressure.

Distribution Systems - The first gas pipelines in the United State was made of relatively short hollow wood pipes used to move gas in upper New York state. However, over 1 million miles (1,609,000 km) of steel pipelines with different diameters now exist, as illustrated in Figure 3. Moreover, a growth rate of about 7,000 miles/year of transmission lines is expected through the

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year 2000. Although modern steel pipeline can resist high operating pressure, plastic pipelines are becoming popular recently due to low cost and resistance to corrosion (American Gas Association 1974).

Waste Aspects of Natural Gas Production

A comprehensive schematic developed through this research for a natural gas production system with respect to generation of wastewaters from wellhead to consumer market is shown in Figure 4. Produced water and other wastes are often stored in open-air pits or holding reservoirs. While the exact volumes of brine are not known nationwide because not all the states maintain records (Miller 1980), large volumes of brine can be produced in oil and natural gas producing states. For example, from 32, 172 gas wells producing water in New Mexico during an eleven-month period in 1982, more than six billion gallons of brine was recorded. The total annual U.S. brine from oil and gas production was estimated at 460 billion gallons in 1980 (Miller 1980).

In waste disposal pits located near natural gas wells, produced water is often found with a hydrocarbon phase, which is either originally present at saturation with the water or more likely is carried over with water due to imperfect control by floatation valves in separators at field-treatment unit. Although water contamination by salts in brine has been reported studies on presence of C_8 to C_{30} in liquid wastes from these disposal pits is not widely known. An exception is work by Middleditch (1982) in which nearly 200 volatile organic constituents including C_3-C_{16} alkanes, benzene, alkyl aromatic hydrocarbons were identified in the produce water from the Buccaneer gas and oil field in the Gulf of Mexico. These wastewaters are usually disposed of either into land pits or reinjected into wells. Another wastewater is generated in glycol dehydrator unit when spent glycol solution is regenerated through heating to remove the absorbed water. The volume of

this waste is believed to be much smaller compared to produced water, a total of a few hundred gallons per well per year.

The presence of large hydrocarbons in the gas phase during natural gas production and distribution is reduced at well-heads where they are separated from natural gas through a rapid drop in pressure. While this process is reasonably efficient, later formation of additional condensation in gathering lines and distribution pipelines through reduction of temperature and pressure has been a reoccurring problem in distribution of natural gas (Orange 1973).

Figure 3. Natural gas pipline and movements, 1974.

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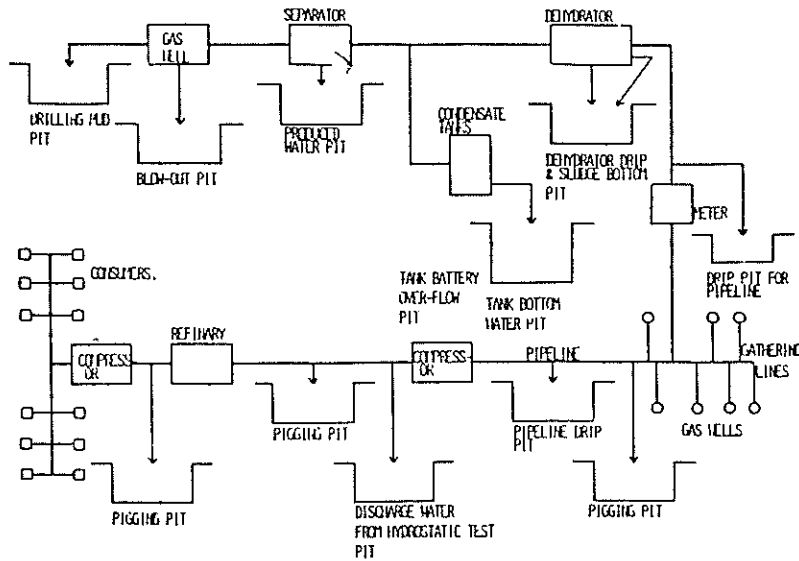
Figure 4. Summary diagram of waste sites associated with natural gas production, processing and distribution.

Such waste is removed at strategic locations and usually stored in surface pits called drip pits. Few records are available to assess the total volume of condensate dripping, but the problem can be severe, as demonstrated in an extreme event where as many as 1,534 gallons of condensate were formed daily during a week period of cold weather in Chalmers Station near Detroit (Katz 1976); similar problems were also reported in Europe. Even though a major research program (Bergman et. al. 1975) was used to address this problem, little detailed information is available on composition of condensate and presence of condensate in other consumer distribution lines. Another source of reasonably large amount of wastes generated in natural gas distribution is discharge water from hydrostatic testing (DWHT) of natural gas pipelines.

Hydrostatic testing, a common practice in the natural gas industry, is used to examine the physical integrity of the pipelines and also to maintain flow efficiencies through removal of deposits (Eiceman, et. al. 1983). During a hydrostatic test, a pipeline is filled with water obtained typically from nearby water sources such as rivers, lakes, and ponds. Then, pipelines are pressurized using air or natural gas to detect any flaws or leaks and lines are subsequently emptied. The process of removing the hydrostatic test water is commonly called "pigging", an the term "pig" refers to any device used to brush, scrape, or remove the fluids and residues from the pipeline. Clear distinction must be made between old pipelines that have been in use for 2 to 15 years and new pipelines (or section of pipelines) in which virtually no condensate from natural gas should be found. Concentration of organic compounds in this condensate may be large, with COD values as high as 100,000 mg/L. Furthermore, volatile organic compounds including benzene, C_1 to C_5, alkylated benzenes, alkylated disulfide, and others have been detected in these wastewaters. Test waters are usually released either directly into rivers or stored in lined or unlined earthen pits.

As it is shown in Figure 4, several other wastes are generated in natural gas production. One example is drilling fluid in which water is the major component by volume (Georg et. al. 1980). The term drilling fluid includes all the components used to aid tools in the creation of a borehole in the earth. Neither the exact volume nor the composition of these wastes are known. However, drilling of over 83,000 oil and gas wells in the United States in 1984 alone (McClasin 1985) portends generation of large amounts of potentially hazardous drilling fluid wastes.

Environmental Impact of Waste Disposal

At least one half of the population of the United States depends upon groundwater as a source of drinking water. Yet, a large number of occurrences

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of ground and surface water contamination have been documented and attributed

to natural gas exploration and development activities (Fryberger 1972;

Oklahoma Water Resources Board 1975; Lehr 1969). Disposal of wastes in

surface pits was a favorite technique in natural gas production and processing

between 1930 to the 1970s and is still widely practiced in the United States

Southwest, particularly in northwest New Mexico. Of special concern in

groundwater protection are those pits that are unlined or lined with clay,

which is known to degrade in organic solvents (Green 1979). Seepage of

aqueous contents of such pits and eventual migration into groundwater have

been observed (Fryberger 1975; Baker aned Brendecke 1983; Sperster et. al.

1983; Rown and Deul 1983). For example, 93% of brine water in an unlined pit

in Utah seeped from pits into nearby soil and only 7% evaporated. In

addition, evaporation is significantly suppressed if the disposal pond is

covered by a thin layer of floating crude oil. Under favorable conditions,

one gallon of oil was enough to cover a 2-acre water surface. The contents of

these pits might pose serious contamination problems with those aquifers

classified as vulnerable (close physically and hydrologically), but few

studies on fate and movement of wastes from pits were available prior to this

research. The few reports which are available have conflicting conclusions:

both extensive and limited migration of hydrocarbon wastes through soils have

been reported. Waste pits that are abandoned or not in use may also be a

source of concern should a hydrocarbon residue remain and gradually migrate

into ground water.

While hydrostatic testing of natural gas pipelines is a regular if not

frequent operation, neither the magnitude of these operations nor

environmental impact from release of these waters untreated or poorly treated

has been addressed, particularly for hazardous organic compounds including

polycyclic aromatic hydrocarbons. However, the presence of over 1,000,000 km

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of pipeline mains with an unknown length of branches in the United States

(Cory 1976) is sufficient magnitude for concern. In some pipelines, a pig is

forced through a pipeline to remove a large fraction of condensate before

hydrostatic testing. While the composition of wastes from dry-pigging also

has not been thoroughly analyzed with regard to toxic organic compounds, this

discharge may reasonably be expected to contain higher concentrations of

whatever is found in the discharge water from hydrostatic testing.

Condensation of hydrocarbons from C_4 to C_{20} in pipelines leads to formation of

liquid wastes that are usually removed from pipelines in geographical low

regions and are placed in earthen drip pits. Few records are available to

assess the total volume of condensate drippings. Virtually no information is

available on their composition of wastes in these drip pits and on the

potential for impact on shallow groundwater. Moreover, no information on the

composition of wastes from regeneration of dehydrator/sweeteners is generally

available. Volatilization, adsorption, photodecomposition, and biodegredation

have all been identified as possible mechanisms for environmental loss of

hydrocarbons and PAH (Sims and Overcash 1983; Pettyjohn and Hounslow 1983;

Newsom 1985). However, contamination of groundwater by these compounds at

several places in the United States, (Fried et. al. 1979; Yazicigi and

Sendlein 1981) represents a certain (but unknown) longevity and shows that

complete loss of hydrocarbons does not occur rapidly through the mechanisms

for loss or decomposition. Moreover, natural gas wells and associated waste

pits are often found in flood plains of river valleys particularly in New

Mexico. Since groundwater can be found at depths as lows as 1.8 meters in the

same area, mobility of organic compounds from waste pits through these soils

should be known for prediction of impact on ground water quality. However,

suitable models and supporting studies on mobility of hydrocarbons and PAH in

complex aqueous mixtures through these soils are unavailable. For example

water seepage from another waste pits has been shown to be extensive in Utah

(Bake and Brendeke 1983) and portends possible migration of hazardous and

toxic organic compounds from waste pits into nearby soil and shallow

groundwater. Little detailed information is available on composition of

natural gas wastes particularly for organic compounds and potential for

deleterious environmental effects from uncontrolled discharge of such wastes.

These pollution problems have been substantial due to uncontrolled discharge

to surface waters or to evaporation pits, as well as other improper waste

disposal practices. Evaporation pits, which are unlined shallow earthen pits,

are still used in northwest New Mexico, eventual impact on groundwater may be

expected. For example, in a recent series of articles in the Wall Street

Journal, substantial water quality degredation and unusual high level of

cancer and illness have been documented in Southern Louisiana, in areas of

heavy oil and gas production, where thousands of open pits are filled with

brine (Petzinger and Getschow 1984).

ABSORPTION OF HIGH MOLECULAR WEIGHT CONTAMINANTS

IN NATURAL GAS ON TENAX-GC

Background

Adsorption traps for atmospheric monitoring of human exposure to toxic,

volatile, organic compounds have become widely accepted in the practice of

industrial hygiene (Marchello and Kelly 1975; Nonhebel 1972). Atmospheric

sample is drawn through a trap containing an adsorbent such as charcoal,

silical gel, alumina or a synthetic macroporus resin, and organic compounds

are retained in the trap while common atmospheric gases are largely

unretained. Advanced designs of this principle have developed for specialized

environmental projects including analyses of incinerator stack emission

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(Parsona and Mitzner 1975), water analyses (Dowly et. al. 1975), and blood analyses for xenobiotics (Zlatkis et. al. 1973).

One major characteristic of adsorption traps is finite capacity for retention of particular components in sample during collection of sample. Movement of a component completely through an adsorbent trap is called breakthrough and occurs for components when a sufficient volume of gaseous sample (the breakthrough volume) is drawn through trap. Different components will have different breakthrough volumes if retention characteristics on the adsorbent are significantly different. Failure to account for the breakthrough phenomenon in adsorption traps, regardless of accuracy of final instrumental measurements of trap contents, will lead to serious quantitative errors.

Breakthrough processes on adsorbent beds in sampling traps have been treated extensively in gas chromatography as frontal analysis (Classon 1946; Blueckauf 1954; Kridge and Pretorius 1965; Reilly et. al. 1962) in which the sample is introduced continuously into the column (Harris et al 1980). As in regular elution chromatography, the mechanism for retention (or breakthrough) is based on the partition coefficient (K) which is inversely proportional to vapor pressure and activity coefficient (Karger et al 1973). For compounds with large values of K, breakthrough measured as retention time or volume will also be large.

Numerous adsorbent materials are available for breakthrough studies but Tenax-GC (poly 2,6-diphenyl para phenylene oxide) was chosen due to several favorable properties, namely: 1) relative low hydroscopic character, 2) well-defined and large breakthrough volumes for hydrocarbons (Brown and Purnell 1979) and 3) wide use in actual sampling procedures (Bertsch et. al. 1975; Pellizzano et. al. 1975; Renberg 1978; McCooye and Gardner 1976).

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Organic Compounds in Laboratory-Supplied Natural Gas

Results from GC analysis of condensed washings of the cold trap are shown in Figure 5 and included 50 to 80 organic compounds. These components were present originally in laboratory-supplied natural gas and were condensed during passage of natural gas through the cold trap.
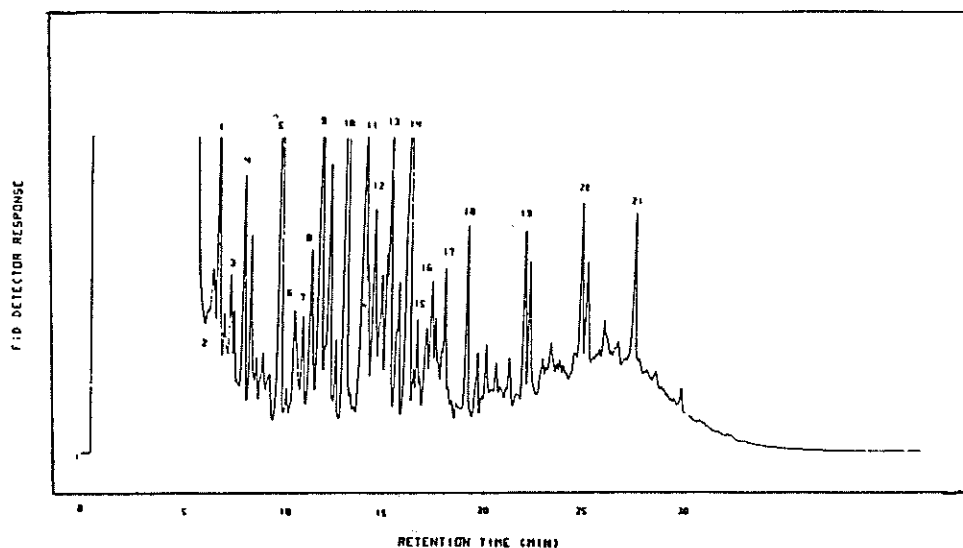
Figure 5. Chromatogram from GC-FID analysis of condensate in natural gas supplied to laboratory. Identification of components referenced to Table 3 using numbers near peaks.

Solvent and procedure blanks were free of detectable levels of such compounds. Total concentration of this mixture in natural gas at standard temperature and pressure was established at 100 mg/m^3, not corrected for efficiency of collection and sample preparation. Thus, this value may be slightly lower than actual concentration. Retention indices for these components, calibrated using C_{12} to C_{34} n-hydrocarbons, showed most compounds with carbon numbers of C_{10} to C_{19}. While large molecular weight compounds have been reported in natural gas, compounds of C_{12+} have not been reported in natural gas in consumer distribution lines. Identitites of major compounds shown in Figure 5

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are given in the Table 3. Of the 21 major components detected, most were

aliphatic hydrocarbons with a few aromatic hydrocarbons.

Breakthrough Studies Using Natural Gas

Results from breakthrough studies in which laboratory-supplied natural

gas was passed through solid adsorbant traps in series are shown in Figure 6

as bar plots. In a bar plot, chromatograms are reduced in form to allow

convenient comparison of several complex chromatograms (Clement 1976). Since

trap 1 was the first trap in the series, the presence of a compound in trap 2

at any period of time (3 to 24 h) is evidence of breakthrough for that

compound on trap 1. Similarly, presence of compounds on trap 3 means

breakthrough (of only those compounds) on trap 2. In Figure 6, several trends

in breakthrough can be observed and employed to explain principles of

breakthrough. For example, in a gas-solid adsorbent system for molecules of

similar chemical characteristics, breakthrough is inversely proportional to

vapor pressure as a first approximation. Since a similar statement can also

be made regarding gas chromatography (for nonpolar solutes with nonpolar

liquid phases), first components to breakthrough traps should also be early

eluting components (i.e., compounds with high vapor pressure) in GC analysis.

This pattern can be seen in Figure 6 if the composition of trap 2 is inspected

as a function of time (or volume) of gas passed through the trap. On trap 3

(E) only a few early-eluting components are seen in GC plots. However, larger

molecular weight compounds (i.e., lower vapor pressure, and thus later-eluting

GC peaks) are seen at increasingly larger concentrations with increasing

volume (D to A), which means breakthrough on trap 1. Similar patterns may

also be seen in trap 3 and regarded as breakthrough on trap 2.

Table 3. Organic compounds at low concentrations in natural gas.

R-T*	Peak No.**	Compound	Vapor pressure at 25°C (mmHg)
7.62	1	$n-C_{12}H_{26}$	0.286
8.08	2	$C_{13}H_{28}$ (branched)	--
9.18	3	$C_{13}H_{28}$ (branched)	--
9.46	4	Methyl-naphthalene	--
10.58	5	$n-C_{13}H_{28}$	0.093
11.98	6	Biphenyl	0.057
12.40	7	Ethyl-naphthalene	--
12.74	8	Dimethyl-naphthalene	--
13.12	9	Ethyl-naphthalene	--
13.70	10	$n-C_{14}H_{30}$	0.035
15.16	11	(Methylbiphenyl + alkylbenzene)	--
15.76	12	Isopropyl-naphtalene	--
16.36	13	Dimethyl-biphenyl isomer	--
16.76	14	$n-C_{15}H_{32}$	0.012
17.86	15	Dimethyl-biphenyl isomer	--
18.32	16	Dimethyl-biphenyl isomer	--
18.70	17	Butyl-naphthalene	--
19.78	18	$n-C_{16}H_{34}$	0.005
22.66	19	$n-C_{17}H_{38}$	0.003
25.42	20	$n-C_{18}H_{38}$	0.002
28.08	21	$n-C_{19}H_{40}$	0.0001

*R-T - Retention time in minutes

**See Figure 5
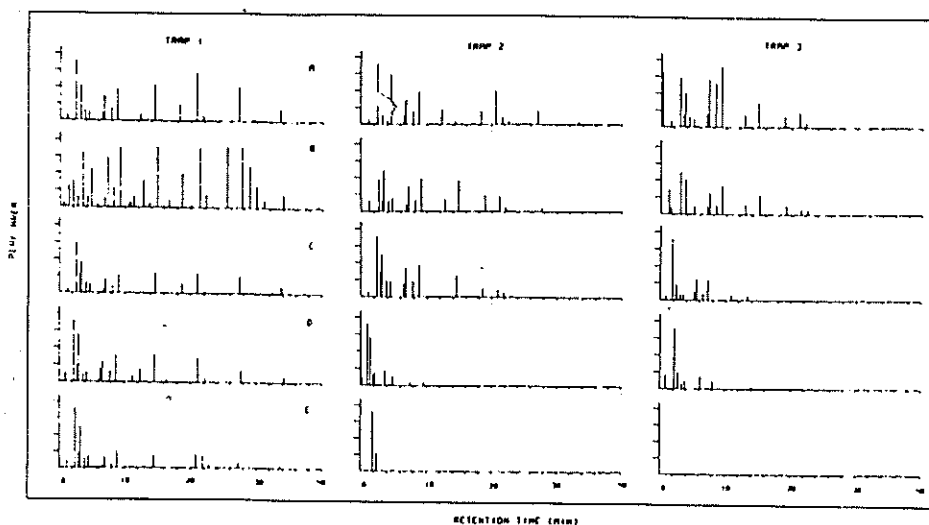
Figure 6. Bar plots of GC analyses of adsorbent traps in breakthrough studies. Letters are for trap systems in which sampling time was: A. 4 hrs.; B. 28 hrs.; C. 12 hrs.; D. 6 hrs.; and E. 3 hrs at gas flow rate of 375 mL/min.

Although breakthrough processes are reasonably apparent in GC plots that were normalized to reduce influence of absolute concentration on visual recognition of patterns, another method to present results for illustration of breakthrough is a plot of concentration of a component on trap 2 versus volume of gas passed, as shown in Figure 7. Several compounds with a range of molecular weights (or vapor pressure) were selected from the GC results for presentation. No attempts were made to use results here for precise measurements and none are possible using these data. However, the breakthrough principle using natural gas has been established and natural gas has been satisfactory for these studies.

A better experimental design for collection of precise breakthrough data would involve continuous monitoring of effluent comparison using detectors. While such designs have been successful in frontal analysis GC where components are present in 1 percent (v/v) concentrations, attempts to use FID and electron capture detectors (for aromatic compounds) connected directly to traps were unsuccessful. With each detector, large amounts of methane were thought responsible for low sensitivity and poor performance generally. However, use of flow-through cells in certain optical spectroscopic methods may be promising for continuous detection of trap effluent.
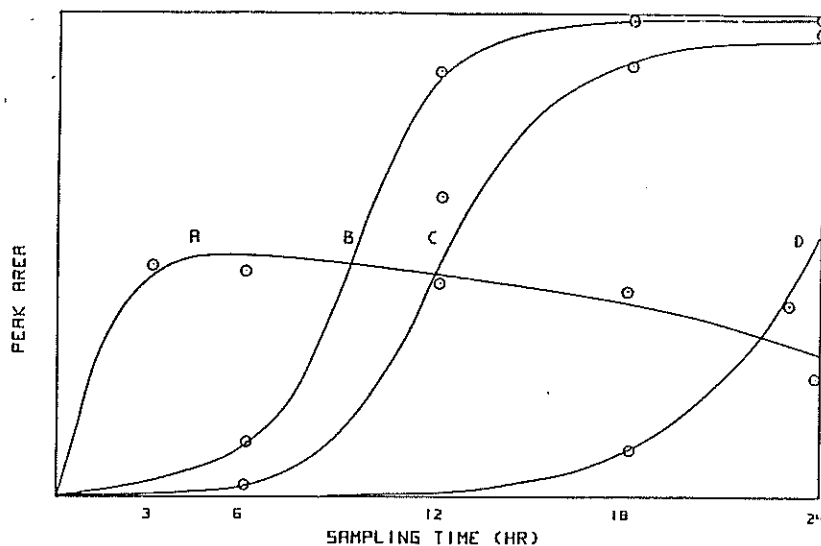
Figure 7. Plots of peak area versus sampling time (hrs) for components found in Trap 2. Peak areas were taken from GC analyses of trap extracts as shown in Figure 3. Components were A. low molecular weight compound possibly dodecane, B. hexadecane, C. octadecane, and D. nonadecane.

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POLYCYCLIC AROMATIC HYDROCARBONS IN NATURAL GAS FROM CONSUMER

DISTRIBUTION PIPELINES

Natural Gas Composition

In this section, natural gas samples drawn from a limited number of

consumer distribution lines were analyzed using GC and GC/MS techniques for

organic compounds with molecular weights above 128 amu or C_{9+}. In our

analyses, more than 50 organic compounds between C_{11} to C_{19} hydrocarbons were

identified at total concentrations of near 100 mg/m^3. In Figure 8,

results are shown for GC analyses of eight gas samples drawn in identical

manner from five urban centers in a wide geographical range, as was

illustrated in Figure 9. Results are displayed in Figure 8 as bar plots of

concentration (ug/m^3) versus retention index. Since the concentrations have

been normalized for sample volume and have been quantified using an average

FID response factor of 14.7 area counts per ng, direct comparisons between

samples can be made through bar plots. As shown in Figure 8, GC
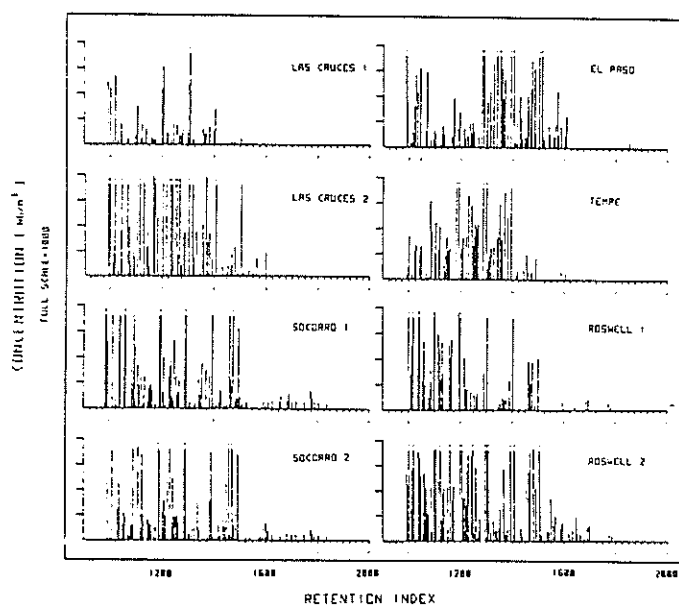
Figure 8. Bar plots of concentration (mg/L; Full Scale Value=50) versus
Retention Index from GC analyses of condensate from natural gas sampled using
Tenax-GC traps.

RETENTION INDEX
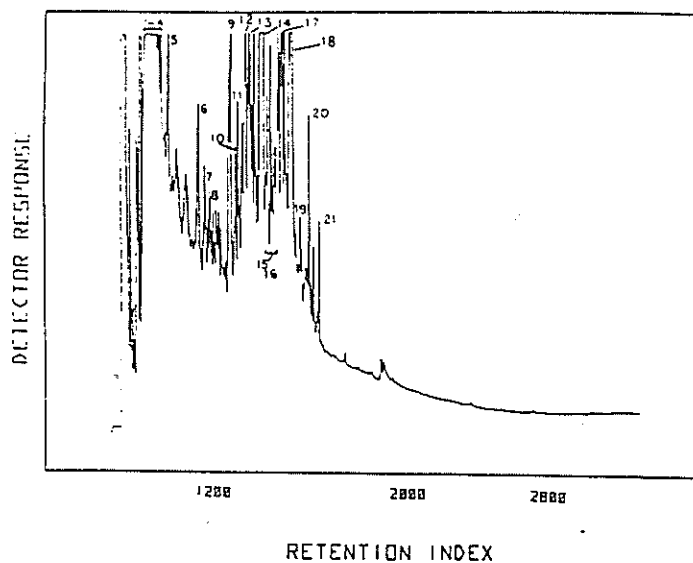
Figure 9. Chromatogram from GC-FID analysis of gas condensate from El Paso, TX. Major components are numbered and listed in Table 3.

patterns typical of complex mixtures were found with all samples, which were all reasonably similar in composition qualitatively. Samples were similar with a range of hydrocarbons from C_9 to C_{20}. However, some samples differed quantitatively in relative composition of components to those in other samples. For example, in the El Paso sample, the majority of major of components were between C_{13} to C_{15} with few major components below C_{12}. In contrast, for samples from Las Cruces 2 and Roswell, most major components were between C_9 and C_{14}. No clear explanation of these results are known or proposed here.

Large differences existed between samples with regard to absolute concentrations (mg/m^3) of organic compounds estimated for each sample from integrated GC data and using FID average response factor were the following:

Las Cruces 1, 0.33; Las Cruces 2, 2.7; Socorro 1, 1.9; Socorro 2, 3.0; El Paso, 2.5; Tempe, 0.98; Roswell 1, 1.2; and Roswell 2, 0.23. These differences are not particularly surprising since samples were drawn with gas supplied from different gas fields or from different locations along a pipeline form the same gas field. Moreover, certain volatile (C_5 to C_8) organic compounds, including benzene and alkylated benzenes, that were found in trap extracts may have been lost largely through the breakthrough phenomenon or by volatilization during condensation of extract using rotary evaporation. For example, breakthrough volumes for the following compounds on Tenax-GC traps in methane carrier were estimated from earlier data: $C_{12}H_{26}$, 45 1/g; $C_{16}H_{34}$, 135 L/g; $C_{18}H_{38}$, 450 L/g and $C_{19}40$, 1080 L/g. Since the volume/mass values for these samples ranged from 180 to 380 L/g, breakthrough should not affect exact quantification for compounds above C_{17} to C_{18}. However, results from GC determination of compounds with molecular weights below values of C_{15} may be considered only semi-quantitative, and breakthrough may account for some quantitative errors in these results. Therefore, these must be considered minimum concentrations and actual concentration should be much larger especially when masses from benezene, alkylated benzenes, and lighter alkanes are included.

Results from scanning GC/MS analyses for the El Paso sample are summarized in Table 4 for major constituents in these samples, although all samples contained the same components but at different concentrations. Since very similar chromatographic conditions were used in GC and GC/MS analyses, favorable comparisons of GC and GC/MS chromatographic patterns, along with mass spectral data and standards, aided assignment of identity to particular GC peaks. The chromatogram in Figure 8 for the El Paso sample was representative of the large complexity of all natural gas samples and resolution of components was considered satisfactory, especially in presence

of an excess abundance of normal and branched alkanes and alkenes. In these samples, adequate mass spectra were obtained for many of the major components, including aromatic hydrocarbons. Apart from a few references (Herlan and Mayer 1978), larger molecules including aromatic, alkylated aromatic, polycyclic aromatic (PAH), and alkylated polycyclic aromatic hydrocarbons have not been widely considered as components in natural gas. However, these results showed relatively large abundances of these compounds in samples from throughout the Southwestern United States. Analytical data that support these results may be found in reports from Germany (van Rossum and Wokote 1980), U.S. Gulf Coast (Jonker et al 1979), U.S. Midwest, and East Coast regions. However, in other reports on natural gas analyses, such compounds have been ignored or unreported (Gouw and Jentolts 1972).

More detailed information on the gas samples was collected by using selected ion monitoring (SIM) for PAH and alkylated-PAH. An 11-ion SIM plot is shown in Figure 10 for the El Paso gas condensate sample. Furthermore, selected quantitative results from SIM analysis of all samples are summarized in Table 5. As shown in Figure 10, naphthalene, biphenyl, anthracene, and alkylated members of each PAH were detected in natural gas from all consumer distribution pipelines studied here. As a general trend, the larger the molecular weight of a component (with a smaller vapor pressure), the lower the gas phase concentration of that component. While this is consistent with liquid-gas vapor pressure behavior, absence of details on the liquid residue inside pipelines made precise conclusions on behavior uncertain. Nevertheless, the general pattern held among all samples and concentrations of individual PAH ranged from 2 ug/m^3 to 240 ug/m^3, which seemed surprisingly large until residues in pipelines were analyzed.

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Table 4. Major components from natural gas preconcentrated using Tenax traps.

Peak No.	Retention Index*	Identity (Retention Time)	Methods of Idenitifcation**
1	0082	Xylene (2.72)	RI, MS
2	0948	C_3-Benxene isomer (4.28)	MSI
3	0955	C_3-Benzene isomer (4.46)	MSI
4	0976	C_3-Benzene isomer (4.94)	RI, MS
5	1000	$C_{10}H_{22}$ (5.52)	RI, MS
6	1100	$C_{11}H_{24}$ (7.90)	RI, MS
7	1126	C_5-Benzene (8.56)	MSI
8	1143	Naphthalene (9.00)	RI, MS
9	1200	$C_{12}H_{26}$ (10.44)	RI, MS
10	1229	C_6-Benzene isomer (11.20)	MSI
11	1235	C_6-Benzene isomer (11.36)	MSI
12	1248	C_1-Naphthalene isomer (11.72)	MS
13	1253	C_1-Naphthalene isomer (11.84)	MS
14	1300	$C_{13}H_{28}$ (13.08)	RI, MS
15	1313	Branched $C_{13}H_{28}$ (13.38)	MSI
16	1327	Alkene (13.70)	MSI
17	1377	Branched alkane (14.86)	MSI
18	1400	$C_{14}H_{30}$ (15.40)	RI, MS
19	1425	$C_{14}H_{28}$ (15.82)	RI, MS
20	1436	Branched alkane (16.00)	MSI
21	1500	$C_{15}H_{32}$ (17.08)	RI, MS

* On DB-5 phase

** RI = retention index of standard, MS = mass spectrum of standard under same conditions, MSI = match to mass spectrum in data base.
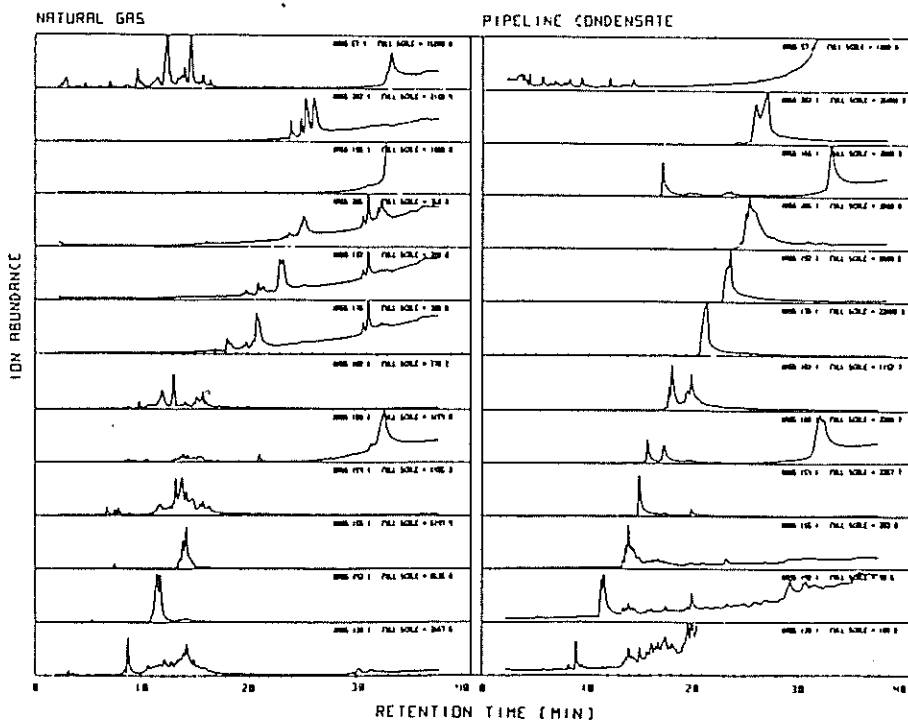
Figure 10. SIM plots from GC/MS analysis of a) natural gas condensate and b) residue washed from natural gas pipelines. An additional ion monitored was m/Z 202.1 amu for pyrene and 57.1 amu for saturated hydrocarbons.

Pipeline Samples

Results from GC analyses of condensed washes are shown in Figure 11. In GC analyses for pipeline washes, the chromatographic patterns were typical of complex mixture with a large amount of unresolved material between RI units of 2000 and 3000 as shown in Figure 11. Extensive pre-fractionation procedures were necessary to isolate the compounds of interest (PAH) despite use of high resolution GC column due to extreme complexity of samples. Results from prefractionation may be seen in Figure 3-8 in which a majority of unresolved organic mass was removed and only a few well-resolved components (PAH) remained as detected with GC/FID. The isolated fractions were analyzed

Table 5. Concentrations of selected PAH in natural gas (ug/m^3).

	Location and Concentration (ug/m^3)			
Compound	Las Cruces 2	Las Cruces 1	Roswell 1	Roswell 2
Naphthalene	26	68	40	21
C_1-Naphthalene	29	154	232	28
C_2-Naphthalene	24	50	156	28
Biphenyl	4	33	15	7
C_1-Biphenyl	5	28	16	4
C_2-BIphenyl	6	26	16	5

	Socorro 1	Socorro 2	Tempe, AZ	El Paso, TX
Naphathalene	55	45	21	46
C_1-Naphthalene	48	41	27	240
C_2-Naphthalene	32	32	23	132
Biphenyl	4	4	3	42
C_1-Biphenyl	7	5	2	39
C_2-Biphenyl	7	6	6	44

by GC/MS using SIM and results are shown in Table 6 and Figure 10 (right panel). Polycyclic aromatic hydrocarbons were found in every ion used in SIM analyses and interesting trends were found as related to the gas-phase composition. Lower molecular weight compounds such as naphthalene were present at relatively low amounts of 4 to 13 ug/m^2 of inner-surface area. However, the larger molecular weight compounds were found at high concentrations, up to 2400 ug/m2.
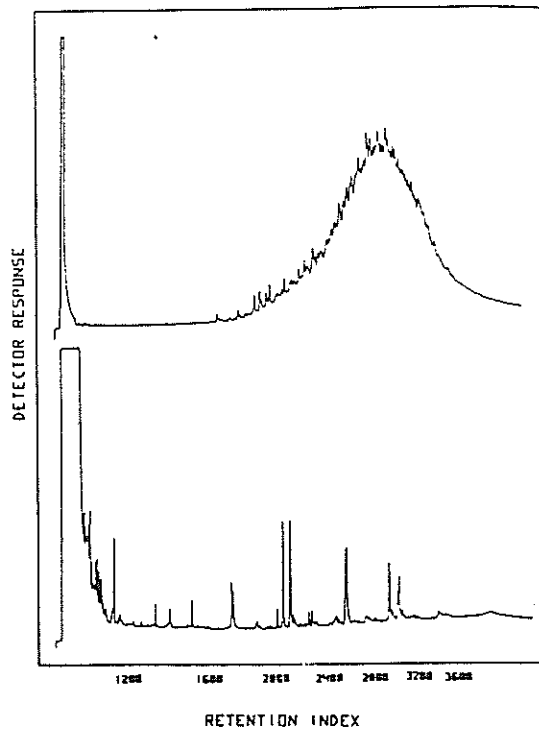
Figure 11. Chromatograms from GC-FID analysis of residue from natural gas pipelines with a) no prefractionation and b) prefractionation of residue for PAH.

Table 6. Concentrations of selected PAH inside natural gas pipelines.

Compound	Location**	1	2	3	4	
Naphthalene		4	6	11	13	
C1-Naphthalenes		9	2	3	1	
C2-Naphthalenes		18	2	5	4	
Biphenyl		75	16	22	1	
C1-Biphenyls		66	8	16	4	
C2-Biphenyls		71	2	22	3	
Anthracenes		1200	84	130	18	
C1-Anthracenes		460	22	37	13	
C2-Anthracenes		280	14	45	10	
Pyrene		2400	160	110	26	
C1-Pyrenes		1030	45	37	4	
C2-Pyrenes		290	20	25	2	

*   Concentrations are expresssed in ug of PAH per m^2 of surface area of innerwall of pipelines.

** Locations are in reference to Table 2-1 and Figure 2-2 and are 1) University and Haggerty: 2) Howell and 5th St.; 3) Ethel and 5th St.; and 4) Palmer and 5th St.
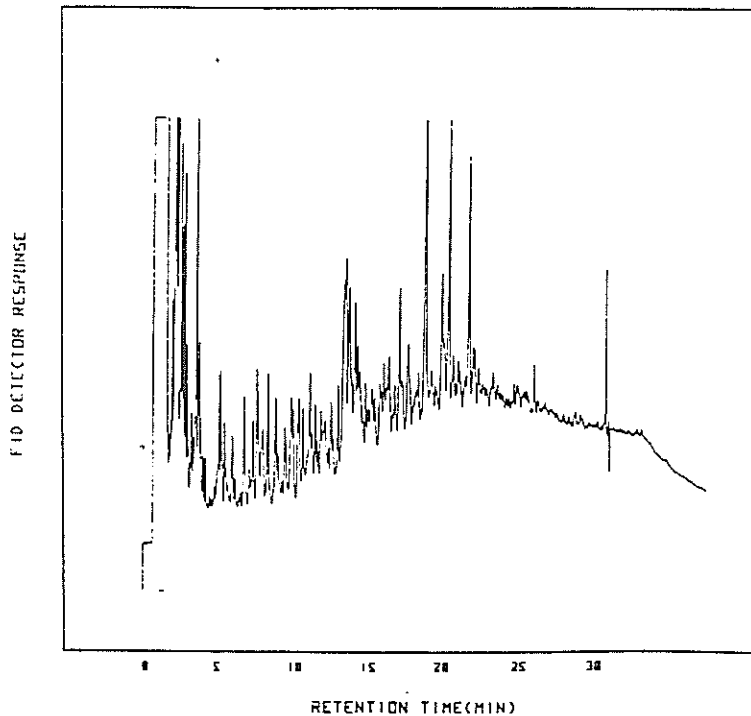
Figure 12. Chromatogram from GC-FID analyses of condensed PAH isolated fraction of DWHT sample Al.

Environmental Assessment and Conclusion

Production of natural gas has been evaluated from a point source

perspective for atmospheric pollution of light hydrocarbons and inorganic

gases and from a point of view of toxic metal ions. However, the result of

this study are the first results to propose the movement of toxic and

carcinogenic compounds widely throughout natural gas distribution lines

systems. The presence of larger molecular weight compounds in natural gas is

reasonable based on vapor pressures and the abundance of same compounds in

pipeline residues, as shown in Figure 10.

The presence of high molecular weight organic compounds in pipelines can be attributed to a phenomenon termed retrograde condensation, which is defined as liquid formation by isothermal expansion of a fluid. Formation of a liquid by isothermally decreasing the pressure of on a gas is unlike that for a pure substance. Methane in natural gas can be considered a supercritical fluid at ambient temperature and under conditions of high pressure. An important consequence of this condition is increased solubility of large molecular weight compounds in the supercritical fluid (Fjeldsted and Lee 1984). However, as natural gas is passed through a pressure drop in production equipment or pipelines, the solubility of large molecular weight components is decreased and condensation occurs. The condensate may be carried through the system by flow of gas. Since these compounds are present in pipeline condensate and in the natural gas, same compounds may be reasonably expected in aqueous wastes from pipeline maintenance including hydrostatic testing. Moreover, the same compounds should be expected in produced water.

Discharge Water from Hydrostatic Testing of Natural Gas Pipelines

Discharge water from hydrostatic testing of natural gas pipelines was found upon simple solvent extractions and direct analysis of condensed extracts using gas chromatography, to be too complex a mixture even for moderate resolution although high resolution capillary column was used. The presence of saturated, unsaturated, and branched aliphatic hydrocarbons was evident in GC/MS determination of a large shifting baseline, which has been called the hydrocarbon hump. Even selected ion monitoring in GC/MS analysis of extracts for selective detection of PAH showed the same general pattern of baseline rise and was unsatisfactory for selective determination of PAH. Thus, prefractionation of extracts was necessary despite additional handling of samples, glassware, and solvents. While several prefractionation schemes were possible, extensive solvent extraction technique was used since the

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samples were so complex and since only readily available glassware (no specialized chromatographic equipment) was needed. This procedure was used as described above with a single addition to correct for variations in extraction efficiencies: known amounts of deuterated PAH was spiked into samples before extraction procedures in order to accurately quantify PAH in samples through SIM analyses.

Results from prefractionation were successful in that over 90 percent of the mass associated with the hydrocarbon hump was reduced as determined through comparison of GC analyses of PAH fraction and those of unfractionated extract of DWHT sample. However, losses in extraction efficiency through use of multistep extraction procedures were also substantial and range in recovery efficiencies were determined for individual PAH as naphthalene, 29-100 percent; anthracene, 21-90 percent; fluorene, 20-92 percent; and pyrene, 45-109 percent. These large variations were believed due to large differences in matrices of samples. In final quantification of PAH in DWHT, corrections for total extraction efficiencies were made using deuterated PAH with same or closest structural ring system to particular PAH. The absence of the hydrocarbon hump in PAH fraction from a DWHT sample with characteristics largely oil in nature is shown in Figure 12. Despite extensive prefractionation, a chromatogram with over 30 to 50 resolved components is apparent and suggests presence of complex mixture of PAH. Nevertheless, peak shapes were good and the resolution were also acceptable. Improved ratios in PAH concentration/background hydrocarbon concentration were also seen in SIM analysis of the same sample for regular PAH shown in Figure 13 as a SIM plot.
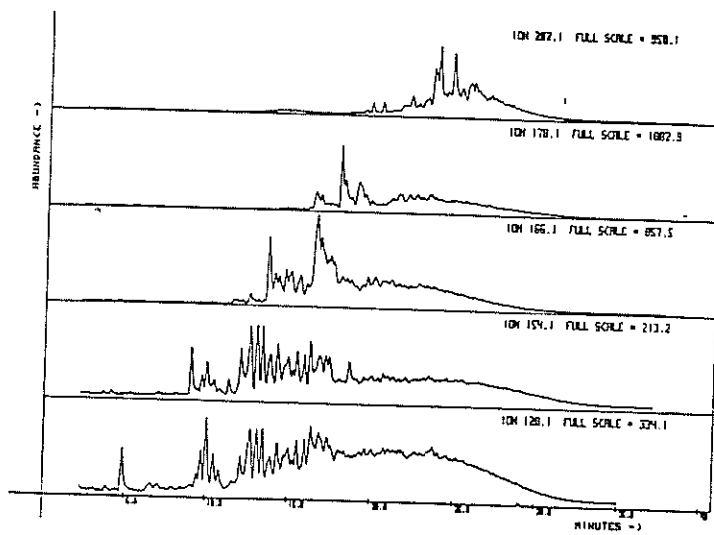
Figure 13. Results from SIM analyses using GC/MS of DWHT sample A1 fro PAH. A) Napthalene, 128 amu; B) biphenyl, 154 amu; C) fluorene, 166 amu; D) anthracene, 178 amu; and E) pyrene, 202 amu.

In Figure 13, the presence of several common PAH in this sample was seen
well above either background hydrocarbons or other interferences. Peak shape
was narrow and symmetrical with numbers of theoretical plates for naphthalene,
3,000; biphenyl, 10,000; fluorene, 30,000; anthracene, 50,000; and pyrene,
90,000. Each sample of DWHT and the condensate sample from natural gas lines
used to supply our laboratory was extracted and analyzed with identical
procedures. Moreover, samples were analyzed using GC/MS for SIM
qunatification over a period of two days in order to eliminate variations in
column resolution and mass spectrometer performance toward more reliable
intersample comparison. Results from quantification of PAH and alkylated PAH
in these samples are given in Table 7. These results show clearly the
complexity of DWHT samples including just the PAH fraction. The number of
substitutional isomers seen and those possible for not only naphthalene but
also other PAH families is given in Table 7. Apart from the regular C_1 and C_2
species, not all possible isomers were detected through either incomplete
resolution or absence of particular isomers. The DWHT sample that was most
oily in appearance and that also coincided with the start of dewatering
operations with this pipeline. All other samples of DWHT and the
laboratory-collected natural gas condensate showed similar complexity but at
different concentrations. Confirmation of identity of PAH was through use of
internal deuterated standard which had the same retention properties as
nondeuterated PAH from the sample and through the use of mass spectra of
standards analyzed using same conditions. Identification of alkylated PAH was
based upon relative retention properties and mass spectra taken using scanning
of GC/MS of the same sample. Mass spectra of alkylated PAH are distinct
showing as a pattern loss of 15 or 29 amu from a molecular ion. Typically,
the molecular ion is moderate in relative intensity and the base ion is
usually the M+ or $M-1^+$ ion. Amounts of these compounds in the PAH fraction

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were sufficient to collect satisfactory mass spectra that were matched favorably with standard spectra in the EPA/NIH mass spectral database. The values of PAH concentrations in these water samples followed as regular trend, as seen in Figure 14, with a decrease in concentration as a decrease in chemical oxygen demand. This of course followed the extent of dewatering and may reflect variations in solubility in the water phase as the composition of this phase varied in content from largely oil to largely water. No similar pattern in concentration was seen earlier with volatile compounds which had uniform concentrations for the same samples drawn from throughout dewatering. Differences in concentration gradients for PAH versus volatile compounds in not known but may be related to less influence on solubility of lower molecular weight aromatic hydrocarbons from changes in composition of DWHT. While these results were for a single pipeline test from a used pipeline, few general conclusions were possible. However, should these patterns be observed in other discharges, several consequences for environmental impact and engineering solutions may exist, namely; a) single grab sample or composite sample may yield skewed characterization of environmental loading from release of DWHT; b) the fraction of the discharge which may pose greatest impact to environment with respect to PAH may constitute only a part of the total volume and waste treatments schemes should be designed to address this feature; and c) unabated release of waters in to unlined holding ponds or directly into aquatic environments will result in contamination similar to oil spills on off-shore oil platforms. However, these sites for pollution may occur in locations far removed from oil production and refinery activities.

Table 7. Amounts of PAH and alkylated-PAH in samples of discharge water from hydrostatic testing of natural gas pipeline and in natural gas supplied to laboratory.

| | | CONCENTRATION (ug/L) ** | | | NATURAL |
COMPOUND	MAXIMUM NO. OF ISOMERS DETECTED	A1	A2	A4	GAS** (ug/m^3)
Naphthalene	1	86	57	150	11
C1-Naphthalene	2	990	99	1,900	147
C2-Naphthalene	5	2,200	1,300	2,200	79
C3-Naphthalene	7	4,000	190	610	44
C4-Naphthalene	∙ 11	5,000	150	170	17
Biphenyl	1	120	78	540	12
C1-Biphenyl	3	250	78	520	4
C2-Biphenyl	7	1,100	59	160	20
C3-Biphenyl	5	2,400	66	130	9.5
C4-Biphenyl	4	2,000	78	790	5.3
Fluorene	1	160	7	33	2.1
C1-Fluorene	2	1,100	18	17	1.7
C2-Fluorene	4	2,900	46	36	2.5
C3-Fluorene	5	3,000	64	40	3.8
C4-Fluorene	8	2,200	71	30	3.8
Anthracene	3	320	40	52	2.6
C1-Anthracene	2	740	68	48	4.2
C2-Anthracene	4	860	120	72	5.5
C3-Anthracene	7	90	21	46	3.6
C4-Anthracene	10	750	78	20	1.1
Pyrene	3	860	46	22	2.3
C1-Pyrene	5	400	24	15	0.6
C2-Pyrene	5	280	26	16	0.6
C3-Pyrene	6	300	26	15	0.7
C4-Pyrene	3	250	24	17	0.8
TOTAL	114	32,356	2,834	7,649	384.7

** Data only satisfactory to two (2) significant figures.

* These numbers may vary slightly based upon resolution and assignment of identity.

(1) Quantified versus nephthalene. All others quantified versus same compounds.

A. CHEMICAL OXYGEN DEMAND(COD)

B. NAPHTHALENE AND NAPHTHALENES (CI-4)

C. FLUORENE AND FLUORENES (CI-4)

D. BIPHENYL AND BIPHENYLS (CI-4)

E. ANTHRACENE AND ANTHRACENES (CI-4)

F. PYRENE AND PYRENES (CI-4)

CONCENTRATION (UG/L) *10⁻³

COD (MG/L) *10⁻³

PERCENT OF DISCHARGE
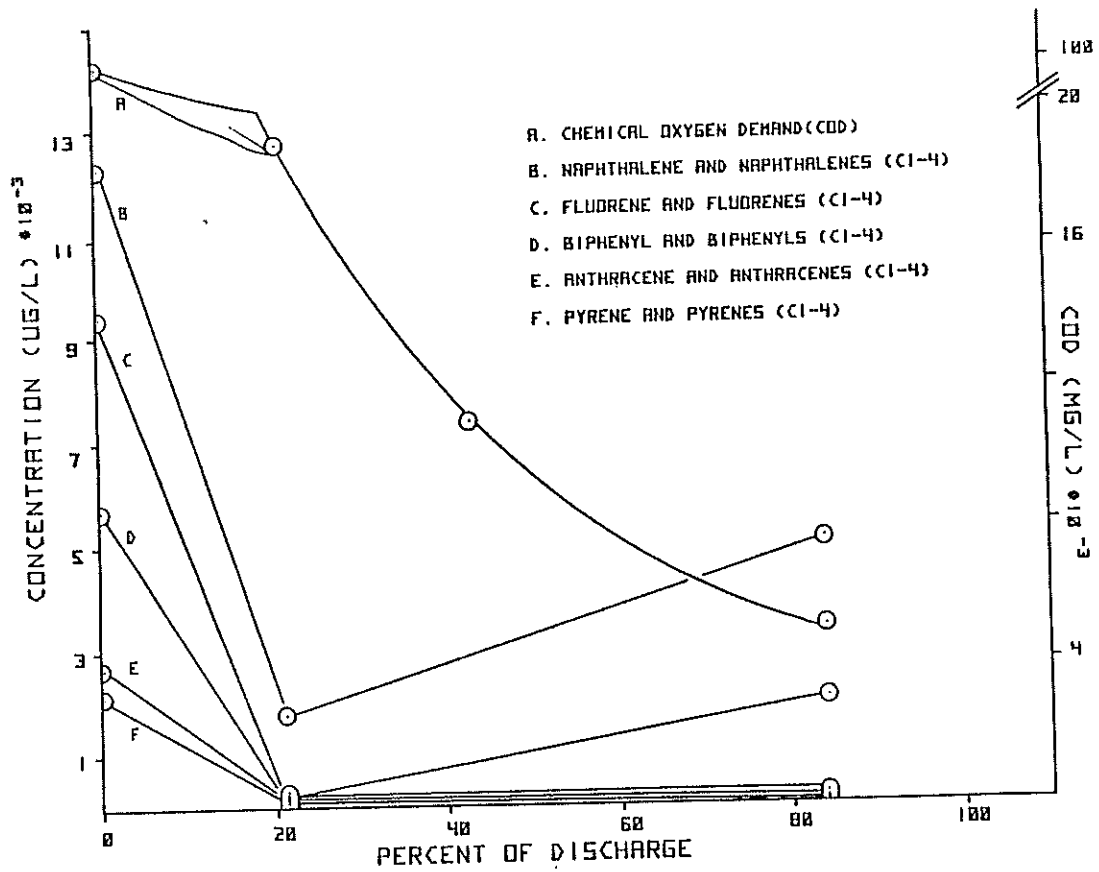
<u>Figure 14</u>. Plots of concentrations of groups of PAH and COD versus volume

present of discharge.

CHARACTERIZATION OF LIQUID WASTES FROM DISPOSAL PITS

Volatile Constituent of Waste Pits

Although contents of waste pits had been exposed to ambient atmosphere at temperature as great as 32°C for unknown duration, a discernible odor was detected in aqueous and non-aqueous phases as present in each sample. Results from GC/MS characterization of volatile organic compounds in the aqueous phase are given in Table 8 and in Figure 15. In Figure 15, a total ion chromatogram (TIC) is shown from GC/MS analyses of the aqueous portion of the Cuba sample for volatile organic compounds. At least 40 resolved or partially resolved components were seen in the TIC and were representative of results found with other water samples. The identities of major components in this and other samples are listed in Table 8 along with abundance values as a rough measure of relative concentrations. In the water phase, the range of estimated total concentrations of volatile compounds was 34 to 500 mg/L. These results were only estimated concentrations since matrices were too complex for accurate external standardization and a broad range of deuterated alkylated benzenes was not available for internal standardization. Moreover, large amounts of volatile organic compounds to the atmosphere was initially believed to result in trace concentrations of these compounds in all waste pit liquids, particularly aqueous phases. Two major classes of compounds were detected in these samples and were alkanes/alkenes and benzene/alkylated benzenes. Such compounds were also major constituents in a sample of produced water from the Gulf of Mexico. Furthermore, the same compounds have been identified in other wastes generated downstream in natural gas production and in samples of natural gas in consumer distribution lines.
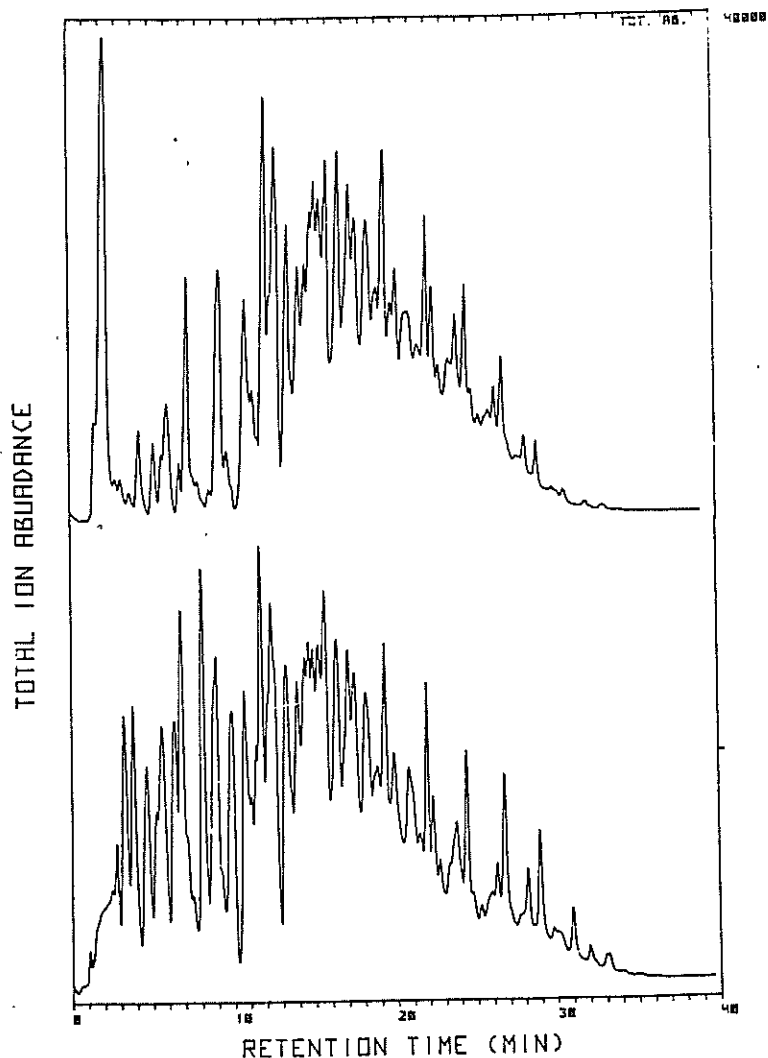
Figure 15. Total ion chromatogram from GC/MS analysis of a) aqueous wastes from Cuba sample and b) non-aqueous wastes for some sample for volatile organic compounds.

Composition of the aqueous fraction of liquid wastes in disposal pits was clearly a complex mixture even for the volatile organic compounds alone. Additional evidence for the large complexity is shown in Figure 16 as mass chromatograms from the same scanning GC/MS analysis shown in Figure 15. Mass chromatograms are shown for benzene, toluene, and alkylated C2 to C8 benzenes. More than 20 compounds from this class were resolved, as shown in Figure 16, (aqueous phase) and retention times were consistent with mass spectral results

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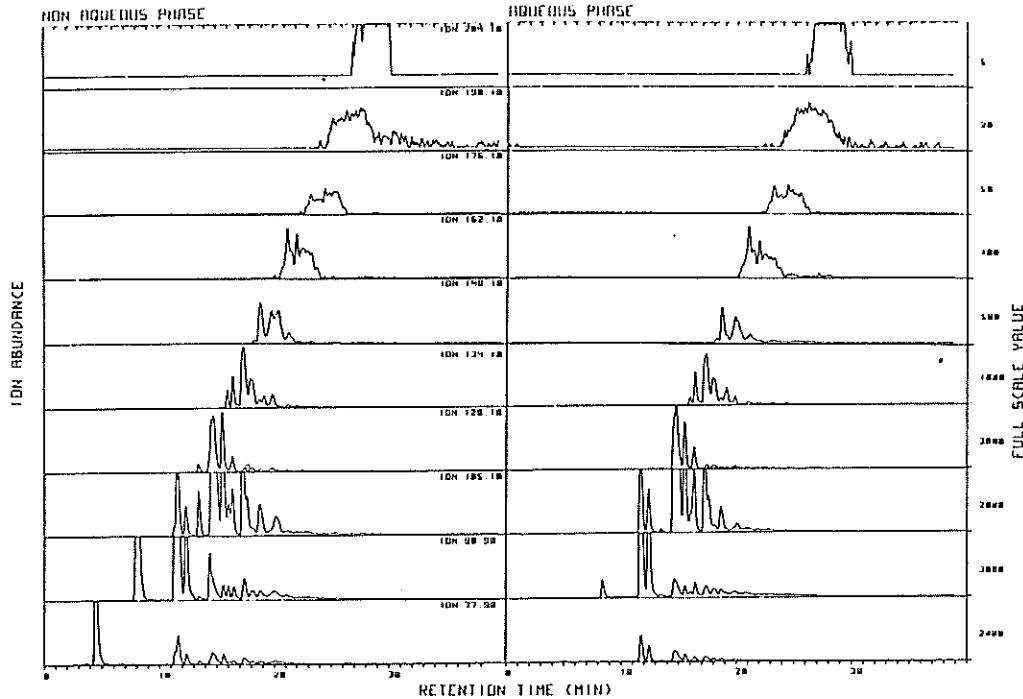
Figure 16. Mass chromatograms for benzene and alkylated benzene from scanning GC/MS analyses non-aqueous (A) and aqueous (B) phase from Cuba sample.

in Table 8. In Table 8, apparent differences in composition amongst samples were sometimes actual differences and not every component was detected in every sample. In contrast, some compounds were present in all samples but not detected due to differences in concentrations of compounds. If concentrations were below a certain threshold, those compounds, even though present, were not recorded or recognized with the data system of the GC/MS. Nevertheless, since in-field history of samples was unknown, generally few conclusions on fresh produced water composition could be made from these results. Also, particularly striking was the composition of the volatile fraction in the non-aqueous wastes in contract with the wastewater as described in Figure 16. Similarities between the aqueous and non-aqueous phases were strong and patterns were nearly identical in range of molecular weights of compounds and relative composition. However, major differences in relative composition may

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Table 8. Summary of volatile organic compounds in aqueous phase of waste pits.

Retention Index	Compounds	Cuba	Archuleta	Bloomfield	Flora Vista IE(A)
			ABSOLUTE MS ABUNDANCE		
693	C_4H_i (alKene)	1431	ND	–	ND
715	C_6H12 (alkene)	1190	–	1762	–
727	C_7H_{16} branched alkane	681	–	–	–
729	Benzene	–	3117	–	–
733	C_7H_{14} isomer	1159	–	1679	–
756	C_7H_{16} branched alkane	1249	–	2243	–
766	C_7H_{14} isomer	3945	–	3920	–
805	Toluene	730	3729	–	–
822	C_8H_{16} alkene	3984	–	–	–
820	C_8H_{16} alkene isomer	5589	–	6767	–
844	C_8H_{18} branched alkane	2843	–	–	–
849	Alkene (U)	–	287	–	–
851	C_8H_{18} branched alkane	–	–	5618	–
868	C_8H_{16} alkene	3599	351	–	–
873	C_8H_{16} alkene	–	–	3721	–
895	Xylene	13911	2848	26834	–
900	$n\text{-}C_9H_{20}$	2040	–	–	–
905	Branched alkane/alkene	–	–	–	3789
912	Xylene isomer	6025	758	14604	–
917	C_9H_{18} alkene	–	–	–	9488
932	Branched alkane C_9H_{22}	6114	806	7616	–
946	C_9H_{18} isomer	2073	1672	1735	–
954	$C_{10}H_{22}$ isomer	1226	–	–	–
959	$C_{10}H_{20}$ alkene	1436	–	–	1837
971	C_3-benzene	5995	425	6989	–
976	$C_{10}H_{20}$ alkene	–	–	–	1315
993	C_3 benzene isomer	6283	395	8713	–
998	$C_{10}H_{20}$ alkene isomer	–	–	–	3630
1000	$n\text{-}C_{10}H_{22}$	7506	743	1345	–

Table 8. continued

Retention Index	Compounds	Cuba	Archuleta	Bloomfield	Flora Vista IE(A)
			ABSOLUTE MS	ABUNDANCE	
1030	$C_{10}H_{20}$ isomer	2313	–	1615	–
1040	C_4-benzene	1955	–	1067	–
1067	Mixture C_4-benzene with unidentified alkane	2909	458	–	–
1070	C_4-benzene	–	–	1513	–
1089	C_5-benzene	952	–	393	–
1100	n-$C_{11}H_{22}$	7781	814	6063	–
1114	Branched alkane	544	–	428	–
1159	Nephthalene	2169	–	789	–
1200	n-$C_{12}H_{26}$	7555	–	2252	–
1231	$C_{12}H_{24}$ alkene	887	–	–	–
1300	n-$C_{13}H_{28}$	7528	1124	1376	–
1337	$C_{13}H_{26}$	5439	–	–	–
1353	Saturated alkane	5033	–	–	–
1373	Branched alkene	–	–	541	–

*Abundance for external benzene standard – 39460. Abundance Units for 14 mg/L.

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be seen in Figure 15 at retention times of 3.0, 6.0, 7.8, and 9.8 min. These compounds were present at large relative concentrations in the non-aqueous phase but at very low concentrations in the aqueous phase. Thus, description of contents of waste pits in terms of aqueous phase alone will be incomplete and inaccurate, particularly since the non-aqueous phase may have comprised as much as 50% or more by volume of contents in pits based on observations of this sampling procedure. Amounts of evaporation of water from pits has been determined as low ·(5 percent), even in the arid Southwest and most loss of water was due to seepage, perhaps into local groundwater.

Extractable Composition of Waste Liquids in Pits

In addition to volatile organic compounds, waste pit samples were analyzed for less volatile extractable organic compounds with carbon numbers 10 to 35. Results from simple direct GC analysis of samples with little or no pretreatment apart from liquid-liquid extract of the aqueous phase and dilution of the non-aqueous phase are shown in Figures 17 and 18, respectively. Results are shown as bar plots of chromatographic data as concentration versus retention index. Concentration units were ng/L for the aqueous phase (Figure 17) and ug/g for the non-aqueous Phase (Figure 18), which In some samples had become solid upon storage in the laboratory at 22°C. Total concentration of organic compounds in samples, as determined from integration of GC total peak area with use of an average response factor, were the following: Bloomfield, 200 ug/L; Cuba, 11,000 ug/L; Flora Vista 1E, 10,400 ug/L; Archuleta, 11,700 ug/L; and Flora Vista 1E(A), 23,500 ug/L. Total organic compounds estimated from GC data for the non-aqueous phase were (in g/kg) Flora Vista 1E, 39; Archuleta, 15; Flora Vista 1E(A), 11; Flora Vista 1, 44, and Aztec, 402. Results for both phases for all samples were not reported here since both phases were not always found in all pits. In certain pits (Bloomfield, Cuba) only an aqueous phase was found while in other

45
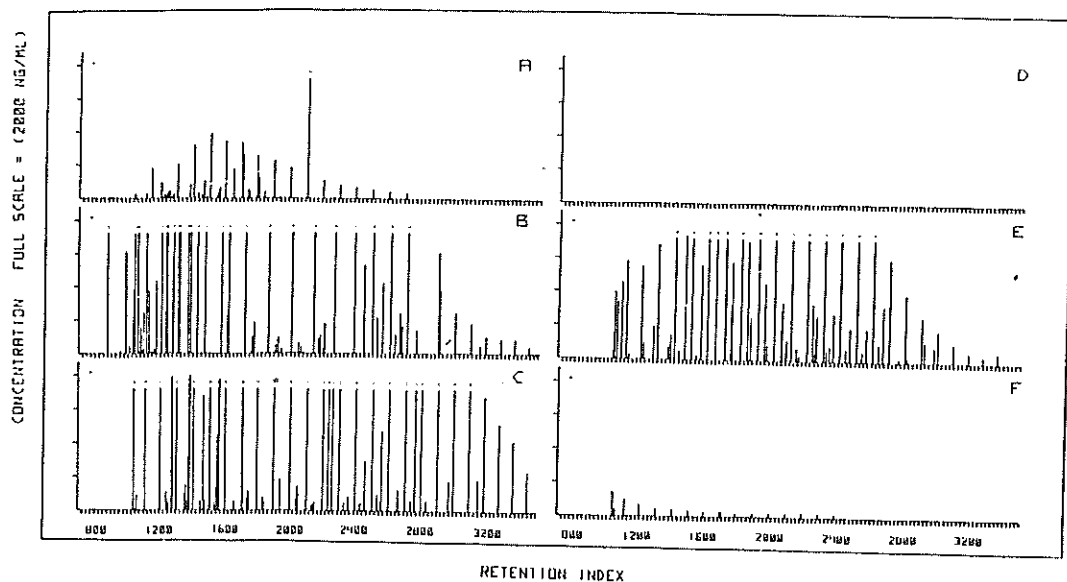
Figure 17. Bar plots from GC/FID analyses of aqueous phase from waste pits for extractable compounds. Samples were A) Cuba, B) Flora Vista 1E, C) Flora Vista, 1, D) Procedure Blank, E) Archuleta, and F) Bloomfield.

(Aztec, Flora Vista 1) only a non-aqueous phase was present and collected.

Although organic compounds were present in non-aqueous wastes at

concentrations greater than 1000x those for the aqueous phase, both patterns

of bar plots and range of molecular weights in general were very similar.

Such results were evident that when phases are present together, transfer of

compounds between two phases should be expected. Nearly all samples were

complex mixtures with 20 to 130+ components, as has been found in discharge

water from hydrostatic testing and in pipeline condensate with a carbon number

range between 10 to 30 with a maximum relative abundance seen at C_{14} to C_{18}.

46
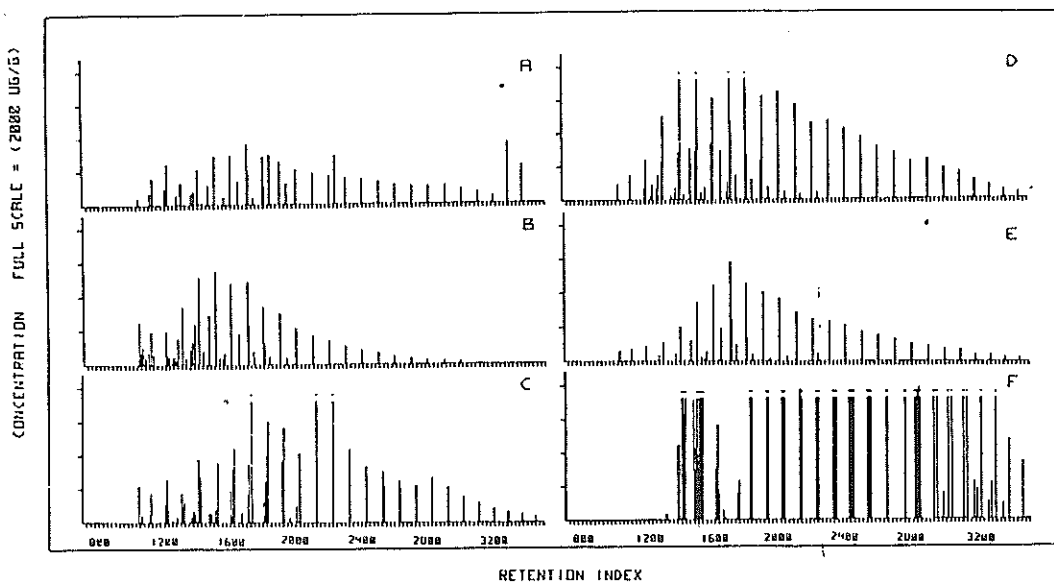
Figure 18. Bar plots from GC/FID analyses of non-aqueous phase from waste pits for extractable compounds. Samples were A) Cuba, B) Flora Vista 1E(A), C) FLora Vista, D) Flora Vista 1E, E) Archuleta, and F) Aztec.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons were found throughout natural gas consumer distribution lines and in natural gas supplied to consumers. This class of compounds was also found in discharge water from hydrostatic testing of natural gas pipeline. Therefore, the presence of PAH in waste disposal pits may reasonably be expected since natural gas was believed the source of PAH in these earlier studies. Results from SIM analyses of aqueous and non-aqueous wastes in disposal pits for PAH are shown in Figure 19 and Tables 8 and 9. In Figure 19, SIM plots are given for 12 molecular ions for PAH and alkylated PAH in both phases for a single waste pit. The presence of each PAH was measured against deuterated internal PAH for qualitative identification

and quantitative content. Patterns in composition of PAH in both phases, as shown in Figures 19 for the Cuba sample, were similar and consistent with the concept of equilibrium between phases. In those pits in which both phases exist and the aqueous phase is covered or protected from ambient atmosphere by the non-aqueous (hydrocarbon) phase, major changes in composition due to
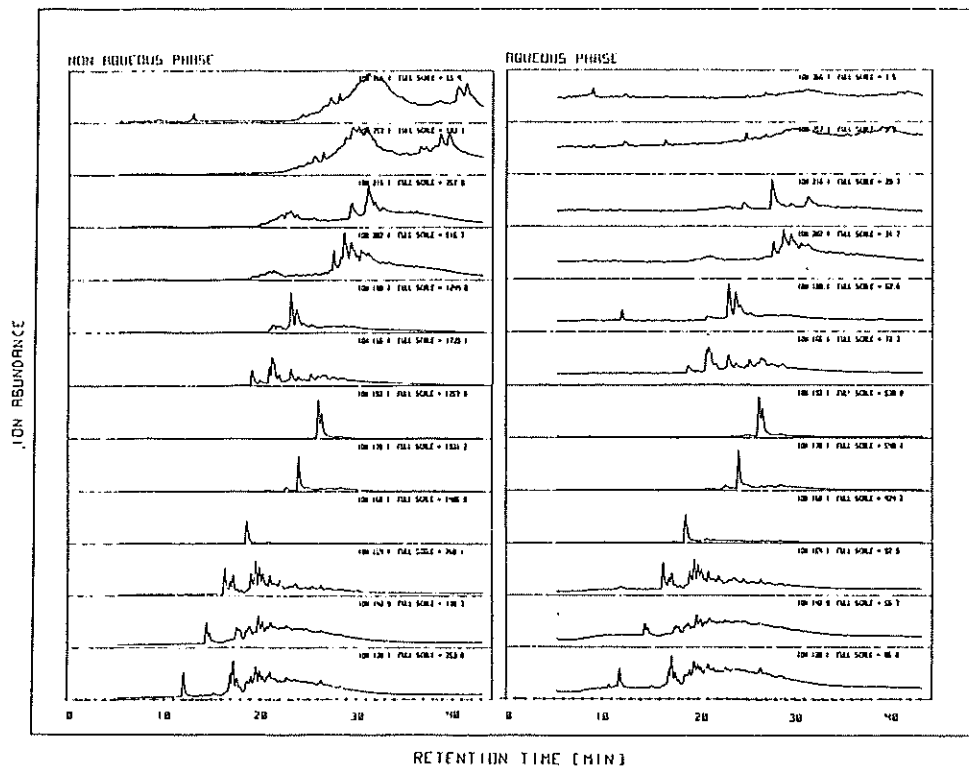
Figure 19. SIM plots from GC/MS analyses of non-aqueous (A) and (B) phases from waste pits from Cuba sample for polycyclic aromatic hydrocarbons.

Table 9. Concentrations of PAH in aqueous phase of waste pits from natural gas production.

	Cuba	Archuleta	Flora Vista 1E	Bloomfield	Flora Vista 1E(A)
			Concentration(ug/L)		
Naphthalene	850	480	ND	ND	500
C_1-Naphthalene	770	390	"	"	1,900
C_2-Naphthalene	1,300	2,500	"	"	4,200
C_3-Naphthalene	1,400	2,400	"	"	3,600
Biphenyl	680	480	"	"	450
C_1-Biphenyl	850	720	"	"	1,400
C_2-Biphenyl	1,000	1,700	"	"	1,400
C_3-Biphenyl	1,100	920	"	"	960
Anthracene	200	430	3.5	130	530
C_1-Anthracene	290	560	5.2	ND	1,900
C_2-Anthracene	260	380	ND	"	2,200
C_3-Anthracene	180	170	"	"	1,700
Fluorene	82	140	ND	ND	320
C_1-Fluorene	180	360	"	"	650
C_2-Fluorene	140	390	"	"	870
C_3-Fluorene	78	430	"	"	650
Pyrene	13	200	300	ND	410
C_1-Pyrene	65	130	1,400	"	260
C_2-Pyrene	46	100	ND	"	280
C_3-Pyrene	33	160	"	"	280
Benzopyrene	ND	ND	ND	ND	ND
C_1-Benzopyrene	"	"	"	"	"
C_2-Benzopyrene	"	"	"	"	"
C_3-Benzopyrene	"	"	"	"	"
TOTAL	9,517	14,740	1,709	130	24,460

ND - Not Detected

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Table 10. Concentrations of PAH in non-aqueous phase of waste pits from natural gas production. .Concentration (mg/kg).

	Cuba	Archuleta	Flora Vista 1E	Flora Vista 1E(A)	Flora Vista	Aztec
Naphthalene	160	23	240	80	375	ND
C_1-Naphthalene	110	22	290	410	250	"
C_2-Naphthalene	1,500	190	4,700	1,000	2,600	1,100
C_3-Naphthalne	1,600	170	3,400	590	1,200	360
Biphenyl	54	23	390	72	230	ND
C_1-Biphenyl	230	86	1,200	250	450	33
C_2-Biphenyl	420	120	1,100	280	300	160
C_3-Biphenyl	320	85	650	270	45	130
Anthracene	130	52	220	17	150	26
C_1-Anthracene	240	66	400	120	280	33
C_2-Anthracene	140	34	290	130	200	15
C_3-Anthracene	99	23	190	79	99	14
Fluorene	27	11	66	30	38	8
C_1-Fluorene	39	27	130	61	56	10
C_2-Fluorene	36	54	84	86	41	10
C_3-Fluorene	30	56	19	92	32	10
Pyrene	24	10	26	13	13	6
C_1-Pyrene	24	8.6	24	28	13	5
C_2-Pyrene	10	8.6	19	30	12	ND
C_3-Pyrene	9	11	11	33	11	ND
Benzopyrene	ND	ND	ND	ND	ND	ND
C_1-Benzopyrene	"	"	"	"	"	"
C_2-Benzopyrene	"	"	"	"	"	"
C_3-Benzopyrene	"	"	"	"	"	"
TOTAL	5,202	1,055	13,449	3,541	11,895	1,920

ND - Not detected.

evaporation or decomposition from weathering may not occur rapidly. However, this is speculation and further study is needed on weathering of disposal pits in hot dry climates as are found in the southwestern United States.

Environmental Conclusions

The concentration of PAH in either phase was sufficiently large for concern should these wastes reach ground water destined for human consumption. While movement of PAH in certain soils is relatively slow, additional study on PAH transport is necessary with sand-like soils in parts of New Mexico and perhaps elsewhere. Results from these analyses show caution is necessary in extrapolating results from waste pits in a small geographical area insomuch that major differences were seen in composition of aqueous and non-aqueous phases in these samples. The origin for differences is presently unknown. However, considerable amounts of a large number of EPA regulated priority pollutents were found in these waste disposal pits and warrant further investigations on movement and fate of toxic and hazardous organic compounds that are generated from production of natural gas.

ORGANIC COMPOUNDS IN SOILS AND SEDIMENTS FROM UNLINED WASTE DISPOSAL PITS

Gas Chromatographic Analyses

A complex mixture of volatile organic compounds (VOC), large molecular weight alkanes and PAH were found in liquid wastes from disposal pits for natural gas production in the San Juan basin of New Mexico as described above. Concentrations for environmentally significant compounds in the aqueous phase were high at 10 to 50 mg/L for VOC and 25 mg/L for total PAH. In the non-aqueous phase concentrations were even greater at 1050 to 13,500 mg/kg for total PAH. Possibilities for these compounds to be adsorbed on bottom soil in pits and to remain in soil after water has percolated through soil were

unknown when contrasted to possible evaporation. This part of the study was initiated as a preliminary characterization of soils in dry wastes pits before extensive survey studies or a depth profile were attempted.

Condensed extracts for every pit sample with each successive extraction solvent were highly colored from intense yellow to dark brown. The viscosity of the extracts was from moderately viscous to semi-solid at 25°C. However, all extracts became completely fluid with warming to 35 to 40°C. Corresponding condensèd extracts for the soil blank were either colorless or had a slight yellow tint and were not viscous. Results from GC-FID analyses of hexane condensate are shown a chromatograms in Figure 20. While the soil blank shown in plot D was free of detectable levels of contamination, complex mixtures of 40 to 70 components were resolved or partially resolved in each pit soil sample, as shown in plots A to C. Chromatographic profiles were typical for petroleum-based samples with a shifting baseline characteristic of unresolved alkane/alkane isomers despite between 31,000 to 113,000 effective theoretical plates with these capillary columns. The range of carbon numbers was 11 to 13 and consistent with liquid contents from similar waste pits and with wastewater from hydrostatic testing of old natural gas pipelines. Although some quantitative differences existed in GC-FID results, neither pit history nor the wastes placed in the pits were well known. Therefore, no general quantitative conclusions were possible. Rather, similarities in range of molecular weights and relative abundances of components were striking even though samples were taken from wastes in different segments of natural gas production, namely, the well head (B) and (C) and compressor station (A). The total concentration of extracted organic mass was determined as residue through evaporation of solvent. Values were (in mg per g of soil) as follows: compressor station pit #1, 100; production pit #1, 85; and production pit #2, 49. No detectable residue was found in soil blank.

While each solvent extract for every sample was colored, no peaks were detected in GC-FID analyses of benzene or methanol extracts. However, in UV scans between 400 to 200 nm, presence of aromatic hydrocarbons was evident in absorbance profiles, as shown in Figure 21, with maximum absorbence at wavelengths between 230 to 250 nm. Quantitative comparison of samples and soil blank is shown for each extract with absorbance values at 254 nm in Table 11. These values, particularly in the benzene and methanol extract, are likely due to complex polar aromatic hydrocarbons which were not sufficiently volatile for GC analysis. While the initial hexane extraction was successful in removing 100 percent of GC suitable components, even after benzene extraction, some compounds presumably highly polar were not removed until extraction with a highly polar solvent, methanol. Composition or complexity of these benzene and methanol extracts were not explored further here but were certainly not naturally present in nearby soil as seen in absorbance values for the soil blank. Although the electron capture detector is normally considered selective for holagen-containing compounds, the detector also has moderate selectivity for oxygenated compounds and PAH (Zltakis 1981) in comparison to alkanes. A GC-ECD was used here for rapid scan for ECD-sensitive compounds, particularly possible presence for PAH. Results from GC-ECD analysis of hexane extracts of same samples are shown in Figure 22 and may be directly compared to results in Figure 22 and may be directly compared to results in Figure 20. No ECD-sensitive compounds were detected in analysis of benzene and methanol extracts. A few components, possibly phthalate ester contaminants, were detected at low concentration in the soil bank in plot D. However, the presence of complex mixtures of ECD-sensitive compounds in the waste pit extracts was preliminary rapid instrumental evidence for PAH in pit soil. The only conclusion possible from these results was that organic compounds other than alkanes were present in these samples. The

Table 11. Absorbance values at 254 nm for extracts of soil in waste pits.

	Absorbance* at 254 nm		
Sample**	Hexane	Benzene	Methanol
Compressor Station Pit #1	4260	246	729
Production Pit #1	4910	30	132
Production Pit #2	3240	45	199
Soil Blank	3	0.1	12

* All values for absorbance were measured between 0 to 3 for dilute solutions of sample. Corrections for concentration were then made to the absorbance values for the original 10 mL condensate of soil extracts.

**Samples were extracted in series with hexane first then benzene and methanol.

possibility that these compounds were alkenes rather than aromatic compounds was unlikely since the shifting baseline in FID data eluted compared to results in Figure 20. No ECD-sensitive compounds were detected in analysis of benzene and methanol extracts. A few components, possibly phthalate ester contaminants, were detected at low concentration in the soil bank in plot D. However, the presence of complex mixtures of about 10 min before elution of the ECD-sensitive compounds. However, ECD may be further modified to improve selectivity toward PAH through more regulated O_2 doping and might be useful in future survey studies. The GC-ECD was tested with mg amounts of alkanes with no response to preclude possible artifact formation here.
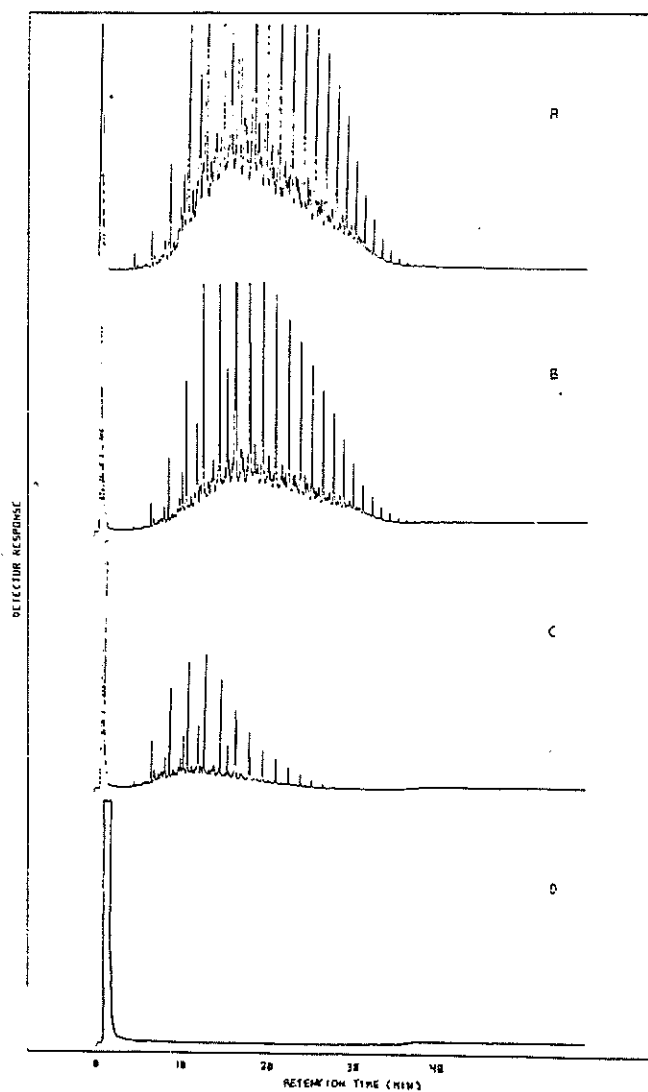
Figure 20. Chromatograms from GC-FID analysis of hexane extract from soil and sediment samples from waste pits A) Compressor Station pit #1, B) Production pit #1, C) Production pit #1, and D) Soil blank.
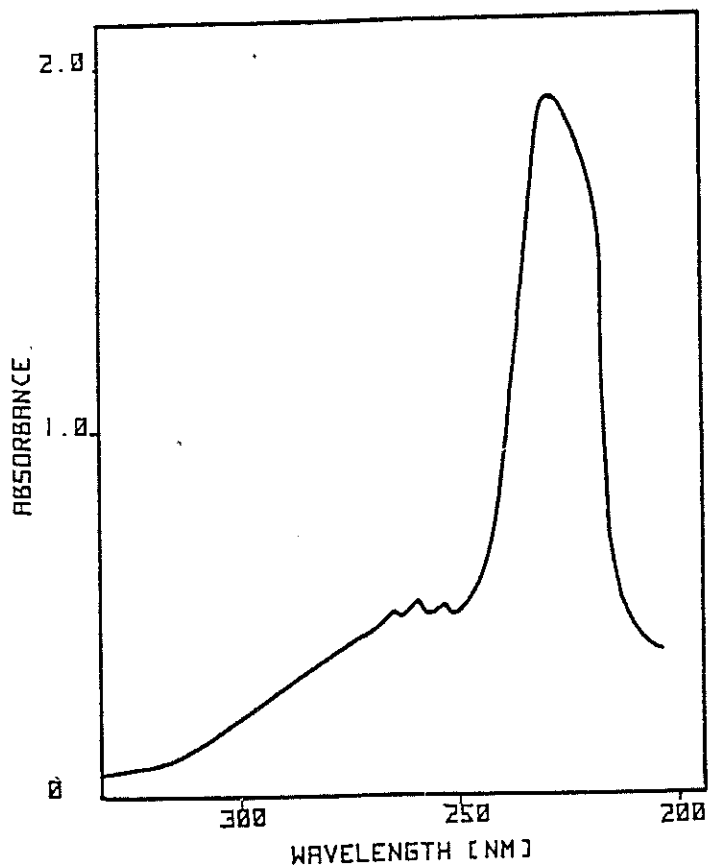
Figure 21. Ultraviolet spectrum of hexane extract from sample Production Pit #1. The scan range rate was 100 nm/min. Cell path was 1 cm and the dilution factor was 1:10,000.

Figure 22. Chromatograms from GC-ECD analysis of extracts of soil and sediment samples. (See Figure 20 for details).

Figure 23. SIM Plots from GC/MS analysis of hexane extracts of soil samples A) Production Pit #1 and B) Compressor Station Pit #1. Legend for ions is given in Table 11.
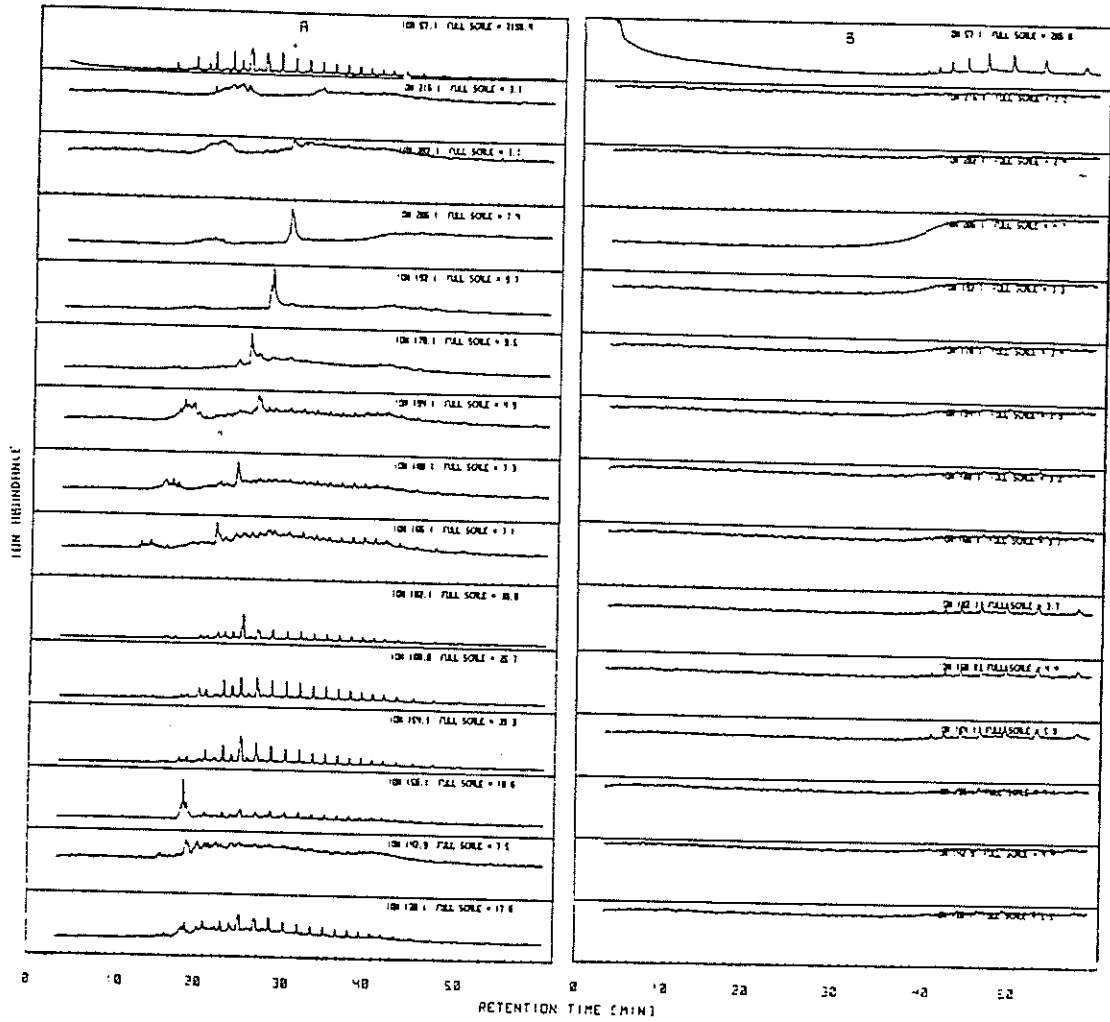
Figure 24. SIM Plots from GC/MS analysis of hexane extracts of soil samples A) Production Pit #2 and B) soil blank.

Gas Chromatography/Mass Spectrometry

Scanning GC/MS was used to aid in identification of components and SIM technique was used for improved selectivity with quantification of PAH in hexane extracts. All major components in chromatograms in Figure 20 were identified as n-hydrocarbons using mass spectra from scanning GC/MS analyses. Side peaks to major components were branched alkanes and large amounts of unsaturated alkanes were found in the background of the shifting baseline. Results from SIM analyses were remarkable since PAH were distinctly detected in the presence of the alkanes, as shown in SIM plots in Figures 23 and 24. In past studies on wastes from natural gas production, extensive prefractionation was necessary to isolate PAH from alkane background normally 1000 to 10,000 times greater in concentration than PAH. Even in SIM analyses, large molecular weight alkanes can be substantial interferences for PAH detection and quantification. However, in these samples, alkanes were interferences only in detection of naphthalene, alkylated napthalenes, biphenyl and alkylated biphenyl as shown in the lower six SIM plots. In other plots for PAH, better resolution was observed for higher molecular weight PAH and alkylated PAH which were consistent with the lower hydrocarbon background expected at higher mass range. The top plot was for ion 57.1 amu, which is the base peak in mass spectra from most n-alkanes. In SIM Plots in Figures 23 and 24, PAH from major families of aromatic compounds were detected and included fluorene, alkylated fluorences, anthracene, alkylated anthracenes, pyrene, and alkylated pyrenes. Assignment of identity was made using retention times for standards and selected ions. Soil blank was free of detectable amount of alkanes or PAH. External calibration without correction for recovery efficiency in extraction was used in preliminary measurement of PAH concentrations in soils as shown in Table 12. Concentrations were large in the range of 15 to 276 micrograms per gram of soil.

Table 12. Concentrations (ug/g) Of PAH in soils from waste pits.

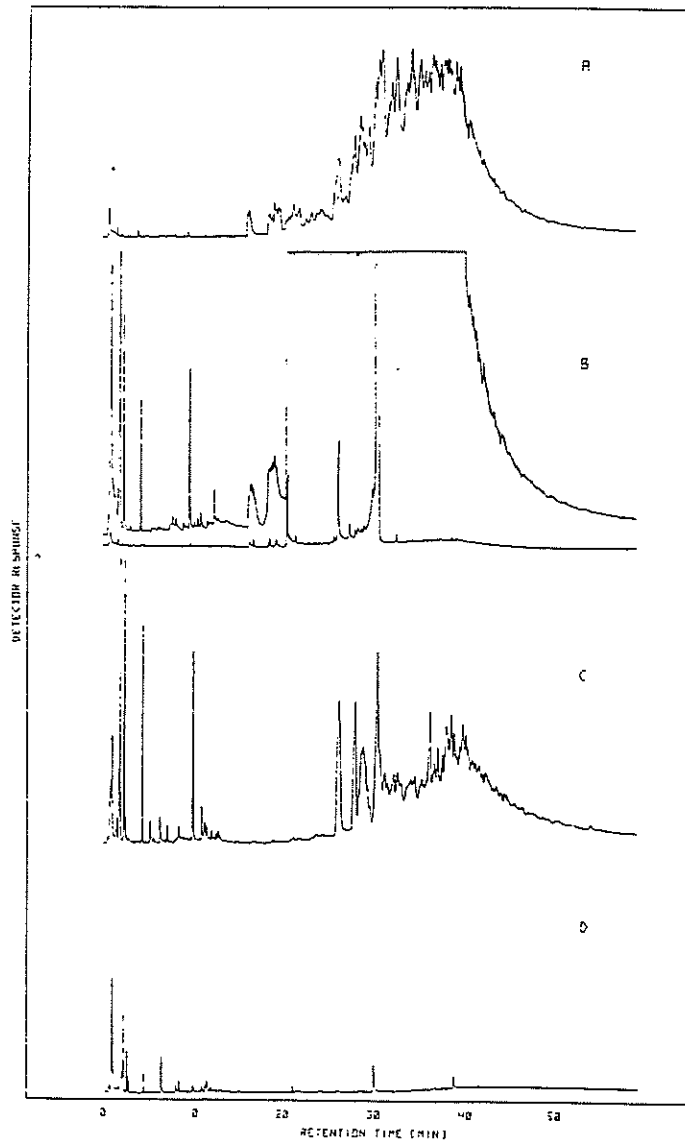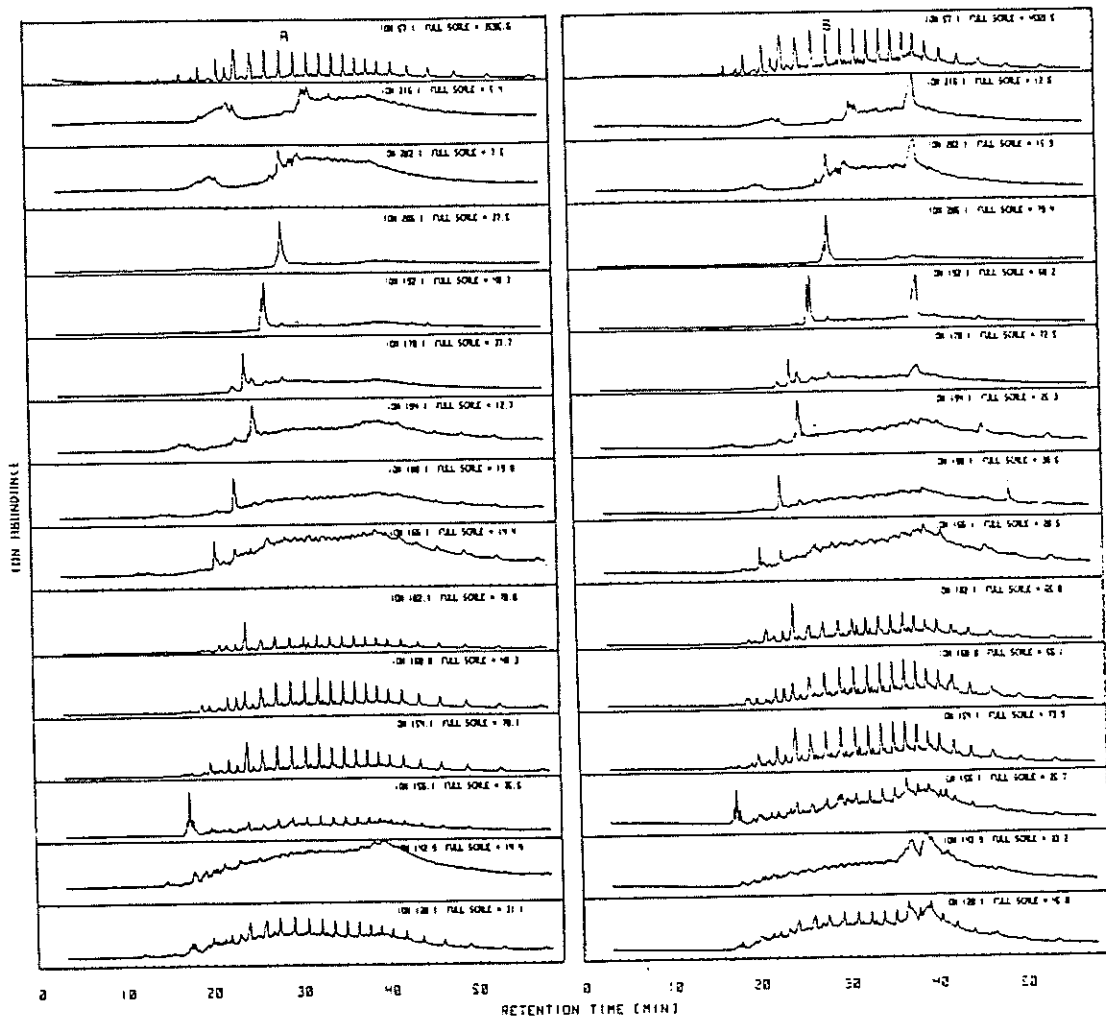| Compound	Compressor Station Pit #1	Production Pit #1	Production Pit #2
C_2-Naphthalenes	53	53	105
C_2-Biphenyls	66	42	91
Fluorene	33	18	42
C_1-Fluorenes	55	15	48
C_2-Fluorenes	52	17	47
Anthracene*	94	36	105
C_1-Anthracenes	205	49	276
C_2-Anthracenes	178	31	138
Pyrene**	25	5	20

*Including phenanthrene

**Including benzanthracene

Environmental Significance

Although this study was designed only for preliminary study of waste pits, certain specific conclusions can be made. Soils from waste pits in natural gas production contains hazardous organic compounds that that been found in wastes generated throughout natural gas production and processing. However, amounts of PAH were substantially lower than expected based on pit contents in nearby wells. Should evaporation of percolation lead to reduction in concentrations of PAH in soil (near the air-soil interface) removal will still not be complete and PAH residues may exist in unused or abandoned waste pits for an undetermined duration. Moreover, these results in combination with prior studies in liquid contents of waste pits portent possible serious ground water contamination from unlined earthen waste pits. More detailed studies on environmental transformations, migration of waste to groundwater, and rates of evaporation are supported by these results. Should results from Baker and Brendecke be found widespread and accurate in New Mexico as seen in parts of Utah, use of earthen waste pits for impoundment of wastes from natural gas may be an uncertain practice environmentally. In the next section, the results on depth profiles of organic compound including PAH in soils from the production, processing, and distribution of natural gas will address this problem in detail.

DEPTH PROFILES FOR HYDROCARBONS AND PAH IN SOIL BENEATH WASTE DISPOSAL PITS

Gas Chromatographic Analysis

Results from GC-FID analysis of soil extracts from the pipeline drip pit at four depths are shown as chromatograms in Figure 25. The depths 1 to 4 correspond to values given in the experimental section. A complex mixture of more than 60 major resolved components was found at each depth and the size of

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the components was between carbon numbers of 10 to 45. The regular spacing, peak shape, and comparison to retention times for the Kovats standard were consistent with the presence of alkanes as the major components as later confirmed in GC/MS analyses. In addition, the shape of the baseline was consistent with a large mass of unresolved hydrocarbons (alkenes/branched alkanes). In range of carbon numbers, as well as the complexity of the mixtures, these samples very much resembled condensate inside consumer distribution pipelines and the non-aqueous phase in a produced water pit. Since a pipeline drip pit is positioned (in terms of a diagram for gas flow) between the well-head and the consumer distribution lines, similarities in samples from each stage should not be surprising and actually might be expected. However, the depth profiles shown in Figure 25 were chromatograms may be compared directly were remarkable. At each depth, a similar chromatographic pattern was obtained across the range of carbon numbers even with the high molecular weight components near C_{45}. A slight attenuation of the total unresolved mass was seen between depth 1 and other depths, but no change was seen with this mass between depths 3 and 4, suggesting a leveling effect in the mechanism for attenuation. A dramatic increase in the abundance of components at carbon ranges from 10 t 20 at depth 4 was especially striking and may be due to either degradation of larger compounds through some unknown mechanism or lack of aeration and volatilization in more shallow zones. Nevertheless, while hydrocarbons, particularly large hydrocarbons, are often described as having strong adsoption to lipophilic organic matter in soil and should be relatively immobile, the zones of earth under this pit clearly have been saturated and little, if any, significant attenuation of mobility for these compounds is evident from these results. Similar results in terms of carbon range, baseline patterns, and depth profiles, were also seen with the produced water pit and the dehydrator pit.

Preliminary survey of these extracts, using GC/MS with SIM methods for PAH content, showed major interference from saturated alkanes, which precluded reliable quantification. A rapid column prefractionation scheme was used to isolate the PAH and results from GC-FID analysis of these isolated fractions for the drip pit samples are shown in Figure 26. Since all experimental and instrumental conditions were unchanged, chromatograms within Figure 26 may be compared directly and may be compared also to those hydrocarbon patterns were minor if present at all in these fractions. Despite this prefractionation, a large number of compounds was still detected at every depth. However, for the drip pit samples as shown in Figures 26, some attenuation was evident, particularly at the bottom Depths 3 and 4, based on GC-FID results. A more specific means for quantification of individual PAH compounds is through use of SIM with GC/MS. Although the pits chosen and the pipeline were related only by a common gas field origin and were not connected, results for the produced water pit and for the dehydrator pit were similar, but not identical, to those for the drip pit. As shown in Figure 27, the PAH fraction for these other pits showed similar complexity to the drip pit samples. Also as expected, the concentration of components in the dehydrator waste pit was less then in the produced water pit which preceded the dehydrator in gas flow. The procedure blank was clean for both total extractable hydrocarbon as well as for analyses of PAH fractions.
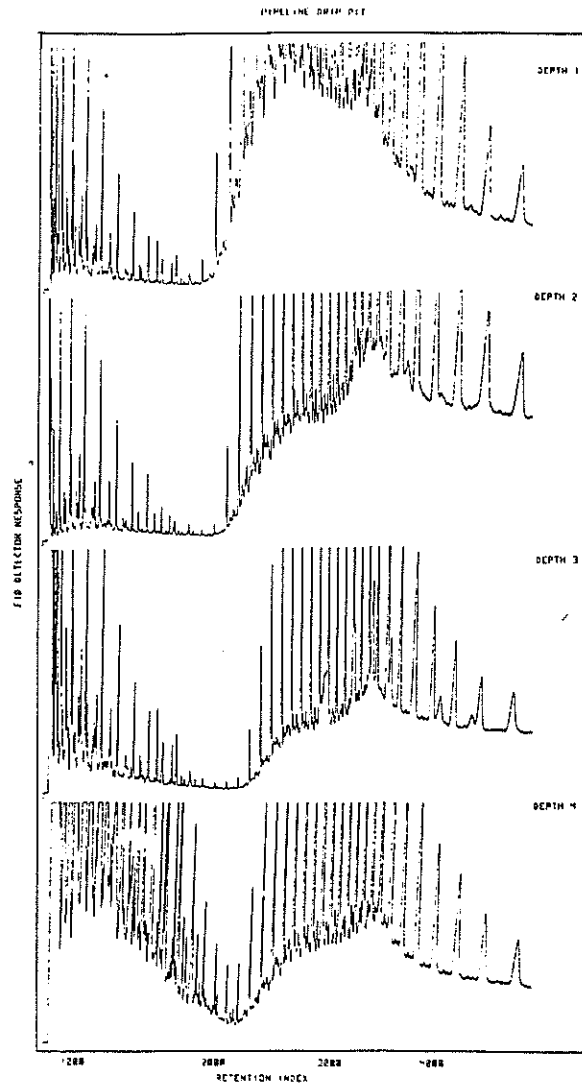
64

Figure 25. Chromatograms from GC–FID analysis of hexane extracts for soil samples from a natural gas pipeline drip pitr. Depths were 3) 60 to 90 cm, and 4) 90 to 120 cm.
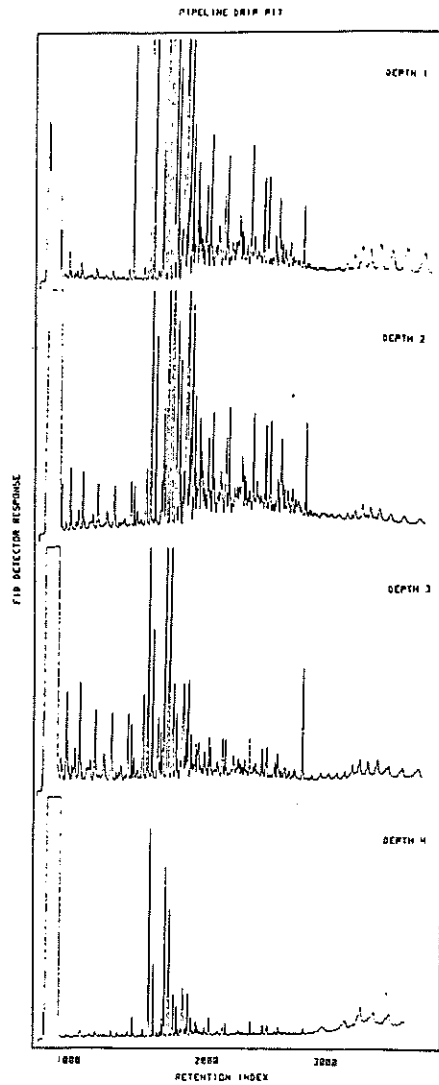
Figure 26. Chromatograms from GC-FID analysis of PAH fraction from same samples shown in Figure 25.

Selected Ion Monitoring for PAH

Results from GC/MS analysis using SIM techniques for PAH fractions of soil extracts are shown in Figure 28 and Figure 29 and Table 13. In Figures 28 and 29, SIM plots for all depths from the pipeline drip pit are shown for 14 PAH and alkylated PAH. While the lowest plot is for the base peak in alkanes, m/z 57.1 amu. For most ions chosen, the major peaks in SIM plots correspond to the correct retention time for the appropriate PAH. Exceptions were for naphthalene, where two components at 18 minute retention were major peaks, for biphenyl, where a set of barely resolved components with retention times near 20 minutes were present at relatively high concentration. The interferences for naphthalene were fragments from the dimethylnaphthalene (m/z = 156.1), which also seemed to interfere in the bipheny plot (m/z = 154.1 amu). However, these interferences could be distinguished from the PAH peak of importence. Otherwise, the SIM plots for all samples were regular with no complications for quantification. The presence of PAH in the soils is also consistent with prior studies where PAH have been found in natural gas and pipeline condensate produced water, and surface soils near waste pits.

Environment Impact

Concentration values are listed in Table 13 for PAH in soils from every pit at each depth and the results are displayed in Figure 30. The concentrations were determined using external standards carried through the prefractionation steps. However, values reported here have not been corrected for extraction efficiency, which was considered exhaustive based on prior study. The total concentrations of PAH at various depths for pits were 557 to 683 mg/kg for pipeline drip pit, 45 to 399 mg/kg for the produced water pit, and 30 to 54 mg/kg for the dehydrator pit. In general, total concentrations
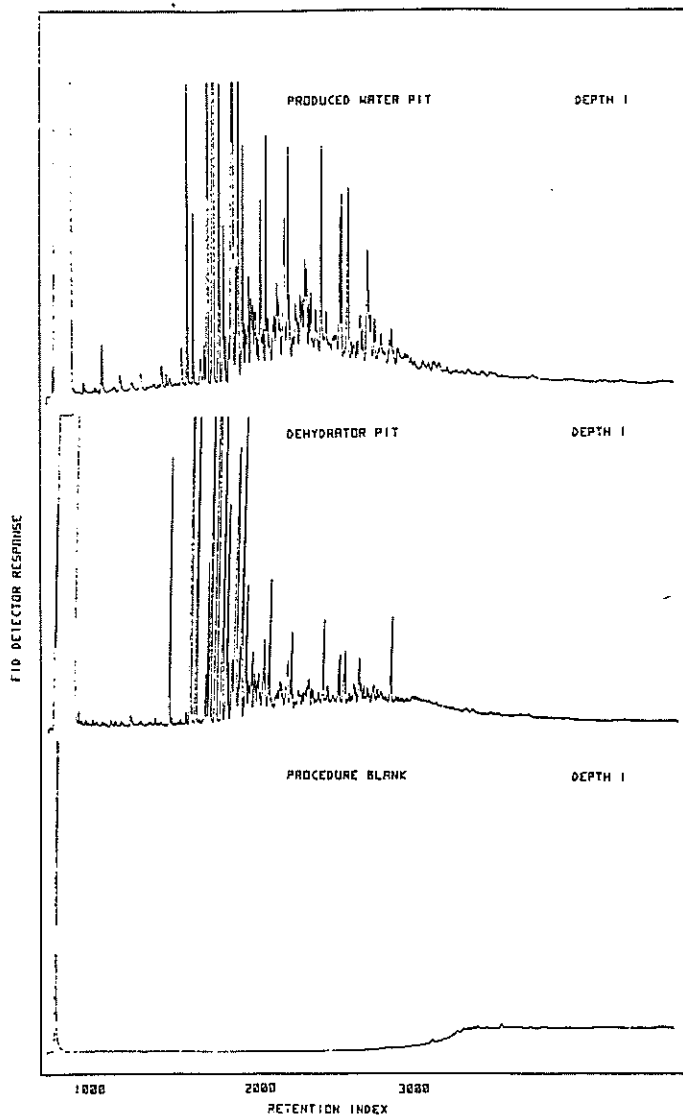
Figure 27. Chromatogram from GC-FID analysis of PAH fraction for soil samples from a produced water pit, dehydrator waste pit, and a procedure blank.
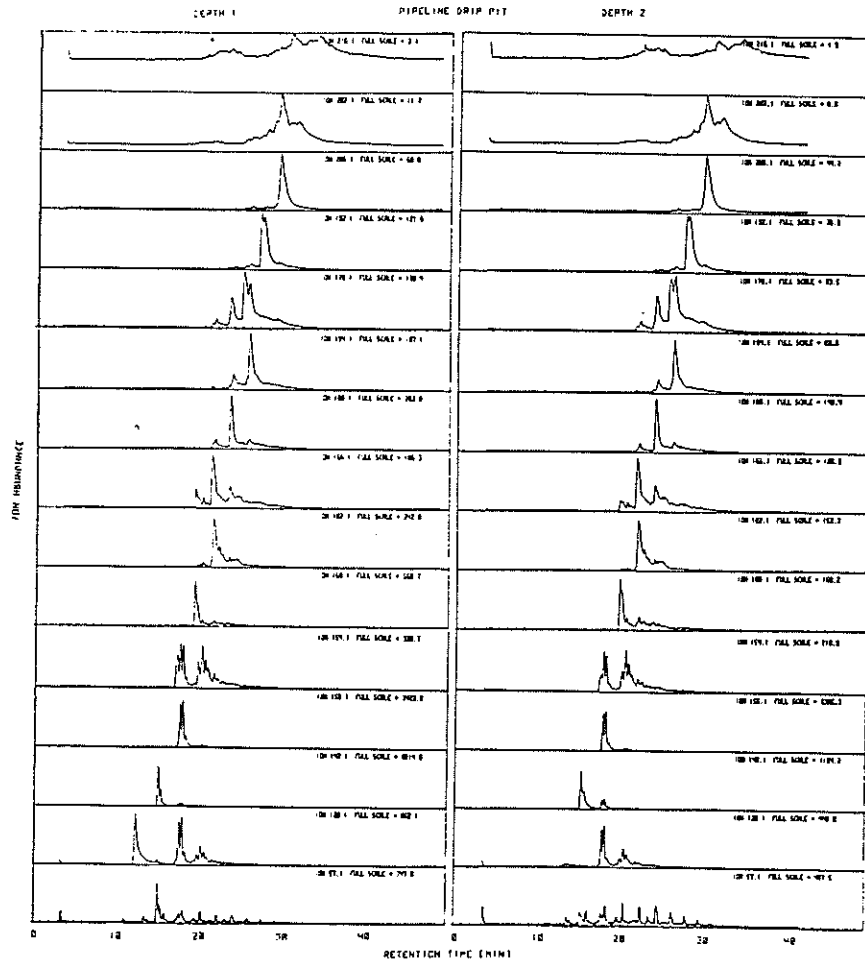
Figure 28. SIM plots for soil samples from pipeline drip pit.
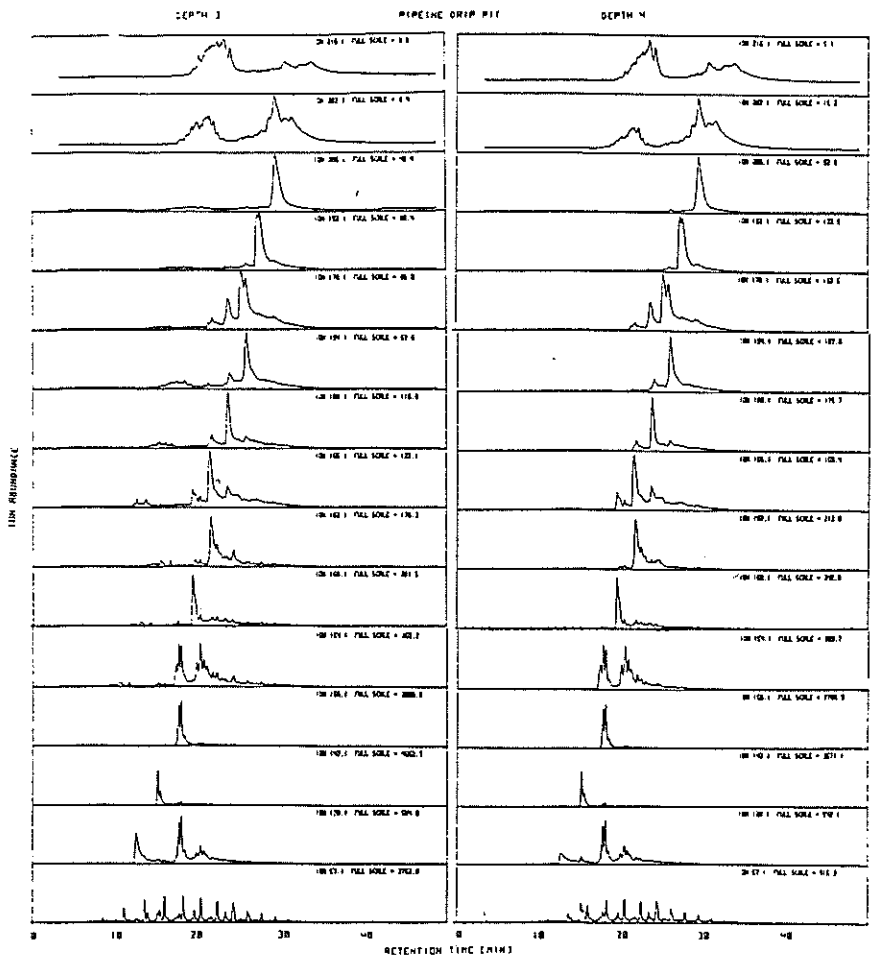
Figure 29. SIM plots for soil samples from pipeline drip pit.

Table 13. Concentration (ug/kg) of PAH in soils at different depth levels.

Pipeline Drip Pit

PAH[b] STM ION DEPTH	NA 128.1	C_1-NA 142.1	C_2-NA 156.1	BP 154.1	C_1-BP 168.1	C_2-BP 182.1	FL 166.1	C_1-FL 180.1	C_2-FL 194.1	AN 178.1	C_1-AN 192.1	C_2-AN 706.1	PY 202.1	C_1-PY 216.1	total mg/kg
1	31,000	320,000	320,000	1,600	3,900	2,500	760	800	600	600	580	420	210	210	683
2	ND	53,000	7,300	910	1,400	1,500	530	600	490	470	450	340	190	190	617
3	18,000	260,000	300,000	1,500	2,900	2,400	800	780	620	650	620	500	270	260	589
4	6,200	260,000	280,000	1,500	3,200	2,400	760	820	670	670	690	490	240	230	557

Produced Water Pit

	NA	C_1-NA	C_2-NA	BP	C_1-BP	C_2-BP	FL	C_1-FL	C_2-FL	AN	C_1-AN	C_2-AN	PY	C_1-PY	total
1	ND	68,000	270,000	1,200	1,700	2,600	1,400	1,300	690	600	640	340	190	190	349
2	ND	130,000	260,000	1,500	1,400	1,900	850	850	530	470	470	470	330	190	399
3	ND	3,400	24,000	330	290	890	420	510	470	650	450	340	190	190	132
4	ND	3,000	37,000	380	300	880	460	540	500	660	500	380	214	190	45

Dehydrator Pit

	NA	C_1-NA	C_2-NA	BP	C_1-BP	C_2-BP	FL	C_1-FL	C_2-FL	AN	C_1-AN	C_2-AN	PY	C_1-PY	total
1	ND	22,000	27,000	1,700	1,400	310	280	270	260	260	260	240	290	---	54
2	ND	24,000	4,500	2,400	1,800	200	340	330	330	310	310	310	190	---	35
3	ND	13,000	13,000	1,800	1,300	310	340	340	330	310	310	310	190	---	31
4	ND	13,000	11,000	1,800	1,800	280	380	360	360	340	340	340	210	---	30

[a]Data only satisfactory to two significant figures.
[b]NA = naphthalene, BP = biphenyl, FL = fluorene, AN = anthracene, PY = pyrene.

decreased slightly with increasing depth with the most dramatic reduction

occurring at the produced water pit. These reductions show that PAH are

either being degraded at lower depths or that an adsorptive mechanism is still

partly effective. This pattern seems especially pronounced for the small PAH,

such as naphthalenes and byphenyls, which actually dominate and skew the total

PAH values are shown in Figure 30. For example, the concentration in

methylnaphthalene in the produced water pit decreased by 20-fold from 68 mg/kg

at depth 1 to 3 mg/kg at depth 4. In the same pit, demethylnaphthalene

decreased from 270 mg/kg at depth 1 to 37 mg/kg at depth 4. However, these

patterns in decrease were not found with large PAH, and were not even

consistent in all the waste pits, despite presence of the same soil in a small

geographic region. In the pipeline drip pit, changes in concentration for

napththalenes and biphenyls were irregular at best. Trends are seen clearly

in Figure 30 where the fluorenes, anthracenes and pyrenes were Largely

unabated as a function of depth, while napthalenes and biphenyls were

dramatically reduced in some but hardly reduced in others (biphenyls in

dehydrator pit and pipeline drip pit).

Of the five major mechanisms or fates of hydrocarbons in soils, namely

volatilization from soil, adsorption, biodegradaton, migration due to partial

or complete saturation of soil, and photodecomposition, the predominant effect

in these studies was migration. Since ground water in flood plains in New

Mexico can be within 1 to 2 m from land surface and since this depth profile

extended from 2 to 3 m from the land surface, contamination of groundwater in

such regions is not only probable, but should be expected. Moreover, based on

recent results on phototoxicity of PAH with fish, (Bowling et al 1983) shrimp

(Morgan and Warshawsky 1977), and other organisms (Kagan et al 1984), presence

of PAH in soils at depths of 2 to 3 m and thus shallow ground water, portend

serious complications for a total quatic environment. These PAH, which gave

toxic responses only at extremely high concentrations of over 10 ppm, were

found to be lethal to fish, frogs, and insects at low ppb concentrations when

exposed to light. In this work, only mobility of PAH and largely hydrocarbons

through soils common to northwest New Mexico (but not the contamination of an

quifer) was verified. However, pipeline drip pits, which along with produced

water pits can pose threats to water quality, have not been included in a

recent state survey of impoundment pit (McQuillen 1984) and should be

accounted in future descriptions of industrial waste sites in New Mexico and

nationwide.

POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL AT GROUND WATER LEVEL

NEAR WASTE DISPOSAL PIT

General Observations at Study Site

The waste pit and area chosen for study were located in flood plains of

the San Juan River in northwest New Mexico between Shiprock and Farmington,

NM. The site was similar to at least 1,500 other nearby wells on the flood

plains in that the soil was largely a light-brown sand with a assortment of

rocks and stones which seemed to comprise a substantial fraction by volume of

the soil. The land surface in the flood plain was nearly flat over the region

studied with less than 0.3 m difference in elevation, as estimated from visual

inspection, and the vegetation was sparse. The waste pit contained nearly 60

cm of produced water with a thin film of hydrocarbon phase on the surface.

Dark stains on sides of the pit suggested greater holding volume of the pit in

the recent past. The pit was nearly 1.5 m deep and ground water was found at

1.8 m in the test pits dug near the waste pit. As each test pit was dug,

water filled in the pit to a certain level from one side of the pit, which

corresponded to a high pressure condition. At about 15 minutes after a pit

was dug, the inflow had stopped and water samples were collected; then, water

levels were measured in each pit. From earlier test pits, a hydrologic

gradient was estimated. Based on this gradient, direction of any plume from

the waste pit was predicted and test pits were dug at sites shown in Figure

31. During the digging of test pits 1-4, 8 and 9 (down-gradient), zones of

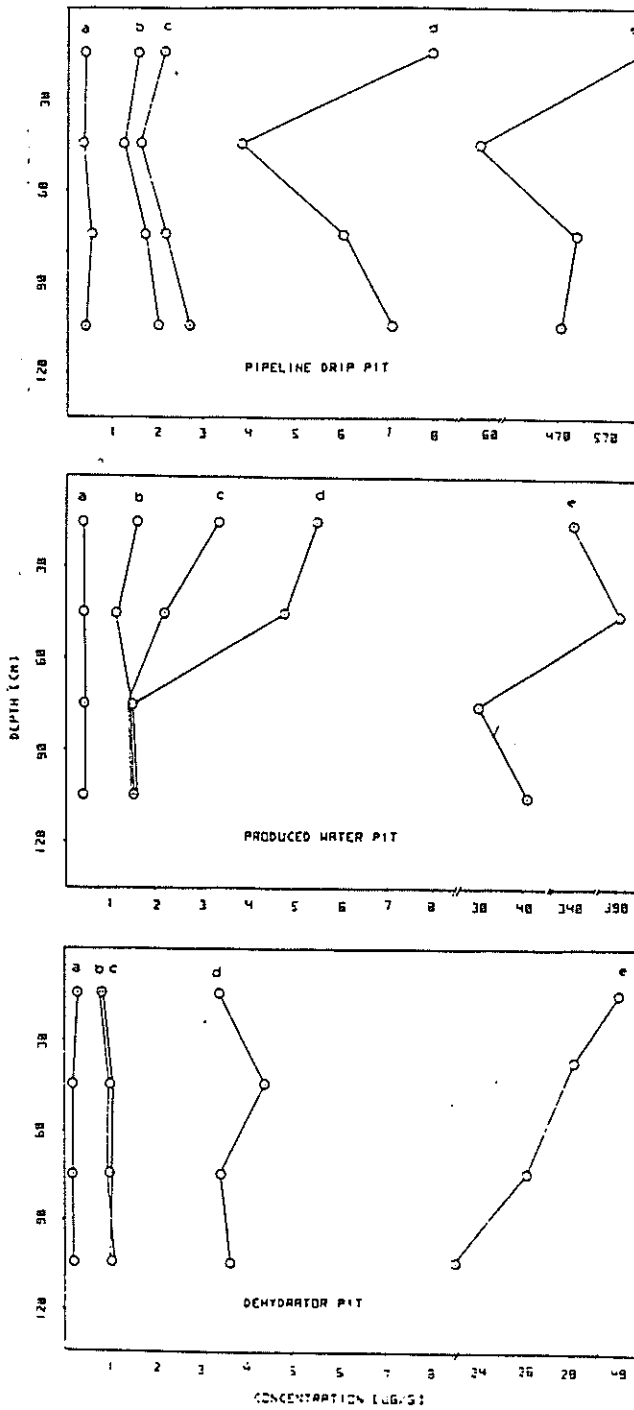black earth were found at about 1.7 m depth, and as the water filled in test

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Figure 30. Depth profiles for PAH in soil from three waste pits.

pit, a distinct hydrocarbon oder was discernible in the air and an oil-sheen film was observed on the ground water. In pits 5-7 (up-gradient), odor or sheen were not observed and the soil was a light brown blue throughout the depth of test pit. Clearly, even pending chemical analyses, the groundwater down-gradient from the test pit was different in composition than groundwater up-gradient, based on smell and properties of light reflection, and this difference strongly supported groundwater contamination by hydrocarbons from the waste pit.

Soil Composition

Results from GC/FID analysis of soil extracts are shown as chromatograms in Figure 32 for several test pits shown in Figure 31. For pits at 25 m down-gradient from the waste pit, complex mixtures of hydrocarbons at approximately 200 to 500 mg/kg total organic mass were detected for components with a range of 12 to 30 carbons. This carbon range was consistent with a possibility for two to four ring PAH samples. Moreover, the chromatographic pattern included a nonresolved shifting baseline characteristic of petroleum-based matrices and the center of mass for the envelope created by this unresolved mass was about C_{16} to C_{18}. Chromatograms for test pits 1, 3, and 8 were virtually identical apart from slight differences in absolute concentration. Extracted hydrocarbons were not detected using GC/FID in any of the pits up-gradient of the waste pit or detected at very low concentrations in test pits at 50 m down-gradient from the waste pit. Soil from test pit no. 4 was free of detectable hydrocarbons, as shown in Figure 31 (top plot).

Additional information on sample composition was acquired using GC/MS with SIM analysis. The SIM plots shown in Figure 33 were for the soil extract from test pit 1 and included ion traces for naphthalene (m/z=128), biphenyl (m/z=154), and C_1 and C_4 alkylated analogs to these PAH. While some SIM plots
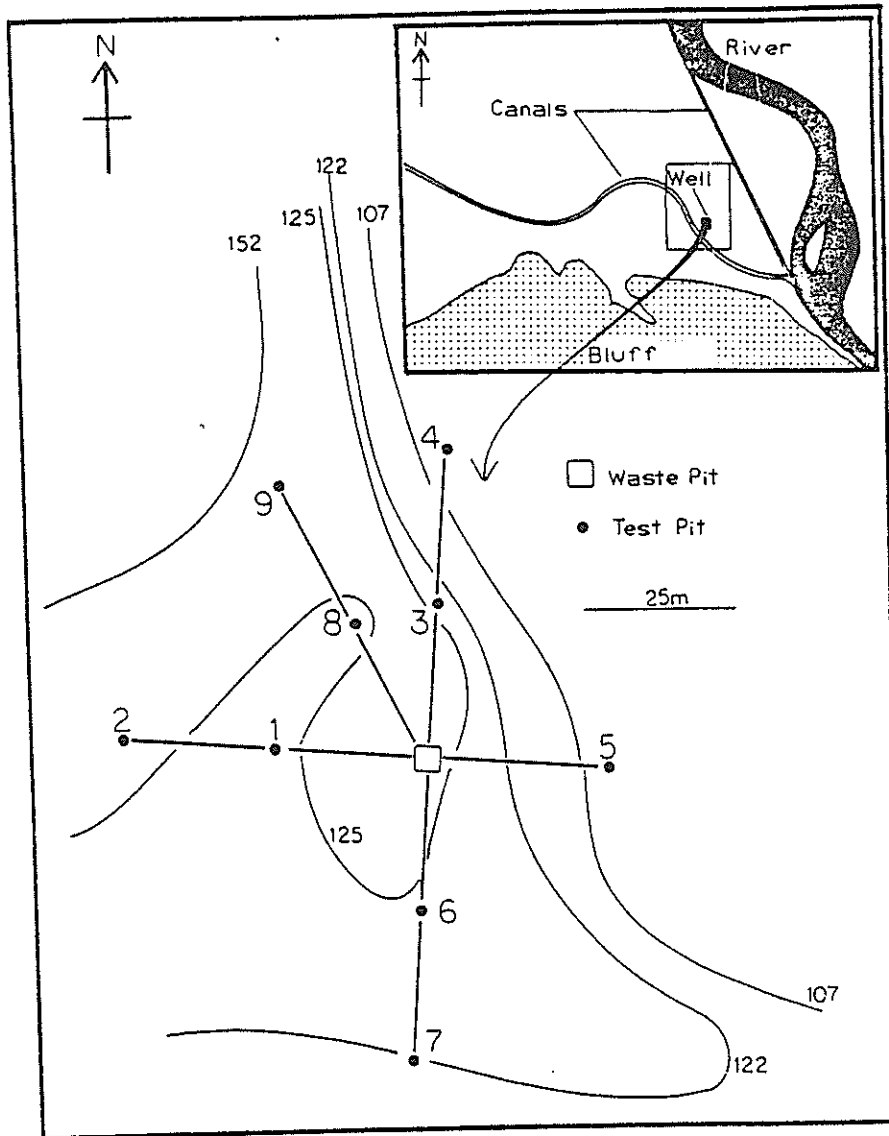
75

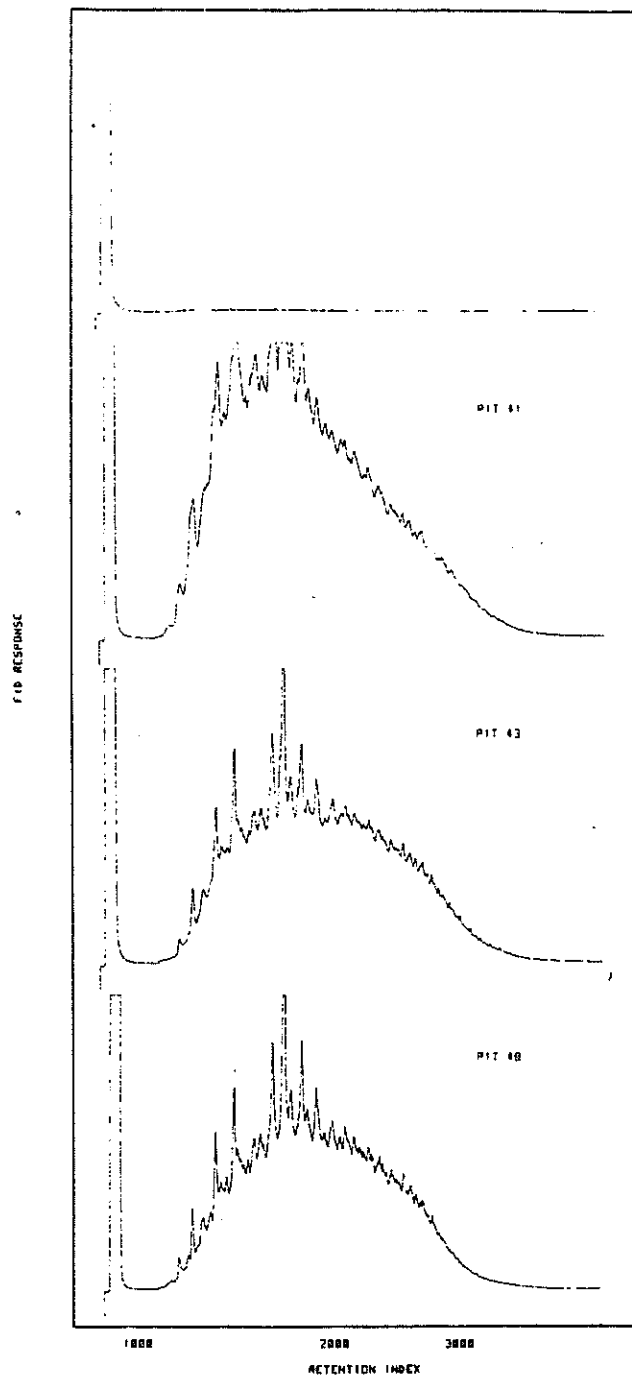**Figure 31.** Map of Test Site in Duncan Oil Field in NW New Mexico.

Figure 32. Detector response versus Kovats Retention Index from GC analysis of soil extracts.
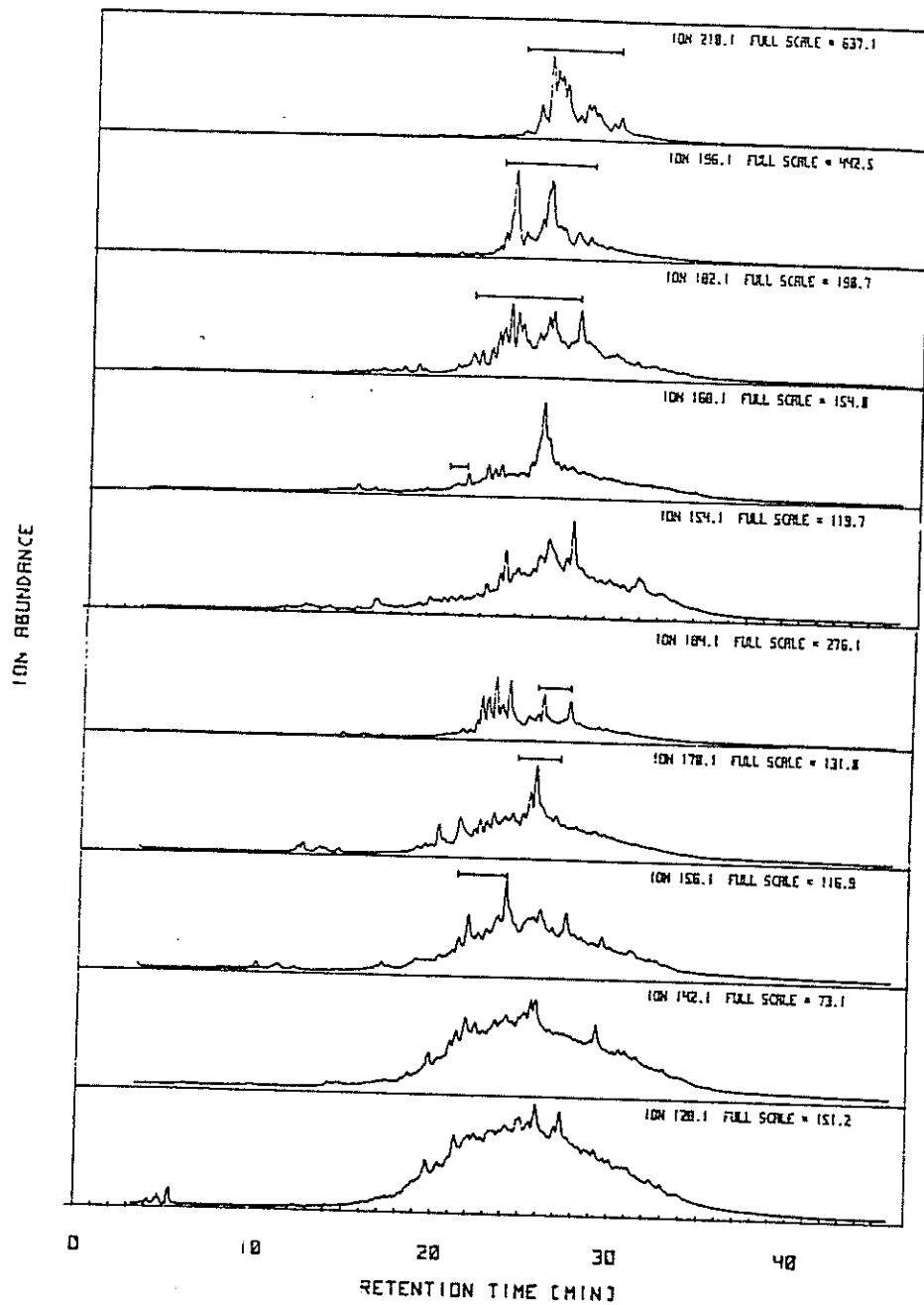
Figure 33. SIM plots for PAH and alkylated PAH.

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such as the C_3-substituted fluorenes showed major peaks within the correct range of retention times, other ion traces showed secondary (interfering) peaks in the same plot. Often this was due to fragmentation ions from higher alkylated PAH from the analogous PAH ring system. Nevertheless, PAH and alkylated PAH were present in the soil down-gradient from the waste pit and quantification for PAH is shown in Table 14. The greatest concentration for total PAH were in test pit 1,3, and 8 as expected since these pits were test pits closet to the waste pit and were down-gradient at a distance of 25 m. The individual concentrations ranged from not detected (ND) to as much as 1900 ppb for C_4-biphenyls in test pit 1. Total concentrations in these three pits were comparable from 2003 to 4860 ppb. However, not all possible PAH were detected using these SIM Table 14. Concentrations (ug/kg) of PAH in soils conditions and other PAH not selected for SIM analysis may be present. Therefore, reported concentrations may be low for a complete reduction for individual and total PAH between soil at 25 and at 50 m was dramatic and as great as 150-fold or larger.

The presence of detectable levels of PAH in soil from up-gradient pits was inconsistent with prior funding in which groundwater from the same pits was free of detectable amounts of hydrocarbons. Nevertheless, low levels of PAH were detected in extracts for test pits 5, 6, and 7. Apart from natural background concentrations for PAH, several mechanisms may be used to account for these findings, including backdiffusion against the hydraulic gradient and dispersion of wastes during flooding in the plain. Of these two, the more likely explanation is flooding, which occurs annually in the spring. For example, less than two months after these samples were collected, snow melt in watershed for the San Juan River caused severe and uncontrolled flooding with inundation of all earthen waste pits in the Duncan Oil Field. The contents of this and other waste pits were swept from the pits and dispersed in the flood

Table 14. Concentrations (ug/kg) of PAH in soils.

TEST PIT NUMBER

Compound	Mass (amu)	1	2	3	4	5	6	7	8	9
Naphthalene	128.1	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND
C_1-Naphthalenes	142.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
C_2-Naphthalenes	156.1	240	ND	ND	ND	ND	ND	ND	ND	ND
C_3-Naphthalenes	170.1	230	9.1	ND	9.8	ND	3.9	6.1	530	1.0
C_4-Naphthalenes	184.1	18	39	480	80	10	29	31	280	7.2
Biphenyl	154.1	8.4	ND	7.9	ND	2.8	ND	ND	13	ND
C_1-Biphenyls	168.1	32 ·	ND	58	15	ND	2.3	ND	18	0.18
C_2-Biphenyls	182.1	830	0.53	40	6.5	ND	5.9	3.1	680	0.62
C_3-Biphenyls	196.1	1300	11	70	10	ND	16	7.3	730	0.47
C_4-Biphenyls	210.1	1900	0.92	750	230	37	0.16	83	110	
Fluorene	116.1	2.9	ND	0.66	0.032	ND	ND	ND	0.52	0.076
C_1-Fluorenes	180.1	4.9	ND	3.9	0.25	1.2	0.61	0.28	13	0.10
C_2-Fluorenes	194.1	68	12	38	0.78	ND	2.85	0.82	120	0.22
C_3-Fluorenes	208.1	110	89	130	19	5.5	18	9.4	170	11
C_4-Fluorenes	222.1	53	4.5	88	0.42	0.72	0.43	0.26	80	0.10
Anthracene[c]	178.1	0.51	ND	0.25	0.068	0.16	0.14	0.10	0.69	0.12
C_1-Anthracenes	192.1	0.0020	0.15	7.1	0.034	0.20	0.088	0.058	18	0.032
C_2-Anthracenes	206.1	19	5.4	20	0.70	0.23	1.4	0.56	22	0.39
C_3-Anthracenes	220.1	24	0.85	26	0.078	0.084	0.21	0.11	27	0.14
C_4-Anthracenes	234.1	8.3	2.3	10	0.44	0.55	0.57	0.26	9.8	0.15
Pyrene[d]	202.1	2.8	0.056	12	0.030	0.072	0.024	0.043	1.6	0.056
C_1-Pyrenes	216.1	6.2	0.013	33	0.0080	0.034	0.017	0.012	5.2	ND
C_2-Pyrenes	230.1	1.4	0.39	17	0.033	0.042	0.056	0.023	4.3	0.010
C_3-Pyrenes	244.1	0.41	0.39	17	ND	0.014	ND	ND	0.80	ND
C_4-Pyrenes	258.1	0.19	0.074	6.7	ND	0.012	0.004	0.20	ND	
Summed Concentrations		4900	270	2000	370	59	89	140	3400	22

[a] Satisfactory to two significant figures.
[b] ND = not detected.
[c] Including Phenanthrene
[d] Including benzanthracene

plain.   Since another waste pit was located up-gradient by several hundred

meters from the study waste pit, contamination of soil through flooding was

possible.   But the probability for this process is presently unknown.

Environmental Evaluation

While these results may be used to suggest only limited mobility of PAH

in soil/groundwater systems, this pit was only 10 years old and may be

considered an average producer of waste water.   In earlier studies, (section

3.6.1) core samples were taken from earthen waste pits from natural gas

production and PAH were found at depths up to 1.8 m from the pit bottom or

about 2.5 m from land surface.   Depth profiles showed that PAH were found at

every level tested and the sandy soil of northwest New Mexico showed limited

abatement properties including low capacity.   For most PAH, concentrations at

the pit bottom were the same as those concentrations at 1.8 m depth.   Thus,

movement of produced water in earthen waste pit into nearby groundwater was

predicted to be extensive and was later confirmed for aliphatic and aromatic

hydrocarbons.   Since groundwater was found at 1 to 1.5 m from land surface in

the Duncan Oil Field, contamination of groundwater and subsequent transport of

PAH along the hydraulic gradient should not be surprising.   Moreover, since

the groundwater and soil seem in intimate contact and since adsorption of PAH

from water onto soil may be favorable, presence of PAH in these soils was

consistent with prior findings.

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