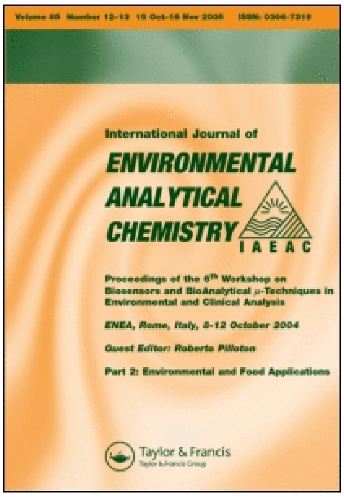

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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**To cite this Article** Davani, B. , Gardea, J. L. , Dodson, J. A. and Eiceman, G. A.(1985) 'Hazardous Organic Compounds in Liquid Wastes from Disposal Pits for Production of Natural Gas', International Journal of Environmental Analytical Chemistry, 20: 3, 205 — 223

**To link to this Article: DOI:** 10.1080/03067318508077058

**URL:** http://dx.doi.org/10.1080/03067318508077058

*Intern. J. Environ. Anal. Chem.*, 1985, Vol. 20, pp. 205–223
0306-7319/85/2004-0205 $18.50/0

Printed in Great Britain

# Hazardous Organic Compounds in Liquid Wastes from Disposal Pits for Production of Natural Gas

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(*Received October 26, 1984; in final form December 3, 1984*)

Samples of liquid waste found in disposal pits from natural gas production were collected at sites selected in northwest New Mexico and were characterized for hazardous and other organic compounds using GC and GC/MS techniques. Purge and trap pretreatment was used in GC/MS determination of volatile organic compounds while solvent extraction, prefractionation and preconcentration were used for isolation of polycyclic aromatic hydrocarbons (PAH) and alkylated polycyclic aromatic hydrocarbons in the same waste samples. Benzene and alkylated benzenes were present at estimated concentrations of 10 to 50 mg/L in aqueous portions of pit wastes. Selected ion monitoring with capillary GC/MS with deuterated PAH as internal standards was used to quantify PAH in both aqueous and non-aqueous liquid phases. Over 50 PAH were detected at total concentrations of 130 μg/L to 24,500 μg/L for aqueous phases and 1055 mg/kg to 13,500 mg/kg for non-aqueous phases in pit wastes. In addition, total organic compounds detected in GC analyses of pit wastes were estimated as 200 μg/L to 235 mg/L for aqueous phase and 11 g/kg to 402 g/kg for the non-aqueous phase. Consequences to aquatic environment from disposal practices in natural gas production are evaluated and discussed based on these results.

## INTRODUCTION

Natural gas is believed to have origins similar to oil and is often but not always found in contact with oil and water at pressures between 100–2000 psig.[1, 2] Oil may actually be produced simultaneously with natural gas from the same well and in New Mexico a natural gas well is defined as a well in which the gas/oil ratio is over 100,000 cubic feet of gas per barrel oil. In high pressure wells, natural gas is not a pure substance but is typically a mixture of $C_1$ to $C_4$ alkanes, and several inorganic gases with methane at 70 to 95+%mole ratio.[1] In addition, a complex mixture of minor components including $C_5$ to $C_{10}$ alkanes and aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAH) have been found in natural gas.[3–8]

In production and transport of natural gas, two major aqueous wastes are generated: produced water (or brine water) and discharge water from hydrostatic testing (DWHT) of natural gas pipelines.[8, 9] Produced water which is stored in open-air pits or holding reservoirs is the wastewater separated from natural gas and hydrocarbon condensate at well-heads. The volume of these wastewaters can be quite large. For example, from 31,172 gas wells producing water in New Mexico in an eleven month period of 1982, over six billion gallons of produced water were recorded.[10] Wastes are disposed using underground injection and waste pits on land surfaces. While pits in the U.S. commonly are lined and discharge to unlined pits is now largely prohibited, in northwest New Mexico most waste pits in natural gas production are unlined. Eventual migration of aqueous contents of such pits into ground water has been observed.[11–13] Even in pits which are lined with clays, formation of cracks or ruptured linings may develop from contact of clay with certain organic wastes.[14] Since DWHT was found to contain hazardous organic compounds at individual concentrations of 7 to 860 $\mu$g/L in prior studies in this research program, presence of hazardous organic compounds in such pits was thought possible and considered potentially serious based on composition and magnitude of wastes and on the number, characteristics and locations of such waste pits near vulnerable aquifers.

The presence of high molecular weight organic compounds in produced water and DWHT can be attributed in part to a phenomenon termed retrograde condensation, which is defined as liquid formation by isothermal expansion of a fluid on a dew point gas stream.[1] Formation of liquid by pressure reduction on a gas is a peculiar behavior for fluid mixtures in the critical region and is unlike that for pure substances.[1] 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.[16–18] However, as natural gas is passed through a pressure drop in production equipment or pipelines, the solubility of larger molecular weight components is decreased and condensation occurs.

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 of flotation valve in separators at field-treatment units. Although water contamination by salts in brine has been reported,[12,13] presence of high molecular weight toxic organic compounds in liquid wastes from these disposal pits is not widely known. An exception is work by Middleditch[15] in which near 200 volatile organic constituents including $C_3$–$C_{16}$ alkanes, benzene, alkyl benzene, naphthalene, and alkyl aromatic hydrocarbons were identified in the produced water effluent from the Buccaneer Gas and Oil field in the Gulf of Mexico. The objective of this present work is to characterize and quantify when possible organic and toxic organic compounds in liquid wastes including produced water in disposal pit contents located in the San Juan Basin of northwest New Mexico. This work is also expected to provide a base of data for assessment of movement and release of toxic compounds into ground waters as well as into domestic atmospheric environments.

## EXPERIMENTAL

### Instrumentation

A Hewlett-Packard model 5880A gas chromatograph was equipped with flame ionization detector (FID), automated splitless injector, and DB-5, 10 m long, 0.25 cm ID fused silica capillary column.

Conditions for analysis of all samples were: initial temperature, 30°C; program rate, 6°C/min; final temperature, 260°C; final time, 5 min; injector port temperature, 250°C; FID temperature 270°C; carrier gas, nitrogen at 30 cm/s average linear velocity; time for splitless injection, 1.5 min; chart speed 0.5 cm; and area reject, 10. A Hewlett-Packard model 5995A gas chromatograph/mass spectrometer (GC/MS) was equipped with jet separator, model 5885M disk drive, model 7225B X-Y plotter, automated splitless injection port and 10 m OV-1 fused silica capillary column. Chromatographic conditions were identical for scanning GC/MS and GC–FID analyses. Mass spectrometer conditions for scanning analyses were: lower mass, 45 amu; upper mass, 600 amu; scan speed, 690 amu/s; delay between scans, 0.1 s; electron multiplier voltage, 1400 V; and MS detection threshold, 10 linear counts. Mass spectrometer conditions for SIM analyses were: electron multipler voltage, 1800V; SIM window size, 0.2 amu; intergrate sensitivity, 0.05; area threshold, 10.00; smoothing factor, 1.000; selected polycyclic and alkylated polycyclic aromatic hydrocarbon with ions chosen for SIM analyses have been given.[8] Volatile organic compounds were determined using instrumentation already described in detail.[9] Sample volumes in GC and GC/MS analyses were 0.5 to 2 $\mu$l delivered using a model no. 701N 10 $\mu$l syringe (Hamilton Co., Las Vegas, NV). Conditions other than these will be noted as necessary.

## Reagents and standard solutions

Dicloromethane (HPLC grade; Fisher Scientific Co., NJ), cyclohexane (pesticide grade; Fisher Scientific Co., NJ), methanol (Burdick and Jackson Laboratories Inc., Muskegon, MI), and nitromethane (Spectrograde; Eastman Kodak Co., Rochester, NY) were used as purchased. Two types of deuterated PAH standards were used at various stages of this research and included: (A) a mixture containing acenaphthene ($d_{10}$), naphthalene ($d_8$), benz(a)anthracene ($d_{12}$), chrysene ($d_{12}$), anthracene ($d_{10}$), fluorene ($d_{10}$), and pyrene ($d_{10}$) in $CD_2Cl_2$ and $C_6D_6$ with individual concentrations of 1 mg/mL purchased from MSD Isotopes (Merck Chemical Division, St. Louis, MO) and (B) a mixture of naphthalene ($d_8$), phenanthrene ($d_{10}$), and anthracene ($d_{10}$) in methylene chloride at individual concentrations of 0.66 mg/ml was obtained from

Supleco, Inc. (Houston, TX). Additionally, 1 ml of 1:50 dilution of saturated solution of benzene (Pesticide grade, Fisher Scientific Co., Fair Lawn, NJ) was used as external standard to estimate the approximate relative concentration of benzene and alkylated benzene in purge and trap analysis of waste samples.

## Samples

Grab samples were drawn from waste pits using a 3 meter sampling rod with container attached to end of pole. Attempts were made to collect both aqueous and non-aqueous (surface film) without concern over mass balance of phases. Exact locations and descriptions of pits with quadrant location and informal names used in this study were: (1) Cuba, 15 miles west of Cuba, NM, Sec. 29 T22N R3W, 5 x 5 m unlined pit, 5 cm thick black film on surface, water below surface was dark brown; (2) Bloomfield, within 60 feet of San Juan River in flood plain, Sec. 27 T29N R11W, 5 x 5 m unlined pit with very little liquid wastes but dark stain on sides of pit, waste has slight oil sheen; (3) Archuleta, Sec. 16 T30N R8W, several miles upstream on NW bank of San Juan River from intersection of highways 173 and

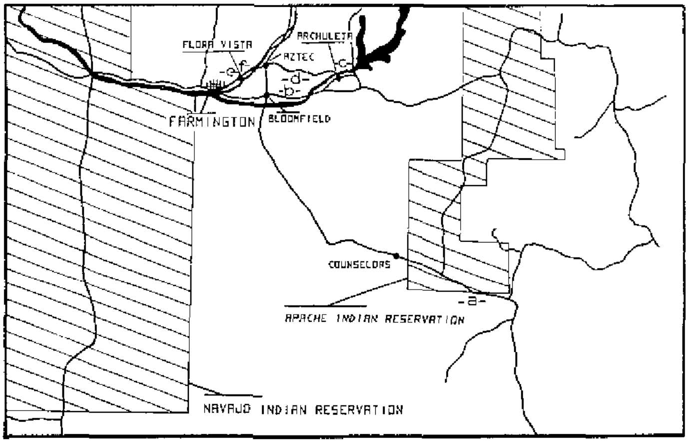

FIGURE 1 Map of locations of waste pits. Locations on map designated by letter is referenced to text according to: (a) Cuba, (b) Bloomfield, (c) Archuleta, (d) Aztec, (e) Flora Vista 1E and (f) Flora Vista 1. Attempt was made to locate letter in general vicinity of associated waste pit.

511 near Archuleta, pit was 3 to 4 m diameter, fiberglass pit with 5 to 10 cm of thick oil-like phase on surface; (4) Flora Vista 1E, Sec. 23 T30N R12W at SW4/SW4, well located in the community of Flora Vista and within 10 to 20 m of Animas River on a flood plain, fiberglass pit with dark oily brown surface phase and murky brown aqueous phase; (5) Flora Vista 1E(A), same pit sampled four months earlier and stored at 1–2 C; (6) Flora Vista 1, near Flora Vista, NM at Sec. 23 T30N R12W at NW4/NW4, largely solid non-aqueous wastes in fiberglass pit; (7) Aztec, location off highway 173 halfway between Aztec and Archuleta, NM, Sec. 27 T30N R9W at SE4NW4F, 10 × 10 m unlined pit on mesa above San Juan River, virtually no water with yellow wax contents and dark high water mark near top of pit nearly 1 meter above surface.

## Procedures

Samples were analyzed for volatile organic compounds using purge and trap method.[9] Conditions for purging were: sample size, 1–5 mL; flow rate of purge gas ($N_2$), 40 mL/min; time of purge, 12 min; and size of Tenax-GC sorbent trap, 100 mg. Contents of traps were then analyzed using packed column GC/MS with direct thermal desorption of Tenax-GC traps. A 2 m long × 2 mm ID borosilicate glass column packed with 3% OV-101 on Chromosorb W was used for analysis. Conditions for desorption were: temperature for desorption, 150°C; time of desorption, 1.5 min after a 0.5 min period of preheating; and switching valve temperature; 150°C.

A solvent-extraction procedure described by Bartel *et al.*[19] and modified by Eiceman *et al.*[8] was used for isolation and concentration of PAH in the samples. Liquid wastes usually but not always had two phases, aqueous and non-aqueous. The non-aqueous phase had viscous properties with distinct petrochemical odor. The aqueous samples were highly colored and also had a petrochemical odor. Samples were separated into aqueous and non-aqueous phases when both were available, however in all cases phases were extracted individually. In each analysis prior to extraction, samples of 50 mL produced water (aqueous phase) and 2 grams of the non-aqueous phase were spiked with 20–30 $\mu$L of deuterated PAH standards. In analysis of each aqueous liquid phase, 50 mL of sample were extracted in triplicate with 50 mL of methylene chloride. Extracts were condensed to ca. 3 mL using rotary evaporator (Buchii Brinkmann Co., NY) and further reduced in volume to 1 mL using a gentle stream of nitrogen gas prior to prefractionation procedures. In analysis of non-aqueous phases, 0.45 gram of sample was diluted to 1 mL with methylene chloride and analyzed directly by GC without any preextraction. A procedure blank was used to insure no contamination from solvent or glassware. Extraction efficiency of PAH as well as confirmation of identity using retention indices was possible through comparison of results to those for deuterated PAH standards.

## RESULTS AND DISCUSSION

### Volatile constituents of waste pits

Although contents of waste pits had been exposed to ambient atmosphere at temperatures as great as 32°C for unknown duration, a discernable 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 1 and in Figure 2A. In Figure 2A, a total ion chromatogram (TIC) is shown from GC/MS analyses of aqueous portion of the Cuba sample for volatile organic compounds. At least 40 resolved or partially resolved components were seen in the TIC and are representative of results found with other water samples. The identities of major components in this and other samples are listed in Table 1 along with abundance values as 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 reported here only as estimated concentration 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 were unexpected since evaporation of volatile compounds to the atmosphere was initially believed to result in trace concentrations of these compounds in all waste pit liquids, particularly aqueous phase. Two major classes of compounds were detected in these samples and were alkane/alkenes and benzene/alkylated

TABLE I

Summary of volatile organic compounds in aqueous phase of waste pits from natural gas production.

| Retention index | Compound | Absolute MS abundances[a] | | | |
|---|---|---|---|---|---|
| | | Cuba | Archuleta | Bloomfield | Flora Vista 1E(A) |
| 693 | $C_4H_8$(alkene) | 1,431 | ND | — | ND |
| 715 | $C_6H_{12}$(alkene) | 1,190 | — | 1,762 | — |
| 727 | $C_7H_{16}$ branched alkane | 681 | — | — | — |
| 729 | Benzene | — | 3,117 | — | — |
| 733 | $C_7H_{14}$ isomer | 1,159 | — | 1,679 | — |
| 756 | $C_7H_{16}$ branched alkane | 1,249 | — | 2,243 | — |
| 766 | $C_7H_{14}$ isomer | 3,945 | — | 3,920 | — |
| 805 | Toluene | 730 | 3,729 | — | — |
| 822 | $C_8H_{16}$ alkene | 3,984 | — | — | — |
| 820 | $C_8H_{16}$ alkene isomer | 5,589 | — | 6,767 | — |
| 844 | $C_8H_{18}$ branched alkane | 2,843 | — | — | — |
| 849 | Alkene (U) | — | 287 | — | — |
| 851 | $C_8H_{18}$ branched alkane | — | — | 5,618 | — |
| 868 | $C_8H_{16}$ alkene | 3,599 | 351 | — | — |
| 873 | $C_8H_{16}$ alkene | — | — | 3,721 | — |
| 895 | Xylene | 13,911 | 2,848 | 26,834 | — |
| 900 | $n$-$C_9H_{20}$ | 2,040 | — | — | — |
| 905 | Branched alkane/alkene | — | — | — | 3,789 |
| 912 | Xylene isomer | 6,025 | 758 | 14,604 | — |
| 917 | $C_9H_{18}$ alkene | — | — | — | 9,448 |
| 932 | Branched alkane $C_9H_{22}$ | 6,114 | 806 | 7,916 | — |
| 946 | $C_9H_{18}$ isomer | 2,073 | 1,672 | 1,735 | — |

| | | | | | |
|---|---|---|---|---|---|
| 954 | $C_{10}H_{22}$ isomer | 1,266 | — | — | — |
| 959 | $C_{10}H_{20}$ alkene | 1,439 | — | — | 1,837 |
| 971 | $C_3$-benzene | 5,995 | 425 | 6,989 | — |
| 976 | $C_{10}H_{20}$ alkene | — | — | — | 1,315 |
| 993 | $C_3$ benzene isomer | 6,283 | 395 | 8713 | — |
| 998 | $C_{10}H_{20}$ alkene isomer | — | — | — | 3,630 |
| 1,000 | $n$-$C_{10}H_{22}$ | 7,506 | 743 | 1,345 | — |
| 1,030 | $C_{10}H_{20}$ isomer | 2,313 | — | 1,615 | — |
| 1,040 | $C_4$-benzene | 1,955 | — | 1,071 | — |
| 1,067 | Mixture $C_4$-benzene with unidentified alkane | 2,909 | 458 | — | — |
| 1,070 | $C_4$-benzene | — | — | 1,513 | — |
| 1,089 | $C_5$-benzene | 952 | — | 393 | — |
| 1,100 | $n$-$C_{11}H_{22}$ | 7,781 | 814 | 6,063 | — |
| 1,114 | Branched alkane | 544 | — | 428 | — |
| 1,159 | Naphthalene | 2,169 | — | 789 | — |
| 1,200 | $n$-$C_{12}H_{26}$ | 7,555 | — | 2,252 | — |
| 1,231 | $C_{12}H_{24}$ alkene | 887 | — | — | — |
| 1,300 | $n$-$C_{13}H_{28}$ | 7,528 | 1,124 | 1,376 | — |
| 1,337 | $C_{13}H_{26}$ | 5,439 | — | — | — |
| 1,353 | Saturated alkane | 5,033 | — | — | — |
| 1,373 | Branched alkene | — | — | 541 | — |

[a] Abundance for external benzene standard = 39,460. Abundance Units for 14 mg/L.

benzenes. Such compounds were also major constituents in sample of produced water from the Gulf of Mexico.[15] 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.[8, 9]

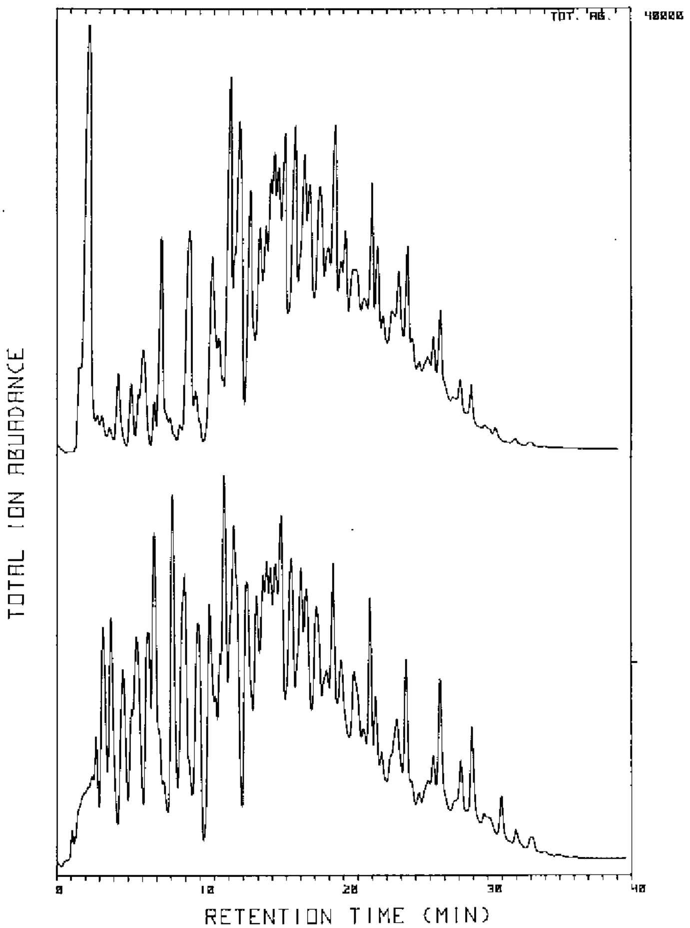

FIGURE 2 Total ion chromatogram from GC/MS analysis of (A) aqueous wastes from Cuba sample and (B) non-aqueous wastes for same sample for volatile organic compounds.

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 3B as mass chromatograms from the same scanning GC/MS analysis shown in Figure 2A. Mass chromatograms are shown for benzene, toluene, and alkylated $C_2$ to $C_8$ benzenes. Over 20 compounds from this class were resolved as shown in Figure 3B and retention times were consistent with mass spectral results in Table 1. In Table 1, 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 is unknown, generally few conclu-

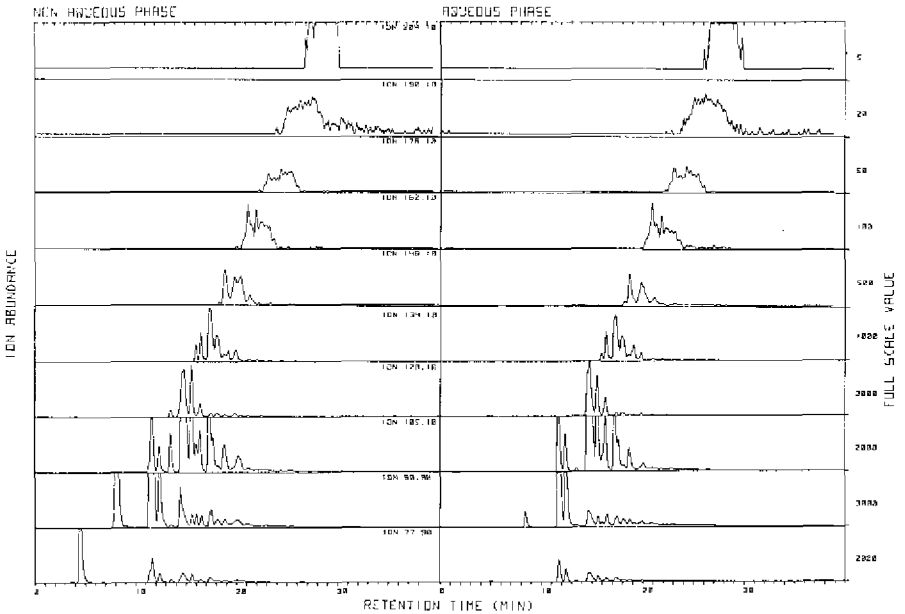

FIGURE 3 Mass chromatograms for benzene and alkylated benzenes from scanning GC/MS analysis of non-aqueous (A) and aqueous (B) phases from Cuba sample.

sions on fresh produced water composition can be made from these results. Also, particularly striking was the composition of volatile fraction in the non-aqueous wastes in contact with the wastewater described in Figures 2A and 3B. Similarities between the aqueous and non-aqueous (Figures 2B and 3A) 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 be seen in Figure 2 at retention times of 3.0, 6.0, 7.8 and 9.8 min. These compounds were present at large relative concentrations in 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 program. Amount of evaporation of water has been determined as low ($<5\%$), even in the arid Southwest and most loss of water was due to seepage perhaps into local groundwater.[12]

## 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 $C_{10}$ to $C_{35}$. Results from simple direct GC analysis of samples with little or no pre-treatment apart from liquid–liquid extract of aqueous phase and dilution of non-aqueous phase are shown in Figures 4 and 5, respectively. Results are shown as bar plots of chromatographic data as concentration versus retention index. Concentration units were ng/L for aqueous phase (Figure 4) and $\mu$g/g for non-aqueous phase (Figure 5) which in some samples had become solid upon storage in the laboratory at 22°C. Total concentrations of organic compounds in samples as determined from integration of GC total peak area with use of an average response factor were: Bloomfield, 200 $\mu$g/L; Cuba, 11,000 $\mu$g/L; Flora Vista 1E, 10,400 $\mu$g/L; Archuleta, 11,700 $\mu$g/L; and Flora Vista 1E(A), 23,500 $\mu$g/L. Total organic carbon 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

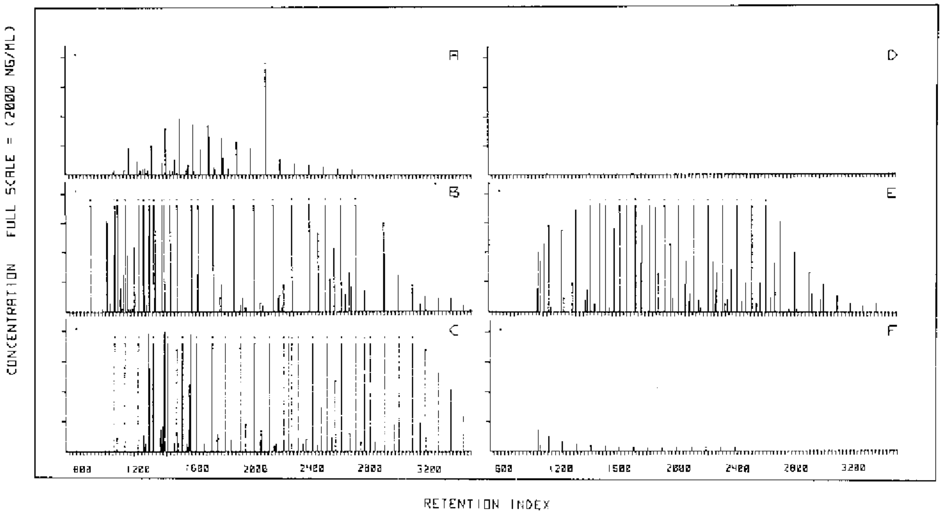

FIGURE 4 Bar plots from GC/FID analyses of aqueous phase from waste pits for extractable compounds. Samples were: (A) Cuba, (B) Flora Vista 1E, (C) Flora Vista 1, (D) Procedure Blank, (E) Archuleta and (F) Bloomfield.

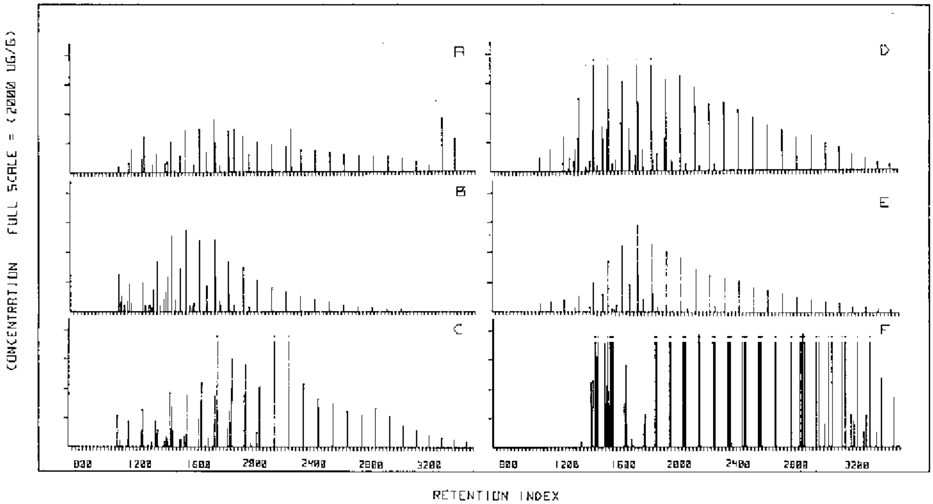

FIGURE 5 Bar plots from GC/FID analyses of non-aqueous phase from waste pits for extractable compounds. Samples were: (A) Cuba, (B) Flora Vista 1E(A), (C) Flora Vista, (D) Flora Vista 1E, (E) Archuleta and (F) Aztec.

were not always found in all pits. In certain pits (Bloomfield, Cuba) only an aqueous phase was found while in others (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 1000 × those for the aqueous phase, both patterns of bar plots and range of molecular weights in general were very similar. Such results are evidence that when phases are present together, movement of compounds between two phases may 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 carbon number range between $C_{10}$ to $C_{30}+$ with a maximum relative abundance seen at $C_{14}$ to $C_{18}$.

## Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons have been found throughout natural gas consumer distribution lines and in natural gas supplied to consumers.[20] This class of compounds has also been found in discharge water from hydrostatic testing of natural gas pipelines.[8] 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 6 and Tables 2 and 3. In Figure 6, 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 6A and 6B 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 may not occur rapidly in compositions from weathering leading to evaporation or decomposition. However, this is speculation and further study is needed on weathering of disposal pits at high altitude in hot dry climates such as is found in the US Southwest.

## Environmental conclusions

The concentrations of PAH in either phase are sufficiently large for concern should these wastes reach groundwater 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 even 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 pollutants were found in these waste disposal pits

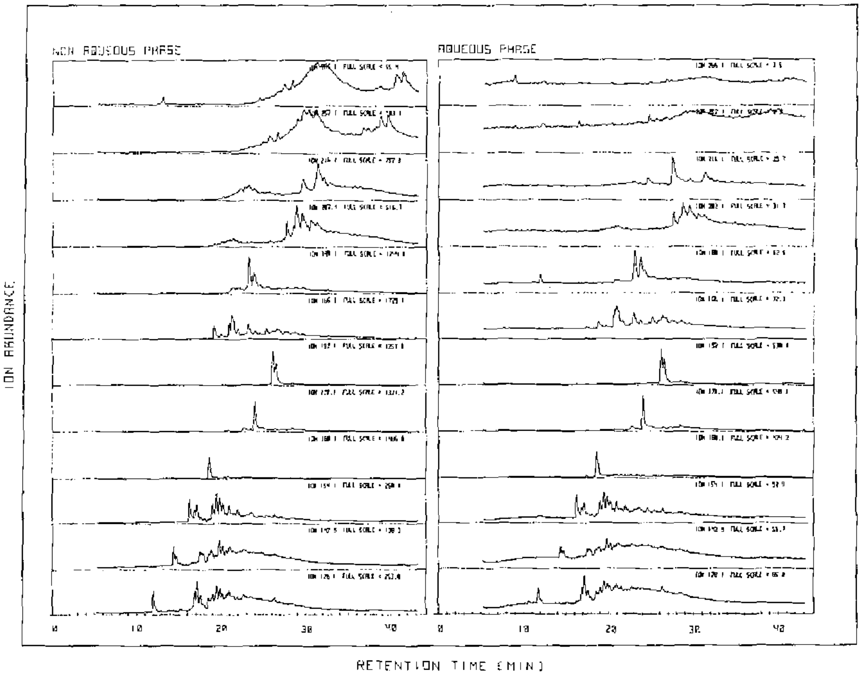

FIGURE 6 SIM plots from GC/MS analyses of non-aqueous (A) and aqueous (B) phases from waste pits from Cuba sample for polycyclic aromatic hydrocarbons.

TABLE II

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

| | Concentration ($\mu g/L$) | | | | |
|---|---|---|---|---|---|
| | Cuba | Archuleta | Flora Vista 1E | Bloomfield | Flora Vista 1E(A) |
| Naphthalene | 850 | 480 | ND | ND | 500 |
| $C_1$-Naphthalene | 770 | 390 | ND | ND | 1,900 |
| $C_2$-Naphthalene | 1,300 | 2,500 | ND | ND | 4,200 |
| $C_3$-Naphthalene | 1,400 | 2,400 | ND | ND | 3,600 |
| Biphenyl | 680 | 480 | ND | ND | 450 |
| $C_1$-Biphenyl | 850 | 720 | ND | ND | 1,400 |
| $C_2$-Biphenyl | 1,000 | 1,700 | ND | ND | 1,400 |
| $C_3$-Biphenyl | 1,100 | 920 | ND | ND | 960 |
| Anthracene | 200 | 430 | 3.5 | 130 | 530 |
| $C_1$-Anthracene | 290 | 560 | 5.2 | ND | 1,900 |
| $C_2$-Anthracene | 260 | 380 | ND | ND | 2,200 |
| $C_3$-Anthracene | 180 | 170 | ND | ND | 1,700 |

| | | | | | |
|---|---|---|---|---|---|
| Fluorene | 82 | 140 | ND | ND | 320 |
| $C_1$-Fluorene | 180 | 360 | ND | ND | 650 |
| $C_2$-Fluorene | 140 | 390 | ND | ND | 870 |
| $C_3$-Fluorene | 78 | 430 | ND | ND | 650 |
| Pyrene | 13 | 200 | 300 | ND | 410 |
| $C_1$-Pyrene | 65 | 130 | 1,400 | ND | 260 |
| $C_2$-Pyrene | 46 | 100 | ND | ND | 280 |
| $C_3$-Pyrene | 33 | 160 | ND | ND | 280 |
| Benzopyrene | ND | ND | ND | ND | ND |
| $C_1$-Benzopyrene | ND | ND | ND | ND | ND |
| $C_2$-Benzopyrene | ND | ND | ND | ND | ND |
| $C_3$-Benzopyrene | ND | ND | ND | ND | ND |
| TOTAL | 9,517 | 14,740 | 1,709 | 130 | 24,460 |

ND—Not detected.

TABLE III

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 | ND |
| $C_2$-Naphthalene | 1,500 | 190 | 4,700 | 1,000 | 2,600 | 1,100 |
| $C_3$-Naphthalene | 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 | ND | ND | ND | ND | ND | ND |
| $C_2$-Benzopyrene | ND | ND | ND | ND | ND | ND |
| $C_3$-Benzopyrene | ND | ND | ND | ND | ND | ND |
| TOTAL | 5,202 | 1,055 | 13,449 | 3,541 | 11,895 | 1,920 |

ND—Not detected.

and warrant further investigations on movement and fate of toxic and hazardous organic compounds which are generated from production of natural gas.

## Acknowledgements

This research has been supported by New Mexico Water Resource Research Institute and New Mexico Environmental Improvement Division (EID) and has been developed during a program of investigating discharge of toxic organic compounds into water from activities of natural gas industry. Aid in collection of samples is gratefully acknowledged for the following: Dennis McQuillan, Dave Tomko, and Janet King all of New Mexico EID.

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