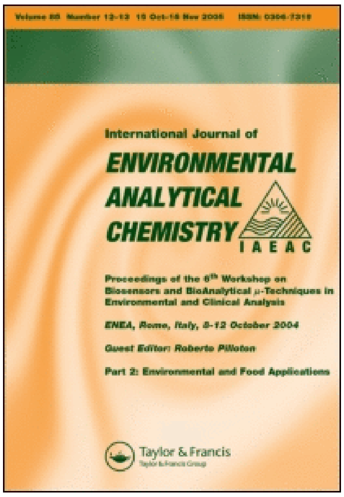

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Determination of Polycyclic Aromatic Hydrocarbons in Drilling Muds and Reserve Pits by Isotope Dilution GC/MS with Selected Ion Monitoring

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Shale cuttings, spent fluids, and drilling muds from natural gas exploration were analyzed for extractable hydrocarbons including polycyclic aromatic hydrocarbons (PAH) and alkylated-PAH. Complex mixtures of aliphatic hydrocarbons with carbon numbers from 10 to 32 were found in three phases coexisting in waste pits where extractable hydrocarbons were 45–990 mg/L in wastewater and 265–59 000 mg/kg in drilling muds/pit sediments. Over 20 members of 2–4 ring PAH and alkylated-PAH were isolated using chemical prefractionation and quantified by isotope dilution GC/MS with selected ion monitoring. Concentrations of total PAH assessed at three sites including a central waste storage site followed the trend: hydrocarbon film > oil-based muds > water-based muds > shale cuttings > aqueous phase and ranged from 15 mg/L for reserve pit water to > 24 000 mg/kg for oil-based drilling muds. Inhomogeneity of large reserve pits due to mechanical dispersion of wastes was illustrated using solution/sediment distribution ratios. Relative standard deviations with isotope dilution GC/MS determination of PAH were 1.9–27% and were generally 1.2 to 6-fold better than those using external calibration methods.

KEY WORDS: Polycyclic aromatic hydrocarbons (PAH), isotope dilution GC/MS, selected ion monitoring.

INTRODUCTION

During the last four years,[1–5] the hydrocarbon composition of liquid and solid wastes from production and processing of natural gas has been determined using high resolution gas chromatography/mass spectrometry (GC/MS). Complex mixtures of aliphatic hydrocarbons with carbon numbers of 10 to 40 were found in such wastes along with 2 to 4-ring polycyclic aromatic hydrocarbons (PAH) and alkylated analogs of these PAH. Since aqueous wastes, a hydrocarbon film, and sediment can co-exist as three separate phases in these pits, phases were analyzed separately for chemical composition. Total PAH concentrations have been as large as 24 mg/L in produced water; 13 g/kg in hydrocarbon films floating on the aqueous phase; and 0.68 g/kg in sediments collected at sites in New Mexico. A central concern from these findings was the environmental fate of PAH in wastes that were placed in earthen unlined pits during the last 25–40 years. Contamination of soil and groundwater by hydrocarbons and PAH from an earthen waste pit near the San Juan River[6,7] was documented. This contamination episode agreed with prior mobility profiles for hydrocarbons in comparable soils[5] and with findings that 93% of wastes percolated into soil below pits while only 7% evaporated in arid climates that favor evaporation.[8] Serious groundwater contamination has occurred in other geographic regions as illustrated in Utah[8] and in Ohio.[9] Although an initial comprehensive assessment of waste production and composition for natural gas production might be prepared using our findings, a complimentary description of wastes generated during exploration was incomplete and unavailable. One objective of the present work was to characterize drilling wastes including drilling muds for hazardous organic compounds such as PAH.

During exploration for natural gas, drilling muds and fluids are used to bore and maintain holes as wells. Drilling techniques, specialized chemicals, and waste disposal practices can be extraordinarily diverse[10,11] although some features are common to most drilling sites. In general, a small portable tank called a working pit is used to contain, recover, and recycle drilling muds while a reservoir called the reserve pit is used to retain excess fluids, cutting wastes and some drilling mud. Earthen unlined pits have been used regularly as reserve pits and are reclaimed once drilling is finished.

In one reclamation technique, water is drained through trenches dug radially from pits so sub-surface strata can be penetrated rapidly by pit fluids; later pits are filled with nearby soil.[12] While several publications or conferences have been devoted to the composition, management, and environmental impact[13–16] of drilling wastes, attention has been directed almost wholly on inorganic metals and salts. Unlined reserve pits may be completely forbidden in the future, but present use and the formation of leachate plumes from pits reclaimed over 25 years ago[12] suggests possible long-term releases into the environment from such pits. Thus, a detailed description of hazardous organic compounds in drilling wastes is necessary for future assessment of environmental impact from disposal practices of drilling wastes.

The composition and environmental importance of organic compounds in drilling muds was recognized only recently. Strosher concluded that 71% of aquatic toxicity in drilling wastes[17] was caused by hydrocarbons that comprised only 7% of total organic carbon the bulk of which is due largely to nontoxic polymer additives. The origin of hydrocarbons in these wastes was attributed to diesel oil but minor amounts might also come from use of spent brine water in drilling.[2] Hydrocarbon composition in aqueous fluids from drilling wastes was comprised of a complex mixture of aliphatic hydrocarbons with carbon numbers of 10–30 at 0.2–2920 mg/L. While detailed composition for PAH isomers was not reported, 2–4 ring PAH were found at 0.1–1410 mg/L from gas chromatographic analysis with a non-specific (flame ionization) detector. Nonetheless, PAH compounds differ in toxicity or carcinogenicity and quantification of individual PAH is needed for advanced toxicology assessments. Suitable selectivity with complex samples may be achieved through simple prefractionation schemes but additional sample handling can cause sample-to-sample variations so external standardization is inaccurate and imprecise. While selected ion monitoring (SIM) analysis with GC/MS instrumentation has previously been found selective for PAH isomers in natural gas wastes,[1–5] SIM measurements for PAH by isotope dilution may yield improved precision over external standardization. Another goal for this work was a comparison of precision between calibration methods for SIM analysis with complex hydrocarbon samples.

A final interest in this study was the partition of PAH between separate phases in the waste pits. Distribution of compounds between sediment and water should be affected in an actual environmental system by the complex mixtures that can saturate each phase and cause solubilities to differ from laboratory-based measurements.[18] Thus, a final objective was to examine hydrocarbon/water/soil distribution of PAH in reserve pits in a general manner without predefined goals.

EXPERIMENTAL

Collection and storage of samples

Samples were obtained at three locations in the San Juan Basin region of northwest New Mexico and sites included (A) a central facility located on State Highway 44 north of Bloomfield for receiving wastes from drilling sites throughout the basin, (B) a drilling site still in operation at SE/4 Sec 10 W, (C) a site where a natural gas well had just been successfully installed and reclamation started at SE/4 Sec 26 T31N R11W. At site A, an unlined earthen pit with dimensions 100 m long × 20 m wide by 6 m deep contained an aqueous phase of which 15% of the surface was covered by a thin hydrocarbon film in patches. A uniformly colored sediment was aqueous-based drilling muds and a single well-defined pile of mud on the bank was oil-based drilling mud. This mud was over 50 cm deep and was not mixed with the other contents of the pit. At site B, a reserve pit was fed from a working pit/shale shaker and appeared to contain mostly water and shale cutting. The pit was 50 m wide × 100 m long × 10 m deep and was about 30% filled. The site was exposed to strong winds and a floating hydrocarbon film was pushed into the windward part of the pit. The pit was also divided by an earthen spit so settling of solids could occur as wastes entered the pit and clarified water could be removed for use in drilling. A distinct difference in sediment coloration was noted at leeward and windward corners of the pit and samples were obtained at both regions. In the last site (C), the working pit was located directly in the reserve pit which was lined with plastic. The size of the reserve pit was 18 m long by 6 m wide and had been drained completely of water with only a grey solid remaining from cuttings. Drilling muds had been removed from the working pit and no drilling muds were noticed in the reserve pit. Another pit called the blow pit was practically unsoiled and had been placed near the well for a possible blow-out. The site was nearly reclaimed and represented a well-managed drilling site. Sampling locations for every site are illustrated in Figure 1. Grab samples were taken of each phase (water, sediment, and hydrocarbon film) as distinct samples and stored separately. Samples were kept in glass jars with screw caps and liners of Teflon or aluminum foil. Samples were stored at 0 °C in a portable, ice-filled cooler, returned to Las Cruces, and refrigerated at 5 °C before analysis.

Extraction and purification of samples

Solids were dried in air at 25 °C for 4–5 days and manually ground with morter and pestle to a free-flowing powder. A portion of sample was removed and an aliquot of deuterated PAH stock solution was added to each sample when placed in a glass fritted extraction thimble. The samples were then extracted using 200 mL of benzene (EM Science, Gibbstown, NJ) in a Soxhlet apparatus for 48 hrs. The extracts were condensed to several mL and placed on a column containing 9 g of 80–200 mesh neutral alumina (Bio-Rad Chem. Div., Richmond, CA) activated to 100 °C. The aliphatic components were eluted using 20 mL of hexane and discarded whereafter the PAH fraction was eluted using 50 mL of benzene. The PAH fraction was condensed to 3 mL using a rotary evaporator and further condensed to 1.0 mL using a gentle stream of dry nitrogen gas. Both condensed PAH fractions and raw untreated extracts were analyzed using GC and GC/MS with SIM. Extracts were all stored at -5 °C until analysis.

Instrumentation

A Hewlett–Packard gas chromatograph model 5880A level 3 was equipped with flame ionization detector (FID), automated splitless injector, and 10 m long, 0.25 mm ID fused silica capillary column containing a DB-5 stationary phase. Conditions for analysis were: initial temperature, 50 °C; initial time, 2 min; oven temperature program rate, 5 °C/min; final temperature, 250 °C, and final time, 10 min. Injector conditions were: split time, 1.0 min and temperature,

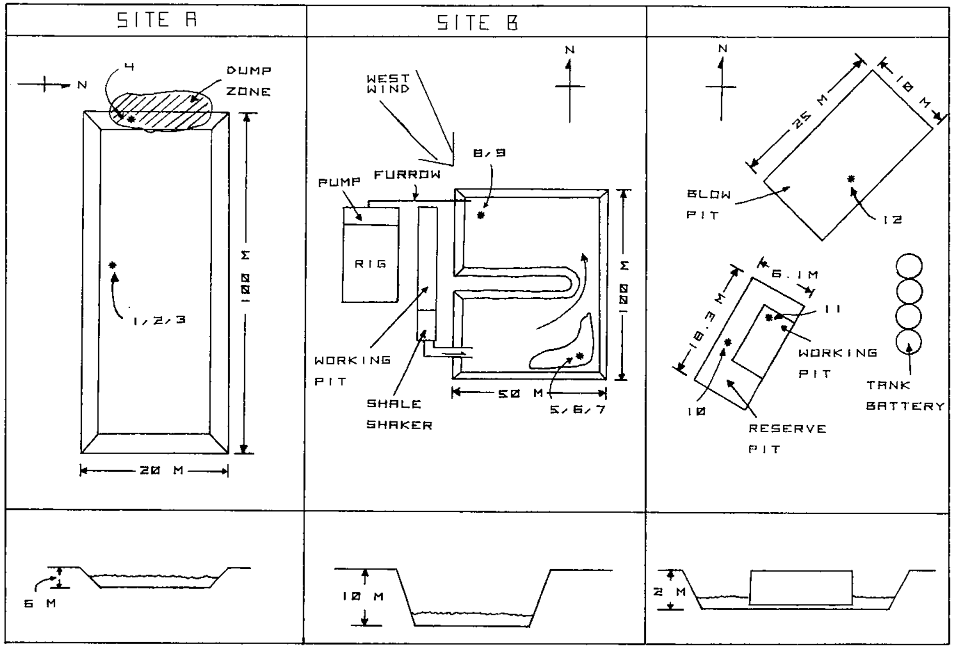

Figure 1 Sampling sites for waste pits for drilling muds and fluids in northwest New Mexico. The sites and details on sample collection are described in the text. The samples are numbered in the figures and were for water-based drilling muds (1), aqueous phase (2), hydrocarbon film on the water (3), oil-based drilling mud (4), sediment from reserve pit on leeward side (5), water (6) and film (7) from the leeward side, sediment (8) and water (9) from the windward side, sediment from a reserve pit (10), residual mud from a working pit (11), and water (12) from an emergency blow pit.

250 °C. Detector temperature was 270 °C. A Hewlett–Packard GC/MS model 5995A was equipped with jet separator, electron impact ion source, 5885M disc drive, 7225B X–Y plotter, automated splitless injector, and 10 m long DB-5 capillary column. Chromatographic conditions for GC/MS were initial temperature, 85 °C; initial time, 3 min; oven temperature program rate, 8 °C/min; and final temperature, 270. Mass spectrometer conditions were electron multiplier voltage, 1800 V; SIM window size, 0.2 amu; and area threshold, 10. Ion masses for SIM analysis were chosen for five PAH ring systems and C1 and C4 alkylated PAH derivatives for each PAH and have been reported earlier in this Journal.[7]

Use of deuterated PAH in isotope dilution MS measurements

The procedures for quantitation by isotope dilution were prescribed by EPA for priority pollutant screening by scanning GC/MS.[19] In isotope dilution methods, a calibration curve is prepared using standard solutions of PAH in combination with a fixed concentration of deuterated (d)-PAH. Relative response (PAH/d-PAH) is plotted versus concentration of PAH and used with the analysis of unknown samples. Aliquots of d-PAH stock solution are added to samples before prefractionation and concentration to account for sample-to-sample variation. Concentrations of d-PAH in final condensates should be identical to those in calibration solutions when no loss of analyte occurred during sample handling. The d-PAH standard solution contained d8-naphthalene, d10-fluorene, d10-anthracene, and d10-pyrene (Merck Sharp & Dohme/Isotopes, St. Louis, MO). In a study of precision, a homogeneous sample of diesel engine oil was analyzed using six replicates by isotope dilution methods with SIM analysis.

RESULTS AND DISCUSSION

Wastes at a central disposal site

Wastes at Site A were from throughout northwest New Mexico and samples from this one site might be considered a weighted measure of waste composition at drilling sites in the region. Results from a

GC-FID screening of unpurified extracts for water-based drilling mud and the hydrocarbon film floating on the associated wastewater are shown as chromatograms in Figures 2. Distinct hydrocarbon patterns were evident in the extract of both samples as peaks at regularly-spaced retention times and the carbon numbers ranged from 10 to 32. These and all other samples contained over 50 major, well-resolved components which were identified using scanning GC/MS as saturated hydrocarbons and alkenes. Attempts to detect PAH in unpurified extracts using GC/MS by scanning or SIM methods without chemical prefractionation was precluded by ion masses from large abundances of alkanes which strongly interfered in mass spectra for PAH. Differences in hydrocarbon patterns between the mud and petroleum film may reflect either actual differences in chemical composition or preferences from particular mechanisms of association. For example, organic compounds will partition into mud through adsorption which will be governed by size such that large molecules are favored. Size dependence for solubility of compounds in the hydrocarbon film should not be exhibited so distinctly with the low molecular weight (short retention time) components. A procedure blank was free of detectable amounts of contamination.

In Figure 3, results from GC analysis for other phases at Site A are shown as bar plots for convenient comparison of complex samples. The range of molecular weights (i.e. retention indices or carbon numbers), chemical complexity, and relative distributions of compounds were reasonably similar especially for the muds. Some slight differences existed between the aqueous phase and the water-based muds where poorly resolved components with low molecular weights were found in the water at concentrations greater than in the mud. A substantial bulk of these compounds were alkenes and simple aromatic hydrocarbons. These compounds undergo dipole-induced dipole interactions with water that compete with London dispersion forces present in the nonpolar muds and increase aqueous solubility. Since London forces are small for small molecules, low molecular weight alkanes and aromatic hydrocarbons should be more soluble in water than large hydrocarbons. This seems to occur for hydrocarbons with carbon number 10–14 that are found in the water at relatively large abundances. Although slight differences between water, muds and film existed, the phases actually have comparable, if not identical, features and interphase communication

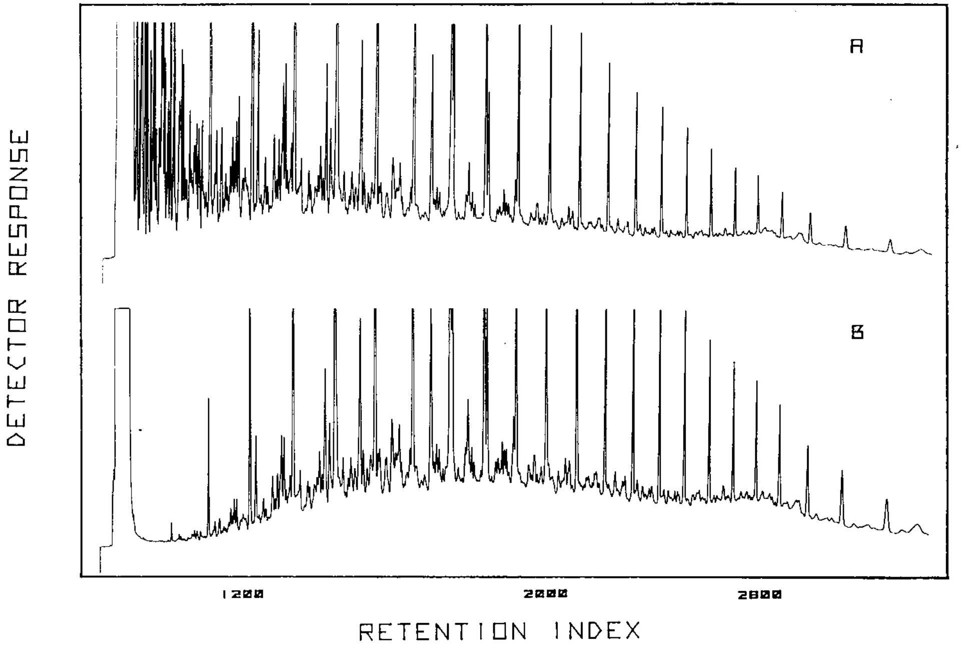

Figure 2 Chromatogram from GC-FID analysis of drilling fluid wastes including hydrocarbon film on wastewater (A) and water-based drilling muds (B). Chromatograms were obtained under identical conditions and may be directly compared.

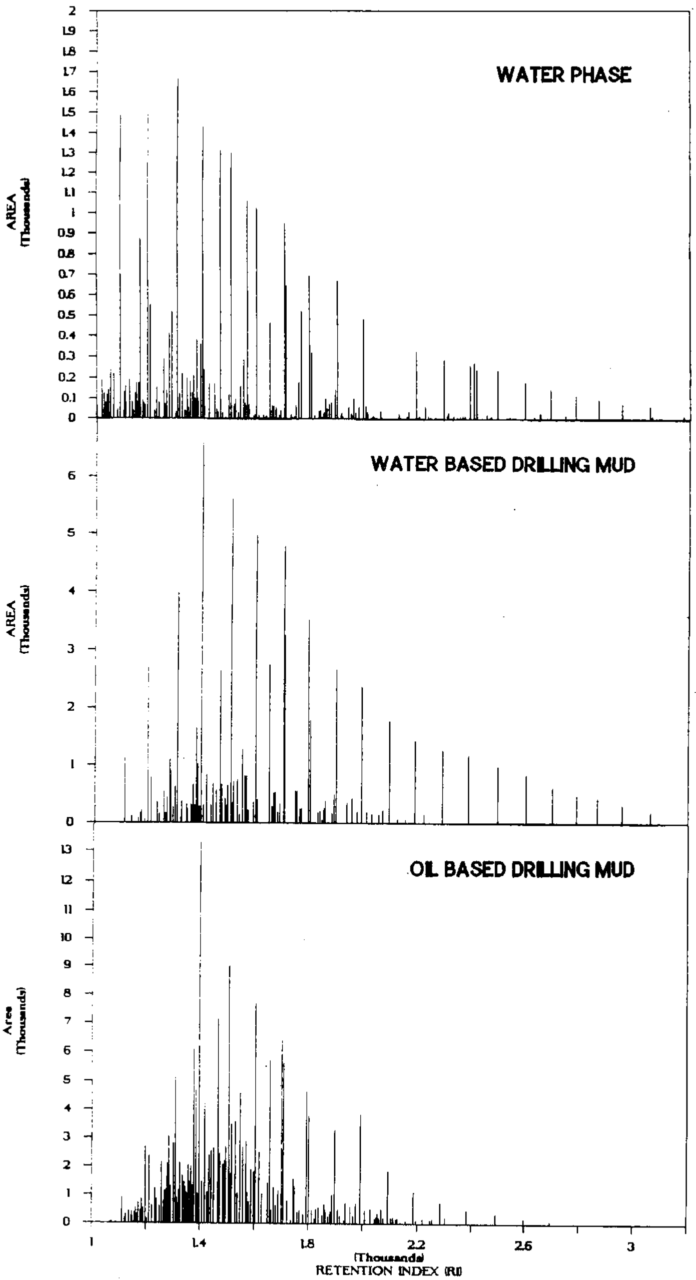

Figure 3 Bar plots from GC-FID analysis of samples at site A. Sample designation and locations correspond to drawings in Figure 1. Concentration axis are reported as peak areas and normalized to the largest component. Comparison of absolute concentrations can be made using extractable organic mass values shown in Table 1.

between the water and water-based drilling muds was suggested by these findings. The total extractable hydrocarbon concentrations ranged from 45 mg/L for the water to 58 600 mg/kg for oil based drilling mud as shown in Table 1. These values were comparable to Strosher's values of 0.2 to 2920 mg/L for wastewaters[17] and to Davani's value of >44 g/kg for oil soaked sediments from brine pits.[5]

Results from SIM analysis of Site A samples for PAH by capillary GC/MS with isotope dilution quantification are also shown in Table 1. Clearly, the PAH content decreased in the trend: hydrocarbon film>drilling muds>aqueous phase for which the total PAH content was 1.4 mg/L. Some striking differences in concentrations were seen between PAH and corresponding alkylated-PAH in the drilling wastes. For example, alkylated-PAH were 2- to >50-fold larger for a given PAH ring structure and incomplete reporting of total PAH content might occur when alkylated-PAH are not determined. This has gained new significance now that certain alkylated-PAH have become incorporated into water quality standards in New Mexico and also appear on EPA priority pollutant list. The oil-based drilling mud sample was taken from an isolated, freshly dumped portion of mud and represents sampling at a single site. Nonetheless, PAH concentrations in oil-based muds were up to 2-fold greater than those for water-based muds. Since muds are often recycled and not discharged in every reserve pit, the composition of these samples do not reflect fairly the actual composition of a reserve pit and estimates of environmental impact may be inaccurately portrayed. Assessment of pits at separate drilling sites was needed.

Waste pits at drilling sites

Results from GC-FID analysis of unpurified extracts of all samples at site B are shown in Figures 4 and 5 and PAH content is given in Table 1. Comparison of bar plots from GC chromatograms shows that the sediment and water had virtually identical compositions on the leeward side with compounds at roughly the same relative abundances of major components. This was seen also with the windward side which included an additional phase, a hydrocarbon film that had a relative composition similar to the water. However, concentrations of total extractable organic mass in the phases differed greatly and were 15–31 mg/L in water, 1600 mg/L for the

Table 1 Concentration of PAH and alkylated PAH in samples from drillings muds and fluids in waste pits

	Concentrations (in mg/L or mg/kg)														
Site:	A				B					C					
Phase:	Mud (Oil)	Mud (Water)	Water	Film	Water	Sed.	Water	Sed.	Film	Mud	Shale cuttings	Blow pit water	Soil blank	Diesel oil	Typical no. isomers
					(Windward)		(Leeward)								
Compound															
Naphthalene	62	23	0.72	700	0.83	4.7	0.70	4.8	4.6	[b]	[b]	nd	0.035	27	1
C1-Napth.	2000	500	nd	2100	5.3	2.4	2.7	79	38	[b]	[b]	nd	nd	46	2
C2-Napth.	6900	1500	nd	2900	8.0	3.9	4.3	245	110	[b]	[b]	nd	nd	100	5
C3-Napth.	7400	1100	nd	2100	5.4	1.9	2.9	215	340	[b]	[b]	nd	nd	160	6
C4-Napth.	3700	410	nd	4.9	0.028	0.83	1.2	100	42	[b]	[b]	nd	nd	120	5
Fluorene	88	50	0.075	310	1.1	1.2	0.24	7.8	47	0.35	0.093	0.18	0.002	3.9	1
C1-Fluor.	410	190	0.065	310	2.9	0.81	0.26	9.1	60	1.2	0.22	nd	0.065	31	2
C2-Fluor.	660	230	0.009	380	1.9	0.84	0.26	10	70	6.1	0.19	0.13	0.009	99	3
C3-Fluor.	450	200	0.005	320	0.92	0.80	0.25	9.7	42	1.4	0.077	nd	0.005	29	4
C4-Fluor.	440	120	nd	200	0.29	0.78	0.24	1.9	14	0.44	0.033	nd	nd	32	6
Anthracene	240	44	0.110	260	1.2	10	0.09	0.054	210	1.1	0.25	nd	0.039	66	1
C1-Anthra.	370	100	0.158	420	1.7	7.7	1.2	0.41	328	2.0	0.36	0.17	0.055	150	2
C2-Anthra.	350	73	0.168	240	0.68	3.4	0.53	0.21	170	1.1	0.21	0.24	0.055	110	2
C3-Anthra.	350	60	0.080	230	0.27	2.1	0.17	0.13	89	0.73	0.11	0.12	0.047	87	5
C4-Anthra.	93	18	0.052	103	0.07	0.86	0.12	0.067	39	0.37	0.065	0.046	0.035	32	6
Pyrene	34	6.8	nd	14	0.012	0.18	0.007	0.53	3.5	0.015	nd	0.026	nd	0.028	1
C1-Pyrene	47	26	nd	56	0.042	0.96	0.079	2.4	8.9	0.42	0.20	nd	nd	23	4
C2-Pyrene	53	30	nd	47	0.027	0.77	0.069	1.0	8.3	0.19	0.085	nd	nd	1	4
C3-Pyrene	15	22	nd	24	0.011	0.42	0.027	0.50	4.6	nd	nd	nd	nd	nd	4
C4-Pyrene	1.6	11	nd	15	nd	0.18	0.079	0.13	1.2	nd	nd	nd	nd	nd	4
Total PAH	24 000	4700	1.4	11 000	31	45	15	690	1600	19	5.3	0.91	0.35	1100	69
Total extracted hydrocarbons:	58 600	28 800	45	[a]	990	265	55	26 600	22 200	177	78	5.7	15.6	[a]	—

[a] This value was difficult to determine satisfactorily since the sample was virtually all hydrocarbon.

[b] The amounts of naphthalene and alkylated naphthalenes were less than 1 mg/kg in these samples but degredation of the *d*-naphthalene standard precluded reliable determinations.

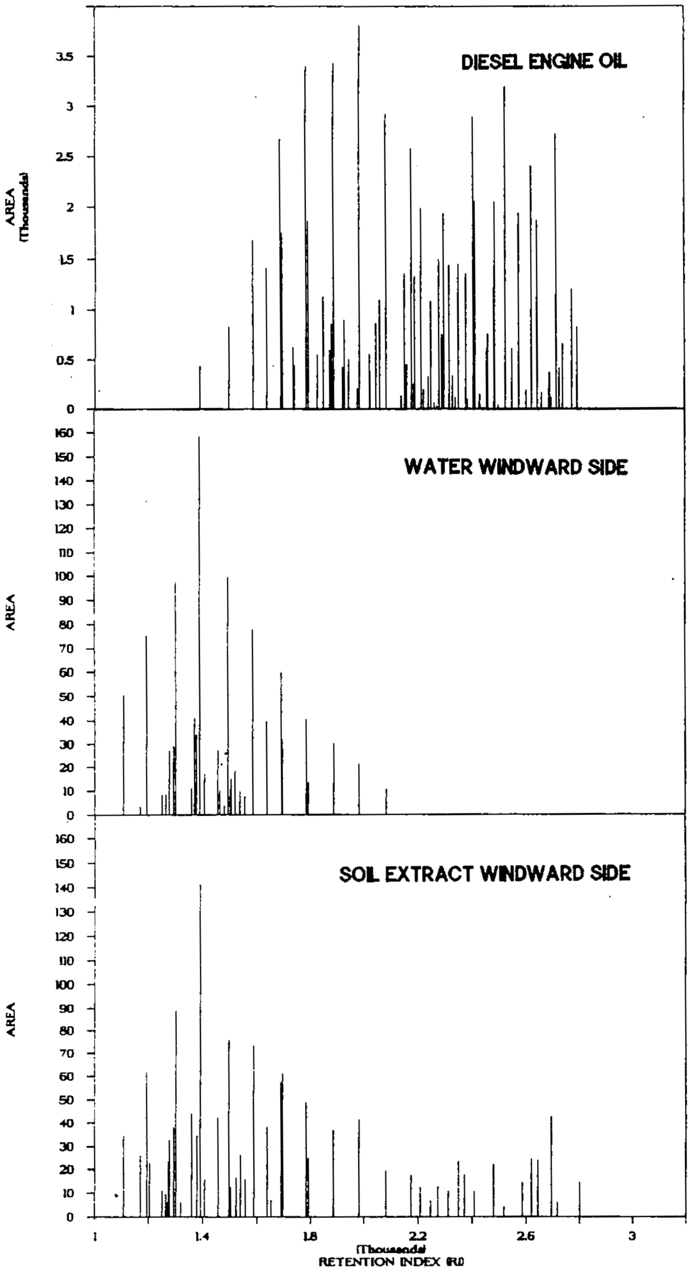

Figure 4 Bar plots from GC-FID analysis of samples from reserve pit at site B. See caption for Figure 3.

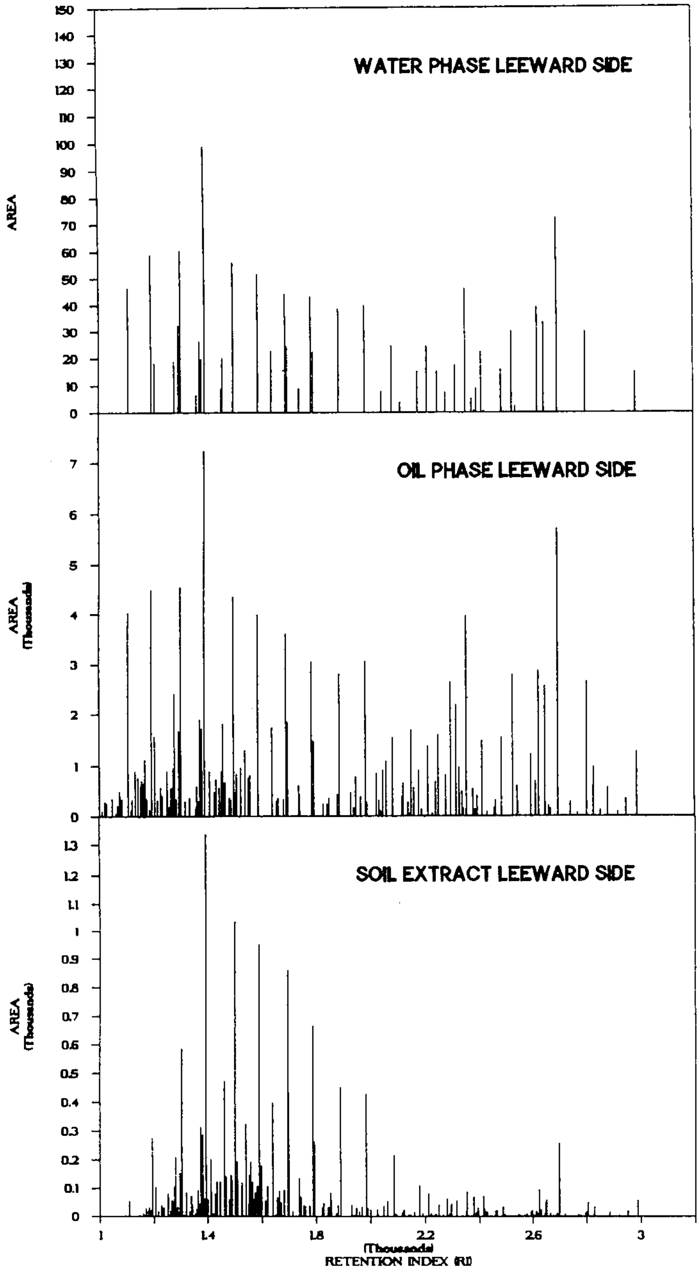

Figure 5 Bar plots from GC-FID analysis of samples from reserve pit at site B. See caption for Figure 3.

film, and 45–690 mg/L for the sediment. Concentrations for PAH listed in Table 1 parallel extractable organic mass although hydrocarbon and PAH content in the pit sediments at Site B were less than those seen for drilling muds alone at Site A. This suggests that hydrocarbons are adsorbed preferentially on to muds over shale cuttings and that hydrocarbon burdens in pits might be controlled when the muds are prevented from entering the reserve pit. With an efficient working pit, only shale cuttings and some fluids should enter the reserve pit while drilling muds should be recovered in the working pit for recycling. Thus, the relatively low amounts of PAH and hydrocarbons in the sediments of this reserve pit were consistent with efficient recycling of mud even though these levels are still large compared to most brine pits. At site B, one immediate source of hydrocarbons was fluids dripping from large diesel engines used in drilling from which a continuous albeit small stream of leaking oil was introduced into the reserve pit. Since such a flow might constitute a large volume over a period of days or weeks and a sample of used diesel oil was obtained and analyzed for preliminary identification of hydroarbon sources for the reserve pit. Bar plots for diesel oil analysis shown in Figure 5 were clearly different from waste pit samples and supported the conclusion that diesel engine oil was not the only source of hydrocarbons in the pit.

In a final site (C), samples were drawn from a reserve pit that had been dewatered in anticipation of last stages of reclamation. From visual inspection, the reserve pit contained principally shale cuttings with no visible amounts of drilling mud. The working pit contained residual drilling mud. The samples labelled shale cutting and mud respectively had chemical composition the same as those in Site B but absolute concentrations for hydrocarbons and PAH were very low as shown in Table 1. The sample from the working pit was only a fraction of that for other mud samples at Site A and the shale cuttings were about the same magnitude as the sediments at Site B. This was consistent with the contention that drilling muds rather than cuttings or fluids contribute (and concentrate) the bulk of hydrocarbons and PAH in waste pits from natural gas exploration. The blow pit was effectively baseline levels for organic compounds. The sampling and transportation blank was a sample of soil near Site C which was also near a major thoroughfare. Trace amounts of PAH may have originated with aerial deposition of particulate matter from combustion engines of nearby traffic.

Partition of PAH in reserve pit phases

Some communication chemically between separate phases at Site B was expected and hydrocarbon partitioning between aqueous solution and sediment should be governed by thermodynamics at the molecular level and by kinetics of mechanical events in the pit. Partition ratios for PAH from Table 1 were calculated for sediment/water and hydrocarbon film/water and are listed in Table 2. Partition ratios for sediment/water at windward and leeward locations in the pit were dramatically different even though the concentrations in

Table 2 Calculated distribution ratios for PAH in reserve pit under current use (Site B) and from produced water pits

	Sediment/water (1)		Oil/water (2)			
	Windward side	Leeward side	Site B	Cuba	Archuleta	Flora Vista
Compound						
Naphthalene	2.7	2.5	2.3	190	48	160
C1-Naphthalene	0.24	12	6	140	56	220
C2-Naphthalene	0.26	25	11	1200	76	240
C3-Naphthalene	0.19	32	51	1100	71	160
C4-Naphthalene	[a]	36	15	[a]	[a]	[a]
Fluorene	0.274	12	69	330	79	94
C1-Fluorene	0.17	9	58	220	75	94
C2-Fluorene	0.40	11	74	260	140	99
C3-Fluorene	0.29	17	74	380	130	140
C4-Fluorene	0.40	9.4	65	[a]	[a]	[a]
Anthracene	1.4	15	120	650	120	32
C1-Anthracene	1.6	13	120	830	120	63
C2-Anthracene	1.9	13	150	540	89	59
C3-Anthracene	2.9	24	270	550	140	46
C4-Anthracene	5.3	7.7	180	[a]	[a]	[a]
Pyrene	4.3	5.9	35	1800	50	32
C1-Pyrene	7.0	10	35	370	66	110
C2-Pyrene	7.5	4.9	37	220	86	110
C3-Pyrene	7.6	4.4	36	270	69	120
C4-Pyrene	20	0.9	5	[a]	[a]	[a]

1) Calculated for samples from Site B the only reserve pit in active use during sample collection.

2) Calculated for hydrocarbon film/water ratios from produced water pits reported by Davani, *et al.*, reference 2.

[a] Indicates data were not available for these compounds.

water were about the same. The windward side of the pit is where the heavy shale cuttings fell to the pit bottom while suspended muds were carried to the leeward side before deposition. A clear progression in distribution ratios was: film > leeward side (muds) > windward side (shale cuttings) with some small inconsistencies for certain compound groups. Since distribution will be governed by aqueous solubilities (affected by total soluble matrix) in competition with adsorption of solids, intermolecular forces should be expected to influence ratios. Trends appear within each set of phases but irregular patterns preclude broad conclusions. These were an uncontrolled set of samples and the central element of this finding is that pits can be heterogeneous at a macroscopic and molecular level. The differences in a pit may correspond to mechanical mixing in Site B and such differences in a single site should be considered in future strategies for sampling of pits with such large dimensions.

In Table 2, distribution ratios are shown for PAH between brine water and hydrocarbon films in produced water pits. These values were taken from an earlier study published in this Journal[2] and were calculated for comparative purposes. All values including reserve pit calculations showed agreement within a factor of 10 generally despite differences in absolute concentrations and possibly differences in original content. Actually, the degree to which the water has been modified by hydrocarbons other than PAH may alter or effect phase distribution ratios. Clearly, these data are preliminary attempts to describe complex physical and chemical processes that are completely undescribed at present. Determination of distribution ratios under controlled conditions is necessary for preparation of an improved model.

Precision in isotope dilution GC/MS

Although PAH composition of wastes have been based on isotope dilution GC/MS in this laboratory during the last two years, precision and errors have not been documented. Typically, relative standard deviations in sample preparation in prior studies were as large as 60% despite attempts to refine a simple, rapid, three-state technique to isolate PAH.[4] Use of external calibration thus may cause serious quantitative errors even for samples prepared and analyzed by the same person with identical instrumentation. In

Table 3 Comparison of precision for PAH determination by GC/MS using isotope dilution or external calibration

Per cent relative standard deviation[a] (Isotope dilution-external calibration)				
Naphthalene	C1-Naphthalene	C2-Naphthalene	C3-Naphthalene	C4-Naphthalene
3.4–3.6	12–10	17–17	21–19	20–18
Fluorene	C1-Fluorene	C2-Fluorene	C3-Fluorene	C4-Fluorene
5.6–19	7.7–17	27–21	18–14	23–10
Anthracene	C1-Anthracene	C2-Anthracene	C3-Anthracene	C4-Anthracene
2.9–11	1.9–12	3.4–11	13–15	13–7.8
Pyrene	C1-Pyrene	C2-Pyrene	C3-Pyrene	C4-Pyrene
2.8–14	5.2–5.7	17–13	6.1–11	6.1–9.7

[a] Based on 5 replicate determinations of the diesel oil sample listed in Table 1. The external calibration technique showed concentrations typically 1–10 mg/L lower than those from the isotope dilution method.

Table 3, standard deviations from determinations of PAH in diesel oil are shown both for isotope dilution and for external calibration. For regular and C1-substituted PAH which may be somewhat volatile, external calibration showed greater imprecision than isotope dilution methods. Even so the worse deviation was 19% RSD for fluorene and showed that reproducibility was reasonably good at 1–100 ppb level. However, these trends were not observed for PAH with C3 and C4 substitution perhaps since these are less affected by volatilization losses. The regular deuterated PAH were used in quantification of these PAH and isotope dilution was actually worse than external calibration since the d-PAH and not the C4-PAH may have been more susceptible to variations in sample preparation. These figures suggest generally imprecision of 2–20% RSD for trace PAH determinations but matrix effects from dramatically different samples and accuracy were not considered. For example, in recovery of PAH from hydrocarbon laden sediments, the amount and type of hydrocarbons in the soil might alter recovery efficiences. These variables must be addressed using rigorous assured or synthetically prepared samples and was beyond the scope of the present study.

CONCLUSIONS

Wastes in reserve pits contain complex mixtures of hydrocarbons including PAH at concentration levels that can be equal or greater than any other waste pits in the production of natural gas. In addition to chemical composition of wastes initially at the effluent source, physical parameters of large pits should be considered as factors when chemical models of these waste pits are constructed. Calculated distribution ratios directly illustrate that even within a single pit, composition differences in sediments can exist and complicate certainty or environmental conclusions from a single grab sample. A continuous study of a single pit to assess these influences is recommended. Isotope dilution mass spectrometry can be used for quantification of PAH at 1 to 100 ppb levels with relative standard deviations of 2–20% using simple prefractionation techniques designed for large throughput of samples.

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