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Polycyclic Aromatic Hydrocarbons in Soil at Groundwater Level Near an Earthen Pit for Produced Water in the Duncan Oil Field

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Hydrocarbons, polycyclic aromatic hydrocarbons (PAH), and alkylated PAH with two to four rings were found in soil at groundwater level down-gradient from an earthen waste disposal pit for produced water, in the Duncan Oil Field of NW New Mexico. Depth to groundwater was only 1 to 1.5 m in this flood plain of the San Yuan River. Complex mixtures of hydrocarbons with carbon numbers from 12 to 30 were detected in solvent extracts of soil samples collected 25 m and 50 m down-gradient from the waste pit. The concentration of total extracted organic mass was as large as 500 ppm at 25 m, but a reduction in concentration of 90 to 100% was seen for samples at 50 m on the same axes. No similar contamination was found in soil samples located on axes drawn up-gradient from the waste pit. Concentrations for total PAH in soil at 25 m distance from the waste pit were as large as 4900 ppb and 37 ppb at 50 m on the same axis. Detectable but trace amounts of PAH in samples up-gradient from the pit may be evidence for a secondary dispersion mechanism such as flooding of the region. While groundwater contamination with organic compounds from an earthen waste disposal pit has been demonstrated here, mobility, partition, and fate of PAH in complex mixtures in a soil/groundwater system remain undetermined.

INTRODUCTION

In production of oil and natural gas, large amounts of wastewater called produced water are generated at the wellhead.^{1,2} Alkanes,

aromatic hydrocarbons (benzenes), and polycyclic aromatic hydrocarbons (PAH) have been found in complex mixtures in produced water from natural gas wells throughout the San Yuan basin of northwest New Mexico.³ However, many of these same wells, while classified as natural gas wells, also produce oil or a hydrocarbon condensate which is recovered in a phase separator and stored for later refining. In waste disposal pits which are located near wellheads and are used to store produced water, aqueous waste may be covered with a hydrocarbon film with thickness from 0.5 to 3 cm. The total concentration of PAH can be as great as 15 ppm in the waste pit water and 150 ppm in the hydrocarbon film.³ Although earthen waste disposal pits were intended for evaporation of the produced water, presence of the hydrocarbon film covering the aqueous phase can lead to decreased rate of evaporation and as much as 93% of produced water can migrate into groundwater.⁴ Lining the earthen pits with clay has been used to decrease permeation into nearby soils, but, these liners may degrade with loss in retaining capacity.⁵ Since groundwater can be found at depths as low as 1.5 m in flood plains of the San Yuan River, migration of aromatic hydrocarbons and PAH from earthen unlined waste pits into groundwater has become a serious concern.

Migration of produced water from waste pits into aquifers has been determined for inorganic compounds or salts.¹ However, contamination of groundwater with aromatic hydrocarbons from produced water in a waste pit from oil or natural gas production has been documented only recently.⁶ Groundwater near an unlined waste pit for an oil well in the Duncan Oil Field was characterized for purgable organic compounds including alkane and aromatic hydrocarbons. Contamination was found in groundwater from test pits dug on the downside of a hydraulic gradient, but no contamination was detected in groundwater up-gradient from the same pit. Volatile compounds, such as benzene, in the produced water were largely undetected in groundwater at 25 m from the pit and were presumably lost through volatilization. In contrast, less volatile compounds such as C₂ to C₄ alkylated benzenes were detected in groundwater at distance of 50 m down-gradient. In that initial study, larger solvent-extractable alkanes seemed to have limited mobility likely from an adsorption mechanism.

Groundwater and associated soil may possibly exist in a chemical

equilibrium for partially soluble organic compounds. Certainly, partition onto soil particularly for the larger organic compound including PAH should be favored. The objective for the present work was to determine if the pattern or distribution of PAH in soils, collected at groundwater level, was comparable to those for aromatic and aliphatic hydrocarbons found in the groundwater from the same waste pit. The intent was to determine if PAH in an actual environmental circumstance could persist and migrate despite available pathways for attenuation such as adsorption and biodegradation.⁷⁻⁹

EXPERIMENTAL

Collection and treatment of samples

A description of the study area and procedures for collection of each sample has been given in detail⁶ and the location of numbered test wells is shown in Figure 1. Samples of soil were collected at groundwater level which was at depths of 1.07 m up-gradient and 1.52 m down-gradient from the waste pit. Samples of soil were collected using a small spade, placed in glass jars with screw cap lids and Teflon liners, stored on ice and returned to the laboratory. The amount of soil was about 1.2 kg and was collected from the zone of darkly stained earth. Samples were air dried at 25°C for five days and 50 g of soil were extracted in a Soxhlet apparatus using 200 mL of benzene (distilled in glass grade, Burdick and Jackson, Co. Muskegon, MI) for 48 h. Based on prior findings,¹⁰ extraction conditions were suitable for exhaustive removal of soluble organic compounds. Four deuterated PAH were added to extracts as internal standards³ for later detection and determination of efficiency for sample handling and storage. The extracts were condensed to 2 mL in a rotary evaporator and adjusted to a final volume of 1 mL using a nitrogen gas stream. The extracts were separated into two fractions using a class separation method with neutral alumina adsorption chromatography^{11,12} aliphatic compounds were recovered in a hexane elution of the alumina column while PAH were removed in a benzene elutant. Fractions were reduced in volume to 500 μ L using rotary evaporator and nitrogen gas. Condensed extracts were analyzed using capillary gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring

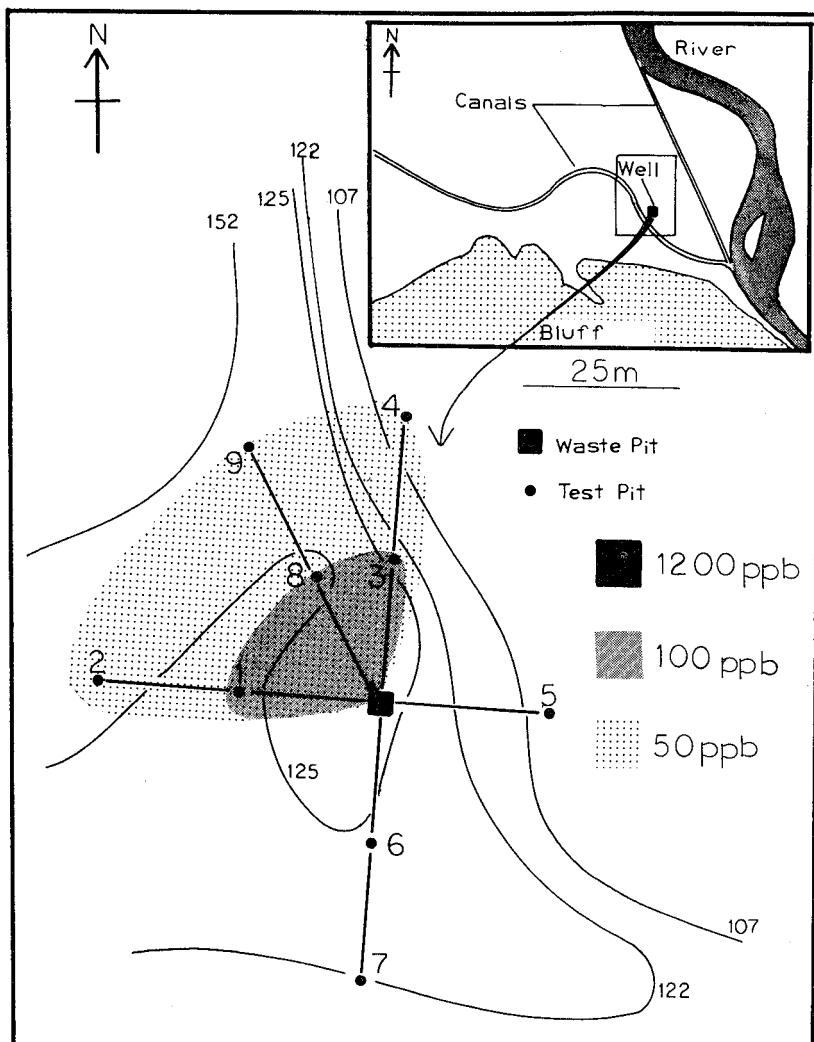


FIGURE 1 Drawing of Waste Pit, Test Pits, and Depth to Groundwater in the Duncan Oil Field (insert). Depth to groundwater is shown in cm next to contours. An estimated hydraulic gradient would extract from shallower to deeper groundwater. The crosshatched region is for concentration of purgable aromatic hydrocarbons in a groundwater plume aligned with the estimated hydraulic gradient. Concentrations of PAH in soil at groundwater level are given in Table 1 were found and followed a comparable pattern. The canal was not in active use and was dry.

(SIM). A mixture of PAH (naphthalene, biphenyl, fluorene, anthracene, and pyrene) with a Kovats Retention Index Standard (C₁₀-C₃₄) was made at three concentrations, prefractionated, and analyzed under identical conditions with those for the sample extracts to establish a working curve, based on complete recovery efficiency in all steps except extraction. All procedure blanks were free of detected contamination.

Instrumentation

A Hewlett-Packard model 5880A GC 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 GC/MS was equipped with jet separator, model 5885M disk drive, model 7225B X-Y plotter, automated splitless injection port and 10 m DB-5 fused silica capillary column. Chromatographic conditions were identical for scanning GC/MS, SIM analysis, and GC-FID analysis. 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 min; electron multiplier voltage, 1400; and MS detection threshold, 10 linear counts. Mass spectrometer conditions for SIM analyses were: electron multiplier voltage, 1600 V; SIM window size, 0.2 amu; integrate sensitivity, 0.05; area threshold, 10; smoothing factor, 1; selected polycyclic and alkylated polycyclic aromatic hydrocarbons with ions chosen for SIM analyses are listed in Table 1. Sample volumes in GC and GC/MS analyses were 0.5 to 2 μ L delivered using a model No. 701N 10 μ L syringe (Hamilton Co., Las Vegas, NV). Conditions other than these will be noted as necessary.

RESULTS AND DISCUSSION

General evaluation

In the study area shown in Figure 1, estimated hydraulic gradients

were superimposed on locations of the earthen waste pit and test pits. Additionally, plumes for purgable hydrocarbons in the groundwater determined in a previous study are depicted as cross-hatched areas. For purgable compounds in groundwater, the plume from the waste pit was aligned with the expected direction of flow for groundwater. Soil collected at test pit nos. 1 to 4, 8, and 9, all had a discernable hydrocarbon odor while soil in pits 5 to 7 was free of such odors. Moreover, in pits 1, 3, and 8 (located at 25m from the waste pit) in the purgable hydrocarbon plume, the soil samples had a dark brown/black hue. In contrast, samples up-gradient from the waste pit were light-brown without dark stains. This preliminary observation was consistent with prior study where a hydrocarbon sheen and odor was found in the groundwater down-gradient but not up-gradient at this same waste pit.⁶ The dark stain in the soil was preliminary support that some hydrocarbons, had migrated through the groundwater/soil system at 1 to 1.5m in depth.

Instrumental analysis

Results from GC/FID analysis of soil extracts are shown as chromatograms in Figure 2 for several test pits as identified in Figure 1. For pits at 25m 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 12 to 30 in carbon numbers. This range of carbon numbers was consistent with the possible presence of two to four ring PAH compounds. Moreover the chromatographic pattern included an unresolved 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 and that detected at very low concentrations in some pits 50m downgradient from the waste pit. Soil from test pit no. 4 was free of extracted hydrocarbons as shown in Figure 2 (top plot).

Additional information on sample composition was acquired using GC/MS with SIM analysis. The SIM plots shown in Figures 3 and 4 were for the soil extract from test pit no. 1 and include ion traces for

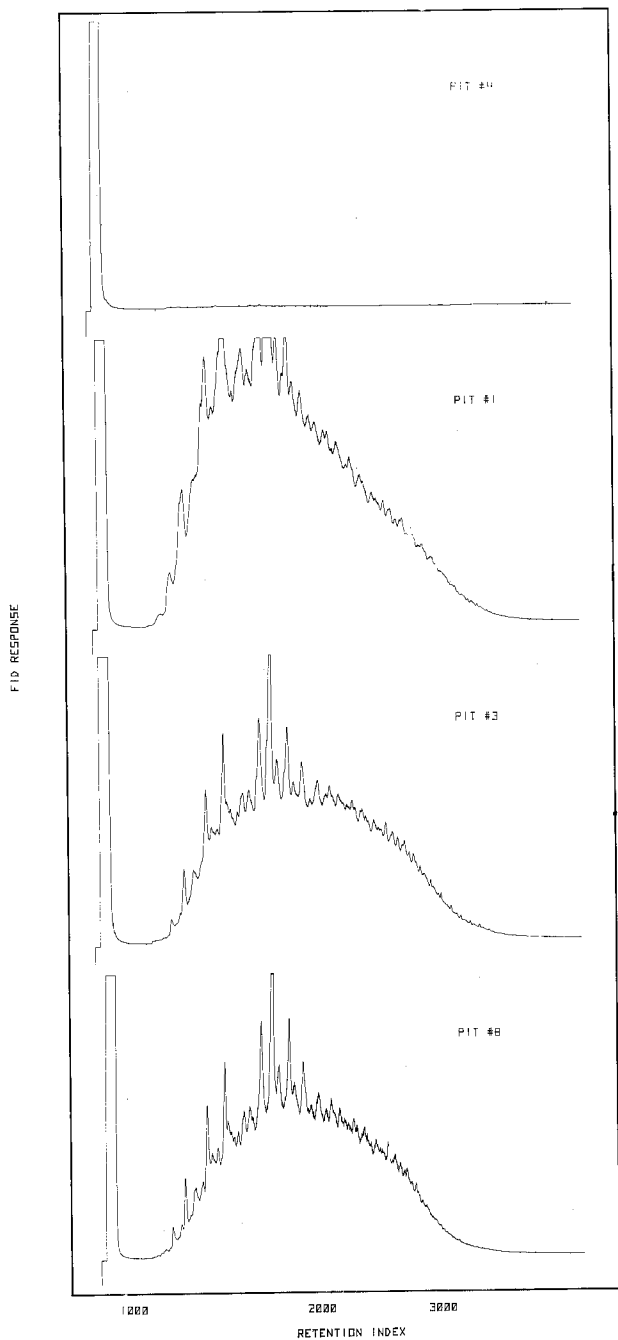


FIGURE 2 Plots of Detector (FID) Response versus Kovats Retention Index from GC Analysis of Soil Extracts. Pit numbers correspond to assignments shown in Figure 1. Results may be directly compared as attenuation and concentration factors were identical in each analyses.

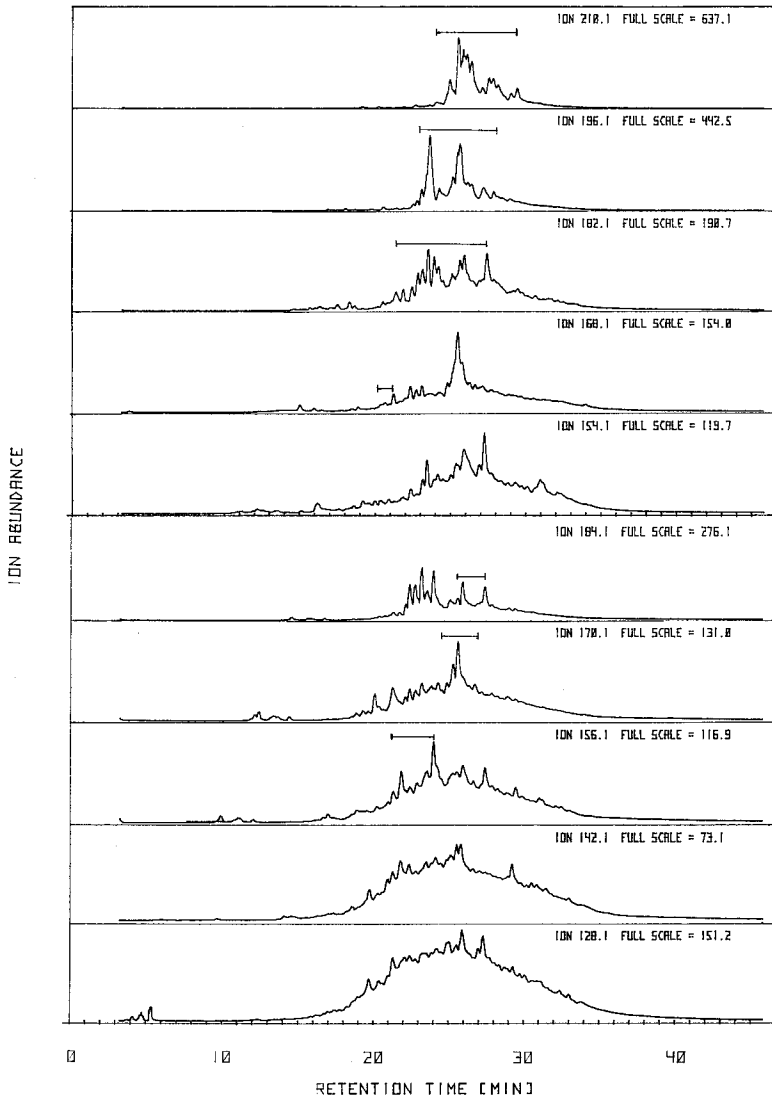


FIGURE 3 Plots of Ion Abundance versus Retention Time from SIM Analysis of PAH Fraction for Soil Extract (Test Pit No. 8). The retention time range for authentic standards or from scanning mass spectrometry identification is shown as horizontal bars. Since alkylated PAH congeners can have different number of isomers based upon length of carbon chain, the length of bars was not the same in every SIM plot.

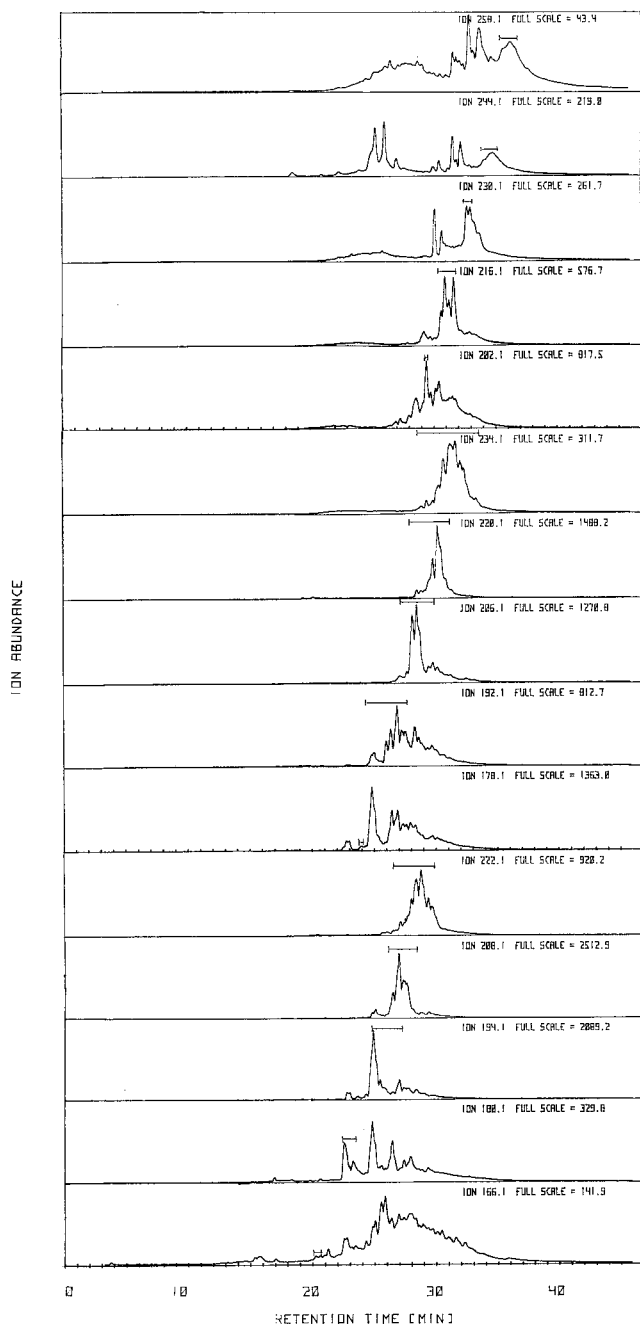


FIGURE 4 SIM Plots for PAH and Alkylated PAH. See caption for Figure 3.

naphthalene (m/z 128), biphenyl (m/z 154), fluorene (m/z 166), anthracene (m/z 178), pyrene (m/z 202), and C_1 to C_4 alkylated congeners of these PAH. While some SIM plots such as the C_3 -alkylated fluorenes showed molecular ion peak within the known range of retention times, other ion traces showed secondary (interfering) peaks in the same plots. These interferences were due to ions from fragmentation of higher alkylated PAH with the same or analogous 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 1. The greatest concentration for total PAH were in test pit nos. 1, 3, and 8 as expected since these pits were pits closest to the waste pit and were down-gradient at a distance of 25 m. The concentrations for individual PAH ranged from not detected (ND) to as much as 1900 ppb for C_4 -alkylated biphenyls in test pit no. 1. Total concentrations of PAH and C_1 to C_4 -alkylated PAH in these three pits were comparable from 2003 to 4860 ppb. However, not all possible PAH were detected using these SIM conditions and other PAH not selected for SIM analysis could have been present. Therefore, reported concentrations may be low for a complete total PAH content. In pits 2, 4 and 9 at 50 m in the purgable hydrocarbon plane, concentrations of total PAH in soil were 22 to 370 ppb. But concentration reductions for certain individual PAH in soil from 25 to 50 m was dramatic and as large as 150 fold or greater.

The presence of detectable levels of PAH in soil from up-gradient pits is inconsistent with prior findings in which groundwater from the same pits was free of detectable amounts of purgable hydrocarbons.⁶ Nevertheless, low levels of PAH were detected in extracts for test pit nos. 5, 6, and 7 although differences in concentration between these samples may not be significant. Apart from natural background concentrations for PAH, several mechanisms may be used to account for these findings including back diffusion 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 spring. For example, less than two months after these samples were collected, snow melt in watershed for the San Yuan 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 pit and dispersed in

TABLE I
Concentrations ($\mu\text{g}/\text{Kg}$)^a of PAH in Soil Samples Collected at Groundwater Level as shown in Figure 1.

Compound	Test pit number								
	1	2	3	4	5	6	7	8	9
Naphthalene	128.1	ND ^b	ND	ND	ND	ND	ND	ND	ND
C ₁ -Naphthalenes	142.1	ND	ND	ND	ND	ND	ND	ND	ND
C ₂ -Naphthalenes	156.1	240	ND	ND	0.68	8.0	ND	ND	ND
C ₃ -Naphthalenes	170.1	230	9.1	9.8	ND	3.9	6.1	530	1.0
C ₄ -Naphthalenes	184.1	18	39	80	10	29	31	280	7.2
Biphenyl	154.1	8.4	ND	7.9	2.8	ND	ND	13	ND
C ₁ -Biphenyls	168.1	32	ND	15	ND	2.3	ND	18	0.18
C ₂ -Biphenyls	182.1	830	0.53	40	6.5	5.9	3.1	680	0.62
C ₃ -Biphenyls	196.1	1300	11	70	10	16	7.3	730	0.47
C ₄ -Biphenyls	210.1	1900	0.92	750	230	37	83	1100	ND
Fluorene	166.1	2.9	ND	0.66	0.032	ND	ND	0.52	0.076
C ₁ -Fluorenes	180.1	4.9	ND	3.9	0.25	1.2	0.61	13	0.10
C ₂ -Fluorenes	194.1	68	12	38	0.78	ND	2.85	120	0.22
C ₃ -Fluorenes	208.1	110	89	130	19	5.5	18	170	11
C ₄ -Fluorenes	222.1	53	4.5	88	0.42	0.72	0.43	80	0.10
Anthracene ^c	178.1	0.51	ND	0.25	0.068	0.16	0.14	0.10	0.12
C ₁ -Anthracenes	192.1	0.0020	0.15	7.1	0.034	0.20	0.088	0.058	0.032
C ₂ -Anthracenes	206.1	19	5.4	20	0.70	0.23	1.4	22	0.39
C ₃ -Anthracenes	220.1	24	0.85	26	0.078	0.084	0.21	27	0.014
C ₄ -Anthracenes	234.1	8.3	2.3	10	0.44	0.55	0.57	9.8	0.15
Pyrene	202.1	2.8	0.056	12	0.030	0.072	0.024	1.6	0.056
C ₁ -Pyrenes	216.1	6.2	0.013	33	0.0080	0.034	0.017	5.2	ND
C ₂ -Pyrenes	230.1	1.4	0.39	17	0.033	0.042	0.056	4.3	0.010
C ₃ -Pyrenes	244.1	0.41	ND	5.6	ND	0.014	ND	0.80	ND
C ₄ -Pyrenes	258.1	0.19	0.074	6.7	ND	0.012	ND	0.20	ND
Summed concentrations	4900	270	2000	370	59	89	140	3400	22

^aSatisfactory to two significant figures.

^bND = not detected.

^cIncluding phenanthrene.

the flood plain. Since another waste pit was located up-gradient by several hundred meters from the study waste pit, contamination of soil through prior flooding was possible. However, 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 should be considered an average producer of wastewater. In earlier studies, core samples were taken from earthen waste pits from natural gas production and PAH were found at depths up to 1.8 m from 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 at 1.8 m in depth. Thus, movement of produced water from an earthen waste pit to shallow groundwater was predicted to be extensive and later was confirmed for purgable aliphatic and aromatic hydrocarbons.⁶ 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. Unknown variables in this study were possible degradation of PAH by bacteria and accurate hydraulic information over a year period. In this study, only the distribution and not the movement of PAH in soil near groundwater was demonstrated. In order to measure movement of PAH, permanent wells and extended monitoring of soil and water samples are needed.

Acknowledgements

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References

1. D. W. Miller, *Waste Disposal Effects on Ground Water* (Premier Press, Berkeley, California, 1980), 294–321.
2. J. S. Fryberger, *Groundwater* **15**, 155 (1975).
3. B. Davani, J. A. Dodson, J. L. Gardea and G. A. Eiceman, *Intern. J. Environ. Anal. Chem.* **20**, 205 (1985).
4. F. G. Baker and C. M. Bredecke, *Ground Water* **21**, 317 (1983).
5. W. J. Green, G. F. Lee and R. A. Jones, *Impact of Organic Solvents on Integrity of Clay Lines for Industrial Waste Disposal* (1979), PB-81-213423.
6. G. A. Eiceman, J. T. O'Connon, M. Zaman, C. Sheuy and D. Earp, *Intern. J. Environ. Anal. Chem.*, (1985), accepted for publication.
7. R. C. Sims and M. R. Overcash, *Residue Reviews* **88**, 1–68, (Springer-Verlag, N.Y., Inc. WA, 1983).
8. W. A. Pettyjohn and A. W. Hounslow, *Ground Water Monitoring Review* 41–47 (Fall, 1983).
9. M. J. Newson, *Ground Water Monitoring Review* 29–36 (Spring, 1985).
10. B. Davani, J. Ingram and G. A. Eiceman, *Water, Air, and Soil Pollution* (in press).
11. D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong and D. L. Vassilaros, *Anal. Chem.* **53**, 1612 (1981).
12. G. A. Eiceman, B. Davani and J. Ingram, *Environ. Scien. and Technol.* (accepted for publication).