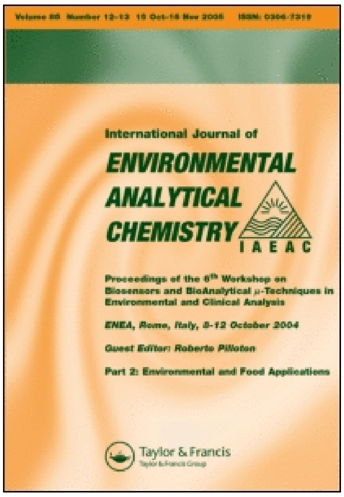

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Discharge Water from Hydrostatic Testing of Natural Gas Pipelines as Source of PAH Loading into Aquatic Environments

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A complex mixture of polycyclic aromatic hydrocarbons (PAH) and alkylated polycyclic hydrocarbons has been identified and quantitatively determined in discharge water from hydrostatic testing (DWHT) of natural gas pipelines. The PAH were quantified in water samples drawn from throughout dewatering procedures using selected ion monitoring of particular molecular ions referenced to deuterated PAH internal standards with capillary GC/MS techniques. Over 100 PAH or alkylated PAH were detected in portions of DWHT using solvent extraction for prefractionation. Concentration of total PAH content showed a clear decreasing trend throughout dewatering from a high value of 32,000 ug/L at start to less than 8,000 ug/L toward end of discharge. This trend was parallel with bulk hydrocarbon concentrations in the aqueous samples. Consequences for environmental release and disposal practices are discussed based on these results.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) and release, movement, and fate of PAH in the total environment have been the subject of intense study for nearly fifteen years.[1–4] While generation of PAH in atmospheric environments is related largely to combustion phenomenon,[5,6] release of this class of pollutants into aquatic environments is less well defined apart from activities of oil production and refinement.[7,8] In earlier work, a complex mixture of volatile organic compounds including alkylated disulfides, alkylated benzenes, and alkanes was found in samples of discharge water from hydrostatic testing (DWHT) of natural gas pipelines. The objective of this present study was to evaluate further several of these same samples as potential source of PAH in surface and ground water especially in regions where no apparent oil-based activities are found but where DWHT is released.

Hydrostatic testing of natural gas pipelines is a regular if not frequent operation used in cleaning and testing both old and new pipelines. Neither the magnitude of these operations nor environmental impact from release of these waters untreated or otherwise has been addressed in particular for toxic organic compounds including PAH. In hydrostatic testing, pipelines are filled with water, water is pressurized using air or natural gas, and drops in pressure are monitored in order to determine presence of flaws in pipelines at specified pressures. The water used in this operation is then removed from the pipeline with the aid of a pig which also accomplishes an additional purpose of cleaning condensate from pipelines. 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 be expected reasonably to contain higher concentrations of whatever is found in the discharge water which follows from hydrostatic testing. Clear distinction must be made between old pipelines which have been in use for 2 to 15 years and new pipelines (or sections of pipeline) in which virtually no condensate from natural gas should be found. In this work, samples are studied from only old pipeline where condensate may be found depending on the purity of gas being carried.

Magnitude of water pollution from release of toxic organic compounds in untreated or poorly treated DWHT is unknown since compilations of quality of water in DWHT has been largely undocumented. However, over 1,000,000 km of pipeline main exist in the U.S. with an unknown length of branches off these mains.[7] Condensation of large molecular weight organic compounds in pipelines during transportation of gas through pipelines has been described by Katz *et al.*[8, 9] and partial chemical analysis of condensate was completed. Amongst compounds found by Katz and another group[10] were alkanes, alkenes, benzenes, substituted benzenes and certain PAH. Since many of these same compounds were seen in DWHT in earlier analyses,[11] the presence and con-concentration of PAH in DWHT seemed a reasonable next phase of analysis following preliminary screening. Results from these investigations are described below with regard to environmental impact and abatement of future pollution.

EXPERIMENTAL

Instrumentation

A Hewlett–Packard model 5880A gas chromatograph was equipped with flame ionization detector (FID), automated splitless injector, and 10 m long, 0.25 mm ID fused silica capillary column. Conditions for analyses of all samples were: initial temperature, 90°C; initial time, 2 min; oven temperature program rate, 5°C/min; final temperature, 250°C; final time, 5; injection port temperature, 270°C; FID temperature, 270°C; carrier gas, nitrogen at 30 cm/s average linear velocity; time for splitless injection 1 min; chart speed, 0.5 cm/min; area reject, 10; and threshold, 2. A Hewlett–Packard model 5995A gas chromatograph/mass spectrometer (GC/MS) was equipped with jet separator, model 9885M 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/sec; delay between scans; 0.5 s, electron multiplier voltage, 1400; and MS detection threshold, 10 linear counts. Mass spectrometer conditions for SIM analyses were: electron multiplier voltage, 1400 V; SIM fat peaks, 1; SIM window size, 0.2; integrate sensitivity, 0.05; area threshold, 10; smoothing factor, 1.000; selected polycyclic and alkylated polycyclic aromatic hydrocarbon with ions chosen for SIM analyses are presented in Table I.

Reagents and standard solutions

Dichloromethane (HPLC grade; Fisher Scientific Co., Fair Lawn,

TABLE I
Masses of ions for compounds determined using selected ion monitoring.

Compound	Mass (amu)
Naphthalene	128.1
C1-Naphthalenes	142.1
C2-Naphthalenes	156.1
C3-Naphthalenes	170.1
C4-Naphthalenes	184.1
Biphenyl	154.1
C1-Biphenyls	168.1
C2-Biphenyls	182.1
C3-Biphenyls	196.1
C4-Biphenyls	210.1
Fluorene	166.1
C1-Fluorenes	180.1
C2-Fluorenes	194.1
C3-Fluorenes	208.1
C4-Fluorenes	222.1
Anthracene	178.1
C1-Anthracenes	192.1
C2-Anthracenes	206.1
C3-Anthracenes	220.1
C4-Anthracenes	234.1
Pyrene	202.1
C1-Pyrenes	216.1
C2-Pyrenes	230.1
C3-Pyrenes	244.1
C4-Pyrenes	258.1

NJ), cyclohexane (pesticide grade; Fisher Scientific Co.), methanol (Burdick & Jackson Laboratories Inc., Muskegon, MI), and nitromethane (spectro grade; Eastman Kodak Co., Rochester, NY) were used as purchased. A mixture of deuterated PAH standards 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 concentration of 1 mg/mL for each component was obtained from MSD Isotopes (Merck Chemical Division, St. Louis, MO).

Samples

Two types of samples were analyzed in this work. The first was DWHT and only a selected number of these samples (i.e., samples taken from the start, middle, and the end of the dewatering procedures) was chosen for quantitative analyses. The specifications of these samples are given in detail by Eiceman *et al.*[11] as samples A1, A2, and A4, respectively. The second sample was condensate from laboratory supplied natural gas collected for 53 hours at the gas jet using a cold trap technique with dry ice and acetone for cooling. Flow rate of the gas was estimated as 15 L/min.

Procedure

The procedure described by Bartel *et al.*[12] was used for isolation and concentration of PAH in the samples. The procedure was modified slightly since separated waste phases were not reextracted. In addition, 5 × 100 mL nitromethane was used instead of dimethylsulphoxide (DMSO) since partition coefficients with DMSO are less favorable than with nitromethane for methyl-derivative of PAH.[12] Samples of 100 mL of DWHT and 10 mL of natural gas condensate from cold trap were spiked with 10 μL of deuterated PAH standards and extracted as described above.

RESULTS AND DISCUSSION

Discharge water from hydrostatic testing of natural gas pipelines was found upon simple solvent extractions and direct analysis of condensed extracts using gas chromatography, too complex a mixture even for moderate resolution although high resolution capillary columns were used. The presence of saturated, unsaturated, and branched aliphatic hydrocarbons was evident in GC/MS determination in 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 suitable determination of PAH. Thus, prefractionation of extracts was necessary despite additional handling of samples, glassware, and solvents. While several prefractionation schemes are available, an extensive solvent extraction technique was used since the samples were so complex and since only readily available glassware and 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 were 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% of the mass associated with the hydrocarbon hump was reduced as determined through comparison of GC analyses of PAH fraction and those for unfractionated extract of DWHT sample. However, losses in extraction efficiency through use of a multistep extraction procedure were also substantial and range in recovery efficiencies were determined for individual PAH as: naphthalene, 29–100%; anthracene, 21–90%; fluorene, 20–92%; and pyrene, 45–109%. These large variations are 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 PAH of same structure. The absence of the hydrocarbon hump in PAH fraction from a DWHT sample with characteristics largely oil in nature is shown in Figure 1. Despite extensive prefractionation, a chromatogram with over 30 to 50 resolved components is apparent and suggests presence of complex mixture of PAH. Nevertheless, peak shape was good and resolution was 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 2 as a SIM plot.

In Figure 2 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 gaslines used to supply our laboratory was extracted and analyzed with identical procedures. Moreover, samples were analyzed using GC/MS for SIM quantification over a period of two days in order to eliminate variations in column resolution and mass spectrometer performance toward more reliable intersample comparisons. Results from quantification of PAH and alkylated PAH in these samples are given in Table II and illustrated in Figures 3 to 5. In Figure 3, a SIM plot is

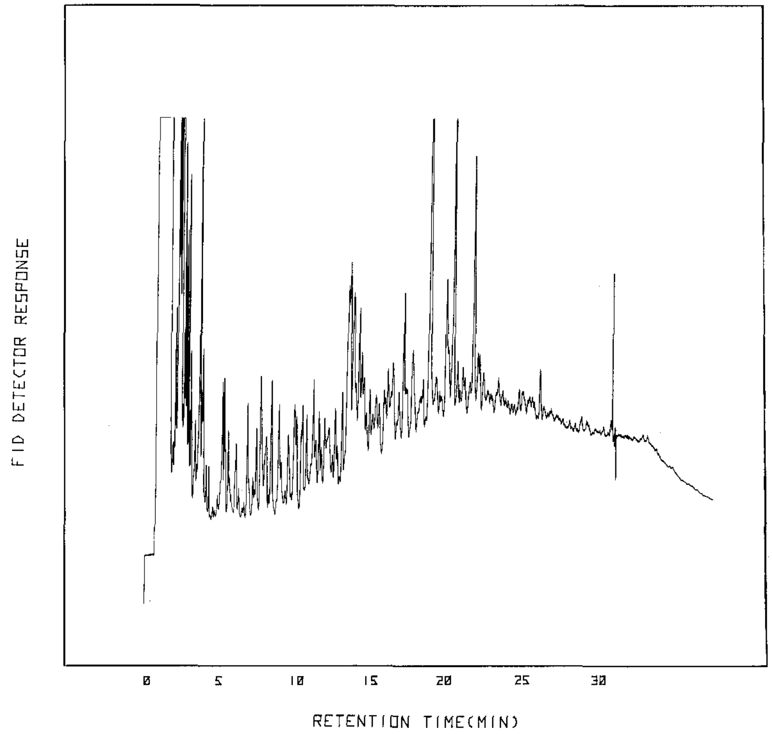

FIGURE 1 Chromatogram from GC-FID analyses of condensed PAH isolated fraction of DWHT sample A1.

shown for naphthalene and alkylated naphthalenes with C1 to C4 substitutions. 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 II. Apart from the regular, C1 and C2 species, not all possible isomers were detected through either incomplete resolution or absence of particular isomers. In Figures 4 and 5, SIM plots for other PAH and alkylated PAH are shown only for comparison to Figure 3. Figures 3 to 5 were all taken from analyses of the DWHT sample which was most oily in appearance and which also coincided with the start of dewatering operations with this pipeline. All other samples of DWHT and the laboratory-collected natural gas condensate showed

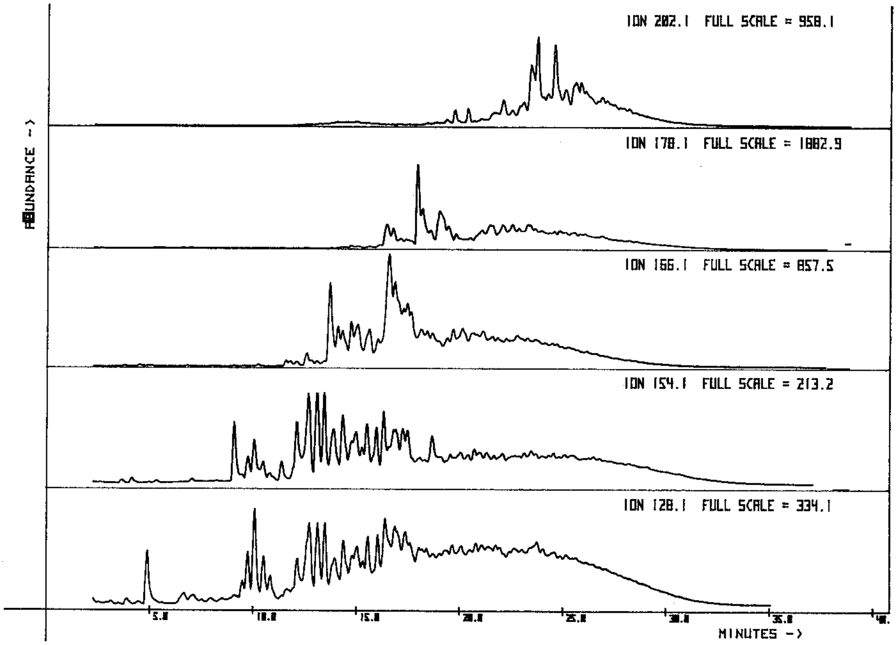

FIGURE 2 Results from SIM analyses Using GC/MS of DWHT sample A1 for PAH. a. naphthalene, 128 amu; b. biphenyl, 154 amu; c. fluorene, 166 amu; d. anthracene, 178 amu; and e. pyrene, 202 amu.

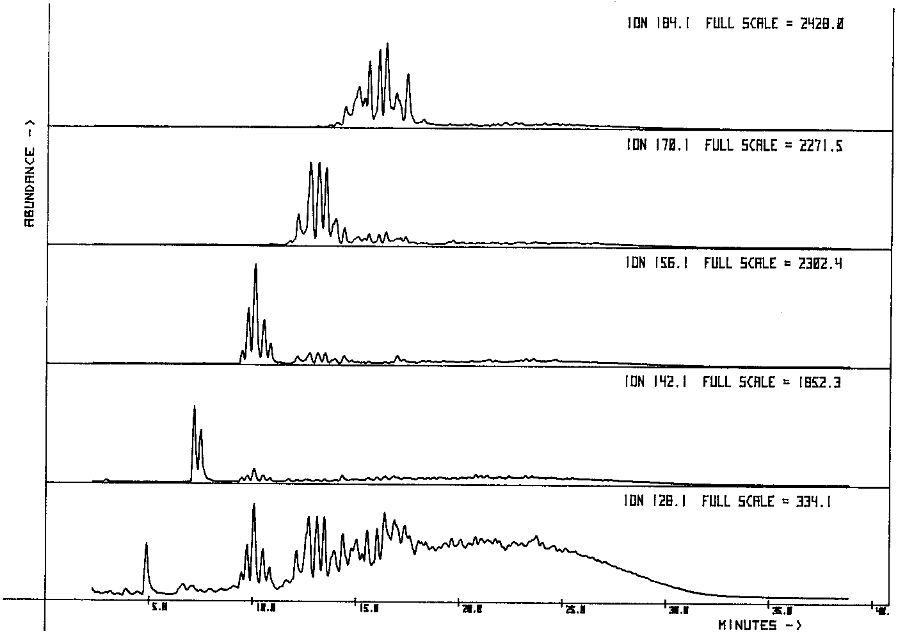

FIGURE 3 SIM plots for Naphthalenes in DWHT sample A1.

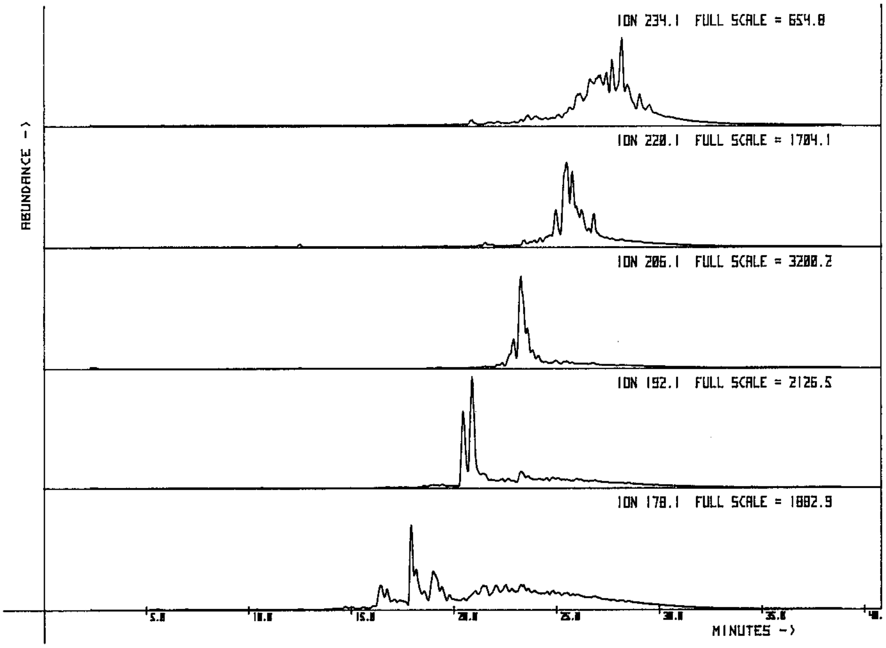

FIGURE 4 SIM plots for Fluorenes in DWHT sample A1.

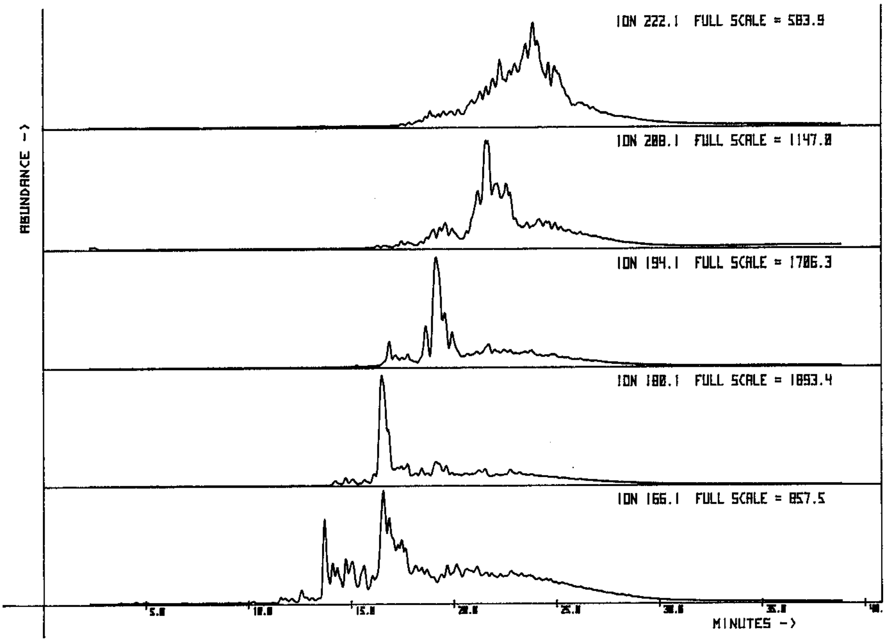

FIGURE 5 SIM plot for Anthracenes in DWHT sample A1.

TABLE II

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.

Compound	Maximum no. of isomers detected[b]	Concentration (ug/L)[a]			Natural gas[a] (μg/m^3)
		A1	A2	A4	
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[c]	1	120	78	540	12
C1-Biphenyl	3	250	78	160	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	100	7	33	2.1
C1-Fluorene	2	1,100	18	17	1.7
C2-Fluorene	4	2,900	46	36	2.5
D3-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

[a] Data only satisfactory to two (2) significant figures.

[b] These numbers may vary slightly based upon resolution and assignment of identity.

[c] Quantified versus naphthalene. All others quantified versus deuterated PAH of same structure.

similar complexity but at different concentrations. Confirmation of identity of PAH was through use of internal radiolabelled standards which had the same retention properties as unlabelled PAH from 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 GC/MS of the same samples. 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-15 amu ion. Amounts of these compounds in the PAH fraction as seen in Figure 1 were sufficient to collect satisfactory mass spectra which were matched favorably with standard spectra in the EPA/NIH mass spectral data base. The values of PAH concentrations in these water samples followed a regular trend as seen in Figure 6 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 on the water phase as the composition of this phase varied from largely oil to largely water in content. No similar pattern in concentration was seen earlier with volatile compounds which had uniform concentrations for the same samples drawn from throughout dewatering.[11] Differences in concentration gradients for PAH versus volatile compounds is 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 are for a single pipeline test from a used pipeline, few general conclusions can be made. However, if these patterns are seen in other discharges several consequences for environmental impact and engineering solutions may exist. These include: (a) single grab samples or composite samples may yield skewed characterization of environmental loading from release of DWHT; (b) the discharge which may pose greatest impact to environment may constitute only a fraction of total volume with respect to PAH and waste treatments schemes should be designed to address this feature; and (c) release of these waters unabated into unlined holding ponds or directly into aquatic environments will result in contamination similar to oil spills[13] or off-shore oil platforms. However, these sites for pollution may occur in locations well-removed from oil production and refinery activities.

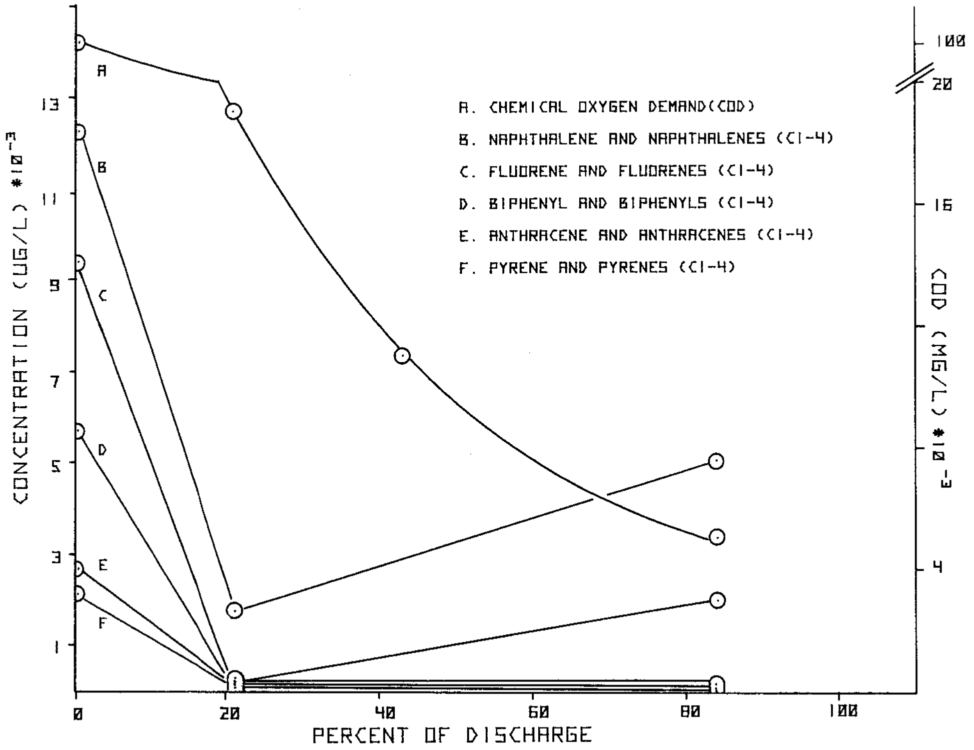

FIGURE 6 Plots of concentrations of groups of PAH and COD versus volume percent of discharge.

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