

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 074-0188

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1. AGENCY USE ONLY (Leave blank)**2. REPORT DATE**

1995

3. REPORT TYPE AND DATES COVERED

Proceedings of International Symposium Feb. 22-24, 1995

4. TITLE AND SUBTITLE

The Influence of PAH Concentration and Distribution on Real-Time In-Situ Measurements of Petroleum Products in Soils Using Laser Induced Fluorescence

5. FUNDING NUMBERS

N/A

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8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

SERDP
901 North Stuart St. Suite 303
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

N/A

11. SUPPLEMENTARY NOTES

Proceedings of an Air and Waste Management Association International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, NV, pp.837-862, 22-24 February 1995. This work was supported in part by Naval Facilities Engineering Command. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.

12a. DISTRIBUTION / AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 Words)

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Discrete soil samples collected from SCAPS boreholes were extracted and analyzed for total petroleum hydrocarbons (TPH), by gas chromatography with flame ionization detection (GC/FID), and 16 parent and over 100 alkyl substituted PAH compounds by gas chromatography with mass spectrometry detection (GC/MS). This method provides a basis for evaluating the relationship between TPH and PAH concentrations in the soil samples and laser induced fluorescence measurements from the soil borings.

14. SUBJECT TERMS

SERDP, LIF, SCAPS, hydrocarbon, GC/MS, GC/FID, principal component analysis, total petroleum hydrocarbons

15. NUMBER OF PAGES

27

16. PRICE CODE

N/A

17. SECURITY CLASSIFICATION OF REPORT

unclass

18. SECURITY CLASSIFICATION OF THIS PAGE

unclass

19. SECURITY CLASSIFICATION OF ABSTRACT

unclass

20. LIMITATION OF ABSTRACT

UL

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ABSTRACT

Real-time laser induced fluorescence (LIF) *in situ* measurements of soil samples provide a reliable and cost-effective screening tool for hydrocarbon site assessments. The site characterization and analysis penetrometer system (SCAPS), is a truck-mounted cone penetrometer probe modified with a sapphire window and connected to a laser by fiber optics. The pulsed nitrogen laser 337-nm excitation source induces fluorescence in polynuclear aromatic hydrocarbons (PAHs), which are present in petroleum products. The fluorescence response of these compounds is measured with a fluorometer. The SCAPS can provide continuous hydrocarbon screening measurements to soil depths greater than 100 feet.

Discrete soil samples collected from the SCAPS boreholes were extracted and analyzed for total petroleum hydrocarbons (TPH), by gas chromatography with flame ionization detection (GC/FID), and 16 parent and over 100 alkyl substituted PAH compounds by gas chromatography with mass spectrometry detection (GC/MS). This method provides a basis for evaluating the relationship between TPH and PAH concentrations in the soil samples and laser induced fluorescence measurements from the soil borings.

We have used principal component analysis (PCA) to evaluate the spectral fluorescence wavelengths that were useful for resolving product types in the soil sample data set. Wavelengths 377 nm, 409 nm, 460 nm, 524 nm, and 625 nm proved to be most useful. PCA analysis of the fluorescence output provided enough resolution to identify product similarities and differences in the data set (e.g., light end products versus heavy products) which were validated by the chemical data (e.g., GC/FID chromatogram). These five wavelengths were added to the PAH soil data set for PCA. The scores and loadings results for principal component #1 (PC1) indicate that heavy product separation is influenced by C₂- and C₃-chrysenes and wavelengths 524 nm and 625 nm, whereas

light product separation is influenced by C₄- and C₃-naphthalenes and fluorescence wavelengths 377 nm and 409 nm.

Although TPH was strongly correlated with total PAH (TPAH) for all samples, the relative fluorescence intensity was not linearly related to TPH or TPAH at this site. However, when the relative fluorescence intensity was normalized to TPAH and plotted versus the total naphthalenes/total chrysenes ratio, a strong correlation was observed ($R^2 = 0.84$). These results suggest that the relative-fluorescence-intensity/TPAH ratio is dependent on product type and degree of degradation (e.g., weathering and biodegradation) and must be considered when evaluating quantitative data from soil LIF analyses.

INTRODUCTION

Fluorescence has been used as a hydrocarbon screening tool in soil, water, and oil samples for the last three decades (Katz et al., 1991, Kennicutt and Brooks 1983). Most of these measurements are carried out on samples collected in the field and analyzed later in the laboratory, although some fluorescence measurements in water samples have been performed *in situ* and in real-time (Katz et al., 1991). The use of in-situ fiber optical measurements to provide continuous real-time hydrocarbon contamination data in soils is a recent development (Lieberman et al., 1992). A fiber-optic-pulsed-laser system has been developed through a joint Army-Navy-Air Force program to provide *in situ* continuous fluorescence measurements in soils at depths exceeding 100 feet. The measurements are made through a sapphire window on a cone penetrometer probe mounted on a truck (Inman et al., 1990, Lieberman et al., 1991, Lieberman et al., 1992). Continuous soil measurements are preferred for hydrocarbon site assessments due to the heterogeneous nature of hydrocarbon distributions in soils. The ability to rapidly evaluate hydrocarbon contamination is a dramatic advantage over the time-consuming and costly discrete sampling/analysis methods traditionally used for placing site monitoring wells, monitoring remediation countermeasures, or tracking hydrocarbon contamination sources.

The SCAPS currently provides fluorescence measurements that are calibrated with hydrocarbon product types to provide a screening measurement of soil hydrocarbon concentration. The spectral distribution and intensity of PAH fluorescence in soil systems is complex and may be affected by moisture, soil type, hydrocarbon product type (Apitz et al., 1992), degree of weathering and biodegradation. Unfortunately, laboratory studies, although useful for the understanding of basic principals, cannot reproduce the complex nature of field environments. Calibrating the fluorescence based screening tool with a laboratory-based measurement technique can provide more detailed information concerning the fate and transport of hydrocarbons in the environment (Katz et al., 1991). The purpose of this study is to increase our current understanding of the factors that effect LIF response in petroleum-contaminated soils so that quantitative and qualitative information derived from the SCAPS may be optimized for hydrocarbon site assessment surveys. This study will focus on the complete soil system (e.g., contaminated soil sample from the field), and use detailed chemical TPH and PAH analyses to 1) determine if the LIF spectral fingerprint can reliably classify the petroleum products in the data set, and 2) evaluate the LIF/PAH relationship for the purpose of improving LIF quantitation accuracy.

METHODS

Field Methods

Real-time soil petroleum hydrocarbon measurements were made using laser (377 nm excitation) induced fluorescence through a sapphire window of a probe that was pushed into the soil from a cone penetrometer test system. The field sampling methods are described in Lieberman et al., (1991) and Lieberman et al., (1992). After removal of the soil probe, a split spoon coring system was used to collect discrete soil samples from the push hole. The core was then sent to the laboratory for processing and analysis.

Analytical Methods

The soil sample from each core tube was extruded and homogenized in a precleaned class 200 jar. The samples were then transferred to 500-mL wide mouth jars and stored frozen until analysis. The PAH target analytes that were used for this study, are presented in Table 1. The analytical methods used to measure aromatic and total petroleum hydrocarbons in oil and sediment samples are described in Douglas et al., 1994, Page et al. 1995, Douglas et al., 1992, and Sauer and Boehm 1991.

In summary, the soil samples were spiked with the surrogate internal standard compounds ortho-terphenyl, naphthalene-d₈, fluorene-d₁₀, and chrysene-d₁₂, mixed with equal amounts or more of sodium sulfate until the mixture was free flowing, then serially extracted three times with methylene chloride using a combined shaker table sonication (EPA Method 3550, USEPA 1986) technique. The combined extracts were then filtered through a 293-mm Gelman Type A/E glass-fiber filter and sodium sulfate to remove any additional water and concentrated to approximately 1 mL. Residue weights were determined on a small aliquot of the soil extracts, then the extract was passed through an alumina cleanup-column using USEPA Method 3611 (USEPA, 1986) to remove polar interferences, and the F₁ (saturated) and F₂ (unsaturated aromatic) hydrocarbon fractions were combined. The combined aliphatic/aromatic hydrocarbon fraction was then concentrated using Kuderna-Danish and nitrogen evaporation techniques to the appropriate pre-injection volume (PIV). The extract was then spiked with the quantitation internal standards 5 α -androstane, acenaphthene-d₁₀, phenanthrene-d₁₀, and benzo(a)pyrene-d₁₂, and analyzed by capillary gas chromatography with flame ionization detection (GC/FID) and capillary gas chromatography with mass spectrometry (GC/MS) operated in the selected ion mode (SIM) to improve analyte sensitivity.

Quality control for the GC/FID and GC/MS methods included the analysis of a procedural blank, a laboratory reference oil, a matrix spike, and a matrix spike duplicate. Surrogate compound recoveries were also examined for acceptability in each sample (surrogate and matrix spike criteria is 40% to 120% recovery). High precision and low detection limits were required to resolve hydrocarbon relationships in environmental samples. This was achieved through (1) the use of a single analyst and instrument for each method, (2) analysis of a standard quality control oil sample with each analytical batch, (3) use of SIM, increased samples sizes, and reduced final extract volumes to improve analytical sensitivity (sediment and water samples), and (4) the manual integration of all multi-component alkyl-PAH analytes.

Approximate GC/FID TPH method detection limits for soil samples (50 g dry weight) are 2 mg/kg for PHC. Approximate method detection limits for PAHs and dibenzothiophenes in soils are 1 μ g/kg. Method detection limit studies were based on the EPA protocol entitled "Definition and Procedure for the Determination of the Method Detection Limit" Code of Federal Regulations 40 CFR Part 136. For this study, seven sediment replicates were prepared by spiking 0.1mg topped crude oil into each clean sediment replicate and analyzed for the target analytes in Table 1.

Interpretive Methods

Principal component analysis of fluorescence wavelength and PAH data was used to capture important chemical information in complex data matrices and transform it into two smaller matrices that are linear combinations of the original data set. The new scores matrix contains information about "sample patterns" in the data, while the new loadings matrix reflects the influence each variable has in the sample patterns. These new matrices or *principal components* (PC) are created in order of decreasing variance, so the first PC accounts for most of the variance of the data, the second PC less, and so on. For hydrocarbon fingerprinting studies, the first PC is often related to weathering of the sample, and source indices are often the second and/or third PC. This technique is used to 1) minimize analyst bias when defining source relationships in large data sets, 2) explore the data set to determine how samples are related and what are the characteristics that make them similar or different, 3) reduce large complex data sets to detect relationships and patterns that may have been

missed or misinterpreted, and 4) classify samples into related groups. For this study, the Sirius for Windows Version 1.2 software was used on normalized wavelength and PAH data.

RESULTS AND DISCUSSION

Sample Screening

Figure 1 shows the results of a SCAPS push at station 44. The vertical profile information includes cone pressure, sleeve friction, soil classification, raw fluorescence and wavelength at peak. Cone pressure, sleeve friction and soil classification are physical measurements used to determine soil physical characteristics and are discussed elsewhere (Lieberman et al., 1992). Soil samples were collected at the following intervals in this boring 2 to 2.5 ft (sample 44-1), 3.5 to 4 ft (sample 44-2), 6 to 6.5 ft (sample 44-3), 8.5 to 9 ft (sample 44-4), 11.5 to 12 ft (sample 44-5), and 13.5 to 14 ft (sample 44-6). The TPH measurements confirmed the raw fluorescence data and were used to screen the samples prior to PAH analysis. Based on the screening protocol only samples 44-2 (TPH= 11000 ppm), 44-3 (TPH=480 ppm), and 44-4 (TPH=990 ppm) were analyzed for PAH in this boring. Only those samples that were analyzed for PAH were evaluated for this study (Table 2).

Sample Chemical Distributions

The GC/FID chromatograms provide a general indication of product type. The GC/FID data for samples 44-4 and 44-2 are presented in Figures 2a and 2b respectively. The data indicate that sample 44-4 is a biodegraded diesel fuel and sample 44-2 is a biodegraded mid-range fuel oil. The PAH concentration data for both samples are presented in Figures 3a and 3b respectively and have distributions that are characteristic of the two product types with the lighter diesel product exhibiting petrogenic (petroleum related) PAH distributions from naphthalenes through dibenzothiophenes and the heavier biodegraded mid-range fuel oil exhibiting petrogenic PAH from naphthalenes through chrysenes and (Douglas et al., 1992, Douglas 1991, Page et al., 1995). The relative fluorescence spectra for the same two samples are presented in Figures 4a and 4b respectively. These spectra are also characteristic of each fuel type with a narrow spectral width and maximum in the 409-nm range for the diesel product and a broader spectral width and maximum in the 500-nm range for the fuel oil. We focus on these two samples because they exhibit the largest chemical variance for all three analyses, and LIF/PAH variations would be expected to exhibit the largest differences between these two contaminated soils.

Fluorescence Product Signatures

The detection of PAH/fluorescence chemical trends is dependent on the ability to reliably measure fluorescent spectral differences between soils contaminated with different product types (e.g., diesel versus residual fuel). If spectral patterns are not resolvable then it will be difficult to determine which PAH grouping is responsible for the observed fluorescence. As noted above, there is a large difference in the fluorescence spectra for samples 44-2 and 44-4, however resolution of fluorescence spectra for the other samples in the data set is not as resolved. To improve the ability to detect spectral differences between samples, exploratory principal component analysis (PCA) was used to evaluate if samples with different types of oil contamination could be separated, and which fluorescence spectral wavelengths were most important for sample resolution. This approach could be useful to determine chemical linkages between samples in the field and increase our understanding of soil transport pathways.

The PCA results for the fluorescence spectral analysis are presented in Figure 5 and the associated PC1 and PC2 loadings presented in Figure 6a and 6b respectively. PC1 accounts for 86% of the variance and PC2 accounts for 11% of the variance in the sample data set. Samples 44-4 and 44-2 are easily resolved using this approach. In addition samples that are similar are clustered together (e.g., 45-1, 45-2, 45-3, and 45-4). In most cases the GC/FID results agreed with the PCA analysis in terms of similarity or differences. The wavelengths that received the most weight in the

sample resolution analysis are presented in the loadings data. For example, in PC1 sample 44-4 (degraded diesel fuel) is enriched in the spectral area with a maximum at 409 nm and depleted in the spectral area with a maximum 524 nm, where the opposite is true for sample 44-2 (degraded fuel oil) resulting in a clear separation between the two samples. PC2 keys on three wavelengths for sample resolution 377 nm, 460 nm, and 625 nm. These five wavelengths were then used with the PAH data to examine fluorescence PAH trends in the soil samples.

The PCA scores and loadings results for the PAH concentration data and the relative fluorescence intensities for the five wavelengths identified by the PCA loadings is presented in Figure 7. The sample separations are driven primarily by an enrichment in C₄-naphthalenes (N4) and C₃-naphthalenes (N3) PAHs and 377 nm and 409 nm wavelengths (e.g., sample 44-4) in products with lighter hydrocarbons and a corresponding depletion in C₁-chrysenes (C1), C₂-chrysenes (C2), C₃-chrysenes (C3), pyrene (Py) and fluoranthene (Fl). Separation of samples 44-2, 42-4, and 42-7 was based on an enrichment in C1, C2, C3, Py, Fl, and 524 nm and 625 nm wavelengths in products with heavier hydrocarbons and a corresponding depletion of N4 and N3. Some products appear to have both heavy and light hydrocarbons and PC2 separation demonstrates enrichment in N1 and N2 (e.g., 45-1 and 45-4). The important information gained from this analysis is the fact that the N4 and N3 are associated with wavelengths 377 nm and 409 nm, and the chrysenes and pyrenes and fluoranthenes are associated with wavelengths 524 nm and 625 nm.

The intensity of laser induced fluorescence in soils is a function of many variables including soil moisture, soil type, surface effects, level of contamination, type and weathering state of the contaminants. For this study equilibrium is assumed and the major influence on fluorescence is assumed to be concentration of petroleum product contamination, product type (i.e., PAH distribution in the sample), and degree of weathering, which effects distribution of PAH in the sample (Elmendorf et al., 1994, Douglas et al., 1994).

As expected, the relationship between TPH and TPAH is linear with an $R^2 = 0.98$ (Figure 8). Regression analysis of fluorescence versus TPAH (and PHC) however does not provide a linear relationship for the samples within this data set (Figure 9a and b). The general trend for most of the samples suggests that relative-fluorescence-intensity/TPAH ratio is greater in the samples containing "light-end" petroleum products (e.g., sample 44-4 diesel) than in heavier petroleum products (e.g., sample 44-2 residual fuel). This will have an impact on the estimation of TPH from fluorescence in the samples from this site due to the variety of petroleum product types. This would probably not be a problem for sites with only one product type (e.g., jet fuel bulk storage facility).

To understand which PAH compound classes influence fluorescence intensity, and to address weathering of the sample, a double ratio plot of relative-fluorescence-intensity/TPAH versus total naphthalenes/total chrysenes (N/C) was examined. This type of plot would quantify the observations made from Figure 9 and compare those observations to a combination product type/weathering ratio. The PCA analysis indicated that naphthalenes (particularly C₄-naphthalenes) and lower fluorescence wavelengths (e.g., 377 nm, and 409 nm) were associated with products with light hydrocarbon fractions in the gasoline (GRO)/diesel (DRO) boiling point range. PCA analysis also indicated that heavy boiling range hydrocarbons (e.g., asphalt, residual oils) were separated based on the enrichment of 3- and 4-ring PAHs (primarily the 4-ring chrysenes). Therefore a ratio of N/C could be used to characterize this chemical separation of the product types. This ratio is also sensitive to PAH weathering (Bence and Burns, 1994) with a decrease in the ratio as the oil degrades in the environment due to biodegradation. Therefore a plot of relative-fluorescence-intensity/TPAH versus N/C would include the major factors responsible for the fluorescence output (Figure 10). Linear regression analysis of this double ratio plot indicate a relationship between the variables ($R^2 = 0.84$) suggesting that for this sample data set, the fluorescence intensity is not only a function of the concentration of the contaminants, but of the product type and weathering state of the product as

well. And finally that naphthalenes and chrysenes are two classes of PAH that are most highly correlated with the fluorescence output of the SCAPS.

CONCLUSIONS

Fluorescence response in soils can vary by several orders of magnitude due to soil type, moisture, presence of other fluorescing or fluorescence-quenching organic compounds, oil type, degree of biodegradation, and concentration of contamination. This study has assumed that equilibrium between the soil and oil has been reached due to the age of the contamination at the site, and that the major factors influencing fluorescence are concentration, product type, and degree of biodegradation. As expected, TPAH was highly correlated with PHC ($R^2 = 0.98$), however for the diverse product types and levels of oil degradation at this site, TPAH and PHC were not linearly related to SCAPS fluorescence. This is because of variations in PAH distribution and fluorescence response. Two different product types (e.g., diesel fuel and residual fuel) with orders of magnitude different TPAH concentrations may yield the same soil fluorescence outputs, with heavier products having lower relative-fluorescence-intensity/TPAH ratios (e.g., residual fuels) than lighter petroleum products (jet fuels, and diesel fuels). Heavier residual fuel products and biodegraded oils contain asphaltenes and polar compounds which are not present in substantial amounts in lighter fuels. When fluorescence is normalized for TPAH, LIF can be related to the relative proportion of total naphthalenes and total chrysenes in the sample. This ratio may represent the major chromophores in the sample based on relative compound fluorescence and concentration in the samples, or may simply be defining product type and weathering state which may act to quench some unidentified chromophore class present in heavy petroleum products. The SCAPS fluorescence spectral outputs can be used to identify wavelength ranges for product class separations. These separations are similar to PCA separations based on PAH distributions in the samples. Lower wavelength fluorescence (377 nm and 409 nm) are associated with naphthalenes and higher wavelength fluorescence (524 nm and 625 nm) appear to be associated with chrysenes, fluoranthenes, and pyrenes.

Laser induced fluorescence provides valuable real-time and continuous data for hydrocarbons site assessment studies. Quantitative precision at each site will vary depending on the diversity and biodegradation of product types. Sites involving one fuel type (e.g., bulk fuel storage facility of diesel) will have higher quantitative precision relative to TPH and TPAH measurements than sites where several product types have been spilled (e.g., refinery). For improved product resolution and quantitative accuracy, the laser induced fluorescence analysis should be intercalibrated with a detailed PAH analysis and TPH analysis to define LIF/TPAH and LIF/TPH relationships at each individual site. This information, combined with the spectral data may be used to develop a simple model that could correct the TPH concentrations based on the spectral distribution (e.g., product class).

ACKNOWLEDGEMENTS

I would like to thank Helda Costa and Roger Prince for their review of this work. Funding for this study was provided by the Naval Facilities Engineering Command.

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Table 1. Target analyte list.

Compound	Abbreviation	# Rings	Primary Ion (M/z)	Secondary Ion (M/z)
<i>Polycyclic Aromatic Hydrocarbons (PAH)</i>				
naphthalene ^a	N	2	128	127
C ₁ -naphthalenes	N1	2	142	141
C ₅ -naphthalenes	N2	2	156	141
C ₃ -naphthalenes	N3	2	170	155
C ₄ -naphthalenes	N4	2	184	169
biphenyl	B1	2	154	152
acenaphthylene ^a	AE	3	152	153
Dibenzofuran	D1	3	168	169
acenaphthene ^a	AC	3	154	153
fluorene ^a	F	3	166	165
C ₁ -fluorenes	F1	3	180	165
C ₂ -fluorenes	F2	3	194	179
C ₃ -fluorenes	F3	3	208	193
anthracene ^a	A	3	178	176
phenanthrene ^a	P	3	178	176
C ₁ -phenanthrenes/anthracenes	P1	3	192	191
C ₂ -phenanthrenes/anthracenes	P2	3	206	191
C ₃ -phenanthrenes/anthracenes	P3	3	220	205
C ₄ -phenanthrenes/anthracenes	P4	3	234	219
dibenzothiophene	D	3	184	152
C ₁ -dibenzothiophenes	D1	3	198	184
C ₂ -dibenzothiophenes	D2	3	212	197
C ₃ -dibenzothiophenes	D3	3	226	211
fluoranthene ^a	FL	4	202	101
pyrene ^a	PY	4	202	101
C ₁ -fluoranthene/pyrenes	FP1	4	216	215
benz[a]anthracene ^a	B	4	228	226
chrysene ^a	C	4	228	226
C ₁ -chrysenes	C1	4	242	241
C ₂ -chrysenes	C2	4	256	241
C ₃ -chrysenes	C3	4	270	256
C ₄ -chrysenes	C4	4	284	269
benzo[b]fluoranthene ^a	BB	5	252	253
benzo[k]fluoranthene ^a	BK	5	252	253
benzo[e]pyrene	BE	5	252	253
benzo[a]pyrene ^a	BA	5	252	253
perylene	PER	5	252	253
indeno[1,2,3-c,d]pyrene ^a	IP	6	276	277
dibenz[a,h]anthracene ^a	DA	5	278	279
benzo[g,h,i]perylene ^a	BP	6	276	277

Table 1. Target analyte list (continued).

Compound	Abbreviation	# Rings	Primary Ion (M/z)	Secondary Ion (M/z)
<i>PAH Surrogate and Quantitation Internal Standards</i>				
naphthalene-d ₈ (SIS)	Nd ₈	2	136	134
fluorene-d ₁₀ (SIS)	Fd ₁₀	3	176	174
chrysene-d ₁₂ (SIS)	Cd ₁₂	4	240	236
acenaphthene-d ₁₀ (QIS)	Ad ₁₀	3	164	162
phenanthrene-d ₁₀ (QIS)	Pd ₁₀	3	188	184
benzo[s]pyrene-d ₁₂ (QIS)	BAPd ₁₂	5	264	260
<i>PHC Surrogate and Quantitation Internal Standards</i>				
ortho-terphenyl ^c (SIS)	NA	0	230	NA
5 α -androstane ^c (QIS)	NA	0	245	NA
<i>QA/QC Standards</i>				
crude oil control samples				
<i>Reporting Limits (soils)</i>				
PHC, 10 mg/kg				
PAH, 0.001 mg/kg				

^a Target analyte is a priority pollutant PAH

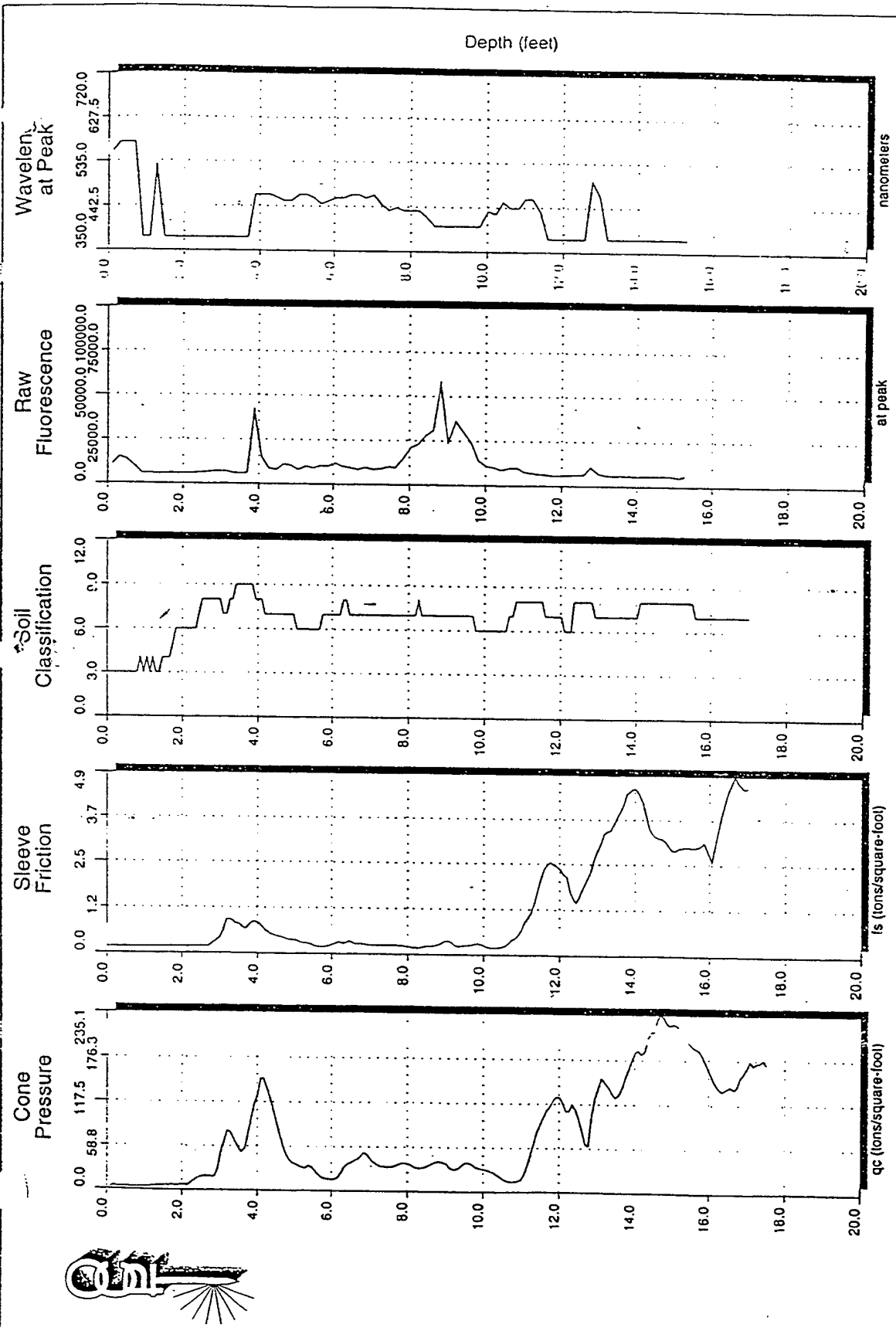
^b Not applicable

^c Target analyte concentration determined by GC/FID analysis (GC/MS M/z is generic for saturated hydrocarbon type)

Table 2. Sample Information.

Sample ID	Depth Interval	TPH Conc. Mg/Kg	TPAH Conc. µg/Kg	Fluorescence Avg. of Interval	Product Classification
41-4	8-9.5'	13000	300000	92273	DHFO
41-6	9-9.5'	48000	1400000	86169	DHFO
42-2	5.5-6'	18000	550000	203232	GRO/DMFO
42-4	7.5-8'	1200	32000	174340	GRO/DRO
42-6	12.5-13'	5700	120000	79970	GRO/DRO/DMFO
42-7	16-16.5'	110	4900	18116	GRO/DRO
43-2	9.5-10'	690	11000	9205	GRO/DRO/DMFO
44-2	3.5-4'	11000	320000	23488	DMFO
44-3	6-6.5'	480	4700	11047	DHFO
44-4	8.5-9'	988	4400	44022	DRO
45-1	6.5-7'	11000	200000	256909	GRO/DRO/DHFO
45-4	14-14.5'	470	8800	10626	GRO/DRO/DHFO
41-5	8.5-9'	646	7600	70992	DHFO

GRO - Gasoline range product
DRO - Diesel range product
DMGO - Degraded mid-range fuel oil
DHFO - Degraded heavy fuel oil



Time: 07:03:32
 Date: 04-06-1994
 Version: 0.95

Push: C:\BA\IC71\DATA\ALA13P44.PSH
 Probe: C:\BA\IC71\DATA\PROBEL1.PRB
 Calibration: C:\BA\IC71\DATA\I06APRDFM.CAL

Figure 1. Real-time SCAPS soil characterization and fluorescence output for Station 44.

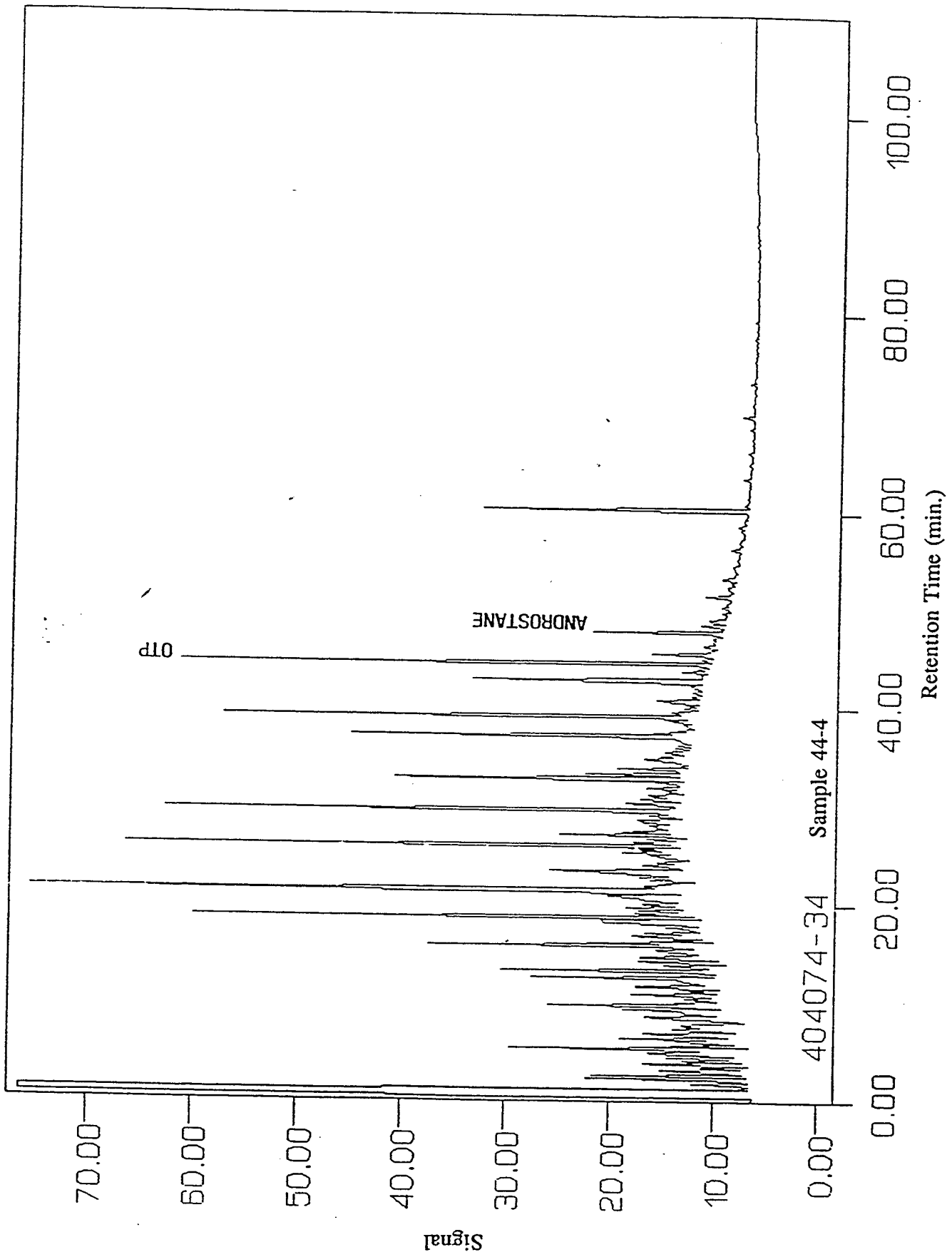


Figure 2a. Gas chromatography with flame ionization chromatograms for a) Sample 44-4 and b) Sample 44-2.

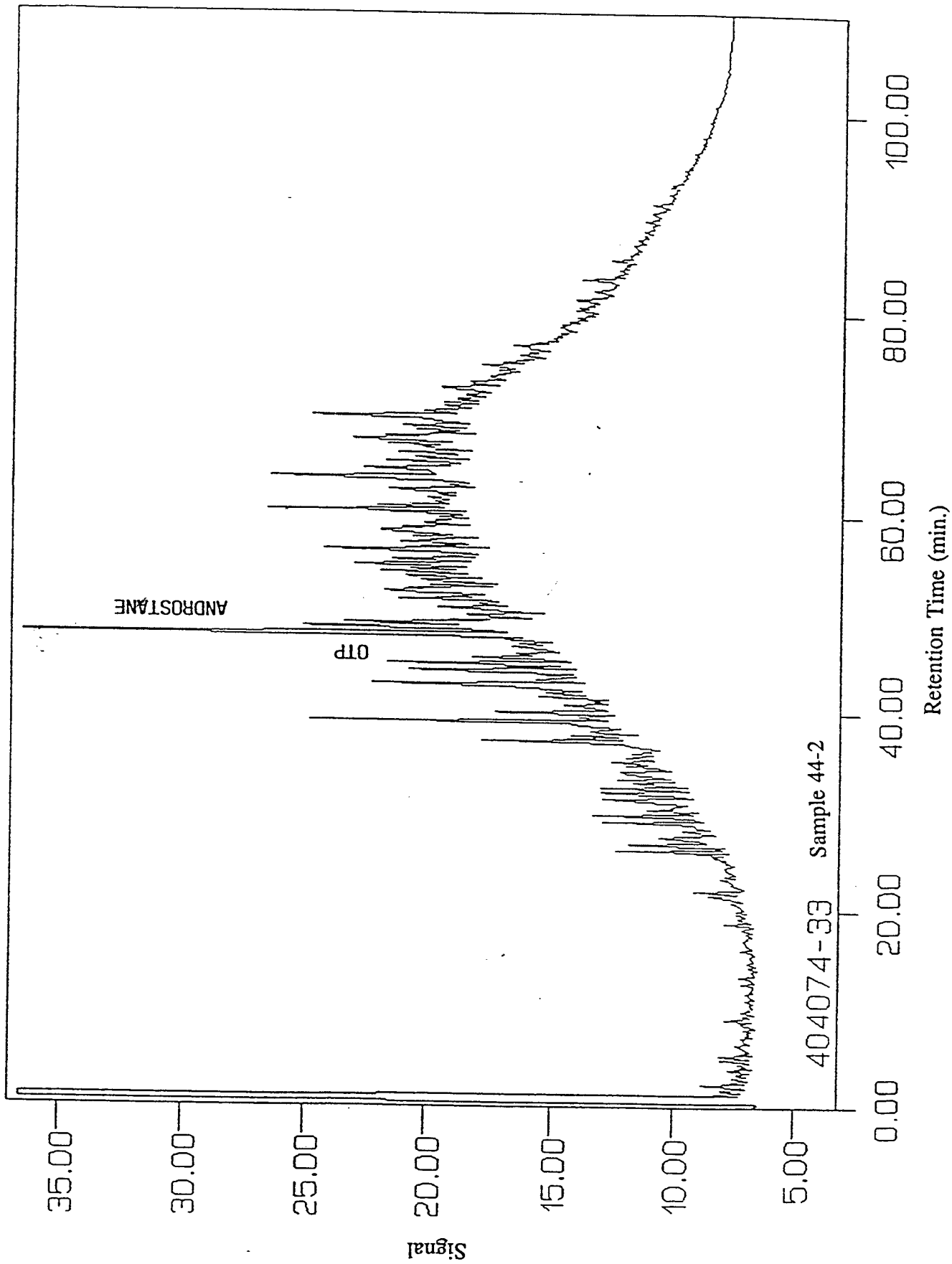


Figure 2b. Gas chromatography with flame ionization chromatograms for a) Sample 44-4 and b) Sample 44-2.

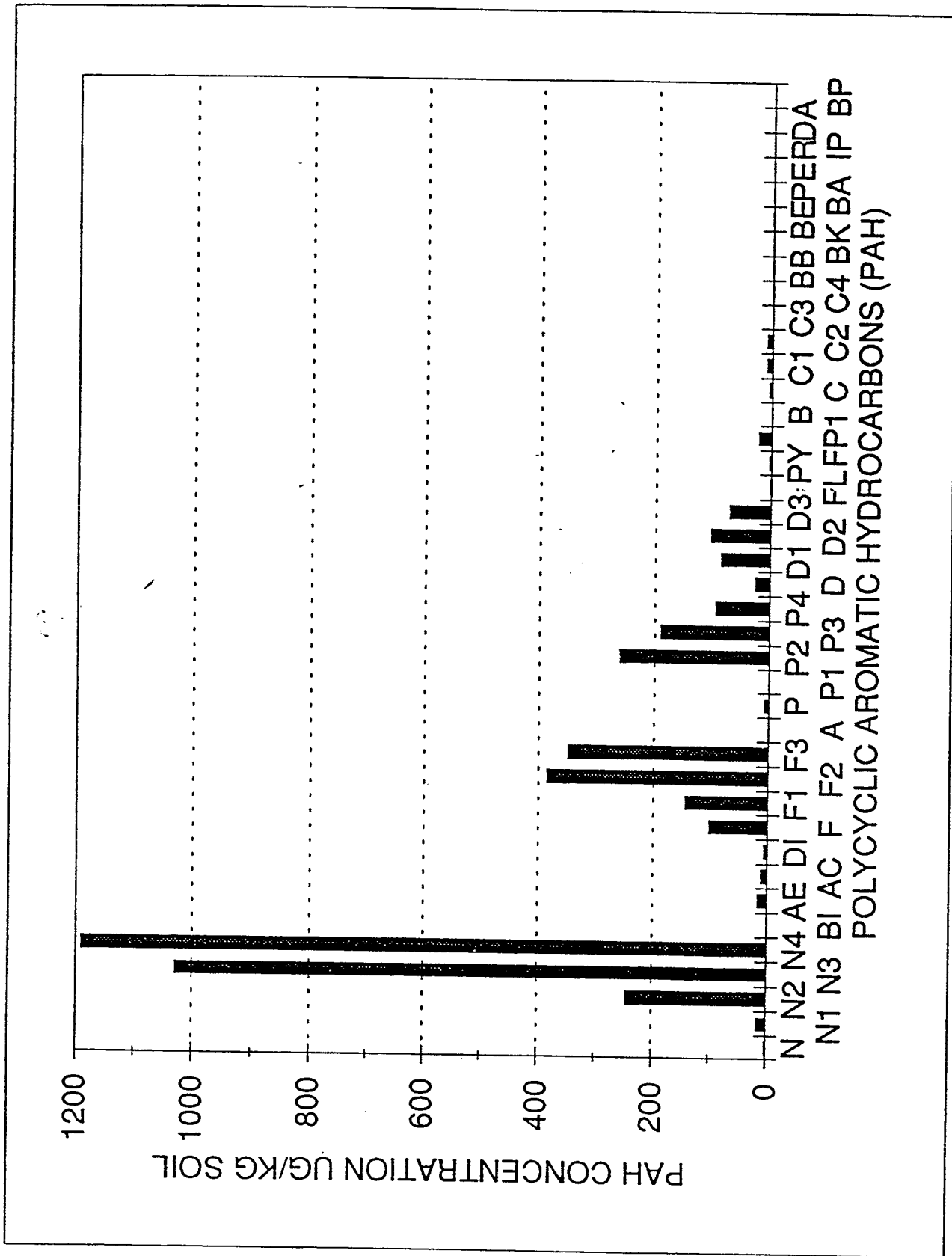


Figure 3a. Polycyclic aromatic hydrocarbon concentrations for a) Sample 44-4 and b) Sample 44-2.

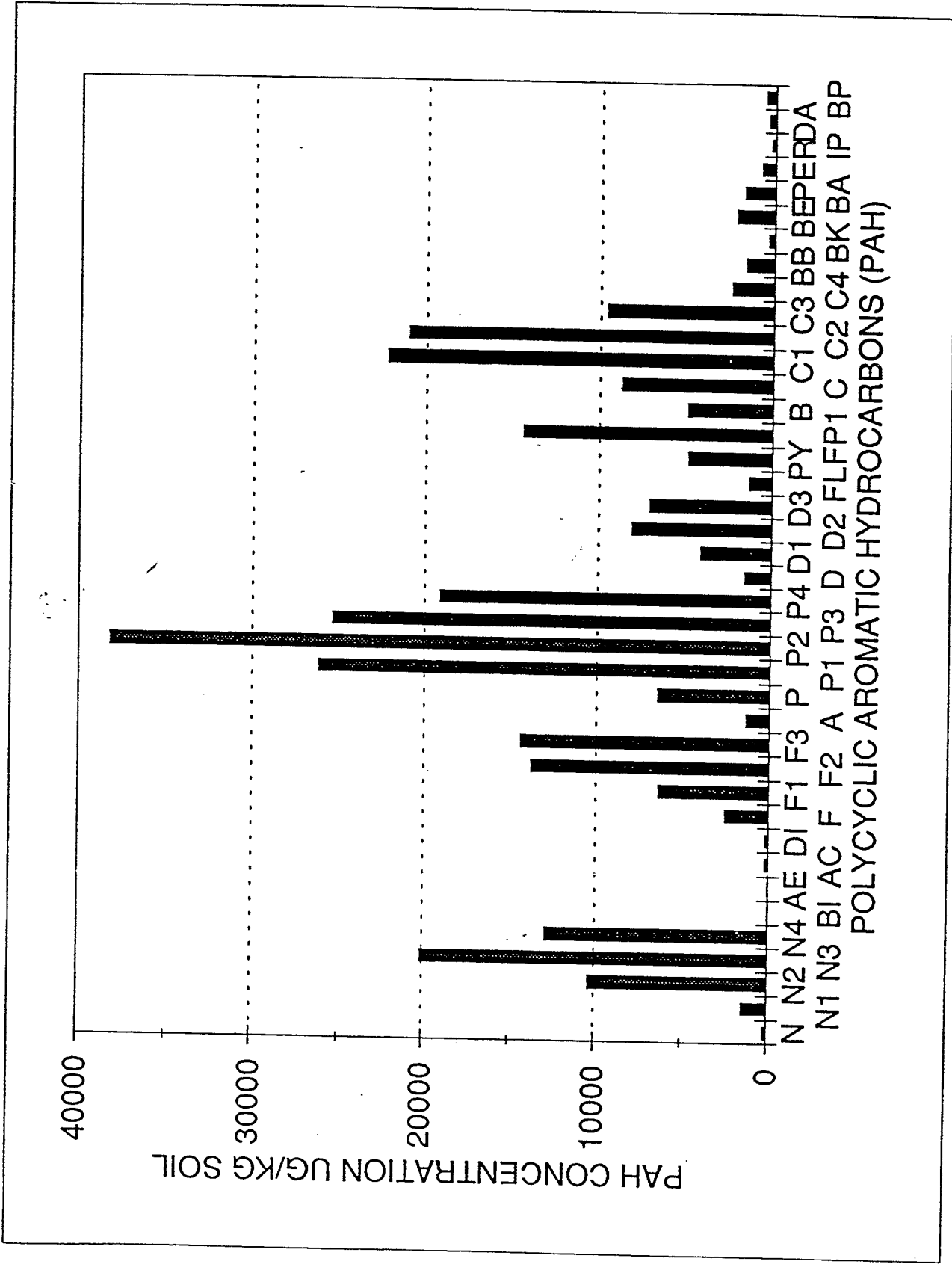


Figure 3b. Polycyclic aromatic hydrocarbon concentrations for a) Sample 44-4 and b) Sample 44-2.

Sample 44-4

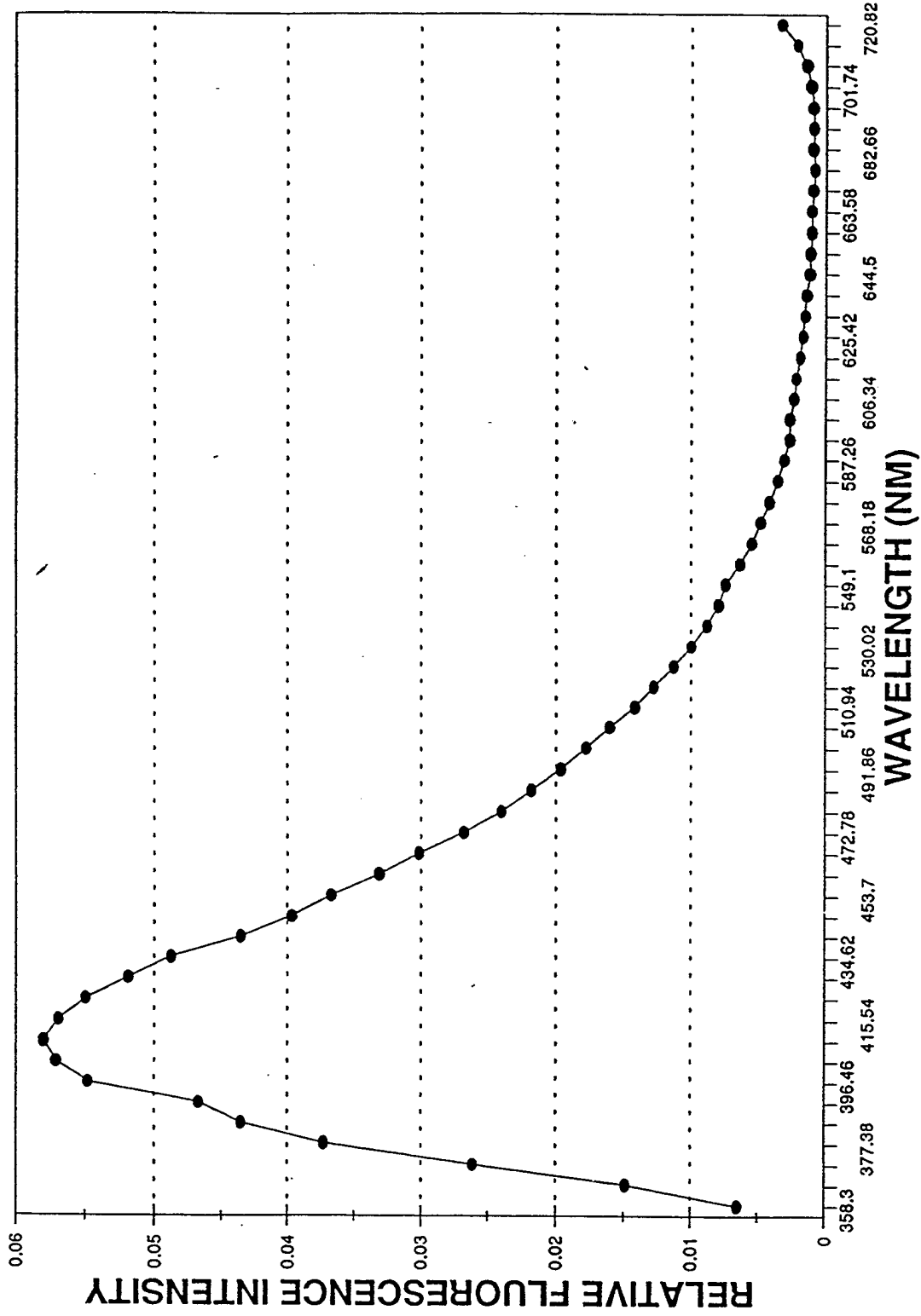


Figure 4a. Relative fluorescence intensity versus wavelength for a) Sample 44-4 and b) Sample 44-2.

Sample 44-2

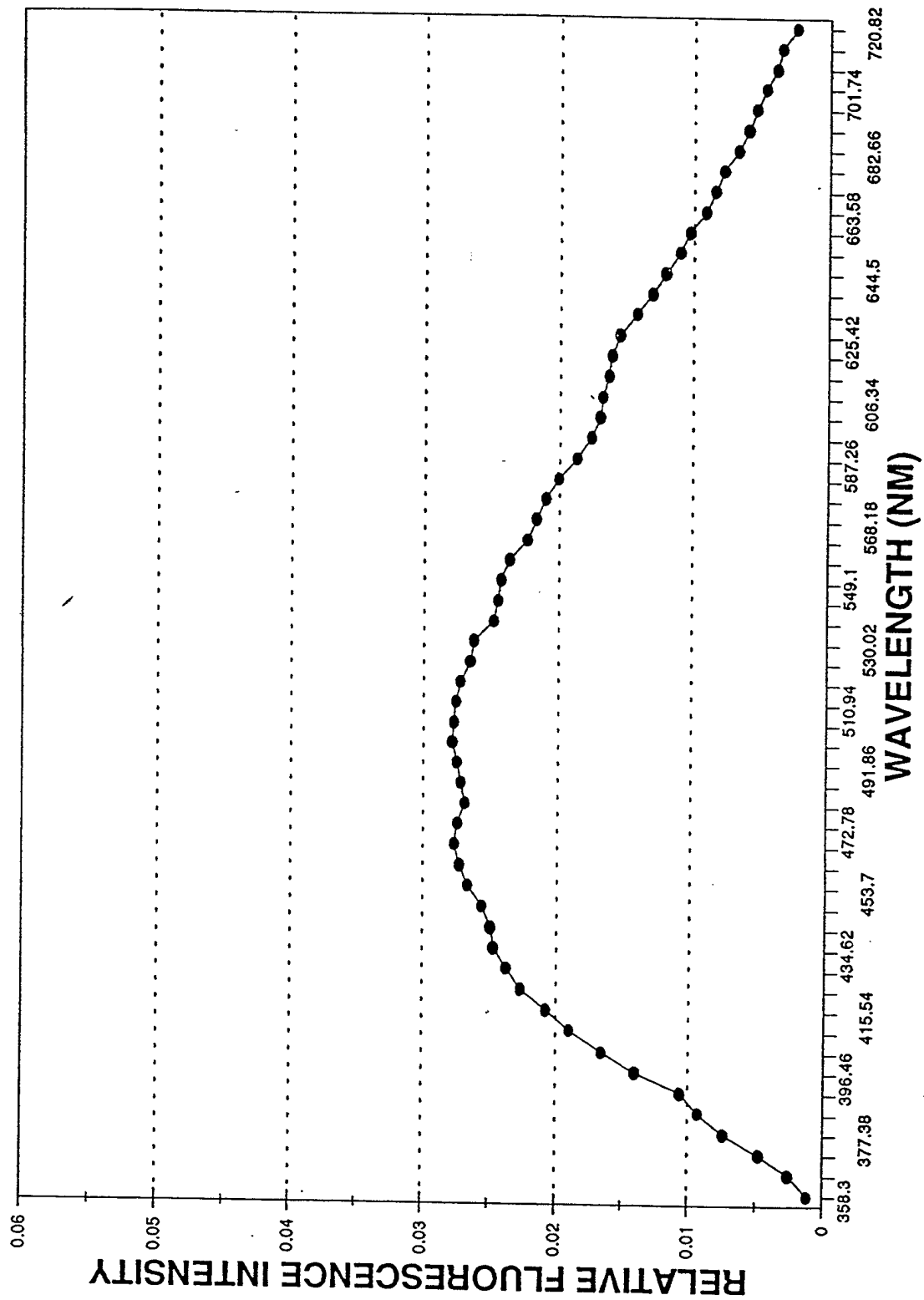


Figure 4b. Relative fluorescence intensity versus wavelength for a) Sample 44-4 and b) Sample 44-2.

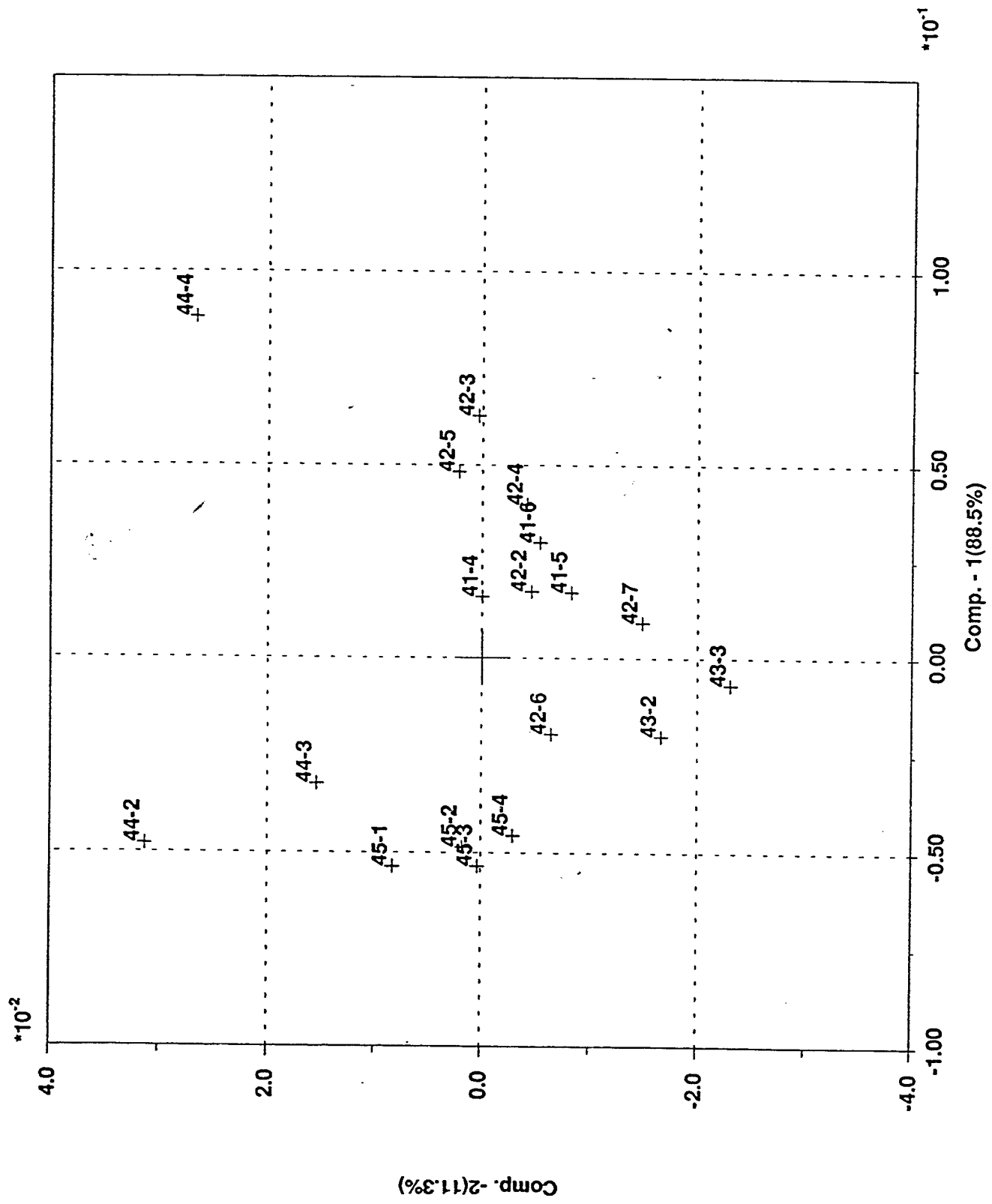


Figure 5. Plot of PC1 versus PC2 scores for the relative fluorescence versus wavelength data for samples in Table 2.

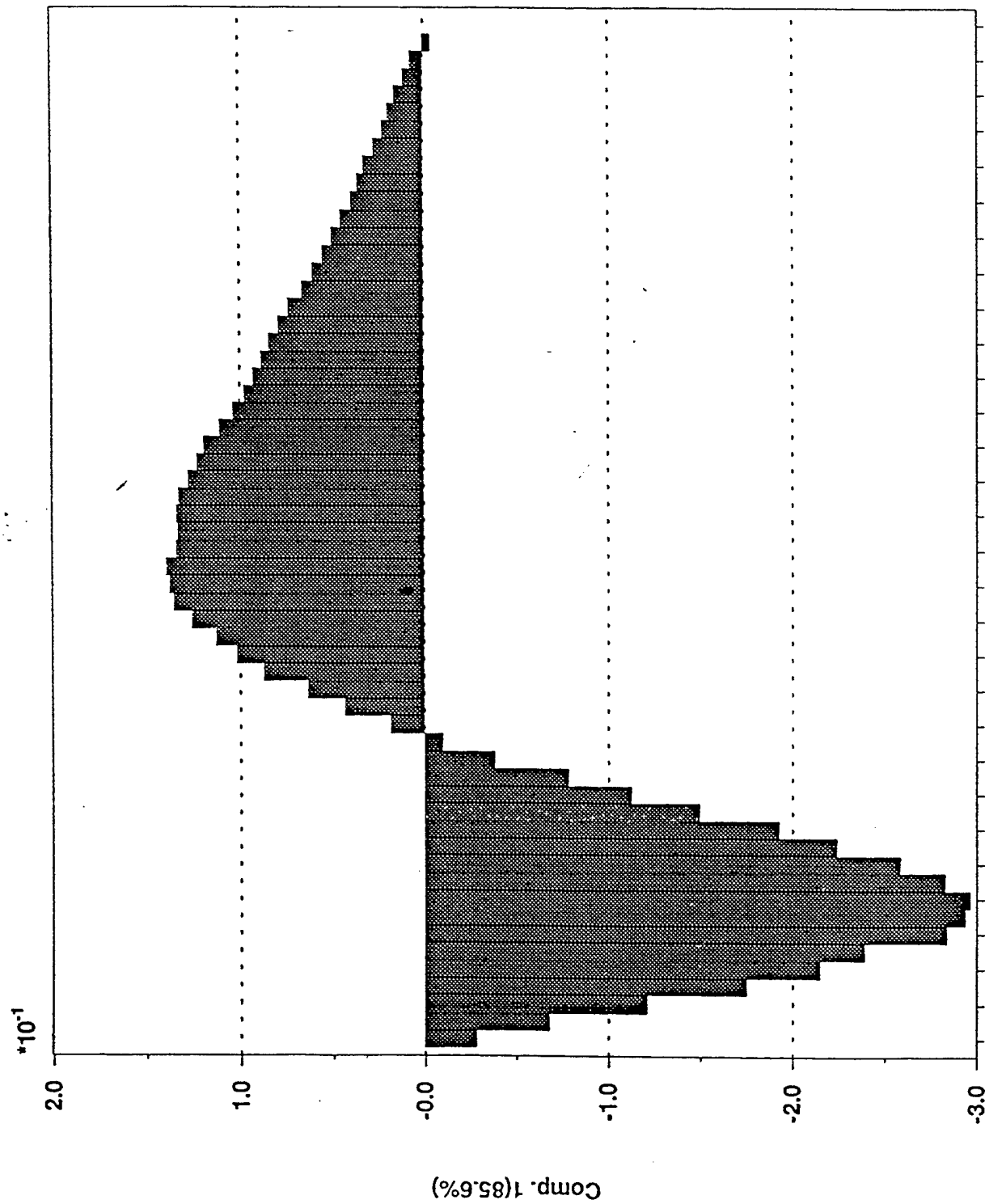


Figure 6a. Wavelength loadings for fluorescence/wavelength PCA. a) PC1 and b) PC2.

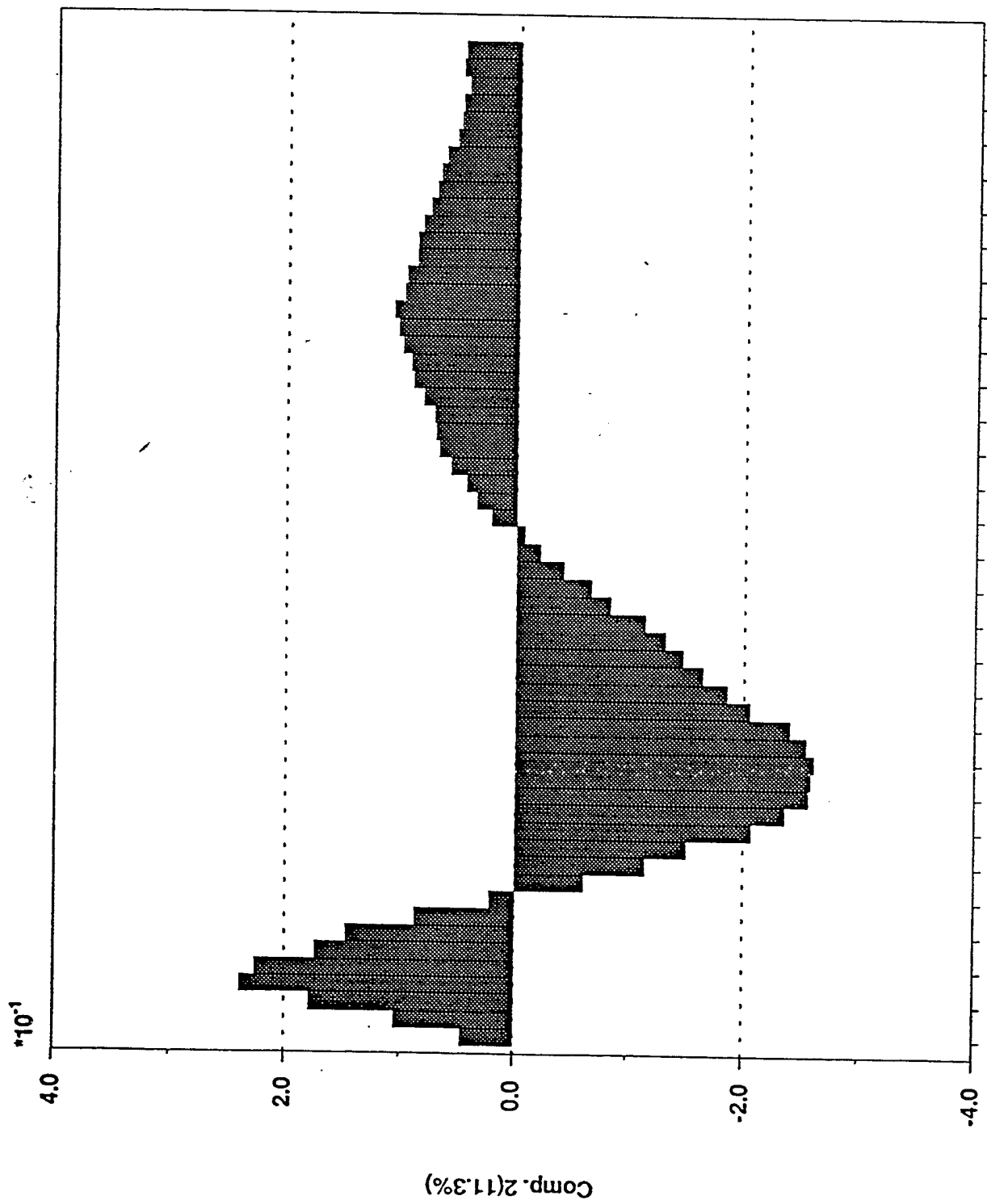


Figure 6b. Wavelength loadings for fluorescence/wavelength PCA. a) PC1 and b) PC2.

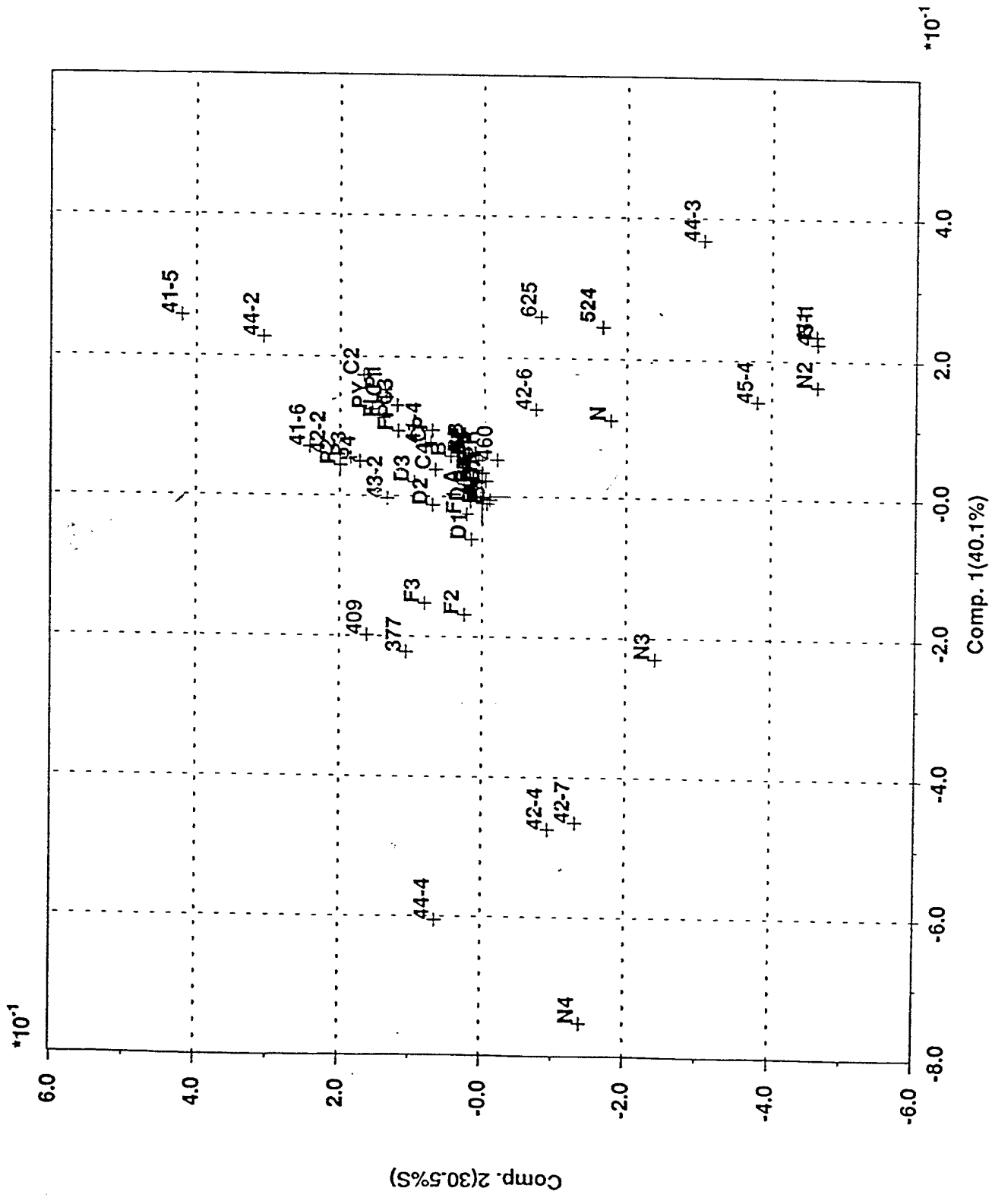


Figure 7. Plot of PC1 versus PC2 scores and loadings for combined PAH and fluorescence wavelength data for the samples in Table 2.

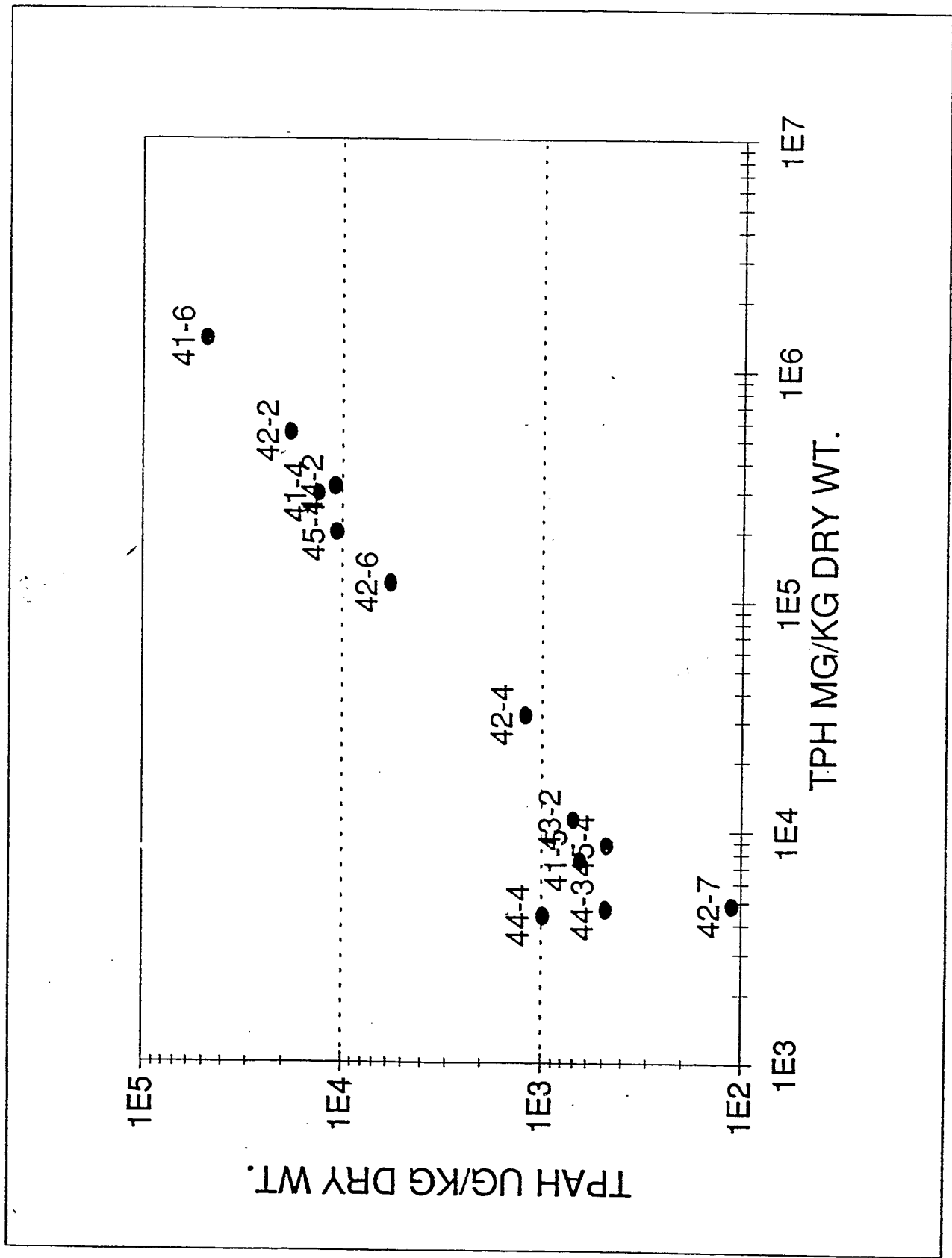


Figure 8. Plot of TPH versus TPAH for the soil samples listed in Table 2.

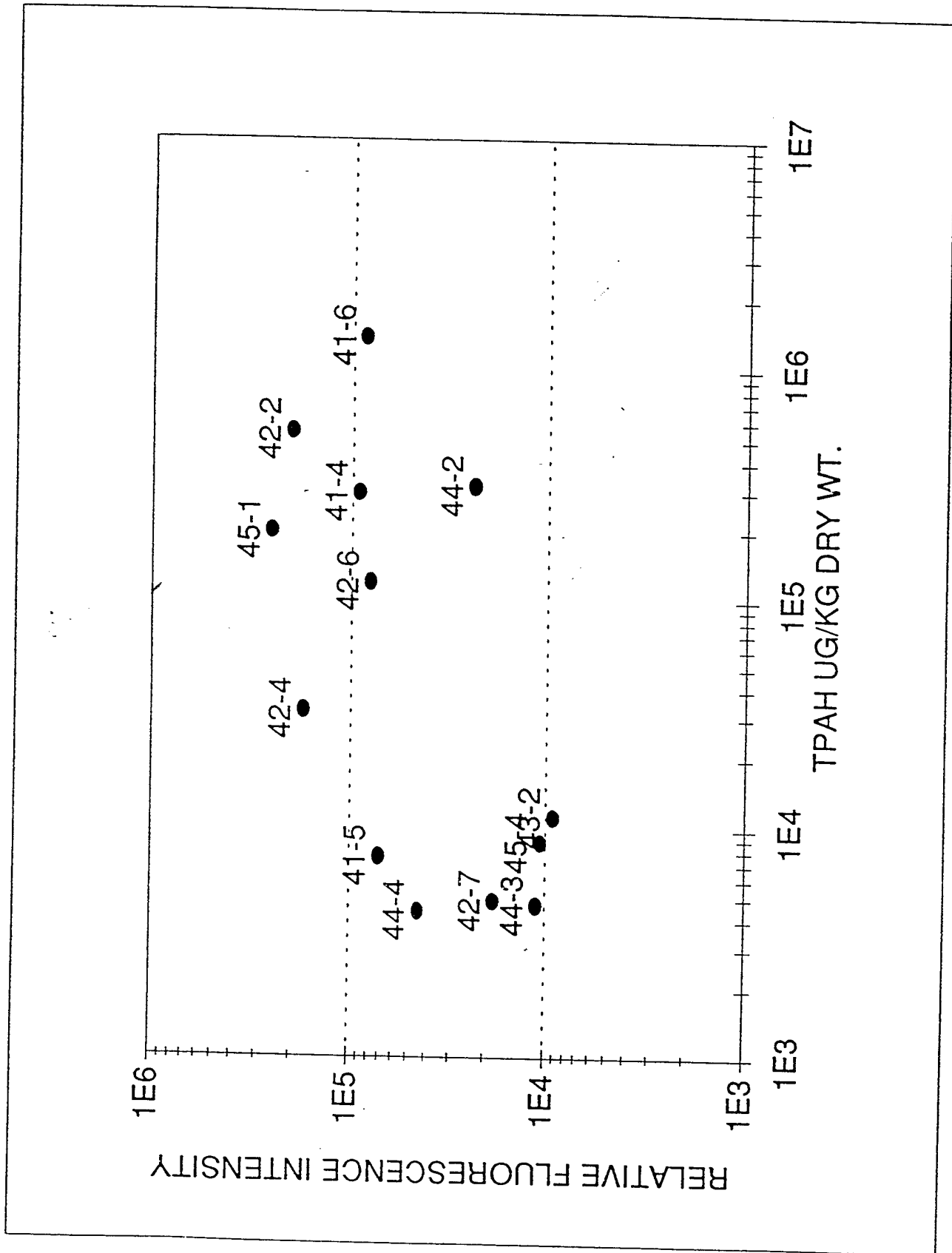


Figure 9a. Plots of fluorescence versus a) TPAH and b) TPH for the samples listed in Table 2.

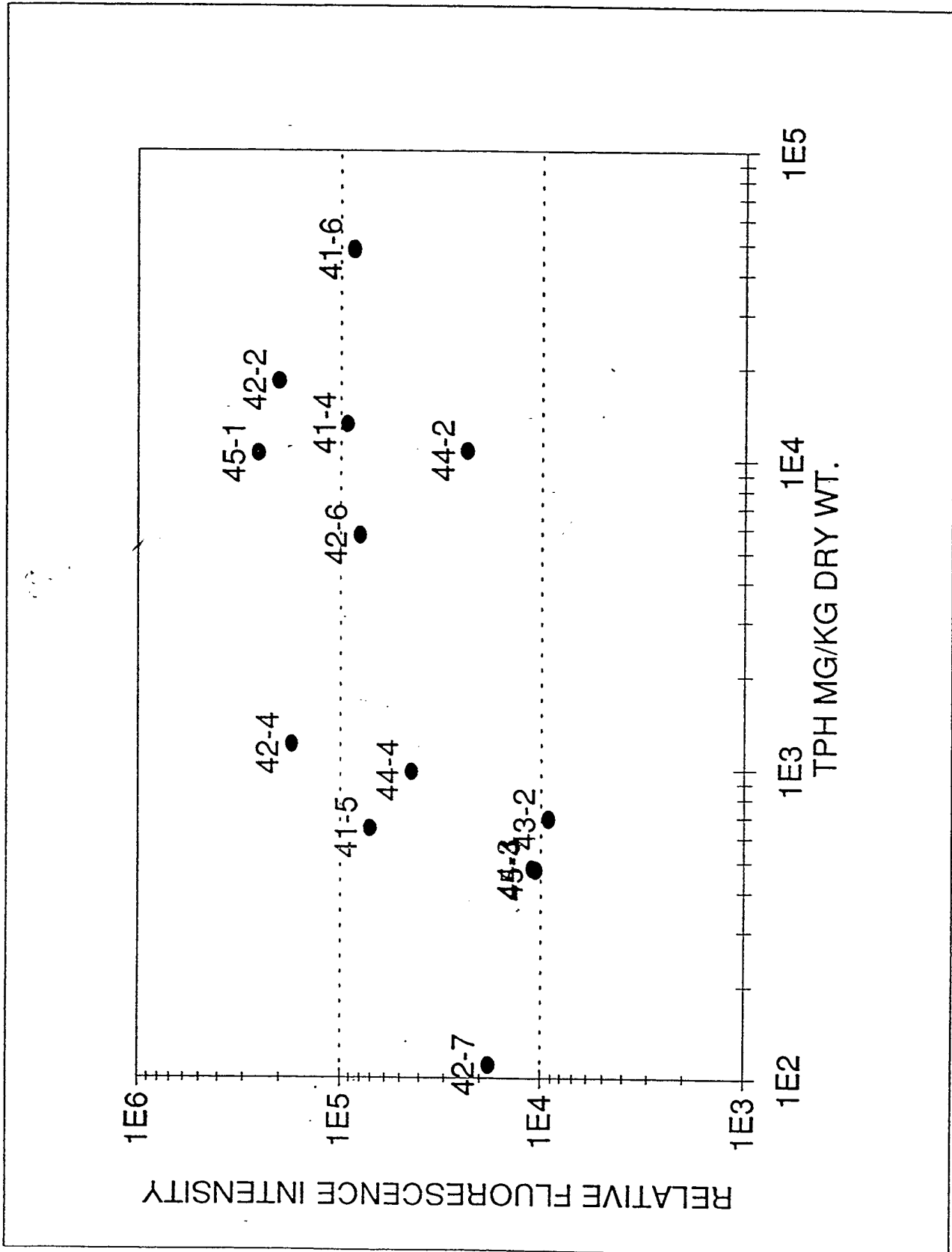


Figure 9b. Plots of fluorescence versus a) TPAH and b) TPH for the samples listed in Table 2.

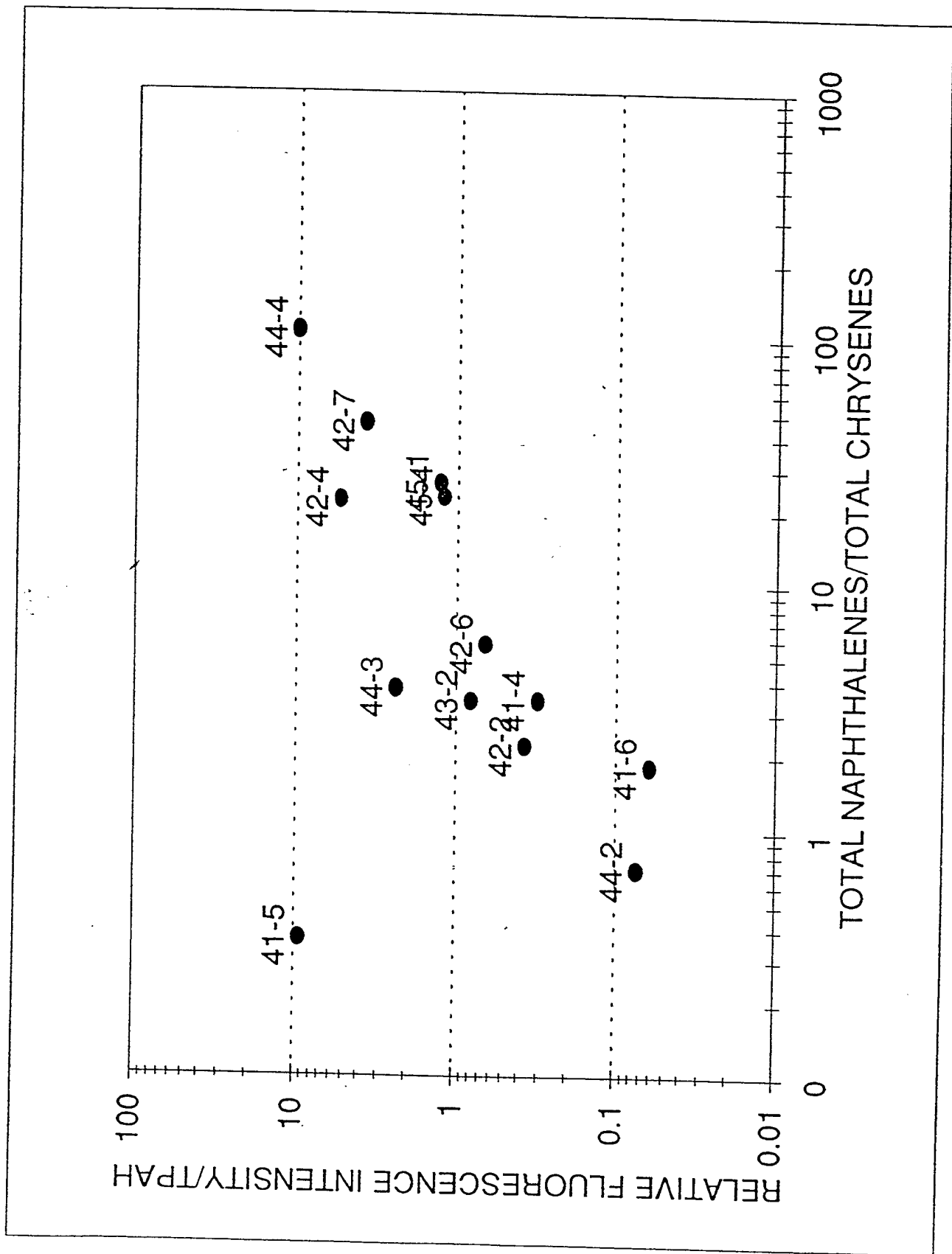


Figure 10. Plot of fluorescence/TPAH versus Naphthalenes (N)/Chrysenes (Cr).

Key Words

Laser fluorescence

Cone penetrometer

Aromatic hydrocarbons

Petroleum hydrocarbons

Site investigation

In situ