

Analyses of Water Samples from the Deepwater Horizon Oil Spill: Documentation of the Sub-Surface Plume

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(1) Surface and sub-surface water samples were collected in the vicinity of the Deep Water Horizon (DWH) wellhead in the Gulf of Mexico. Samples were extracted with dichloromethane and analyzed for a toxic component, polycyclic aromatic hydrocarbons (PAH), using total scanning fluorescence (TSF) and by gas chromatography/mass spectrometry (GC/MS). An aliquot of fresh, floating oil from a surface sample was used as a DWH oil reference standard. Twelve of 19 samples collected from 24 May 2010 to June 6, 2010 on the R/V Walton Smith cruise contained TSF maximum intensities above background (0.7 µg/L based on 1L sample size). These 12 samples had total petroleum hydrocarbon (TPH) concentrations ranging from 5 to 1,300 µg/L. Quantitative GC/MS analysis of these twelve samples resulted in total PAH concentrations ranging from 0.01 to 59 µg/L. Low molecular weight, more water soluble naphthalene and alkylated naphthalene dominated the PAH composition patterns for eleven of the twelve water samples. The 12th sample exhibited substantially

reduced concentrations of naphthalenes relative to other PAH compounds. The total PAH concentrations were positively correlated ($R^2 = 0.80$) with the maximum fluorescence intensity (MFI). TSF is a simple, rapid technique providing an accurate prediction of the amount of PAH present in a sample when compared to the TSF from the discharged oil. TSF-derived estimates of the relative contribution of PAH present in the oil provided evidence that PAH represented ~10% of the higher molecular weight TPH. A good correlation between *in-situ* colored dissolved organic matter (CDOM) fluorescence and total PAH concentration was observed based on the analysis of 36 additional water samples collected during the R/V Pelican cruise from the 9th to the 16th of May 2010 (Diercks et al., 2010). A stronger correlation was obtained between *in-situ* CDOM fluorescence and total phenanthrenes, which are less soluble in water. The subsurface oil plume was traced using the CDOM fluorometer and discrete water samples were collected to ground truth these measurements in the vicinity of the DWH. This study validates the use of fluorescence techniques (CDOM and TSF) to characterize PAH distributions associated with sub-surface oil.

1. Introduction

(2) The Deepwater Horizon (DWH) Spill was unique as gas, oil and dispersants were all released at a depth of approximately 1500 m. This mixture resulted in significant dispersion of the liquid oil at depth. The purpose of this study was to determine whether the higher molecular weight components (C10 to C34) of the oil from the DWH oil spill were present in samples from the sub-surface plume. Gaseous components of the oil are outside the scope of this work as they have very different long-term fates compared to the components examined in this study [Valentine et al. 2010; Kessler et al. 2011, Joye et al., 2011]. A cruise of opportunity three weeks after

the spill on the R/V Pelican detected CDOM fluorescence subsurface maxima that were thought to represent subsurface oil plumes [Diercks et al., 2010, Joye et al., 2011]. The components of oil responsible for its fluorescent properties and toxicity [Barron et al., 2003; Yamada et al., 2003] are the polycyclic aromatic hydrocarbons. In order to confirm that these subsurface fluorescence maxima were due to the presence of oil, water samples were collected in the plumes and analyzed for PAH. In addition, a sample of oil collected from a surface slick in the vicinity of the wellhead was analyzed for TSF, PAH and TPH to document the oil signature of plume using relatively un-weathered surface oil.

Methods

(3) Water samples were processed as previously described [Wade et al., 2011 this volume]. Briefly, samples (~0.4L to 1L) were placed in separatory funnels, acidified to a pH of less than 2 with sulfuric acid, aliphatic surrogate standards added, extracted with dichloromethane and the dichloromethane extracts combined into a 250 ml flat bottom flasks. The sample extracts were reduced in volume and solvent exchanged to hexane. The samples extracts along with procedural blanks were then analyzed by total scanning fluorescence. Samples were diluted, when necessary, to minimize quenching effects. Estimates of total oil equivalents (TOE) of DWH oil were based on the MFI measured at an excitation wavelength of 260 nm and an emission wavelength of 370 nm corresponding to MFI from a sample of DWH oil obtained with a bucket from the sea surface near the spill. The practical quantitation limit (PQL) for the TSF method was estimated as 0.70 $\mu\text{g/L}$ for a 1L sample [Wade et al. 2011 this volume]. All procedural blanks were below the PQL. Sample extracts were reduced in volume to 1 mL and analyzed for TPH by GC with a flame ionization detector (GC/FID) and polycyclic

aromatic hydrocarbons (PAH) by gas chromatography with a mass selective detector [Short et al., 1996].

Results and Discussion

(4) The TSF plot for DWH oil collected from the water surface is provided in Figure 1. We found a strong relationship between MFI and the total PAH concentration (range from 0.1 to 59 $\mu\text{g/L}$) from GC/MS (Figure 3). The correlation (R^2 of 0.80) is expected as the PAH are the fluorescent components of oil. TPH concentrations ranged from 5 to 1,300 $\mu\text{g/L}$. TPH and TSF maximum intensity were also strongly correlated with an R^2 of 0.80 (Figure 3). There was a strong correlation between PAH and TPH with an R^2 of 0.73 (Figure 4). These results indicate fluorometry is an excellent means to screen samples for the presence of oil. Using high MFI values to select impacted samples, more sophisticated analyses can be employed in a more cost effective manner to determine compositional information that can indicate a source of the oil. The distribution of nC10 to nC35 n-alkanes, pristane and phytane are typical of a freshly oiled pattern/fingerprint. Examples for a sample collected 1.2 miles from the blowout site at a depth of 1240 meters (Station 6) and 3.4 miles from the blowout site at a depth of 900 meters (Station 4) are provided in Figures 5 and 6, respectively. The TPH concentration at the near site (Station 6) and the distant site (Station 4) were 442 and 232 $\mu\text{g/L}$, respectively. The dominant n-alkane in the near station was nC14 while the highest for the more distant station was nC17. This pattern was consistent with preferential loss of lower molecular weight, more water soluble n-alkanes from the plume with time, using distance as a surrogate. The average odd n-alkane to even n-alkane ratio for samples with TPH concentrations over 130 $\mu\text{g/L}$ was 1.06 which is in

good agreement with that of oil collected from the surface in the vicinity of the spill (1.05). A ratio near one is a good indicator of fresh oil [Stoudt et al., 2003]. The ratio slightly above one in these samples suggested the presence of lower molecular weight n-alkanes nC11, nC13, nC15 and nC17 which are components common to both oil and marine phytoplankton. The average (for samples with TPH greater than 130 µg/L) pristane/nC17 ratio was 0.60 and phytane/nC18 ratio was 0.54. The pristane/nC17 ratio and phytane/nC18 ratio of oil collected from the surface in the vicinity of the spill were 0.58 and 0.46, respectively. The average ratios are very close to those of the surface oil suggesting little biodegradation of the n-alkanes in samples with concentrations greater than 130 µg/L. The distribution of PAH in the water samples at near and distant stations (C65167 and C65165) with total PAH concentration of 59 and 9.9 µg/L, respectively are provided in Figures 8 and 9. The PAH distributions were markedly different at these two sites with the total naphthalenes (naphthalene + C1+C2 + C3 +C4) in the near sample location accounting for 83.6% and only 56.2 % of the total PAH at the more distant station. The percentages of the total PAH to TPH were 13.3% and 4.5% for the near and distant stations, respectively, indicating a preferential loss of lower molecular weight, more water soluble PAH.

(5) Natural petroleum seepage into the Gulf of Mexico is a widespread phenomenon and a significant source of hydrocarbons into the marine environment [Kennicutt et al., 1988a,b]. Kennicutt et al. [1988a] documented linkage of sea slicks and tar balls with the subterranean reservoir oil based on the distributions of PAH and biomarkers in the northern with the subterranean reservoir oil based on the distribution of PAH and biomarkers in the northern Gulf of Mexico. Wade et al. [2011] reviewed previous work

from the Gulf of Mexico and adjacent areas for the magnitude of near surface and subsurface hydrocarbons. Dissolved hydrocarbon concentrations near the Loop Current at depths of 1 meter below the surface to 500 meters ranged from 1 to 75 $\mu\text{g/L}$ [Iliffe and Calder, 1974]. A recent study of 282 water samples collected in the vicinity of the Loop Current [Wade et al., 2011 this volume] at various depths in the water column reported hydrocarbon concentrations ranging from 0.70 $\mu\text{g/L}$ to 160 $\mu\text{g/L}$. Neither of these studies documented a subsurface plume. The concentration range from this study for total hydrocarbon concentrations was from 5 to 1,300 $\mu\text{g/L}$. The highest concentrations were five times higher based on prior literature. The highest concentration reported here is more than five times less than that for samples collected 2 meters below the surface from the Ixtoc oil spill of 7,010 $\mu\text{g/L}$ [Boehm et al., 1982]. In the late seventies a subsurface plume was reported at a depth of 200 meters in the southwest North Atlantic and eastern Caribbean [Harvey et al. 1979] with concentrations ranging from 3,000 to 12,000 $\mu\text{g/L}$. Requejo and Boehm [1985] attributed the source of this plume as a massive oil seep from the Venezuelan shelf at a depth of 200 meters where the concentrations reached almost 10 times the highest concentrations found in this study. The ephemeral nature of these natural seeps is evidenced by their inability to detect this plume 11 months later [Harvey et al. 1979]. It seems highly unlikely that oil from the DWH will be detectable at high concentrations in the water column over one year after the incident.

Conclusions

- (6) These analyses confirm the presence of subsurface plumes of oil (the higher molecular weight components) near the DWH wellhead. Extraction techniques used in

this study provide measurements of both dissolved and particulate oil (samples were unfiltered). The detected oil lost some of the lower molecular weight components suggesting preferential dissolution or biodegradation of the lower molecular weight, more water soluble components. Biodegradation processes did not modify the n-alkanes in subsurface samples on the basis of the ratios of odd to even n-alkanes, pristane/n-C17 and phytane/n-C18. How the use of dispersants affected these processes can not be determined from our data. The use of CDOM fluorometers was confirmed to be a valuable tool in detecting sub-surface oil. TSF is an effective method for rapid screening of samples to estimate oil concentrations. Additional analysis by more sophisticated techniques (e.g., TPH, PAH, biomarkers, etc.) is required to adequately fingerprint the oil to a specific source or to document its weathering history.

(7) Acknowledgments

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Figure 1. Total scanning fluorescence fingerprint of fresh DWH surface oil

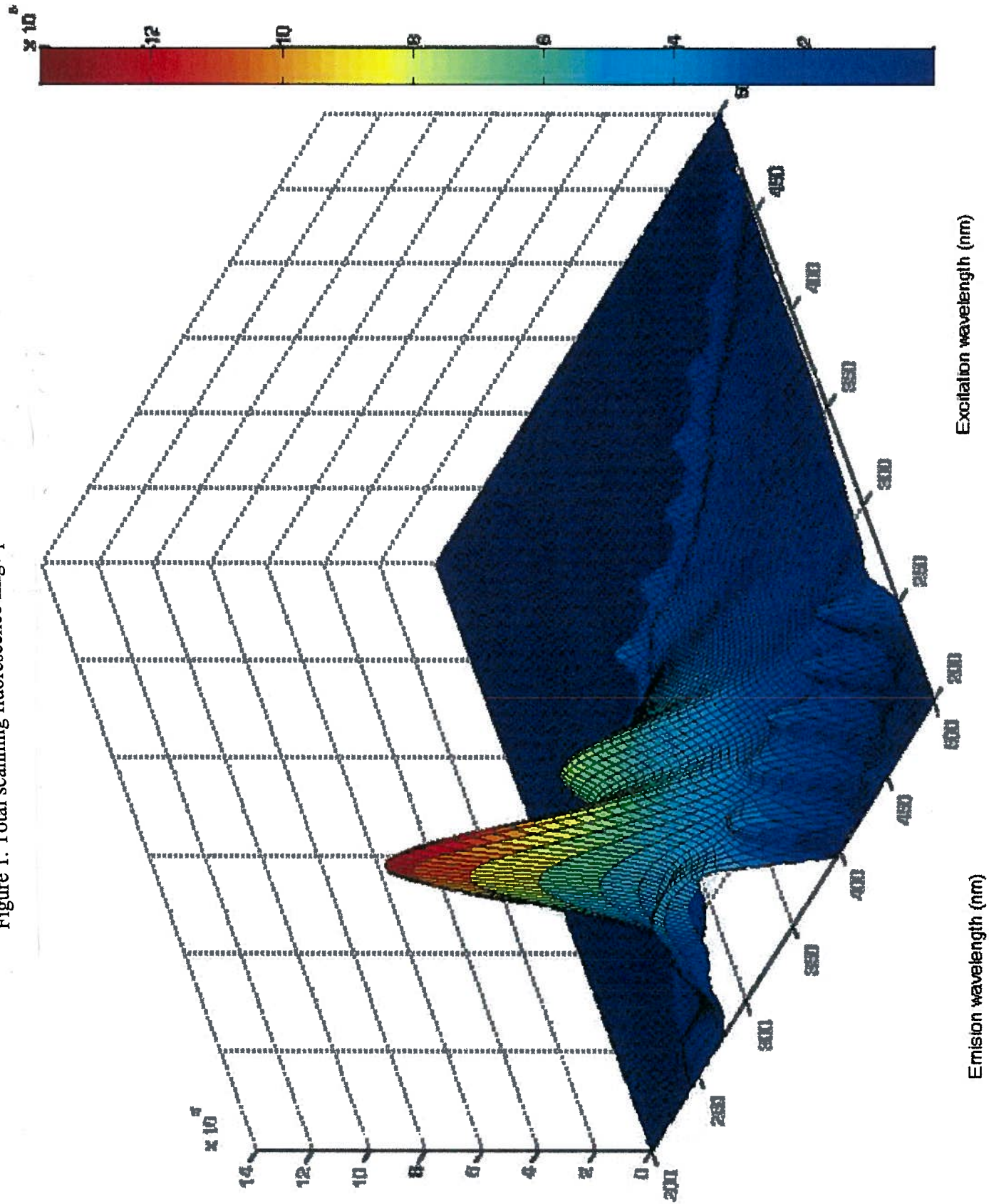


Figure 2. Total Scanning Fluorescence versus PAH

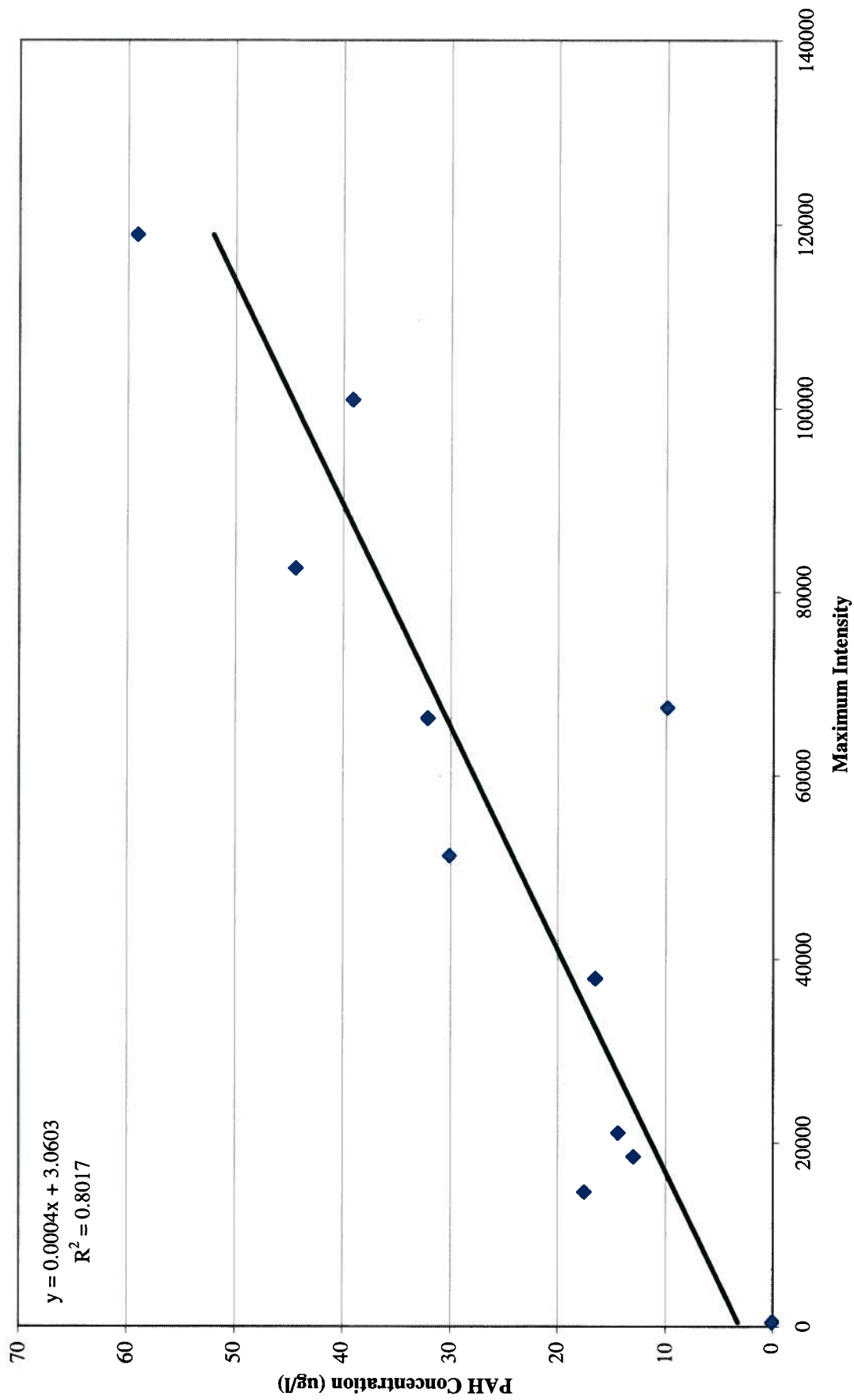


Figure 3. Total Scanning Fluorescence versus TPH

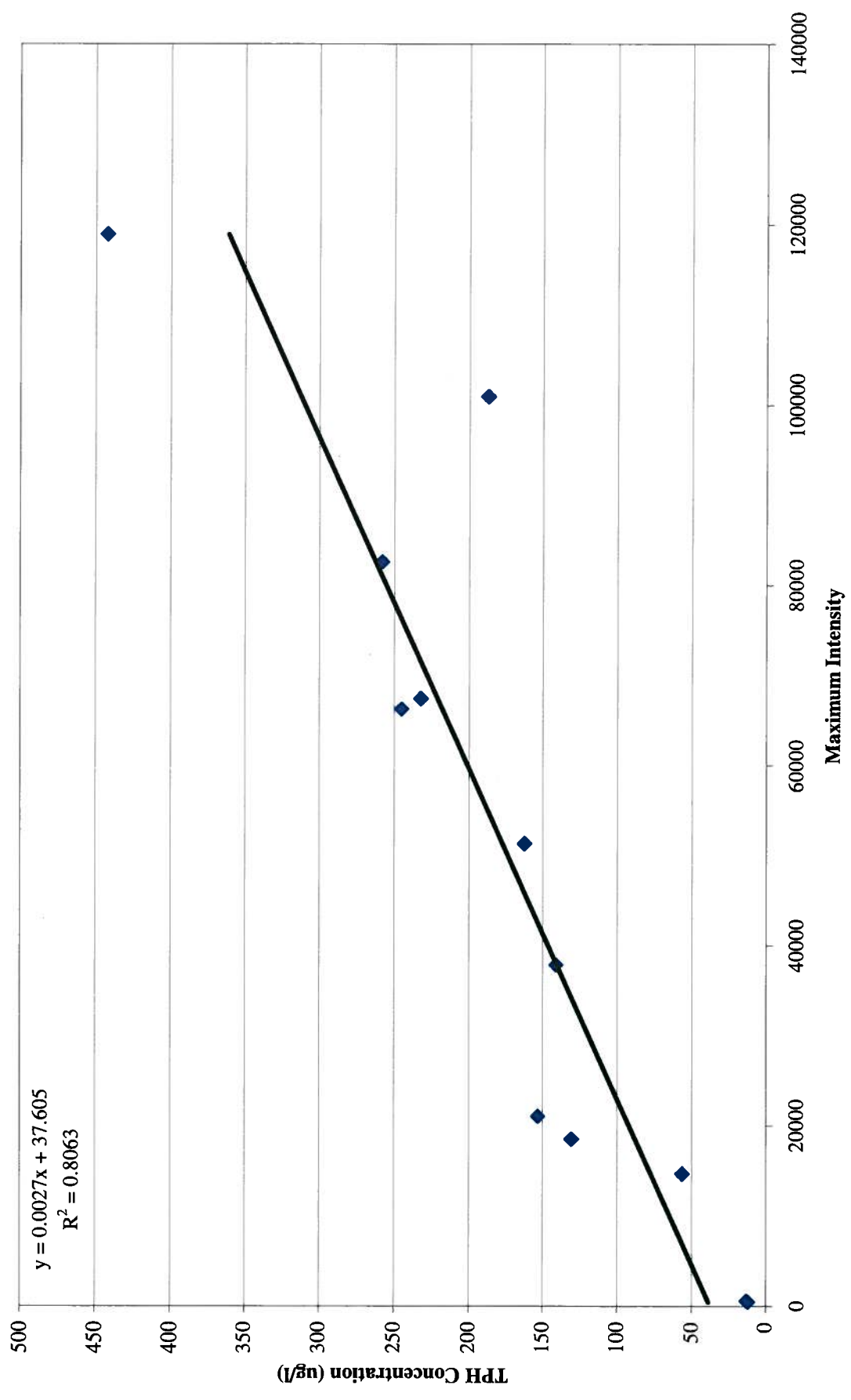


Figure 4. TPH Versus Total PAH

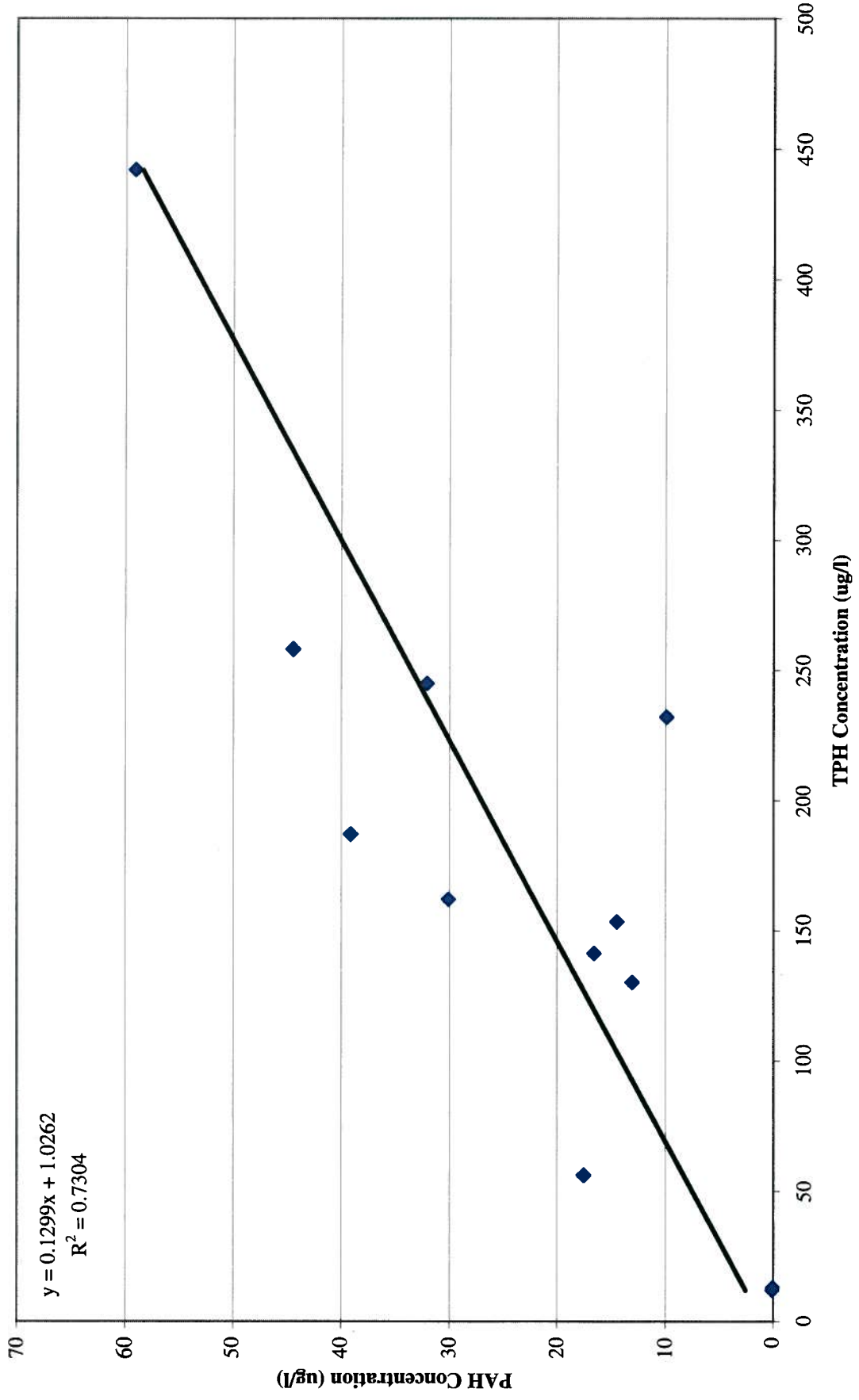


Figure 5. Aliphatic distribution station 6 (1.2 miles from DWH at 1240 meters).

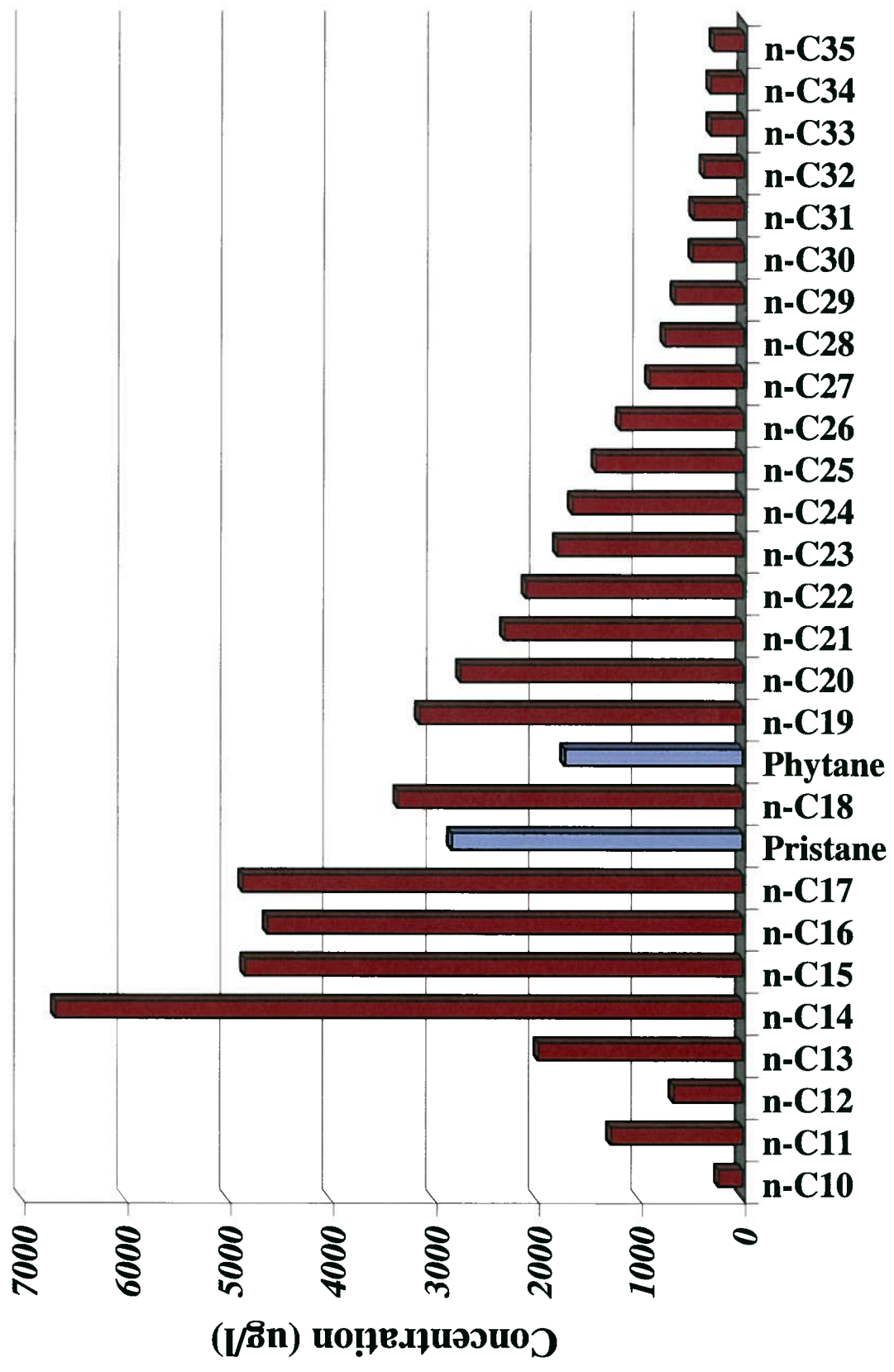


Figure 6. Aliphatic distribution Station 4 (3.5 miles from DWH at 900 meters)

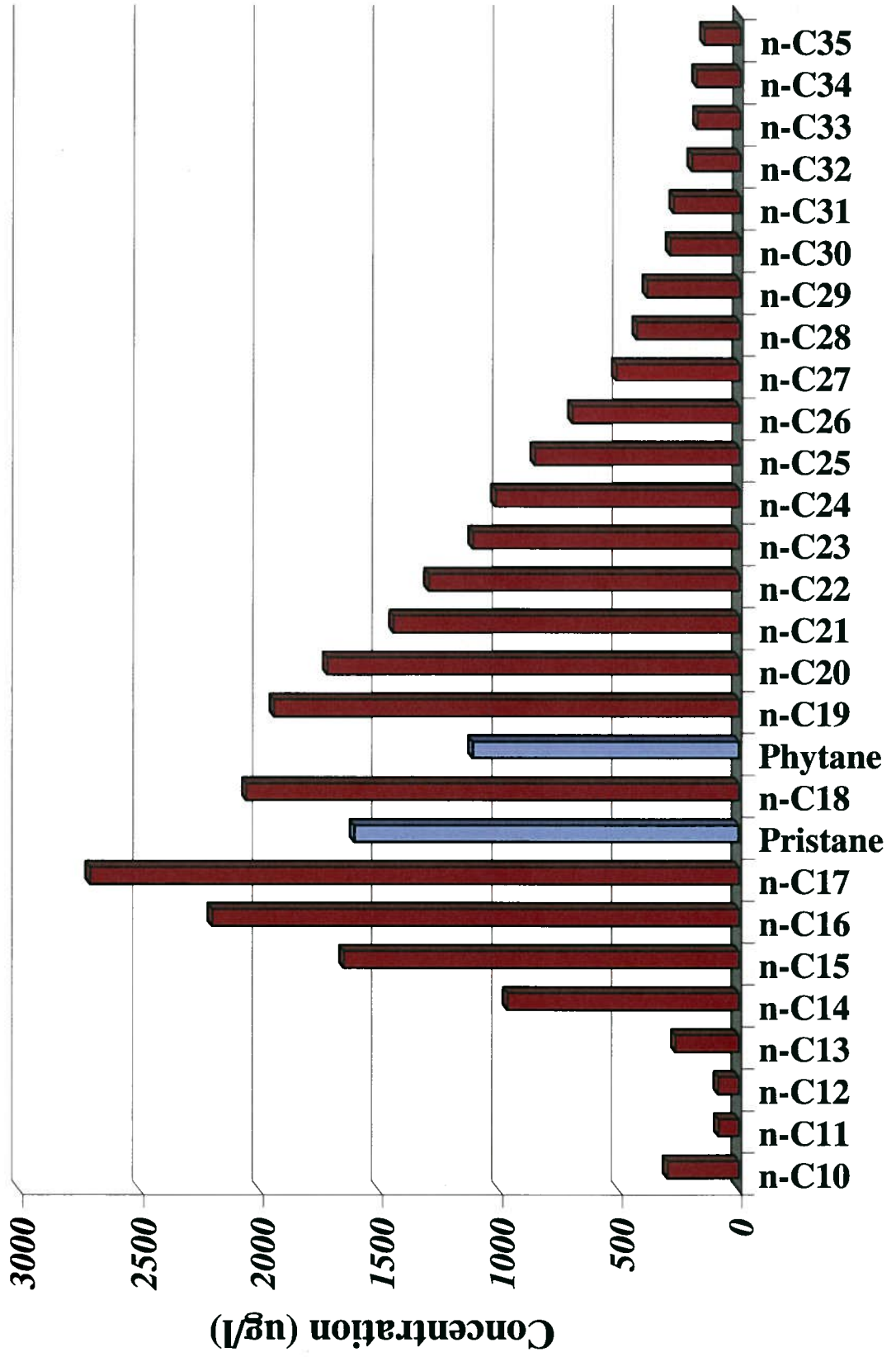


Figure 7. PAH distribution at Station 6 (1240) meters depth

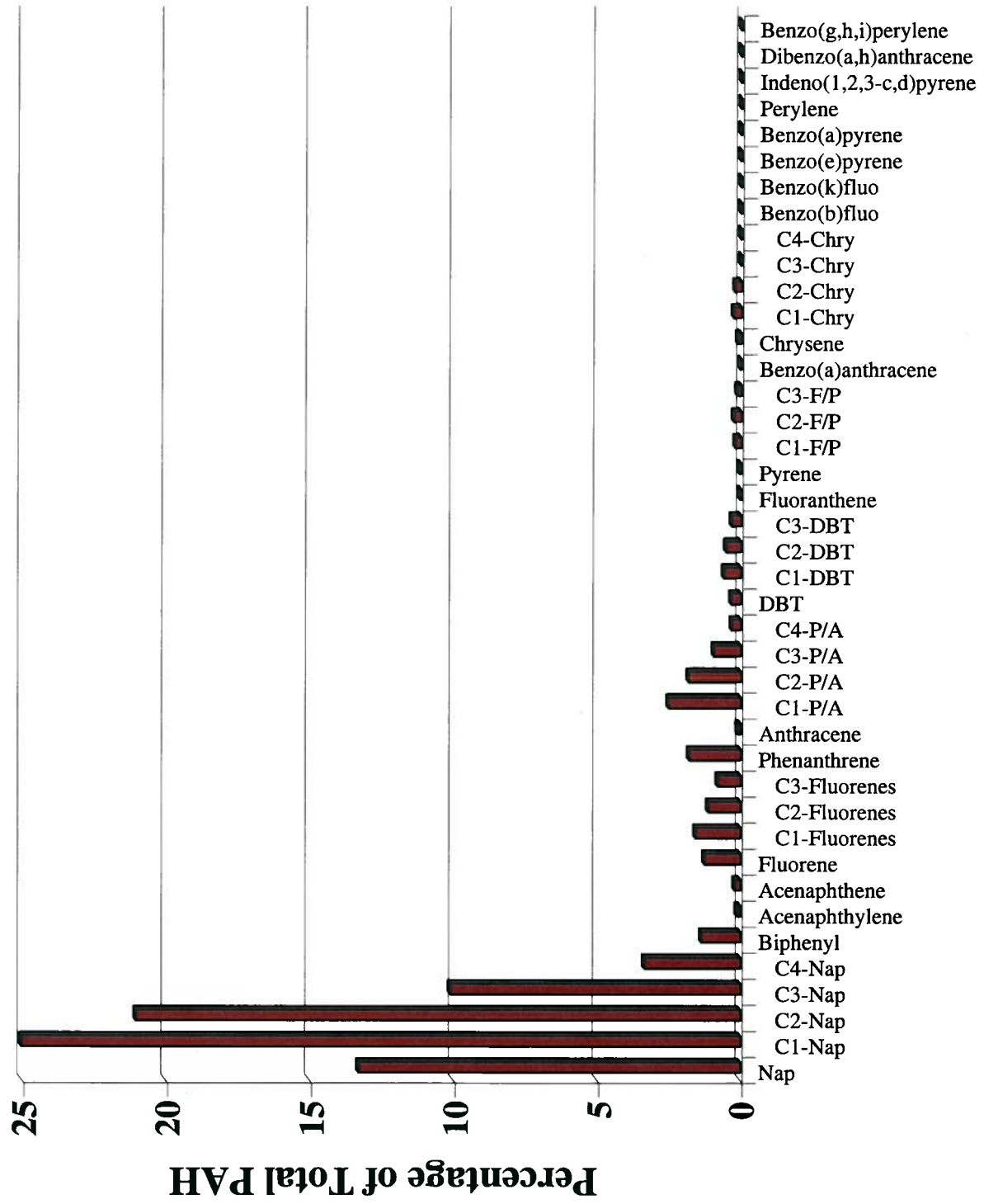


Figure 8. PAH distribution at Station 4 (900 meters)

