

Field Screening of Polycyclic Hydrocarbons Contamination in Soil using a Portable Synchronous Scanning Spectrofluorometer

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) contamination is a considerable problem at various hazardous waste sites. Sources of PAH contamination include incomplete combustion processes, wood preservatives, and the fuel industry (1). The development of rapid, cost-effective field screening techniques to qualitate or quantitate potential PAH contamination could result in improved remediation efficiency. We have recently developed a portable spectrofluorometer (2) for screening potential PAH contaminants at field sites using the synchronous fluorescence approach.

Synchronous fluorescence differs from the more conventional excitation or emission fluorescence as both monochromators are scanned simultaneously with a constant wavelength offset ($\Delta\lambda$) between the two. The principles of synchronous fluorescence have been explained in detail by Vo-Dinh (3,4). For a single molecular specie, the resulting spectra are typically reduced to a single peak with a narrower bandwidth than convention fluorescence spectra. In the analysis of PAH mixtures, the location of the peak offers the user a qualitative device for determining the type of PAH contaminant present.

The portable spectrofluorometer was developed at Oak Ridge National Laboratory (ORNL) for the U.S. Environmental Protection Agency (EPA), National Exposure Research Laboratory, and recently field tested at the American Creosote Works Superfund Site in Jackson, Tennessee (5). The unit demonstrated the capability for screening PAH contamination in soil samples and also provided fingerprint identification of specific groups of contaminants. Hot spots could be readily identified rapidly on-site following measurements performed in 10-15 mins.

In this paper, the portable spectrofluorometer was used to field screen several contaminated soil areas located at the Morristown Industrial Site in Morristown, Tennessee using the synchronous fluorescence technique. An attempt to quantify PAH contamination was performed using the NIST 1647a Priority pollutant standard to generate a calibration curve. Representative samples were subsequently related to the results obtained from standard laboratory measurements.

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2. SITE DESCRIPTION

The City of Morristown faced a unique problem at a site located in an industrial park and owned by the City. Soil from another property had been moved to the industrial park based on the assumption that this soil was only contaminated with petroleum hydrocarbons. However, the site of origin had been previously owned by a railroad company and the State of Tennessee Department of Health and Environment requested additional sampling and analysis to determine if polyaromatic hydrocarbons were present in the contaminated soil piles.

The soil was arranged in a series of eleven elongated piles at the industrial park (Figure 1). All the soil piles, with the exception of pile 9 appeared to be relatively uniform in content. Twenty samples were collected from each of the ten uniform soil piles. Distinct color and odor differences between the northern and southern portions of soil pile #9 were observed at the time of sampling. Samples were taken from the northern portion of the pile, which appeared to be more contaminated. The samples were stored on ice and submitted to a commercial lab for analysis of combined benzene, toluene, ethylbenzene and total xylenes (BTEX) in accordance with EPA methods 8020 and 5030 and total petroleum hydrocarbons (TPH) in accordance with the Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) methods of the Tennessee Department of Environment and Conservation (TDEC), Division of Underground Storage Tanks.

Based on a suggestion by the TDEC, the commercial laboratory was directed to run a base/neutrals and acids (BNA) analysis on the same soil samples for comparison purposes. The resulting analyses provided data on petroleum hydrocarbon as well as volatile organic concentrations in the samples taken from soil piles 9 and 10, which required further study. The other nine soil piles appeared to be below state action levels for petroleum hydrocarbon as well as polyaromatic hydrocarbon concentrations.

Additional study on piles 9 and 10 proceeded using the portable spectrofluorometer as a qualitative tool to select a range of appropriate sampling locations which could be sampled and analyzed at a commercial laboratory. The goal was two fold: first, to correlate the synchronous results with the laboratory results and second to minimize the cost of analysis.

3. EXPERIMENTAL

3.1 Instrumentation

The portable spectrofluorometer has been previously described in detail (1). Briefly, the unit consists of a flashlamp (EG&G) as the excitation source, two monochromators (Optometrics, 2400 lines/mm) and a photomultiplier detector (Hamamatsu, R1527) arranged in the conventional 90° excitation-emission configuration. The instrument is battery operated and can use either standard quartz sample cells or a fiberoptic probe. The unit is controlled via the RS232 port with a notebook computer using software developed at ORNL.

3.2 Field sampling

Composite samples were taken from pile 9 and 10 and split in two similar portions for

analysis using either synchronous fluorescence or GC analysis. A total of 22 samples were taken from the two piles. All samples were screened using synchronous luminescence. Five of the 22 samples (based on their synchronous signals) were then selected for analysis at Kenwill Analytical Laboratories in Maryville, Tennessee using EPA method 8270 for PAHs and the Tennessee Method for Determination of Gasoline and Diesel Range Organics.

The soil samples for synchronous fluorescence analysis were prepared as follows: 1-g of soil was weighed into a 20-mL vial and extracted by adding 5-mL cyclohexane and shaken for 1 min. After the mixture was allowed to settle (3-5 min), the supernatant was drawn off with a pipette and transferred to a 20-mL vial. The soil sample was extracted a second time with another 5-mL portion of cyclohexane and combined with the first supernatant. The sample was allowed to settle and a 2-mL portion of the extract transferred to a cuvette and scanned in the synchronous mode. Prior to analysis, the color of the extract was examined. If the extract had a distinct yellow or black color, the extract was diluted 1:10 or 1:100 prior to analysis. The samples were scanned from 300-510 nm with a $\Delta\lambda = 10$ nm with 3.3-nm slits. The average duration of the scan is 4.5 min. Spectra were processed using SpectraCalc (Galactic Industries Corp). The total area (300-500 nm) under the peaks was calculated using the mathematical algorithm provided in the SpectraCalc software. The total area was compared to a calibration curve established using the NIST 1647a reference samples of PAHs as standard. If the sample area was not within the linear range of the calibration curve, it was diluted with cyclohexane until the signal fell within the linear dynamic range. The area of the blank samples was negligible and was not subtracted from those of the samples.

Two quality assurance measures were implemented in this study. An anthracene standard was prepared and analyzed in the laboratory and in the field. No significant difference was observed between the laboratory and field spectra indicating the unit was working properly. Also, cyclohexane blanks were periodically measured throughout the day to ensure no contamination had occurred.

4. RESULTS AND DISCUSSION

In a previous field trial (5), the portable spectrofluorometer could easily identify relative PAH contamination, and also provide qualitative data as to the identification of some of the PAHs. Figure 2 shows representative synchronous spectra of soil extracts taken from the Morristown Industrial Site. As seen from the various dilutions and their respective signals, the spectrofluorometer can easily identify relative levels of PAHs in soil at the field site. This screening procedure can help focus remediation efforts at the more contaminated areas, therefore decreasing the cost of environmental monitoring.

Table 1 lists some of the NIST Priority Pollutant PAH and their respective synchronous fluorescence peaks ($\Delta\lambda = 10$ nm). The prominent peaks in Figure 2 at 430-440 nm correspond to perylene while those at 401-411 nm could be attributable to fluoranthene and benzo(a)pyrene. The lower wavelength peak at 376-386 nm corresponds to anthracene derivatives and the 369 nm peak fits the profile for chrysene. An important consideration for the identification of PAH using synchronous fluorescence is the trend that the higher number of aromatic rings, correlates with longer wavelengths (4).

Although the portable spectrofluorometer can determine relative PAH contamination levels, it would be more useful if the Total PAH (TPAH) concentration could be determined on site. In order to accomplish this goal, a suitable standard must be developed which would accurately represent the field site samples. In general, it is not possible to develop a single typical standard for the synchronous method due to the large number and variety of PAHs present at various sites. However, the NIST 1647a standard reference material of PAH Priority Pollutant could be identified as a representative standard. The reference material contains 16 PAH compounds commonly found in environmental samples Table 1. A calibration curve was developed with a linear dynamic range between a TPAH of 0.315 ppm and 11.4 ppm ($r= 0.9976$). The concentration of each field sample was determined using this calibration curve. Based on these results, 5 of the 22 samples were then analyzed using EPA Method 8270. A comparison of the 5 samples showed the synchronous results have some relationship with the TPAH data when compared to the Method 8270 results (see Table 2). A regression analysis of the data was then performed and a linear relationship established between the two data sets ($r=0.9602$). For pile sections which were not analyzed, predicted values for PAH contamination were established using this linear relationship and presented in Table 2. Based on these results, it was suggested that the soil be disposed of in a new RCRA subtitle D landfill as a special waste.

5. CONCLUSION

This field study demonstrated the usefulness of the portable synchronous fluorescence instrument for field monitoring. The device is self-contained and can be operated using batteries. The results indicated that the instrument can provide screening data that can decrease the number of unnecessary laboratory analyses. The linear relationship between laboratory data and that using the portable spectrofluorometer could provide quantitative results in the field and thereby reduce the cost of remediation efforts.

6. ACKNOWLEDGEMENTS

This work was sponsored by the U.S. Environmental Protection Agency (Interagency Agreement EPA No. DW8993-3900-02, DOE No. 1824-B124-A1) and the Office of Health and Environmental Research, U.S. DOE under Contract DE-AC0584OR21400 with Lockheed Martin Energy Systems. Although research described in this article has been funded in part by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore, does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute Agency endorsement of this product.

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Table 1. Wavelengths for PAHs- Synchronous Fluorescence Peaks.

<u>Compound</u>	<u>Wavelength (nm)</u>	<u>Compound</u>	<u>Wavelength (nm)</u>
Anthracene	380	Chrysene	365
Benz (a) anthracene	385	Benzo (b) fluoranthene	407
Benzo (a) pyrene	404	Benzo (k) fluoranthene	402
Pyrene	375	Benzo (g,h,i) perylene	404
Napthalene	325	Dibnz (a,h) anthracene	395
Acenaphthene	330	Indeno (1,2,3-cd) pyrene	468
Fluorene	315	Fluoranthene	408
Phenanthrene	358	Perylene	439

Table 2. Concentration of TPAH using synchronous fluorescence and EPA Method 8270.

<u>Sample</u>	<u>TPAH*</u>	<u>SF</u>	<u>TPAH (predicted)</u>
9-13			144
9-14			0.5
9-15			5
9-16			0.5
9-17			5
9-18*	42	90	1
9-19			7
9-20			7
9-21*	60	376	
9-22			233
10-1*	194	3630	
10-2			10
10-3			5
10-4*	298	4855	
10-5			94
10-6			0
10-7			65
10-8			2
10-9			73
10-10			79
10-11*	360	5360	
10-12			16

*Analyzed at Kenwill Laboratories, Method 8270

PAH= Polyaromatic hydrocarbon (ppm)

SF= Synchronous fluorescence (ppm)

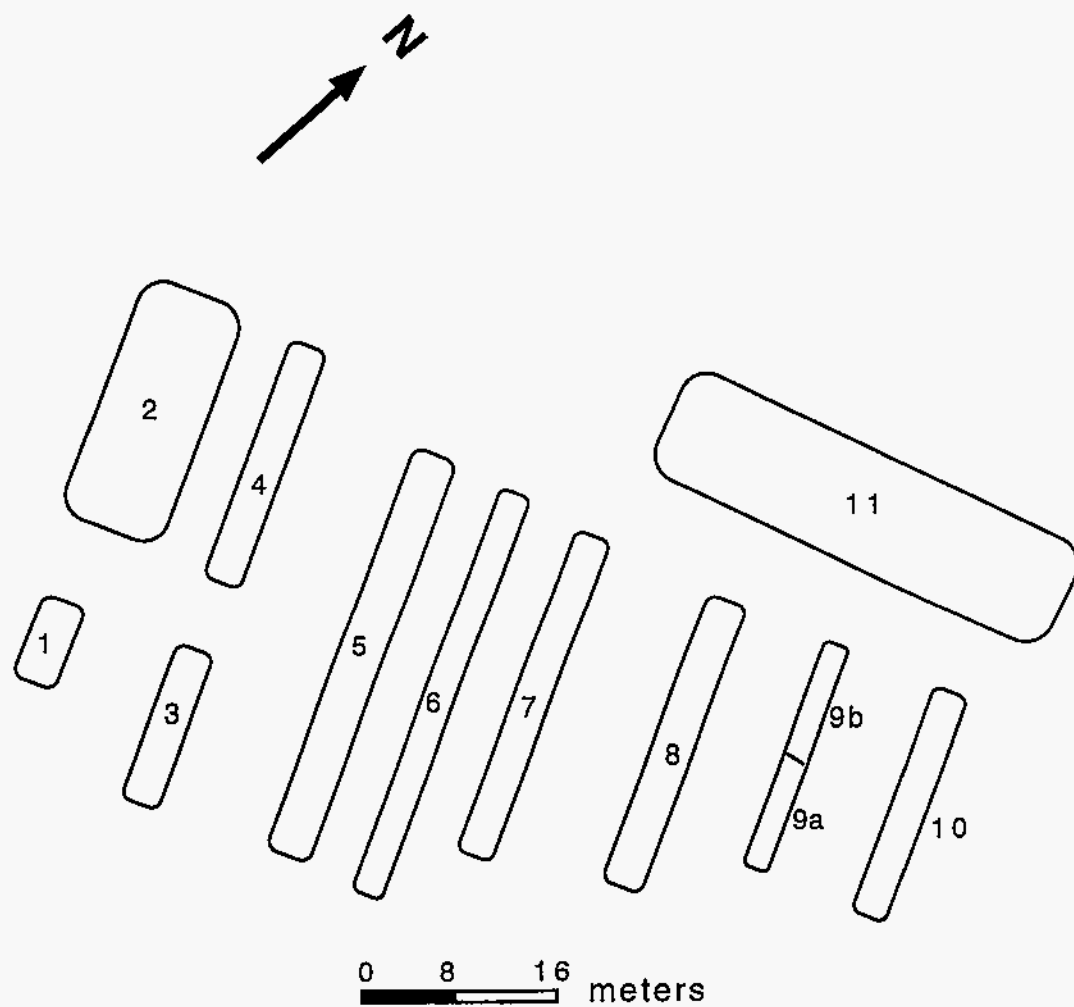


Figure 1. Site map showing location of soil removed from the proposed City of Morristown office building site.

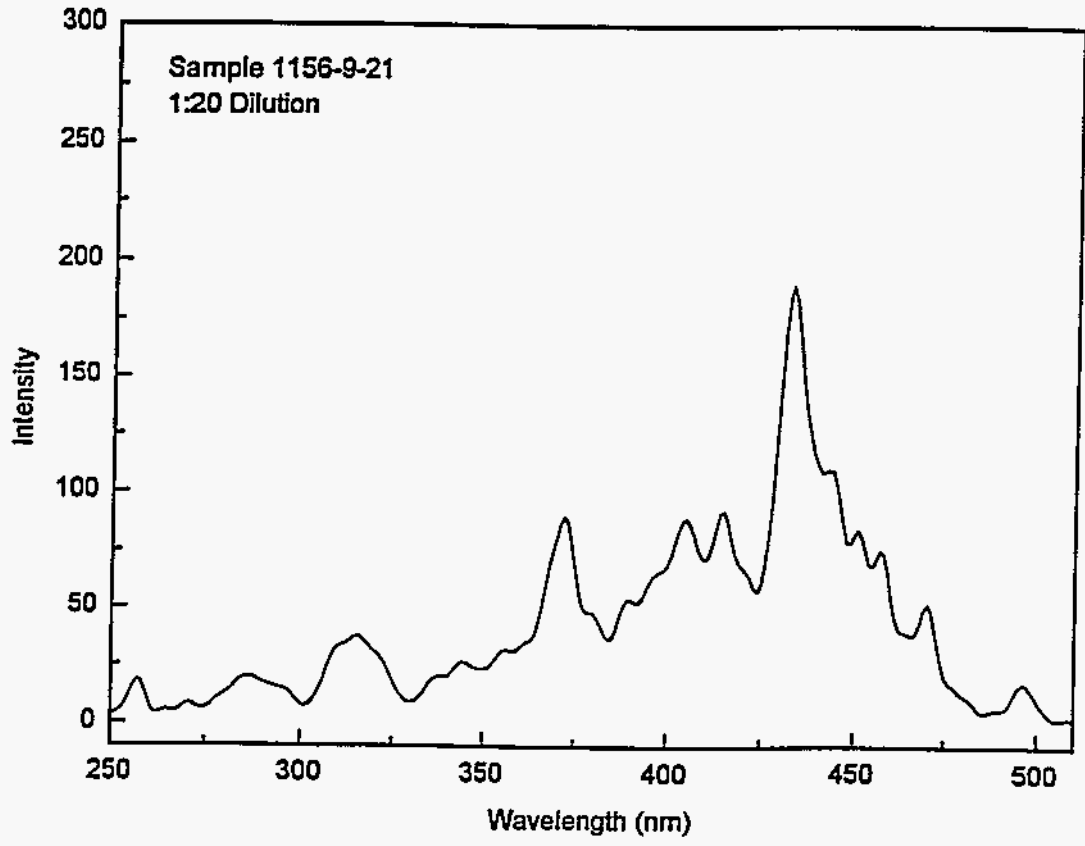
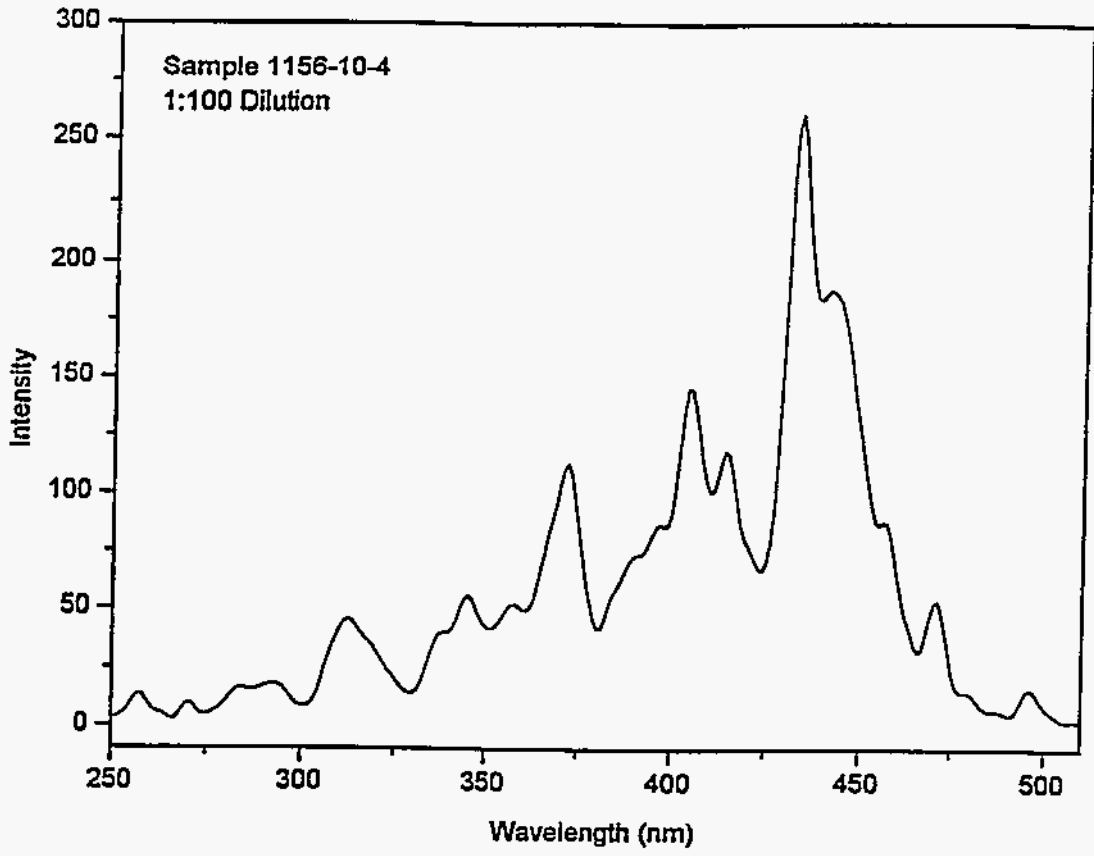


Figure 2. Representative synchronous spectra of soil extracts.