

Article

Polycyclic Aromatic Hydrocarbons in Soil Samples from Diboll, East Texas (USA)

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Abstract: Concentrations of six polycyclic aromatic hydrocarbons (benzanthrone, benz[a]anthracene, chrysene, fluoranthene, pyrene, and triphenylene) of soil samples from Diboll, an East Texas city (USA), were analyzed with gas chromatography-mass spectrometry (GC-MS). Samples were collected from five sites; Old Orchard Park, two heavy traffic intersections (Judd Street and Lumberjack Drive), an industrial site (West Borden Drive), and a truck stop. Acetone and dichloromethane extracts in all samples showed the presence of fluoranthene and pyrene. The sum of fluoranthene and pyrene concentrations in sites followed the order West Borden Drive > Judd Street > Lumberjack Drive > Old Orchard Park > truck stop. Concentrations of fluoranthene and pyrene were in the range 12.3 – 396.5 $\mu\text{g kg}^{-1}$ (ppb) and 13.6 – 209.8 $\mu\text{g kg}^{-1}$ (in dry soil), respectively. Benzanthrone, benz[a]anthracene, chrysene, and triphenylene concentrations were < 2 ppb levels. The higher concentrations in soils were associated with sites close to heavy traffic and vehicular emissions.

Keywords: Soil; PAHs; Diboll; fluoranthene; pyrene; gas chromatography-mass spectrometry

1. INTRODUCTION

The increased use of fossil fuels raises global concerns that stem from environmental contaminations [1]. Of particular note are polycyclic aromatic hydrocarbons (PAHs), environmental pollutants that exhibit health hazardous risks including carcinogenic and/or mutagenic effects to humans and other organisms [2-5]. PAHs are produced mainly by oil derivatives and high temperature processes. Because of the toxic properties of PAHs and their mutagenicity, extraction methods have been developed for quantitation of PAHs in water, soil and air particulates [6][7-10].

The United States Environmental Protection Agency (USEPA) [10] has classified PAHs into various categories based on their mutagenic and carcinogenic effects [11]. Of the sixteen priority PAHs, seven are classified as human carcinogens by the International Agency for Research on Cancer (IARC, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a]anthracene, and indeno[1,2,3-c,d]pyrene) or as non-carcinogenic (acenaphthene, acenaphthylene, anthracene, benzo[g,h,i]perylene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene). The ubiquitous and persistent nature of PAHs in environmental matrices such as soils, makes humans directly or indirectly exposed to PAHs.

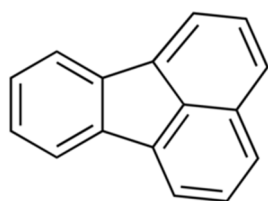
Ninety percent of PAHs in the environment accumulate in soils, which acts as a sink for atmospheric deposition [13]. Besides, other possible sources of PAHs in soils include disposal and/or use of wastewater sewage sludge, urban run-off and cultivation of crops using compost or fertilizers [13, 14]. The analysis of PAHs, especially the 16 priority PAHs in soils have been investigated in the

USA and the world. The analysis of soils and sediments for PAHs reflect the contamination sources and concentrations, and the anthropogenic inputs into the environment [15].

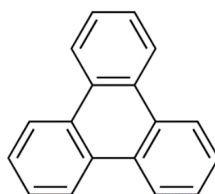
Various methods including supercritical fluid extraction, microwave-assisted solvent extraction, Soxhlet extraction, ultra-sonication, and mechanical agitation [7, 16, 17] are often used for extracting PAHs from soil and sediment. Some disadvantages of Soxhlet method include the large amount of solvent used for extraction and reflux time. Up to 150 mL of solvent may be used for a 10 g soil extraction with a reflux time of 24 hours per solvent system [17], while other researchers have used 50 mL for 8 hrs [17]. Reports show that Soxhlet extractions may produce gas chromatograms with artifact peaks, in addition to humic substances and n-alkanes co-extracted along with PAHs [18, 19]. Ultra-sonication uses the acoustic energy of ultrasonic waves to create rapid compression and rarefaction of fluid movement [16]. Advantages of ultra-sonication include decreased extraction times of 30 – 60 minutes per extraction, decreased sample size (~1 g), and reduced solvent usage [20]. Sun *et al.* [21] showed that ultra-sonication methods yielded PAHs at higher efficiencies than Soxhlet method. However, prolonged exposure to irradiation from ultra-sonication might degrade the PAHs [22]. In addition, ultra-sonication requires additional work-up which consists of centrifugation or filtration prior to collection of the supernatant mixture.

Mechanical agitation uses a mixing action to agitate the soil samples, via magnetic stirring or placement of the soil/solvent mixture on a rotary shaker. Mechanical agitation, however, requires additional work-up such as centrifugation or filtration of the extract. Published reports show mechanical agitation to yield low PAH extraction efficiency (< 75%) compared to Soxhlet or ultra-sonication methods (> 95%) [17, 18]. The reported low efficiencies are however for short extraction times of 5 minutes and 10 mL of solvent. Increased extraction times, sample sizes, and solvent normally increases the extraction efficiency [23]. Because of ease of use of method, and minimal glassware requirements, mechanical agitation was utilized for the extraction of six PAHs (benzanthrone (BA), benz[a]anthracene (BaA), chrysene (CHR), fluoranthene (FLT), pyrene (PY), triphenylene (TP)) in soil samples from Diboll, Texas (See Scheme 1).

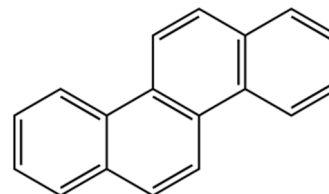
The aim of the present study was to determine concentrations of six PAHs (BA, BaA, CHR, FLT, PY, TP, shown in Scheme 1) from top soils close to the Highway-69 (a major highway) and industrial sites collected from Diboll, a city in East Texas, USA, using gas chromatography-mass spectrometry (GC-MS). The choice of the six PAHs was based on their reported abundancies (FL and PY), their ring structures (4 rings) and their mutagenic potencies to animals. While BaA is a carcinogen [24], it is the nitrated, hydroxyl, and other metabolites of BA, BaA, CHR, FLT, PY, TP that are known carcinogens or mutagenic substances [25-34]. Thus, the monitoring of PAHs in the environment is essential for the planning of sound environmental actions, evaluating potential health risks posed to humans and organisms. This research is essential to understanding the sources and apportionment of PAHs from a busy traffic passing through a major highway.



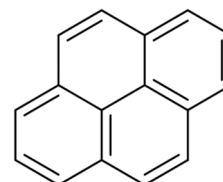
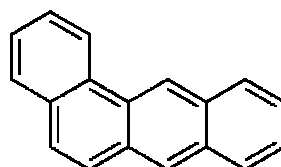
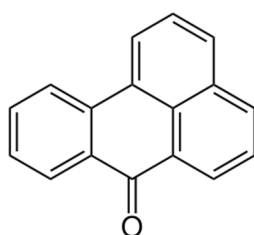
A: Fluoranthene (FLT)



B. Triphenylene (TP)



C: Chrysene (CHR)



D. Benzanthrone (BA) E. Benz(a)anthracene (BaA) F. Pyrene (PY)

Scheme 1. Structures of six PAHS studied in Diboll soils.

2. EXPERIMENTAL DETAILS

2.1. Study Site and Soil Sample Collection

Diboll city is located in Angelina County, East Texas (USA) at latitudes N 31.1861/-94.781 and longitudes W 94.7854. The city is ~ 110 miles northeast of Houston and has a population ~ 5,500. Five sampling sites (Figure 1), namely, Old Orchard Park, an intersection of Lumberjack Drive with U.S. Highway-59, the intersection of Judd Street with U.S. Highway-59, a truck stop site, and West Borden Drive, were selected for the study. The selection of sites (especially intersections and truck stop) was based on their close proximity to Highway-59 and the frequent traffic of from diesel vehicles. The West Borden Drive site, which is in close proximity to four industrial locations and railroad lines, is near an industrial area (and one mile from Highway-59). The Old Orchard Park experiences less vehicle traffic, is one mile from the Highway-59, and two miles east of an industrial site. The other sites (West Borden, Lumberjack Drive, a truck stop) are near to heavy traffic areas but have low vehicle traffic.

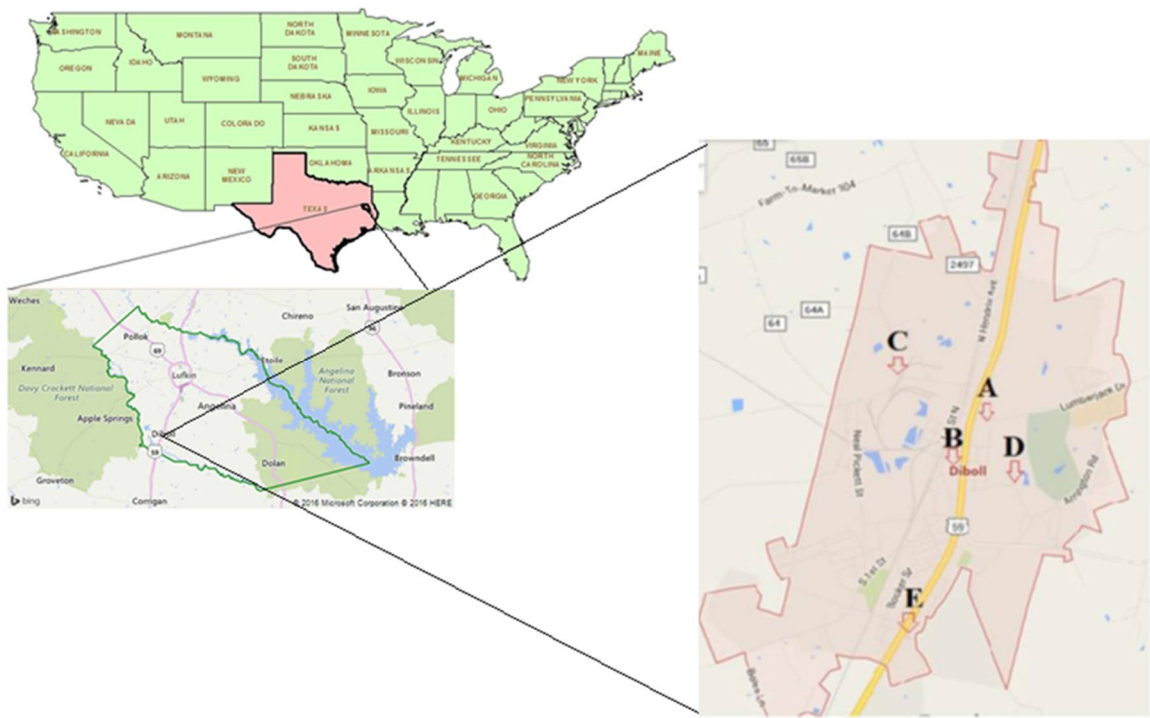


Figure 1. Map of USA, Texas, and Angelina County in East Texas. The five soil sampling sites (Intersection of Lumberjack Drive (A), intersection of Judd Street (B), West Borden Drive (industrial site, C), Old Orchard Park (D), and a truck stop (E)) in Diboll, TX are shown in the inset.

2.2. Reagents

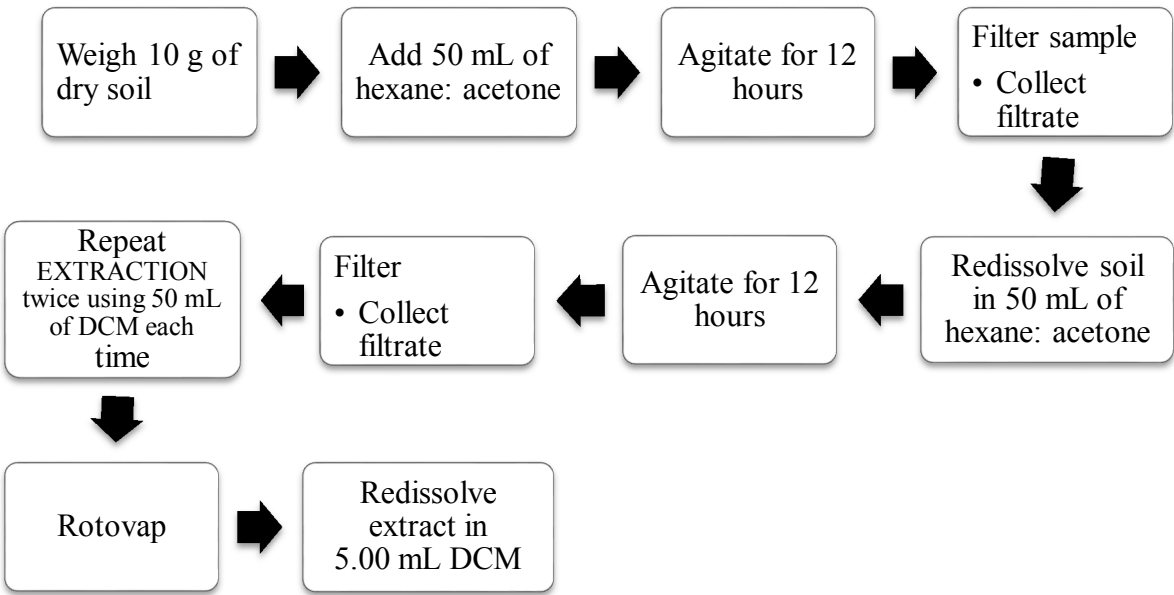
High purity ($\geq 98\%$) benzanthrone (BA), triphenylene (TP), benz[a]anthracene (BaA), chrysene (CHR), fluoranthene (FLT), and pyrene (PY) were purchased from Sigma-Aldrich or Alfa-Aeser. The PAHs were dissolved in dichloromethane (DCM, HPLC grade, 99.8%, Sigma-Aldrich) and used as calibration reference standards. Mixtures of standard solutions ($5 - 500 \text{ mg L}^{-1}$) containing the six PAHs were prepared in cyclohexane (Merck) and stored in the dark at 4°C before use.

2.3. Soil Sample Physical Chemical Characteristics

Soil physico-chemical properties of the soil samples from Diboll were characterized in the lab and summarized in Table 1. Previous characterization [35] is included in Table 1. During analysis soil samples were air-dried and passed through a 2-mm mesh screen. The pH was determined using the suspension of soil to water (1:1 w/v) following USEPA method 9045D [36]. The CEC (Cation Exchange Capacity) was measured by summing Na, K, Mg, and Ca concentrations.

2.4. Extraction and Analysis of PAHs from Soils

Top soil samples (0 - 10 cm depth) from Highway-59 or close to the road were collected in triplicate from the five locations in June 2015. The samples were cored from the soils using plastic pipes, put in nanopure-washed ziplock bags, labeled on site, and transported to the laboratory. To minimize contaminations, soil samples were handled with gloves, plastic spoons or using plastic pipes. Scheme 2 summarizes the soil sample collection and analysis protocol. The samples were homogenized by mixing thoroughly with a stainless steel spatula. Ten grams of dried soil was placed into an Erlenmeyer flask filled with 50 mL of a hexane: acetone (1:1, v/v) solution, and agitated in an orbital shaker for 12 hours (200 RPM at 25 °C). The solution was filtered and the filtrate collected. The soil was mixed with a further 50 mL of the hexane: acetone solution (v/v) and the extraction procedure repeated. Further extraction was repeated 3 more times using 50 mL of dichloromethane (DCM) each time. The collected filtrates were pooled and concentrated using rotary evaporator, and re-dissolved in 5.00 mL of DCM. Aliquots of the soil extract solutions were then analyzed using GC-MS.



Scheme 2. Protocol used for extraction of PAHs from soil.

2.5. Instrumentation

A Varian 450-GC gas chromatograph equipped with an autosampler (Varian CP-8400) was coupled to an ion-trap mass spectrometer (Varian 240-MS). A Phenomenex, Zebron ZB-5 fused silica capillary column (60 m, 0.25 mm i.d., 0.25 µm film thickness) was interfaced to Varian 240-MS mass selective detector operating in the scan mode for GC-MS analyses. A 1.0 µL sample was injected using a splitless mode (20% split ratio). The injection port, transfer line, and ion-trap temperatures were set at 240 °C, 250 °C, and 230 °C, respectively. The carrier gas (helium gas, 99.999% purity), was maintained at a constant flow rate of 1 mL min⁻¹. The oven temperature, initially held at 50 °C, was temperature-programmed at a ramp rate of 20 °C min⁻¹ to 300 °C (hold time 35.00 minutes). The GC-MS Varian mass-selective detector was operated in the scanning mode. The six PAHs BaA, CHR, FLT, PY (four USEPA priority PAHs), BA and TP, and soil extracts, were ionized by electron impact ionization. The total ion chromatogram (TIC) obtained was confirmed with standard mass spectral

fragmentation patterns. Identification of PAHs was achieved using the selected ion mode (SIM) with m/z values 202.2, 228.5, and 230.4. Calibration curves, with $r^2 \geq 99.9\%$, obtained in CH_2Cl_2 were used for the quantitation of PAHs.

2.6. Identification of PAHs in Soil Samples

Prepared standard solutions of BA, BaA, CHR, FLT, PY, and TP were initially analyzed independently on GC-MS and identified based on their retention times and the full scan mass spectral data. To minimize contaminations laboratory procedures were used for quality control and quality assurance including the analyses of method solvent blanks and spiked PAH blanks. Figure 2 shows GC elution profiles of standards, namely, FLT, PY, and BA with retention times (t_r) 19.4, 19.7, and 22.6 minutes, respectively. The elution profile is in agreement with known or calculated dipole moments (BaA = 0.00D, FLT = 0.35 Debye, BA = 3.85 D, CHR = 0.00 D, PY = 0.00D, TP = 0.000 D [30, 37, 38]). Because of similar polarities, dipole moments [37, 38], molecular weights, size, and ring structure, BaA, CHR, and TP eluted from ZB-5 column with close retention times 22.2, 22.3, and 22.3 minutes (Figure 2), respectively.

Figures 3(a) and 3(b) show FLT and PY MS data, with $m/z = 202.3$ exhibiting similar fragmentation patterns. Figures 4(a), 4(b) and 4(c) show that MS fragmentation patterns for BaA, CHR, and TP ($m/z = 228.5$) are the same. Figure 4(d) shows MS spectral data for BA ($M^+ = 230.4$). The concentrations for BaA, CHR, and TP in soil samples were below LOD = 0.2 ppb. Calibration curves from 0 - 500 ppb for the determination of fluoranthene and pyrene (FLT and PY) were constructed, and equations derived, namely, Intensity (MCOUNTS) = 378.35Conc. (FL). ($r^2 = 0.999$, for FLT) and Intensity (MCOUNTS) = 368.63[PY] ($r^2 = 0.997$; for PY) derived.

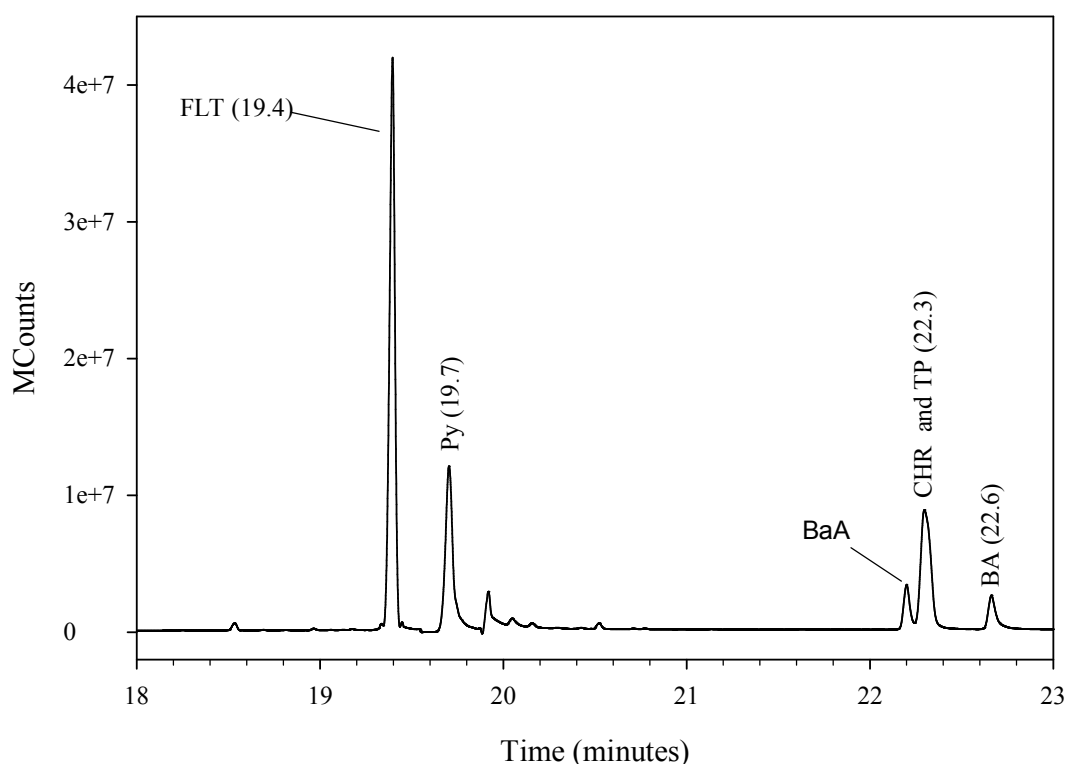


Figure 2. Gas chromatographic profiles of PAH standards benzo[a]anthracene (BaA), benzanthrone (BA), chrysene (CHR), fluoranthene (FLT), pyrene (PY), and triphenylene (TP). A Zebron ZB-5 capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness; Phenomenex, Torrance, CA) was used with a temperature-program: hold time 5 minutes, initial oven temperature held at 50 $^{\circ}\text{C}$, ramp rate of 20 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C}$, run time = 35.00 minutes.

2.7. Quantification, Detection, and Statistical Analysis of PAHs in Soil Samples

Standard solutions in the range 0.0 – 500.0 ppb of PAHs (BA, BaA, CHR, FLT, PY, and TP) were prepared for making calibration curves. By plotting peak areas versus concentration, linear calibration curves with $r^2 = 0.9968 - 0.9990$ were established. The method limit of detection ($LOD = \frac{3s}{m}$; $S/N = 10$ for the LOQs) of the standard solution was evaluated through signal/noise ratios using 10 replicates and a standard deviation (σ); where s is the standard deviation of at least 10 replicate measurements at the 99 % confidence level. The calculated LOD was ≤ 0.2 ppb for fluoranthene, BA, BaA, CHR, and TP, and 0.4 ppb for pyrene.

2.8. Quality Assurance of Measurements

To avoid any contamination, HPLC analytical grade solvents were used throughout the analytical procedures. All glassware was washed and dried using nanopure water and appropriate solvents. Quality control samples analyzed included fifteen laboratory blanks and at least three triplicates at each site. Identification and quantification of individual PAHs, were carried out by comparing their retention times with a standard PAH mixture. The PAHs namely, benzanthrone, benz[a]anthracene, chrysene, fluoranthene, pyrene, and triphenylene with purity > 98% were dissolved in dichloromethane (DCM, HPLC grade, $\geq 99.8\%$, Sigma-Aldrich) and used as calibration reference standards. Several blanks ($n = 3$) were treated in same way as samples. Method blanks, spiked blanks, and sample triplicates were analyzed along with the field samples in this study. The recoveries calculated using the formula:

(% recovery = $\frac{C_{\text{spiked sample}} - C_{\text{unspiked sample}}}{C_{\text{added}}} \times 100\%$) were determined $\geq 88\%$ (% recoveries: BA = $92 \pm 4\%$, BaA = $89 \pm 5\%$, CHR = $93 \pm 2\%$, FLT = 87 ± 3 , PY = $97 \pm 2\%$, and TP = $88 \pm 4\%$).

3. Results

3.1. Physical and Chemical Characterization of Soil samples

The physico-chemical soil characteristics from Diboll are summarized in Table 1. These soils are characterized as fine-silty, siliceous, superactive, thermic Albic Glossic Natraqualfs [35] The determined pH was in the range 7.6 – 8.9 (Table 1). The loamy soils are capable of holding contaminants in their lattice structure. Macroelements including Ca, Mg, Na, K are present in the A horizon, although typically deficient of Al, Si, Mn, Na, C, S and organic matter. Table 1 shows that within the 1-13 cm depth, the Diboll soils have K (64.1 - 90.99 ppm), Ca (1178 - 4428 ppm), and Mg (76.5 – 192 ppm), organic matter (1.6 – 5.5 ppm), total N (0.13 - 0.30 wt %). The available P follows the trend: 9.197 ppm (Old Orchard) < 9.968 ppm (West Borden Dr.) < 25.475 ppm (Truck Stop) < 53.905 (Judd Street) < 54.479 (Lumberjack Drive). The cation exchange capacity was earlier determined to be (0.062, Table 1). In the current determination the electrical conductivity of the soils is in the range $9.27 \mu\text{S}/\text{cm} - 10.1 \mu\text{S}/\text{cm}$ vi-a-vis earlier determination of $\sim 4 \mu\text{S}/\text{cm}$ [35].

TABLE 1. Physico-chemical properties of Diboll soils at 0 -10 cm depths.

| Parameter. | Value** | Old Orchard Park | West Borden Drive | Lumberjack Drive | Judd St. | Truck Stop |
|--------------------------------------|--------------------------|---------------------|----------------------|---------------------|--------------------|--------------------|
| pH | | 8.0 | 7.85 | 7.7 | 8.9 | 7.6 |
| Bulky density (g cm^{-3}) | 1.50 - 1.51 ^a | ND | ND | ND | ND | ND |
| Chemical properties | | | | | | |
| C/N ratio | 13 ^a | 6.289 | 9.442 | 8.722 | 9.484 | 9.51 |
| Potassium (K), ppm | | 70.4 \pm 1.5 | 63.7 \pm 0.6 | 65.6 \pm 0.5 | 70.31 \pm 2.0 | 90.99 \pm 1.01 |
| Calcium (Ca), ppm | | 3662 \pm 335 | 4428 \pm 235 | 1095 \pm 108 | 3796 \pm 307 | 1178 \pm 122 |
| Magnesium (Mg), ppm | | 192.0 \pm 45.3 | 133 \pm 57 | 76.5 \pm 28.5 | 115.24 \pm 18.76 | 117.02 \pm 21.76 |
| Cation exchange capacity (CEC) | 0.62 ^a | 3923 \pm 11.5 | 4625 \pm 18.2 | 1237 \pm 6.56 | 3982 \pm 10.39 | 1386 \pm 7.2 |

| | | | | | | |
|---|-------------------|-------------|------------|-------------|-------------|-------------|
| Ammonium nitrogen (NH ₄ ⁺ -N) ppm | 5.4 ^a | 6.13 ±1.20 | 6.51± 0.39 | 7.57 ± 4.21 | 8.63 ± 0.42 | 5.79 ± 0.01 |
| Organic matter | | 1.65 ± 0.07 | 4.78 ±1.10 | 2.73 ± 0.08 | 5.47 ±0.35 | 3.08 ± 0.04 |
| Organic carbon (% wt., OC) | 1.66 ^a | 0.83 ± 0.01 | 2.39 ±0.02 | 2.73 ± 0.01 | 2.74 ± 0.01 | 1.54 ± 0.01 |
| Total nitrogen (% wt) | 0.080 | 0.13 ± 0.07 | 0.25 ±0.04 | 0.16 ± 0.02 | 0.29 ± 0.04 | 0.16 ±0.05 |
| Total phosphorus (ppm) | | 9.197 | 9.968 | 54.479 | 53.905 | 25.475 |
| Electrical conductivity μS/cm | 8.2 ^a | 9.70±0.20 | 10.1±0.30 | 9.58 ± 0.04 | 9.27 ±0.40 | 9.27± 0.35 |

ND = Not determined. ****Data from Ref # [35].** All other measurements were performed in the lab in this study.

The parameters such as organic matter and total organic carbon may influence the PAH distributions in the soils. The lowest organic carbon (TOC) content was found at the Old Orchard Park (0.826 %) and the Truck stop (1.54%) sites (Table 1). Higher TOCs in other sites increased in the order West Borden Drive (2.39 %) < Lumber Jack Drive (2.73 %) ≈ Judd Street (2.74 %). The low TOC values vis-à-vis higher concentration sites may be due to the low adsorption capacity of the sandy (quartz soils) present at the Old Orchard Park and Truck Stop sites.

3.2. Concentrations of Polycyclic Aromatic Hydrocarbons in Soil Samples

The selected ion mode (SIM) has the advantage of enhancing the peak intensity of selected ions while ignoring undesired peaks that occur at low concentrations (ppb). The *m/z* = 202.2 (FLT and PY), 228.5 (BaA, CHR, and TP), and 230.4 (BA) were selected for SIM mode analysis. The concentrations of PAHs determined from each sampling site are presented below.

Old Orchard Park: Figure 5(a) shows the SIM chromatogram of soil samples from Old Orchard Park site. Of the six PAHs analyzed, FLT and PY were detected in all soil samples in concentrations > 0.2 ppb. FLT was detected in all samples and quantified (via peak area) in samples at 24.2 ± 18.4 μg kg⁻¹ (ppb, in dry soil).

Although PY was detected in all sites, the concentrations found at the Old Orchard Park and Truck stop were less than 0.4 ppb (See Table 2). Samples from Old Orchard Park showed the second lowest fluoranthene concentrations. This park receives regular vehicular traffic and is about a mile from U.S. Highway-59. The large standard deviation suggests that the soil samples extracted were inhomogeneous, which may result from the uneven deposits of PAHs into the soil.

West Borden Drive (Industrial Site): Figure 5b shows the SIM chromatogram of soil samples from the West Borden Drive, an industrial site. The FLT concentrations 142 - 397.7 μg kg⁻¹ (in dry soil (ppb) (Table 2) were 11-fold higher than that found in samples from Old Orchard Park 5.8 - 42.6 μg kg⁻¹ (ppb, dry soil). The pyrene concentrations were determined to be 1477.9 -1590.7 μg kg⁻¹ (in dry soil). Other PAHs (benzanthrone (BA), benz[a]anthracene (BaA), chrysene (CHR), and triphenylene (TP)) were < 0.2 ppb. Due to its proximity to several industrial plants and a railroad line, high concentrations of PAHs were expected for this site; as shown in Table 2.

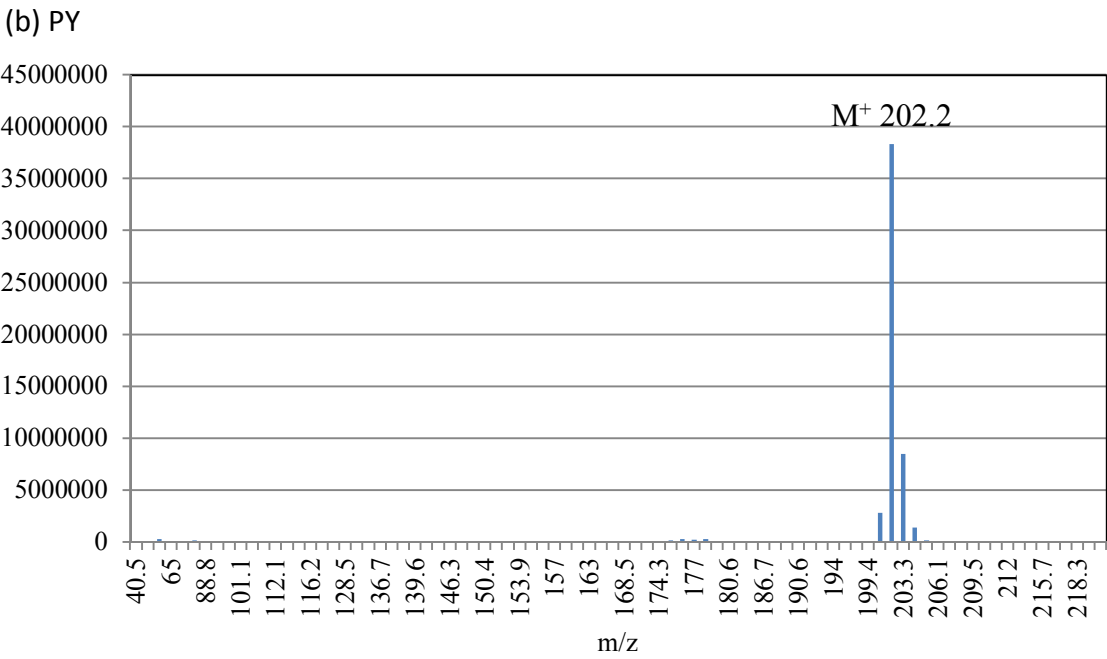
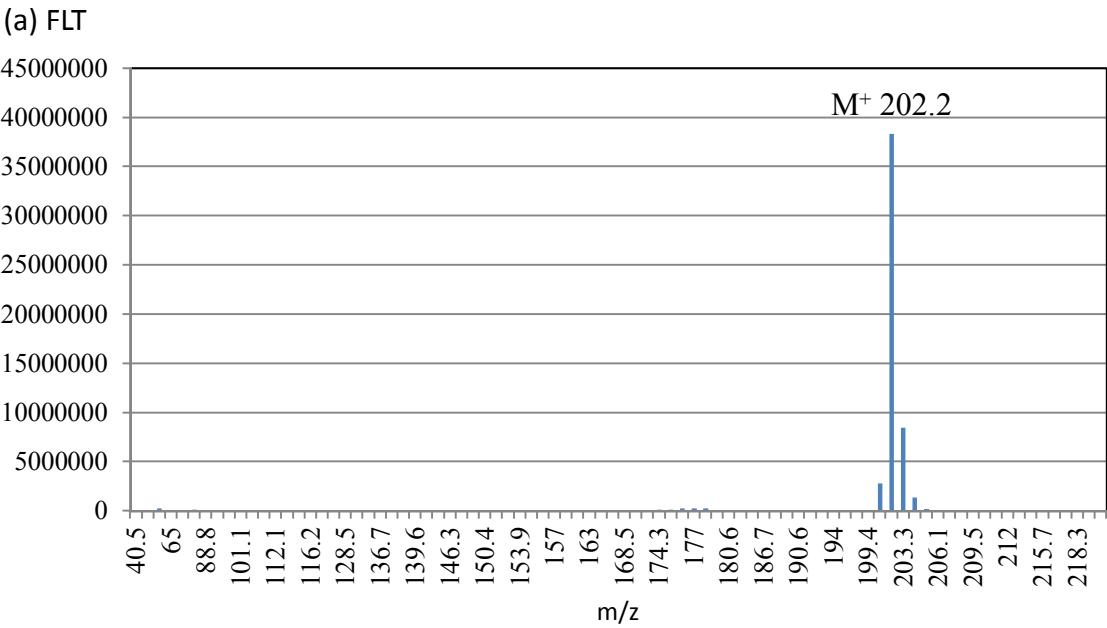


Figure 3. Mass spectra of fluoranthene (a), and pyrene (b). Fragmentation patterns are similar, and both compounds have an M⁺ of 202.2.

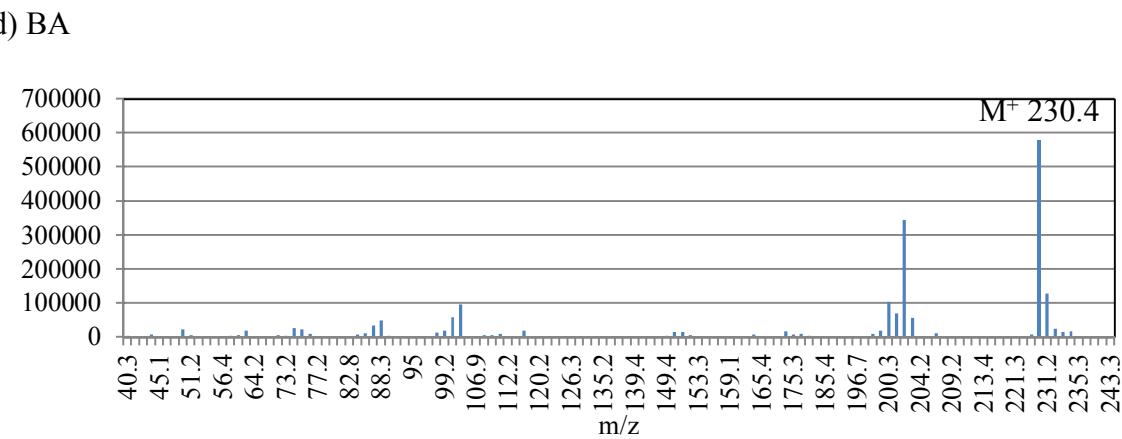
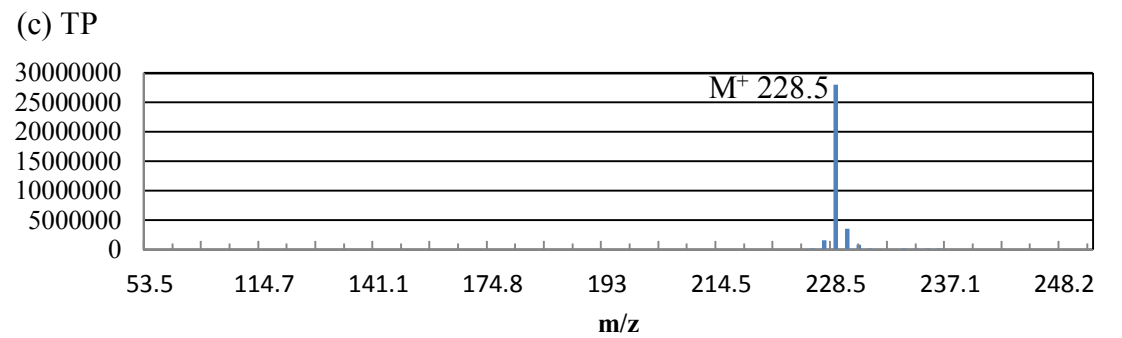
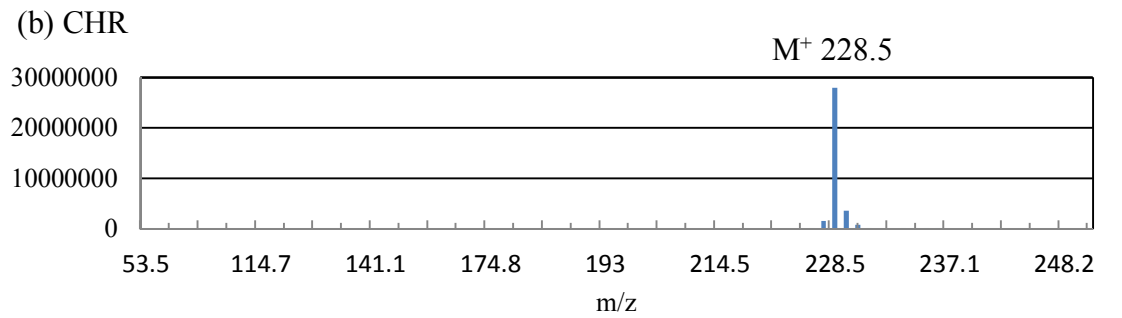
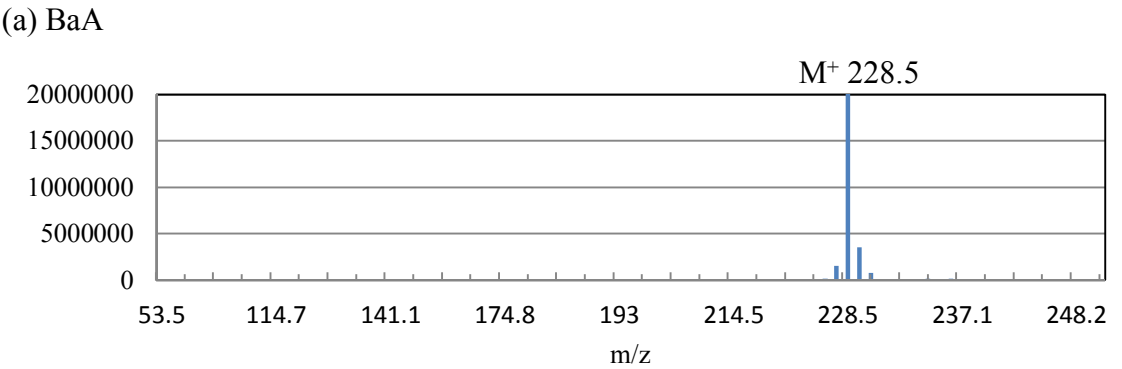


Figure 4. Mass spectra of benz[a]anthracene (a), chrysene (b), triphenylene (c), and benzanthrone (d, with a m/z⁺ = 230.4). The fragmentation patterns of benz[a]anthracene, chrysene, and triphenylene with M/z⁺ = 228.5 amu are identical.

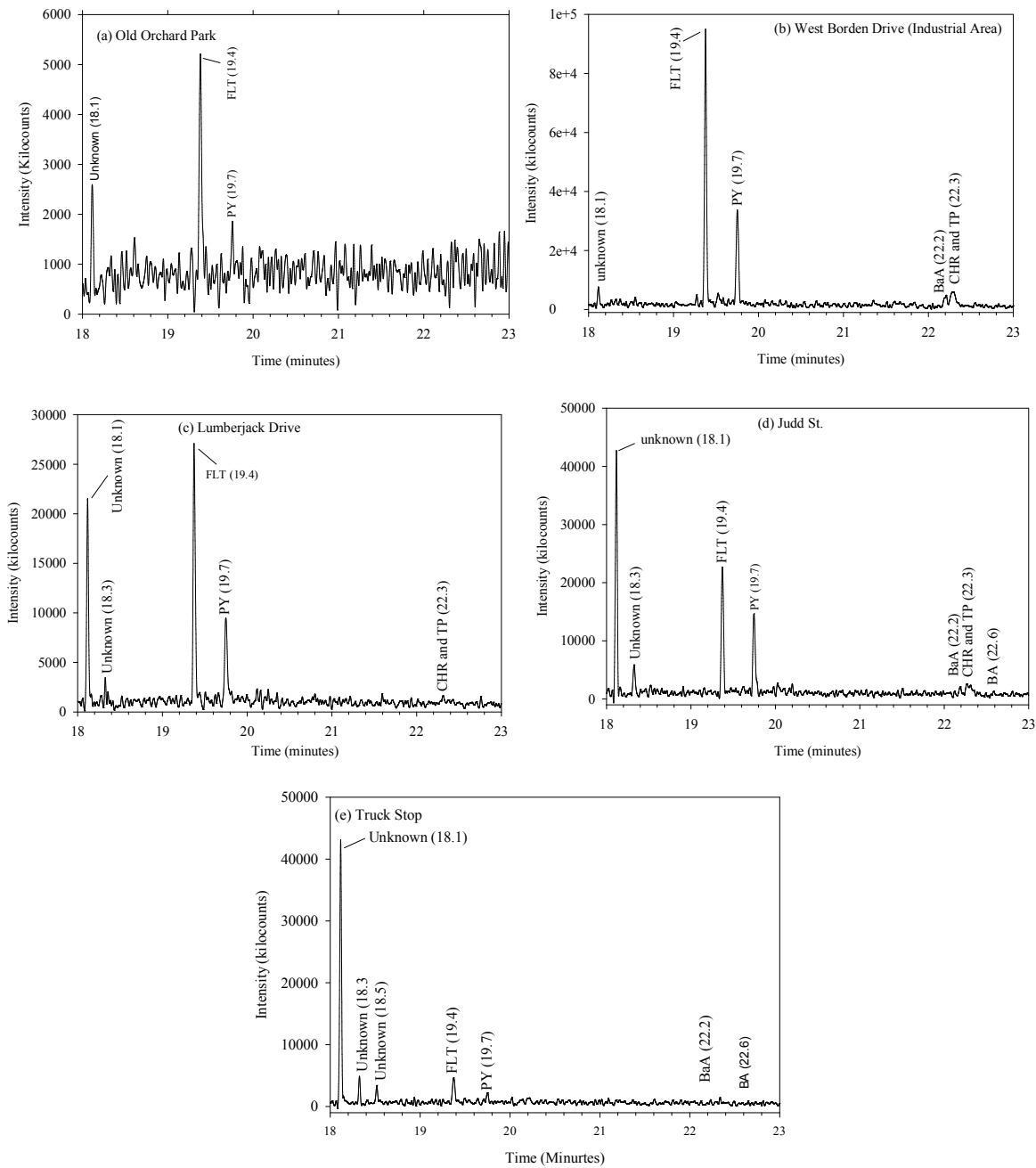


Figure 5. Selected ion spectrum (SIS) gas chromatograms of soil extracts from sample sites and retention times in the 18.0 – 20.0 minutes region: Old Orchard Park (a), West Borden industrial site (b), Lumberjack Drive (c), Judd Street (d), and Truck Stop (e). Selected ions with m/z 202.2, 228.5, and 230.4 were chosen. Conditions used: Zebron ZB-5 capillary column (60 m, 0.25 mm i.d., 0.25 µm film thickness; Phenomenex, Torrance, CA); a temperature-program: hold time 5 minutes, initial oven temperature held at 50 °C, ramp rate of 20 °C min⁻¹ to 300 °C, run time = 35.00 minutes. Chromatograms were detected with a UV-Vis (DAD) detector.

TABLE 2. Concentrations (µg kg⁻¹, in dry soil) of fluoranthene, pyrene, benzanthrone, benz[a]anthracene, chrysene, and triphenylene in soil samples collected from five sites from Diboll, East Texas (USA). n = 3.

| Sampling site/PAH | | Fluoranthene (FLT) | Pyrene (PY) | BA | BaA | CHR | TP |
|-------------------|-----------------|--------------------|-------------|------|------|------|------|
| | Conc. and range | | | | | | |
| Old Orchard Park | Conc. | 24.2 ± 18.4 | 0.4 | <0.2 | <0.2 | <0.2 | <0.2 |
| | Range | 5.8 – 42.6 | | | | | |

| | | | | | | | |
|--|-------|---------------|----------------|------|------|------|------|
| West Borden Drive (Industrial Site) | Conc. | 270.0 ± 127.7 | 1534.6 ± 56.7 | <0.2 | <0.2 | <0.2 | <0.2 |
| | Range | 142.3 – 397.7 | 1477.9 -1590.7 | | | | |
| Lumberjack Drive | Conc. | 46.9 ± 28.0 | 19.4 ±8.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| | Range | 18.9 – 74.9 | 11.2 - 27.6 | | | | |
| Judd St. | Conc. | 86.0 ± 64.0 | 41.2 ± 12.9 | <0.2 | <0.2 | <0.2 | <0.2 |
| | Range | 22.0 -150.0 | 28.3 - 54.1 | | | | |
| Truck Stop | Conc. | 18.1 ± 8.2 | < 0.4 | <0.2 | <0.2 | <0.2 | <0.2 |
| | Range | 9.9 - 26.3 | | | | | |

Note: BA = Benzanthrone, BaA= benz[a]anthracene, CHR = chrysene, and TP = triphenylene were below detection levels in all sampling sites; BD = Below Detection limit of 0.2 ppb.

Lumberjack Drive: Figure 5(c) depicts the SIM gas chromatogram in soil samples from the intersection of Lumberjack Drive with U.S. Highway-59. The detected FLT and PY concentrations in samples were 14.9 – 74.9 $\mu\text{g kg}^{-1}$ and 11.2 -27.6 $\mu\text{g kg}^{-1}$ (in dry soil), respectively. The minimum and maximum FLT concentrations are two-fold higher vis-a-vis Old Orchard Park samples. This is feasible because the intersection of Lumberjack Drive site is located along the busy U.S. Highway-59. Notably, opposite the Lumberjack Drive is a tractor trailer weigh station used by various industrial plants in the city. The engines of the many tractor trailers often run on “idle mode” at this intersection prior to weighing. In addition, Lumberjack Drive intersection has a STOP light where vehicles engines may idle. The heavy traffic and its exhaust emissions may contribute to higher PY and FLT concentrations. Notably, BA, BaA, CHR, and TP concentrations were at < 2 ppb this site (Table 2).

Judd Street intersection: Figure 5(d) depicts the SIM gas chromatogram of soil extracts from the intersection of Judd Street and U.S. Highway-59. Although BA, BaA, CHR, and TP concentrations were found below detection limits (< 0.2 ppb), FLT and PY concentrations in samples were detected in the range of 20.6 -148.6 $\mu\text{g kg}^{-1}$, in dry soil) (ppb) and 28.3 - 54.1 $\mu\text{g kg}^{-1}$ (ppb, in dry soil) respectively. The fluoranthene concentrations in sites follow the order: West Borden Drive (Industrial Site) (142.3 – 398.4 $\mu\text{g kg}^{-1}$) > Judd Street (22.0 -150.0 $\mu\text{g kg}^{-1}$) > Lumberjack Dr. (18.9 – 74.9 $\mu\text{g kg}^{-1}$) > Truck stop (9.9 -26.3 $\mu\text{g kg}^{-1}$ (in dry soil). The pyrene concentrations follow the order: 1477.9-1590.7 $\mu\text{g kg}^{-1}$ (Western Borden Drive) > 28.3 -54.1 $\mu\text{g kg}^{-1}$ (Judd Street) > 11.2 -27.6 $\mu\text{g kg}^{-1}$ (Lumber jack Dr.) > Old Orchard park \approx Truck Stop (< 0.2 ppb, in dry soil). The Judd Street sampling site showed the second highest maximum FLT and PY concentrations. This intersection is further away from a weigh station and receives much less idle traffic vis-a-vis Lumberjack Drive intersection. However, this site receives many moving vehicular traffic, which operate at higher revolutions per minute (RPM) in contrast to idling vehicles. This is in agreement with studies that show that PAH concentrations in vehicle exhaust emissions increase with increasing RPM [34]. The Judd Street intersection is the site of the only bus stop in the city with frequent bus stops, which could contribute to higher FLT, PY, BaA, CHR, TP and BA amounts.

Truck Stop: Figure 5(e) shows the SIM gas chromatogram of soil samples from a Truck Stop site. The concentrations of FLT in these samples was 9.9 - 26.3 $\mu\text{g kg}^{-1}$ (ppb, in dry soil), while PY was detected at low concentrations (\sim < 0.4 ppb). The Truck Stop (showing the second lowest FLT concentration) is the first refueling station in a 30-mile span of U.S. Highway-59, and is visited constantly by tractor trailers and personal vehicles. Considering the number of vehicles at this sampling site, the PAH concentrations were surprisingly low. Such results could be explained by the PAH change from the vapor phase to particulate phase with increasing molecular weight. The lower molecular weight compounds may be volatile and photooxidative in the atmosphere or under atmospheric conditions, in contrast to higher molecular weights that are associated with the soil particles [39].

3.3. Possible isomers of Fluorathene and Pyrene, and Analysis of Unknown Peaks in Soil Samples

In addition to detecting PY, FLT, BaA, CHR and TP as major PAHs in the Diboll soils, other unidentified peaks were found in the in the soils. A possibility of the existence of isomers of FLT and PY may be envisaged. A possible reason for this is presented here. Wise et al [40] analyzed PAHs

mixtures in two standard reference air particular samples. Various 4-ring cata-condensed isomers of pyrene and fluoranthene, namely, chrysene, triphenylene were found in the study. Using a normal-phase LC on an aminosilane column, the analysis showed that pyrene chrysene, benz[a]anthracene eluted from the column albeit having close dipole moments. The 4-ring cata-condensed isomers eluted from the column at different retention times, and separately from PY and FLT. In the present study the proper identification of FLT and PY was determined from the use of known standards as well as the spiking of samples.

Figures 5(a), 5(b), 5(c), 5(d), and 5(e) show unidentified peaks with retention times ~18.1, 18.3, and 18.5 minutes, with corresponding m/z peaks 229.0, 149.0, and 201.0, respectively. From a NIST library database, these peaks could be assigned (possibly) to n-butyl myristate, dibutyl phthalate, and isobutyl laurate (Figure 6), respectively. These compounds are commonly used as plasticizers in cellulosic plastics and polyvinyl chlorides (PVC) [41]. It is also possible that the identities of compounds may include other organic species derived from humic and fulvic substances; products of biodegradation of dead organic matter. Humic and fulvic derivatives constitute a great part of dissolved organic matter in surface soils [7, 41]. However, the identity of these peaks could not be positively confirmed without the use of standard samples or further spectroscopic techniques such as NMR.

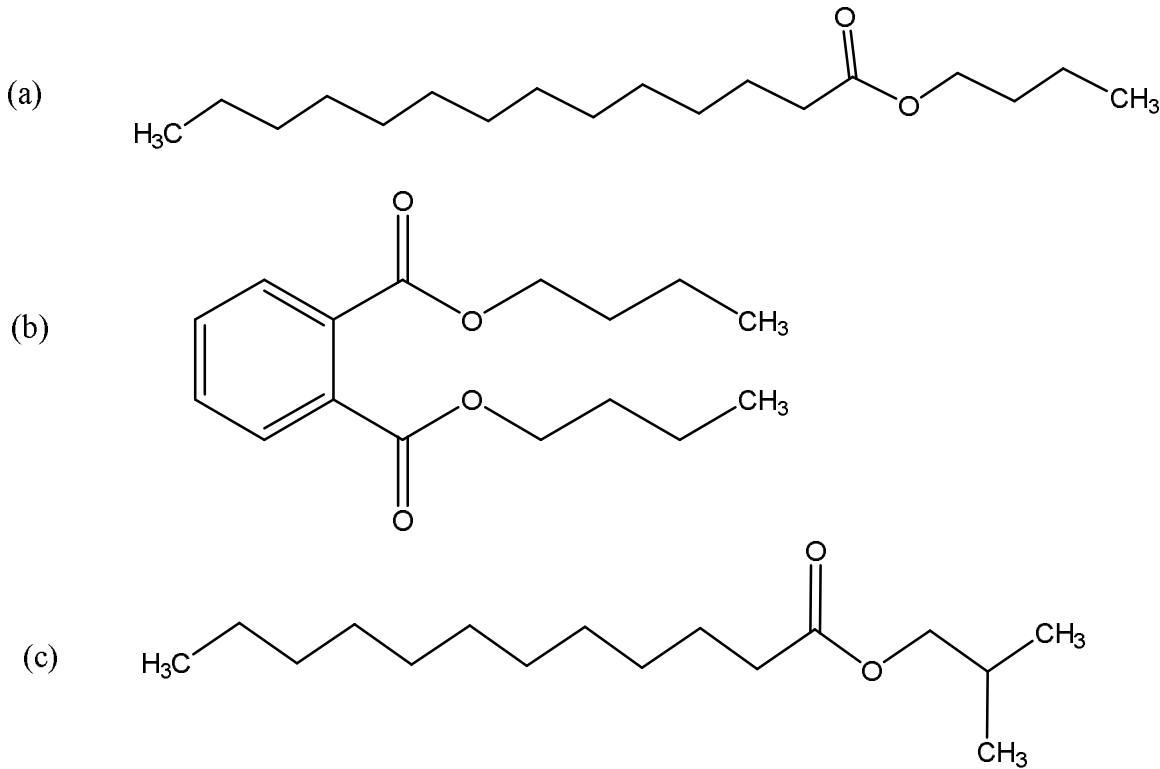


Figure 6. Possible structures of unknown compounds (n-butyl myristate (a), dibutyl phthalate (b), and isobutyl laurate (c)) in soil sample extracts.

4. DISCUSSION

4.1. Comparison of Present Studies to Previous Studies

Fluoranthene (FLT) and pyrene (PY) were detected in soil samples in the range 12.3 – 396.5 and 13.6 – 209.8 $\mu\text{g kg}^{-1}$ (ppb, in dry soil), respectively. From these investigations it is concluded that determined concentrations are comparable with reported FLT concentrations from 565 – 3,167 $\mu\text{g kg}^{-1}$ (ppb) in urban areas and 28 – 65 $\mu\text{g kg}^{-1}$ (ppb) in United States rural areas [42-46]. PY concentrations have been reported from 692 - 3,463 $\mu\text{g kg}^{-1}$ (ppb) in United States urban areas and 25 - 62 $\mu\text{g kg}^{-1}$ (ppb) in United States rural soils [42-47]. The FLT and PY concentrations are comparable to studies

in India [48]. However, concentrations of FLT and PY were determined up to 20 times higher (381 – 6,461 ppb) in one study in Taiwan [49]. In the present study, internal comparisons show that the West Borden Drive site has the highest PY and FLT concentrations. The West Borden Drive sampling area is located at the center of four industrial plants in Diboll. Previously, one of the industrial sites near this sampling site received regular deliveries of coal-tar base creosote by rail car. The creosote was used majorly for the preservation of wood and petrified wood products. FLT and PY are major contaminants of creosote, and are among the more predominant and regulated PAHs in coal tar [47, 50]. Remnants of creosote are likely causes for the elevated concentrations in this area.

The presence of FLT and PY in low traffic areas is usually indicative of FLT and PY emitted to high concentrations of in the environment [51, 52]. As would be expected areas of high vehicular traffic (Lumberjack Drive and Judd Street) had higher PAH concentrations than low traffic areas (Old Orchard Park). However, the “Truck Stop”, which is frequented on a daily basis by hundreds of diesel and gasoline powered vehicles, showed the lowest concentrations of FLT or PY. Most of the diesel vehicles remain idle while powered on in this location. Consequently, PAHs are released from vehicular exhaust emissions to the atmosphere.

Notably, other organic species were detected at these sampling sites. Although the NIST mass spectral library identifies them as carboxylic acids, possibly resulting from being likely derivatives of humic and fulvic substances extracted from the soil [7]. However, the identities of these signals have not been positively confirmed. The detection of benzanthrone (BA), benz[a]anthracene (BaA), chrysene (CHR), triphenylene (TP) and other PAH-derivatives at low concentrations shows their low abundancies in soils at these sampling sites. The detection of these PAHs and their derivatives would be improved by extracting larger amounts of soil (> 10 g) and concentrating the extracts to smaller volumes (< 5.00 mL). Additionally, a standard addition method would be explored for PAHs extractions from soil samples. These would help detect and quantitation of the low quantities of these PAHs.

TABLE 3. Diagnostic ratios of fluoranthene and pyrene (FLT/(FLT+Pyr)) ratios and possible source identification. Ratios are also reported in Ref. # [48].

| PAH ratios | Ratio | Possible Sources | Reference | Present Study |
|--------------|-----------|-------------------------|-----------|---|
| FLT/(FLT+PY) | < 1.0 | Gasoline, Diesel engine | [53] | 0.09 - 0.20 (West Borden Drive) 0.94 (Old Orchard park) > 0.99 (Truck Stop) 0.63 - 0.73 (Lumberjack Drive) 0.29 - 0.84 (Judd St.) |
| | < 0.4 | Petrogenic | [54] | |
| | > 0.4 | Gasoline, diesel engine | [55] | |
| | 1.0 -1.4 | Coal combustion | [53] | |
| | 0.3 - 0.7 | Diesel engine | [56] | |

4.2. Possible Source Identification of Fluoranthene and Pyrene

PAHs of varying molecular weights are released to the environment from varied sources. Diagnostic ratios of PAHs are valid tools of PAH sources analysis because isomer pairs are diluted to a similar extent and distributed similarly to environmental media [57]. Diagnostic ratios are often applied for identification and apportionment of the probable environmental sources [58, 59]. Table 3 shows the diagnostic ratios [53-56] often used for predicting probable PY and FLT sources. Studies show that combustion derived PAHs (pyrogenic) usually contain high molecular weight PAHs, normally generated at high temperatures [60] while petroleum derived residues (petrogenic) contain a high abundance of low molecular weight PAHs (LMW-PAHs) [53-56]. A FLT/PY ratio greater than 1.0 most likely predicts that the PAHs originate from pyrolytic sources [53-56], while a FLT/PY ratio less than 1.0 predicts petrogenic sources. Other studies show that FLT / (FLT+PY) ratio < 0.4 indicate pyrogenic sources, values of 0.4 - 0.5 indicate fuel combustion, and > 0.5 suggests grass/coal/wood combustion sources [60]. The calculated FLT/(FLT+PY) ratios of 0.94, < 0.99 (Table 3) were obtained at the Old Orchard Park, and Truck Stop, respectively, which implicates the gasoline and diesel engine sources. The FLT/ (FLT +PY) ratios of 0.09- 0.20 and 0.63 - 0.73 were calculated at the West

Borden Drive (Industrial Site) and Lumberjack Drive, respectively. This shows that possible PAH sources at the West Borden Drive (Industrial Site) and Lumberjack Drive may be from gasoline and diesel engines; diesel-powered engines/or machines are commonly used at the West Borden Drive site (0.09 - 0.20 ratio). Based on the calculated ratios we conclude that the major PAH sources are diesel combustion, gasoline, wood combustion, vehicle emission, coal combustion and traffic emissions. This is in accord with other studies from rural areas [60, 61].

4.3. Implications of this Study

The concentrations of FLT, PY and other PAHs in the soil samples might raise concerns about human exposure to these PAHs, albeit classified as non-carcinogenic to humans [62-65]. The U.S. Environmental Protection Agency (USEPA) provides guideline exposure limits of FLT and PY in soil samples as 3,100 mg kg⁻¹ and 2,300 mg kg⁻¹ (ppm) [66]. However, their degradation derivatives such as nitrated-PAHs are known carcinogens. Notably, 3-nitrofluoranthene (3-NFLT) and 1-nitropyrene (1-NPY), and other nitro-PAHs (NPAHs) exhibit mutagenic and carcinogenic properties [29, 67, 68]. Although nitrated compounds were not investigated or identified in the soil samples legitimate concerns and pertinent investigations will be sought in future to ascertain their absence. Larger sample sizes and analysis of standard NPAH standards will be needed to determine their presence at the ppb, ng or lower detection levels. Such studies will chart future research into the apportionment of concentrations of PAHs in Diboll, a rural city.

5. CONCLUSIONS

Six polycyclic aromatic hydrocarbons (PAHs) were determined in soil samples from Diboll, East Texas (USA) by using GC-MS. Whereas fluoranthene and pyrene were found most abundant in all soils [69, 70], BaA, BA, CHR, and TP were detected in soil sample extracts at low concentrations. This analysis provides the following conclusions. Firstly, mechanical agitation is an appropriate method for the extraction of PAHs from soil samples when the extraction time is increased to 12 hours. Secondly, the sum of the concentrations of FLT and PY in soil samples decreased in the order of West Borden Drive (industrial site) > Judd Street > Lumberjack Drive > Old Orchard Park > truck stop. Thirdly, GC-MS detected other compounds in the soil samples, with shorter retention times than FLT and PY, indicating that they are likely more polar. Fourthly, the extraction of PAHs from soil samples via mechanical agitation identified unidentified organic substances in soils samples. Although this investigation only used the agitation method, other extraction methods including Soxhlet and ultrasonication will be explored in future. It is further noted that pre-concentration methods would be beneficial to the detection of benzanthrone (BA), benz[a]anthracene (BaA), chrysene (CHR), triphenylene (TP) in environmental samples.

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