

APPENDIX IV

MATES III

FINAL REPORT

**Measurements of Ambient Naphthalene and Other Polycyclic Aromatic
Hydrocarbons**

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Appendix IV

Measurements of Ambient Naphthalene and Other Polycyclic Aromatic Hydrocarbons

IV-1 Background

Naphthalene is the most abundant PAH present in the atmosphere and exists primarily in the gas phase under ambient conditions. Major sources of naphthalene are shown in Figure IV-1. The total estimated inventory of naphthalene in the South Coast Air Basin (Basin) is 1,535 lbs./day for 2005 (see Chapter 3 of this report).

Naphthalene was identified in 1990 as a Hazardous Air Pollutant (HAP) and classified by ARB in 1993 as a toxic air contaminant (TAC). The National Toxicology Program has recently listed naphthalene as a human carcinogen. Additionally, the California EPA Office of Environmental Health Hazard Assessment (OEHHA) has determined ambient naphthalene as a health risk and as a toxic air contaminant under California's Air Toxics Program with a unit risk value of $3.4 \times 10^{-5} (\mu\text{g}/\text{m}^3)^{-1}$.

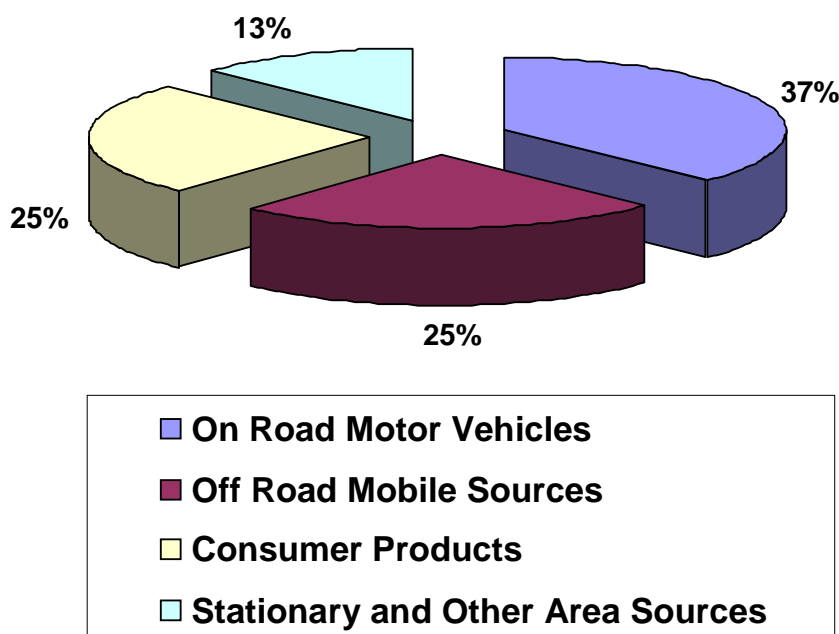


Figure IV-1: Naphthalene Emission Inventory in the South Coast Basin

Particle-bound PAHs are an important class in the complex mixture of chemical compounds observed in ultrafine particles. PAHs and the organic carbon component of ultrafine particles have been shown to be directly correlated to markers for oxidative stress (Li, et al. 2000; Li, et al. 2003; Cho, et al. 2003). Past monitoring in the Basin has shown that individual particle-

bound PAHs are minor contributors to risk (SCAQMD, 2000), despite their high carcinogenicity, because of their low ambient air concentrations which have been decreasing over time (Figure IV-2). Also, some PAHs, such as benzo[*g,h,i*]pyrene, have been suggested to be a tracer for light-duty vehicle exhaust (Miguel, et al. 2005).

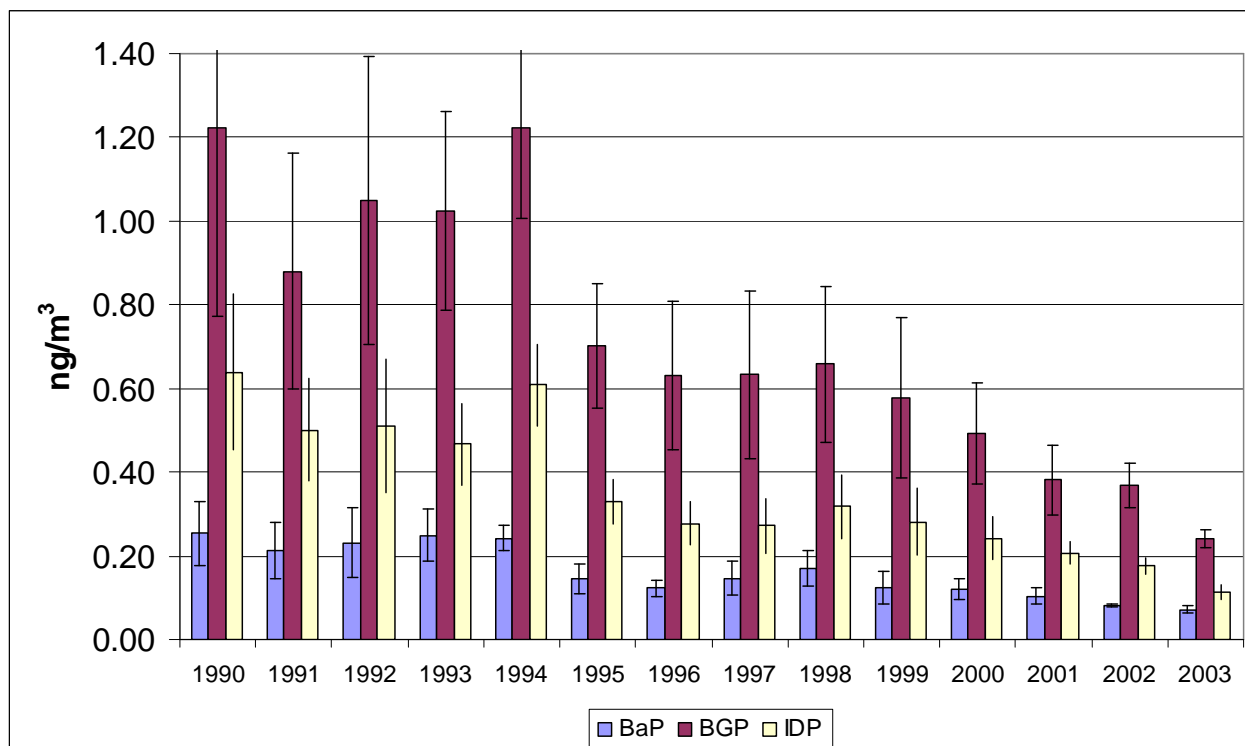


Figure IV-2: CARB Trend Data from 1990 through 2003 for Benzo[*a*]Pyrene (BaP), Benzo[*g,h,i*]perylene (BGP), and Indeno[1,2,3-*cd*]pyrene (IDP)

The MATES II cancer risk assessment showed that the particle-bound PAH contribution-to-cancer risk was insignificant compared to other sources. However, the assessment did not include the semi-volatile or the volatile PAHs such as naphthalene (SCAQMD, 2000). Before 1994, measurements (Table IV-1) showed ambient naphthalene ranging from 750 to 1,300 ng/m³ in the spring with concentrations reaching more than 4,000 ng/m³ during high NO_x or ozone events. In 1996 California Phase II reformulated gasoline (RFG) was introduced which decreased the amounts of alkenes, aromatics, sulfur compounds, and total volatility. Kirchshstetter, et al. (1999) showed that the concentrations of naphthalene and benzene in RFG sampled in Berkeley, California were reduced significantly. After implementation of RFG, significantly lower concentrations ranging from 200 to 575 ng/m³ were observed in the Los Angeles Basin as shown in the Southern California Children's Health Study (CHS) from 2001 to 2002 and subsequent studies by Reisen and Arey (2005). Recent measurements have shown that annual averages of naphthalene are at levels about 1,000 times higher than those of other PAHs (Eiguren-Fernandez, 2004).

Table IV-1 Previous measurements of ambient naphthalene in the South Coast Air Basin

| Period of Measurement | Location | [Naphthalene] ng/m ³ (day) | [Naphthalene] ng/m ³ (night) |
|---|---------------------|---------------------------------------|---|
| 1986 (late winter, high NO _x episode) ¹ | Torrance | 3,315 | 2,875 |
| 1986 (summer, smog episode) ² | Glendale | 3,100 | 4,300 |
| 1987 (spring) ³ | Reseda | 750 | 1,300 |
| 1993 (fall, smog episode) ⁴ | Los Angeles | 6,000 | |
| 1995 ⁵ | Redlands | 348 to 715 | |
| 2001 to 2002 ⁶ | Southern California | 200 to 575 | |
| 2002 (summer) ⁷ | Los Angeles | ~ 350 | ~ 140 |
| 2002 (summer) ⁷ | Riverside | ~ 225 | ~ 40 |
| 2003 (winter) ⁷ | Los Angeles | ~ 1,400 | ~ 1,000 |
| 2003 (winter) ⁷ | Riverside | ~ 500 | ~ 150 |

¹Arey, et al. 1987; ²Arey, et al. 1989; ³Atkinson, et al. 1994; ⁴Fraser, 1998; ⁵Gupta, 1995; ⁶Calvert, et al. 2002; Eiguren-Fernandez, et al. 2004; ⁷Reisen, 2003

PAHs were measured at three of the MATES III monitoring stations using EPA method TO-13A as a guideline. The West Long Beach and Central Los Angeles sites were selected because of their proximity to mobile emissions sources. Also, Lu, et al. (2005) incorporated ambient data from the Southern California CHS and showed the highest naphthalene emissions rate in those regions. The Rubidoux site was selected as a receptor site and also for its particle-bound PAH measurement history as part of the ARB toxics network. Also, collocated samples were done once a month at the Rubidoux site. Table IV-2 provides a list of the 16 PAHs analyzed as part of MATES III.

Table IV-2: List of PAHs Measured in the MATES III Study

| | |
|----------------------|------------------------|
| Acenaphthene | Chrysene |
| Acenaphthylene | Dibenzo[a,h]anthracene |
| Anthracene | Fluoranthene |
| Benzo[a]anthracene | Fluorene |
| Benzo[a]pyrene | Indeno[1,2,3-cd]pyrene |
| Benzo[b]fluoranthene | Napthalene |
| Benzo[g,h,i]perylene | Phenanthrene |
| Benzo[k]fluoranthene | Pyrene |

IV-2 Methodology

IV-2-1 Sampling

The sampling protocol was based on EPA TO-13A in which 24-hour integrated air samples were collected at eight cubic feet per minute (cfm) in a Tisch TE-1000 PUF (polyurethane foam) monitor. The particle phase sample was collected on a quartz fiber filter (102 mm) located upstream from a glass cartridge holding 20 grams of XAD-4 which collected the semi-volatile and vapor phase PAHs. XAD-4 was selected as the sampling media because it has more surface area than XAD-2, allowing for higher collection efficiency of the PAHs. A comparison was done with the PUF/XAD-4/PUF sandwich to ensure that results would not differ significantly from other sampling methodologies, and a breakthrough study was done to ensure that PAHs were not escaping through the XAD-4 cartridge.

Since ambient PAH concentrations in the South Coast Basin have shown seasonal variation (Eiguren-Fernandez, 2004) with higher and more variable concentrations in the winter and lower concentrations in the spring and summer, the samples were collected every third day in the winter of 2004 and 2005 and every sixth day in the spring and summer of 2005. After collection, the samples were chilled and transported to Southwest Research Institute for extraction and analysis.

IV-2-2 Sample Extraction

As with sample collection, the extraction protocol was based on EPA TO-13A. The method was enhanced by using higher internal standard (IS) concentrations of the more volatile PAHs and lower concentrations of the particle-bound PAHs which are reflective of the ratios found in ambient air. This differs from TO-13A which just uses the same concentration for each compound in the IS. Prior to extraction, 25 μ l of deuterated PAH IS mixture was added into each sample. The deuterated PAH IS mixture contained the following compounds: Naphthalene-d8 (1000 ng/ μ l), Acenaphthylene-d8 (300 ng/ μ l), 100 ng/ μ l each of Phenanthrene-d10 and Fluoranthene-d10, and 5.0 ng/ μ l each of Benzo[a]anthracene-d12, Chrysene-d12, Benzo[b]fluoranthene-d12, Benzo[a]pyrene-d12, Indeno[1,2,3-cd]pyrene-d12, Dibenz[a,h]anthracene-d14, and Benzo[g,h,i]perylene-d12.

The XAD-4 glass cartridge and the matching filter were extracted together using 1-Liter Soxhlet extractor with dichloromethane (DCM) as the extracting solvent. The extraction lasted for eight hours with a siphoning rate of 3-4 siphons per hour. At the end of the extraction, the sample extracts were concentrated to about 20 ml by using a rotary evaporator under a gentle vacuum.

With each batch of field samples, four lab QC samples were created and extracted alongside the field samples as follows: solvent blank, XAD-4 blank, lab control spike (LCS), and lab control spike duplicate (LCS-D). The solvent blank had 350 ml of DCM only. The XAD-4 blank consisted of 20 grams of clean XAD-4. The LCS and LCS-D each had 20 grams of clean XAD-4 and one clean filter and each was spiked with 25 μ l of target PAH mix with the concentration similar to that of the PAH IS. Prior to the extraction, each of the QC samples was spiked with the same amount of PAH IS mixture as described above.

IV-2-3 Sample Extract Cleanup for PAH Analysis

One quarter of each sample extract was archived as reserve. The remaining extract was solvent exchanged into 0.5 ml of hexane. Six ml of hexane was then added to the extract. The extract was then vigorously partitioned with 2.0 ml of 25% sulfuric acid in water for 20 seconds.

A disposable pipette (8 mm i.d. x 30 cm long) packed with 5" of activated silica gel was used for sample extract cleanup. The column was pre-cleaned first with 20 ml of distilled DCM and then with 5 ml of hexane. The hexane layer of the acid-washed sample extract was quantitatively transferred onto the silica gel column using hexane as a rinsing solvent. Ten ml of hexane (~3 ml at a time) was used to elute the column and the collected eluent discarded. The PAH fraction was then eluted with 23 ml of DCM/pentane (60/40, ~3 ml at a time).

The collected PAH fraction was mixed well and divided into two parts. The first portion of the cleaned-up extract was carefully blown down to a final volume of 1.0 ml in DCM using a gentle stream of charcoal-filtered nitrogen. This final extract was used for naphthalene through pyrene analysis plus two PAH surrogates.

The second portion of the cleaned-up extract was carefully blown down to 100 µl in two stages. This final extract was used for benzo[a]anthracene through benzo[g,h,i]perylene analysis.

IV-2-4 Sample PAH Analysis by GC/MS

The GC/MS (gas chromatograph/mass spectrometer) used was an Agilent 6890N GC interfaced with an Agilent 5973N MSD (mass spectrometer detector). The column used was a DB-5ms 30 m x 0.25 mm i.d. with 25 µm film thickness. The GC injector and GC/MS interface temperature were held at 290°C. The GC oven temperature program was as follows: 40°C held for 1.5 minutes, 15°C/min to 220°C, then 8°C/min to 310°C and held for 3.5 minutes. The carrier gas was helium at a constant flow rate of 1.5 ml/min.

The GC/MS was operated under EI/PI/SIM mode (electron impact/positive ion/selective ion monitoring). Only the characteristic ions such as molecular ions of PAH ISs, and molecular and major fragment ions of PAH targets were monitored. Acenaphthene-d10, pyrene-d10, and benzo[e]pyrene-d12 were used as recovery standards (RSs). These RSs were spiked into the final sample extracts just prior to GC/MS analysis and were used to quantify the recoveries of the 11 PAH ISs.

The GC/MS analysis was carried out in two stages: the first GC/MS analysis quantified for naphthalene through pyrene on diluted sample extract (1.0 ml); the second GC/MS analysis quantified for benzo[a]anthracene through benzo[g,h,i]perylene on a concentrated sample extract (0.1 ml). Also the lowest calibration point was 10 pg/µl instead of 100 pg/µl as listed in Table 4 of TO-13A.

A five-point initial calibration (ICAL) curve was established using five PAH standard mixtures containing all PAH targets, PAH ISs, surrogates, and RSs. The PAH targets in the five-point curve were at five different levels namely 10, 30, 100, 300, and 1000 pg/µl. The relative response factors (RRFs) of the PAH targets were established using the five-point curve. The relative standard deviation (RSD) of the RRF of each PAH target had to be equal to or less than 25% in order for the ICAL to be considered valid. The RRFs for the ISs relative to the RSs were also established for the five calibration standards in the same way. The ISs and RSs were at 750 pg/µl for all calibration standards.

At the beginning of each sample analysis sequence, a continuing calibration (CC) PAH standard mixture at 300 pg/μl was analyzed. The RRF of each PAH target was established using this CC standard. The percent difference of the RRF of each PAH target in the CC compared with the mean RRF of the ICAL had to be equal to or less than 25%. This CC criterion had to be met before the sample analysis could proceed. The same calibration criterion applied to the ISs as well.

IV-2-5 Analysis of Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST)

The PAH SRM 1597 was diluted 160 folds and 320 folds in DCM. An aliquot of each of the diluted SRM was then spiked with the same PAH IS mix which had been spiked into the field and lab QC samples prior to their extraction. The two NIST PAH SRM solutions were then analyzed alongside the field and lab QC samples.

The analytical concentrations of various PAHs in the diluted SRM solutions were then compared with that of the expected PAH concentrations based on the NIST certified values. A list of PAH concentration ratios, expected/found, was established for those PAHs which had a value in the SRM certificate of analysis. These ratios were used as correction factors to adjust the found PAH concentrations of the field ambient air samples. This is an improvement from TO-13A which just calls for stating the percent recovery of the particular component.

IV-3 Results

The monthly averages for naphthalene over the monitoring period for PAHs are shown in Figure IV-3.

Table IV-3 summarizes the results of the PAH ambient monitoring for MATES III year 2.

Consistent with other studies, the highest levels of naphthalene were measured during the fall and winter season. This is also consistent with measurements of other volatile organic compounds, such as benzene, that are higher during this time period. This is likely due to cooler temperatures and lower mixing height.

The levels of the other PAHs measured were substantially lower than naphthalene. This is also consistent with previous measurements in the Basin.

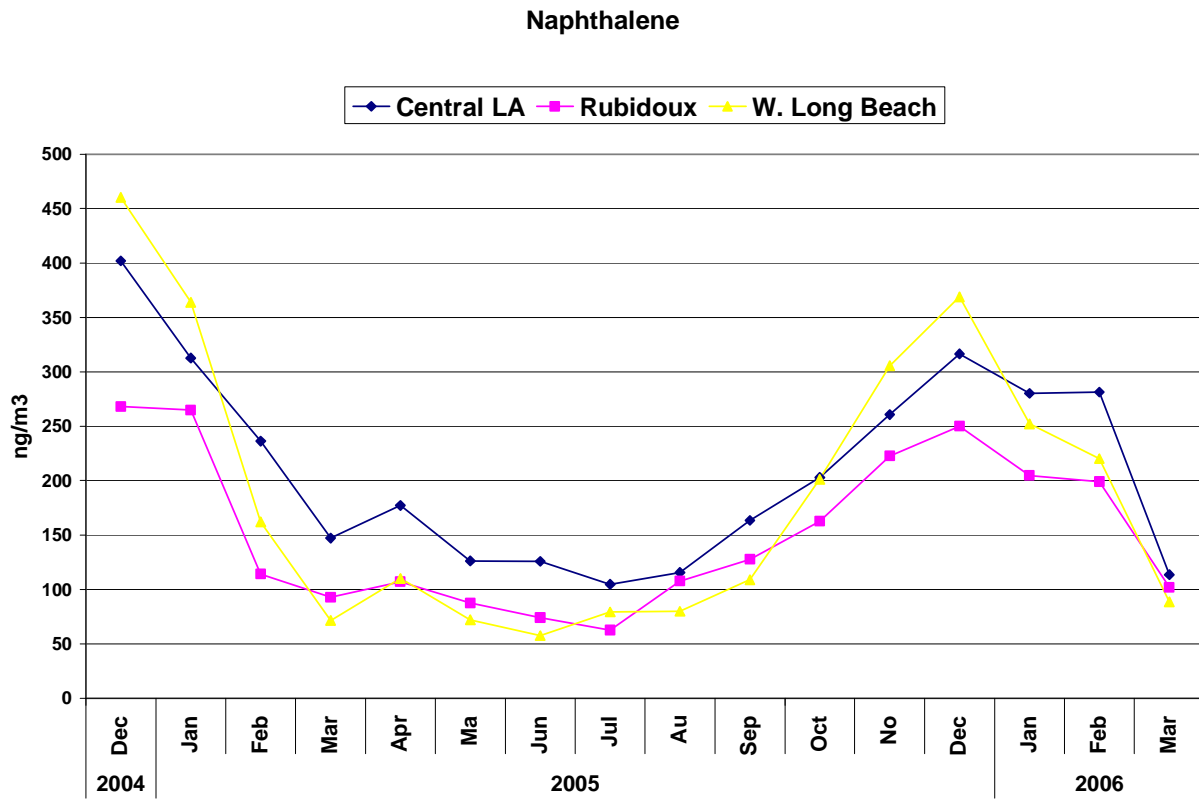


Figure IV-3 Monthly Average Levels of Naphthalene

Table IV-3 MATES III Year 2 Monitored PAH Levels (ng/m³)

| | | Site | | |
|--------------------------|--------|--------------|----------|---------------|
| | | Central L.A. | Rubidoux | N. Long Beach |
| Acenaphthene | Avg | 7.61 | 4.65 | 8.49 |
| | SD | 4.76 | 2.92 | 6.70 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.98 | 0.60 | 1.38 |
| | Max | 21.39 | 13.42 | 34.78 |
| | Min | 0.85 | 0.80 | 1.46 |
| Acenaphthylene | Avg | 5.08 | 4.40 | 5.23 |
| | SD | 4.05 | 4.50 | 5.38 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.83 | 0.92 | 1.10 |
| | Max | 16.02 | 20.92 | 24.68 |
| | Min | 0.51 | 0.29 | 0.56 |
| Anthracene | Avg | 1.19 | 0.72 | 1.07 |
| | SD | 3.07 | 1.62 | 2.53 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.63 | 0.33 | 0.52 |
| | Max | 21.64 | 10.67 | 22.34 |
| | Min | 0.09 | 0.06 | 0.12 |
| Benz(a)Anthracene | Avg | 0.10 | 0.12 | 0.14 |
| | SD | 0.08 | 0.12 | 0.13 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.02 | 0.03 | 0.03 |
| | Max | 0.34 | 0.46 | 0.65 |
| | Min | 0.01 | 0.01 | 0.01 |
| Benzo(a)pyrene | Avg | 0.12 | 0.14 | 0.18 |
| | SD | 0.10 | 0.15 | 0.17 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.02 | 0.03 | 0.04 |
| | Max | 0.51 | 0.62 | 0.82 |
| | Min | 0.01 | 0.02 | 0.02 |
| Benzo(b+j+k)Fluoranthene | Avg | 0.34 | 0.40 | 0.39 |
| | SD | 0.26 | 0.37 | 0.37 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.05 | 0.08 | 0.08 |
| | Max | 1.03 | 1.38 | 1.59 |
| | Min | 0.04 | 0.03 | 0.03 |

Table IV-3 MATES III Year 2 Monitored PAH Levels (ng/m³)

| Substance | | Site | | |
|------------------------|--------|--------------|----------|---------------|
| | | Central L.A. | Rubidoux | N. Long Beach |
| Benzo(ghi)perylene | Avg | 0.35 | 0.33 | 0.40 |
| | SD | 0.24 | 0.31 | 0.36 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.05 | 0.06 | 0.07 |
| | Max | 1.04 | 1.33 | 1.85 |
| | Min | 0.04 | 0.04 | 0.04 |
| Chrysene | Avg | 0.32 | 0.35 | 0.43 |
| | SD | 0.19 | 0.29 | 0.31 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.04 | 0.06 | 0.06 |
| | Max | 0.89 | 1.15 | 1.51 |
| | Min | 0.08 | 0.03 | 0.05 |
| Dibenz(a,h)anthracene | Avg | 0.03 | 0.04 | 0.06 |
| | SD | 0.02 | 0.05 | 0.06 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.01 | 0.01 | 0.01 |
| | Max | 0.13 | 0.44 | 0.53 |
| | Min | 0.00 | 0.00 | 0.00 |
| Fluoranthene | Avg | 2.12 | 1.37 | 1.90 |
| | SD | 0.86 | 0.64 | 1.07 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.18 | 0.13 | 0.22 |
| | Max | 4.37 | 3.09 | 4.84 |
| | Min | 0.48 | 0.33 | 0.54 |
| Indeno(1,2,3-cd)pyrene | Avg | 0.17 | 0.18 | 0.18 |
| | SD | 0.12 | 0.16 | 0.17 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.02 | 0.03 | 0.03 |
| | Max | 0.53 | 0.60 | 0.70 |
| | Min | 0.02 | 0.02 | 0.01 |
| Naphthalene | Avg | 201.29 | 154.91 | 183.78 |
| | SD | 110.52 | 110.68 | 150.79 |
| | N | 91 | 91 | 91 |
| | 95% CI | 22.71 | 22.74 | 30.98 |
| | Max | 447.60 | 533.56 | 726.14 |
| | Min | 35.29 | 24.30 | 29.95 |

Table IV-3 MATES III Year 2 Monitored PAH Levels (ng/m³)

| Substance | | Site | | |
|--------------|--------|--------------|----------|---------------|
| | | Central L.A. | Rubidoux | N. Long Beach |
| Phenanthrene | Avg | 14.35 | 8.96 | 13.65 |
| | SD | 6.52 | 4.39 | 8.40 |
| | N | 91 | 91 | 91 |
| | 95% CI | 1.34 | 0.90 | 1.73 |
| | Max | 34.54 | 20.99 | 37.59 |
| | Min | 2.62 | 2.24 | 3.47 |
| | | | | |
| Pyrene | Avg | 1.67 | 1.19 | 1.68 |
| | SD | 0.73 | 0.70 | 1.01 |
| | N | 91 | 91 | 91 |
| | 95% CI | 0.15 | 0.14 | 0.21 |
| | Max | 3.41 | 3.56 | 5.09 |
| | Min | 0.42 | 0.25 | 0.39 |
| | | | | |

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