

Effectiveness of Microbe Application to Petroleum Spills at Crash Sites

Final Report 600
March 2012



Arizona Department of Transportation
Research Center

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Federal Highway Administration

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| 16. Abstract Each year vehicular accidents cause gasoline and diesel spills on Arizona roadways. ADOT currently uses Micro-Blaze [®] , a commercially available microbial solution, as a supplement to natural degradation of vehicular petroleum spills in soils. With an emphasis on minimizing or eliminating environmental and public health hazard, ADOT is interested in determining cost-effective methods to address spills involving petroleum products from roadway vehicular accidents. This study investigated whether Micro-Blaze, Hydro Clean [®] , Miracle-Gro [®] , or water accelerated the degradation process significantly over natural processes and that it will help to determine their effectiveness in accelerating the remediation of petroleum products (diesel No. 2 and unleaded gasoline) on predominant Arizona soil types from roadway vehicular accidents. The soil types evaluated were aridisols from Burro Creek, alfisols from Show Low, and entisols from Mesa. All three soil types contaminated with gasoline showed a reduction in BTEX levels to below ADEQ's SRLs within 21 days, even in the absence of added microorganisms or nutrients. In none of the sample treatments was the diesel (total petroleum hydrocarbon) concentration below either residential or non-residential SRLs by day 83. The results are discussed referencing ADEQ's SRL in effect for 2006; ADEQ changed SRLs in 2007. When compared to the new 2007 levels, BTEX are below SRL and there is no longer an ADEQ SRL for total petroleum hydrocarbon. | | | | | |
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

| Symbol | When You Know | Multiply By | To Find | Symbol |
|--|----------------------------|-----------------------------|-----------------------------|-------------------|
| LENGTH | | | | |
| in | inches | 25.4 | millimeters | mm |
| ft | feet | 0.305 | meters | m |
| yd | yards | 0.914 | meters | m |
| mi | miles | 1.61 | kilometers | km |
| AREA | | | | |
| in ² | square inches | 645.2 | square millimeters | mm ² |
| ft ² | square feet | 0.093 | square meters | m ² |
| yd ² | square yard | 0.836 | square meters | m ² |
| ac | acres | 0.405 | hectares | ha |
| mi ² | square miles | 2.59 | square kilometers | km ² |
| VOLUME | | | | |
| fl oz | fluid ounces | 29.57 | milliliters | mL |
| gal | gallons | 3.785 | liters | L |
| ft ³ | cubic feet | 0.028 | cubic meters | m ³ |
| yd ³ | cubic yards | 0.765 | cubic meters | m ³ |
| NOTE: volumes greater than 1000 L shall be shown in m ³ | | | | |
| MASS | | | | |
| oz | ounces | 28.35 | grams | g |
| lb | pounds | 0.454 | kilograms | kg |
| T | short tons (2000 lb) | 0.907 | megagrams (or "metric ton") | Mg (or "t") |
| TEMPERATURE (exact degrees) | | | | |
| °F | Fahrenheit | 5 (F-32)/9 or (F-32)/1.8 | Celsius | °C |
| ILLUMINATION | | | | |
| fc | foot-candles | 10.76 | lux | lx |
| fl | foot-Lamberts | 3.426 | candela/m ² | cd/m ² |
| FORCE and PRESSURE or STRESS | | | | |
| lbf | poundforce | 4.45 | newtons | N |
| lbf/in ² | poundforce per square inch | 6.89 | kilopascals | kPa |

APPROXIMATE CONVERSIONS FROM SI UNITS

| Symbol | When You Know | Multiply By | To Find | Symbol |
|-------------------------------------|-----------------------------|-------------|----------------------------|---------------------|
| LENGTH | | | | |
| mm | millimeters | 0.039 | inches | in |
| m | meters | 3.28 | feet | ft |
| m | meters | 1.09 | yards | yd |
| km | kilometers | 0.621 | miles | mi |
| AREA | | | | |
| mm ² | square millimeters | 0.0016 | square inches | in ² |
| m ² | square meters | 10.764 | square feet | ft ² |
| m ² | square meters | 1.195 | square yards | yd ² |
| ha | hectares | 2.47 | acres | ac |
| km ² | square kilometers | 0.386 | square miles | mi ² |
| VOLUME | | | | |
| mL | milliliters | 0.034 | fluid ounces | fl oz |
| L | liters | 0.264 | gallons | gal |
| m ³ | cubic meters | 35.314 | cubic feet | ft ³ |
| m ³ | cubic meters | 1.307 | cubic yards | yd ³ |
| MASS | | | | |
| g | grams | 0.035 | ounces | oz |
| kg | kilograms | 2.202 | pounds | lb |
| Mg (or "t") | megagrams (or "metric ton") | 1.103 | short tons (2000 lb) | T |
| TEMPERATURE (exact degrees) | | | | |
| °C | Celsius | 1.8C+32 | Fahrenheit | °F |
| ILLUMINATION | | | | |
| lx | lux | 0.0929 | foot-candles | fc |
| cd/m ² | candela/m ² | 0.2919 | foot-Lamberts | fl |
| FORCE and PRESSURE or STRESS | | | | |
| N | newtons | 0.225 | poundforce | lbf |
| kPa | kilopascals | 0.145 | poundforce per square inch | lbf/in ² |

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

METRIC CONVERSION FACTORS PAGE (FURNISHED BY ATRC)

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ACRONYMS

| | |
|-------|--|
| ADEQ | Arizona Department of Environmental Quality |
| ADHS | Arizona Department of Health Services |
| ADOT | Arizona Department of Transportation |
| BTEX | benzene, toluene, ethylbenzene, and xylene |
| CCV | continuing calibration verification standard |
| DRO | diesel range organics |
| EPA | Environmental Protection Agency |
| FID | flame ionization detector |
| GC/MS | gas chromatography/mass spectrometry |
| HPLC | high performance liquid chromatography |
| PAHs | polycyclic aromatic hydrocarbons |
| PID | photo ionization detector |
| QA/QC | quality assurance/quality control |
| RPD | relative percent difference |
| SRLs | Arizona soil remediation levels |
| VOCs | volatile organic compounds |

EXECUTIVE SUMMARY

Each year vehicular accidents cause gasoline and diesel spills on Arizona roadways. Reduction of petroleum products in soils occurs naturally through degradation from physical and biological processes; it is of interest that an increase in the degradation rate of petroleum products may occur with the application of bioremediation products. Arizona Department of Transportation (ADOT) currently uses Micro-Blaze[®], a commercially available microbial solution, as a supplement to natural degradation of vehicular petroleum spills in soils. However, its effectiveness in accelerating the biodegradation of gasoline- or diesel-contaminated soils in Arizona has never been tested.

ADOT contracted with N. Weiss Associates, Inc., to determine the effectiveness of Micro-Blaze as a commercial bioremediation product to remediate native soils contaminated with gasoline or diesel fuels from vehicular accidents. With an emphasis on minimizing or eliminating environmental and public health hazards, ADOT is interested in determining cost-effective methods to address petroleum product spills from roadway vehicular accidents. For this report, the specific issue investigated was whether Micro-Blaze accelerated the degradation process significantly over natural processes. During research for this project, other commercially available degradation products (Hydro Clean[®] and Miracle-Gro[®]) were found and they, as well as water, were included in the study. Micro-Blaze, Hydro Clean, Miracle-Gro, and water were studied to determine their effectiveness in accelerating the remediation of petroleum products (diesel No. 2 and unleaded gasoline) from roadway vehicular accidents on predominant Arizona soil types.

ADOT responds to spills throughout the state of Arizona, encountering different soil and climates. Arizona has three predominant soil types: aridisols, alfisols, and entisols. To ensure that each soil type was represented, soil samples were taken from three geographical areas (see Figure A for locations). The soils considered for the purpose of this study are representative of soils found in Arizona.

- Burro Creek is representative of aridisols. Aridisols have relatively low organic matter and low moisture storage capacity; they are common in dry regions.
- Show Low has alfisol soils. Alfisols have relatively low organic matter with high base saturation; they are common in high elevations in semiarid and subhumid regions.
- Mesa has significant entisols. Entisols have a thin surface with some accumulation of organic matter and variable moisture content.

Show Low soil is the most porous, while the Mesa soil sample has the highest bulk and particle density. Samples' soil orders were distinguished using the dominant soil order distribution maps of the United States Department of Agriculture (2008).



Figure A: Location of Soil Samples.

METHODOLOGY

The soils considered for the purpose of this study are considered representative of soils found in Arizona. To obtain a consistent soil sample, each soil type was mixed thoroughly and screened to remove larger particles, such as rocks and plant materials. To determine the surface area and the water saturation capacity of the soil samples, a picnometer was then used to measure the samples' density, percent of dry mass, and porosity.

The homogenized and mixed soil samples were contaminated with diesel No. 2 or unleaded gasoline to create petroleum-spiked samples. The diesel and gasoline were purchased on April 15, 2008, from a local retailer in Mesa, Arizona, and were used without modifications. Solutions of the bioremediation products Micro-Blaze, Hydro Clean, or Miracle-Gro fertilizer mixed with water were then added to the spiked samples. Ultrapure water was used in place of bioremediation products for blank samples.

To represent physical degradation through evaporation or dissolution, the sample tubes were uncapped and placed outside in the sunlight for 48 hours. After this time, the initial extraction and analysis was performed. The spiked samples were still wet, but excess liquid was not present. These initial analyses represented the starting point for measuring the rate of degradation of gasoline or diesel in the spiked samples. Extraction of diesel and gasoline from the spiked soil samples was conducted by using appropriate solvents and a centrifuge to separate the dissolved contaminant and the soil. Following extraction, gas chromatography was used to analyze the diluted contaminant solutions.

The contaminated diesel and gasoline samples were evaluated and compared by using a ranking methodology. First, scores for each sample were determined by comparing different types of soil exposed under the same conditions and by comparing different types of microorganisms and nutrients. Each gasoline sample was assigned a total cumulative score for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, and *o*-xylene. Each diesel sample was assigned a score by analyzing the C₁₀-C₂₂ range and comparing the milligrams of C₁₀-C₂₂ in a kilogram of dry soil to initial levels. Second, the rate of change was calculated between the first and last day of evaluation. Third, the lowest

value for the rate of change was assigned a score of one, and scores were assigned successively to the last sample. The lowest score represented the best remediation option analyzed for the type of soil (Hristovski et al. 2008). Also, the different types of soil, remediation, and added nutrients were compared using this technique.

CONCLUSIONS

All three soil types contaminated with gasoline showed a reduction in benzene, toluene, ethylbenzene, and xylene (BTEX) levels to below Arizona Department of Environmental Quality's (ADEQ's) soil remediation levels (SRLs) within 21 days, even in the absence of added microorganisms or nutrients. However, in trying to compare the rates of degradation among various options, some degree of quantification can be obtained by normalizing the BTEX concentration and measuring the rate of decay. This was done by comparing the change in concentration by the number of days between measurements, resulting in a rate of degradation suitable for comparison.

The most effective treatment for gasoline-contaminated Mesa soils was to add Miracle-Gro. For Burro Creek and Show Low soils, Miracle-Gro was the second most effective treatment for gasoline contamination, with the most effective being to leave the soils alone (without adding water or other products). Micro-Blaze treatment was rated either number 3 or 4, while Hydro Clean was rated number 3, 4, or 5 out of the five possible treatment options. However, the most important observation is that all soil samples contaminated with gasoline were below the residential Arizona SRLs by day 21, no matter what treatment option was employed. There was some acceleration with certain treatments, but all samples ultimately decayed to approximately the same levels of BTEX.

The situation with diesel-contaminated soils was quite different. In none of the sample treatments was the diesel (total petroleum hydrocarbon) concentration below either residential or non-residential SRLs by day 83. For Burro Creek and Show Low soils, the optimal treatment was with Hydro Clean, and this was the second-best treatment option for Mesa soils. Micro-Blaze was the optimal treatment for Mesa soils and the second best for Burro Creek soils. In all soils, treatment with Miracle-Gro resulted in an actual increase in measured diesel range organics (DRO) after 83 days; Micro-Blaze also had this effect in Show Low soils. This is likely due to a division of long chain organics into smaller fragments, which are still included in the DRO sampling range.

RECOMMENDATIONS

Even though the State of Arizona no longer has an SRL for total petroleum hydrocarbons, it is prudent to take action to remediate. Clean-up of petrochemical hydrocarbons will protect stormwater and surface water and eliminate environmental and public health hazards.

Further research in the area of polycyclic aromatic hydrocarbons (PAHs) in soils from diesel fuel spills and from incomplete combustion of carbon-containing fuels should be considered.

Changes in research design should be considered to include in situ application of remediation products. The research was performed in a laboratory situation. The rate at which volatile organic compounds (VOCs) decayed was in days as opposed to weeks, which would have been expected if research occurred in situ.

Further research with gas chromatography/mass spectrometry (GC/MS) may be useful to confirm the breakdown of DRO into smaller hydrocarbon chains. The increase in DRO may be a result of larger-chain hydrocarbon being broken down from large chains to smaller chains, causing DRO numbers to increase.

It also would be prudent to consider further evaluation of other products listed on the Environmental Protection Agency's (EPA) National Contingency Plan Subpart J Product Schedule of dispersants, other chemicals, and oil spill mitigating devices and substances that may be used to remove or control oil discharges. Research associated with the control of oil from rubberized asphalt and other asphaltic materials is a related area that warrants further investigation.

1.0 INTRODUCTION

The Arizona Department of Transportation (ADOT) is interested in determining cost-effective methods that would minimize or eliminate environmental and public health hazards from petroleum product spills in roadway vehicular incidents. ADOT contracted with N. Weiss Associates, Inc., to determine whether commercial bioremediation products might be used to remediate soils contaminated with gasoline or diesel fuels. N. Weiss Associates, Inc., subcontracted with the Environmental Technology Management program at Arizona State University to conduct laboratory-based experiments to evaluate the feasibility of this approach.

ADOT currently uses a microbial solution called Micro-Blaze[®] for soil remediation in small accidents. However, its effectiveness in accelerating the biodegradation of gasoline- or diesel-contaminated soils has never been tested. Natural degradation of petroleum products can occur through physical processes such as evaporation or dissolution and also through biodegradation from naturally occurring organisms in soils. The specific issue to be tested was whether Micro-Blaze accelerated the degradation process significantly compared to natural processes.

Other commercially available biodegradation products were discovered during the literature review for this project. Two materials—Hydro Clean, made by Desert Shield, and a plant fertilizer made by Miracle-Gro[®]—were tested in addition to Micro-Blaze. A fourth set of experiments was conducted with no additional product except water applied to the contaminated soils.

Because ADOT must respond to spills throughout Arizona, different soil types and climates are encountered. There are three predominant soil types in Arizona:

- Aridisols with relatively low organic matter and low moisture storage capacity; common in dry regions
- Alfisols with relatively low organic matter with high base saturation; common in high elevations in semiarid and subhumid regions
- Entisols have a thin surface with some accumulation of organic matter and variable moisture content.

In this project, three different soil samples from different geographic areas of the state were selected. Aridisols are found in soils from Burro Creek; alfisols are found in soil from Show Low; and entisols are found in soils from Mesa.

2.0 BACKGROUND

Of interest to this study, the Arizona Soil Remediation Level (SRL) Rule for remediating sites with soil contaminations changed during the course of this project. Included in Tables 1 and 2 are the old and new standards. The new standard does not include hydrocarbon remediation levels. This project began prior to the change, and the results reference the old standard. However, the change in standard does not affect the project findings as shown in Tables 1 and 2.

Table 1: Old Soil Remediation Levels.

| Chemical Name | SRL Residential (mg/kg) | SRL Non-Residential (mg/kg) |
|---|----------------------------|--------------------------------|
| Benzene | 0.62 | 1.4 |
| Ethylbenzene | 1500 | 2700 |
| Toluene | 790 | 2700 |
| Xylene | 2800 | 2800 |
| Hydrocarbon C ₁₀ -C ₃₂ | 4100 | 18000 |

Table 2: New Soil Remediation Levels.

| Chemical Name | SRL Residential (mg/kg) | SRL Non-Residential (mg/kg) |
|---|----------------------------|--------------------------------|
| Benzene | 0.65 | 1.4 |
| Ethylbenzene | 400 | 400 |
| Toluene | 650 | 650 |
| Mixed Xylene | 270 | 420 |
| Hydrocarbon C ₁₀ -C ₃₂ | None | None |

3.0 METHODOLOGY

3.1 SOILS PREPARATION

Soil samples of native Arizona soils were obtained from Burro Creek, Show Low, and Mesa (see Figure 1 for locations). Each soil type was homogenized and mixed thoroughly using a trowel, and then sieved through a screen with a 2 mm diameter opening (Standard test sieve, ASTM E-11 specification, US Mesh No. 10) to remove larger particles such as rocks and plant materials. The prepared loose soils were stored in capped glass containers at room temperature.



Figure 1: Location of Soil Samples.

A picnometer was employed to determine density, percent of dry mass content, and porosity of the soil samples. The following steps were undertaken using a 30 mL picnometer:

1. The picnometer was dried in the oven at 105° C for one hour.
2. The picnometer was cooled in a desiccator to room temperature.
3. The picnometer was weighed, and the mass of the dry picnometer was recorded.
4. A sample of sieved soil was added to the picnometer; it was weighed, and the mass was recorded.
5. The picnometer with the soil sample dried overnight at 105 °C to constant mass, and it was cooled to room temperature in a desiccator.
6. The picnometer with the soil was weighed, and the mass was recorded.
7. Ultrapure water was added to the picnometer filled with soil. The picnometer was weighed, and the mass was recorded.
8. The extra water was removed, and the picnometer with wet soil was weighed.

The porosity ε was determined once the bulk density ρ_b and the particle density ρ_p were known, using the following equation (Sontheimer et al. 1988).

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p}$$

The bulk density ρ_b represents the ratio of the mass of dry solids to the bulk volume of the soil V , and it was calculated using

$$\rho_b = \frac{m_s - m_a}{V}$$

The particle density ρ_p was determined using

$$\rho_p = \frac{m_s - m_a}{V - \frac{(m_{st} - m_a) - (m_{sw} - m_a)}{\rho_w}}$$

where ρ_w is the density of the water, m_s is the picnometer weight containing the soil sample dried in the oven, m_a is the empty (air-filled) picnometer weight, m_{sw} is the picnometer weight when filled with soil and water, and m_{st} is the picnometer weight with

$$V = \frac{v - m_{sw} - m_{st}}{\rho_w}$$

where v is the picnometer volume. Wilke (2005) used the following equation to obtain the dry mass content m_{dm} expressed in percentage by mass, where m_m is the mass of the picnometer filled with soil sample that was not dried. The obtained results for the different types of soils are shown in the Results section of this report.

$$m_{dm} = \frac{m_s - m_a}{m_m - m_a} \times 100$$

3.2 PREPARATION OF SAMPLES

Soil samples from Burro Creek, Show Low, and Mesa were prepared by weighing 45 g of soil into 60-mL pre-cleaned glass vials that were cleaned to U.S. Environmental Protection Agency (EPA) standards. Spiked soil samples were prepared using diesel No. 2 and unleaded gasoline, which were purchased on April 15, 2008, from a local supplier, Circle K (4353 S. Power Rd., Mesa, AZ 85212), and used without modifications. Dilutions of 5 % v/v of the commercial gasoline and diesel in methanol and dichloromethane, respectively, were prepared to determine the fuel compositions by gas chromatography. Details of the gas chromatographic analysis are provided later in this section. Aqueous solutions of the bioremediation products Micro-Blaze or Hydro Clean or the fertilizer Miracle-Gro were then added to the spiked samples. Ultrapure water was used in place of bioremediation products for blank samples.

Soil Sample Procedures for Soil-Gasoline-Water Blanks

Forty-five grams of soil were weighed in a 60-mL pre-cleaned glass vial, and 10 mL of commercial gasoline were added. The vial was capped, and the sample was homogenized by shaking until the soil was saturated with the contaminant. Five mL of ultrapure water were added, and the sample was homogenized by shaking until the soil was saturated.

Soil Sample Procedures for Soil-Diesel Blanks

The sample was prepared by weighing 45 g of soil in a 60-mL pre-cleaned glass vial, and 10 mL of commercial diesel fuel were added. The vial was capped, and the sample was homogenized by shaking until the soil was saturated with the contaminant. Five mL of ultrapure water were added, and the sample was homogenized by shaking until the soil was saturated.

Soil Sample Procedures for Soil-Treatment Product Blanks

Samples were prepared by weighing 45 g of soil in a 60-mL pre-cleaned glass vial and 5 mL of an aqueous solution of Micro-Blaze, Hydro Clean, or Miracle-Gro were added. The vial was capped and the sample was homogenized by shaking until the soil was saturated with the solution.

Soil Sample Procedures for Soil-Gasoline-Treatment Product Blanks

Forty-five grams of soil were weighed in a 60-mL pre-cleaned glass vial, and 10 mL of commercial gasoline were added. The vial was capped, and the sample was homogenized by shaking until the soil was saturated with the contaminant. Five mL of Micro-Blaze, Hydro Clean, or Miracle-Gro solution were then added, and the sample was homogenized by shaking until the soil was saturated.

Soil Sample Procedures for Soil-Diesel-Treatment Product Blanks

Forty-five grams of soil were weighed in a 60-mL pre-cleaned glass vial, and 10 mL of commercial diesel fuel were added. The vial was capped, and the sample was homogenized by shaking until the soil was saturated with the contaminant. Five mL of Micro-Blaze, Hydro Clean, or Miracle-Gro solution were then added, and the sample was homogenized by shaking until the soil was saturated.

Tables 3, 4, and 5 describe the designation for the samples prepared during the study.

Table 3: Soil Blank Sample Denomination.

| Sample No. | Soil | Contaminant | Treatment |
|------------|----------|-------------|-----------|
| 1 | α | | X |
| 2 | β | | X |
| 3 | δ | | X |
| 4 | α | | Y |
| 5 | β | | Y |
| 6 | δ | | Y |
| 7 | α | | Z |
| 8 | β | | Z |
| 9 | δ | | Z |

*Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil;
X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro. No contaminant added.*

Table 4: Soil Gasoline Sample Denomination.

| Sample No. | Soil | Contaminant | Treatment |
|------------|----------|-------------|-----------|
| 1 | α | | X |
| 2 | β | | X |
| 3 | δ | | X |
| 4 | α | | Y |
| 5 | β | | Y |
| 6 | δ | | Y |
| 7 | α | | Z |
| 8 | β | | Z |
| 9 | δ | | Z |

*Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil;
X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.
Contaminant type is gasoline for all samples.*

Table 5: Soil Diesel Sample Denomination.

| Sample No. | Soil | Contaminant | Treatment |
|------------|----------|-------------|-----------|
| 25 | α | D | |
| 26 | β | D | |
| 27 | δ | D | |
| 28 | α | D | X |
| 29 | β | D | X |
| 30 | δ | D | X |
| 31 | α | D | Y |
| 32 | β | D | Y |
| 33 | δ | D | Y |
| 34 | α | D | Z |
| 35 | β | D | Z |
| 36 | δ | D | Z |

*Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil;
 X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.
 Contaminant type is gasoline for all samples.*

3.3 EXTRACTION AND ANALYSIS

All of the sample tubes listed in Tables 3–5 were uncapped and placed outside in the sunlight for 48 hours. The initial extraction and analysis were conducted after 48 hours. At this point, the spiked samples were still wet, but there was no excess liquid present. These initial analyses represented the starting point for measuring the rate of degradation of gasoline or diesel in the spiked samples.

Diesel Extraction

The diesel extraction was conducted by weighing 1 g of soil sample from the 60 mL vial and placing it in a 20 mL vial (20 mL, clear w/septa, I-CHEM). The samples were capped immediately to prevent contaminant loss due to evaporation and labeled with the sample's name and date.

Diesel range organics, C₁₀-C₂₂, were extracted from the soil samples using anhydrous dichloromethane (99.9+ %, Alfa Aesar, Lot # D125037). A volume of 10 mL of dichloromethane (99.9+ %, Alfa Aesar, Lot # D125037) was added to each 20 mL glass vial, and the samples were sonicated for a period of 15 min. The samples were centrifuged at F ~ 1300 G for a period of 5 minutes to separate the soil and dichloromethane. The extraction process of all the samples was completed during the same day to ensure the same experimental conditions. Duplicate samples were prepared

for every 10 samples using the same procedures. All samples were cooled to $4 \pm 2^\circ \text{C}$ and analyzed within 14 days of sampling.

The diesel-containing samples were diluted with anhydrous dichloromethane by a factor of 20. Syringes were used to make the dilutions, and the samples were stored in a 2 mL glass vial (2 mL, 9 mm, Ultra, wide-mouth screw vial).

Diesel Analysis

The dilutions were analyzed using gas chromatography following Method 8015AZ-Revision 1.0 for detection of C_{10} - C_{22} hydrocarbon range in soil. Quantitative and qualitative analysis of C_{10} - C_{22} diesel range was determined using a Varian Model 3800 gas chromatograph equipped with VARIAN Capillary column, Select Mineral Oil, 15 m, 0.32 mm #CP7491, a Model 1079 injector, a Model 8200 auto-sampler and a flame ionization detector operating at 340°C . The analyzed dilutions were prepared in 2-mL Varian Ultra gas chromatography/mass spectrometry (GC/MS) vials (clear glass wide-opening screw-top vials with ultra GC/MS liners). Component identification was conducted by comparing the resident times of purchased standards, *n*-decane (1000 mg, neat, 442669, Supelco, Lot # LB45279) and *n*-docosane (1000 mg, neat, 442670, Supelco, Lot # LB32530). All samples were analyzed using the Star Chromatography Workstation version 6.3. Table 6 summarizes instrument conditions necessary to achieve separation between the diesel fuel components.

Table 6: Operating Conditions for Diesel Analysis.

| | |
|--------------------------|-----------------------------------|
| Injection | split ratio 2 |
| Injector pressure | 8 psi |
| Injector temperature | 270°C |
| Injection rate | 5 $\mu\text{l}/\text{sec}$ |
| Injected amount | 1 μl |
| Initial oven temperature | 35°C (3 min hold) |
| Rate | 10°C per min |
| Final temperature oven | 310°C (9 min hold) |
| Run time | 39.50 min |

The instrument was calibrated using a five-point linear calibration curve (not forced to zero). Calibration standards of 30, 100, 200, 500, and 1000 $\mu\text{g}/\text{mL}$ were obtained by

dilution of a composite No. 2 diesel fuel standard solution (50,000 µg/mL in dichloromethane; ULTRA Scientific; Lot # M-1431) in anhydrous dichloromethane (99.9+ %, Alfa Aesar, Lot # D125037). The goodness of fit (R^2) was 0.9977 using linear regression. The calibration curve for the C_{10} - C_{22} range is shown in Section 4, Results.

Diesel range (C_{10} - C_{22}) concentrations were reported between 1.4 min. and 20 min. to assure the C_{10} - C_{22} range, as the *n*-decane (C_{10}) retention time was 1.570 min. and the *n*-docosane (C_{22}) retention time was 18.957 min., and those have a little variation. The *n*-decane and *n*-docosane chromatogram and retention times are shown in Section 4.2, Qualitative Analysis. The mass of diesel range aliphatic hydrocarbons (C_{10} - C_{22}) was calculated by determining the total area of the peaks between retention times 1.4 min. and 20 min. and then comparing it to the total area obtained from the calibration curve. The mass was reported in nanograms (ng). All the obtained data were analyzed and presented as milligrams of contaminant per kilogram of dry soil (mg/kg).

Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) procedures were followed using blanks, spikes, and standard solutions. QA/QC equations and procedures from Arizona Department of Health Services (ADHS) Method 8015AZ- Revision 1.0 (1998) were used. A method blank, dichloromethane (99.9+ %, Alfa Aesar, Lot # D125037), was run before every analysis of diesel samples. A continuing calibration verification standard (CCV) solution, composite No. 2 diesel fuel standard solution (500 µg/mL), was analyzed at the beginning of each analytical run and after every 10 samples analyzed. An acceptable percent recovery of the CCV was between 70% and 130% of the true value. Percent recovery was calculated using the following equation:

$$\text{Percent recovery} = \frac{R_1}{R_2} \times 100$$

where R_1 is the measured amount of the analyzed component and R_2 is the true value.

A spiked sample, a soil sample in dichloromethane with composite No. 2 diesel fuel standard solution (500 µg/mL), was prepared using the same procedures as the other diesel samples and was run every time the GC was used to guarantee the accuracy of the method. The following equation was used to calculate the spike recovery:

$$\text{Percent Spike Recovery} = \frac{S - R}{C} \times 100$$

where S is the measured spiked sample result, R is the concentration of the sample before the spike, and C is the actual spike concentration. An acceptable percent spike recovery was between 70% and 130%.

Relative percent difference (RPD) was used to calculate the precision from duplicate samples measured. The following equation was used for calculating the percent RPD:

$$\% \text{ RPD} = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100$$

where X_1 and X_2 are the two measurements being compared. An acceptable RPD was between 0 and 20%.

Gasoline Extraction

Gasoline was extracted from soil samples by weighing 1 g of soil from the 60 mL vial sample and suspending it in 10 mL methanol (99.9+%, Sigma-Aldrich Chemie GmbH, GC grade, Batch # 04555 BD) in 20 mL pre-cleaned vials. To make possible the extraction of the contaminants from the soil, all sample vials were placed in a sonicator bath for 15 min. After sonication, the vials were centrifuged for 5 min. at $F \sim 1300G$. Syringes were utilized to prepare the dilutions of the soil sample to be analyzed in a gas chromatograph purge and trap. Syringes were cleaned by rinsing them three times with 99%+ methanol solution.

Gasoline Analysis

Method 8015AZ, revision 1.0, was used for benzene, toluene, ethylbenzene, and xylene (BTEX) detection and quantification in soil (Arizona Department of Health Services, 1998). Analysis was performed using a SRI 8610B gas chromatograph purge and trap (SRI Instruments, Inc.), equipped with two detectors: a flame ionization detector (FID), and a photo ionization detector (PID). The results were obtained using a Restek fused silica, phase MTX-1, 60 m column (0.53 mm, cat #70183-273, serial # 815473) and helium as a gas carrier. Table 7 illustrates the temperature profile used during the 29.666 min. analysis. Table 8 shows the event program for the purge and trap unit, which was used during analysis of the gasoline samples. The BTEX separation peaks attained using these conditions are shown in Section 4, Results.

Table 7: Purge and Trap Temperature Profile.

| Initial temperature | Hold | Ramp | Final temperature |
|---------------------|------|------|-------------------|
| 40 | 8 | 15 | 200 |
| 200 | 10 | 0 | 200 |
| 200 | 0 | 10 | 210 |

Table 8: Purge and Trap Unit Event Program.

| Time | Event |
|--------|------------------------------|
| 0.100 | E ON (sparge gas ON/OFF) |
| 5.100 | E OFF (sparge gas ON/OFF) |
| 5.900 | B ON (trap bake setpoint) |
| 6.000 | C ON (trap# 2 heat) |
| 6.050 | F ON (trap# 1 heat) |
| 8.000 | G ON (valve# 1 LOAD/INJECT) |
| 8.100 | G OFF (valve# 1 LOAD/INJECT) |
| 12.000 | E ON (sparge gas ON/OFF) |
| 12.900 | B OFF (trap bake setpoint) |
| 13.000 | H ON (valve# 2 LOAD.INJECT) |
| 13.050 | H OFF (valve# 2 LOAD.INJECT) |
| 14.900 | F OFF (trap# 1 heat) |
| 15.100 | C OFF (trap# 2 heat) |
| 15.300 | E OFF (sparge gas ON/OFF) |

Identification of the gasoline constituents was based on the retention times. BTEX components were selected as representative fingerprint components to determine the concentration of gasoline in the samples. Retention times were identified for the BTEX components using purchased standards. Information about the purchased standards and their retention times is presented in Section 4, Results.

After identification of each BTEX compound, dilutions of BTEX standard solutions were analyzed to calibrate the equipment. *m*-Xylene and *p*-xylene were reported together because there was no peak separation between these compounds under these operating conditions. Five dilutions of a BTEX mix standard solution (2,000 µg/mL in methanol; Supelco; Lot # LB46930) at concentrations of 10 µg/mL, 20 µg/mL, 50 µg/mL, 100 µg/mL, and 200 µg/mL in methanol (99.9+%, Sigma-Aldrich Chemie GmbH, GC grade, Batch #04555 BD) were prepared and analyzed to create a calibration curve. Linear calibration (not forced to zero) was conducted over the range of 10-200 µg/mL for the five target BTEX compounds with a run time of 29.666 min and a purge volume of 5 mL high performance liquid chromatography (HPLC) grade water (Fluka). All the analyzed

samples were purged, from a Pyrex culture tube 16x125 mm, with 5 mL of HPLC grade water (Fluka).

The data for the instrument calibration and samples analyzed were processed using PeakSimple 3.59 software. An R^2 of 0.995 or better of acceptance criteria was used in the construction of the BTEX calibration curves. The calibration curves of BTEX compounds are illustrated in Section 4, Results. The mass of each BTEX component was calculated by determining the area of representative peak and by comparing it to the area obtained from the calibration curve. The mass was reported in nanograms (ng). All data obtained from soil samples were analyzed and presented as milligrams of contaminant per kilogram of dry soil (mg/kg).

Quality Assurance and Quality Control

To ensure that the instrument was properly calibrated, the calibration curve was validated every time the instrument was used by running a BTEX standard solution with a concentration of 50 $\mu\text{g/mL}$ and examining the percent recovery of the target analytes. The percent recovery was calculated in the same manner as for the diesel samples.

Blank standards were run using 5 mL of HPLC grade water (Fluka) to ensure that there was no carryover contamination. A purchased standard solution of α,α,α -trifluorotoluene (1000 mg, neat, 442429, Supelco, Lot No LB33410) was used as an internal standard. Each sample was injected with 10 μL of α,α,α -trifluorotoluene (100 $\mu\text{g/mL}$ in methanol) to ensure proper instrument operation. The acceptance range for internal standard recovery was between 70% and 130% of true value as defined by ADHS Method 8015AZR1 (1998).

Duplicate samples were analyzed every 10 samples to estimate sample variability. The results from the duplicate samples were compared and evaluated using RPD. A CCV standard solution, standard BTEX (20 $\mu\text{g/mL}$) solution in methanol, was analyzed at the beginning of each analytical run and for every 10 samples analyzed. The percent recovery of the CCV was between 70% and 130% of the true value. Percent recovery was calculated as described above.

A gram of spiked sample in methanol with a known amount of standard BTEX (50 $\mu\text{g/mL}$) was analyzed every 20 analytical runs to check the appropriateness of the method for the soil matrix. The percent spike recovery, as described above, was used to evaluate the accuracy of the method.

3.4 RANKING METHODOLOGY

A ranking methodology was used to evaluate and compare different diesel and gasoline contaminated samples. Also, the different types of soil, remediation, and added nutrients were compared using this technique.

Gasoline Ranking Methodology

For gasoline samples, the benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene normalized values ((mg/kg)/(mg/kg)₀) were each analyzed comparing different types of soil exposed under the same conditions. Next, the benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, and *o*-xylene normalized values ((mg/kg)/(mg/kg)₀) were each analyzed comparing different types of microorganism and nutrient treatments. Third, a number was obtained from the rate of change of the normalized values $d((\text{mg/kg})/(\text{mg/kg})_0)/dt$, which was calculated from the first and last data obtained from the first and last day of analyses. Fourth, the lowest rate of change $d((\text{mg/kg})/(\text{mg/kg})_0)/dt$ was assigned a score of 1, the second lowest value was assigned a score of 2, and so on successively to the last sample. A total cumulative score for each sample was calculated by adding the scores for benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, and *o*-xylene. The sample with the lowest total score represented the best of the remediation options studied for a type of soil (Hristovski et al. 2008).

Diesel Ranking Methodology

In the diesel range (C₁₀-C₂₂), the following ranking methodology was used to evaluate the results obtained from different samples. First, the C₁₀-C₂₂ range was analyzed in all samples, and the amounts were normalized to initial milligrams of C₁₀-C₂₂ per kilogram of soil for different types of soil and treatment products. Second, the rate of change $d((\text{mg/kg})/(\text{mg/kg})_0)/dt$ between the first and last day of evaluation was calculated. Third, the lowest value of $d((\text{mg/kg})/(\text{mg/kg})_0)/dt$ was assigned a score of 1, and higher values were assigned successive numbers to the last sample. The lowest score represented the best remediation option analyzed for the type of soil (Hristovski et al. 2008).

4.0 RESULTS

4.1 PHYSICAL PROPERTIES OF THE SOILS USED IN THE PROJECT

The soils considered for the purpose of this study are considered representative of soils found in Arizona. Table 9 summarizes the types of soils used in the study and some of their physical properties. Show Low soil is characterized by highest porosity, while the Mesa soil sample has the highest bulk and particle density. Samples' soil orders were distinguished using the dominant soil order distribution maps of the United States Department of Agriculture (2008).

Table 9: Physical Properties of the Soils.

| Properties | Soil Samples | | |
|---------------------------------------|--------------|-------------|----------|
| | Mesa | Burro Creek | Show Low |
| Dry mass content | 97.51% | 96.29% | 98.24% |
| Bulk Density [g/cm ³] | 1.28 | 1.18 | 1.15 |
| Particle Density [g/cm ³] | 2.46 | 2.33 | 2.35 |
| Porosity | 47.89% | 49.11% | 51.06 % |
| Soil Order | Entisol | Aridisol | Alfisol |

4.2 QUALITATIVE ANALYSIS

Gasoline

Aliquots of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene standard solution were injected in a SRI 8610B gas chromatograph purge and trap. These samples were analyzed to determine the retention time of each BTEX compound at working settings in the equipment (i.e., the operating conditions of the chromatograph). Figure 2 shows the peak separation and retention times of each BTEX compound. BTEX compounds have different boiling points; consequently, their retention times are different. Table 10 details the retention times obtained by analyzing standards of each BTEX compound under these operating conditions.

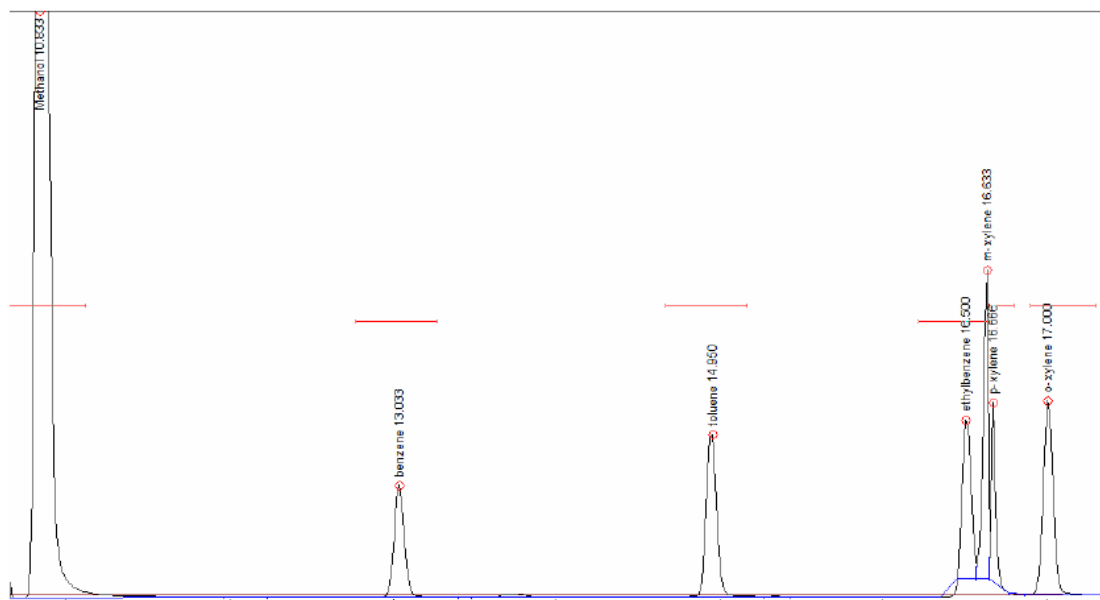


Figure 2: BTEX Chromatogram.

Table 10: BTEX Retention Times in Minutes.

| Compound | Concentration | Manufacture | Lot # | Detector | |
|--------------|---------------|------------------|---------|----------|--------|
| | | | | FID | PID |
| Benzene | 100 µg/ml | ULTRA Scientific | CC-0009 | 13.016 | 13.015 |
| Toluene | 1000 µg/ml | ULTRA Scientific | CC-2781 | 14.866 | 14.833 |
| Ethylbenzene | 100 µg/ml | ULTRA Scientific | T-0336A | 16.383 | 16.385 |
| m-Xylene | 1000µg/ml | ULTRA Scientific | CC-0173 | 16.556 | 16.550 |
| p-Xylene | 5000 µg/ml | ULTRA Scientific | R-09442 | 16.580 | 16.593 |
| o-Xylene | 5000 µg/ml | ULTRA Scientific | U-0201A | 16.916 | 16.916 |

Diesel

Standard solutions of *n*-decane and *n*-docosane were analyzed in a Varian Model 3800 gas chromatograph to identify the limits and retention times of C₁₀-C₂₂ diesel range. Figure 3 shows the identification and retention time of *n*-decane and *n*-docosane. Table 11 shows the retention times of *n*-decane and *n*-docosane under these operating conditions.

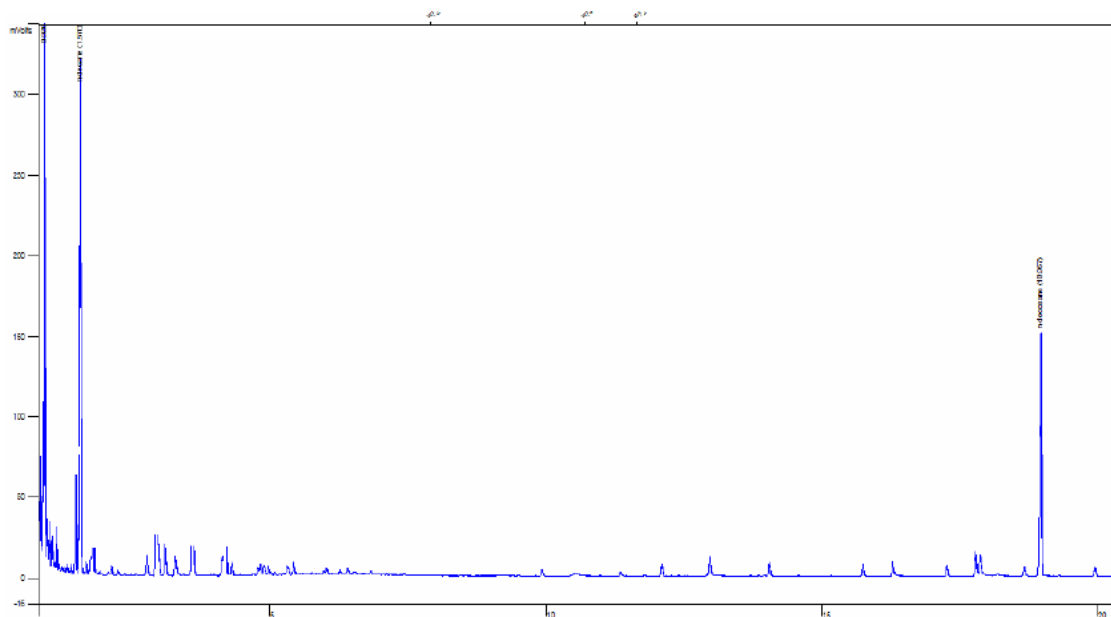


Figure 3: Chromatogram of *n*-Decane and *n*-Docosane.

Table 11: *n*-Decane and *n*-Docosane Retention Times.

| Compound | Retention time (min) |
|---------------------------------------|----------------------|
| <i>n</i> -decane (C ₁₀) | 1.570 |
| <i>n</i> -docosane (C ₂₂) | 18.957 |

4.3 QUANTITATIVE ANALYSIS

Gasoline Calibration Curves

The level of gasoline contamination in soil was expressed as the mass of BTEX compounds contained in a kilogram of dry soil. To quantify the BTEX contained in soil, the equipment was calibrated using dilutions of BTEX standard solution in methanol. Table 12 shows the correlation coefficients obtained for each BTEX compound calibration curve using a FID detector. The BTEX compound calibration curves obtained by using a FID detector are showed in Figures 4 through 8.

Table 12: BTEX Correlation Coefficients.

| Compound | Correlation coefficient |
|--------------|-------------------------|
| Benzene | 0.9988 |
| Toluene | 0.9953 |
| Ethylbenzene | 0.9974 |
| m-p Xylene | 0.9959 |
| o-Xylene | 0.9974 |

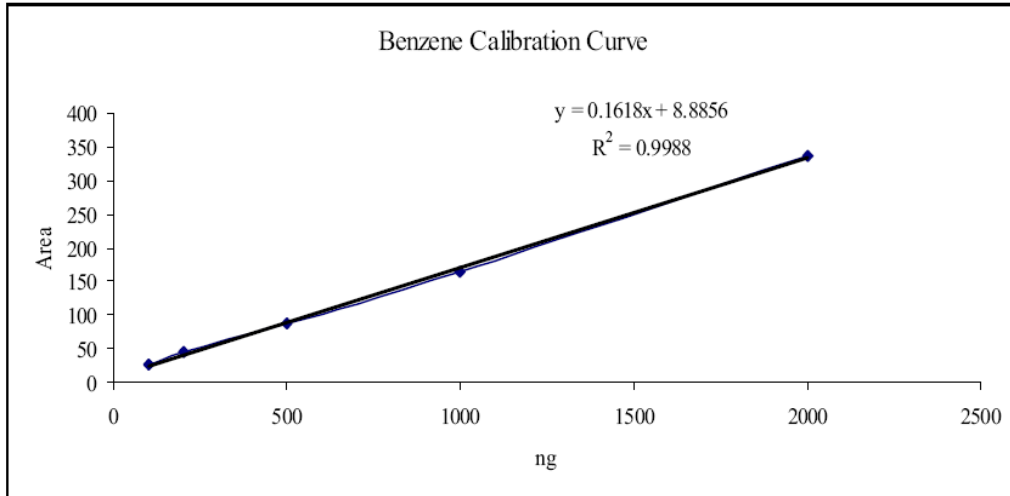


Figure 4: Benzene Calibration Curve.

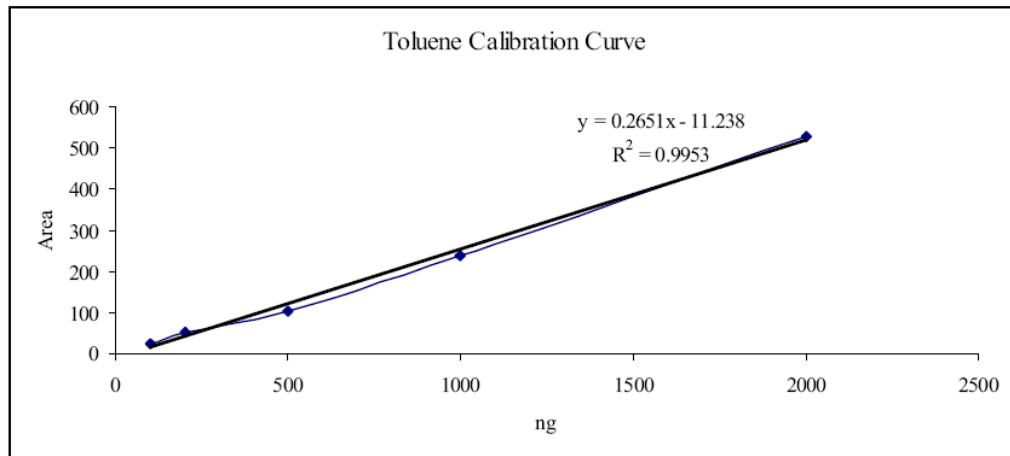


Figure 5: Toluene Calibration Curve.

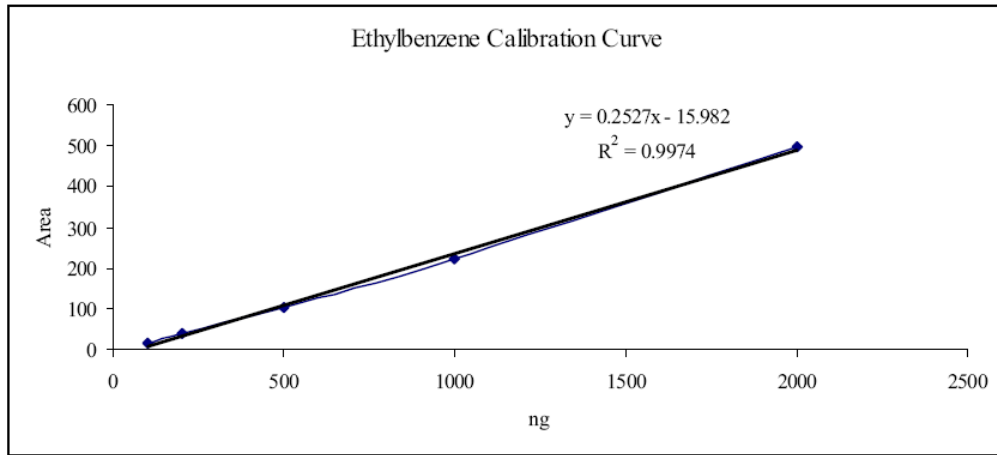


Figure 6: Ethylbenzene Calibration Curve.

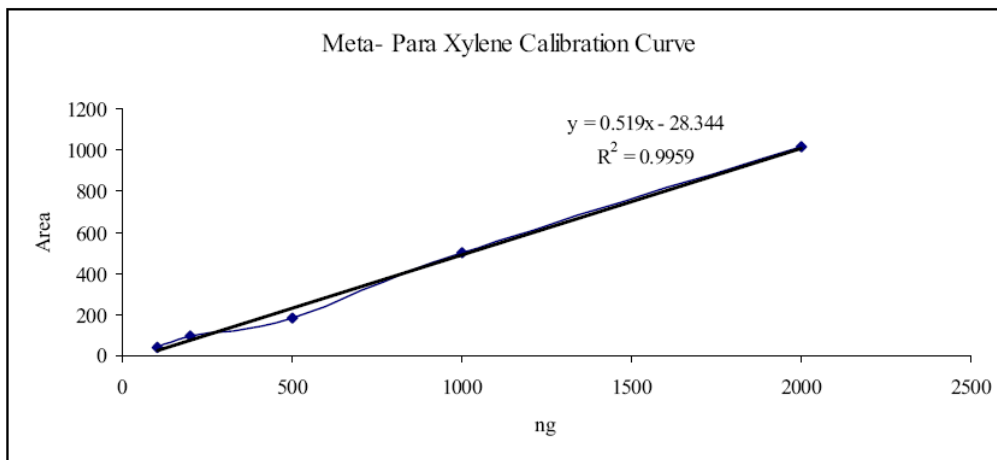


Figure 7: *m*- and *p*-Xylene Calibration Curve.

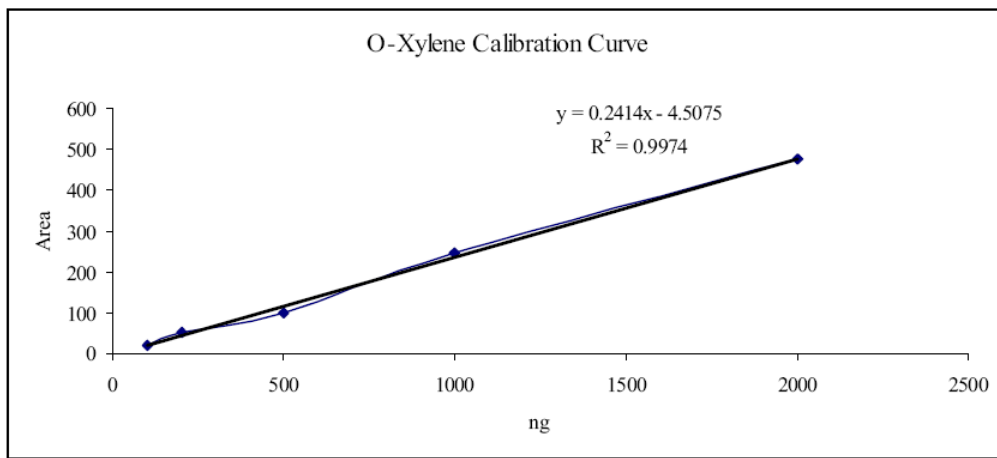


Figure 8: *o*-Xylene Calibration Curve.

Diesel Calibration Curve

The diesel range organics (DRO) range of C₁₀-C₂₂ was analyzed in samples contaminated with diesel No. 2. Before soil analysis, dilutions of composite No. 2 diesel fuel standard solution (50,000 µg/mL in dichloromethane) were used to calibrate the equipment. The calibration curve for the C₁₀-C₂₂ range is exhibited in Figure 9.

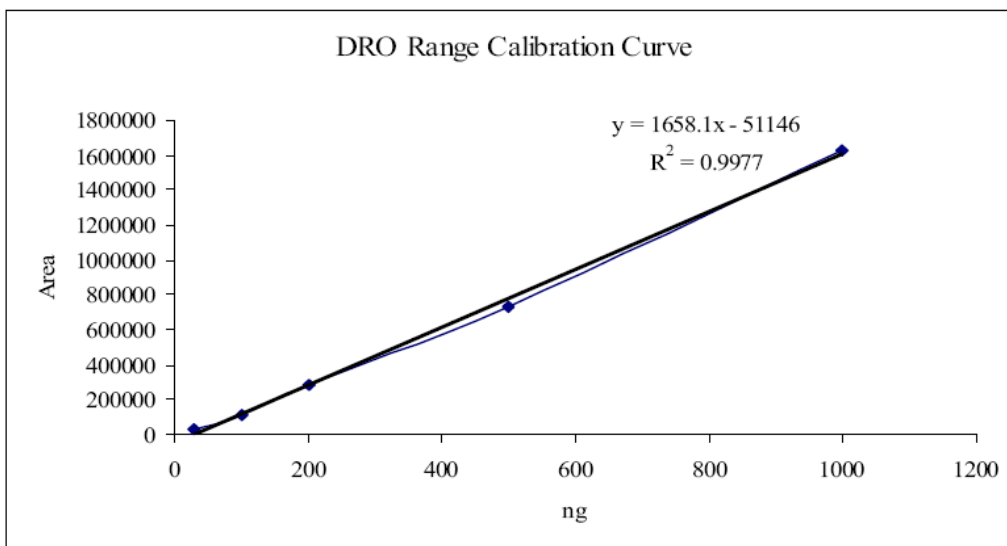


Figure 9: C₁₀ – C₂₂ Calibration Curve.

4.4 ANALYSIS OF SOIL AND TREATMENTS

Soil Blanks Purge and Trap Analysis

The initial contamination of each type of soil was tested by placing a gram of soil in a test tube with 5 mL of ultrapure water. The mixture was analyzed in a purge and trap GC under the same conditions as the contaminated samples. During the soil blank analysis, no background BTEX contamination above detection levels was found in any of the three types of soil.

Soil-Treatment Product Blanks Purge and Trap Analysis

The two different types of microorganisms and an aqueous solution of the added nutrients utilized in this study were first analyzed, without gasoline contamination, by purge and trap analysis. The soil-treatment product blanks were prepared and tested under the same conditions as the gasoline-contaminated samples. No BTEX contaminants were observed in the analysis of Micro-Blaze, Hydro Clean, or Miracle-Gro in the three different types of soil.

Soil Blanks Diesel Range Organic Analysis

Before DRO analysis, each type of soil was analyzed alone to identify possible initial DRO contamination. In this analysis, 1 g of soil was placed in a 20 mL vial with 10 mL of dichloromethane, and an aliquot was analyzed in the Model 3800 GC. No DRO contamination above detection limits was found in any of the three types of soil.

Soil-Treatment Product Blanks Diesel Range Organic Analysis

Micro-Blaze, Hydro Clean, and Miracle-Gro products were initially tested without diesel contamination by the GC 3800. The procedures used to prepare the samples were the same as those used for the diesel-contaminated soil samples (described in Section 3.2). The results showed no DRO-range contamination above detection limits in the commercial products and soils tested.

4.5 GASOLINE-CONTAMINATED SOIL

The results from the analysis of gasoline-contaminated soil samples were expressed in milligrams of contaminant contained per kilogram of dry soil. The results are shown only for toluene, ethylbenzene, *m*-xylene, *p*-xylene, and *o*-xylene. Benzene results were not shown because benzene concentrations were out of range of the benzene calibration curve (lower than the lowest benzene calibration point) by the second time that the samples were analyzed. 100 µg of benzene per kilogram of soil was the minimum detection limit for the method described in Section 3, Methodology. The Arizona Department of Environmental Quality's (ADEQ) benzene soil remediation level is 0.62 mg/kg for residential soils and 1.4 mg/kg for non-residential soils. ADEQ's benzene residential SRL was attained before day 7 of the study. An example of the benzene peak disappearance can be seen in Figure 10, where the progressive degradation of BTEX compounds can be observed.

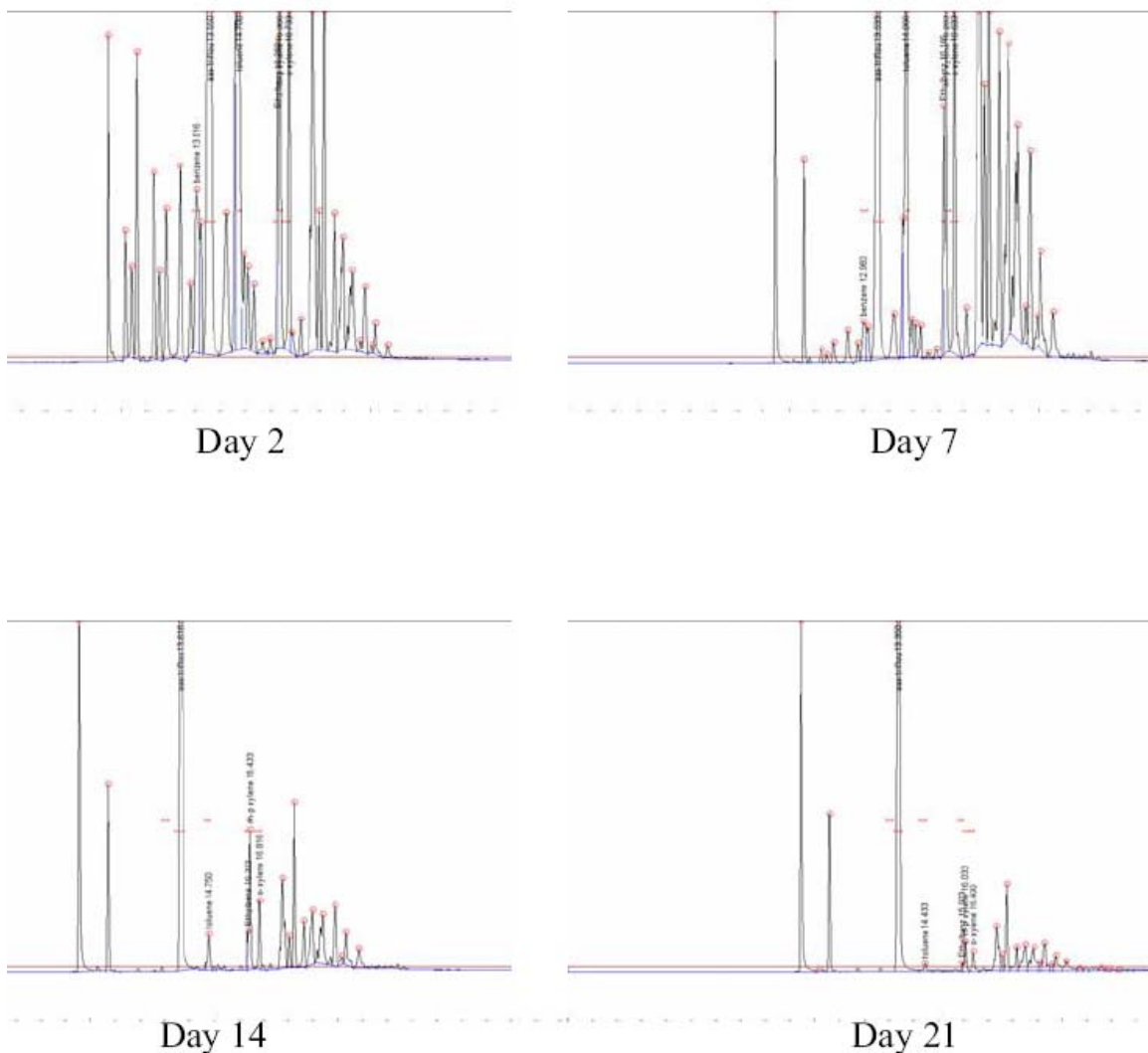


Figure 10: Show Low Soil Contaminated with Gasoline and Treated with Micro-Blaze. Note the Rapid Disappearance of the Benzene Peak.

Soil-Gasoline-Water Blanks

The three different types of soil were contaminated with gasoline and 5 mL of ultrapure water was added in each sample. These samples were prepared to compare untreated gasoline-contaminated samples with gasoline-contaminated samples that were treated with different microorganisms or nutrients. Both types of contaminated samples, those receiving no treatment and those treated with microorganisms or nutrients, had the same moisture level. Table 14 illustrates the results obtained for toluene, ethylbenzene, and xylenes. Benzene was not included because it was below the detection limit by the second measurement.

Duplicate samples for every 10 samples were prepared and analyzed to determine precision of measurements. ADEQ's toluene, ethylbenzene, and xylenes SRLs were

attained in less than 21 days when the three different types of soil were treated only with water. Graphic results of toluene levels in different types of soil treated with water can be seen in Figure 11. Figure 11 demonstrates that the toluene levels in the three types of soil become lower than ADEQ's toluene SRL (see Table 13).

Table 13: ADEQ's Soil Remediation Levels for BTEX and DRO Petroleum Hydrocarbons.

| Chemical name | CAS # | Residential (mg/kg) | Non-Residential (mg/kg) |
|--|-----------|------------------------|----------------------------|
| Benzene | 71-43-2 | 0.62 | 1.4 |
| Ethylbenzene | 100-41-4 | 1500.0 | 2700.0 |
| Toluene | 108-88-3 | 790.0 | 2700.0 |
| Xylene (mixed) | 1330-20-7 | 2800.0 | 2800.0 |
| Hydrocarbons (C ₁₀ to C ₃₂) | N/A | 4100.0 | 18000.0 |

Note: N/A = Not Applicable.

Table 14: Soil Types Contaminated with Gasoline and Treated with Water.

| Sample | Day | Toluene | Ethylbenzene | m-p Xylene | o-Xylene |
|----------------|-----|---------|--------------|------------|----------|
| | | mg/kg | mg/kg | mg/kg | mg/kg |
| α GW | 2 | 1352.16 | 439.47 | 680.82 | 546.25 |
| α GW | 7 | 321.88 | 186.07 | 304.07 | 273.54 |
| α GW | 14 | 58.95 | 73.42 | 72.97 | 47.10 |
| α GW | 21 | 58.62 | 71.49 | 70.46 | 41.75 |
| β GW | 2 | 7386.58 | 1603.41 | 2749.80 | 2413.31 |
| β GW | 7 | 1351.10 | 437.97 | 834.16 | 820.46 |
| β GW | 14 | 79.49 | 119.58 | 173.70 | 206.15 |
| β GW | 21 | 54.16 | 59.45 | 64.91 | 49.55 |
| *2- β GW | 21 | 45.58 | 59.18 | 62.76 | 45.86 |
| δ GW | 2 | 3484.44 | 944.95 | 1598.44 | 1364.56 |
| δ GW | 7 | 195.92 | 90.95 | 125.96 | 100.90 |
| δ GW | 14 | 66.16 | 84.11 | 96.24 | 83.53 |
| δ GW | 21 | 54.89 | 66.66 | 66.00 | 42.79 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; W= Water.
Mg/kg=milligrams of contaminant contained in a kilogram of dry soil.
*= Duplicate sample.

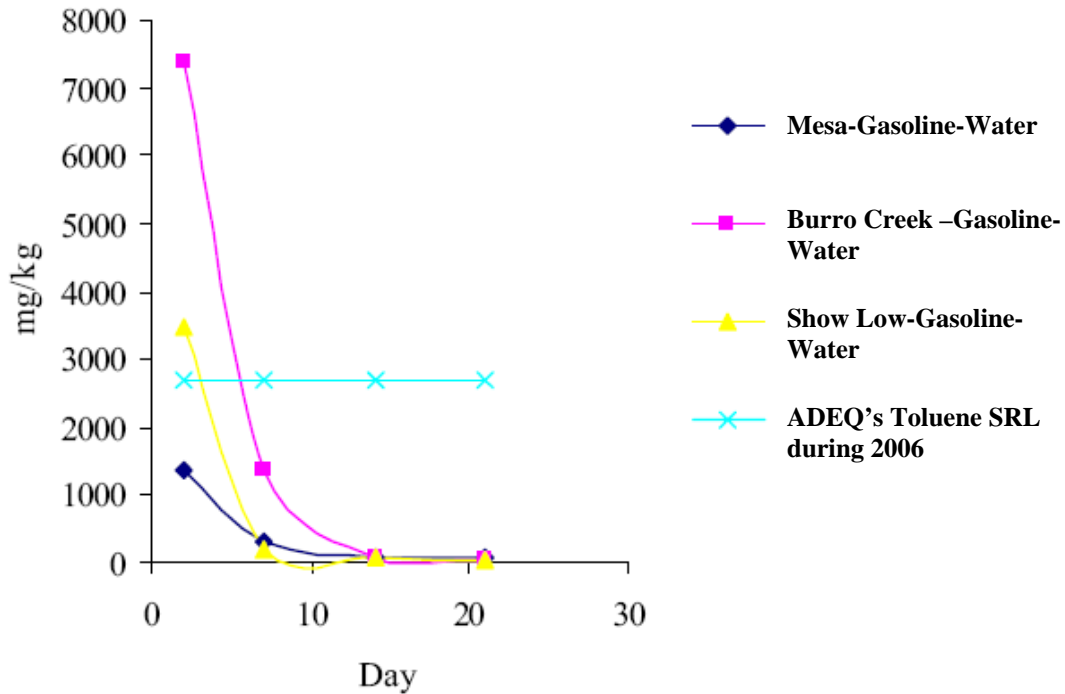


Figure 11: Toluene Levels in Soils Treated with Gasoline and Water.

Soil-Gasoline Blanks

Samples prepared with three different types of soil and commercial gasoline, without added water, were also analyzed. Table 15 describes the results obtained for toluene, ethylbenzene, and xylenes. The precision of the method was assured by a relative percent difference lower than 20 in duplicate samples. Figure 12 shows the gasoline evaporation rate for the three different types of soils and shows that the ADEQ's toluene SRL was attained by the second sampling date, on day 7 of the study. However, the final levels after day 21 were slightly higher than the final levels in samples to which water was added (shown in Table 14).

Table 15: Gasoline-Contaminated Soil Samples.

| Sample | Day | Toluene mg/kg | Ethylbenzene mg/kg | m-p Xylene mg/kg | o-Xylene mg/kg |
|----------------|-----|------------------|-----------------------|---------------------|-------------------|
| α G | 2 | 7268.39 | 1754.70 | 3051.53 | 2707.74 |
| α G | 7 | 938.64 | 381.47 | 606.50 | 644.44 |
| α G | 14 | 121.17 | 191.11 | 331.02 | 359.30 |
| 2- α G* | 14 | 113.89 | 221.79 | 384.54 | 421.46 |
| α G | 21 | 91.54 | 128.73 | 212.26 | 226.21 |
| β G | 2 | 7278.22 | 1744.14 | 2799.88 | 2511.34 |
| β G | 7 | 472.78 | 331.23 | 520.03 | 517.26 |
| 2- β G* | 7 | 575.25 | 344.89 | 577.21 | 538.93 |
| β G | 14 | 96.09 | 201.89 | 379.07 | 408.20 |
| β G | 21 | 88.12 | 123.09 | 193.53 | 207.80 |
| δ G | 2 | 8239.81 | 1408.55 | 2792.49 | 2503.05 |
| 2- δ G* | 2 | 8803.39 | 1673.79 | 3033.14 | 2689.23 |
| δ G | 7 | 777.55 | 302.65 | 542.29 | 487.92 |
| δ G | 14 | 103.91 | 106.20 | 190.16 | 182.25 |
| δ G | 21 | 100.55 | 88.18 | 119.82 | 120.21 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; G= Gasoline.
Mg/kg=milligrams of contaminant contained in a kilogram of dry soil.
*= Duplicate sample.

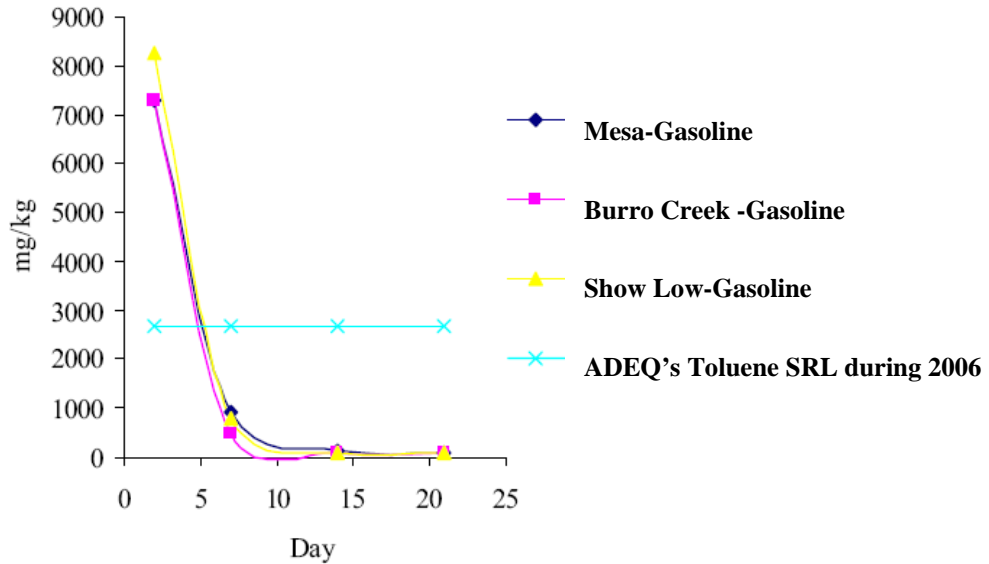


Figure 12: Toluene Levels in Soils Contaminated with Gasoline.

Soil-Gasoline-Treatment Product Blanks

The three commercial products, Micro-Blaze, Hydro Clean, and Miracle-Gro, were tested under the same conditions in different types of gasoline-contaminated soils. The precision of the method was assured by acceptance criteria of a relative percent difference of less than 20% in duplicate samples.

Table 16 details the results obtained during the analysis of the three products treating Mesa soil contaminated with gasoline. Table 17 shows the results for Burro Creek soil and Table 18 the results for Show Low soil. Figures 13 through 15 show the toluene levels in Mesa, Burro Creek, and Show Low soils, respectively, after no treatment, treatment with water, and treatment with each of the three products.

The results for all three soil types and treatment methods are similar to those in Tables 14 and 15, where no commercial treatments were applied. In all cases, the final concentrations by day 21 were below ADEQ's SRLs.

**Table 16: Gasoline-Contaminated Mesa Soil
Treated with Different Products.**

| Sample | Day | Toluene | Ethylbenzene | m-p Xylene | o-Xylene |
|-----------------|-----|----------|--------------|------------|----------|
| | | mg/kg | mg/kg | mg/kg | mg/kg |
| α GX | 2 | 5133.48 | 1987.29 | 3419.71 | 3143.39 |
| α GX | 7 | 525.39 | 229.00 | 422.60 | 413.61 |
| α GX | 14 | 59.11 | 89.44 | 110.79 | 134.22 |
| α GX | 21 | 46.00 | 58.94 | 56.16 | 30.79 |
| α GY | 2 | 10276.48 | 2049.92 | 3594.72 | 3132.80 |
| α GY | 7 | 1213.98 | 390.03 | 764.96 | 770.49 |
| α GY | 14 | 60.65 | 103.92 | 150.76 | 181.21 |
| α GY | 21 | 60.06 | 75.62 | 79.01 | 53.06 |
| *2- α GY | 21 | 52.60 | 67.42 | 65.19 | 54.00 |
| α GZ | 2 | 4938.43 | 939.07 | 1534.01 | 1103.58 |
| α GZ | 7 | 85.78 | 69.44 | 83.31 | 58.46 |
| α GZ | 14 | 59.83 | 68.82 | 66.65 | 41.13 |
| *2- α GZ | 14 | 51.51 | 58.00 | 62.60 | 33.95 |
| α GZ | 21 | 45.28 | 55.12 | 52.43 | 30.83 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; G= Gasoline; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro. Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample.

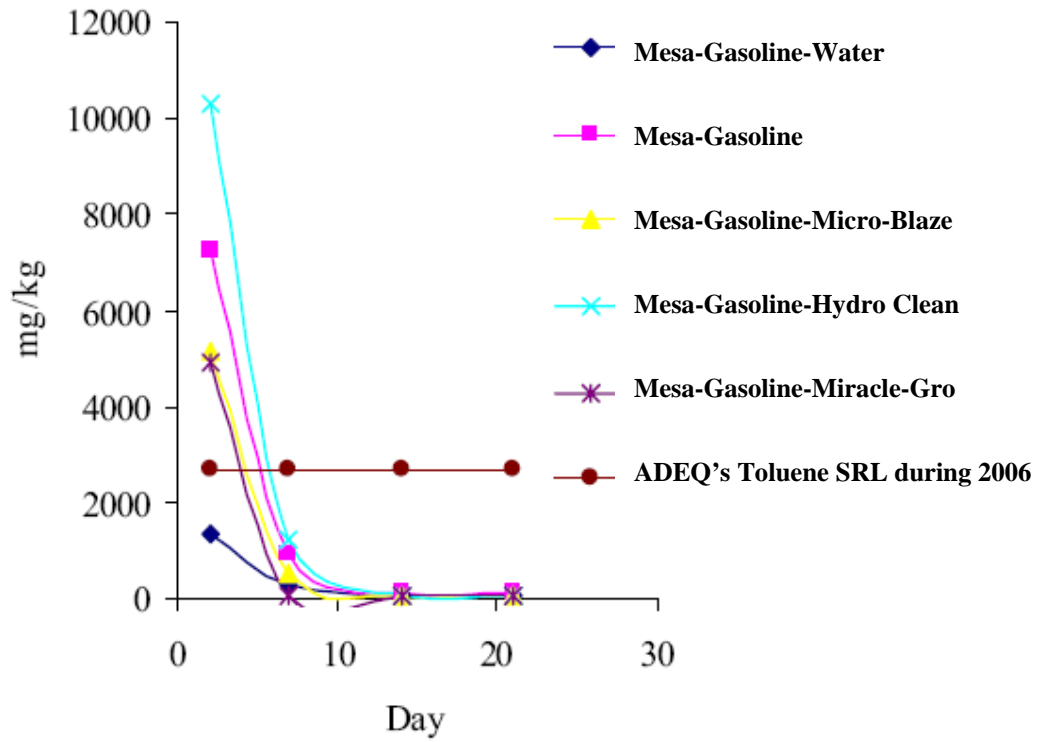


Figure 13: Toluene Levels in Mesa Soil.

**Table 17: Gasoline-Contaminated Burro Creek Soil
Treated with Different Products.**

| Sample | Day | Toluene | Ethylbenzene | m-p Xylene | o-Xylene |
|--------|-----|----------|--------------|------------|----------|
| | | mg/kg | mg/kg | mg/kg | mg/kg |
| βGX | 2 | 11352.85 | 2254.75 | 4109.74 | 3774.64 |
| βGX | 7 | 1620.08 | 572.66 | 1137.00 | 1155.38 |
| βGX | 14 | 82.97 | 125.19 | 200.68 | 202.98 |
| βGX | 21 | 67.59 | 79.32 | 81.17 | 57.53 |
| βGX | 2 | 6816.20 | 1359.39 | 2229.11 | 1960.47 |
| *2-βGY | 2 | 5759.16 | 1166.21 | 2147.83 | 1961.19 |
| βGY | 7 | 916.71 | 301.32 | 620.38 | 604.72 |
| βGY | 14 | 79.54 | 124.92 | 198.26 | 191.36 |
| βGY | 21 | 73.39 | 82.54 | 98.88 | 83.85 |
| βGZ | 2 | 1622.35 | 438.19 | 758.80 | 584.24 |
| βGZ | 7 | 287.49 | 127.59 | 151.14 | 134.99 |
| βGZ | 14 | 64.70 | 103.33 | 149.98 | 132.03 |
| βGZ | 21 | 61.92 | 80.68 | 87.73 | 66.99 |

Note: β = Burro Creek soil; G= Gasoline; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro. Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample.

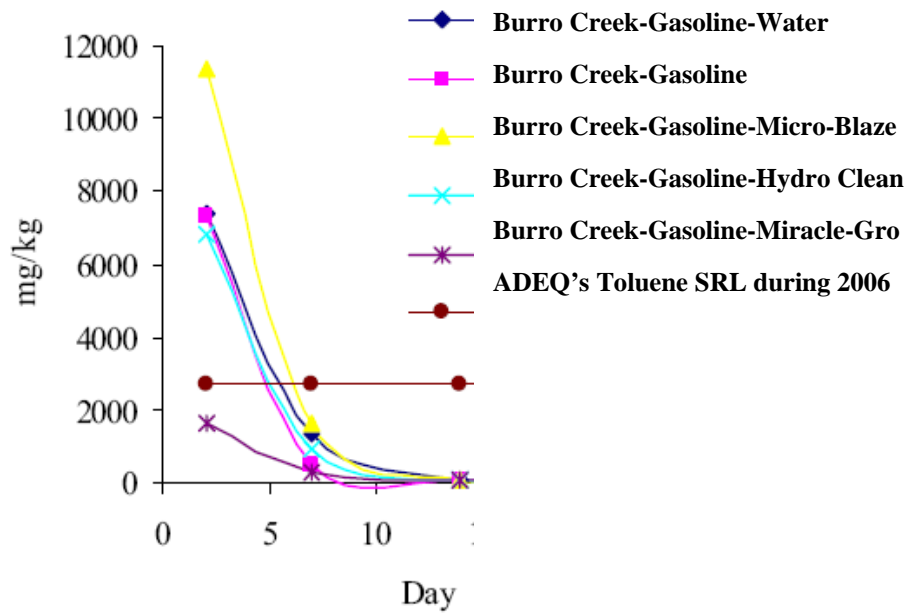


Figure 14: Toluene Levels in Burro Creek Soil.

**Table 18: Gasoline-Contaminated Show Low Soil
Treated with Different Products.**

| Sample | Day | Toluene | Ethylbenzene | m-p Xylene | o-Xylene |
|--------|-----|---------|--------------|------------|----------|
| | | mg/kg | mg/kg | mg/kg | mg/kg |
| δGX | 2 | 7900.93 | 1529.75 | 2121.25 | 2322.48 |
| δGX | 7 | 1572.48 | 556.58 | 973.93 | 1130.90 |
| δGX | 14 | 119.64 | 111.53 | 185.86 | 167.91 |
| δGX | 21 | 44.38 | 58.46 | 66.74 | 54.79 |
| δGY | 2 | 5759.01 | 1095.19 | 2440.11 | 2420.81 |
| δGY | 7 | 1981.72 | 621.83 | 958.30 | 959.45 |
| *2-δGY | 7 | 2392.48 | 743.01 | 1141.04 | 1072.89 |
| δGY | 14 | 75.37 | 114.91 | 178.27 | 169.43 |
| δGY | 21 | 69.11 | 80.71 | 83.12 | 62.48 |
| δGZ | 2 | 7248.42 | 1342.22 | 2283.44 | 1980.54 |
| δGZ | 7 | 881.61 | 294.04 | 553.09 | 536.49 |
| δGZ | 14 | 78.18 | 108.91 | 144.32 | 123.61 |
| δGZ | 21 | 63.82 | 78.56 | 75.61 | 47.06 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; G=Gasoline; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro; RPD% = Relative Percent Difference; Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample.

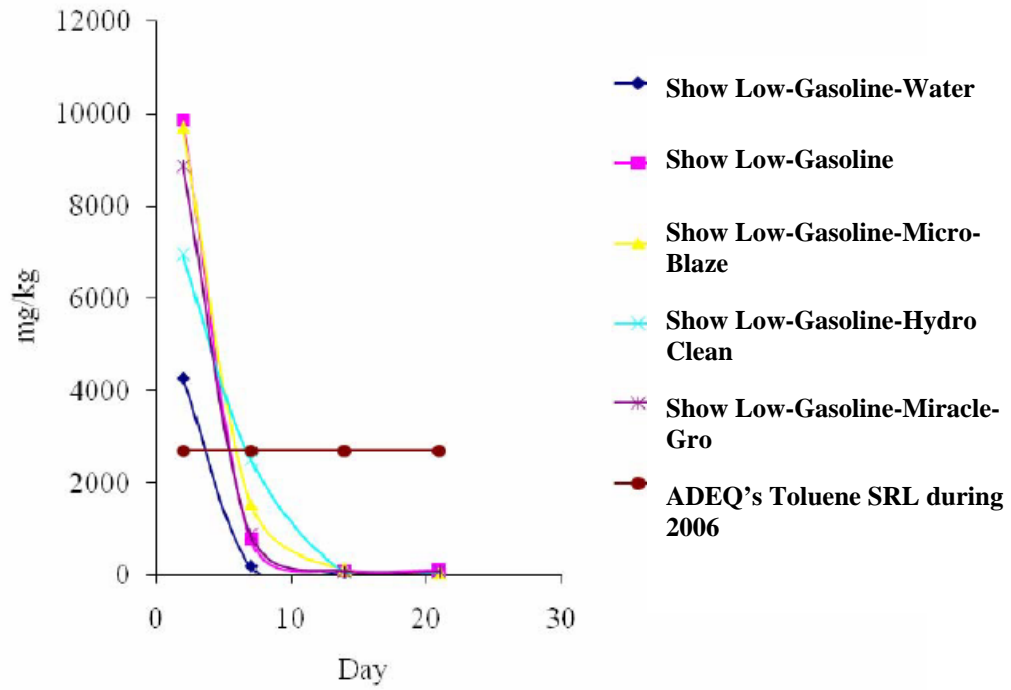


Figure 15: Toluene Levels in Show Low Soil.

4.6 DIESEL-CONTAMINATED SOIL

Soil-Diesel Blanks

Diesel range organics C₁₀-C₂₂ were analyzed, according to the methodology described in Section 2.2, from the three different types of soil contaminated with commercial diesel No. 2 without any added treatments. The results are shown in Table 19. After 83 days, the DRO concentration in soil was still greater than the ADEQ diesel limits for soils.

Table 19: Diesel Blank Samples.

| Day | Sample | mg/kg | RPD% |
|-----|--------|----------|------|
| 2 | αD | 70075.67 | 4.40 |
| 2 | *2-αD | 67058.78 | |
| 83 | αD | 65922.05 | |
| 2 | βD | 79748.74 | |
| 83 | βD | 78873.06 | |
| 2 | δD | 67714.08 | |
| 83 | δD | 57997.74 | |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; D = Diesel;
Mg/kg=milligrams of contaminant contained in a kilogram of dry soil.
*= Duplicate sample.

Soil-Diesel-Treatment Product Blanks

The three commercial products, Micro-Blaze, Hydro Clean, and Miracle-Gro, were applied to the different types of soil contaminated with the same amount of diesel No. 2. Table 20 shows the results obtained from the treatment of Mesa soil. Figure 16 shows the DRO degradation level for each remediation product applied in Mesa soil. After 83 days, levels of diesel contamination were still above the SRL enforced by ADEQ even with treatments. Table 21 and Figure 17 show the results for Burro Creek soil, and Table 22 and Figure 18 show the results for Show Low soil.

Table 20: Mesa Soil Treated with Different Products.

| Day | Sample | mg/kg |
|-----|--------|----------|
| 2 | αDX | 79462.57 |
| 83 | αDX | 39009.71 |
| 2 | αDY | 93263.02 |
| 83 | αDY | 61343.15 |
| 2 | αDZ | 47554.53 |
| 83 | αDZ | 67134.72 |

Note: α = Mesa soil; D= Diesel; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro.
Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample.

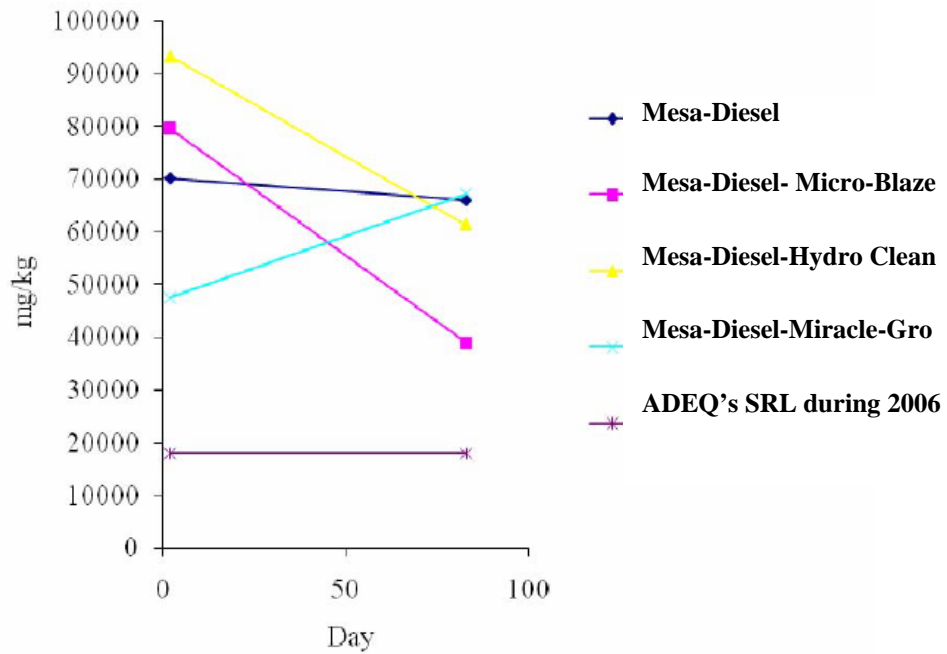


Figure 16: Mesa Soil Contaminated with Diesel.

Table 21: Burro Creek Soil Treated with Different Products.

| Day | Sample | mg/kg | RPD% |
|-----|--------|----------|-------|
| 2 | βDX | 79843.07 | |
| 83 | βDX | 78218.94 | |
| 2 | βDY | 90404.21 | |
| 83 | βDY | 66257.03 | 15.05 |
| 83 | *2-βDY | 77042.66 | |
| 2 | βDZ | 54705.31 | 6.18 |
| 2 | βDZ | 51423.73 | |
| 83 | βDZ | 66837.39 | |

Note: β = Burro Creek soil; D= Diesel.; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro; RPD% = Relative Percent Difference; Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample.

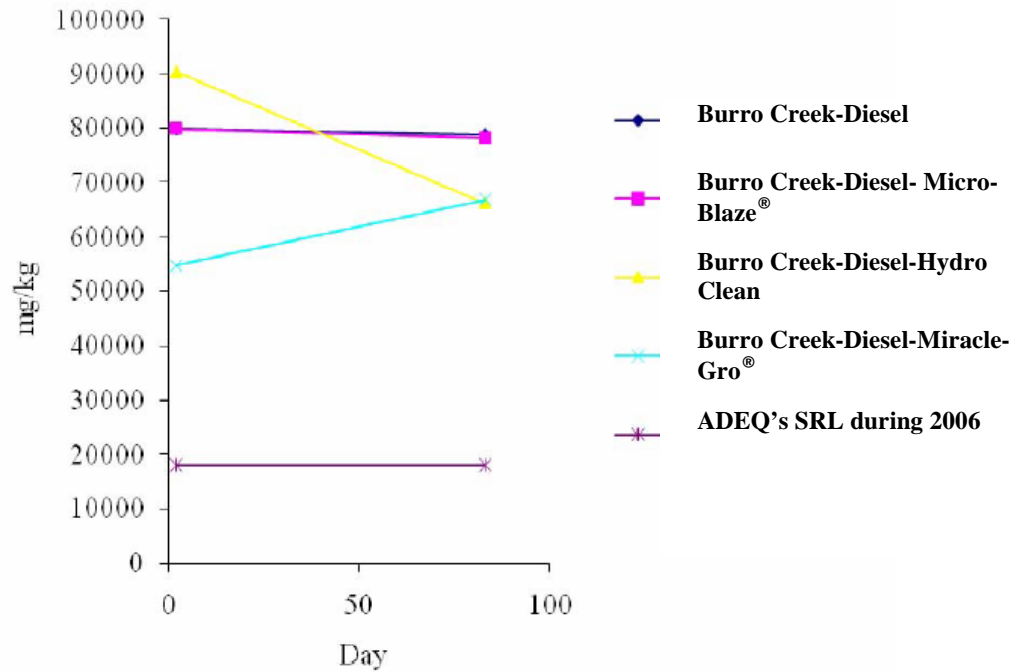


Figure 17: Burro Creek Soil Contaminated with Diesel.

Table 22: Show Low Soil Treated with Different Products.

| Day | Sample | mg/kg |
|-----|--------|-----------|
| 2 | δDY | 106523.79 |
| 2 | *2-δDY | 114646.54 |
| 83 | δDY | 55551.48 |
| 2 | δDX | 63437.14 |
| 83 | δDX | 83909.05 |
| 2 | δDZ | 41542.85 |
| 83 | δDZ | 70294.15 |

Note: δ = Show Low soil; D=Diesel; X=Micro-Blaze; Y= Hydro Clean; Z= Miracle-Gro; RPD%= Relative Percent Difference; Mg/kg=milligrams of contaminant contained in a kilogram of dry soil. *= Duplicate sample; Area= Peaks under C₁₄-C₂₂ Range.

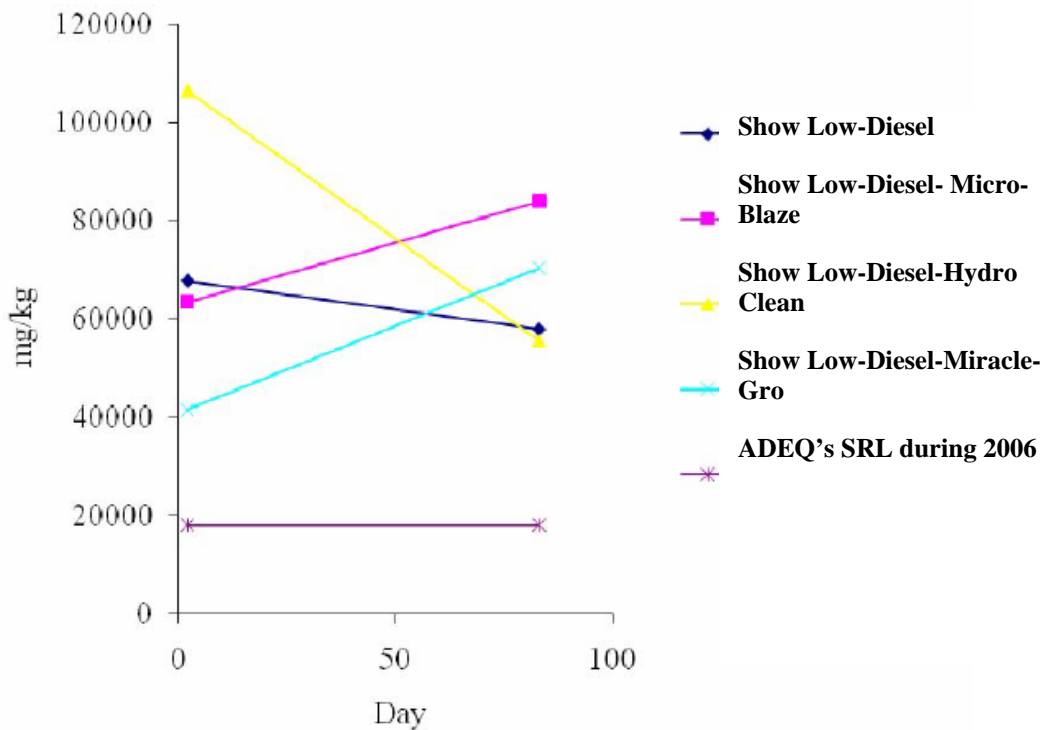


Figure 18: Show Low Soil Contaminated with Diesel.

5.0 CONCLUSIONS

5.1 GASOLINE

All three soil types contaminated with gasoline showed a reduction in BTEX levels to below ADEQ's SRLs within 21 days, even in the absence of added microorganisms or nutrients. However, in trying to compare the rates of degradation among various options, some degree of quantification can be obtained by normalizing the BTEX concentration and measuring the rate of decay.

Thus, the concentration of an individual contaminant at a given time is divided by the initial concentration measurement, and the change in normalized concentration is then divided by the number of days between measurements. The initial measurement of BTEX was performed on day 2. For example, in Table 14, for α GW, the toluene concentration on day 2 is 1352 mg/kg. Its normalized value is $1352/1352 = 1$. The concentration after day 7 is 322 mg/kg for a normalized value of $322/1352 = 0.238$. Thus, the initial rate of decay is

$$\begin{aligned} \text{Rate} &= \text{change in normalized concentration} / \text{change in time.} \\ &= (1 - 0.238) / 5 \\ &= 0.152 \end{aligned}$$

After 14 days, the rate of decay is $(1 - 0.044) / 12 = 0.080$.

In Table 15, where no water was added, the rate of decay for toluene after seven days was 0.174. After 14 days, it was 0.082. Thus, the initial contaminant reduction rate for toluene was slightly greater when no water was added, and the rates after 14 days were similar.

Table 23 shows the normalized initial rates of decay for toluene, ethylbenzene, *m*- and *p*-xylene, and *o*-xylene for all three soil types contaminated with gasoline without added water and with added water (data from Tables 14 -18) from days 2 and 7.

Table 24 shows scores for each treatment method for each contaminant. The highest normalized initial rate was assigned a score of 1, the next highest assigned a score of 2, etc. The total for all components was then added for each soil type and treatment method. The more effective treatment options correspond to lower total scores.

Table 25 arranges the total scores by soil type in order to compare the effectiveness of treatment options.

Table 23: Normalized Initial Rates (5 Days) of Decay for Gasoline-Contaminated Soils.

| Sample | Toluene | Ethylbenzene | <i>m</i> - and <i>p</i> -Xylene | <i>o</i> -Xylene |
|-------------|---------|--------------|---------------------------------|------------------|
| α G | 0.174 | 0.157 | 0.16 | 0.152 |
| β G | 0.187 | 0.162 | 0.163 | 0.159 |
| δ G | 0.182 | 0.164 | 0.164 | 0.164 |
| α GW | 0.152 | 0.115 | 0.111 | 0.01 |
| β GW | 0.163 | 0.145 | 0.14 | 0.132 |
| δ GW | 0.189 | 0.181 | 0.184 | 0.185 |
| α GX | 0.18 | 0.177 | 0.175 | 0.174 |
| α GY | 0.176 | 0.162 | 0.157 | 0.151 |
| α GZ | 0.197 | 0.185 | 0.189 | 0.189 |
| β GX | 0.171 | 0.149 | 0.145 | 0.139 |
| β GY | 0.168 | 0.148 | 0.142 | 0.138 |
| β GZ | 0.165 | 0.142 | 0.16 | 0.154 |
| δ GX | 0.16 | 0.127 | 0.108 | 0.103 |
| δ GY | 0.131 | 0.086 | 0.121 | 0.121 |
| δ GZ | 0.176 | 0.156 | 0.152 | 0.146 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; W = Water; G = Gasoline; X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.

Table 24: BTEX Scores; Lower Scores Indicate Greater Effectiveness.

| Sample | Toluene | Ethylbenzene | <i>m</i> - and <i>p</i> -Xylene | <i>o</i> -Xylene | Total |
|-------------|---------|--------------|---------------------------------|------------------|-------|
| α G | 8 | 7 | 6 | 7 | 28 |
| β G | 3 | 5 | 5 | 5 | 18 |
| δ G | 4 | 4 | 4 | 4 | 16 |
| α GW | 13 | 14 | 14 | 15 | 56 |
| β GW | 11 | 11 | 12 | 12 | 46 |
| δ GW | 2 | 2 | 2 | 2 | 8 |
| α GX | 5 | 3 | 3 | 3 | 14 |
| α GY | 6 | 5 | 8 | 8 | 27 |
| α GZ | 1 | 1 | 1 | 1 | 4 |
| β GX | 8 | 9 | 10 | 10 | 37 |
| β GY | 9 | 10 | 11 | 11 | 41 |
| β GZ | 10 | 12 | 6 | 6 | 34 |
| δ GX | 12 | 13 | 15 | 14 | 54 |
| δ GY | 14 | 15 | 13 | 13 | 55 |
| δ GZ | 6 | 8 | 9 | 9 | 32 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; W = Water; G = Gasoline; X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.

Table 25: BTEX Scores According to Soil Type.

| Sample | Toluene | Ethylbenzene | <i>m</i> - and <i>p</i> -Xylene | <i>o</i> -Xylene | Total |
|-------------|---------|--------------|---------------------------------|------------------|-------|
| α G | 8 | 7 | 6 | 7 | 28 |
| α GW | 13 | 14 | 14 | 15 | 56 |
| α GX | 5 | 3 | 3 | 3 | 14 |
| α GY | 6 | 5 | 8 | 8 | 27 |
| α GZ | 1 | 1 | 1 | 1 | 4 |
| β G | 3 | 5 | 5 | 5 | 18 |
| β GW | 11 | 11 | 12 | 12 | 46 |
| β GX | 8 | 9 | 10 | 10 | 37 |
| β GY | 9 | 10 | 11 | 11 | 41 |
| β GZ | 10 | 12 | 6 | 6 | 34 |
| δ G | 4 | 4 | 4 | 4 | 16 |
| β GW | 11 | 11 | 12 | 12 | 46 |
| δ GX | 12 | 13 | 15 | 14 | 54 |
| δ GY | 14 | 15 | 13 | 13 | 55 |
| δ GZ | 6 | 8 | 9 | 9 | 32 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; W = water; G = Gasoline; X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.

Table 25 indicates that the most effective treatment for gasoline-contaminated Mesa soils was to add Miracle-Gro (indicated by the letter Z). For Burro Creek and Show Low soils, Miracle-Gro was the second most effective treatment, with the most effective being to leave the soils alone without adding either water or other products. Micro-Blaze treatment (letter X) was rated number 2, 3, or 4, while Hydro Clean (letter Y) was rated number 3, 4, or 5 out of the five possible treatment options.

However, the most important observation is that all soil samples contaminated with gasoline were below the residential Arizona SRLs by day 21, no matter what treatment option was employed. There was some acceleration with certain treatments, but all samples ultimately decayed to approximately the same levels of BTEX.

5.2 DIESEL

The situation with diesel-contaminated soils was quite different. In none of the sample treatments was the diesel concentration below either residential or non-residential SRLs by day 83. Normalized diesel scores according to soil type are shown in Table 26.

**Table 26: Normalized Diesel Scores
According to Soil Type After 83 Days.**

| Sample | Score | Rank Order |
|--------------------|----------|------------|
| α D (blank) | 0.000732 | 3 |
| α DX | 0.00628 | 1 |
| α DY | 0.00423 | 2 |
| α DZ | -0.00508 | 4 |
| β D (blank) | 0.000136 | 3 |
| β DX | 0.000251 | 2 |
| β DY | 0.00330 | 1 |
| β DZ | -0.0032 | 4 |
| δ D (blank) | 0.00177 | 2 |
| δ DX | -0.0040 | 3 |
| δ DY | 0.00614 | 1 |
| δ DZ | -0.0085 | 4 |

Note: α = Mesa soil; β = Burro Creek soil; δ = Show Low soil; W = Water; D= Diesel; X = Micro-Blaze; Y = Hydro Clean; Z = Miracle-Gro.

Normalized diesel scores were calculated in the same manner as scores for gasoline-contaminated soils. For Burro Creek and Show Low soils, the optimal treatment was with Hydro Clean, which was the second-best treatment option for Mesa soils. Micro-Blaze was the optimal treatment for Mesa soils and the second-best for Burro Creek soils.

In all soils, treatment with Miracle-Gro resulted in an actual increase in measured DRO after 83 days, as did treatment with Micro-Blaze in Show Low soils. This is likely due to a division of long-chain organics into smaller fragments, which are still included in the DRO sampling range.

6.0 RECOMMENDATIONS AND SUGGESTIONS

Even though the State of Arizona no longer has an SRL for total petroleum hydrocarbons, it is prudent to take action to remediate. Cleaning up petrochemical hydrocarbons will protect stormwater and surface water and eliminate environmental and public health hazards.

Further research in the area of polycyclic aromatic hydrocarbons (PAHs) in soils from diesel fuel spills and from incomplete combustion of carbon-containing fuels should be considered.

The research was performed in a laboratory situation. The rate at which volatile organic compounds (VOCs) decayed was in days as opposed to weeks, although decay would have taken weeks if research had occurred in situ. Changes in research design should be considered to include in situ application of remediation products.

The increase in DRO may be a result of larger-chain hydrocarbons being broken down to smaller chains, causing DRO numbers to increase. Further research with GC/MS may be useful to confirm the breakdown of DRO into smaller hydrocarbon chains.

It is also prudent to consider further evaluation of other dispersants, chemicals, and oil spill mitigating devices and substances listed on the EPA National Contingency Plan Subpart J Product Schedule. Research associated with the control of oil from rubberized asphalt and other asphaltic materials is a related area that warrants further investigation.

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