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EVALUATION OF SOIL WASHING TECHNOLOGY: Results of Bench-Scale Experiments on Petroleum-Fuels Contaminated Soils

by

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16. ABSTRACT

The U.S. Environmental Protection Agency through its Risk Reduction Engineering Laboratory's Releases Control Branch has undertaken research and development efforts to address the problem of leaking underground storage tanks (USTs). Under this effort, EPA is currently evaluating soil washing technology for cleaning up soil contaminated by the release of petroleum products from leaking underground storage tanks. Soil washing is a dynamic physical process which remediates contaminated soil via two mechanisms--particle separation and dissolution of the contaminants into the washwater. As a result of the washing process, a significant fraction of the contaminated soil is cleaned and can be returned into the original excavation or used as cleaned "secondary" fill or aggregate material. Since the contaminants are more concentrated in the fine soil fractions, their separation and removal from the bulk soil increases the overall effectiveness of the process. Subsequent treatment will be required for the spent washwaters and the fine soil fractions.

The soil washing program evaluated the effectiveness of soil washing technology in removing petroleum products (unleaded gasoline, diesel/home heating fuel, and waste crankcase oil) from an EPA-developed Synthetic Soil Matrix (SSM) and from actual site soils. Operating parameters such as contact time, washwater volume, rinsewater volume, washwater temperature, and effectiveness of additives were investigated.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, may threaten both human health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural resources to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication presents information on current research efforts and provides a vital communication link between the researcher and the user community.

An area of major concern to the Risk Reduction Engineering Laboratory is the impacts associated with uncontrolled releases of petroleum hydrocarbons from underground storage tanks. This document provides information on soil washing technology for cleaning up soils contaminated with petroleum products.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The U.S. Environmental Protection Agency through its Risk Reduction Engineering Laboratory's Release Control Branch has undertaken research and development efforts to address the problem of leading underground storage tanks (USTs). Under this effort, EPA is currently evaluating soil washing technology for cleaning up soil contaminated by the release of petroleum products from leaking underground storage tanks. Soil washing is a dynamic physical process which remediates contaminated soil via two mechanisms - particle separation and dissolution of the contaminant into the washwater. As a result of the washing process, a significant fraction of the contaminated soil is cleaned, and can be returned into the original excavation or used as cleaned "secondary" fill or aggregate material. Since the contaminants are more concentrated in the fine soil fractions, their separation and removal from the bulk soil increases the overall effectiveness of the process. Subsequent treatment will be required for the spent washwaters and the fine soil fractions.

The soil washing program evaluated the evaluated the effectiveness of soil washing technology in removing petroleum products (unleaded gasoline, diesel/home heating fuel, and waste crankcase oil) from an EPA-developed Synthetic Soil Matrix (SSM) and from actual site soils. Operating parameters such as contact time, washwater volume, rinsewater volume, washwater temperature and effectiveness of additives were investigated. The additives investigated were CitriKleen (a biodegradable degreasing agent) and an organic surfactant. Actual soils from UST sites in Ohio and New Jersey were washed using the optimum parameters derived from the SSM.

This report was submitted in fulfillment of Contract No. 68-03-3409 by CDM Federal Programs Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1989 to August 1990, and work was completed as of August 1990.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA	--	Atomic Absorption
ASTM	--	American Society for Testing and Materials
BDAT	--	Best Demonstrated and Available Technology
BTEX	--	Benzene, Toluene, Ethylbenzene, Xylenes
CEC	--	Cation Exchange Capacity
COD	--	Chemical Oxygen Demand
EPA	--	U.S. Environmental Protection Agency
G	--	Grams
GC	--	Gas Chromotograph
GP	--	Supelco Trade Name
IR	--	Infrared
MEQ	--	Milliequivalents
MSWS	--	Mobile Soil Washing System
PAH	--	Polycylic Aromatic Hydrocarbons
PI	--	Plasticity Index
PID	--	Photoionization Detector
PL	--	Plastic Limit
ppb	--	Parts per Billion
ppm	--	Parts per Million
PSD	--	Particle Size Distribution
USDA	--	U.S. Department of Agriculture
UST	--	Underground Storage Tank
RREL	--	Risk Reduction Engineering Laboratory
SP	--	Supelco Trade Name
SSM	--	Synthetic Soil Matrix
TOC	--	Total Organic Carbon
TPH	--	Total Petroleum Hydrocarbons
TSS	--	Total Suspended Solids
XRD	--	X-Ray Diffraction
XRF	--	X-Ray Fluorescence

SYMBOLS

cm	--	Centimeter
ft^3	--	Cubic Foot
gal	--	Gallon
Hz	--	Hertz
kg	--	Kilogram
kW	--	Kilowatt

(Continued)

SYMBOLS (Continued)

lb	--	Pound
ml	--	Milliliters
ml/s	--	Milliliters per Second
mm	--	Millimeter
S	--	Second
°	--	Degree
%	--	Percent

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SECTION 1

INTRODUCTION

Based on the Hazardous and Solid Waste Amendments of 1984 and its Land Ban Regulations, EPA has discouraged the excavation and landfill disposal practices of the past for contaminated soils resulting from leaking underground storage tanks (USTs). EPA has encouraged the use of on-site treatment technologies, however, problems have plagued the development of on-site treatment technologies for petroleum contaminated soils. Technical support is needed to develop effective, long-term corrective actions at leaking UST sites, design cleanup program guidance, and help implement state programs.

The U.S. Environmental Protection Agency, through its Risk Reduction Engineering Laboratory's Release Control Branch, has undertaken research and development efforts to address the problem of leaking USTs. The remedial options available for the treatment of contaminated soils from UST sites are broadly segregated into two main categories, namely those which remove the contaminants without excavation (in situ techniques) and those which require excavation of the soil and subsequent cleaning on-site. The former group of remedial options have not yet been demonstrated for high efficiency removal of contaminants from the subsurface. These techniques are plagued by the uncertainty of soil contamination levels in the subsurface after treatment. Soil excavation followed by extensive cleaning of the soil will ensure a more complete removal of contaminants over in situ techniques.

On-site soil washing of excavated soils is a viable alternative to in situ techniques and has been shown to be effective for the cleanup of hazardous waste contaminated soils (EPA, 1988). The goal of this effort is to determine the feasibility of soil washing for cleanup of petroleum contaminated soils.

SOIL WASHING THEORY

Soil washing is a physical process in which excavated soils are contacted with a liquid medium, usually water, as shown in Figure 1. The soils undergo intimate contact with washing and rinsing solutions to promote contaminant transport from the solid to the liquid phase which result in a treated soil and a washwater, the latter requiring further treatment. The washwater treatment involves the removal and residuals management of the fine particulate material that is carried over into the washwater.

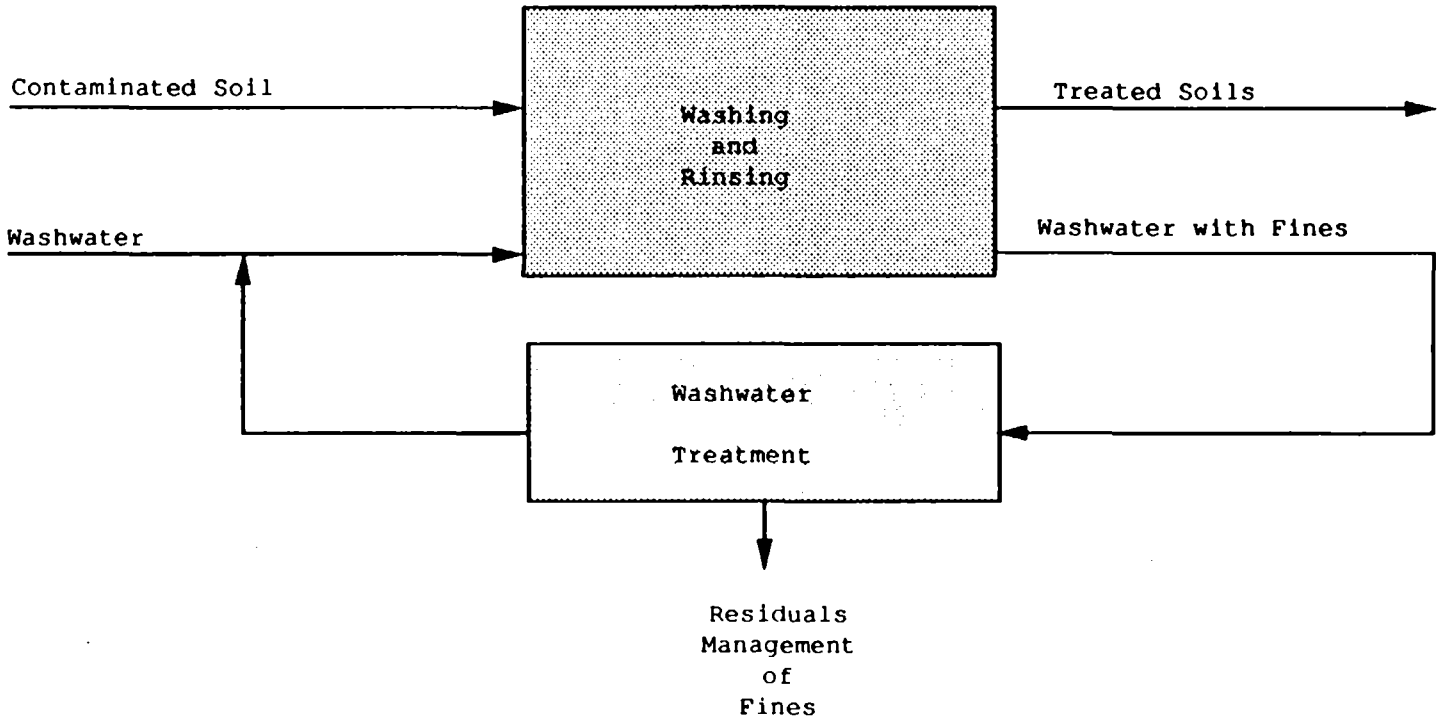


Figure 1. Soil Washing Process Diagram.

The two principle cleaning mechanisms include the dissolution of the contaminants into the extractive agent and/or the dispersion of the contaminants into the extraction phase in the form of particles (suspended or colloidal). The separation of the highly contaminated fine soil particles (silts, clay and colloidal) from the bulk of the soil matrix can result in volume reduction of the contaminated soil. As a result, a significant fraction of the contaminated soil is cleaned and can be put back into the original excavation. Since the contaminants are more concentrated in the fine soil fractions, their removal from the bulk soil increases the overall effectiveness of the soil washing process.

Subsequent treatment will be required for the spent washwaters and the fine soil fractions. The washwaters will contain suspended solids which can be removed by using technologies such as coagulation, precipitation, sedimentation, and cyclones. A resultant sludge will be produced which is ultimately treated or disposed with incineration or landfilling. In addition to removal of the particulates from the washwater, solubilized contaminants must be removed before discharge. Viable technologies for this application include air stripping and carbon adsorption.

LITERATURE REVIEW

A literature review was completed to obtain information on prior work done with soil washing processes. The information obtained included references on:

full scale soil washing,
pilot scale soil washing tests,
soil washing selection at Superfund sites,
liquid/solid extraction (leaching operations),
tar sands extraction and oil recovery,
oil/water emulsions/solubility,
liquid/solid separation (greater than 100 um by sedimentation & less than 100 um by hydroclones/flotation /filtration),
oily wasterwater treatment,
sludge residual management,
clay/silt dewaterability and hydrometallurgy.

The references cited in this literature review are included in the Bibliography.

The treatment of contaminated soils by extractive methods has been investigated by researchers/commercial vendors, and several field applications have been undertaken for the removal of organic and inorganic contaminants. Soil washing technology has been selected for several Superfund sites (Koppers Texarkana TX, Zellwood FL, United Scrap Lead OH, South Cavalcade Street TX, and L.A. Clarke & Sons VA). The technology has been demonstrated in support of the best demonstrated and available technology (BDAT) determination for the RCRA land ban rules (Esposito, 1988). Several commercial vendors have developed soil washing technology for contaminated soils (Chilcote, Trost). Several European companies have

also developed soil washing technology for the cleanup of contaminated soils (Assink, Heimkard, and Sonnen).

The literature indicates that the application of the soil washing process at the various sites involves several steps. The soil is pretreated to remove large objects such as tree roots, boulders and debris, as well as the breaking down of soil lumps. The soil and washing solution are then vigorously contacted to either dissolve or disperse the contaminants into the washing solution. The next stage involves the separation of the soil and the washing solution. The sand particles can be separated by sedimentation, while the silt and clay particles may require froth flotation or hydrocylonic action for removal from the washing solution. The washing solution is then treated by either chemical/physical or biological methods for recycling into the extraction process. The clean sand can be placed back into the excavation, while the silt/clay sludge may require dewatering and further treatment.

Biotrol (Chilcote) has completed an on-site demonstration of their pilot scale soil washing system at a Minnesota Superfund site contaminated with pentachlorophenol and creosote. The pilot study demonstrated pentachlorophenol and creosote removal of 85 to 99 percent with a total soil recovery of 73 to 83 percent of the contaminated soil. The process water was successfully treated and recycled back to the soil washing process. Similar treatment performance has been experienced at several sites in Europe.

Several documents were reviewed dealing with the subject of oil spill cleanup technology. "An Overview of Spill Cleanup Technology" (Griffiths) contains a review of equipment and techniques for responding to spills of dangerous cargoes from ocean vessels. These techniques are more concerned with the emergency response cleanups than long term corrective actions of oil in soils. The "Field Guide to Inland Oil Spill Cleanup Techniques" (Beynon) outlined several methods for cleaning up oil contaminated soils. These included soft surface cleaning, hard surface cleaning, solidification, sludge farming, and incineration. Soft surface cleaning consists of utilizing farm machinery to aerate the oily soils for increased biodegradation. Hard surface cleaning required a hot water or steam jet to wash down pavement or concrete areas. Beach cleaning trials at Pendine Sands (Warren Spring Lab) described techniques for scraping heavy oil emulsions into narrow trenches for removal via vacuum tank trucks.

The known reserves of tar sands (also known as oil sands and bituminous sands) throughout the world has led to the development of several techniques for the extraction and recovery of the trapped oil in the sand matrix. The recovery of oil from tar sands is economically viable through the mining of the tar sands followed by above ground oil extraction utilizing hot and/or cold water with additives (Camp, Deynoyers, Margeson). Cold water separation also termed sand reduction process has been accomplished with water alone and with the addition of kerosene and soda ash. The hot water process consists of a water/NaOH mixture at temperature of 180-200°F. Oil recoveries of up to 75% can be accomplished with the hot water process.

The extraction of metals from natural ores has been accomplished since the early days of civilization. The principles of hydrometallurgy (also known as solids leaching) may help us develop appropriate techniques for removal of contaminants from soil (Canterford, Coyle, Schmidt). The extraction of zinc, copper, and nickel have been accomplished with sulfuric acid and water solutions. Uranium mine tailings have also been treated by acid leaching to remove residual contaminants (Haque).

SOIL WASHING RESEARCH PROGRAM

The research program reported in this document consisted of several sequential steps which built upon the work performed in each previous step. This section outlines the various phases of work which were performed and are reported in this document.

SSM Preparation

The program required the preparation of the contaminated synthetic soil matrices (SSM), which were the soils to be tested. Prior to preparing the quantities of SSM needed for the bench scale tests, bench scale experiments were performed to develop a dose/response relationship between the quantity of petroleum added to the soil matrix and the analysis quantification. The petroleum products evaluated during this study included unleaded gasoline, diesel oil and waste crankcase oil. The dose/response tests investigated the relationship between the concentration of gasoline or diesel added to the soil and the analytical BTEX (benzene, toluene, ethylbenzene and xylenes) and TPH (total petroleum hydrocarbon) results, respectively.

The results of these tests were used to prepare the full scale SSM batches at predetermined concentration levels. The soils were prepared at the EPA Soil Blending Facility in Edison, NJ. TPH analysis was performed to verify the concentration levels for diesel oil and waste oil, and BTEX analysis was performed to verify the concentration levels for gasoline. SSM was prepared in 23 kilograms (50 pound) batches and stored in sealed 19 liter (5-gallon) metal pails until used.

The bench scale experiments were designed to simulate the EPA-developed pilot-scale Mobile Soil Washing System (MSWS). Specifically, the bench scale experiments were designed to simulate the drum-screen washer which separates the >2-mm soil fraction (coarse material) from the <2-mm soil fraction (fines) by use of a rotary drum screen. A high pressure water knife operates at the head of the system to break up soil lumps and strip the contaminants from the soil particles.

Phase I Bench Scale Experiments

The bench scale soil washing experiments consisted of several tasks with various objectives. The first task was to determine the sensitivity of various washing parameters on the removal effectiveness of contaminated SSM. Operating parameters such as contact time, washwater mass, rinsewater mass, washwater temperature and effectiveness of washwater additives

(surfactant, and CitriKleen - a biodegradable degreasing agent) were investigated.

It was expected that gasoline contaminated soils would have different optimal washing parameters than diesel contaminated soils. Therefore, identical sets of experiments were conducted on soils containing high levels of gasoline and diesel contamination. The experiments consisted of sets of experiments where all parameters but one were kept constant and the effect of the varied parameter observed. The result of these experiments was the selection of a set of "optimal" washing parameters for SSM contaminated with gasoline and diesel.

Phase II Bench Scale Experiments

The next phase involved the use of the "optimal" parameters to investigate the removal effectiveness of soil washing on soils at varying levels of contamination. The "optimal" washing parameters were applied to all matrices of SSM prepared including the waste oil contaminated matrices.

The "optimal" conditions were applied to soils from actual UST sites from Ohio and New Jersey. Four site soils were used and the results compared to those obtained with the SSM.

Field Analytical Program

In support of the soil washing experiments, a field analytical program was developed to analyze soils for BTEX constituents. The description, results and conclusions of this program are included in this report.

TPH Procedure Investigation

Finally, an investigation of the laboratory procedures used to analyze TPH in soil was conducted. The method currently used by most laboratories is the Soxhlet extraction method. However, the Sonication extraction method has been found to be quicker, easier, and equally effective in extracting petroleum constituents from soil. The two methods were compared via multiple analysis of the same soil using both methods and statistical evaluation of the results are included in this report.

SECTION 2

CONCLUSIONS

1. The Phase I experiments indicated that very high removals of BTEX and TPH (>90%) were obtained when treating the SSM with soil washing. Various operating conditions were tested for their effect on the soil washing results. Table 1 summarizes the relative effect of the tested parameters on the SSM soil washing efficiency.

TABLE 1. RELATIVE EFFECT OF TESTED PARAMETERS ON SOIL WASHING EFFICIENCY OF SSM

Varied Parameter	Range	Effect On Contaminant Removal*	Effect On Particle Separation
Contact Time	10-30 min	0/+	+
Soaking Time	15-30 min	0	0
Soil/Washwater Ratio by mass	0.5-2	+	0
Rinsewater/Washwater ratio	3-10	0	0/+
Citrikleen Addition	0-0.7%	-	0
Temperature	13-82°C	0	0/+
0.13% CitriKleen/Temp.	13-82°C	+	0
0.5% Surfactant/Temp.	24-49°C	0/+	+

* (+) = improvement, (0) = no effect, (-) = negative effect

NOTE - Rating system based on an increasing value of the parameter.

The high removals were, for the most part, independent of the washing conditions evaluated. It was also observed that most parameters, except for soil/washwater ratio and contact time, did not change the effectiveness of the separation of the soil particles into the various sieve fractions.

The results also indicated that the addition of CitriKleen actually decreased the contaminant removal efficiency of the soil washing process. This may be attributed to enhanced adsorption of contaminants onto the soil matrix with increased CitriKleen concentration.

2. The "optimal" parameters for washing the SSM, as determined by the Phase I experiments, were as follows:

contact time	30 minutes
soil/washwater mass ratio	1:1
rinsewater/washwater mass ratio	3:1
washwater additives	none
washwater temperature	ambient

These parameters were the same for both gasoline and diesel contaminated SSM. The parameters were selected based on achieving high removals as cost-effectively as possible.

3. The Phase II SSM experiments indicated that the high removals of contaminants were independent of the initial concentration of petroleum contaminants in the SSM. Greater than 90% removals of BTEX and TPH were obtained for SSM containing gasoline, diesel, or waste oil at all concentrations.

4. The removals achieved using actual soils (Phase II) were significantly lower (50 to 90%) than the removals from the SSM (>90%) using the same washing conditions. The particle size distributions of the actual site soils show that these soils contained less fine material than the SSM. The washwater Total Suspended Solids (TSS) levels in SSM experiments were much higher (>23% or 230,000 mg/l) than the actual site soils (3 to 4% or 30,000 to 40,000 mg/l).

These results indicate that a major mechanism responsible for contaminant removal during washing of the SSM is particle separation. The majority of the contaminants seem to be adhered to the finer particles, and since these particles make up approximately 44% of the SSM matrix, removal of these particles assists the high removal of petroleum contamination. This would explain why the washing results were independent of most washing conditions which serve to enhance solubilization of the contaminants into the washwater. As long as the fines were effectively removed from the bulk matrix, high removals were obtained.

The removals obtained from the site soils were much lower than those obtained with the SSM. This may be due to the decreased amount of fines present in these soils. Since particle separation was a major contaminant removal mechanism during the washing process, high removals similar to the SSM matrix were not expected or obtained from these soils.

5. Comparison of the Soxhlet and Sonication extraction methods for TPH analysis of soils indicated that the results are statistically equivalent using either method. Since there are several advantages to using the Sonication method, including lower cost and quicker turn-around time, it may be desirable to substitute the Sonication method for the Soxhlet method.

6. The field program developed for analysis of benzene, toluene, ethylbenzene, and xylenes proved to be a useful tool for screening of soils and for quantification of contaminant concentration within an order of magnitude. However, the high detection limits obtained with the existing analytical equipment limited the potential use of this equipment to fully quantify soil concentrations in lieu of an off-site lab.

SECTION 3

RECOMMENDATIONS

The particle size distributions of the SSM allowed a full understanding of the effect of the particle removal mechanism during the washing process. The use of a synthetic matrix also provided a consistent scientific basis for experimental testing with highly reproducible results. However, to further characterize the other parameters which affect the solubility of the contaminants in the washwater, such as temperature and chemical additives, it is recommended that future soil washing work be conducted on soils with less fines than the SSM. This could incorporate the development of another synthetic matrix containing less fines, or actual sandy soils could be used.

A great asset of the SSM was the homogeneity of the matrix which produced good reproducibility of the experiments. Actual soils are inherently less homogeneous that a synthetic matrix. It is recommended that for future work conducted on site soils, an attempt should be made to homogenize the soils prior to testing. This may be accomplished by mixing contaminated soils in the EPA Soils Blending facility prior to testing.

The experimental procedures and analytical protocols used were effective for the bench scale determination of soil washing effectiveness. It is recommended that pilot scale experiments be conducted and compared to the bench scale results to assess how representative the bench scale tests are for predicting larger scale results.

SECTION 4

MATERIALS AND METHODS

PURE PRODUCT DESCRIPTION

The gasoline, diesel, and waste crankcase oil used for the preparation of the respective SSM blends were collected from various sources within the vicinity of Edison, NJ. Gasoline and diesel were collected from five sources each. The waste crankcase oil was collected from three sources. Each product was stored in individual plastic gas cans for later use.

The sources of product were as follows:

Regular Unleaded Gasoline	- Shell, Citgo (Route 1), Sunoco, Amoco and McGas
Diesel	- Citgo (Route 1), Citgo (Route 27), McGas, Exxon and Hess
Waste Crankcase Oil	- Rollins Truck Leasing, Lease Line Truck Rentals and UPS

Equal volumes of product from the various sources were blended to obtain a total of 5 liters for each of the three petroleum product blends. The blending occurred immediately prior to the preparation of the respective SSM blends.

SYNTHETIC SOIL MATRIX CHARACTERIZATION

The basic formula for the SSM was determined by others (Traver, 1989) from an extensive review of Superfund sites and a review of the composition of eastern U.S. soils. The samples of SSM were collected from the mixture of clay, silt, sand, top soil and gravel prepared by others in two 6,800 kilograms (15,000 pound) batches.

A review of the existing soil characteristics was made and additional tests were conducted to further delineate the physical and chemical properties of the SSM. The tests, listed in Table 2, included particle size distribution, moisture retention curve, Atterberg limits, cation exchange capacity, base saturation, organic matter, chemical constituents, and mineralogy.

TABLE 2. INVESTIGATED CHARACTERISTICS OF SYNTHETIC SOIL MATRIX

- Particle Size Distribution
- Moisture Retention Curve
- Atterberg Limits
- Cation Exchange Capacity
- Base Saturation
- Organic Matter
- Chemical Constituents
- Mineralogy

Quantification and assessment of these specific properties will assist the technical community to understand the differences that may be observed between the performance of soil washing technology on the SSM and on actual UST site soils.

The particle size distribution (PSD) of the SSM was determined from mechanical and hydrometer analysis using the U.S. Department of Agriculture (USDA) classification system. The sand fraction was determined from sieve Nos. 10, 18, 35, 60, and 200. Silt and clay fractions were determined by hydrometer analysis. The Moisture-retention curve of the SSM sample was developed from determining moisture content at matric potentials of 0, 0.1, 0.3, 1, 3, and 1,500 kilopascals using a pressure plate apparatus. The moisture content was calculated from triplicate samples of oven dried soil (105°C) and soil at the various matrix potentials. Atterberg limits testing was conducted in accordance with the method outlined by the ASTM standards (ASTM D 4318-84). Phosphorous concentration of the SSM was determined by Bray P_1 and Bray P_2 methods. Exchangeable potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) were determined by extraction with neutral 1.0 N ammonium acetate and atomic absorption (AA) spectrometry. The pH was determined from a mass ratio of 1:1 soil to water solution. Base saturation was calculated from the cation exchange capacity (CEC) and AA analysis of individual cations. Organic matter content was determined by wet combustion using chromic acid digestion. The mineralogy of the SSM was evaluated with x-ray diffraction (XRD) analysis.

SYNTHETIC SOIL MATRIX BLENDING PROCEDURES

The specific blends of SSM required for the bench scale tests were prepared at the EPA Soil Blending Facility located in Edison, New Jersey. The soil was blended in a Marion Tilt-Tub batch mixer Model BPS 2436. The mixer was made of 316 Stainless Steel and had a 280 liter (10 cubic foot) mixing capacity. The 4 mixing blades were spaced along a rotating shaft situated along the cylindrical axis of the mixer. This shaft was driven by a 7.5 kilowatt (10 HP) explosion-proof electric motor. The mixer cavity had

a removable stainless steel cover with a fitting to allow for hook-up to a nitrogen source to provide a nitrogen blanket within the cavity.

The procedures used to prepare the SSM blends were essentially the same for each of the three petroleum products (gasoline, diesel, and waste oil). First, 91 kilograms (200 pounds) of dry SSM was mixed with 15 liters (4 gallons) of water to prepare a base SSM mix containing approximately 17 percent water content by mass. This moisture content was selected because past experience has shown that this is the optimal moisture content for physical handling of the SSM. Low, medium and high concentration SSM blends for each product were prepared by adding the product to the SSM in pre-measured doses as determined by the dose response tests (discussed in Section 6).

The low concentration was prepared first by adding the product to the wetted soil (91 kilograms of soil, dry weight) and allowing to mix for 15 minutes with a nitrogen blanket applied. At the completion of mixing, 23 kilograms (50 pounds) of soil (wet weight) was removed, placed into a 19 liter (5 gallon) pail and sealed. The second dose was added to the remaining soil (approximately 68 kilograms of soil, dry weight) and mixed for 15 minutes with a nitrogen blanket applied. Again, 23 kilograms (50 pounds) of soil was removed, placed in 19 liter (5 gallon) pails and sealed. The final dose was added to the 45 kilograms remaining (100 pounds) of soil and mixing commenced as before. All remaining soil was placed in pails and sealed. The individual doses of each product are provided in Table 3.

TABLE 3. PURE PRODUCT DOSES DURING THE SSM BLENDING OPERATIONS

Blend No. (EPA SSM No.)	Product	Approximate Soil Weight (kg dry wt.)	Product Added in Sequence	Quantity of SSM Blend Removed (kg)
1 (7)	Gasoline	91	120 ml	23
2 (8)	"	68	1290 ml	23
3 (9)	"	45	2150 ml	41
4 (10)	Diesel	91	800 ml	23
5 (11)	"	68	810 ml	23
6 (12)	"	45	1810 ml	41
7 (13)	Waste Oil	91	635 g	23
8 (14)	"	68	635 g	23
9 (15)	"	45	1451.5 g	45

The soils were prepared in this manner to minimize preparation of excess soils (which would later require off-site disposal). It was determined that about 23 kilograms (50 pounds) of each soil blend would be required, but the minimum efficient capacity of the blending facility was 45 kilograms (100 pounds) of soil for any one batch. By starting with 45 kilograms (200 pounds) of soil and preparing the batches of soils sequentially, a minimum of excess soil was prepared while always containing at least 95 kilograms (100 pounds) of soil in the blender.

While placing the soil blends into pails, samples were collected from each blend in duplicate for laboratory analysis. Samples were also collected from the clean wet SSM in duplicate. The analyses of the soils was conducted by the CDM Laboratory and the parameters analyzed included:

- o total petroleum hydrocarbons (TPH)
- o polyaromatic hydrocarbons (PAHs)
- o benzene, toluene, ethylbenzene and xylenes (BTEX)
- o metals (sum of lead, cadmium and zinc)
- o total organic carbon (TOC)

Analysis for TPH, PAH and BTEX were conducted using methods 907/418.1, 625/8270 and 624/8240 respectively. Although the analyses for benzene, toluene, ethylbenzene and the three xylene isomers, ortho-, meta-, and para-, were conducted separately, the results were summed and presented as a single parameter, which throughout this report, are referred to as BTEX. Metals were also analyzed separately and summed as a single parameter. Cadmium and zinc analyses were performed using method 6010. The lead analysis was performed using method 7421. TOC analyses was performed using two different methods depending on the phase of the sample. Liquid samples were analyzed using method 9060. This method, however, is not directly applicable to soil samples. The method used for this analysis is adapted from the determination of organic carbon in soils as presented in the report "Evaluation of Small Scale Retardation Tests for BTX in Groundwater PACE Report No. 87-3, prepared for Environment (PACE), the American Petroleum Institute (API) and University of Waterloo. The method consists of treatment of the soil with sulfuric acid to eliminate carbonates. The treated soil is rinsed with reagent water and an aliquot of the prepared soil sample is placed in a combustion furnace with an oxygen purge. The carbon present in the soil is converted to carbon dioxide which is detected by a non-dispersive infrared detector. The signal is compared to that of TOC standards based on Potassium Hydrogen Phthalate. The instrument used for this analysis was a Xertex/Dohrmann Total Organic Carbon system.

Four samples were also collected from the medium diesel batch from within the mixer at different locations to try to determine the extent of homogenization during the blending process.

The level of worker health and safety protection used was level C for the gasoline blends and level D for the diesel and waste oil blends. The blending facility is equipped with an overhead ventilation fan which was used for the gasoline and diesel blends, but not required for the waste oil

blends. An HNu photoionization meter was used during the blending activities. Readings were as follows:

gasoline	0-10 ppm in general blending area 100 ppm at open mixer
diesel	0-25 ppm at open mixer
waste oil	0-2 ppm at open mixer

The blending facility was originally designed to prepare large batches of SSM. Certain problems were encountered in preparing the small batches required for the bench scale tests. Mixing efficiency decreased during the blending of the high concentration gasoline and diesel blends. Soil built up on the sides of the mixer and on the blades with a small quantity of free product found at the bottom of the mixer. After about eight minutes, the mixer was stopped and the soil was manually scraped from the sides and blades. Mixing was then resumed for the remainder of the 15 minute mixing period. For all of the waste oil blends, mixing efficiency was decreased due to the high viscosity of the oil. The mixer was periodically stopped to scrape the sides and paddles to redistribute the soil for more efficient mixing.

Following the blending of the gasoline and diesel high concentration blends, the mixer was decontaminated by scraping the remaining soil from the sides of the mixer followed by a high pressure water spray and towel wiping. Decontamination following the waste oil high concentration blends consisted of cleaning the mixer by scraping the sides and washing with detergent, which was then followed by a high pressure water wash.

SECTION 5

EXPERIMENTAL PROCEDURES

BENCH SCALE SOIL WASHING STANDARD OPERATING PROCEDURES

This section describes the Bench Scale Soil Washing Standard Operating Procedure used for all bench scale experiments. The procedures were field developed specifically for this project. A general description of the procedures and equipment used is provided followed by a step by step protocol.

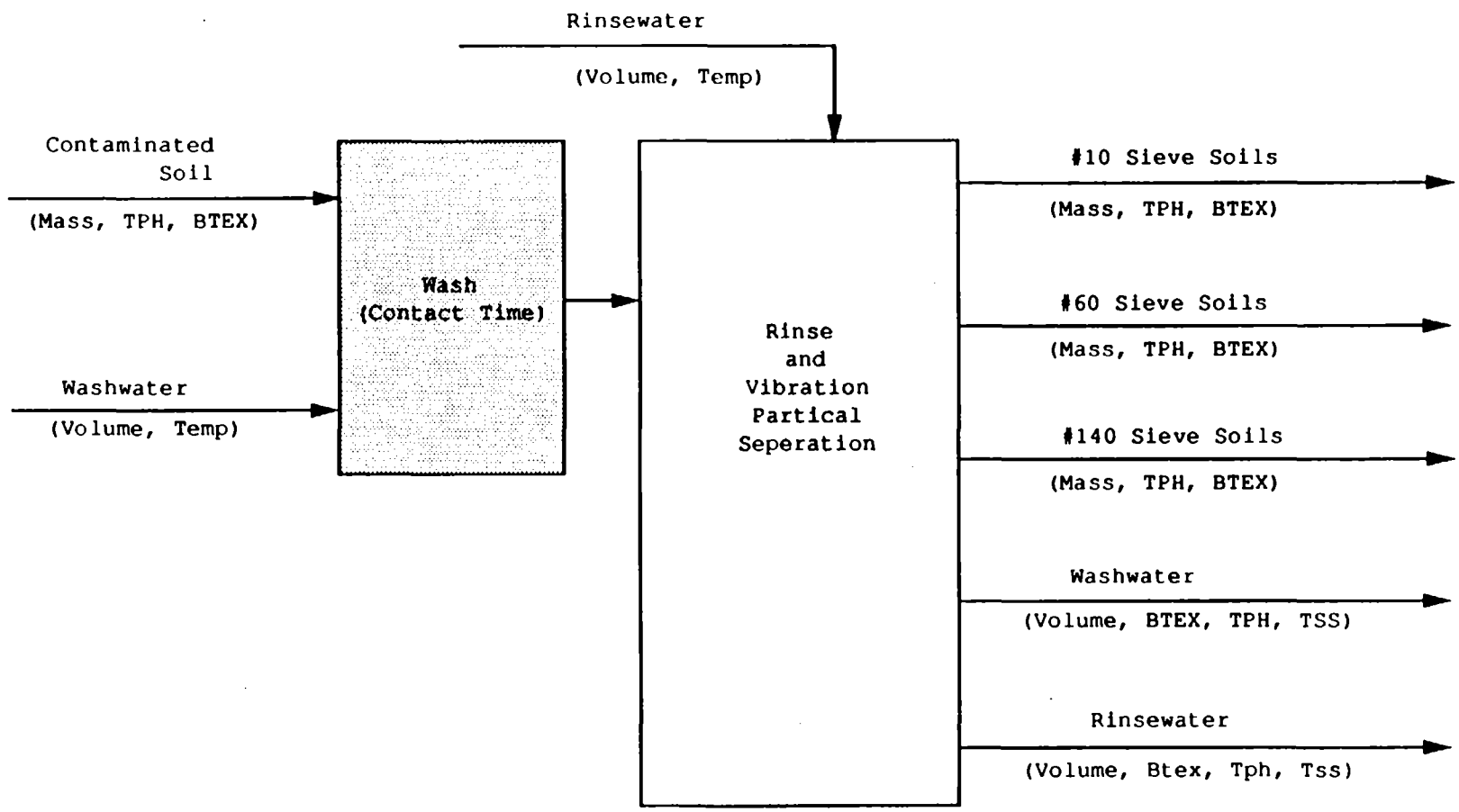
The soil washing process used for the bench scale studies, as shown in Figure 2, consisted of initially contacting the contaminated soil with a washing solution for a set period of time, and then separating out the soil particles while rinsing with water. Low frequency vibration was used to assist with particle separation. Soil was collected on three sieves of decreasing pore size (U.S. Standard Sieve Numbers 10, 60 and 140) with the soil fines passing with the wash solution and rinse water. Samples were collected of the soil contained on the individual sieves, the wash water and the rinse water.

Several experiments were conducted to determine the optimum process conditions for the bench scale studies by varying several operation parameters. The objectives for selection of the operation parameters were to minimize the quantities of washwater and rinsewater used while obtaining maximum contaminant removal. Once the optimum conditions were selected, they were used for the remaining experiments. To assure data quality, several quality control measures were performed including duplicates, field blanks, and experiment replicates.

The following parameters were varied to determine optimum operating conditions:

- Soil-Washwater contact time
- Washwater additive
- Washwater additive concentration
- Washwater temperature
- Soil/Washwater mass ratio
- Washwater/Rinsewater mass ratio

The mass of soil used for each experiment was 1.4 kilograms. This mass was chosen to allow for enough soil volume to remain on the individual sieves for subsequent sampling.



Note: Items In Italics Are Parameters Which Were Measured For Each Experiment.

Figure 2. Bench scale soil washing experiment schematic.

The soil washing step took place on a shaker table. The soil and washwater were combined in a 9 liters (2-gallon) glass container, sealed, strapped to the shaker table with bungi cords, and allowed to shake for the predetermined amount of time. The stroke and frequency of the shaker table was 4 centimeters (1.6 inches) and 4 Hertz respectively.

Once the washing step was completed, the soil-washwater mixture was transferred to a wet sieve unit for the particle separation and rinsing steps. The unit used for these experiments was the Gilson Wet-Vac Model WV-1. The wet sieve unit is equipped with three 31 centimeter (12 inch) diameter sieves stacked vertically and has a cover spray system utilizing a rotating bar with six spray nozzles to rinse the material on the sieves. The unit has an adjustable electromagnetic vibration option, which was utilized during the experiments. With the variable transformer (rheostat) set at 100%, the frequency and stroke of vibration was 60 hertz and approximately 0.5 millimeters (0.02 inch) respectively (based on correspondence with Gilson technical representative).

The unit is equipped with a vacuum water recycle system, however this was not utilized for the work performed here since the experiments were designed to simulate full scale operation. The vacuum was disconnected by simply unplugging the vacuum unit.

To allow for better control of the influent and effluent streams to and from the sieves, the recycle holding tank was disconnected from the system. This was accomplished by connecting an influent hose directly to the influent side of the water pump and also disconnecting the discharge hose from the bottom of the sieve well and attaching a separate effluent hose to allow drainage to be collected in buckets. This allowed for more accurate measurement of the respective streams. The pumping rate was measured to be approximately 110 milliliters per second.

Upon completion of the washing and rinsing steps, five distinct fractions remained which were sampled for analysis: #10 sieve soils (>2 mm), #60 sieve soils (0.25-2mm), #140 sieve soils (0.106-0.25 mm), washwater, and rinsewater. Samples of #10 and #60 soils and washwater were collected for analysis from each experiment. Occasional samples of #140 soil and rinsewater were also collected for analysis.

Samples were placed in appropriately labeled glass or plastic jars, with preservative if required, and submitted to the CDM Laboratory for analysis. Laboratory analyses conducted include TPH, BTEX, metals (sum of lead, cadmium and zinc), TOC, PAHs and COD. Holding times and sampling procedures as outlined in the QAPP, were strictly adhered to.

Following collection of the washwater and rinsewater for CDM Lab analyses, additional samples were collected for Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD) analyses in the field on the respective waters. TSS analysis was performed using a Millipore Pressure Filter with 0.45 micron filters. A pressure filter was used (instead of a vacuum filter) to minimize loss of volatiles in the filtrate. The filtrate was used for the COD test. HACH Co. COD digestion vials were

used for the COD analysis with a Spectronic 20 analyzer for absorbance determination.

Standard Operating Procedure

Below is a step-by-step standard operating procedure for the bench scale tests. Figure 3 is a schematic of the procedure, and the numbered steps in the figure correspond to the steps below.

1. Decontaminate the following equipment: sieve trays, stainless steel bowls and other sampling implements, graduated cylinders, washwater/rinsewater collection buckets, and pressure filter apparatus by rinsing with water, followed by a methanol rinse, then a final water rinse.

2. Bring washwater to the temperature required for the experiment.

3. Prepare the appropriate quantities of washwater and additive in a graduated cylinder.

4. Weigh out 1.4 kg of contaminated soil in a glass container.

5. Combine soil and washwater in the glass container, cover, place on shaker table and secure with bungi cords.

6. Set timer to 30 minutes or other predetermined time period and begin shaking (washing).

7. Bring rinsewater to the temperature required for the experiment.

8. Measure appropriate quantity of rinsewater in a bucket or a large graduated cylinder.

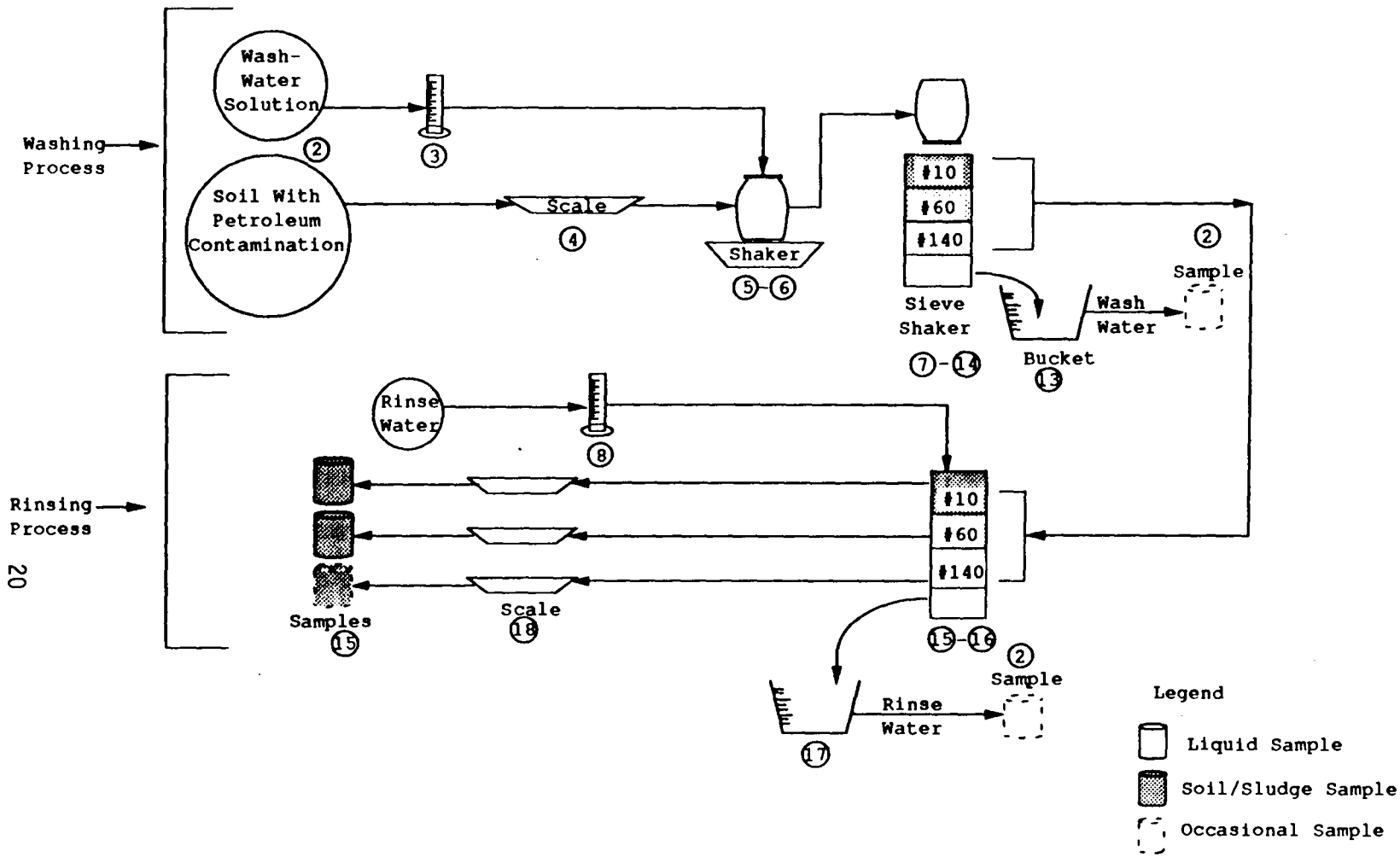
9. Weigh the three decontaminated sieves (No. 10, 60, and 140) while they are still wet to obtain a wet tare weight for each.

10. Situate the three sieves on the Wet Sieve unit with the cover spray piece in the up position. Fill influent hose with water to prime the pump (approximately 200 milliliters) and place in rinsewater container. Ready two decontaminated graduated buckets for washwater and rinsewater collection. Drain effluent hose.

11. Prepare sample jars and sampling equipment.

12. At end of the shaking period, remove the glass container from the shaker table. Measure temperature of the washwater.

13. Swirl container to resuspend solids and pour over sieves (make sure that effluent hose is secured in washwater collection bucket to avoid spillage). Rinse container with 100 milliliters of water and pour over sieves. Manually break up any mud balls remaining from the shaking step with a decontaminated implement such as a spoon and



Note: Numbers correspond to steps in the standard operating procedure

Figure 3. Soil washing standard operating procedure.

distribute materials over the surface of the sieve. Close the wet sieve unit by positioning the cover spray over the sieves and locking in place. Note: Perform these actions as quickly as possible to avoid unnecessary loss of volatiles.

14. Start vibration at 100 percent. Collect washwater in the washwater bucket until no more water can be recovered. Place effluent hose into rinsewater collection bucket.

15. Start the rinse step by turning the water pump on while leaving on the vibration. Continue until water has reached the bottom of the container and immediately turn the water pump off. Do not run the pump dry.

16. Leave vibration on for one additional minute. Turn vibration off and allow to drain for another 4 minutes.

17. Measure washwater and rinsewater volumes. Collect the respective washwater and rinsewater samples. Also collect an additional 250 milliliters of each water fraction for TSS and COD field analysis.

18. After the sieves have drained for the 4 minute period, remove each sieve and weigh. After weighing, collect the soil samples from the respective sieves for analysis of BTEX, TPH, etc.

19. Properly dispose of remaining soil and water fractions.

20. Perform TSS and COD analyses on the washwater and rinsewater.

FIELD ANALYTICAL PROGRAM

As part of this work assignment, a field analytical program was developed to analyze soils for benzene (B), toluene (T), ethylbenzene (E), and ortho-, meta-, and para-xylenes (X). This section contains a description of the field analytical program employed during the soil washing project at the EPA test site in Edison, N.J.

The analytical equipment used was supplied by EPA RREL and consisted of an HNu 321 gas chromatograph with a photoionization detector and a Spectra-Physics SP-4270 integrator.

The field analysis of soil samples was based on the EPA method 8240. This method requires methanol extraction of the soil to be analyzed and GC (gas chromatograph) analysis of the extract. All extracts were analyzed through injection into the GC equipped with a 8′ x 1/8" stainless steel column packed with GP 5% SP-1200/1.75% Bentone 34 on 100/120 Supelcoport at an oven temperature of 105°C and a photoionization detector (PID) operating at 202°C.

Each of the BTEX compounds were identified through comparison of peak retention times on the chromatographs to known standards. The retention times for each compound and the GC conditions are shown in Table 4.

TABLE 4. GC RETENTION TIMES FOR BTEX COMPOUNDS

Compound	Retention Time (min) Oven Temp = 105°C	Oven Temp = 80°C
Benzene	3.2	5.0
Toluene	5.2	9.8
Ethylbenzene	8.6	18.4
p-Xylene	9.9	20.6
m-Xylene	9.9	22.1
o-Xylene	11.3	25.5

NOTES: Operating conditions on HNu 321 include use of 8'x1/8" stainless steel column packed with GP 5% SP 1200/1.75% Bentone 34 on 100/120 Supelcoport. PID operating temperature was 202°C.

Total run time for all gasoline constituents to elute through the column was about 1 hour at 105°C oven temperature and 2 hours at 80°C.

A stock standard solution (supplied by Supelco) of 200 micrograms per milliliter of each of the six BTEX compounds was prepared in high grade methanol to create a series of standard concentration solutions. These standards included a 2 ppm, 20 ppm, 50 ppm, 100 ppm, and 150 ppm BTEX concentration. These various standard solutions were injected into the HNu 321 in duplicate and the calibration curve was developed from the resulting chromatographs. A response factor for each analyte was obtained from the ratio of the known standard concentration injected, to the area under the peak as recorded by the Spectra-Physics SP-4270 integrator. These response factors were then used to determine the BTEX concentrations for all samples.

It should be noted that para- and meta-xylene, at higher concentrations (i.e., >50 ppm), despite eluting as individual peaks, could not be resolved individually with the integrator. In developing the calibration curve, para- and meta-xylene were identified as one peak and one response factor was calculated. Where the isomeric peaks were resolved individually, the concentration was calculated by multiplying the response factor by the summation of the two reported peak areas.

A review of the initial calibration curve determined that the chromatograms for the 2 ppm standard did not depict adequate resolution of the BTEX peaks. Therefore standards of 5 ppm and 10 ppm were created to establish a lower concentration range and detection limits for the field analytical program. Standard injections were made at the beginning of each day to serve as a baseline for sample injections. If the calculated

concentrations for benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene were not within +/- 15 percent of the injected concentration then a second injection was made. If these concentrations were not within the criteria specified then new standard solutions were prepared and the above process was repeated.

The HNu 321 was set at the following conditions:

- o Carrier gas (Grade 5 Nitrogen) - flow A - 12 milliliters per minute at 124 kilopascals
- o Input - Detector A - low
  Output - Detector A - 1024
- o Nitrogen tank regulator - 276 kilopascals

The Spectra-Physics SP-4270 was set at the following conditions:

- o Attenuation - 1024
- o Chart speed - 0.5 centimeters per minute

All soil samples were refrigerated until ready for analysis. Sample preparation for field analysis consisted of weighing approximately two grams of soil, placing the soil into a 15-milliliter vial, and adding 5 milliliters of high grade methanol as the extraction solvent. The vial was mixed for five minutes using a mechanical shaker to ensure sufficient contact of the soil sample with the methanol. The vial was subsequently centrifuged to separate the liquid and solid phases. An aliquot of 1 to 4 microliters of liquid sample, dependent on the concentration expected, was injected into the GC.

Due to problems with the integrator, the concentrations of BTEX compounds were hand-calculated from the areas identified by the integrator with the respective response factors determined from the calibration curves. The concentration of BTEX compounds calculated represented the concentration in the liquid extract phase. To determine the concentration in the soil, the liquid phase concentration was multiplied by the volume of the methanol used as the extraction solvent divided by the mass of soil sample, as shown in Figure 4.

$$\text{Conc. in Soil (mg/kg)} = \text{Conc. in Extract (mg/l)} \times \text{Amount of Solvent in Extract (l) (usually 0.005 l)} \times \frac{1}{\text{Mass of Sample (kg) (usually 0.002 kg)}}$$

Figure 4. Soil BTEX Concentration Equation.

Standard Operating Procedure

Below is a step-by-step standard operating procedure used for the field analysis of the BTEX compounds in soil.

1. Change the septum on injection port A of the HNu 321 each day.

2. Lower the temperature of the oven, which is increased to 150°C after each day of analysis to purge the column of heavier gasoline constituents, to 105°C and turn the PID lamp on.

3. All syringes prior to and after each sample injection were decontaminated with methanol. This was performed by extracting 5 microliters of the methanol and ejecting it into a waste container and then flushing the barrel of the syringe several times with additional methanol. Typically, methanol blanks were performed on a daily basis or when deemed appropriate following the analysis of a highly contaminated sample.

4. Inject 1 microliter of a BTEX standard (standard runs took approximately 15 minutes to completely elute). If the calculated concentrations exceeded the $\pm$15 percent factor then a second BTEX standard was injected.

5. A 5 microliter liquid tight syringe was utilized to extract 5 microliters of sample into the syringe and eject into a waste container. This procedure was then repeated.

6. Depending on the expected concentration of the sample, 1 to 4 microliters of liquid sample was extracted and then injected into port A. The syringe was pushed into the injection port through the septum and the sample was injected.

7. The syringe was immediately removed from the injection port and the "INJA" button was depressed on the integrator keyboard to begin the run. The syringe was then decontaminated with methanol as discussed in step 3.

8. Following the completion of a sampling run (approximately 60 minutes for soil containing gasoline contamination), a hard copy printout of the chromatogram was obtained from the SP-4270 integrator.

9. All samples injected were logged into a notebook which also contained the chromatograms. Daily observations were recorded in a field log book.

10. At the end of each sampling day the oven temperature was increased to 150°C and the detector was turned off.

11. All samples prior to and after analysis were stored in the refrigerator on site.

FIELD TSS & COD PROCEDURES

Field analyses for TSS and COD were performed on the washwater and rinsewater streams collected from the bench scale tests. This section contains a summary of the procedures used. The TSS analysis was required to characterize the washwater and to calculate a soil material balance during the experiment. The COD was used to obtain a quick field-determined characterization of the level of organics transferred into the washwater and rinsewater. The TSS and COD data are reported in Appendices C and D.

Total Suspended Solids Procedure

The total suspended solids analyses were conducted using a pressure filter to minimize loss of volatiles during the filtration process. This was an important requirement because the filtrate from the filtration process was used for COD analysis, which is further described in the following section.

The sample was first shaken to re-suspend any solids that may have settled during storage. The sample was then allowed to sit for 15 minutes to allow the heavier soil fines to settle. During this period, a piece of 142 millimeter diameter 0.45 micron pore size filter paper (Millipore No. HAWP 142) was labeled and weighed. The filter apparatus, Millipore Hazardous Waste Filtration System Model YT 30 142 HW, was then assembled with the filter in place and a sample vial prepared for the filtrate. Following the 15 minute wait period, 95 to 100 millimeters of sample was poured into a graduate cylinder and the volume recorded. This sample volume was then poured into the top of the pressure filter, sealed, and pressurized to a maximum of 483 kilopascals (70 pounds per square inch). The first 5 to 10 milliliters of filtrate was discarded, then approximately 40 milliliters was collected in a sample vial with the remainder of the filtrate discarded.

The apparatus was then disassembled and the filter paper with sludge removed and placed into an oven to dry. The filter paper and sludge was allowed to dry for a minimum of 2 hours. After the material was dried, the filter was removed and allowed to cool, and then weighed. TSS was calculated by subtracting the mass of the tared filter paper from the mass of the dried solids and filter paper then dividing by the initial volume of sample.

$$\text{TSS (mg/l)} = \frac{\text{(mass of filter + sludge) - tared filter mass (mg)}}{\text{volume of sample (liters)}}$$

Figure 5. TSS Concentration Equation.

Chemical Oxygen Demand Procedure

COD digestion was performed on the filtrates using HACH Co. COD vials and reactor. Two ranges of COD vials were available, 0-1500 ppm and 0-150

ppm. Initially, the 0-1500 ppm range was used for the washwater and the 0-150 ppm range was used for the rinsewater. Since the COD analysis method used was based on light transmittance, the samples required filtration prior to analysis. The filtrate from the TSS analyses were used for these analyses.

The samples were digested (according to the directions provided by HACH) by pipetting 2 milliliters of sample into the vial, shaken to mix the reactants with the sample, and placed in the COD reactor. The HACH COD Reactor is factory preset to 150°C. The vials were kept in the reactor for a minimum of 2 hours to allow the reaction to reach completion and were then removed and allowed to cool.

The vial was then placed in a Baush & Lomb Spectronic 20 spectrometer to measure the transmittance of light at the wavelength required by the method. The wavelengths used were 620 nanometers for the 0-1500 ppm vials and 420 nm for the 0-150 ppm vials. The percent transmittance was compared to a chart supplied by Bausch and Lomb to convert to ppm COD. When the particular concentration was out of range, the sample was diluted and re-digested or the next higher (or lower) concentration range vial was used for re-digestion of the sample to obtain a more accurate reading depending upon the particular circumstance.

SECTION 6

RESULTS AND DISCUSSION

SYNTHETIC SOIL MATRIX (SSM) BLENDING

SSM Characterization Test Results

The SSM was characterized in accordance with the test procedures outlined in Section 4. The tests conducted include:

- o particle size distribution
- o moisture content
- o Atterberg Limits
- o cation exchange capacity
- o pH
- o base saturation
- o x-ray fluorescence
- o x-ray diffraction

The test results indicate that the SSM is composed of 60 percent sand, 19 percent silt and 21 percent clay as determined by particle size distribution analysis (Table 5 and Figure 6).

TABLE 5. SYNTHETIC SOIL MATRIX PARTICLE SIZE DISTRIBUTION (USDA)

Soil Fraction	Percentage Distribution	
	USDA Method	USCS Method
Gravel	--	--
Sand (Total)	60.0	58
Very Coarse (1 to 2 mm)	16.0	
Coarse (0.5 to 1 mm)	8.8	
Medium (0.25 to 0.5 mm)	11.7	
Fine (0.1 to 0.25 mm)	23.5	
Silt	19.0	15.2
Clay	21.0	26.8

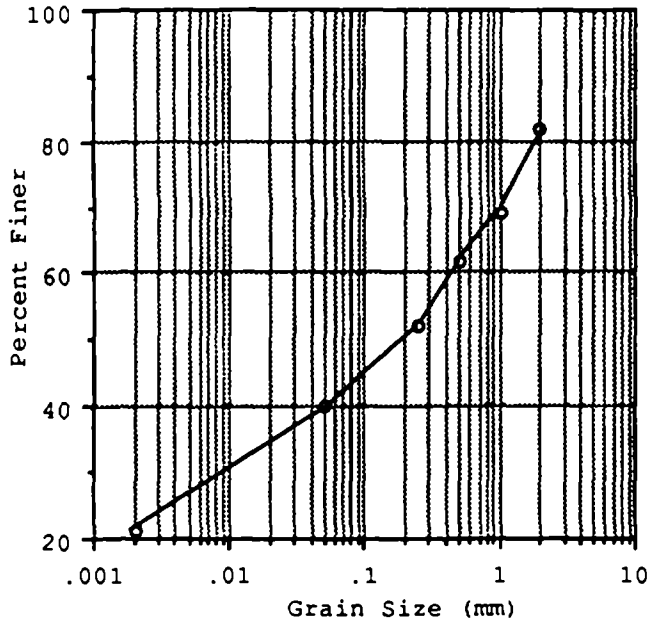


Figure 6. SSM particle size distribution plot - USDA method.

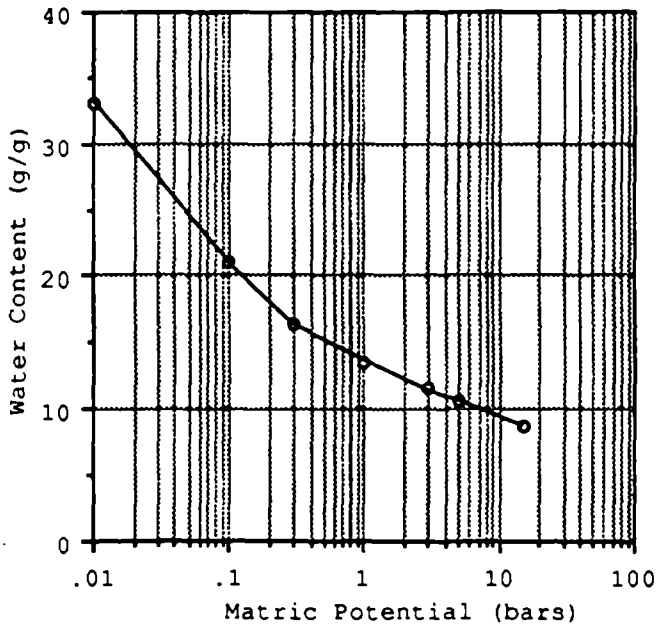


Figure 7. SSM moisture retention plot.

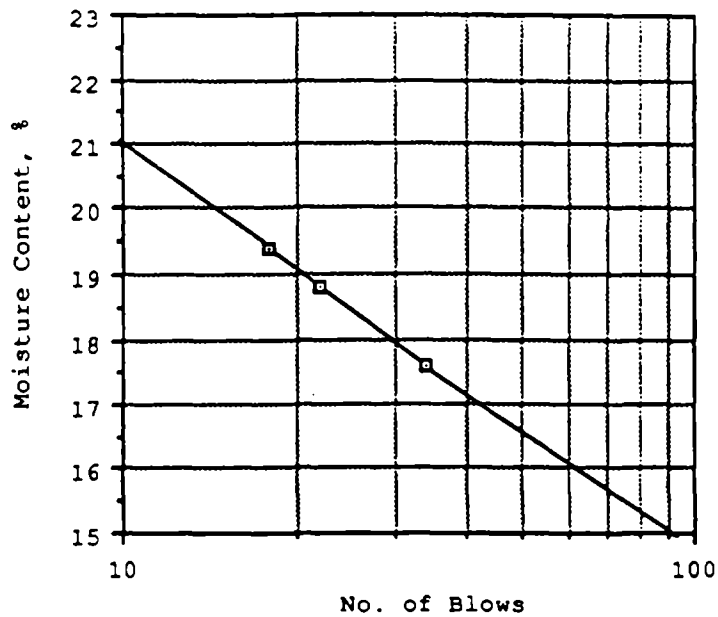


Figure 8. Liquid limit determination.

Based on this composition the SSM would be classified (USDA) as having a sandy clay loam texture. Particle size distribution data may be used to estimate hydraulic properties (Mishra et al., 1989), residual saturation (Hoag and Marley, 1986), capillary movement, bulk density, and surface area of the soil prior to more extensive analyses.

The moisture content of the SSM ranged from 33.1 percent at saturation (0 pacals) to 8.7 percent at the permanent wilting point (1,500 kilopascals). The moisture content at field capacity (10 pascals) was 21.0 percent. The moisture-retention curve (Figure 7), which is a measurement of the degree to which moisture is held within a soil matrix and was developed from the moisture content data, was indicative of a finer textured soil. The moisture retention curve is a plot of the matric potential (which is the applied pressure force) versus the water content remaining in the soil. The moisture content data, can be used to evaluate moisture and chemical characteristics of the SSM. For example, the amount of soil water that can be extracted from the SSM under typical environmental conditions (0 to 1,500 kilopascals) will be 24.4 percent.

The remaining soil water is considered as "unavailable", which can be removed by artificially induced vacuums or pressures. Some similarities exist between the moisture content and residual saturation of petroleum hydrocarbons in the soil. Generally, stronger competitive absorption of water for soil occurs and displaces nonionic organic chemicals that are present in petroleum in petroleum hydrocarbons (Chiou et al, 1989). Residual saturation will be dependent on moisture content and decrease with increasing moisture.

The SSM has a plastic limit (PL) of 15 percent, liquid limit of 19 percent and plasticity index (PI) of 4. A plot of these results on the Plasticity Chart (Figure 8) indicated that the SSM is a CL-ML material (inorganic silt or clay) using the Unified Soil Classification System (USCS). The activity of the clay material, which was calculated from Atterberg Limit tests and a clay content of 26.8, was 0.6 using the formula: A = PL/%Clay

Atterberg limits testing indicated that the clay fraction of the SSM was inactive, which means that it will swell very little volumetrically with addition of water. The estimated swell or heave of the SSM was only 1 percent of the mineral's original volume. This data may indicate the relative absence of swelling clays such as montmorillinite in the SSM.

Analysis of the SSM for concentrations of various exchangeable ions indicated that phosphorus was moderate, potassium was low, and both magnesium and calcium were very high (Table 6).

TABLE 6. SYNTHETIC SOIL MATRIX CHEMICAL CHARACTERISTICS

PARAMETER	UNITS	VALUE
Organic Matter	%	1.3
pH	-	8
Cation Exchange Capacity (CEC)	meq/100g	21.7
Base Saturation	%	99
Ca		86.2
Mg		12.4
K		1.3
H		0
Available Phosphorus	ppm	
Weak Bray		20
$NaHCO_3$		31
Potassium	ppm	112
Magnesium	ppm	324
Calcium	ppm	3740

The pH of the SSM was 8.0. This pH value is generally the result of the presence of bases such as Ca^{2+} and Mg^{2+} ions. Such bases may be readily removed with addition of water and/or other ions which may displace the Ca^{2+} and Mg^{2+} ions and thus lower the pH. The pH of the SSM will in part affect the CEC of the pH dependent fraction of the soil (primarily organic matter), and the adsorption of metals. Mobility of most metals such as lead (Pb) will be minimal as long as the SSM pH exceeds a value of 6.5.

Cations exchange capacity of the SSM was 21.7 milliequivalents per 100 grams. This CEC value is somewhat typical of soil with a texture finer than a sandy loam or with elevated organic carbon content. Determination of CEC is essential in the evaluation of the fate and transport of charged ionic species, but will have little influence on the non-ionic organic compounds present in petroleum hydrocarbons.

The base saturation of the SSM was 99.9 percent, and was dominated by the Ca^{2+} ion (86.2 percent). Addition of water or any leaching solution should considerably reduce the base saturation of the SSM as the Ca^{2+} is replaced by H^{+} and Al^{3+} ions.

The organic matter content of the SSM was 1.3 percent, which is equivalent to an Organic Carbon (C) content of 0.76 percent (using a conversion factor of 1.724; Nelson and Sommers, 1982). Organic matter content determination for soils high in inorganic C (carbonates) requires their removal prior to analysis. The organic matter fraction of the SSM will contribute to the CEC, but is, more importantly, the primary means by which nonionic organic compounds are bound to the soil media. A partitioning occurs in which the nonionic organic compounds are taken up into soil organic matter from the water (Chiou et al, 1989).

X-ray fluorescence (XRF) analysis of the SSM indicated that elevated Ca^{2+} and Mg^{2+} concentrations were present when compared to typical U.S. soils (Lindsay, 1979). Heavy metals such as cobalt (Co), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) were within the range of common soils (Tables 7 and 8).

TABLE 7. SYNTHETIC SOIL MATRIX X-RAY FLUORESCENCE ANALYSIS - MAJOR CONSTITUENTS

PARAMETER	SSM SAMPLE #1 (PPM)	SSM SAMPLE #2 (PPM)	COMMON RANGE* (PPM)
Silica Dioxide (SiO_2)	37.9	39.6	49-75
Calcium Oxide (CaO)	21.5	22.3	1-70
Aluminum Oxide (Al_2O_3)	7.85	8.1	2-57
Magnesium Oxide (MgO)	4.03	4.25	0.1-1.0
Magnetite (Fe_2O_3)	3.64	3.78	1-79
Potassium Monoxide (K_2O)	1.38	1.44	0-3.6
Titanium Dioxide (TiO_2)	0.44	0.45	0.2-1.7
Sodium Monoxide (Na_2O)	0.34	0.37	0-1.0
Phosphoric Acid (P_2O_5)	0.31	0.33	0-1.2
Manganese Oxide (MnO)	0.15	0.15	0-4.0
Barium Oxide (BaO)	0.03	0.04	0-0.3
Chlorine (Cl)	0.02	0.02	0-0.0009
Sulfur	<0.05	<0.05	0-1.0

* Lindsay (1979)

TABLE 8. SYNTHETIC SOIL MATRIX X-RAY FLUORESCENCE ANALYSIS - TRACE ELEMENTS

PARAMETER		SSM SAMPLE #1 (PPM)	SSM SAMPLE #2 (PPM)	COMMON RANGE* (PPM)
Strontium	(Sr)	369	390	50 - 1000
Zirconium	(Zr)	349	370	60 - 2000
Chromium	(Cr)	131	135	1 - 1000
Vanadium	(V)	57	58	20 - 500
Zinc	(Zn)	46	46	10 - 300
Rubidium	(Rb)	41	46	50 - 500
Ytterbium	(Y)	43	40	25 - 250
Wolfram	(W)	28	32	--
Lead	(Pb)	22	25	2 - 200
Nickel	(Ni)	14	15	5 - 500
Copper	(Cu)	12	14	2 - 100
Tin	(Sn)	<50	<50	2 - 200
Arsenic	(As)	<20	<20	1 - 50
Thallium	(Th)	<10	12	--
Molybdinum	(Mo)	<10	<10	0.2 - 5
Uranium	(U)	<10	<10	--
Niobium	(Nb)	<10	<10	--
Cobalt	(Co)	<10	<10	1 - 40

* Source: Based on Lindsay (1979).

X-ray diffraction (XRD) analysis indicated that the SSM was composed of 27 percent calcite, 27 percent quartz, 18 percent dolomite, 8 percent plagioclase feldspar, 8 percent potassium feldspar and a small percent of clays (Table 9).

TABLE 9. SYNTHETIC SOIL MATRIX X-RAY DIFFRACTION CLAY MINERALOGY

MINERAL	% BY WEIGHT*
Quartz	27
Calcite	27
Dolomite	18
Plagioclase feldspar	8
K-feldspar	8
Smectite/vermiculite	5*
Kaolinite	<5*
Mica/illite	--
Chlorite	--
Polygorskite/attapulgit	--
"Unidentified"	<5

* Estimated concentration. Quantification not possible due to low concentration of mineral.

The calcite and dolomite (45 percent), as determined by XRF, indicate the presence of a considerable amount of dolmitic limestone in the SSM. Comparison of the XRD data to the PSD data can be useful in evaluating the SSM. Sand content as determined by PSD was 60 percent of the SSM by weight, while quartz content was only 27 percent according to XRD analysis. The remainder of the sand fraction (33 percent) may include both of the feldspar minerals (16 percent) and the coarser fraction of the limestone (17 percent). The silt fraction (19 percent PSD) appears to be primarily limestone. The clay fraction (21 percent) is made up of some montmorillinitic and kaolinitic clays along with the finer limestone fraction. The XRD analysis only tentatively identified both montmorillinite and kaolinite.

Bench Scale Dose/Response Test

The purpose of the dose/response test was to determine the appropriate amounts of gasoline or diesel fuel which should be added to the SSM to obtain the desired concentration mixes. Various mixtures of SSM and gasoline or diesel were prepared and the soil analyzed for benzene, toluene (T), ethylbenzene (E) and xylenes (X) (the concentrations were summed and are henceforth referred to as BTEX) and total petroleum hydrocarbons (TPH).

The procedure used was to place approximately 500 grams of SSM into each of eight 500 milliliter glass wide mouth jars. Water was added to the jars to make a SSM mixture containing 20 percent water by mass. The water and soil were mixed by hand with metal laboratory spatulas until the soil was of even consistency throughout the jar. The gasoline or diesel was measured out volumetrically with pipets and poured into the jars. The jars were then mixed by hand for a period of five minutes. The jars were then capped and submitted to the lab for analysis of BTEX and TPH. The density of the gasoline and diesel were determined by weighing the contents of a 100 milliliter volumetric flask of both gasoline and diesel.

The result of the dose/response tests are shown in Table 10. The lab tests indicate that the soils reach a level of liquid saturation at about 23 percent liquid (both water and gas or diesel). The tests were conducted such that the soils were all prepared to a 20 percent water level. However, this limited the amount of gas or diesel which could be mixed into the soil mixture.

At 20 percent water, the highest achievable BTEX concentration was about 3,000 milligrams per kilogram. For diesel, at a water content of 20 percent, the highest TPH concentration was 60,000 milligrams per kilogram.

The dose/response curves are plotted in Figures 10 and 11. A linear regression of the data yielded the following relationships for dose/responses: $G=13.33(B)-375$ and $D=0.675\ (T) + 6268$ with correlation coefficients of 0.998 and 0.995 respectively. Where "G" is the gasoline concentration in milligrams per kilograms, "B" is the BTEX concentration in milligrams per kilogram, "D" is the diesel fuel concentration in milligrams per kilogram and "T" is the TPH concentration in milligrams per kilogram.

TABLE 10. SOIL WASHING DOSE/RESPONSE BENCH SCALE TESTS

Jar No.	Soil (g)	Water (ml)	Gasoline (ml)	Gasoline (mg)	Gasoline Concentration (mg/kg)	% Water	Lab Determined BTEX Concentration (mg/kg)	Lab Determined TPH Concentration (mg/kg)	Dose/Response Ratio*
1	486	100	4	2,964	6,100	21	406	NT	15.0
2	491	100	20	14,820	30,200	20	2,200	NT	13.7
3	635	100	50	37,050	58,300	16	4,420	390	13.2
4	506	100	10	7,410	14,600	20	1180 (1380)	NT	11.4
9	500	50	58	42,987	86,000	10	4,670	NT	18.4

Jar No.	Soil (g)	Water (ml)	Diesel (ml)	Diesel (mg)	Diesel Concentration (mg/kg)	% Water	Lab Determined BTEX Concentration (mg/kg)	Lab Determined TPH Concentration (mg/kg)	Dose/Response Ratio
5	511	100	4	6,200	6,200	20	NT	1,950	3.2
6	496	100	10	16,000	16,000	20	NT	13,300	1.2
7	510	100	20	31,000	31,000	20	NT	33,500	0.9
8	498	100	30	47,700	47,700	20	98.3	59,200 (67,700)	0.8

NOTES:

() - denotes duplicate analysis
NT - Not Tested
* - Dose/response ratio is the ratio of the petroleum additive concentration to the analyte concentration (gasoline concentration to lab determined BTEX concentration or diesel concentration to lab determined TPH concentration).

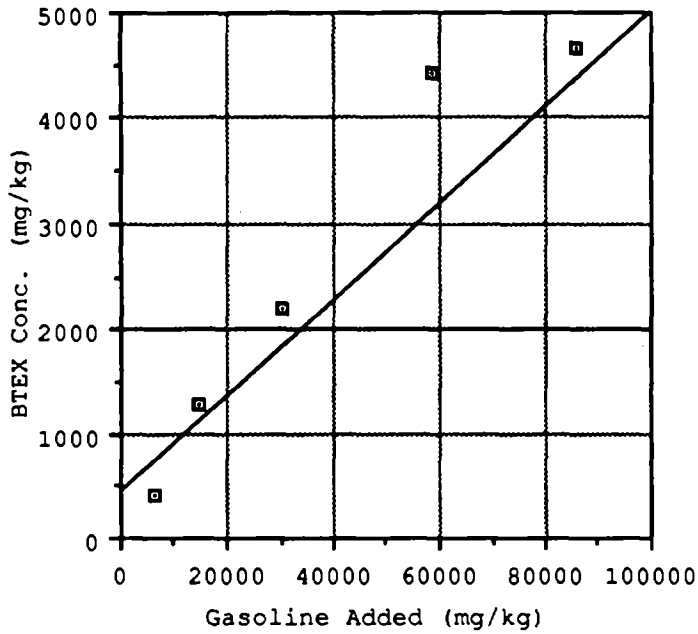


Figure 9. Dose/Response curve for gasoline

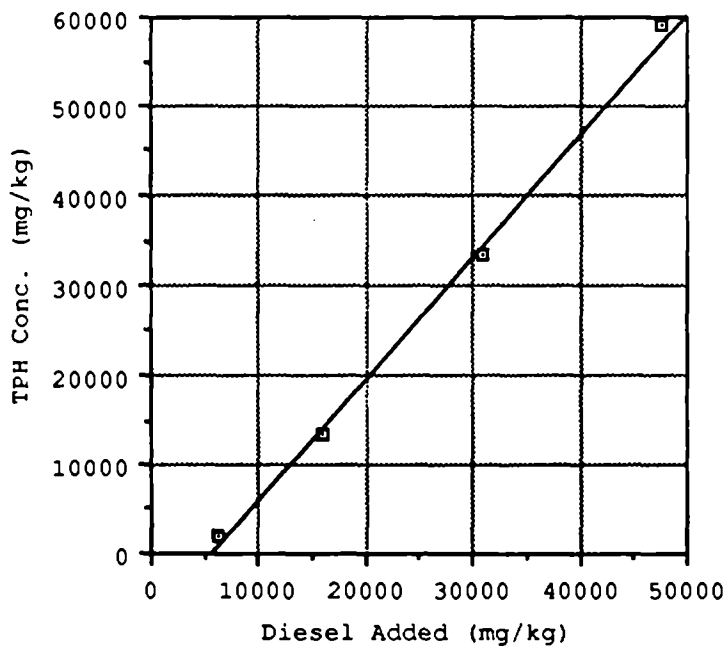


Figure 10. Dose/Resonse curve for diesel fuel

An additional experiment was conducted to determine if a higher level of BTEX could be achieved if a lower moisture content was used. In this experiment, a sample of soil was moistened to a 10 percent water content and then saturated with gasoline. The results, shown in Table 10 as "Jar 9", indicated that the BTEX content was increased to 4670 milligrams per kilogram.

Based on the previous gasoline concentration and diesel concentration calculations, estimates were made to determine the amount of gasoline and diesel fuel to add to the SSM to obtain the desired concentrations of BTEX and TPH for the bench scale experiments. The SSM blends were prepared in the EPA SSM Blending Facility in Edison, NJ in 23 kilogram (50 pound) batches for use in the bench scale soil washing experiments.

Full Scale SSM Blending Results

Based on the results of the bench scale dose/response tests, the appropriate "formulas" were determined for preparation of the full scale SSM blends. The blends were prepared in the EPA Soil Blending Facility in Edison, NJ.

All nine blends were sampled immediately upon preparation, and additionally prior to use. In total, all blends were sampled at least three times and analyzed for BTEX (for gasoline blends) and TPH (for diesel and waste oil blends). The average of the sampling results are presented in Table 11. The values presented in this table are the initial soil concentrations subsequently used to calculate the percent removals from the soils after the washing experiments.

TABLE 11. INITIAL CONCENTRATION OF NINE SSM BLENDS

SSM BLEND	CONCENTRATION (mg/kg)	
Low Gasoline	21	(BTEX)
Medium Gasoline	766	
High Gasoline	2067	
Low Diesel	917	(TPH)
Medium Diesel	1839	
High Diesel	18,425	
Low Waste Oil	1117	(TPH)
Medium Waste Oil	9327	
High Waste Oil	28,533	

NOTE: Above results are averages of several samples taken for each blend.

After the blending results were obtained, a comparison was made of the actual blending results to the predicted results from the bench scale dose/response tests. These results are presented in Table 12.

TABLE 12. COMPARISON OF BENCH SCALE TO ACTUAL DOES/RESPONSE TESTS

Blend	Concentration Goal* (mg/kg)	Actual Concentration (mg/kg)	Actual Concentration As Percentage of Goal
Low Gasoline	100 mg/kg BTEX	21 mg/kg	21
Med. Gasoline	1150	766	67
High Gasoline	3800	2067	54
Low Diesel	1000 mg/kg TPH	917 mg/kg	92
Med. Diesel	15,000	1,839	12
High Diesel	62,000	18,425	30

* As predicted by bench-scale dose/response tests.

As the table shows, the actual results were much lower that the predicted results. The full scale BTEX concentration was as low as only 21 percent of that predicted in the bench scale tests and TPH was as low as 12 percent of the predicted value. In other words, for any given amount of gasoline or diesel added to the soil, the actual BTEX or TPH results obtained in the soil blend was lower than that predicted by the dose/response tests.

These results may be explained by the fact that the mixing was much more vigorous in the full scale blending process than in the bench scale tests. Therefore, more volatiles may have been lost during the full scale blending process thus lowering the organic content in the SSM blends.

A test of the homogeneity of the SSM blending process was conducted by sampling the medium diesel blend six times and analyzing for TPH. The results, presented in Table 13, show that the mean TPH result was 2054 milligrams per kilograms with a standard deviation of 1024 milligrams per kilogram.

TABLE 13. HOMOGENEITY TEST FOR BLENDING OF MEDIUM DIESEL SSM

DUPLICATE NO.	TPH CONCENTRATION (mg/kg)
1	2120
2	1160
3	3300
4	570
5	2840
6	2320
Average	2052
Stand. Dev.	1024

Confidence Level*	Range
50 percent	1750-2350
90 percent	1200-2900

* Calculation based on Student-t test evaluation of data

The standard deviation of the samples was about 50 percent of the sample mean which indicates that the sampling results fell within a wide range. For example, according to these results, for any sample of the mixture taken, there is a 60 percent confidence level that the results will fall within the range of 1182 - 2922 milligrams per kilograms TPH and a 90 percent confidence level that the results fall within 362 - 3942 milligrams per kilograms.

PHASE I - DETERMINATION OF OPERATIONAL PARAMETERS

The objective of this phase of experimental work was to determine the optimal washing conditions for the high gasoline and high diesel SSM blends. The parameters which were varied and investigated include: contact time, soaking time, soil/washwater mass ratio, rinsewater/washwater mass ratio, addition of surfactant to washwater, addition of CitriKleen to washwater, and temperature of washwater.

Table 14 summarizes the ranges within the above parameters were varied.

TABLE 14. PARAMETERS INVESTIGATED IN SOIL WASHING EXPERIMENTS

Contact Time	10-30 min.
Soaking Time	15-30 min.
Soil/Washwater Mass Ratio	0.5-2
Rinsewater/Washwater Mass Ratio	3-10
Citrikleen Addition	0-0.7%
Washwater Temperature	55-180
0.13% CitriKleen/Temp.	55-180
0.5% Surfactant/Temp.	75-120

The selection of these experimental conditions were based on results of previous soil washing work (PEI Associates, Inc., 1988). All experiments were conducted for both diesel and gasoline SSMs and duplicates of each experiment were performed with results averaged.

Description of Varied Parameters

The contact time is the amount of time that the soil and washwater were allowed to shake together in the mixing jar as described as Step 6 of the Standard Operating Procedure. The contact time was varied within the range of 10 to 30 minutes. This parameter is important because in full scale operation, the larger the contact time required, the lower the possible hourly throughput. The goal of varying this parameter was to determine the minimum required contact time.

The soaking time is the amount of time that the soil and washwater were in contact together in the jar but not actively shaking. Active shaking (or mixing) in a full scale system would be energy intensive. Soaking time was investigated to determine the effectiveness of contact between the soil and washwater without actively shaking to promote mass transfer from the soil to the washwater.

The soil/washwater ratio is the mass ratio of the soil and washwater. A higher soil/washwater ratio would result in a lower volume of washwater to be treated. The goal of varying this parameter was to determine the highest ratio which would result in adequate removals. Similarly, the lower the rinsewater/washwater ratio, the less rinsewater in generated requiring further treatment.

CitriKleen, which is a biodegradable solvent, was used as a washwater additive to determine if it would enhance the removal of petroleum contamination. The additive was used in the washwater solution up to 0.7 percent by mass. The goal of varying this parameter was to see how much, if any, benefit was obtained by using this additive.

In general, petroleum compounds are more soluble in hot water than cold water. The washwater temperature was varied between 55 and 180°F to determine if enhanced removal was obtained with increased washwater temperature. The effect of temperature variation was also investigated in experiments using CitriKleen and surfactant additives.

Results of Experiments

A total of 67 experiments were performed on the gasoline and diesel spiked SSM, including duplicates and field blanks. Each experiment involved several analyses and/or measurements of the five resultant fractions (three soil fractions, washwater, and rinsewater). These measurements include: temperature, volume, mass, BTEX, TPH, TSS, and COD. The results of all measurements and analyses of Phase I experiments are shown in Appendix C.

Since a major mechanism of soil washing is separation of the fine particles from the bulk soil, the particle size distribution (which is an indicator of how well the particles were separated) was observed for each experiment. The SSM characterization test results in Section 6 describe the dry SSM particle size distribution. The closer the experimental distribution reached the dry distribution, the better the particle separation during the experiment.

For each set of experiments, a sensitivity analysis curve was generated to show the effect of varying the parameter while keeping all others constant. These curves for all experiments are found in Appendix A. Each sensitivity analysis curve has a corresponding curve which shows the effect of the varied parameter on the particle size distribution. These curves are found in Appendix B.

The effectiveness of soil washing on each experiment was evaluated by the percent removal of TPH or BTEX (Figure 11).

$$\text{Percent Removal} = \frac{(\text{Bulk soil conc.}) - (\text{Sieve Soil conc.})}{(\text{Bulk soil conc.})} \times 100$$

Figure 11. TPH or BTEX Percent Removal Equation.

The percent removal equation in Figure 11 uses the initial bulk soil concentration, rather than the initial concentrations on the individual sieves, as a basis for percent removal. This is done because it is not possible to separate wet contaminated soil for analysis by dry sieve methods. Using the equation in Figure 11, a distinct removal was calculated for each of the three soil fractions.

Three of the curves are shown in Figures 12, 13 and 14. Figure 12 shows the percent BTEX removal on the high gasoline SSM when varying the rinsewater to washwater ratio. Figure 13 shows the percent TPH removal as

a function of washwater temperature on the high diesel SSM where the washwater contains 0.13 percent CitriKleen. Figure 14 shows the particle size distribution as a function of contact time for the high diesel SSM. The ordinate on the particle size distribution curves is percent passing each sieve. To calculate the percent retained on a sieve, the value of the percent passing that sieve should be subtracted from the percent passing the sieve above it. For example, the percent retained on the No. 60 sieve is the percent passing the No. 10 sieve minus the percent passing the No. 60 sieve.

The percent removals for several experiments are shown in Table 15.

TABLE 15. REMOVAL EFFICIENCIES FOR SSM SOIL WASHING EXPERIMENTS

Soil Contaminant	Initial Concentration	Washing Solution	Percent Removal		
			No. 10 Sieve	No. 60 Sieve	No. 140 Sieve
Gasoline	2,100 mg/kg BTEX	77°F Water	99	99	99
Gasoline	2,100 mg/kg BTEX	77°F 0.5% Surfactant	93	98	94
Diesel	18,000 mg/kg TPH	77°F Water	99	98	98
Diesel	18,000 mg/kg TPH	77°F 0.67% CitriKleen	99	97	—
Diesel	18,000 mg/kg TPH	178°F Water	99	99	99

These experimental results are a sampling of the experiments conducted, and the results for all experiments can be found in Appendix C. As the table indicates, the removals obtained were very high, all greater than 90 percent for the No. 10, 60 and 140 sieves. The experiments shown in this table represent a wide variety of operating conditions, and yet they all obtained very high removals. These high removals were demonstrated across the board for gasoline and diesel experiments.

Since the removals were very high, improvements in removal efficiency based on varying operating conditions, were difficult to detect. Regardless of the operating conditions used, the removals for both BTEX and TPH were usually greater than 90 percent.

Some parameters affected the particle size distribution. A contact time of 30 minutes was found to provide the best particle separation because the longer mixing time allowed the soil "clumps" to brake up more readily. Although mixing times greater than 30 minutes were not tested,

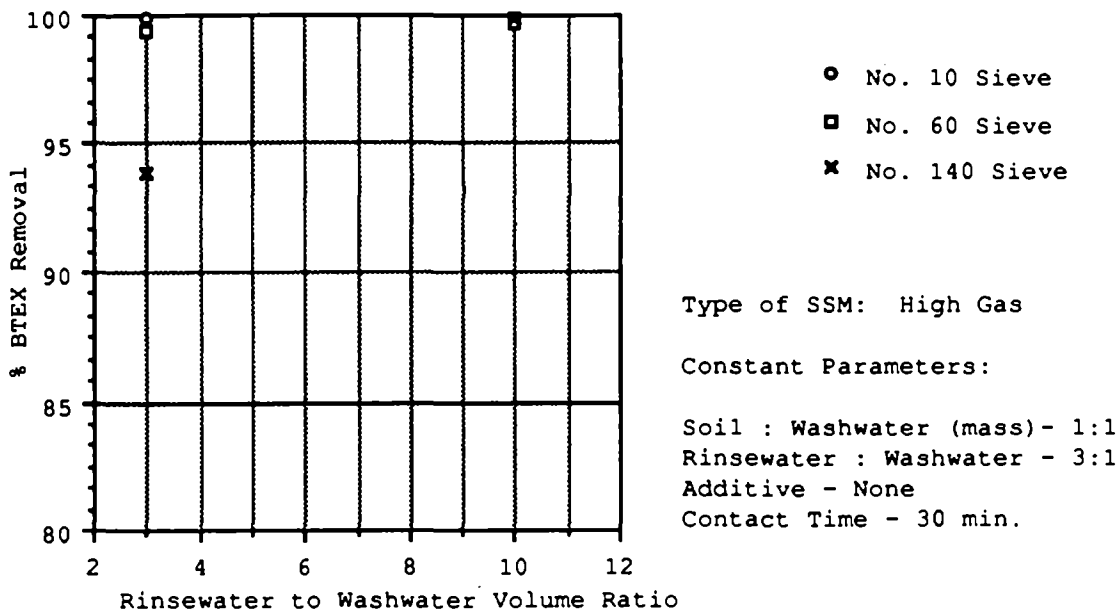


Figure 12. Rinsewater to washwater ratio effect on percent BTEX removal.

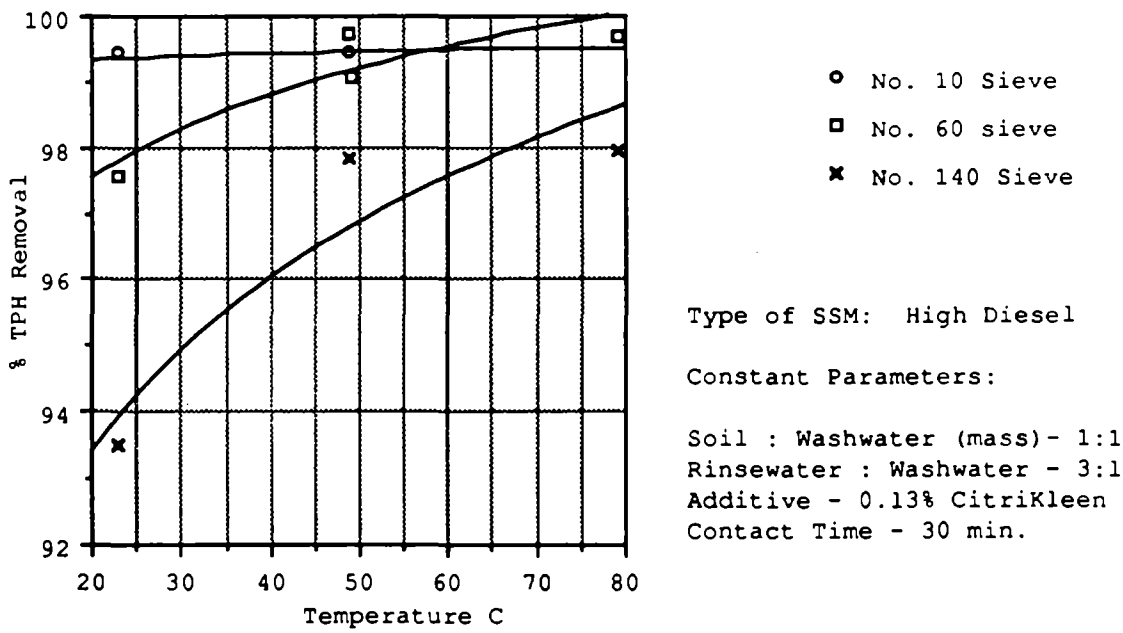


Figure 13. Temperature effect on percent TPH removal with 0.13% CitriKleen.

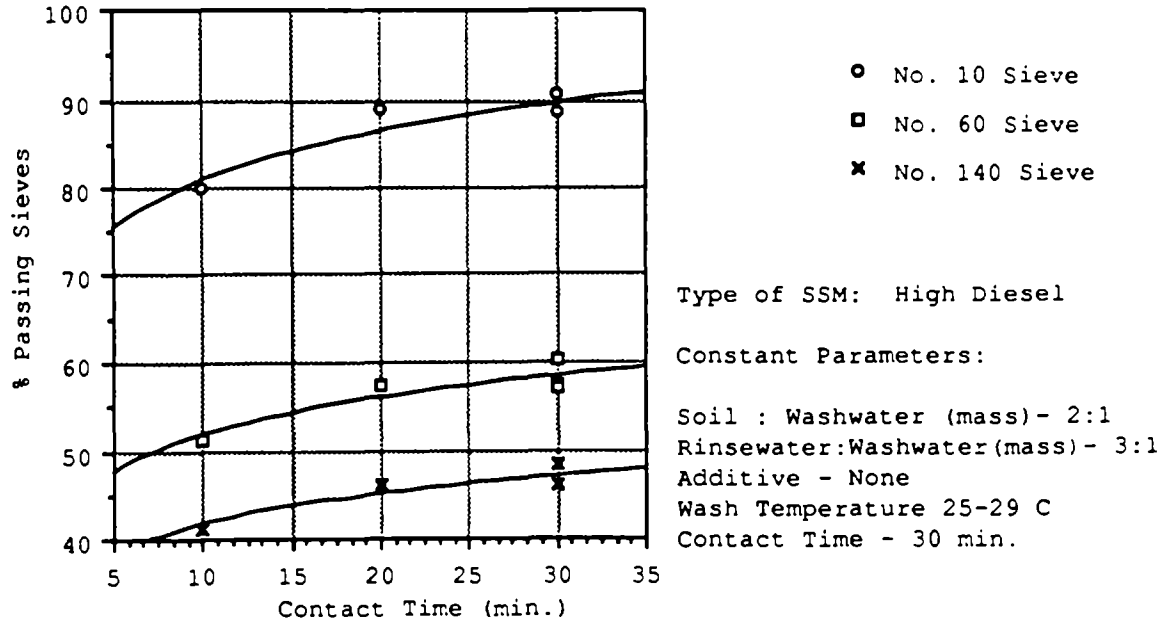


Figure 14. Contact time effect on partical size distribution for diesel contaminated soil.

the data in Figure 14 indicates that the predicted particle separation for mixing times greater than 30 minutes is not expected to significantly improve. The soil/washwater mass ratio also affected the particle separation. Ideally, the largest soil to washwater mass ratio which results in good removal should be used because a minimum quantity of washwater would be generated. A 1:1 mass ratio was the highest soil/washwater ratio which gave effective particle separation. The remainder of the studied parameters did not significantly affect the particle separation.

Selection of "Optimal" Conditions

Based on the Phase I findings, an "optimum" set of operating conditions was selected. The Phase I results did not show a significant difference between the gasoline and diesel experiments. Therefore, the same "optimal" conditions were selected for both gasoline and diesel. The conditions are as follows: a contact time of 30 minutes; a soil to washwater ratio of 1 to 1, a rinsewater to washwater ratio of 3 to 1; ambient temperature; and no additives.

These conditions were selected such that upon scale up to a full scale system, they would provide the most effective contaminant removals at minimum operational cost. This set of operating conditions was used for the Phase II experiments.

Mass Balance Results

For several experiments, sufficient data was taken to perform a material balance of the system during the bench scale soil washing test. A mass balance of the soil was done by comparing the dry mass of soil used in the test to the dry mass of soil recovered in the three soil fractions and the suspended solids content of the washwater and rinsewater. A mass balance of the contaminants was also conducted in a similar fashion by calculating the mass of contaminant (BTEX of TPH) recovered in each fraction.

The mass balance results are shown in Table 16, and indicate that, on average, 83 percent of the soil was accounted for.

TABLE 16. PHASE I - EXPERIMENT MASS BALANCE RESULTS

Experiment Number	Percent Soil Accounted For	Percent Contaminant Accounted For
5	76	66 (BTEX)
6A	94	52 (BTEX)
15	90	26 (BTEX)
19	96	35 (TPH)
22	89	99 (TPH)
23	56	50 (TPH)
33A	80	37 (BTEX)
	Average = 83	
	Stand. Dev. = 14	

The percent recovery for TPH and BTEX experiments ranged from 26 to 99 percent. These fluctuations in the recoveries may be due to measurement errors, inherent analytical variations (as shown in Appendix E), volatilization of the contaminants, and soils adhering to the equipment.

The mass balance required the use of the total suspended solids measurement of the washwater and rinsewater. This analysis is performed with a glass fiber filter. Any colloidal particulates smaller than the filter paper pore size were not accounted for in the mass balance.

PHASE II - FULL MATRIX SOILS TESTING

The soils used in the Phase I experiments were the high gasoline and high diesel SSM blends, and the results indicated that the "optimal"

washing conditions were the same for both gasoline and diesel. The experiments in Phase II incorporated the "optimal" washing conditions determined in Phase I on all the other remaining SSM matrices (the low and medium blends of gasoline and diesel SSM, and all the waste soil SSM blends). The goal was to determine if the same levels of removals could be achieved with varying soil contaminant concentration.

In addition, actual soils were obtained from sites in Ohio and New Jersey where leaking underground storage tanks resulted in petroleum contaminated soils. These soils were washed using the "optimum" conditions to compare the SSM washing results with those of real soils.

Full Matrix Results

A total of 15 experiments were conducted for completion of experiments on all SSM matrices. The same procedures were used for these experiments as for the Phase I experiments. All measurements and analysis results are presented in Appendix D.

The removals of contaminants in this set of experiments were similar to the results obtained in Phase I. The effectiveness of the washing process was greater than 90 percent for most of the experiments as shown in Table 17.

TABLE 17. RESULTS OF PHASE II EXPERIMENTS

SOIL CONTAMINANT	INITIAL CONCENTRATION	PERCENT REMOVAL		
		NO. 10 SIEVE (<2 mm)	NO. 60 SIEVE (0.25-2mm)	NO. 140 SIEVE (0.106-0.25mm)
Gasoline (low)	21 mg/kg BTEX	99	99	99
Gasoline (med)	766 mg/kg BTEX	99	97	97
Diesel (low)	917 mg/kg TPH	98	98	98
Diesel (med)	1,839 mg/kg TPH	97	97	98
Waste Oil (low)	1,117 mg/kg TPH	97	98	85
Waste Oil (med)	9,327 mg/kg TPH	96	98	92
Waste Oil (high)	28,533 mg/kg TPH	88	98	85

NOTE: Results presented in this table are averages of duplicate experiments.

These results indicate that the effectiveness of the soil washing process on the SSM was independent of the concentration or type of contaminant in the soil blend.

Actual Site Soil Results

Soils were collected from four sites with contaminants as shown in Table 18.

TABLE 18. UST SITE SOILS USED FOR PHASE II EXPERIMENTS

SITE LOCATION	SOIL CONTAMINANT	SOIL CONCENTRATION
Grove City, OH	Gasoline	243 mg/kg BTEX
Mahwah, NJ	Gasoline	23.8 mg/kg BTEX
Princeton, NJ	Home Heating Fuel	1,375 mg/kg TPH
Holmdel, NJ	Kerosine	215 mg/kg TPH

Optimal soil washing parameters vary for each type of soil and contaminant condition. However, for the sake of comparison, each site soil was washed using the "optimal" conditions obtained from Phase I. The purpose was not to optimize the removal of contaminants from the site soils, but to compare the removals with those of the SSM.

Each experiment was done in duplicate. The results of these experiments are shown in Table 19.

TABLE 19. SOIL WASHING RESULTS FOR UST SITE SOIL

SITE LOCATION	PERCENT REMOVAL		
	NO. 10 SIEVE	NO. 60 SIEVE	NO. 140 SIEVE
Grove City, OH	10	49	49
(gasoline)	67	50	
Mahwah, NJ	16	80	14
(gasoline)	77	89	
Princeton, NJ	82	72	83
(home heating fuel)	86	~0	
Holmdel, NJ	91	54	48
(kerosine)	97	91	70

NOTE: Experiments performed in duplicate. Results of each experiment are shown in this table.

The removals from these soils were significantly lower than those obtained from the SSM experiments. Although most removals were in the range of 50 to 90 percent, there were some results which were substantially lower.

It should be noted that the experiments using site soils were less reproducible than the SSM experiments. Table 19 shows the duplicate results for each experiment which range from being very close together to varying widely. This is markedly different from the SSM experimental duplicates which were generally within a few percentage points of each other.

Another major difference between the SSM and the site soils was the resultant particle size distribution. Table 20 shows the particle size distribution for the various soils compared with the SSM.

TABLE 20. PARTICLE SIZE DISTRIBUTION OF SOILS

	PERCENT IN EACH FRACTION			
SOIL	NO. 10 SIEVE (>2 mm)	NO. 60 SIEVE (0.25-2mm)	NO. 140 SIEVE (0.106-0.25mm)	WASHWATER & RINSEWATER (<0.25 mm)
SSM	13	31	11	45
Grove City, OH	30	50	4	16
Mahwah, NJ	26	43	21	10
Princeton, NJ	23	12	8	43
Holmdel, NJ	14	67	12	7

The particle size distribution in the table is presented as percent by weight of soil which remained in the No. 10 sieve, No. 60 sieve, No. 140 sieve, and passed into washwater and rinsewater. As the table shows, 45 percent of the original SSM mass becomes part of the washwater and rinsewater, indicating that at least 45 percent of the soil mass is smaller than the No. 140 sieve opening size. On the other hand, the site soils had much lower percentages of soil mass in the washwater and rinsewater. These soils had less fine material in the bulk matrix than the SSM.

These results are also evident in the comparison of SSM and site soil washwater and rinsewater total suspended solids (TSS) concentration presented in Table 21.

TABLE 21. TOTAL SUSPENDED SOLIDS (TSS) LEVELS IN WASHWATERS AND RINSEWATERS

SOIL	TSS (mg/l) WASHWATER	RINSEWATER
SSM	228,000	6,070
Grove City, OH	33,000	3,100
Mahwah, NJ	40,600	3,060
Princeton, NJ	110,000	6,180
Holmdel, NJ	40,600	6,820

The SSM washwater contained about 23 percent solids by weight. The other soils had washwaters with TSS levels in the order of 3 to 11 percent solids.

FIELD ANALYTICAL PROGRAM RESULTS

BTEX analyses on soil samples were performed in the field using a portable gas chromatograph in addition to samples being submitted to an off-site laboratory. The results obtained from the field analyses were compared to the results of the laboratory analyses in an effort to correlate the field data to the laboratory data. The intent of this correlation was to minimize the need for sending samples from future work (e.g., pilot and full scale demonstrations) to an off-site laboratory.

The results of this comparative analysis are tabulated in Table 22 and presented graphically in Figure 15. This includes graphs of the individual BTEX compounds and a graph of total BTEX (sum of all individual compounds). The graphs on the left side of the page represent the results of all the field and laboratory BTEX results. The graphs to the right present the same data as the graphs on the left with the axis scales expanded to focus on the lower concentration data. The field GC results are plotted on the ordinate and the laboratory results are plotted on the abscissa. The closer the data point is to the 45° line drawn onto the graph, the closer the field value is to the lab-obtained value.

The average percent difference between the results obtained in the field and in the laboratory is about 90 percent. This indicates that the field GC results can predict the soil concentrations within an order of magnitude.

TABLE 22. COMPARISON OF FIELD AND LAB BTEX DATA FOR SOIL SAMPLES.

	BENZENE (PPM)				TOLUENE (PPM)			
EXPERIMENT	FIELD	LAB	AVERAGE	% DIFFER	FIELD	LAB	AVERAGE	% DIFFER
EXP 3 SIEVE 10	ND	0.03	-	-	ND	0.35	-	-
EXP 3 SIEVE 60	1.00	0.24	0.62	123%	3.20	3.40	3.30	-6%
EXP 3 SIEVE 140	1.00	1.10	1.05	-10%	5.50	23.00	14.25	-123%
EXP 5 SIEVE 10	1.30	0.17	0.74	154%	3.80	2.30	3.05	49%
EXP 5 SIEVE 60	1.30	<.4	-	-	12.20	3.20	7.70	117%
EXP 5 SIEVE 140	7.20	19.00	13.10	-90%	162.00	330.00	246.00	-68%
EXP 6 SIEVE 60	ND	0.18	-	-	9.70	2.30	6.00	123%
EXP 6 SIEVE 140	ND	0.01	-	-	ND	0.21	-	-
EXP 6A SIEVE 60	6.10	0.48	3.29	171%	19.30	4.20	11.75	129%
EXP 6A SIEVE 140	ND	<.4	-	-	ND	2.30	-	-
EXP 33 SIEVE 60	6.60	3.00	4.80	75%	8.90	33.00	20.95	-115%
EXP 33 SIEVE 140	36.00	6.90	21.45	136%	60.00	110.00	85.00	-59%
EXP 33A SIEVE 10	ND	0.28	-	-	5.50	2.30	3.90	82%
EXP 33A SIEVE 60	ND	0.79	-	-	6.70	11.00	8.85	-49%
EXP 33A SIEVE 140	ND	1.40	-	-	8.60	59.00	33.80	-149%
EXP 9 SIEVE 10	ND	0.20	-	-	37.00	3.00	20.00	170%
EXP 9 SIEVE 60	ND	1.10	-	-	ND	11.00	-	-
FB1 SIEVE 60	ND	<.001	-	-	ND	<.001	-	-
EXP 7 SIEVE 10	ND	0.62	-	-	7.51	7.80	7.66	-4%
EXP 7 SIEVE 60	ND	0.60	-	-	2.00	6.70	4.35	-108%
EXP 7 SIEVE 140	ND	0.47	-	-	2.30	20.00	11.15	-159%
EXP 8 SIEVE 60	ND	0.89	-	-	9.75	9.80	9.78	-1%
EXP 8 SIEVE 140		4.40	-	-	15.07	76.00	45.54	-134%
EXP 10 SIEVE 10	ND	0.46	-	-	41.60	24.00	32.80	54%
EXP 10 SIEVE 60	ND	0.82	-	-	3.90	11.00	7.45	-95%
EXP 10 SIEVE 140	2.50	<.20	-	-	4.50	15.00	9.75	-108%
EXP 10A SIEVE 60	ND	0.88	-	-	9.51	11.00	10.26	-15%
EXP 10A SIEVE 140	6.44	1.40	3.92	129%	15.44	28.00	21.72	-58%
EXP 11 SIEVE 60	ND	0.77	-		2.50	8.70	5.60	-111%
EXP 11 SIEVE 140	6.80	1.50	4.15	128%	18.20	28.00	23.10	-42%
EXP 11A SIEVE 60	ND	0.16	-	-	6.30	1.70	4.00	115%
EXP 12 SIEVE 10	ND	0.60	-	-	2.17	7.50	4.84	-110%
EXP 12 SIEVE 60	ND	0.44	-	-	22.96	5.00	13.98	128%
EXP 12 SIEVE 140	ND	0.01	-	-	1.43	0.04	0.73	190%
EXP 13 SIEVE 10	ND	1.60	-	-	3.30	22.00	12.65	-148%
EXP 13 SIEVE 60	3.00	0.66	1.83	128%	10.80	10.00	10.40	8%
EXP 13 SIEVE 140	ND	0.23	-	-	1.90	10.00	5.95	-136%

(continued)

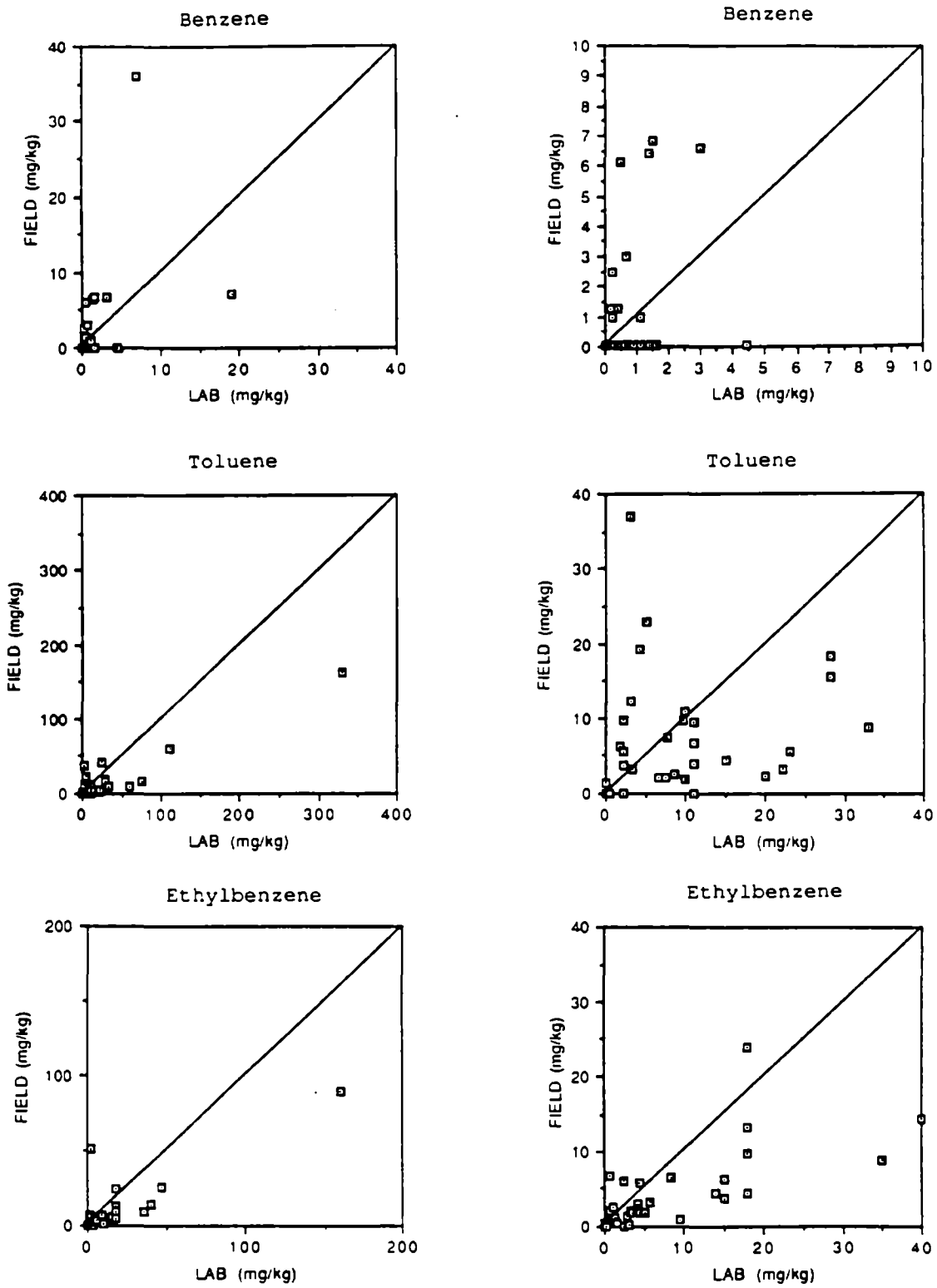
TABLE 22. (continued)

EXPERIMENT	ETHYLBENZENE (PPM) FIELD	LAB	AVERAGE	% DIFFER	TOTAL XYLENES (PPM) FIELD	LAB	AVERAGE	% DIFFER
EXP 3 SIEVE 10	ND	0.14	-	-	ND	0.85	-	-
EXP 3 SIEVE 60	1.20	1.30	1.25	-8%	6.60	7.10	6.85	-7%
EXP 3 SIEVE 140	6.30	15.00	10.65	-82%	40.00	87.00	63.50	-74%
EXP 5 SIEVE 10	1.00	1.00	1.00	0%	5.50	5.20	5.35	6%
EXP 5 SIEVE 60	6.00	2.50	4.25	82%	32.00	16.10	24.05	66%
EXP 5 SIEVE 140	90.00	160.00	125.00	-56%	479.00	860.00	669.50	-57%
EXP 6 SIEVE 60	2.10	0.67	1.39	103%	11.10	3.50	7.30	104%
EXP 6 SIEVE 140	ND	0.17	-	-	ND	0.97	-	-
EXP 6A SIEVE 60	2.60	1.20	1.90	74%	13.70	6.10	9.90	77%
EXP 6A SIEVE 140	ND	2.50	-	-	2.10	17.60	9.85	-157%
EXP 33 SIEVE 60	3.70	15.00	9.35	-121%	20.90	91.00	55.95	-125%
EXP 33 SIEVE 140	26.00	46.00	36.00	-56%	143.00	242.00	192.50	-51%
EXP 33A SIEVE 10	0.90	0.61	0.76	38%	3.70	3.14	3.42	16%
EXP 33A SIEVE 60	3.00	4.10	3.55	-31%	17.20	24.20	20.70	-34%
EXP 33A SIEVE 140	8.80	35.00	21.90	-120%	56.00	176.00	116.00	-103%
EXP 9 SIEVE 10	0.40	1.60	1.00	-120%	2.50	9.10	5.80	-114%
EXP 9 SIEVE 60	3.30	5.70	4.50	-53%	10.20	34.00	22.10	-108%
FB1 SIEVE 60	ND	<.001	-	-	ND	<.001	-	-
EXP 7 SIEVE 10	2.04	3.40	2.72	-50%	6.71	19.70	13.21	-98%
EXP 7 SIEVE 60	1.34	2.80	2.07	-71%	8.63	16.90	12.77	-65%
EXP 7 SIEVE 140	4.40	14.00	9.20	-104%	23.60	82.00	52.80	-111%
EXP 8 SIEVE 60	2.27	4.10	3.19	-57%	11.94	25.50	18.72	-72%
EXP 8 SIEVE 140	14.51	40.00	27.26	-94%	72.82	199.00	135.91	-93%
EXP 10 SIEVE 10	24.00	18.00	21.00	29%	116.70	104.00	110.35	12%
EXP 10 SIEVE 60	1.90	4.50	3.20	-81%	9.60	24.60	17.10	-88%
EXP 10 SIEVE 140	9.80	18.00	13.90	-59%	50.00	100.00	75.00	-67%
EXP 10A SIEVE 60	1.92	5.10	3.51	-91%	12.03	30.20	21.12	-86%
EXP 10A SIEVE 140	4.42	18.00	11.21	-121%	28.52	99.00	63.76	-111%
EXP 11 SIEVE 60	1.80	3.50	2.65	-64%	7.70	18.20	12.95	-81%
EXP 11 SIEVE 140	13.20	18.00	15.60	-31%	65.00	86.00	75.50	-28%
EXP 11A SIEVE 60	6.80	0.69	3.75	163%	16.90	2.02	9.46	157%
EXP 12 SIEVE 10	0.27	3.00	1.64	-167%	3.42	15.70	9.56	-128%
EXP 12 SIEVE 60	51.66	2.40	27.03	182%	36.92	14.20	25.56	89%
EXP 12 SIEVE 140	0.45	0.06	0.25	154%	3.26	0.49	1.88	148%
EXP 13 SIEVE 10	1.00	9.60	5.30	-162%	5.60	51.00	28.30	-160%
EXP 13 SIEVE 60	5.80	4.40	5.10	27%	30.90	24.30	27.60	24%
EXP 13 SIEVE 140	6.60	8.50	7.55	-25%	29.70	51.00	40.35	-53%

(continued)

TABLE 22. (continued)

EXPERIMENT	TOTAL BTEX (PPM) FIELD	LAB	AVERAGE	% DIFFER
EXP 3 SIEVE 10	ND	1.37	-	-
EXP 3 SIEVE 60	12.00	12.04	12.02	0%
EXP 3 SIEVE 140	52.80	126.10	89.45	-82%
EXP 5 SIEVE 10	11.60	8.67	10.14	29%
EXP 5 SIEVE 60	51.50	22.20	36.85	80%
EXP 5 SIEVE 140	738.20	1369.00	1053.60	-60%
EXP 6 SIEVE 60	22.90	6.65	14.78	110%
EXP 6 SIEVE 140	ND	1.36	-	-
EXP 6A SIEVE 60	41.70	11.98	26.84	111%
EXP 6A SIEVE 140	2.10	22.80	12.45	-166%
EXP 33 SIEVE 60	40.10	142.00	91.05	-112%
EXP 33 SIEVE 140	265.00	404.90	334.95	-42%
EXP 33A SIEVE 10	10.10	6.33	8.22	46%
EXP 33A SIEVE 60	26.90	40.09	33.50	-39%
EXP 33A SIEVE 140	73.40	271.40	172.40	-115%
EXP 9 SIEVE 10	39.90	13.90	26.90	97%
EXP 9 SIEVE 60	13.50	51.80	32.65	-117%
FB1 SIEVE 60	ND	<.001	-	-
EXP 7 SIEVE 10	16.26	31.52	23.89	-64%
EXP 7 SIEVE 60	11.97	27.00	19.49	-77%
EXP 7 SIEVE 140	30.30	116.47	73.39	-117%
EXP 8 SIEVE 60	23.96	40.29	32.13	-51%
EXP 8 SIEVE 140	102.40	319.40	210.90	-103%
EXP 10 SIEVE 10	182.30	146.46	164.38	22%
EXP 10 SIEVE 60	15.40	40.92	28.16	-91%
EXP 10 SIEVE 140	66.90	133.20	100.05	-66%
EXP 10A SIEVE 60	23.46	47.18	35.32	-67%
EXP 10A SIEVE 140	54.82	146.40	100.61	-91%
EXP 11 SIEVE 60	11.90	31.17	21.54	-89%
EXP 11 SIEVE 140	103.20	133.50	118.35	-26%
EXP 11A SIEVE 60	30.00	4.57	17.29	147%
EXP 12 SIEVE 10	5.86	26.80	16.33	-128%
EXP 12 SIEVE 60	111.54	22.04	66.79	134%
EXP 12 SIEVE 140	5.14	0.60	2.87	158%
EXP 13 SIEVE 10	9.80	84.20	47.00	-158%
EXP 13 SIEVE 60	50.50	39.36	44.93	25%
EXP 13 SIEVE 140	38.20	69.73	53.97	-58%



(continued)

Figure 15. Comparison of field and lab analytical data.

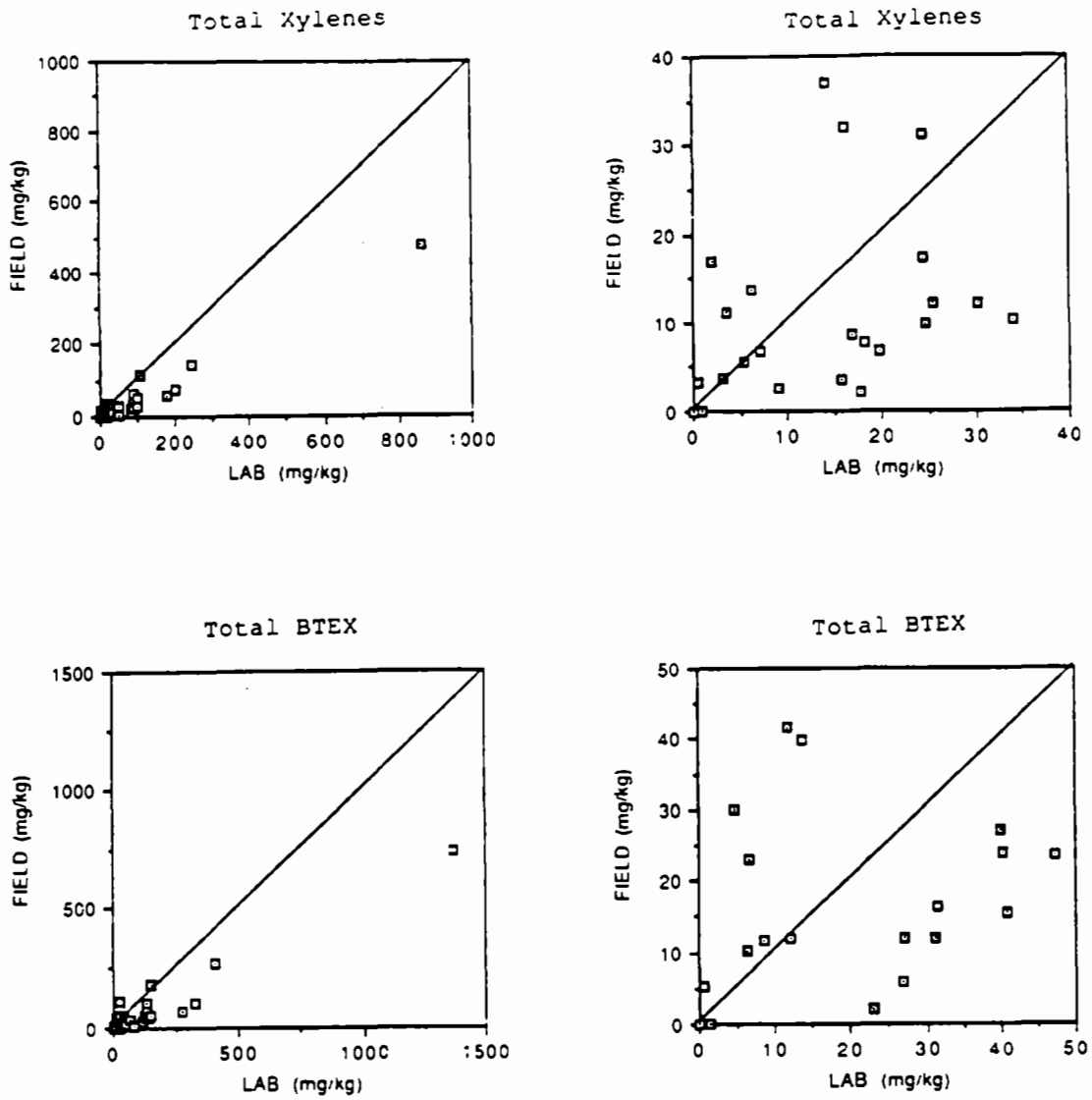


Figure 15. (continued)

As shown on the graphs, the concentrations determined in the field were more often lower than the concentrations reported by the laboratory. This may be due to the methodology used in the extraction procedure. The ability to extract the BTEX compounds from the soil to the liquid phase may not have been as controlled in the field as it is in the laboratory. For the field data, the detection limit is approximately 5 parts per million whereas the laboratory reported a detection limit of 1 part per billion. However, for comparative purposes a reported non-detect for the field data was assigned a value of 0.05 parts per million. This is particularly evident in the benzene graphs.

Since benzene is the most stringently regulated of the BTEX compounds, it was important to be able to quantify benzene. Predominantly, however, the concentration of benzene was not quantified because the benzene peak eluted out at a similar time as the peak of the extraction solvent. Different techniques were employed with the instrumentation available including lowering the oven temperature of the GC from 105°C to 80°C. An improvement in separation and quantitation of the benzene peak was observed, however this increased the sample run time to two hours. The problem encountered was that techniques to separate the early eluting BTEX peaks caused the run times to increase. The late eluting gasoline constituents could take up to several hours to pass through the column.

Various time functions were programmed into the integrator to either ignore or integrate the methanol peak in an attempt to isolate the benzene peak. This did not resolve the difficulties in quatifying benzene. Recommendations were made to modify the field program for the next phase of work including the purchase of a different column and accessing temperature programming capabilities with the microcontroller unit of the HNu 321.

In summary, the results of the field program indicate that the data may only be suitable for screening of soils to determine relative concentrations of BTEX compounds and should only be utilized to supplement the off-site laboratory results.

TOTAL PETROLEUM HYDROCARBON ANALYTICAL STUDY

Total Petroleum Hydrocarbon (TPH) is a parameter often used to determine the extent of contamination present in soils contaminated with petroleum products such as diesel oil and waste oils. The analytical method to do this analysis involves the extraction of the soil with a solvent and the subsequent analysis of the extract using infrared spectroscopy.

There are two methods available to perform the extraction of the soils: Soxhlet Extraction (EPA Test Method 3540, U.S. EPA Test Methods for Evaluation Solid Waste, Third Edition, SW-846, November 1986) and Sonication Extraction (EPA Test Method 3550). The method currently used by most laboratories is the Soxhlet method, although the Sonication method is considered to be a quicker and simpler method.

As part of the soil washing work assignment, a study was conducted to determine if the extraction efficiencies of the two methods were statistically equivalent.

Procedure

The soil washing evaluation project required the preparation of various blends of SSM with gasoline, diesel fuel, or waste crankcase oil. A 2000 gram sample of the medium level diesel spiked SSM and waste oil spiked SSMs were submitted to the Camp Dresser & McKee laboratory for analysis of the two soil samples using both extraction methods. Based on discussion with Lisa Moore, Statistician, EPA RREL, a sample size of 14

analyses per method was considered adequate to determine, with a 90 percent confidence level, if the analytical results for the two methods were within 10 percent of each other.

The sample preparation was conducted by placing the entire sample submitted to the lab in a stainless steel mixing bowl and thoroughly homogenizing. Twenty-gram sample aliquots were used for Soxhlet extraction and ten-gram aliquots were used for Sonication extraction.

Sonication Methodology --

Approximately 10 to 15 grams of sample were accurately weighed into a 250 milliliter beaker. The sample was homogenized prior to aliquots being taken to ensure uniform subsamples. The aliquot was acidified with concentrated sulfuric acid (0.5 to 1 milliliters) and mixed. Approximately 30 grams of dried magnesium sulfate monohydrate was added to the sample and mixed to absorb water. The prepared sample was then extracted with 80 milliliters of freon. The extraction was performed using the Tekmar Sonic Disruptor (with a 3/4" horn, 3 minute cycle at 50 percent pulsed duty cycle). The solvent was then decanted off and filtered through phase separator paper (Whatman). The sample was then extracted two more times with 80 milliliter freon per extraction with the extracts filtered and combined. The final extract was brought to 250 milliliter total volume (freon) in a volumetric flask. The samples were analyzed by EPA method 418.1 (i.e. spectrophotometry). The final results were corrected to dry weight based on a total solids determination (overnight drying at 103-105°C).

Soxhlet Methodology --

Approximately 20 to 30 grams of sample were accurately weighed into a 250 milliliter beaker. The sample was acidified to a pH of 2 with concentrated sulfuric acid (0.5 to 1 milliliters). Magnesium sulfate monohydrate was added to dry the sample. The sample was then transferred to a cellulose extraction thimble. If necessary, a piece of Whatman 4 filter paper wetted with freon was used to obtain a quantitative transfer of the material; if used, the filter paper was added to the thimble. The thimble was then covered with a plug of glass wool to prevent soil from spilling out of thimble. The thimble was placed in the Soxhlet extraction apparatus and extracted with 100 milliliter of freon for four hours with the apparatus operating at a minimum of 4 cycles per hour. After the four hours of extraction, the apparatus was allowed to cool and the freon transferred into a 100 milliliter volumetric flask and brought up to volume with fresh freon. The samples were analyzed by EPA method 418.1 (i.r. spectrophotometry). The final results were corrected to dry weight based on a total solids determination (overnight drying at 103 to 105°C).

Experimental Results

The data collected by the Soxhlet and Sonication extraction methods for medium-level diesel spiked SSM are shown in Table 23.

TABLE 23. TPH RESULTS FOR DIESEL-SPIKED SSM

Replicate Number	TPH Concentration (mg/kg dry basis) Sonification	Soxhlet
1	4,980	6,300
2	7,760	5,680
3	4,580	7,500
4	4,190	9,000
5	4,760	8,150
6	6.680	7,540
7	8,100	5,210
8	10,300	7,170
9	5,220	3,570
10	4,750	5,970
11	5,360	4,150
12	4,300	5,690
13	8,530	4,790
14	5,630	5,660
Average Concentration	6,081	6,170
Standard Deviation	1,817	1,489
n	14	14
Maximum	10,300	9,000
Minimum	4,190	3,570

The data represent fourteen separate extractions. Blank samples consisting of clean wet SSM were also submitted as a QA check. The TPH concentration of the blank was less than 10 milligrams per kilogram using both extraction methods indicating that cross contamination is not a concern in the data for either extraction process.

The first question of concern is whether the two population averages are equal. If the averages are not equal, the second question is whether or not there is a difference of 10 percent or more between the results. Each population is assumed to be normally distributed and independent. The null hypothesis is that the two groups have equal averages, and the alternate hypothesis is that the averages are unequal. The comparison of means has 26 degrees of freedom. The critical student-t test value, t_{cr}, is 1.706 at the 90 percent level of confidence. The test t-value is computed using the equations in Figures 16 and 17.

$$t = \frac{\bar{X}_1 - \bar{X}_2}{S_{sp}\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

NOTE: n_1 and n_2 are the number of data values in each set, and $\bar{X}_1$ and $\bar{X}_2$ are the respective averages.

Figure 16. Test T-Value Equation.

Where S_{sp} is the pooled estimate of the population standard deviation computed as

$$S_{sp} = \sqrt{\frac{(n_1-1)S_1^2+(n_2-1)S_2^2}{n_1 + n_2 - 2}}$$

NOTE: S_1 and S_2 are the standard deviations and n_1 and n_2 are the number of data values in each set.

Figure 17. Pooled Estimate of the Population Standard Deviation Equation.

Table 23 lists the values of the standard deviations and averages along with the individual data points. Figures 18 and 19 show the evaluations of the equations presented in Figures 16 and 17 for diesel spiked soil.

$$t = \frac{6081 - 6170}{1661\sqrt{\frac{1}{14} + \frac{1}{14}}} = -0.14$$

Figure 18. Pooled estimate of the Population Standard Deviation Calculation for TPH Results for Diesel Spiked Soil.

$$S_{sp} = \sqrt{\frac{(13)(1817)^2 + (13)(1489)^2}{26}} = 1661 \text{ mg/kg}$$

Figure 19. T-Value Calculation for TPH Results for Diesel Spiked Soil.

Since the test value of the t-variable (Figure 16) is within $\pm t_{cr}$, the null hypothesis can not be rejected. That is, the differences computed are not significant at the 90 percent level of confidence. This follows the intuitive feel since the averages were only 89 milligrams per kilogram different on averages on the order of 6,000 milligrams per kilogram. Since the averages were found to be statistically equal, the difference between them is less than 10 percent.

A similar procedure was followed using the SSM spiked with waste oil. The laboratory Soxhlet apparatus can only do 11 extractions in one batch, so to obtain the 14 extractions required, two batches were extracted. The TPH extraction data for the waste-oil matrix using the Soxhlet method are shown in Table 24.

TABLE 24. TPH RESULTS FOR WASTE-OIL SPIKED SSM USING SOXHLET EXTRACTION METHOD

	TPH Concentration (mg/kg dry basis)		
	9/19/89	9/21/89	9/25/89
Replicate Number		(Extraction Date)	
1	3,250	6,770	2,060
2	3,000	14,000	2,580
3	6,850	13,500	3,080
4		12,100	
5		8,680	
6		5,590	
7		6,110	
8		6,730	
9		9,700	
10		6,070	
11		9,370	
Average Concentration	4,367	8,965	2,573 mg/kg
Standard Deviation	1,750	2,927	416 mg/kg
n	3	14	11 mg/kg
Maximum	6,850	14,000	3,080 mg/kg
Minimum	3,000	5,590	2,060 mg/kg

NOTE: The CDM laboratory recommends that the data obtained from the extraction on September 19 and 25th be excluded from the reported results.

Three samples were extracted on 9/19 and eleven were extracted on 9/21. Upon examination of the data of the samples extracted on 9/19, the mean of

these samples were significantly lower than the mean of those extracted on 9/21. Three more extractions were done on 9/25, and this data also appeared to fall out of the range of those analyzed on 9/21. The determination from the laboratory was that the data obtained on 9/19 and 9/25 should not be used in the statistical evaluation.

The first question is whether the laboratory analysts correctly recommended eliminating the results from a statistical perspective. The only physical difference noted in the extraction process was the date of extraction. The two sets of three extractions can be considered as a comparison to the original 11 in the same manner as the TPH comparisons made for the medium diesel oil tests (Figures 20 and 21).

$$S_{sp} = \sqrt{\frac{(10)(8965)^2 + (2)(4367)^2}{10}} = 2767 \text{ mg/kg}$$

Figure 20. Pooled Estimate of the Population Standard Deviation.

$$t = \frac{8965 - 4367}{2767\sqrt{\frac{1}{11} + \frac{1}{3}}} = 3.0$$

Figure 21. Test T-Value Calculation For TPH Results for Waste Oil Spiked SSM Using Soxhlet Extraction Method.

With 12 degrees of freedom, the alternate hypothesis can not be rejected. There is evidence to support the conclusion that they are not equivalent. The critical t value is 1.782 for this application.

The second three extractions (9/25/89 extraction date) were conducted as substitutes for the three originally excluded. The results yield a test value of 6.0, again lending support for excluding them from the analysis. Statistically, these extraction results are outliers resulting from unknown factors on the different days. Statistically, the lab was correct in excluding these from the presentation of the data.

Table 25 lists the reported results from the laboratory for the accepted results for the TPH determinations by Soxhlet extraction and Sonication.

TABLE 25. TPH RESULTS FOR WASTE OIL SPIKED SSM

Replicate Number	TPH Concentration (mg/kg dry basis) Sonication	Soxhlet
1	4,640	6,770
2	10,900	14,000
3	9,190	13,500
4	12,600	12,100
5	10,100	8,680
6	7,960	5,590
7	9,930	6,110
8	11,000	6,730
9	7,550	9,700
10	8,010	6,070
11	6,510	9,370
12	7,330	
13	8,110	
14	9,500	
Average Concentration	8,813	8,965
Standard Deviation	1,990	2,927
n	14	11
Maximum	12,600	14,000
Minimum	4,640	5,590

Applying the same procedures to compare the Soxhlet and Sonication extractions, the null hypothesis is stated that the averages are equal for the methods. The application of the same procedures listed above yield a test value to the t variable of -0.16. This is within the range that does not allow rejection of the null hypothesis. There is no statistical evidence to believe that there is a difference in the reported results based on the extraction method.

An argument can be presented that it is impossible, by definition, to have outliers in this procedure. All data, no matter the numerical values must be considered. When this arbitrary rule is applied, the test t value computed is 1.64. This, too, is within the range that does not allow the rejection of the null hypothesis at the 90 percent confidence level.

In summary,

(1) The data presented for the determination of TPH in the diesel spiked SSM by the two methods is statistically equivalent at the 90 percent confidence level.

(2) There is statistical support for the elimination of data outliers at the 90 percent confidence level.

(3) The data found to be acceptable by the laboratory for the analysis of waste-oil and diesel spiked SSM by Soxhlet extraction is statistically equivalent to the Sonication extraction data at the 90 percent confidence level.

(4) The waste oil TPH determination by Soxhlet extraction is equivalent to the TPH determined by Sonication extraction even when all data is forced to be included in the data sample population at the 90 percent confidence level.

Comparison of Extraction Methods

Since the analytical results of both methods were found to be statistically equivalent, it is of interest to compare the two methods to determine if there is any advantage in using one over the other. In order to make a comparison, the CDM laboratory personnel were asked to prepare a summary of the material and labor time required to analyze a batch of samples using each of the methods. A batch size of 10 samples was chosen because the Soxhlet apparatus can only process 12 samples at a time, and each batch must also be accompanied by either one or two QA samples, such as duplicates or blanks. The Sonication apparatus processes 1 sample at a time, and this assumption was used in developing the cost of sample preparation.

Each sample analysis for total petroleum hydrocarbon consists of the following steps: sample preparation, extraction, analysis by infrared spectrophotometry, and cleanup of extraction and analytical apparatus.

A summary of the costs and labor required for each extraction method is presented in Tables 26 and 27. The sample preparation and analysis by i.r. is similar for both methods. However, a significant difference can be seen in the amount of time required for the extraction process.

The Soxhlet method requires 1.6 hours per sample of interactive labor for all activities such as cleanup and reporting of data. This amount of time per sample is a total amount. Therefore, if two chemists were working to perform the analysis, one sample could be completely prepared with 0.8 hours of labor for each chemist. However, each batch of samples require an extraction time of four hours in addition to the 1.6 hours per sample. A batch of 10 samples would take 16 labor hours plus 4 hours of extraction time.

The Sonication method requires less time than the Soxhlet method. The total amount of time required per sample, including time extracting in the Sonication apparatus, is 1.4 hours per sample.

The capital equipment costs and expendable item cost is comparable for the two methods, as shown in Tables 26 and 27. The expendable item cost for the Soxhlet method is 17.2 dollars per sample and the cost for the Sonication method is 15.4 dollars per sample.

TABLE 26. COST SUMMARY OF SOXHLET METHOD OF TPH ANALYSIS

Activity	Time Requirement In Total Labor Hours	Expendable Items	Capital Equipment Cost
Sample Preparation	0.2 hr/sample	Acid $0.2/Sample Magnesium Sulfate $1.8/sample	Beakers, 250 ml Heavy Duty $3.25/each
Extraction	0.3 hrs for sample set up and breakdown time	Freon $3.0/sample Extraction thimble $2.00/sample	Extract Glassware $160.00/each
Analysis by I.R. Spectrophotometry (To Report Stage)	0.9 hr/sample	Freon $5.0/sample Silica Gel $1.2/sample	IR Spectrophotometer IR Cells $1100-$1500/pair
Cleanup of Extraction and Analytical Apparatus	0.2 hr/sample	Acids and Freon $4.00/sample	Drying Oven
Summary	1.6 hr/sample interactive labor 4 hr/batch extraction time	$17.2/sample	

TABLE 27. COST SUMMARY OF SONICATION METHOD OF TPH ANALYSIS

Activity	Time Requirement In Total Labor Hours	Expendable Items	Capital Equipment Cost
Sample Preparation	0.2 hr/sample	Acid $0.2/Sample Magnesium Sulfate $1.8/sample	Beakers, 250 ml Heavy Duty $3.25/each
Extraction	0.2 hr/sample	Freon $6.2/sample	Sonication Extractor $4,000 Extraction Beakers $3.25/each
Analysis	0.9 hr/sample	Freon $5.0/sample Silica Gel $1.2/sample	IR Spectrophotometer IR Cells $1100-$1500/pair
Cleanup of Extraction and Analytical Apparatus	0.1 hr/sample	Acids and Freon $1.00/sample	Drying Oven
Summary	1.4 hr/sample	$15.4/sample	

Since both methods produce statistically similar results, the Sonication method is preferable for use for several reasons. Since the extraction time for the sample is about 10 minutes versus 4 hours for the Soxhlet method, a sample can be quickly turned-around by the laboratory for more immediate results. The lab can produce results using the Sonication method as quickly as two hours after receipt of the sample. Another advantage to Sonication is that this method can easily handle water samples with high solids content, whereas the Soxhlet method can be used only for solid matrix samples. In addition, the Sonication method requires less transferring of sample from various laboratory glassware thus reducing the chance of spill, breakage, and loss of sample. The Sonication extraction unit takes up less lab space than the Soxhlet apparatus, and the unit does not have to be placed in a hood (although it should be vented through tubing into a hood) whereas the Soxhlet method should be placed in a hood to capture any escaping freon vapors.

One disadvantage of using the Sonication extractor is that the unit is somewhat loud, and noise reduction housing is required for use of the unit.

Summary and Conclusions

A sample of SSM spiked with diesel and waste-oil were submitted to the CDM laboratory for analysis of total petroleum hydrocarbon using both the Soxhlet and Sonication method. Both soil matrices were analyzed at least 14 times using each of the two methods and the results were statistically evaluated. The statistical evaluation indicates that within a 90 percent confidence level, the sample results from the two methods are within a 10 percent range.

The Sonication method is preferable for use because, although the material cost is similar, the time required for sample preparation is less. The Soxhlet method requires that the samples extract for four hours, whereas the Sonication method requires only 10 minutes per sample of extraction time. The reduced extraction time provides the benefit of increased flexibility for lab scheduling, and quicker turnaround of sample results, if needed.

No drawbacks are currently known regarding the use of the Sonication method over the Soxhlet method, except for the requirement of noise reduction housing on the Sonication apparatus for lab personnel safety.

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APPENDICES

APPENDIX A

SENSITIVITY ANALYSIS CURVES FOR OPERATIONAL PARAMETERS ON GASOLINE AND DIESEL CONTAMINATED SSM - PHASE I

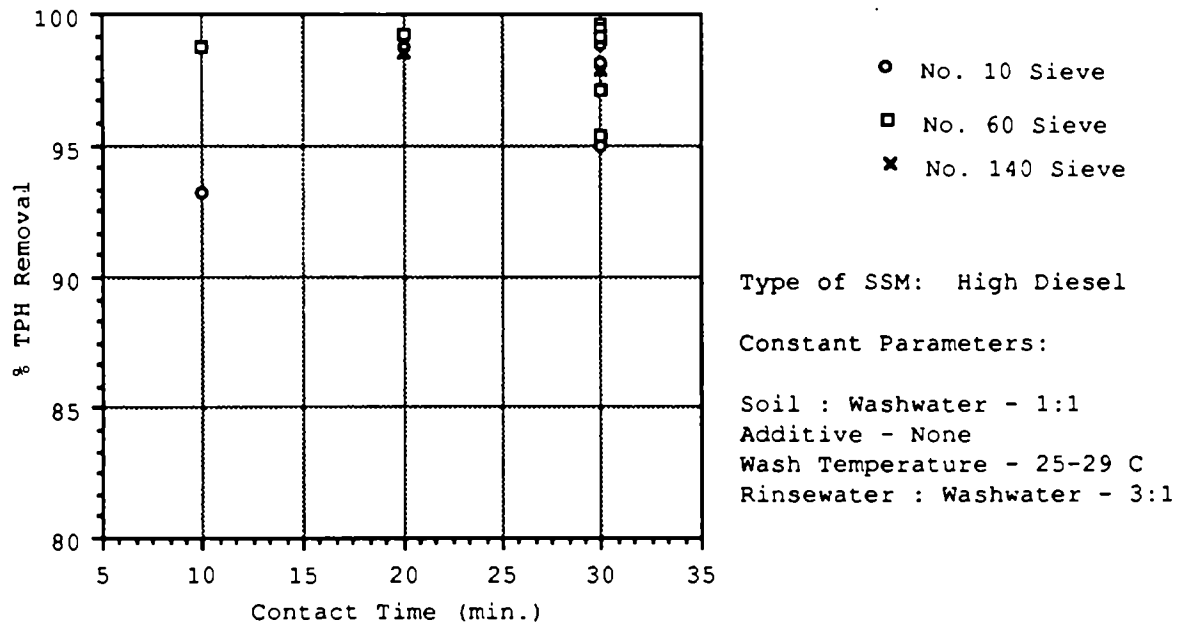


Figure A1. Contact time effect on percent TPH removal.

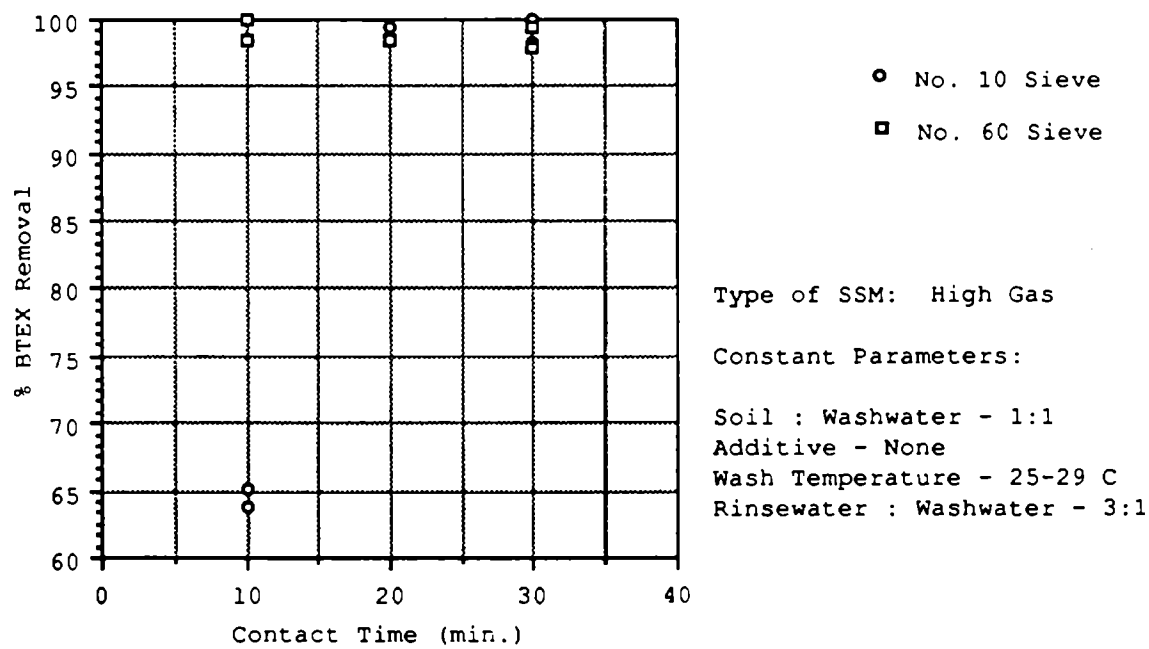


Figure A2. Contact time effect on percent BTEX removal.

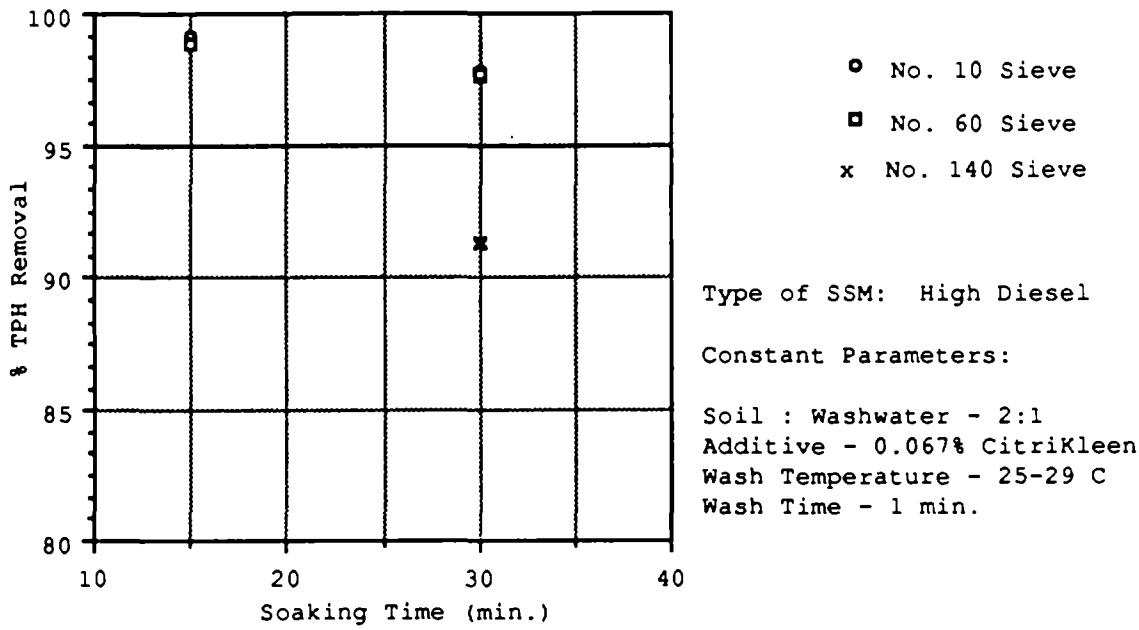


Figure A3. Soaking time effect on percent TPH removal with 0.067% CitriKleen.

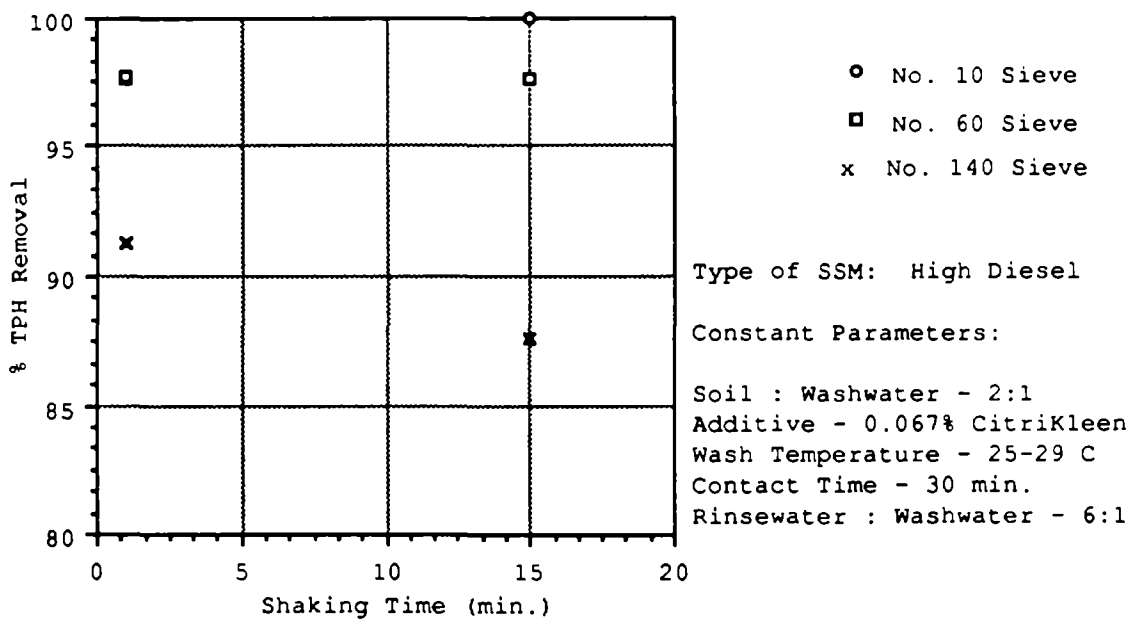


Figure A4. Shaking time effect on percent TPH removal with 0.067% CitriKleen.

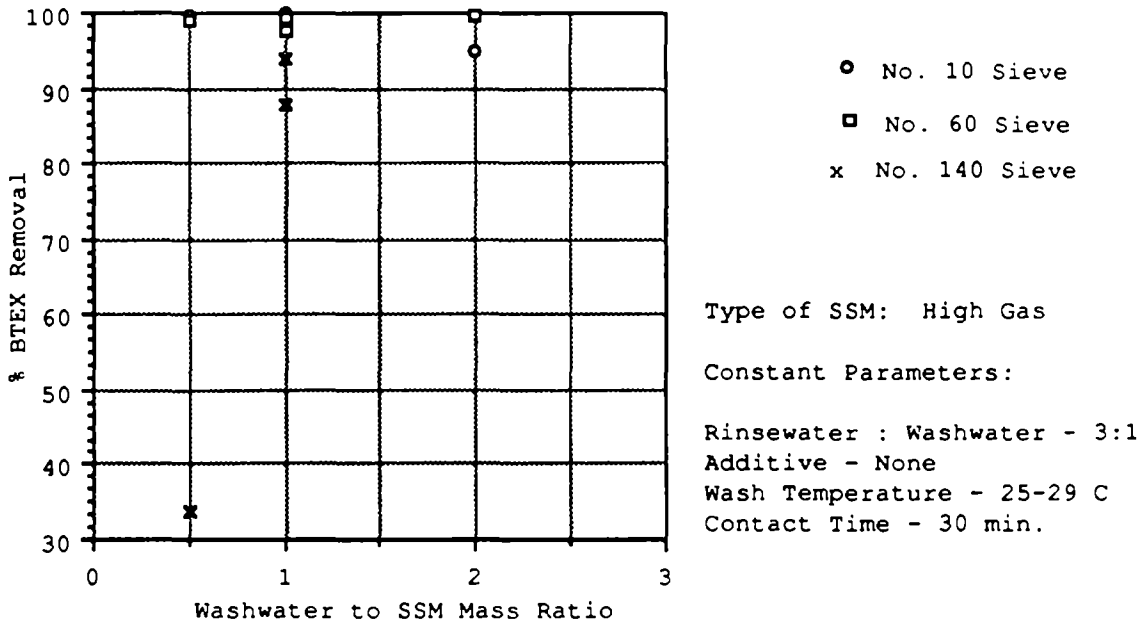


Figure A5. Washwater to soil ratio effect on percent BTEX removal.

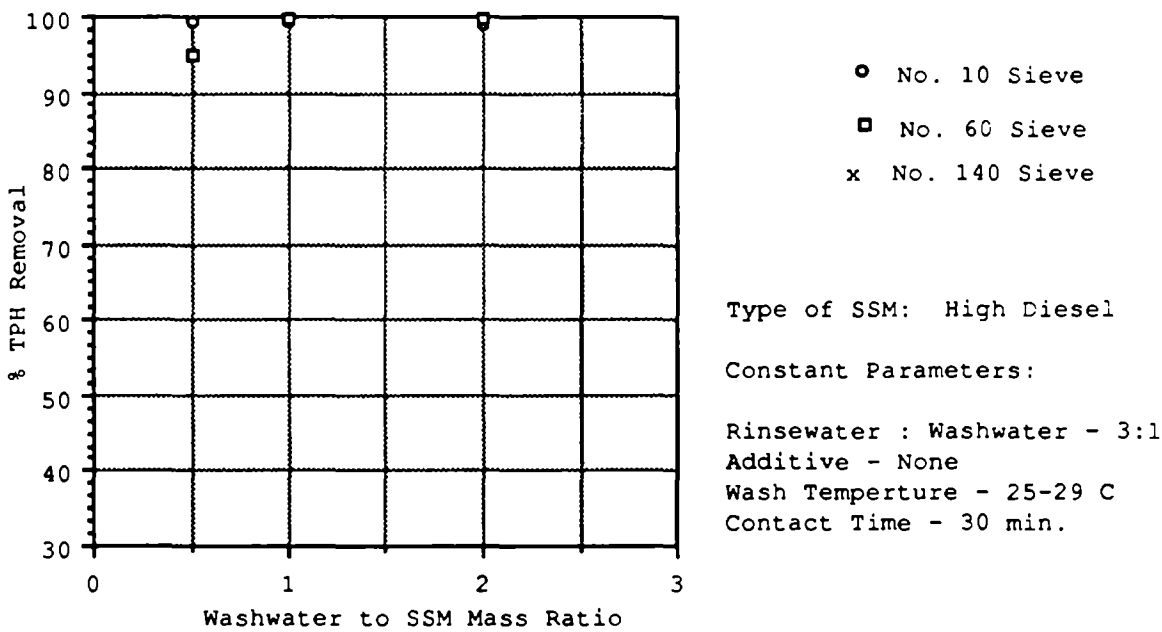


Figure A6. Washwater to soil ratio effect on percent TPH removal.

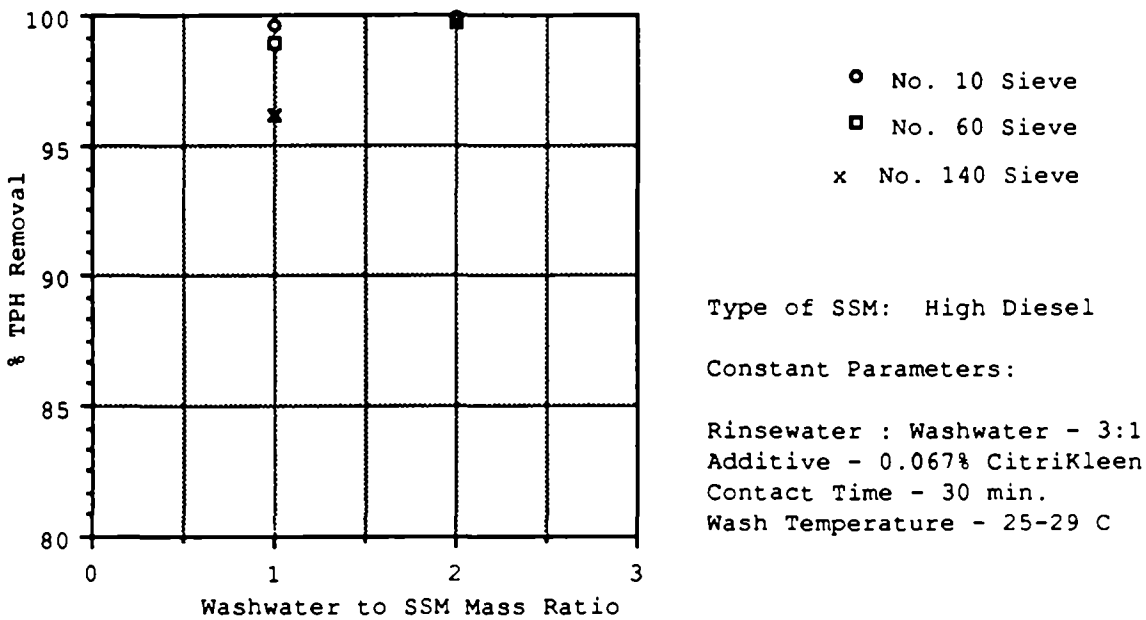


Figure A7. Washwater to soil ratio effect on percent TPH removal with 0.067% CitriKleen.

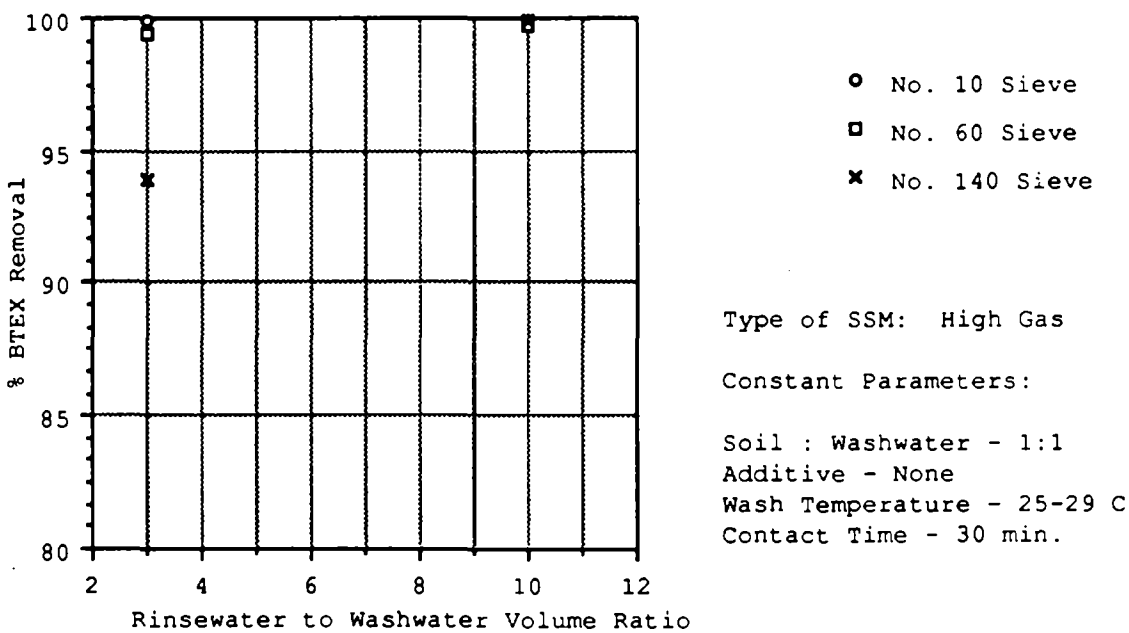


Figure A8. Rinsewater to washwater ratio effect on percent BTEX removal.

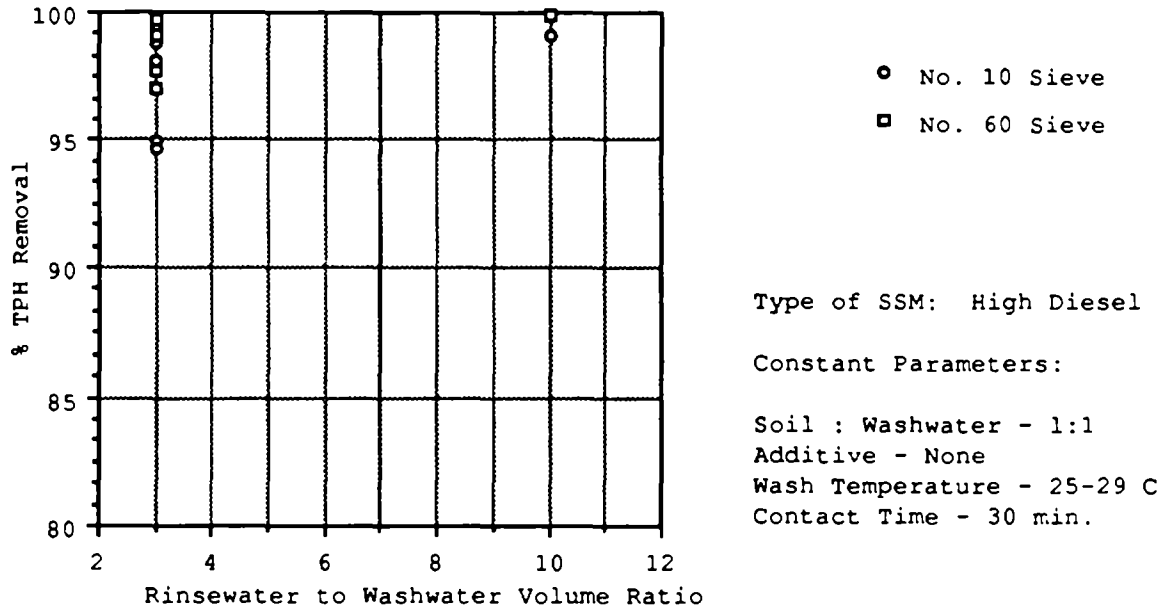


Figure A9. Rinsewater to washwater ratio effect on percent TPH removal.

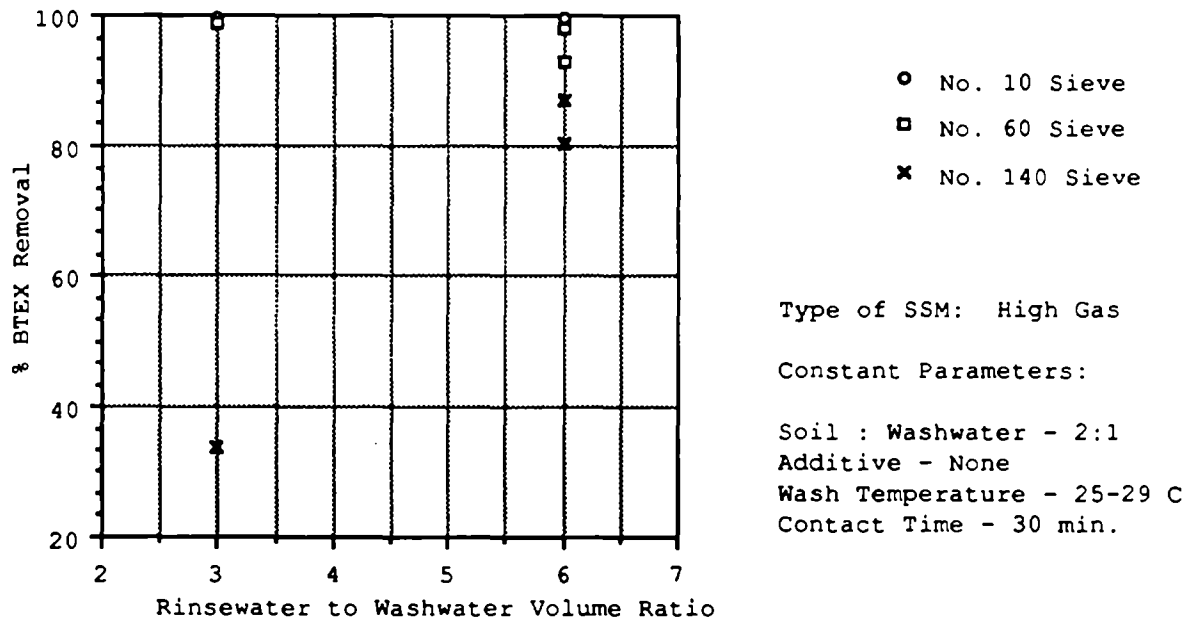


Figure A10. Rinsewater to washwater ratio effect on percent BTEX removal.

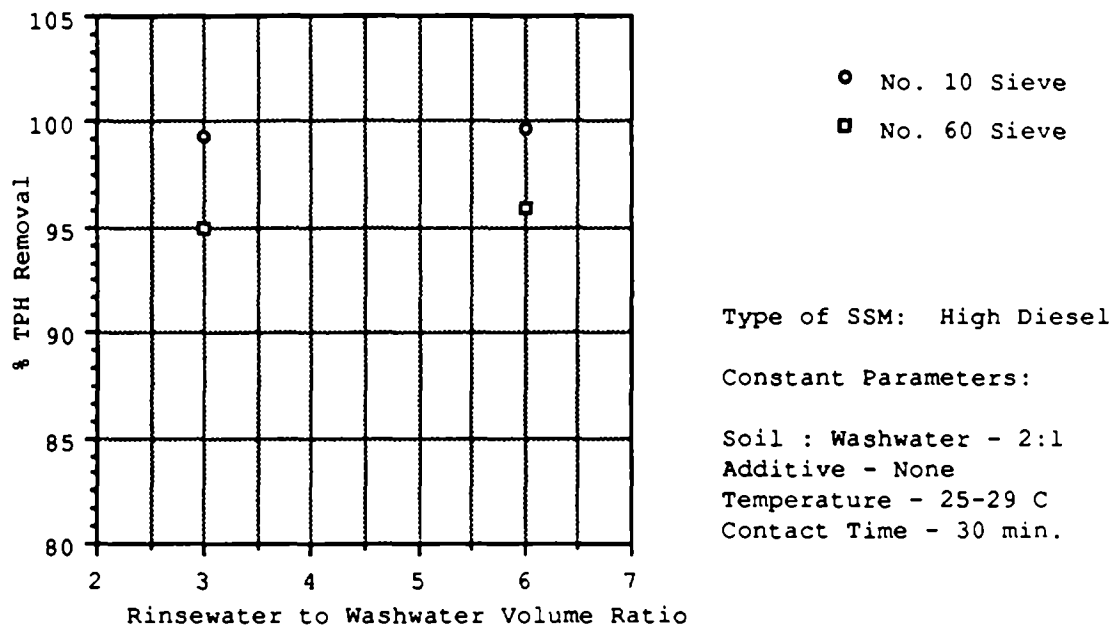


Figure A11. Rinsewater to washwater ratio effects on percent TPH removal.

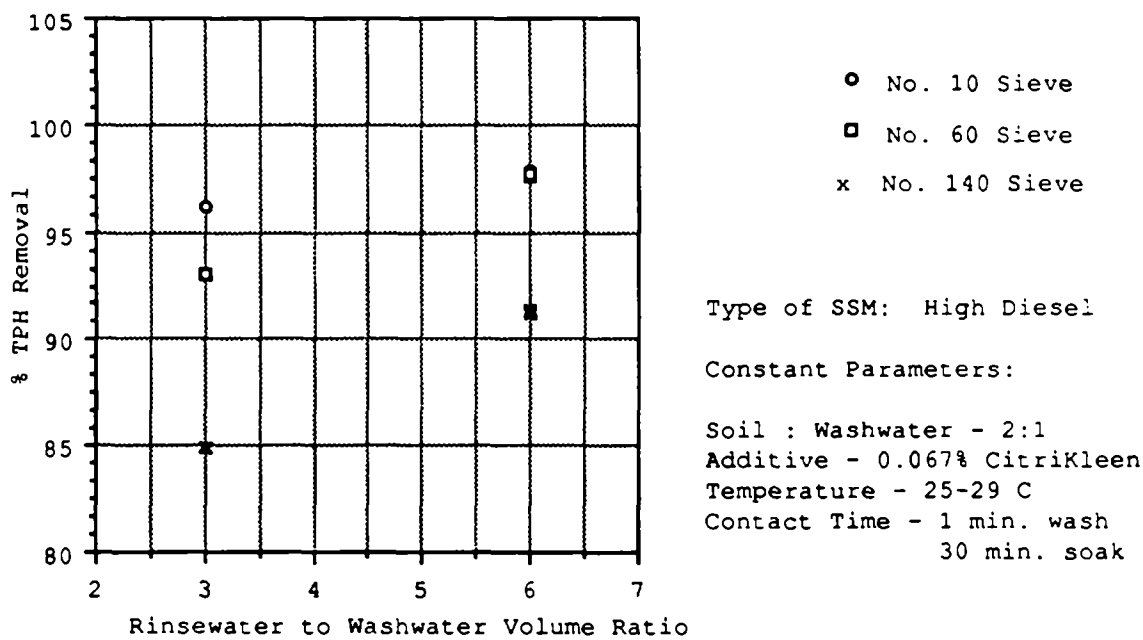


Figure A12. Rinsewater to washwater ratio effect on percent TPH removal.

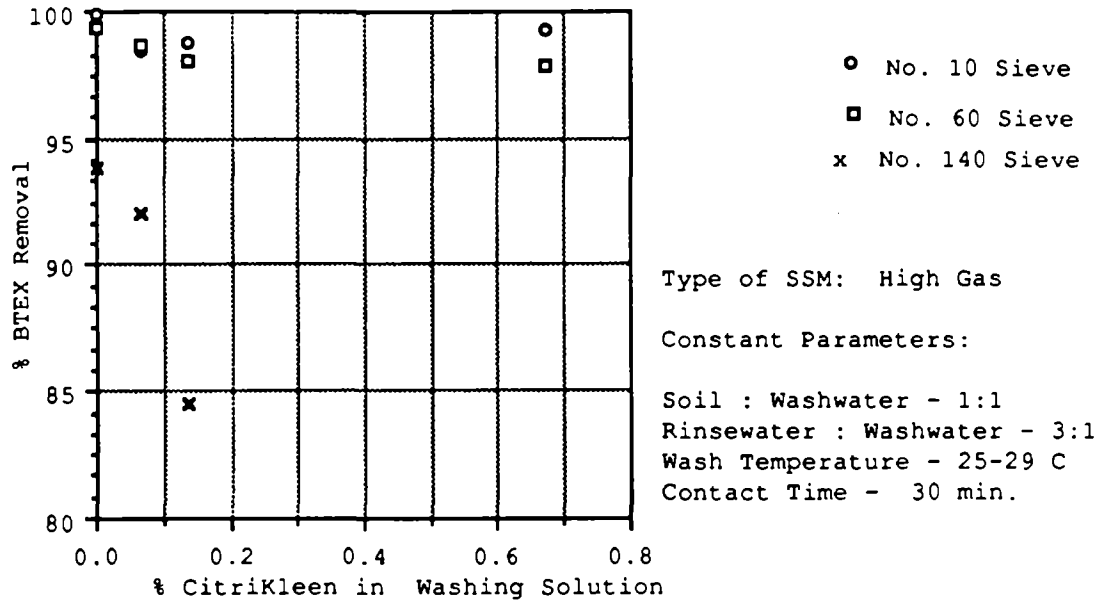


Figure A13. Percent CitriKleen effect on percent BTEX removal.

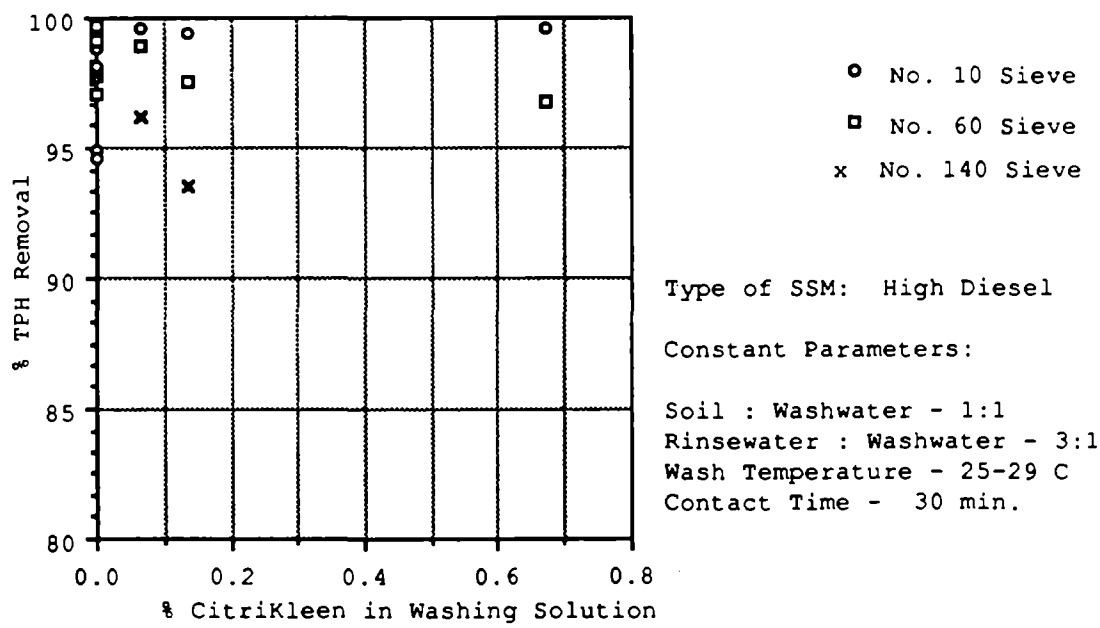


Figure A14. Percent CitriKleen effect on percent TPH removal.

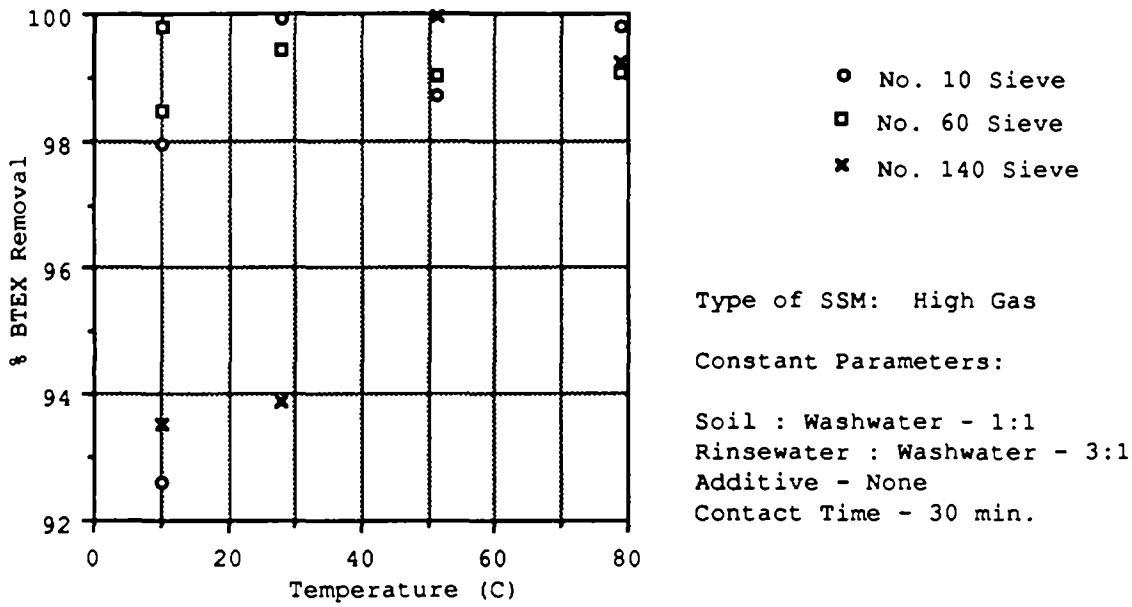


Figure A15. Temperature effect on percent BTEX removal

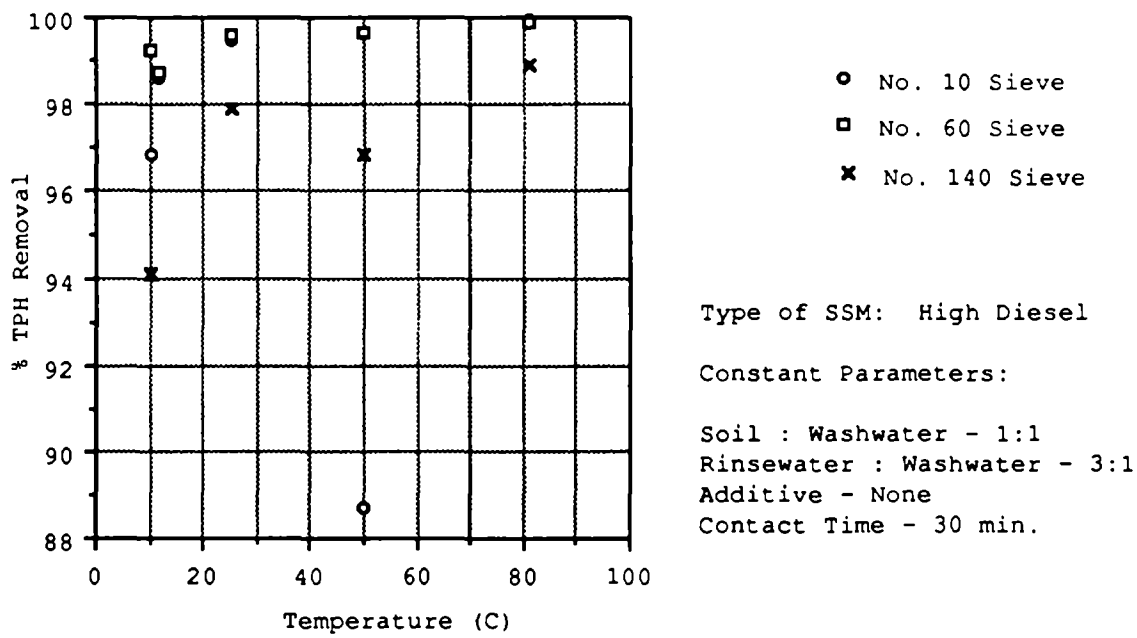
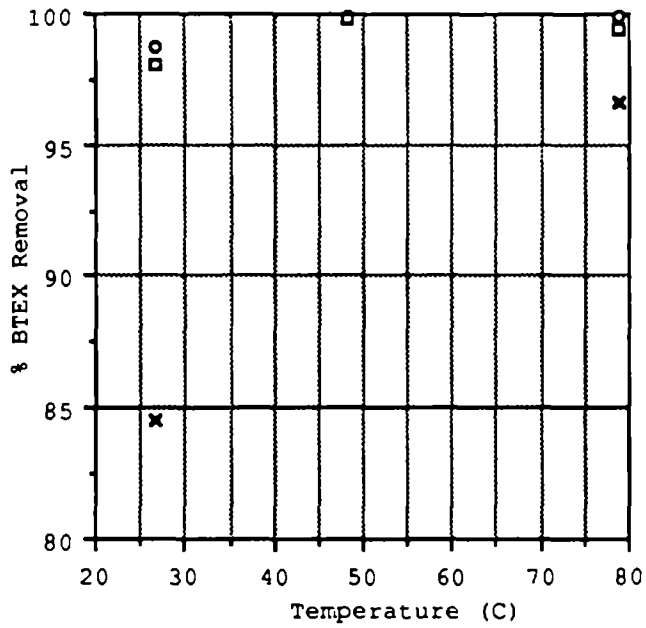


Figure A16. Temperature effect on percent TPH removal



No. 10 Sieve

No. 60 Sieve

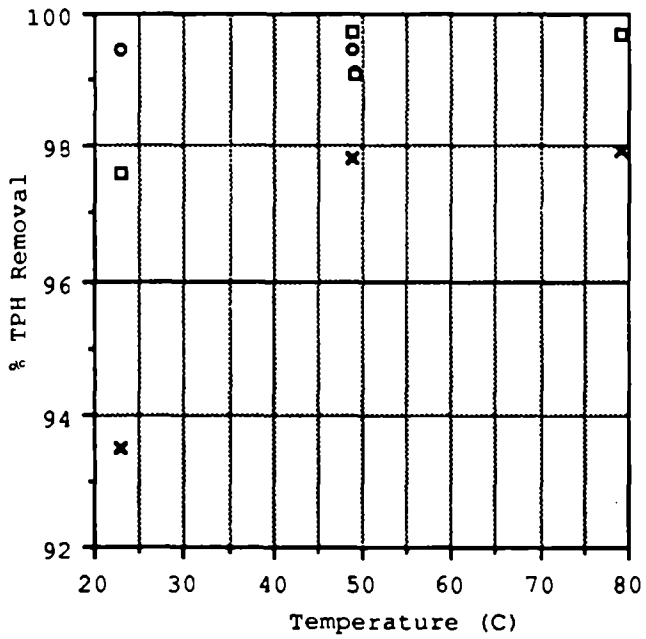
No. 140 Sieve

Type of SSM: High Gas

Constant Parameters:

Soil : Washwater - 1:1
Rinsewater : Washwater - 3:1
Additive - 0.13% CitriKleen
Contact Time - 30 min.

Figure A17. Temperature effect on percent BTEX removal with 0.13% CitriKleen



No. 10 Sieve

No. 60 sieve

No. 140 Sieve

Type of SSM: High Diesel

Constant Parameters:

Soil : Washwater (mass)- 1:1
Rinsewater : Washwater - 3:1
Additive - 0.13% CitriKleen
Contact Time - 30 min.

Figure A18. Temperature effect on percent TPH removal with 0.13% CitriKleen.

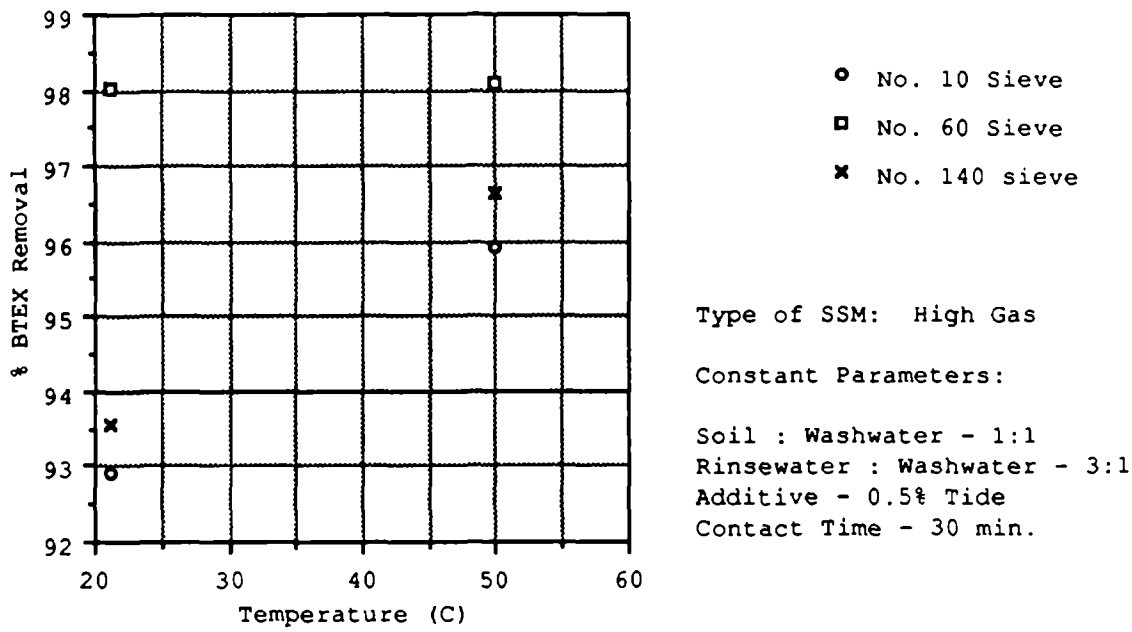


Figure A19. Temperature effect on percent BTEX removal with 0.5% Tide.

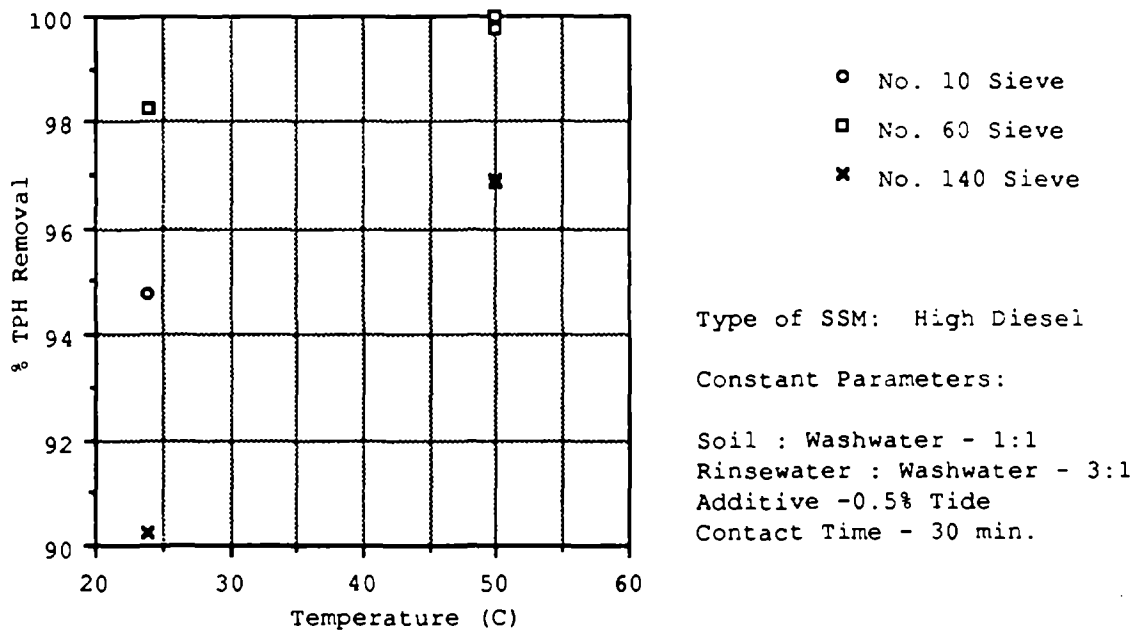


Figure A20. Temperature effect on percent TPH removal with 0.5% Tide.

APPENDIX B

PARTICLE SIZE DISTRIBUTION CURVES FOR BENCH SCALE SSM SOIL WASHING EXPERIMENTS - PHASE I

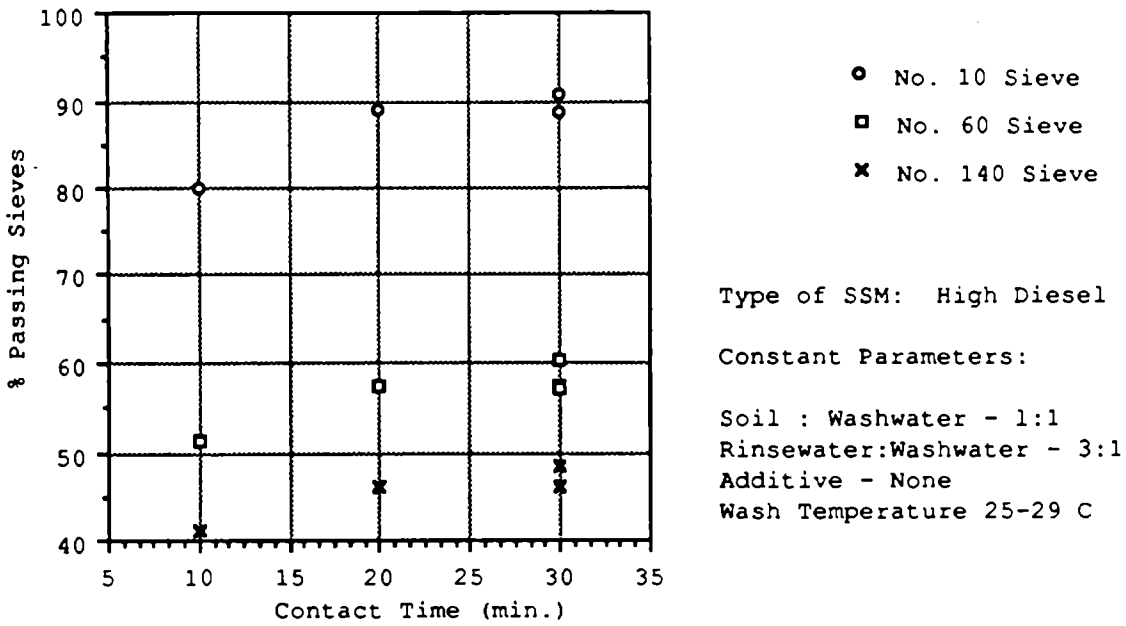


Figure B1. Contact time effect on particle size distribution for diesel contaminated soil.

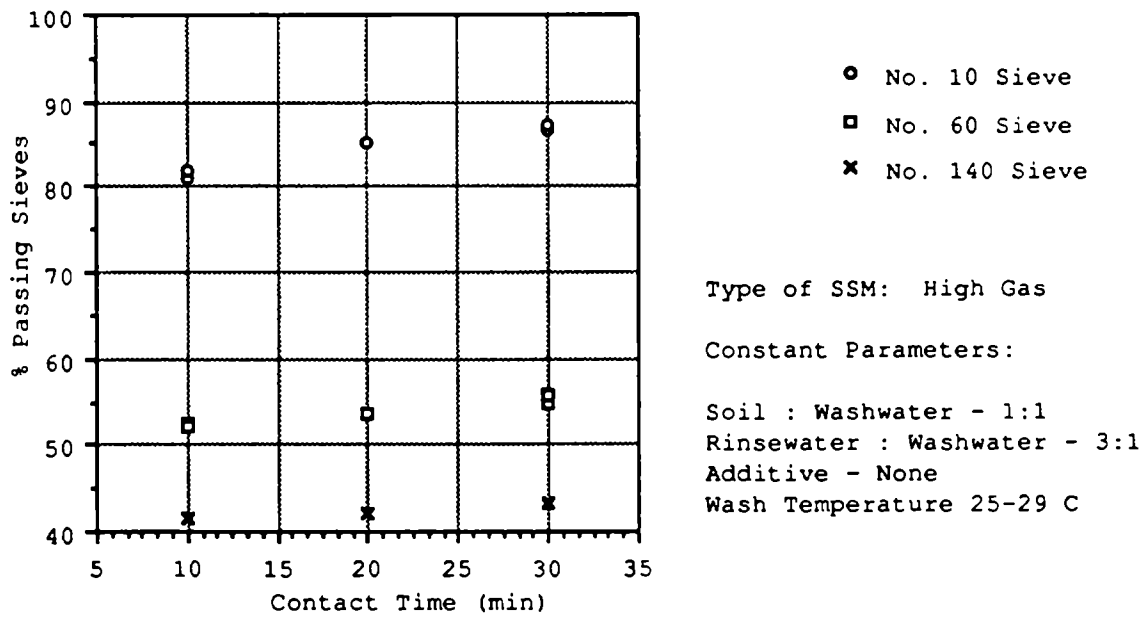


Figure B2. Contact time effect on particle size distribution for gasoline contaminated soil

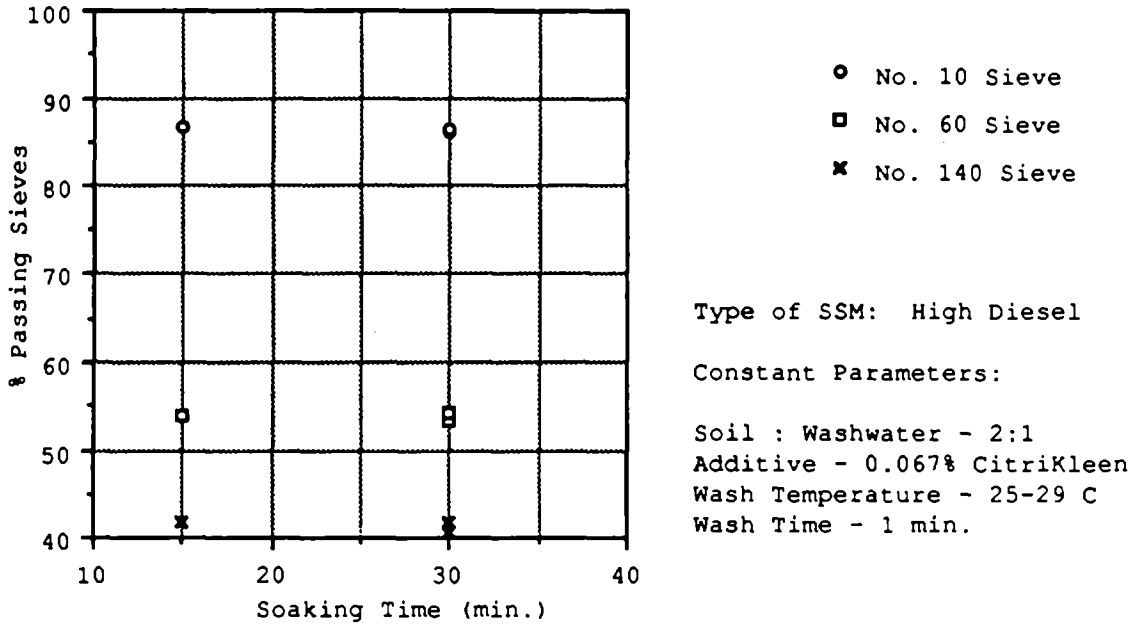


Figure B3. Soaking time effect on particle size distribution for diesel contaminated soil.

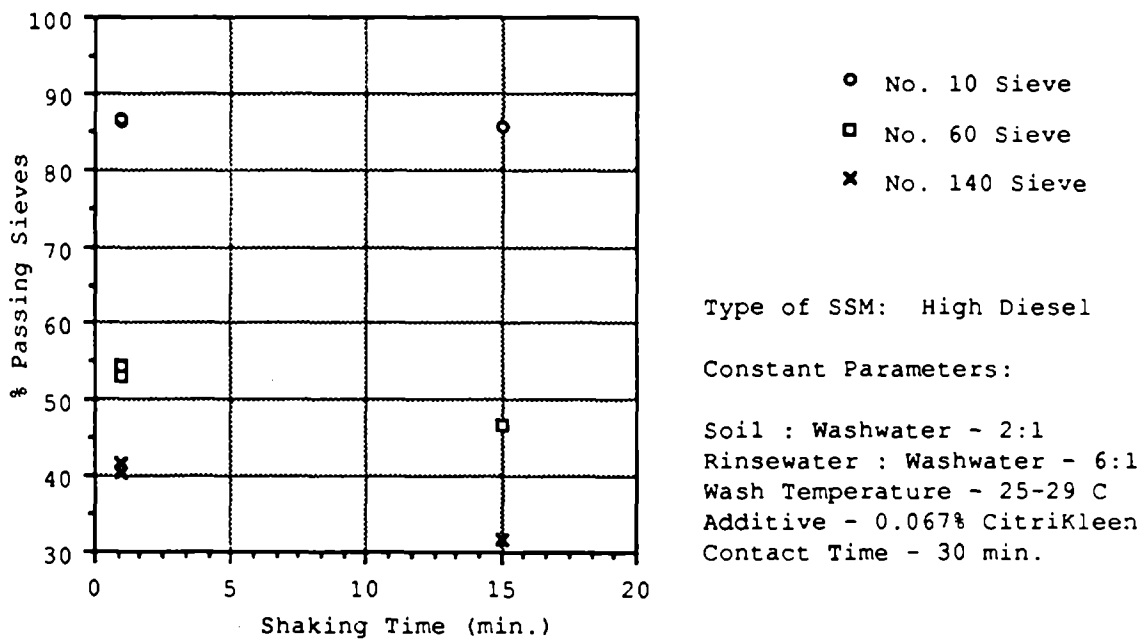


Figure B4. Shaking time effect on particle size distribution for diesel contaminated soil.

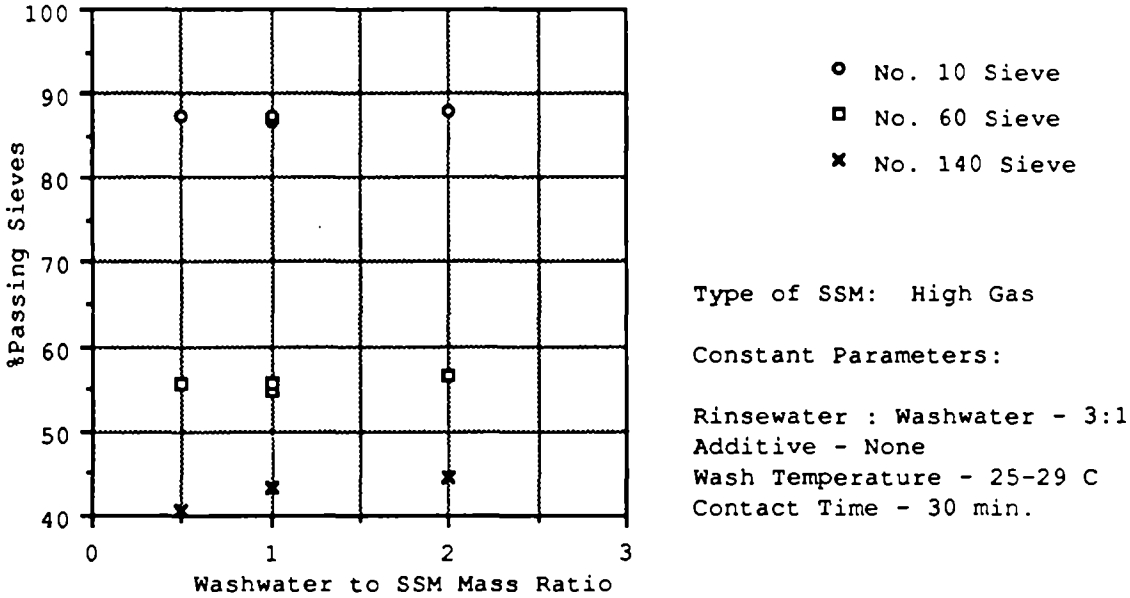


Figure B5. Washwater to soil ratio effect on particle size distribution for gasoline contaminated soil.

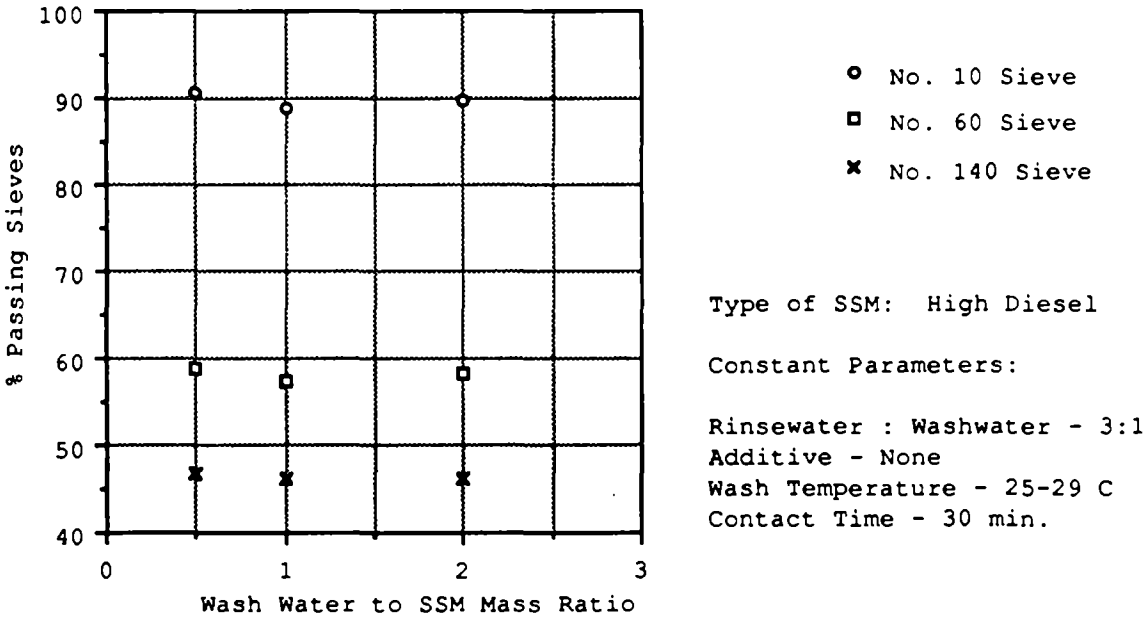
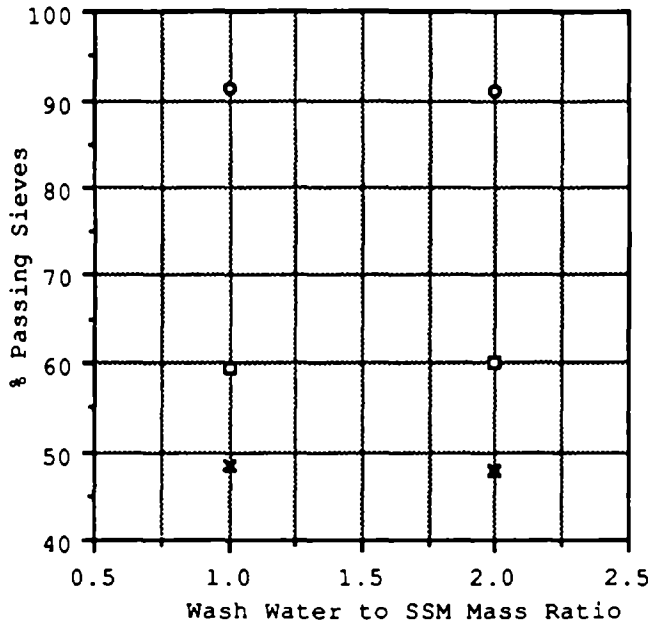


Figure B6. Washwater to soil ratio effect on particle size distribution for diesel contaminated soil.



No. 10 Sieve

No. 60 Sieve

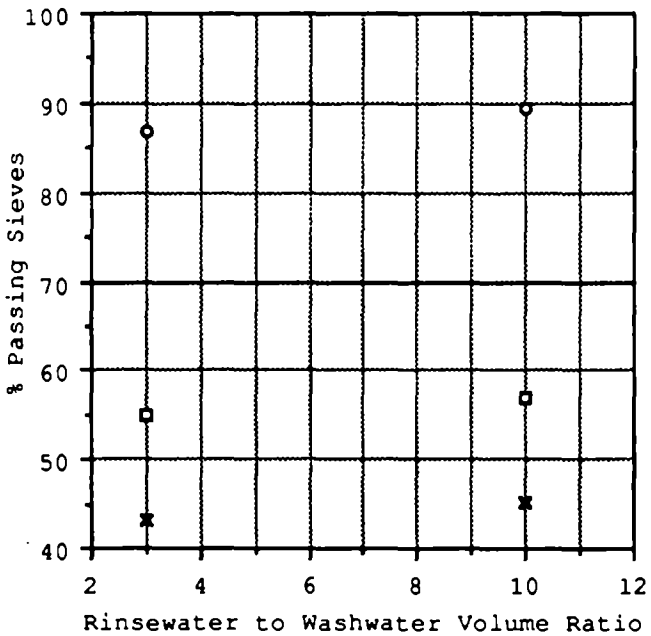
No. 140 Sieve

Type of SSM: High Diesel

Constant Parameters:

Rinsewater : Washwater - 3:1
Additive - 0.067% CitriKleen
Wash Temperature - 25-29 C
Contact Time - 30 min.

Figure B7. Washwater to soil ratio effect on particle size distribution for diesel contaminated soil with 0.067% CitriKleen.



No. 10 Sieve

No. 60 Sieve

No. 140 Sieve

Type of SSM: High Gas

Constant Parameters:

Soil : Washwater - 1:1
Additive - None
Wash Temperature - 25-29 C
Contact Time - 30 min.

Figure B8. Rinsewater to washwater ratio effect on particle size distributio for gasoline contaminated soil.

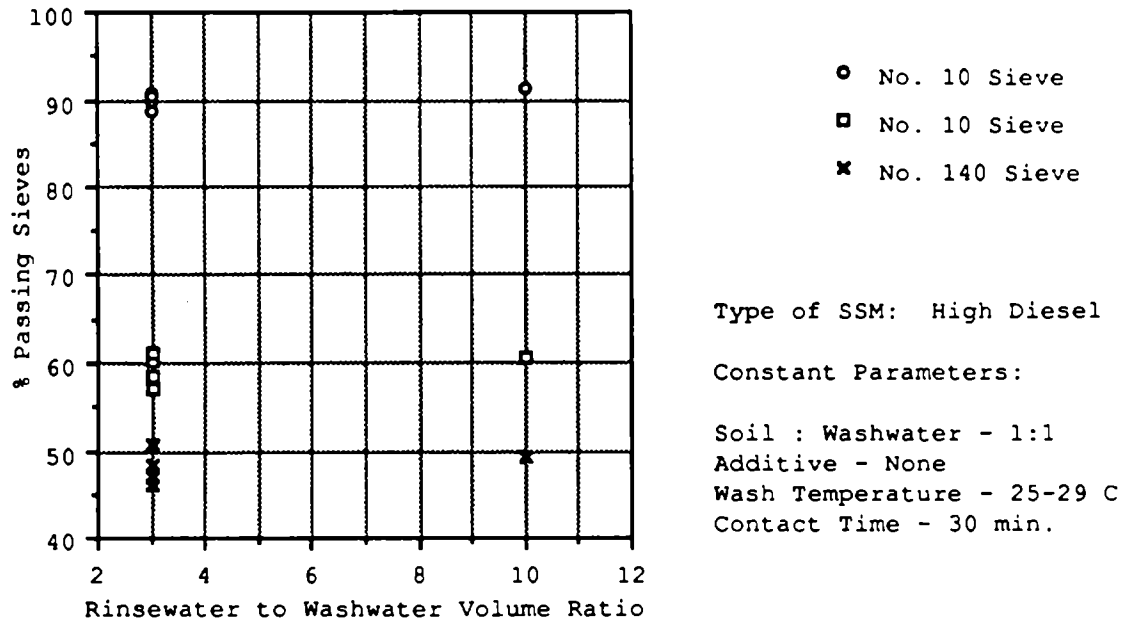


Figure B9. Rinsewater to washwater ratio effect on particle size distribution for diesel contaminated soil.

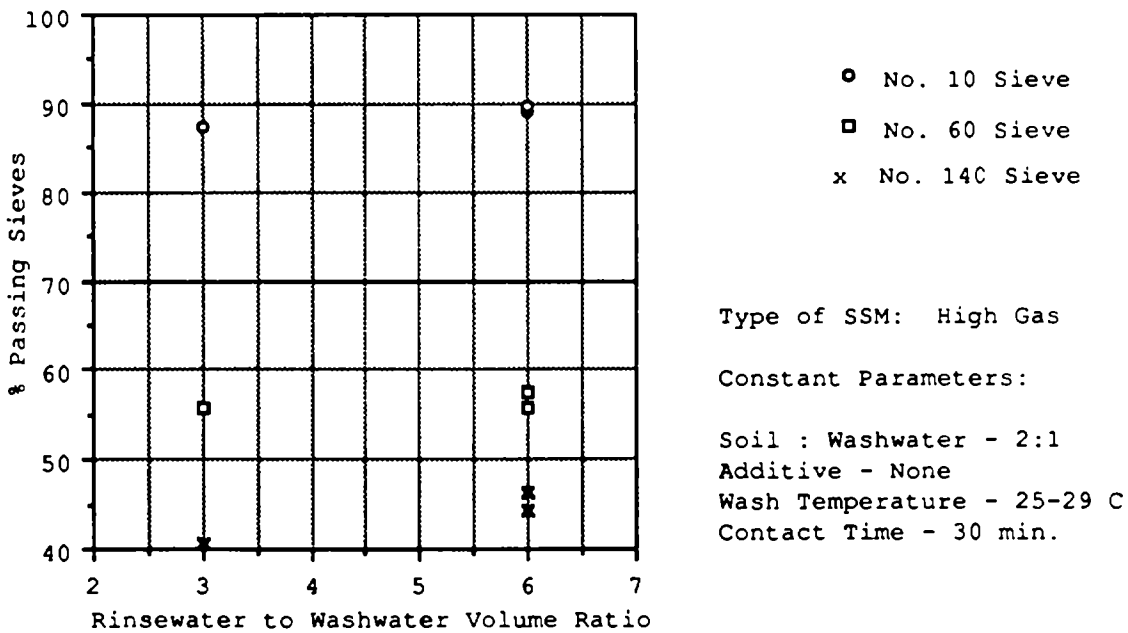


Figure B10. Rinsewater to washwater ratio effect on particle size distribution for gasoline contaminated soil.

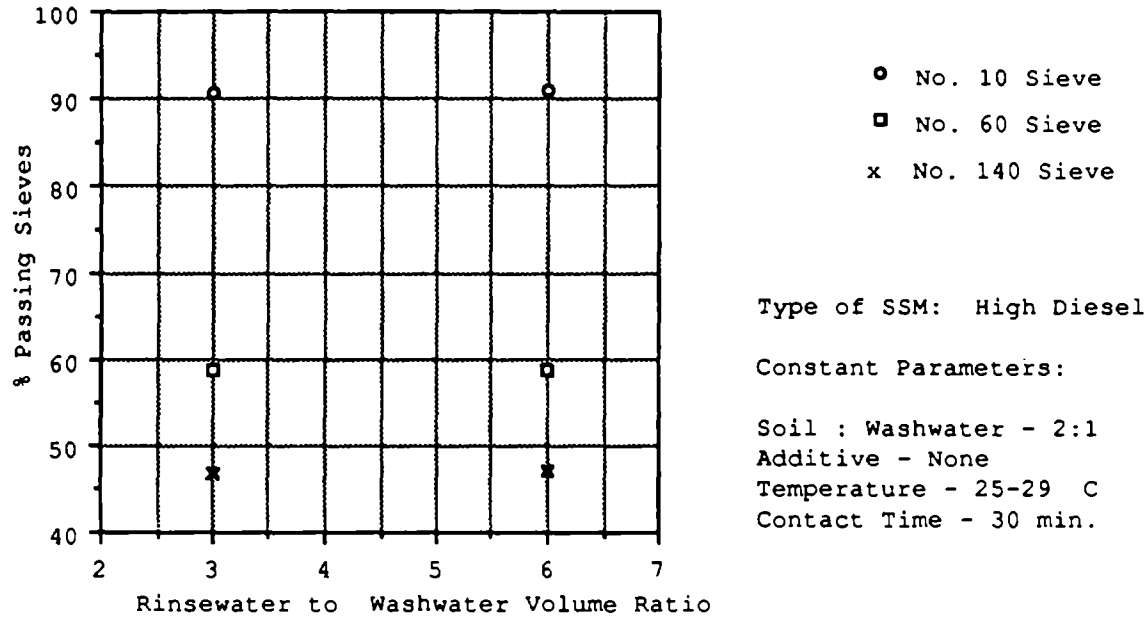


Figure B11. Rinsewater to washwater ratio effect on particle size distribution for diesel contaminated soil.

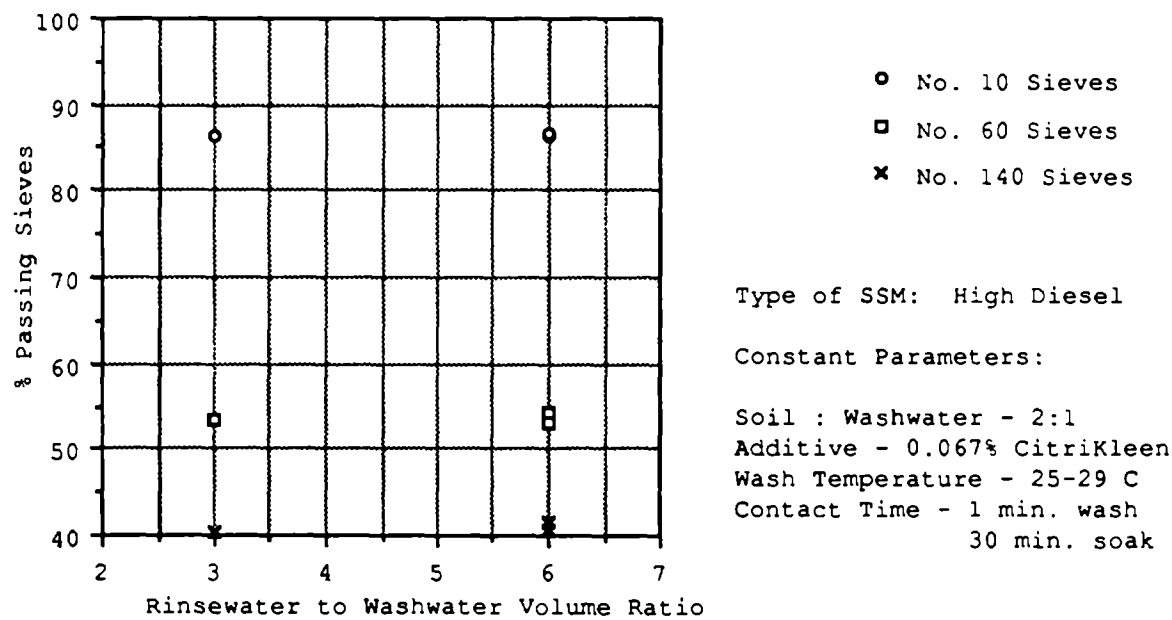


Figure B12. Rinsewater to washwater ratio effect on particle size distribution for diesel contaminated soil.

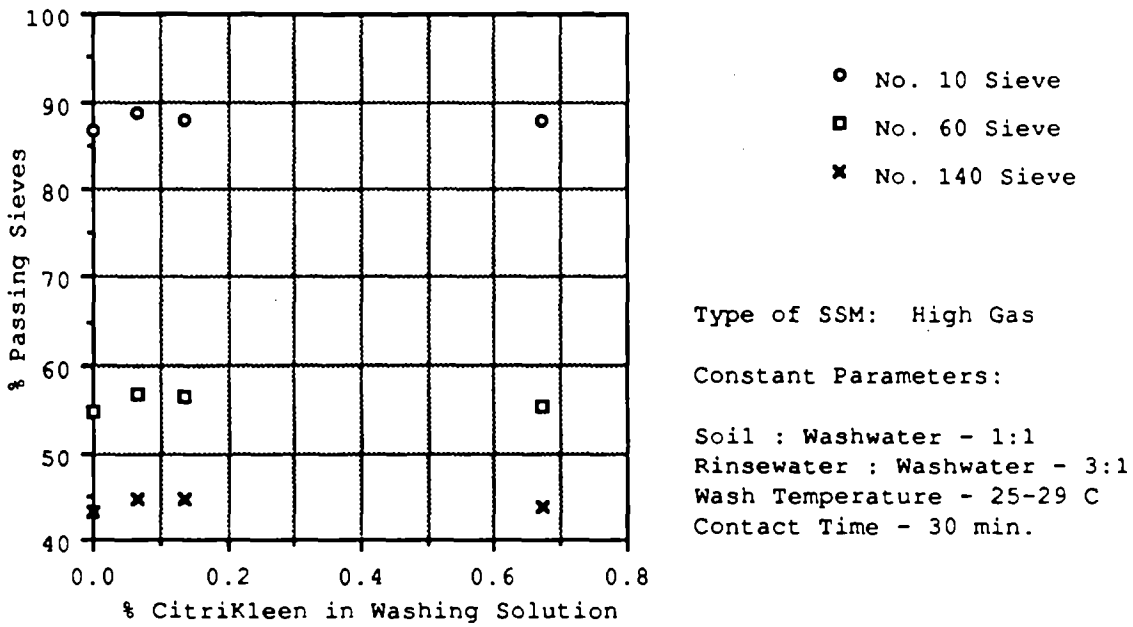


Figure B13. Percent CitriKleen effect on particle size distribution for gasoline contaminated soil.

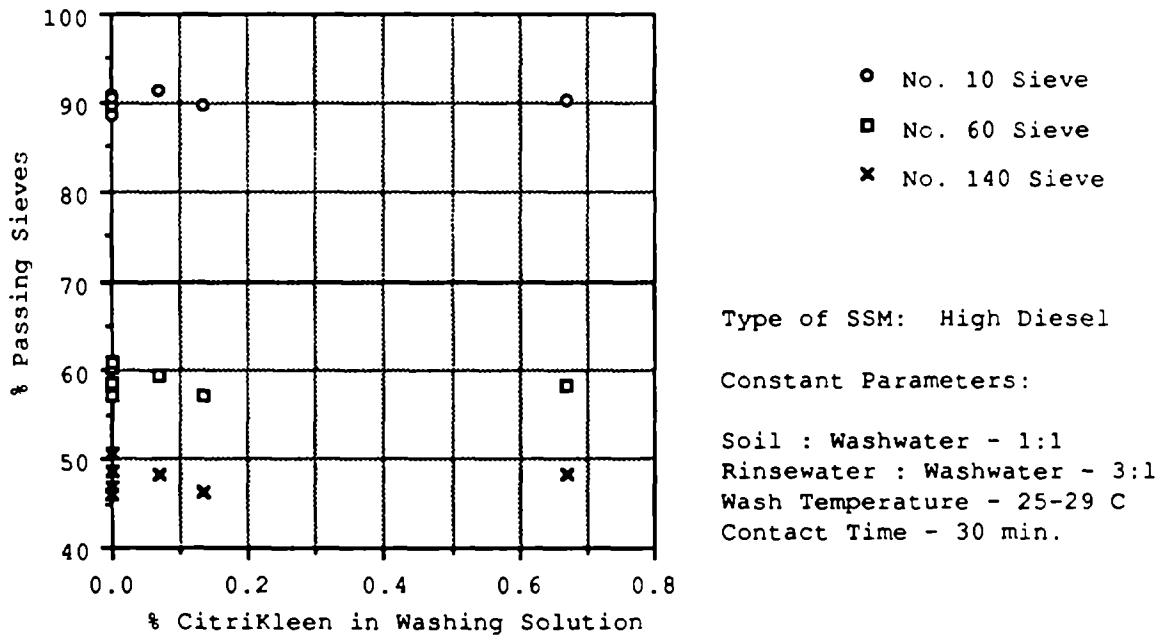


Figure B14. Percent CitriKleen effect on particle size distribution for diesel contaminated soil.

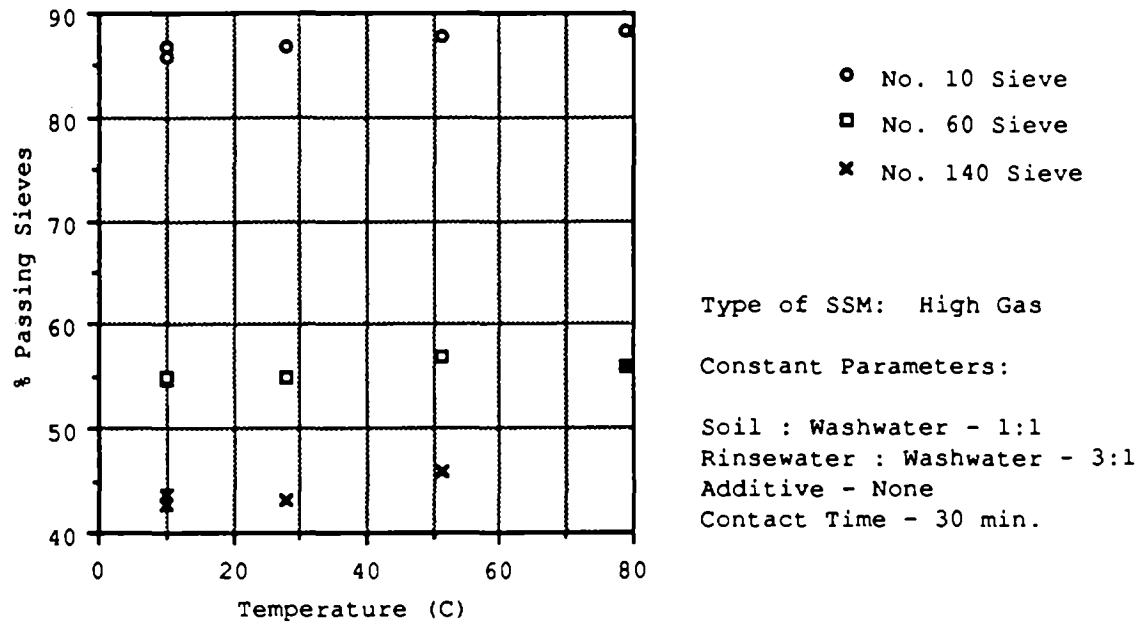


Figure B15. Temperature effect on particle size distribution for gasoline contaminated soil.

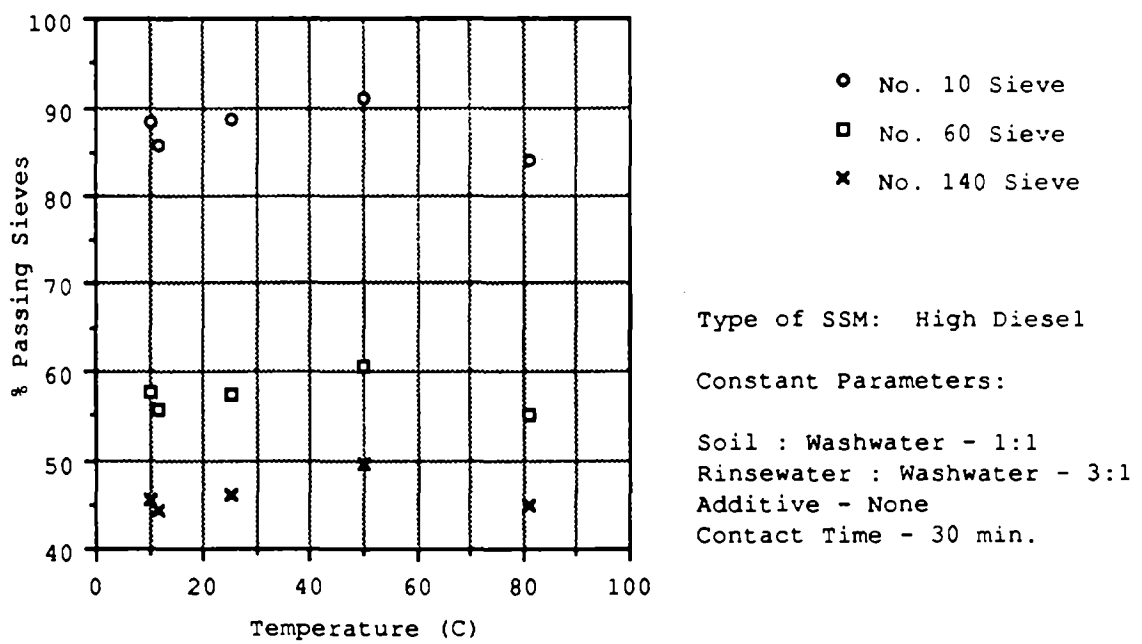


Figure B16. Temperature effect on particle size distribution for diesel contaminated soil.

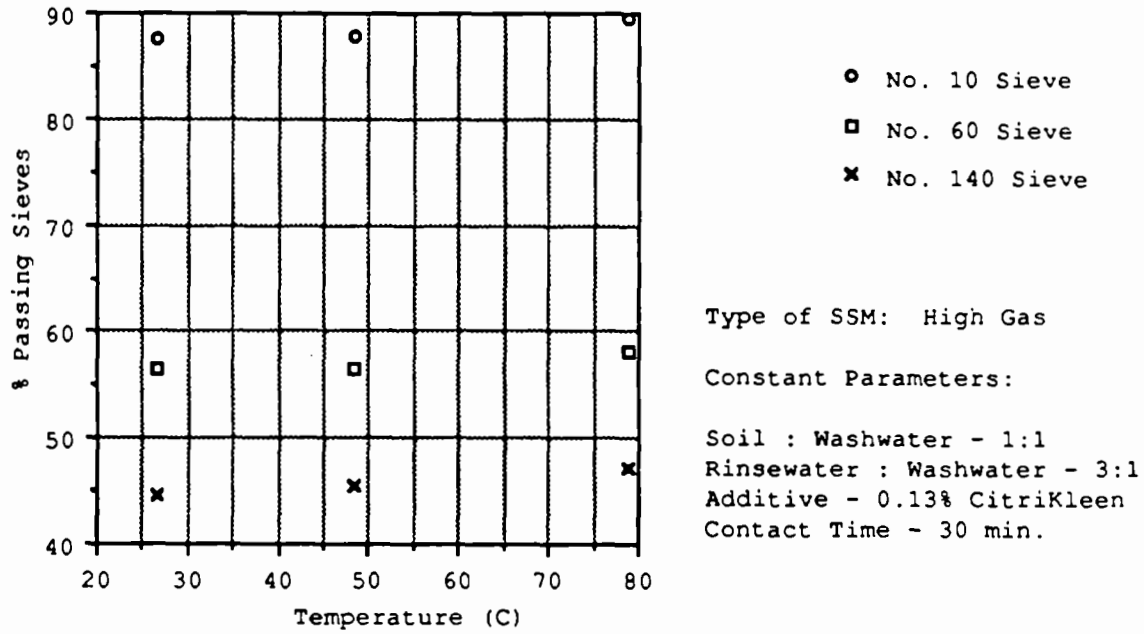


Figure B17. Temperature effect on particle size disribution for gasoline contaminated soil with 0.13% CitriKleen.

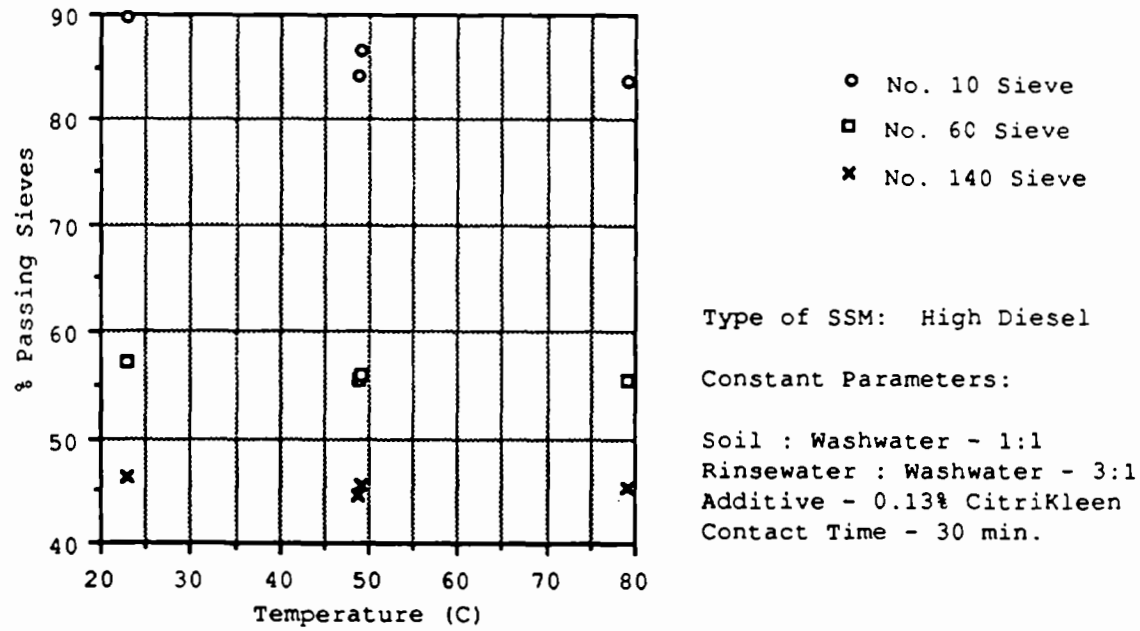
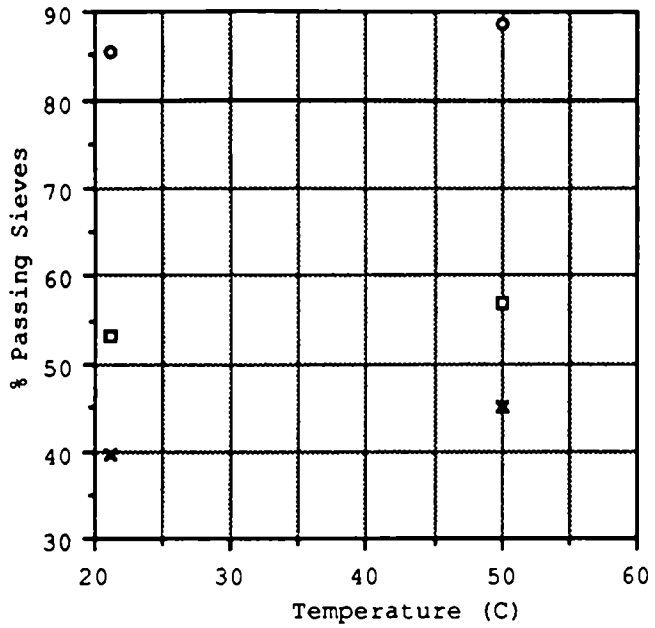


Figure B18. Temperature effect on particle size distribution for diesel contaminated soil with 0.13% CitriKleen.



No. 10 Sieve

No. 60 Sieve

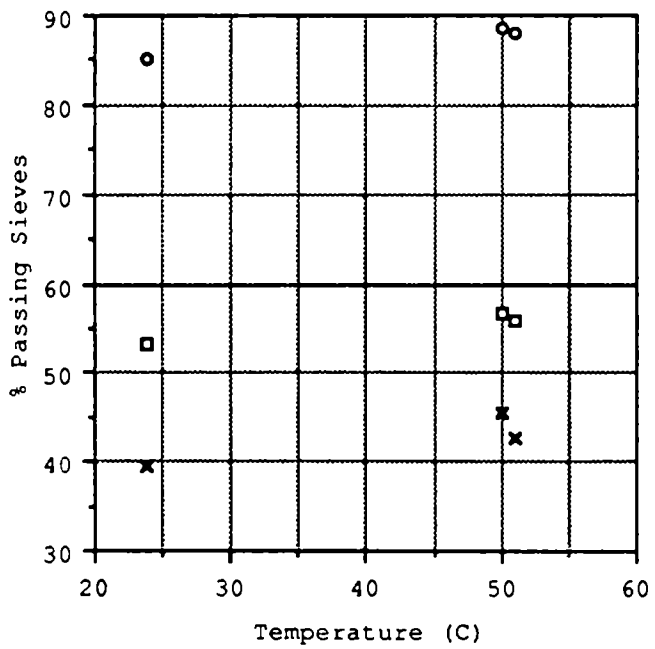
No. 140 Sieve

Type of SSM: High Gas

Constant Parameters:

Soil : Washwater - 1:1
Rinsewater : Washwater - 3:1
Additive - 0.5% Tide
Contact Time - 30 min.

Figure B19. Temperature effect on particle size distribution for gasoline contaminated soil with 0.5% Tide.



No. 10 Sieve

No. 60 Sieve

No. 140 Sieve

Type of SSM: High Diesel

Constant Parameters:

Soil : Washwater - 1:1
Rinsewater : Washwater - 3:1
Additive - 0.5% Tide
Contact Time - 30 min.

Figure B20. Temperature effect on particle size distribution for diesel contaminated soil with 0.5% Tide.