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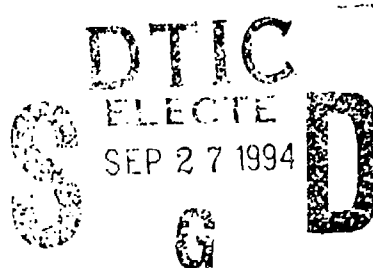
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September 1994

## Interactions of Liquid Propellant/LP XM46 with Soils

by Judith C. Pennington, Cynthia B. Price, Douglas Gunnison,  
Donald W. Rathburn, Tommy E. Myers, Ann B. Strong,  
Jesse M. Harrington, Jimmy L. Stewart, Jennifer A. Busby, WES

Donald Dean Adrian, Louisiana State University

John R. Marcev, American Scientific International Corporation



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Jesse M. Harrington, Jimmy L. Stewart, Jennifer A. Busby

U.S. Army Engineer  
Waterways Experiment Station  
3909 Halls Ferry Road  
Vicksburg, MS 39180-6199

Donald Dean Adrian

Louisiana State University  
Department of Civil Engineering  
Baton Rouge, LA 70803

John R. Marcev

American Scientific International Corporation  
1365 Beverly Road  
McLean, VA 22101

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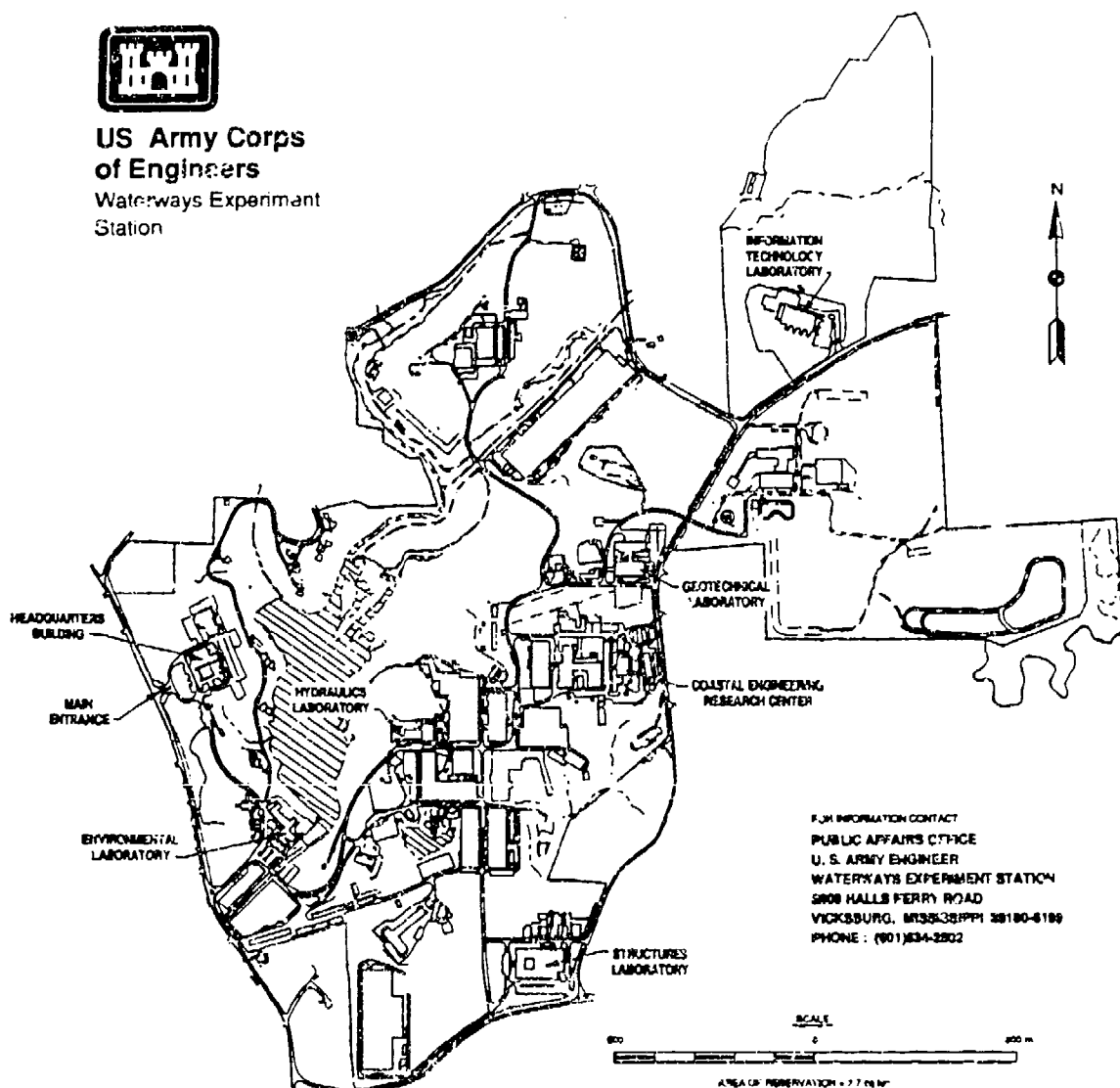
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# Preface

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The studies reported herein were conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The research was sponsored by the Office of Program Manager, Advanced Field Artillery System (AFAS)/Future Armored Resupply Vehicle (FARV), SFAE-FAS-AF Bldg 3159, Picatinny Arsenal, NJ.

The chapters of this report were authored by the following individuals:

|            |                                                                                                                                                                                                              |
|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chapter 1  | Judith C. Pennington, Cynthia B. Price, Jesse M. Harrington, Jimmy L. Stewart, and Jennifer A. Bushy, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL |
| Chapter 2  | Judith C. Pennington and Cynthia B. Price                                                                                                                                                                    |
| Chapter 3  | Donald Dean Adrian, Louisiana State University, and Tommy E. Myers, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL                                                     |
| Chapter 4  | Douglas Gunnison and Judith C. Pennington, EPEB, and John R. Marcev, American Scientific International (ASCI) Corporation                                                                                    |
| Appendix A | Donald W. Rathburn and Ann B. Strong, EED                                                                                                                                                                    |
| Appendix B | Donald W. Rathburn and Ann B. Strong                                                                                                                                                                         |

Technical advice was given by Mr. Richard A. Kam, Environmental Chemistry Branch (ECB), EED, and Dr. William M. Davis, EPEB. Technical assistance with Fourier Transform Infrared Spectroscopy (FTIR) on contact screening tests was provided by Ms. Cameron L. Young, Engineering and Science Branch (ESB), Concrete Technology Division (CTD), Structures Laboratory (SL), WES. Technical assistance with FTIR on asphalt characteristics and asphalt/liquid propellant interactions was provided by Mr. Larry N. Lynch, Materials Research and Construction Technology Branch, Pavement Systems Division, Geotechnical Laboratory (GL), WES. Assistance with soil collection was provided by Mr. Richard A. Price, Fate and Effects Branch, EPED, and by site personnel. Cement samples and characteristics of cements were provided by Dr. Toy S. Poole, Engineering Materials Group, ESB. Soil characterization tests were conducted by ECB; Soil Testing Facility, Soil Research Center, Soil and Rock Mechanic Division (S&RMD), GL; and Pettiet Agricultural Services, Leland, MS. Soils were classified according to the Unified Soil Classification System by Mr. Jesse C. Oldham, Soil Testing Facility, Soils Research Center,

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The study was conducted under the direct supervision of Dr. Richard E. Price, Acting Chief, EPEB; Mr. Norman R. Francinque, Jr., Chief, ERB; and Ms. Ann B. Strong, Chief, ECB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED; Dr. Raymond L. Montgomery, Chief, EED; and Dr. John W. Keeley, Director, EL.

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# Conversion Factors, Non-SI to SI Units of Measurement

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Non-SI units of measurement used in this report can be converted to SI units as follows:

| Multiply              | By       | To Obtain        |
|-----------------------|----------|------------------|
| feet                  | 0.3048   | meters           |
| gallons (U.S. liquid) | 3.785412 | cubic decimeters |
| inches                | 25.4     | millimeters      |
| pounds (force)        | 4.448222 | newtons          |

# Summary

---

Development of an effective spill response plan required elucidation of the potential interactions between soils and the spilled liquid propellant (LP). Determining the potential immediate hazards of a spill to exposed personnel, as well as immediate and longer term hazards to the environment, required an understanding of some of the basic chemical and physical interactions of LP with soils. The studies reported herein provide the data necessary to anticipate these interactions.

The research was conducted in the following four parts: soil characterization and contact screening; batch sorption; runoff, infiltration and movement; and effects on soil microflora. In addition to these tests, an analytical method was developed to detect environmentally significant concentrations of LP components in soils and water.

Liquid propellant/LP XM46 is composed of approximately 60.8-percent hydroxylammonium nitrate (HAN), 19.2-percent triethanolamine nitrate (TEAN), and 20.0-percent water. The HAN, a strong oxidizing agent, poses potentially dramatic interaction problems with soils or other surfaces upon which LP may be spilled. The contact screening tests were performed to qualitatively evaluate the vigor of the oxidation reaction, the character of any gases emitted, and the effects of extreme environmental temperatures upon reactions. Contact with LP did not result in violent decomposition of the LP, but visible bubbling and foaming were observed immediately in some soils. The volume of total gases produced varied from soil to soil and increased with temperature. The only gases detected were oxygen, nitrogen, carbon dioxide, and, in several soils at 60 °C only, nitrous oxide. No carbon monoxide, nitrogen dioxide, or nitric oxide were detected. Contact with LP resulted in dramatic decreases in pH and increases in soil nitrate/nitrite-nitrogen. Appropriate precautions for handling acidic materials of pH less than 4 should be advised when responding to an LP spill. Local soil conditions, hydrology, and terrain should be considered to determine the potential for surface or groundwater contamination by nitrate.

Soil sorption of HAN and TEAN may be a significant environmental fate process in the event of an accidental spill. Batch partitioning tests were conducted with soils from five sites to determine the rate and extent of HAN and TEAN adsorption and to identify soil properties correlating with adsorption.

The HAN reacted with the soils producing gases that volatilized. Therefore, HAN would persist and migrate until it contacted with enough soil for complete reduction to gases. Reactivity was slightly correlated ( $R^2 = 0.5$ ) with total organic carbon, total Kjeldahl nitrogen, oxalate extractable iron, and percent silt. The TEAN did not react with the soil, but exhibited limited adsorption. Adsorption of TEAN correlated best with percent clay, cation exchange capacity, oxalate extractable iron, total organic carbon, oxalate extractable aluminum, and total iron. Results indicated that soil sorption would not prevent migration of TEAN through the soil profile in a spill event.

The objectives of the runoff, infiltration, and transport studies were to relate the distance LP flowed and its rate of infiltration to soil and LP properties, and to measure how undiluted and diluted LP reacted with soils. Spill of LP onto soils was studied with five soils, China Lake B, Picatinny A, Socorro P, WFS Reference, and Yuma 2A, which were selected for their content of sand, organic matter, clay, silt, and silty sand, respectively. The distance a volume of LP traveled along the soil surface and infiltrated into the soil was related through dimensionless variables to the soil and liquid properties. LP reactions with dry soils were studied in open-top column experiments in which dry soil was covered by LP-saturated soil that contained 858,000-mg HAN/L and 286,000-mg TEAN/L. The LP-saturated soil was covered by water. LP was diluted to 8,580-mg HAN/L and 2,860-mg TEAN/L, then reacted with China Lake B and Picatinny A soil in enclosed columns. After completion of tests of diluted LP in enclosed columns, a chloride ion tracer was applied to measure whether any changes in soil mixing properties occurred. Equations developed to describe undiluted LP runoff were less reliable than equations that describe undiluted LP infiltration due to data scatter. Undiluted LP interacted with soils to produce gases that resulted in immediate soil expansion. The soil remained expanded even after gas escaped. Picatinny A expanded the greatest amount, 52 percent, and WFS Reference expanded the least, 26 percent. As LP infiltrated into dry soil, both HAN and TEAN were adsorbed and reacted, so their concentrations were near zero at the wetting front. Behind the wetting front, the concentration of HAN and TEAN increased rapidly, but not to their original concentrations. WFS Reference and Socorro P adsorbed TEAN in preference to HAN. Diluted LP reacted more rapidly with China Lake B soil than with Picatinny A soil. HAN from diluted LP adsorbed more strongly to Picatinny A soil than to China Lake B soil, while the reverse was true for TEAN. Diluted LP conditioned both soil surfaces so that a pulse input of approximately 100 mg of chloride ion from salt, which usually does not react with or adsorb to soil surfaces, reacted and adsorbed. When diluted LP flowed through soils prior to a chloride ion tracer, each species, HAN, TEAN, and chloride ion, had different dispersion coefficients, contrary to expectations. Undiluted LP flowed the shortest distance on Picatinny A soil, followed in order by China Lake B, Yuma 2A, Socorro P, and WFS Reference soils, respectively. Undiluted LP reacted immediately with all soils except China Lake B to cause permanent soil expansion. HAN and TEAN concentrations were the lowest at the wetting front due to their removal by reaction and adsorption when undiluted LP flowed into dry soil. The reactions of HAN and

TEAN in diluted LP which flowed in soils was not predicted from the behavior of undiluted LP when it flowed in soils, and vice versa.

Because microorganisms respond rapidly to changes in their environment, they are sensitive indicators of possible toxic effects of contaminants. The purposes of the microbial tests were to determine immediate and long-term effects of diluted and undiluted LP on the soil microflora, and to compare these effects with the effects of comparable concentrations of nitric acid ( $\text{HNO}_3$ ). Soils were cultured for numbers of native actinomycetes, bacteria, and fungi after contact with LP or nitric acid. Effects of washing the soil with water immediately after contact with LP were also examined.

The LP sterilized the soils within 1 hr of contact, and no microorganisms were recovered from these soils over a 90-day contact period. This effect mimicked the effect of 1.0-N  $\text{HNO}_3$  treatment under the same test conditions. Diluted LP (50 percent by volume) killed all microorganisms; however, this effect failed to be mimicked by contact with 0.1-N  $\text{HNO}_3$  from which actinomycete populations recovered. Dilution of LP by flushing with water within the first hour or two of the spill would mitigate long-term impacts on the soil microflora. However, immediate impacts occur so quickly that the site may be temporarily depauperate of microflora.

Results of this research were incorporated into "Guidance Document for Preparation of Liquid Propellant XM46 Spill Response Plans" developed in cooperation with the Waterways Experiment Station by Arthur D. Little, Inc., Acorn Park, Cambridge, MA.

# 1 Soil Characterization and Contact Screening Tests<sup>1</sup>

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## Introduction

### Background

Liquid propellant/LP XM46 (LP<sup>2</sup>) is composed of approximately 60.8-percent hydroxylammonium nitrate (HAN), 19.2-percent triethanolammonium nitrate (TEAN), and 20.0-percent water. The HAN, a strong oxidizing agent, poses potentially dramatic interaction problems with soils or other surfaces upon which LP may be spilled. The HAN is a salt of hydroxylamine (HA) and nitrate. Complete dissipation of HA in soils has been documented (Bremner, Blackmer, and Waring 1980; Nelson 1978). Therefore, unconfined contact screening tests were performed to qualitatively evaluate the vigor of the oxidation reaction and the character of any gases emitted. Once the reaction had been observed, necessary safety measures were designed into all subsequent tests that required confinement of the test system while LP contacted soil.

Confined contact screening tests were designed to identify and quantify gases resulting from LP interaction with the soils. This information contributed to the development of proper spill response planning based on the hazard, stability, and environmental compatibility of LP in soils. Finally, reactivity was evaluated at three environmental temperatures, since temperature was expected to exert an effect upon reaction rates.

### Objectives

The objective of soil characterization was to evaluate the pertinent properties of the soil that may be important to soil interactions with LP. The objective of the unconfined contact screening test was to evaluate qualitatively the

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<sup>1</sup> By Judith C. Pennington, Cynthia B. Price, Jesse M. Harrington, Jimmy L. Stewart, and Jennifer A. Busby, U.S. Army Engineer Waterways Experiment Station.

<sup>2</sup> For convenience, symbols and abbreviations are listed in the notation (Appendix C).

reactions of LP with all of the test soils. The objectives of the confined contact screening tests were to (a) identify and quantify volatile products released and (b) determine the effects of temperature on composition and quantity of gases evolved.

## Materials and Methods

### Soil collection

Fourteen soils from five LP test sites were selected for laboratory testing. Soils were selected to represent the broadest possible range in properties so that results of tests could be extrapolated to additional potential spill sites. Surface soils were collected from the U.S. Army Armament, Research, Development, and Engineering Center (ARDEC), Picatinny, NJ; U.S. Army Ballistics Research Laboratory (BRL), Aberdeen Proving Ground, MD; U.S. Army Yuma Proving Ground, AZ; Naval Air Warfare Center (NAWC), China Lake, CA; and New Mexico Institute of Mining and Technology (NMIMT), Socorro, NM. Two additional soils were obtained to serve as reference soils; these included a U.S. Army Engineer Waterways Experiment Station (WES) reference soil collected at WES in Vicksburg, MS, and Yokena clay collected in a field south of Vicksburg. Two asphalt samples were obtained from the Geotechnical Laboratory, WES, and five cement samples were obtained from the Structures Laboratory, WES.

**Picatinny samples.** Two 30-gal<sup>1</sup> drums of soil were collected from one site at the ARDEC, Picatinny, NJ. After vegetation, litter, and rocks were scraped from the soil surface (typically the top 1 to 2 in.), a smooth vertical cut of approximately 3 ft was made. The site had been reworked many times in the past; therefore, a distinct soil profile was not evident. Nevertheless, an effort was made to sample the top 6 to 8 in. (Picatinny A) and the underlying 12 to 20 in. (Picatinny B). Soils in the area are typically from the Ridgebury Soil Series. The Series is described as deep, poorly drained stony soil with a very stony loam surface and a moderately developed fragipan occurring 12 to 24 in. below the surface (Soil Conservation Service (SCS) 1976).

**BRL samples.** Two (A and B horizons) 30-gal drums of soil were collected from each of two sites at BRL, Aberdeen Proving Ground, MD. Both samples were collected from the general area of 76° 05' west longitude and 39° 27' north latitude on Spesutie Island. No information was available on these soils.

**Yuma samples.** Two 55-gal drums of soil were collected from each of two sites at the Yuma Proving Ground, AZ. Both samples were collected from the general area of 114° 16' west longitude and 33° 06' north latitude. Both A and

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<sup>1</sup> A table for converting non-SI to SI units of measurement is presented on p xi.

B soil horizons were collected at each site. Soils from site 1 (Yuma 1-A and Yuma 1-B, the A and B horizons of which ranged from the surface to 12 in. of depth and from 12 to 24 in. of depth, respectively) were collected in a well-stratified drainage basin belonging to the Riverbend Family-Carrizo Family Complex Soil Series. Riverbend Family soils are classified as sandy-skeletal, mixed hyperthermic typic calciorthids (SCS 1992). Soils from site 2 (Yuma 2-A and Yuma 2-B having horizon depths comparable to those described above for site 1) were collected on a raised area above the drainage basin from which the first samples were collected. These soils also belong to the Riverbend Family-Carrizo Family Complex Soil Series.

**China Lake samples.** Two 55-gal drums of soil were obtained from one site at the NAWC, China Lake, CA. The sampling site was located at approximately 117° 28' west longitude and 35° 41' north latitude. One sample was taken from the top 4 to 8 in.; the other, at 12 to 16 in. The extremely sandy soil in this arid area has not been classified by the SCS.

**Socorro samples.** Two 55-gal drums of soil were collected at NMIMT, Socorro, NM. Both samples were collected from the Big Eagle Testing Range located at approximately 106° 58' west longitude and 34° 3.5' north latitude (SCS, Soil Survey of Socorro County Area, NM, Section 8, SE 1/4, SE 1/4, Section 8, R1W, T3S). One sample (Socorro S) was a composite of four subsamples collected from different locations on the test-pad surface to a depth of 3 in. Since site construction in 1985 disturbed the original soil horizons, vertical cuts indicated a fairly homogeneous soil structure. The second sample (Socorro P) was collected on the periphery of the test pad along a shallow drainage ditch encircling the test pad. The test pad was set in a small horseshoe-shaped canyon of rock having very little soil filling the crevices. Construction had also altered the original soil profile at this site. The composite sample (Socorro P) was taken from L-shaped wedges cut into the bank at five locations. Although disturbed, the soil type probably most closely approximates the Turney Variant, which is typical for the surrounding area. The SCS classifies Turney Variant soils as fine-loamy, mixed, thermic typic calciorthids (SCS 1988). Both samples were mixed and screened through a 1/4-in. wire mesh before transport to WES. Any chunks of dirt were broken and rubbed through the mesh. Stones were discarded.

**WES Reference soil.** WES Reference soil is a silt collected from the grounds of a designated site at the WES. The soil is classified as clayey over loamy, montmorillonitic, nonacid, thermic, vertic haplaquept (SCS 1964). The soil is used as an internal laboratory silt control in the Environmental Processes and Effects Division (EPED), Environmental Laboratory, WES.

**Yokena clay.** Yokena soil is a heavy clay collected in the vicinity of WES (approximately 90° 58' west longitude and 32° 15' north latitude). Yokena is an agricultural surface soil from the Mississippi River floodplain. The soil is classified as a very fine, montmorillonitic, nonacid, thermic, vertic haplaquept (SCS 1964). The soil is used as an internal laboratory clay control in the EPED.

## Soil characterization

Soils were classified according to the Unified Soil Classification System (USCS) (WES 1960). This classification system assesses the engineering properties of soils. The USCS classifies coarse-grained soils according to their grain size distributions, and fine-grained soils according to their plasticity. Only a sieve analysis and the Atterberg limits are necessary to completely classify the soils. The Yuma and China Lake soils had been sieved through a 0.625-cm (0.25-in.) sieve before shipment to remove rocks. Therefore, the classification of these two soils ignores the >0.625-cm fractions.

Soils for chemical and physical characterization were sieved to 2 mm (0.08 in.) and thoroughly mixed. Total organic carbon (TOC) was determined by American Public Health Association (APHA) (1989) Method 5310 D. Percent organic matter was determined by the Wakley-Black method as modified by De Bolt (De Bolt 1974). Soil pH was determined on magnetically stirred soil slurries (1:1, soil: distilled deionized water) using a Beckman Model SS-3 pH meter (Beckman Instruments Inc., Fullerton, CA) (U.S. Environmental Protection Agency (EPA) 1986). Cation exchange capacity (CEC) was determined by the ammonium saturation method (Plumb 1981). Extracts for CEC determinations were analyzed according to EPA Standard Method 350.1 (EPA 1982). Conductivity and salinity were determined according to the procedure of Rhoades (1982). Particle size distribution was determined by the method of Day (1956) as modified by Patrick (1958). Additional analysis included nitrate nitrogen ( $\text{NO}_3\text{-N}$ ), total Kjeldahl nitrogen (TKN), ammonia nitrogen ( $\text{NH}_3\text{-N}$ ), and organic nitrogen (ON) (EPA 1990). Total iron (Fe) was determined by EPA SW846 Methods 3050 and 6010 (EPA 1990). Oxalate extractable Fe, aluminum (Al), manganese (Mn), and calcium (Ca) were determined according to the method of Brannon and Patrick (1985). Metals were assayed on a Beckman Spectra Span IIIB Argon Plasma Emission Spectrophotometer (Applied Research Laboratories, Dearborn, MI). All soils from sites where explosives are used or have been used in the past are tested for explosives by EPA SW-846 Method 8330 (EPA 1990). Analytes included 2,4,6-trinitrotoluene (TNT); 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX); 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine (HMX); tetryl; 1,3-dinitrobenzene (DNB); 1,3,5-trinitrobenzene (TNB); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); and 4-amino-2,6-dinitrotoluene (4ADNT).

Several characteristics of soils were anticipated to change significantly after contact with LP. Soils were assayed for these parameters after LP contact under controlled conditions. Soil pH was determined 24 hr after contacting each soil with undiluted LP using EPA Method 9045 (EPA 1986). Total Kjeldahl nitrogen and ammonia nitrogen by EPA Method 351.2 (EPA 1986) and nitrate/nitrite nitrogen by EPA Method 353.2 (EPA 1986) were also determined on these samples. A qualitative test on all soils for the presence of inorganic carbon (calcite, dolomite, soluble- $\text{CO}_3^{2-}$  and  $\text{HCO}_3^{-1}$ ) was also conducted (Nelson and Sommers 1982). The buffering capacity of China Lake A and B, Socorro S and P, Picatinny B, Yuma 2A, Yokona, and WES Reference for LP was determined by adding undiluted LP one to several drops at a time

to a 1:4 soil to water slurry while monitoring pH. Titration was continued until a total of 20 mL of LP had been added.

### **Cement and asphalt characterization**

Cements were characterized before contact with LP according to American Society for Testing and Materials (ASTM) methods (ASTM 1992d,g). Asphalts were characterized before contact with LP according to ASTM methods (ASTM 1992e,f,h,i). Asphalts were also characterized before and after contact with LP by Fourier-Transform Infrared Spectroscopy (FTIR) using attenuated total internal reflectance (ATR). A Nicolet 510P FTIR spectrometer (Nicolet Instrument Corp., Madison, WI) containing a Michelson Interferometer and a Deuterium Triglyceride detector was used. Individual spectra were obtained by ratioing the background signal through an internal reflectance element (IRE) only with the sample to IRE signal. The IRE was a germanium crystal. Samples of asphalt for analysis were dissolved in toluene and poured onto the crystal. The toluene was allowed to evaporate leaving a thin film of asphalt cement deposited on the crystal. The IRE was placed into the FTIR, and the sample container was purged with nitrogen ( $N_2$ ) to remove carbon dioxide ( $CO_2$ ), and water vapor. The collection parameters used to obtain the spectra were 32 scans at a resolution of  $4\text{ cm}^{-1}$ .

### **Unconfined contact screening tests**

The unconfined contacting screening tests consisted of contacting 1 g of each soil on an oven dry weight (ODW) basis, asphalt, or cement with 150  $\mu\text{L}$  of LP. Tests were conducted at 23 and 60  $^{\circ}\text{C}$ . The soils and other materials were heated in aluminum weighing pans on a programmable hot plate for high temperature tests. The LP was added through a syringe, one drop at a time. Physical changes such as bubbling, foaming, and color variation were noted over a 24-hr period.

### **Confined contact screening tests**

Selection of soils for confined contact screening tests was based on observed reactivity in the unconfined contact screening test and soil characteristics. Soils selected for testing included China Lake A, Yuma 2A, Yokena, and WES Reference. Tests were conducted in 20-mL Warburg flasks on a Gilson Differential Respirometer (Gilson Medical Electronics, Inc., Middleton, WI) at 5, 22 and 60  $^{\circ}\text{C}$ . An aqueous reference flask was run concurrently with each sample. The 0.25-g (ODW) soil and 100  $\mu\text{L}$  of LP were placed so that the LP was spatially separated from the soil in the bottom of the flasks. Flasks were sparged with helium gas for 5 min before the manometer was allowed to equilibrate for 20 to 30 min. After equilibration, flasks were tilted to allow the LP to contact the soil. After 30 min, the change in pressure was read, and a sample of the head space gases was withdrawn for gas liquid

chromatographic (GLC) and FTIR analysis using a gas-tight syringe equipped with a needle valve.

Total gas was determined by correcting volume measured on the respirometer to standard temperature (273 °K) and pressure (760 torr) (STP) using the following equation:

$$G' = \frac{273 \times (B - W_p) \Delta G}{760 T} \quad (1)$$

where

$G'$  = actual volume of gas produced ( $\mu\text{L}$ )

$B$  = barometric pressure (torr)

$\Delta G$  = change in gas volume in the respirometer flask ( $\mu\text{L}$ )

$W_p$  = water vapor pressure at test temperature (torr)

$T$  = temperature of water bath (°K)

Gas samples (100  $\mu\text{L}$ ) were analyzed on a Hewlett Packard (HP) 5890 Series II gas chromatograph using a Supelco Carboxen 1000 column. The initial temperature was 35 °C for 1 min; then the temperature was ramped at a rate of 25 °C/min to a final temperature of 200 °C, which was held for 10 min. The detector was a thermal conductivity set for high sensitivity. Injection temperature was 180 °C, and detector temperature was 210 °C.

For FTIR analysis, 10 mL of gas was forcefully withdrawn from the respirometer flask and injected into a pre-evacuated 10-cm Beta Gas Cell (International Crystal Laboratories, Garfield, NJ) having a 25 × 4 mm NaCl disc. The gas cell was kept in a desiccator at ambient temperature until analyzed on a Nicolet 510P FTIR spectrometer (Nicolet Instrument Corp., Madison, WI) containing a Michelson Interferometer and a Deuterium Triglyceride detector. Purge gas was  $\text{N}_2$ . Thirty-two scans were performed per sample at a resolution of 4  $\text{cm}^{-1}$ .

Qualitative identification of gases produced in confined contact screening tests was made by comparing the sample gas chromatograms and FTIR spectra with chromatograms and spectra obtained from the analysis of a standard gas (Scott Specialty Gas, Inc., Houston, TX) containing 1 percent (moles) of each of the following gases:  $\text{CO}_2$ , carbon monoxide (CO), nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ ), and nitrous oxide ( $\text{N}_2\text{O}$ ). To quantify analytes detected by GLC, integrated peak areas were converted to  $\mu\text{L}$  of analyte at STP using a standard curve generated based on the analysis of varying volumes of the same standard gas mixture. The FTIR spectrum of the standard gas mixture was

compared to spectra for  $\text{NO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{N}_2\text{O}$  obtained from Sadtler Research Laboratories, Inc., Philadelphia, PA. To quantify analytes detected by FTIR, the height of the most prominent peak for a given analyte was compared with the height of the same peak in the standard using a standard curve for that analyte, which was generated based on the analysis of varying volumes of the same standard gas mixture. The thermal conductivity detector on the GLC is not sensitive to  $\text{NO}_2$  or  $\text{NO}$ , while the FTIR is not sensitive to  $\text{N}_2$ .

## Results

### Characteristics of soils

According to the USCS classification, the soils used in this study tended to be sandy with a brown color (Table 1). Although selection of soils was based on planned locations for LP testing, soils exhibited a broad range in chemical and physical properties (Table 2). Particle size ranged from high percent sand (China Lake B soil, 97.5 percent), silt (WES Reference soil, 93.8 percent), and clay (Yokena soil, 48.75 percent) to no sand (Wes Reference soil), silt (China Lake B soil), and only 2.5-percent clay (China Lake B soil). Two of the soils represented the upper limits of particle size distribution in soils across the country: China Lake B was 97.5-percent sand, and WES Reference was 93.8-percent silt. Yokena was 48.8 percent clay, which is a relatively high clay percentage. Total organic carbon ranged from 176 mg/kg in China Lake A to 24,010 mg/kg in Yokena. Cation exchange capacity ranged from 3.5 meq/100 g in China Lake A to 38.9 meq/100 g in Yokena. All of the Socorro and Yuma soil samples were saline. The pH values of the soils were generally within the typical range of 4 to 8 (Millar, Turk, and Foth 1958) except for China Lake and Socorro soils, which were more alkaline. Some of the soils were positive for inorganic carbon: Yuma 2A, China Lake A, Socorro S, and Socorro P. Nitrate/nitrite nitrogen varied from a high of 290.4 mg/kg in Yuma 2A soils to less than detectable levels in the China Lake soils. No explosives or TNT transformation products were detected in any of the soils. Detection limits for explosives analysis were generally lower than 2 ppm.

Soil pH dropped dramatically after contact with undiluted LP (Table 3). Mean pH for all soils before contact with LP was  $7.1 \pm 0.4$ ; after contact, the mean was  $3.0 \pm 0.3$ . The pH of the undiluted LP was 0.36. The buffering capacity of the soils for LP was poor as demonstrated by titrating several of the soils with LP (Figure 1). The graph illustrates how soil pH would change as the volume of LP increases in a spill event. An insufficient number of soils were analyzed to perform a valid correlation analysis of buffering capacity and soil properties. However, if an arbitrary inflection point is defined as the point on the curve at which the pH decreases by less than 5 percent from the pH at the previous LP addition, the pH values at the inflection points for the different soils can be compared as shown in the following tabulation.

| Soil          | Inflection Point | Original Soil pH |
|---------------|------------------|------------------|
| Yuma 2A       | 6.2              | 8.0              |
| Wes Reference | 4.8              | 6.2              |
| Yokona        | 5.0              | 6.4              |
| China Lake A  | 4.6              | 9.3              |
| China Lake B  | 5.6              | 9.1              |
| Picatinny B   | 4.1              | 6.1              |
| Socorro P     | 6.5              | 8.1              |
| Socorro S     | 6.2              | 8.1              |

**Table 1**  
**Soils Characterized According to the Unified Soil Classification System**

| Soil                       | Classification                                          |
|----------------------------|---------------------------------------------------------|
| China Lake A               | Silty Sand (SP-SM), Brown; Trace of Gravel <sup>1</sup> |
| China Lake B               | Sand (SP), Gray; Trace of Gravel <sup>1</sup>           |
| Socorro P                  | Sandy Clay (CL), Gray                                   |
| Socorro S                  | Sandy Clay (CL), Brown                                  |
| Picatinny A                | Silty Clayey Sand (SC), Brown                           |
| Picatinny B                | Silty Clayey Sand (SC), Brown; Trace of Gravel          |
| Yuma 1-A                   | Silty Sand (SM), Brown <sup>1</sup>                     |
| Yuma 1-B                   | Silty Sand (SM), Brown <sup>1</sup>                     |
| Yuma 2-A                   | Silty Sand (SM), Brown <sup>1</sup>                     |
| Yuma 2-B                   | Clayey Sand (SC), Brown <sup>1</sup>                    |
| BRL-SAS A                  | Silt (ML), Gray; with Sand                              |
| BRL-SAS B                  | Silty Clay (CL), Brown; with Sand                       |
| BRL-MAR A                  | Clayey Silt (ML), Brown, with Sand                      |
| BRL-MAR B                  | Silty Clay (CL), Brown; with Sand                       |
| Yokona                     | Clay (CH), Gray                                         |
| WES Reference <sup>2</sup> | Silt (ML), Gray                                         |

<sup>1</sup> These soils had been sieved through a 0.625-mm screen before classification

<sup>2</sup> WES Reference is the Waterways Experiment Station in-house reference soil.

**Table 2**  
**Physical and Chemical Characteristics of Soils**

| Soil                       | TOC <sup>1</sup><br>mg/kg | OM<br>% | pH  | Salinity<br>ppt | CEC<br>meq/100g | Conductivity<br>millimhc/cm | Particle Size       |                      |                    |
|----------------------------|---------------------------|---------|-----|-----------------|-----------------|-----------------------------|---------------------|----------------------|--------------------|
|                            |                           |         |     |                 |                 |                             | % Sand<br>>50 $\mu$ | % Silt<br>50-2 $\mu$ | % Clay<br><2 $\mu$ |
| China Lake A <sup>2</sup>  | 176                       | 0.20    | 9.3 | 0               | 3.5             | 0.11                        | 92.5                | 2.5                  | 5                  |
| China Lake B               | 226                       | 0.16    | 9.1 | 0               | 3.7             | 0.38                        | 97.5                | 0                    | 2.5                |
| Socorro P                  | 1,172                     | 0.53    | 8.1 | 3               | 27.3            | 3.53                        | 42.5                | 30                   | 27.5               |
| Socorro S                  | 762                       | 0.53    | 8.1 | 3               | 34.0            | 3.55                        | 37.5                | 35                   | 27.5               |
| Picatinny A                | 10,937                    | 2.92    | 5.9 | 0               | 13.2            | 0.16                        | 55                  | 37.5                 | 7.5                |
| Picatinny B                | 6,344                     | 2.23    | 6.1 | 0               | 9.8             | 0.15                        | 62.5                | 32.5                 | 5                  |
| Yuma 1A                    | 581                       | 0.38    | 8.5 | 2               | 5.4             | 0.36                        | 77.5                | 12.5                 | 10                 |
| Yuma 1B                    | 265                       | 0.24    | 8.0 | 2               | 8.6             | 3.67                        | 92.5                | 2.5                  | 5                  |
| Yuma 2A                    | 347                       | 0.21    | 8.0 | 0.5             | 5.4             | 3.0                         | 75                  | 20                   | 5                  |
| Yuma 2B                    | 363                       | 0.22    | 8.0 | 7               | 14.1            | 6.5                         | 75                  | 17.5                 | 7.5                |
| BRL-SAS A <sup>3</sup>     | 10,536                    | 2.5     | 4.5 | 0               | 13.7            | 0.336                       | 18                  | 68                   | 14                 |
| BRL-SAS B                  | 11,445                    | 2.6     | 5.9 | 0               | 10.9            | 0.353                       | 19                  | 67                   | 14                 |
| BRL-MAR A <sup>3</sup>     | 4,562                     | 0.6     | 5.6 | 0               | 8.3             | 0.343                       | 18                  | 63                   | 19                 |
| BRL-MAR B                  | 3,711                     | 0.9     | 5.7 | 0               | 8.1             | 0.353                       | 1 <sup>*</sup>      | 65                   | 17                 |
| Yokena                     | 24,010                    | 4.46    | 6.4 | 0               | 39.9            | 0.32                        | 13.75               | 37.54                | 48.75              |
| WES Reference <sup>4</sup> | 5,670                     | 2.81    | 6.2 | 0               | 12.4            | 0.30                        | 0                   | 93.75                | 6.25               |

(Continued)

<sup>1</sup> TOC is total organic carbon; OM is organic matter; CEC is cation exchange capacity.

<sup>2</sup> A indicates sample taken from soil surface; B indicates sample taken from below surface; P indicates sample taken from periphery of test pad; S indicates sample taken from surface of test pad.

<sup>3</sup> SAS is Sassafras Loam; MAR is Tidal Marsh Soil.

<sup>4</sup> WES Reference is the Waterways Experiment Station in-house reference soil.

Table 2 (Concluded)

| Chemical      |                                                  |                  |                                 |                 |          |                                         |      |       |      |
|---------------|--------------------------------------------------|------------------|---------------------------------|-----------------|----------|-----------------------------------------|------|-------|------|
| Soil          | NO <sub>3</sub> /NO <sub>2</sub> -N <sup>2</sup> | TKN <sup>3</sup> | NH <sub>3</sub> -N <sup>4</sup> | ON <sup>5</sup> | Total Fe | Oxalate Extractable Metals <sup>1</sup> |      |       |      |
|               |                                                  |                  |                                 |                 |          | Al                                      | Ca   | Fe    | Mn   |
| China Lake A  | <2.68                                            | 40.17            | <3.0                            | 40.17           | 9,597    | 75.9                                    | 12.2 | 68.4  | 21.8 |
| China Lake B  | <2.21                                            | 20.1             | <3.0                            | 20.1            | 8,599    | 35.1                                    | 6.51 | 90.8  | 5.97 |
| Socorro P     | 117.7                                            | 190              | <3.0                            | 190             | 10,500   | 80.7                                    | 11.8 | 541   | 30.4 |
| Socorro S     | 37.26                                            | 224              | <3.0                            | 224             | 10,100   | 70.6                                    | 7.51 | 78.8  | 13.6 |
| Picatinny A   | 8.83                                             | 289              | <3.0                            | 289             | 21,000   | 335                                     | 41.7 | 1,463 | 63.3 |
| Picatinny B   | 10.14                                            | 358              | <3.0                            | 358             | 25,000   | 7,980                                   | 64.3 | 1,087 | 57.5 |
| Yuma 1-A      | 13.94                                            | 76.1             | <3.0                            | 76.1            | 15,000   | 85.7                                    | 7.06 | 231   | 12.4 |
| Yuma 1-B      | 75.41                                            | 70.1             | <3.0                            | 70.1            | 12,000   | 75.0                                    | 13.0 | 783   | 45.0 |
| Yuma 2-A      | 290.4                                            | 86.4             | <3.0                            | 86.4            | 12,000   | 95.0                                    | 6.94 | 97.7  | 14.2 |
| Yuma 2-B      | 87.64                                            | 47.5             | <3.0                            | 47.5            | 13,000   | 104                                     | 7.42 | 97.8  | 16.3 |
| BRL-SAS A     | 7.72                                             | 471              | <3.0                            | 471             | 15,000   | 253                                     | 2.85 | 478   | 127  |
| BRL-SAS B     | 14.8                                             | 499              | <3.0                            | 499             | 14,600   | 220                                     | 2.48 | 403   | 112  |
| BRL-MAR A     | 27.4                                             | 335              | <3.0                            | 335             | 21,600   | 116                                     | 1.48 | 366   | 32.3 |
| BRL-MAR B     | 40.9                                             | 337              | <3.0                            | 337             | 19,400   | 138                                     | 1.75 | 381   | 66.1 |
| Yokena        | 6.01                                             | 604              | 10.1                            | 594             | 30,900   | 5,570                                   | 57.6 | 2,128 | 131  |
| WES Reference | 20.3                                             | 830              | 7.14                            | 823             | 9,970    | 184                                     | 47.9 | 715   | 153  |

<sup>1</sup> Al, Ca, Fe, and Mn are aluminum, calcium, iron, and manganese, respectively<sup>2</sup> NO<sub>3</sub>/NO<sub>2</sub>-N is nitrate/nitrite nitrogen.<sup>3</sup> TKN is total Kjeldahl nitrogen<sup>4</sup> NH<sub>3</sub>-N is ammonia nitrogen.<sup>5</sup> ON is organic nitrogen. These values were obtained by subtracting NH<sub>3</sub>-N from TKN

**Table 3**  
**Soil pH Before and After 24-hr Contact with Undiluted LP**

| Soil          | pH <sup>1</sup>     |                    |
|---------------|---------------------|--------------------|
|               | Before <sup>2</sup> | After <sup>3</sup> |
| China Lake A  | 9.25 $\pm$ 0.015    | 3.30 $\pm$ 0.027   |
| China Lake B  | 9.07 $\pm$ 0.042    | 3.33 $\pm$ 0.027   |
| Socorro P     | 8.07 $\pm$ 0.047    | 3.81 $\pm$ 0.013   |
| Socorro S     | 8.12 $\pm$ 0.015    | 3.92 $\pm$ 0.0080  |
| Picatinny A   | 5.91 $\pm$ 0.049    | 1.88 $\pm$ 0.0033  |
| Picatinny B   | 6.07 $\pm$ 0.0033   | 2.02 $\pm$ 0.0088  |
| Yuma 1A       | 8.51 $\pm$ 0.015    | 3.83 $\pm$ 0.055   |
| Yuma 1B       | 7.99 $\pm$ 0.060    | 4.30 $\pm$ 0.038   |
| Yuma 2A       | 8.02 $\pm$ 0.020    | 4.39 $\pm$ 0.043   |
| Yuma 2B       | 7.96 $\pm$ 0.015    | 4.14 $\pm$ 0.047   |
| BRL-SAS A     | 4.54 $\pm$ 0.0033   | 1.95 $\pm$ 0.013   |
| BRL-SAS B     | 5.85 $\pm$ 0.037    | 2.11 $\pm$ 0.025   |
| BRL-MAR A     | 5.62 $\pm$ 0.039    | 1.50 $\pm$ 0.0033  |
| BRL-MAR B     | 5.68 $\pm$ 0.032    | 1.67 $\pm$ 0.018   |
| Yokena        | 6.42 $\pm$ 0.029    | 2.55 $\pm$ 0.0033  |
| WES Reference | 6.20 $\pm$ 0.027    | 2.43 $\pm$ 0.012   |

<sup>1</sup> Values are mean of three replicates  $\pm$  standard error.  
<sup>2</sup> Measured in 1:1 soil to water ratio (EPA 1986).  
<sup>3</sup> Measured in 1:1 soil to undiluted liquid propellant slurries

The China Lake A and B soils exhibited the greatest change in pH. The poor buffering capacity of these soils is probably due to low TOC, since the soils that exhibited the least change, Yokena and WES Reference, have high TOC.

Nitrate/Nitrite-nitrogen, total Kjeldahl nitrogen, ammonia nitrogen, and organic nitrogen increased dramatically in soils contacted with LP (Table 4). These results are a reflection of residual NO<sub>3</sub> and triethanolamine (TEA) remaining in the soils. Undiluted LP had a NO<sub>3</sub>/NO<sub>2</sub>-N level of 132,000 mg/kg and a TKN concentration of 19,700 mg/kg. (The sample was diluted 1:10,000 to conduct the analyses.) This NO<sub>3</sub>/NO<sub>2</sub>-N value is about 3.5 times lower than the calculated value of 453,280 mg/kg for undiluted LP (exclusive of transformations of the amines to NO<sub>3</sub>/NO<sub>2</sub>). In this test, LP was diluted 1:1 with the soil. The calculated concentration of NO<sub>3</sub>/NO<sub>2</sub>-N available in the test is 267,186 mg/kg. The actual NO<sub>3</sub>/NO<sub>2</sub>-N values average only about 10 percent of this value (Table 4). Therefore, a possibility exists that some of the N<sub>2</sub> released when undiluted LP contacts the soil is derived from

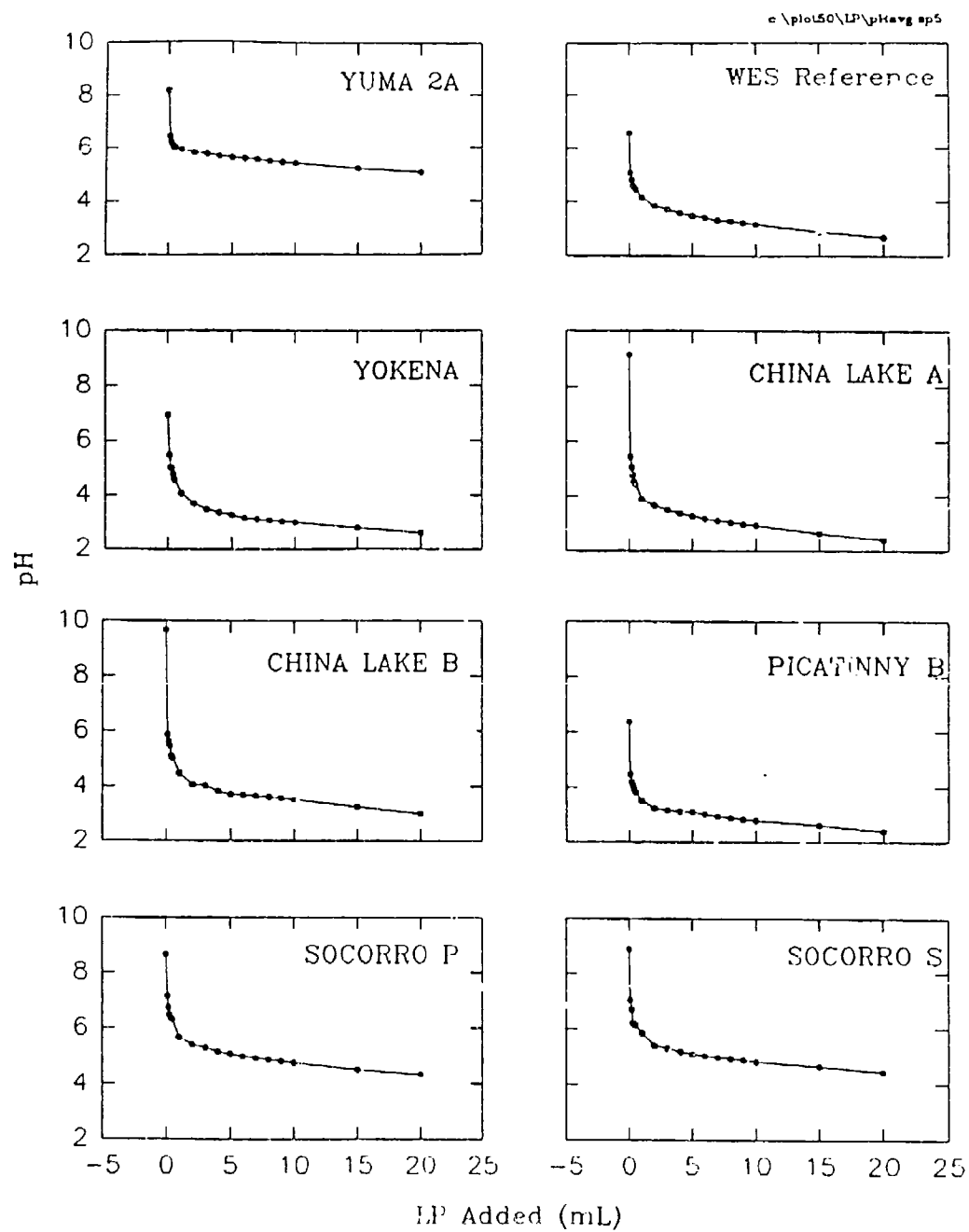


Figure 1. Buffering capacity of eight soils for undiluted LP

| Table 4<br>Nitrogen in Soils Before and After 24-hr Contact with Undiluted LP           |                                              |              |                             |             |                                              |                                    |                             |             |  |  |
|-----------------------------------------------------------------------------------------|----------------------------------------------|--------------|-----------------------------|-------------|----------------------------------------------|------------------------------------|-----------------------------|-------------|--|--|
| Soil                                                                                    | Before Contact with LP                       |              |                             |             |                                              | After Contact with LP <sup>1</sup> |                             |             |  |  |
|                                                                                         | NO <sub>3</sub> /NO <sub>2</sub> -N<br>mg/kg | TKN<br>mg/kg | NH <sub>3</sub> -N<br>mg/kg | ON<br>mg/kg | NO <sub>3</sub> /NO <sub>2</sub> -N<br>mg/kg | TKN<br>mg/kg                       | NH <sub>3</sub> -N<br>mg/kg | ON<br>mg/kg |  |  |
| China Lake A                                                                            | <2.68                                        | 40.17        | <3.0                        | 40.17       | 19,867<br>(639)                              | 2,817<br>(193)                     | 496<br>(32.7)               | 2,321       |  |  |
| Picatinny B                                                                             | 10.14                                        | 358          | <3.0                        | 358         | 43,033<br>(6,342)                            | 5,650<br>(936)                     | 1,058<br>(16.7)             | 4,592       |  |  |
| Yuma 2A                                                                                 | 290.4                                        | 86.4         | <3.0                        | 86.4        | 24,770<br>(3,993)                            | 4,300<br>(175)                     | 957<br>(10.1)               | 3,343       |  |  |
| <sup>1</sup> Means of three replicates with standard errors of the mean in parentheses. |                                              |              |                             |             |                                              |                                    |                             |             |  |  |

breakdown of  $\text{NO}_3$ . Extrapolating to a spill scenario in which no  $\text{NO}_3$  breaks down when the LP contacts the soil, each kilogram of LP could release approximately 326,000 mg of  $\text{NO}_3/\text{NO}_2\text{-N}$ . The local soil conditions, hydrology, and terrain should be considered when determining the potential for surface or groundwater contamination by  $\text{NO}_3$ .

### **Characteristics of cements and asphalt**

Two of the five portland cement samples were Type I (155 and 156), two were Type II with fly ash added (133F and 158F), and one was Type II without fly ash (157). Characterization data on the Type I cements were unavailable, but the chemical characterization data on the Type II cements are given in Table 5. All cement samples met the cited ASTM specifications. Selected characterization data for the two asphalt sample (VS5 and VA20) are presented in Table 6. The table gives the vacuum capillary viscosity at 60 °C (Method D 2171, ASTM 1992i), the kinematic viscosity at 135 °C (Method D 2170, ASTM 1992e), the penetration at 25 and 4 °C (Method D 5, ASTM 1992f), and the softening point (Method D 36, ASTM 1992h). The VS5 sample had a low viscosity and would, therefore, be used in colder regions to minimize thermal cracking of the pavement. The VA20 would be very brittle at low temperatures, but would be stable at high temperatures. The VA20 would be used in warmer climates to minimize deformation tendencies of the pavement.

### **Unconfined contact screening tests**

Results of unconfined contact screening tests indicated that LP interactions with soils were not vigorous enough to produce splattering hazards. Reactions with Yuma 2A and Socorro P soils were immediately visible at ambient temperature as frothing or bubbling (Figure 2), presumably as HAN oxidized soil components (Table 7). In other soils, no reaction was immediately visible, but bubbles slowly developed; in others, no reaction was evident over the 24-hr observation period. Only one cement sample, 156, exhibited immediate foaming when contacted by LP (Table 7). However, all but one cement sample developed at least some bubbling at 50 °C. A color change was observed in three of the cement samples. Asphalts exhibited no visible reaction with LP. The FTIR spectra before and after contact of LP with the asphalt samples were identical (Figures 3 and 4).

### **Confined contact screening tests**

Soils for the confined contact screening tests were selected on the basis of visible reaction with LP in the unconfined tests and on soil properties. China Lake A was selected to represent soils with limited reaction potential because of its slow reactivity with LP and its high percentage of sand. China Lake A was also low in TOC, CEC, conductivity, and  $\text{NO}_3/\text{NO}_2\text{-N}$ . Yuma 2A was

**Table 5**  
**Chemical Composition of Test Cements<sup>1</sup>**

| Test                                                                                   | Sample          |                |                |
|----------------------------------------------------------------------------------------|-----------------|----------------|----------------|
|                                                                                        | 133F            | 158F           | 157            |
| ASTM Specification <sup>2</sup>                                                        | C 618, Class F  | C 618, Class F | C 150, Type II |
| Chemical Analysis                                                                      |                 |                |                |
| SiO <sub>2</sub>                                                                       | 50.0            | 51.2           | 22.8           |
| Al <sub>2</sub> O <sub>3</sub>                                                         | 24.1            | 17.8           | 3.2            |
| Fe <sub>2</sub> O <sub>3</sub>                                                         | 15.4            | 15.5           | 4.0            |
| Sum SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> | 89.5            | 84.4           | NA             |
| CaO                                                                                    | NA <sup>3</sup> | NA             | 61.7           |
| MgO                                                                                    | 1.1             | 0.7            | 3.8            |
| SO <sub>3</sub>                                                                        | 1.3             | 1.4            | 2.5            |
| Na <sub>2</sub> O                                                                      | NA              | NA             | 0.07           |
| K <sub>2</sub> O                                                                       | NA              | NA             | 0.72           |
| TiO <sub>2</sub>                                                                       | NA              | NA             | 0.16           |
| P <sub>2</sub> O <sub>3</sub>                                                          | NA              | NA             | 0.10           |
| Moisture content                                                                       | 0.3             | 0.2            | NA             |
| Loss on ignition                                                                       | 1.0             | 0.9            | 0.8            |
| Available alkalis (28 day)                                                             | 1.0             | NA             | 0.54           |

<sup>1</sup> All units are percent.

<sup>2</sup> ASTM designation of specifications (ASTM 1992 a,b) and test procedures (ASTM 1992 d,g)

<sup>3</sup> This test not conducted or not required for the material tested

**Table 6**  
**Characterization of Test Asphalts**

| Test                            | Sample |       |
|---------------------------------|--------|-------|
|                                 | VS5    | VA20  |
| Viscosity, 60 °C (poises)       | 411    | 1,748 |
| Viscosity, 135 °C (centistokes) | 160    | 330   |
| Penetration, 25 °C (× 0.1 mm)   | 158    | 55    |
| Penetration, 4 °C (× 0.1 mm)    | 48     | 22    |
| Softening Point (°C)            | 47     | 49.5  |

chosen because it exhibited the most immediate and vigorous reaction with LP and because of its high NO<sub>3</sub>/NO<sub>2</sub>-N and moderate salinity. Yokena was selected to represent highly organic soils with substantial clay content. Yokena was also high in CEC and total Fe. WES Reference was selected for its moderate reaction characteristics and its high percentage of silt and ammonia.

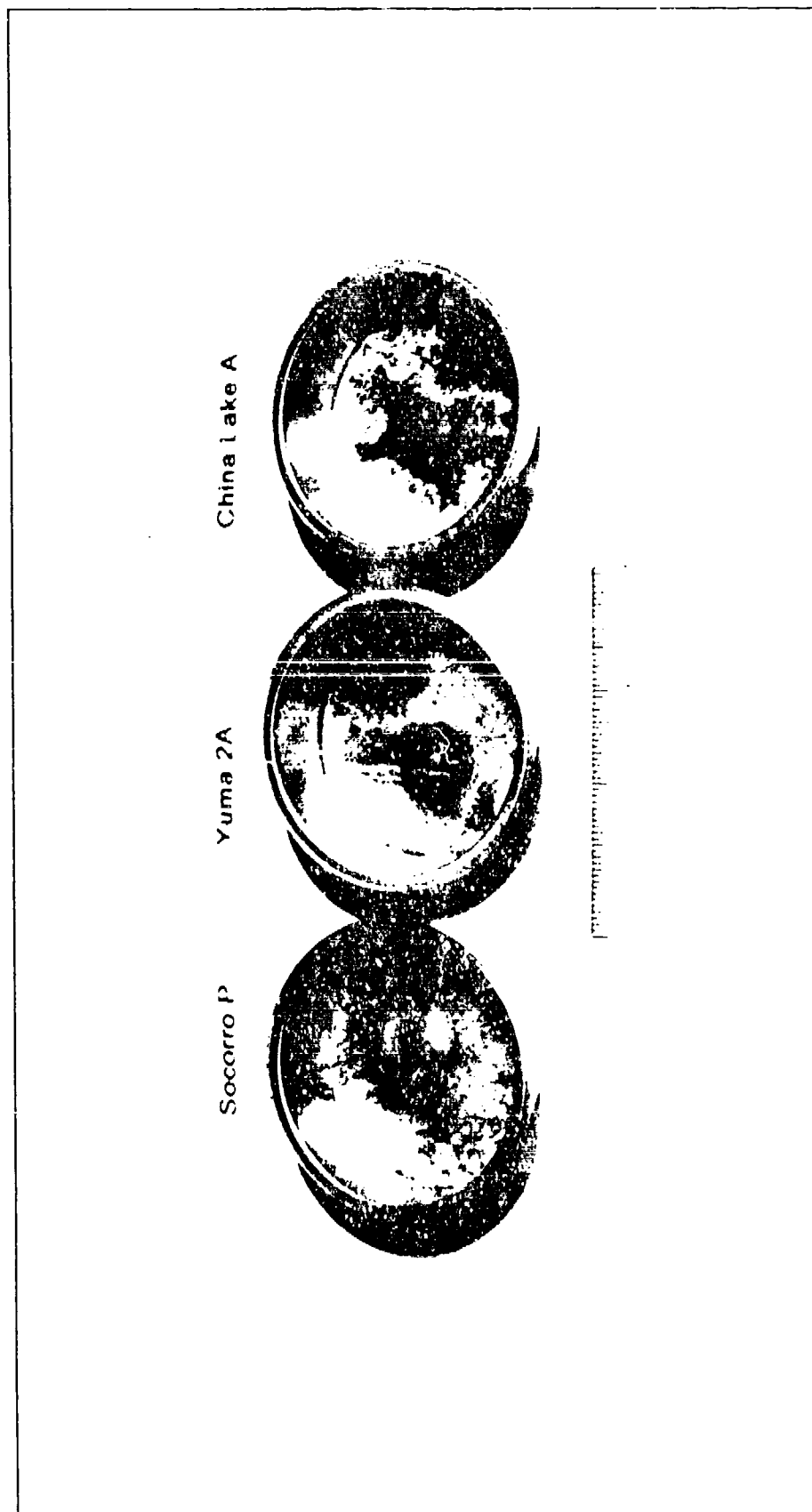


Figure 2. Visible reactions of undiluted LP with three soils. These reactions occurred immediately upon contact. Socorro P and Yuma 2A exhibit bubbling and foaming; China Lake A exhibits no reaction

**Table 7**  
**Visible Reactions of Soils, Cements, and Asphalts Contacted with Undiluted LP in Unconfined Contact Screening Tests**

| Soil          | 23 °C Immediate <sup>1</sup> | 24 hr | 50 °C Immediate             | 24 hr      |
|---------------|------------------------------|-------|-----------------------------|------------|
| China Lake A  | no reaction                  |       | small, fine bubbles         |            |
| China Lake B  | no reaction                  | red   | no reaction                 |            |
| Socorro P     | bubbling and foaming         | black | foaming, soil swelled       |            |
| Socorro S     | bubbling and foaming         |       | much bubbling and foaming   |            |
| Picatinny A   | small amount of bubbling     |       | much bubbling               |            |
| Picatinny B   | no reaction                  |       | no reaction                 |            |
| Yuma 1A       | no reaction                  |       | bubbling                    |            |
| Yuma 1B       | slight bubbling              |       |                             |            |
| Yuma 2A       | bubbling and foaming         |       | bubbling                    |            |
| Yuma 2B       | no reaction                  |       | slight foaming              |            |
| BRL-SAS A     | no reaction                  |       | no reaction                 |            |
| BRL-SAS B     | no reaction                  |       | no reaction                 |            |
| BRL-MAR A     | pooled up, fine bubbles      |       | fine bubbling, soil swelled |            |
| BRL-MAR B     | no reaction                  |       | fine bubbling, soil swelled |            |
| Yokena Clay   | no reaction                  | black | slight bubbling             |            |
| WES Reference | no reaction                  |       | slight bubbling             |            |
| Cement 133F   | no reaction                  |       | slight bubbling             | dark brown |
| Cement 155    | no reaction                  | tan   | much bubbling               | red        |
| Cement 156    | foaming                      | brown | slight bubbling             |            |
| Cement 157    | no reaction                  |       | no reaction                 |            |
| Cement 158F   | no reaction                  |       | much fizzing, swelled       |            |
| Asphalt VA20  | no reaction                  |       | no reaction                 |            |
| Asphalt VS5   | no reaction                  |       | no reaction                 |            |

<sup>1</sup> Observable results consisted of color change in the soil, generally from brown/gray to color indicated in the column. Bubbling/foaming did not persist at 24 hr

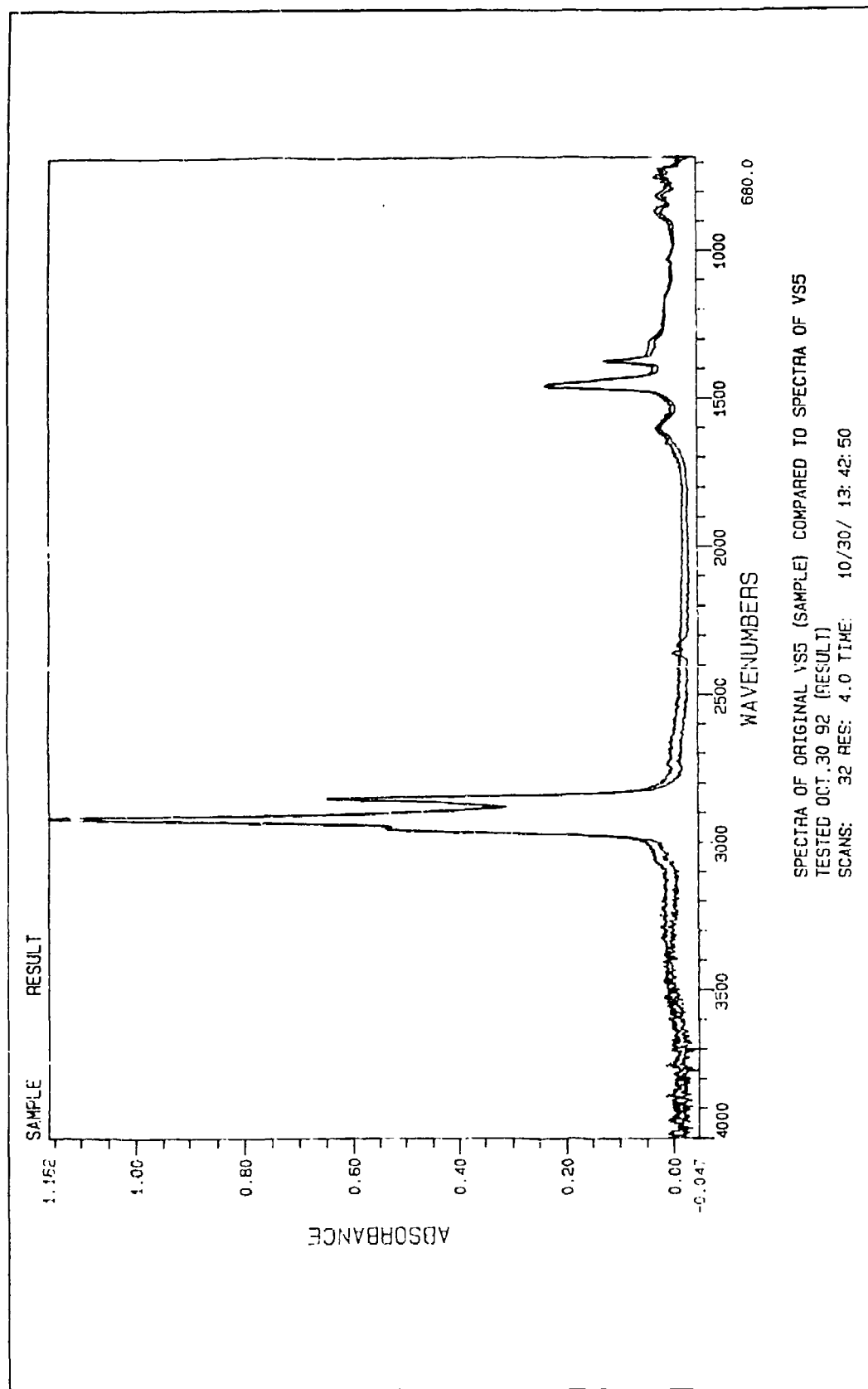


Figure 3. FTIR scan of VS5 asphalt sample before (higher baseline) and after (lower baseline) contact with LP

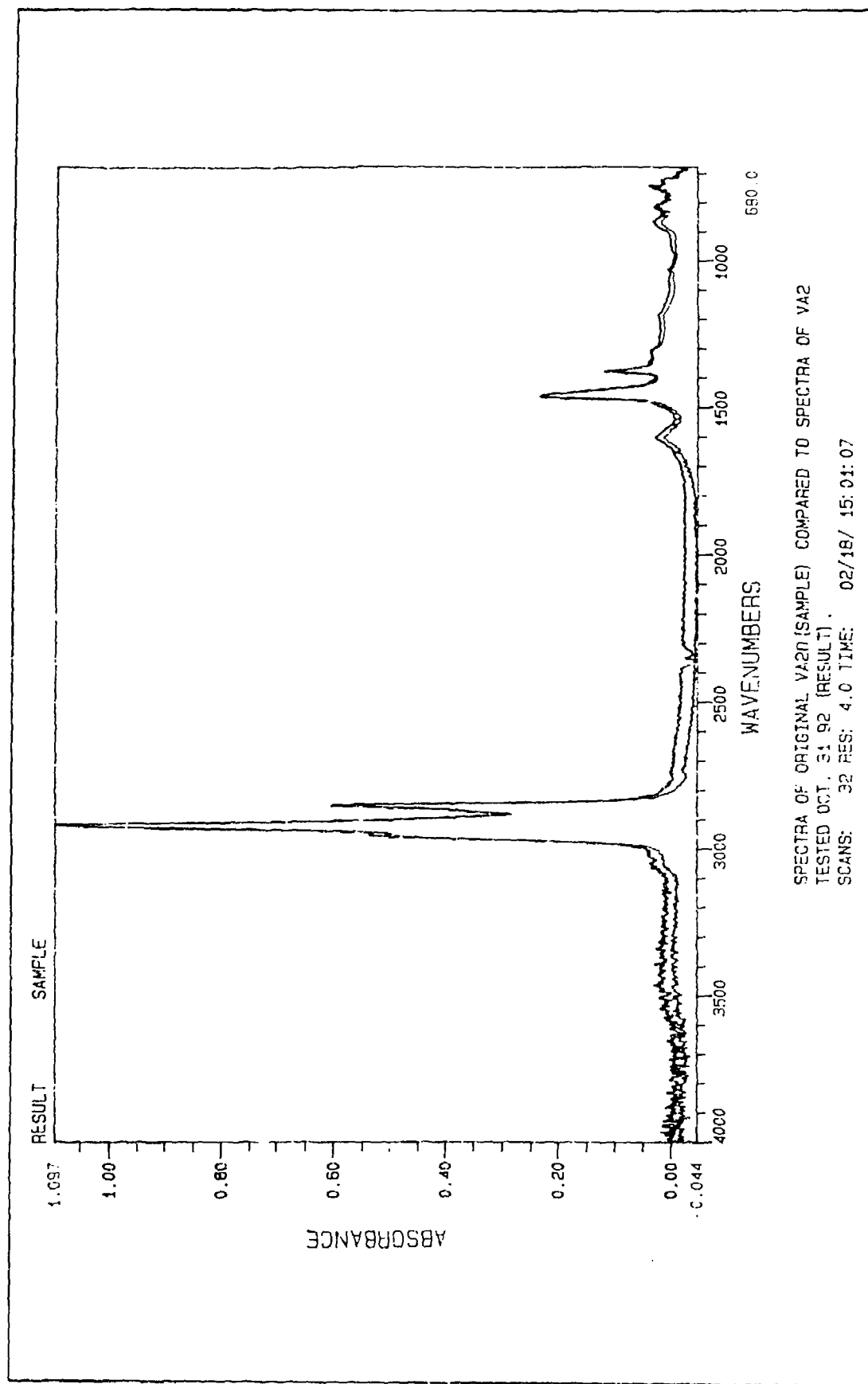


Figure 4. FTIR scan of VA20 asphalt sample before (lower baseline) and after (higher baseline) contact with LP

Results of GLC analysis of gases produced in the confined contact screening tests indicated production of relatively large volumes of gas (Figure 5). One hundred  $\mu\text{L}$  of LP generated approximately 800 to 4,000  $\mu\text{L}$  of total gas at STP. The GLC analysis showed that oxygen ( $\text{O}_2$ ),  $\text{N}_2$ , and  $\text{CO}_2$  predominated at all three test temperatures (Tables 8 through 10). No CO was detected. Nitrous oxide ( $\text{N}_2\text{O}$ ) was detected by both GLC and FTIR in several soils at 60 °C only. Nitric oxide (NO) is unstable in the presence of  $\text{O}_2$ , rapidly converting to nitrogen dioxide ( $\text{NO}_2$ ). Therefore, the presence of NO was unlikely, given the consistent presence of  $\text{O}_2$ . Neither NO nor  $\text{NO}_2$  was detected.

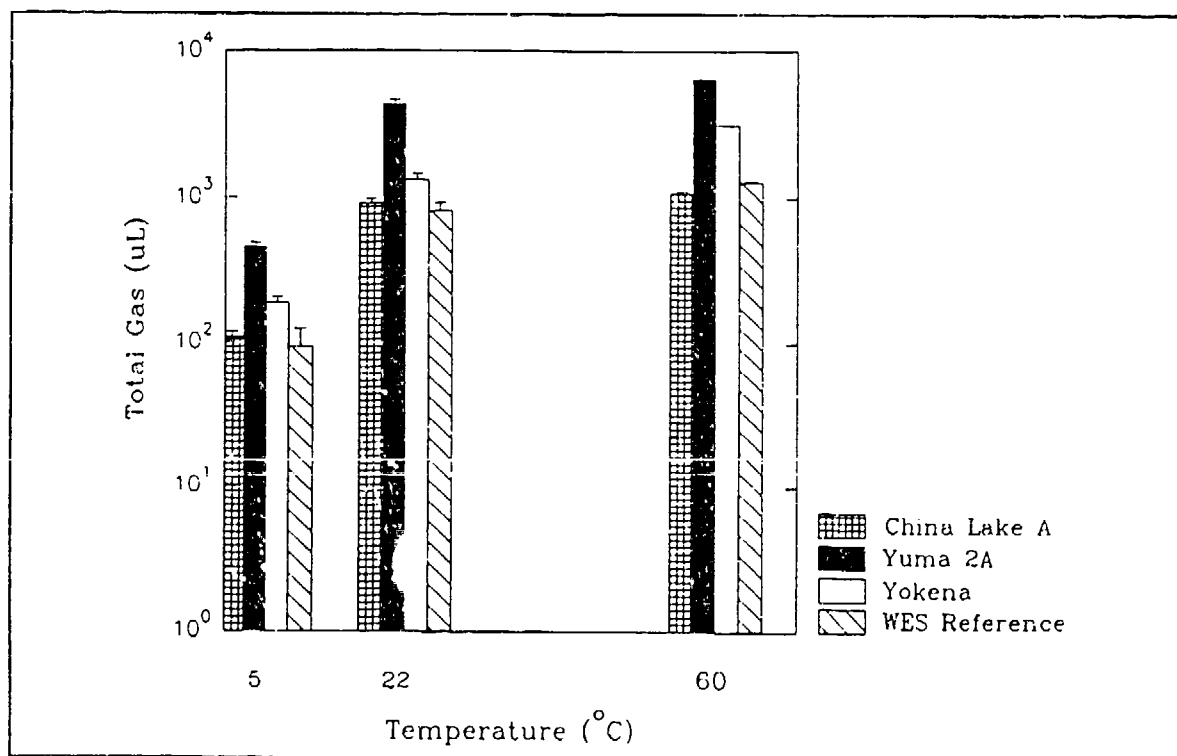


Figure 5. Total gas (STP) produced when 0.25 g of soil was contacted with 100  $\mu\text{L}$  of LP

Oxygen was produced in the highest volume of any gas (Tables 8 through 10). Hazards associated with elevated oxygen levels should be considered in the event of a spill in a confined area or in conjunction with fire hazards.

The sum of analyte volumes determined by GLC plus FTIR analyses did not account for the total volume of gases produced in the respirometer. However, quantifying the volume of gas removed from the respirometer was difficult because of the small size of the manometer and the relatively large volume of samples withdrawn. Withdrawal of a 100- $\mu\text{L}$  sample for GLC analysis presented little difficulty, but removal of 10 mL from the 25-mL respirometer flask was above the range of the constant manometer. Therefore, determination of the exact volume of sample removed from the respirometer

**Table 8**  
**Gases Evolved from Contacting 0.25-g Soil with 100- $\mu$ L**  
**Undiluted LP at 5 °C as Determined by GLC ( $\mu$ L, STP)<sup>1</sup>**

| Soil          | Total | O <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub> | N <sub>2</sub> O |
|---------------|-------|----------------|----------------|-----------------|------------------|
| China Lake A  | 108.5 | 0.580          | 0.938          | 0.039           | ND <sup>2</sup>  |
| Yuma 2A       | 458   | 16.6           | 7.18           | 1.67            | ND               |
| Yokena        | 190.9 | 1.82           | 1.61           | ND              | ND               |
| WES Reference | 93.3  | 1.54           | 0.735          | ND              | ND               |

<sup>1</sup> All values represent means of three replicates.

<sup>2</sup> ND = none detected.

**Table 9**  
**Gases Evolved from Contacting 0.25-g Soil with 100- $\mu$ L**  
**Undiluted LP at 23 °C as Determined by GLC ( $\mu$ L, STP)<sup>1</sup>**

| Soil          | Total | O <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub> | N <sub>2</sub> O |
|---------------|-------|----------------|----------------|-----------------|------------------|
| China Lake A  | 907.5 | 319            | 101.8          | 2.27            | ND               |
| Yuma 2A       | 4,323 | 55.3           | 49.8           | 2.95            | ND               |
| Yokena        | 1,319 | 131            | 40.019         | ND              | ND               |
| WES Reference | 806.3 | 262            | 104.9          | ND              | ND               |

<sup>1</sup> All values represent means of three replicates.

**Table 10**  
**Gases Evolved from Contacting 0.25-g Soil with 100- $\mu$ L**  
**Undiluted LP at 60 °C as Determined by GLC ( $\mu$ L, STP)<sup>1</sup>**

| Soil          | Total | O <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub> | N <sub>2</sub> O    |
|---------------|-------|----------------|----------------|-----------------|---------------------|
| China Lake A  | 1,061 | 7.044          | 11.09          | 1.60            | 0.1025 <sup>2</sup> |
| Yuma 2A       | 6,466 | 677            | 220            | 3.97            | ND                  |
| Yokena        | 3,179 | 101.57         | 38.4           | ND              | 4.96                |
| WES Reference | 1,277 | 22.8           | 13.9           | ND              | 0.237 <sup>2</sup>  |

<sup>1</sup> All values represent means of three replicates.

<sup>2</sup> Detected in one replicate only.

for FTIR analysis relied upon the assumption that an insignificant amount of analyte remained in the sealed flask

The gas of greatest potential concern is  $\text{NO}_2$  (Oxley and Brower 1988, Wojciechowski and Leveritt 1991). It can be detected by FTIR, but not GLC. In order to determine the confidence that can be placed in the FTIR data, comparison between an analyte detected by both GLC and FTIR was made. Nitrous oxide, which was detected by both GLC and FTIR, was used to compare quantities determined by the two methods (Table 11). The values agree within an order of magnitude at the 95-percent confidence level (i.e., mean  $\pm 2$  units of standard error). Standard curves for both  $\text{N}_2\text{O}$  and  $\text{NO}_2$  were constructed by converting from volume of standard injected to moles of  $\text{N}_2\text{O}$  and  $\text{NO}_2$  in the FTIR cell using the Ideal Gas Law (Figure 6). Assuming 10 times signal to noise (3 mm signal/0.3 mm noise, response measured as peak height), the conservative detection limits for FTIR determination of either  $\text{N}_2\text{O}$  or  $\text{NO}_2$  is a peak height of 3 mm. The detection limit for  $\text{N}_2\text{O}$  from the standard curve was  $4.6 \times 10^{-8}$  moles; the detection limit for  $\text{NO}_2$  was  $7.6 \times 10^{-8}$  moles. Therefore, with 95-percent confidence, the  $\text{NO}_2$  level was no more than an order of magnitude above the detection limit of  $7.6 \times 10^{-8}$  moles.

**Table 11**  
**Nitrous Oxide Detected in Gases Evolved from Contacting**  
**0.25-g Soil with 100- $\mu\text{L}$  Undiluted LP at 60 °C: Comparison**  
**Between GLC and FTIR Results (Standard Errors)<sup>1</sup>**

| Soil          | GLC                                                  | FTIR                                               |
|---------------|------------------------------------------------------|----------------------------------------------------|
| China Lake A  | $1.719 \times 10^{-6}$<br>( $1.719 \times 10^{-6}$ ) | $8.77 \times 10^{-6}$<br>( $8.77 \times 10^{-6}$ ) |
| Yckena        | $3.606 \times 10^{-6}$<br>( $1.504 \times 10^{-6}$ ) | $9.44 \times 10^{-6}$<br>( $4.69 \times 10^{-6}$ ) |
| WES Reference | $1.002 \times 10^{-6}$<br>( $8.19 \times 10^{-8}$ )  | $2.87 \times 10^{-7}$<br>( $1.09 \times 10^{-7}$ ) |

<sup>1</sup> All values are means of three replicates, although  $\text{N}_2\text{O}$  was detected in only one replicate of China Lake A by GLC and FTIR and in only one replicate of WES Reference by GLC (zeros were averaged in for the other replicates).

Results of soil interaction studies indicated that TEAN does not decompose immediately when LP contacts the soil (see Chapter 2), and  $\text{NO}_3$  appears to remain unreacted in the soil (Table 4). Therefore, the assumption can be made that the gases produced are primarily products of HAN decomposition. In a worst case scenario, if all the nitrogen in 1 mole of hydroxylamine (HA) were converted to  $\text{NO}_2$ , 1 mole of  $\text{NO}_2$  would be produced. Since 100  $\mu\text{L}$  of LP contains  $9.15 \times 10^{-4}$  moles of HA, the same amount of  $\text{NO}_2$  can be anticipated after interaction with soil. Therefore, the maximum potential production of  $\text{NO}_2$  from 100  $\mu\text{L}$  of LP *if only the HA decomposes to gases* is 0.421 g, or about 30 mL at 20 °C and standard pressure. (This amount greatly exceeds the total gas observed in the present studies.) Therefore, in a worse case scenario,

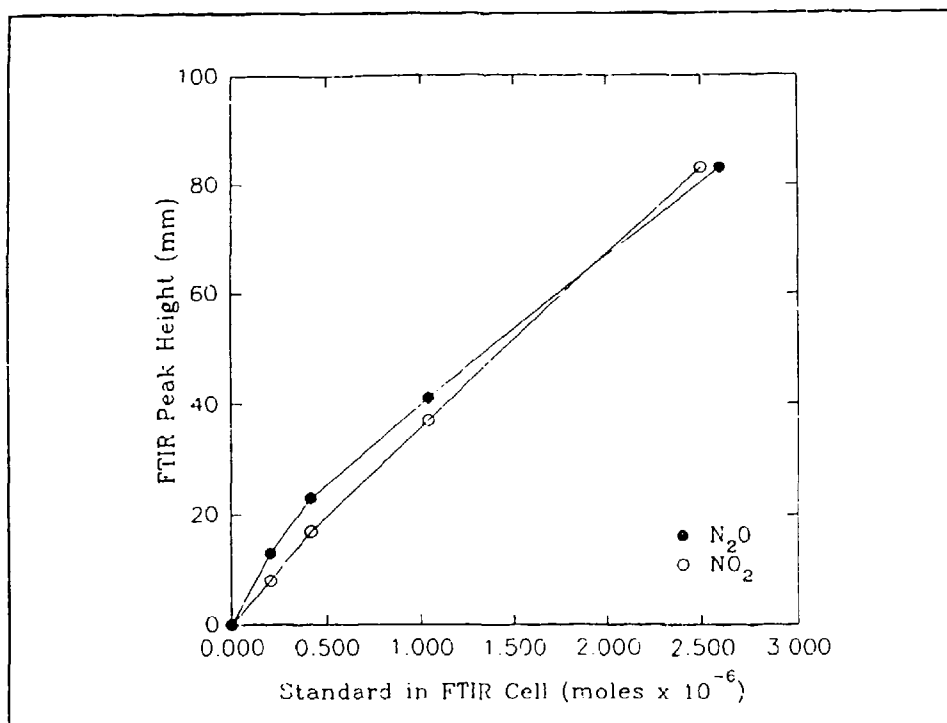


Figure 6. Standard curve relating FTIR peak height for N<sub>2</sub>O and NO<sub>2</sub> and moles ( $\times 10^{-6}$ ) of standard in the FTIR cell.

a spill of 100 L of LP could generate a maximum of 30,000 L of NO<sub>2</sub> at 20 °C. However, based on the FTIR limit of detection for NO<sub>2</sub>, no more than 2.48 L of NO<sub>2</sub> (at 20 °C) would result from a spill of 100 L of LP.

## Conclusions

The 16 test soils exhibited a wide range in properties and were considered suitable for assessing LP interactions with soils. Initial contact with soils did not result in a violent decomposition of LP, but visible bubbling and foaming were observed immediately in some soils. The volume of total gases produced when LP contacted soils varied from soil to soil and increased with temperature. The only gases detected were O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and, in several soils at 60 °C only, N<sub>2</sub>O. No CO, NO<sub>2</sub>, or NO were detected.

Potential hazards resulting from gas production when LP is spilled onto soils are limited to elevations in oxygen levels. Failure to detect the more noxious gases, NO<sub>2</sub> and NO, suggest low toxic gas hazard. However, GLC analysis of confined contact tests did not account for the total volume of gases produced. Quantitative delineation of all gases produced will require a specialized additional study. In a spill onto soil in a confined space, small quantities of toxic gases may be important.

Liquid propellant contact with soils in a spill will result in a dramatic increase in  $\text{NO}_3/\text{NO}_2\text{-N}$  and a decrease in soil pH. Final soil pH after LP contact varied with soil type, ranging from 1.5 to 4.4. The soils exhibited very poor buffering capacity for LP. High  $\text{NO}_3$  and low pH in soils following a spill have important implications for spill response and environmental hazard. Appropriate precautions for handling acidic materials of pH less than 4 should be taken. Local soil conditions, hydrology, and terrain should be considered to determine the potential for surface or groundwater contamination by  $\text{NO}_3$ .

## 2 Soil Sorption<sup>1</sup>

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### Introduction

#### Background

Adsorption and desorption processes potentially exert a controlling influence upon movement of contaminants through unsaturated (vadose) and saturated (aquifer) soils (Freeze and Cherry 1979; Thibodeaux 1979; Curtis, Roberts, and Reinhard 1986; Brusseau and Rao 1989; Mercer, Skipp, and Giffin 1990; Travis and Doty 1990). Partitioning of contaminants between soil solids and pore water is termed *interphase transfer*. Interphase transfer of contaminant into the soil solids phase is termed *adsorption*, whereas movement of the contaminant from the solid into the aqueous phase is referred to as *desorption*. Slow rates of desorption can greatly limit leaching rates and availability of the contaminant for absorption by plants and animals and for degradation by soil microflora. Rapid rates of desorption can speed contaminants through the soil to groundwater and render the contaminant readily available to plants, animals, and the soil microflora.

Batch partitioning tests in which the contaminant is allowed to equilibrate between soil and water phases under carefully controlled conditions are useful in describing interphase transfer. Results of these tests can also be used to identify soil properties exerting the greatest influence on retention and release of the contaminant by soils and, ultimately, allow development of predictive equations based on correlation of soil properties and partitioning coefficients. Field transport processes such as convective flow must be simulated in column tests (see Chapter 3).

#### Objectives

Objectives of the study were the following: (a) to determine the rate of adsorption of HAN and TEAN when soils are contacted with LP, and (b) to identify soil properties controlling adsorption.

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<sup>1</sup> By Judith C. Pennington and Cynthia B. Price, U.S. Army Engineer Waterways Experiment Station.

## Materials and Methods

### Preliminary tests

Batch tests were conducted by shaking soil, water, and the compound of interest until a steady-state distribution between phases was achieved. Several preliminary tests were necessary to develop the best operational conditions for conducting the batch tests. Preliminary tests included the following.

- a. *Contact screening.* Identification of LP interactions with soils that may generate hazards in the confined test system.
- b. *Tolerance to centrifugation.* The centrifugation time and speed necessary for removing particles greater than 0.5- $\mu$ m diameter from the solution phase while maintaining the integrity (safety) of the LP.
- c. *Biodegradability.* The significance of microbial growth during the test period.
- d. *Ratio test.* The ratio of soil to LP that would assure a measurable solution phase concentration of analyte.
- e. *Adsorption kinetics.* The time needed to attain an equilibrium distribution between solid and aqueous phases.

**Contact screening.** The contact screening test was originally envisioned to provide a qualitative indication of the vigor of reaction of LP with soil so that the shake partitioning tests could be designed for safety. Since gas production is an important fate process for LP in soils, more quantitative tests were also conducted. Descriptions of both qualitative and quantitative tests are presented in Chapter 1.

**Tolerance to centrifugation.** The solution phase was centrifuged after all visible reaction between the LP and the soil had dissipated. Centrifugation times at various speeds were calculated from the following equation (EPA 1991):

$$t_c = 1.41 \times 10^6 [\log R_2/R_1]/N^2 \quad (2)$$

where

$t_c$  = centrifuge time, minutes

$R_2$  = distance from centrifuge spindle to deposition surface of centrifuge tube

$R_s$  = distance from spindle to surface of sample

$N$  = number of revolutions of centrifuge per minute (rpm)

Values of  $N$  tested were 5,000, 6,000, and 11,000 rpm which are equivalent to 2,000, 2,800, and 9,400 relative centrifugal force (RCF). Tests were conducted consecutively from 5,000 to 11,000 so that the sealed centrifuge tubes could be examined for breakage after tests at each speed.

**Biodegradability.** Tests were conducted to measure the change in microbial numbers after 5 days under typical test conditions. Test results were used to determine the necessity for inhibiting microbial growth in subsequent tests. Five grams (ODW) of soil (Yuma 2A and Picatinny A) were placed in test flasks and left either unautoclaved or autoclaved at 121 °C and 15 lb of pressure for 15 min. Undiluted LP (20 mL) was added to each test. Tests were replicated three times. All flasks were placed on a rotating shaker (200 rpm). After 5 days, the solution phase was cultured for microbial activity (see Chapter 4), and a subsample was analyzed for HAN and TEAN.

**Ratio test.** A ratio test was performed to determine the ratio of soil to LP that would result in solution phase concentrations sufficiently high for accurate quantifications. The ratios tested were 1:3, 1:4, 1:5, and 1:6 soil to LP. Tests were performed with Yuma 2A and Picatinny A soils and 1,000 ppm LP. Twenty milliliters of diluted LP was added to a 50-mL Erlenmeyer flask with sufficient soil (ODW) to produce the desired ratios. Three replicates of each soil/LP ratio were placed on a rotating shaker for 48 hr, centrifuged at 11,000 rpm (9,400 RCF) for 15 min, and the solution phase was analyzed for HAN and TEAN by ion chromatography (Appendix A).

**Adsorption kinetics.** To determine the time required to establish a steady state of distribution between soil and LP components, three adsorption kinetics tests were conducted using Yuma 2A and Picatinny A soils. The tests differed in the concentration of LP used. Concentrations were (a) undiluted, (b) a 50-percent dilution of LP, and (c) 1,000 ppm LP. Tests were conducted by equilibrating 5 g (ODW) soil with 20 mL of LP or LP solution on a rotating shaker at 200 rpm in three replicates for 0.5, 1, 2, 6, 24, 48, and 120 hr. For 1,000-ppm tests, the first two sampling times (0.5 and 1 hr) were dropped, and a 72-hr sample was added. Three replicates of undiluted and of diluted LP without soil (controls) were analyzed at each sampling time to assess the stability of the LP components under the shaking conditions of the test. For the 1,000-ppm test, only one "no soil" control was tested with each "soil" test. Concentrations of HAN and TEAN in undiluted LP were determined to provide time zero data for the controls.

## Adsorption Isotherms

Adsorption isotherms were determined for each of the 16 soils. LP was partitioned between aqueous and soil phases in the same test system described

above for adsorption kinetics. Five concentrations of LP were tested: 100, 500, 1,000, 1,500, and 2,000 ppm. Soil to solution ratio was 1:4, and the equilibration time was 48 hr. Three replicates for each soil/LP concentration were tested. The aqueous phase was analyzed for HAN and TEAN. The soil phase was analyzed for HAN and TEAN in two soils only, Yuma 2A and Picatinny A. Soil phase concentrations for all other soils were calculated by difference from aqueous phase concentrations. Isotherm data were fit to one linear and two nonlinear models (the Langmuir Isotherm Model and the Freundlich Isotherm Model) that are commonly used to relate solid and aqueous phase contaminant concentrations in soils. Equations for each model are presented below (Weber 1972).

$$\text{Linear} \quad q = K_d C \quad (3)$$

$$\text{Langmuir} \quad q = QbC/(1+bC) \quad (4)$$

$$\text{Freundlich} \quad q = K_f C^{1/n'} \quad (5)$$

where

$q$  = solid phase concentration of TEAN (mg/kg)

$K_d$  and  $K_f$  = adsorption coefficients for the linear (L/kg) and Freundlich [ $\text{mg}^{(n-1)/n} \times \text{L}^{1/n}/\text{kg}$ ] equations, respectively

$C$  = equilibrium solution concentration of TEAN (mg/L)

$Q$  = monolayer sorption capacity (mg/kg)

$b$  = Langmuir constant related to entropy (L/mg)

$n'$  = Freundlich characteristic constant

Parameters for the two nonlinear models were determined by fitting the experimental data to the linearized forms of the Langmuir and Freundlich models as given below (Equations 6 and 7, respectively) (Voice and Weber 1983).

$$1/q = (1/Q) + (1/bQ)(1/C) \quad (6)$$

$$\ln q = \ln K_f + (1/n') \ln C \quad (7)$$

The coefficients of determination, R Square, of the linear regression for each model were compared to determine which model best fit the isotherm data.

The  $K_d$  values were correlated with 13 soil properties using the Pearson Product-Moment Correlation. This correlation test measures the degree of association between two variables without assigning independence to any variable. The correlation coefficient,  $r$ , is defined by the following equation:

$$r = \frac{\sum(X-\bar{X})(Y-\bar{Y})}{\sqrt{\sum(X-\bar{X})^2 \sum(Y-\bar{Y})^2}} \quad (8)$$

where

$r$  = Pearson Product-Moment Correlation Coefficient

$X$  = variable 1

$\bar{X}$  = mean of variable 1

$Y$  = variable 2

$\bar{Y}$  = mean of variable 2

The square of the correlation coefficient, R Square, is an indicator of linearity between the two variables. If the R Square is equal to 1, the straight line describes the relationship between the variables perfectly.

A predictive equation was generated using the results of the correlation analysis. The equation was generated by regressing  $K_d$  with the soil properties exhibiting high correlation (R Square > 0.5). All properties making an insignificant contribution to the prediction were eliminated.

## Results

### Preliminary tests

**Contact screening.** Results of the contact screening tests (presented in Chapter 1) indicated a need for an open flask rather than the standard sealed tube shake test. Therefore, all subsequent tests were performed in 50-mL erlenmeyer flasks with puff plug stoppers to allow escape of any pressure generated by release of gases from the tests. All tests were conducted on a rotating shaker under a fume hood.

**Centrifugation.** No breakage of centrifuge tubes was observed at any centrifugation speed. Therefore, centrifugation was considered to be a safe procedure for separating aqueous and solid phases in subsequent tests. A speed of 11,000 rpm for 15 min was selected.

**Biodegradability.** No colonies were detected in either autoclaved or unautoclaved tests at 5 days. Concentrations of HAN and TEAN in abiotic and biotic tests did not differ significantly ( $P > 0.05$ ). Therefore, no effort was made to control microbial growth in subsequent tests.

**Ratios test.** TEAN concentrations in the aqueous phase of both Yuma 2A and Picatinny A tests were measurable. HAN concentrations were not

measurable in the Picatinny A tests at any ratio and were measurable in the Yuma 2A tests at 1:5 and 1:6 ratios only. Detection of HAN in the 1:5 and 1:6 ratios indicates the presence in the aqueous phase of either unreacted or unadsorbed HAN. Since active bubbling and frothing of the soil were visible in these tests, the reason for the lack of HAN in the aqueous phase was assumed to be due to HAN reactions with the soil rather than to sorption. Results of subsequent sorption isotherms in which the soil phase was also analyzed for HAN and TEAN showed no detectable HAN in Yuma 2A and Picatinny A soils with up to 2,000 ppm LP. Since concentrations of TEAN were measurable at any of the tested ratios and HAN sorption was precluded by reactions with the soil, the 1:4 soil to LP ratio was selected for subsequent testing.

**Adsorption kinetics.** Results indicated very limited adsorption of either HAN or TEAN by the two test soils at any of the tested LP concentrations (Figures 7 and 8). Even though HAN reacted visibly with the soils when tested with undiluted or 50-percent diluted LP, concentrations in the aqueous phase remained only slightly changed from time zero values (Table 12). This is presumably due to the large excess of LP which left large quantities of unreacted HAN in solution. In the 1,000-ppm test, HAN concentrations fell to zero in 24 hr in the Picatinny A soil and in 48 hr in the Yuma 2A soil (Figure 8). These results are attributed to HAN reaction with the soil to produce gases. This reactivity precludes assessment of the sorption capacity of soils for HAN. In subsequent tests in which the soil was analyzed, no HAN was detected. Concentrations of TEAN varied little in either soil at any concentration indicating limited reactivity and sorption.

In undiluted LP tests, the concentration of HAN in controls containing no soil were fairly stable (Figure 7). The concentration of TEAN in controls containing no soil remained stable with diluted and undiluted LP, except in the set run with Picatinny soil tests in which TEAN concentration increased. This increase may be due to loss of water by evaporation. The variability in the 1,000-ppm control was higher than in tests (Figure 8). This is likely due to the fact that one of the two replicate controls was run with each soil test at slightly different times. The concentration of HAN in the control decreased slightly during the test, but the difference was not significant.

### **Adsorption Isotherms**

Model parameters and statistical information for batch adsorption of TEAN onto test soils are presented in Table 13. Isotherms models (solid lines) are plotted with a scatter plot of the data (closed dots) for four of the soils which are representative of other isotherms (Figure 9). Concentrations of HAN and TEAN in soil as well as solution phases were obtained for Picatinny A and Yuma 2A isotherms (Table 14). The soil concentrations are plotted in Figure 9 for these two soils, whereas all other soil values were determined by difference from solution phase analyses.

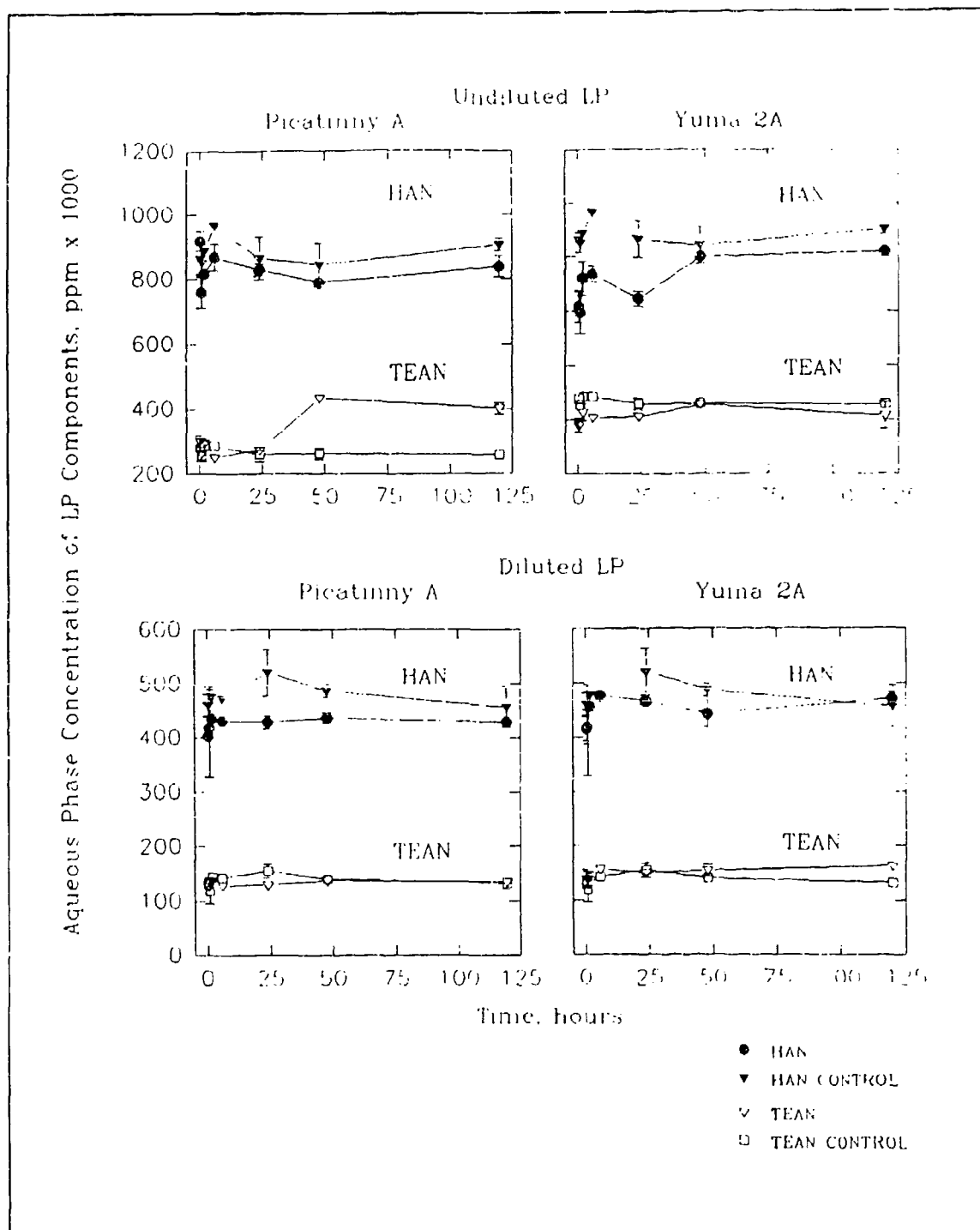


Figure 7. Adsorption kinetics of HAN and TEAN from undiluted and diluted LP on Picatinny A and Yuma 2A soils. Each datum point represents the mean of three replicates. Vertical bars are standard errors of the mean

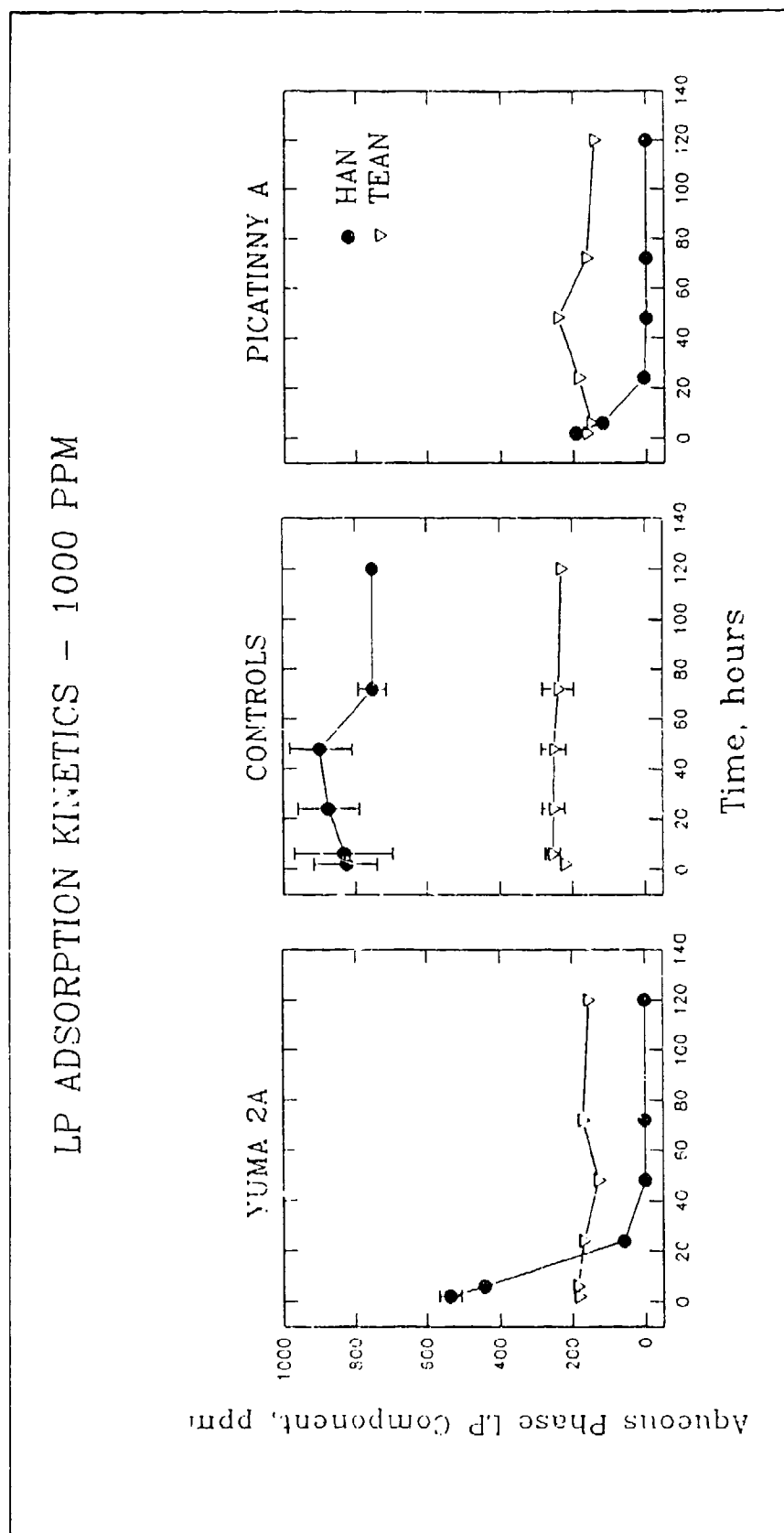


Figure 8 Adsorption kinetics of HAN and TEAN using 1,000 ppm LP on Picatinny A and Yuma 2A soils. Each datum point represents the mean of three replicates. The control graphs (center) contained LP only - no soil. Vertical bars are standard errors of the mean

**Table 12**  
**Concentrations of HAN and TEAN In Undiluted LP, a 50-Percent Dilution of LP and 1,000 ppm LP  $\pm$  One Standard Deviation Unit**

| Dilution                   | HAN Concentration (ppm) | TEAN Concentration (ppm) |
|----------------------------|-------------------------|--------------------------|
| Undiluted <sup>1</sup>     | 996,000 $\pm$ 30,000    | 312,000 $\pm$ 19,800     |
| 50 % Dilution <sup>2</sup> | 498,000                 | 156,000                  |
| 1,000 ppm <sup>2</sup>     | 996                     | 312                      |

<sup>1</sup> Values determined in three replicate analyses by ion chromatography.  
<sup>2</sup> Values determined by calculation from undiluted values.

**Table 13**  
**Linear Regression Parameters for TEAN Adsorption Data with Three Models**

| Soil          | Langmuir              |        |         | Freundlich |                |      | Linear   |                |
|---------------|-----------------------|--------|---------|------------|----------------|------|----------|----------------|
|               | R Square <sup>1</sup> | Q      | b       | R Square   | K <sub>f</sub> | n'   | R Square | K <sub>o</sub> |
| Picatinny A   | 0.989                 | 623    | 0.012   | 0.915      | 15.1           | 1.5  | 0.86     | 1.3            |
| Picatinny B   | 0.893                 | -333   | -0.021  | 0.462      | 32.2           | 1.3  | 0.16     | 2.0            |
| Yuma 1A       | 0.999                 | -981   | -1.9    | 0.995      | 1.39           | 0.89 | 0.98     | 2.8            |
| Yuma 1B       | 0.999                 | -548   | -0.0024 | 0.992      | 0.923          | 0.86 | 0.97     | 2.0            |
| Yuma 2A       | 1.000                 | 1,272  | 0.0018  | 0.999      | 2.70           | 1.09 | 1.0      | 1.7            |
| Yuma 2B       | 0.970                 | 664    | 0.039   | 0.798      | 62.6           | 2.4  | 0.78     | 1.7            |
| Yokota        | 0.999                 | 1,977  | 0.019   | 1.00       | 39.3           | 1.2  | 1.0      | 20.1           |
| WES Reference | 0.980                 | 500    | 0.069   | 0.996      | 44.2           | 2.0  | 0.94     | 2.6            |
| BRL-SAS A     | 0.995                 | 250    | 0.010   | 0.943      | 6.30           | 1.6  | 0.67     | 0.48           |
| BRL-SAS B     | 0.787                 | 250    | 0.066   | 0.756      | 24.9           | 2.0  | 0.69     | 1.5            |
| BRL-MAR A     | 0.989                 | 554    | 0.022   | 0.760      | 34.36          | 2.0  | 0.18     | 0.63           |
| BRL-MAR B     | 0.976                 | 549    | 0.018   | 0.973      | 14.79          | 1.4  | 0.95     | 2.8            |
| China Lake A  | 0.957                 | -111   | 0.0076  | 0.923      | 0.411          | 0.69 | 0.95     | 3.1            |
| China Lake B  | 0.999                 | 877    | 0.0026  | 0.992      | 7.78           | 1.2  | 0.96     | 1.5            |
| Socorro P     | 0.999                 | -3,654 | 0.0016  | 0.993      | 5.20           | 0.95 | 0.97     | 0.9            |
| Socorro S     | 0.996                 | -945   | -0.0035 | 0.990      | 2.98           | 0.92 | 0.99     | 4.4            |

<sup>1</sup> R square = square of correlations coefficient; Q = monolayer sorption capacity; b = Langmuir constant related to entropy (L/mg); K<sub>f</sub> = adsorption coefficients for Freundlich equation [mg<sup>1/n'</sup>  $\times$  L<sup>1/n'</sup>/kg]; n' = Freundlich characteristic constant; K<sub>o</sub> = adsorption coefficient for linear (L/kg) equation.

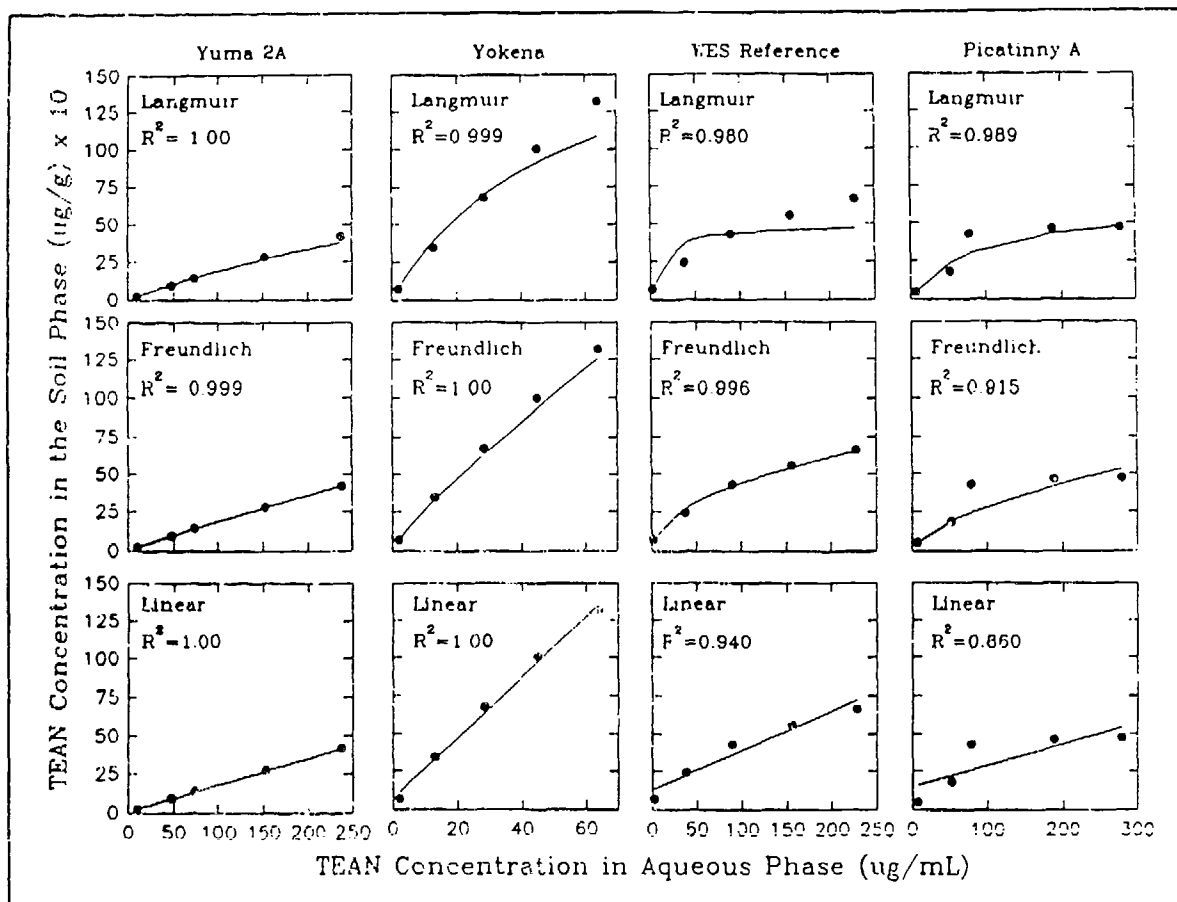


Figure 9. Adsorption isotherms of TEAN in four soils: Yuma 2A, Yokena, WES Reference, and Picatinny A. Isotherms models (solid lines) are plotted with a scatter plot of the data (closed dots). These isotherms are somewhat representative of isotherms for other soil. Each datum point represents the mean of three replicates. Soil concentrations were determined by difference from solution phase concentrations except for Picatinny A and Yuma 2A soils for which the soil phase as well as solution phase was analyzed

Adsorption isotherms of TEAN fit the Langmuir model better than the other models except for Yokena and WES Reference soil, for which the three models differed very little. Only two soils exhibited an R Square less than 0.9 with the Langmuir model. Both of those, Picatinny B (0.89) and BRL-SAS B (0.79), were nonetheless good fits. Eleven of the sixteen soils were also fit by the Freundlich model and ten by the linear model. The consistency between models occurs because the amount of TEAN sorbed by soils is directly proportional to the concentration in solution. This results in small  $n$  and  $b$  values (near 1) for the Freundlich and Langmuir models, respectively. Partition coefficients ( $K_d$ s) for TEAN from the linear model were relatively low, ranging

**Table 14**  
**Concentrations and Standard Errors of HAN and TEAN**  
**(ppm) in Soil and Water Phases of Adsorption Isotherms for**  
**Picatinny A and Yuma 2A Soils**

| Soil        | Phase | LP Concentration (ppm) | HAN             | SE  | TEAN  | SE   |
|-------------|-------|------------------------|-----------------|-----|-------|------|
| Picatinny A | Water | 100                    | <1 <sup>1</sup> | <1  | 10.50 | 0.41 |
|             |       | 500                    | <1              | <1  | 47.7  | 1.7  |
|             |       | 1,000                  | <1              | <1  | 73.7  | 0.72 |
|             |       | 1,500                  | 168             | 18  | 152   | 8.3  |
|             |       | 2,000                  | 288             | 12  | 238   | 6.2  |
|             | Soil  | 100                    | <5              | <5  | 8.33  | 0.72 |
|             |       | 500                    | <5              | <5  | 66.3  | 26   |
|             |       | 1,000                  | <5              | <5  | 205.0 | 12   |
|             |       | 1,500                  | <5              | <5  | 346   | 12   |
|             |       | 2,000                  | <5              | <5  | 356   | 8.8  |
| Yuma 2A     | Water | 100                    | <1              | <1  | 7.33  | 0.27 |
|             |       | 500                    | <1              | <1  | 52.7  | 0.98 |
|             |       | 1,000                  | <1              | <1  | 78.7  | 0.72 |
|             |       | 1,500                  | 2.67            | <1  | 190   | 0.54 |
|             |       | 2,000                  | 77.0            | 2.2 | 278   | 6.6  |
|             | Soil  | 100                    | <5              | 2.3 | 23.7  | 0.72 |
|             |       | 500                    | <5              | <5  | 93.5  | 2.02 |
|             |       | 1,000                  | <5              | <5  | 151   | 4.5  |
|             |       | 1,500                  | <5              | <5  | 283   | 1.5  |
|             |       | 2,000                  | <5              | <5  | 402.7 | 23   |

<sup>1</sup> Values represent means of three replicates. Aqueous phase detection limits were 1 ppm; soil phase detection limits were 5 ppm

from 0.48 to 20.1 with a mean for all soils of  $3.5 \pm 1.2$ . Low partition coefficients indicate limited adsorption of TEAN. When a compound fails to adsorb to the soil and remains in the water, the compound is free to migrate through the soil to the groundwater. The low  $K_{ds}$  mean that soil adsorption will not prevent TEAN from becoming diluted by rainfall events or applications of water to spills and, subsequently, being washed through the soil. However, these events are governed by the flow dynamics of each soil which cannot be extrapolated from the batch partitioning results presented here. The fate of TEAN in the soil profile under various hydrodynamic regimes is the subject of the column studies (see Chapter 3).

Calculated partition coefficients for several important environmental contaminants have been derived from log octanol-water partition coefficient (log  $K_{ow}$ , EPA/USACE (1991)) for China Lake A, Picatinny A, and Socorro P soils (Table 15). Calculations were based upon the relationship among  $K_d$ ,  $K_{ow}$ , and the fraction of organic carbon (fOC) in the soils (DiToro et al. 1991). The  $K_d$  values were derived by multiplying fraction of organic carbon in each soil by  $K_{ow}$  of each contaminant of interest. These values are presented for comparison with the empirically determined  $K_d$  of TEAN in the same soils. Partition coefficients of TEAN are in the range of other relatively low molecular weight organic contaminants.

**Table 15**  
**Adsorption Coefficients of Some Important Environmental Contaminants and TEAN**

| Contaminant              | Octanol/Water Partition Coefficient <sup>1</sup><br>log $K_{ow}$ | $K_d$ <sup>2</sup>  |                     |                     |
|--------------------------|------------------------------------------------------------------|---------------------|---------------------|---------------------|
|                          |                                                                  | China Lake A        | Picatinny A         | Socorro P           |
| PCB 1260                 | 6.9                                                              | $1.398 \times 10^5$ | $8.688 \times 10^6$ | $9.310 \times 10^5$ |
| 2, 3, 7, 8-TCDD (dioxin) | 6.1                                                              | $2.215 \times 10^4$ | $1.377 \times 10^6$ | $1.475 \times 10^5$ |
| 4, 4'-DDT                | 5.7                                                              | 155                 | $5.481 \times 10^5$ | $5.874 \times 10^4$ |
| 1, 1, 1-Trichloroethane  | 2.5                                                              | 5.566               | 345.86              | 37.0                |
| Trichloroethene          | 2.4                                                              | 4.421               | 274.73              | 29.44               |
| Toluene                  | 2.2                                                              | 2.789               | 173.34              | 18.57               |
| Nitrobenzene             | 1.9                                                              | 1.398               | 86.88               | 9.31                |
| Dichloromethane          | 1.3                                                              | 0.351               | 21.82               | 2.34                |
| Bromomethane             | 1.0                                                              | 0.176               | 10.94               | 1.17                |
| N-Nitrosodimethylamine   | 0.6                                                              | 3.98                | 0.070               | 4.34                |
| TEAN                     | -                                                                | 3.1                 | 1.3                 | 6.9                 |

<sup>1</sup> Data compiled in EPA/USACE (1991).

<sup>2</sup> Values derived by multiplying fraction of organic carbon in each soil by  $K_{ow}$  (DiToro et al. 1991), except for TEAN where values are empirical.

The Pearson Product-Moment Correlation of TEAN sorption coefficients ( $K_d$ s) and soil properties resulted in strongest correlations with percent clay and CEC (Table 16). These results suggest several possible mechanisms of TEAN sorption in soils. TEAN very likely exists in the soil as protonated TEA, a cationic form. Adsorption of cations occurs through exchange of functional groups such as -COOH and phenolic-OH in the organic matter, or by displacement of inorganic cations such as Fe or Al from clay surfaces (Khan 1980). The presence of three hydroxyl groups and an amine also make TEA susceptible to hydrogen bonding with the abundant similar functional groups in soil organic matter.

**Table 16**  
**Pearson Product-Moment Correlation Coefficients for Correlation**  
**of TEAN Sorption Coefficients ( $K_d$ s) with 16 Soil Properties<sup>1</sup>**

| Soil Property <sup>1</sup> | Correlation Coefficient | Probability |
|----------------------------|-------------------------|-------------|
| Percent clay               | 0.872                   | <0.001      |
| Cation exchange capacity   | 0.871                   | <0.001      |
| Oxalate extractable iron   | 0.692                   | 0.009       |

<sup>1</sup> Only soil properties for which probabilities of no significant correlation were less than 0.05 are presented. Probabilities greater than 0.05 indicate no significant relationship between the  $K_d$  and the soil property.

Partition coefficients ( $K_d$ s) for TEAN can be predicted from percent clay in soils using the following relationship:

$$K_d = -1.019 + 0.354(\%Clay) \quad (9)$$

where %Clay is percent clay. Other soil properties that exhibited positive correlation with  $K_d$  made insignificant contributions to the prediction and were eliminated from the equation. The predictive equation is based on  $K_d$  and properties of thirteen of the test soils; three soils (Socorro S, Yuma 2A, and BRL-SAS B) were withheld from the database to serve as checks on the predictive equation. When percent clay for these soils is substituted into Equation 9, the predicted values shown below can be compared with the empirical values:

| <u>Soil</u> | <u>Predicted <math>K_d</math></u> | <u>Empirical <math>K_d</math></u> |
|-------------|-----------------------------------|-----------------------------------|
| Socorro S   | 8.7                               | 4.4                               |
| Yuma 2A     | 0.75                              | 1.7                               |
| BRL-MAR B   | 3.9                               | 2.8                               |

The predicted and actual values agree within a factor of approximately 2.

Solution phase concentrations of HAN in isotherm tests showed reaction and dissipation of the HAN until the reactive soil component(s) was depleted in the sample and unreacted HAN accumulated in the solution phase of the test (Table 17). Results demonstrate that the soils vary widely in reactivity with HAN. China Lake, which was high in sand, showed the least reactivity. Socorro P and BRL-SAS B showed the greatest reactivity. Results of analysis for HAN in Picatinny A and Yuma 2A soils indicated no HAN at any LP concentration; all of the unreacted HAN was present in the solution, not the soil, phase. Therefore, HAN had not partitioned into the soils.

**Table 17**  
**Concentration of HAN  $\pm$  Standard Error (ppm) in Aqueous Phase**  
**of Sorption Isotherm Tests**

| Soil          | 100            | 500            | 1,000          | 1,500           | 2,000          |
|---------------|----------------|----------------|----------------|-----------------|----------------|
| Unreacted HAN | 60.8           | 306            | 613            | 920             | 1 226          |
| Picatinny A   | <1             | <1             | <1             | <1              | 77 $\pm$ 4.0   |
| Picatinny B   | <1             | <1             | 7.0 $\pm$ 1.5  | 18.0 $\pm$ 0.58 | 212 $\pm$ 24   |
| Yuma 1A       | <1             | 150 $\pm$ 0.50 | 386 $\pm$ 26   | 568 $\pm$ 57    | 676 $\pm$ 77   |
| Yuma 1B       | <1             | 67.0 $\pm$ 2.6 | 277 $\pm$ 4.4  | 527 $\pm$ 8.2   | 910 $\pm$ 36   |
| Yuma 2A       | <1             | <1             | <1             | 168 $\pm$ 22    | 288 $\pm$ 14   |
| Yuma 2B       | <1             | <1             | 97 $\pm$ 10    | 394 $\pm$ 15    | 754 $\pm$ 14   |
| Yokena        | <1             | <1             | <1             | 6.33 $\pm$ 0.33 | 49 $\pm$ 0.58  |
| Wes Reference | <1             | <1             | 20 $\pm$ 0.58  | 154 $\pm$ 6.8   | 341 $\pm$ 8.3  |
| BRL-SAS A     | <1             | <1             | 66 $\pm$ 4.4   | 232 $\pm$ 9.5   | 511 $\pm$ 49   |
| BRL-SAS B     | <1             | <1             | <1             | <1              | <1             |
| BRL-MAR A     | <1             | 42 $\pm$ 1.5   | 130 $\pm$ 2.6  | 441 $\pm$ 4.9   | 790 $\pm$ 6.3  |
| BRL-MAR B     | <1             | 10 $\pm$ 5.4   | 161 $\pm$ 16   | 337 $\pm$ 14    | 228 $\pm$ 6.5  |
| China Lake A  | 20.7 $\pm$ 2.8 | 261 $\pm$ 23   | 532 $\pm$ 3.3  | 843 $\pm$ 9.6   | 1,212 $\pm$ 51 |
| China Lake B  | <1             | <1             | 7.0 $\pm$ 1.5  | 18.0 $\pm$ 0.58 | 212 $\pm$ 24   |
| Socorro P     | <1             | <1             | <1             | <1              | <1             |
| Socorro S     | <1             | <1             | 50.67 $\pm$ 14 | 205.0 $\pm$ 36  | 452 $\pm$ 16   |

Results of Pearson Product-Moment Correlation of HAN concentration in the solution phase of the 2,000-ppm LP isotherm test yielded no strong correlations (Table 18). Reactivity of HAN with soils correlated best with TOC, TKN, oxalate extractable Fe, and percent silt. Lack of stronger correlation with metals was surprising, since HAN is known to be reactive with certain metals (Schmidt 1990, Hansen 1988, Backof 1989). However, metals are infrequently present in elemental form in soils. The Fe, Al, and Mn extracted from the soil with the oxalate procedure consist of metals in organic complexes or noncrystalline hydrous oxides. The total Fe procedure assays Fe in all of its potential forms, which include soluble and insoluble forms, oxidized ( $\text{Fe}^{+3}$ ) or reduced ( $\text{Fe}^{+2}$ ) states, free oxides, complexes, or elemental form. Apparently, HAN is not as reactive with these various forms of Fe, Al, or Mn as with elemental forms. The positive correlation with percent sand is consistent with other results that indicate limited reactivity of HAN with sand, for example, the limited reactivity of HAN with the China Lake B soil as indicated by solution phase concentrations (Table 17).

**Table 18**  
**Pearson Product-Moment Correlation Coefficients for Correlation**  
**of Concentration of HAN in Solution Phase of 2,000-ppm LP**  
**Isotherm Tests and 16 Soil Properties<sup>1</sup>**

| Soil Property            | Correlation Coefficient | Probability |
|--------------------------|-------------------------|-------------|
| Total Organic Carbon     | -0.563 <sup>2</sup>     | 0.023       |
| Total Kjeldahl Nitrogen  | -0.557                  | 0.025       |
| Oxalate Extractable Iron | -0.519                  | 0.040       |
| Percent Silt             | -0.499                  | 0.049       |
| Percent Sand             | 0.592                   | 0.016       |

<sup>1</sup> Only soil properties for which probabilities were less than 0.05 are presented. Probabilities greater than 0.05 indicate no relationship, positive or negative, between the soil property and the solution phase concentration of HAN.

<sup>2</sup> A negative correlation coefficient indicates an inverse relationship; that is, the concentration of HAN in solution decreases as the soil property increases.

## Conclusions

The two components of LP, HAN and TEAN, differ significantly in interaction with soils. The HAN reacts with oxidizable soil components producing gases that volatilize from the soil. In the sorption tests, when undiluted or a 50-percent diluted LP was used, the amount of LP greatly exceeded the available oxidizable materials in the soil, so that the concentration of HAN was virtually unchanged in the solution phase of the test. However, when 1,000-ppm LP was partitioned into soils, the concentration of HAN dropped to zero within 24 to 48 hr as a result of reaction with soil components. In a field setting, excess HAN would persist only until the HAN migrated into unreacted soil. Reactivity as indicated by decreases in solution phase concentrations of HAN in the 2,000-ppm LP isotherm correlated only slightly ( $R^2 = 0.5$ ) with soil properties. Properties exhibiting significant correlation ( $P \leq 0.05$ ) were TOC, TKN, oxalate extractable Fe, and percent silt. Results of this study revealed no evidence of significant soil adsorption of HAN.

Concentrations of TEAN in the solution phase of tests with undiluted and diluted LP varied only slightly from initial values over 5 days. Even when 1,000-ppm LP was tested, TEAN concentrations were relatively stable over time. These results indicate very limited adsorption of TEAN by the soils. The Langmuir Isotherm Model best described sorption of TEAN in most of the soils, but all three models performed well. Partition coefficients were relatively low. Mean  $K_d$  for all soils was 3.1. Adsorption correlated best with percent clay, CEC, oxalate extractable Fe, TOC, oxalate extractable Al, and total Fe. These results are consistent with ionic interaction between TEAN, or the cationic TEA, with these soil components.

# 3    **Runoff, Infiltration, and Transport<sup>1</sup>**

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## **Introduction**

### **Background**

One of the broad objectives of the research conducted in support of a spill response plan for LP was to determine how fast LP runs off soils while it infiltrates into the ground and begins its decomposition process. Little information is available about what happens in different time periods (minutes, hours, days, and months) after a spill. LP can flow and puddle on the ground surface (time periods of seconds to hours) until it soaks into the ground (time periods of minutes to hours), where it can continue to migrate (time periods of days to months). The volume of the spill and the rate of leakage help to define the delay between discovery of a spill and the choice of corrective actions. The extent of the zone of soil contamination depends upon the area that comes into contact with the flowing LP and the depth of soil that is exposed. Diking to contain and redirect the spill flow is likely to be the first intervention. Shortly thereafter, intervention may consist of reducing the hazards of personnel contacting the spilled liquid on the ground surface by erecting barriers around the spill area, covering the contaminated area, applying solvents, or washing down the ground surface. After the immediate threat of human injury is removed, attention can shift to environmental protection.

The pH conditions that prevail in a soil after an LP spill are related not only to the soil type but also to the concentration of the LP in the soil, as LP is miscible with water. The duration of a low pH condition in a soil brought about by a spill may be modified by chemical reactions and LP mixing with water. LP is expected to migrate through the soil under the impetus of its weight and capillary forces.

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<sup>1</sup> By Donaka Deen Adnan, Louisiana State University; Tommy E. Myers, U.S. Army Engineer Waterways Experiment Station.

Important questions for which there is insufficient information in the literature include:

- How far is spilled LP likely to flow across the ground surface from a spill site?
- How fast is spilled LP likely to soak into the ground?
- How quickly can LP be washed from saturated soil?
- How does undiluted and diluted LP react with soils?
- Do HAN and TEAN migrate through the soil at the same rate, or are they subject to sorption and retardation on the soil?
- To what extent can knowledge of water runoff and infiltration into soils be translated to describe runoff and infiltration of LP?

## Objectives

Specific objectives of the study were as follows:

- a. To compare the runoff and infiltration behavior of LP and water on five soils.
- b. To describe the transport of undiluted HAN and TEAN through soils when their migration rates are increased by water applied over a spill as in rainfall events or spill response dilution efforts.
- c. To simulate the transport of HAN and TEAN through soils after their concentration has been reduced by dilution.

## Theory

### Runoff

Fluid flow down a slope may be classified as either laminar or turbulent, depending on the dimensionless Reynolds number  $N_{Re}$ , which is defined as

$$N_{Re} = \frac{U\eta_0}{\mu} \quad (10)$$

where

$U$  = average velocity of flow, cm/s

$B$  = depth of flow, cm

$\rho$  = fluid density, g/cm<sup>3</sup>

$\mu$  = fluid viscosity, g/cm-s

When the Reynolds number is less than 500, the flow is laminar. Laminar flow is associated with shallow flows on gentle slopes as would be most typical of LP spills. Turbulent flow is associated with deep, fast flow, such as flow in a stream. Turbulent flow could occur for a large LP spill on a steep slope, especially if the flow were constrained so that it took place in a rut or a furrow.

The equation for the average LP velocity in laminar flow on a plane surface,  $U$  (cm/s), is (Streeter and Wylie 1979)

$$U = \frac{\rho g \sin \theta B^2}{6\mu} \quad (11)$$

where the terms are as defined above, and

$g$  = acceleration of gravity, cm/s<sup>2</sup>

$\theta$  = slope of ground surface, radians

$T$  (s) is the time required for LP to flow a distance  $L'$  (cm) at a velocity  $U$ , so Equation 11 becomes

$$L' = \int_0^T U dt = \frac{\rho g \sin \theta}{6\mu} \int_0^T B^2 dt \quad (12)$$

Since the functional relationship between the depth of flow,  $B$ , and time is difficult to define, the integral cannot be evaluated. However, if  $B$  is approximated by its average value,  $B_{avg}$ , which is easier to determine, the equation for  $L'$  becomes

$$L' = \frac{\rho g \sin \theta}{6\mu} B_{avg}^2 T \quad (13)$$

To understand the effects of vegetative ground cover on the laminar flow of LP in the event of a spill, several equations should be examined. Hammer and Kadlec (1986) reviewed water flow equations proposed for vegetated slopes.

Most equations were based on Manning's equation for turbulent flow, so they are not applicable to laminar LP flow through vegetation (Streeter and Wylie 1979). Hammer and Kadlec (1986) cited one empirical equation that fit creeping flow (this may have been laminar flow) in shallow wetlands containing vegetation (water depth varied from 0 to 100 cm) where the distance travelled by a parcel of water was less than 100 m/day. The equation is

$$U = \alpha B^\beta \theta_s \quad (14)$$

where

$\alpha$  = hydraulic friction law,  $M^{1-\beta}/\text{day}$

$\beta$  = hydraulic friction law exponent

$\theta_s$  = slope of water surface

They found that  $\beta = 2$  or  $3$  worked well for wetland water flow data sets; as  $\beta$  is similar to the exponent in Equation 13, Equation 14 might represent LP flow through vegetation.

Adrian and Martel (1989) proposed an equation that took into account laminar flow through grass on a slope. Their equation is

$$U = \frac{2\rho g \sin \theta}{G\eta\mu} \left[ 1 - \frac{1}{\beta} \sqrt{\frac{2}{G\eta}} \tanh \left( \sqrt{\frac{G\eta}{2}} \beta \right) \right] \quad (15)$$

where

$G$  = grass density, stalks per unit area

$\eta$  = constant for the equation  $C_D = \frac{\eta}{N_{Re}}$

$C_D$  = drag coefficient, dimensionless

They suggested that grass cover decreased the average flow velocity as predicted by Equation 11 by factors of 10 to 20.

Agricultural researchers have developed equations for the movement of irrigation water across a field, so the equations may be applicable to LP flow. The equations take into account infiltration into the soil and overland flow. However, the overland flow is turbulent, so it is described by the Manning equation (Yu 1982).

## Infiltration

The volume of water lost to infiltration during irrigation of fields is described through the Kostiakov equation (Kostiakov 1932)

$$Z = k\tau^a + c\tau \quad (16)$$

where

$Z$  = volume of water infiltrated per unit length

$k$  = constant, area/time

$\tau$  = time since start of flooding

$a$  = dimensionless constant

$c$  = constant, area/time

A limitation of the Kostiakov equation is that it is only applicable during the period of ground flooding, so it would not apply to LP migration in soils after the LP disappeared from the soil surface.

Dimensional analysis provides a method of formulating dimensionally correct semi-empirical LP flow and infiltration equations (Bridgman 1931, Streeter and Wylye 1979). A volume of liquid,  $V$ , spilled on a slope flows a distance  $L'$ , where it stops at time  $T$  as all of the volume has infiltrated.  $L'$  is postulated to be a function of the liquid, soil, and other properties:

$$L' = f(V, g, \rho, \mu, \sigma, n, \theta, d, T) \quad (17)$$

where the new symbols and their dimensions are

$n$  = porosity, dimensionless

$d$  = soil particle size, cm

These variables are regrouped into seven dimensionless numbers

$$\frac{L'}{V^{1/3}} = f\left(\frac{\mu}{\rho\sqrt{g}V}, \frac{\sigma}{\rho g V^{2/3}}, n, \theta, \frac{d}{V^{1/3}}, \frac{\sqrt{g}T}{V^{1/6}}\right) \quad (18)$$

The equation for LP runoff distance that is consistent with the laminar flow equation, the application time, the surface tension effect, and the particle size effect is

$$\frac{L'}{V^{1/3}} = K \left[ \left( \frac{\rho \sqrt{g} V}{\mu} \right) \theta \left( \frac{\sqrt{g} t}{V^{1/6}} \right) \right]^A \left[ \frac{\sigma}{\rho g V^{2/3}} \right]^{-B} \left[ \frac{d}{V^{1/3}} \right]^{-C} \quad (19)$$

where the coefficient  $K$  and exponents  $A$ ,  $B$ , and  $C$  are determined from experimental results. For example, the surface tension is expected to increase the infiltration rate so that the runoff distance is decreased. Thus, the surface tension has a negative exponent. Similarly, the particle size is expected to be inversely related to the runoff distance so it has a negative exponent. Time is now interpreted as the application time, or the spill time, so that it has been designated as  $t$  rather than  $T$ .

The variables involved in describing infiltration include the distance the wetting front is below the ground surface,  $y$ , at time  $t$ , and many of the variables from Equation 17

$$y = f(V, t, g, \rho, \mu, \sigma, n, d, \theta) \quad (20)$$

where the symbols have the same meaning as previously defined. The subscripts on the  $y$  and  $t$  variables can be dropped when both are recorded at the same time. The variables are regrouped into seven dimensionless numbers:

$$\frac{y}{V^{1/3}} = f \left( \frac{\mu}{\rho \sqrt{g} V}, \frac{\sigma}{\rho g V^{2/3}}, n, \theta, \frac{d}{V^{1/3}}, \frac{\sqrt{g} t}{V^{1/6}} \right) \quad (21)$$

The LP infiltration distance is the product of the velocity of flow in the soil times the elapsed time. The velocity of liquid flow,  $U$ , in soil, such as LP velocity, is given by the Darcy equation (Domenico and Schwartz 1990)

$$U = KI \quad (22)$$

where

$K$  = coefficient of hydraulic conductivity, cm/s

$I$  = hydraulic gradient, dimensionless

The hydraulic gradient for vertical flow approaches 1.0 as the infiltration gets deeper. The coefficient of hydraulic conductivity,  $K$ , is related to soil and fluid properties by

$$K = \frac{md^2\rho g}{\mu} \quad (23)$$

where

$m$  = dimensionless constant

Large values of the surface tension will typically increase the infiltration rate. Also, the soil slope will be related inversely to the infiltration depth since the fluid runs off a steep slope faster. Thus, the infiltration equation form is

$$\frac{y}{V^{1/3}} = K \left[ \left( \frac{\rho \sqrt{g} V}{\mu} \right) \left( \frac{\sqrt{g} t}{V^{1/6}} \right) \left( \frac{d^2}{V^{2/3}} \right) \right]^A \left( \frac{\sigma}{\rho g V^{2/3}} \right)^B \theta^{-C} \quad (24)$$

where the coefficient  $K$  and the exponents  $A$ ,  $B$ , and  $C$  are determined from experimental data.

### Expansion of the soil

The unconfined expansion of the soil in contact with LP can be defined as the relative change in volume of soil per unit volume of soil (Domenico and Schwartz 1990). A column constrains the soil so it can expand only vertically. Then soil expansivity is defined as

$$\beta_s = \frac{1}{K_s} = \frac{\Delta L'}{L'} \quad (25)$$

where

$\beta_s$  = soil expansivity, dimensionless

$K_s$  = bulk modulus of expansion, dimensionless

$\Delta L'$  = change of length of soil column, cm

$L'$  = original length of the soil, cm

### Dispersion, reaction, and sorption

The dispersion coefficient, first-order reaction rate coefficient, and retardation factor may be calculated from one of two models, depending upon which

one is appropriate for the experimental conditions. One model is appropriate for an instantaneous injection of LP, while the other is appropriate for a step increase in LP concentration. LP contains two constituents, HAN and TEAN, either or both of which can be applied in the appropriate model.

The equation describing the effluent concentration of LP injected into column feed as an instantaneous mass source is (Carslaw and Jaeger 1963, Thomann and Mueller 1987)

$$C(L',T) = \left[ \frac{\left( \frac{M}{A} \right)}{\sqrt{\frac{4\pi DTL'}{Rv}}} \right] \text{EXP} \left[ -\frac{L'Rv(1-T)^2}{4DT} - \frac{kTL'}{v} \right] \quad (26)$$

where

$C(L',T)$  = HAN, TEAN concentration at location  $L'$ , time  $T$ , mg/L

$M$  = HAN, TEAN mass input, mg

$A$  = pore area,  $\text{cm}^2$

$D$  = dispersion coefficient,  $\text{cm}^2/\text{s}$

$T$  = pore volume eluted (dimensionless time), dimensionless

$L'$  = column length, cm

$R$  = retardation coefficient, dimensionless,  $R = 1 + \frac{\rho_b K_d}{n}$

$\rho_b$  = bulk density,  $\text{g}/\text{cm}^3$

$K_d$  = adsorption distribution coefficient,  $\text{cm}^3/\text{g}$

$k'$  = first-order reaction rate,  $\text{s}^{-1}$

$v$  = average pore fluid velocity,  $\text{cm}/\text{s}$

The measured concentrations of HAN versus pore volumes eluted,  $T$ ; TEAN versus  $T$ ; and chloride ion versus  $T$  are supplied to the above equation. Then a nonlinear curve-fitting program, TableCurve<sup>TM</sup> (Jandel Scientific, Corte Madera, CA) is used to estimate for the soil and the flow conditions the values of the HAN, TEAN, or chloride ion dispersion coefficient, reaction rate coefficient, and retardation coefficient. These values represent the mixing, transformation rate, and sorptive properties of the LP constituents, or other tracers, as they flow in soil.

When the step increase in LP concentration is applied to the influent of the column, the appropriate equation for  $C(L', T)$  becomes (van Genuchten and Alves 1982):

$$C(L', t) = \frac{C_0}{2} \exp \left( \frac{vL'}{2D} - \sqrt{\frac{\lambda}{D}} L' \right) \operatorname{ERFC} \left( \frac{L'}{\sqrt{4Dt}} - \sqrt{\lambda t} \right) + \frac{C_0}{2} \exp \left( \frac{vL'}{2D} + \sqrt{\frac{\lambda}{D}} L' \right) \operatorname{ERFC} \left( \frac{L'}{\sqrt{4Dt}} + \sqrt{\lambda t} \right) \quad (27)$$

where terms which have not been defined with Equation 26 are

$C_0$  = HAN, TEAN input concentration, mg/L

$\exp(*)$  = exponential function of  $(*)$

$$\lambda = \frac{v^2}{4D} + k'$$

$\operatorname{ERFC}(*)$  = complementary error function of  $(*)$

$(*)$  = any function can replace  $*$ , for example,

$$* = \frac{vL'}{2D} - \sqrt{\frac{\lambda}{D}} L'$$

When the retardation coefficient,  $R$ , and the dimensionless time,  $T$ , measured in pore volumes are introduced, the equation becomes:

$$C(L', T) = \frac{C_0}{2} \exp \left( \frac{vL'}{2D} - \sqrt{\frac{\lambda R}{D}} L' \right) \operatorname{ERFC} \left( \frac{L'}{\sqrt{\frac{4DL'T}{Rv}}} - \sqrt{\frac{\lambda L'T}{v}} \right) + \frac{C_0}{2} \exp \left( \frac{vL'}{2D} + \sqrt{\frac{\lambda R}{D}} L' \right) \operatorname{ERFC} \left( \frac{L'}{\sqrt{\frac{4DL'T}{Rv}}} + \sqrt{\frac{\lambda L'T}{v}} \right) \quad (28)$$

where

$$\lambda = \frac{v^2}{4DR} + \frac{k'}{R}$$

Again, TableCurve™ can be used to carry out the nonlinear fitting of the experimental data to the equations so as to calculate the values of  $D$ ,  $R$ , and  $k$ . These values represent the mixing, retardation (sorptive), and transformation rate properties, respectively, of the soil and LP constituents as they flow in the soil. The dispersion coefficient,  $D$ , measured from any of several chemical species, including HAN, TEAN, and chloride ion, is expected to be nearly identical for a given soil and a given flow velocity. Each chemical species is expected to have its own retardation coefficient,  $R$ , for each soil. The transformation rate constant,  $k'$ , is expected to be unique to each chemical species and each soil. Transformation rate constants are not expected to vary with the velocity of flow through a column.

## Materials and Methods

### Runoff and Infiltration experiments

Table 19 shows the experimental matrix for the runoff and infiltration experiments for the five soils investigated. Table 20 shows the characterization of the soils. The experiments were carried out in Plexiglas chambers whose slope could be adjusted by placing shims under one end (see Figure 10) to produce slopes of  $X_1$ ,  $X_2$ ,  $X_3$ . Measured weights of soil were packed in the chambers in 1-in. lifts. The surface was scarified; then the procedure was repeated several times until the desired total depth of 3 to 6 in. was obtained. The top surface of the soil was then leveled. LP in 5-, 10-, or 15-mL volumes was applied to the soil surface as shown in Figure 11. The distance the liquid propellant ran down the slope and an outline of the wetting front in the soil were recorded. All experiments were duplicated with water applied to the soil.

### Movement and reactions of undiluted LP in soils

The five soils were packed dry into burets to study the movement of undiluted LP (Figure 12). Table 21 shows the weight of each soil and its porosity after being packed to a depth of 4 in. at the bottom of the buret. Two inches of LP-saturated soil were placed over the dry soil, followed by two inches of water. Table 22 shows the weights of the soil and LP mixed to make the LP-saturated soils and also the weight of water poured onto the saturated soil.

Immediately after water was added to the buret, the stopcock was opened. The position of the wetting front in the formerly dry soil was recorded. Liquid was collected by a fraction collector for chemical analysis as soon as discharge

**Table 19**  
**Experimental Matrix for Runoff and Infiltration Studies**

| Soil                                   | Slope 1                | Slope 2                | Slope 3                |
|----------------------------------------|------------------------|------------------------|------------------------|
| China Lake B<br>LP (mL)<br>Water (mL)  | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 |
| Picatinny A<br>LP (mL)<br>Water (mL)   | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 |
| Socorro P<br>LP (mL)<br>Water (mL)     | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 |
| WES Reference<br>LP (mL)<br>Water (mL) | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 |
| Yuma-2A<br>LP (mL)<br>Water (mL)       | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 | 5, 10, 15<br>5, 10, 15 |

**Table 20**  
**Soil Characteristics**

| Soil         | % Sand | % Silt<br>% Clay | % Org.<br>Matter | % Water | d (cm)<br>50 % size | Spec.<br>Grav. | Class               |
|--------------|--------|------------------|------------------|---------|---------------------|----------------|---------------------|
| China Lake B | 97.5   | 0.0<br>2.5       | 0.53             | 1.1     | 0.040               | 2.59           | Silty Sand<br>SP-SM |
| Picatinny A  | 55.0   | 37.5<br>7.5      | 2.92             | 11.5    | 0.0075              | 2.65           | Sandy Silt<br>ML    |
| Socorro P    | 42.5   | 30.0<br>27.5     | 0.53             | 12.9    | 0.0040              | 2.76           | Sandy Clay<br>CL    |
| WES Ref.     | 0.0    | 93.75<br>6.25    | 2.81             | 3.2     | 0.0019              | 2.54           | Clay Silt<br>ML     |
| Yuma 2A      | 75.0   | 20.0<br>5.0      | 0.21             | 3.1     | 0.0079              | 2.69           | Silty Sand<br>SM    |

from the buret began. The position of the water surface and the position of the soil-liquid interface were recorded for all soils except China Lake B.

Visual observations were made as warranted and included the presence of gas bubbles, foam, and cavities in the soil. The liquid fractions were collected in glass vials and sent to the Environmental Chemistry Branch, Environmental Laboratory, WES, for analysis of HAN and TEAN.

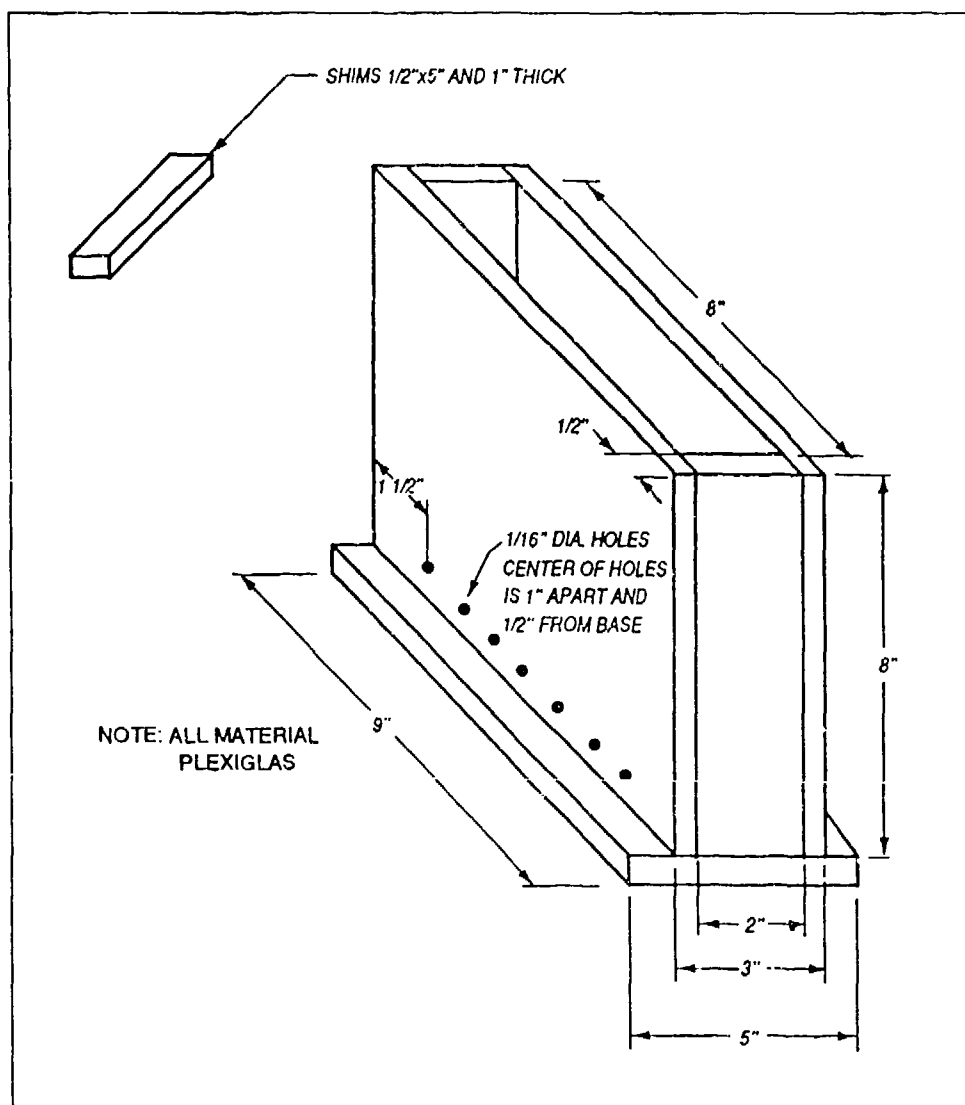


Figure 10. Chamber used for infiltration and runoff experiments

The 45.8 g of LP used to saturate the China Lake B soil (see Table 22) was dyed with 30-ppm methylene blue in solvent. The liquid eluted from the China Lake B buret was divided so that one portion could be analyzed for methylene blue concentration while the other portion was analyzed for HAN and TEAN.

### Transport of diluted LP in soil columns

Soil column experiments were conducted in stainless steel columns (15 × 4.4 cm inside diameter) (Figure 13). China Lake B and Picatinny A soils were packed into the columns in six increments using preweighed soil with light tamping. The surface was scarified to minimize formation of bedding planes before adding the next increment. The experimental matrix is



Figure 11. Liquid propellant application and runoff

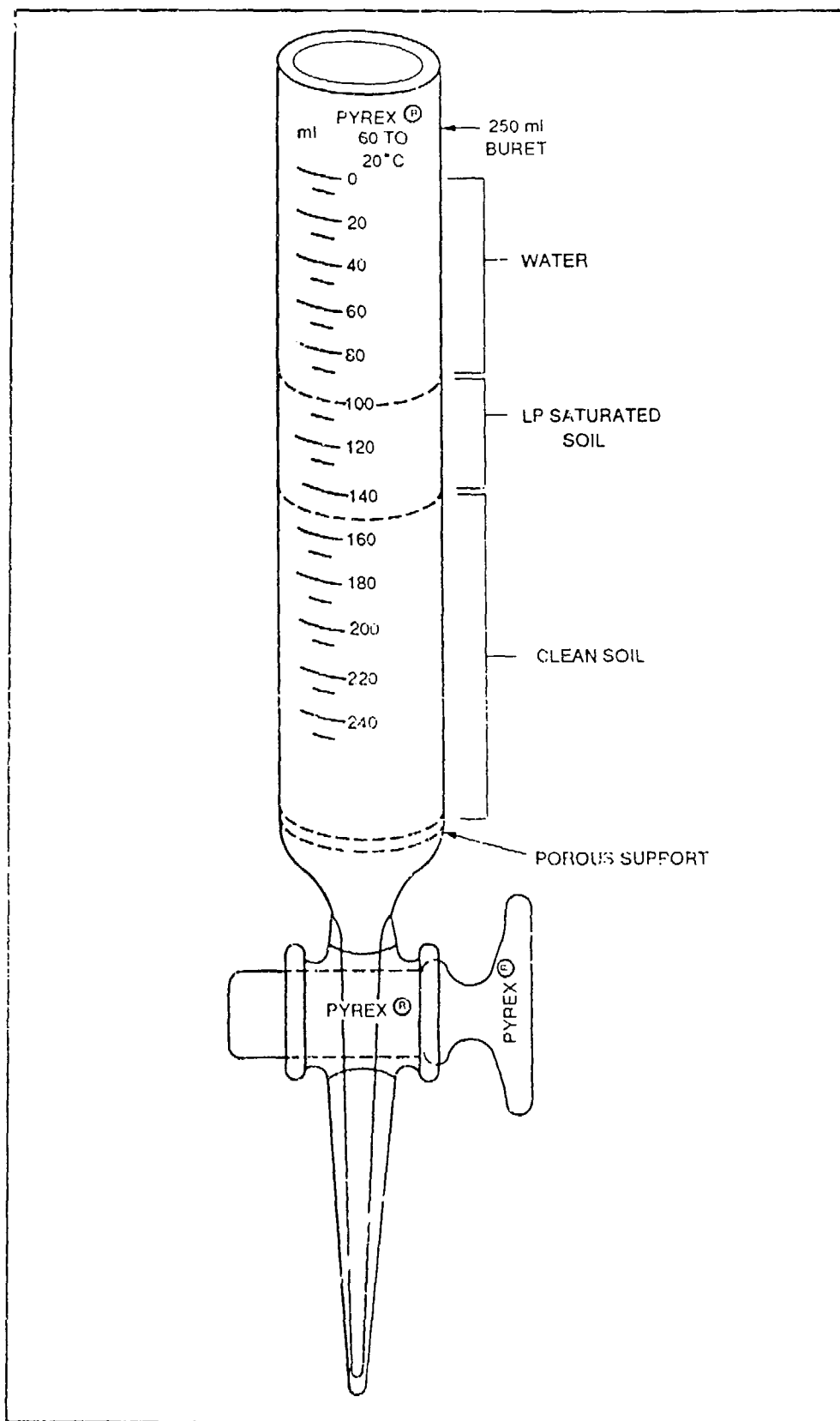


Figure 12. Burets used in experiments on washing LP-saturated soils with water

**Table 21**  
**Porosity of Dry Soils Packed at Bottom of Buret**

| Soil          | Weight of Air Dry Soil, g | Water Content | $\rho_s$ g/cm <sup>3</sup> | Porosity |
|---------------|---------------------------|---------------|----------------------------|----------|
| China Lake B  | 319.0                     | 0.011         | 2.59                       | 0.340    |
| Picatinny A   | 295.9                     | 0.115         | 2.65                       | 0.321    |
| Socorro P     | 280.9                     | 0.129         | 2.76                       | 0.366    |
| WES Reference | 259.6                     | 0.032         | 2.54                       | 0.414    |
| Yuma 2A       | 308.1                     | 0.031         | 2.69                       | 0.375    |

**Table 22**  
**Weights of Soil and LP Used to Make a Saturated Mixture and Weight of Water Applied**

| Soil          | LP-Saturated Soil |               | Water Applied, g |
|---------------|-------------------|---------------|------------------|
|               | Soil Weight, g    | LP Applied, g |                  |
| China Lake B  | 160.0             | 45.8          | 94.8             |
| Picatinny A   | 149.0             | 46.5          | 94.6             |
| Socorro P     | 140.6             | 50.7          | 94.8             |
| WES Reference | 160.2             | 97.0          | 91.6             |
| Yuma 2A       | 154.1             | 51.7          | 94.8             |

shown in Table 23. Flow in an upflow mode was held fixed for each column during a test. The minimum velocity was  $1.75 \text{ E-4}$  and  $1.23 \text{ E-4}$  cm/s, and the maximum velocity was  $19.27 \text{ E-4}$  and  $4.63 \text{ E-4}$  cm/s for China Lake B and Picatinny A soil, respectively. Flow was pumped through a constant volume metering pump. Column discharge was collected in a fraction collector (Figure 14).

After soil loading, hydraulic conditions were stabilized by pumping deaired, distilled, deionized water at steady flow through the columns for approximately 2 weeks, yielding at least 13 pore volumes of throughput for the China Lake B soil and 9 pore volumes of throughput for the Picatinny A soil. Tests started then of transport of dilute LP. Effluent samples for HAN and TEAN analysis were collected by the fraction collector. Samples were stored at  $5^\circ\text{C}$  until analyzed by ion chromatography (Appendix A).

After the LP tests were completed, columns were kept full of water and rested for approximately 1 month. Deaired, distilled, deionized water was then pumped at steady flow through the columns for approximately 1 week, flushing at least 6 pore volumes through the China Lake B soil and 4 pore volumes

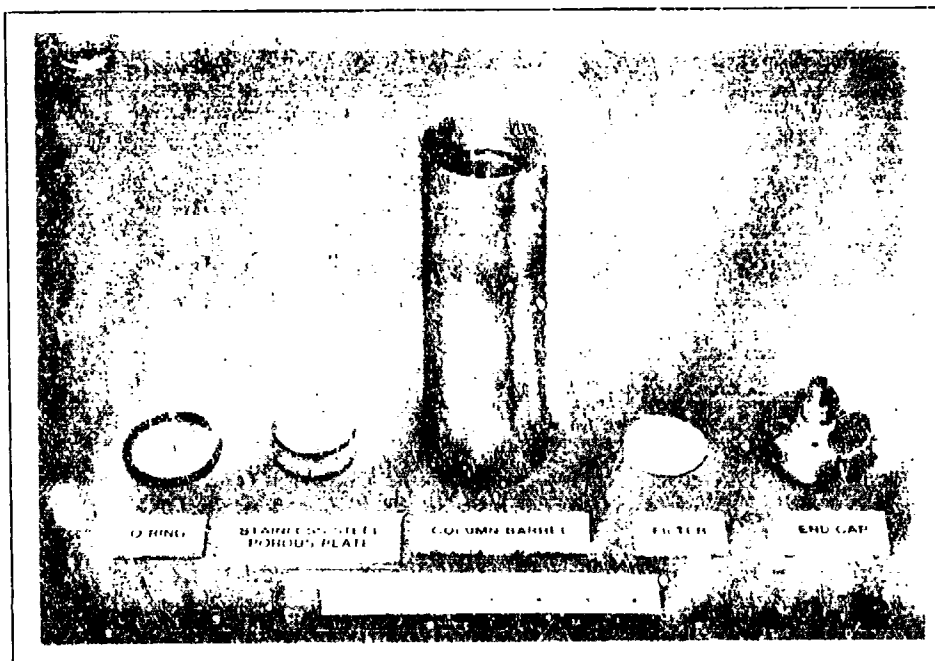


Figure 13. Stainless steel column and components

| <b>Table 23</b><br><b>Experimental Matrix for Transport of Dilute LP in Soil</b> |                                                              |
|----------------------------------------------------------------------------------|--------------------------------------------------------------|
| Soil/Liquid Loaded                                                               | Application method                                           |
| China Lake 3<br>LP<br>Salt Tracer                                                | Instantaneous mass loading<br>Instantaneous mass loading     |
| Picatinny A<br>LP<br>Salt Tracer                                                 | Step increase in concentration<br>Instantaneous mass loading |

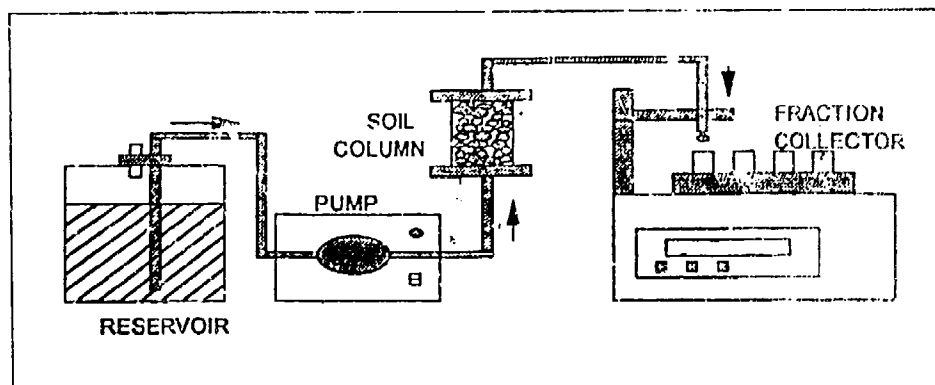


Figure 14. Soil column test apparatus

through the Picatinny A soil. Salt tracer was injected into the flow, and the chloride ion was monitored. The effluent fractions were analyzed for chloride ion concentration.

## Results

### LP runoff

The data from each experiment conducted in a runoff and infiltration chamber and the properties of the fluids were grouped into dimensionless variables which consisted of  $L'/V^{1/3}$ ,  $\mu/(\rho\sqrt{gV})$ ,  $\sigma/(\rho g V^{2/3})$ ,  $n$ ,  $\theta$ ,  $d_p/V^{1/3}$ , and  $(\sqrt{g})t_a/V^{1/6}$ , where

$\sigma$  = surface tension of the fluid

$d_p$  = mean soil particle size

$t_a$  = application time of the fluid

The dimensionless variables were fitted to Equation 19, the dimensionless runoff equation, which reduces to

$$\frac{L'}{V^{1/3}} = K' \left[ \frac{\rho g \theta V^{1/3} t}{\mu} \right]^A \left[ \frac{\sigma}{\rho g V^{2/3}} \right]^B \left[ \frac{d}{V^{1/3}} \right]^C \quad (29)$$

The data were subdivided into two groups, data for LP and data for water. The exponents  $A$ ,  $B$ , and  $C$  and the proportionality constant  $K'$  were determined from the data by the nonlinear regression program in Sigma Plot™ (Jandel Scientific, Corte Madera, CA). Norm of the regression analysis provided a measure of the *goodness* of fit of the data to the equation. The norm is defined in Sigma Plot™ as

$$NORM = \sqrt{\sum (Residuals)^2}$$

where a residual is the difference between a measured runoff function value,  $L'/V^{1/3}$ , and a runoff function value calculated from Equation 29. The smaller the value of the norm, the more closely the data fit the regression equation. Figures 15 and 16 present the experimental runoff data for LP and water, respectively, plotted as the measured  $L'/V^{1/3}$  versus the value of  $L'/V^{1/3}$  from Equation 29 with the optimized coefficient  $K'$  and exponents  $A$ ,  $B$ , and  $C$ . Table 24 summarizes the runoff equation coefficients, exponents, and norm for the five soils that were tested.

**Table 24**  
**Summary of Runoff Equation Coefficients and Exponents for the**  
**Five Soils with LP and Water**

| Soil and Fluid      | K         | A      | B      | C      | Norm |
|---------------------|-----------|--------|--------|--------|------|
| China Lake B<br>LP  | 3.333 E-2 | 0      | 0.1748 | 0.9019 | 1.85 |
| Water               | 5.654 E-4 | 0      | 0.6886 | 1.094  | 1.60 |
| Picatinny A<br>LP   | 3.080 E-1 | 0.2310 | 0      | 0      | 9.05 |
| Water               | 1.096 E-7 | 0.2351 | 2.742  | 0.4575 | 3.17 |
| Socorro P<br>LP     | 6.482 E-4 | 0.2115 | 1.533  | 0      | 4.39 |
| Water               | 1.228 E-4 | 0.1699 | 2.019  | 0      | 4.03 |
| WES-Reference<br>LP | 3.429 E-6 | 0.5096 | 1.938  | 0      | 5.27 |
| Water               | 3.195 E-5 | 0.2499 | 1.974  | 0      | 2.47 |
| Yuma 2A<br>LP       | 6.315 E-9 | 0.2078 | 0      | 3.218  | 2.90 |
| Water               | 6.500 E-4 | 0.1436 | 0.8157 | 0.6891 | 3.83 |

In four of the soils, the regression equation for water had a lower norm than the regression equation for LP. Yuma 2A was the exception in that the regression equation for LP fit the data better than the regression equation for water. The Picatinny A soil had the largest norm of any soil for LP.

The magnitude of the exponent A provides a measure of how closely the runoff distance was described by flow without infiltration down a sloping plane surface. When  $A = 1$ , runoff distance is described by flow rather than infiltration. When  $A = 0$ , the sloping plane surface model is not applicable. In all soils, the exponent ranged in value from zero to about one half, suggesting that the sloping plane surface portion of the model provided at best only part of the explanation for the runoff distance.

Values of exponent A for LP and for water were consistent in most of the soils. China Lake B soil had exponents of 0 for LP and water, meaning that the runoff distance for the sandy China Lake B soil was not described as flow on a sloping plane surface. Picatinny A soil had almost the same exponents, 0.2310 and 0.2351 for LP and water, respectively. Socorro P soil had similar exponents of 0.2115 and 0.1699, respectively, for LP and water. The exponent for WES Reference soil for LP was nearly twice as large as the exponent for water. Yuma 2A soil had a larger exponent for LP than it did for water. In summary, three of the soils had larger exponents A for LP than for water, while the exponents were equal for two soils. For all the soils the exponents were zero, or small compared with 1, suggesting that other factors in addition to flow without infiltration on a sloping plane surface are needed to predict the runoff distance.

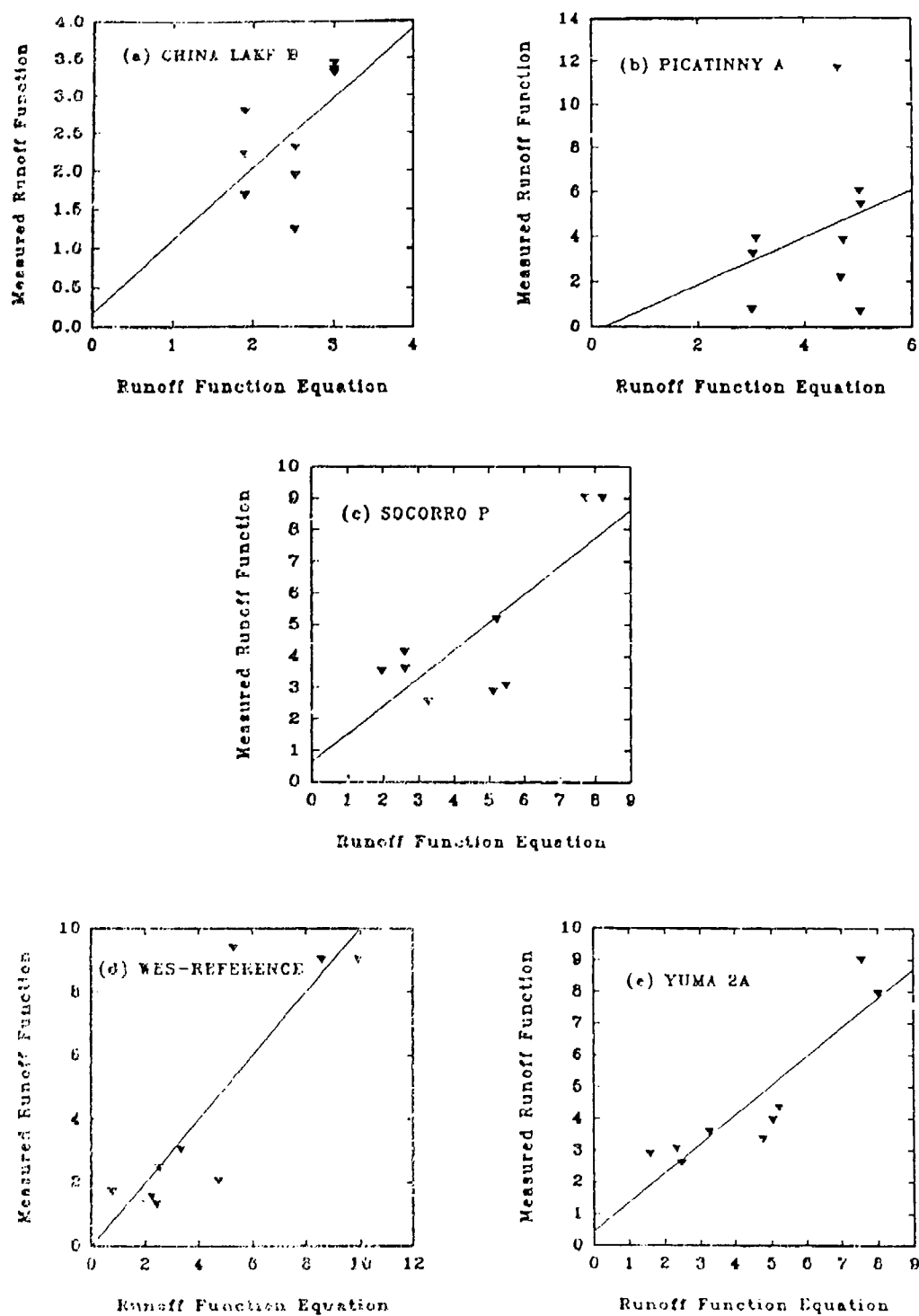


Figure 15. Comparison of runoff function,  $L'/V^{1/3}$ , with optimized function of soil and LP properties

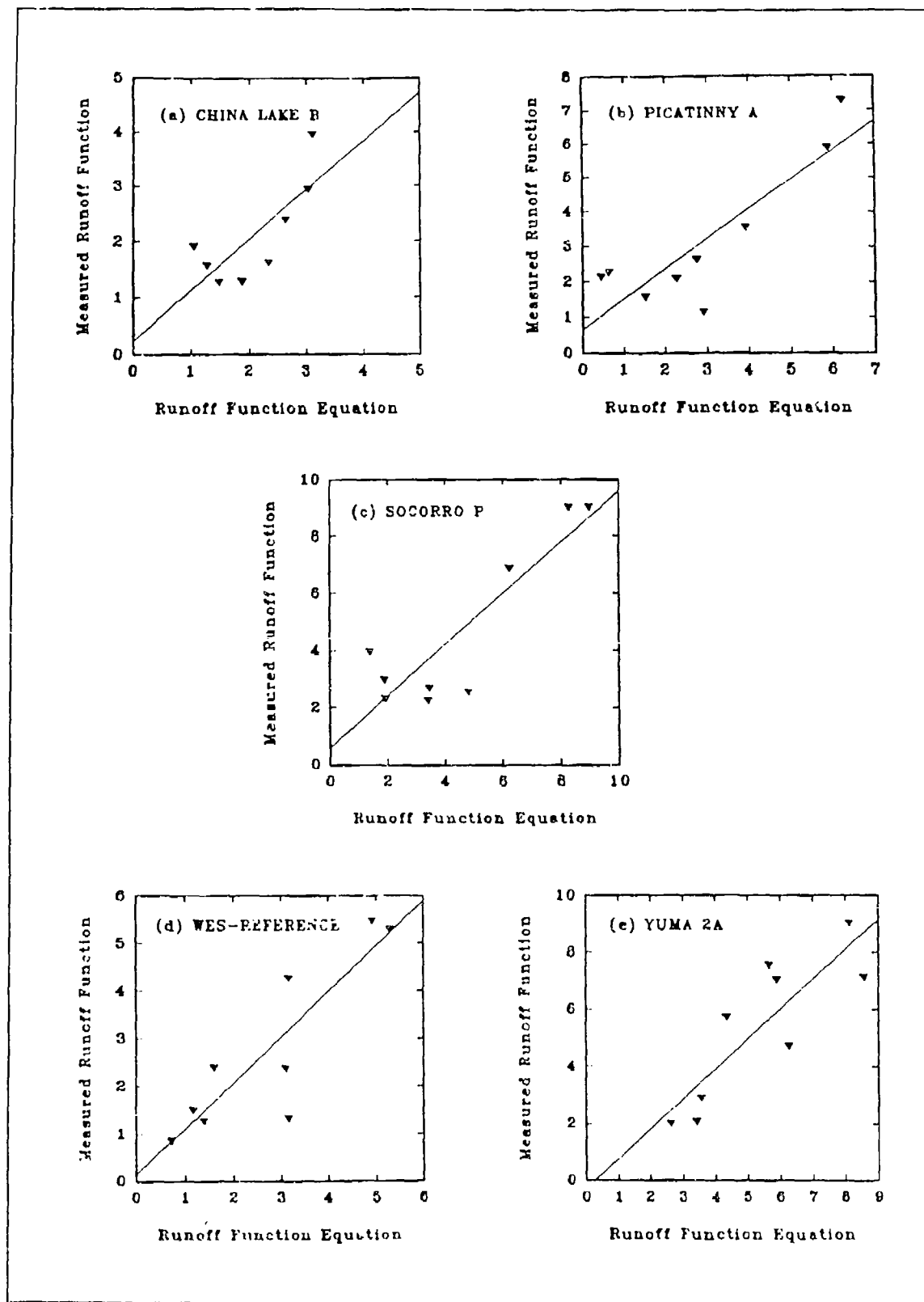


Figure 16. Comparison of runoff function,  $L'/V^3$ , with optimized function of soil and water properties

The magnitude of the exponent  $B$  provides a measure of the role of surface tension in predicting the runoff distance. Values of  $B > 0$  mean that capillary forces play an important role in reducing the runoff distance by increasing the infiltration rate. Table 24 shows that the magnitude of  $B$  varied from 0 for Picatinny A and Yuma 2A soils with LP to 2.742 for Picatinny A soil with water. For all soils, the exponent was smaller for LP than it was for water. This result suggests that surface tension is less important in infiltration of LP than it is for water. The contrast in the effects was most noticeable for Picatinny A and Yuma 2A soils, where the surface tension dimensionless group played no role in the runoff distance for LP, while it played a larger role for water. For China Lake B, Socorro P, and WES Reference soils, the surface tension dimensionless group was important in influencing the runoff distance for both LP and for water.

Exponent  $C$  related the dimensionless particle size to the dimensionless runoff distance. For Socorro P and WES Reference soils receiving water and LP, and for Picatinny A soil with LP, the exponent was zero, showing no influence of particle size on runoff distance. In all other cases, the exponent showed that dimensionless particle size was related to the runoff distance.

The runoff equations should be used within the range of experimental conditions under which they were developed (Table 19). The data sets for which the equations were developed were small, and the equations have not been verified by comparing their predictions against independent measurements of runoff distance. The proportionality coefficients  $K'$  and the exponents  $A$ ,  $B$ , and  $C$  generally vary from soil to soil and between LP and water. Yet patterns in the exponents are evident. While exponents for LP and water were similar in China Lake B, Socorro P, and the WES Reference soils, exponents for LP differed from water in Picatinny A and Yuma 2A soils. Examination of Table 20 on the soil characteristics provides no clues for the above groupings.

Figures 15 and 16 show graphs containing a regression line between the measured runoff function and the runoff function equation. If there were no error, all of the data would plot on a straight line passing through the origin, having a slope of one.

Runoff data for China Lake B soil showed considerable scatter (Figures 15 and 16). The measured runoff function was related in a nonlinear manner to the runoff function equation. The nonlinear behavior is particularly apparent for water runoff (Figure 16). As has been shown, the runoff function equation was not related to the dimensionless theoretical velocity times application time term, but was related to the surface tension and particle size dimensionless numbers (Table 24). The high sand content of the China Lake B soil is the likely reason for the inability of the runoff function equation to predict runoff length. For example, if the applied liquid tends to soak into the soil without running off, then predictions of runoff distance are poor.

Picatinny A soil showed a wide scatter of data for LP and a smaller scatter for water (Figures 15 and 16). The nonn, also a reflection of the scatter in the

data, was large for Picatinny A soil to which LP was applied (Table 24). The relationship between the predicted and measured runoff function was nonlinear (Figure 16).

The predictions of the runoff function equations for LP and water for Socorro P soil were similar (Figures 15 and 16). These results are consistent with the similarity between exponents and norms for LP and water in Socorro P soil (Table 24). The relationship between the predicted and measured was nonlinear.

### LP Infiltration into soils

The data for each infiltration experiment and the properties of the fluids were regrouped into dimensionless variables which consisted of

$$\frac{Y_i}{V^{1/3}}, \frac{\mu}{(\rho V^{2/3})}, \frac{\sigma}{(\rho g V^{2/3})}, n, \theta, \frac{d_p}{V^{1/3}}, \sqrt{\frac{g t_i}{V^{1/6}}}$$

where the terms have been defined previously, except,

$Y_i$  = vertical distance from the original soil surface to the deepest part of the wetting front

$t_i$  = the time since the start of experiment at which  $Y_i$  was measured

The dimensionless variables were analyzed by fitting the data to Equation 24, the dimensionless infiltration equation, which reduces to

$$\frac{Y_i}{V^{1/3}} = K' \left[ \frac{\rho g d^2 t_i}{\mu V^{1/3}} \right]^A \left[ \frac{\sigma}{\rho g V^{2/3}} \right]^B \theta^{-C} \quad (30)$$

The data were subdivided into two groups, data for LP and for water. The exponents  $A$ ,  $B$ , and  $C$  and the proportionality constant  $K'$  were determined by the nonlinear regression program in Sigma Plot™ (Jandel Scientific, Corte Madera, CA). Table 25 summarizes the infiltration equation coefficients, exponents, and norm (which measures the goodness of fit) for the five soils that were tested. All of the soils had small values of the norm indicating that the fit to the equations was good. Figures 17 and 18 present the experimental results,  $Y_i/V^{1/3}$ , plotted against the optimized Equation 30 for LP and water, respectively.

**Table 25**  
**Summary of Infiltration Equation Coefficients and Exponents for**  
**the Five Soils and for LP and Water**

| Soil and Fluid | $K'$   | $A$    | $B$    | $C$    | Norm |
|----------------|--------|--------|--------|--------|------|
| China Lake B   |        |        |        |        |      |
| LP             | 0.2378 | 0.1626 | 0      | 0      | 3.20 |
| Water          | 0.1667 | 0.1868 | 0      | 0      | 2.02 |
| Picatinny A    |        |        |        |        |      |
| LP             | 0.3103 | 0.0771 | 0      | 0.0849 | 1.45 |
| Water          | 0.8273 | 0.1144 | 1.239  | 0      | 1.22 |
| Socorro P      |        |        |        |        |      |
| LP             | 0.6594 | 0.1499 | 0.3112 | 0      | 0.52 |
| Water          | 2.2610 | 0.1298 | 0.4976 | 0      | 0.67 |
| WES-Reference  |        |        |        |        |      |
| LP             | 2.685  | 0.1162 | 0.5178 | 0      | 0.72 |
| Water          | 4.167  | 0      | 0.4463 | 0.0697 | 0.62 |
| Yuma 2A        |        |        |        |        |      |
| LP             | 0.3193 | 0.1680 | 0.0609 | 0.0287 | 1.92 |
| Water          | 2.4700 | 0.0997 | 0.3670 | 0.0411 | 1.44 |

The magnitude of the exponent  $A$  measures how closely the infiltration distance conformed to the predicted infiltration distance developed from Darcy's equation. When  $A = 1.0$ , Darcy's equation was followed exactly. The exponent  $A$  values were much smaller than 1.0, ranging in magnitude from 0.0 for WES Reference soil with water to 0.1868 for China Lake B soil with water. These small values indicate that Darcy's equation required modification to resemble the Kostiaikov expression, Equation 16, to better describe the infiltration distance. Also, the actual hydraulic conductivity was likely to have decreased as infiltration took place due to the infiltrating water filling only part of the soil pore space. This would produce unsaturated flow, which is characterized by low values of hydraulic conductivity.

The magnitude of the exponent  $B$  provides a measure of the role that surface tension plays in describing infiltration distance. A value of  $B > 0$  means that capillary forces played a role in increasing the infiltration depth. Table 25 shows that  $B = 0$  for China Lake B soil for both LP and for water and also for Picatinny A with LP. For Yuma 2A soil with LP,  $B$  was low (0.0609). By contrast,  $B$  varied from 0.3112 to 1.239 for the other soils and fluids. These results demonstrated that surface tension effects were important in describing the infiltration depth for Picatinny A soil with water, for Socorro P soil for both LP and for water, for WES Reference soil for both LP and for water, and for Yuma 2A soil for water. But, in general for LP, surface tension was unimportant (except in Socorro P and WES Reference) and less important than it was for water (except for WES Reference).

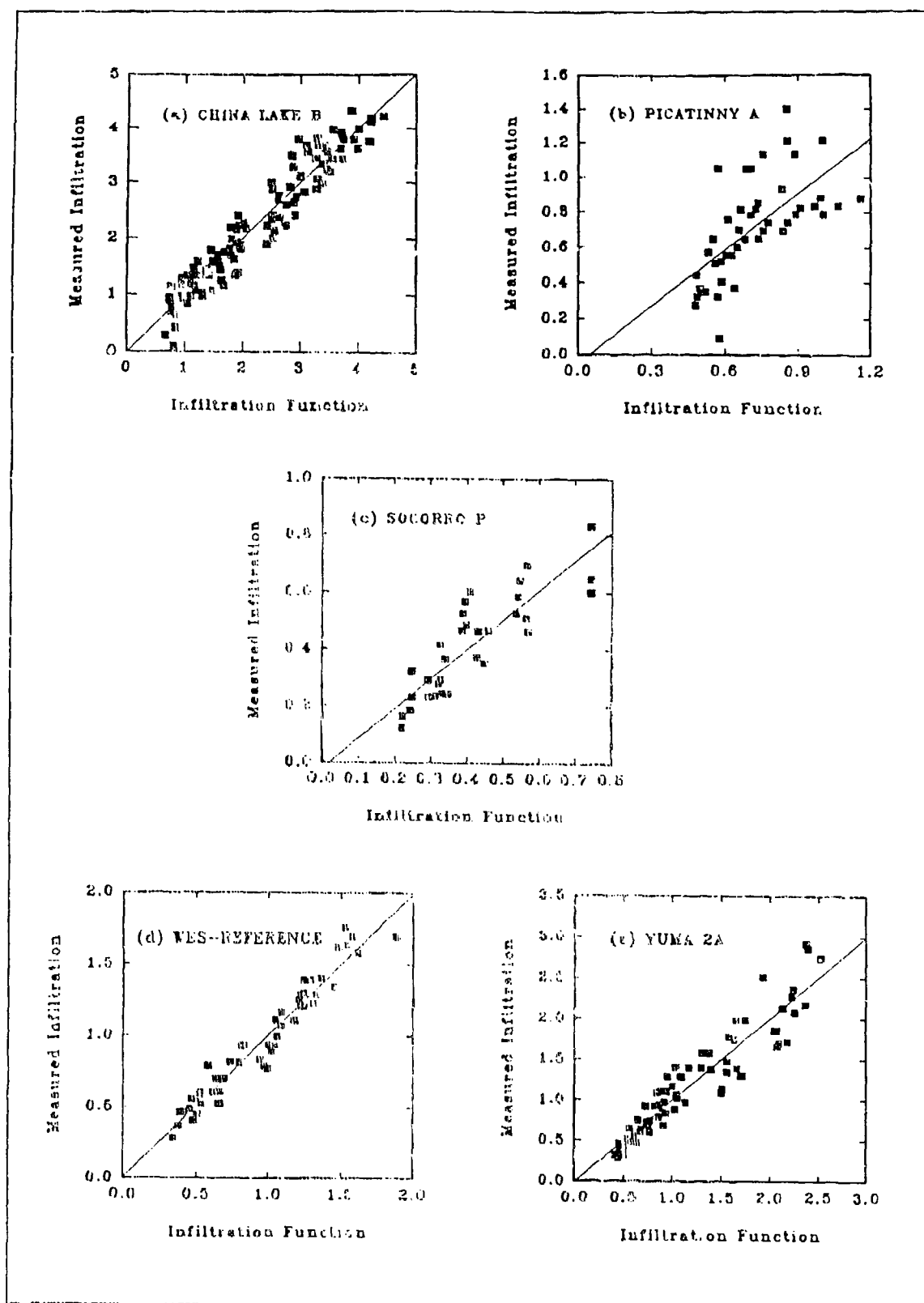


Figure 17. Comparison of infiltration function  $Y/V^{1/3}$ , with optimized function of soil and LP properties

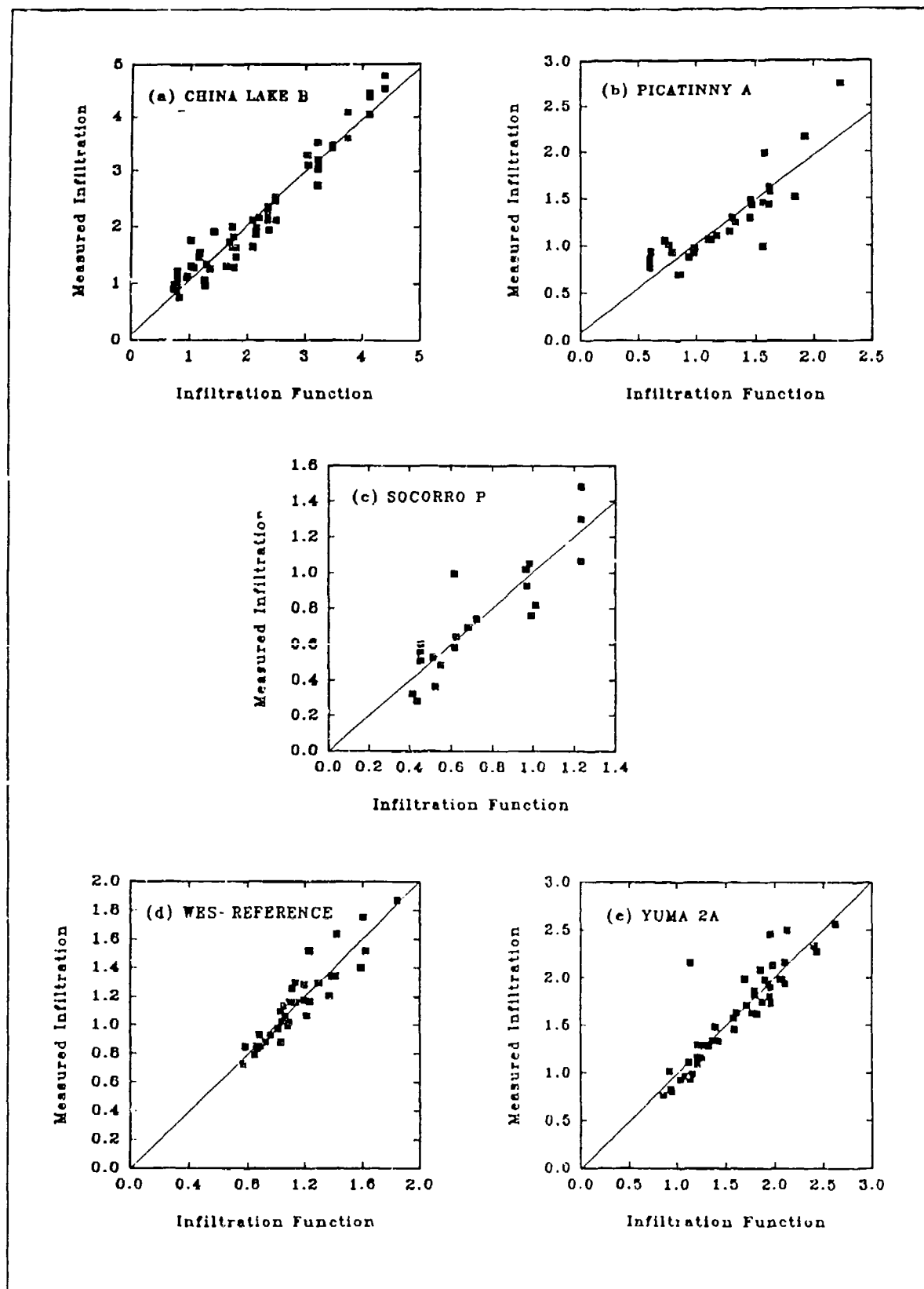


Figure 18. Comparison of infiltration function,  $Y/V^{1/3}$ , with optimized function of soil and water properties

The exponent  $C$  was zero or small in all cases, showing that the soil slope had no, or only limited, effect upon infiltration depth.

Picatinny A soil showed (Figures 17 and 18) a greater scatter of points, especially for LP, than for other soils. The wetting front in Picatinny A soil was difficult to distinguish for both LP and for water. The black soil showed very little color change between wet and dry states, creating difficulty in identification of the wetting front. Socorro P soil also showed relatively little color change between wet and dry states when LP or water was used, resulting in the collection of fewer data points. Data for WES Reference soil were closely clustered about the regression line, especially for LP. Even though Yuma 2A soil showed the greatest tendency of any of the soils to react with LP, infiltration functions were similar to those for water (Figures 17 and 18).

The infiltration equations that were developed should be used within the range of experimental conditions shown for which they were developed (Table 19). The infiltration equations have not been verified by comparing their predictions against independent data sets.

The regression line between the predicted and measured infiltration depth functions in all cases comes close to passing through the origin and having a slope of one (Figures 17 and 18). The data are scattered near the regression line, indicating reasonable agreement between predicted and measured infiltration.

### **Movement and reaction of undiluted LP**

The movement and reaction of undiluted LP in the five test soils were observed in terms of swelling, production of gas bubbles, visibility of the wetting front, time to elution, cavities formation, and rate of percolation of water through the LP saturated soil (Figures 19 and 20). The dashed reference lines show the original position of the soil surface and the water level. The time at which liquid elution started and the time at which cavities formed are indicated.

**China Lake B.** The China Lake B soil showed very little reaction with the LP as evidenced by soil swelling and production of gas bubbles (Figure 19a). The wetting front position was clearly visible and progressed the 4 in. through the dry soil to the porous plate in less than an hour. A lag time of several minutes was observed as the wetting front progressed through the porous plate; then liquid drained into the fraction collector. Two hours were required for drainage of the water standing above the soil to drop to the top of the soil. Almost immediately the drainage rate dropped. A small amount of drainage occurred over the next 12 hr, and then halted. The position of the water level and the soil surface were not recorded.

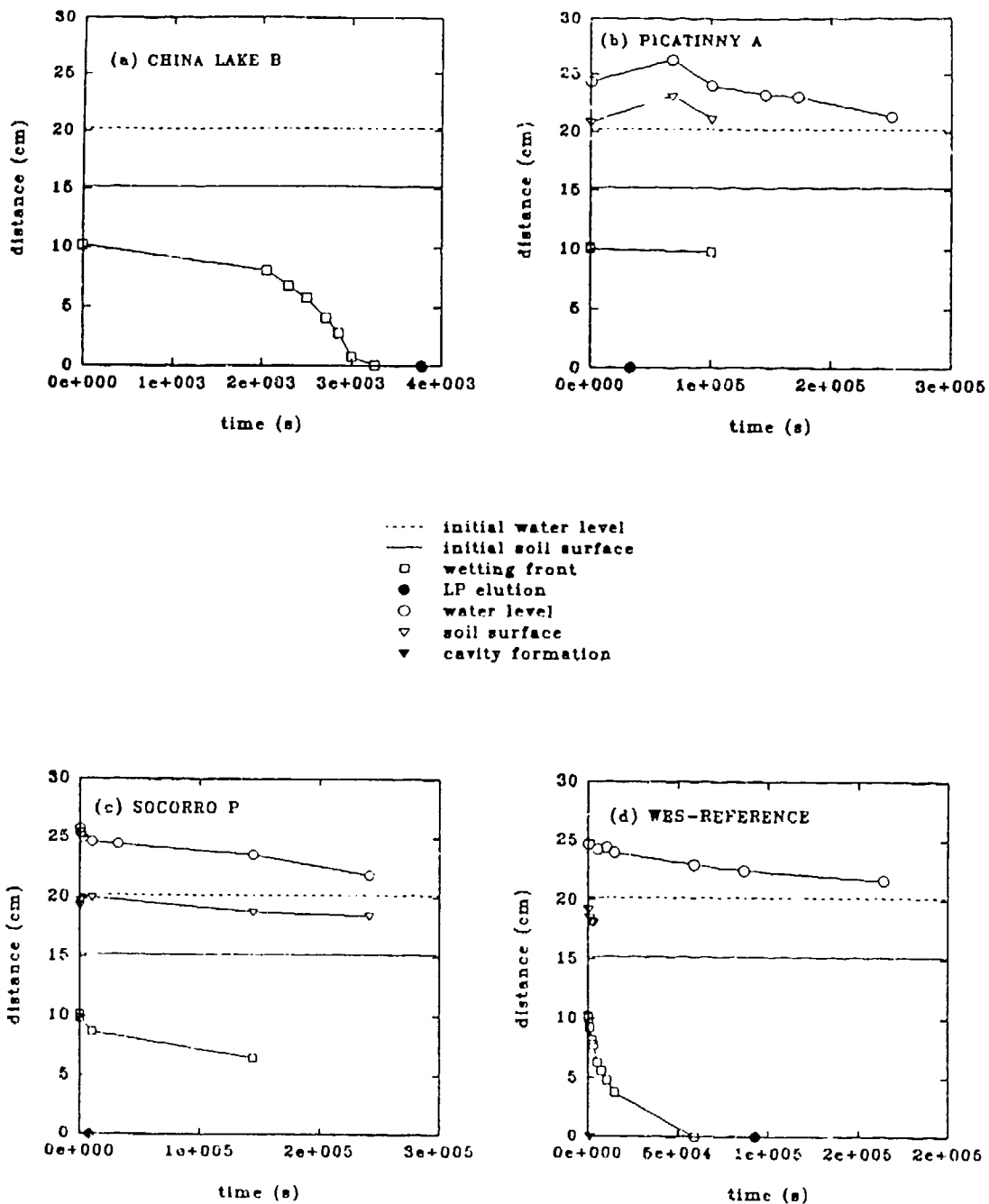


Figure 19. Undiluted LP movement in four soils

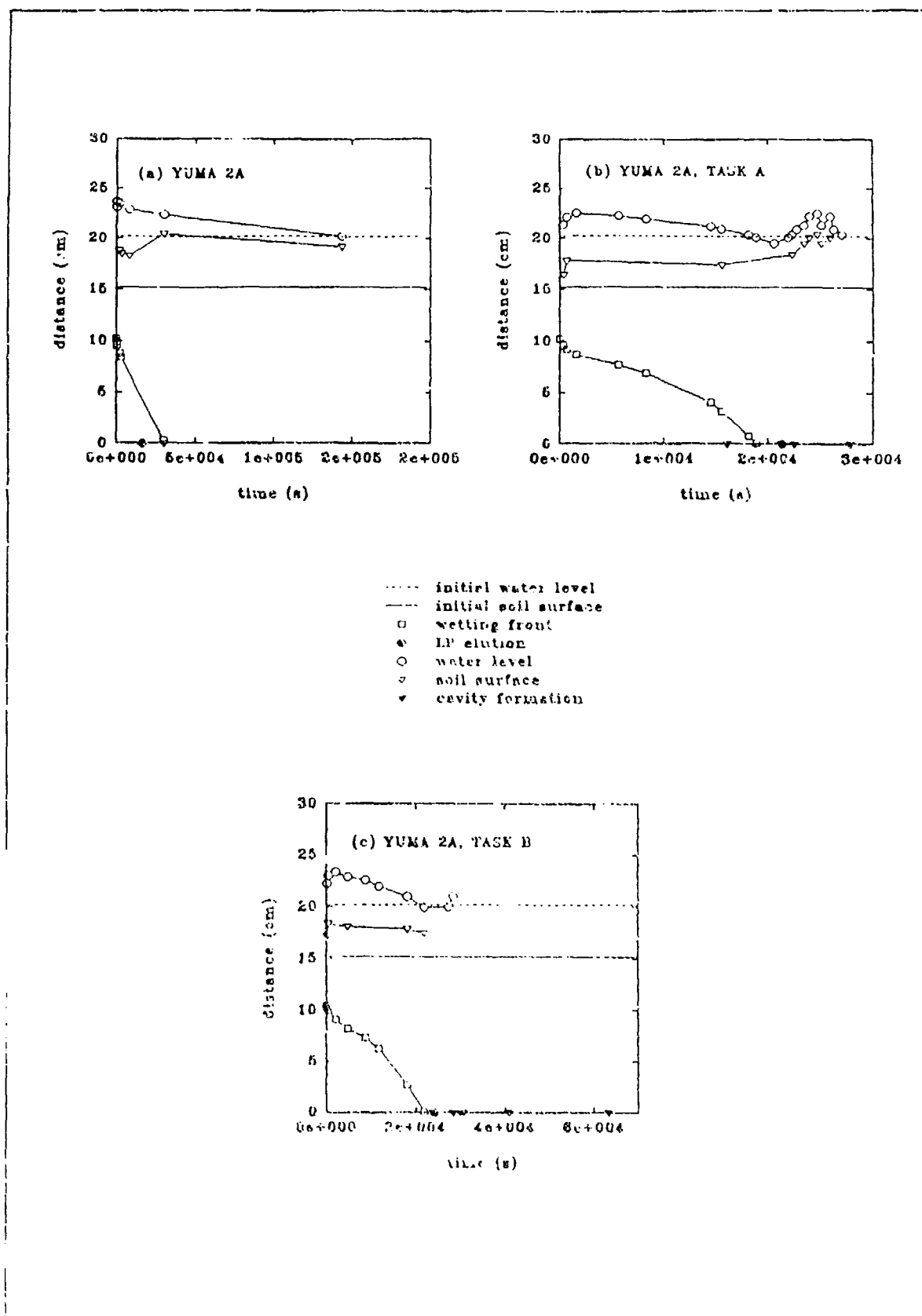


Figure 20 Undiluted LP movement in Yuma 2A soil

**Picatinny A.** Picatinny A soil showed an immediate swelling of 5.6 cm when contacted with LP (Figure 19b). The swelling lifted the water surface and raised the soil surface 7.9 cm in 19 hr. The soil and water levels subsequently declined, but the soil level remained above its original position.

The lack of contrast between wet and dry Picatinny A soil made the advance of the liquid into the soil difficult to observe. In fact, Figure 19b shows that the observed position of the wetting front did not change in the first day of observations. Yet, LP elution occurred after about 9 hr. Obviously, the barely distinguishable wetting front that appeared not to move was not an accurate representation of the position of the liquid in the soil. No attempt to document the position of the wetting front was made after 10<sup>5</sup> sec.

After nearly 3 days, the water level had not declined to its original elevation, even though drainage of liquid had taken place into the fraction collector. Much of the soil swelling was permanent in the sense that after liquid ceased to elute from the buret, the soil surface was still higher than it was in its original position. Part of the soil swelling was due to gas formation in the soil. The gas occupied pore volume and separated the soil particles. Another part of the soil swelling may have been due to expansion of soil particle by wetting.

**Socorro Periphery.** The Socorro Periphery soil underwent an immediate swelling of 4.1 cm upon coming into contact with LP. About 3 hr later, the soil reached its maximum expansion, a total of 4.8 cm. The water surface was lifted from its original position by the soil swelling. The wetting front was poorly visible, so no data are available after X time. As shown in Figure 19c, the recorded wetting front position was several centimeters above the porous plate support even after liquid elution began. Clearly, the poorly visible wetting front was a poor indicator of the liquid position in the soil. After about 10 min, the water level reached its maximum elevation and proceeded to drop as infiltration took place.

**WES Reference.** WES Reference soil followed the trend of other soils in undergoing a rapid expansion when brought into contact with LP (Figure 19d). The soil expanded by 4.0 cm, its maximum expansion, almost immediately. The soil surface dropped as the wetting front advanced. The water level was lifted 4.5 cm by the swelling soil, but dropped as infiltration occurred. The wetting front was visible and reached the porous support after about 16 hr. A 9-hr delay ensued before elution of the liquid started. Part of the delay at the porous support is due to the time required for the wetting front to advance through the 1-cm support. However, the more likely attributable delay is to the difference in pore size of the support and the WES Reference soil. The support has larger pores, producing smaller capillary forces than the fine-grained soil. The capillary forces act to hold the liquid in the WES Reference soil while filling up pore spaces that had been bypassed in the initial infiltration. When the pore space had been filled sufficiently, the wetting front advanced into the porous support to be followed by liquid elution.

One notable feature of the LP advance into the WES Reference soil was the formation of a cavity after about 18 min. The cavity was a gas-filled opening in the wet soil which was visible for a short time before the gas rose through the wet soil and bubbled off. The cavity formed about the time the soil reached its maximum expansion.

**Yuma 2A.** Yuma 2A soil underwent immediate swelling after coming into contact with LP (Figure 20a). The increase was about 3.6 cm in half an hour. The wetting front moved downwards steadily, and the water level showed an early rise as it was lifted by the swelling soil, then a decline as the wetting front advanced. Liquid elution occurred after about 4.5 hr. The visible wetting front had not yet reached the porous support, suggesting that the wetting front was a poor indicator of the liquid position in the soil. About 8 hr after the experiment started, a large cavity was observed extending completely across the soil in the buret. The soil was separated by a gas-filled cavity into an upper portion. Remnants of this cavity were visible several hours later, as were indications that other cavities had formed and collapsed when no observers were present.

Two more experiments were set up to determine whether the formation of large cavities could be duplicated and to obtain more observations of conditions before and after cavity formation. Four cavities were observed in Yuma 2A, Task A (Figure 20b), and six cavities were observed in Yuma 2A, Task B (Figure 20c). In Task A, the first cavity formed without lifting the soil surface. Task B lifted the soil surface only slightly initially, then more as two additional cavities formed.

Table 26 summarizes the soil expansions brought on by concentrated LP. Soil expansion discussions in the literature focus on clay volume changes with an increase in moisture content (Tariq and Durnford 1993).

| Table 26<br>Expansion of Soils Due to Contact with LP |             |                 |                                    |                          |
|-------------------------------------------------------|-------------|-----------------|------------------------------------|--------------------------|
| Soil                                                  | $L'_0$ , cm | $L'_{max}$ , cm | $\Delta L' = L'_{max} - L'_0$ , cm | $\beta = \Delta L'/L'_0$ |
| China Lake B                                          | 15.2        | *               | --                                 | --                       |
| Picatinny A                                           | 15.2        | 23.1            | 7.9                                | 0.52                     |
| Socorro P                                             | 15.2        | 20.0            | 4.8                                | 0.32                     |
| WES-Reference                                         | 15.2        | 19.2            | 4.0                                | 0.26                     |
| Yuma 2A                                               | 15.2        | 20.5            | 5.3                                | 0.35                     |
| Yuma 2A-Task A                                        | 15.2        | 20.4            | 5.2                                | 0.34                     |
| Yuma 2A-Task B                                        | 15.2        | 18.4            | 3.2                                | 0.21                     |
| * $L'_{max}$ was not recorded for China Lake B soil   |             |                 |                                    |                          |

**Relationship of chromatographic effect to reactions of LP with soils:** It was noted that cavities formed in the wet region above the wetting front. Gases generated at the wetting front could move downwards and escape through the porous support. However, the chromatographic effect may provide an explanation for gas formation behind the wetting front.

When LP percolates into the soil, its chemical constituents may travel at the same velocity as the liquid carrier, or they may move at a slower velocity if they undergo adsorption and desorption on the soil. HAN and TEAN undergo sorption on the soil, but the sorption intensity is different for each species and for each soil. The sorption intensity is expressed through the retardation coefficient. A large value of the retardation coefficient indicates a chemical species that is strongly sorbed. It will appear to move slowly, much slower than the carrier fluid, since it spends so much time attached to the soil. On the other hand, a low retardation coefficient indicates a chemical species that travels almost as fast as the carrier fluid. A retardation coefficient of one signifies that the chemical species does not undergo sorption, so it moves at the same speed as the carrier fluid. HAN and TEAN have retardation coefficients that are less than five for China Lake B and Picatinny A soil. TEAN has a larger retardation coefficient than HAN. The retardation coefficients were not measured for Yuma 2A soil, but if they had the same relative magnitude for Yuma 2A soil, the chromatographic effect could explain the cavity formation.

HAN will move faster than TEAN as TEAN has a larger retardation coefficient. Thus, flowing LP will separate into its constituents because the adsorption and desorption process allows each species to move at a different speed. The fluid at the wetting front will become depleted in HAN and TEAN concentrations as they undergo sorption. The highest concentration of HAN will lag behind the wetting front due to retardation. The HAN concentration front will fall back more and more from the wetting front as infiltration proceeds over greater distances. The TEAN will lag behind the HAN as TEAN is retarded more. These phenomena are shown in Figure 21. In the buret experiments, there was also a chromatographic effect at the top of the column of soil where the water was placed on top of the LP-saturated soil.

The chromatographic effect is important in the transport of a reactive and sorbing solute such as LP, for it suggests that the chemical reactions taking place during infiltration will take place behind the wetting front. The distance behind the wetting front will depend on whether the reaction involves HAN or TEAN. Furthermore, if the reaction produces gas as a reaction product, the gas will be generated in a liquid-filled porous medium. Capillary forces will tend to hold the gas in the soil interstices. However, if the interstices are large enough, the bubble formed can migrate upward under the influence of buoyant forces. Fine-grained soils can produce larger capillary forces, which will make it more difficult for the bubble to migrate. In this case, the bubble may be trapped. If a sufficient number of bubbles are trapped, they may allow formation of a cavity in the soil. At any rate, the trapped bubbles would promote swelling of the soil as the gas bubbles would pry the soil grains farther apart.

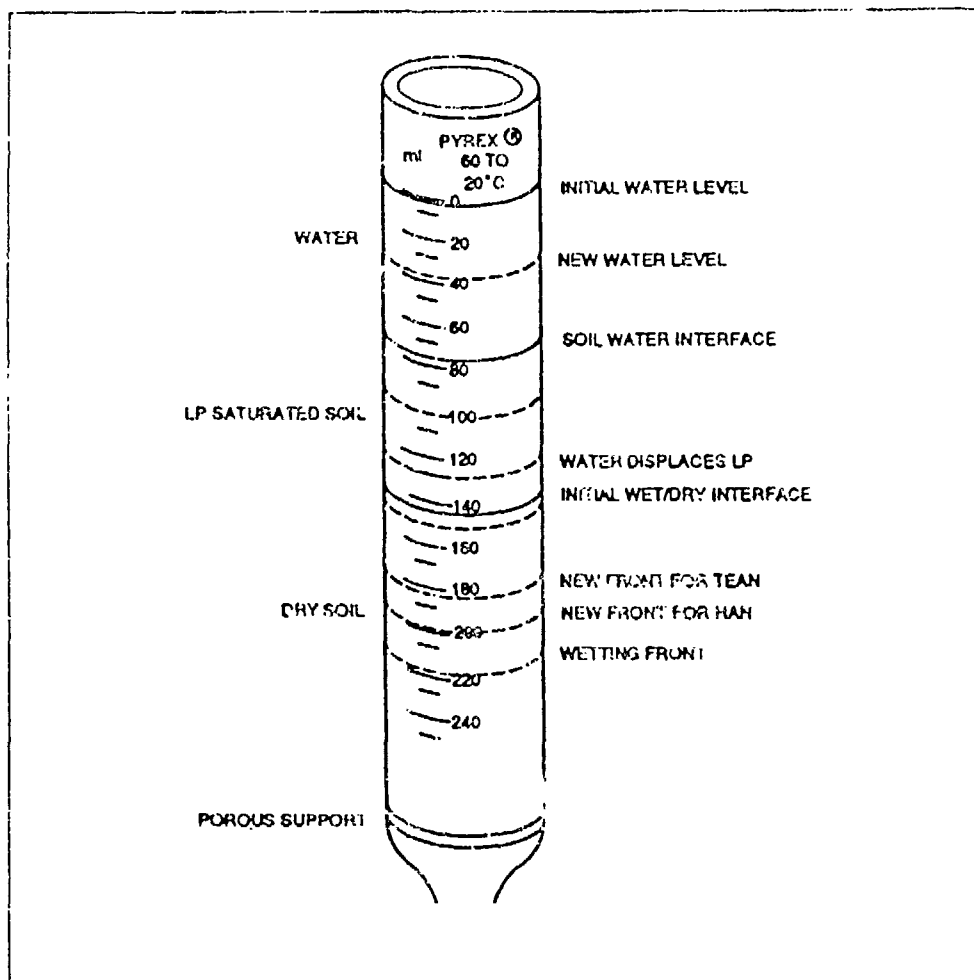


Figure 21. Chromatographic effect in a soil through which LP is percolating

### Elution studies of undiluted LP from soil columns

The concentration of TEAN in the initial eluate sample was zero in Picatinny A (Figure 22b), Socorro P (Figure 22c), WES Reference (Figure 22d), and one of the three Yuma 2A soil samples (Figure 23b) and near zero in China Lake B (Figure 22a), and two of the three Yuma 2A soils samples (Figure 23a,b). The zero or near zero concentrations of TEAN in the initial eluate could evolve in two ways: (a) the overlying water could have migrated through the LP-saturated soil or (b) the initial eluate sample was made up of water and HAN so that it appeared to move faster through the pores of the saturated soil than the TEAN. Subsequent results support the second explanation. The TEAN concentration increased as more fluid eluted, suggesting that the TEAN had been immobile at first, then became mobile later. Initial adsorption decreased the TEAN concentration to zero or near zero in the leading edge of the flow. Then, as the adsorption capacity of the soil was exhausted, the concentration of TEAN in the mobile phase increased.

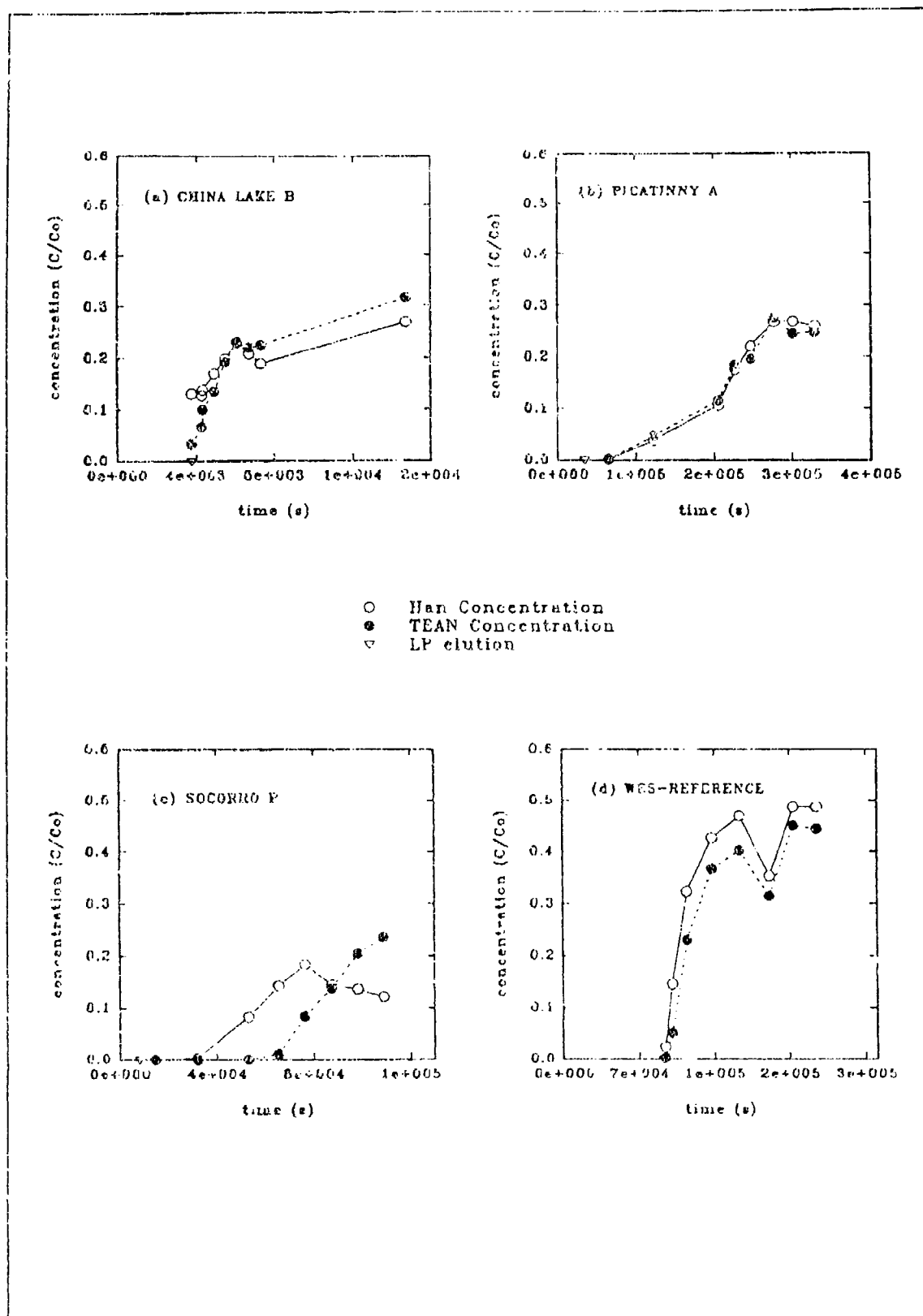


Figure 22. HAN and TEAN concentrations upon elution from four soils

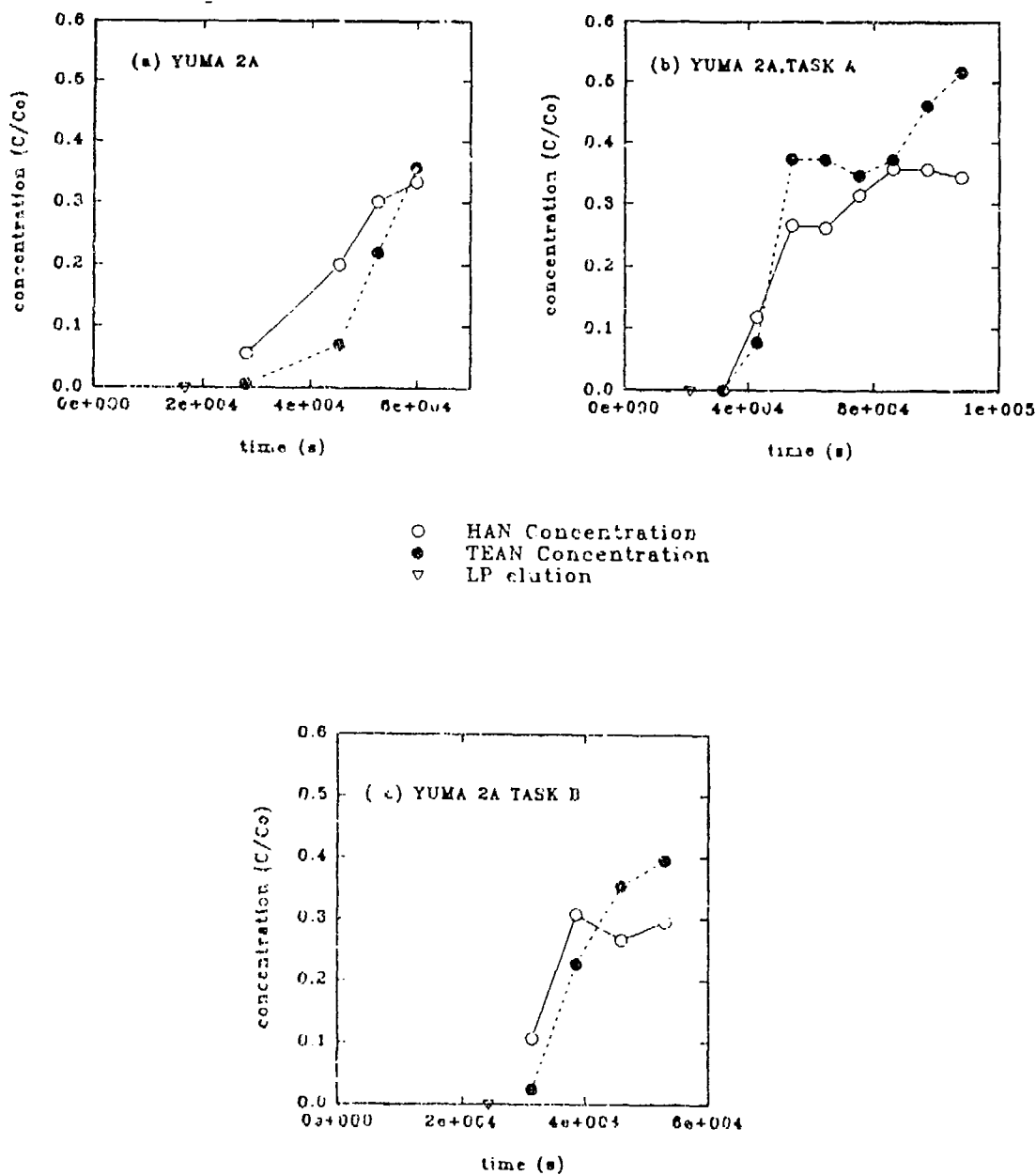


Figure 23. HAN and TEAN concentrations upon elution from Yuma 2A soils

TEAN concentrations in the eluent reached a plateau, a  $C/C_0$  value of about 0.25 for Picatinny A soil and about 0.15 for WES Reference soil. The development of a plateau suggests that (a) the TEAN had degraded or (b) dilution with water decreased the TEAN concentration. In the other soils, the maximum concentration of TEAN was reached when elution stopped. A mathematical model of TEAN transport in the soil was not developed because of the limited amount of data collected and the complexities of the variable flow rate.

The HAN concentration in the initial eluant was zero for Picatinny A, Socorro P, and one Yuma 2A soil (Figure 23b) and near zero for WES Reference soil. The concentration was about 0.13 for China Lake B soil, 0.05 for one Yuma 2A soil (Figure 23a), and 0.1 for another Yuma 2A soil (Figure 23c). Thus, HAN degradation and sorption in the soils was evident, but was not quantified.

The behavior of HAN and TEAN in China Lake B soil was similar after differences in initial concentrations (Figure 22a). Each species underwent a temporary reduction in concentration midway through the flow process, then both climbed to a maximum when flow ceased.

The HAN and TEAN relative concentrations paralleled each other for Picatinny A soil (Figure 22b). Thus, their degradation and adsorptive behaviors were similar.

Socorro P soil adsorbed TEAN to a greater extent than HAN as the TEAN elution curve was delayed relative to the HAN elution curve (Figure 22c). Also, HAN reached a peak concentration midway through elution, then declined in concentration. By contrast, once TEAN appeared after its delayed elution, the concentration climbed continuously until elution stopped. The decrease in HAN concentration after reaching a peak could be evidence for enhanced adsorption.

WES Reference soil showed HAN and TEAN eluted in a similar manner, but HAN maintained a greater relative concentration (Figure 22d).

In Yuma 2A soil, the HAN concentration increased more rapidly than the TEAN concentration early in the test; then the relative concentrations reversed, with the TEAN concentration being larger than the HAN concentration later in the test (Figure 23a,b,c). Part of the explanation for the difference in behavior of HAN and TEAN in the three Yuma 2A soil samples may be attributable to the formation and location of the cavities. A cavity interrupts the flow; then, release of gas bubbles through the soil stirs up the soil opening and closing flow channels. These channels could provide a means for water to enter different depths in the Yuma 2A soil. Also, the chromatographic effect provides some longitudinal segregation of HAN and TEAN in the soil. Thus, if a cavity forms a path for water entry to a region of soil containing TEAN but no HAN, then extra TEAN could be pushed out while the oncoming HAN was delayed.

## Methylene blue dye as a quantitative indicator of LP concentration

The concentration of methylene was very low, in the fraction of a mg/L, even when the applied concentration was as high as 30 mg/L. The China Lake B soil was stained, showing that the dye was adsorbed and almost completely removed from the liquid. The survival of methylene blue as it percolated through other soils with LP was not tested since other soils were likely to sorb more efficiently than China Lake B.

## Transport of diluted LP in soil columns

For China Lake B soil (Columns A, B, and C) (Table 27) Picatinny A soil (Columns D, E, and F) (Table 28), the values of  $\alpha$ , the ratio of the dispersion coefficient (D), and the velocity (V) are within the range found by other investigators (Tomerico and Schwartz 1990). However, the  $\alpha$  values are not the same for HAN, TEAN, and the chloride ion, indicating that the dispersion coefficients are species dependent. For China Lake B soil, the dispersion coefficients are consistent in that each one increases with velocity. Picatinny A soil did not show a consistent trend of having the dispersion coefficient increase with velocity.

The reaction rate coefficient,  $k'$ , for China Lake B soil showed a consistent trend in which the rate coefficient increased with velocity. The increase in the rate coefficient with velocity could be due to more mixing of the reactants in the soil pores, or to a decrease in the fluid boundary layer around each soil particle so as to enhance surface reactions. Picatinny A soil showed no trend in the magnitude of the reaction rate coefficient relative to velocity. The lack of a trend is expected for reactions that take place in the fluid.

An unexpected result was that the chloride ion was not conservative, but decayed through some chemical reaction in the columns. Chloride ion is usually a conservative tracer in porous media studies; however, the results showed it was not conservative when applied after LP. Apparently, the LP altered the soil surfaces so that the chloride ion took part in a surface reaction.

A comparison between soils shows that both HAN and TEAN disappeared more rapidly from China Lake B soil than from Picatinny A soil. China Lake B was classified as silty sand and Picatinny A was classified as sandy silt (see Table 19). Picatinny A had a higher organic matter content than did China Lake B, 2.92 percent versus 0.53 percent, which may have contributed to the stability of both dilute HAN and TEAN in Picatinny A soil. The pH of the effluent from the soil columns was not measured, so its role in reducing the transformation rate of dilute HAN and TEAN in Picatinny A soil is not known.

The values of the partition coefficient,  $K_d$ , were nearly constant for each species in each soil with no trend of  $K_d$  increasing or decreasing with velocity.

**Table 27**  
**Dispersion, Adsorption, Reaction, and Partitioning**  
**Characteristics of China Lake B Soil for the Tracers HAN, TEAN,**  
**and Chloride Ion**

| Column | $\alpha$<br>cm | $V$<br>cm <sup>3</sup> /s | $D$<br>cm <sup>2</sup> /s | $R$    | $k$<br>s <sup>-1</sup> | $K_d$<br>cm <sup>3</sup> /g | $r^2$ |
|--------|----------------|---------------------------|---------------------------|--------|------------------------|-----------------------------|-------|
| A-HAN  | 0.412          | 19.27<br>E-4              | 7.94<br>E-4               | 1.587  | 25.8<br>E-5            | 0.112                       | 0.98  |
| B-HAN  | 0.714          | 9.41<br>E-4               | 6.72<br>E-4               | 1.308  | 5.57<br>E-5            | 0.083                       | 0.96  |
| C-HAN  | 0.753          | 2.23<br>E-4               | 1.68<br>E-4               | 1.473  | 0.989<br>E-5           | 0.095                       | 0.98  |
| A-TEAN | 2.152          | 19.27<br>E-4              | 41.46<br>E-4              | 13.385 | 43.16<br>E-5           | 2.371                       | 0.98  |
| B-TEAN | 3.194          | 9.41<br>E-4               | 30.06<br>E-4              | 10.514 | 15.06<br>E-5           | 2.564                       | 0.95  |
| C-TEAN | 2.368          | 2.23<br>E-4               | 5.28<br>E-4               | 11.061 | 4.13<br>E-5            | 2.015                       | 0.89  |
| A-Cl   | 0.267          | 19.3<br>E-4               | 5.15<br>E-4               | 1.381  | 7.09<br>E-5            | 0.072                       | 0.97  |
| B-Cl   | 0.223          | 9.48<br>E-4               | 2.11<br>E-4               | 1.000  | 1.69<br>E-5            | 0.000                       | 0.99  |
| C-Cl   | 0.417          | 1.75<br>E-4               | 0.73<br>E-4               | 1.081  | 0.23<br>E-5            | 0.016                       | 0.99  |

The chloride ion had a small  $K_d$  for both China Lake B and Picatinny A soils, which is consistent with enhanced chloride ion adsorption.

The partition coefficient is expected to be constant, regardless of flow velocity for a particular soil exposed to a particular species of chemical such as HAN or TEAN. This expectation was confirmed (Tables 27 and 28).

The values of  $r^2$  were high in all cases, indicating a close fit between the mathematical model and the measured data.

The effluent concentration distribution curves show the influence of dispersion, retardation, and reactions. Dispersion is manifested as a spreading out of the effluent concentration over more pore volumes. If there were no dispersion, then the effluent concentration distribution would appear as a high, narrow spike at a pore volume of 1 (retardation could delay the appearance of the spike, but would not change its shape). Figures 24, 25, and 26 show the spreading effect of dispersion.

Reaction or transformation of a species is manifested as a decrease in the area under the effluent distribution curve. Reaction or transformation is

**Table 28**  
**Dispersion, Adsorption, Reaction, and Partitioning Characteristics of Picatinny A Soil for the Tracers HAN, TEAN, and Chloride Ion**

| Column | $\alpha$<br>cm | $V$<br>cm/s | $D$<br>cm <sup>2</sup> /s | $R$   | $K'$<br>s <sup>-1</sup> | $K_d$<br>cm <sup>3</sup> /g | $r^2$ |
|--------|----------------|-------------|---------------------------|-------|-------------------------|-----------------------------|-------|
| D-HAN  | 0.472          | 1.36<br>E-4 | 0.651<br>E-4              | 2.347 | 0.24<br>E-5             | 0.586                       | 0.98  |
| E-HAN  | 1.431          | 3.51<br>E-4 | 3.024<br>E-4              | 2.634 | 0.00                    | 0.773                       | 0.96  |
| F-HAN  | 0.115          | 4.63<br>E-4 | 0.537<br>E-4              | 2.101 | 1.054<br>E-5            | 0.504                       | 0.98  |
| D-TEAN | 1.359          | 1.38<br>E-4 | 1.875<br>E-4              | 2.882 | 0.231<br>E-5            | 0.918                       | 0.97  |
| E-TEAN | 2.101          | 3.51<br>E-4 | 7.375<br>E-4              | 2.859 | 0.046<br>E-5            | 0.879                       | 0.96  |
| F-TEAN | 0.711          | 4.53<br>E-4 | 3.290<br>E-4              | 2.293 | 1.235<br>E-5            | 0.592                       | 0.98  |
| D-C1   | 0.431          | 1.23<br>E-4 | 0.530<br>E-4              | 1.263 | 1.975<br>E-5            | 0.103                       | 0.99  |
| E-C1   | 0.691          | 1.87<br>E-4 | 1.293<br>E-4              | 1.452 | 3.523<br>E-5            | 0.192                       | 0.99  |
| F-C1   | 0.726          | 4.55<br>E-4 | 3.305<br>E-4              | 1.286 | 1.208<br>E-5            | 0.118                       | 0.99  |

difficult to document from a single concentration distribution curve as shown in Figures 24, 25, and 26.

Retardation, which comes about from a species adsorbing and then desorbing from the soil, manifests itself as a delay in appearance of the species in the column effluent. If there were no retardation, then the peak concentration would appear at a pore volume of 1.

The theoretical model, Equation 26, permits the simultaneous determination of the dispersion, decay, and retardation characteristics of HAN, TEAN, and chloride ion in China Lake B soil. The solid curves in Figures 24, 25, and 26 are the best fit of the theoretical model to the experimental data. The curves show that TEAN had a greater retardation in China Lake B soil than did HAN. The value of  $K_d$ , the distribution coefficient, is calculated from the retardation coefficient by an equation defined with Equation 26. From the shape of the TEAN and HAN distribution curves, TEAN has a larger  $K_d$  than does HAN.

Figures 27, 28, and 29 show the effluent concentration distribution curves for HAN, TEAN, and chloride ion for Picatinny A soil. The chloride ion was injected into the column as an instantaneous mass loading so the interpretation

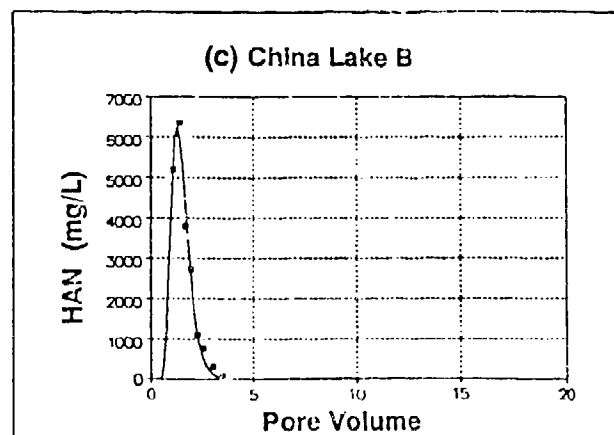
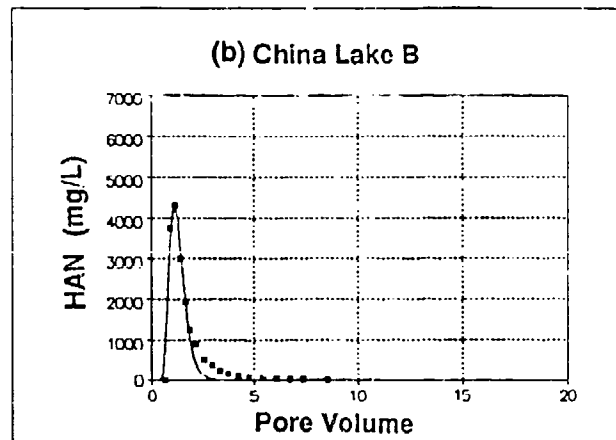
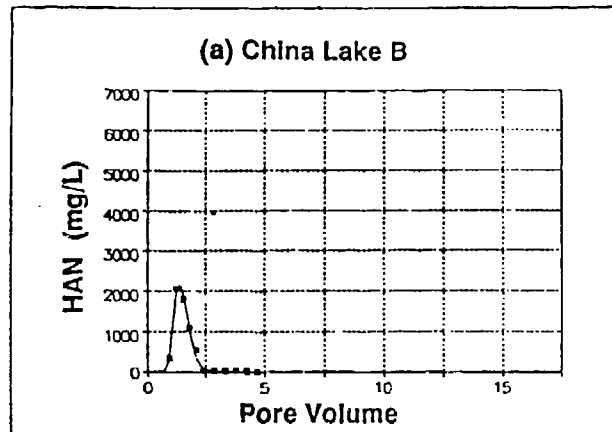


Figure 24. HAN outflow concentration from China Lake B soil

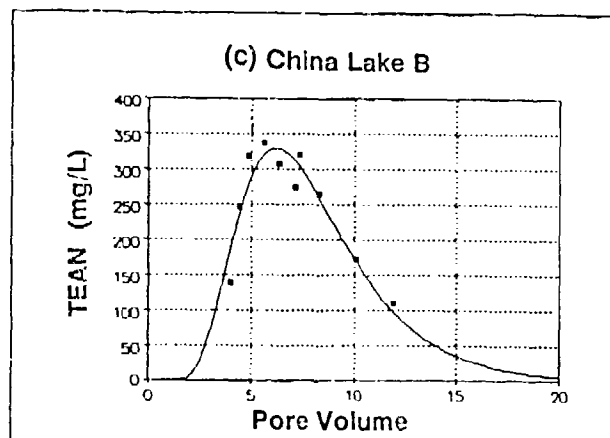
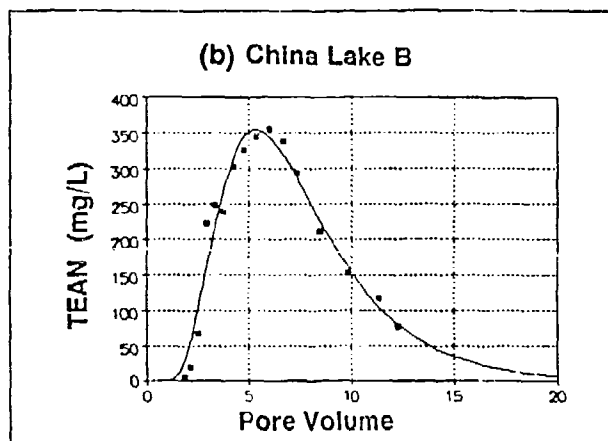
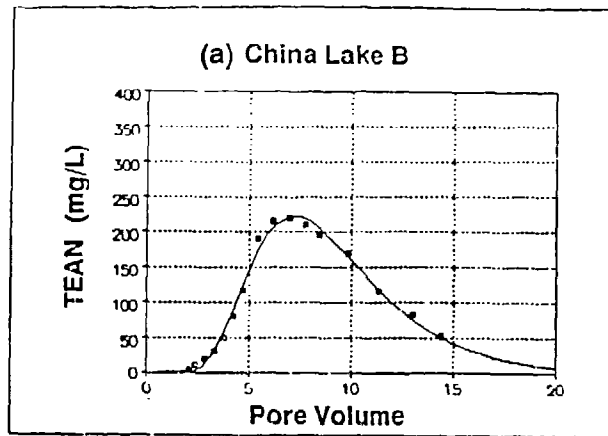


Figure 25. TEAN outflow concentration from China Lake B soil

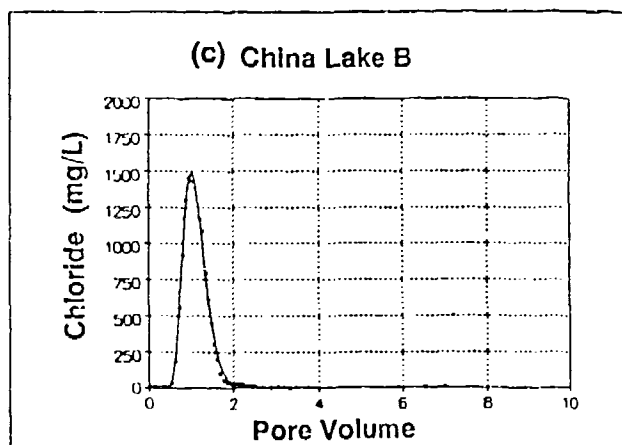
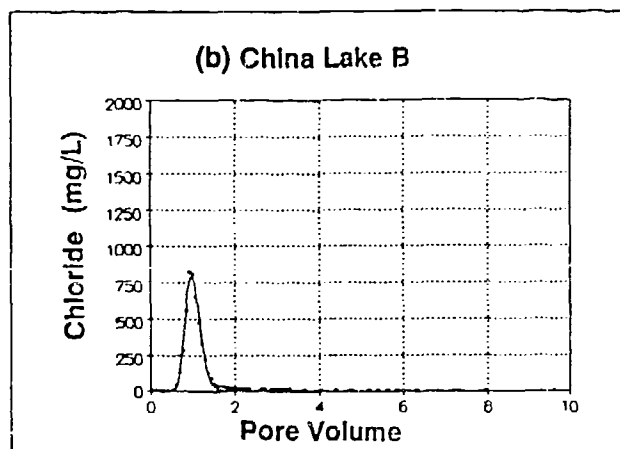
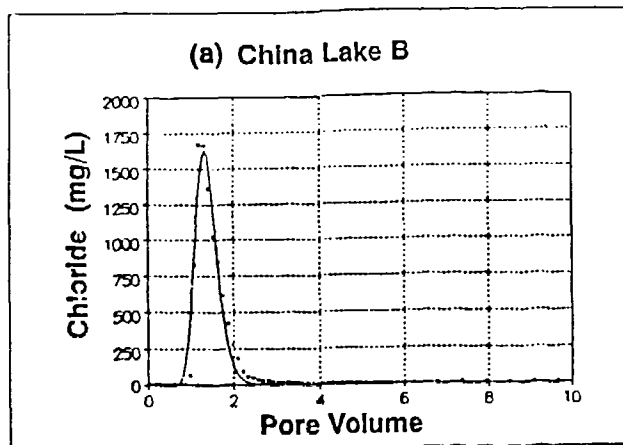


Figure 26. Chloride discharge concentration from China Lake B

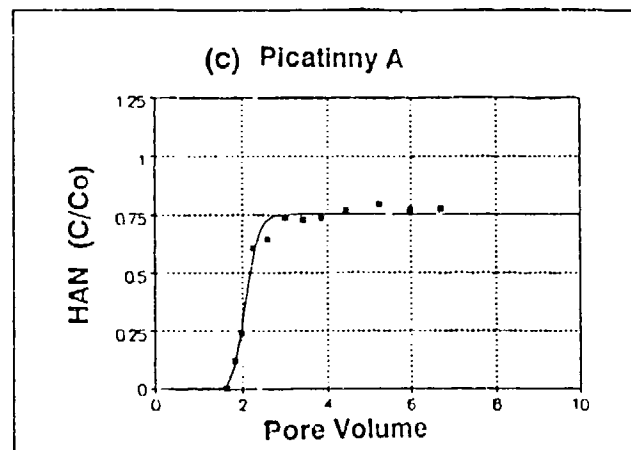
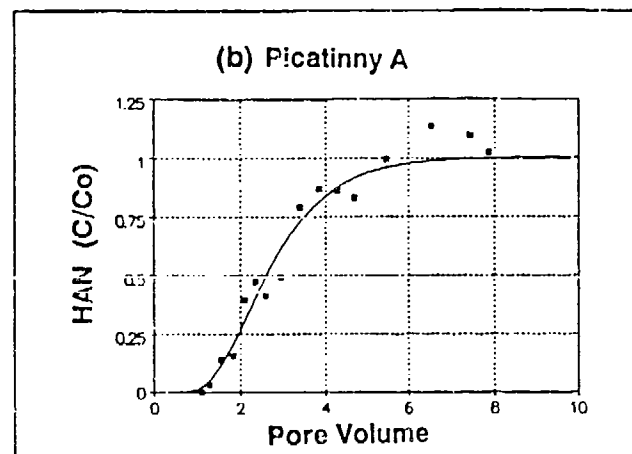
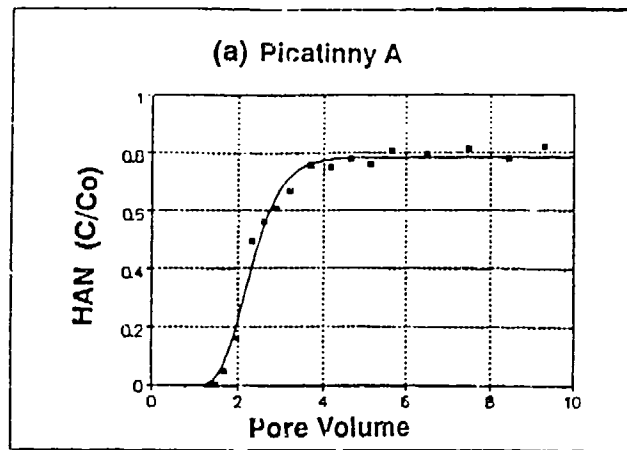


Figure 27. HAN discharge from Picatinny A soil

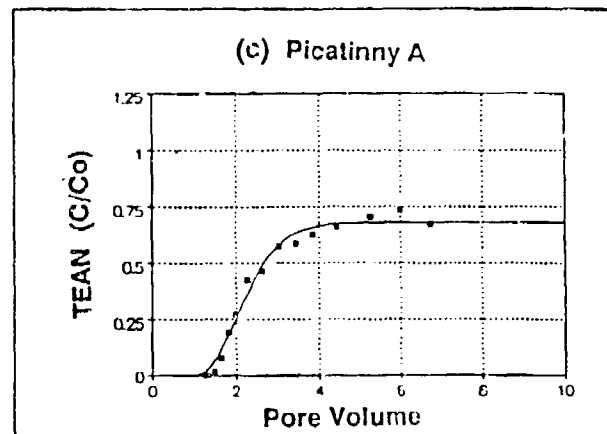
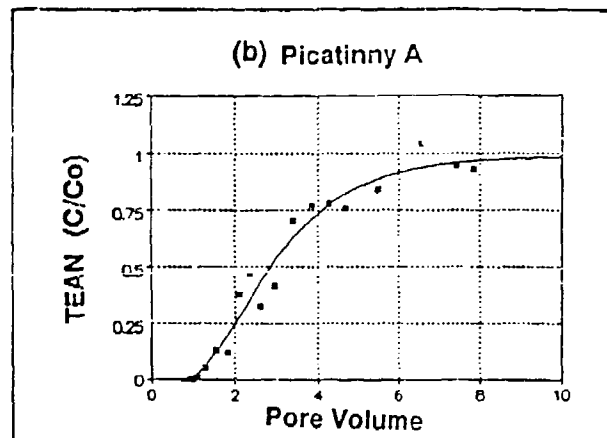
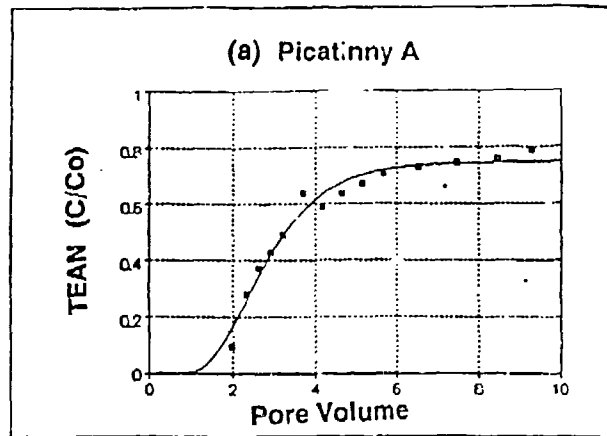


Figure 28. TEAN discharge from Picatinny A soil

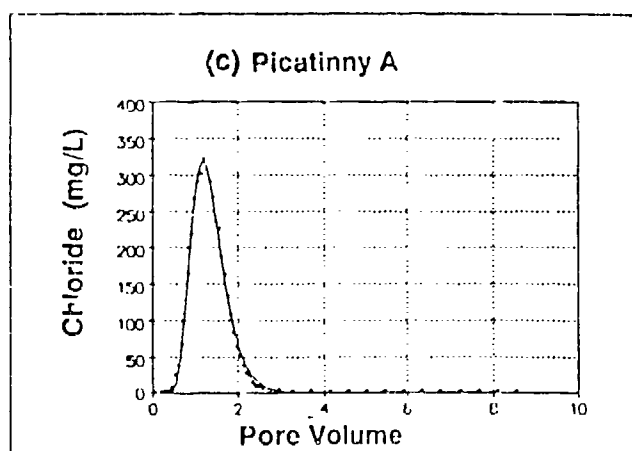
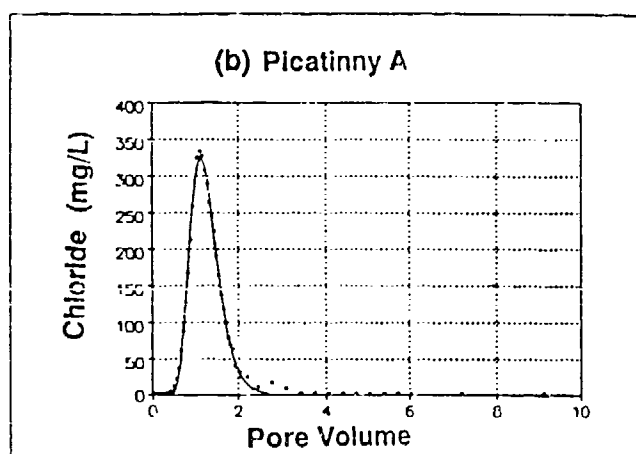
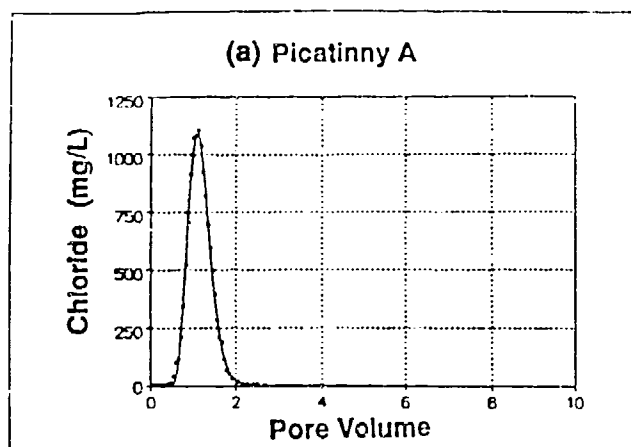


Figure 29. Chloride discharge from Picatinny A soil

of the effluent distribution curves in Figure 29 is the same as it was for China Lake B soil. Chloride ion showed a small retardation and reaction. These results show that the previously applied LP altered the Picatinny A soil surface so it reacted with and adsorbed chloride ion.

The LP loading to Picatinny A soil was a step increase in concentration (see Table 23). The effluent concentration distribution is described by Equation 28. Dispersion manifests itself on Figures 27 and 28 through the slope of the rising limb of the concentration distribution curve. A small dispersion value results in a steep slope to the concentration distribution curve. For example, HAN in column E, Figure 27, has a larger dispersion coefficient than it does in columns D or F.

Reaction or transformation is manifested by the value of  $C/C_0$  leveling off to a value of less than 1. For example, in Figure 27, HAN shows a transformation reaction in Picatinny A soil in columns D and F, but not in column E. Similarly, in Figure 28, TEAN shows more transformation in columns D and F than it does in column E.

Retardation is shown in Figures 27 and 28 by a delay in HAN and TEAN being measured in the effluent. If there were no retardation, the effluent concentration ratio  $C/C_0$  at 1 pore volume should be half of the final effluent concentration. Both HAN and TEAN show the impact of retardation on the concentration distribution curve.

## Conclusions

### Runoff and Infiltration conclusions

When spilled onto soil surfaces, LP runoff and infiltration behavior does not differ significantly from the behavior of water.

Equations to predict how far a given volume of spilled LP will flow on a soil surface before infiltrating into the soil are subject to large errors for both LP and water as each frequently prefers to flow as a rivulet rather than as a thin sheet. A rivulet will travel farther than a thin sheet for the same volume of spill.

Both LP and water infiltrate into soil in a well-behaved manner and show relatively little data scatter. Both fluids continue to migrate deeper into the soil after the free liquid disappears from the soil surface. A combination of gravity and capillary forces keeps the fluids moving.

## **Movement of undiluted LP in soils**

LP reacted by producing gas bubbles as it flowed through Picatinny A, Socorro P, WES Reference, and Yuma 2A soils. The chemical reaction disturbs the soil surface, increasing porosity and resulting in a froth on the pooled LP.

LP expanded the volume of the soils except for China Lake B. Picatinny A soil expanded by 52 percent, Socorro P by 32 percent, WES Reference by 26 percent, and Yuma 2A by 21 to 35 percent.

HAN and TEAN underwent decay and sorption when undiluted LP flowed into dry soil under the driving force of gravity and applied water. The concentrations of HAN and TEAN were reduced by at least 50 percent in China Lake B, Picatinny A, Socorro P, WES Reference, and Yuma 2A soils after flowing through 10 cm of formerly dry soil.

Flow velocities for HAN and TEAN were less than that of the bulk liquid during flow into dry soils. This retardation is evidence of sorption. In addition, HAN and TEAN retardation promotes chemical reactions behind the wetting front with the result that gaseous reaction products sometimes became trapped. In Yuma 2A soil, the gaseous reaction products formed temporary cavities in the soil.

## **Dilute LP movement in soils**

Dilute concentrations of HAN and TEAN exhibited mixing or dispersion characteristics that are distinct to each species even when both flowed at the same time.

Dilute concentrations of HAN and TEAN decay as they flow through China Lake B and Picatinny A soils.

## **Other conclusions**

Methylene blue dye is removed from LP by adsorption as it percolates through China Lake B soil.

Chloride ion that was applied to China Lake B or Picatinny A soil after diluted LP had percolated through was partially removed by reaction and adsorption. This removal is in contrast to the usual conservative behavior of the chloride ion, which does not react or adsorb in soils.

## 4 Effects on Soil Microflora<sup>1</sup>

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### Introduction

#### Rationale

Very little is known about the interactions between LP and the soil biota. Microorganisms respond rapidly to changes in their environment and are therefore particularly sensitive indicators of possible toxic effects of LP on the other soil biota. For this reason, recovery of microorganisms from adverse effects of LP can also demonstrate the effectiveness of spill remediation measures in removing toxicity.

Since LP is used in a highly concentrated form, reactions between LP and the soil fabric and between LP and the soil microorganisms will likely be most intense immediately following a spill. Both positive and negative impacts are possible. The high nitrogen content of LP may make an excellent fertilizer for soil. If this is the case, then the net effect of a spill will be to stimulate microbial growth, and spill response measures will be quite different than if toxicity is observed. Alternatively, the spill may rapidly eliminate the soil microorganisms.

The purpose of this test was to correlate changes in LP associated with soil sorption or LP reaction with the soil to changes in numbers of soil microorganisms. An immediate toxic effect may require that the LP be neutralized soon after the spill. To determine immediate effects of LP, the soil microflora was monitored for changes in levels of selected groups of microorganisms during a soil sorption test. If a delayed toxic effect occurs, the next consideration is the length of contact time required for the toxic effect to be exerted. If LP requires several hours of contact to begin impacting soil microorganisms, the spill response team will have some time following the spill to prevent any harmful long-term effects. Required response time may be sufficient to allow consideration and selection of the most appropriate measure(s) for a given site. Alternatively, several days of contact may be required for a toxic effect to

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<sup>1</sup> By Douglas Gunnison and Judith C. Pennington, U.S. Army Engineer Waterways Experiment Station; John R. Mercer, American Scientific International Corp.

become evident. If this is the case, the question is whether or not a detrimental effect will occur if the spill is left unattended. In this event, the concentration of the LP contacting the soil may be important, i.e., whether the LP entering the soil is undiluted or whether it is diluted to some extent by mixing with water present at the soil surface. If dilution is selected as an immediate remediation measure, what response will the microorganisms make, or what effect will dilution have on LP interactions with the microbes? Each of these scenarios was examined in short- and long-term contact tests during which the fate of LP components and a broad spectrum of soil microorganisms was observed.

If LP exerts a toxic effect on the soil microflora, can this be described in terms that can be easily understood? One possible means of accomplishing this is to compare the impact of LP with the impact of a common laboratory chemical on the same soil microorganisms. LP was observed to have an acid pH; also, it contains nitro groups. In addition, nitric acid is apparently one of the main reactants during LP decomposition. For these reasons, nitric acid was selected for the comparison. Concentrated nitric acid (typically 11 N for 70 percent by weight) was expected to have strong interactions with soil, immediately digesting many soil components, including any microorganisms present. For this reason, 1.0 normal (1.0N) nitric acid was used as the strength of nitric acid comparable to undiluted LP during the testing. One-tenth normal (0.1N) nitric acid was used as the strength of nitric acid comparable to dilute LP during the tests. Nitric acid testing was also conducted in short- and long-term contact studies to provide testing comparable to that done to determine the impact of LP on soil microorganisms. During these tests, the same microorganisms were evaluated as for the short- and long-term LP contact tests.

## **Objectives**

The objectives of this study were to determine the immediate and long-term effects of diluted and undiluted LP on the soil microflora. The short- and long-term effects of 0.1N and 1.0N nitric acid on the soil microflora were also determined to provide a reference to a common laboratory chemical. The microorganisms examined in both studies were restricted to native populations of actinomycetes, bacteria, and fungi.

## **Materials and Methods**

Effects of LP on the soil microflora were evaluated by conducting three tests: (a) a soil sorption kinetics test, (b) a short-term contact test, and (c) a long-term contact test. The effects of short- and long-term contact tests with LP were then compared with short- and long-term tests conducted with 0.1 and 1.0N nitric acid ( $\text{HNO}_3$ ). Microorganisms in Picatinny A and Yuma 2A soils only were monitored during adsorption kinetics tests in which both soils were exposed to undiluted LP and to LP diluted 50:50 with distilled water (diluted

LP). In short-term contact tests with LP, microbial populations in BRL-SAS B, Picatinny A, and Yuma 2A soils were monitored over time following a brief (1 hr) contact with diluted or undiluted LP. Long-term contact tests were monitored to assess microbial recovery after exposing the three soils to diluted or undiluted LP for 90 days. In the comparative studies, microbial populations in Picatinny A soil were monitored over the same short- and long-term contact period using diluted (0.1N) or undiluted (1.0N)  $\text{HNO}_3$  rather than diluted and undiluted LP.

A literature review was conducted with the DIALOG<sup>TM</sup> Search System (databases given in Attachment 1) to obtain a better understanding of the effect of  $\text{HNO}_3$  and pH on soil microorganisms. Search categories included bacteria, fungi, actinomycetes, microorganisms, nitric acid, nitrate, nitrate fertilizers, toxicity, inhibition, and pH effects.

### **Enumeration of microflora in control and test samples**

Oven dry weights were obtained for each soil and for each soil slurry in order to calculate the number of microorganisms per gram. This was done by drying 10 g of moist soil to constant weight at 105 °C.

To enumerate microorganisms in each soil before contact with LP or  $\text{HNO}_3$  (controls), the equivalent of 10-g ODW soil were placed into a dilution bottle containing 90 mL of phosphate-buffered saline (PBS). The slurry was carried through a tenfold dilution series using conventional techniques. One-tenth mL from each dilution was spread onto peptone-tryptone-yeast extract-glucose agar (PTYG) to enumerate bacteria, glycerol agar (GA) to enumerate actinomycetes, and potato dextrose agar (PDA) to enumerate fungi (Table 29). Dilutions of soils in contact with LP were also spread on basal salts agar with LP (BSA-LP) to enumerate microorganisms utilizing LP as a carbon source and basal salts agar with LP, but lacking an additional nitrogen source (BSA-N-LP) to enumerate microorganisms utilizing LP as both a carbon and a nitrogen source (Table 29). Soils in contact with  $\text{HNO}_3$  were spread on basal salts agar with 0.1N  $\text{HNO}_3$  (BSA-DNA) or basal salts agar with 1.0N  $\text{HNO}_3$  (BSA-CNA) to enumerate microorganisms able to tolerate 0.1N or 1.0N  $\text{HNO}_3$ , respectively (Table 29).

In order to enumerate microorganisms in each contact test slurry, 5 mL of each slurry was placed into a dilution bottle containing 95 mL of PBS. The slurry was carried through a twentyfold dilution series using conventional techniques. One-tenth mL from each dilution was spread onto each of the above media under the conditions described.

All plates were incubated at room temperature. After incubation colonies were counted on plates containing 30 to 300 colonies.

| <b>Table 29</b><br><b>Media for Enumeration of Soil Microflora</b>                                               |                                                                                                                                                                                                                                                                                               |                                                                           |
|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Medium                                                                                                           | Contents                                                                                                                                                                                                                                                                                      | Microbial Specificity                                                     |
| PTYG <sup>1</sup>                                                                                                | 0.5-g glucose, 0.5-g peptone, 0.25-g tryptone, 0.5-g yeast extract, 0.25-g magnesium sulfate, 0.07-g calcium chloride, 15-g agar, 1-L reverse osmosis (RO) water                                                                                                                              | Bacteria                                                                  |
| Potato dextrose agar (PDA) <sup>2</sup>                                                                          | 39-g potato dextrose, 1-L tap water                                                                                                                                                                                                                                                           | Fungi                                                                     |
| Glycerol agar (GA)                                                                                               | 10-g glycerol, 1-g sodium asparaginate, 1-g sodium asparaginate, 1-g potassium phosphate, 15-g agar, 1-L tap water                                                                                                                                                                            | Actinomycetes                                                             |
| Basal salts agar with liquid propellant (BSA-LP)                                                                 | 0.4-g ammonium nitrate, 0.1-g potassium phosphate, 0.05-g potassium diphosphate, 0.05-g magnesium sulfate, 0.02-g manganese chloride, 0.005-g calcium chloride, 0.005-g ferrous chloride, 0.2-g calcium carbonate, 1-L tap water, and 5-mL LP                                                 | Microbes utilizing liquid propellant as a sole carbon source              |
| Basal salts agar with liquid propellant, without additional nitrogen (BSA-N-LP)                                  | 0.1-g potassium phosphate, 0.05-g potassium diphosphate, 0.05-g magnesium sulfate, 0.02-g manganese chloride, 0.005-g calcium chloride, 0.005-g ferrous chloride, 0.2-g calcium carbonate, 1-L tap water, and 5-mL LP                                                                         | Microbes utilizing liquid propellant as a sole carbon and nitrogen source |
| Phosphate-buffered saline (PBS)                                                                                  | 7.8-mL (0.1M) sodium phosphate, 2.2-mL (0.1M) potassium phosphate, 90.0-mL 90-mL (0.85%) saline                                                                                                                                                                                               | Dilution medium                                                           |
| Basal salts agar with 0.1N HNO <sub>3</sub> (BSA-DNA) or 1.0N HNO <sub>3</sub> (BSA-CNA)                         | BSA-DNA: Mix 900 mL of BSA containing 15 g of agar made as for BSA-LP with 100 mL of 1.0N HNO <sub>3</sub> , after autoclaving each separately. BSA-CNA: Mix 900 mL of BSA containing 15 g of agar made as for BSA-LP with 100 mL of 10N HNO <sub>3</sub> , after autoclaving each separately | Acid tolerant bacteria                                                    |
| <sup>1</sup> PTYG = Peptone-tryptone-yeast extract-glucose agar.<br><sup>2</sup> Commercially available mixture. |                                                                                                                                                                                                                                                                                               |                                                                           |

### Acridine orange direct count of microbes

Soil samples from the short- and long-term contact tests with and without LP and with 0.1N and 1.0N HNO<sub>3</sub> were also prepared for acridine orange direct count (AODC) using the acridine orange staining procedure of W. F. Ghiorse and L. Anguish (personal communication, Cornell University, April 1993), which is summarized below.

Soil samples were fixed immediately upon retrieval from tests and then stored at 4 °C. The fixation procedure was as follows. Three 2.5-g subsamples of each soil were weighed aseptically into separate tared, sterile Erlenmeyer flasks. These were sealed with sterile rubber stoppers. Twenty-two mL of sterile 0.1-percent sodium pyrophosphate (Na<sub>2</sub>P<sub>2</sub>O<sub>4</sub>•10 H<sub>2</sub>O) adjusted to pH 7.0 was added. This represented a 1:10 dilution of the original sample. The flasks were mixed on a rotary shaker at 150 rpm at 25 °C for

45 min. After shaking, the suspension was allowed to settle for 2 min, permitting the large particles to settle out and leaving a homogeneous suspension in the supernatant. A 9.0-mL portion of the suspension was transferred aseptically from each flask to an autoclaved 25-mL scintillation vial. A 1.0-mL portion of molten 1-percent aqueous Noble agar containing 0.1 mL of 50-percent glutaraldehyde was added to each of the vials. The vials were immediately mixed on a vortex mixer and stored at 25 °C until the staining procedure described below was executed the same week.

To stain the fixed soil samples, two 5- $\mu$ L samples from each vial were spread uniformly onto a glass microscope slide having two 1.1- $\mu$ m inside diameter ceramic circles stamped into the surface. Smears were air-dried and stained for 2 min with a few drops of 0.01-percent acridine orange containing 0.5  $\mu$ g/mL of 4,6-diamidino-2-phenyl-indole (DAPI) dihydrochloride. The smears were washed with 20 mL of 1 M NaCl and rinsed briefly with water. After excess water was allowed to evaporate, 15  $\mu$ L of a 0.2- $\mu$ m filtered DABCO (1,4-Diazabicyclo[2,2,2]octane) was dropped onto the smear. The smear was then covered and sealed with a 50:50 mixture of vaseline and paraffin.

An agar blank was prepared by mixing 9 mL of 0.1-percent sodium pyrophosphate with agar and glutaraldehyde as described in the above fixation procedure. The blank was prepared on each batch of slides to give a background count.

All smears were examined under phase contrast and blue light epillumination using 40X and 100X oiled phase contrast and bright field objectives with 10X wide field eyepieces. Fields counted were 1 mm from the border of the stamped circular area in a region of average soil thickness. Living heterotrophic bacteria fluoresce green, while inactive cells (dead) or soil particles fluoresce red or yellow. Ten to twenty fields were observed for each subsample. Fields with 10 to 100 cells were considered optimal for counting. The most accurate counts were obtained when the 100X bright field objective lens was employed with epi-illumination because this permitted identification of smaller cells. Phase contrast microscopy was used to distinguish between cells and other fluorescent organic matter when distinctions were difficult.

### **Adsorption kinetics tests**

Bacteria in Picatinny A and Yuma 2A soils were enumerated during the adsorption kinetics test at 1 hr, 6 hr, 24 hr, 2 days, and 5 days. Ten-millimeter samples were taken from slurries containing a 1:4 ratio of soil to undiluted LP or to a 50:50 dilution of LP in sterile RO water. Five milliliters were also used in a twentyfold dilution series to determine the microbial number, and five milliliters were used to determine the ODW of the slurry aliquot.

### Short-term contact tests

A 1:5 slurry of sieved (<2 mm) soil (ODW) to undiluted LP, diluted LP, 0.1N HNO<sub>3</sub>, or 1.0N HNO<sub>3</sub> was placed into individual centrifuge bottles stoppered with puff plugs. The bottles were placed onto an orbital water bath shaker beneath the hood and incubated for 1 hr at 30 °C and 75 rpm. The bottles were removed, and the soil was washed three times with sterile RO water. Phases were separated each time by centrifugation at  $4,976 \times g$  for 15 min. Soils were resuspended in RO water to the 1:5 ratio.

After the final wash, soils were diluted (1:5) in RO water and transferred to 125-mL Erlenmeyer flasks stoppered with sterile puff plugs. These flasks were incubated on an orbital shaker at 30 °C and 75 rpm. Samples were taken immediately for AODC and associated nutrient agar plate counts, and for analysis of HAN and TEAN. Results from the short- and long-term LP contact studies indicated good correspondence between AODC results and the values obtained on nutrient agar (see results section). Consequently, nutrient agar plate counts were not made for the HNO<sub>3</sub> treatments. A second sample for AODC was taken after 5 days of incubation with 0.1N or 1.0N HNO<sub>3</sub>. Additional samples for microbial enumeration by plate count were taken after 6 hr, 24 hr, 5 days, 28 days, and 90 days of incubation. A final Picatinny A sample was collected after 90 days of incubation for AODC in the LP and HNO<sub>3</sub> treatments and to determine HAN and TEAN concentrations in the LP treatment.

### Long-term contact tests

A 1:5 slurry of soil to either undiluted LP, a 50:50 dilution of LP in RO water, 1.0N HNO<sub>3</sub>, 0.1N HNO<sub>3</sub>, or RO water alone (control) was incubated in 125-mL Erlenmeyer flasks, as previously described. All slurries were sampled for microbial enumeration by dilution plating after 1 hr, 6 hr, 24 hr, 5 days, 28 days, and 90 days of contact. Slurries containing undiluted or diluted LP were sampled for AODC microbial enumeration, and HAN and TEAN concentrations after 1 hr, 5 days, and 90 days. Slurries containing 1.0N or 0.1N HNO<sub>3</sub> were sampled for AODC microbial enumeration after 1 hr, 5 days, and 90 days. Control slurries were sampled for HAN and TEAN concentrations after 1 hr and 90 days. These samples were used to detect any background interferences in the analytical procedure. Since LP and HNO<sub>3</sub> remained in slurry samples, samples could not be heated to obtain ODW. Therefore, dry weights for all tests were based on ODW of the controls sampled after 1 hr and 45 days.

### Processing of samples from short- and long-term contact tests

**AODC, HAN, and TEAN samples.** The shaker speed was increased from 75 to 300 rpm for sampling. A 5-mL sample from each replicate was centrifuged at  $7,433 \times g$  for 15 min. The supernatant was analyzed for HAN and

TEAN, and the pellet was analyzed for microorganisms after serial dilution and plate count.

**Microbial enumeration.** Five milliliters of slurry were carried through a conventional dilution series in PBS. A 0.1-mL sample of the solution was plated for colony counting.

## Results

### Microbial populations before contact with LP (controls)

Bacteria were detected in BRL-SAS B, Picatinny A, and Yuma 2A soils cultured on PTYG (Table 30). However, levels of bacteria in Yuma 2A soils were extremely low, while the levels in BRL-SAS B and Picatinny A were typical of those normally found in soils (Alexander 1977). Fungi and actinomycetes were also present in BRL-SAS B and Picatinny A soils, but not in Yuma 2A. No microorganisms able to utilize LP as sources of nitrogen or carbon were detected in any of the soils.

| <b>Table 30</b><br><b>Numbers of Microorganisms in Soils Prior to Contact with LP</b> |                                                                                    |                                       |                                       |
|---------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|---------------------------------------|---------------------------------------|
| Medium                                                                                | Colony-Forming Units Per Gram Dry Weight of Soil $\pm$ Standard Error <sup>1</sup> |                                       |                                       |
|                                                                                       | BRL-SAS B                                                                          | Picatinny A                           | Yuma 2A                               |
| PTYG                                                                                  | $5.4 \times 10^6 \pm 3.1 \times 10^5$                                              | $1.1 \times 10^6 \pm 1.2 \times 10^5$ | $3.9 \times 10^3 \pm 4.2 \times 10^2$ |
| PDA                                                                                   | 0.0                                                                                | $8.8 \times 10^3 \pm 2.5 \times 10^3$ | 0.0                                   |
| GA                                                                                    | $4.3 \times 10^5 \pm 5.2 \times 10^4$                                              | $8.8 \times 10^5 \pm 1.0 \times 10^5$ | 0.0                                   |
| BSA LP                                                                                | 0.0                                                                                | 0.0                                   | 0.0                                   |
| BSA-N LP                                                                              | 0.0                                                                                | 0.0                                   | 0.0                                   |

<sup>1</sup> The lowest dilution used for each soil sample was  $1 \times 10^2$ .

### Adsorption kinetics

No microorganisms were recovered over the 5-day monitoring period on any of the media with Yuma 2A soil in contact with either undiluted or diluted LP. This reflects the initial low populations in this soil (Table 30) from which any decrease dropped the levels below the detection limit of  $1 \times 10^2$  microorganisms per gram ODW.

No microorganisms were recovered from Picatinny A soil samples in contact with undiluted LP on any media. The initial levels of bacteria and

actinomycetes present in Picatinny A soil declined by one to two orders of magnitude within the first hour of contact with dilute LP (Table 31). After 24 hr of contact, neither bacteria nor actinomycetes grew (Table 31). The lack of a sufficiently large microbial population in Yuma 2A soil and the lack of any growth with undiluted LP in Picatinny A soil obscured relationships between microbial responses and the physical-chemical responses of soils to LP. Likewise, the rapid decrease in microbial numbers in Picatinny A soil contacting dilute LP provided insufficient data to correlate trends in microbial numbers with physical-chemical responses. Nevertheless, these results were indicative of the inhibitory effects of LP on microbes which were later confirmed in other parts of the study.

**Table 31**  
**Numbers of Microorganisms Present in Picatinny A Soil Treated with Dilute LP in Adsorption Kinetics Study**

| Medium <sup>1</sup> | LP Contact <sup>1</sup> hr | Colony-Forming Units Per Gram Dry Weight Soil $\pm$ S.E. <sup>2</sup> |
|---------------------|----------------------------|-----------------------------------------------------------------------|
| PTYG                | 0                          | $1.1 \times 10^6 \pm 1.2 \times 10^5$                                 |
|                     | 0.5                        | $7.2 \times 10^4 \pm 1.7 \times 10^4$                                 |
|                     | 1                          | $2.3 \times 10^4 \pm 3.5 \times 10^3$                                 |
|                     | 2                          | $2.0 \times 10^4 \pm 6.0 \times 10^3$                                 |
|                     | 6                          | $1.4 \times 10^4 \pm 8.5 \times 10^3$                                 |
|                     | 24                         | $9.3 \times 10^4 \pm 1.0 \times 10^4$                                 |
|                     | 48                         | 0.0                                                                   |
|                     | 120                        | 0.0                                                                   |
| GA                  | 0                          | $8.8 \times 10^5 \pm 1.0 \times 10^4$                                 |
|                     | 0.5                        | 0.0                                                                   |
|                     | 1                          | $3.7 \times 10^3 \pm 2.0 \times 10^3$                                 |
|                     | 2                          | $1.9 \times 10^4 \pm 2.5 \times 10^3$                                 |
|                     | 6                          | $1.8 \times 10^4 \pm 2.7 \times 10^3$                                 |
|                     | 24                         | $2.6 \times 10^4 \pm 5.8 \times 10^3$                                 |
|                     | 48                         | 0.0                                                                   |
|                     | 120                        | 0.0                                                                   |

<sup>1</sup> Contact with LP prevented growth of microbes on the other media used in this test at all contact times. Therefore, these media were not entered into the table.

<sup>2</sup> The lowest dilution used for each soil sample was  $1 \times 10^2$  therefore, the detection limit was 100 CFUs/g of soil (ODW).

### Short- and long-term contact tests

**Changes in LP components.** Due to lack of homogeneity in variances, discussions are confined to trends in the data. Recoveries of HAN and TEAN from the aqueous phase of controls and the short- and long-term contact tests are shown in Table 32. The trace of HAN detected in control samples from each of the soils at 1 hr should be regarded as an artifact of the analysis, since it is well below the 1,000-ppm region, where the detection of these compounds is at maximum sensitivity. The three rinses removed most of the HAN and

**Table 32**  
**HAN and TEAN Recoveries for Aqueous Phase of Short- and Long-Term Contact Tests**

| Soil                                                                                                                                                                                                                                                                                                                                                                                                      | Treatment            | LP Contact Time | Concentration of LP Component (ppm) (Mean + S.E.) <sup>1</sup> |                               |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|-----------------|----------------------------------------------------------------|-------------------------------|
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      |                 | HAN                                                            | TEAN                          |
| BRL-SAS B                                                                                                                                                                                                                                                                                                                                                                                                 | Control <sup>2</sup> | 1 Hour          | 5 ± 0                                                          | 0 <sup>3</sup>                |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Short-term contact   | 1 Hour          | 322 ± 74                                                       | 125 ± 303 <sup>3</sup>        |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Long-term contact    |                 |                                                                |                               |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Undiluted LP         | 1 Hour          | 854,633 ± 8,177                                                | 295,967 ± 7,244               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 803,000 ± 30,000                                               | 283,000 ± 18,500              |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 858,250 ± 41,550                                               | 282,500 ± 24,500              |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Diluted LP           | 1 Hour          | 368,000 ± 0                                                    | 153,500 ± 5,500               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 418,667 ± 7,311                                                | 151,000 ± 6,245               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 852,000 ± 34,000                                               | 268,000 ± 4,000 <sup>4</sup>  |
| Picatinny A                                                                                                                                                                                                                                                                                                                                                                                               | Control              | 1 Hour          | 5 ± 0                                                          | 0 <sup>3</sup>                |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         |                                                                |                               |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Short-term contact   | 1 Hour          | 175 ± 29                                                       | 88 ± 9 <sup>3</sup>           |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Long-term contact    |                 |                                                                |                               |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Undiluted LP         | 1 Hour          | 862,567 ± 3,453                                                | 295,800 ± 2,178               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 819,667 ± 3,528                                                | 283,000 ± 4,933               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 839,500 ± 30,500                                               | 240,150 ± 58,850 <sup>4</sup> |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Diluted LP           | 1 Hour          | 407,667 ± 3,844                                                | 148,333 ± 3,180               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 428,667 ± 3,711                                                | 163,000 ± 7,572               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 585,000 ± 4,854                                                | 171,053 ± 4,953 <sup>4</sup>  |
| Yuma 2A                                                                                                                                                                                                                                                                                                                                                                                                   | Control              | 1 Hour          | 5 ± 1                                                          | 0 <sup>3</sup>                |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Short-term contact   | 1 Hour          | 189 ± 27                                                       | 184 ± 32 <sup>3</sup>         |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Long-term contact    |                 |                                                                |                               |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Undiluted LP         | 1 Hour          | 866,667 ± 9,034                                                | 301,233 ± 14,664              |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 848,000 ± 8,000                                                | 265,500 ± 13,500              |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 801,600 ± 38,000                                               | 267,500 ± 500 <sup>4</sup>    |
|                                                                                                                                                                                                                                                                                                                                                                                                           | Diluted LP           | 1 Hour          | 445,300 ± 6,426                                                | 140,600 ± 6,700               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 5 Days          | 393,000 ± 11,240                                               | 145,000 ± 2,500               |
|                                                                                                                                                                                                                                                                                                                                                                                                           |                      | 90 Days         | 167,800 ± 19,200                                               | 106,867 ± 2,748               |
| <sup>1</sup> Based on three replicate treatments. Detection limits for HAN were 3,000 ppm and for TEAN were 1,000 ppm except where otherwise noted.<br><sup>2</sup> Controls received no LP treatment<br><sup>3</sup> Detection limits were: HAN - 3 ppm, TEAN - 1 ppm.<br><sup>4</sup> Detection limits were: HAN - 1 ppm, TEAN - 3 ppm<br><sup>5</sup> Detection limits were: HAN - 1 ppm, TEAN - 1 ppm |                      |                 |                                                                |                               |

TEAN from the soils in the short-term test, but significant levels were still present in 1-hr samples of all three soils.

Concentrations of HAN in undiluted long-term tests changed little over time. This is consistent with insufficient quantities of soil with which HAN could react, i.e., a large excess of HAN in the test. Concentrations of HAN in the diluted long-term tests for Yuma 2A soil, which has been demonstrated to be the most reactive of test soils with LP, decreased over time, an indication that reaction was still occurring.

HAN and TEAN concentrations in the BRL-SAS B and Picatinny A soils with diluted LP generally increased between 1 hr and 5 days and between 5 and 90 days. This increase is attributable to a decrease in water because of evaporation over the prolonged test period. However, because of continued reactivity with HAN, this trend in the data was not observed in the Yuma 2A soil.

**Changes in soil microflora exposed to LP.** Only actinomycetes and heterotrophic bacteria were recovered with dilutions made from the BRL-SAS B and Picatinny A soils during the control and short-term contact tests (Figure 30). In all cases, the initial effect of short-term contact was to drop the population levels by one to several orders of magnitude. Populations recovered to near control levels by 5 days, except for heterotrophic bacteria in Picatinny A soil, which failed to recover. Microorganisms in the Yuma 2A soil remained at or below the detection limit of  $1 \times 10^2$  colony forming units (CFUs)/gram ODW of soil in both controls and short-term contact tests (no graph shown).

No microorganisms were detected from any of the soils on any of the media in the short- or long-term contact tests with undiluted LP. This result indicated that undiluted LP is toxic to all the microbial groups in the soil. The pH of undiluted and diluted LP was 0.63 and 1.77, respectively. The low pH is very likely a significant factor in the decreases in the numbers of microorganisms contacted with diluted LP and the toxicity of undiluted LP.

Liquid propellant in the media as a carbon and/or nitrogen source failed to support growth of microorganisms in any treatments. Either LP was toxic to the microorganisms, or the microorganisms were incapable of utilizing LP as a growth substrate, or both. In order to serve as a sole carbon and nitrogen source, LP concentrations would have to be significantly lower than those used in this study.

Although used on 1-hr, 5-day and 90-day LP samples only, AODC and nutrient agar plate counts generally substantiated results obtained with other media for most of the treatments (Table 33). Results for controls and short-term contact tests in the three soils were comparable, indicating that properties of the soils exerted no influence on results. In long-term contact tests, undiluted LP sterilized all three soils within the first hour of contact, and no subsequent recoveries in microbial populations were observed over the 90-day period. In long-term contact tests with dilute LP, some residual microorganisms were present at 1 hr in Picatinny A and Yuma 2A soils, but not in BRL-SAS B soil. Both BRL-SAS B and Picatinny A (but not Yuma 2A) soils showed some regrowth by 90 days. The AODC method produces higher numbers than the direct plate counts because AODC enumerates *all* microorganisms visible in the soil sample, whereas the plate count method enumerates only those microorganisms able to grow on the specific artificial media used.

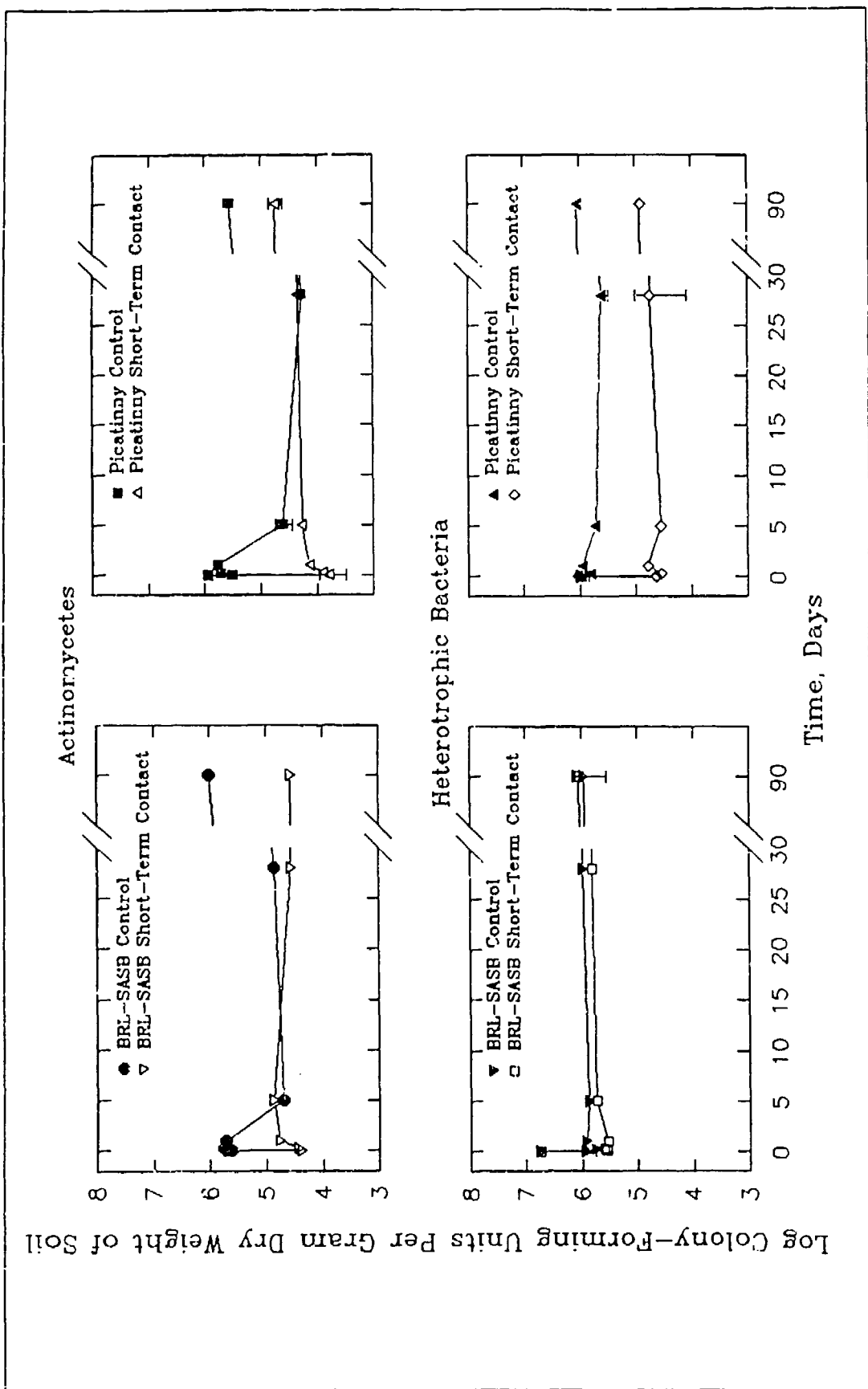


Figure 30. Comparison of microorganisms recovered on glycerol (actinomycetes) and PTYG agars (bacteria) from the control and short-term contact tests. Open and closed symbols are means, and vertical bars are standard errors

**Table 33**  
**Comparison of Total Microorganisms Determined by AODC and**  
**Nutrient Agar Plate Counts**

| Soil           | Treatment <sup>1</sup> | LP<br>Contact<br>Time | Microorganisms per Gram Dry Weight of<br>Soil <sup>2</sup> |                                       |
|----------------|------------------------|-----------------------|------------------------------------------------------------|---------------------------------------|
|                |                        |                       | Direct Count<br>(cells/g soil)                             | Plate Count<br>(CFUs/g)               |
| BRL-<br>SAS B  | Control                | 1 Hour                | $2.7 \times 10^5 \pm 1.0 \times 10^5$                      | $9.8 \times 10^4 \pm 1.5 \times 10^3$ |
|                | Short-term contact     | 1 Hour                | $9.6 \times 10^4 \pm 4.3 \times 10^4$                      | $1.0 \times 10^5 \pm 9.4 \times 10^4$ |
|                | Long-term contact      | 1 Hour                | 0.0                                                        | 0.0                                   |
|                | diluted LP             | 5 Days                | 0.0                                                        | 0.0                                   |
|                |                        | 90 Days               | $1.2 \times 10^5 \pm 5.5 \times 10^4$                      | $2.3 \times 10^5 \pm 2.5 \times 10^2$ |
| Picatinny<br>A | Control                | 1 Hour                | $5.7 \times 10^4 \pm 1.2 \times 10^4$                      | $8.0 \times 10^4 \pm 0$               |
|                | Short-term contact     | 1 Hour                | $3.1 \times 10^5 \pm 1.6 \times 10^5$                      | — <sup>3</sup>                        |
|                | Long-term contact      | 1 Hour                | $5.3 \times 10^3 \pm 2.6 \times 10^3$                      | $7.2 \times 10^1 \pm 3.1 \times 10^0$ |
|                | diluted LP             | 5 Days                | 0.0                                                        | 0.0                                   |
|                |                        | 90 Days               | $3.7 \times 10^5 \pm 1.7 \times 10^5$                      | $3.1 \times 10^4 \pm 5.8 \times 10^2$ |
| Yuma 2A        | Control                | 1 Hour                | 0.0                                                        | $3.1 \times 10^1 \pm 3.1 \times 10^0$ |
|                | Short-term contact     | 1 Hour                | 0.0                                                        | —                                     |
|                | Long-term contact      | 1 Hour                | $2.7 \times 10^5 \pm 1.4 \times 10^5$                      | —                                     |
|                | diluted LP             | 5 Days                | 0.0                                                        | 0.0                                   |
|                |                        | 90 Days               | 0.0                                                        | 0.0                                   |

<sup>1</sup> No microorganisms were detected by either method in undiluted long-term contact tests. Therefore, these negative data were omitted from the table

<sup>2</sup> Acridine orange direct counts were determined on only the 1-hr short-term contact tests

<sup>3</sup> — Sample lost during processing

**Changes in soil microflora exposed to HNO<sub>3</sub>.** The initial effect of short-term contact with 0.1N HNO<sub>3</sub> was a drop in populations of all microbial types by one to several orders of magnitude. However, populations recovered by 5 days to near initial levels (Figure 31). One normal HNO<sub>3</sub> short-term contact tests also caused an immediate drop in populations of all microbial types, but populations failed to recover.

Long-term contact with 0.1N and 1.0N HNO<sub>3</sub> caused populations of all microbial types to drop initially by one to several orders of magnitude (Figure 32). Populations of microbes contacted with 0.1N HNO<sub>3</sub> recovered to near initial levels by 28 days, while populations contacted with undiluted HNO<sub>3</sub> failed to recover.

The AODC indicated that the same numbers of total bacteria were present in the 0.1N and 1.0N HNO<sub>3</sub> short- and long-term contact treatments (Figures 31 and 32). Moreover, these levels apparently did not change over the course of the test. However, the bacteria in the 0.1N HNO<sub>3</sub> treatment fluoresced bright green, indicating that these microorganisms were alive, while those in the 1.0N HNO<sub>3</sub> treatment were orange, indicating that these cells were dead. No living microorganisms were recovered from the undiluted treatment using any of the different plated media (Figure 31). Apparently, the 1.0N HNO<sub>3</sub> killed all of the microorganisms on contact, but also preserved the cells.

The pH of treatments in long-term contact tests were 0.73 with 1.0N HNO<sub>3</sub> and 1.63 with 0.1N HNO<sub>3</sub>. Soil washing after short-term contact resulted in increases in pH to 3.29 in 1.0N HNO<sub>3</sub> tests and 3.41 in 0.1N tests. These pH values would require microorganisms to be very acidophilic (acid loving), even for the 0.1N HNO<sub>3</sub> treatments.

### **Comparison of the Impacts of LP and HNO<sub>3</sub>**

The initial effect of short-term contact with diluted LP and 0.1N HNO<sub>3</sub> was to decrease the numbers of microorganisms present. Over the course of the tests, bacteria and actinomycetes exposed to LP for the short-term generally recovered slightly from the lowest levels achieved during the first 1 to 6 hr, but never returned to the initial population levels. The same was true for the population levels of heterotrophic bacteria and actinomycetes in the 0.1N HNO<sub>3</sub> test. The undiluted LP and 1.0N HNO<sub>3</sub> each sterilized the soil within the first hour of contact, and no microorganisms were recovered after this.

The long-term contact tests with the dilute LP and 0.1N HNO<sub>3</sub> showed some differences. All heterotrophic bacteria and actinomycetes in diluted and undiluted LP long-term contact tests were killed. By contrast, heterotrophic bacteria in the 0.1N HNO<sub>3</sub> long-term contact tests dropped 2 to 3 orders of magnitude and then recovered. Fungi, actinomycetes, and acid-tolerant bacteria in the 0.1N HNO<sub>3</sub> long-term contact tests dropped off to less than detection levels and then recovered, suggesting that the conditions selected for acid-resistant forms that could then repopulate the slurry over the long term. This indicates that the 0.1N HNO<sub>3</sub> treatment was somewhat milder than the dilute LP treatment. The pH level for the 0.1N HNO<sub>3</sub> long-term contact test (1.63) was in the same range as for the diluted long-term LP (1.77). This indicates that other factors than pH alone may have been responsible for the impact of dilute LP on microorganisms.

### **Observations**

Microorganisms vary widely in their responses to acidity. An acidic pH between 4 and 6 and an alkaline pH between 8 and 9 are normally the limits for growth of most bacteria (Thimann 1963). Most bacteria do not tolerate pH

Log Number of Microorganisms Per Gram Dry Weight of Soil

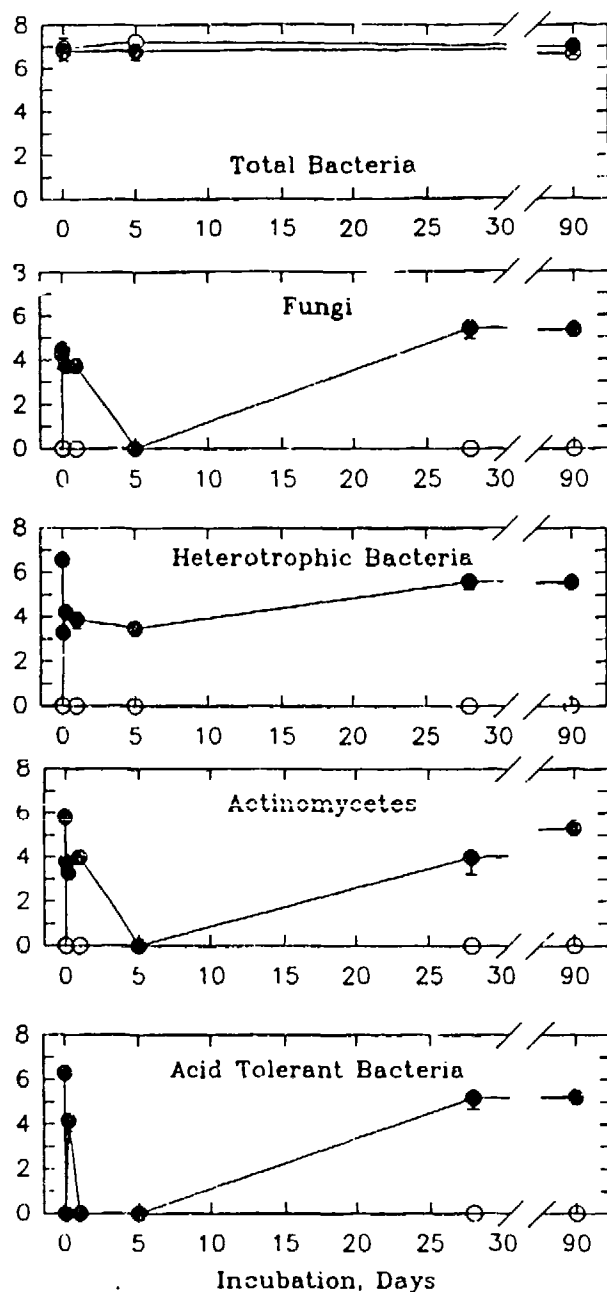


Figure 31. Response of microflora in Picatinny A soil to 1 hr of contact with HNO<sub>3</sub>; • - 0.1N HNO<sub>3</sub> treatment; o - 1.0N HNO<sub>3</sub> treatment. Values given are the means of three replicates  $\pm$  standard error of the mean

Log Number of Microorganisms Per Gram Dry Weight of Soil

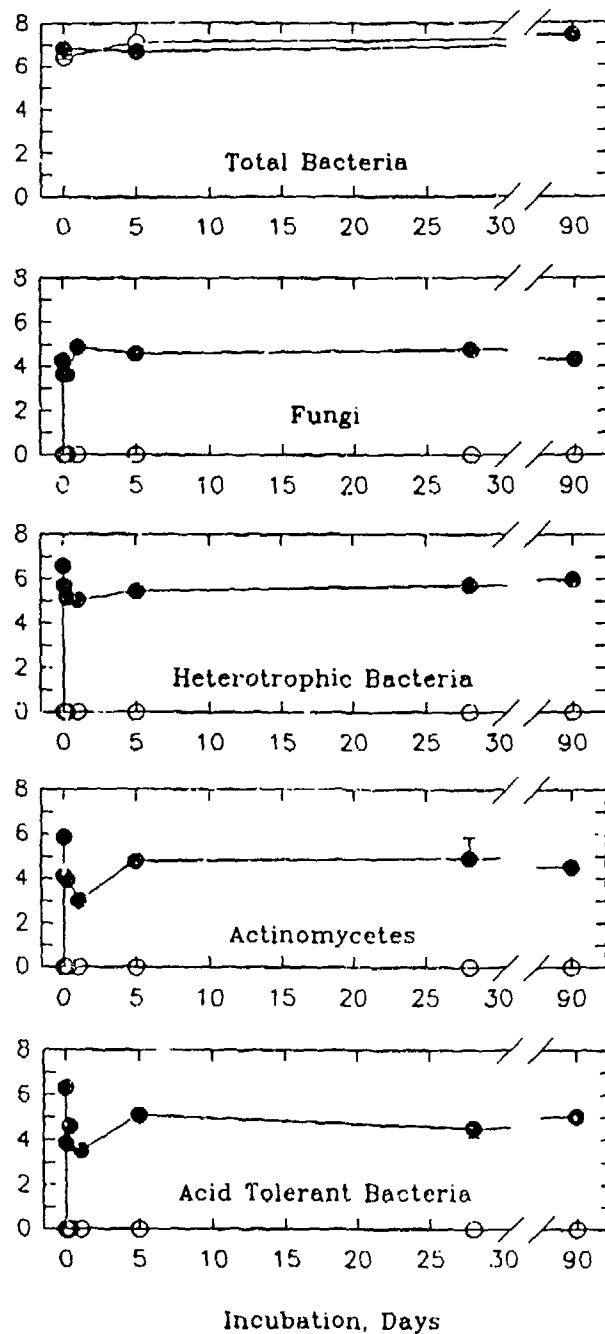


Figure 32. Response of microflora in Picatinny A soil to 90 days of contact with HNO<sub>3</sub>: • - 0.1N HNO<sub>3</sub> treatment; ○ - 1.0N HNO<sub>3</sub> treatment. Values given are the means of three replicates  $\pm$  standard error of the mean

levels less than 4. However, not all bacteria respond negatively to low pH conditions, and many acidophilic species are known. Some of those able to tolerate the most acidic conditions include *Acetobacter* (vinegar-producing bacteria) and the *Thiobacilli* (sulfur oxidizers) (Thimann 1963). In addition, microbial species often are able to adapt to altered soil pH (Parkin, Sexstone, and Tiedje, 1985). For example, soil bacteria are exposed to arid conditions when atmospheric deposition of  $\text{NO}_x$  (mostly  $\text{NO}_2$ ) and its reaction products add  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to the soil system. Acidic deposition can also affect populations of soil bacteria by altering the soil chemical environment and organic matter cycling (Myrold 1990). Bacterial tolerance of low pH is strongly influenced by other environmental factors including desiccation and temperature (Evans, Wallace, and Dobrowolski 1993) and carbon substrate level (Clarke, Dilworth, and Glenn 1993).

Fungi do quite well under mildly acidic conditions. In fact, most yeasts and fungi are markedly acidophilic; several fungi can grow in acid stronger than pH 2 (Griffin 1972). Ectomycorrhizal fungi are often able to grow well at pH 3 (Hung and Trappe 1983), although the mycorrhizal infection of seedlings may decrease as a result of soil acidification (Myrold 1990). Rates of respiration by fungi are not affected much by pH levels in the range of 5 to 8, although pH can impact these microorganisms by affecting environmental factors such as solubility of nutrients (Griffin 1972). Actinomycetes are the most acid intolerant of the microorganisms examined; their optimum pH is approximately 8.5 (Thimann, 1963).

Based on the above information, the effects of pH on levels of microorganisms in soil observed in this study are not surprising; i.e., in long-term 0.1N  $\text{HNO}_3$  treatments, some bacteria were killed off, but the remaining acid-tolerant bacteria were able to repopulate the treatment slurry; fungi generally fared better than the other microorganisms; and the actinomycetes were extremely sensitive to the presence of acid. The bacteria and fungi recovered on plated media from the 0.1N  $\text{HNO}_3$  treatments were not identified to genus and species level to determine changes in diversity over time. However, based on colony morphology, very few species were recovered (D. Gunnison, unpublished observation), although the numbers of microorganisms of a given species were quite high. This is a typical response to a severe environmental stress (Lynch and Poole 1979).

Contact with 1.0N  $\text{HNO}_3$  and both undiluted and diluted LP may have caused osmotic shock in the microorganisms as a result of high solute concentrations. That is, the concentration of dissolved components was so high that water was forced to leave the microbial cells to dilute the high concentration of solute outside the cell; this caused cells to desiccate and die (plasmolysis). The opposite would occur if chemicals enter the cells rapidly. Water would enter, attempting to dilute the chemicals; this occurrence would cause the cells to swell and burst (osmolysis). The pH effect and the osmotic shock acting in concert may help to explain why 1.0N  $\text{HNO}_3$  and undiluted and diluted LP had such lethal impacts on the soil microorganisms in comparison to  $\text{HNO}_3$ .

The literature search located very little relevant literature. However, a brief discussion of findings is given in Attachment 2.

## Conclusions

Similar results were observed for all contact tests with undiluted LP and 1.0N HNO<sub>3</sub>. Each of these substances sterilized the soil within the first hour of contact; no microorganisms were recovered after this. Similar results were also observed for the initial effects of short-term contact with diluted LP and 0.1N HNO<sub>3</sub>; both of these substances decreased the numbers of microorganisms present, but did not eliminate them. The long-term contact tests with the dilute LP and 0.1N HNO<sub>3</sub> showed some differences. All heterotrophic bacteria and actinomycetes in the diluted and undiluted LP long-term contact tests were killed. By contrast, the numbers of heterotrophic bacteria in the 0.1N HNO<sub>3</sub> long-term contact tests dropped by 2 to 3 orders of magnitude and then recovered. The numbers of actinomycetes dropped below detection, and then recovered nearly to initial levels.

The LP toxicity observed in this study is likely related to the low pH of the LP, possibly in combination with osmotic shock to the microbes, and perhaps to reactions between the HAN and the soil. These reactions resulted in a significant pH drop and the rapid oxidation of readily oxidizable soil, and perhaps, microbial components. Because of the generally lethal effects of low pH, measurement of soil pH at a spill site may be sufficient to indicate the severity of impacts on the soil microflora.

Removal or dilution of LP within the first 1 to 2 hr after the spill would mitigate impacts on soil microflora. Therefore, water is an effective flushing agent to quickly reduce LP concentrations in the soil. However, concentrations remaining may be sufficient to cause an immediate toxic effect on soil microbes. Results from short-term contact tests with diluted LP suggest that the soil microbes have the potential to recover from these immediate impacts. For this reason, removal or dilution of the LP as soon after a spill as possible, rather than waiting for rainfall or snowmelt to dilute the LP, is important.

Spilled LP may be neutralized by adding a base. However, since the extent of impact resulting from osmotic shock is not known, negative impacts from the spill may already have occurred, rendering neutralization efforts of little consequence.

## Attachment 1: Dialog Databases Searched

Databases examined included Energy, Science, and Technology (1974-Aug 1993), Federal Register (Jan 1988 - Aug 1993), Chem Abstracts Search (1967-1993), Biosis Previews (1969-1993), NTIS (1964-1993), Ei Compindex Plus (1970-1993), Oceanic Abstracts (1964-1993), Enviroline (1970-1993), Pollution

Abstracts (1970-1993), Aquatic Science Abstracts (1979-1993), PAIS International (1976-1993), CAB Abstracts (1972-1993), Geoarchive (1974-1993), CRIS/USDA (1993), Environmental Bibliography (1974-1993), EMBASE (EXCERTPA MEDICA)(1974-1993), DIALOG Sourceone (Sm) Engineering, Academic Index (1976-1993), Toxline (1965-1993), Newsearch, Geobase (1980-1993), Public Opinion Online (1940-1993), PTS Newsletter Database (1987-1993), BNA Daily News (1990-1993), Federal News Service (1991-1993), and Environment<sup>1</sup> Bibliography (1974-1993).

## **Attachment 2: Summary of Literature Reviewed**

Nitrate is important because of its impact on higher organisms. In mammals, microbial reduction of nitrate to nitrite may result in nitrite poisoning (Marais et al. 1988). Nitrite is also a precursor in the formation of carcinogenic N-nitroso compounds (Kunisaki and Hayashi 1979). Plants may be burned by concentrated nitrate fertilizer. As a whole, addition of nitrate tends to stimulate microbial growth. Nitrate serves as a source of nitrogen and can also be used as an alternate electron acceptor under anaerobic conditions. However, excessive nitrate inhibits nodulation of legumes by nitrogen-fixing bacteria (Yoshioka and Maruyama 1990) and reduces  $N_2O$  to  $N_2$  by soil microorganisms (Blackmer and Bremner 1978). Ammonium nitrate may inhibit the activity of denitrifying bacteria in soil (El-Shinnawi and Aboel-Naga 1981). Synergistic bactericidal activity was more effective when equimolar solutions of urea and ammonium nitrate were used against a variety of plant pathogenic bacteria (Veverka, Kádela, and Oliberius 1988). Nitrite also reduces the cellulolytic, xylanolytic, and total microbial populations in the rumen of cattle (Marais et al. 1988).

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# Appendix A

## Ion Chromatography of Liquid Propellants Using an Electrochemical Detector: Water Analysis<sup>1</sup>

---

### Introduction

#### Background

In order to characterize the environmental effects of Liquid Propellant/LP XM46 (LP), a method for reducing detection limits below levels currently achievable with titrametric methods for the components of LP, hydroxylammonium nitrate (HAN), and triethanolammonium nitrate (TEAN) in soil and water matrices was needed.

#### Objective

The objective of this study was to develop methods for analyzing LP, a homogeneous liquid composed of 60.8-percent HAN, 19.2-percent TEAN, and 20.0-percent water by weight having a density of 1.450 g/cc at 20 °C (Sasse 1990<sup>2</sup>). A method was needed that would separate and quantify HAN and TEAN in the presence of interfering ions such as nitrate.

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<sup>1</sup> By Donald W. Rathburn and Ann B. Strong, U.S. Army Engineer Waterways Experiment Station.

<sup>2</sup> See Reference at the end of the main text.

## Experimental Methods

### Ion chromatography

Ion chromatography (IC) was selected because of its specificity and ability to obtain low detection limits. The two major components of the IC system are the column and the detector. A new isocratic method using a cationic column which simultaneously analyzes monovalent/divalent cations and low molecular weight amines and alkanolamines was adapted for use (Waters Chromatography Division 1991). This column separated the HAN and TEAN components and eliminated the problem of high nitrate and other negative ions in the samples.

Past chromatography analyses used colorimetric or conductivity detectors. The problem with a colorimetric detector is that alkanolamines and HAN have no chromophores (chemical groups that produce color in compounds) in the ultra-violet or visible regions. Derivatization with compounds containing ultra-violet chromophores is possible, but the reagents available for derivatization are unreliable and prone to interferences. Chemically, HAN is a very reactive compound, and derivatization may be possible using a chromophoric ketone to form an oxime (Sasse 1990), but this would not work for TEAN.

Conductivity detectors are the most commonly used detectors for IC and applicable to compounds having ions with fairly high equivalent conductance. Both hydroxyamine and triethanolamine are weak conductors and are not good candidates for this type detection.

More recently, electrochemical detectors (ECD) using direct current or pulsed current have been adapted for use by IC, and this seemed to be a viable alternative to the traditional detectors for LP components. Interfering compounds which co-elute can be discriminated against through the proper selection of the cell potential. Because of the instability of alkanolamines at low pH and hydroxyamine at high pH, a method was developed that would accommodate the limitations of both compounds. A pulsed mode of operation was selected that would allow detection of the ions of interest yet maintain the integrity of the sample compounds.

### Analytical system

The IC system employed for separating and detecting HAN and TEAN consisted of a Waters Model 510 pump, Waters Model 717 Autosampler, Waters Post Column Reaction System, and the Waters Model 464 Pulsed Electrochemical Detector. The basis for the separation was a Waters IC-PAK Cation Exchange Column (No. 36570). A data system using a NEC Power Mate 386/25 was used for operational control of the system and for data storage and retrieval.

The eluant for the chromatographic system contained 5-percent methanol, 0.1-mM ethylenediaminetetraacetic acid, and 3-mM ultrex nitric acid per liter of solution. The post-column eluant was 0.3-M sodium hydroxide using carbon dioxide free water. Flow rates were 1.0 mL per minute for the chromatographic column and 0.2 mL per minute for the post-column.

All water was purified using a Milli-Q PLUS Reagent Grade Water System (Millipore Corporation, Bedford, MA). The mobile phase and post-column elution phase were vacuum filtered through a Millipore Type GV filter to remove particulates and to degas the solution.

The ECD system contained a gold electrode as the working electrode. The reference electrode was a 400-mM sodium hydroxide saturated sodium chloride/silver chloride electrode. The gold electrode was selected because of its resistance to electrolytic corrosion.

The following ECD settings were used:

|                          |                         |
|--------------------------|-------------------------|
| E1 100 mv                | T1 20 cycles 0.333 sec  |
| E2 880 mV                | T2 20 cycles 0.333 sec  |
| E3 -520 mv               | T3 10 cycles 0.333 sec  |
| I Range 0 - 10 microamps | Total pulse - 0.999 sec |

E1, E2, and E3 are the voltages applied to the eluant as it passed through the electrode cell. E1 is the voltage controlling the reduction of the analyte; E2 and E3 are voltages applied to maintain the electrode in a state of preparedness. T1, T2, and T3 are the times applied to the cells at E1, E2, and E3. I refers to the current range. Peak areas associated with each component were made automatically using the data station.

### Detector linearity

The linearity of the detector can be observed in Figures A1 and A2. Solutions containing 3-, 6-, 15-, 20-, and 34-ppm hydroxylammonium nitrate and 1-, 2-, 5-, 8-, and 10-ppm triethanolammonium nitrate were used for this study. The measured areas of the peaks are shown in Tables A1 and A2. A 25- $\mu$ L sample was injected.

A typical chromatogram of hydroxylamine and triethanolamine is shown in Figure A1. Retention times for hydroxylamine and triethanolamine were 3.33 min and 6.42 min, respectively. Retention time is sensitive to the pH of the eluant, and slight variations have an effect. The retention times of both compounds decrease as pH decreases.

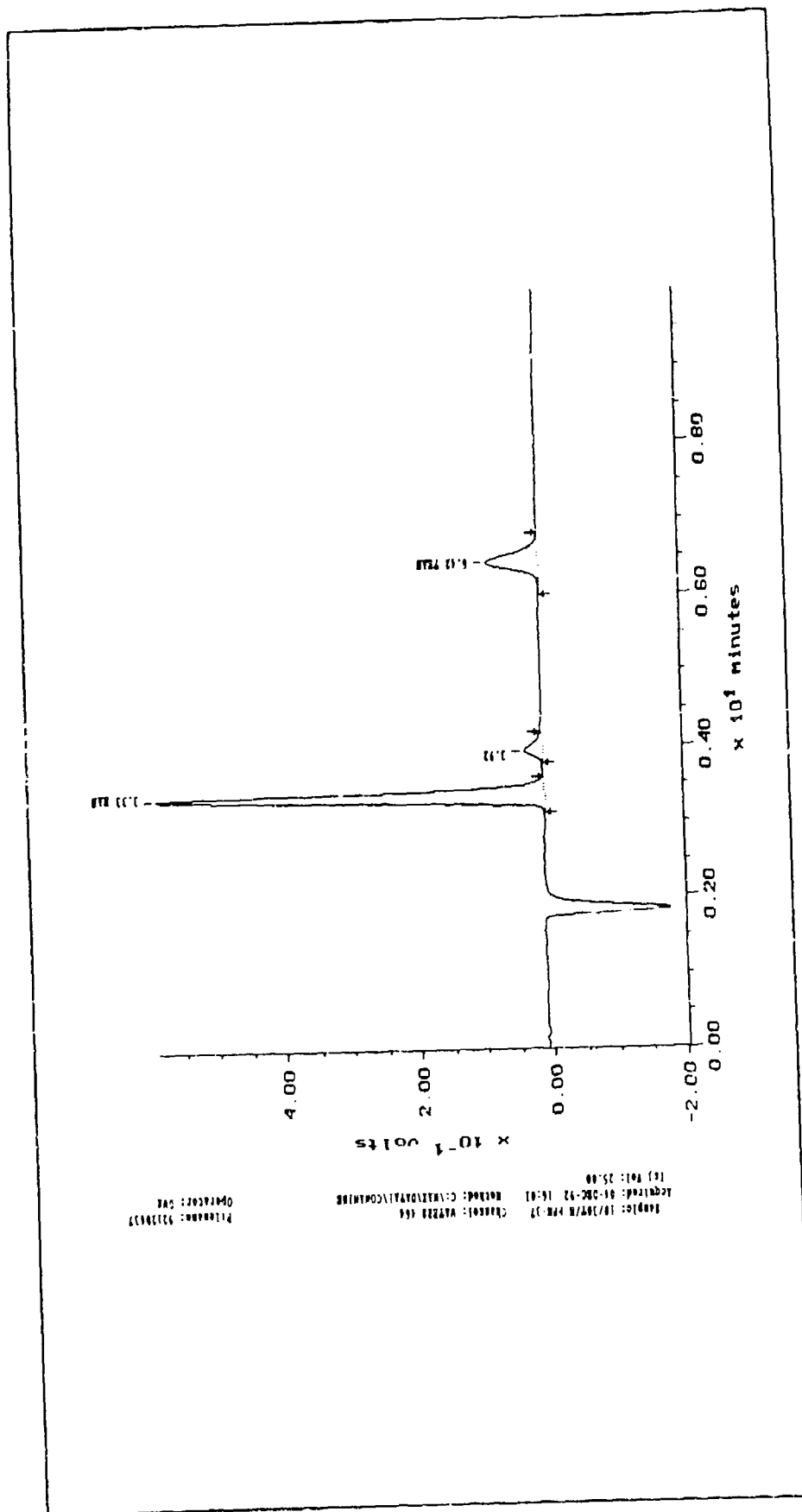


Figure A1. Chromatogram of hydroxylamine (30 ppm) and triethanolamine (10 ppm) generated by the ion chromatograph using an electrochemical detector

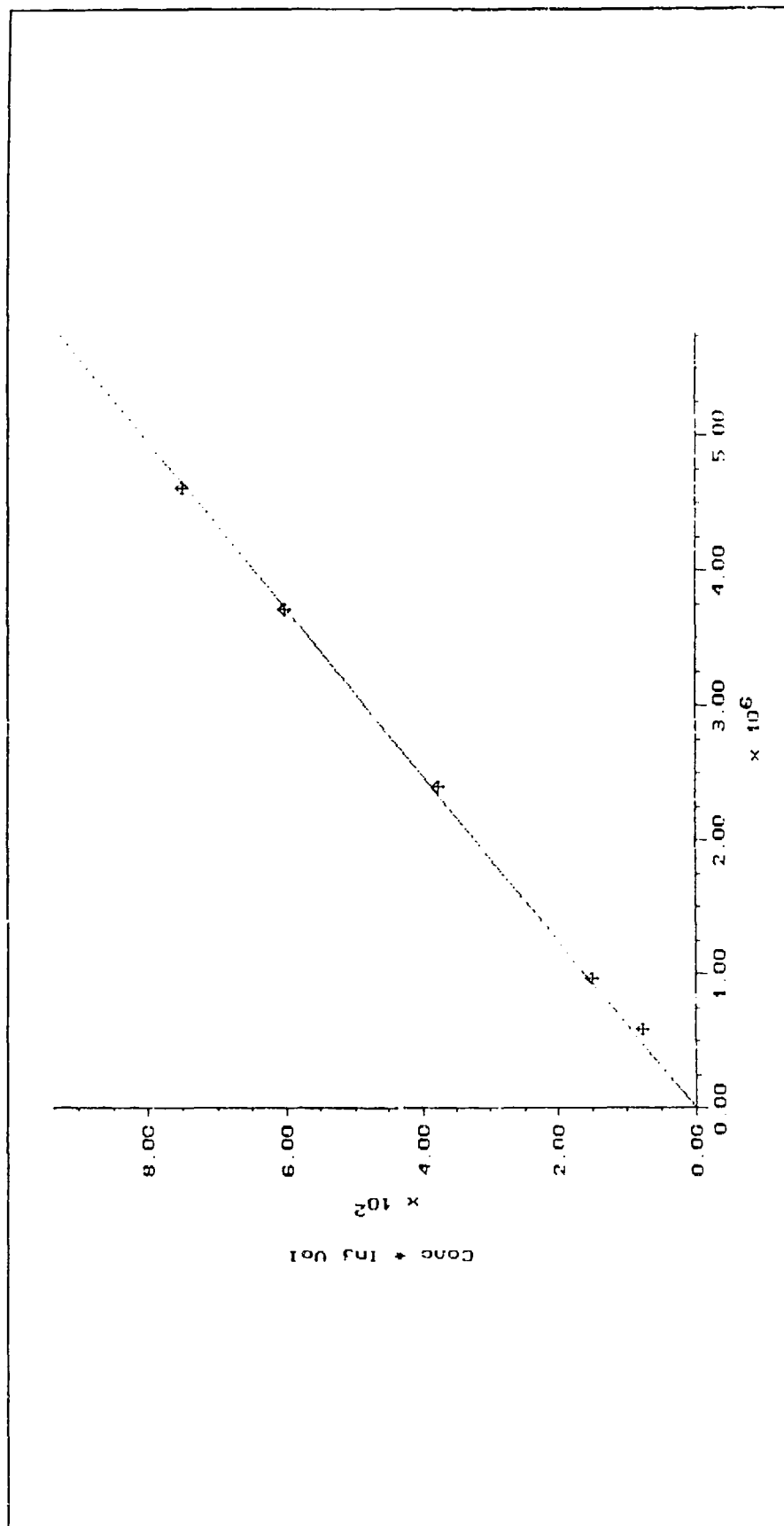


Figure A2. Calibration curve for hydroxylammonium nitrate from a 25- $\mu$ L injection

| Table A1<br>Peak Areas of Hydroxylammonium Nitrate |             |
|----------------------------------------------------|-------------|
| Concentration, ppm                                 | Area, uVSec |
| 3                                                  | 588,670     |
| 6                                                  | 969,370     |
| 15                                                 | 2,390,000   |
| 24                                                 | 3,704,000   |
| 30                                                 | 4,618,000   |

| Table A2<br>Peak Areas of Triethanolammonium Nitrate |             |
|------------------------------------------------------|-------------|
| Concentration, ppm                                   | Area, uVSec |
| 1                                                    | 100,000     |
| 2                                                    | 179,300     |
| 5                                                    | 516,500     |
| 6                                                    | 828,400     |
| 10                                                   | 1,042,000   |

### Limit of detection

The limits of detection were estimated by comparing peak height to the noise level. The peak height from a 120-ppb HAN solution was compared with the noise level at this concentration. Using three times the noise level as the limit of detection, a value of 20 ppb was determined for HAN. Using a 400-ppb solution for TEAN, the detection limit was 220 ppb.

### Reproducibility

The reproducibility of HAN and TEAN measurements was evaluated by measuring the peak areas from a repeated number of analyses at the same concentration. Results are presented in Table A3.

### Calibration standards

No standard analytical reference material is available for HAN and TEAN. The calibration standards were prepared from a previously analyzed LP sample as a reference source (Figure A3). Standards were prepared in plastic vials to minimize sources of positive ions that can damage the analytical column.

**Table A3**  
**Reproducibility Data for Hydroxylammonium Nitrate and**  
**Triethanolammonium Nitrate**

| Component, ppm | No. of Injections | Average Area, uVSec    | %RSD |
|----------------|-------------------|------------------------|------|
| HAN 3.0        | 19                | 976,797 $\pm$ 26,265   | 2.69 |
| HAN 5.0        | 20                | 2,093,082 $\pm$ 37,306 | 1.78 |
| TEAN 1.0       | 19                | 209,421 $\pm$ 14,056   | 6.71 |
| TEAN 5.0       | 20                | 465,403 $\pm$ 20,490   | 4.50 |

### Quality assurance/quality control (QA/QC)

The QA/QC for this study consisted of running samples in duplicates, preparing matrix spikes and matrix spike duplicates, and using a separate LP sample as a reference source. Matrix spikes were prepared from the reference sample.

### Conclusions

Ion chromatography using a cation column for separation coupled with an electrochemical detector was effective in analyzing HAN and TEAN. The system responds well to both hydroxylamine and triethanolamine with low levels of detection. Good separation of ions was achieved with no major chemical interferences.

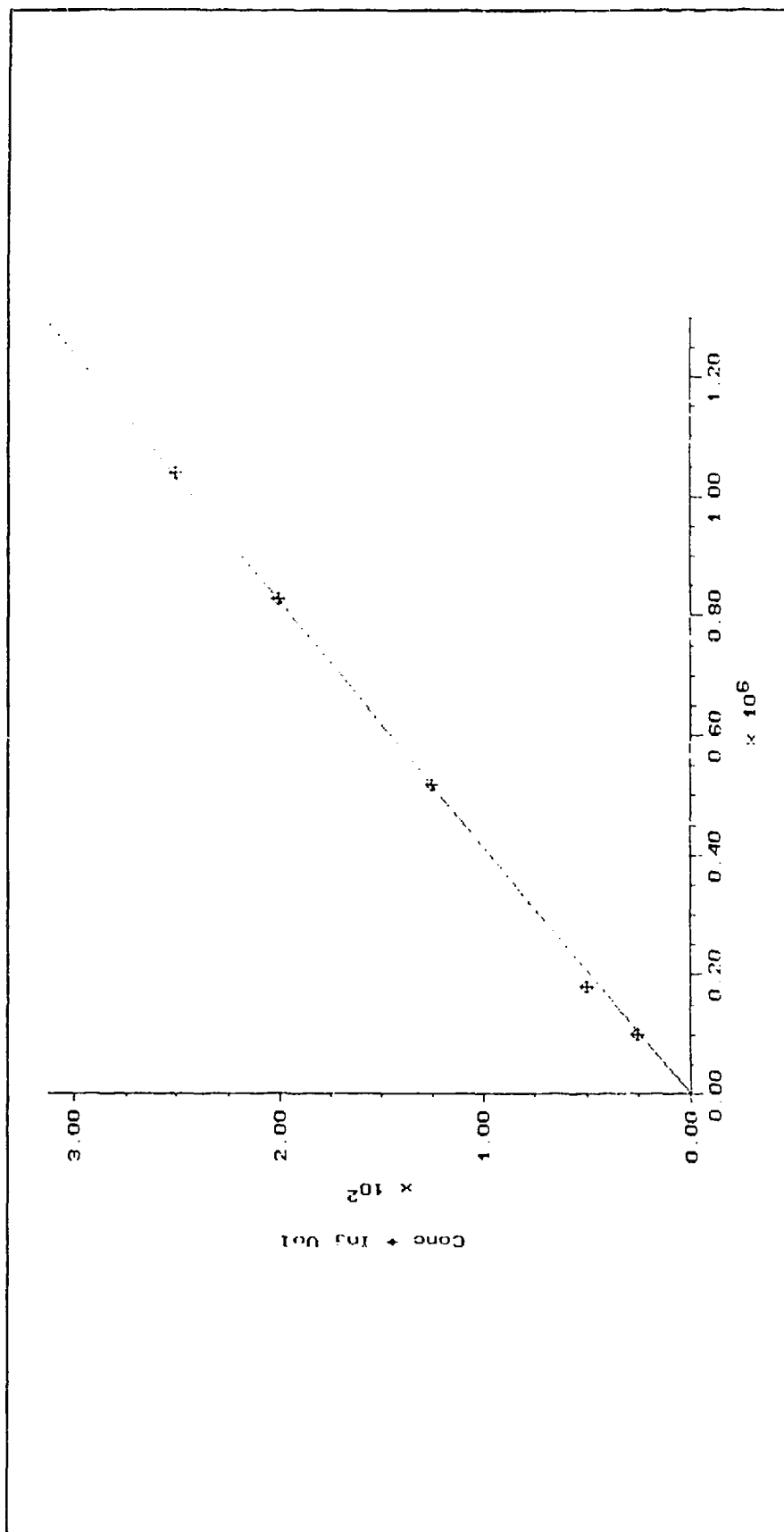


Figure A3. Calibration curve for triethanolammonium nitrate from a 25- $\mu$ L injection

# **Appendix B Ion Chromatography of Liquid Propellant Using an Electrochemical Detector: Soil Analysis<sup>1</sup>**

---

## **Introduction**

### **Background**

Liquid propellant (LP) contains three major ions: the hydroxylammonium cation, the triethanolammonium cation, and the nitrate anion. As an analytical indicator in soils, neither the nitrate ion nor the hydroxylammonium ion are good choices because both nitrate and ammonia are natural soil components and the hydroxylammonium ion is rapidly degraded in most soils. Thus, the triethanolammonium ion represents the best choice for analytically expressing the concentration of LP in soils.

Previous methods for the determination of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) in water were developed using ion chromatographic separation and electrochemical detection of the two major cations (Appendix A). This procedure is an extension of that methodology.

### **Objective**

The objective of this study was to develop a method of analysis for LP components in soils.

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<sup>1</sup> By Donald W. Rathburn and Ann E. Strong, U.S. Army Engineer Waterways Experiment Station.

## Experimental Methods

### Soil extraction:

The following extraction procedures were investigated.

- a. Neutral extraction with 5-percent methanol.
- b. Acid extraction with hydrochloric acid.
- c. Soxhlet extraction with hexane and sodium sulfate.
- d. Basic extraction with sodium hydroxide in 5-percent methanol.

Only the basic extraction procedure yielded acceptable recovery values of 80-percent or better for the triethanolammonium ion component of TEAN. The extracting liquid is a basic solution of 5-percent methanol in water (v/v) and is compatible with the liquid chromatography eluent, thus eliminating the need for solvent change. The concentration of sodium hydroxide is minimized to decrease the possibility of damage to the ion exchange column in the ion chromatograph (IC) system.

### Chemicals

The LP was employed in the early phases of this project for preparing standards and spiking solutions. However, the purity of the propellant, especially the HAN component, became suspect as the ratio of HAN to TEAN began to fluctuate over time. Thus, the use of analytical grade triethanolamine and hydroxylamine hydrochloride replaced LP as calibration standards for the cations of TEAN and HAN. Monoethanolamine, diethanolamine, and triethanolamine were purchased from Aldrich Chemical Company (Milwaukee, WI). The hydroxylamine hydrochloride was purchased from J. T. Baker, Inc. (Phillipsburg, NJ). Ammonium nitrate was from Fisher Scientific Company (Pittsburgh, PA).

All water was purified using a Milli-Q PLUS Reagent Grade Water System (Millipore Corporation, Bedford, MA).

### Preparation of standards

All solutions were prepared by diluting compounds of interest to 10 mL: hydroxylamine hydrochloride - 0.54 g/10 mL; ammonium nitrate - 0.91 g/10 mL; monoethanolamine and diethanolamine - 0.20 g/10 mL; and triethanolamine - 2.01 g/10 mL.

The above solutions were used for preparing standard curves and spiking soil samples. Standard curves were prepared with lower limits of 1 ppm for HAN and TEAN, and 0.1 ppm for ammonia, monoethanolamine, and diethanolamine. Upper limits varied from 10 to 50 ppm for HAN and TEAN, depending upon the concentration range of interest in the environmental studies.

### **Ion chromatography**

The IC system consisted of a Waters Model 510 pump, Waters Model 717 Autosampler, Waters Post Column Reactor System, and the Waters Model 464 Pulsed Electrochemical Detector (ECD). The basis for the separation was a Waters IC-PAK Cation Exchange Column (No. 36570). A data system using a NEC Power Mate 386/25 was used for operational control of the system and for data storage and retrieval.

The eluant for the chromatographic system contained 5-percent methanol, 0.1-mM ethylenediaminetetraacetic acid, and 3-mM ultrex nitric acid per liter of solution. The post-column eluant was 0.3-M sodium hydroxide using carbon dioxide free water. Flow rates were 1.0 mL per minute for the chromatographic column and 0.2-mL per minute for the post-column eluant. Injection volume was normally 25  $\mu$ L.

The ECD system contained a gold electrode as the working electrode. The reference electrode was a 400-mM sodium hydroxide saturated sodium chloride/silver chloride electrode equipped with a Teflon frit.

The following ECD settings were used: E1 = 100 mv, T1 = 20 cycles 0.333 sec, E2 = 880 mv, T2 = 20 cycles 0.333 sec, E3 = -520 mv, T3 = 20 cycles 0.333 sec, Total pulse = 0.999 sec and I range = 0 - 10 microamps.

### **Extraction procedure**

The ratio of extracting solvent to soil was 6:1 (mL/g). Plastic centrifuge tubes with caps were used for extraction. Extraction steps were as follows:

- a. A soil sample weighing between 500 to 1,000 mg was placed into a plastic centrifuge tube.
- b. An appropriate volume (6:1 mL/g) extracting liquid was added to the soil sample in the tube.
- c. The soil and extraction liquid were thoroughly mixed on a vortex-mixer.
- d. The NaOH (100  $\mu$ L of 0.3 N) was added to the tube and the components vortex-mixed.

- e. The pH was checked using indicator strips. If the pH were less than 11, an additional 100  $\mu$ L of NaOH was added and the vortex-mixing repeated. This procedure was repeated until the pH remained 11 or above.
- f. The tubes were placed on a mechanical shaker and agitated for 1 hr.
- g. The tubes were removed and placed in a table-top centrifuge for 5 min. at maximum revolutions per minute.
- h. The supernatant was filtered through a 5.0- $\mu$  and 0.45- $\mu$  filter using a 10-cc plastic syringe.
- i. The samples were diluted, if necessary, at this point.
- j. The samples were analyzed using IC-ECD. Injection volume was normally 25  $\mu$ L.
- k. Chromatographic run times were 15 min to ensure elution of all ions from the column.

## Results

Multiple samples of several soil types were spiked at various concentrations of hydroxylamine and triethanolamine proportioned as in LP. Table B1 presents the recoveries of triethanolammonium cation (as TEAN).

study of detection limits was made using the WES Reference soil. The TEAN peak height was compared with the baseline noise, assuming the detection limit to be 10 times the baseline noise. The limit of detection by peak height was 4 mg/kg. However, because of negative peaks and drifting baseline problems, 100 mg/kg probably represents a working detection limit under these conditions.

## Discussion

Figure B1 is a chromatogram of the five cations used or anticipated to be found in this study. Although the monoethanolammonium and diethanolammonium cations were anticipated, they were never observed in large amounts. The ammonium ion was always present, even in the unspiked samples, probably as a contaminant in the soil or laboratory water. Comparisons of Figures B2, B3, B4, and B5 showed very little ammonium from Cement 157 and Picatinny B; while with Socorro P and WES Reference, the ammonium ion increased.

| <b>Table B1</b><br><b>TEAN Recovery <math>\pm</math> Standard Error</b> |                                               |                                            |                    |
|-------------------------------------------------------------------------|-----------------------------------------------|--------------------------------------------|--------------------|
| <b>Soil</b>                                                             | <b>Spike Amount, <math>\mu\text{g}</math></b> | <b>Recovered, <math>\mu\text{g}</math></b> | <b>Recovery, %</b> |
| Yuma 2A                                                                 | 85                                            | $82 \pm 6$                                 | 97                 |
| Picatinny A                                                             | 85                                            | $81 \pm 4$                                 | 95                 |
| BRL-SAS A                                                               | 85                                            | $71 \pm 1$                                 | 84                 |
| China Lake A                                                            | 95                                            | $75 \pm 1$                                 | 79                 |
| Cement 157                                                              | 95                                            | $89 \pm 1$                                 | 94                 |
| Cement 158 F                                                            | 95                                            | $91 \pm 1$                                 | 96                 |
| WES Reference                                                           | 95                                            | $93 \pm 1$                                 | 98                 |
| BRL-SAS B                                                               | 95                                            | $97 \pm 1$                                 | 102                |
| Socorro P                                                               | 95                                            | $79 \pm 4$                                 | 83                 |
| Picatinny B                                                             | 95                                            | $87 \pm 1$                                 | 92                 |
| Yuma 2A                                                                 | 8,500                                         | $8,880 \pm 720$                            | 104                |
| Picatinny A                                                             | 8,500                                         | $8,420 \pm 800$                            | 99                 |
| BRL-SAS A                                                               | 8,500                                         | $6,910 \pm 450$                            | 81                 |

The failure to routinely extract HAN cannot be clearly explained. The HAN is probably reacting with a soil constituent. Certain soils do not completely degrade HAN (Figure B2). In other cases, HAN is almost totally absent (Figures B3, B4, and B5).

During the IC analysis of soils, strong negative peaks appeared often in the chromatograms. Figure B2 has a large negative peak at approximately 8.7 min. This peak was frequent, but reproducibility for all negative peaks was poor, probably because of the heterogeneous nature of the soil. Occasionally, a broad negative peak was observed from 1.5 to 6 min. (Figure B5). Thus, the time for analysis was extended to 15 min, 10 min normally being adequate for water samples (Appendix A). No effort was made to identify these negative peaks.

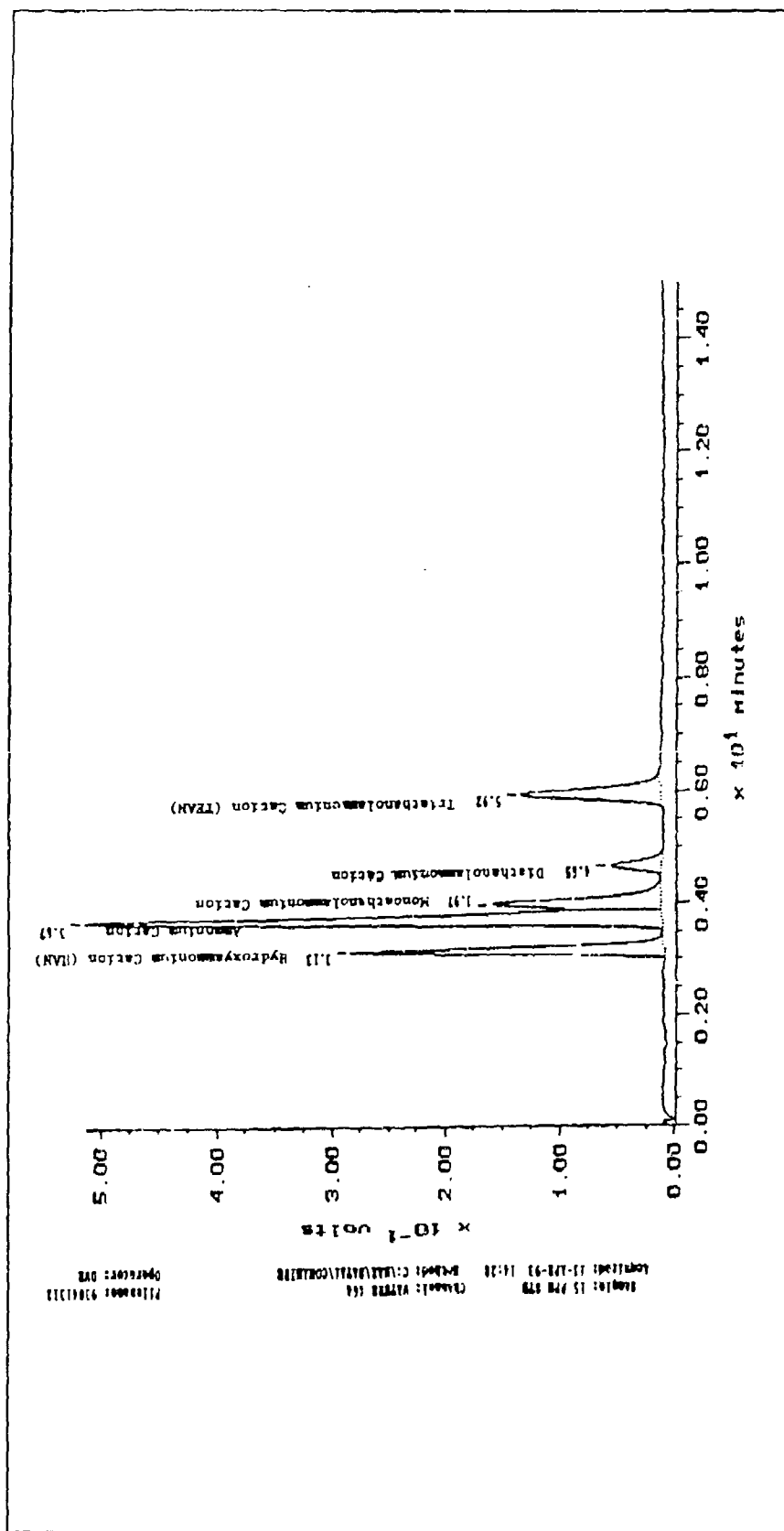


Figure B1. Chromatogram of cations in LP by ion chromatography

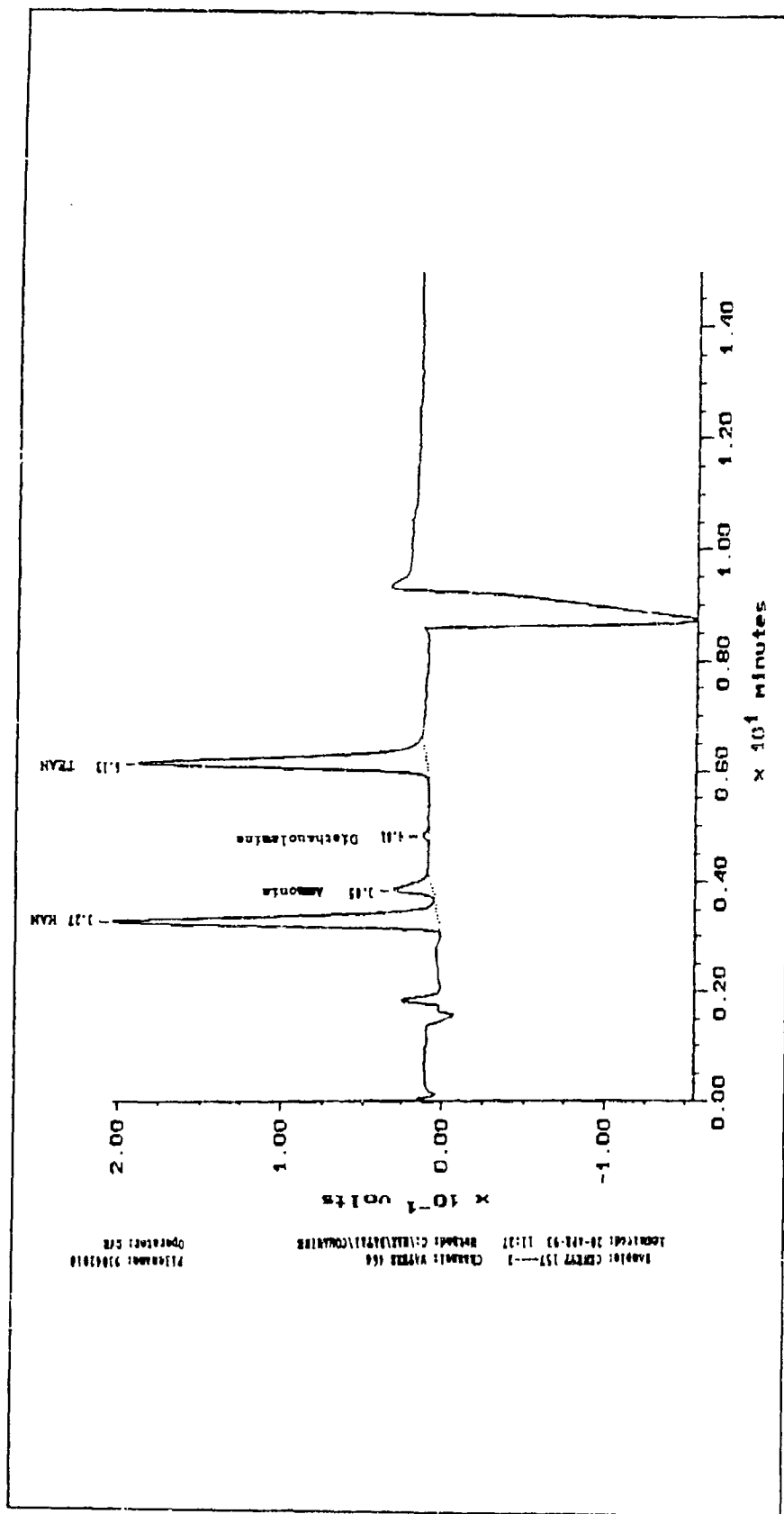


Figure B2. Chromatogram of LP components extracted from cement 157

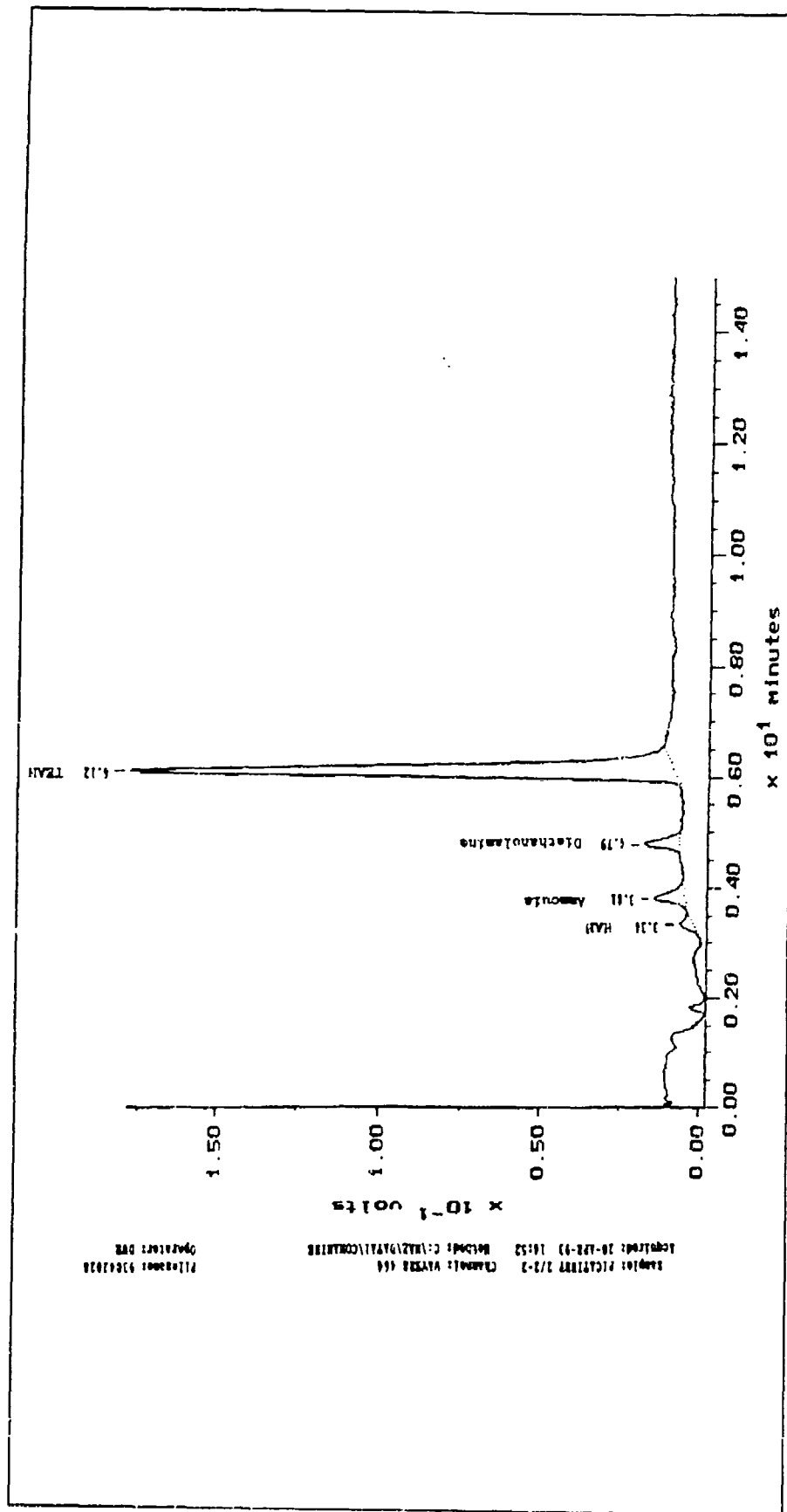


Figure B3. Chromatogram of LP components extracted from Picatinny B soil

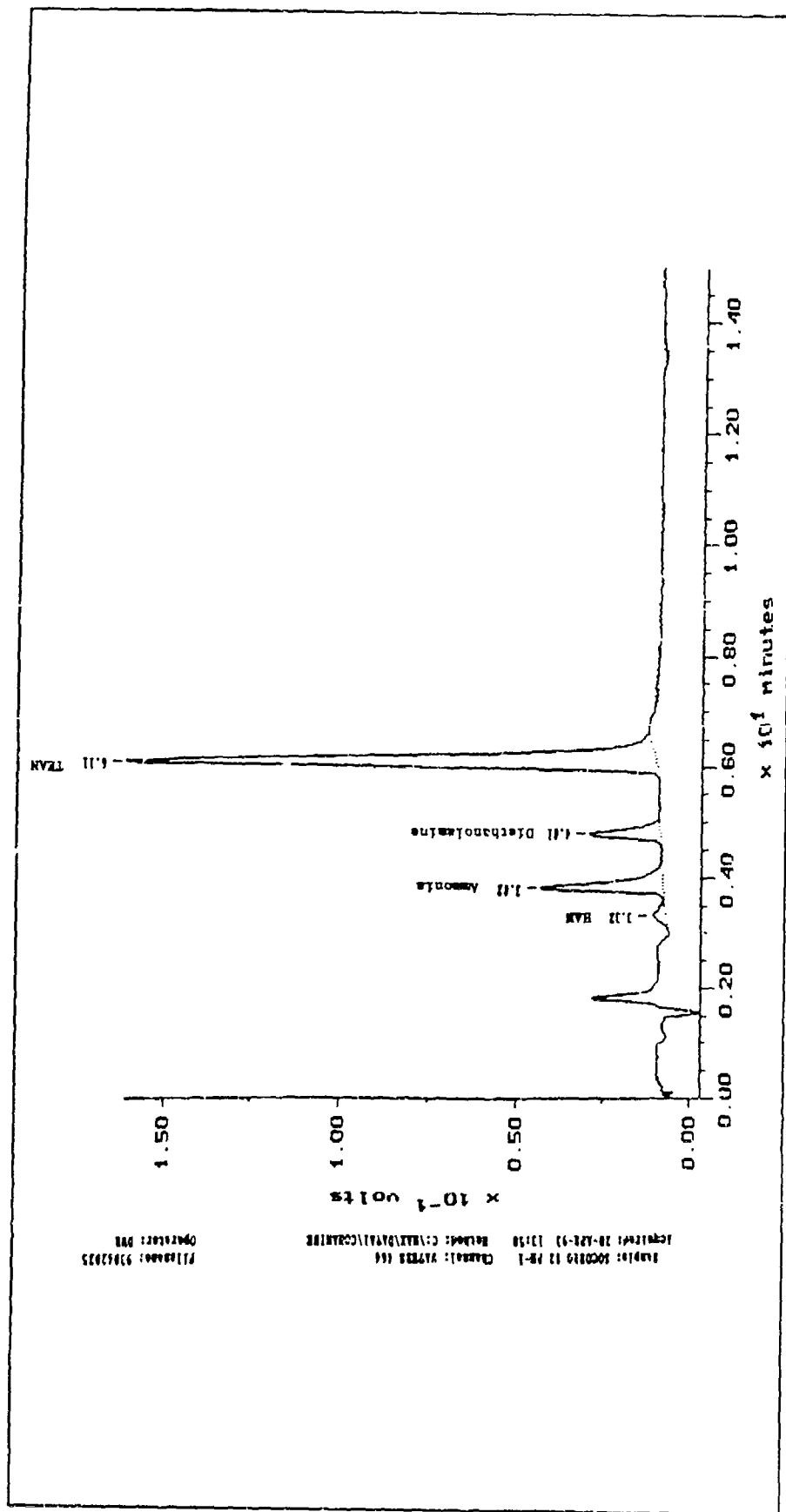


Figure B4. Chromatogram of LP components extracted from Socorro P soil

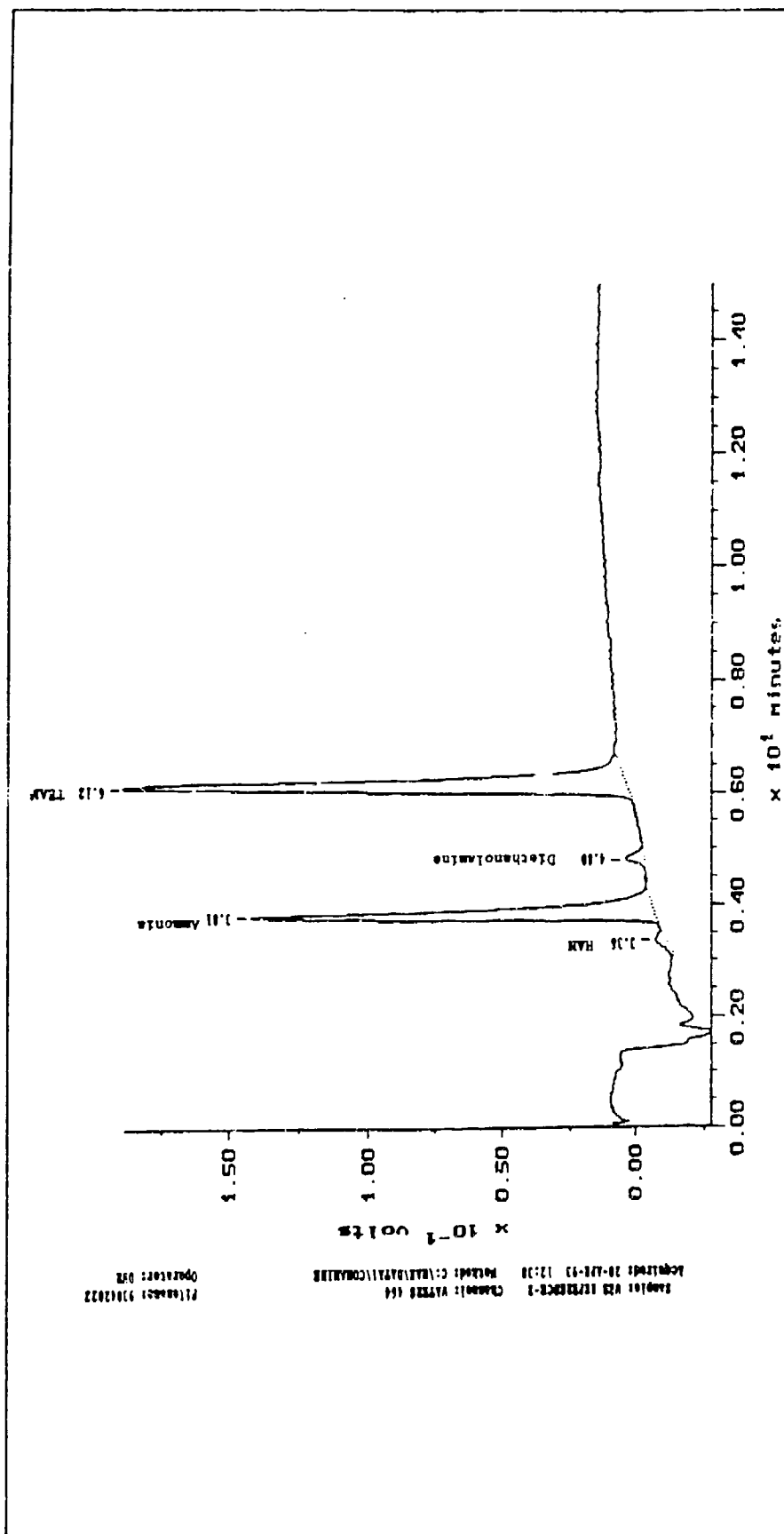


Figure B5. Chromatogram of LP components extracted from WES Reference soil

# Appendix C

## Notations

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### Abbreviations

|                                     |                                                       |
|-------------------------------------|-------------------------------------------------------|
| %OC                                 | Percent organic carbon                                |
| 2, 4-DNT                            | 2, 4-dinitrotoluene                                   |
| 2, 6-DNT                            | 2, 6-dinitrotoluene                                   |
| 4 ADNT                              | 4-amino-2, 6-dinitrotoluene                           |
| Al                                  | Aluminum                                              |
| AODC                                | Acridine orange direct count                          |
| ATR                                 | Attenuated total internal reflectance                 |
| Ca                                  | Calcium                                               |
| CEC                                 | Cation exchange capacity                              |
| CFU                                 | Colony forming unit                                   |
| CO                                  | Carbon monoxide                                       |
| CO <sub>2</sub>                     | Carbon dioxide                                        |
| DAPI                                | diamidino-2-phenyl-indole                             |
| DNB                                 | 1, 3-dinitrobenzene                                   |
| Fe                                  | Iron                                                  |
| FTIR                                | Fourier Transform Infrared Spectroscopy               |
| GA                                  | Glycerol agar                                         |
| GLC                                 | Gas Liquid Chromatography                             |
| HA                                  | Hydroxylamine                                         |
| HAN                                 | Hydroxylammonium nitrate                              |
| HMX                                 | 1, 3, 5, 7-tetranitrooctahydro-1, 3, 5, 7-tetrazoline |
| HNO <sub>3</sub>                    | Nitric acid                                           |
| IRE                                 | Internal reflectance element                          |
| LP                                  | Liquid popellant/LP XM46                              |
| Mn                                  | Manganese                                             |
| NO <sub>3</sub> -N                  | Nitrate nitrogen                                      |
| NO <sub>3</sub> /NO <sub>2</sub> -N | Nitrate/nitrite nitrogen                              |
| NO <sub>2</sub> -N                  | Nitrite nitrogen                                      |
| NH <sub>3</sub> -N                  | Ammonia nitrogen                                      |
| N <sub>2</sub> O                    | Nitrous oxide                                         |
| NO <sub>2</sub>                     | Nitrogen dioxide                                      |
| NO                                  | Nitric oxide                                          |

|                |                                                |
|----------------|------------------------------------------------|
| N <sub>2</sub> | Nitrogen                                       |
| O <sub>2</sub> | Oxygen                                         |
| ODW            | Oven dry weight                                |
| ON             | Organic nitrogen                               |
| PBS            | Phosphate-buffered soils                       |
| PDA            | Potato dextrose agar                           |
| PTYG           | Peptone-tryptone-yeast extract glucose agar    |
| RDX            | 1, 3, 5- trinitro -1, 3-, 5- hexahydrotriazine |
| STP            | Standard Temperature and pressure (1-10)       |
| TEA            | Triethanolamine                                |
| TEAN           | Triethanolammonium nitrate                     |
| TKN            | Total Kjeldahl nitrogen                        |
| TOC            | Total organic carbon                           |
| TNB            | 1, 3, 5-trinitrobenzene                        |
| TNT            | 2, 4, 6-trinitrotoluene                        |
| RO             | Reverse osmosis                                |

## Symbols

|                      |                                                                                              |
|----------------------|----------------------------------------------------------------------------------------------|
| <i>a</i>             | dimensionless constant                                                                       |
| <i>A</i>             | pore area, cm <sup>2</sup>                                                                   |
| <i>b</i>             | Langmuir constant related to entropy, L/mg                                                   |
| <i>B</i>             | depth of flow, cm                                                                            |
| <i>c</i>             | constant, area/time                                                                          |
| <i>C</i>             | equilibrium solution concentration                                                           |
| <i>C<sub>D</sub></i> | drag coefficient, dimensionless                                                              |
| <i>C(L,T)</i>        | concentration at location ( <i>L</i> '), time ( <i>T</i> ), mg/L                             |
| <i>C<sub>o</sub></i> | input concentration, mg/L                                                                    |
| <i>d</i>             | soil particle size, cm                                                                       |
| <i>d<sub>p</sub></i> | mean particle size, cm                                                                       |
| <i>D</i>             | dispersion coefficient, cm <sup>2</sup> /s                                                   |
| ERFC                 | complementary error function of                                                              |
| EXP                  | exponential function of                                                                      |
| FOC                  | fraction of organic carbon                                                                   |
| <i>g</i>             | acceleration of gravity, cm/s <sup>2</sup>                                                   |
| <i>G</i>             | grass density, stalks per unit area                                                          |
| <i>I</i>             | hydraulic gradient, dimensionless                                                            |
| <i>k'</i>            | first order reaction rate, s <sup>-1</sup>                                                   |
| <i>k</i>             | constant, area/time                                                                          |
| <i>K</i>             | coefficient of hydraulic conductivity, cm/s                                                  |
| <i>K'</i>            | proportionality coefficient, dimensionless                                                   |
| <i>K<sub>d</sub></i> | adsorption distribution coefficient, cm <sup>3</sup> /g                                      |
| <i>K<sub>f</sub></i> | adsorption coefficient for Freundlich equation<br>mg <sup>(n-1)</sup> × L <sup>1/n</sup> /kg |
| <i>K<sub>s</sub></i> | bulk modulus of expansion, dimensionless                                                     |
| <i>L'</i>            | distance, cm                                                                                 |

|              |                                                                         |
|--------------|-------------------------------------------------------------------------|
| $L'/V^{1/3}$ | difference between measured runoff function value,<br>dimensionless     |
| $m$          | dimensionless constant                                                  |
| $M$          | mass input, mg                                                          |
| $n'$         | Freundlich characteristic constant                                      |
| $n$          | porosity, dimensionless                                                 |
| $N$          | number of revolutions of centrifuge per minute                          |
| $N_{Re}$     | Reynolds number, dimensionless                                          |
| $Q$          | monolayer sorption capacity (mg/kg)                                     |
| $q$          | solid phase concentration, mg/kg                                        |
| $r^2$        | correlation coefficient, dimensionless                                  |
| $r$          | Pearson Product-Moment Correlation Coefficient,<br>dimensionless        |
| $R_1$        | distance from centrifuge spindle to deposition surface of<br>centrifuge |
| $R_2$        | distance from centrifuge spindle to deposition surface of<br>centrifuge |
| $R$          | retardation coefficient, dimensionless                                  |
| $t, t_a$     | application time of the fluid, s                                        |
| $t_c$        | centrifuge time, min                                                    |
| $T$          | time, s                                                                 |
| $T$          | pore volumes eluted, dimensionless                                      |
| $U$          | average velocity of flow, cm/s                                          |
| $v$          | average pore water velocity, cm/s                                       |
| $V$          | volume of fluid applied to soil, cm <sup>3</sup>                        |
| $y_i$        | distance wetting front is below ground surface, cm                      |
| $Y_i$        | vertical distance from soil surface to deepest wetting front,<br>cm     |
| $Z$          | volume of water infiltrated per unit length, cm <sup>3</sup> /cm        |
| $\rho$       | fluid density, g/cm <sup>3</sup>                                        |
| $\mu$        | fluid viscosity, g/cm-s                                                 |
| $\epsilon$   | the slope of the ground surface, radians                                |
| $\alpha$     | hydraulic friction law, m <sup>1-b</sup> /day                           |
| $\beta$      | hydraulic friction law exponent                                         |
| $\theta_i$   | slope of the water                                                      |
| $\eta$       | constant for the equation $C_D = \eta/N_{Re}$                           |
| $\tau$       | time since start of flooding, s                                         |
| $\beta_s$    | soil expansivity, dimensionless                                         |
| $\rho_b$     | bulk density, g/cm <sup>3</sup>                                         |
| $\sigma$     | surface tension of the fluid, g/s <sup>2</sup>                          |
| $*$          | any function                                                            |

# REPORT DOCUMENTATION PAGE

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