



Preliminary Assessment of Soil Remediation Technologies for Application to Liquid Propellant XM46-Contaminated Soils

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Preliminary Assessment of Soil Remediation Technologies for Application to Liquid Propellant XM46-Contaminated Soils

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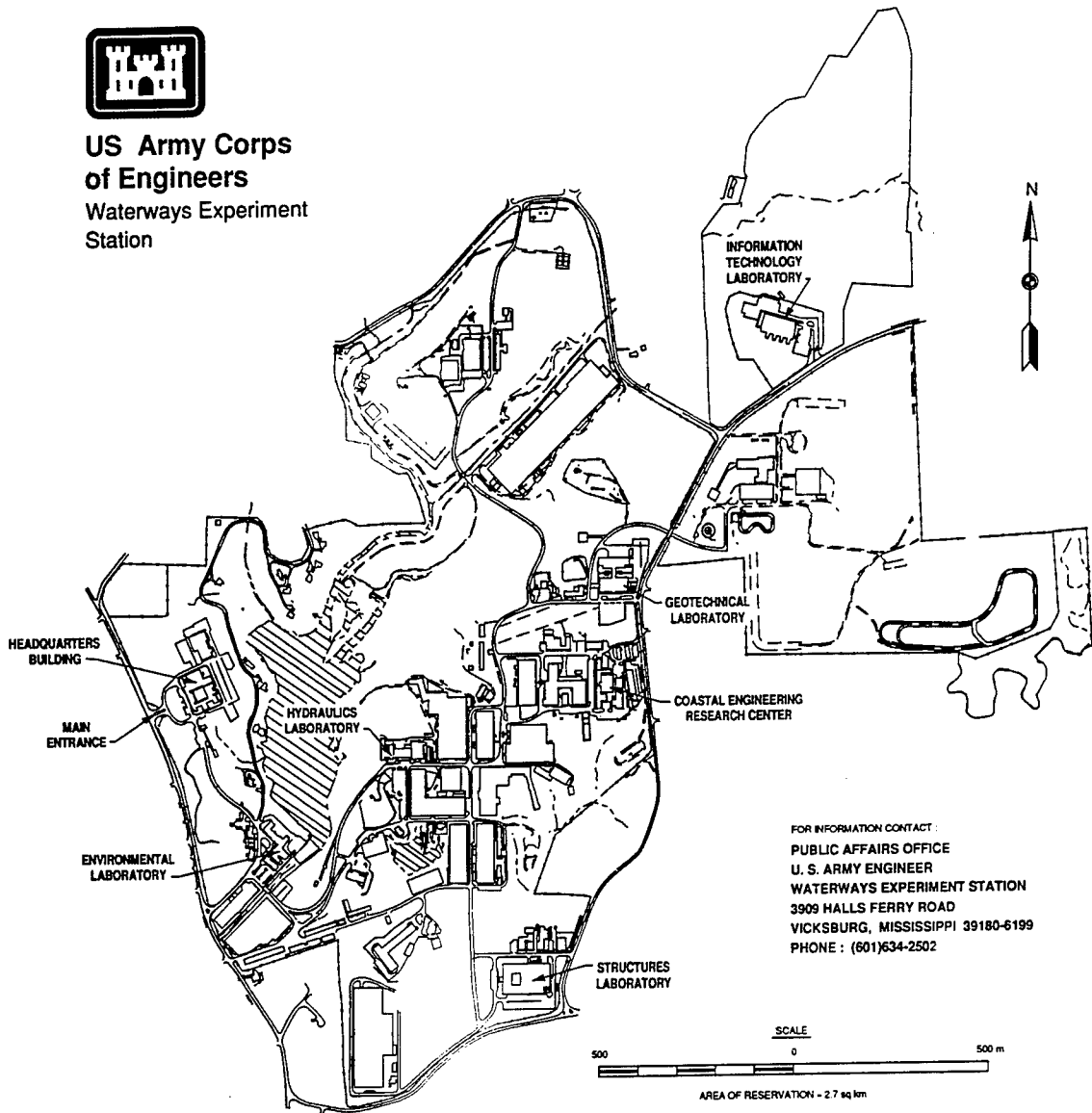
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Preface

The studies reported herein were conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS, in association with Dr. Donald D. Adrian, Department of Civil and Environmental Engineering, Louisiana State University, Baton Rouge, LA, Mr. Dan Townsend, student contractor, North Carolina State University, Raleigh, NC, Dr. Jimmie C. Oxley, University of Rhode Island, Kingston, RI, and Arthur D. Little, Inc., Acorn Park, Cambridge, MA. The research was sponsored by the Office of Program Manager, Crusader, SFAE-FAS-CR-M Bldg 3159, Picatinny Arsenal, NJ.

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Conversion Factors, Non-SI to SI Units of Measurement

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

Multiply	By	To Obtain
cubic yards	0.7645549	cubic meters
feet	0.3048	meters
gallons (U.S. liquid)	3.785412	liters
inches	2.54	centimeters
pounds (force)	4.448222	newtons

Summary

Commitment to development of an environmentally responsible handling protocol for the new generation liquid propellant XM46 (LP) lead the Crusader Program to the development of spill response guidance for installations and activities handling the propellant. A spill response guidance document was prepared by Arthur D. Little, Inc., under U.S. Army Engineer Waterways Experiment Station (WES) contract. The guidance document was based on technical research performed at WES describing LP interactions with soils in the event of a spill. This report extends the existing database to technologies for remediation of soils contaminated with LP and fills data gaps from the original technical study.

Section I examines the applicability of several remediation technologies to LP-contaminated soils. Section II describes experiments conducted to assess soil washing effectiveness. Section III is a review of recent pertinent literature on bioremediation of LP and LP components. Section IV provides the engineering data needed to evaluate the potential for nitrate loading to groundwater from LP-contaminated soil. Section V extends gas evolution data obtained in earlier studies. The following is a summary of each section.

Results of previous studies indicated that the greatest potential for environmental hazards from LP-contaminated soils were high soil pH, leaching of nitrate to groundwater, and soil sterilization. These results in combination with chemical properties of LP suggested several potential soil remediation methods which are discussed in Section I. These include soil washing, bioremediation, and enhanced natural attenuation. The most promising of these is dependent upon location and circumstances of the spill, e.g., spill volume, permeability of soil, and distance to local receptors.

Results reported in Section II demonstrated that soil washing is an effective procedure for removing HAN and TEAN from LP-contaminated soils. A single wash column was not capable of completely eliminating carryover of fine solids that may carry sorbed LP components; therefore, a series of at least two successive columns is recommended. The volume of wash water required depends upon soil properties, but can be estimated from results and equations presented herein. For the soils tested, wash water volumes ranged from 10 to 50 l/kg of soil. Total volume can be reduced by filtering and

recycling the water back through the system. One potential limitation is disposal of wash water, which may be high in nitrate.

The literature review reported in Section III indicated that bioremediation of LP-contaminated soils offers some potential. Careful consideration must be given to LP concentration, since high levels of LP are toxic to microflora. Biotreatment systems will very likely require pH adjustment to accommodate the microflora, since the pH of soils is significantly lowered by LP contamination.

Results of studies on nitrate leachate levels given in Section IV indicated that spills to sandy soils pose a greater potential hazard to groundwater than spills to less permeable soils. The mass loading of nitrate averaged 0.078 g NO_2 plus NO_3 nitrogen per gram of LP spilled and varied little with soil type. Although soil pH dropped initially, pH rose to 6 or greater after 2 to 3 pore volumes of water were eluted. At high pH (6 or greater), adsorption of the nitrate ion is insignificant. Therefore, nitrate movement away from an LP spill is expected to vary with the velocity of the soil water in the vadose zone and with the velocity of the groundwater in the aquifer.

Application of a mathematical model for determining the maximum concentration of NO_2 plus NO_3 nitrogen directly beneath an LP spill exhibiting little surface runoff of LP indicated that the concentration is directly proportional to the mass of the spill and decreases with vertical distance from the soil surface. With worst case assumptions (spill of a drum of LP, 208.3 kg, onto a sandy soil having a water table depth of 10 m), the maximum concentration of NO_2 plus NO_3 nitrogen that could reach the water table would exceed the drinking water standard of 10 mg/l. Models are presented to describe migration patterns and concentrations of NO_2 plus NO_3 nitrogen in various spill scenarios. Results of model applications are that concentrations in an aquifer decrease rapidly with mixing, a bimodal distribution of nitrate ion in the aquifer is typical, and aquifer boundaries exert little effect on the distribution of nitrate ion.

An important conclusion of the various model scenarios, which are presented as an appendix, is that vigorous intervention and remediation efforts should be implemented as soon as practical after an LP spill. Immediate excavation of the soil contaminated by LP to interrupt migration is warranted when spill volume is significant. Even if spill response is late, the soil should be removed, since it may remain a reservoir that feeds nitrate to the groundwater aquifer for a significant period of time. As an interim response, an impermeable barrier can be placed on the spill site to reduce the supply of infiltrating rainwater. In the event of major contamination to groundwater, pump and treat remediation should be initiated as soon as practical to restrict the spread of nitrate and minimize the volume of water that must be removed. If contamination is slight, natural mixing may preclude intervention. This can be confirmed by groundwater monitoring for nitrate/nitrite.

Results of additional studies on gas formed when LP interacts with soils are reported in Section V. Results confirm results of earlier studies that

identified the following gases that evolved as LP interacts with soil: N_2 , O_2 , (attributed to ambient air present in the test chamber), CO_2 , and N_2O . No noxious NO_x compounds were detected. Total volume of gas produced was positively correlated ($R^2 = 0.92$, $P = 0.03$) with total inorganic carbon in the soils. Therefore, acid hydrolysis of carbonates by LP is a likely source of the CO_2 generated. A hazard of high CO_2 generation may exist if LP is spilled onto high carbonate soils in a confined space.

Section I

Evaluation of Available Technologies for Remediation of Liquid Propellant Spills

1 Introduction

Studies of liquid propellant (LP) interactions with the environment were reviewed, evaluated, and summarized to assess potential LP spill remediation technologies. Guidance was provided to the U.S. Army Engineer Waterways Experiment Station (WES) on what technologies might be most suitable for remediation of LP spilled to the environment, focusing specifically on the evaluation of the three most promising technologies (biodegradation, natural attenuation, and soil washing). The scope of this project was focused on remediation of LP spills to soils, including minimization of LP impacts to groundwater. The objective of the study was to help steer future LP remediation research efforts towards the most viable remediation technologies.

Under Delivery Order No. 7 (DO 7) of Contract No. DACA 39-92-D-0014 with WES, Arthur D. Little, Inc., has been contracted to provide "Site Support and Spill Remediation of Liquid Propellant (LP) XM46." The work to be conducted for this Delivery Order was broken down into two separate tasks: Task 1 was entitled "Support for Development of Site Specific Spill Response Plans"; Task 2 was entitled "Evaluation of Available Technologies for Remediation of LP Spills."

Section I of this report presents the results of the DO 7 - Task 2 activities, which were conducted in accordance with the 27 January 1995 scope of work received from WES. The Task 1 Deliverable was submitted to WES under separate cover and is not included in this report.

Purpose and Scope

The purpose of the DO 7 - Task 2 activities was to review, evaluate, and summarize the results of past research conducted by others on LP interactions with the environment and LP spill remediation technologies. The results of this review should help identify any perceived data gaps to be addressed prior to identification of a preferred remedial technology. The 27 January 1995 scope of work prepared by WES also requested that guidance be provided to WES on what technologies might be most suitable for remediation of LP spilled to the environment, and what additional data might facilitate the selection and implementation of an LP spill remediation technology. An additional

purpose listed in the Task 2 scope of work was that any promising remediation technology be identified that warranted additional research or development.

The scope of this task was negotiated between WES and Arthur D. Little personnel during the preliminary phases of the Task 2 activities. The work for this task focused on the evaluation of past research conducted on the two to three most promising technologies for the remediation of spilled LP. Biodegradation, natural attenuation, and soil washing were chosen as the three technologies to be considered. The scope was further limited to remediation of LP spills to soils, as air emissions from LP spills are expected to be minimal, and remedial approaches for spills to surface water bodies are anticipated to be ineffective.

This review of the past research conducted on the transport, fate, and possible remediation of spilled LP was anticipated to be used to direct future LP remediation research efforts towards the most promising remediation technologies.

This study of potential LP spill remediation technologies was not intended to address remedial action at sites with other health or safety hazards such as fire episodes or confined space entries. Personnel protective equipment (PPE) selection is discussed, but the suggested field PPE should be reviewed by personnel implementing any remedial measures prior to field work to ensure that the equipment is protective for the particular remediation situation.

Section Organization

This section has been organized into chapters that discuss the following:

- a. The purpose and scope of the study, as well as the organization of the section (Chapter 1, Introduction).
- b. The physical characteristics of LP, the health hazards known to be associated with the use of LP, the personal protective equipment suggested to be worn by personnel remediating spilled LP, and the likely transport means and packaging of LP (Chapter 2, LP Characteristics and Use).
- c. Results of studies conducted to date on LP interaction with soils and groundwater (Chapter 3, Current Status of Research—LP Interactions With the Environment).
- d. Results of studies conducted to date on potential LP spill remediation technologies (Chapter 4, Current Status of Research Into LP Spill Remediation Technologies).

- e.* Recommendations for the next steps to be taken to support the selection and implementation of an LP spill remediation technology (Chapter 5, Recommendations to Support the Selection and Implementation of an LP Spill Remediation Technology).
- f.* References used to prepare this section.

2 LP Characteristics and Use

LP is an aqueous mixture of the salts hydroxylammonium nitrate (HAN), approximately 61 percent and triethanolammonium nitrate (TEAN), approximately 19 percent, with the balance made up of water. It is an ionic, strongly oxidizing, acidic ($\text{pH} < 0.5$) solution that has a vapor pressure of 11.5 mm of mercury at 25 °C primarily due to the water component. The LP freezing point has not been observed, but a boiling point of 123.7 °C at atmospheric pressure has been calculated. LP is not considered carcinogenic based upon negative mutagenicity data and information on HAN and TEAN. The toxic effects to human health from LP will most commonly be due to direct contact with the eyes and skin, as the low vapor pressure results in a minimal inhalation hazard under ambient conditions. The size of any spill and, therefore, the toxic effects will be limited by the packaging of LP in 40-gal¹ containers, which minimizes the potential for large spills. Based on the methods developed for handling LP, the most common LP spill, spill due to a transportation accident, will be of less than 10 gal with a large spill being approximately 150 gal.

Physical Characteristics

As manufactured, LP is clear in color and has no odor, although colorants and odorants may be added to enhance the ability to distinguish it from water. The propellant remains a homogeneous liquid (does not separate) over the entire range of temperatures and pressures expected in normal handling operations.

The composition of LP varies slightly between lots, but is 60.8-percent HAN, 20-percent water, and 19.2-percent TEAN on a mass basis. The elemental weight composition is approximately 6.5-percent carbon, 6.2-percent hydrogen, 20.3-percent nitrogen, and 67-percent oxygen. No actual molecular weight can be given because LP is a mixture; the mean molecular weight, 54.6 g (1.95 oz) per mole, has been used for some calculations. No freezing

¹ A table of factors for converting non-SI units of measurement to SI units is presented on page viii.

point has been observed for LP, but a boiling point of 123.7 °C (255 °F) at atmospheric pressure has been calculated (Decker et al. 1987). The LP is a strongly oxidizing acidic solution that does not readily vaporize; the vapor pressure for LP, which is primarily due to the water component, is approximately 11.5 mm of mercury (0.015 atmospheres) at 25 °C (77 °F). The density of the LP is approximately 1.43 g/milliliter (11.9 lb/gallon) at 25 °C (77 °F), and the kinematic viscosity of the material has been reported as 5.16 centistokes at 25 °C (77 °F) (Billack 1993).

Toxicity Information

The toxicity information summarized in this section is taken from a guidance document prepared to assist installation personnel responsible for the preparation of LP spill response plans (Arthur D. Little, Inc. 1994).

LP is considered to be moderately toxic. Its toxicity is primarily a result of the acidic and strong nitrate components, HAN and TEAN, with the majority of the toxic effects associated with HAN. LP and its components have been associated with both short- and long-term health effects. Adverse effects may occur locally at the site of contact or be systemic and affect various bodily systems.

Impact to human health from LP will most commonly result from direct contact with the eyes and skin as well as from skin absorption. In addition, LP may be toxic if accidentally ingested. Based on extrapolation of the median oral lethal dose fifty (LD₅₀) of a closely related compound (LP 1845), the lethal dose of LP XM46 would be approximately 720 mg/kilogram (0.011 oz/lb) of body weight. This dosage rate corresponds to approximately 41 ml of LP for a 180-lb person.

Prolonged skin contact with LP can cause severe irritation and damage. Depending on the duration of contact, symptoms may include rash, blistering, burning sensation, and, in extreme cases, necrosis similar to a third degree burn. Although LP causes strong allergic skin sensitization in guinea pigs, preliminary results indicate that it did not cause skin sensitization in human volunteers.

Eye exposure can also result in severe irritation and injury. Effects can include corneal opacities with temporary loss of vision. Eye contact may also result in inflammation of the iris and conjunctival redness and swelling. LP remediation personnel must be aware of the potential threat posed by contact of LP-contaminated soils with the eye.

LP does not present a significant inhalation hazard under normal ambient conditions because LP does not readily vaporize, and because its primary volatile component is water. Inhalation of aerosolized LP may cause local respiratory irritation. However, in animal studies, single 8-hr exposures to LP vapors did not cause toxic effects. As the spill event will have typically

occurred some period of time before the remediation efforts are initiated, the likelihood that remediation personnel will encounter aerosol phase LP is limited.

Although of lesser concern than acute short-term effects in a spill remediation situation, LP has also been associated with potential long-term or chronic human health effects. Based on animal studies, long-term overexposure to LP may result in spleen and liver enlargement and anemia. In addition, HAN has caused altered liver function, enlarged heart, and blood cell imbalance in test animals. These systemic effects may be caused by absorption of LP through the skin and/or inhalation of aerosolized LP.

Medical conditions that could put remediation personnel at increased risk from exposure to LP include significant coronary artery disease, stroke, or conditions causing cyanosis, as well as restrictive and obstructive pulmonary disease.

In summary, LP presents a manageable toxicity risk to human health. The toxic effects from LP are similar to those of other acidic materials and will most commonly result from contact with the eyes and skin, as the low vapor pressure of LP minimizes the inhalation hazard. Immediately rinsing LP-contaminated eyes and skin with water has been found to reduce the effect of the LP. In addition, LP is not considered carcinogenic based upon negative mutagenicity data and information on HAN and TEAN. Appropriate use of personnel protective equipment is crucial to ensure that personnel remediating an LP spill are protected against the potentially toxic effects of LP.

Suggested Personal Protective Equipment

Personnel must wear protective equipment when participating in spill remediation activities. In selecting personal protective equipment, both material compatibility and chemical resistance must be considered.

A penetration and degradation study using LP has been conducted on various materials currently used for the protection of soldiers. The results indicated that the following materials displayed adequate penetration resistance and degradation resistance when subjected to casual LP contact: water repellent coated nylon cotton field coat and water repellent coated Battle Dress Overgarment. Protection from gross liquid contact can be achieved using the woven nylon/Goretex, polyethylene coated polyolefin, polyurethane coated fabric, butyl coated cloth, butyl rubber (gloves), nitrile rubber (gloves), polyvinyl chloride (boots), and polycarbonate lens material. Preliminary results from a second phase of this study suggest that LP contact duration and the temperature and humidity of the surrounding environment affect LP interaction with PPE materials. Therefore, all LP-exposed materials should be promptly (within 8 hr of exposure) rinsed with sufficient water and evaluated by the user prior to reuse (Arthur D. Little, Inc. 1994).

The Environmental Protection Agency (EPA) has defined four levels of personal protective equipment ranging from a high protective factor "Level A" to a low of "Level D." The Army has also designated PPE according to alphabetized levels, but the Army-defined levels do not necessarily correspond to the similar EPA-defined level. This report was prepared based upon the EPA-defined levels, which are more universally recognized. Regardless of the definition chosen, the use of each of these protection levels is dictated by the nature of the materials spilled and subsequent site conditions.

In general, Level A equipment must be worn when the highest level of respiratory, skin, and eye protection is needed, while Level B equipment should be used when the highest level of respiratory protection is needed, but a lesser level of skin protection is required. Level C protection relies on the same type of chemical-resistant clothing as Level B, but is distinguished from Level B protection by the equipment used to protect the respiratory system. Level C protection can only be used when the criteria for using air-purifying respirators are met. Level C equipment worn without respiratory protection is known as Modified Level C and is designed for providing skin and eye protection in confirmed absence of respiratory threats. Level D protection is not designed for spill remediation activities and is considered to function only as a work uniform. Personal protective equipment requirements for Levels A, B, C, Modified C, and D are summarized in Table 1.

Table 1 Summary of EPA Personal Protective Equipment Requirements				
Level A	Level B	Level C	Modified Level C	Level D
Gas-tight fully encapsulating chemical-resistant suit	Fully encapsulating nongas-tight or nonencapsulating chemical-resistant clothing	Nonencapsulating chemical-resistant clothing	Nonencapsulating chemical-resistant clothing	Coveralls
Gloves (inner, outer) chemical resistant	Gloves (inner, outer), chemical resistant	Gloves (inner, outer), chemical resistant	Gloves (inner, outer), chemical resistant	Gloves ¹
Boots, chemical resistant, steel toe and shank and boot covers (outer) ¹	Boots (outer), chemical resistant, steel toe and shank and boot covers (outer) ¹	Boots (outer), chemical resistant, steel toe and shank and boot covers (outer) ¹	Boots (outer), chemical resistant, steel toe and shank and boot covers (outer) ¹	Boots/shoes, leather or chemical resistant, steel toe and shank
Disposable gloves ¹ (worn over encapsulating suit)	Gloves (outer, inner), chemical resistant	Gloves (outer, inner), chemical resistant	Gloves (outer, inner), chemical resistant	Safety glasses/chemical splash goggles
SCBA or pressure-demand, airline respirator	SCBA or pressure-demand, airline respirator	Air-purifying, full face-piece, canister equipped respirator	Respirators not required	Respirators not required
Hard hat ¹	Hard hat ¹	Hard hat ¹	Hard hat ¹	Hard hat ¹
Note: Source: Arthur D. Little, Inc. 1994. ¹ Optional depending on spill scenario.				

Respiratory protection will not be required for typical remedial activities because LP remediation activities should not produce airborne LP. Since LP does not readily vaporize, and because its primary volatile component is water, LP is not considered to present a significant inhalation hazard under normal ambient conditions. Therefore, Modified Level C equipment should provide adequate protection from LP exposure for the personnel responsible for implementing the remedial technology and is described in greater detail below.

Modified Level C equipment consists of chemical resistant impervious clothing, gloves, and boots. Each component of the modified Level C ensemble is described below. Note that modified Level C protection is not adequate for use during remediation activities involving fire or permit-required confined spaces. This study of potential LP spill remediation technologies was not intended to address remedial action at sites with other health or safety hazards.

Nonencapsulating chemical resistant clothing required for Modified Level C may consist of hooded, one- or two-piece chemical-splash suits, or disposable chemical resistant, one-piece suits. Nonencapsulating suits, unlike gas-tight fully encapsulating suits (see Level A requirements, Table 1), are not gas tight and do not provide maximum protection against vapors or airborne particulate. However, taping the wrist, ankle, and neck joints will provide protection against splashes.

In most cases, Modified Level C ensembles have chemically resistant, steel-toed and shank boots. Disposable, chemical-resistant outer boot covers are optional. All steel-toed safety shoes must meet the requirements of American National Standards Institute (ANSI) Z41.1 PT91. Depending on site conditions, a hard hat may also be required for Modified Level C. Hard hats must meet ANSI Z89.1-1986 specifications for protection. The use of a chin strap is recommended when work involves bending and ducking.

The use of compatible chemical-resistant gloves is also required for Modified Level C. Sleeve cuffs should generally be worn over glove cuffs and the seam taped to minimize leakage of liquid into the gloves. The use of Silver Shield or 4-H under gloves is highly recommended. Heavy leather gloves may be worn over chemical-protective gloves when handling abrasive or sharper objectives, but must be discarded if they become contaminated.

Level D dermal protection should not be worn when remediating LP-contaminated materials. Level D does not provide protection against skin irritation hazards and can only be worn in areas where no possibility of contact with contamination due to splashes or immersion exists.

LP Transportation and Packaging

The transportation and packaging proposed for LP during full-scale use, along with other variables such as operator responsibilities and the design of the equipment used to transfer LP into the Crusader artillery, will impact the likely size of typical LP spills, and therefore, the methods for remediation. This section summarizes the packaging and the transportation schemes most likely to be used for LP following full-scale deployment to quantify a range of typical spill volumes. The remediation technologies reviewed later in this report were assessed assuming that the following approach identifies, within an order of magnitude, the most likely range of LP spill volumes.

Transportation-related spill

LP is currently packaged in 30-gal (115-ℓ) triple pack transportation containers (Goll 1994). In full-scale manufacture, the LP will be packaged immediately following manufacture into containers, projected to be 40-gal (151-ℓ) drums, which will then be assembled, four per pallet, for transportation. The palletized drum design will minimize the risk for contamination of the LP due to transfers typically associated with liquid transport from manufacturing plant to tanker to destination bulk vessel, etc.

LP is and will continue to be transported over public highways using any of several different commercial or military vehicles with current Army and Department of Transportation (DOT) approval. The projected typical capacities of the vehicles range from a heavy expanded mobility tactical truck (HEMTT) capable of carrying 9 pallets, or 1,440 gal of LP, to a van, semi-van, or trailer capable of transporting 18 pallets, or 2,880 gal of LP (Billack 1993).

The LP packaging and proposed transportation plans both suggest that spills are unlikely during transport and will be limited in size if a spill does occur. Spills during transport often occur during tank-to-tank bulk liquid loading or unloading activities. This particular concern is minimized for LP, because the LP will not be transferred from the manufacturer-filled drums until the LP is ready for field use.

Transportation-related spills are expected to be infrequent and of low volume due to the integrity of the LP packaging, the volume contained in a single container, and the care with which explosives are transported. A likely spill size might range from one to four drums of LP, or up to approximately 150 gal.

Bulk-storage-related spill

The LP will be removed from the transport vehicles using forklifts, moved into an explosives-rated storage area, and stored in palletized drums at the

Army Storage Depots. The potential spill scenarios will vary at each facility depending upon the location of the LP unloading area, but LP is expected to be removed from the transport truck within a contained area that is sealed to be impervious to LP. The LP will then be moved into a storage area designed for explosives storage. Both of these techniques will decrease the potential for releases to the environment. The quantity of LP likely to be spilled during storage will be proportional to the total amount of LP stored, as the LP will be stored in the 40-gal containers filled by the manufacturer, and not in bulk storage tanks.

The most likely spill scenario is due to pallet movement using a forklift. The spill could occur during removal of the pallet from the truck, during transportation of the palletized drums to the LP storage area, or while attempting to place the pallet in the appropriate storage location. The spill would, therefore, most often be to a sealed area designed for containment of LP spills, and should not impact the environment. LP spilled to a contained area can be collected for disposal, eliminating the need for remediation.

If LP spilled during storage activities reaches the environment, the spill would be managed similarly to field testing and use-related spills. Therefore, spills related to bulk-storage activities are not discussed separately in this letter report.

Field testing and use-related spills

Several Army installations are currently testing prototypes of an LP artillery system. LP transfer operations at these sites are likely to be conducted under close scrutiny and should subsequently be less susceptible to operator error. Therefore, the most common single event spill scenarios may involve the small drip-sized volumes typically associated with liquid transfer operations, or up to a gallon if a loading hose ruptures. As a worst case scenario, one to two drums (40 to 80 gal) of LP could be punctured or overturned during the transfer operations; however, the risk is extremely low.

During full-scale use, LP spills may occur more frequently than during the fixed gun test firing phase due to the increased level of activity. The largest likely spill volume during deployment may be estimated on the basis of the size of the LP storage tanks on both the artillery weapon itself and the vehicle used to supply it with LP. The artillery resupply vehicle will be used to refill the LP storage tanks of the artillery vehicle. Currently, palletized LP drums are envisioned to drain into an internal tank within the resupply vehicle, which will then be used to fill an internal tank on the artillery vehicle. Either or both vehicles will be serviced by a portable tank designed to download contaminated LP.

The design of the vehicles has not been finalized, but the artillery and resupply vehicles will likely have a capacity of approximately 250 gal (950 ℓ)

and 500 gal (1,900 ℓ), respectively.¹ These vessels will be provided with secondary containment to capture spilled LP. This report was prepared assuming that either vehicle would release, at most, 10 percent of its capacity in a single-event, worst case spill. Therefore, the remediation technologies reviewed for use during full-scale deployment must be capable of remediating a spill of up to 50 gal, assuming that the vehicle secondary containment tank is somehow drained or spilled during fieldwork activities.

¹ Facsimile Correspondence, 1994, Christopher Goll, Department of the Army, to Mr. Kevin Cahill, Arthur D. Little, Inc.

3 Current Status of Research—LP Interactions With the Environment

Several studies have been conducted on the interactions between LP and various soils to predict the potential consequences of LP spills. Fewer studies have been conducted on the interactions between LP and water. The LP/soil studies have indicated that one active component of LP, HAN, will react with most soils to produce an offgas and release nitrate to the soils, while the other active component, TEAN, will pass through the soil column to the groundwater, as it does not react or adsorb well. The composition of the offgas produced when LP reacts with the soil depends upon the type of soil contacted, but none of the soils reacted explosively with the LP. The LP/water interaction study results indicate that the dissociated TEAN will degrade quite slowly upon contact with groundwater, and the LP dissociation could cause exceedances of groundwater nitrate standards.

LP Interactions With Soils and Impact on Groundwater

Current status of studies

Potential environmental impacts associated with the use of LP have been investigated during overall development of the LP-based artillery system. This letter report is based primarily on the results of those previous investigations and studies, which were completed to assess the interactions between spilled LP and several soils. The study results are presented in a summary report (Pennington et al. 1994a) that includes separate chapters on the following:

- Soil Characterization and Contact Screening Tests (Pennington et al. 1994b).
- Soil Sorption (Pennington and Price 1994).

- Runoff, Infiltration, and Transport (Adrian and Myers 1994).
- Effects on Soil Microflora (Gunnison, Pennington, and Marcev 1994).

Each of these chapters will be referenced separately in this letter report. The References at the end of this section include a listing for the overall Pennington et al. (1994) report as well as each of the four chapters, as each could be considered as a separate study.

The first chapter/study (Pennington et al. 1994b) was completed to investigate the interactions between spilled LP and several soils. The objectives of the study were to evaluate the pertinent properties of the soil that may be important to LP/soil interactions; evaluate qualitatively the reactions of LP with the test soils; identify and quantify the volatile products released; and determine the effects of temperature on composition and quantity of gases evolved. Fourteen soils from five LP test sites were selected for testing; the fourteen soils were chosen to represent the broadest possible range in properties so that the test results could be extrapolated to any potential spill site.

Contact between the LP and soils was conducted in both confined and unconfined testing equipment. The unconfined testing was completed to determine if the reactivity or offgas generation would prohibit the use of the confined test equipment. The confined testing was subsequently conducted to evaluate the offgas produced by the reaction of the LP with the soils.

The unconfined tests were conducted at 23 and 60 °C by contacting 1 g (oven-dry weight basis, ODW) of soils with 150 μl of LP. As the LP was added to the soils one drop at a time, it reacted producing physical changes such as bubbling, foaming, and color variation over the 24-hr test period.

The confined contact tests were conducted at 5, 22, and 60 °C by contacting 0.25 g (ODW) of five soil types with 100 μl of LP. The soil and LP were allowed to interact for 30 min, at which time the change in headspace pressure was noted, and a sample of the headspace gas was withdrawn for analysis. Qualitative identification and quantification of the gases generated were conducted.

The Results of the confined and unconfined studies indicated that contact and subsequent reaction with undiluted LP resulted in various changes to the soils. The following results were noted:

- a. LP interactions with soils were not vigorous enough to produce violent LP decomposition or splattering hazards. Reactions with the soils varied: reactions in several soils were immediately visible at ambient temperature as frothing or bubbling; no reaction was immediately visible in others, but did form later in the 24-hr test period; and some soils exhibited no visible reaction at all over the entire 24 hr.

- b. Soil pH dropped dramatically after contact with LP; mean pH for all soils before contact with LP was 7.1 ± 0.4 , whereas after contact the mean was 3.0 ± 0.3 . The LP pH was 0.36.
- c. The buffering capacity of the soils for LP was poor as demonstrated by titrating several of the soils with LP. The poor buffering capacity of these soils was concluded to be due to low total organic carbon (TOC), since the soils that exhibited the least change had high TOC.
- d. Nitrate/nitrite-nitrogen, total Kjeldahl nitrogen, ammonia nitrogen, and organic nitrogen increased dramatically in soil contacted with LP. On the basis of soil contact testing, each kilogram of LP could release approximately 326,000 mg of nitrate/nitrite nitrogen ($\text{NO}_3/\text{NO}_2\text{-N}$) if no nitrate breaks down when the LP contacts the soil.
- e. One hundred microliters of LP generated approximately 800 to 4,000 μl of total gas, consisting of oxygen, nitrogen, and carbon dioxide. Two of the five soils tested for their ability to generate gas when mixed with LP produced relatively large quantities of gas, composed primarily of carbon dioxide (96 percent) with the balance consisting of nitrous oxide. This result was attributed to LP oxidation of a carbonaceous component of the soil, possibly carbonate. Two of the other soils generated almost no gas, but the generated gas was 81-percent nitrous oxide with the balance composed of carbon dioxide. The researchers concluded that this gas was mostly a result of LP degradation. The fifth soil produced an unusually large amount of gas over a long period of time (approximately 24 hr), and the oxygen was noticeably depleted. In all other soils, the oxygen to nitrogen ratio observed in the gaseous LP/soil emissions remained equal to that found in ambient air.
- f. TEAN did not decompose immediately when LP contacted the soil, and nitrate remained unreacted in the soil. Therefore, the researchers concluded that the gases produced are primarily products of HAN decomposition.

The results of this study reveal several complications to consider when remediating LP spills. The results discussed above indicate that soils impacted by spilled LP will have a low pH, so the need to quickly neutralize the soils is necessary to protect human health and the environment; the use of personal protective equipment is warranted during remediation activities. The spilled LP is unlikely to pose a splattering hazard based upon the observed LP/soil reactions. Results of the offgas analyses indicate that inhalation would not be an expected exposure pathway and that respiratory protection is not required for the remediation team. Reaction of LP with the soils could reduce the available oxygen; therefore, if the site affected by the spill is confined, care should be taken to confirm that adequate oxygen remains in the spill area prior to implementation of remedial activities.

The nitrate/nitrite-nitrogen, total Kjeldahl nitrogen, ammonia nitrogen, and organic nitrogen increased dramatically in soils contacted with LP due to residual nitrate and triethanolamine (TEA) remaining in the soils. This increased loading of nitrogen in the site soils could lead to nitrate contamination of the groundwater if the nitrate does not degrade or sorb strongly to the site soils. The results of this study indicate that nitrate/nitrite-nitrogen contamination will be the major remediation concern.

LP degradation and sorption in soil was the subject of a second study (Pennington and Price 1994). The rate and extent of HAN and TEAN adsorption when LP contacted soils was determined, and soil properties correlating with adsorption were identified. Several tests were conducted with soil from five LP test sites to identify the optimum parameters to be used during the LP sorption tests. These tests included a contact screening test to assess whether the sorption studies could be conducted in confined test equipment; a biodegradability test to determine whether microbial growth was likely to cause interference; a ratio test to determine the ratio of soil to LP that would ensure a measurable solution phase concentration of HAN and TEAN; and an adsorption kinetics test to determine the time needed to reach sorption equilibrium.

The contact screening test results from a previous study (Pennington et al. 1994b) were used to conclude that subsequent testing would be conducted in an open flask. The biodegradability test was conducted by adding 20 ml of LP to 5 g of both autoclaved and unautoclaved soil, placing the sample on a rotating shaker for 5 days, and then culturing the sample for microbial activity. The ratio test was conducted using soil and a 1,000-part-per-million (ppm) LP solution, and soil:LP solution ratios ranging from 1:3 to 1:6 based upon 20 ml of the LP solution. The sample was placed on a rotating shaker for 2 days, centrifuged, and the solution was then analyzed for HAN and TEAN concentrations. The adsorption kinetics test was conducted by contracting 20 ml of either LP, 50-percent diluted LP, or a 1,000-ppm solution of LP with 5 g of soil. The sample was then placed on a rotating shaker for time ranging from 30 min to 120 hr.

Results of this LP degradation and sorption study confirmed several of the results indicated by the first study discussed above, primarily that the two active LP components, HAN and TEAN, react differently with soils and water.

Specific results of these sorption studies indicated the following:

- a. In the ratio tests using 1,000 ppm of LP, the HAN concentration fell to less than detection limits within 48 hr due to reaction with the soils. No sorption could be determined for HAN due to its reactivity. In the adsorption kinetics tests using undiluted or 50-percent diluted LP, concentrations of HAN were detected in the solution at equilibrium, due presumably to the overwhelming excess of LP.

- b. The 1,000-ppm LP adsorption kinetic tests indicated limited adsorption and limited reactivity for TEAN, as the TEAN concentration was relatively stable over time. The authors of this study noted that 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 authors concluded that the low soil adsorption capacity and lack of reactivity will allow the TEAN to migrate during rainfall events or when water is applied to the spill area.
- c. HAN sorption results indicated less than detectable HAN concentrations on the soil while HAN remained in the solution; any HAN that migrated from the solution into the soil would react, producing an offgas. Reactivity of HAN with soils correlated best with total organic carbon, total Kjeldahl nitrogen, oxalate extractable iron, and percent silt. The results did indicate a wide variation in the reactivity of the different soils with HAN.

Results indicate that HAN, which is the major constituent of LP, degrades and/or dissociates relatively quickly in the environment. The HAN in spilled LP would persist and migrate only until the LP had contacted sufficient soil to reduce the HAN. Nitrate produced by HAN degradation and dissociation will remain in the environment and continue to migrate. During the same test, the TEAN did not react with the soil and exhibited limited adsorption, indicating that soil sorption would not prevent migration of TEAN through the soil profile if LP is spilled in sufficient quantity. Remediation of LP-contaminated soils will, therefore, most effectively protect groundwater resources if it slows the movement of unreacted TEAN through the soil column and remediates the nitrate.

A third study (Adrian and Myers 1994) was conducted to assess the potential impact to groundwater from an LP spill. The testing apparatus consisted of 4 in. of dry soil placed in the bottom of a buret, topped by 2 in. of LP-saturated soil, which was then topped by 2 in. (94.8 g) of water. The five soils investigated using this experimental setup were contacted with between 46 and 97 g of LP. As the water flowed through the soils, the effluent was periodically sampled and analyzed to determine how the effluent composition differed from the composition of the original LP.

Similar to the discussion presented earlier, 4 in. of soil beneath the 2 in. of LP-saturated soil may have provided a worst case model of environmental conditions. LP spilled to the environment will most likely move more slowly through the impacted soil (without the driving force of 2 in. of water), and soil columns in the environment are likely to provide a much longer migration pathway for HAN to react within. Both of these factors should allow the HAN to react with sufficient soil to degrade completely.

The results of the soil column elution studies using undiluted LP varied slightly depending upon the type of soil tested. The first pore volume eluted from the majority of soils tested contained below detectable or near detection

limit concentrations of TEAN. The TEAN concentration continued to increase as additional pore volumes eluted from the soils and never peaked during the test runs.

The HAN concentration in the first pore volume eluted was zero or near zero for approximately half of the soils tested. For the remaining soils, the first pore volume contained a significant HAN concentration (i.e., approximately 5 to 10 percent of the HAN concentration in undiluted LP). The HAN eluate concentration over time varied depending on the soil tested, but the HAN concentration did peak and begin to decrease in four of the five soils tested.

The researchers concluded that HAN and TEAN underwent decay and sorption when undiluted LP contacted the dry soil beneath the LP-saturated soil. This conclusion was based on the observation that flow velocities for HAN and TEAN were less than that of the bulk liquid during flow into the dry soils. The results of tests conducted using diluted LP were similar to those of the undiluted LP; decay and sorption were both observed. One interesting result of the tests conducted using undiluted LP was that both HAN and TEAN disappeared more rapidly from the soil with a lower organic matter content. The researchers concluded that the higher organic content may have contributed to the stability of the diluted HAN and TEAN. The higher organic matter content might also have increased the HAN and TEAN sorption.

The results of this study indicated that the impacts of an LP spill are heavily dependent upon the size of the spill and the characteristics of the impacted soils. Smaller spills may be degraded within the uppermost layer of the ground surface, especially if the soil infiltration rate is relatively slow. Larger spills have the potential to migrate a considerable depth into the soil column, continually releasing nitrate as the HAN undergoes dissociation and/or reaction. LP remediation efforts must be undertaken considering the amount of LP spilled and the type of soil impacted by the spill. A relatively large spill to a sandy soil may allow unacceptable nitrate concentrations to reach the groundwater, while a smaller spill to an organic-rich soil may result in little more than an increase in the soil nitrate concentration.

The final study (Gunnison, Pennington, and Marcev 1994) included in the overall study was conducted to determine the immediate and long-term effects of diluted and undiluted LP on the soil microflora. The diluted LP tests were conducted with LP diluted 50:50 (volume basis) with deionized water. The effects were evaluated by conducting three tests: a soil sorption kinetics test, a short-term contact test, and a long-term contact test.

The adsorption kinetics testing was conducted by exposing two different soils to a 1:4 ratio of soil to either LP or diluted LP. Soil bacteria were then quantified at various times over the 5-day test. For the short-term contact tests, a 1:5 slurry of soil to either LP or diluted LP was used. The slurry was placed on a shaker and incubated for 1 hr at 30 °C. Following the

incubation, the soil was washed several times, transferred to incubation flasks, and sampled for microbial enumeration, HAN and TEAN. The long-term contact tests were conducted in a similar manner, except that the LP or diluted LP was not rinsed from the slurry until the end of the test. Microbial enumeration and analysis for HAN and TEAN were conducted at various times during the 90-day incubation period.

These tests are likely to be more representative of surface soils than subsurface soils due to the relatively high LP loading (5:1 LP to soil) ratio used for the short- and long-term tests. This soil to LP ratio would adequately represent the relationship between surface soils impacted by LP, but might not represent the sorption kinetics of deeper soils. By the time LP infiltrated through the top few inches of soil, the HAN concentration would presumably have decreased, the nitrate concentration would have increased, and the infiltrating liquid would not be as acidic due to neutralizing reactions with the soils. Therefore, the use of the sorption parameters derived from this study may not extrapolate to accurately predict the sorption of LP-related contaminants as the spill infiltrates deeper into the impacted soils. The column leaching tests discussed in LP Spill Impacts on Groundwaters below investigated the sorption effects due to deeper LP spills.

Results of microbiological testing indicated that no microorganisms in any of the soils could use LP as a sole source of nitrogen or carbon. Undiluted LP permanently sterilized each of the soils within the first hour of contact, while diluted LP decreased the number of microorganisms present, but allowed later regrowth of microorganisms. Study results indicated that HAN concentrations in undiluted long-term tests varied little during the 90-day test period, while the HAN concentration in the diluted long-term test decreased over time due, the researchers concluded, to continued reaction.

This study concluded that removal or dilution of LP within the initial 1 to 2 hr after the spill would mitigate impacts on soil microflora, and that removal or dilution of LP as soon after a spill as possible is important. The authors further concluded that although spilled LP may be neutralized by adding a base, the negative impacts from the spill on the microorganisms may already have occurred.

This final point has important implications for potential remedial measures. Understanding whether microbes can survive contact with spilled LP that is immediately neutralized with a weak alkali such as baking soda or soda ash is critical. If the microbes are capable of surviving such an incident, natural processes including plant growth may remove the nitrate from the soil and reduce the potential groundwater impacts of the spill. Microbes could potentially reduce the nitrogen content in the LP-contaminated soils if postspill soil conditions allow microbial regrowth.

Perceived data gaps

No significant data gaps were identified in the studies discussed above that would impact selection of an LP spill remediation scheme. Results indicated that LP spilled to soils is not likely to react explosively, but that the LP/soils interaction will produce gases. The soil sorption results indicated that even soils with a high organic carbon content will not significantly retard the movement of TEAN through the vertical soil profile, while the HAN will persist only as long as it takes to contact a sufficient amount of soil to completely react.

One area that should be further reviewed is the impact of "realistic" LP spills on the microbes and how to minimize that impact. Undiluted LP sterilized the soils tested, while diluted LP only temporarily reduced the microbial population. The data gap is that no testing has been conducted to assess whether soil microflora can recover from a spill of undiluted LP that is neutralized reasonably quickly. Data on how soil biota respond, over time, to an LP spill followed by neutralization will determine whether natural attenuation would be effective for the remediation of spills.

LP Spill Impacts on Groundwaters

Current status of studies

An additional study (Section IV of this report) was conducted to investigate the rate of LP-derived nitrate movement through various soil types and to develop predictive computer models. Three separate mathematical models were developed to predict how different pathways and conditions affect the nitrate ion concentration in the soils and groundwater beneath an LP spill site. To support development of these models, three soil column experiments were performed in which one-half pore volume of LP was applied to 800 g of each of the soils. The LP was eluted by applying five pore volumes of deionized water.

Results indicated that the pH of the eluate rose from an initial range of 2 to 3 to a range of 6 to 8 after elution of three pore volumes. Models developed based upon these soil column results predicted that the concentration of nitrate ion would decrease rapidly near a 245-gal (1,316 kg) spill site due to mixing with the aquifer water, so that the nitrate concentration would soon be reduced to below the 10-mg/l drinking water standard for the United States.

This report stated that experimental measurements show the retardation coefficient for HAN varied from 1.3 in China Lake soil (sandy) to 2.6 in Picatinny soil (silty), while the TEAN retardation coefficient ranged from 2.3 in Picatinny soil to 13.5 for China Lake soil. The nitrate ion retardation coefficient was estimated as being equal to one, or not retarded.

The conclusions drawn from this study included the following:

- a. An LP spill will soak vertically into a sandy soil near the spill site, while an LP spill onto clay or silty soils will have time to flow over the soil surface for a greater distance before soaking into the soil.
- b. An LP spill onto a sandy soil will pose a greater potential for groundwater contamination than a similarly sized spill onto a clay or a silty soil.
- c. A mathematical model was used to calculate the maximum concentration of nitrite/nitrate nitrogen that could be present directly under an LP spill onto sandy soils. In a worst case scenario, the maximum concentration of nitrite/nitrate nitrogen that could reach a water table that is 10 m below the soil surface is likely to exceed the drinking water standard if a drum (≥ 208.3 kg) or more of LP is spilled onto a sandy soil.
- d. A second mathematical model was developed to predict how the nitrate concentration might vary with distance and time after the spilled LP and its transformation products reach the groundwater table. The results were based on the assumption that spilled LP would spread out over the soil surface area before infiltration and mixing with the groundwater. The maximum concentration of nitrate was predicted to be directly proportional to the mass of LP spilled. The maximum concentration of nitrate decreased rapidly with mixing so that a spill of a full LP drum (208.3 kg) was unlikely to exceed the 10-mg/l U.S. drinking water standard except directly under the spill.
- e. A third mathematical model was used to assess the results of a spill that seeped vertically from the surface through the vadose zone, which then discharged to the aquifer. The results indicated that a bimodal maximum concentration occurred; one peak remained under the spill, while the second peak was carried along with the flowing groundwater.
- f. The authors stated that an "unmistakable" conclusion from the computer modeling conducted for this study was that vigorous intervention and remediation efforts should be implemented as soon as practical after an LP spill. It was further concluded that immediate excavation of the LP-contaminated soil to prevent migration is warranted when the spill volume is significant.
- g. Excavation of the contaminated soil from the vadose zone directly under the spill site was recommended even after the passage of considerable time. The computer models indicated that contaminated soil could act as an LP reservoir that feeds to the groundwater aquifer for a substantial period of time. As an interim spill response, an impermeable barrier (tarpaulin or other water-tight barrier) could be placed on the spill site surface to reduce the supply of infiltrating water. Without

infiltrating water, the spilled LP will be held longer in the vadose zone, which is more accessible for removal.

This study was conducted on the premise that a full drum of LP, as a worst case, was released to the environment. Given that volume as an initial condition, it is not surprising that the computer modeling results indicated that LP-derived nitrate groundwater contamination could occur. The researcher's conclusion that soil excavation is warranted to reduce the threat of groundwater contamination was based upon the size of the modeled spill. Soil excavation may not be required to protect the groundwater from nitrate contamination due to small LP spills. This uncertainty supports the concept that the appropriate remedial response to an LP spill must be based upon knowledge of the particular spill size and impacted area.

Data gaps

A data gap was identified based upon a comparison of the results of the studies described in earlier sections. The data gap is that the soil studies discussed earlier indicated that soil sorption would not be sufficient to maintain an LP residual source in the spill site soils, while the third mathematical model discussed immediately above predicts that the spill area soils will continue to act as a residual groundwater contamination source. The question of whether spill area soils can act as a continual source of LP contamination must be answered before an appropriate remediation strategy can be developed.

The timing of when the LP is flushed from an LP spill site is a critical point because that timing will affect the spill response activities. If the spill occurs during a rainstorm and a moderate amount of LP is spilled, remediation of the soil may not be practical because most of the LP might already have washed through the soil column. Conversely, if the LP is spilled to a soil with poor vertical hydraulic conductivity and a high organic carbon content, spill remediation may be practical for a period of several weeks or longer after the spill.

4 Current Status of Research Into LP Spill Remediation Technologies

Previous laboratory studies assessed soil washing and bioremediation for remediation of LP spills to soil. The soil washing study indicated that LP could be effectively removed from the soils investigated, although significant concentrations of HAN and TEAN sorbed to one soil. The bioremediation results were less conclusive but did indicate that TEAN biodegradation was possible. Concentrated LP solutions (greater than 1,000 mg/l) were shown to be toxic to microorganisms, while more dilute solutions (less than 100 mg/l) did not inhibit bacterial growth. No studies have been conducted to assess the potential effectiveness of enhanced natural attenuation, but past TEAN biodegradation results and groundwater models of nitrate loadings suggest that enhanced natural attenuation could be an attractive remedial option.

Soil Washing

Conclusions of studies conducted to date

Soil washing and soil flushing are technologies used to remove contaminants from soil by flushing the soil with a fluid in which the contaminant is soluble. The process is typically known as soil flushing when conducted in situ and soil washing when conducted ex situ. These terms will be used interchangeably in this report, as both in situ and ex situ processing of LP-contaminated soils may potentially be used. Although water is often used as the extracting or flushing agent, other materials including triethanolamine have been used to removed water-insoluble soil contaminants.

A study (Section II of this report) investigating the potential use of soil flushing as a remediation technology for LP-contaminated soils was recently completed. Laboratory tests were conducted to determine the effectiveness of soil washing by placing contaminated soil in a vertical column and backflushing the soil with water. The objective of this study was to determine whether the soluble LP components could be removed from the soils without also

washing out a significant portion of the finer soil particles. Four soils were selected to offer a wide range of soil properties and were tested to assess any correlation between LP removal and soil particle-size distribution.

The testing was carried out by loading LP-saturated soil into a column with sufficient freeboard to allow for bed expansion during the flushing. The soil was prepared by adding 345.7 g LP to 3,000 g soil. Backwash fractions were collected from the top of the column while the soil was flushed, and these fractions were analyzed for HAN, TEAN, TKN, and nitrate/nitrite-nitrogen. Two tests were conducted for each of the four soils varying the rate at which the soil was flushed to investigate the impact of the flushing rate on the solids wash rate. The "high" and "low" wash rates varied depending on the soil being tested, but averaged 1.0 and 0.50 ℓ per minute, respectively. Backwash volumes per mass of soil ranged from 10 ℓ /kg soil to 50 ℓ /kg soil.

The results of this study indicated that the soil washing effectively removed HAN and TEAN from the LP-contaminated soil. The residual HAN and TEAN concentrations in the soils were comparable after the low flow and high flow washing. The amount of HAN and TEAN remaining in the soils after flushing varied according to the flush rate and the soil type, but most of the LP components were removed in all cases. Of the approximately 200 g of HAN and 70 g of TEAN added to the soils, less than 1 g of HAN and TEAN remained in the soil following seven of the eight test runs. In the eighth test run, conducted with the low flushing rate and the soil with the highest organic matter content, approximately 27 g of HAN and 15 g of TEAN remained in the soil. The researchers concluded that the HAN and TEAN had sorbed onto organic matter.

The results of this study indicate that the soil flushing was extremely effective in removing the LP components from the soils. Because the amount of HAN and TEAN left in the soils was, on average, slightly greater for the low flush rate than the high flush rate test runs, the HAN and TEAN were concluded to adsorb preferentially to the smaller sized soil particles that were washed out of the column at the higher wash rate.

Nitrate was detected in seven of the eight test soils after washing and was the predominant contaminate in five of the eight soil tests. The presence of nitrate raises an additional concern for LP spill remediation; removal of LP from the soils is only one aspect of LP remediation. Nitrate must be treated to prevent exceedances of the nitrate groundwater standard.

The researchers concluded that if a column-type soil washing technology were implemented for remediation of LP-contaminated soils, provisions would have to be made to minimize the solids washed out of the column. This conclusion was based on the observation that the high flushing rate was more effective at removing the LP components, but also led to the wash out of smaller soil particles on which the HAN and TEAN could be sorbed. The researchers cautioned that a solids separation unit may be appropriate after the backwashing operation to recover the solids.

These results clearly demonstrate that soil washing can be used to remove LP from contaminated soils. Although the researchers used a column for this study, other processing schemes could be designed that might decrease the amount of water required to remove the LP, thereby increasing the attractiveness of this technology. The study did generate ambiguous results relating LP removal efficiency to a backwash volume, but can be used as a starting point towards the development of more efficient soil washing schemes.

Evaluation of soil washing as an LP spill remediation technology

Soil washing has a strong potential as a remedial technology for contaminated soils. Although questions remain on how to dispose of the LP-contaminated rinsate produced by implementation of this technology, it remains the one technology demonstrated to be capable of removing the LP components from a heavily contaminated soil matrix. The test results discussed in the section above indicate that soil washing is effective even with a soil with a relatively high organic matter content, which would tend to increase LP sorption to the soil matrix.

A comparison of various remediation technologies (Department of Defense Environmental Technology Transfer Committee 1994) was reviewed to estimate probable soil washing costs. This reference source stated that ex situ soil washing-based remediation can typically be completed for between \$120 and \$200 per ton assuming 15,000 yd³ of material. The costs for implementing soil washing for remediation of LP-contaminated soil would most likely be in the \$125 to \$150 per ton range, as LP does not sorb strongly to soils. This cost estimate would vary depending on factors including geographic location of the spill, the quantity of contaminated soils, and the depth of contaminated soils.

A concern with the use of soil washing is that the process generates a wastewater stream that may be difficult to treat. The HAN and TEAN, together with their degradation and dissociation products, will remain in the wastewater. A treatment process for this wastewater would have to be identified or developed prior to implementation of soil washing as an LP remediation technology.

Perceived data gaps

Several data gaps were identified based upon the results of this study, but none of these data gaps diminish the overall result that soil washing appears to be a potential remediation technology for LP-contaminated soils. One significant data gap is the same data gap discussed earlier, namely the effect that sorption may have on remediation of LP-contaminated soils. The LP/soil interaction study results (Pennington et al. 1995) discussed earlier indicated that neither HAN nor TEAN would adsorb to soils, but that they would be flushed through the soil profile. The results of the soils washing study,

however, indicated that a significant portion of the HAN and TEAN remained in the soil with the highest organic matter content. A more focused sensitivity analysis on the impact of LP sorption to organic matter on soil washing effectiveness would be useful for review prior to implementing soil washing as a remediation technology for LP-contaminated soil.

Another unanswered question with regard to implementation of the soil washing technology is what could be done with the backwash water generated by this process. Various studies have demonstrated that HAN and TEAN do not readily degrade when LP is diluted with water, but may be dissociate, releasing nitrate and either hydroxylamine (HA) or triethanolamine (TEA). Residual nitrate contamination may limit disposal options for the backwash water unless biological industrial and/or municipal treatment plants can be demonstrated to effectively treat dilute concentrations of HAN and TEAN.

Bioremediation

Conclusions of studies conducted to date

Although studies have successfully demonstrated bioremediation of TEAN, bioremediation of LP-contaminated soils has not been proven. One study (Kaplan et al. 1984) was conducted to assess the biodegradability of several ammonium nitrate-based propellants in aqueous and soil matrices under a variety of conditions. Both aerobic and anaerobic systems were operated for periods of up to 177 days, with the progress of the biodegradation reaction monitored using radiolabeled propellants.

The study showed that TEAN was biodegradable under both aerobic and anaerobic conditions, and that no significant concentrations of intermediates were formed. One particular experiment demonstrated that a 500-ppm TEAN solution could be degraded by a typical garden soil containing 6.7-percent organic matter, while another demonstrated that HAN was chemically unstable above a pH of approximately 5.9. The researchers concluded that HAN would not persist under most environmental conditions due to its instability above pH 5.9 and the chemical reactions likely to occur with inorganic and organic soil components.

Another experiment conducted for the Kaplan study with relevance to LP-contaminated soil remediation demonstrated TEAN to be mineralized in an aerobic batch reactor in which TEAN was the sole source of carbon and nitrogen. The researchers noted that this result indicated that a biological process water treatment system would be feasible for remediation of TEAN-contaminated aqueous solutions. If the TEAN mineralization results could be confirmed, an aerobic reactor might be capable of treating LP-contaminated wastewater generated by a soil washing process of extracted groundwater.

TEAN dissociates into triethanolamine (TEA) and nitrate. A study (Frings et al. 1994) has demonstrated a biodegradation pathway for TEA. An

anaerobic bacterium isolated from sewage sludge was shown to be able to use TEA as its sole source of energy and organic carbon, and degraded the TEA into acetate and ammonium. These results, along with the results of the Kaplan study discussed above, suggest that bioremediation of dilute solutions of both TEAN and TEA should be possible.

A literature search revealed only one study (IT Corporation 1995) that was conducted specifically to assess the potential use of biodegradation for industrial waste treatment as well as remediation of LP contamination. This investigation was conducted in three phases: a preliminary screening for LP-tolerant microbes; an evaluation of LP biodegradation in soil matrices; and an evaluation of LP biodegradation in aqueous matrices.

The microbe screening process was conducted by subjecting soils and sludges from 14 sources to a solution containing 1,000 ppm LP in a mineral salt media adjusted to a pH of 7.0. No bacteria could be grown in the solution, so isolates were successively subjected to increasing amounts of LP with supplemental nutrient sources until two aerobic isolates achieved tolerance to 800 ppm LP. A third isolate, tolerant of greater than 300 ppm, was also selected for further study. The lowest concentration of the nutrient broth that could sustain microbial growth in the presence of LP was 1,200 mg/ℓ.

The study results indicated that LP could not serve as a sole source of carbon or nitrogen for any of the isolates. Although a specific threshold for toxic or inhibitory effects was not determined, 100 ppm of LP did not appear to have an effect while concentrations of 1,000 ppm inhibited all microbial growth. The threshold for the particular strains used for this study must be presumed to fall within the 100- to 1,000-ppm concentration range.

This result indicates that LP-contaminated wastewaters might be amenable to treatment in an activated sludge wastewater treatment plant (WWTP) where LP would not serve as the primary carbon or nitrogen source. If a facility remediating an LP spill has an existing WWTP, the microbial mass in that WWTP may be capable of treating the very dilute LP wastewaters from remedial activities.

The soil studies were conducted by exposing the three selected isolates to both autoclaved and unautoclaved soil containing 800-ppm LP, lime for pH control, and a nutrient media. The HAN and TEAN concentrations were monitored by weekly analysis, and nitrate and nitrite were also analyzed to confirm HAN or TEAN degradation.

Results confirmed several conclusions of past LP/soil interaction studies. In particular, the HAN concentration was observed to decrease quickly in the soil that had been neutralized with lime. This result confirmed the conclusion noted above, that HAN degrades quickly at a pH of greater than 5.9.

TEAN concentrations were observed to decrease after 3 weeks in native soils and 4 to 5 weeks in autoclaved soil samples that had been amended with

LP-tolerant cultures. The researchers concluded that the observed TEAN degradation was the result of biological activity and not adsorption because the size of the bacterial population increased during the test and because the abrupt change in TEAN concentration occurred too late for adsorption. The soil study authors did indicate that the addition of LP-tolerant microbes did not enhance biodegradation of the TEAN. However, the results did not clearly demonstrate that biodegradation was responsible for this decrease, as the observed decrease could have been due to other factors such as variability in the analytical data.

The aqueous LP degradability tests were conducted in two phases: a preliminary assessment of LP stability in groundwater and seawater and a detailed analysis of LP fate in deionized water and simulated groundwater. The preliminary assessment was conducted by adding LP to both matrices at 2, 10, and 100 times the TEAN detection limit and analyzing the sample after 24 hr of storage at 4 °C.

The detailed study was conducted by combining 800 ppm of LP, sodium hydroxide for pH adjustment, and a nutrient mixture in four 1-ℓ vessels and varying the addition of a mixed consortia of microbial cultures, soil, and water. A total water and soil volume of 1 ℓ was used for each of the four experiments, and the pH of each sample was adjusted to between 7.0 and 7.5. The tests were conducted for 8 weeks without adding nutrient amendments or adjusting the pH. Samples were collected every 14 days and analyzed for HAN, TEAN, nitrate, nitrite, and other potential LP breakdown products.

The aqueous biodegradation results showed that HAN disappeared rapidly from water treatments that were amended with soil, but the rate of HAN reduction in water treatments without soil was at least 100 times slower. The TEAN results were more difficult to interpret. A slow decomposition of TEAN occurred in the soil-water slurries, but microbial growth did not contribute to TEAN degradation. No definitive conclusions could be drawn regarding what was causing the decomposition.

Sequencing batch reactors (SBRs) using activated sludge supplemented with LP-tolerant isolates were also used to investigate LP biodegradation. The reactors were operated with a hydraulic residence time of 2 days and a biological solids retention time (BSRT) of 5, 10, or 20 days for a period of four sludge ages. Samples were analyzed periodically during the course of the experiments to monitor potential TEAN degradation.

The results of SBR testing led the researchers to conclude that TEAN was not degraded by any of the SBR tests. HAN was reduced in the SBR tests; HAN reductions of 44, 55, and 73 percent were reported for the SBRs with BSRTs of 5, 10, and 20 days, respectively.

The overall result of the IT Corporation study was that LP biodegradation was not conclusively demonstrated. This indicates that finding an effective consortia of microbes will be difficult. The SBR test results, in particular,

showed that a microbial population may require extended contact with LP to evolve the capability to use LP as a substrate.

Evaluation of bioremediation as an LP spill remediation technology

Bioremediation has not been demonstrated to be a feasible LP spill remediation technology due to the inhibitory effect of LP on microbial growth. However, biodegradation of LP may be useful for treatment of residuals from remedial activities such as wastewaters from soil washing or extracted groundwater. Demonstration that LP can be biodegraded would also support the potential use of enhanced natural attenuation for LP remediation.

Additional studies should be conducted to definitively answer whether the LP components are capable of being biologically degraded in the environment and at low concentrations with other organics in a WWTP. The IT study results did not conclusively demonstrate that the TEAN component of LP was biodegradable, while the TEAN degradation data generated by Kaplan et al. (1984) suggested that it should be amenable to biological degradation. Based upon these results, it could be concluded that bioremediation of soil and aqueous matrices highly contaminated with LP is not feasible, but that natural attenuation of soils and biodegradation of dilute aqueous wastes may be possible.

Perceived data gaps

Several studies conducted to date have indicated that LP components should be amenable to biodegradation, but LP bioremediation has not been demonstrated to be achievable. The Kaplan et al. (1984) study investigating biodegradation of TEAN, not LP, indicated that TEAN was biodegradable at concentrations of up to 1,000 ppm in soils. The Frings et al. (1994) study demonstrated that TEA could be biodegraded. However, the IT Corporation (1995) study investigating bioremediation of LP did not conclusively demonstrate that LP could be biodegraded in soil cultures or in SBRs. Although it is doubtful that biodegradation can be demonstrated for LP concentrations that would enhance the economic viability of bioremediation, biodegradation of trace LP concentrations may support the use of natural attenuation.

Enhanced Natural Attenuation

Conclusions of studies conducted to date

In this letter report, the term "enhanced natural attenuation" has been defined to refer to the process of natural attenuation enhanced only by pH adjustment. When used in reference to soil remediation, natural attenuation

typically refers to the natural processes by which soil contaminant concentrations are reduced by chemical reactions, physical transport mechanisms, or other means. To achieve the desired level of human health and environmental protection, the enhanced natural attenuation process would have to bioremediate TEAN and denitrify residual nitrate.

No studies could be found in the literature describing investigations of LP-contaminated soil remediation by enhanced natural attenuation processes, but data from other studies can be used to assess the potential use of this method. An LP/soil contact study referenced previously (Gunnison, Pennington, and Marcev 1994) noted that undiluted LP sterilized soils. However, when LP was diluted 50:50 (volume basis) with water before spilling onto soil, all microflora were killed unless the soil was washed with water within 1 hr of contact. When contacted by the diluted LP, microbial population levels dropped by one to several orders of magnitude, then recovered to near control levels within 5 days.

The results of these soils studies indicate that prompt spill response activities would need to be taken if enhanced natural attenuation is to be a viable remedial response. Spilled LP could be neutralized using baking soda, soda ash, or any other comparable weak alkali to reduce the dermal contact risk. The fate of the residual LP-derived nitrate contamination would depend upon the types of microbes that returned to repopulate the impacted area.

Evaluation of enhanced natural attenuation as an LP spill remediation technology

The LP/soil interaction study result discussed earlier indicates that if soils impacted by spilled LP are flushed within 1 hr, the natural microbial population has a chance to recover. Results of a second study (Kaplan et al. 1984) indicate that HAN is not stable above a pH of approximately 5.9. Therefore, for incidental drips, spills, or other releases of LP to a soil matrix, soil flushing with a mildly alkaline solution may both allow the recover of prespill microbial populations and degrade the HAN.

Enhanced natural attenuation might be an especially attractive option for periodic incidental LP releases or small spills, neither of which are likely to result in an unacceptable nitrate loading in the groundwater. Therefore, if the dermal contact risk is reduced by mixing baking soda, soda ash, or a similar alkali into the surficial soils, and microbial growth returns to the impacted area, enhanced natural attenuation may sufficiently reduce the potential health and environmental risks.

One of the studies reviewed (Section III of this report) noted that denitrifying bacteria, which are capable of converting nitrate to volatile nitrogen, are sensitive to low soil pH (values less than 4). As the pH of soils used in the Adrian investigation was reduced to values ranging from 1.5 to 4.5 after saturation with LP, the potential for ready denitrification of LP-contaminated

soil is limited unless LP-contaminated soils are neutralized. If a weakly alkaline material is added to raise the soil pH above 4, the denitrifying bacteria have a chance to survive and potentially utilize the HAN released nitrate and the remaining TEAN as substrates.

The costs of implementing a natural attenuation alternative are difficult to estimate, as they will vary depending upon the size of the LP spill. For spills of less than 40 gal, modeling work previously conducted (Section IV of this report) suggests that there will be no adverse impacts in even a worst case scenario of unreactive soils and a relatively high groundwater table. For larger spills of greater than 40 gal, the costs will range from minimal to only slightly less than that of soil washing. The enhanced natural attenuation option, although not a "technology," is also not a completely "hands-off" approach. A significant amount of effort would be required to demonstrate that the environment is being protected from a larger spill and that the nitrate is being reduced. This demonstration often requires extensive computer modeling using site-specific information and laboratory demonstration that the endogenous microflora are capable of denitrifying the remaining contaminants. The costs of this work will vary according to geographical location of the personnel conducting the modeling and laboratory work, the proximity of sensitive receptors, and the requirements of the local regulatory code.

Perceived data gaps

Several data gaps exist before implementation of enhanced natural attenuation could be considered for use as a remedial technology. The two primary concerns with LP spilled to the environment are the potential for dermal contact with the highly acidic soil and the potential for nitrate contamination of the groundwater.

The dermal contact risk could be reduced by adding dry baking soda, soda ash, or a similar alkali to neutralize soils impacted by an LP spill. No studies have been conducted to assess whether microbes could recolonize LP-contaminated soils that were subsequently neutralized by the addition of a mild alkali. Tests could also be conducted to determine if rototilling baking soda, soda ash, or a similar alkali into the soils would improve the microbial regrowth following the LP contact.

The more crucial question is whether nitrate produced by the HAN and TEAN degradation and/or dissociation would typically reach the groundwater before the endogenous microflora were able to recolonize the impacted area and denitrify the soils. If the nitrate is likely to be flushed quickly, the test results discussed under Current status of studies (Section IV of this report) could be used to estimate the potential nitrate impact to groundwater. A potential data gap to be addressed is the likelihood that native microbes, not microbes cultured to be LP tolerant, would be able to denitrify the soils prior to the nitrate reaching the groundwater. The viability of enhanced natural

attenuation would increase in direct proportion to the amount of denitrification produced by typical endogenous microflora in LP-contaminated soils.

5 Recommendations to Support the Selection and Implementation of an LP Spill Remediation Technology

Additional biological studies should be conducted to conclusively establish whether TEAN is susceptible to biodegradation. The rate of HAN and TEAN sorption in soils with high organic content should also be established using LP concentrations more closely approximating conditions subsequent to an LP spill during field use. Consideration should also be given to conducting investigations to determine whether enhanced natural attenuation is capable of protecting human health and environmental concerns following spills of less than 40 gal.

The selection of an LP remediation technology must be based upon the quantity of LP spilled and the environmental sensitivity of the impacted area. Because LP will be packaged in individual 40-gal containers and stored prior to use, the typical LP spill size is anticipated to be less than 40 gal. Spills due to leaks and drips during LP transfer from the original container into the artillery equipment will likely be less than 10 gal.

Environmental concerns due to spilled LP are primarily due to the resultant low soil pH, increased nitrate, and TEAN concentrations in both soils and water. HAN degrades relatively quickly in the environment, so HAN does not present a long-term environmental concern except for residual nitrate. TEAN is expected to dissociate in the environment, releasing nitrate and TEA, a compound that has been shown to be biodegradable by acclimated anaerobic bacteria. Neutralization of the LP-impacted soils following a spill should promote microbial recolonization in the area. Past groundwater modeling efforts indicate that a 10-gal spill of LP should not lead to exceedances of the U.S. 10-mg/l nitrate standard, and that a 40-gal spill should only temporarily exceed the standard; so the nitrate from most spills should not adversely impact groundwater resources. The most significant uncertainty impacting the selection of a remedial alternative appears to be whether, and, if so, how

quickly typical native soil and groundwater microflora can degrade concentrations of TEAN/TEA and nitrate resulting from an LP spill.

Recommendations to Address Perceived Data Gaps in LP/Environmental Media Studies

Chapter 3 described the studies conducted on interactions of LP with soils, water, asphalt, and concrete. Results of these studies were summarized, and data gaps were identified where the results relate to potential remedial strategies. This section discusses how these data gaps could be addressed to yield results that could be used to assess potential LP spill remediation technologies.

A significant data gap identified from the results of the LP/soils interactions studies was the extent to which TEAN would adsorb to spill area soils. Soil sorption study results (Pennington et al. 1994) indicate that even soils with a high organic carbon content will not significantly retard the movement of TEAN through the vertical soil profile, while modeling efforts (Section IV of this report) predict that LP spill area soils will continue to act as a residual groundwater contamination source. The longer the LP spill contaminants are sorbed to the soil, the more likely it is that soil microbes will be able to degrade or mineralize the contaminants.

The question of whether spill area soils can act as a continual source of LP contamination must be answered before an appropriate remediation strategy can be developed. The speed at which the LP degradation/dissociation products move vertically through the spill site soils is a critical point because that timing will affect the spill response activities. If the spill occurs during a rainstorm and a moderate amount of LP is spilled, remediation of the soil may not be practical because the majority of the LP might already have washed through the soil column. Conversely, if the LP is spilled to a soil with low vertical hydraulic conductivity and a high organic carbon content, spill remediation may be practical for a period of several weeks or longer after the spill to limit the potential groundwater impact.

Another data gap exposed by a review of the LP/environmental media studies was that full-strength LP sterilized the soils tested while diluted LP only temporarily reduced the microbial population. To assess whether neutralization of LP-contaminated soils will be effective, a soil study could be conducted by contacting undisplaced soils, if possible, with LP followed by mixing with an alkali powder such as soda ash. The study could also be conducted in a laboratory using a large patch of soil that is only contacted with LP in the middle. This would give the microbes from the unaffected perimeter a chance to recolonize the impacted center of the soil sample. Data on how quickly soil biota recolonize sterilized soils later neutralized with an alkali will determine whether natural attenuation will be sufficient or whether ex situ technologies will be required to remediate soils impacted by an LP spill.

Recommendations to Address Perceived Data Gaps in LP Remediation Studies

Three potential LP spill remediation technologies were reviewed, as described in Chapter 4. The first potential LP remediation technology reviewed was soil washing, which was demonstrated to be capable of reducing LP contamination in several types of soil. One data gap identified in the soil washing study reviewed is the effect that sorption may have on remediation of LP-contaminated soils. As soil washing was shown to be capable of successfully treating soils with a relatively high organic matter content, the impact of LP sorption due to organic matter does not impact the viability of soil washing as much as it does bioremediation- and natural attenuation-based processes.

A more important question with regard to implementation of the soil washing technology is what could be done with the contaminated water generated by this process. One potential alternative would be to discharge the wastewater to an operating biological wastewater treatment plant. The TEA remaining in the soil washing wastewater should be susceptible to biodegradation in the presence of large quantities of other biodegradable organic carbon. Therefore, the TEA content should not prohibit the discharge of LP-contaminated soil washing wastewater to a reasonably sized municipal or industrial biological wastewater treatment plant.

The second potential LP remediation technology reviewed was bioremediation. A study (IT Corporation 1995) conducted to investigate bioremediation of LP did not demonstrate that the LP could be biodegraded in soil cultures or in sequencing batch reactors. Although up to 1,000 ppm TEAN in soils has been shown (Kaplan et al. 1984) to be susceptible to biodegradation, the bioremediation potential has not been demonstrated to be achievable for LP. Based upon the IT Corporation study results, additional bioremediation studies are not warranted at this time.

The third and last remedial technology investigated was the enhanced natural attenuation process. Enhanced natural attenuation would be implemented by neutralizing the surface soils impacted by an LP spill with a weak alkali, followed by monitoring for possible LP contaminant degradation as natural endogenous microflora repopulate the area. No studies have been conducted to assess whether denitrifying microbes could recolonize LP-contaminated soils that were subsequently neutralized with an alkali. A test could be conducted to determine how fast microbes would return to the soils impacted by the LP, and whether these microbes could remove nitrate and TEAN/TEA from the subsurface soils. Samples collected over time should show the rate at which nitrate and TEAN/TEA are attenuated from the soils. Tests could also be conducted to determine if rototilling the soils would improve the microbial regrowth following the LP contact and application of the neutralizing agent.

Recommendations for Future LP Remediation Studies

For the immediate future, soil washing may be the best remedial option for larger spills to soils. Environmental impacts of an LP spill of a specified volume will vary according to the type of soil impacted, the slope of the impacted area, and the proximity of environmental receptors. For this letter report, the term "larger" spills will be estimated to be a volume range centered near the 245-gal volume indicated to be capable of causing groundwater nitrate concentrations directly beneath the spill of greater than 10 mg/l by a previously referenced study (Adrian et al. 1995). The models were developed using conservative "worst case" values for many parameters, but still indicated that the nitrate plume produced by a 40-gal spill would disperse quickly, and that the nitrate concentration would quickly decrease to less than 10 mg/l. Of the three technologies addressed by this study, soil washing is the only technology demonstrated to be capable of removing significant quantities of LP from soils in a reasonable amount of time.

For "smaller" spills, which are more likely to occur, enhanced natural attenuation may be adequate to protect both human health and the environment. The release of a full drum of LP is unlikely, so the majority of spills are likely to pose an environmental threat that may be adequately controlled through enhanced natural attenuation processes. Human health would be protected by the neutralization of the impacted surface soils. Neutralization would decrease the likelihood of skin irritation due to contact with the acidic soils. The environment would also be protected because the smaller spill size would be unlikely to cause an exceedance of the 10-mg/l U.S. drinking water standard.

The primary focus of future studies, therefore, should be to evaluate whether enhanced natural attenuation provides adequate groundwater protection, as soil neutralization is expected to protect human health. A literature search was conducted to find results of any studies conducted to assess whether naturally occurring denitrifying bacteria could reduce nitrate concentrations in soils and groundwater. This search revealed studies that indicated soils or groundwater systems that were (Bottcher et al. 1990; Fustec et al. 1991) and that were not (Schwan, Kramer, and Gericke 1984) able to remove nitrates by conversion to nitrogen. A more detailed study of nitrate fate in the environment could be conducted to answer this question.

The recommendation is that the Army consider implementation of enhanced natural attenuation for LP spills that do not pose an immediate threat to a groundwater supply. Mathematical models simulating nitrate impacts to groundwater from a spilled LP drum indicated that compliance with the groundwater nitrate standard would be maintained in a typical aquifer everywhere but directly beneath the spill site. Further efforts should be focused on evaluating the natural degradation of TEA and nitrate in soils and groundwater following neutralization of spill area soils.

References

- Adrian, D. D., and Myers, T. E. (1994). "Chapter 3: Runoff, infiltration and transport." "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Arthur D. Little, Inc. (1994). "Guidance document for preparation of liquid propellant XM46 spill response plans," prepared for the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Billack, J. (1993). "Liquid propellant ammunition system - XM46 - preliminary draft exposure study."
- Bottcher, J., Strebel, O., Voerkelius, S., Schmidt, H. (1990). "Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer," *Journal of Hydrology* 114, 413-424.
- Decker, M., Klein, N., Greedman, E., Leveritt, C., Wojciechowski, J. (1987). "HAN-based liquid gun propellants: Physical properties," BRL-TR-2684, U.S. Army Ballistic Research Laboratory.
- Department of Defense Environmental Technology Transfer Committee. (1994). "Remediation technologies screening matrix and reference guide," 2nd ed., EPA/542/B-94/013, NTIS PB95-104782, October 1994.
- Frings, J., Wondrak, C., Schink, B. (1994). "Fermentative degradation of triethanolamine by a homoacetogenic bacterium," *Arch. Microbiol.* 162, 103-107.
- Fustec, E., Mariotti, A., Grillo, X., and Sajus, J. (1991). "Nitrate removal by denitrification in alluvial groundwater: Role of a former channel," *Journal of Hydrology* 123, 337-354.
- Gunnison, D., Pennington, J., and Marcev, J. R. (1994). "Chapter 4: Effects on soil microflora." "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

- IT Corporation. (1995). "Biodegradation of liquid gun propellant formulation 1846," Technical Report No. SFIM-AEC-ETD-CR-95026, U.S. Army Environmental Center, Aberdeen Proving Ground, MD.
- Kaplan, D. L., Riley, P. A., Emerson, D. J., Kaplan, A. M. (1984). "Degradation of ammonium nitrate propellants in aqueous and soil systems," *Environmental Science and Technology* 18(9), 694-699, Published by American Chemical Society.
- Pennington, J. C., and Price, C. B. (1994). "Chapter 2: Soil Sorption." "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathburn, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994a). "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, Prepared for Office of Program Manager, Advanced Field Artillery System/Future Armored Resupply Vehicle, Picatinny Arsenal, Prepared by U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Pennington, J. C., Price, C. B., Harrington, J. M., Stewart, J. L., and Busby, J. A. (1994b). "Chapter 1: Soil characterization and contact screening tests." "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Schwan, M., Kramer, D., and Gericke, C. (1984). "Simulation of nitrate in groundwater," *Journal of Groundwater Chemistry and Biology* 2, 163-171.

Section II

Soil Washing

1 Introduction

Background

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. Since the active components of LP are readily soluble salts, soil washing for removal of LP from soils contaminated by LP spills is a reasonable approach for remediation. Soil washing is also a potentially cost-effective remediation alternative, since the greatest expense is likely to be actual excavation costs. Furthermore, soil washing results in a finished product that is little different from the prespill soil and can, therefore, be readily reassimilated into the environment.

Soil washing is a process by which soluble contaminants are removed by repeated flushing of excavated soil with water. Wastewater containing the removed contaminant can be further reduced by evaporation of water or by passing the water through a filtration system designed to remove the contaminant.

A discussion of the theory of backwashing and contaminant transport is presented below. The design of the experiments subsequently described (Materials and Methods) are based on these theories. An evaluation of available technologies for remediation of LP spills, including soil washing, can be found in Section I of this report.

Soil Backwashing Theory for Particulate Matter Removal

During the twentieth century, the water treatment industry has employed a filtration process for removing particulate matter from wastewaters. The treatment system uses filters called "rapid sand filters" or "rapid rate filters" consisting most commonly of sand and less commonly of crushed anthracite, called "anthrafilt." The process water applied to rapid sand filters is typically pretreated with coagulating and flocculating agents and processed through a sedimentation basin where larger and heavier particles are removed. Thus,

the function of the rapid sand filter is to remove small, light particles. After filtering a certain volume of water, the particulate material, which is captured in the filter, is removed in a process called backwashing.

Backwashing consists of reversing the direction of water flow in the filter from its normal downward direction to an upward direction. The filter bed expands as the upward flow velocity increases until its thickness increases by 25 to 40 percent. The expanded bed allows the captured particulate material to be dewatered and prepared for disposal. When the backwash process is completed, the flow direction is reversed, and the clean filter is placed back into operation to again remove particulate matter from the process water. Backwashing can be applied to the removal of contaminants such as LP from soil. The LP-contaminated soil takes the place of sand or anthrafil in the wash unit. Soil washing utilizes an upward direction of flow of wash water to expand the soil bed and to facilitate removal of LP.

Backwashing theory has been developed to describe the process of expanding the filter bed to allow the captured particulate matter to be washed from the filter. Backwash theory is readily available in textbooks including Clark and Viessman (1965), Steel and McGhee (1979), and Weber (1972). Steel and McGhee (1979) state that the velocity that just begins to expand the bed (U_b) is

$$U_b = \frac{0.3682 (D_{60})^{1.82} [\rho (\rho_s - \rho)]}{\mu^{0.88}} \quad (1)$$

where

U_b = backwash velocity, m/min

D_{60} = effective size of filter particles, mm (60 percent by weight of filter material is smaller in diameter than D_{60} size)

ρ = water density, g/cm³

ρ_s = density of filter material, g/cm³

μ = viscosity of water, centipoise

The backwash velocity at 20 °C for sand ($\rho_s = 2.65$ g/cm³) is typically less than

$$U_t = 10 D_{60} \quad (2)$$

While for anthracite ($\rho_s = 1.55$ g/cm³)

$$U_t = 4.7 D_{60} \quad (3)$$

since too high a velocity will wash out the finer portions of the filter material. U_t in Equations 2 and 3 is the terminal velocity (meters per minute) of particles of size D_{60} . The bed is completely fluidized when

$$U_b = U_t n^{4.5} \quad (4)$$

where n (dimensionless) is the porosity of the medium.

Particulate matter is removed by shear from the backwash water flowing past filter particles and by abrasion when suspended particles collide with each other. Maximum abrasion occurs when

$$U_b = 0.1 U_t \quad (5)$$

Contaminant Dilution and Washout Theory

Since LP is soluble in water, washout of LP from soil can be visualized in a simplified manner. The expanded bed of soil in the washing column can be treated as a completely mixed region. The remainder of the volume of the wash column above the expanded bed is a highly mixed region. The influent wash water dilutes the liquid in the wash column, which then washes out with the effluent. The dilution equation is

$$C(V) = C_o \exp \left[-\frac{V}{V_T - V_S} \right] \quad (6)$$

where (See note below on units)

$V = Q \times t = \text{volume of wash water eluted, length}^3$

$Q = \text{washwater flow rate, length}^3/\text{time}$

$C_o = \text{initial concentration in wash water, mass/length}^3$

$\exp[.] = \text{exponential function, dimensionless}$

$V_T = \text{volume of completely mixed region of wash column, length}^3$

$V_S = \text{volume of soil solids in wash column, length}^3$

Note: When units are expressed as length^3 , $\text{mass}/\text{length}^3$, or $\text{length}^3/\text{time}$, the meaning is that any consistent set of units can be used such as cgs (centimeter, gram, second) or mks (meter, kilogram, second).

Objective

The objective of the soil washing studies was to provide the technical data necessary for implementation of soil washing as a remediation method for soils contaminated with LP.

2 Materials and Methods

Soil Amendment

Four soils from previous experiments (Pennington et al. 1994) were tested. The soils were selected to represent a variety of compositions including sand (Table 1 and Figures 1, 2, 3, and 4). Figures 1, 2, 3, and 4 show the gradation curves of the China Lake, Picatinny, Socorro, and Yuma soils as determined by the U.S. Army Engineer Waterways Experiment Station (WES) Geotechnical Laboratory (26 April 1993). The China Lake soil is silty sand (SP-SM), Picatinny is sandy silt (ML), Socorro is sandy clay (CL), and Yuma is silty sand (SM). The silt plus clay fraction of each can be used to rank the soils in terms of fine particles: Socorro (62 percent), Picatinny (50 percent), Yuma (48 percent), and China Lake (7 percent). Foaming occurs as a result of HAN reactions in the soil (Pennington et al. 1994).

Table 1
Characteristics of Soils

Soil	Sand Percent	Silt Percent	Clay Percent	Organic Matter Percent	Water ¹ Percent	Size, mm		Uniformity Coefficient ²
						D ₁₀	D ₆₀	
China Lake	97.5	0.0	2.5	0.53	1.1	0.092	0.5	5.25
Picatinny	55.0	37.5	7.5	2.92	11.5	0.042	0.12	2.86
Socorro	42.5	30.0	27.5	0.53	12.9	<0.001	0.068	>68
Yuma	75.0	20.0	5.0	0.21	3.1	0.007	0.11	15.71

¹ (Weight of water, g/Weight of solids, g) × 100.

² D₆₀/D₁₀, where D₆₀ and D₁₀ are the sieve sizes that pass 60 and 10 percent by weight of a soil sample, respectively.

Soils (3,000 g on a wet weight basis) were amended with undiluted LP (345.7 g) by manual stirring. The amount of soil was chosen to provide a column depth of soil large enough for practical observations and measurements of bed expansion during washing. The amount of LP was chosen so that the soils would be somewhat saturated with LP, simulating the upper layer of an actual LP spill. Before loading into the backwashing apparatus,

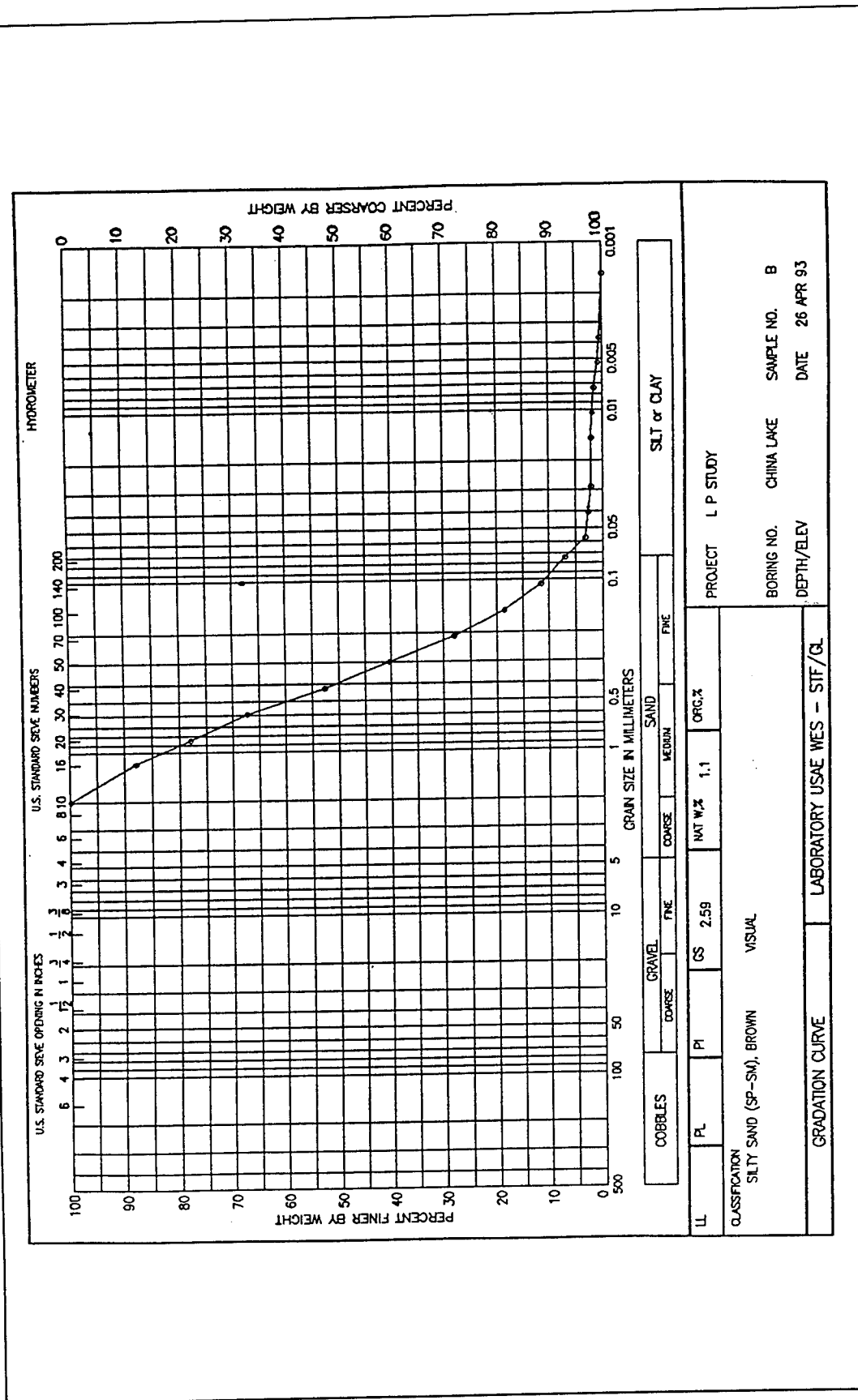


Figure 1. Size gradation curve for China Lake soil

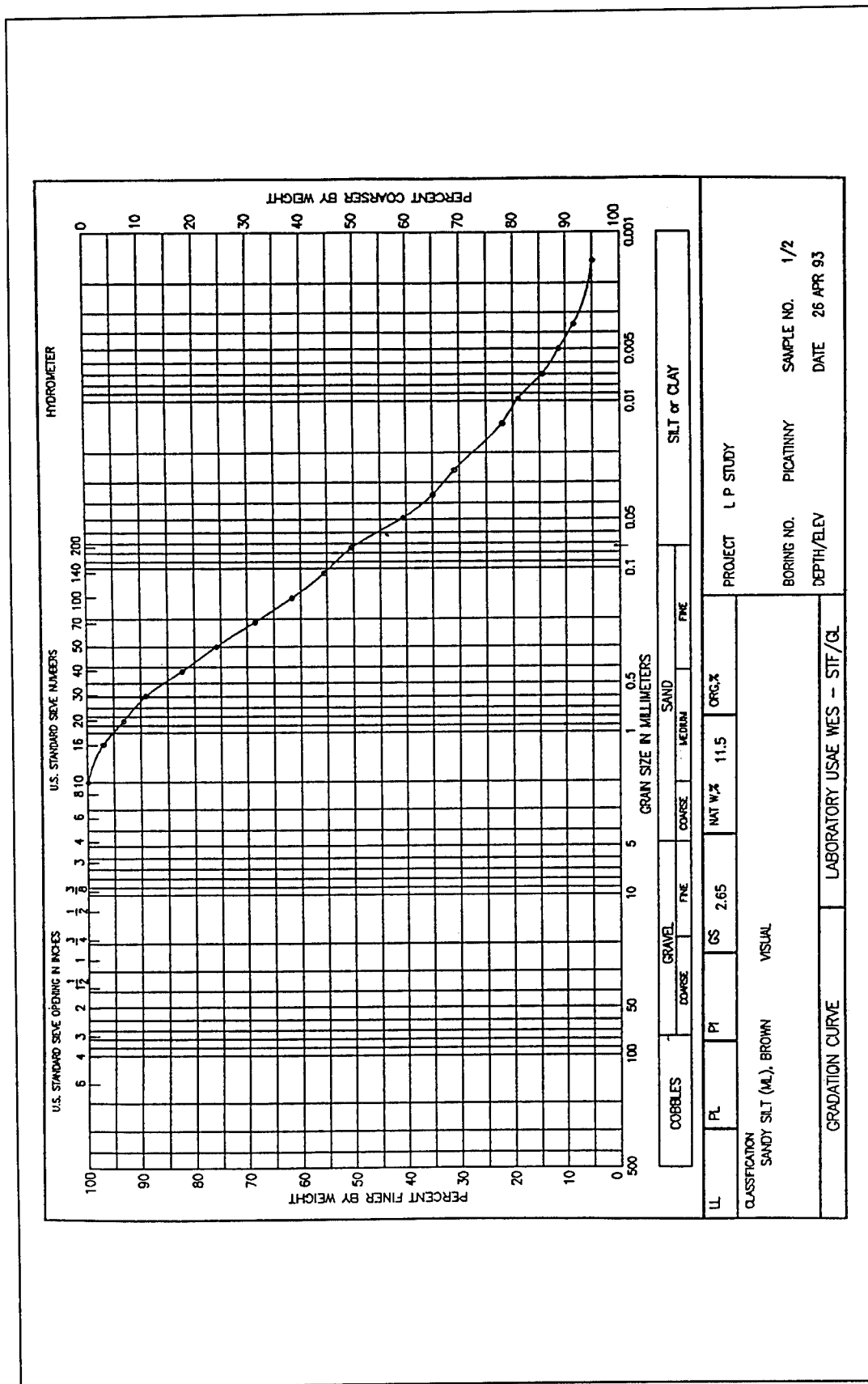


Figure 2. Size gradation curve for Picatinny soil

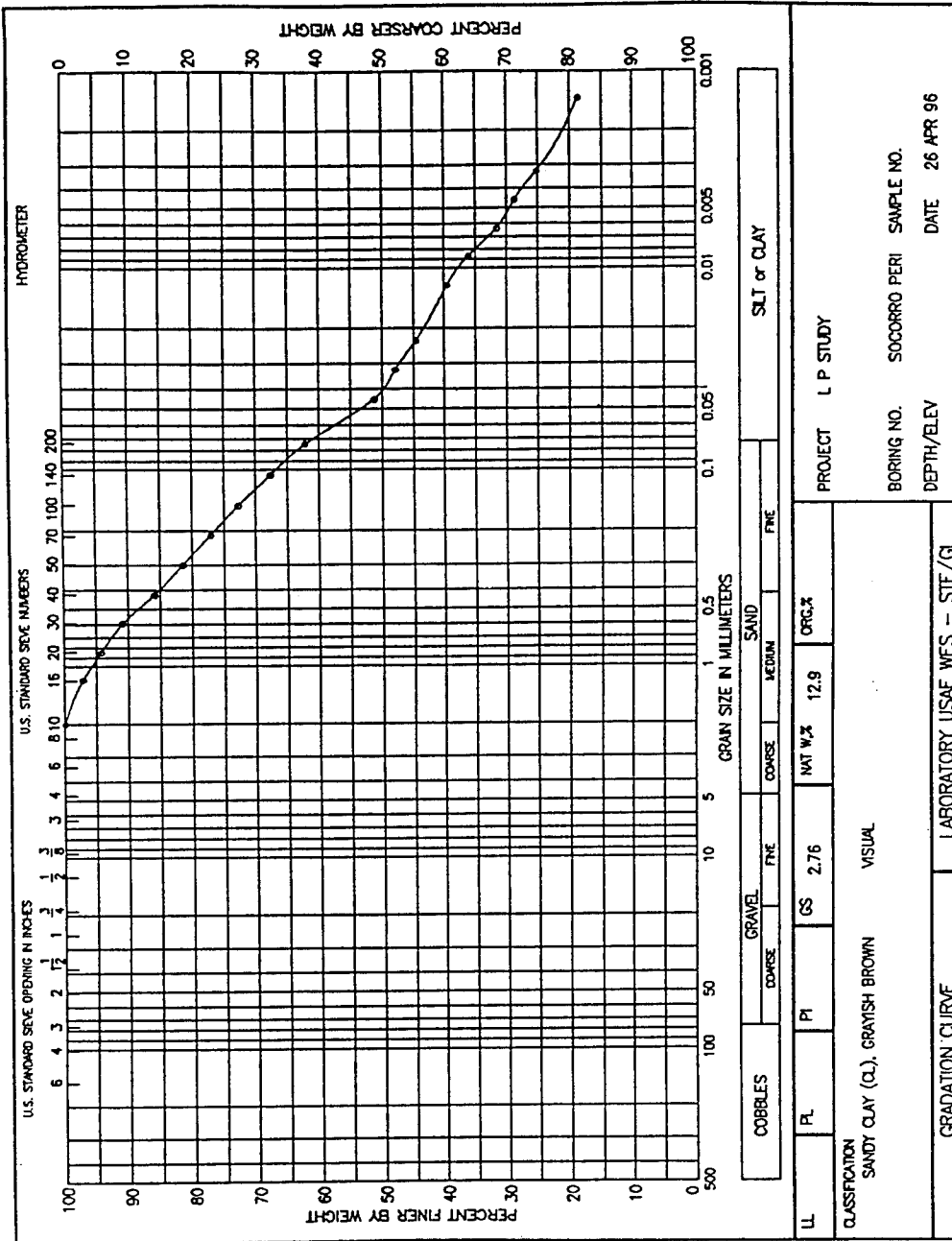


Figure 3. Size gradation curve for Socorro soil

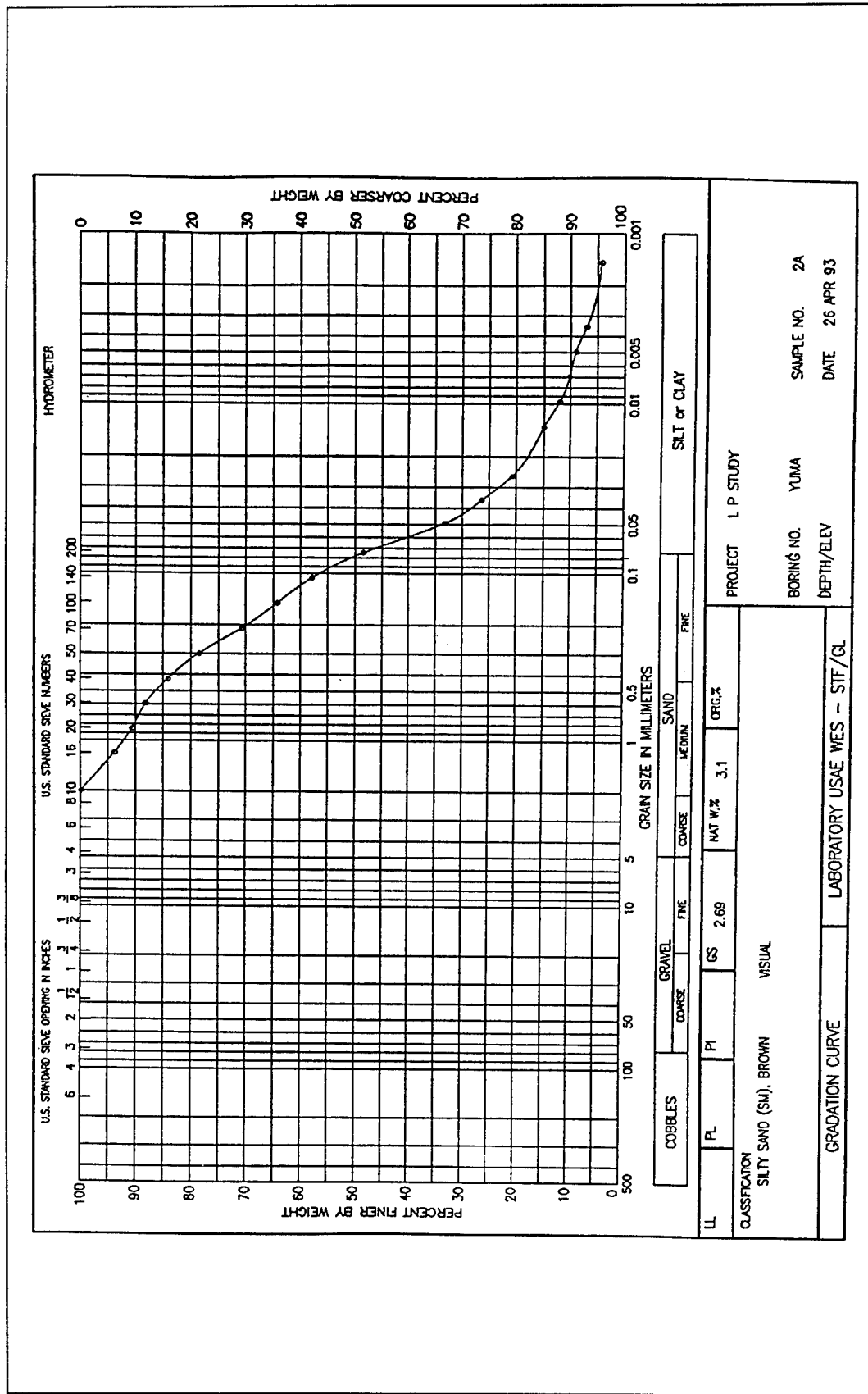


Figure 4. Size gradation curve for Yuma soil

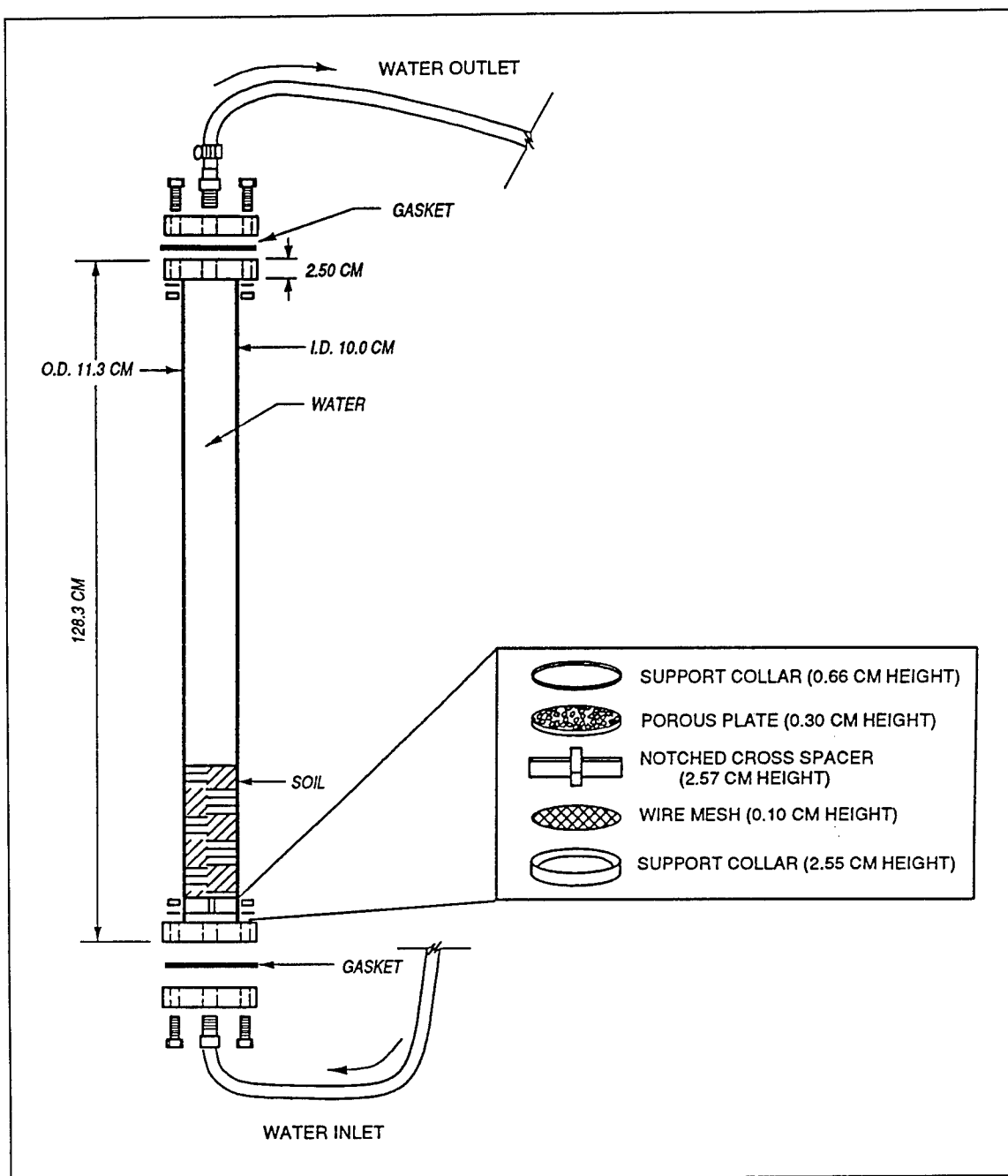


Figure 5. Soil backwashing apparatus

soils were allowed to stand for 1 hr to allow the LP to penetrate the sample thoroughly.

Backwashing Apparatus and Procedure

The backwashing apparatus consisted of a plexiglass column 128.3 cm (50.5 in.) long and 10.0 cm (4 in.) in diameter (Figure 5). The amended soil

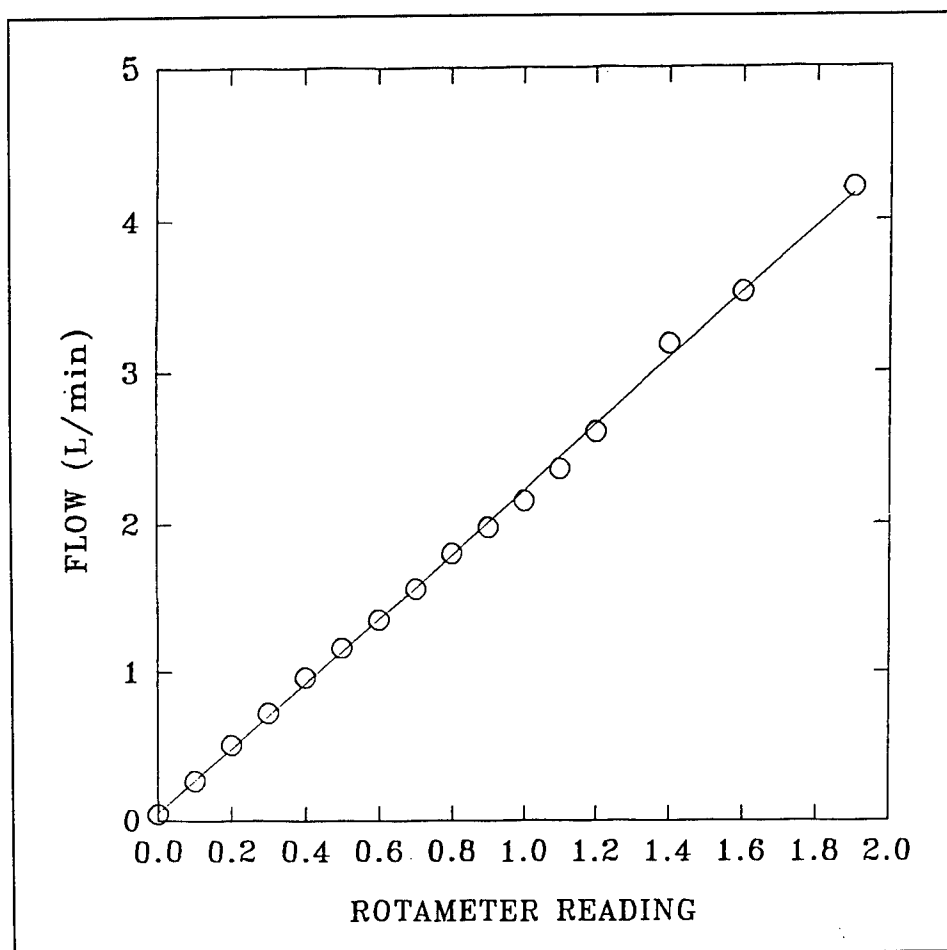


Figure 6. Calibration curve for rotameter used for measuring flow rate to soil backwashing column

was supported in the column by a porous plate at the bottom. Before loading the amended soil into the column, the apparatus was backflushed from the bottom to fill the intake lines with water all the way to the top of the porous plate. A total of 2 l of water was also added through the top of the column to bring the water to a depth of 25.4 cm (10 in.). After transferring the LP-amended soil into the column and allowing the mixture to settle for about 10 min, the soil depth was measured. Water from a cold water tap was forced through the bottom of the column after passing through a rotameter (Model #D6428, Gilmont Instruments, Inc., Barrington, IL) and a pressure gauge (Catalogue #AS1004, Ashcroft Instrument Division, Berea, KY) to control and monitor flow rate. The rotameter was calibrated (Figure 6) prior to the backwash experiments. The water temperature from this tap was measured at the beginning of each experiment. The column was equipped with outlet tubing at the top from which backwash fractions were collected into 500-ml high density polyethylene sample bottles. Samples were collected periodically (minutes to hours) until about 50 samples were obtained. The volume of each sample was approximately 500 ml. Periodically, soil depth

was measured and visual observations were recorded describing soil appearance and presence of foaming.

Experimental Conditions

Two runs, one at high and one at low flow rates, were conducted for each of the four soils. After removing a small subsample for total suspended solids (TSS) analysis (U.S. Environmental Protection Agency (EPA) 1982), each sample was filtered through a glass microfiber filter (Whatman GF/F) and split into two subsamples. One subsample of 250 ml was preserved with 1 ml H_2SO_4 and analyzed for total Kjeldahl nitrogen (TKN) (EPA 1990) and nitrate/nitrite-nitrogen (NO_3/NO_2 -nitrogen) (EPA 1990). The other subsample of approximately 20 ml was transferred to an amber glass vial for HAN and TEAN analysis by ion chromatography (Pennington et al. 1994). At the end of each experiment except the first, the soil in the column was exuded and sectioned into three parts: top, middle, and bottom. Each section was analyzed for HAN, TEAN, TKN, and NO_3/NO_2 -nitrogen by methods cited above. In the first experiment, the soil layer was exuded, but was not sectioned before analysis.

3 Results and Discussion

Soil Washout From Column

For each experiment, the applied backwash velocity was calculated using Equation 1. The size of a hypothetical particle that would just wash from the column was calculated by equating the particle's downward settling velocity, which is a function of particle size, with the upward velocity of water in the column. From these results and the soil gradation curves, the fraction of soil that was expected to be washed from the wash column was calculated.

Applied backwash rates and projected and measured soil washout data are shown in Table 2. Projected soil washout values were consistently 1 to 3 times larger than measured soil washout values. Two plausible reasons for this discrepancy are (a) the cohesive nature of the soils investigated and (b) shortcomings in the theory behind Equation 1. Some of the smaller individual grains of soil clumped together and behaved like a larger sized single particle. Larger sized particles have a larger settling velocity than smaller particles, so a clump of small particles would remain in the backwash column contrary to predictions made on the basis of each particle's size. The second reason for discrepancy between Equation 1 and the experimental values of soil washout data is due to the fact that Equation 1 was developed for the

Table 2
Backwashing Rate Applied to Each Soil and Projected and Measured Soil Washout From Column

Soil	Wash Rate ℓ/min	U_b m/s	Critical Size Particle mm	Soil Fraction Smaller Than Critical Size Percent	Initial Mass of Soil in Column g	Projected Soil Washout g	Measured Soil Washout g
China Lake	0.76	2.60E-03	0.039	2.5	2,967	74.2	36
	1.7	1.61E-03	0.019	3	2,967	89	46.7
Picatinny	0.51	1.08E-03	0.014	24	2,691	645.8	322.2
	0.96	2.04E-03	0.024	32	2,691	861.1	994.6
Socorro	0.26	5.50E-04	0.008	35	2,657	930	297
	0.51	1.08E-03	0.014	42	2,657	1,115.9	508.9
Yuma	0.38	8.10E-04	0.01	12	2,910	349.2	N
	0.96	2.01E-03	0.023	21	2,910	611.1	N

Note: N = Not measured.

expansion of sand or anthracite filters. These filters are characterized by a narrow range of particle sizes; therefore, Equation 1 is being applied beyond the limits for which it was developed. Although caution is advised when predicting solids carryover loads for cohesive soils using Equation 1, the projected washout values were conservative for the experiments with the sole exception of Picatinny soil at high flow, where the measured washout was slightly larger than projected.

Washout of HAN, TEAN, NO_3 , and TKN

Examination of Figures 7, 8, 9, and 10 shows that backwashing was effective in rapidly reducing the concentration of HAN and TEAN from each of the LP-contaminated soils. The relative order of cleaning HAN and TEAN from each soil was China Lake $\approx$ Yuma $>$ Picatinny $>$ Socorro, while the respective volumes of backwash water applied to the above soils was 30, 30, 100, and 150 ℓ .

The term $V_T - V_S$ in Equation 6 represents the total volume of water in the expanded bed of soil inside the wash column. If the contaminants in the wash column washed out according to Equation 6, then the concentration of HAN, TEAN, NO_3 , and TKN would decline exponentially with wash water volume as shown in Table 3. The washout of each species generally followed an exponentially declining curve (Figures 7, 8, 9, and 10) with certain exceptions for China Lake low flow.

Table 4 presents the results of fitting Equation 6 to each species shown in Figures 7, 8, 9, and 10. The experimental data shown in the figures were fit to Equation 6 by using a math transform function in SigmaPlot (Jandel Corp., Corte Madera, CA). The parameter $V_T - V_S$ and C_o were treated as unknowns. The parameters in the column labeled "Calculated $V_T - V_S$ " and "Calculated C_o " were generated by the SigmaPlot program. The column labeled "Experimental $V_T - V_S$ " was determined from the dimension of the wash column, V_T , and the volume of soil in the column at the beginning of an experiment, V_S . In effect, the "Calculated $V_T - V_S$ " was determined by assuming that the soil expanded to fill the entire backwash column. As soil washed from the column during an experiment, V_S would decrease and the experimental $V_T - V_S$ term would increase. The maximum value of $V_T - V_S$ if all of the soil washed out of the column is $V_T = 10.19 \ell$. The ratio of "Calculated $V_T - V_S$ " to "Experimental $V_T - V_S$ " represents the fraction of total volume inside the column that exhibited complete mix behavior, and is labeled the "active zone factor" (Table 4). An average active zone factor for HAN is 0.76 and for TEAN is 0.86. Combining the results for HAN and TEAN yields an overall active zone factor of 0.81.

Socorro soil at the high flow rate was the only soil in which the calculated $V_T - V_S$ was larger than the experimental $V_T - V_S$ value. This behavior indicates short circuiting in the wash column as the high silt and clay content of

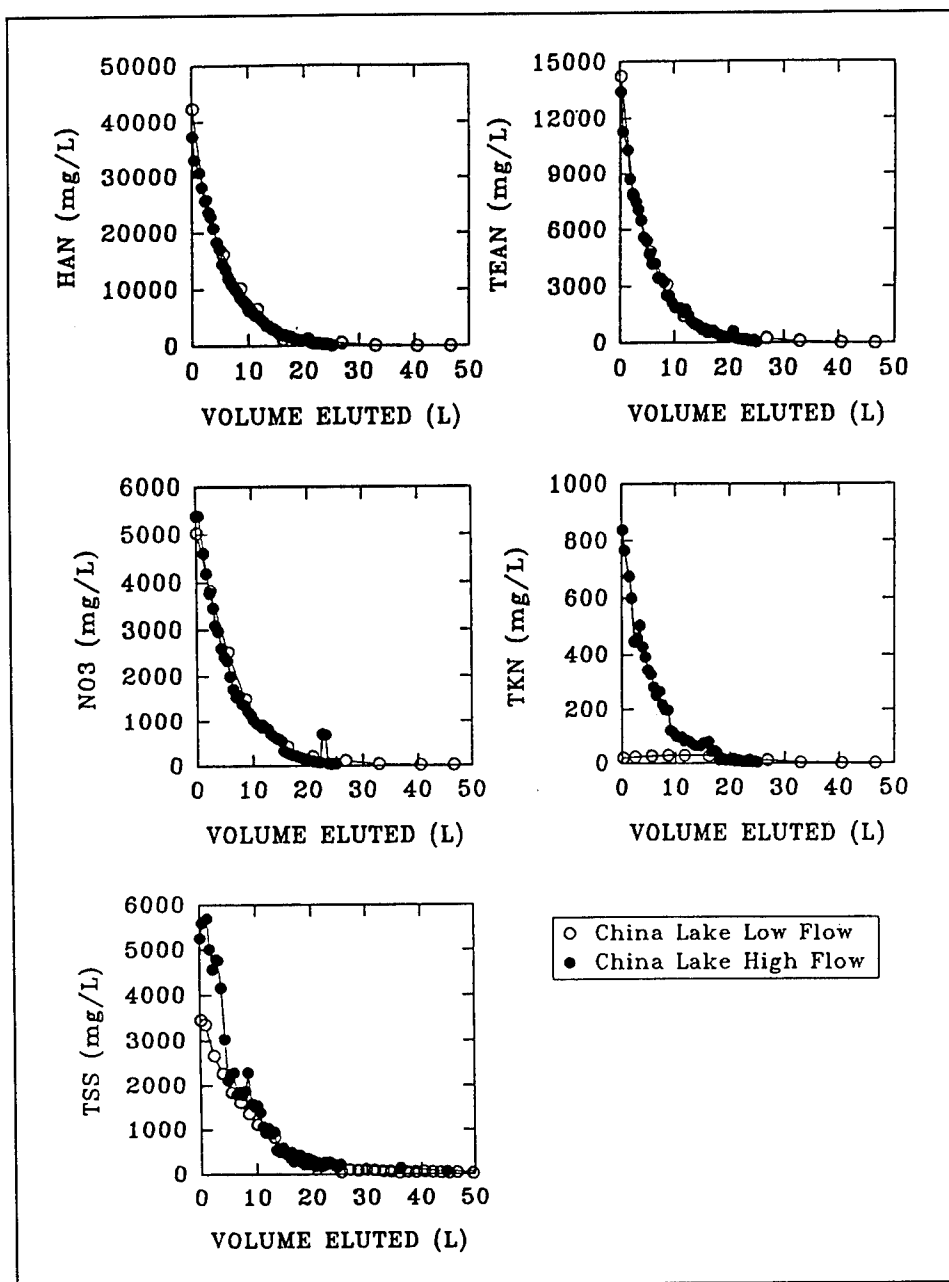


Figure 7. Effluent concentration of HAN, TEAN, NO₃, TKN, and TSS for China Lake soil

Socorro soil added to its cohesion to encourage the flow to take place through a few large channels, resulting in less efficient soil washing.

The removal of TKN from the soil columns was sometimes described by Equation 6. TKN represents organic nitrogen and ammonia. As HAN and TEAN dissociate, the concentration of ammonium ion should predominate over the concentration of organic nitrogen. The ammonium ion has a

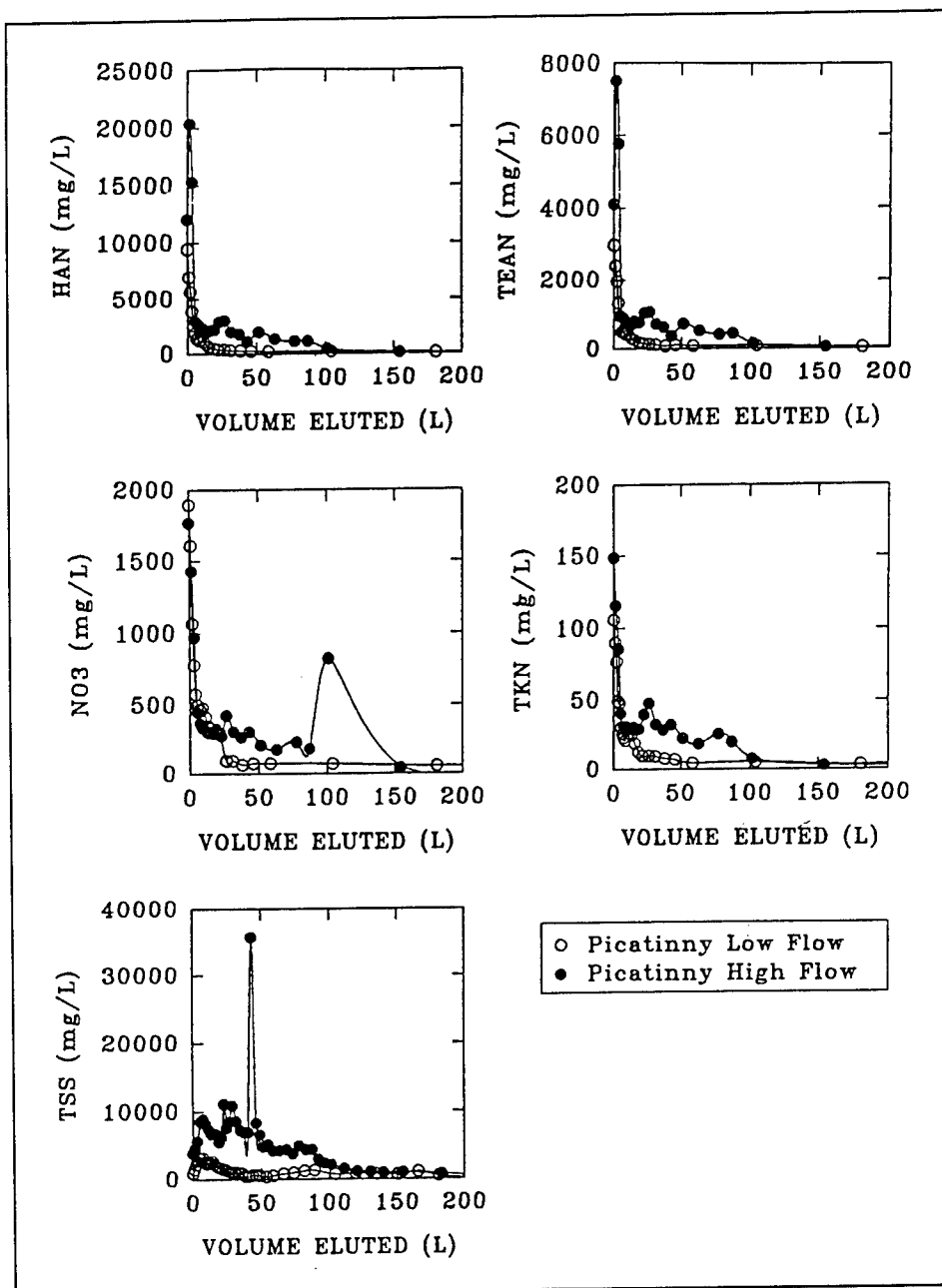


Figure 8. Effluent concentration of HAN, TEAN, NO₃, TKN, and TSS for Picatinny soil

tendency to adsorb to the soil particles. Thus, TKN washout is likely to be dependent upon factors not included in Equation 6.

The calculated values of C_0 are based on a fit of the experimental data to Equation 6 by use of SigmaPlot software. The values of C_0 represent the initial concentration that washed out of the soils reasonably well (see Figures 7, 8, 9, and 10).

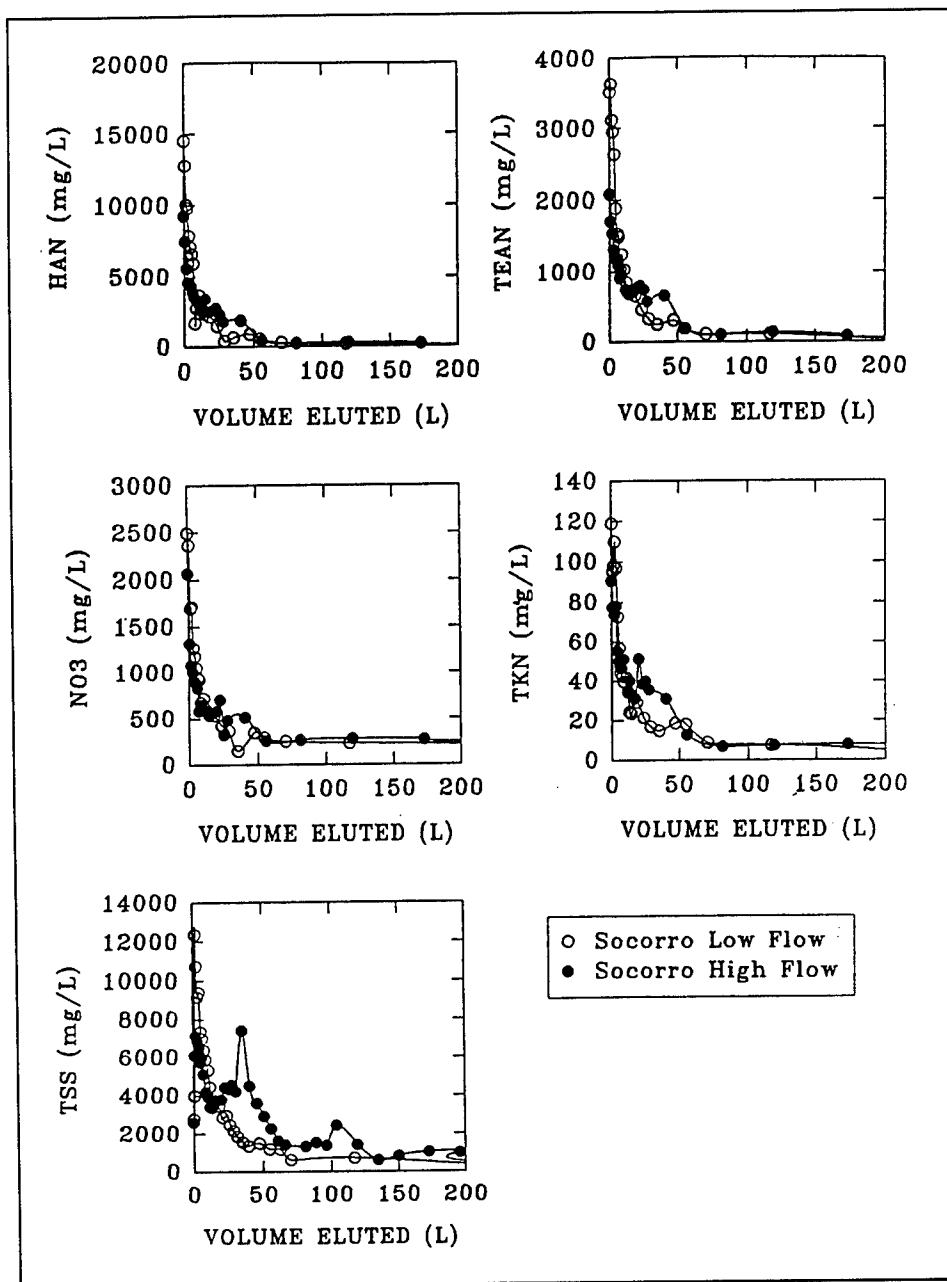


Figure 9. Effluent concentration of HAN, TEAN, NO₃, TKN, and TSS for Socorro soil

Residual Contaminant Concentration in Washed Soils

Except for China Lake with high flow, the soil remaining in the column after soil washing was divided by length into thirds, which were labeled bottom, middle, and top. China Lake high flow soil was mixed, and one

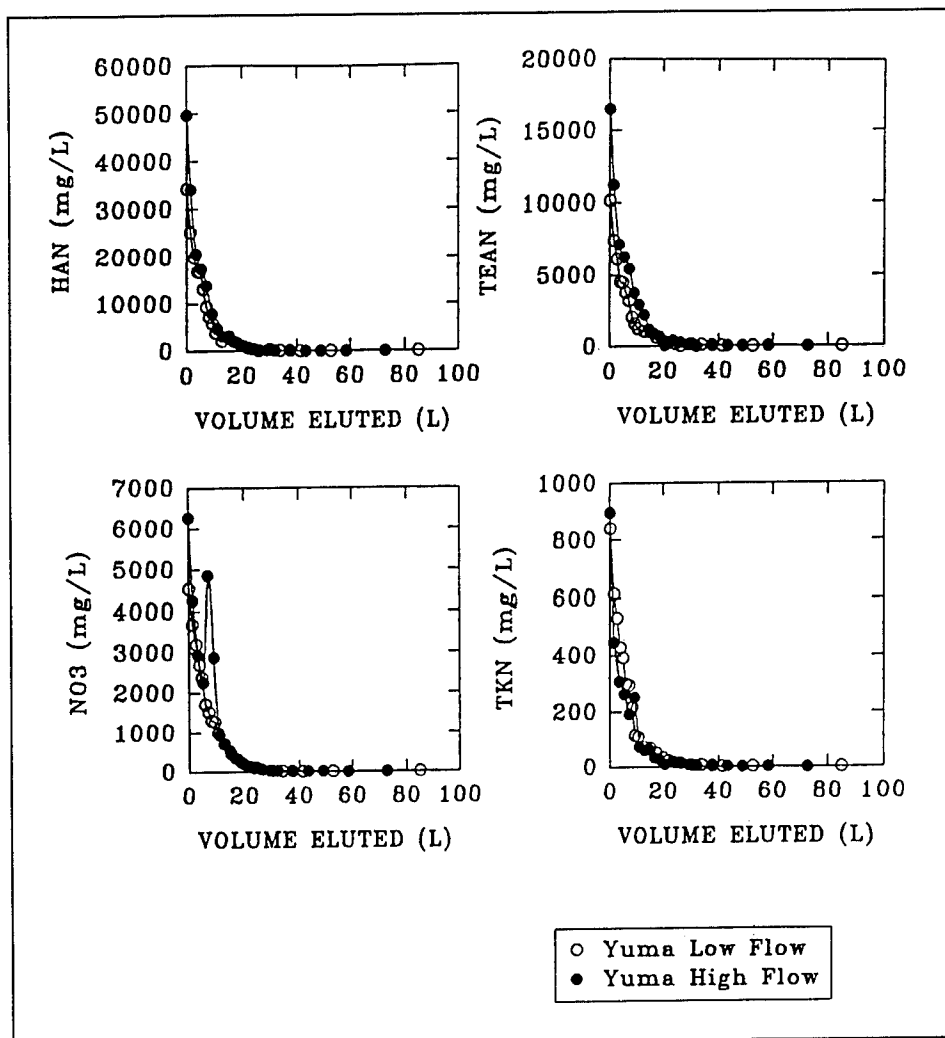


Figure 10. Effluent concentration of HAN, TEAN, NO₃, and TKN for Yuma soil

Table 3 Reduction in Concentration of LP Components as a Function of Wash Water Volume for a Completely Mixed Wash Column	
No. of Wash Water Volumes $V/(V_T - V_S)$	Concentration Remaining as a Percent of Original Concentration, C/C_o
1	36.8
2	13.5
3	5.0
4	1.8

Table 4
Contaminant Washout Parameters for Soil Washing

Soil	Wash Rate ¹ ℓ/min	Experimental $V_r V_s$, ℓ	Calculated $V_r V_s$, ℓ					Calculated C_o , mg/ℓ					Calculated Active Zone Factor	
			HAN	TEAN	NO ₃	TKN	HAN	TEAN	NO ₃	TKN	HAN	TEAN	HAN	TEAN
China Lake	0.76	8.93	5.58	4.92	6.97	29.9	43,460	14,560	5,326	29.5	0.62	0.55	0.62	0.55
	1.7	8.93	5.74	5.43	5.9	5.36	39,010	13,110	5,736	859	0.64	0.61	0.64	0.61
Picatinny	0.51	9.06	3.7	3.89	5.51	5.88	9,991	3,237	1,812	105.8	0.41	0.43	0.41	0.43
	0.96	9.06	6.73	6.7	6.61	8.93	17,700	6,360	1,745	132.7	0.74	0.74	0.74	0.74
Socorro	0.26	9.11	6.57	7.69	8.36	9.53	14,320	3,828	2,330	118.4	0.72	0.84	0.72	0.84
	0.51	9.11	16.31	22.88	18.97	30.18	6,966	1,624	1,347	72.9	1.8	2.5	1.8	2.5
Yuma	0.38	9	5.56	5.52	6.69	5.77	34,790	10,260	4,705	854.9	0.62	0.61	0.62	0.61
	0.96	9	4.62	5.45	7.28	4.41	50,700	16,270	6,021	839.5	0.51	0.61	0.51	0.61

Note: The calculated parameters are for the exponential equation $C = C_o \exp[-V/(V_T - V_S)]$.

¹ First value for each soil represents low flow; second value represents high flow.

subsample was drawn from the mix for analysis. Each portion of the soil was analyzed for HAN, TEAN, NO₃, and TKN. The results of the analyses for each species are shown in Figures 11, 12, 13, and 14.

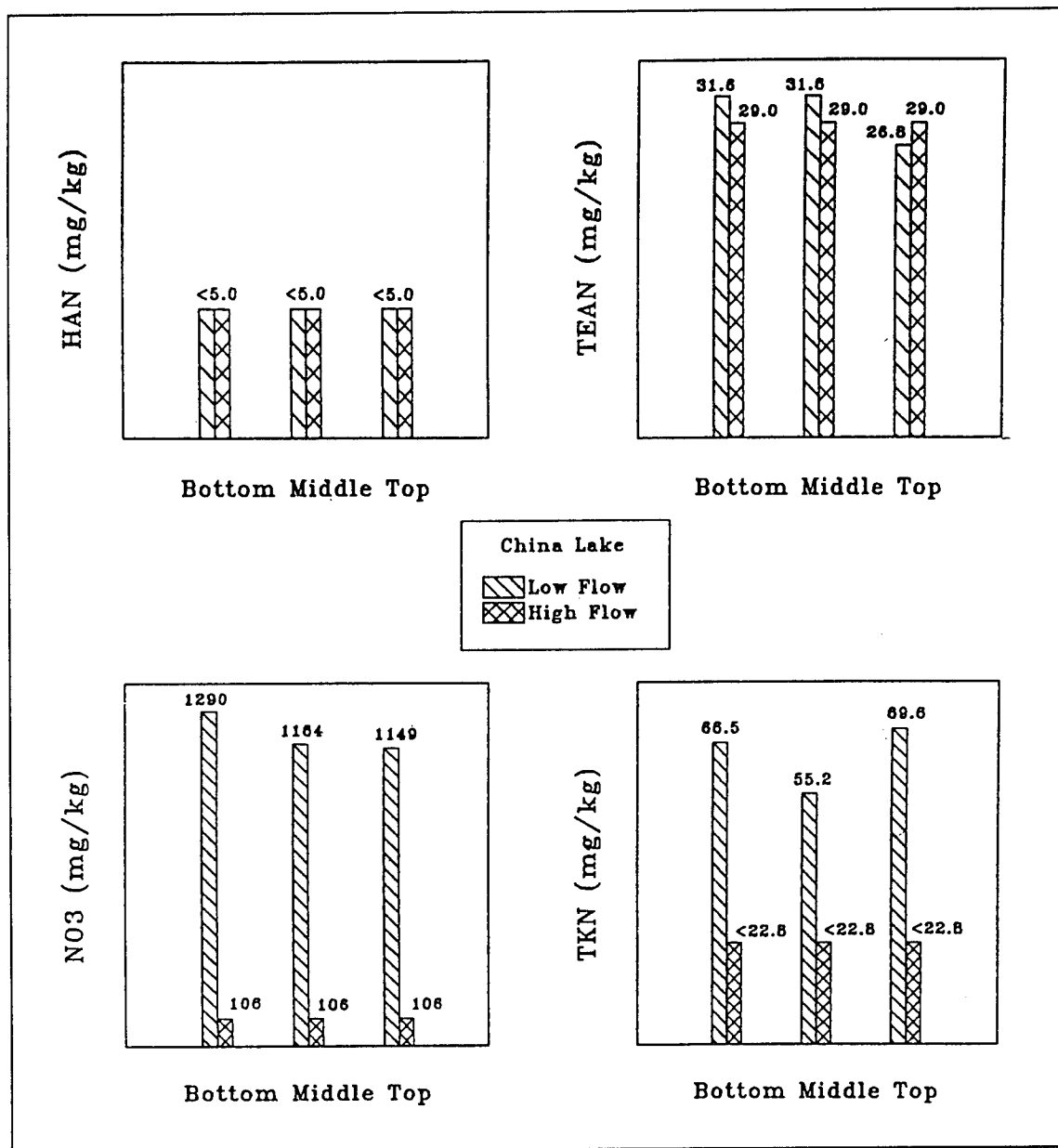


Figure 11. Residual concentrations of HAN, TEAN, NO₃, and TKN in China Lake soil after completion of washing (Concentrations are milligrams per kilogram of wet soil)

As expected, residual concentrations were generally higher after low flow than after high flow when values were above detection limits. Residual concentration of each species was directly related to the smaller sized particles. The higher flow rate washed out more soil from the column, but the smaller

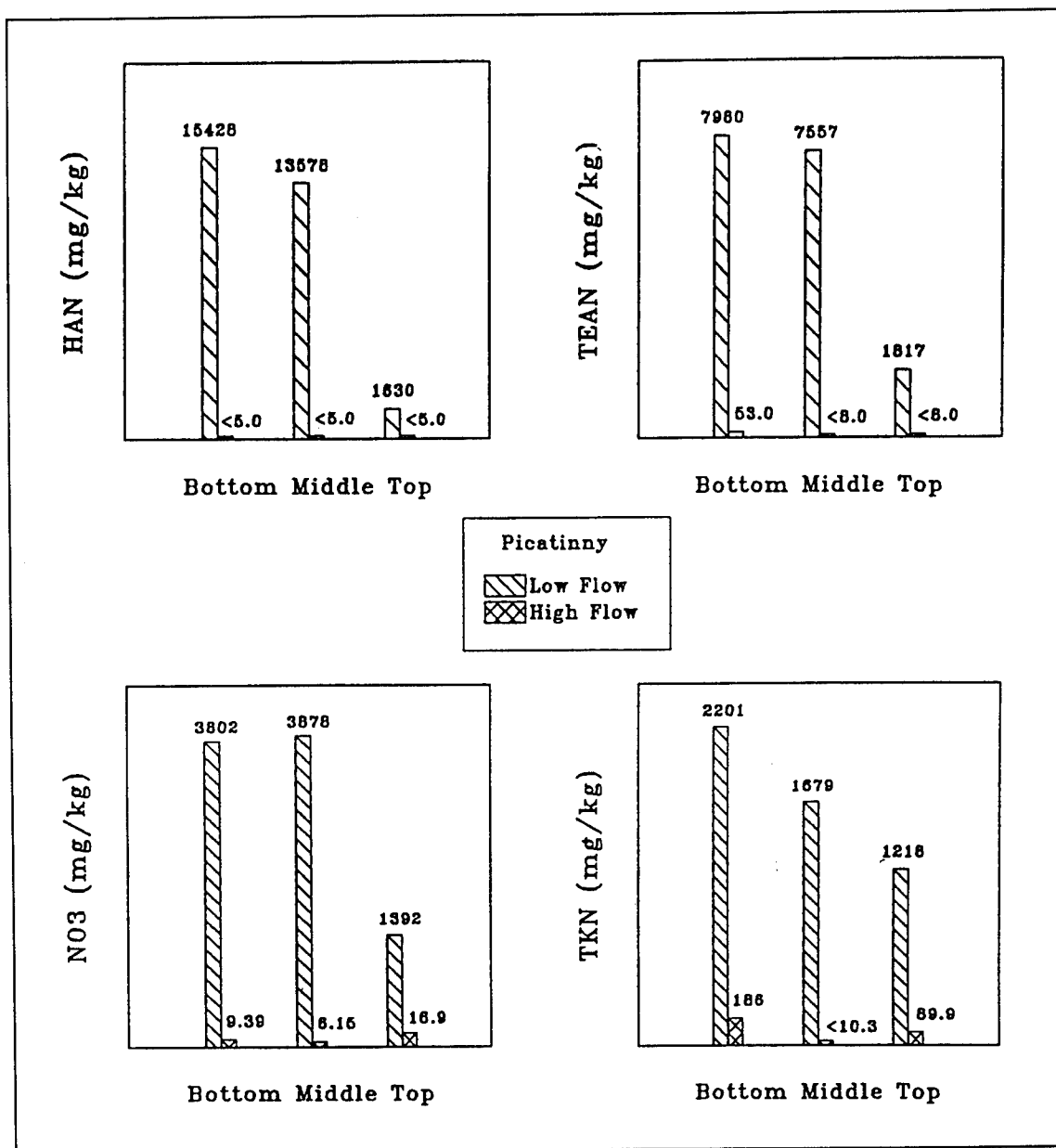


Figure 12. Residual concentrations of HAN, TEAN, NO₃, and TKN in Picatinny soil after completion of washing (Concentrations are milligrams per kilogram of wet soil)

sized soil particles were removed in preference to larger sized particles (see Table 2 for projected soil washout of each soil).

One of the exceptions to the general tendency for residual concentration to be associated with particle size occurred with Socorro soil (see Figure 13). HAN and TEAN concentrations were larger after the low flow washing in the bottom third of the soil than they were after the high flow washing. This is most likely due to short circuiting in the Socorro soil at the high wash rate, which also limited interpretation of the NO₃ and TKN data. In Yuma soil, the

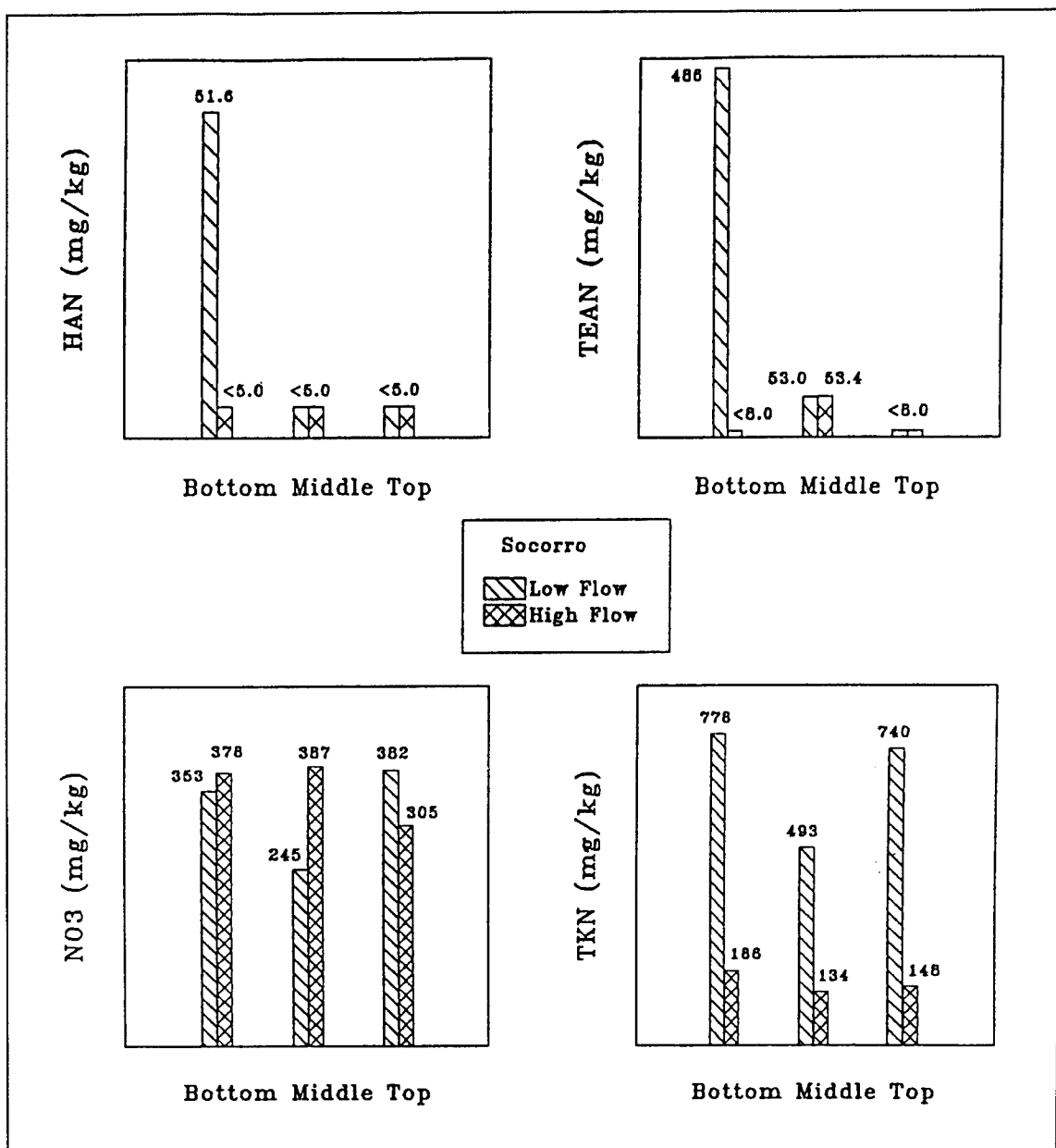


Figure 13. Residual concentrations of HAN, TEAN, NO₃, and TKN in Socorro soil after completion of washing (Concentrations are milligrams per kilogram of wet soil)

TEAN concentration was lower in the top third of the soil after the high flow rate than it was after the low flow rate. This result was expected. However, the TEAN concentration in the bottom and middle third of the soil was larger after the high flow rate than after the low flow rate. No explanation is known for this observation.

The area under the curves shown in Figures 7, 8, 9, and 10 represents the mass of constituent in the wash water discharged from the column. These results are presented in Table 5. The mass of each constituent in the soil

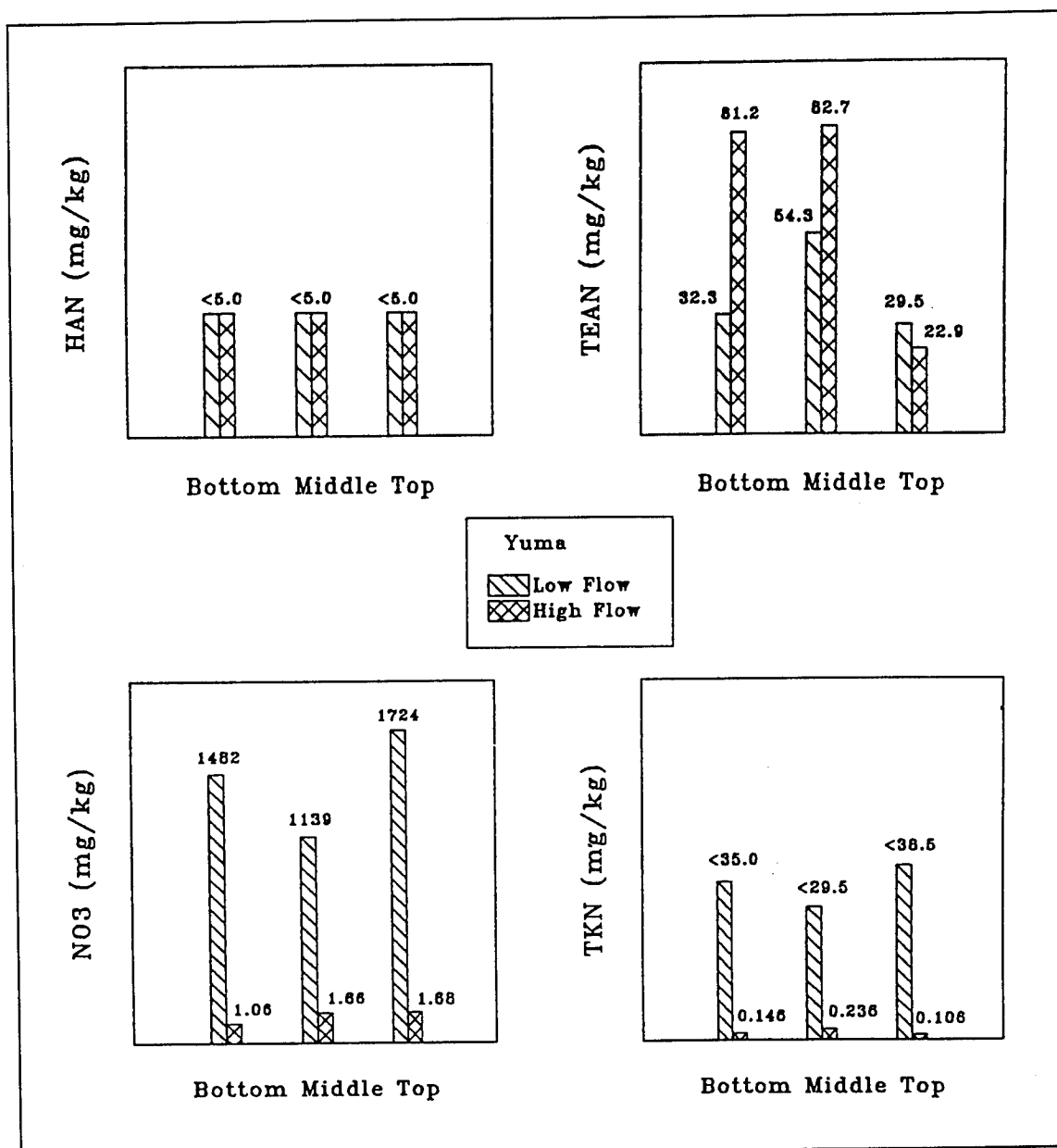


Figure 14. Residual concentrations of HAN, TEAN, NO₃, and TKN in Yuma soil after completion of washing (Concentrations are milligrams per kilogram of wet soil)

remaining in the wash column can be calculated from the concentration information presented in Figures 11, 12, 13, and 14, and the wet weight of the soil remaining in the wash column. For Yuma soil, the amount washed out was taken from the "projected soil washout" column of Table 2. The mass of HAN, TEAN, NO₃⁻, and TKN in the soil are shown in Table 6. Concentrations below the minimum detection level are reported as zero.

Tables 5 and 6 provide a measure of the effectiveness of soil backwashing in removing LP from soil. Except Picatinny soil at low flow, only a small part of the HAN and TEAN that had been applied to any soil remained after

Table 5
Mass of HAN, TEAN, NO₃⁻, TKN, and Soil Washed From Column

Soil	Wash Rate ℓ/min	Mass Washed Out, g				
		HAN	TEAN	NO ₃ ⁻	TKN	Soil
China Lake	0.76	243.8	76.4	58.0	0.96	36.0
	1.7	213.8	69.0	33.1	4.44	46.7
Picatinny	0.51	96.6	38.0	45.6	2.3	322.2
	0.96	264.2	95.2	83.3	3.7	994.6
Socorro	0.26	154.3	58.3	154.7	9.3	297.7
	0.51	182.6	63.2	192.6	4.8	508.9
Yuma	0.38	198.1	70.1	35.1	5.2	*
	0.96	244.9	96.6	54.0	4.6	*

Note: * = Soil washout was not measured for Yuma soil.

Table 6
Mass of HAN, TEAN, NO₃⁻, and TKN Remaining in Soil After Washing

Soil	Wash Rate ℓ/min	Mass Remaining, g			
		HAN	TEAN	NO ₃ ⁻	TKN
China Lake	0.76	0	0.09	3.5	0.19
	1.7	0	0.09	0.3	0
Picatinny	0.51	27.0	15.3	8.0	4.5
	0.96	0	0.03	0.02	0.2
Socorro	0.26	0.04	0.48	0.87	1.8
	0.51	0	0.04	0.87	0.4
Yuma	0.38	0	0.10	3.8	0
	0.96	0	0.15	0	0

backwashing. Slightly more TEAN than HAN remained in the backwashed soil except in Picatinny soil at low flow. The slightly higher organic matter content of Picatinny soil may have influenced these results. If HAN and, to a greater extent, TEAN were associated with the fine particles of organic matter in the soil, less would be washed out than in soils with lower organic matter content, especially at the low backwash rate. The HAN and TEAN concentrations remaining in the Picatinny soil after the high backwash rate were as low (for HAN) and lower (for TEAN) than in any other soil at any backwash rate.

Mass Balance

The initial mass of HAN and TEAN added to each soil was calculated from the mass of LP added and the fraction by weight of LP that is HAN and TEAN, namely, 60.8 and 19.2 percent, respectively. These calculations resulted in 210,200 mg of HAN added to each soil except Socorro for the low flow test in which 211,200 mg was added. Similar calculations for TEAN addition showed 66,400 mg was added to all soils except for Socorro during the low flow test when 66,700 mg was added. The mass balance was calculated for HAN and TEAN by the equation

$$\text{Mass Accounted For} = \left[\frac{\text{Mass Washed Out} + \text{Mass Left in Soil}}{\text{Mass Added to Soil}} \right] 100 \quad (7)$$

A mass balance was not carried out for NO_3^- and TKN, as these constituents were not added to the soil. The mass balances for HAN and TEAN are shown in Table 7. Table 7 shows that greater than 100 percent of the HAN was recovered in four out of eight experiments, while greater than 100 percent of the TEAN was recovered in five out of eight experiments. The experiments with Yuma soil can be omitted from the mass balance of HAN and TEAN discussion, as the weight of the soil washed from the column was estimated on indirect evidence of the size of soil particles that would be washed out rather than on direct measurements. Three possible sources of error in the mass balance for the other soils are as follows:

- The amount of HAN and TEAN added to the soil is incorrectly high.
- The HAN and analytical data were incorrectly elevated.
- The flow rates recorded during the soil washing experiments were too large.

Table 7 Mass Balance for HAN and TEAN in Soil Washing Tests			
Soil	Wash Rate, l/min	HAN Accounted for Percent	TEAN Accounted for Percent
China Lake	0.76	116.0	115.3
	1.7	101.7	104.0
Picatinny	0.51	58.8	80.2
	0.96	125.7	143.4
Socorro	0.26	73.1	88.1
	0.51	86.9	95.2
Yuma	0.38	94.2	105.8
	0.96	116.5	145.7

The LP applied to the soil was analyzed for stability of the HAN and TEAN components at the beginning of experimentation. Results indicated that the LP had the appropriate composition of HAN and TEAN, 60.8 percent HAN and 19.2 percent TEAN. Therefore, decomposition of LP in the test product did not occur. An error in measuring the quantity added to the tests is possible, but consistently measuring too much LP in each test is unlikely.

The second possible source of error is inconsistent with the quality control procedures carried out routinely during the chemical analysis. The large volume of prior testing evidenced no such inflation in analytical data. Therefore, analytical error is unlikely.

The third possible source of error that the flow measurements were incorrectly large is also difficult to justify. Flow measurement plays an essential role in the mass balance calculations since the mass of HAN and TEAN washed from the soil was calculated by integrating the area under the curves (concentration versus volume) in Figures 7, 8, 9, and 10. Flow rate was measured with a rotameter in the backwash experiments. Prior to using the rotameter, it was calibrated with water over the range of flow rates used in the experiments (Figure 6). Rotameter calibration was thorough, so that the flow rate used in the backwashing experiments involved interpolating between calibration data points rather than extrapolating beyond the calibration points. The rotameter was placed in the water supply line upstream of the soil wash column, so it was not subject to density variations in the metered water. As a check for rotameter accuracy, the mass of wash water was measured in the China Lake high flow run. This independent measurement showed less than 1-percent error in the rotameter reading. An independent accuracy check was not performed on the remaining runs, however. Therefore, no compelling evidence is apparent that the flow rates were measured incorrectly. Nevertheless, the flow meter data contain the greatest potential source of variability and, therefore, of error.

4 Conclusions

The soil washing apparatus studied in this experiment was effective in demonstrating removal of HAN and TEAN from a contaminated soil by backwashing. A small amount of HAN and TEAN remained in the washed soil at the end of an experimental run (Table 6). The amount of HAN and TEAN left in the soil, while small, was greater in most cases after low flow washing than after high flow washing (Figures 11, 12, 13, and 14). This suggests that HAN and TEAN adsorb preferentially to the smaller sized soil particles that were washed out of the column at a higher wash rate. In Picatinny soil, which had the highest organic matter content, the HAN and TEAN that failed to wash out may have been adsorbed to the organic matter.

Some washout of soils from a backwash column is inevitable. Equation 1 is useful, but not highly accurate, as an aid in estimating the fraction of soil that will wash out. Soils containing high relative proportions of silt- and clay-sized particles exhibit carryover of some soil with the wash water. Some carryover of fine-sized soil particles with wash water is inevitable for soils that contain colloidal-sized particles. Additional carryover with wash water is inevitable, as the wash rate increases to expand the soil bed. Design of a single wash column capable of achieving soil bed expansion while also minimizing carryover of solids is not feasible. A solids separation unit may be appropriate after the backwashing operation recovers the solids.

An alternative soil washing design would be to have two or more columns in series. Each successive column could be of a larger diameter so that the upward velocity would decrease in the sequence of columns. This design would allow segregation of different size fractions of soil in different columns, while expanding each size fraction to achieve thorough washing.

Evidence of short circuiting during washing of Socorro soil was evident, yet removal of HAN and TEAN was still effective (Table 6). Short circuiting while washing a cohesive soil could be reduced if a mixing device were installed in the wash column to stir the soil during the initial period of washing, breaking up clods.

The volume of wash water required to remove most of the HAN and TEAN from the soil was a function of the soil properties. The approximate volumes of wash water were the same for HAN as for TEAN: China Lake,

30 ℓ; Yuma, 30 ℓ; Picatinny, 100 ℓ; and Socorro 150 ℓ. As the backwashing units were all charged with the same amount of soil (3,000 g), the backwash volumes per mass of soil were as follows: China Lake, 10 ℓ/kg soil; Yuma, 10 ℓ/kg soil; Picatinny, 33 ℓ/kg soil; and Socorro, 50 ℓ/kg soil.

The backwash water volumes used in soil backwashing could be reduced by recycling the water through the backwash unit. In this case, the recycled water should be filtered prior to recycle to remove fine soil particles to which HAN and TEAN may adsorb preferentially. A small volume of clean wash water would be available, e.g., $4 \times (V_T - V_S)$, for a final polishing of the soil.

References

Clark, J. W., and Viessman, W., Jr. (1965). *Water supply and pollution control*. International Textbook Co., Scranton, PA.

Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathburn, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Steele, E. W., and McGhee, T. J. (1979). *Water supply and sewerage*. McGraw-Hill, New York.

U.S. Environmental Protection Agency. (1982). *Methods for chemical analysis of water and wastes*. EPA 600/4-79-020, March 1979 and EPA 600/4-82-055 December 1982, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

_____. (1990). "Method 8330" *Methods for chemical analysis of water and wastes*. SW-846, 3rd ed., November 1990 revision, USEPA Office of Solid Waste and Emergency Response, Washington, DC.

Weber, W. J., Jr. (1972). *Physicochemical processes for water quality control*. Wiley-Interscience, New York.

Section III

Bioremediation

1 Introduction

Three important consequences of an LP spill to soils are (a) sterilization of the soil, (b) low soil pH, and (c) high soil nitrate (Pennington et al. 1994). The following discussion will explore the ramifications of each of these factors on bioremediation of LP-contaminated soils.

Soil Sterilization

One immediate effect of an LP spill is sterilization of the soil. Results of microbial survival tests demonstrated that undiluted LP killed all the soil microorganisms, including bacteria, fungi, actinomycetes, and acid-tolerant bacteria, within the first hour of contact (Pennington et al. 1994). Sterilization of the soil may be attributable to several possible mechanisms, which include low pH, high ionic strength due to high nitrate, and the strong oxidizing ability of the HAN. Impacts of low pH on survival of the soil microflora are discussed below. In typical soils, nitrate loading does not inhibit the microflora due to the denitrifying capability of the soil microflora. However, in the case of an LP spill to soils, the ionic strength in the immediate vicinity may be sufficient to cause osmotic shock of the microbial cells and lead to their death by dehydration. The HAN component of LP is such a strong oxidizing agent that rapid "fume off" as frothing and bubbling is observed when LP contacts soils. Any organic material, including living microbial cells, is susceptible to oxidation by the HAN. Such oxidation could result in destruction of the soil microflora.

When LP was diluted 50:50 (v/v) with water before spilling onto soil, all the microflora were killed unless the soil was washed with water after 1 hr of contact. In the latter case, microbial population levels dropped by one to several orders of magnitude, then recovered to near control levels by 5 days in most soils. These results suggest that microbial populations in the immediate vicinity of an LP spill will be significantly impacted, but will recover in time especially if the LP is diluted. If only LP saturated or nearly saturated soils are to be bioremediated, as for example in a bioslurry reactor, the native microflora may be inadequate. In the environment, amelioration of the initial spill impacts may occur by dilution of the LP in the soil by leaching of

rainwater followed by recolonization by microflora from surrounding communities.

If the soil is excavated and treated in bioslurry reactors, inoculation with suitable microbes may be effective, particularly if other adjustments in the soil are made to optimize bioremediation (see discussion of bioremediation methods below). For example, the influent feed rate of contaminated soil could be adjusted to prevent lethal effects of LP on the viable microflora in the reactor. The reactor microflora would be obtained from a source other than the contaminated soil being treated, e.g., soil from the same site, but uncontaminated with LP, or sludge from a municipal waste treatment system.

Low Soil pH

Immediate demise of the microbial community observed in prior studies may have several causes. The most likely cause is low soil pH resulting from the LP. Potential effects of pH values less than 4 on the native soil microflora include (a) demise of the bacteria and actinomycetes (however, soils of pH 3 often contain many bacteria), (b) bacterial toxicity due to solubilization of toxic cations, e.g., Al^{+3} and Mn^{+2} , and (c) flourishing of the fungi that are more tolerant of acidic conditions. Fungi are much more tolerant to pH extremes than other soil microflora, often tolerating pH as low as 2 to 3 or as high as 9 and above; fungi often dominate low pH soils due to reduced competition for food caused by the demise of bacteria and actinomycetes. Pennington et al. (1994) found that soil pH 24 hr after saturation with LP was reduced by about half. This reduction resulted in soil pH values of 1.5 to 4.5. As indicated in the previous paragraph, none of the soil microorganisms, including the fungi, survived contact of the soil with undiluted LP. Due to concern for nitrate loading of groundwater following an LP spill, it is important to note that denitrifying bacteria, which are capable of converting nitrate to volatile nitrogen, are sensitive to low soil pH (values less than 4). Furthermore, pH affects not only the rate of denitrification, but also the final products. Much more N_2O and NO are released from acid soils than from other soils. While not of great concern as local air pollutants, these compounds can contribute to ozone depletion in the upper atmosphere (Alexander 1977).

In the application of bioslurry treatment, the pH of the influent feed could be adjusted by addition of a base such as sodium hydroxide.

High Soil Nitrate

One kilogram of LP has the potential to generate 326 g of $\text{NO}_3/\text{NO}_2\text{-N}$. However, only about 10 percent of this amount was actually observed in soils contacted with undiluted LP, probably due to release as N_2 as HAN interacted with the soils (Pennington et al. 1994). Therefore, about 32.6 g of $\text{NO}_3/\text{NO}_2\text{-N}$ per kilogram of spilled LP may actually remain in the soil.

Two potential natural mechanisms of removal of nitrate from soils include leaching to the groundwater and denitrification by soil bacteria. As discussed previously, initial impacts of an LP spill include soil sterilization and low pH. Therefore, the potential for ready denitrification of LP-contaminated soil is limited.

For bioslurry treatment of LP-contaminated soils, a limited soil washing pretreatment step may be useful to reduce the nitrate concentration and the concentration of any residual hydroxylamine and triethanolamine. The reactor could be inoculated with denitrifying bacteria for improved nitrate removal.

2 Literature Review

A literature review was conducted to define the current state of the art in bioremediation of LP or LP components. A search of the computerized literature database, Dialog, revealed only one referred publication (Kaplan et al. 1984) that focused on components of LP, HAN and TEAN, which were tested independently of each other. The literature search produced several articles on biodegradation of triethanolamine. The following literature review begins with a summary and comments on recent research available as a contract report, but not yet appearing in the referred literature (Graves, Rightmyer, and Hoyer 1995). This report is reviewed first, since it specifically addresses biodegradation of the LP formulation of interest. The Kaplan et al. (1984) paper and the papers on triethanolamine are reviewed last.

Review of Report by Graves, Rightmyer, and Hoyer (1995)

Preliminary screening for LP-tolerant microbes

Soils and sludges from 14 sources were screened for microbes tolerant to LP. Tests were conducted by exposing inoculum source to 1,000-ppm LP in mineral salts medium and adjusting the pH to 7. Although some bacteria survived in this concentration of LP as evidenced by microscopic examination, the bacteria did not grow. By successively subculturing surviving isolates on increasing amounts of LP with supplemental nutrient sources, tolerance to a high of 800-ppm LP was achieved by two isolates. Six isolates were tolerant to more than 300-ppm LP. The LP could not serve as a sole source of carbon or nitrogen for any of the isolates. Only aerobic microbes were tolerant. Three isolates were taken to the next stage of testing. These were isolated from crude oil-degraders, mushroom cultivation compost, and Bunker C fuel oil.

Biodegradation in soil samples

Soil tests consisted of exposing the three test isolates to soils containing (a) 800-ppm LP, (b) powdered lime to adjust the pH, and (c) a nutrient

medium. Results were consistent with results of contact tests conducted at WES (Pennington et al. 1994). The HAN failed to persist in the soil, probably due to chemical decomposition during oxidation of soil components. Only about 25 percent of the added TEAN was recovered from the soil at time zero. Low time zero TEAN concentrations were attributed to extraction inefficiency and adsorption (See discussion below concerning analytical procedures). Variability in data, e.g., standard error or standard deviation, was not given. Since extraction efficiencies reported in the analytical sections of the report demonstrate that variability was high (34 percent at 6 days, Table 6, Appendix A), lack of significant differences among data points cannot be dismissed. An unexplained aspect of the time series data is a 65- to 75-percent increase in TEAN concentration after 5 days. This result may also be consistent with high variability in the data.

The soil used for generating the data shown in Figures 4 and 5 of the report was not indicated, and no characteristics data on soils used in the study were included in the report. However, based on quantity of TEAN added and on partitioning coefficients determined previously (K_d s of 2 and 20 for soils having extremely high sand and extremely high clay content, respectively; Pennington et al. 1994), soil adsorption could account for the observed data over the first 20 days. (Solution phase concentrations of 51 and 7 mg TEAN per liter for sandy and clayey soils may be observed, respectively.) A dramatic drop in TEAN concentration to less than 15 mg per kilogram after Day 15 was attributed to biological activity. The autoclaved soil also exhibited a drop in TEAN concentration a little later, i.e., after 20 days. However, microbial populations in the autoclaved soils had recovered to levels comparable with those in the unautoclaved soils by Day 12. Therefore, the drop in TEAN concentration after 15 days may be due to degradation in both soils, provided that the differences in values are not accounted for by experimental variability. Addition of LP-tolerant isolates failed to enhance biodegradation.

Biodegradation in aqueous samples

Preliminary tests were conducted to determine the stability of LP in groundwater and in seawater. Water samples were spiked with LP at 2, 10, and 100 times detection limits for TEAN (10.5, 53, and 527 mg/l) and stored at 4 °C for 72 hr before analysis. Recoveries for HAN were generally low to none, probably due to chemical decomposition. Recoveries of TEAN, on the other hand, were generally higher than 100 percent due to analytical interferences.

Biodegradation in water was evaluated using deionized water with 5-percent soil added to simulate groundwater. Microbial nutrients and LP-tolerant isolates were also added. Eight hundred milligrams LP per liter were added, and the pH was neutralized with sodium hydroxide. Samples were collected every other week for 8 weeks and analyzed for HAN, TEAN, nitrate, nitrite, ammonium, DEA, EA, pH, and microbial density.

The HAN dissipated from all test systems. Disappearance from treatments containing added soil were faster than from treatments containing water only. Initial concentrations of TEAN were consistent with adsorption of TEAN onto the small amount of soil in the test. Concentrations decreased by about 40 mg per liter over 8 weeks. Without data on variability among replicates, these data are difficult to interpret. If variability is high, the observed decrease may be insignificant. Results in the treatment containing autoclaved soil were comparable with treatments containing unautoclaved soil. Therefore, the observed degradation of TEAN was not attributed to microbial degradation.

Biodegradation in a sequencing batch reactor

Sequencing batch reactors (1-ℓ volume) were tested using activated sludge supplemented with LP-tolerant isolates. The reactors were operated by removing a measured volume of treated waste and introducing an equal volume of influent waste. The biological solids retention times were 5, 10, and 20 days. Twelve-hour composites of grab samples of effluent were analyzed for HAN, TEAN, and other parameters.

Concentrations of HAN dropped by 44, 54.6, and 72.6 percent in the 5-, 10-, and 20-day tests, respectively. Decomposition resulting from chemical reactions and from microbial degradation reaction cannot be distinguished in the reactors. However, considering the high organic carbon content of the reactors, chemical decomposition of HAN is likely to be significant. Concentrations of TEAN failed to decline in the 20-day test, but dropped 5 to 15 percent in other tests. The authors conclude that TEAN is recalcitrant to degradation in sequencing batch reactors.

Analytical method

Details necessary to adequately assess the analytical problems are not given in the report. Details concerning the electrochemical detection system, chromatographic eluents, standards, and reagents are not provided. However, examination of chromatograms presented has allowed the identification of the following five important technical problems with the analytical procedures reported by Graves, Rightmyer, and Hoyer (1995).

- a. High detection limits may be the result of relatively low sample injection volume. The 10-μℓ injection loop used is appropriate for high concentrations of LP, e.g., greater than 1-ppm TEAN. Lower detection limits necessitate increasing the injection volume. The report does not indicate the use of larger sample volumes for improving detection limits.
- b. Analysis of HAN and TEAN require the use of a base resistant Ag/AgCl reference electrode. With nonbase resistant reference electrodes, the pH of the electrode varies with the time of exposure to the

postcolumn reagent (0.3 molar NaOH). Such electrodes typically exhibit a gradual drift in electrode potential and response factors. Such drift can exert significant impacts on precision and accuracy of results.

- c. Background currents of the electrochemical detector are not specifically reported, but examination of the chromatograms presented in Appendix A reveal a minimum background current of 1,000 nA with detection currents on the order of 30 to 100 nA for TEAN. Such high background currents result in greater signal to noise ratio and raise detection limits. High background currents can also be responsible for the inconsistencies reported in the analyses. Several of the many possible reasons for high background currents include improperly degassed solvents, mobile phase contamination, improperly distilled and deionized water, and dirty or damaged electrode surfaces.
- d. The report refers to interferences encountered in soil analysis that are attributed to soil-TEAN interactions. A significant number of soil samples have been analyzed over the last 3 years at WES. These soils represent a very broad range in soil properties (Pennington et al. 1994). Such interferences have never been encountered.
- e. Examination of the chromatograms presented in the report reveal great instability in baselines, low signal to noise ratio, and, as noted by the authors, poor reproducibility. These are significant problems in chromatographic performance.

Review of Other Literature

The only prior study of microbial degradation research on ammonium nitrate propellants is the work of Kaplan et al. (1984). They tested HAN, TEAN, and two other ammonium nitrate propellants independently in batch reactors in which the propellant was the sole source of carbon and nitrogen, and in continuous flow reactors under both aerobic and anaerobic denitrifying conditions. The HAN was found to degrade rapidly above pH 4.9 in soils. This finding is consistent with WES research results (Pennington et al. 1994) and with research results of Graves, Rightmyer, and Hoyer (1995). The TEAN, however, persisted and served as the sole source of carbon and nitrogen in batch reactors where approximately 45 percent of added radiolabeled TEAN was recovered as $^{14}\text{CO}_2$. This is confirmation of complete mineralization of 45 percent of the added TEAN. In continuous flow reactors under aerobic conditions, TEAN was effectively decomposed at a 4.0-day retention time, i.e., 45- to 60-percent mineralized to $^{14}\text{CO}_2$. The concentrations of TEAN in these continuous flow reactors was 500 and 1,000 ppm. Under anaerobic denitrifying conditions, the 1,000-ppm concentration of TEAN required a 9.5-day retention time for effective mineralization (80.8-percent mineralization). For these studies, isolates were obtained by combining isolates from aerobic and anaerobic sewage sludge and soil.

Several early reports describing triethanolamine (TEA) degradation studies were found. In one study of microbial degradation of TEA and several other water-soluble lubricants, no degradation of TEA by sewage sludge microorganisms was observed (Geiger, Bennett, and Gannon 1984). In another study, isolates capable of using industrial cutting fluids were grown in TEA, diethanolamine, and several other substituted diethanolamines independently as the sole carbon and nitrogen source (Gannon, Adams, and Bennett 1978). Optimal growth was obtained with 500-ppm TEA, and inhibition was observed at 1,000 ppm. Triethanolamine accounted for 17 percent of the theoretical biochemical oxygen demand (BOD) of the system at 500 ppm. When a sewage sludge culture that had been acclimated to TEA for 5 days was used as an inoculum, the BOD attributable to TEA rose to 22.1 percent of the theoretical value. In a third study, Frings, Wondrak, and Schink (1994) report isolation of a homoactinogenic bacterium capable of fermentative degradation of TEA. The isolate was obtained from a municipal sewage sludge and identified as an *Actinobacterium* species. The TEA served as the sole source of energy and organic carbon for the isolate. The authors propose a degradation pathway in which TEA is degraded to acetate and ammonia.

Although the above evidence suggests that TEA and TEAN are biodegradable, the study of Graves, Rightmyer, and Hoyer (1995) is the only one in which TEAN and HAN were tested together in the LP XM46 formulation. The strong oxidizing power of HAN, the rapid and dramatic pH drop, and the high nitrate concentration imposed upon the test system by LP are likely to exert a significant impact upon the microflora. Therefore, the effects of the chemical processes occurring when LP interacts with the remediation matrix must be understood and taken into account when designing a biotreatment system. For example, neutralization of LP to prevent the effects of low pH on the microflora is likely to significantly change the LP components. These changes may affect the activity and viability of the microflora and the effectiveness of microbial enzyme systems to degrade the post neutralization "remnants" of the LP.

3 Feasibility of Bioremediation of LP-Contaminated Soil

Based on the demonstrated biodegradability of TEA reported in the literature, LP-contaminated soils should be amenable to biotreatment. However, results of the study conducted by Graves, Rightmyer, and Hoyer (1995) demonstrate a need to define the chemical reactions occurring when LP or LP-contaminated soil interacts with the biotreatment matrix. Furthermore, remediation efforts should be focused on finding degraders rather than microbes that are merely tolerant to LP. Previous studies demonstrate that the pH of the contaminated soil is likely to be quite low (Pennington et al. 1994). Therefore, pH adjustment will probably be required. When the soil is neutralized, the chemical composition of the contaminant is likely to be affected. Neutralization may also impact the microflora. Therefore, an understanding of the chemical composition of the system presented to the microbial community is essential.

Development of a microbial isolate or consortium capable of biodegrading LP can be approached in two steps. First, a screening test for mineralization of radiolabeled TEAN by isolates from a variety of sources would identify sources of true degraders. The advantage of using radiolabeled TEAN is the ability to readily detect radiolabeled carbon dioxide coming from the degradation of TEAN. Carbon dioxide from the TEAN is conclusive evidence that the TEAN has been degraded. Once obtained, increasing tolerance for higher LP concentrations by these isolates would be developed to improve performance. This can be accomplished by continuous culture under optimal conditions for the diverse community of microorganisms containing LP degrading activity. The system initially supports a broad community of microorganisms; but as time progresses, growth conditions can be gradually altered to favor the degrading community to the exclusion of extraneous microflora. Simultaneously, tolerance to higher LP concentrations can be developed by increasing concentration.

Once effective isolates are developed, the treatment system can be optimized for maximum throughput of LP-contaminated soil. The finished product must be further characterized to ensure compatibility with environmental constraints such as nitrate/nitrite concentration and pH. Based on results of this characterization, disposal options can be recommended.

References

- Alexander, M. (1977). "Introduction to soil microbiology." 2nd ed., John Wiley and Sons, New York.
- Frings, J., Wondrak, C., and Schink, B. (1994). "Fermentative degradation of triethanolamine by a homoacetogenic bacterium," *Arch Microbiol* 162, 103-107.
- Gannon, J. E., Adams, M. C., and Bennett, E. O. (1978). "Microbial degradation of diethanolamine and related compounds," *Microbios* 23(91), 7-18.
- Geiger, R. M., Bennett, E. O., and Gannon, J. E. (1984). "Microbial degradation of selected water-soluble lubricants." *Developments in industrial microbiology*. Proceedings of the 40th General Meeting of the Society for Industrial Microbiology, Sarasota, FL, August 14-19, 1983.
- Graves, D., Rightmyer, J., Hoyer, R. (1995). "Biodegradation of liquid gun propellant formulation 1846," Report No. SFIM-AEC-ETD-CR-95026, Final Report, IT Corporation, Cincinnati, OH for U.S. Army Environmental Center, Aberdeen Proving Ground, MD.
- Kaplan, D. L., Riley, P. A., Emerson, D. J., and Kaplan, A. M. (1984). "Degradation of ammonium nitrate propellants in aqueous and soil systems," *Environmental Science and Technology* 18, 694-699.
- Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathburn, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Section IV
Nitrate Loading to Groundwater
Aquifers From Spills of Liquid
Propellant/LP XM46 Onto Soils

1 Introduction

Background

Groundwater may become contaminated by the nitrite ion, NO_2^- , or the nitrate ion, NO_3^- . The nitrite ion usually transforms rapidly to the nitrate ion. Under many environmental conditions, the nitrate ion is stable. Nitrates not taken up by plants travel down to the aquifer with percolating water. Fertilizer addition, acid rain precipitation, leachate from septic tanks, and other uncontrollable natural sources typically contribute to the nitrate budget in groundwater.

The main public health problem with nitrate-contaminated water is its toxicity to infants for whom it can cause a condition known as methemoglobinemia, or blue babies, a condition of too little oxygen in the blood. The maximum permissible concentration of nitrite plus nitrate nitrogen in drinking water is 10 mg/l as nitrogen (U.S. Environmental Protection Agency (EPA) 1991; Tchobanoglous and Schroeder 1985). Nitrate concentrations may be reported in two ways: (a) the concentration of the ion as NO_3^- , and (b) the concentration of the nitrogen portion of the ion, referred to as nitrate-nitrogen, or as $\text{NO}_3^- \text{-N}$. Nitrate nitrogen is calculated from NO_3^- concentration by the formula (Snoeyink and Jenkins 1980)

$$\text{NO}_3^- - \text{N} = 14 \text{ NO}_3^- / 62 \quad (1)$$

The transport of nitrate ions to a groundwater aquifer is a complex process (Figure 1). Numerous factors affect the transformation of the different nitrogen forms; the type of soil, rainfall, plants, temperature, pH, land use, and the presence of heavy metals or pesticides that may inhibit microbiological transformations of different nitrogen-containing species. Under many conditions, the adsorption of NO_3^- to soils is insignificant, and the nitrate ion may be treated as a conservative species. However, in soil of pH less than 6, adsorption of the nitrate ion increases.

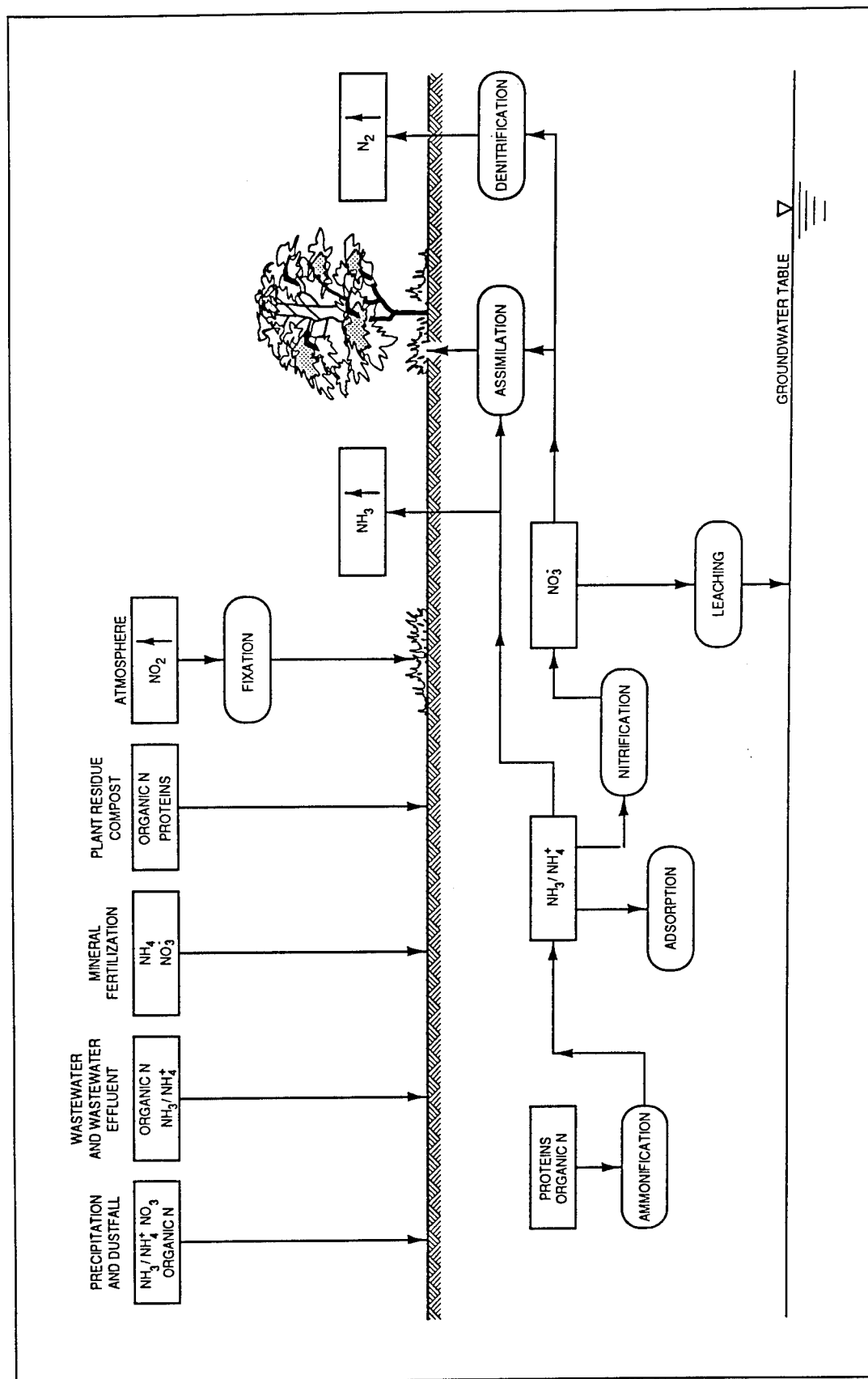


Figure 1. Nitrogen cycle in soil and groundwater (U.S. EPA 1975)

The nitrate concentration of groundwater is below the drinking water limit of 10-mg/l NO_3^- -N under many conditions. Below are results of a study conducted in the United Kingdom to relate the concentration of nitrate in drainage water to land utilization (Tester and Carey 1985).

Land Uses	NO_3 -N in Drainage Water, mg/l
Fertilized arable land	10-40
Fertilized grassland	4-10
Rough grazing, unfertilized grassland, woodland	1-2

Any undissociated ammonium nitrate, NH_4NO_3 , is expected to have a limited tendency to adsorb to soil particles and would be carried with flowing groundwater. For dissociated ammonium nitrate, the ammonium ion, NH_4^+ , is less mobile in groundwater than the nitrate-ion, NO_3^- , since the ammonium ion tends to adsorb more (Craig and Wolburn 1982). The nitrate ion tends not to adsorb unless the pH is reduced below 6.

One method of removing the nitrogen from nitrogen-containing compounds is through the process of denitrification. Denitrification takes place through the action of microorganisms that remove the oxygen from NO_3^- and produce nitrogen gas, N_2 , which can bubble off into the atmosphere. However, the presence of compounds that are toxic to microorganisms can inhibit the denitrification process (Yeoman and Bremner 1985a,b).

Objectives

The objectives of this study were as follows: (a) to quantify liquid propellant (LP) components and the transformation products resulting from LP application to three soils, and (b) to develop a mathematical model with which to predict the rate at which the nitrate ion concentration decreases because of its transport in a groundwater aquifer.

2 Materials and Methods

Experiments were performed by applying water to the top of the soil columns and collecting elution fractions at the bottom (Figure 2). Soil columns were 250-ml burets having an inside diameter of 4.91 cm at the base (Figure 3, Ace Glass, Inc., Vineland, NJ) and containing a porous plate (70 to 100 μm). Measured weights of the soil (Table 1) were packed into the buret in 80-g layers. A packer weighing 371.5 g was raised about 5 cm above the soil layer and dropped 40 times to remove voids from the soil. The soil surface was scarified and another soil layer added. This procedure was repeated until 10 soil layers were added. The mass of the soil in each buret was 800 g. Soil depth averaged 25.4 cm, and pore volume ranged from 107.8 to 285.5 cm^3 (Table 2). Characteristics of dry soils in the burets were similar except for water content, which varied from 1.1 to 12.9 percent of weight (Table 3).

One-half of the pore volume of the soil was calculated, and this volume of LP was applied to the soil surface. Five pore volumes of distilled deionized (DDI) water followed (Table 4). The position of the wetting front, the liquid surface, and the soil-liquid interface were recorded for each soil. Liquid was collected by a fraction collector (Eldex Laboratories, Inc., Napa, CA) for chemical analysis as soon as discharged from the buret.

Visual observations were made as warranted and included noting gas bubbles, foam, and cavities in the soil. The liquid fractions were collected in 20- and 40-ml glass vials. After weighing the vials, pH was measured with a Beckman 45 pH meter (Model pH I 45, Serial No. 167432). The mass of liquid collected was totaled and divided by 20. Ten was subtracted from this number to get an approximate amount of liquid needed for 20 samples to be analyzed for nitrate, nitrite, total Kjeldahl nitrogen (TKN), ammonia nitrogen, and organic nitrogen (Table 5). Starting from the first collected vial, 10 ml was extracted or composited for analysis of pH, hydroxylammonium nitrate (HAN), and triethanolammonium nitrate (TEAN). This sample was not preserved. Then the amount designated for the nitrogen tests was extracted or composited, and this volume was diluted to approximately 250 ml. This volume of liquid was preserved with three drops of sulfuric acid. The procedure was repeated until 20 samples were obtained for nitrogen species, HAN, and TEAN analysis. Samples were analyzed by the Environmental Chemistry

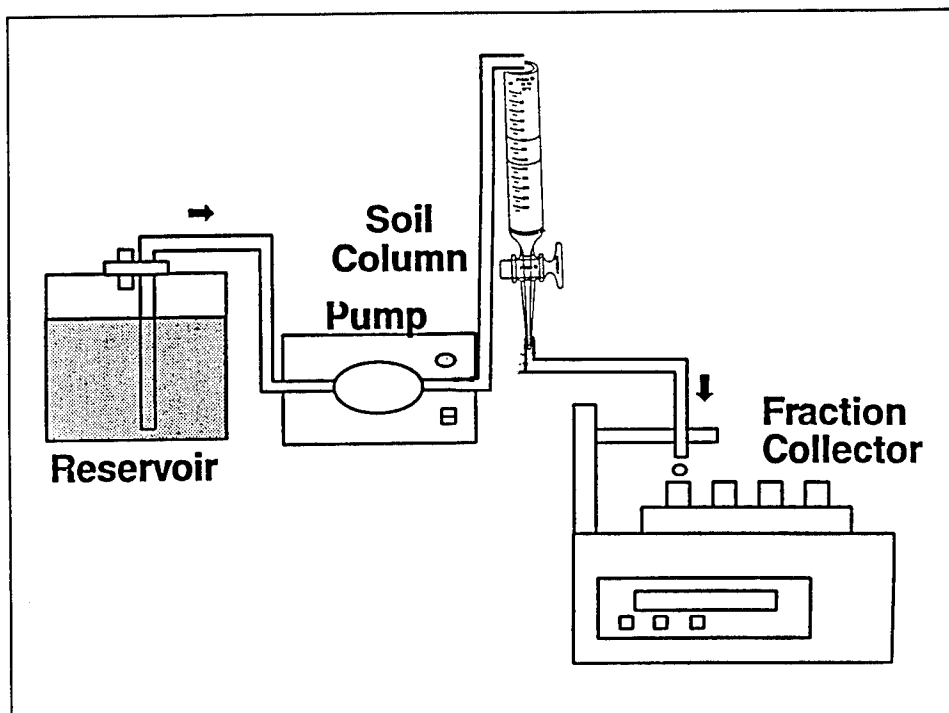


Figure 2. Soil column test apparatus

Branch, Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station.

Contaminant Transport in Vertical Flow Models

The vertical movement of LP in unsaturated soil can be described by the equation

$$\frac{\partial C}{\partial t} + \frac{V}{\theta} \frac{\partial C}{\partial z} = \frac{D_x}{\theta} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{\theta} \frac{\partial^2 C}{\partial y^2} + \frac{D_z}{\theta} \frac{\partial^2 C}{\partial z^2} - \frac{KC}{\theta} - \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} \quad (2)$$

where

C = concentration of species being transported,
mass/volume

t = time

V = vertical velocity, in soil interstices length/time

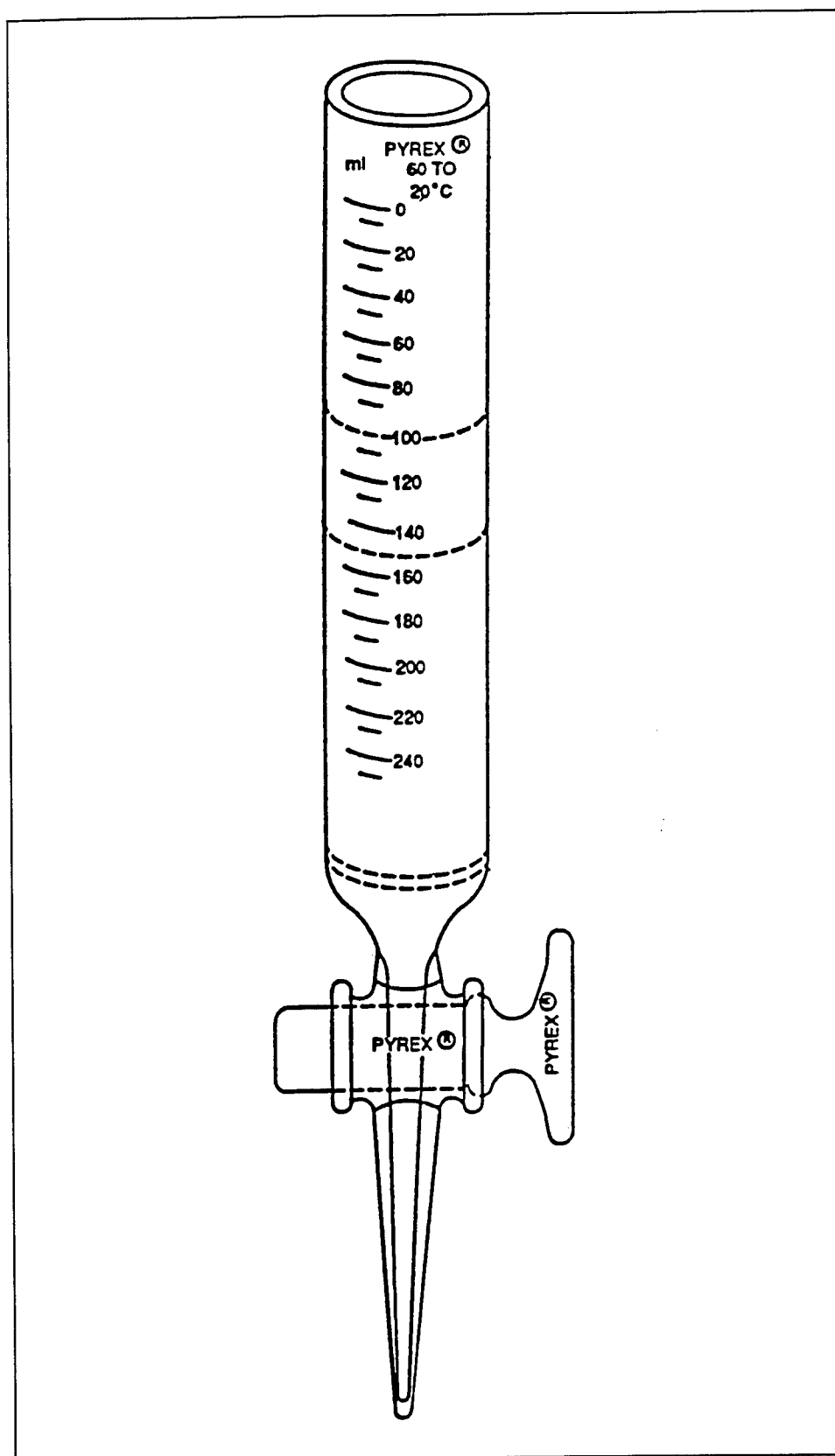


Figure 3. Burets used in experiment

Table 1 Soil Characteristics							
Soil	% Sand	% Silt % Clay	% Organic Matter	% Water	d, cm 50 % Size	Specific Gravity	Class
China Lake B	97.5	0.0 2.5	0.53	1.1	0.040	2.59	Silty Sand SP-SM
Socorro P	42.5	30.0 27.5	0.53	12.9	0.0040	2.76	Sandy Clay CL
Yuma 2A	75.0	20.0 5.0	0.21	2.5	0.0079	2.69	Silty Sand SM

Table 2 Soil Placement Characteristics in Burets		
Soil	Pore Volume, cm ³	Height, cm
China Lake B	107.8	21.8
Socorro P	285.5	28.4
Yuma 2A	201.5	26.0

Table 3 Porosity of Dry Soils Packed Into Burets				
Soil	Weight of Air Dry Soil, g	Water Content %	Density, g/cm ³	Porosity
China Lake B	800.0	1.1	2.59	0.240
Socorro P	800.0	12.9	2.76	0.339
Yuma 2A	800.0	2.5	2.69	0.369

Table 4 Weights of LP and DDI Water Pumped Onto Soils in Burets		
Soil	LP Weight, g	DDI Water Weight, g
China Lake B	141.4	910.8
Socorro P	230.6	1,532.5
Yuma 2A	237.5	1,644.1

Table 5 Weight of Liquid Available for Nitrogen Tests	
Soil	Liquid Weight, g
China Lake B	approximately 35
Socorro P	approximately 50
Yuma 2A	approximately 50

θ = moisture content, varies between 0 and n ,
dimensionless

n = porosity, dimensionless

x , y , and z = spatial coordinates, length

D_x , D_y , and D_z = dispersion coefficients in x , y , or z directions,
respectively, length²/time

K = chemical transformation rate, time⁻¹

ρ_b = bulk density of soil, mass/ volume

S = mass of adsorbed species per unit mass of soil,
dimensionless

$$S = K_d C \quad (3)$$

If linear adsorption takes place according to the relationship and if one lets

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (4)$$

where

ρ_b = soil bulk density, mass/volume

K_d = linear adsorption coefficient, volume/mass

R = retardation factor, dimensionless

then the transport equation simplifies to

$$\frac{\partial C}{\partial t} + \frac{V}{R\theta} \frac{\partial C}{\partial z} = \frac{D_x}{R\theta} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R\theta} \frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R\theta} \frac{\partial^2 C}{\partial z^2} - \frac{KC}{R\theta} \quad (5)$$

Baetsle (1969) and Csanady (1980) presented a solution to the equation without the transformation term ($KC/R\theta$). Their solution, modified to apply to the equation above, is

$$C(x,y,z,t) = \frac{M}{[(2\pi)^{1/2}(\sigma_x\sigma_y\sigma_z)^{1/3}]^3} \times \exp \left[-\frac{x^2}{2\sigma_x^2} - \frac{y^2}{2\sigma_y^2} - \frac{\left[z - \frac{Vt}{R\theta}\right]^2}{2\sigma_z^2} - \frac{Kt}{R\theta} \right] \quad (6)$$

where

M = mass of the contaminant added

$$\sigma_x = \left[\frac{2D_x t}{(R\theta)} \right]^{\frac{1}{2}}, \text{ length} \quad (7)$$

$$\sigma_y = \left[\frac{2D_y t}{(R\theta)} \right]^{\frac{1}{2}}, \text{ length} \quad (8)$$

$$\sigma_z = \left[\frac{2D_z t}{(R\theta)} \right]^{\frac{1}{2}}, \text{ length} \quad (9)$$

$\exp(.)$ = exponential function, dimensionless

This solution is for the mass introduced as an instantaneous point source. The maximum concentration ($C_{\max}$) is along a line through the center line of the plume, at the location where $z = Vt/(R\theta)$. Along this line the maximum concentration at any time is

$$C_{\max} = \frac{M(R\theta)^{3/2} \exp \left[-\frac{Kt}{R\theta} \right]}{[8(\pi t)^{3/2}(D_x D_y D_z)^{1/2}]} \quad (10)$$

In some of the following developments of the model, the source of the contaminant spill is placed off the origin of the coordinate system. For example, if the spill location has coordinates (X_1, Y_1, Z_1, τ) rather than $(0,0,0,0)$, then Equation 6 can be modified by a shift in the coordinate system to describe the new spill location. Equation 6 is modified to

$$C(x,y,z,t) = \frac{M}{[(2\pi)^{1/2}(\sigma_x\sigma_y\sigma_z)^{1/3}]^3} \times \exp \left[-\frac{(x-x_1)^2}{2\sigma_x^2} - \frac{(y-y_1)^2}{2\sigma_y^2} - \frac{\left[z-z_1 - \frac{V(t-\tau)}{R\theta} \right]^2}{2\sigma_z^2} - \frac{K(t-\tau)}{R\theta} \right] \quad (11)$$

with the further condition that

$$C(x,y,z,t) = 0 \quad \text{if } t < \tau \quad (12)$$

For the contaminant added at time τ , Equation 7, 8 and 9 become

$$\sigma_x = \left[\frac{2D_x(t-\tau)}{(R\theta)} \right]^{\frac{1}{2}} \quad (13)$$

$$\sigma_y = \left[\frac{2D_y(t-\tau)}{(R\theta)} \right]^{\frac{1}{2}} \quad (14)$$

$$\sigma_z = \left[\frac{2D_z(t-\tau)}{(R\theta)} \right]^{\frac{1}{2}} \quad (15)$$

The location of the maximum concentration would be along the vertical center line. The vertical distance below the land surface to the point of maximum concentration would be where $z = V(t-\tau)/(R\theta)$. At this location, the maximum concentration would be

$$C_{\max} = \frac{M(R\theta)^{3/2} \exp \left[-\frac{K(t-\tau)}{R\theta} \right]}{[8(\pi t)^{3/2}(D_x D_y D_z)^{1/2}]} \quad (16)$$

and

$$C_{\max} = 0 \quad \text{if } t < \tau \quad (17)$$

If the spill of contaminant spreads out over an area instead of being concentrated at a point, Equation 11 can be modified to describe the new scenario. Consider that a mass M of contaminant is added instantaneously over an area A at time zero. The area A is taken for simplicity to be rectangular, having length $x_2 - x_1$, and width $y_2 - y_1$. The concentration then becomes

$$C(x,y,z,t) = \int_{x_1}^{x_2} \int_{y_1}^{y_2} \frac{M}{A \left[(2\pi)^{\frac{1}{2}} (\sigma_x \sigma_y \sigma_z)^{\frac{1}{3}} \right]^3} \times \exp \left[-\frac{(x-x_1)^2}{2\sigma_x^2} \right. \\ \left. - \frac{(y-y_1)^2}{2\sigma_y^2} - \frac{\left[z-z_1 - \frac{Vt}{R\theta} \right]^2}{2\sigma_z^2} - \frac{Kt}{R\theta} \right] dx_1 dy_1 \quad (18)$$

This expression integrates to

$$C(x,y,z,t) = \frac{M}{(x_2 - x_1)(y_2 - y_1)(\sigma_z)(32\pi)^{\frac{1}{2}}} \\ \times \exp \left[-\frac{\left(z - z_1 - \frac{Vt}{R\theta} \right)^2}{2\sigma_z^2} - \frac{Kt}{R\theta} \right] \\ \times \left[\operatorname{erf} \left[\frac{(x_2 - x)}{\sqrt{2}\sigma_x} \right] - \operatorname{erf} \left[\frac{(x_1 - x)}{\sqrt{2}\sigma_x} \right] \right] \\ \times \left[\operatorname{erf} \left[\frac{(y_2 - y)}{\sqrt{2}\sigma_y} \right] - \operatorname{erf} \left[\frac{(y_1 - y)}{\sqrt{2}\sigma_y} \right] \right] \quad (19)$$

where $\text{erf}(\cdot)$ = the error function, dimensionless.

Since the mass source, M , was added at $t = 0$, σ_x , σ_y , and σ_z can be calculated from Equations 7, 8, and 9, respectively.

In some situations, the bulk of contaminant flow is in the vertical direction with only a small amount of lateral dispersion in the x or y coordinate direction. Equation 19 may be considered too cumbersome, and a simpler, one-dimensional model can be applied. Cleary and Adrian (1973) cite a one-dimensional model to describe contaminant transport. The model they cite can be modified to describe the concentration from a source of mass, M , which is applied over an area, A , at vertical location, z_1 . The contaminant is subject to transformation and adsorption while flowing with velocity, V , through soil having a moisture content of θ . The equation for these conditions is

$$C(z,t) = \frac{M}{A \left[\frac{4\pi D_z t}{R\theta} \right]^{\frac{1}{2}}} \exp \left[- \frac{\left[z - z_1 - \frac{Vt}{R\theta} \right]^2}{\left[\frac{4D_z t}{R\theta} \right]} \right] \quad (20)$$

This equation states that the maximum concentration at any time will occur when $z - z_1 = Vt/R\theta$.

Contaminant Transport in Horizontal Flow Models

The contaminant transport because of horizontal flow in a bounded aquifer model is based on a model presented by Cleary and Adrian (1973). Developed to describe mixing in a river, the model must be modified to apply to a contaminant flowing with groundwater. The modified model describes transport in an aquifer of width, W , and height, H . This type of aquifer could be found in a mountain valley, for example, where sedimentary aquifer materials are confined laterally between impervious walls of the adjacent mountains. The dimension, H , represents the height of water in the aquifer above an impermeable base. The model can be applied to aquifers that have lateral boundaries spaced far apart by increasing the value of the width, W . The transformation rate of the contaminant is given by the first order reaction with rate constant, K . Linear sorption of the contaminant is included in the modified model.

For saturated flow conditions that exist in the aquifer, the moisture content of Equation 2 becomes $\theta = n$, and the solute transport equation for horizontal flow becomes

$$\begin{aligned}
n \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - KC \\
- \rho_b \frac{\partial S}{\partial t} + M \delta(x - x_1) \delta(y - y_1) \delta(z - z_1) \delta(t - \tau_1)
\end{aligned} \tag{21}$$

where the new terms are

U = horizontal interstitial flow velocity

M = an instantaneous point source of mass

(x_1, y_1, z_1, τ) = coordinates, having units of lengths, of point
where point source of mass is released at time τ

$\delta(x-x_1), \delta(y-y_1), \delta(z-z_1)$ = Dirac delta functions of space coordinates,
length⁻¹

$\delta(t - \tau)$ = Dirac delta function of time, units are time⁻¹

Equation 20 is modified by the linear sorption relationship, Equation 3,
and the retardation factor

$$R = 1 + \frac{\rho_b K_d}{n} \tag{22}$$

where K_d and R have been defined earlier and n is the dimensionless porosity.

The solution by Cleary and Adrian can be modified to account for contaminant transformation and adsorption. The model becomes

$$\begin{aligned}
C(x,y,z,t) = & \frac{\left[\frac{M}{R} \right] \exp \left[\frac{-R \left[x - x_1 - \frac{ut}{R} \right]^2}{4D_x t} - \frac{Kt}{R} \right]}{WH \left[\frac{4\pi D_x t}{R} \right]^{\frac{1}{2}}} \\
& \times \left[1 + 2 \sum_{N=1}^{\infty} \exp \left[-\frac{\mu_N^2 D_z t}{R} \right] \cos \mu_N z \cos \mu_N z_1 \right] \\
& \times \left[1 + 2 \sum_{m=1}^{\infty} \exp \left[-\frac{\beta_m^2 D_y t}{R} \right] \cos \beta_m y \cos \beta_m y_1 \right]
\end{aligned} \tag{23}$$

where

$$\mu_N = \frac{N\pi}{H}, \quad \beta_m = \frac{m\pi}{H}, \quad N, m = 1, 2, 3, \dots \tag{24}$$

The effect of sorption is expressed in two ways in Equation 23. First, sorption acts through the retardation coefficient, R , to decrease the apparent magnitude of the mass addition of contaminant through the term M/R . The second effect of sorption is to act through the retardation coefficient, R , as if time were slowed down by the term t/R .

As for the vertical flow model, an area source of contamination as well as a point source should be considered for the horizontal flow model. In a contaminant spill scenario, the contaminant may first drain in a vertical direction through the unsaturated zone, then encounter the top of the groundwater aquifer where flow becomes horizontal.

The modified model of Cleary and Adrian (1973), Equation 23, was modified further to accept contamination from a rectangular area on top of an aquifer. Furthermore, because an LP spill will produce a loading over a small area, the model was modified to accept a uniform instantaneous loading that extended from coordinates x_1 to x_2 and y_1 to y_2 , where the contaminated area extended only part of the distance, W . For the concentration of contaminant at any location

$$\begin{aligned}
C(x,y,z,t) = & \frac{M}{2WHAR} \left[1 + 2 \sum_{N=1}^{\infty} \exp \frac{(-\mu_N^2 D_z t)}{R} \cos(\mu_N z) \cos(\mu_N H) \right] \\
& \times \exp \left[\frac{-Kt}{R} \right] \left[\operatorname{erf} \left[\frac{x_2 - \left[x - \frac{Ut}{R} \right]}{2 \sqrt{\frac{D_x t}{R}}} \right] - \operatorname{erf} \left[\frac{x_1 - \left[x - \frac{Ut}{R} \right]}{2 \sqrt{\frac{D_x t}{R}}} \right] \right] \\
& \times \left[(y_2 - y_1) + 2 \sum_{m=1}^{\infty} \frac{\exp \left[\frac{-\beta_m^2 D_y t}{R} \right]}{\beta_m} \cos(\beta_m y) (\sin \beta_m y_2 - \sin \beta_m y_1) \right]
\end{aligned} \quad (25)$$

where

$$\mu_N = N\pi/H, \beta_m = m\pi/W, N, m = 1, 2, 3, \dots$$

M = an instantaneous horizontal area source of mass M

A = horizontal area over which mass is applied, length²

U = horizontal velocity of flow in aquifer, length/time

The maximum concentration of LP would occur if the LP flowed only a minimal vertical distance before encountering a shallow water table. After reaching the water table, the maximum concentration would occur at the top of the aquifer and along the line of flow of the groundwater.

Contaminant transport may take place in an aquifer that is wide and deep. In such a situation, the aquifer may be appropriately considered to be unbounded. In this situation, the model presented by Baetsle (1969) and Csanady (1980), Equation 6, can be modified slightly and applied to describe the contaminant concentration. Equation 6 is modified to

$$\begin{aligned}
C(x,y,z,t) = & \frac{2M}{\left[\sqrt{2\pi} (\sigma_x \sigma_y \sigma_z)^{1/3} \right]^3} \times \exp \left[- \frac{\left[x - x_3 - \frac{u(t - \tau)}{R} \right]^2}{2\sigma_{x_\tau}^2} \right. \\
& \left. - \frac{(y - y_3)^2}{2\sigma_{y_\tau}^2} - \frac{(z - z_3)^2}{2\sigma_{z_\tau}^2} - \frac{K(t - \tau)}{R} \right]
\end{aligned} \quad (26)$$

where the mass, M , has been introduced to the aquifer at location (x_3, y_3, z_3) and at time τ . The factor of 2 in the numerator of Equation 26 is necessary because the aquifer that is described as "unbounded" is still bounded or limited on the top by the water table. The terms σ_x , σ_y , and σ_z in Equation 6 are designated with an additional subscript, τ , in Equation 26 when their meaning is:

$$\sigma_{x_\tau} = \left[\frac{2D_x(t - \tau)}{(R)} \right]^{\frac{1}{2}}, \text{ length} \quad (27)$$

$$\sigma_{y_\tau} = \left[\frac{2D_y(t - \tau)}{(R)} \right]^{\frac{1}{2}}, \text{ length} \quad (28)$$

$$\sigma_{z_\tau} = \left[\frac{2D_z(t - \tau)}{(R)} \right]^{\frac{1}{2}}, \text{ length} \quad (29)$$

A constraint on Equation 26 is that $C = 0$ when $t < \tau$.

The contaminant transport model in an unbound aquifer can be modified further to accept a loading in which the applied mass is spread over a horizontal area instead of being applied at a point. In this case, the mass is assumed to be applied over an area, A , which extends in the x direction from x_1 to x_2 , and in the y direction from y_1 to y_2 . The model to describe the contaminant concentration is

$$\begin{aligned} C(x,y,z,t) = & \frac{M}{(32\pi)^{\frac{1}{2}} A \sigma_{z_\tau}} \\ & \times \exp \left[- \frac{\left[z - z_1 - \frac{u(t - \tau)}{R} \right]^2}{2\sigma_{z_\tau}^2} - \frac{K(t - \tau)}{R} \right] \\ & \times \left[\operatorname{erf} \left[\frac{(x_2 - x)}{\sqrt{2} \sigma_{x_\tau}} \right] - \operatorname{erf} \left[\frac{(x_1 - x)}{\sqrt{2} \sigma_{x_\tau}} \right] \right] \\ & \times \left[\operatorname{erf} \left[\frac{(y_2 - y)}{\sqrt{2} \sigma_{y_\tau}} \right] - \operatorname{erf} \left[\frac{(y_1 - y)}{\sqrt{2} \sigma_{y_\tau}} \right] \right] \end{aligned} \quad (30)$$

Sequential Contaminant Transport From Vertical Flow to Horizontal Flow

A contaminant plume from a spill on the soil surface will move downward until it encounters an aquifer that will have largely horizontal flow. Therefore, contaminant transport from vertical flow must be connected to contaminant transport in horizontal flow. The transport rate for vertical flow is given by

$$\left(VC - D_z^{-1} \frac{\partial C}{\partial z} \right) \Big|_{A_{z=H}} \quad (31)$$

where the various expressions in Equation 31 are obtained from Equation 20. Also, D_z^{-1} designates the dispersion coefficient in the vadose zone. Equation 31 becomes

$$\left(VC - D_z^{-1} \frac{\partial C}{\partial z} \right) \Big|_{A_{z=H}} = C \left[V + \frac{R\theta \left[z - z_1 - \frac{Vt}{R\theta} \right]}{2t} \right] \Big|_{z=H} \quad (32)$$

When contaminant transport from the vertical flow model is linked to contaminant transport in the horizontal model, the two models should use the same coordinate system. The coordinate system that has been used in the horizontal flow model is adopted, so that the z coordinate is positive pointing upward in the vertical direction, and the x and y coordinate are in the horizontal plane. Flow in the horizontal aquifer is in the x direction. The z_1 coordinate of a spill on the ground surface will be $z_1 = H + B$ with the origin of the coordinate system at the bottom of a horizontal aquifer of thickness, H . The ground surface is a distance, B , above the top of the aquifer.

The rate of transfer of mass from the vadose zone to the horizontal aquifer then becomes from Equation 32

$$\begin{aligned} \left(VC - D_z^{-1} \frac{\partial C}{\partial z} \right) \Big|_{A_{z=H}} &= \frac{M \left[V - \frac{R\theta}{2t} \left[B + \frac{Vt}{R\theta} \right] \right]}{\left[\frac{4\pi D_z^{-1} t}{R\theta} \right]^{\frac{1}{2}}} \\ &\times \exp \left[- \frac{\left[B + \frac{Vt}{R\theta} \right]^2 R\theta}{4D_z^{-1} t} - \frac{Kt}{R\theta} \right] \end{aligned} \quad (33)$$

where D_z^1 is the dispersion coefficient (units length²/time) in the vadose zone. Two precautions apply to this equation: first, the downward velocity, V , is a negative quantity since it is in the direction opposite to the positive z coordinate, and second, the mass transfer rate is negative when it is in the downward direction as the positive z coordinate is directed upward. Therefore, the mass transfer rate may have to be multiplied by -1 for some applications.

Now the mass transfer rate from Equation 33 can be applied as a loading function onto the horizontal aquifer. By combining Equations 25 and 33, the result is

$$\begin{aligned}
 C(x,y,z,t) = & \frac{M}{2WH} \int_0^t \frac{\left[V - \frac{R\theta}{2\tau} \left(B + \frac{V\tau}{R\theta} \right) \right]}{\left[\frac{4\pi D_z^1 \tau}{R\theta} \right]^{\frac{1}{2}}} \exp \left[- \frac{\left(B + \frac{V\tau}{R\theta} \right)^2 R\theta}{4D_z^1 \tau} - \frac{K\tau}{R\theta} \right] \\
 & \times \left[1 + 2 \sum_{N=1}^{\infty} \exp \left[-\mu_N^2 D_z \left\{ \frac{t-\tau}{R} \right\} \right] \cos(\mu_N z) \cos(\mu_N H) \right] \\
 & \times \left[\operatorname{erf} \left[\frac{x_2 - x + \frac{U(t-\tau)}{R}}{2 \left[D_x \frac{(t-\tau)}{R} \right]^{\frac{1}{2}}} \right] - \operatorname{erf} \left[\frac{x_1 - x + \frac{U(t-\tau)}{R}}{2 \left[D_x \frac{(t-\tau)}{R} \right]^{\frac{1}{2}}} \right] \right] \\
 & \times \left[(y_2 - y_1) + 2 \sum_{m=1}^{\infty} \frac{\exp \left[-\beta_m^2 D_x \left\{ \frac{t-\tau}{R} \right\} \right]}{\beta_m} \cos(\beta_m y) (\sin \beta_m y_2 - \sin \beta_m y_1) \right] d\tau
 \end{aligned} \tag{34}$$

where τ is a dummy variable of integration. Equation 34 will be multiplied by -1 to give positive concentrations. The spill of mass, M , covers an area, A , on the ground surface, where $A = (y_2 - y_1)(x_2 - x_1)$.

The horizontal aquifer may be considered to be unbounded by impermeable layers if the aquifer is deep and wide. In this situation, the mass transfer rate from the vertical flow model, Equation 32, must be combined with the unbounded horizontal flow model, Equation 26. The coordinate system is oriented with the origin on top of the horizontal aquifer, with the z axis vertical, the x axis in the direction of flow in the horizontal aquifer, and the y axis on the surface of the horizontal aquifer. Under these conditions Equations 32 and 26 combine to yield

$$\begin{aligned}
C(x,y,z,t) = & \frac{M}{(2^3\pi)^{\frac{1}{2}}} \int_0^t \frac{\left[V - \frac{R\theta}{2\tau} \left[B + \frac{V\tau}{R\theta} \right] \right]}{\sigma_{z_\tau} \left[\frac{4\pi D_z^1 \tau}{R\theta} \right]^{\frac{1}{2}}} \\
& \times \exp \left[- \frac{\left[B + \frac{V\tau}{R\theta} \right]^2 R\theta}{4D_z^1 \tau} - \frac{K\tau}{R\theta} \right] \\
& \times \exp \left[- \frac{z^2}{2\sigma_{z_\tau^2}} - \frac{K(t-\tau)}{R\theta} \right] \quad (35) \\
& \times \left[\operatorname{erf} \left[\frac{x_2 - x + \frac{U(t-\tau)}{R}}{\sqrt{2}\sigma_{x_\tau}} \right] - \operatorname{erf} \left[\frac{x_1 - x + \frac{U(t-\tau)}{R}}{\sqrt{2}\sigma_{x_\tau}} \right] \right] \\
& \times \left[\operatorname{erf} \left[\frac{y_2 - y}{\sqrt{2}\sigma_{y_\tau}} \right] - \operatorname{erf} \left[\frac{y_1 - y}{\sqrt{2}\sigma_{y_\tau}} \right] \right] d\tau
\end{aligned}$$

where τ is a dummy variable of integration. The coordinate z will be negative within the horizontal aquifer. Because the mass transfer from the vadose zone is opposite the direction of the positive z axis, Equation 35 will be multiplied by -1 to give positive concentrations. Again, the spill of mass, M , is considered to cover an area, A , where $A = (y_2 - y_1)(x_2 - x_1)$.

Estimates of Parameters in Contaminant Transport Models

Contaminant transport models contain a number of parameters that describe the magnitude of the spill, the area over which the spill took place, the migration velocities of water, the porosity and moisture content of the aquifer, the retardation coefficient, dispersion coefficients, and reaction rate constants. The parameters tend to be spill and site specific, so generalizing about them prior to a spill is difficult. Nevertheless, having information about the role of different parameters in describing the concentration in an aquifer resulting from a spill is helpful.

Volume or mass of a spill

The mass of a spill may be estimated crudely from the size of containers involved. Arthur D. Little (ADL) (1994) reported that an individual LP container is anticipated to hold 115 ℓ (30 gal). This volume is projected to increase to 151 ℓ (40 gal) in the future under full-scale production conditions. Using these tentative amounts, if four such containers were packed into a pallet, the projected capacity of a vehicle transporting LP can be described (Table 6).

Table 6 Projected Typical Capacity of Vehicles Transporting LP			
Vehicle	Pallets	Liter (gal)	Kg (lb)
Van, Semivan, or Trailer	18	10,990 (2,880)	15,600 (34,300)
Intermodal Shipping-Overseas (ISO) Container	16-0	9,700-12,100 (2,560-3,200)	13,800-17,300 (30,400-38,000)
Palletized Load System (PLS) Flatrack	14	8,500 (2,240)	12,100 (26,700)
Heavy Expanded Mobility Tactical Truck (HEMTT)	9	5,400 (1,440)	6,200 (13,600)

Area covered by a spill

The area covered by an LP spill is a function of the soil type. For example, gravel and coarse sand have an open, porous structure that lends itself to high percolation or infiltration rates. High infiltration rates are associated with a spill covering a small surface area. Silt or clay soils are generally associated with lower infiltration rates, so the area covered by a spill may be relatively large. Terrain also will influence the area covered by a spill, as steep terrain will promote LP runoff in rivulets or streams. Methods for estimating the length of an LP spill are provided in Pennington et al. (1994). Examples are provided in ADL (1994). The spill width is expected to depend upon the spill conditions and the local terrain—for examples, into a ditch, upon a flat surface, or upon a hillside. A crude estimate of the tendency for a spill to infiltrate, or run off, can be made from the Universal Soil Classification System (Table 7). A spill onto soils appearing at the top of the table (coarse-grained soils) will infiltrate rapidly, generating approximately a point source, while a spill on soils appearing at the bottom of the table (fine-grained soils) will tend to run off, approximating an area source loading.

Table 7
Universal Soil Classification System

Major Divisions			Group Symbols ²	Typical Names	Field Identification Procedures (excluding particles larger than 75 mm and basing fractions on estimated weights)
1	2		3	4	5
Coarse-grained Soils More than half of material is larger than No. 200 ¹ (75 μ m) sieve size. The No. 200 sieve size is about the smallest particle visible to the naked eye.	Gravels More than half of gravel fraction is larger than No. 4 sieve size (4.75 mm) (for visual classification, 5 mm may be used as equivalent to the No. 4 sieve size)	Clean Gravels (little or no fines)	GW	Well-graded gravels, gravel sand mixtures, little or no fines.	Wide range in grain sizes and substantial amounts of all intermediate particle sizes.
			GP	Poorly graded gravels, gravel-sand mixture little or no fines.	Predominantly one size or a range of sizes with some intermediate sizes missing.
		Gravels with Fines (appreciable amount of fines)	GM	Silty gravels, gravel-sand silt mixtures.	Nonplastic fines or fines with low plasticity (for identification procedures see ML below).
			GC	Clayey gravels, gravel-sand-clay mixtures.	Plastic fines (for identification procedures see CL below.)
	Sands More than half of coarse fraction is smaller than No. 4 sieve size. (4.75 mm)	Clean Sands (little or no fines)	SW	Well-graded sands, gravelly sands, little or no fines.	Wide range in grain sizes and substantial amounts of all intermediate particle sizes.
			SP	Poorly graded sands, gravelly sands, little or no fines.	Predominantly one size or a range of sizes with some intermediate sizes missing.
		Sands with Fines (appreciable amount of fines)	SM	Silty sands, sand-silt mixtures.	Nonplastic fines or fines with low plasticity (for identification procedures see ML below).
			SC	Clayey sands, sand-clay mixtures.	Plastic lines (for identification procedures see CL below.)

(Continued)

Note: U.S. Army Engineer Waterways Experiment Station (1960) and Howard (1977).

¹ All sieve sizes on this chart are U.S. Standard.

² Boundary classifications: soil, possessing characteristics of two groups are designated by combinations of group symbols. For example, GW-GC, well-graded gravel/sands mixture with clay binder.

Table 7 (Concluded)

Major Divisions		Group Symbols ²	Typical Names	Field Identification Procedures (excluding particles larger than 75 mm and basing fractions on estimated weights)		
1	2	3	4	5		
Fine-grained Soils More than half of the material is smaller than No. 200 (75 μm) sieve size.	Silts and Clays Liquid limit less than 50			Identification Procedures on Fraction Smaller than No. 40 Sieve Size		
				Dry Strength (crushing characteristics)	Dilatancy (reaction to shaking)	Toughness (consistency near PL)
		ML	Inorganic silts and very fine sands, rock flour, silty or clayey fine sands or clayey silts with slight plasticity.	None to slight	Quick to slow	None
		CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays.	Medium to high	None to very slow	Medium
		OL	Organic silts and organic silty clays of low plasticity	Slight to medium	Slow	Slight
		MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts.	Slight to medium	Slow to none	Slight to medium
		CH	Inorganic clays of high plasticity, fat clays	High to very high	None	High
		OH	Organic clays of medium to high plasticity, organic silts.	Medium to high	None	High
	Highly Organic Soils		Pt	Peat and other highly organic soils.	Readily identified by color, odor, spongy feel, and frequently by fibrous texture.	

Aquifer dimensions

Some of the models presented in this report require the dimensions of an aquifer, specifically thickness and width. The thickness of an aquifer is likely to be unknown unless geological information and drilling records are available for the site. In some cases, such as a spill in a mountain valley, the aquifer width can be estimated from the distance between canyon walls. In most cases, the aquifer can be treated as unbounded, i.e., the aquifer is wide and deep, and more precise dimensions are unnecessary.

Porosity and soil water content

Porosity, n , and soil water content, sometimes called moisture content, θ , appear as parameters in some equations. Porosity is likely to fall between values of 0.2 to 0.5 with an estimate of 0.35 being a first approximation. Better values are obtained by soil testing.

The soil water content, θ , represents the volume of water per unit volume of soil. In an aquifer, all of the pore space is assumed; content is the porosity, n . In the vadose zone, the soil water content may vary from a low value of 0.10 to a value equal to the porosity. The soil water content will reflect the local climate. In arid areas, soil water content will be low; while in areas of high rainfall, soil water content will be high, but cannot exceed n , the porosity.

Seepage velocity in vadose zone

The seepage velocity of water in the vadose zone is in the downward direction because of the influence of gravity. Seepage velocity is calculated by Darcy's equation

$$V^1 = KI \quad (36)$$

where

V^1 = seepage velocity, length/time

I = hydraulic gradient, dimensionless

K = hydraulic conductivity, length/time

For unsaturated soil, the hydraulic conductivity, K , is a function of the soil water content and may be written as $K(\theta)$ to show the functional relationship. The value of $K(\theta)$ is determined experimentally and varies greatly with the soil water content, decreasing as the soil water content decreases. Figure 4 shows the hydraulic conductivity as a function of the soil water content for a sandy

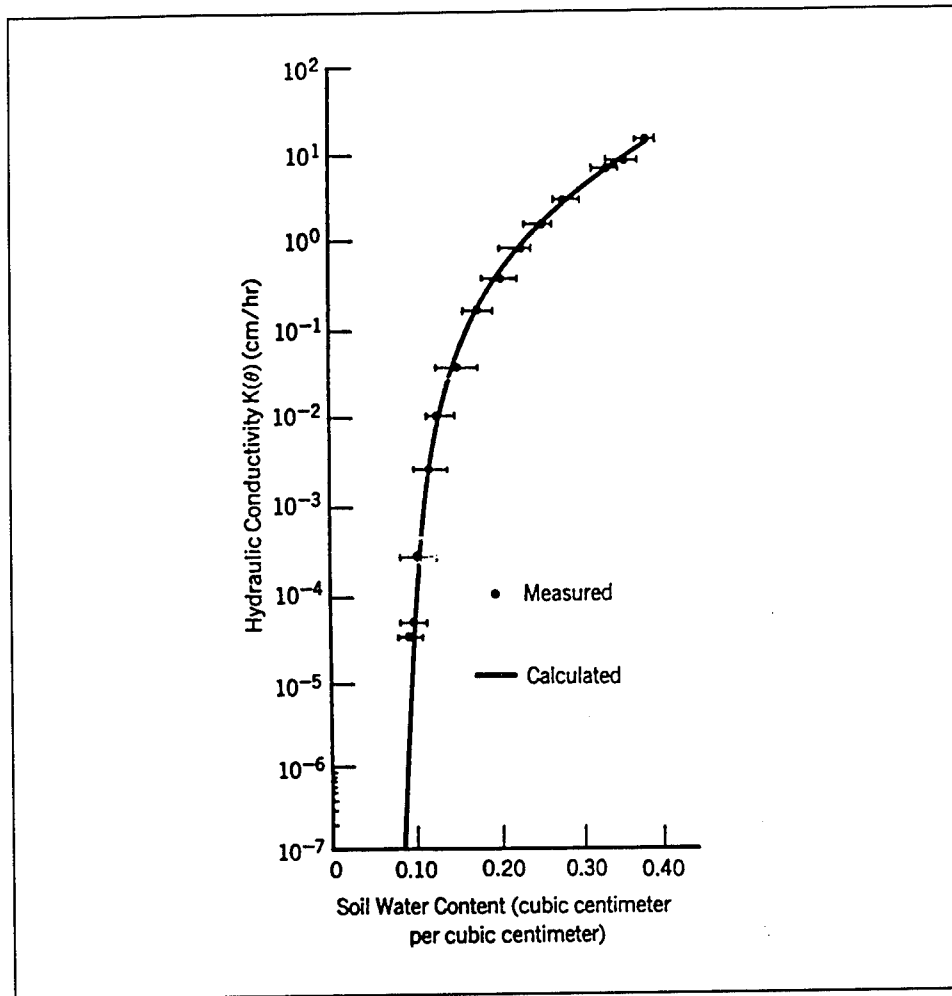


Figure 4. Hydraulic conductivity in vadose zone related to soil water content (cubic centimeter per cubic centimeter)

soil. The variation in magnitude of $K(\theta)$ is so large that no "typical value" can be given.

The hydraulic gradient, I , is easy to predict in the vadose zone since the gradient will approach a value of $I = 1.0$.

Seepage velocity in an aquifer

The seepage velocity in an aquifer, U^1 , is not a function of the soil water content since the pore space in an aquifer is saturated with water. The seepage velocity is calculated from Darcy's equation

$$U^1 = KI \quad (37)$$

where

U^1 = seepage velocity in an aquifer, length/time

K = saturated hydraulic conductivity, length/time

I = hydraulic gradient, dimensionless

The hydraulic conductivity varies greatly from one type of aquifer material to another. Table 8 gives a range of values for different types of aquifer materials. The values of the hydraulic conductivity in sedimentary rocks in Table 8 can be correlated with the classifications of soil in Table 7 to provide a crude relationship between soil particle size and hydraulic conductivity.

The hydraulic gradient, I , in an aquifer is difficult to determine without measurements in observation wells. The hydraulic gradient will be < 1 , typically much less than one. A crude approximation of the hydraulic gradient may be made by observing the slope of the land surface. A drop in the land surface of 1 m per 100 m may correspond to a hydraulic gradient of 1/100.

Darcy equation velocity versus pore water velocity

The Darcy equation for vertical flow, Equation 36, or horizontal flow, Equation 37, provides the flow rate per unit area or the seepage velocity. However, when considering contaminant transport, the velocity of the water in the pores must also be determined. A simple conversion between the seepage velocity and the pore water velocity can be made. The appropriate equation for flow in the vadose zone is

$$V = \frac{V^1}{\theta} \quad (38)$$

where V is the pore water velocity in the vadose zone, length/time.

The equation that is applicable for the pore water velocity in an aquifer is

$$U = \frac{U^1}{n} \quad (39)$$

where U is the pore water velocity, length/time.

Table 8
Representative Values of Hydraulic Conductivity for Various Rock Types

Material	Hydraulic Conductivity, m/sec
Sedimentary	
Gravel	3×10^{-4} - 3×10^{-2}
Coarse sand	9×10^{-7} - 6×10^{-3}
Medium sand	9×10^{-7} - 5×10^{-4}
Fine sand	2×10^{-7} - 2×10^{-4}
Silt, loess	1×10^{-9} - 2×10^{-5}
Till	1×10^{-12} - 2×10^{-6}
Clay	1×10^{-11} - 4.7×10^{-9}
Unweathered marine clay	8×10^{-13} - 2×10^{-9}
Sedimentary Rocks	
Karst and reef limestone	1×10^{-6} - 2×10^{-2}
Limestone, dolomite	1×10^{-9} - 6×10^{-6}
Sandstone	3×10^{-10} - 6×10^{-6}
Siltstone	1×10^{-11} - 1.4×10^{-8}
Salt	1×10^{-12} - 1×10^{-10}
Anhydrite	4×10^{-13} - 2×10^{-8}
Shale	1×10^{-13} - 2×10^{-9}
Crystalline Rocks	
Permeable basalt	4×10^{-7} - 2×10^{-2}
Fractured igneous and metamorphic rock	8×10^{-9} - 3×10^{-4}
Weathered granite	3.3×10^{-6} - 5.2×10^{-5}
Weathered gabbro	5.5×10^{-7} - 3.8×10^{-6}
Basalt	2×10^{-11} - 4.2×10^{-7}
Unfractured igneous and metamorphic rocks	3×10^{-14} - 2×10^{-10}

Diffusion and dispersion coefficients

Three mixing coefficients, D_x , D_y , and D_z , appear in the contaminant transport equations (where the subscript indicates the coordinate direction for which the coefficient is applicable). Each mixing coefficient is made up of two components, a molecular diffusion component and a mechanical-mixing component. The molecular diffusion component is independent of the

coordinate direction. Figure 5 shows diffusion coefficients for various environments. Note that molecular diffusion coefficients range in magnitude from approximately 10^{-9} cm²/sec to 10^{-4} cm²/sec.

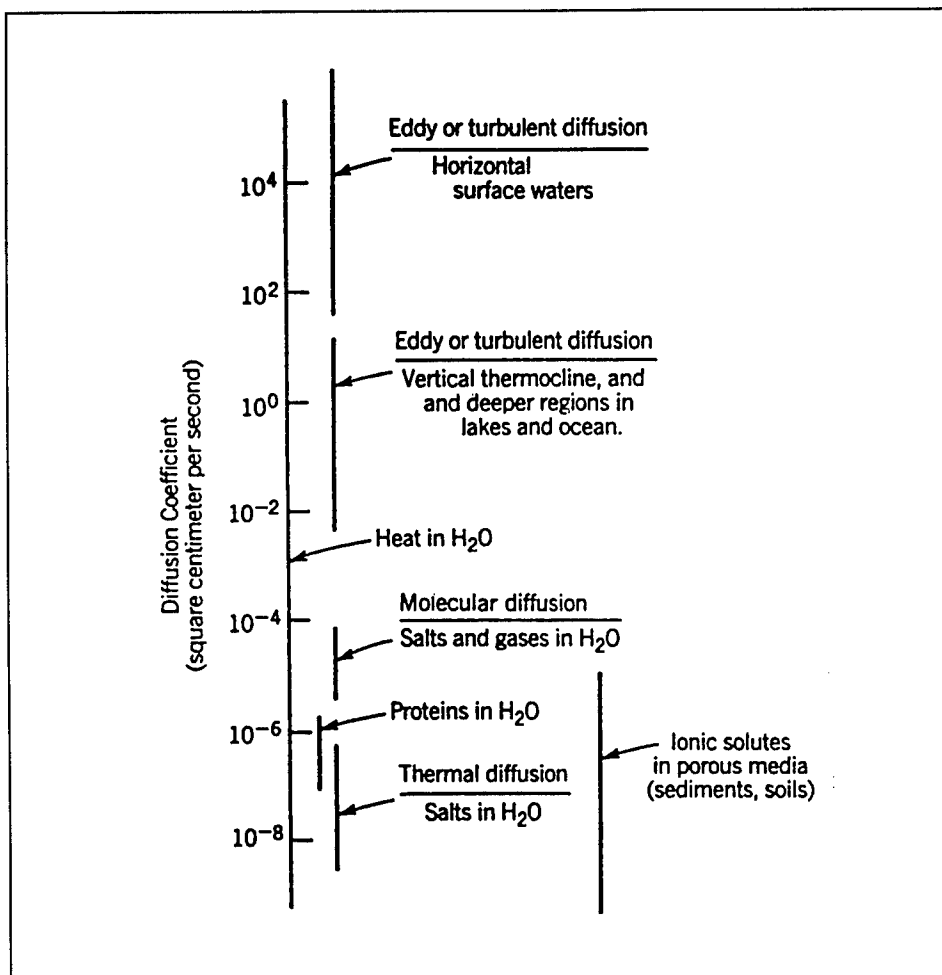


Figure 5. Diffusion coefficients characteristic of various environments

Mechanical mixing coefficients are directly proportional to the water velocity, V or U . The dispersion coefficient is the sum of the molecular diffusion coefficient and the mechanical mixing coefficient. Using the pore water velocity, U , in the X direction one has

$$D_x = D_m + \alpha_L U \quad (40)$$

where

D_x = dispersion coefficient in direction of flow, length²/time

D_m = molecular diffusion coefficient, length²/time

α_L = longitudinal dispersivity in direction of flow, length

U = pore water velocity in X direction, length/time

In nearly all cases, $\alpha_L U$ is much larger than D_m , so the usual approximation is that

$$D_x = \alpha_L U \quad (41)$$

The longitudinal dispersivity, α_L , varies with the scale of the experiment (Figure 6). The scale of an experiment refers to the distances that are involved. For example, if a spill occurs on the ground surface and the spilled material seeps 10 m into the ground, the scale would be 10 m. On the other hand, if a spill seeped 100 m in a horizontal aquifer to a well, the scale would be 100 m.

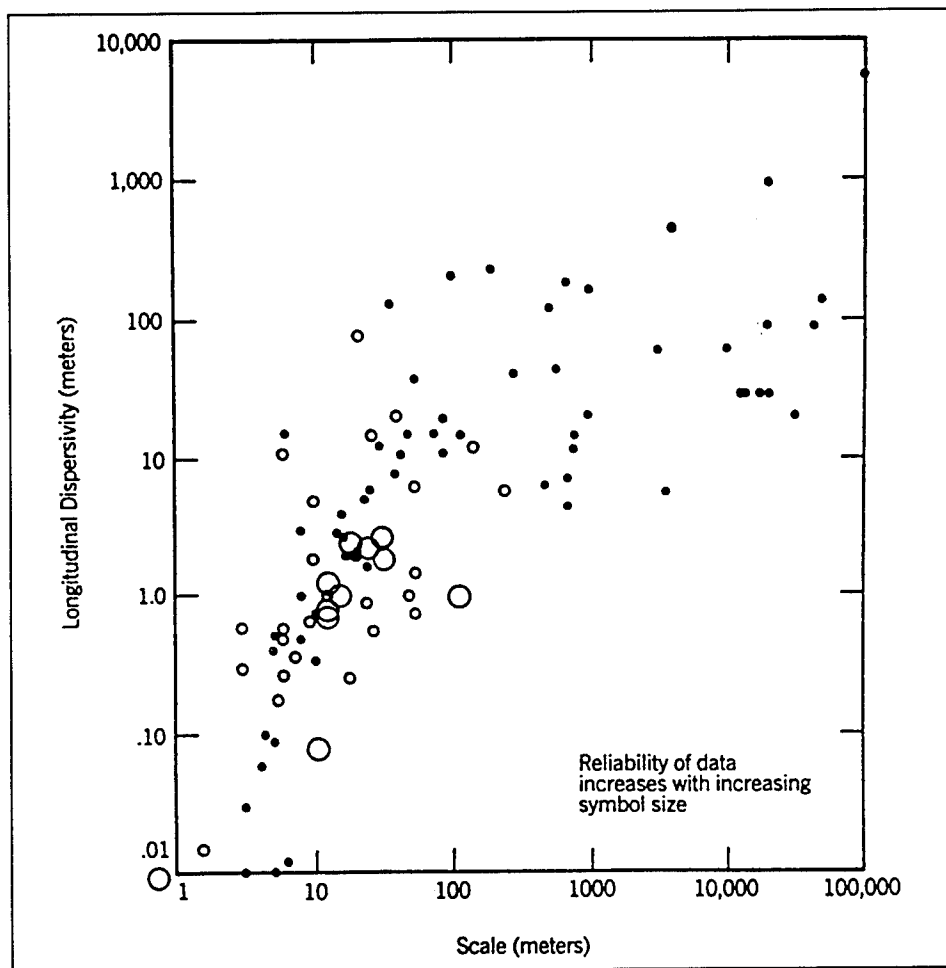


Figure 6. Scale of observation versus longitudinal dispersivity: reliability classification

The dispersion coefficients that are applicable to the directions perpendicular to the flow direction are given by the equations

$$D_y = D_m + \alpha_T U \quad (42)$$

and

$$D_z = D_m + \alpha_T U \quad (43)$$

where the meaning of the terms corresponds to previous definition, but α_T is the transverse dispersivity with units of length. Again, molecular diffusion is usually neglected and

$$D_y \text{ or } D_z = \alpha_T U \quad (44)$$

The value of α_T is approximately 10 percent of the magnitude of α_L . Thus, as a first approximation, Figure 6 can be used to estimate the longitudinal dispersivity in the direction of flow. Then the lateral, or transverse, dispersivity can be taken as 10 percent of the longitudinal dispersivity.

The dispersion characteristics in the vadose zone are not likely to be the same as in a saturated aquifer. In the absence of more specific guidance, the same procedure can be used to estimate the dispersion coefficients in the unsaturated zone as in the saturated zone.

Retardation coefficient

The retardation coefficient, R , should be determined by experiment until a larger body of experimental data sets are available. Experimental measurements show the value of R (dimensionless) for HAN varied from 1.3 in China Lake soil to 2.6 in Picatinny soil (Pennington et al. 1994). The corresponding values of R for TEAN ranged from 2.3 for Picatinny soil to 13.5 for China Lake soil. The retardation coefficient for the NO_3^- ion is usually estimated as $R = 1$, i.e., not retarded.

Transformation rate

Transformation rate is expressed as a first order process. The rate constant, K , expresses the transformation rate through the equation

$$\frac{dC}{dt} = -KC \quad (45)$$

where

C = concentration of species being transformed, mass/volume

t = time

K = first order transformation rate, 1/time

A conservative (worst case) assumption is that $K = 0$ for a spill. In such a case, HAN would leach rather than react with the soil as has been documented.

Summary example of measured coefficients

Adrian and Myers (Pennington et al. 1994) reported results of two experiments in which LP was added to China Lake (Table 9) and Picatinny soils (Table 10). The experiments took place in columns 15.2 cm long, so this provides an estimate of the scale of the experiment. The flow in the columns was one dimensional, so no estimate of transverse mixing was possible. All terms in the tables have been defined previously.

Table 9 Dispersion, Adsorption, Reaction, and Partitioning Characteristics of China Lake Soil (reprinted from Pennington et al. 1994)						
Column	α cm	V cm/sec	D cm ² /sec	R	K sec ⁻¹	K_d cm ³ /g
A-HAN	0.412	19.27 E-4	7.94 E-4	1.587	25.8 E-5	0.112
B-HAN	0.714	9.41 E-4	6.72 E-4	1.308	5.57 E-5	0.083
C-HAN	0.753	2.23 E-4	1.68 E-4	1.473	0.989 E-5	0.095
A-TEAN	2.152	19.27 E-4	41.46 E-4	13.385	43.16 E-5	2.371
B-TEAN	3.194	9.41 E-4	30.06 E-4	10.514	15.06 E-5	2.564
C-TEAN	2.368	2.23 E-4	5.28 E-4	11.061	4.13 E-5	2.015

Table 10
Dispersion, Adsorption, Reaction, and Partitioning Characteristics
When LP Was Added to a Column of Picatinny Soil (reprinted from
Pennington et al. 1994)

Column	α cm	V cm/sec	D cm ² /sec	R	K sec ⁻¹	K_d cm ³ /g
D-HAN	0.472	1.38 E-4	0.651 E-4	2.347	0.24 E-5	0.586
E-HAN	1.431	3.51 E-4	5.024 E-4	2.634	0.00	0.773
F-HAN	0.116	4.63 E-4	0.537 E-4	2.101	1.054 E-5	0.504
D-TEAN	1.359	1.38 E-4	1.875 E-4	2.882	0.281 E-5	0.818
E-TEAN	2.101	3.51 E-4	3.290 E-4	2.859	0.046 E-5	0.879
F-TEAN	0.711	4.63 E-4	5.28 E-4	2.293	1.235 E-5	0.592

3 Results and Discussion

Observation of Liquid Propellant Movement and Reaction in Soils

All three soils expanded upon contact with LP (Figure 7). The LP migrated through each soil within the first several minutes. Profiles for migration of water levels varied with soil.

China Lake B

Of the three soils, China Lake B soil reacted least with the liquid propellant as evidenced by soil swelling and production of gas bubbles. The wetting front was clearly visible and progressed through the dry soil to the porous plate in several minutes. Small, temporary cavities were formed as the liquid progressed through the soil, but the soil was coarse enough to allow the gas bubbles to travel upwards and exit from the top of the column. No ponding was evident on the soil surface during the first few minutes after LP application started, but within a few minutes temporary ponding was observed. As water displaced LP in the column, gas production stopped, the liquid infiltrated easily into the soil, and ponding stopped.

Socorro Periphery

Of the three soils, elution of liquid through Socorro P was the slowest. Socorro P soil immediately swelled upon coming into contact with LP. Within a few minutes after the start of the experiment, the soil reached its maximum expansion, having expanded to a total length of 37.8 cm. The soil remained expanded during the remainder of the experiment. Ponding on the soil surface started almost as soon as LP was applied. Ponding continued throughout the experiment regardless of whether the applied liquid was LP or water. The position of the wetting front was difficult to identify in Socorro P soil because of the lack of contrast in color between wet and dry soil. Gas production from LP produced many cavities in the soil. Small cavities tended to persist for long periods of time.

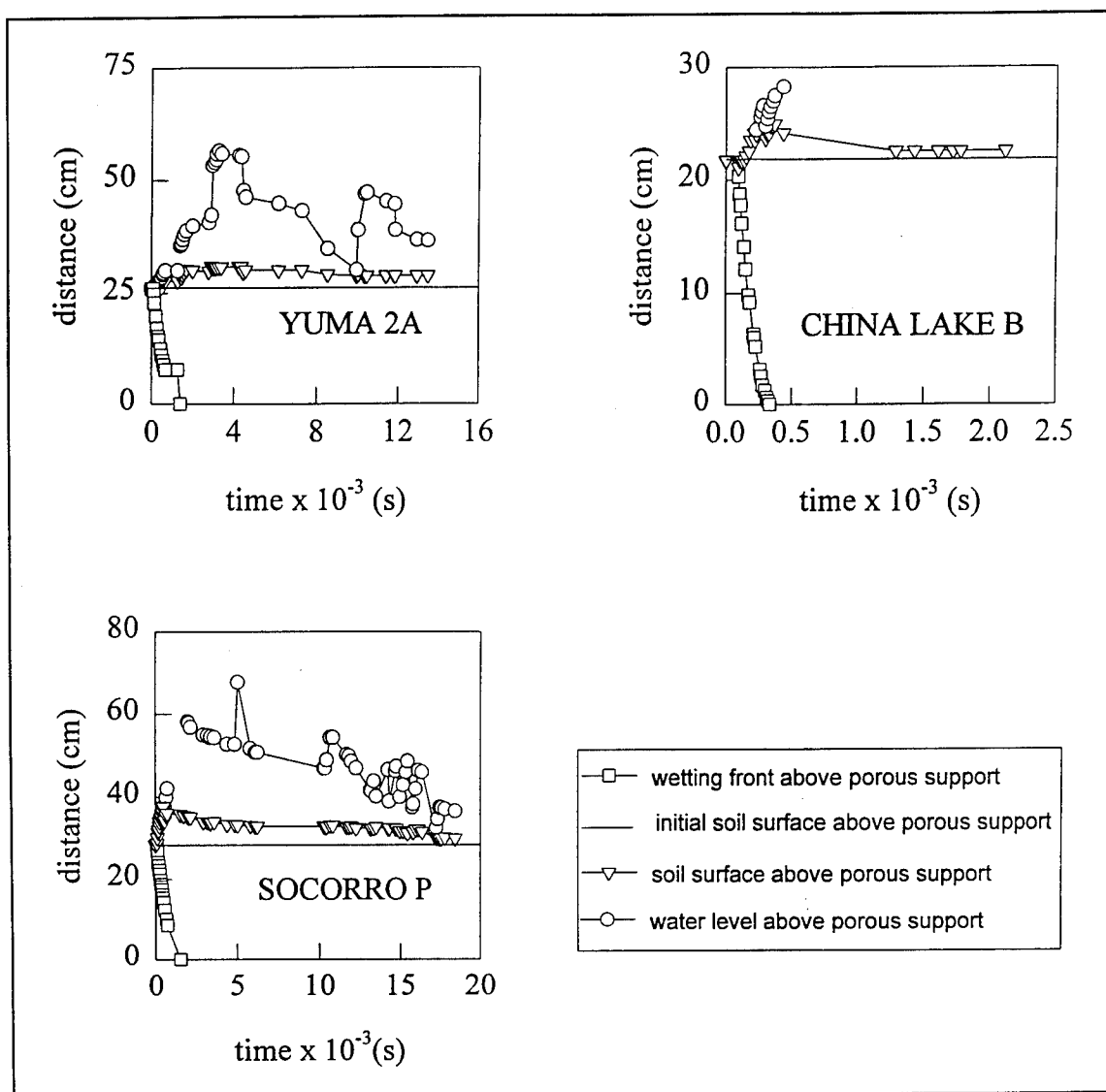


Figure 7. Infiltration characteristics of LP in test soils

Yuma 2A

Yuma 2A soil produced gas immediately upon contact with LP resulting in soil swelling. The wetting front moved down steadily, but was interrupted by cavity formation. Ponding on the soil surface occurred soon after LP was applied, and ponding continued throughout the experiment. However, the depth of liquid ponded on the soil surface increased and decreased, depending on the formation and disappearance of cavities in the soil. Cavities, which were larger than in the other two soils, interrupted the flow more often.

Elution of HAN, TEAN, and Other Nitrogen-Containing Species

In each of the soils, the peak concentration of HAN in the effluent was greater than the peak concentration of TEAN (Figure 8). However, the relative peak concentrations of HAN and TEAN differed considerably from soil to soil. The ratio of TEAN to HAN in Socorro P soil was about 4:5, in Yuma 2A soil 3:5, and in China Lake B soil 3:10. The ratio in China Lake B soil approximates the ratio of HAN to TEAN in undiluted LP, which is approximately 1:3. The soils also showed distinctly different abilities to transform HAN and TEAN. The peak HAN concentrations in effluents from China Lake B, Yuma 2A, and Socorro P soils were 730, 300, and 230 g/l, respectively. The peak TEAN concentrations were 230, 180, and 190 g/l in the same soil, respectively. An exception to the general trend was a TEAN concentration greater than the HAN concentration in Socorro P soil during a washout period.

One of the measures of transformation is the form of nitrogen occurring in the highest concentration in the eluate. Yuma 2A and Socorro P soils eluted peak concentrations of TKN of 160 g/l and 110 g/l, respectively, while the peak concentration in China Lake B soil was about 20 g/l (Figure 9). Organic nitrogen occurred in the second highest concentration in the eluate of Yuma 2A and Socorro P soils. Concentrations were 140 g/l and 110 g/l, respectively. China Lake B soil produced a peak concentration of 20 g/l. By contrast, NO_2 plus NO_3 nitrogen occurred in the highest concentration in eluants from China Lake B soil (120 g/l). Yuma 2A and Socorro P yielded peak concentrations of 80 g/l and 70 g/l, respectively. The NH_3 -nitrogen occurred in the lowest peak concentrations in all soils; China Lake B, Yuma 2A, and Socorro P yielding concentrations of 16, 15, and 3 g/l, respectively.

The NO_2 plus NO_3 nitrogen presents a significant public health concern. An LP spill onto a sandy soil, like China Lake B soil, has the potential to produce a higher peak concentration of NO_2 plus NO_3 nitrogen in groundwater than a spill onto soils that contain higher concentrations of silt and clay, such as Yuma 2A and Socorro P soils (Figure 8).

The mass of NO_2 plus NO_3 nitrogen in eluants were 10.70, 19.55, and 17.58 g for China Lake B, Socorro P, and Yuma 2A soils, respectively. These masses represent the potential loading of an aquifer.

Potential Nitrate Loading of an Aquifer

Loading factors define the quantity of NO_2 plus NO_3 nitrogen generated per unit mass of LP spilled or per unit volume of LP spilled (Table 11). Loading

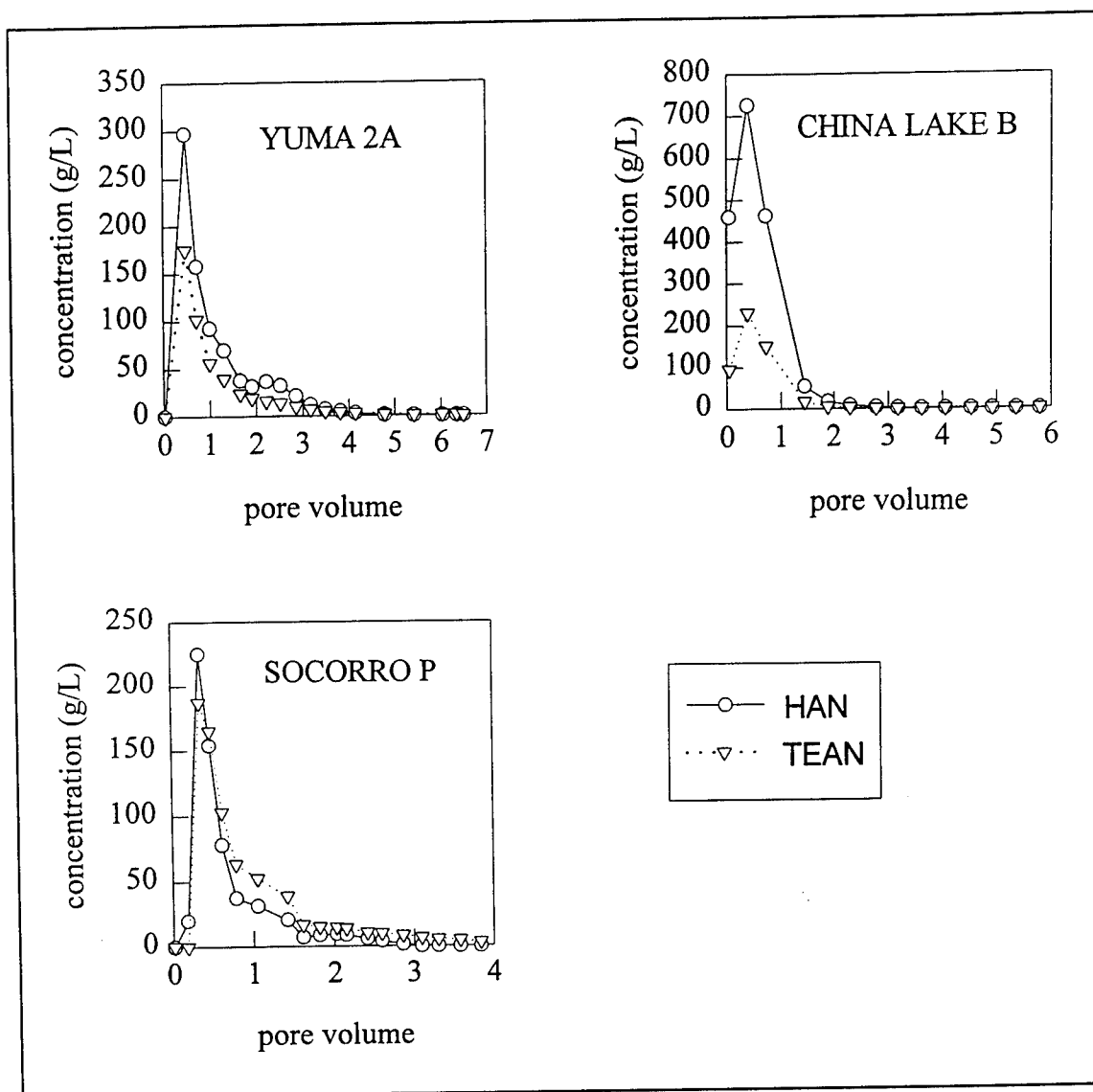


Figure 8. HAN and TEAN elution from test soils

factors are developed from the measurements of NO_2 plus NO_3 nitrogen eluted from each soil and the mass of LP applied to the soil (Table 11). Two examples are presented below that illustrate the use of loading factors to estimate nitrate concentrations reaching a shallow aquifer and the time required to reach the aquifer.

pH Behavior in Soil

Since HAN and TEAN were concentrated in the first eluate, finding the lowest pH in that eluant from both China Lake B and Socorro P soils was not surprising (Figure 10). After the first pore volume, the pH increased with the amount of liquid eluted until stabilizing in the 6 to 8 pH range. Part of the

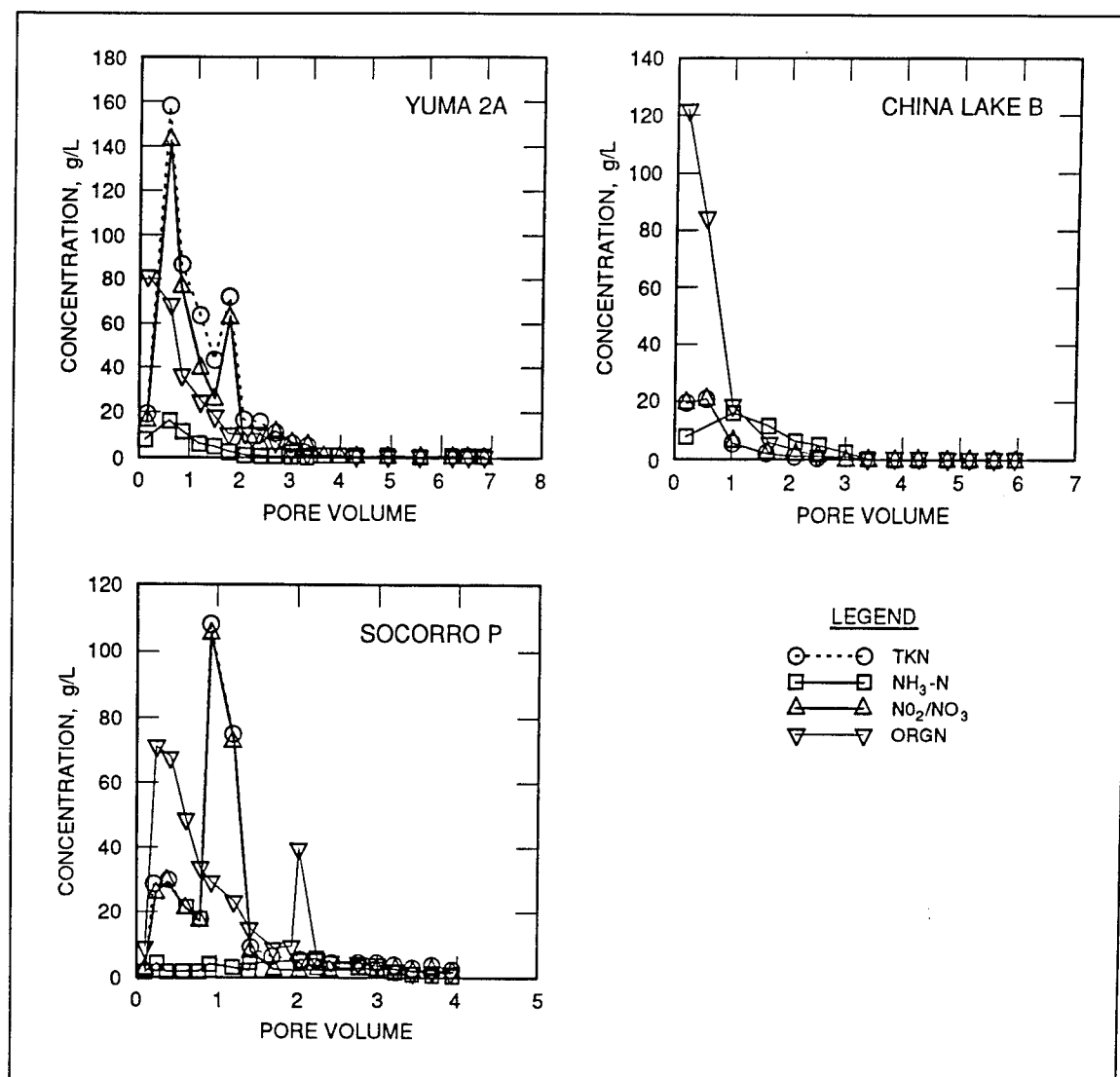


Figure 9. Distribution of nitrogen species eluted from soils

Table 11 NO₂ Plus NO₃ Nitrogen Loading Factors for LP Spilled Onto Soil					
Soil	LP Mass Applied, g	LP Volume Applied, cm ³	NO ₂ Plus NO ₃ Nitrogen Generated, g	Load Factor g NO ₃ per g, LP	Load Factor g NO ₃ per cm ³ LP
China Lake B	141.4	98.9	10.70	0.076	0.11
Socorro P	230.6	161.3	19.55	0.085	0.12
Yuma 2A	237.5	166.1	17.58	0.074	0.11

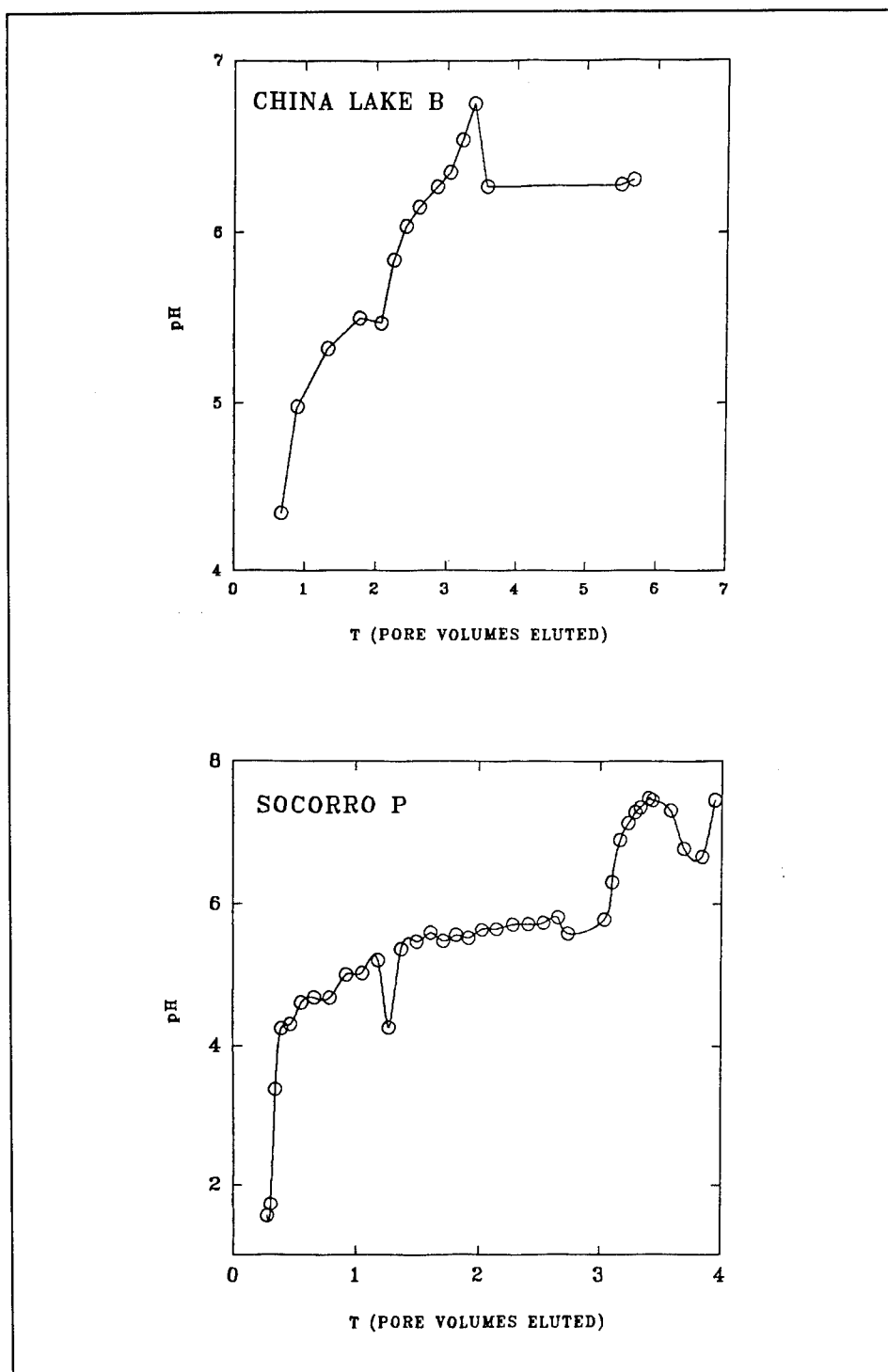


Figure 10. pH in liquid eluted from China Lake B and Socorro P soils

increase in pH was due to the soil contact with LP, while part was due to dilution of the applied LP with the feed water. The pH in China Lake B soil stabilized in the range 6 to 7, while the pH in Socorro P soil fluctuated with the pore volumes of eluted liquid, but remained within the 6 to 8 pH range.

Application of Mathematical Models

The remainder of this chapter is devoted to the results obtained when the mathematical models, which were presented in the "Materials and Methods" section, were applied to predict the concentration of nitrate ion as a result of various LP spill scenarios. In the remainder of the chapter, the combination NO_2^- plus NO_3^- will be referred to as nitrate or nitrate ion. More precisely, the meaning will be nitrate-nitrogen, NO_3^- -N.

Most of the results obtained by applying the mathematical models are lengthy and tedious to follow. To help reduce the number of tables that must be applied to obtain concentrations of nitrate in groundwater, some of the results are presented in graphical form (Appendix A). The results of applying the mathematical models will be presented in the following three examples:

- a. Example 1 is a short calculation of the maximum concentration of nitrate ion that could result from an LP spill defined as a point source.
- b. Example 2 is a model of an LP spill that occurs on an aquifer that is nearly at the ground surface. Such a scenario could occur near a wetland or in a river valley after prolonged rainfall. The spilled LP spreads out over an area before infiltrating. The model output to support Example 2 are contained in a series of lengthy tables (Appendix A).
- c. The model output for Example 3 is a series of figures (Appendix B) showing LP infiltrating into the soil, seeping downward, intercepting the groundwater aquifer, and being carried along by the flowing groundwater.

Example 1. Calculation of maximum nitrate concentration beneath a point source LP spill

A shipment of LP on a trailer is damaged in an accident so that one container is ruptured. The LP spills onto a soil having the characteristics of China Lake B soil. The spill is considered a point source. The water table is 10 m beneath the soil surface, and the vertical flow velocity of water through the soil is 2 m/day. The maximum concentration of nitrate ion is calculated at the water table.

Assume that the soil has the following characteristics:

θ = moisture content = 0.5

R = retardation coefficient = 1.0

K = chemical transformation rate = 0

$D_x = D_y$ = lateral dispersion coefficients = $2.6 \times 10^{-6} \text{ m}^2/\text{sec}$

D_z = longitudinal dispersion coefficient = $2.3 \times 10^{-5} \text{ m}^2/\text{sec}$

Equation 16, which gives the maximum concentration for vertical flow, will be used. The following calculation steps are appropriate:

Step 1. Calculate the mass of LP spilled. State that if a trailer carries 15,000 kg of LP, which is contained in 18 pallets, each of which contains 4 drums (ADL 1994), then mass spilled = $15,000 \text{ kg} / (18 \text{ pallets} \times 4 \text{ drums/pallet}) = 208.3 \text{ kg} = 208,300 \text{ g}$.

Step 2. Calculate the mass of nitrate ion generated from the spilled LP. For China Lake B soil, a load factor of $0.076 \text{ g NO}_3/\text{g LP}$ has been determined empirically (Table 6). Therefore, the mass of nitrate generated = $208,300 \text{ g LP} \times 0.076 \text{ g NO}_3/\text{g LP} = 15,830 \text{ g NO}_3$.

Step 3. Calculate the time that will elapse between the spill and the LP reaching the water table. Calculate $t = \text{length/velocity} = 10 \text{ m} / (2 \text{ m/day}) = 5 \text{ day} = 432,000 \text{ sec}$.

Step 4. Calculate C_{max} , the maximum nitrate concentration at the water table. $C_{max} = [M(R\theta)^{3/2} \exp(-Kt/R\theta)] / [8(\pi t)^{3/2} (D_x D_y D_z)^{1/2}] = [15,830 (1 \times 0.5)^{3/2} \exp(-0)] / [8(\pi 432,000)^{3/2} (2.6 \times 10^{-6} \times 2.6 \times 10^{-6} \times 2.3 \times 10^{-5})^{1/2}] = [15,830 \times 0.3536 \times 1] / [8 \times 1.582 \times 10^9 \times 1.247 \times 10^{-8}] = 35.47 \text{ g/m}^3 = 35.47 \text{ mg/l}$.

A larger or smaller spill of LP would produce a nitrate concentration that is directly proportional to the spill mass, as long as the spill is assumed to take place as a point source. For example, if two LP drums were spilled, the maximum concentration for the conditions given in the example would be $C_{max} = 2 \times 35.47 \text{ mg/l} = 70.94 \text{ mg/l}$. Example 1 is modeled with slightly different variables and for several periods of lapsed time after a spill (10, 20, 30, 40, 50, 60, 80, 100, 125, 150, 200, 250, 300, 400, and 500 days) in Appendix B (pages B2-B18).

Example 2. Calculation of nitrate concentration in an aquifer near the ground surface

In this example, the aquifer is considered to be so near the ground surface that the vertical travel distance can be neglected. The LP can be assumed to mix into the groundwater as it flows in an almost horizontal direction. This example will make use of the horizontal flow model, Equation 25.

Suppose the conditions at the spill site were such that the LP spill mass = 1,316 kg, and the spill takes place over an area that measures 10 by 10 m. The aquifer is assumed to be 100 m wide and 10 m deep and has a seepage velocity of $1.0 \times 10^{-6} \text{ m/sec} = 0.0864 \text{ m/day}$. The longitudinal dispersion coefficient, D_x , is $10^{-4} \text{ m}^2/\text{sec}$; both the lateral and the vertical dispersion coefficient, D_y and D_z , are $10^{-5} \text{ m}^2/\text{sec}$.

Step 1. Calculate the nitrate loading on the spill area. Nitrate loading = (LP mass spilled $\times$ load factor)/spill area = $(1,316 \text{ kg} \times 1,000 \text{ g/kg} \times 0.076 \text{ g NO}_3/\text{g LP})/(10 \text{ by } 10 \text{ m}) = 1,000 \text{ g/m}^2$.

Step 2. Calculate the nitrate concentration in the aquifer. The calculations use the horizontal flow model equations and are carried out on a computer. The results are shown in a series of tables in Appendix B. The tables show the concentration as a function of the x , y , z , t coordinates in the aquifer, where x is in the longitudinal direction, y is in the lateral direction, and z is in the vertical direction with $z = 0$ at the bottom of the aquifer. Time is stated in the tables in seconds after the spill takes place. The spill area is assumed to cover the space from $x = 0$ to $x = 10 \text{ m}$, and from $y = 45 \text{ m}$ to $y = 55 \text{ m}$. Thus, the line $y = 50 \text{ m}$ is a line of symmetry, so that only half the calculated values of concentration need be presented.

Some of the calculated concentrations are as follows:

- a. At the downstream end of the spill $x = 10 \text{ m}$. The nitrate concentration 1 day (86,400 sec) after the spill at the top of the aquifer, $z = 10 \text{ m}$, and at the center line, $y = 50 \text{ m}$, is read as 303.29 mg/l . At the same time, the nitrate concentration 5 m from the bottom of the aquifer, and with the same values of x and y coordinates, is 0.22 mg/l .
- b. After 30 days, the nitrate concentration at $x = 10 \text{ m}$, $y = 50 \text{ m}$, and $z = 10 \text{ m}$ has decreased from its former value of 303.29 mg/l , when $t = 1 \text{ day}$, to a value of 10.23 mg/l .

Example 2 is modeled for several periods of lapsed time after a spill (10, 20, 30, 40, 50, 60, 80, 100, 125, 150, 200, 250, 300, 400, and 500 days) in Appendix B (pages B19-B35).

Example 3. Contaminant transport simulations for vertical flow discharging to horizontal flow in a bounded aquifer

A spill onto the ground surface is likely to seep vertically downward until the plume intercepts an aquifer, so that contaminant transport first occurs in the vertical direction, then in the horizontal direction. Equation 34 models such a transport scenario when the aquifer is bounded, i.e., is of limited width and depth. A set of figures is presented to show how a contaminant will spread, mix, and travel as a function of time after a spill when the aquifer is considered bounded (Figures 11 and 12). The spilled LP may be visualized in cross section as it spreads out on the ground surface, then infiltrates into the vadose zone where it eventually discharges to a groundwater aquifer (Figure 11a). The "Downward Infiltration" into the vadose zone may be represented on a shading scale (Figure 12a) where the shading indicates the numerical concentration in grams/cubic meter (key to concentrations indicated on the horizontal shading scale to the left on Figure 12a). The discharge from

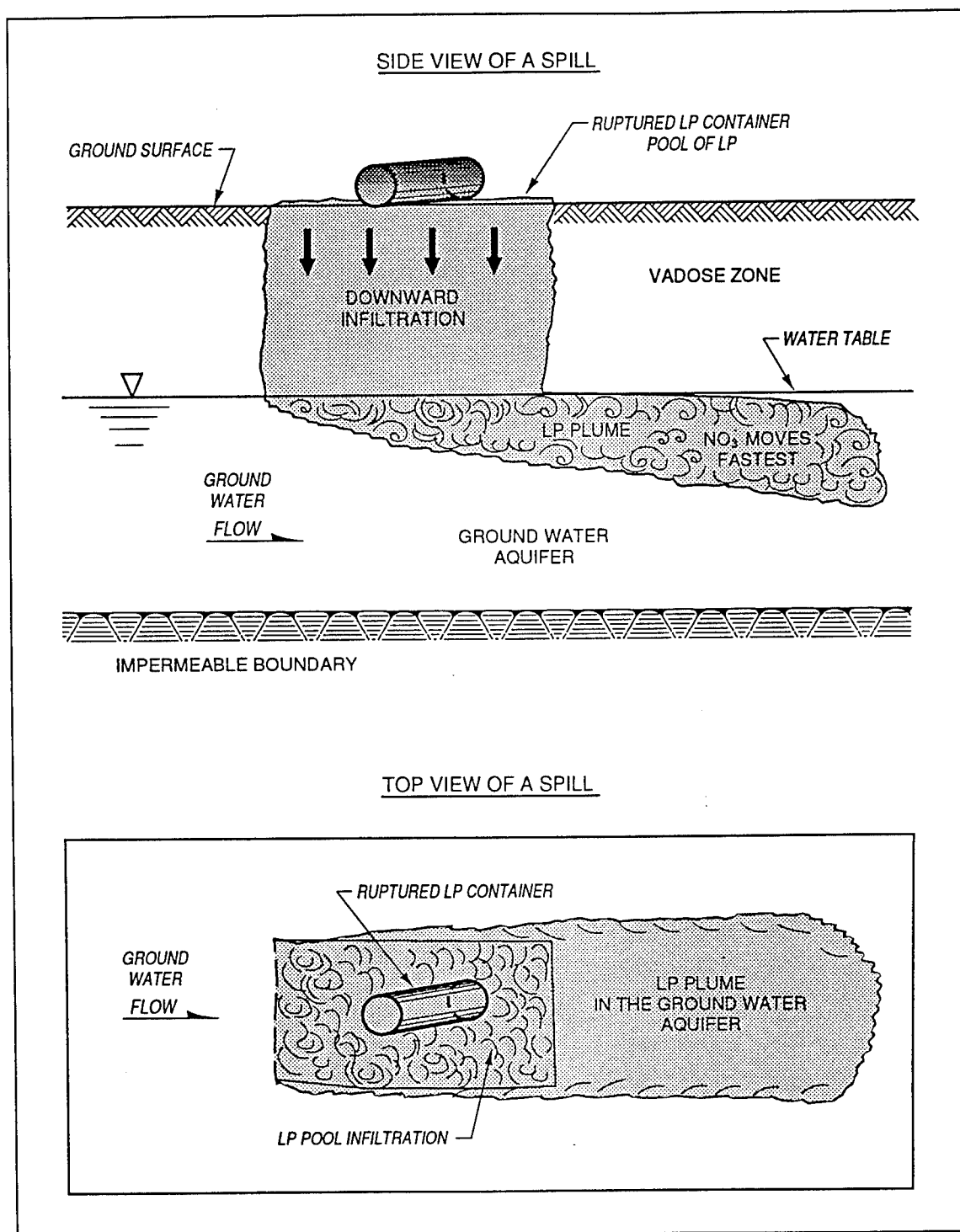


Figure 11. Identification and transport processes in vadose zone and in groundwater aquifer

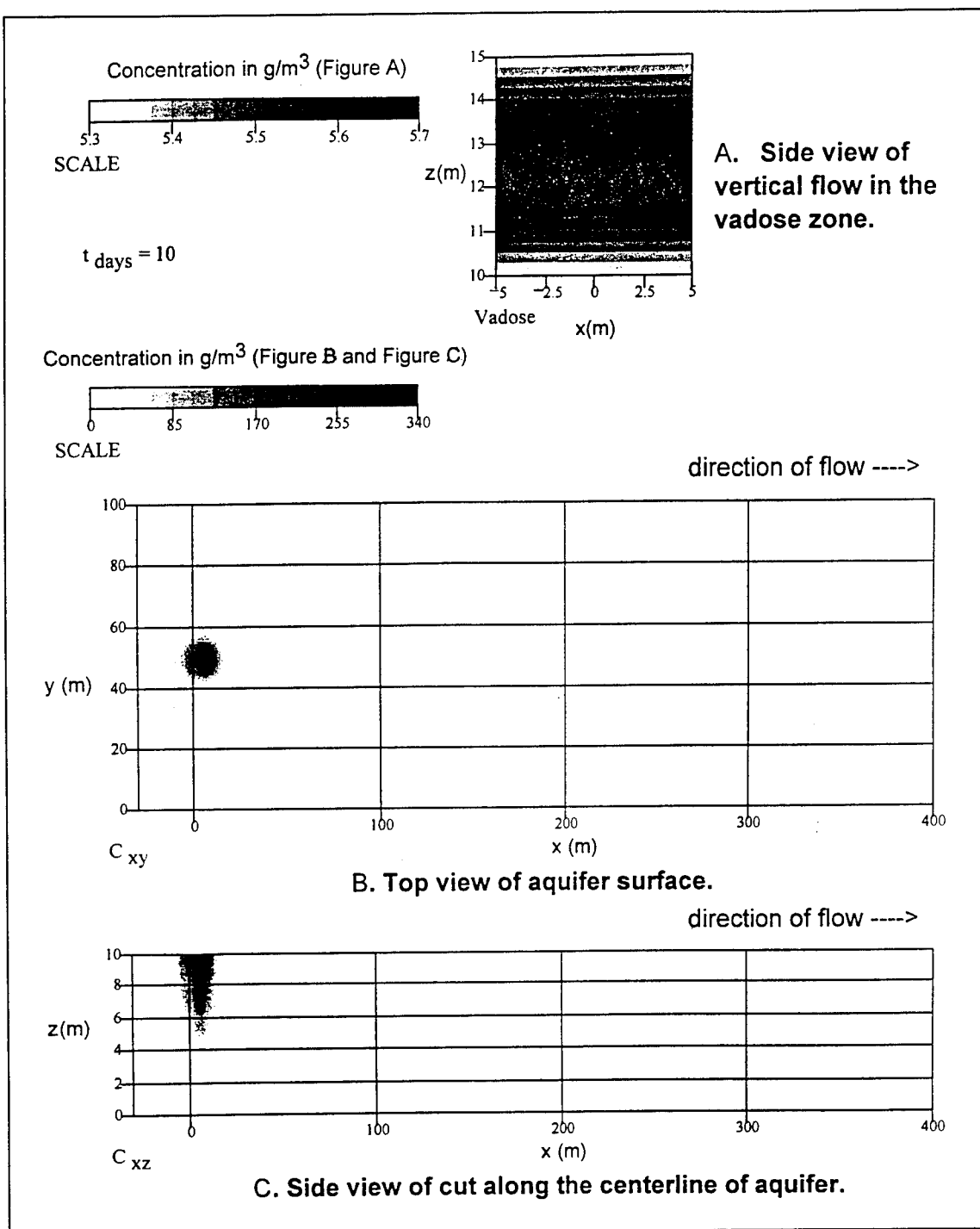


Figure 12. Model of LP plume under standard conditions and unbounded flow after a lapsed time of 10 days

the vadose zone into the groundwater aquifer forms a plume as the LP constituents mix with the groundwater (Figure 11a and 11b). This plume may be represented by the model in a "bird's eye" view (Figure 12b) and in cross section (Figure 12c, key to concentrations indicated on the horizontal shading scale just above Figure 12b).

The time that has elapsed since the LP spill in this example is " $t_{days} = 10$ ". The model boundaries of the plume become wavy as time increases (Appendix B, pages B36-B41). The waviness is a mathematical artifact of applying the error function for large times and distances. Actual plumes would have smooth, not wavy boundaries, except perhaps when affected by subsurface heterogeneities.

Examples 4 through 8. Contaminant transport simulations for vertical flow discharging to horizontal flow in a bounded aquifer

Equation 35 models transport when the aquifer is unbounded, i.e., is very wide and very deep, which is typical of most potential spill sites. The migration of the LP plume for standard model condition (Table 12) of unbounded flow after 10, 20, 50, 100, and 200 days is presented in Appendix B (pages B42-B47). Unbounded flow with low horizontal velocity is modeled for lapsed times of 10, 20, 50, 100, and 200 days in Appendix B (pages B48-B53). Unbounded flow with two retardation factors, $R = 2$ (Appendix B, pages B54-B59) and $R = 10$ (Appendix B, pages B60-B65), which are greater than the standard of $R = 1$, is modeled for 10, 20, 50, 100, and 200 days. Finally, unbounded flow with $R = 10$ and a high flow velocity of 8×10^{-5} m/sec is modeled (Appendix B, pages B66-B71).

General Guidance for Spill Response Time

To summarize results of experimentation and modeling of the potential nitrate hazard associated with a spill of LP onto soils, a table generalizing to minimum recommended spill response time has been generated (Table 13). The guidance is provided for various volumes of LP, depths to water table, and soil types. Response, as used in the table, means containment of the spill and/or excavation of the LP-containing soil.

Table 12
Parameters Used in Standard Model for Combined Vertical
Transport Followed by Horizontal Transport for an Aquifer of Finite
Width and Depth

Symbols	Name or Description	Value	Units	Comment
M	Nitrate portion of mass spilled	10,000	g	The calculated nitrate concentration will be directly proportional to the value M .
V	Vertical velocity	-1×10^{-6}	m/sec	The negative sign signifies a downward velocity. The vertical velocity is estimated by using the Darcy equation.
D_{22}	Vadose zone dispersion coefficient	-1×10^{-5}	m ² /sec	Little guidance is available on dispersion coefficient in unsaturated zone. In the absence of other information, select from Figure 6.
U	Horizontal velocity	8×10^{-6}	m/sec	This velocity would be estimated using the Darcy equation.
θ	Soil water content	1	cm ³ of water cm ³ of soil	This value is too large, as the soil water content cannot be larger than the porosity. A value in the range of 0.3 to 0.5 would be realistic.
D_x	Dispersion coefficient in x direction	1×10^{-5}	m ² /sec	The value is selected using Figure 6. The value of the dispersion coefficient in the flow direction is usually larger than in the transverse direction.
D_y, D_z	Dispersion coefficients in y and z direction	1×10^{-5}	m ² /sec	These values would be about 10 percent of the magnitude of D_x in most cases.
B	Depth of vadose zone from surface to aquifer	5	m	This value will depend on the specific dimensions found at the spill site.
W	Width of aquifer	10	m	This value will depend on the dimensions at the spill site. The concentration usually is not sensitive to W except for large times.
H	Height of aquifer	10	m	This value will depend on the aquifer depth at the spill site. The concentration usually is not sensitive to H for small times.
(Continued)				

Table 12 (Concluded)				
Symbols	Name or Description	Value	Units	Comment
R	Retardation coefficient	1	dimensionless	Retardation factor will be 1 for nitrate ion. It may be about 2 for HAN and about 10 for TEAN.
K	Chemical transformation rate	0	1/sec	It is suggested $K = 0$ unless one knows reaction mechanisms and knows that conditions in a plume favor transformation.
$(x1, x2, y1, y2)$	Initial loading area boundaries	(-5, 5, 45, 55)	m	These coordinates were used in the example simulation. Other values can be selected to fit spill conditions.
N_{max}	Number of summation steps	100	dimensionless	The value of 100 works well. Trial may allow the number to be reduced.
M_{ax}	Number of summation steps	100	dimensionless	The value of 100 works well. Trial may allow the number to be reduced.

Table 13
Minimum Recommended Response Time for LP Spills of Various
Quantities Onto Three General Soil Types

Spill Size, ℓ , gal	Distance to Water Table, m, ft	Soil Type	Minimum Recommended Response Time ¹
< 189, 50	3.05, 10	Sandy Silty Clayey	< 24 hr < 72 hr < 1 wk
	> 3.05, 10 < 15.2, 50	Sandy Silty Clayey	< 48 hr < 1 wk < 1 wk
	> 15.2, 50	Sandy Silty Clayey	< 72 hr < 1 wk < 2 wk
> 189, 50 < 1,892, 500	< 3.05, 10	Sandy Silty Clayey	< 24 hr < 48 hr < 1 wk
	> 3.05, 10 < 15.2, 50	Sandy Silty Clayey	< 24 hr < 48 hr < 1 wk
	> 15.2, 50	Sandy Silty Clayey	< 48 hr < 1 wk < 2 wk
> 1,892, 500	< 3.05, 10	Sandy Silty Clayey	ASAP ² < 24 hr < 72 hr
	> 3.05, 10 < 15.2, 50	Sandy Silty Clayey	ASAP < 24 hr < 1 wk
	> 15.2, 50	Sandy Silty Clayey	< 24 hr < 72 hr < 1 wk

¹ Initiation of material recovery.
² As soon as possible.

4 Conclusions

Spilled LP reacted with all three test soils as soon as infiltration began. Visible indicators of reactions were foam on the soil surface, gas bubbles, and soil swelling.

The infiltration rate of LP and water into each soil varied with the soil type and with time. An indication of the infiltration rate was provided by the duration of ponding on the soil surface. Durations of ponding were 500, 14,000, and 18,000 sec for China Lake B, Socorro P, and Yuma 2A soils, respectively. As expected, the hydraulic conductivity of China Lake B soil, which has a high sand content, was larger than the hydraulic conductivity of Socorro P and Yuma 2A soils, which contain primarily silt and clay. A practical result of the brief duration of ponding on China Lake B soil is that an LP spill will soak into sandy soil near the spill site. By contrast, an LP spill on Socorro P or Yuma 2A soil will have time to flow over the soil surface for a greater distance before soaking into the soil.

The peak concentration of HAN eluted from each of the three soils was always greater than the peak concentration of TEAN. However, the peak concentration of HAN and TEAN was attenuated differently by each soil. The relative ranking of the soils in terms of the peak HAN concentration was China Lake B > Yuma 2A > Socorro P. The corresponding ranking of each soil in terms of the peak concentration of TEAN was China Lake B > Socorro P > Yuma 2A.

The peak concentration of NO₂ plus NO₃ nitrogen eluted from each of the three soils was dependent on the soil type. China Lake B soil had the largest peak NO₂ plus NO₃ nitrogen concentration eluted, followed by Yuma 2A and Socorro P soils. Since NO₂ plus NO₃ nitrogen is the nitrogen-containing species for which a drinking water standard has been defined (10 mg/ℓ), an LP spill onto a sandy soil will pose a greater potential hazard to drinking water than a spill onto a clay or a silty soil.

The total loading of NO₂ plus NO₃ nitrogen generated from an LP spill showed little variation from soil to soil. Loading factors were calculated in the following two ways: first, as the mass (grams) of NO₂ plus NO₃ nitrogen produced per mass (grams) of LP applied; and as the mass (grams) of NO₂ plus NO₃ nitrogen produced per cubic centimeter of LP applied. The

respective mass loading factors for China Lake B, Socorro P, and Yuma 2A soils were 0.076, 0.085, and 0.074 NO_2 plus NO_3 nitrogen per gram LP applied. Too little data are available for statistical analysis of these loading factors, but the average loading factors of 0.078 g NO_2 plus NO_3 nitrogen per gram of LP and 0.11 g of NO_2 plus NO_3 nitrogen per cubic centimeter of LP are likely to be representative of values for other soils.

The pH results show a difference in buffering capacity of the two soils. The initial eluate from China Lake soil had a pH of 4.3, while the initial eluate from Socorro soil had a pH of 1.6. Dilution of LP with water probably contributed to the rise in pH, although the soil buffering effect cannot be completely separated from the dilution effect. The pH rose to 6 or above after 2.3 pore volumes were eluted from China Lake soil and after about 3.0 pore volumes were eluted from Socorro soil. These results are significant with respect to transport of the nitrate ion, since adsorption of the nitrate ion to aquifer solids is likely to be insignificant when the pH is above 6. Thus, a reasonable conclusion about nitrate ion movement away from an LP spill site is that the nitrate ion moves with the velocity of the soil water in the vadose zone and with the velocity of the groundwater in an aquifer.

A mathematical model was applied to calculate the maximum concentration of NO_2 plus NO_3 nitrogen directly under an LP spill onto soils that would support rapid infiltration with little surface runoff of LP. The mathematical model showed that the maximum concentration of NO_2 plus NO_3 nitrogen directly under a spill of LP is directly proportional to the mass (or the volume) of the spill. The maximum concentration decreased with vertical distance from the soil surface as a complex function of LP transformation rate, dispersion rate, and the flow time. In a worse case scenario, the maximum concentration of NO_2 plus NO_3 nitrogen that could reach a water table that is, for example, 10 m below the soil surface is likely to exceed the drinking water standard if a drum of LP (of at least 208.3 kg) is spilled onto a sandy soil.

A second mathematical model was presented to show how the concentration of NO_2 plus NO_3 nitrogen is expected to vary with distance and time after the spilled LP and its transformation products reach the water table. In this model, the spilled LP was assumed to spread out over an area before infiltration and mixing with the aquifer water. The model showed that the maximum concentration of NO_2 plus NO_3 nitrogen was directly proportional to the mass of LP spilled. Also, the maximum concentration of NO_2 plus NO_3 nitrogen in the aquifer decreased rapidly with mixing, so that a spill of a drum of LP (208.3 kg) was unlikely to exceed the drinking water standards except directly under the spill.

A third type of mathematical model accounted for a spill of LP occurring on the ground surface so that vertical seepage would occur through the vadose zone, which would discharge to the groundwater flow in an aquifer. Simulations with this model showed that a bimodal concentration distribution of nitrate ion in the aquifer was the rule rather than the exception. One nitrate

concentration peak would remain under the spill site at the intersection of the discharge location from the vadose zone and the top of the aquifer. A second nitrate concentration peak would be carried along with the flowing groundwater. The position of this second peak will vary with time.

Other applications of the combined transport by vertical flow in the vadose zone followed by horizontal flow in the groundwater aquifer showed that aquifer boundaries had little effect on the nitrate ion concentration distribution. An increase in the retardation factor, which signifies greater nitrate ion adsorption to soil, slowed the advance rate of the nitrate plume. However, this result has little practical significance since nitrate adsorption to soils is negligible when the pH is 6 or above.

The unmistakable conclusion from application of the several computer simulation models is that vigorous intervention and remediation efforts should be implemented as soon as practical after an LP spill. Immediate excavation of the soil contaminated by LP to interrupt migration is warranted when spill volume is significant.

In the event that groundwater becomes contaminated from an LP spill, a pump and treat remediation system should be installed as early as practical. Such early intervention will restrict the spread of LP so that the volume of water to be treated will be minimized.

Excavation of the contaminated soil from the vadose zone directly under the spill site is advisable even after passage of considerable time. The models indicate that contaminated soil acts as an LP reservoir that feeds to the groundwater aquifer for a long time. As an interim spill response, an impermeable barrier, e.g., plastic sheeting, can be placed on the spill site to reduce the supply of infiltrating water. Without infiltrating water, e.g., rainfall, the spilled LP will be held longer in the vadose zone from which removal is easier.

References

- Arthur D. Little, Inc. (ADL). (1994). "Guidance document for preparation of liquid propellant XM46 spill response plants," Final Report, June 6, 1994, prepared for U.S. Army Engineer Waterways Experiment Station by ADL, Acorn Park, Cambridge, MA. Reference No.: 63933, Task Order No. 03, DACA 39-92-D-0014.
- Baetsle, L. H. (1969). "Migration of radionuclides in porous media." *Progress in Nuclear Energy Series XII, Health Physics*. A. M. F. Duhamel, ed., Pergamon Press, Elmsford, NY, 1969, 707-730.
- Cleary, R. W., and Adrian, D. D. (1973). "New analytical solutions for dye diffusion equations," *Journal of the Environmental Engineering Division, American Society of Civil Engineers* 99(EE3), 213-227.
- Craig, J. R., and Wolburn, A. G. (1982). "Ammonia volatilization soil nitrogen changes after urea and ammonium nitrate fertilizer of *Pinus Taeda*," *Soil Science Society of American Journal* 46, 409-414.
- Csanady, G. T. (1980). *Turbulent diffusion in the environment*. D. Reidel Publishing Co., Boston, MA, 14-22.
- Howard, A. K. (1977). "Laboratory classification of soils - Unified Soil Classification System," Earth Science Training Manual No. 4., U.S. Bureau of Reclamation, Denver, CO.
- Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathburn, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Snoeyink, V. L., and Jenkins, D. (1980). *Water chemistry*. John Wiley and Sons, New York, 16.
- Tchobanoglous, G., and Schroeder, E. D. (1985). *Water quality: Characteristics, modeling, modification*. Addison Wesley, Reading, MA, 192.

- Tester, D. J., and Carey, M. A. (1985). "The prediction of nitrate pollution in chalk groundwater-derived potable supplies and the renovation of an affected source," *Journal of International Water Pollution Control* 84(3), 366-379.
- U.S. Army Engineer Waterways Experiment Station. (1960). "The unified soil classification system," Technical Memorandum No. 3-357. Appendix A, "Characteristics of soil groups pertaining to embankments and foundations, 1953;" Appendix B, "Characteristics of soil groups pertaining to roads and airfields, 1957," Vicksburg, MS.
- U.S. Environmental Protection Agency. (1991). Code of Federal Regulations 56FR3526, Drinking Water Regulations and Health Advisories, Washington, DC.
- _____. (1975). *Process design manual for nitrogen control*. 2-7.
- Yeoman, J. C., and Bremner, J. M. (1985a). "Denitrification in soil: Effects of herbicides," *Soil Biology and Biochemistry* 17(4), 447-452.
- _____. (1985b). "Denitrification in soil: Effects of insecticides and fungicides," *Soil Biology and Biochemistry* 17(4), 453-456.

Appendix A

Program Used to Solve Three-Dimensional Models for Liquid Propellant Spills

```

{ ***** }
{ *   This program is used to solve the 3-D dye diffusion equations   * }
{ *   with instantaneous surface loading. (Dec. 1994)                 * }
{ ***** }
PROGRAM DYE_3D;      {DYE-3D.PAS}
CONST
  GSA=1000.0;        { surface loading, gm/sq.m. }
  X1=0.0;            { X=longitudinal dimension, m }
  X2=10.0;           { m }
  Y1=45.0;           { Y=lateral dimension, m }
  Y2=55.0;           { m }
  Z1=10.0;           { Z=Vertical dimensionm, m. at surface: Z1=H }
  H=10.0;            { average depth, m }
  W=100.0;           { average width, m }
  U=1.0E-6;          { average velocity, m/s }
  DX=1.0E-4;         { turbulent diffusion coeff. in X direction, sq.m./s }
  DY=1.0E-5;         { turbulent diffusion coeff. in Y direction, sq.m./s }
  DZ=1.0E-5;         { turbulent diffusion coeff. in Z direction, sq.m./s }
  N=100;             { summation times }
  M=10;              { # of intervals in Y direction }
  P=10;              { # of intervals in Z direction }
  Q=1000;            { steps used in calculations of error function }
TYPE
  CTYPE=ARRAY[0..M,0..P] OF DOUBLE;
  YTYPE=ARRAY[0..M] OF DOUBLE;
  ZTYPE=ARRAY[0..P] OF DOUBLE;
  EYTYPE=ARRAY[0..Q] OF DOUBLE;
VAR
  DYE:TEXT;
  C:CTYPE;           { concentration, mg/L }
  T:DOUBLE;          { time, sec. }
  Y:YTYPE;
  Z:ZTYPE;
  EY,EZ:EYTYPE;
  I,J,K,A:INTEGER;
  X,SP,SP1,SP2,E1,E2,EE,ER,ER1,ER2,V1,V2,T1,D:DOUBLE;

PROCEDURE SUMP (Y:YTYPE; Z:ZTYPE; VAR SP:DOUBLE);
{ *** To calculate the summation terms, SP1 and SP2. *** }
BEGIN
  SP1:=0.0;          SP2:=0.0;
  FOR I:=1 TO N DO
    BEGIN
      V1:=DZ*SQR(I*PI/H)*T;
      IF V1<10000.0 THEN
        BEGIN
          SP1:=SP1+EXP(-DZ*SQR(I*PI/H)*T)*COS(I*PI*Z[K]/H)*COS(I*PI*Z1/H);
        END
      ELSE
        BEGIN
          SP1:=SP1;
        END;
      V2:=DY*SQR(I*PI/W)*T;
      IF V2<10000.0 THEN
        BEGIN
          SP2:=SP2+EXP(-DY*SQR(I*PI/W)*T)*W/I/PI*COS(I*PI*Y[J]/W)
            *(SIN(I*PI*Y2/W)-SIN(I*PI*Y1/W));
        END
      ELSE
        BEGIN
          SP2:=SP2;
        END;
    END;
  END;

```

```

        END;
        SP:=(1+2*SP1)*(Y2-Y1+2*SP2);
    END;
END;

PROCEDURE ERF (EE:DOUBLE; VAR ER:DOUBLE);
{ *** To calculate the error function.
  BEGIN
    EY[0]:=EE;
    FOR A:=1 TO Q DO
    BEGIN
      EY[A]:=(-1)*EY[A-1]*(2*(A-1)+1)*EE*EE/A/(2*A+1);
      EZ[A]:=EZ[A-1]+EY[A];
    END;
    ER:=EZ[Q]*2/SQRT(PI);
  END;
}

{ *** Main program.
  BEGIN
    ASSIGN (DYE,'B:\D1-A180.DAT');
    REWRITE (DYE);
    WRITELN (DYE,' ');
    X:=1.0;
    D:=180.0;
    T:=D*86400;
    WRITELN (DYE,'***** X=',X:6:1,' m *****',
              '*****');
    WRITELN (DYE,'          ,D:6:1,' days after application.',
              '(T= ',T:12,' sec.)');
    WRITELN (DYE,'_____');
    WRITELN (DYE,'          Y (m)');
    WRITE (DYE,'(m) ');
    FOR J:=0 TO M DO
    BEGIN
      Y[J]:=50.0-5.0*J;
      WRITE (DYE,Y[J]:4:1,' ');
    END;
    WRITELN (DYE,' ');
    WRITELN (DYE,'Concentration (mg/L) ');
    WRITELN (DYE,'-----');
    FOR K:=P DOWNT0 0 DO { * Z * }
    BEGIN
      Z[K]:=H/P*K;
      WRITE (DYE,K:2);
      FOR J:=0 TO M DO { * Y * }
      BEGIN
        Y[J]:=50.0-5.0*J;
        SUMP (Y,Z,SP);
        E1:=(X2-X+U*T)/2/SQRT(DX*T);
        IF E1<-3.0 THEN BEGIN ER1:=-1.00; END
        ELSE
        IF E1>3.0 THEN BEGIN ER1:=1.00; END
        ELSE
        IF ABS(E1)<0.0001 THEN BEGIN ER1:=0.00; END
        ELSE
        BEGIN
          ERF(E1,ER);
          ER1:=ER;
        END;
        E2:=(X1-X+U*T)/2/SQRT(DX*T);
        IF E2<-3.0 THEN BEGIN ER2:=-1.00; END
        ELSE

```

```

      IF E2>3.0 THEN          BEGIN  ER2:=1.00;  END
      ELSE
      IF ABS(E2)<0.0001 THEN  BEGIN  ER2:=0.00;  END
      ELSE
        BEGIN
          ERF(E2,ER);          ER2:=ER;
        END;
      C[J,K]:=GSA/2/W/H*SP*(ER1-ER2);
      WRITE (DYE,' ',ABS(C[J,K]):6:2);
      END;
      WRITELN (DYE,' ');
    END;
  CLOSE (DYE);
END.

```

***** X= 1.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	347.48	337.59	173.76	9.94	0.02	0.00	0.00	0.00	0.00	0.00	0.00
9	260.18	252.77	130.11	7.44	0.02	0.00	0.00	0.00	0.00	0.00	0.00
8	109.21	106.10	54.61	3.12	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	25.70	24.97	12.85	0.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	3.39	3.29	1.70	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.25	0.24	0.13	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 1.0 m *****
2.0 days after application. (T= 1.728E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	211.62	194.09	106.57	19.04	0.76	0.01	0.00	0.00	0.00	0.00	0.00
9	183.11	167.95	92.22	16.48	0.66	0.01	0.00	0.00	0.00	0.00	0.00
8	118.64	108.81	59.75	10.68	0.43	0.00	0.00	0.00	0.00	0.00	0.00
7	57.55	52.79	28.98	5.18	0.21	0.00	0.00	0.00	0.00	0.00	0.00
6	20.90	19.17	10.53	1.88	0.08	0.00	0.00	0.00	0.00	0.00	0.00
5	5.69	5.21	2.86	0.51	0.02	0.00	0.00	0.00	0.00	0.00	0.00
4	1.16	1.06	0.58	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.18	0.16	0.09	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 1.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	150.46	133.66	77.40	21.07	2.17	0.08	0.00	0.00	0.00	0.00	0.00
9	136.62	121.37	70.29	19.13	1.97	0.07	0.00	0.00	0.00	0.00	0.00
8	102.30	90.88	52.63	14.32	1.48	0.05	0.00	0.00	0.00	0.00	0.00
7	63.16	56.11	32.49	8.84	0.91	0.03	0.00	0.00	0.00	0.00	0.00
6	32.15	28.56	16.54	4.50	0.46	0.02	0.00	0.00	0.00	0.00	0.00
5	13.50	11.99	6.94	1.89	0.20	0.01	0.00	0.00	0.00	0.00	0.00
4	4.67	4.15	2.40	0.65	0.07	0.00	0.00	0.00	0.00	0.00	0.00
3	1.33	1.18	0.69	0.19	0.02	0.00	0.00	0.00	0.00	0.00	0.00
2	0.31	0.28	0.16	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.06	0.06	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 1.0 m *****
5.0 days after application. (T= 4.320E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	91.32	79.89	50.08	19.80	4.46	0.54	0.03	0.00	0.00	0.00	0.00
9	86.18	75.40	47.27	18.68	4.21	0.51	0.03	0.00	0.00	0.00	0.00
8	72.45	63.39	39.73	15.71	3.54	0.43	0.03	0.00	0.00	0.00	0.00
7	54.24	47.46	29.75	11.76	2.65	0.32	0.02	0.00	0.00	0.00	0.00
6	36.18	31.65	19.84	7.84	1.77	0.21	0.01	0.00	0.00	0.00	0.00
5	21.49	18.80	11.79	4.66	1.05	0.13	0.01	0.00	0.00	0.00	0.00
4	11.37	9.95	6.24	2.47	0.56	0.07	0.00	0.00	0.00	0.00	0.00
3	5.36	4.69	2.94	1.16	0.26	0.03	0.00	0.00	0.00	0.00	0.00
2	2.27	1.99	1.25	0.49	0.11	0.01	0.00	0.00	0.00	0.00	0.00
1	0.92	0.81	0.51	0.20	0.05	0.01	0.00	0.00	0.00	0.00	0.00
0	0.56	0.49	0.31	0.12	0.03	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 1.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	41.08	36.80	26.21	14.52	6.09	1.90	0.43	0.07	0.01	0.00	0.00
9	39.91	35.75	25.47	14.10	5.92	1.84	0.42	0.07	0.01	0.00	0.00
8	36.59	32.78	23.35	12.93	5.43	1.69	0.38	0.06	0.01	0.00	0.00
7	31.67	28.37	20.21	11.19	4.70	1.46	0.33	0.05	0.01	0.00	0.00
6	25.88	23.18	16.51	9.15	3.84	1.19	0.27	0.04	0.01	0.00	0.00
5	19.99	17.91	12.76	7.06	2.97	0.92	0.21	0.03	0.00	0.00	0.00
4	14.64	13.11	9.34	5.17	2.17	0.68	0.15	0.03	0.00	0.00	0.00
3	10.26	9.19	6.55	3.63	1.52	0.47	0.11	0.02	0.00	0.00	0.00
2	7.08	6.35	4.52	2.50	1.05	0.33	0.07	0.01	0.00	0.00	0.00
1	5.18	4.64	3.31	1.83	0.77	0.24	0.05	0.01	0.00	0.00	0.00
0	4.55	4.08	2.90	1.61	0.68	0.21	0.05	0.01	0.00	0.00	0.00

***** X= 1.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	9.87	9.38	8.04	6.22	4.34	2.72	1.54	0.78	0.35	0.14	0.05
9	9.81	9.32	7.99	6.18	4.31	2.70	1.53	0.77	0.35	0.14	0.05
8	9.62	9.14	7.84	6.06	4.22	2.65	1.50	0.76	0.34	0.14	0.05
7	9.33	8.86	7.60	5.88	4.10	2.57	1.45	0.73	0.33	0.14	0.05
6	8.96	8.51	7.30	5.64	3.93	2.47	1.39	0.71	0.32	0.13	0.05
5	8.55	8.12	6.96	5.39	3.75	2.36	1.33	0.67	0.31	0.12	0.05
4	8.14	7.73	6.63	5.13	3.57	2.24	1.27	0.64	0.29	0.12	0.04
3	7.77	7.38	6.33	4.90	3.41	2.14	1.21	0.61	0.28	0.11	0.04
2	7.48	7.11	6.09	4.71	3.28	2.06	1.16	0.59	0.27	0.11	0.04
1	7.29	6.93	5.94	4.59	3.20	2.01	1.13	0.57	0.26	0.11	0.04
0	7.23	6.87	5.89	4.55	3.17	1.99	1.12	0.57	0.26	0.11	0.04

***** X= 1.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	3.01	2.79	2.22	1.52	0.89	0.45	0.19	0.07	0.02	0.01	0.00
9	3.01	2.79	2.22	1.52	0.89	0.45	0.19	0.07	0.02	0.01	0.00
8	3.01	2.79	2.22	1.52	0.89	0.45	0.19	0.07	0.02	0.01	0.00
7	3.01	2.79	2.22	1.52	0.89	0.45	0.19	0.07	0.02	0.01	0.00
6	3.01	2.79	2.22	1.52	0.89	0.45	0.19	0.07	0.02	0.01	0.00
5	3.01	2.79	2.22	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00
4	3.01	2.79	2.22	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00
3	3.01	2.78	2.22	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00
2	3.00	2.78	2.22	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00
1	3.00	2.78	2.22	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00
0	3.00	2.78	2.21	1.51	0.89	0.45	0.19	0.07	0.02	0.01	0.00

***** X= 1.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
9	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
8	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
7	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
6	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
5	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
4	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
3	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
2	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
1	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06
0	1.50	1.44	1.28	1.05	0.80	0.56	0.37	0.22	0.13	0.08	0.06

***** X= 1.0 m *****
360.0 days after application. (T= 3.110E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
9	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
8	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
7	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
6	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
5	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
4	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
3	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
2	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
1	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20
0	0.73	0.71	0.67	0.61	0.53	0.45	0.37	0.30	0.25	0.21	0.20

***** X= 2.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	Y (m)											
	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0	
Concentration (mg/L)												
10	395.38	384.13	197.72	11.31	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	296.04	287.62	148.04	8.47	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	124.27	120.73	62.14	3.55	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	29.24	28.41	14.62	0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	3.86	3.75	1.93	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.29	0.28	0.14	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 2.0 m *****
2.0 days after application. (T= 1.728E+0005 sec.)

Z (m)	Y (m)											
	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0	
	Concentration (mg/L)											
10	230.02	210.97	115.84	20.70	0.83	0.01	0.00	0.00	0.00	0.00	0.00	
9	199.04	182.55	100.24	17.91	0.72	0.01	0.00	0.00	0.00	0.00	0.00	
8	128.96	118.28	64.94	11.60	0.46	0.00	0.00	0.00	0.00	0.00	0.00	
7	62.56	57.38	31.50	5.63	0.23	0.00	0.00	0.00	0.00	0.00	0.00	
6	22.72	20.84	11.44	2.04	0.08	0.00	0.00	0.00	0.00	0.00	0.00	
5	6.18	5.67	3.11	0.56	0.02	0.00	0.00	0.00	0.00	0.00	0.00	
4	1.26	1.15	0.63	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
3	0.19	0.18	0.10	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
2	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

***** X= 2.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	Y (m)											
	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0	
	Concentration (mg/L)											
10	160.03	142.16	82.33	22.41	2.31	0.08	0.00	0.00	0.00	0.00	0.00	
9	145.31	129.09	74.76	20.35	2.10	0.07	0.00	0.00	0.00	0.00	0.00	
8	108.80	96.66	55.97	15.24	1.57	0.06	0.00	0.00	0.00	0.00	0.00	
7	67.17	59.68	34.56	9.41	0.97	0.03	0.00	0.00	0.00	0.00	0.00	
6	34.20	30.38	17.59	4.79	0.49	0.02	0.00	0.00	0.00	0.00	0.00	
5	14.35	12.75	7.38	2.01	0.21	0.01	0.00	0.00	0.00	0.00	0.00	
4	4.97	4.41	2.56	0.70	0.07	0.00	0.00	0.00	0.00	0.00	0.00	
3	1.42	1.26	0.73	0.20	0.02	0.00	0.00	0.00	0.00	0.00	0.00	
2	0.33	0.30	0.17	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
1	0.07	0.06	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
0	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

***** X= 2.0 m *****
5.0 days after application. (T= 4.320E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	95.17	83.26	52.19	20.63	4.64	0.56	0.03	0.00	0.00	0.00	0.00
9	89.81	78.58	49.26	19.47	4.38	0.53	0.03	0.00	0.00	0.00	0.00
8	75.50	66.06	41.41	16.37	3.69	0.44	0.03	0.00	0.00	0.00	0.00
7	56.53	49.46	31.00	12.26	2.76	0.33	0.02	0.00	0.00	0.00	0.00
6	37.70	32.99	20.68	8.17	1.84	0.22	0.01	0.00	0.00	0.00	0.00
5	22.40	19.59	12.28	4.86	1.09	0.13	0.01	0.00	0.00	0.00	0.00
4	11.85	10.37	6.50	2.57	0.58	0.07	0.00	0.00	0.00	0.00	0.00
3	5.59	4.89	3.07	1.21	0.27	0.03	0.00	0.00	0.00	0.00	0.00
2	2.37	2.07	1.30	0.51	0.12	0.01	0.00	0.00	0.00	0.00	0.00
1	0.96	0.84	0.53	0.21	0.05	0.01	0.00	0.00	0.00	0.00	0.00
0	0.58	0.51	0.32	0.13	0.03	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 2.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	42.08	37.70	26.85	14.87	6.24	1.94	0.44	0.07	0.01	0.00	0.00
9	40.88	36.62	26.09	14.45	6.06	1.89	0.43	0.07	0.01	0.00	0.00
8	37.49	33.58	23.92	13.25	5.56	1.73	0.39	0.06	0.01	0.00	0.00
7	32.44	29.06	20.70	11.47	4.81	1.50	0.34	0.06	0.01	0.00	0.00
6	26.51	23.75	16.92	9.37	3.93	1.22	0.28	0.05	0.01	0.00	0.00
5	20.48	18.34	13.07	7.24	3.04	0.95	0.21	0.04	0.00	0.00	0.00
4	14.99	13.43	9.57	5.30	2.22	0.69	0.16	0.03	0.00	0.00	0.00
3	10.51	9.42	6.71	3.71	1.56	0.49	0.11	0.02	0.00	0.00	0.00
2	7.26	6.50	4.63	2.56	1.08	0.33	0.08	0.01	0.00	0.00	0.00
1	5.31	4.75	3.39	1.88	0.79	0.24	0.06	0.01	0.00	0.00	0.00
0	4.66	4.18	2.97	1.65	0.69	0.22	0.05	0.01	0.00	0.00	0.00

***** X= 2.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	9.99	9.49	8.14	6.29	4.39	2.75	1.55	0.79	0.36	0.15	0.05
9	9.92	9.43	8.08	6.25	4.36	2.73	1.54	0.78	0.36	0.14	0.05
8	9.73	9.25	7.93	6.13	4.27	2.68	1.51	0.77	0.35	0.14	0.05
7	9.44	8.97	7.69	5.95	4.14	2.60	1.47	0.74	0.34	0.14	0.05
6	9.06	8.61	7.38	5.71	3.98	2.50	1.41	0.71	0.32	0.13	0.05
5	8.65	8.22	7.05	5.45	3.80	2.38	1.34	0.68	0.31	0.13	0.05
4	8.23	7.82	6.71	5.19	3.62	2.27	1.28	0.65	0.29	0.12	0.04
3	7.86	7.47	6.40	4.95	3.45	2.17	1.22	0.62	0.28	0.11	0.04
2	7.57	7.19	6.16	4.77	3.32	2.08	1.18	0.60	0.27	0.11	0.04
1	7.38	7.01	6.01	4.65	3.24	2.03	1.15	0.58	0.26	0.11	0.04
0	7.31	6.95	5.96	4.61	3.21	2.01	1.14	0.58	0.26	0.11	0.04

***** X= 3.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z	Y (m)										
(m)	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	433.44	421.10	216.75	12.40	0.03	0.00	0.00	0.00	0.00	0.00	0.00
9	324.53	315.30	162.29	9.28	0.02	0.00	0.00	0.00	0.00	0.00	0.00
8	136.23	132.35	68.12	3.90	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	32.06	31.15	16.03	0.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	4.23	4.11	2.12	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.31	0.30	0.16	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 3.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z	Y (m)										
(m)	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	167.43	148.74	86.14	23.45	2.42	0.09	0.00	0.00	0.00	0.00	0.00
9	152.04	135.07	78.22	21.29	2.20	0.08	0.00	0.00	0.00	0.00	0.00
8	113.84	101.13	58.56	15.94	1.65	0.06	0.00	0.00	0.00	0.00	0.00
7	70.28	62.44	36.16	9.84	1.02	0.04	0.00	0.00	0.00	0.00	0.00
6	35.78	31.79	18.41	5.01	0.52	0.02	0.00	0.00	0.00	0.00	0.00
5	15.02	13.34	7.73	2.10	0.22	0.01	0.00	0.00	0.00	0.00	0.00
4	5.20	4.62	2.67	0.73	0.08	0.00	0.00	0.00	0.00	0.00	0.00
3	1.48	1.32	0.76	0.21	0.02	0.00	0.00	0.00	0.00	0.00	0.00
2	0.35	0.31	0.18	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.06	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 3.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z	Y (m)										
(m)	50.0	47.5	45.0	42.5	40.0	37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	42.87	38.40	27.35	15.15	6.36	1.98	0.45	0.07	0.01	0.00	0.00
9	41.65	37.31	26.57	14.72	6.18	1.92	0.44	0.07	0.01	0.00	0.00
8	38.19	34.21	24.37	13.50	5.67	1.76	0.40	0.07	0.01	0.00	0.00
7	33.05	29.61	21.09	11.68	4.90	1.53	0.35	0.06	0.01	0.00	0.00
6	27.01	24.19	17.23	9.55	4.01	1.25	0.28	0.05	0.01	0.00	0.00
5	20.86	18.69	13.31	7.37	3.09	0.96	0.22	0.04	0.00	0.00	0.00
4	15.27	13.68	9.75	5.40	2.27	0.71	0.16	0.03	0.00	0.00	0.00
3	10.71	9.59	6.83	3.78	1.59	0.49	0.11	0.02	0.00	0.00	0.00
2	7.39	6.62	4.72	2.61	1.10	0.34	0.08	0.01	0.00	0.00	0.00
1	5.41	4.84	3.45	1.91	0.80	0.25	0.08	0.01	0.00	0.00	0.00
0	4.75	4.25	3.03	1.68	0.70	0.22	0.05	0.01	0.00	0.00	0.00

***** X= 3.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	10.09	9.58	8.22	6.35	4.43	2.78	1.57	0.79	0.36	0.15	0.05
9	10.02	9.52	8.16	6.31	4.40	2.76	1.56	0.79	0.36	0.15	0.05
8	9.83	9.34	8.01	6.19	4.32	2.71	1.53	0.77	0.35	0.14	0.05
7	9.53	9.05	7.76	6.00	4.18	2.63	1.48	0.75	0.34	0.14	0.05
6	9.15	8.69	7.45	5.77	4.02	2.52	1.42	0.72	0.33	0.13	0.05
5	8.73	8.30	7.11	5.50	3.83	2.41	1.36	0.69	0.31	0.13	0.05
4	8.31	7.90	6.77	5.24	3.65	2.29	1.29	0.66	0.30	0.12	0.04
3	7.94	7.54	6.47	5.00	3.49	2.19	1.23	0.63	0.28	0.12	0.04
2	7.64	7.26	6.22	4.81	3.35	2.10	1.19	0.60	0.27	0.11	0.04
1	7.45	7.08	6.07	4.69	3.27	2.05	1.16	0.59	0.27	0.11	0.04
0	7.38	7.01	6.01	4.65	3.24	2.03	1.15	0.58	0.26	0.11	0.04

***** X= 3.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	4.59	4.46	4.11	3.57	2.94	2.29	1.68	1.17	0.77	0.48	0.28
9	4.59	4.46	4.10	3.57	2.94	2.29	1.68	1.17	0.77	0.48	0.28
8	4.58	4.45	4.10	3.56	2.93	2.28	1.68	1.17	0.77	0.48	0.28
7	4.57	4.44	4.09	3.56	2.93	2.28	1.68	1.17	0.77	0.48	0.28
6	4.55	4.43	4.07	3.54	2.92	2.27	1.67	1.16	0.77	0.48	0.28
5	4.53	4.41	4.06	3.53	2.91	2.26	1.66	1.16	0.76	0.47	0.28
4	4.52	4.39	4.04	3.52	2.89	2.25	1.66	1.15	0.76	0.47	0.28
3	4.50	4.38	4.03	3.51	2.89	2.25	1.65	1.15	0.75	0.47	0.28
2	4.49	4.37	4.02	3.50	2.88	2.24	1.65	1.15	0.75	0.47	0.28
1	4.48	4.36	4.01	3.49	2.87	2.24	1.65	1.15	0.75	0.47	0.28
0	4.48	4.36	4.01	3.49	2.87	2.23	1.64	1.14	0.75	0.47	0.28

***** X= 3.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	3.05	2.99	2.83	2.57	2.25	1.90	1.54	1.20	0.90	0.65	0.45
9	3.05	2.99	2.83	2.57	2.25	1.90	1.54	1.20	0.90	0.65	0.45
8	3.05	2.99	2.83	2.57	2.25	1.90	1.54	1.20	0.90	0.65	0.45
7	3.05	2.99	2.83	2.57	2.25	1.89	1.54	1.20	0.90	0.65	0.45
6	3.05	2.99	2.83	2.57	2.25	1.89	1.54	1.20	0.90	0.65	0.45
5	3.05	2.99	2.82	2.57	2.25	1.89	1.54	1.20	0.90	0.65	0.45
4	3.05	2.99	2.82	2.57	2.25	1.89	1.53	1.20	0.90	0.65	0.45
3	3.05	2.99	2.82	2.57	2.25	1.89	1.53	1.20	0.90	0.65	0.45
2	3.05	2.99	2.82	2.57	2.25	1.89	1.53	1.20	0.90	0.65	0.45
1	3.05	2.99	2.82	2.57	2.25	1.89	1.53	1.20	0.90	0.65	0.45
0	3.05	2.99	2.82	2.57	2.25	1.89	1.53	1.20	0.90	0.65	0.45

***** X= 4.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m)					
						37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	458.32	445.27	229.19	13.11	0.03	0.00	0.00	0.00	0.00	0.00	0.00
9	343.16	333.40	171.61	9.82	0.02	0.00	0.00	0.00	0.00	0.00	0.00
8	144.05	139.95	72.03	4.12	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	33.90	32.93	16.95	0.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	4.47	4.35	2.24	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.33	0.32	0.17	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 4.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m)					
						37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	172.33	153.09	88.66	24.13	2.49	0.09	0.00	0.00	0.00	0.00	0.00
9	156.49	139.02	80.50	21.91	2.26	0.08	0.00	0.00	0.00	0.00	0.00
8	117.17	104.09	60.28	16.41	1.69	0.06	0.00	0.00	0.00	0.00	0.00
7	72.34	64.26	37.21	10.13	1.05	0.04	0.00	0.00	0.00	0.00	0.00
6	36.83	32.72	18.95	5.16	0.53	0.02	0.00	0.00	0.00	0.00	0.00
5	15.46	13.73	7.95	2.16	0.22	0.01	0.00	0.00	0.00	0.00	0.00
4	5.35	4.75	2.75	0.75	0.08	0.00	0.00	0.00	0.00	0.00	0.00
3	1.53	1.36	0.79	0.21	0.02	0.00	0.00	0.00	0.00	0.00	0.00
2	0.36	0.32	0.18	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.06	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 4.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m)					
						37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	43.43	38.91	27.71	15.35	6.44	2.00	0.45	0.07	0.01	0.00	0.00
9	42.19	37.80	26.92	14.91	6.26	1.95	0.44	0.07	0.01	0.00	0.00
8	38.69	34.66	24.69	13.67	5.74	1.79	0.41	0.07	0.01	0.00	0.00
7	33.48	29.99	21.37	11.83	4.97	1.55	0.35	0.06	0.01	0.00	0.00
6	27.36	24.51	17.46	9.67	4.06	1.26	0.29	0.05	0.01	0.00	0.00
5	21.13	18.93	13.48	7.47	3.14	0.98	0.22	0.04	0.00	0.00	0.00
4	15.47	13.86	9.87	5.47	2.30	0.71	0.16	0.03	0.00	0.00	0.00
3	10.85	9.72	6.92	3.83	1.61	0.50	0.11	0.02	0.00	0.00	0.00
2	7.49	6.71	4.78	2.65	1.11	0.35	0.08	0.01	0.00	0.00	0.00
1	5.48	4.91	3.50	1.94	0.81	0.25	0.06	0.01	0.00	0.00	0.00
0	4.81	4.31	3.07	1.70	0.71	0.22	0.05	0.01	0.00	0.00	0.00

***** X= 4.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	10.17	9.66	8.28	6.40	4.46	2.80	1.58	0.80	0.36	0.15	0.05
9	10.10	9.59	8.23	6.36	4.43	2.78	1.57	0.80	0.36	0.15	0.05
8	9.90	9.41	8.07	6.24	4.35	2.73	1.54	0.78	0.35	0.14	0.05
7	9.60	9.12	7.82	6.05	4.22	2.65	1.49	0.76	0.34	0.14	0.05
6	9.22	8.76	7.51	5.81	4.05	2.54	1.43	0.73	0.33	0.13	0.05
5	8.80	8.36	7.17	5.54	3.86	2.43	1.37	0.69	0.32	0.13	0.05
4	8.38	7.96	6.83	5.28	3.68	2.31	1.30	0.66	0.30	0.12	0.04
3	8.00	7.60	6.52	5.04	3.51	2.20	1.24	0.63	0.29	0.12	0.04
2	7.70	7.31	6.27	4.85	3.38	2.12	1.20	0.61	0.28	0.11	0.04
1	7.51	7.13	6.11	4.73	3.30	2.07	1.17	0.59	0.27	0.11	0.04
0	7.44	7.07	6.06	4.69	3.27	2.05	1.16	0.59	0.27	0.11	0.04

***** X= 4.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	4.62	4.49	4.13	3.60	2.96	2.30	1.70	1.18	0.78	0.48	0.28
9	4.62	4.49	4.13	3.59	2.96	2.30	1.69	1.18	0.78	0.48	0.28
8	4.61	4.48	4.12	3.59	2.95	2.30	1.69	1.18	0.77	0.48	0.28
7	4.60	4.47	4.11	3.58	2.94	2.29	1.69	1.17	0.77	0.48	0.28
6	4.58	4.45	4.10	3.57	2.94	2.28	1.68	1.17	0.77	0.48	0.28
5	4.56	4.44	4.08	3.55	2.92	2.28	1.68	1.17	0.77	0.48	0.28
4	4.55	4.42	4.07	3.54	2.91	2.27	1.67	1.16	0.76	0.48	0.28
3	4.53	4.41	4.05	3.53	2.90	2.26	1.66	1.16	0.76	0.47	0.28
2	4.52	4.39	4.04	3.52	2.90	2.25	1.66	1.15	0.76	0.47	0.28
1	4.51	4.39	4.04	3.51	2.89	2.25	1.66	1.15	0.76	0.47	0.28
0	4.51	4.38	4.03	3.51	2.89	2.25	1.66	1.15	0.76	0.47	0.28

***** X= 4.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	47.5	45.0	42.5	40.0	Y (m) 37.5	35.0	32.5	30.0	27.5	25.0
Concentration (mg/L)											
10	3.07	3.01	2.84	2.59	2.26	1.91	1.55	1.21	0.91	0.66	0.46
9	3.07	3.01	2.84	2.59	2.26	1.91	1.55	1.21	0.91	0.66	0.46
8	3.07	3.01	2.84	2.59	2.26	1.91	1.55	1.21	0.91	0.66	0.46
7	3.07	3.01	2.84	2.59	2.26	1.91	1.55	1.21	0.91	0.66	0.46
6	3.07	3.01	2.84	2.58	2.26	1.91	1.55	1.21	0.91	0.66	0.46
5	3.07	3.01	2.84	2.58	2.26	1.90	1.54	1.21	0.91	0.66	0.46
4	3.07	3.01	2.84	2.58	2.26	1.90	1.54	1.21	0.91	0.65	0.46
3	3.06	3.01	2.84	2.58	2.26	1.90	1.54	1.21	0.91	0.65	0.46
2	3.06	3.01	2.84	2.58	2.26	1.90	1.54	1.20	0.91	0.65	0.46
1	3.06	3.01	2.84	2.58	2.26	1.90	1.54	1.20	0.91	0.65	0.46
0	3.06	3.01	2.84	2.58	2.26	1.90	1.54	1.20	0.91	0.65	0.46

***** X= 5.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z	Y (m)										
(m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	467.82	233.94	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	350.28	175.16	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	147.04	73.53	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	34.60	17.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	4.57	2.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.34	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 5.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z	Y (m)										
(m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	174.49	89.77	2.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	158.45	81.51	2.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	118.64	61.03	1.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	73.25	37.68	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	37.29	19.18	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	15.65	8.05	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	5.42	2.79	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.55	0.80	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.36	0.19	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 5.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z	Y (m)										
(m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	43.76	27.92	6.49	0.46	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	42.51	27.13	6.31	0.45	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	38.98	24.87	5.78	0.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	33.74	21.53	5.00	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	27.57	17.59	4.09	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	21.29	13.59	3.16	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	15.59	9.95	2.31	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.93	6.97	1.62	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.55	4.82	1.12	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.52	3.52	0.82	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.85	3.09	0.72	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 5.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	10.23	8.33	4.49	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.16	8.27	4.46	1.58	0.36	0.05	0.01	0.00	0.00	0.00	0.00
8	9.96	8.12	4.37	1.55	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.66	7.87	4.24	1.50	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.28	7.56	4.07	1.44	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.85	7.21	3.89	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.43	6.87	3.70	1.31	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	8.05	6.56	3.53	1.25	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.74	6.31	3.40	1.20	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.55	6.15	3.32	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.48	6.10	3.29	1.16	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 5.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	4.64	4.15	2.98	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
9	4.64	4.15	2.97	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
8	4.63	4.15	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
7	4.62	4.13	2.96	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
6	4.61	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
5	4.59	4.11	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
4	4.57	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
3	4.56	4.08	2.92	1.67	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.54	4.07	2.91	1.67	0.76	0.28	0.08	0.02	0.00	0.00	0.00
1	4.54	4.06	2.91	1.67	0.76	0.28	0.08	0.02	0.00	0.00	0.00
0	4.53	4.06	2.90	1.66	0.76	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 5.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	3.09	2.86	2.28	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
9	3.09	2.86	2.28	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
8	3.09	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
7	3.08	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
6	3.08	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
5	3.08	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
4	3.08	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
3	3.08	2.86	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
2	3.08	2.85	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
1	3.08	2.85	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00
0	3.08	2.85	2.27	1.55	0.91	0.46	0.20	0.07	0.02	0.01	0.00

***** X= 6.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	461.10	230.58	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	345.25	172.65	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	144.92	72.47	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	34.11	17.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	4.50	2.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.33	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 6.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	173.80	89.41	2.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	157.82	81.19	2.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	118.17	60.79	1.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	72.96	37.53	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	37.14	19.11	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	15.59	8.02	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	5.40	2.78	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.54	0.79	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.36	0.19	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 6.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	43.85	27.98	6.50	0.46	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	42.60	27.18	6.32	0.45	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	39.06	24.92	5.79	0.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	33.80	21.57	5.01	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	27.62	17.63	4.10	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	21.34	13.61	3.17	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	15.62	9.97	2.32	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.95	6.99	1.62	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.56	4.82	1.12	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.53	3.53	0.82	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.86	3.10	0.72	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 6.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	10.27	8.36	4.51	1.60	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.20	8.31	4.48	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
8	10.00	8.15	4.39	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.70	7.90	4.26	1.51	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.31	7.59	4.09	1.45	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.89	7.24	3.90	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.46	6.89	3.72	1.32	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	8.08	6.58	3.55	1.26	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.77	6.33	3.41	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.58	6.17	3.33	1.18	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.51	6.12	3.30	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 6.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
9	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
8	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
7	4.64	4.15	2.97	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
6	4.63	4.14	2.96	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
5	4.61	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
4	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
3	4.58	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.56	4.08	2.92	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.56	4.08	2.92	1.67	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.55	4.07	2.92	1.67	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 6.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	2.33	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
9	2.33	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
8	2.33	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
7	2.33	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
6	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
5	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
4	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
3	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
2	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
1	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01
0	2.32	2.19	1.84	1.38	0.92	0.55	0.29	0.14	0.06	0.02	0.01

***** X= 7.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	438.75	219.41	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	328.52	164.28	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	137.90	68.96	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	32.45	16.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	4.28	2.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.32	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 7.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	170.30	87.61	2.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	154.65	79.56	2.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	115.79	59.57	1.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	71.49	36.78	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	36.39	18.72	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	15.28	7.86	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	5.29	2.72	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.51	0.78	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.36	0.18	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 7.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	43.69	27.88	6.48	0.46	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	42.45	27.09	6.30	0.44	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	38.92	24.84	5.77	0.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	33.69	21.49	5.00	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	27.53	17.56	4.08	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	21.26	13.57	3.15	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	15.57	9.93	2.31	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.91	6.96	1.62	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.53	4.81	1.12	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.51	3.52	0.82	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.84	3.09	0.72	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 7.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	10.29	8.38	4.52	1.60	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.22	8.32	4.49	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
8	10.02	8.17	4.40	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.72	7.92	4.27	1.51	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.33	7.60	4.10	1.45	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.91	7.26	3.91	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.48	6.91	3.72	1.32	0.30	0.05	0.00	0.00	0.00	0.00	0.00
3	8.10	6.59	3.56	1.26	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.79	6.35	3.42	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.60	6.19	3.34	1.18	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.53	6.13	3.31	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 7.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.67	4.18	2.99	1.71	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.66	4.17	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
6	4.64	4.15	2.97	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.62	4.14	2.96	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
4	4.61	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
3	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.57	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.57	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 7.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	2.34	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
9	2.34	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
8	2.34	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
7	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
6	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
5	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
4	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
3	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
2	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
1	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01
0	2.33	2.20	1.85	1.39	0.92	0.55	0.29	0.14	0.06	0.02	0.01

***** X= 8.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	Y (m)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	402.77	201.41	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	301.57	150.81	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	126.59	63.30	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	29.79	14.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	3.93	1.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.29	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 8.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	Y (m)		20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	164.16	84.45	2.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	149.07	76.69	2.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	111.61	57.42	1.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	68.91	35.45	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	35.08	18.05	0.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	14.73	7.58	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	5.10	2.62	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.45	0.75	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.34	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.07	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 8.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	Y (m)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	43.30	27.63	6.42	0.45	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	42.07	26.84	6.24	0.44	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	38.57	24.61	5.72	0.40	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	33.38	21.30	4.95	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	27.28	17.41	4.05	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	21.07	13.44	3.13	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	15.43	9.84	2.29	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.81	6.90	1.60	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.47	4.76	1.11	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.46	3.48	0.81	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.80	3.06	0.71	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 8.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	10.29	8.38	4.52	1.60	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.22	8.33	4.49	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
8	10.03	8.17	4.40	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.72	7.92	4.27	1.51	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.33	7.60	4.10	1.45	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.91	7.26	3.91	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.48	6.91	3.72	1.32	0.30	0.05	0.00	0.00	0.00	0.00	0.00
3	8.10	6.60	3.56	1.26	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.79	6.35	3.42	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.60	6.19	3.34	1.18	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.53	6.13	3.31	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 8.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.67	4.18	2.99	1.71	0.79	0.29	0.08	0.02	0.00	0.00	0.00
6	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.64	4.15	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
4	4.62	4.13	2.96	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.60	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 8.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
9	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
8	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
7	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
6	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
5	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
4	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
3	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
2	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
1	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01
0	2.34	2.21	1.86	1.39	0.93	0.55	0.29	0.14	0.06	0.02	0.01

***** X= 9.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	356.29	178.17	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	266.77	133.40	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	111.98	56.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	26.35	13.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	3.48	1.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.26	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 9.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	155.66	80.08	2.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	141.35	72.72	2.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	105.84	54.45	1.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	65.34	33.62	0.94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	33.26	17.11	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	13.96	7.18	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	4.83	2.49	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.38	0.71	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.32	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.06	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 9.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	42.68	27.23	6.33	0.45	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	41.46	26.46	6.15	0.43	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	38.02	24.26	5.64	0.40	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	32.90	20.99	4.88	0.34	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	26.89	17.16	3.99	0.28	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	20.77	13.25	3.08	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	15.21	9.70	2.26	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.66	6.80	1.58	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.36	4.70	1.09	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.38	3.43	0.80	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.73	3.02	0.70	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 9.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	Y (m)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	10.27	8.37	4.51	1.60	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.20	8.31	4.48	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
8	10.01	8.15	4.39	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.70	7.90	4.26	1.51	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.32	7.59	4.09	1.45	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.89	7.24	3.90	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.47	6.90	3.72	1.32	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	8.08	6.58	3.55	1.26	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.78	6.34	3.42	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.58	6.18	3.33	1.18	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.52	6.12	3.30	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 9.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	Y (m)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	4.70	4.21	3.01	1.73	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.70	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.68	4.18	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
6	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.64	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
4	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.61	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
2	4.60	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.59	4.11	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 9.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	Y (m)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
9	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
8	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
7	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
6	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
5	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
4	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
3	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
2	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
1	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
0	2.35	2.22	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01

***** X= 10.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	303.29	151.67	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	227.09	113.56	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	95.32	47.67	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	22.43	11.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	2.96	1.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.22	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 10.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	145.20	74.70	2.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	131.85	67.83	1.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	98.72	50.79	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	60.95	31.36	0.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	31.03	15.96	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	13.02	6.70	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	4.51	2.32	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	1.29	0.66	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.30	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.06	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 10.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	41.83	26.69	6.21	0.44	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	40.64	25.93	6.03	0.43	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	37.26	23.78	5.53	0.39	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	32.25	20.58	4.78	0.34	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	26.35	16.82	3.91	0.28	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	20.35	12.99	3.02	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	14.90	9.51	2.21	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.45	6.67	1.55	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.21	4.60	1.07	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.28	3.37	0.78	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.63	2.96	0.69	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 10.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	Y (m) Concentration (mg/L)						
					30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	10.23	8.34	4.49	1.59	0.37	0.05	0.01	0.00	0.00	0.00	0.00
9	10.17	8.28	4.46	1.58	0.36	0.05	0.01	0.00	0.00	0.00	0.00
8	9.97	8.12	4.38	1.55	0.36	0.05	0.01	0.00	0.00	0.00	0.00
7	9.67	7.88	4.25	1.50	0.35	0.05	0.00	0.00	0.00	0.00	0.00
6	9.28	7.56	4.08	1.44	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.86	7.22	3.89	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.44	6.87	3.70	1.31	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	8.05	6.56	3.54	1.25	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.75	6.31	3.40	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.56	6.16	3.32	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.49	6.10	3.29	1.16	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 10.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	Y (m) Concentration (mg/L)						
					30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	4.70	4.21	3.01	1.73	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.70	4.21	3.01	1.73	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
6	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
4	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.61	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
2	4.60	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 10.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	Y (m) Concentration (mg/L)						
					30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
9	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
8	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
7	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
6	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
5	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
4	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
3	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
2	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
1	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01
0	2.36	2.23	1.87	1.40	0.93	0.55	0.29	0.14	0.06	0.02	0.01

***** X= 11.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	248.03	124.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	185.71	92.87	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	77.96	38.98	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	18.35	9.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	2.42	1.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.18	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 11.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	40.77	26.02	6.05	0.43	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	39.61	25.28	5.88	0.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	36.32	23.18	5.39	0.38	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	31.44	20.06	4.66	0.33	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	25.69	16.39	3.81	0.27	0.01	0.00	0.00	0.00	0.00	0.00	0.00
5	19.84	12.66	2.94	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	14.53	9.27	2.16	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	10.18	6.50	1.51	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	7.03	4.49	1.04	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	5.14	3.28	0.76	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.52	2.88	0.67	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 11.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	10.18	8.29	4.47	1.58	0.36	0.05	0.01	0.00	0.00	0.00	0.00
9	10.11	8.24	4.44	1.57	0.36	0.05	0.01	0.00	0.00	0.00	0.00
8	9.92	8.08	4.35	1.54	0.36	0.05	0.00	0.00	0.00	0.00	0.00
7	9.61	7.83	4.22	1.49	0.34	0.05	0.00	0.00	0.00	0.00	0.00
6	9.23	7.52	4.05	1.44	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.81	7.18	3.87	1.37	0.32	0.05	0.00	0.00	0.00	0.00	0.00
4	8.39	6.83	3.68	1.30	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	8.01	6.52	3.52	1.25	0.29	0.04	0.00	0.00	0.00	0.00	0.00
2	7.71	6.28	3.38	1.20	0.28	0.04	0.00	0.00	0.00	0.00	0.00
1	7.51	6.12	3.30	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.45	6.07	3.27	1.16	0.27	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 11.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	4.70	4.21	3.01	1.73	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.70	4.20	3.01	1.73	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
6	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
4	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.61	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
2	4.60	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.59	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 11.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	2.36	2.23	1.88	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
9	2.36	2.23	1.88	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
8	2.36	2.23	1.88	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
7	2.36	2.23	1.88	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
6	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
5	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
4	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
3	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
2	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
1	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01
0	2.36	2.23	1.87	1.40	0.94	0.56	0.29	0.14	0.06	0.02	0.01

***** X= 11.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
9	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
8	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
7	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
6	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
5	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
4	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
3	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
2	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
1	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
0	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06

***** X= 12.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	194.54	97.28	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	145.66	72.84	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	61.14	30.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	14.39	7.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.90	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.14	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 12.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	39.53	25.22	5.86	0.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	38.40	24.50	5.70	0.40	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	35.21	22.47	5.22	0.37	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	30.47	19.44	4.52	0.32	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	24.90	15.89	3.69	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	19.23	12.27	2.85	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	14.08	8.99	2.09	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	9.87	6.30	1.46	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6.82	4.35	1.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	4.99	3.18	0.74	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.38	2.79	0.65	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 12.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	10.10	8.23	4.44	1.57	0.36	0.05	0.01	0.00	0.00	0.00	0.00
9	10.04	8.18	4.41	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
8	9.84	8.02	4.32	1.53	0.35	0.05	0.00	0.00	0.00	0.00	0.00
7	9.54	7.77	4.19	1.48	0.34	0.05	0.00	0.00	0.00	0.00	0.00
6	9.17	7.47	4.02	1.42	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.75	7.12	3.84	1.36	0.31	0.05	0.00	0.00	0.00	0.00	0.00
4	8.33	6.78	3.66	1.29	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	7.95	6.48	3.49	1.24	0.28	0.04	0.00	0.00	0.00	0.00	0.00
2	7.65	6.23	3.36	1.19	0.27	0.04	0.00	0.00	0.00	0.00	0.00
1	7.46	6.08	3.28	1.16	0.27	0.04	0.00	0.00	0.00	0.00	0.00
0	7.39	6.02	3.25	1.15	0.26	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 12.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	4.70	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.69	4.20	3.01	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.69	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.67	4.18	2.99	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
6	4.66	4.17	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.64	4.15	2.97	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
4	4.62	4.14	2.96	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.61	4.12	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.60	4.11	2.94	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.59	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 12.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
9	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
8	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
7	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
6	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
5	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
4	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
3	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
2	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
1	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
0	2.37	2.23	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01

***** X= 12.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
9	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
8	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
7	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
6	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
5	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
4	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
3	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
2	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
1	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
0	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06

***** X= 13.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	146.10	73.06	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	109.39	54.70	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	45.92	22.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	10.81	5.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.43	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.11	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 13.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	38.11	24.32	5.65	0.40	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	37.02	23.62	5.49	0.39	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	33.94	21.66	5.04	0.36	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	29.38	18.75	4.36	0.31	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	24.01	15.32	3.56	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	18.54	11.83	2.75	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	13.58	8.66	2.01	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	9.52	6.07	1.41	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6.57	4.19	0.97	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	4.81	3.07	0.71	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.22	2.69	0.63	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 13.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	10.01	8.15	4.40	1.56	0.36	0.05	0.01	0.00	0.00	0.00	0.00
9	9.94	8.10	4.37	1.55	0.36	0.05	0.00	0.00	0.00	0.00	0.00
8	9.75	7.94	4.28	1.52	0.35	0.05	0.00	0.00	0.00	0.00	0.00
7	9.45	7.70	4.15	1.47	0.34	0.05	0.00	0.00	0.00	0.00	0.00
6	9.08	7.40	3.99	1.41	0.33	0.05	0.00	0.00	0.00	0.00	0.00
5	8.67	7.06	3.81	1.35	0.31	0.05	0.00	0.00	0.00	0.00	0.00
4	8.25	6.72	3.62	1.28	0.30	0.04	0.00	0.00	0.00	0.00	0.00
3	7.88	6.42	3.46	1.22	0.28	0.04	0.00	0.00	0.00	0.00	0.00
2	7.58	6.17	3.33	1.18	0.27	0.04	0.00	0.00	0.00	0.00	0.00
1	7.39	6.02	3.25	1.15	0.26	0.04	0.00	0.00	0.00	0.00	0.00
0	7.32	5.97	3.22	1.14	0.26	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 13.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	4.69	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.68	4.19	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
8	4.67	4.18	3.00	1.72	0.79	0.29	0.08	0.02	0.00	0.00	0.00
7	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
6	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
5	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
4	4.61	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
3	4.60	4.11	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.58	4.10	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.57	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 13.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
9	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
8	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
7	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
6	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
5	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
4	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
3	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
2	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
1	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
0	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01

***** X= 13.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
	Y (m) Concentration (mg/L)										
10	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
9	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
8	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
7	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
6	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
5	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
4	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
3	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
2	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
1	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06
0	1.58	1.52	1.35	1.11	0.84	0.59	0.39	0.23	0.13	0.08	0.06

***** X= 14.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	104.89	52.45	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	78.53	39.27	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	32.97	16.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	7.76	3.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.02	0.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 14.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	36.54	23.31	5.42	0.38	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	35.49	22.65	5.27	0.37	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	32.54	20.77	4.83	0.34	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	28.17	17.97	4.18	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	23.02	14.69	3.41	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	17.78	11.34	2.64	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	13.02	8.31	1.93	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	9.12	5.82	1.35	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6.30	4.02	0.93	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	4.61	2.94	0.68	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	4.05	2.58	0.60	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 14.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	9.90	8.06	4.35	1.54	0.35	0.05	0.00	0.00	0.00	0.00	0.00
9	9.83	8.01	4.32	1.53	0.35	0.05	0.00	0.00	0.00	0.00	0.00
8	9.64	7.86	4.23	1.50	0.35	0.05	0.00	0.00	0.00	0.00	0.00
7	9.35	7.62	4.11	1.45	0.33	0.05	0.00	0.00	0.00	0.00	0.00
6	8.98	7.31	3.94	1.40	0.32	0.05	0.00	0.00	0.00	0.00	0.00
5	8.57	6.98	3.76	1.33	0.31	0.05	0.00	0.00	0.00	0.00	0.00
4	8.16	6.65	3.58	1.27	0.29	0.04	0.00	0.00	0.00	0.00	0.00
3	7.79	6.35	3.42	1.21	0.28	0.04	0.00	0.00	0.00	0.00	0.00
2	7.50	6.11	3.29	1.17	0.27	0.04	0.00	0.00	0.00	0.00	0.00
1	7.31	5.95	3.21	1.14	0.26	0.04	0.00	0.00	0.00	0.00	0.00
0	7.24	5.90	3.18	1.13	0.26	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 14.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
					Y (m) Concentration (mg/L)						
10	4.67	4.18	2.99	1.71	0.79	0.29	0.08	0.02	0.00	0.00	0.00
9	4.67	4.18	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
8	4.66	4.17	2.99	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
7	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
6	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
5	4.62	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
4	4.60	4.11	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
3	4.58	4.10	2.94	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.57	4.09	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.56	4.08	2.92	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
0	4.56	4.08	2.92	1.67	0.77	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 14.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
					Y (m) Concentration (mg/L)						
10	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
9	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
8	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
7	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
6	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
5	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
4	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
3	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
2	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
1	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
0	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01

***** X= 14.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
					Y (m) Concentration (mg/L)						
10	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
9	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
8	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
7	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
6	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
5	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
4	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
3	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
2	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
1	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06
0	1.58	1.52	1.35	1.11	0.85	0.60	0.39	0.23	0.14	0.08	0.06

***** X= 15.0 m *****
1.0 day after application. (T= 8.640E+0004 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	71.87	35.94	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	53.82	26.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	22.59	11.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	5.32	2.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.70	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.05	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 15.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	34.84	22.23	5.17	0.36	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	33.84	21.59	5.02	0.35	0.01	0.00	0.00	0.00	0.00	0.00	0.00
8	31.03	19.80	4.60	0.32	0.01	0.00	0.00	0.00	0.00	0.00	0.00
7	26.86	17.14	3.98	0.28	0.01	0.00	0.00	0.00	0.00	0.00	0.00
6	21.95	14.00	3.26	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	16.95	10.82	2.51	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	12.41	7.92	1.84	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	8.70	5.55	1.29	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6.01	3.83	0.89	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	4.39	2.80	0.65	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	3.86	2.46	0.57	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 15.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	Y (m) Concentration (mg/L)										
	50.0	45.0	40.0	35.0	30.0	25.0	20.0	15.0	10.0	5.0	0.0
10	9.77	7.96	4.29	1.52	0.35	0.05	0.00	0.00	0.00	0.00	0.00
9	9.70	7.91	4.26	1.51	0.35	0.05	0.00	0.00	0.00	0.00	0.00
8	9.52	7.75	4.18	1.48	0.34	0.05	0.00	0.00	0.00	0.00	0.00
7	9.23	7.52	4.05	1.43	0.33	0.05	0.00	0.00	0.00	0.00	0.00
6	8.86	7.22	3.89	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
5	8.46	6.89	3.71	1.31	0.30	0.04	0.00	0.00	0.00	0.00	0.00
4	8.05	6.56	3.54	1.25	0.29	0.04	0.00	0.00	0.00	0.00	0.00
3	7.69	6.26	3.38	1.20	0.28	0.04	0.00	0.00	0.00	0.00	0.00
2	7.40	6.03	3.25	1.15	0.26	0.04	0.00	0.00	0.00	0.00	0.00
1	7.21	5.88	3.17	1.12	0.26	0.04	0.00	0.00	0.00	0.00	0.00
0	7.15	5.82	3.14	1.11	0.26	0.04	0.00	0.00	0.00	0.00	0.00

***** X= 15.0 m *****
60.0 days after application. (T= 5.184E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
9	4.65	4.16	2.98	1.71	0.78	0.29	0.08	0.02	0.00	0.00	0.00
8	4.64	4.15	2.97	1.70	0.78	0.29	0.08	0.02	0.00	0.00	0.00
7	4.63	4.14	2.97	1.70	0.78	0.28	0.08	0.02	0.00	0.00	0.00
6	4.61	4.13	2.96	1.69	0.78	0.28	0.08	0.02	0.00	0.00	0.00
5	4.60	4.11	2.95	1.69	0.77	0.28	0.08	0.02	0.00	0.00	0.00
4	4.58	4.10	2.93	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
3	4.56	4.08	2.92	1.68	0.77	0.28	0.08	0.02	0.00	0.00	0.00
2	4.55	4.07	2.92	1.67	0.77	0.28	0.08	0.02	0.00	0.00	0.00
1	4.54	4.07	2.91	1.67	0.76	0.28	0.08	0.02	0.00	0.00	0.00
0	4.54	4.06	2.91	1.67	0.76	0.28	0.08	0.02	0.00	0.00	0.00

***** X= 15.0 m *****
120.0 days after application. (T= 1.037E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
9	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
8	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
7	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
6	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
5	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
4	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
3	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
2	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
1	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01
0	2.37	2.24	1.88	1.41	0.94	0.56	0.29	0.14	0.06	0.02	0.01

***** X= 15.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
	Concentration (mg/L)										
10	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
9	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
8	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
7	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
6	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
5	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
4	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
3	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
2	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
1	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
0	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06

***** X= 20.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	28.95	14.89	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	26.29	13.52	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	19.68	10.12	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	12.15	6.25	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	6.19	3.18	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	2.60	1.34	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.90	0.46	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.26	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.06	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 20.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	25.27	16.13	3.75	0.26	0.01	0.00	0.00	0.00	0.00	0.00	0.00
9	24.55	15.67	3.64	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	22.51	14.37	3.34	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	19.49	12.43	2.89	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	15.92	10.16	2.36	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	12.30	7.85	1.82	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	9.01	5.75	1.34	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	6.31	4.03	0.94	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	4.36	2.78	0.65	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	3.19	2.03	0.47	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	2.80	1.79	0.42	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 20.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	8.89	7.24	3.90	1.38	0.32	0.05	0.00	0.00	0.00	0.00	0.00
9	8.83	7.20	3.88	1.37	0.32	0.05	0.00	0.00	0.00	0.00	0.00
8	8.66	7.06	3.80	1.35	0.31	0.05	0.00	0.00	0.00	0.00	0.00
7	8.40	6.84	3.69	1.31	0.30	0.04	0.00	0.00	0.00	0.00	0.00
6	8.07	6.57	3.54	1.25	0.29	0.04	0.00	0.00	0.00	0.00	0.00
5	7.70	6.27	3.38	1.20	0.28	0.04	0.00	0.00	0.00	0.00	0.00
4	7.33	5.97	3.22	1.14	0.26	0.04	0.00	0.00	0.00	0.00	0.00
3	7.00	5.70	3.07	1.09	0.25	0.04	0.00	0.00	0.00	0.00	0.00
2	6.73	5.49	2.96	1.05	0.24	0.04	0.00	0.00	0.00	0.00	0.00
1	6.57	5.35	2.88	1.02	0.24	0.03	0.00	0.00	0.00	0.00	0.00
0	6.51	5.30	2.86	1.01	0.23	0.03	0.00	0.00	0.00	0.00	0.00

***** X= 20.0 m *****
 90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	3.09	2.87	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
9	3.09	2.87	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
8	3.09	2.87	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
7	3.09	2.87	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
6	3.09	2.87	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
5	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
4	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
3	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
2	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
1	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00
0	3.09	2.86	2.28	1.56	0.91	0.46	0.20	0.07	0.02	0.01	0.00

***** X= 20.0 m *****
 180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
9	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
8	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
7	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
6	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
5	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
4	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
3	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
2	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
1	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06
0	1.59	1.53	1.36	1.12	0.85	0.60	0.39	0.24	0.14	0.08	0.06

***** X= 20.0 m *****
 360.0 days after application. (T= 3.110E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
9	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
8	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
7	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
6	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
5	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
4	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
3	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
2	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
1	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
0	0.79	0.77	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22

***** X= 30.0 m *****
3.0 days after application. (T= 2.592E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.03	0.53	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.94	0.48	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.70	0.36	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.43	0.22	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.22	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.09	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 30.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	8.79	5.61	1.30	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	8.54	5.45	1.27	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	7.83	5.00	1.16	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	6.78	4.32	1.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	5.54	3.53	0.82	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	4.28	2.73	0.63	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	3.13	2.00	0.46	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	2.20	1.40	0.33	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	1.52	0.97	0.22	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	1.11	0.71	0.16	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.97	0.62	0.14	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 30.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	6.39	5.20	2.81	0.99	0.23	0.03	0.00	0.00	0.00	0.00	0.00
9	6.35	5.17	2.79	0.99	0.23	0.03	0.00	0.00	0.00	0.00	0.00
8	6.23	5.07	2.73	0.97	0.22	0.03	0.00	0.00	0.00	0.00	0.00
7	6.04	4.92	2.65	0.94	0.22	0.03	0.00	0.00	0.00	0.00	0.00
6	5.80	4.72	2.55	0.90	0.21	0.03	0.00	0.00	0.00	0.00	0.00
5	5.53	4.51	2.43	0.86	0.20	0.03	0.00	0.00	0.00	0.00	0.00
4	5.27	4.29	2.31	0.82	0.19	0.03	0.00	0.00	0.00	0.00	0.00
3	5.03	4.10	2.21	0.78	0.18	0.03	0.00	0.00	0.00	0.00	0.00
2	4.84	3.94	2.12	0.75	0.17	0.03	0.00	0.00	0.00	0.00	0.00
1	4.72	3.84	2.07	0.73	0.17	0.03	0.00	0.00	0.00	0.00	0.00
0	4.68	3.81	2.05	0.73	0.17	0.02	0.00	0.00	0.00	0.00	0.00

***** X= 30.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	2.86	2.65	2.11	1.44	0.85	0.43	0.18	0.07	0.02	0.01	0.00
9	2.86	2.65	2.11	1.44	0.85	0.43	0.18	0.07	0.02	0.01	0.00
8	2.86	2.65	2.11	1.44	0.85	0.43	0.18	0.07	0.02	0.01	0.00
7	2.86	2.65	2.11	1.44	0.84	0.43	0.18	0.07	0.02	0.01	0.00
6	2.86	2.65	2.11	1.44	0.84	0.43	0.18	0.07	0.02	0.01	0.00
5	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00
4	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00
3	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00
2	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00
1	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00
0	2.86	2.65	2.11	1.44	0.84	0.42	0.18	0.07	0.02	0.01	0.00

***** X= 30.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
9	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
8	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
7	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
6	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
5	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
4	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
3	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
2	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
1	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06
0	1.57	1.51	1.34	1.11	0.84	0.59	0.38	0.23	0.13	0.08	0.06

***** X= 30.0 m *****
360.0 days after application. (T= 3.110E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
9	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
8	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
7	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
6	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
5	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
4	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
3	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
2	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
1	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
0	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22

***** X= 40.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.76	1.12	0.26	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	1.71	1.09	0.25	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	1.57	1.00	0.23	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	1.35	0.86	0.20	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	1.11	0.71	0.16	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.86	0.55	0.13	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.63	0.40	0.09	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.44	0.28	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.30	0.19	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.22	0.14	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.19	0.12	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 40.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	3.80	3.09	1.67	0.59	0.14	0.02	0.00	0.00	0.00	0.00	0.00
9	3.77	3.07	1.66	0.59	0.14	0.02	0.00	0.00	0.00	0.00	0.00
8	3.70	3.01	1.62	0.58	0.13	0.02	0.00	0.00	0.00	0.00	0.00
7	3.59	2.92	1.58	0.56	0.13	0.02	0.00	0.00	0.00	0.00	0.00
6	3.45	2.81	1.51	0.54	0.12	0.02	0.00	0.00	0.00	0.00	0.00
5	3.29	2.68	1.44	0.51	0.12	0.02	0.00	0.00	0.00	0.00	0.00
4	3.13	2.55	1.37	0.49	0.11	0.02	0.00	0.00	0.00	0.00	0.00
3	2.99	2.43	1.31	0.46	0.11	0.02	0.00	0.00	0.00	0.00	0.00
2	2.88	2.34	1.26	0.45	0.10	0.02	0.00	0.00	0.00	0.00	0.00
1	2.80	2.28	1.23	0.44	0.10	0.01	0.00	0.00	0.00	0.00	0.00
0	2.78	2.26	1.22	0.43	0.10	0.01	0.00	0.00	0.00	0.00	0.00

***** X= 40.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m)					
						25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
9	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
8	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
7	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
6	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
5	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
4	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
3	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
2	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
1	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00
0	2.48	2.30	1.83	1.25	0.73	0.37	0.16	0.06	0.02	0.01	0.00

***** X= 40.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
9	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
8	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
7	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
6	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
5	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
4	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
3	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
2	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
1	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06
0	1.50	1.44	1.28	1.06	0.80	0.56	0.37	0.22	0.13	0.08	0.06

***** X= 40.0 m *****
360.0 days after application. (T= 3.110E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
9	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
8	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
7	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
6	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
5	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
4	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
3	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
2	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
1	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22
0	0.80	0.79	0.74	0.67	0.59	0.50	0.41	0.33	0.27	0.23	0.22

***** X= 40.0 m *****
540.0 days after application. (T= 4.666E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
9	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
8	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
7	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
6	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
5	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
4	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
3	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
2	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
1	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28
0	0.54	0.53	0.51	0.48	0.45	0.41	0.37	0.33	0.31	0.29	0.28

***** X= 50.0 m *****
10.0 days after application. (T= 8.640E+0005 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.20	0.13	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.20	0.12	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.18	0.11	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.16	0.10	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.13	0.08	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.10	0.06	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.07	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.05	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.03	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

***** X= 50.0 m *****
30.0 days after application. (T= 2.592E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.87	1.52	0.82	0.29	0.07	0.01	0.00	0.00	0.00	0.00	0.00
9	1.85	1.51	0.81	0.29	0.07	0.01	0.00	0.00	0.00	0.00	0.00
8	1.82	1.48	0.80	0.28	0.07	0.01	0.00	0.00	0.00	0.00	0.00
7	1.76	1.44	0.77	0.27	0.06	0.01	0.00	0.00	0.00	0.00	0.00
6	1.69	1.38	0.74	0.26	0.06	0.01	0.00	0.00	0.00	0.00	0.00
5	1.62	1.32	0.71	0.25	0.06	0.01	0.00	0.00	0.00	0.00	0.00
4	1.54	1.25	0.68	0.24	0.06	0.01	0.00	0.00	0.00	0.00	0.00
3	1.47	1.20	0.65	0.23	0.05	0.01	0.00	0.00	0.00	0.00	0.00
2	1.41	1.15	0.62	0.22	0.05	0.01	0.00	0.00	0.00	0.00	0.00
1	1.38	1.12	0.61	0.21	0.05	0.01	0.00	0.00	0.00	0.00	0.00
0	1.37	1.11	0.60	0.21	0.05	0.01	0.00	0.00	0.00	0.00	0.00

***** X= 50.0 m *****
90.0 days after application. (T= 7.776E+0006 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
9	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
8	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
7	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
6	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
5	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
4	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
3	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
2	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
1	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00
0	2.02	1.87	1.49	1.02	0.60	0.30	0.13	0.05	0.02	0.00	0.00

***** X= 50.0 m *****
180.0 days after application. (T= 1.555E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
9	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
8	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
7	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
6	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
5	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
4	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
3	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
2	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
1	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06
0	1.39	1.33	1.19	0.98	0.74	0.52	0.34	0.21	0.12	0.07	0.06

***** X= 50.0 m *****
360.0 days after application. (T= 3.110E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
9	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
8	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
7	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
6	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
5	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
4	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
3	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
2	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
1	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22
0	0.79	0.78	0.73	0.66	0.58	0.49	0.40	0.33	0.27	0.23	0.22

***** X= 50.0 m *****
540.0 days after application. (T= 4.666E+0007 sec.)

Z (m)	50.0	45.0	40.0	35.0	30.0	Y (m) 25.0	20.0	15.0	10.0	5.0	0.0
Concentration (mg/L)											
10	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
9	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
8	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
7	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
6	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
5	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
4	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
3	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
2	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
1	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28
0	0.54	0.54	0.52	0.49	0.45	0.41	0.37	0.34	0.31	0.29	0.28

Appendix B

Examples of LP Plume Migration Based on Transport Models

bounded LP flow model
(standard conditions)

$\theta := 1$ <--moisture content
 $K := 0$ <--chemical transformation rate
 $R := 1$ <--retardation factor
 $M := 10000$ <--mass of the contaminant added
 $V := (-1 \cdot 10^{-6})$ <--vertical velocity

 $D_x := 1 \cdot 10^{-5}$ $D_y := 1 \cdot 10^{-5}$ $D_z := 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturate zone

 $D_{zz} := 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

 $x_1 := -5$ $x_2 := 5$ <-- initial loading area boundaries
 $y_1 := 45$ $y_2 := 55$

 $W := 100$ <--aquifer dimensions
 $H := 10$

 $N_{\max} := 100$ <--number of summation steps
 $m_{\max} := 100$

 $B := 5$ <--depth of aquifer

 $U := 8 \cdot 10^{-6}$ <--horizontal velocity

Example 1. Vertical flow from a spill at a point source (bound aquifer) (Sheet 1 of 17)

$$d_y := y_2 - y_1 \quad C := \frac{M}{2 \cdot W \cdot H}$$

$$f_1(z, t, \tau) := 1 + 2 \cdot \sum_{N=1}^{N_{\max}} \exp \left[- \left(\frac{N \cdot \pi}{H} \right)^2 \cdot D_z \cdot \frac{t - \tau}{R} \right] \cdot \cos \left[\left(\frac{N \cdot \pi}{H} \right) \cdot z \right] \cdot \cos \left[\left(\frac{N \cdot \pi}{H} \right) \cdot H \right]$$

$$f_2(x, t, \tau) := \left[\operatorname{erf} \left[\frac{x_2 - x + U \cdot \frac{t - \tau}{R}}{2 \cdot \sqrt{D_x \cdot \frac{t - \tau}{R}}} \right] - \operatorname{erf} \left[\frac{x_1 - x + U \cdot \frac{t - \tau}{R}}{2 \cdot \sqrt{D_x \cdot \frac{t - \tau}{R}}} \right] \right] \cdot \exp \left(- \frac{K \cdot t}{R} \right)$$

$$f_3(y, t, \tau) := d_y + 2 \cdot \sum_{m=1}^{m_{\max}} \frac{\exp \left[- \left(\frac{m \cdot \pi}{W} \right)^2 \cdot D_y \cdot \frac{t - \tau}{R} \right]}{\left(\frac{m \cdot \pi}{W} \right)} \cdot \cos \left[\left(\frac{m \cdot \pi}{W} \right) \cdot y \right] \cdot \left[\sin \left[\left(\frac{m \cdot \pi}{W} \right) \cdot y_2 \right] - \sin \left[\left(\frac{m \cdot \pi}{W} \right) \cdot y_1 \right] \right]$$

$$C(x, y, z, t) := C \cdot \int_1^t \frac{V - \frac{R \cdot \theta}{2 \cdot \tau} \cdot \left(B + \frac{V \cdot \tau}{R \cdot \theta} \right)}{\left(\frac{4 \cdot \pi \cdot D_z \cdot \tau}{R \cdot \theta} \right)^{\frac{1}{2}}} \cdot \exp \left[- \frac{\left(B + \frac{V \cdot \tau}{R \cdot \theta} \right)^2 \cdot R \cdot \theta}{4 \cdot D_z \cdot \tau} - \frac{K \cdot \tau}{R \cdot \theta} \right] \cdot f_1(z, t, \tau) \cdot f_2(x, t, \tau) \cdot f_3(y, t, \tau) \, d\tau$$

$$z_1 := B + H$$

$$C_v(z, t) := \frac{M}{\sqrt{\frac{4 \cdot \pi \cdot D_z \cdot t}{R \cdot \theta}} \cdot (x_2 - x_1) \cdot (y_2 - y_1)} \cdot \exp \left[- \frac{\left(z - z_1 - \frac{V \cdot t}{R \cdot \theta} \right)^2}{\left(\frac{4 \cdot D_z \cdot t}{R \cdot \theta} \right)} - \frac{K \cdot t}{R \cdot \theta} \right]$$

$$P := 35$$

$$i := 0..P \quad j := 0..P$$

$$\text{SCALE} := \begin{bmatrix} 1 & 1 \\ 2 & 2 \\ 3 & 3 \\ 4 & 4 \\ 5 & 5 \\ 6 & 6 \\ 7 & 7 \\ 8 & 8 \\ 9 & 9 \end{bmatrix}$$

Example 1. (Sheet 2 of 17)

$t_{\text{days}} := 10$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 8.64 \cdot 10^5$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := C_v(z_i, t)$$

$$\text{VERT}_{1,i} := C_v(z_i, t)$$

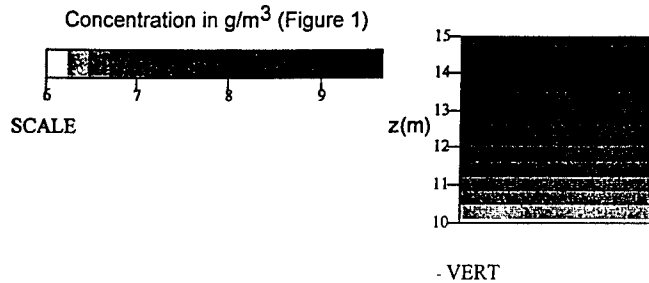
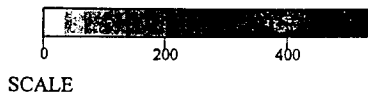


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy_{i,j}} := C(x_i, y_j, z, t)$$

direction of flow ---->

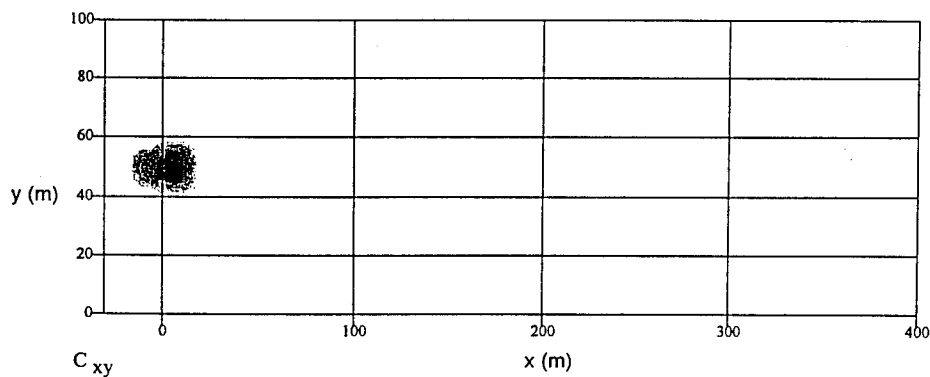


Figure 2. Top view of aquifer surface.

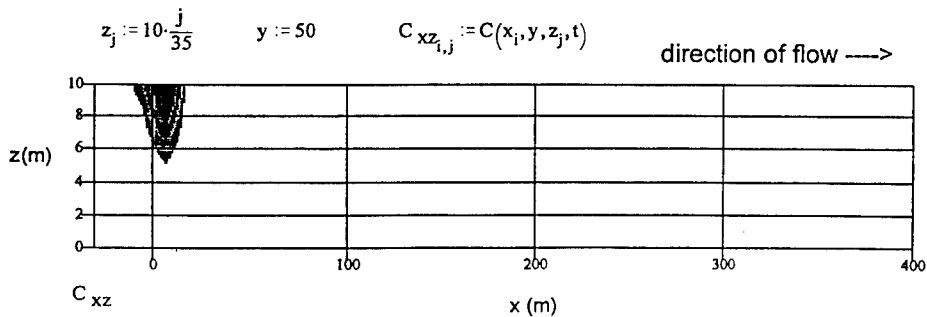


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 20$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.728 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

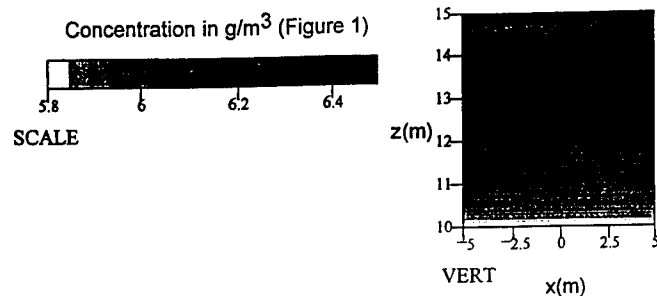


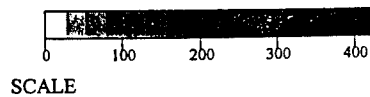
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

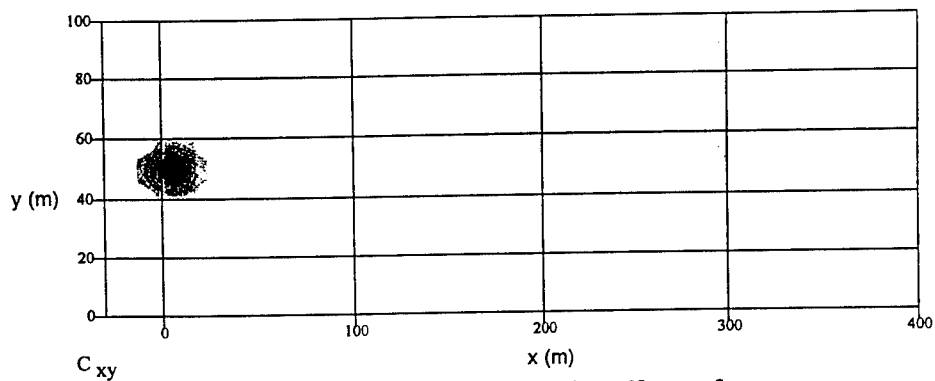


Figure 2. Top view of aquifer surface.

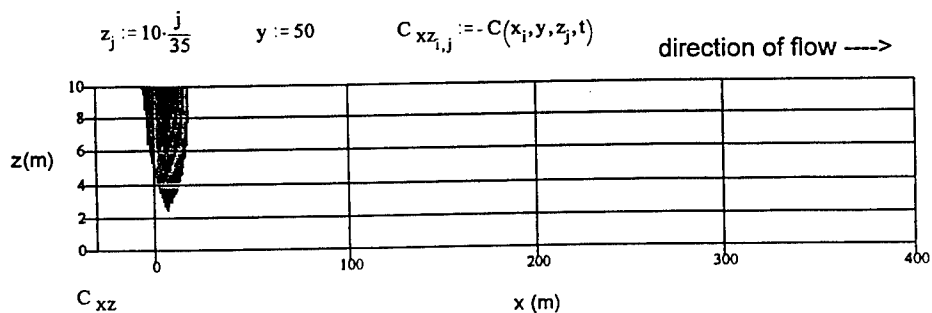


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 4 of 17)

$t_{\text{days}} := 30$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.592 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

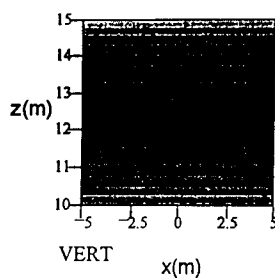
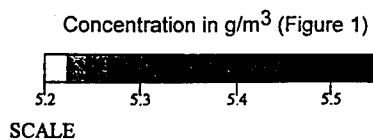
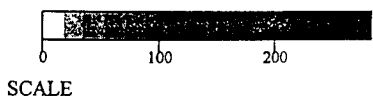


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy_{i,j}} := C(x_i, y_j, z, t)$$

direction of flow ---->

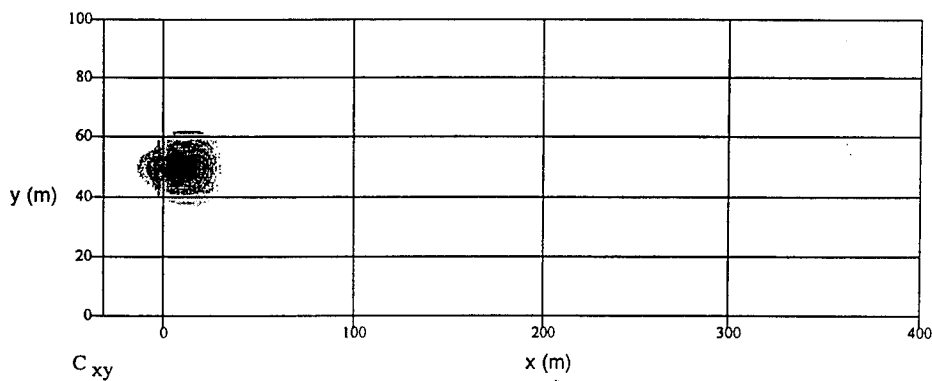


Figure 2. Top view of aquifer surface.

$$z_j := 10 \cdot \frac{j}{35}$$

$$y := 50$$

$$C_{xz_{i,j}} := C(x_i, y, z_j, t)$$

direction of flow ---->

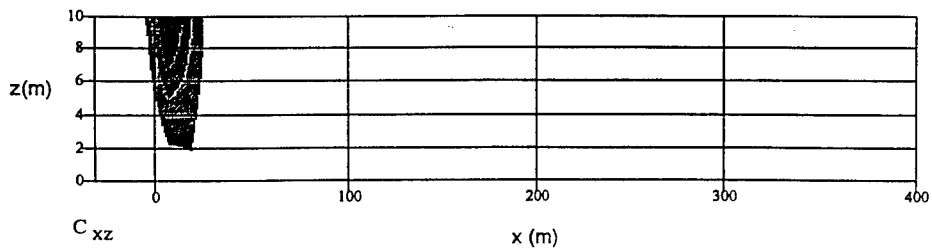


Figure 3. Side view of cut along the centerline of aquifer.

$$t_{\text{days}} := 40 \quad \leftarrow \text{time (days)} \quad t := 3600 \cdot 24 \cdot t_{\text{days}} \quad t = 3.456 \cdot 10^6 \quad \leftarrow \text{time (seconds)}$$

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

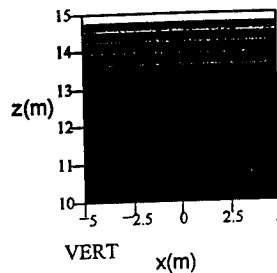
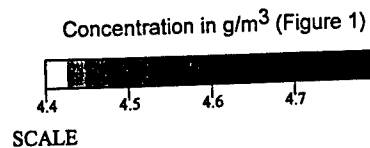
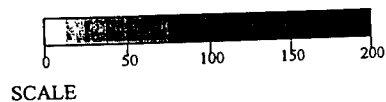


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 10$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

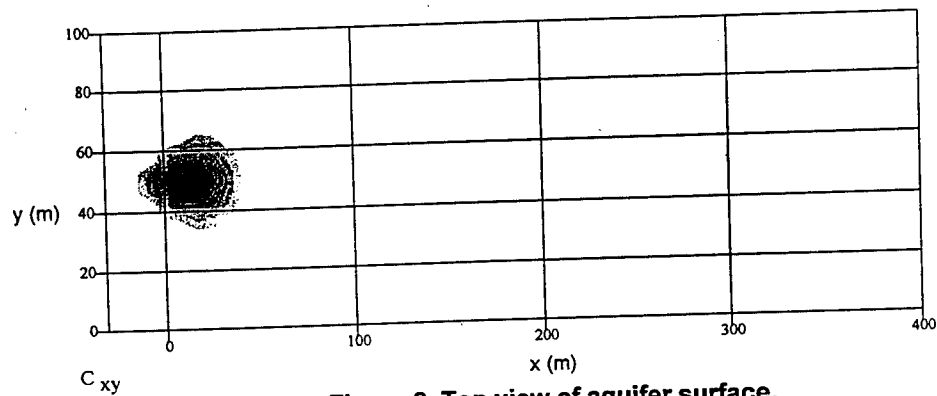


Figure 2. Top view of aquifer surface.

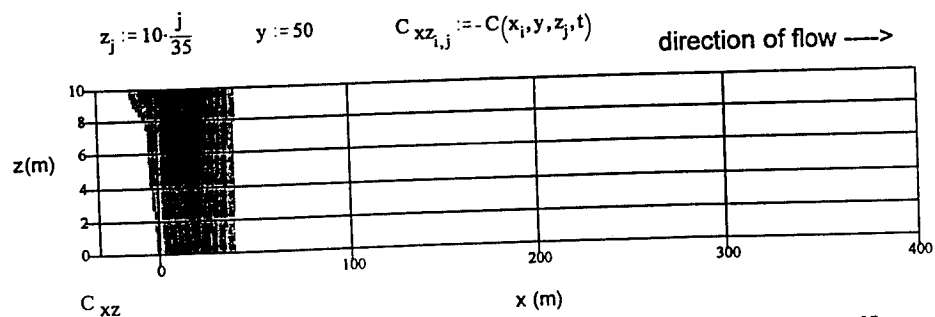


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 6 of 17)

$t_{\text{days}} := 50$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 4.32 \cdot 10^6$ <-- time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

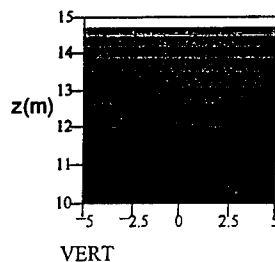
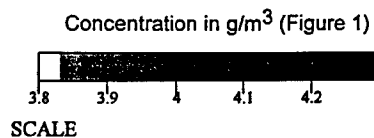
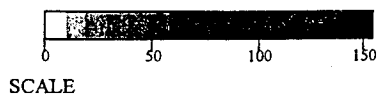


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

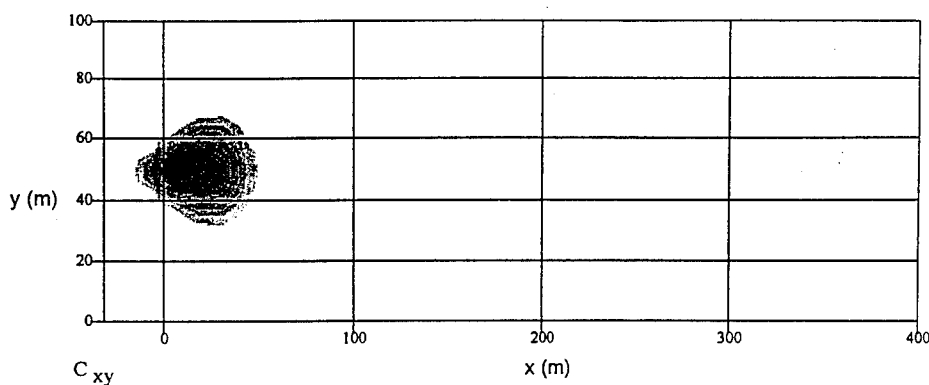


Figure 2. Top view of aquifer surface.

$$z_j := 10 \cdot \frac{j}{35}$$

$$y := 50$$

$$C_{xz,i,j} := -C(x_i, y, z_j, t)$$

direction of flow ---->

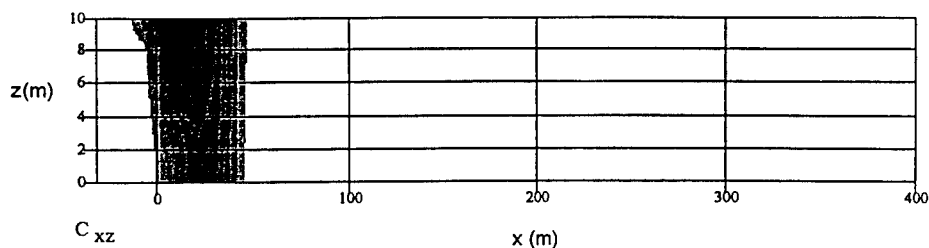


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 60$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 5.184 \cdot 10^6$ <-- time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

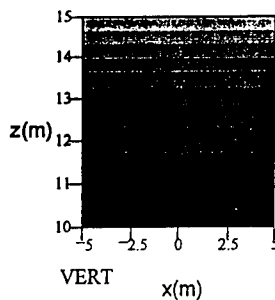
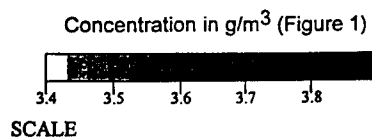
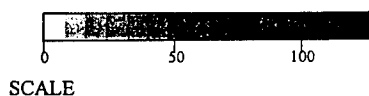


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

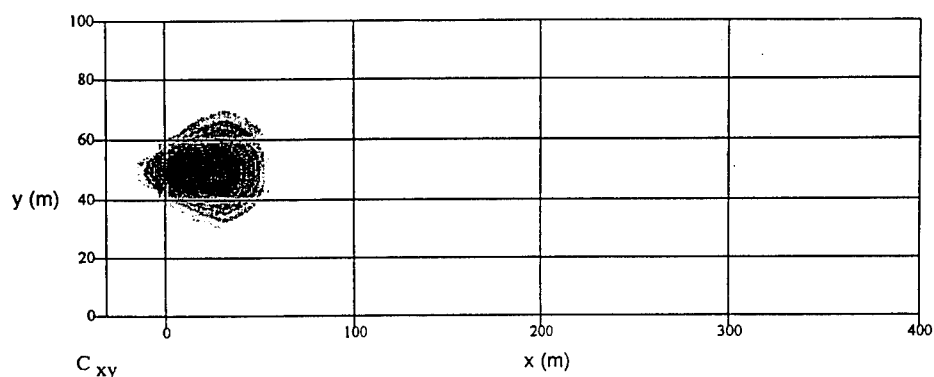


Figure 2. Top view of aquifer surface.

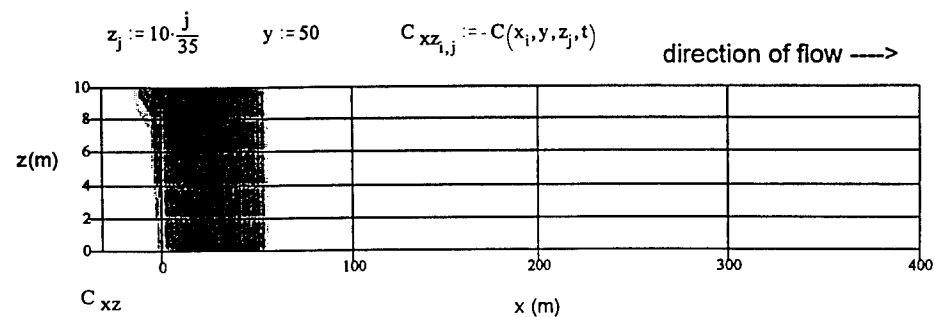


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 8 of 17)

$t_{\text{days}} := 80$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 6.912 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

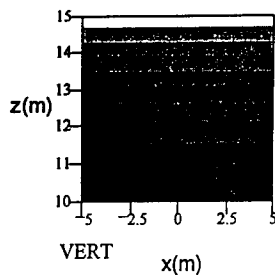
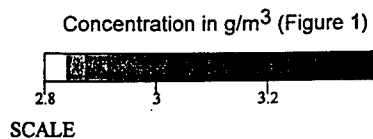
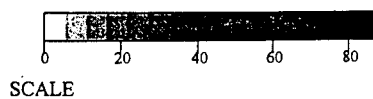


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow $\longrightarrow$

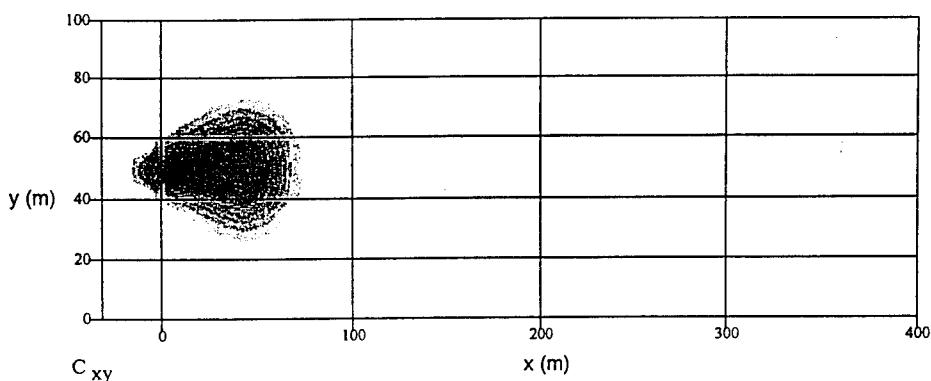


Figure 2. Top view of aquifer surface.

$$z_j := 10 \cdot \frac{j}{35}$$

$$y := 50$$

$$C_{xz,i,j} := -C(x_i, y, z_j, t)$$

direction of flow $\longrightarrow$

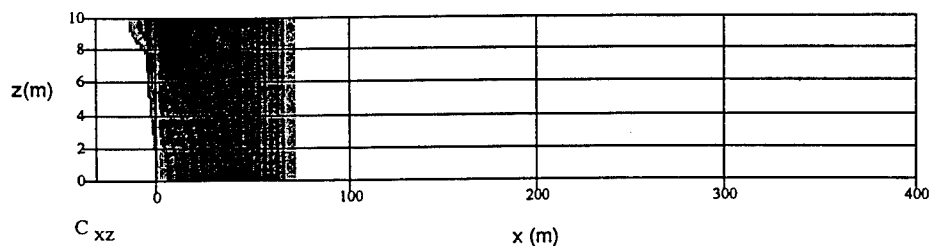


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 100$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 8.64 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

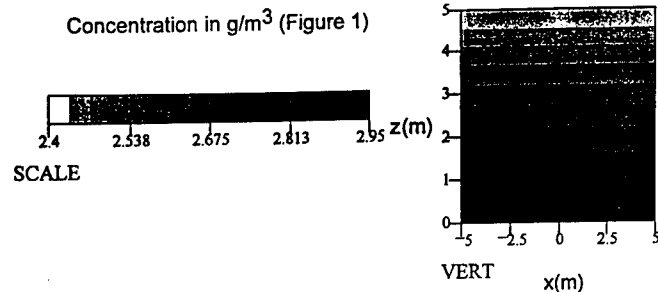


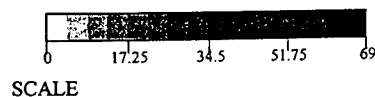
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

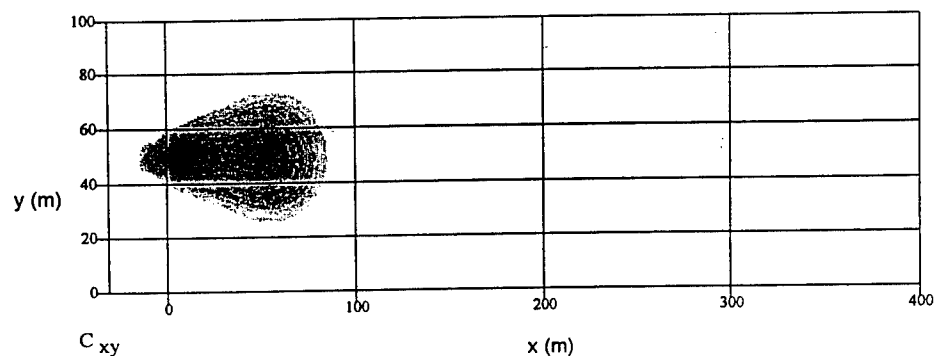


Figure 2. Top view of aquifer surface.

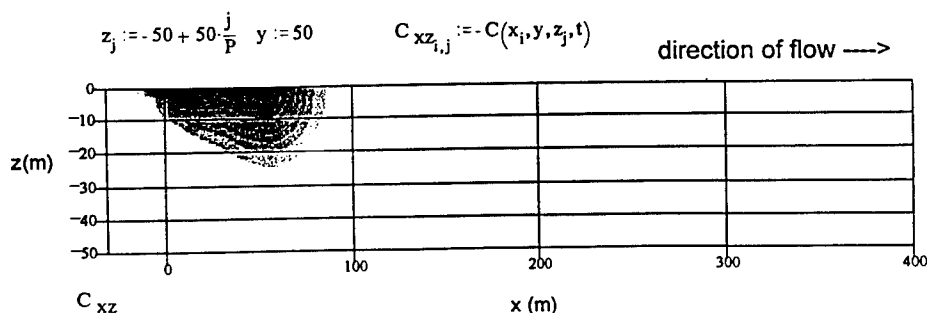


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 10 of 17)

$t_{\text{days}} := 125$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.08 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{I,i} := -C_v(z_i, t)$$

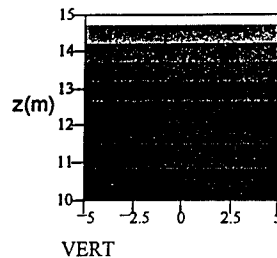
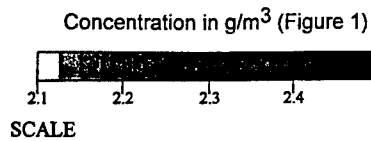
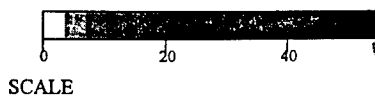


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow $\rightarrow$

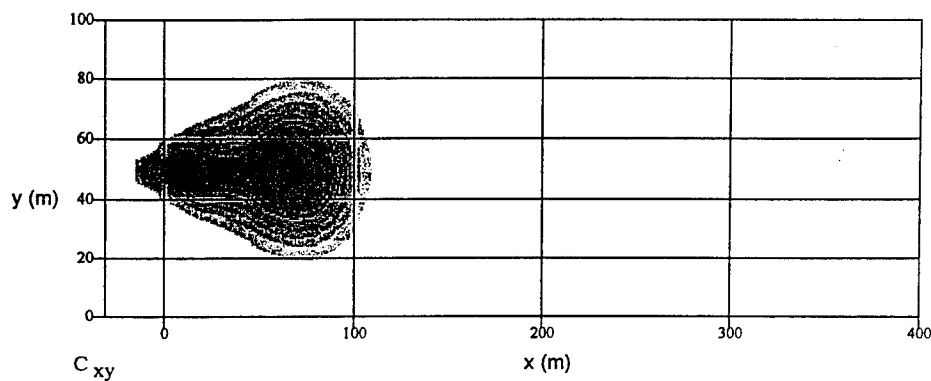


Figure 2. Top view of aquifer surface.

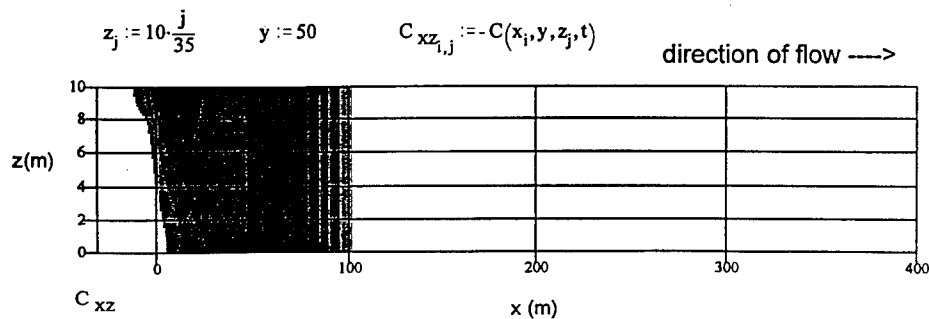


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 150$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.296 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

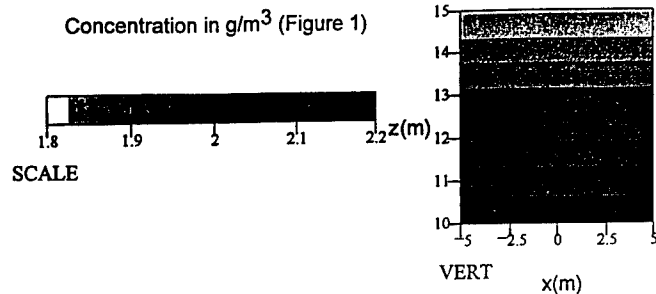
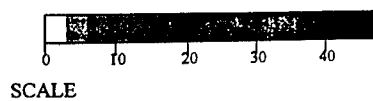


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 10$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

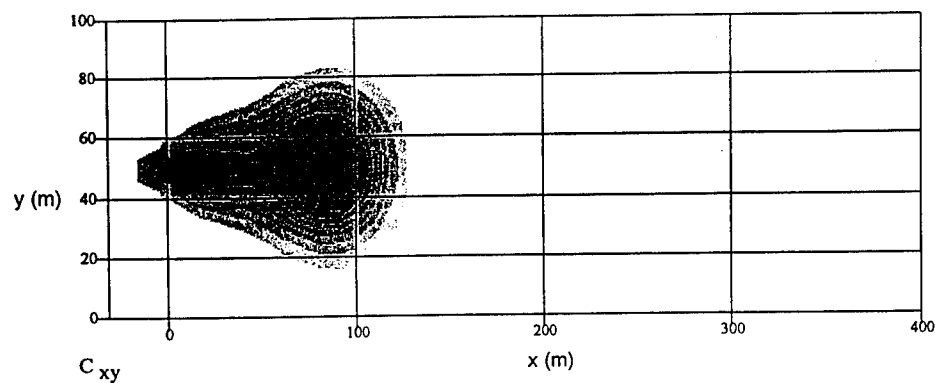


Figure 2. Top view of aquifer surface.

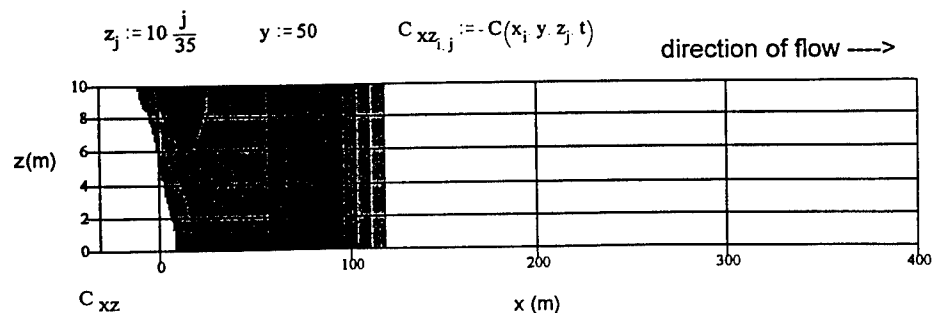


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 12 of 17)

$t_{\text{days}} := 200$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.728 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

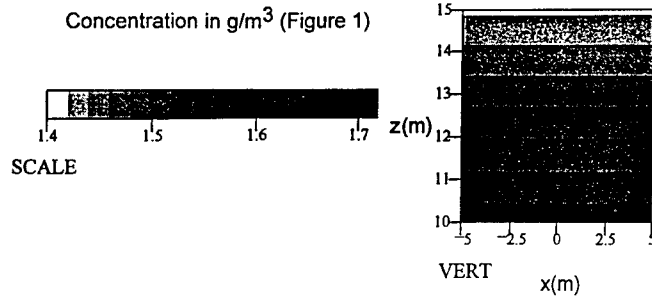


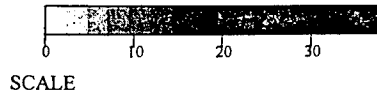
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow $\rightarrow$

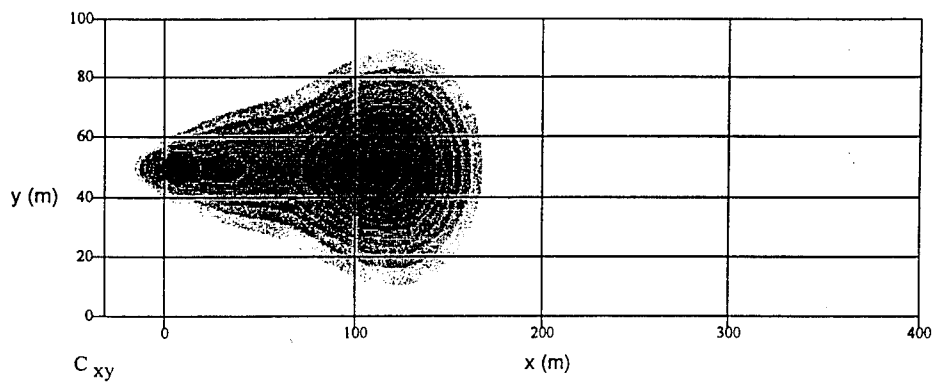


Figure 2. Top view of aquifer surface.

$$z_j := 10 \cdot \frac{j}{35}$$

$$y := 50$$

$$C_{xz_{i,j}} := -C(x_i, y, z_j, t)$$

direction of flow $\rightarrow$

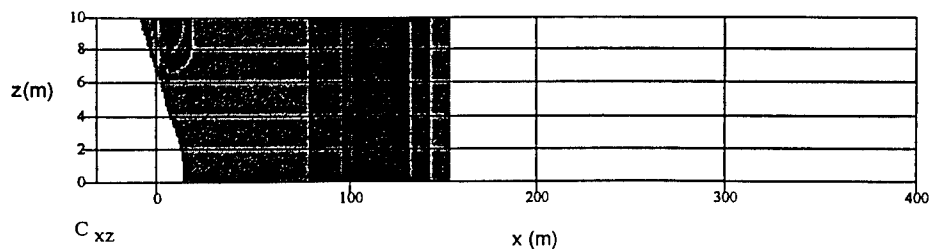


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 250$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.16 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

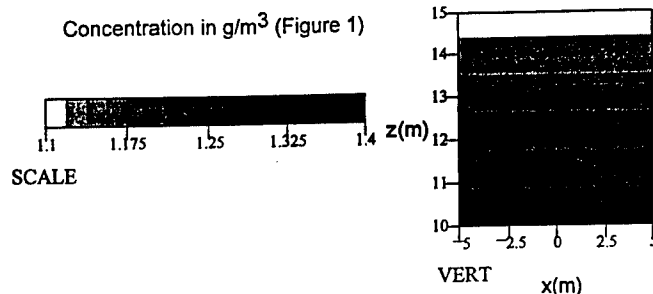


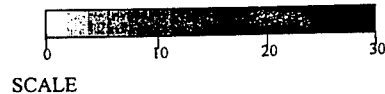
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$



$$C_{xy_{i,j}} := C(x_i, y_j, z, t)$$

direction of flow ---->

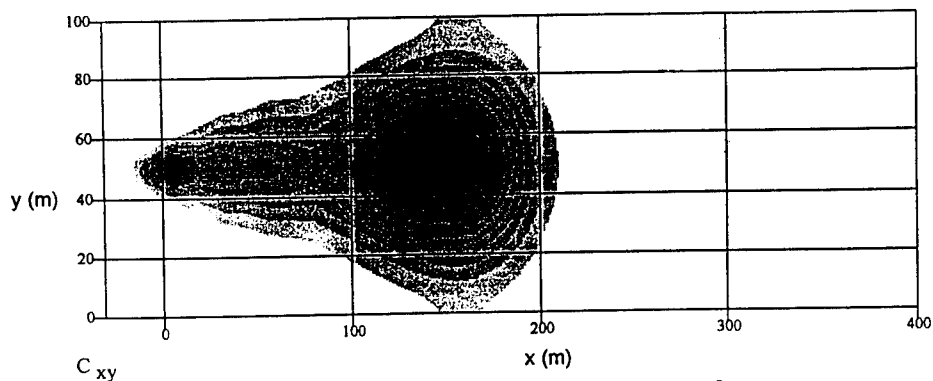


Figure 2. Top view of aquifer surface.

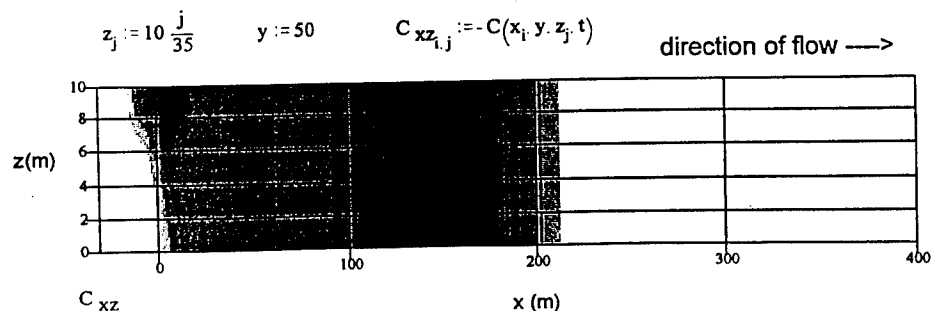


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 14 of 17)

$t_{\text{days}} := 300$ <- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.592 \cdot 10^7$ <- time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

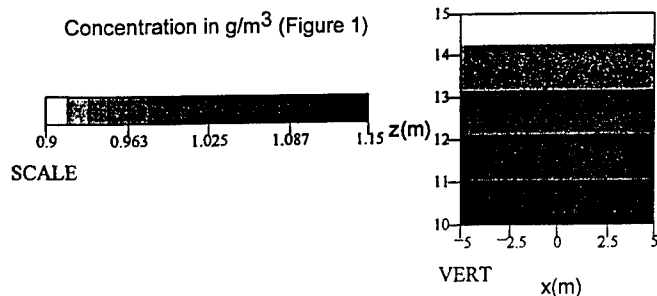


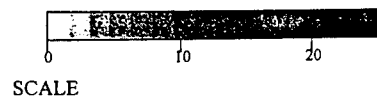
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

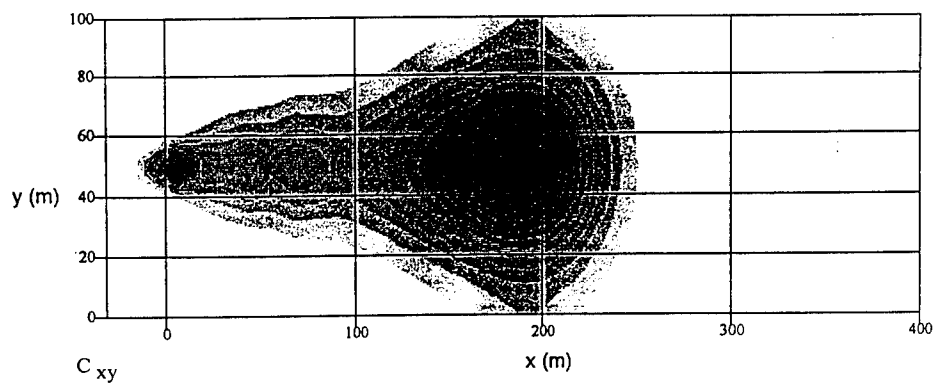


Figure 2. Top view of aquifer surface.

$$z_j := 10 \cdot \frac{j}{35}$$

$$y := 50$$

$$C_{xz_{i,j}} := -C(x_i, y, z_j, t)$$

direction of flow ---->

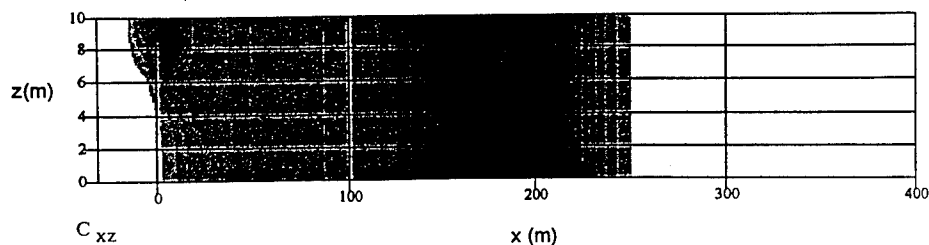


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 400$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 3.456 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

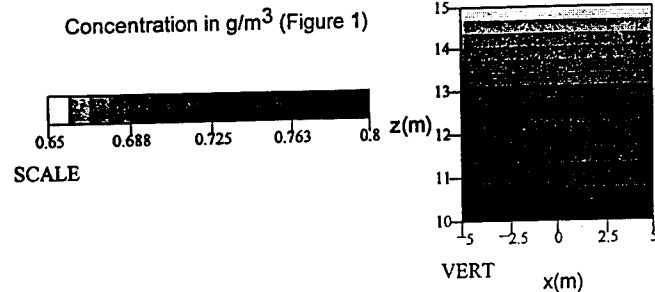


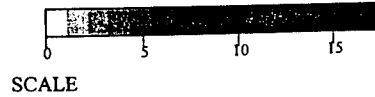
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow $\rightarrow$

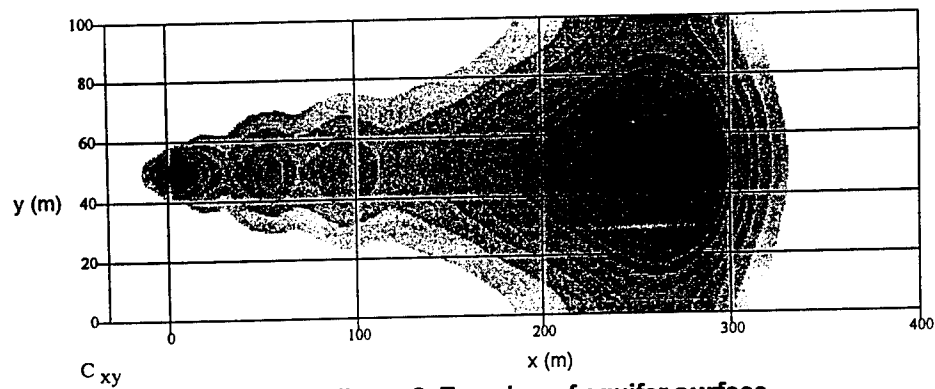


Figure 2. Top view of aquifer surface.

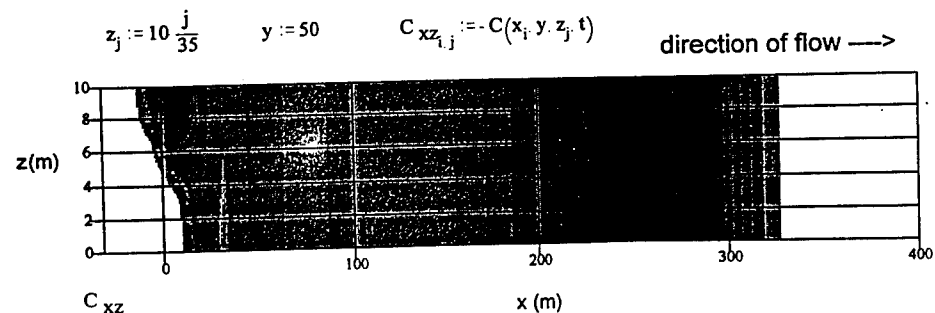


Figure 3. Side view of cut along the centerline of aquifer.

Example 1. (Sheet 16 of 17)

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$t_{\text{days}} := 500$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 4.32 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P} + H$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

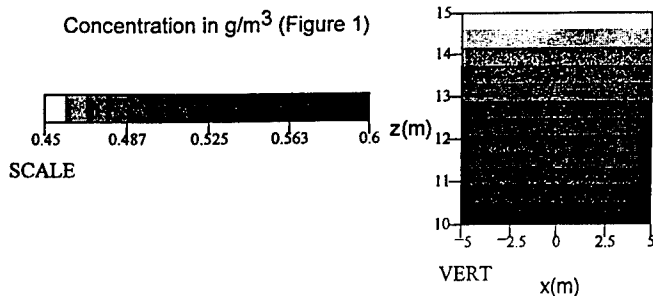
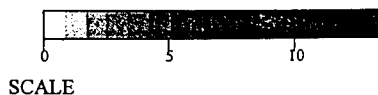


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 10$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

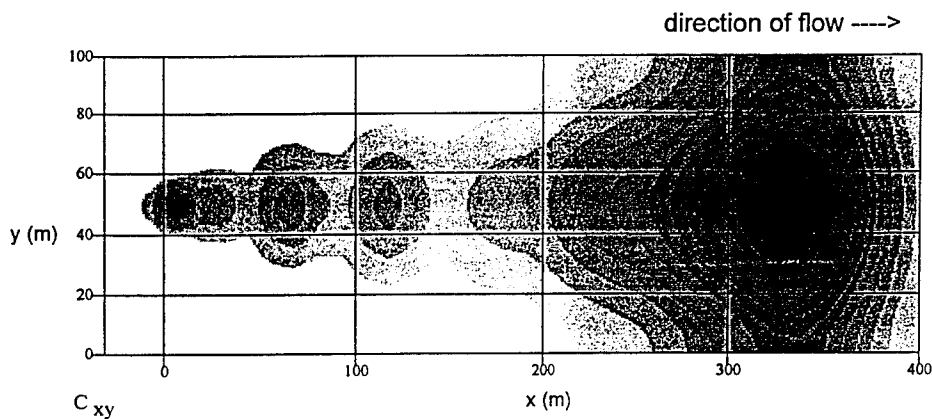


Figure 2. Top view of aquifer surface.

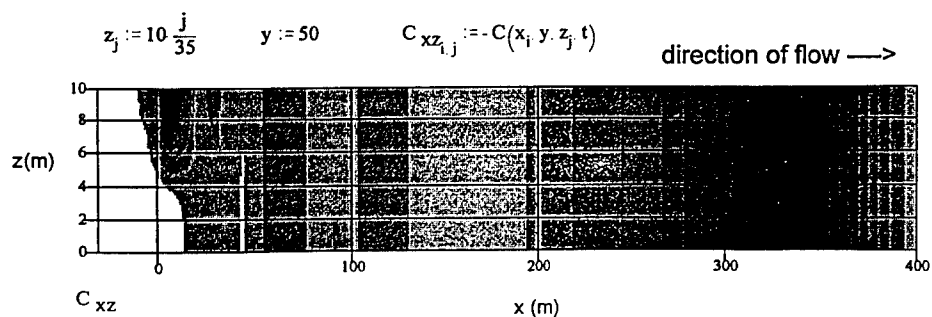


Figure 3. Side view of cut along the centerline of aquifer.

unbounded LP flow model
(standard conditions)

```

θ := 1      <--moisture content
K := 0      <--chemical transformation rate
R := 1      <--retardation factor
M := 10000  <--mass of the contaminant added

V := (-1·10-6) <--vertical velocity

Dx := 1·10-5  Dy := 1·10-5  Dz := 1·10-5  <--dispersion coefficients in the saturate
                                                    zone
Dz2 := 1·10-5  <--dispersion coefficients in the vadose
                                                    zone

x1 := -5      x2 := 5      <-- initial loading area boundaries
y1 := 45      y2 := 55

B := 5      <--depth of aquifer

U := 8·10-6  <--horizontal velocity

```

Example 2. A spill over an area when the water table is at the ground surface (unbound aquifer) (Sheet 1 of 17)

$$f_1(x,t,\tau) := \left[\operatorname{erf} \left[\frac{x_2 - x + \frac{U \cdot (t - \tau)}{R \cdot \theta}}{\sqrt{2 \cdot \left[\frac{2 \cdot D_x \cdot (t - \tau)}{R \cdot \theta} \right]}} \right] - \operatorname{erf} \left[\frac{x_1 - x + \frac{U \cdot (t - \tau)}{R \cdot \theta}}{\sqrt{2 \cdot \left[\frac{2 \cdot D_x \cdot (t - \tau)}{R \cdot \theta} \right]}} \right] \right]$$

$$f_2(y,t,\tau) := \left[\operatorname{erf} \left[\frac{y_2 - y}{\sqrt{2 \cdot \left[\frac{2 \cdot D_y \cdot (t - \tau)}{R \cdot \theta} \right]}} \right] - \operatorname{erf} \left[\frac{y_1 - y}{\sqrt{2 \cdot \left[\frac{2 \cdot D_y \cdot (t - \tau)}{R \cdot \theta} \right]}} \right] \right]$$

$$f_3(z,t,\tau) := \exp \left[-\frac{(z)^2}{2 \cdot \left[\frac{2 \cdot D_z \cdot (t - \tau)}{R \cdot \theta} \right]} - \frac{K \cdot (t - \tau)}{R \cdot \theta} \right] \quad F := \frac{M}{2^2 \cdot \pi^2}$$

$$C(x,y,z,t) := F \cdot \int_1^t \frac{V - \frac{R \cdot \theta}{2 \cdot \tau} \cdot \left(B + \frac{V \cdot \tau}{R \cdot \theta} \right)}{\left(\frac{4 \cdot \pi \cdot D_z \cdot \tau}{R \cdot \theta} \right)^{\frac{1}{2}} \cdot \left[\frac{2 \cdot D_z \cdot (t - \tau)}{R \cdot \theta} \right]^{\frac{1}{2}}} \cdot \exp \left[-\frac{\left(B + \frac{V \cdot \tau}{R \cdot \theta} \right)^2 \cdot R \cdot \theta}{4 \cdot D_z \cdot \tau} - \frac{K \cdot \tau}{R \cdot \theta} \right] \cdot f_3(z,t,\tau) \cdot f_1(x,t,\tau) \cdot f_2(y,t,\tau) \, d\tau$$

$$z_1 := B$$

$$C_v(z,t) := \frac{M}{\sqrt{\frac{4 \cdot \pi \cdot D_z \cdot t}{R \cdot \theta}} \cdot (x_2 - x_1) \cdot (y_2 - y_1)} \cdot \exp \left[-\frac{\left(z - z_1 - \frac{V \cdot t}{R \cdot \theta} \right)^2}{\left(\frac{4 \cdot D_z \cdot t}{R \cdot \theta} \right)} - \frac{K \cdot t}{R \cdot \theta} \right]$$

$$P := 35$$

$$i := 0..P \quad j := 0..P$$

$$\text{SCALE} := \begin{bmatrix} 1 & 1 \\ 2 & 2 \\ 3 & 3 \\ 4 & 4 \\ 5 & 5 \\ 6 & 6 \\ 7 & 7 \\ 8 & 8 \\ 9 & 9 \end{bmatrix}$$

Example 2. (Sheet 2 of 17)

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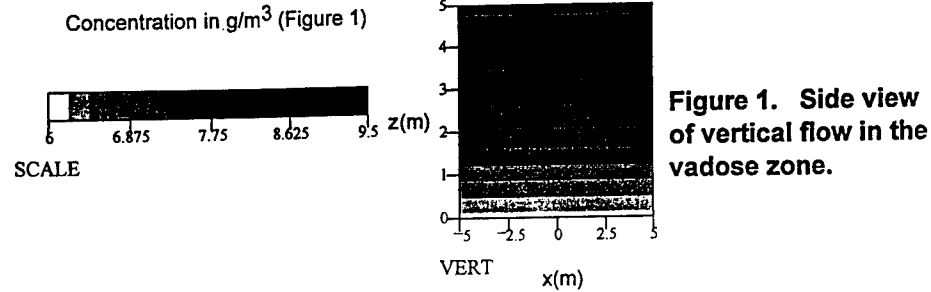
Section IV Appendix B Examples of LP Plume Migration

$$t_{\text{days}} := 10 \quad \leftarrow \text{time (days)} \quad t := 3600 \cdot 24 \cdot t_{\text{days}} \quad t = 8.64 \cdot 10^5 \quad \leftarrow \text{time (seconds)}$$

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

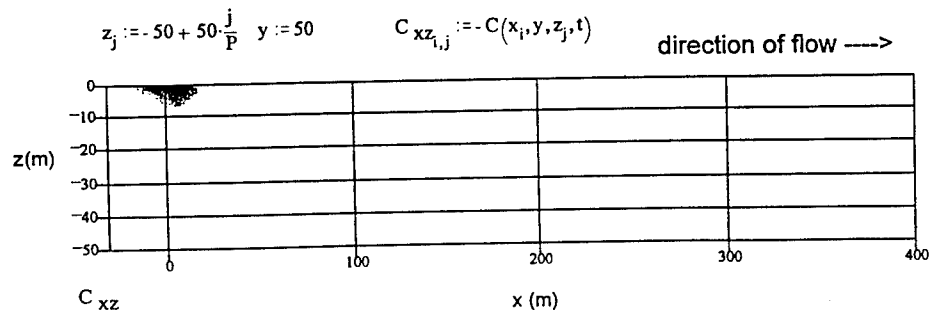
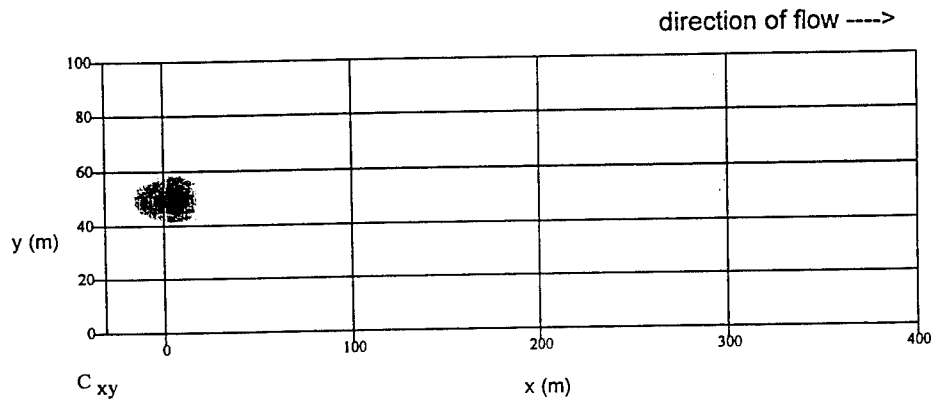
$$\text{VERT}_{1,i} := -C_v(z_i, t)$$



Concentration in g/m³ (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 0$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$



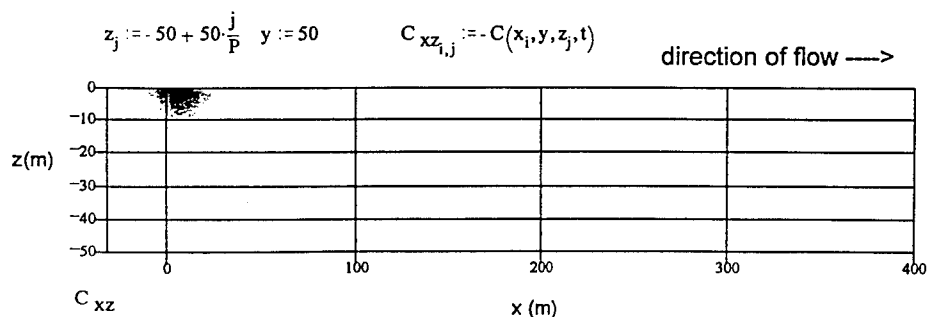
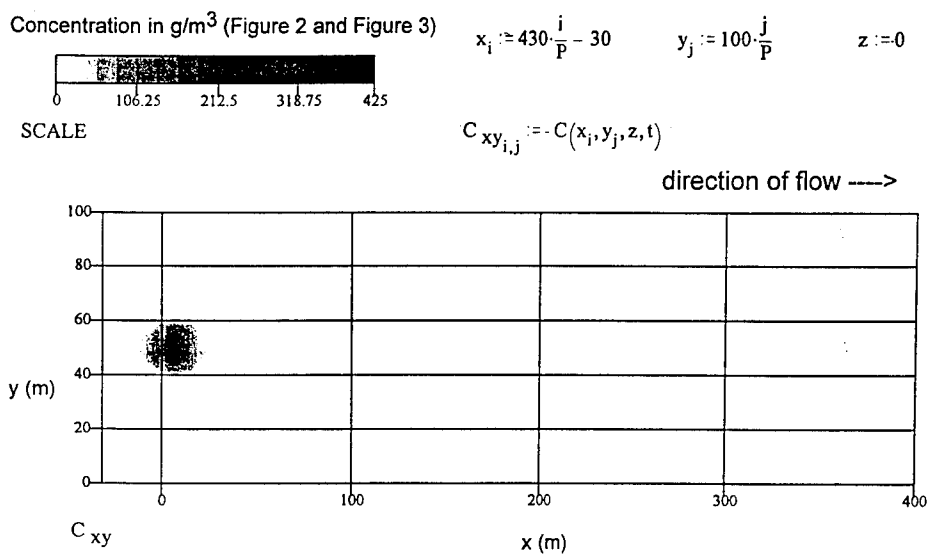
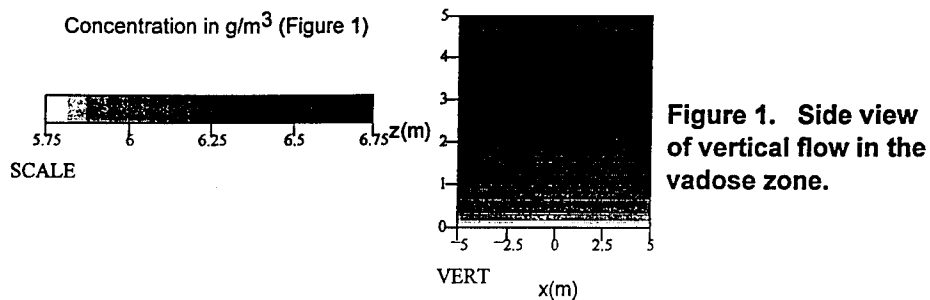
Example 2. (Sheet 3 of 17)

$t_{\text{days}} := 20$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.728 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$



$t_{\text{days}} := 30$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.592 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

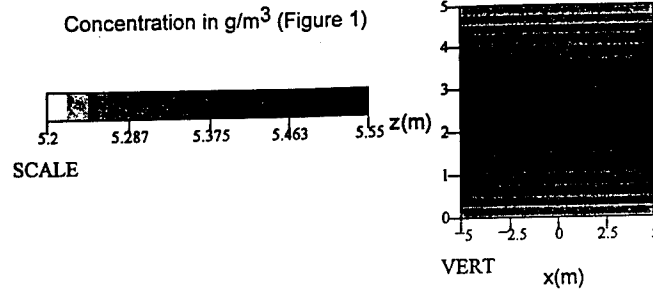


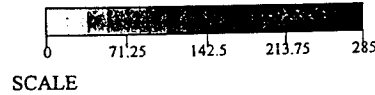
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m³ (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

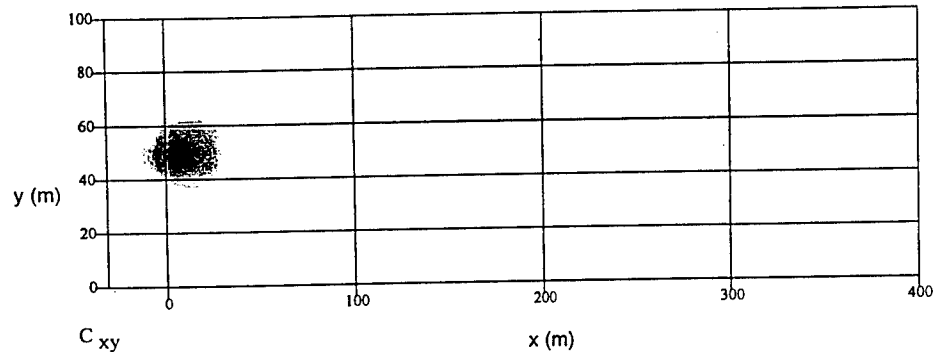


Figure 2. Top view of aquifer surface.

$$z_j := -50 + 50 \cdot \frac{j}{P} \quad y := 50$$

$$C_{xz_{i,j}} := -C(x_i, y, z_j, t)$$

direction of flow ---->

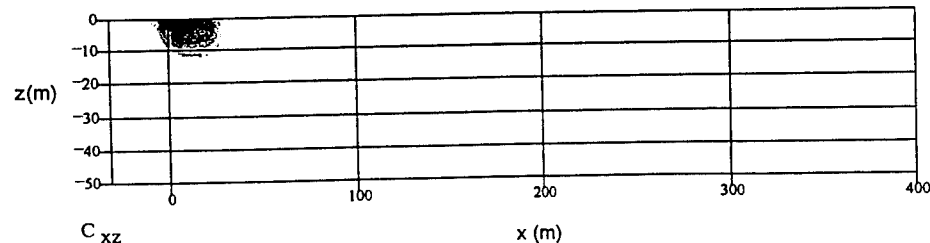


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 5 of 17)

$t_{\text{days}} := 40$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 3.456 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

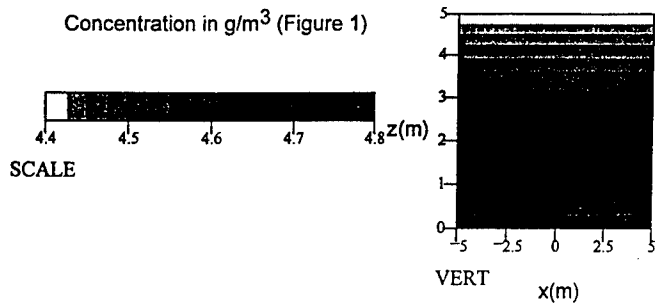
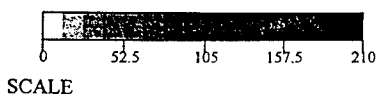


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

$$C_{xy,i,j} := C(x_i, y_j, z, t)$$

direction of flow ---->

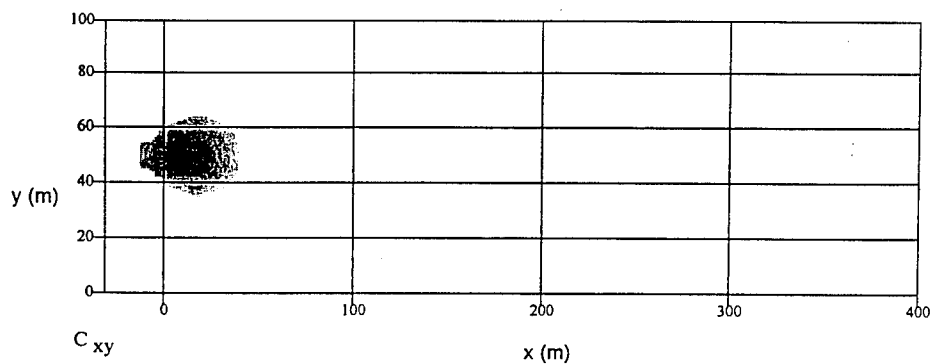


Figure 2. Top view of aquifer surface.

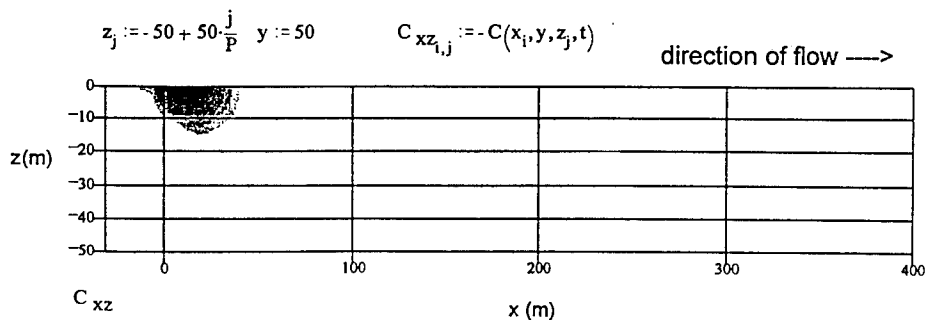


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 50$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 4.32 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

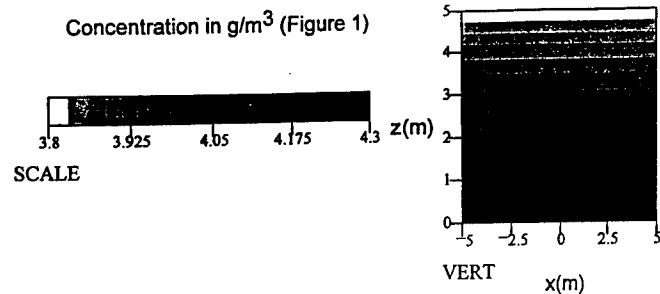


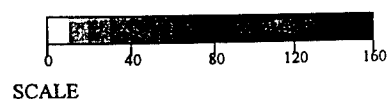
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

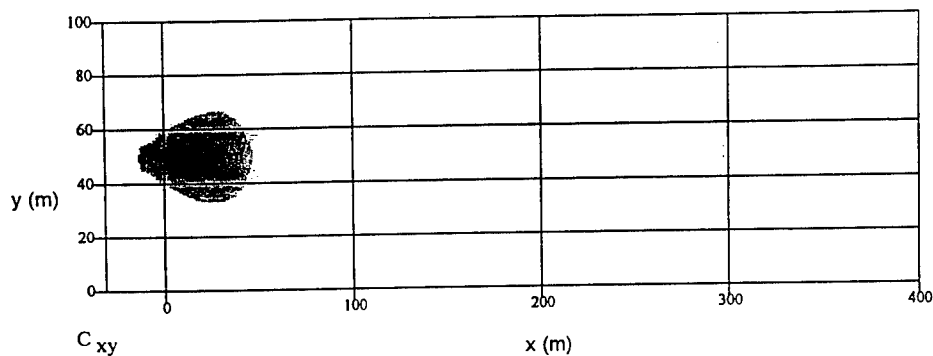


Figure 2. Top view of aquifer surface.

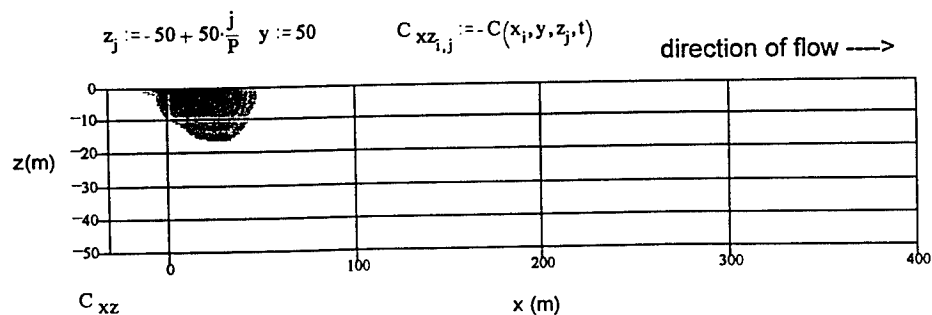


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 7 of 17)

$t_{\text{days}} := 60$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 5.184 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

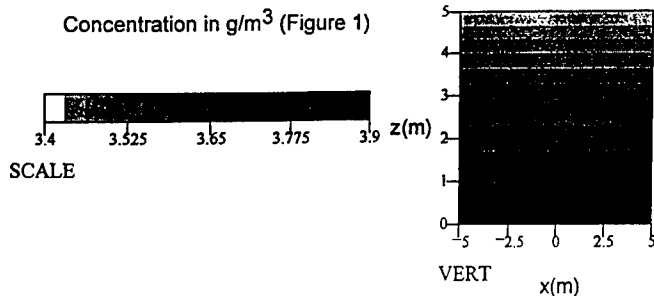


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

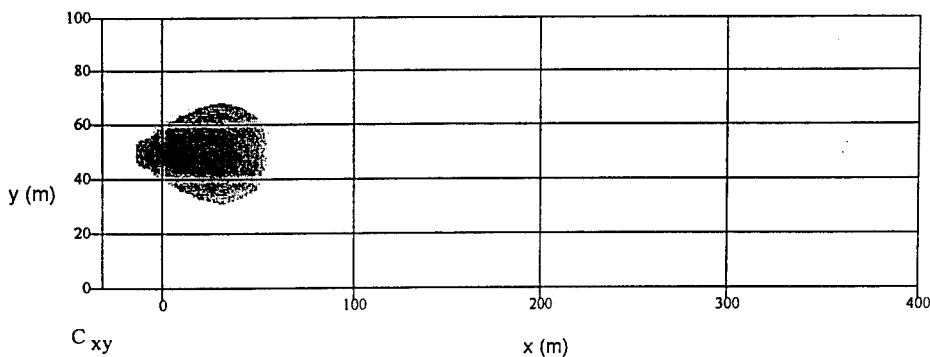
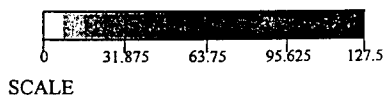


Figure 2. Top view of aquifer surface.

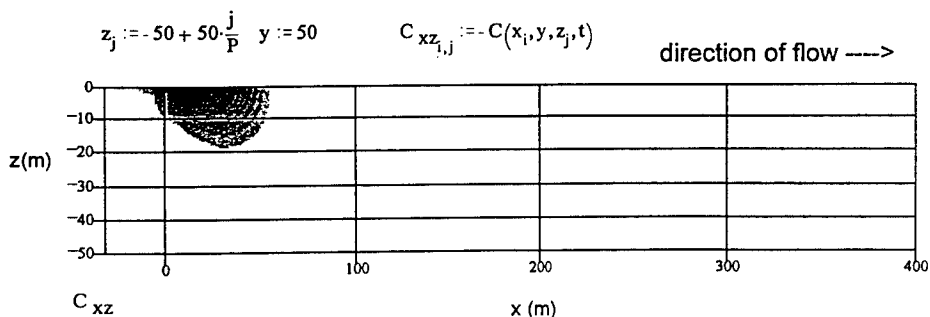


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 80$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 6.912 \cdot 10^6$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

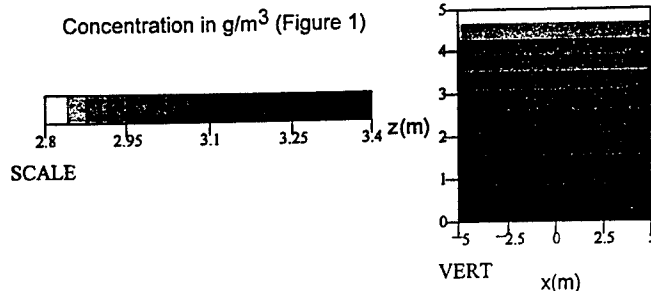
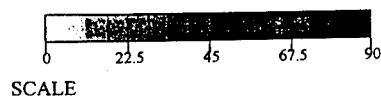


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 0$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow $\rightarrow$

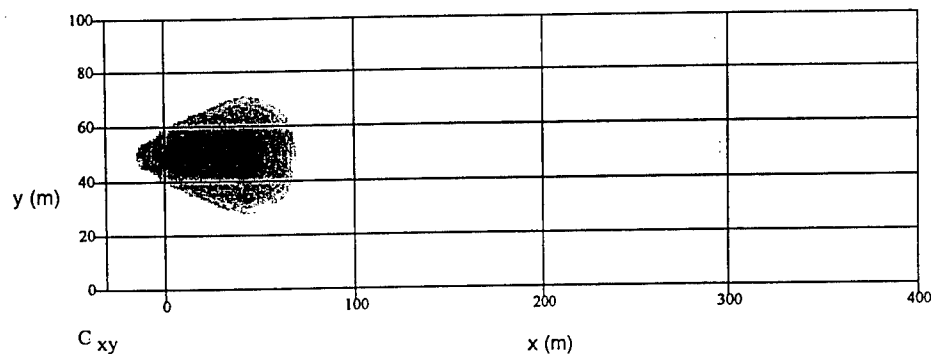


Figure 2. Top view of aquifer surface.

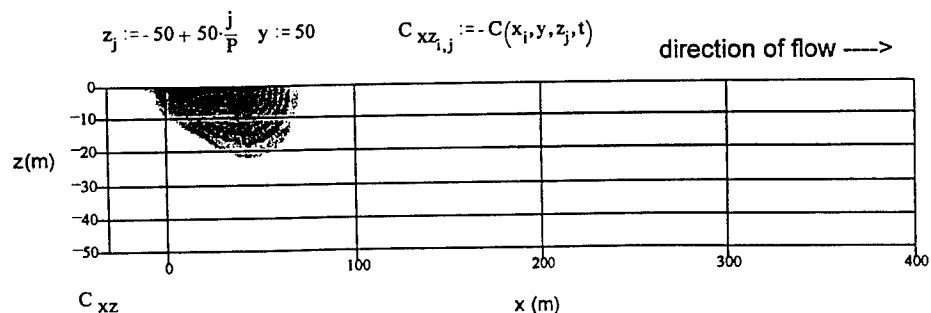


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 9 of 17)

$t_{\text{days}} := 100$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 8.64 \cdot 10^6$ <-- time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

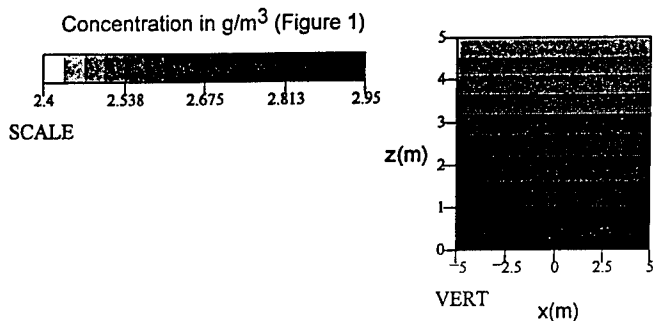
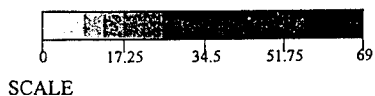


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

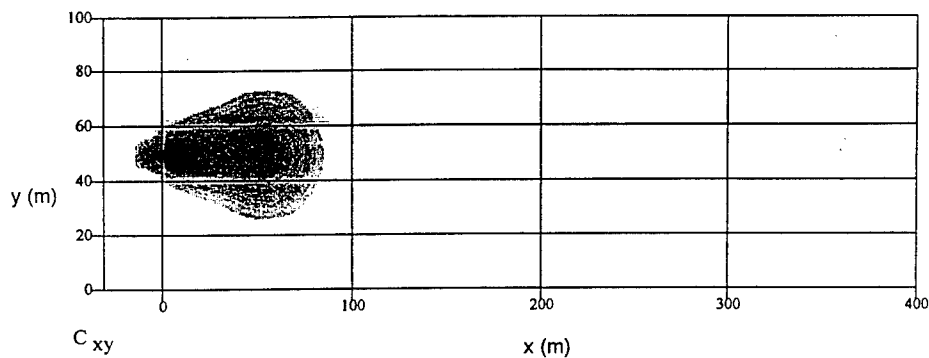


Figure 2. Top view of aquifer surface.

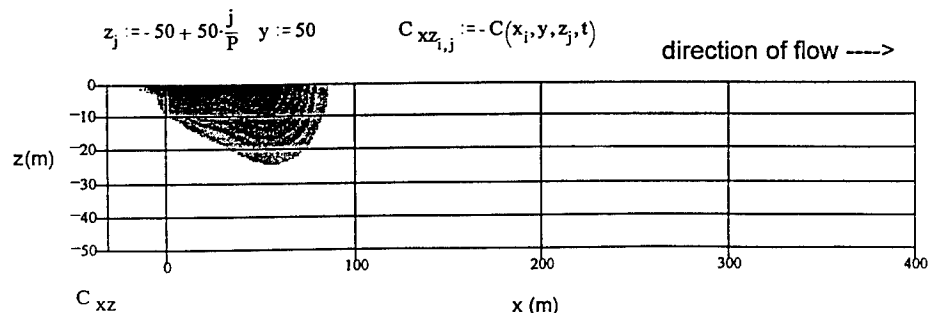


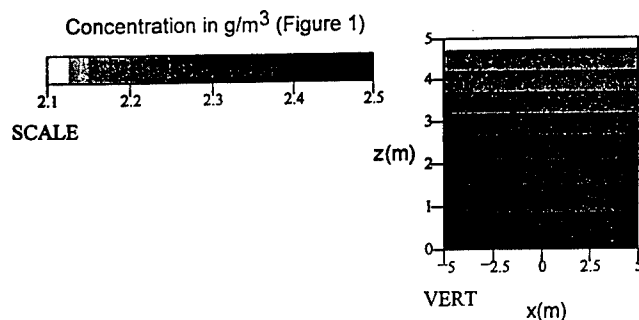
Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 125$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.08 \cdot 10^7$ <-- time (seconds)

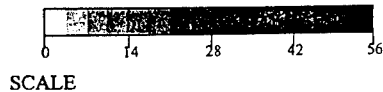
$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$



Concentration in g/m³ (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

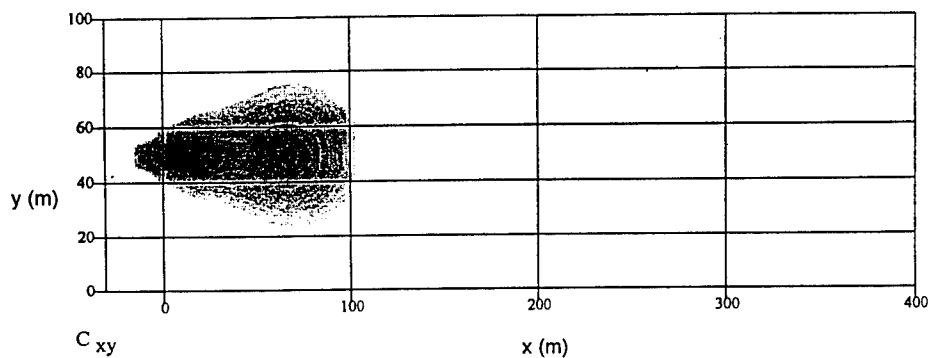


Figure 2. Top view of aquifer surface.

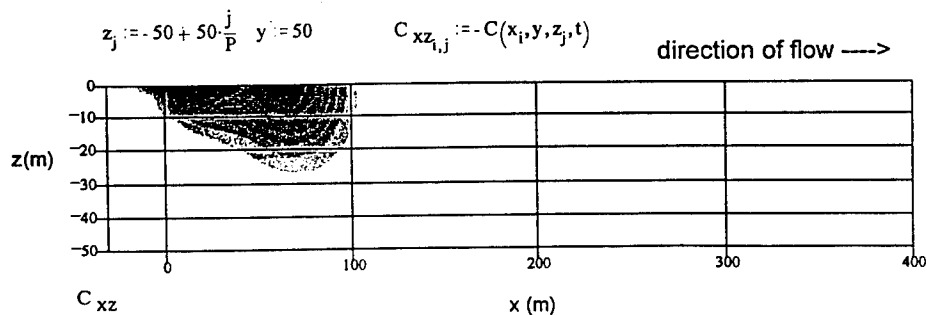


Figure 3. Side view of cut along the centerline of aquifer.

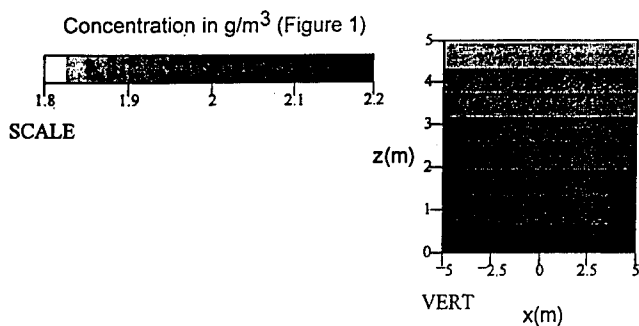
Example 2. (Sheet 11 of 17)

$t_{\text{days}} := 150$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.296 \cdot 10^7$ $\leftarrow$ time (seconds)

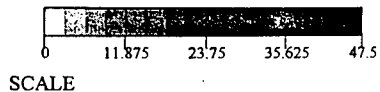
$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$



Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow $\longrightarrow$

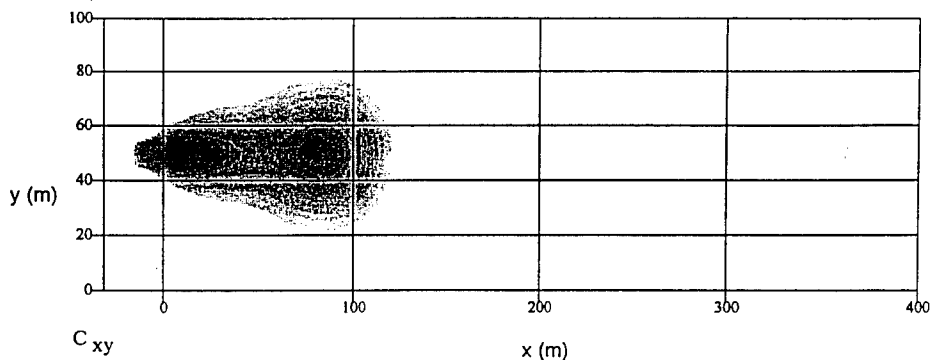


Figure 2. Top view of aquifer surface.

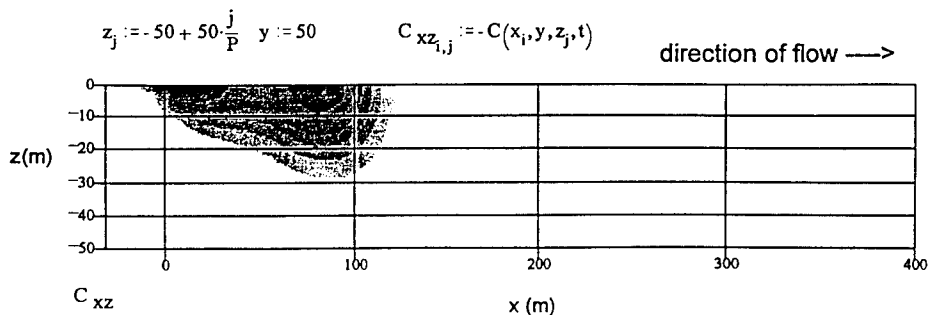


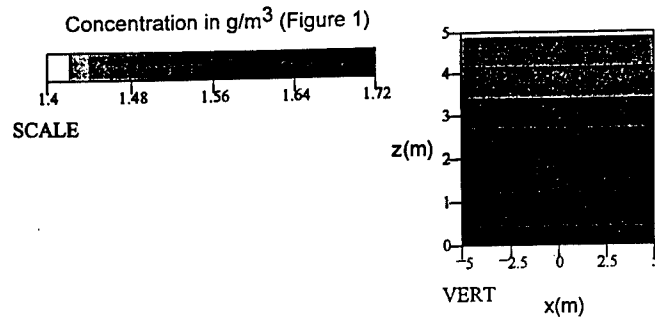
Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 200$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 1.728 \cdot 10^7$ <-- time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

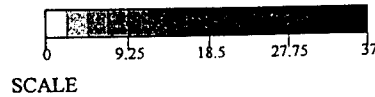
$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$



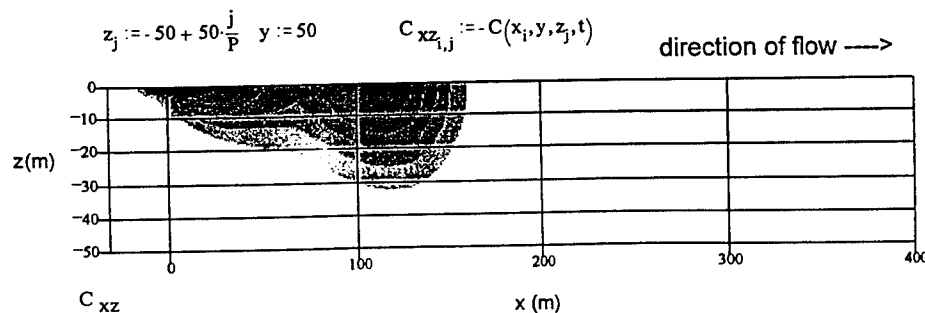
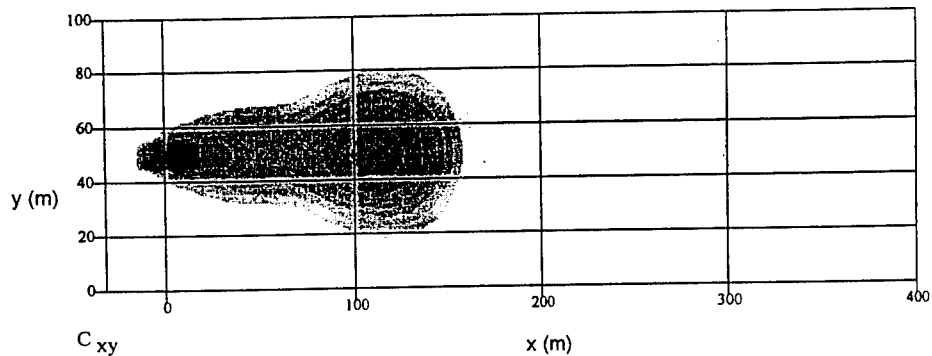
Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 0$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->



Example 2. (Sheet 13 of 17)

$t_{\text{days}} := 250$ <-- time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.16 \cdot 10^7$ <-- time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

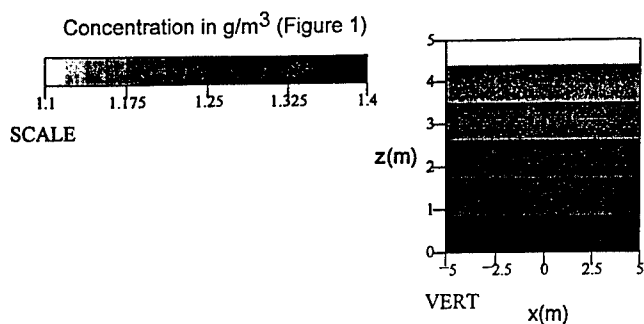


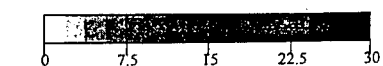
Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$



$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow ---->

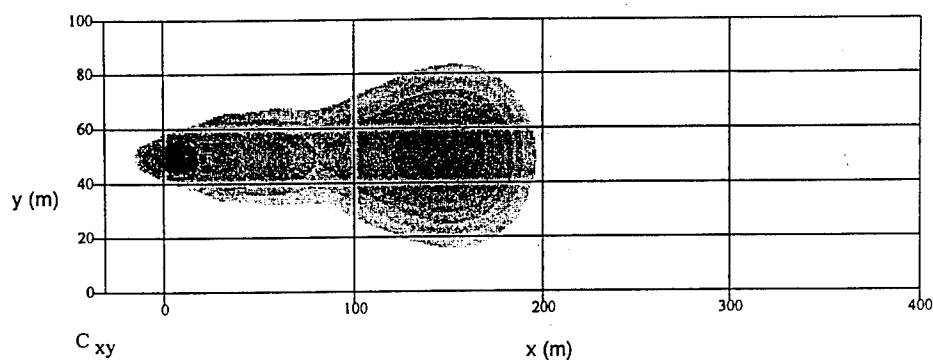


Figure 2. Top view of aquifer surface.

$$z_j := -50 + 50 \cdot \frac{j}{P} \quad y := 50$$

$$C_{xz,i,j} := -C(x_i, y, z_j, t)$$

direction of flow ---->

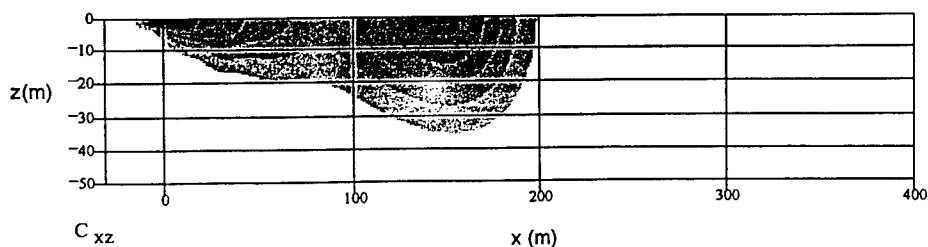


Figure 3. Side view of cut along the centerline of aquifer.

$t_{\text{days}} := 300$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 2.592 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

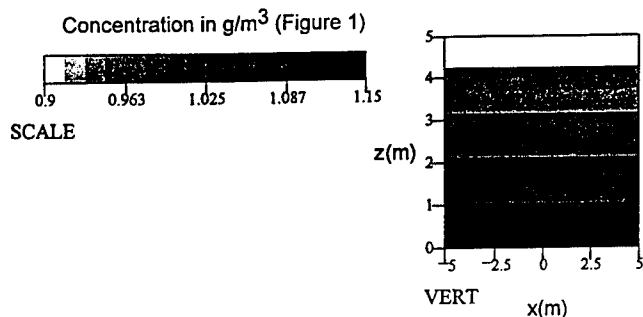
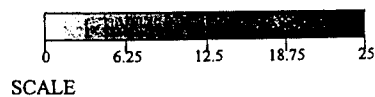


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)

$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 0$$



$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

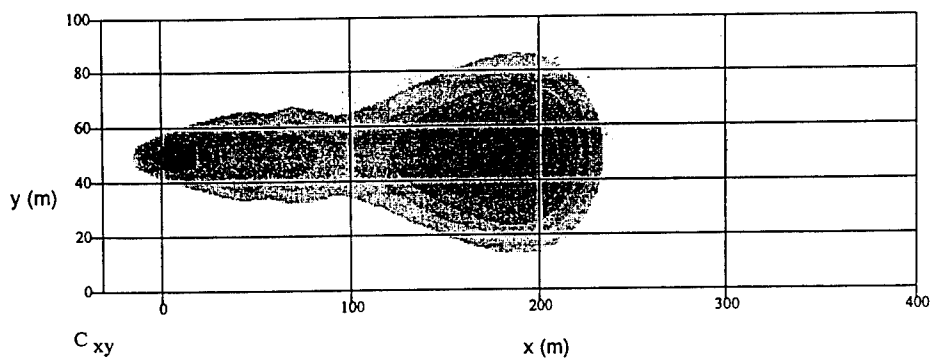


Figure 2. Top view of aquifer surface.

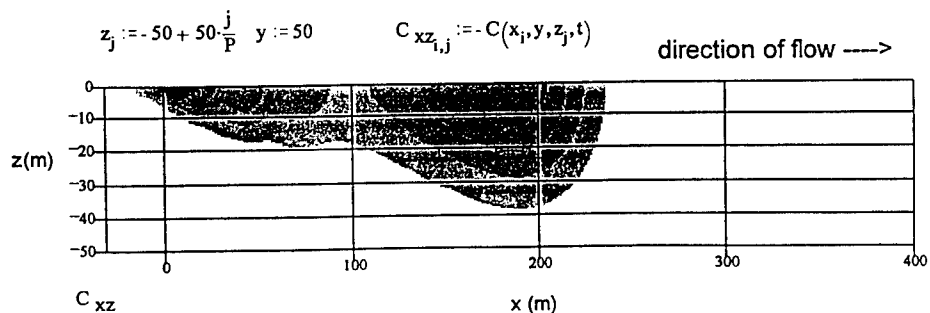


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 15 of 17)

$t_{\text{days}} := 400$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 3.456 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

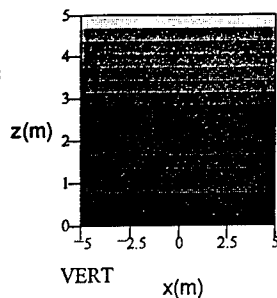
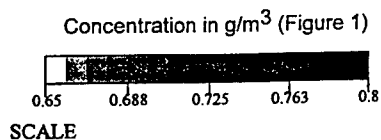
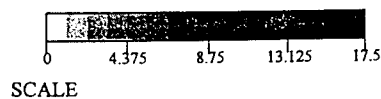


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30$$

$$y_j := 100 \cdot \frac{j}{P}$$

$$z := 0$$

$$C_{xy_{i,j}} := -C(x_i, y_j, z, t)$$

direction of flow ---->

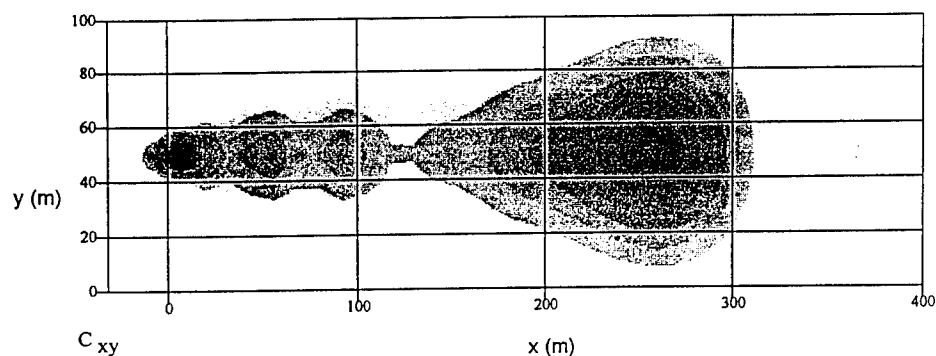


Figure 2. Top view of aquifer surface.

$$z_j := -50 + 50 \cdot \frac{j}{P} \quad y := 50$$

$$C_{xz_{i,j}} := -C(x_i, y, z_j, t)$$

direction of flow ---->

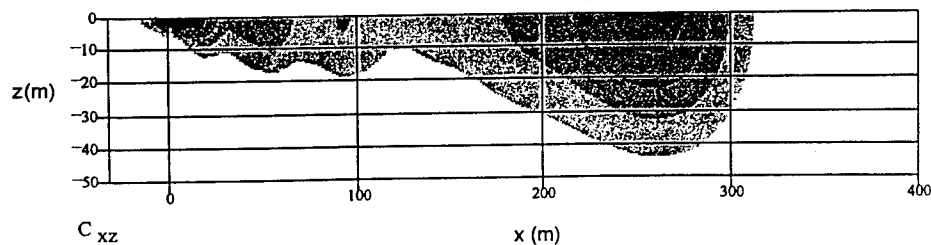


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 16 of 17)

$t_{\text{days}} := 500$ $\leftarrow$ time (days) $t := 3600 \cdot 24 \cdot t_{\text{days}}$ $t = 4.32 \cdot 10^7$ $\leftarrow$ time (seconds)

$$z_i := B \cdot \frac{i}{P}$$

$$\text{VERT}_{0,i} := -C_v(z_i, t)$$

$$\text{VERT}_{1,i} := -C_v(z_i, t)$$

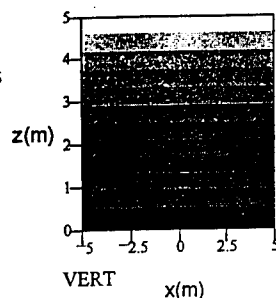
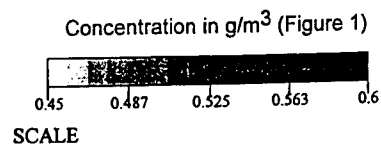
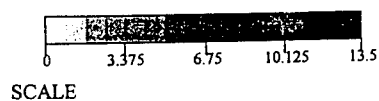


Figure 1. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure 2 and Figure 3)



$$x_i := 430 \cdot \frac{i}{P} - 30 \quad y_j := 100 \cdot \frac{j}{P} \quad z := 0$$

$$C_{xy,i,j} := -C(x_i, y_j, z, t)$$

direction of flow $\longrightarrow$

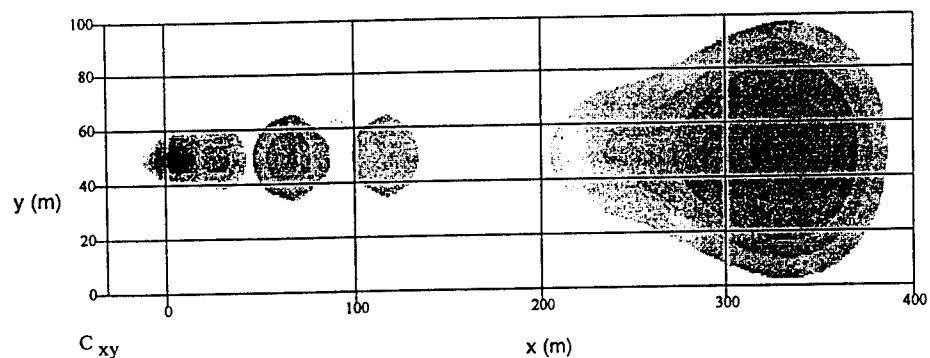


Figure 2. Top view of aquifer surface.

$$z_j := -50 + 50 \cdot \frac{j}{P} \quad y := 50$$

$$C_{xz,i,j} := -C(x_i, y, z_j, t)$$

direction of flow $\longrightarrow$

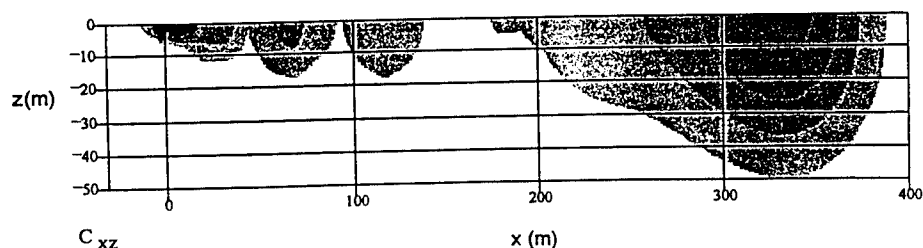


Figure 3. Side view of cut along the centerline of aquifer.

Example 2. (Sheet 17 of 17)

Bounded LP flow model
(standard conditions)

$\theta = .35$ <--moisture content
 $K = 0$ <--chemical transformation rate
 $R = 1$ <--retardation factor
 $M = 10000$ <--mass of the contaminant added
 $V = (-1 \cdot 10^{-6})$ <--vertical velocity

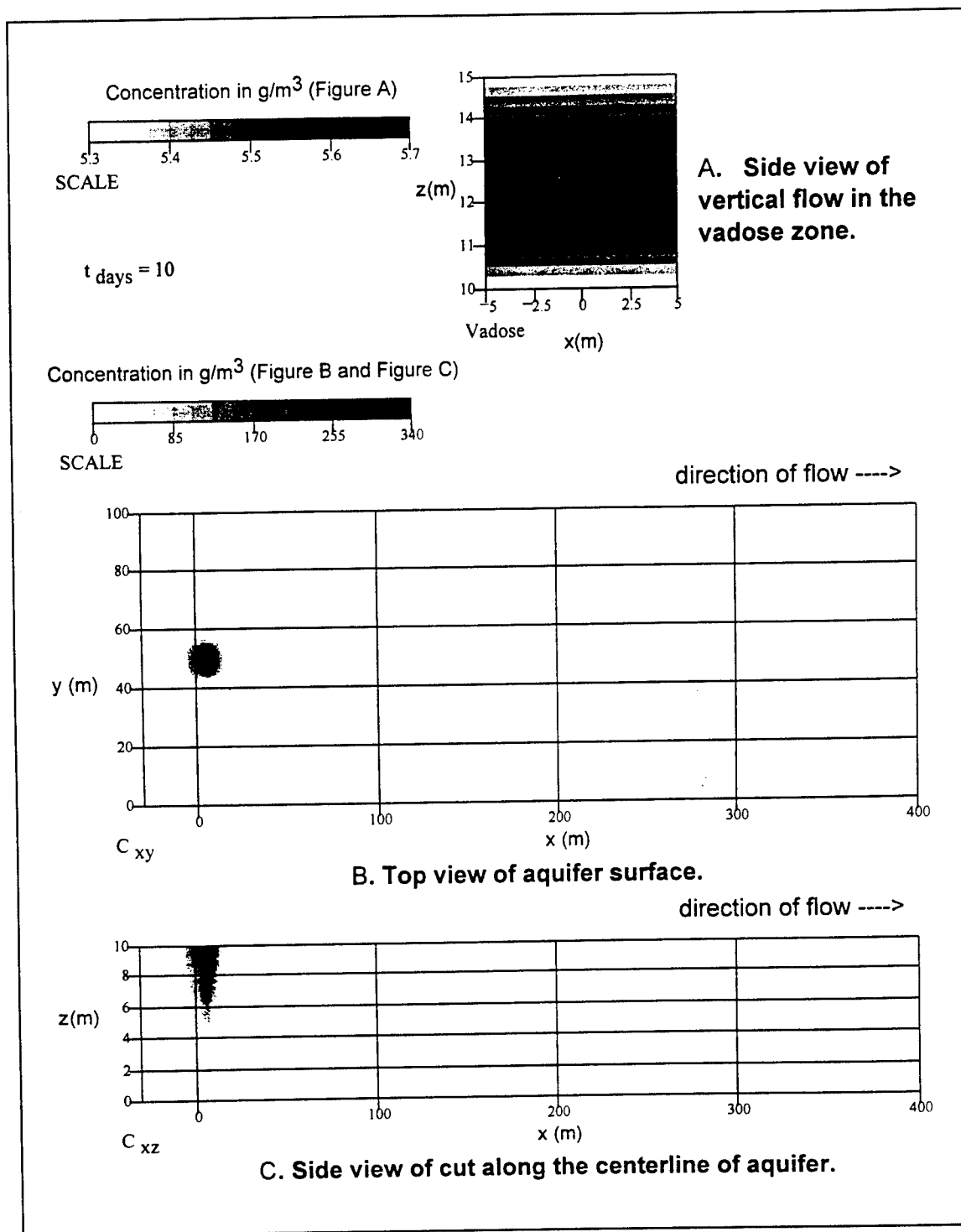
 $D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$
 $D_{zz} = 1 \cdot 10^{-5}$ <--dispersion coefficients

 $x_1 = -5$ $x_2 = 5$
 $y_1 = 45$ $y_2 = 55$ <-- initial loading area boundaries

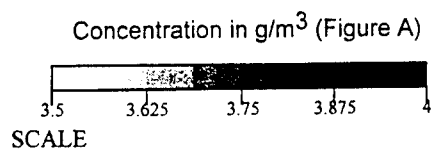
 $W = 100$ <--aquifer dimensions
 $H = 10$
 $N_{\max} = 100$ <--number of summation steps
 $m_{\max} = 100$
 $B = 5$ <--depth of aquifer

 $U = 8 \cdot 10^{-6}$ <--horizontal velocity

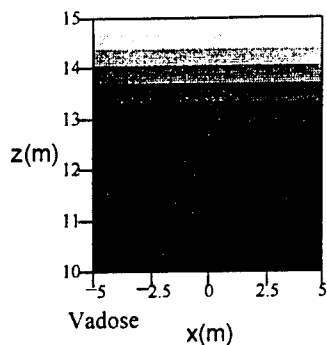
Example 3. Bound LP flow model (standard conditions) (Sheet 1 of 6)



Example 3. (Sheet 2 of 6)

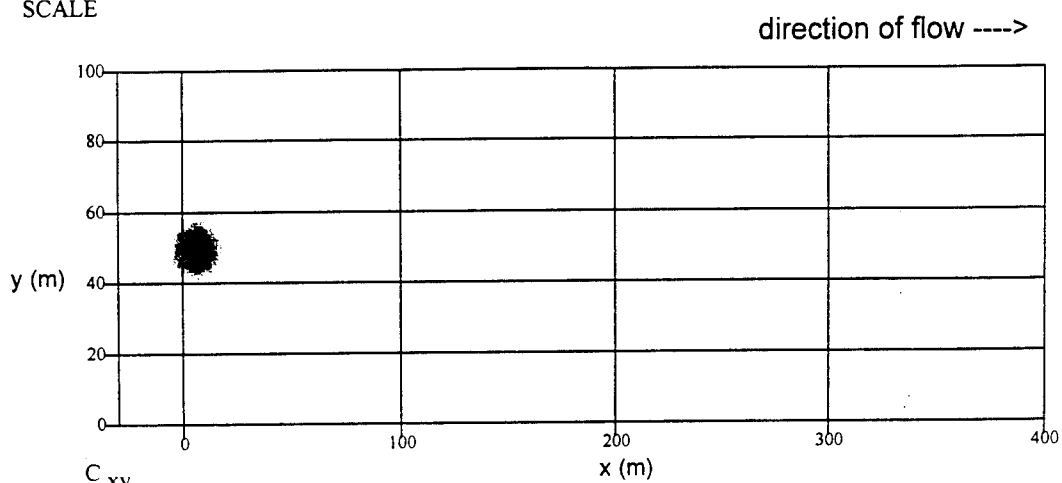
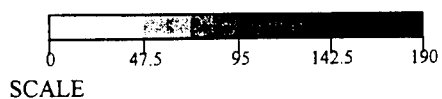


$t_{\text{days}} = 20$

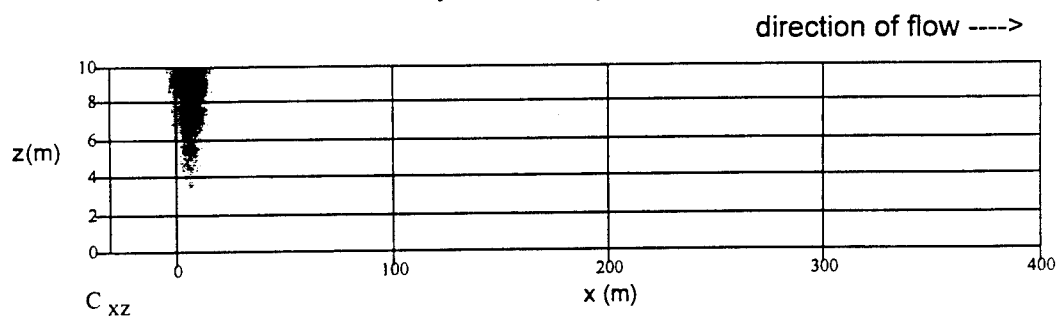


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

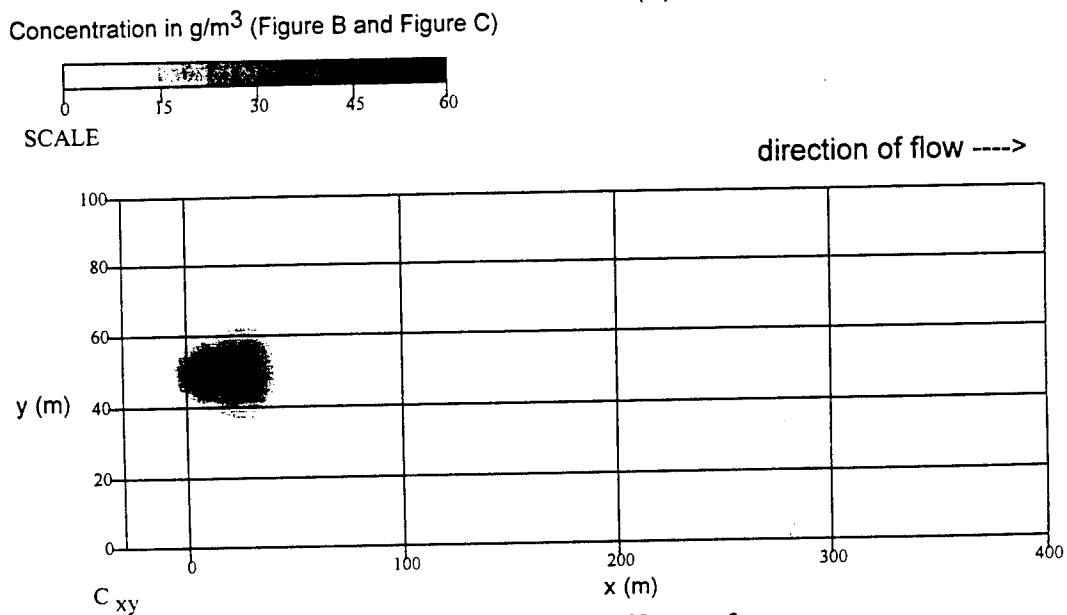
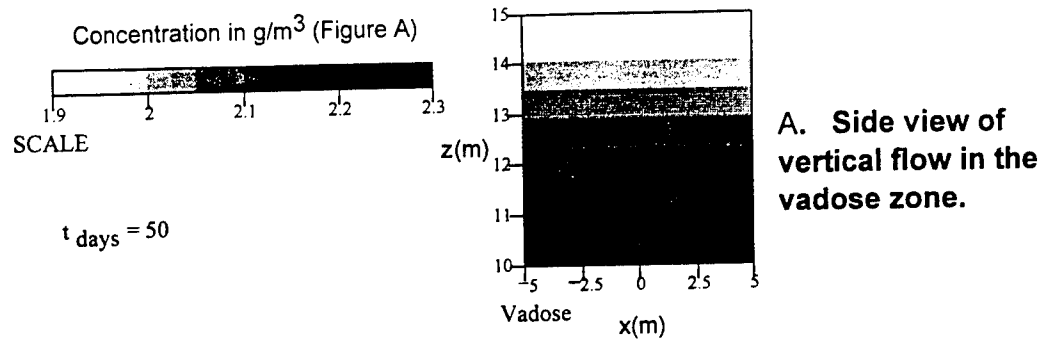


B. Top view of aquifer surface.

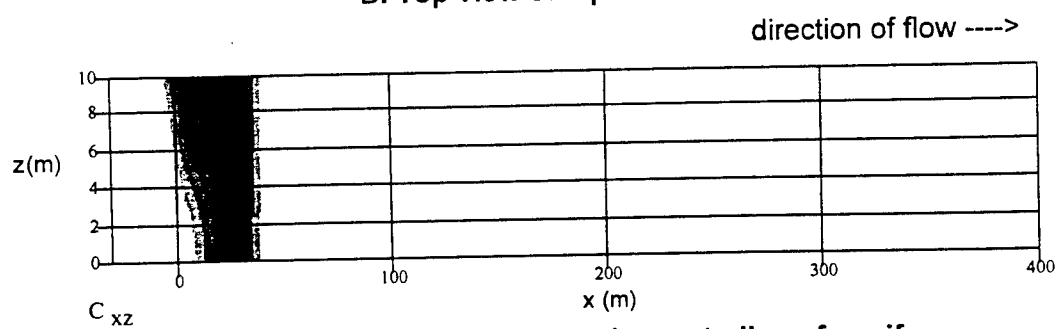


C. Side view of cut along the centerline of aquifer.

Example 3. (Sheet 3 of 6)

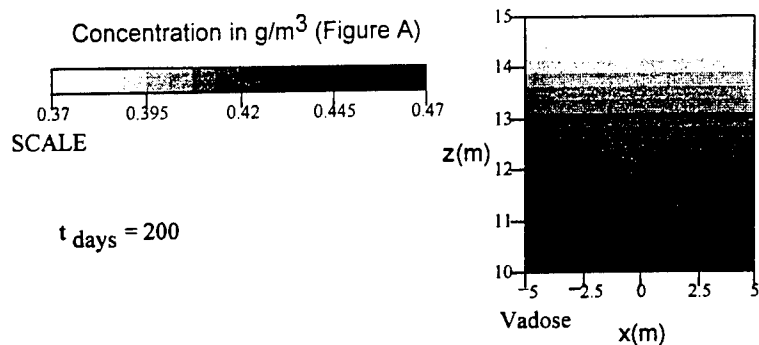


B. Top view of aquifer surface.



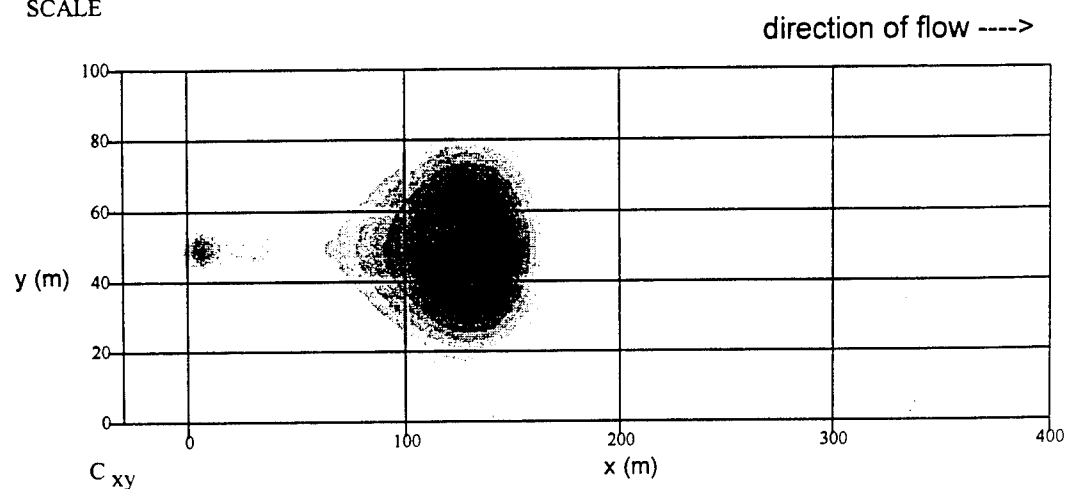
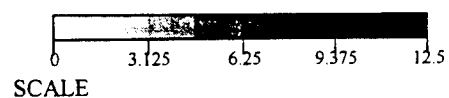
C. Side view of cut along the centerline of aquifer.

Example 3. (Sheet 4 of 6)

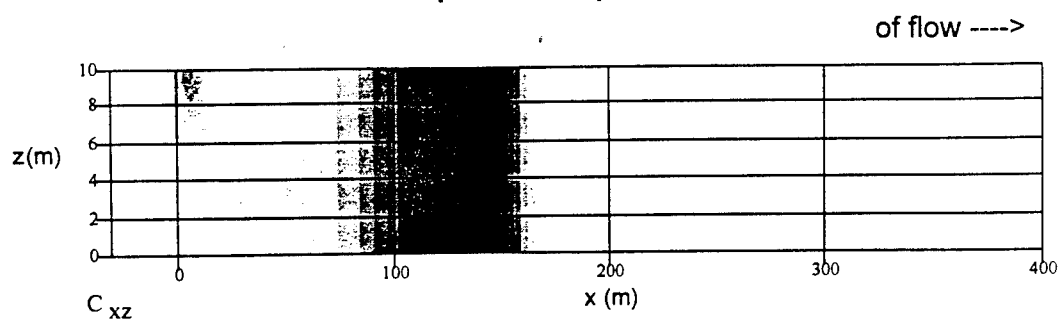


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

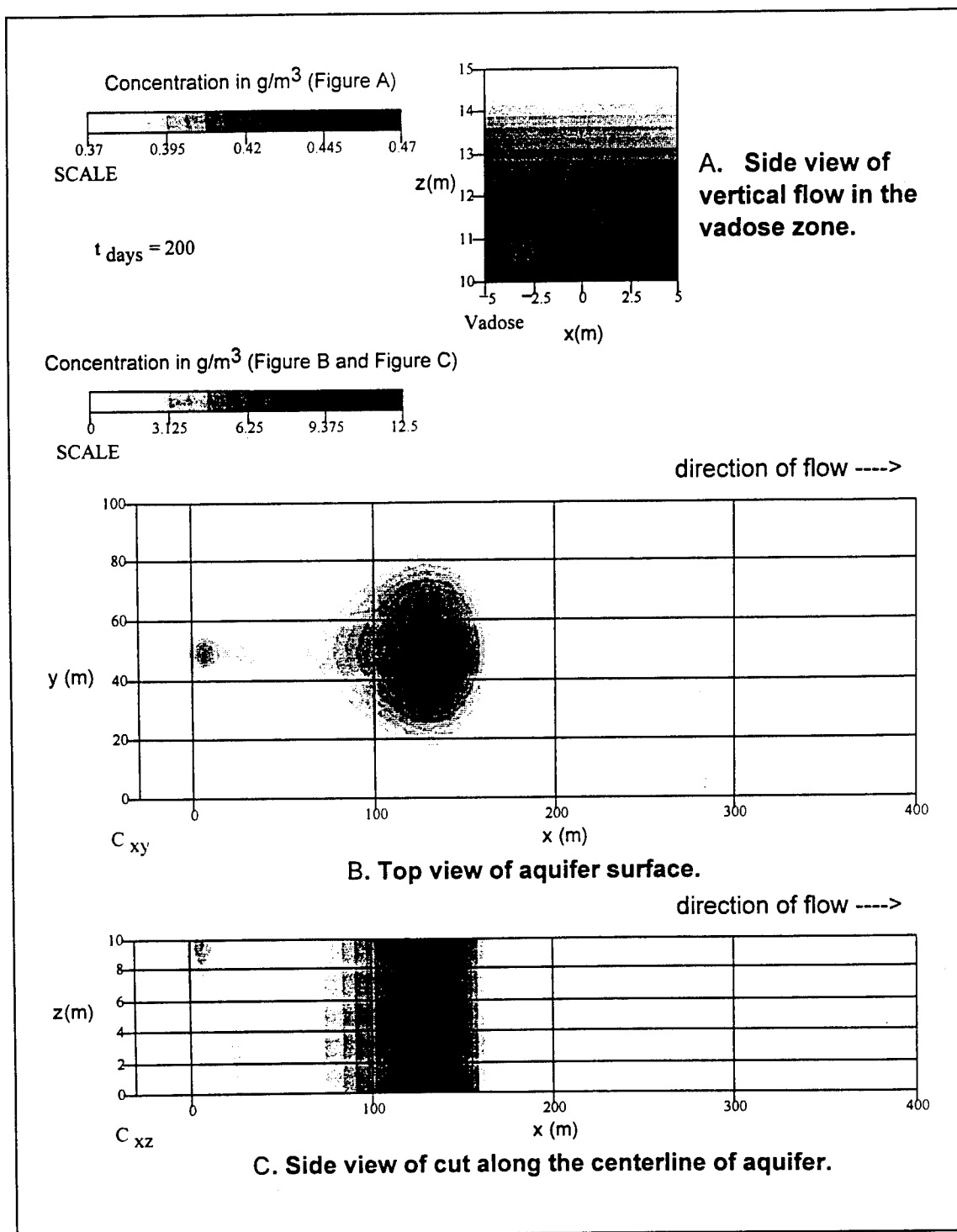


B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 3. (Sheet 5 of 6)



Example 3. (Sheet 6 of 6)

Unbounded LP flow model
(standard conditions)

$\theta = .35$ <--moisture content

$K = 0$ <--chemical transformation rate

$R = 1$ <--retardation factor

$M = 10000$ <--mass of the contaminant added

$V = (1 \cdot 10^{-6})$ <--vertical velocity

$D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturated zone

$D_{z2} = 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

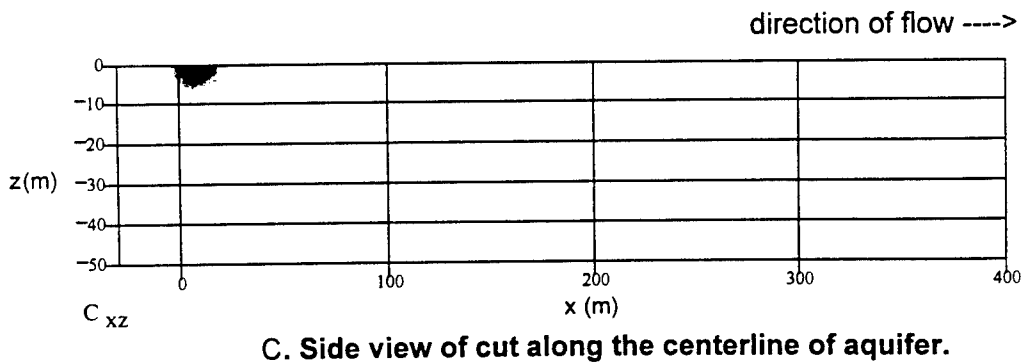
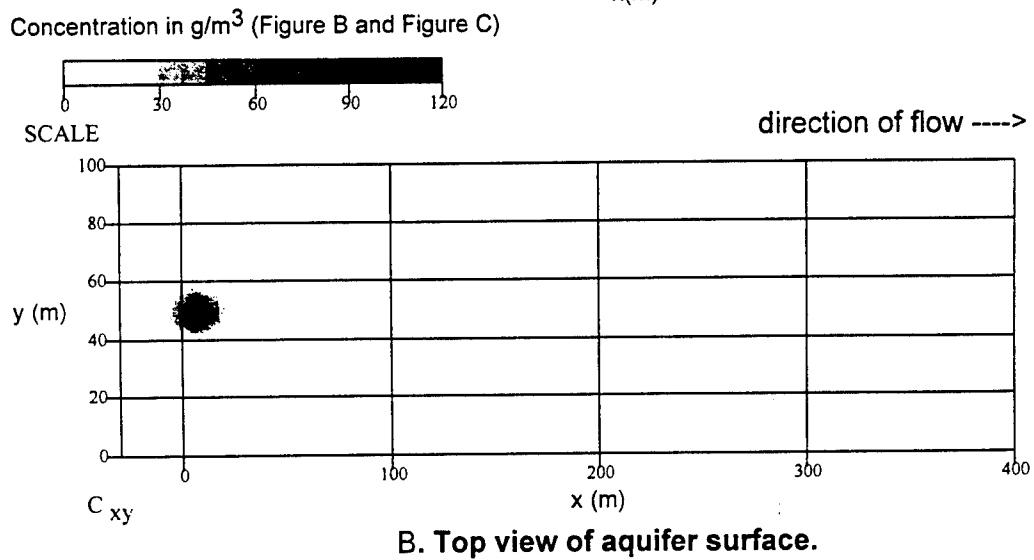
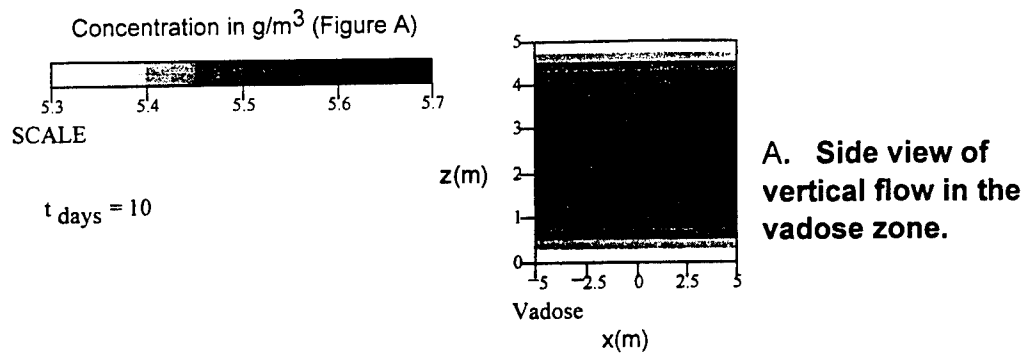
$x_1 = 5$ $x_2 = 5$ <-- initial loading area boundaries

$y_1 = 45$ $y_2 = 55$

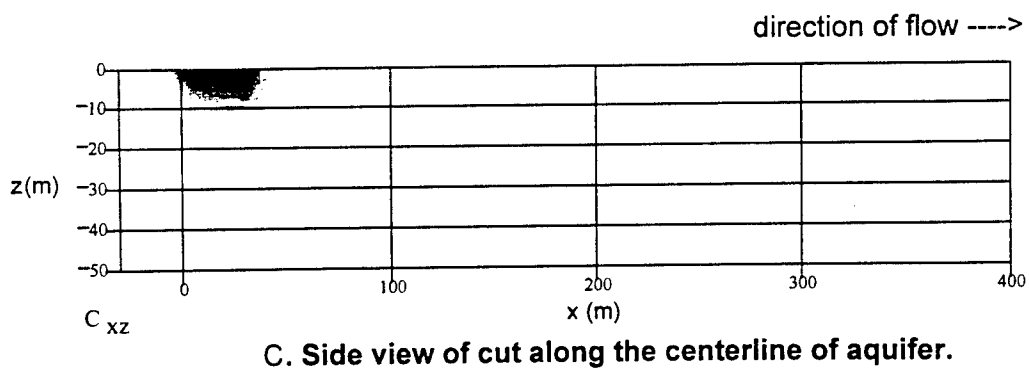
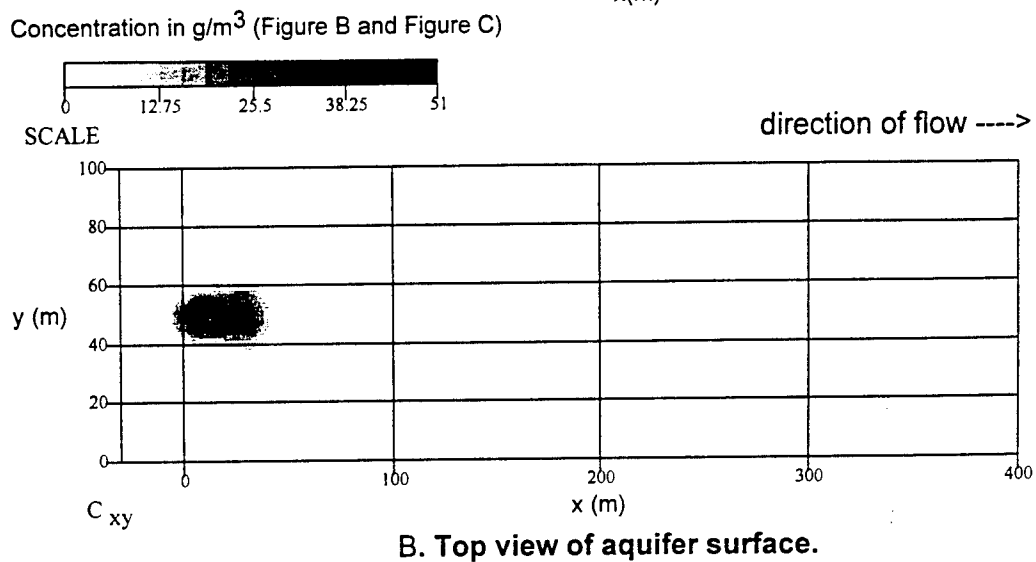
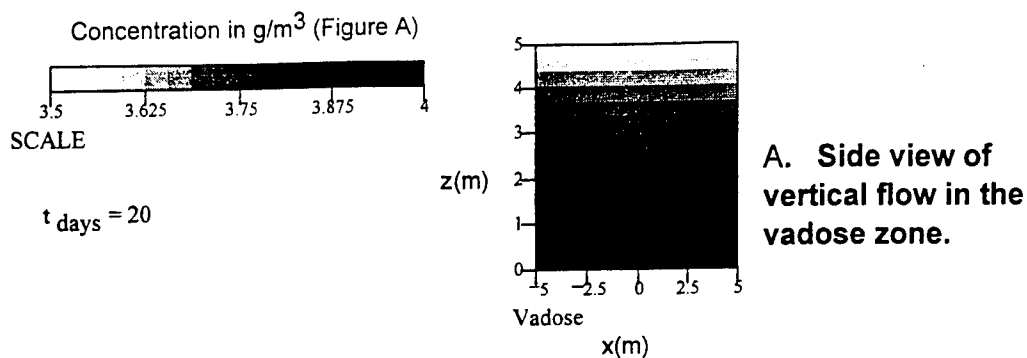
$B = 5$ <--depth of aquifer

$U = 8 \cdot 10^{-6}$ <--horizontal velocity

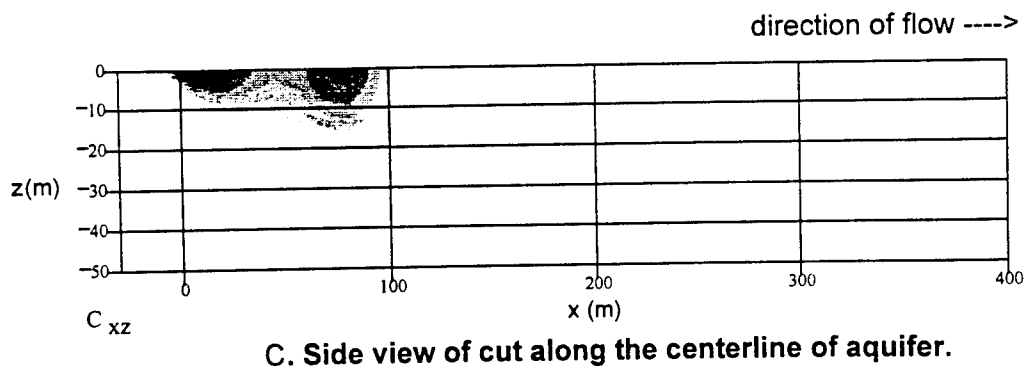
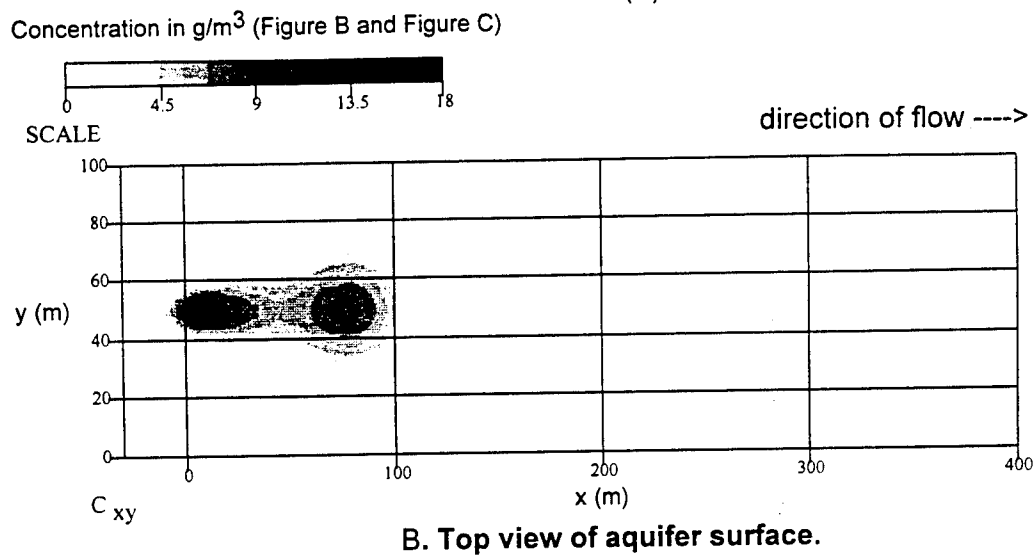
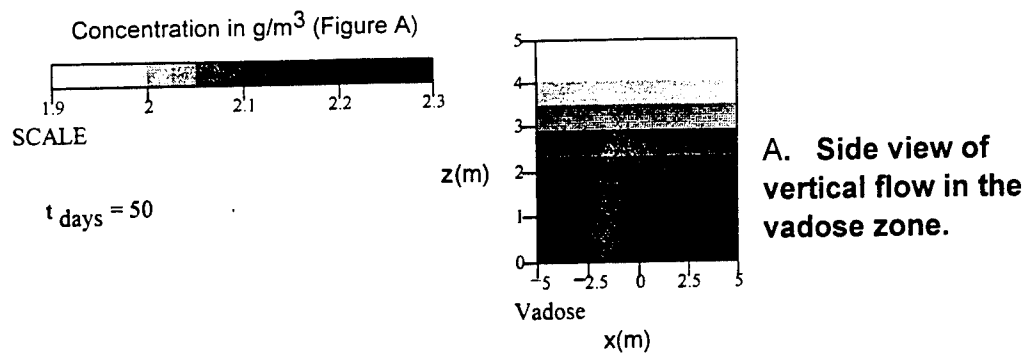
Example 4. Unbounded LP flow model (standard conditions) (Sheet 1 of 6)



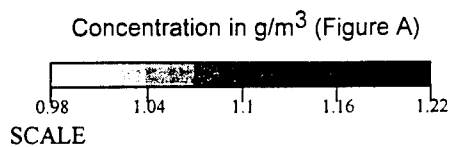
Example 4. (Sheet 2 of 6)



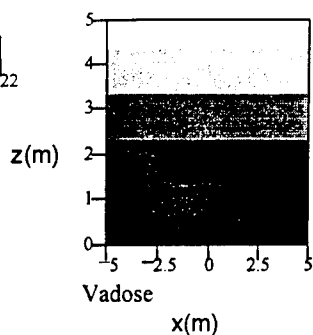
Example 4. (Sheet 3 of 6)



Example 4. (Sheet 4 of 6)

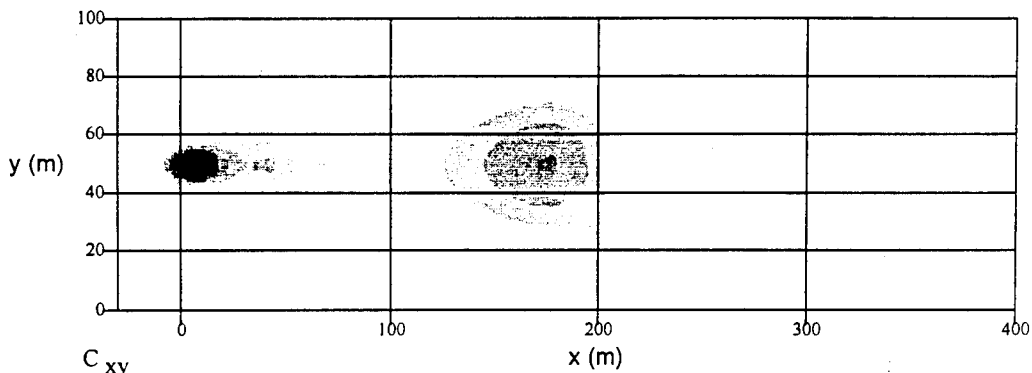
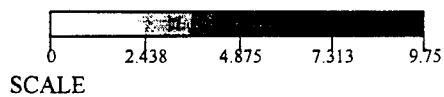


$t \text{ days} = 100$

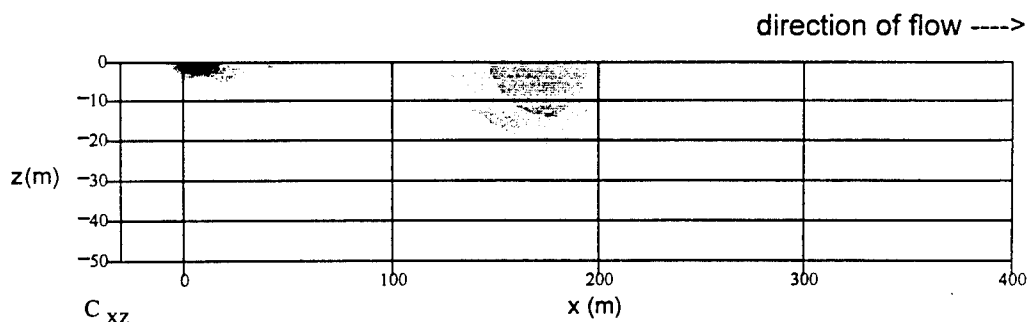


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

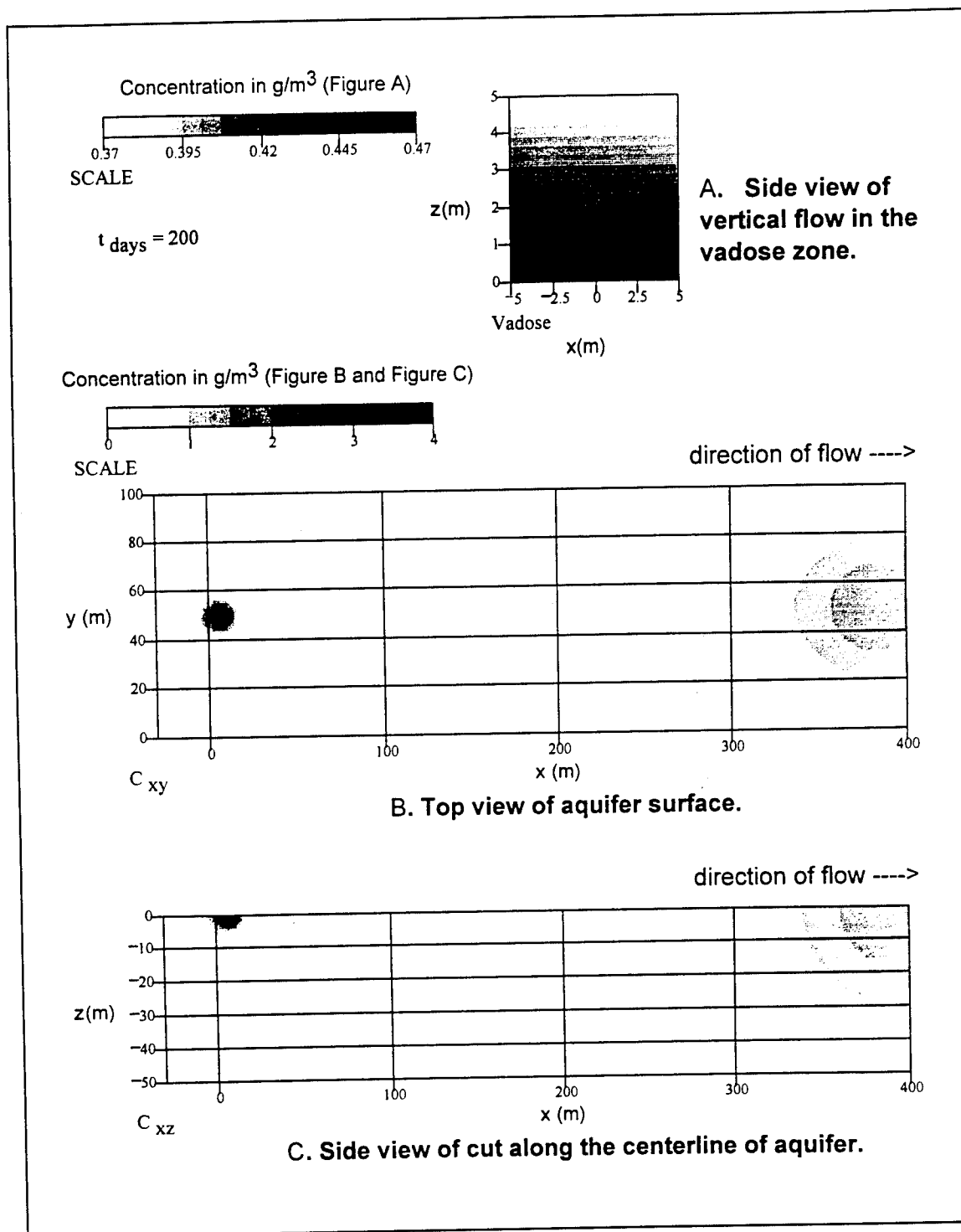


B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 4. (Sheet 5 of 6)



Example 4. (Sheet 6 of 6)

Unbounded LP flow model
(low horizontal velocity)

$\theta = .35$ <--moisture content

$K = 0$ <--chemical transformation rate

$R = 1$ <--retardation factor

$M = 10000$ <--mass of the contaminant added

$V = (1 \cdot 10^{-6})$ <--vertical velocity

$D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturated zone

$D_{z2} = 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

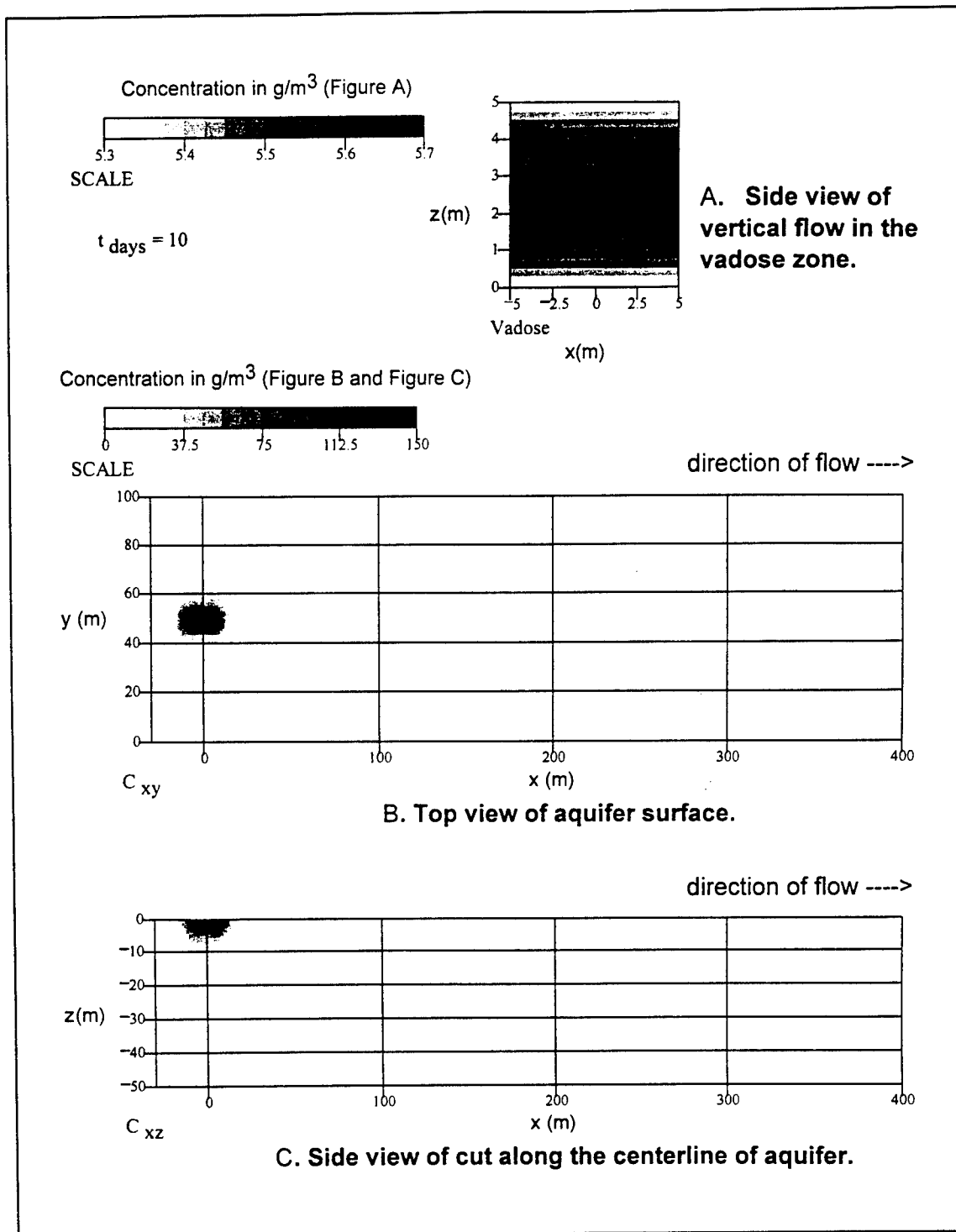
$x_1 = .5$ $x_2 = 5$ <-- initial loading area boundaries

$y_1 = 45$ $y_2 = 55$

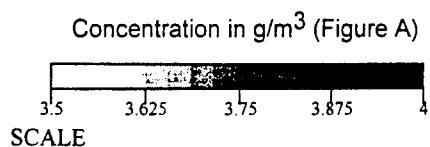
$B = 5$ <--depth of aquifer

$U = 8 \cdot 10^{-7}$ <--horizontal velocity

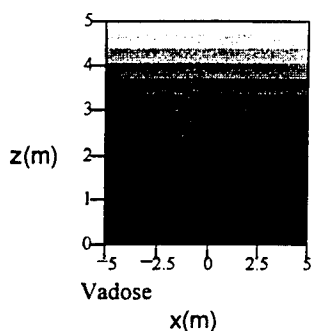
Example 5. Unbounded LP flow model (low horizontal velocity) (Sheet 1 of 6)



Example 5. (Sheet 2 of 6)

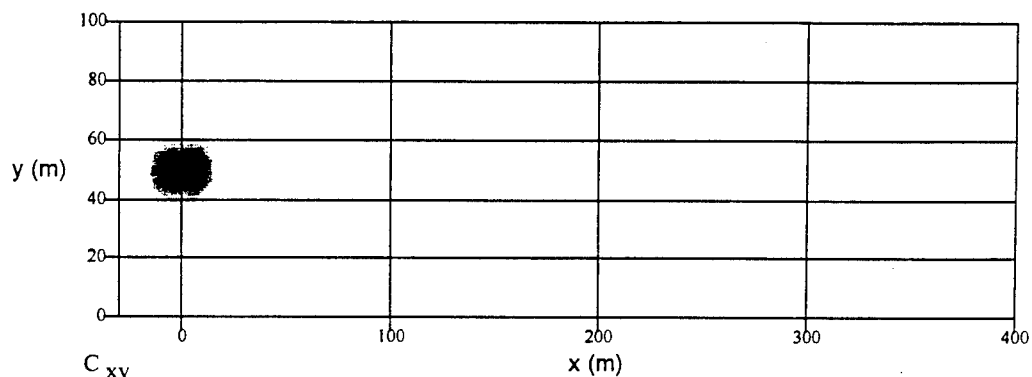
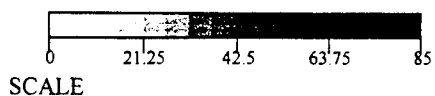


$t_{\text{days}} = 20$

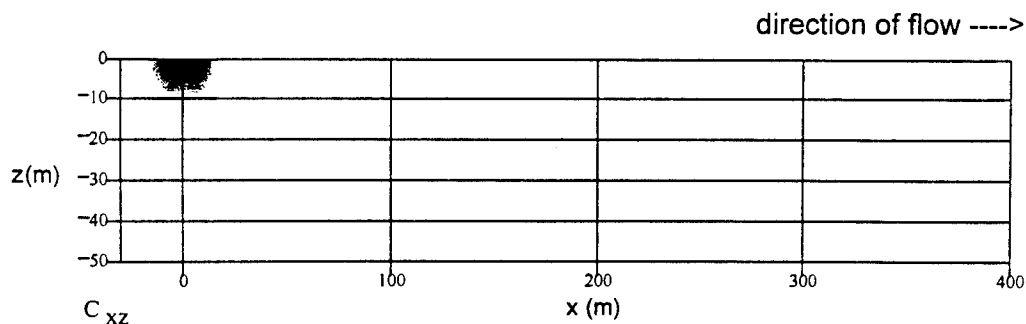


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

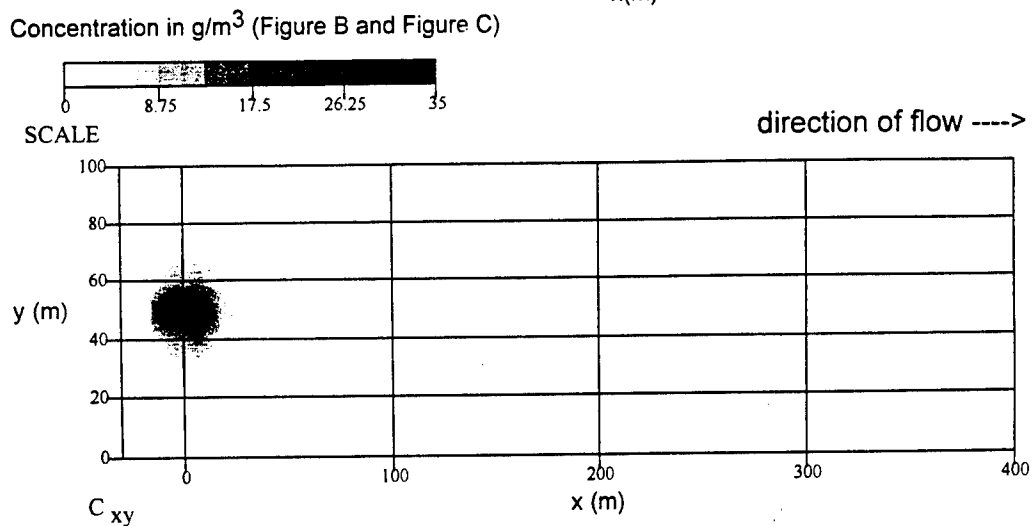
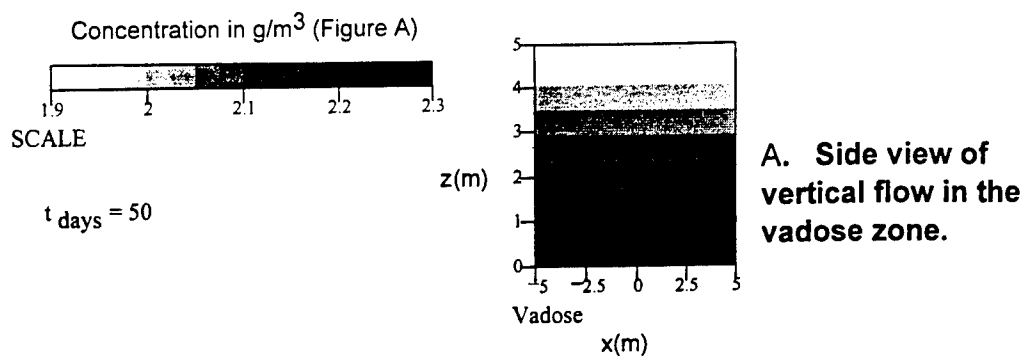


B. Top view of aquifer surface.

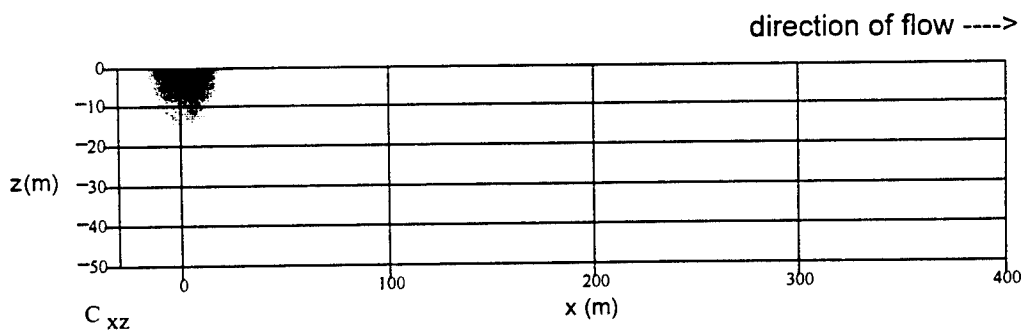


C. Side view of cut along the centerline of aquifer.

Example 5. (Sheet 3 of 6)

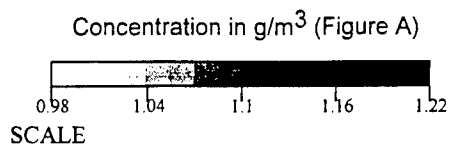


B. Top view of aquifer surface.

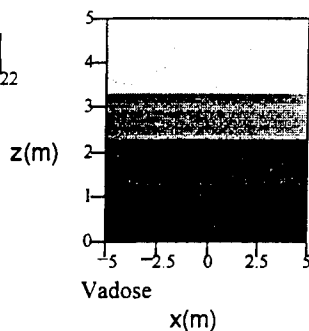


C. Side view of cut along the centerline of aquifer.

Example 5. (Sheet 4 of 6)

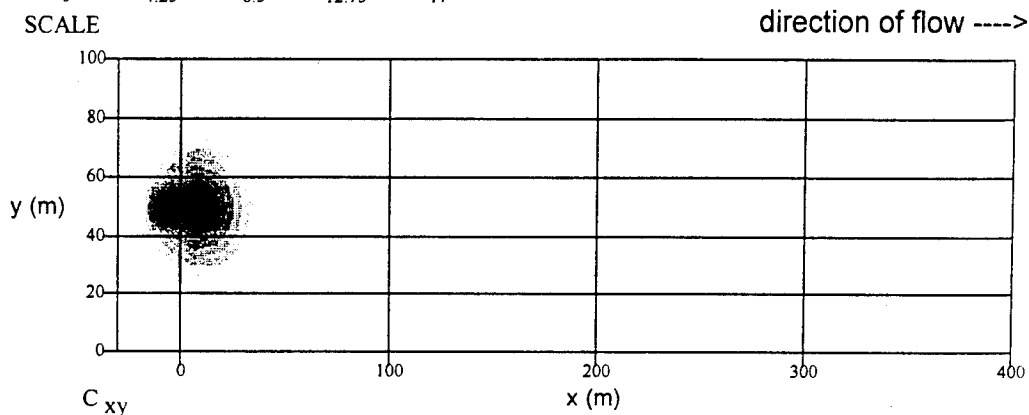
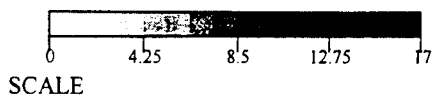


$t_{\text{days}} = 100$

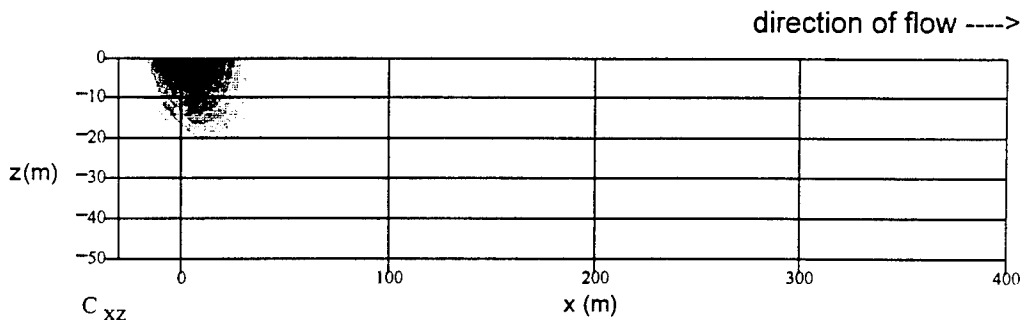


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

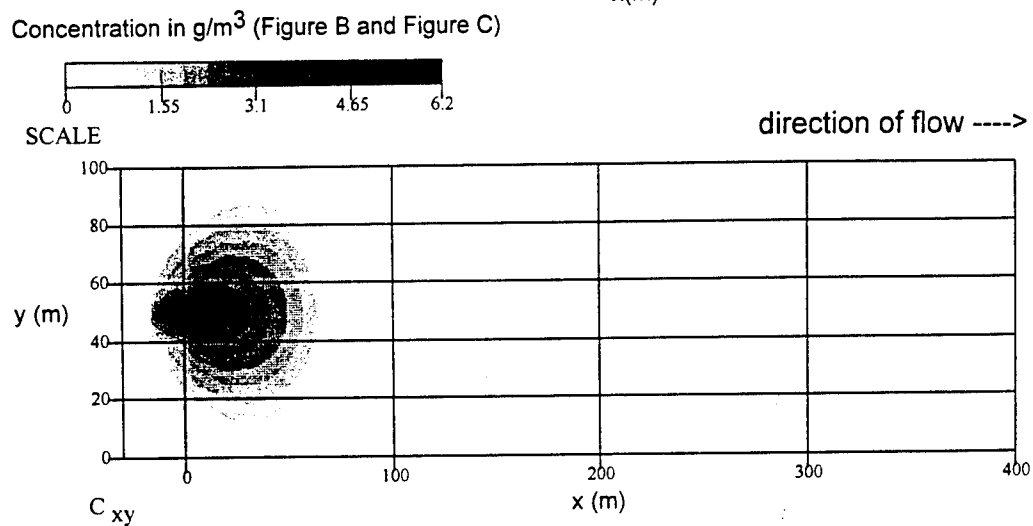
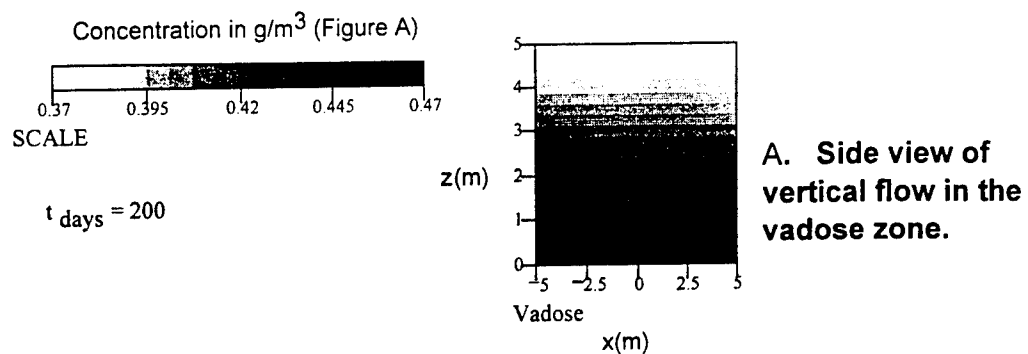


B. Top view of aquifer surface.

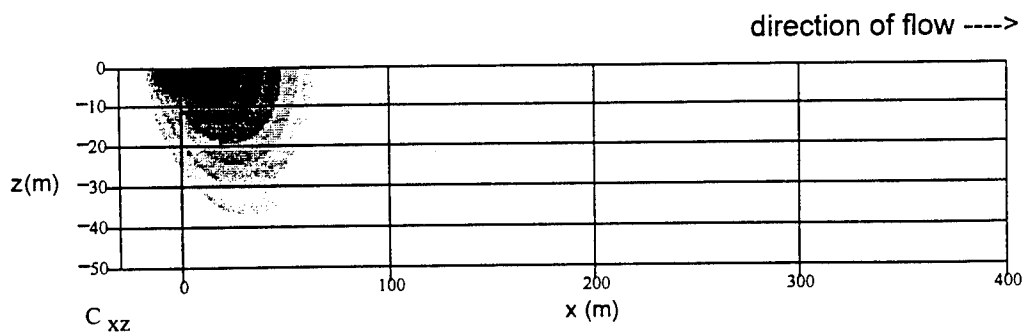


C. Side view of cut along the centerline of aquifer.

Example 5. (Sheet 5 of 6)



B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 5. (Sheet 6 of 6)

Unbounded LP flow model
(retardation factor = 2)

$\theta = .35$ <--moisture content

$K = 0$ <--chemical transformation rate

$R = 2$ <--retardation factor

$M = 10000$ <--mass of the contaminant added

$V = (1 \cdot 10^{-6})$ <--vertical velocity

$D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturated zone

$D_{z2} = 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

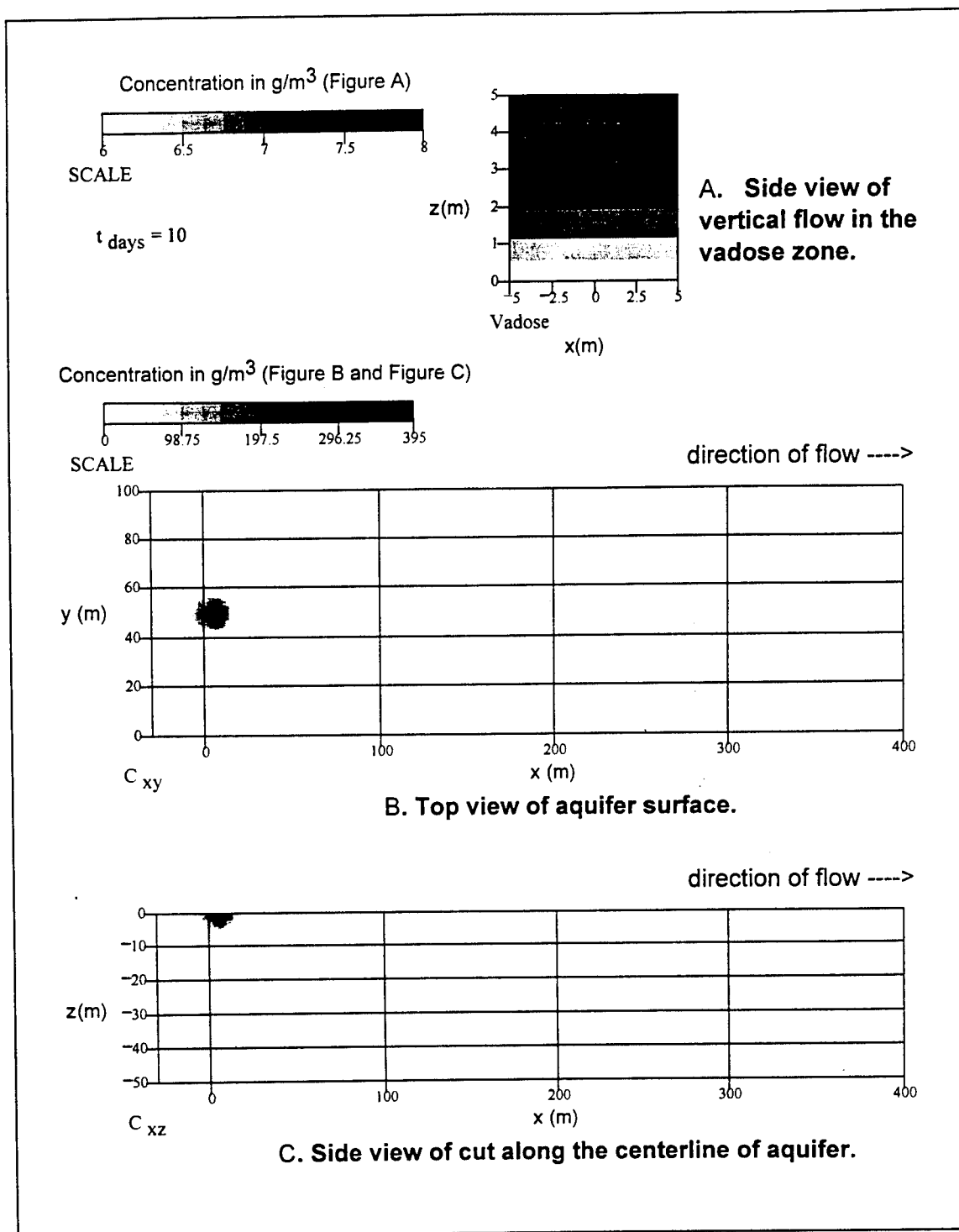
$x_1 = -5$ $x_2 = 5$ <-- initial loading area boundaries

$y_1 = 45$ $y_2 = 55$

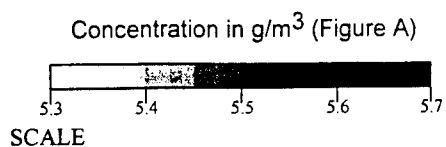
$B = 5$ <--depth of aquifer

$U = 8 \cdot 10^{-6}$ <--horizontal velocity

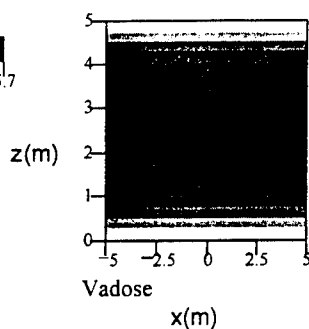
Example 6. Unbounded LP flow model (retardation factor = 2) (Sheet 1 of 6)



Example 6. (Sheet 2 of 6)

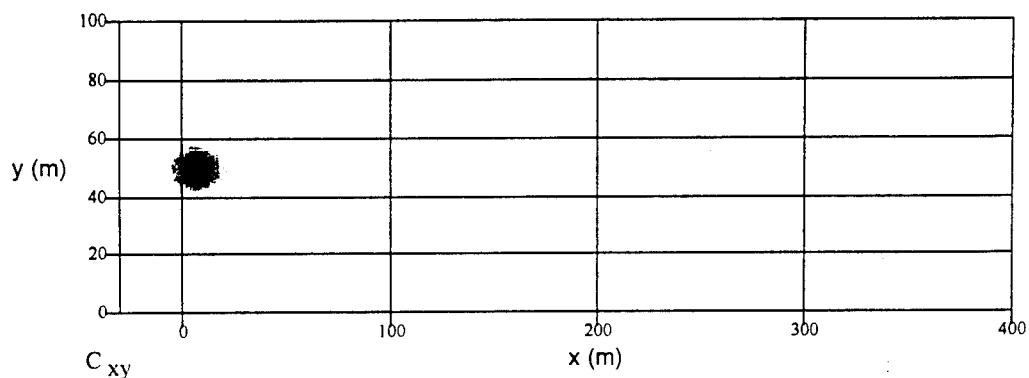
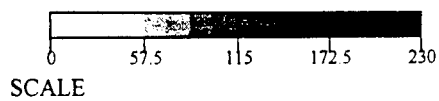


$t_{\text{days}} = 20$

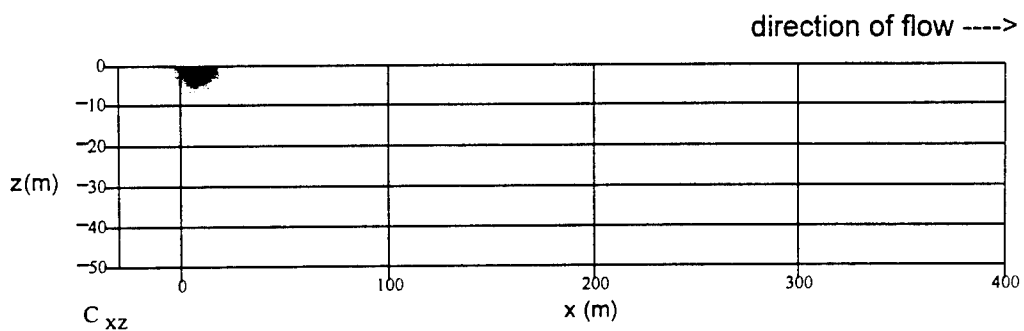


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

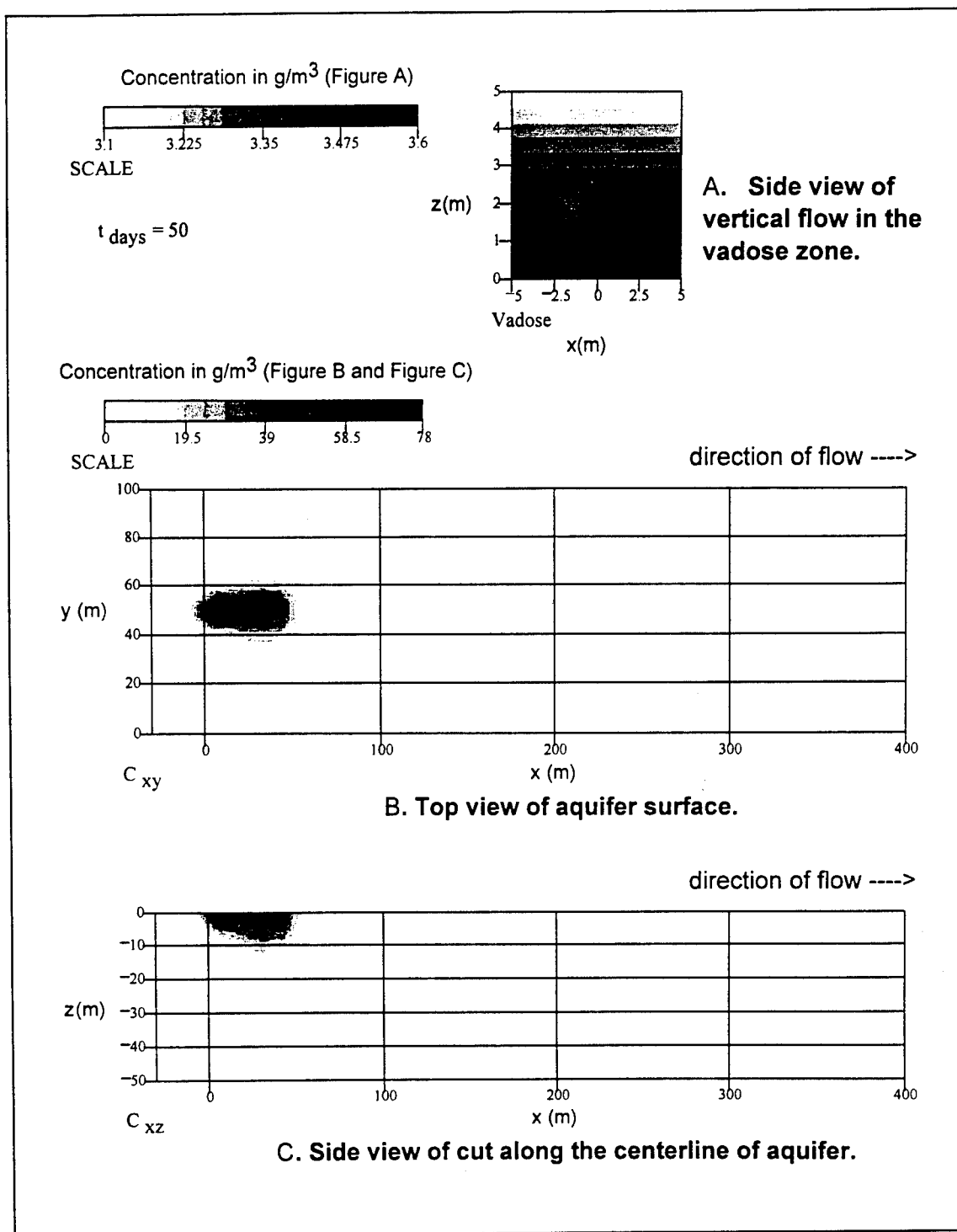


B. Top view of aquifer surface.

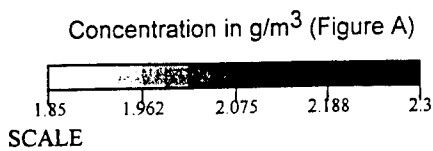


C. Side view of cut along the centerline of aquifer.

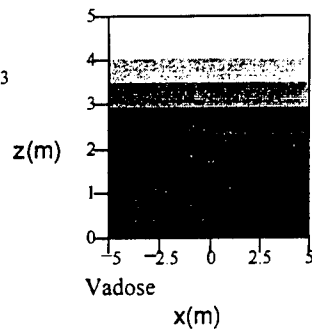
Example 6. (Sheet 3 of 6)



Example 6. (Sheet 4 of 6)

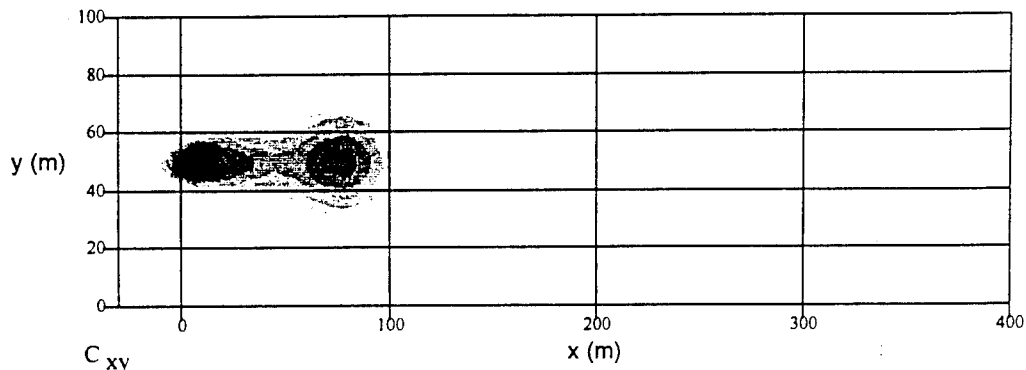
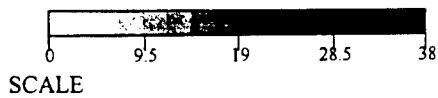


$t_{\text{days}} = 100$

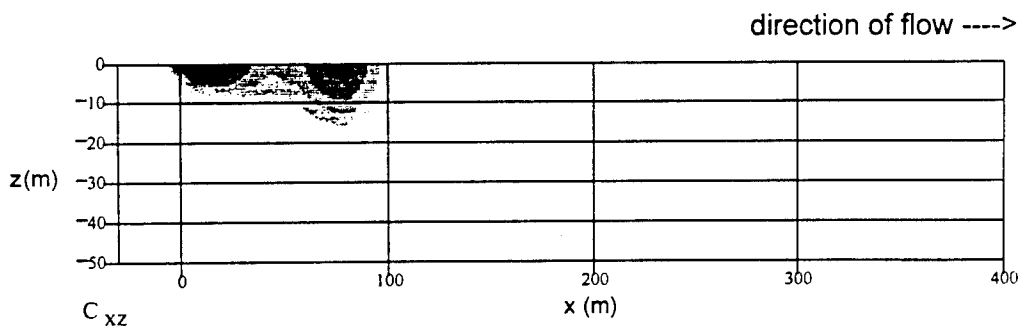


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

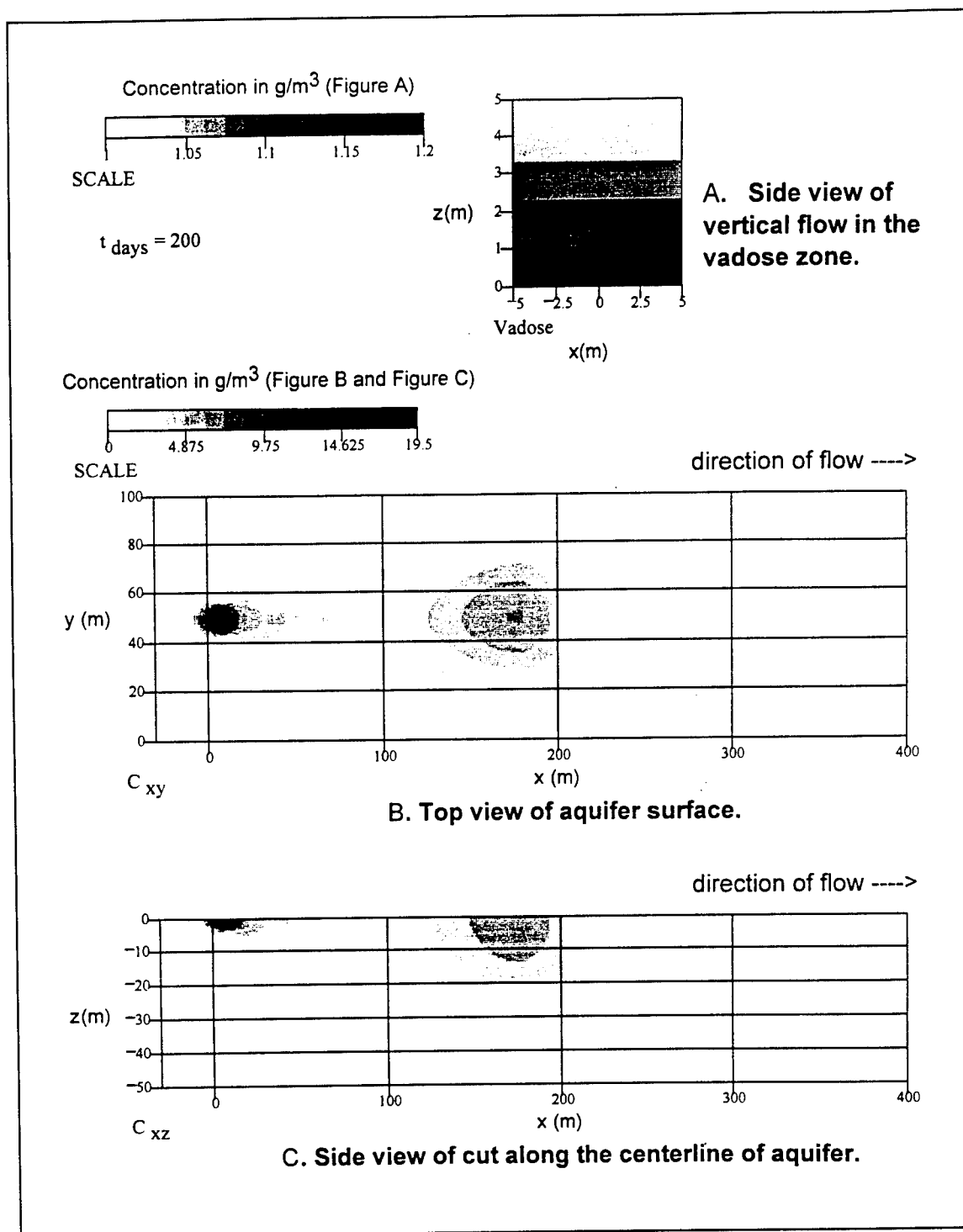


B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 6. (Sheet 5 of 6)



Example 6. (Sheet 6 of 6)

Unbounded LP flow model
(retardation factor = 10)

$\theta = .35$ <--moisture content

$K = 0$ <--chemical transformation rate

$R = 10$ <--retardation factor

$M = 10000$ <--mass of the contaminant added

$V = (-1 \cdot 10^{-6})$ <--vertical velocity

$D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturated zone

$D_{z2} = 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

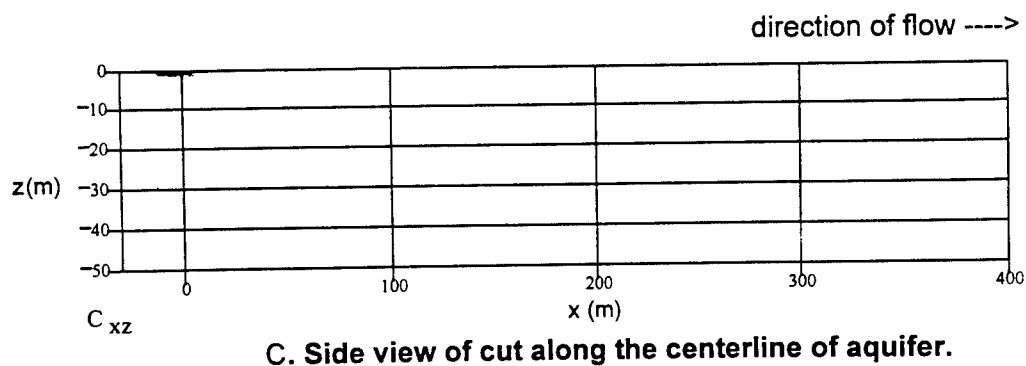
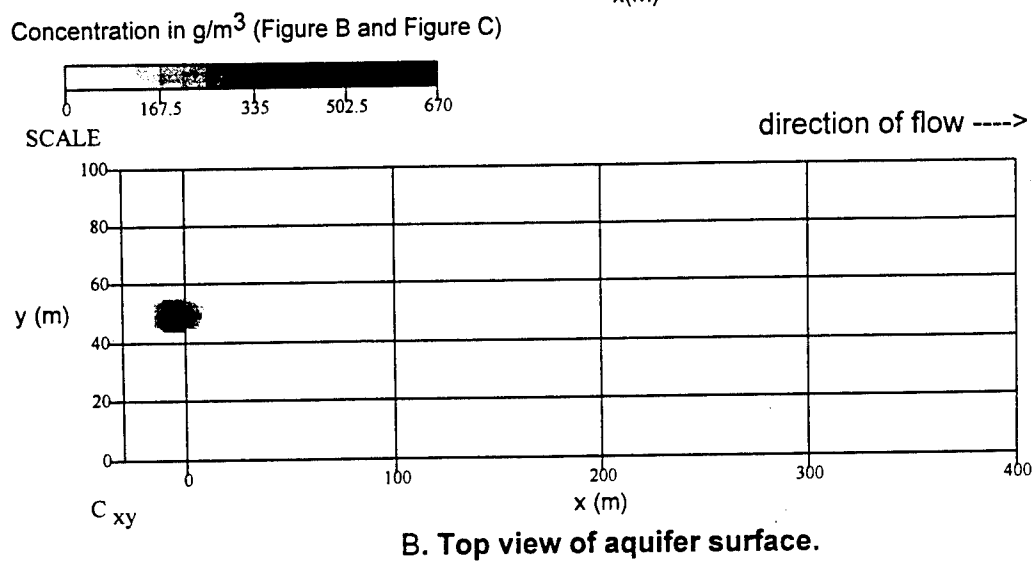
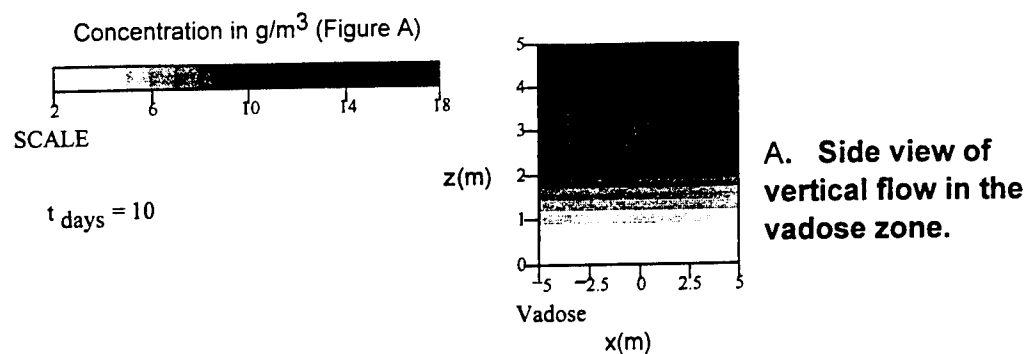
$x_1 = -5$ $x_2 = 5$ <-- initial loading area boundaries

$y_1 = 45$ $y_2 = 55$

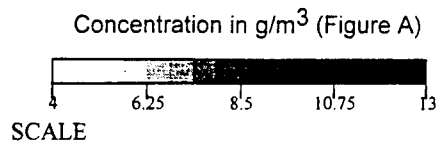
$B = 5$ <--depth of aquifer

$U = 8 \cdot 10^{-6}$ <--horizontal velocity

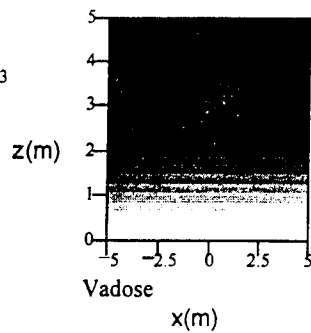
Example 7. Unbounded LP flow model (retardation factor = 10) (Sheet 1 of 6)



Example 7. (Sheet 2 of 6)

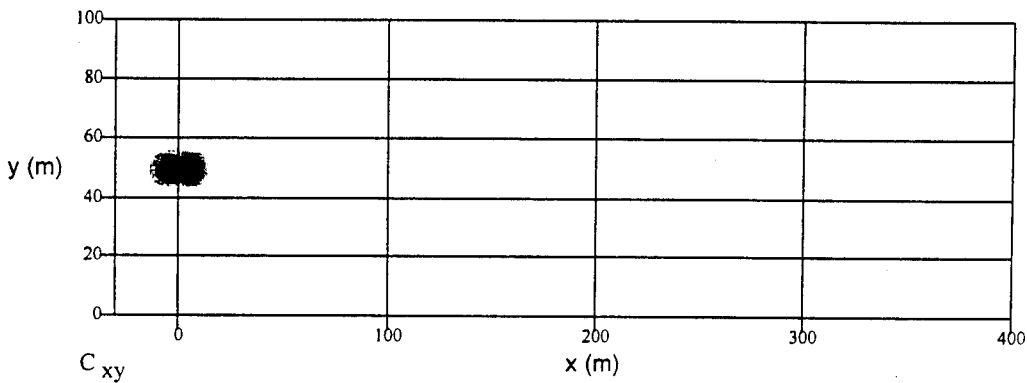
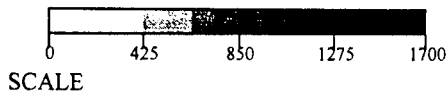


$t \text{ days} = 20$

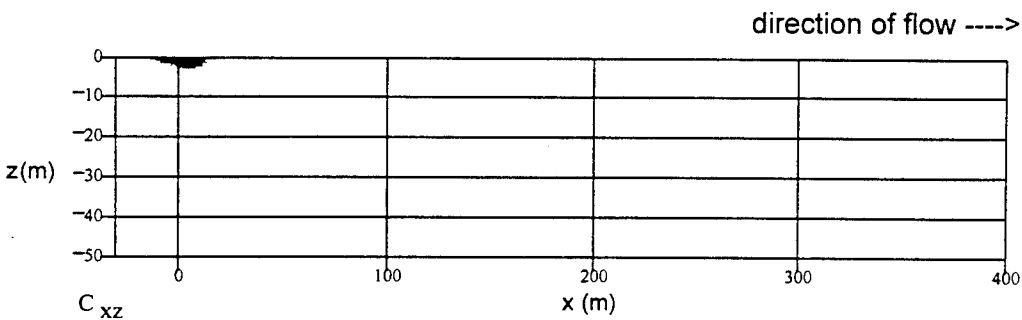


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

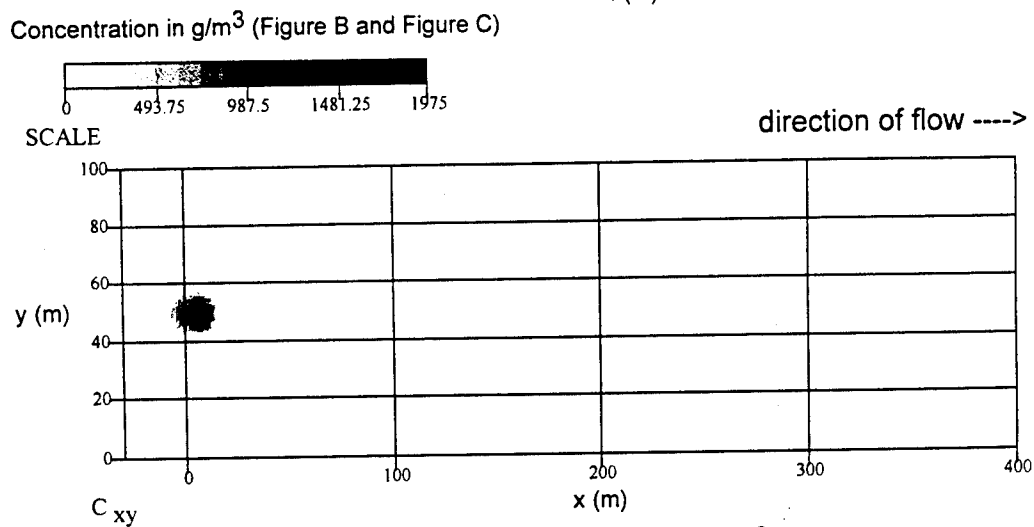
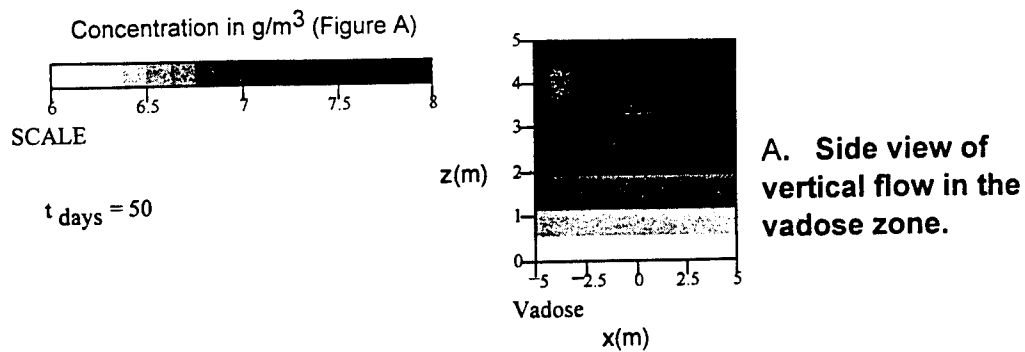


B. Top view of aquifer surface.

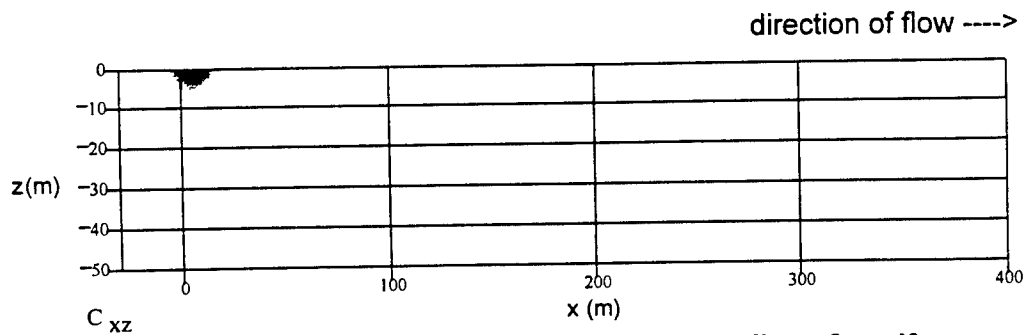


C. Side view of cut along the centerline of aquifer.

Example 7. (Sheet 3 of 6)

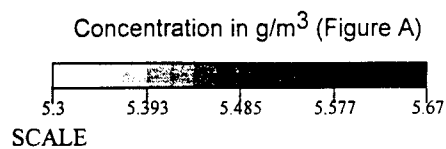


B. Top view of aquifer surface.

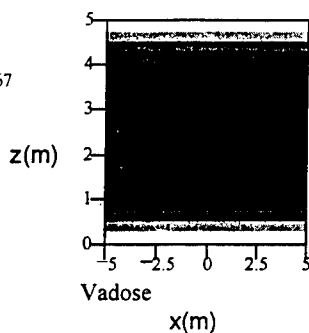


C. Side view of cut along the centerline of aquifer.

Example 7. (Sheet 4 of 6)

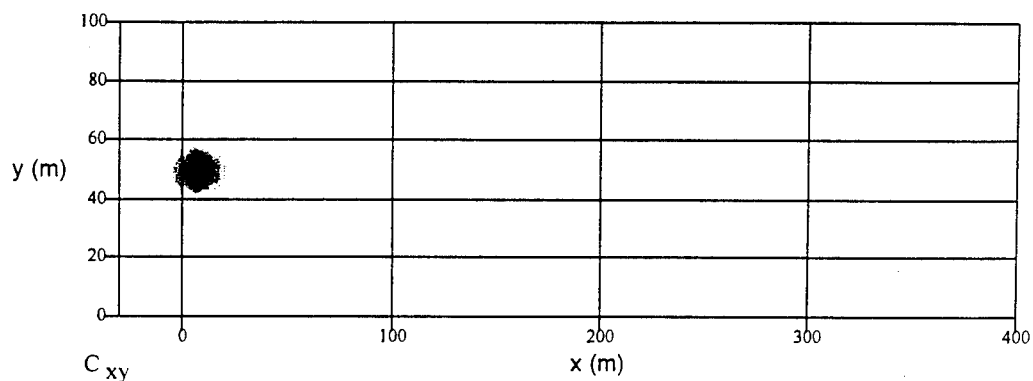
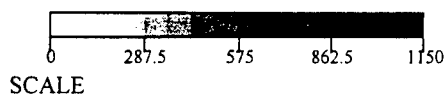


$t_{\text{days}} = 100$

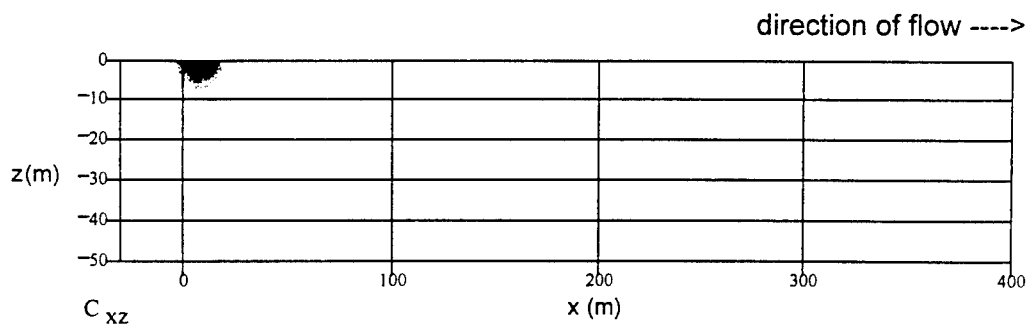


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

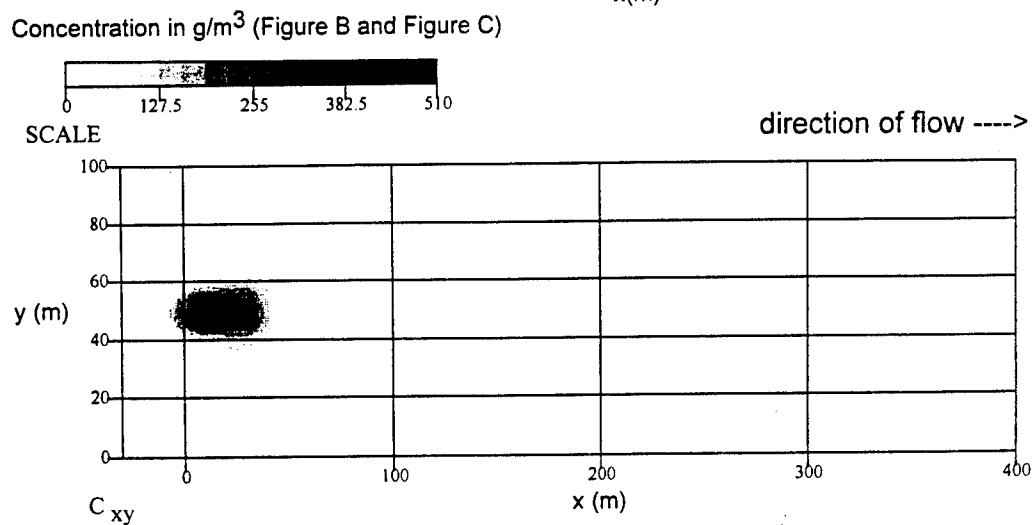
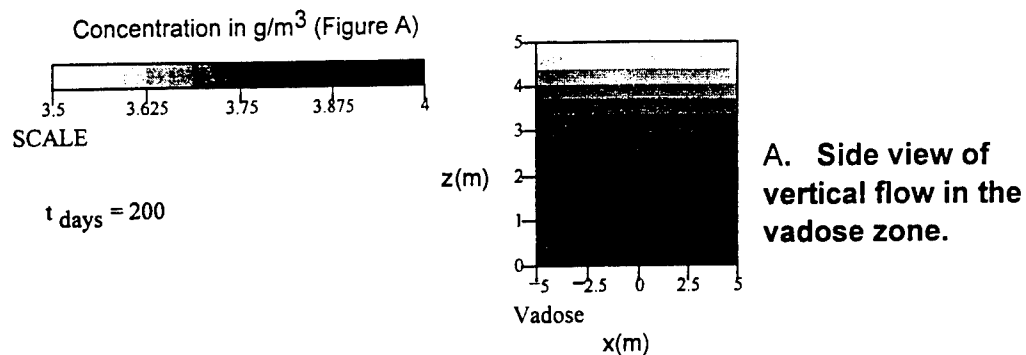


B. Top view of aquifer surface.

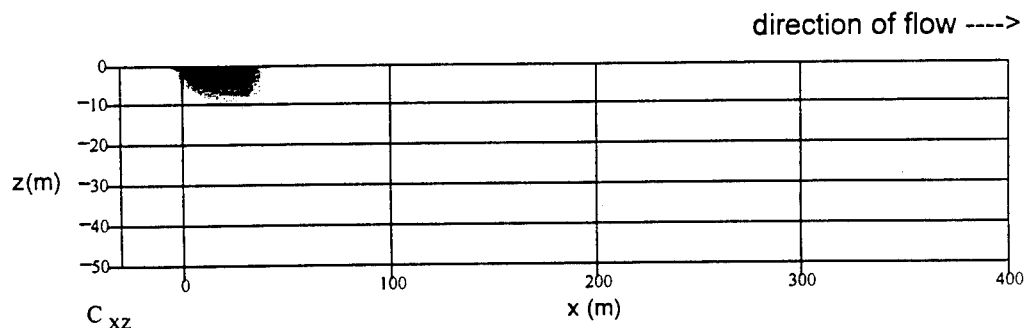


C. Side view of cut along the centerline of aquifer.

Example 7. (Sheet 5 of 6)



B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 7. (Sheet 6 of 6)

Unbounded LP flow model
(high velocity and R=10)

$\theta = .35$ <--moisture content

$K = 0$ <--chemical transformation rate

$R = 10$ <--retardation factor

$M = 10000$ <--mass of the contaminant added

$V = (-1 \cdot 10^{-6})$ <--vertical velocity

$D_x = 1 \cdot 10^{-5}$ $D_y = 1 \cdot 10^{-5}$ $D_z = 1 \cdot 10^{-5}$ <--dispersion coefficients in the saturated zone

$D_{z2} = 1 \cdot 10^{-5}$ <--dispersion coefficients in the vadose zone

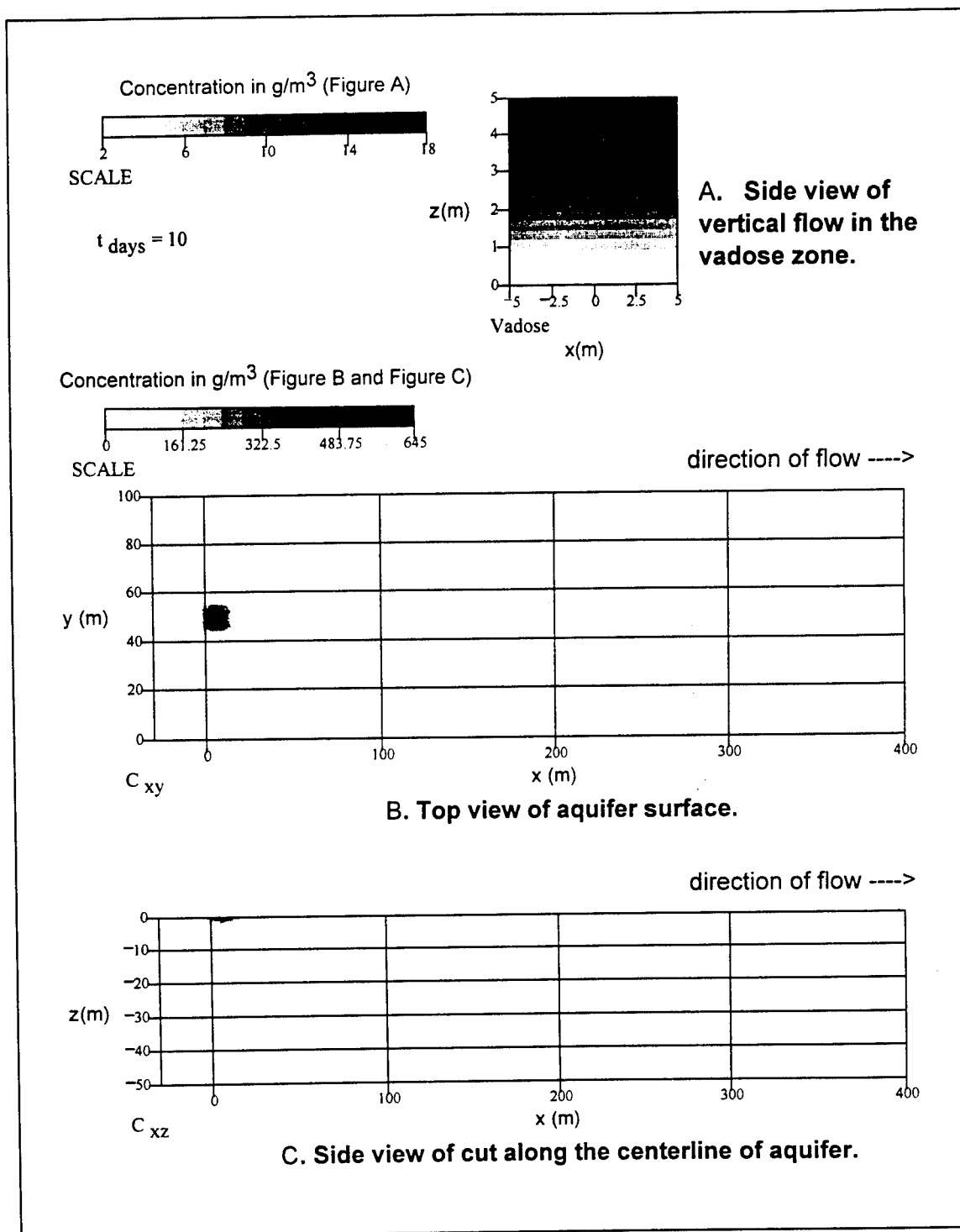
$x_1 = -5$ $x_2 = 5$ <-- initial loading area boundaries

$y_1 = 45$ $y_2 = 55$

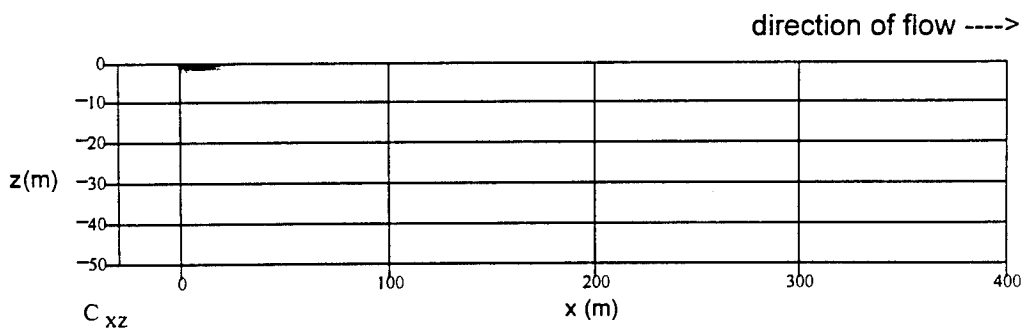
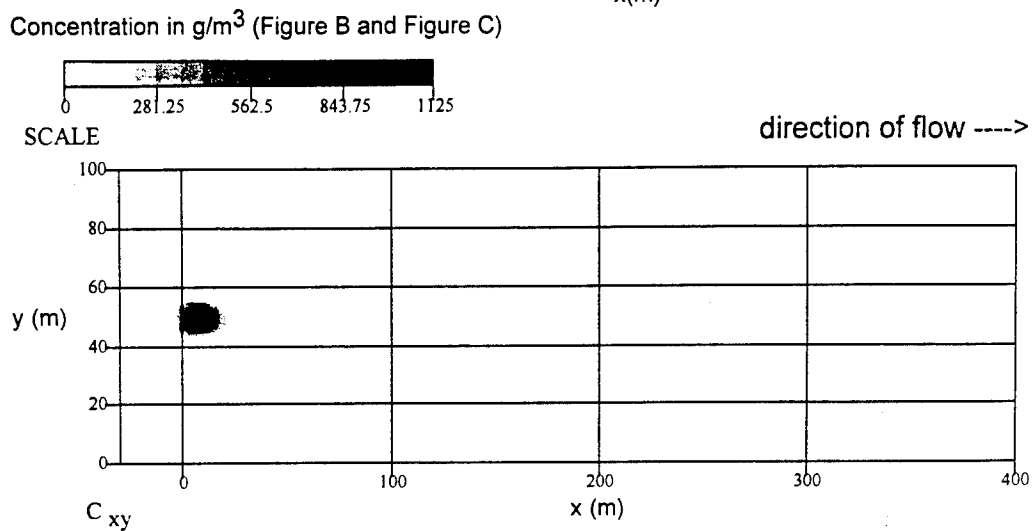
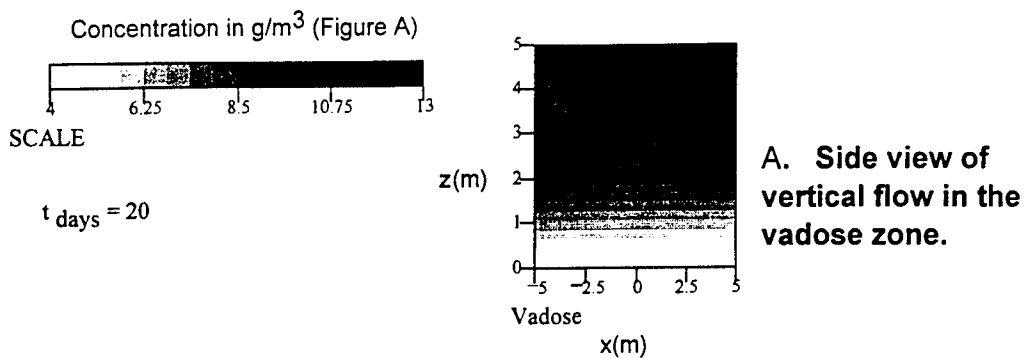
$B = 5$ <--depth of aquifer

$U = 8 \cdot 10^{-5}$ <--horizontal velocity

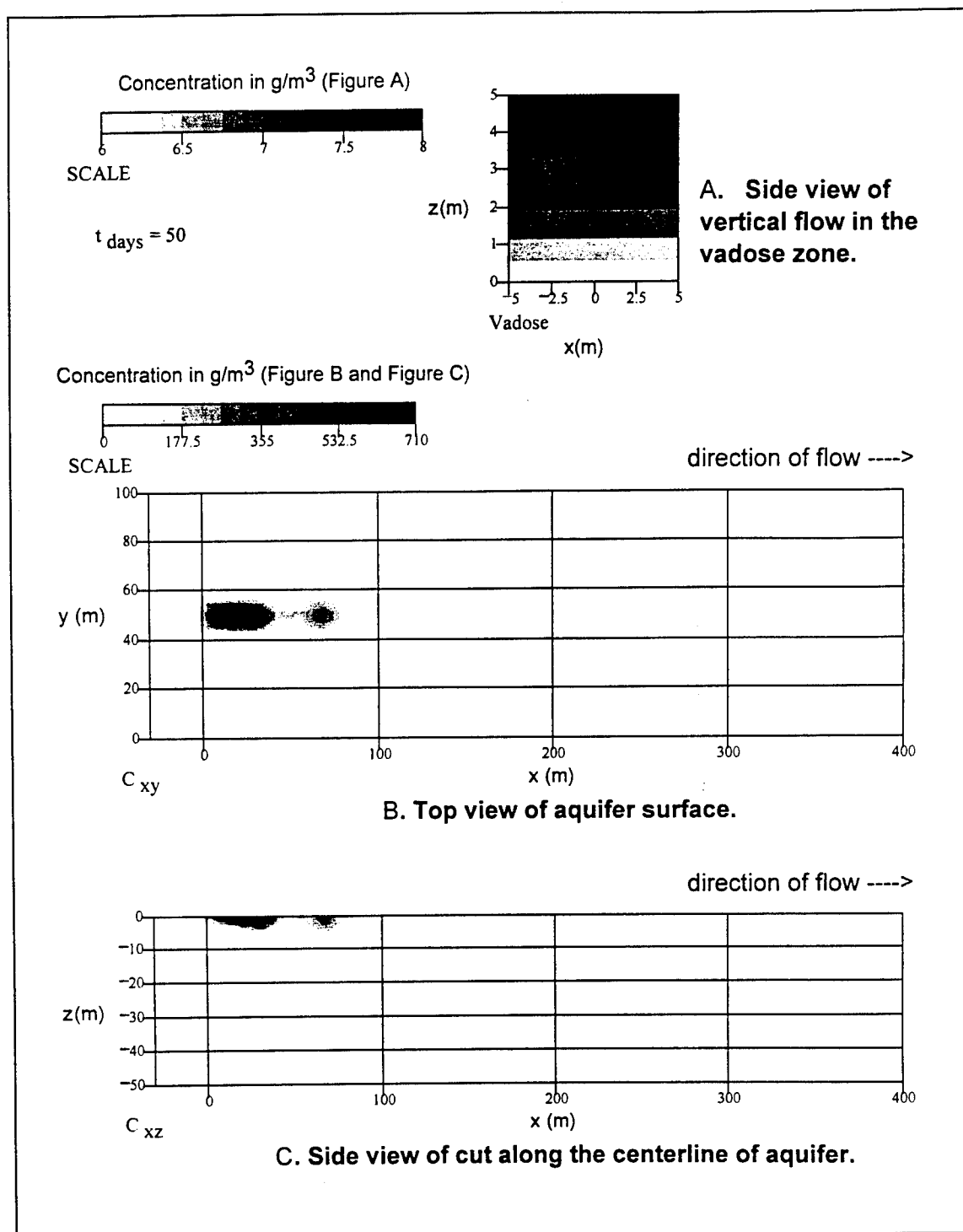
Example 8. Unbounded LP flow model (high velocity and retardation factor = 10) (Sheet 1 of 6)



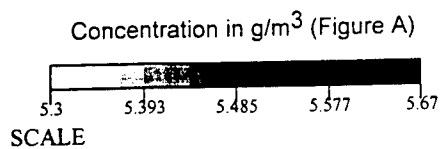
Example 8. (Sheet 2 of 6)



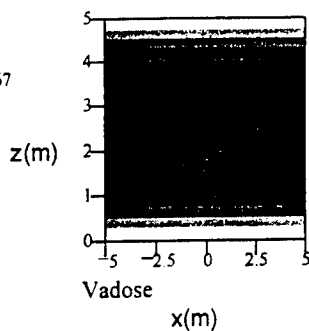
Example 8. (Sheet 3 of 6)



Example 8. (Sheet 4 of 6)

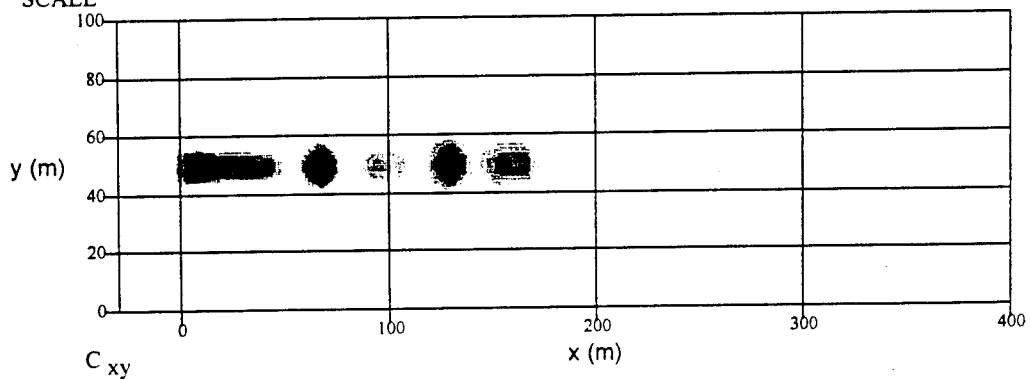
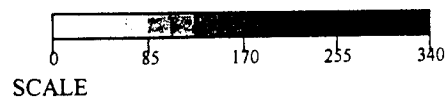


$t_{\text{days}} = 100$

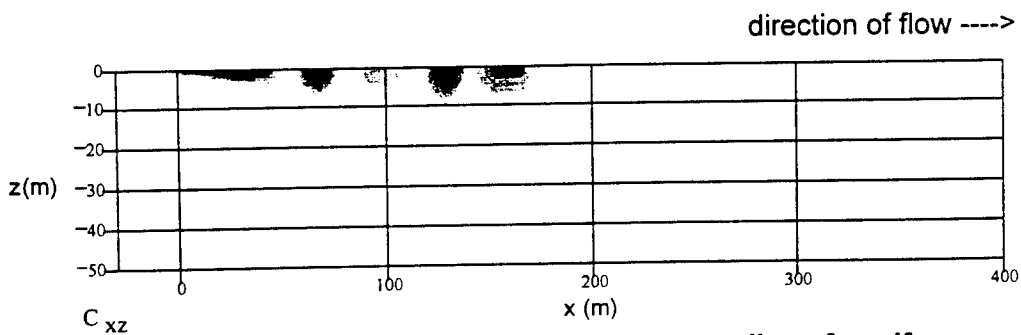


A. Side view of vertical flow in the vadose zone.

Concentration in g/m^3 (Figure B and Figure C)

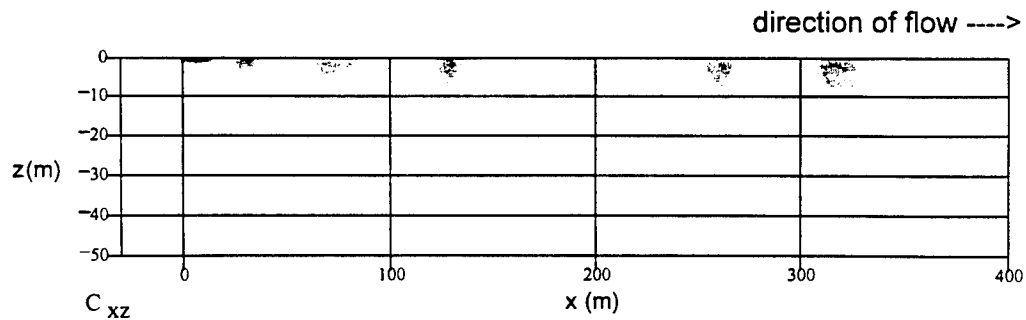
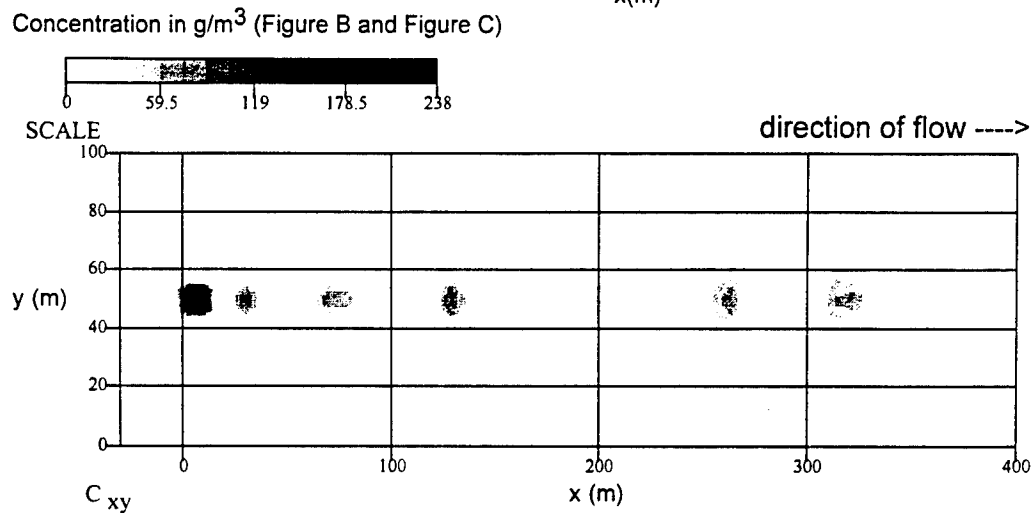
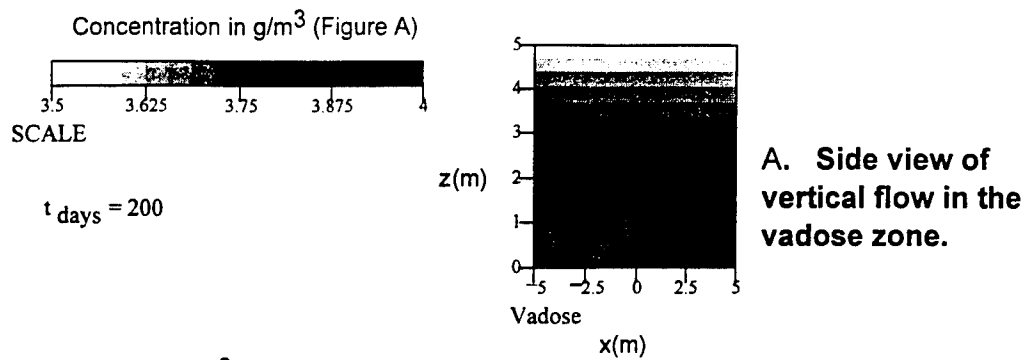


B. Top view of aquifer surface.



C. Side view of cut along the centerline of aquifer.

Example 8. (Sheet 5 of 6)



Example 8. (Sheet 6 of 6)

Section V
Gas Production from Interaction
of Liquid Propellant XM46 With
Soil

1 Background

Explosive contamination of the soil at military bases is a difficult and costly problem faced in all major military facilities. With the wisdom of experience, the military is now examining, early in the development program, potential environmental problems caused by new energetic materials. Liquid Propellant (LP) XM46, containing 61-percent hydroxylammonium nitrate (HAN), 19-percent triethanolammonium nitrate (TEAN), and 20-percent water, has been shown to be quite chemically reactive. In an effort to more fully assess the potential interaction of LP with soil, the gas production caused by 1 ml of LP contacting approximately 15 g of soil was determined for five soils previously screened by the U.S. Army Engineer Waterways Experimental Station (WES).¹

¹ Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathbum, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XPM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

2 Experimental Section

Five soils obtained from geographically diverse locations¹ were analyzed for total insoluble carbonates² and evaluated for their ability to generate gas when mixed with LP. In addition to determining the total volume of gas evolved, the composition of the gas as mole percents nitrogen (N₂), oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂), and nitrous oxide (N₂O) was determined by gas chromatography. Analyses were conducted as four replicates for each soil type. A schematic of the apparatus is shown in Figure 1. A closed system initially containing soil and air, at ambient temperature and pressure, approximates a real-world environment for the study of soil/LP interactions. For each replicate, accurately measured amounts of soil ranging from approximately 13.4 to 20.6 g (Table 1) were introduced into a 25-ml round bottom flask with a 19/22 ground glass joint and a 4.5-mm ID side arm. Under these conditions, the soil was considered in excess compared with the amount of LP added. The ground glass joint was connected to a thermometer adapter. Supelco Thermogreen septa (7/16 in.) were inserted into the end of the adapter. The side arm was connected directly to a standard Valco 6 port gas sampling valve with 100- μ l sample loop in line with a Varian Model 3600 gas chromatograph equipped with a Hayesep DB column (30 ft by 1/8 in. by 0.085 in. 100/120 mesh) and thermal conductivity detection (GC). The injector and detector temperatures were 150 and 140 °C, respectively. The oven was held at 35 °C for 10 min, then ramped to 180 °C at 30 °C/min. The system was pressure tested to ensure an airtight seal prior to each experiment.

The pressure of the system was monitored with an Omega meter/pressure transducer (Model DP205-E/PX800-010GV) assembly connected to the outlet port of a gas sampling valve (Figure 1). For each soil, the volume displacement of 1 ml of liquid (water) was correlated with the pressure transducer measurements in order to correct for the addition of the 1 ml of liquid LP introduced at the onset of the actual experiment. (Liquid calibrations are

¹ Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathbum, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XPM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

² Hesse, P. R. (1971). *A textbook of soil chemical analysis*. Chemical Publishing Co., Inc., New York.

Table 1
Summary of Gas Chromatograph Results (Heights responses)

Soil	Sample Number	Amount Soil, g	Height N ₂	Height O ₂	Height CO	Height CO ₂	Height N ₂ O	Ratio N ₂ /O ₂
Yuma 2A	2	13.8356	167344	36146		46783	1259	4.630
	3	14.0892	166776	35524		48708	1551	4.695
	4	14.0470	168486	36416		49336	1577	4.695
	5	13.6800	170346	36549		49102	1737	4.661
	25	13.4744						
China Lake A	6	14.2189	-	-			-	
	7	15.3485	194054	42038		25375	891	4.616
	8	20.5842	-	-			-	
	9	14.1575	188605	41118		27523	994	4.587
	10	14.8322	189581	41132		28804	1071	4.609
	23	12.5253						
Yokena Clay	11	14.4502	201214	43133		618	2583	4.665
	12	14.3838	201470	43421		588	2301	4.640
	13	13.5435	200038	42946		681	2815	4.658
	14	14.5	201698	43150		792	2512	4.674
WES Reference	15	13.4084	201798	43860		486	2156	4.601
	16	13.7124	199489	43275		trace	1835	4.610
	17	13.5188	199158	43439		trace	2399	4.585
	18	13.9320	199930	43223		409	2149	4.626
Socorro P	19	14.2794	169865	14144	1583	127467	7060	
	20	14.1484	147618	3977	1239	121572	10574	
	21	14.7817	162211	660	1315	106308	14517	
	22	14.6895	162256	502	1283	104164	12162	
	24	14.4524						
Average								4.632
Standard Deviation								0.032

shown in Table 2.) It was found that 1 ml of liquid added to the system corresponded to a volume displacement of 1.09 to 1.36 ml, depending on the soil type. The pressure transducer gauge, itself, was calibrated prior to each run whether LP or water was to be added to the soil. Volumes of air in 1-ml increments, up to 5 ml, were added by a 1-ml gastight syringe through the

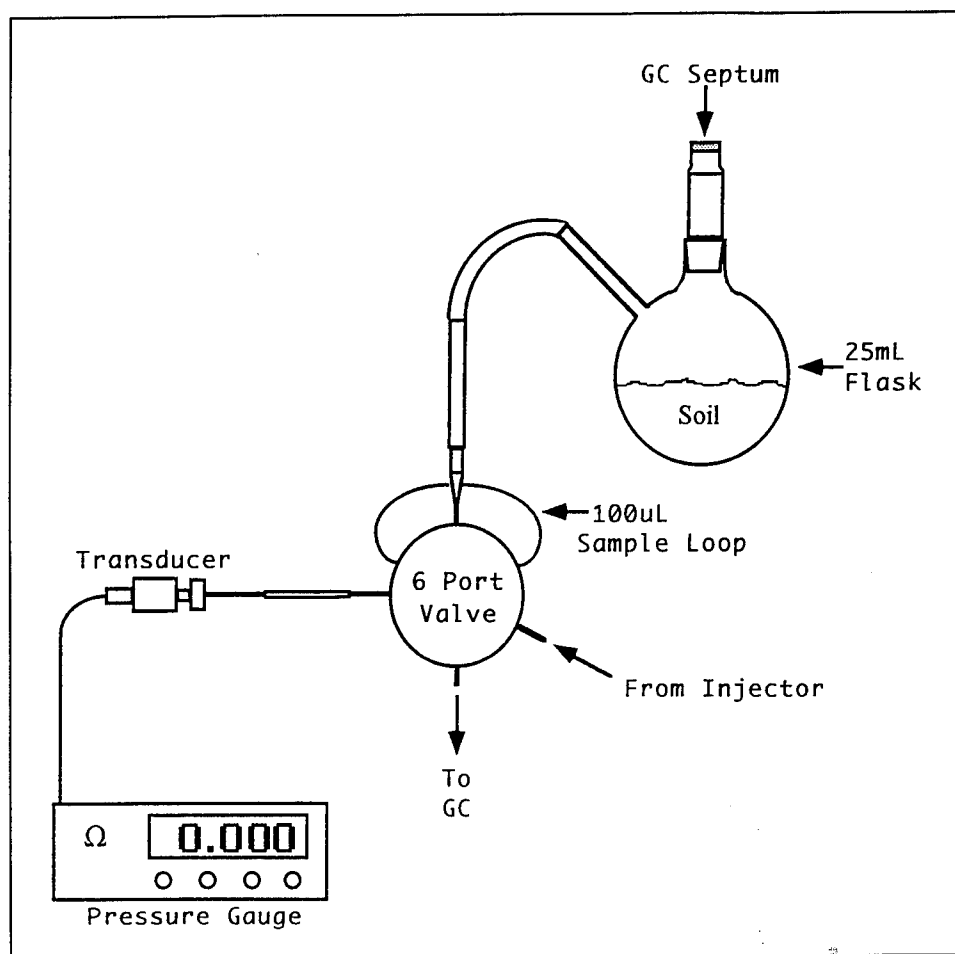


Figure 1. Apparatus used for pressure readings

septum, and pressure transducer counts were related to the gas volume introduced. (Gas volume calibrations are shown in Tables 3-7.) After the gas calibration was complete, excess air was vented from the system prior to addition of the desired liquid. For the actual tests, 1 ml of LP was added to the soil, and the pressure transducer measurements of the sealed system were monitored until equilibration was reached, i.e., no further pressure rise was detected over a 5-min period. This usually required about 30 min except for the samples using Socorro P soil (Table 7). Samples 19 and 20, using Socorro P soil and 1 ml of added LP, produced sufficient gas to exceed the pressure maximum of the gauge in 2.25 and 3.75 hr, respectively. In samples 21, 22, and 24, using Socorro P soil and only 0.5 ml of LP, substantially longer times were required to achieve the criteria for equilibration (8, 11, and 16.5 hr, respectively). The volume of gas produced was determined by multiplying the gas calibration factor by the maximum pressure transducer reading (Tables 3-7). Total gas produced from the interaction of LP on each soil is shown in Table 8. Values in the far right column have been converted to volumes at standard temperature and pressure (STP), assuming ambient conditions were 22 °C and 0.85 atmospheres.

Table 2
Liquid Calibration

Soil Type	Gas Calibration ¹			Liquid Calibration ²		
	Air Injected ml	Gauge Reading ct	Calibration Factor ³ (ml/ct) × 10 ⁻²	Gauge Reading ct	Liquid Adjustment ml	Liquid Adjustment μmol
Yuma 2A	1	17	5.88	22	1.29	45.4
	2	34				
	3	51				
China Lake A (#1)	1	24	4.35	31	1.35	47.3
	2	47				
	3	70				
	4	93				
	5	116				
China Lake A (#2)	1	25	4.02	34	1.37	47.9
	2	51				
	3	76				
	4	100				
	5	125				
Yokena Clay	1	23	4.26	31	1.32	46.3
	2	47				
	3	70				
WES Reference	1	23	4.35	29	1.26	44.3
	2	46				
	3	69				
Socorro P	1	24	4.35	25	1.09	38.2
	2	47				
	3	70				

¹ See Experimental Section and Table 3.

² One milliliter of water was used for the liquid calibration; see Experimental Section.

³ For the calibration factor in μmole/ct, multiply by 35.11 μmole/ml.

After the total amount of evolved gas had been calculated from pressure transducer readings, the gas was vented from the system through a 100-μl sample loop. The sample loop containing gas from the sealed system at ambient temperature and pressure was connected on line with the GC. The GC was configured to separate and detect N₂, O₂, CO, CO₂, and N₂O. Calibration gases were used to quantify the individual gas components. Prior to

Table 3
Yuma 2A—Gas Volume Calibrations and LP + Soil Results

Sample Number	Gas Calibration ¹			Sample Results ²			
	Air Injected ml	Gauge Reading ct	Calibration Factor (ml/ct) × 10 ⁻²	Gauge Reading ct	Uncorrected Gas Evolved ml	Corrected Gas Evolved ml	Corrected to STP, ml
2	1	18	5.56	135	7.51	6.21	4.88
	2	36					
	3	54					
3	1	17	5.59	150	8.38	7.09	5.58
	2	35					
	3	52					
	4	70					
	5	87					
	6	104					
	7	121					
	8	138					
4	1	18	5.68	168	9.54	8.25	6.49
	2	36					
	3	53					
	4	71					
5	1	17	4.78	155	8.95	7.66	6.03
	2	35					
	3	52					
	4	69					
25	1	22	4.65	242	11.3	10.0	7.87
	2	43					
	3	64					
	4	86					
	5	108					
Average							6.17
Standard deviation							1.12

¹ The calibration factor in ml/ct is the slope of ml versus ct lines. To obtain the calibration factor in $\mu\text{moles/ct}$, multiply by $35.11 \mu\text{moles/ml}$.

² The calibration factor multiplied by the gauge reading gives uncorrected gas evolved at ambient temperature and pressure. The corrected gas evolved is obtained by subtracting liquid adjustment (Table 2) for the specified soil type.

Table 4
China Lake A—Gas Volume Calibrations and LP + Soil Results

Sample Number	Gas Calibration ¹			Sample Results ²			
	Air Injected ml	Gauge Reading ct	Calibration Factor (ml/ct) $\times 10^{-2}$	Gauge Reading ct	Uncorrected Gas Evolved ml	Corrected Gas Evolved ml	Corrected to STP ml
6	1	18	5.78	77	4.45	3.09	2.43
	2	35					
	3	53					
	4	70					
	5	87					
7	1	18	5.72	81	4.63	3.27	2.57
	2	36					
	3	53					
	4	71					
	5	88					
8	1	22	4.41	108	4.75	3.39	2.67
	2	45					
	3	68					
	4	90					
	5	113					
9	1	22	4.50	99	4.36	3.00	2.36
	2	45					
	3	68					
	4	90					
	5	113					
10	1	23	4.39	103	4.52	3.16	2.49
	2	46					
	3	69					
	4	92					
	5	114					
23	1	23	4.44	97	4.31	2.95	2.32
	2	45					
	3	68					
Average							2.47
Standard Deviation							0.13

¹ The calibration factor in ml/ct is the slope of ml versus ct lines. To obtain the calibration factor in $\mu\text{moles/ct}$, multiply by 35.11 $\mu\text{moles/ml}$.

² The calibration factor multiplied by the gauge reading gives uncorrected gas evolved at ambient temperature and pressure. The corrected gas evolved is obtained by subtracting liquid adjustment (Table 2) for the specified soil type.

Table 5
Yokena Clay—Gas Volume Calibrations and LP + Soil Results

Sample Number	Gas Calibration ¹			Sample Results ²			
	Air Injected ml	Gauge Reading ct	Calibration Factor (ml/ct) × 10 ⁻²	Gauge Reading ct	Uncorrected Gas Evolved ml	Corrected Gas Evolved ml	Corrected to STP ml
11	1	25	4.29	44	1.89	0.57	0.45
	2	48					
	3	72					
	4	95					
	5	118					
12	1	24	4.20	45	1.89	0.57	0.45
	2	48					
	3	72					
	4	96					
	5	119					
13	1	24	4.22	44	1.86	0.54	0.42
	2	48					
	3	72					
	4	95					
	5	118					
14	1	24	4.17	44	1.83	0.51	0.40
	2	48					
	3	72					
	4	96					
Average							0.43
Standard Deviation							0.02
¹ The calibration factor in ml/ct is the slope of ml versus ct lines. To obtain the calibration factor in $\mu\text{moles/ct}$, multiply by 35.11 $\mu\text{moles/ml}$.							
² The calibration factor multiplied by the gauge reading gives uncorrected gas evolved at ambient temperature and pressure. The corrected gas evolved is obtained by subtracting liquid adjustment (Table 2) for the specified soil type.							

chromatographic analysis of the gases generated from soil/LP interaction, a standard calibration gas was run to obtain response factors for CO, CO₂, and N₂O (Table 9). The composition of the calibration gas, purchased from Scott Specialty Gases, was 35.578 mole percent N₂, 5.952 mole percent CO, 30.16 mole percent CO₂, and 28.31 mole percent N₂O. The response factors for N₂ and O₂ were obtained from air controls that were run concurrently with soil/LP experiments. The composition of air was taken to be 79 mole percent N₂ and 21 mole percent O₂. All gas components were identified by the

Table 6 WES Reference—Gas Volume Calibrations and LP + Soil Results							
Sample Number	Gas Calibration ¹			Sample Results ²			
	Air Injected ml	Gauge Reading ct	Calibration Factor (ml/ct) × 10 ⁻²	Gauge Reading ct	Uncorrected Gas Evolved ml	Corrected Gas Evolved ml	Corrected to STP ml
15	1	23	4.35	31	1.35	0.09	0.06
	2	46					
	3	69					
	4	92					
16	1	24	4.29	32	1.37	0.11	0.09
	2	47					
	3	70					
	4	94					
17	1	24	4.29	38	1.46	0.20	0.16
	2	47					
	3	70					
	4	94					
18	1	23	4.22	36	1.52	0.26	0.20
	2	47					
	3	71					
	4	94					
Average							0.13
Standard Deviation							0.06
¹ The calibration factor in ml/ct is the slope of ml versus ct lines. To obtain the calibration factor in $\mu\text{moles/ct}$, multiply by 35.11 $\mu\text{moles/ml}$. ² The calibration factor multiplied by the gauge reading gives uncorrected gas evolved at ambient temperature and pressure. The corrected gas evolved is obtained by subtracting liquid adjustment (Table 2) for the specified soil type.							

characteristic retention times. A typical chromatogram is shown in Figure 2. The N₂O composition (Table 10) ranged from 0.28 mole percent to 4.13 mole percent. These values were obtained using response factors from a calibration gas with substantially greater amounts of N₂O (28.31 mole percent). Great confidence cannot be placed in the absolute accuracy of these amounts since response factors used to calculate sample compositions were not obtained from standards with comparable N₂O mole percent compositions. However, these values are believed to provide a good indicator of relative amounts of N₂O. Independently, efforts were made to detect the presence of ammonia in the evolved gases. This was accomplished using a Hayesep Q column (6 ft by 1/8 in. by 0.085 in. and 80/100 mesh) connected to the same system mentioned above. The injector was set at 75 °C and the detector 130 °C. The

Table 7
Socorro P—Gas Volume Calibrations and LP + Soil Results

Sample Number	Gas Calibration ¹			Sample Results ²			
	Air Injected ml	Gauge Reading ct	Calibration Factor (ml/ct) × 10 ⁻²	Gauge Reading ct	Uncorrected Gas Evolved ml	Corrected Gas Evolved ml	Corrected to STP ml
19	1	23	4.35	570	24.8	23.7	18.6
	2	46					
	3	69					
	4	92					
	5	115					
20	1	24	4.29	659	28.3	27.2	21.4
	2	47					
	3	70					
	4	94					
	5	117					
21 ³	1	24	4.44	585	26.0	25.5	20.1
	2	47					
	3	71					
	4	94					
	5	117					
22 ³	1	23	4.27	585	25.0	24.4	19.2
	2	47					
	3	70					
	4	93					
	5	117					
24 ³	1	24	4.26	652	27.8	27.2	21.4
	2	48					
	3	71					
	4	95					
	5	118					
Average ⁴							20.2
Standard Deviation							1.1
¹ The calibration factor in ml/ct is the slope of ml versus ct lines. To obtain the calibration factor in μmoles/ct, multiply by 35.11 μmoles/ml.							
² The calibration factor multiplied by the gauge reading gives uncorrected gas evolved at ambient temperature and pressure. The corrected gas evolved is obtained by subtracting liquid adjustment (Table 2) for the specified soil type.							
³ 0.5 ml LP was injected instead of 1 ml.							
⁴ Average of Samples 21, 22, and 24.							

Table 8
Summary Total Gas Generated

Soil	Sample Number	Calibration Factor ¹ μmol/ct	Gauge Reading ct	Equivalent Gas, μmol	Liquid Adjust- ment ² μmol	Total Gas μmol	Total Gas ³ , ml
Yuma 2A	2	1.95	135	263	45.4	218	4.88
	3	1.96	150	294		249	5.58
	4	2.00	168	335		290	6.49
	5	2.03	155	315		269	6.03
	25	1.63	242	395		350	7.87
	Average					275	6.17
China Lake A	6	2.03	77	156	47.6 ⁴	109	2.43
	7	2.01	81	163		115	2.57
	8	1.55	108	167		120	2.67
	9	1.55	99	153		106	2.36
	10	1.54	103	159		111	2.49
	23	1.56	97	151		104	2.32
	Average					111	2.47
Yokena Clay	11	1.51	44	66	46.3	20	0.45
	12	1.48	45	66		20	0.45
	13	1.48	44	65		19	0.42
	14	1.46	44	64		18	0.40
	Average					19	0.43
WES Reference	15	1.53	31	47	44.3	3.1	0.06
	16	1.51	32	48		4.0	0.09
	17	1.51	34	51		7.0	0.16
	18	1.48	36	53		9.0	0.20
	Average					5.8	0.13
Socorro P	19	1.53	570 ⁵	870	38.2	831	18.6
	20	1.51	659 ⁵	993		955	21.4
	21 ⁶	1.56	585	882	19.1	863	20.1
	22 ⁶	1.50	585	878		859	19.2
	24 ⁶	1.49	652	974		955	21.4
	Average for Samples 21, 22, 24					892	20.2

¹ See Tables 3-7.

² See Table 2.

³ Standard temperature and pressure.

⁴ This is the average of two liquid adjustments; see Table 2.

⁵ Sample had not equilibrated.

⁶ 0.5 ml LP was injected instead of 1 ml.

Table 9
Gas Chromatograph Standard Gas Calibration Data¹

For Sample Number		N ₂	O ₂	CO	CO ₂	N ₂ O
2-3	Height Response	191312	40958	13057 13419	93854 96311	84441 86650
	Response Factor (× 10 ⁻⁴)	4.129	5.127	4.496*	3.172*	3.309*
4	Height Response	191929	41994	14285	101727	91591
	Response Factor (× 10 ⁻⁴)	4.116	5.001	4.167	2.965	3.091
5	Height Response	194695	42188	13998	99798	89749
	Response Factor (× 10 ⁻⁴)	4.058	4.978	4.252	3.022	3.154
7,9-10	Height Response	197450	42959	14298	101636	91358
	Response Factor (× 10 ⁻⁴)	4.001	4.888	4.163	2.967	3.099
11-14	Height Response	202162 199169	43859 43535	14519	103326	93002
	Response Factor (× 10 ⁻⁴)	3.937*	4.806*	4.099	2.919	3.044
15	Height Response	201220	43908	14348	102553	92208
	Response Factor (× 10 ⁻⁴)	3.926	4.783	4.148	2.941	3.070
16-18	Height Response	200828	43980	14003	99730	89790
	Response Factor (× 10 ⁻⁴)	3.934	4.775	4.251	3.024	3.153
19-20	Height Response	200552	43807	14212	100805	90638
	Response Factor (× 10 ⁻⁴)	3.939	4.794	4.188	2.992	3.123
21	Height Response	200263	43784	15545	110374	99396
	Response Factor (× 10 ⁻⁴)	3.945	4.796	3.829	2.733	2.848
22	Height Response	197850	43980	14243	101237	91140
	Response Factor (× 10 ⁻⁴)	3.993	4.775	4.179	2.979	3.106

¹ A standard gas was used to compute response factors for CO, CO₂, and N₂O. The N₂ and O₂ response factors were computed from ambient air controls.
Note: * Response factor is the average of two runs.

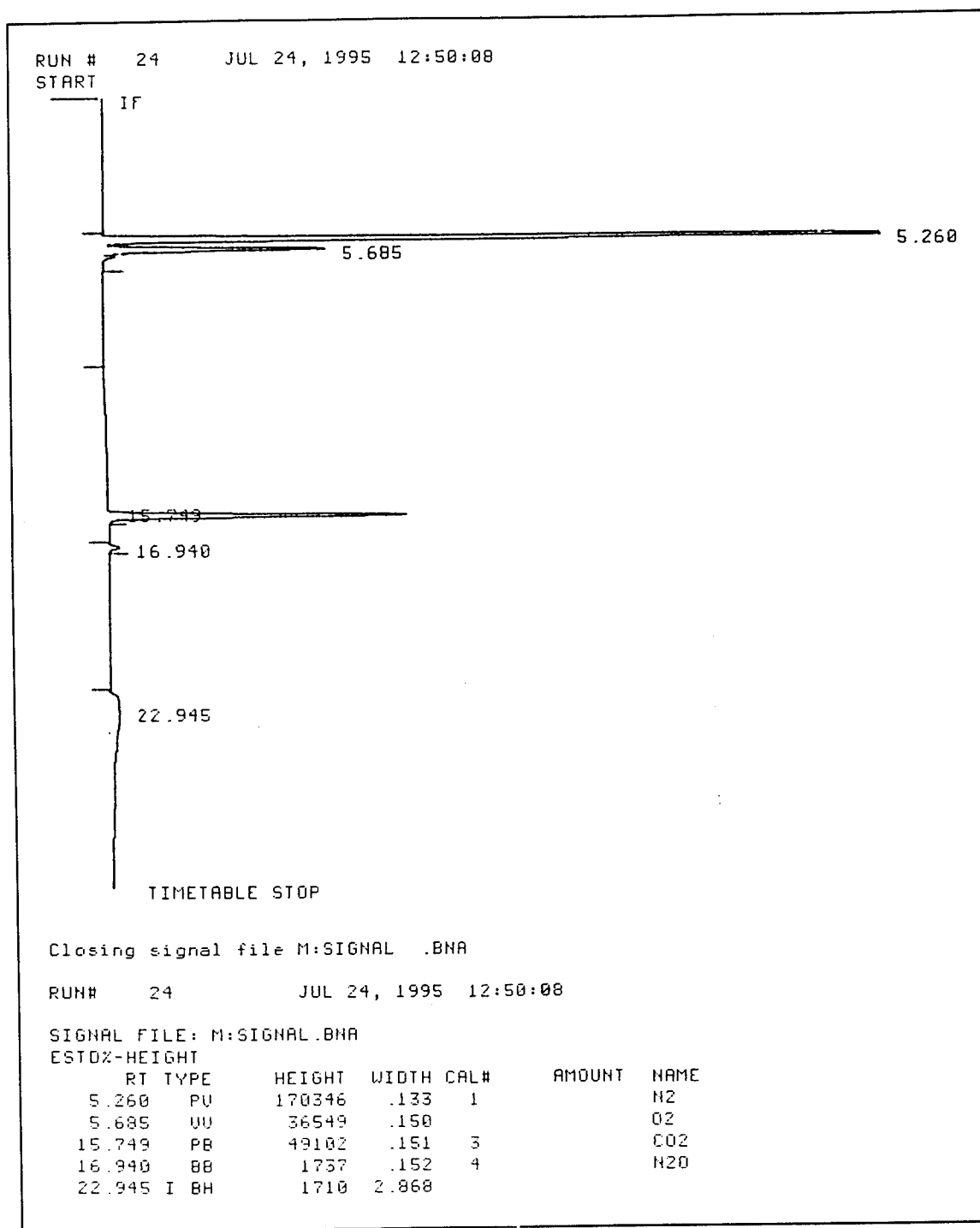


Figure 2. Gas chromatogram: A typical chromatogram of evolved gas from a soil sample (Yuma A sample #5) (Retention times for N₂, O₂, CO₂ and N₂O are 5.260, 5.685, 15.749 and 16.940 respectively. No CO was observed in this sample)

Table 10
Summary of Gas Chromatograph Results¹ in Mole Percent

Soil	Sample Number	N ₂	O ₂	CO	CO ₂	N ₂ O	Total
Yuma 2A	2	69.10	18.53	nd ²	14.84	0.42	102.84
	3	68.86	18.21	nd ²	15.45	0.51	103.03
	4	69.35	18.21	nd ²	14.63	0.49	102.68
	5	69.13	18.19	nd ²	14.84	0.55	102.71
China Lake A	7	77.64	20.55	nd ²	7.53	0.28	106.00
	8	-	-	nd ²	-	-	
	9	75.46	20.10	nd ²	8.17	0.31	104.04
	10	75.85	20.11	nd ²	8.55	0.33	104.84
Yokena Clay	11	79.22	20.73	nd ²	0.18	0.79	100.92
	12	79.32	20.87	nd ²	0.17	0.70	101.06
	13	78.76	20.64	nd ²	0.20	0.86	100.46
	14	79.41	20.74	nd ²	0.23	0.76	101.14
WES Reference	15	79.23	20.98	nd ²	0.14	0.66	101.01
	16	78.48	20.66	nd ²	trace	0.58	99.72
	17	78.35	20.74	nd ²	trace	0.76	99.85
	18	78.65	20.64	nd ²	0.12	0.68	100.09
Socorro P	19 ³	66.91	6.78	0.66	38.14	2.21	114.70
	20 ³	58.15	1.91	0.52	36.37	3.30	100.25
	21 ⁴	63.99	0.32	0.50	29.05	4.13	98.44
	22 ⁴	64.79	0.24	0.54	31.03	3.79	100.39

¹ Includes composition of air + gas evolved when 1 ml LP contacted 15 g soil for 30 min.

² None detected.

³ Sample had not equilibrated.

⁴ 0.5 ml LGP was injected instead of 1 ml.

oven condition was isothermal at 50 °C. A sample of dilute ammonia in air gave a peak at a retention time of about 2.5 min. Chromatographic analysis of samples did not reveal the presence of ammonia.

3 Results and Discussion

Three of the test soils were below the detection limit (0.10 percent) in total inorganic carbon. The other two soils, Yuma 2A and Socorro P, had 6.67 and 9.85 percent, respectively.

Total volume of gas evolved from the five soil types is summarized in Table 8. For Samples 2 to 20, the observed gas was produced by 1 ml of LP on an excess of soil (13.4 to 20.6 g, Table 1). For Samples 2 to 18, equilibration times were about 30 min. The system was judged to be equilibrated when the digital pressure gauge reading did not change for a 5-min interval of time. These criteria required much longer times for the Socorro P Samples (19-24). Samples 19-20, where 1 ml of LP was added, had not achieved equilibrium after 2.25 and 3.75 hr, respectively; furthermore, the pressure gauge readings were approaching maximum limits when the readings were taken. For Samples 21, 22, and 24, only 0.5 ml of LP was used, and final pressure readings were taken after 8, 11, and 16.5 hr. The largest producer of gas was the Socorro P soil, averaging about 20.2 ml (892 μ moles) of gas at STP, when 0.5 ml of LP was used. Both Yuma 2A and China Lake A produced moderate amounts of gas, averaging 6.17 ml (275 μ moles) and 2.47 ml (111 μ moles), respectively, at STP, when 1 ml of LP was added. Production of gas was low for Yokena Clay, averaging 0.43 ml at STP, and barely detectable for WES Reference soils, at 0.13 ml (5.8 μ moles) at STP.

Gas composition results are summarized in Tables 1, 10, and 11. The raw height response data is given in Table 1. Two calibration gases were used to relate this information to gas compositions. One calibration gas consisted of 35.578 mole percent N_2 , 5.952 mole percent CO, 30.16 mole percent CO_2 , and 28.31 mole percent N_2O . This gas was used to calculate response factors for CO, CO_2 , and N_2O , and these were used to calculate compositions given in Table 10 from raw data in Table 1. The other calibration gas was ambient air. The mole percent compositions for N_2 and O_2 in ambient air was taken to be 79 mole percent and 21 mole percent, respectively. All calibration data and response factors are in Table 9. Gas composition, in mole percent, is given in Table 10.

In all samples for all soils, N_2 and O_2 were observed, but this was attributed to the ambient air in the reaction chamber for two reasons. First, the chromatograph height responses for soil/LP samples (Table 1) ranged from

Table 11
Composition of Evolved Gases¹ (ml)

Soil Type	Sample Number	Gas Evolved + Air (see Table 1)			Gas Evolved ²				
		Mole Percent CO ₂	Mole Percent N ₂ O	Mole Percent Total	Normalized Mole Percent		Total ml	CO ₂ ml	N ₂ O ml
					CO ₂	N ₂ O			
Yuma 2A	2	14.84	0.42	15.26	97.25	2.75	4.88	4.75	0.13
	3	15.45	0.51	15.96	96.80	3.20	5.58	5.40	0.18
	4	14.63	0.49	15.12	96.76	3.24	6.49	6.28	0.21
	5	14.84	0.55	15.39	96.43	3.57	6.03	5.81	0.22
Average		14.94	0.49	15.43	96.81	3.19	6.17	5.97	0.20
China Lake A	7	7.53	0.28	7.81	96.41	3.59	2.43	2.34	0.09
	9	8.17	0.31	8.48	96.34	3.66	2.36	2.27	0.09
	10	8.55	0.33	8.88	96.28	3.72	2.49	2.40	0.09
Average		8.08	0.31	8.39	96.34	3.66	2.47	2.38	0.09
Yokena Clay	11	0.18	0.79	0.97	18.56	81.44	0.45	0.08	0.37
	12	0.17	0.70	0.87	19.54	80.46	0.45	0.09	0.36
	13	0.20	0.86	1.06	18.87	81.13	0.42	0.08	0.34
	14	0.23	0.76	0.99	23.23	76.77	0.40	0.09	0.31
Average		0.20	0.78	0.97	20.05	79.95	0.43	0.09	0.34
WES Reference	15	0.14	0.66	0.80	17.50	82.50	0.06	0.01	0.05
	16	nd ³	0.58	0.58	-	-	0.09	-	-
	17	nd ³	0.76	0.76	-	-	0.16	-	-
	18	0.12	0.68	0.80	15.00	85.00	0.20	0.03	0.17
Average		0.13	0.69	0.82	15.82	84.18	0.13	0.02	0.11
Socorro P	21	29.05	4.13	33.18	87.55	12.45	20.10	17.60	2.50
	22	31.03	3.79	34.82	89.12	10.88	19.20	17.11	2.09
Average		29.22	3.85	33.07	88.37	11.63	20.20	17.85	2.35

¹ Gases evolved when 1 ml LP (Samples 21 and 22 used 0.5 ml LP) contacted approximately 15 g soil for about 15 min. Observed N₂ and O₂ are assumed to be from air and are removed.

² Standard temperature and pressure.

³ None detected.

approximately 107000 to 202000. Air controls gave height responses ranging from about 191000 to 201000 (Table 9). If a significant amount of N₂ was generated by soil/LP interactions, then increases in the height response, above ambient values, would be expected. Where other gases besides N₂ are produced, the N₂ height responses should decrease in proportion to the evolved gas volume (0.1 to 6 ml) compared with the volume of the test chamber (30 to 35 ml). For Yokena Clay and WES Reference samples, where only slight

amounts of gas were produced, N₂ and O₂ compositions are nearly those of the ambient air. Decreasing values for N₂ and O₂ composition in Yuma 2A and China Lake A samples appear to be associated with dilution by the evolved gas. Second, the average height response N₂/O₂ ratios for Yuma 2A, China Lake A, Yokena Clay, and WES Reference soils (Table 1) is 4.632 with a standard deviation of 0.032, while the average for air controls is 4.585 and standard deviation of 0.040 (Table 12). Since these values are not significantly different, it is believed that neither N₂ nor O₂ was produced from Yuma 2A, China Lake A, Yokena Clay, or WES Reference soils. For samples using Socorro P soils, N₂ peak heights are somewhat lower than observed with the other soils. This is probably due to the large amount of gas production associated with these samples. The fact that the nitrogen peaks are not lower might even argue that nitrogen is produced in the reaction of LP with this soil. However, the remarkable thing about these samples is the dramatic decrease in O₂ composition. This seems to be correlated with the production of large quantities of CO₂.

Table 12
Gas Chromatograph Height Responses for Air Controls

Soil	Sample Number	N ₂ Height	O ₂ Height	N ₂ /O ₂ Ratio
Yuma 2A	2-3	191312	40958	4.671
	4	191929	41994	4.570
	5	194695	42188	4.615
China Lake A	6-10	197450	42959	4.596
Yokena Clay	11-14	202162	43859	4.609
		199169	43535	4.575
WES Reference	15	201220	43908	4.583
	16-18	200828	43980	4.566
Socorro P	19-20	200552	43807	4.578
	21	200263	43784	4.574
	22	197850	43980	4.499
Average				4.585
Standard Deviation				0.040

According to chromatographic results, the interaction of LP with Yuma 2A, China Lake A, Yokena Clay, and WES Reference soils produced carbon dioxide and nitrous oxide. While a small amount of generated nitrogen might have gone undetected, ammonia and oxygen were not produced. For the Yuma 2A and China Lake A soils, the composition of the evolved gas was primarily CO₂ with a small amount of N₂O. In contrast, Yokena Clay and WES Reference soils produced predominately nitrous oxide. For Socorro P soil, interpretation was complicated due to consumption of O₂ and production of CO₂ (Table 10). (The detection of CO is considered insignificant.)

Results of Pearson Product Moment Correlation Analysis revealed high positive correlation (correlation coefficient of 0.92 at a P-value of 0.03) between total gas and total inorganic carbon. Therefore, acid hydrolysis of soil carbonates by LP is a likely source of CO₂ generation. A hazard of high CO₂ generation may exist if LP is spilled onto high carbonate soil in a confined space. Exceedance of the Occupational Safety and Health Agency (OSHA) permissible exposure limit of 5,000 ppm (0.5 percent) may result in health effects.¹

As shown in Table 10, N₂O was detected in all samples. For samples using Yuma 2A, China Lake A, Yokena Clay, or WES Reference soils, the amount of nitrous oxide generated was relatively constant. Since WES has already shown that residual HAN is not detected in the soils that were treated with LP, nitrous oxide is probably the major decomposition product of LP treated with soil.² For Yuma 2A and China Lake A soils, the production of N₂O is overshadowed by the oxidation of the soil resulting in CO₂; but for Yokena Clay and WES Reference soils, which have little carbonaceous materials available for oxidation, nitrous oxide becomes the principal LP decomposition product.

¹ National Institute for Occupational Safety and Health. (1987). "NIOSH pocket guide to chemical hazards," U.S. Department of Health and Human Resources, Washington, DC.

² Pennington, J. C., Adrian, D. D., Price, C. B., Gunnison, D., Rathbum, D. W., Myers, T. E., Strong, A. B., Harrington, J. M., Stewart, J. L., Busby, J. A., and Marcev, J. R. (1994). "Interactions of liquid propellant/LP XPM46 with soils," Technical Report EL-94-10, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

4 Conclusions

While it is obvious that the LP reacts with soils, the actual interaction is dependent on soil properties. Some soils respond mainly to the acidic nature of the LP, e.g., reaction of LP with carbonate in the soil. This is evidenced by the high CO_2 content of the evolved gas. Other soils degrade LP, evidenced by the high N_2O and low CO_2 content of the evolved gas. One soil was unique in its response to LP; oxygen depletion in conjunction with CO_2 production was observed. A hazard of high CO_2 generation may exist if LP is spilled onto high carbonate soil in a confined space.

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Environmentally responsible handling of a new liquid propellant formulation (LP XM46) led the Crusader Program to sponsor research on remediation technologies potentially useful in the event of an LP spill onto soil. Based on interactions of LP with soils described by previous research, a technology review and several laboratory-scale research projects were conducted. The technology review assessed suitability of soil washing, bioremediation, and enhanced natural attenuation. Research addressed implementation of soil washing, rate of potential nitrate loading to groundwater after a spill, and identification of gases evolved when LP initially contacts soils.

Results confirmed that soil washing is an effective procedure for removing LP components from soils. A potential limitation to soil washing is disposal of the high nitrate wash water. Bioremediation and natural attenuation have some potential if the highly acidic soil resulting from an LP spill can be adjusted and the LP diluted to reduce toxicity to soil microflora. Results of nitrate studies suggest that immediate containment/remediation response will be necessary to ensure protection of groundwater from nitrate contamination in the event of large spills. Although gas production from LP reactions with soils is often visible as frothing of the soil surface, no noxious gases, such as NO_x, were detected. However, spills to high carbonate soils in a confined space may present a CO₂ health hazard.

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All three of the technologies for remediation of LP-contaminated soils are promising. Each will require additional development; however, soil washing and enhanced natural attenuation are probably closer to readiness than is bioremediation.

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Leaching
Liquid propellant
Natural attenuation

Nitrate
Soil remediation
Soil washing
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