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THE FATE AND BEHAVIOR OF LEAD ALKYLS IN THE SUBSURFACE ENVIRONMENT

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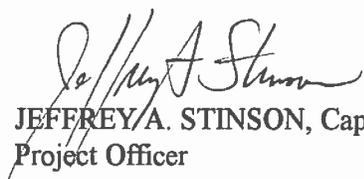
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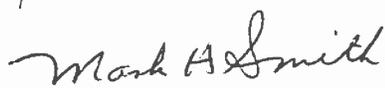
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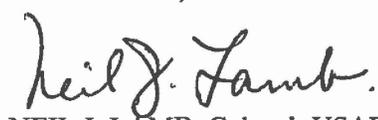
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14. Abstract   The transformation and sorption properties of lead (Pb) alkyls in the subsurface were determined to assist the Air Force in predicting the migration of, and risks associated with, Pb alkyls in soil and groundwater. Studies included Pb alkyl sorption/desorption in representative soils; sorption and degradation in soils of tetraethyl lead (TEL) in hexane and microemulsion phases; fate and transport of TEL in water-saturated sand and loam soil columns; fate and transport of triethyl lead (TREL) in water-saturated sand soil columns; impact of leaded gasoline in-water (LG/W) microemulsion flow on the transport of TEL, total Pb, and gasoline through a sand soil column; and biodegradation of Pb alkyls in soil samples in contact with aqueous solutions of Pb alkyls.

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PREFACE

This study, entitled "The Fate and Behavior of Lead Alkyls in the Subsurface Environment", was initiated under Contract F08635-90-C-0064 from the Battelle Memorial Institute in Columbus, Ohio, with the Armstrong Laboratory Environics Directorate (AL/EQ), Tyndall Air Force Base, Florida 32403-5323. This work was performed between 30 September 1990 and November 1995.

This final report describes investigations of sorption/desorption, fate and transport, and biodegradation of lead alkyls in subsurface environments conducted by the Soil and Water Science Department, University of Florida, Gainesville, Florida 32611. Dr. R. Mansell was the project leader and principal investigator. Dr. L. Ou and Dr. R. Rhue were investigators. Dr. Y. Ouyang was a postdoctural research associate at the University of Florida during the performance of the studies reported here.

The AL/EQW technical project officers were Mr. Paul Carpenter (during the initial stage of the project) and Capt Jeffrey A. Stinson (during the latter stage). In addition, Dr. Robert Olfenbuttel, Director of DoD Programs Development at Battelle, managed the overall effort.

EXECUTIVE SUMMARY

A.   OBJECTIVES

This research, conducted under the Environics Task Order Contract No. F08635-90-C-0064, investigated:

- Sorption/desorption of lead (Pb) alkyls in soils when the soils were placed in contact with leaded gasoline or analytical lead alkyls

- Sorption and degradation in soils of tetraethyl lead (TEL) in hexane and microemulsion phases

- Fate and transport of TEL in water-saturated Arredondo sand and Madison loam soil columns during immiscible flow of leaded gasoline with a sequential flushing of soil columns by aqueous solution and surfactant-cosurfactant mixture

- Fate and transport of triethyl lead (TREL) in water-saturated Leon sand soil columns during miscible flow of an aqueous solution

- Impact of flow of leaded-gasoline-in-water microemulsion on the transport of TEL, total lead, and gasoline through Astatula sand soil column

- Biodegradation of lead alkyls in samples of soils that have been placed in contact with aqueous solutions of lead alkyls.

B.   BACKGROUND

Pb contamination is a nationwide public health problem. It is prevalent in urban metropolitan areas and in sites where there have been leakages and spills of automobile and aviation leaded gasoline from underground s. rage tanks. Pb in the bloodstream has been shown to produce toxic effects in children, such as low red intelligence and dysfunctional behavior. In senior adults, Pb exposure causes high blood pressure, which is associated with increased risks of heart attack, stroke, and death. The source of most Pb cont. mination is the past use of vehicles using leaded gasoline. Other sources include the production of Pb-acid storage batteries and the use of Pb-based paint on houses.

Lead alkyl species used in automobile and aviation transportation include TEL, tetramethyl lead, triethylmethyl lead, dimethyldiethyl lead, and trimethylethyl lead compounds. All of these compounds have been used as antiknock agents and have provided a convenient and inexpensive means of enhancing octane ratings. Use of leaded gasoline was almost global for more than 50 years, from 1925 to 1975. The amount of Pb released in automobile exhaust during that time accounted for more than half of the total yearly Pb pollution of the entire earth. Production of leaded gasoline in the United States peaked in early 1970 and steadily declined after 1975. Now only Pb-free gasoline may be used as an automotive fuel in the United States, but leaded gasoline still is used in many countries for aviation and automotive fuel. Extensive use of Pb antiknock additives in gasoline has made Pb perhaps the most widely distributed toxic heavy metal in the urban environment.

Soils at Air Force bases may have become contaminated with lead alkyls from leaded aviation gasoline through leakage from storage tanks, accidental spillage near storage facilities, and previous disposal of fuel sludge from storage tanks. Soils in the vicinity of storage areas are known to be susceptible to Pb contamination during leakage and accidental spillage, but very little research has been reported on the interactions of lead alkyls in soil and groundwater. Therefore, there is a need to investigate the fate and transport of lead alkyls in subsurface environments. This research work was designed to satisfy that need.

C.   SCOPE

This report is presented in 13 sections. Section I gives an introduction to lead-alkyl contamination problems in subsurface environments. Sections II and III examine the sorption/desorption behaviors of lead alkyls in soils. Sections IV through VI present results from the investigations of fate and transport of TEL, TREL, and leaded-gasoline-in-water (LG/W) microemulsion through soil columns. Section VII describes a new method for measuring TEL and total Pb in organic solvents. The method was created during the course of this research. Sections VIII, IX, and X describe the biodegradation of lead alkyls in soils. Conclusions and recommendations are given in Sections XI and XII, respectively. References cited in the text and tables are given in Section XIII.

D.   SUMMARY OF KEY FINDINGS

Degradation and sorption by Arredondo sand soil of TEL in gasoline and LG/W microemulsion were studied. Results showed that TEL is unstable in the soil and undergoes a dealkylation to TREL. TREL is toxic and highly water-soluble. Leakage of leaded gasoline with TEL as a major Pb species may contaminate groundwater due to the dealkylation of TEL into water-soluble TREL and inorganic Pb^{+2}.

Investigations of the fate and transport of TEL during the immiscible flow of gasoline in Madison loam and Arredondo sand soils with velocities of 1.5 and 2.5 cm h^{-1}, respectively, were performed. Results showed that TEL can transport through the soil columns due to the migration of gasoline. Speciation of the TREL and diethyl lead (DEL) derived from TEL that were found in the effluent and soil samples indicated that TEL was unstable during the immiscible flow of gasoline. An aqueous solution (i.e., NaCl solution) may be used to displace some of the gasoline that is mobile in the soil pores, but not the residual gasoline. Residual analysis showed that remediation efficiency of the water-surfactant-cosurfactant mixture for removing gasoline and total Pb in Arredondo sand soil experiments was 100 percent, whereas it was 94.1 percent and 93.4 percent, respectively, for gasoline and for total Pb in Madison loam soil experiments.

Experiments were conducted to investigate the fate and transport of TREL in water-saturated Leon sand soil columns. Total Pb but not TREL was found in the effluent and soil samples at the end of the experiments, indicating that TREL is very unstable and degrades into other Pb species. A mass balance analysis show that only 22 percent of total Pb was washed out from the soil columns by the NaCl solution. This indicates that most of the total Pb was adsorbed by the soils.

The use of surfactants to remove hydrocarbons from soil has shown significant potential. However, one of the most important problems with this remediation technique — the formation of emulsion — has been ignored. Flow of macroemulsion has been shown to inhibit the transport of hydrocarbons through soil. In contrast, flow of microemulsion may enhance the transport of gasoline and Pb through soils. An experiment was conducted to compare the influence of the LG/W microemulsion miscible flow with that of the LG/W immiscible flow upon the transport of gasoline, TEL,

and total Pb in Astatula sand soil columns. Results showed that the LG/W microemulsion flow enhances the transport of gasoline, TEL, and total Pb. A major factor causing a difference in the behavior of gasoline-water flow and LG/W microemulsion flow is the size of gasoline droplets in aqueous phase. Gasoline droplets are very large in gasoline-water flow because the two liquids are immiscible. In microemulsion flow, the size of the gasoline droplets ranges from 0.01 to 0.1 μm, which is comparable to the soil pore size; therefore, clogging of soil pores by droplets is greatly minimized.

Measuring TEL and total Pb contents in organic solvent with current techniques is time-consuming and expensive. A simple technique called the Iodine Monochloride (ICl) Digestion Method was developed in this study. TEL contained in samples first was converted to Pb^{+2} by 0.1 M ICl solution, and then the total Pb content was measured using atomic absorption spectrophotometry (AAS). Finally, the concentration of TEL was estimated through a back calculation using the molecular fraction of Pb in TEL. This method seems efficient and cost-effective compared to other methods. It has a recovery rate ranging from 92.7 to 102.3 percent and a coefficient of variability (CV) ranging from 1.02 to 1.9 percent for all measurements in this experiment. The high recovery rate and low CV indicate that the ICl Digestion Method can be applied to measure both TEL and total Pb content in organic solvents.

TEL in gasoline and hydrocarbon solvents (e.g., hexane and benzene) is very stable under dark conditions, but TEL in nonsterile and autoclaved surface and subsurface soils rapidly degrades. Biological and chemical degradation are both responsible for the degradation of TEL in surface and subsurface soils. Of the two, chemical degradation is the major factor. Biological degradation is estimated to be responsible for up to 20 percent of TEL degradation in nonsterile soils. Degradation of TEL in surface soils generally is more rapid than in subsurface soils.

E.   APPLICATIONS AND RECOMMENDATIONS

This research work provides a better understanding of the sorption/desorption, biodegradation, fate and transport, and remediation of lead alkyls or gasoline in soils. Results from this research should be of most interest to researchers and scientists interested in the fate, transport, and remediation of contaminants in subsurface environments. Increasing concerns over soil and groundwater contamination have caused rapid growth of research on the fate and transport, remediation, and modeling of contaminants. Knowledge of the various physical, chemical, and biological processes of contaminants in subsurface environments is crucial for such research.

Based on our findings, the following recommendations are offered for future research into the fate, transport, and remediation of non-aqueous-phase liquids (NAPLs) and heavy metals.

1.   Laboratory studies should be conducted to explore the fate and transport of heavy metals and NAPLs in heterogeneous and layering soil systems.

2.   Research should be initiated on the long-term abiotic and biotic transformations of residual NAPLs. These transformations would affect its mobilization, composition, and ability to dissolve into groundwater.

3.   Soil and NAPL interactions should be examined in the laboratory to provide an assessment of the importance of NAPL wettability and permeability.

4.   Further laboratory- and field-scale investigations of the formation, stability, and flow of microemulsions in heterogeneous soil systems should be conducted, because the use of

microemulsions to remediate NAPLs and heavy metals from contaminated soils has high potential.

5. Research should be directed toward developing and applying mathematical models to guide contaminant remediation practices. These models would provide information on the stability and flow of NAPL-in-water microemulsions; such information is needed to optimize the use of surfactants and cosurfactants.

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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

A	cross section area
AAS	atomic absorption spectrophotometry
AFB	Air Force Base
Al	aluminum
ASTM	American Society for Testing and Materials
BTC	breakthrough curve
Bu-DEL	butylized diethyl lead
Bu-TREL	butylized triethyl lead
C	carbon
CEC	cation exchange capacity
CV	coefficient of variability
ρ_b	bulk density
DEL	diethyl lead
DI	deionized
EDTA	ethylenediaminetetraacetic acid
Fe	iron
GC	gas chromatograph, gas chromatography
HP	Hewlett-Packard
ICl	Iodine Monochloride Digestion Method
K_{oc}	adsorption coefficient of organic carbon
KOH	potassium hydroxide
L	column length
LG/W	leaded-gasoline-in-water
LSC	liquid scintillation counting
MEL	monoethyl lead
NaDDTC	sodium diethyldithiocarbamate
NAPL	non-aqueous-phase liquid
N_c	capillary number
Pb	lead
SDS	sodium lauryl sulfate
Si	silicon

TEL	tetraethyl lead
THF	tetrahydrofuran
TLC	thin layer chromatography
TML	tetramethyl lead
TREL	triethyl lead
TRML	trimethyl lead
UV	ultraviolet
V	Darcy velocity
W/O	water/oil
W/S/CoS	water-surfactant-cosurfactant

SECTION I

INTRODUCTION

A.   OBJECTIVES

The purpose of this research was to investigate the fate and transport in soils of lead (Pb) alkyls in the form of leaded aviation gasoline or analytical alkyl Pb compounds. Air Force Base (AFB) soils may have become contaminated with Pb alkyls from leaded aviation gasoline through leakage from storage tanks, accidental spillage near storage facilities, and previous disposal of fuel sludge. Leaded aviation gasoline and analytical Pb alkyl compounds were applied to soils to provide spiking with Pb alkyls. These Pb alkyl-contaminated soil samples were used to perform sorption/desorption investigations. Microbial degradation investigations were performed by applying analytical Pb alkyl compounds to soil samples. Mobility transport investigations were performed by displacing a pulse of leaded aviation gasoline through water-saturated columns of uncontaminated soils, displacing the leaded gasoline with an aqueous solution and a water-surfactant-cosurfactant mixture, and determining concentrations of Pb alkyls, total Pb, and gasoline in column effluent and soil samples.

Three types of soils were used in the experiments. A first soil sample (Madison loam soil) included materials from A and B horizons collected from an area adjacent to an old tank at Dobbins AFB in Georgia. A second soil sample, taken from Tyndall AFB in Florida, is Leon sand, which is a typical Spodosol from A, E, and Bh horizons. Finally, samples from A and B horizons of an Arredondo soil were collected from a location near the University of Florida campus in Gainesville, Florida.

The main objectives of this research, conducted under the Environics Task Order Contract No. F08635-90-C-0064, were as follows:

1.   Investigate the sorption/desorption of Pb alkyls with these soils by (a) determining sorption isotherms for TEL on soil, specimen clay minerals (kaolinite and montmorillonite), and oxides (Fe, Al, and Si); (b) determining the extent of desorption of TEL and TREL into aqueous solutions from the adsorbents; and (c) determining the partitioning of TEL between gasoline and water.

2.   Investigate the mobility of Pb alkyls through soil columns by (a) evaluating the fate and transport of TEL and its degradation products through soil columns with Darcy flow velocities of 1.5 and 2.5 cm h^{-1} during flow of leaded gasoline, water, and surfactant-cosurfactant mixture; (b) evaluating the fate and transport of TREL through soil columns during miscible flow of TREL and aqueous solutions; and (c) comparing the influence of the LG/W microemulsion flow and the leaded-gasoline-water flow on the transport of gasoline and Pb species through soil columns.

3.   Evaluate the biodegradation of Pb alkyls in samples of soils that have been placed in contact with Pb alkyls by (a) determining the role of microorganisms on degradation of TEL and its two suspected weathering products (TREL and DEL) in subsurface soils; (b) determining biodegradation rates of TEL and the two weathering products in these soil samples; (c) isolating microorganisms capable of degrading TEL and the two weathering products from these soil samples and from leaded gasoline-contaminated soils

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(if available); and (d) testing their capacity to detoxify TEL and the two weathering products from contaminated soils.

B. BACKGROUND

Pb contamination is a nationwide public health problem and is prevalent in urban metropolitan areas (Mielke et al., 1983) and in sites where automotive and aviation leaded gasoline has leaked and spilled from underground storage tanks. Pb in the bloodstream has been shown to produce toxic effects in children, such as lowered intelligence and dysfunctional behavior. In senior adults, Pb exposure causes high blood pressure, which is associated with increased risk of heart attack, stroke, and death (Driscoll et al., 1992). Most Pb contamination is caused by emissions from vehicles using leaded gasoline (Adriano, 1986). Other sources of Pb contamination include the production of Pb-acid storage batteries and the use of lead-based paint on houses (Mielke et al., 1983; Rhue et al., 1992).

TEL is a major alkyl Pb species in leaded gasoline. It was introduced as a commercial antiknock agent in 1923 by the General Motors Development Company in Dayton, Ohio (Lewis, 1985; Nickerson, 1954; Shapiro and Frey, 1968). Production of TEL rose during the 1930s and increased enormously during World War II (Lewis, 1985). By 1950, most gasoline was leaded.

The large estimated values derived by Bauer (1986) for the organic carbon adsorption coefficient K_{oc} for TEL ($1,058 \times 10^4$) by Bauer (1986) indicate that both Pb-containing compounds tend to be immobilized by organic matter generally present in the surface horizons of most soils. However, in sandy soils containing low concentrations of organic matter, TEL should migrate readily downward to the underlying groundwater. Once degraded to TREL, the mobility of the contained Pb would be expected to increase because of the greater water solubility of these substances.

Very little is known about the biodegradation of TEL compounds and their associated weathering products in soil-sediment systems. Microorganisms capable of degrading TEL compounds have not been reported. It is likely that the weathering products of TEL, such as trialkyl lead and dialkyl lead, may be degraded biologically in soil and water. A soil bacterium (*Arthrobacter* sp.) and a wood decay fungus (*Phaceolus schweinitzii*) were found to have some capacity to degrade trimethyl lead.

The mobility of alkyl lead compounds in sludge-contaminated soils is largely unknown primarily because of the unknown chemical reaction or sorption by mineral and organic soil components. As rainwater infiltrates into soils, the leachability of Pb alkyls will be determined largely by sorption reactions. An unknown but finite potential exists for leachability of organolead compounds from soils previously used for disposal of fuel sludge. The high water solubility of TREL and trimethyl lead (TRML) organic cations makes these compounds particularly suspect for mobility in soil systems during periods of net water infiltration into the soil.

In the past, disposal of all such sludges was performed by removing the liquid through evaporation, sedimentation, or centrifugation; resuspension of the solids in water; and dispensing this slurry into evaporation/settling pools. Exposure to oxygen in the presence of sunlight allowed the TEL species to photodegrade to elemental ionic Pb and to combine with oxygen to form water-insoluble Pb oxide (Jarvie, 1988). Any excess ionic Pb was assumed to be adsorbed to organic material in the bottom of the pool. All other components were assumed to decompose to nonhazardous materials. The sediments in these pools were usually scraped up and placed in "secure" landfills or sold to companies involved in the reclamation of used Pb. However, in many cases the sediment was simply spread over fields and plowed under. This procedure offers questionable safety. The environmental acceptability of

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this method is based on the unproven assumption that most or all of the organoleads initially present were in forms inaccessible to organisms by the time the water had evaporated from the pools.

Soils near storage areas for leaded gasoline are known to be susceptible to Pb contamination during leakage and accidental spillage. However, very little research has been reported (Rhue et al., 1992) for interactions of Pb alkyls in soil and groundwater. Therefore, there is a need to investigate the fate and transport of Pb alkyls in subsurface environments. This research work was designed to satisfy this need.

C.   SCOPE

The mechanisms of soil retention of TEL and its derivatives are very complex and involve adsorption/desorption, exchange reactions, precipitation, occlusion, microbial metabolism, and complexation with native soil organics. Batch equilibrium studies were conducted to determine sorption/desorption isotherms, and an effort was made to identify the exact reactions between TEL and soil constituents.

There is no published experimental information on the biodegradation of TEL in either microbial cultures or soil substrates. Little is known about the biodegradation of TEL and its weathering products (principally TREL and DEL) in surface and vadose zone soils and groundwater or in microbial cultures. Therefore, it is essential that we demonstrate the role of microorganisms in the degradation of these chemicals in soils.

The fate and transport of Pb alkyls through subsurface environments in soils contaminated with leaded gasoline are not understood because the chemical, physical, and biological reactions of Pb alkyls in soil and groundwater environments are not known. To assess the impacts that soils contaminated with leaded gasoline have on local groundwater supplies, it is necessary to determine the fate and transport mechanisms of Pb alkyls during net water flow through the soil.

This report presents laboratory investigations into the fate and transport of Pb alkyls and gasoline in subsurface environments. It provides an improved understanding of the basic mechanisms of (1) the fate and transport of TEL, TREL, and gasoline through water-saturated soil columns; (2) the degradation and sorption of TEL in soil environments; (3) the flow of the LG/W microemulsion and its effect on the transport of total Pb and gasoline in saturated soil; (4) the remediation of total Pb and gasoline using a microemulsion technique; and (5) the biodegradation of Pb alkyls. In addition, a method for measuring the total Pb and TEL in organic solvents was developed during the course of the investigations. Detailed experimental procedures and analytical methods are given in each section.

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SECTION II

DEGRADATION, SORPTION, AND DESORPTION OF TETRAETHYL LEAD
IN GASOLINE AND MICROEMULSION BY SOILS

A.   INTRODUCTION

Degradation of organic alkyl lead species, such as tetraethyl lead (TEL), in soils and aquatic systems is an important factor in determining their distribution in subsurface environments. Incorporating degradation of TEL in soils into mathematical models and environmental remediation practices is crucial in predicting the fate and transport of Pb species through soil and groundwater. Degradation of TEL occurs through a series of dealkylation steps and eventually results in Pb^{+2} (Rhue et al., 1992). That is, TEL first degraded to triethyl lead (TREL), then to diethyl lead (DEL), and finally to inorganic Pb^{+2}. Bauer (1986) reported that K_{oc} (adsorption coefficient of organic carbon) for TEL was 1.058×10^4. This large value was estimated from the relationship between K_{oc} and water solubility for other hydrophobic organic compounds. To our knowledge, the K_{oc} values for TEL have not been verified by experimentation. However, estimates based on solubility often are correct to within a factor of 2 to 3. Bauer concluded that TEL can be immobilized by soil organic carbon and that, in soils containing low concentrations of organic carbon, TEL can migrate readily. Bauer's inherent assumption is that there is negligible sorption of TEL from solution onto soil mineral surfaces. This may not be true and thus requires experimental validation.

Jarvie et al. (1981) investigated the decomposition of organolead compounds adsorbed onto silica gel (100 to 200 m h). The authors noted that TEL in aqueous suspensions adsorbed onto the glass walls of the containers and could be recovered by benzene extraction. Sorption to the walls is not surprising when one considers that the authors made the TEL "solutions" exceed the solubility limit of TEL in water by more than 100 times. The authors reported that TEL was totally adsorbed from aqueous solution onto silica. The adsorbed species were rapidly degraded to TREL, which was the only detectable organolead product. In contrast, Schmidt and Huber (1976) reported no adsorption of TEL compounds by sediments. This discrepancy was explained by the fact that inorganic Pb compounds displace alkyl lead compounds from silica and sediment surfaces, thus showing the strongly competitive nature of inorganic relative to organic Pb compounds. This suggests that, in a sludge material dominated by inorganic Pb compounds, the potential mobility of the highly toxic alkyl lead compounds may be quite high. In the absence of inorganic Pb, TREL was totally adsorbed from aqueous solution by silica.

Ripley and Towner (1984) investigated sorption of Pb alkyls (10^{-5} M) onto amorphous iron (III) hydrous oxide (specific surface area of 300 m^2 g^{-1}, zero point of charge of 7.9). They found that no TREL adsorbed to any detectable extent over the pH range from 5 to 10. Edwards et al. (1975) performed work on the sorption of TEL vapor onto alumina, silica, carbon black, and graphitized carbon black, which were assumed to simulate atmospheric dust components. These materials adsorbed a substantial amount of TEL when exposed to the vapor. Edwards et al. (1975) present vapor-phase sorption isotherms of TEL onto these materials. Laxen and Harrison (1977) reported that dialkyl lead salts appeared to decompose rapidly when adsorbed onto atmospheric dust, whereas tetra- and trialkyl lead compounds did not. Values of adsorbed organic Pb range from 39 to 140 μg Pb per gram of atmospheric dust. However, these values generally represented < 1 percent of the total particulate Pb. Because atmospheric dust probably would have much greater surface areas and much lower quantities of adsorbed water than soil particles, vapor-phase sorption in soils may be of little importance. A search

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of published literature has not revealed any investigations of adsorption of alkyl lead compounds onto soils and sediments.

The objectives of this study were (1) to investigate the degradation and sorption of TEL in gasoline and gasoline-in-water microemulsion by Arredondo soil at times of 2, 6, 24, and 48 hours; and (2) to investigate the speciation of TREL from leaded gasoline-contaminated soil.

B.   MATERIALS AND METHODS

1.   Degradation and Sorption of TEL in Gasoline by Soil Experiment

a.   Materials

Unleaded gasoline was purchased from a local gasoline station in Gainesville, Florida. Analytical-grade TEL was purchased from All-Chemie Ltd., Ft. Lee, New Jersey. All other chemicals were analytical grade.

Arredondo fine sand was used for the batch experiments. Soil samples were collected at 0 to 15 cm depth from a site on the campus of the University of Florida, in Gainesville. Selected soil properties are shown in Table 1. Before the experiments, the soil samples were analyzed for initial TEL using gas chromatography (GC). No TEL was found in the background soil.

TABLE 1. SELECTED SOIL PROPERTIES OF ARREDONDO SOIL USED FOR THIS STUDY.

Soil Depth (cm)	pH	Water Content g/kg^{-1} soil	Organic C	Sand (%)	Salt (%)	Clay (%)
0-15	5.5	55	11.8	92	7	1
15-30	4.6	46	4.7	93	5	2
30-45	5.6	28	3.9	93	4	3

Leaded gasoline stock solution was prepared by spiking 72 μL analytical grade TEL into a 200-mL volumetric flask and diluting it with unleaded gasoline. Concentration of TEL in the stock solution was calculated to be 591.1 $\mu g/mL^{-1}$. Analytical-grade TEL was dissolved in hexane to make working standards at concentrations of 0.01, 0.05, 0.1, 1, 5, and 10 $\mu g/mL^{-1}$.

b.   Procedures

Triplicate 5-mL aliquots of leaded gasoline (containing 591.1 μg TEL/mL^{-1}) and 5 grams of wet Arredondo sand soil were added to the 50-mL test tubes and shaken for 2, 6, 24, and 48 hours, respectively. The test tubes were rotated end-over-end manually for 2 minutes and then put on the shaker to ensure complete mixing. Then the soil samples were centrifuged at 2000 rpm for 10 minutes with an International Model HN-S centrifuge. TEL in the clear supernatant liquids was extracted

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by hexane and analyzed using GC. The differences between the initial concentration and the concentrations for samples were taken as the amount of TEL degradation in the soil at a given time.

Spike analysis was conducted to ensure that TEL in gasoline can be measured by GC. Triplicate 1-mL aliquots of the leaded gasoline stock solution were transferred into a 100-mL volumetric flask and diluted with hexane. Concentrations of TEL in the solution were measured by GC.

A Hewlett-Packard (HP) 5710A gas chromatograph was used for sample quantitation. Operating conditions of this system were as follows: (1) injection sample volume, 20 μL; (2) detector temperature, 300°C; (3) injection port temperature, 150°C; (4) oven temperature, 120°C; (5) gas flowrate, 81 mL/min^{-1}.; and (6) GC column length, 6 feet with an inner diameter of 4 mm. These conditions are similar to those reported by Chakraborti et al. (1989a).

2. Degradation and Sorption of TEL in Microemulsion by Soil Experiment

a. Materials

A mixture of water-surfactant-cosurfactant (W/S/CoS) was made by mixing 4.3 grams of sodium lauryl sulfate (SDS), 8.7 grams of n-pentanol, and 87 grams of deionized (DI) water. Leaded-gasoline-in-water (LG/W) microemulsion was then prepared by mixing 2 grams of leaded aviation gasoline and 98 grams of W/S/CoS mixture. Analytical-grade TEL was dissolved in hexane to make working standards with concentrations of 0.01, 0.05, 0.1, 1, 5, and 10 μg/mL^{-1}. The leaded aviation gasoline was dissolved in n-hexane to make working standards with concentrations of gasoline at 120, 480, and 1500 μg/mL^{-1}.

b. Procedures

Duplicate 5-gram aliquots of dry Arredondo sand and 15 mL of LG/W microemulsion were added to test tubes and shaken for times of 6, 12, 24, and 48 hours, respectively. Control samples were prepared by adding 15 mL of LG/W to test tubes containing no soil for 24 hours. Then the samples were centrifuged at 2000 rpm for 20 minutes. An aliquot of 0.3 mL supernatant was transferred into 10 mL hexane for analyzing TEL using GC.

Spike LG/W microemulsion was prepared first by mixing 1 gram of unleaded gasoline, 0.05 mL of 5000 μg TEL, and 49 grams of W/S/CoS mixture. The TEL concentration in the microemulsion was 4.95 μg/mL^{-1}. Then 0.3 mL of this microemulsion was pipetted into 10 mL of hexane. Finally, 1 mL of 1 μg TEL/mL^{-1} was spiked into a 1-mL aliquot solution. This mixture has 1.074 μg TEL/mL^{-1}.

3. Speciation of TREL Gasoline-Saturated Soil Experiment

a. Materials

Analytical grades of KI, KIO$_3$, NaCl, EDTA, NaDDTC, and concentrated NH$_4$OH were purchased from Fisher Scientific (Orlando, Florida). All other chemicals used in this experiment are given in Section II, B.1.a. Solvent for extracting TREL from aqueous solution was prepared by mixing 2 grams of EDTA disodium salt and 2 mL of 0.25 M NaDDTC.3H$_2$O into a 100-mL volumetric flask. The solvent mixture was adjusted to pH = 9 with NH$_4$OH and diluted with DI water. Working standards of TREL were 0.2, 1, and 10 μg/mL^{-1}.

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b. Procedures

Soil samples from the degradation study described in Section II.B.1 were used for this washout study, and 10 mL of DI water was added to the leaded gasoline-saturated soil samples, which were then shaken for 3 hours. The samples were centrifuged for 10 minutes at 2000 rpm and decanted. The samples in soil phase, water phase, and residual gasoline phase were saved for measurement of TEL and TREL. Volumes of the residual gasoline were measured by graduated cylinder. Samples for measuring TEL concentrations in residual gasoline were prepared by adding duplicate 0.1-mL aliquots of residual gasoline into 25-mL volumetric flasks; the samples were diluted with hexane. TEL concentrations in the samples were measured by GC.

TREL in water phase was analyzed by the following procedure: (1) Pipette 5 mL of the water phase sample and 10 mL of the TREL extracting solvent into 125-mL separatory funnels and shake for 1 minute; (2) Add 5 mL of hexane into the separatory funnels and shake for 2 minutes; separate layers and save hexane phase; (3) Add 5 mL of hexane to the aqueous phase and shake for 2 minutes; separate and save hexane phase; (4) Combine hexane layers and discard aqueous phase; (5) Dry hexane with anhydrous Na_2SO_4, decant, and save hexane phase; (6) Rinse anhydrous Na_2SO_4 with 5 mL of hexane and add the hexane phases together; (7) Evaporate to dryness using evaporator; (8) Add 1 mL of 1.9 M Grignard reagent (2.0-M butylmagnesium chloride in tetrahydrofuran [THF]); (9) Swirl for 1 minute and add 10 mL of 1 N H_2SO_4 and 1 mL of hexane; (10) Shake for 2 minutes, separate, and save hexane phase; and (11) Analyze the samples for TREL by GC.

C. RESULTS AND DISCUSSION

A spike analysis of TEL in leaded gasoline stock solution shows that the average recovery rate fu the triplicate measurements was 99 percent (Table 2). This high recovery rate indicates that TEL in gasoline can be measured using GC.

TABLE 2. INITIAL TEL CONCENTRATION IN GASOLINE PREPARED BY MIXING TEL WITH UNLEADED GASOLINE.

Sample	Measured Concentration $(\mu g/mL^{-1})$	Average Concentration $(\mu g/mL^{-1})$	Theoretical Concentration $(\mu g/mL^{-1})$	Recovery Rate (%)
1	577.4	591.1	597*	99.01
2	681.7			
3	604.8			

* Theoretical TEL concentration = $(1.659 \times 10^{-8} \times 0.072)/200 = 597 \ \mu g/mL^{-1}$.

Figure 1 shows the decrease of TEL in gasoline as a function of time after contact with Arredondo sand soil. Although 55 percent of the TEL in gasoline disappeared within the first 2 hours of the experiments, only 3.4 percent disappeared from 24 to 48 hours. The dramatic decrease in TEL concentration initially was due to the degradation and sorption of TEL by the soil.

TABLE 3. SORPTION AND DEGRADATION OF TEL IN
MICROEMULSION BY ARREDONDO SOIL.

Time (hr)	Rep. #	Sample	Average
0	1	19.8	19.8
	2	19.8	
6	2	2.29956	2.29956
	2	—	
12	1	1.57536	1.549747
	2	1.524133	
24	1	1.03272	1.262107
	2	1.491493	
48	1	0.92936	1.01878
	2	1.1082	

TABLE 4. TEL CONTENT IN RESIDUAL GASOLINE DISPLACED BY WATER.
SAMPLES WERE FROM 24- AND 48-HOUR EXPERIMENTS IN SECTION II.

Sample from	Rep. #	Conc. (μg/mL^{-1})	Average (μg/mL^{-1})	Vol. of Residual Gasoline (mL)
24 hr	1	288.8	268.0	0.5
24 hr	2	247.1		0.7
48 hr	1	418.0	406.4	0.6
48 hr	2	394.7		0.6

TABLE 5. TREL CONTENT IN WATER PHASE.

Samples from	Rep. #	Sample Conc. (μg/mL^{-1})	Average (μg/mL^{-1})
24 hr	2	0.62	0.53
24 hr	3	0.43	
48 hr	2	0.98	0.84
48 hr	3	0.70	
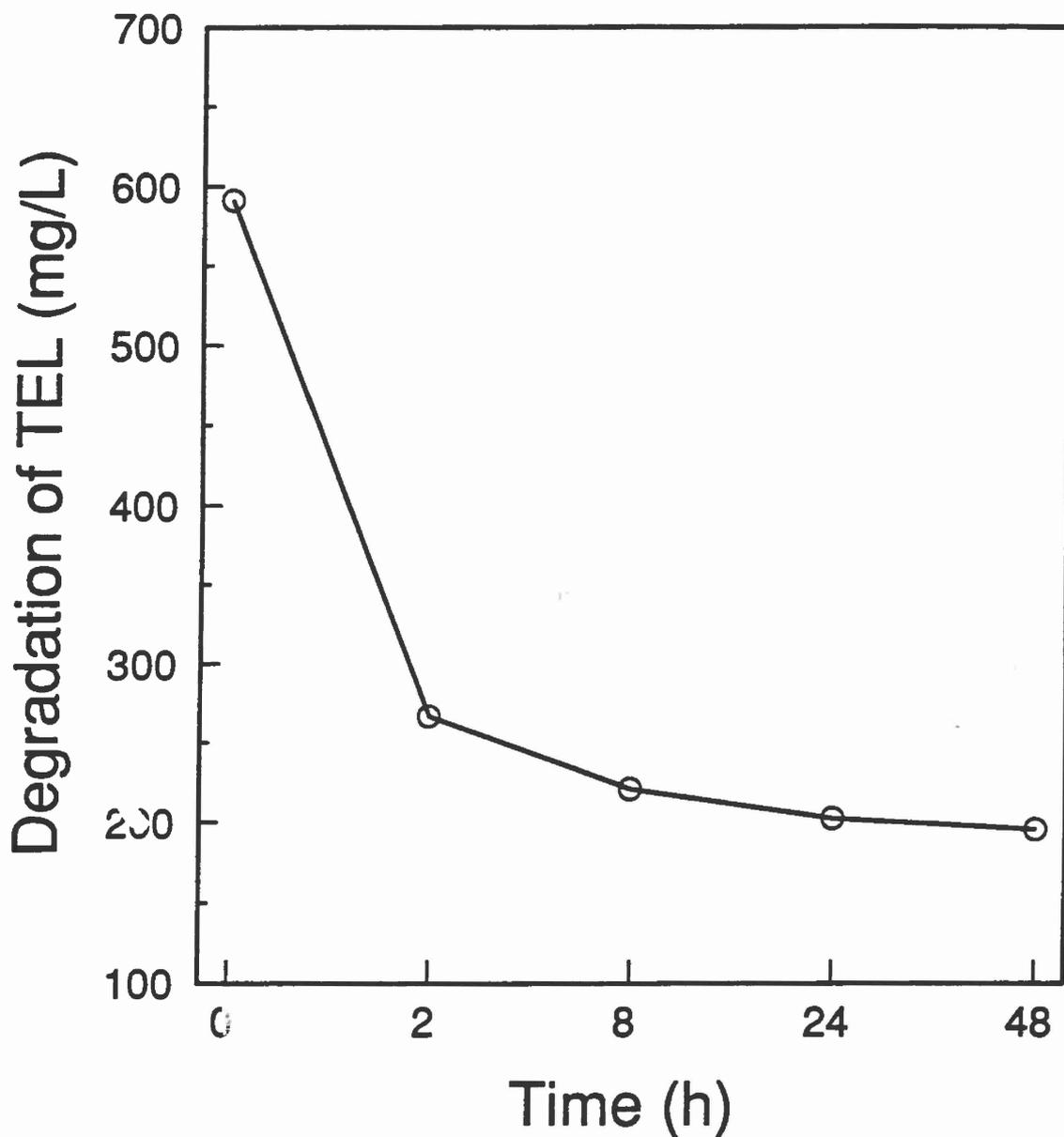
Figure 1. Degradation of TEL in Leaded Gasoline by Arredondo Soil.

A spike analysis of TEL in LG/W microemulsion shows that average recovery rate was 94.7 percent. This high recovery rate indicates that TEL in LG/W microemulsion can be measured using GC.

The decrease in TEL concentration in microemulsion at times of 0, 6, 12, 24, and 48 hours is shown in Table 3. A plot of reduced concentration as a function of time appears in Figure 2. The results obtained for TEL in LG/W microemulsion were similar to those for the leaded gasoline experiment. That is, TEL decreased dramatically during the first 6 hours and decreased slowly thereafter.

The TEL content in the residual gasoline is shown in Table 4. There were variations in TEL concentrations for all the samples because the residual gasoline contained organic matter and colloidal
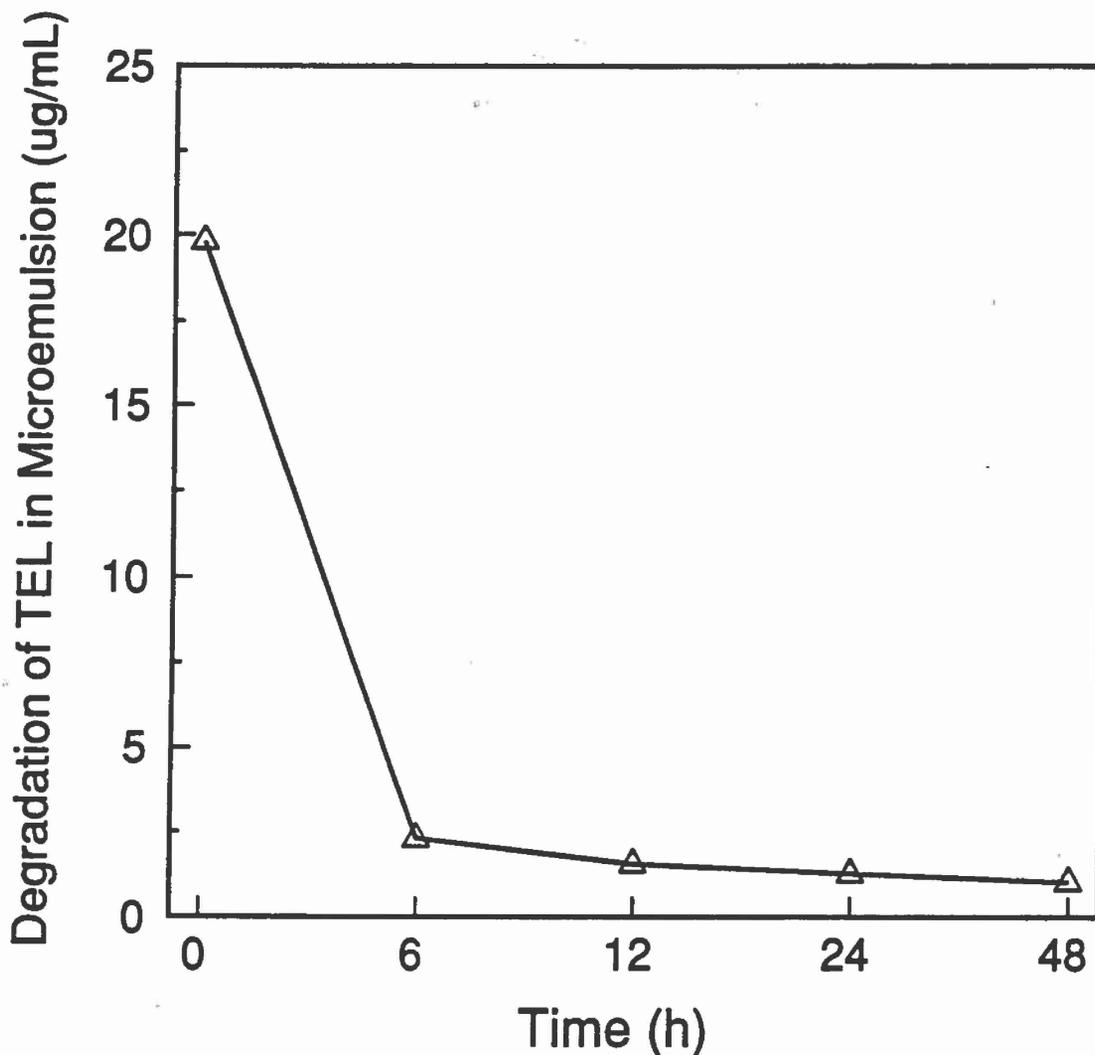
Figure 2. Degradation of TEL in LG/W Microemulsion by Arredondo Soil.

particles even after the samples were centrifuged. TEL in gasoline may adsorb onto the surfaces of organic matter and colloid particles, leading to variations in experimental results.

Table 5 shows speciation of TREL in water phase from TEL in gasoline after contact with soil and washing by DI water. Concentrations of TREL ranged from 0.53 to 0.84 μg mL^{-1}, indicating that TEL in gasoline can degrade into TREL species after coming into contact with the soil.

D. CONCLUSIONS

The results of studying the degradation, sorption, and desorption of TEL in gasoline and gasoline-in-water microemulsion after contact with Arredondo soil showed that TEL is very unstable in the soil environment and undergoes a dealkylation to triethyl lead (TREL), which is highly water-soluble and toxic. Therefore, leakage of leaded gasoline with TEL as a major Pb species may contaminate ground-water because TEL dealkylates into ionic TREL.

SECTION III

SORPTION EXPERIMENTS FOR TEL DISSOLVED
IN HEXANE AND GASOLINE

A.   PARTITIONING OF TEL BETWEEN GASOLINE AND WATER

The purpose of this exercise was to determine the partition coefficient for TEL between gasoline and water. It was expected that water containing TEL at this equilibrium concentration could be equilibrated with soil and a partition coefficient, K_d, between the soil and water phases measured.

A 41.5-μL sample of pure liquid TEL was pipetted into a 100-mL volumetric flask and brought to volume with unleaded gasoline, giving a TEL concentration of 688 μg/mL^{-1}. Next, 10 mL of this leaded gasoline and 10 mL of deionized water were mixed and equilibrated for 6, 24, and 48 hours. After equilibration, TEL was measured in both the gasoline and water phases.

TEL concentrations in both the gasoline and water phases are shown in Table 6. Using the 48-hour concentrations, the partition coefficient, defined as the ratio of TEL in water to that in gasoline, was about 9×10^{-5}. A 48-hour equilibration between the above-water phase containing 0.054 μg/mL^{-1} of TEL and a sample of Arredondo surface soil resulted in no detectable TEL in solution. As shown later, Arredondo soil has a high sorption capacity for TEL, even when the latter is dissolved in gasoline.

TABLE 6. DISTRIBUTION OF TEL BETWEEN GASOLINE AND WATER
PHASES AT THREE EQUILIBRATION TIMES.

Phase	Equilibration Time		
	6 Hours	24 Hours	48 Hours
	(μg/mL^{-1})		
Water	0.034	0.051	0.054
Gasoline	611	672	608

The 0.05 μg/mL^{-1} TEL in the water phase may represent a quasi "steady-state" concentration resulting from (1) the mass transfer of TEL from the gasoline phase to the water phase and (2) the simultaneous decomposition of TEL to inorganic lead. Thus, the use of the above partition coefficient, based on the assumption of equilibrium, may not be warranted. In their study of TEL solubility in water, Feldhake and Stevens (1963) observed losses of TEL from aqueous solutions that they could not explain. Their data showed losses ranging from 9 to 40 percent for equilibration times of 2.5 hours or less. In spite of this difficulty, they reported a solubility of TEL in water at 24.7°C of 0.29 μg/mL^{-1}.

Due to the instability of TEL in pure aqueous systems, it was decided to test its stability in a mixed solvent system. If successful, this system would have two additional advantages: (1) organic compounds have much greater solubility in water/cosolvent systems, thereby allowing much higher initial

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concentrations to be used, and (2) sorption to soil components is reduced, thereby facilitating the measurement of sorption isotherms. By measuring sorption from water/cosolvent mixtures at three or more water contents, the sorption behavior in pure water can be derived by extrapolation of data to zero cosolvent content. This method has been used successfully for many hydrophobic organic compounds of low water solubility (Nkedi-Kizza et al., 1985).

To test this approach, TEL at an initial concentration of 10 $\mu g/mL^{-1}$ was added to a mixed solvent system consisting of water and methanol at a 1:1 ratio. The concentration of TEL was then measured after 6, 12, 24, and 48 hours. After only 6 hours, more than 98 percent of the TEL had already decomposed. At this point, attempts to measure sorption of TEL from aqueous solutions or water/cosolvent systems were abandoned. It was decided to concentrate on measurements of sorption from non-aqueous solvents such as gasoline and hexane, because TEL is stable in these liquids for long periods of time. This was demonstrated by two experiments. In one, a hexane solution of TEL was equilibrated with water, and in the second, a hexane solution was equilibrated with a 1:1 water/methanol mixture. In both cases, TEL concentrations in the hexane phase were little affected, even after equilibration periods of 12 to 48 hours.

B.   SORPTION OF TEL FROM ORGANIC LIQUIDS

1.   Sorption from Gasoline Onto Arredondo Soil

In this series of experiments, Arredondo surface soil was equilibrated with gasoline to which various amounts of TEL had been added. The soil-to-solution ratio was 1 gm:1 mL. Figure 3 shows the TEL remaining in solution after various equilibration times. Initial TEL concentrations ranged from 180 $\mu g/mL^{-1}$ to 720 $\mu g/mL^{-1}$. In each case, a rapid initial loss of TEL from the gasoline was followed by a much slower rate of loss. There was no evidence of sorption equilibrium being attained, even after 1 week. For an initial concentration of 180 $\mu g/mL$, TEL was not detectable in solution after 2 days.

2.   Sorption from Hexane Onto Kaolinite Clay

An experiment similar to the one above for Arredondo soil was conducted using kaolinite clay, in which 1 gram of kaolinite was equilibrated with 10 mL of a hexane solution containing 305 μg TEL mL^{-1}. The amount of TEL remaining in solution was determined after 24, 48, 72, and 96 hours. After 24 hours, only of a trace of TEL remained in solution. None was detectable at the other three equilibration times. The total lead concentrations in these hexane solutions, measured by the ICl method (Ouyang et al., 1994), were below detection limits, indicating no other organic or inorganic lead compounds were present in the hexane solutions.

Following sorption of TEL from hexane, the kaolinite samples were extracted with 1.0 M KCl followed by 1.0 M HCl, each at a soil-to-solution ratio of 1:20. Lead in these extracts was then measured by atomic absorption spectrophotometry. The results are given in Table 7. There was a trend for the KCl-extractable lead to increase and HCl-extractable lead to decrease with equilibration time.

A second experiment was conducted to determine the maximum amount of TEL that the kaolinite clay could adsorb. In this experiment, 1-g samples of clay were equilibrated with 10 mL of a solution containing 300 μg TEL per mL of hexane. After 48 hours, the suspensions were centrifuged, the hexane solution decanted, and the clay resuspended in fresh TEL solution for another 48 hours. The amount of TEL remaining in solution after each equilibration was measured, and the cumulative sorption was calculated.

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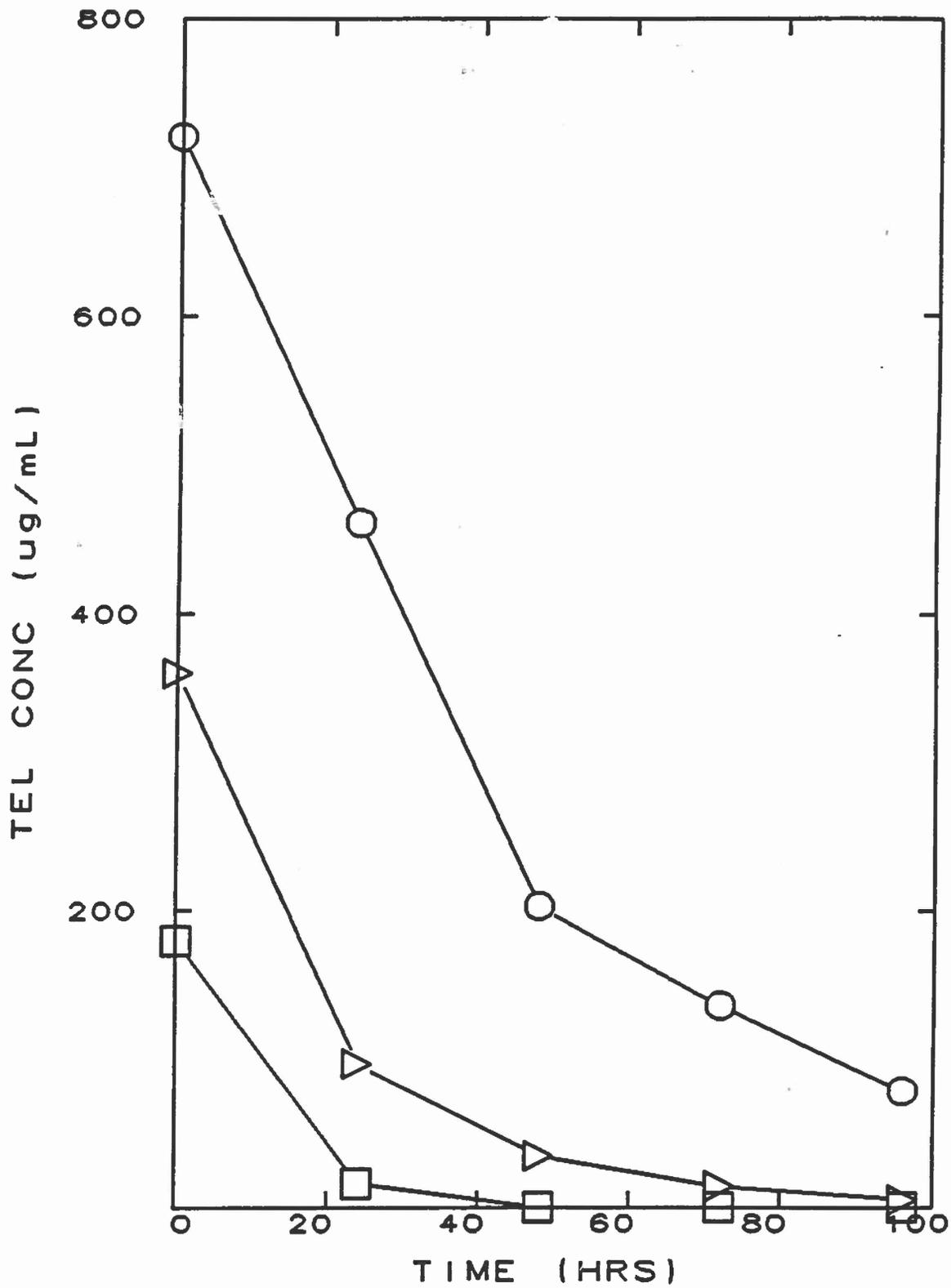
Figure 3. TEL Remaining in Gasoline After Equilibrating
with Arredondo Soil.

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TABLE 7. AMOUNTS OF TEL SORBED FROM HEXANE BY KAOLINITE CLAY
AND THE AMOUNTS REMOVED BY SEQUENTIAL EXTRACTIONS
WITH KCl AND HCl.

| Time (hr) | Amount Sorbed | | Extractable Lead* | |
| | (μg/g^{-1}) | | | |
	As TEL	As Lead	With KCl	With HCl
24	2,089	1,337	260 (19)	775 (58)
48	2,567	1,643	353 (21)	746 (45)
72	2,559	1,638	323 (20)	769 (47)
96	2,145	1,373	330 (24)	522 (38)

* Numbers in parentheses are percentages of the total lead sorbed.

Figure 4 shows the cumulative sorption of TEL after 8 consecutive equilibrations with the above hexane solutions of TEL. Total TEL sorption approached 15 mg/g^{-1} of clay after 8 equilibrations. The KCl and HCl extraction data for these samples are shown in Table 8. The percentage of adsorbed lead extracted with KCl was greater and the percentage extracted with HCl was less than that shown in Table 7. The recovery of lead from these four samples was essentially 100 percent.

Sorbed and KCl-extractable lead values for two additional kaolinite samples are shown in Table 9. The sorbed lead values for these two samples were intermediate between those of the two previous data sets. The trend in Tables 7, 8, and 9 suggests that as the loading rate increased, the percentage of KCl-extractable lead increased. Thus, an increasing fraction of lead at the high loading appears to be in exchangeable forms.

TABLE 8. AMOUNTS OF TEL SORBED FROM HEXANE BY KAOLINITE CLAY
DURING SEQUENTIAL EQUILIBRATIONS AND THE AMOUNTS REMOVED
BY SEQUENTIAL EXTRACTIONS WITH KCl AND HCl.

| Rep. # | Amount Sorbed | | Extractable Lead* | |
| | (μg/g^{-1}) | | | |
	As TEL	As Lead	With KCl	With HCl
1	14,400	9,216	6,947 (75)	3,263 (35)
2	14,500	9,280	6,791 (73)	3,213 (35)
3	15,017	9,611	6,053 (63)	3,116 (32)

* Numbers in parentheses are percentages of the total lead sorbed.
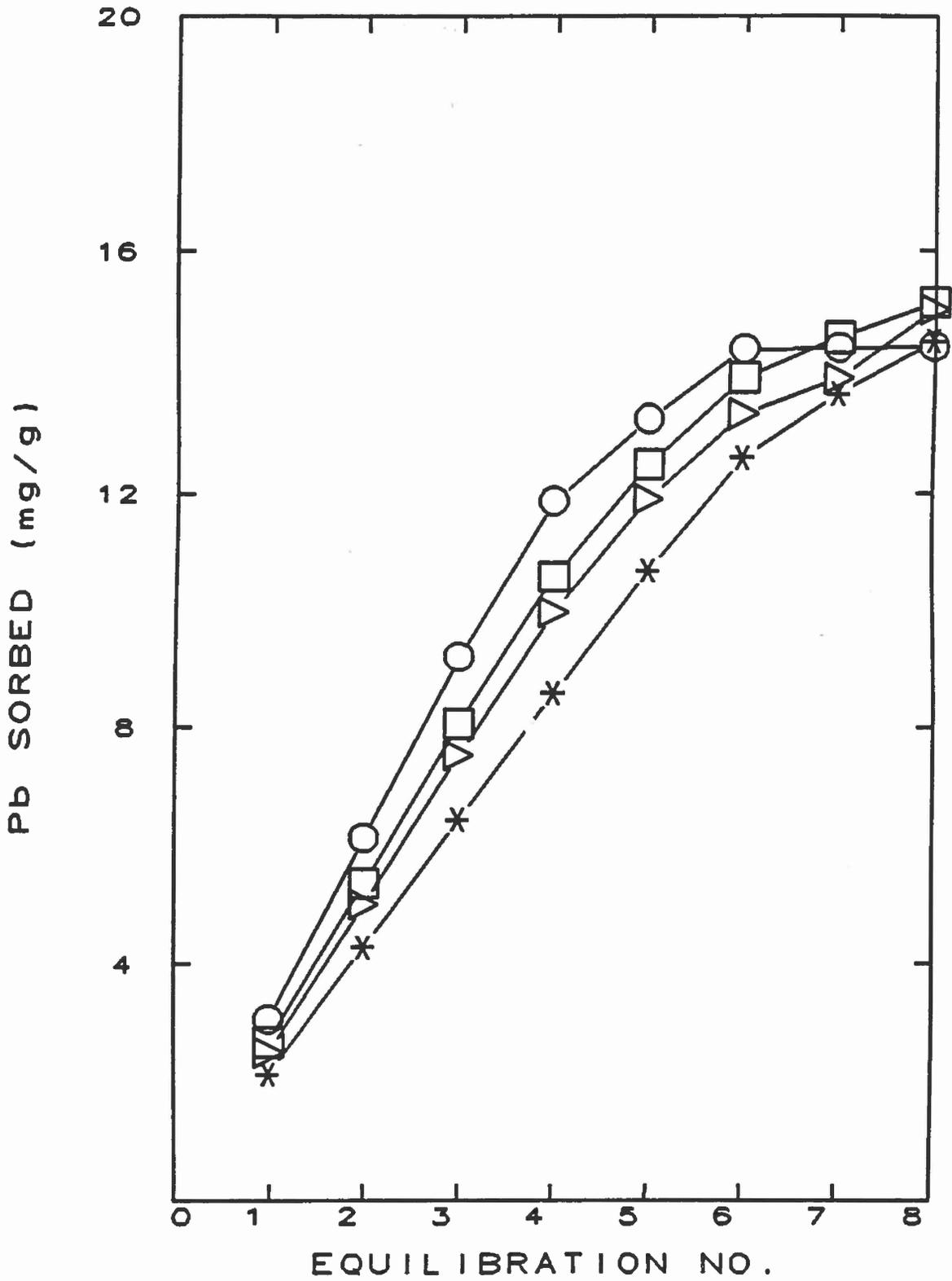
Figure 4. Cumulative Lead Sorption by Kaolinite Clay During
Sequential Equilibrations with Hexane Solutions Containing
300 $\mu g/mL^{-1}$ TEL. Four replications are shown.

TABLE 9. SORBED AND EXTRACTABLE LEAD VALUES AND TREL
AND DEL CONCENTRATIONS IN THE KCl EXTRACTS FOR TWO
SOIL MATERIALS AND KAOLINITE CLAY.

Sample	Amount Sorbed ($\mu g/g^{-1}$)		KCl Extractable* ($\mu g/g^{-1}$)	Concentration in KCl ($\mu g/mL^{-1}$)		
	As TEL	As Lead		TREL	DEL	Total
Kaolinite						
1	8,270	5,293	1,659 (31)	0	0	59
2	7,070	4,525	1,392 (31)	2	2	59
E Horizon of Spodosol						
1	2,215	1,418	12 (<1)	0	0	0.5
2	1,852	1,185	24 (2)	0	0	1.2
Bh Horizon of Spodosol						
1	1,837	1,176	402 (34)	1	<1	20
2	2,096	1,341	382 (28)	7	0	14

* Numbers in parentheses are percentages of the total lead sorbed.

3. Exchangeable TREL and DEL on Kaolinite

KCl extractable lead could include the ionic organic species, TREL and DEL, as well as inorganic Pb^{+2}. Therefore, the KCl extract following a sorption experiment was analyzed for TREL, DEL, and total lead. In addition to kaolinite clay, soil samples taken from the 6- to 12- and 12- to 18-inch depths of a Spodosol located at Tyndall AFB were used; 1 gram of soil and 1 gram of kaolinite were each equilibrated with 20 mL of a hexane solution containing 300 μg TEL mL^{-1} for 48 hours.

The total amount of lead sorbed and the amount subsequently extracted with KCl are shown in Table 9. No HCl extraction was conducted on these six samples. The 6- to 12- and 12- to 18-inch soil samples were from the E and Bh horizons of the Spodosol, respectively. The E horizon is a stripped sand layer, very low in organic matter and clay, i.e., low cation exchange capacity (CEC). The Bh horizon is characterized by the accumulation of clay and metal-organic complexes. It is interesting that while the E and Bh samples adsorbed almost identical amounts of lead, the E horizon sample had very low KCl-extractable lead levels compared to the Bh horizon sample. This suggests that the CEC of the soil, although it did not affect the total amount of lead adsorbed by the E and Bh samples, did affect the amount of sorbed lead that was exchangeable with KCl.

The results of the TREL and DEL analyses are shown in Table 9. The results for the TREL and DEL are somewhat erratic. However, it appears that the organic species comprise only a small

percentage of the total lead extracted with KCl for both soil and clay samples. TREL and DEL were not measured in the KCl extracts of the kaolinite samples in Table 8. However, it is possible that a significant percentage of the KCl-extractable lead was present as TREL and DEL in those samples. If all the lead in the KCl extracts of these samples were present as Pb^{+2}, it would represent 6.3 $cmol_c/kg^{-1}$ of clay. This exceeds the CEC of the clay which was 5.0 $cmol_c/kg^{-1}$. Thus, as much as 25 percent of the KCl-extractable lead at these high loading rates may have been present as TREL and other lead complexes with valences lower than two.

C.   CONCLUSIONS

The inherent instability of TEL in aqueous systems that was observed in this study precluded measurements of TEL sorption from aqueous solutions or from water/cosolvent systems. This instability of TEL in aqueous systems that also has been observed by others suggests that aqueous solubility data found in the literature may be suspect. The instability also precludes the use of estimates of K_{oc} based on water solubility, a practice common with other organic compounds of low water solubility.

Sorption of TEL from hexane and gasoline by soil and clay materials was characterized by a rapid initial loss of TEL from solution followed by slower rate of loss. No evidence of sorption equilibrium was observed in any system even after 1 week of equilibration. In many cases, TEL loss from solution continued until it was no longer detectable. Analysis of the liquid phase showed that the TEL had been adsorbed and not simply converted to other lead species in solution (i.e., TREL, DEL, Pb^{+2}, etc.)

Sequential equilibrations of kaolinite clay with TEL in hexane suggested that its sorption capacity for TEL may be in excess of 15 mg/g^{-1}. KCl extractable lead ranged from <1 to >70 percent of the total lead sorbed depending on initial lead concentrations, time of equilibration, soil and clay characteristics, etc. Inorganic Pb^{+2} was probably the dominant lead species in the KCl extracts, because TREL and DEL were either present in relatively small concentrations or not detectable in the KCl extracts. The one exception might have been the kaolinite samples from the sequential equilibration study where the CEC of the clay was insufficient to account for all the lead extracted if it were present as Pb^{+2}.

SECTION IV

FATE AND TRANSPORT OF TETRAETHYL LEAD DURING IMMISCIBLE
FLOW OF GASOLINE IN SOIL COLUMNS

A.   INTRODUCTION

Growing concern about the dissemination and adverse health impacts of toxic substances in the natural environment has led to intensified research on the occurrence, source, mobility, degradation, and eventual fate of heavy metals and hydrocarbons. Among the most prevalent toxic compounds found in the subsurface environment are lead and gasoline. Pb alkyl species used by automobile-related industries include tetraethyl lead (TEL), triethylmethyl lead, dimethyldiethyl lead, trimethylethyl lead, and tetramethyl lead compounds. All of these compounds have been used as antiknock agents and have provided a convenient and inexpensive means of enhancing octane rating for gasoline (Caplun et al., 1984).

Following TEL's introduction as a commercial antiknock agent in gasoline in 1923, use of leaded gasoline was almost global for more than 50 years during 1925 to 1975. The amount of Pb released in automobile exhausts during that time accounted for more than half of the total yearly Pb pollution of the entire earth (Settle and Patterson, 1980; Caplun et al., 1984). Production of leaded gasoline in the United States peaked in early 1970 and steadily declined after 1975 (Grandjean and Nielsen, 1979). Although only Pb-free gasoline may now be used as an automobile fuel in the United States, leaded gasoline still is used commonly as an aviation fuel in the United States and as an automobile fuel in many countries in the world (Driscoll et al., 1992; Rhue et al., 1992). Extensive use of Pb antiknock additives in gasoline has made Pb perhaps the most widely distributed toxic heavy metal in the urban environment (Brown and Hem, 1984).

Over the past 20 years, there has been increased concern about the problem of Pb contamination of soil due to the use of leaded gasoline and other leaded products. This concern exists although the use of leaded gasoline in autos has greatly decreased. At present there are no federal regulations addressing the acceptable level of Pb in the soil for public health protection and remedial action. However, soil and drinking water with Pb concentrations > 500 ppm and 15 ppb, respectively, are considered toxic waste by EPA (Rhue et al., 1992).

Mobility of Pb alkyl compounds in soil contaminated by leaded gasoline is largely unknown primarily because of the unknown chemical reaction or sorption by mineral and organic soil components. As rainwater infiltrates into soils, the leachability of Pb alkyls will be determined largely by sorption and degradation reactions. An unknown but finite potential exists for organolead compounds to leach from soils previously used for disposal of fuel sludge. The high water solubility of ionic triethyl lead (TREL) and ionic diethyl lead (DEL) species makes these compounds particularly suspect for mobility in soil systems during periods of water infiltration into the soil. Unfortunately, no laboratory experiments have been conducted to investigate the fate and transport of Pb alkyls in soils contaminated with leaded gasoline.

This study was designed to (1) investigate the fate and transport of gasoline and TEL through a loam soil and sand soil with two degrees of leaded gasoline saturations (i.e., 3 and 30 percent saturation of columns, respectively); (2) examine the speciation of TREL and DEL from TEL during the immiscible flow of leaded gasoline; and (3) test the remediation efficiency of gasoline and TEL by NaCl solution followed by a mixture of water-surfactant-cosurfactant (W/S/CoS).

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B. MATERIALS AND METHODS

1. Materials

a. Reagents

Analytical grades of TEL and TREL chloride were purchased from All-Chemie Ltd. (Ft. Lee, New Jersey). Pb standard solution and sodium lauryl sulfate were purchased from Fisher Scientific (Orlando, Florida). All other chemicals such as concentrated HCl, n-hexane, n-pentanol, KI, KIO_3, NaCl, concentrated HNO_3, NaCl, EDTA disodium salt, NaDDTC, Na_2SO_4, 1.9 M of Grignard reagent (2.0-M butylmagnesium chloride in tetrahydrofuran [THF]), and concentrated NH_4OH were analytical grades. Leaded aviation gasoline was purchased locally from the Gainesville Regional Airport in Gainesville, Florida. The major Pb species in this gasoline is TEL. Properties of TEL are given in Table 10.

TABLE 10. BENCHMARK PROPERTIES OF TEL AND SODIUM LAURYL SULFATE.

Parameter	Value/Unit	Reference
TEL		
Formula	$Pb(C_2H_5)_4$	Mackison et al., 1981
Molecular Wt.	323.4	
Density	1.65 g/mL^{-1} (20°C)	Mackison et al., 1981
Solubility		
in Water	Insoluble (<0.1 mg/L^{-1})	Mackison et al., 1981
in Hexane	Soluble	
Toxicity	LD$_{50}$ (Oral) 250 mg/kg^{-1}	Grandjean and Nielsen, 1979
Sodium Lauryl Sulfate		
Formula	$CH_3(CH_2)_{10}CH_2OSO_3Na$	
Molecular Wt.	288	
Toxicity	None	
Ionic Nature	Anionic	
Critical Micel. Concentration		
in Water	0.0081 mole L^{-1}	Hiemenz, 1986
in 0.1 M NaCl	0.00139 mole L^{-1}	Hiemenz, 1986

Arredondo fine sand from Gainesville, Florida and a Madison loam soil from Dobbins Air Force Base in Georgia were used for the experiments. Selected soil properties are shown in Table 11.

TABLE 11. SELECTED PROPERTIES OF ARREDONDO AND MADISON SURFACE SOILS USED FOR THIS STUDY.

Property	Arredondo Soil	Madison Soil
pH	5.5	4.7
Organic C	11.8%	6.1%
Sand	92%	43%
Silt	7%	40.3%
Clay	1%	16.7%
Soil Depth	0-15 cm	0-15 cm

A mixture of W/S/CoS was made by mixing 4.3 grams of sodium lauryl sulfate, 8.7 grams of n-pentanol, and 87 grams of deionized (DI) water. This mixture was used to solubilize and mobilize residual gasoline in the soils by producing a gasoline-in-water microemulsi ̣ system. Solvent for extracting TREL and DEL from effluent was prepared by mixing 2 grams of E₁ TA disodium salt and 2 mL of 0.25 M NaDDTC·3H₂O into a 100-mL volumetric flask. Then the solvent was adjusted to pH = 9 with NH₄OH and diluted with DI water.

Analytical-grade TEL was dissolved in n-hexane to make working standards of TEL at concentrations of 0.01, 0.05, 0.1, 1, 5, and 10 μg/mL^{-1}. Leaded aviation gasoline was dissolved in n-hexane to make working standards of gasoline at concentrations of 120, 480, 1500 μg/ mL^{-1}. A 0.1 M ICl solution was prepared by mixing 40 mL DI water, 44.5 mL concentrated HCl, 11.0 grams of KI, and 7.5 grams of KIO₃. This solution was used to convert the TEL into Pb^{+2} so that th ̣ total Pb content in the effluent could be measured by atomic absorption spectrophotometry (AAS) (Ouyar. ̣ et al., 1994). Working standards of Pb solution for measuring total Pb content in effluent were made by adding standard Pb solution in 3:1 DI water:0.1 M ICl solution at concentrations of 1, 10, and 20 μg/mL^{-1}. Working standards of Pb for measuring total Pb content in soil before and after the experiments were prepared according to the EPA Method 3050 (U.S. EPA, 1986).

b.   Standards

A 100 μg/mL^{-1} ionic TREL solution was prepared by dissolving 0.025 gram of analytical TREL chloride salt into a 250-mL volumetric flask and diluting the contents with DI water. TREL and DEL are highly water soluble but are not soluble in organic solvent such as hexane. Therefore, to measure TREL and DEL by GC, it is necessary to convert ionic TREL and DEL into butylized TREL (Bu-TREL) and butylized DEL (Bu-DEL), which are both soluble in hexane. The procedures for butyl-ization of TREL and DEL (modified from Chau et al., 1984) are as follows: (1) pipette 5 mL of the 100 μg/mL^{-1} ionic TREL solution and 20 mL of the extracting solvent into a 125-mL separatory funnel

and shake for 10 minutes; (2) add 5 mL of n-hexane to the separatory funnel and shake for another 5 minutes; (3) separate the layers and save n-hexane solution; (4) repeat procedure 2 by adding another 5 mL of n-hexane to aqueous phase solution and shaking for 2 minutes; (5) separate the layers and save the hexane phase; (6) combine the hexane solutions and discard the aqueous phase; (7) dry the hexane solution with anhydrous Na_2SO_4 (about 1 scoop), decant, and save the hexane phase; (8) rinse anhydrous Na_2SO_4 with 5 mL hexane; (9) add all hexane solution together and evaporate the hexane solution to dryness by evaporator; (10) add 1 mL of 1.9 M Grignard reagent (butylmagnesium chloride in THF) by syringe and swirl for 1 minute; (11) add 5 mL of n-hexane and 10 mL of 1 NH_2SO_4 and shake for 2 minutes; (12) separate and save hexane phase. Concentration of Bu-TREL in the hexane solution was verified using an iodine monochloride method (Ouyang et al., 1994). That is, to measure the Bu-TREL content in hexane phase indirectly, the Bu-TREL was converted to Pb^{+2} by ICl solution. Then the Pb^{+2} content was measured by AAS. Therefore, Bu-TREL content in organic solvent can be calculated as follows:

$$C_{TREL}^{B} = \frac{W_{TREL}^{B} \, C_{Pb}}{W_{Pb}} \tag{1}$$

where C_{TREL}^{B} is the concentration of Bu-TREL ($\mu g/mL^{-1}$), W is the molecular weight of Bu-TREL (408.2), C_{Pb} is the concentration of Pb^{+2} in the samples ($\mu g/mL^{-1}$), and W_{Pb} is the molecular weight of Pb^{+2} (207.2). After verification working standards of Bu-TREL at concentrations of 0.2, 1, and 5 $\mu g/mL^{-1}$ were prepared by diluting the Bu-TREL solution with hexane.

The same procedures were used to make the working standards for Bu-DEL as for Bu-TREL except that a 0.1 M ICl solution was added to the ionic TREL solution to convert TREL into DEL before extraction and butylization (Hancock and Slater, 1975).

c.   Column Packing

Duplicate glass cylinders with a 4.8-cm inner diameter were used to hold 15.75-cm soil columns. To fill the cylinders, air-dried Madison loam soil (or Arredondo sand soil) was crushed, passed through 0.5-mm screen, poured into the cylinders in 2-cm increments, and stirred to prevent layering. The columns were tapped to settle the soil to the desired volume. The masses of the empty columns and the packed columns were weighed to determine the bulk densities of columns.

The columns initially were saturated by 0.1 M NaCl solution with an upflow mode and a peristaltic pump was used to establish a low column flowrate (6 mL/h^{-1}) for 30 hours until the soil columns were saturated. After saturation, the soil columns were weighed to determine the pore volumes (i.e., the mass difference between the dry soil columns and saturated soil columns). Then the column flow was increased to have a desired Darcy flow velocity of 1.5 cm h^{-1}. Experimental conditions for these columns are given in Table 12.

2.   Displacement Experiments in Columns of Madison Loam Soil

After the NaCl solution flow reached a steady-state condition (1.5 cm/h^{-1}), 48 mL leaded gasoline (about 30 percent saturation of the columns) was pumped through the soil columns. Then the columns were flushed by 1.6 pore volumes of NaCl solution and the column flow was stopped overnight. The next morning, the soil columns were washed by 6.4 pore volumes of the W/S/CoS mixture next morning with the same flow velocity.

TABLE 12. EXPERIMENTAL PARAMETERS.

Parameters	Madison Soil	Arredondo Soil
Bulk density, ρ_b (g/cm^{-3})	1.02	0.98
Darcy velocity, V (cm/h^{-1})	1.5	2.5
Column length, L (cm)	15.75	15.75
Cross section area, A (cm^2)	18.1	18.1
Applied leaded gasoline (mL)	48	2.3
Saturated water content (cm^3/cm^3)	0.54	0.55
Pore volume (mL)	154.5	157
Viscosity of water at 20°C, μ (N h m^{-2})	3.6	3.6

All effluents were collected in test tubes in an automatic fraction collector with a time interval of 10 minutes. All test tubes and soil columns were wrapped in aluminum foil before the experiment started to prevent photodegradation of TEL. For analyzing TEL and gasoline in the effluent flushed by NaCl solution, 0.8 mL effluent was pipetted into 10 mL of n-hexane and shaken for 30 minutes. The same procedures were used to analyze the TEL and gasoline in effluent washed by the W/S/CoS equal mixture, except that a small amount of NaCl salt was added to the samples to break the possible coalescence of hexane and effluent.

After the column flows had been terminated, the soils were analyzed for residual gasoline, TEL, and total Pb. To analyze TEL and gasoline in the soil samples, 1 gram of wet soil was added into 10 mL of hexane and shaken for 1 hour. Then the samples were centrifuged at 2000 rpm for 20 minutes and decanted. The clear supernatants were used to measure TEL and gasoline by GC and ultraviolet (UV) spectrophotometer, respectively. The method for measuring background and residual soil total Pb is described by EPA 3050 Method (U.S. EPA, 1986). The moisture contents of the wet soils at the end of experiments were measured by oven drying.

Gasoline contains more than 200 components. It is time-consuming, if not difficult, to measure all these components. Current methods for detecting gasoline-contaminated sites include analysis for benzene, toluene, xylene, ethylbenzene, total petroleum hydrocarbons, or immunoassay (Allen et al., 1992). In this study, we used the UV spectrophotometer to measure components of aromatic and unsaturated bonds in gasoline as an indicator of gasoline. We assumed that concentration of gasoline is proportional to the concentration of aromatic and unsaturated components in effluent and soil samples. Our preliminary study shows that the chromatograms generated by UV spectrophotometer for gasoline in effluent and in soil samples extracted by hexane have the same distributed pattern. Therefore, the use of a UV spectrophotometer to measure aromatic and unsaturated bonds as indicators of gasoline is justified.

About a 5-mL aliquot sample was poured into a cuvette for analyzing the gasoline using UV spectrophotometer with the scanning wavelengths ranging from 240 to 300 nm. A 20-μL aliquot sample was injected into the GC to analyze the TEL concentration with GC conditions reported by Chakraborti et al. (1989b). The method for measuring the total Pb in the effluent was developed by Ouyang et al. (1994).

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3. Displacement Experiment in Columns of Arredondo Sand Soils

The same procedures were used in this displacement experiment as in the Madison soil experiments except that a 2.3 mL of leaded gasoline (about 3 percent saturation of the soil columns) with a Darcy velocity of 2.5 cm/h^{-1} was pass through the columns. Then the columns were flushed by 2 pore volumes of 0.1 M NaCl solution, followed by 3.2 pore volumes of the W/S/CoS mixture. Experimental parameters for the displacement experiments are given in Table 12.

4. Degradation and Adsorption of TEL in Arredondo Soil

Triplicate 5-mL samples of leaded gasoline and 5-gram samples of wet Arredondo soil were added to the 50-mL test tubes and shaken for 2, 6, 24, and 48 hours, respectively. The test tubes were rotated end-over-end manually for 2 minutes and put on the shaker to ensure complete mixing. Then the soil samples were centrifuged at 2000 rpm for 10 minutes with an International Model HN-S centrifuge. The clear supernatants were analyzed for TEL using GC. The differences between the initial concentration and the concentrations for equal samples were taken as the amount of TEL degradation and adsorption by the soil at a given time.

A 20-μL hexane solution was injected into a GC (HP 5710A Gas Chromatograph) for analyzing the TEL concentration with the following conditions: (1) detector temperature 300°C; (2) injection port temperature is 150°C; (3) attenuation is 32; (4) slop sensitivity is in AUTO position; (5) area reject is 10; (6) oven temperature is 120°C; (7) gas flowrate is 81 mL/min^{-1}; and (8) GC column length is 6 feet with an inner diameter of 4 mm. These conditions are similar to those reported by Chakraborti et al. (1989b).

C. RESULTS AND DISCUSSION

1. Displacement of Leaded Gasoline in Columns of Madison Loam Soil

Figure 5 shows that 34 percent of applied gasoline was displaced from the leaded gasoline-contaminated soil columns by 1.6 pore volumes of 0.1 M NaCl solution. Concentration of gasoline in the effluent ranged from a maximum of 286.9 grams of L^{-1} to a minimum of 0.17 gram of L^{-1}. The rest of the gasoline remained as residuum in the soil pores. This phenomenon can be explained by capillary trapping mechanisms. When gasoline flowed through the water-saturated soil columns, capillary attractive forces caused some gasoline being displaced from relatively large pores but not from small pores. No matter how much water flowed through the columns, a certain amount of residual gasoline remained entrapped. Wilson et al. (1990) reported that when two fluid phases flow through a soil system, and the non-wetting fluid is being displaced by the wetting fluid, there are two major mechanisms for capillary trapping of gasoline: (1) snap-off and (2) by-passing. Snap-off occurs as non-wetting fluid in a pore is displaced from a pore body into a pore throat. The mechanism strongly depends on wettability and the aspect ratio of pore body diameter to pore throat diameter (Wardlaw, 1982).

In the case of NaCl solution, displacing the gasoline from the soil columns in our experiments, the walls of soil pores were strongly water wet and the water contact angle was acute. The water-gasoline interface was curved and the water phase wicked along the wall (Figure 6A). When a thin layer of water phase reached the exit pore throat, a large blob of gasoline still remained in the pore. Snap-off occurred as the water continued through the exit pore throat leaving behind the now disconnected singlet blob.

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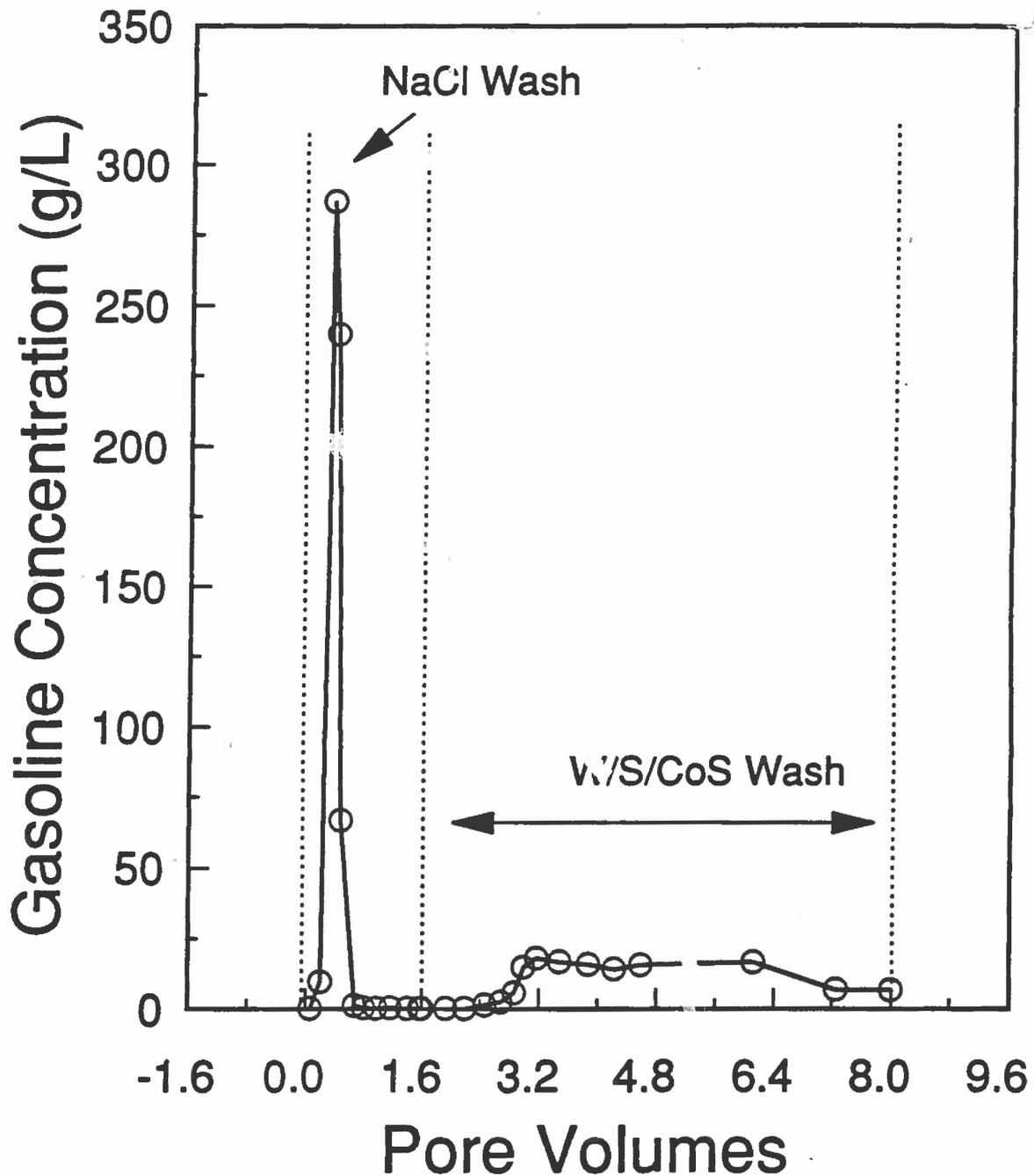
Figure 5. BTC for Gasoline in Madison Loam Soil Experiments. The experiments started with pumping 48 mL of leaded gasoline through the water-saturated soil column, followed by 1.6 pore volumes of NaCl and 6.4 pore volumes of W/S/CoS mixture washing.

The pore doublet model has been used to describe the gasoline by-passing mechanism on a microscopic scale (Chatzis et al., 1983). A pore doublet consists of a tube that splits into two pores, one generally more narrow than the other, and rejoins (Figure 6B). Water entered the narrow pore first. As water reached the stream node, it did not stop because no stable interface was formed (Figure 6B,

PORE BODY

COLLAR OF WATER

A. SNAP-OFF

STEP 1

STEP 2

STEP 3
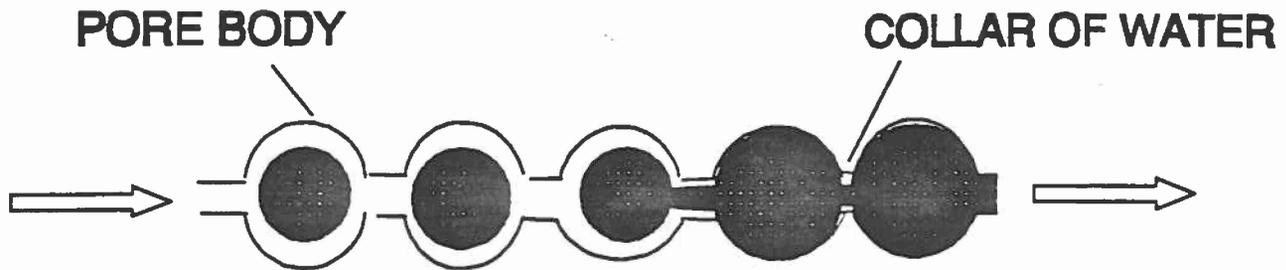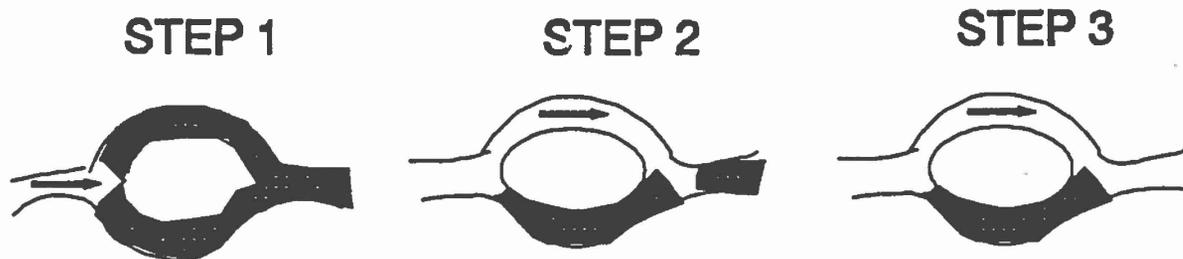
B. BY-PASSING

Figure 6. Capillary-Trapping Mechanisms for
Gasoline Flow in Water-Saturated Soil.

Step 1). The gasoline in the wider pore became disconnected from the main body of gasoline and was now unstable to draw from the pore. This gasoline has begun to bypass the advancing water (Step 3).

The mobilization of gasoline droplets can be quantified by the capillary number. The capillary number is a dimensionless ratio of viscous to capillary forces. It provides a measure of how strongly residual oil is trapped within a given porous medium (Taber, 1981). Gupta and Trushenski (1979) reported that the mobilization of gasoline entrapped in the soil usually begins at a capillary number of about 10^{-5} (the critical capillary number), and complete oil recovery occurs at a high value of capillary number of about 10^{-2}. The capillary number for these experiment was 6.7×10^{-6}, which was below the critical capillary number. Therefore, some of the gasoline was trapped by the soil pores.

When the soil columns were washed with the W/S/CoS mixture, 44 percent of the gasoline was removed from the soil columns. This was a result of the formation of a gasoline-in-water micro-emulsion due to the use of W/S/CoS. A surfactant is a substance that lowers the surface or interfacial tension of the medium in which it is dissolved. The important properties of a surfactant are its amphipathic

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structure, monolayer orientation at interfaces, and adsorption at interfaces. A surfactant molecule is made up of two fundamental groups, a hydrophilic head and a lipophilic carbon chain. The two groups line up between the gasoline and water phases with their opposing ends dissolved in the respective phases. This arrangement creates a third layer at the interface, decreasing the interfacial tension between the gasoline and water. The balance between the head group and the carbon tail determines which phase the surfactant molecule will dissolve into more easily. That is, if the balance favors the head group more than carbon group, the surfactant as a whole will be more water soluble. In this case, it will tend to pull gasoline into solution as droplets encased in a shell of surfactant molecules. This balance is called the hydrophilic-lipophilic balance (Shinoda and Friberg, 1986).

An emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible. A microemulsion is a special kind of stabilized emulsion in which the dispersed droplets are extremely small (effective diameter $< 0.1 \mu m$) and it is transparent (Schramm, 1992). The important features of microemulsions are their thermodynamic stability, high solvent power (Shinoda and Friberg, 1986), and relatively smaller size of droplets compared to those of macroemulsions. Table 13 shows the average diameters for colloid particles, macroemulsion droplets, microemulsion droplets, and soil micropores. Unlike colloids and macroemulsions, a microemulsion has a much smaller droplet diameter than that of soil micropores. Therefore, capture of gasoline droplets by soil pores is minimized in the microemulsion system.

TABLE 13. DIAMETERS OF COLLOIDAL PARTICLES, MOLECULAR SOLUTIONS, MACROEMULSION DROPLETS, MICROEMULSION DROPLETS, AND SOIL MICROPORES.

Parameter	Diameter	Reference
Colloid Particles	0.1-2 μm	Martel et al., 1993
Molecular Solutions	$<0.001 \mu m$	Martel et al., 1993
Macroemulsion Droplets	1-10 μm	Martel et al., 1993
Microemulsion Droplets	0.01-0.1 μm	Martel et al., 1993
Soil Micropores	$< 30 \mu m$	Glinski and Lipiec, 1990

A similar breakthrough pattern was observed for TEL (Figure 7). That is, 51.5 percent of TEL was recovered from the soil columns by NaCl solution flush and 33.6 percent of TEL was removed by the W/S/CoS mixture wash. About 0.04 percent TEL was detected in soil samples from the columns at the end of the experiments. An estimation of total TEL mass shows that only 85.2 percent of TEL was recovered. This low recovery rate of TEL was attributed to the biotic and abiotic degradation of TEL in the soils. TEL is a toxic hydrocarbon compound that is very unstable when in contact with soil. Degradation of TEL occurs through a series of sequential dealkylation steps and eventually to Pb^{+2} (Rhue et al., 1992). That is, non-ionic TEL was first degraded to monovalent TREL, which in turn degraded to divalent DEL and finally to inorganic Pb^{+2}.

Comparison of breakthrough curves (BTCs) for gasoline (Figure 5) and TEL (Figure 7) shows that TEL can be transported through the soil columns with the migration of gasoline.
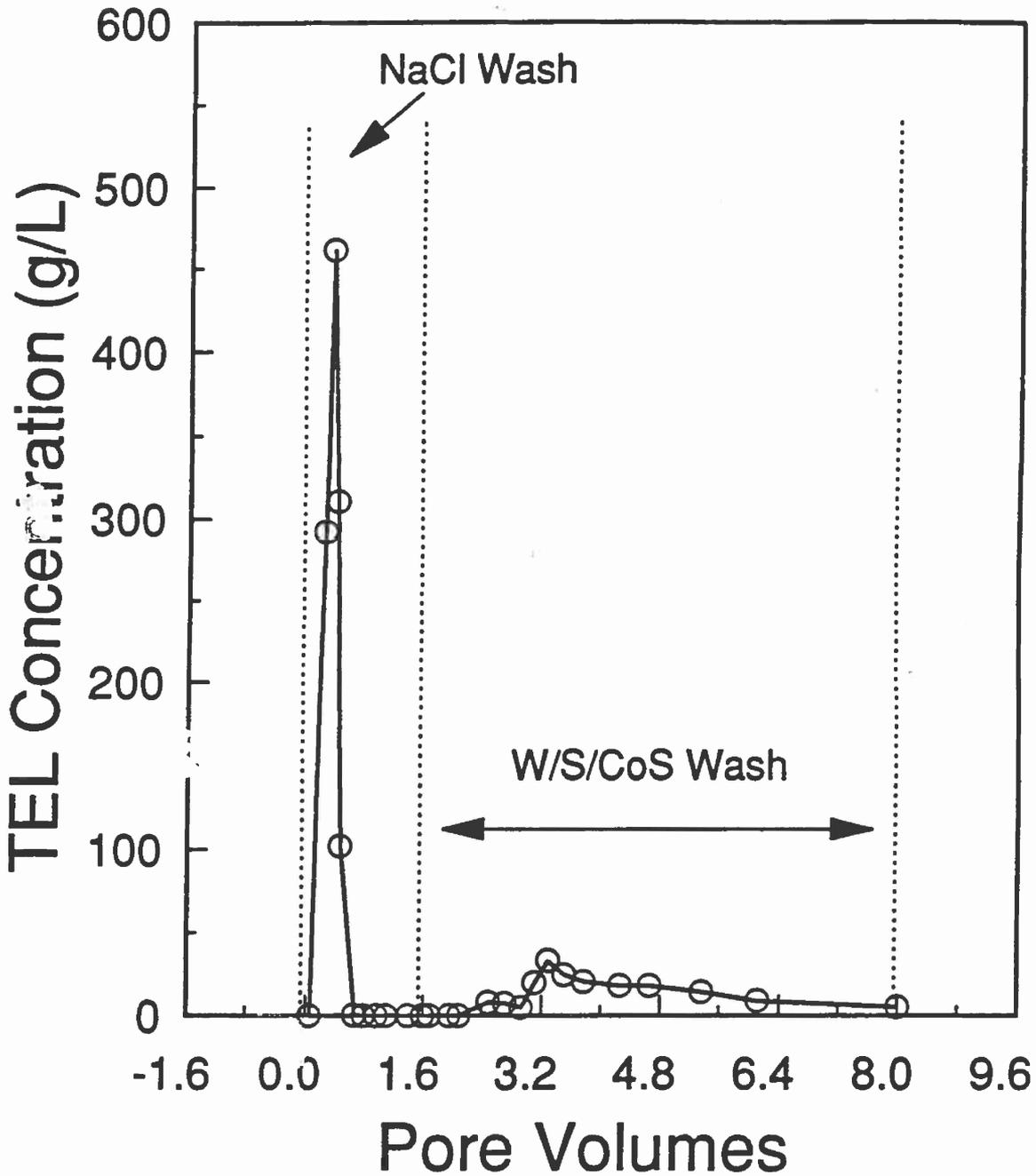
Figure 7. BTC for TEL in Madison Loam Soil Experiments. The experiments started with pumping 48 mL of leaded gasoline through the water-saturated soil column, followed by 1.6 pore volumes of NaCl and 6.4 pore volumes of W/S/CoS mixture washing.

The BTC for total Pb, which is the sum of Pb in TEL, TREL, DEL, and Pb^{+2} species, is shown on Figure 8. Inorganic ionic Pb^{+2} cannot be washed out by NaCl solution although a certain amount of Pb^{+2} adsorbed onto the surface of soil particles or organic matter may be washed out by the W/S/CoS mixture. Therefore, the breakthrough of total Pb was a result of the breakthrough of TEL and
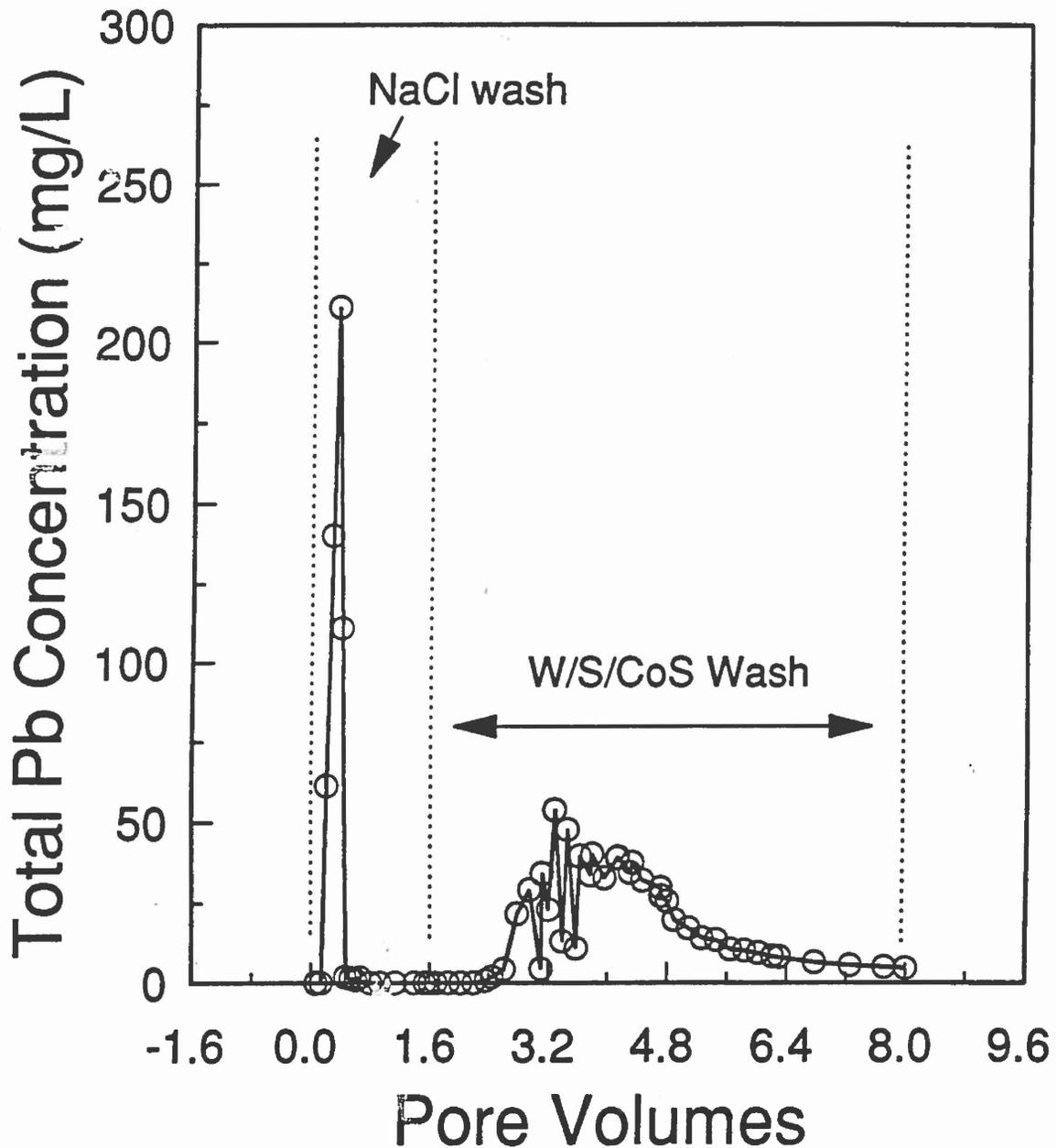
Figure 8. BTC for Total Pb in Madison Loam Soil Experiments. The experiments started with pumping 48 mL of leaded gasoline through the water-saturated soil column, followed by 1.6 pore volumes of NaCl and 6.4 pore volumes of W/S/CoS mixture washing.

its degradation products moved along with gasoline or microemulsion and TREL and DEL moved along with NaCl solution or microemulsion. A mass balance analysis of TEL for the experiments may not be adequate due to the unstable nature of TEL in the soil. However, a mass balance analysis of total Pb for the experiments can provide information about the accuracy of the experiments. The equation used to estimate the mass balance of total Pb is as follows:

$$\text{Mass Balance \%} = (Pb_{effluent} + Pb_{residual}) / (Pb_{input} + Pb_{back}) \tag{2}$$

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where $Pb_{effluent}$ is total Pb in the effluent, $Pb_{residual}$ is residual total Pb in the soil column at the end of experiment, Pb_{input} is total Pb input to the soil column, and Pb_{back} is total background Pb in the soil before the experiments. Values for parameters in Eq. (1) are given in Table 14. The average total Pb mass balance for the experiments was 101 percent. This high mass balance rate indicates good experimental measurements.

2.   Speciation of TREL and DEL from TEL

Spot checking shows that DEL exists in the effluent washed by both 0.1 M NaCl (ranging from 0.93 to 0.05 $\mu g/mL^{-1}$) and surfactant solutions (ranging from 0.61 to 0.04 $\mu g/mL^{-1}$), whereas TREL was found only in the effluent washed by surfactant solution (ranging from 10.7 to 0.3 $\mu g/mL^{-1}$). Speciation of DEL in the soils at the end of experiments ranged from 20.9 to 0.1 $\mu g\ g^{-1}$ dry soil. No TREL was found in the soil column at the end of the experiments. Results show that speciation of TREL and DEL from TEL occurred during the flow of leaded gasoline through soil columns. However, the fact that no TREL was detected in the soil samples does not necessarily mean that DEL is more stable than TREL in the soil. It has been reported that both TREL and DEL were unstable in the soil (Rhue et al., 1992), but the stability of the two species was not compared. DEL may have been found in the soil samples because of the length of sampling time. Our experiments lasted for about 24 hours. Therefore, TREL in the soil may have changed to DEL when the soil samples were prepared at the end of the experiments.

TABLE 14. MASS BALANCE OF Pb FOR THE COLUMN FLOW EXPERIMENTS IN MADISON AND ARREDONDO SOILS.

Parameter	Madison Soil	Arredondo Soil
Mass in Background Soil	18.2 mg	15.7
Mass in Influent	21.5 mg	1.03
Mass in Effluent	20.4 mg	2.4
Mass in Soil at the End of Experiment	19.6 mg	13.1
Mass Balance	101%	93%

3.   Displacement of Leaded Gasoline in Columns of Arredondo Soil

Figure 9 shows that no gasoline was displaced from the soil column by 2 pore volumes of NaCl solution flush. This result indicates that all the gasoline was captured by this soil enriched by organic C (12 percent). However, after application of 3.2 pore volumes of the W/S/CoS mixture, all the gasoline entrapped in the soil was removed from the columns because no gasoline was found in the soil samples at the end of the experiments. This occurred because a gasoline-in-water microemulsion system was produced as explained above in the displacement experiments for Madison loam soils.

A similar BTC was observed for TEL (Figure 10). No TEL was recovered from the soil columns by NaCl solution, but all of the TEL that was not degraded was removed by the W/S/CoS mixture because no TEL was detected at the end of the experiments. However, an estimate of the area under the BTC showed that only 45.4 percent of applied TEL was recovered. The low recovery rate for TEL was attributed to the biotic and abiotic degradation of TEL in the soil and confirmed by our batch study results for the degradation of TEL in the same soil (Figure 11). Figure 11 shows that 55.3 percent of
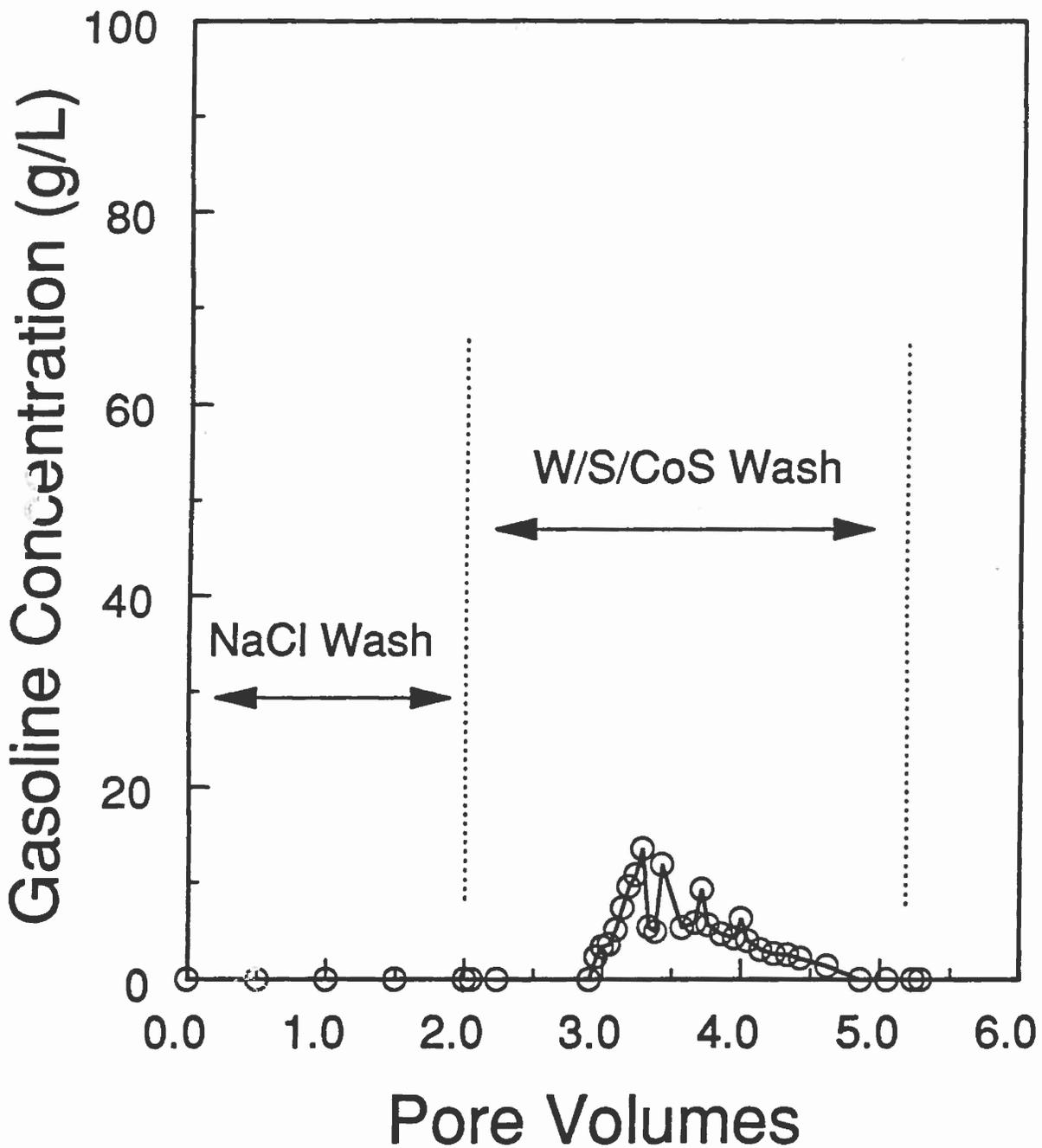
Figure 9. BTC for Gasoline in Arredondo Sand Soil Experiments. The experiments started with pumping 2.3 mL of leaded gasoline through the water-saturated soil column, followed by 2 pore volumes of NaCl and 3.2 pore volumes of W/S/CoS mixture washing.

the TEL disappeared or that 44.7 percent of the TEL was left in the soil within the first 2 hours and 64.8 percent of the TEL disappeared or 35.2 percent of the TEL was left in the soil after 24 hours, which was the total time period used for the column experiments. The discrepancy between the recovery rates of TEL in the batch study (45.4 percent) and column study (35.2 percent) at 24 hours was due to the
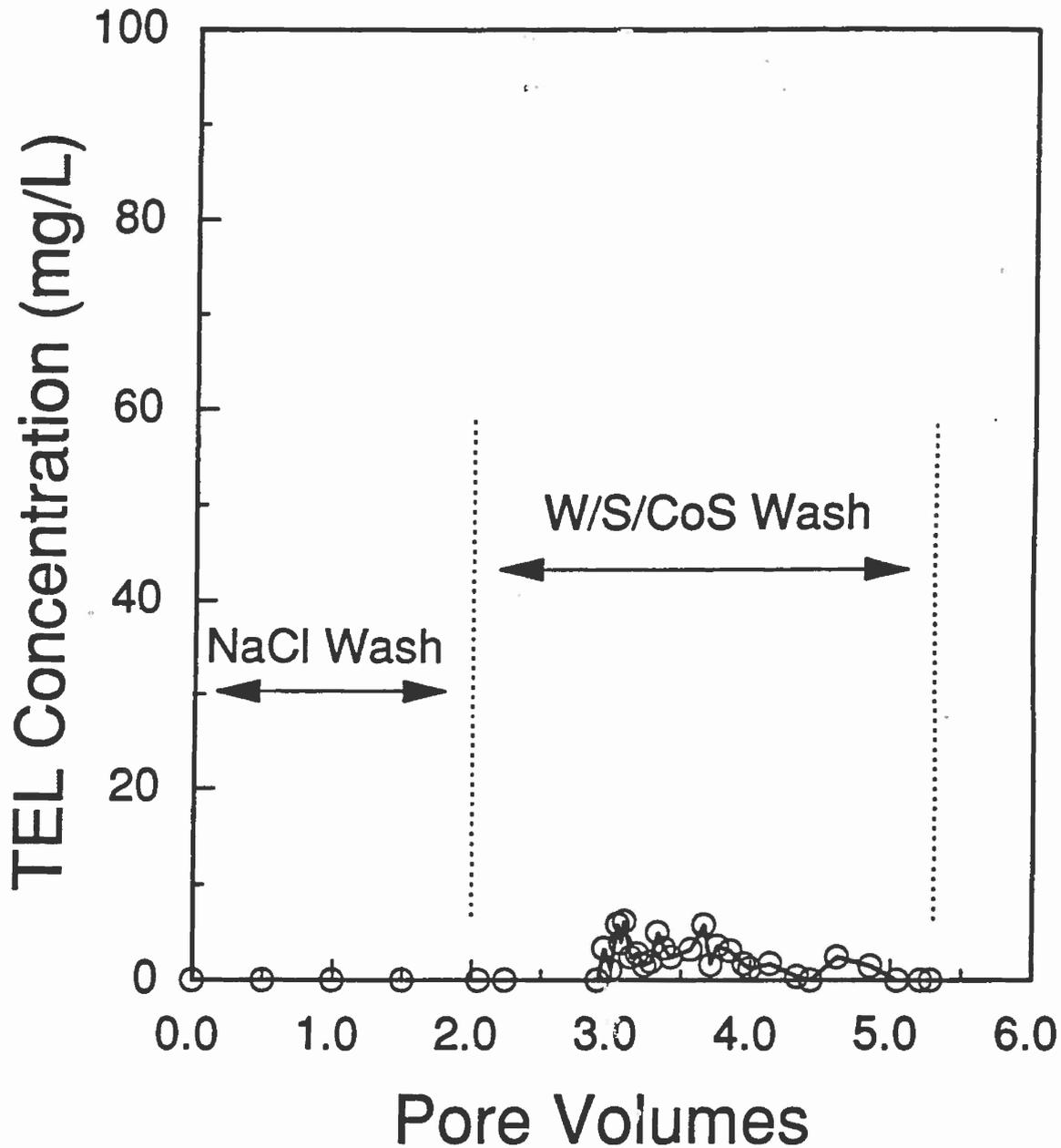
Figure 10. BTC for TEL in Arredondo Sand Soil Experiments. The experiments started with
pumping 2.3 mL of leaded gasoline through the water-saturated soil column, followed
by 2 pore volumes of NaCl and 3.2 pore volumes of W/S/CoS mixture washing.

time of TEL contact with the soil. The column flow involved a shorter contact time and nonequilibrium
reactions between TEL and soil due to the removal of TEL by the W/S/CoS mixture, whereas the batch
study involved a longer contact time and equilibrium reactions between TEL and soil due to the complete
mixture of TEL and soil with shaking. A mass balance analysis showed that the average total Pb recov-
ery rate for the experiments was 93 percent, indicating that experimental measurements were reasonable.
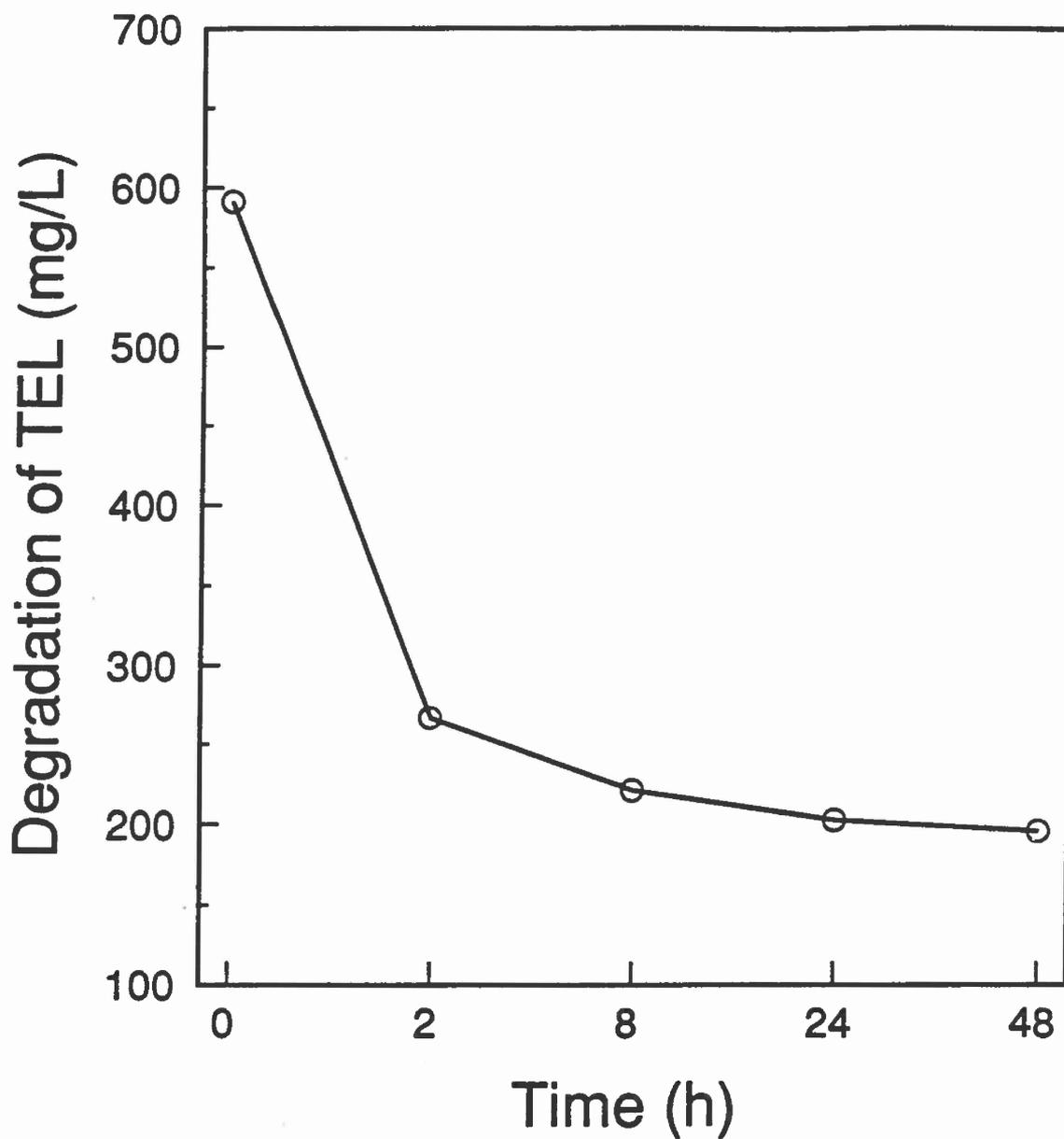
Figure 11. Degradation of TEL in Arredondo Sand Soil Experiments at Times
of 2, 8, 24, and 72 Hours.

4.   **Remediation Efficiency of Gasoline in Soils**

A residual analysis found no gasoline in the soil samples at the end of the experiments in Arredondo sand soil. This implies that a 100 percent remediation efficiency was achieved when the soil columns saturated with 3 percent of gasoline were washed by 3.2 pore volumes of the W/S/CoS mixture, because no gasoline was found by the NaCl solution flush. A residual analysis for experiments in Madison loam soil showed that 5.89 percent of gasoline was left in the soil at the end of the experiments. This result indicates that a 94.11 percent remediation efficiency was achieved when the soil columns saturated with 30 percent of gasoline were washed by 1.6 pore volumes of NaCl solution and 6.4 pore volumes of the

W/S/CoS mixture. The results indicate that the NaCl solution can be used to displace a certain amount of gasoline that is mobile in the soil pores but not the immobile residual gasoline. The use of the W/S/CoS mixture had a high remediation efficiency for removing gasoline and total Pb from soil columns.

D.   CONCLUSIONS

Soil contamination by hydrocarbons and heavy metals such as gasoline and Pb is widespread and is of public concern. Leaks and spills of leaded gasoline from storage tanks may contaminate soils and groundwater with toxic TEL and its degradation products. TEL is very unstable in soil and is subject to a series of sequential dealkylation steps. TEL first degrades to TREL, which in turn degrades to DEL, and finally to inorganic Pb^{+2}. Comparison of BTCs for gasoline and TEL shows that TEL can be transported through soil columns due to the migration of gasoline. Speciation of the TREL and DEL from TEL found in the effluent and soil samples indicates that TEL was unstable during the immiscible flow of gasoline. NaCl solution may be used to displace a certain amount of gasoline that is mobile in the soil but not the residual gasoline. Residual analysis shows that a 100 percent remediation efficiency was obtained for experiments in Arredondo sand with the application of the W/S/CoS mixture, whereas a 94.11 percent remediation efficiency was obtained for the experiments in Madison loam soil with the application of NaCl solution and the W/S/CoS mixture. Further study is needed to test the remediation efficiency of the W/S/CoS mixture in unsaturated soil before a given solution is used at field scale.

SECTION V

FATE AND TRANSPORT OF TRIETHYL LEAD IN SOIL COLUMNS

A.   INTRODUCTION

Leakage of leaded gasoline from underground storage tanks and the use of leaded gasoline from the 1920s to 1975 may lead to the production of ionic triethyl lead (TREL) in the soil and groundwater because of the dealkylation of TEL in the gasoline in the soil environment. TREL is very toxic and is water soluble. Production of TREL from leaded gasoline may contaminate soil and groundwater, and therefore poses a threat to public health. The objective of this study was to investigate the fate and transport of TREL in water-saturated soil columns of Leon soil.

B.   MATERIALS AND METHODS

1.   Materials

Analytical grades of TREL chloride was purchased from All-Chemie Ltd. (Ft. Lee, New Jersey). Pb standard solution was purchased from Fisher Scientific (Orlando, Florida). All other chemicals such as concentrated HCl, n-hexane, KI, KIO_3, NaCl, concentrated HNO_3, NaCl, EDTA disodium salt, NaDDTC, Na_2SO_4, 1.9 M Grignard reagent (MgBuCl in THF), and concentrated NH_4OH were analytical grades. Leon fine sand collected from Tyndall Air Force Base in Tyndall, Florida was used for the column experiments. Selected soil properties are presented in Table 15.

TABLE 15. SELECTED PROPERTIES OF TYNDALL SOIL.

Property	Value/Unit
pH	5.03
Organic C	0.11%
Sand	96.19%
Silt	0.34%
Clay	3.47%
Soil depth	15-30 cm

Solvent for extracting TREL from effluent was prepared by mixing 2 grams of EDTA disodium salt and 2 mL of 0.25 M NaDDTC·$3H_2O$ into a 100-mL volumetric flask. The solution was adjusted to pH = 9 with NH_4OH and diluted with DI water.

A 0.1-M ICl solution was prepared by mixing 40 mL DI water, 44.5 mL concentrated HCl, 11.0 grams of KI, and 7.5 grams of KIO_3. This solution was used to convert the TREL into Pb^{+2} so that the total Pb content in the effluent could be measured by atomic absorption spectrophotometry (AAS). Working standards of Pb solution for measuring the total Pb content in the effluent were made

by adding standard Pb solution in 3:1 DI water:0.1 M ICl solution at concentrations of 1, 10, and 20 μg/mL^{-1}. Working standards of Pb for measuring the total Pb content in the soil before and after the experiments were prepared according to EPA Method 3050 (U.S. EPA, 1986).

A 100 μg TREL/mL^{-1} solution was prepared by dissolving 0.025 gram of analytical TREL chloride salt into a 250-mL volumetric flask and diluting with DI water. TREL is highly water soluble but is not soluble in organic solvent such as hexane. Therefore, to measure TREL by GC, it is necessary to convert ionic TREL into butylized TREL (Bu-TREL), which is soluble in hexane. The procedures are given in Section IV of this report.

2.   Column Packing

Duplicate glass cylinders with a 4.8-cm inner diameter were used to hold 15.75-cm soil columns. To fill the cylinders, air-dried Leon find sand was crushed, passed through a 0.5-mm screen, poured into the cylinders in 2-cm increments, and stirred to prevent layering. The columns were tapped to settle the soil to the desired volume. The masses of the empty columns and the packed columns were weighed to determine their bulk densities (Table 16).

TABLE 16. EXPERIMENTAL PARAMETERS.

Parameters	Leon Soil
Bulk density, ρ_b (g/cm^{-3})	1.02
Darcy velocity, V (cm/h^{-1})	1.5
Column length, L (cm)	15.75
Cross section area, A (cm^2)	18.1
Pore volume (mL)	154.5

The columns initially were saturated with 0.1 M NaCl solution in an upward-flow mode, and a peristaltic pump was used to establish a low column flowrate (6 mL/h^{-1}) for 30 hours until the soil columns were saturated. After saturation the soil columns were weighed to determine the pore volumes (i.e., the mass difference between the dry soil columns and saturated soil columns). Then, the column flow was increased to have a desired Darcy flow velocity of 2.5 cm/h^{-1}. Experimental conditions for these columns are given in Table 16.

3.   Displacement of TREL through Soil Columns

When a designated flow velocity of 2.5 cm h^{-1} was reached, 1 pore volume of 100 μg TREL/mL^{-1} solution was pumped into the columns, followed by 1.5 pore volumes of 0.1 M NaCl solution washing. Effluent samples were collected by an automatic fraction collector to analyze TREL and total Pb using GC and AAS. Soil in the columns was analyzed for residual TREL and total Pb at the end of the experiments. Procedures for measuring TREL and total Pb in the effluent and the soil samples are given in Section IV of this report.
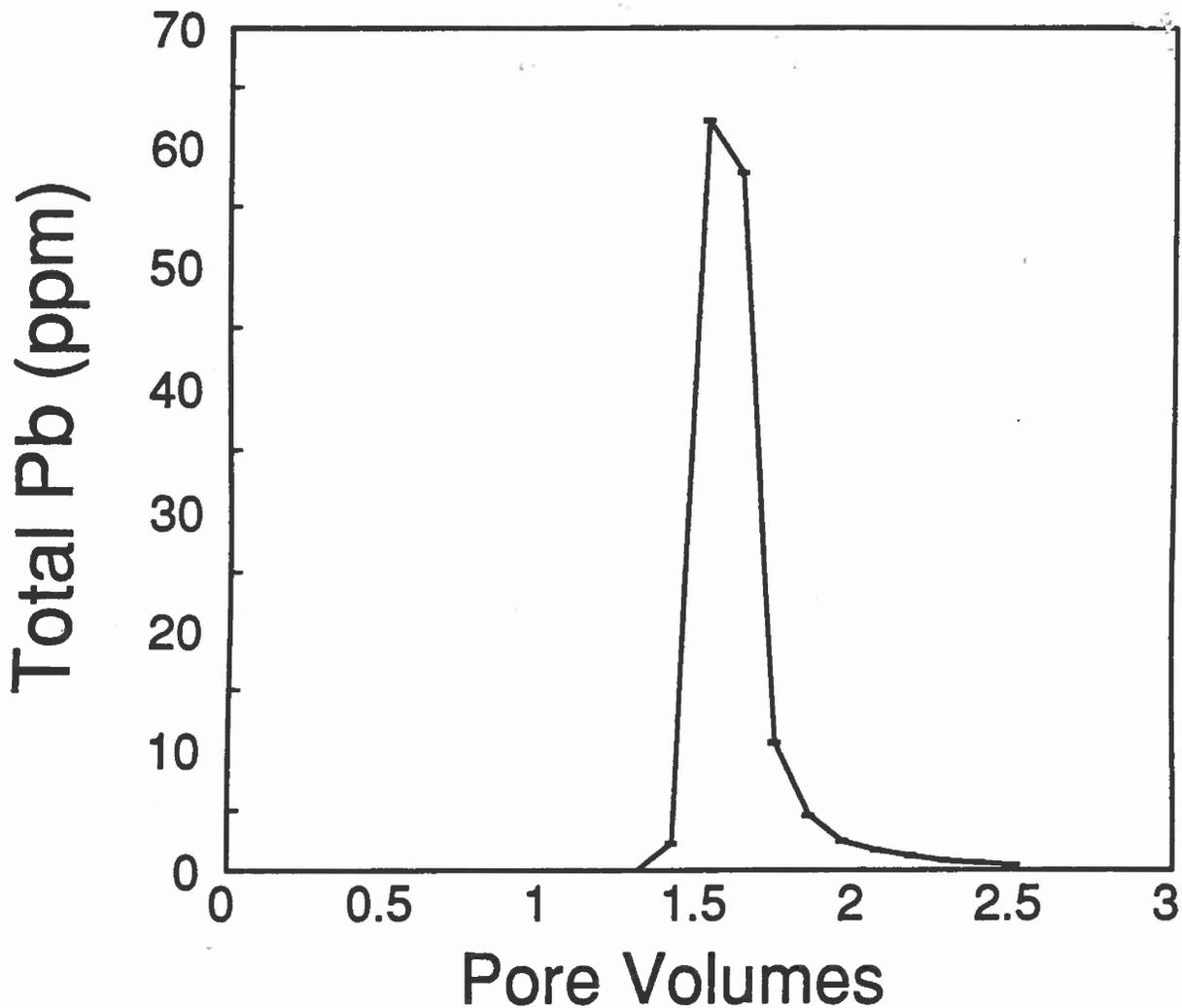
Figure 12. Average BTC for Total Pb in Leon Sand Soil Experiments.

C.   RESULTS AND DISCUSSION

No TREL was found in the effluent and the soil samples at the end of the experiments. Results show that TREL is unstable ionic alkyl lead in the soil environment. The mass balance analysis of the breakthrough curve (Figure 12) for total Pb from the experiments indicates that 78 percent of the total Pb was adsorbed by the soil.

D.   CONCLUSIONS

We have conducted a study to investigate the fate and transport of TREL in saturated soil columns. Results show that TREL is very unstable and degrades into other Pb species, because total Pb but not TREL was found in the effluent and soil samples at the end of the experiments. A mass balance analysis shows that only 22 percent of total Pb was washed out from the soil columns by the NaCl solution.

SECTION VI

FLOW OF LEADED-GASOLINE-IN-WATER MICROEMULSION
THROUGH WATER-SATURATED SOIL COLUMN

A.   INTRODUCTION

Soil contamination by hydrocarbons such as gasoline and heavy metals such as Pb is widespread and is of great public concern.   One technique currently used to remediate the problem is to wash the hydrocarbon-contaminated soil using surfactants (surface active agents).   Although this technique has shown significant potential for application in environmental remediation practices (Nasr-El-Din, 1992; Abdul et al., 1992; Pennell et al., 1993), a major obstacle for obtaining adequate washing efficiency is the potential clogging of soil pores due to the formation of unstable macroemulsions. Flow of emulsions may influence the transport of hydrocarbons through soil. Knowledge of such a phenomenon is crucial to a successful and cost-effective remediation of hydrocarbons from soil.

When two immiscible liquids such as gasoline and water are mechanically shaken together, two distinct layers commonly form. However, if a surfactant is added to lower the interfacial tension between the liquids and shaken, the milling together of the constituents causes one of the liquids to be dispersed in the other, thus producing an emulsion (Hiemenz, 1986). An emulsion is a dispersion of droplets of one liquid into another with which it is completely immiscible. A microemulsion is a special kind of emulsion which consists of water, gasoline, surfactant, and cosurfactant components, and is thermodynamically stable. Dispersed droplets in the microemulsion are so small that the microemulsion is transparent (Shinoda and Friberg, 1986). A major difference between macroemulsions and microemulsions is the droplet size in the dispersed phase. The droplets of a macroemulsion have diameters ranging from 1 to 10 μm. In a microemulsion, they range between 0.01 and 0.1 μm, which are larger than molecular solutions (<0.001 μm) but smaller than colloidal dispersions of polymers or clays (0.1 to 2 μm). A macroemulsion behaves more like a dispersion, whereas a microemulsion is closer to a true solution (Martel et al., 1993). Table 17 summarizes major differences in the physical-chemical properties of macroemulsions and microemulsions.

TABLE 17. MAJOR DIFFERENCES IN PHYSICAL-CHEMICAL PROPERTIES
OF MACROEMULSIONS AND MICROEMULSIONS.

Property	Macroemulsion	Microemulsion	Reference
Droplet Size	1-10 μm	0.01-0.1 μm	Martel et al., 1993
Stability	Thermodynamically unstable	Thermodynamically stable	Schramm, 1992
Color	Milky	Transparent	Shinoda and Friberg, 1986
Solvent power	Median	High	Shinoda and Friberg, 1986

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In general, there are two types of emulsions, depending on which liquid forms the continuous phase (Becher, 1965; Shinoda and Friberg, 1986; Schramm, 1992): (1) oil/water (O/W), where non-aqueous-phase liquids (NAPLs) such as oil or hydrocarbons are dispersed in a water phase, such as milk; and (2) water/oil (W/O), where water is dispersed in an oil or hydrocarbon phase, such as margarine. Various combinations of these two categories may occur. For instance, an O/W/O type emulsion is a multiple emulsion containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The type of emulsion that may form depends on a number of factors. If the ratio of phase volumes is either very large or very small, the phase having the smaller volume frequently is the dispersed phase. If the ratio is close to unity, the outcome depends on other factors such as the nature of the surfactants. Surfactants that are more soluble, dispersible, or wettable in or by oil favor the development of W/O emulsions (Ca^{2+} soaps are an example). In contrast, surfactants that are more soluble, dispersible, or wettable in water favor the development of O/W emulsions (Na^+ soaps are an example). Commonly occurring emulsifying agents found in petroleum emulsions are aphalthenes, resinous substances, oil-soluble organic acids (such as naphthenic acid), finely divided carbonate scales, silica, clays, metal sulfates, metal sulfides, or chemical additives. These substances usually stabilize droplet interfaces between external and internal phases of emulsions.

Emulsions can be found in almost every aspect of petroleum production and recovery processes — in reservoirs, wellheads, many parts of the refining process, and transport pipelines (Schramm, 1992). Soo and Radke (1984, 1986a, 1986b) reported that emulsion flow in porous media can occur by accident or by design in industrial processes such as in enhanced oil recovery. Pal et al. (1986) stated that crude oils produced from secondary and tertiary oil recovery processes often involve the formation of O/W emulsions.

Emulsions also may form naturally in the presence of natural organic acids in some crude oils, especially esphetic crude oils. These acids may eliminate the need for expensive surfactants to form emulsions. They react with strong alkalis (usually NaOH) to form petroleum soaps. These soaps diffuse into the oil-water interface, decrease interfacial tension, and form emulsions. Many researchers have used dilute alkali solutions (about 0.1 wt percent NaOH) to form O/W emulsions (Nasr-El-Din, 1992).

Investigations of emulsion flow through porous media have focused predominantly on petroleum recovery areas (Prince, 1977; Soo and Radke, 1984; Shinoda and Friberg, 1986; Kokal et al., 1992; Schramm, 1992). McAuliffe (1973) first proposed using dilute, stable emulsions as mobility control agents for oil recovery processes. He investigated their influence on transient permeability behavior of porous media. Pal et al. (1986) studied the flow behavior of concentrated O/W emulsions with oil concentrations ranging from 40 to 50 percent by volume. These authors found that the flow of emulsions was time-independent, non-Newtonian at higher dispersed phase concentrations. The emulsion viscosity increased sharply with an increase in the dispersed phase volume. In contrast, Devereux (1974) investigated the linear flow behavior of emulsions in sandstone by experimental measurement and mathematical modeling when the concentration of the dispersed phase was low (0.1 to 5 percent). Results obtained by Alvarado and Marsden (1979) for the flow of emulsions in both capillary tubes and porous media also showed that emulsions with an oil concentration less than 50 percent behaved like Newtonian fluids, whereas those with an oil concentration greater than 50 percent behaved like pseudoplastic fluids.

The use of surfactants as a remediation technique to remove toxic hydrocarbons from contaminated soil and groundwater has received considerable attention and has been explored in some detail. However, microemulsion flow through soils as a remediation technique and its influence on the transport of hydrocarbons and heavy metals has not been investigated. The objectives of this study were (1) to investigate the flow of the leaded-gasoline-in-water (LG/W) microemulsion through a water-saturated soil column and its influence on the transport of gasoline and Pb alkyls; (2) to compare the flow of the leaded gasoline and the LG/W microemulsion through water-saturated soil; (3) to evaluate the

washing efficiency of water-surfactant-cosurfactant (W/S/CoS) mixture on soil contaminated by leaded gasoline; and (4) to monitor the pressure changes during the process of column flow to track the possible clogging of soil pores by gasoline droplets.

B.   MATERIALS AND METHODS

1.   Materials and Column Packing

Leaded aviation gasoline was obtained from the Gainesville Regional Airport in Gainesville, Florida. The major organic Pb species in this gasoline is tetraethyl lead (TEL). Analytical grade TEL was purchased from All-Chemie LTD (Ft. Lee, New Jersey). Pb standard solution and sodium lauryl sulfate (SDS) were purchased from Fisher Scientific (Orlando, Florida). All other chemicals such as concentrated HCl, n-hexane, n-pentanol, KI, KIO_3, NaCl, and concentrated HNO_3 were analytical grades. Astatula fine sand (hyperthermic, uncoated typic quartzipsamments) was used for the column experiments. Soil samples were collected from the Ocala National Forest in Ocala, Florida. Selected soil properties are shown in Table 18.

TABLE 18. SELECTED PROPERTIES OF ASTATULA SOIL
USED FOR THIS STUDY.

Property	Value
pH	4.9
Organic C	0.1%
Sand	96.3%
Silt	1.9%
Clay	1.8%
CEC	0.68 cmol/kg $^{-1}$

A W/S/CoS mixture was made by mixing 4.3 grams of SDS and 8.7 grams of n-pentanol in 87 grams of deionized (DI) water. The LG/W microemulsion was prepared by mixing 2 grams of aviation leaded gasoline and 98 grams of the W/S/CoS mixture. Analytical-grade TEL was dissolved in n-hexane to make working standards with concentrations of 0.01, 0.05, 0.1, 1, 5, and 10 ppm. The leaded aviation gasoline was dissolved in n-hexane to make working standards with gasoline concentrations at 120, 480, and 1500 $\mu g/mL^{-1}$. A 0.1-M ICl aqueous solution was prepared by mixing 40 mL DI water, 44.5 mL concentrated HCl, 11.0 grams of KI, and 7.5 grams of KIO_3. This solution was used to convert the TEL into Pb^{+2} so that the total Pb content in the effluent could be measured by atomic absorption spectrophotometry (AAS). Working standards of Pb solution were made by adding standard Pb solution to 3:1 DI water:0.1 M ICl solution at concentrations of 1, 10, and 20 $\mu g/mL^{-1}$.

A glass cylinder with a 4.8-cm inner diameter was used to hold a 15.75-cm soil column. To fill the cylinder, air-dried Astatula sand was crushed, passed through 0.5-mm screen, poured into the cylinder in 2-cm increments, and stirred to prevent layering. The soil column was tapped to settle the soil to the desired bulk density of 1.6 g cm^{-3}.

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2. Column Flow for the Leaded Gasoline Displacement

The column initially was saturated by 0.1 M NaCl solution with an upflow mode using a peristaltic pump to establish steady-state water flow (0.33 cm/h^{-1}) until the soil column was saturated. A low velocity favored more complete displacement of air out of the soil column. After saturation, the soil column was weighed to yield a pore volume of 82.4 mL (i.e., the difference between the dry soil column and saturated soil column). Then the flowrate was increased to the desired Darcy flow velocity of 2.5 cm/h^{-1}. The water pressure drop along the column was measured by connecting the positive side of a pressure transducer to the in-flow end of the column and the negative side to the out-flow end of the column (Figure 13). After the 0.1-M NaCl solution flow reached a steady-state condition (2.5 cm/h^{-1}), 0.03 pore volume (or 2.3 mL) of leaded gasoline was pumped into the soil column. Then the column was washed by 4.5 pore volumes of 0.1 M NaCl solution, followed by 3.5 pore volumes of W/S/CoS mixture.
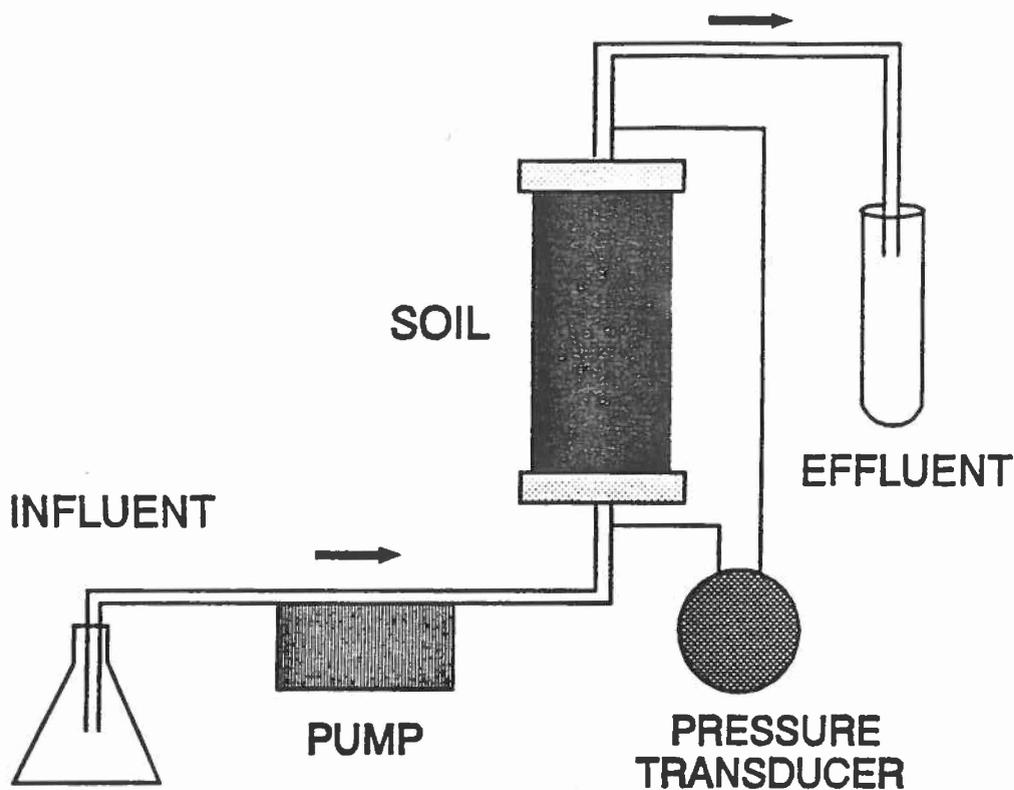
Figure 13. Schematic Diagram of the Experimental Apparatus.

Column effluent was collected in test tubes using a fraction collector and the tubes were covered immediately by parafilm-wrapped rubber stoppers. All test tubes and soil columns were wrapped by aluminum foil before the experiment started to minimize TEL transformation. The column pressure drop monitored by a pressure transducer was recorded every 10 minutes. A semidark area was used for this experiment to prevent the photodegradation of TEL into ionic Pb species. Samples were analyzed for gasoline and TEL immediately to avoid evaporative loss of gasoline and transformations of TEL in the effluent. After the column flow was terminated, the soil in the column was analyzed for residual TEL and gasoline.

3. Column Flow for the LG/W Microemulsion Displacement

All experimental procedures in this experiment were the same as in the leaded gasoline displacement experiment, except that one pore volume of the LG/W microemulsion rather than 0.03 pore volume of the leaded aviation gasoline was pumped through the soil column. However, the amount of the leaded gasoline used in both displacement experiments was exactly 2.3 mL. Experimental conditions for the leaded gasoline and the LG/W microemulsion displacement experiments are given in Table 19.

TABLE 19. COMPARISON OF EXPERIMENTAL CONDITIONS FOR THE LG/W MICROEMULSION DISPLACEMENT AND THE LEADED GASOLINE DISPLACEMENT EXPERIMENTS.

Parameters	LG/W Microemulsion Experiment	Leaded Gasoline Experiment
Bulk density (g/cm^{-3})	1.6	1.6
Velocity (cm/h^{-1})	2.5	2.5
Soil materials	Astatula sand	Astatula sand
Column length (cm)	15.75	15.75
Column I.D. (cm)	4.8	4.8
Applied leaded liquids (mL)	82 mL LG/W microemul. (containing 2.3 mL leaded gasoline)	2.3 mL leaded gasoline

4. Analysis of Column Effluent and Residuum

Effluent from the column experiments was analyzed for concentrations of gasoline, TEL, and total Pb to establish BTCs. Such extensive analyses are essential for deciphering the flow behaviors of the leaded gasoline and the LG/W microemulsion through the water-saturated soil columns. To analyze gasoline in the effluent in the absence of W/S/CoS mixture (i.e., when the leaded gasoline-contaminated soil column was washed by NaCl solution alone), 1 mL effluent was pipetted into 10 mL hexane solution and shaken for 2 minutes. Then, the gasoline in hexane phase was determined by ultraviolet (UV) spectrophotometry using the gasoline standards described earlier. Similar procedures were used to determine the gasoline concentrations in the effluent in the presence of W/S/CoS mixture, except that a small amount of NaCl salt was added to the mixture of aqueous phase plus hexane phase to enhance extraction into hexane. Samples prepared for measuring the gasoline also were used to analyze TEL concentrations by injecting the hexane phase into a gas chromatograph (GC).

A 20-μL hexane solution was injected into a GC for analysis of the TEL concentration with GC conditions similar to those reported by Chakraborti et al. (1989b). The total Pb content in the effluent was analyzed by the iodine monochloride method developed by Ouyang et al. (1994).

At the end of the experiments, soil in the columns was extracted and analyzed for residual gasoline, TEL, and total Pb content. One gram of wet soil and 10 mL hexane were added to test tubes and shaken for 30 minutes. Then the samples were centrifuged at 2000 rpm for 20 minutes and decanted. The hexane

phase solution was analyzed for gasoline and TEL by UV spectrophotometry and GC, respectively. The total Pb content in the soil was measured using U.S. EPA Method 3050 (U.S. EPA, 1986).

C.   RESULTS AND DISCUSSION

1.   Displacement of Leaded Gasoline through the Soil Column

This experiment was chosen to evaluate the displacement of the leaded gasoline through the water-saturated soil column followed by sequential flushing with 0.1 M NaCl solution and a W/S/CoS mixture. The experiment began with displacement of 2.3 mL (0.03 pore volume) aviation leaded gasoline through the water-saturated soil column, followed by 4.5 pore volumes of 0.1 M NaCl flushing solution and 3.5 pore volumes of W/S/CoS washing mixture. BTCs for gasoline, TEL, and total Pb as a function of relative pore volume (V/V_o) are shown on Figures 14, 15, and 16. No residual gasoline, TEL, or total Pb was found in the soil column at the end of the experiment.

Figure 14 shows that approximately 40 percent of the applied gasoline was displaced from the soil column contaminated by leaded gasoline by 4.5 pore volumes of 0.1 M NaCl solution. The remaining 60 percent occurred as residue in the soil pores. Capillary attractive forces resulted in some gasoline being displaced from relatively large pores but not from small pores. No matter how much the NaCl solution flowed through the column, a certain amount of residual gasoline remained entrapped.

Residual gasoline entrapped in the soil can be qualified by a capillary number. The capillary number N_c is a dimensionless ratio of viscous to capillary forces. It provides a measure of how strongly trapped residual oil is within a given porous medium (Taber, 1981)

$$N_c = \frac{\upsilon\mu}{\delta} \tag{3}$$

where υ is Darcy flow velocity, μ is the viscosity of the displacing phase, and δ is the interfacial tension between the displaced and displacing phases. Gupta and Trushenski (1979) reported that, for the oil phase, mobilization of residual oil usually begins at a capillary number of about 10^{-5} (the critical capillary number), and complete oil recovery occurs at a high value of capillary number of about 10^{-2}. The capillary number for this experiment was 2.4×10^{-7}, ($\upsilon = 0.025$ m/h^{-1}, $\mu = 2.8 \times 10^{-7}$ N/h/m^2, $\delta = 0.03$ N/m^{-1}), which was below the critical capillary number. Entrapment of residual gasoline was confirmed by the experiment.

The BTC for gasoline was observed to be a multimodal distribution during the NaCl solution flushing process (Figure 14). Multiple peaks resulted from immiscible displacement of gasoline droplets. When the column was flushed by the NaCl solution, gasoline droplets in the large pores were assumed to be displaced out of the column. Gasoline droplets in the smaller pores were strained until a sufficiently high capillary pressure was reached at which the gasoline droplets were pushed through the soil pores. A snap-off model given by Chatzis et al. (1983) was used to explain this phenomenon. In this model, NAPL (gasoline) initially fills a series of connected pore bodies. The surface of each pore wall is assumed to be water-wet and is coated with a thin film of water. The capillary pressure varies with the path and tends to be highest at the pore throat. As water flows into pores, some NAPL will be entrapped. But if the capillary pressure becomes high enough, the NAPL phase will be snapped off into globules within the pores in the flow path and may be squeezed out of the pore throats. Snap-off begins to occur as the ratio of maximum pore diameter to pore throat diameter exceeds a critical value.

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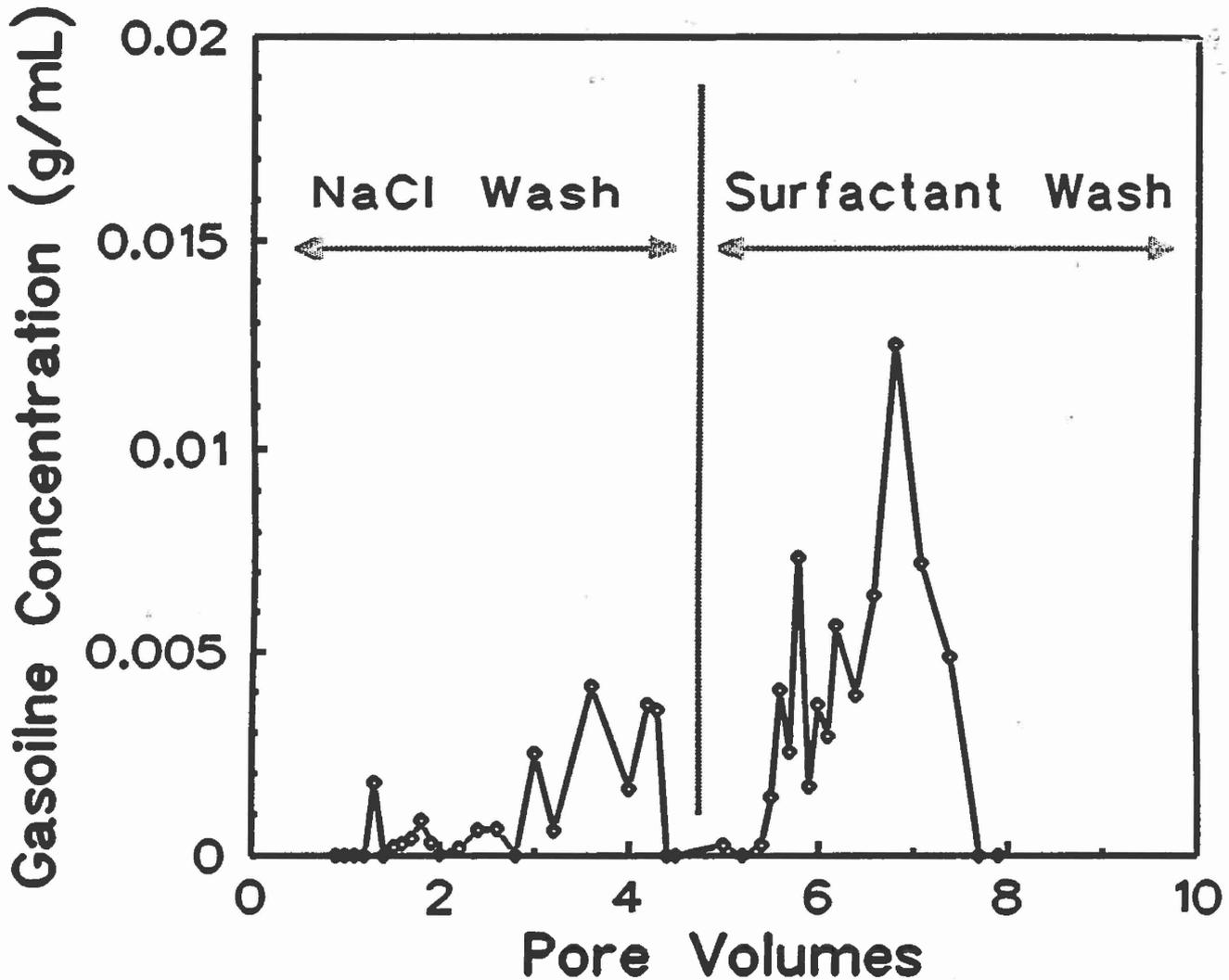
Figure 14. BTC for Gasoline in the Leaded Gasoline Displacement Experiment. The experiment started with pumping 0.03 pore volume of the leaded gasoline through the water-saturated soil column, followed by 4.5 pore volumes of NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

After flushing with the NaCl solution, a W/S/CoS mixture was used to flush the residual gasoline that was entrapped in the soil pores (Figure 14). No gasoline was detected within the column soil at the end of the experiment. When the W/S/CoS mixture was pumped into the column, the interfacial tension between the water and gasoline phases was extremely low, leading first to displacement of gasoline due to the formation of an LG/W microemulsion. The gasoline droplets in the microemulsion ranged in size from 0.01 to 0.1 μm, which was comparable to the soil pore size. Therefore, the flow behavior of the microemulsion was closer to that of a true solution (Martel et al., 1993). As a result, clogging of the gasoline droplets by the soil pores was eliminated by the W/S/CoS mixture, and all the residual gasoline was removed from the column.

No measurements were conducted to characterize the size of the gasoline droplets to determine if the effluent was a macroemulsion or microemulsion in this experiment due to the lack of
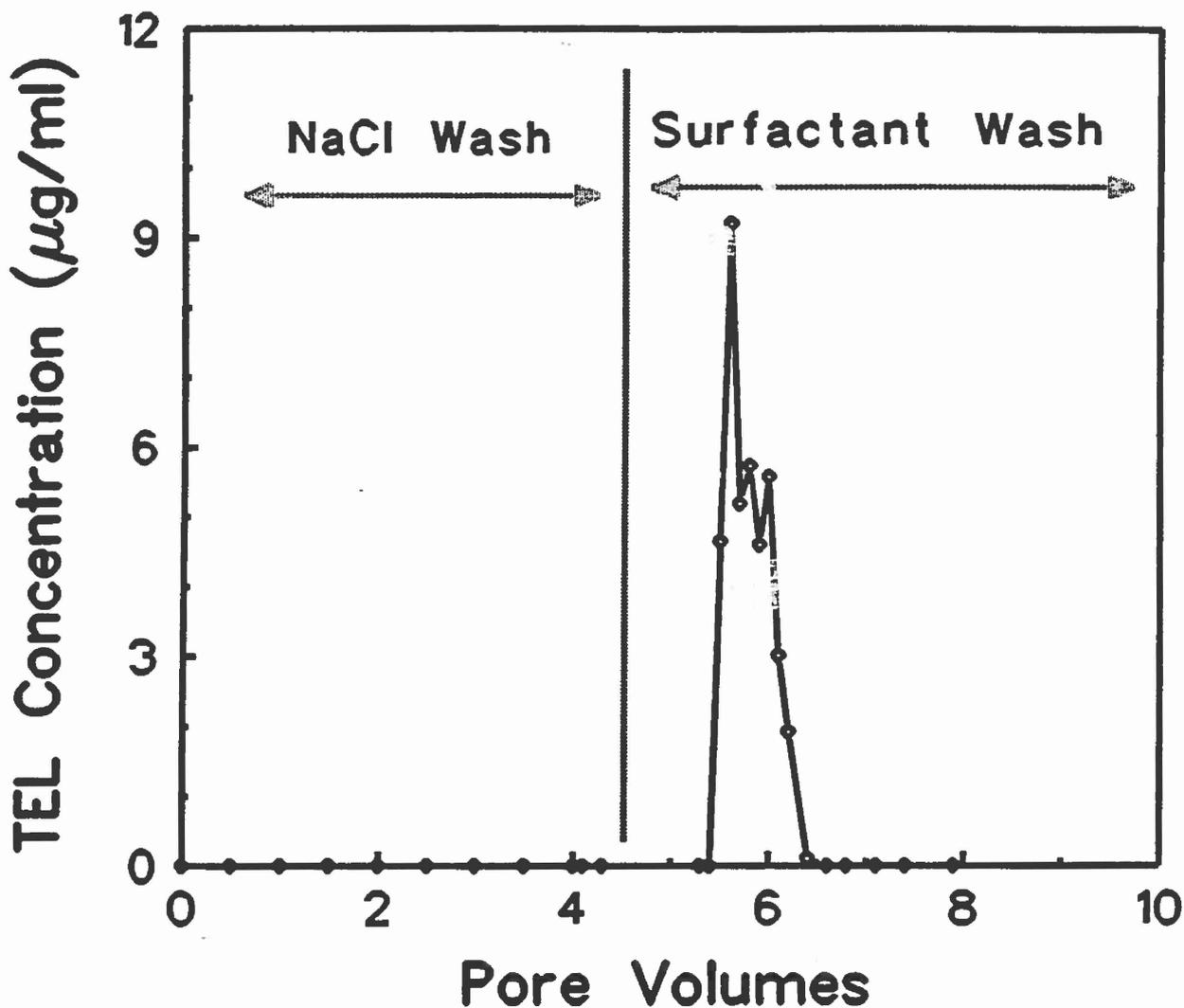
Figure 15. BTC for TEL in the Leaded Gasoline Displacement Experiment. The experiment started with pumping 0.03 pore volume of the leaded gasoline through the water-saturated soil column, followed by 4.5 pore volumes of NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

appropriate equipment in our laboratory. We assumed that the effluent obtained was a microemulsion when the W/S/CoS mixture occurred in the effluent, except for the first couple of effluents that were turbid and cloudy due to the low concentration of the W/S/CoS mixture. This assumption was justified because (1) no separation of gasoline and water phases was observed in the effluent and (2) the components of gasoline, W/S/CoS mixture, and water were verified to exist in the effluent by our measurements. These facts indicate that the effluent contained an emulsion. Furthermore, no Tyndall effect (Hiemenz, 1986), which is characteristic of a macroemulsion, was observed for the effluent. Therefore, the transparent and clear effluent that was observed obviously was a microemulsion.

Changes in TEL concentrations as a function of relative pore volume (V/V$_o$) for the experiment are shown on Figure 15. No TEL was found in the effluent when the soil contaminated with leaded gasoline was flushed by NaCl solution. As reported by Feldhake and Stevens (1963), TEL is a
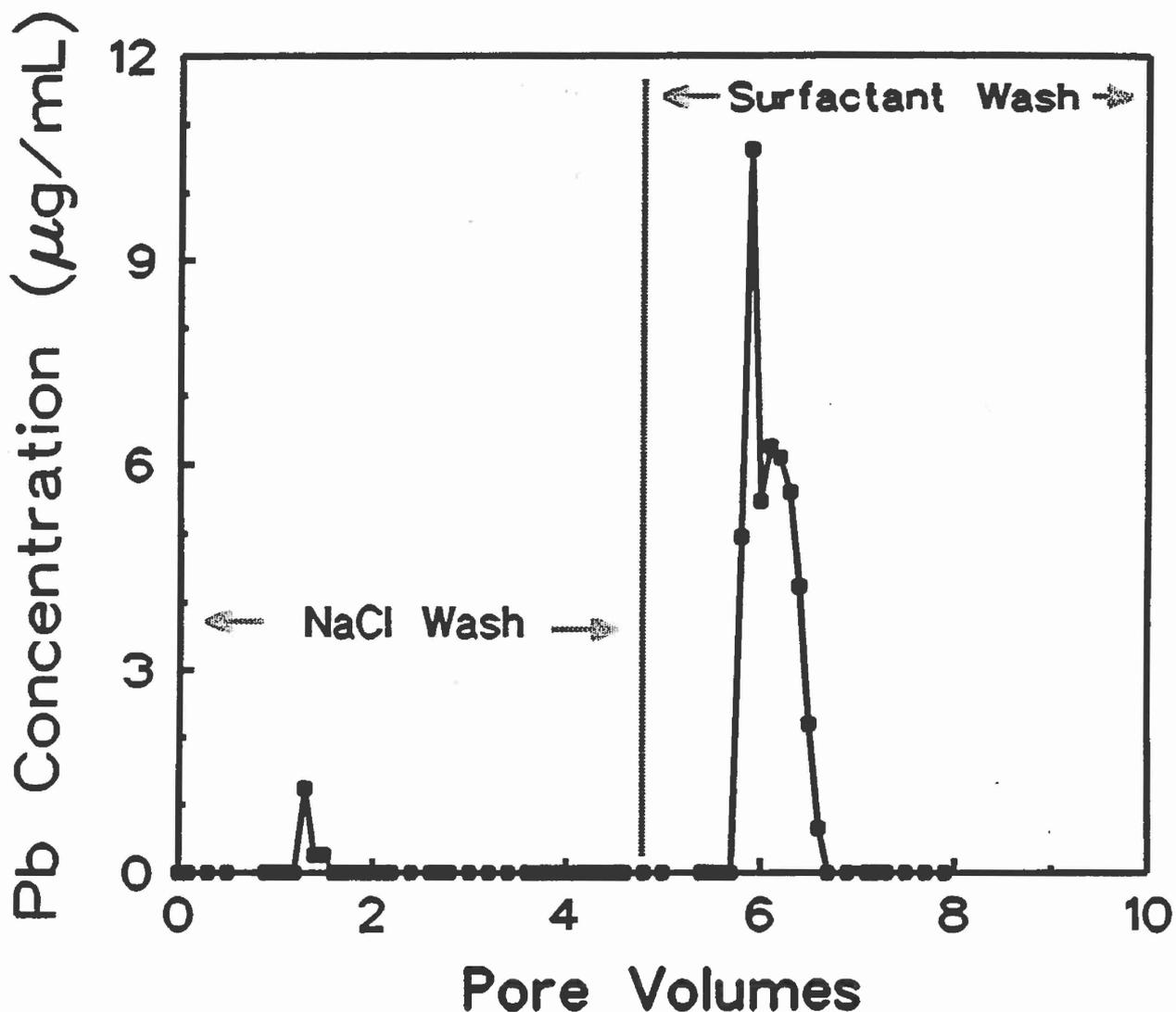
Figure 16. BTC for Total Pb in the Leaded Gasoline Displacement Experiment.
The experiment started with pumping 0.03 pore volume of the leaded
gasoline through the water-saturated soil column, followed by 4.5 pore
volumes of NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

hydrophobic compound with very low water solubility and is very unstable when in contact with soil.
As a result, no TEL was found in the effluent washed by the NaCl solution. The opposite result was
obtained for TEL when the soil column was washed by the W/S/CoS mixture (Figure 15). The break-
through of TEL in the effluent resulted from the breakthrough of gasoline dispersed in the microemul-
sions. TEL in microemulsion was removed along with the gasoline from the soil column. A similar BTC
was obtained for total Pb as obtained for TEL, except that a smaller peak was observed when the soil
column was flushed by NaCl solution (Figure 16). This occurred because TEL is very unstable when
in contact with soil and undergoes a series of sequential dealkylation steps to end up eventually as Pb^{+2}.

2.   Displacement of the LG/W Microemulsion through Soil Column

This experiment was chosen to investigate the influence of the miscible flow of an LG/W
microemulsion upon the transport of gasoline, TEL, and total Pb in the water-saturated soil column

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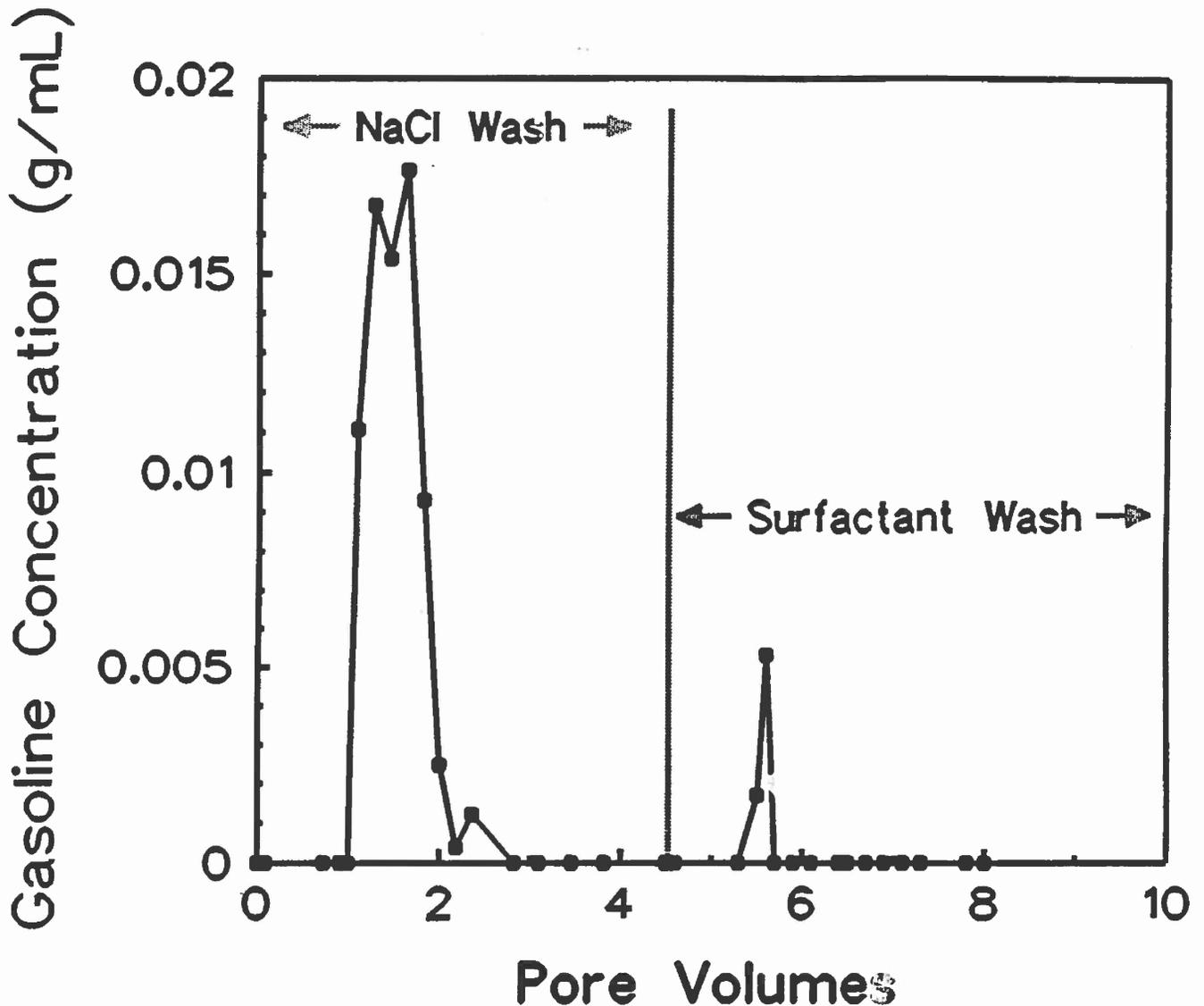
Figure 17. BTC for Gasoline TEL in the LG/W Microemulsion Displacement Experiment.
The experiment started with pumping 1 pore volume of the leaded gasoline
through the water-saturated soil column, followed by 4.5 pore volumes of
NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

during a period of sequential flushing with a NaCl solution and a W/S/CoS mixture. The experiment started with pumping one pore volume of the LG/W microemulsion through the water-saturated column, followed by 4.5 pore volumes of 0.1 M NaCl flushing solution and 3.5 pore volumes of W/S/CoS washing mixture. BTCs for gasoline, TEL, and total Pb as a function of relative pore volumes (V/V_o) are shown in Figures 17, 18, and 19, respectively.

About 90 percent of the total input of gasoline in the microemulsion was flushed out by NaCl solution, with only 10 percent of the gasoline remaining as residue in the soil pores (Figure 17). This occurred because the droplet size of the gasoline in the microemulsion was small compared to the pore size. Therefore, most of the gasoline was miscibly flushed out by NaCl solution. There are two
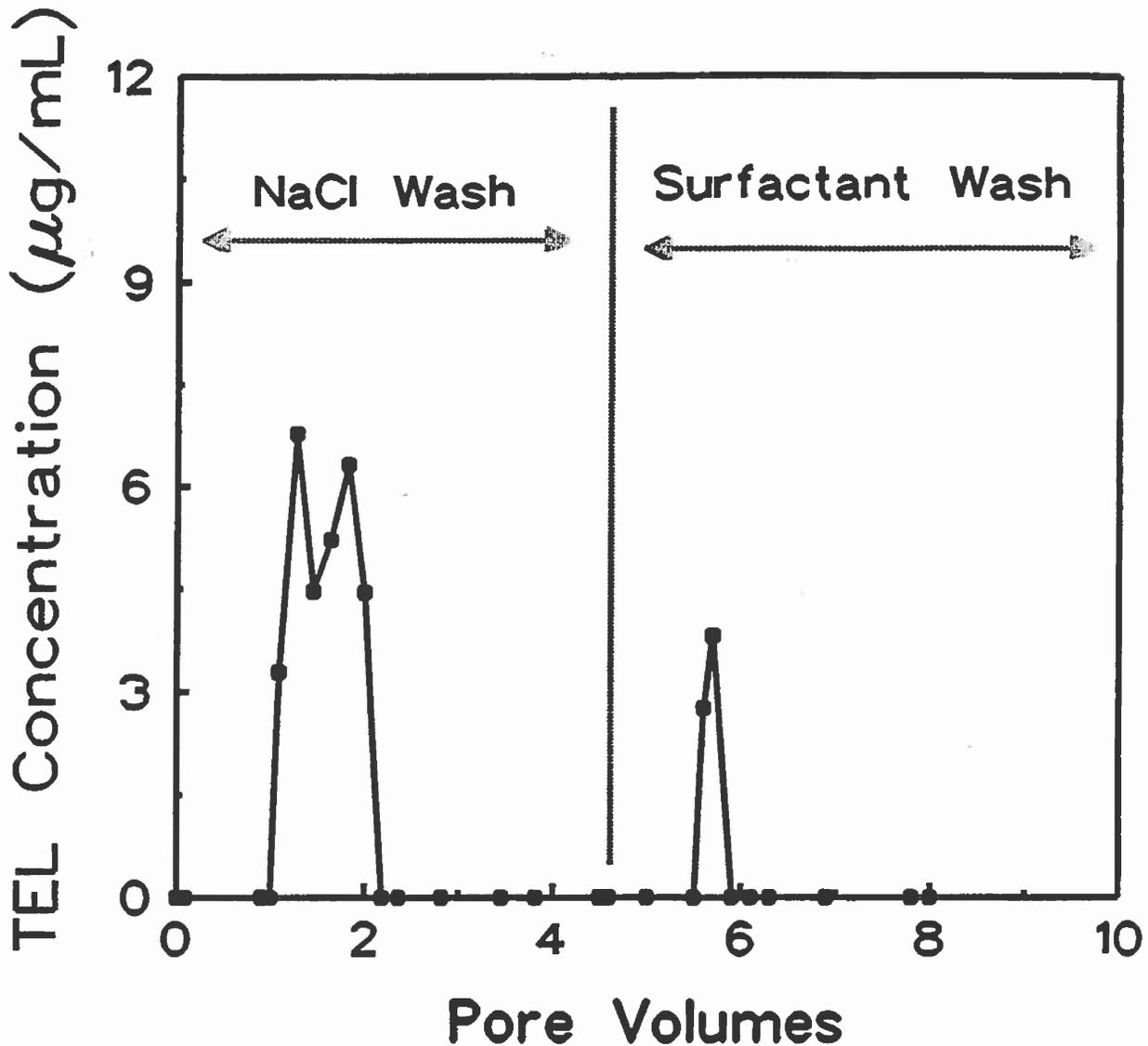
Figure 18. BTC for TEL in the LG/W Microemulsion Displacement Experiment.
The experiment started with pumping 1 pore volume of the leaded
gasoline through the water-saturated soil column, followed by 4.5 pore
volumes of NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

possible explanations for the small amount of residual gasoline (10 percent) that clogged the soil pores.
First, dilution of the LG/W microemulsion by the NaCl solution may have resulted in demulsification,
separating the gasoline from the water phase and leading to multiple-phase flow and pore clogging.
Second, some of the gasoline droplets were captured by small pore necks and could not be removed by
NaCl solution.

After flushing with the NaCl solution, the W/S/CoS mixture was pumped through the soil
column. Because no gasoline was detected in the column soil at the end of the experiment, it was
concluded that all the residual gasoline (approximately 10 percent of the total input of gasoline) that had
clogged the soil pores was washed out by the W/S/CoS mixture (Figure 17).
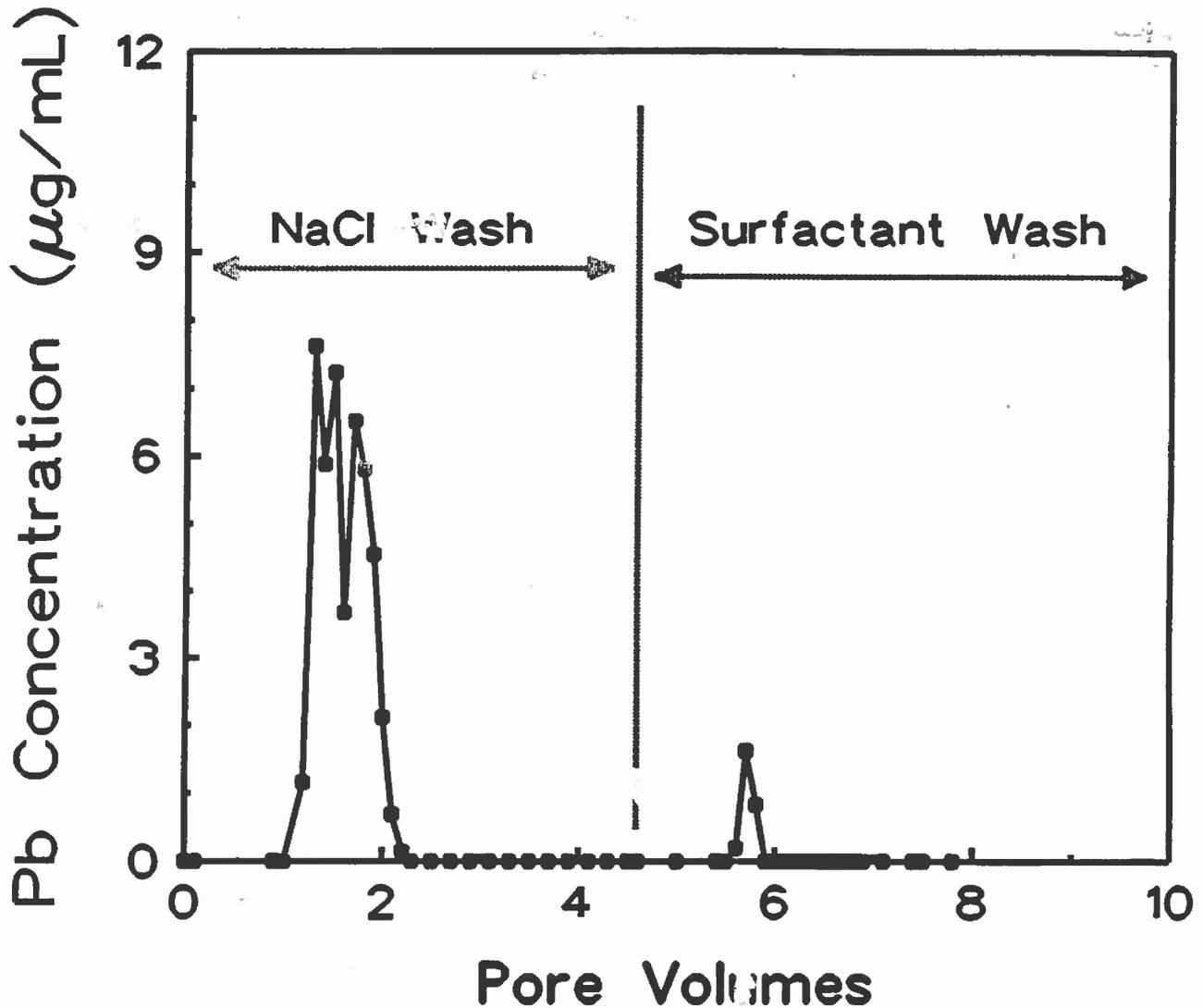
Figure 19. BTC for Total Pb in the LG/W Microemulsion Displacement Experiment. The experiment started with pumping 1 pore volume of the leaded gasoline through the water-saturated soil column, followed by 4.5 pore volumes of NaCl and 3.5 pore volumes of W/S/CoS washing mixture.

Changes in TEL concentrations in the effluent during the LG/W microemulsion displacement are shown on Figure 18. A graphical analysis shows that about 80 percent of the TEL in the gasoline droplets, which was not degraded into ionic forms, was flushed out by the NaCl solution and the remaining 20 percent was removed by flushing with the W/S/CoS mixture. A similar BTC also was obtained for total Pb (Figure 19).

3.   Leaded Gasoline vs. LG/W Microemulsion Displacement

Table 19 compares the experimental conditions for the leaded gasoline displacement and the LG/W microemulsion displacement experiments. All experimental conditions were the same in both

displacement experiments, except that 0.03 pore volume of leaded aviation gasoline was used in the leaded gasoline displacement experiment, whereas one pore volume of the LG/W microemulsion was used in the LG/W microemulsion displacement experiment. However, the amount of leaded aviation gasoline used in both displacement experiments was exactly the same (2.3 mL), so that the mass comparison of leaded gasoline components between the two displacement experiments was available.

Comparison of BTCs for gasoline (Figure 20) between the two displacement experiments shows that the flow of the LG/W microemulsion enhanced the migration of gasoline within the soil, because 90 percent of the gasoline was flushed out by NaCl solution in the microemulsion displacement experiment, whereas only 40 percent was flushed out in the leaded gasoline displacement experiment by the same solution. This occurred because gasoline was dissolved in the microemulsion with its droplet
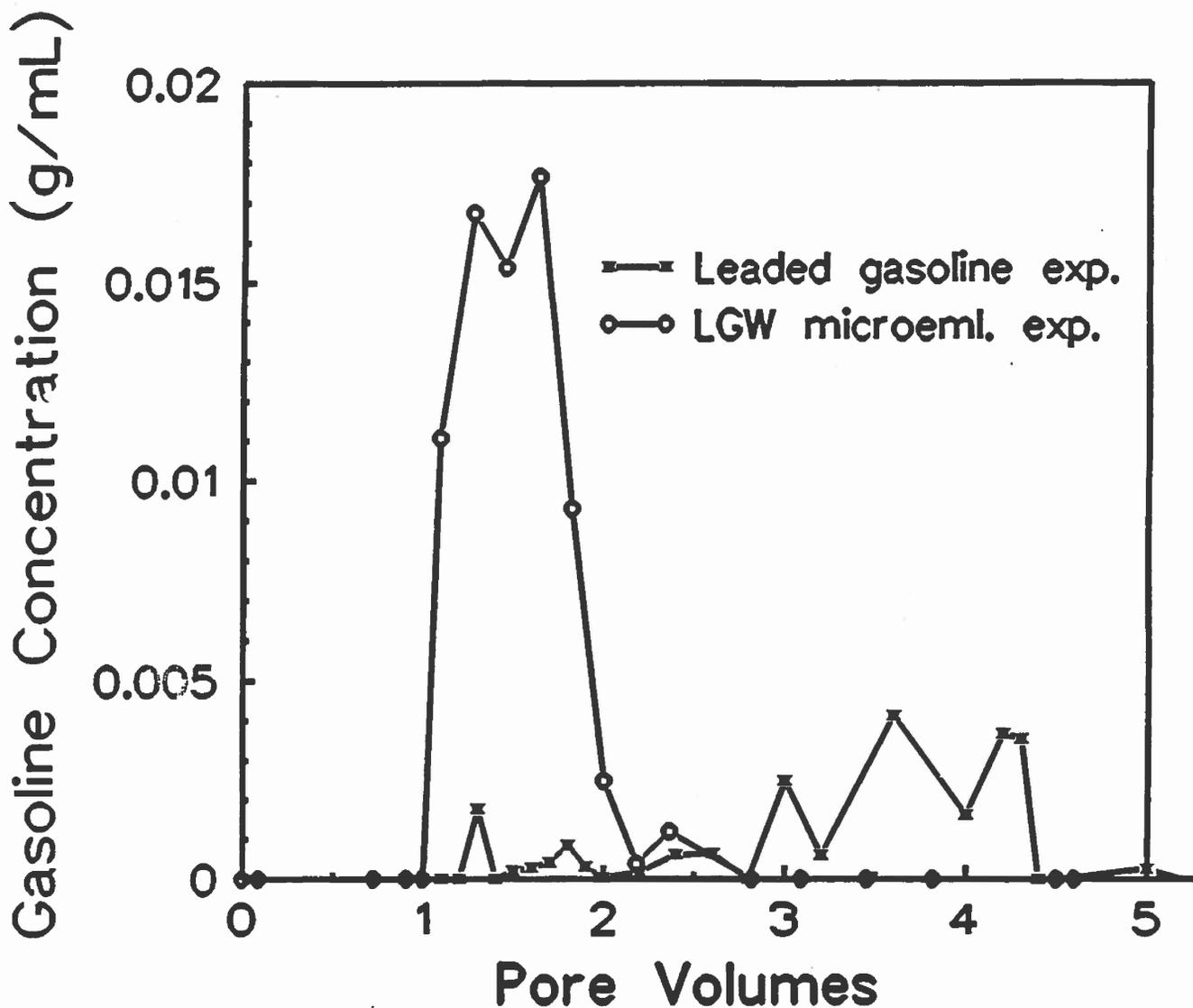
Figure 20. Comparison of Gasoline BTCs between the Leaded Gasoline Displacement and the LG/W Microemulsion Displacement Experiments.

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size comparable to the pore size, whereas in the leaded gasoline displacement experiment the gasoline was immiscible with NaCl solution and became trapped in the soil pores by capillary attractive forces.

The results obtained for total Pb were similar to those for gasoline (Figure 21). That is, the flow of the LG/W microemulsion enhanced the transport of total Pb through the soil column. About 90 percent of total Pb was flushed out in the LG/W microemulsion displacement experiment when the column was washed by NaCl solution alone, whereas only 10 percent of total Pb was flushed out in the leaded gasoline displacement experiment. This occurred because the total Pb existed mostly as TEL and was dissolved in gasoline, which became entrapped in the soil pores in the immiscible displacement
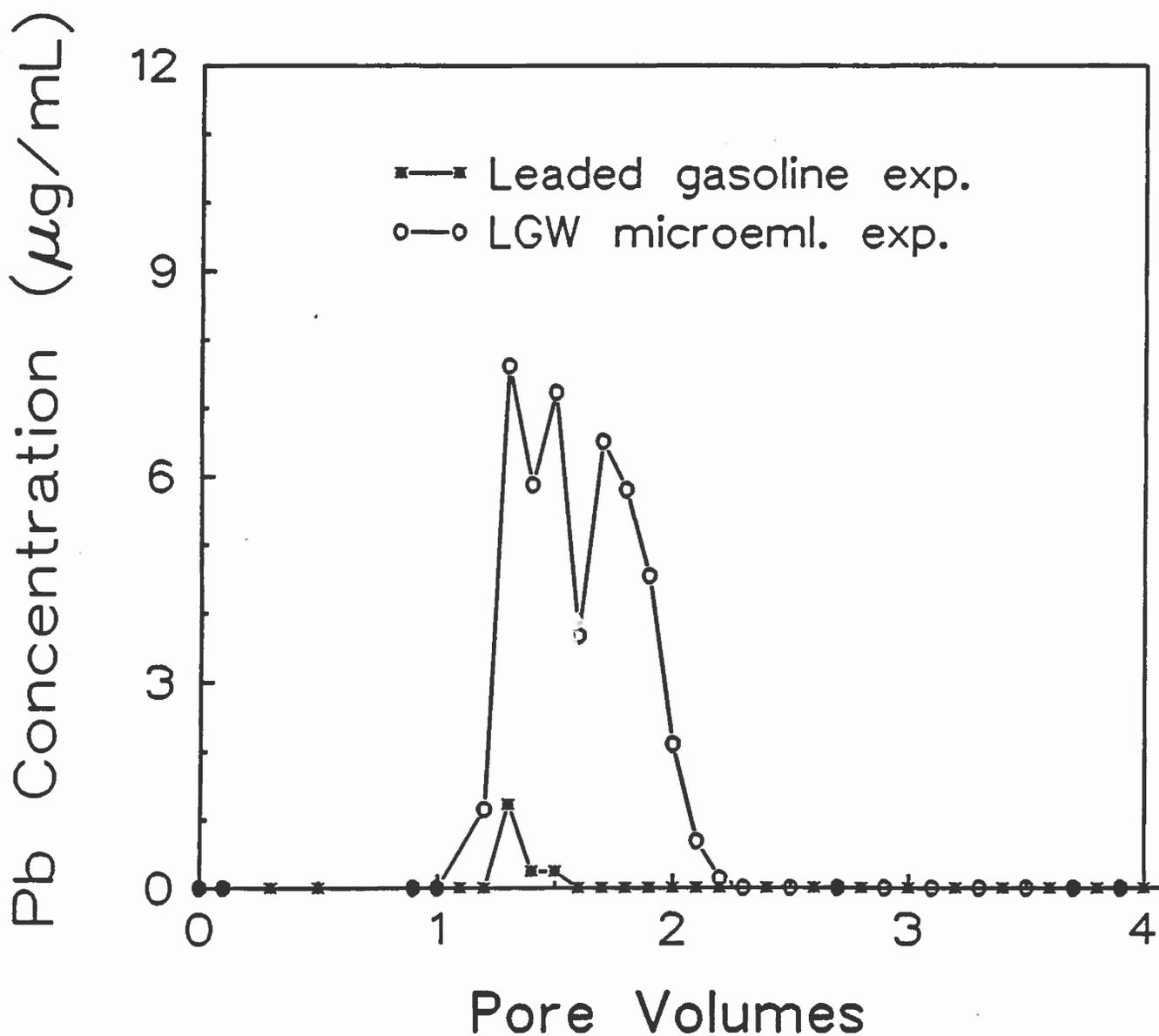
Figure 21. Comparison of Total Pb BTCs between the Leaded Gasoline Displacement and the LG/W Microemulsion Displacement Experiments.

of leaded gasoline experiment, but the total Pb in the miscible displacement of LG/W microemulsion experiment was mobile with less pore clogging. As a result, more total Pb was flushed out by NaCl solution in the LG/W microemulsion displacement experiment.

Possible trapping cf gasoline droplets in the two displacement experiments was evaluated by monitoring the changes in pressure-head drop along the soil column during the experiments (Figure 22). The column pressure-head drop initially was adjusted to zero. Column pressure began to increase to about 34 cm in the leaded gasoline displacement experiment right after the leaded gasoline was pumped through the soil column. The increase occurred because some of the soil pores were clogged by gasoline blobs due to the capillary force. As a result, a high pressure-head drop was observed within the soil column. Then, from 0.2 to 1 pore volume, the pressure decreased from 30 to 10 cm. This phenomenon was a result of gasoline droplets being squeezed out of some pore necks or throats due to the
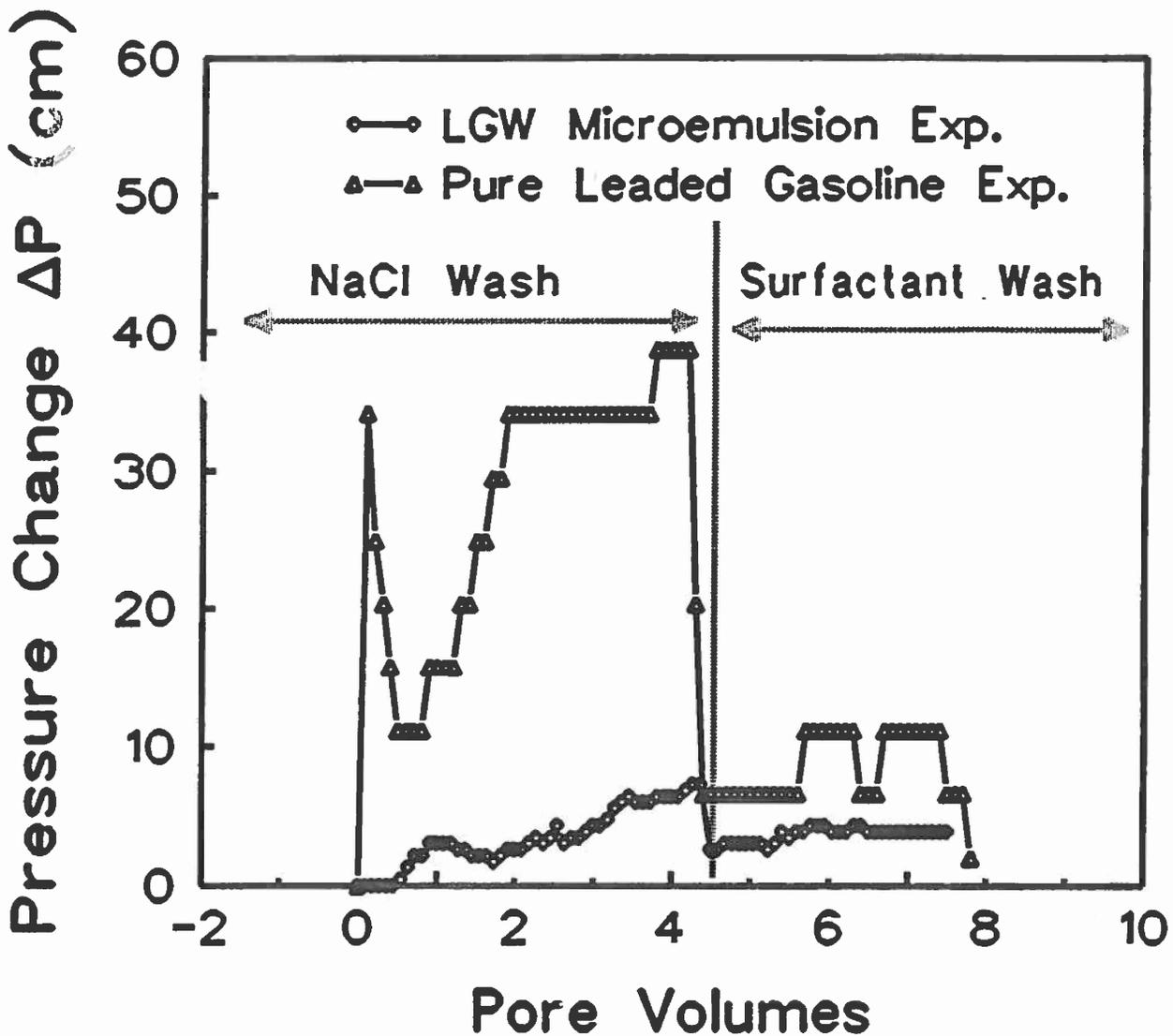

Figure 22. Comparison of Column Pressure-Head Drops between the Leaded Gasoline Displacement and the LG/W Microemulsion Displacement Experiments.

high pressure accumulated in those pores. As the NaCl solution was continuously pumped through the soil column, more and more gasoline droplets were strained by smaller soil pores, causing an increase in the column pressure-head drop from 10 to 38 cm for pore volumes from 1 to 4.5.

After the column was flushed with the NaCl solution, W/S/CoS mixture was used to remove the residual leaded gasoline that was entrapped in the soil pores. The column pressure-head drop immedi...:ely decreased from 38 to 5 cm right after the W/S/CoS mixture was applied. Then the pressure-head drop fluctuated in a range from 5 to 10 cm during the surfactant washing process, and finally dropped to about 2 cm. This result indicates that pore clogging by gasoline droplets was minimized by the W/S/CoS mixture. In contrast, the pore clogging by oil in a macroemulsion flow system was not minimized. Soo and Radke (1986a,b) reported that the flow of dilute, stable macroemulsion in porous media such as in sand columns reduces the permeability of the soil. These authors concluded that, at steady-state condition, large-drop-size macroemulsions reduce permeability more than small-drop-size macroemulsions.

Theoretically, the column pressure-head should drop down to the original setting (i.e., zero at the beginning) after all the residual gasoline has been washed out by the W/S/CoS mixture. Our experiments ... ow that the column pressure-head dropped close to zero. This may be a result of slight pore cloggi.ng ...y soil particles due to the high pressure-head drop at the time when the leaded gasoline was pumped through the soil column and flushed by NaCl solution. This high column pressure-head may change the pore space arrangement and cause the clogging by soil particles.

In contrast, the column pressure-head drops in the LG/W microemulsion displacement experiment were much smaller than in the leaded gasoline displacement experiment, although a similar pressure-head drop pattern was observed in both displacement experiments. That is, the column pressure-head increased with the N. .l solution flushing and decreased with the W/S/CoS mixture washing. This result indicates that pore clogging by gasoline droplets (or permeability reduction) was greatly minimized during the flow of the LG/W microemulsion.

D.   CONCLUSIONS

Contamination of soil and g:oundwater with NAPLs such as gasoline and hydrocarbon is wide-spread and of great public concern. Although the use of surfactants as a remedial technique to clean up NAPLs from soil has shown significant potential for application, one of the most important problems that has not been adequately explored is the formation of macroemulsions or microemulsions due to the use of surfactants. Flow of unstable macroemulsions has been shown to inhibit the transport of NAPLs through soil (Buist and Ross, 1987). In contrast, flow of stable microemulsions enhances the transport of gasoline and Pb through soil, as reported in this study. A major factor causing a difference in flow behavior between macroemulsions and microemulsions is the size of the NAPL droplets dispersed in the aqueous phase. The NAPL droplets in the macroemulsion range in diameter from 1 to 10 μm. In a microemulsion, they range from 0.01 to 0.1 μm, which is comparable to the pore size, greatly minimizing clogging of soil pores.

A macroemulsion may be produced if a single surfactant component is used to wash hydrocarbons from soil. This will result in low remedial efficiency due to the pore clogging by a large size of the hydrocarbon droplets. Our study suggests that a successful and cost-effective remediation of NAPLs from soil could be achieved if a mixture of W/S/CoS is used to produce a microemulsion. Further study in needed to test the formation and flow of microemulsions in unsaturated and heterogeneous soil columns before a given solution is used at field scale.

A METHOD FOR MEASURING TETRAETHYL LEAD
AND TOTAL LEAD IN ORGANIC SOLVENTS

A.   INTRODUCTION

The public health concern over the Pb content in the subsurface environment has necessitated development of a method to determine Pb content (both organic and inorganic species) that is accurate but is not demanding of time, technique, or special equipment. Currently, American Society for Testing and Materials (ASTM) Standard Method D3237 is used to measure the total Pb content in leaded gasoline (Kashiki et al., 1971; ASTM, 1988). The ASTM method is time-consuming, expensive, and tedious compared to the method presented in this document.

Newman et al. (1947) reported that TEL in leaded aviation gasoline can be determined by the iodimetric method. The chemical reaction for the procedure was expressed as:

$$Pb(C_2H_5)_4 + I_2 = Pb(C_2H_5)_3I + C_2H_5I \tag{4}$$

First, an excess of iodine was added to a measured volume of gasoline. After complete reaction, the unreacted iodine was titrated with sodium thiosulfate. The authors concluded that the method was applicable to all aviation gasoline and had a maximum deviation of ± 0.05 mL of TEL per gal when compared with the ASTM results.

Conversion of TEL and triethyl lead (TREL) to diethyl lead (DEL) using iodine monochloride (ICl) solution has been reported by Hancock and Slater (1975), Chau et al. (1979), and Noden (1980). However, TEL degrades through a series of sequential dealkylation steps, including TREL and, in turn, DEL, and finally degrading to inorganic Pb^{+2} (Rhue et al., 1992). Because the ICl solution can be used to convert TEL and TREL to DEL, it might convert TEL directly to Pb^{+2}. If this is so, TEL and total Pb contents in organic solvents can be determined easily. That is, TEL can be converted to Pb^{+2}, which can be measured by atomic absorption spectrophotometry (AAS), and then TEL content can be estimated using a back calculation according to the molecular fraction of Pb present in TEL.

The objective of the study described in this section was to develop a simple ICl digestion method for measuring both TEL and total Pb content in organic solvents. Two types of samples were used: TEL in gasoline and TEL in hexane. In addition, an experiment was conducted to verify that the above procedures indeed convert TEL to inorganic Pb^{+2} and not to a mixture of the intermediate TREL and DEL species, which are highly soluble in water.

B.   MATERIALS AND METHODS

Analytical-grade TEL and Pb standard solution were purchased from All-Chemie Ltd. (Ft. Lee, New Jersey) and Fisher Scientific (Orlando, Florida), respectively. Unleaded gasoline was obtained at a local gasoline station in Gainesville, Florida. All other chemicals (e.g., concentrated HCl, n-hexane, KI, KIO_3, EDTA, NaDDTC) were analytical grade. A 0.1-M ICl aqueous solution was prepared by mixing 40 mL deionized water (DI), 44.5 mL concentrated HCl, 11.0 grams of KI, and 7.5 grams of KIO_3. This solution was used to convert the TEL to Pb^{+2}. Solvent for extracting TREL and DEL from aqueous solution was prepared by mixing 2 grams of EDTA disodium salt and 2 mL of 0.25-M

NaDDTC·3H$_2$O into a 100-mL volumetric flask, adjusting it to pH = 9 with NH$_4$OH, and diluting with DI water.

Leaded gasoline samples were prepared by spiking a known amount of TEL into the unleaded gasoline. Two leaded gasoline concentrations used in this study were 5 and 10 mg TEL/L^{-1}. Hexane samples were prepared by dissolving TEL in *n*-hexane solution in volumetric flasks wrapped with aluminum foil at concentrations of 5 and 10 mg TEL/L^{-1}. Standard Pb solution was made by adding analytical grade Pb standard solution in 3:1 DI water:0.1 M ICl solution at concentrations of 1, 10, and 20 mg Pb L^{-1}. All of the samples were prepared in a semidark condition to avoid photodegradation of TEL.

Triplicate 3-mL aliquots of these samples and 1 mL of 0.1 M ICl solution were added to test tubes and shaken for 30 minutes. After TEL had been converted to Pb^{+2}, 3 mL of DI water was added to the test tubes, and the test tubes were shaken mechanically for another 30 minutes. The fact that Pb^{+2} is insoluble in organic solvent but is highly soluble in water allowed Pb^{+2} to dissolve in the water phase. Then the samples were transferred to separatory funnels for phase separation. The Pb^{+2} content in the water was analyzed by AAS. Blank samples were prepared by mixing 3 mL of DI water and 1 mL of 0.1-M ICl solution.

An additional experiment was conducted to verify that the above procedures actually convert TEL to inorganic Pb^{+2} and not to a mixture of the intermediate TREL and DEL species, which are highly water-soluble. Triplicate samples of 10 mL of TEL at a concentration of 40 mg/L^{-1} and 3.3 mL of 0.1-M ICl solution were added to test tubes and shaken for 30 minutes. After addition of 10 mL of DI water, the test tubes were shaken for another 30 minutes. The samples were transferred to separatory funnels for phase separation, and 3-mL aliquots of water samples were used to analyze the contents of Pb^{+2} using . AS. To verify the possible existence of TREL and DEL species during the conversion of TEL to Pb^{+2} by the ICl Digestion Method, triplicate 5-mL aliquots of the water samples and 20 mL of solvent (a mixture of EDTA, NaDDTC, and DI water) were added to the test tubes and shaken for 10 minutes. Then 10 mL of *n*-hexane was added to the test tubes, which were shaken for another 10 minutes. This removed TREL and DEL from the water phase (Blais and Marshall, 1986). Finally, the samples were transferred into separatory funnels for phase separation. The Pb^{+2} content in the water samples was measured by AAS.

C.   RESULTS AND DISCUSSION

TEL is a hydrophobic compound with very low solubility in water (< 0.1 mg/L^{-1}) but it is highly soluble in hydrophobic solvents such as gasoline and hexane (Feldhake and Stevens, 1963). To determine the TEL content in organic solvents indirectly, TEL was converted to Pb^{+2} by ICl solution and then the Pb^{+2} content was measured by AAS. Therefore, the TEL content in organic solvent can be calculated as follows:

$$C_{TEL} = \frac{W_{TEL} \times C_{Pb}}{W_{Pb}} \tag{5}$$

where C_{TEL} is the concentration of TEL (mg/L^{-1}), W_{TEL} is the molecular weight of TEL (323.4), C_{Pb} is the concentration of Pb^{+2} in the samples (mg/L^{-1}), and W_{Pb} is the molecular weight of Pb^{+2} (207.2).

Table 20 presents a comparison of theoretical values and experimental measurements for TEL in leaded gasoline and hexane, obtained with the ICl Digestion Method. Each type of sample had two treatments done in triplicate. TEL concentrations for samples in Table 20 were obtained by using Eq. (2) to

TABLE 20. THEORETICAL VALUES OF TEL AND EXPERIMENTAL MEASUREMENTS OF TEL AND TOTAL Pb BY ICI METHOD.

Rep. #	Theoretical Concentration (mg TEL/L⁻¹)	Measured Concentration (mg TEL/L⁻¹)	Average Concentration (mg TEL/L⁻¹)	CV (%)	Recovery Rate (%)	Total Pb Concentration (mg/L⁻¹)
Leaded Gasoline Samples						
1	5.0	4.74	4.64	1.90	92.7	3.04
2	5.0	4.64				2.97
3	5.0	4.53				2.90
1	10.0	9.71	9.67	1.34	96.7	5.22
2	10.0	9.81				6.29
3	10.0	9.49				6.08
Hexane Samples						
1	5.0	5.08	5.01	2.07	100.2	3.26
2	5.0	4.86				3.11
3	5.0	5.08				3.26
1	10.0	10.15	10,23	1.021	102.3	6.50
2	10.0	10.15				6.50
3	10.0	10.37				6.64

convert the AAS-measured Pb concentrations into TEL. Average recovery rates for TEL in leaded gasoline samples at concentrations of 5 and 10 mg/L^{-1} were 92.7 percent and 96.7 percent, respectively. Coefficient of variability (CV) among the triplicates ranged from 1.34 percent to 1.90 percent. Such high recovery rates and low CV values suggest that ICl digestion is a valid method of measuring TEL content in leaded gasoline samples.

Similar results were obtained in hexane solutions. Average TEL recovery rates at concentrations of 5 and 10 mg/L^{-1} were 100.2 percent and 102.3 percent, respectively. The CV values ranged from 1.02 percent to 2.07 percent. The TEL content values observed in this experiment slightly overestimated the theoretical values for the hexane sample, but slightly underestimated the theoretical values for the leaded gasoline samples.

No difference in Pb^{+2} concentration was observed in the water samples before and after TREL and DEL were extracted by the solvent (a mixture of EDTA, NaDDTC, and DI water). This indicates that no TREL and DEL existed in the water samples and that all the TEL was converted to inorganic Pb^{+2} by the ICl Digestion Method.

This investigation shows that TEL can be converted not only to TREL (Newman et al., 1947) and DEL (Hancock and Slater, 1975) but also to total Pb^{+2}. The chemical reaction for the process may be expressed as

$$Pb(C_2H_5)_4 + 4I^{+1} = Pb^{+2} + 4(C_2H_5)I \tag{6}$$
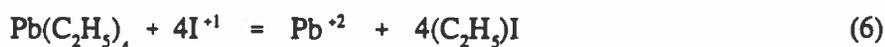
D. CONCLUSIONS

The measurement of TEL and total Pb content in organic solvent by current techniques is time-consuming and expensive. A simple technique known as the Iodine Monochloride (ICl) Digestion Method for the determination of TEL and total Pb has been introduced. Samples containing TEL were converted to Pb^{+2} by 0.1-M ICl solution and then the total Pb content was measured using AAS. Finally, the concentration of TEL was estimated through a back calculation according to the molecular fraction of Pb in TEl. This method seems to be efficient and cost-effective compared to current methods. It has a recovery rate ranging from 92.7 percent to 102.3 percent and a coefficient of variability (CV) ranging from 1.02 percent to 1.9 percent for all measurements in this experiment. Such a high recovery rate and low CV lead to a conclusion that the ICl Digestion Method can be applied to measure TEL, as well as total Pb content in organic solvents.

SECTION VIII

PRELIMINARY STUDIES ON TETRAETHYL LEAD DEGRADATION IN SOIL

A.   INTRODUCTION

The extensive use of leaded gasoline in automobiles began with tetraethyl lead (TEL) in 1923 (Noden, 1980; Rhue et al., 1992). An analogous chemical, tetramethyl lead (TML), was introduced in 1960. Like TEL, TML was added to gasoline, in amounts of 3 to 5 grams per gallon, either separately or in combination to achieve the desired octane numbers. TEL was suitable for high-speed engines, whereas TML was good for low-speed engines (Grandjean and Nielsen, 1979). Although leaded gasoline was completely phased out for use in automobiles in early 1980 in the United States, leaded gasoline containing TEL is still used in aircraft engines. Apparently there is no substitute for TEL in gasoline for high-speed engines.

With the advent of more sensitive analytical techniques in the late 1970s and early 1980s, mainly through the improvement of GC-AAS techniques, alkyl lead compounds were found to be ubiquitous in the environment. Alkyl lead compounds were detected in aerosol dusts (Laxen and Harrison, 1977), rainwater (Radojevic and Harrison, 1987a), surface water (Chau et al., 1979), snow (Van Cleuvenbergen et al., 1986), sediments (Chau et al., 1984), soils (Blais and Marshall, 1986), fish (Chau et al., 1984), and leaves (Van Cleuvenbergen et al., 1990). Ionic trialkyl lead − triethyl lead (TREL) and trimethyl lead (TRML) − are the major species found in the environment. Because the use of leaded gasoline in automobiles has been discontinued, the levels of alkyl lead in the environment should decline.

Degradation pathways of tetraalkyl lead compounds in soil are not known. However, degradation pathways for tetraalkyl lead in aqueous solutions were proposed to proceed through a series of dealkylation steps, eventually resulting in inorganic lead (Rhue et al., 1992). For example, TEL first degrades to monoionic TREL, which in turn degrades to diionic diethyl lead (DEL), and finally to Pb^{2+}. The fate of tetraalkyl lead in subsurface soils underneath old, leaking underground leaded gasoline storage tanks is not known.

There have been no reports of microorganisms capable of degrading TEL and other forms of tetraalkyl lead. However, microbial degradation could be partially responsible for the disappearance of TRML in soil. Blais et al. (1990) reported that the levels of TRML in nonsterile soil were lower than levels in corresponding autoclaved soil after 24 hours of incubation.

This section discusses an investigation of the rates for biological and chemical transformation of TEL to ionic organolead forms (TREL and DEL) and for mineralization of TEL in surface and subsurface soils. To achieve these objectives, ^{14}C-labeled TEL was used so that (1) conversion from non-ionic form to ionic form could be determined easily and (2) evolution of CO_2 from the mineralization of TEL could be measured.

B.   MATERIALS AND METHODS

Ethyl-1-labeled ^{14}C-tetraethyl lead (TEL) was purchased from American Radiolabeled Chemicals, Inc. (St. Louis, Missouri). Analytical-grade TEL was obtained from All-Chemie Ltd. (Ft. Lee, New

Jersey). Both ^{14}C-TEL and TEL were dissolved in n-hexane in glass bottles wrapped with aluminum foil at a radio dosage of 1 μCi/mL and a concentration of 2,000 μg/mL, respectively.

Arredondo fine sand (Grossarenic Paleudult) was used for this study. Soil samples were collected at 15-cm increments from a virgin forest site on the campus of the University of Florida, Gainesville, Florida. Selected soil properties are shown in Table 21.

TABLE 21. SELECTED PROPERTIES OF SOIL SAMPLES USED FOR THIS STUDY.

Soil Depth (cm)	pH (g/kg soil)	Soil/Water Content (g/kg soil)	Organic Carbon (g/kg soil)	Sand (%)	Silt (%)	Clay (%)
0 - 15	5.5	55	11.8	92	7	1
15 - 30	4.6	46	4.7	93	5	2
30 - 45	5.6	28	3.9	93	4	3

To avoid volatilization loss of TEL, 50 grams of soil (oven-dry weight basis) was transferred to a 250-mL Erlenmeyer flask with a Teflon™-lined screw cap. After adding 0.1 μCi of ^{14}C-TEL and 1,000 μg/g of TEL, an additional 50 grams of the soil was added immediately to the top of the soil in the flask. After a brief but thorough mixing, the flask was closed tightly with a Teflon™-lined screw cap under which a stainless steel vial (3-mL capacity) containing 0.5 mL of 8 N KOH was hung, supported by a stainless steel wire. At predetermined intervals, all vials were replaced with new vials containing fresh KOH. The KOH in the removed vials was diluted with deionized H$_2$O to 5 mL, and 0.5 mL of the diluted KOH was used for determination of total ^{14}C-activity in the KOH traps by liquid scintillation counting (LSC). In addition, 2 mL of the KOH was transferred to a plastic centrifuge tube that had contained 0.5 mL of BaCl$_2$ (200 g/L), resulting in the formation of insoluble BaCO$_3$, including Ba^{14}CO$_3$. After centrifugation, ^{14}C in the supernatants was quantified by LSC. The difference between ^{14}C in the KOH and ^{14}C in the supernatant was considered to be ^{14}CO$_2$ (Ou, 1989). To reduce photodecomposition, all flasks were wrapped with aluminum foil, and the experiments were carried out in semidarkness. The flasks were incubated at 25°C for 28 days, after which 10 grams of soil from each flask was transferred to a 50-mL glass tube for solvent extraction as described below. The ^{14}C remaining in the solvent-extracted soil samples was combusted to ^{14}CO$_2$ by a sample oxidizer and quantified by LSC. Identical experimental procedures were carried out for autoclaved Arredondo soil.

To determine TEL-to-ionic-species (TREL and DEL) transformation rates, a series of 30-mL glass centrifuge tubes wrapped with aluminum foil were prepared and 5 grams of the Arredondo soil was added to each tube. Then 0.05 μCi of ^{14}C-TEL and 100 μg of TEL were applied to the surface of the soil, and another 5 grams of the soil was added immediately. The tubes were closed with Teflon™-lined screw caps and mixed in a reciprocal shaker for 5 minutes. The tubes were incubated in the dark at 25°C. At pre-determined intervals, two tubes from each depth were extracted with 10 mL of n-hexane and 10 mL of EDTA (2 grams of disodium EDTA/100 mL of deionized H$_2$O, pH 9.0). The tubes were shaken for 1 hour in a reciprocal shaker and then centrifuged at 2,000 rpm for 20 minutes. After centrifugation, the hexane phase appeared on the top and the EDTA phase under it. A 0.5-mL quantity was carefully removed from each phase for determination of ^{14}C activity by LSC. Identical experimental procedures were carried out for autoclaved Arredondo soil. All experiments were duplicated.

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C. RESULTS AND DISCUSSION

TEL is a hydrophobic compound with very low solubility in water (Feldhake and Stevens, 1963) but high solubility in hydrophobic solvents such as gasoline, benzene, and hexane. On the other hand, ionic ethyl lead species (TREL and DEL) are highly water-soluble but are not soluble in hydrophobic solvents. This study took advantage of these two contrasting properties: hydrophobic TEL would be fractionated into hexane, but ionic ethyl lead species would remain in the aqueous phase. Thus, ^{14}C-TEL would be used to determine easily the rates at which TEL transforms to ionic forms in soil. This is analogous to hexane being used successfully to separate the organophosphorus insecticide methyl para-thion from its polar hydrolysis product p-nitrophenol in bacterial culture fluids (Ou and Sharma, 1989).

It was observed consistently that ^{14}C in hexane (^{14}C-TEL) initially disappeared in nonsterile soil samples more rapidly than in the corresponding autoclaved soil samples (Figure 23), especially for surface samples. The disappearance rate leveled off earlier in the nonsterile samples than in the corresponding autoclaved samples. The time required for 50 percent disappearance of ^{14}C-TEL in the three layers of nonsterile samples (depths of 0 to 15, 15 to 30, and 30 to 35 cm) was 2, 1.5, and 2 hours, respectively. In contrast, the time required for 50 percent disappearance of ^{14}C-TEL in the corresponding sterile samples was 14, 7, and 8 hours, respectively (Figure 23).

Ionic ^{14}C (^{14}C-TREL and ^{14}C-DEL) slowly but steadily increased in the EDTA phase in nonsterile samples but leveled off after 3 to 6 hours of incubation (Figure 23). More ionic ethyl lead species were formed in subsurface than in surface samples, and up to 23 percent of the applied ^{14}C was associated with the ionic forms. Similar patterns for the formation of ionic ^{14}C were observed for the corresponding autoclaved samples, but the levels of ionic ^{14}C in the autoclaved samples were generally lower than in the corresponding nonsterile samples. The time required for 50 percent disappearance of non-ionic ^{14}C plus ionic ^{14}C in the three layers of nonsterile samples (depths of 0 to 15, 15 to 3 and 30 to 45 cm) was 14, 7, and 8 hours, respectively. The time required for 50 percent disappearance of non-ionic ^{14}C and ionic ^{14}C in the corresponding layers of the autoclaved samples was 17, 12, and 12 hours, respectively (Figure 23).

Figure 24 shows the distribution of the ratio of ^{14}C activity fractionated into aqueous EDTA solution to ^{14}C activity fractionated into hexane phase (^{14}C in EDTA/^{14}C in hexane) in nonsterile and autoclaved Arredondo soil. If ^{14}C in EDTA/^{14}C in hexane is smaller than 1, more TEL than ionic TREL and DEL is present in the soil. If ^{14}C in EDTA/^{14}C in hexane is larger than 1, less TEL is present than the ionic forms. Less than 1 percent of ^{14}C-TEL standard could be fractionated into the EDTA phase, indicating that radiopurity of ^{14}C-TEL was more than 99 percent. Once ^{14}C-TEL was applied, ^{14}C in EDTA/^{14}C in hexane increased in all nonsterile and sterile soil samples. Because TEL disappeared and ionic forms formed more rapidly in nonsterile soil than in the corresponding autoclaved soil (Figure 23), ^{14}C in EDTA/^{14}C in hexane in the nonsterile samples would be expected to be larger than in the corresponding autoclaved samples. In fact, values of ^{14}C in EDTA/^{14}C in hexane in the three layers of nonsterile soil were consistently larger than in the corresponding autoclaved samples during 48 hours of incubation. This suggests that both chemical degradation and biological degradation play roles in the transformation of TEL to ionic TREL and DEL.

The ^{14}CO$_2$ initially evolved rapidly from ^{14}C-TEL-treated surface and subsurface soil (Figure 25) and leveled off after 3 days of incubation. Total amounts of ^{14}CO$_2$ evolved from these samples were progressively smaller with soil depth. No ^{14}CO$_2$ was evolved from ^{14}C-TEL-treated autoclaved soil (data not shown). Thus, mineralization of TEL in soil is a microbially mediated process. Total ^{14}C recoveries from the three layers of soil after 28 days of incubation were poor (Table 22), ranging from 17.6 percent

59
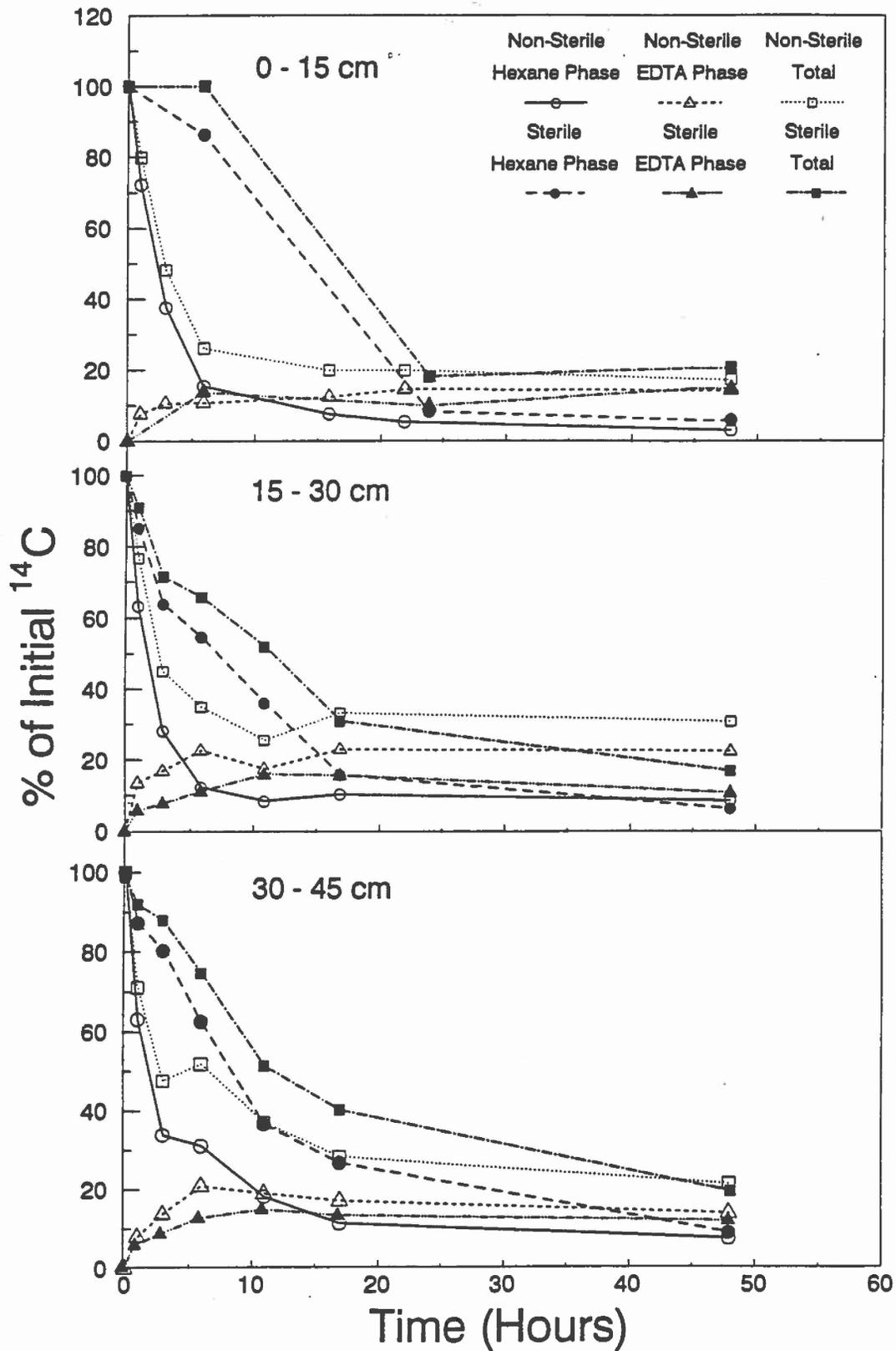
Figure 23. Distribution of ^{14}C in Hexane and ^{14}C in EDTA in Nonsterile and Autoclaved Soil.

60
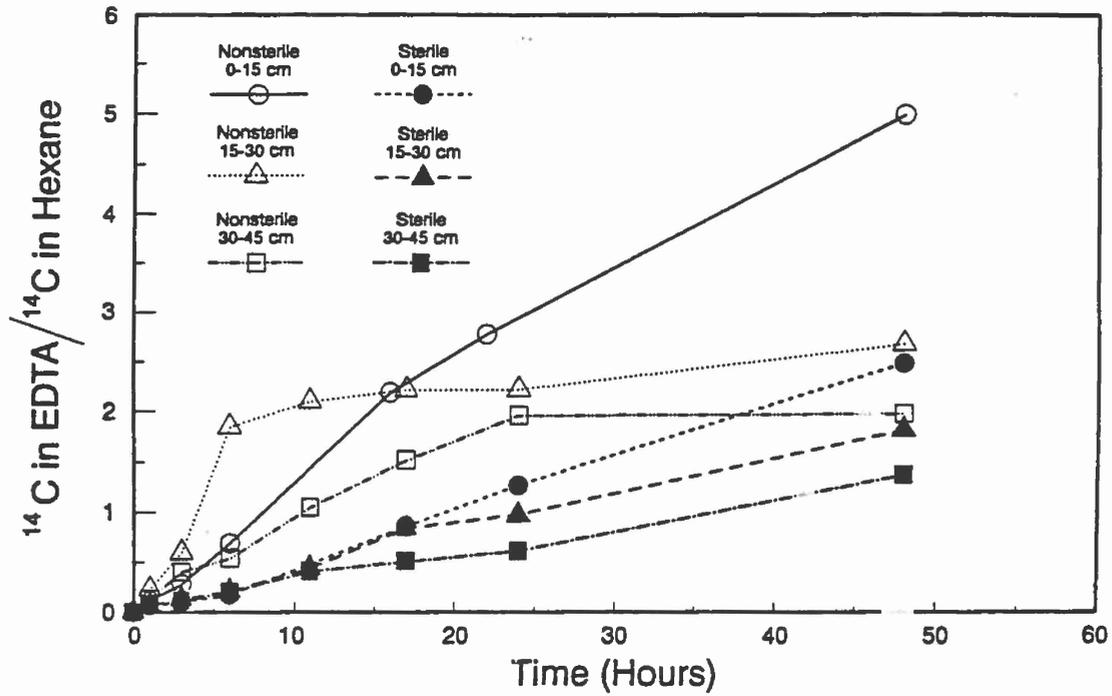
**Figure 24.** Distribution of ^{14}C in EDTA/^{14}C in Hexane Extracted from Nonsterile and Autoclaved Arredondo Soil Treated with ^{14}C-TEL.
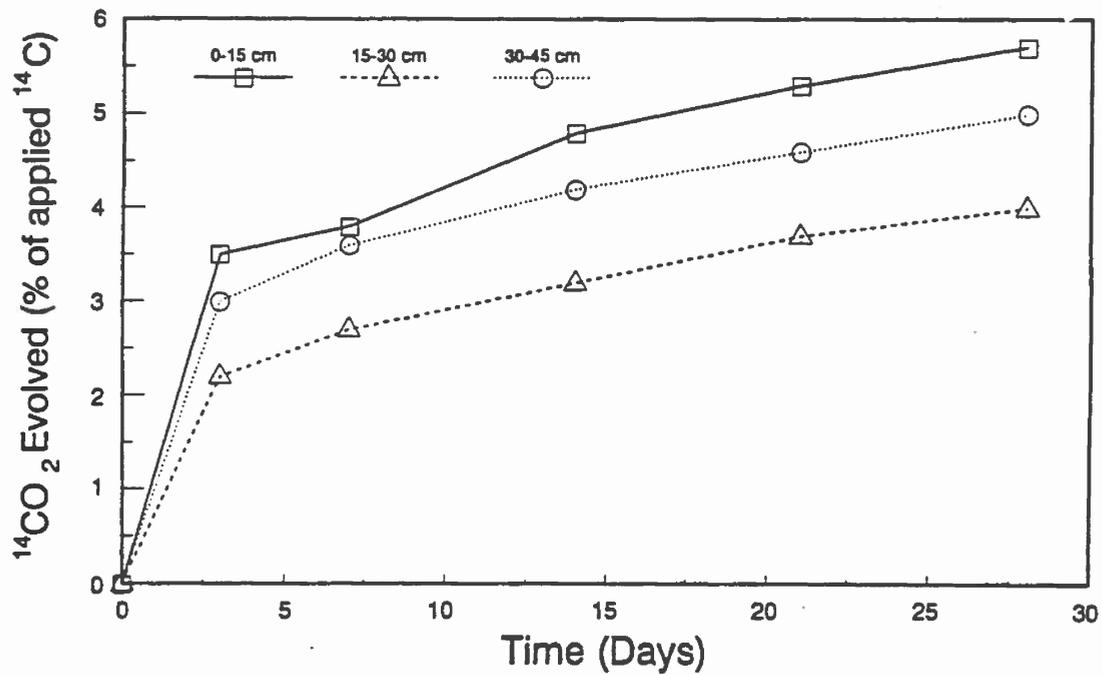
Figure 25. $^{14}CO_2$ Evolution from Arredondo Soil Treated with ^{14}C-TEL.

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to 28.0 percent of the applied ^{14}C. Because the majority of ^{14}C trapped in KOH traps was $^{14}CO_2$ and only 0.2 percent or less of the applied ^{14}C trapped in the KOH traps was associated with ^{14}C organics (possibly ^{14}C-TEL), it is likely that the ^{14}C not accounted for was associated with volatile ^{14}C organics (possibly volatile degradation products) which had little capacity to be trapped in KOH. No ^{14}C was found in hexane extracts, and 3.9 percent to 6.2 percent of the applied ^{14}C was found in EDTA phase (Table 22). This indicated that, after 28 days, TEL in nonsterile soil was degraded completely to ionic forms and other unknown volatile products.

TABLE 22.   DISTRIBUTION OF ^{14}C IN NONSTERILE ARREDONDO SOIL AFTER 28 DAYS OF INCUBATION WITH ^{14}C-TEL.

	$^{14}CO_2$	^{14}C Organics	^{14}C in Hexane	^{14}C in EDTA	Nonextract-able ^{14}C	Recovery
Depth (cm)	Percent of applied ^{14}C					
0 - 15	5.7	0.1	0	6.2	16.0	28.0
15 - 30	4.0	0.2	0	3.9	9.5	17.6
30 - 45	5.0	0.2	0	5.7	13.0	23.9

The results indicate that transformation of TEL to ionic forms in soil occurred both biologically and chemically. It is well known that autoclaving to sterilize soil alters the physical and chemical charac-teristics of the soil (Skipper and Westermann, 1973). Therefore, chemical degradation rates of TEL in nonsterile and autoclaved soils may not be the same. Nevertheless, biological degradation certainly contributes to the disappearance of TEL in soil. Mineralization of TEL did occur in nonsterile soil.

After 28 days of incubation, no TEL could be detected in the Arredondo soil and considerable amounts of ionic ethyl lead species were present. This suggests that TEL is less persistent in soil than its degradation products, ionic ethyl lead species. This finding is in agreement with the fate of tetraalkyl lead compounds and ionic alkyl lead species in water, where ionic lead species are considerably more stable than tetraalkyl lead compounds (Radojevic and Harrison, 1987b). This study did not investigate the distribution of individual ionic ethyl lead species; it remains to be determined whether triethyl lead or diethyl lead is the dominant species.

SECTION IX

DEGRADATION OF TRIETHYL LEAD AND DIETHYL LEAD IN SOIL

A.   INTRODUCTION

Alkyl lead species have been found to be ubiquitously present in the environment. Alkyl lead compounds were detected in roadside soils (Blais and Marshall, 1986), sediments (Chakraborti et al., 1989b; Chau et al., 1979), rain and surface waters (Chakraborti et al., 1984, 1989b; Chau et al., 1979; Radojevic and Harrison, 1987a; Van Cleuvenbergen et al., 1986), fish (Chau et al., 1979, 1984), grass, and tree leaves (Van Cleuvenbergen et al., 1990). Ionic triethyl lead (TREL) and trimethyl lead (TRML) were the dominant species found in the environment (Radojevic and Harrison, 1987b; Rhue et al., 1992). In aqueous solutions, TEL and TML degrade first to the respective ionic trialkyl lead species, which are then degraded to ionic dialkyl lead species, and eventually to inorganic Pb^{2+} (Jarvie et al., 1981; Radojevic and Harrison, 1987b).

Little information is available regarding the pathways of TEL and TML in soil. Blais and Marshall (1986) reported that only two ionic ethyl lead species, TREL and diethyl lead (DEL), were detected in street dusts and roadside soils and no tetraalkyl lead species were detected. Ou et al. (1994) found that TEL rapidly disappeared in soil under laboratory conditions and completely disappeared after 28 days of incubation. At the same time, ionic ethyl lead species rapidly formed and persisted throughout the entire 28 days of incubation. Although individual species of ionic ethyl lead compounds in soil were not determined, the results of this study suggested that TEL, similar to the degradation patterns in aqueous media, also could be first degraded to TREL, and then to DEL. Furthermore, it was found that both biological and chemical degradation were responsible for the disappearance of TEL in soil.

This investigation was initiated to determine degradation and metabolism of the two ionic ethyl lead species, TREL and DEL, in soil under laboratory conditions. Specifically, the mineralization rates, disappearance rates, and metabolite formation in nonsterile and sterile soils were determined so that contributions from biological and chemical degradation could be assessed.

B.   MATERIALS AND METHODS

1.   Soil

Soil samples were collected from a virgin forest site at the campus of the University of Florida, Gainesville Florida. A composite of four soil cores was collected using a 10-cm-diameter bucket auger at 15-cm increments to 45-cm depth. The soil was classified as Arredondo fine sand (loamy, siliceous, hyperthermic Grossarenic Paleudults). Organic C contents and pH values of the soil samples at 0 to 15, 15 to 30, and 30 to 45 cm depth were 11.8, 4.7, and 3.9 g/kg soil, and 5.5, 4.6, and 5.6, respectively. Detailed key soil properties were reported previously (Ou et al., 1994). All soil samples were stored in the dark at 4°C and used within 3 months after collection.

2.   Chemicals and Reagents

TREL and TEL were purchased from All-Chemie Ltd. (Ft. Lee, New Jersey). Ethyl-1-^{14}C-TEL (specific activity 0.74 GBq/mmol and radiopurity > 99 percent) were obtained from American Radiolabeled Chemicals (St. Louis, Missouri). The ^{14}C-TEL was used as a starting chemical for synthesis

to ethyl-1-^{14}C-TREL and ethyl-1-^{14}C-DEL. The synthesis methods are described in the following sections. Because alkyl lead compounds are sensitive to light and subject to photodecomposition, all the alkyl lead compounds were stored in the dark at $-20°C$. All other chemicals were either analytical grade, scintillation grade, or the highest grade commercially available.

Iodine monochloride (ICl) solution (0.1 mol/L) was prepared as described by Chau et al. (1984): 11 grams of potassium iodide (KI) was added to a brown glass bottle containing a mixture of 40 mL of deionized H_2O and 44.5 mL of concentrated HCl, to which 7.5 grams of potassium iodate (KIO_3) was slowly added with mechanical stirring. This solution was stable for several months. Sodium diethyl-dithiocarbamate (NaDDTC) solution (0.065 mol/L) was prepared by dissolving 2.00 grams of NaDDTC in 100 mL of deionized H_2O.

3.   Conversion of ^{14}C-TEL to ^{14}C-TREL

The method used to convert ^{14}C-TEL to ^{14}C-TREL was a modification of the method for converting nonlabeled TEL to TREL yielded at gram quantities (Moss and Browett, 1966; Newman et al., 1947). The modified method was able to convert μgram quantities of ^{14}C-TEL to ^{14}C-TREL. One mL of n-hexane containing 3 μCi of ^{14}C-TEL (48 μg) was placed in a 10-mL glass tube with a Teflon™-lined screw cap. The tube was wrapped with aluminum foil to block light. To avoid photodecomposition, this experiment and all subsequent experiments were carried out under semidark conditions. After 15 μL of 0.1 mol/L ICl was added to the tube, the tube was tightly closed and shaken by a vortex mixer for 10 minutes. Then 1 mL of deionized H_2O was added to the tube, and the tube was shaken for an additional 2 minutes.

After the two liquid phases had separated, the upper layer was removed and discarded with a Pasteur glass pipette. Following addition of 1 mL of 0.065 mol/mL NaDDTC, the remaining solution was extracted with 1 mL hexane by shaking with a vortex mixer for 2 minutes. The upper layer (hexane) then was carefully transferred to a clean glass tube. The remaining aqueous solution was again treated with 15 μL of the ICl solution and extracted with NaDDTC and hexane as described above. All hexane extracts were combined.

The hexane solution was spotted to a preparative silica gel G thin layer chromatography (TLC) plate and the plate was developed in acetone/n-hexane/propionic acid (30:70:2, v/v/v). After the plate had air-dried, it was exposed to an SB-5 X-ray film (Eastman Kodak, Rochester, New York) for 14 to 16 hours. The silica gel band corresponding to TREL was scraped and eluted with ethyl acetate. The radiopurity of the purified ^{14}C-TREL was checked by TLC-autoradiographic assays and liquid scintillation counting (LSC) and found to be better than 99 percent. The final yield ranged from 15 to 30 percent. ^{14}C-TREL in ethyl acetate was stable for 1 month if stored in an opaque tube at $-20°C$.

4.   Conversion of TREL to DEL

Conversion of nonlabeled TREL to DEL followed the procedure described by Chau et al. (1984). Briefly, 4 mL of aqueous TREL solution (100 μg/mL Pb) in a 20-mL brown glass bottle received 4 drops of 0.1 mol/L ICl solution. This conversion was instantly completed. Conversion of ^{14}C-TREL to ^{14}C-DEL was carried out in a similar manner. All DEL solutions were synthesized immediately prior to usage.

5. Mineralization Studies

For the mineralization studies, 100 grams each of the Arredondo surface and subsurface soil samples (oven-dry weight basis) were transferred to a 250-mL Erlenmeyer flask with a Teflon™-lined screw cap that had contained 1,000 μg of nonlabeled TREL and 1.5 kBq of ^{14}C-TREL in 0.25 mL of deionized H_2O. After mixing, the flask was weighed and closed tightly with a Teflon™-lined screw cap under which a small stainless steel vial (3 mL capacity) containing 0.5 mL of 8 mol/L KOH was hung using a stainless wire. The flasks were wrapped with aluminum foil and incubated in the dark at 28°C. At predetermined time intervals all vials were removed; after the weights of the flasks were checked and compensated for water loss, new vials containing fresh KOH were hung. Each removed KOH trap was diluted with deionized H_2O to 5 mL in a small beaker. The ^{14}C in the diluted KOH solutions was quantified by LSC. At the end of incubation, 10 grams of soil were removed and placed in a 40-mL glass centrifuge tube with a Teflon™-lined cap. The soil was extracted with an equal volume of 0.1 mol/L phosphate buffer (pH 7.2) and n-hexane. The extraction procedures are given in the next section. The ^{14}C activity remaining in the extracted soil samples was determined by combusting to $^{14}CO_2$ in a sample oxidizer (Ou et al., 1982) and by LSC.

6. Metabolite Formation of TREL

A series of 500-mL glass bottles wrapped with aluminum foil was set up in which 100 grams of the Arredondo surface or subsurface soil samples had been added earlier. Then 1,000 μg of TREL and 180 kBq of ^{14}C-TREL in 0.5 mL of deionized H_2O were applied to each sample. The soil samples were mixed, weighed, and incubated in the dark at 25°C. At predetermined intervals, after the weights of the bottles were checked and compensated for water loss, 10 grams of soil were removed from each bottle and transferred to a 40-mL glass centrifuge tube. After 15 mL of phosphate buffer had been added to the tube, the tube was shaken in a reciprocal shaker for an additional 5 minutes, and then 1 mL of 0.07 mol/L NaDDTC and 5 mL of n-hexane were added and shaken for 5 minutes. The tubes were centrifuged at 2,000 rpm for 10 minutes to facilitate the separation of the two phases. The upper hexane layer was carefully removed with a Pasteur pipette and transferred to a clean centrifuge tube. Next, 1 mL of 0.07 mol/L NaDDTC and 5 mL of n-hexane were added to the tube containing phosphate buffer and soil, and the tube was shaken for 5 minutes. The hexane layer was removed and combined with the hexane removed earlier.

The hexane extracts were transferred to cone-shaped glass tubes wrapped with aluminum foil and concentrated under a gentle stream of N_2 gas to 0.1 mL under semidark conditions. The concentrated hexane extracts and standards of ^{14}C-TREL and ^{14}C-DEL were spotted on silica gel G TLC plates and developed using a solvent system of acetone-hexane-propionic acid (35:65:2, v/v/v). After the plates were dried, SB-5 X-ray films (Eastman Kodak, Rochester, New York) were placed on the plates for autoradiographic analysis. The ^{14}C-activity in the radioactive area on the plates was quantified by LSC using the procedures described by Ou et al. (1982).

7. Metabolite Formation of DEL

The experimental procedures used for DEL were similar to those described above for determining the disappearance of TREL in soil. Briefly, 1,000 μg of DEL and 140 kBq of ^{14}C-DEL were mixed with 100 grams of soil, and the soil samples were incubated in the dark at 25°C. At appropriate intervals, subsamples (10 grams) were extracted with phosphate buffer, NaDDTC, and hexane. After ^{14}C determination in the hexane and phosphate buffer, ^{14}C in the hexane was separated by TLC and

quantified by LSC. The ^{14}C remaining in the extracted soil samples was quantified by combusting to ^{14}CO$_2$ in a sample oxidizer and by LSC.

8.   Confirmation by GC-AAS

The existence of ^{14}C-TREL, ^{14}C-DEL, and their ^{14}C-metabolites in soils detected by TLC-autoradiography assays and LSC was confirmed by the established gas chromatography-atomic absorption spectrometer (GC-AAS) technique (Chakraborti et al., 1984; Chau et al., 1984). Soil treatment and solvent extraction procedures were similar to those for the soil samples treated with ^{14}C-TREL and non-labeled TREL or with ^{14}C-DEL and nonlabeled DEL, with the exception that no ^{14}C-labeled chemical was added. A nickel tubing was used to interface a Hewlett-Packard 5890 GC equipped with an autosampler and an integrator, and a Perkin-Elmer AAS, equipped with a Perkin-Elmer Pb detector with a deuterium background corrector. The instrument parameters and operating conditions were as follows: column, glass, 6 feet long and 0.25-inch i.d., packed with 10 percent OV-101 on Chromosorb W (80 mesh); temperatures for column oven, injector, and transfer line: 120 to 220°C/min with 10°C ramp, 150°C and 160°C, respectively; gas flow for nitrogen (carrier gas), hydrogen, acetylene, and air: 65 mL/min, 80 mL/min, 30 L/min, and 50 mL/min, respectively; Pb hollow cathode lamp set at 217.0 nm wavelength and 0.7 nm slit width; and injection volume, 2 μL. Hexane extracts containing TEL were injected directly into the instrument without any modification. Ionic TREL and DEL in hexane-NaDDTC extracts were butylated with magnesium butylchloride and then injected into the GC-AAS. Retention times for TEL, TREL, and DEL were 3.9, 6.7, and 8.5 minutes, respectively.

C.   RESULTS AND DISCUSSION

1.   Mineralization of TREL and DEL

The ^{14}C-TREL in surface and subsurface samples (0 to 15, 15 to 30, and 30 to 45 cm depth) of Arredondo soil initially mineralized rapidly during the first 3 days of incubation (Figure 26), and mineralized more slowly thereafter. Rates of mineralization for the three layers of samples were very close, and at the end of 31 days of incubation, 15.4, 16.0, and 16.2 percent of the applied ^{14}CO$_2$ were mineralized from the three layers of samples. ^{14}C recoveries after 31 days were much better compared to the recoveries for ^{14}C-TEL-treated Arredondo soil (Ou et al., 1994). Ou et al. (1994) reported that, after 28 days of incubation, less than 30 percent of the applied ^{14}C was recovered in the ^{14}C-TEL-treated surface (0 to 15 cm) and subsurface (15 to 30 and 30 to 45 cm) Arredondo samples. TEL is volatile, whereas TREL and DEL are not. After 31 days, 25.3 to 33.5 percent of the applied ^{14}C in the ^{14}C-TREL treated surface and subsurface Arredondo samples was not accounted for (Table 23). The ^{14}C recovery was better in the surface sample than in the two subsurface layers. Unaccounted for ^{14}C could be associated with gaseous degradation products. After 31 days, 20.7 to 22.1 percent of the applied ^{14}C could be extracted with hexane-NaDDTC, which was associated with ionic ethyl lead species (TREL and DEL). Apparently other unknown polar metabolites, possibly not structurally related to ionic ethyl lead species, were formed in small amounts. Between 3 and 9.4 percent of the applied ^{14}C remained in the phosphate buffer. The ^{14}CO$_2$ was not evolved from the autoclaved Arredondo soil samples treated with ^{14}C-TREL (data not shown). This indicates that mineralization of TREL is a biological process.

The ^{14}C-DEL in Arredondo soil initially was mineralized more slowly during the first 3 days of incubation than was ^{14}C-TREL (Figure 26). However, after 3 days, mineralization rates of ^{14}C-DEL in the three depths of Arredondo soil were higher than those for ^{14}C-TREL in the respective layers. The initial mineralization rate for ^{14}C-DEL was progressively lower with soil depth. However, after 7 days the situation was reversed, such that more mineralization occurred in the subsurface layers

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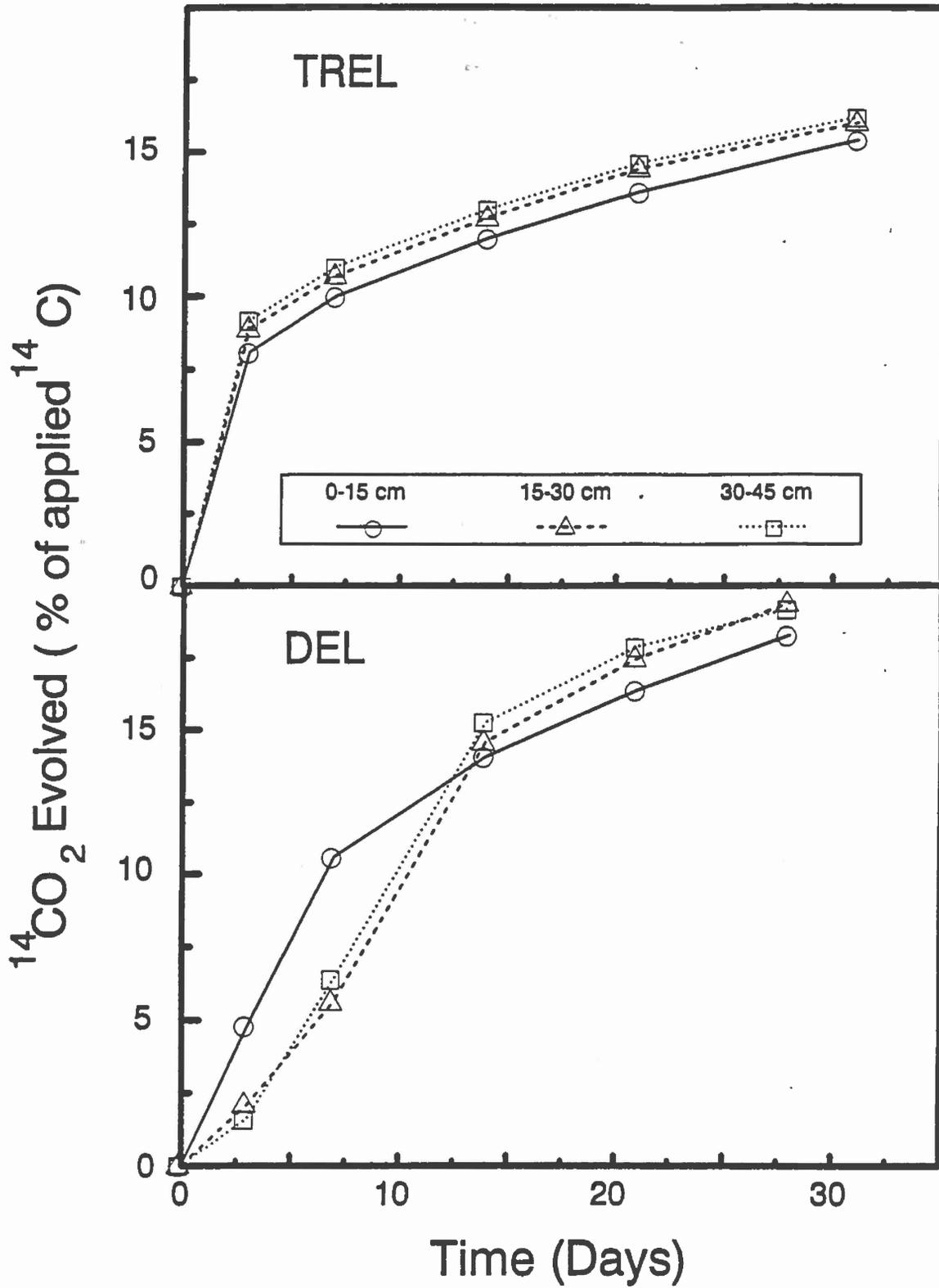
Figure 26. Mineralization of ^{14}C-TREL and ^{14}C-DEL in Arredondo Soil during 31 or 28 Days of Incubation.

TABLE 23. ^{14}C DISTRIBUTION IN ^{14}C TREL-TREATED SOIL AND ^{14}C-DEL-TREATED SOIL AFTER 31 AND 28 DAYS OF INCUBATION, RESPECTIVELY.

Depth (cm)	$^{14}CO_2$	Hexane-NaDDTC	Phospate Buffer	Nonextract-able ^{14}C	Recovery
	Percent of applied ^{14}C				
^{14}C-TREL					
0 - 15	15.4	22.1	9.4	27.8	74.7
15 -30	16.0	20.7	6.0	23.8	66.5
30 - 45	16.2	20.7	3.0	28.5	68.4
C-DEL					
0 - 15	18.3	23.5	11.2	37.0	90.0
15 - 30	19.4	7.6	10.3	32.7	70.0
30 - 45	19.2	8.3	6.0	21.2	54.7

than in the surface layer. After 28 days of incubation, 18.3, 19.4, and 19.2 percent of the applied ^{14}C-DEL were mineralized in soil samples of 0 to 15 cm, 15 to 30 cm, and 30 to 45 cm depth, respectively. Total ^{14}C recoveries in the ^{14}C-DEL-treated subsurface samples, especially those from the deepest layer (30 to 45 cm), were poor (Table 23) and were much lower than recovery in the surface sample. Much lower amounts of ^{14}C could be extracted with hexane-NaDDTC in the two subsurface layer samples than in the surface sample. This indicates that more DEL was degraded in the subsurface layers than in the surface layer. Similar to the ^{14}C-TREL-treated autoclaved Arredondo samples, mineralization was not observed in the ^{14}C-DEL-treated autoclaved Arredondo samples.

2. Disappearance and Metabolites of TREL in Soil

In both nonsterile and autoclaved Arredondo soil, the ^{14}C that could be extracted with hexane-NaDDTC decreased rapidly (Figures 27 and 28). The hexane-NaDDTC extractable ^{14}C in nonsterile samples initially declined more rapidly than it did in the corresponding autoclaved samples. The initial disappearance of hexane-extractable ^{14}C was more profound in the nonsterile subsurface sample than in the corresponding autoclaved sample. The disappearance of hexane-NaDDTC extractable ^{14}C in nonsterile and autoclaved surface samples leveled off after 2 days of incubation. After 3 days, more hexane-NaDDTC extractable ^{14}C was found in the nonsterile surface sample than in the autoclaved surface sample. The disappearance of hexane-NaDDTC extractable ^{14}C in the nonsterile subsoil also leveled off after 2 days of incubation. In the autoclaved subsoil, the disappearance of hexane-NaDDTC ^{14}C declined continuously during the entire 28-day incubation period, and less hexane-NaDDTC extractable ^{14}C was found after 28 days in this sample than in the corresponding nonsterile sample.

Only one organolead metabolite, DEL, was detected in both nonsterile and autoclaved samples (Figure 29). The appearance of ^{14}C-DEL in the nonsterile and autoclaved surface samples was brief. The ^{14}C-DEL was detected in the nonsterile surface sample 3 hours after the treatment of ^{14}C-TREL and in the autoclaved surface sample only once, 1 day after the treatment of ^{14}C-TREL. No ^{14}C-DEL was detected in either surface sample thereafter. The appearance of ^{14}C-DEL in the nonsterile and autoclaved subsurface samples (30 to 45 cm depth), especially the autoclaved sample, lasted longer
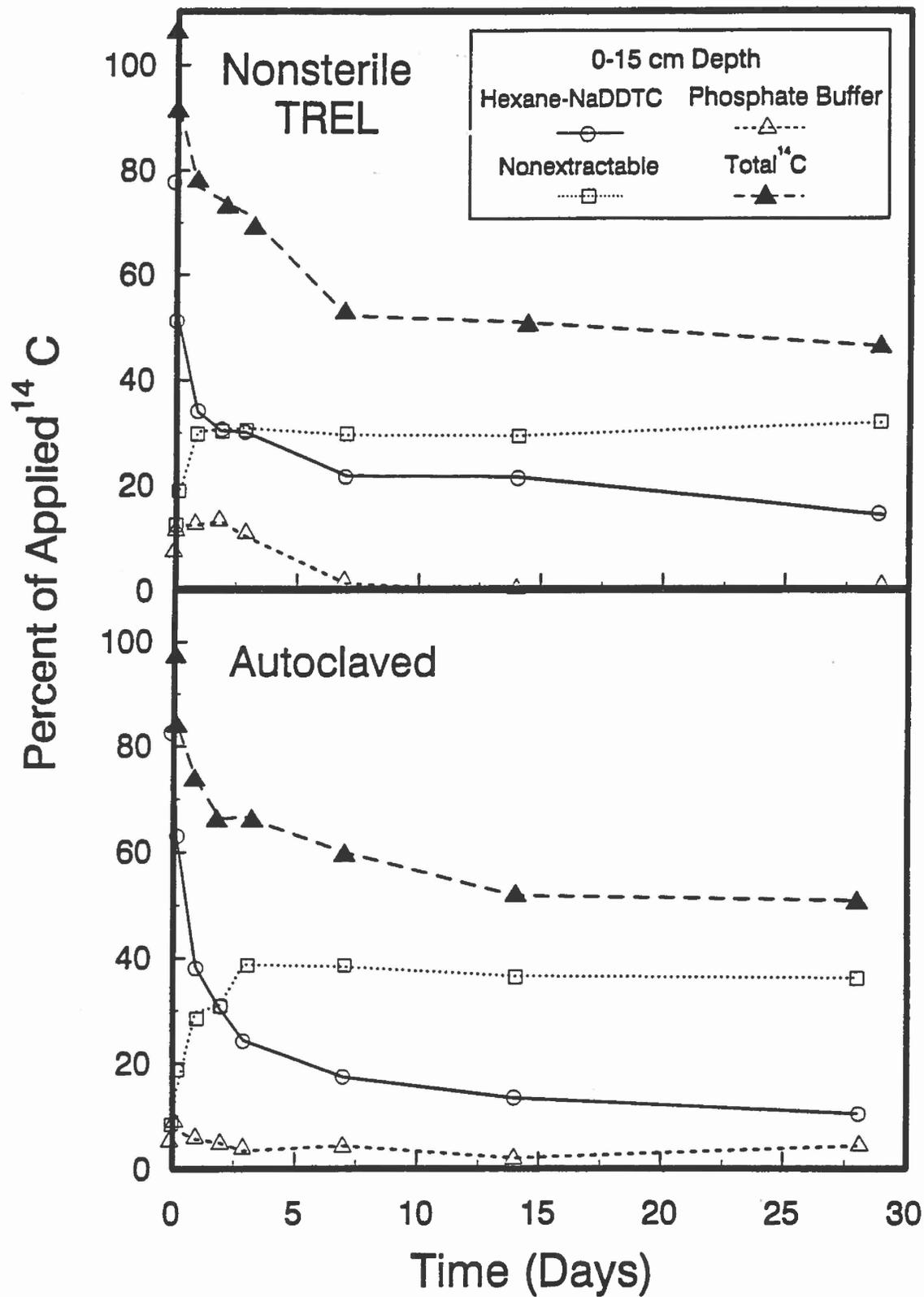
Figure 27. Distribution of ^{14}C in Hexane-NaDDTC Phase, Phosphate Buffer Phase, Nonextractable, and Total Recovery from the ^{14}C-TREL-Treated Nonsterile and Autoclaved Arredondo Surface Soil (0 to 15 cm) during 28 Days of Incubation.
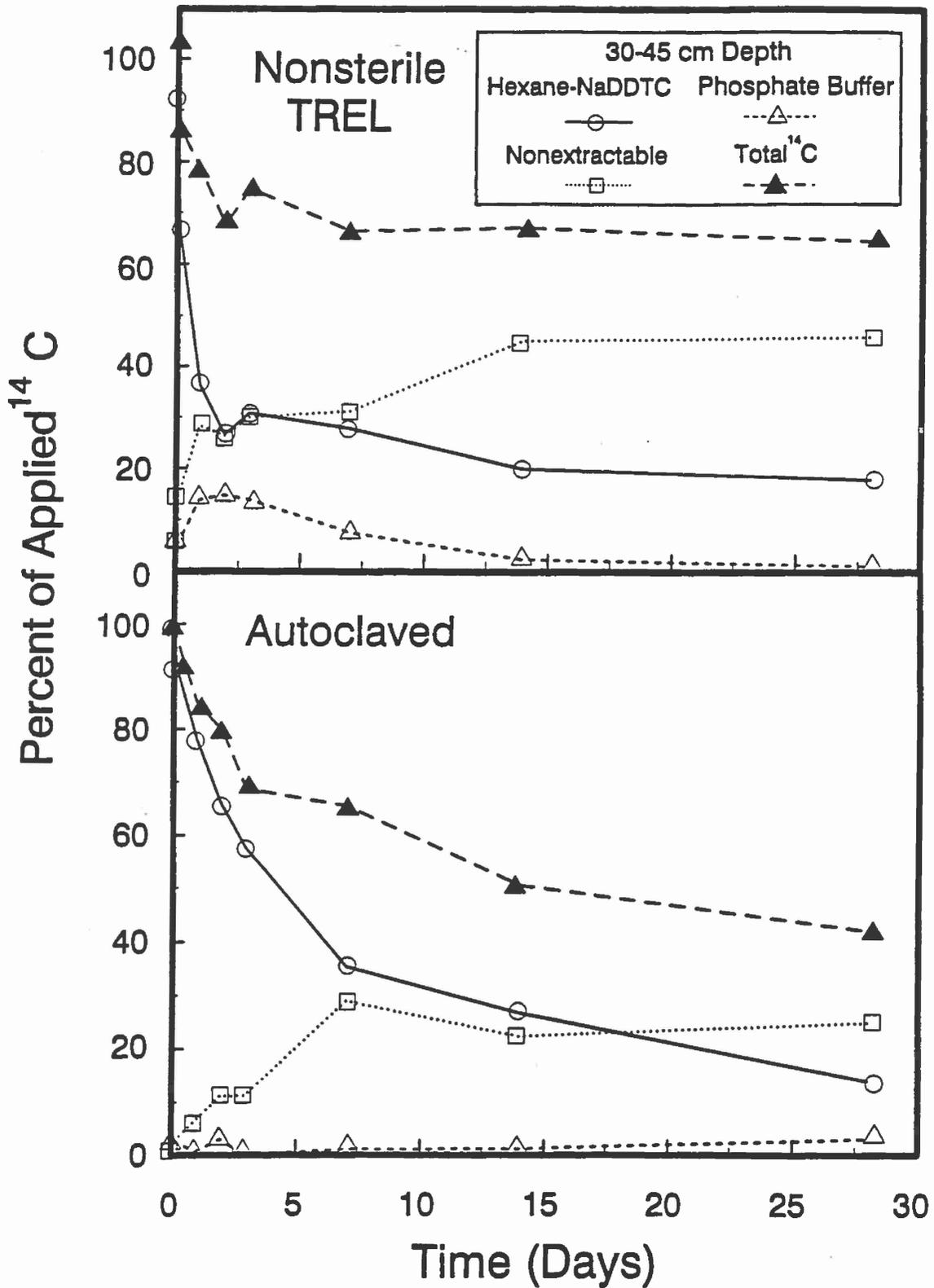
Figure 28. Distribution of ^{14}C in Hexane-NaDDTC Phase, Phosphate Buffer Phase, Nonextractable, and Total Recovery from the ^{14}C-TREL-Treated Nonsterile and Autoclaved Arredondo Subsurface Soil (30 to 45 cm) during 28 Days of Incubation.
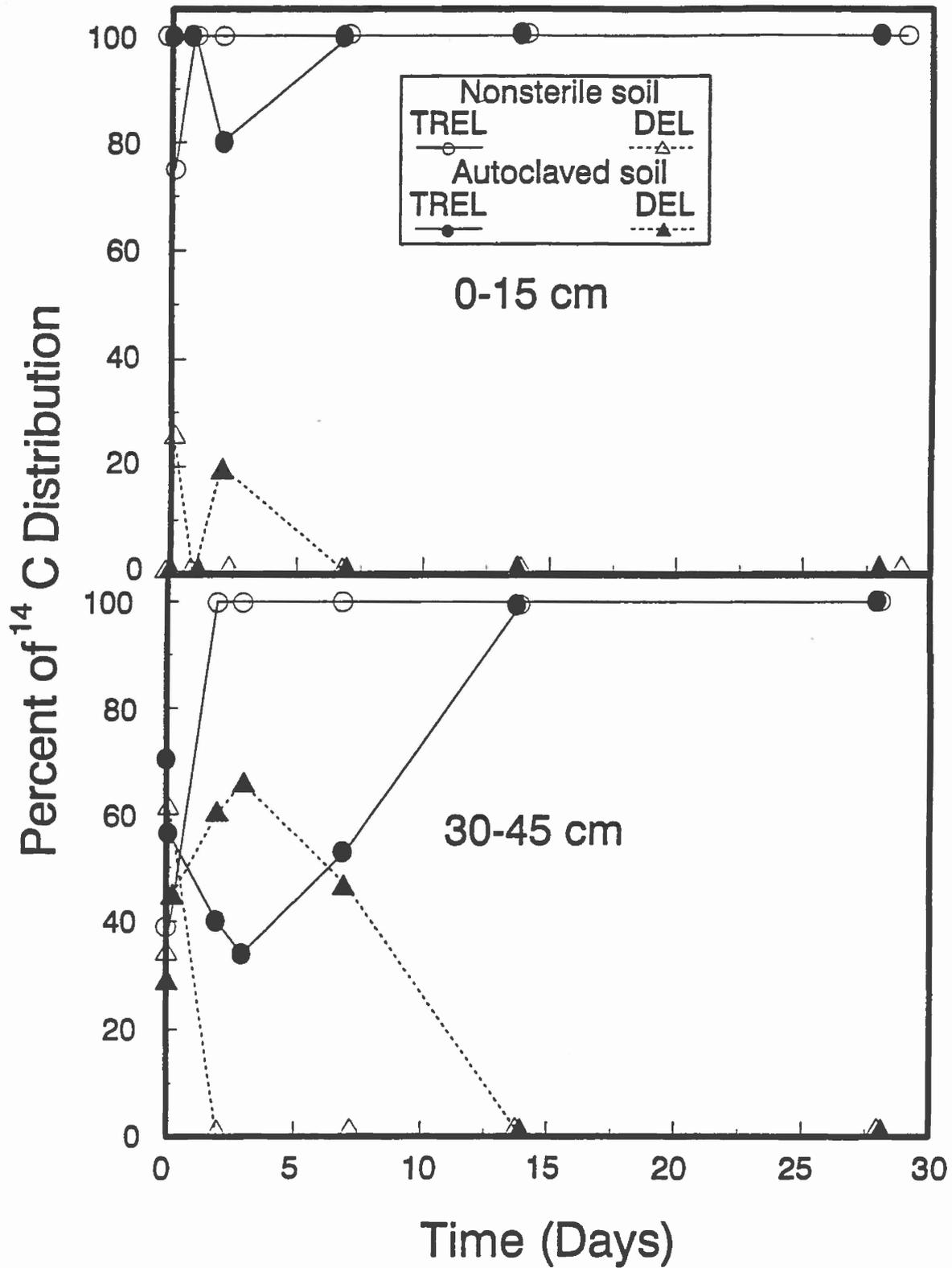
Figure 29. Distribution of ^{14}C-TREL and Its Metabolite ^{14}C-DEL in ^{14}C-TREL-Treated Nonsterile and Autoclaved Arredondo Surface and Subsurface Soil during 28 Days of Incubation.

than in the surface samples. The ^{14}C-DEL in the nonsterile and autoclaved samples persisted for 3 and 14 days, respectively, after the treatment of ^{14}C-TREL. GC-AAS confirmed the formation of DEL in nonsterile and autoclaved samples during the early stage of incubation.

Small amounts of ^{14}C generally were found in phosphate buffer extracts of nonsterile and autoclaved samples (Figures 27 and 28). The ^{14}C in the phosphate buffer that could not be extracted with hexane-NaDDTC appears to be associated with compounds of more polar nature than ionic triethyl lead and diethyl lead. More ^{14}C was extracted by phosphate buffer in the nonsterile surface sample during the first 3 days of incubation than in the autoclaved surface sample. After 3 days, the situation was reversed. In fact, no ^{14}C was found after 7 days in the phosphate buffer extract of the nonsterile surface sample. This would indicate that ^{14}C-metabolites in the nonsterile surface sample that could be extracted with phosphate buffer were further degraded, most likely to their final oxidation products, CO_2 and H_2O. Whereas more ^{14}C was extracted by phosphate buffer during the first 14 days of incubation in the nonsterile subsurface sample than in the autoclaved subsurface sample, substantial amounts of ^{14}C became nonextractable (bound residues) in both nonsterile and autoclaved samples.

Nonextractable ^{14}C in the nonsterile and autoclaved samples, with the exception of the autoclaved subsurface sample, initially increased rapidly and leveled off after 1 day. Nonextractable ^{14}C in the autoclaved subsurface sample initially increased slowly and leveled off after 7 days. More non-extractable ^{14}C, up to 38.8 percent of the applied ^{14}C, was formed in the autoclaved surface sample than in the nonsterile surface sample. In contrast, for the subsurface samples, more nonextractable ^{14}C was formed in the nonsterile sample than in the autoclaved sample.

Total ^{14}C recoveries in surface and subsurface samples decreased with time. At the end of 28 or 29 days of incubation, 46.2 and 64.5 percent of the applied ^{14}C were recovered in the nonsterile surface and subsurface samples, and 50.9 and 42.2 percent of the applied ^{14}C were recovered in the autoclaved surface and subsurface samples. However, total ^{14}C recovery did not include $^{14}CO_2$. Even if $^{14}CO_2$, which ranged from 15 to 16 percent of the applied ^{14}C, were included, total ^{14}C recoveries in the nonsterile samples still would be well below 100 percent, about 60 to 80 percent. Furthermore, as stated above, no $^{14}CO_2$ production from the autoclaved samples was observed. Thus, 49 to 58 percent of the applied ^{14}C in the autoclaved samples was not accounted for. It is likely that volatile degradation products, other than $^{14}CO_2$, formed chemically. Judging from a rapid decrease in total ^{14}C recovery, once ^{14}C-TREL came into contact with soil, especially with autoclaved soil, these chemicals rapidly degraded to unknown volatile products. It is well known that soil physical and chemical properties are altered significantly after autoclaving (Skipper and Westermann, 1973). It appeared that autoclaved soil was more active chemically in degrading TREL in these experiments.

3.   Disappearance and Metabolites of DEL in Soil

Hexane-NaDDTC extractable ^{14}C in ^{14}C-DEL-treated nonsterile and autoclaved soil samples initially disappeared more rapidly than in the corresponding ^{14}C-TREL-treated samples (Figures 30 and 31). In nonsterile soil, hexane-NaDDTC extractable ^{14}C in the subsurface sample declined more rapidly than in the surface sample, and at the end of 28 days of incubation, 5 and 0 percent of the applied ^{14}C in the surface and subsurface samples could be extracted with hexane-NaDDTC, respectively. In the autoclaved samples, although hexane-NaDDTC extractable ^{14}C in the surface sample initially declined more rapidly than in the subsurface sample, after 3 or 4 days, hexane-NaDDTC extractable ^{14}C in both samples leveled off. At the end of 28 days of incubation, less than 1 percent of the applied ^{14}C in the autoclaved surface and subsurface samples could be extracted with hexane-NaDDTC. The only ^{14}C chemical found in hexane-NaDDTC extracts in all nonsterile and autoclaved soil samples was ^{14}C-DEL.
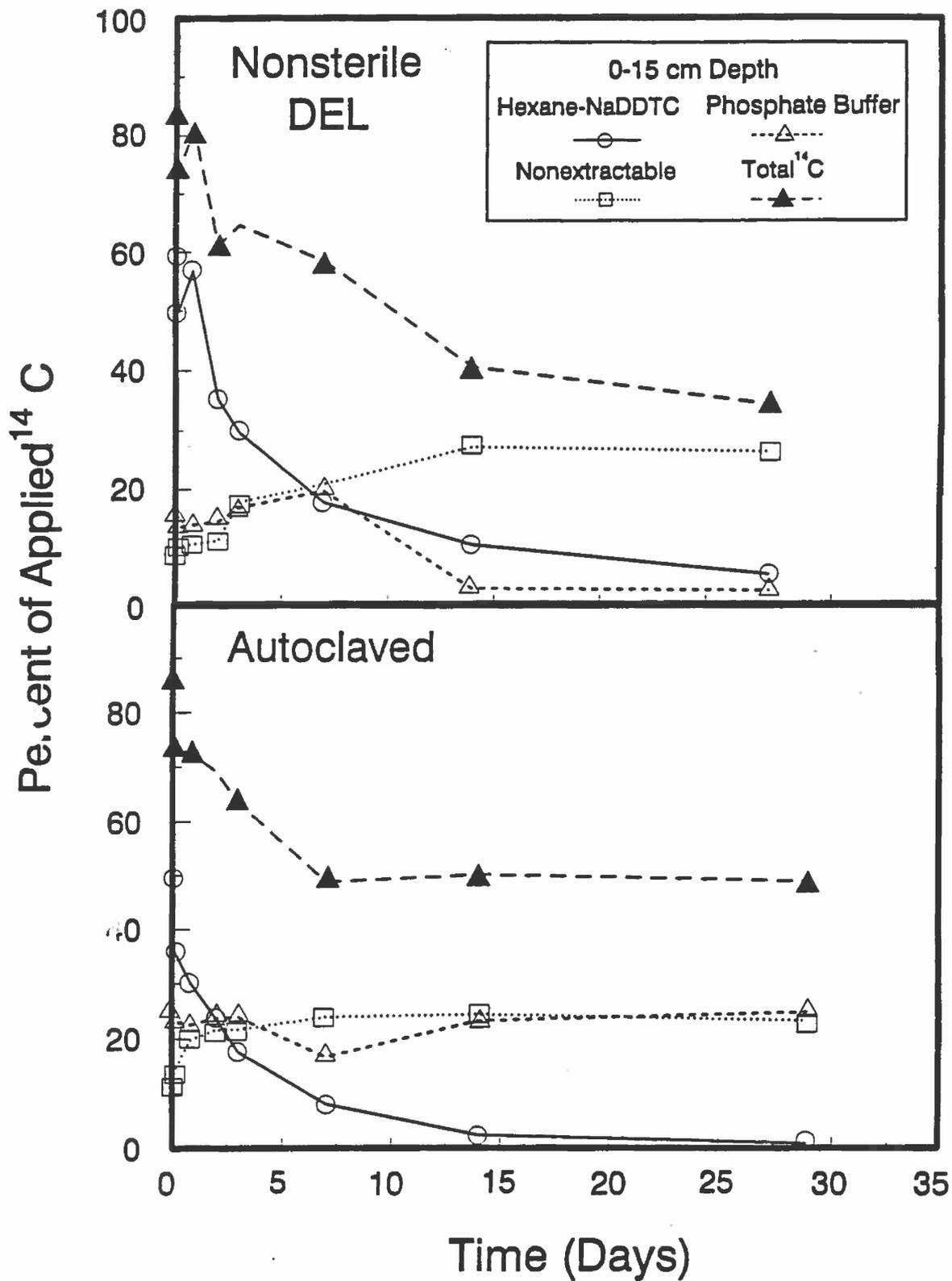
Figure 30. Distribution of ^{14}C in Hexane-NaDDTC Phase, Phosphate Buffer Phase, Nonextractable, and Total Recovery from the ^{14}C-DEL-Treated Nonsterile and Autoclaved Arredondo Surface Soil (0 to 15 cm) during 28 Days of Incubation.
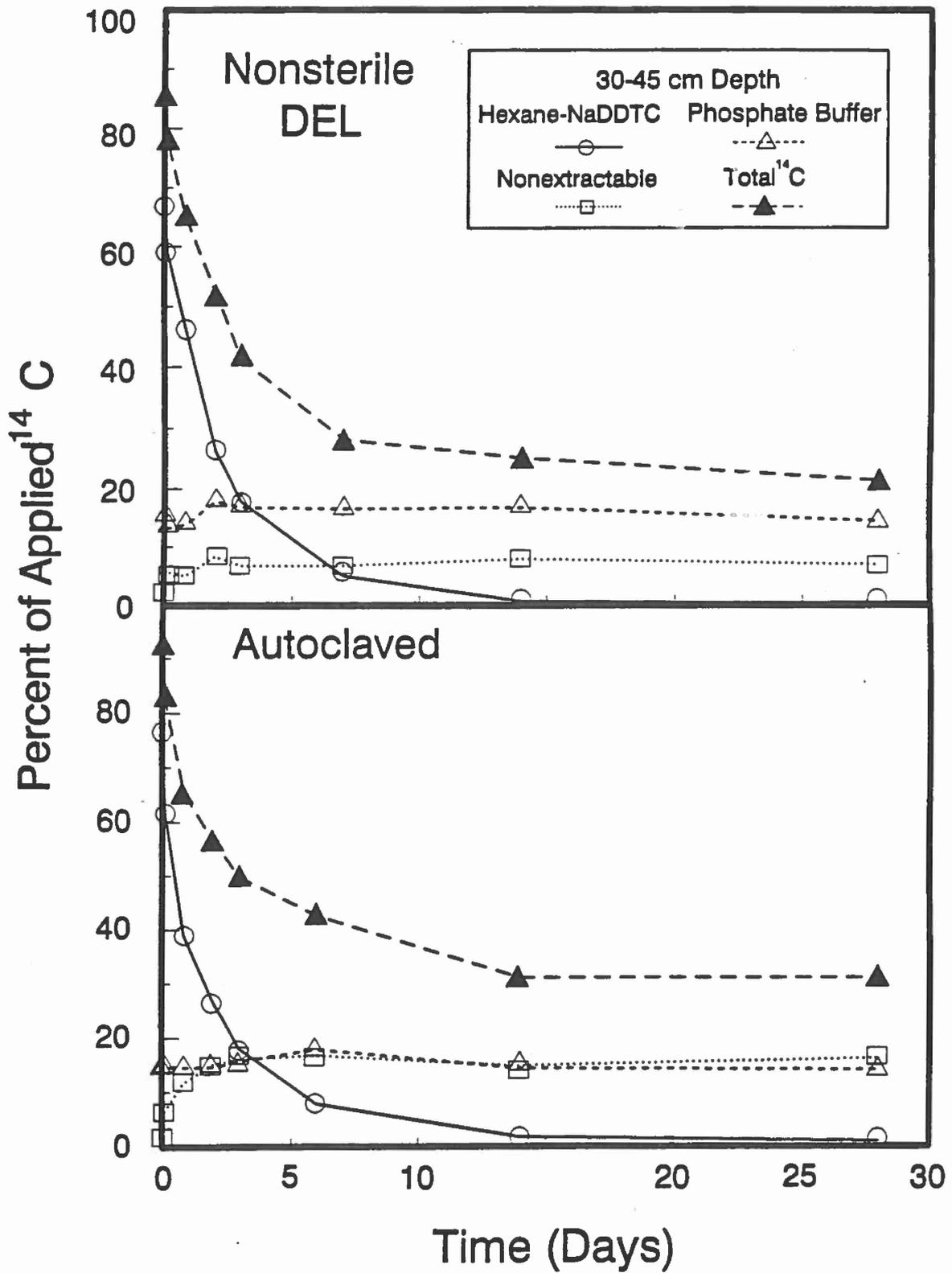
Figure 31. Distribution of ^{14}C in Hexane-NaDDTC Phase, Phosphate Buffer Phase, Nonextractable, and Total Recovery from the ^{14}C-DEL-Treated Nonsterile and Autoclaved Arredondo Subsurface Soil (30 to 45 cm) during 28 Days of Incubation.

Apparently monoethyl lead is chemically unstable and, in fact, this chemical was never detected in the environment. Thus, degradation of DEL in soil is a one-step process yielding to inorganic Pb^{2+}, and is mainly a chemical process in nature. GC-AAS confirmed the results of the TLC-autoradiographic assays.

The levels of phosphate buffer-extractable ^{14}C for all soil samples, with the exception of the nonsterile surface sample after 14 days of incubation, were nearly unchanged during the entire incubation periods. The levels of ^{14}C in phosphate buffer in the nonsterile surface sample after 14 days were much lower than at 7 days or earlier. Nonextractable ^{14}C in the ^{14}C-DEL-treated surface sample was higher than in the subsurface sample. Nonextractable ^{14}C in the ^{14}C-DEL-treated samples initially was formed more rapidly than in the ^{14}C-TREL-treated samples, but the levels of nonextractable ^{14}C were lower than in the ^{14}C-TREL-treated samples. Total ^{14}C recoveries, which did not include $^{14}CO_2$, in the nonsterile samples initially declined rapidly; at the end of 28 or 29 days of incubation, 21.1 to 48.9 percent of the applied ^{14}C had been recovered. Total ^{14}C recovery in the nonsterile samples was higher than in the autoclaved samples. The discrepancy may be related to the fact that mineralization of ^{14}C-DEL did not occur in the autoclaved samples. In the autoclaved samples, 51 to 69 percent of the applied ^{14}C was not accounted for. The ^{14}C not accounted for could be associated with volatile ^{14}C products not related to $^{14}CO_2$. Similar to TREL, poor ^{14}C recoveries in ^{14}C-DEL-treated autoclaved soil also could be due to greater chemical degradation than in the nonsterile soil.

If maintained in the dark, both TREL and DEL were fairly stable in water (Jarvie et al., 1981). Both were much less stable under sunlight or in the presence of silica. Both characteristics were especially true of TREL. In the presence of silica and under dark conditions, small amounts of DEL were formed in water treated with TREL; after 84 days of incubation, 25 percent of the applied TREL was not accounted for (Jarvie et al., 1981). The TREL not accounted for either degraded to inorganic Pb^{2+} or adsorbed to the silica surface. Jarvie et al. (1981) found also that no organic degradation product of DEL was found in water containing silica. In this study, both TREL and DEL were rapidly transformed through chemical degradation in either nonsterile or autoclaved soil under dark conditions; in the case of TREL, small amounts of DEL appeared briefly. More of the applied TREL or DEL was unaccounted for in soil than in water, even though in water TREL or DEL adsorbed onto silica surfaces was not determined. Therefore, it was postulated that ^{14}C not accounted for in the ^{14}C-TREL- or ^{14}C-DEL-treated soil was lost due to formation of volatile and/or gaseous ^{14}C-products, such as ^{14}C-ethanol or ^{14}C-ethane. Furthermore, it was not clear whether microorganisms can directly mineralize ^{14}C-TREL and ^{14}C-DEL to $^{14}CO_2$, or whether formation of $^{14}CO_2$ is due to the mineralization of degradation products such as ^{14}C-ethanol or ^{14}C-ethane.

Attempts to isolate microorganisms capable of mineralizing TEL from the three soils and a Pb gasoline-contaminated soil have not been successful. Macaskie and Dean (1990) reported that an *Arthrobacter* sp. had a limited capacity to transform trimethyl lead to inorganic Pb^{+2}. It was not clear that in the course of transforming trimethyl lead to Pb^{+2}, the organism had the capacity to mineralize trimethyl lead.

SECTION X

DEGRADATION AND METABOLISM OF TETRAETHYL LEAD IN THREE SOILS

A. INTRODUCTION

The extensive past use of leaded gasoline in automobiles had made TEL, TML, and their degradation products, ionic Pb alkyl compounds, ubiquitous in the environment prior to the late 1980s (Radojevic and Harrison, 1987b; Rhue et al., 1992). Ionic Pb alkyl compounds were the major species detected in surface water, rain water, and sediments (Chau et al., 1979, 1984; Radojevic and Harrison, 1987a,b). TEL in aqueous solutions appeared to undergo a series of sequential deethylations, first to triethyl lead, then to diethyl lead, and eventually to Pb^{2+} (Rhue et al., 1992). Little information is available regarding the fate of TEL in soil. Triethyl lead and diethyl lead were the only organolead compounds detected in soil samples collected from an urban area (Blais and Marshall, 1986). Ou et al. (1994) reported that TEL in both nonsterile and autoclaved surface and subsurface soils transforms rapidly to ionic ethyl lead species, presumably to triethyl lead and diethyl lead, and that both biological and chemical degradation contribute to the degradation of TEL. Furthermore, in addition to degradation of ionic ethyl lead species and CO_2, unknown volatile products also could be formed.

The objectives of this study have been to determine (1) the mineralization rates of ^{14}C-TEL in nonsterile Leon sand and Madison loam; (2) disappearance rate for ^{14}C-TEL and formation of degradation products in nonsterile and autoclaved Arredondo fine sand, Leon, and Madison soils; and (3) mass balance of ^{14}C in the three soils treated with ^{14}C-TEL.

B. MATERIALS AND METHODS

1. Soils

Soil samples were collected at 15-cm increments to 45-cm depth from three forest sites located at the University of Florida, Gainesville, Florida; Tyndall Air Force Base (AFB), Florida; and Dobbins AFB, Georgia; they were classified as Arredondo fine sand, Leon sand, and Madison loam, respectively. The soil samples were stored in the dark at 4°C and used within 3 months after collection. Selected soil properties of the three soils are shown in Table 24.

2. Chemicals

Analytical-grade TEL and TREL chloride salt were obtained from All-Chemie Inc. (Ft. Lee, New Jersey). Ethyl-1-^{14}C-TEL with a specific activity of 0.74 GBq/mmol and radiopurity of better than 99 percent was purchased from American Radiolabeled Chemicals (St. Louis, Missouri). We found that more than 99 percent of the ^{14}C-TEL was fractionated into hexane (see Section VIII). This finding indicates that more than 99 percent of ^{14}C was associated with a hydrophobic type of chemical and TEL is a hydrophobic chemical. The ^{14}C-TREL, ^{14}C-DEL, and nonlabeled DEL were obtained from chemical conversions from ^{14}C-TEL, ^{14}C-TREL, and analytical-grade TREL chloride salt, respectively, as described in Section IX.B. All other chemicals were either analytical grade, scintillation grade, or the highest grade commercially available.

TABLE 24. SELECTED SOIL PROPERTIES OF ARREDONDO FINE SAND, LEON SAND, AND MADISON LOAM USED FOR THIS STUDY.

Soil Depth (cm)	pH	Soil-Water Content	Organic C	Sand	Silt	Clay
			g/kg soil			
Arredondo						
0 - 15	5.5	55	11.8	920	70	10
15 - 30	4.6	46	4.7	930	50	20
30 - 45	5.6	28	3.9	930	40	30
Leon						
0 - 15	5.1	40	15.5	900	30	70
15 - 30	5.0	21	1.1	960	10	30
30 - 45	5.1	87	11.0	820	90	90
Madison						
0 - 15	4.7	320	6.1	430	400	170
15 - 30	4.7	206	2.8	500	330	170
30 - 45	4.6	180	1.5	540	300	160

3. Mineralization Studies

The experimental setup for mineralization of ^{14}C-TEL in nonsterile soil was similar to the procedure described in the Section IX, with slight modifications. In short, 50 grams of nonsterile soil (oven-dry weight basis) was transferred to a 250-mL Erlenmeyer flask, to which 0.1 μCi of ^{14}C-TEL and 1,000 μg of TEL were added. An additional 50 grams of new soil was added immediately to the top of the soil in the flask. After a brief but thorough mixing, the flask was closed tightly with a Teflon™-lined screw cap under which a stainless steel vial containing 3 mL of 8 mol/L KOH was hung. All flasks were wrapped with aluminum foil and incubated in the dark at 28°C. At predetermined intervals, all vials were removed and replaced with new vials containing fresh KOH. The removed vials were placed individually in small glass beakers, and the KOH was diluted with deionized H_2O to 5 mL. Then 0.5 mL of the diluted KOH was used for ^{14}C determination by liquid scintillation counting (LSC). To reduce photodecomposition, all operations were carried out under semidark conditions. At the end of this incubation period (28 days), 10 grams of soil from each flask was transferred to a 50-mL glass centrifuge tube for solvent extraction as described below. The ^{14}C remaining in the solvent-extracted soil samples was combusted to $^{14}CO_2$ by a sample oxidizer and quantified by LSC (Ou et al., 1982).

The experimental setup for determining the mineralization rates of ^{14}C-TREL and ^{14}C-DEL in Leon and Madison soil was similar to that for ^{14}C-TEL mineralization.

4. Disappearance of TEL and Metabolite Formation

A series of 50-mL glass centrifuge tubes wrapped with aluminum foil was set up; each contained 5 grams of nonsterile or autoclaved soil. After 100 μg of TEL and 2 kBq of ^{14}C-TEL was

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added to each tube, an additional 5 grams of the same soil was added to the top of the soil in the tube. The tubes were tightly closed with Teflon™-lined screw caps and immediately shaken in a reciprocal shaker at 250 strokes per minute for 5 minutes. Two tubes from each treatment immediately received 10 mL of n-hexane and 10 mL of EDTA solution (20 grams of disodium EDTA in 1 liter of deionized H_2O), and were shaken for 30 minutes. The two tubes were then centrifuged at 500xg for 10 minutes for separation of the two phases, hexane and EDTA. After 0.5 mL was removed from the hexane phase for ^{14}C determination by LSC, the rest of the solution was transferred to a 50-mL plastic centrifuge tube. The two tubes were centrifuged at 25,000xg for 10 minutes. After removal of the hexane and the EDTA layers from the tube, 10 mL each of hexane and EDTA solution were added to soil in the tubes. The two tubes were again subjected to the above process, i.e., shaking, centrifugation, and phase separation. The ^{14}C in the combined hexane extract and the combined EDTA fraction were quantified by LSC. The EDTA fraction then received 5 mL of n-hexane and 1 mL of sodium diethyldithiocarbamate (NaDDTC, 20 grams/1 liter H_2O), and the tubes were shaken for 15 minutes. After the hexane-NaDDTC phase was removed, the aqueous phase was subjected to the same hexane-NaDDTC extraction. The combined hexane-NaDDTC then was concentrated under a gentle stream of N_2 gas to 0.1 mL. The rest of the tubes were incubated in the dark at 28°C. At predetermined intervals, two tubes from each treatment were removed for hexane and hexane-NaDDTC extractions. The ^{14}C remaining in the extracted soil samples was combusted to $^{14}CO_2$ in a sample oxidizer and quantified by LSC. All operations were carried out under semidark conditions, and all experiments were duplicated.

The concentrated hexane-NaDDTC extracts were spotted on silica gel G TLC plates, and the plates were developed in acetone/n-hexane/propionic acid (30:70:2, v/v/v). After air-drying, the plates were covered with X-ray films (SB-5, Eastman Kodak, Rochester, New York). After 21 days of exposure, the films were developed, and the silica gel in the radioactive areas was scraped off and transferred to scintillation vials for ^{14}C determination by LSC.

5. Confirmation by GC-AAS

Degradation products of ^{14}C-TEL and ^{14}C-TEL in nonsterile and autoclaved soils were confirmed by established gas chromatography-atomic absorption spectrometry (GC-AAS) techniques (Chakraborti et al., 1984; Chau et al., 1984). A detailed description is given in Section IX.B for confirmation of TREL, DEL, and their degradation products in soil. Briefly, a GC (Hewlett-Packard 5890, equipped with an autosampler and an integrator) was interfaced with an AAS (Perkin-Elmer, equipped with a Perkin-Elmer Pb detector with a deuterium background corrector) through nickel tubing. Soil samples treated with analytical-grade TEL were extracted first with n-hexane and then with n-hexane-NaDDTC. The hexane extracts were injected directly into the GC-AAS for determination of TEL. Prior to injection into the instrument, ionic ethyl lead compounds in the hexane-NaDDTC extracts were butylated with magnesium butylchloride. Retention times for TEL, TREL, and DEL were 3.9, 6.7, and 8.5 minutes, respectively.

C. RESULTS AND DISCUSSION

1. Mineralization of TEL in Leon and Madison Soils

Similar to the mineralization of ^{14}C-TEL in nonsterile Arredondo soil (see Section VIII.C), ^{14}C-TEL in nonsterile Leon and Madison soils initially was mineralized rapidly. Mineralization during the first 7 days accounted for more than half of the total mineralization during the entire 28 days of incubation (Figure 32). After 7 days, mineralization of ^{14}C-TEL leveled off in all samples, and TEL in these samples was mineralized at near-constant rates, ranging from 0.06 to 0.10 percent of the applied

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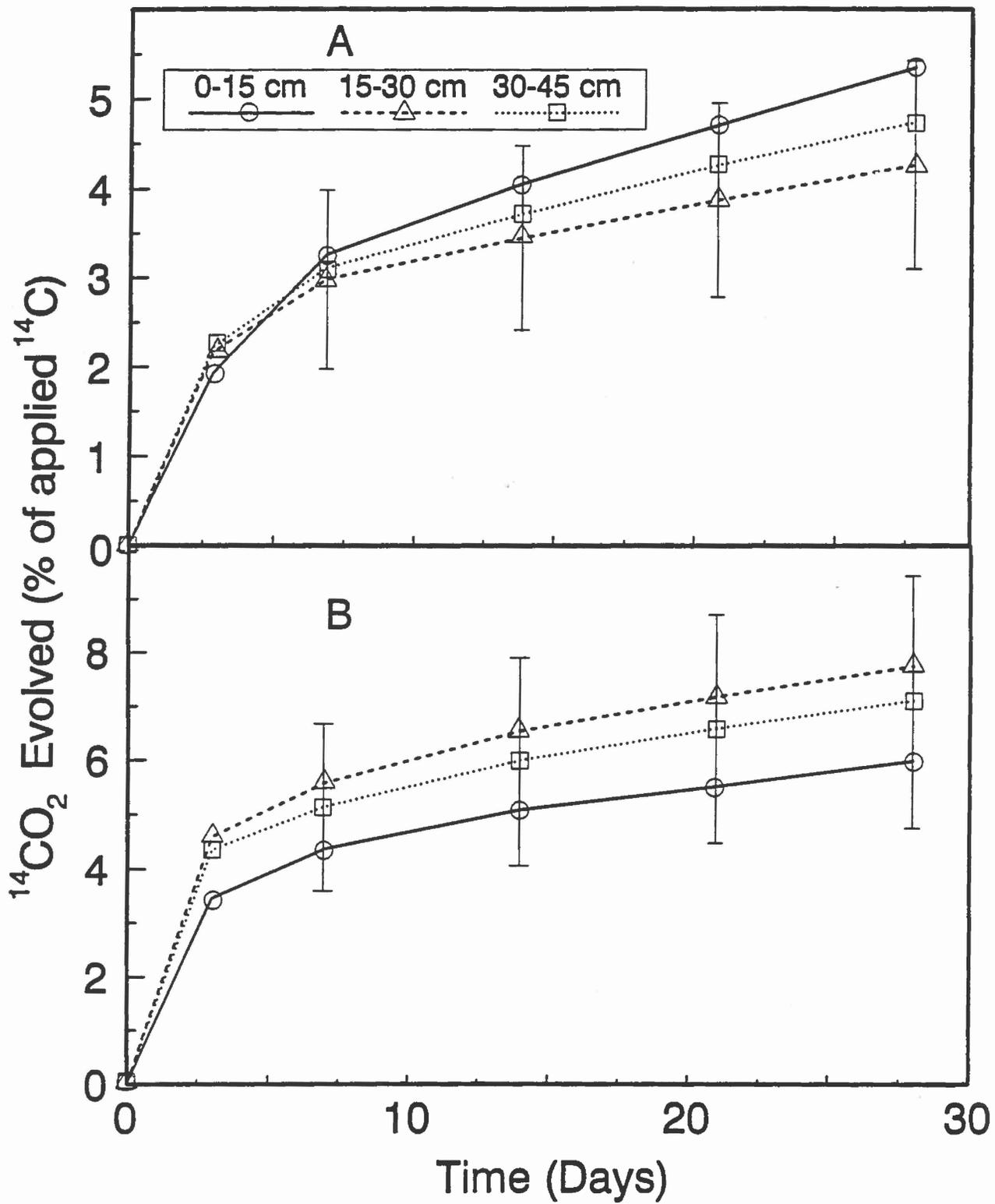
Figure 32. Mineralization of ^{14}C-TEL in Leon (A) and Madison (B) Soils during 28 Days of Incubation.

^{14}C mineralized per day. Similar to the Arredondo soil, in Leon soil more ^{14}C-TEL was mineralized in the surface sample than in the subsurface samples. In contrast to Arredondo and Leon soils, more ^{14}C-TEL was mineralized in the subsurface samples of the Madison soil than in the surface sample. After 28 days only 4.26 to 5.35 percent and 5.98 to 7.74 percent of the applied ^{14}C was mineralized in the Leon and Madison soils, respectively. The mineralization results shown in Figure 32 also include small amounts of volatile ^{14}C organics, most likely ^{14}C-TEL, which could amount to a very small fraction of the total ^{14}C trapped in KOH (less than 0.2 percent of the applied ^{14}C, see Section VIII.C). No attempt was made to determine the mineralization rates of autoclaved Leon and Madison soil samples. No mineralization of TEL was observed in autoclaved Arredondo soil samples during 28 days of incubation (see Section VIII.C). Obviously, mineralization of TEL in soil is a microbially mediated process. Thus, it is expected that mineralization of TEL also would not occur in autoclaved Leon and Madison soils.

At the end of 28 days of incubation, total ^{14}C recoveries in the ^{14}C-TEL-treated Leon and Madison soils were poor (Table 25), ranging from 18.88 to 28.70 percent for the Leon samples and from 24.41 to 33.55 percent for the Madison samples. Total ^{14}C recoveries in the surface samples were better than in their respective subsurface samples. Patterns of ^{14}C recoveries in the two soils were similar to those in Arredondo soil samples in which total ^{14}C recoveries were poor and more ^{14}C was recovered in the surface sample than in the subsurface samples (see Section VIII.C). The ^{14}C not accounted for could be associated with volatile and/or gaseous degradation products, such as ^{14}C-ethane or ^{14}C-ethanol.

TABLE 25. DISTRIBUTION OF ^{14}C IN NONSTERILE LEON AND MADISON SOILS
AFTER 28 DAYS OF INCUBATION WITH ^{14}C-TEL.

Soil Depth	^{14}CO$_2$	^{14}C in hexane	^{14}C in EDTA	Nonextractable ^{14}C	Total ^{14}C
(cm)	Percent of applied ^{14}C				
			Leon		
0 - 15	5.36	0.80	6.75	15.80	28.70
15 - 30	4.26	1.57	6.62	6.44	18.88
30 - 45	4.74	0.60	5.58	7.62	20.52
			Madison		
0 - 15	5.98	0.23	1.55	25.80	33.55
15 - 30	7.74	0.42	1.19	16.40	25.77
30 - 45	7.10	0.45	0.75	17.60	24.41

Ionic ^{14}C-TREL was the major metabolite of TEL in Leon and Madison soils, respectively (see below). Therefore, mineralization rates of ^{14}C-TREL in nonsterile Leon and Madison soils were investigated. Mineralization of ^{14}C-TREL in nonsterile surface and subsurface samples of the two soils initially was rapid. More than half of the applied ^{14}C was mineralized during the first 3 days, with the exception of the shallow subsurface sample (15 to 30 cm depth) of Leon soil (Figure 33). In this sample, more than half of the applied ^{14}C was mineralized in 7 days. More ^{14}C-TREL was mineralized in the surface sample of the Madison soil than in the corresponding subsurface samples. In Arredondo soil, the ^{14}C-TREL also was initially mineralized rapidly and, after 3 days of incubation, more than half of the applied ^{14}C in the surface and subsurface samples was mineralized (see Section IX.C). More ^{14}C-TREL than ^{14}C-TEL was
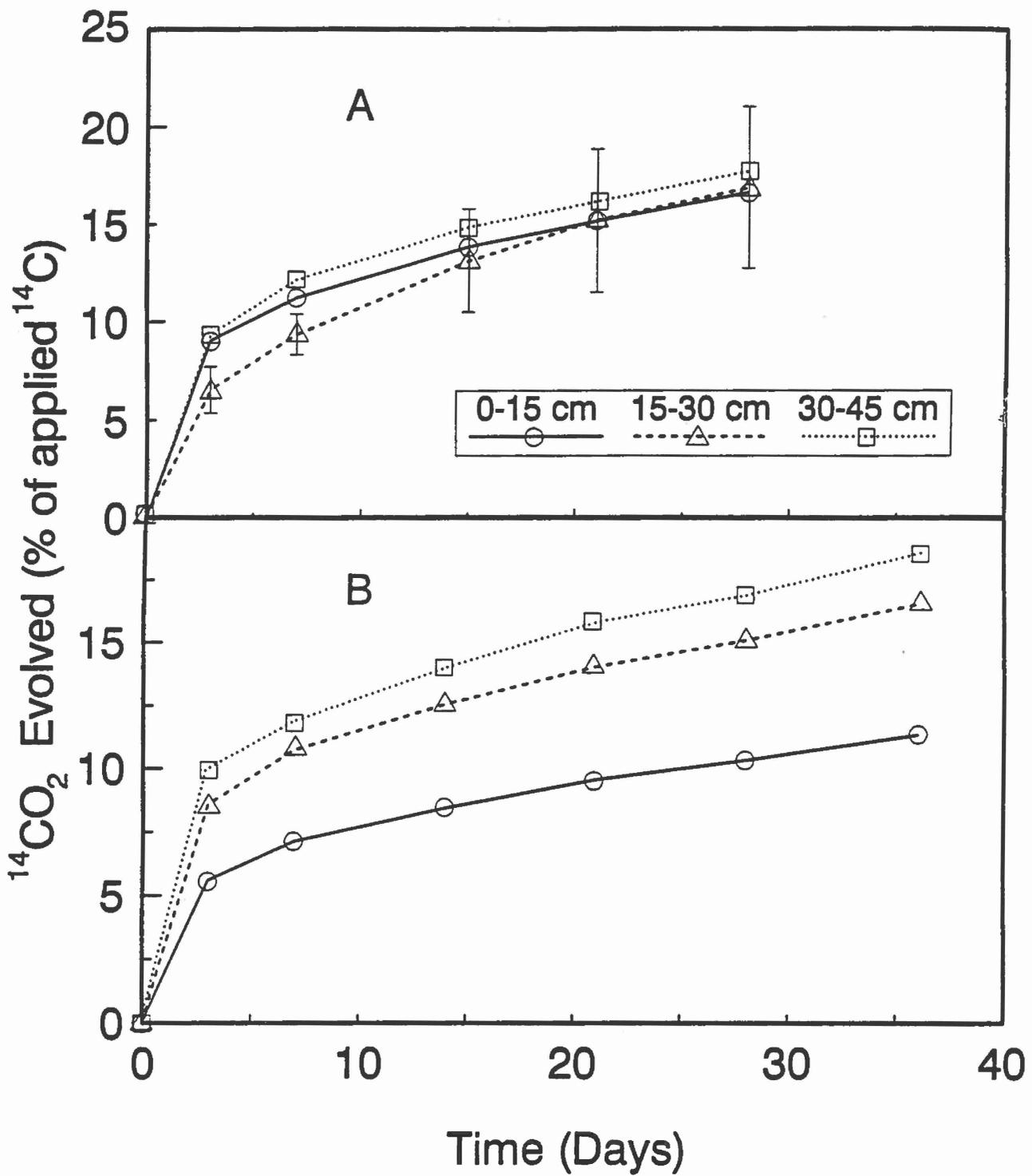
Figure 33. Mineralization of ^{14}C-TREL in Leon (A) and Madison (B) Soils during 28 and 36 Days of Incubation, Respectively.

mineralized during the 28 to 36 days of incubation. Because TREL is water-soluble and TEL is not, it is likely that TREL would be more easily utilized by microorganisms, resulting in a higher level of mineralization.

Although the ^{14}C-DEL in surface samples of Leon and Madison soils initially was mineralized rapidly (Figure 34), the ^{14}C-DEL in the deeper subsurface samples (30 to 45 cm depth) and the shallow subsurface samp!, (15 to 30 cm depth) of the Leon was mineralized at a much lower rate. The ^{14}C-DEL in these samples was mineralized more or less steadily throughout the entire incubation period. At the end of 28 days of incubation, much more ^{14}C-DEL was mineralized in the surface sample of the Leon soil than in the corresponding subsurface samples, whereas, to a smaller extent, more ^{14}C-DEL was mineralized in the subsurface samples of the Madison soil than in the corresponding surface sample. In Section IX.C we reported that ^{14}C-DEL in the surface sample of Arredondo initially was mineralized more rapidly than in the corresponding subsurface samples, and at the end of 28 days of incubation nearly 20 percent of tl applied ^{14}C was mineralized in the surface and subsurface samples.

2.   TEL Disappearance and Formation of Ionic Ethyl Lead Compounds

TEL has a very low water solubility but is highly soluble in hydrophobic types of solvents such as hexane, benzene, and gasoline (Feldhake and Stevens, 1963; Rhue et al., 1992). Ou et al. (1994) took advantage of these unique properties for the separation of TEL from ionic ethyl lead compounds and unknown nonlead water-soluble organic compounds in soil. This study went a step further to separate ionic ethyl lead compounds from water-soluble nonlead organic compounds in soil. Non-ionic ^{14}C-TEL in soil first was fractionated into hexane, and the remaining ionic ^{14}C-ethyl lead compounds then were fractionated into hexane-NaDDTC. The remaining ^{14}C in aqueous solution is considered to be associated with water-soluble nonlead organic compounds. Because ^{14}C-TEL was used, TEL, ionic ethyl lead compounds, and unknown nonlead organic compounds could be quantified easily by LSC. The unknown water-soluble nonlead compounds were possibly more polar than ionic ethyl lead compounds.

The ^{14}C-TEL in nonsterile and autoclaved surface (0 to 15 cm depth) and subsurface (30 to 45 cm depth) samples of Leon and Madison soils all rapidly disappeared (Figures 35, 36, 37, and 38). The ^{14}C-TEL in nonsterile samples disappeared more rapidly during the first 3 to 7 days than in the corresponding autoclaved samples, and the ^{14}C-TEL in surface samples disappeared more rapidly than in the corresponding subsurface samples. These differing rates indicated that both biological and chemical degradation were involved in the disappearance of TEL from soil, with chemical degradation being the major factor contributing to the disappearance of TEL in soil. It is estimated that biological degradation was responsible for about 20 percent and 10 percent of the ^{14}C-TEL in the Leon and Madison soils, respectively, during the first day of incubation. Smaller disappearance rates in subsurface samples probably reflected the fact that these samples had low microbial activity (nonsterile samples) and low organic matter contents.

With the rapid disappearance of the hexane-extractable ^{14}C, which is associated with ^{14}C-TEL in nonsterile and autoclaved samples, ^{14}C in the EDTA fraction and the nonextractable ^{14}C (bound residues) were rapidly formed and the ^{14}C levels in both phases rapidly leveled off (Figures 35, 36, 37, and 38). Total ^{14}C recoveries in nonsterile and autoclaved samples initially declined rapidly, and after 1 day the declination had either leveled off or stabilized. At the end of 28 days of incubation, total ^{14}C recoveries in all samples were poor, ranging from 18.9 to 42.1 percent of the applied ^{14}C. Because $^{14}CO_2$ production was not determined in nonsterile samples, based on the results of the Section X.C.1, the total $^{14}CO_2$ evolution during 28 days in nonsterile surface and subsurface samples of Leon and Madison soils was relatively small, ranging from 4.3 to 7.7 percent. Even if these values were used,

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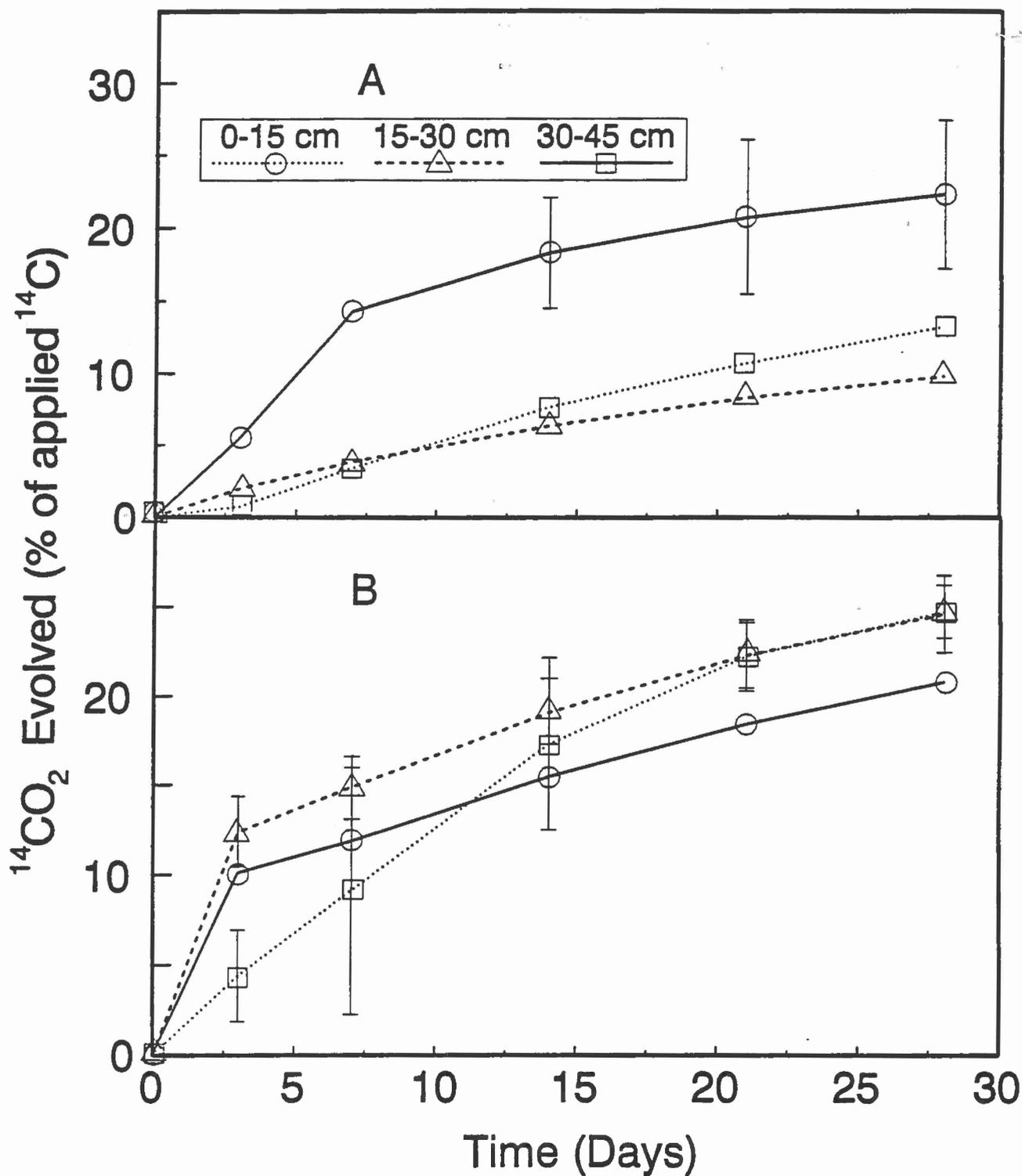
Figure 34. Mineralization of ^{14}C-DEL in Leon (A) and Madison (B) Soils during 28 Days of Incubation.
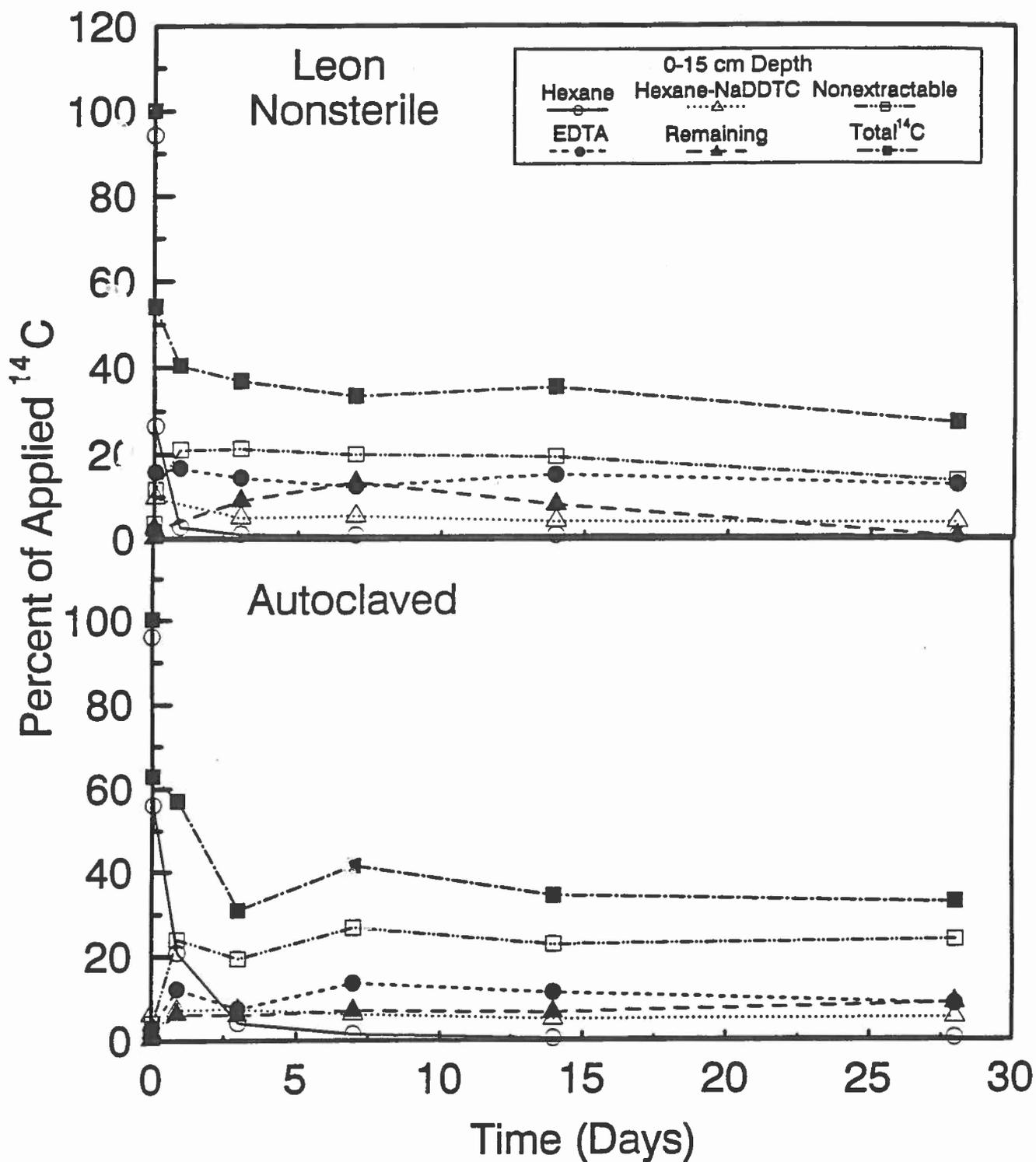
Figure 35. Distribution of ^{14}C in Hexane Phase, EDTA Phase, Hexane-NaDDTC Phase, [14]C Remaining, Nonextractable, and Total Recovery from ^{14}C-TEL-Treated Nonsterile and Autoclaved Surface Samples of Leon Soil.
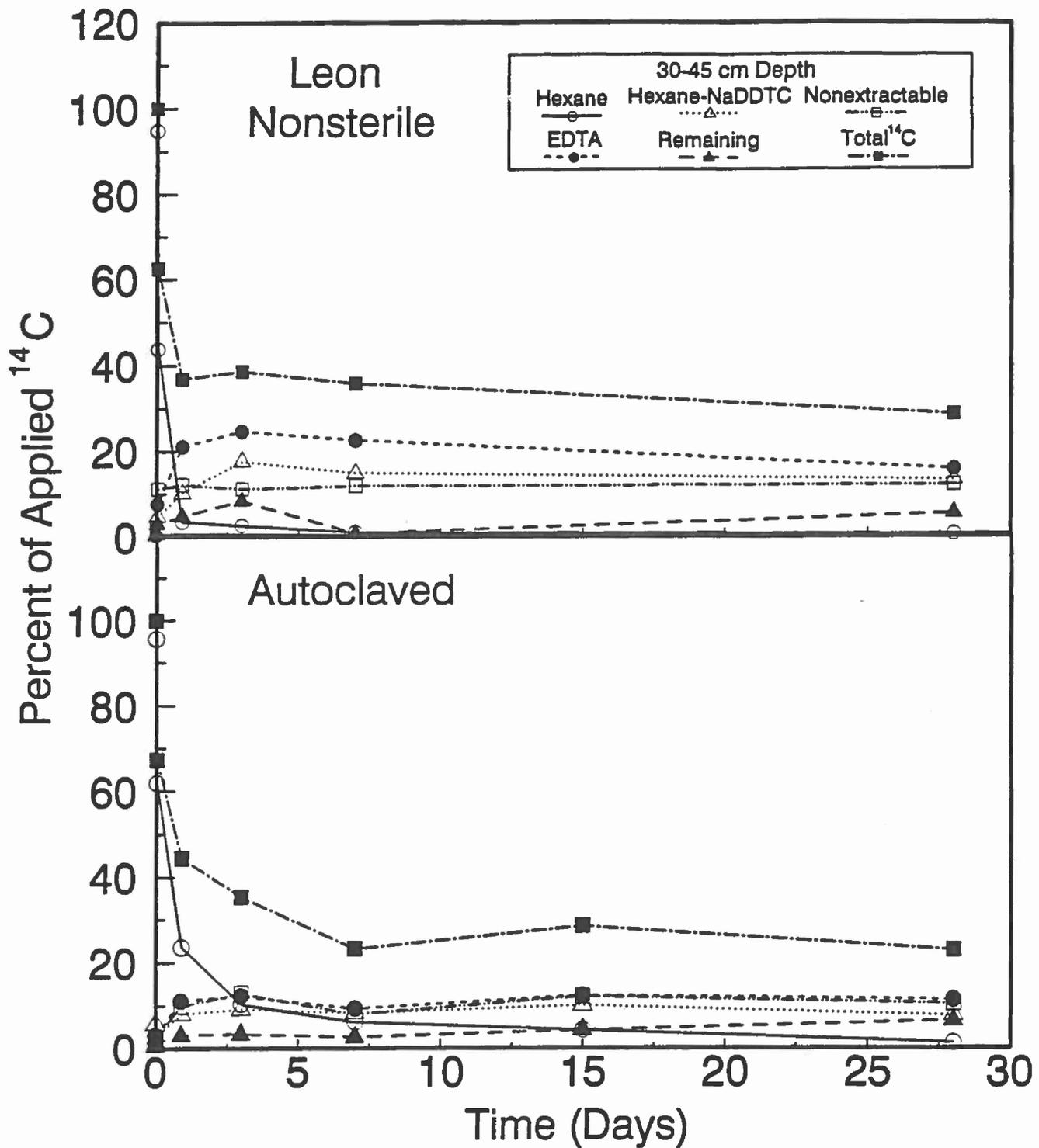
Figure 36. Distribution of ^{14}C in Hexane Phase, EDTA Phase, Hexane-NaDDTC Phase, ^{14}C Remaining, Nonextractable, and Total Recovery from ^{14}C-TEL-Treated Nonsterile and Autoclaved Subsurface Samples of Leon Soil.
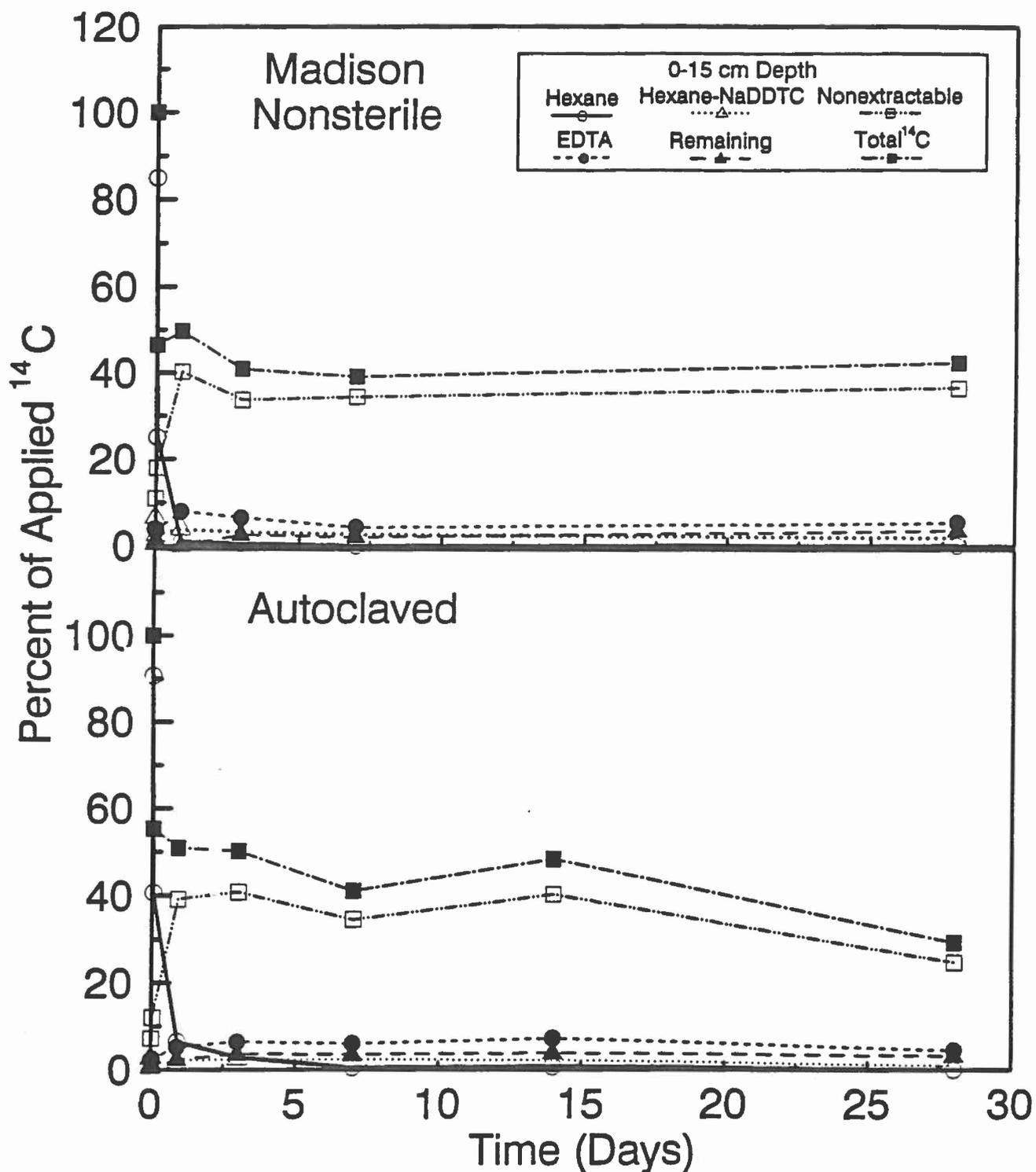
Figure 37. Distribution of ^{14}C in Hexane Phase, EDTA Phase, Hexane-NaDDTC Phase, [14]C Remaining, Nonextractable, and Total Recovery from ^{14}C-TEL-Treated Nonsterile and Autoclaved Surface Samples of Madison Soil.
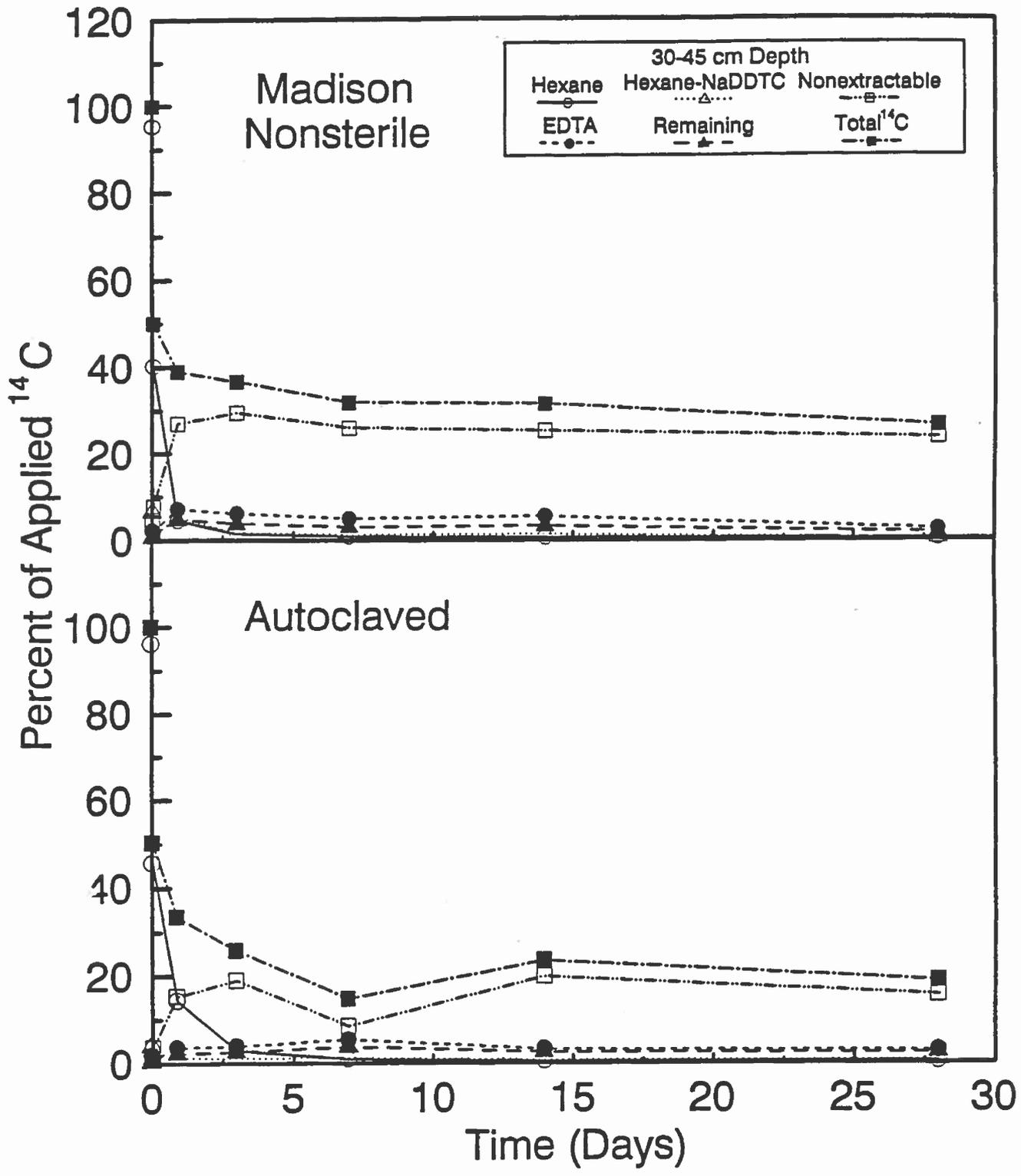
Figure 38. Distribution of ^{14}C in Hexane Phase, EDTA Phase, Hexane-NaDDTC Phase, ^{14}C Remaining, Nonextractable, and Total Recovery from ^{14}C-TEL-Treated Nonsterile and Autoclaved Subsurface Samples of Madison Soil.

total ^{14}C recoveries for all nonsterile soil samples were still very poor, below 50 percent. The rapid disappearance of ^{14}C in conjunction with the rapid declination of total ^{14}C recovery in nonsterile and autoclaved samples indicated that during TEL degradation unknown volatile and/or gaseous ^{14}C-products, besides $^{14}CO_2$, were formed. The majority of the ^{14}C-products appeared to escape into the atmosphere. A small fraction of the products remained in soil and was subsequently mineralized to $^{14}CO_2$. Based on the chemical structure of TEL, the unknown volatile and/or gaseous products could be ^{14}-ethanol or ^{14}-ethane. More unknown volatile and/or gaseous products were formed in autoclaved samples than in nonsterile samples.

The ^{14}C fractionated into the EDTA fraction represents water-soluble organic metabolites, including ionic ethyl lead species and nonlead organic compounds. The ^{14}C associated ethyl lead compounds were fractionated into hexane-NaDDTC, and the remaining ^{14}C in the aqueous phase was associated with water-soluble nonlead organic compounds. Ionic ethyl lead compounds were detected in ^{14}C-TEL treated nonsterile and autoclaved Leon and Madison samples during the entire 28 days of incubation (Figures 35, 36, 37, and 38). Small amounts of ^{14}C remained in the aqueous phase throughout the entire incubation period. Levels of ^{14}C remaining in the aqueous phase were generally more stable in autoclaved samples than in nonsterile samples.

Figures 39, 40, and 41 show the ratio of ^{14}C in hexane extract to ^{14}C in hexane-NaDDTC extract (^{14}C in hexane/^{14}C in hexane-NaDDTC), and the ratio of ^{14}C remaining in aqueous phase after the hexane-NaDDTC extraction to ^{14}C in hexane-NaDDTC extract (^{14}C remaining/^{14}C in hexane-NaDDTC) in nonsterile and autoclaved Leon, Madison, and Arredondo soils. If the value of ^{14}C in hexane/^{14}C in hexane-NaDDTC is one, this indicates that the amount of ^{14}C-TEL and the amount of ionic ^{14}C-ethyl lead species are the same. The rapid decrease in values of ^{14}C in hexane/^{14}C in hexane-NaDDTC in all nonsterile and autoclaved samples indicates that TEL disappeared rapidly and at the same time ionic ethyl lead compounds were rapidly formed. The values of ^{14}C in hexane/^{14}C in hexane-NaDDTC in nonsterile samples during the first 3 days were larger than in corresponding autoclaved samples. This indicated that, in addition to chemical conversion, biological degradation also contributed to the disappearance and formation of ionic ethyl lead compounds. The ratio of ^{14}C remaining in aqueous phase to ^{14}C in hexane-NaDDTC generally increased steadily with time. An increase in the value of ^{14}C remaining/^{14}C in hexane-NaDDTC indicates that ^{14}C associated with water-soluble nonlead organic compounds increases while ^{14}C associated with ionic ethyl lead species decreases.

3. Ionic Ethyl Lead Metabolites

It has been demonstrated that TEL in nonsterile and autoclaved soils partially degrades to ionic ethyl lead compounds (Ou et al., 1994; Sections VIII.C and IX.C). However, no attempts were made by Ou et al. (1994) to identify the nature of the ionic metabolites. In this study, ionic ethyl lead species in the hexane-NaDDTC extracts were separated, detected, and quantified by TLC-autoradiographic assays and LSC. In the ^{14}C-TEL-treated nonsterile surface samples of Leon and Madison soils, only ^{14}C-TREL was detected during the entire 28 days of incubation, with the exception of the Leon soil. In this sample, ^{14}C-DEL was detected once, 1 hour after incubation; ^{14}C-TREL was the principal or only ionic ethyl lead product in the autoclaved surface samples of Madison and Leon soils, respectively. The ^{14}C-DEL appeared briefly (at 1 and 23 hours after incubation) in the autoclaved Leon surface sample, and the ^{14}C-DEL in this sample accounted for 75 and 25 percent of total ionic ^{14}C-ethyl lead species at 1 and 23 hours of incubation, respectively. This indicates that TEL in soil initially degrades to TREL, which then degrades to DEL, again suggesting that degradation involves both chemical and biological mechanisms, with chemical degradation being the major factor.
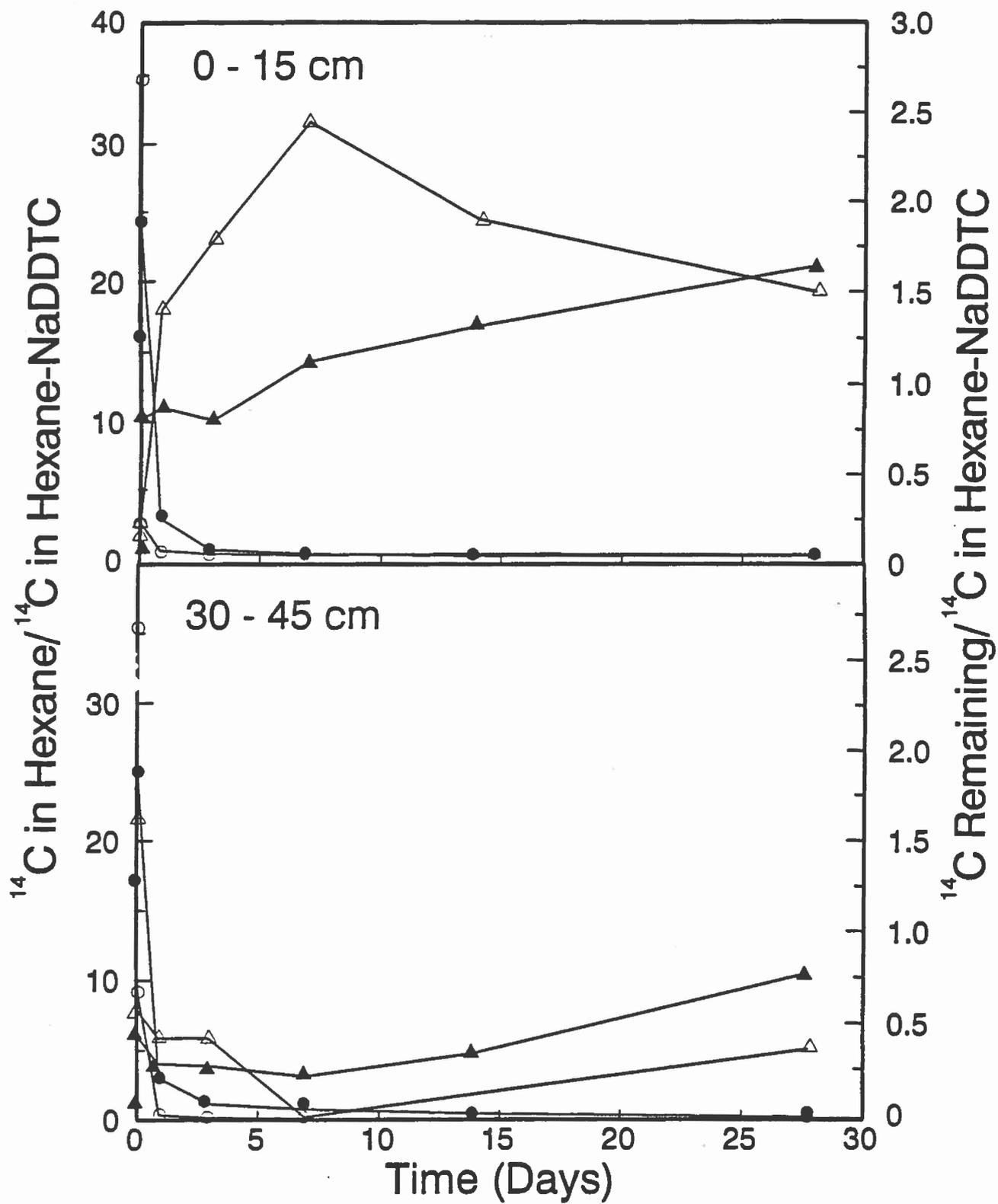
Figure 39. Distribution of ^{14}C in Hexane/^{14}C in Hexane-NaDDTC ($\bigcirc$,$\bullet$), and ^{14}C Remaining/^{14}C in Hexane-NaDDTC ($\triangle$,$\blacktriangle$) in Nonsterile (Open Symbols) and Autoclaved (Closed Symbols) Leon Soil.
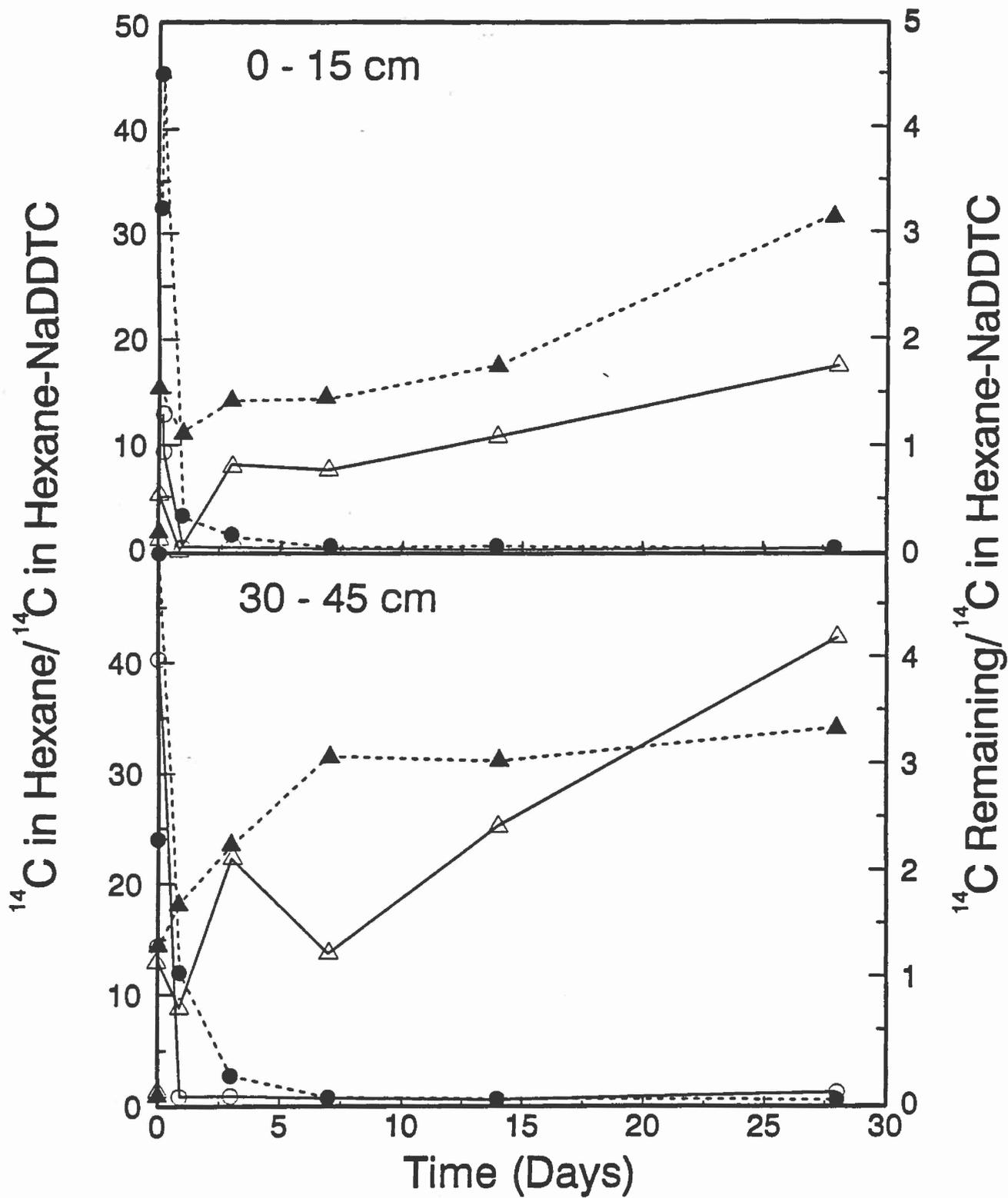
Figure 40. Distribution of ^{14}C in Hexane/^{14}C in Hexane-NaDDTC ($\bigcirc$,$\bullet$), and ^{14}C Remaining/^{14}C in Hexane-NaDDTC ($\triangle$,$\blacktriangle$) in Nonsterile (Open Symbols) and Autoclaved (Closed Symbols) Madison Soil.
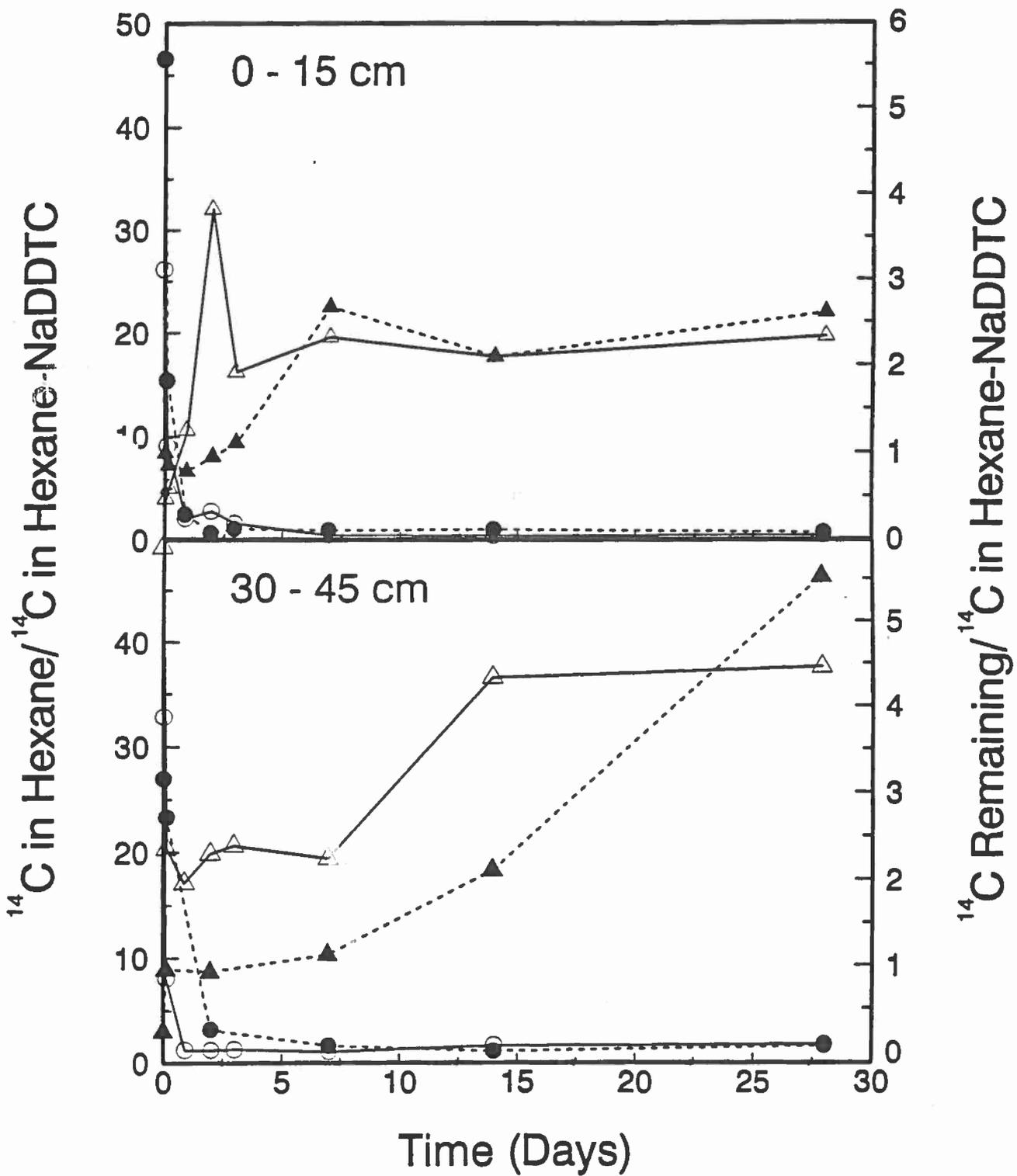
Figure 41. Distribution of ^{14}C in Hexane/^{14}C in Hexane-NaDDTC (○,●), and ^{14}C Remaining/^{14}C in Hexane-NaDDTC (△,▲) in Nonsterile (Open Symbols) and Autoclaved (Closed Symbols) Arredondo Soil.

Similar to the nonsterile and autoclaved surface samples of the Madison soil, ^{14}C-TREL was the only ionic ethyl lead species detected in the nonsterile and autoclaved subsurface samples (30 to 45 cm depth) of Madison soil during the entire 28 days of incubation, whereas, in addition to ^{14}C-TREL, ^{14}C-DEL also was detected in the nonsterile and autoclaved subsurface samples of Leon soil. The appearance of ^{14}C-DEL in the two samples, though brief, lasted longer than in the corresponding surface samples; ^{14}C-DEL was detected in the nonsterile and autoclaved subsurface samples between 1 and 23 hours and between 23 hours and 7 days, respectively. The levels of ^{14}C-DEL in the two samples declined progressively with time. The results of the formation of ^{14}C-TREL and ^{14}C-DEL in the subsurface samples confirmed the results in the surface samples that both biological and chemical degradation contributed to the formation and subsequent degradation of TREL and DEL. The longer appearance of DEL in the nonsterile and autoclaved subsurface samples probably was due to the low microbial activity and low organic matter content in the subsurface samples. It appears that the DEL in the soil rapidly degraded to inorganic Pb^{2+}, without the formation of monoethyl lead (MEL). MEL appears to be chemically unstable. This chemical never was detected in the environment (Radojevic and Harrison, 1987b; Rhue et al., 1992). GC-AAS confirmed the results of the TLC-autoradiographic analysis.

Both ^{14}C-TREL and ^{14}C-DEL were detected in the nonsterile surface Arredondo soil during the first 3 days of incubation. After 3 hours of incubation, the level of ^{14}C-DEL declined progressively with time. After 7 days, only ^{14}C-TREL was detected in the nonsterile surface sample. In the autoclaved surface sample, in addition to ^{14}C-TREL and ^{14}C-DEL, two unknown organolead products also were detected during the first 3 days of incubation. After 15 days, only ^{14}C-DEL was detected. In the nonsterile subsurface sample (30 to 45 cm depth), both ^{14}C-TREL and ^{14}C-DEL were detected during the first 3 days of incubation. After 15 days, only ^{14}C-DEL was detected, whereas in the autoclaved subsurface sample, in addition to ^{14}C-TREL and ^{14}C-DEL, two unknown ionic organolead metabolites also were detected during the first 7 days of incubation. After 14 days, only ^{14}C-DEL was detected. It was not clear why, after 14 or 15 days, ^{14}C-DEL but not ^{14}C-TREL was detected in the nonsterile subsurface sample and in the autoclaved surface and subsurface samples of Arredondo soil.

In conclusion, ^{14}C-TEL in nonsterile surface and subsurface soil samples of the three soils rapidly degraded to ^{14}C-TREL, ^{14}C-DEL, ^{14}CO$_2$, water-soluble nonlead ^{14}C-organic products, unknown volatile and/or gaseous ^{14}C-products, and bound residues. Both biological and chemical degradation were responsible for the degradation (with the exception of ^{14}CO$_2$ evolution), with chemical degradation being the major factor. The ^{14}C-TREL was the major ionic ethyl lead metabolite in nonsterile and autoclaved soils.

SECTION XI

CONCLUSIONS

The intent of this research has been to better understand the fate and transport of Pb alkyls and gasoline through the subsurface environment. In this section, we review our conclusions to the investigations. The conclusions are divided into seven categories according to the investigations.

A. FATE AND TRANSPORT OF TEL DURING THE IMMISCIBLE FLOW OF GASOLINE IN SOIL COLUMNS

Leaks and spills of leaded gasoline from storage tanks may contaminate soils and groundwater with the toxic tetraethyl lead (TEL) and its degradation products. TEL is very stable in gasoline but unstable in soil. It is subject to a series of sequential dealkylation steps. That is, TEL first degrades to TREL which in turn degrades to DEL, and finally to inorganic Pb^{+2}. Results show that TEL can be transported through the soil columns due to the migration of gasoline. Speciation of TREL and DEL from TEL found in the effluent and soil indicates that TEL is unstable during the immiscible flow of gasoline. NaCl solution may be used to displace a certain amount of gasoline that is mobile in the soil pores, but not the residual gasoline. Residual analysis shows that the remediation efficiency of the water-surfactant-cosurfactant (W/S/CoS) mixture for removing gasoline and total Pb in the Arredondo sand soil experiments was 100 percent, whereas in the Madison loam soil experiments, the remediation efficiency was 94.1 percent and 93.4 percent, respectively. Further study is needed to test the remediation efficiency of the W/S/CoS mixture in unsaturated and heterogeneous soil systems before a given solution is used at field scale.

B. DEGRADATION AND SORPTION OF TEL IN GASOLINE AND MICROEMULSION BY SOILS

The degradation and sorption of TEL in gasoline and a gasoline-in-water microemulsion by Arredondo sand soil have been studied. Results show that TEL is unstable in the soil and undergoes dealkylation to TREL. TREL is a highly water-soluble and toxic chemical. Leakage of leaded gasoline with TEL as a major Pb species may contaminate groundwater due to the dealkylation of TEL into water-soluble TREL and inorganic Pb^{+2}.

C. FATE AND TRANSPORT OF TREL IN WATER-SATURATED SOIL COLUMNS

Experiments have been conducted to investigate the fate and transport of TREL in water-saturated soil columns. Total Pb but not TREL was found in the effluent and soil samples at the end of the experiments, indicating that TREL is very unstable and degrades into other Pb species. A mass balance analysis shows that only 22 percent of the total Pb was washed out from the soil columns by the NaCl solution.

D. FLOW OF LEADED-GASOLINE-IN-WATER MICROEMULSION THROUGH WATER-SATURATED SOIL COLUMNS

Hydrocarbon contamination of soil and groundwater is widespread and is of great public concern. Although the use of surfactant as a remediation technique to clean up hydrocarbons from soil has shown a significant potential for application, one of the most important problems that has been ignored is the formation of emulsions due to the use of surfactants. The flow of a macroemulsion has been shown to

inhibit the transport of hydrocarbons through soil. In contrast, the flow of a microemulsion enhances the transport of gasoline and Pb through soil, as reported in this study. A major factor causing a difference in flow behavior between macroemulsions and microemulsions is the size of hydrocarbon (or oil) droplets dispersed in the aqueous phase. The size of hydrocarbon droplets in macroemulsions ranges in diameter from 1 to 10 μm. In microemulsions, the size ranges from 0.01 to 0.1 μm, which is comparable to the soil pore size, and thereby droplet clogging by soil pores is greatly minimized.

A macroemulsion may be produced if a single surfactant component is used to wash hydrocarbons from soil, resulting in low remedial efficiency due to the pore clogging by the large size of the hydrocarbon droplets. Our study suggests that a successful and cost-effective remediation of hydrocarbons from soil can be achieved if a mixture of W/S/CoS mixture is used to produce a microemulsion. Further study is required to test the formation and flow of microemulsions in unsaturated and heterogeneous soil columns before a given solution is used at field scale.

E. A METHOD FOR MEASURING TETRAETHYL LEAD AND TOTAL LEAD IN ORGANIC SOLVENTS

The measurement of TEL and total Pb contents in organic solvent by current techniques is time-consuming and expensive. A simple technique called the Iodine Monochloride (ICl) Digestion Method for the determination of TEL and total Pb is introduced here. Samples containing TEL first were converted to Pb^{+2} by 0.1 M ICl solution, then the total Pb content was measured using atomic absorption spectrophotometry (AAS). Finally, the concentration of TEL was estimated through back calculation according to the molecular fraction of Pb in TEL. This method seems to be an efficient and cost-effective approach compared to current methods. It has a recovery rate ranging from 92.7 to 102.3 percent and a coefficient of variability (CV) ranging from 1.02 to 1.9 percent for all measurements in this experiment. Such a high recovery rate and low CV lead to a conclusion that the ICl Digestion Method can be applied to measure TEL as well as total Pb contents in organic solvents.

F. DEGRADATION AND METABOLISM OF TEL IN SURFACE AND SUBSURFACE SOILS

Although TEL in gasoline and hydrocarbon solvents (e.g., hexane and benzene) is very stable under dark conditions, TEL in nonsterile and autoclaved surface and subsurface soils rapidly degrades. Both biological and chemical degradation are responsible for the degradation of TEL in surface and subsurface soils, with chemical degradation being the major factor. It is estimated that biological degradation could be responsible for up to 20 percent of TEL degradation in nonsterile soils. Degradation of TEL in surface soils generally is more rapid than in subsurface soils. Ionic TREL was the major organolead degradation product detected in nonsterile and autoclaved soils, with DEL being the minor degradation organolead product. In addition, a small fraction of TEL (up to 7.7 percent in 28 days) in nonsterile soils was mineralized to CO_2. Unknown water-soluble nonlead organic products in small amounts also were formed in nonsterile and autoclaved soils. Less than 50 percent of the applied ^{14}C-TEL in nonsterile and autoclaved soils could be accounted for. Thus, it is likely that unknown volatile and/or gaseous products were formed and could be the major degradation products of TEL in soils.

G. DEGRADATION AND METABOLISM OF TREL AND DEL IN SURFACE AND SUBSURFACE SOILS

Ionic TREL and DEL rapidly degraded in nonsterile and autoclaved surface and subsurface soils, and the two chemicals generally degraded more rapidly in surface soil than in subsurface soil. Both

biological and chemical degradation were responsible for the degradation of TREL and DEL, with chemical degradation being the major factor. Mineralization of TREL and DEL occurred only in the nonsterile surface and subsurface soils. Up to 16 percent of the applied ^{14}C-TREL and up to 20 percent of the applied ^{14}C-DEL were mineralized to ^{14}CO$_2$ in 31 and 28 days, respectively. DEL was the only organolead product detected in the TREL-treated soils. No organolead products were detected in the DEL-treated soils. Apparently DEL degraded directly to Pb^{2+}. The mass balance for TREL and DEL in soils was better than for TEL, yet 10 to 50 percent of applied TREL or DEL could not be accounted for. Therefore, unknown volatile and/or gaseous products also could be formed.

SECTION XII

RECOMMENDATIONS

Based on our investigations of the fate, transport, and remediation of Pb alkyls and gasoline through soils, five categories of recommendations are offered for future research into the transport and remediation of heavy metals and non-aqueous-phase liquids (NAPLs). These five categories are discussed below.

A. INVESTIGATION OF PROCESSES IN HETEROGENEOUS SOIL SYSTEMS

We have three recommendations:

1. Laboratory studies should be conducted to explore the fate and transport of heavy metals and NAPLs in heterogeneous and layering soil systems.

2. Research should be initiated on the long-term abiotic and biotic transformations of residual NAPLs. These transformations would affect the mobilization, composition, and ability of NAPLs to dissolve into groundwater.

3. Soil and NAPL interactions should be examined at laboratory scale to provide an assessment of the importance of wettability and permeability of NAPLs.

B. APPLICATION OF MICROEMULSION TECHNIQUE FOR REMOVING NAPLS AND HEAVY METALS

The use of the microemulsion technique to remediate NAPLs and heavy metals from contaminated soils has high potential in applications as demonstrated in this study. Further studies should be devoted to investigating the formation, stability, and flow of microemulsions in heterogeneous soil systems at both laboratory and field scale.

C. MODELING THE REMEDIATION EFFICIENCY OF CONTAMINANTS FROM VADOSE ZONE AND GROUNDWATER USING MICROEMULSION TECHNIQUE

Research should be directed toward the development and application of a mathematical model to guide the contaminant remediation practices. This model should provide information about the stability and flow of the NAPL-in-water microemulsion associated with the optimized use of surfactant and cosurfactant for cost-effective application.

D. USE OF MICROORGANISMS TO DETOXIFY TEL AND/OR TREL AND DEL IN LEADED GASOLINE-CONTAMINATED SOILS AND GROUNDWATER

Bioremediation is an emerging technique for safe and economical removal of toxic contaminants from soils, sediments, surface water, groundwater, and wastes. Microorganisms capable of degrading TEL and/or ionic TREL and DEL should be isolated from subsurface soils, sediments, and groundwater for use in decontaminating TEL in leaded gasoline-contaminated sites and TEL-contaminated sites.

E. DETERMINATION OF DEGRADATION RATES OF TEL AND IONIC TREL AND DEL IN LEADED GASOLINE-CONTAMINATED SOILS AND GROUNDWATER

Degradation rates of TEL and ionic TREL and DEL in leaded gasoline-contaminated vadose zone soils and groundwater should be determined, especially in conjunction with the degradation of gasoline (hydrocarbons). TEL in gasoline-contaminated soil mainly remains in the hydrocarbon phase, which protects TEL from chemical and biological degradation. Both aerobic and anaerobic degradation need to be investigated.

SECTION XIII

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