Revised

Technical Memo for Laboratory Microcosm and Column Studies to Investigate In Situ Treatment of Perchlorate-Impacted (Source Area) Groundwater

Lockheed Martin Corporation, Beaumont Site 2
Beaumont, California

Prepared for:

LOCKHEED MARTIN

TETRA TECH

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TC# 22289-0202 / July 2010

RESPONSE TO COMMENTS, TECHNICAL MEMO FOR LABORATORY MICROCOSM AND COLUMN STUDIES TO INVESTIGATE IN-SITU TREATMENT OF PERCHLORATE-IMPACTED (SOURCE AREA) GROUNDWATER AND SOIL
LOCKHEED MARTIN CORPORATION, BEAUMONT SITE 2
TETRA TECH, INC.
APRIL 2010

Comments from Daniel Zogaib, DTSC		
Comment	**Response**	**Proposed Action**
Comment 1. Section 2.3, Analytical Procedures: Besides the testing conducted by the UCR laboratory, please describe the other parameters and analytical methods (e.g., anions, cations, and metals) listed on Tables 8 and 9, and the laboratory that performed these analyses.	Soil and groundwater samples were analyzed by Emax Laboratories of Torrance, California, a California DPH-certified laboratory. The laboratory reports were previously submitted to DTSC in Attachment 1 of the *Technical Memo for Laboratory Microcosm and Column Studies to Investigate Biobarrier Application for Treatment of Perchlorate-Impacted Groundwater* (Tetra Tech and UCR, 2009).	Tables 8 and 9 will be revised to identify Emax as the laboratory and to reference the report where these results were previously submitted.
Comment 2. Section 2.4, QA/QC: Please elaborate on the procedures used in the column studies to ensure test reproducibility (e.g., multiple samples collected or columns sacrificed, and possible major sampling uncertainties associated with the microcosm and column studies.	Analytical duplicate and matrix spike samples were analyzed at a rate of 1 per 20 samples, as described in Section 2.4 of the text. All amended and control microcosms were run in triplicate, as indicated in Section 2.4 of the text. Running duplicate column tests was not included in the approved work plan, and was therefore not performed as part of this study. However, the data and trends observed during the column tests are highly consistent, which is indicative of the validity of the results. Procedures used to minimize heterogeneity in the as-received soil samples included screening out material greater than ¼-inch and homogenizing the soil prior to conducting the microcosm and column tests. Processed soil was stored at 3 °C prior to use. Soil samples from the microcosms and columns were collected sacrificially by emptying the microcosm or column, homogenizing the soil, and randomly selecting a representative 10 gram aliquot for analysis.	Procedures used for homogenizing and handling of the as-received soil, and for collecting soil samples from the microcosms and columns will be added to Sections 2.1 and 2.2 of the text, respectively

Comments from Daniel Zogaib, DTSC		
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Comment 3. Section 3.2, Source Area Vadose Zone Soil: Please clarify the intent of the two soil samples listed on Table 9; it is not clear whether the aquifer soil sample was used in the studies. On Table 9, please also include the analytical results of the new source area vadose zone soil (high perchlorate and organic content) used in the column testing for completeness.	The aquifer soil from Table 9 was used in both the source area groundwater microcosm and column tests. The vadose zone soil from Table 9 was used in the vadose zone soil microcosm tests. Additional vadose zone soil collected from boring K-54-SB116 during the Dynamic Site Investigation (Tetra Tech, 2010) was used for the vadose zone column tests.	Table 9 will be revised to include the analytical data for the additional soil samples from boring K-54-SB116. Electronic copies of the E.S. Babcock & Sons laboratory reports for these samples will be provided as an appendix.
Comment 4. Section 4.1.2, Groundwater Column Testing: While the general conclusion that EOS as a soil amendment may have significant advantages over glycerin for treating groundwater appears reasonable, additional testing should be performed to determine the optimal dose of EOS-amended soil in field conditions. Figures 8 and 9 indicate that the EOS-amended column might be near the "break-through" point at the end of the 120-day test.	Evaluating optimal amendment dosages for the groundwater column tests was not included in the approved work plan (Tetra Tech, 2008), and was therefore not performed as part of this study. The column tests in this study were not specifically designed to define breakthrough because field conditions are, in general, very different from laboratory conditions. These differences include the following: a) In the column tests, substrate was uniformly mixed with soil. In a deep hot-spot treatment or well-type barrier application, mixing the substrate directly into the aquifer material may not be possible. b) The soil used in the column tests was screened and recompacted per ASTM procedures, a process which disrupts the soil structure. Natural soils under field conditions are expected to exhibit behavior which may differ from the laboratory columns. c) The approach velocity used in this study (and in most studies of this type) is at the upper end of the groundwater velocity range, in order to maximize the number of pore volumes flushed through the columns over the experiment time frame. In the field, groundwater	No changes to text are proposed.

Comments from Daniel Zogaib, DTSC		
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	velocities could be considerably lower, which may result in different substrate kinetics. d) In general, field conditions are characterized by large-scale heterogeneities that are difficult or impossible to replicate in bench-scale laboratory tests, but which may be controlling factors in pilot-scale or full-scale implementation. In general, the experience of most practitioners has been that the information obtained in laboratory column tests is useful for evaluating conditions at a specific applied dosage that would result in complete perchlorate removal. This goal has been achieved by the column tests. The exact response, breakthrough, and replenishment needs are generally better ascertained in a pilot test, because of laboratory limitations and the significant differences between laboratory and field conditions as described above. The half-life of EOS in the subsurface is generally in the order of months, will be assessed in the field through a pilot study.	
Comment 5. Section 4.2.2, Vadose Zone Column Testing: DTSC concurs that the recirculation treatment is promising for treating source area soil up to 100 mg/kg, additional testing is needed to confirm perchlorate reduction stimulated by natural organic contents and the minimum TOC level (and other factors) necessary for such application to be effective in the field.	We concur that additional evaluation of MNA, including verification of perchlorate reduction using naturally-occurring organic carbon as an electron donor, should be conducted at the site, and LMC will be proposing additional field studies. Such work is out of the scope of the column testing work plan.	No changes to text are proposed.
Comment 6. DTSC believes that for optimal design of the pilot groundwater treatment system more	Evaluating substrate kinetics was not included in the approved work plan (Tetra Tech, 2008), and was therefore not performed as	A copy of the glycerine half-life calculation is attached. No

Comments from Daniel Zogaib, DTSC		
Comment	**Response**	**Proposed Action**
information is needed regarding the kinetics of the substrate. Additional testing should be conducted to determine the kinetics and thus the time to "break-through" point as indicated in comment 4 above.	part of this study. In practice, glycerin is known to have a very short half-life (on the order of minutes to hours), whereas EOS is known to have a much longer half-life (on the order of months to several months). In response to DTSC's comment, we have estimated the half life of glycerine substrate based on the column test results. The estimated half-life (0.2 days) is within the expected range. A copy of the calculation is provided as an attachment. As discussed in the response to Comment 4 above, we do not believe that quantifying substrate kinetics based on the laboratory studies will provide useful design data. The relevant data will be obtained during a field pilot test.	changes to text are proposed.

Project: Lockheed Martin Corporation - Beaumont Site 2 **Bench-Scale Treatability Studies**
Task: Glycerin Half Life Calculation

Objective:
The objective of this calculation is to find out the half life of glycerin in the column study conducted by University of California, Riverside for the Lockheed Martin Corporation Beaumont Site 2 to investigate in situ treatment of perchlorate.

Data Source:
This calculation is based on the data presented in Figure 10. Perchlorate Reduction in Source Area Glycerin-Amended Columns in *Draft Technical Memo For Laboratory Microcosm and Column Studies to Investigate In Situ Treatment of Perchlorate-Impacted (Source Area) Groundwater and Soil*, Lockheed Martin Corporation Beaumont Site 2, prepared by Tetra Tech, Inc. and University of California, Riverside, September 3, 2009. (referred to as "The Memo" in this calculation.)

Plug Flow Equation
The flow in a column can be viewed as plug flow and the consumption of glycerin can be considered as first order reaction. The change of glycerin concentration overtime equals to the difference between influent and effluent glycerin concentration minus glycerin degradation. This can be expressed as the equation below:

$$\frac{d \cdot C}{dt} \cdot V_{Column} = F_{in} C_{in} - F_{out} C_{out} - \int kC \, dV_{Column} \qquad (1)$$

C = Concentration of glycerin in the column at time t
V_{Column} = Volumn of the Column
t = Time
F_{in} = Influent flow rate
F_{out} = Effluent flow rate
C_{in} = Influent glycerin concentration
C_{out} = Effluent glycerin concentration
k = First order reaction rate constant

At steady state, $\frac{d \cdot C}{dt} \cdot V_{Column} = 0$ and $F_{in} = F_{out}$

The above equation (1) can be simplified and integrated to:

$$0 = F_{in}\left(C_{in} - C_{out}\right) - kCV_{Column}$$

Based on Chemical Engineers' Handbook (5th Edition) by Robert H. Perry and Cecil H. Chilton, McGraw-Hill, 1973, Table 4-11 on page 4-23, for a plug flow with first order reaction:

$$\theta = \frac{1}{k \cdot \left(C_{G_0}\right)^{(n-1)}} \cdot \int_{X_{G_0}}^{X_G} \frac{1}{\left(1 - X_G\right)} dX_G \qquad (2)$$

θ = Hydraulic Residence Time (HRT)

X_G = Percent conversion of glycerin = $\left(1 - \frac{C_G}{C_{G_0}}\right)$

C_G = Glycerin concentration in the column
C_{G0}= Influent glycerin concentration
n = 1 for first order reaction

Above equation (2) can be simplified and integrated to:

$$\theta = \frac{-1}{k} \ln\left(1 - X_G\right) \Big|_{X_0}^{X_G}$$

$$\theta = \frac{1}{k} \ln\left(\frac{1 - X_0}{1 - X_G}\right)$$

Given X_0 =0, $\theta = \frac{1}{k} \ln\left(\frac{1}{1 - X_G}\right)$

Based on the defination of θ as HRT, $\theta := \frac{L}{\nu}$

ν = velocity; L = length of column

$$\nu := \frac{Q}{A\varepsilon}$$

Q = Flow Rate
A = Column cross section area
ε = Porosity

So, $\theta := \frac{LA\varepsilon}{Q}$

Therefore, $\frac{LA\varepsilon K}{Q} = \cdot \ln\left(\frac{1}{1 - X_G}\right)$ (3)

Glycerin consumption rate, K, is a function of $\ln\left(\frac{1}{1 - X_G}\right)$ and $\frac{LA\varepsilon}{Q}$

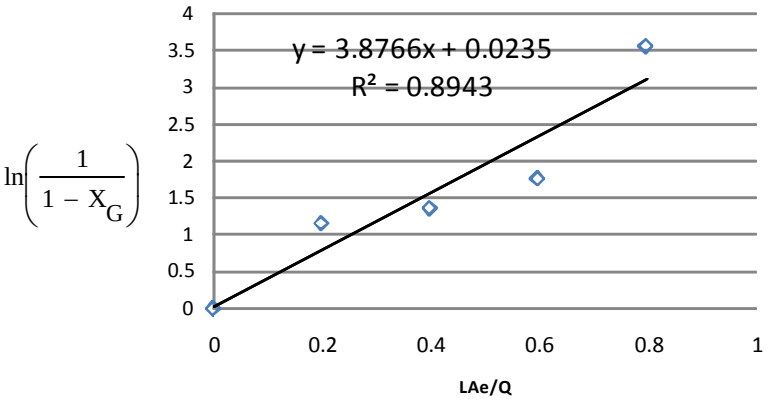
Data Interpretation:
Based on the data presented in Figure 10. in the Memo,

- When the influent concentration of glycerin was 60 mg/L, only 10-40% perchlorate was removed, indicating insufficient glycerin;
- When the influent concentration of glycerin was 300 mg/L, complete perchlorate removal was reached rapidly, indicating residual glycerin;
- So, the minimum glycerin concentration required to sustain complete perchlroate removal is between 60-300 mg/L.
- When the influent concentration of glycerin was 120 mg/L, complete perchlroate removal was reached with some flucturation by the end of the study.
- Therefore, with available data, it is reasonable to use data from 120 mg/L influent glycerin to conduct kinetics calculation.

Kinetics Calculation:
As shown in Figure 10 in the Memo, with 120 mg/L influent glycerin and 70 mg/L perchlorate, the column reached steady state at about 80 days. Therefore, the 80-day data will be used to calculate the first reaction rate. The glycerin consumption rate was assumed to be equal to the perchlroate removal rate.

	Column Length (in)				
	0	6	12	18	24
$C_{perchlorate}$	70	22	18	12	2
$X_{perchlorate}$	0%	69%	74%	83%	97%
$X_{glycerin}$	0%	69%	74%	83%	97%
$\ln(1/(1-X_G))$	0	1.157453	1.358123	1.763589	3.555348
L(ft)	0	0.5	1	1.5	2
LAe/Q (d)	0	0.199064	0.398127	0.597191	0.796254

Plot $\ln\left(\frac{1}{1-X_G}\right)$ as y-axis and $\frac{LA\varepsilon}{Q}$ as x-axis, we can obtain K from the slope:



k = 3.8766/day

Half-life = $\frac{\ln\left(\frac{1}{1-0.5}\right)}{k}$ = $\frac{\ln(2)}{3.8766} = 0.179$ day

Conclusion:

- The half life of glycerin in the column study is 0.2 days.
- This is a very fast half life. The reaction is limited by stoichiometry and the field condition.
- Since this half life is calculated based on 80 days data where the perchlorate concentration in 6" and 12" columns were still reducing, the real half life will be even shorter than this calculated value.
- This half life will have little practical value on guiding treatment design.
- The stoichiometry and hydraulics will drive the treatment design instead.

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LOCKHEED MARTIN

July 15, 2010

Mr. Daniel Zogaib
Southern California Cleanup Operations
Department of Toxic Substances Control
5796 Corporate Avenue
Cypress, CA 90630

Subject: Submittal of the Revised *Technical Memo for Laboratory Microcosm and Column Studies to Investigate In Situ Treatment of Perchlorate-Impacted (Source Area) Groundwater and Soil, Lockheed Martin Corporation, Beaumont Site 2, Beaumont, California*

Dear Mr. Zogaib:

Please find enclosed one hard copy and two CDs containing Adobe pdf files of the revised *Technical Memo for Laboratory Microcosm and Column Studies to Investigate In Situ Treatment of Perchlorate-Impacted (Source Area) Groundwater and Soil, Lockheed Martin Corporation, Beaumont Site 2, Beaumont, Califomia*, revised in accordance with responses to DTSC comments submitted on April 20, 2010 and accepted by DTSC on June 23, 2010.

If you have any questions or comments regarding this submittal, please contact me at 408.756.9595 or denise.kato@lmco.com.

Sincerely,

Denise Kato
Remediation Analyst Senior Staff

Enclosure

Copy w/Enclosure:
Gene Matsushita, LMC (1 pdf and 1 hard copy)
John Eisenbeis, Ph.D, Camp, Dresser, McKee (1 pdf)
Thomas J. Villeneuve, Tetra Tech, Inc. (1 pdf and 1 hard copy)
Hans Kernkamp, Riverside County (1 pdf)

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Technical Memo for Laboratory Microcosm and Column Studies to Investigate In Situ Treatment of Perchlorate-Impacted (Source Area) Groundwater and Soil, Lockheed Martin Corporation Beaumont Site 2, Beaumont, California

July 2010
T#: 22289-0202

Prepared for:
Lockheed Martin Corporation
Burbank, California

Prepared by:
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ABBREVIATIONS AND ACRONYMS

%	percent
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µs	microsiemens
ASTM	American Society for Testing and Materials
cm	centimeters
DI	deionized
EOS	emulsified oil substrate
EPA	United States Environmental Protection Agency
ft/d	feet per day
g	grams
g/L	grams per liter
HFCS	high fructose corn syrup
LPG/H_2/CO_2	liquefied petroleum gas/hydrogen gas/carbon dioxide
L/d	liters per day
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mL	milliliter
mL/min	milliliter per minute
Site	Lockheed Martin Corporation's Beaumont Site 2
t	time
TM	Technical Memo
TOC	total organic carbon
UCR	University of California, Riverside
v/v	volume-to-volume
w/w	weight-to-weight

1.0 INTRODUCTION

This Technical Memo (TM) presents a summary of the results of the laboratory microcosm and column studies performed at the University of California, Riverside (UCR) to investigate applications for treatment of perchlorate-impacted source area groundwater and vadose zone soil at Lockheed Martin Corporation's Beaumont Site 2 (herein referred to as the "Site"). An overview of the experimental procedures used to test potentially applicable amendments for effectiveness in stimulating biological reduction of perchlorate is also provided within this report. The results of this study should be considered when making preliminary recommendations regarding potential treatment possibilities for saturated zone groundwater and vadose zone soils at the Site.

In addition to the information summarized in this report, other studies were undertaken to test potential amendments for treating perchlorate in groundwater near the property boundary in a biobarrier application. Results of these additional studies were previously submitted to the California Department of Toxic Substances Control in January 26, 2009 [1]. A summary of the drilling and sampling program that collected and tested the media used as part of both that study and this study was included as an appendix to the earlier study report. The results are included and discussed herein either as part of this TM, or by reference.

1.1 SUMMARY OF APPROACH

For this laboratory study, the suitability of several pre-selected electron donor amendments were assessed for effectiveness in stimulating biological perchlorate reduction and treatment of both groundwater in the source area aquifer matrix as well as the source area vadose zone soil. These tests included both microcosms and column work for both media (groundwater and vadose zone soil). Microcosms were used to screen selected amendments in terms of effectiveness, and to gain a general understanding of the potential rate of treatment. In addition, the effects of nutrient addition (groundwater and soils) and moisture content (soils) were assessed.

Following microcosm testing, column testing was conducted for both the groundwater and soils to provide a preliminary assessment of likely field performance. Source area groundwater and aquifer material collected from the Site were used for the groundwater columns. Vadose zone soil collected from the Site and local (Riverside) dechlorinated tap water with added amendments were used for the vadose zone soil columns.

For the groundwater column study, source area groundwater was passed through sets of columns of differing lengths to gain an understanding of the rate of perchlorate removal and develop breakthrough curves as a function of length of operation. For the vadose zone column study, amended tap water was

applied to soil columns to assess two simplified application scenarios: 1) batch flooding to simulate batch application of the soluble donor in a wet/dry cycling approach and 2) continuous wetting to simulate recirculation of the leachate through the vadose zone. These experiments provided a basic understanding of how perchlorate treatment is affected by amendment/moisture application to the vadose zone and the time required to achieve effective perchlorate reduction.

1.2 OBJECTIVES

The overall goal of the source area groundwater and vadose zone microcosm tests was to determine the most effective of the selected amendments in stimulating perchlorate bioreduction in the groundwater and vadose zone soil collected from the Site. Specific information sought in the microcosm testing included:

- Assessment of various amendments in terms of effectiveness in stimulating biological perchlorate reduction; and
- The general rate of perchlorate bioreduction.

The goal of the source area groundwater column tests was to:

- Compare the individual treatment performances of two selected amendments to the source area aquifer soil.

Based on results obtained from the vadose zone microcosm tests, significant perchlorate degradation was not observed under unsaturated conditions at moisture contents of 15% and 25% with any of the tested amendments. However, in a supplemental test, it was determined that perchlorate biodegradation was achievable under saturated conditions (using sodium acetate as an amendment). These results are presented in Section 4.0 of this TM. Thus, the focus of the vadose zone column test was to:

Determine the likely performance of two application scenarios for two selected amendments that were successful in stimulating perchlorate biodegradation in the earlier biobarrier groundwater treatment and the source area groundwater treatment;

- Generate comparative data to help elucidate which of the two substrates may be more preferable in a full-scale system; and
- Determine relative kinetics of perchlorate removal for each substrate.

Because the amendments themselves degrade over time, long-term treatment performance (beyond the initial installation period) was not determined in any of these relatively short tests.

2.0 SUMMARY OF METHODOLOGY

Source area groundwater as well as aquifer and vadose zone soil samples were collected from the Site and sent to UCR for the study. Details of the sampling and analytical procedures and results were summarized in a previous report [1]. Data relevant to the bench-scale tests are presented and summarized in the following sections.

2.1 MICROCOSM PROCEDURES AND METHODS

Microcosm experiments were conducted to evaluate potential amendments for treatment of source area groundwater and vadose zone soil. Prior to conducting the microcosm experiments, the as-received soil was homogenized by screening out material greater than ¼-inch, followed by hand-mixing on a tarp. The processed soil was stored in a cold room at 3 °C prior to use. Experiments were conducted both with and without nutrient addition. The procedures and methods for each experiment are outlined below.

2.1.1 Source Area Groundwater

Microcosm experiments were used to evaluate five amendments for source area groundwater treatment, both with and without nutrient (diammonium phosphate) addition. These amendments are summarized in Table 1.

Table 1
Electron Donor Amendments used in Source Area Microcosm Tests

Material	Source
Emulsified Oil Substrate (EOS 598)	EOS Remediation, Inc.
Glycerin	US Glycerin
High fructose corn syrup (HFCS 42)	Sweetener Products Company
Acetic acid	Fisher Scientific
Sodium acetate	Fisher Scientific

For the source microcosms, Emulsified Oil Substrate (EOS 598), high fructose corn syrup (HFCS 42), glycerin, acetic acid, and sodium acetate were mixed with site soil and then placed into the microcosms. These amendments were added at dosages as listed in Table 2. Groundwater from the contaminant source area was added to the microcosm in a solid/groundwater ratio of 1:4 (weight-to-weight [w/w]) in 250 milliliters (mL) glass serum bottles with a minimal headspace. The bottles were sealed with a septum cap that allowed for withdrawal of solution from the bottle. The microcosms were mixed by inversion three times per day to promote mixing of the solid substrate with the groundwater.

Microcosms containing as-collected soil/groundwater [1:4 (w/w)] with no amendments were utilized as controls to quantify potential perchlorate degradation/loss from natural attenuation and other mechanisms.

All amended and control microcosms were run in triplicate. Table 2 provides a summary of the microcosm test conditions.

Table 2
Summary of Source Area Microcosm Test Conditions

Ground-water source	Soil mass + ground -water volume	Soil only control	EOS[a]	Glycerin	High fructose corn syrup	Acetic acid	Sodium acetate
Aquifer underlying source area High perchlorate concentration	50 g soil in 200 mL of GW	Aquifer soil under-lying source area	EOS added to GW at 0.1 & 0.5% (v/v). For nutrient amended microcosms, 1 g/L of diammonium phosphate was added to the solution.	Glycerin added to GW at 0.1 & 0.5% (v/v). For nutrient amended microcosms, 1 g/L of diammonium phosphate was added to the solution.	High fructose corn syrup added to GW at 0.1 & 0.5% (v/v). For nutrient amended microcosms 1 g/L of diammonium phosphate was added to the solution.	Acetic acid added to GW at 280 and 1,440 mg/L. For nutrient amended microcosms, 1 g/L of diammonium phosphate was added to the solution.	Sodium acetate added to GW at 1000 and 5000 mg/L. For nutrient amended microcosms, 1 g/L of diammonium phosphate was added to the solution.

Notes:

a 0.1percent emulsified oil substrate solution is recommended by the manufacturer for laboratory testing.
EOS – emulsified oil substrate
g – grams
mL – milliliters
GW – groundwater
% – percent
v/v – volume-to-volume
g/L – gram per liter
mg/L– milligram per liter

Water samples were withdrawn using a syringe and filter [0.45 micrometer pore size]. Perchlorate, nitrate, and total organic carbon (TOC) were measured periodically over an 18-day or shorter period. This included time (t) = 0 (immediately following addition of amendments) and four additional time points for both perchlorate and nitrate. Specific analytical methods are provided in a later section. TOC was measured at t = 0 and the final sampling event.

Concomitant with perchlorate reduction, remedial efforts may alter site geochemistry, which could lead to mobilization of certain naturally occurring inorganic constituents such as arsenic, iron, and manganese. This may have negative implications with respect to general groundwater quality in the immediate

vicinity of treatment during field applications. Other parameters to assess general geochemistry and potential metal mobilization were also measured.

2.1.2 Vadose Zone Soil

Microcosm experiments were used to evaluate five amendments for vadose zone soil treatment. These amendments are summarized in Table 3.

Table 3
Electron Donor Amendments used in Vadose Zone Microcosm Tests.

Material	Source
Glycerin	U.S. Glycerin
High Fructose Corn Syrup	Sweetener Products Company
Sodium Acetate	Fisher Scientific
Ethyl Acetate	Fisher Scientific
Liquefied Petroleum Gas/Hydrogen Gas/Carbon Dioxide	Local supplier/Praxair/Praxair

The vadose zone soil microcosm testing assessed the impact of amendments, moisture content, amendment concentrations, and the addition of a nutrient (diammonium phosphate) on perchlorate biodegradation.

For the microcosm tests, the as-received vadose zone soil was deemed to be unrepresentative of the established or expected perchlorate contamination levels. Therefore, perchlorate was added to the concentrated amendment solution as needed to bring the soil perchlorate concentration to a level of approximately 4,000 micrograms per kilogram (µg/kg).

In addition to spiking with perchlorate, the soil moisture content was raised to 15 percent (%) using dechlorinated tap water. For the soluble amendments, substrate was added to the tap water to bring the amendment/soil ratio to the desired level. The gaseous electron donors, ethyl acetate and liquefied petroleum gas/hydrogen gas/carbon dioxide mixture were introduced into the headspace after sealing the microcosm. The ethyl acetate was allowed to evaporate and the flask was shaken 30 seconds to ensure homogeneous distribution of ethyl acetate. For the control microcosms, no amendments were added. A summary of the test conditions for the vadose zone microcosms is given in Table 4. Only one dosage rate was tested for the gaseous donors.

For the vadose zone microcosms, each 250-mL microcosm bottle contained 200 grams (g) of amended soil and was sealed using air-tight caps with septa. Headspace was purged with nitrogen for the soluble amendments or the gaseous donor. The microcosms were then incubated at room temperature. For microcosms containing ethyl acetate, 60 microliters of ethyl acetate was injected directly through the

septum onto the inside surface of the glass bottle. The microcosms were then incubated at room temperature. At designated times, a set of microcosms (three per each amendment and control) was opened and sacrificially sampled to determine perchlorate degradation after incubation for a selected period of time. Soil samples were collected by emptying the microcosm, homogenizing the soil by hand mixing, and randomly selecting a representative 10 gram aliquot for analysis.

Table 4
Summary of the Vadose Zone Microcosm Test Conditions, 15% Moisture

Soil source	Amendment					
	Soil only control	**Glycerin**	**High fructose corn syrup**	**Sodium acetate**	**Ethyl acetate**	**LPG/H_2/CO_2**
Vadose zone soil from source area High perchlorate concentration	Soil with DI water added to test field moisture content.	Glycerin added to soil at 100 and 500 mg/kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammoniu m phosphate will be added to the solution.	High fructose corn syrup added to soil at 100 and 500 mg/ kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammonium phosphate will be added to the solution.	Sodium acetate added to DI water soil at 100 and 500 mg/ kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammonium phosphate will be added to the solution.	Soil with DI water added to the target moisture content. Ethyl acetate (60 microliters) was added and evaporated in the headspace of the microcosm.	Soil with DI water added to the target moisture content. A mixture of LPG/H_2/CO_2 (80%/10%/10 %) will be added to fill the void & headspace of the microcosm.

Notes:

DI – deionized water
mg/kg– milligram per kilogram
g/L – gram per liter
LPG/H_2/CO_2 – liquefied petroleum gas/hydrogen gas/carbon dioxide
% – percent

Because of the lack of significant perchlorate degradation during the 15% moisture content microcosm tests, a second set of vadose zone soil microcosms was set up with an increased moisture content of 25%. At 15% moisture content, the vadose soil can be qualitatively described as being somewhat cohesive and crumbly. At 25% moisture content, the vadose zone soil was found to be cohesive and had the characteristics of modeling clay (able to hold a definitive shape while being molded by hand). Therefore, at 25% moisture content only, soluble amendments were tested in microcosms – glycerin, sodium acetate, and HFCS. These amendments were added to the water used to increase the soil moisture content. A summary of the test conditions for the 25% moisture content microcosms is provided in Table 5.

A third vadose zone microcosm test was conducted due to lack of perchlorate degradation at the 25% moisture content condition. To check whether perchlorate degrading bacteria were present and could be stimulated, the third microcosm test was conducted by saturating the vadose zone soil using only sodium acetate as the electron donor at an amendment dosage of 500 milligrams per kilogram (mg/kg), both with and without nutrient addition. At the end of the microcosm study period, the final microcosms were analyzed for pH, nitrate, nitrite, and TOC.

Table 5
Summary of the Vadose Zone Microcosm Test Conditions, 25% Moisture

Soil source	Amendment			
	Soil only control	**Glycerin**	**High fructose corn syrup**	**Sodium acetate**
Soil from source area High perchlorate concentration	Soil with DI water added to test field moisture content.	Glycerin added to soil at 100 and 500 mg/kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammonium phosphate will be added to the solution.	High fructose corn syrup added to soil at 100 and 500 mg/ kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammonium phosphate will be added to the solution.	Sodium acetate added to DI water soil at 100 and 500 mg/ kg soil at the target field moisture content. For nutrient amended microcosms 1 g/L of diammonium phosphate will be added to the solution.

Notes:
DI – deionized water
mg/kg– milligram per kilogram
g/L – gram per liter

2.2 COLUMN PROCEDURES AND METHODS

American Society for Testing and Materials (ASTM) Test Method D 4874-95 (Standard Test Method for Leaching Solid Material in a Column Apparatus) was used as a general guide for the column tests. The method is a standard laboratory procedure for generating aqueous leachate from materials using a column apparatus. The method provides for the passage of an aqueous fluid through porous media. Analysis of column effluent provides information on the leaching characteristics of material under the conditions used in the test. It is intended that the sample used in the procedure be physically, chemically, and biologically representative of the material from the Site. While not intended to be the sole basis for engineering design, the method is expected to produce results that can be used, along with other information, as design

input for the full-scale treatment system. A detailed discussion regarding the methodology can be found in [2].

Prior to conducting the column tests, the as-received soil samples were homogenized by screening out material greater than ¼-inch, followed by hand-mixing on a tarp. The processed soil was stored in a cold room at 3 °C prior to use.

2.2.1 Source Area Groundwater

Three sets of four parallel 2-inch (5.1 centimeters [cm]) diameter polyvinyl chloride pipe columns were constructed in lengths of 6 inches (15 cm), 12 inches (30 cm), 18 inches (45 cm) and 24 inches (60 cm). The three sets of columns were used to assess treatment performance by (1) aquifer soil alone (control), (2) EOS-amended aquifer soil, and (3) glycerin-amended aquifer soil to obtain treatment performance as a function of column travel. EOS and glycerin were both mixed with Site source area aquifer soil at ratios of 0.3% (w/w) prior to column packing. Multiple, smaller diameter parallel columns were used instead of one large column to reduce the volume of water needed to run the tests.

This approach simplified the sample collection procedure by allowing for collection of sufficient sample volume (20 to 25 mL) from the bottom of each column (representing the various distances from inlet to sampling point) for the various analyses in a reasonable time period, and prevented significant disruption of the flow through the column during sampling. If samples were taken from ports down the length of a single column, samples would need to be withdrawn by syringe. At low flow rates, if the sample is taken in a reasonable time period (5 minutes), a significant amount of the water is withdrawn from the column (not just at the sampling port), disrupting the bulk flow. Thus, the sample may not be representative of the flow at the sampling location. For this low flow rate, the sampling time for a sufficient volume was on the order of 1.5 to 2.0 hours per location. By using individual columns for the different lengths, the effluent from the columns were collected as a composite to represent performance as a function of length.

Columns were set up by compacting soil and then saturating with source area groundwater by pumping upward to allow pore gases to escape. Following saturation, source area groundwater was introduced into the columns at a rate equal to an approximate approach velocity of 0.5 feet per day (ft/d) [15 centimeters per day] or about 0.31 liters per day (L/d) and 1.24 L/d per column and set of columns, respectively. This velocity is in the higher range of groundwater velocities expected at the Site. No nutrient was added to the site groundwater. Samples were collected periodically from each column and analyzed for perchlorate, pH, nitrate, and TOC.

2.2.2 Vadose Zone Soil

The baseline vadose zone soil sample did not contain the expected level of perchlorate contamination and there was insufficient volume remaining for the column testing. Therefore, for the vadose zone soil column study, a new soil sample from the Site was collected from a different location, one that was known to be in the "hot" zone. The perchlorate concentration of this new soil sample was found to be 100 mg/kg in subsequent testing and more representative of perchlorate levels in source area soil.

Six-inch (15 cm) long columns, with a 2 inch (5 cm) inner diameter, were packed with site soil. The vadose zone columns were amended with the electron donor by applying a specified volume of solution amended with the substrate. The substrate solution consisted of local (Riverside) dechlorinated tap water containing the amendment at a concentration of 0.5% (w/w) and 20 mg/L of diammonium phosphate. The substrate solution application was done in either a batch mode (Treatment Scenario 1) or recirculating mode (Treatment Scenario 2).

Treatment Scenario 1

The columns used for this scenario were used to simulate soil flooding, followed by natural drainage. This process simulates one time application of an amendment. Approximately two pore volumes of water, 300 mL, were pumped upward into the packed vadose zone columns at a rate of about 1 milliliter per minute (mL/min) to saturate the soil. Influent water contained EOS or glycerin at 0.5% volume-to-volume (v/v) to ensure that the electron donor was not limiting. In addition, 20 mg/L of diammonium phosphate was added as a nutrient supplement. The nutrient dosage was kept relatively low, based on the desire to supply nutrients, but to limit addition of nitrogen to the system, which may be of concern in the field application. Once the solution was added and the columns were saturated, the effluent port was opened and the column was allowed to drain. Collected leachate was analyzed for perchlorate, nitrate, pH, and TOC. Once the columns were drained, the effluent ports were closed and the columns were left with the top open to the atmosphere.

Columns were sampled on a sacrificial basis by emptying the colum, homogenizing the soil by hand-mixing, and randomly selecting a representative 10 gram aliquot for analysis. Representative soil samples from each column were measured for perchlorate, nitrate, pH, TOC, and moisture content at 0.5, 1, 2, 4, and 8 weeks. Due to time and budget constraints, only one cycle was assessed. Simulating additional wet/dry cycling was beyond the scope of this effort.

Treatment Scenario 2

A set of columns was used to simulate a recirculation approach in which an initial application of electron donor is applied to the surface and allowed to migrate into the underlying groundwater. In this approach,

the vadose zone soil is maintained at nearly saturated conditions by pumping the underlying groundwater and applying it over the surface.

For this treatment scenario, donor/water solutions (specified above) were applied on a recirculating basis at a rate of about 0.1 mL/min, which is equivalent to about one pore volume per day. Like Treatment Scenario 1, influent water contained EOS or glycerin at a concentration of 0.5% (w/w) with nutrient (diammonium phosphate) at 20 mg/L, or no amendment (control). The solution was pumped from and returned to a reservoir to simulate the recirculation process. Columns were also sampled on a sacrificial basis as described above under Treatment Scenario 1. Representative soil samples from each column were measured for perchlorate, nitrate, pH, TOC, and moisture content at 0.5, 1, 2, 4, and 8 weeks. Also, recirculated water from the reservoir was analyzed for perchlorate, nitrate, pH, and TOC.

Table 6 summarizes the set up/analysis of vadose zone columns.

Table 6
Summary of the Vadose Zone Column Conditions

Treatment Scenario (see above)	Amendments	Sampling Frequency	Total number of columns	Conditions
1	Emulsified Oil Substrate, Glycerin, None (control)	0, 0.5, 1, 2, 4, 8 weeks	18	Saturate initially, allow to drain
2	Emulsified Oil Substrate, Glycerin, None (control)	0, 0.5, 1, 2, 4, 8 weeks	18	Maintain saturated conditions via recirculation

Notes:

1. Influent water contained emulsified oil substrate or glycerin at 0.5% (weight-to-weight) or no amendment, and ammonium phosphate at 20 milligrams per liter.
2. At specified times, columns were sacrificed and soil analyzed for perchlorate, nitrate, total organic carbon, pH, and moisture content.

2.3 ANALYTICAL PROCEDURES

Analytical testing was conducted by the UCR laboratory. A summary of the analytical methods that were generally followed during this study is given in Table 7.

Table 7
Summary of Analyses Used for Liquid Samples

Parameter	Analytical Method
pH	U.S. Environmental Agency (EPA) 150.1
Oxidation/reduction potential	Standard Method 2580 [3]
Total organic carbon	EPA 415.1
Perchlorate	EPA 314.1
Nitrate	ASTM D4327-03 [4]

For the soil analysis, the soil from each column was removed and mixed to homogenize the soil from which a representative sample was taken. The extraction procedure of Nozawa-Inoue et al. [5] was be used to determine soil perchlorate and nitrate concentration.

2.4 QUALITY ASSURANCE/QUALITY CONTROL

The data quality objective is to collect data with a high enough degree of certainty to distinguish performance differences between non-amended controls and beneficial performance in treatment microcosms upon addition of one or more electron donors. Alternatively, there should be sufficient data to state that performance under the various conditions are statistically similar. This objective requires accurate quantitative data for all measured constituents and a reasonable degree of certainty for the degradation rates determined. To ensure that these data quality objectives are met, analytical instruments were calibrated using commercially available reference standards for each set of samples. Matrix spikes and analytical duplicates were analyzed at least once in every twenty samples to assess accuracy. Triplicate microcosm samples were conducted for replication and possible statistical analyses. Observations and data collected in the laboratory were recorded in permanently bound, dedicated lab books.

3.0 ASSESSMENT OF THE AS-RECEIVED SOIL AND GROUNDWATER SAMPLES

Source area aquifer groundwater, and aquifer and (initial) vadose zone soil samples were collected from the site. Analytical results of the collected groundwater and soil samples are provided in Tables 8 and 9.

3.1 SOURCE AREA GROUNDWATER AND AQUIFER SOIL

As shown in Table 8, the initial perchlorate level was approximately 60,000 micrograms per liter (µg/L) in the collected source area groundwater. This value is assumed to be a representative perchlorate concentration. The groundwater pH was about 7.8 and the aquifer soil pH was 8.8 (see Table 9). A pH between 6.0 and 8.5 is generally favorable for biological treatment, with the optimal pH for perchlorate degradation occurring at neutral pH conditions (i.e., 7) [6][7]. TOC concentrations were 2.62 mg/L in groundwater and 28.1 mg/kg in soil. Based on a stoichiometric evaluation, the groundwater TOC value is not sufficient to completely degrade source area perchlorate. Although the soil may be an additional TOC source, the presence of nitrate as the predominant nitrogen form suggests that its availability and suitability as an electron donor is unlikely; otherwise, the nitrate would be reduced. These conditions are consistent with perchlorate persistence in the area.

Cation and anion groundwater data do not suggest any anomalous conditions that could adversely affect treatment. In contrast, the presence of sulfate in groundwater and soil samples (approximately 56 mg/L and 19 mg/kg, respectively) may be beneficial, as reduced sulfur species (sulfides) resulting from biotreatment can enhance precipitation of some solubilized metals, if this occurs. Trace metal concentrations were near the detection limits in groundwater samples from the source area (Table 8). Iron and manganese, typical of most soils, are present in the source area aquifer soil at low levels (Table 9).

Sulfide detections in aquifer and vadose soil were unexpected and may be associated with natural sulfide minerals. However, because sulfate is also present, it may be possible (although unlikely) that microbial sulfate reduction occurred at some point with subsequent mineral precipitation.

With regard to nutrients, Total Kjeldahl nitrogen - the sum of free-ammonia and organic nitrogen - was detected in groundwater at a very low concentration (0.46 mg/L). Ammonia in the groundwater was also low (<0.2 mg/L as nitrogen); however nitrate was present at 8 to 9 mg/L as nitrogen (Table 8). Since nitrate biodegradation consumes electron donor, this requirement should be taken into account in design of the full-scale treatment system, in addition to the demand from sulfate bioreduction. Total phosphorus was detected at trace levels in both soil and groundwater samples; however ortho-phosphate (the predominant biologically available form) was low in groundwater (0.13 mg/L) and below the detection limit in the soil (Tables 8 and 9). These results indicate the presence of these macronutrients, albeit at

Table 8
Results of Analysis of As-Received Groundwater Samples

		Wet Chemistry (mg/L)					Nutrients (mg/L)						Alkalinity (mg/L)		
Sample Name	**Perchlorate (µg/L)**	**pH (unitless)**	**Total Organic Carbon**	**Electroconductivity (µs)**	**Hardness (as calcium carbonate)**	**Total Dissolved Solids**	**Ammonia (as Nitrogen)**	**Total Kjeldahl Nitrogen**	**Nitrate (as Nitrogen)**	**Ortho-Phosphate**	**Total Phosphorus**	**Total Sulfur**	**Total Alkalinity**	**Bicarbonate (HCO_3)**	**Carbonate (CO_3)**
Source Area Groundwater:															
TT-MW2-17D[1]	57,800	--	2.62	--	240 c	670	0.135	0.462	9.0	0.126	0.107	20.1	97.5	97.5	< 1.0
TT-MW2-17D[2]	64,100	7.76	--	1350	--	839	--	--	8.6	<0.5	--	--	96	--	--

		Anions (mg/L)		Cations (mg/L)				Trace Metals (mg/L)		
Sample Name	**Perchlorate (µg/L)**	**Chloride**	**Sulfate**	**Calcium**	**Magnesium**	**Potassium**	**Sodium**	**Arsenic**	**Iron**	**Manganese**
Source Area Groundwater:										
TT-MW2-17D[1]	57,800	305	55.6	73.5	13.7	3.47	187	< 0.0400	< 0.0666 Jq	0.0325
TT-MW2-17D[2]	64,100	--	--	--	--	--	--	--	--	--

Notes:

-- - not analyzed
µg/L – micrograms per liter
mg/L – milligrams per liter
µs –microsiemens
1 – analyzed by Emax Laboratories [1]
2 – analyzed by University of California, Riverside laboratory
J – the analyte was positively identified and the result is usable; however, the analyte concentration is an estimated value
c – by calculation
q – the analyte detection was below the practical quantitation limit

Table 9
Results of Analysis of As-Received Soil Samples

		Soil Results (mg/kg unless otherwise notes)										
Sample Identification Location and Depth	**Zone**	**Arsenic**	**Iron**	**Manganese**	**Perchlorate (µg/kg)**	**pH (unitless)**	**Ortho-Phosphate**	**Total Phosphorus**	**Total Sulfide**	**Sulfate**	**Total Kjeldahl Nitrogen**	**Total Organic Carbon**
Source Area Soil:												
15B-20'[1]	Vadose	< 4.27	20,700	369	< 10.7	9.3 Je	0.395 Jq	1.02 Jq	16.0	5.28 Jq	17.6 Ba	102
15B-70'[2]	Aquifer	< 4.63	22,300	417	18,000	8.8	< 0.232	0.869 Jq	20.0	18.7	8.37 Ba	28.1
K-54-SB116-20[3]	Vadose	-	-	-	130,000	-	-	-	-	-	-	-
K-54-SB116-25[3]	Vadose	-	-	-	18,000 Jc	-	-	-	-	-	-	-

Notes:

µg/kg – micrograms per kilogram
mg/kg – milligrams per kilogram
- indicates not analyzed.
1. Vadose zone soil sample used for microcosm tests. Analyzed by Emax Laboratories [1]
2. Aquifer soil sample used for microcosm and column tests. Analyzed by Emax Laboratories [1]
3. Additional vadose zone soil sample used for column tests. Sample used for testing was collected between 20 and 25 feet below ground surface. Analyzed by E.S. Babcock & Sons, Inc.

B – the sample result is less than 5 times (10 times for common organic laboratory contaminants) the amount of blank contamination. The result is considered not to have originated form the environmental sample, because cross-contamination is suspected.
J – the analyte was positively identified and the result is usable; however, the analyte concentration is an estimated value
a – the analyte was found in the method blank
c – The MS and/or MSD recoveries were outside control limits.
e – a holding time violation occurred
q – the analyte detection was below the practical quantitation limit

relatively low levels. Finally, previous microbiological testing showed that perchlorate-reducing bacteria were present in soil samples [1].

3.2 SOURCE AREA VADOSE ZONE SOIL

As shown in Table 9, the perchlorate level in the initial soil sample (15B-20') was <10.7 µg/kg and less than previously reported values of 4,000 µg/kg. Therefore, as outlined in the work plan for the vadose zone microcosms, the initial soil sample was spiked with perchlorate. Because the initial soil sample had low perchlorate concentrations, an additional source area vadose zone soil sample was collected for use in the column tests. The additional sample was collected during the recent Dynamic Site Investigation [18], from boring K-54-SB116 between 20 and 25 feet bgs. Perchlorate results for samples collected at depths of 20 and 25 feet bgs were 130 and 18 mg/kg, respectively (Table 9).

In the initial sample, the TOC concentration was 102 mg/kg, which is one-hundredth of one percent. The soil pH was 9.3, which is quite alkaline but consistent with soils in arid/semi-arid areas with carbonate minerals. Literature suggests that a pH between 6.0 and 8.5 is generally favorable for biological treatment of perchlorate [6][7]; therefore, site conditions appear to influence perchlorate persistence in the area.

Total phosphorus in the initial sample was detected at a low level, 1.0 mg/kg, and the ortho-phosphate (the predominant biologically available form) was about 40% of the total phosphorus. These results indicate the presence of these macronutrients, albeit at relatively low levels. The potential effects of enhancing these nutrients were assessed in the microcosm tests. Finally, microbiological testing showed that perchlorate-reducing bacteria were present in soil samples [1].

4.0 RESULTS AND DISCUSSION

4.1 SOURCE AREA GROUNDWATER TREATMENT

Results for the source area groundwater microcosm and column tests, and brief discussions are provided in the following subsections.

4.1.1 Source Area Groundwater Microcosm Tests

Source microcosm results are included as Figures 1 though 4. Microcosm results without nutrient addition for the lower and higher amendment dosages without nutrient addition are shown in Figure 1. Results for the lower and higher amendment dosages with nutrient addition are shown in Figure 2.

Reduction of Perchlorate without Nutrient Addition

As shown in Figure 1, nearly complete perchlorate reduction was observed in microcosms receiving EOS, glycerin, and sodium acetate (at both the lower and higher dosages) in 17 days or less. Limited perchlorate reduction was also observed using HFCS 42 at the lower dosage after 13 days. Little or no perchlorate removal occurred with acetic acid. Based on comparisons in Figure 1, the effects of higher dosages vary somewhat, but are likely not significant. In the case of EOS, the onset of perchlorate degradation occurred a few days earlier for higher dosages compared with the other donors. There was very little difference between the higher and lower dosages for the glycerin trials. With sodium acetate, the higher dosage actually resulted in a delay in perchlorate degradation. This same delay may have also occurred with HFCS 42, if this were tested. Overall, the observed differences between higher and lower dosages and the various carbon substrates did not appear to be significant to warrant the use of the higher dosage to serve the desired perchlorate treatment objective.

Reduction of Perchlorate with Nutrient Addition

As shown in Figure 2, nearly complete perchlorate reduction was observed in microcosms receiving EOS, glycerin, and sodium acetate at both dosages. Limited perchlorate reduction was also observed using HFCS 42 at either dosage, although the higher dosage was slightly more effective. Little or no perchlorate removal occurred with acetic acid. Based on comparisons in Figure 2, the effects of higher dosages vary somewhat, but again are likely not significant. In the case of the EOS microcosms, perchlorate degradation was complete a few days earlier in the higher dosage treatment compared to the lower dosage treatment. For the glycerin trial, there was a lag in the initiation of the perchlorate degradation and an even longer delay for sodium acetate at the higher dosage. For HFCS, there was little difference in perchlorate degradation initiation. Again, the differences that were observed did not appear to be significant to the desired perchlorate treatment objective.

The results presented in Figures 1 and 2 suggest that EOS, glycerin, and sodium acetate appear to promote efficient perchlorate degradation. However, to minimize salt/ion additions to the aquifer, EOS and glycerin would likely be preferable to sodium acetate. As a result, the focus of the column tests was the use of EOS and glycerin.

Individual microcosm results for EOS and glycerin are shown in Figures 3 and 4, respectively. As can be seen in both Figures 3 and 4, nutrient addition seemed to provide limited benefit to perchlorate reduction with either EOS or glycerin at both the lower and higher dosages (even though the initial characterization suggested that nutrient levels were relatively low). Complete reduction occurred with and without nutrient addition within a timeframe ranging from 8 to 18 days. As a result, no nutrients were added to the aquifer soil or source area groundwater in the subsequent column testing.

Reduction of Nitrate Relative to Perchlorate

Nitrate reduction typically precedes perchlorate reduction in groundwater where these anions co-exist. As can be seen in Figures 5 and 6, nitrate was completely reduced prior to the onset of perchlorate reduction for both EOS and glycerin.

Water Quality Changes

Biological perchlorate reduction requires reduced conditions. Following addition of an organic substrate, water undergoes a change from oxidizing to reducing conditions. Under these conditions, arsenic, iron, and manganese can be reduced to more soluble species, and thus may be mobilized in the subsurface. In addition, nitrite-nitrogen may be formed via reduction of nitrate. Nitrite was observed at low concentrations in the control microcosms at the end of the test, but not in the treated microcosms. Nitrite, a product of denitrification, is transient in nature in reducing environments. Thus, nitrite is generally not expected to be an issue in the field application. Initial and final water quality analyses for these constituents are provided in Tables 10 through 12.

Table 10
Initial-Final Water Analyses for Control Microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as Nitrogen	0.090	ND	1.2	ND	1.8
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	ND	ND	ND	ND

Notes:
MDL – Method Detection Limit
mg/L – milligrams per liter
ND – not detected

Table 11
Initial-Final Water Analyses for EOS Amended Microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as Nitrogen	0.090	1.7	ND	4.7	ND
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	0.083	0.39	ND	0.22

Notes:
EOS – Emulsified Oil Substrate
MDL – Method Detection Limit
mg/L – milligrams per liter
ND – not detected

Table 12
Initial-Final Water Analyses for Glycerin Amended Microcosms

Parameter	MDL, mg/L	Without Nutrient		With Nutrient	
		Initial, mg/L	Final, mg/L	Initial, mg/L	Final, mg/L
Nitrite as N	0.090	0.57	ND	1.1	ND
Arsenic	0.070	ND	ND	ND	ND
Iron	0.15	ND	ND	ND	ND
Manganese	0.070	ND	ND	ND	ND

Notes:
MDL – Method Detection Limit
mg/L – milligrams per liter
ND – not detected

There was no increase in concentrations of arsenic and iron for either the EOS or glycerin amended microcosms (Tables 11 and 12, respectively). However, minor solubilization of manganese appears to have occurred in the EOS microcosms (Table 11). Solubilization of manganese occurs under reducing conditions induced by application of a substrate, but manganese is generally reoxidized and immobilized as conditions return to normal following substrate depletion.

4.1.2 Source Area Groundwater Column Testing

Column data are presented in Figures 7 through 10. As shown in these figures, perchlorate reduction was observed in the soil columns amended with either EOS or glycerin (Figures 8 and 9), but not in the control column (Figure 7). In Figures 7 through 10, perchlorate concentrations from the influent, 6 inches (15 cm), 12 inches (30 cm), 18 inches (45 cm), and 24 inches (60 cm) columns are shown.

No perchlorate degradation was seen in any of the control set of columns as expected (see Figure 7). Thus, it is unlikely that natural attenuation of perchlorate will occur in the groundwater as it passes through the source area aquifer soil.

EOS-Amended Columns

In the EOS-amended soil columns (Figure 8), perchlorate degradation began gradually over the first two weeks and then progressed rapidly. After about 20 days, perchlorate removal was nearly complete in the 12 inch column, and complete in the 18 inch and 24 inch columns. Perchlorate reduction reached a maximum of about 35% in the 6 inch column after 20 days. After about 50 days of operation, a gradual decrease in perchlorate reduction was observed in the 6 inch and 12 inch column. After about 90 days of operation, a gradual decrease in perchlorate reduction was observed in the 18 inch column. After 20 days, effluent perchlorate concentrations from the 24 inch column remained well below 1 mg/L for the duration of the column testing.

Perchlorate reduction profiles for the EOS column at various times during the column testing are shown in Figure 9. As can be seen, there is a general decrease in the degradation rate over the 120-day test period. Effluent perchlorate concentration profiles are generally observed to be shifting to the right as seen in the figure with the increase in number of days of operation.

Glycerin-Amended Columns

In the glycerin-amended soil column, glycerin at a concentration of 0.3% (mass basis) was mixed into the soil prior to packing. From Figure 10, it can be seen that after approximately 20 days, no perchlorate degradation was observed. In contrast, perchlorate degradation was initiated in the similarly amended EOS columns (see Figure 8) within that same time frame.

To help induce perchlorate degradation, 300 mg/L of glycerin was added to the influent on Day 25, which is equivalent to about five times the stoichiometric amount needed for perchlorate/nitrate biodegradation. After glycerin addition, perchlorate degradation was observed, but subsided when glycerin supplementation was discontinued. At Day 53, glycerin addition was temporarily discontinued. Within a few days, little or no perchlorate degradation was observed in the effluent from the 6 inch, 12 inch, 18 inch, and 24 inch columns.

At Day 68, glycerin addition into the source area groundwater influent was again initiated, except at a concentration of 120 mg/L, or only about two times the stoichiometric amount for perchlorate/nitrate degradation. Significant perchlorate degradation was then observed in each of the columns, with about 90 percent removal in the 24 inch column.

At Day 96, the glycerin addition into the source area groundwater influent was lowered to 60 mg/L, or about the stoichiometric amount needed for perchlorate/nitrate biodegradation. After Day 96, perchlorate biodegradation decreased significantly at all column lengths until the end of the testing.

Nitrate reduction in the glycerin-amended columns is shown in Figure 11. Prior to Day 25, partial to nearly complete nitrate reduction in the columns occurred. However, after that time, nitrate reduction began to decrease. This trend is most likely due to the rapid loss of glycerin (in comparison to EOS) from the soil during this period due to biodegradation and/or leaching. Due to the lack of sufficient electron donor, the denitrification rate decreased. Without complete denitrification, perchlorate biodegradation is inhibited. Hence, no perchlorate degradation was observed when incomplete denitrification occurred. It was not until additional glycerin (300 mg/L) was added to the source area groundwater influent that complete denitrification occurred and concomitant perchlorate reduction was observed. In contrast, complete denitrification was observed in the EOS-amended columns at all times (data not shown).

4.2 Source Area Vadose Zone Soil Treatment

Results for the source area vadose zone microcosm and column tests and brief discussions are provided in the following subsections.

4.2.1 Source Area Vadose Zone Microcosm Tests

Vadose zone microcosm results are included as Figures 12 though 18. Microcosm results without nutrient addition for the lower and higher amendment dosages at a 15% moisture content are shown in Figure 12. Results for the lower and higher amendment dosages with nutrient addition at the same 15% moisture content are shown in Figure 13.

As shown in Figure 12, minimal perchlorate reduction was observed in the vadose zone microcosms during the nearly 80-day test period for any of the tested amendments at a moisture content of 15% without nutrient added. The use of higher dosages of the soluble amendments also did not result in any significant perchlorate removal. Results were similar when nutrient (diammonium phosphate) was added (see Figure 13), showing minimal perchlorate degradation.

Based on the results of the 15% moisture content microcosms, additional vadose zone microcosms were tested with a 25% moisture content with the soluble donors only. Results are shown in Figure 14. As seen with the 15% moisture content, minimal perchlorate degradation was observed with or without nutrient addition after 40 days.

To verify that perchlorate-degrading bacteria were present, a further microcosm test was conducted by saturating the vadose zone soil using sodium acetate at a dosage of 500 mg/kg of soil as the electron

donor, with and without nutrient addition. The results of this microcosm test are shown in Figure 15. In this saturated microcosm test, perchlorate reduction was initiated within 5 to 7 days with and without nutrient addition. Perchlorate treatment was nearly complete after 9 days without nutrient addition and 6 days with nutrient addition.

Based on these results, perchlorate biodegradation can be stimulated in the vadose zone soil. It appears that a favorable biodegradation environment was not produced by the mere addition of electron donor and nutrient at a soil moisture content of either 15% or 25%. The limiting condition that results in perchlorate inhibition was not determined. Successful perchlorate biodegradation under saturated conditions and minimal (at best) perchlorate degradation at 15% and 25% soil moisture conditions indicates the possibility of a dilution effect. The soil has a readily desorbable perchlorate and salinity component. The concentration of these constituents in the aqueous phase is a function of the soil moisture content. There is more water in the soil at 25% moisture content than 15%. At saturation, the soil moisture content is the highest it can be and the concentration of the desorbed components will be at its lowest level. The measured soil moisture content at saturated conditions was found to be 64% for the source area vadose zone soil. The measured field moisture capacity was 35% (the field moisture capacity is the soil moisture capacity after the soil has been allowed to naturally drain). The initial soil moisture content of the source area vadose zone soil was 9%.

There are a wide range of possible reasons for ineffective perchlorate biodegradation in the partially saturated vadose zone treatment including:

- High perchlorate concentration (Bardiya and Bae [8])
- High salinity (Park and Marchand [9]; Chung et al. [10]; Logan et al. [11])
- High or low pH (Wang et al. [6]; Xu et al. [7])
- Moisture content (Nozawa-Inoue et al. [5]; Evans and Trute [12]).
- Presence of inhibitory constituents (Song and Logan [13]; Attaway and Smith [14]) or production of inhibitory metabolites from incomplete fermentation in unsaturated conditions
- Lack of sufficient macronutrients (e.g. nitrogen) and/or micronutrients (e.g. molybdenum) (Hatzinger et al. [15]; Chaudhuri et al. [16])
- High oxidation/reduction potential conditions and/or aerobic conditions (Coates and Achenbach [17])
- Combinations of the above

The results of an extraction analysis performed on the vadose zone soil indicate that the readily dissolvable solids are about 3,300 mg/kg (dry weight basis) from the soil. For a moisture content of 15% and 25%, the average salinity in the pore water is on the order of 22,000 and 13,200 mg/L, respectively. At saturated conditions, the pore water salinity would be on the order of 5,000 mg/L. Park and Marchand

[9] found inhibition of perchlorate biodegradation at 4% salinity (~40,000 mg/L) for some bacteria, whereas other bacteria were able to degrade perchlorate at 4% salinity. Similar observations were made by Logan et al. [11] who found that the source of bacteria (fresh versus saline water) determined their ability to degrade perchlorate under salinity conditions in the 1% to 7% range.

Based on the initial perchlorate soil concentration of 4,000 µg/kg, the average perchlorate concentration in the pore water at 15% moisture content would be in the range of 27 mg/L. Reported perchlorate inhibition occurs at concentrations of 7,000 mg/L (Bardiya and Bae [8]). Clearly, the expected level of pore water perchlorate concentration is well below this concentration. Further, the perchlorate was readily degraded in the source area groundwater at concentrations of 60 mg/L. Thus, perchlorate inhibition is unlikely.

With respect to pH, soil pH measurements are made by mixing 100 g of soil with 100 g of deionized water. This is equivalent to 100% moisture content. The measured pH of the vadose zone soil was 9.3 (see Table 9). At a moisture content of 15%, there is a likelihood that the pore water pH is higher than 9.3. Little or no perchlorate biodegradation has been shown to occur at this pH by some researchers (Wang et al. [6]; Xu et al. [7]). On the other hand, Evans *et al.* reported that perchlorate in vadose zone soil can be reduced at an initial pH value between 9.3 and 9.8 [12].

Overall, salinity or pH inhibition or unbalanced fermentation may be primary factors for the lack of perchlorate degradation observed in the unsaturated microcosm tests at 15% and 25% moisture content, and the complete perchlorate biodegradation that was observed under saturated conditions. These inhibitive effects may be overcome via dilution. It would appear that moisture content between 25% and 65% may provide the necessary dilution.

4.2.2 Source Area Vadose Zone Column Testing

During the vadose zone microcosm testing, it was found that none of the tested amendments, with or without nutrient addition, was able to yield the desired perchlorate biodegradation. Perchlorate biodegradation only occurred when the vadose zone soil was saturated. Thus, the vadose zone columns were operated in such a way to create saturated conditions at least temporarily. Donor solutions were applied in either a batch mode (Treatment Scenario 1) or recirculating mode (Treatment Scenario 2).

The electron donor used in the saturated vadose zone microcosm was sodium acetate. However, as noted in the source area groundwater column study, sodium acetate was considered to be less desirable than EOS or glycerin, which minimized added ions to the groundwater due to the treatment process. Therefore, for the vadose zone columns, EOS and glycerin were selected as the two test electron donors.

To confirm the effectiveness of EOS and glycerin to stimulate perchlorate degradation under saturated conditions, a saturated vadose zone microcosm test was conducted with the new source area vadose zone soil collected from the site that was found to have a perchlorate concentration of 100 mg/kg. The amending solution contained EOS or glycerin at a concentration of 0.5% (w/w) with 20 mg/L of diammonium phosphate. The results of this microcosm test are shown in Figure 16. Both EOS and glycerin were shown to stimulate effective perchlorate degradation in the vadose zone soil under saturated conditions.

Batch Application (Treatment Scenario 1)

Results from Treatment Scenario 1 (batch amendment application) are given in Figure 17 through Figure 19. Little or no overall perchlorate degradation was observed under this batch application approach (see Figure 17) and approximately 30% to 40% of the perchlorate in the soil was leached out as a result of the batch application. (Note: The column bottoms were sealed after one day.) Most of the water from these columns drained within 30 minutes; the moisture content after draining for one hour was approximately 40%. Perchlorate was found to be highly mobile in the soil and loosely sorbed. Significant migration of the perched perchlorate will be expected to occur as a result of batch flooding with or without added amendments.

The lack of perchlorate biodegradation in the batch vadose zone columns is consistent with the microcosm results. As seen in Figure 18, the soil moisture content in the columns decreased with incubation time, from about 40% (field moisture capacity) to 15% by the end of the eight-week study period. The as-received moisture content of the newer vadose zone soil sample was measured at 11%. The bottom port was sealed after one day of draining; moisture was evaporated via the surface to the atmosphere.

Interestingly, soil nitrate was reduced readily as a result of amendment addition (Figure 19). Within one week of amendment application, the soil nitrate was reduced to below the detection limit in the batch vadose zone columns that had EOS or glycerin applied, whereas minimal nitrate reduction was observed in the control column. Therefore, it appears that the microbial consortia which developed in the columns could overcome the limitations for denitrification but not for perhlorate dechlorination. The reasons for this unexpected disparity are not clear.

Recirculation Application (Treatment Scenario 2)

Results from Treatment Scenario 2 (recirculation application) are presented in Figure 20 for perchlorate reduction. Rapid perchlorate degradation was observed under the recirculation application approach for EOS, glycerin, and the control. Within three weeks, the soil perchlorate was effectively reduced.

A seemingly anomalous result is the reduction of perchlorate in the recirculating control column. In the initial vadose zone microcosms, the soil sample used for those tests was found to have little or no perchlorate and a TOC concentration of 100 mg/kg, or less than 0.1% organic content. The newer vadose zone soil collected for the column work had considerable perchlorate, 100 mg/kg, and an organic content of 2.1%. The soil used in the column work had considerably more organic matter. Based on the recirculation vadose zone column results, the existing organic matter in the site soil may be able to provide sufficient electron donation for perchlorate biodegradation. The recirculation of water through the column appears to provide a suitable condition for this reduction to occur. Although perchlorate reduction in the control was limited in the microcosm test using the new vadose zone soil sample (Figure 16), there was a downward trend in the control perchlorate microcosm towards the end of that test.

Perchlorate biodegradation in the recirculation vadose zone columns is consistent with the microcosm results. In the recirculation approach, the soil moisture content is maintained at or near saturation at all times in contrast to the batch approach in which the soil is saturated for a short period of time, reaches field moisture capacity shortly after the batch application, and then the moisture content decreases steadily with time.

Similar to the batch vadose zone columns, soil nitrate was reduced readily as a result of amendment/water addition. Within one week of amendment application, the soil nitrate concentration was reduced to below the detection limit in the recirculation columns including the control columns (data not shown).

5.0 SUMMARY OF FINDINGS/CONCLUSIONS

In summary, initial source area groundwater, and aquifer and vadose zone soil parameters were measured for samples from the source area to verify perchlorate levels, and provide initial characterization of samples. The perchlorate level in the source area groundwater was found to be consistent with prior measurements; however, the vadose zone soil was found to have little perchlorate and required spiking to 4,000 µg/kg. Additional vadose zone soil was collected for use in the latter stages of the study. This soil had concentrations of perchlorate of approximately 100 mg/L.

5.1 SOURCE AREA GROUNDWATER TESTS

Source area groundwater microcosm tests revealed that complete perchlorate biodegradation occurred with and without nutrient addition using either EOS, sodium acetate, or glycerin within a timeframe ranging from 5 to 12 days. Nitrate was also reduced effectively, preceding perchlorate reduction. Based on a desire to minimize salt ion addition to the groundwater, EOS and glycerin were considered to be preferable amendments for further consideration in column testing.

The effect of adding nutrients in the source area groundwater microcosms, at least in the short term, was to accelerate the timeframe for the initiation of perchlorate biodegradation by approximately two days. Once perchlorate biodegradation was initiated, very little difference in the rate of perchlorate degradation was observed. Thus, the benefit of adding 1 g/L of diammonium phosphate is considered to be minimal. Solubilization of arsenic, manganese, and iron was not observed for either the EOS- or glycerin-amended microcosms. Very minimal solubilization of manganese was observed in the EOS treatment.

In column testing, soil was first amended with EOS or glycerin at a rate of 0.3% (3000 mg/kg) in addition to a control column. Within 10 to 15 days, the columns with EOS-amended soil achieved nearly complete perchlorate and nitrate reduction within the first 12 inches (30 cm) of column length after 20 days of operation. After a period of time, perchlorate degradation efficiency began to decrease at the shorter column lengths. This trend occurs most likely due to the depletion of the available electron donor, EOS, over time. While nearly complete perchlorate degradation was achieved in the 24 inch (60 cm) column during the entire 4-month study period, reduction in perchlorate degradation efficiency would be expected to decrease after a protracted period of some time. In field application, periodic reinjection of EOS will likely be required to maintain electron donor availability.

Major conclusions of the source area groundwater tests are as follows:

- EOS, glycerin, and sodium acetate were shown in microcosm testing to be effective in stimulating biological reduction of perchlorate in site aquifer material.

- The rates of reduction were relatively similar for these three amendments, with complete reduction observed in the microcosms within a timeframe of between 7 and 18 days.
- The addition of 1 g/L of diammonium phosphate resulted in earlier initiation of the perchlorate degradation by about two days, which is not considered significant in remedial timeframes typically undertaken in the field.
- In the column studies, amending soil with EOS had significant advantages over using glycerin as a soil amendment. To be effective in stimulating and maintaining perchlorate degradation, glycerin had to be added directly into the influent. Glycerin, mixed with the soil, had limited effectiveness due to leaching and/or rapid biodegradation. In contrast, a single addition of EOS to the soil resulted in steady removal of perchlorate with a 24-inch (30 cm) column with no additional amendment in the influent feed.
- Results generally indicated no significant (or very minimal) solubilization of metals due to artificially-induced reducing conditions created by EOS or glycerin amendment.

Thus, based on the laboratory study, both EOS and glycerin may be considered to be acceptable alternatives for field implementation in treating the source area groundwater in situ. EOS may be preferable in terms of longevity and avoidance of continuous amendment feed. Glycerin will most likely require continuous feed into the groundwater to maintain perchlorate removal efficiency, whereas a single application of EOS may last four or more months depending on the dimensions of the application zone and the groundwater flow.

5.2 SOURCE AREA VADOSE ZONE SOIL TESTS

Source area vadose zone microcosm tests revealed that none of the pre-selected amendments were able to stimulate perchlorate biodegradation under unsaturated conditions at 15% and 25% moisture content. Perchlorate biodegradation was induced under saturated conditions, however, using sodium acetate as an electron donor. It was later determined in subsequent microcosm tests that EOS and glycerin could also be used as electron donors to induce perchlorate treatment under saturated conditions. These latter electron donors were considered to be preferable amendments for further consideration based on a desire to minimize salt ion addition.

The effect of adding nutrients in the source area vadose zone microcosms under saturated moisture conditions was to accelerate the timeframe for the initiation of perchlorate biodegradation by two or three days. Once perchlorate biodegradation was initiated, very little difference in the rate of perchlorate degradation was observed. Thus, the benefit of adding 1 g/L of diammonium phosphate is considered to be minimal.

For the column tests, two application scenarios were tested, a one-time batch flooding approach and a recirculation approach using donor-amended water. Both EOS and glycerin were used at a solution concentration of 0.5% (w/w) with 20 mg/L of diammonium phosphate added. Within three to four weeks, complete perchlorate degradation was observed in the recirculated columns, including the control

columns. Removal of perchlorate in the control columns, while surprising, occurred most likely due to the significant organic content (2.3%) measured in the second vadose zone soil sample collected from the Site. In contrast, little or no perchlorate degradation was noted in the batch flooded columns during the eight-week testing period.

Major conclusions of the source area vadose zone tests are as follows:

- EOS, glycerin, and sodium acetate were shown in microcosm testing to be effective in stimulating biological reduction of perchlorate in vadose zone soil under saturated conditions only. Minimal perchlorate degradation occurred at 15% and 25% moisture content.
- EOS and glycerin were considered to be preferable electron donors based on a desire to minimize salt ion addition.
- The addition of 1 g/L of diammonium phosphate results in earlier initiation of perchlorate degradation under saturated conditions by about two or three days.
- In the column studies, the recirculation approach was shown to be effective in reducing soil perchlorate in the vadose zone soil, whereas the batch application resulted in minimal perchlorate degradation.
- The specific reason why perchlorate biodegradation occurs only under saturated conditions is not fully understood. It is speculated that salinity, pH conditions, and/or unbalanced fermentation at the low moisture condition may inhibit specific perchlorate-reducing organisms in the vadose zone soil. It should be noted that nitrate bioreduction was not inhibited; the reasons for this disparity are not clear.

Thus, based on the laboratory study, both EOS and glycerin may be considered to be acceptable alternatives for field implementation in treating the source area vadose zone soil, but only under continually saturated conditions. It also may be possible to take advantage of the existing soil organic content in the vadose zone soil in some areas of the site during engineering implementation in the field.

6.0 IMPLICATIONS FOR FULL-SCALE DESIGN

The completed source area groundwater bench-scale tests indicate that biotreatment appears to be a feasible technology to implement in the field. EOS or glycerin may be used to achieve the desired perchlorate degradation; however these amendments would be applied differently in the field. Glycerin would likely require frequent, intermittent, or even continual supplementations. On the other hand, the bench-scale tests indicate that EOS is likely to have greater longevity in the field (estimating the exact longevity of EOS in the bench-sale was beyond the current scope and these estimates are often better determined in the field. Other remedial feasibility factors will be taken into consideration the substrate of choice in the field. The dimensions, location, perchlorate concentrations, and other geochemical factors will play a role in finalizing the type and amount of carbon substrate. Final selection of the substrate to be tested in the field will be conducted based on economic and implementability considerations.

The bench-scale studies also indicated that macronutrients (nitrogen and phosphors) do not appear to be necessary for aquifer treatment. While the lag prior to the onset of perchlorate treatment was marginally greater in the trials for which macronutrients were not added, the timeframe appeared to be in the order of 2 to 3 days which should not be critical in the field where treatment timeframe is in the order of months.

The vadose zone studies indicated that flooding and continual saturation appeared to be the most optimal laboratory method for rapid treatment of perchlorate. Some of the factors obstructing treatment in the vadose zone at near saturation conditions were elucidated but not clearly understood for site specific soils. Saturation of vadose zone can be achieved by flooding the source area with carbon substrate amended water followed by continual flushing with water (to maintain saturated conditions) and potential extracting and recirculating downgradient groundwater to create a closed loop in-situ system. Various engineering mechanisms can be employed for saturating the soil and will be considered during the design of the field systems.

The bench-scale tests also indicated that in areas where sufficient organic carbon is present, natural flushing, which translates to natural bioattenuation, could play a contributing role in overall remediation. One of the vadose zone trial columns with TOC of 2.2% did not appear to need additional carbon substrate and achieved excellent perchlorate removal by continual flushing. This should be a strong consideration for portions of the site when remedial options, in particular monitored natural attenuation, are evaluated.

7.0 REFERENCES

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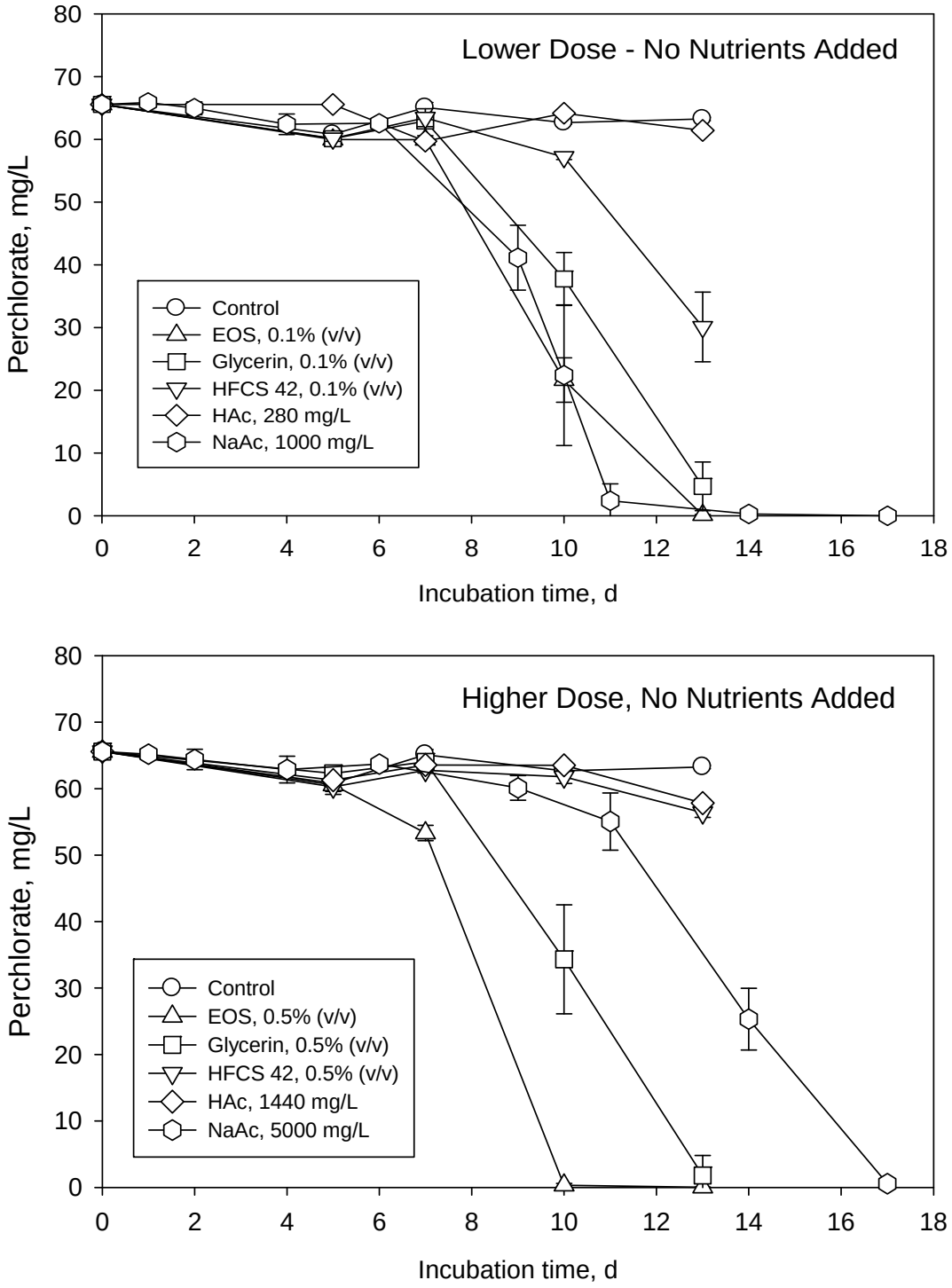
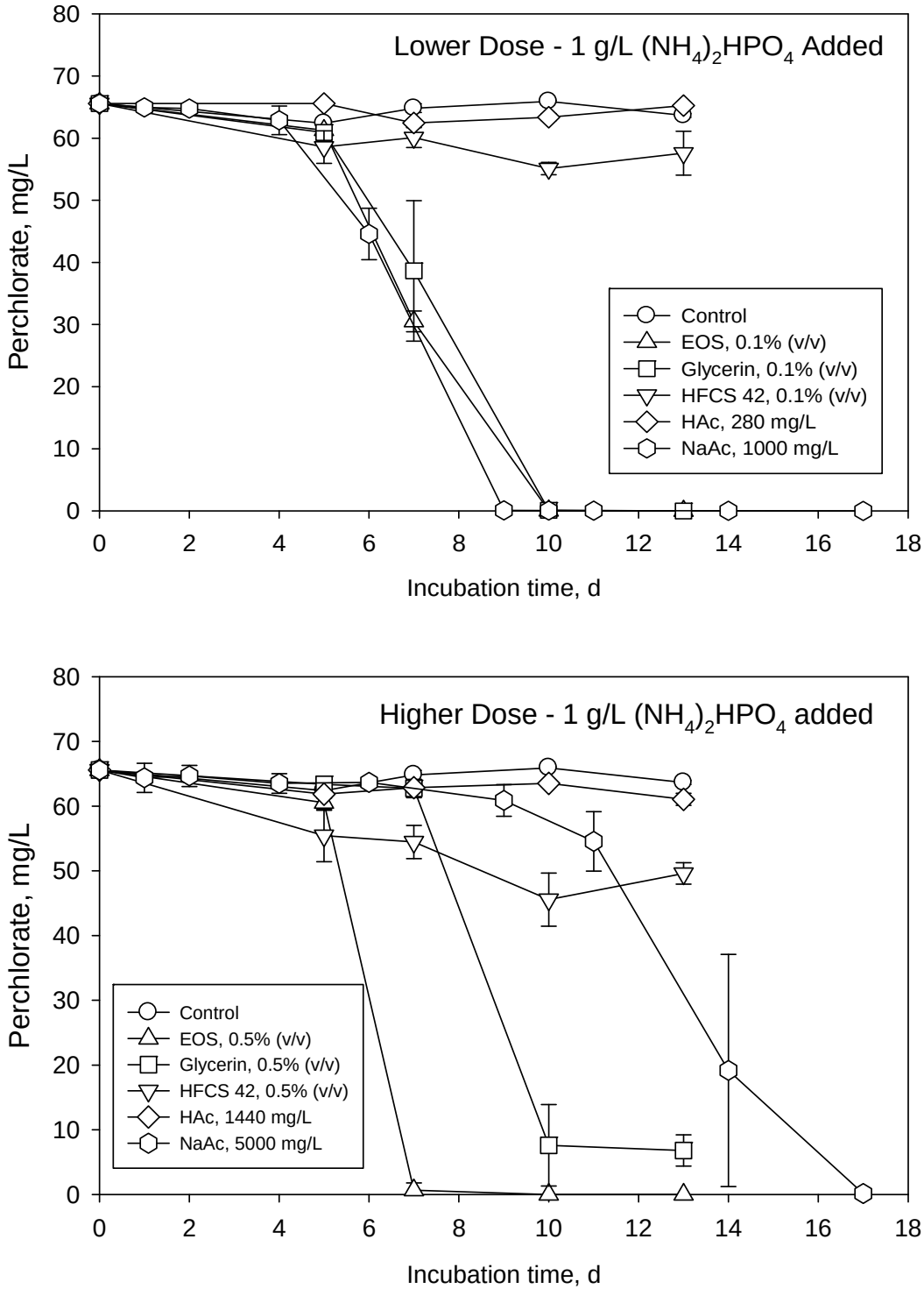
FIGURES



Notes:

d – days
EOS – emulsified oil substrate
mg/L – milligrams per liter
HAc – acetic acid
v/v – volume-to-volume
HFCS – high fructose corn syrup
NaAc – sodium acetate
% –percent

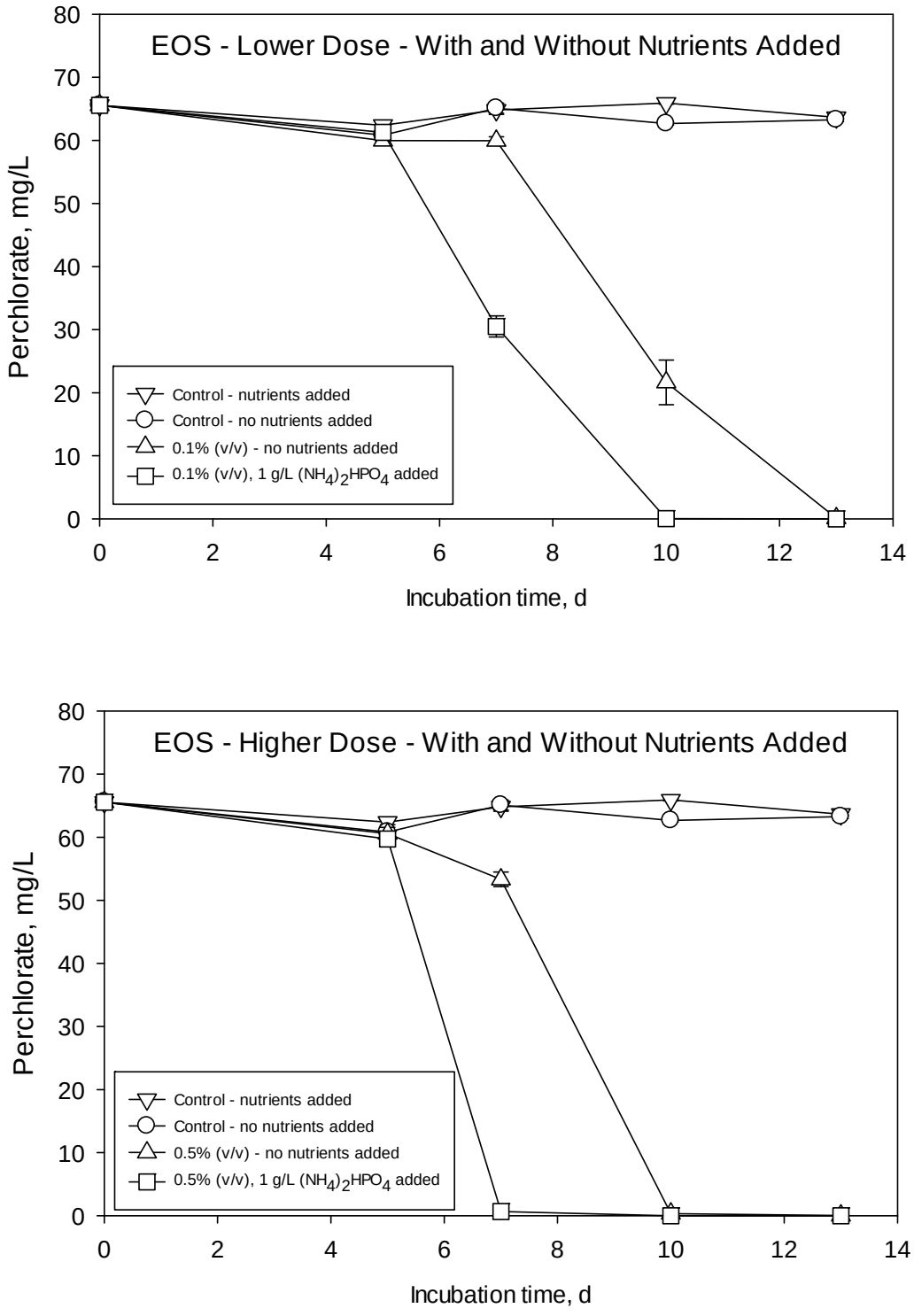
Figure 1 Source Area Groundwater Microcosms, No Nutrients Added (Top: Low Dosage; Bottom: High Dosage)



Notes:

$(NH_4)_2HPO_4$–diammonium phosphate EOS – emulsified oil substrate mg/L – milligrams per liter HAc – acetic acid
v/v – volume-to-volume HFCS – high fructose corn syrup NaAc – sodium acetate d – days % – percent

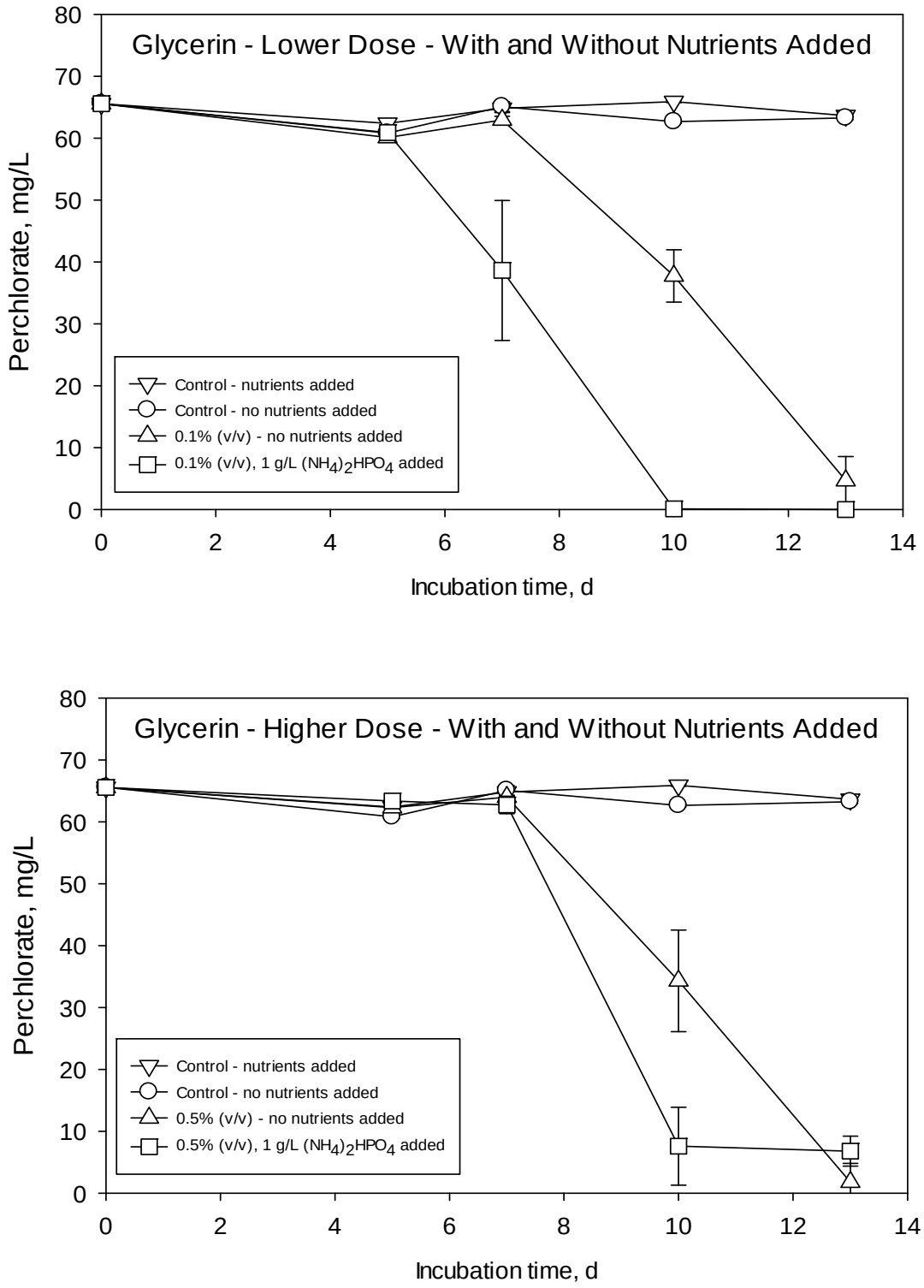
Figure 2 Source Area Groundwater Microcosms, Diammonium Phosphate Added (Top: Low Dosage; Bottom: High Dosage)



Notes:

$(NH_4)_2HPO_4$–diammonium phosphate
v/v – volume-to-volume
EOS – emulsified oil substrate
d – days
mg/L – milligrams per liter
% – percent

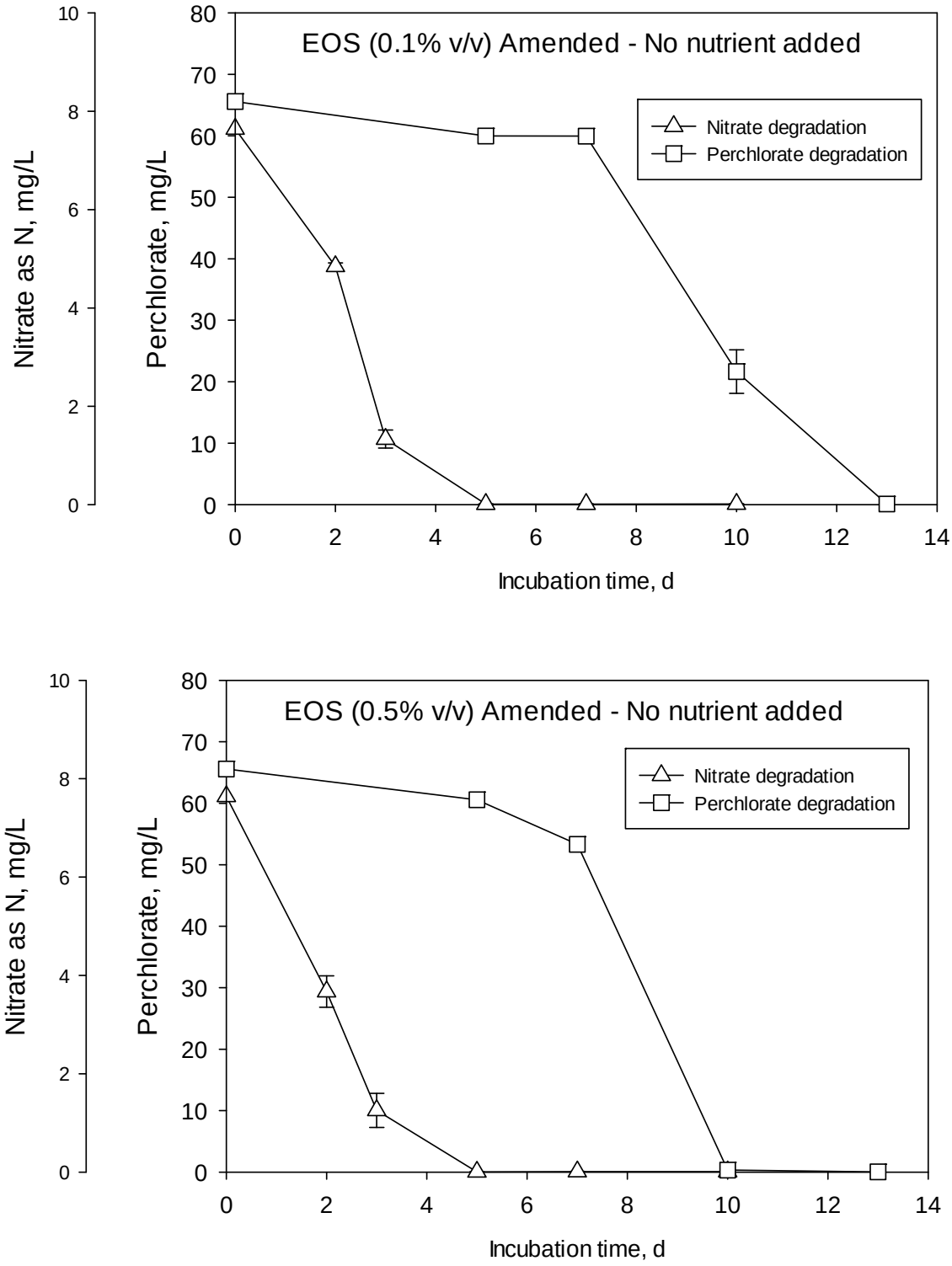
Figure 3 Perchlorate Reduction in EOS Amended Source Area Microcosms (Top: Low Dosage; Bottom: High Dosage)



Notes:

$(NH_4)_2HPO_4$–diammonium phosphate mg/L – milligrams per liter v/v – volume-to-volume d – days **%** – percent

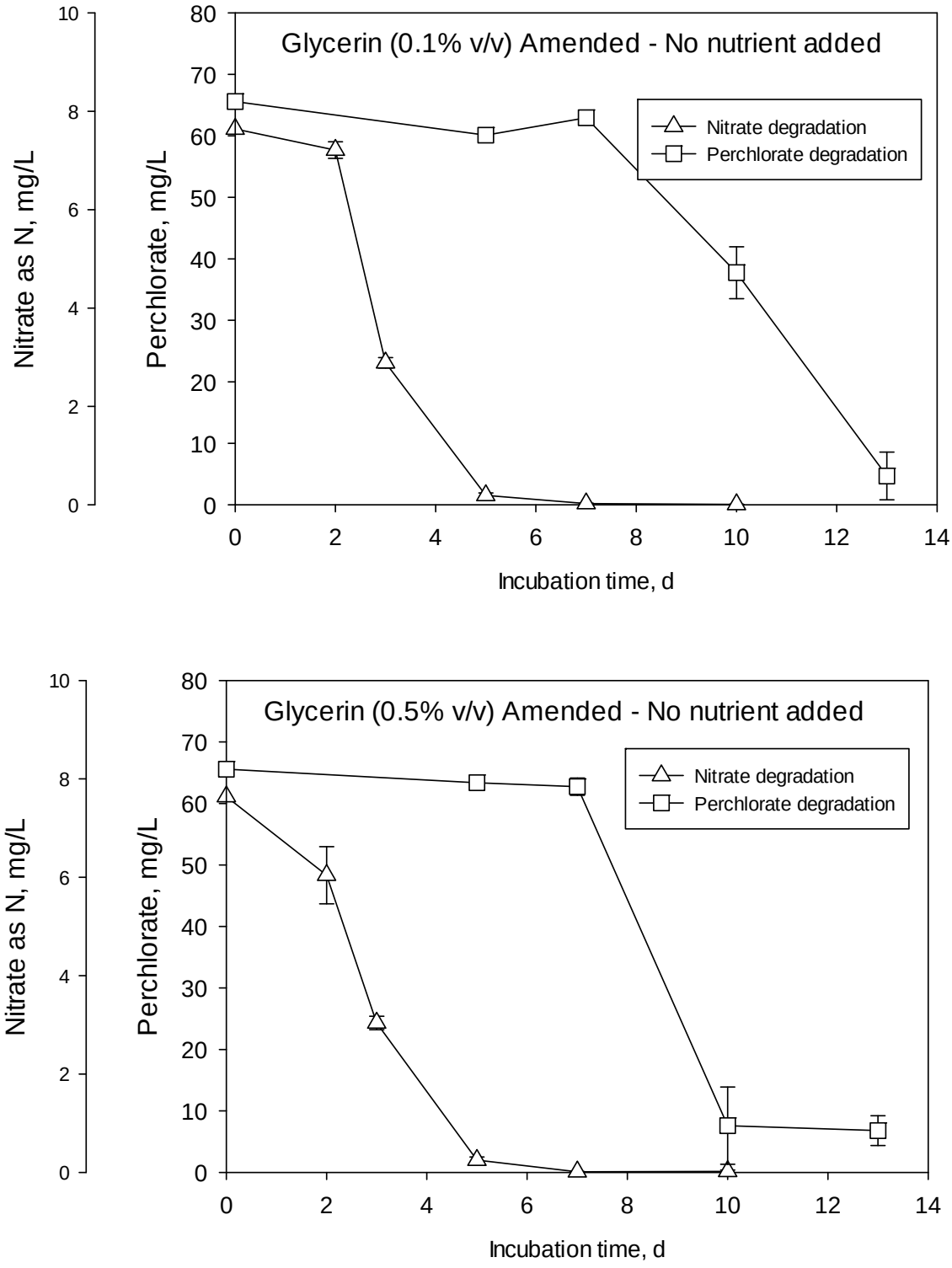
Figure 4 Perchlorate Reduction in Glycerin Amended Biobarrier Microcosms (Top: Low Dosage; Bottom: High Dosage)



Notes:

N–nitrogen EOS – emulsified oil substrate mg/L – milligrams per liter v/v – volume-to-volume
d – days % – percent

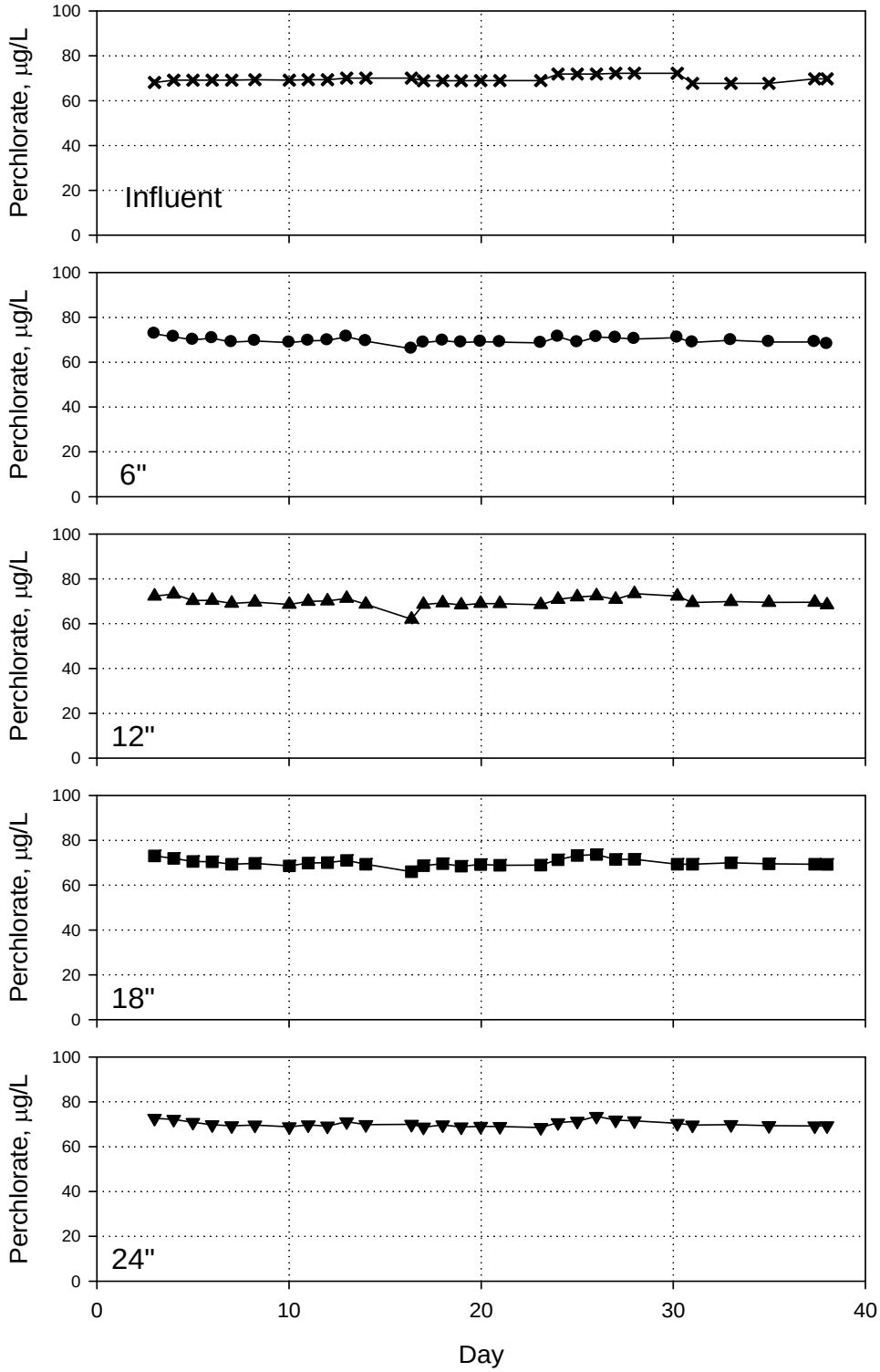
Figure 5 Nitrate and Perchlorate Reduction in EOS Amended Source Area Microcosms



Notes:

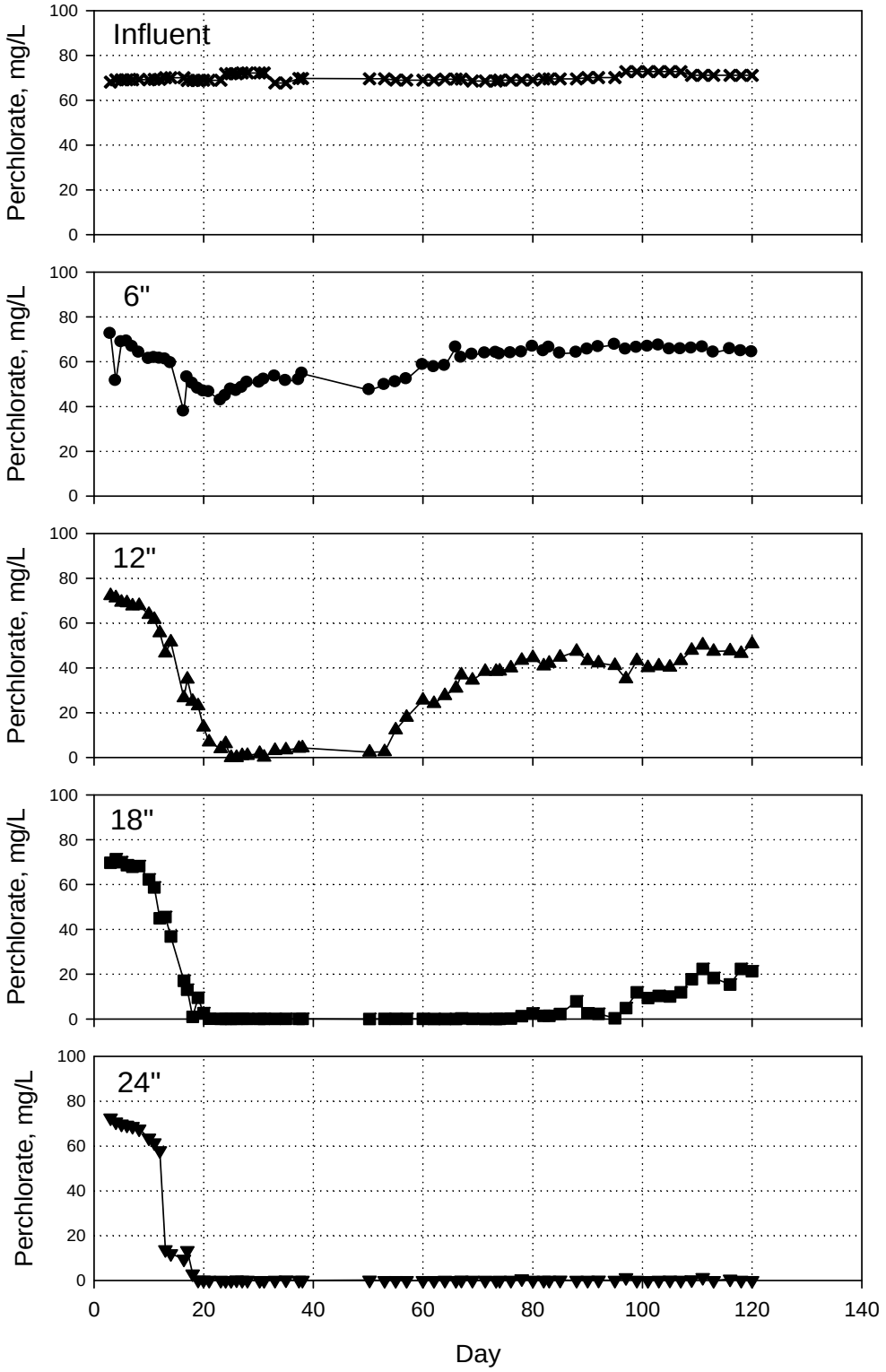
N–nitrogen mg/L – milligrams per liter v/v – volume-to-volume d – days **%** – percent

Figure 6 Nitrate and Perchlorate Reduction in Glycerin Amended Source Area Microcosms



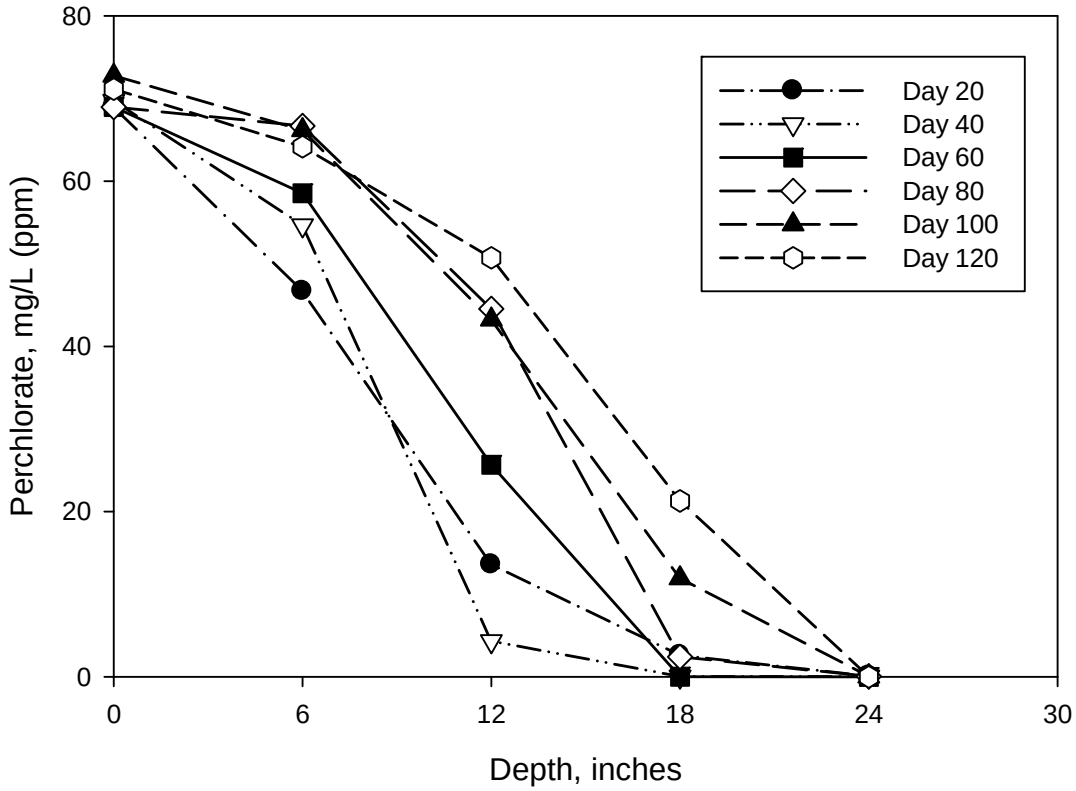
Notes:
µg/L–micrograms per liter

Figure 7 Perchlorate Reduction in Source Area Control Columns



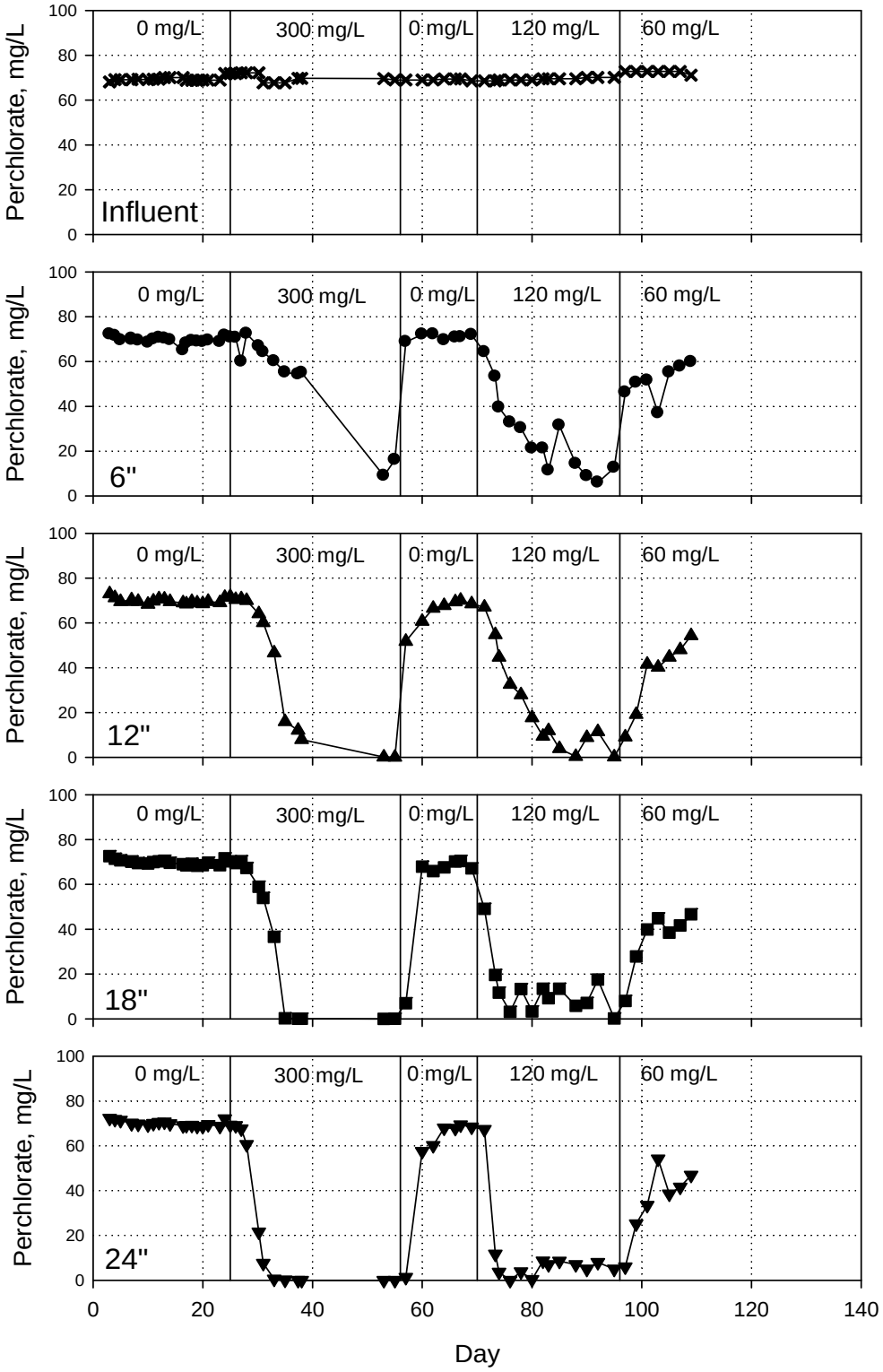
Notes:
mg/L–milligrams per liter

Figure 8 Perchlorate Reduction in Source Area EOS-Amended Columns



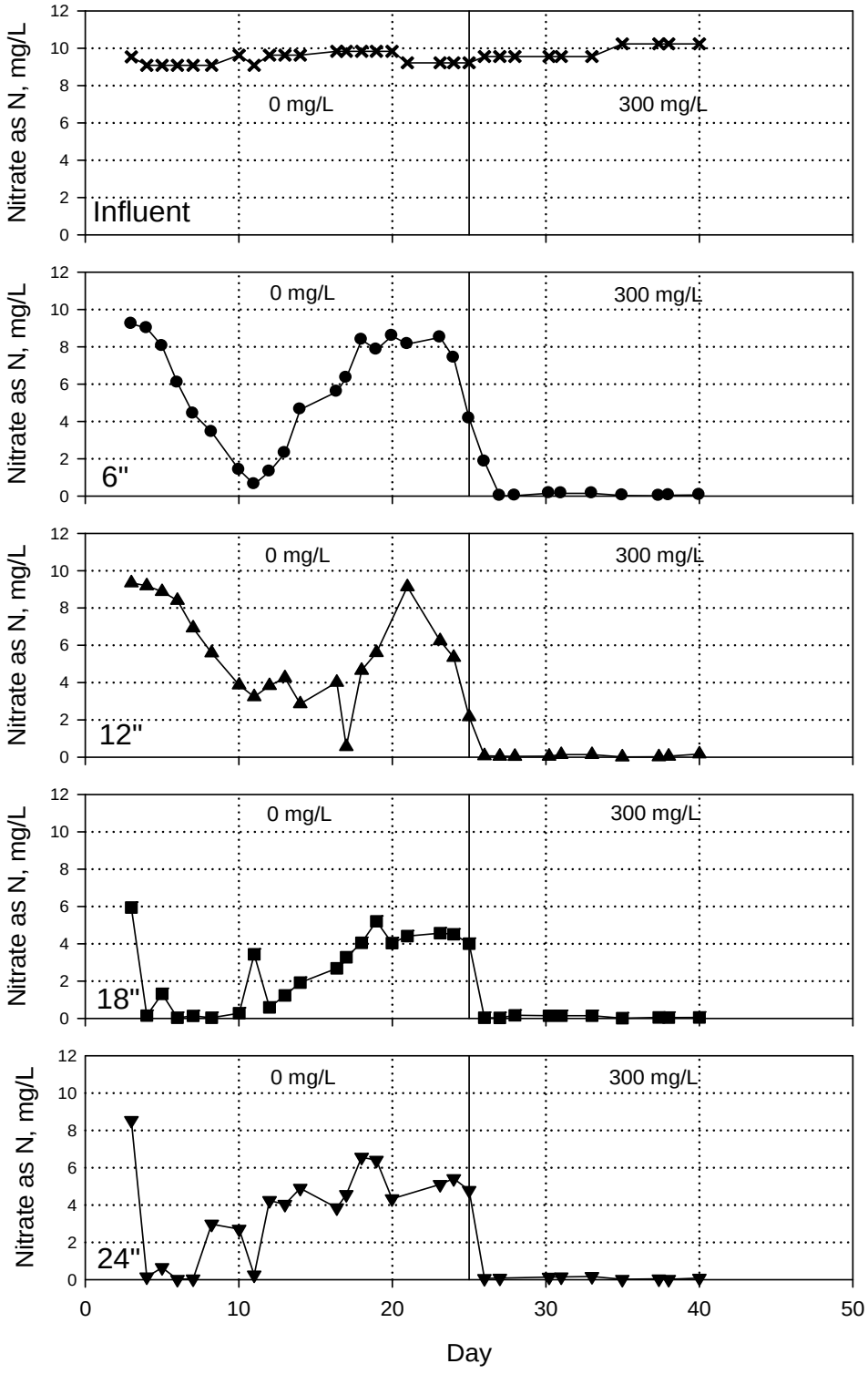
Notes:
mg/L–milligrams per liter ppm – parts per million

Figure 9 Perchlorate Reduction Profiles in EOS Amended Source Area Columns



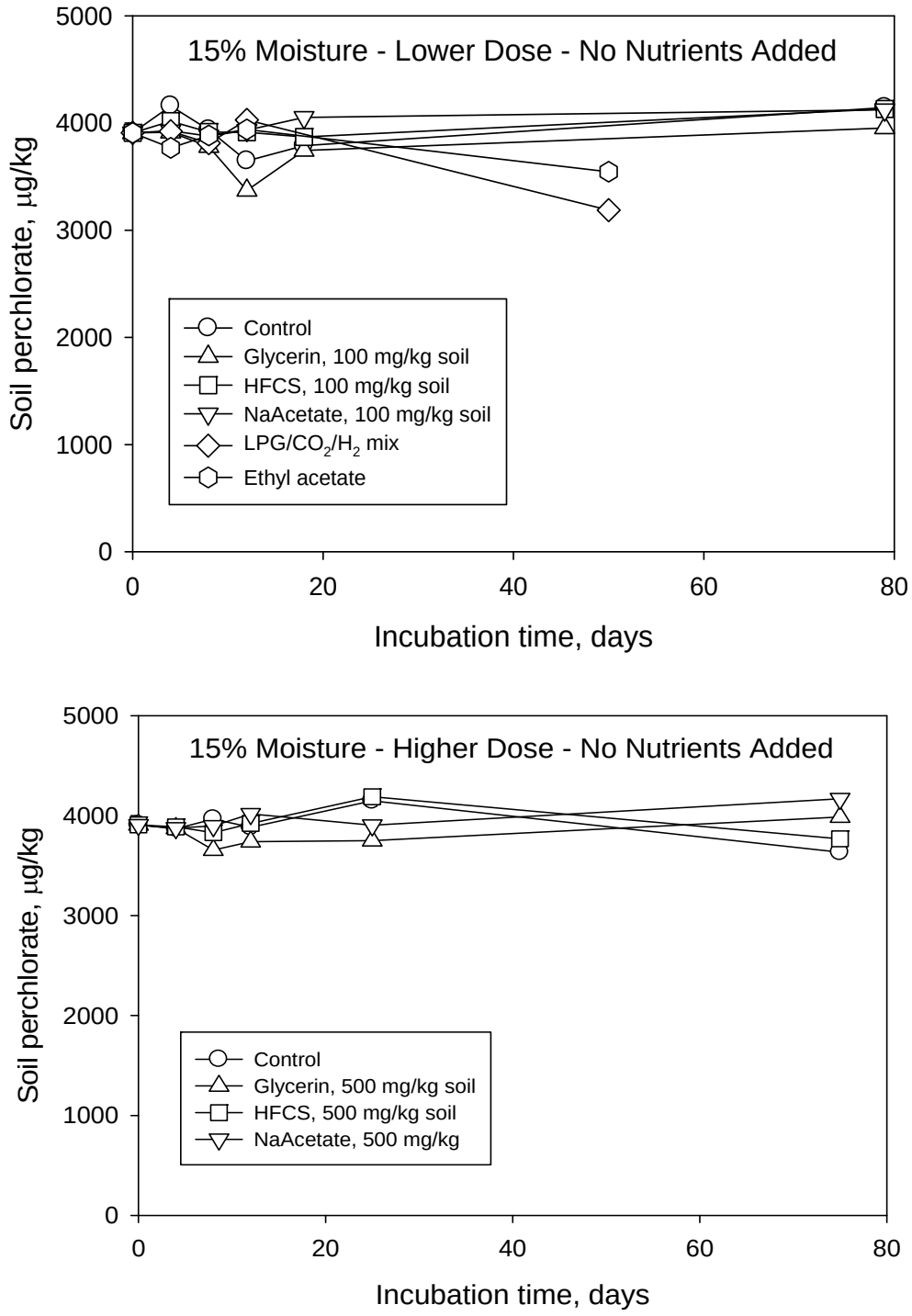
Notes: mg/L–milligrams per liter

Figure 10 Perchlorate Reduction in Source Area Glycerin-Amended Columns Concentration Indicated is Amount of Glycerin Added to Influent



Notes: mg/L–milligrams per liter N – nitrogen

Figure 11 Nitrate Reduction in Source Area Glycerin-Amended Columns Concentration Indicated is Amount of Glycerin Added to Influent



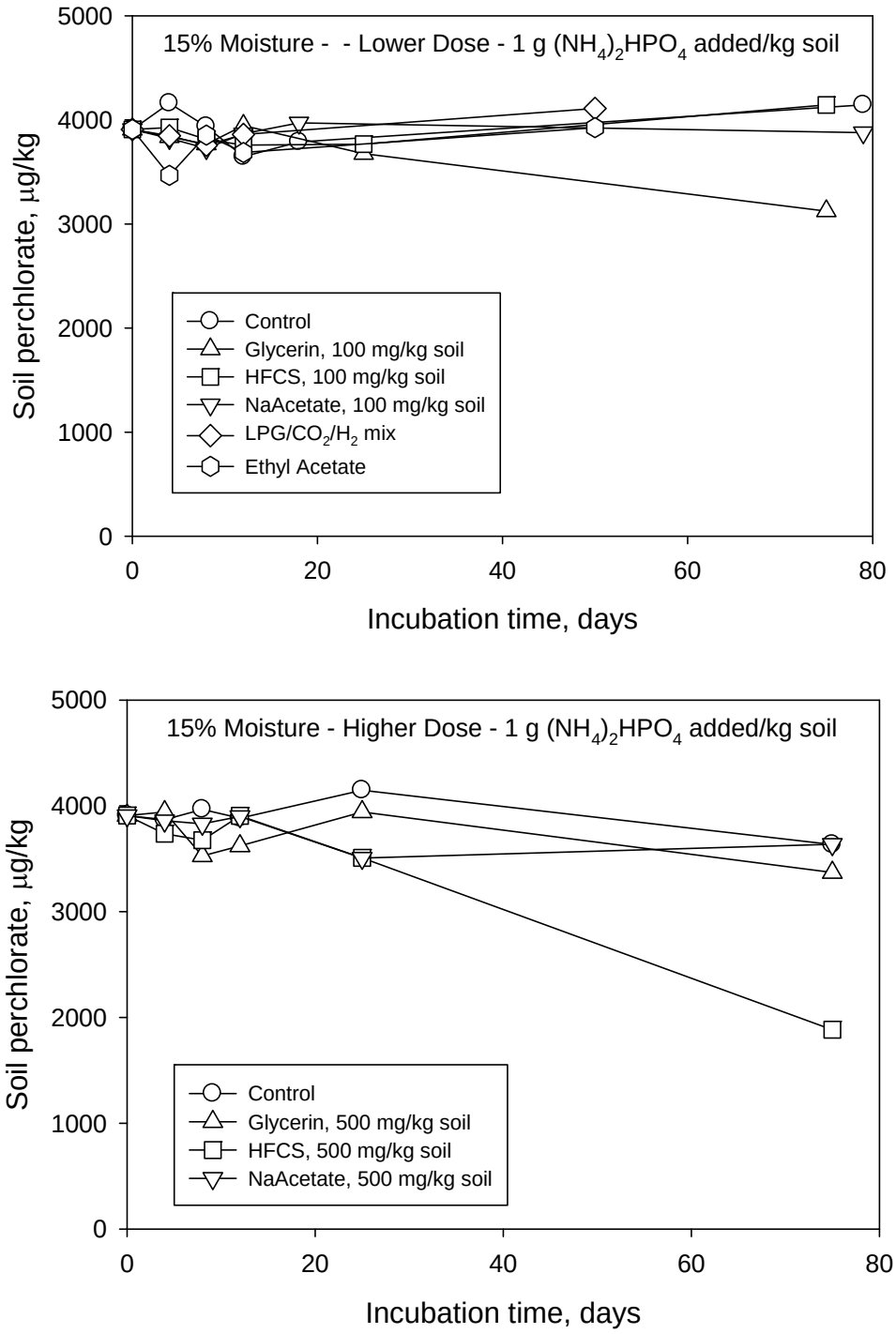
Notes:

LPG/ CO_2/ H_2–liquefied petroleum gas/carbon dioxide/hydrogen gas mg/kg – milligrams per kilogram

µg/kg – micrograms per kilogram HFCS – high fructose corn syrup NaAcetate – sodium acetate % – percent

Figure 12 Vadose Zone Microcosms – 15% Moisture Content
No Nutrient Added, Soil Amended with Perchlorate – 4,000 µg/kg

(Top: Gaseous and Soluble Donors (low dosage); Bottom: Soluble Donors (high dosage)

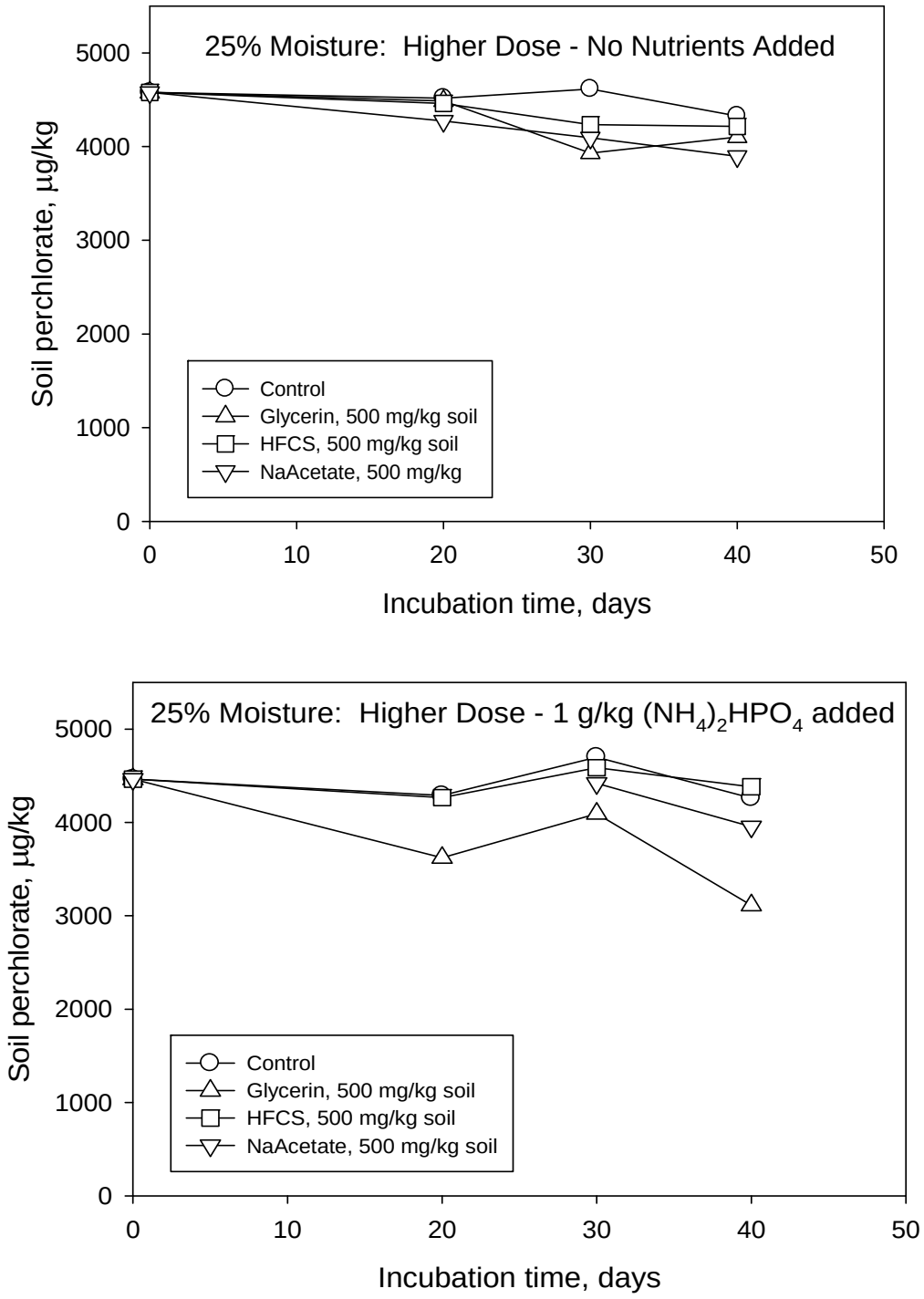


Notes:

LPG/ CO_2/ H_2–liquefied petroleum gas/carbon dioxide/hydrogen gas $(NH_4)_2HPO_4$–diammonium phosphate µg/kg – micrograms per kilogram mg/kg – milligrams per kilogram HFCS – high fructose corn syrup NaAcetate – sodium acetate g/kg – grams per kilogram % – percent

Figure 13 Vadose Zone Microcosms – 15% Moisture Content
Diammonium Phosphate Added, Soil Amended with Perchlorate – 4,000 µg/kg

(Top: Gaseous and Soluble Donors (low dosage); Bottom: Soluble Donors (high dosage)

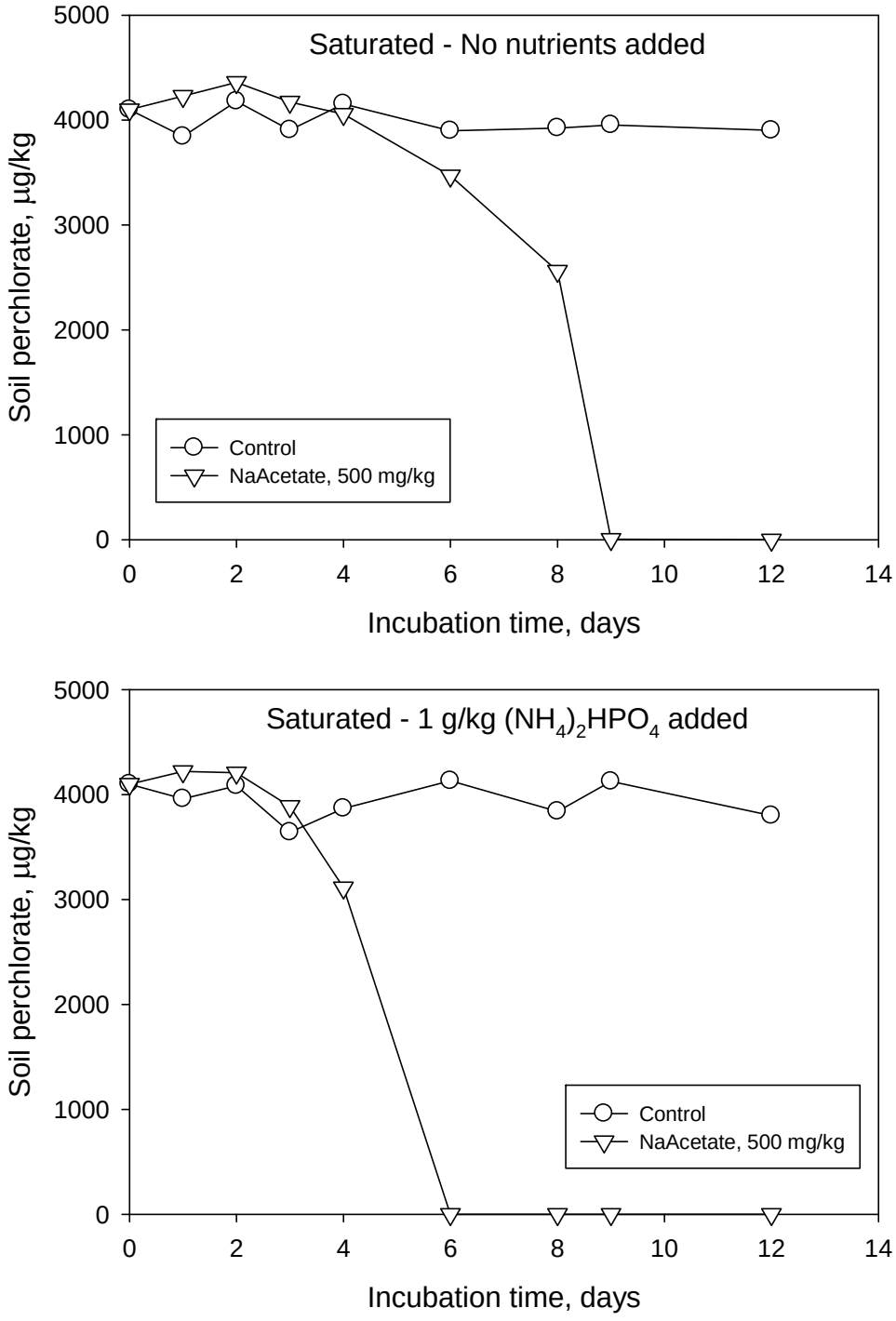


Notes:

$(NH_4)_2HPO_4$–diammonium phosphate µg/kg – micrograms per kilogram mg/kg – milligrams per kilogram
HFCS – high fructose corn syrup NaAcetate – sodium acetate g/kg – grams per kilogram % – percent

Figure 14 Vadose Zone Microcosms – 25% Moisture Content, 500 mg/kg (high dosage) of Soluble Electron Donor Added

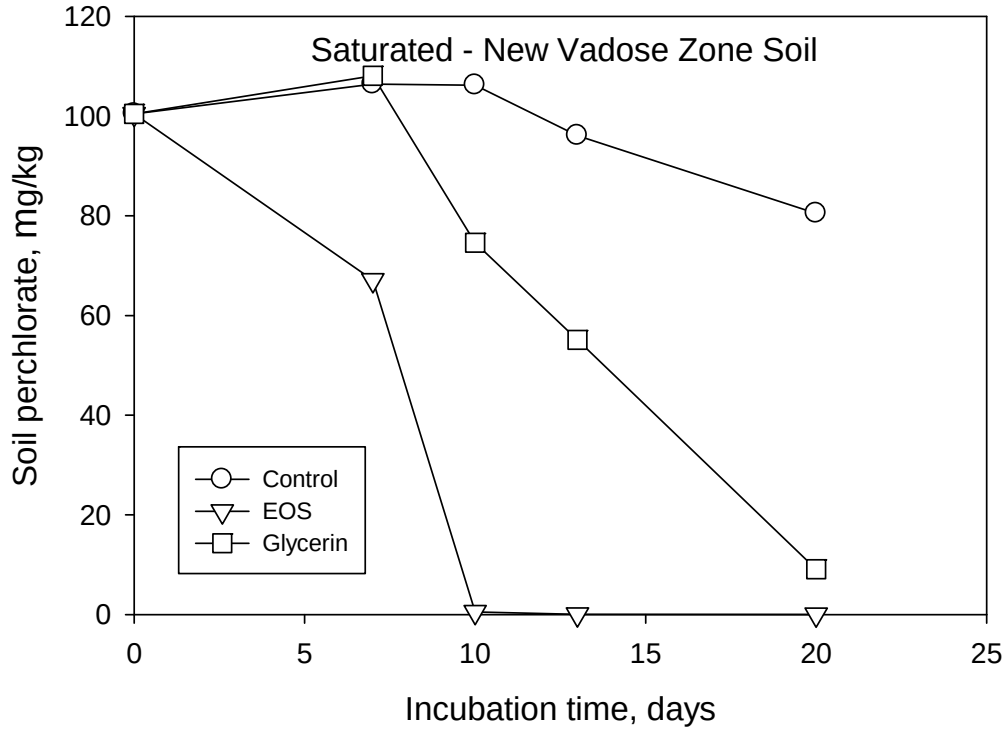
Top: No nutrient added. Bottom: 1 g/L (NH4)2HPO4 added



Notes:

µg/kg – micrograms per kilogram
mg/kg – milligrams per kilogram
NaAcetate – sodium acetate
g/kg – grams per kilogram
$(NH_4)_2HPO_4$–diammonium phosphate

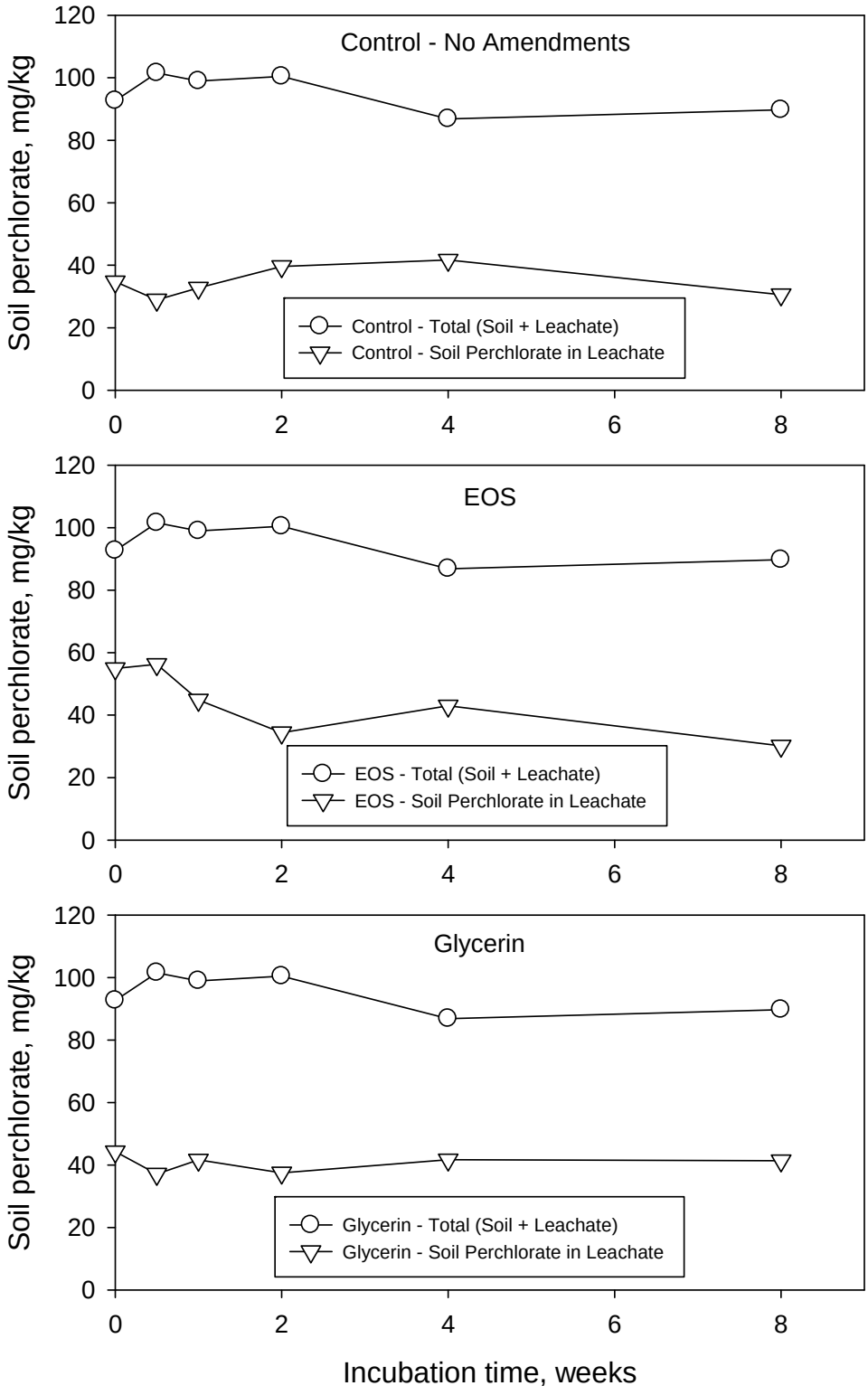
Figure 15 Vadose Zone Microcosms – Saturated, 500 mg/kg (high dosage) of Sodium Acetate Added



Notes:

mg/kg – milligrams per kilogram EOS – emulsified oil substrate

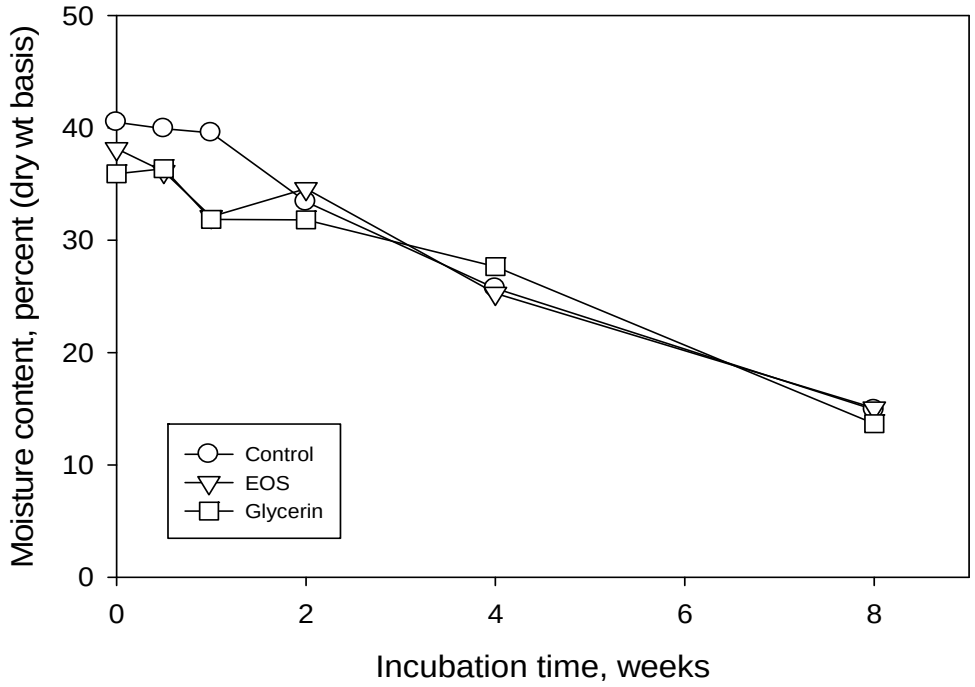
Figure 16 Vadose Zone Microcosms – Saturated, New Vadose Zone Soil Sample, Donor Solution = 0.5% (w/w)



Notes:

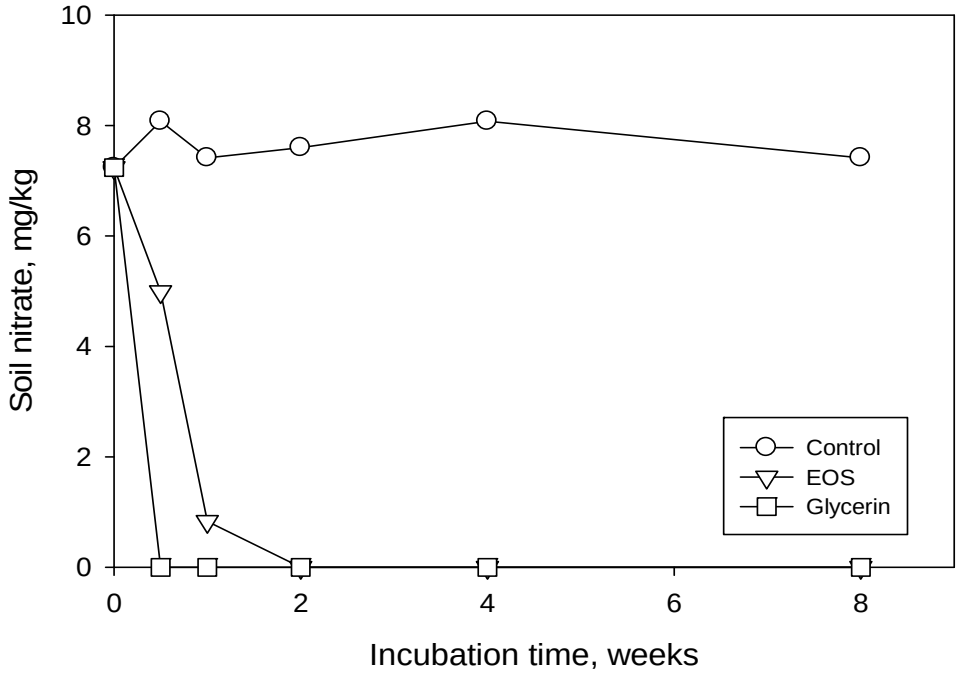
mg/kg – milligrams per kilogram EOS – emulsified oil substrate

Figure 17 Perchlorate Results – Vadose Zone Columns – Batch Application (Scenario 1)



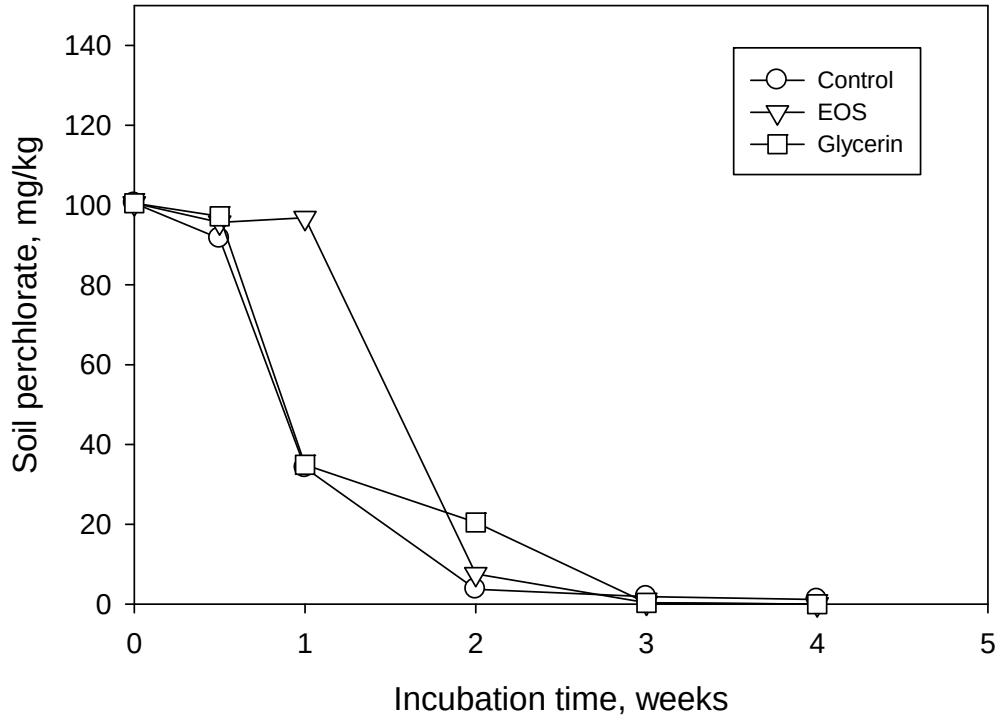
Notes: EOS– emulsified oil substrate

Figure 18 Moisture Content – Vadose Zone Columns – Batch Application (Scenario 1)



Notes: EOS– emulsified oil substrate mg/kg – milligrams per kilogram

Figure 19 Nitrate Removal – Vadose Zone Columns – Batch Application (Scenario 1)



Notes: EOS– emulsified oil substrate mg/kg – milligrams per kilogram

Figure 20 Perchlorate Results – Vadose Zone Columns – Recirculation Application (Scenario 2)

APPENDIX A

LABORATORY REPORTS