Pilot Scale In-Situ Bioremediation Of Perchlorate-Contaminated Soils At The Longhorn Army Ammunition Plant

INVESTIGATORS

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ABSTRACT

Treatability studies were conducted to identify suitable carbon sources for the cleanup of perchlorate-contaminated soils at the Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas. A series of bench-scale experiments to measure the kinetics of perchlorate removal in LHAAP soil were conducted. The use of microorganisms to enhance bioremediation (biostimulation) was evaluated by applying such organic amendments as poultry manure, cow manure, horse manure, cotton waste, methanol and ethanol. The different amendments stimulated the biodegradation of perchlorate in the contaminated soils, with cotton waste resulting in slower rates compared to the other carbon sources. A series of column tests evaluating the transport behavior of ethanol in LHAAP soil suggested that the soil has very low ability to adsorb carbon. Based on the results of these initial treatability studies, a field demonstration study was conducted at the LHAAP site. Three carbon sources (ethanol, horse and chicken manure) were selected for pilot testing at the site.

The distribution of perchlorate across the plots varied widely and the maximum concentration of perchlorate in the selected treatment plots at the start of the pilot study was 400 mg/kg. The field demonstration started in October 2000. Six identical treatment plots (4.57 x 2.74 m) and one control cell (5.5 x 5.5 m) were sectioned off (isolated) using plastic liners. Duplicate cells were treated with the same predetermined concentration of each amendment and no amendment was added to the control cell. Water was applied to all 7 plots to achieve complete saturation only down to the desired treatment depths below ground surface (bgs). Maximum rates of perchlorate removal at the top layer during the start of the test are in the range of 6-7 mg/kg-soil/day. After 120-days of bioremediation, perchlorate concentrations in soil were reduced from initial values ranging from 8.4 to 295.3 mg/kg, down to 0.0 to 223.4 mg/kg. After ten months, we observed complete removal of perchlorate in the surface soils and varied reduction in the deeper layers. At the termination of the pilot study, the concentration of perchlorate in the wettest cells (except for the control) had decreased to non-detectable levels at all treatment depths. The effectiveness of the process varied with the type of organic amendment, wetness of the soils, and depth. It was found that under field conditions, horse manure and ethanol were superior carbon amendments. The results of this pilot study demonstrate that perchlorate-contaminated soils can be treated in-situ by applying the cost-effective techniques we have developed to deliver nutrient amendments to desired depths.

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I. RATIONALE

Background

Past industrial operations, testing, and training activities at numerous Department of Defense (DoD) installations have resulted in the release of many toxic chemicals substances into the soil, surface water, and groundwater. The use of cost-effective technologies to remediate impacted sites assists the U.S. military in meeting its stewardship goals while conserving resources that can be directed to maintaining its readiness capability.

The Longhorn Army Ammunition Plant (LHAAP) site is located in a moist, sub-humid to humid, mild climate with an average annual rainfall of 46 inches, which is fairly evenly distributed throughout the year. The depth to groundwater across the facility ranges from 1 to 70 ft below ground surface, with typical depth to groundwater being 12 to 16 feet. Groundwater generally occurs under unconfined conditions with frequent occurrence of perched and local confining conditions due to the high clay content and highly variable stratigraphy. LHAAP is presently inactive and scheduled to be transferred to the US fish and wildlife service. A 1998 Remedial Investigation/Feasibility Study (RI/FS) for the LHAAP indicates that perchlorate has seriously impacted surface water, groundwater and soils at the site.

Located in the Production Area of Longhorn AAP and in the watershed area of Goose Prairie Creek is Building 25-C. Building 25-C has been identified as a building where ammonium perchlorate was ground prior to being incorporated in rocket motors and flare propellants. A characterization of perchlorate concentrations around building 25-C prior to remedial action is presented in Table 1 and the corresponding soil types in the sampling area is provided in Table 2.

TABLE 1.
Measured perchlorate concentrations around building 25-C at the Longhorn Army Ammunition Plant, (μg/kg), (Sampled 18 August 1998)

		Sampling Location								
		25C1	25C2	25C3	25C4	25C5	25C6	25C7	25C8	25C9
Sampling Depths (ft)	0-0.5'	27,500	84,800	1,920	1,390	2,900	6,050/ 5,880 QC/ 11,000 QA	140,000	1,640	84,200
	4'-5'	58,800	335	22.1/ 23.1QC/ <40QA	36,900	50,700	165,000	3,690	21,900	81,600
	9'-10'	10,700	5,720	12,300	3,570	15,200	118,000	2,310	14,400	8,090

Source: 1998 Remedial Investigation/Feasibility Study (RI/FS) for LHAAP, Texas

The Texas Environmental Protection Division and the U.S. Army have been seeking low cost remedial technologies for the clean up of perchlorate, TNT, and other contaminants at this site. The removal of perchlorate from soils using phytoremediation was considered as one alternative. However, this approach is a very slow process at this site because the tree roots that promote rhizodegradation are not evenly spread out in contaminated soil, thus limiting rhizosphere activity in the absence of organic carbon.

TABLE 2.
Soil sampling description for sampling around building 25-C [Companion table to Table]

		Sampling Location								
		25C1	25C2	25C3	25C4	25C5	25C6	25C7	25C8	25C9
Sampling Depths (ft)	0-0.5'	Yellow Brown silty Sand	Tan silty Sand	Yellow Brown/ Gray silty Sand	Light Brown silty Sand	Brown Silty Sand	Yellow Brown silty Sand	Brown Sand	Mixed Sand/ Gravel	Yellow Brown silty Sand
	4'-5'	Gray-red stiff Clay	Gray clayey Sand	Gray clayey silty Sand (wet)	Gray silty Sand	Mottled Brown/ Gray clayey silty Sand	Gray silty Sand	Gray silty Sand w/dk brown woody type fiber mixed	Brown Gray silty Sand	Mottled Brown/ Gray silty Sand
	9'-10'	Gray clayey Sand (moist)	Yellow Brown clayey Sand (wet)	Brown Sand (wet)	Gray clayey Sand	Gray/Brown clayey Sand	Gray silty Sand	Brown silty Sand (wet)	Gray silty Sand	Gray silty Sand

Source: 1998 Remedial Investigation/Feasibility Study (RI/FS) for LHAAP, Texas

Feasible alternative

A large body of literature suggests that ubiquitous perchlorate-reducing microorganisms are present in groundwater, soils, and sediments. Our work in phytoremediation has confirmed that microbial systems in the rhizosphere contribute significantly to perchlorate transformation. Based on this information, we proceeded to develop a biotreatment system for perchlorate-contaminated soils that addresses the shortcomings of phytoremediation treatment at this site.

The technology employs a system for surface application of amendments that enhance in-situ bioremediation of perchlorate at defined depths. The sandy nature of the topsoils around Building 25C (Table 2) presents favorable conditions for this approach. The biotreatment system is essentially a composting system with suitable carbon sources added at the surface and allowed to infiltrate the soil profile.

The technology is relatively inexpensive and sufficiently effective that it can be implemented on a large scale to clean up many acres of perchlorate contamination in soils within a very short

time. Adding a suitable carbon (electron) source to the soil contaminated with perchlorate results in the enhancement of transformation of perchlorate to chloride. We have identified and tested the best amendments [preliminary bench scale evaluation] for LHAAP in completed laboratory tests using perchlorate-contaminated soils collected from this site. Since soils are very heterogeneous, different types of amendments are required to formulate the most effective system and achieve optimum degradation rates.

Demonstration and validation data of biotreatment systems for perchlorate-contaminated soils is a special need that supports DoD's cleanup efforts and transfer of the technology. Composting-biotreatment like phytoremediation has very low initial startup and maintenance costs, and can attenuate contaminant concentrations to very low levels. Combined with other technologies intended for source removal, this approach can be very effective as a long-range strategy. Therefore, the overall goals of this project were to develop and evaluate the Composting-Biotreatment technology and transfer the technology through an onsite pilot demonstration at LHAAP.

II. OBJECTIVES

- Refine an in-situ bioremediation approach using bench scale testing that will lead to final plans for field scale demonstration.
- Implement field scale demonstrations of surface application of amendments to treat perchlorate-contaminated soils.
- Evaluate feasibility of *in-situ* bioremediation of the vadose zone.
- Conduct batch studies to evaluate kinetics of perchlorate degradation for each carbon source tested in the field.
- Select an inexpensive and effective carbon source that will provide for rapid perchlorate reduction, specifically in soils at the LHAAP.
- Determine the maximum depth to which the soils at the LHAAP site can be treated using Composting-Biotreatment technology.

III. REFINEMENT OF TECHNOLOGY IMPLEMENTATION USING BENCH-SCALE TESTING

A series of bench-scale tests were conducted to evaluate the amount of amendment and the type of amendment that would be most suitable for the soils at LHAAP. Soil samples were obtained from LHAAP around building 25-C and transported to our laboratory. Several organic amendments including cow manure, chicken litter, cotton gin waste, methanol, molasses, and ethanol were evaluated. Table 3 summarizes the types of experiments and duration. Individual experimental procedures and their results are described in the following sections.

TABLE 3.
Summary of bench – scale experiments that were conducted to evaluate amendment-LHAAP soil interactions.[1]

Date of Exp. Start – End	Treatments
May 5, 2000 – June 14-15	LHAAP Soil+ [CM, CL, CGT, MeOH, EtOH][1]
Undated	LHAAP Soil slurry+Amendment [MeOH] Run time 31d
June 15 – July 20	LHAAP Soil slurry+[CL, CGT] Run time 35d
June 28 – July 21	LHAAP Soil slurry+[CM] Run time 22d
Undated	LHAAP Soil+[CL, CGT, Mol] Run time 3.2d
July 25	TIC and TOC on CL extracts in DI water
July 27 – Aug 4	LHAAP Soil+GW+[CL different levels] Run time 8 d
July 28	LHAAP GW+[CL] Run time = 10d

[1]Legend of symbols used:
CM – Cow manure
CME – Cow manure extract prepared by mixing raw cow manure with DI water
CL – Chicken litter [or manure]
CLE – Chicken litter extract prepared by mixing chicken litter with DI water
CGT – Cotton gin trash
DI – Deionized water
MeOH – Methanol
Mol – Molasses
GW – Ground water [from the LHAAP site]

May 5 – Experiment (Refer to Table 3)

Procedure: CME and CLE were prepared by mixing CM and CL with DI water in a ratio of 1:1 (v/v). CGT extract was prepared by mixing CGT with DI water at a 1:2 (v/v) ratio. The LHAAP soil was used in this trial. Water used in this mix was ICT-8 water from LHAAP (contains about 35 ppm perchlorate). In addition DI water was used. Samples were kept in 500 mL Erlenmeyer

flasks and allowed to sit at room temperature for 40 and 41 days before analysis. Table 4 below shows a list of treatments.

TABLE 4.
Summary of treatments and results obtained in bench-scale testing.

Tmt #	Treatment [100 mL DI water was added to each flask after treatment below was prepared]	Final Perchlorate concentration[1, 2] mg/kg	Perchlorate analysis date
1	250 g Soil + 250 mL CME	0.00	June 14
2	250 g Soil + 50 mL CME	0.26	June 15
3	250 g Soil + 50 mL CLE	0.00	June 15
4	250 g Soil + 50 mL CGT extract	0.00	June 15
5	250 g Soil + 50 mL MeOH (at 20% conc.)[3]	184.1	June 15
6	250 g Soil + 50 mL Mol	35.0	June 15
7	250 g Soil + 50 mL Diluted Mol (at 50% conc.)[3]	4.9	June 15
8	250 g Soil + 50 mL Diluted CME (at 50% conc.)[3]	0.26	June 15
9	250 g Soil + 50 mL Water [Control 1]	190.7	June 15
10	250 g Soil + 50 mL Water [Control 2]	187.4	June 15

[1]Average of 2 replicate analysis [not replicated treatment]
[2]Chromatogram says treatment – extracted with 250 mL DI water
[3]Dilutions performed with deionized water analysis showed no perchlorate.

June 15 – Experiment (Refer Table 3)

Procedure: Soil plus one gram chicken manure or one gram cotton waste plus 20 ppm perchlorate. Duplicate samples were sacrificed for perchlorate analysis at predetermined time intervals.

Results: The concentration of perchlorate in the soil slurry over a period of 35 days is shown in Figure 2. Dramatic reduction in perchlorate from 35 mg/L down to less than 1.0 mg/L within five days are seen in the chicken litter amended treatments. Thereafter the concentration remained close to zero in this treatment.

Cotton waste was less effective compared to chicken manure. The high amount of organic carbon and micronutrients in the chicken manure can be the reason for this effectiveness. Previous work has shown that in the presence of organic carbon, indigenous microorganisms are capable of using perchlorate as a terminal electron donor and transforming it to chlorate (Figure 2).

Figure 1. Influence of organic carbon (acetate) on perchlorate degradation in soils.

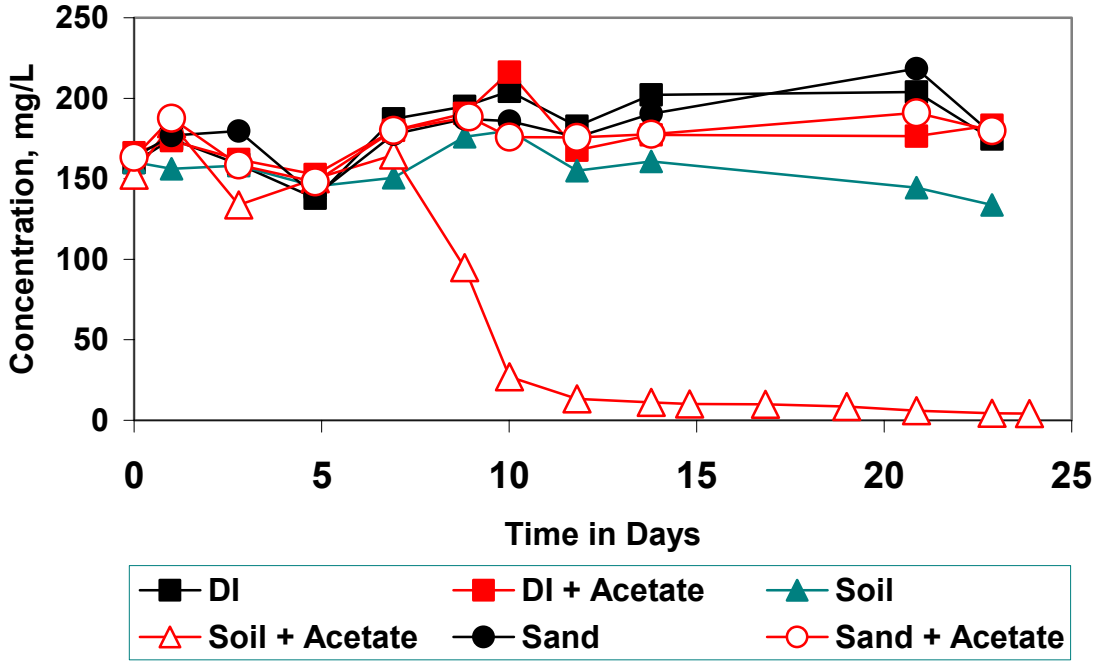
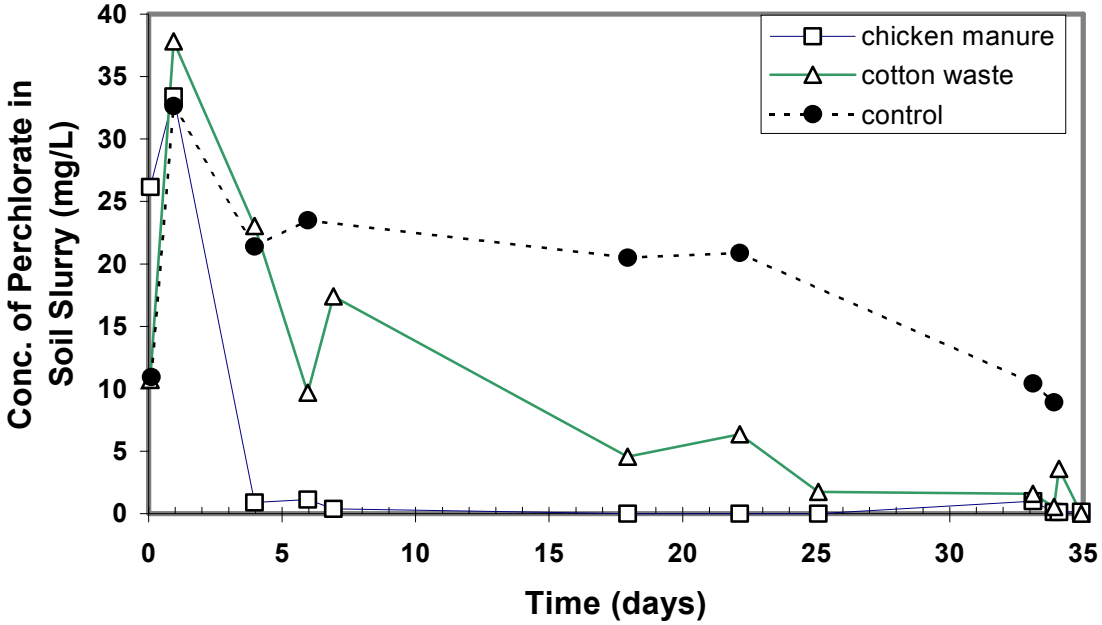


Figure 2. Biodegradation of Perchlorate
Flasks contained 25g Soil+1g Amendment, Control was Umamended

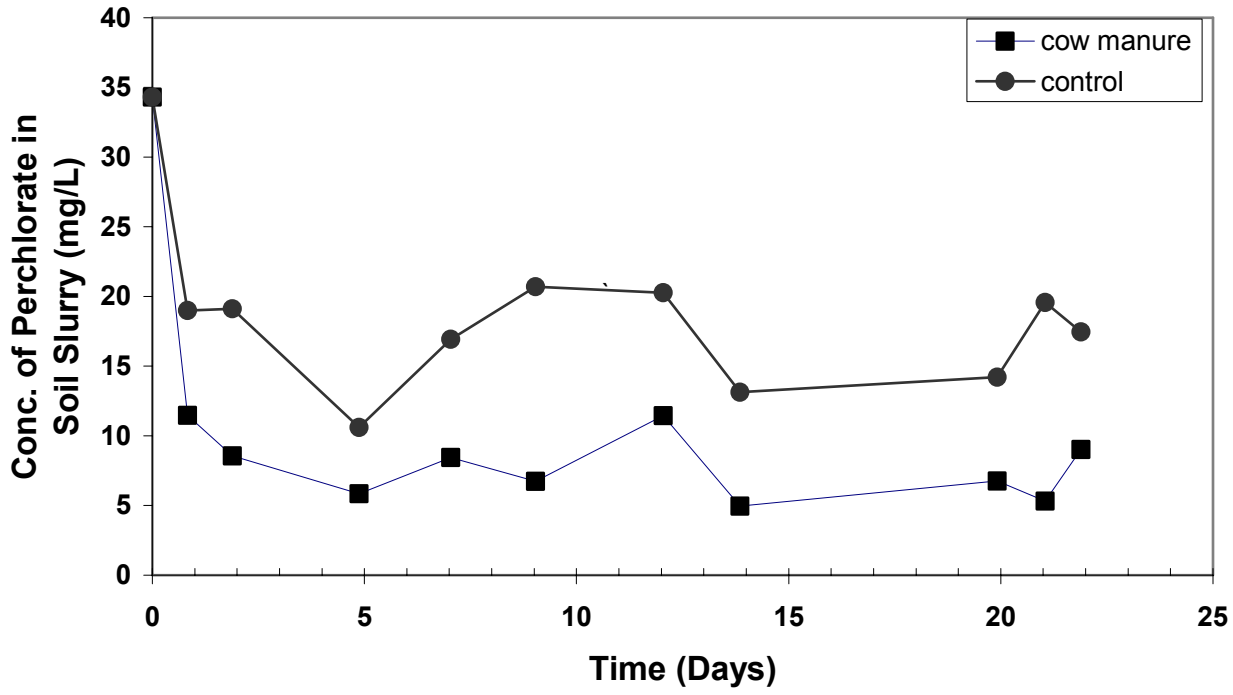


June 28 – Experiment (Refer Table 3)

Procedure: CME was prepared by mixing 500g of dry cow manure with 1 L of DI water. Treatment consisted of mixing 25 g of contaminated soil with 10 mL of CME+ ICT-8 LHAAP of perchlorate-contaminated water (34.3 ppm).

Results: Similar reduction in concentration of perchlorate is seen in the cow manure treated soil slurry (Figure 3). The concentration was reduced from initial values to stable values within three days. In the case of the control, the concentration stabilized at approximately 17 mg/L and remained at that level for the duration of the experiment. The cow manure amended treatment reduced to a lower level of approximately 7 mg/L where it stabilized (Figure 3).

Figure 3. Biodegradation of Perchlorate
Flasks contained 25g Soil + 10mL CME, Control was unamended



July 27 – Experiment (Refer Table 3)

Procedure: CME was prepared by mixing 500 g fresh cow manure with 1 L DI water. Different volumes of CME [0 to 32mL] were mixed with 25g of contaminated Soil and 25mL of GW [ICT-8]. Control was amended with DI water in a volume equal to the CME added to treatments. Flasks were incubated for eight days [July 27 - Aug 4] and analyzed.

Results:
The data obtained in the experiment is provided below in Table 5 for verification. The data have been summarized in Figure 4 following the table. The reduction in perchlorate concentration in various treatments ranged from 86.2 to 100%. In lower dosages of less than 1mL added to the sample solution (25 g soil + 25 mL GW), the removal was in the range of 86.2 to 89.5 % when compared to the controls.

At the higher dosage of cow manure extract (>2 mL per sample solution (25 g soil + 25 mL GW)), the removal was complete within the test period. There appeared to be little advantage in increasing the amount of cow manure extract added to the treatments (Table 5).

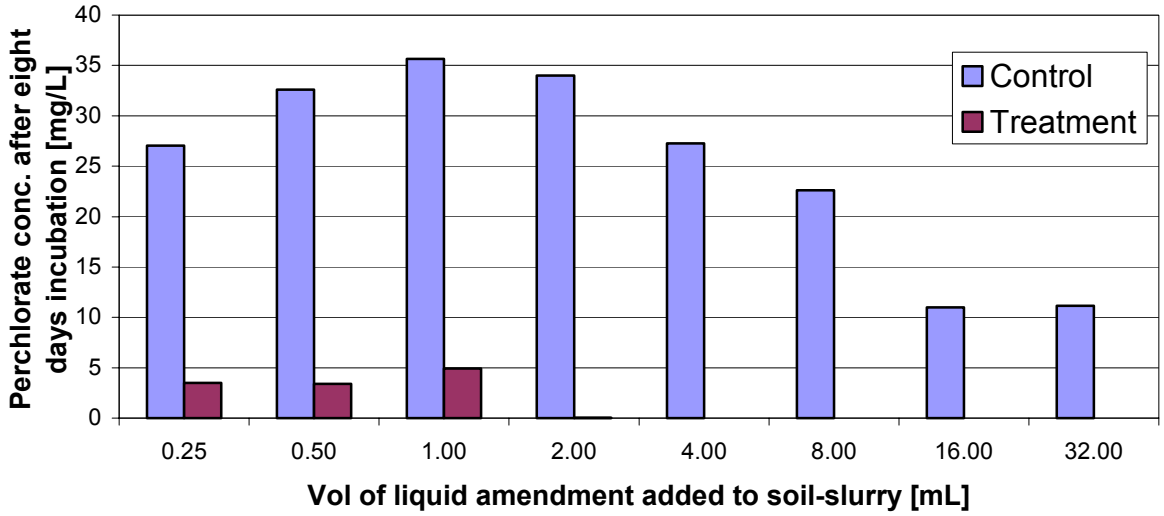
TABLE 5.
Experimental data from July 27: Treatments and concentrations

SAMPLE COMPOSITION:
25g soil (LHAAP), 25ml ICT-8, Different amounts of Cow manure and DI.
EXTRACT COMPOSTION:
Extract made from 500g of fresh cow manure and 1Liter of DI Water.
Prepared on 07/27/00,
Sampled on 8/4/00.

SAMPLE NAME	VOLUME	DILUTION	Conc. Rep1 mg/L	Conc. Rep 2 mg/L	Average Control.	Average Treatment. mg/kg
CM CONTROL1	0ml DI water	10	31.86	33.06	32.46	3.42
CM CONTROL2	0.25ml DI water	10	27.00	27.07	27.04	3.50
CM CONTROL3	0.5ml DI water	10	32.59	32.63	32.61	3.40
CM CONTROL4	1ml DI water	10	35.58	35.71	35.65	4.92
CM CONTROL5	2ml DI water	10	33.97	34.02	33.99	0.03
CM CONTROL6	4ml DI water	10	27.22	27.30	27.26	0.01
CM CONTROL7	8ml DI water	10	22.67	22.60	22.63	0.00
CM CONTROL8	16ml DI water	10	11.00	10.96	10.98	0.00
CM CONTROL9	32ml DI water	10	11.17	11.11	11.14	0.00
		TREATMENTS				
CM 1	0.25ml cow manure	2	3.42	3.40	3.41	
CM 1B	"	2	3.42	3.43	3.42	3.42
CM 2	0.25ml cow manure	2	3.41	3.69	3.55	
CM 2B	"	2	3.41	3.49	3.45	3.50
CM 3	0.5ml cow manure	2	3.40	3.36	3.38	
CM 3B	"	2	3.41	3.42	3.41	3.40
CM 4	1ml cow manure	2	6.31	6.36	6.33	
CM 4B	"	2	3.48	3.54	3.51	4.92
CM 5	2ml cow manure	2	0.00	0.00	0.00	
CM 5B	"	2	0.05	0.07	0.06	0.03
CM 6	4ml cow manure	2	0.00	0.00	0.00	
CM 6B	"	2	0.00	0.03	0.02	0.01
CM 7	8ml cow manure	2	0.00	0.01	0.00	

CM 7B	"	2	0.00	0.00	0.00	0.00
CM 8	16ml cow manure	2	0.00	0.00	0.00	
CM 8B	"	2	0.00	0.00	0.00	0.00
CM 9	32ml cow manure	2	0.00		0.00	
CM 9B	"	2	0.00	0.00	0.00	0.00

Figure 4. Effect of addition of different quantities of Cow Manure Extract on Perchlorate biodegradation



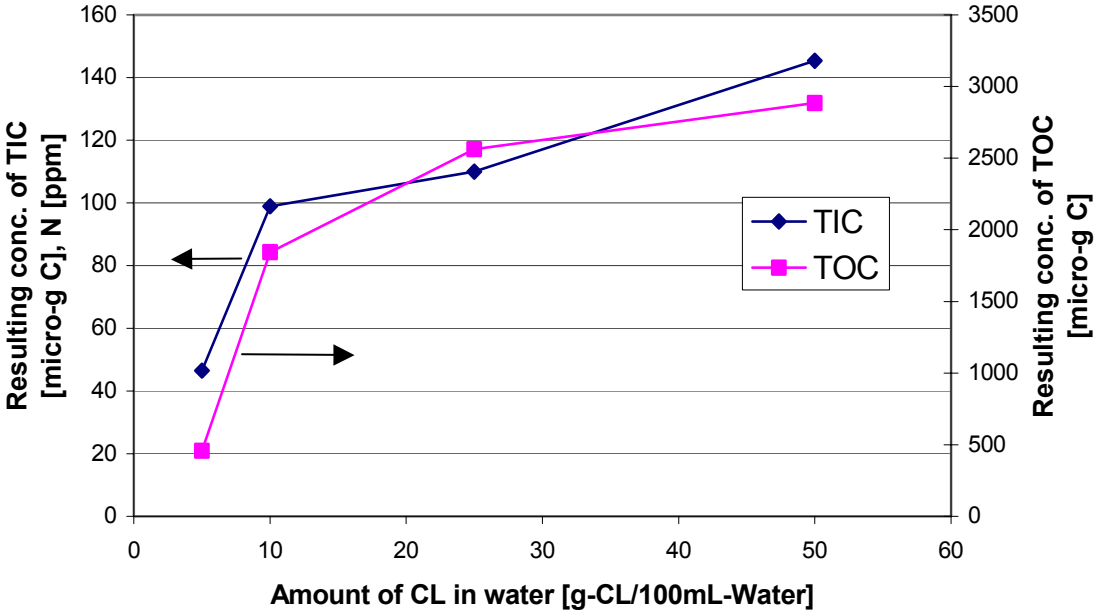
July 25 – TIC/TOC extraction experiment (Refer Table 3)

In order to determine the amount of extractable organic and inorganic carbon in the extracts, TIC/TOC were measured.

Procedure: Different quantities of fresh chicken litter was mixed with DI water to provide extractions of differing concentrations. TOC and TIC were measured on the resulting extracts. The chicken litter/water mixtures were stirred for 2 hours and then filtered with a regular coffee filter.

Results:
As expected, increasing the amount of chicken litter in the extract increased the total organic carbon (Figure 5). There appears to be a point of saturation at approximately 25 g/100 mL. The corresponding TOC extractable was 2600 μg in the 100 mL solution.

Figure 5. Extractable carbon from chicken litter at different mixture strenghts.



IV. FIELD SCALE DEMONSTRATION OF PERCHLORATE REMEDIATION

Objectives

The primary purpose of this part of the project was to determine if sub-surface microbial communities would transform perchlorate, thus demonstrating the feasibility of performing in-situ perchlorate remediation.

Pilot Scale Demonstration Procedures

The pilot scale demonstration study was conducted at a former pilot scale wastewater treatment plant on the LHAAP site and consisted of six 15 x 9 ft treatment plots and an 18 x 18 ft control plot (Figures 6, 7).

Previous soil analysis indicated that perchlorate concentration ranged from 36,200 to 144,000 μg/kg (0-2 ft). Perchlorate groundwater concentration was reported as 22,000 μg/L in one well located at 150 ft from the selected location for the field study. Forty-two soil cores were obtained from the site to determine spatial distribution of perchlorate in the soil and other soil parameters (e.g., TOC). Based on these data, cells to receive carbon source addition were identified. Each cell was tilled to ~12 inches and trenches were dug 24 inches deep to isolate each cell. An attempt to hydraulically isolate each cell was made by installing plastic liners vertically inside the trenches. Liners were hung from a metal frame grid that was installed between adjacent cells.

Solid carbon sources were added to each of the cells and mixed with the tilled soil (Figure 7), and ethanol was added with the water source. Water was added in two stages to saturate the soil down to 12 and then 24 inches. Water saturation was monitored using tensiometers installed at 12, 24, and 36 inches below land surface (Figure 8). Soil cores were periodically obtained at different depths for perchlorate analysis. In addition, oxidation-reduction potentials (ORP) were measured in multiple locations and depths in each cell. Each cell was covered during the incubation period.

Figure 6. Schematic of the pilot scale demonstration test layout.

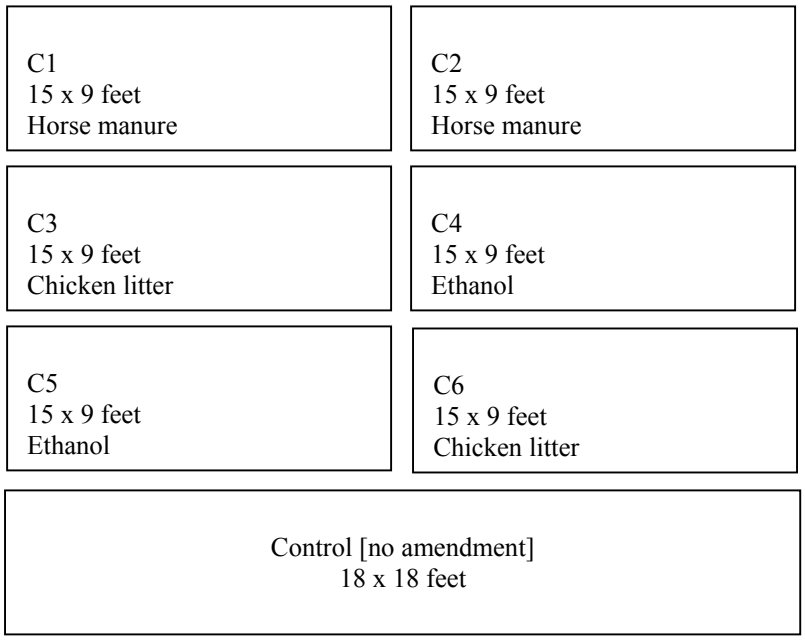


Figure 7. Photographic view of the pilot scale test layout immediately after addition of the liquid amendments.

Figure 8. Tensiometers installed in the pilot scale treatment plots.

RESULTS AND DISCUSSION

The addition of external carbon sources biostimulated the reduction of perchlorate in the site soil within 2 to 5 days. In the batch studies, perchlorate levels were typically reduced from 25-35 ppm to 0-5 ppm depending on the carbon source (Figures 1-3). Time course data for laboratory bench scale studies conducted with methanol and chicken manure indicated that these carbon sources, gave the highest perchlorate transformation rates (Figure 9). Similar data were obtained for ethanol (data not shown here). Ethanol was chosen as a carbon source due to it ease of availability and its greater efficacy to stimulate perchlorate transformation than methanol (determined from comparative studies conducted with different concentrations of ethanol and methanol).

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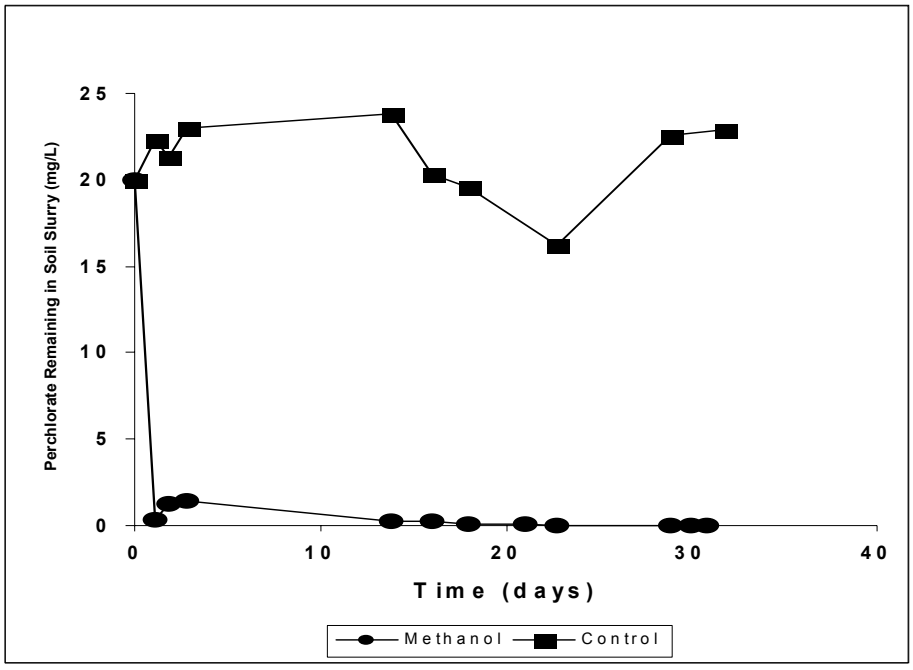
IGURE 9. Effect of methanol on the transformation of perchlorate in batch reactors using LHAAP site soil.



The LHAAP site soils at the pilot study location are characterized as silty clay (Richards, 1965). Tensiometers installed at different depths confirmed saturation to 0.91 m (3 ft) bgs. Negative oxidation-reduction potential values (i.e., Eh values) were observed in treated cells, while positive values were observed in control cells. This indicates anaerobic conditions and high microbial activity in the cells that received amendments. After 3 winter months (November, December and January), the highest rate of perchlorate removal was observed at shallow depths. After 10 months, greater than 95% perchlorate removal was observed in shallow, medium and bottom layers of the wettest cells (cells # 4 and 6). (See Table 6 and Figures 10 and 11). The complete removal of perchlorate in the relatively less saturated plots occurred mostly at shallow depths (1- 2ft). A statistical analysis of the pilot study using SAS System 8.2 confirmed the following order of effectiveness:

Horse biosolids > Ethanol > Chicken biosolids > Control.

The removal of perchlorate from the silty clay LHAAP soils and sediments was influenced by the following two factors:

1. The length of time over which the cells remained saturated within the treatment depth of 0-0.91 m (0 – 3 ft).
2. The form in which the carbon source was applied: solid vs. liquid.

It was observed that while ponded water in treated cells had no detectable concentrations of perchlorate, the ponded water in the control cell showed the presence of perchlorate. This suggested that optimum conditions for biodegradation of perchlorate were not created in the control cell. Based on the HYDRUS-2D model and monitoring wells installed up gradient and down gradient of the treated cell, it was evident that the transport of perchlorate to groundwater was not likely. Therefore, the observed decrease in perchlorate concentration in the control cell was attributed mainly to the redistribution of perchlorate within the cell and not to biodegradation.

Some perchlorate transport is indicated in the top section of the plots (0-12”) due to the measured loss of perchlorate in the control (Figure 11). However, biodegradation of perchlorate is indicated due to the complete exhaustion of perchlorate in the soil treated with ethanol and chicken manure at depths of 24 and 36 inches, relative to a constant perchlorate concentration observed in the control cell at these depths. The results of this pilot study demonstrate that perchlorate-contaminated soils can be treated in a cost-effective manner by employing the techniques we have developed to deliver nutrient amendments to desired depths.

FIGURE 10. Carbon type effect on perchlorate biodegradation at different depths (0-12 in [yellow]; 12-24 in [red]; 24-36 in [blue]). Pilot scale demonstration-LHAAP in Karnack, Texas.

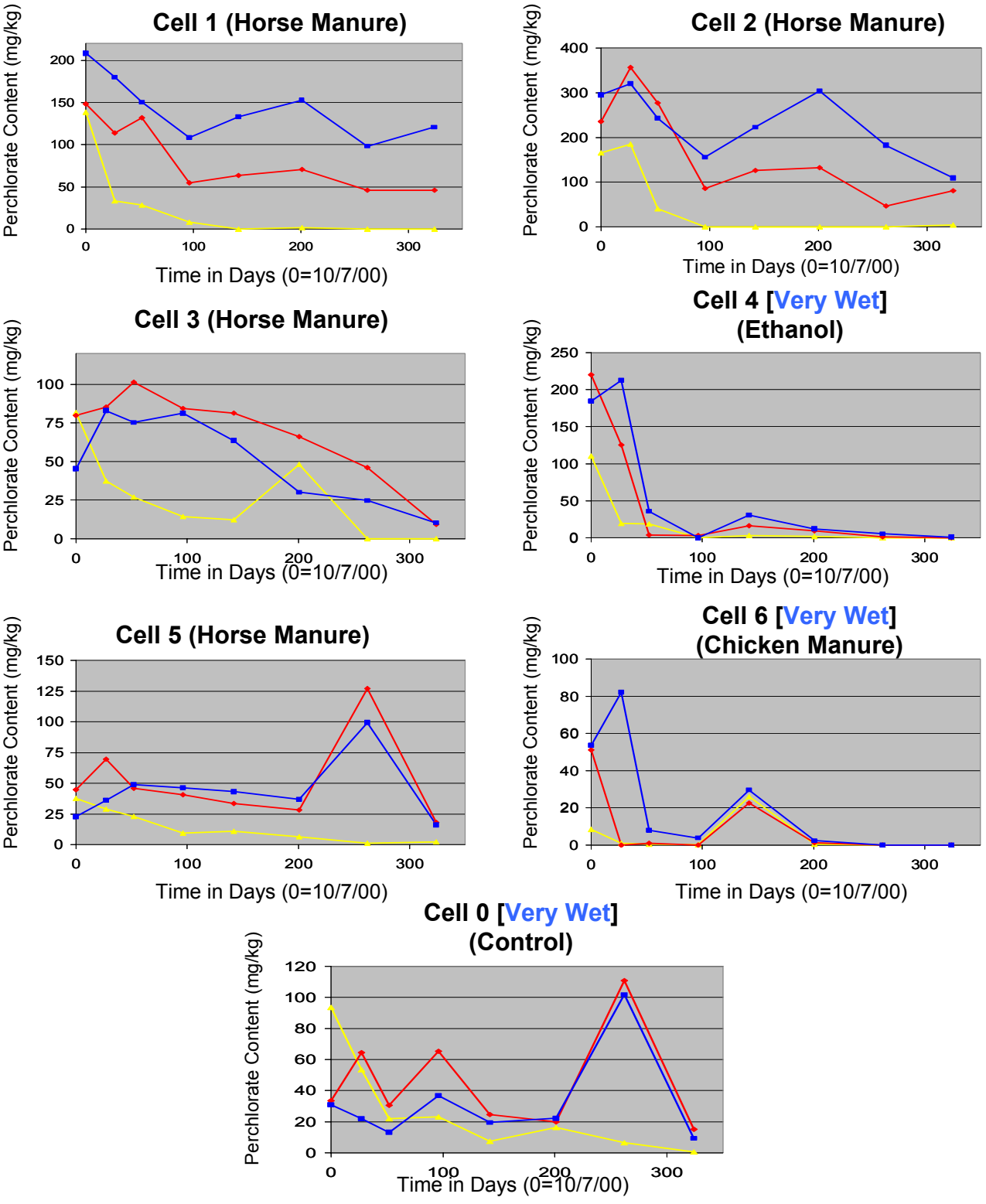
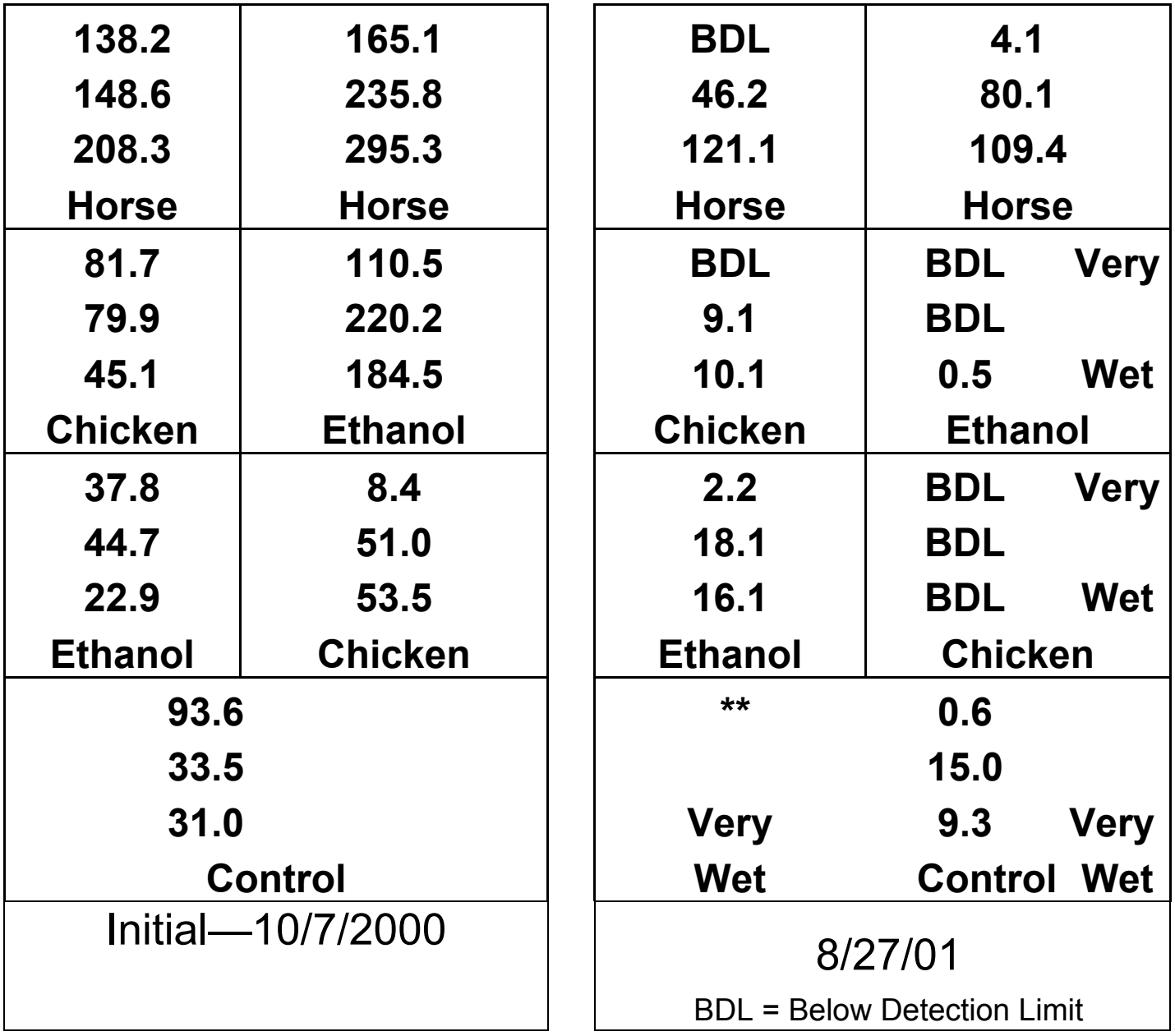
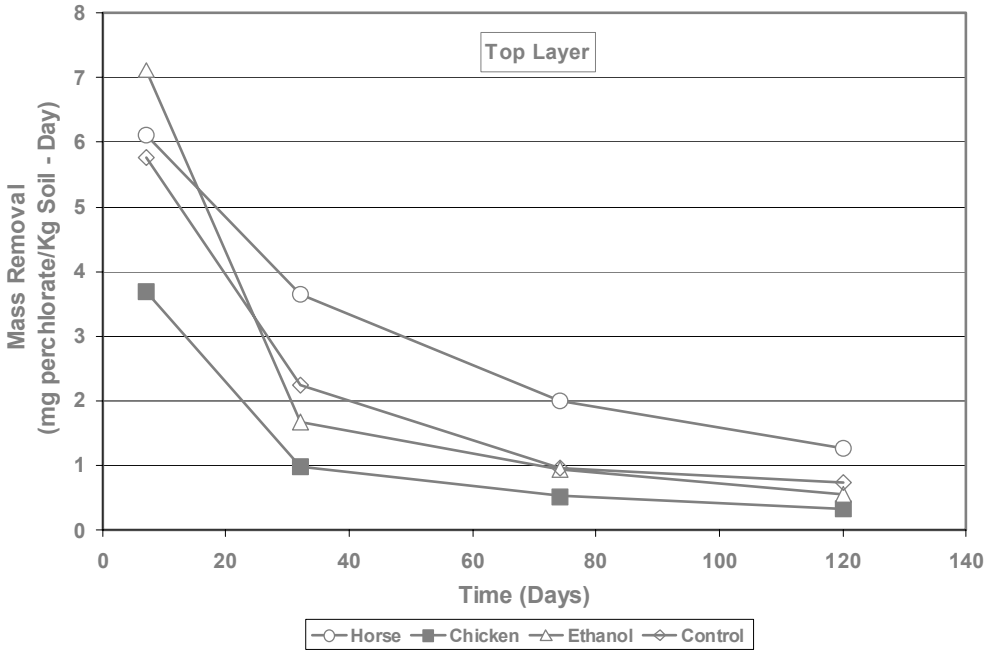


Figure 11. Baseline and final perchlorate concentrations after 10 months of treatment. Three values indicate measurements at the top, middle and bottom layers in depth.



** At the termination of the study a more even distribution of perchlorate was observed in the control but not in the treated cells.

Figure 12 [A, and B] . Mass removal from different layers within the pilot test plots over the test period of 120-days.



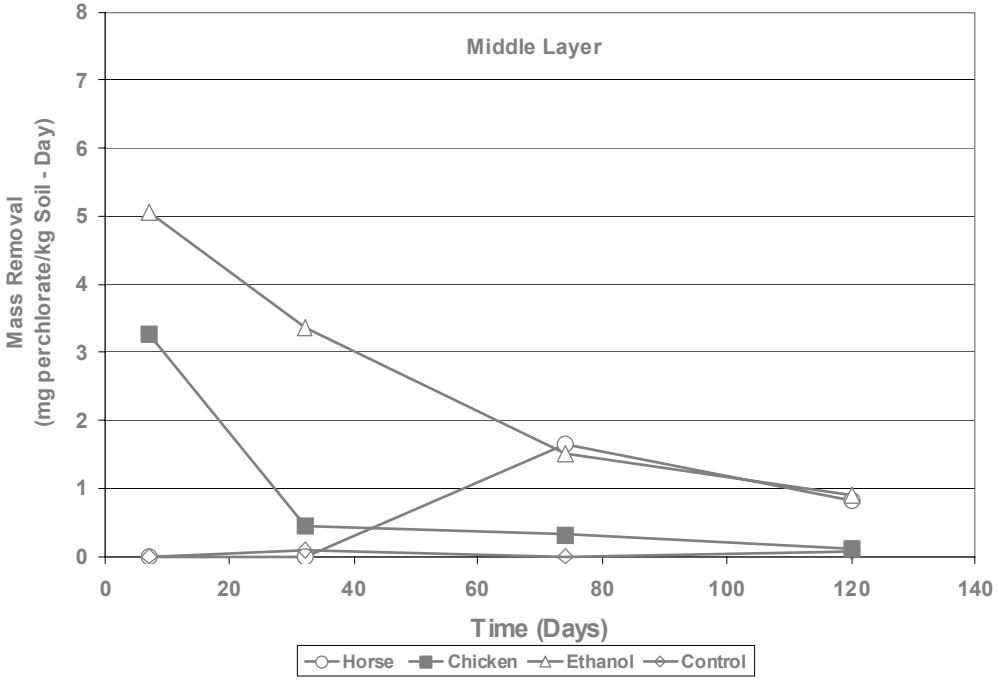
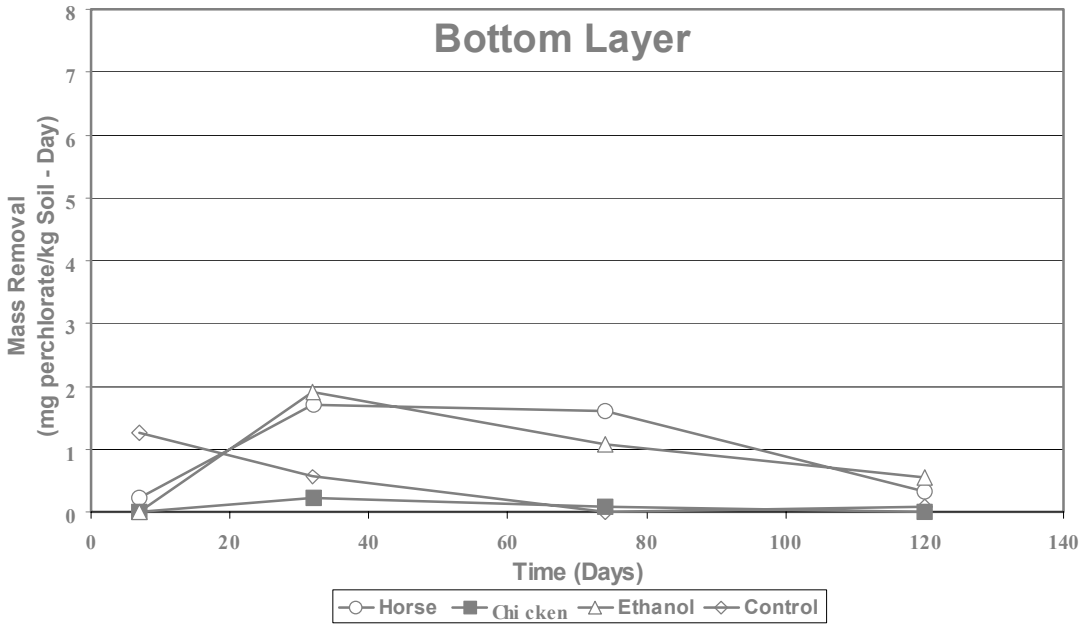


Figure 12 [C] . Mass removal from different layers within the pilot test plots over the test period of 120-days.



Figures 12 [A-C] indicate the kinetics of reduction over the 120-day duration of monitoring. In the top and middle layers, significant reduction in concentration is seen at the start of the test period. In contrast, in the bottom layer the rate of perchlorate removal [mg/kg/day] was low initially and then increased around the 30th day. This could be a result of the time required for organic carbon to reach that layer. In the initial stages, the carbon is consumed in the upper layers. Towards the 30th day, the organic carbon utilization in the upper layers has decreased, thus allowing carbon to reach the bottom layer.

Unlike the bench scale test, where chicken manure was the most effective amendment, in field tests, horse manure followed by ethanol were the most effective. One reason for this may be that that ethanol was able to disperse more easily into the soil and transport to lower layers. The manures tested were high in particulates and this could have clogged the soil pores initially, restricting organic carbon transport and biodegradation at depth. This issue needs to be addressed before further full-scale implementation.

**** control had a the smallest and very uneven distribution of perchlorate at start of study**

Plot ID	Carbon Source	Percent (%) Perchlorate Removed from		
		Top layer	Middle layer	Bottom
1	Horse manure	100	68.9	41.9
2	Horse manure	97.5	65.9	62.9
3	Chicken manure	100	88.6	77.6
4 Very Wet	Ethanol	100	100	99.7
5	Ethanol	94.3	59.5	28.8
6 Very Wet	Chicken manure	100	100	100
Control Very Wet	None	99.4**	55.1	69.8

Table 6: Percent removal of perchlorate at different depths.

V. OTHER RELATED WORK

MODELING

HYDRUS-2D was used to model water and solute transport, and perchlorate biodegradation in the vadose zone (Simunek et al., 1999). The flow equation utilized in this model is a two-dimensional variably saturated form of the Richard's Equation.

Model parameters were estimated in the following manner. A Guelph permeameter was used to determine the in-situ saturated hydraulic conductivities of the soils beneath the pilot scale location. Soil samples were collected and transported to the University of Georgia. These soil samples were utilized to further refine the saturated hydraulic conductivities using falling head permeameter methods (Lambe, 1951). Other soil samples were used to determine the water retention curves for each of the soil horizons using Tempe cells. The relationship of pressure (ψ) versus volumetric soil moisture content (θ) and hydraulic conductivity (K_u) necessary to solve the flow and transport equations were determined from the water retention curves for each soil sample using Tempe cells (Richards, 1965). The soil samples were also used to determine size fraction, cation exchange capacity, bulk density, porosity, and percent organic carbon. Biodegradation rate constants were estimated from the batch treatability studies and K_d values for perchlorate and the carbon sources determined via batch partition studies.

VI. DETERMINATION OF PARTITION COFFECIENT OF ETHANOL WITH LHAAP SOILS.

In order to determine the partition coefficient of ethanol with the LHAAP soil, a series of column studies were conducted. The evaluated transport behavior of ethanol could be used in modeling transport before further full-scale remediation. In addition, the partition coefficient can be used to directly estimate the amount of organic carbon that would be transported to defined depths based on application rates. These data and parameters would serve as design parameters when developing full-scale remediation strategies for several hundred acres.

Figures 13 and 14 show the adsorption and desorption curves for ethanol being supplied to a column of LHAAP soil. It is evident that even at very low infiltration rates, within a period of 3 to 4 days, the outlet concentration equals the inlet concentration. This indicates that the soil has very low capacity to hold organic carbon. This proposition is supported by the partition coefficient experiment (Figure 15). The calculated value of K_d based on these data is $3.1X10^{-5}$ L/kg (0.03 mL-Carbon/kg-Soil). This value appears to be much smaller than originally anticipated. Further work to evaluate the consistency and accuracy of these measurements is required.

Figure 13. Breakthrough curve of ethanol transport through a column of LHAAP soil. Inlet concentration of ethanol was 16 mg/L.

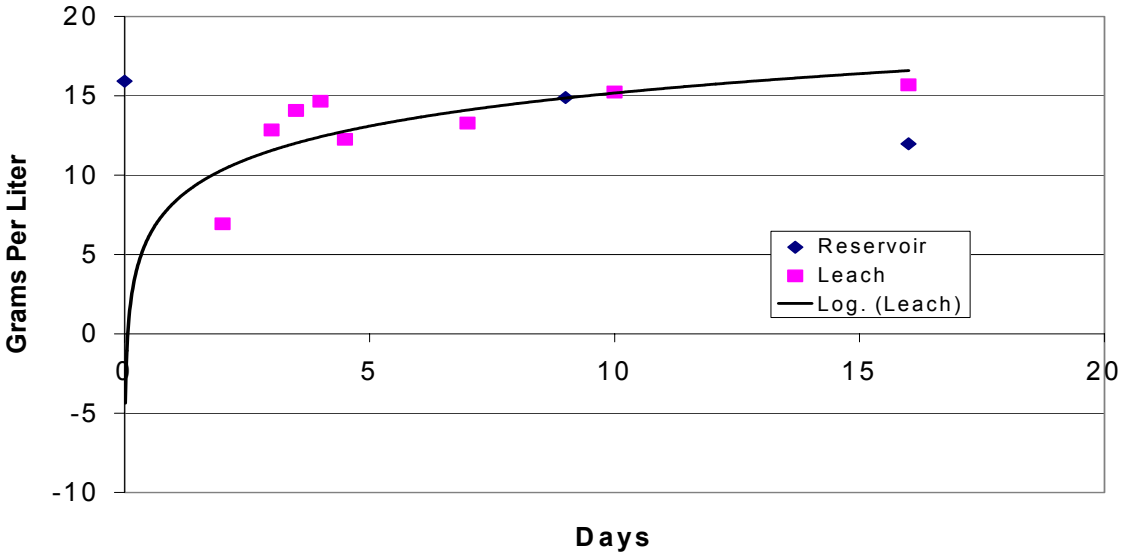


Figure 14. Breakthrough curve [Desorption] of ethanol transport through a column of LHAAP soil

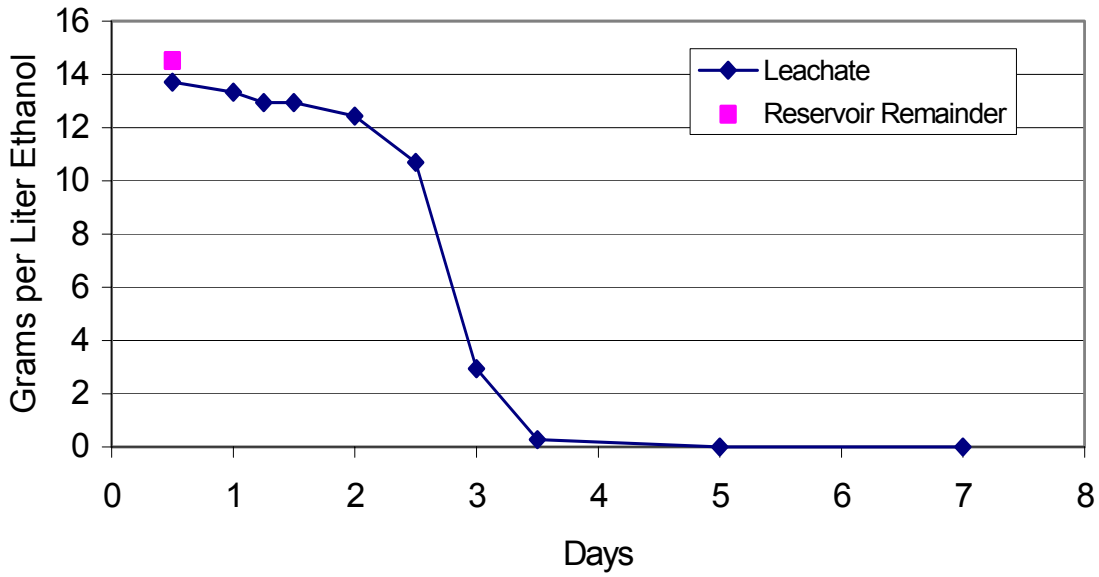
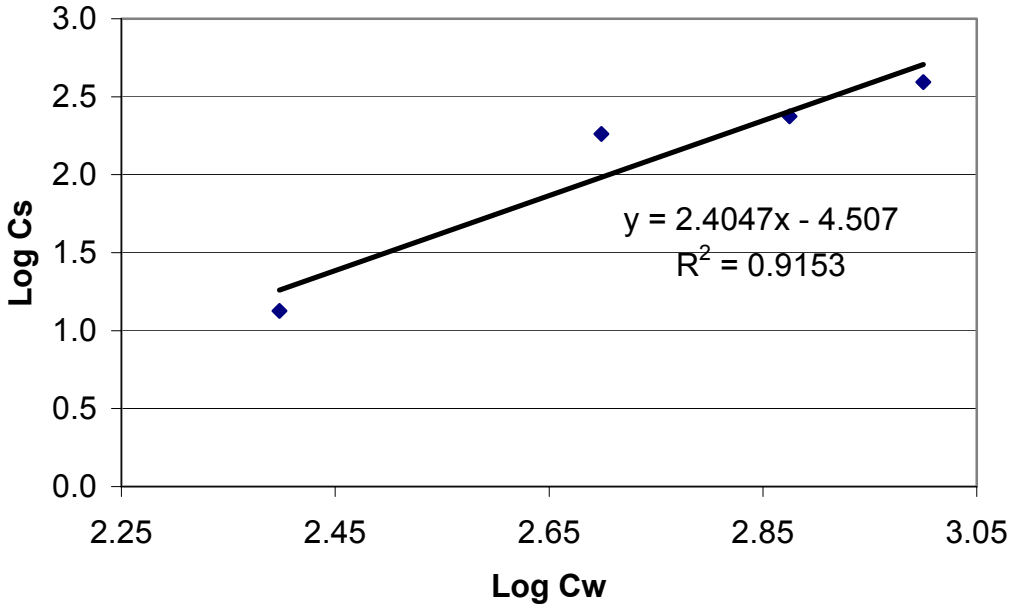


Figure 15. Freundlich isotherm for organic carbon [in ethanol] partitioning between water and LHAAP soil. EQUATION: Log C_s= Log K_d + n Log C_w is used to evaluation the partitioning coefficient K_d.



If, however, the results of these tests (Figure 15) were correct, then the strategy of supplying a continuous stream of very low concentration carbon would be required. If excess carbon is supplied, the soil's inability to absorb it will lead to lower efficiency of the system.

VII. SOIL EXTRACTION AND ANALYSIS PROCEDURES

In general, for each soil sample analyzed, six 10 g portions were weighed and placed into six extraction containers. The soil was extracted several times by homogenizing for 10 min with 100 mL of solution in a tissue homogenizer. For soils rich in organic matter (10% by weight), most of the sorbed perchlorate was desorbed using 10 mM NaOH solution. On average, three extractions were needed to completely extract the extractable perchlorate from most soils. Perchlorate is very soluble in water and does not sorb strongly to soils.

Slurry samples were sonicated for 30 minutes and allowed to cool to room temperature. The extract was separated from the aqueous-soil phase by centrifugation at 20,000 RPM for 30 minutes. The supernatant from the centrifuged samples was passed through a cartridge of prewashed activated alumina and 0.2 um Gelman Acrodisk ion membranes (Fisher Scientific, Fairlawn, NJ). These original extracts were diluted as needed before analysis by IC.

The extraction of sample and control soil samples was necessary to further verify the QA/QC of the method. Control soils would not have been exposed to perchlorate at any stage of the process. The method was validated earlier by extraction of sample and control soils dosed with $^{36}ClO_4^{1-}$ used in controlled greenhouse tests. This information was used for mass balance determination and in previous greenhouse tests, we have achieved recoveries of >92%.

VIII. PERCHLORATE MEASUREMENT PROCEDURES

Perchlorate concentration measurements in this project were conducted on water extracts using a Dionex 500 Ion Chromatograph with Conductivity Detector [IONPAC® AG11 guard column (4 x 50 mm) and IONPAC® AS 11 analytical column (4 x 250 mm)] IONPAC® AS 16 guard column (4 x 50 mm) and IONPAC® AS 16 analytical column (4 x 250 mm)

The IC is equipped with a Dionex AI-450 Chromatography Automation System and the Advanced Computer Interface Module (ACI). It has an autosampler with a holding capacity of sixty 5-mL vials. Sample injection volume of 25 µL was used for high perchlorate concentrations (ppm) or 500 uL for low concentrations (ppb). Both an IONPAC® AG16 guard column (4 x 50 mm) and IONPAC® AS 16 analytical column (4 x 250 mm) was used.

The analytical conditions developed by Dionex Corporation for analysis of low concentrations of perchlorate in drinking water and ground water by Ion Chromatography was followed. Flow rate of eluent was 1 mL/min. 50 mM NaOH solution was used for the perchlorate ion measurement. The working perchlorate concentration range will be 80-1000 ppb and the conductivity was maintained at less than 0.3 µS. The detection limit for perchlorate for the above method was 2 µg/L. The run time for this method was 15 minutes. Deionized water (resistance of 18.0 - 18.2 MΩ-CM) was used as a system blank sample to establish the baseline and to confirm the lack of

contamination in the system. Low and/or high concentration calibration curves were daily to ensure accurate quantification of perchlorate.

IX. CONCLUSIONS

Several stages of bench-scale experiments were conducted to evaluate the best organic amendment for *in-situ* soil bioremediation of perchlorate. Based on a series of column tests evaluating the transport behavior of ethanol in LHAAP soil, it appears that the soil has very low ability to adsorb carbon. This suggests that organic carbon (electron sources) can be easily transported to greater depths.

Following the initial bench scale treatability studies, a field scale test of remediation was conducted at the LHAAP site. Results show that remediation occurs with varying degrees at different depth layers. Maximum rates of perchlorate removal at the top layer during the start of the test are in the range of 6-7 mg/kg-soil/day (Figure 12A).

Initial concentrations in the test site were 8.4 to 165.1 mg/kg at the surface and 31.0 to 295.3 mg/kg at the bottom layer. After a period of 120 days, concentrations reduced to 0.0 to 0.7 mg/kg at the surface and 0 to 223.4 mg/kg at the bottom layer.

Although laboratory experiments indicated that poultry litter was a preferable amendment and had higher capacity to remediate perchlorate, the pilot test confirmed that horse manure (substitute of cow manure) and ethanol were superior amendments for in-situ bioremediation of perchlorate in LHAAP site soils.

The results of this pilot study demonstrate that perchlorate-contaminated soils can be treated in-situ by applying the techniques we have developed to deliver nutrient amendments to desired depths. We also demonstrated that the in-situ bioremediation of perchlorate-contaminated clay-rich soils could be achieved in winter, as well as summer months.