Remediation of a spill of crude oil and brine without gypsum

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ABSTRACT

The empowerment of small independent oil and gas producers to solve their own remediation problems will result in greater environmental compliance and more effective protection of the environment, as well as making small producers more self-reliant. Here, we report on the effectiveness of a low-cost method of remediation of a combined spill of crude oil and brine in the Tallgrass Prairie Preserve in Osage County, Oklahoma. Specifically, we have used hay and fertilizer as amendments for remediation of both the oil and the brine. No gypsum was used. Three spills of crude oil plus produced water brine were treated with combinations of ripping, fertilizers and hay, and a downslope interception trench in an effort to demonstrate an inexpensive, easily implemented, and effective remediation plan. No statistically significant effect of treatment on the biodegradation of crude oil was, however observed. Total petroleum hydrocarbon (TPH) reduction clearly proceeded in the presence of brine contamination. The average TPH half-life considering all impacted sites was 267 days. The combination of hay addition, ripping, and a downslope interception trench was superior to hay addition with ripping or ripping plus an interception trench in terms of rates of sodium and chloride leaching from the impacted sites. Reductions in salt inventories (36 months) were 73% in the site with hay addition, ripping, and an interception trench, 40% in the site with hay addition and ripping only, and less than 3% in the site with ripping and an interception trench.

INTRODUCTION

The smallest independent oil producers produce from the marginal or stripper wells in fields with an aging infrastructure left behind by the majors. Yet these marginal wells account for 20% of domestic crude oil production (Independent Petroleum Association of America). However, unlike the majors, there is no vertical depth to their businesses; they are totally dependent on the sale of oil and gas. They are vulnerable to the instability of crude oil prices, and

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without a technical staff, they are commonly easy prey for snake oil salesmen who promise them quick fixes or cheap solutions. The bottom line is that a critical fraction of our domestic energy needs is supplied by small businesses that are commonly operating with a thin profit margin from an aging infrastructure. A recent analysis of the Oklahoma Corporation Commission's complaint database, covering 1993–2002, revealed that, in Oklahoma alone, 620,000 bbl of crude oil and more than 1 million bbl of produced water brine were reported spilled during this 10-yr period (Fisher and Sublette, 2005). With an average total dissolved solids (TDS) of about 150,000 mg/L TDS, that is 2800 t of salt entering Oklahoma's environment each year during this period. Further analysis of the database revealed that about 80% of these spills were caused by corrosion in tanks and pipelines.

There is no doubt that these spills harm Oklahoma's environmental quality. Especially troublesome are spills of saltwater, which can result in erosion and loss of topsoil as well as salt contamination of surface waters and groundwater. This problem needs to be addressed on two fronts. The first is obviously prevention. Preventive maintenance, particularly the replacement of old gathering lines with new polymer pipes, would go a long way toward preventing these spills. However, given the instability of crude oil prices, preventive maintenance is seen by small producers as pure expense. Overcoming this perception is a matter of education concerning the economic value of being proactive. States could also help by providing tax credits or other incentives for replacing aging equipment. The second front is the development and demonstration of low-cost methods for the treatment of oil and brine spills that are easy for small producers to understand and implement. The empowerment of small independent producers to solve their own remediation problems will result in greater environmental compliance and more effective protection of the environment, as well as making small producers more self-reliant.

Here, we report on the effectiveness of a low-cost method of remediation of a combined spill of crude oil and brine. Specifically, we have used hay and fertilizer as amendments for remediation of both the oil and the brine. No gypsum was used. Gypsum typically adds significantly to the cost of brine-spill remediation because of both the cost of the gypsum and the cost of transportation and spreading. However, the effect of gypsum in mobilizing sodium from clays is manifested only to the depth to which it is applied (Robbins, 1986). Furthermore, the addition of large amounts of gypsum to the soil has the potential to interfere with phosphorous cycling (Sample et al., 1980). We propose that reducing the salinity of brine-impacted soils using hay and fertilizer will generally allow revegetation with salt-tolerant native plants in 1–2 yr. Hay increases macropores in the soil, and fertilizer addition supports biodegradation of hay, which provides products that increase the stability of soil aggregates. Plant roots exude organic compounds, increasing the stability of soil aggregates and build soil structure, which increases the hydraulic conductivity of the soil and further increases rates of

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salt removal by natural precipitation. In addition, in calcareous soils, CO_2 production from both microbial biodegradation and root respiration will increase the solubility of calcite in the soil, producing soluble Ca^{2+} displacing Na^+ from clays. Unlike gypsum, the effect of plant roots on soil structure extends to the depths of the root zone (Robbins, 1986). Salt-tolerant plants give way to less tolerant and commonly more desirable vegetation as salinity is further reduced. If crude oil is spilled along with the brine (a common occurrence), hay and fertilizer also stimulate the biodegradation of the oil by increasing oxygen penetration into the soil and providing nutrients for microorganisms.

SITE DESCRIPTION

The site used in this work is located in the Tallgrass Prairie Preserve in Osage County, Oklahoma. During the fall of 1999, three different spills of produced fluids (oil + brine) caused by corrosion in a single steel gathering line resulted in three separate lobes of contamination, which extended west from the gathering line down a slope of about 5%. The immediate effect of each spill was a loss of vegetation cover. The three contaminated sites are very close together separated by a strip of unimpacted native grass about 3–5 m (10–16 ft) wide. The amount of crude oil and brine spilled is not known, but most of the crude oil was retained in the upper two-thirds of each spill area by vegetation. The three lobes of contamination are referenced here according to their respective positions. The contaminated site, which is northernmost, is referred to as the north site (N), the one that is farthest south is the south site (S), and the third, which is between these two, is the middle site (M). The north site was the first one to be contaminated, around September 18, 1999. The middle site was contaminated between September 18 and 24, 1999, and the south site was discovered in early January 2000. An area adjacent to the south site was used as an unimpacted control. The unimpacted control is dominated by tallgrass prairie climax vegetation. The dimensions of each site are as follows: north, 80 × 7.5 m (262 × 24 ft) (600 m^2; 6458 ft^2); middle, 33 × 7 m (108 × 23 ft) (230 m^2; 2475 ft^2); south, 60 × 16 m (196 × 52 ft) (960 m^2; 10,333 ft^2).

This area of the preserve is very rocky, and the topsoil is, on average, about 15 cm (6 in.) deep at the top of the hill and thicker at the bottom of the hill. Soil textures at the site are given in Table 1. As noted above, the volumes of oil and brine spilled in each case is unknown; however, typically in this area, the water/oil ratio in produced fluids is 10–15:1. Produced water brine in this area typically has a TDS of about 105,000 mg/L (U.S. Geological Survey), and the composition of oil produced in this area is shown in Table 2. As will be discussed below, TPH biodegradation and leaching of Na^+ and Cl^- were modeled as first-order reactions, and linear regressions were performed on ln [TPH], ln [Na^+], and ln [Cl^-] vs. time data for each site. Estimates of initial TPH and brine component concentrations were obtained from the intercepts at $t = 0$. These initial concentrations with 95% confidence intervals are given in Tables 3 and 4.

REMEDIATION PROTOCOL

As shown in Figure 1, this area is extremely rocky. Initially, enough rocks were removed by hand on June 13, 2000 to allow the sites to be ripped to blend in amendments on the following 2 days. Tilling was not possible; therefore, mixing of amendments with the contaminated soil was not optimal. Amendments were added to the north and south sites as shown in Table 5 and ripped in. Hay application rates were approximately six small square bales per 100 m^2 (1076 ft^2). Fertilizers were added based on initial estimates of TPH using a field analytical method, which was subsequently shown to be unreliable. The middle site was ripped as well, but no amendments were added.

Salt must have a pathway out of the root zone if vegetation is to be reestablished. The slope of these sites provided a natural pathway for lateral movement and overland transport of brine components. However, given the significant slope of these sites, there was the potential for transport of brine components into the unimpacted areas downslope at a rate that could be damaging. To be protective of the downslope areas, an interception trench was installed at the bottom of the north and middle sites. No trench was installed at

Table 1. Soil Textures at the Brine- and Oil-Contaminated Sites

Plot	Sand (%)	Silt (%)	Clay (%)
North	29.6	45.0	25.4
Middle	34.2	41.1	24.8
South	37.7	39.6	22.7
Control	36.9	38.1	25.0

Table 2. Approximate Composition of Oil Spilled at the Study Site

Component	Percent by weight*
Aliphatics	
>C6 to C8	0.5
>C8 to C10	7.5
>C10 to C12	8.7
>C12 to C16	18.8
>C16 to C21	15.3
>C21 to C35	16.7
Aromatics	
>C7 to C8	trace
>C8 to C10	2.2
>C10 to C12	3.2
>C12 to C16	4.8
>C16 to C21	3.1
>C21 to C35	9.0

*Remainder > C35.

the bottom of the south site to determine whether the trenches had any effect on the rate of leaching of salt from the soil in the impacted areas. Trenches were about 7.5 m (24 ft) long, 0.15 m (0.49 ft) wide, and 0.6 m (1.9 ft) deep. In each trench was placed a 10.2-cm (4-in.)-diameter slotted drainage pipe covered with a polyethylene fiber sock to prevent clogging of the pipe. The whole assembly was surrounded by limestone gravel to create a highly permeable zone around the slotted pipe. A small 15-cm (6-in.) earthen berm was also constructed just below the interception trench to restrict the flow of the water. A polymer pipe 5 cm (2 in.) in diameter was used to connect the interception trench to a natural drainage area (a gully system that eventually drained into an intermittent creek). The lengths of the pipes from the bottom of the north and middle contaminated sites to the natural drainage area were about 61 and 91.5 m (200 and 300 ft), respectively. Natural precipitation was the only source of water to leach brine components from the site. Figure 2 provides monthly precipitation levels from June 2000 to August 2003 compared to historical normal precipitation. As seen in Figure 2, there were two significant periods of below-normal rainfall or drought during this experiment: July–December 2000 and June 2001 to March 2002. This leaves about 23 months with sufficient rainfall to potentially produce effective leaching of brine components from the soil in the impacted sites. Biodegradation of hydrocarbons was also likely to have been negatively affected during periods of insufficient rainfall.

SAMPLING AND ANALYSIS

Sites of this type are highly heterogeneous even after tilling. Nicknamed ''the rock garden,'' these three sites were even more heterogeneous because of the rocky conditions that prevented tilling with mixing of amendments accomplished by ripping only. To account for as much heterogeneity as possible at each sampling event, fourfold composite samples were collected from three regions of each impacted site. Each composite sample was composed of soil taken from four holes adjacent to a line perpendicular to the axis of each impacted site. Sampling lines were approximately equally spaced along the axis of the impacted sites (north sampling lines: 8.0–9.5, 32.5–33.5, and 60.5–62.0 m [26.2–31.1, 106.6–109.9, and 198.4–203.4 ft] from the pipeline; middle sampling lines: 3.5–4.5, 14.5–15.5, and 27.0–28.0 m [11.4–14.7, 47.5–50.8, and 88.5–91.8 ft] from the pipeline; and south sampling lines: 12.0–14.0, 32.5–34.0, and 59.5–61.0 m [39.3–45.9, 106.6–111.5, and 195.2–200.1 ft] from the pipeline). Samples for analysis of brine components (Na^+ and Cl^-) were collected from both the 0–15- and 15–30-cm (0–6- and 6–12-in.) depth intervals. Brine components were extracted from approximately 120 g of homogenized, oven-dried (110°C) soil with deionized water using a 1:1 ratio of dried soil/deionized water. Extracts were allowed to settle overnight and then vacuum filtered. The electrical conductivities of the extracts were used to calculate appropriate dilutions for analysis of Na^+ and Cl^- by ion chromatography (IC) using a DX-120 ion chromatograph (Dionex Corp.) (Harris, 1998). The anion buffer solution was prepared by diluting 9 mL of a 3.5:1.0 mixture of 0.5 M sodium bicarbonate and 0.5 M sodium carbonate solution to 1 L with deionized water. The cation buffer

Table 3. Estimated Initial TPH Concentrations in the Brine-Impacted Sites

Site	$[\mathrm{TPH}]_o$ (mg/kg)	95% Confidence Intervals
North	1300	130–13,000
Middle	5200	1040–27,700
South	2100	270–13,000

Table 4. Estimated initial Na^+ and Cl^- Concentrations in the Brine-Impacted Sites

Site	$[Na^+]_o$ (mg/kg)	95% Confidence Intervals (mg/kg)	$[Cl^-]_o$ (mg/kg)	95% Confidence Intervals (mg/kg)
North	1400	1130–1800	2600	1600–4160
Middle	1100	780–1600	1600	1030–2500
South	1580	980–2450	3000	2100–4200

solution was prepared by dissolving 1.9822 g of methanesulfonic acid in 1 L of deionized water. An ionPac AS14 4-mm (0.15-in.) column was used for the anions, whereas an ionPac CS12A 4-mm (0.15-in.) column was used for the cations. The calibration standards used for the IC were Five Anion Standard and Six Cation Standard (Dionex Corp.) for the anions and cations, respectively.

TPH samples were collected in the impacted areas and unimpacted control from the 0–15-cm (0–6-in.) depth interval in glass jars with Teflon-lined lids. Sample bottles were placed immediately on ice in the field and later shipped overnight cold to Continental Laboratories in Salina, Kansas, for analysis (Environmental Protection Agency 418.1).

At each sampling event, sixfold composite samples (two places each on three sampling lines) were also collected from each impacted site and the unimpacted control in a 1-gal (3.79-L) Ziploc® bag and homogenized. Composited samples were transferred to sterile Whirl-pak® bags (Fisher-Scientific) and were placed immediately on ice in the field. Samples were stored at 4°C until shipped overnight on ice to Microbial Insight, Inc. (Rockford, Tennessee) for phospholipid fatty acid analysis (PLFA). Phospholipid fatty acid analysis is based on the extraction and separation of lipid classes, followed by quantitative analysis using gas chromatography–mass spectrometry. Lipids are essential components of the cell membranes of all microbial cells. This method is superior to plate counts because both culturable and nonculturable microorganisms are enumerated and characterized. Signature lipid biomarker analysis provides quantitative insight into three important attributes of microbial communities: viable biomass, community structure, and nutritional and physiological status (White et al., 1997).

Figure 1. Close-up photo of rocks in the South impacted site. Note ink pen for scale.

RESULTS AND DISCUSSION

The Impact of Brine on Soil Microbiology

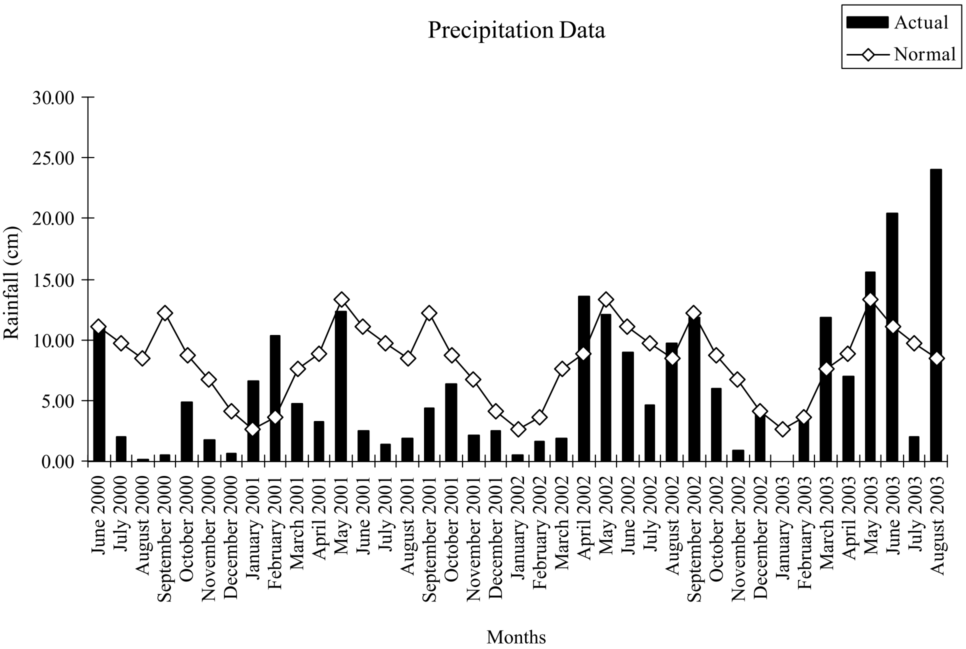
Conventional wisdom in the oil and gas industry is that a brine spill sterilizes soil. Phospholipid fatty acid analysis of soil samples from these impacted sites certainly challenges that belief. Soil microbial populations are greatly influenced by soil moisture and season, as well as a disturbance such as oil or brine contamination. Comparisons between different treatments or simply different sites can only be made with sets of soil samples taken at the same time, so that for each set, soil moistures will be similar, and seasons will be the same. A repeated-measures analysis of variance was used to

Table 5. Amendments to the North and South Lobes of the Study Site

Amendment	North	South
Hay (equivalent small square bales)*	32–36	48–54
NH_4NO_3 (kg)	90.7	45.4
P_2O_5 (kg)	7.0	3.5
K_2O (kg)	3.7	1.5

*Native prairie hay in round bales was used. Approximate conversion to small square bales is provided (8–10 small square bales per round bale).

Figure 2. Monthly precipitation levels compared to historical normal precipitation from June 2000 to August 2003.



test whether a significant difference existed between the samples in terms of prokaryotic (bacteria) and eukaryotic (fungi, protozoa, and algae) PLFA when compared for each sample date. Table 6 presents the mean concentrations of prokaryotic and eukaryotic PLFA observed over the June 2000 to August 2003 period. Also presented (Table 7) is a statistical comparison of the log-transformed means from April 2001 to August 2003 using a Tukey-Kramer multiple comparisons test. As seen in Table 7, none of the impacted sites (north, middle, and south) were different from each other at a 95% confidence level. However, the log-transformed means of prokaryote and eukaryote PLFA concentrations in the impacted sites were statistically different from the unimpacted control. Although PLFA concentrations in the impacted sites were, on average, about 50% lower than in the corresponding control samples, these concentrations represent cell counts of more than 10^8 viable cells/g dry weight of soil (White et al., 1997). The lower concentrations of soil microbes in the brine-impacted sites are not necessarily the direct result of the presence of salt alone. The lack of vegetation, particularly the root structure, caused by the brine spill also directly affects the numbers of soil microbes.

Bacteria tend to produce cyclopropyl fatty acids when cells enter the stationary phase (a period of slow or zero growth) (Guckert et al., 1986). If these cyclopropyl fatty acids and their monoenoic precursors are enumerated, a picture emerges of the overall or average turnover number in the bacterial population in a given soil sample. Overall metabolic status is given by the summation of two ratios of fatty acids derived from phospholipids (cy17:0/16:1ω7c + cy19:0/18:1ω7c). (For a description of the nomenclature for fatty acids, see www.microbe.com.) Larger values of this ratio indicate slower growth rates. Table 6 provides the mean values of this ratio for bacteria in all sites over the period

Table 6. Microbial Parameters in Impacted Sites and the Unimpacted Control

	N	M	S	Control
Prokaryote PLFA	15,300 ± 7600*	17,800 ± 12,000	17,800 ± 8100	34,000 ± 23,000
Eukaryote PLFA	2500 ± 1950	2400 ± 2000	3000 ± 1600	6200 ± 3900
Metabolic status	3.98**	3.61	3.68	2.91
Environmental stress	0.11***	0.10	0.09	0.04

*PLFA = Phospholipid fatty acids (pmol/g dry weight soil).

**Metabolic status = Mean (cy17:0/16:1ω7c + cy19:0/18:1ω7c).

***Environmental stress = Mean (16:1ω7t/16:1ω7c + 18:1ω7t/18:1ω7c).

Table 7. Comparison of the Microbial Parameters, April 2001–August 2003

Site Comparisons	Prokaryote PLFA	Eukaryote PLFA	Metabolic Status	Environmental Stress
N-M	0.45*	1.05	0.95	0.34
N-S	1.26	1.12	0.52	1.26
M-S	1.72	2.17	1.65	0.92
N-C	5.51**	6.80***	11.00***	4.81†
M-C	5.96**	7.85***	10.00***	4.47†
S-C	4.24†	5.68**	11.51***	3.55

N-M is a comparison of the north and middle sites; C = unimpacted control; S = south site as identified in the text. Values for the site were compared using a Tukey-Kramer multiple comparisons. Prokaryote PLFA, eukaryote PLFA = comparison of means of log-transformed values ($\log_{10}$ pmol/g dry weight soil); Metabolic status = (cy17:0/16:1ω7c + cy19:0/18:1ω7c); Environmental stress = (16:1ω7t/16:1ω7c + 18:1ω7t/18:1ω7c).

*q values for Tukey-Kramer, $q > 3.9$ is equal to $p < 0.05$.

**$p < 0.01$.

***$p < 0.001$.

†$p < 0.05$.

June 2000 to August 2003, and Table 7 compares these means for the period from April 2001 to August 2003 using a Tukey-Kraemer multiple comparisons test. As seen here, the impacted sites do not differ from each other at the 95% confidence level. However, the metabolic status indicators in the impacted sites are statistically greater than the control at the 95% confidence level, indicating slower growth in the impacted sites compared to the unimpacted control.

Many bacteria also respond to environmental stress with a change in the fatty acid composition of their cytoplasmic membranes, converting certain cis-monoenoics to corresponding trans-monoenoic versions to modify membrane permeability (Guckert et al., 1986). This effect is also quantified by computing the summation of two ratios (16:1ω7t/16:1ω7c + 18:1ω7t/18:1ω7c). Elevated values of this ratio reflect greater adaptation to stress. Table 6 provides the mean values of this ratio for bacteria in all sites over the period June 2000 to August 2003 and compares these means for the period April 2001 to August 2003 using a Tukey-Kraemer multiple comparisons test. As seen here, the impacted sites do not differ from each other at the 95% confidence level (Table 7). However, in the impacted sites, environmental stress indicators are statistically greater than the unimpacted control at the 95% confidence level, indicating elevated stress levels in the north and middle impacted sites compared to the unimpacted control.

The community structure of a soil microbial community is commonly reflected in the fatty acids enumerated in the PLFA analysis (White et al., 1997). Different structural classes of fatty acids are indicative of different types of bacteria and eukaryotes that make up the community. These structural classes are C16 monoenoics, C18 monoenoics, branched saturated fatty acids, midbranched fatty acids, terminally branched fatty acids, n-saturated fatty acids, and polyenoics. Using these structural groups, a cluster analysis was performed to make gross comparisons of microbial community structure in the impacted sites relative to the control during the June 2000 to August 2003 period (Figure 3). Samples taken in 2000 and 2001 from the impacted areas were similar to each other and different from the majority of the control 2001 samples. The community structures of the impacted sites were clearly impacted by oil and brine spill and subsequent loss of vegetation. However, samples taken from the impacted sites in 2003, especially the September 2003 samples (indicated by an arrow in Figure 3), had greater similarity to the control area. This demonstrates that the impacted sites have become more similar to the unimpacted control over time in terms of microbial community structure.

In summary, the presence of brine components and loss of vegetation in the impacted sites resulted in fewer soil microbes growing at slower rates and experiencing greater stress than microbial communities in the control site. Over time, community structures impacted by brine approached those of the unimpacted control as salt was leached out of the site.

Biodegradation of Hydrocarbons in the Brine-Impacted Sites

The north site was somewhat oil stained over its entire length by the original spill. After amendments were added, crude oil was detected as TPH at each sampling line in this impacted site. The south and middle sites

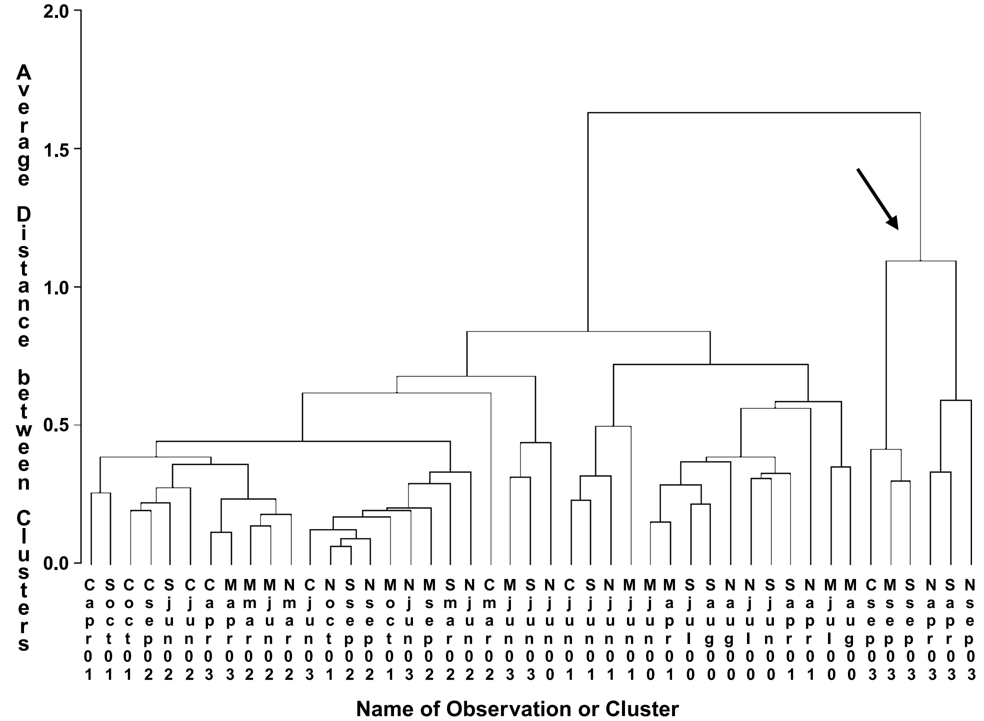


Figure 3. Cluster analysis of PLFA structural groups from samples taken from June 2000 to August 2003. Sites are designated by N (north), M (middle), S (south), and C (control, uncontaminated prairie). The sample month is indicated vertically underneath the site (apr = April, oct = October, etc.), and the sample year is underneath the sample month (00 = 2000, 01 = 2001, 02 = 2002, 03 = 2003). The arrow indicates a cluster of similar samples taken April or September 2003.

were oil stained over the top two-thirds of the sites by the original spills. Removal rates were estimated only where TPH was detected. TPH concentrations were far from uniform in any of the impacted sites at any sampling event given the heterogeneity of the original oil distribution and minimal amendment mixing. At each sampling event, an average TPH concentration was determined for each impacted site from the TPH composite samples.

Biodegradation was assumed to be the operative mechanism for removal of TPH from the impacted sites. No bloom in numbers of soil microbes was observed in the impacted sites with hay and fertilizer additions using PLFA to document viable biomass. Blooms of hydrocarbon degraders that result from the introduction of hydrocarbons or nutrients, like fertilizers, are typically documented by methods that directly enumerate culturable degraders (plate counts) or hydrocarbon-degrading activity (assays of specific genes for enzymes involved in hydrocarbon biodegradation). Phospholipid fatty acid analysis is a measure of the total culturable and nonculturable biomass in the soil. The hydrocarbon-degrading component can be a small fraction of the total soil community. In a related study, we documented a relationship between numbers of hydrocarbon degraders as determined by plate counts and TPH, but no such relationship existed between TPH and PLFA concentrations. In this related study, the hydrocarbon degraders were only about 5% of the total soil community (Sublette et al., 2002).

Biodegradation of crude oil was modeled as a first-order reaction, and a linear regression on the natural logarithm of [TPH] vs. time was performed for each site. First-order rate constants were obtained from the slopes of these lines, and estimates of initial TPH concentrations were obtained from the intercepts at $t = 0$. First-order rate constants are given in Table 8. A statistical comparison of the slopes using a *t*-test showed that there was no significant difference in the rate constants at the 95% confidence level. Therefore, treatment had no significant effect on the biodegradation of crude oil. However, TPH reduction clearly proceeded in the presence of brine contamination. The average half-life considering all impacted sites was 267 days.

Table 8. First-Order Rate Constants for TPH Biodegradation and Removal of Brine Components in the Brine-Impacted Sites

Site	TPH Removal (day^{-1})	Na^+ Removal (day^{-1})	Cl^- Removal (day^{-1})
North	$2.0 \times 10^{-3*}$	1.1×10^{-3}	1.3×10^{-3}
Middle	2.5×10^{-3}	3.0×10^{-5}	0
South	3.9×10^{-3}	5.0×10^{-4}	5.0×10^{-4}

*Student's *t*-test.

Treatment Effects in the Removal of Brine Components from Brine-Impacted Sites

Leaching of brine components from the brine-impacted sites was also modeled as a first-order reaction and a linear regression on the natural logarithm of $[\mathrm{Na}^+]$ or $[\mathrm{Cl}^-]$ vs. time was performed for each site (see Figure 4 for north as example). $[\mathrm{Na}^+]$ and $[\mathrm{Cl}^-]$ concentrations used in this analysis were averaged across each site and over the entire 0–30-cm (0–12-in.) depth interval. No significant differences between the Na^+ and Cl^- removal rate constants in the same sites were observed in any of the impacted sites (north: $t = 0.44$; middle: $t = 0.046$; south: $t = 0.02$, $p > 0.20$ for all three). First-order rate constants for the removal of brine components were compared between pairs of sites using a *t*-test. Comparisons between north, the site with the highest rate of removal of brine components, and middle, the site with the lowest rate, were significant at $p < 0.05$. Comparisons of north or middle with south, the site with the intermediate rates of removal, were not significant at $p < 0.05$.

The purpose of gypsum as an amendment in the remediation of brine spills is to mobilize Na^+ by displacing Na^+ with Ca^{2+} in clay lattices. All of the impacted sites have clay concentrations in the range of 22.7–25%. Evidently, at this clay concentration, the removal of Na^+ was not retarded by the interaction

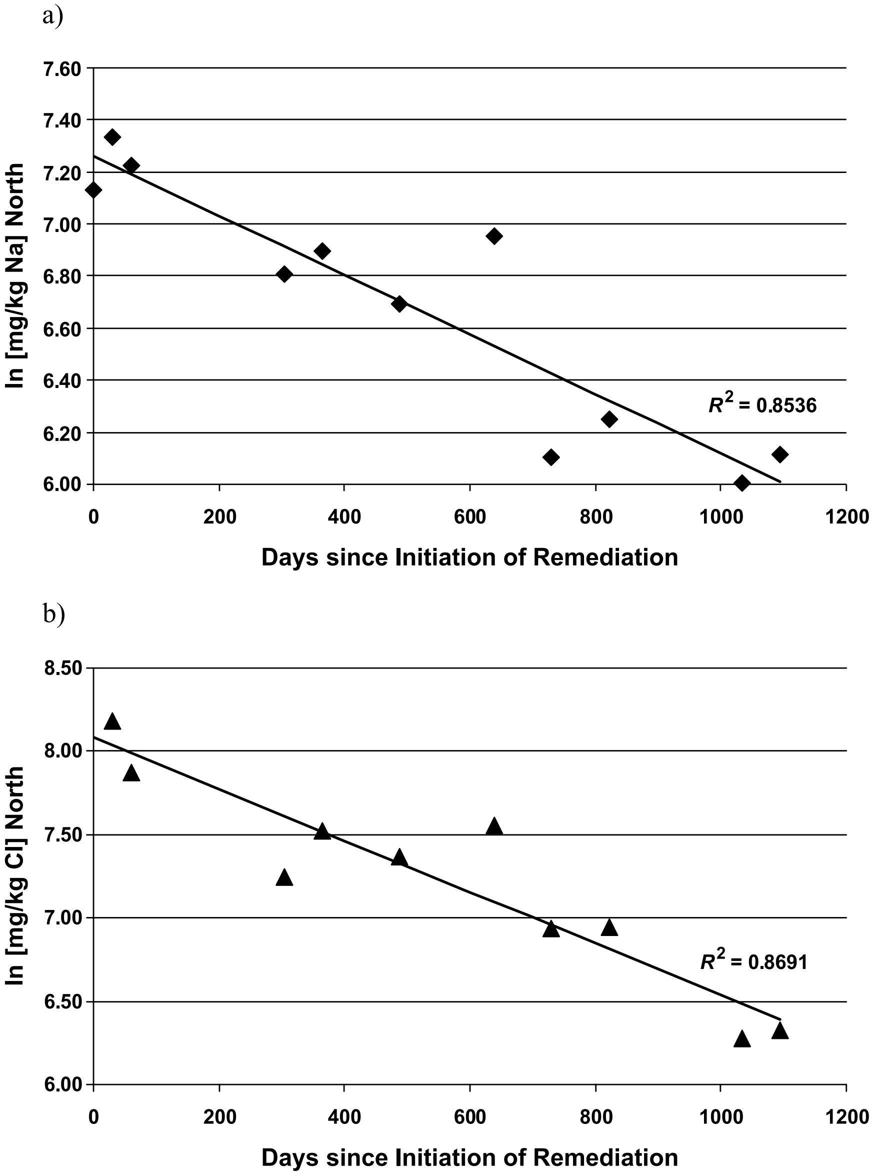


Figure 4. Leaching of (a) Na^+ and (b) Cl^- from the north site during remediation.

Table 9. Comparison of First-Order Rate Constants of Na$^+$ and Cl$^-$ Removal between Treatments

	Na$^+$ Removal	Cl$^-$ Removal
N-M	3.51*, $p < 0.05$	3.00, $p < 0.05$
N-S	1.7, $0.10 < p < 0.02$	1.91, $0.10 < p < 0.02$
M-S	0.95, $p > 0.20$	1.41, $0.10 < p < 0.02$

*Student's *t*-test.

with clay lattices because Na$^+$ and Cl$^-$ leached at comparable rates. The first-order rate constants for Na$^+$ and Cl$^-$ removal were significantly greater in the north site than in the middle site at the 95% confidence level (Tables 8, 9). Na$^+$ and Cl$^-$ removal rate constants were also greater in the north site than the south site at about the 90% confidence level. Rate constants for Cl$^-$ removal in the south and middle sites were significantly different at the 80% confidence level. Rate constants for the removal of Na$^+$ in the south and middle sites were not significantly different.

As shown in Table 5, the north and south sites differed in fertilizer application rates. Nutrients (NO_3^--N and NH_4^+-N) were monitored in all of the impacted sites and the control from March 2002 to August 2003 (Table 10). As seen in Table 10, the mean concentrations of these nutrients did not differ significantly in the impacted sites, but all were greater than in the control during this period. Therefore, during the period of most significant rainfall (Figure 2), there was little difference between the north and south sites in terms of fertilizer nitrogen concentrations, and there may have been significant transfer of nutrients from the north and south sites to the middle site by wind during fertilizer application because the sites are so close together. It must also be noted that the study site is within the bison enclosure in the Tallgrass Prairie Preserve. Bare ground attracts bison, which leave manure and urine behind as sources of organic nitrogen in the soil that are converted to NH_4^+ and NO_3^- by soil bacteria. Given these observations, no conclusions as to the effect of fertilizer addition on the remediation process can be drawn.

The data suggest that the combination of hay addition, ripping, and an interception trench at the low end of the site (north) was superior to hay addition with ripping (south) or ripping alone (no hay amendment) and a downslope interception trench (middle). Based on other work (unpublished data), we believe that the south and middle sites may continue to diverge with time, more clearly delineating the effects of hay addition in this difficult remediation environment. However, it is clear that the interception trench at the bottom of the site had a pronounced effect on the rate of both Na$^+$ and Cl$^-$ leaching with the limited mixing of amendments that characterized this site. The trench may have acted to more effectively drain the north site, resulting in greater infiltration rates following rainfall events and more effective transport of brine components. Subsurface drainage systems similar to the trench employed in this study have been shown to enhance the lateral subsurface transport of brine components during the remediation of historic brine scars (Weathers et al., 1994). The lack of a similar enhancement in the removal of brine components in the middle site, which also employed a downslope interception trench, can be attributed to the absence of the hay amendment in this site and insufficient hydraulic conductivity.

The north site experienced a 73% reduction in salt inventory (total amount of salt in the 0–30-cm [0–12-in.] interval) in 36 months without the addition of gypsum, and by August 2003, about one-third of the north site had revegetated with Bermuda grass and mixed forbs. In contrast, very little revegetation was observed in the south and middle sites, and the 36-month reductions in salt inventory were 40% and less than 3%, respectively.

Table 10. Mean Concentrations (±Standard Deviation) of Nitrate and Ammonium Nitrogen in the Impacted and Control Sites over the Period March 2002–August 2003

	NO_3^--N (mg/kg)	NH_4^+-N (mg/kg)
North	22.7 ± 10.8	9.7 ± 5.7
Middle	20.0 ± 5.1	14.8 ± 6.3
South	31.9 ± 6.8	12.3 ± 7.5
Control	2.2 ± 1.4	8.1 ± 4.4

CONCLUSIONS

Three spills of crude oil plus produced water brine have been treated with combinations of ripping, fertilizers and hay amendments, and a downslope interception trench in an effort to demonstrate an inexpensive, easily implemented, effective remediation plan. The presence of brine components and loss of vegetation in the impacted sites resulted in lower concentrations of soil microbes growing at slower rates and experiencing greater stress than communities in an unimpacted control. However, over time, microbial community structures originally impacted by brine approached those of the unimpacted control as salt was leached out of the site.

No effect of treatment on the biodegradation of crude oil was observed. However, TPH reduction clearly proceeded in the presence of brine contamination. The average half-life, considering all impacted sites, was 267 days.

The combination of hay addition, ripping, and downslope interception trench was superior to hay addition with ripping or ripping plus an interception trench in terms of rates of sodium and chloride leaching from the impacted sites.

From this study, the remediation of produced fluid spills with ripping (or tilling), hay and fertilizer addition, and an interception trench has been shown to be effective in the bioremediation of the hydrocarbons and removal of brine components. This methodology can be easily and inexpensively implemented by small independent oil and gas producers without hiring outside contractors and without the purchase, transportation, and spreading of gypsum. With access to a tractor and tiller and a local source of hay, an independent producer can remediate a 1-ac (0.4-ha) site for about $200. Hiring a contractor to remediate the site with gypsum can cost 10 times that amount. Neither of these cost estimates include the cost of an interception trench, which would depend somewhat on the topography of the site. The interception trench is basically a French drain, which can also be installed by the independent producer as needed.

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