In-situ Biodegradation of Ethanolamine in Low Permeability Soils*

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Abstract

Ethanolamine is commonly used in gas sweetening operations and in some cases, has been found in the soil and groundwater at gas plants. Ethanolamine is reported to be amenable to biodegradation. At certain sites, however, low permeability soils hamper the ability to provide microbial consortia with the necessary nutrients for metabolism. A research program was initiated at a former Edmonton area gas plant site to demonstrate *in-situ* site remediation techniques. A horizontal well was drilled at a depth of 4m below ground surface and hydraulically fractured to increase the permeability of the glacial till soils. Fractures were initiated in 12 locations with a water-based slurry. A sand propant was used to prevent their subsequent closure. Phosphoric acid was added to the well to provide a source of orthophosphate to stimulate the growth of the native bacteria. Well completion failed when the slotted PVC piping parted in tension. A second horizontal well was drilled adjacent to the first and was completed using a pre-tensioned steel cable to prevent the PVC from failing. The horizontal well and fracture network were then

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used as part of a bioventing demonstration. A network of monitoring wells was installed along the horizontal wells to test the pneumatic connection with the fracture network and to monitor bacterial respiration. Oxygen required for the aerobic degradation of the amines and glycols was provided from atmospheric air in two ways; first in a positive pressure mode employing a 1 HP blower and then by vacuum extraction using a 5 HP liquid ring pump. Field results demonstrated oxygen depletion and carbon dioxide production which indicates the presence of biological activity. Pneumatic connection between the monitoring wells and fracture network was relatively poor, possibly due to the invasion of water into the network. While preliminary site characterization did not indicate the presence of shallow groundwater, water-levels in the monitoring wells confirmed groundwater presence. Ethanolamine levels in groundwater extracted from the monitoring wells showed an overall decline in concentration while ammonia levels did not change. Ammonia is a breakdown product of amines and provides further indication of microbial degradation. However, the concentration of ammonia in the groundwater may be sufficiently high to exert a toxic influence on the soil bacteria, preventing additional degradation.

1.0 Introduction

1.1 Overview of the Research Objectives

In order to demonstrate and evaluate the effectiveness of *in-situ* technologies for remediation in low permeability media, a research program was established at a decommissioned natural gas plant near Edmonton, Alberta. The three research objectives at the field site were to evaluate the effectiveness of: drilling a shallow horizontal well, using the horizontal well to induce hydraulic fractures to increase the bulk permeability of the soils at the site, and establishing a pilot bioventing program using the induced fracture network to enhance the biodegradation of ethanolamine-impacted soil. The results from the research program will be presented and discussed after a brief introduction to the issues and the field site.

1.2 *In-Situ* Remediation and Low Permeability Soils

In-situ technologies are designed to remediate impacted soils and groundwater without the need for costly excavation and disposal. Most *in-situ* methods require access to the impacted region via the permeability of the porous media. Thus a limitation of the majority of *in-situ* techniques for the remediation of contaminated soil and groundwater is low permeability porous media. In Canada, low permeability surficial soils such as glacial tills are very common and while they vary significantly in composition, they have relatively low permeabilities (10^{-9} to 10^{-15} cm^2). As a consequence, there are many sites in Canada, which are not amenable to conventional *in-situ* remediation. One technique to improve access to impermeable soils is by inducing fractures within the porous media to serve as conduits for fluid transfer. After increasing the permeability with fractures, it is possible to apply a variety of *in-situ* remediation strategies.

1.3 Hydraulic Fracturing and Horizontal Wells

Environmental fracturing may be accomplished pneumatically or hydraulically by pumping a fluid into a well at a rate and pressure high enough to overcome the confining stress of the geologic material, resulting in a fracture that propagates into the formation (Frank and Barkley, 1995). To prevent the fractures from resealing because of overburden stress, a granular propant (e.g. coarse sand) may be hydraulically pumped into the fracture. The propant filled fractures are significantly more permeable than the formation and may then be used to deliver or withdraw fluids or other constituents from the subsurface. In this way, a much larger volume of impacted soil and groundwater may be targeted in a more reasonable time-frame. In some cases, it is possible that induced fractures will intersect natural porous media fractures, enabling access to an even larger volume of the subsurface in an interconnected fracture network.

Fracturing may be accomplished from either vertical or horizontal wells. While vertical wells are less expensive, horizontal wells can target regions inaccessible to vertical wells (e.g. under buildings or operational facilities).

1.4 Sour Gas Sweetening Operations

Produced natural gas often contains considerable quantities of acid gases such as hydrogen sulfide (H_2S) and carbon dioxide. Gas with significant H_2S concentration is referred to as sour gas. Because of its toxicity, it must be treated to remove the H_2S. Carbon dioxide must also be removed before the gas is transported to the consumer to reduce corrosion problems. One common method for the removal of carbon dioxide and H_2S is to "sweeten" natural gas using a process involving alkanolamines. Alkanolamines are organic derivatives of ammonia (NH_3) and are effective at removing acid gases (CO_2, H_2S) from natural gas because of their basic characteristics. Common types of alkanolamines used in gas sweetening include ethanolamine (also called monoethanolamine, MEA), diethanolamine (DEA), methyldiethylamine(MDEA), and diisopropanolamine (DIPA) (CAPP, 1996). There are reported to be more than 90 gas sweetening operations in Canada and an additional 394 in the United States (Sorensen *et al.*, 1999). Because of the widespread use of alkanolamines for sweetening natural gas, soils and groundwater at some gas plants have been impacted and require remediation.

1.5 Amine properties and Biodegradation

Alkanolamines like such as MEA, DEA, and TEA are high pH organic liquids which are completely miscible with water. Table 1 provides some of the physical properties of MEA. Because MEA is miscible with water in all proportions, it is free to flow with groundwater. However, Sorensen *et al.* (1997) report distribution coefficients (K_d) ranging from 2.21 to 4.91 in the pH range of 6.5-8.5. Clear trends based on pH or concentration were difficult to interpret, but K_d values in this region indicate significant sorption to sediments and therefore limited mobility. One caveat however, is that at pH values above the pK_a of MEA (9.4), MEA would be unprotonated and would likely have increased mobility (Sorensen *et al.*, 1997).

Table 1: General Physical and Chemical Properties of MEA [1,2]

Chemical Formula:	C_2H_7NO	Chemical Structure:	$NH_2\text{–}CH_2\text{–}CH_2\text{–}OH$
Molecular Weight:	61.08	Physical State @ STP:	Liquid
Boiling Point:	170.8 °C	Specific Gravity:	1.0
Freezing Point:	10.5 °C	Odor/Appearance:	Ammoniacal/colorless
Flash Point:	94 °C	Aqueous Solubility:	Completely miscible
Vapor Pressure:	< 0.13 kPa @ 24 °C	Viscosity:	24 centistokes @ 38 °C
Vapor Density:	2.11	pH of 25% aq. soln.:	12.1

[1] (IOR, 1994)
[2] (Budavari, 1996)

There are numerous reports in the literature that amines are biodegradable in both aerobic and anaerobic modes (e.g. Scarlett and Turner, 1976; Williams and Callely, 1982; Knapp *et al.*, 1996; CAPP, 1996; Sorensen *et al.*, 1997). In some cases, amines may provide both a carbon source and a nitrogen source for degradation. While there may be more than one chemical pathway governing alkanolamine degradation depending on the microorganisms present and site conditions, research indicates that both aerobic and anaerobic degradation can mineralize amines such as DEA and MEA to water, carbon dioxide, and ammonia. Figure 1 provides a proposed breakdown pathway for MEA (after Knapp *et al.*, 1996; Williams and Callely, 1982). The MEA is degraded to acetaldehyde with the evolution of ammonia. The acetaldehyde reacts in turn to form either ethanol or acetic acid which are easily mineralized in the soil to water and carbon dioxide. The ammonia, however, may accumulate or may by consumed by nitrifying/denitrifying bacteria to form nitrite, nitrate, and ultimately nitrogen gas. Ammonia speciation is dependent on pH and for water around 10°C-20°C, will be distributed as NH_4^+ at pH values of 8 or less, as a mixture of NH_3 and NH_4^+ at pH values between 8 and 11.5, and as NH_3 at a pH above 11.5. (Viessman and Hammer, 1985). This may play an important role in amine degradation because alkanolamines are basic compounds and NH_3 is significantly more toxic to organisms than the NH_4^+ species (Vershueren, 1983). Additionally, ammonia accumulation without nitrification may inhibit the degradation of amines.

2.0 Site Characterization and Program Methodologies

2.1 Site Characterization

The field site chosen to conduct research is at the location of a decommissioned gas plant. The plant was used to sweeten gas produced from a sour gas well on-site. The site is near the top of a hill with natural drainage boundaries on all sides. The boundaries include deep drainage gullies immediately to the east and west of the site which curve and join to the north of the site. To the south there is a fairly steep drop leading to a lake approximately 500m away. Gas production and treatment operations ceased in 1993 and all infrastructure was removed from the site except for one small building used for storage. The natural gas treatment operations at the site introduced amines and glycols to the surface soils on a raised fill pad at the north end of the site. These compounds migrated into the soil and are found to be within the top 4m below ground surface (bgs). The soils within this zone include a surface fill layer (0.5-1m) followed by a sandy silt with sand lenses grading to a cohesive and dense clay till approximately 3.5m bgs. During initial site characterization, augered test holes did not encounter flowing water. However, after implementation of the bioventing program, seasonal water was found to enter most monitoring wells indicating a fluctuating water table several meters bgs.

Figure 2 provides a plan-view schematic of the portion of the site relevant to this research program. The horizontal well is illustrated and trends from the northwest to the southeast at a depth of approximately 4m becoming shallower prior to exiting the ground at both ends. Monitoring nests (97-1 to 97-13) were placed to interpret the effectiveness of the horizontal well, the fractured network, and the bioventing pilot demonstration. Each of the 13 nests has two 5 cm PVC piezometers. The screened portions (0.75m screened intervals) are at approximately 2m bgs (designated as 97-1A, 97-2A, etc.) and approximately 4m bgs (designated as 97-1B, 97-2B, etc.). All the piezometer nests are placed within the screened interval of the horizontal well. The nests 97-1, 97-2, and 97-3 were intended to represent wells outside the influence of the fracture network. The induced hydraulic fractures are located in twelve 2m intervals from 4m southeast of piezometer 97-4 to approximately 4m northwest of 97-11. Figure 3 provides an illustration in a sectional view along the horizontal well. It shows the fractured region, the location of the monitoring wells and the overall concept of bioventing by either injecting air with a blower or removing it by vacuum extraction.

Figure 2 shows groundwater elevations and flow direction for high watertable conditions during the 1998 field season. The pattern of flow is radially outward from an area upgradient from the horizontal well where an earlier unrelated study had been implemented. The pattern of flow and the boundary conditions imposed by the drainage gullies and the hill suggest that the water is entering the ground predominantly through infiltration. The water present at the site may be perched on the dense clay tills approximately 3.5m-4m bgs.

Initial chemical characterization identified amines (principally MEA) and glycols (principally ethylene glycol and triethyleneglycol) emanating from the treatment pad area which was located in the area northeast of the horizontal well in Figure 2. Only the amines will be considered here. Soil sampling indicated that the MEA had migrated to the southwest. The soil analyses in this relatively small region indicated MEA levels ranging from 4 to 16000 mg/Kg, ammonia levels from 25 mg/kg to 1000 mg/kg, and pH values varying between 7.2 and 9.6. Elevated iron and manganese levels were also recorded. The soil analyses were used to choose the location for the field research program.

2.2 Field Program Chronology

The soil sampling for the field program was conducted in July of 1997 by Komex International Ltd. The initial horizontal drilling and hydraulic fracture program was completed in September 1997. Drilling was contracted to RamCor Directional Drilling Ltd., and the fracture network was installed by Frac Rite Environmental Ltd. using subcontractor Eco Scan Inc. for prediction of fracture propagation. Because of completion difficulties (discussion to follow), a second horizontal well was drilled and completed in October, 1997, followed by installation of the monitoring wells shown in Figure 2. The initial bioventing program was conducted from November 1997, to April 1998, but was hindered by excess water at the site. In April 1998, a bioventing program using vacuum de-watering was used to aerate the subsurface. After de-watering was complete, bioventing by positive pressure air injection continued until the end of the field season in September 1998. In October 1998, an aquifer test was conducted to aid in the interpretation of the groundwater issue. Extensive water sampling programs were conducted in April and September 1998, to evaluate the effectiveness of the bioventing program.

2.3 Chemical Analysis

Soil and water analyses were conducted using standard commercial laboratory methodologies by Philips Analytical Services in Burnaby, BC. Amine analyses were conducted by ion chromatography (IC). It became apparent, however, that the standard IC method was unable to properly separate ammonia and MEA when both are at high concentrations. To solve this problem, CAPP (1996) recommended the use of a Dionex C-14 column using 18-crown-6 ether added to the eluent to increase the separation between the ammonia and MEA peaks. However, the 18-crown-6 ether was found to be detrimental to the system hardware and therefore Dionex has developed an alternative column (C-15) which incorporates the 18-crown-6 ether directly into the column. This column separates the ammonia and MEA peaks well.

3.0 Results and Discussion

3.1 Horizontal Well Installation and Induced Hydraulic Fractures

The horizontal well (5 inch ID) was drilled along a 55m section of the site at a depth of 4m bgs as indicated in Figures 2 and 3. The direction and depth of the well was successfully monitored from the surface by RamCor. Note that this well, unlike some horizontal wells had an entry and exit hole. After drilling the hole from the west side of the site to the east side, Frac Rite Inc. attached their frac tool to the drill string and it was pulled back into the hole to initiate twelve fractures (F1 - F12 in Figure 3). The fractures were spaced two meters apart except for F11 and F12, which were 3m apart. Frac Rite injected a total of 3650 Kg of 20-40 mesh sand (propant) using 5200 Liters of fluid slurry to create and maintain the fractures. Fracture initiation pressures ranged from 0.5 to 1.3 MPa. In several cases (F3, F4, and F11), fracture fluid vented to the surface through the bentonite-grouted test holes used by Komex for soil sampling. Based on their operations, Frac Rite recommends that for future shallow environmental fracturing, test holes should be kept at least 5m away from the fracture zone. This may be unreasonable given the necessity for site characterization. Where necessary, test holes should be grouted with cement rather than bentonite prior to fracturing to prevent extrusion of the bentonite grout and loss of fracture fluid and pressure.

Eco-Scan Inc. was subcontracted by Frac-Rite to predict the orientation of the induced hydraulic fractures. Tiltmeters were placed in an array on the ground surface and were used to measure the ground displacement after each fracture was initiated. Computer modeling by Eco Scan Inc. predicted the magnitude and orientation of each fracture. The computer model assumes that the ground displacement is caused by the addition of a single planar fracture to the subsurface. This precludes the possibility of branched fractures. In general, the predicted fractures were found to propagate sub-horizontal (within 30° from horizontal) from the well with thickness ranging between 1-18mm. Figure 4 shows the predicted fractures superimposed on one another and placed on the site schematic. It is evident that the fracture geometry is variable and it is likely that fractures in the eastern portion may have joined to form a single, larger fracture. Predictions for fracture geometry made on a vertical test-well fractured at the site and later excavated by the University of Calgary (Alfaro and Wong, 1998) were in general agreement with the observed fracture orientations.

After the initiation of the fractures, and prior to well completion, 625 Kg of dissolved phosphate amendment was pumped into the horizontal well as a nutrient to stimulate microbial activity. Because of time constraints, it was necessary to leave the drilled and fractured well open overnight prior to completion. The next day, the drill string was re-advanced into the well. A 15 cm OD backreamer was attached to the drill string followed by the PVC well casing and a tremmie pipe to emplace a sand pack. Unfortunately, the slotted PVC pipe broke while it was being pulled into the horizontal drill hole from the east end, leaving a 17m length of PVC in the subsurface at the east end of the well.

According to the drillers, the pull back force increased substantially just prior to the break. It is interpreted that some kind of hole collapse or partial cave-in occurred, binding the PVC pipe in the drill hole. The pipe then failed in tension at the screen slots. Rather than attempt to re-drill the hole, a second well was drilled and completed at a later date approximately 1m south of the first well. It was anticipated that the well would intersect the fractures from the original well. During completion, a pre-tensioned steel cable was placed inside the PVC casing to prevent it from parting in tension. No sandpack was installed. For future installation using a non-metal casing, it is recommended that a pretensioned cable be used during installation. It is also recommended that completion of the hole be conducted immediately after the horizontal drilling and fracturing operation.

3.2 Pneumatic Connectivity of the Fracture Network

In order to test the pneumatic connectivity and increased permeability of the subsurface due to hydraulic fracturing, two methods of testing were undertaken. The first measured the pressures or vacuum at each of the monitoring points when pressure or suction was applied to the horizontal well or to individual monitoring wells in the system. The second method involved measuring the hydraulic conductivity of the subsurface.

Prior to initiating the first phase of bioventing, a vacuum was applied to the horizontal well, and in turn, to other monitoring wells to assess the pneumatic connectivity. Following this, air pressures were measured routinely in the monitoring points during the initial phase of bioventing (air injection) until the spring of 1998. Because of water infiltration, however, air connectivity in the fractures was difficult to measure. Throughout the testing matrix however, all wells except 97-1, 97-2, and 97-3 showed some response to pressures/vacuum either applied to the horizontal well or to other monitoring wells. The horizontal well had poor pneumatic connection with all the wells except 97-5b, which demonstrated a good connection with the well. This suggests that the second horizontal well did not intersect very many of the hydraulic fractures initiated in the first well or that water interfered with the connectivity.

Water levels rose ubiquitously across the site in the spring of 1998 and in some cases covered the well screens completely. Initial site characterization did not anticipate the presence of so much groundwater. The water interfered with the first phase of bioventing operations and prevented a thorough assessment of pneumatic connectivity. However, the groundwater provided an opportunity to monitor chemical composition spatially with time and a means to assess the permeability of the fracture network hydraulically. The second phase of bioventing was conducted by de-watering the site using a 5 HP liquid ring vacuum pump to withdraw water from the horizontal well and from well 97-8b. At the lowest water levels during de-watering (June 1998) all the monitoring points except for those wells outside of the fracture network (97-1, 97-2, and 97-3) showed a vacuum connection (-0.1 to <-25 KPa). These data indicate the increased connectivity in the fracture zone.

3.3 Hydraulic Conductivity

The high water levels at the site allowed an assessment of the increased hydraulic conductivity (and thus permeability) caused by the fracture network. The hydraulic assessment of permeability included: slug tests conducted on selected monitoring wells before de-watering, the water recovery curves after de-watering, and an aquifer test and additional slug tests conducted after the water levels had recovered. The analysis of the data was conducted by Komex using a variety of standard groundwater analytical techniques.

Table 2 provides a summary of the mean hydraulic conductivity results for three of the different methods used. The results are averages of a number of monitoring wells used in each of the different test methods. The aquifer test and dewatering test are long term tests (several weeks to several months respectively) and target a much larger volume of porous media than the individual slug tests. Thus the aquifer test and especially the de-watering test should give a fair representation of the bulk site hydraulic conductivity. The best data for this bulk value are the recovery tests given that they are the least impacted by local heterogeneity imparted by the fractures. The slug tests provide a more local measure of hydraulic conductivity and may indicate whether or not the fractures have contributed to an increase in conductivity.

Within the fractured area, the mean hydraulic conductivity of the slug tests for the wells measured (4B, 8A, 8B, 9B, 10B, 11B) is over twenty times the value of the aquifer test recovery mean and 45 times the de-watering test mean. This indicates that local permeability is increased in the porous media in the proximity of the fractured zone. However, it must be noted that the unfractured area slug tests along the horizontal well also gave roughly the same value as the fractured area, begging the question of whether or not the fractures really changed the permeability. To respond to this, it was only possible to conduct 2 shallow piezometer slug tests (97-1 and 97-3) in this area because the rest of the wells did not supply enough water. The deeper piezometers measured in an unfractured area upgradient were less permeable than the fractured zone wells. Additionally, only some of the wells within the fracture zone are likely to intersect fractures. The rest will have lower permeability.

Table 2: Log normal mean hydraulic conductivity results (m/s)

Media Type	Aquifer Test		De-watering Recovery	Single Well (slug) Test
	drawdown	recovery		
Unfractured Area	N/A	N/A		6.5x10[illegible]

Unfractured Area (upgradient)	N/A	N/A		$3.0x10^{-8}$
Fractured Area	$9.0x10^{-8}$	$2.9x10^{-8}$	$1.5x10^{-8}$	$7.0x10^{-7}$

To provide a different perspective, Figure 5 shows the scatter of all the measured values split into three categories. The de-watering and aquifer tests are bulked into one category called aquifer test and the others are self-explanatory. This scatter plot more easily demonstrates that the hydraulic conductivity values within the fractured region are higher than those in the unfractured region. The aquifer test values further demonstrate that the fracturing program increases permeability locally compared to background values.

3.4 Bioventing Pilot

The bioventing pilot was initially designed to stimulate the aerobic degradation of amines in the induced fracture network via aeration or suction through the horizontal well. As discussed, the presence of unexpected quantities of water and the difficulties encountered with completion of the horizontal well hampered the proposed bioventing program. Over the course of the research program, the initial design was modified to enable the study to continue. The initial bioventing program operated from November 1997 to April 1998 and involved positive pressure injection of air into the horizontal well using a 1 HP blower. When the water levels rose in the spring of 1998, the de-watering bioventing program was established. While the water hindered the initial bioventing, it provided an analytical means to test the effectiveness of the de-watering bioventing because water samples are more easily taken than soil samples. Thus a suite of samples was taken before and after the bioventing. One point that must be considered, however, is that the water may simply dissolve and dilute the contaminated region and not actually reduce amine concentrations due to bio-degradation. While this remains a critical issue, there are several lines of evidence that suggest that bioremediation occurred at the site. These will be explored.

3.4.1 Carbon Dioxide Evolution and Oxygen Depletion

The initial plans to monitor the progress of remediation were to measure the gas composition at the monitoring wells. As with most aerobic processes, carbon dioxide is produced and oxygen is consumed during the aerobic metabolism of MEA, Throughout the field program oxygen and carbon dioxide were measured using a Nova Instruments Analyzer. Normal atmospheric levels of O_2 and CO_2 are 20.9% and 0.03% respectively. Field results demonstrate that for many of the wells in the fractured region, there is a significant reduction in O_2 and a corresponding increase in CO_2. Some wells in the fractured zone had levels of O_2 below 5% and CO_2 levels as high as 13% of the gas stream. P97-1 and P97-3 on the other hand generally did not show much deviation from atmospheric levels. P97-2 did show deviation. Interestingly, P97-2 was found to contain some amines and glycols while P97-1 and P97-3 are not impacted. Therefore, the presence of groundwater contamination correlates with oxygen consumption and carbon dioxide evolution. What is not well understood is if the amines are necessarily the carbon source being used by the bioactivity.

To confirm the measured O_2/CO_2 tests and to measure rates of oxygen consumption, respiration tests were conducted on three of the piezometers (97-6A, 97-7A, and 97-11A). One set of tests was conducted shortly after piezometer installation and the other after the dewatering program. Both tests were conducted with the blower/vacuum pump turned off. Initially, the wells were aerated and bailed to ensure atmospheric oxygen levels in the well bore. An oxygen sensor (Jensen Instruments) was installed in each of the three wellbores and datalogged for a 24 hour period. Results for the first set of tests are presented in Figure 6. They demonstrate variable oxygen usage for the three wells. During the first test, the screen in 97-6A was covered in water, so only oxygen in the well bore was available and it was consumed relatively quickly. The order of the oxygen depletion rates for the three wells shown in Figure 6 reversed during the second test, indicating dynamic activity in the subsurface and a change perhaps caused by the de-watering program. Once again, there are a variety of reasons why the subsurface might act as an oxygen sink. The presence of multiple carbon sources as well as significant ammonia concentrations could all serve as mediums for oxygen consumption through aerobic degradation or nitrification.

3.4.2 Ethanolamine and ammonia levels.

As previously mentioned, the water encroachment in the bioventing system permitted a more thorough sampling program than would otherwise have been possible without extensive drilling. MEA is completely miscible with water and despite its reported sorption to soils (Sorensen *et al.*, 1997), will partition significantly into the aqueous phase. The ammonia at the pH values encountered at the site is in the ammonium ion species which is also very soluble and mobile in water. Water samples were taken before and after the dewatering bioventing program to determine if MEA degradation was occurring. According to the proposed pathways (Figure 1), ammonia should be evolved during the degradation of MEA. The concentrations ranged from below detection limit (BDL) to 36000 mg/L for the MEA and from BDL to 3700 mg/L for ammonia. Many of the samples contained levels of both MEA and ammonia that are well above levels reported to inhibit amine degradation (Sorensen *et al*, 1997) and nitrification (Vershueren, 1983). However, the site may have become acclimatized to high concentrations or degradation may be occurring at the fringe of the contaminant plume. Figure 7 presents a scatter and means plot for the MEA samples taken in wells before and after the dewatering program. Only the wells with data for both sampling programs were included. The overall mean MEA concentration has error bars that represent the 90% confidence interval. Thus we can say with 90% confidence that the overall average amine concentration was reduced during the dewatering program. In a similar plot prepared for the ammonia, there was an overall increase in the mean ammonia concentration by 300 mg/L, but no statistical difference. Thus MEA was reduced in concentration without a significant change in ammonia levels. This result suggests that dilution is not the sole mechanism for amine reduction.

3.4.3 Microbiological tests

As a final inquiry to help elucidate whether the site had biologically active organisms, several microbiological tests were conducted on groundwater taken from piezometer 97-8B. The groundwater at 8B generally has several thousand mg/kg of both ammonia and MEA. Table 3 presents results from two water samples sent to Olds College for microbial analysis by Dr. Abimbola Abiola. The first sample was collected on October 15, 1998 during the aquifer test at 97-8B. The second sample was collected on October 26, 1998 from the pumped groundwater stored in the tank at the site. Despite the high levels of ammonia and MEA in the samples, total aerobic heterotrophs and total anaerobes were found in significant numbers (10^5-10^6 colony forming units per gram). This does not necessarily mean that there are viable amine degraders in the water, but suggests that the water is by no means sterile.

Table 3: Most probable number determination of aerobes and anaerobes.

Sample Name	Anaerobic Bacteria (cfu/g)	Aerobic Bacteria (cfu/g)
October 15, 1998: 97-8B	3×10^5	3×10^5
October 26, 1998: 97-8B	5×10^5	4×10^6

As a test to try and categorize the types of bacteria present at the site, Biological Activity Reaction Tests (BART^{TM}) donated by Droycon Bioconcepts Inc. were used (Droycon Bioconcepts Inc., 1998). The BART^{TM} kits are tests which indicate the presence and approximate enumeration of different types of bacteria. Test types included heterotrophic aerobic bacteria, nitrifying bacteria, denitrifying bacteria, iron related bacteria and sulfate reducing bacteria. Two samples were used. The first sample was collected on October 15, 1998 from 97-8B shortly after starting the aquifer test. The second sample was collected from 97-8B on October 16, 1998 after 25 hours of pumping. Results are displayed in Table 4 and indicate widespread microbial activity in the groundwater except for nitrifying bacteria. This is consistent with the ammonia accumulation at the site since nitrifiers are necessary for the transformation of ammonia to nitrite and nitrate. It does raise the concern, however, that successful mineralization of MEA will not necessarily remediate soil and groundwater because of ammonia accumulation. As a secondary remedial step, it may be necessary to stimulate nitrifying organisms to ensure the complete minearalization of both amines and ammonia.

Table 4: Biological Activity Reaction Test (BART^{TM}) Results

Sample Name (97-8B)	Heterotrophic Aerobic Bacteria (cfu/mL)	Nitrifying Bacteria (cfu/mL)	Denitrifying Bacteria (cfu/mL)	Iron Related Bacteria (cfu/mL)	Sulfate Reducing Bacteria (cfu/mL)

Oct. 15, '98	10^6	No activity	10^6	$> 10^5$	10^3
Oct. 16, '98	10^6	No activity	10^6	$> 10^5$	10^2

4.0 Conclusions and Recommendations

A field research program was conducted at the site of a decommissioned natural gas sweetening plant to demonstrate the use of a combination of *in-situ* remediation methods. A shallow horizontal well was used to hydraulically induce twelve sand-filled fractures in the subsurface to increase the overall permeability of the porous media. The fractures were successfully introduced into the subsurface and were demonstrated to increase the overall permeability of the fractured region by at least one order of magnitude. Tensile failure of the PVC casing in the initial horizontal well was avoided in a subsequent well by using a pre-tensioned steel cable to reduce tension on the PVC during completion. The second well was not fractured and had relatively poor connectivity to the fracture network. While horizontal wells may provide an efficient means of installing a fracture network, fractured vertical wells may carry less risk of losing access to the whole network during well completion. Bioventing at the site was hindered by unexpectedly high water levels, but a subsequent dewatering bioventing program demonstrated a reduction in MEA concentration. Oxygen depletion, carbon dioxide production, and ammonia accumulation provide evidence of MEA biodegradation. Microbial activity in water samples is moderately high and indicates that despite the high levels of ammonia and MEA, the water is not toxic to all organisms. Bacterial testing provides preliminary evidence that nitrification is not occurring in the groundwater. This may prevent the assimilation of ammonia at the site and must be considered for the bioremedition of this site and others impacted with alkanolamines.

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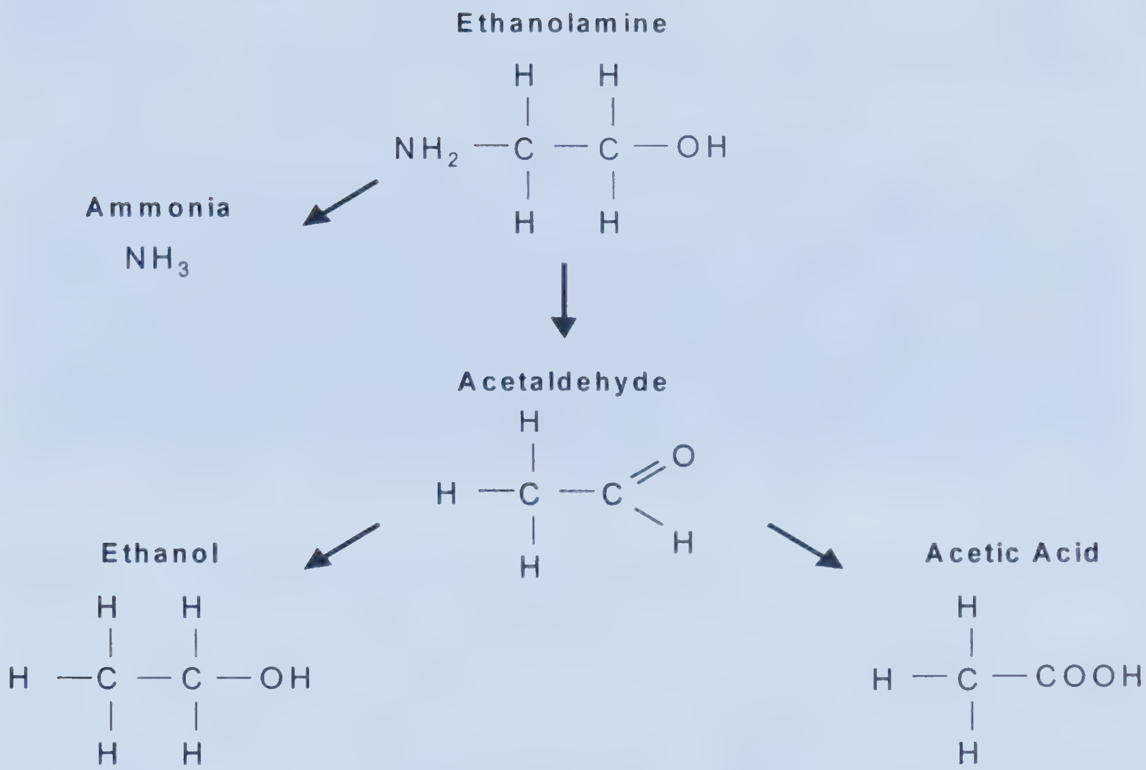

Figure 1 Proposed ethanolamine degradation pathway
(After Knapp *et al*., 1996; Williams and Callely, 1982)

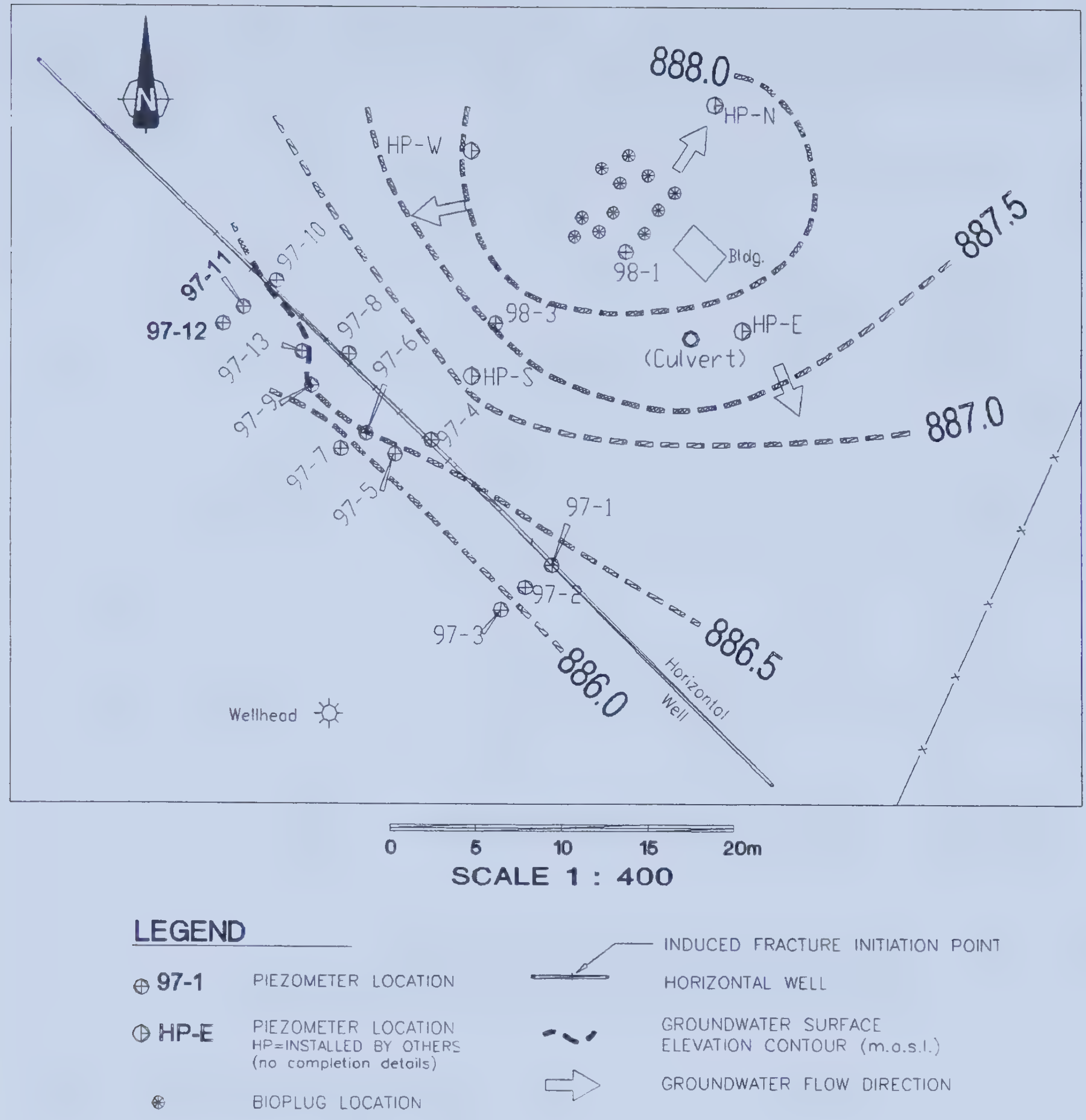

Figure 2 Field Site Schematic

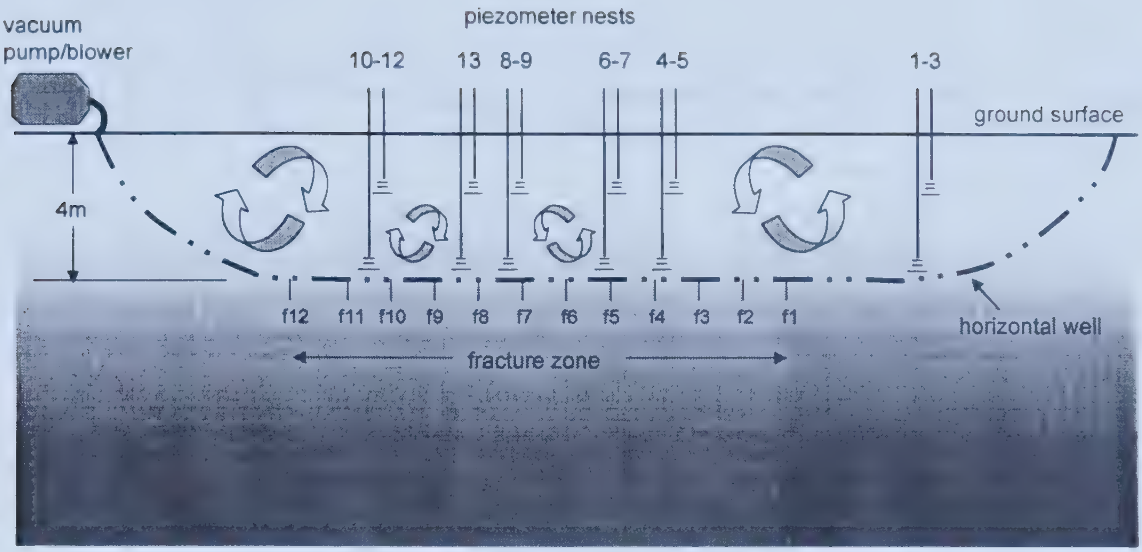

Figure 3 Sectional View Along the Horizontal Well

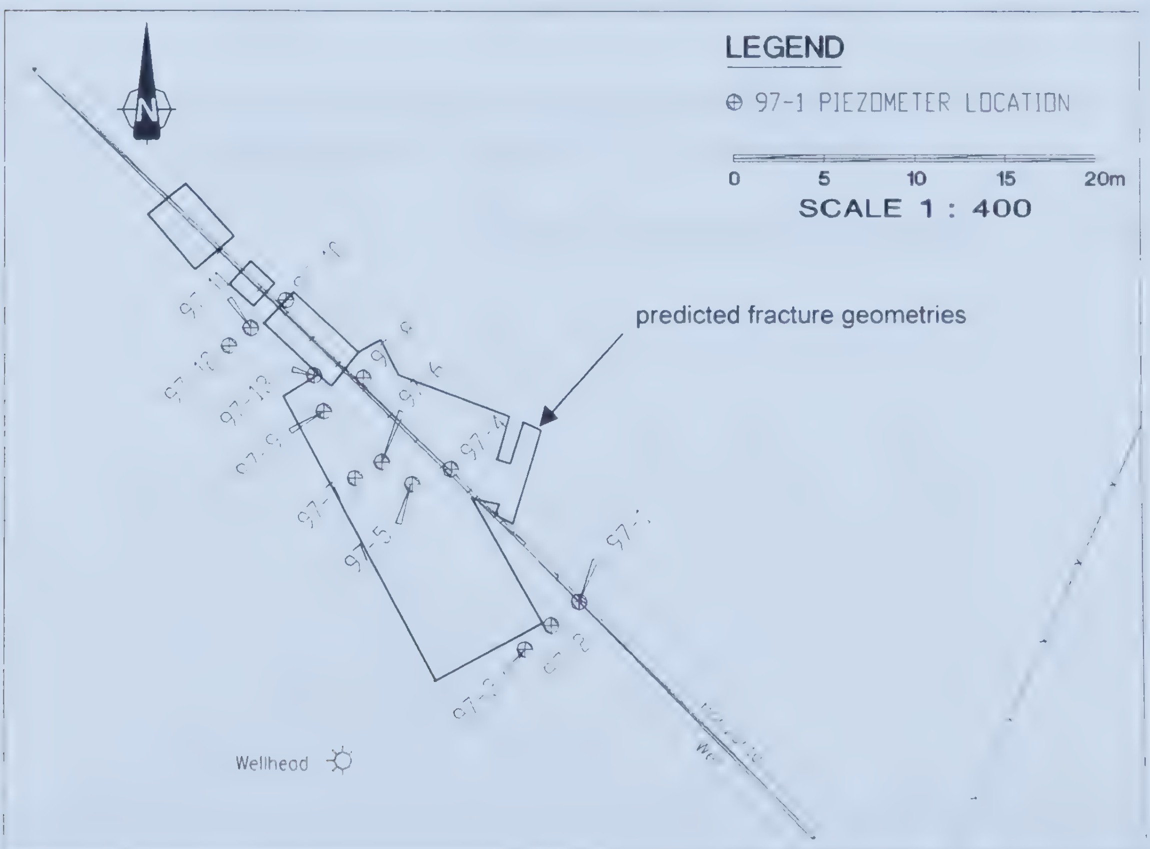

Figure 4 Predicted Fracture Geometries

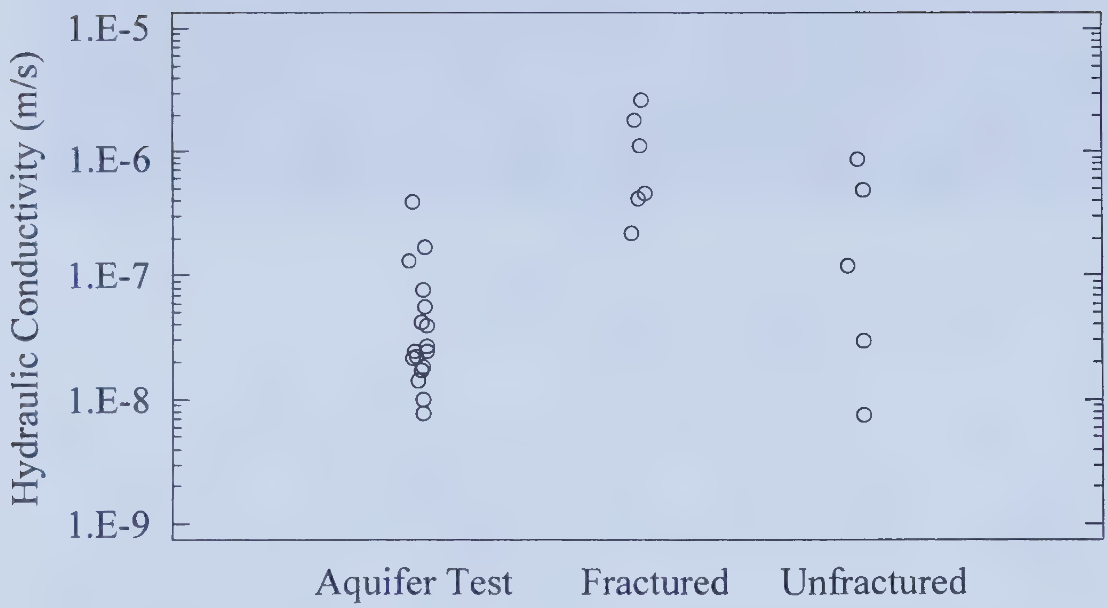

Figure 5 Hydraulic Conductivity Scatter Diagram

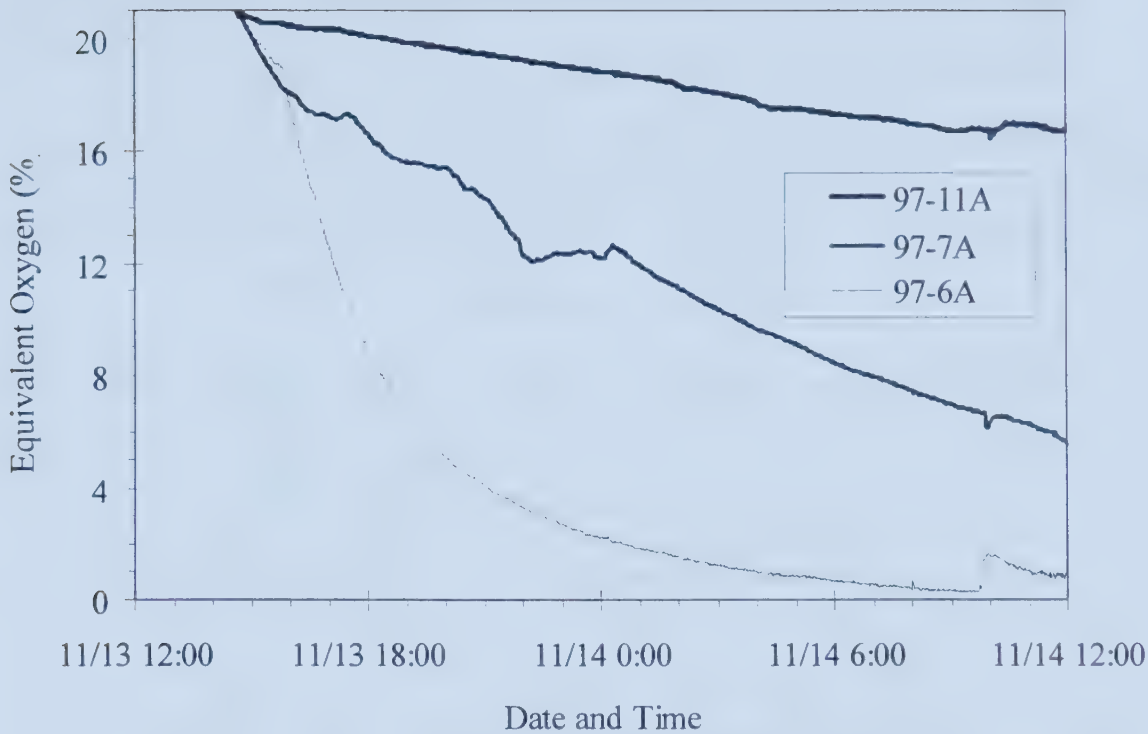

Figure 6 Oxygen Depletion Curves Measured during Initial Bioventing Program

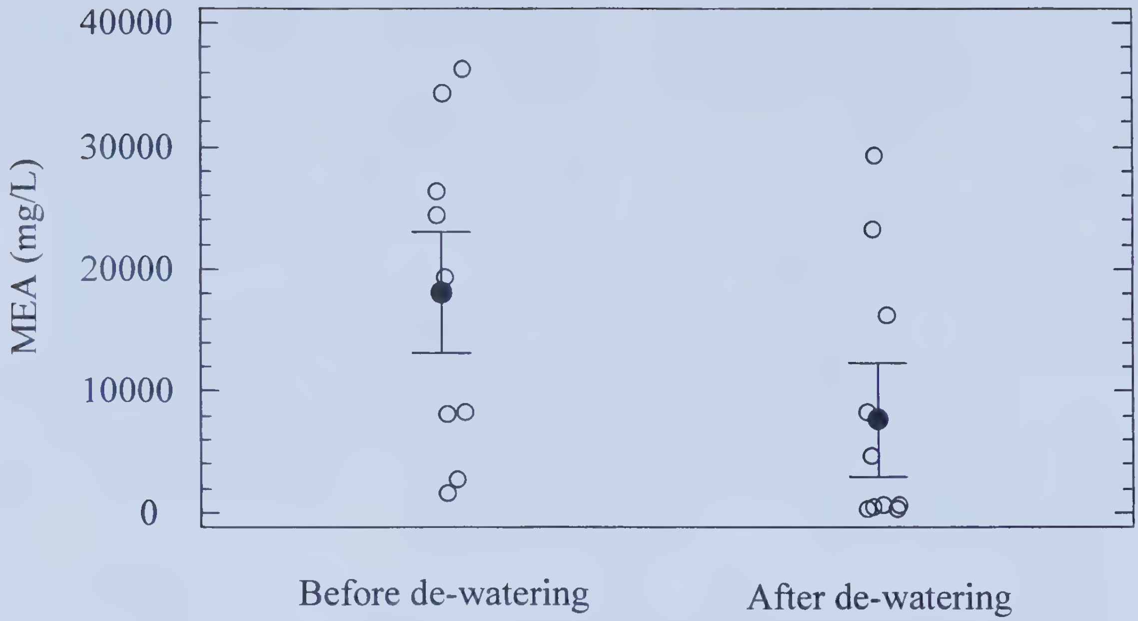

Figure 7 MEA Concentrations Measured before and after De-watering Program

Perspectives in Land Reclamation and Restoration

Presented by:

Canadian Land Reclamation Association/
Association Canadienne De Réhabilitation Des Sites Dégradés

Saskatchewan Environmental Industry and Managers Association

Including the Canadian Land Reclamation Association's
24th Annual Meeting

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Conference Program / Table of Contents

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