

Biodegradation of monoethanolamine in soil monitored by electrical conductivity measurement: an observational approach

R.C.K. Wong, L.R. Bentley, A.W. Ndegwa, A. Chu, M. Gharibi, and S.R.D. Lunn

Abstract: Monoethanolamine (MEA) is commonly used by the natural gas industry to remove acid gases from the natural gas stream. A series of pan test studies was conducted to examine the biodegradability of MEA in soil recovered from a decommissioned sour gas processing plant site. Test results indicate that MEA was successfully biodegraded or transformed into simple compounds under aerobic and anaerobic conditions. The electrical conductivity (EC) of the soil evolved with changing chemical conditions of its by-products during degradation of MEA. Based on experimental observations, five ranges of EC were correlated with five geochemical zones consisting of various concentrations of MEA and its by-products. The five ranges of EC were translated into equivalent in situ EC ranges. Using these in situ EC ranges, an electrical resistivity tomography image was used to create a geochemical interpretation of the subsurface beneath the plant site. The geochemical interpretation can provide useful information for detailed site assessment and remediation design.

Key words: electrical conductivity, biodegradation, monoethanolamine, ammonia, acetate, electrical resistivity tomography, site characterization, observational approach.

Résumé : La monoéthanolamine (MEA) est utilisée couramment par l'industrie de gaz naturel pour enlever les gaz acides des sources de gaz naturel. On a réalisé une série d'études au « pan tests » pour examiner la biodégradabilité de la MEA dans le sol récupéré sur le site d'une usine de traitement de gaz acide abandonnée. Les résultats des essais indiquent que la MEA a été biodégradée avec succès et transformée en des composés simples dans des conditions aérobieques et anaérobiques. La conductivité électrique (EC) du sol a évolué avec les conditions chimiques changeantes de ses sous-produits au cours de la dégradation de la MEA. En partant des observations expérimentales, on a corrélié cinq plages de EC avec cinq zones géotechniques consistant en diverses concentrations de MEA et de ses dérivés. Les cinq plages de EC ont été traduites en des plages équivalentes de EC. En utilisant ces plages de EC in situ, on a utilisé une imagerie tomographique de résistivité pour créer une interprétation géochimique de la surface souterraine sous le site de l'usine. L'interprétation géochimique peut fournir de l'information utile pour l'évaluation détaillée du site et la conception de la rémédiation.

Mots clés : conductivité électrique, biodégradation, monoéthanolamine, ammoniac, acétate, tomographie en résistivité électrique, caractérisation de site, approche observationnelle.

[Traduit par la Rédaction]

1. Introduction

Monoethanolamine (MEA) is a common chemical used by the natural gas industry to remove acid gases from the natural gas in a process called sweetening. Electrical resistivity tomography (ERT) (Wong and Alfaro 2001; Bentley et al. 2001) images from surveys conducted at the site of a decommissioned natural gas plant were found to delineate zones of

high electrical conductivity (EC) that were associated with MEA, glycol, and their degradation products. Time-lapse ERT images show that the in situ electrical conductivity profiles changed with time (Bentley et al. 2001). It was postulated that these EC changes were due to in situ transport and chemical evolution of MEA, glycol, and their degradation products (Mrklas et al. 2001). Consequently, a laboratory program was initiated to investigate the degradation path-

Received 7 April 2003. Accepted 13 April 2004. Published on the NRC Research Press Web site at <http://cgj.nrc.ca> on 27 October 2004.

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Table 1. Summary of pan test study.

Test label	Soil batch	Treatment details
R1-SOIL-1, R1-SOIL-2	1	Site contaminated soil of batch 1 used; aerobic degradation at room temperature
R1-PADD-1, R1-PADD-2	1	KH ₂ PO ₄ added to site contaminated soil of batch 1; aerobic degradation at room temperature
R2-SOIL-1, R2-SOIL-2	1	Site contaminated soil of batch 1 used; aerobic degradation at room temperature
R3-SOIL-1, R3-SOIL-2	2	Site contaminated soil of batch 2 used; aerobic degradation at room temperature
R3-COLD-1, R3-COLD-2	2	Site contaminated soil of batch 2 used; aerobic degradation at 5 °C
R3-SHFT-1, R3-SHFT-2	2	Site contaminated soil of batch 2 used; alternating aerobic–anaerobic degradation at room temperature
R3-NIN-1, R3-NIN-2	2	Nitapryrin added to site contaminated soil of batch 2; alternating aerobic–anaerobic degradation at room temperature
R4-MEA-1, R4-MEA-2	2	Fresh MEA added to site contaminated soil of batch 2; aerobic degradation at room temperature
R4-NITIN-1, R4-NITIN-2	2	Fresh MEA and nitapryrin added to site contaminated soil of batch 2; aerobic degradation at room temperature
R4-ANA-1, R4-ANA-2	2	Fresh MEA added to site contaminated soil of batch 2; anaerobic degradation at room temperature

Note: The labels R1-SOIL-1 and R1-SOIL-2 denote test run 1 (R1), treatment details (SOIL), and replicates 1 and 2 (1 and 2).

ways of MEA under relevant environmental conditions and to measure the EC changes of the soil. Pan test study results on biodegradability of MEA in soil are presented in detail in Ndegwa (2001) and Ndegwa et al. (2004). This paper presents results of laboratory chemistry and EC measurements. Based on the results, an observational method is developed for interpreting geochemical zones from subsurface EC profiles determined using surface electrical resistivity tomography (ERT).

2. Electrical conductivity of bulk soil

The EC of rocks or soils can be modeled with the Waxman–Smits equation (Waxman and Smits 1968):

$$[1] \quad \sigma = S^n \Phi^m (\sigma_w + BQ_v/S)$$

where σ is the formation electrical conductivity, S is the water saturation, Φ is the porosity, σ_w is the electrical conductivity of the pore fluid, m and n are cementation and saturation exponents, B is the equivalent electrical conductance of the solid phase, and Q_v is the cation exchange capacity. The first term on the right-hand side of eq. [1] accounts for conductance through the liquid phase and is known as Archie's law (Archie 1942). The second term accounts for surface conductance in the solid phase and is required when the solid phase contains significant conductive clay content. The Waxman–Smits equation shows that the bulk EC of a soil is a function of porosity, pore fluid EC, saturation, and cation exchange capacity (a function of the amount and type of clay content). In addition, the pore fluid EC is strongly dependent on temperature changing several percent per degree centigrade. Assuming that the formation is relatively homogeneous, the change in bulk (or soil) EC across a site or with time is mainly controlled by variations in the pore fluid EC. Besides temperature, pore water EC is primarily a function of the concentration of dissolved species, the mobility of the ions, and the percent dissociation of the electrolytic species.

3. Test material and methods

3.1. Field site

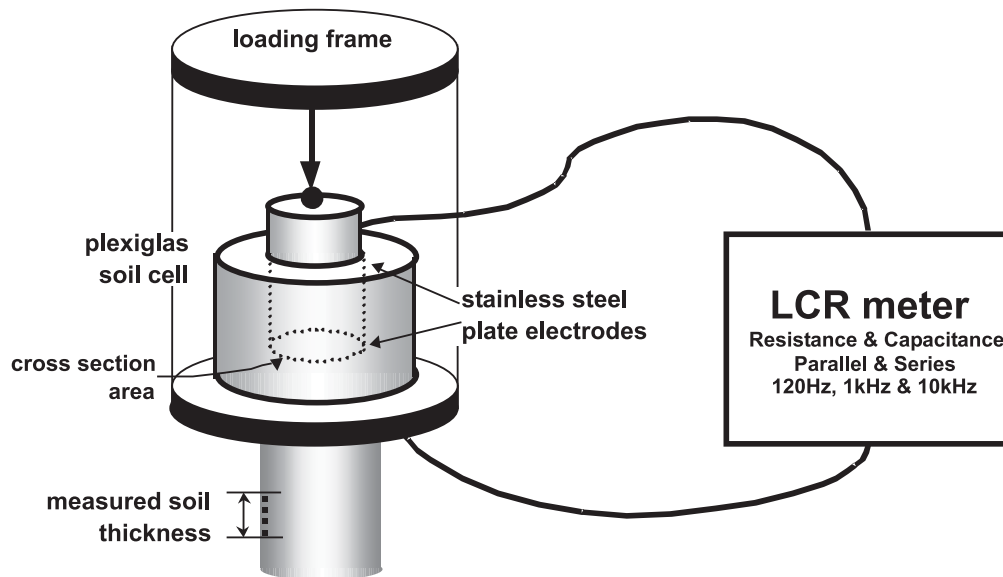
A former gas-processing plant located in northwestern Alberta, Canada, was the site of ERT profiling (Wong and Alfaro 2001; Bentley et al. 2001) and the source of contaminated soil samples for this laboratory study. The site has contained high concentrations of MEA. The near-surface water table fluctuates with seasons, but neutron logs indicate that the soil is close to saturation at depths below 0.3 m, presumably due to the fine-grained nature of the soils. The soil stratigraphy at the site consists of 0–1 m of fill overlying a 5–6 m thick layer of till. The till can be classified as clay with low plasticity. The clayey till consists of 20%–42% silt, 24%–41% clay, and the remainder sand. The liquid and plastic limits lie in ranges of 38%–46% and 15%–23%, respectively, and its in situ density is about 2.02 g/cm³. The in situ hydraulic conductivity of intact till (10⁻⁷ to 10⁻⁸ m/s) is typical of low-permeability soils. The cation exchange capacity is approximately 28 mequiv./100 g.

3.2. Bioremediation pan tests

A series of pan test studies was conducted to examine the biodegradation pathway of MEA in soil under various relevant environmental conditions and to track the bulk electrical conductivity history of the soils during the chemical evolution. Two soil batches of approximately 45 kg each were removed by hand excavation from the plant site and stored in a cold room at 1–4 °C prior to any testing. A concrete mixer was used to homogenize the soil. Then, the soil was placed in a disposable aluminum pan inside an air-tight glass desiccator. To minimize moisture losses from the soil, 100 mL of distilled–deionized water was placed below the pans at the bottom of each desiccator to reduce the evaporation of soil moisture to the headspace of the desiccator. Soil from the pan tests was sampled regularly and analyzed for moisture, temperature, pH, EC, total Kjeldahl nitrogen (TKN), anions, and cations. Headspace gases were also collected and analyzed as a measure of biological activity and volatilization (specifically ammonia).

A total of 20 pan tests (10 aerobic, four nitrification inhibited, two shift aerobic–anaerobic, two coldroom, and two an-

Fig. 1. Setup details of the electrical conductivity (EC) cell.



aerobic) in four separate runs were conducted on the two soil batches from the gas plant remediation site (Ndegwa 2001; Ndegwa et al. 2004). In addition, two control pan studies, an autoclaved control and a sodium azide control, were monitored to confirm respirometric results at room temperature under aerobic conditions. The testing parameters and notation are summarized in Table 1.

For chemical analysis, soil-water slurry was prepared, correcting for the moisture content of the soil, using one part soil and one part distilled-deionized water. The slurry was mixed using a mechanical shaker for approximately 60 min. The slurry was then centrifuged for 45–60 min to settle out most of the particulate matter. The supernatant was drained off and filtered through a sterile 0.45 μm membrane filter to complete the extraction procedure (Bigham 1996). Because the absolute and relative amounts of various solutes are influenced by the water to soil ratio at which the extract is made (Reitemeier 1946), the ratio used to obtain the extract was kept constant to obtain consistent results. Soil water extract was analyzed for EC, pH, major cations and anions, acetate, ammonia, and MEA. Further details can be found in Ndegwa (2001) and Ndegwa et al. (2004).

3.3. Electrical conductivity measurement

3.3.1. Soil extract EC by EC probe

An automatic conductivity meter (Orion Research Inc. model 112) made up of a glass conductivity cell and a thermistor was used to measure the extract electrical conductivity. This conductivity probe has a four-electrode configuration in which two electrodes supply the direct current (DC) and the other two measure the conductance of the extract. The electrode probe was calibrated using a standard potassium chloride (KCl) solution prior to testing (Castellan 1983; Bigham 1996; Lide 1996).

3.3.2. Bulk (soil) EC by EC cell

According to American Society for Testing and Materials (ASTM) standard G57-95a (ASTM 2003), it is recom-

mended that a rectangular cell with a Wenner four-electrode configuration should be used to measure the EC of soil. A DC or alternating current (AC) of low frequency (97 Hz) is applied to both ends of the rectangular soil sample using a pair of end electrodes. Another pair of electrodes is inserted into the sample at a fixed spacing to measure the EC of the soil. This four-electrode configuration eliminates polarization problems at the contacts between the soil material and the end electrodes. This setup requires a large volume of soil, however, and does not have proper control on the soil compaction, yielding a variation in soil density or porosity. To ensure consistency in the soil sample porosity, an oedometer cell with two electrodes was designed and fabricated (Fig. 1). In each EC measurement, a vertical load was applied to a fixed mass of soil inside the oedometer cell and compressed the soil sample to a designated height. Measurement of resistance in soil using DC with two electrodes is not reliable, however, because polarization and accumulation of charges occur at the contact surfaces between the test material and electrodes. To reduce the effect of polarization, frequency-dependent AC was used. At low frequencies, capacitance or charge buildup on the electrodes could be significant. At high frequencies of the megahertz range, molecular polarization becomes active (Smith and Arulanandan 1981). Thus, it is important to conduct a control experiment for validation of the EC cell (two electrodes with AC) with the EC probe (four electrodes with DC) using standard KCl solutions of known concentrations. Figure 1 shows the setup details of soil EC measurement using the oedometer cell. The oedometer cell was made of plexiglas walls (6 cm in internal diameter, 5 cm in height, 2 cm wall thickness, and 1 cm thick base) and two removable top and bottom 2 mm thick stainless steel plates. The two plates were used as electrodes and to apply a vertical load to the sample. A Hewlett-Packard™ 4262A inductance-capacitance-resistance (LCR) meter was used to measure the resistance (R) and capacitance (C) of the soil sample at room temperature. The measured resistance value was then converted to conductivity (σ) using the following expression:

Fig. 2. Setup details of the validation test for the EC cell. I , current; R , resistance; R_{cell} , resistance at the cell; RMS, root mean square; V_1 and V_2 , voltage at voltmeters 1 and 2; V_{cell} , voltage at the cell.

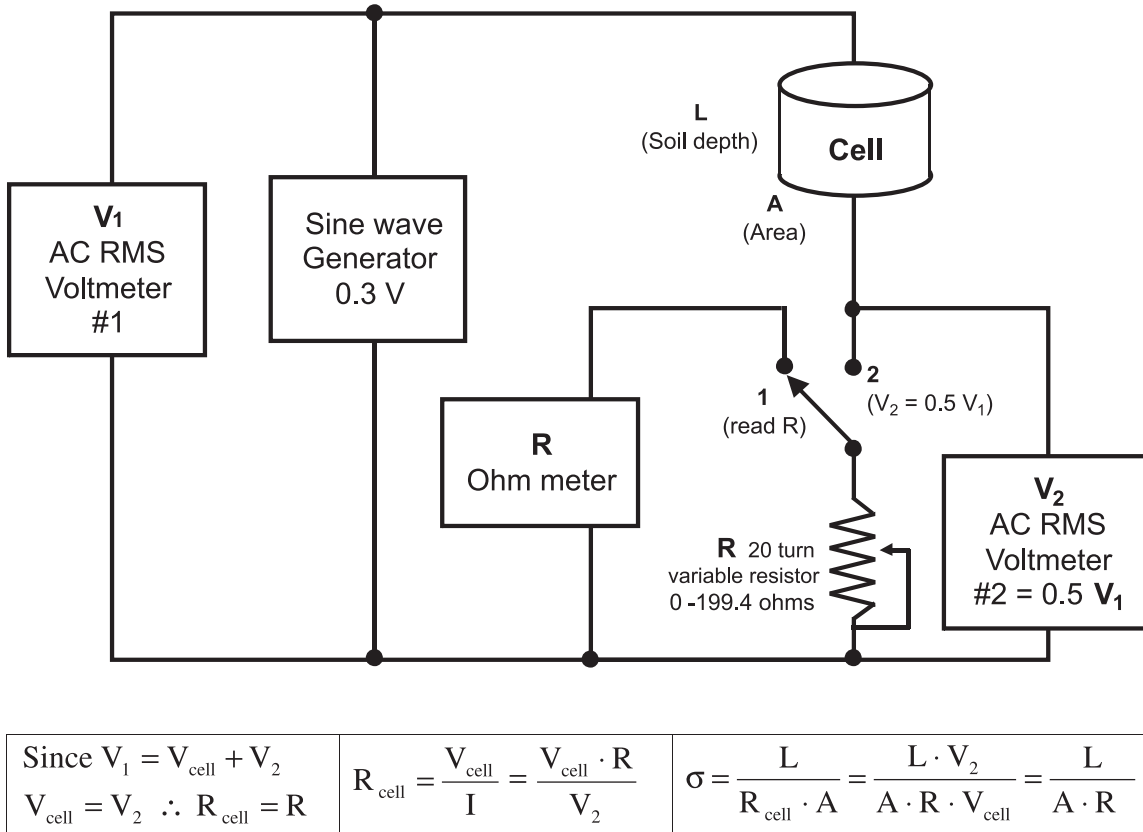


Fig. 3. Electrical conductivity of KCl solution as a function of concentration and measurement frequency (validation tests for EC cell).

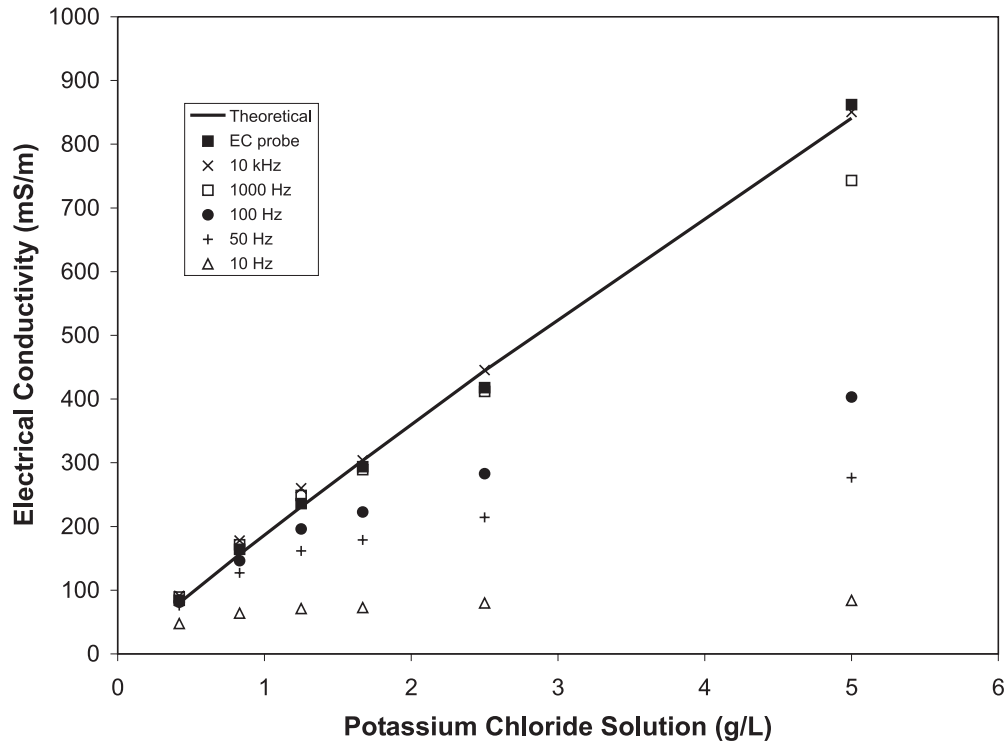
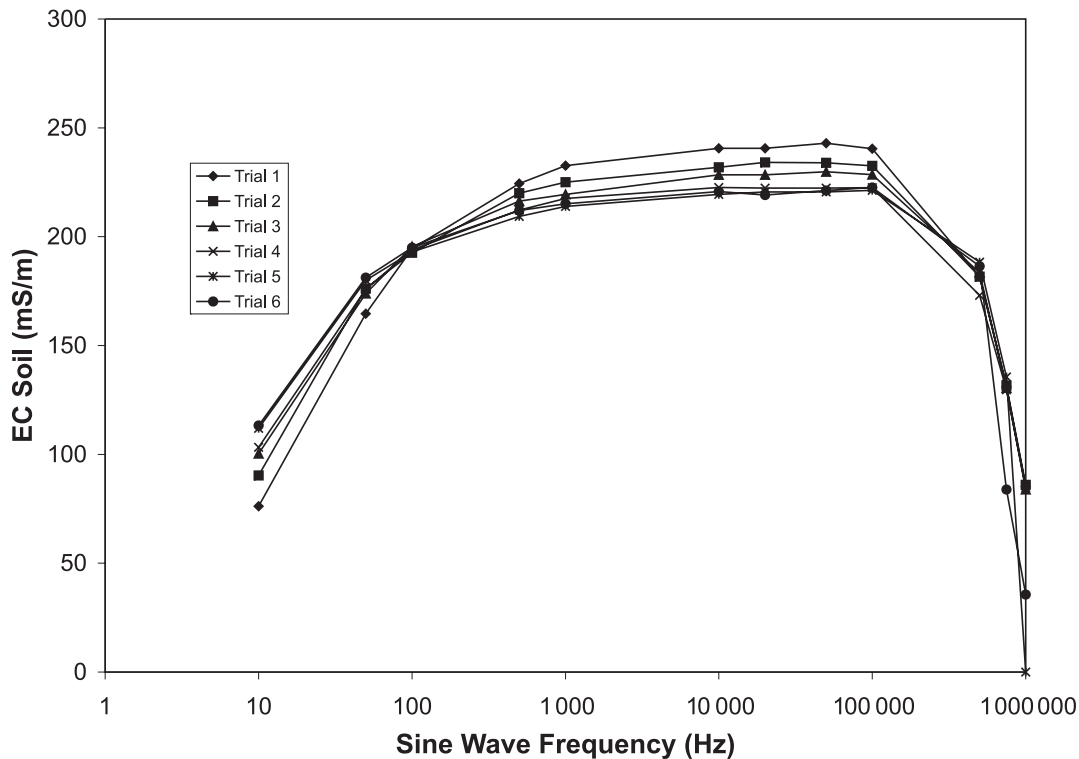


Fig. 4. Electrical conductivity of bulk soil as a function of measurement frequency (repeatability test).



$$[2] \quad \sigma = A/RL$$

where A is the cross-sectional area of the cell, and L is the length of the sample.

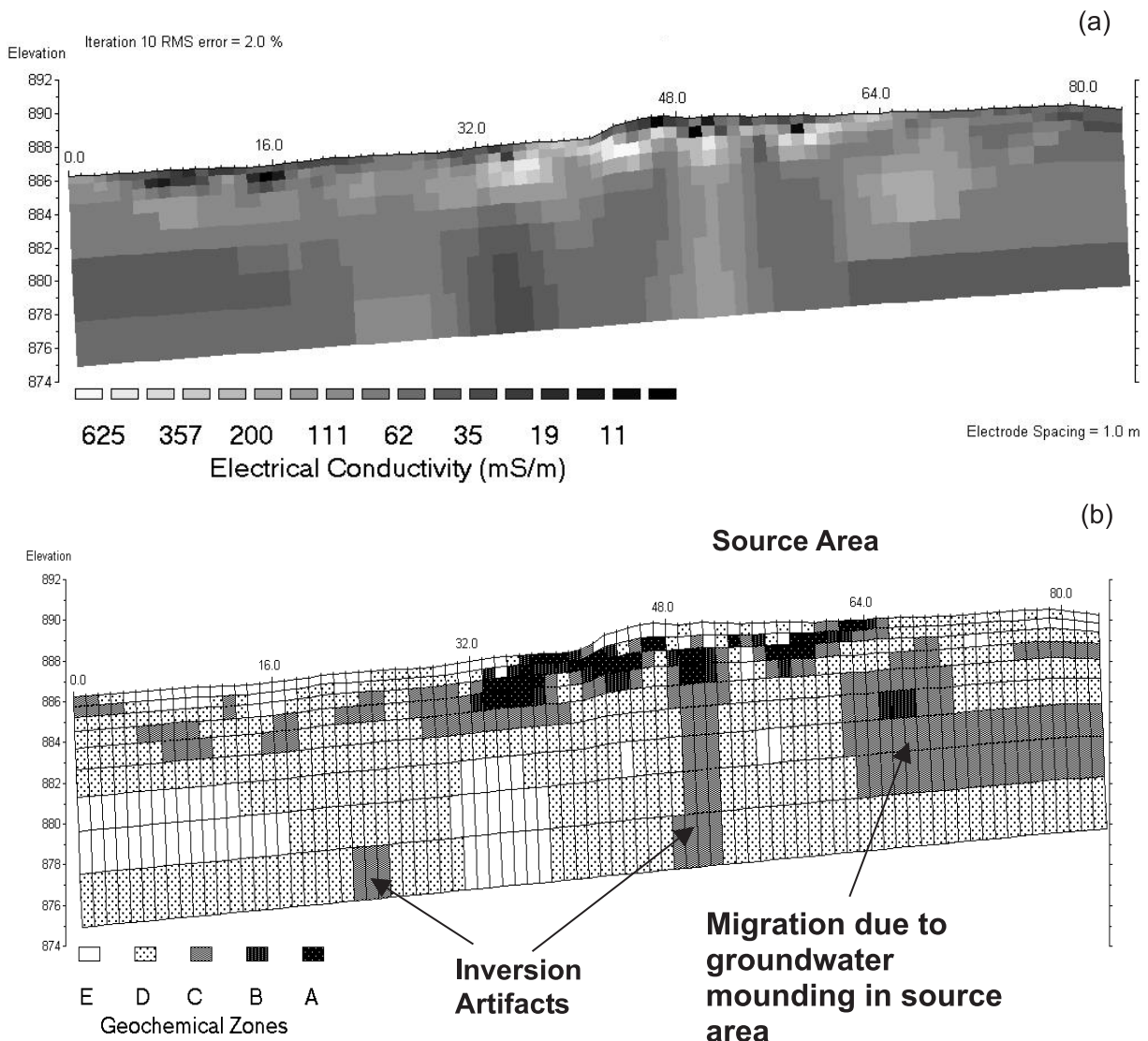
Figure 2 shows the setup details of the validation tests for the EC cell using KCl solutions. An AC electrical circuit was constructed to measure the resistance (or impedance) across the EC cell filled with KCl solutions of known concentrations. A variable resistor was adjusted until the voltmeter 2 value (V_2) matched 0.5 of the input voltage (V_1). A toggle switch was then switched from position 2 to position 1 and the resistance of the variable resistor was read. This resistance is approximately equal to that of the cell filled with KCl solution if the capacitance effect of the EC cell – KCl solution system is negligible. The EC measurement was repeated with varying AC frequencies of 10 Hz to 10 kHz to determine the frequency range at which the capacitance of the system was insignificant. Figure 3 presents the EC values of KCl solutions with varying concentrations at varying AC frequencies, along with those EC measurements of KCl solutions by the EC probe. The EC probe measurements show that the EC values of the KCl solution increase linearly with increasing concentrations. This trend agrees well with the theoretical values predicted from the Debye–Huckel–Onsager equation (Castellan 1983). The results from Fig. 3 indicate that the EC measurements using the EC cell should be made at the high-end frequencies close to 10 kHz. At frequencies lower than 10 kHz, the measured resistances were higher than the actual value due to the capacitance developed at the contacts between the electrodes and the KCl solution.

In addition to the validation tests of the EC cell with the KCl solution, the AC circuit (Fig. 2) was used to investigate

if the soil compaction procedure used in this study would affect the EC measurement. Approximately 130 g of the gas plant soil with a moisture content of 28% was compressed inside the EC cell to a height of 2 cm using a hydraulic loading ram (Fig. 1). The EC reading was taken at a range of frequencies varying from 10 Hz to 1000 kHz. The soil was unloaded, disturbed, and reloaded to the same height to measure the resistance again. This procedure was repeated six times to study its repeatability, and the results are plotted in Fig. 4. Equation [1] indicates that, if all other factors are constant, the soil EC will remain constant if the saturation and porosity do not vary. The EC results of the six trials fall within a narrow band, suggesting that the compaction method used in this study can reproduce consistent porosity values for the soil samples. In addition, Fig. 4 shows that the measured EC of the bulk soil is dependent on the AC frequency used as with the EC measurements of the KCl solution. It is consistent from the validation and repeatability tests that the EC measurement made at a frequency of 10 kHz produces a small capacitive effect and yields the representative EC value of the KCl solution or soil.

For the EC measurement of the contaminated soil, the test procedures were similar to those used in the repeatability test. A 130 g soil sample was removed from the pan inside the desiccator and compressed inside the oedometer cell using the hydraulic loading ram. A vertical force of approximately 2 kN was required to compress the sample to a height of 2 cm, achieving a consistent soil density of approximately $2.0 \pm 0.2 \text{ g/cm}^3$. Upon application of the vertical force, the Hewlett-Packard™ LCR meter was used to measure the resistance (R) and capacitance (C) of the soil sample at room temperature. This measurement was done at a setting of 10 kHz. The LCR meter not only offers quick

Fig. 5. (a) Electrical conductivity profile (line 5, run 4, August 2001) from 2D electrical resistivity tomography image. (b) Geochemical interpretation derived from EC profile in (a). Elevation in metres.



and accurate measurement, but also measures the resistance and capacitance simultaneously, whereas the AC circuit used in the validation and repeatability tests (Fig. 2) can measure the resistance (or impedance) only. The measured specific capacitance values were less than 10 nF/m, confirming that capacitance effects within the EC cell are negligible at 10 kHz.

3.4. Electrical resistivity tomography

Two-dimensional electrical resistivity tomography data are collected by laying out a set of electrodes in a line across the surface of the survey area (Griffiths and Barker 1993). Direct or alternating current is injected into the subsurface through an electrode pair, and the potential difference between another electrode pair is measured. The procedure is repeated using many combinations of locations and separation distance between electrodes. The subsurface profile is divided into constant-resistivity elements. The measurement data are inverted to produce an in situ subsurface resistivity profile (Loke and Barker 1996).

Figure 5a is an example of a two-dimensional (2D) inverted profile across the research site. The results are presented in electrical conductivity. The data were acquired using the Wenner array and direct current. The line was laid out with a 1 m electrode spacing. The line starts (0 m) downgradient of the pad and process area (55 m). Regions of elevated electrical conductivity are observed within the subsurface in the area surrounding the location of the decommissioned processing plant. The converted in situ EC values range from 5 to 625 mS/m.

4. Results and discussions

4.1. Biodegradation of MEA in soil

Pan test study results on the biodegradability of MEA in soil are presented in detail in Ndegwa (2001) and Ndegwa et al. (2004). This paper presents some of the typical results.

One set of aerobic test results is shown in Fig. 6. In this set (R4-MEA-1; Table 2), 2000 mg/kg soil of MEA was added to the existing soil. Extracted MEA was depleted

Fig. 6. Results of aerobic pan tests (R4-MEA-1).

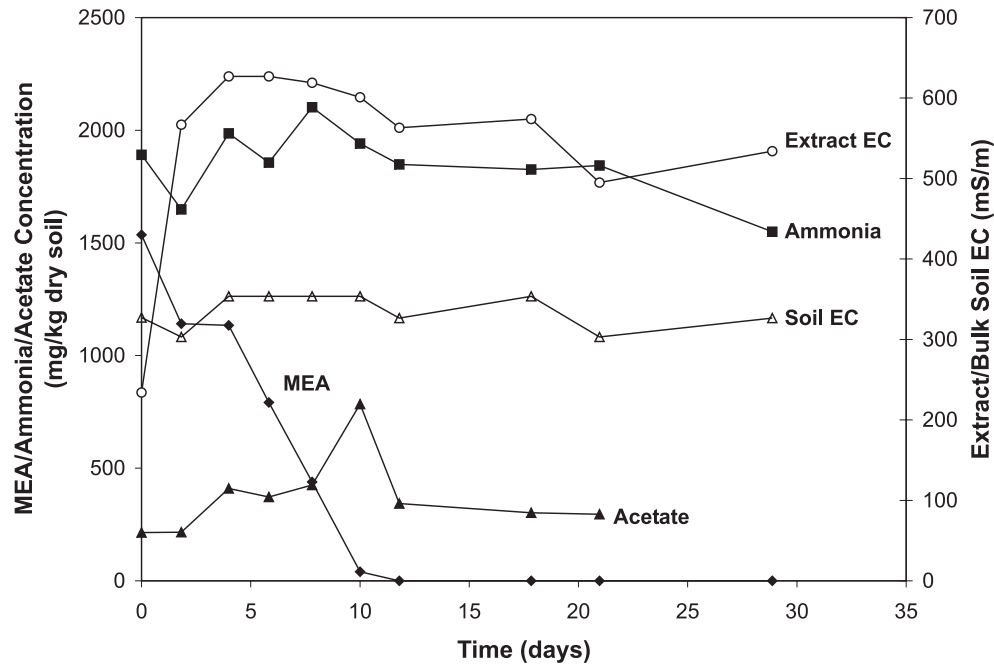


Table 2. Chemical properties of ammonia, acetate, and MEA.

Ion	Equivalent electrical conductivity, Λ ($\times 10^{-4}$ m ² ·S·mol ⁻¹) (Lide 1996) ^a	Dissociation constant, K_a (Breck et al. 1981; Montgomery 1991) ^b
Ammonia	73.5	45%–85% (pH = 9.5–8.3)
MEA	47.2	60%–91% (pH = 9.5–8.3)
Acetate	40.9	100% (pH = 9.5–8.3)

^aThe equivalent electrical conductivity (Λ) is defined as the conductivity of an ion per unit concentration. The values shown are extrapolated to infinite dilution in aqueous solutions at 25 °C.

^bThe percentage of the species that are dissociated into aqueous ions, enhancing the electrical conductivity of the solution. K_a varies with the pH of the solution. The pH values in parentheses were measured in the soil extracts.

within the first 10 days. The extracted ammonia started with an initial concentration of over 1800 mg/kg of dry soil and decreased gradually to 1600 mg/kg of dry soil by the end of the test at 29 days. The soil EC value started at 330 mS/m, increased to a maximum of 370 mS/m as the MEA degraded, and was 330 mS/m at the end of 29 days. The diluted soil extract EC exhibited a rapid increase from 240 to 600 mS/m in the first few days and reached a value of 530 mS/m at the end of the experiment. The extractable acetate increased from 200 mg/kg of dry soil to a maximum of just over 600 mg/kg of dry soil as the MEA degraded. Subsequently, the acetate concentration decreased to 300 mg/kg of dry soil by the end of the experiment. The pH values of the extracts fell within a range of 8.8–9.3. Significant amounts of nitrogen and carbon dioxide gases were produced during the entire period of the pan test. The production curves showed the greatest rates in the first 18 days.

One set of anaerobic test results is shown in Fig. 7. In this set (R4-ANA-1), the degradation rates of MEA were compa-

rable to those observed in aerobic tests. The EC values of bulk soil and soil extract continually increased, as did the concentrations of ammonia and acetate. A small amount of nitrogen and CO₂ gas production was observed at the beginning of the anaerobic tests, but the gas production declined rapidly to zero. Trace amounts of nitrate and nitrite were present at the beginning of the tests but declined rapidly to nondetectable levels.

When interpreting the pan test study results, it is important to note that the soil extract chemistry is not the same as the pore fluid chemistry because the dilution process in the soil extract preparation can induce desorption and possible dissolution of minerals. The soil extract can be used to interpret the geochemical pathways, however, but the concentration values of species and the EC of the extract water are not the same as that of the pore water, even after accounting for the effects of dilution. In summary, most of the residual or freshly added MEA in the soil was biodegraded in all pan tests under aerobic and anaerobic conditions. Results of ion chromatography analyses on soil extracts show ammonia cation and acetate anion were the two dominant transformed by-products. This confirms that the MEA degrades rapidly, producing acetic acid and ammonia. Under aerobic conditions, ammonia and acetate (consumed as a carbon source) were further degraded into carbon dioxide, nitrogen gases, and water. Under anaerobic conditions, ammonia and acetate were accumulated in pore fluid and adsorbed to the clay particles (Ndegwa et al. 2004).

4.2. Observational correlation between EC and geochemistry in pore fluid extract and soil

It is of practical significance and contribution to develop an analytical tool to predict the concentrations of species in contaminated soil from the EC measurement of the soil. The soil EC is controlled by the pore water EC, which in turn is

Fig. 7. Results of anaerobic pan tests (R4-ANA-1).

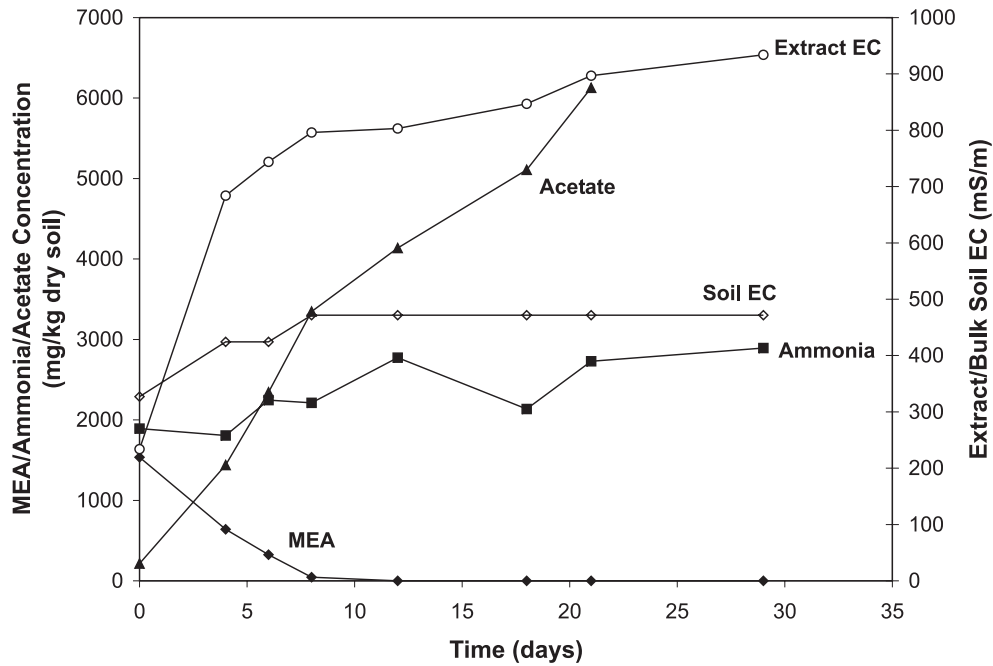


Fig. 8. Correlation between bulk soil EC and ammonia (see Table 2 for explanation of legend labels).

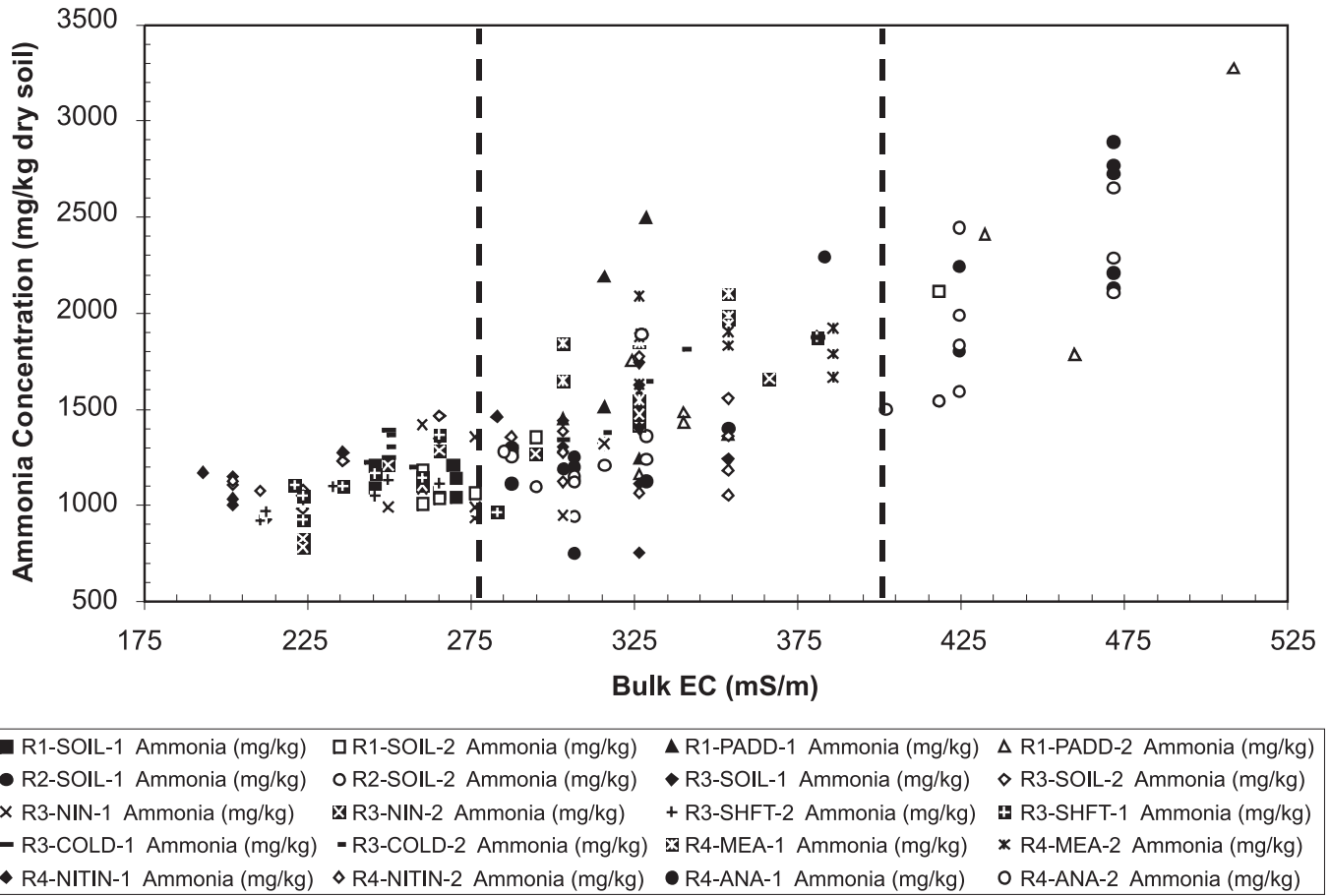
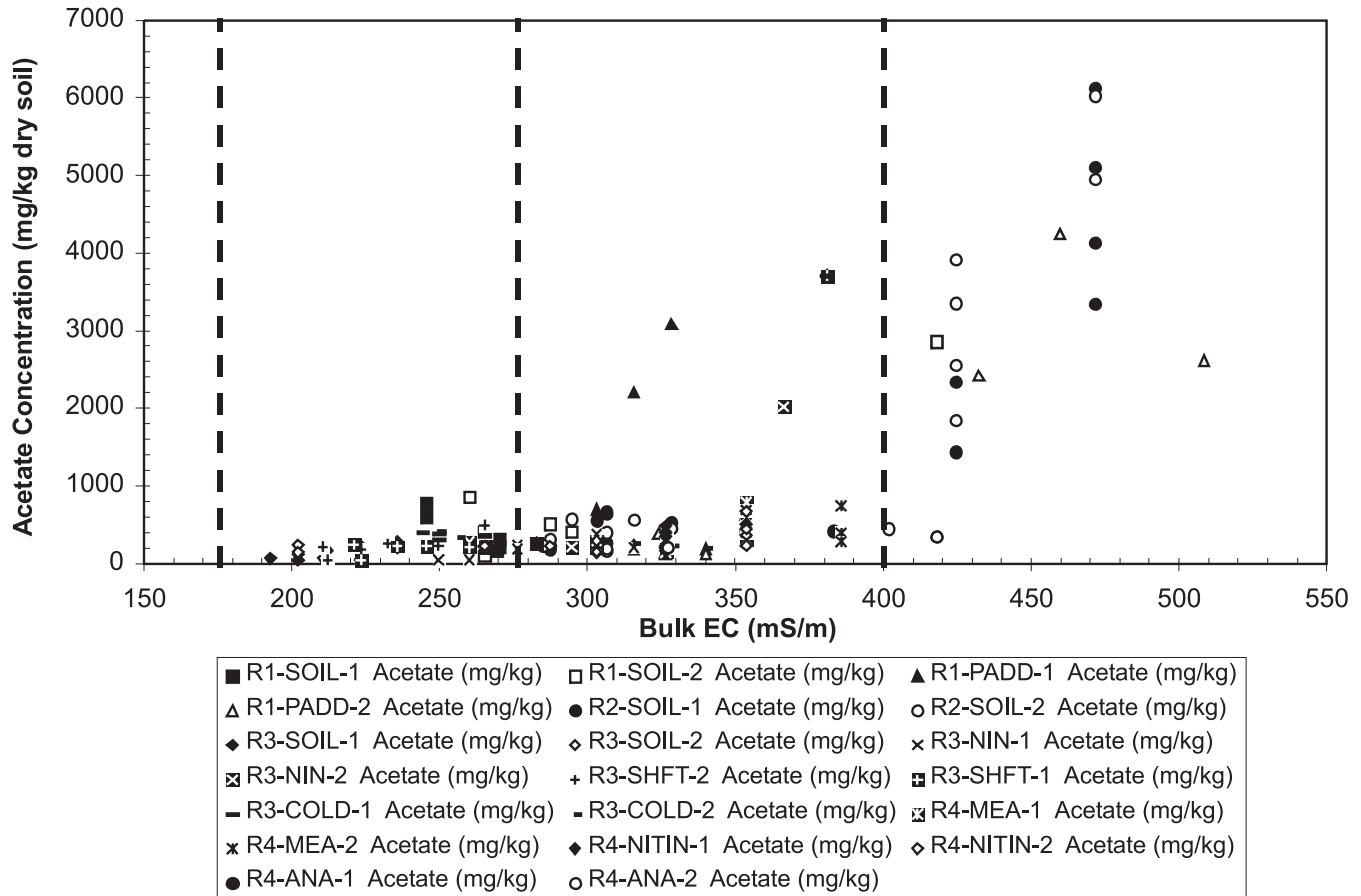


Fig. 9. Correlation between bulk soil EC and acetate (see Table 2 for explanation of legend labels).



primarily a function of the concentrations of dissolved species, the mobility of the ions, and the percent dissociation of the electrolytic species. Assuming all the ionic species of a solution are known, the overall EC of the solution is given as follows:

$$[3] \quad \sigma_s = \sum \Lambda_i (K_a c_i)$$

where σ_s is the EC of the solution; and Λ_i , c_i , and K_a are the equivalent EC, molar concentration, and dissociation constant of ion i in the solution, respectively.

Equation [3] shows that one EC measurement cannot quantify concentrations of all ionic species in a complex solution, i.e., use of EC measurement for determination of ionic concentrations only is applicable in solutions with single ionic species. To make use of EC measurement as an analytical tool, the so-called "observational" approach was adopted in this investigation. In this empirical approach, EC measurements are made in soil samples from the pan test study, which simulates possible environmental conditions encountered in the field. Correlations between soil EC and concentrations of different ionic species may provide some insight into the relationship between the soil EC and its overall geochemistry from which an analytical tool could be developed to map geochemical zones.

The chemistry of pore fluid in the soil water extract does not exactly represent the pore water due to possible dissolution and desorption. The relative soil water extract concentrations are indicative of the chemical state of the soil

system, however. Consequently, observations about the relative concentrations in the soil water extract are used to infer the geochemical state of the soil. Soil extract analysis from the pan study indicates that ammonia, acetate, and MEA are the three dominant species of interest under aerobic and anaerobic conditions.

Figures 8–10 show the soil EC versus concentrations of ammonia, acetate, and MEA, respectively, at laboratory temperatures. From Fig. 8, there is a correlation between the EC and ammonia concentration, i.e., the soil EC increases almost linearly with increasing concentration. This correlation is attributed to the fact that the ammonia concentration and its Λ value are highest among the three species, though its dissociation constant is only half of that of acetate (Table 2). Extract acetate concentrations are always high when the soil EC is greater than 400 mS/m (Fig. 9). Only a few high extract concentrations are found in soils with less than 400 mS/m. The majority of these data come from anaerobic experiments in which acetate was accumulated. With one exception, MEA is found in soil water extract only when the soil EC is greater than 275 mS/m (Fig. 10). From Figs. 8–10 and Table 1, it is evident that ammonia made the biggest contribution to the EC values of extract and soil samples, followed by acetate and MEA.

The soil EC was measured at an average temperature of 22.6 °C. The average temperature of groundwater at the site is 8 °C. From laboratory experiments performed on cores from the site, it was determined that soil EC changes 3%/°C

Fig. 10. Correlation between bulk soil EC and MEA (see Table 2 for explanation of legend labels).

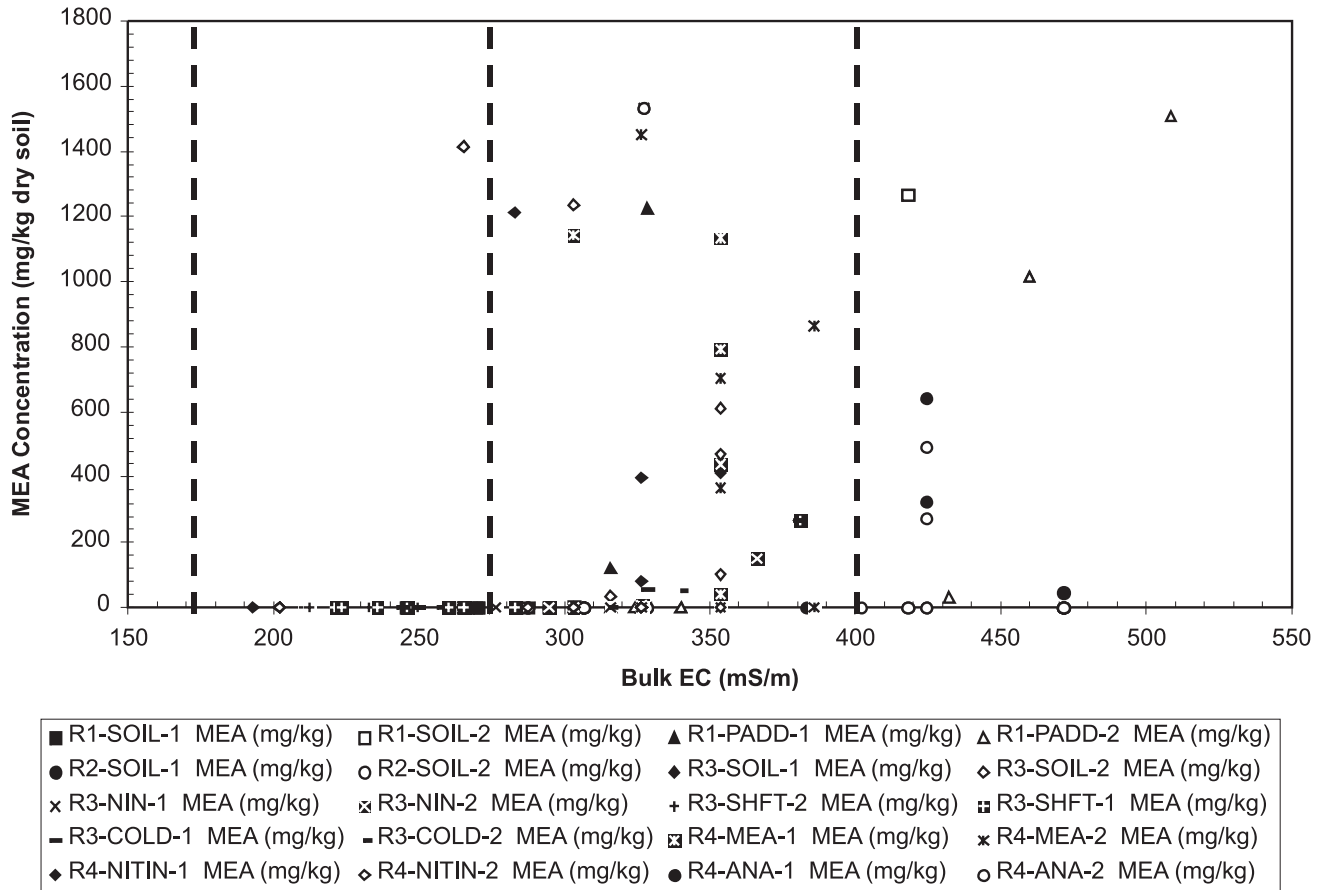


Table 3. Geochemical zones and soil electrical conductivity.

Zone	Laboratory soil EC range (mS/m)	In situ soil EC range (mS/m)	Description
A	400<	224<	Anaerobic, high ammonia, high acetate; possible MEA source area
B	275–400	154–224	High to moderate ammonia, mostly moderate acetate; possible MEA source area
C	175–275	98–154	Moderate ammonia, moderate to low acetate; no MEA
D	87–175	49–98	Possibly background or moderate to low ammonia, moderate to low acetate
E	<87	<49	Background

temperature difference from 22.6 °C. If the average ground-water temperature is the same as the average ground temperature, then the in situ EC can be estimated from the laboratory soil EC using

$$[4] \quad \sigma_T = \sigma_{lab}[1 + 0.03(8 - 22.6)]$$

where σ_T and σ_{lab} are the soil EC values at the in situ ground temperature and laboratory temperature of 22.6 °C, respectively. Using eq. [4], the equivalent in situ EC is 44% less than the laboratory-measured value.

The observed relationships between the soil EC and the three species (shown in Figs. 8–10) lead to a geochemical zonation interpretation of the in situ soil EC values after correcting to in situ temperature (Table 3).

Zone A ($\sigma > 224$ mS/m at in situ temperature) is generally anaerobic, with large concentrations of acetate and ammonium. It may or may not contain MEA source material. The

bulk EC values are the highest because the anaerobic conditions allow the accumulation of the degradation products, ammonium and acetate. Almost all of the points within this zone in Figs. 8–10 are from the anaerobic experiments runs R4-ANA-1 and R4-ANA-2.

Zone B ($154 < \sigma < 224$ mS/m at in situ temperature) contains moderate to high concentrations of ammonia. Acetate levels are generally moderate to low. Zone B may or may not have significant MEA source material.

Zone C ($98 < \sigma < 154$ mS/m at in situ temperature) has moderate concentrations of ammonia and low concentrations of acetate. Zone C does not contain significant MEA.

Zone D ($49 < \sigma < 98$ mS/m at in situ temperature) has low levels of NH_4^+ and acetate to background levels. Although there are few data in this zone, the EC values are interpreted to be in the transition range from the moderate to low levels in zone C and the assured background values of zone E. ERT EC values in this range have been observed in assumed

background regions and in areas with slightly elevated ammonium and (or) acetate.

Zone E ($\sigma < 49$ mS/m at in situ temperature) is definitely background. The background value was set by evaluating ERT inversion EC values in areas of no known impact.

The geochemical zones interpreted for the ERT inversion (Fig. 5a) are shown in Fig. 5b. The processing chemical source area for this site was a plant located in a pad area around 55 m on the profile. The geochemical interpretation of the EC profile indicates that the source is limited to within 3–4 m below ground level. Some inversion artifacts can be seen in the lower part of the image where the inversion is poorly constrained by the data. Possible source materials have migrated to approximately 33 m on the profile. Other areas of elevated ammonium and acetate are found below and around the potential source areas. A large area of geochemical zone C appears at depths to 5 m in the up-gradient direction. This migration is consistent with transport due to groundwater mounding, which has been observed beneath the source area. The interpretation indicates slow migration of process chemicals and the degradation by-products and a limited area of impact.

4.3. Discussion

The pan test results have led to a geochemical interpretation of ERT images. The zones are based on pan test experiments using soils from known MEA source areas. Additional source chemicals, such as glycol, may add additional EC signatures, so the EC to chemical mapping is not necessarily unique. Additionally, geological heterogeneity will lead to variations in the Waxman–Smits parameters and the relationship between bulk EC and pore fluid EC, adding noise to the EC to chemistry mapping. These additional complications must be addressed site by site.

The geochemical zones do not represent sharp boundaries and are gradational. For example, some zone B elements may be nearly or partly anaerobic while other zone B elements may lack source and show moderately elevated levels of ammonium and acetate.

Pan tests were performed on small samples of soil compared with the scale of the blocks in the ERT inversion. The EC values from the ERT inversions represent averages over volumes of soil on the order of 1 m³. At this point in time, the impact of the different scales is not clear and remains an area of future research.

Despite these limitations, the ERT images give a spatially dense and areally extensive estimate of the geochemical variations across the site. ERT data collection is rapid and inexpensive relative to drilling. The interpreted images may be used to estimate the mass and volume of contaminated soils and will prove valuable in the design of remediation programs.

5. Summary

Pan test studies monitored degradation pathways of MEA under simulated natural conditions (Ndegwa 2001; Ndegwa et al. 2004). It was found that MEA degraded aerobically and anaerobically. Aerobic degradation leads to the generation of acetic acid and ammonia. The acetic acid degrades

readily in the presence of oxygen. The ammonia tends to sorb to the soil and the concentration slowly declines. Anaerobic degradation leads to the accumulation of ammonium and acetic acid. In both aerobic and anaerobic cases, the geochemical evolution of the soils was correlated with an EC evolution of the soil.

The bulk EC of the soils was separated into five classes that were associated with geochemical classes (Table 3). Bulk soil electrical conductivity measured in the pan study was converted to equivalent ERT field values using a laboratory-derived temperature correction relationship. The relative trends were generally consistent with the chemical distributions at a decommissioned sour gas plant. Using these classes, the EC values from ERT images were interpreted in terms of geochemical zones. The geochemical zones varied between the extremes of anaerobic, potential source areas to background values.

The relationship between EC and chemistry at a given site must be established in order for a geochemical interpretation of resistivity images. Degradation pathways and the associated electrical conductivity evolution must be established on a site by site basis. In this paper, the relationship was established using laboratory pan test studies. At other sites, the geochemistry may be understood a priori and the EC to chemistry relationship established by correlating core data with ERT images.

Several avenues of research will improve the usefulness and precision of the geochemical interpretation of EC. Better field validation of the ERT chemical interpretations is required to fully understand the uncertainty associated with the geochemical interpretations. The role of scale of observation needs additional investigation. It remains to develop protocols for integrating core, groundwater analytical results and ERT images into a single geochemical interpretation.

Nevertheless, the current study is a step towards geochemical interpretations of ERT images. The geochemical interpretations will prove valuable in-site assessment and the design of site remediation strategies.

Acknowledgements

This study was financially supported by a research grant from the Natural Sciences and Engineering Research Council of Canada (NSERC), Imperial Oil Limited, and the Department of Civil Engineering at the University of Calgary.

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List of symbols

- A cross-sectional area of the cell
- B equivalent electrical conductance of the solid phase
- C capacitance
- I current
- L length of the sample
- m, n cementation and saturation exponents
- Q_V cation exchange capacity.
- R resistance
- R_{cell} resistance of the cell
- S water saturation
- V voltage
- V_{cell} voltage across the EC cell
- V_1, V_2 voltage across voltmeters 1 and 2
- Φ porosity
- σ formation electrical conductivity
- σ_{lab} soil EC values at laboratory temperature of 22.6 °C
- σ_s EC of the solution
- σ_T soil EC values at in situ ground temperature
- σ_w electrical conductivity of the pore fluid
- Λ_i, c_i, K_a equivalent EC, molar concentration, and dissociation constant of ion i in the solution