

PRINCIPAL COMPONENT ANALYSES OF GROUNDWATER CHEMISTRY DATA DURING ENHANCED BIOREMEDIATION

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Abstract. A bioremediation project has been monitored for two years at a former sour gas plant site that had ethanolamine, glycol and their degradation products in the subsurface. The active enhanced bioremediation program consisted of dewatering and bioventing. An extensive groundwater monitoring program mapped the distribution of chemical species. Principal component analysis was used to help organize and interpret the chemical analysis. Three principal components accounted for 75% of the variability in the data. The first component separated contaminated waters from background. The second component indicated aerobic versus anaerobic conditions and the third component was indicative of the accumulation of nitrogen compounds. The site is extremely heterogeneous with preferential pathways due to fractures, sand lenses and a fractured horizontal well. In addition the source and contaminated areas are very heterogeneous. The PCA shows drastically different geochemical conditions residing within relatively small areas. The study site can be conceptualized as a series of small, meter-scale sized reactors that interact and mix due to preferential flow paths and diffusion. The evolution of the chemistry shows that the bioremediation process is successfully removing acetic acid, and it is becoming more aerobic. Enhanced infiltration in the process area is slowly removing the source and degradation products.

Keywords: monoethanolamine, PCA, bioremediation, groundwater, degradation products

Introduction

Sour natural gas is a valuable resource for the global energy sector. Sour natural gas may contain as much as 36 mol% hydrogen sulfide (H₂S) and 8 mol% carbon dioxide (CO₂) (Kroschwitz, 1992; Sorensen *et al.*, 1999). Gas scrubber facilities are used to turn sour natural gas into consumable 'sweet' natural gas. Desulfurization units use alkanolamines to remove acidic components such as hydrogen sulfide from sour natural gas streams (Kroschwitz, 1992). The reaction between the 'lean' amine solution and the sour gas stream occurs within counter current contactors (Smart *et al.*, 1997). The resulting 'rich' amine mixture contains H₂S and CO₂ and is recycled and reused in the sweetening process.

In addition, most sour gas operations employ glycol dehydrator facilities (McQueen *et al.*, 1998). These devices use the hygroscopic properties of

monoethylene glycol (MEG) and triethylene glycol (TEG) to capture and reduce moisture in process natural gas streams and consequently reduce equipment and pipeline corrosion (McQueen *et al.*, 1998). Optimization and modification of natural gas processes has resulted in a diverse composition of alkanolamine mixtures and glycol solutions for specific applications (Polasek *et al.*, 1992; Rooney *et al.*, 1998). Unintentional introduction of both alkanolamines and glycols into the subsurface and groundwater pose a potential hazard to the environment (Fedorak *et al.*, 1997; Lintott *et al.*, 1997; Sorensen *et al.*, 1999; Wrubleski *et al.*, 1997).

After release, alkanolamines and glycols may migrate into the subsurface and groundwater. The high density and high water solubility of these species influence their fate and transport in the subsurface and in groundwater environments (Sorensen *et al.*, 1999). Alkanolamines and glycols are readily biodegradable (Chong *et al.*; 1999, Pitter, 1976; McVicker *et al.*, 1997; Scarlett and Turner, 1976; Williams and Cally, 1982), however the behavior of alkanolamines in concentrations exceeding 3000 mg/L in the presence of high levels of aerobic and anaerobic breakdown products (i.e. ammonium and acetate) is not well understood. In addition, little is known about aerobic and anaerobic biodegradation of TEG in ground water and subsurface environments (Strong-Gunderson *et al.*, 1995). Studies investigating the *in-situ* fate and transport of alkanolamines, glycols and degradation products have been conducted by McVicker *et al.* (1997), Sorensen *et al.* (1999) and Strong-Gunderson *et al.* (1995), but results have been complicated by the strongly heterogeneous study environments.

Mrklas (2002), Mrklas *et al.* (2004) and Ndegwa *et al.* (2004) have summarized the evolution of glycol and alkanolamine in soils and slurries. Briefly, alkanolamine will degrade under aerobic or anaerobic conditions to acetate (Ac) and ammonium (NH₄). However, alkanolamine degradation can be significantly retarded in some areas within this study site soils due to a lack of phosphorus. Glycol degradation produces Ac. Ammonium sorbs to clays through cation exchange. Under aerobic conditions, Ac will be mineralized to CO₂ and water and NH₄ will be oxidized to nitrite (NO₂) and then nitrate (NO₃). Under anaerobic conditions, Ac and NH₄ will accumulate and increase the electrical conductivity of pore fluids. If water containing NO₃ becomes anaerobic and a substrate such as Ac or ethanol is present, the NO₃ can be converted to nitrogen gas, CO₂ and water. Therefore, old industrial sites may experience a range of biodegradation pathways and a range of released and degradation products.

An *in-situ* bioremediation program was initiated at the site of a decommissioned sour gas processing plant in order to reduce elevated levels of monoethanolamine (MEA), glycol, and the degradation products NH₄ and Ac within the subsurface. *In-situ* bioremediation was being studied as an alternative to excavation and burial in an attempt to identify less expensive remediation options. This study assesses the *in-situ* chemical evolution of the site during a two year period of the remediation program. Analysis of the results was complicated by the extreme heterogeneity of the site. Principal component analysis (PCA) proved a valuable tool for simplifying

the analysis of complex chemical relationships that developed. Consequently, in the following, PCA is used as a tool to help organize the data and to differentiate between different chemical environments at the site.

Methods and Materials

STUDY AREA

The study area is a decommissioned sour natural gas plant site located in west-central Alberta, Canada. A MEA desulfurization unit and glycol gas-dehydration unit were operated on-site between 1978 and 1993. After plant closure in 1993, all physical infrastructure was decommissioned and removed from the site. Underground abandoned cables and purged and blanked process lines were located and mapped.

Past on-site construction involved a cut-and-fill method to build the process area or pad area located in the northeast quadrant of the site within the area of Zone 4 (Figure 1). The process area fill material contains a mixture of clay, silt, sand and gravel to up to a 1 m depth. The surficial geology of the site consists of 4–6 m of glacial deposits comprised mainly of sandy-silt till or silty-clay till overlying weathered siltstone bedrock. Sand lenses and some gravel were found within the till in a few of the boreholes. An average cation exchange capacity of 28 meq/100 g was determined from soil samples using the BaCl₂ method (Carter, 1993). The general groundwater flow direction followed the topography from the north recharge area across the site to the south. Average (range) hydraulic gradient, average (range) hydraulic conductivity and groundwater velocity were 0.07 m/m (0.04–0.14), 10⁻⁷ m/s (10⁻⁹–10⁻⁶) and 5 m/year respectively (Butterfield, 2002).

In this study, the site was categorized into four zones (1–4) according to level of contamination and level of employed remediation efforts (shown by the circle and rectangles in Figure 1). Zone 1 is away from source area and remediation efforts and represents background levels of groundwater chemistry (Butterfield, 2002). Zone 2 is the excavated and backfill portion near the horizontal well, and it represents the area that has background chemistry and was affected by remediation efforts. Zone 3 is located in the centre of the site downgradient of the source area and parallels the fractured horizontal well. Zone 3 has high levels of degradation products and was a centre of remediation efforts. Zone 4 contains the former process area and main source area. The groundwater quality was monitored via monitoring wells that were previously installed (shown in Figure 1).

Remediation activities in 1999 introduced hydraulic fracturing using a horizontal well at a depth of approximately 4 m below grade that spanned from northwest to southeast in the centre of the site (Figure 1). The purpose of the hydraulic fracturing was to enhance permeability and improve the circulation of fluids and

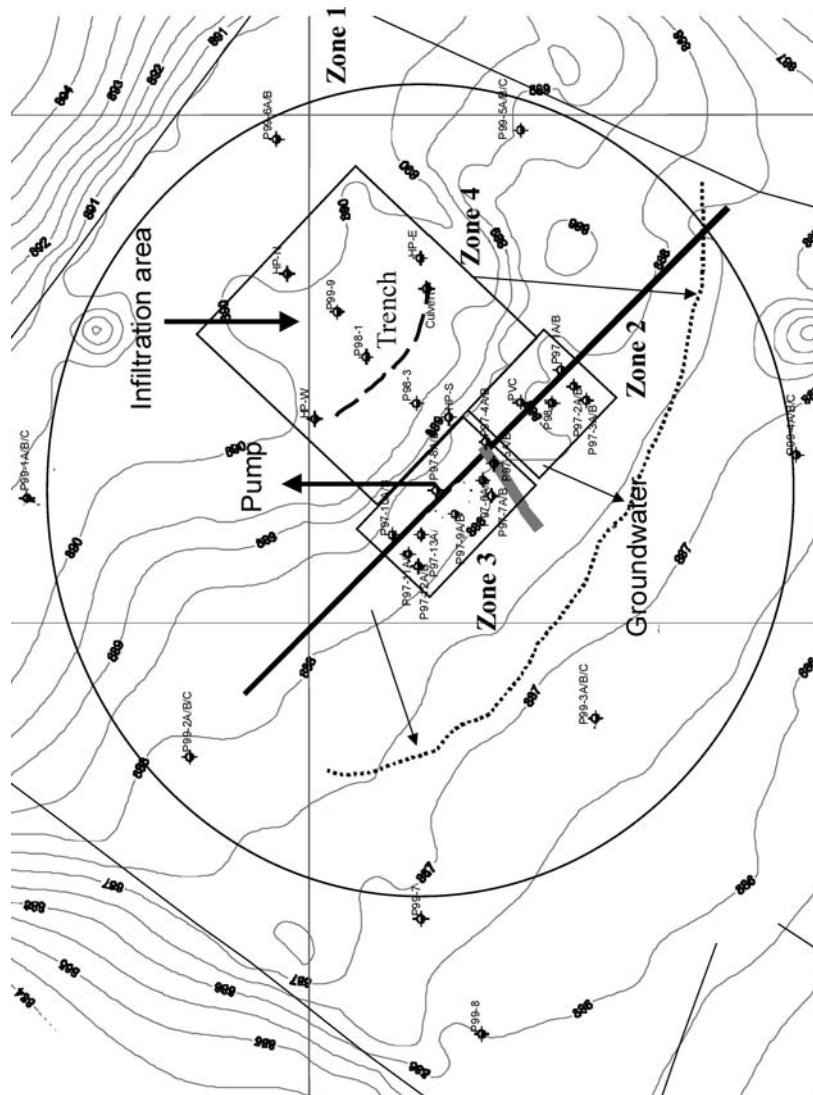


Figure 1. Site topography including monitoring stations, horizontal well (solid line), geomembrane (gray line), culvert trench system (dashed line), anticipated groundwater flow direction (dotted line), main groundwater discharge (pump) and predicted enhanced natural infiltration area. The three rectangular Zones 2, 3 and 4 indicate different geochemical environments within the contaminated and remediation area. Zone 1 is outside of the contamination and remediation area and is considered background.

air. Previously, a bioplug system was constructed within Zone 4 in the pad area on the north end of the site. Bioplugs are boreholes that have been filled with nutrients or other compounds intended to stimulate biodegradation (McDonald and Portier, 2003). Open holes associated with the system acted as an enhanced recharge area and caused groundwater mounding under the pad area. Previous remediation efforts included drilling the previously mentioned horizontal well, inducing fractures in the horizontal well and injecting phosphoric acid into the horizontal well (Wong and Alfaro, 2001). Zone 2 in Figure 1 was excavated and backfilled in order to map induced hydraulic fractures induced along the horizontal well. Zone 2, which did not have process chemicals or their byproducts, was isolated from Zone 3 with an impermeable geomembrane liner during the backfill. Prior to this study, groundwater removal programs were carried out mainly in the centre of the site employing the horizontal well. Numerous smaller excavations, core sampling and push tool investigations were carried out before, during and after this study. Some of the results are discussed elsewhere (Mrklas, 2002; Mrklas *et al.*, 2003; Mrklas *et al.*, 2004; Bentley *et al.*, 2001; Butterfield, 2002).

MONITORING STATIONS

The site is monitored via 55 nested piezometers installed between 1997 and 1999. The monitoring wells were labeled according to depths: A ~ 2 m, B ~ 4 m and C ~ 6 m below ground level (bgl). Additional features include two wells labeled PVC culvert and Culvert. The PVC culvert was installed to monitor groundwater levels in zone 2 and to remove water from the site. The culvert in zone 4 was connected to an interception trench and was used to intercept water moving south from the former process area. Piezometers HP-N, HP-S, HP-W and HP-E were installed to assist the bioplug remediation effort carried out in 1997. These piezometers were fully screened along their entire length to bedrock.

ANALYSES PROCEDURES

MEA and NH_4 concentrations were separated from sodium (Na), magnesium (Mg) and calcium (Ca) and analyzed with cation exchange ion chromatography (IC) technology and water mode suppressed conductivity detection (Mrklas *et al.*, 2003). Acetate, chloride (Cl), NO_2 , NO_3 , phosphate and sulfate (SO_4) were analyzed using anion exchange IC and chemical suppressed conductivity detection (Mrklas *et al.*, 2003). Ethanol, MEG and TEG were analyzed using reverse-phase IC and pulsed amperometric detection (Mrklas *et al.*, 2003). Electrical conductivity (EC) and pH were measured on-site using handheld Orion 105 and Hanna 9025 field meters, respectively. The same meters were used to measure and verify EC and pH of groundwater samples prior to analyses in the laboratory. All EC values were

measured without automatic temperature compensation and subsequently converted to a reference temperature of 8 °C using a correction curve because it is near the mean average groundwater temperature. Results of the chemical analysis for 32 locations are found in Table I.

DEWATERING & BIOVENTING

An active dewatering/bioventing program consisting of two stages and started on July 15, 2000. First, a vacuum pump system was installed and operated from July 2000 to October 2000 to remove groundwater and simultaneously draw air into shallow and deep regions of impacted zones. The system was designed to remove contaminated groundwater and to induce the flow of air into the anaerobic subsurface to accelerate the degradation of MEA, glycol and Ac. The pump was connected to monitoring well P97-8B (~4 m bgl) in the centre of the site (Figure 1). The pump was operated continuously during the 2000 program. Groundwater discharge was captured in an on-site storage tank. The overall removed water volume was estimated at 30–40 m³. There was no exhaust air flow meter installed, therefore, the volume of air pumped through the system is unknown. Networks of fractures and sand lenses may have created shortcuts for preferential air and water pathways to the pump. Therefore, the influence and efficiency of the pumping and extraction operation is uncertain. The water discharge altered the groundwater flow and redirected it partially towards the centre of the site (Butterfield, 2002).

The second stage involved a vacuum pump and operated June 15, 2001 to October 1, 2001. The pump was connected to piezometer P97-8B and operated continuously. There were approximately 50 m³ of groundwater removed, however, air flow rates are unknown. Periodically the pump was used to withdraw groundwater from all P-97 piezometers located in the centre of the site and at the PVC culvert.

As indicated above, for the purpose of analysis the site was divided into four main areas according to level of impact indicated by groundwater chemistry and level of remediation efforts (Figure 1). Background piezometers of Zone 1 (P99-1A/B/C to P99-5A/B/C, P99-6A/B, P99-7, P99-8) were likely outside of the radius of influence of the sources and the influence of pumping (non-impacted/not dewatered). Zone (2) (P97-1A/B to P97-3A/B, PVC culvert and P98-4) had been fractured, excavated, back filled and had background levels of major cations and anions similar to Zone (1) concentrations. Zone (2) was periodically dewatered during the 2000/2001 bioremediation program and, therefore is classified as non-impacted/dewatered. Zone (3) (P97-4A/B to P97-13A/B) spanned the centre of the site where past fracturing and drilling took place. Zone (3) (impacted/dewatered) was directly under pumping influence and some groundwater samples indicated significant MEA, ammonium and acetate concentrations. Zone (4) (HP-N, HP-S, HP-W, HP-E, P99-9, P98-1 and 3 and the Culvert) (impacted/not dewatered) was the former process area, and, due to the low permeability of the glacial till, it is

TABLE I
June 2000 and May 2002 groundwater chemistry at 32 locations

Location Unit	EC (mS/cm)	pH	Ac (mol/L)	Ca (mol/L)	Mg (mol/L)	Na (mol/L)	Cl (mol/L)	SO ₄ (mol/L)	MEA-N (mol/L)	NH ₄ -N (mol/L)	NO _x -N (mol/L)
June 2000											
99-1C	2.83	6.10	70.55	17.99	7.32	9.70	1.52	0.35	ND	ND	ND
99-5B	1.83	6.36	ND	8.92	4.81	7.70	5.61	2.40	ND	ND	ND
99-5C	0.60	7.02	ND	3.15	1.93	2.04	1.10	1.58	ND	ND	ND
99-6B	0.86	6.48	ND	5.65	2.18	1.70	0.37	0.29	ND	ND	ND
P97-1A	0.86	6.40	ND	6.67	2.96	2.65	2.06	0.34	ND	ND	ND
P97-2A	2.13	6.86	ND	2.52	2.80	5.26	0.59	2.30	ND	0.17	ND
P97-2B	0.84	6.88	ND	4.17	2.51	1.04	0.73	0.70	ND	0.43	1.16
P97-3A	1.31	6.70	ND	6.57	4.20	10.40	1.30	0.90	ND	ND	ND
P97-3B	0.93	7.16	ND	5.20	2.59	2.00	0.20	0.75	ND	ND	1.34
P98-4	0.99	6.51	ND	6.62	4.61	0.83	1.61	0.79	ND	ND	0.68
PVC	1.11	6.77	ND	3.25	3.78	1.96	2.03	0.43	ND	0.35	1.20
P97-4A	8.12	6.03	345.08	73.21	24.85	22.40	9.96	1.12	ND	20.19	ND
P97-4B	1.38	6.58	111.35	14.09	24.97	25.58	4.20	1.11	0.07	40.73	ND
P97-5A	1.89	6.50	ND	12.19	8.27	8.31	3.86	0.42	ND	ND	ND
P97-5B	4.88	6.44	104.74	18.04	15.59	6.61	3.98	0.72	ND	31.59	0.21
P97-6A	11.43	6.46	299.80	23.94	22.42	15.22	4.09	1.99	0.01	115.14	3.97
P97-6B	6.90	6.26	186.76	22.29	17.36	7.96	5.50	0.92	ND	58.93	0.11
P97-7A	4.78	6.29	ND	25.71	6.87	6.39	ND	1.94	ND	10.31	15.58
P97-7B	4.40	6.34	104.10	31.46	22.17	5.09	4.77	0.58	ND	7.58	0.09
P97-9A	10.22	7.43	153.80	5.42	11.23	18.05	2.06	1.98	0.21	90.26	1.35
P97-9B	6.48	6.19	107.89	13.79	24.43	24.49	3.84	1.08	0.07	40.69	ND
P97-10B	13.37	5.67	861.42	205.30	29.16	38.54	20.20	1.03	ND	50.05	ND
P97-11A	2.56	6.82	ND	4.92	2.59	10.05	1.02	2.67	ND	17.68	0.93
P97-11B	7.90	6.12	202.15	46.25	20.03	16.92	6.60	3.19	ND	35.32	4.24
P97-12B	1.46	6.71	ND	8.77	5.39	16.92	2.34	1.47	ND	ND	ND
P98-1	2.95	6.89	38.39	4.52	1.73	2.78	1.86	0.59	ND	30.59	ND
P98-3	13.11	6.37	460.66	32.16	39.74	32.19	12.69	1.44	0.11	123.93	ND
HP-N	8.42	6.59	304.98	16.07	9.95	8.83	ND	1.93	0.31	71.93	4.87
HP-S	6.44	6.68	95.77	21.26	14.77	12.31	1.27	1.56	ND	38.91	0.81
HP-W	3.87	6.30	ND	4.57	7.77	14.48	8.46	1.67	ND	22.14	0.81
HP-E	1.54	6.68	11.43	12.77	4.32	3.22	0.90	0.62	ND	0.78	ND
Culvert	4.23	6.52	121.08	15.27	4.90	4.74	5.19	1.15	ND	28.90	ND
Mean	4.39	6.53	210.59	21.33	11.19	10.82	4.00	1.25	0.13	38.03	2.49
May 2002											
99-1C	1.87	6.71	ND	12.09	3.50	10.96	0.11	0.08	ND	ND	ND
99-5B	1.85	6.49	ND	10.79	3.66	7.05	5.61	2.57	ND	ND	0.03
99-5C	0.74	7.17	ND	4.12	1.60	1.87	1.69	1.73	ND	ND	0.04
99-6B	0.91	6.75	ND	6.97	1.97	0.39	0.08	0.18	ND	ND	ND

(Continued on next page)

TABLE I
(Continued)

Location Unit	EC (mS/cm)	pH	Ac (mol/L)	Ca (mol/L)	Mg (mol/L)	Na (mol/L)	Cl (mol/L)	SO ₄ (mol/L)	MEA-N (mol/L)	NH ₄ -N (mol/L)	NO _x -N (mol/L)
P97-1A	0.98	6.60	ND	6.57	0.21	2.13	0.82	0.41	ND	ND	0.08
P97-2A	2.23	7.29	ND	4.00	1.93	3.39	ND	1.07	ND	13.82	2.70
P97-2B	0.64	7.05	ND	3.80	1.73	0.91	0.39	0.55	ND	0.04	0.20
P97-3A	0.72	7.04	ND	2.60	0.78	5.26	ND	0.93	ND	0.30	0.60
P97-3B	0.70	6.94	ND	3.80	1.89	1.04	0.25	1.20	ND	ND	0.28
P98-4	1.53	6.70	ND	8.95	3.50	1.70	1.47	0.59	ND	0.56	1.38
PVC	1.86	6.65	ND	10.84	4.24	2.74	1.95	0.65	ND	0.95	1.80
P97-4A	3.93	6.57	25.59	20.39	6.05	10.83	0.68	0.20	ND	10.53	0.94
P97-4B	3.13	6.81	ND	17.64	9.87	4.57	2.40	ND	ND	8.88	ND
P97-5A	1.91	6.77	6.32	10.69	4.36	6.74	3.36	0.12	ND	ND	ND
P97-5B	2.17	6.98	ND	4.15	3.87	2.78	1.47	0.50	ND	5.07	0.18
P97-6A	13.55	6.57	ND	61.19	14.97	18.01	ND	1.97	ND	61.58	47.13
P97-6B	5.54	6.87	24.93	15.29	18.06	8.26	4.51	7.82	ND	32.93	0.72
P97-7A	10.94	6.34	ND	80.36	7.77	7.79	ND	1.33	ND	6.76	41.53
P97-7B	2.16	6.69	2.12	13.69	5.68	3.09	5.39	0.12	ND	0.61	0.41
P97-9A	9.67	6.63	ND	40.68	8.39	14.05	ND	2.24	ND	55.73	25.62
P97-9B	2.79	7.28	ND	8.35	7.94	10.35	2.65	ND	ND	12.26	0.22
P97-10B	12.75	5.87	143.03	216.44	32.13	26.01	ND	9.55	ND	43.16	ND
P97-11A	9.95	6.41	ND	66.57	8.43	16.83	2.62	2.18	ND	22.79	34.43
P97-11B	9.81	6.00	141.25	93.68	20.03	12.83	5.81	1.64	ND	24.66	12.76
P97-12B	3.88	6.99	12.84	22.16	10.57	8.18	3.24	ND	ND	7.11	ND
P98-1	7.92	7.65	ND	12.62	4.77	4.39	7.84	3.60	ND	76.61	13.09
P98-3	11.99	5.97	254.29	46.60	24.52	27.66	12.95	0.93	ND	117.56	ND
HP-N	14.45	6.47	475.99	57.72	22.54	8.13	0.51	ND	0.88	120.34	ND
HP-S	4.91	6.70	46.35	31.38	13.78	8.66	0.99	ND	ND	18.98	ND
HP-W	2.83	6.74	ND	15.89	6.91	8.48	10.69	ND	ND	4.68	0.11
HP-E	2.47	6.45	29.70	20.69	3.91	4.61	2.54	0.49	ND	0.13	0.01
Culvert	2.50	7.15	ND	11.59	2.30	2.09	0.25	0.81	ND	8.75	5.35
Mean	4.79	6.73	105.67	29.45	8.18	7.87	3.09	1.67	0.88	26.19	8.24

ND: Below detection limit.

MEA: Monoethanolamine.

likely outside the pumping influence. Some locations within zone (4) contained significant MEA, ammonium and acetic acid concentrations.

During the bioremediation program, water was periodically discharged from the PVC culvert in zone (2) using the vacuum pump and/or tanker truck. In order to minimize migration of contaminants out of the former process area (zone 4), the Culvert and trench were kept at a constant water level using a submersible pump with a float actuator and a plastic storage tank. A tanker truck periodically emptied the storage tanks for deep well disposal.

SAMPLING PROTOCOLS

Groundwater sampling of monitoring wells was carried out before, during and after the remediation programs. Samples were initially taken in June 2000, one month prior to starting the pumping program. August 2000 and September 2000 samples were collected during active remediation efforts. The November 2000 ground water samples were taken one month after the pumping had ended. The final sampling was carried out in May 2001, approximately one year after the initial sampling. Prior to sampling, each well was purged for 2–3 cumulative borehole volumes or until the well was dry. Since hydraulic conductivity was low, it was found that a 24 h recovery time was needed prior to collection of the sample. A 30 mL water sample was taken from each piezometer with a bailer, stored in a glass vial on ice and transported to the laboratory for analyses. Samples were frozen at -20°C until analyses. This paper focuses on the June 2000 and May 2001 sample results. Other results are reported by Mrklas (2002)

PRINCIPAL COMPONENT ANALYSES (PCA)

Principal component analysis (PCA) (Mardia *et al.*, 1979) is a method for reducing the dimensionality of multivariate data sets such as the 11 water quality variables that we have presented for each of the monitoring well locations before and after the remediation effort. Since many of the chemical variables are positively or negatively correlated, some of the variables essentially contain the same information. PCA finds a new orthogonal coordinate system of uncorrelated variables to represent the original chemical data. Each coordinate direction (principal vector) is expressed as a linear combination of the original variables. The first principal vector is in the direction of greatest variance in the original data set. The eigenvalues associated with each direction are a measure of the variance accounted for by that direction. Each succeeding principal vector is orthogonal to the preceding vectors and is in the direction of the greatest variance not accounted for by the previous vectors. The dimensionality of the data can be reduced by ignoring the vectors associated with small eigenvalues that account for the least amount of variance. This procedure is also useful for identifying which variables are correlated. Consequently, PCA offers a powerful tool for identifying process and grouping water quality types. The data vectors for each chemical sample are rotated into the new coordinate system by taking a dot product between a weighting matrix and the vector of chemical analysis data. Only the significant components are retained during the subsequent analysis.

We use PCA as a tool to help organize the rather complex set of data and to differentiate between different chemical environments at the site. Table I contains the data from the June 2000 and the May 2002 sampling campaigns. The sample entries contain 11 chemical parameters for each of the 32 sample locations: EC, pH, acetate (Ac), Ca, Mg, Na, Cl, SO_4 , MEA-N, NH_4 -N, and NO_x -N (sum of

NO₂-N and NO₃-N). Before PCA, each column in Table I is converted to a zero mean, unit variance equivalent by subtracting the mean value of the variable and dividing by the standard deviation. This conversion gives each chemical parameter the same magnitude and variance and consequently the same influence in the PCA. The PCA routine within Statgraphics Plus 5^(TM) software was used to analyze the groundwater chemistry data at 32 locations from June 2000 (before remediation) and May 2002 (after two remediation programs).

Results and Discussion

Table II and Figure 2 show the weights for the first three principal components. The eigenvalues are all greater than one, while the eight remaining components have eigenvalues less than one. As can be seen in Table II, the first three principal components account for over 75 % of the variability in the data set, and we will use these three components in the following analysis. Figure 3 shows the values of the first three principal components for the 32 locations for the June 2000 and May 2002 samples. The value of a component of a sample is calculated by multiplying each of the zero mean, unit variance values of that sample by the weight associated with that component and summing. Due to the zero mean, unit variance conversion, parameters that have values that are above the average value for that parameter and that have a positive weight for a component will contribute positively to that component. Parameter values that are below the average and have a positive weight for a component will contribute negatively to that component. Similarly, negative (or below the mean) concentrations with a negative weight contribute positively

TABLE II
Table of component weights for June 2000 and May 2002

Element	Principal component weights		
	CW1	CW2	CW3
EC	0.39	0.14	0.29
pH	-0.28	-0.10	0.34
Acetic acid (Ac)	0.37	-0.31	-0.04
Calcium (Ca)	0.33	0.30	-0.13
Magnesium (Mg)	0.39	-0.05	-0.05
Sodium (Na)	0.38	0.04	-0.15
Chloride (Cl)	0.28	-0.21	-0.42
Sulfate (SO ₄)	0.15	0.46	0.06
Monoethanolamine (MEA-N)	0.14	-0.40	0.56
Ammonium (NH ₄ -N)	0.33	-0.18	0.38
Nitrate + Nitrite (NO _x -N)	0.07	0.06	0.34
Eigenvalues	5.36	1.51	1.46
Cumulative percentage of total variation	48.69	62.46	75.73

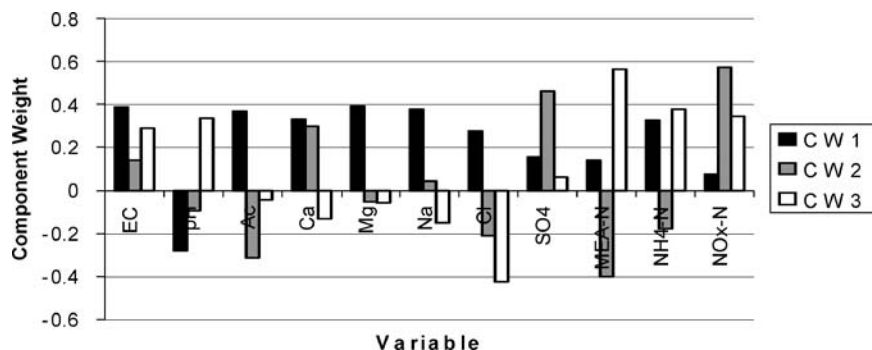


Figure 2. Principal component weights CW1, CW2 and CW3 and variables. (MEA: Monoethanolamine)

and positive (or above the mean) concentrations with a negative weight contribute negatively.

Component 1 (C1) has positive weights for all parameters except pH, which has a large negative weight. Consequently, samples with elevated EC, Ac, NH₄ and low pH will tend to have high values of C1. The high values of EC observed at the site are due to elevated concentrations of Ac and NH₄, which are degradation products of MEA and glycol. The negative weight for pH is apparently associated with the decrease in pH in the presence of Ac. The large weights associated with Ca and Mg are interpreted as due to increased dissolution in the more acidic conditions of significant Ac concentrations. As well, the increase in Na, Ca and Mg concentrations may be due to the replacement of those ions with NH₄ by cation exchange within the clay rich tills. This is consistent with recent laboratory investigations that showed large reservoirs of NH₄ sorbed onto soils from this site during biodegradation experiments (Mrklas *et al.*, 2003; Mrklas *et al.*, 2004). We interpret samples with high values of C1 to come from areas that have significant concentrations of degradation products. In addition, if the samples have elevated concentrations of Ac, the high C1 value would also indicate anaerobic conditions. Negative values of C1 are mainly due to relatively high pH and relatively low concentrations of Ac, Ca, Mg, Na and NH₄. Negative C1 values are consistent with little or no contamination.

Component 2 (C2) has large positive weights for EC, Ca, SO₄, NO_x and large negative weights for Ac, Cl, MEA and NH₄. Samples with large negative values of C2 generally have elevated Ac or NH₄ indicating anaerobic conditions and the presence of degradation products. Samples with large positive C2 values are interpreted as coming from areas that have had significant amounts of degradation products, but are or have been at aerobic conditions. The elevated EC, NO_x and Ca would be due to historic high concentrations of NH₄ and Ac, and the negative weight associated with Ac and NH₄ means that the concentrations are no longer elevated. In addition, the presence of SO₄ would be further evidence that aerobic

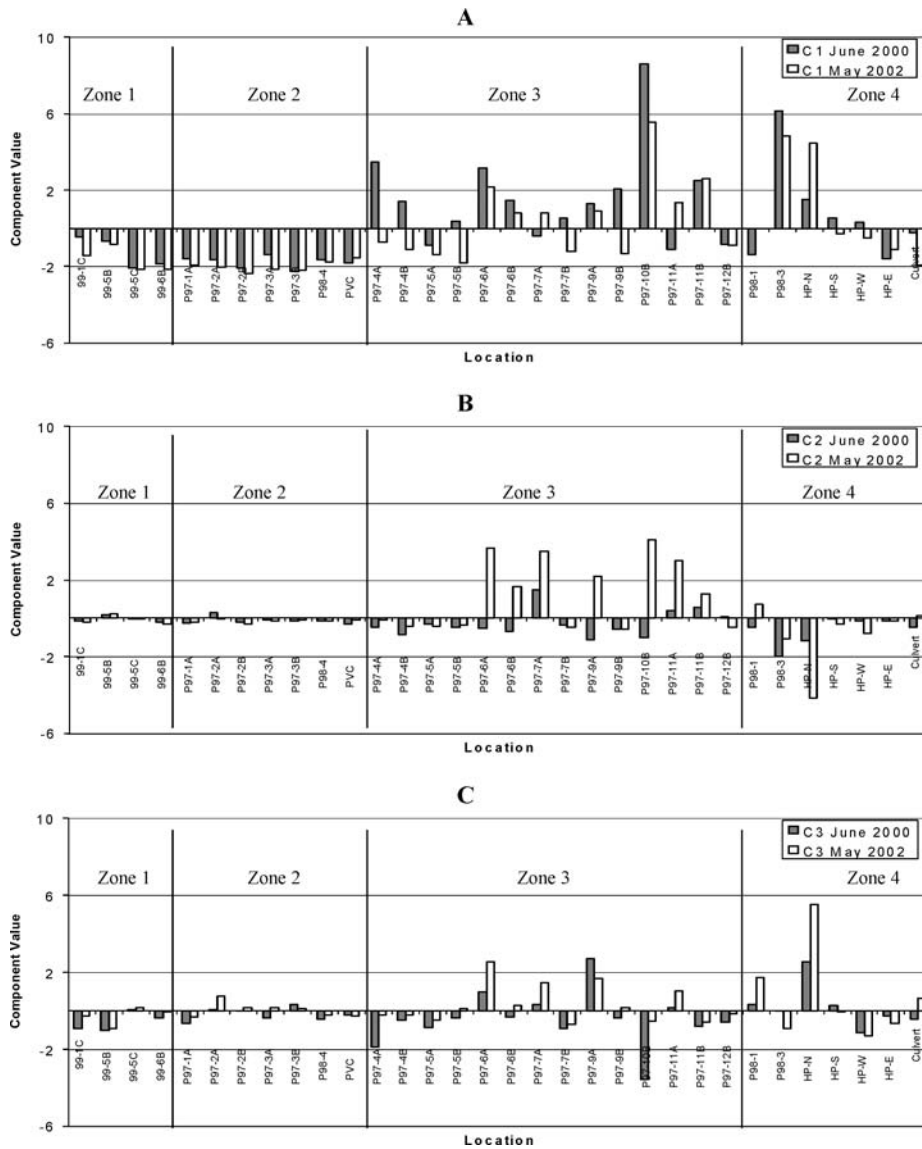


Figure 3. A, B and C. Principal components, C1, C2 and C3. (A) C1 June 2000 versus C1 May 2002, (B) C2 June 2000 versus C2 May 2002 and (C) C3 June 2000 versus C3 May 2002.

conditions have been experienced at the location. Samples with C2 near to zero may come from areas with little or no history of contamination or that are in transition from anaerobic to aerobic conditions.

Component 3 (C3) has large positive weights for EC, pH, NO_x , NH_4 and MEA and large negative weights for Na, Ca and Cl as well as a negative weight for Ac.

The high EC and high pH are correlated with significant concentrations of NH_4 and we interpret the samples with large positive values of C3 as being from zones with elevated quantities of nitrogen, often in the form of NH_4 . Large negative values of C3 are associated with relatively low concentrations of nitrogen compounds and sometimes elevated sodium and chloride and low pH levels.

The first three principal components of zones 1 and 2 show a similar behavior. Both have negative C1 values on the order of -1 to -2 . The low values are indicative of low (below average) concentrations of all ions and below the average EC. Both zones have near zero C2 values and C3 values between $+1$ and -1 . Only minor changes in the principal component values are seen between the June 2000 values and the May 2002 values. The lack of change is expected in zone 1 since it is background. The lack of change in zone 2 indicates that process chemicals and their byproducts have not migrated to the area. In addition, the dewatering and circulation of air have not changed the chemistry in zone 2.

Source materials and degradation products have migrated into or evolved within zone 3. This zone has also been the focus of much of the remediation efforts. Zone 3 has the greatest variance in chemistry before the remediation effort and we interpret that as being due to the heterogeneous nature of the subsurface and uneven distribution of contaminant migration. Zone 3 has also seen the most change in chemistry over the two year period. P97-5A and P97-12B have chemistry similar to zones 1 and 2 and have shown little change and demonstrate that even within this contaminated area, some areas have not been affected. All other wells show signs of changing chemistry towards a more aerobic environment. The most dramatic changes are seen in 97-6A, 97-6B, 97-9A and 97-10B where C1 has declined in value and C2 has gone from negative to a large positive number. The dramatic changes in C3 for 97-10B and 97-4A are mainly due to the decreases in the reported sodium and chloride concentration. In addition, Ac EC, and NH_4 levels have declined. Wells 97-4B, 97-7A, 97-11A, 97-5B and 97-9B no longer have Ac and have started biodegrading NH_4 to NO_x with the shallower wells further along the process than the deeper ones (Table I). Limited mass loss might have been due to water extraction as small volumes of water taken from the site and the low hydraulic conductivity (Butterfield, 2002) of the subsurface likely inhibited contaminant migration in short timeframes thus biodegradation appeared to be the dominant removal mechanism for NH_4 and Ac. Volatilization of NH_4 is a potential pathway for NH_4 removal, but laboratory experiments indicated that this is not a significant sink (Ndegwa *et al.*, 2004). In addition, the evolution of NO_x is consistent with NH_4 degradation (Mrklas *et al.*, 2004). Although the pattern of change is complicated, all of the wells show distinct changes in their principal components. We interpret this complicated pattern to the wells starting and ending in a variety of different points in the chemical evolution. Wells 97-4A, 97-7B and 97-11B are still anaerobic, but have declining values of Ac. Well 97-11B is least far along in the process and has the least change in principal component values between the two surveys. The large positive values of C3 for wells P97-6A, P97-7A,

P97-9A and P97-11A are indicative of the accumulation of NO_x and the lack of chloride.

Clearly extracting water with Ac and the introduction of oxygen into the subsurface is having the desired effect of removing Ac and NH_4 from the system. However, the effect varies locally in both the vertical and horizontal over very small distances. This variability is consistent with the variable distribution of the compounds and preferred flow pathways due to the heterogeneous nature of the permeability distribution due to fractures, the horizontal well and sand lenses. Since aerobic and anaerobic zones with Ac are in close proximity, the lack of accumulation of elevated concentrations of NO_x with the major decline in NH_4 may be partially due to simultaneous nitrification-denitrification that has been hypothesized to explain the results of laboratory experiments (Mrklas *et al.*, 2004; Ndegwa *et al.*, 2004). In addition elevated NO_x concentrations result in the dissolution of sediments due to its acidic nature and consequently Ca and Mg concentrations increase.

Zone 4 is the original source area. It has been subjected to various remediation tests in the past, but it was not affected by the dewatering or air sparging system. However, it is a zone of induced infiltration and groundwater mounding due to ponding in the previous bioplug experimental area. HP-N and P98-3 are within remnant source zones and these samples exhibit elevated concentrations of Ac, NH_4 , high EC and they contain MEA. Both have high values for C1 and negative values for C2 indicating anaerobic conditions. The difference in the C3 value between the two sites is due to the higher concentration of MEA and the lower chloride concentration in HP-N compared to P98-3. The concentration of MEA, Ac, NH_4 and main ions have increased in HP-N in the May 2002 sampling, implying that transport from other locations is playing a role in zone 4. The persistence of MEA for many years after operations ceased is most likely due to phosphorus limitation in the soil (Mrklas *et al.*, 2004).

Well 98-1 has C1 change from slightly negative to near zero, C2 change from slightly negative to slightly positive and C3 change from near zero to positive. These changes are due to the elimination of Ac, an increase in NH_4 , introduction of NO_x and minor increases in ions. Ac has either been oxidized or migrated from the area and the area has become more aerobic. Additionally, nitrogen compounds must have migrated into the area.

HP-E has principal components that are similar to the background wells in zone 1, but it has slightly elevated values of Ac and NH_4 . The well has minor impact from degradation products. HP-S has similar chemistry to HP-E, but higher concentrations of Ac and NH_4 , which accounts for the difference in their principal component values. In contrast, HP-W has minor amounts of NH_4 , no Ac and minor concentrations of NO_x . Consequently, it is more aerobic than HP-E and HP-S. In all cases concentrations of the degradation products are slowly declining.

The Culvert represents an integrated average of the water moving south out of the source area that is captured in the trench. The Culvert sees the elimination of Ac, a general decrease in main ion concentration, lower EC, the reduction in NH_4

concentration and the appearance of NO_x . Component 1 has decreased to a value similar to background. C2 has increased to slightly positive as an indication of more aerobic conditions with some degradation products. C3 has increased to slightly positive in response to the high NO_x concentrations.

Clearly the pad area has a complex distribution of geochemical zones. The high infiltration rates and groundwater mounding seem to be mobilizing both MEA source and degradation products. At least two zones of impact exist in the vicinities of HP-N and P98-3. Since P98-3 is south of the trench, degradation products are probably migrating into zone 3 from zone 1. Although source zones still exist, the overall water quality of zone 4 is improving as evidenced by the gradual reduction in degradation products in HP-W, HP-E, HP-S and the Culvert. The improvement is most likely due to the enhance infiltration of oxygenated water and the removal of nitrogen compounds and acetic acid at the trench. Similar to zone 3, simultaneous nitrification-denitrification may be occurring and contributing to the removal of nitrogen from groundwater. Unfortunately, the source area around HP-N seems to be mobile and persistent.

Conclusions

An *in-situ* bioremediation program at the location of a decommissioned sour gas processing plant was monitored over a two-year period. Principal component analysis was used to help organize the groundwater chemistry data and analyze the chemical processes active at the site. The first three principal components accounted for approximately 75 % of the variability in the data. The first component separated contaminated waters from background. The second component indicated aerobic versus anaerobic conditions and the third component was indicative of the accumulation of nitrogen compounds. PCA was used to help distinguish between different geochemical states and to identify trends in the changing groundwater chemistry as the site was undergoing *in situ* bioremediation.

The site is extremely heterogeneous in the distribution of hydraulic conductivity with preferential flow pathways due to fractures, sand lenses and the fractured horizontal well. The PCA indicates drastically different geochemical conditions in close proximity. We hypothesize that zones of high hydraulic conductivity have preferential air flow and tend to be aerobic. These aerobic zones are located next to dense unfractured zones that tend to be more persistently anaerobic. The site can be conceived of a series of small, meter-sized reactors that interact and mix due to preferential flow paths and diffusion

Different areas of zone 3 had different geochemical starting points and evolved at different rates. However, in general the site is showing a reduction in Ac that is due to extraction of groundwater, oxidation due to increased groundwater and air circulation and fermentation. Onsite soil gas monitoring showed significant methane and carbon dioxide evolution in zone 3 indicating that some locations are anaerobic.

The bioremediation program has removed MEA from zone 3 and is changing zone 3 from an anaerobic to an aerobic environment producing decreases in NH_4 and increases in NO_x and SO_4 . NH_4 is being physically removed with the produced groundwater and it is being biologically oxidized to NO_x . Some losses may be due to volatilization, but soil gas samples and laboratory experiments indicate that this is an insignificant process. We interpret the slow decline in concentration of NH_4 as being due to the release of a large reservoir of cation exchanged NH_4 from the low hydraulic conductivity anaerobic zones that slowly diffuses to more aerobic zones where it is oxidized. On the other hand, NO_x is not accumulating as fast as the declines in NH_4 would indicate and this may, in part, be due to simultaneous nitrification-denitrification that has been observed in laboratory experiments.

These results demonstrate that the chemical evolution of the site cannot be explained without taking into account the complex interactions of flow and transport in a heterogeneous porous medium. The results show that zones with significantly different chemical conditions can exist in close proximity within the subsurface. Clearly, design of in situ remediation programs needs to account for the evolution and interaction of these different zones.

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