
Canadian Association
of Petroleum Producers



Migration of Methane into Groundwater

**from
leaking production wells
near Lloydminster**

March 1995

CAPP Pub. #1995-0001

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1. INTRODUCTION

In the vicinity of Lloydminster, methane is leaking from a number of oil and gas wells to surface, through casing vents and soils (Figure 1; Schmitz et al., 1993; Erno et al., 1994). There is a lack of information on whether this methane also migrates into shallow aquifers (Figure 1), and its impact on the aquifers, if any.

1.1 Background - Vertical Migration of Methane into Soils Surrounding Production Wells

A large number of production well sites in the vicinity of Lloydminster have "plumes" of methane gas that extend one to five meters outward from the wellheads within the soil. These methane plumes often adversely affect the vegetation growing in these soils (Godwin et al., 1990).

Little information is available about the pathways that transport methane rapidly from the deep sources to the soil horizons. The pathways appear to be in the annular space surrounding the production and/or surface casings (Figure 1). There may be permeable zones in the cement between the casings and borehole walls (Figure 1), perhaps interconnected fractures and other macropores. There may be apertures along the contacts between the cement and the casings and/or the borehole walls. Such a fracture or other pore (sometimes referred to as a micro-annulus) may allow relatively rapid upward migration of methane as bubbles through groundwater.

Methane disperses readily as a gas phase in sandy soils, and also along the ubiquitous networks of fractures in fine-grained soils and oxidized subsoils (<10 m below ground). This explains the relatively large size of plumes of methane (up to 5 m diameter) observed in some soils.

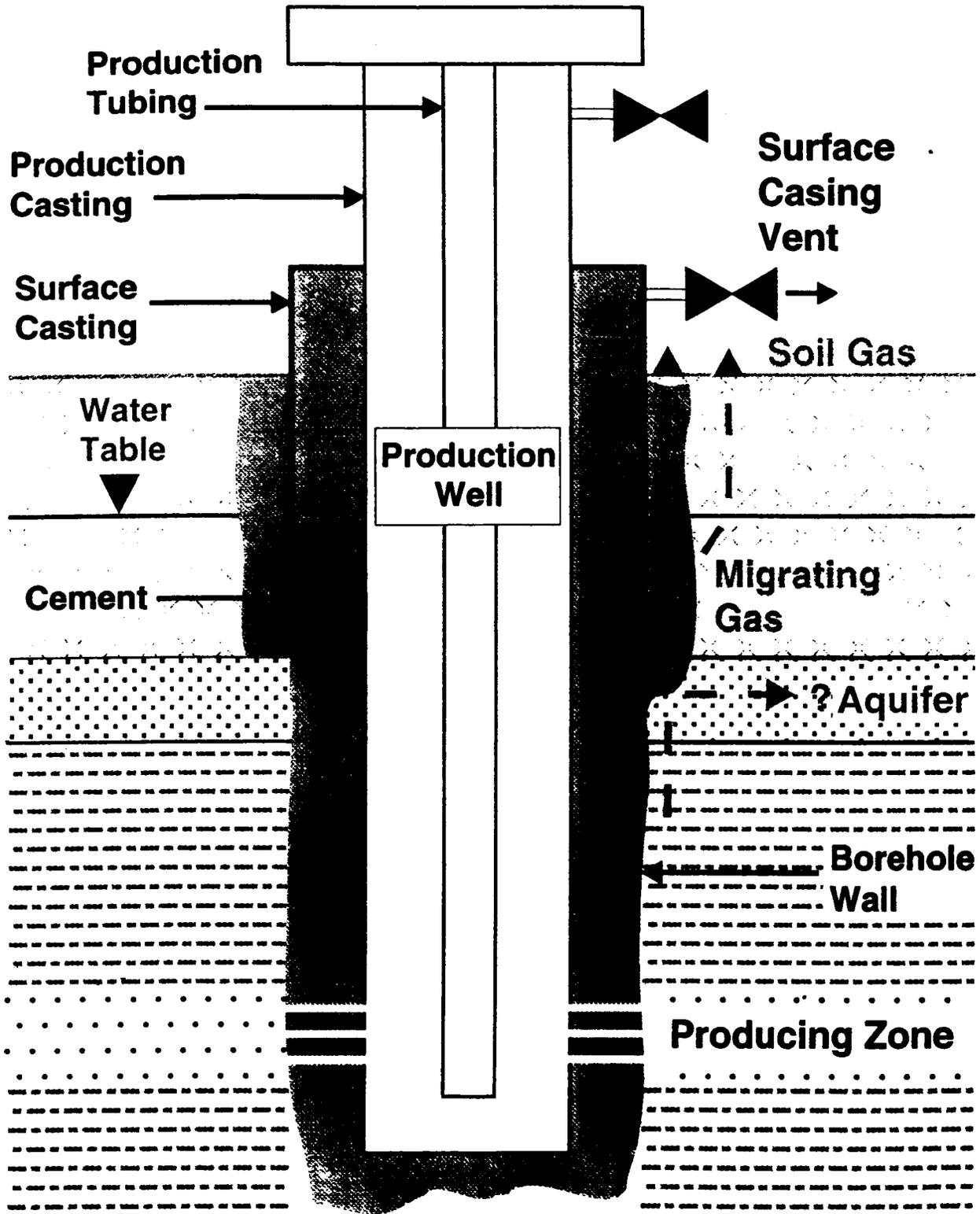


Figure 1 Schematic of gas migration, modified after Schmitz et al (1994).

1.2 Background - Methane in Aquifers

Methane that is being conducted upwards adjacent to the production wells may also spread out laterally into the various geological units intersected by the production well. Lateral diffusion of dissolved methane into fine-grained lithologies (unoxidized shale, clay, till) would occur at slow rates (on the order of 1 meter in 100 years: Freeze and Cherry, 1979, p. 393). In contrast, plumes of dissolved methane may migrate fairly rapidly by advective-dispersive transport into aquifers intersected by production wells (Figure 1; see Sections 4.1.1 and 4.2.4). It is uncertain whether methane also migrates laterally as a gas (bubble) phase within these aquifers .

In addition to possible contributions from leaking production wells, methane occurs naturally in some aquifers (e.g. Barker and Fritz, 1981; Hendry and Schwartz, 1990; Aravena and Wassenaar, 1993). Chemical and biochemical mechanisms have been documented that either produce or consume methane in the subsurface environment, but their significance in shallow aquifers in the vicinity of Lloydminster is not known.

Isotope techniques and methane/(ethane + propane) ratios are useful in distinguishing "thermogenic" methane, from "biogenic" methane (Wiese and Kvenvolden, 1993). Thermogenic methane is produced by chemical reactions at elevated temperatures and pressures, deep below the earth's surface. Biogenic methane is produced in the shallow subsurface (\sim 3 km) by microorganisms. To date, methane sampled from production zones and leaking production wells at surface in the Lloydminster area, consistently has had a biogenic isotopic signature (Rich et al., 1994). This limits the potential to distinguish methane leaking from production wells from methane derived from other, shallow biogenic sources.

2. OBJECTIVES

As outlined above, the migration of methane from leaking oil and gas wells into aquifers may be a problem in the Lloydminster area. No previous data on methane in shallow aquifers in this area are available. The main objectives of this study are the following:

- a) to determine if methane is present in shallow aquifers near leaking wells, and if so:
- b) to determine whether the methane is derived from the leaking wells or occurs naturally in the aquifers,
- c) to determine the concentration gradients and approximate flux rates of methane from leaking wells to shallow aquifers, and
- d) to predict the migration rate of methane in aquifers under various scenarios of time and physicochemical conditions.

3. METHODS OF INVESTIGATION

The primary components of this investigation were:

- 1) selection of research sites;
- 2) drilling of testholes;
- 3) installation of monitoring wells (2 phases);
- 4) purging of wells, pumping tests, and water level monitoring;
- 5) sampling and analyses for dissolved methane and other hydrochemical species;

The timing of some of these components overlapped to some degree.

3.1 Selection of Research Sites

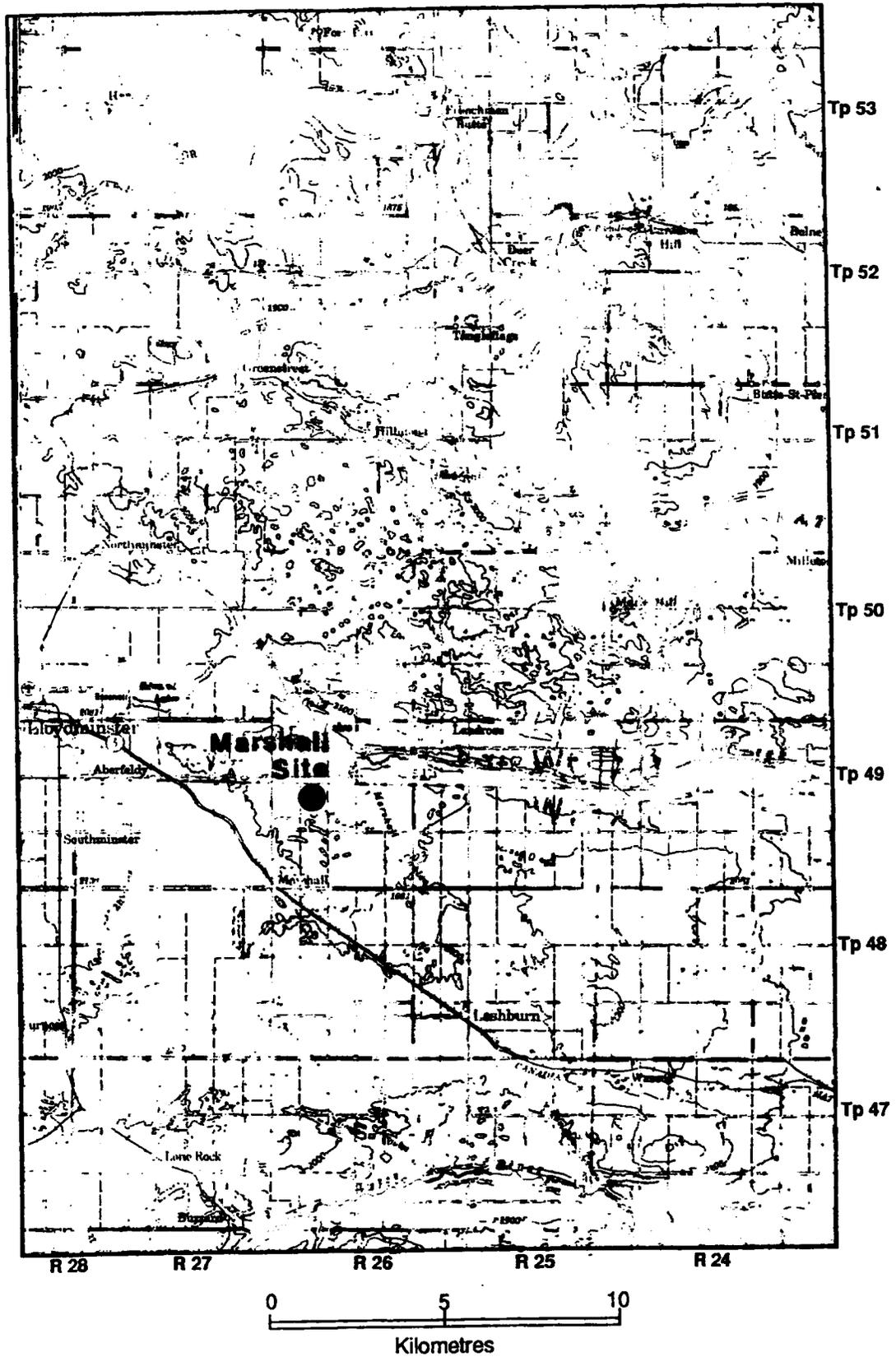
Two sites were chosen in the vicinity of Lloydminster (Figures 2, 3) based on existing information on leaking wells provided by participating oil companies, logs of testholes and water wells, and groundwater and geology maps. The oil wells at both research sites are no longer in production.

3.1.1 SITE 1. Aberfeldy Unit C14-16-49-26, Husky Oil Operations Ltd.

This site, located ~5 km northwest of Marshall, Saskatchewan, is referred to informally as the "Marshall site" (Figures 2, 4). It was chosen for several reasons:

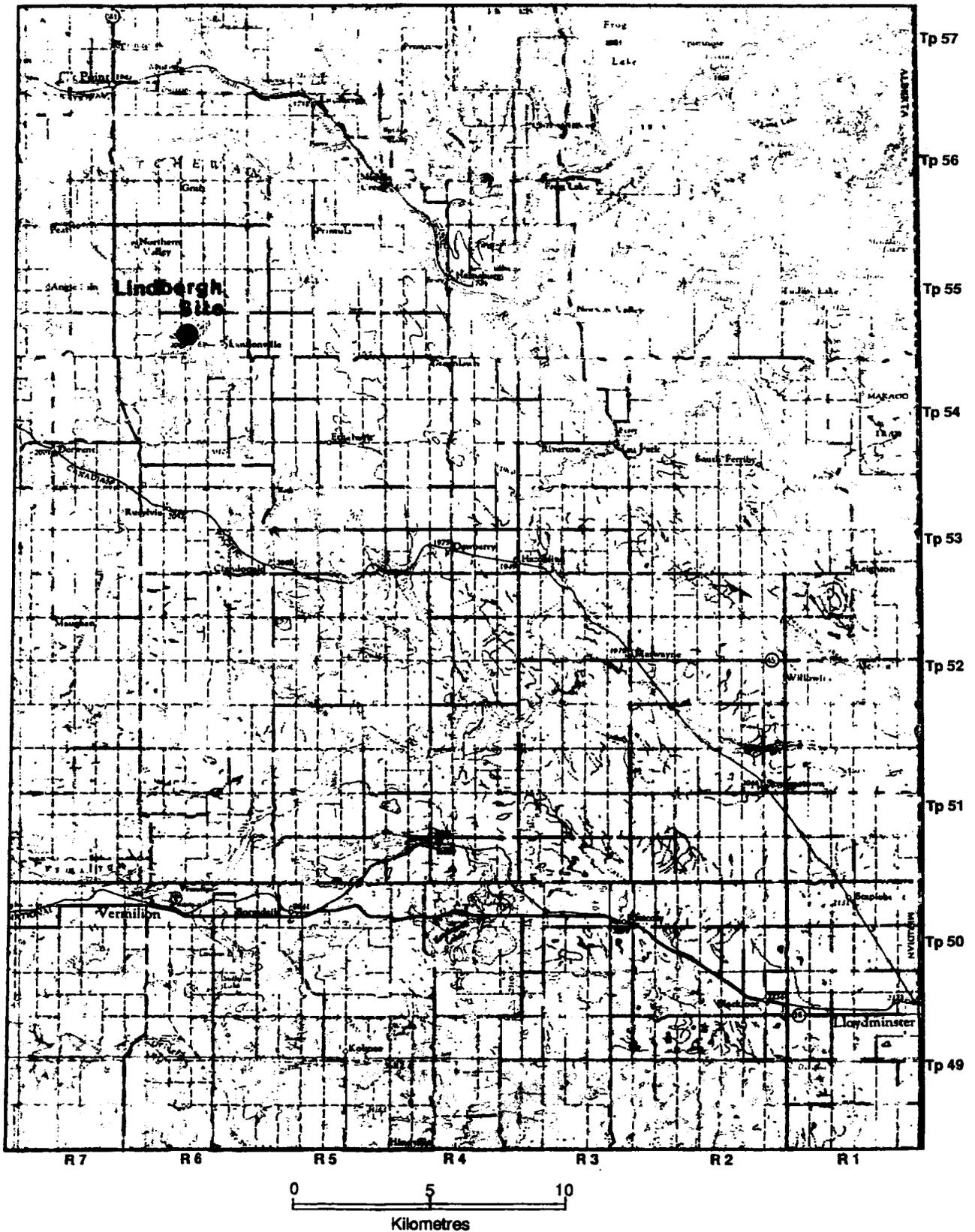
- Very high methane concentrations in soil pores (40% natural gas at the well head, same at 1 m and at 3 m from well head) were measured by an explosion meter on February 11, 1991. However, soil methane was not detectable on other occasions (6/28/90, 6/10/92, 9/30/92, 7/19/94, 8/26/94) (gas leakage history database, Husky Oil Operations Ltd.).
- Recent mapping by the Saskatchewan Research Council (Millard, 1990) indicated that the Ribstone Creek Tongue (Member), a sandy subunit within the Cretaceous Judith River Formation (Figure 5), locally an important water supply, is buried ~20 m below ground surface at this site.
- This site is relatively isolated, located ~500 m from the nearest adjacent production well, and on the northwestern fringe of the Aberfeldy oil field.

The Husky production well at this site was completed in November, 1965. The total depth drilled was 557 m below ground surface. The oil producing horizon, Lower Sparky sand, occurs at 522 to 534 m below ground surface. The borehole diameter is 200 mm (7.875"); the production casing diameter is 140 mm (5.5"). The cement used to



Base map by Energy, Mines and Resources, Ottawa

Figure 2. Location of the Marshall Site



Base map by Energy, Mines and Resources, Ottawa

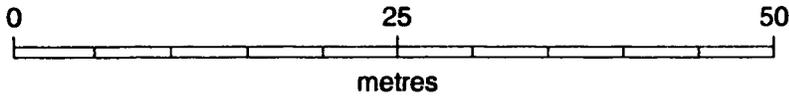
Figure 3. Location of the Lindbergh Site

⊙ MAR 94-04
598.478

598.5

Marshall Site (NW1/4 LSD 14-16-49-26 W3)

Scale 1:500



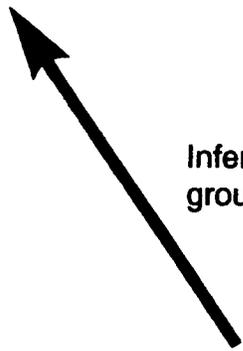
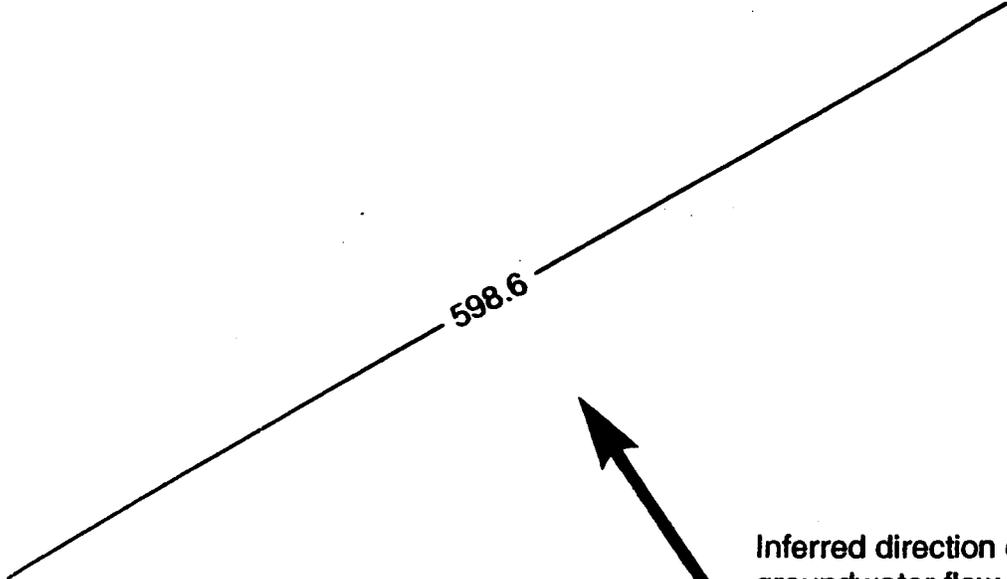
- ⊙ Monitoring well
- ⊕ Production well
- Testhole and monitoring well

Note:
Contours and data at monitoring wells are in units of metres above sea level. Contour interval is 0.1m.

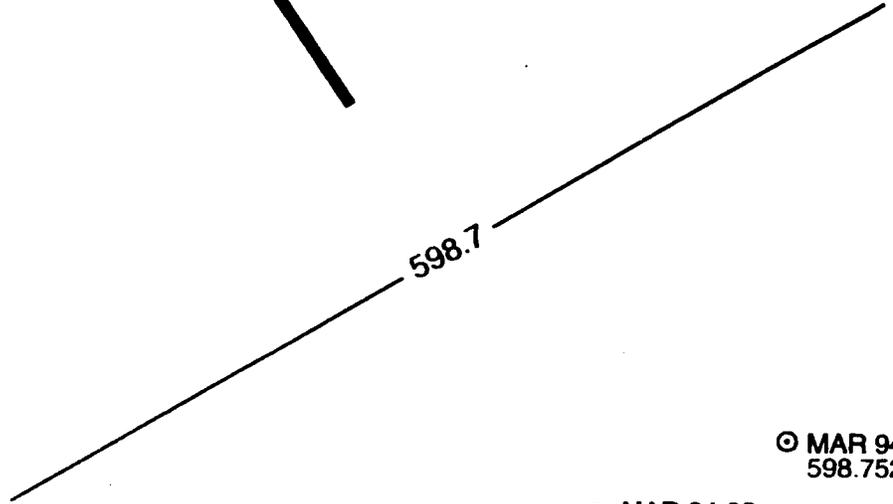
Figure 4 Plan of the Marshall site and water levels measured on Oct. 18, 1994.

E-W fenceline

94
598.5



Inferred direction of groundwater flow

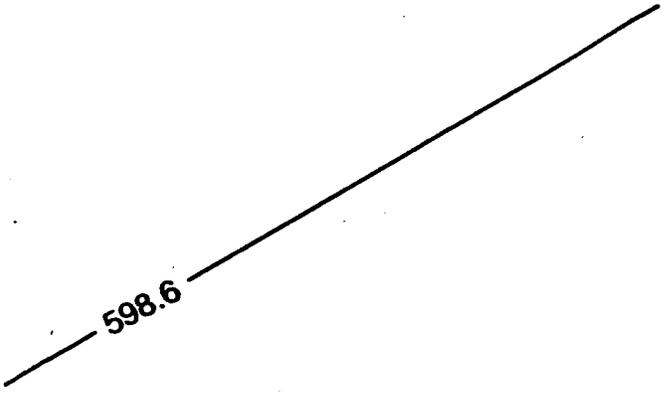


⊙ MAR 94-02
598.752

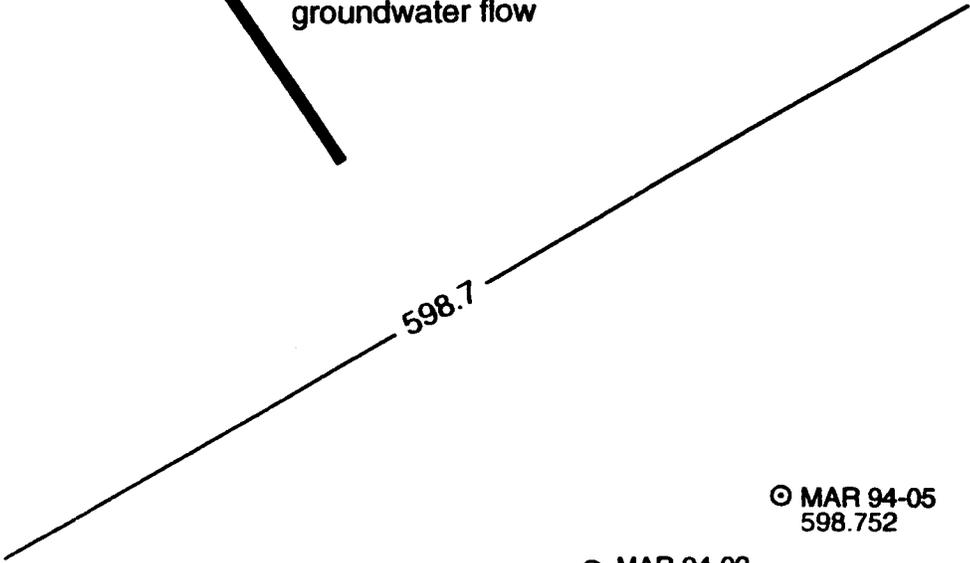
⊙ MAR 94-02
598.747

○ Production well
● MAR 94-01
598.770

E -W fenceline



Inferred direction of groundwater flow

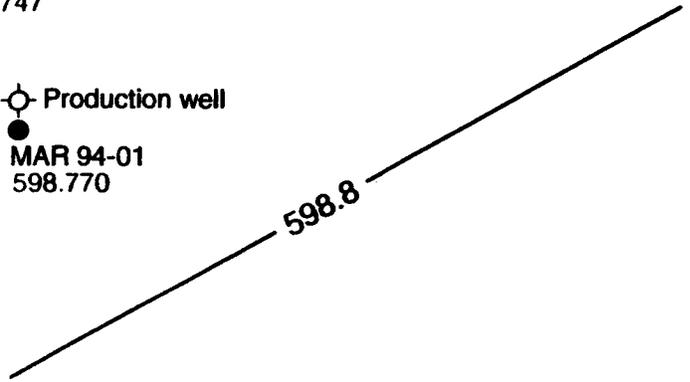


⊙ MAR 94-03
598.749

⊙ MAR 94-05
598.752

⊙ MAR 94-02
598.747

⊙ Production well
● MAR 94-01
598.770



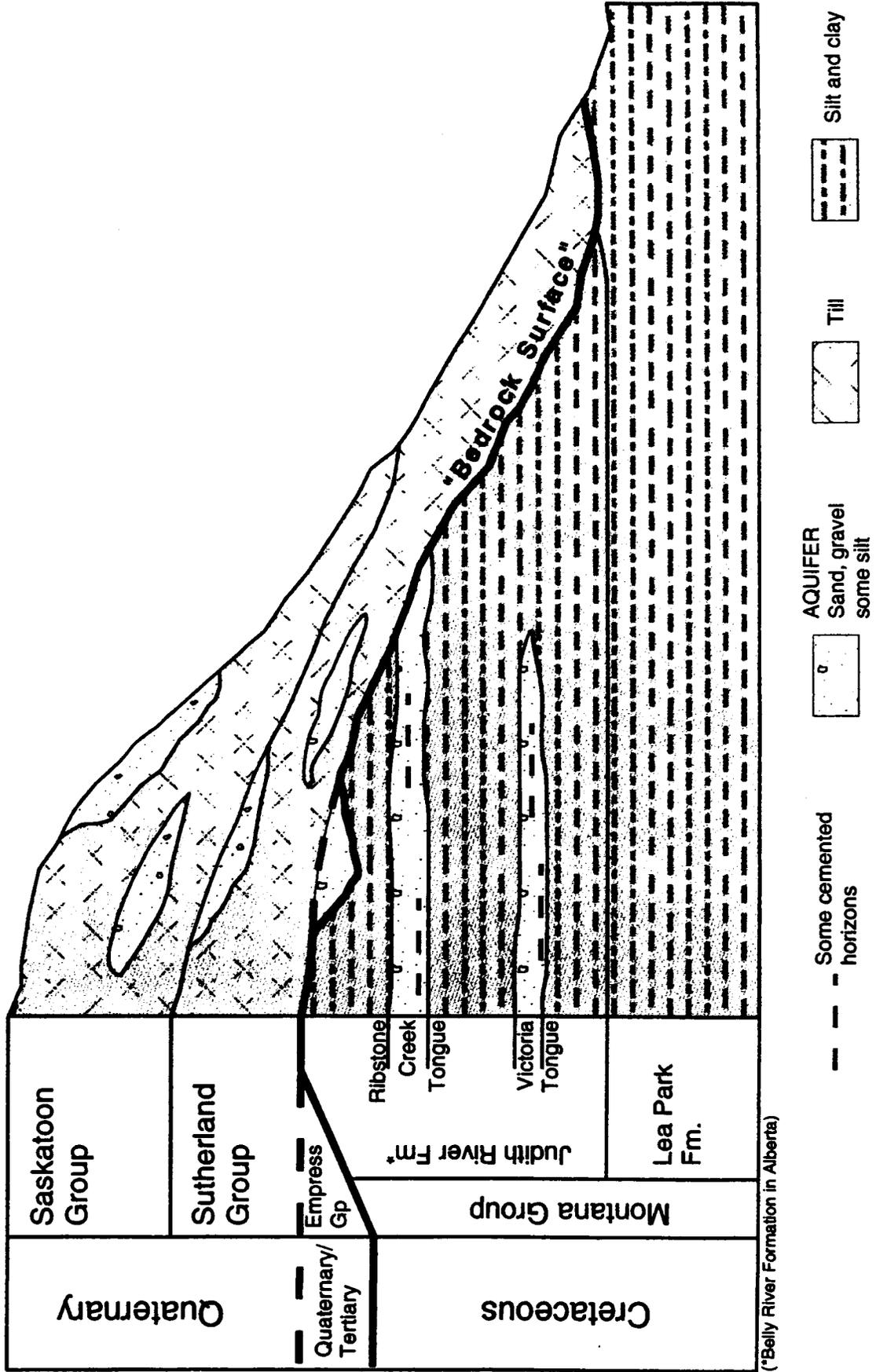


Figure 5 Generalized stratigraphy of the Lloydminster area.

set the casing was a mixture of Oilwell Neat and Standard Portland with 6% gel. Approximately 1 m³ of cement return was observed at the wellhead.

3.1.2 SITE 2. LINDE-1 16-4-55-6-W4, Amoco Canada Ltd.

This site, located ~20 km southeast of Elk Point, Alberta is referred to informally as the "Lindbergh site" (Figures 3, 6). It was chosen for several reasons:

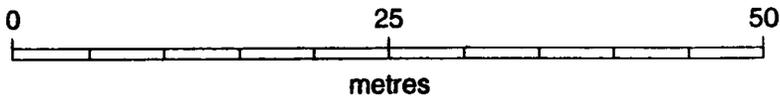
- Methane leakage was noted in 1988 (K. Uhrich, pers. comm.), and continues to bubble out of a pool of water in a cellar surrounding the production wellhead. Relative concentrations and stable isotope measurements of methane and other light hydrocarbons leaking as a gas phase at this wellhead have been determined (Rich et al., 1994, and unpublished data).
- This site is relatively remote from other production wells in the area, on the southern fringe of the Lindbergh oil field.
- Shallow (<50 m) drift and bedrock aquifers are present in the vicinity, as documented by Alberta Environmental Protection (Ozoray et al., 1994; additional reference oil logs and water well records).

The Amoco production well at this site was completed in December, 1983. The total depth drilled was ~640 m below ground surface. A surface casing was installed from ground surface to ~100 m below ground. For this interval, the borehole (drill bit) diameter is 374 mm; the surface casing diameter is 273 mm, and the production casing is 177.8 mm diameter. Class A cement with 3% CaCl₂ was used to set the surface casing. Contaminated cement return was observed at the wellhead. The production casing was set with "Thermal III + 0.7% NFL₂" cement; 1.5 m³ return at surface was noted.

N - S fence line

Lindbergh Site (16-04-55-06-W4)

Scale 1:500



- ⊙ Monitoring well
- ⊕ Production well
- Testhole

Note: Tentative contours and data at monitoring wells are in units of meters above sea level. Contour interval is 0.005m. Differences in water levels are approximately the same order of magnitude as measurement error (accuracy $\sim \pm 0.005\text{m}$), but indicate a consistent gradient (decline to southwest).

Figure 6: Plan of the Lindbergh site and water levels measured on Oct. 17, 1994.

62

E - W fenceline

N - S fenceline

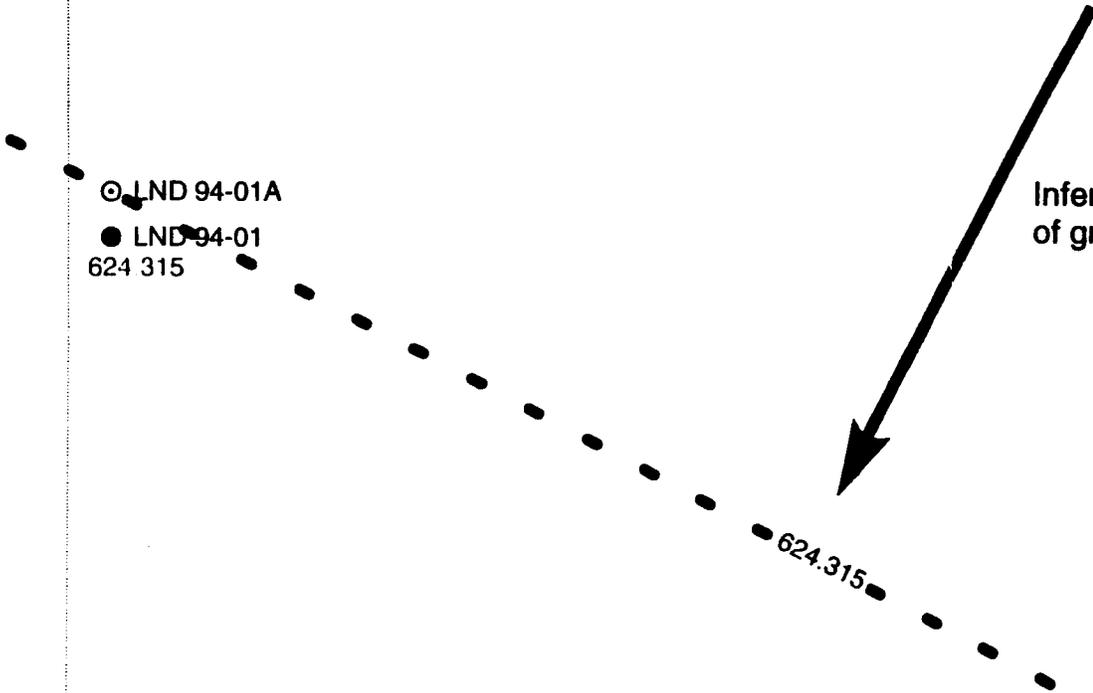
624.31
(anomalous
datum)
⊙
LND 94-03

624.317
⊙
Prod.
well
LND 94-02

⊙ LND 94-01A
● LND 94-01
624.315

Infer
of gi

624.315



E - W fenceline

624.32
LND 94-05

624.320



624.31
(anomalous
datum)
LND 94-03

624.317
LND 94-02
Prod.
well

Inferred direction
of groundwater flow



94-01A
94-01

624.315

LND 94-04 624.315

The oil producing horizons (Lower Cummings B" and "Sparky") occur between -510 to 580 m below ground surface. Oil was produced from this well between February, 1984 and November, 1987.

3.2 Completion of Testholes

In this investigation, one testhole was completed at each site in May, 1994. Mac Millard of the Saskatchewan Research Council conducted the geological interpretations.

A rotary drilling rig (Failing 1250) was used at both sites because coarse gravel and/or cemented bedrock horizons were known to occur in these areas. The drill bits used ranged from 130 to 159 mm (5.125" to 6.25") in diameter. Local supplies of fresh surface water were used for the drilling fluids. Cutting samples were collected for 1.5 m (5') intervals during the drilling. A downhole E-log (spontaneous potential, resistivity) was obtained for each open hole after drilling had been completed.

3.2.1 Marshall Site Testhole (MAR-94-1)

The drift encountered at this site was oxidized (brown) and unoxidized (gray) till (Appendix A). The bedrock surface was encountered at 10.4 m below ground surface. From 10.4 to ~30 m, the lithology varied from clay to silt to silty sand, with a few consolidated horizons of siltstone or sandstone. From 30 to 41 m, the lithology was a more uniform gray shale (silt and clay). The inferred main aquifer zone, consisting of sand(stone) and silt(stone), interpreted as part of the Ribstone Creek member, occurred from 20 to 23 m below ground. This aquifer was targeted as the completion zone for monitoring wells at this site.

3.2.2 Lindbergh Site Testhole (LND-94-1)

About 45 m of drift was encountered at this site, underlain by gray shale (silt and clay) to 53 m below ground surface (Appendix A). The drift consisted mainly of till from ground surface to a depth of 25 m. An intertill sand unit was encountered at 16.2 to 17.4 m. Coarse-grained paleochannel sediments (Empress Group?) were encountered from 25 to 45 m. The uppermost meter and lowermost 3 m of these channel deposits was largely gravel, the rest was mainly medium to coarse sand. This large paleochannel was targeted as the aquifer for the completion of monitoring wells. It is possible that this paleochannel is continuous with a northwest-southeast-trending channel incised into bedrock, that was inferred by Ozoray et al. (1994 their Fig. 3).

This testhole was abandoned with a bentonite slurry grout (Baroid BENSEAL®, water mixture), and backfill from -5 m depth to ground surface.

3.3 Installation of Monitoring Wells

Monitoring wells were installed in two phases:

- 1) Three monitoring wells were installed at each site in May, 1994 (Appendix A). Monitoring well MAR-94-1 was installed in the testhole at the Marshall site. For all other wells, the drilling was terminated 1-2 m below the targeted depths for placement of well screens.
- 2) Two additional monitoring wells were installed at each site in September, 1994, after initial data (water levels, pumping tests, hydrochemical analyses) had been collected and a preliminary assessment of groundwater flow conditions had been conducted.

The drilling for installation of wells was conducted as for the testholes: 1.5 m interval cutting samples were collected, and E-logs were obtained for each open hole (SP logs not available for second phase of drilling) . For all monitoring wells, 5 cm (2")

diameter PVC screens (10 slot Johnson) and Schedule 80 PVC casings (buttress thread with o-rings) were used. Frac. sand (10/20) was placed around the screens, then graded sand to the tops of the completion aquifers, topped by a layer of bentonite pellets, and then a bentonite grout slurry (Baroid BENSEAL® and water mixture) to ground surface. Individual monitoring well completion data, together with lithologic logs, and E-logs are shown in Appendix A.

3.4 Purging of Wells, Pumping Tests, and Water Level Monitoring

Each monitoring well was purged after completion. This procedure was required to remove drilling fluid that had entered the aquifer in the vicinity of the screen. The purging was conducted in two ways: first, "air lifting" with the drilling rig pump (compressed air, generally for 10 to 20 min); second, displacement with a Grundfos® Redi-Flo submersible pump at a rate of 7.5 to 20 L/min for 3 to 13 hours. Purge volumes of between 2200 to 9400 L were removed from each monitoring well. Assuming aquifer porosities of 35%, groundwater within a radius of -1 to 2 m was purged from the aquifer around each screen. Such purging would have disturbed any meter-scale gradients in methane concentrations in the immediate vicinity of the monitoring wells. Pumping tests were conducted in June, 1994 at each site to determine bulk transmissivities, and to infer hydraulic conductivities (Appendix A). MAR-94-02 and LND-94-03 were used as the pumping wells. The tests were conducted with a Grundfos® submersible pump at rates of 7 L/min for 5 hours (Marshall site) and 16 L/min for 3 hours (Lindbergh site).

Water levels were measured periodically between May and October, 1994 to determine hydraulic gradients and flow conditions in the aquifer (Appendix A). The measurements were made manually using an electric water level detector.

3.5 Sampling for Dissolved Methane and other Hydrochemical Components

Special techniques were required to prevent loss of methane by degassing during collection and handling of groundwater samples. Certainly some degassing has occurred from the upper portion of the stagnant water column in each well, combined with upward diffusion. There is also a possibility that some methane has degassed as bubbles from the screened portion of the wells during initial purging and pumping tests, considering that the drawdowns (≤ 2.5 m) decreased the hydraulic pressure at the screens by up to 0.25 atm. This would have been offset by subsequent advection and diffusion from the aquifer surrounding the well screens.

Submersible bladder pumps constructed of stainless steel and Teflon™ (Geotech model # 0510) were used to sample groundwater at each well screen for all of the required hydrochemical analyses (Figure 7). This type of pump operates by cycling the pressure of compressed air in a stainless steel chamber around a Teflon™ bladder between 1 and 9 atm. The bladder in each pump has inlet and outlet check valves. When the bladder is squeezed by compressed air, the groundwater that has entered through the lower check valve is pushed through the upper check valve and eventually pumped through a 1.3 cm (0.5") Teflon™-lined polyethylene flow tube to surface.

For sampling, the pump inlet was placed approximately in the middle of the well screen interval. After determining the quasi-steady drawdown (several cm), the pump was isolated from the water column above by inflating a rubber packer with compressed N₂ (~5 atm) in the casing. This packer was located above and within a meter of the pump and top of screen. Prior to sampling, the bladder pump was used to "micro-purge" the system: ~20 L were removed from each well, equivalent to ~3 to 4 times the combined volume within the packed off interval of the well, bladder and flow tube. During micro-purging and sampling, the pumping rate (90 to 200 mL/min) was maintained at a steady rate for each well.

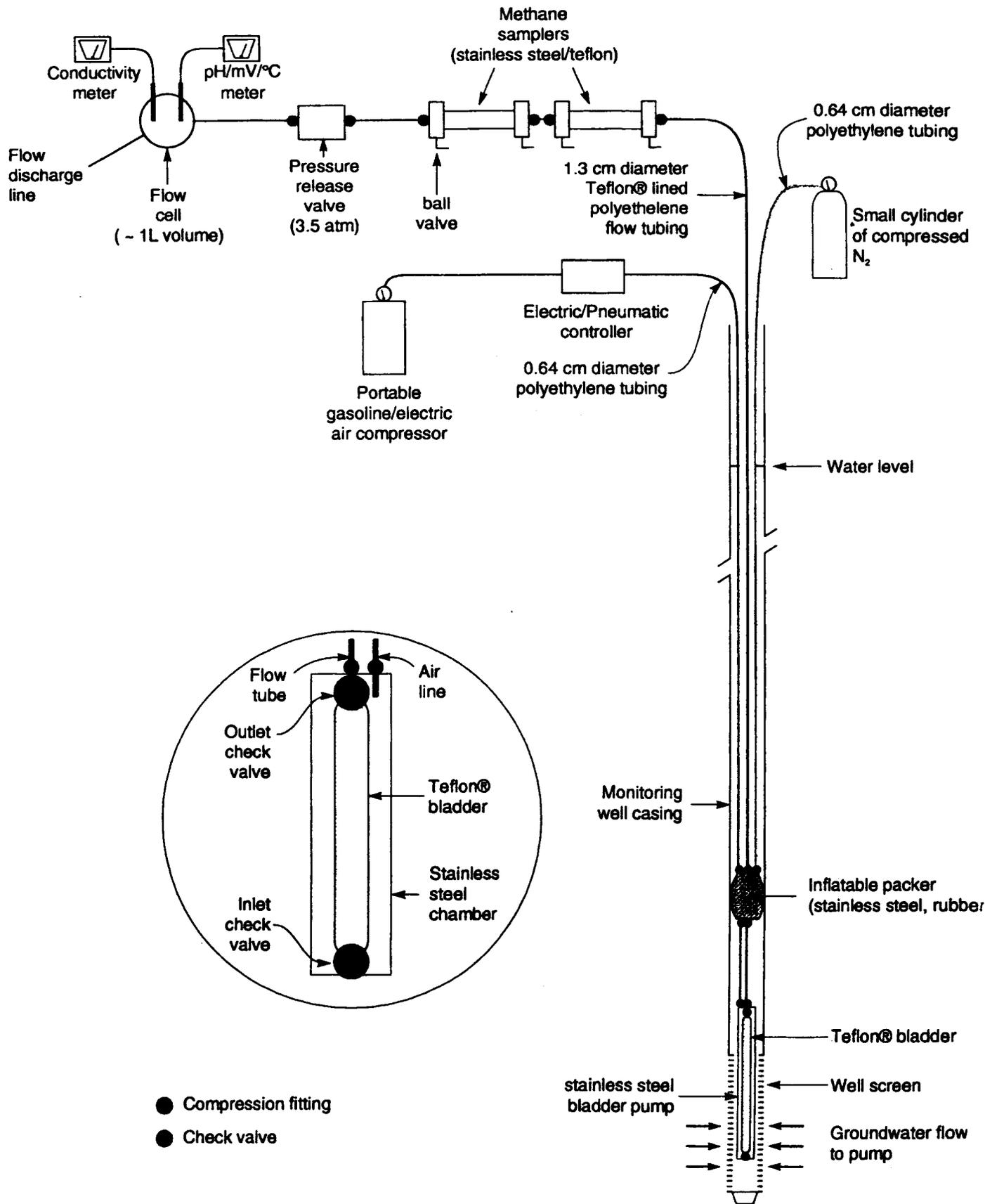


Figure 7 Schematic of the sampling apparatus used in this investigation

3.5.1 Samplers for Dissolved Methane

Stainless steel samplers were constructed to sample methane in groundwater (Figure 7). Each sampler consists of a stainless steel tube (1.3 cm (0.5") diameter, 10 cm long), connected at each end by compression fittings to a 1.3 cm (inside diameter) stainless steel/Teflon™ ball valve (NCS model CF 8M). These valves are rated to withstand pressures up to 136 atm (2000 psi). Each sampler was tested for leaks with compressed air (~7 atm). Negligible leakage was observed over periods of 1 to 5 days. The sampling volume of each sampler is approximate.

At the study sites, these samplers were connected above ground surface with compression fittings to the end of the flow tube leading from the bladder pump (Figure 7). Several samplers were connected in-line for collection of replicate samples. Downflow of the samplers, a brass pressure release valve allows passage of the groundwater when the pressure exerted by the pump exceeds 3.4 atm (50 psi). This valve was used to maintain the pressure in the samplers at or above the hydraulic head of the aquifer, in order to prevent degassing of methane.

After micro-purging, the ball valves on the samplers were closed, the pumping stopped, and the samplers were detached from the flow tubing. The samplers were stored on ice in the field and transferred to a cooler (5°C) for up to 3 weeks before extraction and analysis.

3.5.2 Collection of Other Samples and Field Analyses

After micro-purging, and prior to collection of the methane samples, groundwater that had passed through the pressure release valve downflow of the methane samplers was collected in polyethylene bottles in order to analyze the dissolved major ions (Ca, Mg, Na, K, HCO₃, SO₄, and Cl) and selected redox species (nitrate plus nitrite, Fe and

Mn). The samples for nitrate and nitrite analyses were filtered (0.45 μm) and treated with H_2SO_4 for preservation. The samples for Fe and Mn analyses were also filtered, and treated with HNO_3 for preservation. The analyses of these redox species were required to provide general constraints on the potential mechanisms for oxidation of methane within the aquifer environment.

The conductivity, pH, Eh (mV), and temperature of the groundwater pumped to surface was measured in a flow cell connected with flow tubing to the pressure release valve (Figure 7). A Cole Parmer® Model 1481-40 Conductivity Meter and a Cole Parmer® pH/mV/°C Model RS232 Meter were used for these measurements. The Eh values determined by this method are considered to be only approximate (e.g. Appelo and Postma, 1993).

3.6 Methane Analyses

The method for extraction and analysis of methane in the groundwater samples collected in the 20 mL (nominal) stainless steel samplers was as follows: For each sampler, one ball valve was attached to an evacuated glass manifold (~500 mL) and opened to transfer the groundwater sample (Figure 8). The sampler/manifold connection was not completely air-tight during transfer (a few seconds); a small amount of ambient atmospheric air may also have been introduced as bubbles trapped in deionized water used to reduce the dead volume at the sampler valve. This atmospheric gas was assumed to contain negligible quantities of methane and ethane. In the manifold, the sample was stirred for several minutes during degassing. Then a large, measured fraction of the evolved gas in the manifold was displaced with a reservoir of mercury into a volumetric burette and adjusted to 1 atm pressure. A portion (250 μL)

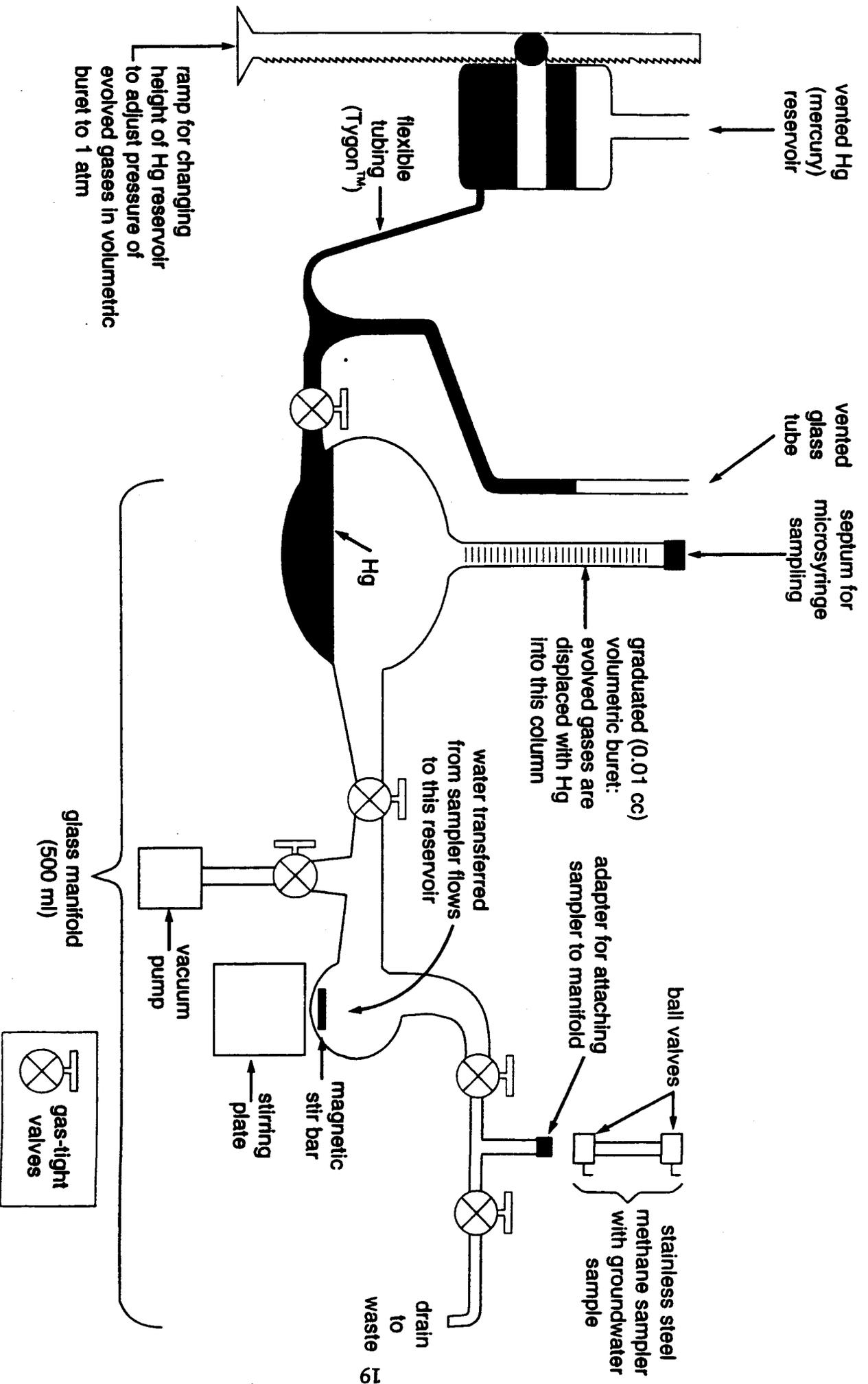


Fig. 8 Schematic of methane extraction apparatus used in this investigation.

of the evolved gas was then extracted through a septum into a micro syringe and injected into a gas chromatograph (HP 5890, Ar carrier) for analysis.

For comparison, duplicate samples from four monitoring wells were analyzed for methane in groundwater at the National Hydrology Research Institute (NHRI). Each sampler was fitted with Luer lock syringe adapters at each end. Two plastic 50 mL syringes fitted with Luer lock 3-way valves were then attached to each adapter. The upper syringe contained 40 mL of methane-free gas. The dead volumes at the valves at each end of the sampler-syringe assembly were purged with the same methane-free gas. Then the sampler valves were opened and the plunger of the upper syringe was pushed so that the methane-free gas acted as a piston to slowly (~5 sec.) displace the 20 mL groundwater sample into the evacuated syringe at the bottom, along with ~20 mL head space (measured). After the valve of the lower syringe was closed, this syringe was detached from the assembly, shaken for several seconds, and allowed to degas and equilibrate for a few minutes. Then a portion of the head space gas in this syringe was injected into a Carle Special Series S Model 311 Analytical Gas Chromatograph (equipped with porapak and molecular sieve columns, and automatic valve switching, He carrier) for analysis.

4. RESULTS AND INTERPRETATION

4.1 Marshall Site

4.1.1 Groundwater Flow

At the Marshall site, the water level data collected from the monitoring wells indicate that the groundwater flow in the aquifer is towards the north-west (Figure 4). Based on measurements made on October 17, 1994, the hydraulic gradient is -0.0022 . Based on Saskatchewan Water Corporation records, the closest farm well completed in

the same Ribstone Creek Tongue is 1.2 km to the northwest (downgradient) of the production well.

The pumping test results for MAR-94-03, drawdown versus time, were interpreted by comparison to the Theis theoretical curve (Appendix B). Matching indicated a transmissivity of $6.84 \times 10^{-5} \text{ m}^2/\text{s}$. Assuming a uniform aquifer zone thickness of 2 m, the hydraulic conductivity of this aquifer zone is $3.4 \times 10^{-5} \text{ m/s}$.

Assuming a uniform porosity of the aquifer zone of 35%, the average linear velocity of groundwater (v) was calculated as follows:

$$v = (3.4 \times 10^{-5} \text{ m/s})(0.0022)/0.35, \text{ equivalent to } -2 \times 10^{-7} \text{ m/s, } -0.017 \text{ m/d, or } -6.1 \text{ m/year.}$$

4.1.2 Methane Concentrations

Methane concentrations measured in the samples collected from the monitoring wells at the Marshall site range from 0.002 to 0.16 mg/L (Table 1). The 1994 data should be viewed as approximate concentrations. The precision for duplicate analyses collected in May was ± 33 to 57%. There were problems with sample transfer for extraction of methane from some of the October samples (Appendix C). Improving the handling and extraction techniques, and achieving greater analytical precision will be priorities for the 1995 monitoring program.

As a general rule, the methane concentrations measured in the various monitoring wells decreased with distance from the production well. The only exception to this pattern is that the concentration of methane in the most distant well, MAR-94-04 (0.027 to 0.055 mg/L), was higher than in several closer wells (MAR-94-02, MAR-94-03, MAR-94-05: 0.002 to 0.039 mg/L). With respect to groundwater flow, MAR-94-04 is almost directly downgradient of the production well. Thus, the relatively high concentration

Table 1. Methane and ethane concentrations in groundwater at the Lindbergh and Marshall sites.

Monitoring Well	Sample Date	methane mg/L	ethane mg/L	Monitoring Well	Sample Date	methane mg/L	ethane mg/L
Lindbergh Site							
LND-94-01A	June 1/94	0.062	ND	MAR-94-01	May 30/94	0.16	ND
	June 1/94	0.063	ND		May 30/94	0.044	ND
	Oct. 18/94	0.02	ND		Oct. 19/94	(0.003**)	ND
LND-94-02	June 1/94	8.6	0.043	MAR-94-02	May 30/94	0.025	ND
	June 1/94	14	0.068		May 30/94	0.012	ND
	June 1/94	12	0.06		May 30/94	0.039	ND
	Oct. 18/94	2.1	0.009		Oct. 19/94	0.022	ND
	Oct. 18/94	6.2*					
LND-94-03	June 1/94	0.02	ND	MAR-94-03	May 30/94	0.002	ND
	June 1/94	0.012	ND		May 30/94	0.004	ND
	Oct. 18/94	0.014	ND		Oct. 17/94	0.003	ND
LND-94-04	Oct. 6/94	(< 0.001**)	ND	MAR-94-04	Sept. 30/94	(0.001**)	ND
	Oct. 18/94	0.03	ND		Sept. 30/94	0.055*	
					Oct. 17/94	0.027	ND
LND-94-05	Oct. 6/94	0.003	ND	MAR-94-05	Sept. 30/94	0.003	ND
	Oct. 6/94	0.025*			Sept. 30/94	0.0063*	
	Oct. 18/94	(0.003**)	ND		Oct. 17/94	0.015	ND

* analysed at the National Hydrology Research Institute, all other analyses at the Saskatchewan Research Council.

** assumed erroneous results because of observed incomplete sample transfers during extractions.

ND = not detectable

Precision for the above SRC analyses ranged from +/-1 to +/-57% (relative to mean concentrations).

of methane at MAR-94-04 may reflect the fact that it is near the center of a methane contaminant plume extending downgradient of the production well. In contrast, MAR-94-03, for example, which is closer (46 m from the production well) may lie outside the methane plume (see Section 4.1.4).

The spatial distribution of methane in the aquifer indicates the presence of a dissolved methane plume, derived from the Husky production well, which may have impacted groundwater more than 130 m downgradient. This extent is reasonable, considering the inferred flow rate (6 m/year) and time elapsed since installation of the production well (29 years). However, the methane concentrations measured in the plume (up to 0.15 mg/L) are low. They are 3 to 4 orders of magnitude below the inferred saturation for dissolved methane in this aquifer (74 mg/L, see Appendix D).

Based on plume modelling, as described in Section 4.1.4, the concentration of methane at MAR-94-03 (0.002 to 0.004 mg/L) may be indicative of "background" methane levels in the aquifer. It is likely that low level methane is an intrinsic property of this aquifer, unrelated to migration from production wells, or other human activities. A study of the same Ribstone Creek Tongue in the Alberta Special Areas district, south of the Lloydminster area (Prairie Farm Rehabilitation Administration, 1993) found methane to be the dominant dissolved gas in this and other bedrock aquifer zones. However, this study did not report absolute concentrations (mass per volume of groundwater) of methane.

Within a larger context, the Ribstone Creek Tongue as part of the Judith River Formation, along with other adjacent Cretaceous sediments, form a shallow, "tight gas reservoir" (biogenic methane) in portions of Saskatchewan, Alberta and the adjacent Northern Great Plains of the United States (Law and Spencer, 1993). Thus, although a thick confining shale sequence is not present above the Ribstone Creek Tongue aquifer

at the Marshall site, it would not be surprising to find low-level, intrinsic methane in this unit, perhaps diffusing slowly from the underlying shale.

4.1.3 Other Hydrochemical Data

Hydrochemical analyses of samples collected from the monitoring wells at the Marshall site indicate that the groundwater is dominated by Ca, Mg, Na, HCO₃ and SO₄, with total dissolved ions ranging from 960 to 1406 mg/L (Table 2). The sulfate concentrations tend to be lowest in the vicinity of the production well (~200 mg/L, MAR-94-01, MAR-94-02). In contrast, the concentration of sulfate is highest (423 - 430 mg/L) at MAR-94-03, which appears to lie outside the methane plume (cf. following section). The pattern of sulfate concentrations at the Marshall site suggests that concurrent microbial oxidation of methane and reduction of sulfate may be significant. The lack of nitrate (<0.01 mg/L), occurrence of dissolved Fe (0.46 to 2.7 mg/L) and Mn (0.16 to 0.67 mg/L), and relatively low Eh (Table 2) indicate reducing conditions, and support the interpretation that sulfate reduction may be occurring. The bulk of any sulfate that has been reduced to sulfide in this aquifer has likely precipitated as mineral sulfide (e.g. FeS). Based on Eqn. 1, one millimole of sulfate (96.07 mg) is required to oxidize one millimole of methane (16.04 mg):



Stated another way, this means that 5.99 mg of sulfate (96.07/16.04) are reduced to oxidize 1 mg of methane. Equation 1 is a simplified, overall reaction, not intended to represent the complexity of concurrent microbially mediated reactions that may actually take place.

Table 2. Groundwater chemistry for the monitoring wells at the Lindbergh and Marshall sites.

Lindbergh Site Monitoring Well	Date Sampled	pH field	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO3 mg/L	SO4 mg/L	Cl mg/L	Fe mg/L	Mn mg/L	NO3 + NO2 mg/L	Eh field mV	Sum of ions mg/L
LND-94-01A	940601	6.66	155	56	123	6	554	390	19	2.8	0.87	<0.01	31.7	1303
LND-94-02	941018	7.02	156	60	132	6.3	569	396	20	2.8	0.87	<0.01	11.9	1343
LND-94-03	940601	6.95	158	58	123	5.8	562	382	19	5.4	2.1	0.01	15.1	1308
LND-94-04	941018	6.9	143	59	106	4.9	581	375	20	4.2	1.5	<0.01	-34.2	1321
LND-94-05	941006	6.99	150	62	111	6.4	590	389	19	0.79	0.82	<0.01	-44.1	1333
	941018		155	61	100	6.6	574	384	18	1.7	0.82	<0.01		1300
	941018		152	61	101	7	574	378	18	0.73	0.32	<0.01		1294
	941006		144	58	90	4.8	546	343	18	0.76	0.35	<0.01		1205
	941018		150	59	90	5	550	347	18			<0.01		1220

Marshall Site Monitoring Well	Date Sampled	pH field	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO3 mg/L	SO4 mg/L	Cl mg/L	Fe mg/L	Mn mg/L	NO3 + NO2 mg/L	Eh field mV	Sum of ions mg/L
MAR-94-01	940530	7.28	125	45	139	7.3	514	338	5	1.4	0.16	<0.01	-38.4	1173
MAR-94-02	941019	7.18	128	50	59	5.5	535	213	2	1.3	0.27	<0.01	-32.6	994
MAR-94-03	940530	6.98	140	50	43	5.8	520	199	2	2.7	0.22	<0.01	-22.4	960
MAR-94-04	941019	7.01	144	51	40	6	622	208	2	0.46	0.67	<0.01	-39.9	1075
MAR-94-05	940530	7.17	201	76	67	6.7	614	423	3	0.87	0.36	<0.01	-45.6	1391
	941017		208	75	59	6	622	430	3			<0.01		1406
	940930		171	62	50	6.2	579	289	4			<0.01		1161
	941017		166	62	59	7.3	579	277	3			<0.01		1154
	940930		170	63	54	6	567	317	4			<0.01		1181
	941019		166	62	62	7.2	568	301	3			<0.01		1170

4.1.4 Modelling of the Methane Plume

Given the complexity of the physicochemical and biochemical processes that may affect the migration and fate of methane in shallow aquifers, the quantitative modelling component of this study is of a preliminary nature. An analytical model, PATCH3D (Sudicky et al., 1988) was used to model the transient transport of dissolved methane.

A number of assumptions are made with this model:

- the aquifer has finite, uniform thickness;
- the groundwater velocity is constant and uniform, and its direction is parallel to the upper and lower aquifer boundaries;
- the contaminant source occurs as a rectangular area ("patch") within the aquifer, which is oriented perpendicular to the direction of groundwater flow;
- the concentration of contaminant at the source may be held constant or decay exponentially;
- the decay of methane (biodegradation) in the plume follows a simple exponential function, or can be ignored;
- sorption of methane along the flow path is described by the retardation equation (Appendix E: Eqn. E.1).

The first PATCH3D scenario ("conservative case" Scenario M1) for the Marshall site assumes that dissolved methane has leaked from a constant, saturated source since the time the well was installed (29 years), and this methane does not decay (i.e. is not biodegraded) within the plume. This scenario is based on a conceptual model that assumes that the "saturated" source is derived from methane bubbles that flow continuously upward through the aquifer at the production well. The methane dissolved in water directly adjacent to such a bubble stream would remain essentially

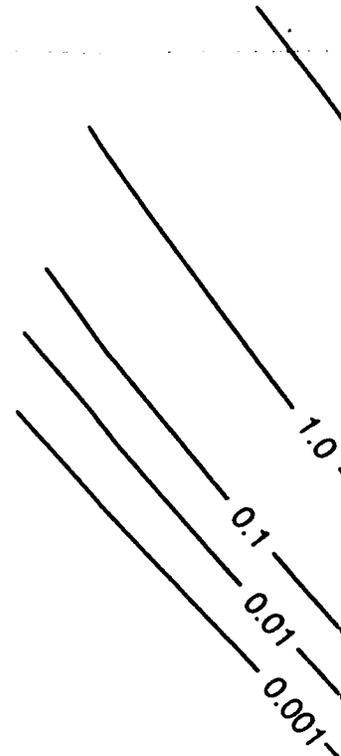
in saturated equilibrium with the methane gas phase (bubbles). This scenario assumes that lateral migration of these bubbles into this aquifer is not important. The estimated parameters used for Scenario M1 are shown in Table 3. Because the methane source is assumed to fully penetrate the aquifer profile (i.e. extends from lower to upper surface of aquifer), this, and all subsequent scenarios given in this report, are essentially two dimensional flow simulations.

The Scenario M1 plume, oriented along the inferred direction of groundwater flow, indicates a methane concentration much higher than measured at MAR-94-02 (Figure 9; Table 4), directly downgradient of the production well. By contrast, the methane concentrations at other monitoring wells are modeled to be below analytical detection, whereas methane has been measured in samples from each. Overall, the modeled concentrations differ greatly from the measured concentrations (Table 4). Thus, Scenario M1 clearly does not give an acceptable match of modeled and measured data.

Of special note, the elevated concentration of methane measured at MAR-94-01 cannot be duplicated with PATCH3D (Figure 9, Table 4). This analytical model assumes that upgradient of the methane source, the methane concentration remains at zero (i.e. background). Similarly, the methane concentration of any other well located outside of the plume, either downgradient or to the side (e.g. MAR-94-03), is assigned a zero concentration by PATCH3D.

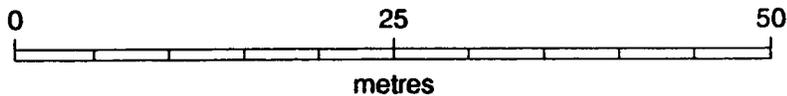
A number of the parameters used in the model PATCH3D (Table 3) can be varied. Most will not independently provide a suitable fit with the measured methane data at the Marshall site. For example, increasing or decreasing the sorption coefficient by an order of magnitude has little effect on modeled methane concentrations close to the

©MAR 94-04



Marshall Site (NW1/4 LSD 14-16-49-26 W3)

Scale 1:500



- ⊙ Monitoring well
- ⊕ Production well
- Testhole and monitoring well

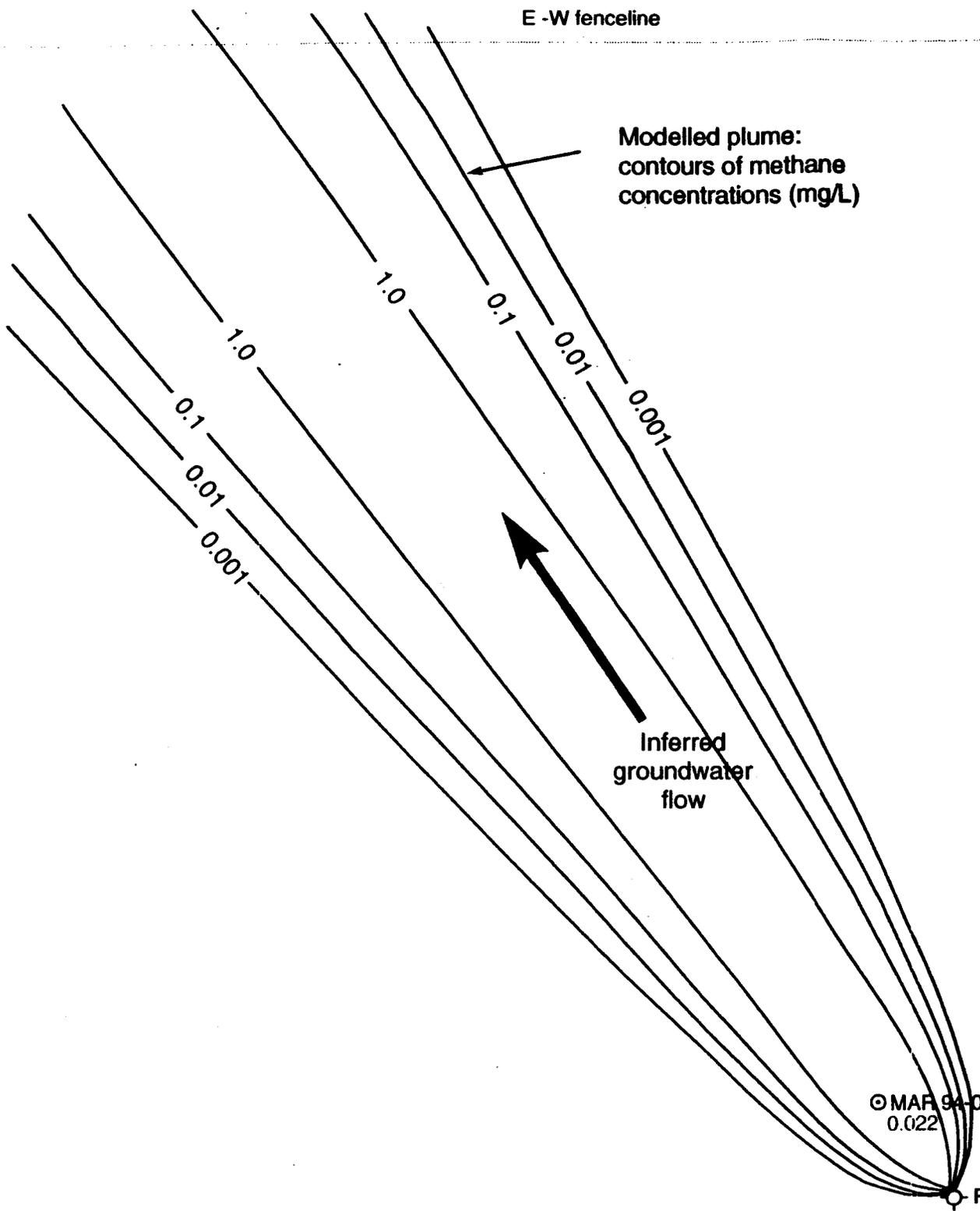
Note: 0.015 - measured methane concentrations (mg/L), sampled Oct. 17 & 19, 1994. 0.16* sampled May 30, 1994, erroneous analysis of Oct. 19 sample

Figure 9 Plan of the Marshall site with measured methane concentrations and contours of concentrations modelled by PATCH3D, Scenario M1 ("conservative case"). Model parameters are given in Table 3.

194-04

E -W fence line

Modelled plume:
contours of methane
concentrations (mg/L)



⊙ MAR 94-02
0.022

● Produc
MAR 94-01
0.016

E -W fenceline

Modelled plume:
contours of methane
concentrations (mg/L)



1.0

0.1

0.01

0.001

Inferred
groundwater
flow

⊙ MAR 94-03
0.003

⊙ MAR 94-05
0.015

⊙ MAR 94-02
0.022

○ Production well

● MAR 94-01
0.016

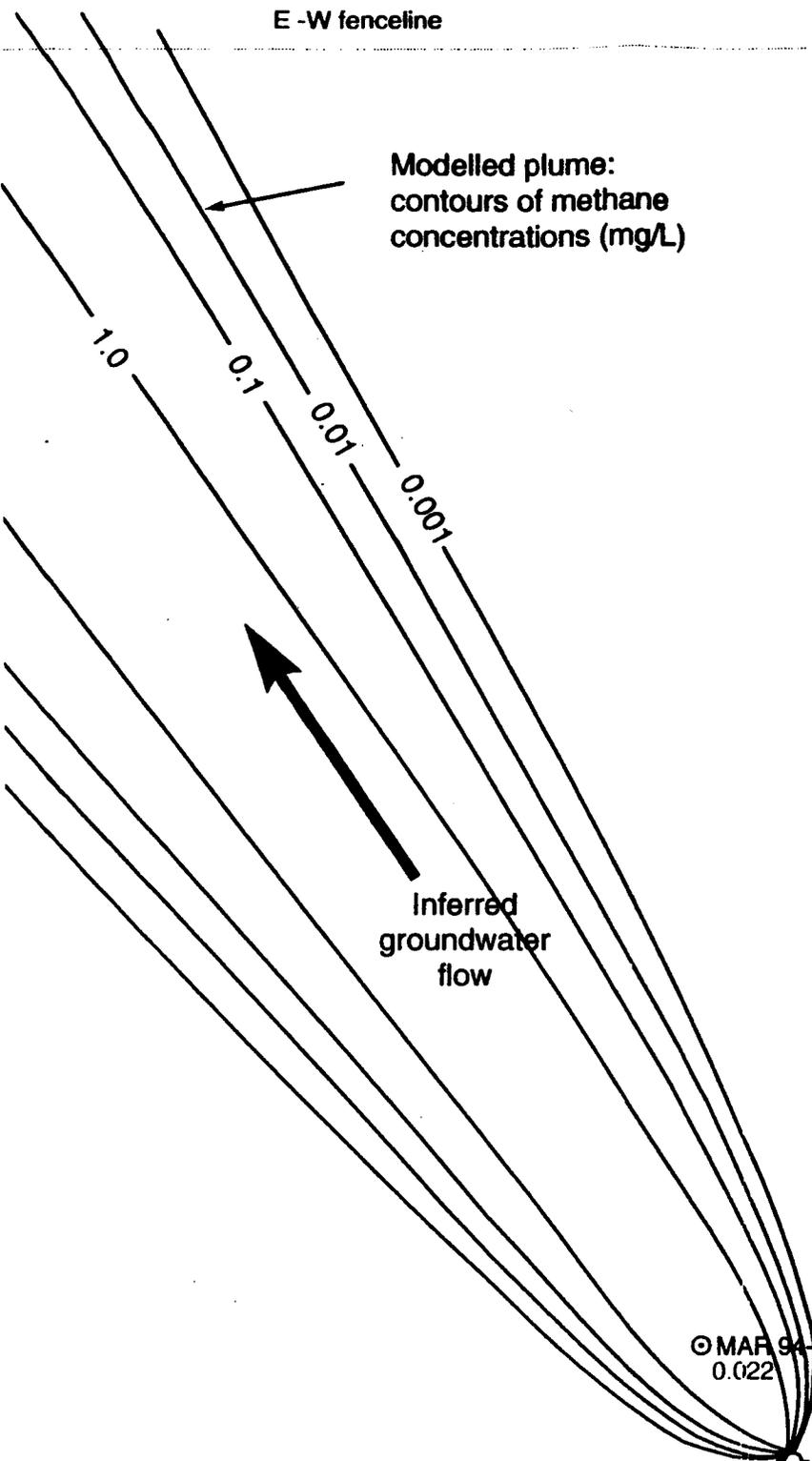


Table 3. Parameters used for PATCH3D Scenario M1 ("Conservative Case"), Marshall Site.

Estimated Parameter	Value	Source
velocity	6 m/year	pumping test and water level data (see Section 4.1.1, Appendix B)
dispersion coefficients - longitudinal - horizontal transverse - vertical transverse	1 m 0.1 m 0.001 m	typical values (Gelhar et al., 1992)
diffusion coefficient	10^{-2} m/year	typical value for dissolved component (Freeze and Cherry, 1979)
methane source dimensions - width - length	0.2 m 2 m	width of production well borehole thickness of aquifer
sorption coefficient	1.06	assuming $K_d = 0.012$, bulk density = 1.8, porosity = 0.35 (Appendix E)
time	29 years	time since production well
methane concentration at source	74 mg/L	saturated concentration in groundwater for field conditions, based on Duan et al., 1992 (Appendix D)

Table 4. Measured versus calculated methane concentrations for Scenarios M1 to M4.

Monitoring Well	Measured Methane (mg/L)	Modelled Methane (mg/L)			
		Scenario M1	M2	M3	M4
MAR-94-01	0.044 to 0.16	0 (upgradient)	0 (upgradient)	0 (upgradient)	0 (upgradient)
MAR-94-02	0.012 to 0.039	3.25	1.82	0.014	0.11
MAR-94-03	0.002 to 0.004	0 (outside plume)	0 (outside plume)	0 (outside plume)	0 (outside plume)
MAR-94-04	0.027 to 0.055	N.D.	0.023	0	0.013
MAR-94-05	0.003 to 0.015	N.D.	0.035	0	0.0036

N.D. = not detectable

source (for example, at MAR-94-02), whereas the concentrations near the perimeter of the plume change by about an order of magnitude. Similarly, changing the diffusion coefficient, estimated groundwater velocity, or elapsed time independently by an order of magnitude do not improve the fit of modeled and measured data much. Reducing the source (patch) width decreases the methane concentrations throughout the plume by about the same order in magnitude. This could help to bring the modeled concentrations closer to measured values at MAR-94-02, but will not improve the fit for the other monitoring wells.

If, the dispersion coefficients (Table 3) are increased by an order of magnitude, the concentrations nearest the source decrease by more than half, and the plume broadens considerably (Figure 10). This Scenario M2 improves the fit of most of the measured versus modeled concentrations, particularly for MAR-94-04 and -05 (compare Figures 9 and 10; Table 4). But this adjustment of dispersion coefficients still leaves the modeled methane concentration at MAR-94-02 much higher than the measured value.

The above discrepancy could be due, in part, to an error in the modeled flow direction, or irregularity in the actual flow path. However, the differences between the measured values at monitoring well MAR-94-02 and those modeled in Scenarios M1 and M2 strongly suggest that either 1) the source of methane is much smaller in size or concentration than modeled in these scenarios, or 2) methane is being oxidized by bacteria in the plume.

When the constant for exponential decay (biodegradation) of methane along the flow path is set at 20.0 (i.e.; half life = 12.6 days: Scenario M3), the PATCH3D modeled concentration at MAR-94-02 (0.014 mg/L) is very similar to the measured values (0.012 to 0.039 mg/L). However, the modeled methane concentrations at monitoring wells

32

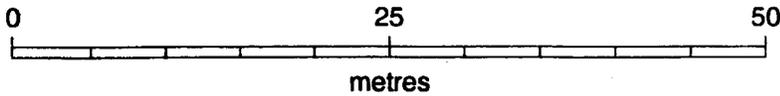
⊙ MAR 94-04
0.027

cor
cor

0.001

Marshall Site (NW1/4 LSD 14-16-49-26 W3)

Scale 1:500



- ⊙ Monitoring well
- ⊕ Production well
- Testhole

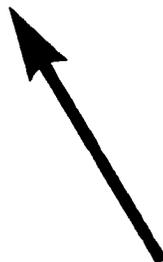
Note: 0.015 - measured methane concentrations (mg/L), sampled Oct 17 & 19, 1994. 0.16* sampled May 30/94, erroneous analysis of Oct. 19 samples.

Figure 10 Plan of the Marshall site with measured methane concentrations and contours of concentrations modeled by PATCH3D, Scenario M2.

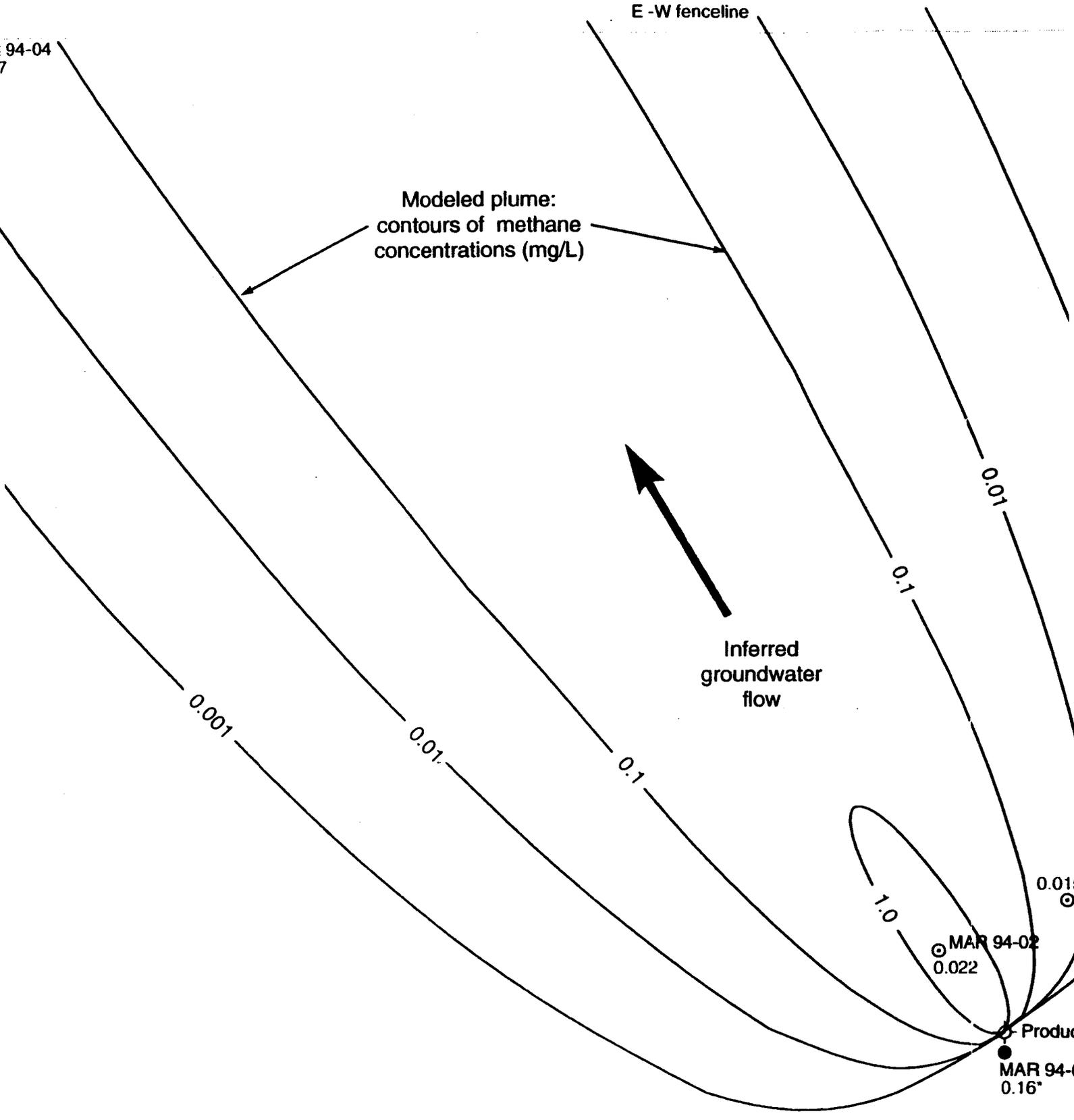
3 94-04
17

E - W fenceline

Modeled plume:
contours of methane
concentrations (mg/L)



Inferred
groundwater
flow



0.015

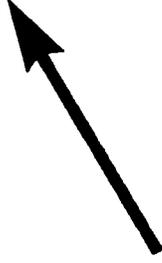
MAR 94-02
0.022

Product
MAR 94-0
0.16

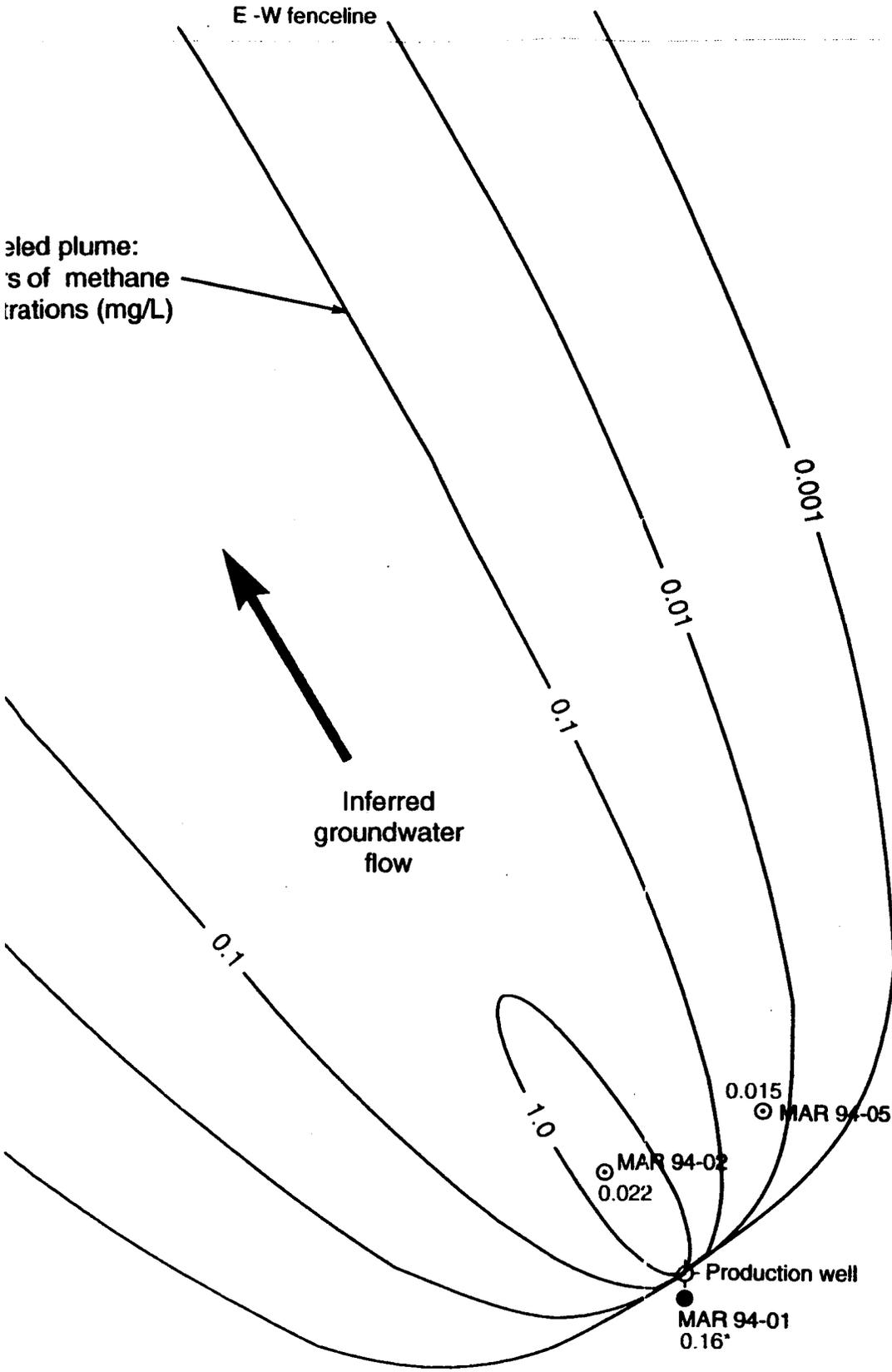
E -W fence line



plume:
s of methane
trations (mg/L)



Inferred
groundwater
flow



⊙ MAR 94-03
0.003

0.015
⊙ MAR 94-05

⊙ MAR 94-02
0.022

● Production well
MAR 94-01
0.16*

MAR-94-04 and -05 become negligible (Figure 11; Table 4), which is not a good fit with the elevated concentrations of methane measured at these sites (Table 4).

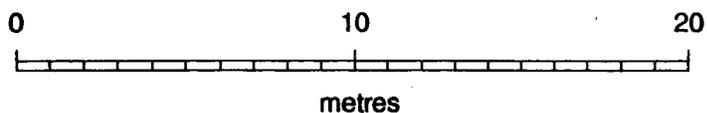
Assuming no decay (biodegradation) in the plume, but an exponential decline of the methane source concentration (constant = 0.1; i.e.; half life = 6.93 years), the modeled methane concentrations at MAR-94-02, -04 and -05 (Scenario M4) are all within an order of magnitude of measured concentrations (Figure 12; Table 4). This is a reasonable fit.

Many uncertainties remain concerning the suitable estimates of parameters for modelling methane migration as outlined above. The processes affecting methane in the plume at the Marshall site, including biodegradation, may not be best represented by simple linear or exponential equations, such as modeled by PATCH3D. Similarly, the assumption that the aquifer is homogeneous at this site may have to be reconsidered in the future. However, given the measured methane concentration data available, the scenarios considered in this section represent an adequate preliminary analysis. When more information is available, the modelling of methane migration at the Marshall site will be developed and refined.

4.1.5 Possible Role of Biodegradation of Methane

As outlined above, the measured concentrations of methane at the Marshall site cannot be satisfactorily modeled by simple advection-dispersion, plus sorption (Scenarios M1 and M2). If the analyses of methane in samples collected from monitoring well MAR-94-04 (relative to MAR-94-03, for example) are reliable indicators of concentrations within the plume, it appears that a source decay term must be used in PATCH3D to simulate the field data (e.g. Scenario M4). This suggests that either:

Marshall Site (NW1/4 LSD 14-16-49-26 W3)

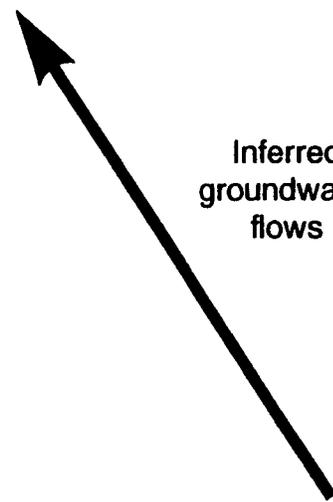


- ⊙ Monitoring well
- ⊕ Production well
- Testhole and monitoring well

Note: 0.015 - measured methane concentrations (mg/L), sampled Oct. 17 & 19, 1994. 0.16* sampled May 30/94, erroneous analysis of Oct. 19 sample

Modeled plume:
contours of methane
concentrations (mg/L)

Inferred
groundwater
flows

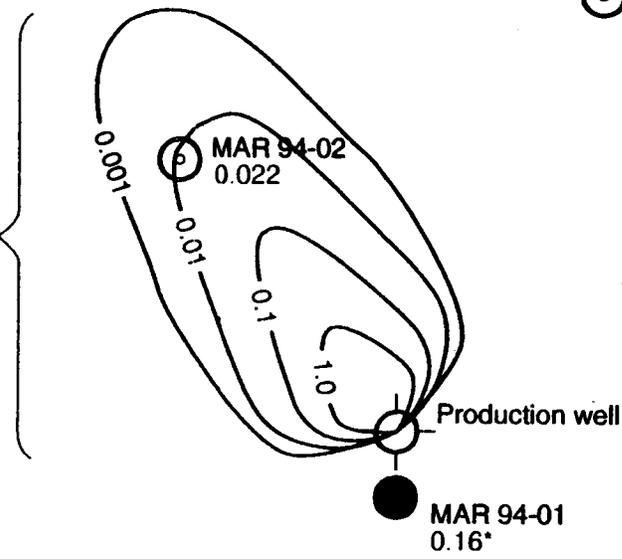


0.001

Figure 11 Plan of the Marshall site with measured methane concentrations and contours of concentrations modeled by PATCH3D Scenario M3. Exponential coefficient for decay (biodegradation) of methane in plume set to 20 (i.e. half-life = 12.6 days); all other parameters as for Scenario M2.

Inferred
groundwater
flows

ume:
methane
ons (mg/L)



MAR 94-05
0.015

MAR 94-02
0.022

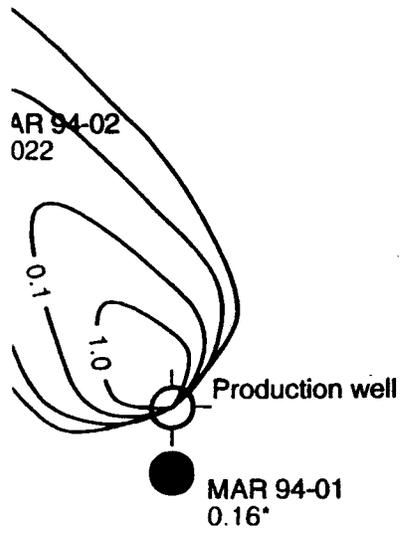
Production well

MAR 94-01
0.16

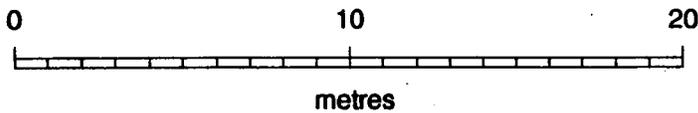


○ MAR 94-03
0.003

○ MAR 94-05
0.015

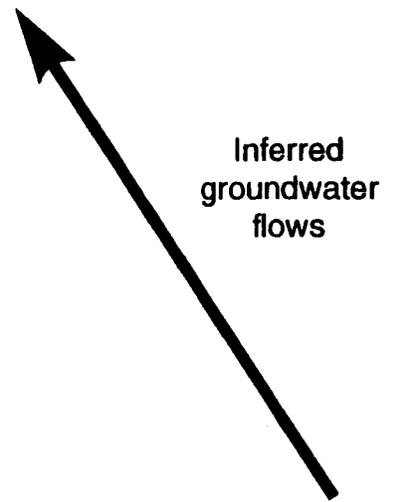


Marshall Site (NW1/4 LSD 14-16-49-26 W3)



- ⊙ Monitoring well
- ⊕ Production well
- Testhole and monitoring well

Note: 0.015 - measured methane concentrations (mg/L), sampled Oct. 17 & 19, 1994. 0.16* sampled May 30/94, erroneous analysis of Oct. 19 sample



Modeled plume:
contours of methane
concentrations (mg/L)

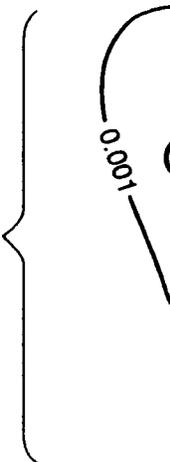
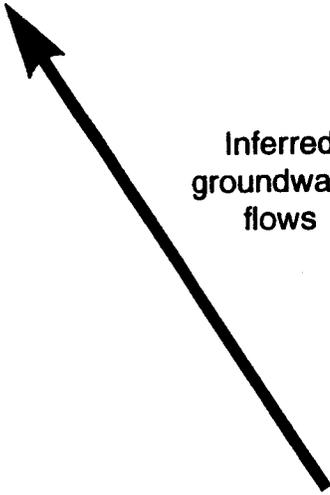


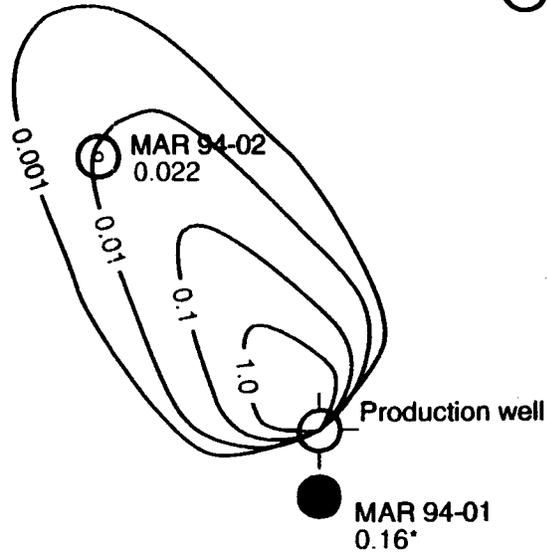
Figure 11 Plan of the Marshall site with measured methane concentrations and contours of concentrations modeled by PATCH3D Scenario M3. Exponential coefficient for decay (biodegradation) of methane in plume set to 20 (i.e. half-life = 12.6 days); all other parameters as for Scenario M2.

Inferred
groundwater
flows



○ MAR 94-05
0.015

Plume:
Contours of methane
concentrations (mg/L)

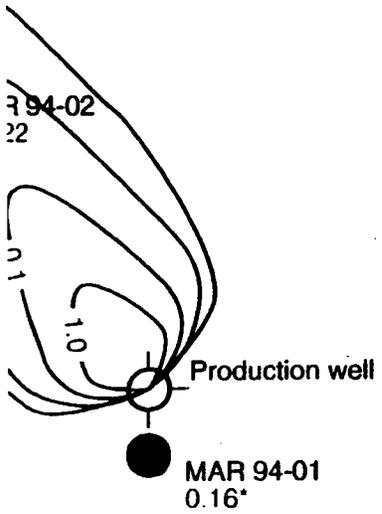


● MAR 94-01
0.16*



⊙ MAR 94-03
0.003

⊙ MAR 94-05
0.015



MAR 94-02
22

Production well

MAR 94-01
0.16

- 1) the flux of methane from the deep source to the aquifer has declined significantly over time; and/or
- 2) the rate of biodegradation of methane in the aquifer close to the point of introduction at the production well has increased over time.

Perhaps a consortium of bacteria, located within the immediate vicinity of the methane source (wellbore), has been able to progressively oxidize methane more efficiently. In this case, the rate of biodegradation of methane downflow in the plume must be very low relative to near the plume source, in order to account for all of the measured methane concentrations inferred to be within the plume, at MAR-94-02, -04 and -05. In either case (1 or 2 above), the data suggest that the concentration of methane at (in close proximity to) the plume source has declined over time.

Based on measured versus modeled concentrations obtained with PATCH3D Scenarios M1 and M2, -2 to 3 mg/L methane may be missing at MAR-94-02 due to biodegradation. If this amount of methane has been depleted, and directly linked to microbial sulfate reduction, the "missing" methane corresponds to -10 to 20 mg/L of sulfate that has been reduced. Yet the sulfate concentration at MAR-94-02 is "depleted" by -200 mg/L relative to MAR-94-03. This comparison suggests that the spatial variation in sulfate concentrations detected at the Marshall site do not relate directly or solely to methane oxidation. This raises several questions:

- Are the lateral variation in sulfate concentrations in the aquifer unrelated to oxidation of methane leaking from the production well?
- Alternatively, is the rate of methane leakage to the aquifer an order of magnitude greater than modeled with PATCH3D, perhaps due to lateral migration as a gas (bubble) phase?

- Are other organic compounds leaking into the aquifer via the production well, inducing most of the sulfate reduction?

The answers to these questions are unknown at the present time. Since both sulfate reduction and methane oxidation are isotope fractionating processes, selected isotope analyses and other data (e.g. tracer determined methane oxidation or sulfate reduction rates) may provide some answers in the future.

4.2 Lindbergh Site

4.2.1 Groundwater Flow

At the Lindbergh site, the water level data collected from the monitoring wells indicate that the groundwater flow in the aquifer is towards the south-west (Appendix B, Figure 4). Based on measurements made on October 18, 1994, the hydraulic gradient is -5×10^{-5} . These determinations of the direction and magnitude of the hydraulic gradient are tentative, given that the measured differences in water levels at this site are similar in magnitude to the measurement accuracy (± 0.005 m). Note however, that except for the LND-94-03 datum, the water levels indicate a consistent gradient from north-east to south-west (Figure 4). This gradient is compatible with the generalized regional groundwater flow patterns outlined by Emond (1989) for the Lindbergh area, which indicated southward flow towards Landon Lake in the vicinity of this research site. However, because of the regional scale of investigation by Emond (60 by 40 km), her study cannot be directly applied to determine flow in the aquifer at the Lindbergh site.

Matching of the pumping test results for LND-94-01A (drawdown versus time) to the Theis curve indicated a transmissivity of 1.4×10^{-3} m²/s (Appendix B). Assuming an aquifer thickness of 19.8 m, the hydraulic conductivity is 7.1×10^{-5} m/s.

The average linear velocity of groundwater (v) was estimated (assuming porosity = 35%):

$$v = (7.1 \times 10^{-5} \text{ m/s})(5 \times 10^5)/0.35 = 9.2 \times 10^9 \text{ m/s} = 7.9 \times 10^4 \text{ m/d, or } -0.3 \text{ m/year.}$$

4.2.2 Methane Concentrations

The dissolved methane concentrations measured closest to the production well at LND-94-02 (6.22 to 13.9 mg/L; Table 2) indicate the presence of a methane plume in the aquifer, derived from the Amoco production well. This concentration range is approximately an order of magnitude lower than the inferred saturated dissolved concentration for this aquifer (112 mg/L; see Appendix D). Low levels of ethane were also detected in this well (Table 2).

The low levels of methane (0.012 to 0.063 mg/L; Table 1) measured in all other monitoring wells at this site (LND-94-01A, -03, -04 and -05) may represent intrinsic ("background") concentrations in the aquifer (see Section 4.2.4), perhaps unaffected by migration from the Amoco production well, or other human activities. As for the Marshall site, the methane in this aquifer may be diffusing from the underlying shale.

4.2.3 Other Hydrochemical Data

Hydrochemical analyses of samples collected from the monitoring wells at the Lindbergh site indicate that the groundwater is dominated by Ca, Na, HCO_3 , and SO_4 , with total dissolved ions ranging from 1205 to 1343 mg/L (Table 2). Significant dissolved Fe and Mn concentrations, negligible nitrate plus nitrite concentrations, and Eh values (Table 2) indicate reducing conditions at this site, similar to those at the

Marshall site. Unlike the Marshall site, there are no obvious spatial trends in sulfate concentrations at the Lindbergh site.

4.2.4 Modelling of the Methane Plume

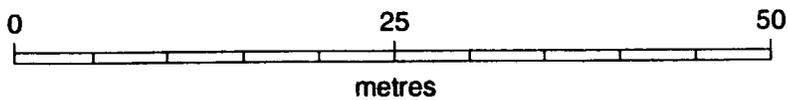
Table 5. Parameters used for PATCH3D "Conservative Case" Scenario of the Lindbergh Site.

Estimated Parameter	Value	Source
velocity	0.3 m/year	pumping test and water level data (see Section 4.2.1)
dispersion coefficients - longitudinal - horizontal transverse - vertical transverse	10 m 1 m 0.01 m	retained from Scenarios M2 to M4 (Section 4.1.4)
diffusion coefficient	10^2 m/year	typical value (Freeze and Cherry, 1979)
methane source dimensions - width - length	0.37 m 19.8 m	width of production well borehole thickness of aquifer
retardation coefficient	1.06	assuming $K_d = 0.012$, bulk density = 1.8, porosity = 0.35 (Appendix E)
time	11 years	time since production well
methane concentration at source	112 mg/L	saturated concentration in groundwater for field conditions, based on Duan et al., 1992 (Appendix D)

A 'conservative case' scenario of dissolved methane migration in the aquifer at the Lindbergh site (Figure 13) was based on the estimated parameters shown on Table 5. Methane was assumed to have migrated laterally as a dissolved phase from a constant, saturated source (112 mg/L) ever since the well was installed (11 years), with no decay (biodegradation) within the plume. The resultant model plume, oriented along the

Lindbergh Site (16-04-55-06-W4)

Scale 1:500



- ⊙ Monitoring well
- ⊕ Production well
- Testhole

Note:

0.02 measured methane concentration, mg/L
(sampled Oct. 6 and 18, 1994)

Figure 13: Plan of the Lindbergh site with measured methane concentrations and contours of concentrations modelled by PATCH3D ("conservative" case). Model parameters are given in Table 5.

E - W fenceline

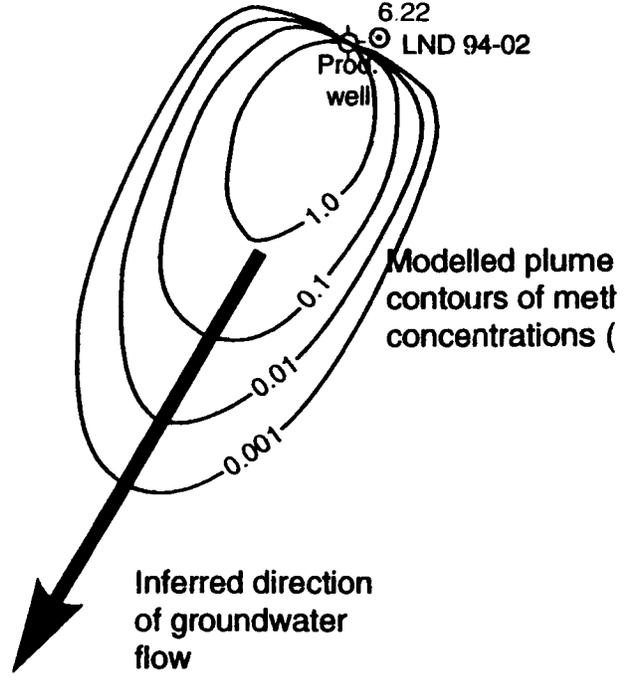
N - S fenceline

0.02
⊙ LND 94-01A
● LND 94-01

0.014
⊙ LND 94-03

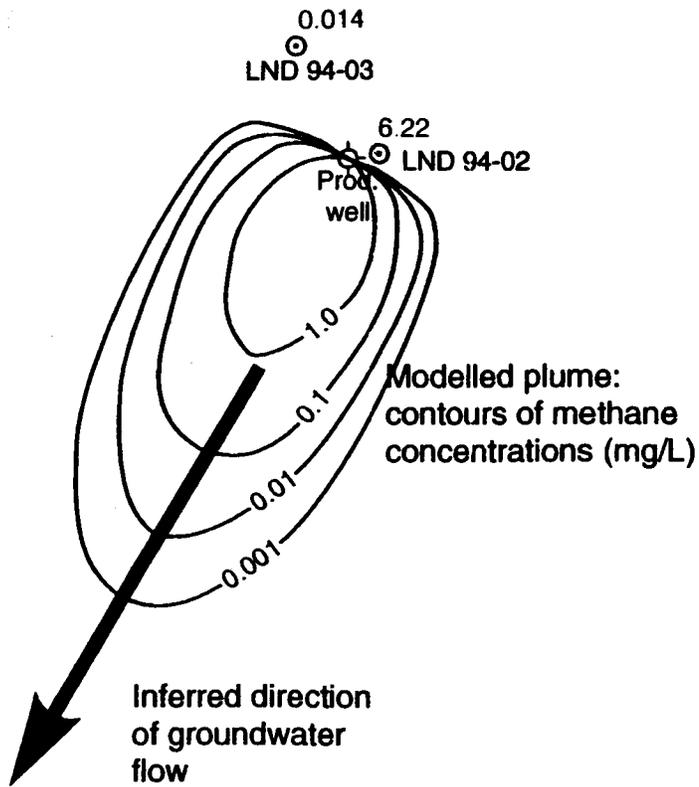
6.22
⊙ LND 94-02

Prod.
well





D 94-01A
D 94-01



LND 94-04 0.03

inferred direction of groundwater flow, extends ~35 m downflow from the production well (Figure 13). According to this result, none of the monitoring wells at this site lie within the methane plume.

As with the Marshall site (MAR-94-01; Section 4.1.4), the upgradient, elevated concentration of methane at LND-94-02 (6.22 to 13.9 mg/L) cannot be duplicated with PATCH3D. However, these relatively high concentrations suggest that, to some extent, methane may be migrating laterally from the Lindbergh production well (including upgradient) within the aquifer as a gas (bubble) phase.

Any well located outside of the plume is assigned a zero concentration by PATCH3D. The measured concentrations, ranging from 0.012 to 0.062 mg/L in LND-94-01A, -03, -04 and -05, may be intrinsic or "background" values, unaffected by methane migrating from the production well. Based on existing data, there may be slightly elevated methane concentrations in LND-94-01A (up to 0.063 mg/L), relative to LND-94-03, -04, and -05. However, even if the estimated groundwater velocity in the aquifer at this site is increased by an order of magnitude to 3 m/year, modelling with PATCH3D indicates that the plume would still have no detectable impact on monitoring well LND-94-01A. This result is based on the tentative groundwater flow direction indicated on Figure 13.

Due to the uncertainty in the groundwater flow direction, the lack of monitoring wells within the inferred methane plume, and the limited data collected so far, further modelling of methane at the Lindbergh site is not warranted at this time.

5. CONCLUSIONS

1. Dissolved methane was detectable in all monitoring wells at the Marshall and Lindbergh research sites, ranging in concentration from 0.002 to 14 mg/L.
2. At each site, relatively high methane concentrations in one or more monitoring wells indicated the presence of a methane plume that has migrated from the production well.
3. Based on the overall distribution of methane concentrations in the monitoring wells, and modeling of the methane plumes (PATCH3D), "intrinsic" methane may be present at low concentrations in the aquifers at each site.
4. Preliminary modeling of the methane plume at the Marshall site suggests that bacterial oxidation of methane may be occurring in the aquifer.

6. RECOMMENDATIONS

1. Because of the low hydraulic gradient at the Lindbergh site, another monitoring well, completed off-lease, ~200 m from the production well, is required to test the inferred groundwater flow direction. Subsequently, it is necessary to install two additional monitoring wells at the Marshall site, and two additional wells at the Lindbergh site, within plumes simulated by PATCH3D, to better compare modeled and measured methane concentrations.
2. Other "leaky" well sites in the Lloydminster area should also be investigated to determine if similar methane plumes are present. Some investigations of possible methane migration into relatively deep aquifers (50 to 200 m below ground) are needed.

3. Monitoring of methane concentrations and other hydrochemical parameters at the research sites should be continued on an annual basis for several years (through 1997 or 1998). This may enable the detection of significant trends that will constrain the modelling of the methane transport at these sites, and further our understanding of the effects of methane migration in the aquifers.
4. Selected analyses of the isotopic composition of dissolved methane, sulfate and bicarbonate (see Equation 1), and of methane-oxidizing micro-organisms present in the aquifers should be conducted. These analyses will either counter or reinforce the hydrochemical evidence for processes such as concurrent methane oxidation and sulfate reduction.
5. It should be determined whether a significant quantity of He or another "inert" gas is migrating from the production wells along with methane. If such a gas can be measured with high precision, it might be a useful conservative tracer to help model and determine the role of sorption and/or biodegradation of methane.
6. More data are required on the occurrence and concentration of intrinsic methane in shallow aquifers in the Lloydminster area. It may also be valuable to determine methane concentration gradients in the aquitards immediately adjacent to these aquifers; to determine intrinsic diffusion fluxes to the aquifers.
7. A more comprehensive model of the migration of methane into aquifers intersected by production wells is anticipated as a continuation of this investigation and further monitoring.
8. The progress of other research projects that examine the vertical migration paths of methane at production wells should be monitored closely. It is anticipated that attention will focus on documenting the leakage pathways, methods for

remediation of existing leakers, and on installation procedures to minimize leakage from new wells.

7. ACKNOWLEDGMENTS

This project was funded by the Canadian Association of Petroleum Producers (CAPP), the Lloydminster Area Operators Gas Migration Team (LAOGMT), the Federal Program on Energy Research and Development (PERD), and the Saskatchewan Research Council (SRC). The Project Steering Committee, which was comprised of Margaret Klebek (Alberta Environmental Protection), Don Roberts (Energy Resources Conservation Board), Les Bernier (Saskatchewan Energy and Mines), Scott Robinson (Saskatchewan Environment and Resource Management), Gary Lorenz (LAOGMT), Harold Seitz (Wascana Energy), Kurt Uhrich (Amoco Canada) and Ron Schmitz (Husky Oil), provided overall direction for the project. Ron Schmitz (Husky Oil Operations Ltd.) coordinated this project on behalf of CAPP, in conjunction with LAOGMT. Garry Lorenz (Husky) and Kurt Uhrich (Amoco) provided information and technical assistance for site selection and conducting the field components of this investigation. Assistance was also provided by other Husky and Amoco personnel. Members of the Project Steering Committee provided comments or additional information.

The drilling of testholes, installation of monitoring wells, and E-logging was conducted by McAllister Waterwells Ltd. of Lloydminster, under the supervision of the authors. Mac Millard (SRC) conducted the geological sampling and interpretation of the testholes. Brian McIntosh, Hans Piek, and Carlos Sardinha (all at SRC) drafted the maps and figures. All sampling and field analyses (pH, Eh, EC, temperature) were conducted by the authors; subsequent analyses of dissolved ions and dissolved methane and ethane

were conducted by the SRC Analytical Laboratory. Wo Yuen (SRC) developed the methane extraction technique. Several duplicate methane analyses were conducted by Ray Kirkland of the National Hydrology Research Institute in Saskatoon.

8. REFERENCES

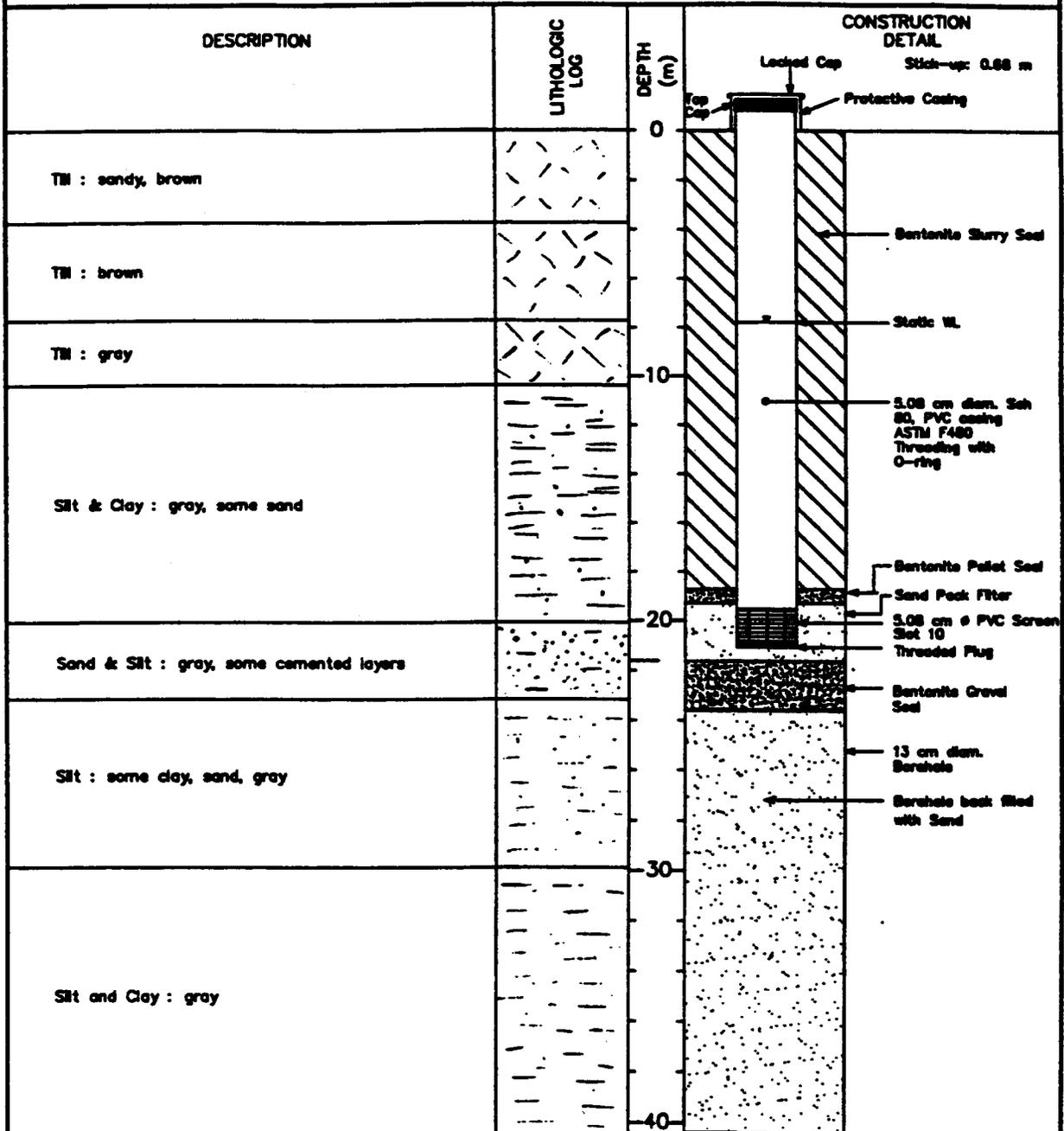
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APPENDIX A. Completion data for production wells, testholes and monitoring wells.

Testhole and Monitoring Well Mar-94-01

PROJECT: Methane Migration	DATE: May 4, 1994	LOCATION: NW14-16-49-26-W3
DRILL RIG: Rotary	TOTAL DEPTH: 41.15 m	UTM: 12/583400E/5898650N
DRILLING CO.: McAllister Water Wells Ltd.	SURF. ELEV.: 606.6 masl	DRILLER: G. McAllister
ELEV. SOURCE: Ref. to Husky Production Well	TOC. ELEV.: 607.28 masl	LOGGED BY: Dale Van Stempvoort*



Saskatchewan Research Council

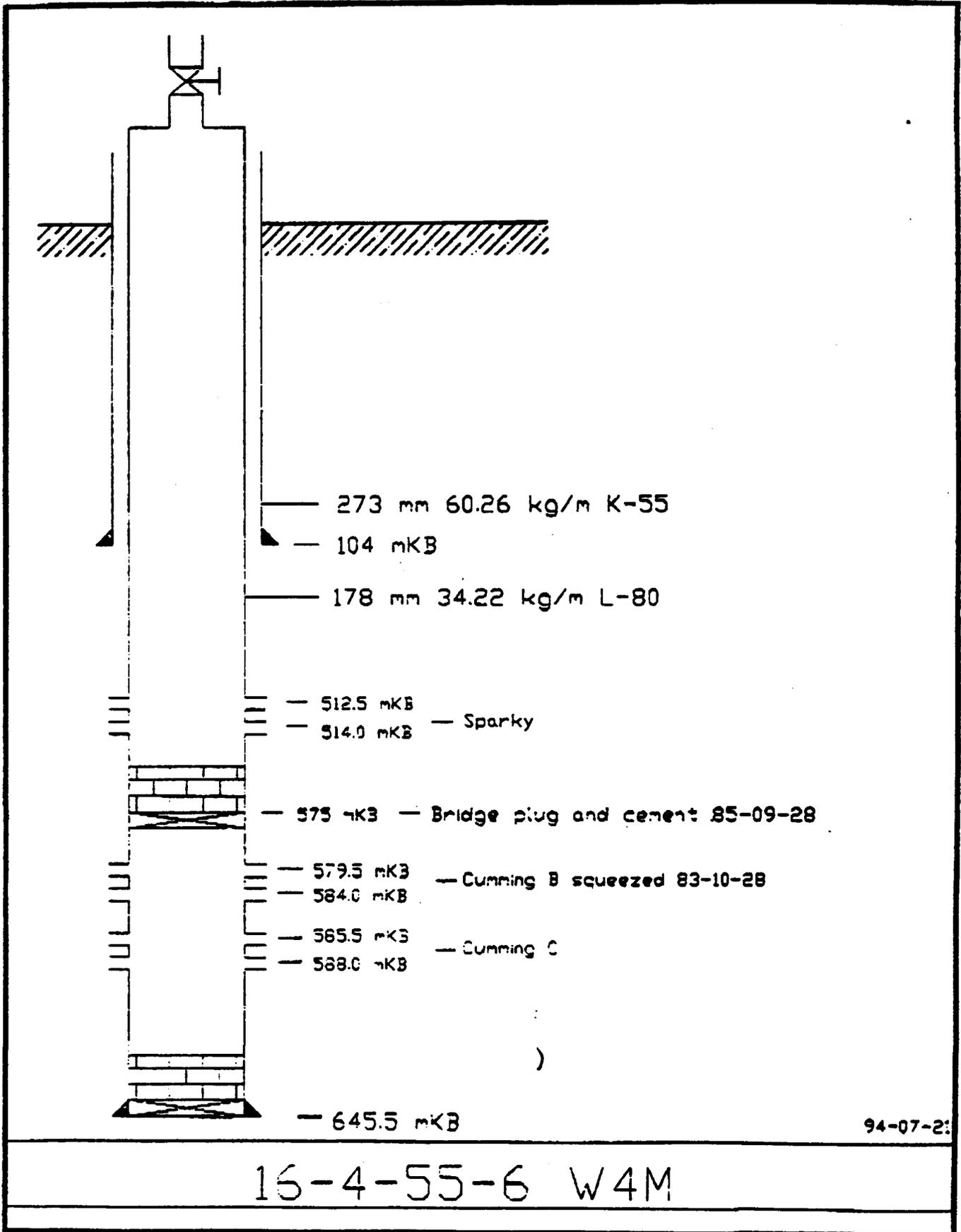
* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

Completion data for monitoring wells and testholes at the Marshall and Lindbergh sites.

LAND LOCATION	NAME	TYPE*	DATE DRILLED	Ground Elevation (m aed)	TOC Elevation (m aed)	Stick-up (m)	DEPTH DRILLED (m)	TOP OF SCREEN TOC (m)	BOTTOM SCREEN TOC (m)	AQUIFER	STATIC WL ELEV BELOW TOC (m)	DATE
14-16-49-26-W3	MAR-94-01	TH/MW	940504	608.60	607.28	0.68	41.2	20.76	21.72	Ribstone Ck.	8.872	940508
14-16-49-26-W3	MAR-94-02	MW	940504		607.97	0.72	22.1	20.10	21.05	Ribstone Ck.	9.574	940508
14-16-49-26-W3	MAR-94-03	MW	940504		607.18	0.68	23.2	20.37	21.31	Ribstone Ck.	8.833	940508
14-16-49-26-W3	MAR-94-04	MW	940927		608.14	0.68	25.1	21.40	22.34	Ribstone Ck.	9.856	941005
14-16-49-26-W3	MAR-94-05	MW	940927		607.33	0.73	25.4	21.08	22.03	Ribstone Ck.	8.580	941005
16-04-55-06-W4	LND-94-01	TH	940503				53.3					
16-04-55-06-W4	LND-94-01A	MW	940505		627.04	0.61	32.6	30.19	31.14	Buried Channel	2.760	940602
16-04-55-06-W4	LND-94-02	MW	940505	625.60	626.09	0.49	29.2	28.71	29.66	Buried Channel	1.809	940602
16-04-55-06-W4	LND-94-03	MW	940506		626.27	0.61	30.0	28.71	29.66	Buried Channel	1.995	940602
16-04-55-06-W4	LND-94-04	MW	940928		626.84	0.66	32.0	30.24	31.08	Buried Channel	2.528	941018
16-04-55-06-W4	LND-94-05	MW	940928		627.16	0.70	32.0	30.23	31.18	Buried Channel	2.837	941018

*MW = monitoring well, TH = testhole

Schematic for Amoco Production Well Completion



	<u>K.B.</u>	<u>DATUM</u>
T.D. (Logger)	1861	+ 126
(Driller)	1860	+ 127

SAMPLE DESCRIPTION None

PEROFRATION DATA 1716-1724 in the Lower Sparky sand.
 No. of shots - 32/ft. Type - Schlumberger Sand C

INITIAL PRODUCTION Date Production Test Began - December 3, 1965
 Date Finished - December 4, 1965
 Term of Test - 2 days
 Type of Test - Pumping

...VED

<u>Production</u>	<u>Hours</u>	<u>Water</u>	<u>Oil</u>	<u>Gas</u>
1st. day	16	0.05	24.95	-
2nd. day	24	0.02	16.98	-
Total		0.07	41.93	-
Daily Average Production		0.04	27.69	-
Gravity - 16.4 ^o API				

REMARKS This well was drilled as a step out on the east side of the Unit, in an area previously thought to be low. The Upper Sparky was found to be silted out but the Lower Sparky came in at +275', 9.0' high to the C12-16 well approximately $\frac{1}{2}$ mile S.W., and 9.0' high to the C16-17 well $\frac{1}{2}$ mile west, and 18.0' high to the C4-21 well approximately $\frac{1}{2}$ mile to the N.W. The Lower Sparky had 14.0' of net oil pay and the G.P. 10.0'.

C. W. Williamson
 Geologist

COMPLETION REPORT

WELL NAME Aberfeldy Unit C14 16 49 26
LOCATION N.W. Lsd, 14, Sec. 16, Twp. 49, Rge. 26W3
CO-ORDINATES 330 ft. S. of N.W. Corner 16-49-26W3
1650 ft. E. of N.W. Corner 16-49-26W3
ELEVATION Ground Level 1977
Kelly Bushing 1987
OPERATOR Husky Oil Canada Ltd.
CONTRACTOR Wardean Drilling
SPOUDED 12:00 noon October 31, 1965
COMPLETED 6:37 a.m., November 2, 1965
TOTAL DEPTH Driller 1860
Logger 1861
HOLE SIZE **FILMED** 7 7/8"
CASING Surface casing - none
Production casing - ran 61 jts. 1857.51', 5 1/2",
14#, J-55 new casing. Shoe set at 1860' K.B.
Insert float valve at 1828' K.B. with 86 sax
of Oilwell neat and 203 sax of Standard Portland
with 6% gel. Completed by Dowell at 6:37 a.m.,
November 2, 1965.
CORED INTERVALS None
DRILL STEM TESTS None
LOGS Induction Electric Survey
STATUS Indicated Lower Sparky oil well.
ABANDONMENT PLUGS None
GEOLOGICAL MARKERS

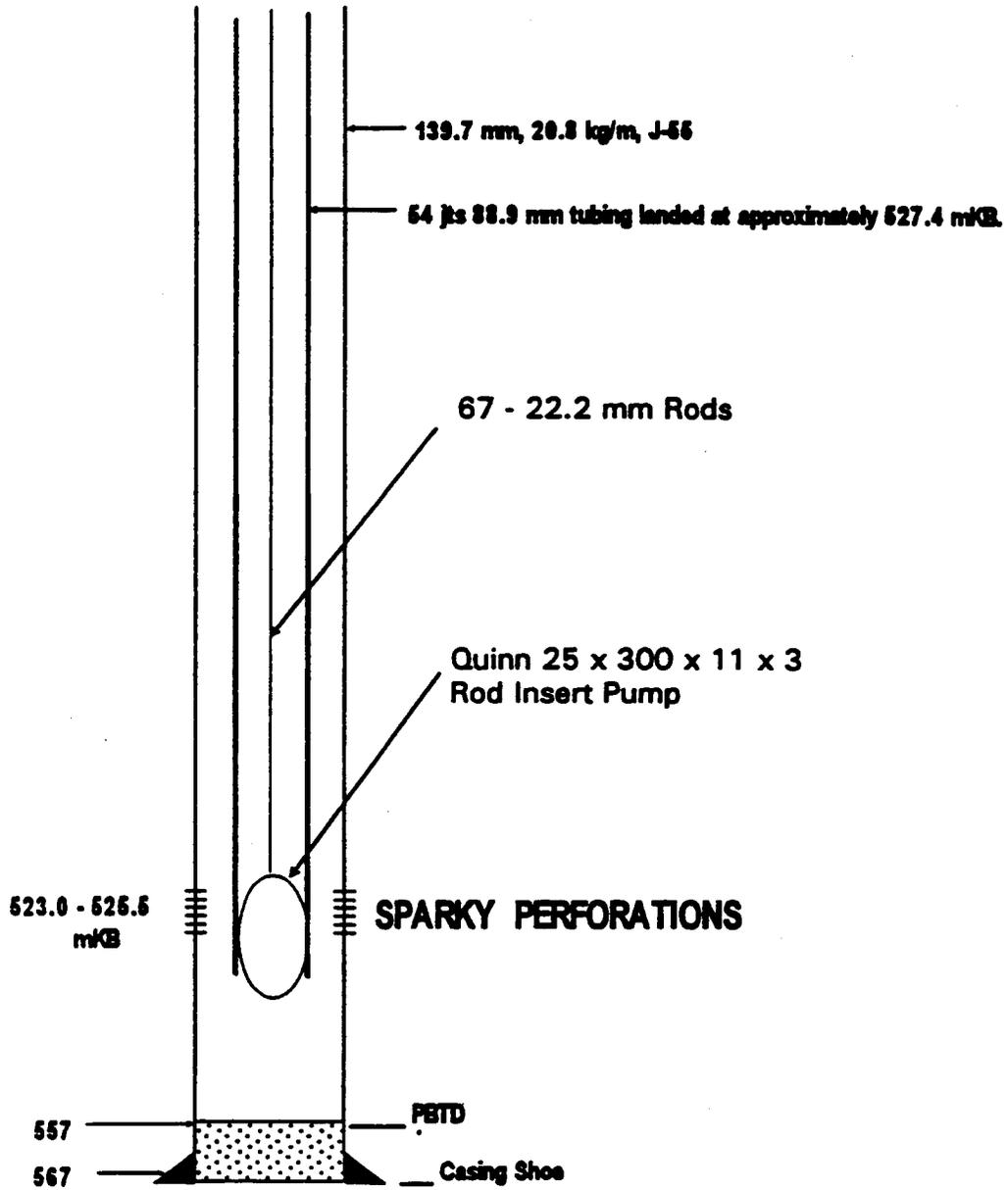
	<u>K.B.</u>	<u>DATUM</u>
Cretaceous		
Core Hole Marker	182	+ 1805
Colorado	869	+ 1118
Second White Specks	1123	+ 864
Base Fish Scales	1245	+ 742
Mannville	1542	+ 445
Upper McLaren	1576	+ 411
Waseca	1621	+ 366
Upper Sparky	1703	+ 284
Lower Sparky	1712	+ 275
G.P.	1752	+ 235
Rex	1797	+ 190

Husky Aberfeldy Unit C14-16-49-26W3

DATE DRAWN
22-NOV-94

DRAWN BY
C.M. Snodden

PLANNED
 AS RUN



CORING SAMPLE DESCRIPTIONS

SP 20 MV

LT, GRAY, SANDY, GRIP, LIGHT REDDISH BROWN

NO, STIV, WOOD, BRN, BROWN, WOOD, GRAY

LT, SLIGHTLY GRAY, WILD, PALE BROWN, VILLOUSIS, BROWN FRAGMENTS

LT, SLIGHTLY GRAY, WOOD, GRAY, VERMILION BROWN FRAGMENTS

LT, NORMAL, WOOD, GRAY, GRAY, OCCASIONAL SANDY FRAGMENTS AND GRAY

LT, NORMAL, WOOD, GRAY, GRAY, GRAY

LT, MASSIVE, NORMAL, WOOD, SANDY, GRAY

ADD, NORMAL, WOOD, VERY FINE, SILENT, GRAY, GRAY, GRAY

LT, NORMAL, WOOD, SANDY, GRAY, SANDY, SILT INTERLARD

LT, N.A. WITH OCCASIONAL SANDY INTERLARD

SECTION 1 100

SILT, NORMAL, MASSIVE, SILTY, WOOD, GRAY, GRANULOMETER SANDY LAMINATION

SILT AND CLAY, NORMAL, WOOD, GRAY

TD 0185'

DRILLER'S LOG

REL 70 OHMS

TILL, BROWN

TILL, GRAY

BEFORE SURFACE OF

SHALE, GRAY

SANDY CLAY SANDSTONE AND SILTY SAND

SANDY SILTY

SILENT SAND

SECTION 2

SANDY SAND

GRAY SAND

Geology by: P.J. CHILCO

CLAY, MUCKY, WITH
SILT, MUCKY, WITH, LIGHT GRAY
SILT, MUCKY, WITH, LIGHT GRAY

SAND (INTERBEDDED)

SILT, MASSIVE, MUCKY, WITH, SANDY, GRAY

SAND, MUCKY, WITH, VERY SILTY, SILTY, GRAY DARK GRAY

SILT, MUCKY, WITH, SANDY, GRAY, SANDY SILT INTERBEDS

SILT, R.D. WITH OCCASIONAL SANDY CUTTINGS

SILT MUCKY, MASSIVE, CLAYEY, WITH, GRAY, MUCKY

SILT AND CLAY, MUCKY, WITH, GRAY

SHALE, GRAY

SANDY SHALE

SANDY SHALE AND MUCKY SANDY INTERBEDS

SILTY SHALE

SILTSTONE

SANDY SHALE

GRAY SHALE

TD = 185'

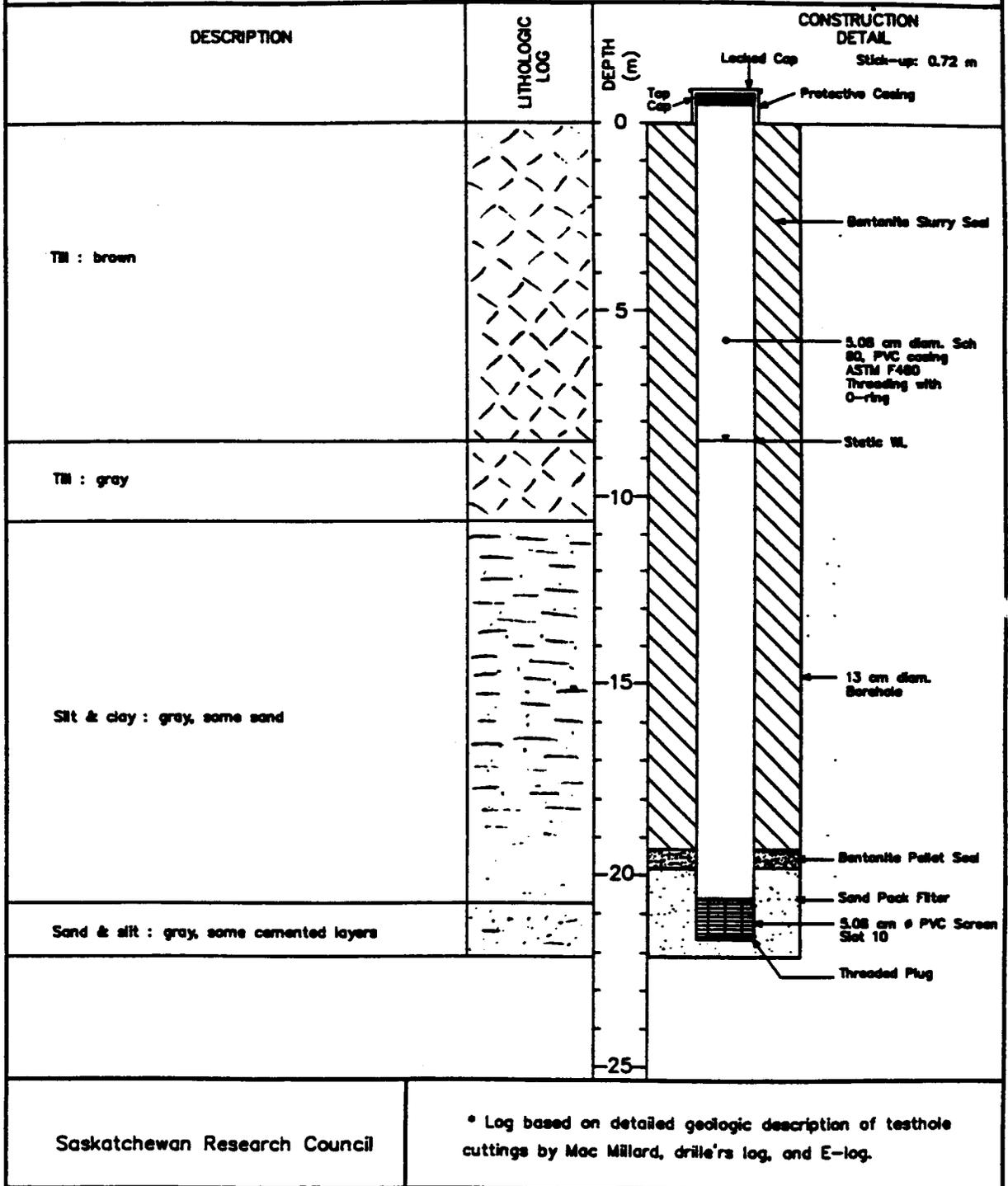
Geology by: P.J. HILL

Monitoring Well Mar-94-02

PROJECT: Methane Migration
 DRILL RIG: Rotary
 DRILLING CO.: McAllister Water Wells Ltd.
 ELEV. SOURCE: Ref. to Husky Production Well

DATE: May 4, 1994
 TOTAL DEPTH: 22.10 m
 SURF. ELEV.: 607.25 masl
 TOC. ELEV.: 607.969 masl

LOCATION: NW14-16-49-26-W3
 UTM: 12/583400E/5898650N
 DRILLER: G. McAllister
 LOGGED BY: Dale Van Stempvoort*

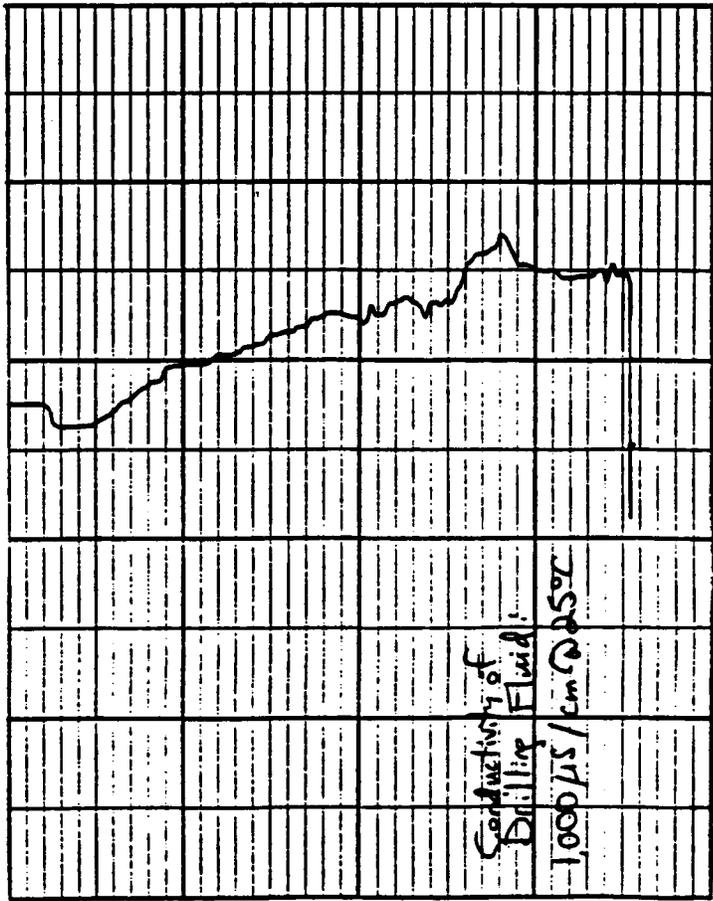


Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

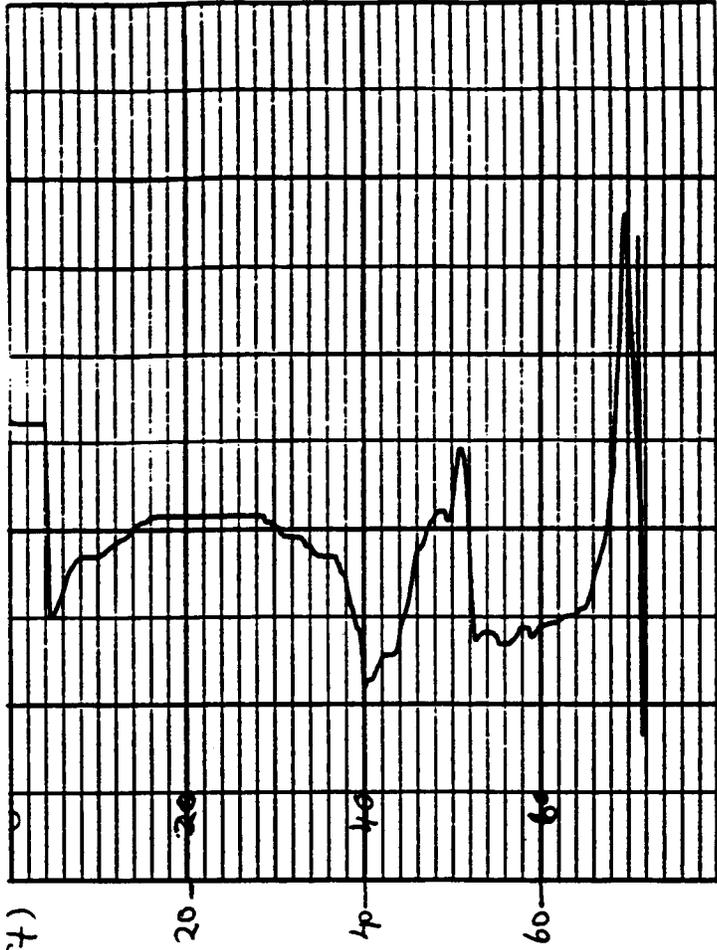
MAR-94-02 May 4/94

SP 20 mV



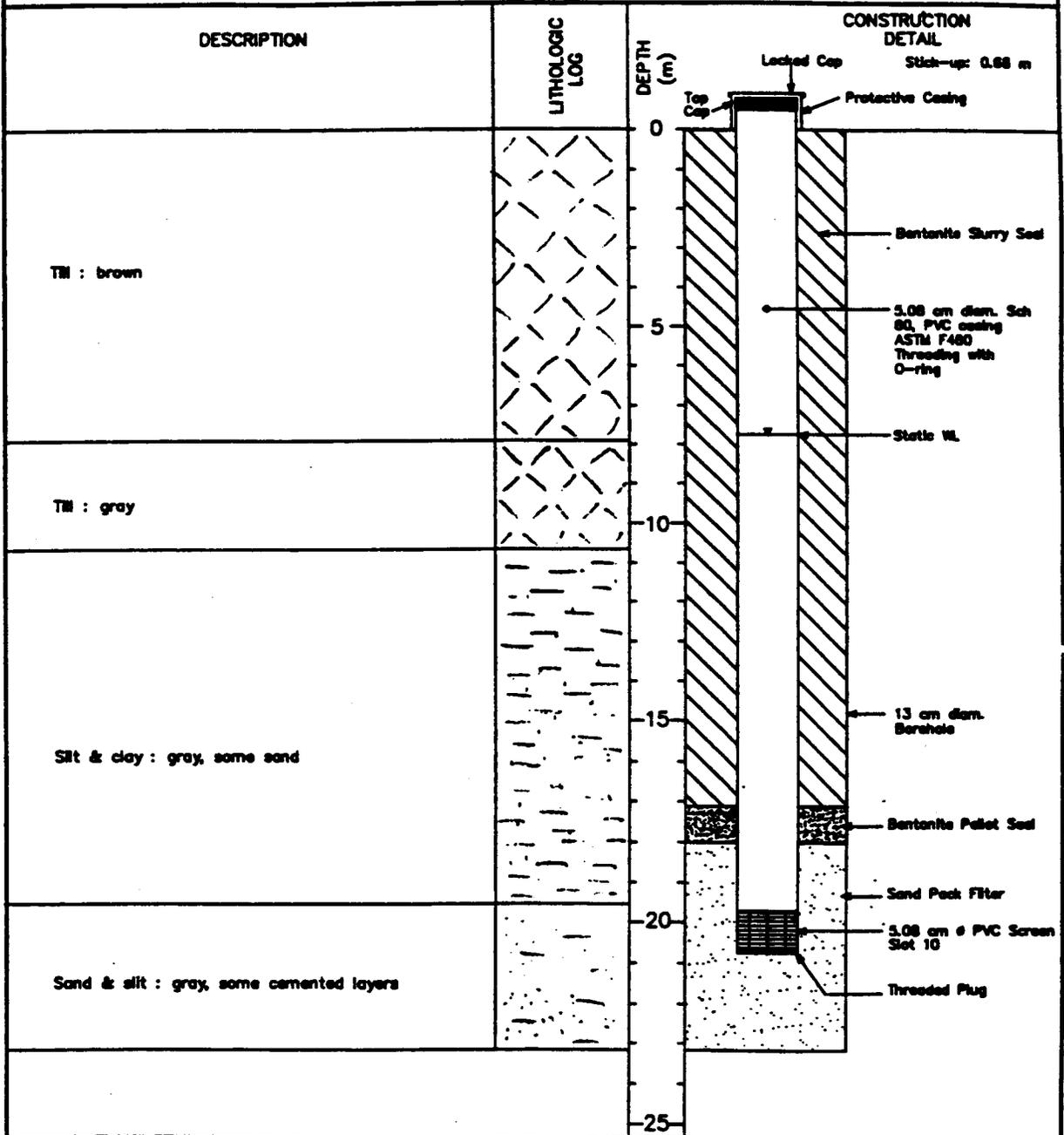
Depth below Ground (ft)

R 10 ohms



Monitoring Well Mar-94-03

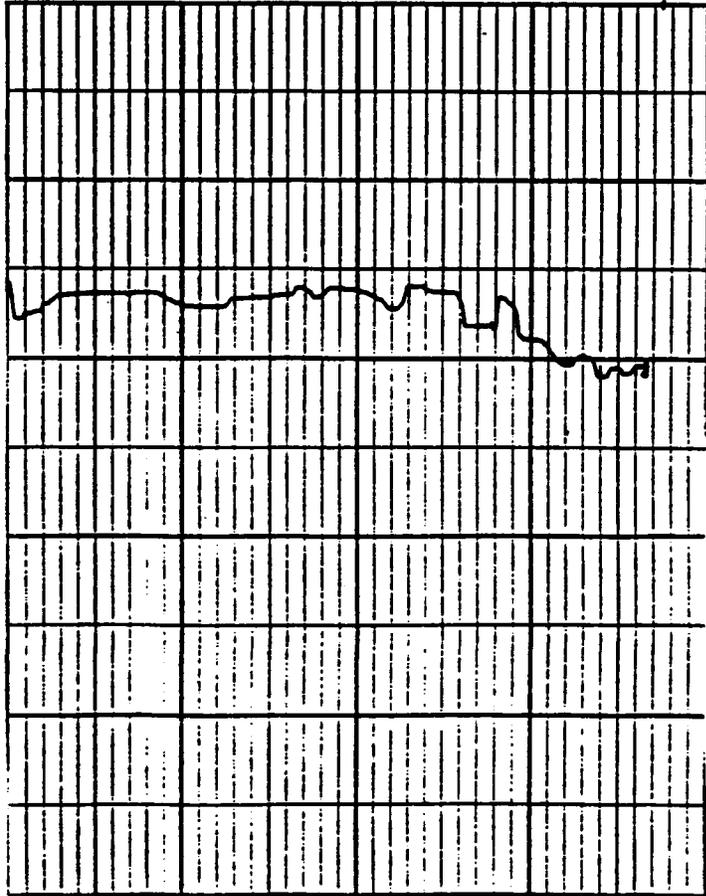
PROJECT: Methane Migration	DATE: May 4, 1994	LOCATION: NW14-16-49-26-W3
DRILL RIG: Rotary	TOTAL DEPTH: 23.16	UTM: 12/583400E/5898650N
DRILLING CO.: McAllister Water Wells Ltd.	SURF. ELEV.: 606.50 masl	DRILLER: G. McAllister
ELEV. SOURCE: Ref. to Husky Production Well	TOC. ELEV.: 607.182 masl	LOGGED BY: Dale Van Stempvoort*



Saskatchewan Research Council	* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.
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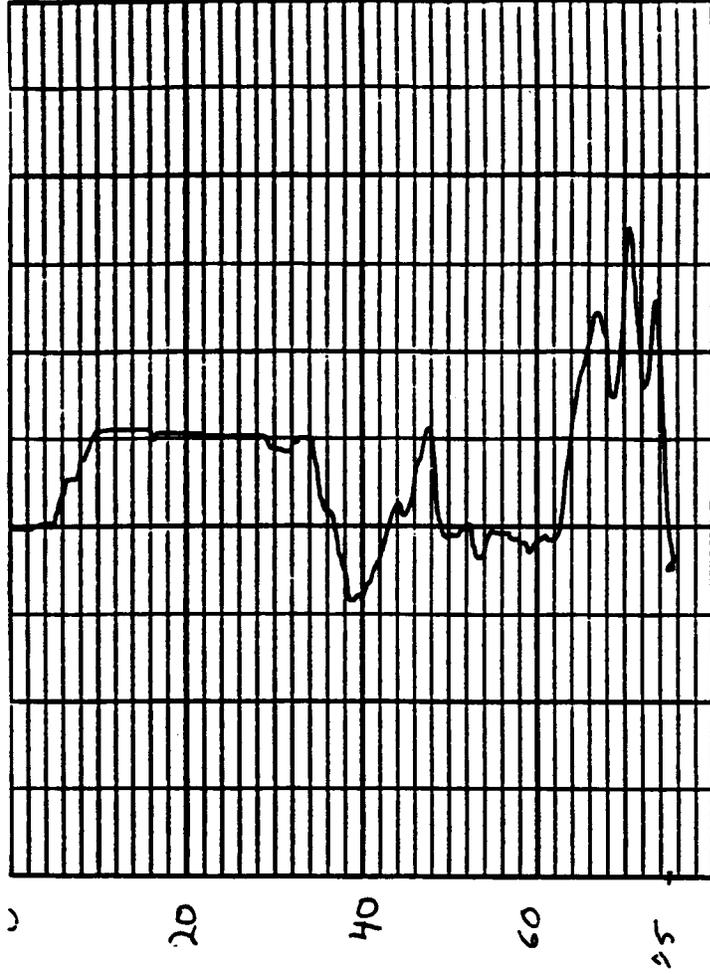
MAR-94-03 May 4/94

SP 20 mV



R 10 ohms

Depth below
Ground

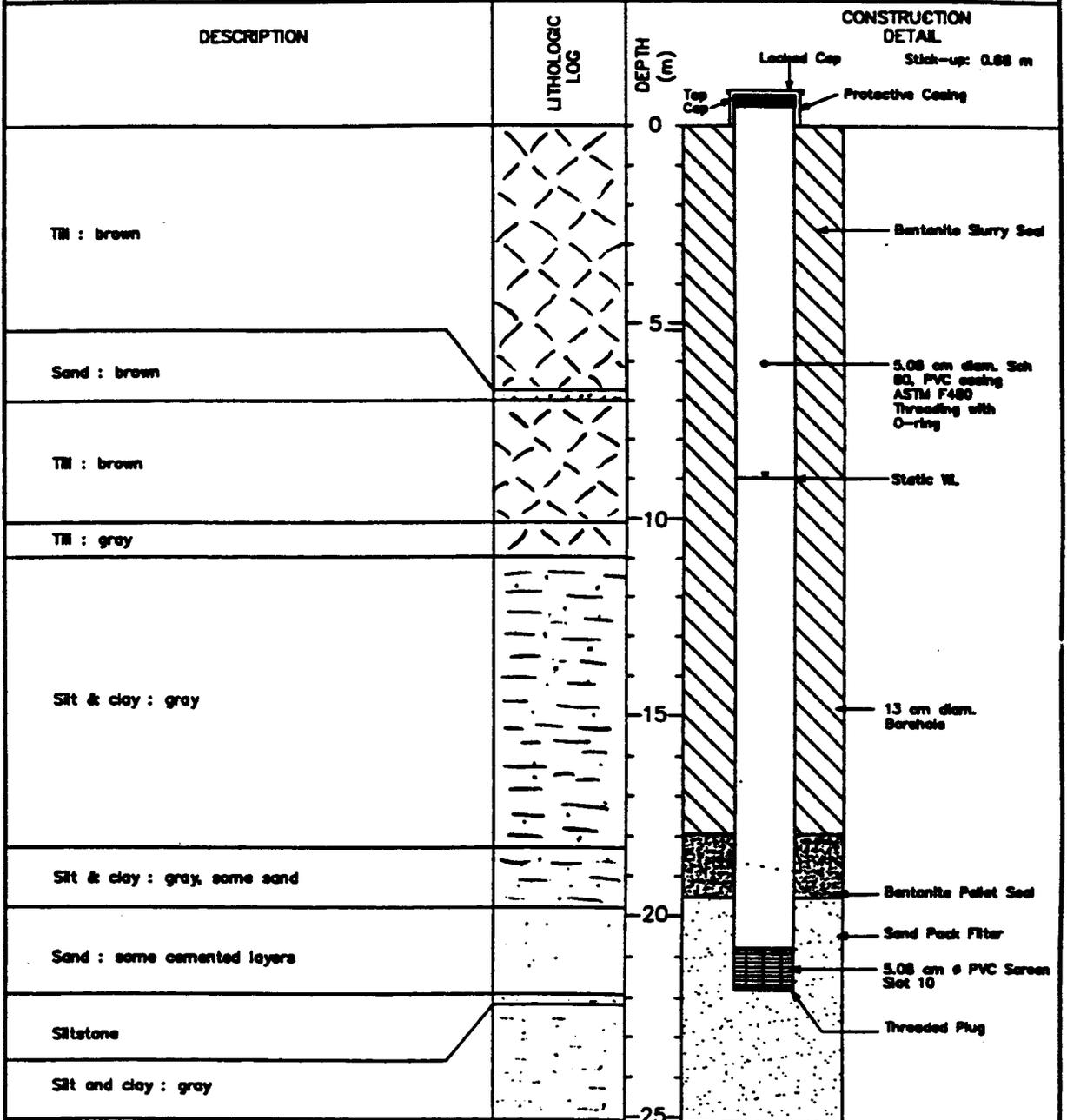


Cond. of drilling mud: $250 \mu\text{s @ } 25^\circ\text{C}$

Monitoring Well Mar-94-04

PROJECT: Methane Migration
 DRILL RIG: Rotary
 DRILLING CO.: McAllister Water Wells Ltd.
 ELEV. SOURCE: Ref. to Husky Production Well

DATE: September 27, 1994 LOCATION: NW14-16-49-26-W3
 TOTAL DEPTH: 25.10 UTM: 12/583400E/5898650N
 SURF. ELEV.: 607.46 masl DRILLER: T. Koppel
 TOC. ELEV.: 608.143 masl LOGGED BY: Dale Van Stampvoort*



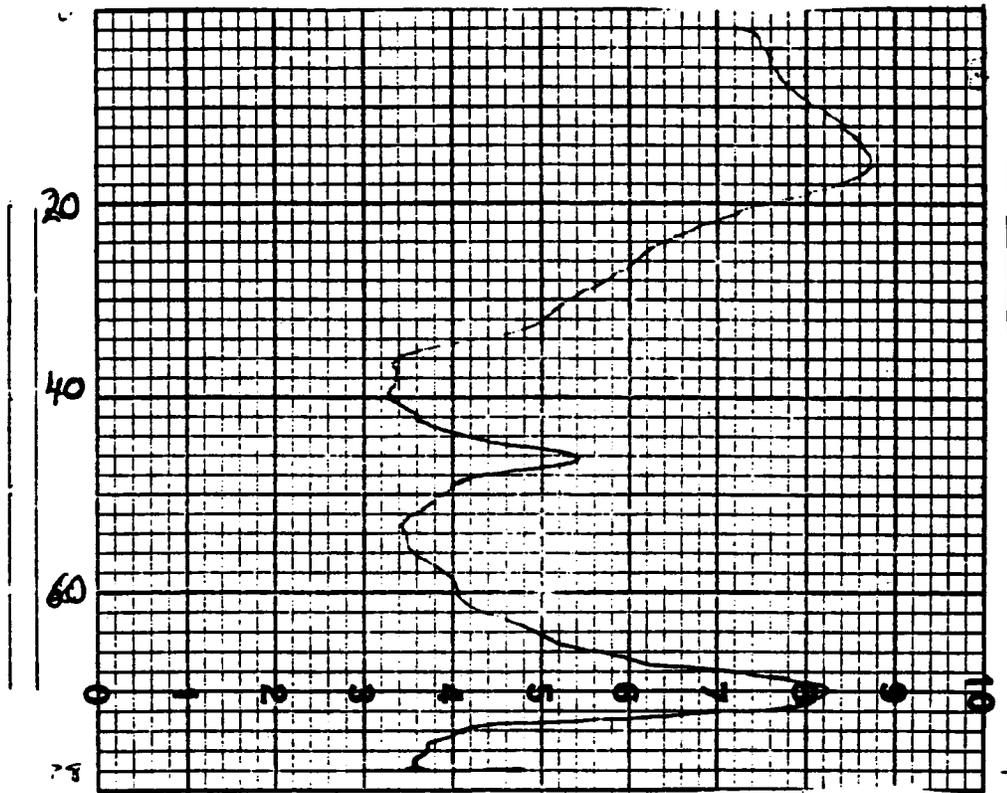
Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

MAR-94-04 Sept 27/94

Depth below
Ground (ft)

R 25 ohms

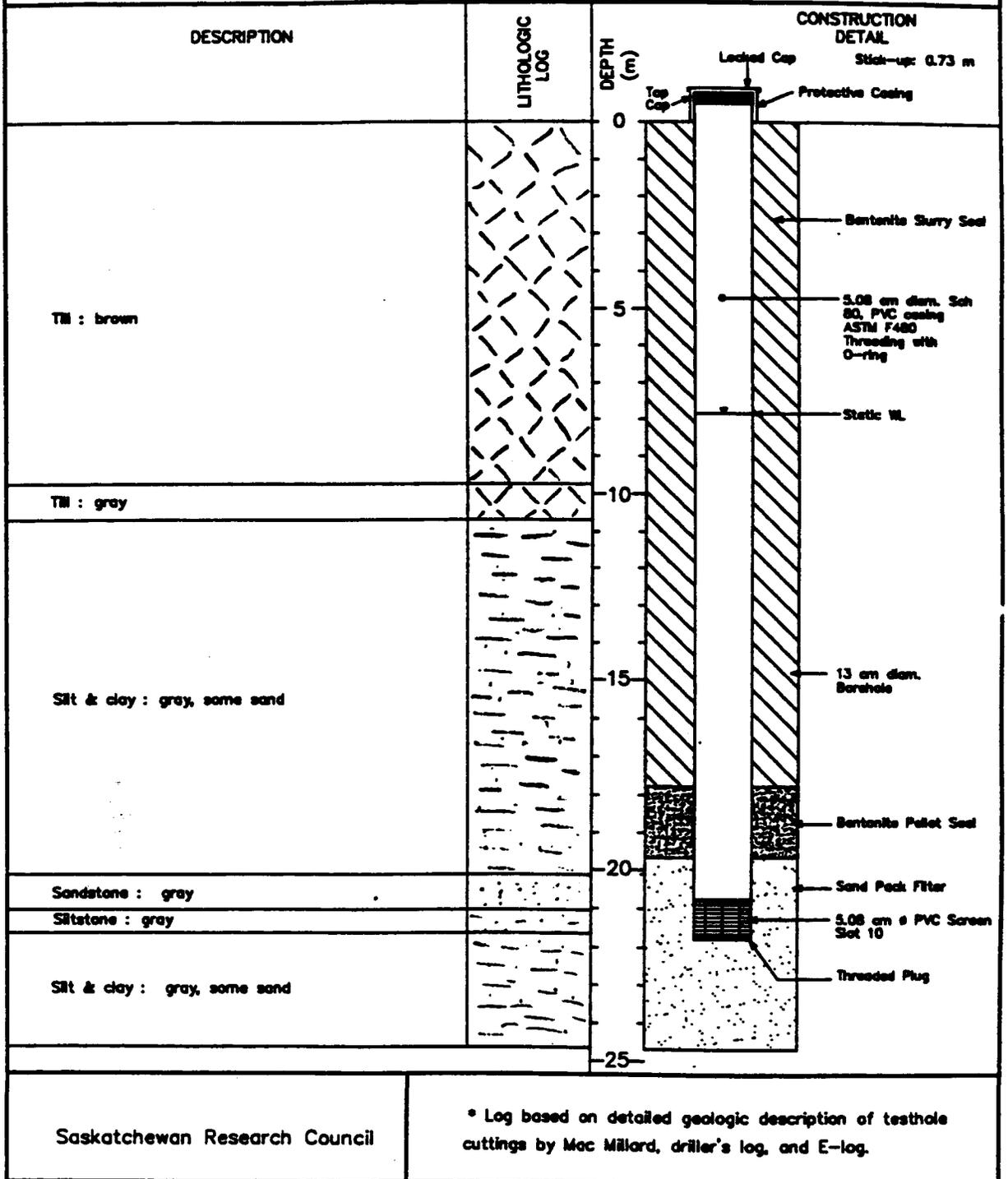


Drilling fluid conductivity: $1875 \mu\text{S}/\text{cm}$ @ 25°C

Monitoring Well Mar-94-05

PROJECT: Methane Migration
 DRILL RIG: Rotary
 DRILLING CO.: McAllister Water Wells Ltd.
 ELEV. SOURCE: Ref. to Husky Production Well

DATE: September 27, 1994 LOCATION: NW14-16-49-28-W3
 TOTAL DEPTH: 25.40 UTM:12/583400E/5898650N
 SURF. ELEV.: 606.60 masl DRILLER: T. Koppel
 TOC. ELEV.: 607.330 masl LOGGED BY: Dale Van Stampvoort*



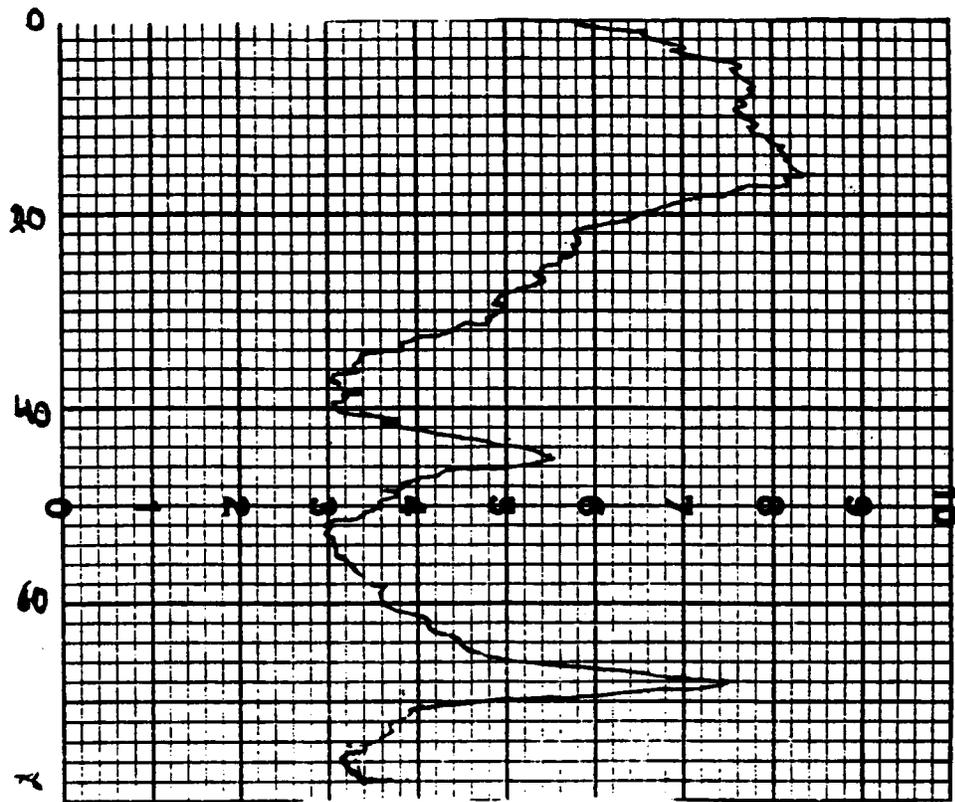
Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

MAR-94-05

Depth below
Ground

R 25 ohms



Drilling fluid conductivity: $1927 \mu\text{S}/\text{cm}$ @ 25°C .

Thin, coarse, fine, gravel - brownish, brown, and white, gray

Thin, sandy, coarse, medium, coarse, gravel - dark gray, gray

Gravel, 50-70%
Sand, medium, coarse, brownish, brown, and white, gray

Medium, coarse, sandy, gravel, light brownish, gray

Thin, coarse, gravel, sandy, gray

Medium, coarse, medium, gravel, sandy, gray

Sand, medium, coarse, gravel, brownish, brown, and white, gray

Sand, medium, coarse, gravel, brownish, brown, and white, gray

Sand, coarse, medium, gravel, brownish, brown, and white, gray

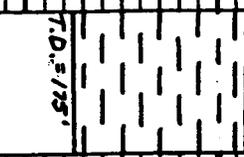
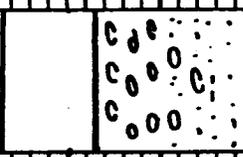
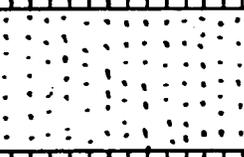
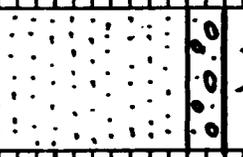
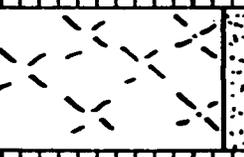
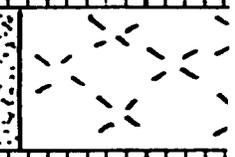
Sand, coarse, medium, gravel, brownish, brown, and white, gray

Gravel, coarse, medium, gravel, brownish, brown, and white, gray

No. sample

Sand, coarse, medium, gravel, brownish, brown, and white, gray

Gravel, coarse, medium, gravel, brownish, brown, and white, gray



Thin, coarse

Sand, medium, brown

Thin, coarse, gravel, sandy

Sand, coarse, medium, gravel

Sand, coarse, medium, gravel

Gravel, coarse, medium, gravel

Gravel, coarse, medium, gravel

Gravel, coarse, medium, gravel

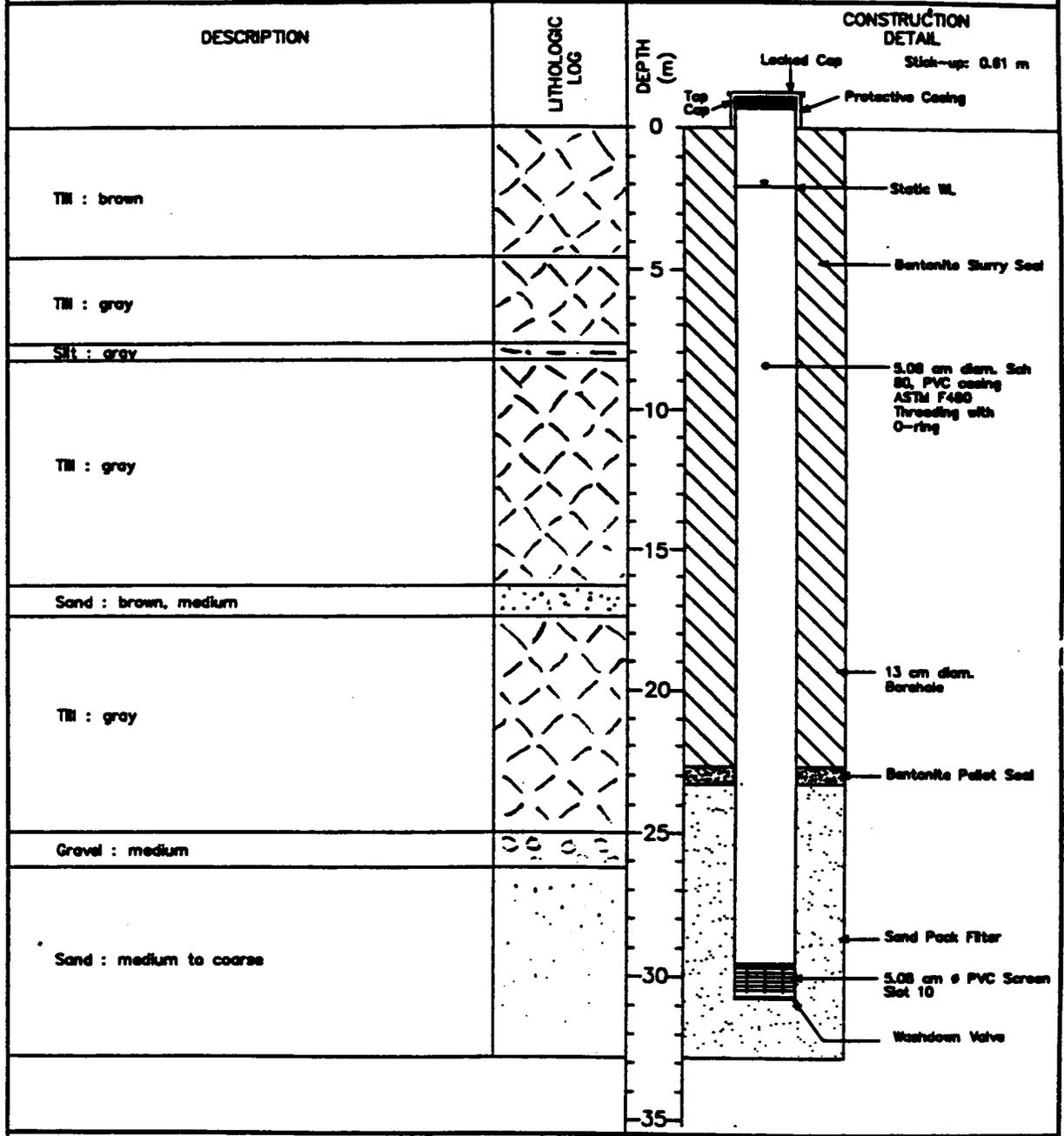
Sand, coarse, medium, gravel

Gravel, coarse, medium, gravel

Strategy by: [unclear]

Monitoring Well Lnd-94-01A

PROJECT: Methane Migration	DATE: May 5, 1994	LOCATION: NE16-04-55-06-W4
DRILL RIG: Rotary	TOTAL DEPTH: 32.80	UTM: 12/511700E/5953100N
DRILLING CO.: McAllister Water Wells Ltd.	SURF. ELEV.: 626.43 masl	DRILLER: G. McAllister
ELEV. SOURCE: Ref. to Amoco Production Well	TOC. ELEV.: 627.041 masl	LOGGED BY: Dale Van Stampvoort*

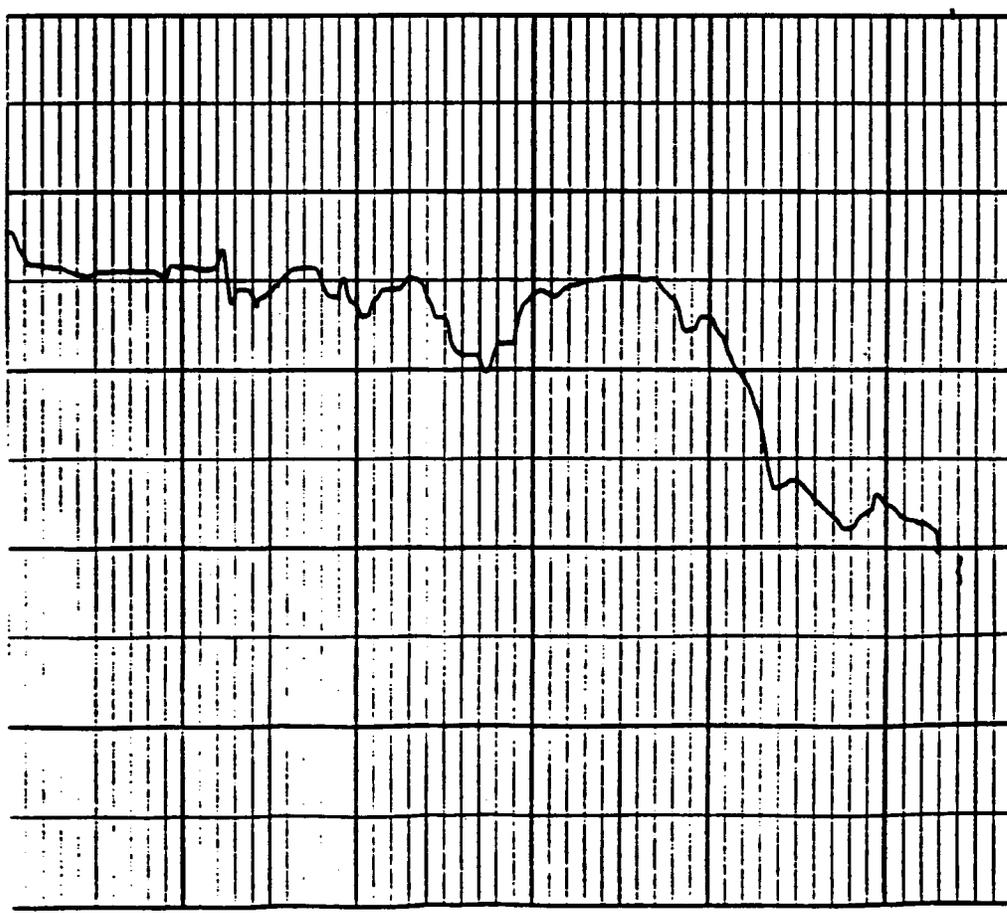


Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

LND-94-01A May 5/94

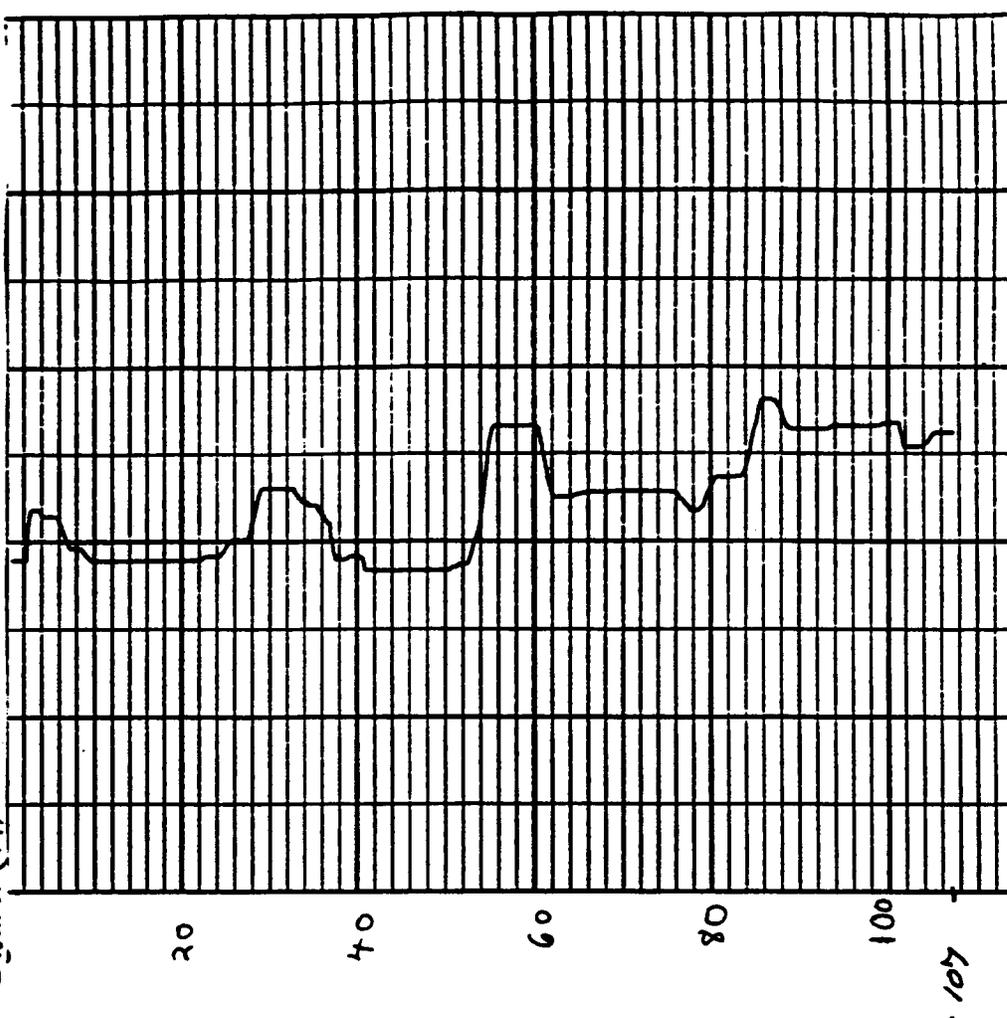
SP 20 mV



Conductivity of drilling fluid:
525 μ S/cm @ 25°C

R 25 ohms

Depth below Ground (ft)



Monitoring Well Lnd-94-02

PROJECT: Methane Migration

DATE: May 5, 1994

LOCATION: NE16-04-55-06-W4

DRILL RIG: Rotary

TOTAL DEPTH: 29.20

UTM: 12/511700E/5953100N

DRILLING CO.: McAllister Water Wells Ltd.

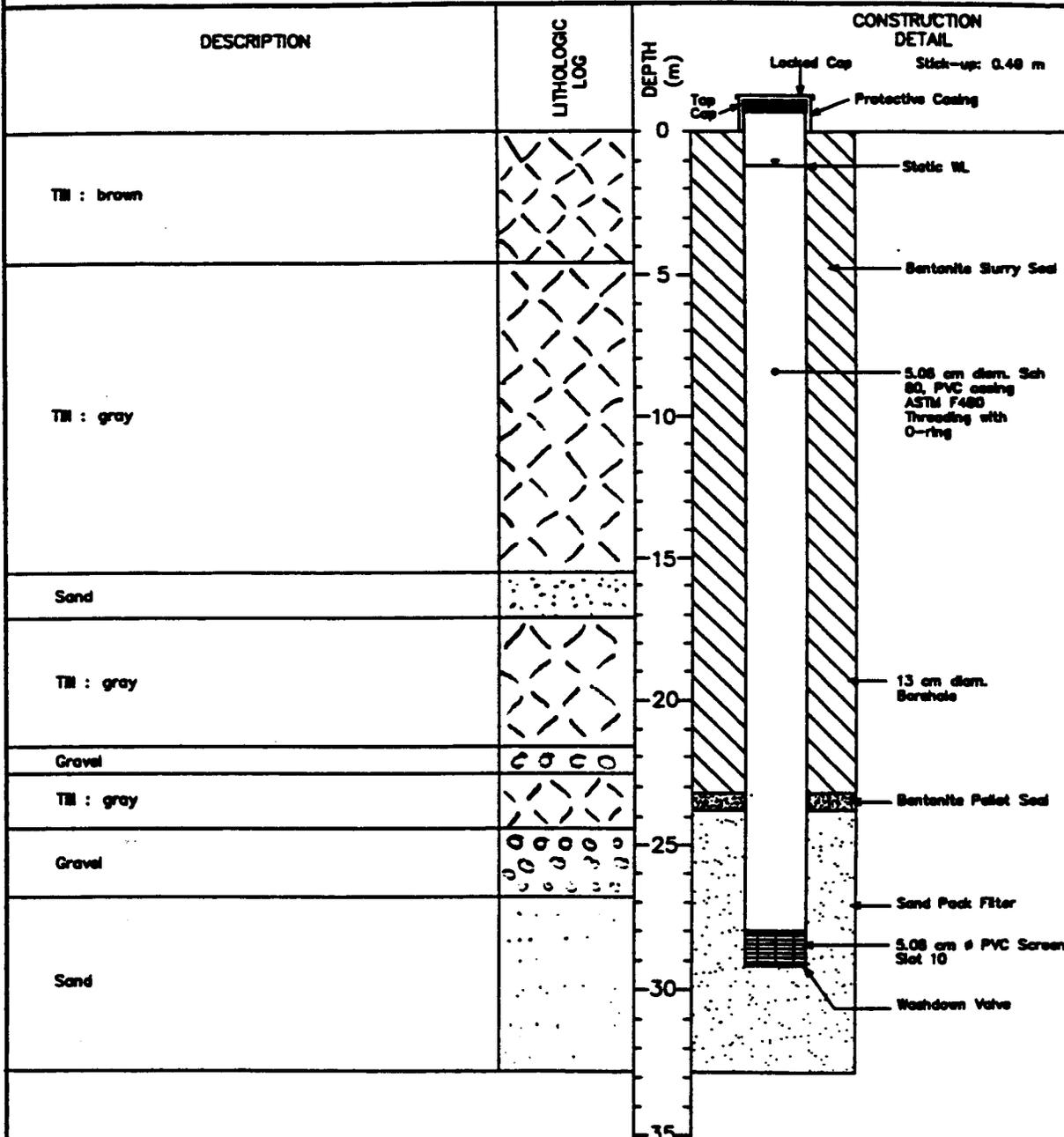
SURF. ELEV.: 625.60 masl

DRILLER: G. McAllister

ELEV. SOURCE: Ref. to Amoco Production Well

TOC. ELEV.: 626.090 masl

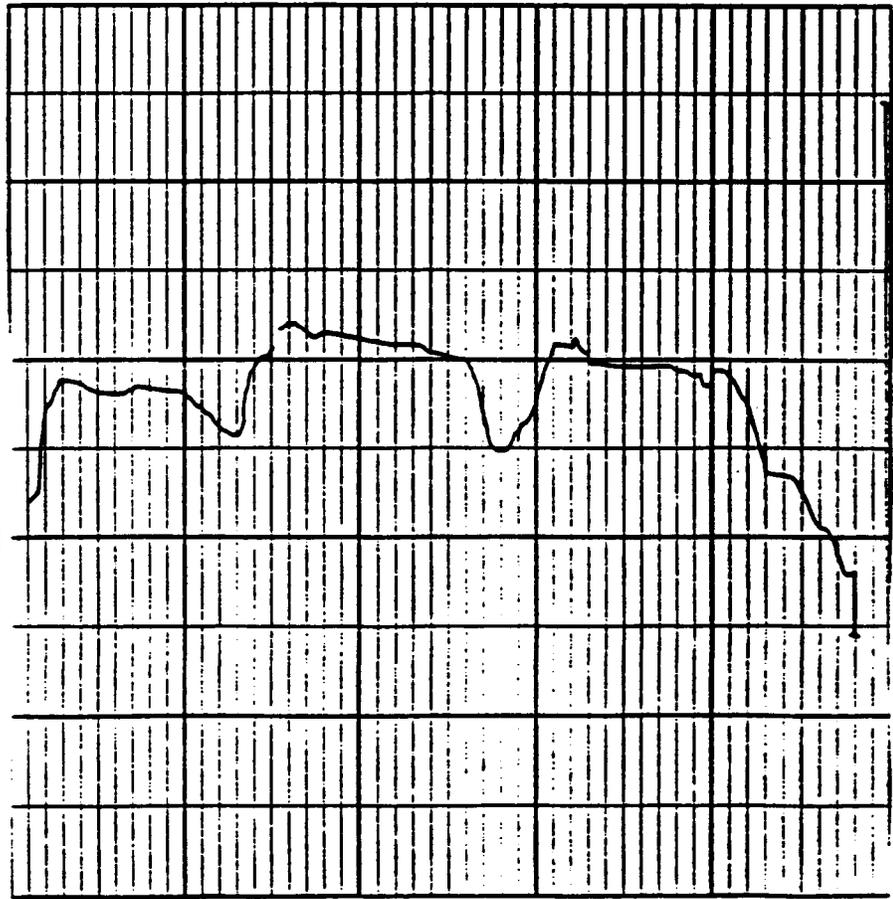
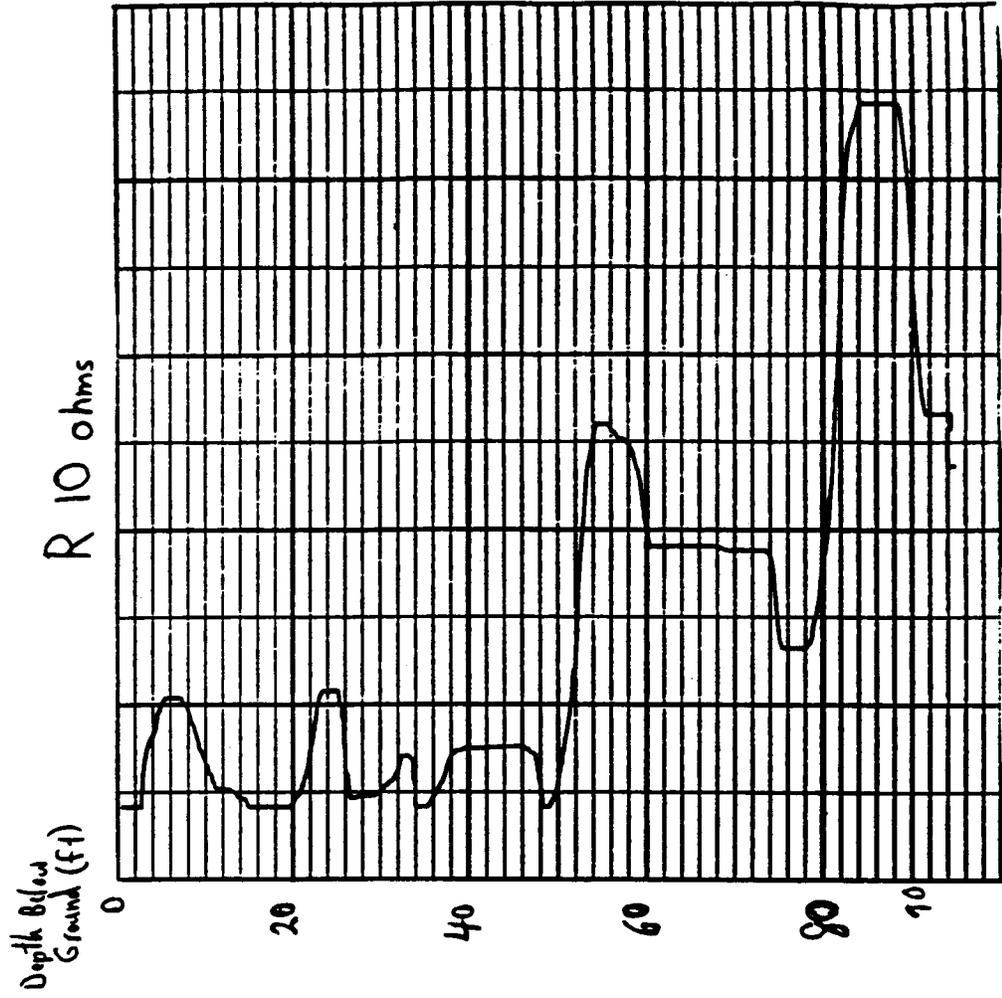
LOGGED BY: Dale Van Stempvoort*



Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

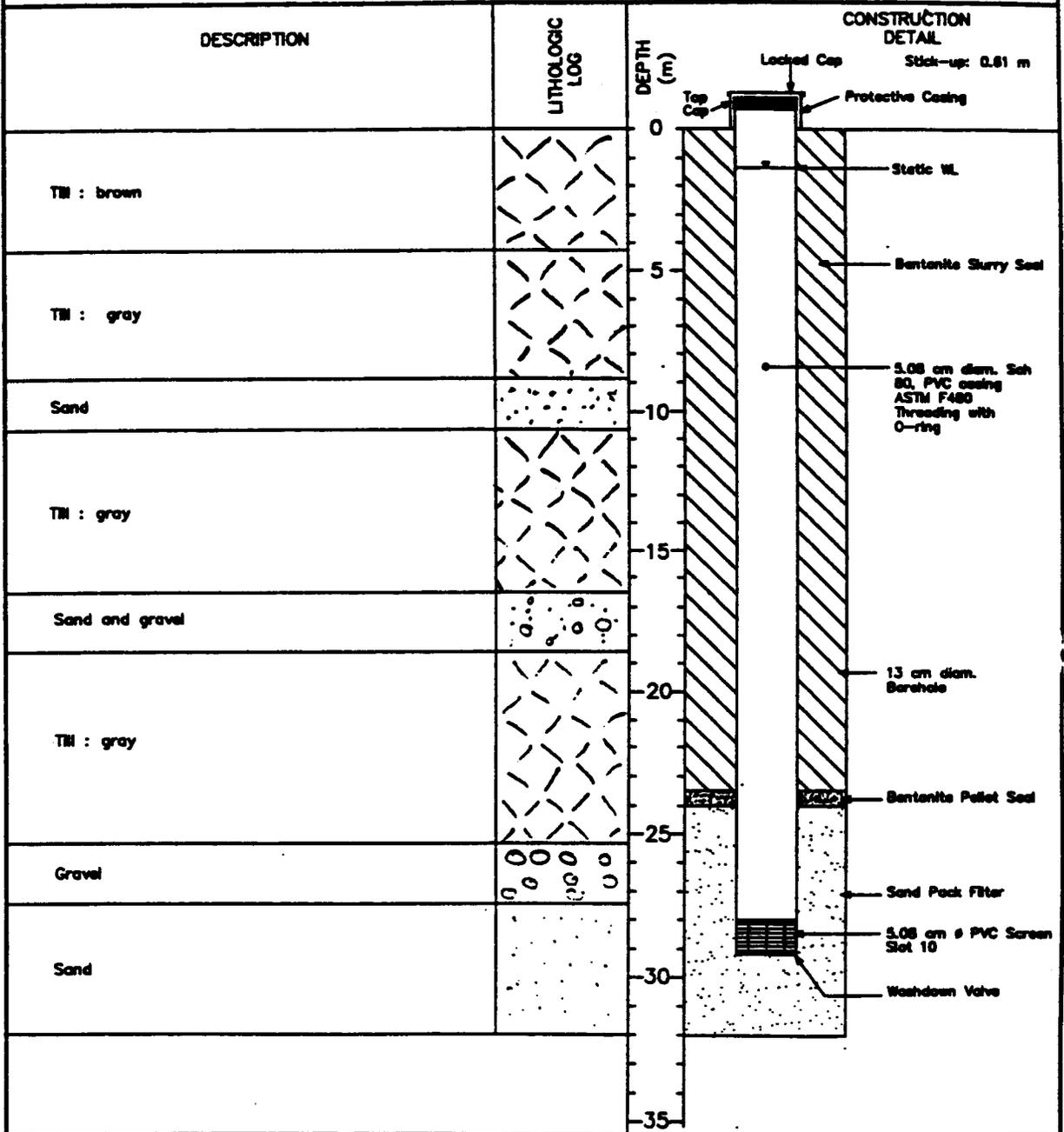
LND-94-02 May 5/94



Conductivity of Drilling Fluid:
700 μ S @ 25°C

Monitoring Well Lnd-94-03

PROJECT: Methane Migration	DATE: May 6, 1994	LOCATION: NE16-04-55-06-W4
DRILL RIG: Rotary	TOTAL DEPTH: 29.20	UTM: 12/511700E/5953100N
DRILLING CO.: McAllister Water Wells Ltd.	SURF. ELEV.: 625.66 masl	DRILLER: G. McAllister
ELEV. SOURCE: Ref. to Amoco Production Well	TOC. ELEV.: 626.269 masl	LOGGED BY: Dale Van Stampvoort*

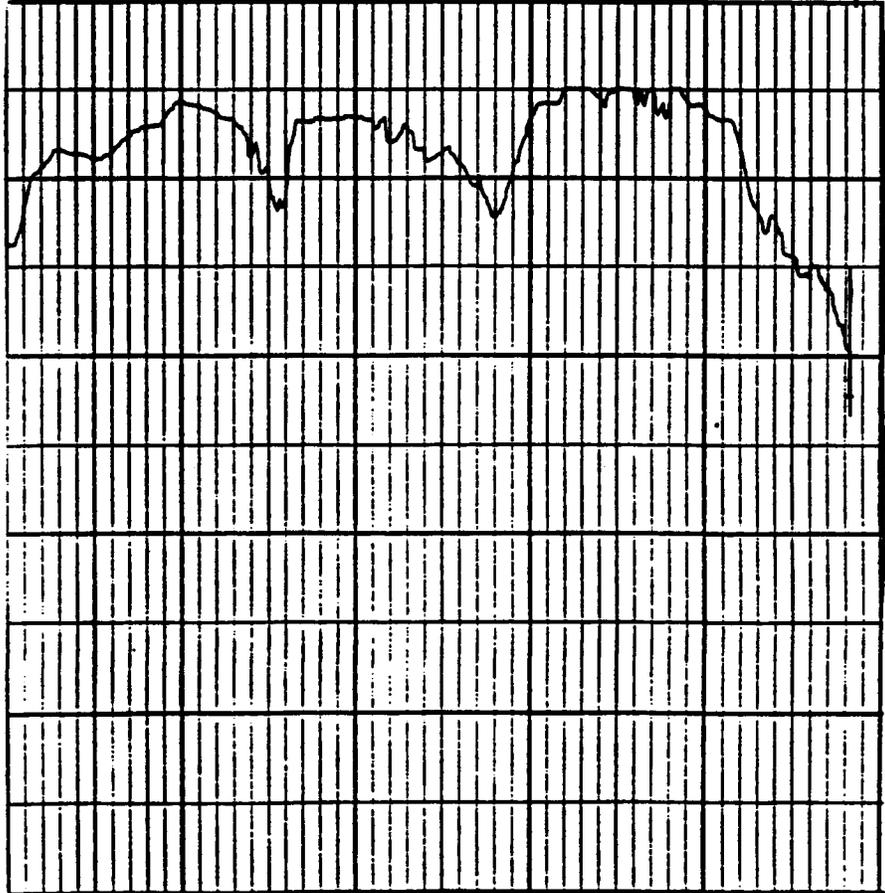


Saskatchewan Research Council

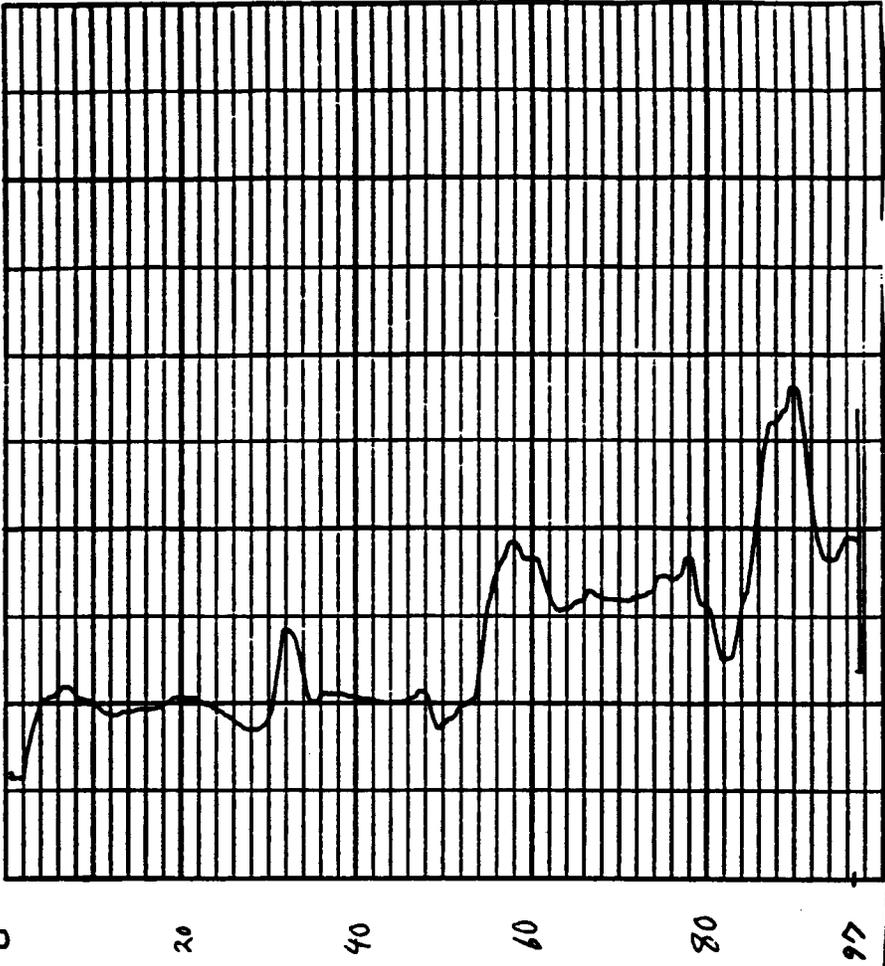
* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

LND-94-03 May 6/94

SP 20 mV



R 25 ohms



Conductivity of drilling fluid:
730 μ S/cm @ 25°C

Monitoring Well Lnd-94-04

PROJECT: Methane Migration

DATE: September 28, 1994 LOCATION: NE16-04-55-06-W4

DRILL RIG: Rotary

TOTAL DEPTH: 32.00 m

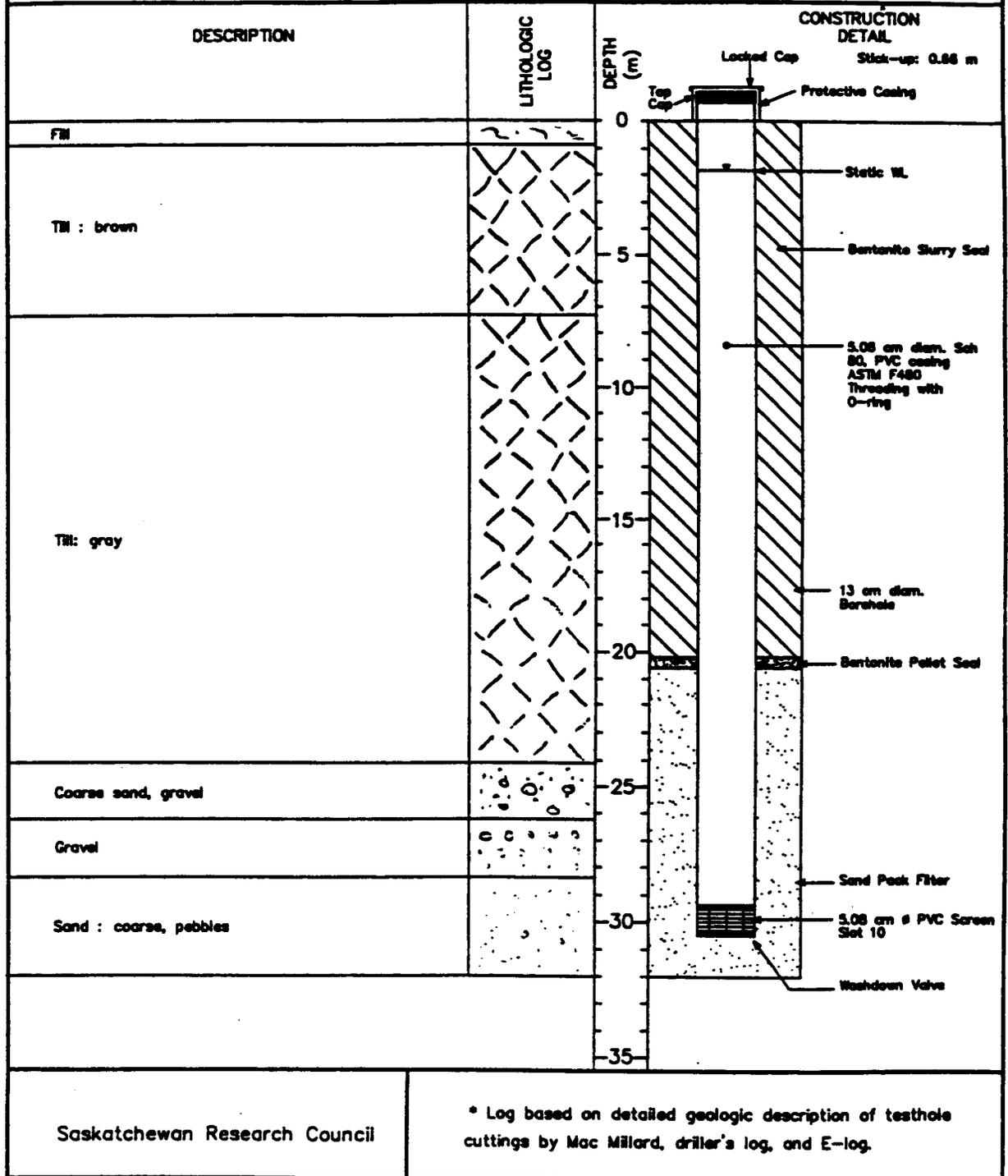
UTM: 12/S11700E/5953100N

DRILLING CO.: McAllister Water Wells Ltd.

SURF. ELEV.: 626.18 masl DRILLER: T. Koppel

ELEV. SOURCE: Ref. to Amoco Production Well

TOC. ELEV.: 626.843 masl LOGGED BY: Dale Van Stempvoort*



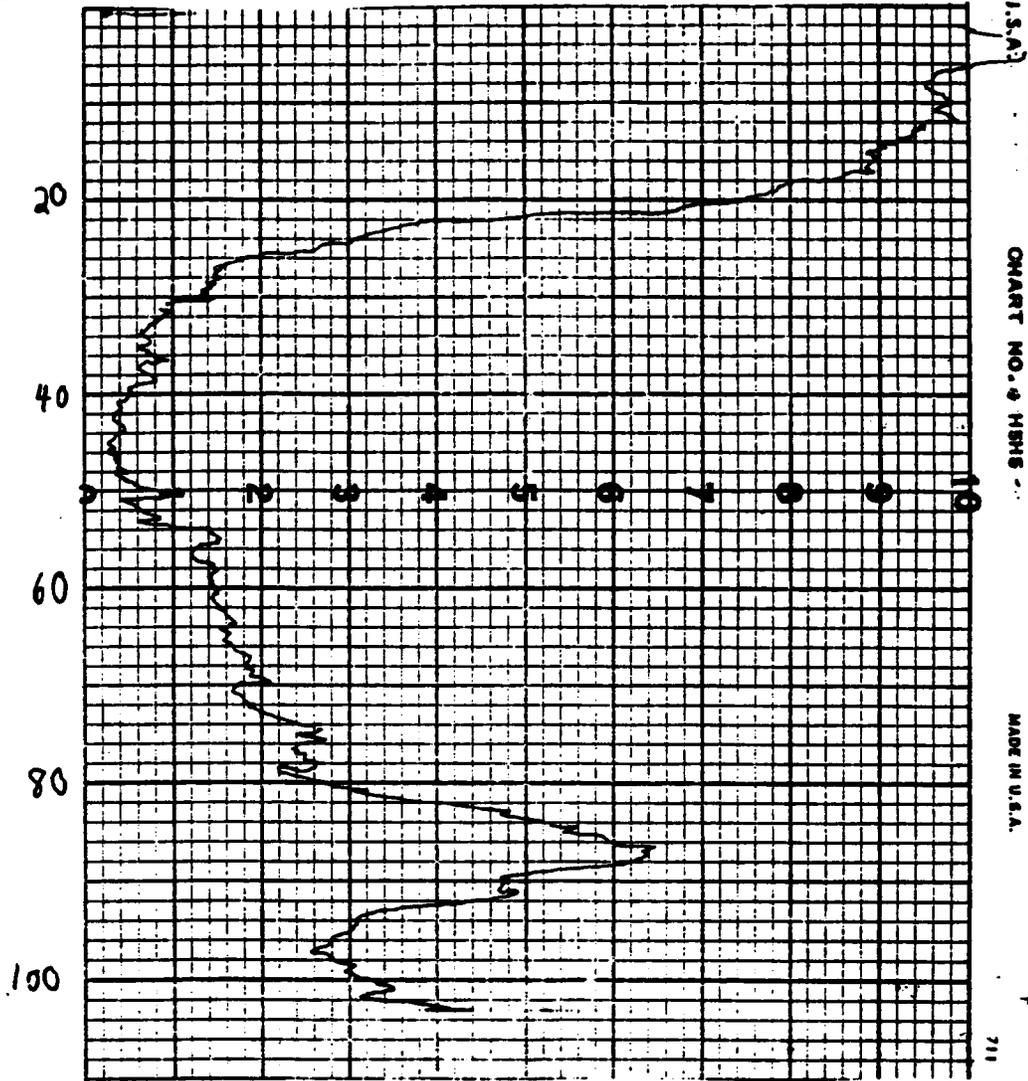
Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

LND-94-04 Sept 28/94

Depth below
Ground (ft)

R 50 ohms

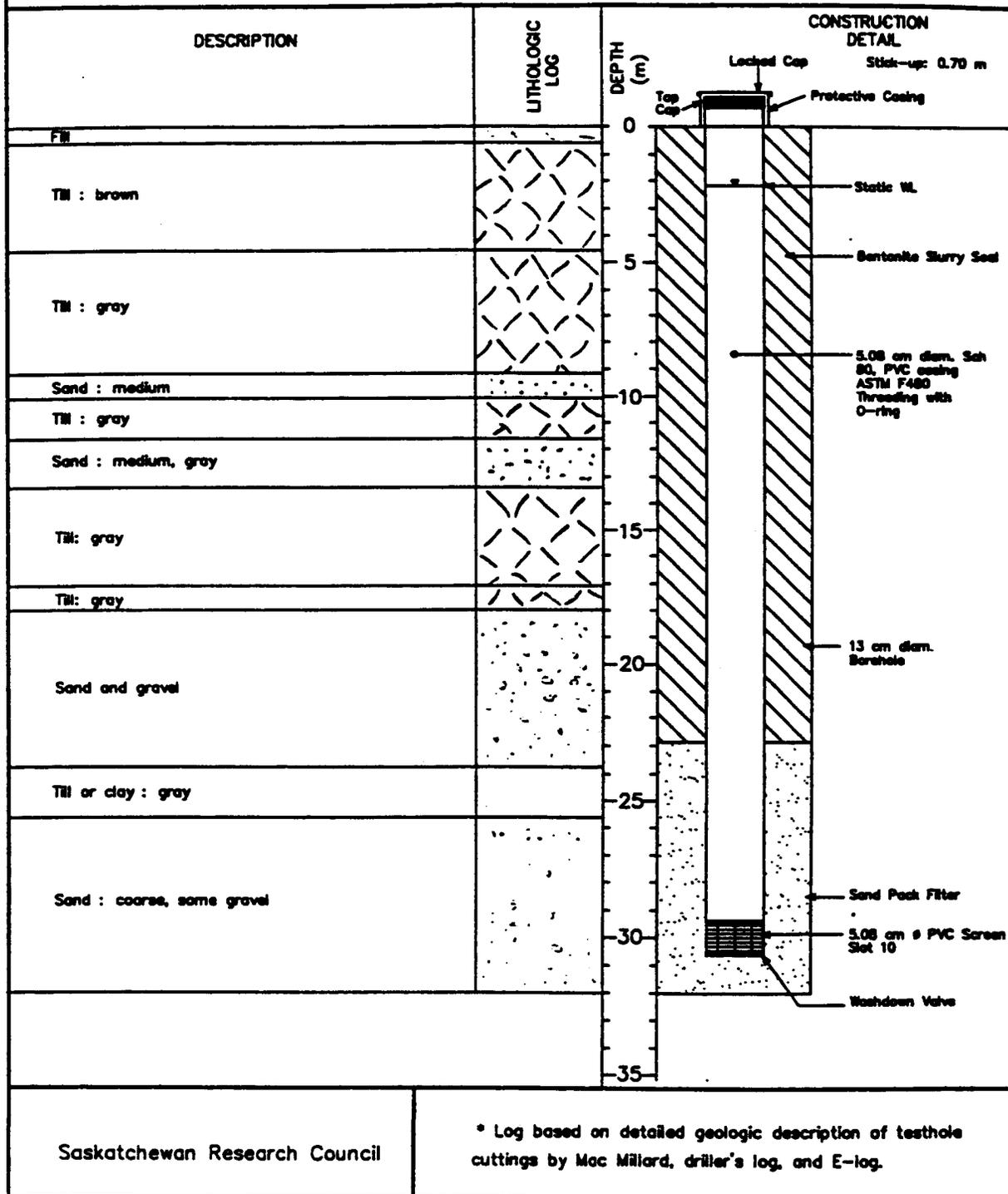


Conductivity of drilling
fluid: $805 \mu\text{S}/\text{cm}$ @ 25°C

Monitoring Well Lnd-94-05

PROJECT: Methane Migration
 DRILL RIG: Rotary
 DRILLING CO.: McAllister Water Wells Ltd.
 ELEV. SOURCE: Ref. to Amoco Production Well

DATE: September 29, 1994 LOCATION: NE16-04-55-06-W4
 TOTAL DEPTH: 32.00 m UTM: 12/S11700E/5953100N
 SURF. ELEV.: 626.46 masl DRILLER: T. Koppel
 TOC. ELEV.: 627.157 masl LOGGED BY: Dale Van Stampvoort*



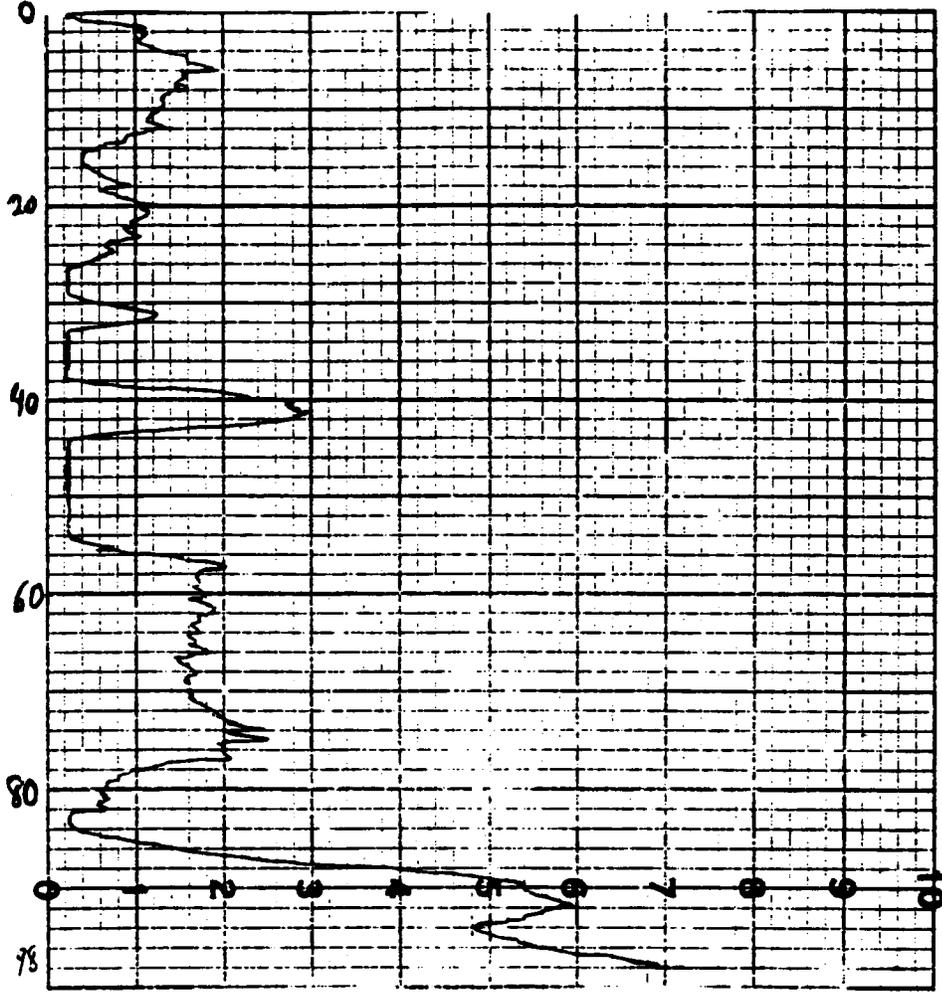
Saskatchewan Research Council

* Log based on detailed geologic description of testhole cuttings by Mac Millard, driller's log, and E-log.

LND-94-05 Sept 29/94

Depth below
Ground (ft)

R 50 ohms



Conductivity of drilling fluid:

APPENDIX B. Water level data, including pumping tests.

Table B.1. Water Level Data for the Monitoring Wells Collected in 1994.

	Date	Ground Elevation (m asl)	TOC Elevation (m asl)	Stick -up	Water Level below TOC	Water Level (m asl)
MAR-94-01	Jun 21/94	606.6	607.28	0.68	8.561	598.719
	Sep 26/94				8.528	598.752
	Oct 5/94				8.513	598.767
	Oct 17/94				8.510	598.770
MAR-94-02	Jun 21/94		607.969	0.72	9.272	598.697
	Sep 26/94				9.240	598.729
	Oct 5/94				9.223	598.746
	Oct 17/94				9.222	598.747
MAR-94-03	Jun 21/94		607.182	0.68	8.489	598.693
	Sep 26/94				8.454	598.728
	Oct 5/94				8.437	598.745
	Oct 17/94				8.433	598.749
MAR-94-04	Oct 5/94		608.143	0.68	9.658	598.485
	Oct 17/94				9.665	598.478
MAR-94-05	Oct 5/94		607.33	0.73	8.580	598.750
	Oct 17/94				8.578	598.752
LND-94-01A	Jun 21/94	625.6	627.041	0.61	2.713	624.328
	Sep 26/94				2.759	624.282
	Oct 18/94				2.726	624.315
LND-94-02	Jun 21/94		626.09	0.49	1.766	624.324
	Sep 26/94				1.804	624.286
	Oct 18/94				1.773	624.317
LND-94-03	Jun 21/94		626.269	0.61	1.948	624.321
	Sep 26/94				1.989	624.280
	Oct 18/94				1.959	624.310
LND-94-04	Oct 18/94		626.843	0.66	2.528	624.315
LND-94-05	Oct 18/94		627.157	0.7	2.837	624.320

Pump Test Conducted on June 21/94 in MAR-94-02

MAR-94-01

time	time (sec)	Drawdown h-h ₀	Water Level
14:08	0	0	8.561
14:14	360	0.309	8.870
14:19	660	0.527	9.088
14:25	1020	0.659	9.220
14:30	1320	0.728	9.289
14:37	1740	0.777	9.338
14:43	2100	0.813	9.374
14:49	2460	0.847	9.408
15:08	3600	0.909	9.470
15:27	4740	0.972	9.533
15:54	7560	1.022	9.583
19:19	18660	1.239	9.800

MAR-94-02

time	time (sec)	Drawdown h-h ₀	Water Level
14:08	0	0	9.272
14:10	120	4.908	14.18
14:11	180	5.888	15.16
14:12	240	6.378	15.65
14:13	300	6.608	15.88
14:18	600	6.948	16.22
14:23	900	7.078	16.35
14:29	1260	7.142	16.414
14:35	1620	6.833	16.105
14:41	1980	6.823	16.095
14:47	2340	6.918	16.19
15:06	3480	6.847	16.119
15:24	4560	6.957	16.229
15:33	5100	7.117	16.389
15:53	6300	7.016	16.288
19:18	18600	7.164	16.436

MAR-94-03

time	time (sec)	Drawdown h-h ₀	Water Level
14:08	0	0	8.489
14:16	480	0.005	8.494
14:21	780	0.016	8.505
14:27	1140	0.031	8.52
14:32	1440	0.047	8.536
14:39	1860	0.062	8.551
14:45	2220	0.078	8.567
14:51	2580	0.089	8.578
15:10	3720	0.121	8.61
15:21	4380	0.137	8.626
15:30	4920	0.15	8.639
15:56	7680	0.18	8.669
19:22	18840	0.317	8.806

Based on data for MAR-94-03, at match point, $h-h_0 = 0.135$, $W(u) = 1$ (Theis curve*)
where

$$T = (Q \cdot W(u)) / (4\pi(h-h_0))$$

$$T = 6.84 \times 10^{-5} \text{ m}^2/\text{s}$$

$$\text{pumping rate } Q = 0.116 \text{ m}^3/\text{s} \times 10^{-3}$$

Assuming $b = 2 \text{ m}$

$$K = 3.4 \times 10^{-5} \text{ m/s}$$

*Theis, C. V. 1935. The relation between the lowering of the piezometric surface and rate and duration of discharge of a well using groundwater storage. Trans. Amer. Geophys. Union, v. 2, p. 519-524.

Pump Test Conducted June 2/94 in LND-94-03

LND-94-01A

time	time (sec)	Drawdown h-h ₀	Water Level
15:11	0	0	2.760
15:16	300	0.013	2.773
15:20	540	0.019	2.779
15:24	780	0.023	2.783
15:30:56	1196	0.027	2.787
15:35	1440	0.028	2.788
15:53:35	2555	0.038	2.798
16:16:54	3954	0.043	2.803
16:47:15	5775	0.053	2.813
17:19	7680	0.057	2.817
17:48	9420	0.059	2.819
18:17	11160	0.062	2.822

LND-94-02

time	time (sec)	Drawdown h-h ₀	Water Level
15:11	0	0	1.809
15:14	180	0.061	1.87
15:18:15	435	0.075	1.884
15:22:35	695	0.085	1.894
15:29:18	1098	0.094	1.903
15:33:35	1355	0.095	1.904
15:51:35	2435	0.109	1.918
16:15:27	3857	0.119	1.928
16:46	5700	0.124	1.933
17:17	7560	0.131	1.94
17:46	9300	0.136	1.945
18:15	11040	0.139	1.948

LND-94-03

time	time (sec)	Drawdown h-h ₀	Water Level
15:11	0	0	2.76
15:16	300	0.013	2.773
15:20	540	0.019	2.779
15:24	780	0.023	2.783
15:30:56	1196	0.027	2.787
15:35	1440	0.028	2.788
15:53:35	2555	0.038	2.798
16:16:54	3954	0.043	2.803
16:47:15	5775	0.053	2.813
17:19	7699	0.057	2.817
17:48	9420	0.059	2.819
18:17	11100	0.062	2.822

Based on data for LND-94-01A, at match point, $h-h_0 = 0.0142$, $W(u) = 1$

where

$$T = (Q \cdot W(u)) / (4\pi(h-h_0))$$

$$T = 1.4 \times 10^{-3} \text{ m}^2/\text{s}$$

$$Q = 0.116 \text{ m}^3/\text{s} \times 10^{-3}$$

Assuming $b = 19.8 \text{ m}$

$$K = 7.1 \times 10^{-5} \text{ m/s}$$

APPENDIX C.

Precision for Methane Analyses

Overall, analyses of methane for the two sites ranged by 4 orders of magnitude (0.002 to 13 mg/L) indicating large spatial variations of methane concentrations occur at the sites (Table 1, excluding unreliable analyses). The highest concentrations at each site were observed in monitoring wells immediately adjacent to the production well.

For gas chromatography of methane, the instrumental precision of the GCs used in this investigation is approximately ± 5 to 10 %. The analytical precision for replicate samples may also be affected by other factors such as sample storage and handling. The precision observed for duplicate samples collected in May/June, 1994, extracted and analyzed at SRC, ranged from ± 1 to ± 57 % (relative to mean concentrations). However, for duplicate samples collected in September/October, 1994, the analyses reported by NHRI were consistently much higher (by 2 to 8 times, ignoring the MAR-94-04 duplicates) than reported by SRC, based on analyses conducted approximately 10 days later. These differences are apparently mainly due to a problem for the October samples analyzed at SRC, in which transfers of samples to the manifold were observed to be incomplete. Thus some of the SRC results, as noted on Table 1, are assumed to be unreliable.

It is possible that partial decomposition of methane during storage may affect analytical precision. Sampling artifacts are less likely to have significant effects because duplicate samples are collected in the same manner at the same time.

Further development of sample handling and extraction techniques will be conducted by SRC in 1995 in order to obtain better precision. The focus will be improvement of the extraction technique. Also, whenever practical, analyses will be conducted within 3 days of sample collection.

APPENDIX D.

Calculations of saturated methane concentrations (mg/L) at the Marshall and Lindbergh sites.

For both sites, assume groundwater temperature, $T = 5^{\circ}\text{C} = 278.15^{\circ}\text{K}$

At this temperature, vapor pressure of pure water = $P_{\text{H}_2\text{O}} = 0.87260 \text{ kPa} = 0.008726 \text{ bar}$
(Haar et al., 1984)

The pressure in the aquifer, $P = P_0 + \rho gh$

where P_0 = atmospheric pressure = 1.013 bar

ρ = fluid density = 1000 kg/m³

g = acceleration due to gravity = 9.81 m/s²

h = height of water column

From Duan et al. (1992; their Eqn 10, Table 4)

$$\ln(m_{\text{CH}_4}) = \ln(\chi_{\text{CH}_4} \phi_{\text{CH}_4} P) - \mu/RT - 2\lambda(m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) - 0.06(m_{\text{SO}_4}) + 0.00624(m_{\text{Na}})(m_{\text{Cl}})$$

where m_{CH_4} is the saturated molal concentration of methane

$\chi_{\text{CH}_4} = (P - P_{\text{H}_2\text{O}})/P$

ϕ = fugacity coefficient

μ = chemical potential (a function of T, P calculated from their Table 2)

λ = interaction parameter (a function of T, P calculated from their Table 2)

$R = 0.083145 \text{ bar}\cdot\text{L}/\text{mol}\cdot\text{K}$

m is molality of a dissolved ion (Na, K, etc.) in the groundwater

At 1 bar, $\phi_{\text{CH}_4} = .9977$

At 20 bar, $\phi_{\text{CH}_4} = .9553$

Assuming linear change, ϕ_{CH_4} decreases .00223 per bar

References:

- Duan, Z., Møller, N., Greenberg, J. and Weare, J. H. 1992. The prediction of methane solubility in natural waters to a high ionic strength from 0 to 250°C and 0 to 1600 bar. *Geochimica et Cosmochimica Acta* 56, p. 1451-1460.
- Haar, L., Gallagher, J.S. and Kell, G. S. 1984. *Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI units.* Hemisphere Publishing Co.

For Marshall site

$$h = 12.9 \text{ m}; P = 1.013 + 1.265 = 2.278 \text{ bar}$$

$$\phi_{\text{CH}_4} = .9977 - (1.278 * .00223) = 0.9949$$

P	T	P _{iso}	χ_{CH_4}	ϕ_{CH_4}	μ/RT	λ
2.278	278.15	0.008726	0.996169	0.9949	6.189031	0.106547

m_{N_2}	m_{O_2}	m_{CO_2}	$m_{\text{H}_2\text{O}}$	m_{SO_4}	m_{Cl}
0.006046	0.000187	0.003119	0.001851	0.003518	0.000141

Based on above equations and data:

$$\ln(m_{\text{CH}_4}) = -5.37834 m_{\text{CH}_4} = 0.00462$$

i.e the saturated methane conc. is 74.0 mg/L

For Lindbergh site

$$h = 27.5 \text{ m}; P = 1.013 + 2.698 = 3.711 \text{ bar}$$

$$\phi_{\text{CH}_4} = .9977 - (2.711 * 0.00223) = 0.9917$$

P	T	P _{iso}	χ_{CH_4}	ϕ_{CH_4}	μ/RT	λ
3.711	278.15	0.008726	0.997649	0.9917	6.192014	0.106641

m_{N_2}	m_{O_2}	m_{CO_2}	$m_{\text{H}_2\text{O}}$	m_{SO_4}	m_{Cl}
0.00535	0.000148	0.003942	0.002386	0.003977	0.000536

Based on above equations and data:

$$\ln(m_{\text{CH}_4}) = -4.89551 m_{\text{CH}_4} = 0.00748$$

i.e the saturated methane conc. is 120.0 mg/L

APPENDIX E.

Estimation of the Sorption Coefficient for Methane in Aquifers at the Marshall and Lindbergh Sites.

A sorption (retardation) coefficient R to account for sorption during transport of methane (or other solute) in an aquifer can be estimated (Freeze and Cherry, 1979, p. 404):

$$R = 1 + \rho_b/n.K_d \quad \text{Eqn E.1}$$

where ρ_b = bulk density of the aquifer,

n = porosity of the aquifer,

K_d = distribution coefficient for sorption in the aquifer = C_m/C_a ,

where C_m is concentration of methane sorbed in the solid mass,
and C_a is dissolved, aqueous concentration.

Since methane is sorbed primarily by solid organic carbon in the aquifer, the parameter K_d can be related to known organic content as follows:

$$K_d = f_{oc}(K_{oc}) \quad \text{Eqn E.2}$$

where K_{oc} is the distribution coefficient for sorption by the solid organic carbon,

f_{oc} = concentration of the solid organic carbon in the aquifer,

In turn, K_{oc} can be estimated by the following empirical equation (Hassett et al., 1983):

$$\log K_{oc} = 0.088 + 0.909(\log K_{ow}) \quad \text{Eqn E.3}$$

where K_{ow} = distribution coefficient for methane the octanol- water system = C_{ow}/C_w ,

where C_{ow} is concentration of methane dissolved in octanol.

From Hansch and Leo (1979), $\log K_{ow}$ for methane = 1.09

From Eqn E.3, $\log K_{ow} = 1.08$, $K_{ow} = 12.02$

From Eqn E.2, assuming $f_{oc} = 0.0001$ to 0.001^* : $K_d = 0.0012$ to 0.012

From Eqn E.1, assuming $\rho_s = 1.8$, $n = 0.30^{**}$: $R = 1.006$ to 1.06

*typical range for glaciofluvial sands (Domenico and Schwartz, 1990)

**typical values for sands, gravels (Freeze and Cherry, 1979)

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