HELIUM AND METHANE ANOMALIES IN DOMESTIC WELL WATERS IN SOUTHWESTERN SASKATCHEWAN, CANADA, AND THEIR RELATIONSHIP TO OTHER DISSOLVED CONSTITUENTS, OIL AND GAS FIELDS, AND TECTONIC PATTERNS

Willy Dyck and Colin E. Dunn

Geological Survey of Canada, Ottawa, Canada

During the summer of 1976 a Abstract. regional groundwater survey was undertaken in an area of 18,000 km² in southwestern Saskatchewan. Approximately 940 domestic wells and springs were sampled at a density of 1 per 13 km^2 , where possible. The samples were analyzed for up to 30 variables, including He, CH4, and many trace and minor elements. The results of the survey are related to regional topographic, geological, and hydrological features. Of particular interest are CH4 and He anomalies associated with known gas and oil reservoirs in the region. Several anomalies of similar magnitude occur away from known reservoirs and hence may point to new ones. The close association of CH4 with He, sample depth and deeper "softer" waters, as indicated by the positive correlations of CH₄ with He, Na, CO_3^2 , HCO_3 and sample depth is postulated to be a good criterion for distinguishing between reservoir CH4 and marsh The coincidence of CH₄ and He anomalies known tectonic features also indicates gas. with fracture leakage from depth and the possible existence of oil and gas fields. Regional surveys of domestic well waters can be of use in delineating areas with proven and potential oil and gas reservoirs at depth.

Introduction

publication of Oil and Gas in The Saskatchewan, the seventh special publication of the Saskatchewan Geological Society (Lorsong and Wilson, 1984), inspired a closer look at CH4 (methane) data obtained during a regional well water survey of the Cypress Hills area (Dyck, 1980b). At the time of the survey it seemed self-evident that the gas and oil fields in the area would be reflected by anomalous CH4 and possibly other trace elements and gases in the groundwaters. However, the usefulness of hydrocarbon and He gases in surficial environments for the search of petroleum deposits is still in debate. The main problem is not in detecting gas anomalies but in interpreting them (Philip and Crisp, 1982). Methane alone is not considered to be a reliable indicator because it is also produced in microbiological processes occurring in soils and sediments. This CH4 can confuse or mask CH4 from a hydrocarbon deposit. Higher C homologues, primarily C_2-C_4 , aid in distinguishing between biogenic and reservoir CH4 (Philip and Crisp, 1982), but they occur in much lower concentrations and hence are often not detectable. Carbon isotopes can also aid in distinguishing between these two types of CH4

Published in 1986 by the American Geophysical Union.

Paper number 5B5723.

(Goth, 1985; Faber and Stahl, 1984) but add considerably to the analytical cost of a survey. Hickey et al. (1983) have applied integrative gas chromotography/mass spectrometry/pattern recognition procedures to characterize fault leakage of C homologues associated with producing areas of petroleum.

During the course of development of reconnaissance uranium exploration techniques, Dyck (1980a) and Dyck et al. (1976a) carried out several regional well water surveys and analyzed these waters for a large number of trace elements and dissolved gases. The first pilot study of this nature involved 130 domestic wells near Ottawa, Ontario. A weak positive CH4-He correlation was observed in one part of the survey area but was dismissed as coincidental because there was no corresponding correlation of CH4 with depth as there was for He and depth. The conclusion in this case was that He from depth was mixing with CH, produced biogenically at the surface.

A more extensive well water survey in eastern maritime Canada (Dyck et al., 1976a) gave no correlation between CH_4 and He, although the spent oil field in the Moncton, New Brunswick, area produced a strong CH_4 anomaly. As in the case of the Ottawa region, several weak CH_4 anomalies were attributed to marsh gas because of coincident swamps and the lack of any depth- CH_4

The well water reconnaissance survey in the Cypress Hills area of Saskatchewan revealed extensive regional CH4 and He anomaly patterns. Not only do these patterns correlate with each other, but both He and CH4 correlate with depth (the deeper the well, the higher the dissolved gas content), with major tectonic features, and This report with known gas and oil fields. describes these anomalies in detail, relates them to regional tectonic features, and employs other geochemical indicators to show that the CH. anomalies are not related to marsh gas near the surface but rather to gas or oil fields at depth. The close association of He and CH4 and major tectonic features may also indicate outgassing of the crust through deep faults (Gold, 1979).

The Survey Area

The area surveyed lies in the extreme southwestern corner of Saskatchewan (Figure 1) and straddles the northwestern edge of the Williston basin, a major gas and oil producing region in the midwestern United States and Canada. The topography is dominated by the Cypress Hills, a remnant of a large plateau that has been extensively eroded during the last 40 million years. The hills rise steeply from the surrounding plains in the west and north at 520 to 760 m, to a plateau with a maximum elevation of 1400 m.



Fig. 1. Location, surficial geology (after Macdonald and Broughton, 1980), gas and oil fields (after Pearce, 1983), and synclines of the Late Mesozoic (after Kamen-Kaye, 1953) of the Cypress Hills well water survey region.

The plateau dips gently southeastward to the level of the plains.

The hills form a divide separating two major watersheds. North of the divide the South Saskatchewan River drains into Hudson Bay, and in the south the Missouri River drains into the Gulf of Mexico. Most of the northward flowing creeks within the Cypress Hills plateau contribute to an interior drainage pattern that flows into a series of alkaline lakes located north of the study area. On the southern slopes of the plateau, most of the creeks flow into an eastwest drainage channel consisting of man-made Cypress Lake and the Frenchman River. Drainages west of Cypress Lake, Battle Creek, and Middle Creek flow southeastward into the United States.

The climate of the plains surrounding the Cypress Hills is semiarid. This area has the lowest precipitation, less than 30 cm, and the highest temperatures found anywhere in the Canadian prairies. In the Cypress Hills the climatic conditions are like those found in the valleys and slopes of the Rockies. There is a greater amount of precipitation, cooler temperatures, and less evaporation here than is found in the surrounding plains.

General Geology

Sediments washed from the mountains to the west during periods of uplift were deposited under fluviatile and marine conditions to form the rock sequence of the present day Cypress Hills.

The sediments exposed within the study area are those of the Judith River, Bearpaw, Eastend, Whitemud, Battle, Frenchman, Ravenscrag, Cypress Hills and reworked Cypress Hills formations, and glacial drift (Figure 1). These predominantly sandy sediments range in age from Upper Cretaceous (Judith River through the Frenchman formations) to Pleistocene (glacial drift). The oldest outcropping sediments occur in the west of the survey area and comprise the Judith River Formation. This formation ranges in thickness from 73 to 235 m and consists of interbedded marine sand, silt, and shales that are carbonaceous and noncalcareous.

The Upper Cretaceous and Tertiary strata are water bearing because the nonmarine formations are permeable, and the marine Eastend, Bearpaw, and Judith River formations contain numerous sand layers. Hence there is a regional aquifer permitting the movement of groundwater over relatively large areas. For more detailed accounts of the geology of the area the reader is referred to Russell (1948), Furniwal (1946), Kupsch (1956), and Macdonald and Broughton (1980).

southwestern Saskatchewan, In structural deformation is limited to slightly dipping strata, slumping, and localized faulting. Strata dip gently toward the southeast because the area is situated on the east limb of the Sweetgrass Arch. Slumping of the formations is widespread in exposures along valleys of the major rivers and creeks. Minor faulting is restricted to localized faults with very small displacements. Kent (1974) has summarized surficial evidence that indicates the existence of deep-seated NE-SW and NW-SE trending linear features in the area. The occurrence of many so-called "pairsets" suggests zones of weakness in the Precambrian cratonic basement, dividing it into a series of juxtaposed blocks.

Mineral Deposits

The extent of gas and oil exploration in the area is evident from the large number of boreholes sunk into the ground and the numerous oil pumps dotting the countryside. By 1976 over 1700 boreholes had been completed with an average depth of 1500 m and a range of 280-2700 m (Buller, 1972).

The first oil discovery in the Williston basin was in Silurian rocks of the Cedar Creek anticline in 1936 (Gerhard et al., 1982; Gallup and Hamilton, 1953).

Within the study area, 22 medium crude oil pools have been defined, most of which were discovered in the 1950's. Production is entirely from the Mesozoic, primarily from the Jurassic Shaunavon Formation, but with some also from the Cretaceous (Roseray and Cantuar Sands). The initial oil in place is estimated to be 150 million m³ (Saskatchewan Energy and Mines, 1983). At the time this study was conducted, about 15 % of the oil had been recovered. A major gas pool (Hatton) occurs in the northwestern part of the study area, north of Maple Creek (Figure 1), and extends a further 70 km to the north. No other gas pool has been defined in southwestern Saskatchewan.

According to van Delinger (1978), oil in basal Cretaceous sand reservoirs appears to represent migrated hydrocarbons from older beds, most probably the Jurassic Upper Shaunavon. Commercial gas production in southwestern Saskatchewan comes from a relatively few reservoirs found in the Cretaceous Colorado and Montana groups. Christopher (1974) and Simpson (1982) have postulated that additional gas reservoirs may be present in marine Cretaceous sandstones and other formations in the survey area. Similar predictions have been made by Rice and Shurr (1978, 1980) for the Williston basin in the United States. These known and postulated fields are believed to be responsible for the strong CH4 and He anomalies in the well waters discussed below.

The source of He is the decay of U and Th in basement rocks (Hitchon, 1963). Burwash and Cumming (1974, 1976) have postulated uranium-rich porphyritic granites along the Precambrian-Cambrian unconformity and circulating formation fluids for the He rich natural gas occurrence in hole B.A. Wilhelm 1-9, located 20 km NE of the survey area (14 km north of Swift Current). The hole produced an inert gas mixture composed of 97% N₂, 2% He, and 1% CO₂ (Sawatzky et al., 1960).

Uraniferous lignite coal seams similar to those in the Dakotas (Denson and Gill, 1965) have been found and investigated in the Cypress Hills area from time to time (Cameron and Birmingham, 1970; Little and Ruzicka, 1970). They occur in the Ravenscrag Formation in narrow bands usually less than 25 cm thick, but thicknesses of 30 m have been encountered. However, thickness and grades encountered have not warranted commercial exploitation of U.

Hydrogeochemistry

Average annual precipitation in the Cypress Hills area ranges from 25 cm north and south of the hills to 45 cm over the hills. This shift in the water balance has a marked effect on the chemical composition of the well waters. Fresh, weakly mineralized waters on the hills gradually turn into mineralized waters in the plains. Evaporation is one of the factors in concentrating trace elements in groundwaters in the plains area. As these waters become more mineralized, their composition tends toward that of seawater. Sinking groundwaters tend to change from Ca- and Mg-rich "hard" to Na-rich "soft" waters as a result of base exchange with clays. Waters in the area are predominantly alkaline because of the nature of the rocks. Mixing of young waters with older, more mineralized waters from depth also contributes to a rise in element concentrations in the wells. The presence of coal and gaseous hydrocarbons in the Ravenscrag and Frenchman formations promote sulphate reduction and results in poorly oxygenated waters. For a more detailed description of Saskatchewan groundwaters, the reader is referred to Rutherford (1966) and Whitaker (1977).

Sampling Procedures

Approximately 940 domestic wells and springs were sampled during the summer of 1976. The location of the surveyed area is shown in Figure 1. A sample density of one sample per 13 km^2 was maintained, where possible, over the $18,000 \text{ km}^2$ survey area. The sample density is somewhat less in the south because of a lack of wells.

Samples were taken from domestic wells, pasture stock wells, and in some areas from springs. At each site, three bottles were filled slowly, completely, and carefully by removing aerators from kitchen taps and letting the water run for about half a minute prior to sampling. To one 310-mL glass bottle was added, prior to collection of the sample, a 2-mL aliquot of 8 M HNO3 to prevent bacteria from consuming CH4 during shipment and storage. The unacidified sample from another 310 mL bottle was analyzed in the field laboratory as soon as possible after collection. The acidified sample and a spare unacidified sample were shipped to Ottawa for analysis of dissolved gases and trace and minor elements.

Analytical Procedures

The procedures adopted for this survey were similar to those used in the 1975 Maritime well water survey (Dyck et al., 1976a).

In the field laboratory the samples were analyzed for U, Rn, F, dissolved O2, Eh, pH, alkalinity, and conductivity. U was determined by the fluorometric method without removal of U quenching components (Smith and Lynch, 1969). Rn was determined by degassing a 120-mL aliquot into a ZnS (silver activated) cell and measuring the alpha-particle emanation rate with a counter (Dyck, 1969). Alkalinity was determined by titrating a 25-mL aliquot to a pH of 4.65 with 0.01 H_2SO_4 (Thomas and Lynch, 1960). F, O_2 , Eh, and conductivity were measured ρH. electrochemically by specific ion or other electrodes.

CH, and He were determined by a mass spectrometer technique developed by Dyck et al. (1976b) in the Geochemistry Subdivision Laboratories, Geological Survey of Canada. In this method a 25 mL aliquot from a completely filled, tightly sealed, acidified sample in a glass bottle was admitted to an inlet system under high vacuum; the gases were extracted by boiling for a few minutes, dried by passage through dry ice-acetone traps, and admitted to the analyzer of the mass spectrometer. The observed ion currents were converted to partial pressures by comparison with standard samples in the case of CH₄ and atmospheric air in the case of He. The routine precision at 95% probability level varied from \pm 10% to \pm 30% depending upon levels of concentration.

Zn, Cu, Pb, Mn, Fe, Ni, Na, K, Ca, and Mg, were analyzed by atomic absorption spectroscopy using a Perkin Elmer 306 and an automated data acquisition facility devised by Bristow (1975). Aliquots were taken from the acidified samples in the glass bottles and analyzed directly for Zn, Mn, and Fe with deuterium background correction for Zn. Cu and Pb were extracted from an 80-mL sample using a mixture of 5-mL sodium acetate buffer (at a pH of 4.75), 2.5 mL 1% ammonium pyrrolidine dithiocarbamate and 6-mL methyl isobutyl ketone.

Chloride determinations were carried out colorimetrically by the thiocyanate method (Environment Canada, 1974).

The sulfate ion was determined spectrophotometrically using a modified 2-aminoperimidine method described by Jones and Stephen (1973).

Sampling and Analytical Controls and Errors

Each set of 20 samples comprised one distilled deionized (blank) water sample, one reference solution, one field duplicate, and 17 routine samples. Nominal concentrations of dissolved gases in these samples were calculated assuming 20°C water in equilibrium with atmospheric air at an altitude of 900 m (average estimated temperature and altitude at Eastend, where samples were prepared). For ionic species, standards were prepared by dissolving weighed amounts of salts in acidic solutions.

The analytical results of these control samples showed that sampling plus analytical errors of samples with concentrations well above the detection limits were small compared with data variability of unknown samples. The paired Student's t values from analytical results of 51 field duplicate pairs showed that none of the pairs were significantly different at the 97% probability level, and only Rn was found to be significantly different at the 95% level, with a probability of difference of 98%.

The random insertion of pure water and reference solutions into sample suites from hydrogeochemical surveys has proven to be valuable in determining the accuracy of the results and the practical detection limits of techniques, and has helped to reveal errors in laboratory and field procedures.

The analyses of replicate sample suites showed that, for samples with element contents well above the detection limits, maximum variation of concentrations in field duplicates and seasonal duplicates was about $\pm 30\%$ relative to the respective mean. A report describing in more detail the results of the precision and accuracy tests is in preparation (W. Dyck, report in preparation, 1985).

Results and Discussion

Factors Responsible for Variations in Element Content

Summary statistics of 23 well and spring water variables are given in Table 1. The skewness of the untransformed and log-transformed data indicates that most of the variables tend toward lognormal distributions. Although not shown here, the spring waters are generally somewhat lower in element content but higher in dissolved oxygen than well waters. When the data are grouped according to the type of drawing system, rock type, pressure system, type of tank, and type of pipe, certain trends, known from other groundwater surveys, are apparent. But in general, these criteria are not as effective in dividing the water into homogenous groups as one might anticipate. The regional nature of the data, the mixing of waters from different aquifers, and the effect evapotransport seems to have on trace element distributions, are probably responsible for the inhomogeneity in the grouped data. The higher O_2 content of springs compared with that of wells is explained by the fact that springs occur in the hills where waters are circulating more actively. The drop in the Rn content of waters from open wells or springs compared with waters from pressure systems is probably due to loss of Rn to the atmosphere. It seems odd, though, that He does not exhibit as pronounced a drop as Rn in these wells. In fact, the well water samples from hand-pumped systems contain essentially as much He as the well water samples from pressure systems. It is believed that a sampling problem is responsible for this apparent discrepancy. It was found that the hand-pump well samples are also much higher in dissolved ionic species, indicating that this particular set of samples came from wells that were tapping more mineralized aquifers. Such waters usually come from greater depth or have spent more time underground. The correlation between He and depth is strong and positive (r = 0.61), and between Rn and depth it is essentially random (r = -0.01). Similarly, the correlation between He and conductivity, and Rn and conductivity, is 0.32 and 0.03, respectively. Waters from the Cypress Hills Formation have the highest O_2 and Rn and the lowest He concentrations, indicating actively circulating In contrast, waters from the younger waters. older Bearpaw Formation have the lowest content of O_2 and the highest content of He and are characterized by generally higher concentrations of trace and major elements. The waters from the two formations of marine origin, namely, Bearpaw and Eastend, contain very high concentrations of Na, Cl, and SOL.

When the results are grouped by type of pressure system, type of tank, and type of pipe using only samples from the Bearpaw Formation, trends are evident, but they are weak and inconclusive. For example, lower O_2 , U, and Rn and higher He and conductivity are probably indicators of older, deeper waters rather than a precharged pressure system. The same reason probably also explains the variations of trace elements when the data are sorted by tank type-except for Zn; the higher Zn values in waters

from galvanized tanks may in fact be due to the Zn coating in these tanks. Similarly, systems with Fe pipes contain more Fe, and systems with Cu pipes contain more Cu in solution. But the increases are not so pronounced as to conclude that they are in fact due to variations in plumbing materials. Other causes, such as changes in rock formation, rainfall, different aquifers, and regional drainage patterns, appear to be the dominant causes of variations in the element patterns of the groundwaters in the area.

Regional Distribution of Elements

The regional distribution of all minor and most trace elements in well and spring waters is very similar to that of conductivity of the waters, shown in Figure 2. The distributions of CH4 and He are shown in Figures 3 and 4, respectively. These contour maps were produced by a computer mapping package (APPMAP) developed by D. J. Ellwood in the Resource Geochemistry Subdivision, Geological Survey of Canada. This package makes use of an Applicon plotter and Applicon library software residing on a CDC Cyber 730 computer at the Computer Science Centre of the Department of Energy Mines and Resources. APPMAP interpolates from the irregularly spaced reconnaissance data grid to a regular $1600-m^2$ data grid. The interpolation is in the form of a moving average where weighting is by an inverse distance function $(1/d^3)$ using the nearest five data points. The effect of this moving average is to filter out minor irregularities in the spatial data and emphasize the broader scale and regional features. For the element maps APPMAP erased the contours in areas greater than 4 km from the nearest sample site.

The most obvious regional feature of the conductivity map is the rise in conductivity in lower, drier areas of the survey. Topography and climate combine to effect an increase in concentration of the dissolved constituents in the groundwaters. Evidently, evapotransport and aquifers of different ages play a role in the enrichment of dissolved solids in the well waters of the region. However, there are notable exceptions to this general trend. Radon, for example, is higher in the waters over and near the Cypress Hills, an observation that confirms the radioactive nature of the Cypress Hills Formation and the radioactive lignites from the subjacent Ravenscrag Formation. Rn cannot survive the journey into the lowlands because of its relatively short half-life of 3.8 days. Radium, the immediate parent of Rn, with its 1600-year half-life, has time to survive the passage into the lowlands but is readily adsorbed on the soils near the source. Uranium, on the other hand, is stable and soluble in surface and near surface (i.e., oxidizing) waters and hence is found in greater concentration the farther the water moves from the hills.

The dissolved oxygen and Eh patterns are similar to that of Rn; the waters on and near the hills are richer in dissolved O_2 than the waters farther away. Younger, more actively circulating waters are responsible for this feature as well as for the generally lower pH in this region.

The He and CH₄ patterns (Figures 3 and 4) are similar to each other but differ from the

TABLE 1. Statistical Parameters

Variable	Unit	Samples	Samples Below Detection	Detection Limit	Minimum*	Median	Maximum
Depth	metres	759	• • •		1.	20.	500.
Rn	pCi/L	938	32	4	2.	285.	4135.
D.O.	pm mqq	938	0	0.2	0.4	2.9	14.0
Eh	mv	940	0	10	7.	397.	906.
s.c.	microm/cm	940	0	5	110.	1160.	15000.
рH	Hq	939	0	1	4.86	7.60	9.00
alka	ppm	940	0	1	8.	354.	1811.
ບໍ່	ppb	940	67	0.2	0.1	4.0	220.0
F	ppm	939	Ó	0.04	0.04	0.22	4.10
S04	ppm	940	69	10	5.	214.	10700.
He	nL/L	936	Ö	10	37.	108.	34000.
CH4	mL/Ļ	939	823	0.02	0.01	0.01	132.00
Zn	ppb	940	40	3	1.0	198.5	75721.1
Çu	ppb	940	52	1	0.5	7.1	1648.6
Pb	ppb	940	363	2	0.5	2.6	174.9
Ni	ppb	940	392	2	1.0	2.3	497.1
C1	ppm	940	20	0.2	0.1	10.1	1500.0
Mn	ppb	940	211	10	5.0	61.4	9637.9
Fe	ppb	940	22	20	10.0	379.	243815,
Na.	ppm	939	0	0.2	2.0	99.5	3426.6
ĸ	ppm	939	0	0.2	0.2	5.1	94.0
Ca	ppm	940	0	0.5	1.5	82.6	686.5
Mg	ppm	939	0	0.5	0.2	38.5	704.4

D.O., dissolved oxygen; S.C., specific conductivity; and alka, total alkalinity. *Minimum value entered is half the detection limit of the analytical method when element is below detection.



of Cypress Hills Well Water Variables

Arithmetic Mean	s.d.	Skew	Kurtosis	Geometric Mean	Log ₁₀ Mean	Log ₁₀ s.d.	Log Skew	Log Kurtosis
29.9	37.8	5.37	49.86	17.7	1.2482	0.4550	-0.02	-0.55
363.0	339.3	3,31	22.23	211.6	2.3255	0.6026	-1.79	3,39
3.89	2.72	1.09	0.38	3.07	0.4869	0.3015	0.09	-0.90
387.6	104.3	-0.54	2.95	364.8	2.5621	0.1866	-4.06	25.17
1451.	1195.	3.28	22.85	1114.	3.0471	0.3187	-0.06	-0.18
7.64	0.37	-0.44	6.11	7.63	0.8823	0.0218	-1.22	11.98
372.7	165.4	1.72	8.94	338.	2.5289	0.2029	-1.11	5.84
11.5	20.5	4.32	28.77	3.3	0.5197	0.7828	-0.29	-0.70
0.29	0.28	7.20	81.64	0.23	-0.6376	0.2708	0.45	1.05
551.	838.	4.02	29.13	193.	2.2864	0.7360	-0.51	-0.33
1026.	3216.	6.75	53.23	204.	2.3095	0.6770	1.08	0.18
0.82	7.00	13.12	199.74	0.02	-1.8077	0.6343	3.89	15.30
964.	3256.	14.63	304.05	196.	2.2926	0.8084	-0.14	0.05
26.7	83.3	12.20	196.53	8.5	0.9284	0.6199	0.29	0.06
4.9	11.6	8.27	86.93	2.6	0.4068	0.4153	0.97	1.39
5.0	23.9	15.24	264.85	2.3	0.3611	0.3857	1.48	4.47
41.7	93.7	7.22	82.72	10.7	1.0312	0.7674	-0.12	-0.17
334.	791.	5.99	51.44	64.	1.8065	0.8396	0.20	-1.03
2330.	11209.	15.96	295.60	486.	2.6863	0.7099	0.34	0.17
191.0	253.4	4.37	39.14	80.0	1.9032	0.6598	-0.39	-0.84
7.1	7.4	5.69	51.92	5.2	0.7149	0.3484	-0.35	1.37
114.1	110.2	2.04	4.60	73.4	1.8657	0.4499	-0.71	0.88
66.3	80.3	3.29	15.84	35.93	1.5555	0.5465	-0.88	1.48

108 109 50 15-METHANE ML/L %TILE .GULL LAKE 132.00 MAX 110 5.80 98 -50 50-95 0.46 0.04 90 0.01 MIN CREE 939 SAMPLES .EASTEND GEOLOGICAL SURVEY OF CANADA ALBERTA DECEMBER 1985 GOVENLOCK 20 30 ۵ 10 40 KILOMETRES SASKATCHEWAN **---**49 108 49 110 109 WYOMING

Fig. 3. Methane concentrations in well waters from the Cypress Hills region.



Fig. 4. Helium concentrations in well waters from the Cypress Hills region.

distribution patterns of trace elements. Anomalies for these gases coincide with depth of water wells to some extent as well as with the The frequency of drilled exploration holes. exploration drill hole density is considerably higher over the producing oil and gas fields than over nonproductive areas (Buller, 1972). Thus leakage from these holes into aquifers tapped by domestic wells could explain the anomalies. And deeper wells, being closer to the hydrocarbon pools, would be richer in these gases. Whether the presence of exploration drill holes can account completely for the observed He and CH4 anomalies is open to debate. However, it is reasonable to assume that nature provides natural vents for these gases in the form of faults and The north-south and east-west fracture zones. trends in the anomaly patterns of these gases do suggest major regional structural features. In fact, the major north trending gas anomalies run strikingly parallel to the Eastend Syncline of the Late Mesozoic, and the east-west trending anomalies in the northern half of the area coincide roughly with the Ponteix Syncline near of the survey the eastern border area (Kamen-Kaye, 1953). These gases appear to leak to the surface along permeable tectonic features, both from the basement and from oil and gas fields at depth along fault and fracture zones. The He and CH4 anomaly patterns also coincide with the rectilinear patterns of the Shaunavon Formation (Christopher, 1964). However, as shown

in Figure 1, the strong north-south trending pattern at about longitude 108°45' coincides with known oil fields (Simpson, 1982; Pearce, 1983). Similarly, the anomalous sites in the northwest corner of the survey area are close to the margin of the commercial gas fields north of Maple Creek. In the southwestern corner of the survey area, wells were scarce, resulting in gaps in the sample density pattern, but the anomalies south of Govenlock, near the U.S. border, are of the same magnitude as those in the commercial fields and hence could be of considerable interest for oil and gas exploration. The wells in this corner also contain high Na and bicarbonate concentrations. Soft waters are usually encountered at greater depth, and there is indeed a noticeable correlation between depth, Na, and bicarbonate over the whole region.

The trace elements Cu, Pb, Ni, Zn, Mn, and F, like U, show a positive correlation with the major elements, suggesting that evapotransport has an influence on these elements. However, sporadic point anomalies of these trace elements suggest local contamination. Occasionally, when taps were opened, pipes under pressure would rattle. This rattle could have dislodged fine particles of scale, rich in trace elements common in the waters of the area or in the materials of plumbing systems. Nickel, not a common metal in the waters or the plumbing systems, gives an unusually strong coherent north-east trending anomaly in the Gull Lake area and a smaller

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	
 Depth	-0.18493	0.66370	0.04151	0.00253	-0.14734	
Rn	-0.04764	-0.14631	0.36157	-0.33230	0.42146	
D.O.*	-0.25636	-0.53662	0.39435	0.11721	-0.27512	
Eh	-0.04624	-0.24541	0.42289	0.06498	-0.20958	
S.C.*	0.80259	0.40453	0.26496	0.01541	-0.06283	
рH	-0.45085	0.45629	0.23839	0.23442	-0.23209	
alka *	0.34027	0.64217	0.21416	0.05297	-0.10834	
U	0.55317	-0.41594	0.36143	0.24368	0.27832	
F	0.04598	0.30900	0.32043	0.38725	0.54373	
S04	0.81892	0.18824	0.16935	-0.20265	-0.18413	
He	-0.09814	0.84698	0.06658	0.02636	-0.01033	
CH4	-0.17336	0.39458	-0.16228	0.46206	0.45658	
Zn	0.33144	-0.18020	-0.28288	0.51504	0.25503	
Cu	0.12433	-0.46234	0.16424	0.44788	- 0.14543	
Pb	0.16057	-0.12570	-0.31627	0.63081	-0.27513	
Ni	0.44929	-0.21096	-0.27405	0.25548	0.33440	
Cl	0.64598	0.24264	0.34123	0.26623	0.03952	
Mn	0.56756	0.27093	-0.49483	-0.17258	0.17165	
Fe	0.27839	0.36891	-0.59657	-0.03646	-0.04429	
Na	0.48693	0.74247	0,28005	0.00040	-0.13259	
K	0.67261	0.09169	-0.07920	-0.14116	-0.21642	
Ca	0.77161	-0.50975	-0.04468	-0.13604	0.03921	
Mg	0.79500	-0.46323	0.02225	-0.14792	0.01386	
Eigenvalue	5.17275	4.38031	2.01895	1.74235	1.37691	
Percentage of variabil	22.5 ity	19.0	8.8	7.6	6.0	
Matnix uses principal factor no iterations estimated						

TABLE 2a. Factor Matrix of Cypress Hills Well Water Variables

Matrix uses principal factor, no iterations, estimated communalities = 1, log transformed data, 749 samples, and 10 factor model. *see table 1 for abbreviations

equally strong anomaly near the western border. One can speculate that the Gull Lake anomaly resulted from spills of Ni-bearing crude oil or waters associated with high-Ni crude. Hodgson (1954) reports higher than average Ni contents in some Canadian oils, particularly those from shallower depth and with lower API gravity.

Several of the anomalous F areas coincide with deep wells, others with Ni and/or Pb. The positive correlations of F with He, CH_4 , Na, and Cl also suggest a deep origin for much of the F in well waters.

Element Associations

The magnitude of the CH4 anomalies, up to 132 mL/L, should cause one to speculate as to its

source, namely, marsh gas or hydrocarbon deposits. There are geochemical indicators that help to resolve the marsh gas versus reservoir CH4 problem. As indicated in the introduction, C isotope analyses and higher C homologues are being used for this purpose. However, common trace and minor elements and He concentrations in groundwaters also help to differentiate between these two types of CH4 sources. In the Cypress Hills well water samples up to 30 variables were determined. Twenty-three of these are listed in Table 1. These can help directly, or indirectly, in solving the nature or source of CH4. A correlation matrix of this many variables is difficult to analyze, but a factor matrix is manageable (Table 2a). The principal component matrix was obtained from log-transformed data

TABLE 2b. Correlation Matrix of Most Significant Variables

	Depth	S.C.	Alka	Не	CH4	Na	Ca	
Correlation Coefficients								
Depth S.C. Alka He CH ₄ Na Ca	1 0.001 0.001 0.001 0.001 0.001 0.001	0.119 1 0.001 0.833 0.001 0.001	0.282 0.565 1 0.001 0.001 0.001 0.978	0.606 0.263 0.439 1 0.001 0.001 0.001	0.155 0.005 0.137 0.307 1 0.142 0.001	0.388 0.789 0.678 0.582 0.090 1 0.007	-0.454 0.412 -0.074 -0.495 -0.311 -0.062 1	

Data in lower left triangle are probabilities that correlation has arisen by chance

using a 10-factor model with principal factors without iteration or rotation. Factors one and two represent two types of water. Factor one characterizes shallow "hard" waters rich in Ca, Mg, K, SO4, and Cl. Factor two represents deep "soft" waters rich in NaHCO3 and Na₂CO3. Both He The positive and CH₄ favor factor two. correlation of He and CH4 with depth and with each other (Table 2b) is probably the most significant indicator of the source of CH4. We know that the main source of He is from basement rocks, because of their high U and Th content relative to the overlying sedimentary rocks in the area. This He dilutes quickly to atmospheric levels near the surface because of its great mobility. Methane generated near the surface will therefore not correlate with He, except in some circumstances when He from depth migrates up a fault that is covered by a CH4-generating peat However, such situations are easily bog. recognized by examining the topography. In the study area no bogs were encountered. The weaker correlation of CH4 and depth relative to He and depth leads one to the conclusion that the source of He is indeed basement rocks, and the source of CH4 the sedimentary rocks above.

Factor three represents an oxidizing environment with respect to U, Fe, and Mn and hence near-surface conditions. In factor four the association of CH4 with the heavy metals can be explained by assuming that some CH4 is associated with heavier hydrocarbons, which dissolved in the groundwater, have complexed the heavy metals. Factor five suggests that some CH4 is associated with U minerals such as fluoroapatite.

Conclusion

Regional surveys of domestic well waters can be of use in delineating areas with proven and potential economic oil and gas deposits at depth. Positive correlations of CH₄ with depth and with He, and characteristic associations with trace and minor elements, help to distinguish between reservoir CH₄ and marsh gas.

<u>Acknowledgments</u>. We would like to acknowledge the assistance of members of the Resource Geochemistry Subdivision of the Geological Survey of Canada in the preparation of this report. In particular, we would like to thank D.J. Ellwood for the preparation of the element maps and members of the laboratory staff, G. Gauthier, W.H. Nelson, and J.C. Pelchat, for the many analyses.

References

- Bristow, Q., A computer-controlled geochemical analysis system for use with existing Perkin Elmer double-beam atomic absorption spectrophotometers, <u>Geol. Explor. 4</u>, 371-383, 1975.
- Buller, J. V., The Saskatchewan Government computerized well information system, <u>Sask.</u> <u>Dep. of Miner. Resour.</u>, <u>Rep. 162</u>, 125 pp., Canada, 1972.
- Burwash, R. A., and G. L. Cumming, Helium sourcerock in southern Saskatchewan, <u>Bull. Can.</u> <u>Petrol. Geol. 22(4)</u>, 405-412, 1974.
- Burwash, R. A. and G. L. Cumming, Uranium and thorium in the Precambrian basement of western

Canada, 1, Abundance and distribution, <u>Can. J.</u> <u>Earth Sci., 13</u>, 284-293, 1976.

- Cameron, A. R. and T. F. Birmingham, Radioactivity in western Canadian coals, Geol. Surv. Can. Pap. 70-52, 35 pp., 1970.
 Christopher, J. E., The Middle Jurassic Shaunavon
- Christopher, J. E., The Middle Jurassic Shaunavon Formation of southwestern Saskatchewan, <u>Sask.</u> <u>Dep. of Miner. Resour., Rep. 95, 95 pp.,</u> Canada, 1964.
- Christopher, J. E., The Upper Jurassic Vanguard and Lower Cretaceous Mannville Groups of southwestern Saskatchewan, <u>Sask. Dep. of</u> <u>Miner. Resour.</u>, <u>Rep. 151</u>, <u>349 pp. Canada</u>, <u>1974</u>.
- Denson, N. M. and J. R. Gill, Uranium bearing lignite and carbonaceous shales in the southwestern part of the Williston Basin - A regional study, <u>U.S. Geol. Surv. Prof.</u> Pap. 463, 1965.
- Dyck, W., Field and laboratory methods used by the Geological Survey of Canada in geochemical surveys, No. 10 Radon determination apparatus for geochemical prospecting for uranium, <u>Geol.</u> <u>Surv. Can. Pap. 68-21</u>, 30 pp., 1969.
- Dyck, W., Uranium, radon, helium, and other trace elements and gases in well waters of parts of the St. Lawrence lowlands (Ottawa region), Canada, J. Geochem. Explor., 13, 27-39, 1980a.
- Dyck, W., Regional well water geochemical reconnaissance data, Cypress Hills, Saskatchewan, <u>Geol. Surv. Can. Open File</u> <u>Rep. 678</u>, 61 pp., 1980b.
- Dyck, W., A. K. Chatterjee, D. E. Gemmell, and K. Murricane, Well water trace element reconnaissance, eastern maritime Canada, J. Geochem. Explor., 6, 139-162, 1976a.
- Dyck, W., J. C. Pelchat, and G. A. Meilleur, Equipment and procedures for the collection and determination of dissolved gases in natural waters, <u>Geol. Surv. Can. Pap. 75-34</u>, 12 pp., 1976b.
- Environment Canada, <u>Analytical Methods Manual</u>, Inland Waters Directorate, Ottawa, 1974.
- Faber, E., and W. Stahl, Geochemical surface exploration for hydrocarbons in the North Sea, <u>Bull. Am. Assoc. Petrol. Geol., 68</u>, 363-386, 1984.
- Furniwal, G. M., Cypress Lake Map-area, Saskatchewan, <u>Geol. Surv. Can</u>. <u>Mem. 176</u>, 137 pp., 1946.
- Gallup, W. B. and G. J. Hamilton, The orogenic history of the Williston Basin, Saskatchewan, in <u>Billings Geological Society Guide-book</u>, Forth Annual Field Conference, edited by J. M. Parker, pp. 123-136, Billings, Montana, 1953.
- Gerhard, L. C., S. B. Anderson, J. A. Lefever, and C. G Carlson, Geological development, origin, and energy mineral resources of Williston Basin, North Dakota, <u>Am. Assoc.</u> <u>Petrol. Geol. Bull., 66</u>(8), 989-1020, 1982.
- Gold, T., Terrestrial sources of carbon and earthquake outgassing, <u>J. Petrol. Geol.</u>, 1(3), 3-19, 1979.
- Goth, M., Indication of methane movement from petroleum reservoir to surface, Lomingen oilfield NW-Germany, <u>J. Geochem. Explor., 23</u>, 81-97, 1985.
- Hickey, J. C., R. W. Klusman and K. J. Voorhees, Fault leakage characterization by integrative gas geochemistry/mass spectrometry/pattern

recognition procedures, (abstract), <u>Bull. Am.</u> <u>Assoc. Petrol. Geol., 67</u>, 1342, 1983. Hitchon, B., Geochemical studies of natural gas,

- Hitchon, B., Geochemical studies of natural gas, 3, Inert gases in western Canadian natural gas, J. Can. Petrol. Technol. 1(4), 165-174, 1963.
- Hodgson, G. W., Vanadium, nickel, and iron trace metals in crude oils of western Canada, <u>Bull.</u> <u>Am. Assoc. Petrol. Geol. 38</u>(12), 2537-2554, 1954.
- Jones, P. A. and W. I. Stephen, The indirect spectrophotometric determination of the sulphate ion with 2-aminoperimidine. <u>Anal.</u> <u>Chim. Acta, 64</u>, 85-92, 1973. Kamen-Kaye, M., The tectonic pattern of south-
- Kamen-Kaye, M., The tectonic pattern of southwestern Saskatchewan, Canada in Billings Geological Society Guidebook, Fourth Annual Field Conference, edited by Guidebook, J. M. Parker, pp. 118-122, Billings, Montana, 1953.
- Kent, D. M., The relationship between hydrocarbon accumulations and basement structural elements in the northern Williston Basin, in <u>Fuels: A</u> <u>geological Appraisal, Spec. Publ. 2</u>, pp. 63-79, Saskatchewan Geological Society, Regina, Canada, 1974.
- Kupsch, W. O., Geology of eastern Cypress Hills (Knollys and Dollar Quadrangles) Saskatchewan, <u>Sask. Dep. of Min. Resour.</u>, <u>Rep. 20</u>, 30 pp., Canada, 1956. Little, H. W. and V. Ruzicka, Uranium in Canada,
- Little, H. W. and V. Ruzicka, Uranium in Canada, Report of activities April to October 1969, Geol. Surv. Can. Pap. 70-1A, 97-101, 1970.
- Lorsong, J. A. and M. A. Wilson (eds.), <u>Oil and</u> <u>Gas in Saskatchewan, Spec. Publ. 7,</u> Saskatchewan Geological Society, Regina, Canada, 1984.
- Macdonald, R. and P. Broughton, Geological map of Saskatchewan, Provisional ed., <u>Sask. Dep. of</u> <u>Miner. Resour.</u>, Saskatchewan Geol. Surv. Regina, Canada, 1980.
- Pearce, R. O., Mineral development map of southern Saskatchewan, Sask. Energy and Mines, Regina, Canada, 1983.
- Philip, R. P. and P. T. Crisp, Surface geochemical methods used for oil and gas prospecting - A review, <u>J. Geochem. Explor.</u>, <u>17</u>, 1-34, 1982.
- Rice, D. D. and G. W. Shurr, Potential for major natural gas resources in shallow, lowpermeability reservoirs of Pre-Northern Great Plains, paper presented at the 1978 Williston Basin Symposium, (Abstract) <u>Montana Geol.</u> <u>Soc.</u>, Billings, Montana, 1978.

- Rice, D. D., and G. W. Shurr, Shallow lowpermeability reservoirs of Northern Great Plains: Assessment of their natural gas resources, <u>Bull. Am. Assoc. Petrol.</u> <u>Geol., 64</u>, 969-987, 1980.
 Russell, L. S., Preliminary report-The Geology of the southern part of the Cypress Hills,
- Russell, L. S., Preliminary report-The Geology of the southern part of the Cypress Hills, southwestern Saskatchewan, <u>Petrol. Geol. Ser.</u> <u>1</u>, 57 pp., Sask. Dep. of <u>Nat. Resourc. and</u> Ind., Canada, 1948.
- Rutherford, A., Water quality survey of Saskatchewan groundwaters, <u>Re. C-66-1</u>, 267 pp., Sask. Res. Counc., Canada, 1966.
- Saskatchewan Energy and Mines, <u>Saskatchewan</u> Energy and Mines Reservoir Annual, Regina, Canada, 1983.
- Sawatzky, H. B., R. G. Agarwal and W. Wilson, Helium prospects in southwestern Saskatchewan, <u>Rep. 49</u>, 26 pp., Sask. Dep. of Miner. Resour., Canada, No. 49, 1960.
- Simpson, F., Low-permeability gas reservoirs in marine Cretaceous sandstones of Saskatchewan: 15 notes on origin, mode of occurrence and probable location of undiscovered accumulations in Colorado and Montana groups (Middle Albian to Campanian) of southern Saskatchewan and adjacent areas. Summary of Investigations 1982, <u>Sask. Geol. Surv.</u>, <u>Misc.</u> <u>Rep. 82-4</u>, pp. 120-125, Canada, 1982.
- Smith, A. Y. and J. J. Lynd, Field and laboratory methods used by the Geological Survey of Canada in geochemical surveys, No. 11, Uranium in soil, stream sediment and water, <u>Geol.</u> Surv. Can. Pap. 69-40, 9 pp., 1969.
- Thomas, J. F. J. and J. J. Lynch, Determination of carbonate akalinity in natural waters, <u>Journal American Water Works Association, 52</u>, 259-268, 1960.
- Van Delinger, D. G., Genetic history of Basal Cretaceous oil in southern Saskatchewan, paper presented at the 1978 Williston Basin Symposium, (Abstract), <u>Montana Geol. Soc.</u>, Billings, Montana, 1978.
- Whitaker, S. H., Geology and groundwater resources of the Cypress area (72-F), Map 22, Sask. Res. Counc. Geol. Div., Canada, 1977.
- C. E. Dunn and W. Dyck, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario Canada K1A 0E8.

(Received July 15, 1985; revised October 31,1985; accepted November 1, 1985.)