

Hydrogeology and hydrochemistry of the Milk River aquifer system, Alberta, Canada: a review*

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Abstract—The Milk River aquifer system consists of 30–60 m of Cretaceous sandstone located within the Milk River Formation, southern Alberta, Canada. The Milk River Formation is confined below by >500 m of shale of the Colorado Group and above by up to 120 m of shale of the Pakowki Formation. The dominant recharge area for the aquifer is the Sweetgrass Hills, Montana, where the aquifer crops out. From the recharge area, the groundwater flows to the north, east and west. Calculated groundwater residence times at the north end of the aquifer (about 100 km north of the recharge area) range from 250 to 510 ka. Limited hydrological data from the confining shales suggest that cross-formational flow does not occur. Systematic patterns are observed in major ions (Na, Cl, $\text{HCO}_3 + \text{CO}_3$, and SO_4), stable isotopes (^{18}O and deuterium), and field pH on a regional scale. Several mechanisms have been proposed to explain the geochemical evolution of the groundwaters.

INTRODUCTION

THE FOCUS of the papers in this special issue is the Milk River aquifer system, southern Alberta, Canada. One reason that this aquifer system was selected for this coordinated study was because of the relatively large number of previous studies that provide a comprehensive picture of the hydrogeological setting and major elements of the aqueous geochemistry (Table 1). More importantly, however, are the strikingly systematic patterns observed in the major ion and stable isotopes on a regional scale.

The Milk River aquifer system in southern Alberta has been studied extensively over the past 10 years. Major published studies include those of SCHWARTZ and MUEHLENBACHS (1979), SCHWARTZ *et al.* (1981), DOMENICO and ROBBINS (1985), PHILLIPS *et al.* (1986), and HENDRY and SCHWARTZ (1988, 1990a).

The objective of this paper is to summarize the state of knowledge of the hydrogeology and hydrogeochemistry in the Milk River aquifer system, thus providing a consistent hydrogeological and geochemical basis upon which the isotopic data, presented in the other papers in this issue, can be discussed.

SITE DESCRIPTION AND GEOLOGY

The area that has been studied in most detail is approximately square and covers ~10,000 km² (Fig. 1). It extends 100 km north from the Canada–U.S.A. border. Over most of this region, the Milk River aquifer is a source of water for domestic and agricultural uses.

The regional land surface slopes from ~915 m above mean sea-level in the south to ~760 m in the north. The surface topography is gently rolling, and is cut by several deeply eroded river channels and glacial melt-water channels. The climate is semi-arid with an annual temperature at Foremost (Fig. 1) of 4.8°C, and an annual precipitation of 355.9 mm (CANADA DEPARTMENT OF ENVIRONMENT, 1982).

Near-surface bedrock is a thick succession of marine and non-marine Cretaceous sediments. The main units of interest in most studies have been, in ascending order, the Colorado Group, the Milk River Formation, and the Pakowki Formation (Fig. 2a). The Colorado Group consists mainly of dark grey to black bentonitic marine shales ranging in thickness from 500 to 650 m. The lower beds contain several thin sandstones, the most important of which is the Bow Island sandstone.

The overlying Milk River Formation varies in thickness from 90 to 145 m and crops out or subcrops in the southern part of the area (Figs 2a and 3). It is

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divided into two units. The lower, or Milk River sandstone, is a succession of massive marine sandstones interbedded with grey shales which conformably overlies the Colorado Group. This unit is informally referred to as the Milk River aquifer. The upper unit consists of a thick succession (20–60 m) of cross-bedded, non-marine sandstones, green shales, carbonaceous shales, thin coal seams, and thin sandstones. To the north, the abundance of sandstones in the Milk River Formation gradually diminishes. To the north of the study area, where the facies change is complete, the Milk River Formation is known as the Alderson Member of the Lea Park Formation (MEIJER DREES and MYHR, 1981).

The Pakowki Formation unconformably overlies the Milk River Formation (Fig. 2a), and consists of grey bentonitic shales with thin bentonite beds. The Pakowki Formation is 120 m thick in the north-eastern part of the study area and thins to the west. Near surface deposits consist of other fine-grained Cretaceous rocks and glacial drift (Fig. 2a).

The dominant structural feature in south-central

Alberta is the Sweetgrass Arch. Uplift at the time the arch formed caused the strata to dip gently toward the north (Fig. 2a). Subsequent erosion of the Upper Cretaceous and Tertiary deposits during the Pliocene and Pleistocene exposed concentric outcrops of Milk River sandstone around the Sweetgrass Hills (Fig. 1). These outcrops are the dominant recharge areas for the aquifer (MEYBOOM, 1960). HENDRY and SCHWARTZ (1988) estimate that erosion exposed the aquifer ~0.5 Ma ago.

According to WESTGATE (1968), five Laurentide glacial advances covered portions of the study area. Only the first two advances, however, covered the recharge area. Little is known about the dates of advance and retreat of these ice sheets. WESTGATE (1968) suggests that the first advance occurred ~50 ka B.P., and the second advance occurred at ~24–20 ka B.P. A sample of wood obtained from the till in the recharge area yielded a ^{14}C decay age of 35 ka B.P. (SWEENEY, 1988, personal communication). Subsequent advances have occurred between this date and around 12 ka B.P.

Table 1. Papers and reports on the hydrogeology and geochemistry of the Milk River aquifer

| | |
|-------------------------------------|--|
| MEYBOOM (1960) | Conducted pioneering work on hydrogeology and geochemistry of the Milk River sandstone |
| HITCHON and FREIDMAN (1969) | Interpreted trends in $\delta^{18}\text{O}$, δD and chemistry data from groundwaters from the western Canadian Sedimentary Basin (including Milk River aquifer) to be due to mixing of surface waters and diagenetically altered seawater |
| HITCHON <i>et al.</i> (1971) | Interpreted trends in the concentrations of 20 dissolved species from the western Canadian sedimentary basin to be due to dilution of connate water. Concentration of ion species was attributed to membrane filtration |
| BORNEUF (1976) | Detailed groundwater hydrology and general geochemistry of the Milk River aquifer in the eastern half of the present study area |
| SCHWARTZ and MUEHLENBACHS (1979) | Interpreted $\delta^{18}\text{O}$, δD and geochemistry of the Milk River aquifer. Postulated several mechanisms for the observed trends |
| SCHWARTZ <i>et al.</i> (1981) | Interpreted $\delta^{18}\text{O}$, δD and geochemistry of groundwaters from six major sandstones in the western Canadian Sedimentary Basin (including Milk River aquifer). Trends were attributed to flushing of connate water by infiltrating meteoric water |
| SWANICK (1982) | Calculated ^{14}C age dates for groundwaters from the Milk River aquifer and interpreted them based on ^{36}Cl and flow modelling |
| DOMENICO and ROBBINS (1985) | Interpreted published trends in Cl data for the aquifer as being the result of displacement of connate waters in the aquifer by recharge water |
| PHILLIPS <i>et al.</i> (1986) | Interpreted Cl and ^{36}Cl trends in the Milk River aquifer water as being the result of ion filtration |
| FABRYKA-MARTIN <i>et al.</i> (1987) | Interpreted I and ^{129}I data from the Milk River aquifer to be from a subsurface source, not ion filtration |
| HENDRY and SCHWARTZ (1988) | Interpreted trends in Cl, I, δD , $\delta^{18}\text{O}$ and ^{36}Cl as being caused by aquitard–aquifer diffusion |
| ROBERTSON (1989) | Interpreted geochemistry δD and $\delta^{18}\text{O}$ to suggest older, possibly pre-glacial water in the recharge area of the Milk River aquifer is being displaced by younger post-glacial recharge water |
| USUNOFF and GUZMAN-GUZMAN (1989) | Used factor and correspondence analyses on existing geochemical data from the Milk River aquifer to categorize waters into three hydrochemical patterns |
| MURPHY <i>et al.</i> (1989) | Interpreted ^{14}C measurements on fractions of dissolved organic C to provide information on the ages of groundwater in the Milk River aquifer |
| HENDRY and SCHWARTZ (1990a) | Interpreted major ion data and dissolved gases in groundwaters from the Milk River aquifer on the basis of aquifer–aquitard diffusion and geological changes in the recharge area |

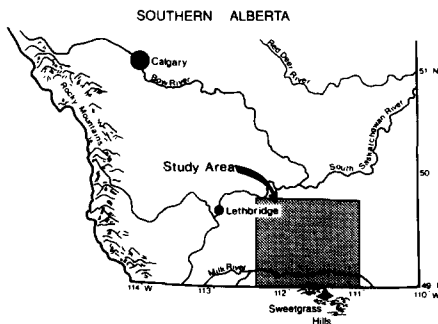
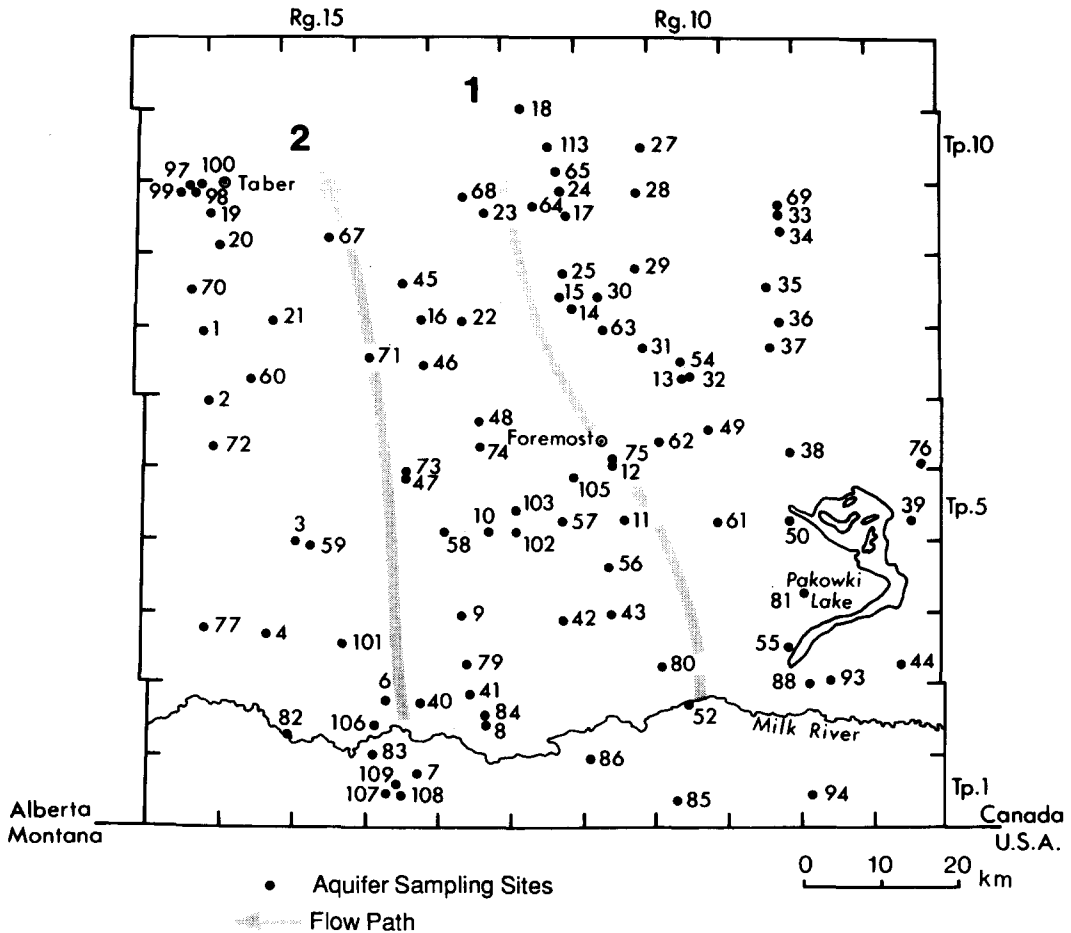


FIG. 1. Study area.

HYDROGEOLOGY

Development of groundwater supplies from the aquifer first began in the early 1900s. Nearly all of these early wells flowed upon completion. However, by the 1960s, long-term withdrawals of groundwater eventually lowered the piezometric surface and reversed gradients in the areas of heaviest use. The modern-day potentiometric surface of the Milk River aquifer is presented in Fig. 4. Many of the data used to prepare Fig. 4 were collected by MEYBOOM (1960). Water levels from the southwestern portion of the study area were collected by the authors in the 1980s.

Accounting for anomalies in the piezometric surface caused by pumping, the best estimate is that groundwater flow generally follows the dip of the aquifer (Fig. 3) toward the north, west and east.

The transmissivity map for the aquifer (Fig. 5) shows that transmissivities decrease from the south toward the north, east and west as a result of aquifer thinning and a decrease in hydraulic conductivity. The transmissivity distribution is strongly influenced by sedimentological trends (MEYBOOM, 1960).

The vertical hydraulic conductivity of the Colorado Group shales was estimated to range from 10^{-10} to 10^{-14} m/s (HENDRY and SCHWARTZ, 1988). Simi-

larities in lithologies and the presence of extensive areas of flowing wells (or once flowing wells) indicate that the vertical hydraulic conductivity of the overlying Pakowki Formation shales is also low. HENDRY and SCHWARTZ (1988) suggested that the vertical hydraulic conductivity of the Pakowki shales is similar to that of the Colorado Group shale. Estimates based on groundwater model studies suggest that the vertical hydraulic conductivity for the Pakowki Formation is about 10^{-13} m/s (PHILLIPS *et al.*, 1986).

Cross-formational flow from the Milk River aquifer to the underlying Bow Island sandstone and the overlying surficial deposits (Fig. 2b) has been proposed (SCHWARTZ *et al.*, 1981; DOMENICO and

ROBBINS, 1985). These flow conditions were interpreted from hydraulic heads measured in the Milk River aquifer, Bow Island sandstone, and in the shallow Cretaceous bedrock and glacial deposits. More recent data collected by TOTH and CORBET (1986) and HENDRY and SCHWARTZ (1988) point to a more complex pattern of flow than is presented in Fig. 2b. Limited hydraulic-head measurements from piezometers completed in the Colorado Group and drillstem test data suggest that the Colorado Group acts as a fluid sink for water from the Bow Island sandstone and the Milk River aquifer. The Colorado Group shale may be behaving as a fluid sink because of elastic rebound following the rapid erosion of

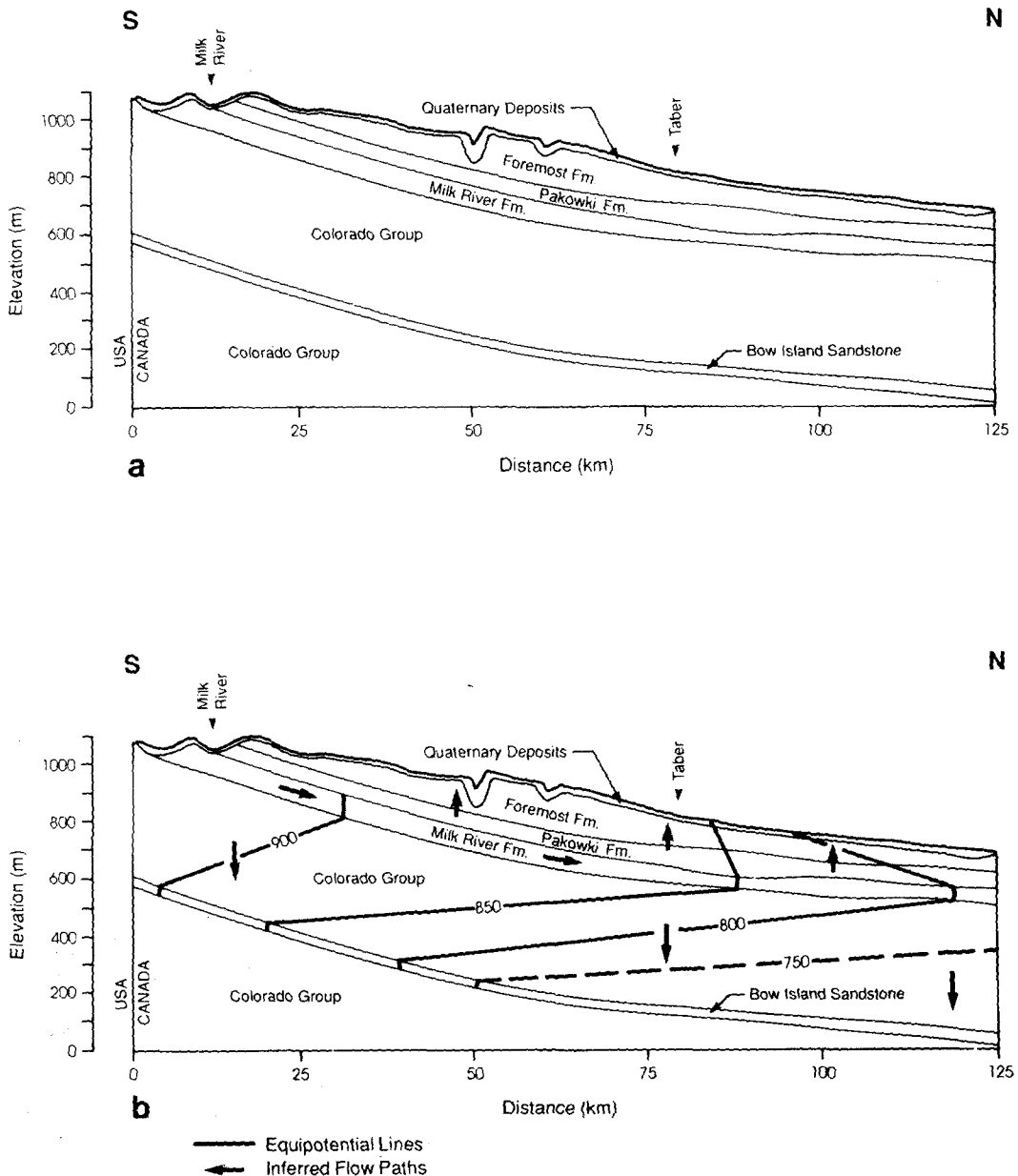


FIG. 2. Geology and conceptual model of groundwater flow in cross-section: (a) geology; and (b) cross-formational flow.

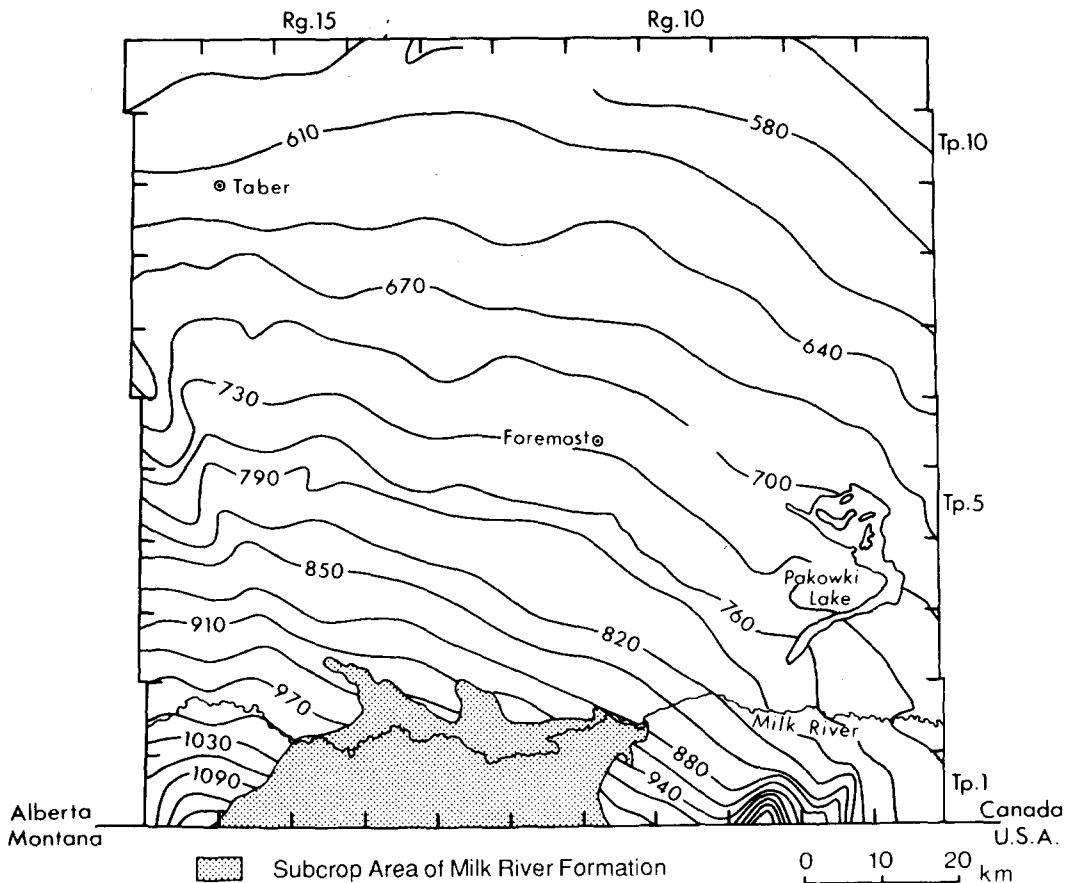


FIG. 3. Elevation of the top of the Milk River Formation (m above sea-level).

>700 m of Tertiary and Upper Cretaceous rocks during Pliocene and Pleistocene times (TOTH and CORBET, 1986). If this is the case, the hydraulic heads in the Colorado shale are still likely to be readjusting to present-day conditions as a consequence of the very low vertical hydraulic conductivity. Elastic rebound was also suggested by HENDRY and BUCKLAND (1990) to explain anomalously low hydraulic heads measured in the Pakowki Formation shale. If the low hydraulic head measurements within the confining shales are typical, then both the Colorado Group and the Pakowki Formation shales may have been acting as fluid sinks for several million years. These observations provide further evidence that the hydraulic conductivities of the shales are very low.

In the southwestern part of the study area, the Milk River is incised into the aquifer (Figs 2 and 3) and intercepts groundwater flowing in the aquifer from farther south (ROBERTSON, 1989). Estimates based on erosional levels indicate that the Milk River has existed in this form since the Pleistocene (COLLIER and THOM, 1918; ALDEN, 1932).

The residence time for groundwater in the aquifer has been estimated by SCHWARTZ and MUEHLENBACHS (1979), PHILLIPS *et al.* (1986) and HENDRY and SCHWARTZ (1988). All three calculated ages are in close agreement. SCHWARTZ and MUEHLENBACHS

(1979) estimated the age as 300 ka based on hydraulic arguments. PHILLIPS *et al.* (1986) used a flow model (BRINKMAN, 1982) to calculate residence times of 500 ka for flow to the northern margin of the aquifer. HENDRY and SCHWARTZ (1988) estimated the age of groundwater at the ends of flow paths 1 and 2 (Fig. 1) to be 250 and 510 ka, respectively. Indications are that the residence time in the southern half of the aquifer is much shorter than in the northern half due to the northward decrease in hydraulic conductivity.

GEOCHEMISTRY

Description of chemical patterns

One of the unique features of the Milk River aquifer is the consistency in the distribution of major ions and environmental isotopes ^{18}O and D. Here, our interest is with the major ions, particularly Ca, Mg, Na, K, Cl, SO_4 , HCO_3 and CO_3 . The discussion in this review is based mainly on analyses from 36 wells reported by HENDRY and SCHWARTZ (1990a), 25 wells reported by SCHWARTZ and MUEHLENBACHS (1979) and 30 from SWANICK (1982). Specific analytical techniques are described by the authors. The sample locations are shown in Fig. 1 and chemical

analyses in Table 2. In most cases, chemical data for water samples yielded ion balances of <7%. Analyses from sites 5 and 7, however, did not fall within this range and were included in the data base. Samples from these sites, however, were sampled for most isotopes discussed in subsequent papers.

The concentration distribution of the most abundant species Cl, Na and $\text{HCO}_3 + \text{CO}_3$ is generally the same (Fig. 6). Concentrations are lowest in the recharge area and increase progressively along the flow system. Chloride concentrations range from <0.05 mmol/l at the southern boundary of the study area to >30 mmol/l at the northwestern margin of the aquifer. Concentrations of Na increase from ~15 mmol/l in the south to >50 mmol/l in the northwest. Concentrations of $\text{HCO}_3 + \text{CO}_3$, which are dominated by HCO_3 , range from <12 mmol/l to >25 mmol/l along the flow system (Fig. 6).

Although the concentrations of these species vary systematically, their patterns are complex. For example, the distribution of Cl, $\text{HCO}_3 + \text{CO}_3$ and Na is marked by a large north-trending bulge of groundwater with low concentrations. This bulge coincides with a zone of higher transmissivity (Fig. 5).

The patterns of variation of Ca and Mg are similar. Concentrations of both ions are typically

<0.1 mmol/l. However, at the northeastern margin of the aquifer, concentrations are >0.1 mmol/l.

In contrast to the species just discussed, the distribution of SO_4 is very different. Sulfate concentrations decrease from >5 mmol/l in the south to <0.1 mmol/l throughout the remainder of the aquifer (Fig. 6).

In the region where the aquifer subcrops (Fig. 3), the patterns in ion distribution differ somewhat from those just discussed. In particular, SO_4 , Na, Ca and Mg concentrations are much higher than expected from trends farther north in the Milk River aquifer (Fig. 6). HENDRY and SCHWARTZ (1990a) attribute these anomalously high concentrations to relatively recent recharge (possibly <40 ka B.P.) through the overlying glacial tills.

With the exception of the zone where the aquifer subcrops, field pH decreases from >9.0 in the south to 8.2 in the north (Fig. 7). Values of pH in the subcrop area are <8.5.

Geochemical processes

The interpretation of the origin of patterns in "nonreactive" ions (and the stable isotopes of O and H) in the Milk River aquifer has been problematical.

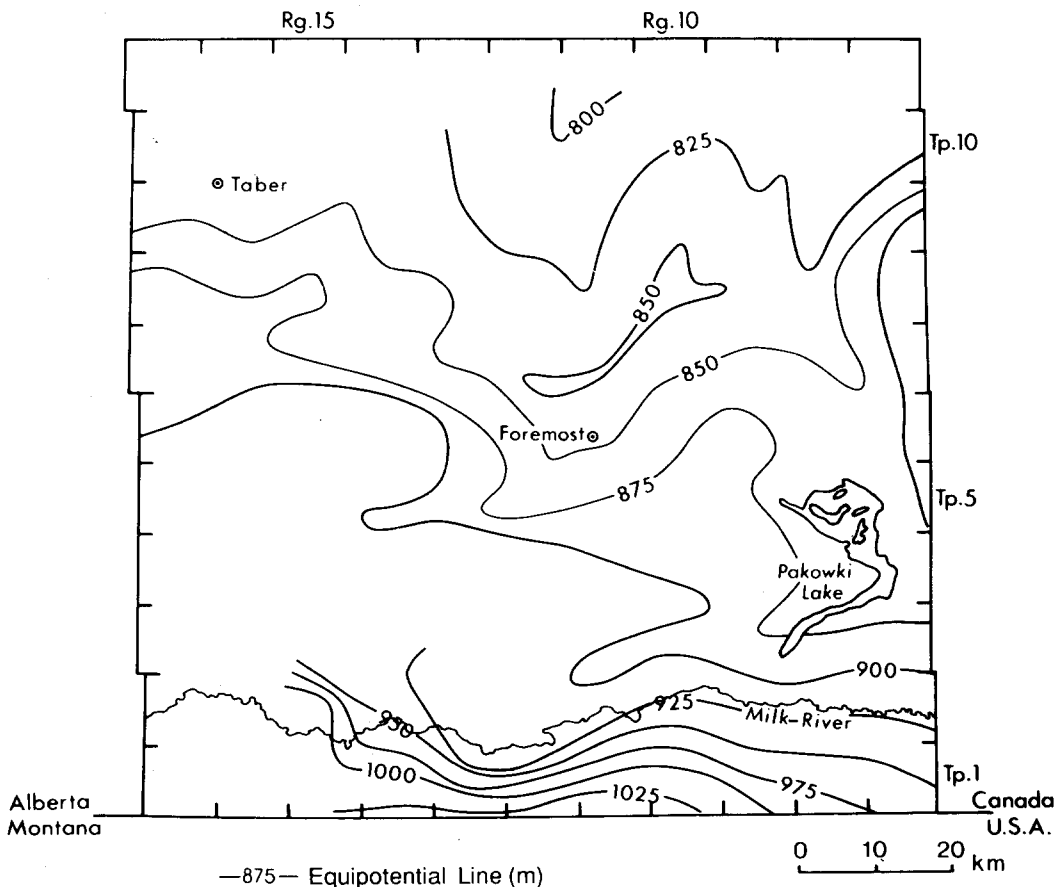


FIG. 4. Present-day piezometric surface in the aquifer (from HENDRY and SCHWARTZ, 1988).

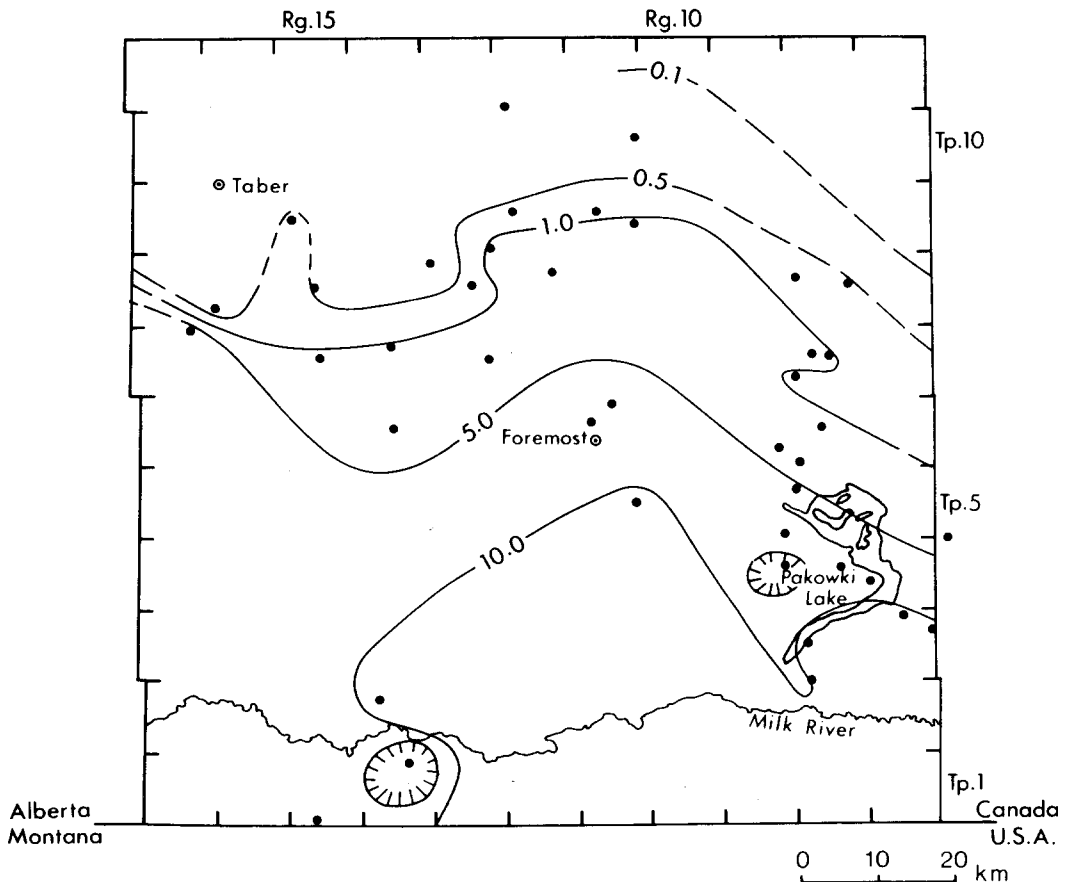


FIG. 5. Transmissivity ($\text{m}^2/\text{s} \times 10^{-5}$) of the Milk River aquifer.

Four mechanisms have been advanced to explain the progressive increase in Cl with distance from the recharge area (Fig. 8). These mechanisms are megascopic dispersion (SCHWARTZ and MUEHLENBACHS, 1979; SCHWARTZ *et al.*, 1981), mixing related to a recharge area of limited extent (DOMENICO and ROBINS, 1985), membrane filtration (PHILLIPS *et al.*, 1986, 1990), and diffusion from the confining Colorado Group shales into the aquifer (HENDRY and SCHWARTZ, 1988, 1990b). The megascopic dispersion model explained the Cl pattern as advectively controlled mixing whereby groundwater entered the aquifer from below, adding water with high Cl concentrations. Mixing between recharging groundwater, with low Cl concentrations, and the deeper groundwater with high Cl concentrations, produced observed Cl concentrations in the aquifer. The limited recharge model proposed that the recharging groundwaters with low Cl concentrations enter the aquifer at the Sweetgrass Hills and mix with more saline groundwater in a more extensive north-flowing system. The diffusion model proposed that the Cl pattern in the aquifer is the result of a diffusion gradient between saline water in the aquitard (Colorado Group shale) and fresher water in the aquifer. Unlike the other hypotheses, which attribute the trends in Cl to mixing, the membrane filtration model

proposed that Cl accumulates because the Colorado Group and Pakowki Formation shales act as semi-permeable membranes. As the water leaks out of the aquifer, the residual solution becomes enriched in Cl.

The classical interpretation of increasing Na concentration along a flow path in an aquifer of regional extent is by cation exchange whereby Na, which was initially on exchange sites in clays in the aquifer, exchanges with Ca and Mg in solution. This mechanism has been advanced by SCHWARTZ and MUEHLENBACHS (1979) and PHILLIPS *et al.* (1986) to explain the increasing concentration in Na along the Milk River aquifer. However, indications are that the Na concentration may be controlled mainly by the same mixing processes that affect the non-reactive species and environmental isotopes. As evidence, HENDRY and SCHWARTZ (1990a) showed that the addition of equimolar amounts of Na and Cl to groundwater from the southern part of the aquifer models the observed distribution of Na and Cl along the aquifer.

The computer code PHREEQE (PARKHURST *et al.*, 1980) has been used to determine theoretical saturation states of calcite, dolomite, gypsum and pCO_2 for the water samples. The mean log saturation indices were calculated to be 0.0 and 0.1 for calcite and dolomite (HENDRY and SCHWARTZ, 1990a). These data indicate that the groundwaters in the

Table 2. Standard water analyses from sampling sites in the Milk River aquifer

| Well number | Field pH | Ca | Mg | Na | HCO ₃ + CO ₃ | Cl | SO ₄ |
|-------------|----------|-------|-------|-------|------------------------------------|-------|-----------------|
| 1* | — | 0.10 | 0.13 | 56.00 | 15.0 | 38.80 | 0.10 |
| 2* | 8.4 | 0.25 | 0.05 | 40.53 | 26.3 | 16.41 | <0.01 |
| 3* | 9.0 | 0.05 | 0.03 | 29.58 | 23.4 | 7.11 | 0.03 |
| 4* | 8.1 | 0.19 | 0.15 | 44.40 | 14.2 | 19.32 | 0.04 |
| 6* | — | 0.15 | 0.15 | 18.00 | 9.9 | 1.50 | 3.35 |
| 8* | 8.4 | 0.15 | 0.10 | 45.72 | 12.9 | 1.55 | 14.28 |
| 9* | 8.6 | 0.10 | 0.05 | 32.38 | 17.4 | 3.96 | 5.37 |
| 10* | 8.3 | 0.15 | 0.10 | 35.39 | 17.5 | 18.16 | 0.34 |
| 11* | 9.0 | 0.02 | 0.01 | 16.97 | 14.6 | 1.30 | <0.01 |
| 12* | 9.1 | 0.02 | 0.01 | 18.31 | 15.1 | 1.33 | <0.01 |
| 13* | 8.8 | <0.05 | <0.05 | 18.73 | 16.2 | 2.12 | 0.02 |
| 14* | 8.6 | 0.04 | 0.01 | 19.40 | 16.8 | 1.42 | <0.01 |
| 15* | 8.8 | 0.03 | 0.02 | 20.71 | 17.6 | 1.83 | <0.01 |
| 16* | 8.5 | <0.05 | <0.05 | 36.30 | 24.8 | 12.50 | 0.03 |
| 17* | 8.8 | 0.04 | 0.02 | 22.92 | 18.6 | 3.84 | <0.01 |
| 18* | 8.3 | 0.09 | 0.07 | 44.44 | 23.1 | 22.98 | <0.01 |
| 19† | 8.3 | 0.06 | 0.05 | 43.50 | 25.0 | 17.69 | 0.02 |
| 20† | 8.5 | 0.05 | 0.05 | 39.59 | 25.9 | 13.96 | 0.02 |
| 21† | 8.2 | 0.08 | 0.06 | 41.76 | 24.6 | 17.21 | 0.07 |
| 22† | — | 0.08 | 0.10 | 36.98 | 25.9 | 11.34 | 0.06 |
| 23† | — | 0.03 | 0.02 | 23.93 | 20.3 | 3.84 | 0.04 |
| 24† | 8.8 | 0.03 | 0.02 | 22.62 | 17.3 | 3.67 | 0.04 |
| 25† | 8.8 | 0.02 | 0.01 | 19.14 | 16.1 | 2.06 | 0.04 |
| 27* | 8.4 | 0.16 | 0.13 | 56.55 | 20.6 | 37.52 | 0.02 |
| 28† | 8.4 | 0.05 | 0.04 | 31.76 | 19.5 | 10.04 | 0.02 |
| 29† | 8.5 | 0.03 | 0.02 | 20.01 | 17.1 | 3.10 | 0.06 |
| 30† | 8.7 | 0.03 | 0.02 | 19.14 | 15.1 | 2.60 | 0.07 |
| 31† | 8.8 | 0.02 | 0.02 | 19.14 | 16.2 | 2.31 | 0.04 |
| 32† | 8.8 | 0.02 | 0.02 | 19.14 | 14.4 | 2.26 | 0.02 |
| 33† | 8.2 | 0.18 | 0.14 | 47.85 | 16.8 | 30.83 | 0.13 |
| 34† | — | 0.14 | 0.12 | 47.85 | 18.7 | 29.71 | 0.02 |
| 35† | 8.4 | 0.07 | 0.06 | 31.76 | 18.8 | 12.24 | 0.02 |
| 36† | 8.3 | 0.09 | 0.07 | 38.28 | 17.2 | 19.72 | 0.02 |
| 37† | — | 0.06 | 0.05 | 33.93 | 21.4 | 12.78 | 0.02 |
| 38† | 8.7 | 0.04 | 0.02 | 19.14 | 15.3 | 2.31 | 0.05 |
| 39† | 8.7 | 0.04 | 0.02 | 19.14 | 15.5 | 2.51 | 0.02 |
| 40† | 8.4 | 0.20 | 0.35 | 34.80 | 15.9 | 2.96 | 9.27 |
| 41† | 8.4 | 0.16 | 0.13 | 60.90 | 15.0 | 1.69 | 21.86 |
| 42† | 8.9 | 0.04 | 0.03 | 22.19 | 13.8 | 8.32 | 0.10 |
| 43† | 9.0 | 0.02 | 0.01 | 16.53 | 12.9 | 1.02 | 0.85 |
| 44† | 9.3 | 0.02 | 0.02 | 17.40 | 15.2 | 2.20 | 0.05 |
| 45† | 8.3 | 0.08 | 0.06 | 42.63 | 23.1 | 17.72 | 0.03 |
| 46† | 8.5 | 0.08 | 0.09 | 30.02 | 21.1 | 8.24 | 0.13 |
| 47† | 8.7 | 0.03 | 0.02 | 25.23 | 19.9 | 3.22 | 0.08 |
| 48† | — | 0.04 | 0.03 | 28.71 | 22.4 | 6.40 | 0.05 |
| 49† | 8.9 | 0.04 | 0.02 | 18.71 | 14.9 | 3.10 | 0.04 |
| 50* | 8.4 | 0.08 | 0.06 | 27.84 | 16.2 | 7.08 | 1.46 |
| 52* | 8.6 | 0.04 | 0.02 | 20.40 | 12.6 | 0.26 | 3.44 |
| 54† | 8.8 | 0.03 | 0.02 | 19.58 | 15.1 | 3.19 | 0.04 |
| 56‡ | — | 0.05 | 0.04 | 39.19 | 15.5 | 23.70 | 0.03 |
| 57‡ | 8.5 | <0.01 | <0.01 | 20.23 | 16.4 | 2.88 | 0.03 |
| 58‡ | — | 0.02 | 0.02 | 29.23 | 19.4 | 3.53 | 2.88 |
| 59‡ | — | 0.03 | 0.02 | 30.06 | 20.8 | 8.04 | 0.03 |
| 60‡ | — | 0.02 | 0.03 | 37.37 | 25.8 | 10.29 | 0.02 |
| 61‡ | — | <0.01 | 0.01 | 18.40 | 12.6 | 1.13 | 1.63 |
| 62‡ | — | 0.02 | 0.02 | 22.88 | 13.5 | 8.46 | 0.02 |
| 63‡ | — | <0.01 | <0.01 | 19.58 | 16.4 | 2.23 | 0.02 |
| 64‡ | — | <0.01 | <0.01 | 21.27 | 17.2 | 3.30 | 0.02 |
| 65‡ | — | 0.01 | 0.01 | 25.53 | 20.0 | 4.01 | 0.02 |
| 67‡ | — | 0.04 | 0.07 | 48.11 | 23.5 | 24.97 | 0.03 |
| 68‡ | — | <0.01 | 0.02 | 25.49 | 19.8 | 4.46 | <0.01 |
| 69* | 8.3 | 0.06 | 0.11 | 46.81 | 18.9 | 32.16 | <0.01 |
| 70‡ | — | 0.03 | 0.05 | 43.24 | 23.7 | 22.57 | 0.02 |
| 71‡ | — | 0.02 | 0.04 | 34.89 | 23.6 | 11.29 | <0.01 |
| 72‡ | — | 0.05 | 0.33 | 41.33 | 22.9 | 18.76 | 0.68 |

Table 2.—Continued

| Well number | Field pH | Ca | Mg | Na | HCO ₃ + CO ₃ | Cl | SO ₄ |
|-------------|----------|-------|-------|-------|------------------------------------|-------|-----------------|
| 73‡ | — | <0.01 | 0.02 | 24.71 | 20.3 | 3.19 | 0.67 |
| 74‡ | — | <0.01 | 0.02 | 25.49 | 20.5 | 5.87 | <0.01 |
| 75‡ | — | <0.01 | <0.01 | 16.62 | 14.8 | 1.83 | 0.01 |
| 76‡ | — | <0.01 | 0.02 | 20.66 | 17.3 | 2.62 | <0.01 |
| 77‡ | — | 0.03 | 0.07 | 20.18 | 18.5 | 0.90 | 0.75 |
| 79‡ | — | 0.04 | 0.04 | 31.93 | 14.8 | 3.19 | 7.30 |
| 80* | 8.7 | 0.03 | 0.01 | 19.53 | 11.9 | 0.39 | 2.87 |
| 81‡ | — | <0.01 | <0.01 | 15.83 | 13.6 | 1.47 | 0.28 |
| 82‡ | — | 0.03 | 0.03 | 21.14 | 13.7 | 0.51 | 3.64 |
| 83‡ | — | 0.14 | 0.41 | 38.11 | 35.3 | 0.85 | 1.87 |
| 84‡ | — | 0.04 | 0.04 | 35.50 | 14.4 | 3.10 | 8.54 |
| 85* | 8.8 | 0.02 | 0.01 | 16.10 | 10.6 | 0.16 | 2.25 |
| 86* | — | 0.02 | 0.07 | 25.93 | 14.1 | 9.25 | 1.25 |
| 88* | 9.5 | 0.03 | 0.05 | 33.10 | 10.7 | 3.10 | 5.50 |
| 93* | 9.2 | <0.05 | <0.05 | 16.00 | 10.7 | 0.40 | 1.70 |
| 94* | 9.1 | 0.02 | 0.01 | 15.20 | 12.9 | 0.40 | 0.55 |
| 97* | 8.6 | <0.05 | <0.05 | 43.90 | 25.1 | 16.40 | 0.25 |
| 98* | 8.6 | <0.05 | <0.05 | 47.40 | 24.8 | 21.90 | 0.25 |
| 99* | 8.5 | <0.05 | <0.05 | 44.80 | 25.2 | 20.90 | 0.25 |
| 100* | 8.5 | <0.05 | <0.05 | 47.80 | 25.5 | 15.40 | 3.40 |
| 101* | — | 0.10 | 0.40 | 22.80 | 13.7 | 2.10 | 4.10 |
| 102* | 8.9 | <0.05 | <0.05 | 19.00 | 14.0 | 2.00 | 1.60 |
| 103* | 9.0 | <0.05 | <0.05 | 19.70 | 14.3 | 2.30 | 1.25 |
| 105* | 8.7 | <0.05 | <0.05 | 17.90 | 13.0 | 2.60 | 0.85 |
| 106* | — | 0.63 | 0.53 | 20.90 | 13.2 | 1.28 | 3.90 |
| 113* | 8.3 | 0.15 | 0.12 | 35.71 | 21.7 | 13.88 | 0.02 |

* From HENDRY and SCHWARTZ (1990a).

† From SWANICK (1982).

‡ From SCHWARTZ and MUEHLENBACHS (1979).

Concentrations are in mmol/l; pH is in pH units.

Potassium ranged from 0.01 to 0.56 mmol/l ($\bar{x} = 0.07$, $s = 0.07$, $n = 114$).

aquifer are at or near equilibrium with respect to calcite and dolomite. MEYBOOM (1960) and LONGSTAFFE (1984) identified both of these minerals as dominant carbonate minerals in the Milk River Formation. The similarity in concentrations between Ca and Mg may be attributed to congruent dissolution of dolomite in the aquifer.

Calculated log pCO₂ values are plotted on Fig. 7. The trend in calculated pCO₂, as one would expect, is similar to that of HCO₃ + CO₃ (Fig. 6) and pH (Fig. 7). As HCO₃ + CO₃ increases so does pH decrease and log pCO₂ increase. Calculated log pCO₂ values range from near-atmospheric (−3.2 to −3.9) in the southeastern part of the study area (near the recharge area) to −2.1 at the north margin of the aquifer.

One possible way of explaining the decrease in SO₄ and increase in HCO₃ + CO₃ and pCO₂ is by SO₄ reduction coupled with carbonate mineral equilibrium. This process was proposed by SCHWARTZ and MUEHLENBACHS (1979) and PHILLIPS *et al.* (1986). This explanation, however, is contradicted by, among other things, the lack of measurable sulfide in gaseous or ionic form (HENDRY and SCHWARTZ, 1990a). HENDRY and SCHWARTZ (1990a) concluded that, although minor SO₄ reduction may be occurring

in the aquifer, the dominant control on the distribution of SO₄ is a geological one. They attribute the presence of SO₄ near the recharge area to relatively recent recharge water (<40 ka B.P.), which is moving through glacial tills rich in SO₄ (HENDRY *et al.*, 1986) before entering the aquifer.

The trend in increasing pCO₂ (and decreasing pH) can be explained by a source of CO₂ in the aquifer. A viable process for the generation of CO₂ is methane fermentation (during decomposition of organic C) represented by 2CH₂O = CH₄ + CO₂. In addition to accounting for the increase in CO₂, this mechanism produces methane gas, the concentration of which is observed to increase down dip in the aquifer. Mass transfer calculations (HENDRY and SCHWARTZ, 1990a) can be used to support this explanation.

From the available geochemical data, it cannot be discerned whether the increasing concentrations in CH₄ and CO₂ with increasing residence time in the aquifer are the result of the decomposition of organic C in the aquifer or in the confining shales. In the latter, the gases would then have to diffuse from the shales in a similar manner to that proposed to explain the concentrations of Cl (and Na) in the aquifer by HENDRY and SCHWARTZ (1988).

SUMMARY AND CONCLUSIONS

The Milk River aquifer is confined above and below by shales of the Pakowki Formation and Colorado Group, respectively. Groundwater flow in the aquifer is in the downdip direction. Overall, it is

estimated that ~500 ka is required for water to move along the aquifer from south to north. Most groundwater recharges in the Sweetgrass Hills immediately south of the study area. Water-level data from the confining shales, flow modeling and hydraulic conductivity measurements suggest that some leakage

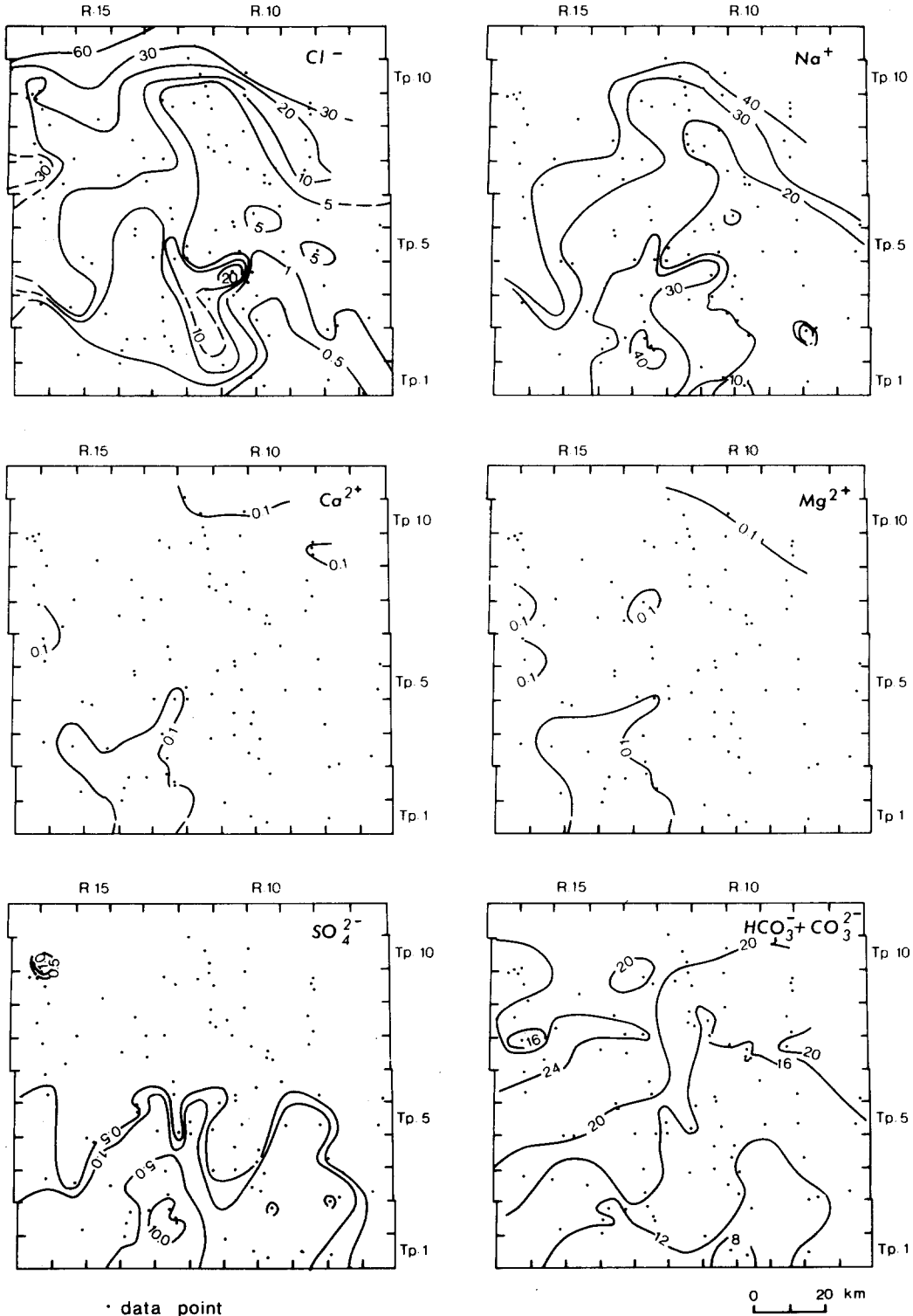


Fig. 6. Spatial variations in dissolved ions (after HENDRY and SCHWARTZ, 1990a).

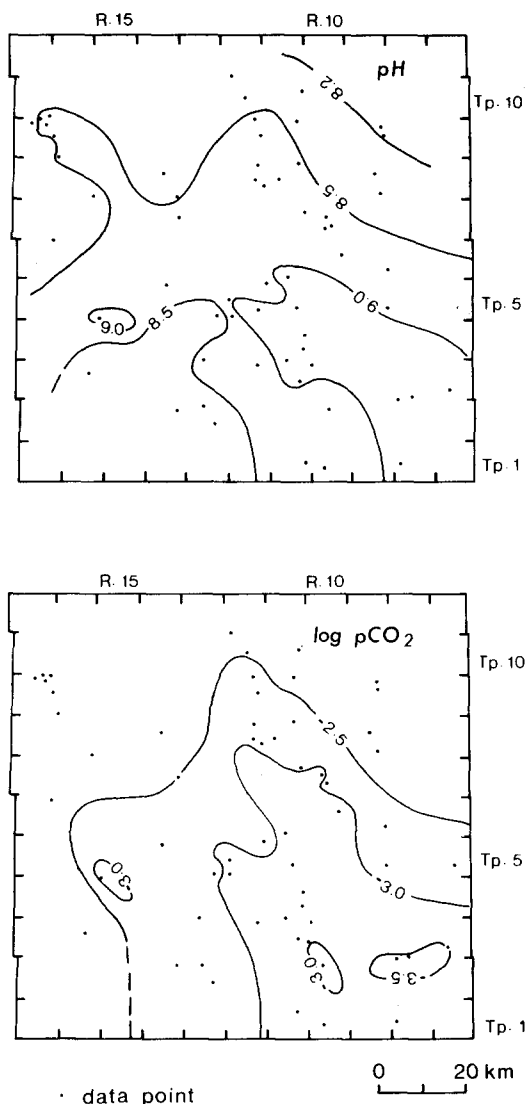


FIG. 7. Spatial variations in field pH, and calculated pCO_2 (after HENDRY and SCHWARTZ, 1990a).

from the aquifer is moving into shales that are under-pressured.

All dissolved ions in the aquifer exhibit well-defined patterns of variability. Concentrations of dissolved Na, Cl, $HCO_3 + CO_3$ and pH increase as a function of travel distance along the flow system while SO_4 and pH decrease. Concentrations of Ca and Mg are typically low.

Although the geochemical trends in the aquifer system are well defined, several mechanisms have been proposed to explain the geochemical evolution of the groundwater. In general, the interpretations of the evolution in the major ion chemistry in the groundwater are based predominantly on mixing. Trends in pH (and calculated pCO_2) and CH_4 can be attributed to the decomposition of organic C. Calcite and dolomite saturation constrain the carbonate system. Anomalously high concentrations of SO_4 , Na,

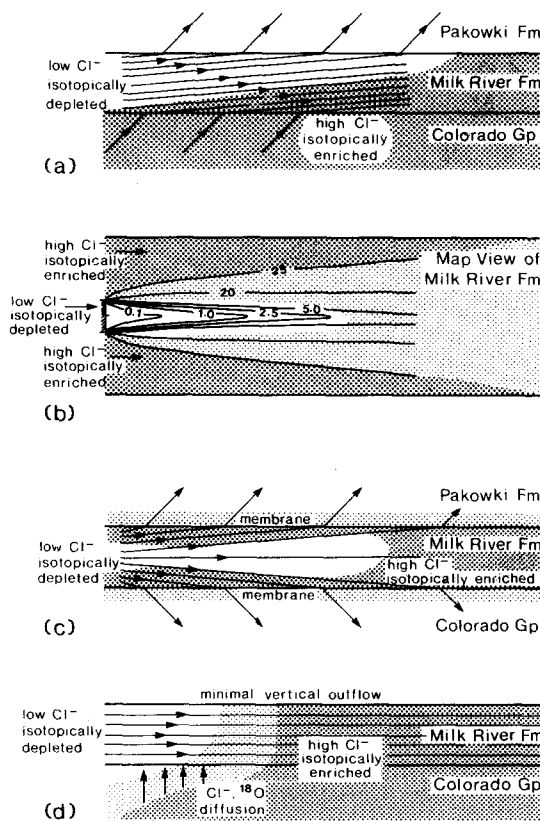


FIG. 8. Conceptual models to explain the origin of Cl pattern in the Milk River aquifer: (a) megascopic dispersion; (b) limited recharge area; (c) membrane filtration; and, (d) aquitard diffusion (after HENDRY and SCHWARTZ, 1988).

Mg and Ca in the southern part of the study area can be attributed to recharge of groundwater through the glacial till, which was deposited approximately 40 ka ago. Although the presence of SO_4 near the recharge area and lack of SO_4 in downdip waters can be explained by geological changes, SO_4 reduction cannot be ruled out as occurring in the aquifer.

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