

Rural groundwater quality surveys: southern and central Manitoba.

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ABSTRACT

Regional groundwater sampling in two major bedrock aquifers in Manitoba has revealed a variety of groundwater geochemical types which show distinct spatial variations in the carbonate rock aquifer and water quality changes with depth in the Odanah Shale aquifer. Groundwater quality in the carbonate rock aquifer is generally excellent, although hard, throughout most of the sampled area. Salinity increases near Lake Manitoba and south of the lake as a regional fresh water-saline water boundary is approached. Poor quality groundwaters are found near the Red River and the Town of Arborg. Groundwater quality is poor within many parts of the Odanah Shale aquifer. Total dissolved solids concentrations exceeded 1000 mg/L many of the samples. Sodium, sulphate and chloride are frequently greater than drinking water guidelines.

Minor and trace parameters, other than iron and manganese, are rarely found at concentrations which exceed drinking water guidelines in either aquifer. Iron and manganese frequently exceed aesthetic based guidelines, particularly in the Odanah Shale aquifer where almost 80% of samples had excessive manganese concentrations.

Nitrate + nitrite is found at concentrations above one mg/L in about 25% of samples in the carbonate rock aquifer and in more than 70% of samples from the Odanah Shale aquifer. Parts of the carbonate rock aquifer overlain by less than 15 metres of tills and clays are particularly susceptible to nitrate contamination. Naturally occurring nitrogen species may account for a considerable amount of the nitrogen found in samples from the Odanah Shale aquifer.

INTRODUCTION

As part of activities carried out under the Canada-Manitoba Agreement on Agricultural Sustainability (CMAAS), funding was made available to a number of organizations to undertake surveys of rural groundwater quality in parts of agro-Manitoba. Two of these surveys will be reported on here: one carried out in the southern and central parts of the Interlake region during 1994, with supplementary sampling in 1996, and a second survey conducted during 1995 in a part of south central Manitoba (Figure 1).

These surveys focussed on the groundwater quality in parts of two major bedrock aquifers found in the province: the carbonate rock aquifer which underlies the Interlake region and the Odanah Shale aquifer which occurs beneath parts of southcentral Manitoba and extends into the west central region of the province. These aquifers were chosen since they form important, and in many parts of the areas, the only, local sources of water supply. Portions of the aquifers within the study areas are also considered sensitive to contamination from near-surface sources.

In each of the two study areas, the region to be sampled was divided into approximately equal sectors based on the number of samples which could be collected and analyzed with the available funding. Private water wells were then selected for sampling within each sector from GWDRILL, the provincial data base of water well logs. Sampling sites were chosen from wells which were completed into either the carbonate rock aquifer or the Odanah Shale aquifer. Selected sampling points included both recently drilled (post 1985) and older (pre 1985) wells; however the selection process was otherwise essentially random within each sector. One hundred and nineteen wells were sampled in the Interlake study area during the fall of 1994, approximately one sample per township (36 square miles), and 98 wells were sampled in the southcentral study area during the fall of 1995, approximately two wells per township. Follow-up sampling in the Interlake was undertaken by the South Interlake Land Management Association and the Water Resources Branch during 1996. This sampling was specifically aimed at examining the distribution of nitrogen species in groundwater in an area of about 1000 km² which was considered particularly susceptible to contamination. Pesticide sampling was also carried out in this area as part of the Water Resources Branch supplementary work.

Each sample was analyzed for a rather complete set of inorganic parameters, bacteria, and some isotopes (Table 1). Analytes were chosen to include a basic set of groundwater quality parameters and additional parameters to satisfy the interests of the various groups involved in each of the two studies. These interests included drinking water quality, impacts from agricultural operations, evaluation of groundwater flow systems and especially the locations of recharge areas, and the presence of dissolved species which could indicate potential ore bodies. Water samples from selected wells were also analyzed for a suite of

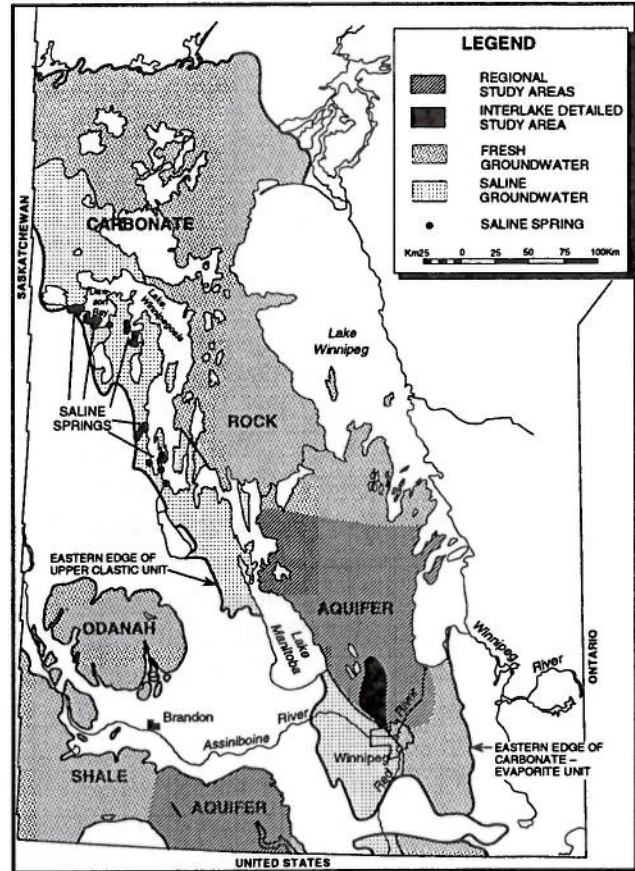


Figure 1. Extent of carbonate rock and Odanah Shale aquifers and locations of study areas within these aquifers.

pesticides although, due to time constraints, the results will not be fully discussed in this paper. Wells for pesticide analysis were selected from regions where the aquifer was thought to be most sensitive to pesticide contamination. These were considered to be regions where the overburden was thin, where annual crops have been grown for a number of years in fields in the vicinity of the selected wells and where nitrate and tritium were found in sampled wells. No pesticide residues were detected in the Interlake sampling and only trace concentrations were found in 5 of 20 wells in the Odanah Shale study.

Table 1. Analyses Carried Out on Groundwater Samples

MAJOR IONS AND GENERAL CHEMISTRY	NUTRIENTS	BACTERIA	MINOR AND TRACE CONSTITUENTS	ISOTOPES
calcium	nitrate + nitrite	total coliform	copper	tritium
magnesium	nitrite*	fecal coliform	lead	oxygen-18
sodium	ammonium	iron bacteria	zinc	deuterium*
potassium	total phosphorus		nickel	nitrogen-15*
alkalinity	dissolved organic		chromium	
chloride	carbon		silver	
sulphate			cadmium	
pH			aluminum	
hardness			iron	
conductivity			manganese	
dissolved oxygen			arsenic	
TDS			barium	
temperature			selenium	
			uranium	
			boron	
			silica	
			fluoride	
			bromine	
			strontium	
			molybdenum	
			antimony*	
			beryllium*	
			bismuth*	
			cyanide*	

* Odanah Shale aquifer study only

** Carbonate Rock aquifer study only

Water samples were collected from outside or inside taps after discussion with the homeowner to ensure that sampling of untreated water would take place. The tap was allowed to run for approximately five minutes or until the water temperature had stabilized. Samples were analyzed for fluid conductivity, pH, temperature and dissolved oxygen in the field during the Interlake sampling and for fluid conductivity, pH and temperature in the Odanah Shale aquifer study. Samples for cation analysis were field filtered through 0.45 micron membrane filters and acidified on arrival at the lab. Samples were stored in ice filled

coolers following collection and generally delivered to the lab within 24 hours. Samples for isotope analysis were stored at room temperature in tightly sealed polypropylene bottles until shipment to the Environmental Isotope Laboratory at the University of Waterloo for analysis. Finally, a form was filled out showing land use in the vicinity of the sampling point, the surface construction of the well, potential sources of contamination in the vicinity, and uses of fertilizers and pesticides on adjacent fields.

INTERLAKE STUDY AREA

The Interlake region is underlain by the carbonate rock aquifer, a sequence of limestones and dolomites of Ordovician through Devonian age. This aquifer varies in thickness from less than 10 metres along the northeastern tip of Hecla Island to more than 300 metres along the eastern shores of lakes Winnipeg and Winnipegosis (McCabe, 1971). The aquifer is overlain by a variable thickness of unconsolidated sediments consisting principally of silt to clay tills. The tills are in turn overlain by lacustrine clays deposited in glacial Lake Agassiz throughout much of the southern and eastern parts of the study area. In general, overburden thickness is greatest in the southeastern part of the study area, where thicknesses greater than 40 metres may be found, and least in the central and western parts of the area where bedrock outcrop is common.

Groundwater flow in the aquifer occurs through a network of subhorizontal bedding planes interconnected by a system of subvertical joints (for brevity, all secondary permeability features will be referred to as fractures). A long history of dissolution has resulted in the development of preferential flow pathways within this fracture network as selected discontinuities have been widened, in places into very large features such as sinkholes, caves and tunnels. Pleistocene glaciation has also produced a highly fractured upper bedrock surface in many areas. Groundwater movement is best thought of as occurring through a complex 3-dimensional dendritic network with occasional very large and permeable dissolution features acting as collectors and conduits of large volumes of groundwater.

The primary recharge area for the aquifer lies in the central part of the Interlake. Recharge has produced a large groundwater mound in this area with flow occurring outward towards lakes Winnipegosis and Manitoba on the west and Lake Winnipeg on the east. Groundwaters are fresh (<2000 mg/L total dissolved solids) in most of the region but become saline near the eastern shores of lakes Winnipegosis and Manitoba and north of the Assiniboine River. The saline groundwaters are part of a continental flow system with its origins in the upland areas of Montana and the Dakotas (Downey, 1984).

It is estimated that there are currently more than 20,000 wells producing groundwater from this aquifer. Wells are constructed as open holes in the bedrock portion of the aquifer with casing set at the top of the bedrock surface or, in areas of thin overburden, to some depth within the aquifer. Most domestic wells will yield from 0.5 to 5.0 L/s while municipal, industrial and irrigation wells may have yields as high as 120 L/s. The aquifer also forms an important thermal energy reservoir for groundwater heating and cooling systems, particularly in the City of Winnipeg.

RESULTS

General Groundwater Quality

Groundwaters show a number of fairly distinct geochemical types within the study area, with well defined spatial trends. Calcium-magnesium-bicarbonate type groundwaters with total dissolved solids (TDS) concentrations of 350-550 mg/L dominate the central part of the area, stretching from the outskirts of Winnipeg northward to encompass most of the area between lakes Winnipeg and Manitoba (Figure 2). Calcium and magnesium concentrations typically vary from 40-80 mg/L in this area producing a fairly hard water; hardness varies from about 350 to 550 mg/L-CaCO₃. Sulphate concentrations are generally less than 100 mg/L. Chloride is typically found at less than 10 mg/L while sodium concentrations generally are less than 20 mg/L. The low chloride concentrations indicate that much of the recharge that occurs in the central uplands part of the Interlake enters the aquifer in a near-direct manner, likely in areas of very thin overburden cover.

The very fresh groundwater zone found in the central part of the Interlake is bordered on the southwest and southeast by zones of significantly more saline groundwaters (Figure 2).

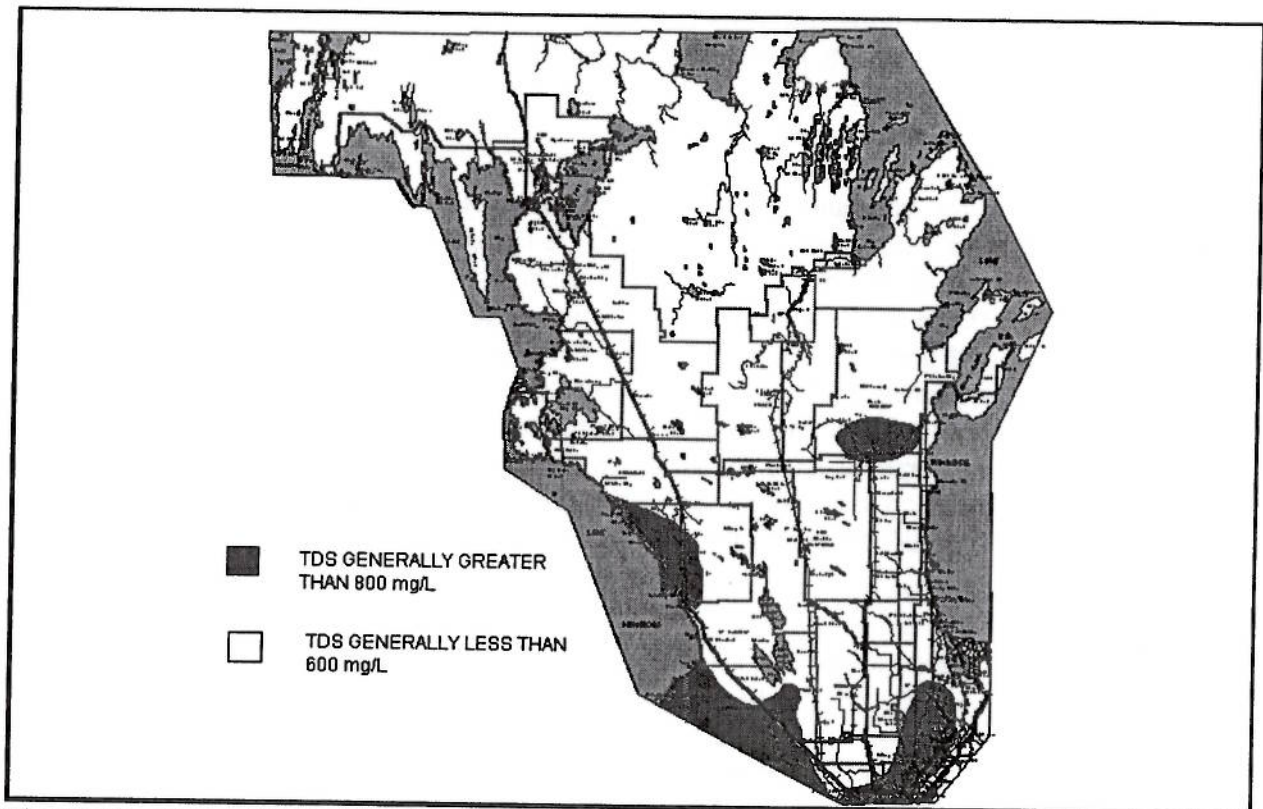


Figure 2. Generalized groundwater chemistry of the carbonate rock aquifer in the Interlake study area.

Sodium-chloride-sulphate type groundwaters with TDS concentrations exceeding 3000 mg/L develop south of the Shoal Lakes and stretch westward to the edge of the study area. A similar water quality change occurs near the eastern shore of the south basin of Lake Manitoba. This marks the transition to sodium-chloride type saline groundwaters and brines that occupy the western extent of the carbonate rock aquifer. In the southeast, groundwaters become geochemically complex to the west of the Red River where TDS concentrations approach 2000 mg/L. These groundwaters contain up to 450 mg/L chloride, several hundred milligrams per litre sodium and locally exceed the 500 mg/L drinking water guideline for sulphate. (All references to drinking water guidelines refer to the 1995 "Guidelines for Water Quality in Canada 1995" published by Health Canada). The origin of these poor quality groundwaters is not well understood. They may be influenced by an upward flux of poor quality water from the underlying Winnipeg Formation aquifer. Water quality improves rapidly east of the River.

An second area of anomalously poor quality groundwater is found in the vicinity of Arborg. Calcium-magnesium-sulphate-bicarbonate type groundwaters with total dissolved solids concentrations near 1000 mg/L occupy an area of about 150 km² near the town. Although sodium and chloride are somewhat elevated in this zone, they do not rise to the very high concentrations found west of the Red River. Again, the source of this poor quality groundwater is not well understood but it is speculated that gypsum may have been incorporated into the local tills during glaciation or may be present in the bedrock aquifer.

Minor and Trace Constituents

The results for trace and minor constituent analyses are summarized in Table 2. Chromium, cadmium, silver and molybdenum were not detected in any of the 119 samples. Nickel and lead were detected in 2 and 3 of the samples respectively. The maximum lead concentration of 0.013 mg/L was found in a sample where a sampling error had occurred and a softened water had been collected. This anomalous lead concentration likely results from dissolution of lead-bearing solder in the plumbing system of the home by the more corrosive softened groundwaters. Excluding this sample, the maximum lead concentration was 0.002 mg/L. Selenium and arsenic were found above detectable levels in 24 and 35 of the samples respectively; however, concentrations were again very low. Aluminum was detected in 16 samples, with the highest concentration of 0.064 mg/L.

Table 2. Analytical Results for Minor and Trace Constituents - Interlake Study Area

PARAMETER	DETECTION LIMIT (mg/L)	DETECTION S (119 SAMPLES)	MAXIMUM VALUE (mg/L)	DRINKING WATER GUIDELINE (mg/L)	NUMBER EXCEEDING GUIDELINE
COPPER	0.01	39	0.16	1.0	0
LEAD	0.002	3	0.013	0.01	1
ZINC	0.01	119	1.36	5.0	0
ARSENIC	0.001	35	0.007	0.025	0
ALUMINUM	0.01	16	0.064		
SELENIUM	0.001	24	0.004	0.01	0
NICKEL	0.005	2	0.006		
CHROMIUM	0.002	0	ND	0.05	0
CADMIUM	0.001	0	ND	0.005	0
SILVER	0.001	0	ND		
MOLYBDENUM	0.005	0	ND		
BARIUM	0.05	55	0.09	1.0	0
URANIUM	0.0002	99	0.033	0.1	0
IRON	0.01	117	3.23	0.3	28
MANGANESE	0.005	88	0.41	0.05	20
BORON	0.05	110	1.74	5.0	0
SILICA	0.2	119	19.8		
FLUORIDE	0.1	119	3.6	1.3	3

Copper and zinc were detected in a higher percentage of samples; zinc was found at or above the detection level (0.01 mg/L) in all but two samples while copper was detected in 39 samples. Anthropogenic sources for these two metals from plumbing systems or well casings are possible. However, both metals have been detected in samples from test wells where there has been no opportunity for contact with plumbing systems and were found in this study at comparable concentrations in samples from wells with PVC casing and wells having steel casings. While anthropogenic sources cannot be ruled out, it does appear that copper and zinc are found naturally in many groundwaters in the carbonate rock aquifer. The major sources are likely sulphide minerals found locally in the aquifer skeleton.

Iron and manganese were found at detectable levels in most samples. Iron exceeded the drinking water guideline of 0.3 mg/L in 28 of the samples while manganese was over the

guideline value in 20 samples. There are abundant natural sources of iron and manganese in the bedrock and glacial deposits as well as from iron casings installed in many of the wells. Both these metals become increasingly soluble under reducing conditions (Hem, 1985).

Uranium was found at trace concentrations in most samples, and exceeded 30 ug/L at two locations. Both locations were in areas of relatively thin overburden with the tills overlain by lacustrine clays. Uranium concentrations are known to be very high in the pore waters of Lake Agassiz clays (Betcher et al., 1988) and it is suspected that the elevated uranium concentrations in these samples result from local recharge of the carbonate rock aquifer with soil waters having undergone geochemical development in the clays.

Fluoride was found above the detection limit in all samples but exceeded the drinking water guideline in only three cases. Fluoride concentrations were generally less than 0.5 mg/L in the very fresh central part of the study area but increased to more than 1.0 mg/L in the softer increasingly sodium-chloride dominated groundwaters found in the southwestern part of the area and along the east shore of Lake Manitoba. The lower calcium concentrations in these groundwaters may allow an increased solubility of fluoride. Three samples had fluoride concentrations greater than the drinking water guideline of 1.5 mg/L with the highest concentration being 3.6 mg/L.

Bacteria

Coliform bacteria were found in 10 of the samples with seven of the 10 also showing the presence of fecal coliforms. The maximum coliform count was 56 CFU/100 ml while the maximum fecal count was 36 CFU/100 ml. Samples containing detectible coliform bacteria were collected from wells having from seven to 42 metres of casing indicating that coliform entry into the aquifer is probably associated with well construction or maintenance. Potential pathways include casing annuli which have not been grouted with cement or bentonite, poor well maintenance or location such that runoff water is directed toward the well, flooding of well pits where the top of the casing in the pit has not been properly sealed, development of corrosion holes in metal casings or failure of pitless adapters. In some cases, unsealed or improperly sealed abandoned wells may also form a pathway for bacterial entry into the aquifer.

Iron bacteria were detected microscopically in 25 of the samples. There appears to be little relationship between the presence of iron bacteria and coliform contamination although wells which did not have coliform contamination during this sampling event could certainly have had previous episodes of contamination. Iron bacteria may be present naturally in parts

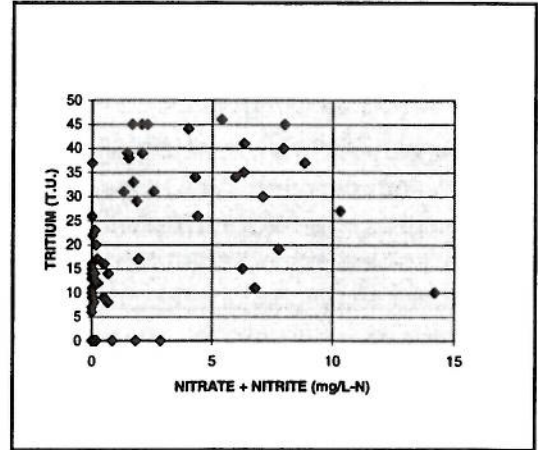


Figure 3. Relationship between nitrate and tritium - Interlake study area. Note that the tritium detection limit is 6 T.U.

of the aquifer, may have been introduced during construction of the well or installation of the pump or may have been introduced with surface water infiltration.

Nutrients

Samples were analyzed for nitrate + nitrite (refer to as nitrate for simplicity), ammonium and total phosphorus. Nitrate (as N) was detected in slightly more than half of the samples, was greater than one mg/L in 29, and equal to or above the drinking water guideline value of 10 mg/L in only two samples. These results are similar to findings from other rural well water surveys carried out in parts of the Interlake since the early 1980's.

Nitrate was found in both tritiated (post-1953) and non-tritiated (pre-1953) groundwaters (Figure 3) with the samples containing the highest tritium concentrations having a high percentage of elevated nitrate concentrations. Nitrate concentrations greater than 1.0 mg/L and detectable tritium were both found primarily in groundwaters from sampling sites where the overburden thickness was less than 15 metres (Figures 4 and 5). The tritium results indicate downward groundwater velocities through the overburden (generally tills in these thin overburden areas) in the order of a few tens of cm/yr, which is in good agreement with detailed soil tritium profiles carried out by the author at a number of sites in the Interlake. Elevated nitrate concentrations in groundwaters in these areas indicate that stable nitrate transport through significant thicknesses of till is occurring on time scales of a few decades.

As a follow-up to these results, in 1996 the South Interlake Land Management Association and the Water Resources Branch undertook more detailed sampling for nitrate in

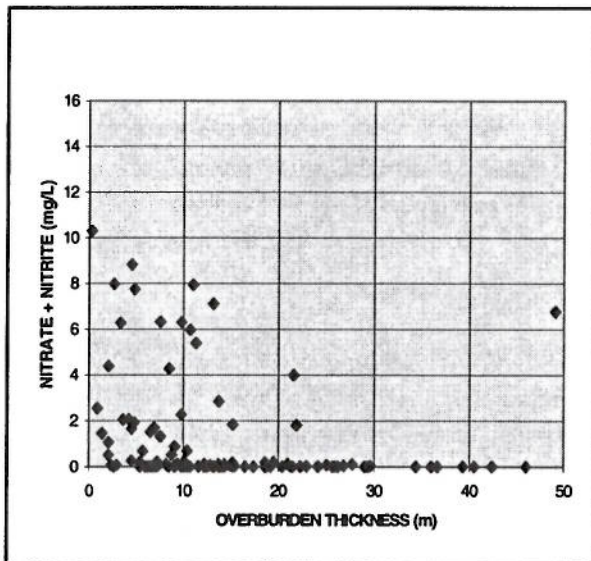


Figure 4. Relationship between nitrate in groundwater and overburden thickness.

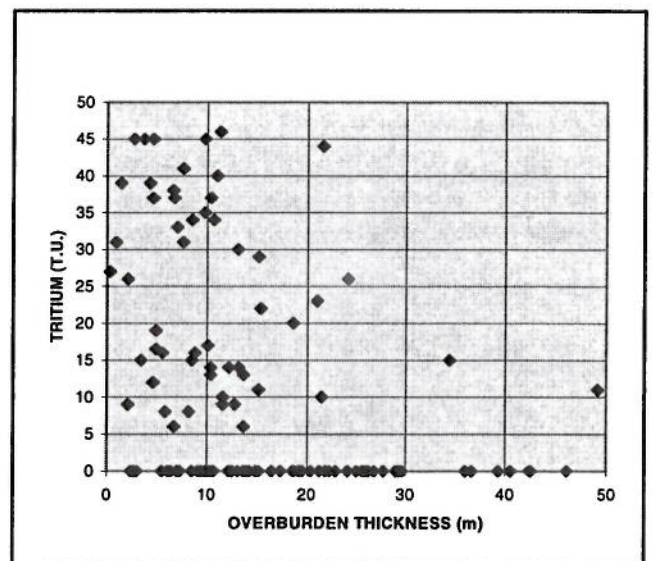


Figure 5. Tritium in groundwater vs overburden thickness.

an area lying to the west of Highway 7 and south of Teulon (Figure 1). Much of this land has been cleared and is currently in grain or livestock production. The bedrock aquifer throughout much of the area is overlain by less than 10 metres of till and lacustrine clay. The water table is generally below the top of the bedrock surface. As a result, overburden sediments are unsaturated, except seasonally or in areas underlying surface ponding. This creates a strong downward gradient and also provides an aerated environment in which nitrate will be stable. Thus, groundwater in the carbonate rock aquifer in this area would be considered to be "sensitive" to nitrate contamination.

A total of 66 individual private wells were sampled during 1996. All samples were analyzed for nitrate, chloride, iron and fluid conductivity while 34 samples were also analyzed for tritium and ammonium. Nitrogen-15 isotopic analysis was carried out on nitrate from twenty-seven of the samples. Fifty-six of the samples contained more than 1 mg/L nitrate, forty-seven more than 5 mg/L and 14 (21%) had nitrate concentrations greater than or equal to the 10 mg/L drinking water guideline. See text for detailed discussion. The model developed above for predicting the locations of nitrate-sensitive groundwater conditions in the Interlake region (less than 15 m till-dominated overburden, water table in bedrock) appears to work quite well.

Possible nitrate sources in this area include animal wastes, septic system discharges, nitrogen fertilizers, soil nitrogen and atmospheric deposition. Nitrogen-15 analyses varied over a considerable range (Figure 6). Fifteen of the 27 samples had $\delta N-15$ values greater than +10‰ which is generally considered to be representative of animal (including human) manures (Coplen, 1993) although Farrell et al. (1996) have shown that isotopic enrichment of soil organic nitrate by denitrification can raise $\delta N-15$ values somewhat above +10‰. The other 12 samples had $\delta N-15$ values from +6.18 to +10‰ which may be attributable to

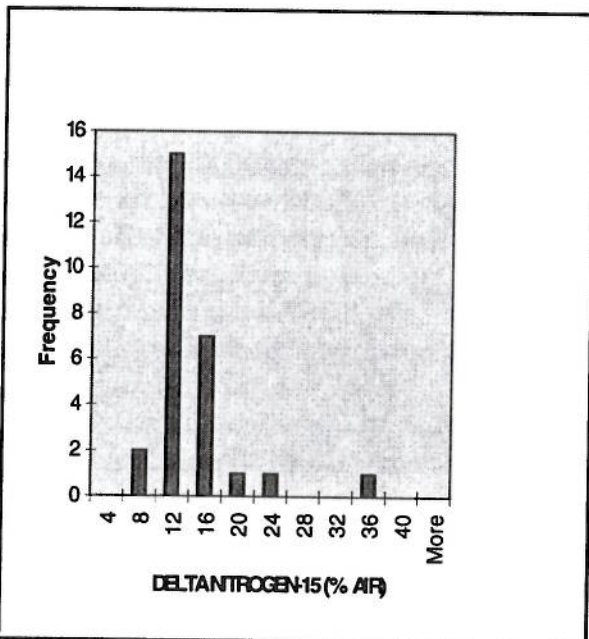


Figure 6. Delta nitrogen-15 analyses of nitrate from selected samples in the detailed study area.

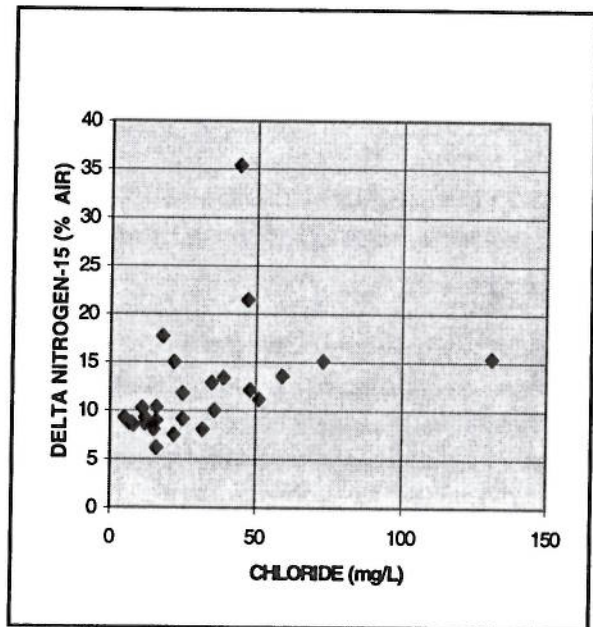


Figure 7. Delta nitrogen-15 vs chloride in samples from the detailed study area.

nitrogen produced by organic decay in the soil or, less likely, to artificial fertilizers in which N-15 enrichment has occurred as a result of denitrification processes.

It was hoped that chloride would serve as a useful indicator of animal wastes but some of the most positive $\delta\text{N-15}$ results were in groundwaters with chloride concentrations less than 20 mg/L while some of the least positive $\delta\text{N-15}$'s were found in samples having 30-50 mg/L chloride. The correlation coefficient between chloride and nitrate was close to zero. More detailed studies of the impacts from individual possible nitrate sources would be useful to sort out which of the many sources is more likely to contribute to nitrate contamination of groundwater in these sensitive areas.

SOUTH CENTRAL STUDY AREA

The sole bedrock unit containing fresh groundwater in this part of Manitoba is the Odanah Shale aquifer. This aquifer is formed by the hard, brittle, and fractured siliceous shales of the Odanah Member of the upper Cretaceous Pierre Shale. This aquifer extends from the Manitoba Escarpment westward into Saskatchewan and northward into the Riding Mountains (Figure 1) although post-Cretaceous erosion has removed the aquifer through parts of the area. In southwestern Manitoba the Odanah Member loses its distinctive hard lithology near the Saskatchewan border (Young and Moore, 1994) and is not considered to form an aquifer in this area. The Odanah Member is typically up to 40-50 metres thick through much of its outcrop area but may exceed 200 metres in thickness beneath Turtle Mountain (Bamburak, 1978). The lower part of the Member contains frequent interbeds of calcium bentonite or bentonitic shale. Ironstone concretions are common.

The Odanah Shale is more properly termed a porcelenite since silica in the form of cristobalite and quartz comprises more than 80% of the bulk rock composition (Young and Moore, 1994). Mixed-layer clays and minor illite form about 10% of the rock. Ironstone concretions are composed of iron and manganese carbonates, calcite and dolomite (Young and Moore, 1994; Spector, 1941). Sulphides, amphiboles and apatites have also been noted.

The Odanah Shale aquifer forms an important source of groundwater in southwestern Manitoba, particularly in parts of the area where Quaternary sand and gravel aquifers are absent. It is estimated that there are several thousand rural domestic wells currently completed into the aquifer. Five communities also rely on the aquifer as their sole source of water supply.

Well yields are generally less than 0.5 L/s but yields greater than 1.0 L/s are not uncommon. A few wells have been drilled which produce more than 10 L/s. There have been no studies completed of regional groundwater flow within the Odanah Shale aquifer. However, it is expected that active local flow systems will have developed in shallow parts of the aquifer in areas with hilly topography and thin overburden cover such as the Tiger Hills region. In areas where the overburden cover is very thick or in the deeper parts of the aquifer, groundwater flow is likely to be more regional in nature and flow velocities are expected to be extremely slow.

RESULTS

General Groundwater Chemistry

Groundwaters in the Odanah Shale aquifer show a highly variable geochemical make-up. However, in contrast to the Interlake area, there appears to be little spatial trend to groundwater quality although, as will be discussed, there are some vertical trends. About 5% of the samples have total dissolved solids concentrations less than 500 mg/L while another 5% have TDS values greater than 4000 mg/L (Figure 8). The average TDS concentration is 1770 mg/L. There is somewhat of a trend of increasing TDS with well depth (Figure 9), yet most depth ranges shown on this figure include both low and high TDS groundwaters. It should be pointed out that deeper wells do not necessarily draw water only from deeper portions of the aquifer. Most well logs report intersecting several water producing zones, each of which supplies a portion of the water being produced by a well. This makes depth trend analysis particularly uncertain.

Groundwater geochemical types also show a great deal of variation. Groundwaters in shallow wells (<15 m) are generally Ca-Mg-HCO₃ to Ca-Mg-HCO₃-SO₄ types, typical of hydrogeochemical development in the carbonate-rich glacial tills found overlying the aquifer throughout much of the study area. Groundwaters from deeper wells (>30 m) tend to be enriched in sodium and sulphate, but not always so, and depleted in calcium and magnesium relative to the shallow wells.

Sodium concentrations exceed 300 mg/L in most deep wells (Figure 10). Chloride concentrations also tend to be elevated in the deep wells relative to the shallow wells, but the

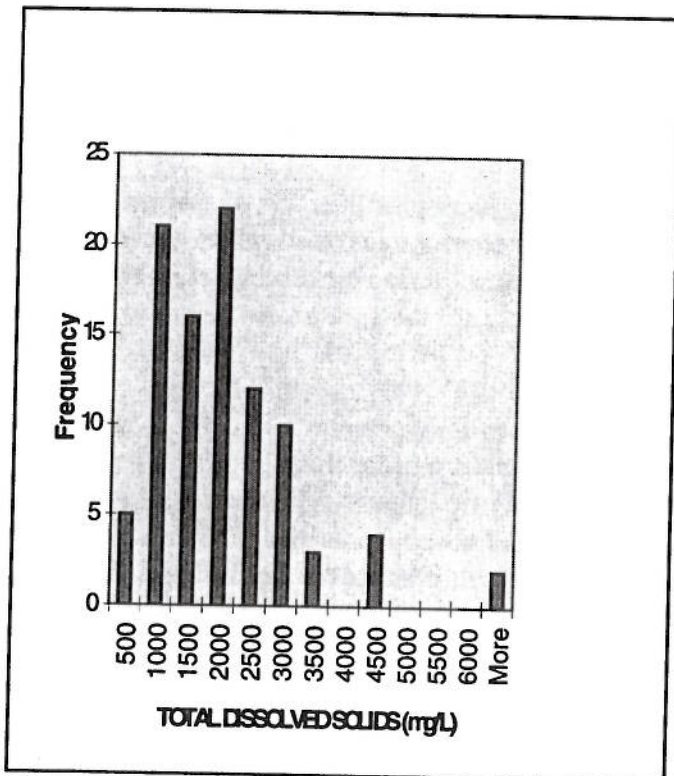


Figure 8. Histogram showing distribution of TDS in the Odanah Shale aquifer.

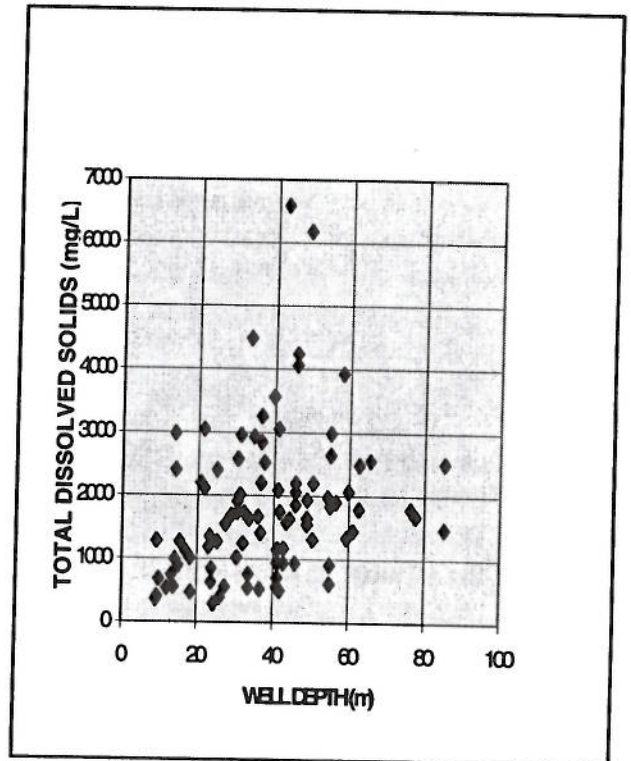


Figure 9. Distribution of total dissolved solids with depth in the Odanah Shale aquifer.

trend is not so pronounced as for sodium.

Chloride and a portion of the sodium are thought to be introduced into solution primarily by diffusion of residual marine waters from the aquifer matrix. This will be more pronounced in the deeper parts of the aquifer where groundwater movement is very slow and flushing of marine waters from the aquifer by post-Mesozoic fresh waters is incomplete. A residual marine source is supported by the linear relationship between chloride and bromide in groundwater as shown in Figure 11. The ratio of sodium to chloride (equivalents per million) in the deeper samples is generally greater than two reflecting the addition of sodium through cation exchange reactions. Calcium and magnesium concentrations have been reduced to less than 10 mg/L in many of these samples.

Sulphate concentrations vary from less than 10 mg/L to more than 1700 mg/L, showing no trends with well depth. Approximately 30% of the samples collected during this survey exceeded the 500 mg/L drinking water guideline. Sulphate is generally found at high concentrations in groundwaters which have undergone geochemical evolution in glacial tills developed over Cretaceous shales. Sources of sulphur may include oxidation of sulphide minerals or dissolution of gypsum incorporated into the tills, or oxidation of organic matter (Hendry et al., 1986). In the bedrock aquifer, sulphur sources may include the oxidation of sulphides and sulphate diffusion from residual marine waters held in the aquifer matrix. A number of samples from deep wells contained sulphate concentrations below the laboratory detection limit (10 mg/L), providing evidence of local biochemical sulphate reduction.

Dissolved oxygen (DO) concentrations were analyzed in 92 of the 98 samples. DO concentrations were less than 0.5 mg/L (a reasonable estimate of zero given the sampling and analysis techniques) in 71 of the samples (77%), indicating that reducing conditions are prevalent in the aquifer.

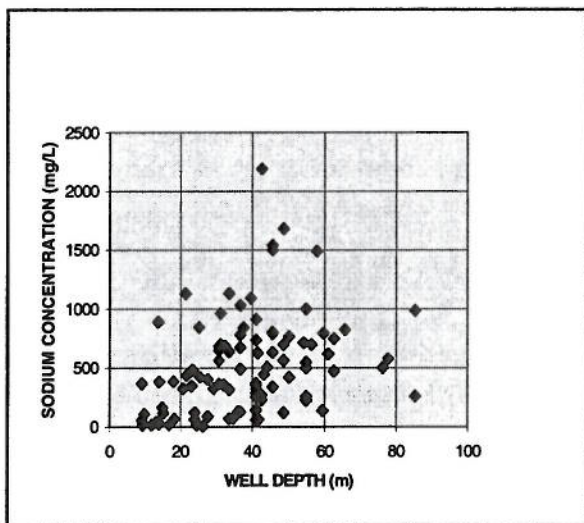


Figure 10. Odanah Shale - sodium vs well depth

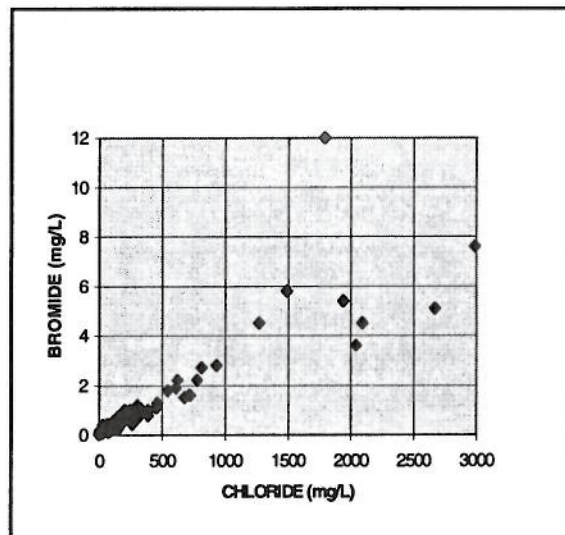


Figure 11. Linear relationship between chloride and bromide, indicating residual marine water origin.

Minor and Trace Constituents

The results of minor and trace constituent analysis are summarized in Table 3. A number of trace constituents of drinking water or potential drinking water interest were not detected in any of the 98 samples. These include chromium, cadmium, silver, molybdenum, antimony, beryllium, cyanide and cobalt. Aluminum, selenium, nickel and bismuth were detected in 20-30% of the samples, but generally at concentrations near detection limits.

Table 3. Analytical Results for Minor and Trace Constituents - Odanah Shale Aquifer

PARAMETER	DETECTION LIMIT (mg/L)	DETECTION S (98 SAMPLES)	MAXIMUM VALUE (mg/L)	DRINKING WATER GUIDELINE (mg/L)	NUMBER EXCEEDING GUIDELINE
COPPER	0.01	37	0.32	1.0	0
LEAD	0.002	4	0.134	0.01	1
ZINC	0.01	77	1.72	5.0	0
ARSENIC	0.001	42	0.020	0.025	0
ALUMINUM	0.01	16	0.064		
SELENIUM	0.001	15	0.010	0.01	0
NICKEL	0.005	14	0.064		
CHROMIUM	0.002	0	ND	0.05	0
CADMIUM	0.001	0	ND	0.005	0
SILVER	0.001	0	ND		
MOLYBDENUM	0.005	0	ND		
URANIUM	0.0002	77	0.1	0.1	0
IRON	0.01	96	6.03	0.3	22
MANGANESE	0.005	93	4.42	0.05	78
ANTIMONY	0.003	0	ND		
BERYLLIUM	0.001	0	ND		
COBALT	0.005	0	ND		
BISMUTH	0.10	28	0.4		
CYANIDE	0.010	0	ND	0.2	0
BORON	0.05	97	5.19	5.0	1
FLUORIDE	0.10	97	2.2	1.5	2
STRONTIUM	0.05	98	3.83		

Copper and zinc were detected in 37 and 77 samples respectively, although, with few exceptions, at concentrations near the detection limit. Lead was detected in four samples although only one sample contained a concentration greater than the drinking water guideline. The lead concentration in this sample (0.134 mg/L) was more than an order of magnitude greater than the drinking water guideline value. However, the sample contains no other unusual metals concentrations and is quite carbonate-rich casting doubt on the accuracy of the result. The well owner was advised and resampling will be carried out in 1997. Copper and zinc concentrations showed similar values in wells completed with steel casing vs. wells with PVC casing. Assuming that the flushing of the water supply was effective in removing stagnant water from the household copper plumbing, it is reasonable to attribute the presence of copper and zinc to natural sources in the aquifer.

Arsenic was detected in 42 water samples although none exceeded the drinking water guideline. Arsenic is found at significant concentrations in a number of shale-rich Quaternary aquifers in Manitoba and North Dakota (Betcher et al., 1995; Roberts et al., 1985) and there was some expectation that groundwaters in the Odanah Shale aquifer may contain elevated values. It is speculated that arsenic concentrations may be relatively low in the Odanah Shale, due to its siliceous nature, compared to older Cretaceous shales which do not form bedrock aquifers in Manitoba. Erosion and redeposition of these older shales may provide a major source of arsenic in some Quaternary aquifers in the province.

Uranium was found above the detection limit of 0.0002 mg/L in 77 samples with an average concentration of 0.0066 mg/L and a maximum value equal to the drinking water guideline of 0.1 mg/L.

Iron and manganese are found at generally high concentrations in groundwater samples from the aquifer, manganese concentrations being particularly elevated. In fact, 78 of the 98 samples collected had manganese concentrations above the drinking water guideline of 0.05 mg/L and seven exceeded 1.0 mg/L. Manganese is abundant in the ironstone nodules in the Shale (which was at one time investigated as a potential source of industrial manganese Spector, 1941). Under the reducing groundwater conditions generally found in the aquifer, this manganese may be redissolved (Hem, 1985).

Fluoride concentrations averaged 0.4 mg/L with only two samples exceeding the drinking water guideline of 1.5 mg/L. One sample had a boron concentration in excess of the guideline value of 5.0 mg/L.

Bacteria

Coliform bacteria were present in 53 of the 98 groundwater samples with fecal bacteria being found in four of the 53 samples. Sampling was carried out during a rather wet fall period but nonetheless, the presence of coliform bacteria in more than half the samples is disturbing.

Many of the bacteria problems are found in wells where the bedrock aquifer is overlain by thin (<6 m) Quaternary deposits. Some of these wells were constructed with very

little surface casing, in places less than five metres. While bacteria problems are not unexpected in these situations, particularly if the well is located in a barnyard, many of the other bacteria contaminated wells were completed with more than 20 metres of casing or are located where thick Quaternary deposits are found. In these cases, inadequate well construction or maintenance is likely allowing the introduction of near-surface waters containing bacteria into the aquifer.

None of the wells sampled during this survey had the casings cement or bentonite grouted; in fact, in order to maximize well yield, in a number of instances the casing was surrounded with a gravel pack which extended to within a few metres of ground surface. If the casing annulus is not properly sealed, it may form a preferential pathway for downward movement of surface waters. It is also common practice in this area to construct a well pit to a depth below the frost line and cut off the casing just above the base of the pit. During wet weather these pits can partially flood and, if the top of the casing is not properly sealed, allow contaminated water to flow into the well.

Iron bacteria were observed microscopically in 26 of the water samples. It is not known if these organisms exist naturally in the aquifer or if they have been introduced during construction of the well, installation or servicing of the pump, or by seepage of surface waters into the well. To prevent the introduction of iron bacteria, considerable care should be taken to prevent the entry of surface waters, to use clean chlorinated drill water and to chlorinate wells whenever a pump is installed or serviced.

Nutrients

Water samples were analyzed for nitrate, nitrite, ammonium and total phosphorus. Nitrate was found in 91 of the samples at concentrations above the detection limit (.01 mg/L-N) with 72 samples containing more than 1.0 mg/L-N. Nineteen of the samples had nitrate concentrations above the drinking water guideline of 10 mg/L-N. The maximum concentration was 201 mg/L-N and the median was 2.2 mg/L-N.

Many of the highest nitrate concentrations were found in wells having high bacteria counts but this was not always the case. Plots of nitrate vs well depth, casing length and drift thickness (only drift thickness plot is shown, Figure 12) show that while many of the samples having the highest nitrate concentrations are found in wells shallower than 20 metres or where the drift thickness is less than 7 metres, there are numerous exceptions. The highest nitrate concentration was actually found in a well having more than 20 metres of casing and a drift thickness just under 20 metres.

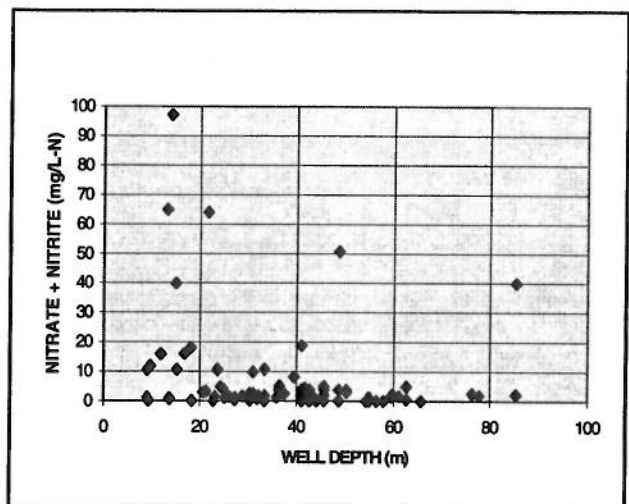


Figure 12. Nitrate concentration vs well depth. Two nitrate values greater than 100 mg/L are not shown.

This points out the difficulty in interpreting regional aquifer conditions from analyses carried out in private wells - the wells themselves may play a significant role in determining local water quality conditions which are not necessarily reflective of regional aquifer conditions. Nonetheless, there are some lines of evidence which indicate that groundwater quality in at least parts of the aquifer is being impacted by seepage of nitrogen-contaminated waters which enter the aquifer by slow seepage through the overlying materials. The first is that higher nitrate concentrations tend to be found in areas of thin drift cover. Seepage into the aquifer will occur most quickly where the aquifer is near the surface. However, it is also recognized that wells in these areas may tend to have less casing installed, making them more likely to allow entry of surface water. The second evidence comes from an examination of nitrate concentrations vs tritium (Figure 13). Groundwaters with no detectible tritium (<6 T. U.) will be composed primarily of pre-1953 infiltration, implying that little of the water originates from the influx of surface waters into the aquifer via the well. Fifty-four samples contained no detectible tritium yet 38 of these samples had nitrate concentrations above 1 mg/L-N and several had concentrations above 5 mg/L-N. This implies an influx of nitrogen through slow seepage through the overburden, (or possibly naturally occurring N species as will be discussed later), not entry by direct access via a well.

Both nitrite and ammonium were found at significant concentrations in many of the groundwater samples, frequently exceeding 1.0 mg/L. The average nitrite-N concentration was 0.85 mg/L while the average ammonium-N concentration was 1.72 mg/L. In the shallow soil zone or in oxygenated groundwaters these species are generally nitrified to nitrate. The presence of reduced nitrogen species is often attributed to nearby sources of organic contamination such as manure piles, with the nitrification process being incomplete. However, this does not account for the presence of nitrite and ammonium in older groundwaters (no detectible tritium) or groundwaters produced from deep wells showing no other evidence of surface water contamination in the study area.

It is suggested that the presence of reduced nitrogen species in parts of the aquifer are naturally occurring, a result of the presence of ancient organic material within the aquifer matrix. At the low Eh conditions that appear to be common in the aquifer, indicated by low dissolved oxygen and very high manganese concentrations, the nitrogen would be present as reduced species. This may be more significant in the deeper parts of the Odanah Shale where the silica content is less and underlying carbonaceous shales are approached. Nitrogen isotopic studies are planned for 1997/98 to examine this issue further.

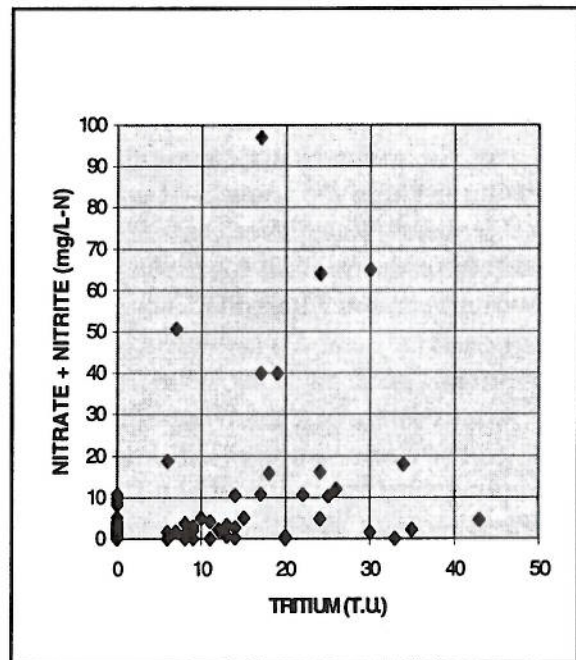


Figure 13. Nitrate vs tritium for samples from the Odanah Shale aquifer.

SUMMARY

Regional groundwater sampling in the carbonate rock and Odanah Shale aquifers has helped to define the general trends in background water quality in the two aquifers. Groundwaters in the carbonate rock aquifer are generally of good quality although naturally high in hardness, iron and manganese. Poorer quality groundwaters are found near the regional fresh water-saline water boundary near Lake Manitoba, west of the Red River and near the Town of Arborg. Anthropogenic impacts have not been large on a regional sense. However, in sensitive areas, significant groundwater quality impacts are found in a high percentage of private wells. Based on the findings from this and other studies, sensitive areas of the Interlake should be mapped and land use policies developed for these areas specifically to minimize the potential for groundwater contamination. There is also considerable evidence that well construction plays a critical role in providing uncontaminated groundwater in the Interlake. Wells should be constructed with cement or bentonite grouted casings and should be completed at the surface in a manner which does not allow surface water infiltration.

Groundwater quality is often poor in the Odanah Shale aquifer, with more saline groundwaters tending to be found at increasing depth. Manganese concentrations exceed drinking water guidelines in most samples and sodium, chloride and sulphate concentrations are also frequently found above drinking water guidelines. Bacteria and nitrate contamination are widespread and, although some of the nitrogen may in fact be naturally occurring, in many cases reflect problems with well construction or maintenance. As suggested for the Interlake, mapping of sensitive areas should be undertaken followed by development of land use policies for these areas to protect groundwater quality. New wells should be constructed with an adequate length of cement or bentonite grouted casing and should be completed at surface in a manner which will not allow direct entry of surface waters.

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