MULTI-ISOTOPE GEOCHEMISTRY OF SURFACE AND GROUNDWATER IN THE AVON RIVER DRAINAGE: HYDROGEOLOGICAL IMPLICATIONS

by

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ABSTRACT

This thesis demonstrates the use of a number of isotopes in gaining an understanding of the groundwater processes in the Maritimes. The study was carried out in the Avon Valley located about 55km northwest of Halifax and stretching roughly 30km along the #14 Highway from Card Lake to Windsor, N.S. This valley was chosen because it straddles two typical Nova Scotian geographic and geologic settings; the granitic highlands and the sedimentary lowlands. Furthermore, the valley is known to host uranium deposits allowing radioisotopes to be a viable part of the study. Samples of lake, stream, and domestic well waters were taken in the summer of 1998 with some follow up sampling in 1999. The samples were analysed for general chemistry as well as isotopes of oxygen, hydrogen, carbon, strontium, and uranium and the concentration of radon. Nitrogen and radium concentrations were below the analytical limits of detection.

Nova Scotian rainfall has a very low concentration sea-salt signature and has low pH due to anthropogenic pollution. Rain collects in the abundant lakes of the granitic highlands where minor additions of the dissolved components of the granites are made to the water which remains low in pH and TDS. The lakes also contain solid and dissolved organic matter, as is shown by the tea-brown colour of the water. As the lake water infiltrates into the ground it becomes further modified by additions of ions from interaction with minerals in the glacial till. The dissolution of limestone and to a lesser extent gypsum, by the low pH water is an important factor in the chemical alteration of the composition of the infiltrating water. By far the dominant component of these waters is calcium carbonate and its addition is reflected in a shift in the carbon and strontium isotopes as well as an increase in uranium concentration due to its higher solubility as a uranyl-carbonate complex. These chemically more mature groundwaters also have the opportunity to mix with older water such that their oxygen isotope signature is closer to the yearly average while the surface waters reflect the current seasonal average. Thus the highlands act as a very short-term recharge area while the lowlands receive the discharge of chemically more mature and mixed waters.

This model suggests high flushing rates, which decrease the sensitivity of the system to natural and anthropogenic pollution. The model also suggests that the highland area is susceptible to groundwater shortage in the event of low rainfall conditions even if those conditions are on the scale of only a few years. The sensitivity of the lowland groundwater depends upon the reservoir capacity of the bedrock both in the highlands and the lowlands.

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about some of those examples). Also to my brother's wives who have treated me as a true brother.

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1.0 INTRODUCTION

1.1 Introduction

The use of multiple isotopes and chemistry to investigate a hydrologic system is unprecedented in Nova Scotia. The initial impetus of this thesis was to create a new database of radionuclide concentrations in water in an area considered anomalous for uranium after exploration in the 1970s and 1980s. Choosing a valley that crossed both granitic and sedimentary bedrock allowed the work to test the question of whether the granite-hosted uranium poses a greater or lesser uranium and radon hazard than the sedimentary-hosted uranium. In addition, analysis for uranium isotopes would show whether uranium series disequilibrium data could add any new and useful information. It was recognized that previous surface and groundwater studies in Nova Scotia were broad, regional, government reports which focussed on water quality and quantity issues (Vaughan and Somers 1980, Porter 1982, Gibb and McMullin 1980, Lin 1970, 1975, and Trescott 1969a, 1969b, 1970). This study included a number of isotopes in order to complete a comprehensive catchment-scale study of rock-water interaction in Nova Scotia. The use of multi-isotope geochemistry in catchment-scale studies of surface and groundwater flow to investigate the interaction of water with geological elements is increasingly being used (Kendall et al. 1998).

1.2 Purpose of Thesis

1) To examine the usefulness of a variety of isotopes in the analysis of surface water and groundwater in Nova Scotia and propose testable hypotheses from these data.

2) To observe the chemical and isotopic evolution of the surface water and groundwater and relate the evolution to influences such as climate and water-rock interactions within a single catchment consisting of granitic rocks upstream and sedimentary rocks downstream.
3) To determine the current levels of uranium, radium and radon in surface water and groundwater in the Avon Valley.
4) To determine the usefulness of uranium isotope ratios in the analysis of a drainage basin containing known sources of concentrated uranium.
5) To provide baseline groundwater data which can be used in future studies to determine change through time and to demonstrate changes in anthropogenic effects.

1.3 Scope and Limitations of the Thesis

This study used commonly analysed elements combined with less commonly used isotopes to gain some understanding of the hydrologic system in the Avon Valley. The analyses include concentration of sodium, potassium, calcium, magnesium, sulfate, chloride, alkalinity, inorganic carbon, strontium, radon, uranium, radium, and nitrogen. Temperature, conductivity, pH, and hardness were also measured. Isotopic analyses included $^{87}Sr/^{86}Sr$, $^{234}U/^{238}U$, $\delta^{13}C$, ^{14}C, $\delta^{18}O$, δD and nitrogen isotopes. Sampling was carried out to obtain data on spatial variation. The data are mainly from shallow groundwater and surface waters. Two drilled well samples were taken. The majority of the sampling was done during two summers (1998 and 1999) that were both noted for long dry periods which caused drought problems for farms near the study area.

1.4 Organisation of Thesis

The first three chapters provide background information for the thesis as a whole, including geology, methodology and a discussion of the analytical errors involved. Chapters 4 through 11 constitute the main portion of the thesis, in which each element is given its own chapter. This organization allows all the information on a given topic to be located in one place. Chapter 12 summarises the conclusions and recommendations of the study.

2.0 STUDY AREA

The study area was chosen because it straddles two major physiographic and geological regions of Nova Scotia, Canada; the granitic highlands and the sedimentary, Carboniferous lowlands including the Horton and Windsor Group rocks (Fig. 2.1 and 2.2). Furthermore, the Avon Valley contains a number of known uranium showings (Ham 1991) making it ideal for a radioisotope study.

The study area is a part of the catchment basin of the South Branch of the Avon River. This branch of the Avon extends from Card Lake in the south to its mouth near Windsor, Nova Scotia (Fig. 2.1 and 2.2). Windsor lies roughly 55km northwest of Halifax and is situated on the Minas Basin on the southern side of the Bay of Fundy. The study area is covered by the National Topographic Data Base (NTDB) maps 21A16, the northernmost part of 21A09 and the southern half of 21H01. Access to the study area is most conveniently by Highway 14, which closely follows the South Branch of the Avon River (hereafter simply referred to as the Avon River). This north to south trend in the sampling pattern was augmented by the addition of two outlying areas (Fig. 2.2). Samples were collected along Mill Brook, a significant tributary located to the east of the Avon River where it flows through the communities of Leminster and Lower Vaughan. Samples were also collected to the west of Windsor from areas that overlie the sedimentary rocks. The surface waters of this area do not drain the South Mountain Batholith and so they provide a comparison to the samples collected within the Avon Valley.

2.1 Bedrock Geology

Bedrock in the study area is dominantly composed of the South Mountain

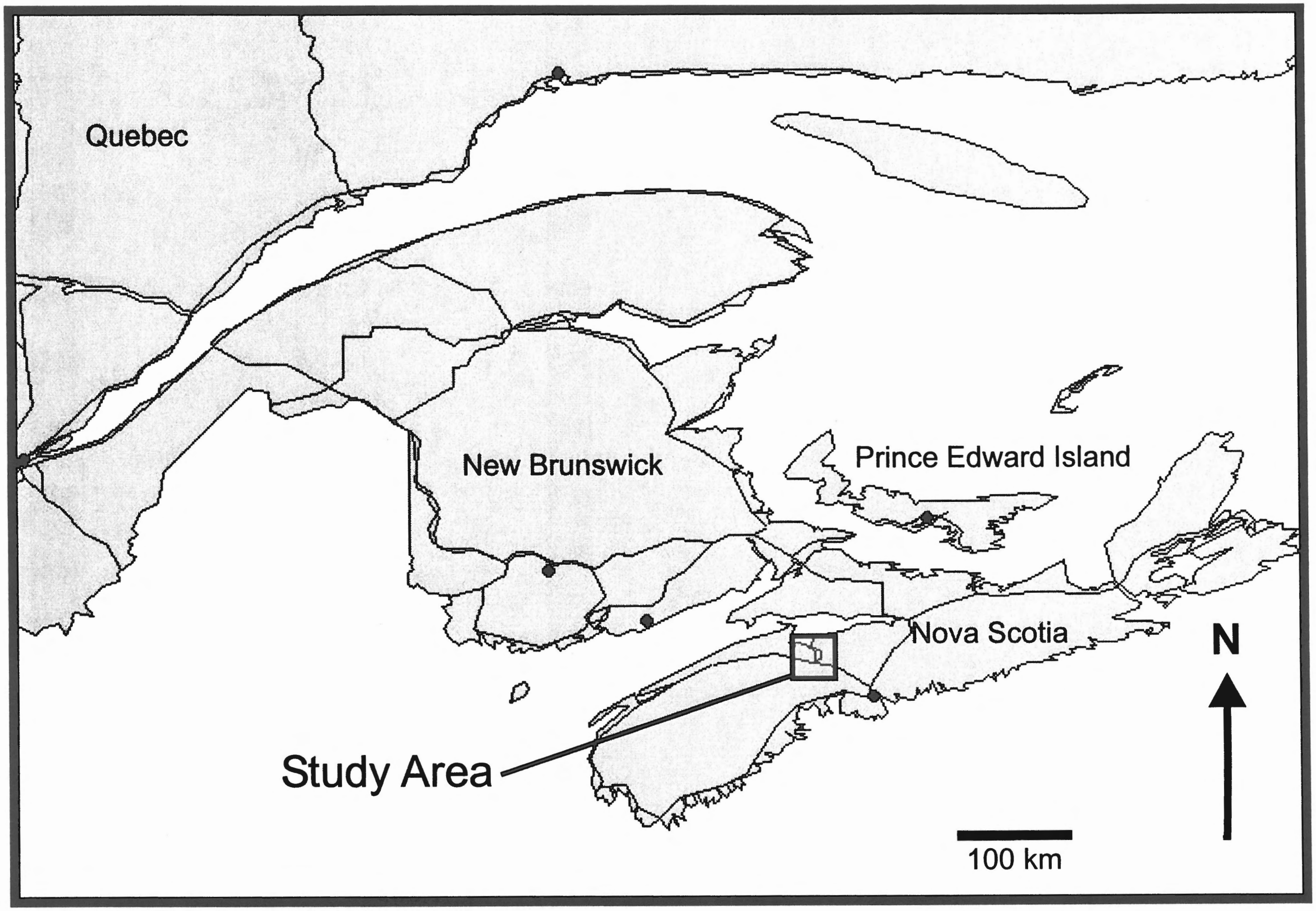

Fig. 2.1: Location of study area within Nova Scotia, Canada.

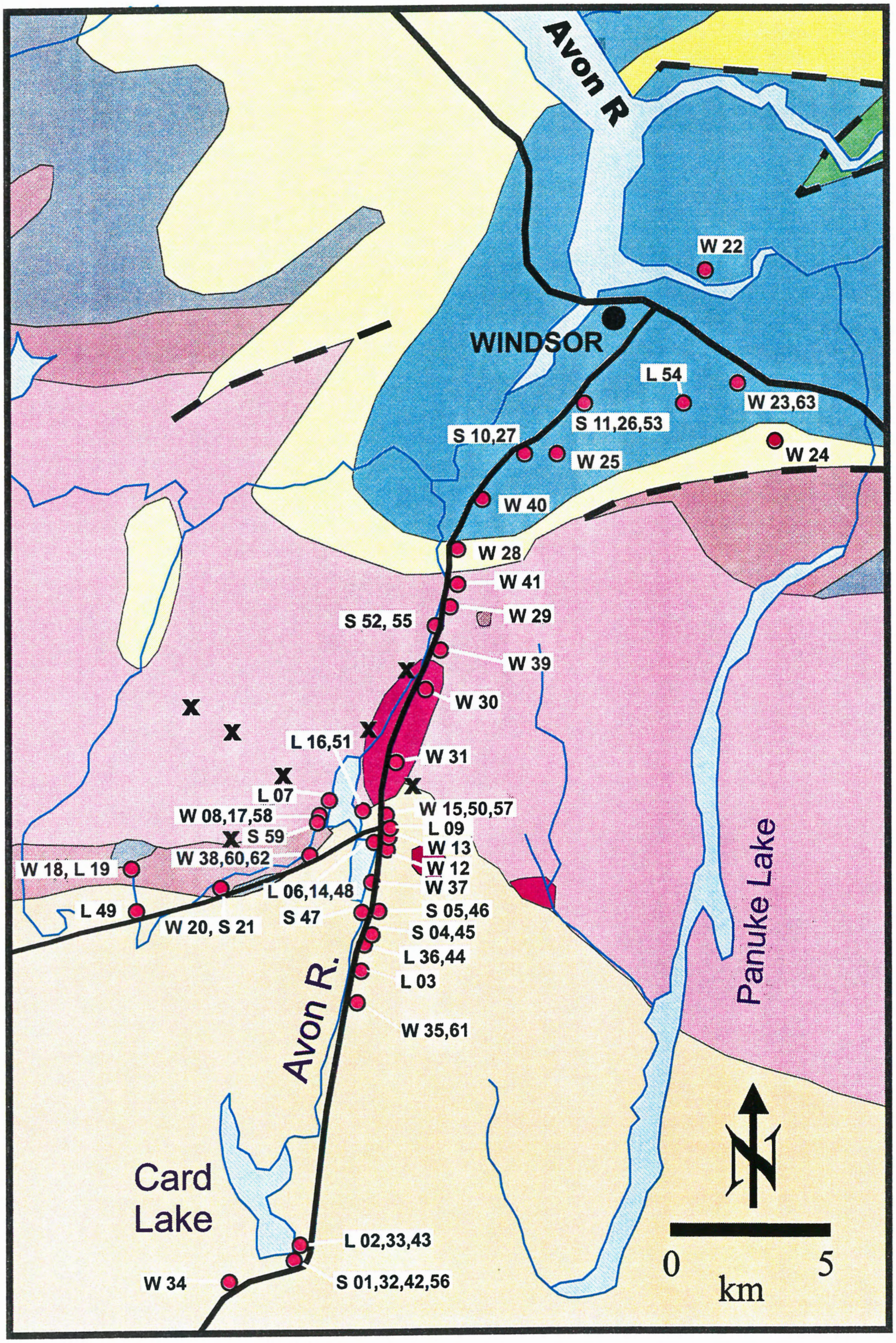

Fig. 2.2: Geology and sample map of the study area (modified after Donohoe and Grantham, 1994). See Figure 2.3 for legend.

Bedrock Geology Legend

Cp	**Pictou Group**
Cc	**Canso Group**
Cw	**Windsor Group**
CH	**Horton Group**
South Mountain Batholith	
Dlm	**leucomozogranites**
Dg	**granodiorites**
OSw	**White Rock et.al. Formations**
COH	**HalifaxSupergroup**
COG	**Goldenville Supergroup**
gn	**Gneiss (unknown age)**
●	**Sample site**
✕	**Uranium Mineralization**
– – –	**Fault**
━━━	**Highway 101**
━━━	**Highway 14**
───	**Side road**

Fig. 2.3: Legend for geology and sample map Fig. 2.2.

Batholith (SMB) in the south and the Carboniferous sedimentary strata of the Minas Basin in the north (Fig 2.2). Topographically, the resistant granites form rolling highlands with a steep, glacially rounded scarp where they contact the Carboniferous strata, which form fairly flat lowlands. The SMB also contains some inliers of Meguma Supergroup rocks and an unnamed and undated gneiss that has in the past been mapped as deformed Meguma Supergroup. These units are described below in chronological order from oldest to youngest.

2.1.1 Unnamed gneiss

These three inliers are suspected of being the oldest rocks in the study area, due to the intensity of metamorphism. They are shown in Fig. 2.2 as irregular, reddish ovals within the South Mountain Batholith. These rocks were originally mapped as Meguma Supergroup but the "style and intensity of deformation is not known to occur within the Meguma Supergroup rocks" (Ham 1991). The unit is significant to the study, because the largest of the three inliers is adjacent to the Avon River and is host to the Hemlock Hill uranium deposit. Additional uranium showings are found around the contact between the gneiss and the granite (Ham 1991).

2.1.2 The Meguma Supergroup

The Meguma Supergroup is a thick sequence of siliciclastic rocks ranging in age from Late Cambrian or older to Early Ordovician (Schenk 1995). The Meguma Supergroup is divided into an underlying Goldenville Group and an overlying Halifax Group. The Goldenville Group is dominantly massive, thick-bedded, quartzose to feldspathic metawacke with minor slate and siltstone. The Halifax Group is made up of grey to black slate that is variably massive, laminated, and rippled, with minor silt and sandstone (Schenk 1995). The Halifax Group and, to a lesser extent, the Goldenville Group are known to contain abundant sulphide minerals including pyrrhotite, pyrite, and arsenopyrite, all of which are known to produce acid rock drainage (e.g. Pupp and Grove 1988).

2.1.3 South Mountain Batholith (SMB)

The SMB is the largest peraluminous granitoid body in the Appalachian Orogen (MacDonald et al. 1992). The study area covers a small portion of the northeastern edge of the pluton. The intrusion of the pluton has been dated at approximately 370 Ma (Fairbairn et al. 1964, Clarke and Halliday 1980, Reynolds et al. 1981, 1987) and is associated with late stages of the Acadian Orogeny. The pluton is a composite intrusion that can be divided into as many as 49 mappable units (MacDonald 1994, MacDonald et al. 1992). The units are assumed to belong to an early intrusive stage (mostly granodiorite and monzogranite) which is found in the central portion of the study area, and to a late stage (mostly monzogranite, leucomonzogranite and leucogranite), which covers the southernmost portion of the study area (MacDonald 1992). Uranium mineralization in the study area is strongly associated with the contacts between these intrusions, although mineralization is also associated with the inliers of Meguma and gneiss (Fig. 2.2). The SMB is on average high in uranium compared to other granitic bodies in Nova Scotia and to the world average for granites (Barkhouse and Laffin 1982).

2.1.4 Horton Group

The western part of the Minas Basin in the vicinity of Windsor is the type area for two major sedimentary units known as the Horton and Windsor Groups. The Horton Group is of Late Devonian – Early Carboniferous age. It was deposited in local half grabens during an extensional phase that followed the Acadian Orogeny (e.g. Martel and Gibling 1996). The Horton Group overlies the Meguma Supergroup with angular unconformity and the SMB granitoids nonconformably (Gibling 1995). Bell (1929) divided the Horton Group into the lower, predominantly lacustrine Horton Bluff Formation and the upper, alluvial Cheverie Formation. The Horton Group consists dominantly of arkosic sandstones and mudstones with some red and grey-green polymictic conglomerates, oil shales, and minor non-marine evaporites (van de Poll et al. 1995, Gibling 1995). There are known to be high concentrations of uranium in the Horton Group (e.g. Page 1999).

2.1.5 Windsor Group

The Windsor Group strata are marine redbed shales, carbonates and evaporites (Bell 1929) of Middle to Late Visean age. Bell (1929) estimated the rock type volumes at roughly 20% gypsum, 25% calcareous beds, and 55% red shales. He recognised five stages of deposition which are thought to be related to marine transgression-regression cycles or to seasonal and climactic fluctuations in aridity (Schenk 1967, 1969 as cited in van de Poll et al. 1995). In addition to the three dominant rock types, there are minor amounts of anhydrite, salt and potash (e.g. van de Poll et al. 1995, Gibling 1995). The calcareous and evaporitic nature of the Windsor Group was expected to exert an important influence on the chemistry of the waters in the lowland area.

2.2 Till Geology

Recent work by Finck and Stea (1995) has produced a map of till units over the SMB. The relevant portion of this map is reproduced in Fig. 2.4 and 2.5. This map shows that Lawrencetown till overlies the majority of the study area with a few pockets of Beaver River Till. It is important to note the outwash and ice contact deposits that follow the course of the Avon River closely. These glaciofluvial deposits suggest that the Avon Valley was a significant meltwater channel, at least during the last glaciation. Furthermore, these deposits are dominantly sand and gravel and make excellent aquifers.

The Lawrencetown till is the oldest till in the study area and is associated with southward iceflow. Referred to as "Silty Till Plain and Drumlins" on the map by Stea et al. (1992) it is noted in the legend to have moderate drainage and stoniness and moderate to good buffering capacity for acid rain because of transported calcareous bedrock components. The till is described as a dark reddish-brown silty matrix till (Finck and Stea 1995). It is matrix-supported and 1-10m thick where it is ground moraine but where the landscape is covered by drumlins it can reach thicknesses of 30-40m. The end member (ideal) Lawrencetown Till can have more than 90% allochthonous clasts from more than 50km up-ice (Finck and Stea 1995). This suggests that the soft Carboniferous sediments to the north may make up a significant portion of the till throughout the study area, which would account for the buffering capacity in this location (Stea et al. 1992).

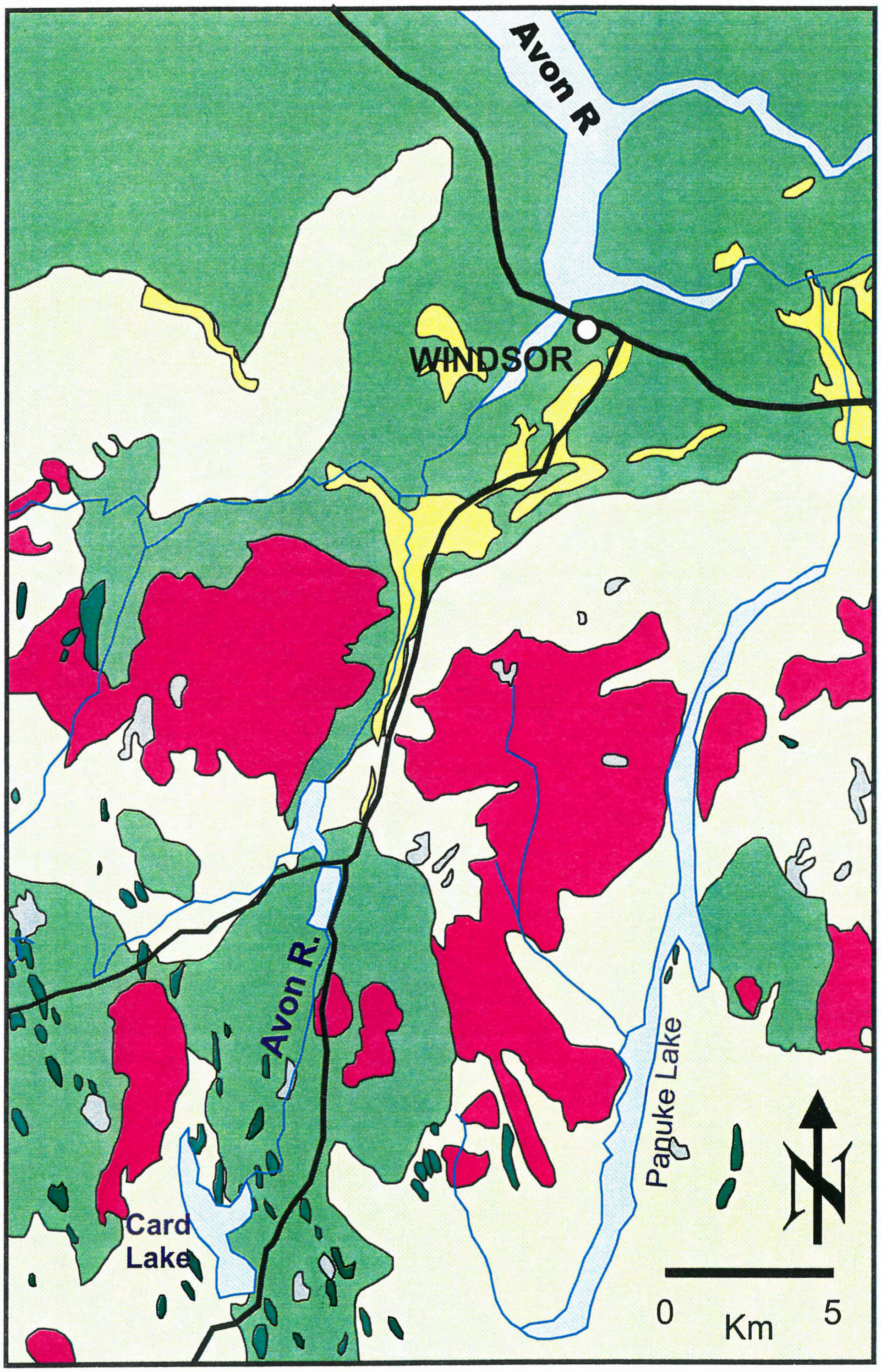

Fig. 2.4: Surficial geology map of the study area (modified from Stea et al. 1992). See Figure 2.5 for legend.

🟨	**Undifferentiated alluvial and glaciofluvial deposits**
▩	**Organic deposits (sphagum moss, peat, gyttja, clay)**
⬮	**Drumlins**
🟩	**Silty till plain (silty matrix, compact) -correlates with Lawrencetown Till**
⬜	**Stony till plain (sandy matrix, stony) -correlates with Beaver River Till**
🟥	**Bedrock**
– – –	**Fault**
━━━	**Highway 101**
━━━	**Highway 14**
───	**Side road**

Fig. 2.5: Legend for surficial geology map Fig. 2.4.

The Lawrencetown till is overlain in places by the Beaver River Till. The latter is subdivided based on clast content, since the clasts closely reflect the local bedrock type. The Beaver River Till usually contains very few clasts coming from more than a kilometre away (Finck and Stea 1995). In the study area there are pockets of greywacke-slate clast-dominated till (Meguma Supergroup clasts) and an area of granite-dominated till (SMB clasts). Clasts of gneissic origin are not differentiated from clasts from the Meguma Supergroup. Classified as a Stony Till Plain and Drumlins (Stea et al 1992), this till category is noted to have rapid drainage, a high water table, and poor buffering capacity for acid rain. The Beaver River Till is described as a loose, stony, sandy till variably clast- to matrix-supported (Finck and Stea 1995).

2.3 Climate and Hydrology of Nova Scotia

The general climate of Nova Scotia is humid and temperate with rainfall ranging from 1000-1500mm per year and average annual temperatures from 5.9 to 7.0 °C (Porter 1982, Lin 1975, Gibb and McMullin 1980, Trescott 1969a, 1969b). Values for the Windsor area were noted by Trescott (1969b). The mean average temperature in Windsor is 44.2 °F (6.8 °C) and precipitation is 42.16 inches (1070.86 mm). It is important to contrast this rainfall figure with the data from a weather station called Avon, which is located in the SMB highlands (44°53'N 64°13'W, 23m elevation). This station reports precipitation of 55inches (1397mm) for the same time period. Those data support the idea that precipitation in the highlands is significantly higher than in the lowlands, and that in general, precipitation in Nova Scotia is highly variable. Hennigar (1972) noted that detailed precipitation monitoring in a single watershed near Truro showed a coefficient of variance (for different monitoring sites at the same time) ranging from 7% to almost 63%. This result suggests that the carrying out of an accurate quantitative study of precipitation in any Nova Scotia watershed would require many precipitation sampling stations.

The general hydrogeology of the Maritimes is very clearly summarised in the following paragraphs:

> "In all of Atlantic Canada, (hydro)geology is determined by the formation of the Appalachians, fold-and-thrust mountains created during the late Precambrian to early Carboniferous age (between 600 to 350 million years ago), and by their subsequent erosion, glaciation and deglaciation. Because of that, one finds igneous, metamorphic and sedimentary rock, often close to each other; one finds extensive fracturing and faulting and separation in bedding planes; one also finds surficial stratified deposits along major river valleys and deltas; one finds uplands where bedrock is exposed or nearly exposed and lowlands with a, generally thin, cover of glacial drift (till and stratified deposits).
>
> The hydrogeological effect of all this is ground water storage and flow that occurs primarily in fractures or in surficial or near-surficial sand and gravel aquifers of limited extent. Significant primary porosity may also be found in soft sedimentary rock of Carboniferous age. Permeability and porosity may change over short distances and, in bedrock, within the same formations. As precipitation is generally high (1000 to 1500mm per year), as recharge may reach 20 to 30% of precipitation, and as permeability is generally high, ground water is usually young and of good quality. Unfortunately the same factors also make shallow groundwater more vulnerable to surface contamination."
>
> (Pupp and Grove 1988)

Pupp and Grove go on to detail some of the differences within the Maritime Provinces:

> "Distinctive features in Nova Scotia may be the carbonate rocks of the Windsor Group with their often high concentrations of chlorides, the Meguma Group with its slate and its content of easily oxidizable pyrite, pyrrhotite and arsenopyrite, and the high yielding sedimentary formations and surficial aquifers in the Annapolis-Cornwallis valley and in the Cumberland Basin."
>
> (Pupp and Grove 1988)

Trescott (1969b) carried out a groundwater resources assessment in the study area as well as in the Annapolis Valley immediately to the west (Trescott 1969a). The following information on hydrologic properties and estimated yields of the various geologic units is summarized from Trescott's reports.

Granite (SMB) and metamorphosed slate and quartzite (Meguma Supergroup) – These rocks are essentially impermeable in an unfractured state. Near surface these rocks are generally fractured due to the release of confining pressure by the erosion of overlying rocks. Weathering increases the dimensions of these fractures, such that the zone of weathered rock may be 10 times more permeable than the unaltered rock. From this zone, the permeability of the rock decreases by about 3 orders of magnitude downwards to a depth of 300ft (after Snow 1968), as confining pressure closes fractures. No information was available for well yield in the granitic rocks in the study area but estimates for the adjacent Western Annapolis Valley average 2gpm/100ft (gallons per minute for every 100 feet of saturated section). The metamorphic slate and quartzite of the Meguma Supergroup are estimated to provide 1.5 to 2gpm/100ft in the Windsor area. The yield of wells in granites and metasediments can range from less than 0.25 gpm to 40 or 50gpm/100ft.

Horton Group – The aquifer properties of this group vary with rock type. The shale sections are poor aquifers. The sandstone sections are good aquifers. Two wells in the Horton Group rocks yielded 2 and 3gpm/100ft while a third well yielded 27gpm/100ft.

Trescott suggests that wells drilled into sandstone produce water an order of magnitude more efficiently than do sections that are predominantly shale.

Windsor Group – Fracture permeability is very important hydraulically in this rock group. The permeability is low in the shales. In limestone and gypsum, where solution channels are present, the permeability is high. An average yield of 10 gpm/100ft has been suggested for this group. Depending on lithology and the presence or absence of solution channels, the yield can vary from 1 to over 100gpm/100ft.

Glaciofluvial Deposits (including outwash and ice contact deposits) – These sorted and stratified glacial deposits are both highly permeable and highly porous. They are more permeable and can store more water per unit volume than any other unit in the area. The permeability is from 10 to 100 times greater than in the Horton Group.

Other Surficial Deposits (glacial till) – These deposits are dominantly fine-grained and poor aquifers. Dug wells in this material satisfy domestic demands due to the storage capacity of the well itself, but problems may be experienced during dry summers when the storage capacity is reduced due to recession of the water table. It should be noted here that Trescott (1969a, b) reported mostly on surficial deposits in the lowlands. He did not comment on the permeability of tills developed over the granitic highlands. These may be slightly less fine-grained due to the more resistant bedrock from which the deposits are locally derived.

2.4 Conclusions of the Nova Scotia Uranium Task Force

The Nova Scotia Department of Health first became aware of potential problems with radionuclides in domestic water in May 1978 (Grantham 1986). Information from the investigations following this, and information summarized from exploration company assessment reports, was summarized by the Nova Scotia Uranium Task Force in a report by David Grantham (1986). This section summarises the relevant conclusions from that report.

The study found that 25% of the 784 wells tested had uranium concentrations higher than 0.02 mg/l, which was the 1986 Canadian Drinking Water Quality Guideline. The 1998 guideline is 4 Bq/l which is equivalent to about 0.154 mg/l (Federal-Provincial Subcommittee on Drinking Water 1998). Of these wells, 99% were drilled wells. The study found that on a province-wide scale, bedrock was a major factor in the occurrence of uranium in well waters. The granite batholiths and alkaline sandstone and shale of the Upper Carboniferous sedimentary basin were found to be most likely to exhibit anomalous uranium concentrations in well water. The granite area was noted to have geographically and chemically variable results due to hydrogeological effects such as locally increased water flow in fracture and shear zones. Furthermore, the more fractionated and silica-rich phases of plutonic intrusion were associated with higher uranium content. Thus, uranium levels were noted to increase from the granodiorites to the monzogranites, to alaskite or leucogranites. Uranium distribution was found to be more uniform in the Carboniferous Basin, possibly as a result of the more uniform groundwater flow system and the geochemical consistency resulting from a roll-front uranium deposit. Higher uranium in well water was associated with high pH, alkalinity, phosphate, silicate, fluoride and arsenic in granites, with hardness and TDS contributing to that list for the Carboniferous Basin. The strongest correlation was found to be with pH. Uranium in water wells was also found to correlate generally with elevated radium and radon gas. Radon was found to be highest in known uraniferous zones, in the monzogranites and alaskite granites, or in wells containing high radium. Radon variability was concluded to be related to rock type, overburden thickness, well depth and aquifer permeability. Uranium and radium concentrations were found to be quite constant through the short term (1 day) and the long term (1 year), though variable well water use could affect the uranium concentration. Radon concentrations were constant on the short term but quite variable over one year, especially with variable water use.

Finally, the report concluded that not all areas that may be susceptible to radionuclide content in domestic water had been investigated and that further work was required to further assess these areas (Grantham 1986).

3.0 METHODOLOGY

3.1 Field Sampling

Sampling was designed to take a representative overview of lakes, streams and groundwater in two contrasting terrains: the granite-dominated uplands and the sediment-dominated lowlands of the Avon River basin. At all sample locations pH, conductivity and total dissolved solids (TDS) were measured using a field meter that was calibrated before, during and after sampling using standard solutions. pH is a measure of the activity (roughly concentration) of H^+ in solution, which is a quantitative measure of acidity. Conductivity is a measure of the ease of conductance of electricity through the water sample. Conductivity rises with increased concentration of dissolved ions in solution, which aid in conducting charge (electricity) through the water. In other words, the cleaner the water is, the lower the conductivity. The Total Dissolved Solids (TDS) measurement is a measure of dissolved solid matter in the solution. In many field meters it is calculated using the conductivity measurement. Temperature was also measured at each location using a standard mercury and glass lab thermometer.

Samples for general chemistry and strontium isotope analysis were collected in 500 ml high-density polyethylene bottles. Samples for carbon, oxygen and hydrogen isotopes were collected in 250 ml high-density polyethylene bottles. Samples for radon and radium were collected in 250 ml brown glass bottles to ensure that the gas phase could not migrate out of the bottle and that reactions with light did not occur. To prevent water / atmosphere gas exchange, all of the bottles were filled with as little air space as possible. The tops of samples to be shipped were dipped in liquid paraffin wax on the day of sampling to ensure a gas-tight seal. Uranium samples were collected in 10 to 20 litre jerry cans and were acidified on the day of sampling to prevent precipitation of uranium and microbial action. All containers were rinsed at least once with the sample water before filling.

Ideally, tap water samples should not be collected until the tap has run for 10 or 20 minutes in order to ensure the lines are flushed. However, since most of the sampling was done during drought conditions in the Avon Valley, it was not always possible to flush the water lines. To offset this, all the bottles were rinsed before filling, and where large samples (such as for uranium) were collected, they were collected first, to ensure that small samples were collected from the longest-running stream of water.

3.2 Analyses

The basic analytical procedures used are described in standard texts such as Clark and Fritz (1997) and Mazor (1991). More detailed analytical information, particularly for the isotopic analyses, was obtained via personal communication with the representatives of the analytical laboratories that were used for the study (as noted with each element).

3.2.1 Water Chemistry

Sampling and analyses were carried out using standard procedures. Water samples 12 through 21 were sent together with radon samples to Israel, where Dr. Joel Kronfeld of the Department of Geophysics at Tel Aviv University in Israel carried out their analysis. Basic water chemistry of the remaining samples was measured at the Queen Elisabeth II Environmental Sciences Laboratory in Halifax, N.S. Table 3.1 lists the analytical techniques used for each parameter and the respective detection limits.

Table 3.1 Water Chemistry Analytical Methods and Detection Limits

Parameter	Analytical Method	Detection Limit
Alkalinity	Colorimetric, automated, bromophenol blue	1.0 mg/l
Chloride	Colorimetric, automated, hydride-molybdenum blue	1.0 mg/l
Nitrogen		
-ammonia	Colorimetric, automated, phenate	0.05 mg/l
-nitrate, nitrite	Colorimetric, automated, hyrazine	0.05 mg/l
Sulphate	Colorimetric, automated, Methylthymol Blue (MTB)	2.0 mg/l
Potassium	Atomic Absorption	0.2 mg/l
Sodium	Atomic Absorption	0.5 mg/l
Calcium	Inductively Coupled Plasma	0.005 mg/l
Magnesium	Inductively Coupled Plasma	0.01 mg/l

3.2.2 Oxygen and Deuterium

Thirty-three oxygen isotope analyses of samples collected in the summer of 1998 were performed at the Quaternary Dating Research Unit (QUADRU) Environmentek laboratory at CSIR in Pretoria, South Africa. Six oxygen and deuterium isotope analyses of samples collected in 1999 were performed at Geochron Laboratories in Cambridge, Massachusetts.

QUADRU uses a SIRA 24 mass spectrometer equipped with a double collector, dual inlet system with both H/D and CNOS ion sources. For oxygen analysis the water is equilibrated with CO_2 gas and then the isotopes are analysed on the mass spectrometer. Geochron Labs uses a Vg Micromass 903 triple collector mass spectrometer for oxygen analysis and a Vg Micromass 602D double collector mass spectrometer for hydrogen analysis. The oxygen is prepared in a similar manner to that described above. The hydrogen uses a uranium reduction method, in which the sample water is passed over heated uranium producing H_2 gas. Both oxygen and hydrogen isotopic analyses were compared to Vienna Standard Mean Ocean Water (VSMOW). This is the current international standard. It differs only slightly from the older Standard Mean Ocean Water (Clark and Fritz 1997). The following standard formula (e.g. Clark and Fritz 1997, Mazor 1991) is used to convert the isotope ratio into delta notation :

$$\delta\text{Heavy ‰} = \frac{(\text{Ratio})_{\text{sample}} - (\text{Ratio})_{\text{standard}}}{(\text{Ratio})_{\text{standard}}} \times 1000$$

This equation compares the isotopic ratio of the analysed sample with that of a standard. Because the heavier isotope is in the numerator of the original ratio, a positive δ number indicates that a sample contains a higher proportion of the heavy than the standard, and a negative number indicates that a sample that contains a lower proportion of the heavy isotope.

3.2.3 Carbon

Thirty-three samples collected in the summer of 1998 for stable carbon isotope analysis were analysed at QUADRU Environmentek laboratory at CSIR in Pretoria, South Africa. The surface waters and four of the groundwater samples had dissolved inorganic carbon concentrations below the isotopic analytical detection limit. Thus, a total of seventeen carbon isotope measurements were obtained from the groundwater sampled in the summer of 1998. In order to obtain data for surface waters, two stream and four lake samples of a larger (1 litre) size were collected in 1999 and sent to Geochron Laboratories in Cambridge, Massachusetts. To complement the $\delta^{13}C$ data, two samples were collected for ^{14}C analysis - one lake and one well. These were also measured at Geochron Laboratories using Accelerator Mass Spectrometry (AMS).

Stable carbon analysis uses the same basic method as the oxygen and hydrogen analyses. CO_2 gas is extracted from the acidified sample and is analysed in the mass spectrometer. For $\delta^{13}C$ analyses QUADRU uses the SIRA 24 mass spectrometer and Geochron Laboratories uses the Vg Micromass 903 triple collector mass spectrometer. The mass spectrometer presents a ratio of ^{13}C over ^{12}C. This ratio is then compared to a standard (Vienna Pee Dee Belemnite or VPDB, again slightly different from the older PDB standard (Clark and Fritz 1997)).

The radioactive isotope ^{14}C is reported as a percentage of modern carbon (pmc). In order to keep analyses between laboratories standardized, the activity of "modern carbon" (100 pmc) is defined as 95% of the ^{14}C activity of the NBS (National Bureau of Standards) oxalic acid standard (e.g. Clark and Fritz 1997).

3.2.4 Nitrogen

Seventeen samples for nitrogen isotope analysis were measured at the QUADRU Environmentek laboratory at the CSIR in Pretoria, South Africa. All the samples contained N_2 at concentrations below the isotopic analysis limit of 2 mg/l.

3.2.5 Strontium

Thirty-three samples collected in the summer of 1998 were analysed for strontium isotopes at the Radiogenic Isotope Laboratory at the Council for Geoscience (Geological Survey of South Africa) in Pretoria, South Africa. Strontium was extracted from the samples using ion exchange columns followed by resin columns. The strontium was then loaded on single Ta filaments and run on a multicollector VG 354 thermal ionisation mass spectrometer with normalization to $^{86}Sr/^{88}Sr = 0.1194$. The $^{87}Sr/^{86}Sr$ ratios were then corrected for machine bias on the basis of analyses of the National Institute of Science and Technology (NIST) standard 987, for which the $^{87}Sr/^{86}Sr$ ratio is 0.710250. Strontium concentrations were determined by ICP mass spectrometry.

3.2.6 Uranium

Samples for analysis for uranium were only collected in the summer of 1998. The sample size ranged from 5 to 10 litres. They were acidified on the day of sampling with 3 ml/l of concentrated HCl in order to ensure that all the uranium complexes remained in solution and to prevent the growth of biological material. The samples were partially processed by the author at Dalhousie University (as described below) to produce a solid concentrate. The concentrate was then shipped to the Department of Geophysics of Tel Aviv University in Israel, where Dr. Joel Kronfeld performed purification and analysis using an alpha spectrometer. The next paragraph describes the concentration process and the following paragraph describes the process performed in Israel.

At Dalhousie University, four litres of sample were placed into an Erlenmeyer flask with 2 ml of calibrated ^{232}U spike and a ferric hydroxide carrier. This isotope does not occur in nature and so, by adding a known amount, the percent yield of the precipitation process can be calculated by alpha spectrometry. The percent yield can be used to calculate the solution concentrations of the naturally occurring isotopes. The solution was boiled for at least 25 minutes to break up the uranyl complexes. Ammonium hydroxide solution was then added until a pH of 9 was reached. This caused the precipitation of ferric hydroxide and the co-precipitation of uranium and other trace metals in the form of a floc. The precipitate was then separated, filtered, rinsed and placed in a Ziploc bag for shipment to Israel.

In Israel the solid precipitate was dissolved in hydrochloric acid and passed through a number of anion exchange columns, which allowed the separation of uranium from other trace metals. The resulting purified uranium was electroplated from an ammonium chloride electrolytic solution onto a platinum planchette. The planchette was then placed in an alpha spectrometer where the number and energy of the alpha particle emissions were detected. For further details on these techniques refer to Bhat et al. (1969), Veselsky (1974), Osmond and Cowart (1976), Lally (1992), and Wolf (1999).

3.2.7 Radon and Radium

The first nineteen radon samples collected during the summer of 1998 were analysed by Dr. Joel Kronfeld at Tel Aviv University in Israel within four days of the sampling date. Two subsequent sample batches totalling sixteen samples were shipped via courier, but no courier was able to get the samples to the lab within a reasonable time for accurate analysis. The time limit for analysis is roughly eight days, which is about two half lives of radon. After this period, the amount of remaining radon is too low to detect accurately at the concentrations present. For this reason a field radon detector was acquired and in the summer of 1999, a further thirteen analyses were made in the field, including some duplicates.

In Israel at Tel Aviv University, the radon was measured using a Scintrex RDU-2 radon analyser. After one month, during which time the excess radon had decayed, the radon gas was re-measured. The radon gas measured at this time represented the radon that was produced by its radium parent, and thus yielded the activity of the soluble radium.

The radon detection instrument used in the field in 1999 was a Durridge RAD 7 Radon detector with the RAD H_2O attachment for measuring radon in water samples. The instrument uses an air bubbling process to strip the radon gas from the water and then to pump it into a chamber containing a solid-state alpha detector. This detector measures the number and energy of alpha decays over a period of time. The decays of radon have a specific energy level and so can be differentiated from the decays of daughter products (RAD-7 manual).

3.3 Analytical Uncertainty

The following paragraphs discuss the errors associated with the field instruments, the water chemistry, the various laboratory analysed isotopes and the radon field instrument:

3.3.1 Field Measurements

The mercury thermometer is considered sufficiently precise that the human reading error is by far the main factor. The thermometer used was marked at each degree Celsius, so error is estimated at +/- 0.5 °C. The field pH, conductivity and TDS meter is listed as having an accuracy of 0.02 pH units and 0.5% conductivity/TDS (manual for The Oyster^{TM} pH + TDS + Conductivity Meter). Experience with daily re-calibration and multiple readings suggest that a conservative estimate would put these error values off by one order of magnitude. Thus, pH data should be considered accurate to +/- 0.2 pH units and conductivity/TDS at +/- 5%. Furthermore, the readout for conductivity and

TDS must be multiplied by 10 to achieve the correct units, which means that a value of 10 or 20 appears on the meter as 1 or 2. Thus, the final digit is not a significant digit. With the very low TDS and conductivity found in the study area this uncertainty is significant. For this reason a precision of +/- 10% is believed to be more representative of the TDS and conductivity readings.

3.3.2 Water Chemistry

The reaction error is determined by comparing the sum of the anions to the sum of the cations divided by the sum of the total dissolved ions. In all samples this was found to be within an acceptable 8%.

3.3.3 Isotope Analyses

The high cost of isotopic analysis prevented the use of duplicate samples. However, part of the standard procedure at Geochron Labs is to perform a duplicate analysis from the same sample. For the six samples collected for oxygen, hydrogen, and stable carbon analysis in 1999, the difference between duplicate analyses for each is: $\delta^{18}O = 0.1‰$, $\delta D = 2.0‰$, and $\delta^{13}C = 0.3‰$. The reported analytical error for the process for each of these isotopes is 0.1‰ for carbon and oxygen and 1‰ for hydrogen. Thus, the stated analytical error and the difference between duplicate measurements are very close.

The analytical errors reported for the ^{14}C analyses were both less than 0.5% modern carbon. The strontium analyses have an associated analytical errors of 0.005% for the $^{87}Sr/^{86}Sr$ ratio and 5% for the strontium concentration.

The uranium and radon analyses have associated statistical counting errors that depend upon the number of counts measured during the time interval, which was generally two to three days per sample for uranium. The radon counting time was approximately one hour per sample in the laboratory and 20 minutes for the field instrument.

4.0 WATER CHEMISTRY

4.1 Background

Ideally, every study of groundwater should include some basic chemistry to assist interpretation. In this study the temperature was measured at each sample location with a standard mercury thermometer. The pH, conductivity, and total dissolved solids (TDS) were measured with a field meter. At each location, a 500 ml sample was taken to be analysed for the four major cations (sodium, potassium, calcium, magnesium) and for three major anions (sulphate, chloride, and alkalinity). Nitrate, nitride and ammonia were also measured.

The methodology and analytical laboratories have been described in chapter 3. Chemical data can be used to group samples according to their chemistry. The Schoeller and Piper diagrams do this effectively using alkalinity (or HCO_3) and six of the most common ions in natural waters: K^+, Mg^{+2}, Na^+, Ca^{+2}, Cl^- and SO_4^{-2}. Fig. 4.1 is an example of a Schoeller diagram using data from samples from Israel (Mazor 1976), to show how chemically related waters may share a similar pattern while varying in concentration values. This example also shows that a change in concentration can be explained by mixing, dilution, or concentration effects.

The Piper diagram or trilinear diagram (Piper 1944, Back 1966) removes the effect of absolute concentrations by grouping certain ions and converts an individual ion concentration into a proportion of the group total. For example, the sodium concentration of a sample is divided by the concentration sum of sodium, magnesium and calcium (note that in many cases the sodium and potassium concentrations are combined into one factor). The results are then plotted on the ternary diagrams shown at the lower right and

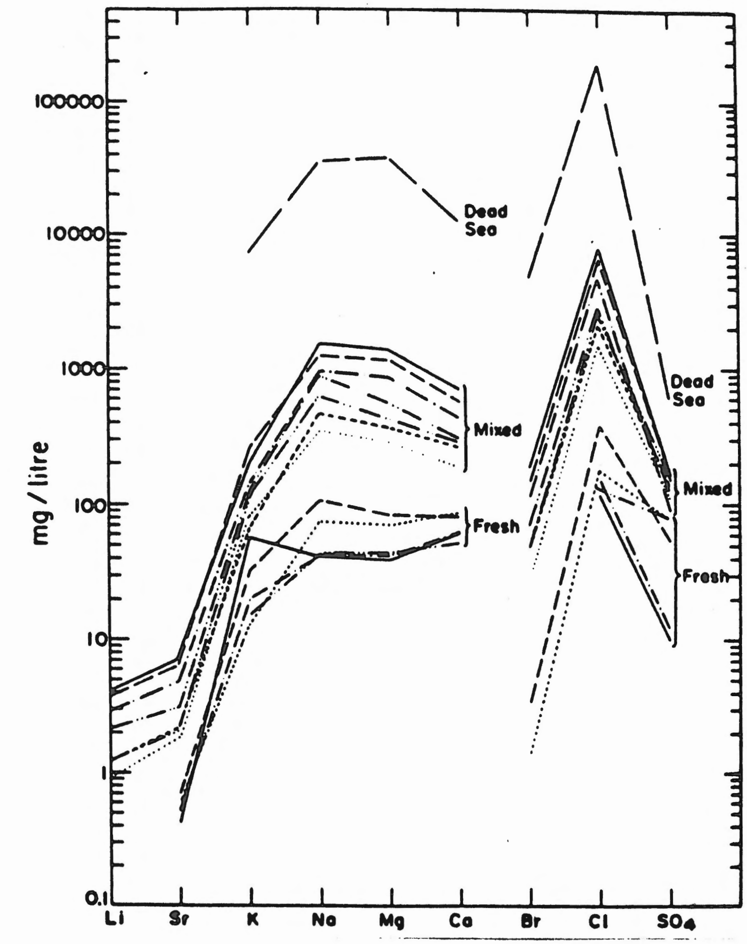

Fig. 4.1 Schoeller plot illustrating how related waters show similar patterns despite very different concentrations. Also note the location of intermediate waters interpreted as mixed. (Mazor 1976)

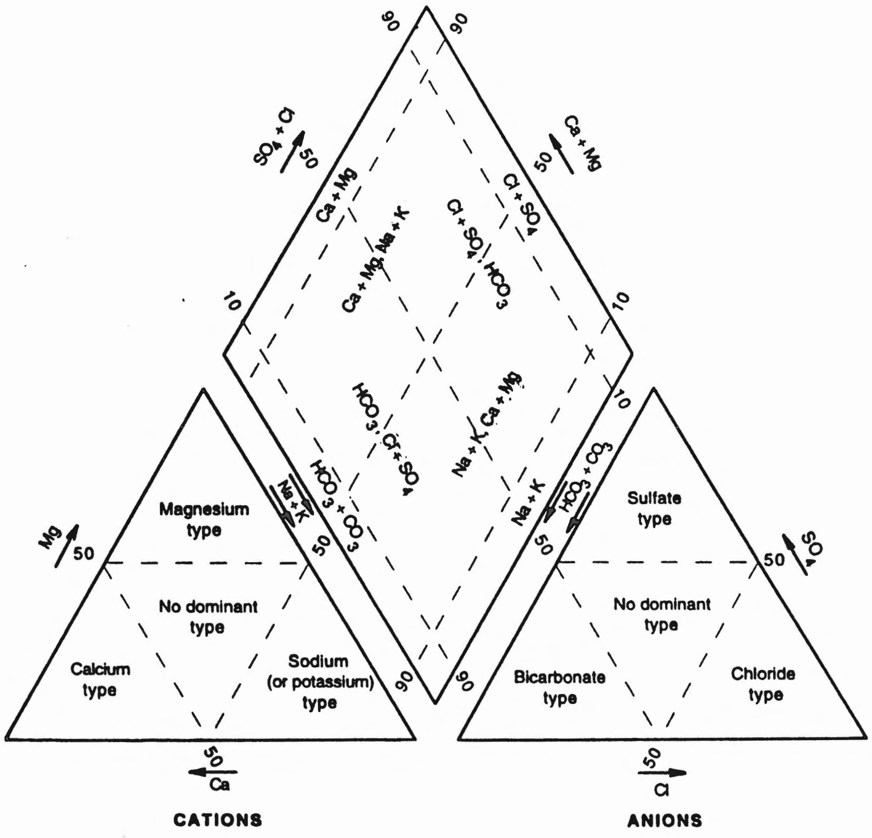

Fig. 4.2 Piper diagram layout showing hydrochemical facies which denote the dominant ions for various areas on the diagram. Note in the central part of the diamond figure, the ions after the comma are present but are less than 50% of the three component ions. (Drever 1997 after Back 1966)

left of Fig. 4.2. These ternary diagrams show which of the three components dominates in a sample. The data from two ternary diagrams can be combined into the tetrahedron shown above and between them (Fig. 4.2). The three plots together allow the sample to be characterized according to all six components. Linear relationships on these diagrams may represent mixing or evolution trends (Piper 1944).

Finally, chemical data can be analysed using standard x-y scatter plots. These plots generally use absolute concentrations in milligrams per litre, although moles per litre, milliequivalents per litre and ion activities are also common. The latter three units are useful when considering chemical reactions, because such reactions are not dependent upon the weight of chemicals but on the ratios in which chemicals combine.

4.2 Data and Interpretation

The data from this study are shown in Table 4.1. Four groupings are recognised based on Schoeller plots. Fig. 4.3 shows the first group, which is characterised by high values for the calcium and carbonate ions and consists solely of well water samples. For brevity this group will be referred to as the bicarbonate waters. Fig. 4.4 shows the second group, which is characterised by low values for the calcium ion and high values for sodium and chloride ions. This group will be referred to as the sodium chloride waters. Of the remaining eleven samples, three are shown in Fig. 4.5 as being characterised by very high values for the calcium and sulphate ions. These three samples will be referred to as outliers. The other eight samples shown in Fig. 4.6 represent a transitional state between the bicarbonate and the sodium chloride groups. Table 4.2 shows which samples are in each grouping.

Table 4.1: Avon Valley Water Chemistry Data

sample code	Temp. (°C)	pH	Conduct. µS/cm	TDS mg/l	Sodium mg/l	Potassium mg/l	Calcium mg/l	Magnesium mg/l	Sulphate mg/l	Chloride mg/l	Alkalinity mg/l
W12	14	5.56	90	50	2.6	0.53	10.1	1.03	3.2	2.5	31
W13	12.5	6	60	40	2.9	0.33	6.3	0.73	2.5	2.9	20
L14	24.5	4.6	20	20	3	0.37	0.94	0.31	1.9	4.5	1.2
W15	8.5	8	280	90	2.8	1.3	62	2	2.5	2.4	150
L16	25	4.9	30	20	2.9	0.27	0.92	0.31	1.8	4.3	1.2
W17	15.5	7.1	80	50	4.8	0.79	12	1.06	4.1	2.5	39
W18	22	6.75	280	190	4.5	0.78	52	2.2	5.5	5.5	126
L19	25	5.1	20	10	1.95	0.26	0.8	0.32	1.8	2.5	1.8
W20	14.5	6.3	600	410	95	2.2	29	2.2	18	260	33
S21	25.5	5.5	20	10	2.1	0.21	0.73	0.29	1.8	3	1.8
W22	10	7.32	320	210	4.3	6.6	57	4.63	12.8	5.2	151
W23	14.5	7.49	520	350	9.2	3.4	90.1	11.9	31.7	8.8	241
W24	12	5.8	190	130	8.8	3.1	22.1	2.38	28.6	14	41
W25	18.5	5.2	310	210	30.1	1.1	28.9	4.24	64.3	54	17
S26	25	7.23	540	360	10.6	1.5	100	3.58	217	19	40
S27	25	7.03	1480	980	9.1	7.2	382	5.09	860	12	82
W28	17.5	6.78	1020	690	101	3.8	97	11.8	26.7	206	169
W29	17	6.51	1110	740	97.7	3.1	102	10.2	13.8	260	122
W30	12.5	6.56	110	70	10.9	0.9	9.81	0.98	5.3	20	21
W31	19	6.46	410	270	18.7	3	55.9	6.17	13.3	48	111
S32	14.5	5.74	130	90	20	1	4.25	1.4	3	32	17
L33	20	5.3	20	20	3.7	0.4	0.7	0.32	2	6.6	1
W34	21	6.97	190	130	5.7	1.5	39.2	2.57	8	6	99
W35	14.5	6.8	360	240	13.4	2.1	71	7.15	14	22	181
L36	24.5	5.5	20	10	3.7	0.5	0.814	0.31	2	6	2.5
W37	14	7.33	120	80	3.8	3	26.2	0.69	5	4.3	72
W38	20	6.02	230	150	36.2	1.8	11	2.03	6.7	58	36
W39	19	6.38	100	60	3.4	0.7	17.1	0.79	2.8	3.8	50
W40	17	6.95	450	300	8.4	1.2	106	3.51	28	16	235
W41	19	5.58	120	80	14.8	1.1	7.77	1.8	9.3	24	18
S42	11	5.24	120	80	20	0.8	3.63	1.21	3	35	9.1
L43	12	4.6	20	10	2.7	0.4	0.68	0.33	3	5.1	1
L48	14	4.86	20	10	2.4	0.5	1.16	0.4	2	4.9	1.7
L49	11.5	4.9	20	10	1.9	0.4	1.1	0.5	2.5	4	1
R52	14	5.54	20	10	2.2	0.5	1.31	0.43	2.5	4.5	1.7
L54	13	7.13	1840	1220	42.7	1.3	426	5.91	950	69	88
S55	14	5.5	20	10	2.2	0.5	1.43	0.41	2	4.9	2
S56	9.5	5.6	130	90	22.6	0.7	2.3	0.77	4.3	36	6
W57	11	7.3	350	230	2.8	1.7	80.4	2.32	2	3	211
W58	11.5	6.7	80	50	4.1	0.9	12.1	1.03	5.3	3.3	39
S59	9.5	5.9	20	10	1.7	0.4	2.32	0.43	2	4	4.2
W60	12.5	5.72	250	170	46.7	2	9.36	2.12	7	71	23

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

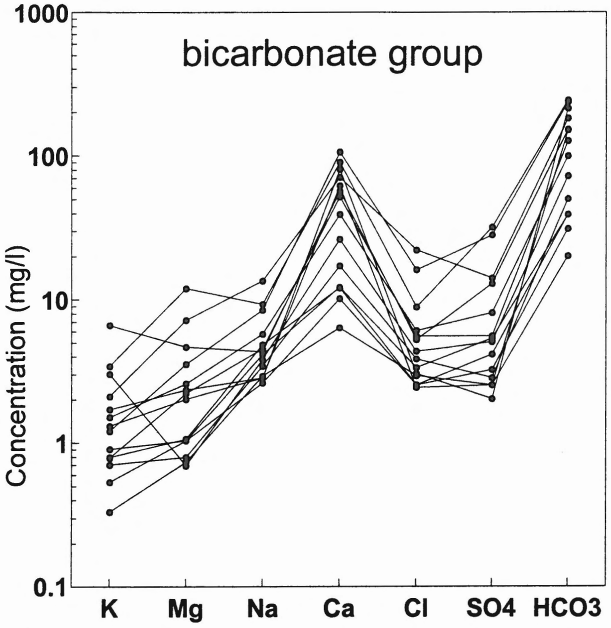

Fig. 4.3

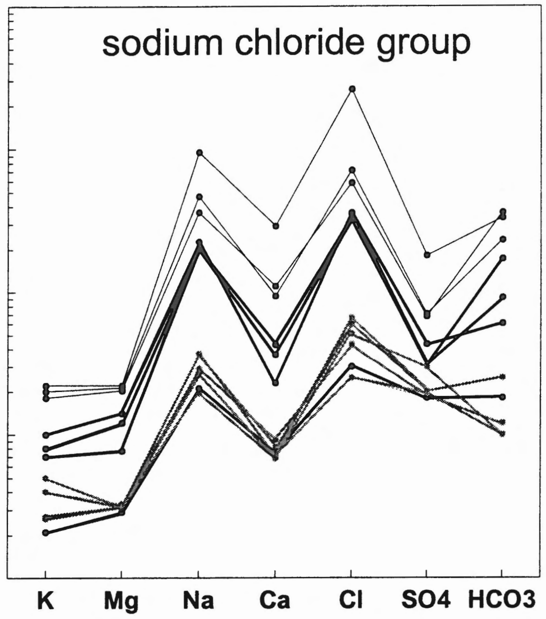

Fig. 4.4

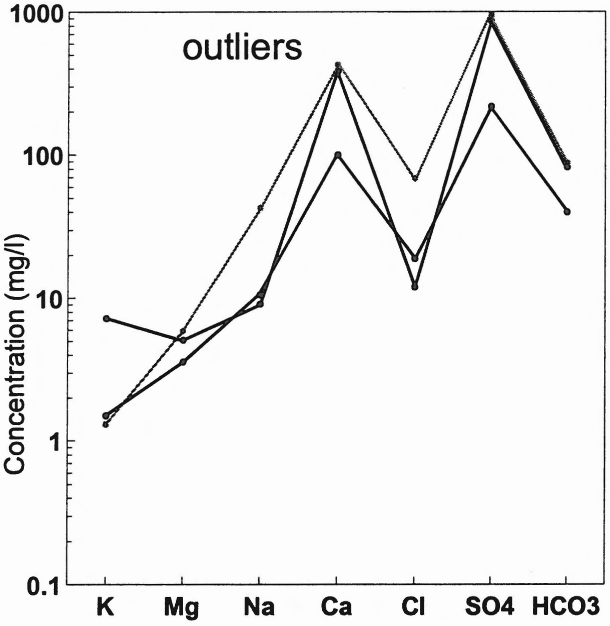

Fig. 4.5

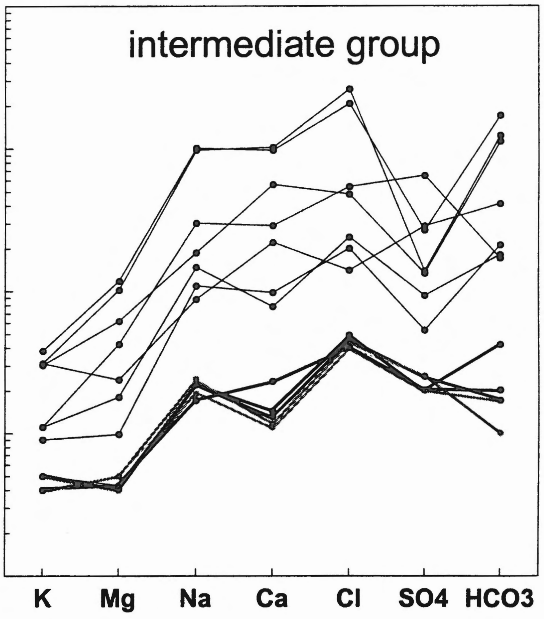

Fig. 4.6

Figs. 4.3-4.6 All Schoeller plots set at the same scale. Note that conventionally the positions of sodium and magnesium are reversed. This pattern is preferable for this data. Graphs show thin black lines for well waters, thick black lines for streams and thick grey lines for lake samples. See Table 4.2 for sample numbers in each group.

Fig. 4.3 This plot includes the samples with calcium and carbonate peaks.

Fig. 4.4 This plot includes the samples with sodium and chloride peaks.

Fig. 4.5 This plot includes the samples with calcium and suphate peaks.

Fig. 4.6 This plot includes the samples that do not fit into the previous three groups.

Table 4.2: Sample Numbers According to Chemical Grouping.

Water Group	Lake Samples	Stream Samples	Groundwater Samples
calcium bicarbonate	none	none	12, 13, 15, (57), 17, (58), 18, 22, 23, 34, 35, 37, 39, 40
sodium chloride	33, (43), 14, (48), 16, 19, 36	32, (42), (56), 21	20, 38, (60)
intermediate	49	52, (55), 59	24, 25, 28, 29, 30, 31, 41
outliers	54	26, 27	none

Note: Samples in brackets represent repeated samplings at the same location as the preceding sample number (see Fig. 2.2).

These groups are also clearly distinguishable on a Piper diagram (Fig 4.7). The bicarbonate waters are all groundwaters and plot in a cluster on the left-hand side of the central tetrahedron. All but three of the sodium chloride waters are surface waters and plot on the far right of the tetrahedron. The three outliers are all surface waters and plot at the very top of the tetrahedron well away from all the other samples. The intermediate waters lie between the bicarbonate and sodium chloride groups but are clearly closer to the sodium chloride samples. This agrees with the concentration pattern of the Schoeller plot in Fig. 4.6.

Fig. 4.8 shows the data points on the central tetrahedron according to the 4 groups that have been defined using the Schoeller plots. Fig. 4.9 shows how the Piper plot allows samples to be categorised by their dominant ions depending on where they plot on the tetrahedron. For example the outliers plot in the area where dominance by calcium and magnesium crosses over the area of dominance by chlorine and sulphate. Thus any or all of those components may dominate the intermediate waters. The ternary diagrams in Fig. 4.7 reveal that only calcium and sulphate are significant components of the

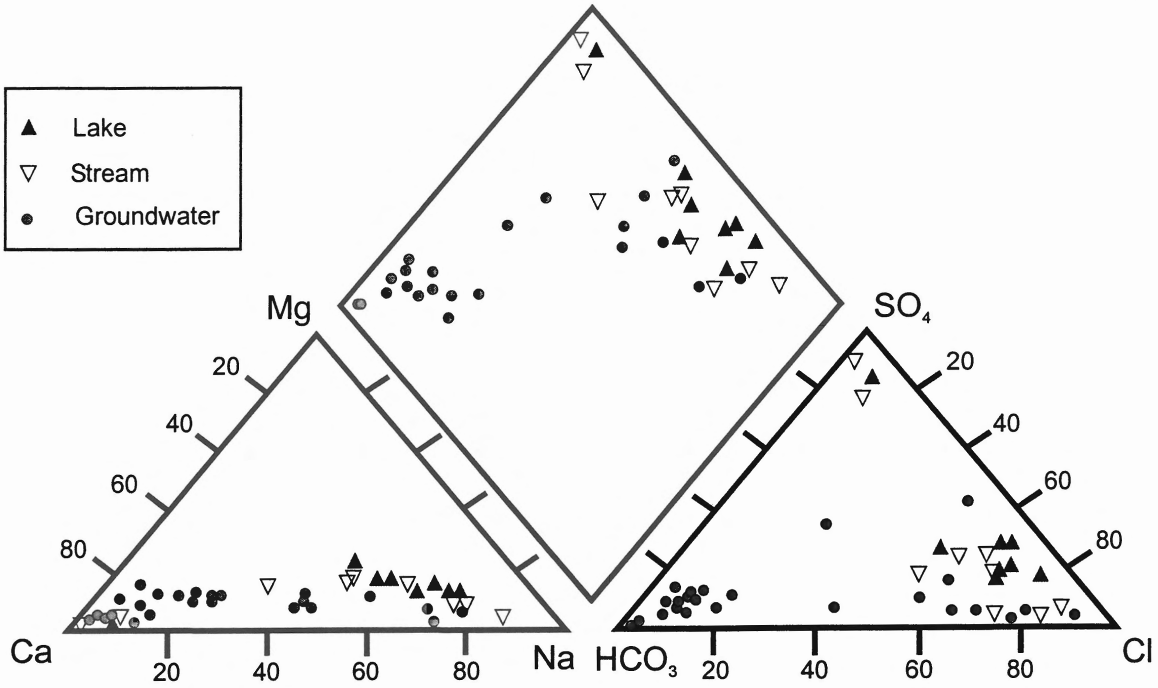

Fig. 4.7

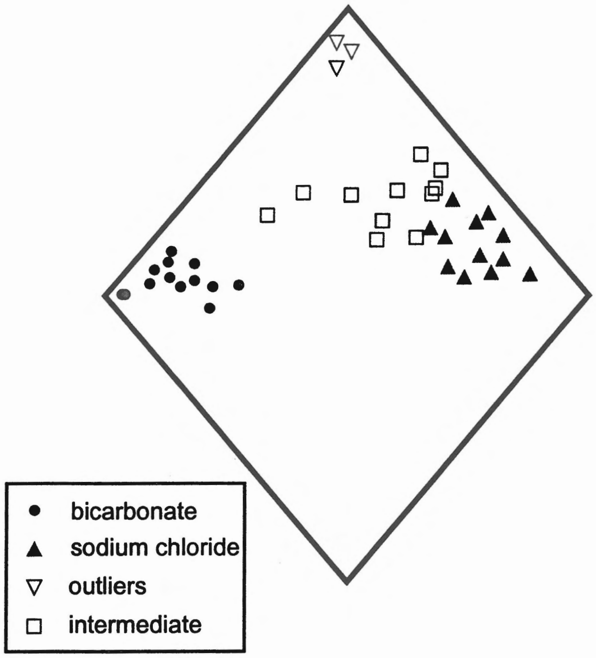

Fig. 4.8

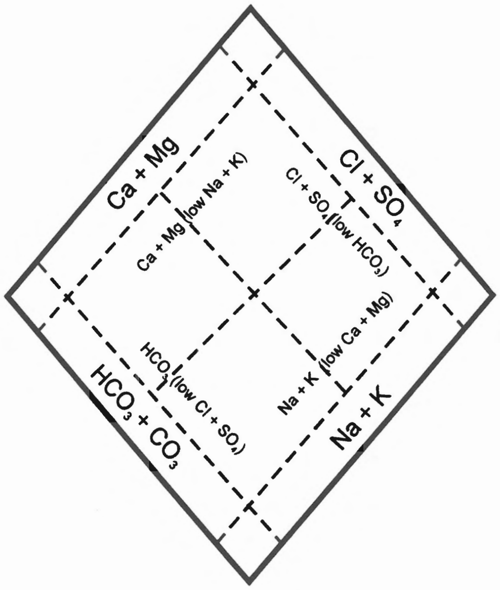

Fig. 4.9

Figs. 4.7 - 4.9 Piper plots. Fig. 4.7 is a complete Piper plot showing the position of lake, stream, and well water samples. These samples can be categorized by their chemistry using the information on Figs. 4.2 and 4.9 (Drever 1997 after Back 1966). These are shown in Fig. 4.8 plotted by chemical water type.

outliers. In this way the water groups identified by the Schoeller diagrams are also characterised on a Piper plot as calcium bicarbonate waters, sodium chloride waters, an intermediate group, and calcium sulphate outliers. The Piper plot shows that the intermediate group lies between the bicarbonate and the sodium chloride groups more clearly than do the Schoeller diagrams (Fig. 4.8).

The water groups are not geographically grouped nor do they correlate with bedrock type with the exception of the three outliers. The outliers are all surface waters that occur directly over Carboniferous sedimentary bedrock (stream samples 26, 27 and lake sample 54). The dissolution of gypsum, known to be present in this bedrock, accounts for the very strong calcium sulphate signature of the outliers. The water chemistry of the remaining groups is dependent upon the extent of water-rock interaction. The sodium chloride waters are interpreted to represent slightly salty rainwater with only minor dissolved mineral content. The bicarbonate waters are groundwaters that have dissolved some calcium carbonate-bearing material. The intermediate waters have had more limited contact with the carbonate material and so have not had the salt-water signature completely overprinted.

This interpretation suggests that the waters of the Avon Valley evolve from immature, slightly salty precipitation on the far right of the Piper diagram to more mature calcium carbonate waters on the left. This is the reverse of the usual interpretation of groundwater evolution on a Piper diagram. Groundwater is typically considered clean and immature when it has a calcium carbonate signature. It matures into a high concentration salty brine due to extensive interaction with aquifer rocks. On the Piper plot this appears as an evolution from left to right. The difference is due to the extreme immaturity of the Avon sodium chloride waters which are essentially rainwater with very low dissolved ion concentration. Thus the bicarbonate group waters can be considered mature only when compared to these very clean samples. The waters sampled in this study have not begun to evolve into what is normally considered mature groundwater. For the sake of simplicity, the bicarbonate waters will be referred to as mature, but that is only relative to the other samples in this study. The remainder of this chapter will discuss further evidence for the interpretation of these water groups.

In Figs. 4.10 and 4.11, chloride is plotted against sodium. The plots include a line with a slope of 1, which is the expected trend for the direct dissolution of salt (NaCl). Also included is a line with a slope of 1.17, which is the ratio of chloride to sodium in sea water. This ratio might be expected in precipitation that includes some ocean aerosol component.

The data in Fig. 4.10 show a good linear correlation ($r^2 = 0.96$). Fig. 4.10 shows three outliers that do not fit either plotted line, having an excess of chloride. The rest of the data show the high concentration sodium chloride waters close to the salt dissolution line. This suggests that these waters have a dissolved salt component. Fig. 4.11 shows the low concentration sodium chloride data surrounding the aerosol line. This suggests that the low concentration sodium chloride waters contain airborne salt. This conclusion is supported by studies in Nova Scotia dating as far back as the work by Gorham in 1957, which shows that ocean salts are common in maritime lakes. Fig. 4.11 shows the bicarbonate data points falling below the salt dissolution line but parallel to it. This

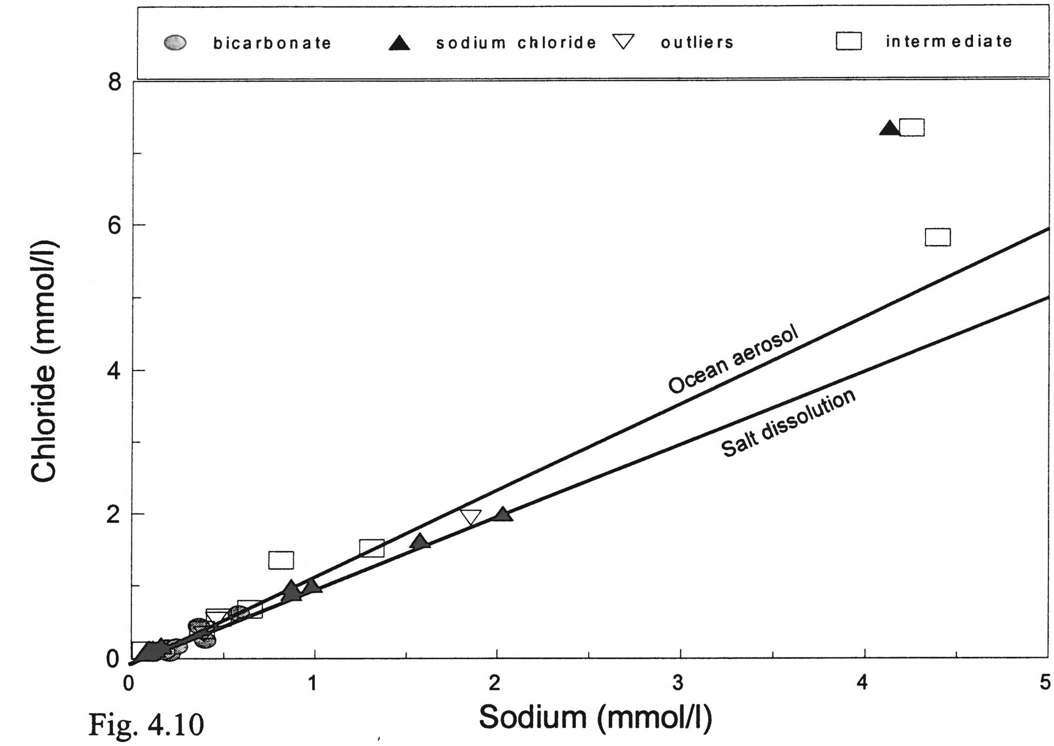

Fig. 4.10

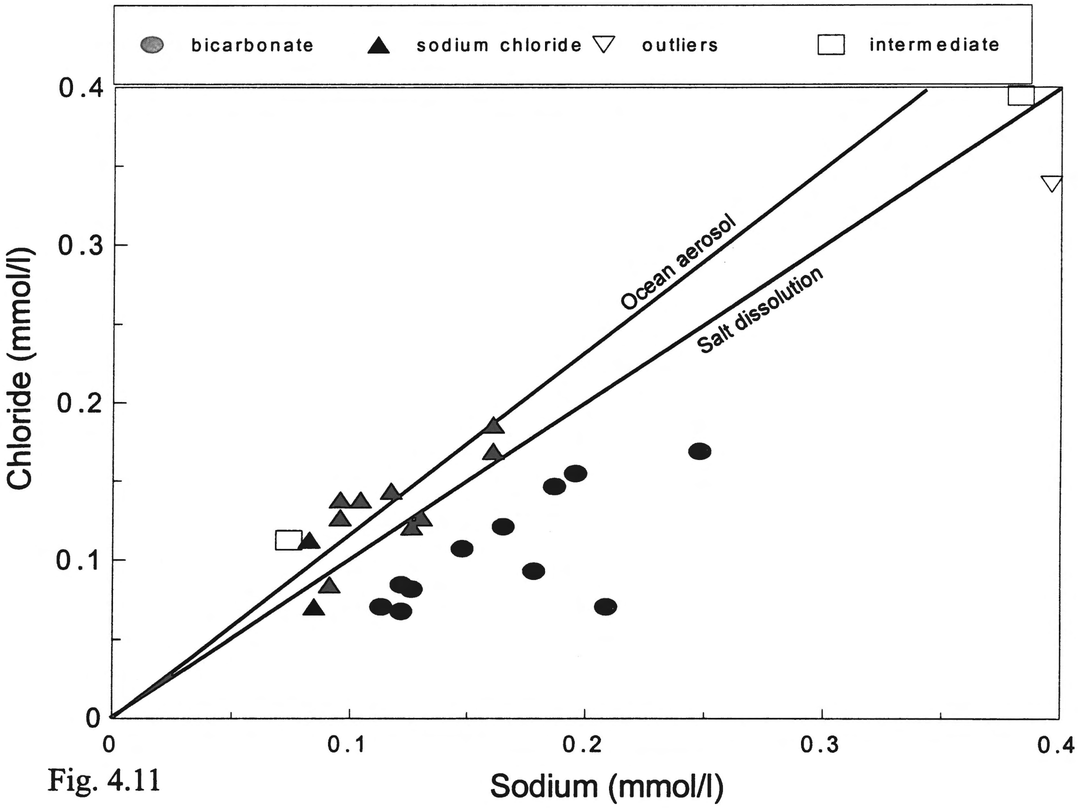

Fig. 4.11

Figs. 4.10-4.11 Plots of sodium vs. chloride showing lines at the slope expected of the ratio of sodium to chloride in airborne sea salt and that expected by direct dissolution of salt. Fig. 4.10 shows all the data and Fig. 4.13 focuses on the lower concentrations.

suggests the addition of sodium from another source, such as the weathering of albite feldspars. This is quite likely, considering that the bicarbonate waters are interpreted as having had more water-rock interaction than the sodium chloride waters. The higher sodium chloride concentration samples can not be explained by airborne sea salt. Dissolution of evaporite salt from the glacial till is a plausible explanation for these data. An alternate explanation is the infiltration of winter road salt in the form of NaCl, which would show the same trend as evaporitic NaCl dissolution. Some of the sample data variability may be due to sources of chlorine and sodium other than salt, such as feldspar and mica weathering.

Further evidence that the surface waters are essentially rainwater is the very low conductivity and TDS readings of the samples of lakes and many of the streams. This 'clean' character can be seen in the fact that the lakes plot very low on the Schoeller diagrams (Fig. 4.3 - 4.6). Groundwaters plot the highest, and streams fall in between, suggesting that the streams are a mixture of ground and surface waters. The surface waters are also characterised by low pH. This has usually been attributed to a mixture of organic acids and acid rain (Gorham 1957). The few stream samples and the lake with higher pH and conductivity belong to the outlier group of samples taken near Windsor which overlie rocks that contain abundant carbonate material (stream samples 26, 27 and lake 54). Thus, their high concentration of dissolved components and high pH can be attributed to dissolution of readily available limestone and gypsum bedrock. Alternatively, their chemistry may be a result of greater groundwater input, which is expected if the lowlands are indeed a recharge area.

The higher ion concentration and pH of the groundwater samples support the idea that the groundwater has experienced greater water-rock interaction, allowing dissolution of ions and buffering of the low pH rainwater.

The interpretation that the bicarbonate waters receive their calcium carbonate from dissolved limestone is supported in two ways. Firstly, all samples except for the outliers show a correlation between alkalinity and calcium (r^2 = 0.90). The linear relationship suggests that both components come from the same source, and the most likely source is calcium carbonate or limestone. Figs. 4.12 and 4.13 show that this correlation is improved when magnesium and sulphate are included (r^2 = 0.98). The improvement in the correlation suggests that the dissolution of gypsum is also a component of the water chemistry. In fact the correlation shown in Figs. 4.12 and 4.13 includes the outliers group, which supports the interpretation that the chemistry of the outliers is a result of gypsum dissolution. Since most of the samples come from the granitic highlands, the source of the limestone is not bedrock in most cases. However, the dominant till in the area is Lawrencetown Till, which is noted to contain abundant material from the Carboniferous units that include limestone and evaporite strata (see sections 2.1 and 2.2). The location of these strata in the northern part of the study area lends further evidence to this idea, since that direction would have been up-ice during some stages of recent maritime glaciation (Finck and Stea 1995). Thus, the chemistry of the bicarbonate waters is most likely a result of water-rock interaction with limestone and gypsum in the glacial till.

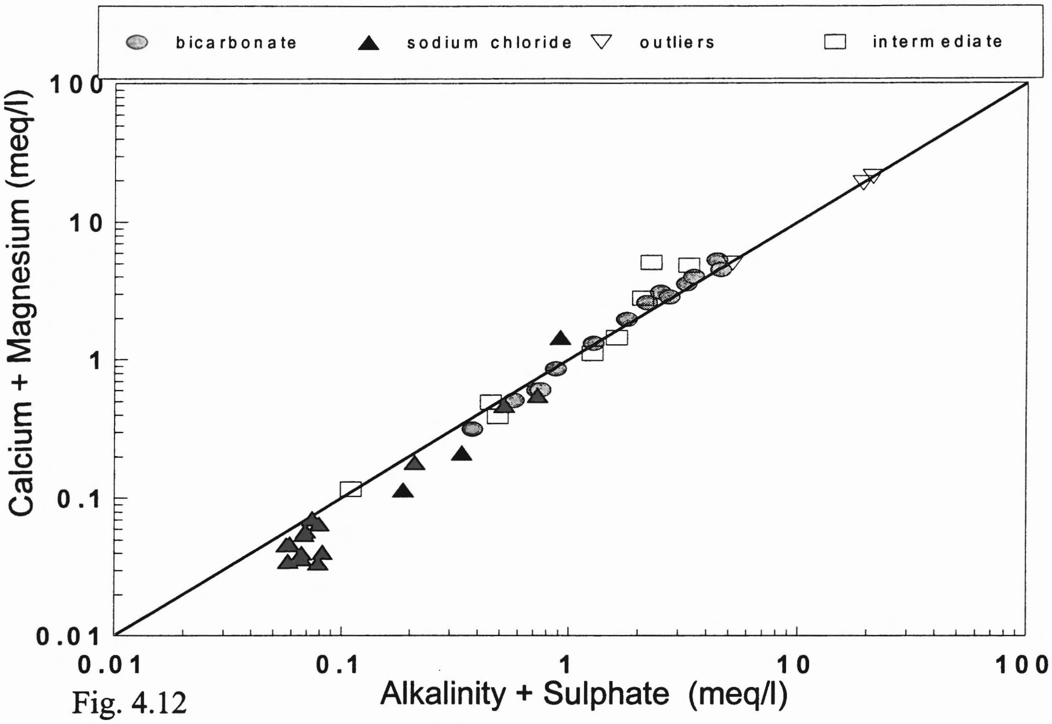

Fig. 4.12

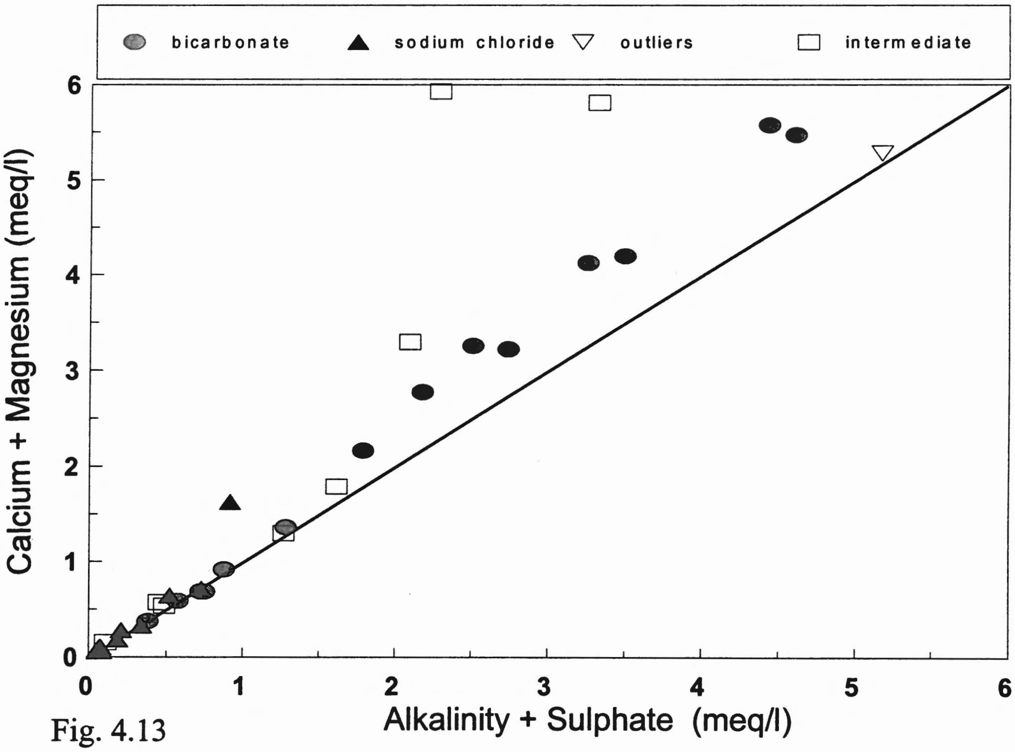

Fig. 4.13

Figs. 4.12-4.13 These plots share the same x and y axis components but Fig. 4.12 has logarithmic axes and Fig 4.13 has linear and does not show the outliers. The plots show a reasonable agreement with the included 1:1 line. This suggests that the chemistry of the samples is a result of dissolution of limestone containing some magnesium along with calcium and some dissolution of gypsum to provide the sulphate.

The second piece of evidence that limestone dissolution is the source of the calcium and alkalinity is the fact that all but two samples are undersaturated with respect to calcite (Fig. 4.14). This means that the waters of the Avon Valley will actively dissolve any calcite they come into contact with. The fact that the groundwaters are closer to saturation supports the interpretation that the groundwaters have experienced more water-rock interaction than have the surface waters. Wells 15 and 23 that are just above saturation in Fig. 4.14 are not used for domestic water supplies and so their water is likely quite stagnant. This would allow more time for the water to dissolve calcite and so become saturated. The program Hydrowin™ was used to calculate the saturation index of various minerals (Appendix 2) which are consistently well below saturation. This suggests that even the 'mature' bicarbonate waters do not have a long residence time in the Avon Valley.

The difference between the chemistry of the lakes and of the groundwater suggests that there is not significant input into the lakes from the groundwater. This situation is not the normal hydrological situation shown in Fig. 4.15 and described in most textbooks (e.g. Judson and Kauffman 1990, Dolgoff 1996). Lakes are generally seen as places where the land surface goes below the water table. As water is removed from the lake, groundwater recharges it. Attanayake (1986) completed a study of some Nova Scotia lakes on granitic bedrock and their groundwater input by using seepage meters. Estimates based on his data suggest that these lakes only received between 16.4 and 3.4% of their volume from groundwater. Looking at the calcium data from this study as an example, it can be seen that the lake water concentrations are between 10 and 100

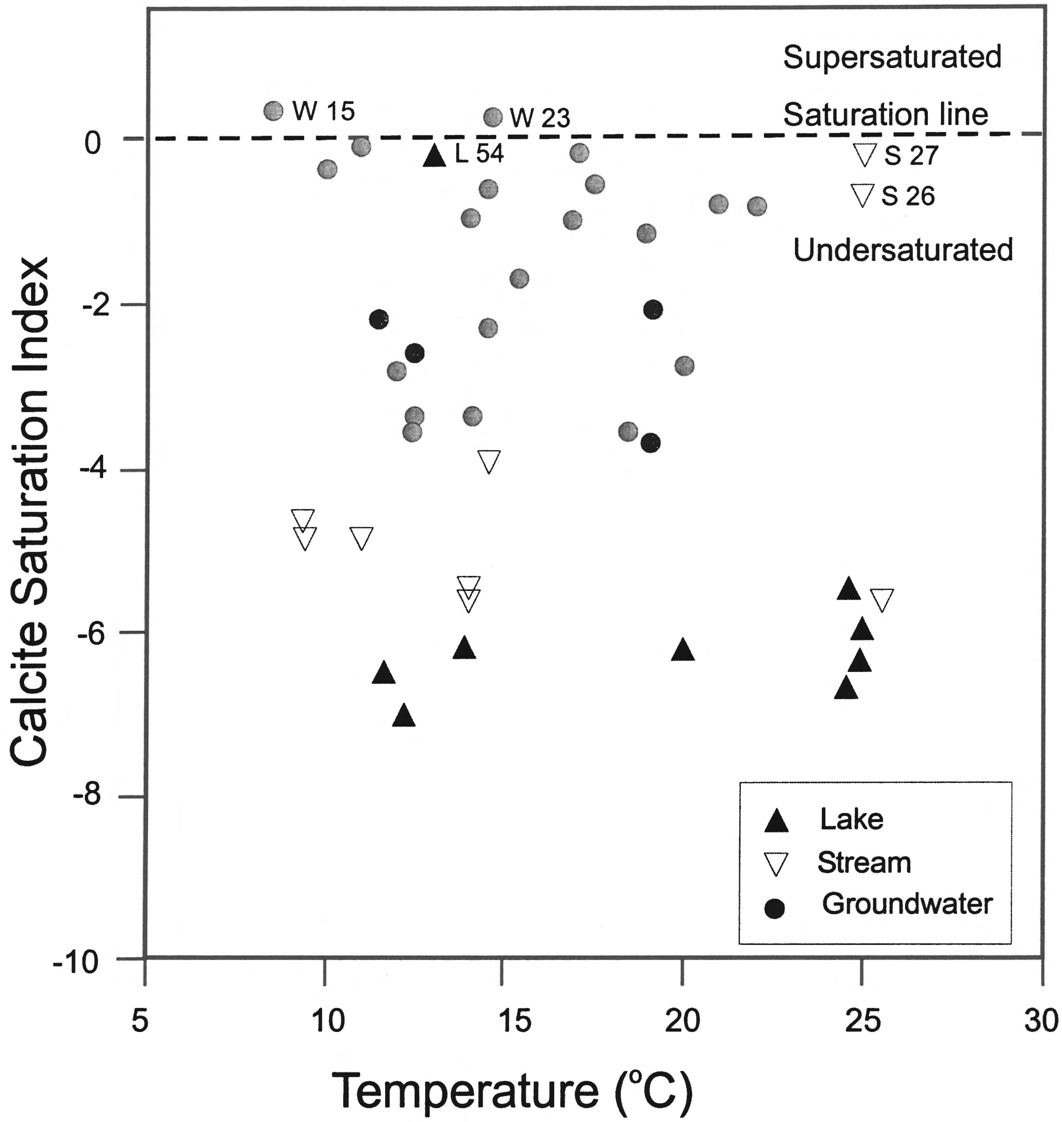

Fig. 4.14 Plot of calcite saturation index vs. temperature with the dashed line at zero representing saturation with respect to calcite. Above that line the sample is supersaturated and below that line it is undersaturated. The only two well waters that are saturated are well 15 and 23, both of which are wells that are not heavily used for domestic needs, thus allowing some stagnation which may explain the degree of saturation. The three surface waters plotting near to saturation (lake 54 and streams 10 and 11) are all from the lowland area and so have abundant carbonate material available to them.

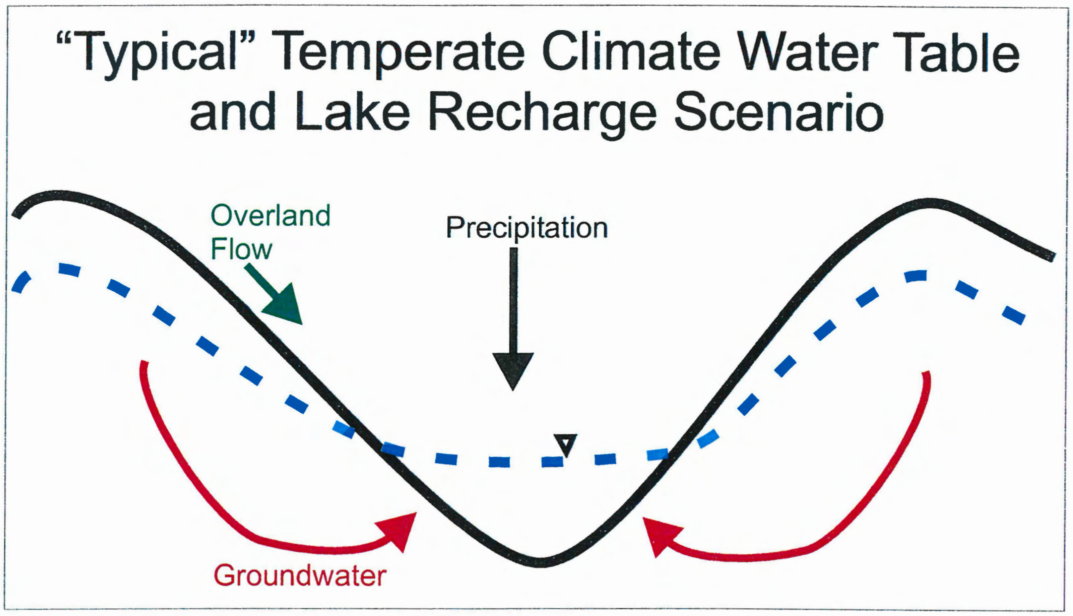

Fig. 4.15 Schematic cross-section showing the typically accepted model for groundwater recharge of surface waters such as lakes and streams.

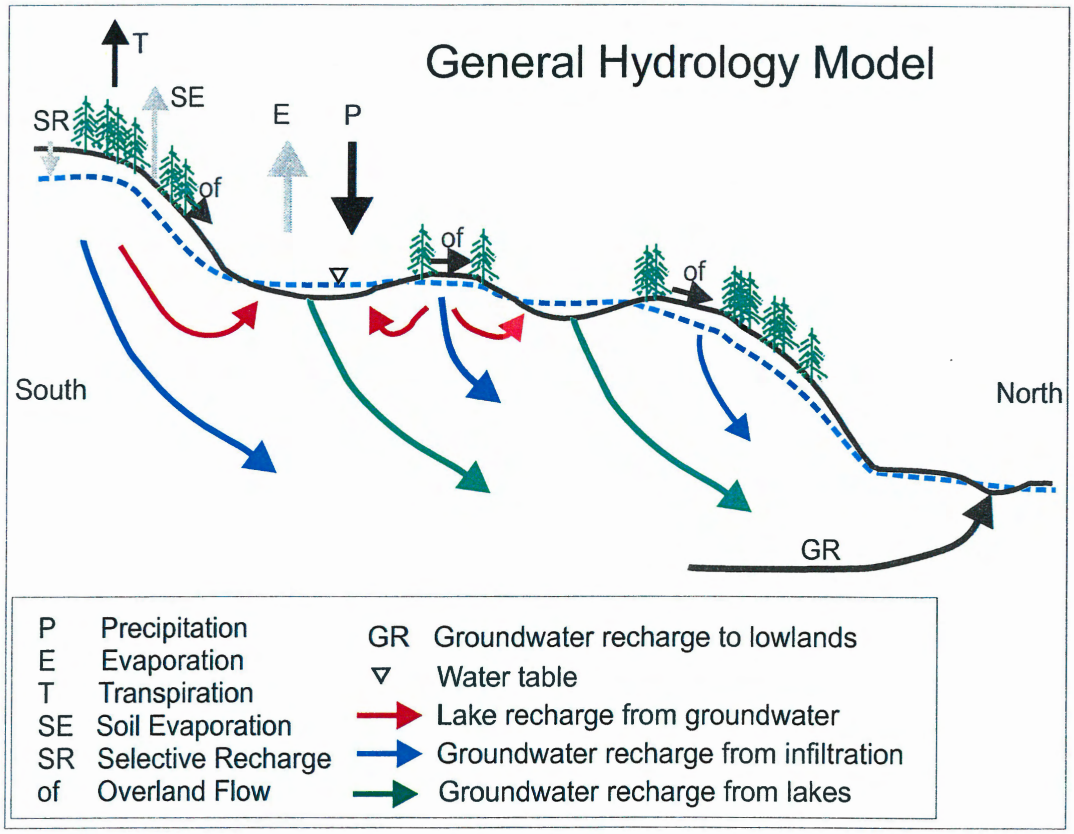

Fig. 4.16 Schematic cross-section of the Avon Valley from south to north showing typical flow patterns and water cycle inputs and outputs.

times lower than the groundwater concentrations (Table 4.1). This suggests that the groundwater input is responsible for between 1 and 10% of the lake volume, which overlaps with the estimates based on the Attanayake data. Fig. 4.16 shows a schematic of the hydrologic flow proposed for the Avon Valley from south to north. In this schematic the granitic highlands in the south are the recharge area for the groundwaters that discharge to the lowland farming areas. The calcium data shown in Fig. 4.17 show that the difference between the lakes and the groundwater does not allow for significant groundwater input into the lakes. To achieve this, lake water must either be cut off from the groundwater system or feed into the groundwater without being recharged by it. The latter possibility is generally only seen in 'losing lakes' which occur in arid climates where the lake surface is higher than the surrounding water table. This situation is unlikely in Nova Scotia, so the former solution of having the lakes cut off from the groundwater is preferable. This would require that the lake bottoms have such low permeability that groundwater is prevented from entering them. Lake cores from this area of Nova Scotia commonly show a thick (>4 inches) layer of dense clay below the modern sediments of the lake and above the glacial till or bedrock (Dr. Ian Spooner, personal communication 2000). This layer could prevent the usual interaction between lakes and groundwater. It also explains why the streams, lacking this clay layer, would show the effect of groundwater input.

In summary, the waters of the Avon Valley can be grouped according to their chemical signature, which is an indication of the extent of their water-rock interaction. The surface waters are also distinct from the groundwaters due to this water-rock

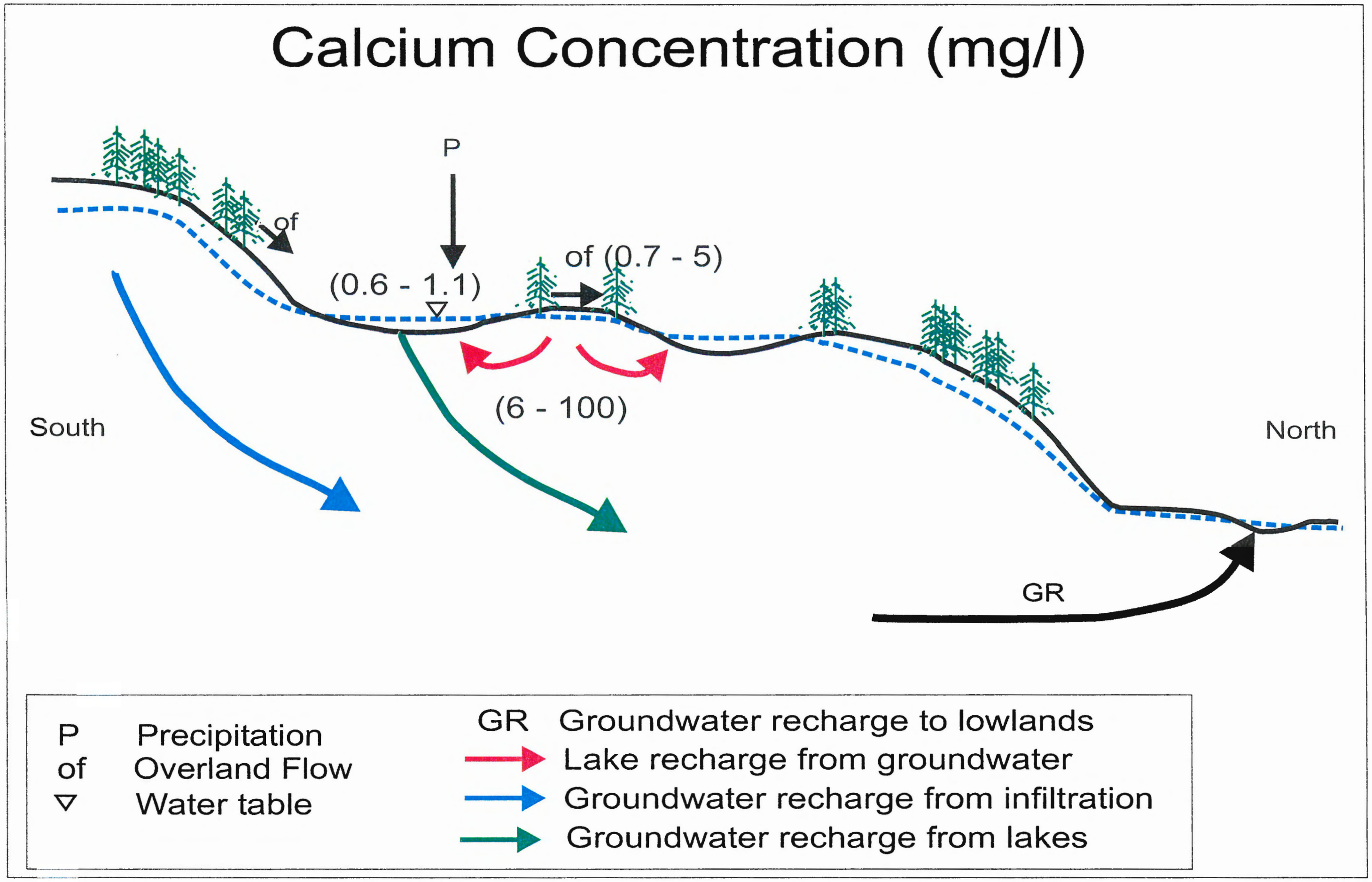

Fig. 4.17 Schematic cross-section of the Avon Valley from south to north showing the range of concentration of calcium for various parts of the system. Note that the lake water is between 10 and 100 times less concentrated than the groundwater. This indicates that the groundwater could not be contributing significantly to lake recharge.

interaction. A sodium chloride signature dominates the lake waters, some of the streams, and a few groundwater samples. This signature appears to be a result of oceanic salt precipitation in the low concentration samples. At higher concentrations, the dissolution of additional salt from another source is required. Current data cannot differentiate between road salt and Windsor Group evaporitic salt.

The majority of the groundwaters shows a calcium bicarbonate signature. The data best fit a system in which limestone and gypsum are both involved in the dissolution. The evolution of these waters from low concentration sodium chloride waters to the calcium bicarbonate waters as shown on the Piper diagram is unusual in that groundwater maturity normally progresses in the reverse direction. This difference is a result of the immaturity of the Avon Valley waters: the more mature waters are just approaching the chemistry that is usually considered immature, while the immature waters are essentially rainwater. The immaturity of the water in the Avon Valley is shown by the fact that all but two samples are undersaturated with respect to calcite. The evolution of the groundwater is illustrated by the linear nature of the relationship between calcium and alkalinity: the waters show an increase in both their alkalinity and their calcium concentration as they dissolve limestone. The concentration difference between lake waters and groundwater suggests that the lakes receive less than 10% of their volume from groundwater input. This may be due to a clay layer on the lake bottom, which prevents groundwater recharge.

5.0 OXYGEN AND HYDROGEN ISOTOPES

5.1 Background

Isotopes of oxygen and hydrogen are very useful in hydrological studies, because they tend to be chemically conservative in low temperature environments (Mazor 1976). This is because the oxygen and hydrogen involved in the isotopic analysis are the atoms of the water molecule itself. Thus, during a simple exchange reaction such as the dissolution of calcite, the number of oxygen atoms added by the calcium carbonate dissolved in a litre of water is insignificant compared to the number of water molecule oxygen atoms present in that litre. The two exceptions to this general rule are high temperature reactions and reactions of small volumes of water with large volumes of rock over geologic time scales (Clark and Fritz 1997, Mazor 1991). Since neither of these exceptions applies in this study, the processes affecting oxygen and hydrogen isotopes are essentially physical processes.

The ultimate source and sink of all surface water is the ocean, and this is where the initial isotopic signature is defined. Meteorological processes, such as evaporation and condensation, fractionate the isotopes and determine the signature of the water that falls as precipitation (Clark and Fritz 1997). The fractionation is controlled by the difference in energy required to transport the different isotopes. Evaporation from the ocean's surface favours the lighter isotopes, since they require less energy to move. Thus, clouds are formed with a lighter isotopic signature than oceanic water. Condensation tends to remove the heavier isotopes, so clouds become further enriched in the light isotope. Since most global evaporation takes place at the equator and the cloud masses move north and south from there, the isotopic signature of precipitation over the globe tends to reflect the fact that clouds are increasingly depleted in the heavier isotopes with distance from the equator. Fig. 5.1 shows a portion of the worldwide pattern for $\delta^{18}O$ in rainfall as a yearly average. This pattern is referred to as the latitude effect (Clark and Fritz 1997). The figure also shows the continental effect: large landmasses tend to cause rainout, which increases the rate at which the isotopic signature becomes more negative.

Clark and Fritz (1997) and Mazor (1991) describe altitude and seasonal effects. Both are reflections of the effect of temperature on water phase changes. The altitude effect is a result of the decreasing temperature and increasing precipitation as vapour is forced to rise over high topography. The result is isotopic depletion (water becoming lighter or more negative) ranging from –0.15 to –0.5‰ per 100m rise in altitude. The seasonal effect also reflects the isotopic depletion due to lower temperature, but it is caused by seasonal temperature variation rather than elevation. It is important to note that the fractionation from gas to solid phase causes greater depletion than from gas to liquid. The result of this is that winter snow precipitation has much more negative values than does summer rainfall. The gas to solid phase fractionation effect is only significant at latitudes that experience snowfall.

These processes are also represented in surface waters that are in contact with the atmosphere. However, once water enters the saturated zone, its oxygen and hydrogen isotopic signature tends to remain constant. For this reason oxygen and hydrogen isotopes are routinely used as tracers to study different bodies of groundwater.

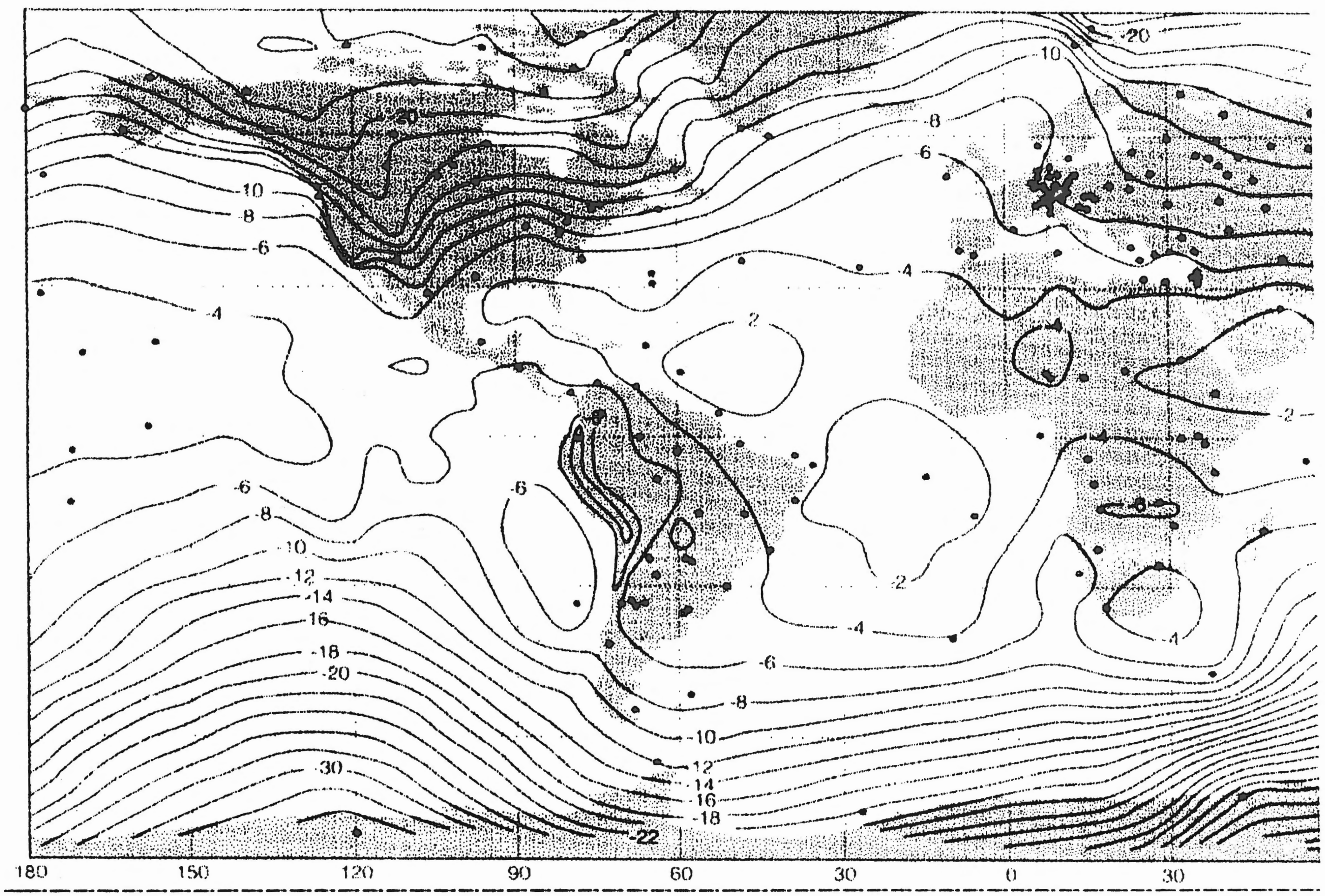

Fig. 5.1 Mean δ^{18}O distribution in precipitation for a portion of the globe including stations with at least 24 months of records. (Based on the IAEA World Meteorological Precipitation monitoring data summarized by Rozanski et al. 1993.) Figure modified from Clark and Fritz (1997).

The seasonal and temperature effects can be seen directly in data from Truro, Nova Scotia, one of the International Atomic Energy Agency and the World Meteorological Organization's (IAEA/WMO) global network of precipitation monitoring stations. The Truro station was used for the collection of meteorological data and the analysis of stable oxygen and hydrogen isotopes in precipitation from 1975 to 1983. These data are available on the web (IAEA/WMO 1998) and are shown in Figs. 5.2 to 5.4. Fig. 5.2 shows the seasonal effect very clearly. The winter months show generally lower $\delta^{18}O$ values reflective of some snow precipitation (average ~ -12‰). The summer months exhibit higher values, reflective of liquid precipitation (average ~ -7‰). Fig. 5.3 shows how well these monthly-averaged $\delta^{18}O$ values correlate to the monthly average temperature (direct temperature effect). Note that the points that fall below -18‰ probably result from months dominated by snow precipitation. Figure 5.4 is a plot of $\delta^{18}O$ vs. $\delta^{2}H$ for the Truro data and for six samples from surface waters in the Avon Valley. The linearity of the data shows that the effect of temperature on isotopic fractionation is a consistent effect on both oxygen and hydrogen isotopes. The result is that colder winter months with snow precipitation plot with very negative numbers, while warm summer rainfall plots closer to zero. The line formed by the data is referred to as a Local Meteoric Water Line (Ingraham 1998). Water samples that plot off this line reveal surface or subsurface processes affecting the water isotopes (Clark and Fritz 1997). The surface process of interest to this study is the potential evaporative effect on the lakes, which would make samples plot lower and to the right of the data in Fig. 5.4 (note dashed line).

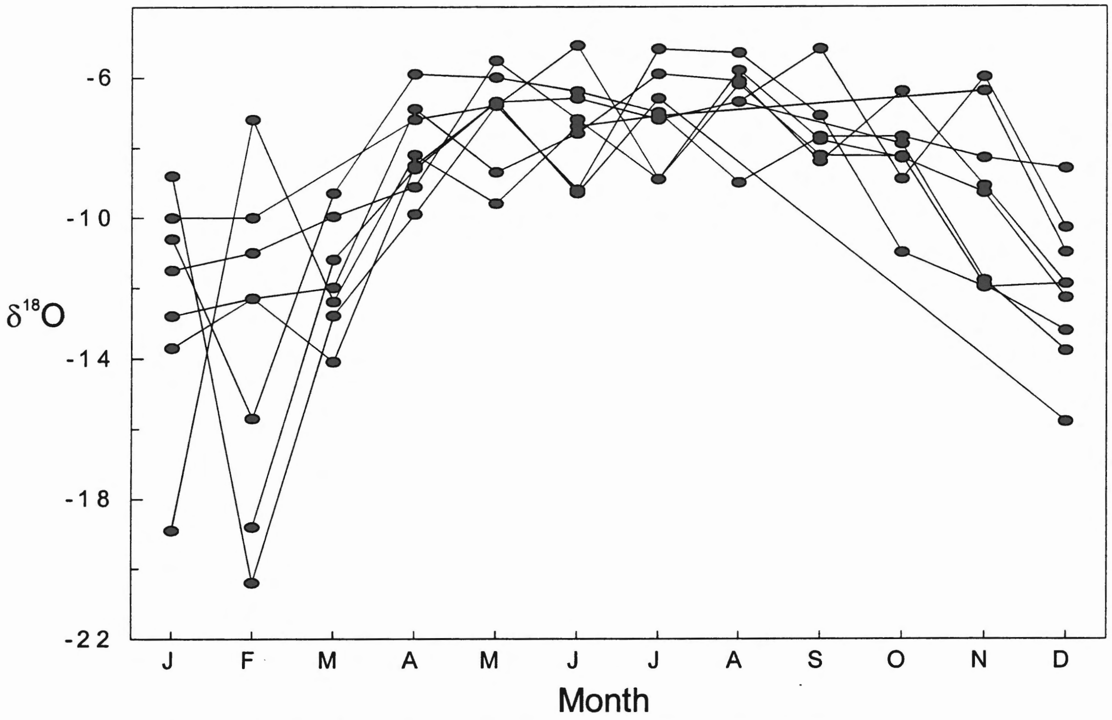

Fig. 5.2: Monthly average rainfall $\delta^{18}O$ for Truro from 1975 to 1983 (data from IAEA/WMO 1999).

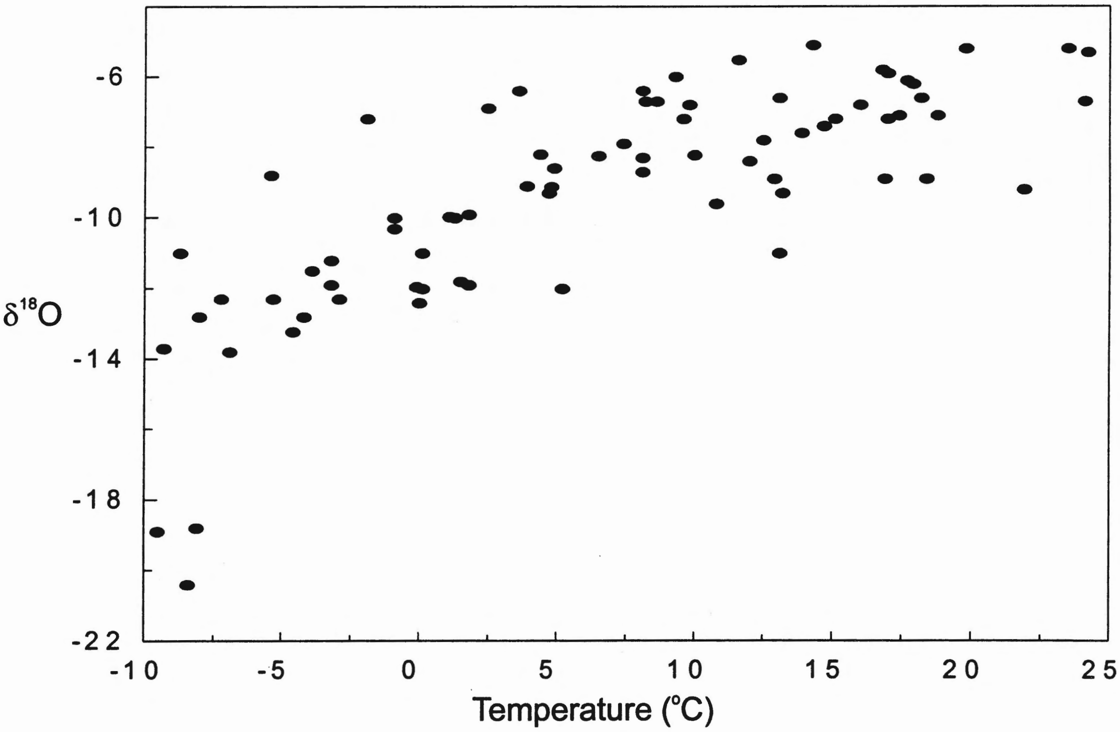

Fig. 5.3: Monthly average rainfall $\delta^{18}O$ versus temperature for Truro from 1975 to 1983.(data from IAEA/WMO 1998).

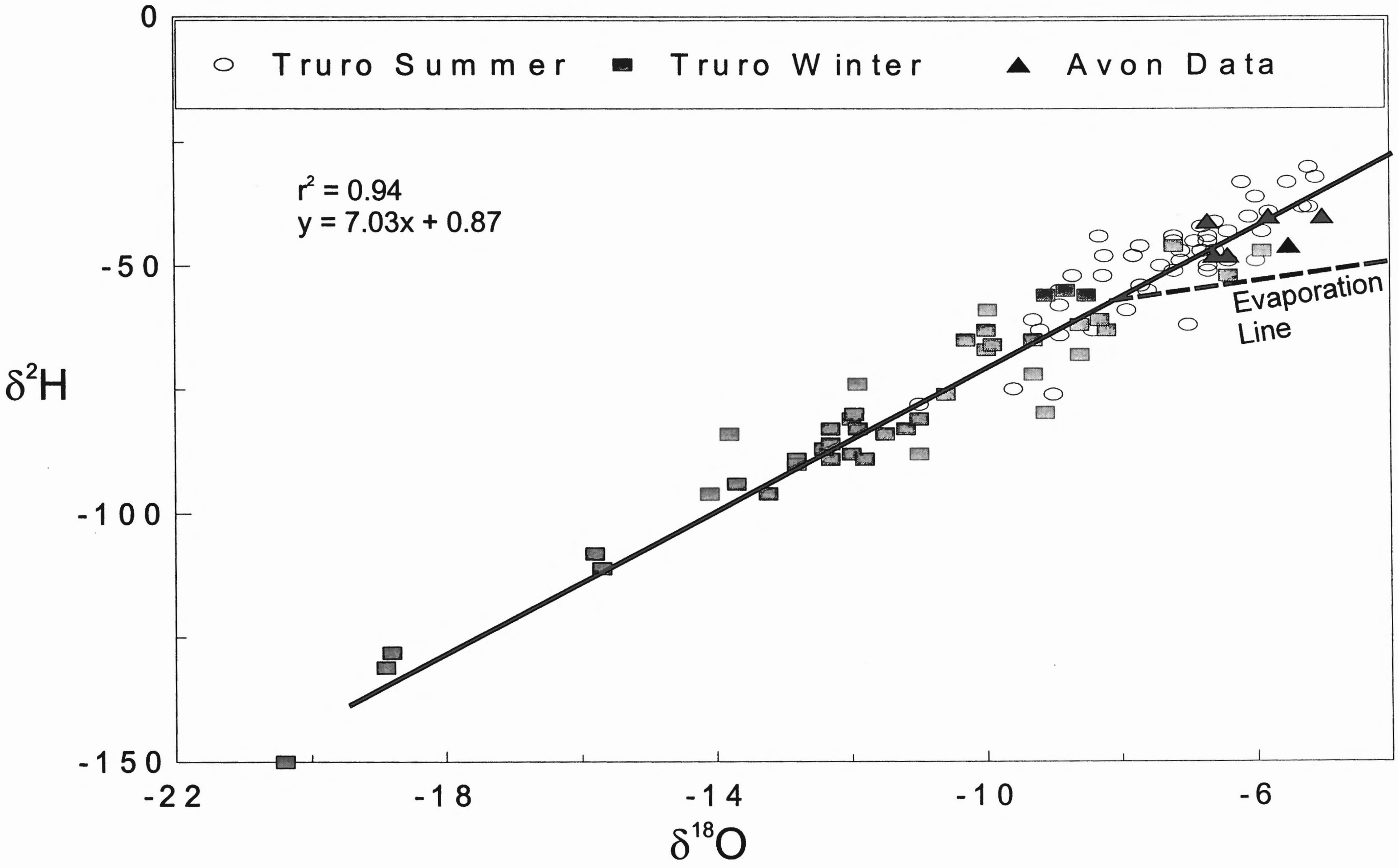

Fig. 5.4 Truro δ^2H vs $\delta^{18}O$ data showing the Local Meteoric Water Line. (Data from IAEA/WMO 1999). The data for this study are shown as "Avon Data". The dashed line shows the trend expected for waters affected by evaporative fractionation.

5.2 Data and Interpretation

The oxygen and hydrogen isotope data for the Avon Valley are shown in Table 5.1. The rainwater samples from Ellershouse and Halifax are shown in Table 5.2. The six Avon Valley samples showing both oxygen and hydrogen data were collected from surface waters in the summer of 1999. These data are plotted with the Truro data on Fig. 5.4. Since they plot within the grouping of data from Truro, it is suggested that surficial evaporation does not affect the isotopic composition of these surface waters. Water that has experienced evaporation would have had its oxygen and hydrogen signature altered such that it would plot below and to the right of the Local Mean Water Line (Clark and Fritz 1997).

The fact that the Avon Valley data fall right on the meteoric water line formed by the Truro data also suggests that the Truro data represent well the precipitation in the study area. Truro is located approximately 80 km east of the study area and, like Windsor, is very close to the Bay of Fundy. In order to validate the use of data from the 1970s and 1980s, rainwater samples were collected in 1999 at Halifax and at Ellershouse, which is only 10 km east of the study area. These data are shown in Table 5.2 and are plotted in Fig. 5.5. The data are highly variable as would be expected from individual rainfall events (Ingraham 1998, Gat 1980) but give a direct average of -6.7‰. This value is consistent with the Truro data summer average. When samples at Halifax and Ellershouse were collected on the same day, July 26th, 1999, their isotopic signatures were the same. This suggests that significant rainfall events provide water of a consistent isotopic signature from Ellershouse to Halifax (~ 45 km apart).

Table 5.1: $\delta^{18}O$ and $\delta^{2}H$ data for waters of the Avon Valley.

Sample Code	$\delta^{18}O$	$\delta^{2}H$
	‰ VSMOW	
S01	-8.0	
L02	-7.6	
L03	-8.2	
S04	-8.9	
S05	-9.0	
L06	-8.4	
L07	-8.2	
L09	-8.2	
S10	-9.1	
S11	-8.9	
W12	-8.8	
W13	-8.9	
W15	-9.2	
W17	-9.2	
W18	-9.3	
L19	-7.5	
W20	-8.3	
S21	-7.5	
W22	-9.8	
W23	-9.6	
W24	-9.3	
W25	-9.0	
W28	-9.1	
W29	-9.9	
W30	-9.7	
W31	-9.1	
W34	-8.5	
W35	-8.5	
W37	-8.8	
W38	-9.1	
W39	-9.7	
W40	-9.6	
W41	-9.7	
S42	-6.6	-48
L43	-6.4	-48
L48	-5.8	-41
L49	-5.0	-40
S52	-5.5	-41
L54	-6.7	-46

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well sample.

Table 5.2: $\delta^{18}O$ data for rainwater collected in Halifax and Ellershouse.

Sample Code	$\delta^{18}O$ ‰ VSMOW	Sample Date
H1	-11.2	21-Jun-99
H2	-3.7	29-Jun-99
H3	-7.4	10-Jul-99
H4	-7.7	14-Jul-99
E5	-9.1	17-Jul-99
H6	-4.4	19-Jul-99
E7	-6.7	23-Jul-99
H8	-5.2	26-Jul-99
E9	-5.3	26-Jul-99
E10	-9.5	07-Aug-99
H11	-7.4	09-Aug-99

Note: The letter prefix of the sample code refers to sample collection site: H for Halifax and E for Ellershouse.

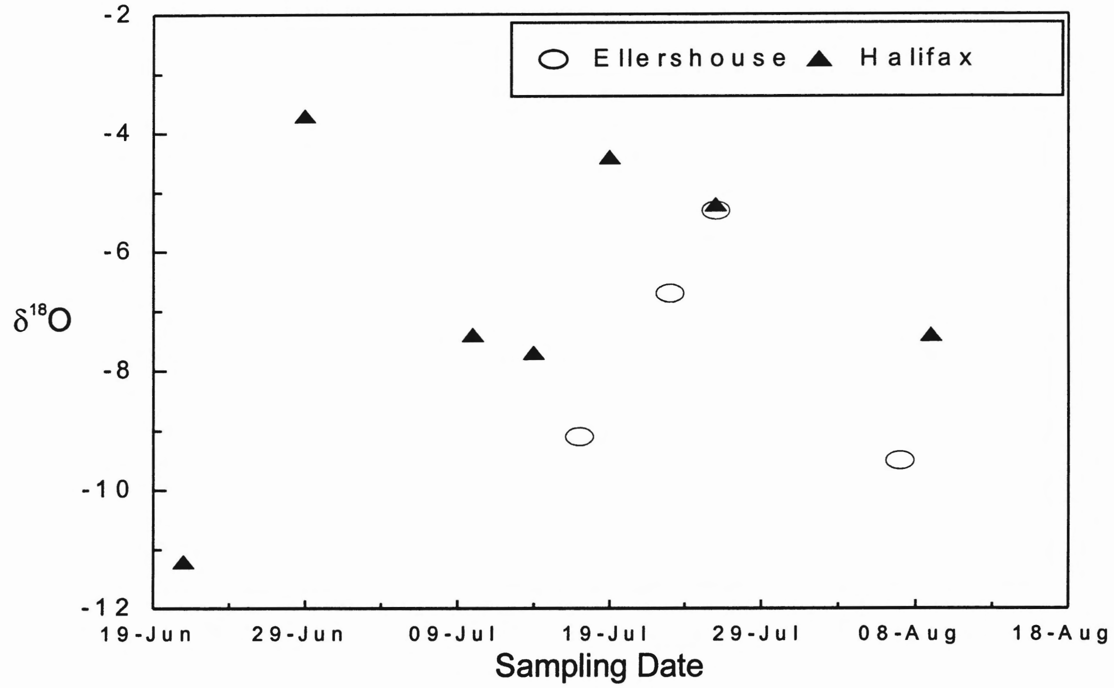

Fig. 5.5 Rainwater $\delta^{18}O$ data collected in the summer of 1999 in Halifax and Ellershouse. The variability for individual rainfalls is common. The average of the data agrees with Truro summer rainfall data. Note that on the one date the sample sets have in common (26th of July), the same isotopic value was reported.

Fig. 5.6 shows the $\delta^{18}O$ values for this study plotted against sample location (in UTM northing). The data range from –7‰ to –10‰, well within the range of data from Truro (Fig. 5.2) and could simply reflect direct rainfall values. These data have an r of -0.67 and an r^2 of only 0.46, suggesting that the correlation is not statistically significant. However, the graph clearly shows a difference between the values in the south (less negative or heavier) and those in the north (more negative or lighter). The change in values appears to be consistent and gradual from south to north, especially if only the mature bicarbonate waters are considered. The bicarbonate waters have an r^2 of 0.74 which is considered a reasonably good correlation. Seasonal attenuation of isotopic variation is the best explanation for the south to north change in isotopic values. The change in values is not explained by altitude effect, latitude effect, or lake evaporation.

Fig. 5.7 shows that the $\delta^{18}O$ values in the surface waters have the heavier values and correspond well with the expected summer rainfall values of about -7‰ (Fig. 5.2). The groundwater values in the northern area, which are lower in the catchment basin, are closer to a combined average value for summer and winter precipitation (~12‰). Clark and Fritz (1997) describe a process called "attenuation of seasonal variations" in which the seasonal variation in $\delta^{18}O$ values of the infiltrating rainfall is reduced with depth by mixing (see Fig. 5.8). Using this model, the surface waters in the southern highlands reflect recent rainfall $\delta^{18}O$ values, but the groundwater experiences a steady mixing of this recent water with older water from the previous season(s). The degree of mixing is increased with flow direction as the waters gather together, particularly where the Avon Valley narrows at the scarp of the South Mountain Batholith. In this way the change in

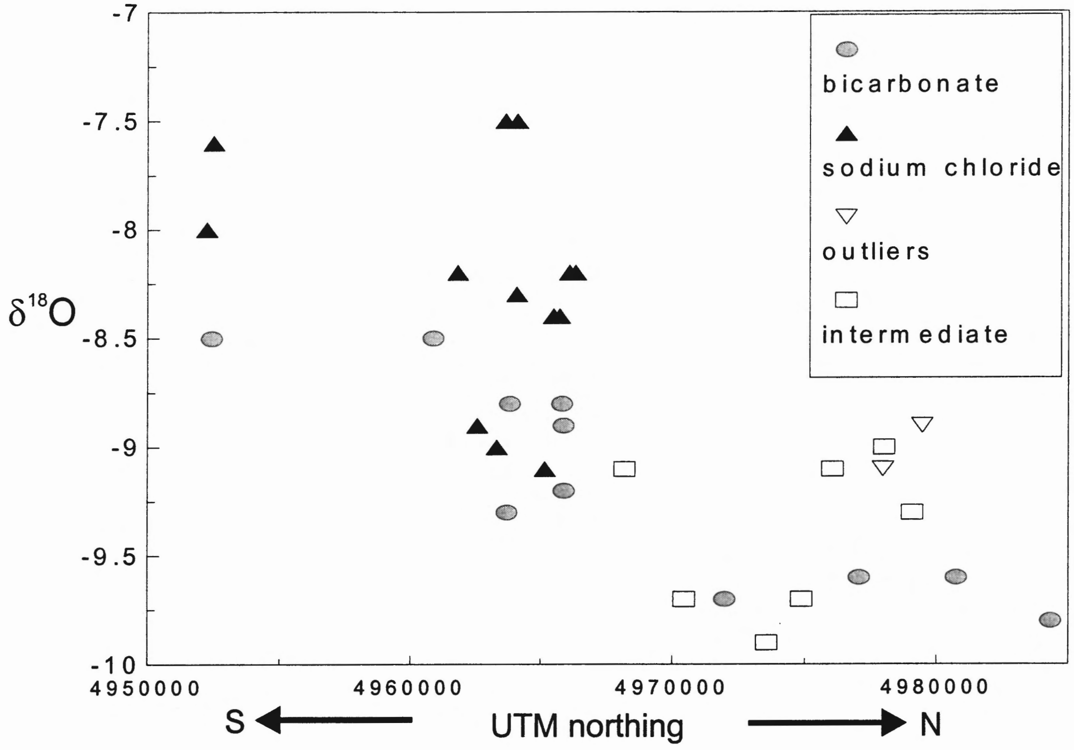

Fig. 5.6 δ^{18}O values plotted against sample location. Note the steady change in values from south to north.

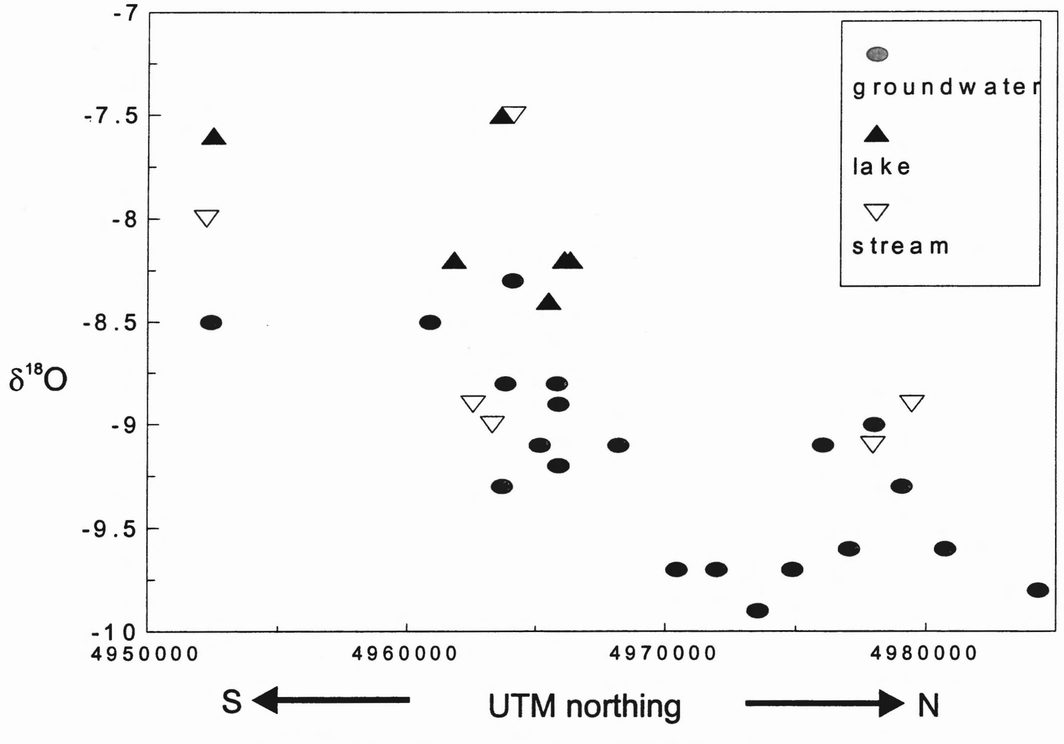

Fig. 5.7 δ^{18}O data for surface and groundwater samples in the Avon Valley plotted against sample location. Surface waters are consistently higher in δ^{18}O value.

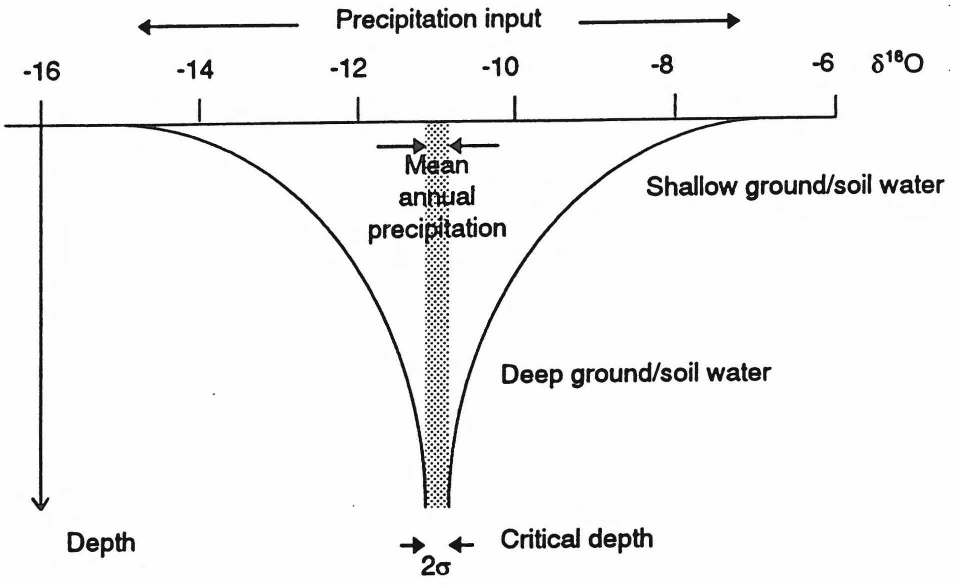

Fig. 5.8 Schematic of the attenuation of seasonal isotope variations in recharge waters during infiltration. (Clark and Fritz 1997).

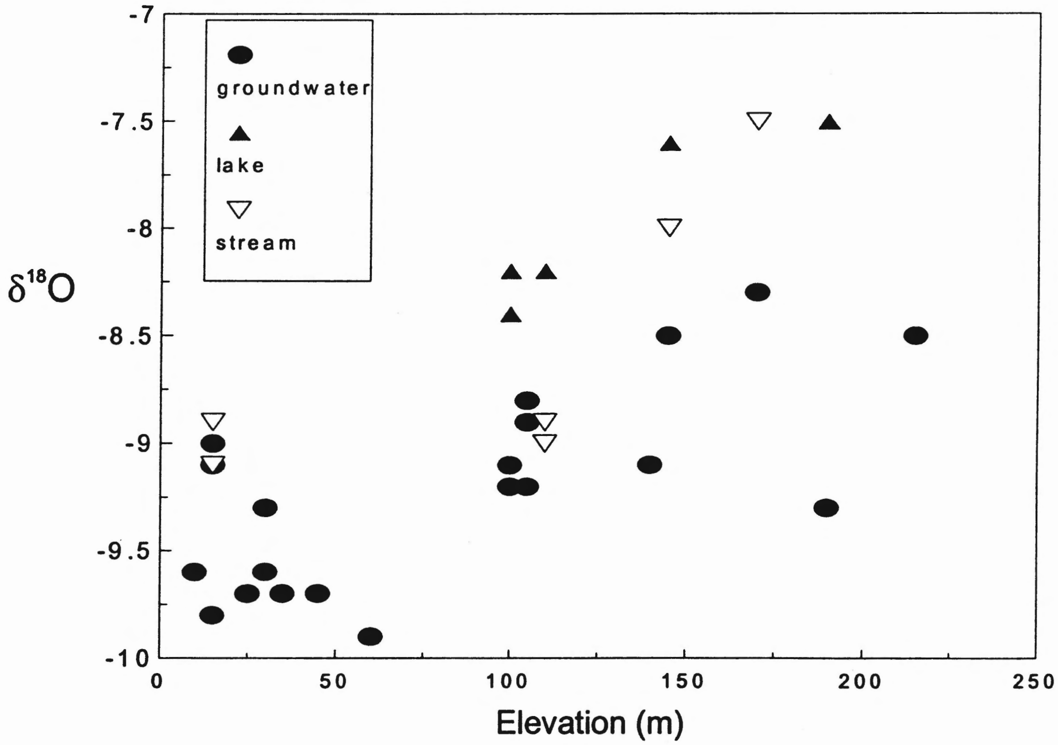

Fig. 5.9 $\delta^{18}O$ values plotted against sample elevation in meters. Note that a change from more negative at low elevation to less negative at higher elevation is the reverse of the change expected from elevation effects. Thus the changes in the data seen in Fig. 5.6 are not explained by the change in sample site elevation.

$\delta^{18}O$ values northwards is a result of increasing mixing of recently infiltrated water with older groundwater from south to north. The overall result is that surface waters reflect recent rainfall $\delta^{18}O$ values while mature groundwater reflects the seasonal average. The mixing and averaging of $\delta^{18}O$ values explains why the mature bicarbonate waters in Fig. 5.6 show a better correlation than the immature waters, which reflect recent rainfall with highly variable $\delta^{18}O$ values.

The latitude effect does not explain the change in $\delta^{18}O$ values, because the study area covers too small a distance to account for the magnitude of the observed change in isotopic values. The elevation effect does not explain the change in $\delta^{18}O$ values either. The Avon Valley data become less negative with increase in elevation (Fig. 5.9), but rainfall that is affected by increasing elevation should decrease in isotopic signature. Furthermore, the r^2 value for the data in Fig. 5.9 is only 0.45, which indicates that there is not a statistically significant correlation between elevation and the change in $\delta^{18}O$ values.

Evaporation causes lighter isotopes to enter the vapour phase preferentially, leaving the heavier isotopes behind. Thus, a lake experiencing evaporation would show an increase in heavier isotopes of water and thus a rise in $\delta^{18}O$. Fig. 5.7 shows that the data points with heavier isotopic values are largely surface waters. Evaporation of the surface waters in the granitic highlands would result in residual high $\delta^{18}O$ water. This water would make its way into the groundwater to mix with directly infiltrated rainwater that is unaffected by evaporation. This mixing would explain both the tendency for groundwater $\delta^{18}O$ values to be lower than surface water values as well as the gradual change northwards. In the northern portion of the study area there are very few lakes or streams, and the presence of sandy and silty meltwater glacial deposits would likely allow rapid infiltration, which in turn would reduce the effect of evaporation and result in lower $\delta^{18}O$ values.

There are two problems with this explanation. Firstly, it does not explain why there is a gradual change in $\delta^{18}O$ values from north to south. The sudden change in topography in the study area at around 49700000 m north (the contact between the granitic highlands and the sedimentary lowlands) correlates with the change from abundant lakes to very few lakes. This would be expected to result in an abrupt change in the evaporation effect. Secondly, Fig 5.10 shows that the six samples collected in the fall of 1999 have the overall highest $\delta^{18}O$ values, which suggests they have been affected the most by evaporation. However, these six points plot on the meteoric water line in Fig. 5.4, which should not be true of waters that have fractionated due to evaporation. Rather, these samples are isotopically enriched, because they were collected shortly after a number of tropical storms had passed over Nova Scotia. The tropical storms carry water that has been transported rapidly from the tropics and so has not experienced the same amount of isotopic depletion as typical summer rainfall.

In summary, the gradual lowering of $\delta^{18}O$ values from south to north is best interpreted as a form of seasonal attenuation. In this scenario the immature surface waters reflect the $\delta^{18}O$ signature of the current season's rainfall. The deeper and more mature (older) waters show $\delta^{18}O$ values that match well with the yearly average, so the deeper waters are probably a mixture of older and younger waters. Fig. 5.11 illustrates this scenario as a schematic cross-section of the Avon Valley from south to north.

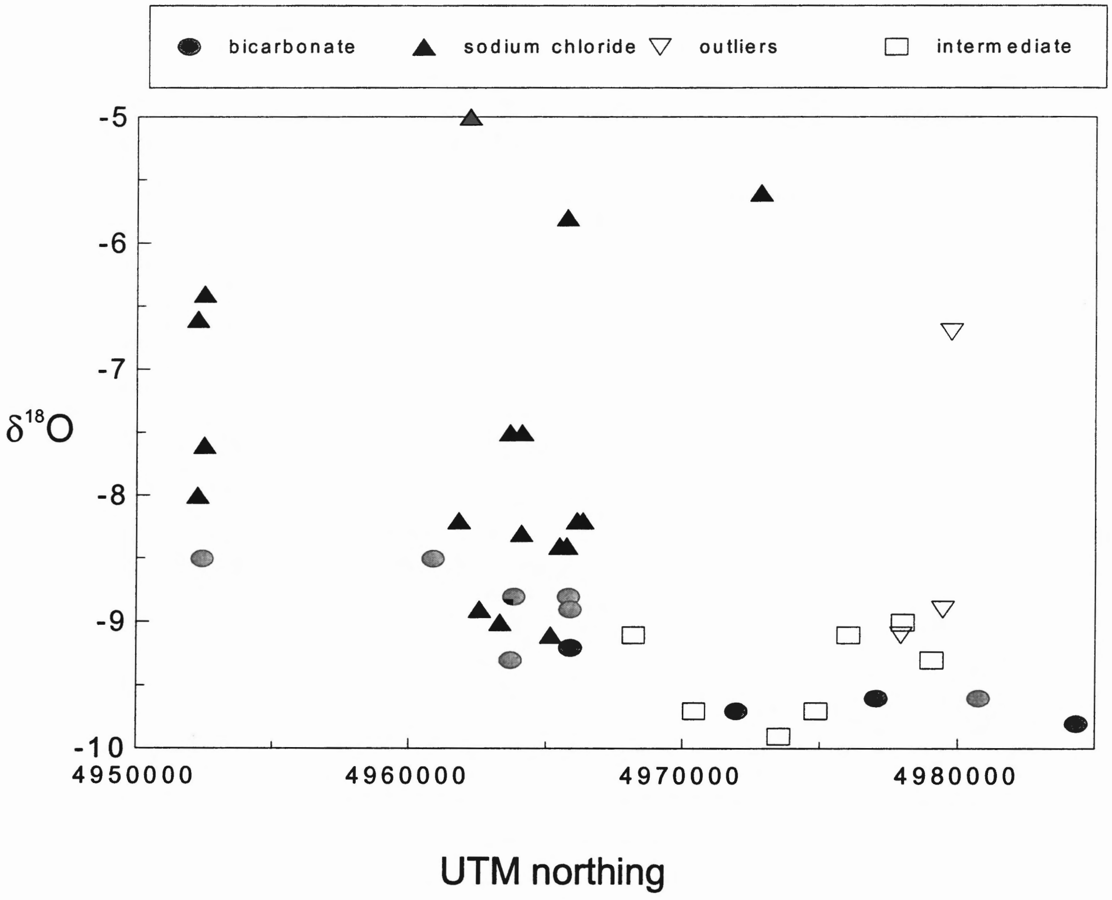

Fig. 5.10 $\delta^{18}O$ values plotted against sample location including the six samples taken in the fall of 1999. All six samples are heavier (higher) than -7. These six samples appear to support the interpretation of lake evaporation causing high $\delta^{18}O$ values. However, they are the result of tropical storm rainfall and their location on Fig. 5.4 shows that they can not be the result of evaporation.

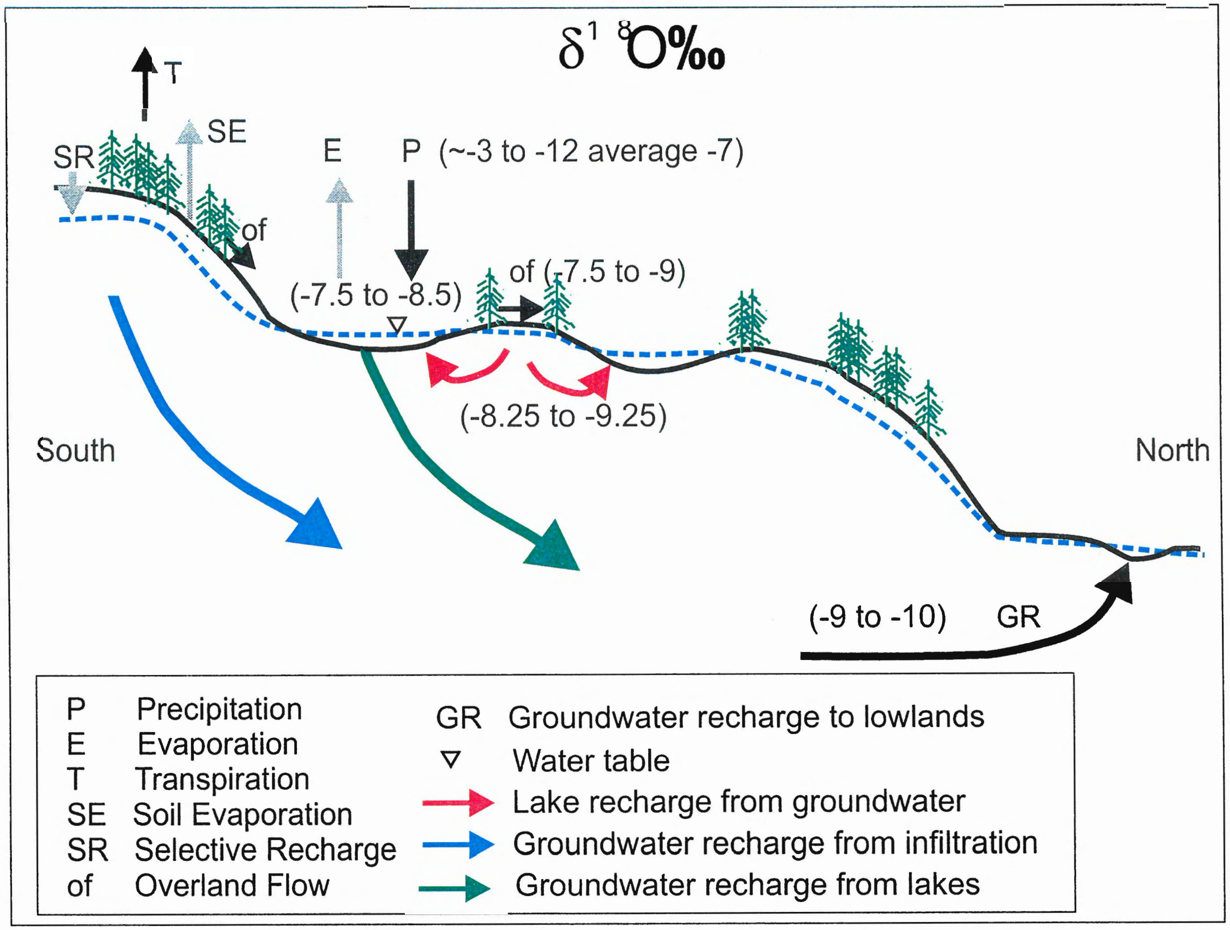

Fig. 5.11 Schematic cross-section of the Avon Valley from south to north showing the decrease in δ^{18}O from south to north and from surface to groundwaters. This diagram supports the interpretation that the lakes do not receive significant recharge from the groundwater. The diagram also suggests increasing mixing of recent precipitation and older water from south to north and from surface to groundwaters.

The diagram shows the $\delta^{18}O$ values for rainfall, lakes, streams, and groundwater in the highlands and in the lowlands. The change in $\delta^{18}O$ values from south to north is clearly illustrated in this diagram. The diagram also supports the idea that groundwater is not feeding the lakes in the highlands, since the lake water values so closely resemble the average rainfall values but are significantly different from groundwater values. In order for seasonal attenuation to work, both the lakes and the shallow groundwater must be rapidly flushed to remove the majority of the precipitation from previous seasons. The observed change in $\delta^{18}O$ values is not explained by the altitude effect, the latitude effect, or surface water evaporation.

6.0 STABLE AND RADIOACTIVE CARBON ISOTOPES

6.1 Background

The $\delta^{13}C$ of dissolved inorganic carbon (DIC) can be used in hydrogeology to trace water-rock interactions (Bullen and Kendall 1998, Clark and Fritz 1997). In order to interpret the $\delta^{13}C$ data, it is necessary to understand the chemistry of inorganic carbon in water and to know the potential sources of this carbon. The following chemical and isotopic information is common to many sources, such as Bullen and Kendall (1998), Clark and Fritz (1997), Mazor (1991), Drever (1997), Mook (1980), and Salomons and Mook (1986).

DIC forms four main species: $CO_{2\,(aq)}$ (dissolved CO_2); H_2CO_3 (carbonic acid), HCO_3^- (bicarbonate ion), and CO_3^{2-} (carbonate ion). According to Clark and Fritz (1997) the net reaction of these dissociations is:

Equation 1:

$$CO_{2(g)} + H_2O \xleftrightarrow{K_{CO_2}} H_2CO_3 \xleftrightarrow{K_1} H^+ + HCO_3^- \xleftrightarrow{K_2} 2H^+ + CO_3^{2-}$$

where K_{CO2} is the equilibrium constant for dissolution of CO_2 in water, K_1 is the equilibrium constant for the dissociation of H_2CO_3, and K_2 is the equilibrium constant for the dissociation of HCO_3^-. The concentration of each species in solution depends upon pH, temperature, and the partial pressure of CO_2.

The source reservoirs of DIC in a watershed are atmospheric CO_2, soil CO_2, and carbon from mineral dissolution. Rainwater gets its carbon from atmospheric CO_2, which is at a partial pressure of about $10^{-3.5}$ (350 ppmv) and has a $\delta^{13}C$ value of about -7‰. Soil contains CO_2 gas from the decomposition of plant matter at partial pressures from 10^{-3} to

10^{-1} (1000 to 100,000 ppmv). These high pressures mean that water in the soil will take up far more CO_2 from the soil than it takes from the atmosphere, and so the soil gas $\delta^{13}C$ signature will dominate in waters that pass through the soil. The soil gas is derived from plant matter that is depleted in ^{13}C due to a combination of processes, including CO_2 diffusion into the leaf stomata, dissolution in the cell sap, and carboxylation in the leaf chloroplasts. The resulting $\delta^{13}C$ value is different for three different groups of plants with slightly differing photosynthetic pathways. The C_3 pathway operates in about 85% of plant species including most major crops. A temperate and high latitude region such as Nova Scotia would be almost exclusively populated by C_3 plants. The C_4 pathway is less common. Generally, only plants in hot, arid ecosystems use it. The CAM pathway is the least common and is generally only used by cacti and other desert plants. The C_3 plants have a range of $\delta^{13}C$ values from -24 to -30‰, with an average of about -27‰. The average soil gas $\delta^{13}C$ in C_3-dominated areas is actually about -23‰, due to diffusion where soil gas comes in contact with the atmosphere.

The third contribution of carbon to natural waters is from mineral dissolution. Carbonate minerals, such as calcite, contribute their own carbon to the system as shown in the following reaction (Mazor 1991):

Equation 2:

$$\underset{\text{soil gas carbon}}{\underline{C}O_{2(g)}} + H_2O + Ca\underset{\text{mineral carbon}}{\underline{C}O_3} \longrightarrow Ca^{2+} + 2H\underset{\text{half soil gas, half mineral carbon}}{\underline{C}O_3^-}$$

Marine carbonates have $\delta^{13}C$ values similar to the reference VPDB which is 0‰. Thus, in waters that have dissolved marine carbonates, the soil gas signature is diluted roughly in half and ranges from -12 to -16‰ (Clark and Fritz 1997). However, in areas dominated by silicate rocks, carbon in weathering reactions is not from other minerals but from the atmosphere or soil gas. This is shown below for the weathering of albite (Mazor 1991):

Equation 3:

$$NaAlSi_3O_8 + \underset{\text{soil gas carbon}}{\underline{C}}O_{2(g)} + {}^{11}/_{2}H_2O \longrightarrow Na^+ + \tfrac{1}{2}Al_2Si_2O_5(OH)_4 + 2H_4SiO_4^{o} + H\underset{\text{soil gas carbon}}{\underline{C}}O_3^-$$

Water in equilibrium with atmospheric CO_2 that has not been in contact with soil gas or carbonates is expected to have a $\delta^{13}C$ value near to the atmospheric value of -7‰. Shallow groundwater in till or soil, or water derived from an area dominated by silicate bedrock (equation 3) is exposed to soil gas CO_2 and so should have a $\delta^{13}C$ signature of about -23‰. Groundwater that has been in contact with marine carbonates and has been exposed to soil gas should have $\delta^{13}C$ values of around -12 to -16‰ (equation 2). These end members are summarized in Fig. 6.1.

^{14}C can be used to determine whether carbonate dissolution is contributing to groundwater DIC content. Radiocarbon is produced in the upper atmosphere by cosmic ray interactions with nitrogen. The ^{14}C so produced oxidizes rapidly to CO_2 and is subsequently incorporated into plant matter through photosynthesis. The activity of radiocarbon produced in the atmosphere is 100 per cent modern (100 pmc). Living plants have the same radiocarbon activity. When plant uptake of ^{14}C is stopped by the death of the organism a type of clock is started as the ^{14}C decays and is not replaced by photosynthesis. As a consequence of the half-life of ^{14}C (5570 y) any organic material

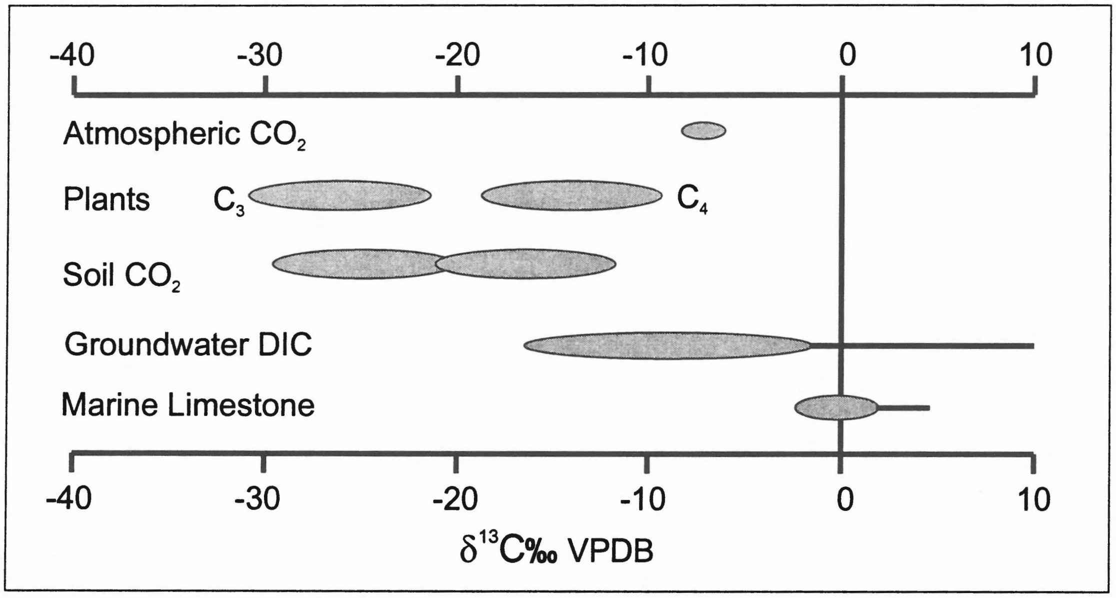

Fig. 6.1 Ranges for $\delta^{13}C$ values in selected natural compounds. Note that the soil CO_2 corresponds to the prevalent plant type and groundwater DIC varies with the combination of input carbon. (Modified after Clark and Fritz 1997).

younger than about 30,000 years old should contain a detectable amount of ^{14}C. Soil gas from decaying plant matter should represent the atmospheric production value of 100 pmc or slightly greater, due to the bomb effect. The bomb effect is a result of atmospheric nuclear testing in the 1960's, which caused the addition of more ^{14}C to the atmosphere than what would normally be present (up to approximately 130pmc). This effect is decreasing with time and atmospheric values are now only slightly greater than 100 pmc. Carbonate rocks that are older than 45 thousand years should contain no radiocarbon. Thus, from Equation 2, waters that have dissolved calcite from carbonate rocks older than Pleistocene age to the point of calcite saturation would contain about 50 pmc.

6.2 Data and Interpretation

The carbon data are listed in Table 6.1. The total inorganic carbon (TIC) concentration ranges from below the detection limit to 4.77 mmol/l and the $\delta^{13}C$ values from –12.9 to –19.6‰ for the samples taken in 1998. In October 1999 four lake samples and two creek samples were taken in 1 litre containers in an attempt to get sufficient carbon for analysis. The $\delta^{13}C$ of these samples range from –12.9 to –27.7‰. At the same time one well and one lake sample were analysed for ^{14}C. The lake sample yielded 103.64 pmc and the well sample 77.72 pmc.

Based on the behaviour of carbon isotopes as described above, we should expect $\delta^{13}C$ values in groundwaters to be very negative in the south where the bedrock is granite without any carbonate. The values would be expected to rise to about -12 to -16‰ in the north where the carbonate bedrock is found. Surface waters might be expected to be in equilibrium with the atmosphere.

Table 6.1: Total Inorganic Carbon (TIC) and $\delta^{13}C$ Data

Sample Code	TIC mM/l	$\delta^{13}C$ ‰ VPDB
W12	0.92	-19.6
W15	2.96	-14.5
W17	0.88	-18.9
W18	2.87	-14.7
W20	0.95	-17.4
W22	3.95	-13.1
W23	4.77	-15.3
W24	0.97	-15.9
W28	3.44	-12.9
W29	2.60	-14.6
W31	2.35	-13.5
W34	2.10	-15.7
W35	3.71	-15.3
W37	1.52	-17.1
W38	0.88	-15.7
W39	1.08	-15.7
W40	4.77	-14.1
S42		-21.5
L43		-25.0
L48		-26.5
L49		-26.9
R52		-24.0
L54		-12.6

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

Fig. 6.2 shows the $\delta^{13}C$ values plotted against UTM northing. The graph shows that all the groundwaters have $\delta^{13}C$ values that require the dissolution of carbonate material. Furthermore, the surface waters clearly show a soil gas signature. This suggests that the lake water CO_2 is dominantly from the decomposition of plant matter or soil gas dissolved in the water. The dissolution of carbonates lowers the $\delta^{13}C$ while raising the conductivity, due to the addition of dissolved ions. A strong correlation between $\delta^{13}C$ and conductivity is indeed in evidence in Fig. 6.3. The plot has an exponential fit with an r^2 of 0.80. This correlation clearly shows that the groundwater has increased its conductivity as it has dissolved calcite and other minerals during infiltration and movement through the till. The higher $\delta^{13}C$ signature of the groundwater clearly reflects this dissolution of marine carbonate. The lake waters do not exhibit the results of

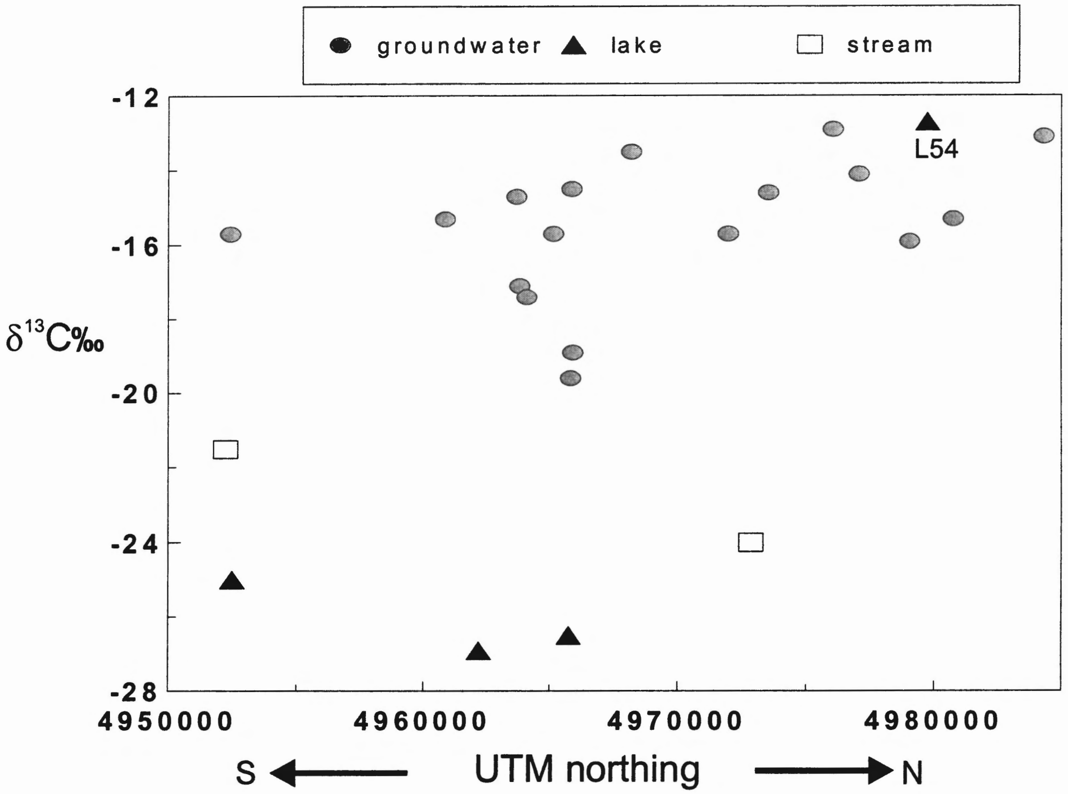

Fig. 6.2 Graph of δ^{13}C vs. sample location by UTM northing. Note the clear separation of lakes, streams and wells by δ^{13}C values. Exception is lake 54, which is located on limestone and gypsum bedrock.

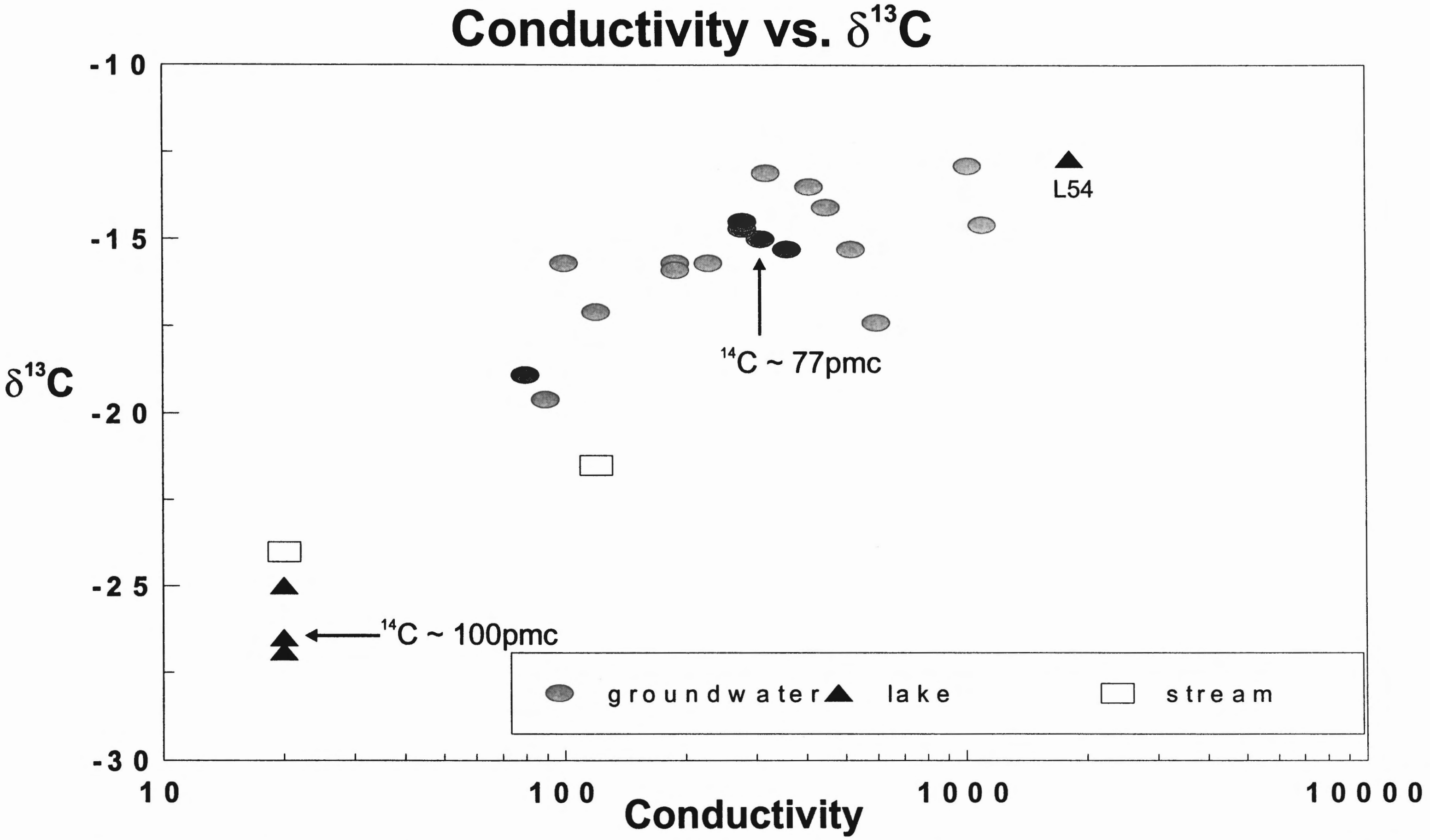

Fig. 6.3 Graph of $\delta^{13}C$ vs. conductivity showing an exponential trend for all samples. The well waters show the effect of carbonate dissolution by having high conductivity and $\delta^{13}C$ values which represent a mixture of carbon from soil gas CO_2 ($\delta^{13}C$~-26‰) and from carbonate mineral carbon ($\delta^{13}C$ ~0‰). The lakes show a pure plant matter $\delta^{13}C$ signature except for lake 54, which is located on gypsum bedrock and so shows the effect of carbonate dissolution. The two ^{14}C samples further support the interpretation that the lakes contain only plant carbon while the wells have a mixture of plant carbon and dissolved carbonate carbon.

any dissolution of carbonate material nor could there be a significant input of groundwater to the lakes without resulting in higher $\delta^{13}C$ values than are observed.

The ^{14}C data serve to confirm the interpretation of the $\delta^{13}C$ data. The lake ^{14}C sample value was 103.64 pmc. The lake water therefore, contained some of the excess ^{14}C from atmospheric nuclear testing. This suggests that most of the carbon in the lakes is younger than 40 years and in fact could be very much younger. This ^{14}C value would not be possible if there were old carbonate material dissolved in the lake waters. The groundwater sampled had a ^{14}C value of 77.72 pmc, which means that some component of old carbonate was mixed with the modern carbon in the soil gas. The fact that the ^{14}C value was not 50 pmc suggests that the water contained a residue of the ^{14}C from the 1960s fallout.

The lake water $\delta^{13}C$ values do not show the effect of mixing with atmospheric CO_2. This is a result of the low partial pressure of CO_2 in the atmosphere compared to that of the lake waters, which are likely higher by an order of magnitude, due to the decay of organic matter in the lake through chemical, biological, and photochemical oxidation. Stream waters tend to fall between the lakes and groundwater, which suggests that the streams are mixtures of lake water and groundwater.

Lake sample 54 has a higher conductivity than any of the groundwaters. It has one of the lowest $\delta^{13}C$ values (-12.6‰). This lake is located near Windsor in an area of limestone and gypsum bedrock and has become almost saturated with respect to calcite (chapter 4). Its $\delta^{13}C$ value is thus exactly what would be expected of water containing equal contributions of carbon from soil gas and marine carbonate (Equation 2).

In summary, the carbon isotopes confirm the idea that all the groundwater in the Avon Valley dissolves marine calcium carbonate. The lack of old carbon or of any carbonate $\delta^{13}C$ signature in the lakes demonstrates conclusively that the lakes do not receive appreciable recharge from the groundwater. This is clearly summarized in Fig. 6.4, which shows how the data relate spatially on a schematic cross-section of the Avon Valley.

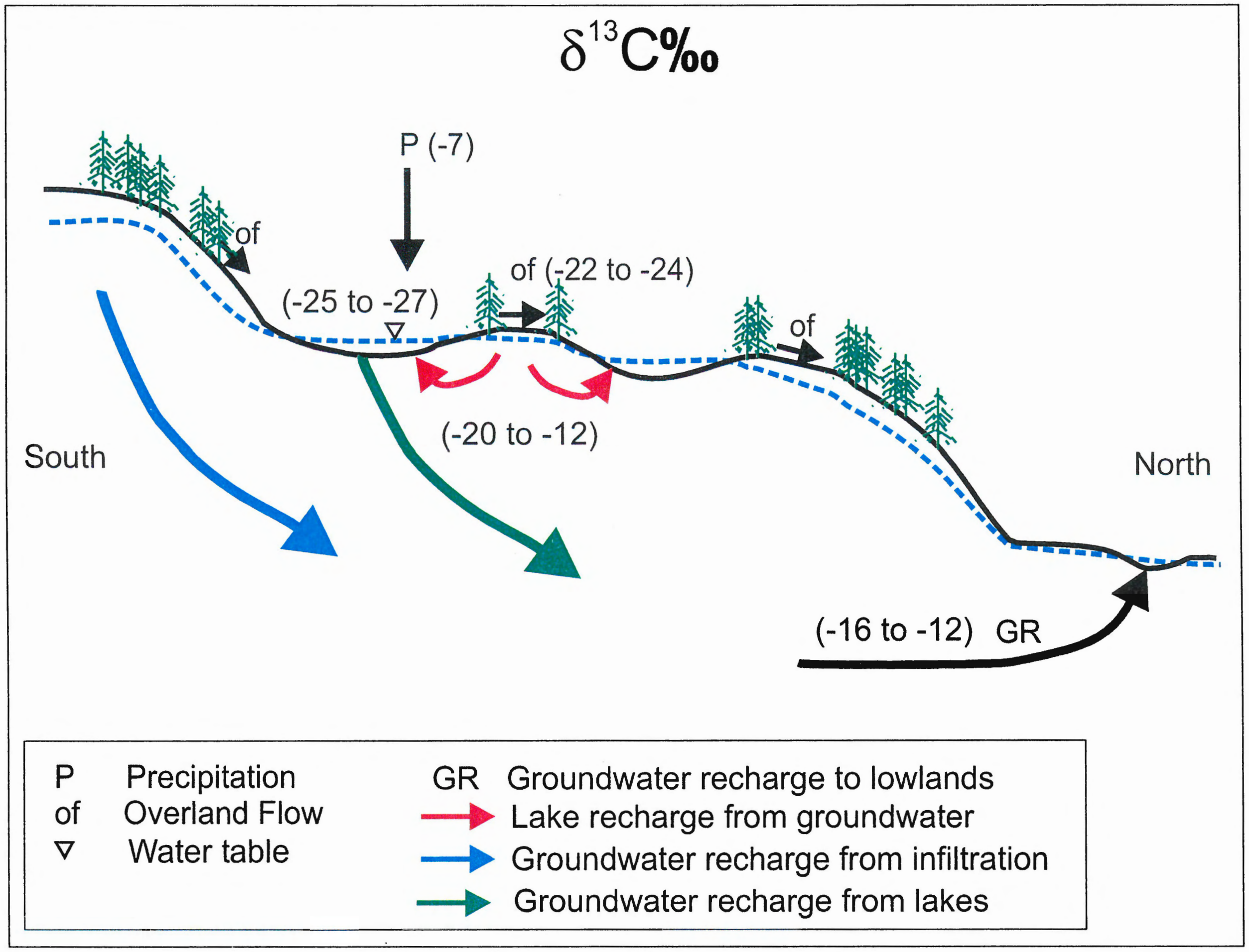

Fig. 6.4 Schematic cross-section of the Avon Valley from south to north showing the change in $\delta^{13}C$ from south to north and from surface to groundwaters. This diagram demonstrates conclusively that there is insignificant lake recharge from groundwater and that groundwaters show an increasing effect of marine carbonate from south to north, which suggests increasing water-rock interaction down the flow path.

7.0 NITROGEN ISOTOPES

7.1 Discussion

Nitrogen compounds are largely derived from organic waste, including human and animal waste products, from fertilizers, and from decayed plant matter (e.g. Kendall and McDonnell 1998). In many places where farming is a dominant land use, unacceptable levels of nitrogen compounds are found in surface and groundwaters (e.g. Clark and Fritz 1997). Poorly placed septic fields can also supply high levels of nitrogen to domestic water supplies. Nitrogen isotopic analyses were included in this study in order to trace the source of nitrogen compounds in the waters of the Avon Valley.

None of the samples contained enough nitrogen to allow isotopic analysis. Table 7.1 lists the concentrations of nitrate + nitrite and of ammonia that were obtained from the analysis of general chemistry. Many samples were also below the analytical chemistry detection limit of 0.5 mg/l.

This data shows clearly that there is no anthropogenic nitrogen compound contamination of the Avon water system, even in the lower valley where farming is common. Since the general chemistry suggests the water system is quickly flushed in this area, a significant amount of nitrogen could be added to the system and be quickly flushed out. The increasing land use of the granitic highlands for summer cottages and permanent residences has clearly not reached a high enough density to cause detectable groundwater pollution.

Table 7.1: Avon Valley Nitrogen Compound Concentration Data

Sample Code	Nitrate+ Nitrite mg/L	Ammonia mg/L
S01	<0.1	<0.1
L02	<0.1	<0.1
L03	<0.1	<0.1
S05	<0.1	<0.1
W12	<0.1	<0.1
W13	<0.1	<0.1
W15	<0.1	<0.1
W17	<0.1	<0.1
W18	0.7	<0.1
L19	<0.1	<0.1
W20	<0.1	<0.1
S21	<0.1	<0.1
W22	2.80	<.05
W23	0.49	<.05
W24	1.24	<.05
W25	<.05	<.05
S26	<.05	<.05
S27	<.05	<.05
W28	4.20	<.05
W29	0.52	<.05
W30	<.05	<.05
W31	3.90	<.05
S32	0.05	0.08
L33	<.05	<.05
W34	0.34	<.05
W35	0.92	<.05
L36	<.05	<.05
W37	0.17	<.05
W38	0.23	<.05
W39	<.05	<.05
W40	0.64	<.05
W41	0.94	<.05
S42	<.05	<.05
L43	<.05	<.05
L48	<.05	<.05
L49	<.05	<.05
R52	<.05	<.05
L54	<.05	<.05
R55	<.05	<.05
S56	<.05	<.05
W57	<.05	<.05
W58	0.22	<.05
S59	<.05	<.05
W60	0.47	<.05

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

8.0 STRONTIUM ISOTOPES

8.1 Background

The greatest potential use of Strontium isotopes in hydrology is to identify salinization due to modern seawater intrusion. This is because modern seawater has a well-defined $^{87}Sr/^{86}Sr$ ratio of 0.7092 and a concentration of 8 mg/l (Faure 1986). The seawater isotopic ratio has changed over time (Fig. 8.1). Marine carbonates and evaporites incorporate the $^{87}Sr/^{86}Sr$ isotopic ratio of the seawater at the time of their deposition. This offers the possibility of tracing groundwater flow through aquifers of differing age. The potential for the use of the strontium isotopic ratio as a tracer is not always realized where the rocks contain appreciable amounts of rubidium-bearing minerals. In such instances the $^{87}Sr/^{86}Sr$ ratio can be altered by the leaching of radiogenic ^{87}Sr derived from the decay of ^{87}Rb. This may be of considerable influence in waters that are in contact with igneous rocks. Since rubidium will readily substitute for potassium, rocks rich in potassium will have high ^{87}Rb and therefore high ^{87}Sr content. This results in a high or 'radiogenic' $^{87}Sr/^{86}Sr$ ratio signature for rocks such as granites that contain micas and potassium feldspar (Faure 1986, Clark and Fritz 1997). According to Clark and Fritz, the $^{87}Sr/^{86}Sr$ ratio for ocean basalt is 0.703, while continental rocks are variably enriched from 0.710 to 0.740.

The oceanic $^{87}Sr/^{86}Sr$ ratio is preserved in marine calcium carbonate rocks, because strontium substitutes for calcium. The carbonate rocks in the study area are Carboniferous in age (corresponding to Mississippian and Pennsylvanian), so $^{87}Sr/^{86}Sr$ values from 0.7083 to 0.7075 are predicted, as shown in Fig 8.1.

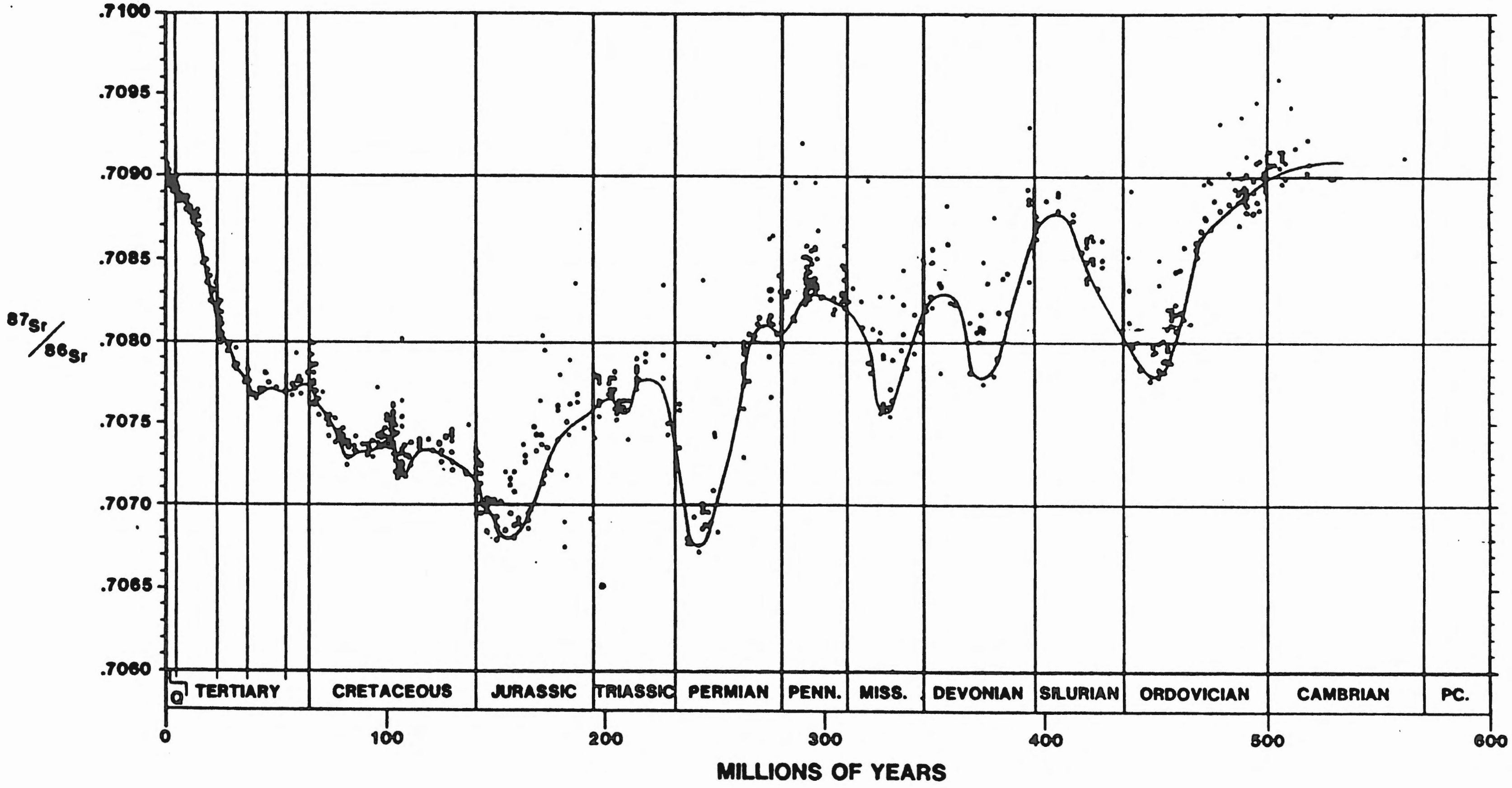

Fig. 8.1 Plot of $^{87}Sr/^{86}Sr$ variation in ocean water through Phanerozoic time. The carbonate rocks in the study area are Carboniferous in age which fits around the Mississippian area on this chart. (Taken from Burke et al.1982).

It was expected that the $^{87}Sr/^{86}Sr$ ratio in Avon Valley waters would have a modern seawater signature of 0.7092 in the precipitation, due to wind-blown aerosol salts, a radiogenic signature in groundwaters in the south, due to dissolution of granite, and a Carboniferous carbonate signature in the north from dissolution of the Windsor and Horton carbonates. Previous studies on strontium isotopes in the South Mountain Batholith (e.g. Clarke and Halliday 1980) have shown that the $^{87}Sr/^{86}Sr$ values vary widely depending upon the intrusive phase and on the proximity to the Meguma Group. The $^{87}Sr/^{86}Sr$ ratios exhibited by the biotite granodiorite average 0.7081, the adamellite average is 0.70942, and the porphyry yields an average ratio of 0.71021. The Meguma group yield highly radiogenic ratios that range from 0.7113 to 0.7177. The granites proximal to this country rock often show $^{87}Sr/^{86}Sr$ values intermediate between the granite and the Meguma Group, due to assimilation of Meguma material. In the Avon Valley there are inliers of Meguma Group and pods of alaskite porphyry that are expected to have high $^{87}Sr/^{86}Sr$ values.

8.2 Data and Interpretation

The strontium data are listed in Table 8.1. Fig. 8.2 shows a gradual south to north change in $^{87}Sr/^{86}Sr$ data from values over 0.717 in the south to values ranging from 0.710 to 0.708 in the samples over the sedimentary rocks in the north. These data generally agree with the expected values. However, the observed change is gradual rather than sharp at the contact between the granitic and sedimentary bedrock. There are even some samples in the granitic area that exhibit values as low as those over the carbonates suggesting that there is a carbonate influence throughout the groundwater of the study area. The lake waters, which are interpreted as essentially rainwater, have the expected seawater signature masked by a contribution of radiogenic ^{87}Sr leached from the bedrock.

Table 8.1: Avon Valley Strontium Concentration and Isotope Data

sample code	Strontium mg/l	^{87}Sr/^{86}Sr
S01	3.2436	0.714114
L02	0.0068	0.717492
L03	0.0054	0.716335
S05	0.0074	0.713829
L06	0.0060	0.715834
L07	0.0061	0.715855
L09	0.0063	0.709119
S10	0.5111	0.708083
S11	0.3792	0.708028
W12	0.0485	0.708301
W13	0.0163	0.710937
W15	0.1109	0.710230
W17	0.0436	0.713721
W18	0.1110	0.710123
L19	0.0064	0.713339
W20	0.0936	0.712943
S21	0.0043	0.716856
W22	0.1415	0.709119
W23	0.6074	0.708846
W24	0.0755	
W25	0.2345	0.708566
W28	0.2146	0.710161
W29	0.3056	0.711934
W30	0.0229	0.712874
W31	0.1168	0.712847
W34	0.0525	0.713361
W35	0.1797	0.712266
W37	0.1009	0.709990
W38	0.0428	0.712755
W39	0.0505	0.710393
W40	0.1732	0.709673
W41	0.0353	0.712667

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

The lower ^{87}Sr/^{86}Sr ratios, coupled with the higher strontium concentrations in the bicarbonate waters, corroborate the finding that the calcium carbonate groundwater has evolved from surface waters through the dissolution of sedimentary rocks (of Carboniferous age). Such a mechanism could also explain the correlation in Fig 8.3 between strontium concentration and calcium concentration in the groundwater (r^2 = 0.56). This correlation supports the idea that the groundwater strontium is derived from the calcite dissolution. This is because, as groundwater interacts with more carbonate material, it gains more of the marine carbonate ^{87}Sr/^{86}Sr ratio signature.

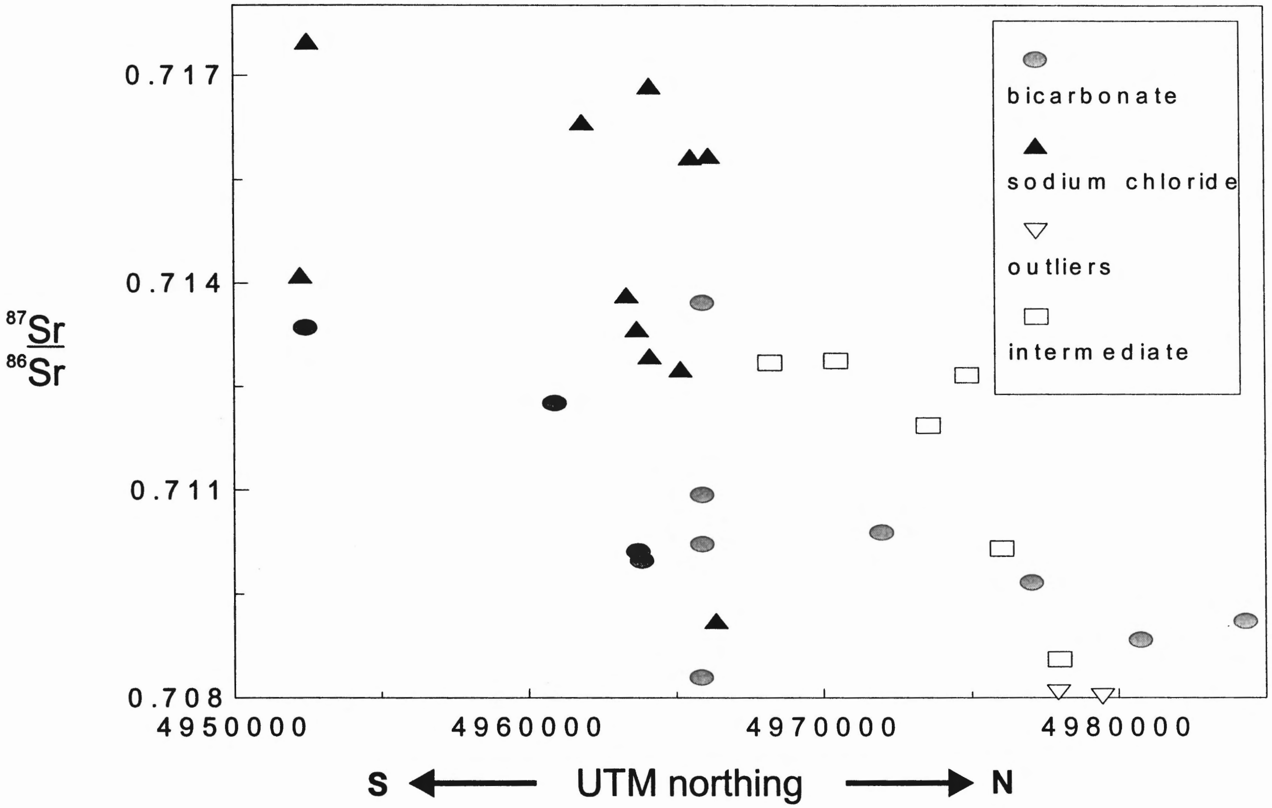

Fig. 8.2 Plot of ^{87}Sr/^{86}Sr against sample location in UTM northing. The plot shows the gradual change in the range of ^{87}Sr/^{86}Sr values from south to north.

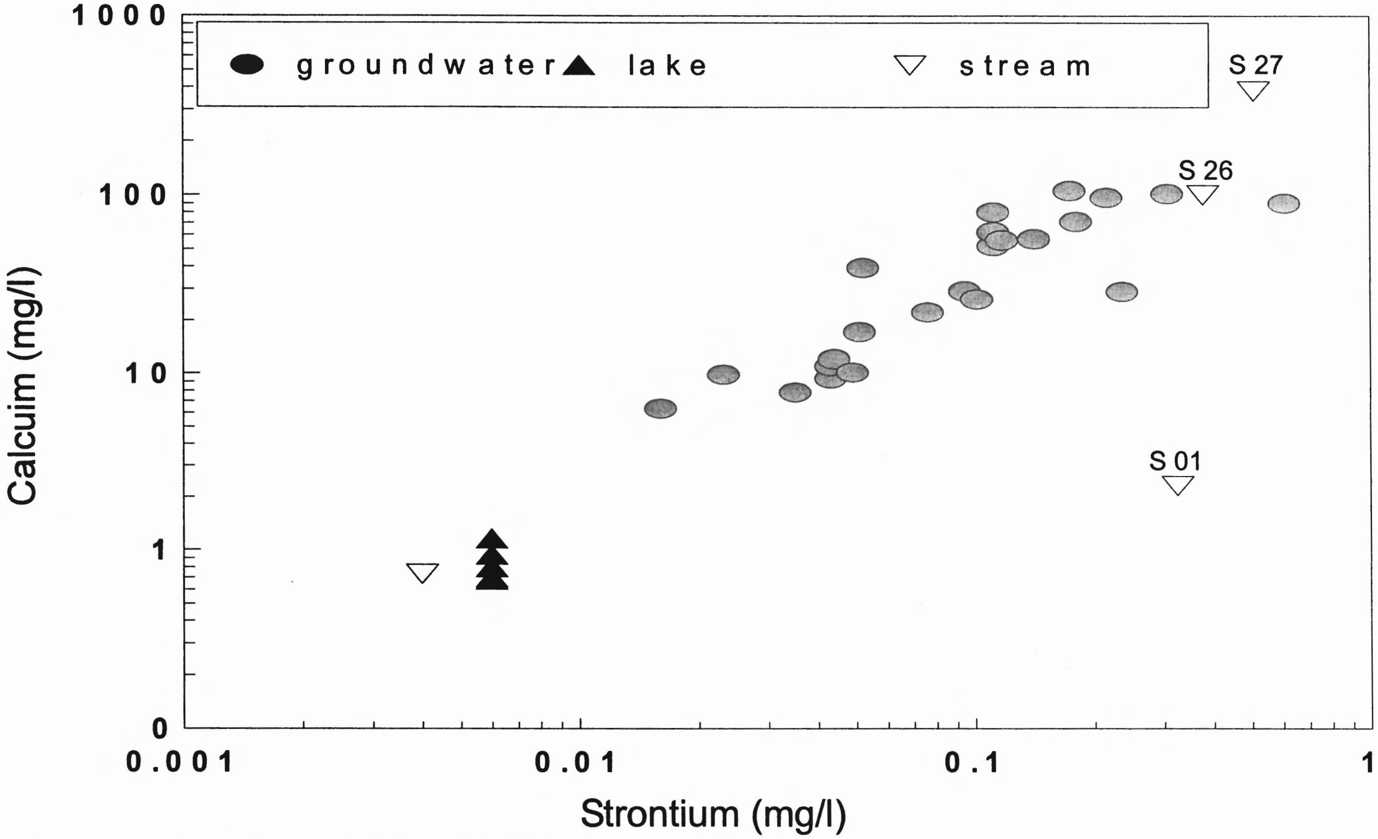

Fig. 8.3 Plot of strontium vs. calcium concentrations showing a clear difference between the surface waters and the groundwaters. The correlation indicates that the strontium gained by the groundwaters is coming from the same source as the calcium since they increase together. This supports the idea that the strontium is coming from marine carbonates of Carboniferous age, giving the more mature waters the same isotopic signature as Carboniferous carbonates. Note that streams 26 and 27 in the lowlands reflect ample dissolution of the carbonate material. Stream 01 is from the granitic highlands near Card Lake. It has more strontium (relative to calcium) than would be expected from dissolution of marine carbonates indicating a local source of mobile strontium other than limestone.

This interaction has been interpreted as increasing towards the north thus explaining the gradual change in isotopic signature.

Since the lakeshores in the south are all covered by granite debris ranging from boulders to sand, it is reasonable to assume that water-granite interactions are occurring. To explain the lakewater isotopic ratio in the highlands, it must be assumed that the rainwater contains so little oceanic strontium that a small amount contributed by the granite dissolution is able to alter the $^{87}Sr/^{86}Sr$ ratio without increasing the overall water conductivity significantly. This is a reasonable assumption, since the ratio of strontium to chloride in the ocean is 0.00042. In the lakes the strontium to chloride ratio averages 0.0014. Thus, at most only 1/3 of the strontium found in the lakes could be of oceanic origin.

In summary, the $^{87}Sr/^{86}Sr$ ratio is strongly radiogenic in the south and gradually changes northwards to match the expected ratio for the Carboniferous carbonates in the lowlands. The strontium isotopic data suggest that, in the low conductivity surface waters in the granitic highlands, there is sufficient water-rock interaction to raise the isotope ratio of the recently precipitated waters above that of modern seawater. The gradual change of the strontium isotope signature in the groundwater from south to north suggests that the effect is an ongoing process of dissolution of carbonate material in the till. Thus, the radiogenic signature acquired by surface waters from the granites is gradually overprinted by the marine carbonate signature with the increasing exposure of groundwater to carbonate minerals in the glacial till. Fig. 8.4 summarises these data on a schematic cross-section of the Avon Valley. This diagram makes it clear that

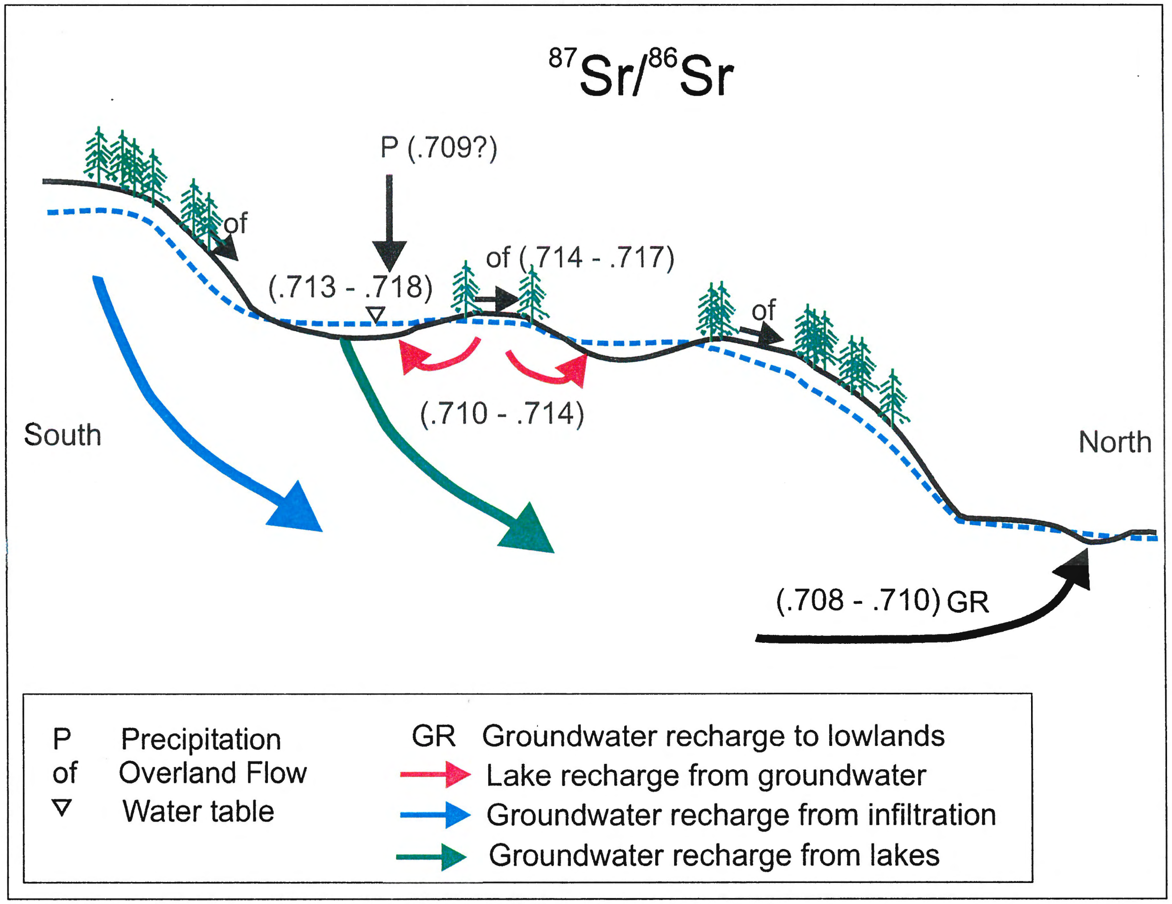

Fig. 8.4 Schematic cross-section of the Avon Valley from south to north showing the decrease in ^{87}Sr/^{8}Sr from south to north and from surface to groundwaters. This diagram supports the interpretation that the lakes do not receive significant recharge from the groundwater. The diagram also suggests increasing interaction with marine carbonates from south to north and from surface to groundwaters.

groundwater cannot be contributing significantly to the lakes, because of the difference in the isotopic ratios of the waters. It is also clear that a gradual progression of water from radiogenic in the south, to marine carbonate in the north is best explained by increasing water-rock interaction as the groundwater flows north.

9.0 URANIUM ISOTOPES

9.1 Background

Uranium isotopes have been used successfully in hydrogeological studies to delineate specific groundwater bodies and to trace flow paths, as well as in prospecting studies (Ivanovich and Harmon 1992). Thus, a study of the uranium isotopes was carried out in the present investigation to evaluate their usefulness for tracing water flow in the Avon Valley.

The solubility of elemental uranium is governed by its valence state. Under reducing conditions U^{4+} is insoluble. Under oxidizing conditions U^{6+} is soluble. It can form various soluble complexes with carbonate, phosphate, sulfate, fluoride and silicate ions as well as adsorb onto organic compounds (Ivanovich and Harmon 1992). The most often encountered complex in natural waters is the soluble uranyl carbonate complex. There is no significant isotopic fractionation in nature between ^{238}U and ^{235}U, each of which heads a decay series, because of the very slight difference in their respective masses. However, uranium isotopes in the ^{238}U-series, which also have only slight mass differences, are readily separated in nature. This is obviously not due to the difference in mass between the parent ^{238}U and its daughter ^{234}U (Fig. 9.1). Rather, it is due to radiogenic processes related to the nuclear transformation from parent to daughter. There are basically two ways to carry out the isotopic separation that goes on between water and solids. One method is to use nuclear transformations to make the daughter isotope preferentially more soluble. This is accomplished by the breaking of chemical bonds, displacement within the crystal structure, the creation of micro-channels that allow for the penetration of water into the mineral grains, and by the auto-oxidation of the resulting

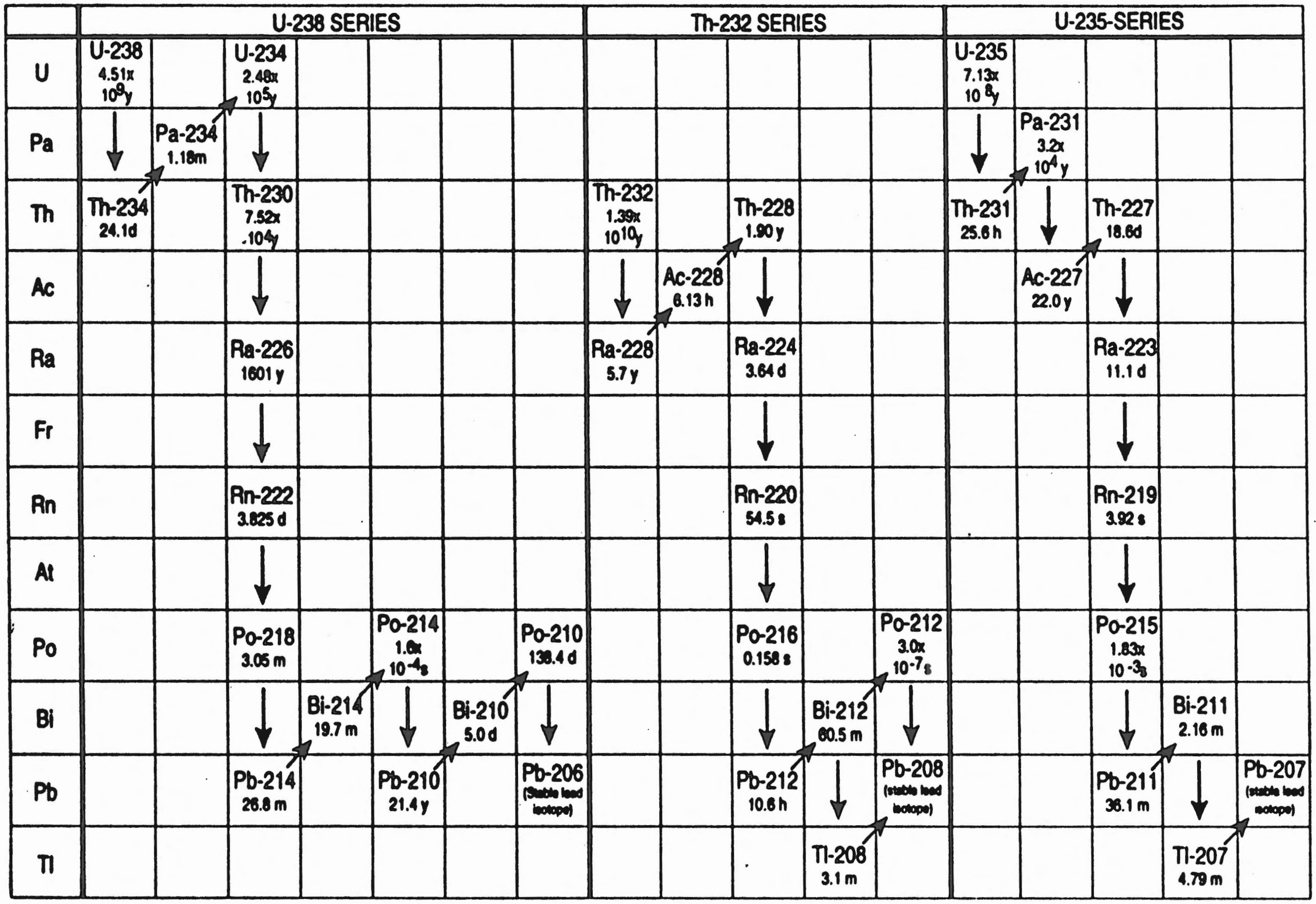

Fig. 9.1 The ^{238}U, ^{232}Th, and ^{235}U decay series. Vertical arrows represent alpha decays and diagonal represent beta. Half-lives are listed in years, days, minutes and seconds. (From Kraemer and Genereux 1998).

daughter nuclide to the soluble plus 6 valence through the loss of the two nuclear betas (Fig. 9.1). In addition to the preferential leaching of the daughter isotope, it is possible to cause the physical ejection of the ^{234}U across grain boundaries, irrespective of the prevailing redox conditions, by alpha-recoil (Fig 9.2)(also Kronfeld 1974).

9.2 Data and Interpretation

The uranium data are shown in Table 9.1.

Table 9.1: Avon Valley Uranium Concentration and ^{234}U/^{238}U Ratio Data

Sample Code	Uranium mg/l	Conc. Error	^{234}U/^{238}U	Ratio Error
S01	0.240	0.010	1.06	0.08
L02	0.250	0.020	1.17	0.10
L03	0.230	0.010	0.98	0.07
S05	0.260	0.020	1.04	0.08
L06	0.240	0.010	1.17	0.08
L07	0.250	0.010	1.15	0.08
S11	0.150	0.010	1.19	0.09
W12	0.060	0.010	1.24	0.27
W13	0.040	0.010	1.10	0.17
W15	0.340	0.020	1.07	0.08
W17	2.310	0.080	1.11	0.04
W18	1.620	0.030	0.98	0.02
L19	0.290	0.020	1.15	0.09
W20	0.370	0.020	1.03	0.08
S21	0.280	0.010	1.11	0.06
W22	0.290	0.010	1.39	0.10
W23	2.590	0.110	1.19	0.06
W24	0.029	0.008	1.33	0.38
W25	0.024	0.004	1.27	0.30
W28	0.530	0.020	1.13	0.06
W29	0.400	0.020	1.05	0.06
W31	0.210	0.010	1.36	0.08
W34	0.450	0.010	1.10	0.04
W35	41.080	0.470	0.99	0.01
W37	0.800	0.040	1.10	0.05
W38	0.660	0.040	1.00	0.09
W39	0.100		1.25	0.39
W40	0.610	0.040	1.13	0.07
W41	0.079	0.003	1.43	0.08

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

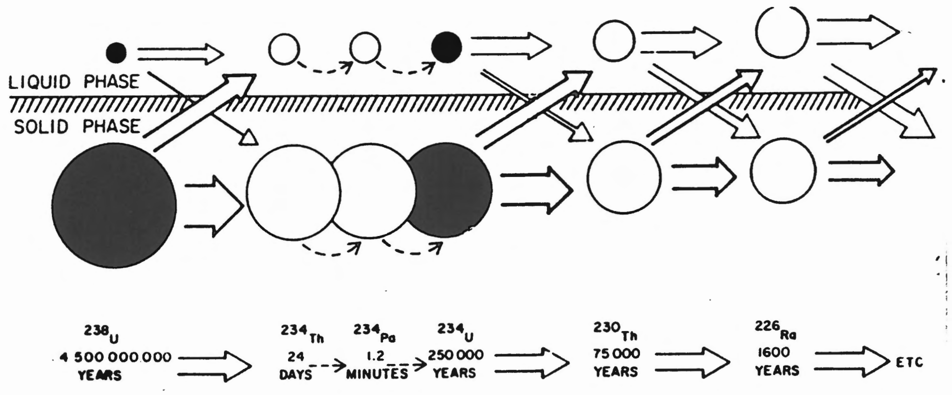

Fig. 9.2 The recoil model of uranium-series isotopic disequilibrium. Decay chains in the fluid and solid phases from ^{238}U through the first several daughters are shown diagrammatically, and result from a series of alpha (solid arrows) and beta (dotted) events. Alpha decay involves recoil displacements and may result in transfer of the atoms from the solid phase to the fluid, or more rarely vice versa. Sizes of atoms and arrows represent relative radioactivity. The commonly measured isotope pair, ^{238}U and ^{234}U, are shaded (from Osmond and Cowart 1982).

With one exception (sample W34), the uranium concentrations ranged from .024 to 2.9 μg/l. Most concentrations fell in the narrower range between 0.2 and 0.6 μg/l. These values were appreciably lower than the 3.3 μg/l that is found in ocean water. Sample W34 yielded an anomalously high 41 μg/l uranium. All uranium values obtained in the study fell below the current permissible level of 0.154 mg/l (154 μg/l) as noted in the Guidelines for Canadian Drinking Water Quality (Federal-Provincial Subcommittee on Drinking Water, 1998).

Uranium concentration does not show any correlation to geographical location or to water chemistry. Uranium is often found to correlate with pH and alkalinity. The Nova Scotia Uranium Task Force (Grantham 1986) did find this correlation in some Nova Scotia groundwaters. The groundwater trend likely results from the increased solubility of uranium with formation of the soluble uranyl carbonate complex (Mangini et al. 1979). Fig. 9.3 shows the relationship of alkalinity to uranium concentration for the Avon data. There is clearly a tendency for groundwater samples with high uranium values to have high alkalinity. However, the r^2 is only 0.12, which indicates that there is not a significant linear correlation. The lack of a strong correlation indicates that uranium concentration is not controlled by carbonate complexation in the Avon Valley. The surface waters in Fig. 9.3 exhibit a very uniform uranium concentration between 0.1 and 0.3 μg/l. This clearly indicates that the uranium concentration in surface waters is totally independent of alkalinity in the Avon Valley. Why the uranium concentration is so uniform at these levels and with concomitant variable alkalinities is not readily apparent. Perhaps the uranium concentration is related to organic complexes in the

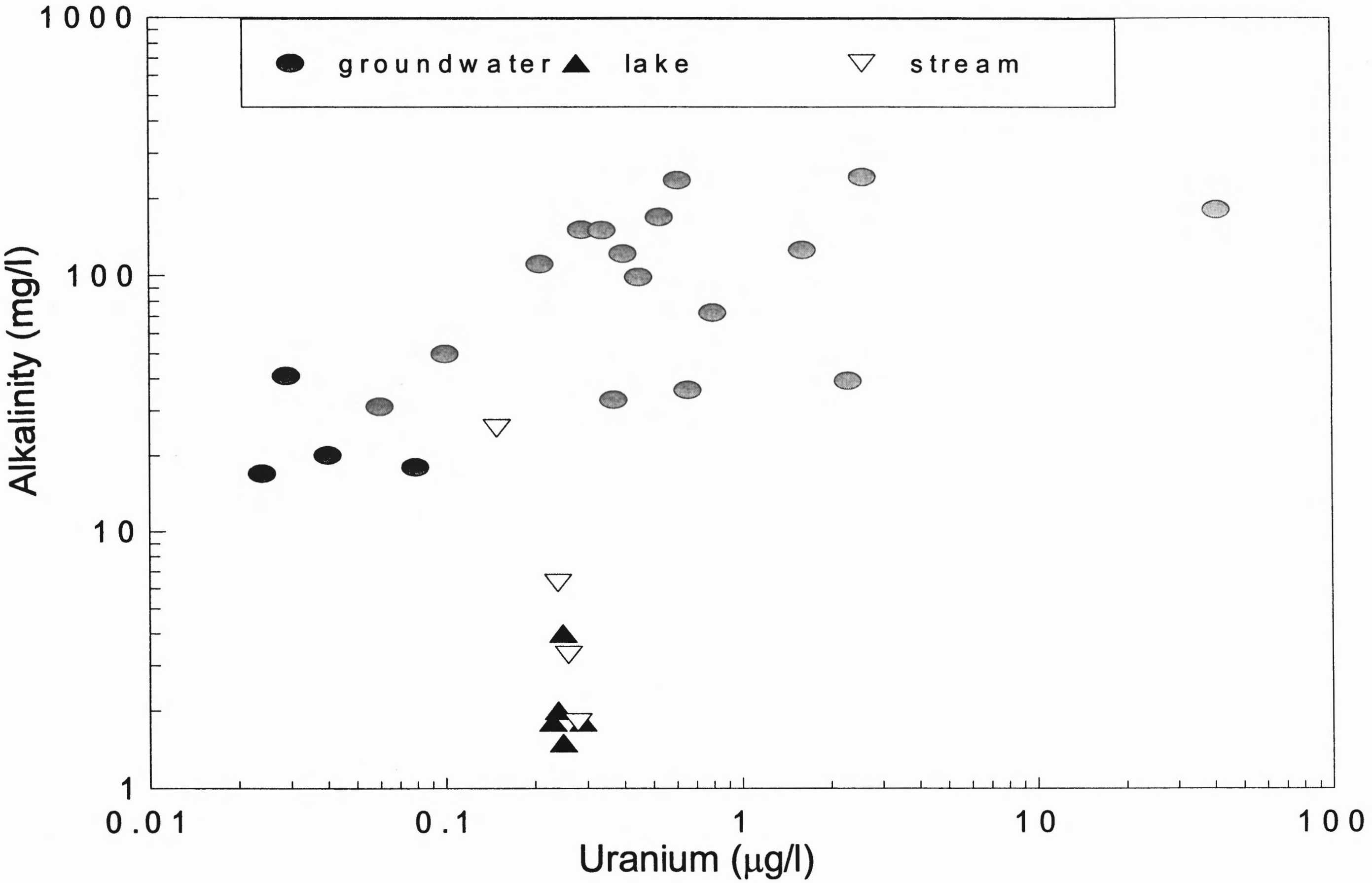

Fig. 9.3 Scatter plot of alkalinity vs. uranium concentration using logarithmic axes. The plot is by sample type to show the difference between groundwaters and surface waters. The groundwaters show an increase in uranium solubility with increasing alkalinity that is likely a result of the formation of soluble uranyl carbonate complexes. Surface waters seem to be nearly uniform in uranium concentration and more concentrated than the alkalinity would predict. This may be a result of adsorption onto dissolved organic compounds in the surface waters.

surface waters which can adsorb uranium and thus keep it in solution (Ivanovich and Harmon 1992, Zielinski et al. 1988) at levels higher than would be expected at these low alkalinity levels.

The $^{234}U/^{238}U$ activity ratios ranged from 0.98 to 1.43. The leaching of primary uranium ores, coupled with high uranium concentrations, should yield activity ratios close to unity (Osmond and Ivanovich 1992). One sample, W34, contained an anomalously high uranium concentration of 41 μg/l and had an activity ratio of unity. It is strongly suspected that this may reflect the proximity to a weathering, near-surface uranium mineralization. However, the rest of the Avon data show higher activity ratios coupled with low concentrations, as would be expected from the weathering of a non-uranium mineralized source under humid conditions. There is no apparent geographical trend of uranium isotopic changes with flow direction along the Avon Valley. What is most apparent here is the dominance of chemical weathering on the uranium concentration and isotopic ratio. For example, if a comparison is made between the values presented here and published values from a similar non-mineralized granitic area in a hyperarid region (personal communication, Kronfeld 1998), the climatic effects on the uranium isotopic ratio become readily apparent (Fig. 9.4). The southern Sinai desert, taken for comparison, receives less than 50 mm of rainfall per year. In this region mechanical weathering is dominant over chemical weathering. The result of this is that new rock surfaces are constantly being formed as the rocks are eroded. Under these conditions new sites of ^{234}U become continuously available to leaching processes. The infrequent rains are thus able to leach the preferentially soluble daughter isotopes that

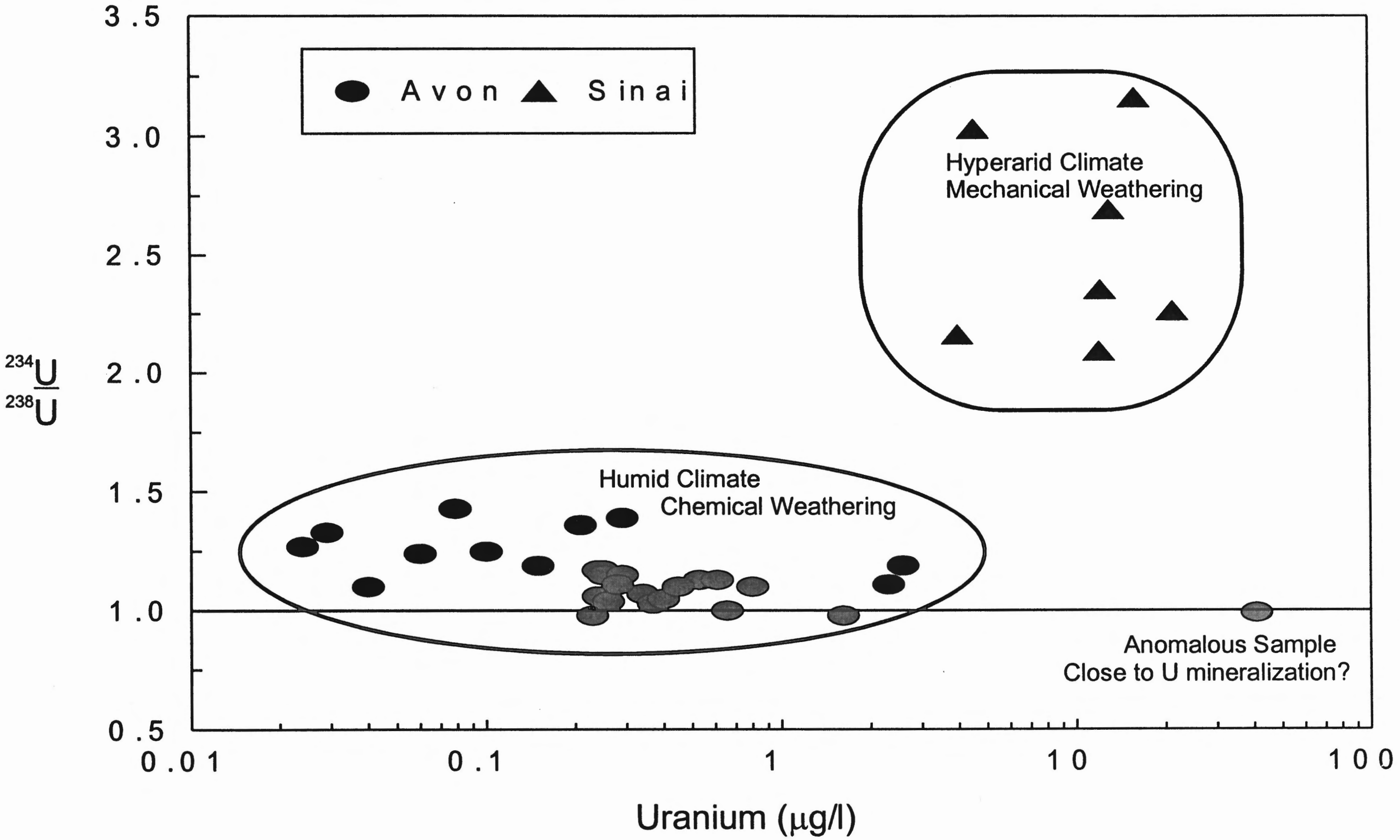

Fig. 9.4 Scatterplot of uranium concentration versus $^{234}U/^{238}U$ activity ratio comparing samples from the hyperarid Sinai region with samples from the Avon Valley. Differences in concentration and activity ratio are attributed to the differing effect of mechanical versus chemical weathering. The anomalous Avon sample combines high concentration with close to unity $^{234}U/^{238}U$ activity ratio suggesting proximal uranium mineralization.

become exposed. This can generate $^{234}U/^{238}U$ activity ratios that range between 2 and 4. Such ratios are appreciably higher than those generated from the same type of granitic rocks in Nova Scotia. The high evaporation in the desert leads to concentration of the elemental uranium, which is leached more effectively at the high ambient temperatures in the desert. In the Avon Valley the lack of production of new surfaces by mechanical weathering results in a paucity of available ^{234}U daughter product. The constant chemical weathering that results from high rainfall removes uranium. However, much of the ^{234}U daughter has previously been leached away without allowing sufficient time for much build up of new daughter product. The result is that the predominant chemical weathering in Nova Scotia leads to dilution of the elemental uranium in solution (low concentration values in the water) and low activity ratios.

10.0 RADON

10.1 Background

Radon is often used as water tracer in groundwater studies, since it is a noble gas and will not be involved in chemical reactions in the aquifer (Kraemer and Genereux 1998). Radon is also known to be a health concern (Grantham 1986). For these reasons radon was included in this study.

Radon is a naturally occurring, noble gas in the ^{238}U decay series (Fig. 9.1). Physical rather than chemical processes govern its mobility. It does not form an ion in solution, nor is it readily adsorbed onto most surfaces (Wanty and Schoen 1991). Radon is soluble in water but favours the gaseous phase. In a water-air system, at 20°C, it will partition itself into the air phase at a ratio of 4 to 1 in favour of air (Weigel 1978 as cited in Niton Electronics 1993). Because of the huge volume of the atmosphere, in which radon concentrations are very low (Wanty and Schoen 1991), water in contact with the air will eventually lose nearly all of its radon. The effect of radon loss due to contact with the atmosphere is hereafter referred to as radon degassing. This degassing makes radon useful as a tracer in hydrological studies since any radon in surface water indicates groundwater input. In the case of a stream, the input must be local, due to the short half-life of radon (Kraemer and Genereux 1998). Since it is so mobile in groundwaters and so easily removed by contact with air, radon is often found to correlate poorly to its parent radionuclide. For this reason, when a correlation does exist, it suggests the proximal presence of the parent radionuclide.

Currently, the Canadian Drinking Water Guidelines do not include a guideline for the maximum permissible radon concentration in water. This is because no studies to date have conclusively shown that ingestion of radon in water causes significant harm (NSDOE 1998). However, in 1991 in the U.S.A., the Environmental Protection Agency (E.P.A.) proposed a Maximum Contaminant Level for the concentration of radon in public drinking water of 300 pCi/l (Federal Register 1991 as cited in Niton Electronics 1993). Radon in air is associated with an increased risk of lung cancer (Grantham 1986). It should be noted that radon in a domestic water supply will degas into the air as the water is used in the home. For this reason elevated levels of radon in well water can lead to elevated levels of radon in indoor air.

10.2 Data and Interpretation

The radon data are summarized in Table 10.1. Radon concentrations varied widely, from less than the level of detection to 17,700 pCi/l. Eight sample sites exceeded the U.S.E.P.A. guideline of 300pCi/l.

Table 10.1: Avon Valley Radon Activity Data

Sample Code	Radon pCi/l	Analytical Error
S01	120.0	25.0
L02	17.0	7.0
L03	12.0	8.0
S04	63.0	21.0
S05	27.0	9.0
L06	19.0	7.0
L07	18.0	7.0
W08	7165.0	217.0
L09	8.0	5.0
S10	1.0	0.0
S11	12.0	6.0
W12	158.0	22.0
W13	829.0	54.0
L14	0.0	3.0
W15	0.0	2.0
W17	4653.0	146.0
W18	2318.0	108.0
L19	28.0	10.0
W20	0.0	3.0
S56	175.0	67.7
W57	23.2	6.3
W58	7620.0	377.0
S59	595.0	75.9
W60	8660.0	306.0
W61	17700.0	462.0
W62	9720.0	952.0
W63	180.0	71.1

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

Radon activity was lowest in the lakes and streams, probably due to continuous degassing to the atmosphere. Radon activity is much higher in the groundwater. There is a tendency for the dissolved radon activity to correlate with the amount of dissolved uranium in groundwater samples (Fig. 10.1). This suggests that radon activity could be used as a tracer to approximate the uranium concentration in this area. Fig. 10.1 shows 7 groundwater samples that fit the suggested correlation reasonably well ($r^2 = 0.71$). Two groundwater samples lacked measurable radon. Well 20 was well ventilated, having screens that allowed the air in the well to exchange with the atmosphere. Well 15 is a Provincial Park pump that is not frequently used. Information concerning its construction and maintenance was not obtained. Here too radon degassing is suspected to be occurring in the pump. One other well (well 23) plots between the radon-free wells and the other well water data points. It is likely a partially degassed sample. This well was also noted to be rarely used, for the well owner used bottled water for all potable water needs. A re-measurement of well 15 showed higher radon content, but it also falls below its expected position on the trend line. Again this is likely due to partially degassing. The surface water points in Fig. 10.1 show a trend away from the correlation line that can be explained by radon degassing. It is important to note that for this correlation to exist, the source of both the radon and the uranium must be nearby, due to the short half-life of radon and the low flow rate of groundwater.

A correlation between uranium and radon has been found in another location in Nova Scotia. Using the data presented in Page (1999), a direct correlation ($r^2 = 0.96$) is found between soluble radon and uranium (Fig. 10.2). This correlation uses data from

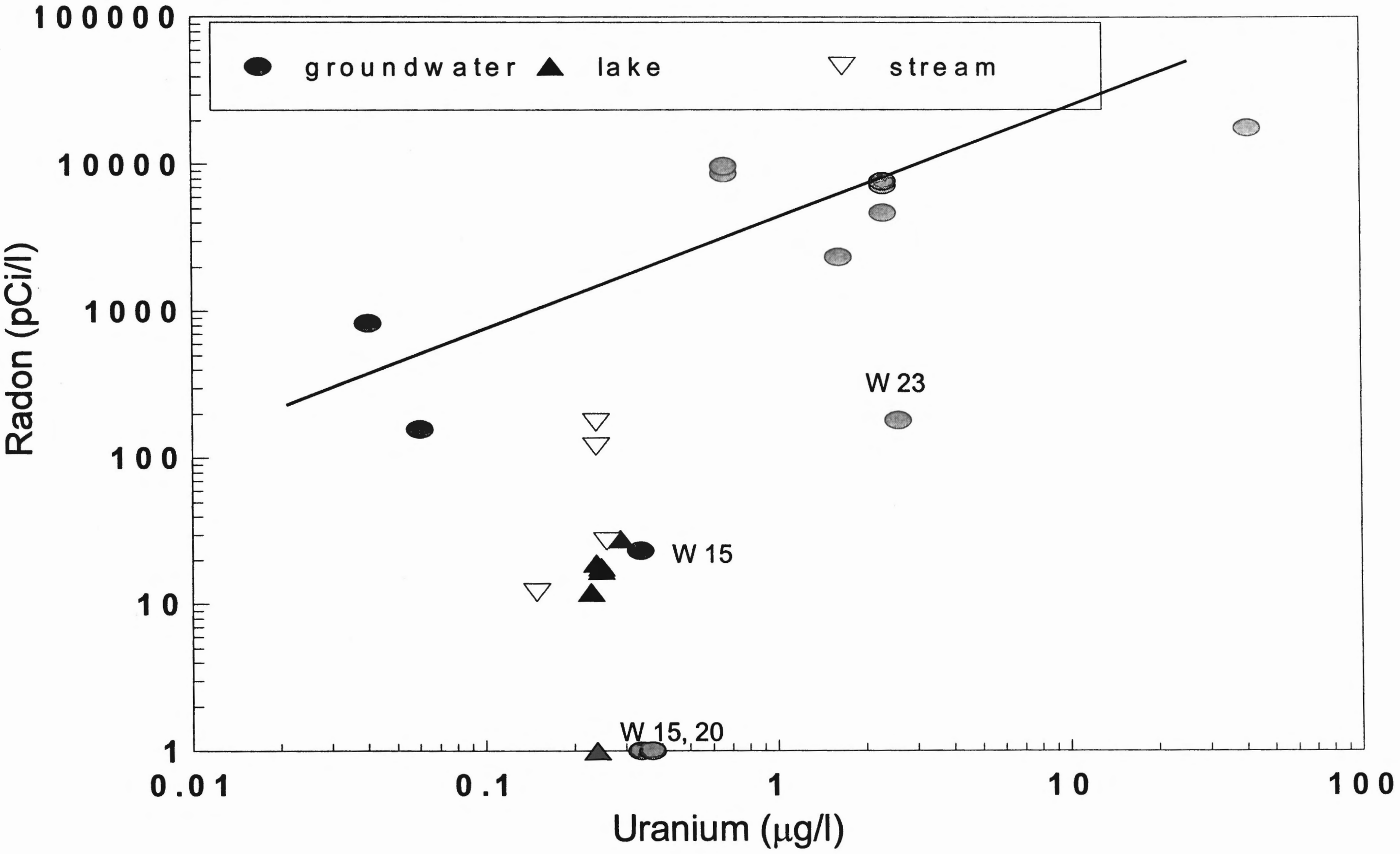

Fig. 10.1 Logarithmic scatterplot of uranium vs. radon concentration The surface water samples and the labeled well samples are believed to have degassed radon as discussed in the text. The remaining well water samples form a trend with an r value of 0.84 and an r^2 of 0.70.

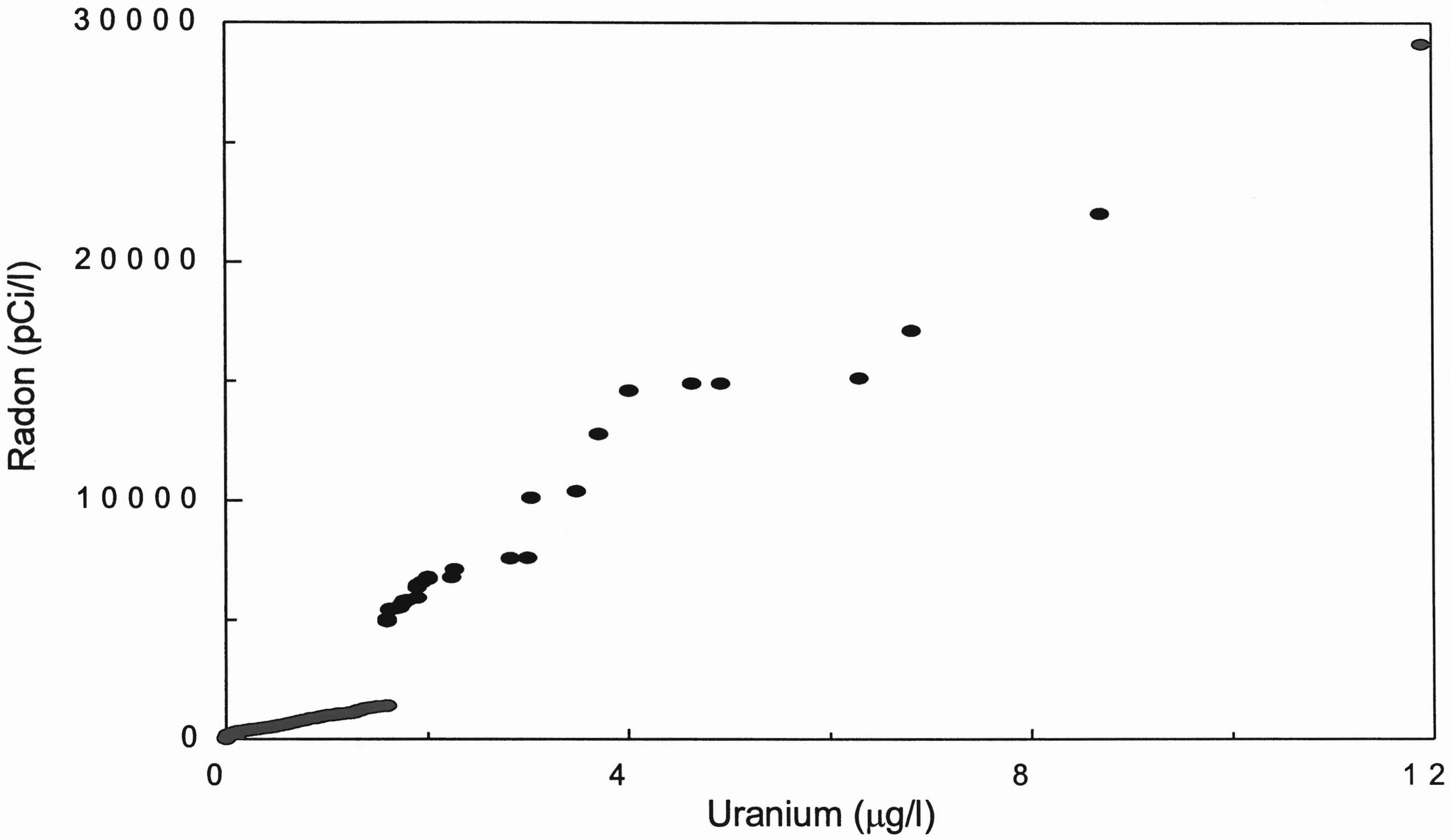

Fig. 10.2 Linear scatterplot of uranium vs radon for well water data put into digital format by Page (1999) from Saarburg-Interplan exploration data. The trend in the data has an r^2 value of 0.96. This data clearly show that a good linear relationship between uranium and radon is possible for waters from Nova Scotia.

631 water wells in the Windsor and Rawdon Hills area immediately adjacent to the present study area. However, data from a number of other areas of Nova Scotia in the Uranium Inquiry study do not show this correlation at all (Grantham 1986).

In summary, the data obtained in this study suggest that samples of radon that have not experienced degassing do correlate with the uranium in solution. The correlation of high radon activity with high uranium activity suggests proximity to uranium-rich sources.

11.0 RADIUM

11.1 Discussion

Radium is a radioactive product of ^{230}Th alpha decay in the ^{238}U decay chain (Fig. 9.1). Radium chemistry is dominated by its ionic state, Ra^{2+} (Fig. 11.1). It is insoluble in the sulphate and carbonate forms, while the ionic form is susceptible to adsorption, ion exchange, and co-precipitation (Wanty and Schoen 1991, Kraemer and Genereux 1998, and Gascoyne 1992). Radium is soluble as radium chloride in water where the chloride anion is dominant.

None of the samples analysed contained detectable radium. Since the waters of the study area are known to contain uranium (the ultimate parent of radium) and radon (the immediate daughter) there must be radium in the system. Previous studies have also found very little radium in Nova Scotia waters (Page 1999, Grantham 1986). Since the waters in the area are generally undersaturated with respect to carbonate and sulphate species, it is unlikely that either precipitation with calcium carbonate/sulphate or formation of radium carbonate/sulphate is the reason for the low levels of radium. Radium is highly soluble as a chlorine complex, but levels of chlorine in the Avon Valley waters are very low. In the present study area, adsorption and ion exchange are thus the most likely processes causing low radium concentrations, which agrees with the generalization of Ku et al. (1992 as cited in Osmond and Cowart 1992) regarding radium solubility. They concluded that: “The removal of radium from solution, is principally by adsorption (Krishnaswami et al. 1982) or cation exchange (Sturchio et al. 1989).”

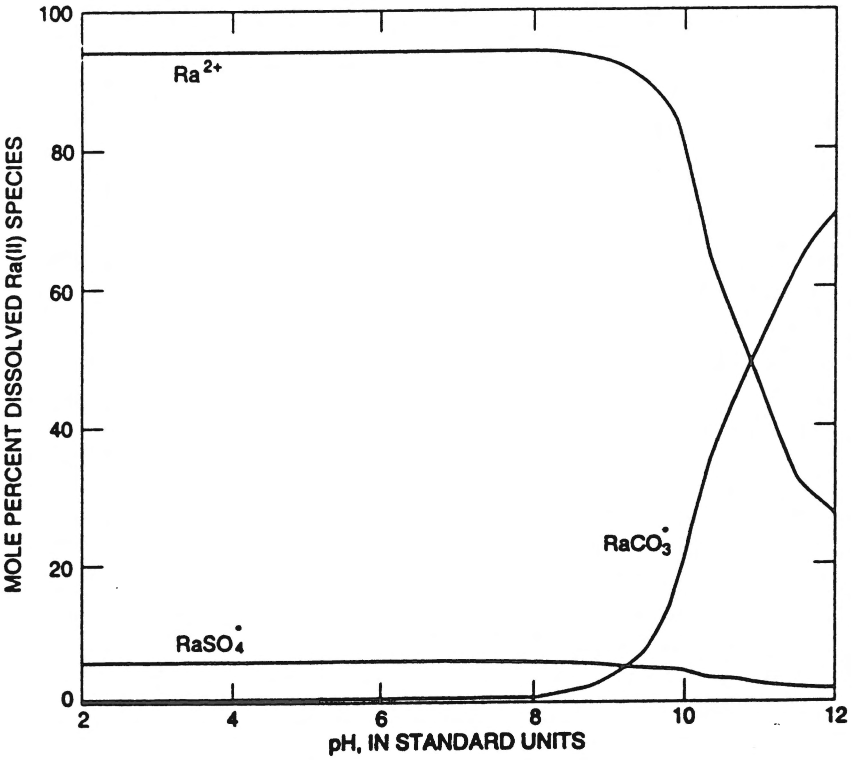

Fig. 11.1 Distribution of inorganic aqueous radium species as a function of pH for the following conditions: $\Sigma CO_3 = 10^{-2}M$, $\Sigma SO_4 = 10^{-4}M$, and $\Sigma cl = 10^{-4}M$. No chloride complexes are sufficiently significant to plot on the diagram (from Wanty and Schoen, 1991).

12.0 SUMMARY

12.1 Conclusions

The use of multiple isotopes and water chemistry in the Avon Valley provided abundant information about the geochemistry of the waters and suggested constraints on the hydrology of the system. Corroborating evidence from more than one isotope strengthens many of the conclusions discussed in this section.

No part of Nova Scotia is far from the ocean, and as a result, the rain falling on it has a dilute component of sea salt. The prevailing winds moving up the industrialized eastern seaboard of the U.S.A. ensure that the rain has a very low pH. The rain has an oxygen isotopic signature that varies consistently from summer to winter. When this rain falls on the Avon Valley, it can take a number of routes (refer to Fig. 4.16). Some water evaporates immediately or experiences evapotranspiration by plants. This water does not enter into the present study. Some falls directly on the lakes in the area, and much more falls onto the land surface. Some of what falls on the land surface becomes overland flow, which is to say that it flows into streams and eventually into the lakes without interacting significantly with the subsurface. The lake waters do show some effects of granite dissolution (e.g. uranium, and radiogenic strontium content). The water chemistry, strontium isotopes, carbon isotopes and oxygen isotopes all indicate that rainfall and/or overland flow recharge the lakes, not groundwater.

Some of the rain that lands on the surface infiltrates into the glacial till, where it interacts with material the glaciers have transported up the Avon Valley, including material from the Windsor and Horton Groups to the north. The water chemistry, the carbon isotopes and the strontium isotopes indicate conclusively that dissolution of limestone and some gypsum accounts for the majority of the resulting groundwater chemistry. Not all wells have dissolved this material to the same degree. It is suggested that the degree of 'maturity' correlates with the length of time the water has been in contact with the till. The temperate climate and high flushing rate of the system are reflected in the observed uranium concentrations and activity ratios.

Stream waters in the highlands tend to have compositions intermediate between those of the lakes and the groundwater. Their chemistry is interpreted to be a mix of lake and/or rainwater with groundwater input. The fact that a few streams in the granitic highlands contained detectable radon suggests that the groundwater input was close to those sample points and the spring sources could be traced using radon concentrations.

Water samples were collected in the lowlands around Windsor as a comparison to the granite-dominated highlands. The chemistry of the groundwater samples at these sites was consistent with the chemistry of the highland samples, but the surface waters showed a very strong influence from the gypsum in the area.

The surface waters and groundwater of the Avon Valley can be chemically divided into two end members with a few samples falling between them. One end member has a salt signature and consists mostly of surface waters with low pH and low conductivity. This water is interpreted to be composed mostly of rainwater. The other end member has a calcium bicarbonate signature and is made up of well waters with higher pH and conductivity. This is interpreted to be mature water, which has undergone some water-rock interaction. The intermediate samples have simply had less contact with till or rock than the mature end member. There are also three outlier samples, which are surface waters characterised by calcium sulphate. These are the surface samples from the lowland area whose chemistry is interpreted to have resulted from the dissolution of gypsum.

Nitrogen was generally below detection levels, and radium was not detected. The low nitrogen concentration is likely due to fairly low anthropogenic inputs coupled with rapid flushing of the system. The presence of radium was expected in the system, since both its daughter and one of its parent radionuclides are found in detectable quantities. The lack of detectable radium indicates that chemical conditions are such that the radium is not mobile in the water system but is adsorbed onto surfaces, either within the bedrock or within the till.

Uranium concentrations throughout the study area were below current Canadian Drinking Water Guidelines in all samples. The isotope activity ratio of U^{234}/U^{238} was found to be useful in characterising the Avon Valley samples in comparison to arid climate groundwaters from a granitic bedrock area. The activity ratio and uranium concentration also allowed the identification of anomalous versus background values.

While there are no Canadian Drinking Water Guidelines for Radon in water, eight samples in the study exceeded the U.S. EPA guideline of 300 pCi/l. Uranium and radon concentrations showed a linear correlation in groundwater samples that have not had an opportunity to degas the radon. This correlation was also found in data from adjoining areas to the north and east of this study area. However, previous studies from other parts of Nova Scotia did not show this correlation.

The great strength of this study is the fact that all of the data point to the same conclusions. The entire hydrologic system is rapidly flushed with rainwater. This conclusion is based on: a) the presence of abundant waters with the chemical signature of rainwater, b) the overall low concentrations of dissolved ions, c) the lack of samples saturated with respect to calcite or gypsum, d) the lack of nitrogen compounds in the waters, e) the low concentration of uranium and f) the near unity in the uranium isotope activity ratios. The lake waters are dominantly composed of recent rainfall, and the dissolution of minerals progresses with groundwater flow to the north. The water chemistry and the isotopes of carbon, oxygen, and strontium support this interpretation. In particular the carbon isotopes leave no doubt about the lack of groundwater input to the lakes. The carbon isotopes also confirm that changes in the groundwater chemistry are largely due to the dissolution of old marine carbonate material. The water chemistry and the strontium isotopes support this conclusion. The oxygen and carbon isotopes indicate that the lakes have a very short residence time, on the order of a few years. The oxygen isotopes suggest that even the groundwater in the highlands is dominated by recent precipitation, while the lowlands receive older water as discharge from the highlands.

This thesis has underlined the strength of a multi-isotope groundwater study. In particular this study has shown the source of the groundwater chemistry in the Avon Valley. The study has also found significant problems with the concept of groundwater-recharged lakes. These results would not have been achieved using only chemical or physical data.

12.2 Recommendations

Since many Nova Scotians rely on well water, and many municipalities rely on lake reservoirs, studies of hydrochemistry and hydrology are important. This study has shown some of the uses of isotopes. Further work could expand on the conclusions of this study and explore further use of isotopes. Further work using physical data would also help to support or refute the ideas proposed in this study. In particular, three concepts warrant further investigation.

1) This study has proposed that the surface and groundwater system is rapidly flushed and that groundwater does not significantly contribute to the highland lakes. A physical study designed to create a detailed catchment basin water budget would help to test this idea. Further chemical and isotopic studies using repeated sampling would test the consistency of this conclusion through time. A tritium isotope study would help to confirm water ages, residence time and trace flow patterns. An oxygen and hydrogen isotope study using rainfall, surface waters and groundwaters through time would also be able to constrain flow patterns and flushing rates.

2) A few repeat samples of water chemistry were found to be very consistent, as was pH and conductivity. A study of the change in chemistry through time at a few sample sites would help to determine how much the system changes with time and whether that change can be correlated with rainfall. If there is not much change with time, it would be useful to know what process keeps the water chemistry so constant.

3) Finally, the radionuclides showed two interesting results. The uranium concentration in the lakes is remarkably constant. What process causes this? Does it

relate to the organic compounds in the lakes? Is uranium building up in the organic-rich lake bottom deposits? The correlation of radon with uranium is also interesting. Is the correlation variable with time? What other areas in Nova Scotia show this relationship? Does the relationship depend on bedrock type, uranium deposit type, or groundwater conditions? Is this relationship useful in predicting high uranium values in groundwater using the much less expensive field radon testing?

It is to be hoped that these and other questions relating to this study will be further investigated in the Avon Valley and in other parts of Nova Scotia.

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Appendix 1: Sample Descriptions

Sample Code	Sample Type	Sampling Date	UTM Easting	UTM Northing	Elevation (m)	Well Depth
S01	stream	05/28/98	399650	4952250	145.00	N/A
L02	lake	05/28/98	399700	4952500	145.00	N/A
L03	lake	05/28/98	401900	4961825	110.00	N/A
S04	stream	05/28/98	402400	4962575	110.00	N/A
S05	stream	05/28/98	402500	4963325	110.00	N/A
L06	lake	05/28/98	402450	4965500	100.00	N/A
L07	lake	05/28/98	401050	4966125	100.00	N/A
W08	well	05/28/98	401025	4965900	100.00	unknown
L09	lake	05/28/98	403110	4966340	100.00	N/A
S10	stream	05/28/98	408300	4977950	15.00	N/A
S11	stream	05/28/98	409450	4979450	15.00	N/A
W12	well	07/24/98	402725	4965825	105.00	~25 ft
W13	well	07/24/98	402750	4965875	105.00	~100 ft (drilled)
L14	lake	07/24/98	402525	4965750	100.00	N/A
W15	well	07/24/98	401850	4965875	105.00	unknown
L16	lake	07/24/98	401825	4965875	105.00	N/A
W17	well	07/24/98	401025	4965900	100.00	unknown
W18	well	07/24/98	395365	4963700	190.00	~130 inches
L19	lake	07/24/98	395375	4963675	190.00	N/A
W20	well	07/24/98	397375	4964100	170.00	~10-15 ft
S21	stream	07/24/98	397375	4964115	170.00	N/A
W22	well	08/06/98	413950	4984320	15.00	~9 ft
W23	well	08/06/98	415950	4980750	30.00	~20 ft
W24	well	08/06/98	416475	4979060	30.00	~25 ft
W25	well	08/06/98	408810	4978000	15.00	~9.5 ft
S26	stream	08/06/98	409451	4979451	15.00	N/A
S27	stream	08/06/98	408301	4977951	15.00	N/A
W28	well	08/06/98	405475	4976040	15.00	~12 ft
W29	well	08/06/98	405110	4973540	60.00	~15 ft
W30	well	08/06/98	404030	4970440	25.00	unknown
W31	well	08/06/98	403410	4968200	100.00	~21 ft
S32	stream	08/13/98	399650	4952250	145.00	N/A
L33	lake	08/13/98	399700	4952500	145.00	N/A
W34	well	08/13/98	397150	4952425	215.00	~12 ft
W35	well	08/13/98	401900	4960875	145.00	~120 ft (drilled)
L36	lake	08/13/98	402300	4962575	110.00	N/A
W37	well	08/13/98	402220	4963825	105.00	~9 ft
W38	well	08/13/98	400675	4965160	140.00	~6 ft
W39	well	08/13/98	404650	4971975	35.00	~9 ft
W40	well	08/13/98	406100	4977050	10.00	~12 ft
W41	well	08/13/98	405175	4974875	45.00	~12 ft
S42	stream	10/09/99	399650	4952250	145.00	N/A
L43	lake	10/09/99	399700	4952500	145	N/A
L44	lake	10/09/99	402300	4962575	110	N/A
S45	stream	10/09/99	402400	4962575	110	N/A
S46	stream	10/09/99	402500	4963325	110	N/A
S47	stream	10/09/99	402250	4963100	105	N/A
L48	lake	10/09/99	402525	4965750	100	N/A

Appendix 1: Sample Description cont.

Sample Code	Sample Type	Sampling Date	UTM Easting	UTM Northing	Elevation (m)	Well Depth
L49	lake	10/09/99	395150	4962200	190	N/A
W50	well	10/09/99	401850	4965875	105	unknown
L51	lake	10/09/99	401825	4965875	105	N/A
R52	stream	10/09/99	404750	4972850	20	N/A
S53	stream	10/09/99	409450	4979450	15	N/A
L54	lake	10/09/99	414000	4979750	35	N/A
R55	stream	10/09/99	404750	4972850	20	N/A
S56	stream	10/22/99	399650	4952250	145	N/A
W57	well	10/22/99	401850	4965875	105	unknown
W58	well	10/22/99	401025	4965900	100	unknown
S59	stream	10/22/99	401025	4965890	100	N/A
W60	well	10/22/99	400675	4965160	140	~6 ft
W61	well	11/02/99	401900	4960875	145	~120 ft (drilled)
W62	well	11/02/99	400675	4965160	140	~6 ft
W63	well	11/02/99	415950	4980750	30	~20 ft

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.

Appendix 2: Mineral Saturation Indices Calculated by Hydrowin

Sample Code	Calcite	Aragonite	Dolomite	Strontianite	Magnesite	Gypsum	Annhydrite	Celestite
W12	-3.27	-3.42	-7.01	-5.03	-4.63	-3.63	-3.88	-4.20
W13	-3.12	-3.27	-6.63	-5.15	-4.44	-3.92	-4.17	-4.78
L14	-6.63	-6.77	-13.38	-8.42	-7.33	-4.82	-5.04	-5.36
W15	0.45	0.29	-.001	-1.65	-1.49	-3.10	-3.36	-4.05
L16	-6.33	-6.47	-12.78	-8.12	-7.02	-4.85	-5.07	-5.38
W17	-1.58	-1.73	-3.72	-3.46	-2.98	-3.46	-3.71	-4.15
W18	-0.68	-0.82	-2.33	-2.79	-2.31	-2.83	-3.06	-3.71
L19	-6.96	-7.11	-13.97	-8.61	-7.58	-4.90	-5.12	-5.30
W20	-2.19	-2.34	-4.99	-4.05	-3.67	-2.62	-2.88	-3.30
S21	-6.20	-6.34	-12.45	-7.99	-6.81	-4.94	-5.16	-5.74
W22	-0.36	-0.52	-1.24	-2.33	-1.87	-2.43	-2.69	-3.24
W23	0.27	0.12	0.18	-1.26	-0.96	-1.94	-2.19	-2.29
W24	-2.78	-2.94	-5.99	-4.64	-4.14	-2.42	-2.67	-3.11
W25	-3.59	-3.73	-7.55	-5.08	-4.72	-2.03	-2.27	-2.31
S26	-0.66	-0.81	-2.43		-2.34	-1.13	-1.35	
S27	-0.16	-0.30	-1.86		-2.27	-0.33	-0.55	
W28	-0.54	-0.69	-1.52	-2.55	-1.77	-2.05	-2.29	-2.85
W29	-0.96	-1.11	-2.45	-2.84	-2.28	-2.31	-2.55	-2.99
W30	-2.59	-2.74	-5.63	-4.64	-3.97	-3.43	-3.69	-4.32
W31	-1.18	-1.32	-2.86	-3.27	-2.43	-2.45	-2.69	-3.33
S32	-3.90	-4.06	-7.78		-4.75	-4.04	-4.29	
L33	-6.20	-6.35	-12.31		-6.82	-4.93	-5.17	
W34	-0.82	-0.97	-2.41	-3.14	-2.27	-2.76	-2.99	-3.85
W35	-0.64	-0.79	-1.75	-2.61	-1.99	-2.35	-2.60	-3.14
L36	-5.48	-5.62	-11.01		-6.11	-4.87	-5.09	
W37	-0.92	-1.07	-2.89	-2.75	-2.86	-3.08	-3.33	-3.73
W38	-2.82	-2.96	-5.93	-4.67	-3.83	-3.35	-3.59	-3.98
W39	-2.07	-2.22	-5.03	-4.06	-3.70	-3.49	-3.73	-4.26
W40	-0.13	-0.28	-1.27	-2.30	-1.93	-1.93	-2.17	-2.89
W41	-3.66	-3.81	-7.51	-5.46	-4.59	-3.31	-3.55	-3.90
S42	-4.81	-4.96	-9.53	-3.09	-5.69	-4.11	-4.36	
L43	-7.04	-7.19	-13.84	-5.92	-7.74	-4.75	-5.01	
L48	-6.24	-6.39	-12.43	-4.81	-7.07	-4.70	-4.96	
L49	-6.53	-6.69	-12.86	-5.03	-7.27	-4.63	-4.88	
S52	-5.59	-5.74	-11.14	-4.31	-6.44	-4.56	-4.81	
L54	-0.18	-0.33	-1.70	-0.90	-2.43	-0.27	-0.52	
S55	-5.48	-5.63	-10.98	-4.23	-6.39	-4.61	-4.87	
S56	-4.81	-4.96	-9.51	-3.20	-5.71	-4.14	-4.40	
W57	-0.06	-0.22	-1.10	-1.50	-2.01	-3.12	-3.38	
W58	-2.13	-2.29	-4.79		-3.61	-3.33	-3.59	
S59	-4.62	-4.78	-9.39	-4.53	-5.78	-4.40	-4.66	
W60	-3.50	-3.65	-7.10		-4.53	-3.40	-3.65	

Note: The prefix of the sample code refers to sample type: L for a lake sample, S for a stream sample and W for a well water sample.