Stable Isotopes Information – more information in Clark and Fritz 1997
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1. Fractionation and precipitation

Kinetic and equilibrium fractionation controls the isotopic signature of meteoric water. Hydrogen has three isotopes: ^{1}H, ^{2}H and ^{3}H of which ^{1}H and ^{2}H are stable and ^{3}H (tritium), is radiogenic. Oxygen has three stable isotopes: ^{16}O, ^{17}O and ^{18}O two of which are commonly used in hydrologic studies. Due to the differences in mass and energy between isotopes of the same element, isotopes will behave differently during kinetic processes. The relative proportion of the heavy to light isotope will fractionate during chemical reactions as one isotope is used preferentially. In the hydrologic cycle during phase changes one stable isotope will be preferentially partitioned into the new phase over another, this process is dependent on temperature and relative humidity and thus so is the isotopic signature of water. Understanding stable isotope compositions in meteoric water begins with an initial oceanic isotope composition, and proceeds through evaporation, condensation, and precipitation.

Both oxygen and hydrogen stable isotopes are usually expressed in delta notation as the relative proportion of the heavy to light isotope (R=^{18}O/^{16}O or ^{2}H/^{1}H) in the sample compared to the proportion in a standard (Equation 1).

The standard used for both oxygen and hydrogen is Vienna Standard Mean Ocean Water (VSMOW). The abundance of the ^{18}O and ^{2}H is much smaller than those of the corresponding light isotopes and so results are expressed in per mil (‰).

Clark and Fritz (1997) detail this fractionation process. The isotopic composition of oceanic water is similar to VSMOW. The first fractionation of isotopes begins as water evaporates from the ocean or other surface water bodies (Figure 1). As water evaporates from the ocean surface the ocean surface waters become increasingly more enriched. Lighter isotopes of water preferentially evaporate with respect to heavier isotopes. Enrichment effects can be seen in the isotopic composition of the water vapor. Enrichment during evaporation fractionation is kinetic, and is affected by humidity, wind speed, and surface water temperature. Once water is evaporated, mixes with the vapor already present in the atmosphere. Within a cloud, equilibrium fractionation between the vapor and the condensate preferentially partitions ^{18}O and ^{2}H (Rayleigh-type distillation process). This process removes the heavier isotopes from the vapor phase.

Equilibrium fractionation during condensation and precipitation causes precipitation to plot near the meteoric waterline (MWL) with a slope of approximately 8.0 (Craig 1961). The global meteoric water line is the relationship between $\delta^{18}O$ and δ^2H in fresh water globally.

Craig (1961) measured samples of precipitation from across the globe and plotted the results of the analyses as $\delta^{18}O$ vs δ^2H, which resulted in the following fit line (Figure 2):

$$\delta^2H = 8 \cdot \delta^{18}O + 10\ ‰ \qquad\qquad\text{(Equation 1)}$$

Later work by Rozanski *et al.* (1993) refined the line; and called it the Global Meteoric Water Line (GMWL) using the VSMOW standard and the International Atomic Energy Agency (IAEA) sampling network:

$$\delta^2H = 8.13\ \delta^{18}O + 10.8\ ‰ \qquad\qquad\text{(Equation 2)}$$

Groundwater, samples that fall on the GMWL can be assumed to be meteoric waters. Samples that fall off the meteoric line are waters that have undergone a chemical or physical process that has caused fractionation. Once precipitation reaches the earth's surface, several factors can affect the isotopic composition of meteoric water. As fractionation processes affect the isotopic composition of water, shifts occur away from the meteoric waterline. Evaporation, condensation, exchange with rock minerals, hydration of silicates, carbon dioxide exchange and (hydrogen sulfide/gas production/ methane) production can all affect the isotopic composition of water, which are graphically shown on a meteoric water plot (Figure 3). It is thought that as water infiltrates the unsaturated zone, the seasonal isotopic composition variations present in precipitation are "smoothed out" by the differential flow paths within the porous medium or in fractures in variably saturated sediments reaching a value close to the average isotopic composition for precipitation (Darling and Bath 1988, Eichinger *et al*. 1984; Clark and Fritz 1997).

1.1 Deuterium Excess

Local differences in the y-intercept and slope of the meteoric waterline require the definition of a local meteoric water line (LMWL). The y-intercept is termed the deuterium excess (d-excess) factor and for a given sample is defined as:

$$ⓓ\ (‰) = \delta^2H - 8 \cdot \delta^{18}O\ \text{(Dansgaard, 1964)} \qquad\qquad\text{(Equation 3)}$$

D-excess is influenced by the temperature and humidity at the precipitation source (Merlivat and Jouzel 1979). During evaporation of seawater at a humidity of 85%, which is considered the average humidity

for atmospheric water vapour formation, the resulting precipitation is displaced from seawater with an excess of deuterium in the amount of +10‰ (Craig 1961; Clark and Fritz 1997). This is the d-excess value of the GMWL. The slope of the GMWL is dependent on the temperature and humidity at the site of precipitation (Merlivat and Jouzel 1979).

The particular isotopic signature of an air mass is dependent on the temperature and humidity at the time of formation. As the mass moves inland and moves to higher elevations the remaining water will become increasingly depleted in $\delta^{18}O$ and δ^2H as the heavy isotopes are preferentially incorporated into the precipitation and subsequent rainout (Dansgaard 1964). Each precipitation event will have an isotopic signature that varies according to the temperature and humidity during the event. These variations are generally removed from the groundwater by mixing and the groundwater will take on an isotopic signature similar to the annual average for the area. Stotler (2003) and Gerber *et al.* (2009) suggest that a seasonal signal may be preserved in the d-excess values of groundwater to a greater extent than in $\delta^{18}O$ and δ^2H. When interpreting isotope data it is important to keep in mind that seasonal variations can be expected in the shallow system (Fritz et al. 1987, Clark and Fritz 1997, Stotler 2003).

Preferential pathways allow groundwater to move more rapidly through the confining aquitard preventing mixing and attenuation of seasonal variations. The mixing of different groundwaters may also cause variation in the isotopic signature of a confined aquifer. The attenuation of seasonal variations with depth observed for $\delta^{18}O$ may be less pronounced for d-excess allowing some variation to be preserved. This has implications for climate research as d-excess may present a better proxy by which to study climate change than $\delta^{18}O$ and δ^2H if variations are better conserved (Stotler, 2003).

Stotler (2003) suggests that monitoring of seasonal variations in groundwater isotopic signatures can yield valuable insight in a number of areas. Shifts in isotopic signatures caused by changing temperature and humidity conditions due to climate change may be preserved in groundwater and observed with repeated monitoring at locations where seasonal variations are observed. In the short term, periods of more extreme weather conditions such as drought/flood, may convey a particularly high/low d-excess value on waters recharged under this conditions. Repeated samplings may also reveal the dominant recharge season and potentially the quantity of recharge. Using d-excess and other tracers (like tritium) could provide information on dispersion processes in the shallow groundwater system with important implications for contaminant transport modeling (Stotler 2003).

In southern Ontario, precipitation results from air masses transported from 5 different sources (Figure 4). Atlantic air masses and tropical air masses from the Gulf of Mexico are dominant; however air streams from the Arctic influence the winter months (Fritz *et al.* 1987). Pacific air masses can also reach the study area. Evaporation from the Great Lakes provides an additional source of precipitation (Gat *et al.* 1994). A wide range in the isotopic signature of precipitation recorded at IAEA stations at Lake Simcoe and Ottawa reflects the differences in air masses from each of the sources listed above.

A secondary vapour source can also influence the isotopic signature of precipitation by increasing the d-excess values downwind from the source (Fritz *et al.* 1987; Gat *et al.* 1994). Evaporation enriches ^{18}O and ^2H in the vapour phase and the resulting evaporation line has a d-excess greater than that of the GMWL. Mixing of the evaporated waters into an atmospheric air mass will increase the d-excess of the resultant mixture (Gat *et al.* 1994).

The $\delta^{18}O$ isotopic signature of modern groundwater given by Fritz and others (1987) for the York Region study area is -9 to -12‰ (Fritz *et al.* 1987) (Figure 5).

2. Tritium Background

^3H is the radioactive isotope of hydrogen and has a half-life of 12.43 years. It is measured in tritium units (TU) with one TU being equivalent to one ^3H atom for every 10^{18} atoms of hydrogen. The method for measurement is liquid scintillation counting. Small amounts of tritium are produced naturally in the atmosphere by cosmogenic rays (Figure 6).

Tritium then enters the hydrologic cycle through precipitation as part of the water molecule ($^1H^3HO$). The level of natural tritium in the atmosphere varies seasonally and geographically with the greatest amount of tritium being transferred from the stratosphere to the troposphere, where it can be incorporated into precipitation, during the spring at mid-latitudes (Clark and Fritz 1997). Natural production and background tritium is relatively low (5 TU, Mazor 1997) and so generally waters recharged before 1950 will not have detectable levels of tritium in them.

During the 1950s and 1960s thermonuclear bomb testing input tritium into the atmosphere (Figure 7). Tritium in the atmosphere increased from approximately 10 TU to a peak of over 2000 TU in the mid-

1960s (IAEA 1983) before decreasing again to modern values of around 15-20 TU in southern Ontario. Current input of tritium into the atmosphere remains higher than natural levels through new tritium contribution from nuclear power generation. If waters have measurable tritium in them they can be considered modern meteoric waters recharged after 1950 if sourced from thermonuclear bomb tritium, or after 1970 if sourced from nuclear power generation (King 1997; Gerber *et al.* 2009).

Classifying older and younger waters can also be useful in interpreting flow systems and showing areas of faster groundwater flow where tritium is found at greater depths or further along a flow system (e.g. Stimson *et al.* 2001). Surface waters that have non-detectable tritium can be an indicative of discharge of older deeper waters.

3. Carbon-14 Background

Carbon-14 dating considers a much longer time scale, on the order of thousands to tens of thousands of years with carbon-14 having a half-life of 5568 years (Libby half-life) and recently Godwin (1962) revised the carbon-14 half-life to 5730 (Clark and Fritz 1997). Like tritium, carbon-14 is generated naturally in the atmosphere.

$$^{14}_{7}N + {}^{1}_{0}n \ \rightarrow \ {}^{14}_{6}C + {}^{1}_{1}P \hspace{3cm} \text{(Equation 6)}$$

The ^{14}C generated by this reaction then oxidizes to form CO_2, which mixes with atmospheric gases. $^{14}CO_2$ gas in the atmosphere can dissolve into the oceans, the largest storehouse of carbon-14, or may also be incorporated into plant matter through the process of photosynthesis.

The amount of the parent radionuclide (^{14}C) that has been lost is need for the determination of a radiocarbon date or age. This initial concentration of carbon-14 present in the system must be known and that carbon-14 is then lost only to radioactive decay and not gained or lost through other sources or sinks. If these two conditions are satisfied then the decay equation (7) may be used:

$$a_t = a_0 \cdot e^{-\lambda t} \hspace{3cm} \text{(Equation 7)}$$

Where a_t is the activity of the parent nuclide initially (a_0) and after some time (t). Carbon-14 is often reported as percent modern Carbon (pmC), (e.g. a groundwater where one ^{14}C half-life, 5730 years, has

passed since recharge would be reported as 50 pmC).

Relative ages calculated from radiocarbon dating are generally reported in radiocarbon years as opposed to calendar years, based on the use of 100 pmC for atmospheric CO_2. The atmospheric carbon-14 record has been reconstructed from the Pleistocene to the Holocene and back to the late Pleistocene by analyzing tree rings and coral (Bard *et al.* 1990). This record shows that atmospheric carbon-14 is not fixed (Stuiver and Quay 1980; Damon *et al.* 1989; Bard *et al.* 1990). To simplify the problem, atmospheric CO_2 is often assumed to be 100pmC.

Similar to tritium, thermonuclear bomb testing since the 1950s has provided a significant input of carbon-14 to the more recent atmosphere. The result of this are many waters identified with carbon-14 concentrations above 100 pmC. Such elevated concentration of carbon-14 is a good indicator of much younger waters (Clark and Fritz 1997).

Figure 8 illustrates the pathway of carbon-14 in CO_2 from creation in the atmosphere to incorporation into vegetation through photosynthesis and the associated fractionation. Root respiration and decay of vegetation create soil CO_2 with further fractionation effects (Figure 8). As soil CO_2 dissolves into infiltrating groundwater dependent on recharge temperature, pH, partial pressure of CO_2 and other weathering reactions taking place in the soil (Clark and Fritz, 1997). The ^{14}C contained in this dissolved CO_2 is the initial input of radiocarbon into the groundwater system. This assumes that no further dilution of ^{14}C occurs along the groundwater flow path, in a perfect closed system. However, the initial concentration of ^{14}C can be reduced through dilution and geochemical reactions and this loss must be accounted for in age dating of groundwaters.

It is important to understand that when interpreting the results of carbon-14 analyses the ages reported are not absolute given that groundwaters are mixtures. A radiocarbon age for a given sample does not indicate that every water molecule in that sample was recharged at the same given age. In reality it is an average of the various ages of waters incorporated in the sample. For example, a sample may have a radiocarbon age of 10,000 years and may also contain a small amount of tritium. The majority of the water may actually be 12,000 years old and a small proportion is less than 50 years old, with the end analyses showing a relative radiocarbon age of 10,000 year.

3.1 NETPATH: Carbon-14 modeling (Plummer *et al.* 1994)

NETPATH is often used to account for dilution of carbon-14 through geochemical reactions along the flow path. It is a geochemical mass balance model that analyses mass-balance reactions along a flow path from initial water to final water. A full description of NETPATH can be found in Plummer *et al.* (1994). NETPATH incorporates several adjustment models to define a_0 (Equation 5), the initial concentration of carbon-14 in the system by adjusting it for sources and sinks of carbon along the flow path.

Further adjustment of radiocarbon ages could be made with the measurement of dissolved organic carbon and CH_4. This would allow adjustment of ages based on total dissolved organic carbon (DOC) instead of only dissolved inorganic carbon (DIC). Although we did measure DOC, CH_4 measurements were not possible during this sampling study. Gas was present in some locations however consistent sample of existing gas were not obtained. Future studies would need to consider adding this as a mandatory parameter.

For the purposes of the York Region 2008-2014 study, several of the initial carbon-14 adjustment models contained in NETPATH were considered: (1) Tamers, (2) Ingerson and Pearson, (3) Fontes and Garnier and (4) Eichinger. Due to the overall complexity of the flow system a simple correction for carbonate dissolution was performed considering only the chemistry of the sampled well and the phases calcite, dolomite and carbon dioxide (CO_2) constrained by calcium, magnesium and carbon. A soil gas $\delta^{13}C$ value of -22‰ and carbon-14 activity of 100 pmc was assumed based on Aravena *et al.* (1995). This was the basic parameter set considered and corrections using these parameters. With the geochemical data available this base parameter set, while quite simplified, provides a rough correction of radiocarbon age.

Apart from the base case, additional models were run to test the sensitivity of the assumed soil gas isotopic composition and sensitivity of each model varied. The Tamers model is not dependent on this parameter and thus varying $\delta^{13}C$ values for soil CO_2 had no effect on the resulting radiocarbon age. The other models considered showed that by assuming a value of - 25‰ instead of -22‰ resulted in an age approximately 1000-1500 years younger. Adjusting the initial carbon-14 present in the soil gas predictably results in adjusted radiocarbon ages. If a value of 95 pmc is used instead of 100 pmc then the resultant radiocarbon age is reduced by 400 years. This is another area where adjustments could be made for future sampling, adding soil gas as a parameter would assist in understanding what are the actual values and

how they affect the radiocarbon data collected.

4. Dissolved Gases: Noble Gases and Chlorofluorocarbons

There are four sources of dissolved gases in groundwater: atmospheric dissolution (gas exchange), radiogenesis, chemical reactions, and terrigenesis.

4.1 Solubility Equilibrium

Gas exchange between water and air occurs in the atmosphere and the unsaturated zone. Henry's Law governs the partitioning of chemical compounds and elements (such as CFCs, He, Ne, Xe, Ar, Kr, O_2, and N_2) between air and water.

Henry's Law constants for groundwater studies must be determined from solubility data for the each chemical compound to estimated recharge temperature. Solubilities typically increase with temperature and atomic mass, with sensitivity to temperature increasing with mass (Stute and Schlossler 2000). But, when considering the temperature range relevant for the groundwater regime, noble gas solubilities in water commonly decrease with increasing temperature (Kipfer *et al.* 2002).

As groundwater moves through the unsaturated zone to the capillary fringe, it is in constant contact with soil gases, constantly re-equilibrating until it enters the saturated zone at which point the concentrations of the dissolved gases are consider to be "fixed". After initial recharge, if the water comes back into contact with the gas-phase of the saturated zone, the gas exchange will at the minimum partially erase the imprint of the earlier equilibration stage (Stute and Schlosser 2000).

4.2 Excess Air

In order to understand the interpretation of certain York Region samples and the data derived an understanding of the concept of excess air is required. Heaton and Vogel (1981) were the first to recognized "excess air". It was determined that some air derived noble gas concentrations were actually higher than the expected atmospheric equilibrium. Gas ratios in excess air are typically equal to the atmospheric ratios (Stute and Schlosser 2000).

Four conceptual models have been developed to explain excess air: unfractionated excess air (Heaton and Vogel 1981), partial re-equilibrium (Stute *et al.* 1995), multi-step partial re-equilibrium (Kipfer *et al.* 2002), and closed-system equilibration (Aeschbach-Hertig *et al.* 2012). At this point only the closed-system

equilibration model seems to adequately explain all of the observed fractionation. In closed-system equilibrium, a rising water table entraps air from the unsaturated zone in the saturated zone. This entrapped air then partially dissolves into groundwater, until equilibrium is reached. Finally the water table drops, leaving behind some entrapped air. It is typical for more air to be entrapped than can be dissolved at the prevailing pressure (Kipfer *et al.* 2002). It is thought that excess air correlates with lithology, amount of precipitation, humidity and climate change (Stute and Schlosser 2000, Aeschbach-Hertig *et al*. 2012). Excess air values of 0 to 3 cc STP/L are considered normal (Stute and Schlosser 2000).

4.3 Recharge Temperature

Recharge temperature is an important component with regards to the interpretation of dissolved gas data. Noble gas equilibrium concentrations record changes in physical conditions during air-water partitioning, such as changes in soil temperature, altitude, pressure, and salinity (Kipfer *et al.* 2002). It is typically assumed that water moving through the unsaturated zone constantly equilibrates with soil gas until it reaches the capillary fringe and the water table (Kipfer *et al.* 2002). This assumption is key for the calculation of recharge, groundwater ages and residence times, as the recharge temperature is the temperature at which dissolved gases establish equilibrium when entering groundwater

When calculating recharge temperature, there are usually two unknown components: equilibrium temperature or recharge temperature and amount of excess air. The first method of determining recharge temperature was through comparison of dissolved N_2 and Ar concentrations (Sugisaki 1961, Mazor 1972). Because N_2 concentration is susceptible to biogeochemical reactions such as denitrification this method is not the most reliable. Using Ne and Xe, is preferred because their solubilities react differently; Ne is strongly affected by excess air and Xe strongly affected by equilibrium temperature (Kipfer *et al.* 2002).

Over long periods of time the entrapped gases record long term seasonal or climate variations. This information can be used along with isotopic data such as ^{18}O and relative dating to understand the potential ages of some water masses/aquifers.

4.4 Chlorofluorocarbons (CFCs)

Chlorofluorocarbons (CFCs) are used as environmental age tracers in groundwater and are useful to date water recharged within the last 50 years (e.g. Busenberg and Plummer 1992, Cook *et al*. 1995, Katz *et al.* 1995, Johnston et al. 1998, Plummer *et a*l. 1998a, Plummer *et al.* 1998b, Plummer *et al*. 2000, Busenberg and Plummer 2000). However it was Thompson and Hayes (1979) who first proposed their use as

groundwater age dating tracers. Henry's Law governs the partitioning of CFCs between water and the gas phase

CFCs were developed in the 1930s as safe alternatives to ammonia and sulfur dioxide for refrigeration (Plummer and Busenberg 2000). By the mid-1970s, atmospheric scientists realized the compounds that were almost completely stable in the lower atmosphere would break apart when exposed to UV radiation, the product of which would attacked the ozone layer (Molina and Rowland 1974, Rowland and Molina 1975). Subsequently, monitoring stations established were established and eventually the compound was banned. As a result of this today's CFC concentrations have stabilized and are diminishing.

The most relevant CFC compounds with respect to groundwater age dating are: CFC-12, CFC-11 and CFC-113. CFCs are susceptible to microbial degradation, sorption, and subsurface contamination (Plummer and Busenberg 2000). For CFC tracers, it is important to correctly interpret recharge temperature and excess air content. If recharge temperature is overestimated or the excess air is interpreted incorrectly, the apparent age will be too young (Plummer and Busenberg 2000). Young groundwater in urban areas often experience atmospheric concentrations that are enriched compared with the global atmospheric curves; resulting in younger than expected groundwater age (Plummer and Busenberg 2000). Groundwater may also erroneously appear older when unsaturated zone travel times are less than 0.25-0.5 m/yr (Schlosser *et al.* 1989) or the unsaturated zone is greater than 10 m (Plummer and Busenberg 2000).
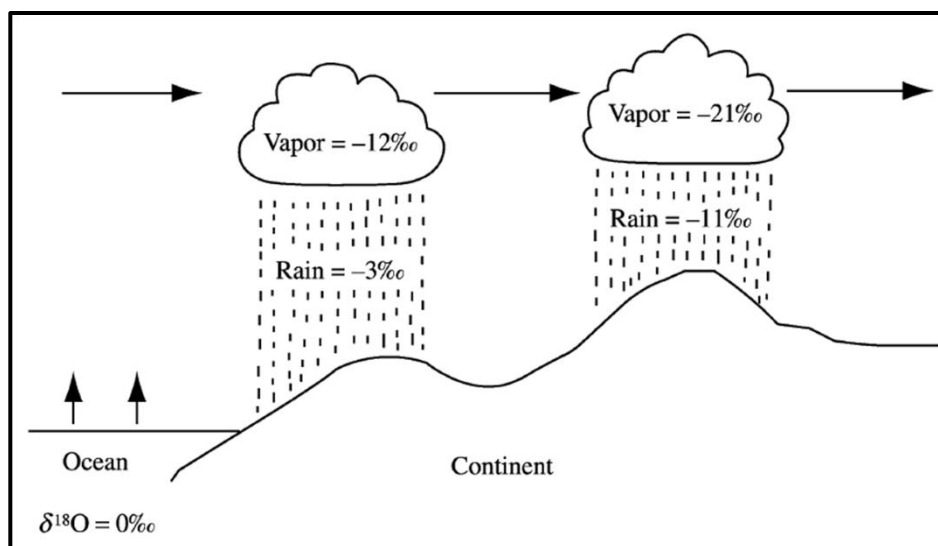
Figure 1: The ^{18}O isotopic abundance decreases with increasing distance to coast. ^{18}O enriched water rains down first while depleting the cloud of its ^{18}O isotope content. (Clark and Fritz 1997).
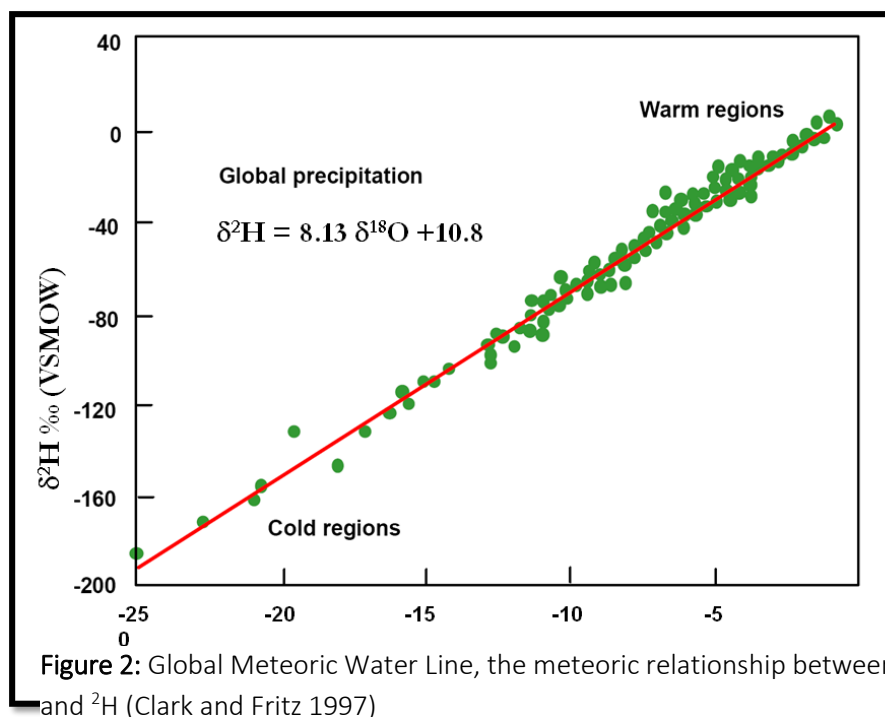

Figure 2: Global Meteoric Water Line, the meteoric relationship between ^{18}O and ^{2}H (Clark and Fritz 1997)
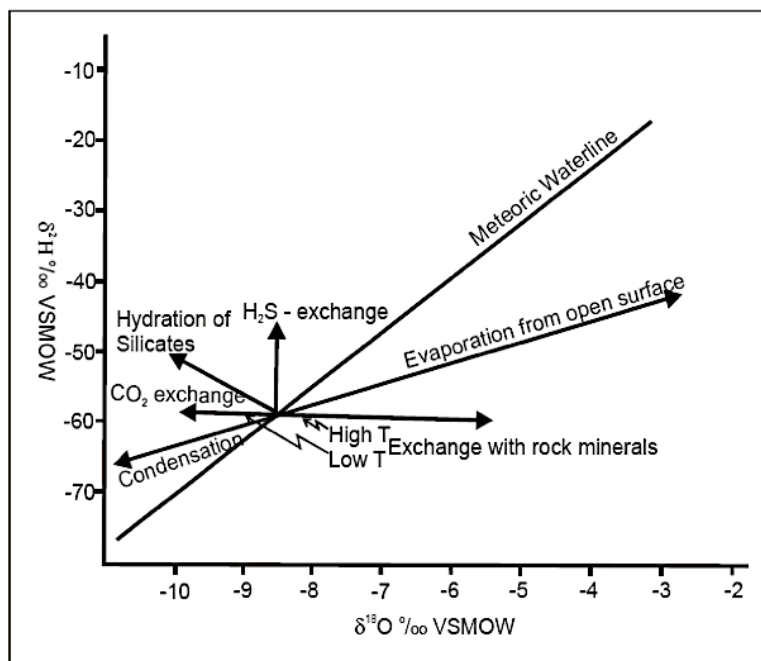
Figure 3: Processes causing fractionation of the stable isotopes deuterium and oxygen-18, causing the isotopic signature of water to deviate from the meteoric water line (IAEA, 1983).
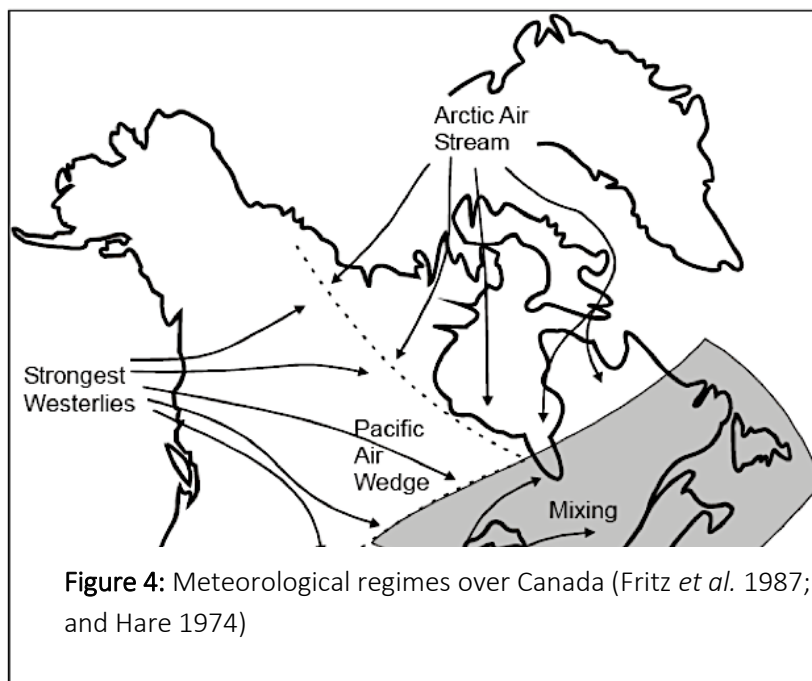
Figure 4: Meteorological regimes over Canada (Fritz *et al.* 1987; Bryson and Hare 1974)
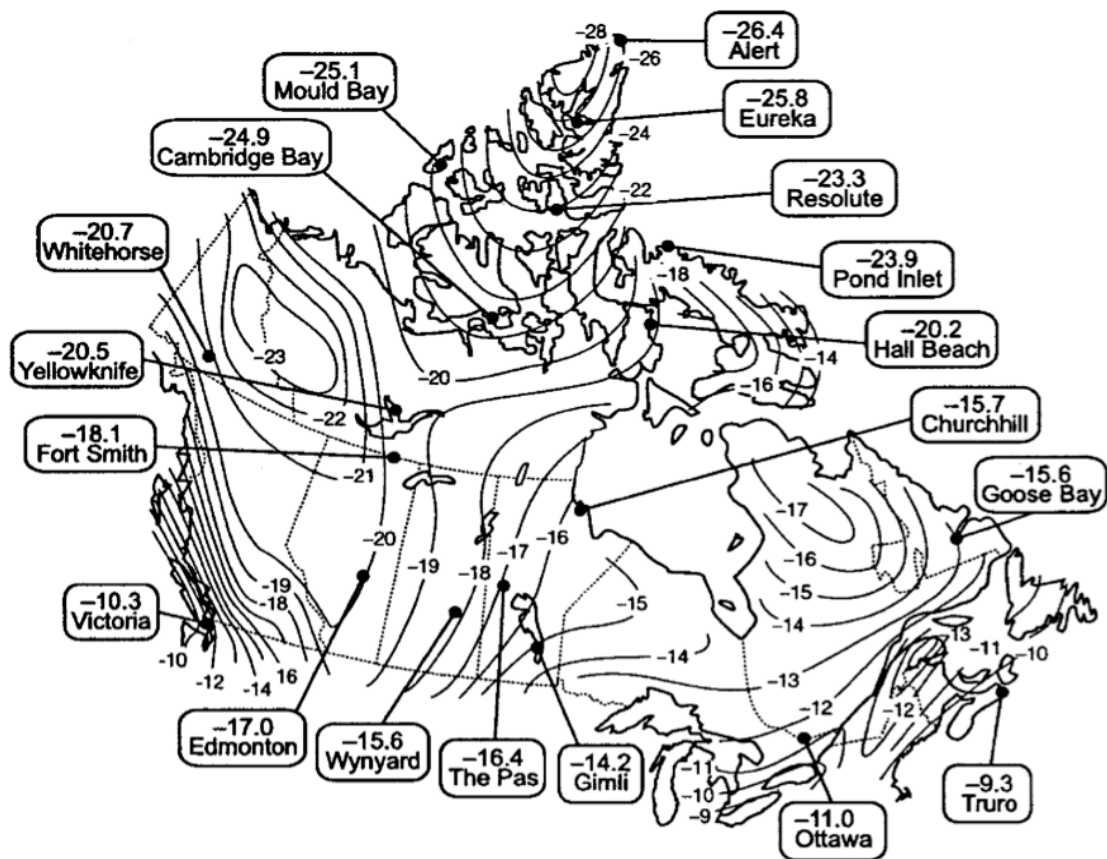
Figure 5: Oxygen-18 distribution across Canada in locally recharged groundwater with the weighted mean δ18O in precipitation at monitoring stations. From Clark and Fritz (1997).
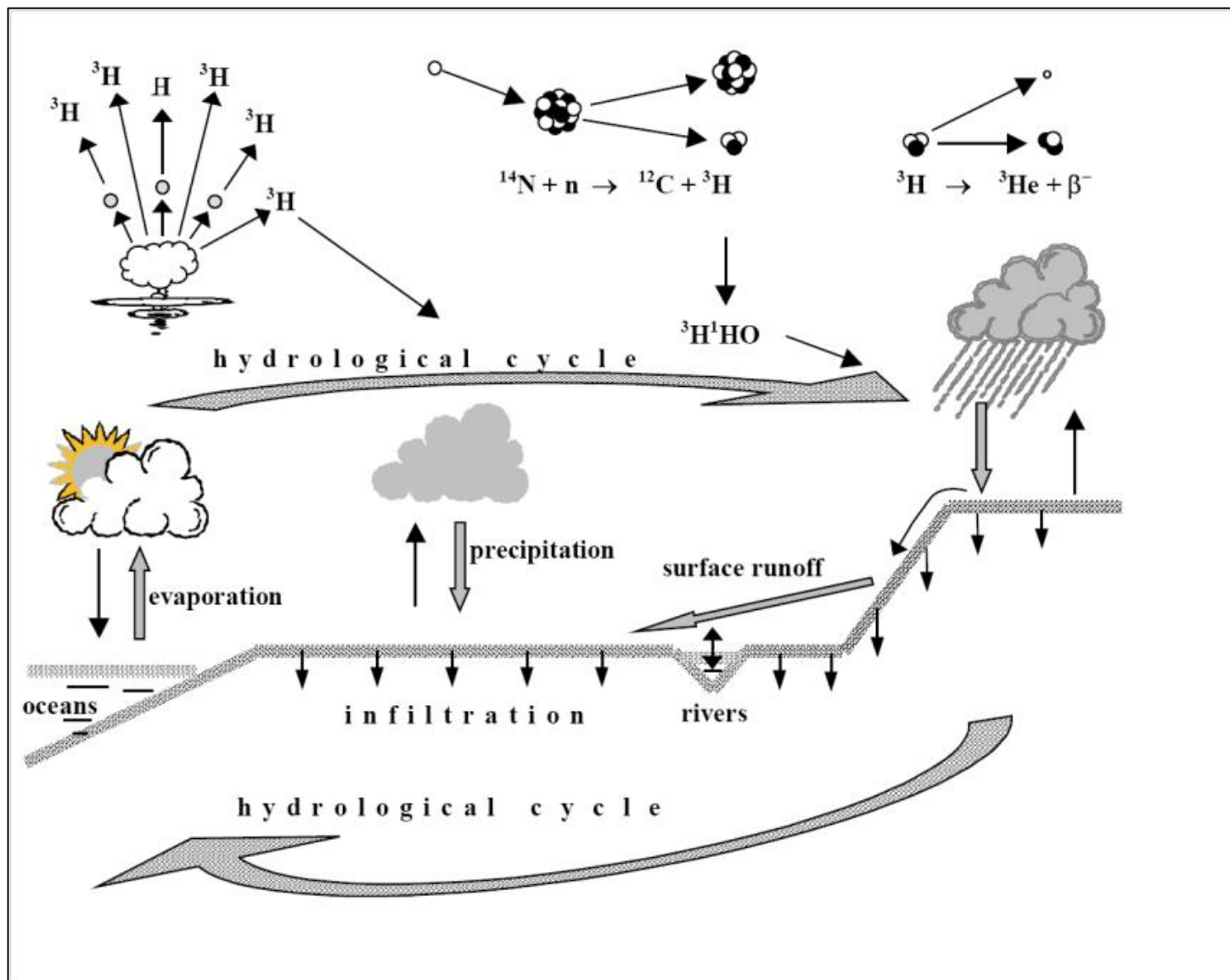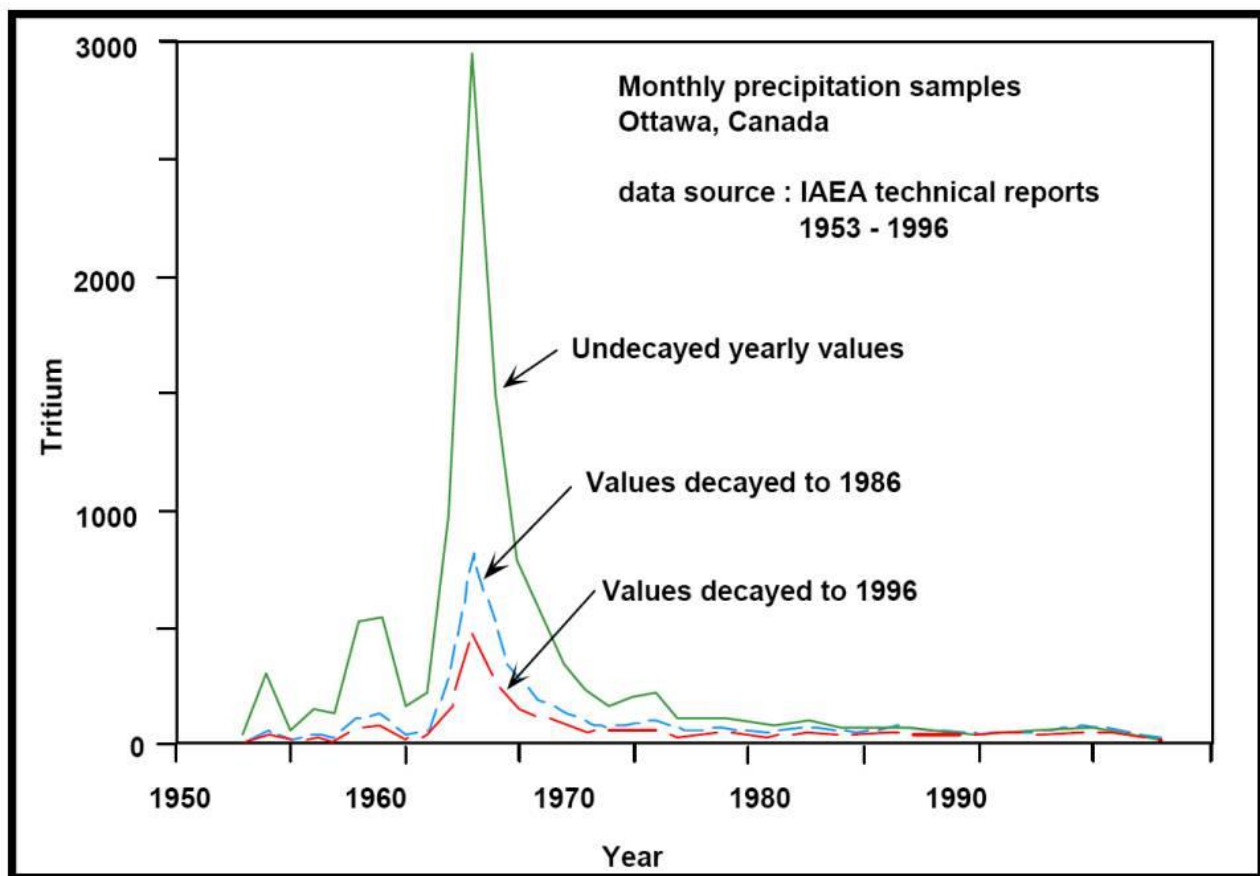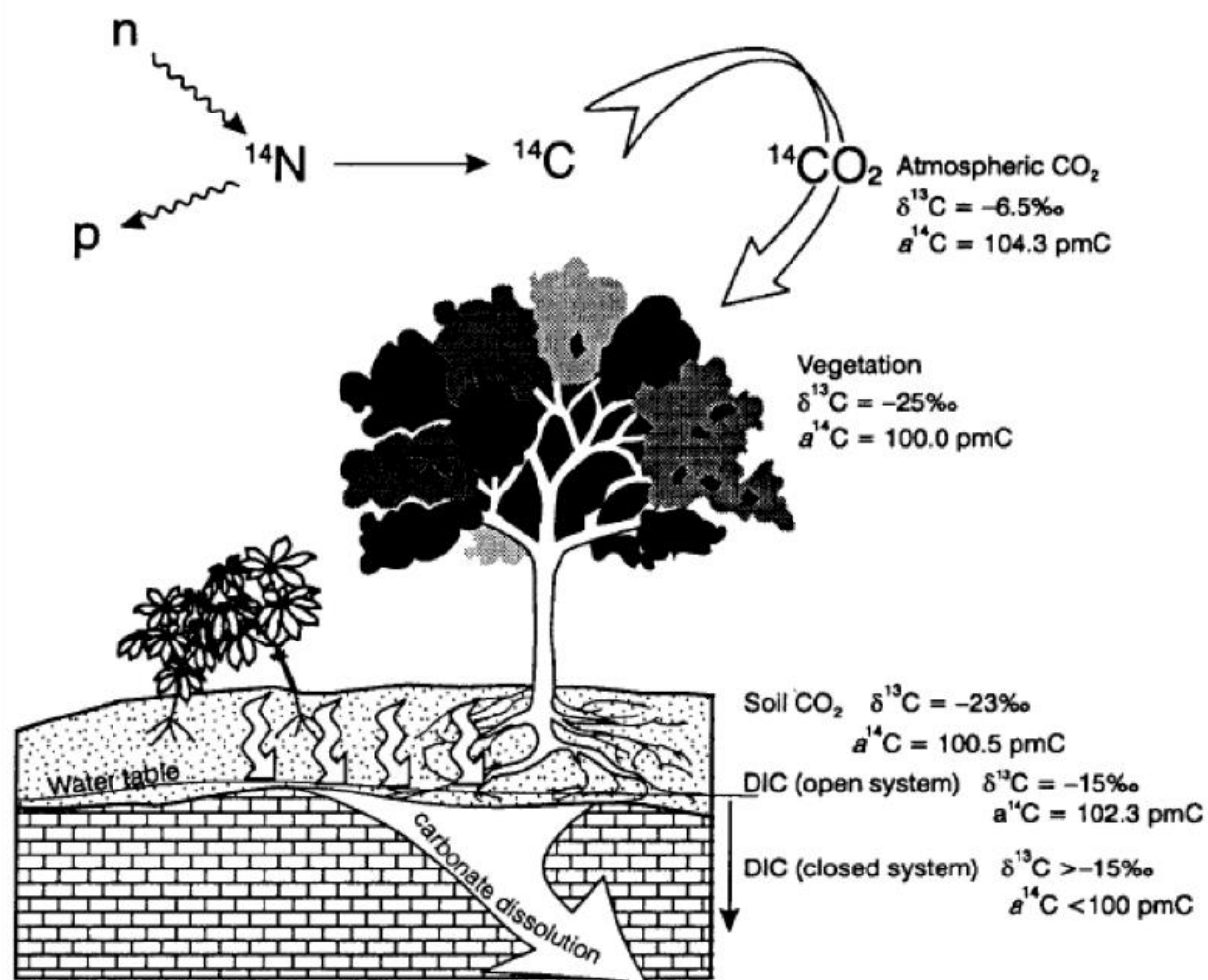
Figure 6: Tritium in the hydrological cycle (IAEA, 2008).

Figure 7: Tritium concentrations measured at the Ottawa IAEA Station including values corrected for decay to 1986 and 1996 levels. (Burke 1997).

Figure 8: Illustration of the pathway ^{14}C takes from the atmosphere to groundwater along with the associated fractionation of both ^{14}C and ^{13}C (Clark and Fritz 1997).

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