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**THE PARTITIONING OF ATMOSPHERIC ^{129}I IN A SHALLOW SAND
AQUIFER AT STURGEON FALLS, ONTARIO**

by

Robert Edward Renaud

**A thesis submitted to the Faculty of Graduate and Postdoctoral Studies
in partial fulfillment of the requirements
for the degree of M.Sc. in Earth Sciences**

OTTAWA-CARLETON GEOSCIENCE CENTRE

AND

UNIVERSITY OF OTTAWA

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ABSTRACT

The transport and partitioning of ^{129}I has been examined for a shallow groundwater flow system at Sturgeon Falls in northeastern Ontario. Recharge into a sandy surficial postglacial deltaic aquifer occurs in the vicinity of a seasonally-wet boreal forest. Concentrations of stable iodine, ^{129}I , tritium, radiocarbon, stable isotopes and major ions were measured on samples of groundwater and precipitation. The present-day tritium profile delineates the position of the early 1960's thermonuclear bomb-pulse at a depth of approximately 12 m.

The concentrations of stable iodine for groundwaters above, near and below the present-day bomb pulse range from 0.07 to 1.7 ppb. Over that same interval ^{129}I concentrations decreased from 1.9×10^6 atoms/L at 9 m, to approximately 1.9×10^5 atoms/L on tritium-depleted waters occurring below the present-day location of the recharging thermonuclear bomb-test peak at 35 m. No substantial increases in the levels of ^{129}I were evident in waters sampled near the present-day location of the thermonuclear bomb peak. A precipitation sample collected at Sturgeon Falls had a stable iodine concentration of 0.2 ppb and an ^{129}I concentration of 8.5×10^7 atoms/L.

The groundwater in the lower aquifer is practically tritium-free (< 2 TU) and is considered to be pre-bomb in age. Its ^{129}I concentration varies between 2 to 4×10^5 atoms/L. These values are considerably greater than published estimates of pre-bomb ^{129}I (10^3 to 10^4 atoms/L – Fabryka-Martin et al., 1985 and Rao and Fehn, 1999), and indicate contribution of ^{129}I from the fissionogenic decay of ^{238}U in the basal granite bedrock or from leaching of ^{129}I from the aquifer grains.

The lesser concentrations of ^{129}I in Sturgeon Falls groundwaters, compared with those from other studies in central Canada, suggest that the levels of ^{129}I in these groundwaters may have been attenuated by complexation or ion exchange with organic materials in the near-surface soil horizons. Such processes have been documented during a previous study on the behavior of ^{129}I in a shallow aquifer near a low-level, radioactive waste management area (Alvarado Quiroz, 1999).

Along a 30 cm soil profile at piezometer nest 28 at the Sturgeon Falls study site, the concentrations of ^{129}I ranged from approximately 4.3×10^8 atoms/g in the uppermost soil litter layer to 5.6×10^7 atoms/g in the siltier bottom soil horizons. Over that same profile, stable iodine varied from 4.7 ppm in the upper layers to 3.9 ppm in the lower layers.

Additionally, the concentrations of ^{129}I in the mine waters of the Con Mine, in Yellowknife, NWT were examined. ^{129}I levels in the deep brines were associated with the fissionogenic decay of ^{238}U , while that of the shallower waters was associated with atmospheric fallout of ^{129}I from the thermonuclear weapons testing and nuclear fuel reprocessing.

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1.0 INTRODUCTION

1.1 ^{129}I Background Information

^{129}I is a nuclear fuel waste radionuclide of concern to scientists, medical health officials and nuclear regulators due to its longevity and its propensity to bioaccumulate in the thyroid gland of higher organisms (Handl et al., 1993). Iodine, an essential element for life, has only one stable isotope, ^{127}I . Iodine has radioisotopes ranging from ^{120}I to ^{135}I . With the exception of ^{129}I , which has a half-life of 15.7 million years, all of the iodine radioisotopes are fairly short-lived (Table 1) (Moran, et al., 1995).

Isotope	Mass	Half-life	Mode of decay
^{120}I	119.91005	1.35 h	EC to ^{120}Te
^{121}I	120.90737	2.12 h	EC to ^{121}Te
^{122}I	121.9076	3.6 m	EC to ^{122}Te
^{123}I	122.90561	13.2 h	EC to ^{123}Te
^{124}I	123.90621	4.18 d	EC to ^{124}Te
^{125}I	124.90462	59.4 d	EC to ^{125}Te
^{126}I	125.90562	13.0 d	EC to ^{126}Te ; β^- to ^{126}Xe
^{128}I	127.90581	25.0 m	EC to ^{128}Te ; β^- to ^{128}Xe
^{129}I	128.90499	1.57×10^7 y	β^- to ^{129}Xe
^{130}I	129.90667	12.36 h	β^- to ^{130}Xe
^{131}I	130.90613	8.040 d	β^- to ^{131}Xe
^{132}I	131.908	2.28 h	β^- to ^{132}Xe
^{133}I	132.90781	20.8 h	β^- to ^{133}Xe
^{134}I	133.9099	52.6 m	β^- to ^{134}Xe
^{135}I	134.91005	6.57 h	β^- to ^{135}Xe

Table 1. Radioisotopes of Iodine. (Source: WebElements™).

Natural production of ^{129}I occurs through several processes. Cosmogenic production of ^{129}I occurs through the interaction of high-energy cosmic rays with stable xenon isotopes

in the upper atmosphere. The spontaneous fission or neutron-induced fission of ^{238}U in the Earth's crust produces fissiogenic ^{129}I (Moran, et al., 1995). Cosmogenic and fissiogenic production of ^{129}I contribute approximately equal amounts of ^{129}I to the hydrosphere (Fabryka-Martin et al., 1985). Volcanic emissions also release fissiogenic ^{129}I produced in the Earth's interior (Fabryka-Martin et al., 1989). These natural sources of ^{129}I were the only sources of the isotope in the pre-nuclear age. During that time, the $^{129}\text{I}/\text{I}$ ratio in hydrosphere and biosphere varied between 5×10^{-12} and 2.5×10^{-9} (Handl, 1996).

Since the dawn of the nuclear age, anthropogenic sources of ^{129}I have increased the $^{129}\text{I}/\text{I}$ ratio at the surface of the Earth by several orders of magnitude (Moran, 1996). Releases of ^{129}I from nuclear fuel reprocessing plants and from thermonuclear weapons testing fallout have completely overwhelmed the natural $^{129}\text{I}/\text{I}$ signal in the last 50 years (Oktay, et al., 2000). Atmospheric weapons testing in the late 1950's and early 1960's released significant amounts of ^{129}I . According to Handl (1996), the $^{129}\text{I}/\text{I}$ ratio in the biosphere increased to a peak value of 10^{-6} during that time, but has been decreasing continuously in the USA since then.

Nuclear fuel reprocessing plants are responsible for the majority of the anthropogenically-produced ^{129}I released to the biosphere. The global inventory of natural ^{129}I in the surface environment is approximately 80 kg, while atmospheric bomb testing contributed an additional 50 kg (Moran et al., 1999). Nuclear accidents, such as the one that occurred at Chernobyl, have released minor amounts (1-2 kg) of ^{129}I into the atmosphere (Raisbeck and Yiou, 1999). These amounts are largely overshadowed by the

^{129}I releases from two commercial nuclear fuel-reprocessing plants in Europe. The plant at Cap de La Hague, France has released approximately 1640 kg of ^{129}I into the English Channel, between 1975 and 1997, while the plant at Sellafield, England has discharged approximately 720 kg of ^{129}I into the Irish Sea, between 1961 and 1997 (Raisbeck and Yiou, 1999).

1.2 Project Objectives

The behavior of ^{129}I in groundwater is not well understood. Given its long half-life, the migration of ^{129}I is of particular concern in the safety assessment of potential nuclear waste repositories, which may be constructed deep into the Precambrian Shield. Previous studies have investigated the transport and partitioning of ^{129}I in a nuclear-waste management area (Alvarado Quiroz, 1999). The purpose of this study was multifold. The primary focus of this study was to investigate the behaviour of ^{129}I in a shallow sand aquifer at Sturgeon Falls, Ontario, a region impacted only by natural background concentrations, fallout from nuclear weapons testing and nuclear fuel reprocessing and to determine pre-bomb ^{129}I concentrations in groundwater. This study also examined the ^{129}I concentrations in mine waters collected from the Con Mine located on the Precambrian Shield. Finally, the column elution method (Ross and Gascoyne, 1995) used to isolate iodine from water samples was modified to suit the large groundwater samples from Sturgeon Falls and the high salinity mine waters. The Sturgeon Falls subject site and the Con Mine subject site are investigated independently in Chapters 2 and 3, respectively.

2.0 STURGEON FALLS, ONTARIO

The field site chosen to investigate the migration of ^{129}I in the natural environment is located near the town of Sturgeon Falls, Ontario ($46^{\circ}19' \text{ N}$ and $79^{\circ}28' \text{ W}$). Sturgeon Falls is located approximately 40 km west of North Bay and roughly 400 km from Ottawa (Figure 1). This site was chosen because it has been well instrumented for previous studies, including the tracing of atmospheric sulfur fallout, tritium dispersion and ^{36}Cl transport (Robertson and Cherry, 1989; Robertson et al., 1989; Solomon et al., 1993; Solomon et al., 1996; Milton et al., submitted).

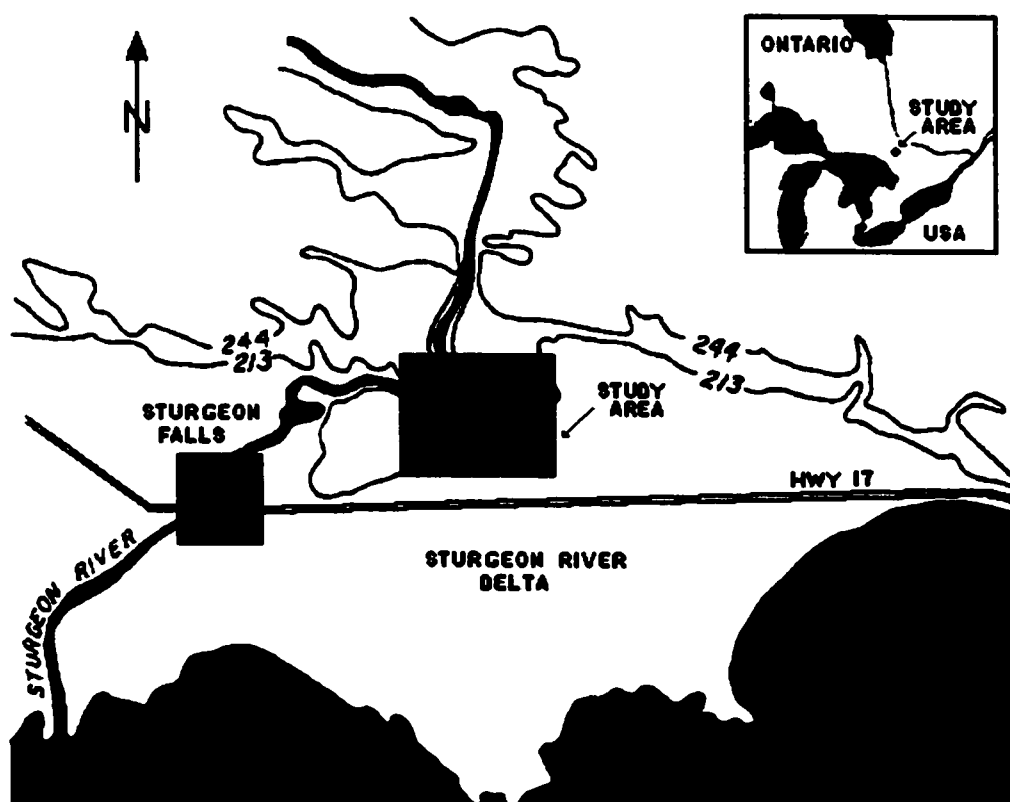
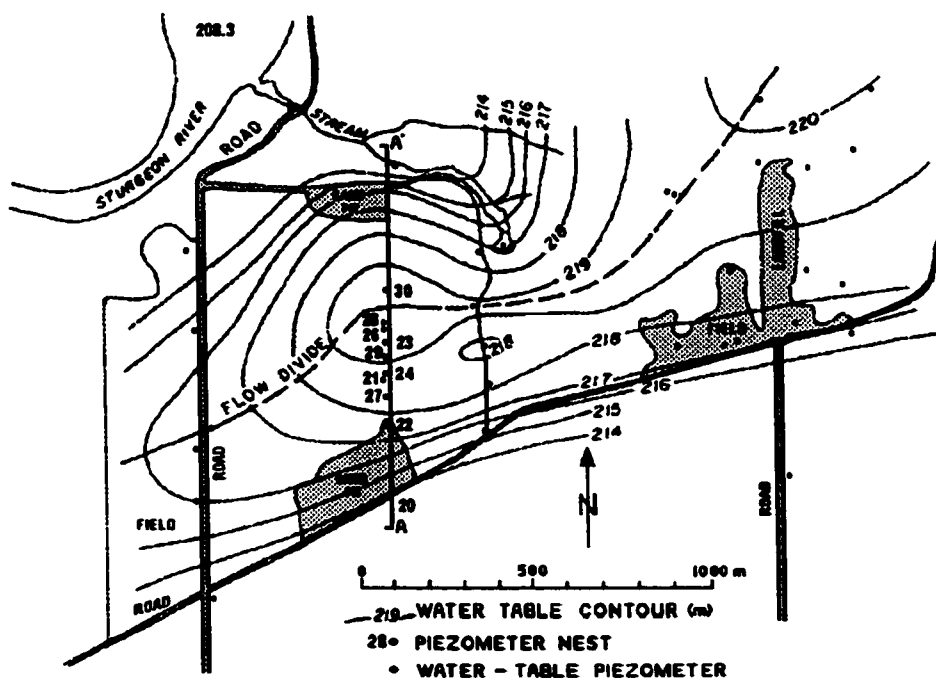


Figure 1. Location and topography of Sturgeon Falls field site.

The site is forested, and in the spring there is often standing water covering a large portion of the study area. The average annual precipitation received at Sturgeon Falls is approximately 97 cm. This is based on the meteorological data collected by Environment Canada for North Bay from 1939-1990. According to Robertson et al., 1989, the forested site has an annual evapotranspiration of about 50 cm/year.

The piezometers selected for sampling are located on a small topographic ridge coincident with the groundwater recharge divide. Figure 2 illustrates the groundwater divide as well as the location of some of the piezometer nests, consisting of mostly drive-point piezometers and three bundle piezometers. Standing water was not present at the sampled nests during the sampling periods. The surface elevation of the sampling nest is approximately 220 mASL.



Source: Robertson & Cherry, 1988.

Figure 2. Water table configuration.

The site has a relatively simple geology (Figure 3) and the hydrogeology is well known (Robertson and Cherry, 1989; Robertson et al., 1989; Solomon et al., 1993; Solomon et al., 1996;). The site has two main aquifers within the surficial postglacial deltaic sediments, separated by an aquitard. The upper aquifer is approximately 25 m thick and is relatively homogeneous. It consists of fine silty sand and silt. At 25 m depth, a varved clay and silt aquitard is encountered. The downward vertical hydraulic gradient is 0.09 in the silty sands and increases to 1 in the lower varved silt and clay (Solomon, et al., 1993). The lower aquifer consists of sands and gravels, which makes it more permeable than the upper aquifer, thereby serving as a basal drain for the upper aquifer (Robertson & Cherry, 1989).

Robertson and Cherry, 1989, conducted a detailed investigation of the aquifer properties. They used laboratory tests on 28 samples of core material from the three augered boreholes to measure the porosities of the sediments and they determined the hydraulic conductivities of the sediments using permeameter tests, where the core samples were recompacted close to their original density. It was determined from 18 permeameter tests that the upper 19 m of the aquifer, consisting of very uniform silty fine sand, had an arithmetic mean hydraulic conductivity of 1.8×10^{-4} cm/s. The upper 12 m appeared structureless in the core samples observed and was assumed to have a low degree of anisotropy. At depths below 12 m, occasional thin (1 – 2 mm) clay lamellae were observed, likely causing a greater degree of anisotropy. From 19 to 23 m below land surface, the arithmetic mean hydraulic conductivity was 2.8×10^{-5} cm/s. Robertson and Cherry were unable to determine the mean hydraulic conductivity of the sediments

collected between 25 and 35 m depth due to the high clay content (10-25%). Below 35 m depth, the arithmetic mean hydraulic conductivity was 6×10^{-3} cm/s.

Robertson and Cherry, 1989, also estimated the bulk vertical hydraulic conductivities of sediment in the area of nest 28, using a mass balance approach, utilizing the observed vertical hydraulic gradients, the flow velocity (0.35 m/year) indicated by the position of the mid-1960s tritium peak and the measured sediment porosity value (0.35). They determined that the zone between 12 and 15 m below land surface had bulk vertical hydraulic conductivities averaging 10^{-5} cm/s. Below that, from 15 to 21 m below land surface, the vertical hydraulic conductivity was determined to be 5×10^{-6} cm/s and from 21 to 35 m, the vertical hydraulic conductivity was 1.1×10^{-6} cm/s. Anisotropy values of about 10 were indicated at depths between 12 and 35 m based on a comparison of the horizontal and vertical hydraulic conductivities. The absence of bedding above 12 m suggested a low degree of anisotropy in that zone (Robertson and Cherry, 1989).

The piezometers installed at the study site consisted primarily of drive-point piezometers. According to Robertson and Cherry (1989), they

“were advanced to depths ranging from 1 to 21 m using a handheld vibrating hammer with adaptive drive head. One type, which was advanced to depths of up to 11 m, was constructed of 2.5 cm diameter, glue-coupled polyvinyl chloride pipe, with a tip consisting of a tapered drive point and a short 0.15-m-long drilled section screened with porous geotextile. The other type, which was advanced to depths below 11 m, was constructed of 1.3 cm diameter thread-coupled steel pipe with 0.15-m-long drilled-tip screened internally with nylon cloth.”

In addition to the drive-point piezometers, a multilevel bundle piezometer (nest 26) was installed in an auger-drilled borehole. Robertson and Cherry (1989) describe it as follows:

“This borehole was advanced using drilling mud for deeper penetration and was terminated at a depth of 35 m when a coarser sand aquifer was encountered. Split-spoon

core samples were retrieved at 2-4 m intervals during drilling and a bundle of five piezometers was installed to the bottom of the borehole.”

The piezometer nomenclature consisted of the nest number, followed by the depth of the piezometer within the nest. For example, piezometer 28-9 is located in nest 28 and is 9 m deep.

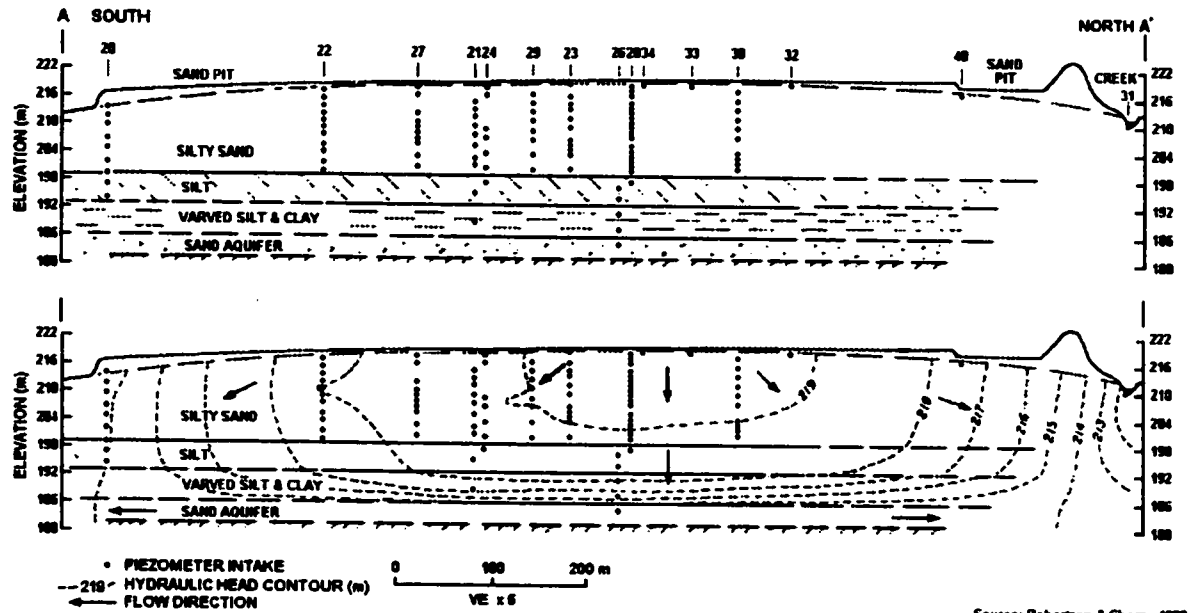


Figure 3. Section A-A': stratigraphy & hydraulic head distribution, Aug. 8, 1986.

2.1 METHODOLOGY

2.1.1 Field Methods

The piezometers sampled for this study are located near the center of the study area. The main piezometer nest sampled was nest 28. At this location, there are piezometers ranging in depth from 1 m to 21 m. In addition to nest 28, 26-35 was also sampled as part of this study. These piezometer nests were chosen because they are located near the

center of the section A-A' (Figure 2) and groundwater flow in that region, as determined by Robertson and Cherry (1989), is vertical (Figure 3).

A preliminary site investigation was done over several days in July 1999. At that time, water level measurements were made using a standard water level meter. Approximately half of the piezometers were pumped until the water level was at the suction lift level of the peristaltic pump. The pH of the waters was measured and alkalinity titrations, using a Hach™ field kit, were performed. Samples were collected for geochemical and isotopic analyses. HDPE bottles were used for all samples with the exception of those taken for ^{13}C and ^{14}C analysis of dissolved inorganic carbon (DIC), which were collected in amber glass bottles.

Further sampling was carried out in the fall of 1999. Efforts were concentrated on three piezometers, 26-35, 28-14 and 28-9, which yielded sufficient water for the large ^{129}I samples required. On the basis of ^3H concentration, the three piezometers sampled provide pre-bomb water, water from the leading edge of the bomb pulse and post-bomb water. Approximately 100 L of water was pumped from each of these piezometers and collected in collapsible water containers for iodine analysis. Smaller samples were also taken for geochemical and isotopic analysis.

In June 2000, field sampling was again carried out at Sturgeon Falls. Along with the standard geochemical and isotopic sampling, large 300 L samples were collected from

the three piezometers for iodine analysis. Pumping rates were kept to approximately 200 mL/min.

In February 2001, one additional trip was made to Sturgeon Falls to collect a snow sample. Three 100 L containers were filled with snow from a site approximately 1 km from piezometer nests. Since the roads into the site are not plowed in the winter, we could not collect the snow sample at the piezometer nests sampled for this study.

During previous studies (Milton, et al., submitted), soil and organic matter samples were collected from the area surrounding nest 28. Portions of these samples were analyzed for iodine and ^{129}I .

2.1.2 Major Ion Analyses

Cation analysis was performed at Accutest Laboratories by ICP-AES, using a Varian Liberty 220 ICP Emission Spectrometer. Anion analysis was primarily performed at Accutest Laboratories, although some samples were also analyzed at AECL-CRL. The instrumentation used for the anion scan was a Dionex DX-100 Ion Chromatograph (HPLC) with a Dionex AS40 automated sampler.

The analytical errors associated with the procedures are generally 10% at analyte concentrations that are greater than 10 times the detection limit, and 100% at

concentrations less than 10 times the detection limit. Errors for NO₂, NO₃ and F results are ± 100% of the reported value. Errors for SO₄ results are ± 10% of the reported value.

2.1.3 Stable Isotope Analyses

Samples were collected for ²H, ¹⁸O and ¹³C. All analyses were performed in the G.G. Hatch Isotope Laboratories at the University of Ottawa. Deuterium analysis involves high temperature reduction of the sample to elemental hydrogen, H₂, using 3 µL of water in evacuated breakseals. The water is frozen and the breakseal is re-evacuated. The analytical precision was ± 1.5 ‰ (2σ).

The δ¹⁸O in water was determined by equilibration with CO₂ in a temperature-controlled bath (25°C), with continuous shaking. The CO₂ is then extracted and analyzed on a SIRA-12 gas source mass spectrometer. The fractionation factor, between CO₂ and H₂O, used by the G.G. Hatch Laboratories, is 1.0412 from Friedman and O'Neil, 1977. The analytical precision was ± 0.10 ‰ (2σ).

The ¹³C of DIC was measured by acidifying the water samples under vacuum to release CO₂. This was then cryogenically purified and analyzed on the SIRA-12 gas source mass spectrometer. Again, the analytical precision was ± 0.10 ‰ (2σ).

2.1.4 ^3H and ^{14}C Analyses

Analysis of ^3H was undertaken at AECL – Chalk River Laboratories (CRL) by direct liquid scintillation counting (LSC). 3.00 mL water samples were transferred to a 22 mL polyethylene scintillation vial and mixed with 15.00 mL of Canberra-Packard Ultima Gold scintillation cocktail. The vial was capped and shaken vigorously. The sample was then loaded into a Canberra-Packard Model 1500 LSC. Tritium activities are expressed in tritium units (TU), where one TU corresponds to one ^3H atom per 10^{18} atoms of hydrogen (1 TU = 0.12 Bq/L). The minimum detection limit was 5 TU.

Samples containing less than 5 TU were sent to the Environmental Isotope Laboratory (EIL) at the University of Waterloo for enriched tritium analysis. Samples are enriched 15 – 100 times by electrolysis and then counted by LSC. EIL uses Canberra-Packard Pico-fluor LLT (Low Level Tritium) scintillation cocktail (Drimmie, et al., 1993). The minimum detection limit was 0.8 TU.

The ^{14}C activity of DIC was measured by tandem accelerator mass spectrometry (AMS) at IsoTrace Laboratory at the University of Toronto. Samples for ^{14}C analysis were prepared at the University of Ottawa using the same CO_2 extraction procedure as used for ^{13}C analysis (sample DIC – 1 mg C). The samples were then sent to IsoTrace in breakseals. The analytical error for the Sturgeon Falls samples ranged from 1 to 3.5% (pMC).

2.1.5 Stable Iodide Measurements

Concentrations of dissolved stable iodine (^{127}I) in the Sturgeon Falls waters were measured at CRL. The basis of the analysis is the formation of a 2-iodo-3-pentanone complex, which is extracted into hexane and is analyzed by gas chromatography (Marchetti et al., 1994; Kramer et al., 2001).

Groundwater and snow samples were analyzed in the following manner. A predetermined volume was weighed and placed in a 125 mL separatory funnel. The amount of sample used depends on the anticipated concentration of iodine in the sample and the requirement for the results to fall within the GC calibration range. The sample in the funnel was made up to 25 mL with double distilled water (Kramer et al., 2001). Using a pipette, 1 mL of 5 M H_2SO_4 , 1 mL of 30% H_2O_2 and 1 mL of 4% v/v 3-pentanone, were added to the separatory funnel. The funnel was then shaken vigorously for 10 seconds and then allowed to vent. The funnel was then allowed to sit for 10 minutes as the 2-iodo-3-pentanone complex formed. Then, 5 mL of hexane was added to the funnel and the funnel was shaken vigorously for 2 minutes, stopping to vent when necessary. After waiting for approximately 5 minutes for the phases to separate, the aqueous phase was drained and discarded. The hexane was then collected in a scintillation vial. The samples, along with iodine calibration standards, processed in the same manner as the samples, were loaded into the GC autosampler and run. The analytical errors associated with these procedures are approximately 20%.

2.1.6 Iodine Extraction by Column Elution for ^{129}I Analysis by AMS

The column separation method, described in Ross and Gascoyne (1995), used to isolate the iodide from water samples prior to precipitating it as AgI for AMS analysis, was modified to suit the large Sturgeon Falls groundwater samples. Large columns (125 mL) were used for all Sturgeon Falls waters. Prior to their introduction to the columns, all the waters had stable iodide added as carrier, in the form of a KI solution. This carrier was needed to increase the amount of iodide present in the sample, thereby making handling of the sample easier. In most cases, ^{125}I ($T_{1/2} = 59.4$ days) was also added to the water sample prior to its introduction to the column as a check of the efficiency of the column-elution procedure. Silica wool was used at the bottom of the columns in place of a frit.

The anion exchange resin used in the columns was Dowex Anion Exchange Resin AG1-X8, 100-200 mesh. Approximately 60 mL of the resin was loaded into each column in the form of a water-based slurry. Care was taken to prevent trapping air bubbles or forming gaps in the resin. Such areas represent locations where exchange will not occur, thus the potential flow through and loss of iodine-laden water was minimized. The resin was pre-conditioned with sodium bisulphate before introducing the sample waters. Approximately 600 mL of NaHSO_4 was passed through the columns. The purpose of this pretreatment was to convert all anions on the exchange sites on the resin from chloride to bisulphate. This allows the maximum exchange of iodide between the sample water and the resin as iodide easily replaces bisulphate on the exchange sites of the resin.

Break-through is a potential problem faced with this type of iodine extraction procedure. Break-through occurs when all of the exchange sites of the resin are occupied and thus additional iodine entering the system is lost. To guard against that possibility, all water that drained from the columns was collected and stored in case reintroduction to the column was necessary. The Sturgeon Falls waters were allowed to flow through the column at a flow rate between 10 and 15 mL/min.

The elution scheme used for the Sturgeon Falls waters consisted of passing 60 mL of hot double-distilled water, then 65 mL of bleach, and finally 110 mL of double-distilled water through the column. The addition of the hot water to the column prior to the introduction of the bleach was to minimize the oxidation of any organic matter in the sample water still present on the resin. Before adding this step to the elution scheme, the addition of bleach resulted in gas bubbling in the resin of several columns.

Following the elution of the sample from the column, the vials were placed on the gamma counter where the amount of ^{125}I present was measured. The vials containing the iodine were combined (for that sample) if the elution process proved to be efficient. If the elution was less than efficient, more bleach and water was added to the column.

The vials containing the iodine eluate (IO_3^-) were combined in a 500 mL separatory funnel for the extraction process. The solution was acidified with 20 mL of HNO_3 . This was done slowly and carefully. The funnel was well shaken to release any Cl_2 produced. When no more Cl_2 was released, 10 mL of 1.0M $\text{NH}_2\text{OH} \cdot \text{HCl}$ was carefully added to the

flask. The flask was shaken to allow the complete mixture of the solutions. $\text{NH}_2\text{OH} \cdot \text{HCl}$ reduces IO_3^- to I_2 . This was evident by a brown colour in the solution.

The I_2 was extracted using CCl_4 . A 10 mL aliquot of CCl_4 was added to the funnel and then it was shaken. After allowing the solutions to settle, the lower purple-coloured layer was run-off into a clean 125 mL separatory funnel. The CCl_4 additions were repeated until the CCl_4 layer was colourless.

Another 5 mL aliquot of $\text{NH}_2\text{OH} \cdot \text{HCl}$ was added to the 500 mL funnel. The extraction was carried out with successive additions of CCl_4 , as before, until the CCl_4 layer was colourless. The solution was then acidified with 10 mL of HNO_3 . The addition of 5 mL of 1.0M NaNO_2 reduced any remaining IO_3^- to I_2 . The I_2 was again extracted using successive volumes of CCl_4 .

Once the extraction procedure no longer yielded any purple colour in the CCl_4 , the back-extraction procedure was performed on the CCl_4 in the 125 mL funnel. 20 mL of distilled, deionized water along with 0.5 mL of 1.0M NaHSO_3 was added to the funnel containing the CCl_4 . When the funnel was shaken, the purple colour disappeared. This occurred as the I_2 was reduced back to I^- by the NaHSO_3 and was now present in the aqueous phase. This CCl_4 phase was then discarded and the aqueous phase was transferred to a 50 mL beaker. A small amount of HNO_3 (0.5 mL) was added to the beaker. The solution was heated to boil off any CCl_4 that remained. The beaker was then allowed to cool and the solution was transferred to a 50 mL centrifuge tube. Several

milliliters of 0.1M AgNO_3 were added to the solution, drop by drop using a disposable pipette. A yellow-coloured precipitate of AgI , as well as a white-coloured AgCl precipitate formed in the centrifuge tube. The tube was then put in the centrifuge for several minutes at a moderate speed. Another drop or two of AgNO_3 was added to check for complete precipitation. If the precipitation was not yet complete, more AgNO_3 was added and the tube was again placed in the centrifuge.

When no more precipitate was formed, the supernatant was decanted. The precipitate was washed with 5 mL of NH_4OH , which dissolved any AgCl and AgBr . The tube was then centrifuged and the supernatant was decanted. If the precipitate was not bright yellow in colour, a small amount of HNO_3 (1 or 2 mL's) was added. This brought the precipitate back to a yellow colour. The tube was centrifuged and the supernatant was decanted.

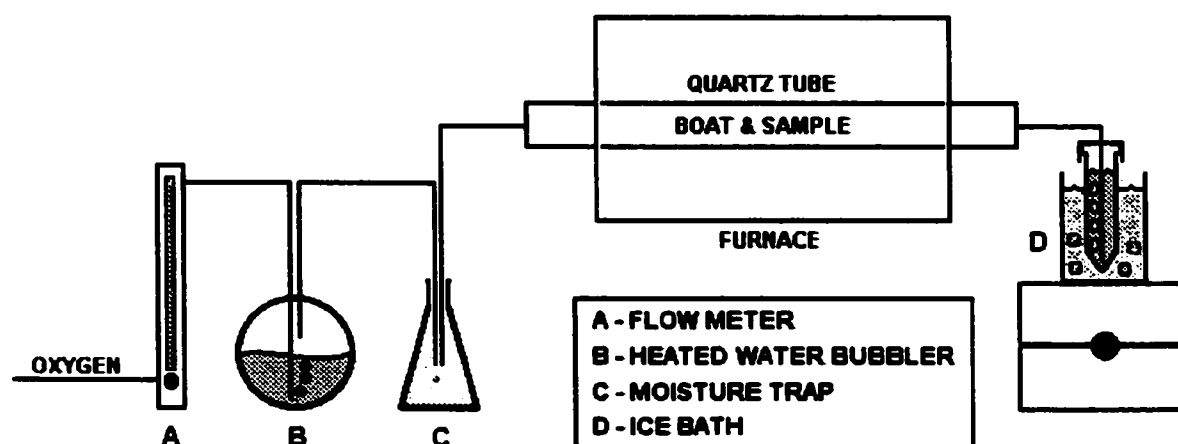
The precipitate was then washed three times with distilled, deionized water and twice with reagent alcohol. Each time, the tube was centrifuged and supernatant was decanted. Using a small amount of alcohol, the precipitate was carefully transferred to a pre-weighed aluminum weighing boat. The weighing boat was covered with aluminum foil and placed in the oven (@ 80°C) for 10 minutes to dry. Once dry, the weighing boat was weighed to determine the amount of AgI recovered. The AgI was carefully transferred from the weighing boat to an amber bottle using a small amount of reagent alcohol. The bottle was placed in the oven briefly to evaporate the reagent alcohol. The bottle was then prepared for shipping to IsoTrace Laboratory at the University of Toronto for ^{129}I

analysis by AMS. All necessary precautions were taken to keep the precipitate in the dark, as AgI is photo-reactive.

2.1.7 Pyrolytic Extraction of Iodine for Soil Sediment and Organic Matter

The extraction of iodine from solid materials involves a different procedure from the extraction of iodine from water samples. The sample is combusted at 1000°C in a stream of moist oxygen. The released iodine is collected in a receiving solution of 0.01 M NaOH (Alvarado Quiroz et al., 1999; Milton et al., 1999; Kramer et al., 2001).

The apparatus used for this procedure is shown in Figure 4. It consists of a tube furnace, a quartz glass combustion tube (I.D. 2.8 cm and 75 cm long), a quartz glass combustion boat (approximately 20 cm long), a cylinder of compressed oxygen, a flow meter (A), a heated water bubbler (B), a moisture trap (C) and a centrifuge tube, containing the NaOH receiving solution, sitting in an ice water bath (D).



Source: Kramer et al., 2001.

Figure 4. Pyrolysis apparatus.

The apparatus was carefully set up as shown in Figure 4. The furnace was heated to 1000°C. The oxygen flow rate was set at 1.6L/min. The clean quartz combustion boats were pre-combusted in the furnace for roughly 15 minutes. While the boats were pre-combusting, the soil and litter samples were crushed with a mortar and pestle. Any large twigs or sticks were removed at this time. The soil and litter samples had previously been soaked in 0.5 N KOH overnight, after which the KOH was decanted and the sample was dried in the oven. The purpose of the KOH was to degrade organic molecules to more easily extract iodine from the sample that was tightly bound to organic matter. The concentrations of iodine in these leaches ranged from 76 µg/L to 113 µg/L.

Approximately 35 mL of 0.01 M NaOH was added to the pre-weighed centrifuge (receiving) tube. The top of the tube was covered with aluminum foil and a small hole was made in the foil to receive the tip of the quartz tube. The receiving tube was placed in an ice bath and raised to the appropriate height using a jack-stand.

The samples were carefully loaded into the combustion boats, leaving empty space at the leading edge of the boat to prevent flash combustion and soot production. The combustion boat containing the sample was eased into the quartz tube until the sample ignited. After the sample finished burning, the boat was pushed to the center of the furnace, where it remained for 15 minutes (Kramer et al., 2001).

The wet oxygen stream removed iodine and other volatiles, which were collected in the NaOH receiving solution (Alvarado Quiroz et al., 1999). After the 15 minutes of combustion, the receiving solution tube was removed, capped and weighed. The combustion boat was then removed from the furnace and allowed to cool. The combustion tube was closed and oxygen was allowed to flow through the tube for 5 minutes. The combustion tube was purged into a centrifuge tube containing water. Background levels were determined by running a procedural blank after the combustion of each sample (Kramer et al., 2001).

The Site 1 & 2 Litter Top sample had very low density due to the large organic matter fraction. As such, after seven combustions, only 55.9 g of the sample had been combusted. In contrast, the Site 1 Litter Bottom sample consisted of mixed organics and crystalline sand. As such, 172.1 g of the sample was combusted over five combustions. The analytical errors associated with these procedures are approximately 20%.

2.1.8 ^{129}I Calculations

Dissolved stable iodine concentrations were measured on all Sturgeon Falls samples examined for this project. This measurement of iodine is crucial in order to calculate the amount of ^{129}I in the samples. The AMS analysis of ^{129}I provides a ratio of radioiodine to total iodine ($^{129}\text{I}/\text{I}$). Generally, the analytical errors associated with the preparation for AMS analysis are approximately 20%. To calculate the amount of ^{129}I present in atoms/L or atoms/g, a number of calculations must be made (see sample calculations below). The $^{129}\text{I}/\text{I}$ ratio was corrected, based on laboratory and procedure blanks. The blank

correction incorporates any “background” that may be present in the lab, the materials used and in the experimenter’s procedure. Corrections were also made to the ratio for dilution, based on the amount of stable iodine added as carrier to the sample. An effort was made to keep the dilutions as small as possible. Table 5 contains the iodine and ^{129}I concentrations, the dilution factors, as well the measured $^{129}\text{I}/\text{I}$ ratios for the Sturgeon Falls samples and the associated blanks.

Sample Calculations:

^{129}I (atoms/L) in groundwaters and precipitation samples:

$$^{129}\text{I} \text{ (in atoms/L)} = \frac{\{\text{dissolved stable iodine (in ppm)}\} \times \{\text{dilution corrected ratio}\} \times (1000^{-1}) \times \{\text{Avogadro's number} / 129\}}$$

Numerical example:

$$^{129}\text{I} \text{ (in atoms/L)} = (0.0004 \text{ ppm}) \times (2.16 \times 10^{-10}) \times (1000^{-1}) \times (6.023 \times 10^{23} / 129)$$

$$^{129}\text{I} \text{ (in atoms/L)} = 4.03 \times 10^{-5} \text{ atoms/L}$$

^{129}I (atoms/g) in soil samples:

Same as above, but final result divided by 1000 to reflect difference in units (i.e., Litres versus grams)

2.2 RESULTS AND DISCUSSION

2.2.1 Tritium Profile

2.2.1.1 Background Information

The thermonuclear tritium profile in the groundwater of Sturgeon Falls was measured. Since recharging groundwaters migrate vertically downward through the aquifer in the vicinity of the piezometers chosen for this study, the thermonuclear tritium profile is preserved. Tritium concentrations in groundwater samples are easily measured and the

location of the thermonuclear tritium peak in the subsurface allows for the calculation of recharge rates and establishes a zone where atmospheric ^{129}I (from thermonuclear fallout) may be found.

Tritium levels in the groundwater at the Sturgeon Falls site were previously measured during investigations by other researchers (Robertson & Cherry, 1989 and Solomon et al., 1993). Robertson and Cherry, during their extensive sampling round in October 1986, collected samples from most of the drive-point piezometers, including those located at nest 28. The samples that they collected were analyzed for tritium at the University of Waterloo by direct liquid scintillation counting. Low-level tritium samples were analyzed by enriched tritium analysis at the Weizmann Institute in Israel.

Robertson and Cherry's data indicate that in 1986, at nest 28, the bomb-pulse was located between 6 m and 11.5 m below land surface, with the bomb-peak located at 8.7 m below surface (Figure 5). They measured a peak tritium value of approximately 218 TU at piezometer 28-9. Below 12 m depth, the samples yielded pre-bomb levels of tritium, which were less than ~ 5 TU in Ottawa precipitation (Brown, 1961 and Robertson and Cherry, 1989).

In November, 1986, Solomon et al., collected samples at nest 28 for ^3H and ^3He analyses. They collected samples in copper tubes. Tritium decays to ^3He , thus ^3He levels increase over time in groundwater. The tritium activities were determined using the $^3\text{H}/^3\text{He}$ ingrowth technique (Solomon et al., 1993). The analytical work was carried out at

McMaster University in Hamilton, Ontario. Solomon et al., found the bomb-pulse and bomb-peak in the same location as Robertson and Cherry did in 1986. Again, pre-bomb levels of tritium were found below 12 m.

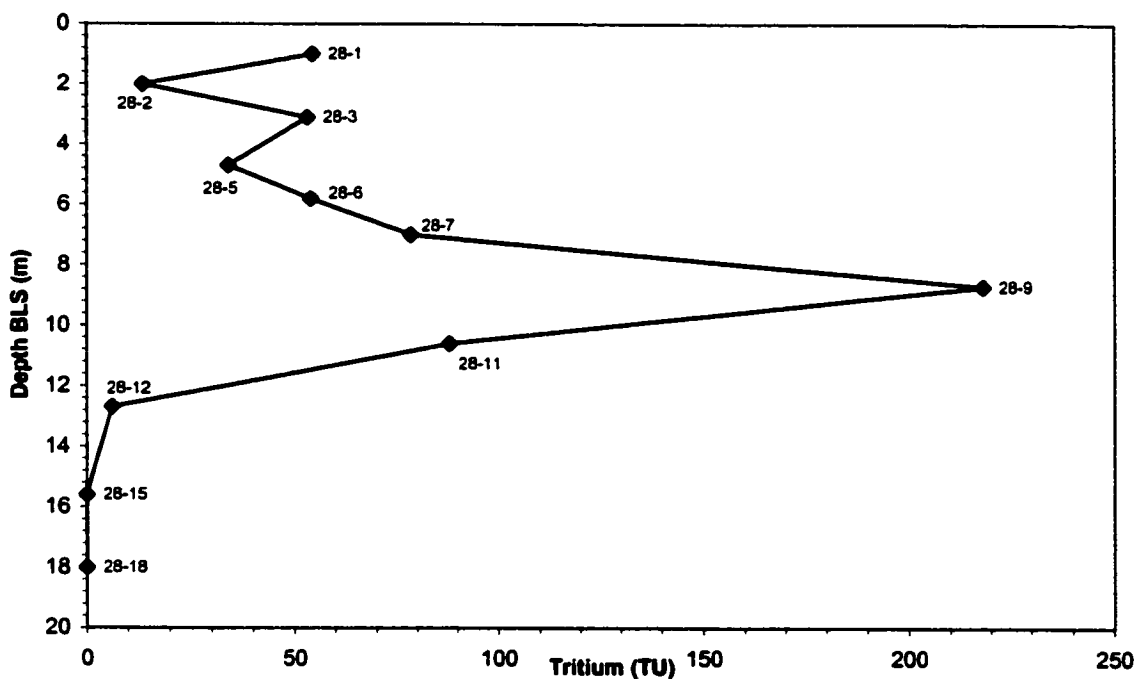


Figure 5. ^3H data for piezometer nest 28 from October, 1986 (Robertson and Cherry, 1989).

Solomon et al., also collected samples for ^3H and ^3He analysis in 1990 and 1991. Those samples were analyzed at the University of Rochester. They determined that in 1990 the bomb-peak (175 TU) was located at 9.8 m below land surface (Figure 6). Samples collected in 1991 indicated that the bomb peak (149 TU) had moved deeper, centering around 10.6 m below land surface. Tritium levels were at pre-bomb levels below 14 m.

2.2.1.2 Current Research

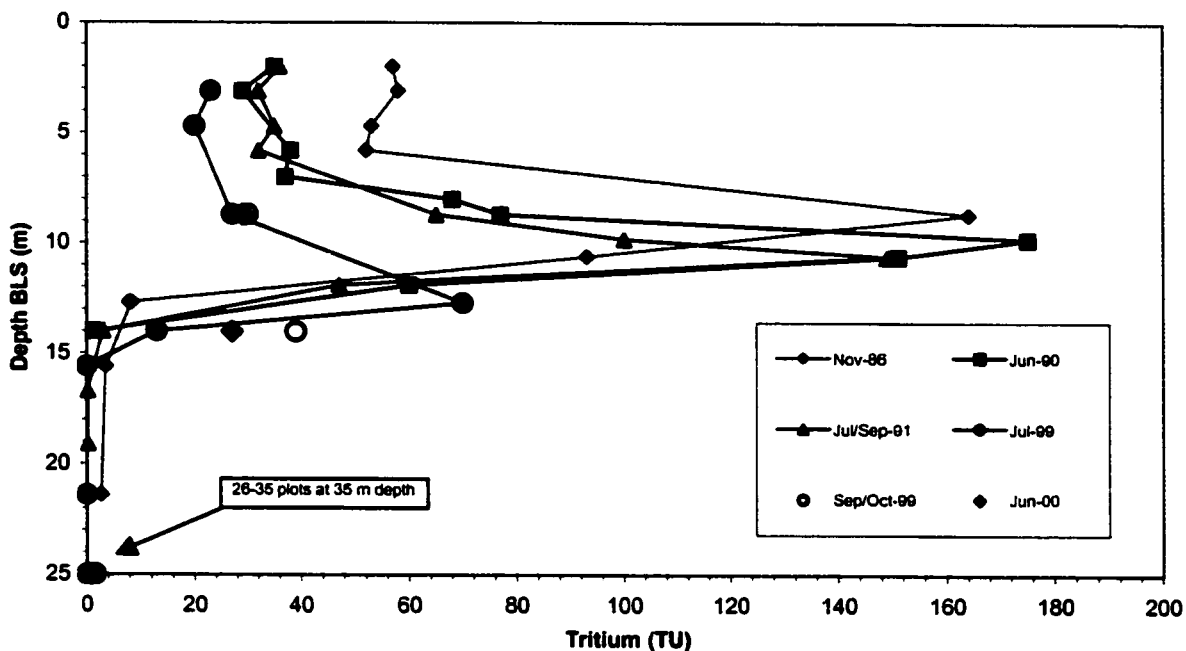


Figure 6. ^3H data from Nov. 1986 to June 2000 (Solomon et al, 1993 and project data).

Using the data collected by Robertson and Cherry (1989) and Solomon et al., (1993), the average vertical velocity of the tritium peak was calculated to be 0.38 m/year. That velocity corresponds to water at a depth of 10.6 m that was approximately 28 years old in 1991, which means it entered the groundwater system in 1963, the peak of ^3H production during nuclear weapons testing.

In July of 1999, the current research project began. At that time, six piezometers (28-9, 28-12, 28-14, 28-15, 28-21 and 26-35) were sampled for tritium. The bomb peak (70 TU) was observed at 12.7 m depth in piezometer 28-12 (Figure 6). Pre-bomb ^3H levels were observed below 14 m depth. Assuming that 1963 groundwater recharged at

the peak of the thermonuclear weapons testing, this gives an average downward velocity of 0.35 m/year (Clark et al., 2001).

In the sampling rounds carried out in September and October, 1999 and in June, 2000, only three piezometers were sampled (28-9, 28-14 and 26-35). Tritium values collected in the autumn of 1999 and in the spring of 2000, while they do not contain values for 28-12, they reveal elevated tritium levels at 28-14, indicating that the bomb peak is continuing to migrate downward.

Based on the low pumping rates used and the slight anisotropy of the sediments below 12 m depth, it is suspected that the collection of the large groundwater samples had a minimal effect on the migration of the tritium bomb peak.

2.2.2 ^{14}C Profile

$^{14}\text{C}_{\text{DIC}}$ was measured on water samples collected in July 1999. ^{14}C , like ^3H , is a radioisotope that was produced in large quantities during the thermonuclear weapons testing of the 1950's and 1960's, and is therefore another tool that aids in the interpretation and understanding of the fate of atmospheric ^{129}I in the subsurface. ^{14}C is still being produced by current nuclear power production, but in much smaller quantities.

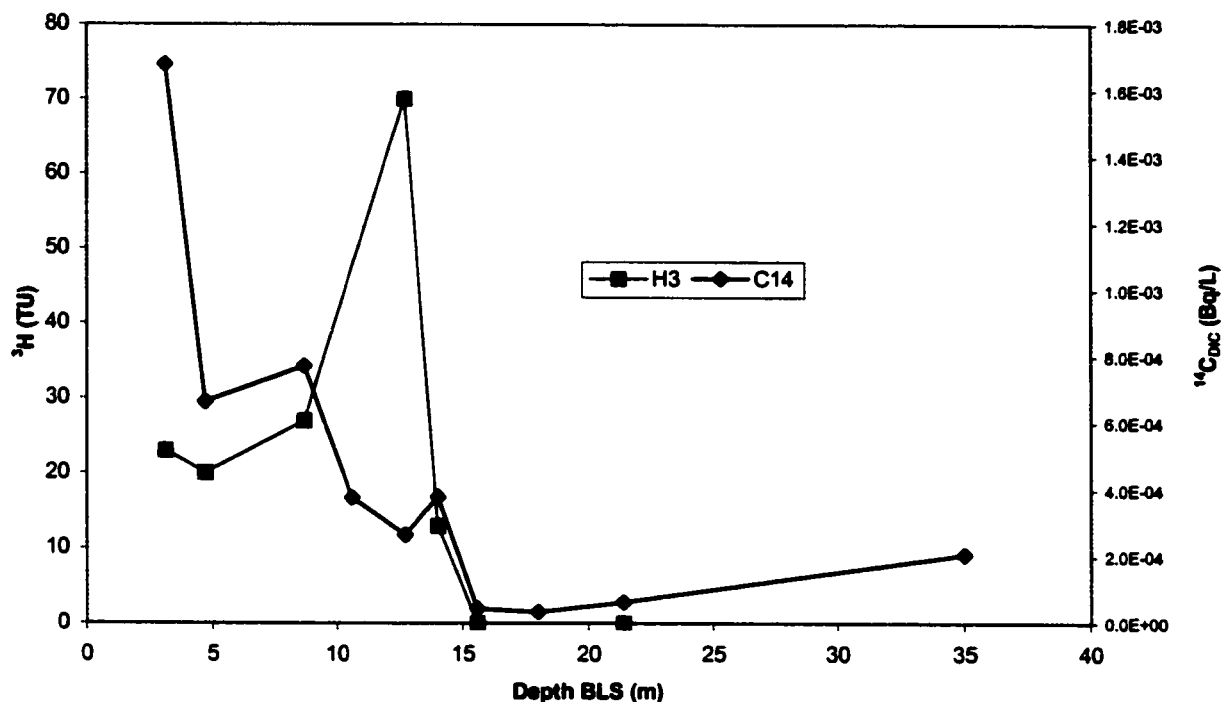
Atmospheric ^{14}C occurs as $^{14}\text{CO}_2$. In this form, it may be taken up directly by vegetation to be used in photosynthesis. In the shallow subsurface, the decay of vegetation produces

soil CO₂, which is ¹⁴C active. Recharging groundwaters then dissolve the soil ¹⁴CO₂ and pick up a dissolved organic carbon signature.

At nests 26 and 28 of the Sturgeon Falls field site, 10 samples were collected for ¹⁴C_{DIC} analysis. The samples, collected in July 1999, range in depth from 3 m to 35 m below land surface. Figure 7 illustrates the differences in the ³H (conservative) and ¹⁴C_{DIC} profiles in July 1999 versus depth below land surface.

As previously shown in Figure 6, the July 1999 ³H peak was observed at 12.7 m depth. This is in sharp contrast to the ¹⁴C_{DIC} bomb-peak, which is observed at 3.1 m depth below surface. In Figure 7, ¹⁴C activities are expressed as Bq/L water, rather than being normalized to the concentration of DIC. In this fashion, dilution of ¹⁴C_{DIC} in the shallow (<14 m) subsurface through enhanced carbonate weathering by H₂SO₄ do not bias the initial ¹⁴C content of the groundwaters gained during recharge. The ¹⁴C_{DIC} level in piezometer 28-3 was determined to be 68.33 pMC. The DIC concentration in that piezometer was measured at 4.32 mmol/L. It is likely that the migration of ¹⁴C_{DIC} bomb-peak, downward through the groundwater system, is being retarded by equilibration reactions in the near surface.

Figure 7. ^3H and $^{14}\text{C}_{\text{DIC}}$ in Sturgeon Falls groundwater (July, 1999).



Note: ^{14}C measurements are normalized to water volume, and are expressed as Bq/L.

2.2.3 Geochemistry and Stable Isotopes

The major ion chemistry and environmental isotope concentrations for Sturgeon Falls groundwater samples are presented in Tables 2 & 3, respectively. Generally, these groundwaters can be classified as dilute Ca-HCO₃ waters with very low chloride concentrations that are near the analytical detection limits. Sulfate levels are above the detection limits for groundwater samples collected 14 m below surface and shallower. Generally, samples collected below 14 m depth are at or below the analytical detection limit for sulfate.

The levels of calcium measured are probably generated due to carbonate mineral dissolution, a hypothesis supported by the HCO_3^- measurements made in July 1999. It is likely that the infiltrating water has a moderately low pH, which is due to the dissolution of soil CO_2 and the presence of H_2SO_4 from smelter fallout from Sudbury. Robertson et al. (1989) used $\delta^{34}\text{S}$ evidence to establish this link to the smelters in Sudbury. SO_4 levels in the upper 14 m of the groundwater are indicative of smelter fallout, while below 14 m depth, sulfate reduction is occurring. The pH of waters collected from piezometers 28-1 (1 m deep) and 28-2 (2 m deep) in July 1999 were measured at 6.04 and 5.63, respectively. This acidity is buffered before reaching deeper piezometers by the dissolution of carbonate minerals. The $\delta^{13}\text{C}_{\text{DIC}}$ values for groundwater at the Sturgeon Falls study site average -11.4‰ (VPDB), slightly enriched with respect to $\delta^{13}\text{C}$ in soil CO_2 , (Table 3) further supporting the argument. This value falls in the middle of the range of typical DIC contents in groundwater following closed system dissolution of carbonate minerals (Clark and Fritz, 1997). The pH of water samples collected from below 14 m depth are significantly higher than shallower samples and are likely due to sulfate reduction which is occurring at those locations. The shallow groundwaters are slightly oversaturated with respect to calcite (Table 4). All groundwaters measured are undersaturated with respect to gypsum, however the gypsum saturation indices (not shown) for groundwaters below 14 m depth are significantly lower than those of waters collected in the top 14 m of the aquifer due to loss of sulfate by sulfate reduction in this zone.

Piezometer	Date	pH	Temp (°C)	Ca	Na	Mg	K	Cl	HCO ₃	Br	F	SO ₄	NO ₂	NO ₃
28-3	Jul-99	7.95	13.3	34.2	2.3	14.6	1.4	<1	-	<0.05	0.19	10.0	<0.1	<0.1
	Sep-99	-	-	47.1	2.5	14.1	1.6	1.0	-	<0.05	0.21	8.0	<0.1	0.2
28-5	Jul-99	8.04	13.6	41.5	1.6	10.6	1.3	1.0	-	<0.05	0.14	11.5	<0.1	<0.1
28-9	Jul-99	8.10	10.3	43.7	2.4	11.9	<0.5	1.0	181	<0.05	0.12	11.5	<0.1	<0.1
	Sep-99	-	-	43.3	2.3	11.2	<0.5	1.0	-	<0.05	0.15	14.0	<0.1	0.1
	Oct-99	7.83	7.8	24.0	3.9	11.3	1.9	1.0	-	<0.05	0.14	12.5	<0.1	<0.1
	Jun-00	7.87	7.6	45.0	2.0	15.0	<1	0.5	-	<0.05	0.08	12.0	<0.1	<0.1
28-11	Jul-99	8.18	10.2	36.7	2.3	9.8	0.7	1.0	-	<0.05	0.12	18.0	<0.1	<0.1
28-12	Jul-99	9.16	12.2	31.2	2.2	11.9	<0.5	1.0	-	<0.05	0.12	13.5	<0.1	0.2
	Sep-99	-	-	6.7	2.4	11.5	<0.5	1.0	-	<0.05	0.10	4.0	<0.1	0.2
28-14	Jul-99	8.15	-	36.5	2.1	12.3	1.5	1.0	150	<0.05	0.16	9.0	<0.1	<0.1
	Oct-99	8.21	10.7	32.7	3.3	9.4	1.0	1.0	-	<0.05	0.16	9.5	<0.1	<0.1
	Jun-00	8.18	10.2	34.0	2.0	12.0	<1	0.6	-	<0.05	0.08	10.9	<0.1	<0.1
28-15	Jul-99	9.44	9.9	10.4	2.8	8.1	0.8	1.0	-	<0.05	0.12	<3	<0.1	<0.1
	Sep-99	-	-	5.0	2.3	10.5	<0.5	1.0	-	<0.05	0.12	<3	<0.1	1.1
28-18	Jul-99	9.35	10.6	6.3	2.6	7.6	<0.5	1.0	-	<0.05	0.19	<3	<0.1	0.2
28-21	Jul-99	9.91	11.2	25.6	3.1	6.0	1.0	1.0	-	<0.05	0.16	<3	<0.1	0.5
	Sep-99	-	-	20.3	2.6	7.7	0.9	1.0	-	<0.05	0.18	<3	<0.1	0.5
26-35	Jul-99	7.75	10.0	29.8	3.8	7.4	1.7	<1	131	<0.05	0.25	<3	<0.1	<0.1
	Sep-99	-	-	33.6	4.1	9.1	<0.5	4.0	-	<0.05	0.29	<3	<0.1	1.1
	Oct-99	7.82	9.8	16.9	3.5	4.1	<0.5	<1	-	<0.05	0.22	<3	<0.1	<0.1
	Jun-00	8.10	10.2	32.0	4.0	11.0	1.0	<1	-	<0.05	0.23	<3	<0.1	0.6

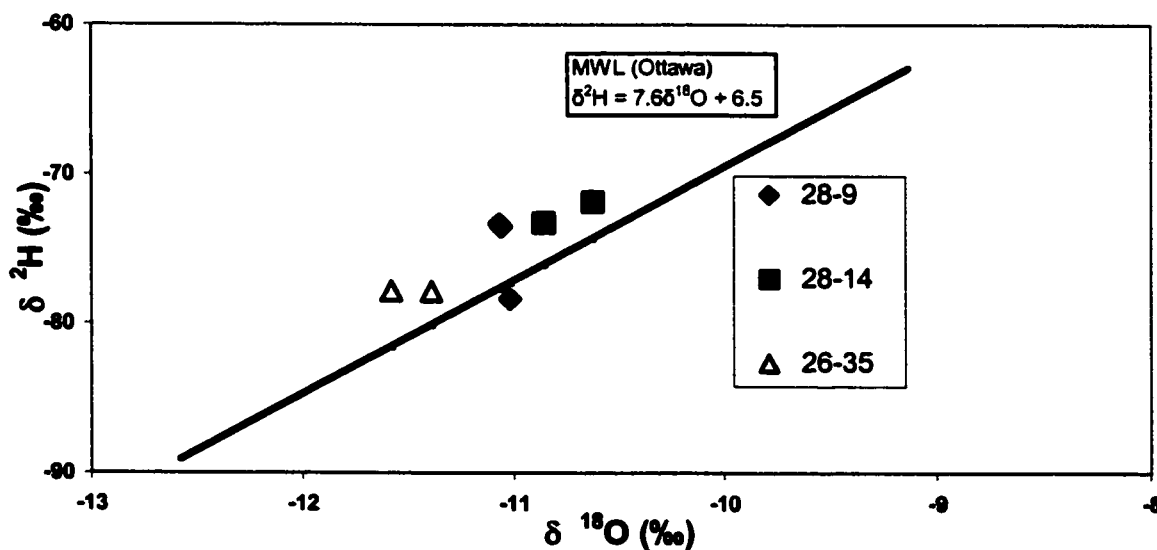
Table 2. Major ion concentrations (in mg/L) in Sturgeon Falls groundwater samples.

Deuterium and oxygen-18 concentrations in the groundwaters collected from 28-9, 28-14 and 26-35 are presented in Figure 8, Table 3. Generally, the ²H and ¹⁸O concentrations are more depleted in the deeper samples from 26-35. This points to a more regional origin for the deep groundwater. As these waters are practically tritium-free (< 2 TU), they are older than the shallow groundwaters.

Table 3. Isotope Data for Sturgeon Falls groundwater.

Piezometer	Date	$\delta^2\text{H}_{\text{VSMOW}} (\text{‰})$	$\delta^{18}\text{O}_{\text{VSMOW}} (\text{‰})$	$\delta^{13}\text{C}_{\text{VPDB}} (\text{‰})$	^{14}C (Bq/L)	^3H (TU)
28-3	Jul-99	-	-	-15.46	1.68×10^{-3}	23
	Sep-99	-	-	-	-	29
28-5	Jul-99	-	-	-13.11	6.63×10^{-4}	20
28-9	Jul-99	-73.57	-11.06	-14.12	7.71×10^{-4}	27
	Sep-99	-78.37	-11.02	-	-	-
	Jun-00	-73.34	-11.07	-	-	29
28-11	Jul-99	-	-	-13.08	3.76×10^{-4}	-
28-12	Jul-99	-	-	-9.91	2.65×10^{-4}	70
	Sep-99	-	-	-	-	72
28-14	Jul-99	-71.84	-10.63	-13.99	3.79×10^{-4}	13
	Jun-00	-73.27	-10.86	-	-	27
28-15	Jul-99	-	-	-0.59	4.30×10^{-5}	BMDL
	Sep-99	-	-	-	-	1
28-18	Jul-99	-	-	-9.19	3.38×10^{-5}	-
28-21	Jul-99	-	-	-13.98	6.18×10^{-5}	BMDL
	Sep-99	-	-	-	-	-
26-35	Jul-99	-77.80	-11.58	-10.88	2.06×10^{-4}	BMDL
	Sep-99	-77.85	-11.39	-	-	1.5
	Jun-00	-	-	-	-	<0.8

Note: BMDL – Below Method Detection Limit (At AECL MDL is approximately 5 TU)

**Figure 8. Stable isotopes of the three principal groundwaters sampled at Sturgeon Falls.**

The inorganic carbon species concentrations in groundwaters collected in September 1999 are presented in Table 4. The speciation was calculated based on the field-

measured pH and the total DIC content of the waters. In water samples with a pH below 8.4, the concentration of CO_3^{2-} was assumed insignificant. Similarly, the concentration of H_2CO_3 in water samples with a pH above 8.4 was assumed insignificant. The calculated HCO_3^- concentrations correspond well with those measured in the field by alkalinity titration.

Table 4. Inorganic carbon speciation in groundwaters collected in July 1999.

Sample	Field pH	DIC mol/L	H_2CO_3 mol/L	CO_3 mol/L	HCO_3 mol/L	Calculated HCO_3 mg/L	Field Measured HCO_3 mg/L	$\log\text{SI}_{\text{cal}}$
28-3	7.95	4.2×10^{-3}	1.1×10^{-4}	-	4.2×10^{-3}	180	-	0.147
28-5	8.04	2.9×10^{-3}	5.8×10^{-5}	-	2.8×10^{-3}	174	-	0.308
28-9	8.10	3.0×10^{-3}	5.3×10^{-5}	-	3.0×10^{-3}	182	181	0.352
28-11	8.18	2.4×10^{-3}	3.5×10^{-5}	-	2.3×10^{-3}	143	148	0.275
28-12	8.62	2.0×10^{-3}	-	3.8×10^{-5}	2.0×10^{-3}	120	-	0.571
28-14	8.15	2.4×10^{-3}	3.7×10^{-5}	-	2.3×10^{-3}	142	150	0.256
28-15	9.44	7.8×10^{-4}	-	8.9×10^{-5}	6.9×10^{-4}	42	-	0.434
28-18	9.78	6.3×10^{-4}	-	1.4×10^{-4}	4.9×10^{-4}	30	-	0.362
28-21	10.00	9.0×10^{-4}	-	2.9×10^{-4}	6.1×10^{-4}	37	-	1.160
26-35	7.75	2.0×10^{-3}	7.6×10^{-5}	-	1.9×10^{-3}	116	131	-0.270

Note: $\log\text{SI}_{\text{cal}} = \log (\text{IAP}/K_{\text{calcite}})$

2.2.4 ^{129}I in Groundwater

The two major sources of anthropogenic ^{129}I are the atmospheric thermonuclear weapons tests, conducted in the 1950's and 60's and the ongoing nuclear fuel reprocessing activities. Current reprocessing activities are concentrated in Europe and have released several thousand kilograms of ^{129}I since the mid-1960's. While the testing of thermonuclear weapons was the dominant source of anthropogenic ^{129}I prior to 1966, nuclear fuel reprocessing is now the primary source. Both of these activities have maintained ^{129}I concentrations in the environment well above natural background levels.

The ^{129}I discharges from Europe's two largest reprocessing plants, at Cap de la Hague in France and at Sellafield in England, have resulted in marine contamination of the English Channel and Irish Sea, respectively. In the northeastern United States, the West Valley, N.Y. reprocessing facility was operational from 1966 to 1975, although reprocessing stopped in 1972. This site released large amounts of ^{129}I during its operation (Rao and Fehn, 1999). The release of ^{129}I from the West Valley facility was primarily through atmospheric emissions (Fehn, pers. comm.).

Table 5 contains iodine and ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios for groundwater samples collected from Sturgeon Falls. The samples generally have sub-ppb levels of dissolved stable iodine. The dissolved stable iodine levels in the groundwater range from 0.07 ppb to 1.7 ppb. A snow sample, collected in February 2001, contained a dissolved stable iodine concentration of 0.2 ppb. ^{129}I concentrations in the groundwater samples range from approximately 1.5×10^5 atoms/L to approximately 1.9×10^6 atoms/L, while the ^{129}I concentration of the snow sample was 8.5×10^7 atoms/L.

Table 5. Sturgeon Falls iodine isotope ratios.

Sample	Dissolved Stable I (ppm)	Dissolved Stable I (mg)	Stable I Carrier (mg)	Total Stable I (mg)	Measured Ratio	Lab Blank Ratio Used	Blank Corrected Ratio	Dilution Factor	Dilution Corrected Ratio	^{129}I (10^6 atoms/L)
28-9 (Oct. '99)	0.0017	0.170	1.929	2.099	7.32E-12	5.82E-12	1.50E-12	12	1.85E-11	0.15 ¹ (± 7.7%)
28-9 (Jun. '00)	0.00067	0.201	6.710	6.911	2.31E-11	5.49E-12	1.76E-11	34	6.04E-10	1.89 (± 3.5%)
28-14 (Jun. '00)	0.00007	0.021	7.012	7.033	2.32E-11	5.49E-12	1.77E-11	335	5.93E-09	1.94 (± 11.2%)
26-35 (Oct. '99)	0.0004	0.040	2.242	2.282	9.61E-12	5.82E-12	3.79E-12	57	2.16E-10	0.40 (± 9.7%)
26-35 (Jun. '00)	0.00015	0.042	6.242	6.284	7.33E-12	5.49E-12	1.84E-12	150	2.75E-10	0.19 (± 5.3%)
Sturgeon Falls Snow	0.0002	0.016	2.074	2.090	7.06E-10	5.49E-12	7.01E-10	131	9.15E-08	85.44 (± 2.1%)
S.F. Site 1 & 2 Litter Top	4.728	0.2644	2.290	2.554	2.22E-09	1.81E-13	2.22E-09	10	2.15E-08	473.55 ² (± 2.2%)
S.F. Site 1 Litter Bottom	3.903	0.6715	2.062	2.734	7.58E-10	2.50E-13	7.58E-10	4	3.08E-09	56.21 ² (± 2.3%)
Combustion Blank Apr.3/01	0.0026	0.0001	2.730	2.730	1.81E-13	-	-	-	-	-
Combustion Blank Apr.4/01	0.0022	0.0001	2.090	2.090	2.50E-13	-	-	-	-	-
Large Test Column	-	-	1.875	1.875	4.23E-12	-	-	-	-	-
Test Column #1	-	-	5.000	5.000	3.01E-12	-	-	-	-	-
Test Column #2	-	-	2.000	2.000	1.02E-11	-	-	-	-	-
Tank Blank	-	-	2.035	2.035	5.49E-12	-	-	-	-	-

¹ this sample had an erroneous yield of 360%

² 10^6 atoms/g.

Rao and Fehn (1999) conducted a large study that measured ^{127}I and ^{129}I in surface waters and soils and examined the sources and reservoirs of anthropogenic ^{129}I . Dissolved stable iodine levels in surface water samples across North America ranged from less than 0.1 ppb to 1.9 ppb, a range very similar to that found in the groundwater samples from Sturgeon Falls, while ^{129}I concentrations ranged from 6×10^6 to 1.4×10^{11} atoms/L. In another study, Alvarado Quiroz (1999) measured dissolved stable iodine and ^{129}I in a shallow aquifer at a low-level nuclear waste management facility at CRL. Stable iodine

levels ranged from 0.23 to 26 ppb, and ^{129}I concentrations ranged from 1×10^8 to 8.3×10^{11} atoms/L. Figure 9 illustrates the relationship between ^{129}I and stable iodine at Sturgeon Falls and in these other two studies. From Figure 9 it is apparent that while the stable iodine concentrations of the Sturgeon Falls groundwater fall within the same range as the surface waters, groundwaters and precipitation samples reported by other researchers, the ^{129}I concentrations of the Sturgeon Falls groundwaters are at least an order of magnitude lower than the ^{129}I concentrations measured in the other samples.

At Sturgeon Falls, where bomb tritium is observed, there may be anthropogenic ^{129}I may be present. Since the bomb peak was determined to be at approximately 12.7 m depth, it follows that pre-bomb levels of ^{129}I may be observed in piezometer 26-35, bomb ^{129}I in 28-14 and post bomb (i.e., modern) ^{129}I in 28-9. The groundwaters sampled from 28-14 likely recharged around 1960 (based on an average vertical groundwater velocity of 0.35 m/year). Since this predates the nuclear fuel reprocessing activities, the ^{129}I found at this level can likely be attributed to the thermonuclear weapons tests. Conversely, the groundwater at 28-9 likely recharged around 1975 and as such, may have contributions of ^{129}I from both thermonuclear weapons testing and nuclear fuel reprocessing (Clark et al., 2001).

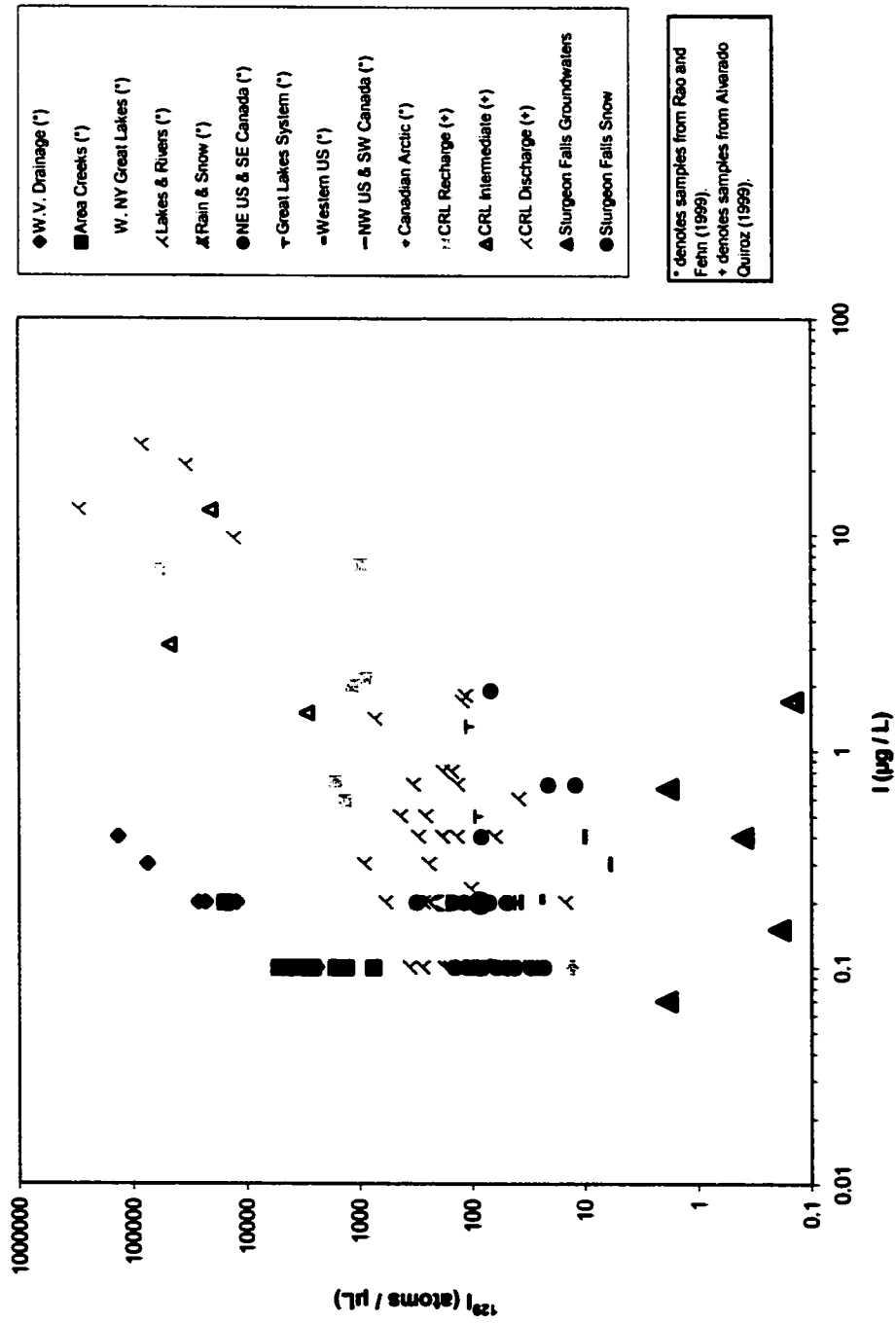


Figure 9. ^{129}I vs. I for surface waters, groundwater and precipitation.

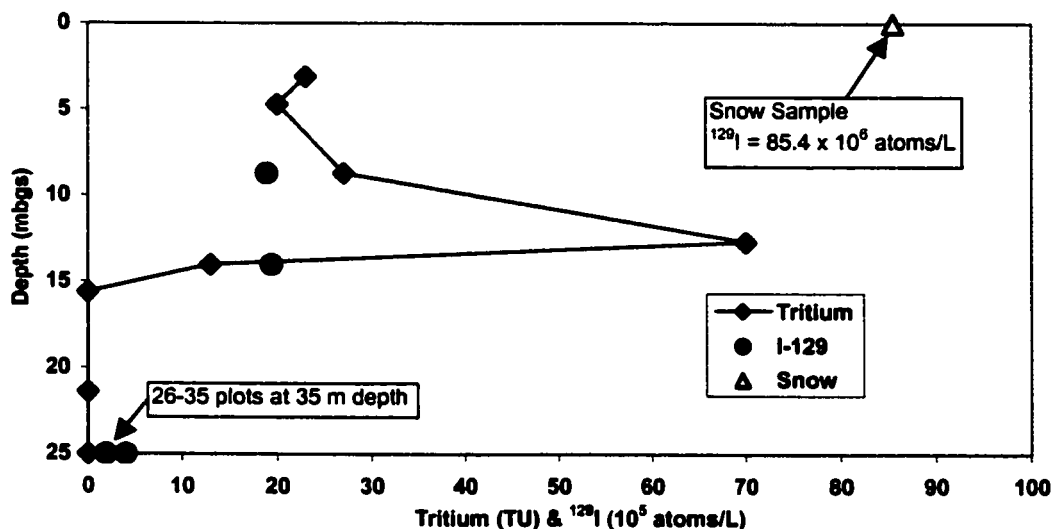


Figure 10. ^{129}I (Oct. 99 & Jun. 00) and ^3H (Jul. 99) in Sturgeon Falls groundwaters.

The practically tritium-free groundwater at 26-35 has higher ^{129}I concentrations than published estimates of pre-bomb ^{129}I levels. Fabryka-Martin et al. (1985) and Rao and Fehn (1999), have estimated pre-bomb ^{129}I concentrations in water to be 10^3 to 10^4 atoms/L. Since the ^{129}I concentrations measured in groundwaters collected from piezometer 26-35 are 1 to 2 orders of magnitude greater than these published estimates, it is likely that there is a geogenic source contributing additional ^{129}I to this deep groundwater. Since piezometer 26-35 is completed in the basal aquifer, which overlies the granitic basement rocks of the Precambrian Shield, it is likely that the granitic bedrock is supplying fissiogenic ^{129}I from the spontaneous fission of ^{238}U . This fissiogenic ^{129}I may be leached by the groundwater. Previous studies have demonstrated that brackish to saline waters in granites can have ^{129}I concentrations between 2 and

340×10^6 atoms/L (Fabryka-Martin et al., 1989; Kotzer et al., 1998). Thus, even a minor fissiogenic contribution from bedrock could provide the excess ^{129}I observed in these pre-bomb waters. Alternatively, the additional ^{129}I could be due to leaching from silicate minerals in the upper aquifer (Clark et al., 2001).

The snow sample collected at Sturgeon Falls in February 2001 has a ^{129}I concentration of 8.5×10^7 atoms/L, which is over 44 times larger than the groundwater sample with the highest ^{129}I concentration. Precipitation samples collected by Rao and Fehn (1999) in the Rochester, N.Y. area, show ^{129}I concentrations ranging from 3×10^7 to 1.3×10^8 atoms/L. The Sturgeon Falls precipitation (snow) sample falls within that range. Regional surface waters measured by Rao and Fehn (1999) had ^{129}I concentrations ranging from 1×10^7 to 1.4×10^{11} atoms/L. The fact that regional precipitation and surface water samples have much larger concentrations of ^{129}I than measured in groundwater samples suggests that ^{129}I is highly attenuated during infiltration. However, the dissolved stable iodine concentrations in the Sturgeon Falls groundwaters fall within the same range as those measured by Rao and Fehn in regional surface waters (1999). This suggests that a disequilibrium exists between dissolved stable iodine and ^{129}I . It is likely that stable iodine is recycled through the biosphere and hydrosphere on a long-term basis while modern ^{129}I is from atmospheric sources (Clark et al., 2001).

2.2.5 ^{129}I in Soil

In order to determine if iodine was being sequestered in the shallow subsurface, two samples of soil and organic litter were combusted and the ^{129}I concentrations were measured. Table 5 contains the iodine and ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios for the soil and litter samples collected from Sturgeon Falls. ^{129}I concentrations in the samples range from approximately 5.6×10^7 atoms/g in the bottom litter to approximately 4.3×10^8 atoms/g at the top of the litter layer. These values are similar to the low-end values obtained by Rao and Fehn in soil cores taken in western New York (1999). Rao and Fehn also found that the upper layers of their cores had ^{129}I concentrations at least an order of magnitude greater than the lower layers, which did not correlate with the stable iodine levels. They concluded that ^{129}I and stable iodine are not in isotopic equilibrium. They estimated pre-bomb concentrations of ^{129}I to be less than 10^5 atoms/g.

A study on the behavior of iodine in a shallow aquifer near a low-level, radioactive waste management area, found differences between stable iodine and ^{129}I with respect to how each species was bound to sediment (Alvarado Quiroz, 1999). It was determined that stable iodine was more tightly bound to organic matter than was ^{129}I . According to Alvarado Quiroz (1999), some of the stable iodine may be incorporated into the mineral or organic structure, while the ^{129}I is more loosely bound to surfaces and bound to iron and magnesium oxyhydroxides.

Stable iodine tends to interact with plants on a long-term basis and is likely recycled through the biosphere. Conversely, ^{129}I in recharge waters may not necessarily be incorporated in plant material on a single pass (Milton, pers. comm.). While Alvarado Quiroz (1999) demonstrated that ^{129}I was taken up rapidly by plants from air and groundwater, his results show that iodine uptake via the stomata was of greater significance than the uptake of iodine via the roots. Previously, other researchers (Milton et al., pers. comm.), working at Sturgeon Falls, found ^{129}I concentrations ranging from 4.2×10^6 atoms/g in cedar leaves to 7.5×10^7 atoms/g in grass. Consequently, ^{129}I in the groundwater is attenuated during recharge and infiltration through the soil zone and ^{129}I concentrations in groundwater are lower than local precipitation and lower than regional surface waters.

2.3 CONCLUSIONS

The Sturgeon Falls groundwaters had dissolved stable iodine concentration ranging from 0.07 ppb to 1.7 ppb. As a result, it was necessary to collect large samples for ^{129}I analysis. The ^{129}I concentrations in the groundwater vary from less than 2×10^5 atoms/L to almost 2×10^6 atoms/L.

The groundwaters of the basal aquifer are geochemically and isotopically distinct from the shallow groundwaters. They are more depleted in ^{18}O , indicating a more regional origin. Although these groundwaters are practically tritium-free, making them pre-thermonuclear bomb groundwaters, ^{129}I concentrations ranging from 2×10^5 to 4×10^5 atoms/L are 1 to 2 orders of magnitude greater than published estimates. Fabryka-Martin et al. (1985) and Rao and Fehn (1999) suggest that background ^{129}I concentrations prior to the thermonuclear weapons testing were on the order of 10^3 to 10^4 atoms/L. It is likely that there is a geogenic source contributing additional ^{129}I to this deep groundwater. The granitic bedrock is likely supplying fissiogenic ^{129}I from the spontaneous fission of ^{238}U . This fissiogenic ^{129}I may be leached from the bedrock by the groundwater. Alternatively, the additional ^{129}I could be due to leaching from silicate minerals in the upper aquifer.

The groundwater collected from piezometer 28-14 (14 m bgs) has an ^{129}I concentration of 1.94×10^6 atoms/L. Based on an average vertical groundwater velocity of 0.35 m/year, the groundwater at 14 m depth likely recharged around 1960. Since this predates the

nuclear fuel reprocessing activities, the ^{129}I found at this level can likely be attributed to thermonuclear weapons testing. The groundwater collected from piezometer 28-9 (8.7 m bgs) has an ^{129}I concentration of 1.89×10^6 atoms/L. This water recharged around 1975 and the source of the ^{129}I may include both thermonuclear weapons testing and nuclear fuel reprocessing. The ^{129}I concentrations at 28-9 and 28-14 are considerably lower than measured by Rao and Fehn in precipitation and in regional surface waters (1999). Also, the lack of correlation between the dissolved stable iodine concentrations in Sturgeon Falls groundwaters, which fall within the range of regional surface waters, and ^{129}I , indicates that no equilibrium ratio exists. Stable iodine is likely recycled in the biosphere on a long-term basis, while the modern ^{129}I is from anthropogenic sources (Clark et al., 2001).

The snow sample collected in February 2001 had a dissolved stable iodine content of 0.2 ppb and an ^{129}I concentration of approximately 8.5×10^7 atoms/L. The ^{129}I concentration of the Sturgeon Falls snow sample falls within the range of ^{129}I concentrations measured by Rao and Fehn (1999) on precipitation samples collected in the state of New York.

The analyses of ^{129}I in soil and organic litter samples reveal that ^{129}I is being sequestered in the near surface environment. The organic litter sample analyzed showed levels of ^{129}I of approximately 4.7×10^8 atoms/g. The lower soil sample, which consisted primarily of the silty sand aquifer material with some organic matter, had an ^{129}I concentration of 5.6×10^7 atoms/g. These samples indicate that ^{129}I in recharging waters is highly

attenuated in the near surface, by ion exchange or by the formation of complexes with the organic matter and that its release to the groundwater is very slow. Measurements of ^{14}C in dissolved inorganic carbon originating from the thermonuclear weapons tests, reveal that the peak of the bomb pulse is located in the shallow subsurface (i.e., 3 m bgs or less). It is likely that the migration of $^{14}\text{C}_{\text{DIC}}$ bomb-peak, downward through the groundwater system, is also being retarded by equilibration reactions in the near surface.

3.0 CON MINE

The Miramar Con Mine is located in Yellowknife, Northwest Territories, ($62^{\circ}27'N$, $114^{\circ}22'W$). Yellowknife is located 966-air km north of Edmonton, Alberta. The ground surface elevation is 206 mASL at the airport. Yellowknife is located on the west side of Yellowknife Bay, which is on the northern arm of Great Slave Lake (Figure 11) (City of Yellowknife, 2001). The Con Mine is located in the southeast corner of the city.

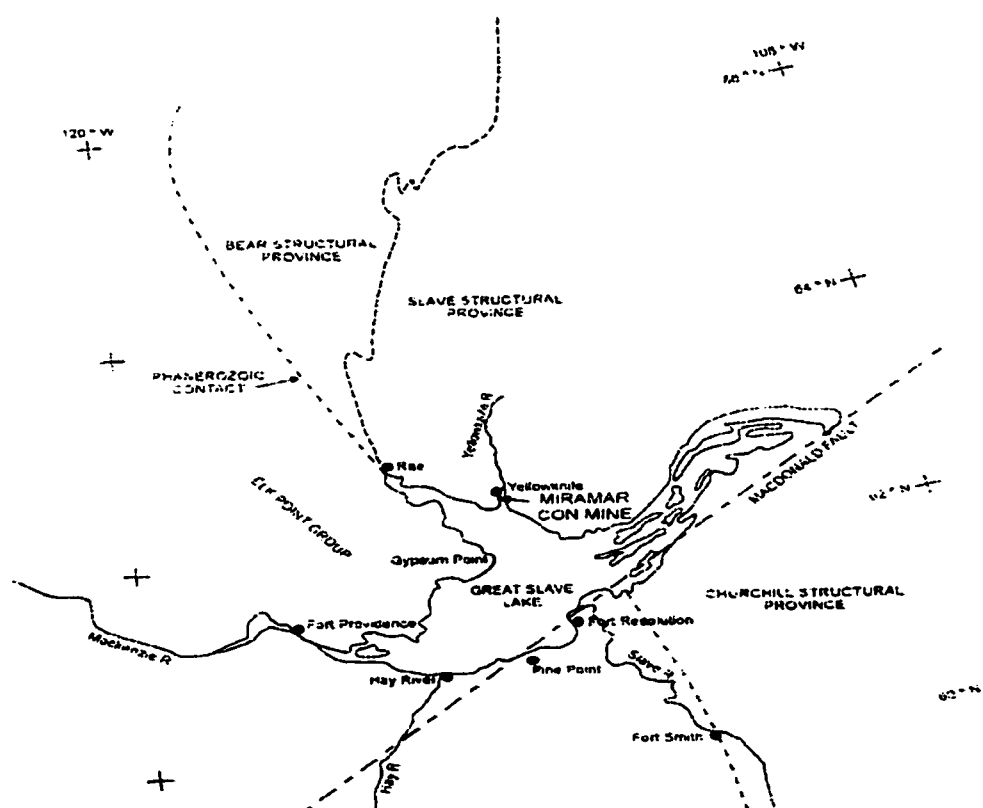


Figure 11. Yellowknife (N.W.T.) location and regional geological features.
(Source: Intera Consultants Ltd, 1997).

The Con Mine is situated within 2.5 to 2.7 billion year old volcanic and sedimentary rocks of the Yellowknife greenstone belt. Gold primarily occurs in quartz-bearing shear zones that crosscut the original rocks (City of Yellowknife, 2001). The main shear zone exploited by the mine is the Campbell Shear, which strikes in a N-S direction (Douglas et

al., 2000). There are three main fault orientations in the area (Figure 12). The oldest is the Negus Fault, which has a NE-SW orientation and it dips steeply to the southeast (Intera Consultants Ltd, 1997). The Negus Fault is offset approximately 290 m by the movement of the Pud Fault. Its orientation is NNE-SSW and dips steeply to the southwest. The Angel-type faults, oriented in a WNW-ESE direction, have a near vertical strike (Intera Consultants Ltd, 1997).

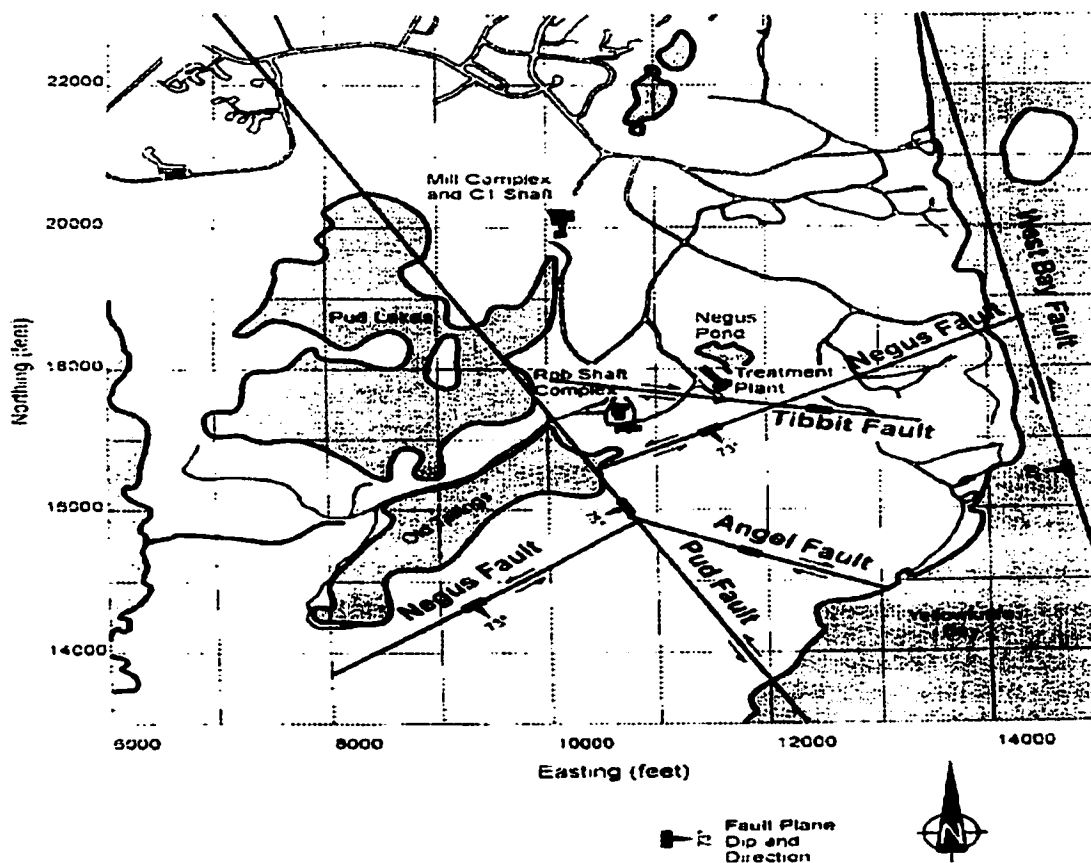


Figure 12. Con Mine site and fault traces.
(Source: Intera Consultants Ltd, 1997).

The mine has two shafts; the C1 (Con) shaft and the Robertson shaft. The excavation of the C1 shaft began in 1937. In 1946, it was sunk to 745 m (2,444'). The Robertson shaft

was sunk to 1,890 m (6,200') beginning in 1974 (Figure 13) (Intera Consultants Ltd, 1997).

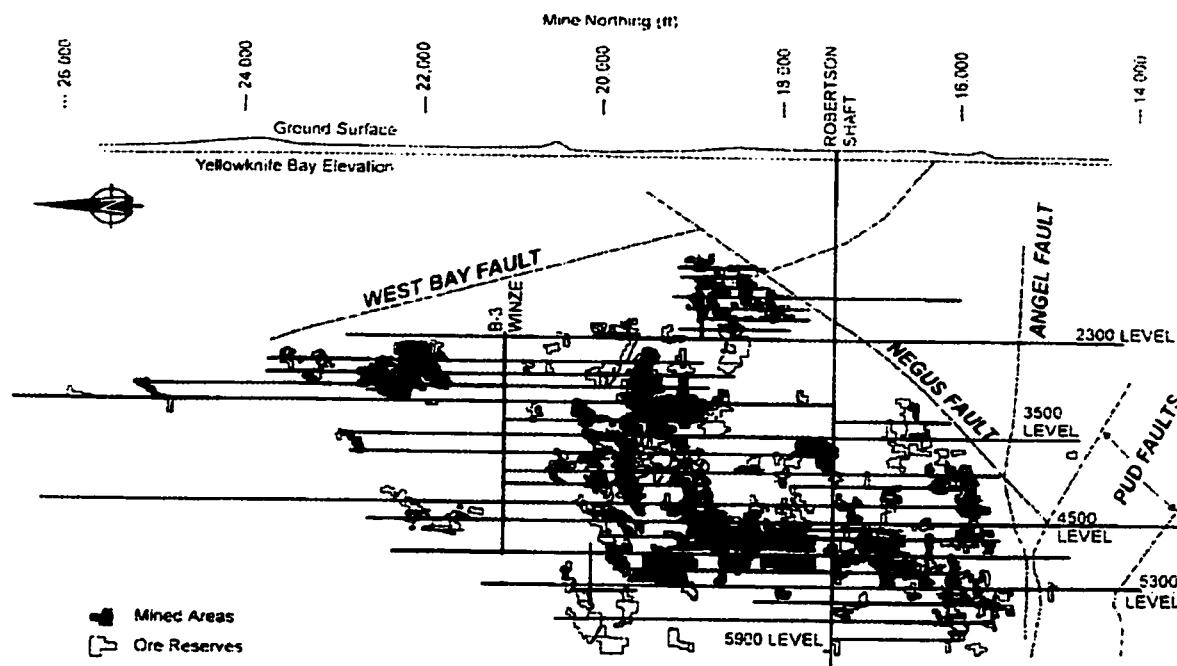


Figure 13. Longitudinal section of the Campbell Shear.
(Source: Intera Consultants Ltd, 1997).

3.1 METHODOLOGY

3.1.1 Field Methods

Con Mine sampling operations were concentrated on four levels. Sampling began on the 5300' level and proceeded to the 4500' level, the 3500' level and finally the 4900' level. Conditions on the lower levels were difficult. The drifts were muddy and slick. The air quality was sub-optimum. The boreholes sampled were approximately 500 m or more away from the main shaft. Due to the hydrostatic pressure, no pump was needed to sample the waters. The water was flowing freely from the boreholes. Samples for iodine

analysis, geochemical analysis and other isotope analyses were taken in HDPE bottles, directly from boreholes. Samples for carbon isotope analysis were taken in amber glass bottles.

Measurements made *in situ* include pH, dissolved oxygen, conductivity and temperature. A flow cell was used for this purpose. On the 5300' level, the waters were particularly saline. For this reason, the electronic meters were protected by plastic bags and the contacts between the meters and the electrodes were protected from corrosion by petroleum jelly. In addition, due to the high solute load of these waters, 10 times (10 x) dilutions were performed before conductivity measurements were made. Figure 14 illustrates the conditions in the drifts.



Figure 14. Underground conditions.

Due to the difficult conditions underground, alkalinity titrations were performed immediately upon return to surface. The titrations were performed using a Hach™ field kit.

3.1.2 Major Ion Analyses

Major ion analyses were carried out in the same manner as for the Sturgeon Falls samples. Cation analysis was performed at Accutest Laboratories by ICP-AES, using a Varian Liberty 220 ICP Emission Spectrometer. Anion analysis was also performed at Accutest using a Dionex DX-100 Ion Chromatograph (HPLC) with a Dionex AS40 automated sampler. Cation and anion concentrations are found in Table 6 (Results Section).

The analytical errors associated with the procedures are generally the same as reported for the Sturgeon Falls samples, with the following exceptions. The analytical error for all Br and Cl results are $\pm 10\%$ of the reported value. Error for SO_4 results for the following samples B8906, B7126, B6790 and B5586, are $\pm 100\%$ of the reported value.

3.1.3 Stable Isotope Analysis

Samples were collected for ^2H , ^{18}O and ^{13}C analyses. This work was performed in the G.G. Hatch Isotope Laboratories at the University of Ottawa. The same analytical procedures, as those performed on the Sturgeon Falls samples, were followed during the

isotopic analyses of the Con Mine waters. The analytical errors associated with these techniques are the same as reported for the Sturgeon Falls samples.

3.1.4 ^3H Analysis

^3H analysis was primarily performed at AECL – Chalk River Laboratories (CRL). Samples containing less than 5 TU were sent to the Environmental Isotope Laboratory (EIL) at the University of Waterloo for enriched tritium analysis (MDL = 0.8 TU). Due to the complex matrix of Con Mine water, azeotropic distillation was performed on samples analyzed for ^3H by liquid scintillation counting (LSC) at AECL. The azeotropes used included the Con Mine water samples and toluene. Azeotropic distillation is described in detail by Revesz and Woods, 1990.

3.1.5 Stable Iodide Measurements

Stable iodide measurements were made on the Con Mine samples using two methods. Measurements were made at CRL, by gas chromatography (GC), following the same procedure used for the Sturgeon Falls samples. The analytical error associated with this procedure is $\pm 20\%$. Additionally, an iodine ion selective electrode (ISE) was also used. All ISE work was carried out at the University of Ottawa. The ISE was used to verify the results obtained using the GC.

The ISE consisted of an Orion 290Aplus portable ion selective meter, an iodide electrode and a double junction reference electrode. Iodide standards ranging from 0.001 ppm to 1000 ppm were prepared by serial dilution from a 0.1 M iodide stock standard (NaI). Before measuring the standards, the slope of the iodide electrode response was verified for linearity. The slope is the change in millivolts observed with a ten-fold change in concentration. Checking the slope of the response ensures that the electrode is working properly. To check the slope, the following procedure was performed. 100 mL of distilled water was placed into a 150 mL beaker. 2 mL of ionic strength adjuster (ISA) were added. The contents of the beaker were stirred at a slow to moderate speed using a magnetic stirrer. With the meter in mV mode, 1 mL of 1000 ppm iodide standard was added to the beaker. Once a stable reading was obtained on the meter, it was recorded and an additional 10 mL of the 1000 ppm iodide standard was added to the beaker. Again, after waiting for a stable reading, the electrode potential (mV) was recorded. The difference in electrode potential should be between 54 and 60 mV per ten-fold change in iodide concentration.

With a properly functioning electrode, the iodide standards were measured. Approximately 25 mL of the standard was transferred to a 250 mL beaker. To this, 0.5 mL ISA was added. The standard was placed on the magnetic stirrer and the electrode potential was measured and recorded. With all of the standards measured, a calibration curve was prepared. This curve would be used to determine the iodide concentration of the samples. Instead of calculating one regression line for all the standard concentrations, 6 regression lines were calculated, one for each ten-fold increase

in iodide concentration. This allows a more precise determination of the iodide concentration of the unknown.

The fresh to brackish (i.e., <40000 ppm Cl⁻) samples were measured in the same way as the standards (i.e., 25 mL of the sample, 0.5 mL ISA). Brine samples (i.e., >50000 ppm Cl⁻) were measured in a slightly different manner. These samples were diluted before measurement. Both 10 times (10 x) and 100 times (100 x) dilutions were performed on these samples. The diluted sample (25 mL) was transferred to a 250 mL beaker as was done previously. Again, 0.5 mL ISA was added. The sample was placed on the magnetic stirrer and the electrode potential was measured. Using the calibration curve and the dilution factor, the iodide concentration of the sample was determined.

3.1.6 Iodine Extraction by Column Elution for ¹²⁹I Analysis by AMS

The procedure used to extract iodine from the Con Mine waters was very similar to the column extraction procedure carried out on the Sturgeon Falls samples. The main differences between the procedures included the size of the column and the volume of the reagents. Small columns (approximately 10 mL + reservoir) were used for all the mine waters. Smaller reagent volumes were also used for the extraction of iodine from the mine waters. With the exceptions noted above, the procedure was virtually identical to that used for the Sturgeon Falls samples.

3.2 RESULTS AND DISCUSSION

3.2.1 Tritium Profile

The Con Mine is considered a “leaky” mine. There are many fractures and faults that cut the volcanic and sedimentary rocks which host the mine. These features allow modern meteoric water to find its way to depths of at least 1372 m (4500’). Large hydraulic gradients due to the open mine works provide the driving force for the modern water to reach depth. A previous study (Clark et al., 2000) characterized the mine waters as mixtures of three end members, namely modern recharge, glacial meltwater and shield brines. Generally, modern recharge waters are found in the upper layers of the mine and saline brines are found in the lower layers.

Field sampling for this study was carried out in the autumn of 2000. Samples were collected on the 3500’, 4500’, 4900’ and 5300’ levels. Tritium levels varied from 0.9 to 26 TU (Table 6). These values closely resemble those measured by Douglas et al., 2000. The presence of tritium in some of the mine waters indicates that there is a fraction of bomb and/or nuclear fuel reprocessing impacted water at depth.

3.2.2 Major Ions and Isotopes

The predominant species in mine water samples collected from level 3500 to level 5300 are Ca^{2+} , Na^+ , Cl^- , and SO_4^{2-} (Table 6). Generally, the waters have increasing salinity with depth, varying from brackish waters to saline brines. There are local variations

where dissolved loads may not follow this trend, in particular borehole B3316 on the 4500' level. Waters collected from this borehole are brines, likely the result of the mixing of waters from other levels controlled by fracture hydraulic conductivity.

The shallower waters are typically Ca-SO₄/HCO₃ waters with minor Na-Cl salinity. Sulfate levels are greatest where chloride levels are below 15 g/L. The deeper waters are Ca/Na-Cl waters, typical of Canadian Shield brines (Clark, et al., 2000, Douglas, et al., 2000 – and references therein). Previous studies (Bottomley, et al., 1994, 1999) have attributed the Cl⁻ salinity of the brines to an evaporitic or cryogenic concentration of a Paleozoic seawater. The chloride-bromide relationship is linear throughout, suggesting a single source, while stable isotopes demonstrate a three-component mixture of glacial meltwaters, modern meteoric water and shield brines (Clark et al., 2000).

Table 6. Ionic and isotopic composition of Con Mine waters (Sep. 2000).

Level (feet)	Borehole	Ca	Na	Mg	K	Cl	HCO ₃	SO ₄	Br	F	I	δ ² H _{VSMOW}	δ ¹⁸ O _{VSMOW}	δ ¹³ C _{VPOB}	³ H (TU)
(Great Slave Lake)		16	5	4	<1	11	-	12	<0.05	0.22	0.01	-133.26	-16.04	-	-
3500	B8906	241	236	31	3	533	340.4	170	5	<0.50	0.01	-154.38	-19.38	-15.08	24
3500	B9362	1780	2040	34	8	5815	39.5	580	46	<0.50	0.15	-161.65	-20.85	-17.91	17
3500	B9452	1210	1110	83	7	3685	139	638	27	<0.50	0.11	-157.33	-19.77	-16.58	26
4500	B3316	36800	21200	211	165	119500	-	15	1190	<0.50	10.58	-99.97	-17.02	-	-
4500	B3362	23900	14700	190	111	73750	-	27.5	683	<0.50	6.20	-129.05	-18.69	-	-
4500	B3450	18900	12400	190	83	52700	-	40.5	525	<0.50	4.97	-135.98	-19.26	-	-
4500	B3457	2800	2500	50	13	8190	39.5	602.5	67	<0.50	0.30	-157.84	-20.10	-17.44	13
4500	B3618	13800	7910	126	55	32100	-	98.5	265	<0.50	2.17	-147.52	-20.19	-	-
4500	B5316	4450	3320	78	21	12250	37.8	587	112	<0.50	0.41	-160.47	-20.47	-17.70	16
4500	B5318	15600	7530	148	51	33900	53.7	69.5	350	<0.50	1.83	-149.92	-19.35	-17.44	18
4900	B5310	21800	11100	294	83	69900	-	36	-	<0.50	6.28	-134.08	-19.72	-	3.2
5300	B5586	81900	33000	153	308	163500	-	4	1600	<0.50	12.50	-80.64	-15.50	-6.91	-
5300	B6790	82700	29800	219	318	169000	18.8	5	1650	<0.50	14.91	-73.30	-15.26	-10.03	1.2
5300	B7126	96100	36900	486	391	168500	17.3	2	1720	<0.50	14.12	-73.30	-14.76	-8.30	0.9

Note: Ionic concentrations in mg/L; isotopic values in ‰; TU = Tritium Units.

3.2.3 ^{129}I and I in Water Samples

Table 7 contains iodine and ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios for mine water samples collected from the Con Mine. The majority of the stable iodide measurements reported in Table 7 were obtained using a gas chromatograph. However, two stable iodide measurements made on the GC were suspect. The concentrations measured by GC for B6790 and B7126 seemed too low, based on sampling conducted during previous studies at the Con Mine. An iodide ion selective electrode was used to investigate this possibility. It was suspected that the high salinity of these two samples interfered with the extraction of the iodo-complex into the hexane, thereby underestimating the iodide concentrations of the samples. To guard against any matrix effects or the effects of the elevated salinity in these samples, it was decided that performing dilutions prior to measurement by ISE was the best course of action. As such, two dilutions were performed on each sample. The samples were diluted 10 times (10 x) and 100 times (100 x). The electrode potential measured was then compared to the calibration curve (Figure 15) derived while measuring iodide standards. The iodide concentration determined from the calibration curve was then multiplied by the dilution factor. The stable iodide values listed in Table 7, as measured by ISE, are mean values for that sample obtained from the two dilutions performed. This mean value was then used to calculate the concentration of ^{129}I in the sample.

The ^{129}I concentrations in the shallower water samples tend to be related more closely to the anthropogenic sources of ^{129}I including fallout from thermonuclear weapons testing and nuclear fuel reprocessing activities. However, the ^{129}I concentrations in the brines

from the deeper levels of the mine have a fissiogenic origin. Evidence supporting these premises can be found in figures 16 through 18.

In Figure 16, several trends may be present. The obvious trend is that there appears to be a linear relationship between the ^{129}I concentration and the dissolved stable iodine concentration in the brine samples. As the dissolved stable iodine concentration of these waters increase, so do the ^{129}I concentrations. These waters are practically tritium-free, therefore older than the thermonuclear weapons testing and nuclear fuel reprocessing activities. The ^{129}I in these waters is from the spontaneous fission of ^{238}U in the host rocks. Interestingly, these waters do not appear to have picked up their dissolved stable iodine from their contact with the host rocks. Bottomley et al, (2002) point out that the stable iodine concentration of the brines could not be produced by leaching of the iodine from typical basaltic rocks. They suggest the source of the iodine was likely an external marine reservoir, with a minimum age of 78 million years (based on geological constraints), but possibly as old as a Middle Devonian (380 million years) seawater.

There are other potential trends in the data presented in Figure 16. It appears that there may be a positive linear relationship between the ^{129}I concentration and the dissolved stable iodine concentration of water samples collected from boreholes on the 4500' level, including B3457, B5316 and B5318 (see inset). This relationship is similar to that seen in the brine samples, however, there is a tritium signature to these waters, indicating that at least a portion of the ^{129}I concentration of these waters may be from anthropogenic sources. There is little or no correlation between the ^{129}I concentration and the dissolved

stable iodine concentration of remaining water samples, including B8906, B9452 and B9362 collected from the 3500' level. The lack of correlation between the ^{129}I and the dissolved stable iodine may indicate that these waters derive a component of their ^{129}I concentration from anthropogenic sources. It has been shown that no $^{129}\text{I}/\text{I}$ equilibrium ratio exists in the nuclear era (Clark et al., 2001). However, since the ^{129}I concentrations of these waters are at least an order of magnitude larger than that of the shallow Sturgeon Falls groundwaters, there must also be a fissiogenic component of the ^{129}I concentrations of these waters.

In Figure 17, there are similar relationships between the ^{129}I concentrations and the chloride salinity of the waters as were evident in Figure 16. The moderate to high salinity samples, i.e., the waters collected from the 4500' and 5300' levels, show positive linear trends between ^{129}I and Cl^- . Like the dissolved iodine in these samples, the dissolved chlorine load is likely due to the possible marine origin of the brines (Bottomley et al., 1999 and Bottomley et al., 2002). Conversely, the low salinity samples collected from the 3500' level show little correlation between these halides. A slight inverse relationship between the ^{129}I and Cl^- concentrations in these samples may be observed but it is unlikely that this relationship is real. The ^{129}I concentration of B8906 has a large statistical error associated with it due to the small amount of AgI precipitated following the column elution procedure, and, as the AgI target yielded ^{127}I currents that were 100 times lower than the reference material, there may be an additional systematic contribution to the error. Furthermore, the chloride concentration of the water collected

from B8906 is an order of magnitude less than that of the other samples collected on the 3500' level.

Figure 18 provides further evidence of the provenance of the ^{129}I in the water samples. This figure contrasts the ^{129}I concentrations and the Cl (salinity) with the ^{18}O concentrations (expressed in the standard ‰ notation). There is a linear relationship between the species. As the ^{129}I concentration increases, the ^{18}O concentration also increases. This is true for the salinity as well. The brine samples (B3316, B6790 and B7126) have the highest ^{129}I concentrations, the highest salinity and have enriched ^{18}O levels. The enriched ^{18}O levels of the brines suggest they are rock-equilibrated waters.

Table 7. Con Mine iodine isotope analyses.

Sample	Dissolved Stable I (ppm)	Dissolved Stable I (mg)	Stable I Carrier (mg)	Total Stable I (mg)	Measured Ratio	Blank Corrected Ratio	Dilution Factor	Dilution Corrected Ratio	¹²⁹ I (atoms/ μ L)
B9906 (3500'L)	0.01	0.01	2.17	2.18	1.10E-11	1.05E-11	198.45	2.09E-09	107.5 ¹ (\pm 12.7%)
B9362 (3500'L)	0.15	0.15	2.45	2.60	4.99E-12	4.53E-12	16.90	7.66E-11	55.1 (\pm 4.6%)
B9452 (3500'L)	0.11	0.11	2.12	2.23	6.70E-12	6.24E-12	20.23	1.26E-10	64.9 (\pm 4.0%)
B3316 (4500'L)	12.00	1.50	2.06	3.56	1.76E-12	1.30E-12	2.37	3.09E-12	173.1 (\pm 8.0%)
B3457-1 (4500'L)	0.40	0.05	2.11	2.16	1.53E-12	1.08E-12	43.22	4.65E-11	86.9 (\pm 6.5%)
B3457-2 (4500'L)	0.30	0.30	2.23	2.53	2.98E-12	2.52E-12	8.36	2.11E-11	29.9 (\pm 7.4%)
B5316 (4500'L)	0.41	0.41	2.59	3.00	4.46E-12	4.00E-12	7.36	2.95E-11	56.0 (\pm 4.9%)
B5316 (4500'L)	1.83	0.91	2.22	3.14	3.84E-12	3.38E-12	3.43	1.16E-11	99.1 (\pm 7.6%)
#41-10 (4900'L)	11.00	1.38	1.90	3.27	2.17E-12	1.71E-12	2.38	4.08E-12	209.4 (\pm 8.8%)
B5586 (5300'L)	17.00	1.02	2.11	3.13	1.83E-12	1.37E-12	3.06	4.21E-12	334.1 (\pm 9.8%)
B6709-3 (5300'L)	18.00	1.08	2.22	3.30	1.73E-12	1.27E-12	3.06	3.90E-12	327.4 (\pm 11.0%)
B6709-4 (5300'L)	18.00	1.08	2.78	3.86	1.26E-12	7.41E-13	3.57	2.65E-12	222.5 (\pm 9.9%)
B6790 (5300'L)	8.03	4.02	0.00	4.02	6.79E-12	6.33E-12	1.00	6.33E-12	237.6 (\pm 8.4%)
B6790 (5300'L)	14.91 (ISE)	7.45	0.00	7.45	6.79E-12	6.33E-12	1.00	6.33E-12	440.7 (\pm 8.4%)
B7126 (5300'L)	8.08	4.04	0.00	7.06	5.74E-12	5.28E-12	1.00	5.28E-12	199.3 (\pm 10.6%)
B7126 (5300'L)	14.12 (ISE)	7.06	0.00	7.06	5.74E-12	5.28E-12	1.00	5.28E-12	348.2 (\pm 10.6%)
Small Test Column	-	-	3.16	3.16	5.16E-13	-	-	-	-
3 Column Blank	-	-	3.19	3.19	1.19E-12	-	-	-	-
Bleach/Extraction Blank	-	-	3.25	3.25	1.09E-13	-	-	-	-
Low pH Blank	-	-	5.16	5.16	2.52E-13	-	-	-	-
Higher pH Blank	-	-	5.24	5.24	2.75E-13	-	-	-	-

¹ Small sample, therefore larger error.

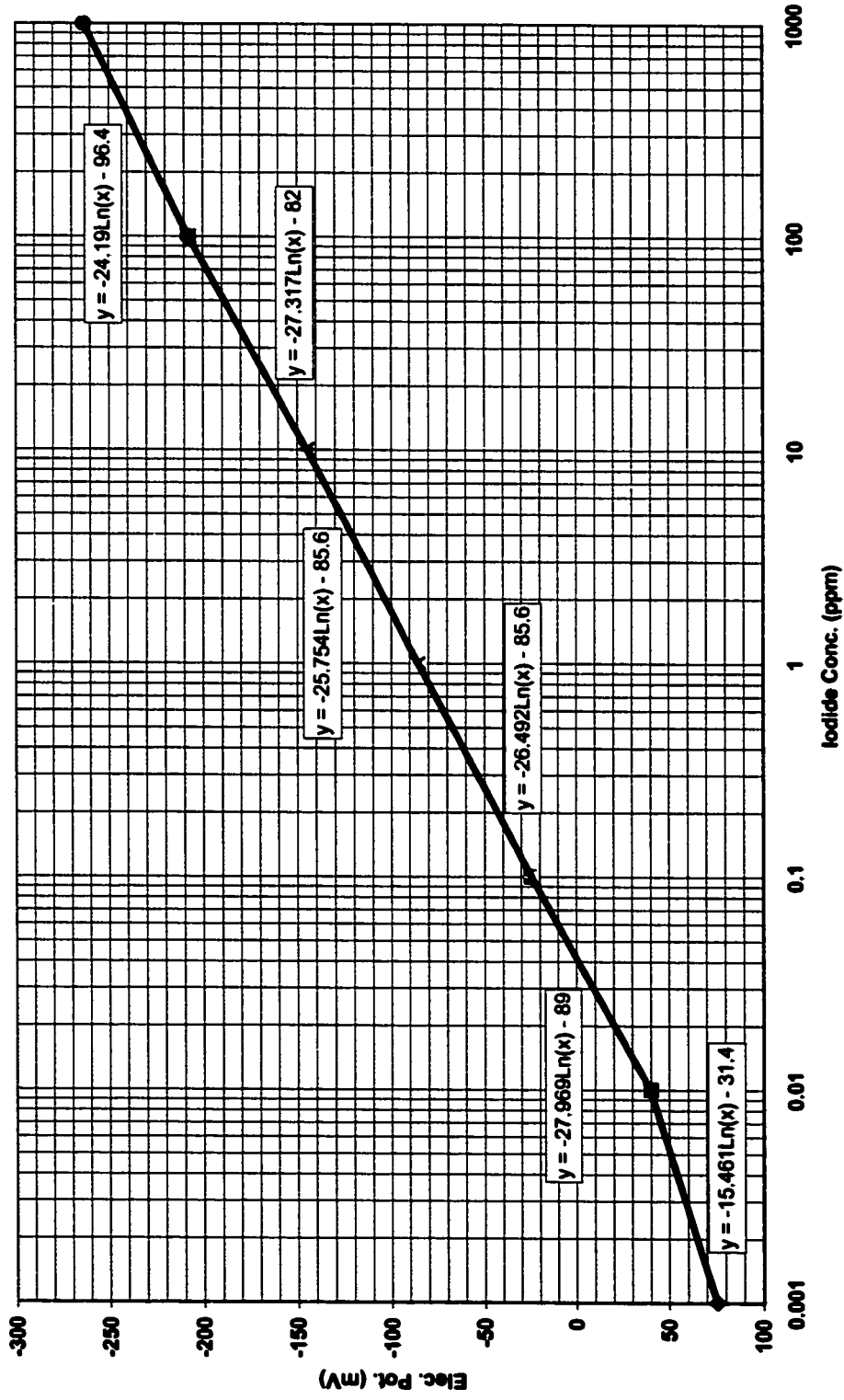


Figure 15. Iodide calibration curve for ISE.

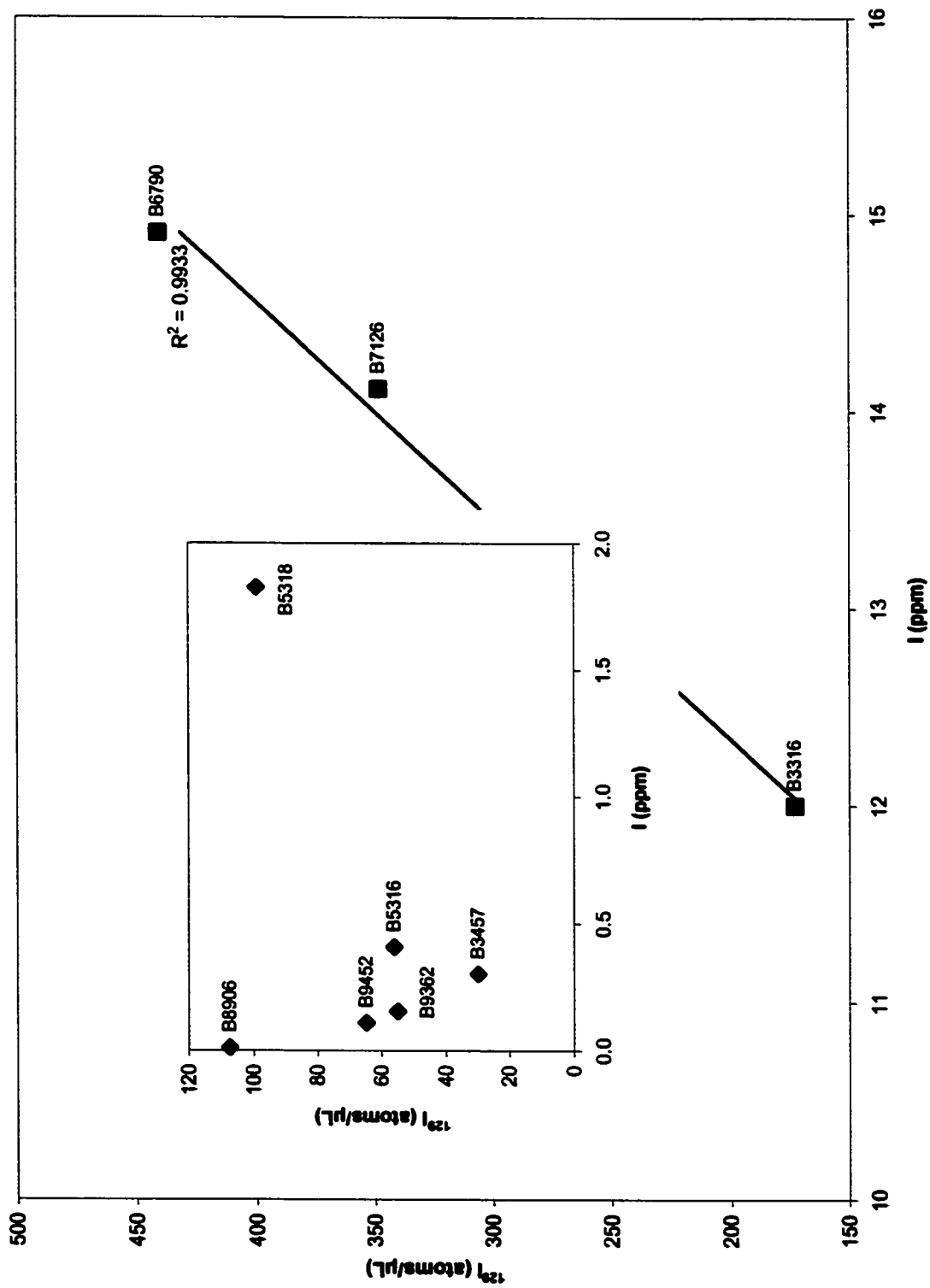


Figure 16. ^{129}I versus dissolved stable iodine.

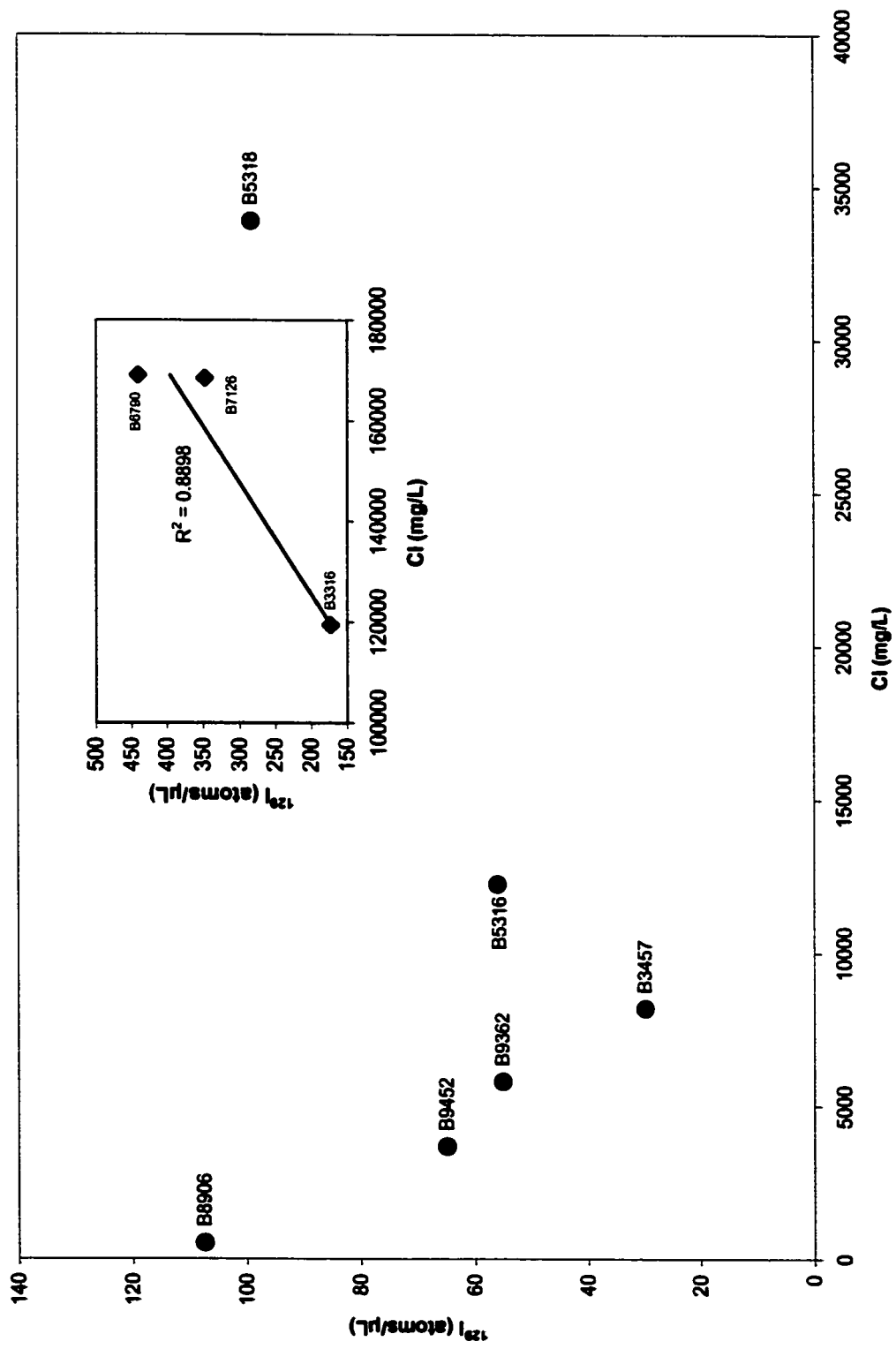


Figure 17. ¹²⁹I versus chloride salinity.

3.3 CONCLUSIONS

There is a good correlation between the dissolved stable iodine concentration and the ^{129}I concentration in the most saline waters collected primarily from the 5300' level. Since these waters are practically tritium-free, they owe their ^{129}I concentration to the spontaneous fission of ^{238}U during their long residence time in contact with the host rocks. These are rock-equilibrated waters based on their enriched ^{18}O levels. These waters also exhibit a good correlation between their chloride salinity and ^{129}I concentration. The high stable iodine and chloride concentration of these waters is likely due to their marine origin (Bottomley et al., 1999 and Bottomley et al., 2002).

The moderate salinity waters collected from the 4500' level have a tritium signature. These waters also show good correlations between dissolved stable iodine and ^{129}I , as well as between chloride salinity and ^{129}I . These correlations suggest a fissiogenic source of ^{129}I , as in brine samples, however their tritium signatures suggest that they derive at least a portion of their ^{129}I concentration from anthropogenic sources (namely thermonuclear weapons testing and nuclear fuel reprocessing). This portion of their ^{129}I content is likely due to mixing with modern meteoric water.

The low salinity waters collected on the 3500' level show little or no correlation between dissolved stable iodine and ^{129}I , as well as between chloride salinity and ^{129}I . The lack of correlation between the ^{129}I and the dissolved stable iodine may indicate that these waters derive a component of their ^{129}I concentration from anthropogenic sources. However, since their ^{129}I concentrations are much larger than the shallow groundwaters of Sturgeon Falls, they must also have a significant proportion of fissiogenic ^{129}I .

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