The mobility of anthropogenic ^{129}I in a shallow sand aquifer at Sturgeon Falls, Ontario, Canada

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Summary. 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 above-ground nuclear weapons pulse at a depth of approximately 12 m.

The concentrations of stable iodine for groundwaters above, near and below the above-ground nuclear weapons 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 in tritium-depleted waters at 35 m, below the present-day depth of the recharging above-ground nuclear weapons peak at approximately 12.7 m. No substantial increases in the levels of ^{129}I were evident in waters sampled near the location of the above-ground nuclear weapons peak.

The ^{129}I values in the lower aquifer are 1 to 2 orders of magnitude greater than published estimates of pre-bomb ^{129}I (10^3 to 10^4 atoms/L), and indicate contribution of ^{129}I from the fissiogenic decay of ^{238}U in the basal granite bedrock or from leaching of ^{129}I from the aquifer grains.

A precipitation sample collected at Sturgeon Falls had concentrations of stable iodine and ^{129}I of 0.2 ppb and 8.5×10^7 atoms/L, respectively. Concentrations of ^{129}I in Sturgeon Falls groundwaters are lower than those reported in other studies in central Canada, suggesting 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.

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.

Introduction

The geochemical behavior of ^{129}I in groundwater is of particular interest. Given its long half-life, the advective transport of ^{129}I is of concern in the safety assessment of future radioactive waste repositories, which may be constructed deep into the Precambrian Shield. Previous studies have investigated the transport and partitioning of ^{129}I in a radioactive-waste management area [1, 2]. The purpose of this study was to investigate the behavior 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-nuclear ^{129}I concentrations in groundwater. Tritium was used to define the location, in the subsurface, of the above-ground nuclear bomb peak, while ^{2}H, ^{18}O and ^{13}C assist in characterizing the isotopic and geochemical make-up of the groundwaters.

The natural production of ^{129}I occurs *via* 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 [3]. Cosmogenic and fissiogenic production of ^{129}I contribute approximately equal amounts of ^{129}I to the hydrosphere [4]. Volcanic emissions also release fissiogenic ^{129}I produced in the Earth's interior [5]. These natural sources of ^{129}I were the only sources of the isotope in the pre-nuclear age. During that time, the ^{129}I/I ratio in the hydrosphere and biosphere varied between 5×10^{-12} and 2.5×10^{-9} [6].

Due to its longevity and its propensity to bioaccumulate in the thyroid gland of higher organisms, ^{129}I is a nuclear fuel waste radionuclide of concern to scientists, medical health officials and nuclear regulators [7]. Iodine, an essential biochemical element, has only one stable isotope, ^{127}I, and has radioisotopes ranging from ^{120}I to ^{135}I. With the

exception of [129]I, the longest-lived radioisotope of iodine ($t_{1/2} = 1.57 \times 10^7$ years), all of the radioisotopes of iodine have fairly short half-lives [3].

Since the start of nuclear weapons testing in the 1940's, the anthropogenic levels of [129]I have increased, raising the [129]I/I ratio at the surface of the Earth by several orders of magnitude [8]. Releases of [129]I from nuclear fuel reprocessing plants and from above-ground nuclear weapons testing fallout have completely overwhelmed the natural [129]I/I signal in the last 50 years [9]. According to Handl [6], the [129]I/I ratio in the biosphere increased to a peak value of 10^{-6} during the above-ground nuclear weapons testing of the late 1950's and early 1960's, but has been decreasing continuously to a value of 1×10^{-8} in the 1970's in the USA.

Moran *et al.* [10] demonstrated that 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 [10]. Nuclear power plant accidents, such as the one that occurred at Chernobyl, have released minor amounts (1–2 kg) of [129]I into the atmosphere [11]. These amounts are largely overshadowed by [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 [11].

Field site

The field site chosen to investigate the geochemical behavior of [129]I in the natural environment is located near the town of Sturgeon Falls, Ontario (46°19′ N and 79°28′ W). Sturgeon Falls is located approximately 40 km west of North Bay and roughly 400 km from Ottawa (Fig. 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 [12–16].

The site is forested, and in the spring there is frequently standing water covering a large portion of the study area. The average annual precipitation received at Sturgeon Falls is approximately 970 mm, based on the meteorological data collected by Environment Canada for North Bay from 1939–1990. According to Robertson *et al.* [13], the forested site has an annual evapotranspiration of about 500 mm/year.

Piezometers are wells used to measure groundwater pressure at discrete intervals. Bundled piezometers or piezometer nests, consist of multiple piezometers, each terminating at a discrete interval, installed to measure vertical hydraulic gradients. The piezometers selected for sampling, consisting of mostly drive-point piezometers and three bundle piezometers, are located on a small topographic ridge (∼ 220 mASL) coincident with the groundwater recharge divide (Fig. 1). Standing water was not present at the sampled nests during the sampling periods in this study.

The geology of the study site is fairly simple, consisting largely of flat-lying silts, sands and clays (Fig. 2). The hydrogeology of the area is well known [12–15]. The site
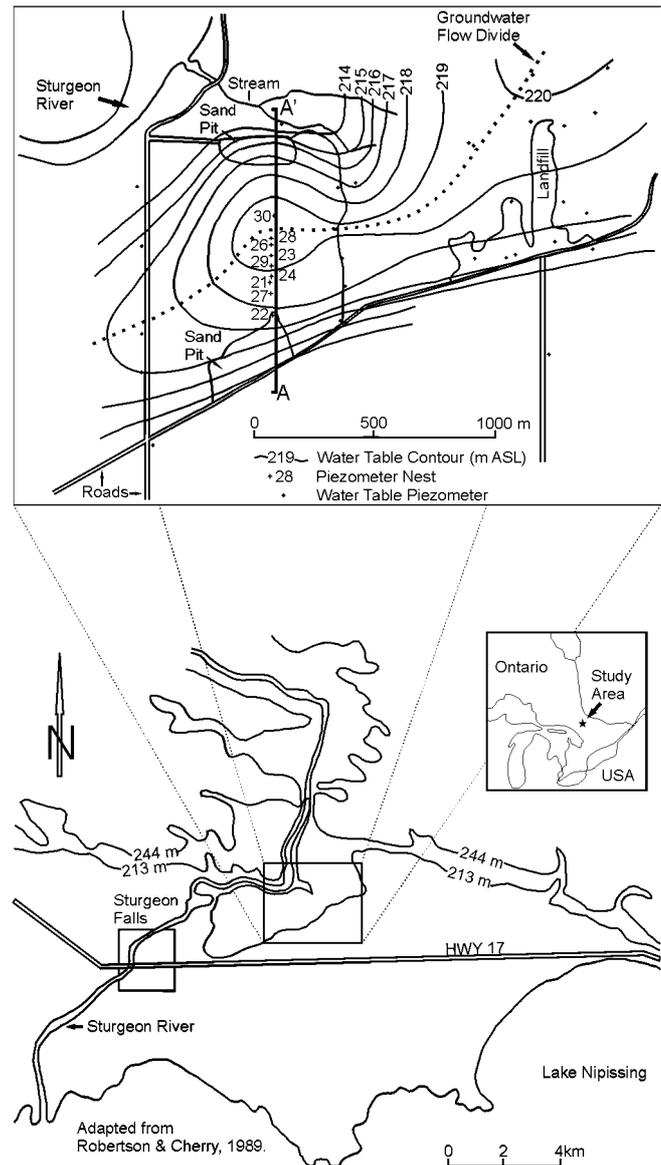

Fig. 1. Location, topography and water table configuration of Sturgeon Falls field site [12].

has two main aquifers within the surficial postglacial deltaic sediments, separated by a varved clay and silt aquitard. The upper aquifer consisted of silt and fine silty sand and is approximately 25 m thick. The downward vertical hydraulic gradient is 0.09 in the silty sands and increases to 1 in the lower varved silt and clay [14]. The lower aquifer consists of higher permeability sands and gravels, thereby serving as a basal drain for the upper aquifer [12].

Robertson and Cherry [12] conducted a detailed investigation of the aquifer properties. Twenty-eight samples of core material from three augered boreholes were measured for their sediment porosities and the hydraulic conductivities of the sediments using permeameter tests, where the core samples were recompacted close to their original density. Core samples collected from the upper 12 m of aquifer appeared structureless and were assumed to have a low degree of anisotropy. However, samples from below 12 m depth were somewhat more anisotropic due to occasional thin (1–2 mm) clay lamellae. Overall, the permeameter tests indicated that the upper 19 m of the aquifer had an arith-
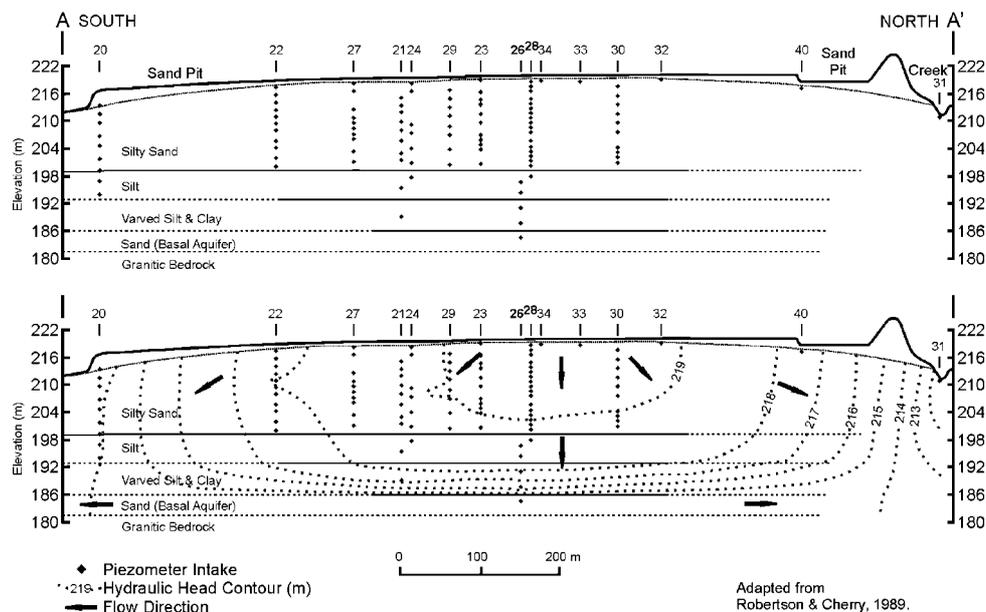
Fig. 2. Section A-A': stratigraphy & hydraulic head distribution, Aug. 8, 1986.

metic mean hydraulic conductivity of 1.8×10^{-4} cm/s. Sediments from 19 to 23 m below ground's surface have a mean hydraulic conductivity of 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.

Using a mass balance approach, Robertson and Cherry [12] estimated the bulk vertical hydraulic conductivities of sediment in the area of nest 28, based on the observed vertical hydraulic gradients, the flow velocity (0.35 m/a) indicated by the position of the mid-1960's tritium peak and a 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, between 15 and 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 [12].

Field methods

At the study site, approximately 68 drive-point piezometers were installed at seven nest locations in June 1986 [12]. Piezometer nest 28 (Fig. 1), sampled in this study, comprises 22 piezometers ranging in depth from 1 m to 21 m in the upper aquifer. An adjacent multi-level piezometer, 26-35 (Fig. 1), completed in the basal sand and gravel aquifer, was also sampled. The two piezometer nests were chosen as they are located near the center of the section A-A' (Fig. 1) and groundwater flow in that region, as determined by Robertson and Cherry [12], is vertical (Fig. 2).

A preliminary site investigation was carried out over several days in July 1999 to determine the water yields from each piezometer and to collect preliminary water samples for iodine, chemical and isotopic analyses. The water level in each well was measured using an electric water level meter. Samples were collected using a battery-operated peristaltic pump and small diameter polyethylene tubing. Prior to sampling, at least two well volumes of water were removed from each piezometer. HDPE bottles were used for all samples with the exception of those for ^{13}C and ^{14}C analysis of dissolved inorganic carbon (DIC), which were collected in amber glass bottles.

Further groundwater 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 amounts of water for ^{129}I measurements. Approximately 100 L of water was pumped from each of these piezometers and collected in collapsible plastic containers for iodine analysis. In addition, smaller volume samples from these piezometers were collected for ^{3}H analysis, as well as geochemical and stable isotopic analyses.

In June 2000, the last major field sampling program was carried out. Along with the collection of small water samples for geochemical and isotopic analysis, 300 L water samples were collected from the three piezometers for stable and radioiodine analyses. These samples were collected in collapsible plastic containers as per previous sampling campaigns.

In February 2001, a 300 L snow sample was collected from a site approximately 1 km from the piezometer nests while at distance of approximately 500 m from the highway.

Soil and organic matter samples were collected from the area around nest 28 during previous studies [16]. Portions of these samples were analyzed for iodine and ^{129}I for this study.

Analytical

Geochemical and stable isotope analyses

Accutest Laboratories in Ottawa provided the major ion geochemical analyses. Cation concentrations were deter-

mined using a Varian Liberty 220 ICP atomic emission spectrometer, while anion concentrations were determined using a Dionex DX-100 ion chromatograph (HPLC). The analytical errors associated with these procedures, as reported by Accutest Laboratories, were generally 10% at analyte concentrations that were greater than 10 times the detection limit, and 100% at concentrations less than 10 times the detection limit.

Stable isotope analyses (^{2}H, ^{18}O, ^{13}C) were performed in the G. G. Hatch Isotope Laboratories at the University of Ottawa. Hydrogen for deuterium/hydrogen isotopic analysis resulted from high temperature reduction of the sample to elemental hydrogen, H_2, using 3 μL of water in evacuated breakseals. D/H ratios in the resultant hydrogen gas were analyzed from zinc reduction with an automated double collector VG 602E mass spectrometer. The analytical precision was ±1.5 ‰ (2σ).

The δ^{18}O values of the water were determined by CO_2–water equilibration. The equilibrated CO_2 is then cryogenically extracted and analyzed on a VG SIRA-12 gas source mass spectrometer with an analytical precision of ±0.10 ‰ (2σ). The currently accepted CO_2-H_2O fractionation factor of 1.0412 was used.

The δ^{13}C values of dissolved inorganic carbon (DIC) in the waters were first measured by acidifying the water samples under vacuum to release CO_2, which was then cryogenically purified and analyzed on the VG SIRA-12 gas source mass spectrometer. Again, the analytical precision was ±0.10 ‰ (2σ).

Tritium analysis was performed at Atomic Energy of Canada Limited (AECL) – Chalk River Laboratories (CRL) by direct liquid scintillation counting (LSC – minimum detection limit = 7 Tritium Units (TU)). Samples containing less that 5 TU were sent to the Environmental Isotope Laboratory (EIL) at the University of Waterloo for enriched tritium analysis (minimum detection limit = 0.8 TU [17]).

The ^{14}C activity of DIC was measured by tandem accelerator mass spectrometry (AMS) at IsoTrace Laboratory at the University of Toronto [18], having an analytical precision ranging from 1 to 3.5 percent modern carbon (pMC).

Iodine

Concentrations of dissolved stable iodine (^{127}I) in the Sturgeon Falls waters were measured at AECL-Chalk River Laboratories. The basis of the analysis is formation of a 2-iodo-3-pentanone complex, extraction into hexane and analyzed by gas chromatography [19, 20]. Analytical error associated with this procedure is estimated to be 20%.

Given that the measured iodine concentrations of all of the samples were quite low, stable iodine was added as a carrier, in the form of a KI solution, prior to any further procedures. The addition of a carrier aided with sample handling.

Direct precipitation of the dissolved iodine in the groundwater and precipitation samples, using $AgNO_3$ [21], was not possible due to the low concentration of iodine. A column separation method using ion selective resin beads was used to collect iodine from the water samples prior to precipitating it as AgI for AMS analysis. This method was based on the method developed by Ross and Gascoyne [22] and was modified slightly to suit the Sturgeon Falls samples. The

resultant AgI precipitates were submitted to the IsoTrace Laboratory at the University of Toronto where the ^{129}I/^{127}I ratios were measured by AMS.

Soil and litter samples were combusted at 1000 °C in a stream of moist oxygen, with the released iodine collected in 0.01 M NaOH [10, 20, 23]. The iodine was then precipitated as AgI and sent to IsoTrace Laboratories where the ^{129}I/^{127}I ratios were measured by AMS. The soil and litter samples had previously been soaked in 0.5 N KOH for 12 hours, after which the KOH was decanted and the sample was dried in the oven. The purpose of the KOH was to degrade organic molecules thereby releasing iodine tightly bound to organic matter. The concentrations of iodine in these leaches ranged from 76 μg/L to 113 μg/L. The analytical errors associated with these procedures are estimated to be 20%.

Results and discussion

Groundwater flow velocity

Present-day maximum tritium concentrations of 70 TU, originating from the 1963 above-ground nuclear bomb peak were observed at 12.7 m depth in the recharge of piezometer 28-12. Below 14 m depth, pre-bomb ^{3}H levels of less than 5 TU were observed. Using the depth of the ^{3}H peak in the Sturgeon Falls groundwaters and the time that has elapsed since 1963, the peak of the above-ground nuclear weapons testing, an average downward flow velocity of 0.35 m/a is obtained, which is comparable to the groundwater flow velocities reported by Robertson and Cherry [12] and Solomon *et al.* [14]. Tritium measurements on groundwaters sampled in the autumn of 1999 and again in June 2000, indicate that the tritiated bomb peak groundwater is continuing to move downwards advectively.

The specific activity of ^{14}C of dissolved inorganic carbon (DIC) was measured on water samples collected in July 1999, to assess the vertical mobility of this tracer. Fig. 3 illustrates the ^{3}H and ^{14}C profiles in July 1999 *versus* depth. In this diagram, ^{14}C activities are expressed as Bequerels/Litre (Bq/L) water, rather than being normalized to the concentration of DIC. In doing so the effects of dead carbon (*i.e.*, ^{14}C-free carbon) dilution of ^{14}C$_{DIC}$ in the shallow (< 14 m) subsurface by enhanced carbonate weathering associated with previously recharged acidic rainfall are minimized.

On the basis of the analysis, the ^{14}C$_{DIC}$ bomb-peak is observed at a depth of 3.1 m, much shallower than the 1963 thermonuclear ^{3}H peak at 12.7 m depth. It is likely that the migration of ^{14}C$_{DIC}$ bomb-peak, downward through the groundwater system, is being retarded by equilibration reactions with organics in the near surface.

Geochemistry

Sturgeon Falls groundwaters can be hydrochemically classified as Ca-HCO$_3$ water with very low chloride concentrations (< 1 ppm – see Table 1). Sulfate concentrations in samples collected below 14 m depth are generally at or below the analytical detection limit for sulfate (3 ppm). Calcium's dominance in the groundwater is probably due to carbonate mineral dissolution, a hypothesis supported by the HCO$_3^-$

Table 1. Anion and cation concentrations and calcite saturation indices for Sturgeon Falls groundwater (July 1999). Data from all piezometers sampled are included to assess the geochemical makeup of groundwaters from upper and basal aquifers.

Piezometer	pH	Temp. (°C)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO$_4$ (mg/L)	HCO$_3$ (mg/L)	F (mg/L)	NO$_3$ (mg/L)	Br (mg/L)	NO$_2$ (mg/L)	TDS (mg/L)	log SI$_{cal}$
28-3	7.95	13.3	34.2	14.6	2.3	1.4	1.0	10.0	180	0.19	0.1	0.05	0.1	244.0	0.147
28-5	8.04	13.6	41.5	10.6	1.6	1.3	1.0	11.5	174	0.14	0.1	0.05	0.1	242.0	0.308
28-9	8.10	10.3	43.7	11.9	2.4	0.5	1.0	11.5	181	0.12	0.1	0.05	0.1	252.3	0.352
28-11	8.18	10.2	36.7	9.8	2.3	0.7	1.0	18.0	148	0.12	0.1	0.05	0.1	216.9	0.275
28-12	8.62	12.2	31.2	11.9	2.2	0.5	1.0	13.5	120	0.12	0.2	0.05	0.1	180.7	0.571
28-14	8.15	10.5	36.5	12.3	2.1	1.5	1.0	9.0	150	0.16	0.1	0.05	0.1	212.8	0.256
28-15	9.44	9.9	10.4	8.1	2.8	0.8	1.0	3.0	42	0.12	0.1	0.05	0.1	68.5	0.434
28-18	9.78	10.6	6.3	7.6	2.6	0.5	1.0	3.0	30	0.19	0.2	0.05	0.1	51.5	0.362
28-21	10.00	11.2	25.6	6.0	3.1	1.0	1.0	3.0	37	0.16	0.5	0.05	0.1	77.5	1.160
26-35[a]	7.75	10.0	29.8	7.4	3.8	1.7	1.0	3.0	131	0.25	0.1	0.05	0.1	178.2	−0.270

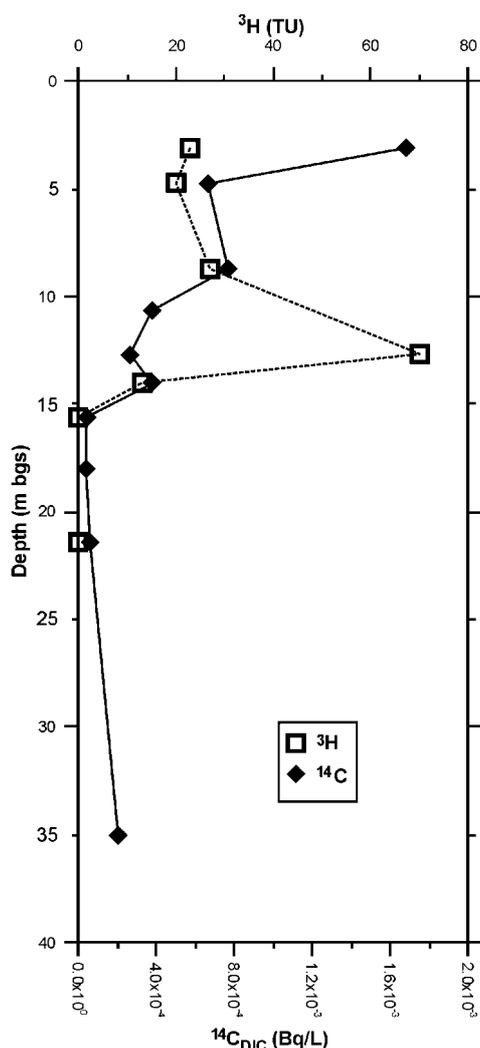Note: log SI$_{cal}$ = log(IAP/$K_{calcite}$); a: Basal Aquifer.

Fig. 3. Comparison between ^{3}H & ^{14}C$_{DIC}$ and groundwater sampling depth at Sturgeon Falls piezometers (July 1999). Radiocarbon measurements are normalized to water volume, and expressed as Bq/L.

measurements made in July 1999, where the concentrations of Ca^{2+} and HCO$_3^-$ peak above 14 m depth. Additionally, the δ^{13}C$_{DIC}$ values for groundwater at the Sturgeon Falls study site average −11.4 ‰ (VPDB), (Table 2). This value falls in the middle of the range of typical DIC contents in groundwater, indicating that approximately half of the DIC is derived from subsurface carbonate sources [24, 25]. 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. The slight acidity of the infiltrating water is due to soil CO$_2$ and the presence of H$_2$SO$_4$ from smelter SO$_2$ fallout from Sudbury [13]. This acidity is buffered before reaching deeper piezometers (> 14 m depth) by the dissolution of carbonate minerals and below about 14 m, sulfate reduction occurs. Robertson *et al.* [13] cite δ^{34}S evidence, which shows a strong enrichment at low SO$_4$ concentrations, typical of sulfate reduction environments. The low bicarbonate concentrations in the groundwater of the upper aquifer below 14 m depth are likely due to sequestering by calcite (CaCO$_2$) precipitation. The saturation index for CaCO$_2$ shows that the groundwater below 14 m depth (in the upper aquifer) is oversaturated with CaCO$_2$. The rise in pH in these waters is likely due to sulfate reduction, an alkaline reaction [25].

Groundwater sampled from the basal aquifer (from piezometer 26-35) does not follow the trend for the overlying groundwaters, as it has a greater Ca-HCO$_3$ component, slightly greater sodium content and a much lower pH (Table 1). It is also undersaturated with respect to calcite. These differences distinguish this basal aquifer groundwater from the shallow groundwaters, and are consistent with the tritium data (Table 2), which shows it to be older.

Iodine-129 in groundwater

The Sturgeon Falls groundwater samples we collected generally have sub-ppb levels of dissolved stable iodine, between 0.07 ppb to 1.7 ppb (Table 3). The snow sample 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 3). The concentration of stable iodine in the Sturgeon Falls groundwaters are very similar to those measured in surface waters across North America [26], however the levels of ^{129}I are at least an order of magnitude lower than those measured elsewhere (Fig. 4). The levels of radioiodine in background sites at Sturgeon Falls and elsewhere in North America are at least 3 orders of magnitude lower than ^{129}I in surface and groundwaters around nuclear facilities (Fig. 4).

Table 2. Summary of stable and radioisotope data for Sturgeon Falls groundwater.

Piezometer	Date	δ^2H_{VSMOW} (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{13}C_{VPDB}$ (‰)	^{14}C (pMC)	^3H (TU)
28-3	Jul-99	–	–	−15.5	68.3	23
	Sep-99	–	–	–	–	29
28-5	Jul-99	–	–	−13.1	60.5	20
28-9	Jul-99	−73.57	−11.06	−14.1	63.6	27
	Sep-99	−78.37	−11.02	–	–	–
	Jun-00	−73.34	−11.07	–	–	29
28-11	Jul-99	–	–	−13.1	50.5	–
28-12	Jul-99	–	–	−9.9	50.2	70
	Sep-99	–	–	–	–	72
28-14	Jul-99	−71.84	−10.63	−14.0	51.9	13
	Jun-00	−73.27	−10.86	–	–	27
28-15	Jul-99	–	–	−0.6	53.0	BMDL
	Sep-99	–	–	–	–	1
28-18	Jul-99	–	–	−9.2	65.1	–
28-21	Jul-99	–	–	−14.0	59.1	BMDL
	Sep-99	–	–	–	–	–
26-35	Jul-99	−77.80	−11.58	−10.9	41.0	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).

Table 3. Summary of Sturgeon Falls iodine isotopic ratios. The ^{129}I concentration was calculated using the measured $^{129}I/^{127}I$ ratio, correcting for laboratory and procedural background and dilution (due to the addition of stable iodine as a carrier).

Sample	Dissolved Stable I (ppm)	Dissolved Stable I (mg)	Stable I Carrier (mg)	Total Stable I (mg)	Measured $^{129}I/^{127}I$ Ratio	Background & Dilution Corrected Ratio	^{129}I (10^6 atoms/L)
28-9 (Oct. '99)	0.0017	0.170	1.929	2.099	7.32×10^{-12}	1.85×10^{-11}	0.15[a] (±7.7%)
28-9 (Jun. '00)	0.00067	0.201	6.710	6.911	2.31×10^{-11}	6.04×10^{-10}	1.89 (±3.5%)
28-14 (Jun. '00)	0.00007	0.021	7.012	7.033	2.32×10^{-11}	5.93×10^{-9}	1.94 (±11.2%)
26-35 (Oct. '99)	0.0004	0.040	2.242	2.282	9.61×10^{-12}	2.16×10^{-10}	0.40 (±9.7%)
26-35 (Jun. '00)	0.00015	0.042	6.242	6.284	7.33×10^{-12}	2.75×10^{-10}	0.19 (±5.3%)
Sturgeon Falls Snow	0.0002	0.016	2.074	2.090	7.06×10^{-10}	9.15×10^{-8}	85.44 (±2.1%)
S.F. Site 1 & 2 Litter Top	4.728	0.2644	2.290	2.554	2.22×10^{-9}	2.15×10^{-8}	473.55[b] (±2.2%)
S.F. Site 1 Litter Bottom	3.903	0.6715	2.062	2.734	7.58×10^{-10}	3.08×10^{-9}	56.21[b] (±2.3%)

a: This sample had an erroneous yield of 360%;
b: 10^6 atoms/g.
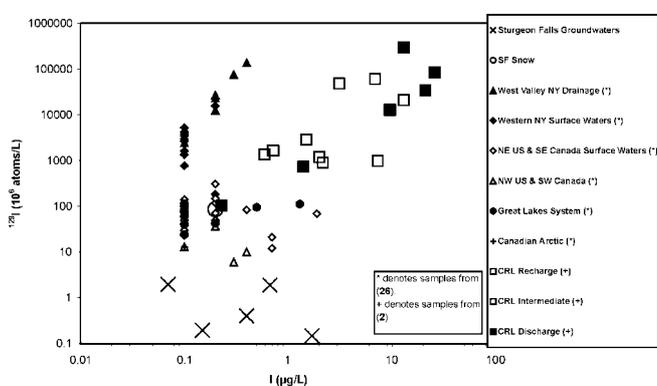
Fig. 4. Comparison of ^{129}I and stable iodine concentrations in surface waters, groundwaters and precipitation from Sturgeon Falls and elsewhere.

Based on the calculated flow velocity of 0.35 m/a (using the location of the 1963 ^3H peak), groundwaters sampled from 28-14 likely recharged around 1960. As this predates nuclear fuel reprocessing activities, the levels of ^{129}I found in 28-14 can likely be attributed to radioiodine from earlier above-ground nuclear weapons tests. However, the groundwater at 28-9 likely recharged around 1975 and as such, may have contributions of ^{129}I from both above-ground nuclear weapons testing and nuclear fuel reprocessing. In contrast, ^{129}I levels in piezometer 26-35 should reflect pre-nuclear weapons radioiodine levels. These processes are largely observed at Sturgeon Falls as trends of decreasing ^{129}I and ^3H concentrations with increasing depth (Fig. 5).

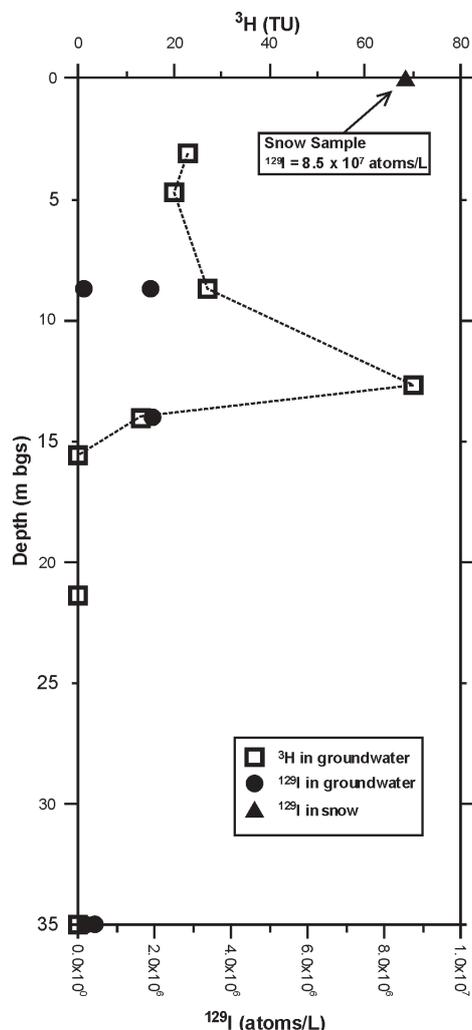Tritium-depleted groundwaters from 26-35 have ^{129}I concentrations (10^5 atoms/L) that are higher than previous

Fig. 5. Concentrations of ^{129}I and ^{3}H in Sturgeon Falls groundwaters sampled in July 1999, October 1999 and June 2000 (data in Tables 2 & 3). Tritium is used as a tracer for the location of the 1963 above-ground nuclear bomb peak.
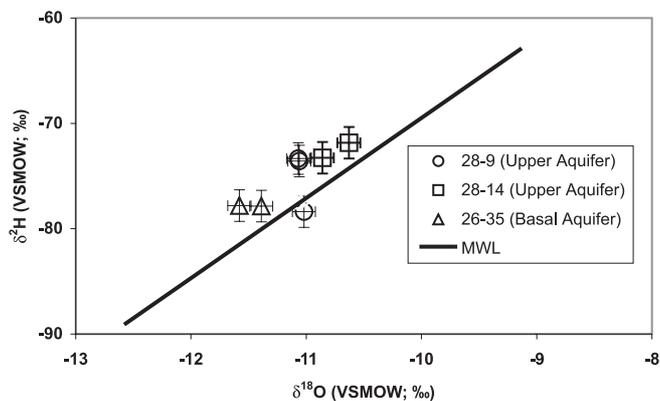

Fig. 6. Stable isotopic composition of groundwaters sampled at Sturgeon Falls from three separate piezometers between July 1999 and June 2000 (data in Table 2). MWL represents the local meteoric water established for Ottawa (δ^2H $= 7.6\,\delta^{18}$O $+ 6.5$ [24]). The analytical precisions for δ^2H & δ^{18}O are 1.5% & 0.1%, respectively. Reference used for isotope ratios: VSMOW (Vienna Standard Mean Ocean Water).

estimates of 10^3 to 10^4 atoms/L for pre-nuclear weapons groundwaters [2, 26]. As this piezometer is located in the basal aquifer, which overlies the granitic basement rocks of the Precambrian Shield, it is likely that ^{129}I from spontaneous fission of ^{238}U is being leached from the granites through water-rock interactions. Previous studies have demonstrated that brackish to saline waters in granites can have ^{129}I concentrations between 2×10^6 and 3.4×10^8 atoms/L [3, 27]. Therefore, only a slight fissiogenic contribution from bedrock could provide the excess ^{129}I observed in these pre-nuclear weapons testing waters. Stable isotope data for groundwater samples collected from 26-35 indicate that the basal aquifer groundwater has a different origin than the groundwater in the upper aquifer. δ^{18}O and δ^2H contents are more depleted in the deep groundwater (Fig. 6), indicating a more regional origin, at higher elevation and possibly residual meltwater remaining in the subsurface since the late Pleistocene [25].

Precipitation, represented in a single snow core collected February 2001, has a much higher ^{129}I concentration (8.5×10^7 atoms/L) than the Sturgeon Falls groundwaters, which have recharged over the last 40 years (1.5×10^5 to 1.9×10^6 atoms/L). The levels of ^{129}I in Sturgeon Falls

snow are comparable to that in precipitation samples in the Rochester, New York area (3×10^7 to 1.3×10^8 atoms ^{129}I/L [26]). If the levels of ^{129}I in the Sturgeon Falls snow sample and in precipitation from Upper New York State are representative of the ambient levels of ^{129}I in precipitation over central Canada, then the much lower ^{129}I levels measured in groundwater samples must be due to attenuation of iodine during infiltration. One problem with this premise is that the concentrations of the dissolved stable iodine in the Sturgeon Falls groundwaters fall within the same range as the local snow sample and more regional surface waters [26]; although the most likely explanation is that the sources for the dissolved stable iodine and ^{129}I are not the same. Here it is proposed that stable iodine is being recycled through the biosphere and hydrosphere on a long-term basis while modern ^{129}I from atmospheric sources follows a different cycle that has not yet resulted in equilibrium between the surface soil and groundwater reservoir.

Iodine-129 in soil

The ^{129}I concentrations in soil samples collected near piezometer nest 28 and within 30 cm of the surface range from 5.6×10^7 atoms/g in the lowermost soil to 4.3×10^8 atoms/g in the upper litter layer. These values fall within the lower range of values for soil cores taken in Western New York state [26]. Those authors also found that the upper layers of their cores had ^{129}I concentrations at least an order of magnitude greater than the lower layers and did not correlate with the concentrations of stable iodine. For example, three soil samples (depths 0–8 cm, 8–20 cm and 20–30 cm) from site S-6 in West Valley, New York, had stable iodine concentrations of 0.67 ppm, 0.80 ppm and 0.99 ppm, respectively, and ^{129}I concentrations of 1.9×10^{10} atoms/g, 1.4×10^{10} atoms/g and 3.2×10^9 atoms/g, respectively. Based on this, they concluded that ^{129}I and stable iodine are not in isotopic and chemical equilibrium. This is also thought to be the case for stable iodine and ^{129}I at Sturgeon Falls. Further evidence for geochemical disequilibrium of iodine in the environment was documented in a study on the behavior of iodine

in a shallow aquifer (and associated wetland) near a low-level, radioactive waste management area [10, 11]. Here, batch leach tests indicated differences between stable iodine and [129]I with respect to how each nuclide was bound to sediment. Overall it was demonstrated that stable iodine was more tightly bound to organic matter than [129]I and radioiodine appeared to be adsorbed onto the surfaces of iron and manganese oxyhydroxides. These differences were also attributed to the length of time over which iodine was considered to be resident in the hydrologic-geologic system, with stable iodine associated with the initial formation of the sandy aquifer and wetlands during the latest Holocene deglaciation and [129]I being largely introduced over the length of time the waste management area has be in operation, approximately 30 years.

Anions such as iodine are necessary elements in plant physiology on a long-term basis and, like chloride, may be recycled through the biosphere [16]. Conversely, dissolved anions such as iodide (and [129]I) are thought to be largely conservative (non-reactive) in recharge waters and may not necessarily be incorporated in plants *via* root transpiration over the short term (*i.e.*, single uptake). Alvarado Quiroz [10] demonstrated that iodine uptake *via* the stomata was of greater significance than the uptake of iodine *via* the roots. Assuming that the sources for [129]I in the plants is largely gaseous methylated iodide for stomata and dissolved iodide for roots, at Sturgeon Falls, [129]I concentrations ranging from 4.2×10^6 atoms/g in cedar leaves to 7.5×10^7 atoms/g in grasses, would suggest the opposite, although detailed evaluations are required. Overall, at Sturgeon Falls the potential uptake of [129]I by plants and adsorption onto soil sediments and organic matter is considered to be the likely cause for attenuation of [129]I in the shallow soil-biologic interface whereby iodine in the groundwater is attenuated during recharge and infiltration through the soil zone, which serves to decrease its observed levels relative to local precipitation and regional surface waters.

Conclusions

At Sturgeon Falls, groundwaters within the basal aquifer contain negligible amounts (< 1.5 TU) of tritium and are geochemically and isotopically distinct from overlying shallow groundwaters, indicating they are part of a separate and more regional groundwater system. Within these lowermost groundwaters, [129]I concentrations range from 2×10^5 to 4×10^5 atoms/L and are 1 to 2 orders of magnitude greater than published estimates of 10^3 to 10^4 atoms/L [5]. Here it is considered that these basal aquifer groundwaters contain a minor contribution of fissiogenic [129]I, which has been leached from the underlying granitic bedrocks.

The tritium profile in the Sturgeon Falls groundwaters clearly defines the above-ground nuclear bomb peak at 12.7 m below ground's surface (bgs), with tritium concentrations near 70 TU. This is considered to be groundwater that recharged during the peak (1963) of the above-ground nuclear weapons testing and establishes a groundwater flow velocity of 0.35 m/a. Iodine-129 found at this depth can

likely be attributed to the above-ground nuclear weapons tests, nuclear fuel reprocessing activities post-date 1963. The groundwater collected from piezometer 28-14 (14 m bgs) has an [129]I concentration of 1.94×10^6 atoms/L, considerably greater than pre-above-ground nuclear weapons levels [5]. 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 the above-ground nuclear weapons testing and nuclear fuel reprocessing activities. The [129]I concentrations at 28-9 and 28-14 are considerably lower than in precipitation and in regional surface waters [26].

The dissolved stable iodine concentrations in Sturgeon Falls groundwaters do not correlate with [129]I, indicating that no equilibrium exists. Stable iodine is likely recycled in the biosphere on a long-term basis, while the modern [129]I is from anthropogenic sources. This finding supports earlier work on the subject [26].

The concentrations of [129]I in shallow soil and upper organic litter layer (5.6×10^7 and 4.7×10^8 atoms/g) demonstrate that [129]I 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.

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