PAPER

Tritium across the hydrologic systems of southern Ontario, Canada: implications for groundwater age dating in the Great Lakes Basin

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Abstract

Modern, ambient tritium concentrations in precipitation are lower and more temporally consistent now that they have recovered from the historic thermonuclear bomb peak of the mid-1960s. With the bomb peak no longer the overriding influence on atmospheric tritium concentrations, anthropogenic point sources, such as nuclear-generating stations (NGS), have the largest influence, though the extent and temporal variability of this influence remains uncharacterized. The lack of precipitation monitoring locations means that spatial trends in tritium concentrations in precipitation are unknown. To address this data gap, tritium concentrations in shallow modern groundwater are interpolated throughout southern Ontario (Canada), at the center of the Great Lakes Basin, and the interpolation is tested as a precipitation proxy with a statistical comparison that shows good agreement between the shallow groundwater and precipitation datasets. The shallow groundwater tritium interpolation is used to delineate the extent of NGS influence as representing 66% of the study area. Recharge timings in the subcropping bedrock aquifers of the study area are interpreted qualitatively in areas outside of NGS influence to be primarily a mix of pre-bomb and modern recharge, with no indication of peak recharge levels remaining. The influence of drift thickness on the proportion of tritium-dead versus tritium-live samples is observed spatially and confirmed by comparing data distributions. The oldest waters (pre-1953) tend to occur in subcropping bedrock aquifers underlying the thickest sediment packages.

Keywords Radioactive isotopes · Groundwater age · Isotopes · Environmental tracers · Canada

Introduction

Today, tritium in precipitation originates naturally from cosmic radiation bombardment of nitrogen in the atmosphere, as well as through anthropogenic inputs from nuclear-generating stations (NGS). Historically, the greatest and overriding source of tritium in the environment was from atmospheric tests of thermonuclear weapons in the 1950s and early 1960s. The 1963 thermonuclear tritium peak in precipitation was a key hydrogeological time marker that was used to roughly estimate groundwater age, or recharge timing, by comparing groundwater concentrations against the precipitation record (Anderson and Sevel 1974; Dincer et al. 1974; Fritz et al. 1991; Roberston and Cherry 1989; Michel et al 1984). Because the tritium peak was ubiquitous across the Northern Hemisphere, it provided a reliable time marker for groundwater age dating regardless of location. Today, the loss of thermonuclear weapons fallout results in lower ambient background tritium concentrations with localized anthropogenic contributions from point source emitters such as nuclear power generating stations. Although tritium concentrations across biota and the hydrolological cycle are often well characterized at NGS sites globally (Janovics et al. 2014; Köllő et al. 2011), characterization is rarely extended to areas where tritium levels fall below regulatory background levels. However, extending such characterization offers insight into the controls on tritium distribution and the transport information needed to predict fluxes and

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fate (Ducros et al. 2018). Now that large-scale, thermonuclear testing inputs are no longer a controlling factor, the main influence on tritium concentrations in precipitation in areas outside of NGS influence is seasonal, related to the origin of the water vapour source, and more locally, weather and storm patterns (Michel et al. 2018; van Rooyen et al. 2021). Tritium levels in precipitation in areas unaffected by nuclear power operations in the Northern Hemisphere have been approaching natural, or "background" levels since the early 2000s (Eastoe et al. 2012), which is ~4–8 TU for central north America (Thatcher 1962; Kaufman and Libby 1954), ~1.2–5.6 TU in coastal California (Harms et al. 2016). Contemporary tritium concentrations in precipitation have recently been estimated to range from 9 to 14 TU in the Laurentian Great Lakes area, predicted from a recent regression model based on environmental and geospatial covariates (Wassmuth et al. 2022). To facilitate recharge timing estimates using tritium in the present day, post-thermonuclear tritium peak era, the spatial variability and temporal trends of tritium in precipitation must be known.

Southern Ontario is located at the centre of the Laurentian Great Lakes Basin, bordering lakes Huron, Erie and Ontario,

forming the 95,000-km^2 study area of this investigation (Fig. 1). Current tritium levels across southern Ontario's hydrologic cycle are influenced by point sources comprising NGS and research sites clustered at three general locations, though the spatial extent of their influence is not well known (Fig. 1). Tritium monitoring in precipitation is restricted to three short-term clustered monitoring areas near NGSs and research sites (1988–2012 and 1988 to present), and a single long-term monitoring site (1953 to present) in Ottawa, Ontario, which is outside of the assumed major influence of present-day nuclear activity (Fig. 1). Long-term tritium monitoring in Ottawa precipitation has been conducted since 1953 as part of the International Atomic Energy Agency, Global Network of Isotopes in Precipitation (GNIP) program (IAEA 2021). Precipitation monitoring at four general locations offers a spatial density of one monitoring station per 24,000 km^2, a dearth of coverage given that the extent of impacts from point sources is unknown.

In this investigation, spatial trends in recent tritium concentrations are interpreted across the hydrologic systems of the study area by integrating recent (2017–2019) data for precipitation at four general locations, surface-water data
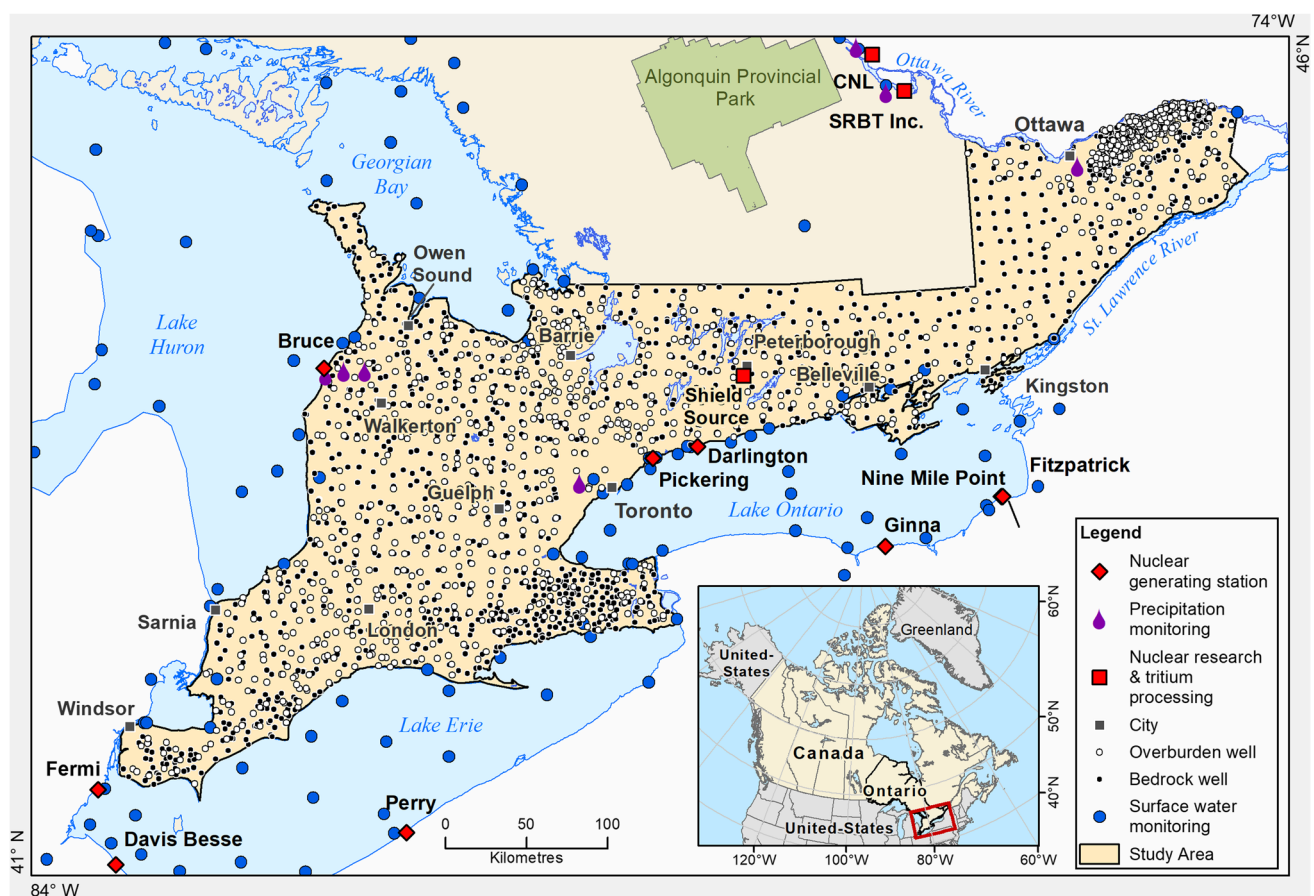

Fig. 1 Study area with nuclear operations in Canada and the United States. Sampling locations are shown for bedrock and overburden wells (Hamilton 2021), stations in the Great Lakes (Dove et al. 2021), tributaries and precipitation (IAEA 2021; Bruce Power 2019)

from 153 locations and groundwater data from 2,516 locations. The recent precipitation data are from the Bruce NGS (Bruce Power 2018, 2019, 2020), from Health Canada monitoring near Toronto (J-F. Mercier, Health Canada, unpublished data, Canadian Radiological Monitoring Network, 2020), from research and industrial sites at or near Canada Nuclear Laboratories (this paper) and the Ottawa GNIP station (IAEA 2021). The surface-water dataset comprises Great Lakes data from Dove et al. (2021), tributary monitoring data from Bruce NGS (Bruce Power 2018, 2019, 2020), Ontario Power Generation (2018, 2019, 2020) and Canadian Nuclear Laboratories (this paper). Tritium concentrations in groundwater at 2516 locations are from Hamilton (2021). Assessing recent spatial trends across the study area, within all components of the hydrologic cycle, enables the delineation of areas influenced by possible point sources such as NGSs, research and tritium processing activities, which are interpreted here within the context of wind and weather patterns. Following this, temporal trends are assessed for each hydrologic system component where data records permit.

The baseline work of this investigation is the characterization of spatial and temporal tritium trends across the hydrologic cycle, an assessment of the suitability of using shallow groundwater as a proxy for precipitation, and the delineation of areas of NGS influence. Following this, the shallow groundwater interpolation is used to inform qualitative estimates of recharge timing in the deeper, subcropping bedrock aquifers of the study area. To investigate the suitability of using shallow groundwater tritium data as a proxy for precipitation, the statistical distributions of the shallow groundwater and precipitation datasets are compared. National surveys by Brown (1970, 1971), and later Gibson et al. (2020), demonstrate that hydrogen isotopes in large Canadian surface waters broadly reflect trends observed in annual precipitation. Thus, where tritium concentrations in shallow groundwater resemble those in annually averaged precipitation and surface water, it is reasonable to use shallow groundwater as a proxy for either.

Study area

The 95,000-km^2 study area is located within the Great Lakes basin, bound in the south by Lake Ontario, Lake Erie and the St. Lawrence River, in the east by the Quebec border, in the north by the Ottawa River, Algonquin Provincial Park and Georgian Bay and in the west by Lake Huron (Fig. 1). Roughly 30% of Ontario residents rely on groundwater, with ~1.3 million people using private domestic wells and 1.9 million relying on centralized municipal groundwater supplies (Sharpe et al. 2013).

The subcropping bedrock geology of southern Ontario is composed of Paleozoic sedimentary rocks that are

Cambrian-age in the east to Devonian-age in the west (Armstrong and Carter 2010). A small portion of the subcropping bedrock is Precambrian, Canadian Shield rock, at the northern study area boundary just south of Algonquin Park. Southern Ontario has a complex glacial history that has shaped the modern landscape. During much of the last 2.6 Ma Quaternary period, the entire province of Ontario was covered by continental ice sheets many times, with the last glaciation ending in southern Ontario by the beginning of the Holocene Epoch at ~10 ka (Barnett 1992). The advance and retreat of glaciers has resulted in the deposition of sediments that are more than 250 m in places (Gao et al. 2007) with a complex range of physiography and permeability that influences the geometry of groundwater flow systems (Sharpe et al. 2013). The climate of the study area is very much moderated by the surrounding Great Lakes, with the greatest annual average precipitation observed leeward of the lakes. Historic annual average precipitation values range from 750–1,100 mm/year (Environment Canada 2021a, b).

The nuclear industry in Ontario started in 1952 with the opening of Atomic Energy of Canada Limited (now Canadian Nuclear Laboratories), located on the Ottawa River, west of Ottawa, with research and development leading to the CANDU power generating technology (CNL 2021). CANDU reactors have been in operation at NGS in Kincardine (Bruce), Pickering and Darlington since 1971, 1971 and 1982, respectively (Ontario Power Generation 2020). CANDU reactors use heavy water for cooling, and they release more tritium into the environment than those that rely on light water for cooling. As a result, the light-water reactors employed in the United States represent smaller point sources of tritium in the environment compared to the Canadian CANDU reactors.

Methodology

Tritium analysis was conducted by liquid scintillation counting, with several datasets analyzed after undergoing electrolytic enrichment to lower detection limits and improve analytical precision. The enrichment process is initiated with salt removal by ion exchange columns, followed by electrolytic reduction and then the tritium-enriched residual is counted for a set period (R. Drimmie, Isotope Tracer Technologies Ltd. (Canada), 'Analysis of tritium in water, Technical Procedure TP 11.0 Rev.02', unpublished report, 2012). In this investigation, the analytical detection limits for samples that have undergone electrolytic enrichment range from 0.8 to 0.1 TU and those that have not undergone electrolytic enrichment range from 6 to 20 TU. For all datasets, the decision to perform electrolytic enrichment was made based on desired detection limits and expected data range, with higher detection limits suitable for areas influenced by

nuclear power generation and research, where tritium concentrations are higher, and lower detection limits needed in areas outside of presumed nuclear influence. For samples analyzed after electrolytic enrichment, samples with concentrations below detection were assigned a tritium concentration of zero, whereas for samples analyzed using the direct method with results below detection, the tritium concentration was assumed to be half of the detection limit. Precision is estimated from the median σ values reported with the analyses. For datasets where precision was not reported, it is assumed to equal the analytical detection limit.

Interpolating tritium in shallow groundwater

The 2,516 stations sampled by Hamilton (2021) from 2007–2018 represent several well types and a range of depths. To establish a subset of data representing shallow modern conditions that would be suitable for use in the tritium interpolation, a well selection process was established (Priebe and Hamilton 2022). The tritium data were first divided into categories based on well type, well depth and aquifer type (Table 2). For bedrock wells, total well depth and overburden thickness were considered in the selection process. Bored wells and sandpoints are well construction types often associated with poor annular well seals, which means these wells can be recharged relatively quickly with precipitation compared to drilled wells (Ontario 2015). Because of this difference, bored wells and sandpoints were

considered independently of drilled wells. Once the data for each category (Table 2) were sorted, cumulative probability plots of tritium concentrations were plotted (Fig. 2).

The tritium data for each category are shown on the cumulative probability plots (Fig. 2). Lines of best fit are shown rather than individual data points for ease of dataset comparison. Cumulative probability plots showing complete datasets, rather than lines of best fit, are provided in Figures S1–S6 in the electronic supplementary material (ESM) (). Two horizontal markers are shown at key tritium concentrations for context; at 15 TU, which is the Ottawa GNIP median tritium value since relative temporal stabilization in 2003 (IAEA 2021), and at 8.6 TU, which is the 10-year piston flow decay from the Ottawa GNIP median value. This two-point criterion for dataset selection ensures that selected data represent the most recently recharge groundwater, and that the distributions are similar in slope. The criteria are broad enough to honour the spatial variability in tritium from point sources, as well as the variability in hydrogeological settings across the large study area. This data selection approach is intended to result in an initial dataset that is later improved in the interpolation process. An initial subset of data representing modern local recharge conditions (Fig. 2b) was selected from the entire groundwater dataset (Fig. 2a) by excluding well categories with a <50% probability of encountering tritium levels ≥15 TU and/or an 80% probability of encountering tritium concentrations ≥8.6 TU. The probability of encountering higher tritium
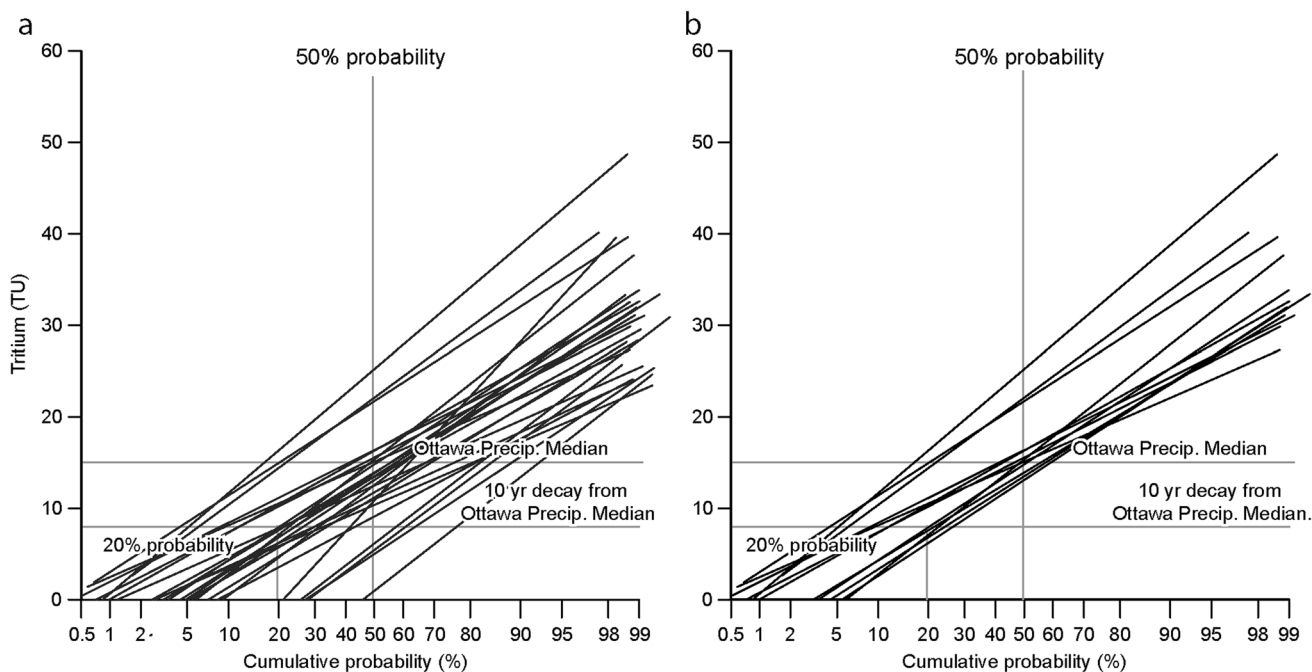

Fig. 2 **a** Probability distributions for all well categories of the groundwater dataset of Hamilton (2021). **b** Probability distributions of tritium concentrations for the well categories selected to represent the most modern local recharge conditions

concentrations decreases with increasing well depth and overburden thickness. Of the 2,516 samples in the dataset, 630 met the criteria for inclusion in the tritium interpolation; henceforth, referred to as the *shallow groundwater dataset.*

Empirical Bayesian Kriging (EBK) was selected as the method for interpreting tritium concentrations from the shallow groundwater dataset. A spatial assessment of tritium concentrations across the study area shows that the data are nonstationary (Priebe and Hamilton 2022) and likely not well represented by a single semivariogram common to standard kriging methods. Rather than relying on a single semivariogram, EBK relies on the best fit of a spectrum of semivariograms that are calculated for overlapping data subsets across the model domain (Krivoruchko 2011; Samsonova et al. 2017). This approach improves the quality of the interpolation for areas with clusters of high tritium.

Because the method of establishing the initial shallow groundwater dataset did not guarantee the exclusion of samples unrepresentative of local recharge conditions, the interpolation was generated and iteratively improved until no further improvement in model statistics (mean error, standardized root mean square and coefficient of determination between measured versus predicted) could be achieved. This process comprised removing samples with the largest relative differences between measured and predicted tritium concentrations, which was observed to have occurred where the measured value was very low compared to the predicted surface. The greatest relative difference was 2.5 times, and these samples were removed first, followed by those with less of a relative difference. Every datapoint removed was investigated for evidence of local groundwater upwelling, resulting in the removal of 59 samples.

The 59 removed samples had either physical evidence of being located at the end of long groundwater flow paths, or chemical evidence including chloride-bromide ratios suggestive of either deep brine (Cl/Br <150) or seawater influence (Cl/Br 350). Samples removed in eastern Ontario, were determined to be influenced by sediments of the Pleistocene Champlain Sea (Lemieux et al 2018). In central Ontario, the samples removed were determined to represent discharge locations at the end of long groundwater flowpaths within the lowlands of the buried Laurentian Valley where the wells are primarily flowing artesian (Priebe et al. 2018). Brine-impacted samples were also removed on the Niagara Peninsula, located between Lakes Ontario and Erie, an area where shallow groundwater is known to be impacted by upwelling fluids related to abandoned oil and gas wells (Smal 2017).

Cross-validation of the final EBK model yields a mean error, which is the average difference between measured and predicted values, of –0.18 indicating the model slightly underpredicts the tritium concentrations. The standardized root mean square is 0.96, indicating that the variability is slightly overestimated in the model and a coefficient of determination (R^2 value) of 0.6 between predicted versus measured tritium concentrations (Priebe and Hamilton 2022). These cross-validation statistics indicate an absence of systemic prediction bias and an acceptable estimation of variability in predictions. Spatially, the magnitude of the prediction error, which ranges from 0 to 20 TU, is greatest in areas where tritium concentrations are highest or where sample density is poor (Priebe and Hamilton 2022).

Results and discussion

Spatial tritium trends

Spatial trends in tritium concentrations are first assessed for shallow groundwater, and then across the entire hydrological cycle using the most recent data available for surface water, groundwater, precipitation, and the Great Lakes. Tritium values for Great Lakes (Dove et al. 2021) and tributaries are from samples collected between 2017 and 2019. Precipitation data from 2017 to 2019 are averaged for this interpolation. To achieve the spatial coverage needed for the assessment, the shallow groundwater dataset covers a much longer data collection period from 2007–2018. Recent data from a short time period (2017–2019), with the exception of groundwater data, are used to reduce the likelihood of temporal changes influencing the spatial assessment.

Spatial tritium trends in shallow groundwater

For context, tritium concentrations in shallow groundwater (Fig. 3), are compared with background concentrations of tritium in precipitation from the high spatial resolution tritium prediction of Wassmuth et al. (2022). Establishing threshold values representing background tritium concentrations is challenging because the interaction of natural and anthropogenic tritium sources within and among the hydrologic systems under investigation is not well understood across the study area. Wassmuth et al. (2022) have created a high spatial resolution map predicting contemporary (2008–2018) tritium concentrations in precipitation using a regression model based on environmental and geospatial covariables such as temperature, latitude, longitude, altitude, land mass fraction, distance to coast, and climate. Their model validation determined that predictions matched measured values within a narrow range of ±20%. Based on the predictive mapping of Wassmuth et al. (2022), background tritium concentrations within the present study area should range from 9 to 14 TU. By subtracting the background interpolation of tritium in precipitation of Wassmuth et al (2022) from the interpolation of tritium in shallow groundwater developed here (Fig. 3), the areas of anthropogenic influence can be easily identified (Fig. 4). Shallow groundwater
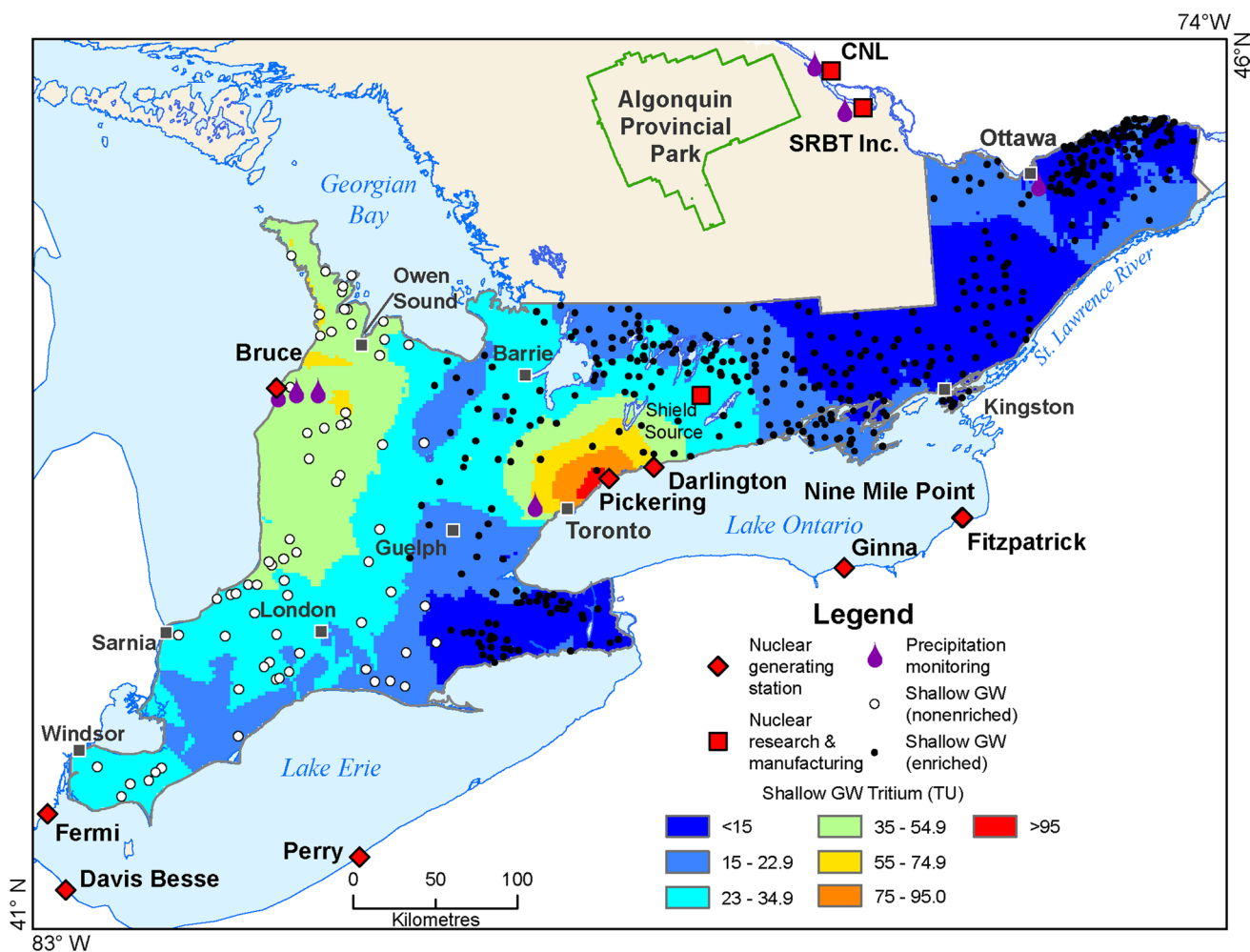
Fig. 3 Wind rose diagrams and nuclear plant locations, including power generating stations and other nuclear sites for tritium reprocessing, nuclear research, etc., overlain on the interpolated shallow groundwater tritium concentrations

tritium is considered to be greater than background when values are 6 TU or more than background levels (Fig. 4), with this threshold selected to reflect higher detection limits and poorer precision of samples analyzed without prior enrichment (Table 1).

Tritium concentrations are highest in shallow groundwater in the vicinity of NGSs Pickering and Darlington on the north shore of Lake Ontario, and at the Bruce NGS on the eastern shore of Lake Huron (Fig. 3). The area of NGS influence on the north shore of Lake Ontario at Pickering and Darlington is associated with concentrations ranging from 35 to 103 TU (Fig. 3), with the area in exceedance of background tritium concentrations extending 125 km to the east and 50 km to the west (Fig. 4). The northern extent of the Pickering and Darlington NGSs influence reaches the study area boundary, and cannot be distinguished from the influence of Bruce NGS (Fig. 4). The extent of NGS influence on shallow groundwater near the Pickering and Darlington NGSs is likely controlled by wind patterns

distributing emissions via precipitation. Wind speed and direction data for the past 30 years show that in the Toronto area, wind direction is disproportionally (33% of the time) from the northwest (Environment Canada 2021a). The relatively small spatial extent of westward impacts to shallow groundwater may be because the winds predominantly move emissions toward the lake (Fig. 3b).

Near the Bruce NGS, tritium concentrations in shallow groundwater are above background to the southwest study area boundary, extending ~100 km to the north beyond the land margin, and becoming indistinguishable from the Pickering and Darlington NGS influence to the east and southeast (Fig. 4). The extent of influence of the Bruce NGS on shallow groundwater is larger than that observed surrounding the Pickering and Darlington NGSs. Wind direction in the south Bruce area, in the past 30 years, is predominately from the west (Fig. 3c; Environment Canada 2021a), with about 5 and 6% coming from the north and south, respectively, and less than 25% coming from an easterly direction. Assuming that
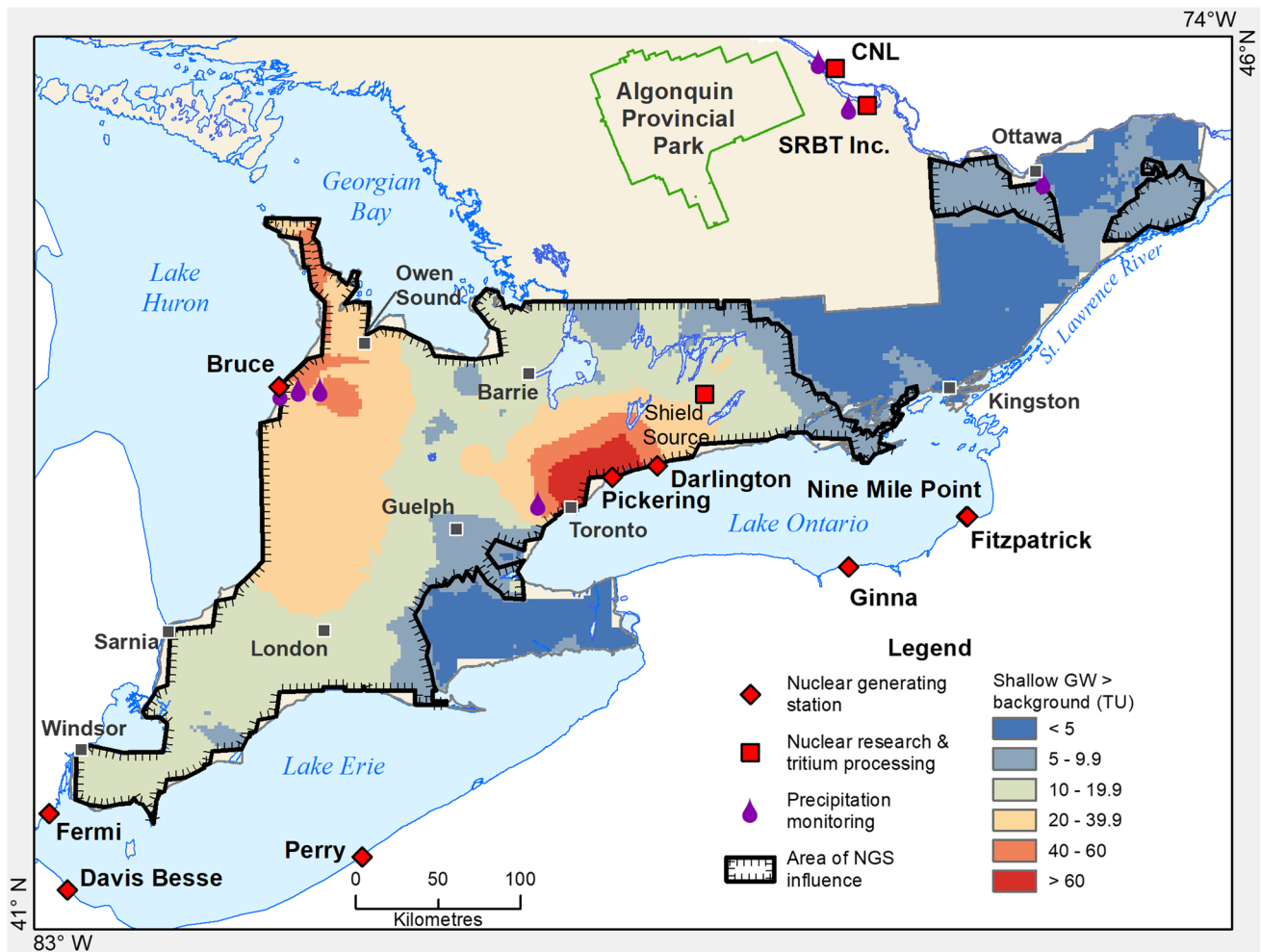
Fig. 4 Difference between the shallow groundwater interpolation (Fig. 3) and the interpolation of contemporary tritium in precipitation by Wassmuth et al. (2022)

emissions are delivered as precipitation by wind, the extent of impacts to shallow groundwater would be highest in the downwind direction towards the east and not as observed in a S–SSE direction from the Bruce NGS. The tritium samples used to develop the shallow groundwater interpolation in the vicinity of the Bruce NGS were not enriched prior to analysis and they have a higher detection limit (6–8 TU, Table 1) and poorer precision (4 TU, Table 1) compared to those that underwent enrichment (grey dots, Fig. 3). Given that tritium concentrations in this area are well above the limit of detection or precision, the trends are not likely impacted by the lack of enrichment prior to analysis. For additional information about the prediction error inherent in the interpolation, the reader is directed to Figure S7 in the ESM.

Outside of the areas near NGSs, tritium in shallow groundwater occurs at concentrations at background at two locations—in eastern Ontario, and in the Niagara Peninsula area located between lakes Ontario and Erie (Fig. 4). In eastern Ontario, tritium in shallow groundwater ranges

resembles background, indicating that the area is not influenced significantly by nuclear activity. The Ottawa GNIP station is located in this part of the study area and the good agreement between tritium concentrations in precipitation and shallow groundwater indicates that the interpolation (Fig. 3) represents local precipitation and recharge conditions as suspected. Eastern Ontario is not proximal to an NGS but is located ~150 km southeast of a research reactor on the Ottawa River that was decommissioned in 2018 (Fig. 3). The dominant wind direction in the Ottawa area for the past 30 years (Environment Canada 2021a) is from the SW ~32% of the time, which would direct emissions from the research reactor primarily to the NE, away from eastern Ontario (Fig. 3a). The second area of low tritium in shallow groundwater is observed on the Niagara Peninsula, with tritium concentrations from <15 and 22 TU (Fig. 3), reflecting background concentrations (Fig. 4). Despite its proximity to the Pickering and Darlington NGSs, the tritium concentrations in the shallow groundwaters of the Niagara Peninsula

Table 1 Detection limits for tritium analyses

Dataset	Data purpose	Detection limit (TU)	Analytical precision (median σ)	Reference
Groundwater	Ontario Geo Survey: background mapping	6–8 ($n=376$) 0.8 ($n=2,140$)	4.0 0.86	Hamilton (2021)
	Bruce and Darlington: NGS site monitoring	20	-	Bruce Power (2018, 2019, 2020)
Precipitation	Bruce NGS: background monitoring	20	-	Bruce Power (2018, 2019, 2020)
	Ottawa: background monitoring	0.8	-	IAEA (2021)
	Health Canada/CRMN background monitoring	0.8	-	J-F. Mercier, unpublished data from the CRMN, 2021
	CNL and SRBL: nuclear research and tritium processing	~10	-	This paper
Surface water	Environment Canada's Great Lakes monitoring	1.0	0.7	Dove et al. (2021)
	NGS background monitoring of lakes and tributaries	~20	-	Bruce Power (2018, 2019, 2020)
	NGS on and near site monitoring lakes	19.5	-	Ontario Power Generation 2018, 2019, 2020)

σ = standard deviation, *NGS* nuclear-generating stations, *CNL* Canadian Nuclear Laboratories, *SRBL* SRB Technologies, *OPG* Ontario Power Generation

remain at background levels (Fig. 4). The Niagara Peninsula is S–SW of the two NGSs in the path of the least common wind direction that crosses over the stations. Approximately 90% of the time, the peninsula would be upwind or across-wind from the NGSs, which accounts for the absence of influence from the Pickering and Darlington NGSs on shallow groundwater in that area (Fig. 3b). For context, even the highest tritium concentrations measured in shallow groundwater fall well below the Canadian drinking-water guideline for tritium which is 59,290 TU (Health Canada 2020).

Spatial tritium trends across the hydrologic cycle

Tritium data from precipitation, tributaries and the Great Lakes (contoured using conventional kriging), are overlain on the shallow groundwater interpolation (Fig. 5), showing good agreement among datasets. Tritium concentrations in tributaries range from <15 to 22 in eastern Ontario and on the Niagara Peninsula, where tritium in shallow groundwater is also the lowest (Fig. 5). Adjacent to these background areas, at the eastern margins of lakes Ontario and Erie, tritium concentrations in the Great Lakes also fall within the low background range of 15–22 TU. Tritium concentrations in tributaries and Great Lakes in excess of 35 TU are observed within 50 km of the Pickering and Darlington NGSs and within 150 km of the Bruce NGS, similar to shallow groundwater trends (Fig. 5). Together, hydrologic datasets show that the spatial extent of nuclear influence is smallest near the Pickering and Darlington NGSs, though the tritium concentrations here are highest with maximum concentrations of 100 TU in groundwater and 115 TU in

Lake Ontario. In comparison, the Bruce NGS has a larger area of influence but with lower concentrations near the NGS with maximum concentrations of 60 TU in groundwater and 95 TU in Lake Huron. The larger area of impact at lower concentrations near the Bruce NGS may result from the higher annual average precipitation trends at this location (1,048 mm/year), compared with the Pickering and Darlington NGS area (786 mm/year), which offers more opportunity for emissions distribution (Environment Canada 2021a). Although the area of impact is larger near the Bruce NGS, precipitation data collected at the NGS, shows an eight-fold decline in tritium concentrations within 20 km from the site, indicating that nuclear operations contribute to low levels at large distances, while high concentrations remain close to the site (Bruce Power 2018, 2019, 2020).

All possible tritium releases and controls were considered when interpreting the connection between Great Lakes tritium trends and those observed in other components of the hydrologic cycle. Releases from Bruce NGS are responsible for ~50% of the tritium in Lake Huron (Klukas and LaMarre 2000; King-Sharp 2009). Sources comprise tritium released to the lake in cooling water plumes, as well as atmospheric emissions (King-Sharp 2009; King-Sharp and Frape 2020). The interactions of these sources with hydrologic components, and the magnitude of their tritium inputs, have not been quantified. Bruce NGS is located just north of the mid-lake ridge that divides the deeper northern basin of Lake Huron from its southern basin. Cooling water plumes are traced upon release and the Lake Huron currents and gyres in the vicinity of the mid-lake ridge and Bruce NGS generally confine them to within several kilometers of the shore
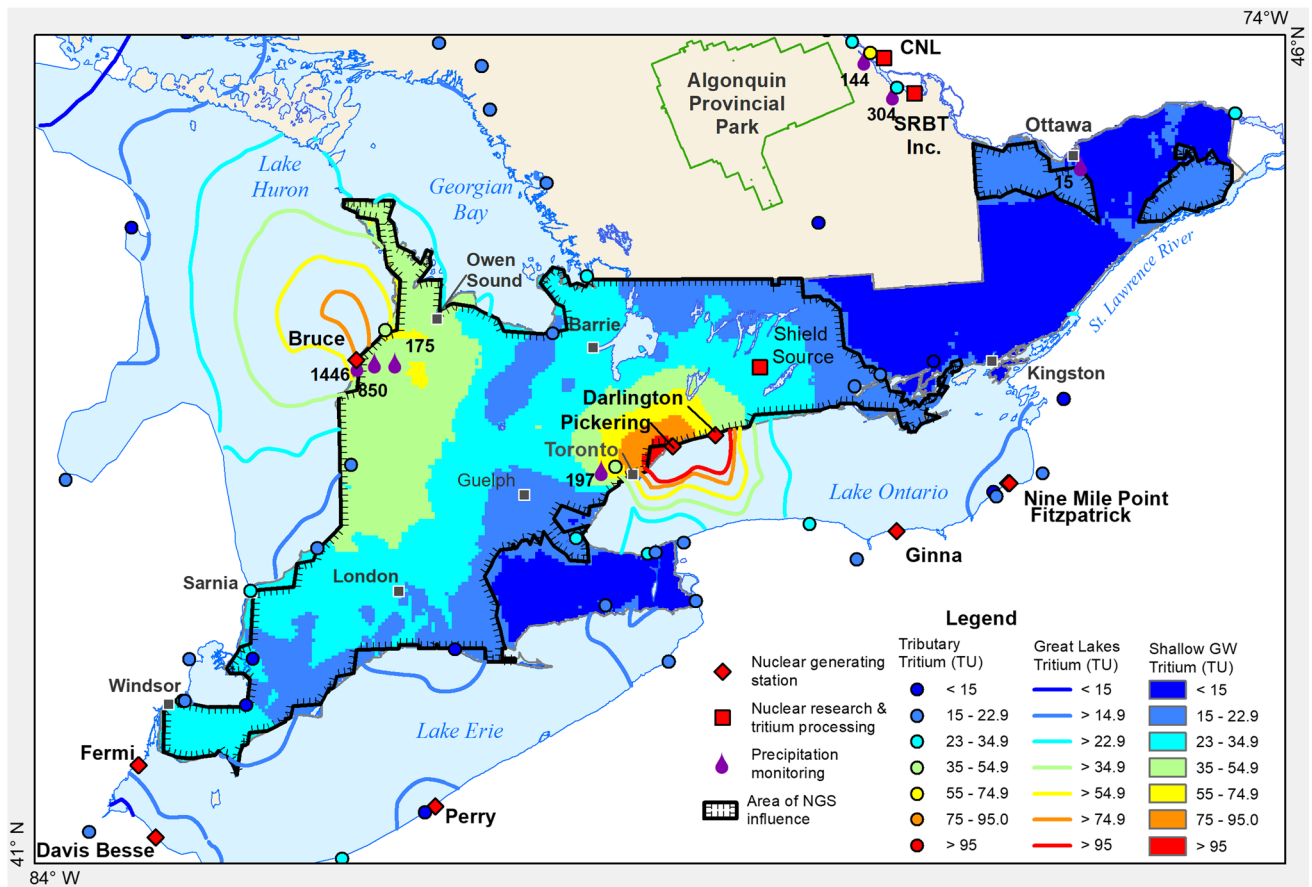
Fig. 5 Tritium across the hydrologic cycle for the period of 2017–2019 including tributaries, Great Lakes (Dove et al. 2021), precipitation—Ottawa (IAEA 2021); Bruce (Bruce Power 2018, 2019, 2020); Toronto (J-F. Mercier, unpublished data from the CRMN, 2021). Shallow groundwater tritium interpolated from data collected during 2007–2018 (Hamilton 2021). Sampling locations, from which interpolations were made are shown in Fig. 1. Average tritium concentrations (TU) in precipitation are presented next to each precipitation monitoring location, which are symbolized with purple raindrops

where they flow northeastward relatively undiluted (NOAA 2022). The cooling water plumes retain integrity past the mouth of Georgian Bay until they reach Manitoulin Island where they mix with lower concentrations from the outlets of Lakes Superior and Michigan. The cooling water plumes described by NOAA (2022) are not perfectly oriented in the direction of tritium trends observed in Lake Huron near the Bruce NGS (Fig. 5). As a result, tritium concentrations in the Great Lakes near NGS sites appear to be influenced by more than cooling water releases. It is likely that precipitation delivers episodic atmospheric emissions from NGSs to the Great Lakes as well as to the adjacent watersheds and shallow aquifers.

The tributary monitoring stations near the Bruce and Darlington NGSs ($n = 2$) have tritium concentrations ranging from 35 to 55 TU, which match the underlying shallow groundwater and adjacent Great Lakes tritium concentrations (Fig. 5). Tritium in groundwater and the Great Lakes show very good agreement in the vicinity of NGSs, with

tritium contours in Great Lakes nearly matching those in shallow groundwater (Fig. 5). The only disagreement occurs in southwestern Ontario, where groundwater values are generally higher than those of the other two datasets, although the trends in the three datasets are similar. As mentioned previously, tritium analysis of groundwater samples collected in southwestern Ontario was performed without enrichment, which resulted in a higher detection limit and poorer analytical precision—locations (Fig. 3); precision (Table 1).

The good agreement between tritium concentrations in shallow groundwater, surface water and precipitation shown here (Fig. 5), demonstrates the interconnectivity among these components, suggesting that they are almost interchangeable at the scale of the study area. The similarity between tributary and shallow groundwater tritium concentrations is not unexpected in the study area given that tributaries within the Great Lakes basin are composed of 40–70% baseflow, i.e. groundwater (Neff et al. 2005).

To further assess the suitability of using shallow groundwater as a proxy for precipitation, probability distributions for tritium concentrations in shallow groundwater and precipitation are compared for the Ottawa area (Fig. 6). The precipitation data represent monthly composite samples from the Ottawa GNIP station (IAEA 2021) for 2012 to 2018 ($n = 77$). The groundwater data are from Hamilton (2021) and comprise samples collected from 2012 to 2018 ($n = 317$) that meet the shallow groundwater criteria established for the tritium interpolation (Table 2).

Probability distributions of tritium concentrations for shallow groundwater and precipitation appear to be similar, and the dataset statistics (median, mean, standard deviation) are also similar (Fig. 6; Table 3). The tritium range for shallow groundwater is larger due to a small portion of samples with low tritium concentrations falling below 6.7 TU, which is the minimum value detected in precipitation (Table 3). At the high end of the tritium concentration range, the two datasets are similar with few samples reaching 28–30 TU (Fig. 6). The two datasets are compared statistically to quantify differences between the distributions, and based on the Shapiro-Wilks test, neither dataset can be considered normally distributed (Table 3). The distributions were therefore compared using the Mann–Whitney test for nonparametric datasets larger than 10 samples. The Mann–Whitney results demonstrated that at a confidence level of $\alpha = 0.05$, the null

Fig. 6 Cumulative probability distribution of tritium concentrations in Ottawa area shallow groundwater (blue symbols) (Hamilton 2021), monthly composite precipitation samples (red symbols) from the Ottawa GNIP station (IAEA 2021) and the annual weighted average values from the Ottawa GNIP station (yellow symbols) (IAEA 2021)

hypothesis of identical distributions is rejected if the absolute value of the test statistic (|z|) is ≥1.96. The calculated test statistic is |z|=0.8, falling outside of the rejection region, indicating that the null hypothesis cannot be rejected and the two distributions may be considered the same.

The good agreement between probability distributions for tritium in shallow groundwater and monthly precipitation confirms that shallow groundwater represents a realistic proxy for monthly composite precipitation in Eastern Ontario (Fig. 6). Unlike large rivers, which are a proxy for annual precipitation averages (Brown 1970), shallow groundwater tritium more closely reflects monthly composites (Fig. 6). Whether tritium concentrations in shallow groundwater or large rivers resemble monthly or annual precipitation values is likely due to storage. Groundwater storage is small compared with large rivers, and may reflect seasonal precipitation inputs, whereas larger rivers, such as the Ottawa River described by Brown 1970), have larger storage capacity allowing for the assimilation of seasonal inputs. Unlike large rivers, the smaller tributaries sampled in this investigation appear to more closely resemble shallow groundwater (Fig. 5), indicating that their storage capacity falls below that required to assimilate seasonal tritium inputs.

The Ottawa GNIP station is the only station in the study area where tritium samples are collected monthly and analyzed after electrolytic enrichment, providing low enough detection limits and confidence intervals to be sure that the data are representative. The Ottawa GNIP station is also considered to be outside of the influence of NGS (Fig. 4), which offers the opportunity to investigate the relationship between shallow groundwater and precipitation at various time intervals without interference from NGS inputs. The geology of the Ottawa area is similar to the rest of the study area in its bedrock geology, geological history and the origin of the regional glacial sediments. As a result, the Ottawa area serves as an analogue for the remaining study area and the relationships between shallow groundwater and precipitation developed in Ottawa are assumed to exist throughout the study area.
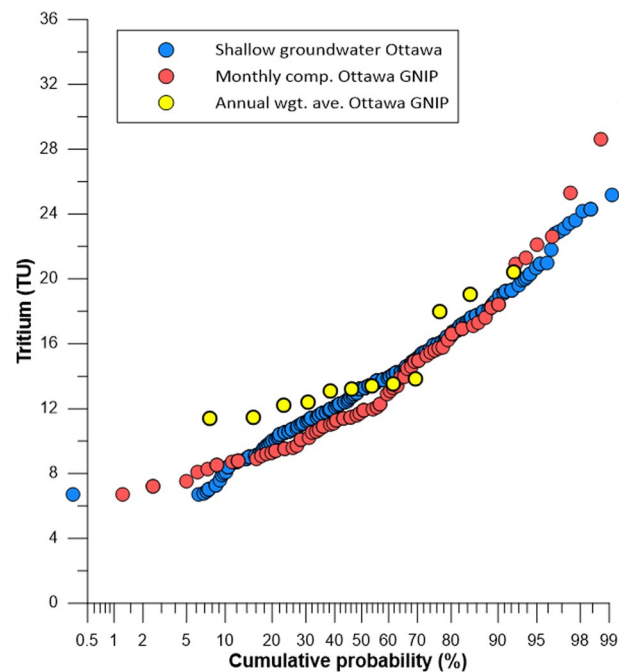
Temporal tritium trends

The preceding investigation delineated the influence of NGSs on tritium concentrations and characterizes the similarities in tritium spatial distribution patterns across the hydrologic cycle. In this section, temporal tritium trends for each hydrologic system component are assessed.

Temporal tritium trends in precipitation

Long-term monitoring of tritium concentrations in precipitation, with records spanning at minimum the past decade,

Table 2 Well information

Well type	Well depth grouping	Number of wells
Bored and sandpoints	<5 m	130
	5–10 m	169
	>10 m	50
Drilled over-burden	<10 m	33
	10–20 m	117
	20–30 m	87
	30–40 m	75
	40–50 m	42
Drilled bedrock Overburden thickness <2 m	<10 m	32
	10–20 m	66
	20–30 m	57
	30–40 m	42
	40–50 m	37
	>50 m	44
Overburden thickness 2–5 m	<10 m	26
	10–20 m	46
	20–30 m	38
	30–40	35
	>40 m	60
Overburden thickness 5–10 m	<10 m	23
	10–20 m	79
	20–30 m	40
	30–40 m	30
	>40 m	36
Overburden thickness 10–20 m	<20 m	119
	20–30 m	116
	30–40 m	42
	>40 m	62

Table 3 Dataset and distribution statistics for monthly precipitation and shallow groundwater from the Ottawa region (IAEA 2021; Hamilton 2021). *SD* standard deviation

Statistic	Shallow groundwater	Monthly precipitation
Median	13.2	11.8
Mean	13.2	13.0
Geomean	12.1	12.3
SD	4.6	4.3
Min	0.8	6.7
Max	30.9	28.6
Skewness	0.3	1.2
Shapiro Wilks test (p)	<0.01	<0.01
Shapiro Wilks W	0.97	0.91
Mann–Whitney U test for $n \geq 10$	$z = -0.8$	$z = -0.8$

(1968) method. The Sen (1968) slope is calculated by taking the median of the slopes of all lines through pairs of points, and the approach is considered to be an accurate alternative for assessing linear trends when a simple linear regression does not offer an acceptable solution, such as for the Ottawa GNIP dataset with an R^2 of 0.4. Since 2003, tritium concentrations at the Ottawa GNIP station have been decreasing, with a (Sen) slope of –0.03 TU (Table 4; Fig. 7). In the Northern Hemisphere, tritium concentrations in precipitation are expected to have decayed to background levels in areas not influenced by nuclear power operations (Eastoe et al. 2012). For the Ottawa area, a background tritium concentration of 14 TU is predicted by Wassmuth et al. (2022), which appears realistic given the time series trend since the year 2003.

In addition to the Ottawa GNIP station, relatively shorter time series precipitation monitoring for tritium is available from Pickering and Darlington NGSs from 1988–2012, Bruce NGS from 1988–2019, Canadian Nuclear Laboratories (CNL) from 2008 to 2019 and SRB Technologies Inc., a tritium-based light manufacturer located just east of CNL, from 2009 to 2019 (locations, Fig. 1 and Table 4). For ease of comparison, these data have been divided into two time periods, before 2003 and after 2003. The year 2003 was selected for separating the datasets because it represents the period of relative stabilization of tritium in precipitation in areas outside of NGS influence (Fig. 7).

At NGS sites Pickering and Bruce, tritium in precipitation is on an overall declining trend prior to 2003, and then stabilizes, based on Mann–Kendall trend analysis (Table 4). At these locations, tritium concentrations in precipitation dropped abruptly from 1988 until ca. 2003 when they stabilize and fluctuate in a narrower concentration range (Fig. 8). At Darlington NGS, tritium in precipitation is stable until 2003 and then decreases (Table 4; Fig. 8a). Stability in

has been conducted at four general locations within the study area. The longest and most complete record of precipitation monitoring is the Ottawa GNIP station which comprises tritium analysis of monthly composite samples since August of 1953 (Fig. 7). The complete precipitation monitoring record shows the tritium peak, or bomb pulse, of 1963 and the subsequent decline in tritium concentrations with the decay of fallout from thermonuclear weapons testing of the 1950s and 1960s. Average annual tritium concentrations in precipitation at Ottawa have been relatively stable since about 2000, though a slight decline in concentrations is observed (Fig. 7). The presence of a temporal trend was assessed using the Mann–Kendall test, and the slope of that trend calculated using the Sen

Fig. 7 Weighted annual average tritium in precipitation (GNIP reference) at the Ottawa and Vienna stations
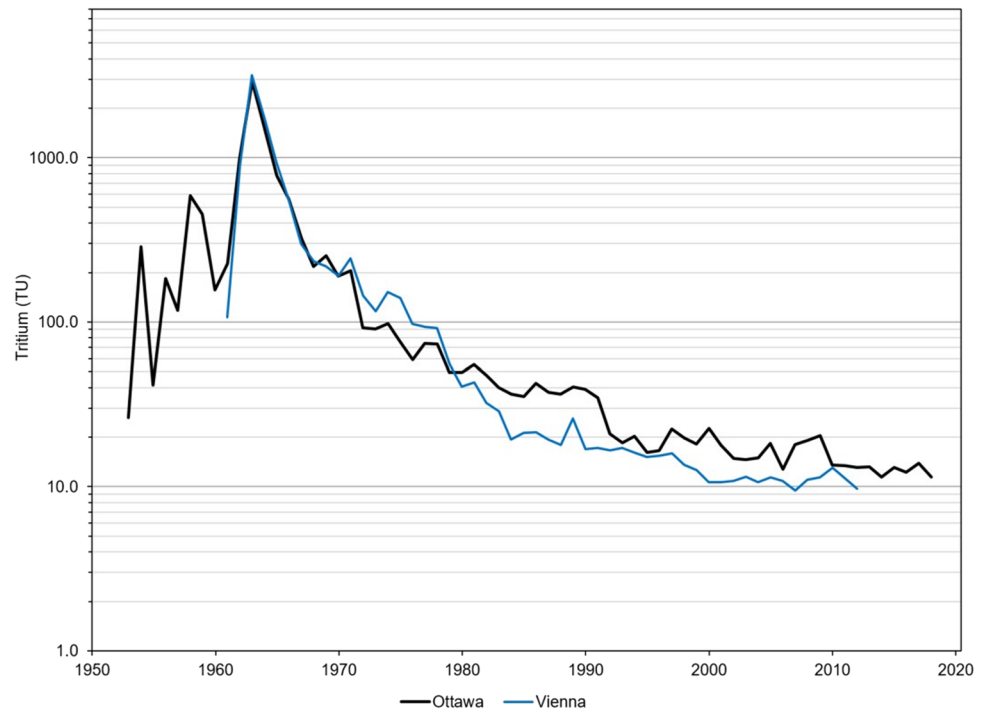
tritium in precipitation in close proximity (10 and 20 km) to the Bruce NGS is also observed since monitoring began at these locations in 2006 (Fig. 8b). At the Bruce NGS, the relatively stable tritium in precipitation from 2003 onward coincides with stability in tritium oxide emissions in air, and they appear to follow the same temporal trend (Fig. 8b). At Pickering and Darlington NGSs, the stability of airborne tritium releases corresponds with a decline in tritium in precipitation (Fig. 8a). At CNL and SRB Technologies Inc., tritium concentrations in precipitation are stable and decreasing,

respectively. These sites are located in eastern Ontario, just outside of the reach of the shallow groundwater interpolation, and cross-wind to the dominant wind direction at the Ottawa GNIP station (Fig. 3d).

Temporal tritium trends in groundwater near NGSs

Groundwater monitoring of tritium concentrations is conducted in the shallow domestic wells within ~20 km of the Bruce (Fig. 8b), Pickering and Darlington (Fig. 8a) NGS sites.

Table 4 Tritium (TU) in precipitation at 6 sites in southern Ontario

| Statistic	Ottawa GNIP, 2003–present	CNL, 2008–present	SRB Inc., 2008–present	Darlington		Pickering		Bruce	
				<2003	2003–2012	<2003	2003–2019	<2003	2003–2019
n	224	145	136	15	10	15	10	15	18
Max	54.1	7,428.2	4,667	1,185.8	338.8	24,563	2,541	4,099.5	2,566.4
Min	5.5	34	70.9	262.6	152.2	2,541	886.6	897.8	726.7
0.9-quantile	23.5	445.5	951.3	982.5	271.6	15,246	2,342.8	3,435.4	1,950
SD	6.9	697.5	588.4	263	50	5,920.9	434.9	972	465.8
Mann–Kendall Test z	–5.39	–5.21	–5.95	1.04	–2.6	–4.22	–1.36	–4.21	–0.57
Significance level (p-value)	<0.001	<0.001	<0.001	>0.1	<0.05	<0.001	>0.1	<0.001	>0.1
Trend (h)	True	True	True	False	True	True	False	True	False
Trend direction	Decreasing	Decreasing	Decreasing	Stable	Decreasing	Decreasing	Stable	Decreasing	Stable
Sen slope	–0.03	–1.35	–3.29		–10.03	–847		–160.93	

SD standard deviation

Shallow groundwater tritium concentrations at these locations are lower than the precipitation trends recorded on-site, at the stations, with which they are plotted (Fig. 8). Concentrations at 20 km from the site are approximately an order of magnitude lower than on-site (Fig. 8b). A number of high tritium concentrations in groundwater do occur at locations near NGSs (100–400 TU near Bruce NGS and 25–225 TU at Pickering and Darling NGSs), although these appear to be relatively stable since monitoring began in the early to mid-2000s, coinciding with the period of stability observed in tritium in precipitation at the on-site monitoring stations (Table 4; Fig. 8). To protect the privacy of residents, the locations of the private wells monitored near NGSs by the environmental monitoring group were not provided. The interpolated shallow groundwater tritium concentration could not incorporate the few wells sampled by the NGS environmental monitoring group because locations are

not provided. Instead, the interpolation relies on groundwater sampling of Hamilton (2021), for which many wells in close proximity to the NGS were included (locations, Fig. 1).

Temporal tritium trends in the Great Lakes

Tritium levels in the Great Lakes water declined consistently in the last 20 years, partly in response to the continued decay of fallout from thermonuclear weapons testing of the 1950s and 1960s (Dove et al. 2021). Previous work simulating tritium concentrations and identifying sources in the Great Lakes suggests that by 2030, this continued loss of thermonuclear tritium will increase the relative proportion of tritium contributed by NGS CANDU reactors to 80% from its previously

Fig. 8 **a** Tritium concentrations in precipitation and groundwater at Pickering and Darlington NGSs (Ontario Power Generation 2018, 2019, 2020). **b** Tritium concentrations in precipitation and groundwater monitoring data at Bruce NGS (Bruce Power 2018, 2019, 2020). Airborne releases are from the Canadian Nuclear Safety Commission (2020). Ottawa GNIP data are from IAEA (2021)
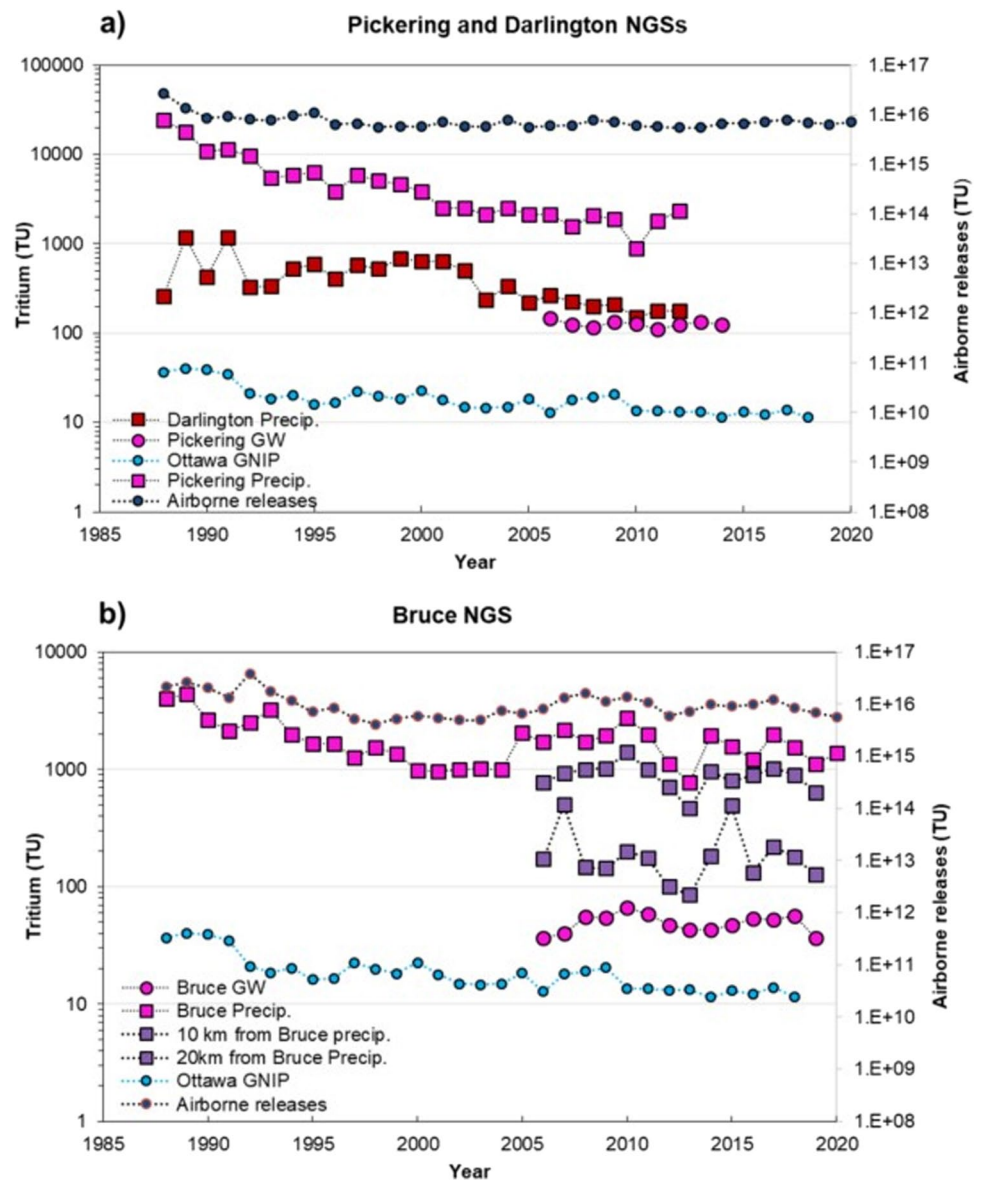
estimated proportion of 65% in 2000 (Klukas and Lamarre 2000; King-Sharp 2009; King-Sharp and Frape 2020).

Assessing temporal tritium trends at wells that have been re-sampled years apart

As part of Ontario Geological Survey's groundwater sampling campaign (Hamilton 2021), between 2010 and 2018, a total of 179 wells across southern Ontario that were originally sampled and analyzed for tritium after enrichment, were resampled at a later time and analyzed for tritium after enrichment. The resampled wells comprise 117 in southwestern Ontario, 34 in south-central Ontario and 28 in eastern Ontario (Fig. 9). When plotted against each other, the original and resampled tritium concentrations generally fall along a 1:1 line and have R^2 values of 0.95 for southwestern Ontario, 0.94 for central Ontario and 0.78 for eastern Ontario. The length of time between the original sample collection and the resample ranges from 1 to 8 years and is expressed (Fig. 9) with proportional symbol sizes. The nearly 1:1 slope and good correlation between the original and resampled tritium values demonstrate that:

1. Tritium in precipitation, the groundwater recharge source, is spatially variable and temporally stable.
2. Tritium in shallow groundwater is spatially variable and temporally stable.
3. Tritium inputs to the shallow groundwater flow systems across the study area are stable over the 8-year investigation period.

Analytical precision for tritium in groundwater was quantified with a Thompson-Howarth error analysis for large, normally distributed datasets (Thompson and Howarth 1978) (grey lines, Fig. 9). The Thompson-Howarth method estimates error as a function of concentration, which offers a more representative range of error values than the single value provided with the analysis. The difference between sample pairs falling inside the precision envelope may be caused by analytical error, but those outside of the envelope have differences larger than the analytical error and are therefore assumed to be due to changes in tritium in groundwater with time. Eighty-five percent of the sample pairs (152/179) fall within the precision envelope, and tritium concentrations at these locations can be considered stable over the resample time period.

Temporal stability across the hydrologic cycle

Outside of areas of NGS influence, where longer-term data records exist, components of the hydrologic cycle
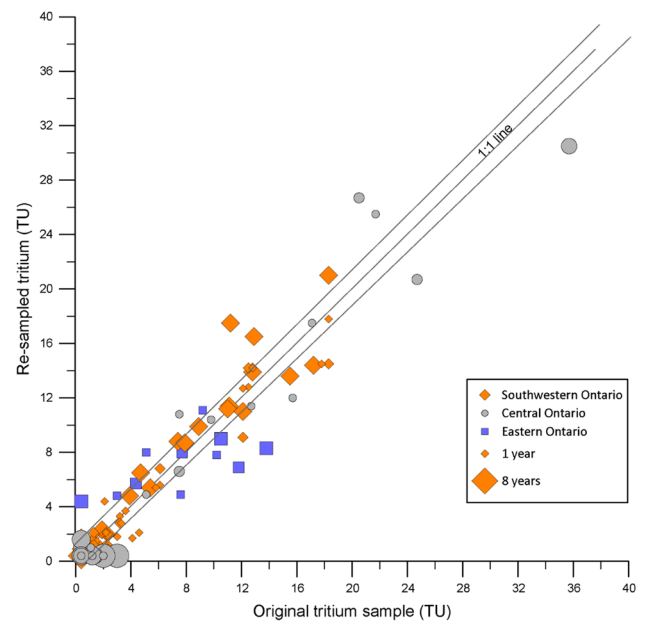

Fig. 9 Comparison of tritium concentrations for groundwater, sampled from the same wells on different occasions. The symbols are coloured by general location across the study area. Symbol sizes are proportional to time between the two samplings, which ranges from 1 to 8 years. Analytical precision is shown as grey lines

show a very slow rate of tritium decline over the past two decades, for example in precipitation at the Ottawa GNIP site (Fig. 7). The rate of decline is such that over the entire period of shallow groundwater data collection by Hamilton (2021) from 2007 to 2018 is 0.33 TU. Such a small decline is below the limits of precision of the groundwater dataset, and negligible in the context of background tritium levels of 9–14 TU (Wassmuth et al. 2022). In the surface waters of the Great Lakes of the study area, tritium concentrations are also declining slowly (Klukas and Lamarre 2000; King-Sharp 2009; King-Sharp and Frape 2020).

Although the suitability of using shallow groundwater as a proxy for precipitation was confirmed in the preceding (Fig. 6), the relative stability among time-series tritium data for all components of the hydrologic cycle (Figs. 8 and 9) demonstrates that shallow groundwater can be a reliable proxy for precipitation from 2003 onward, corresponding to the period when tritium in precipitation has been stable (Pickering NGS, Bruce NGS) or declining negligibly (Ottawa GNIP; Table 4). The repeated sampling of shallow groundwater across the study area shows that within the limits of precision, tritium concentrations have been approximately stable from 2010 to 2018 (Fig. 9), suggesting that the minor declines across the hydrological cycle are negligible during this period.

Estimating groundwater ages with tritium in the Great Lakes Basin

Estimating groundwater ages with tritium requires knowledge of the input function at the time of recharge, as well as an understanding of mixing, dispersion and decay, the processes that influence the tritium concentration in the aquifer under investigation. Near the Ottawa GNIP station, tritium concentrations in groundwater recharged after 1972, decay to resemble the atmospheric scenario, making the input function ambiguous (Clark 2015). To assess this ambiguity in the modern context, now that tritium is relatively stable at the Ottawa GNIP (IAEA 2021), tritium concentrations were estimated for a theoretical confined aquifer using the lumped parameter model, TracerLPM (Jurgens et al. 2012). In the simulation, groundwater flow is represented as piston-flow, with no dispersion or mixing, an assumption that tends to be applicable in confined aquifers with relatively small recharge areas (Jurgens et al. 2012), a suitable assumption in the study area which comprises complex glacial sediments that tend to restrict the size and distribution of recharge areas. Using the Ottawa GNIP data (IAEA 2021) as the T_0, the tritium concentrations in a well sampled in 2012 are estimated annually for recharge times from 1930 and 2012 (Fig. 10). The year 2012 was selected because it represents the middle of the data collection period for the shallow groundwater dataset (Hamilton 2021).

The TracerLPM simulation shows an aquifer containing water recharged any time between ca. 1972 and 2006 would have the same tritium concentration, despite the different tritium inputs (1972 input is 90 TU, 2006 is 10 TU; Fig. 7),

because of decay. Although estimating groundwater age from tritium concentration alone in a groundwater sample cannot be done reliably because of ambiguity (Fig. 10), qualitative estimates are still possible and the shallow groundwater interpolation can inform these estimates by identifying areas of NGS influence (Table 5). In areas within and outside of NGS influence, tritium values below a detection limit of 0.8 TU can be interpreted definitively as having been recharged prior to the beginning of bomb testing in 1953 (Table 5). The recharge period for tritium-live values cannot be qualitatively interpreted in areas within NGS influence, whereas in areas outside of NGS influence, tritium values between 0.8 and 10 can be interpreted as a mix of modern and prebomb groundwaters. Additionally, outside of NGS influence, groundwater recharged after 1970 will have a present-day tritium concentration of 10–20 TU, though the same tritium values may represent a mix of modern and prebomb recharge (Fig. 10 and Table 5). Tritium concentrations greater than 20 TU, in areas outside of NGS influence, can be interpreted as having been recharged sometime during the bomb testing period, from the late 1950s to the late 1960s (Table 5; Fig. 10).

Tritium concentrations in the subcropping bedrock aquifers of the study area are interpreted qualitatively to get a sense of recharge timing where possible. A total of 1,280 groundwater samples collected from wells tapping into the deeper subcropping bedrock aquifers were analyzed for tritium following electrolytic enrichment. Of these, 553 samples were collected within the area of NGS influence and 727 samples were collected outside of the area of NGS influence. Within the area of NGS influence, tritium concentrations

Fig. 10 Theoretical tritium concentrations with time of tritiated groundwater recharged between 1930 and 2012, modelled assuming piston flow with, no dispersion. The Ottawa GNIP data are used, ending in 2012 which is approximately the middle of the sampling period
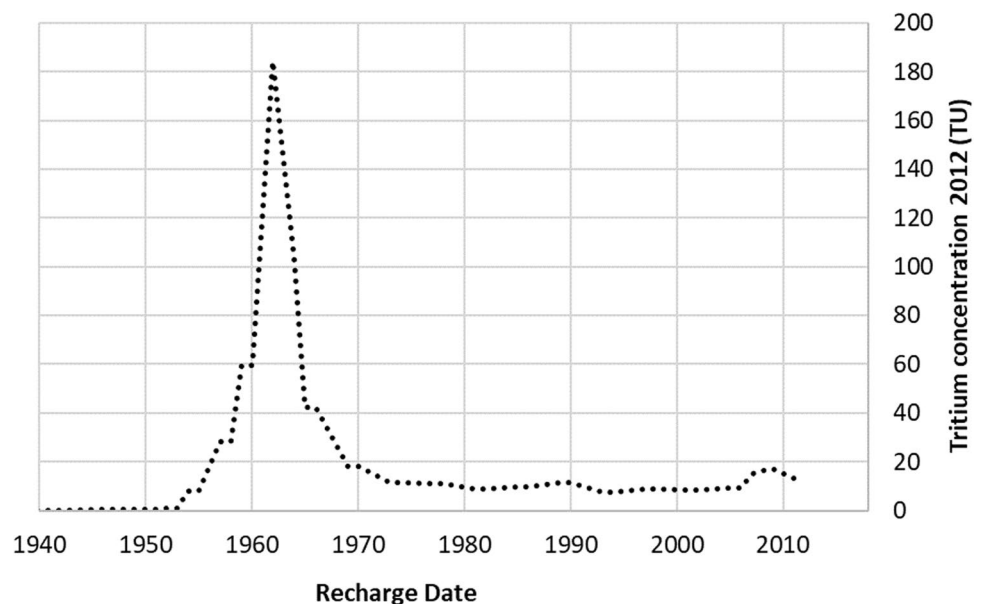
Table 5 Qualitative estimate of recharge period in areas outside of NGS influence

Recharge period	Tritium in groundwater sample (TU)
Recharge between 1958 and 1968 (peak)	>20
Recharge since 1970 OR mix of modern and peak	10–20
Mix of modern and prebomb	0.8–10
<1953	≤0.8

in the subcropping bedrock aquifers have an average of 8.0 TU, a standard deviation of 8.5 TU and minimum and maximum values of <0.8 and 44.4 TU respectively. A total of 203 samples within the area of NGS influence are below detection (0.8 TU), or tritium-dead, and these aquifers were recharged prior to 1953. In areas outside of NGS influence, tritium concentrations in the subcropping bedrock aquifers comprise 229 locations yielding tritium-dead samples, with these aquifers recharged prior to 1953. The average tritium concentration in the subcropping bedrock aquifer outside of

NGS influence is 4.7 TU, with a standard deviation of 4.4 TU and minimum and maximum values of <0.8 and 20.7 TU, respectively. The average value of 4.7 TU indicates that most subcropping bedrock aquifers comprise a mix of modern and pre-1953 recharge. Although the TracerLPM model predicts the recharge timing of samples with tritium levels greater than 20 TU to be from 1950–1968 (the peak, Fig. 10), only one out of 727 subcropping bedrock well samples reports a value over 20 TU, with a value of 20.7 TU, just over the 20 TU threshold, indicating the possibility that recharge occurred during the bomb peak. The absence of samples with tritium concentrations >20 TU in areas outside of NGS influence suggests that either the subcropping bedrock aquifers of the study area were recharged after 1970, or that dispersion and mixing have assimilated the bomb peak. However, if the latter were true, and the peak were just dampened by dispersion and mixing, then the repeated groundwater sampling (Fig. 9) would have likely captured a systemic change between resampling periods, reflecting the different recharge inputs associated with each year of the bomb peak. Instead, only 14% of the resampled pairs are considered to be different than each other.
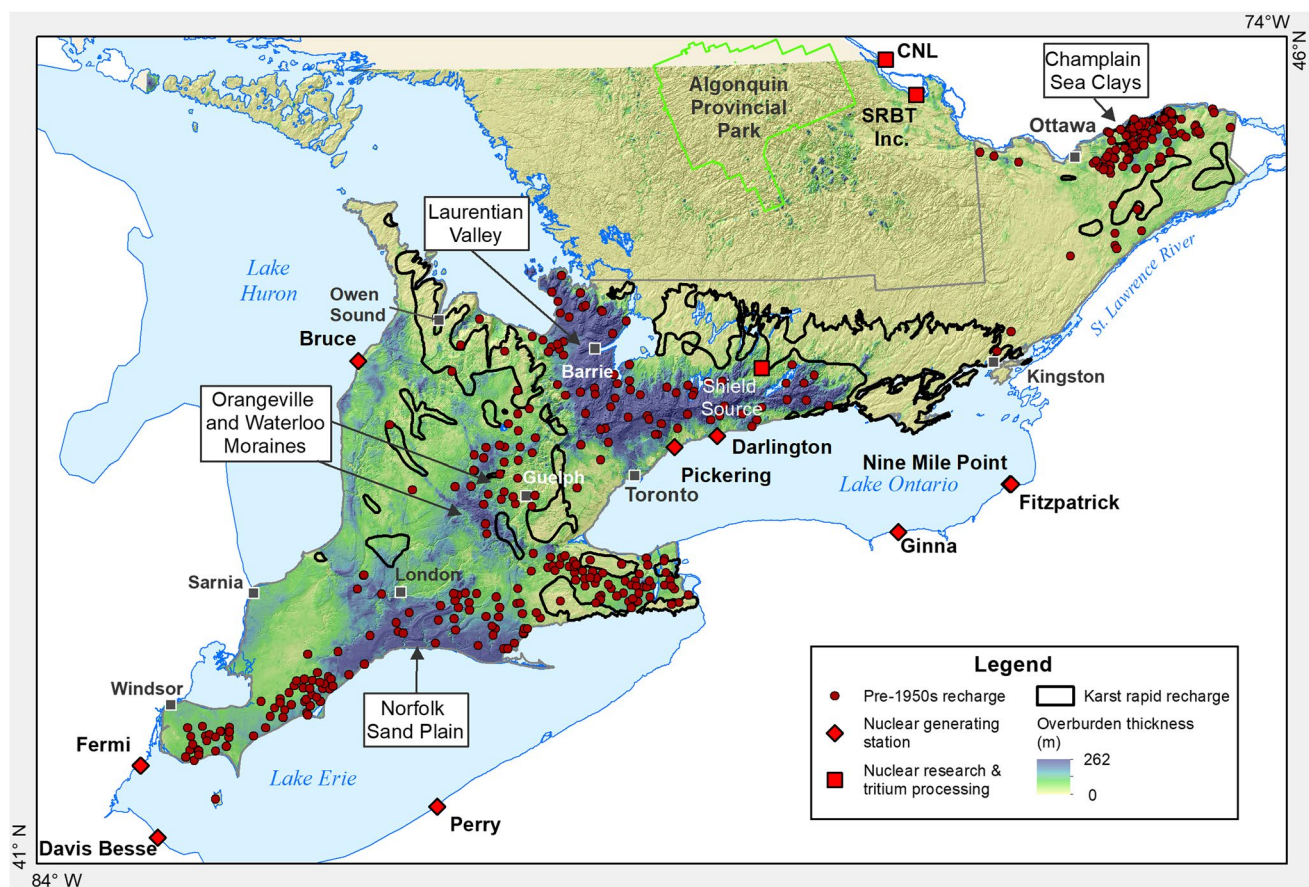

Fig. 11 Groundwater samples in the subcropping bedrock aquifer with groundwater recharged prior to the early 1950s symbolized with red dots overlying the drift thickness (Gao et al. 2007). Samples with detectable tritium concentrations are shown with small black dots

The oldest waters in the subcropping bedrock aquifers of the study area appear to occur primarily in areas overlain by the thickest overburden sediments (Fig. 11). In eastern Ontario, there is a cluster of pre-1950s water in the subcropping bedrock aquifer underlying the Champlain Sea clays (Colgrove 2016; Fig. 11). The low permeability, glaciomarine Champlain Sea clays range in thickness from 10 to 90 m (Charron 1975). Trending northwest of Lake Ontario, there is a large collection of pre-1950s waters in the subcropping bedrock aquifer underlying the sediments of the Laurentian Valley (Fig. 11). The Laurentian Valley is a bedrock depression more than 100 km long and 100 m deep that connects Lake Ontario to Georgian Bay on Lake Huron (Sharpe et al. 2018). Sediments reach a thickness of 200 m within the Laurentian Valley (Sharpe et al. 2018). Isotopic evidence (^{18}O) of Pleistocene-age groundwater has been previously reported for deeper groundwater systems of this area (Aravena and Wassenar 1993) A cluster of pre-1950s groundwater is also found beneath the Orangeville and Waterloo Moraines, which are abutting interlobate features with varied permeability and thicknesses reaching 74 m (Burt AK 2017) and 140 m (Bajc et al. 2014), respectively. There is also a large area of pre-1950s groundwater in the subcropping bedrock aquifers of the Niagara Peninsula extending westward along the north shore of Lake Erie (Fig. 11). With the exception of the thick clay-rich sediments underlying the Norfolk Sand Plain, this area is not covered in thick overburden. However, the moderately thick sediments along the margins of Lakes Erie, Huron and St. Claire are very fine grained, which coupled with the low horizontal groundwater gradients, leads to very sluggish groundwater flow and a Pleistocene age component to some of these waters (Hamilton et al. 2015).

The probability distribution of tritium-dead versus tritium-live samples with respect to drift thickness shows the influence of drift thickness on tritium levels (Fig. 12). There is a 50% probability of subcropping bedrock aquifers being overlain by 38 m of drift for the tritium-dead dataset, while for the tritium-live dataset, there is only a 15% probability of a sample location being overlain with 38 m of drift. For the tritium-live dataset, there is a 50% probability of 12 m of overlying drift, a value less than 3 times that of the tritium-dead dataset. The greater probability of tritium-dead samples collected from areas of thick drift supports the observed the spatial trends (Fig. 11).

Summary and conclusions

The shallow groundwater tritium interpolation established in this investigation was developed with groundwater data from the Ontario Geological Survey groundwater geochemistry database (Hamilton 2021). Groundwater samples were selected for inclusion in the interpolation based on criteria
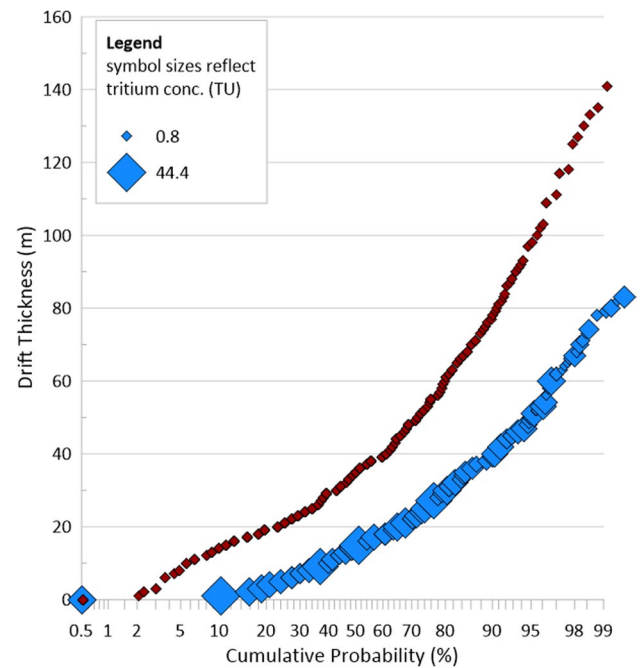

Fig. 12 Probability distribution of tritium-dead (brown diamonds) versus tritium-live samples (bllue diamonds) with respect to drift thickness for the subcropping bedrock aquifers. Symbols are sized to reflect tritium content

established by a combination of aquifer type, well type, well depth and tritium concentration (Fig. 2). Spatial and temporal datasets were examined for tritium in precipitation, shallow groundwater, the Great Lakes and tributaries in southern Ontario (Fig. 5). Similarities in spatial tritium trends across the hydrologic cycle demonstrate the close connection among its components and conceptually support the use of shallow groundwater as a proxy for monthly composite precipitation. A statistical (Table 4) and data distribution comparison (Fig. 6) of the monthly composite Ottawa GNIP precipitation data with the shallow groundwater dataset for the same area, confirms the interchangeability of the two datasets. Temporal results show that with the exception of Darlington NGS, tritium levels in precipitation are relatively stable in areas within and outside of NGSs influence since ca. 2003 (Table 4). Because precipitation monitoring for tritium is not conducted at a sampling density that reflects the spatial trends, the use of shallow groundwater data as a proxy for precipitation has enabled the delineation of the extent of NGS influence (Fig. 4), which appears to be influenced primarily by wind direction (Fig. 3). The area of NGS influence represents 60,000 km^2, which comprises 66% of the 95,000-km^2 study area. Delineating the extent of NGS influence offers predictive capability to nuclear regulators should unexpected releases occur to the natural environment by providing information on background concentrations, controls, probable migration directions and extent.

Estimating recharge timing in deeper groundwater systems is complicated by the ambiguity of the input function through time (Fig. 10), and more recently, by NGS influences. Qualitative estimates of recharge timing are supported with the results of a lumped parameters model, TracerLPM (Jurgens et al. 2012), simulating the tritium concentrations in a recent groundwater sample for waters recharged each year since 1930 (Fig. 10). Recharge timing estimates must be made separately for areas within and outside NGS influence (Table 5) for all tritium-live samples. For tritium-dead samples, NGS influence may be ignored because those waters were recharged prior to the bomb peak and the commissioning of NGSs within the study area. The oldest groundwaters in the subcropping bedrock aquifers, recharged prior to the bomb peak, generally underlie the thickest sediment packages, which can be observed spatially (Fig. 11) and by a comparison of data distributions for tritium-live versus tritium-dead with drift thickness (Fig. 12). More definitive age dating of older waters (pre-1950s) in the subcropping bedrock aquifers of interest should be conducted with additional isotope tools such as radiocarbon.

Tritium remains an invaluable tracer across global hydrologic systems, but only where precipitation inputs are known. The detailed characterization offered here presents essential context, spatial and temporal trends, supporting the interpretation of tritium data across systems. Where groundwater data are available, the application of shallow groundwater tritium trends, as a proxy for precipitation data, enables similar characterization of spatial and temporal trends elsewhere.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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