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Historical Record of Tritium from Tree Cores at the Savannah River Site

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Title: Historical Record of Tritium from Tree Cores at the Savannah River Site
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Abstract

Tree cores from various locations at the Savannah River Site (SRS) and local area were measured for total tritium (T) content and T speciation to include tritiated water (HTO), exchangeable organic bound T (E-OBT) and non-exchangeable organic bound T (NE-OBT) species. The tree cores dated back to the 1960's or prior which provided an opportunity to measure T over the last 60 to 70 years. The total T levels from pine and oak tree cores were consistent with the record of known T atmospheric releases from nuclear activities at the SRS between the mid-1950's and 1990's with a notable peak in T tree core levels during the late 1960's. The T speciation data for some tree core samples from SRS demonstrated elevated levels of OBT:HTO and NE-OBT:E-OBT identified primarily in the last ~20 years due to T inputs from remedial irrigation with OBT-rich pond water. Elevated but lower levels of OBT:HTO and NE-OBT:E-OBT were observed due to inputs from SRS operations during the last 70 years and prior to irrigation with the T-rich pond water.

Environmental Significance Statement

Tritium is an effluent from nuclear processes and anthropogenic activities. It is an environmental contaminant that can be hazardous to biological systems depending on the quantity and chemical form (tritiated water as HTO or organic bound tritium as OBT). This study focuses on coupling total T and T speciation measurements over the history of nuclear-related activities and remediation efforts at the Savannah River Site (SRS). It is expected that the total T data from tree cores will provide a record of T atmospheric releases at the SRS and the OBT:HTO will help to better understand the biological impact of remediation activities.

Introduction

Anthropogenic nuclear activities over the last 75 years have caused the elevated releases of radioactive tritium (T; half-life = 12.3 years) into the environment. Environmental T is of interest because it is an isotope of hydrogen (H), which is an essential element for life, and it is a

biological hazard. Tritium can be found in multiple forms in the environment such as tritiated water (HTO), HT (gas), and organic bound tritium (OBT). Some examples include HTO found in tissues and other matrices, CH_3T (tritiated methane gas), tritiated organics such as specially labeled drugs, amino acids, chemicals, and OBT in environmental media. Tritium is produced by several nuclear processes and anthropogenically-mediated activities. Tritium can be released during the operation of nuclear reactors, from fuel storage and separation activities, from nuclear weapons testing, nuclear research and industrial T handling facility operations.[1] There are many routes of T release into the environment because T can reside in water as HTO, in gas as HT and in organic molecules. Several chemical forms of T can permeate many barrier materials, and this is one route in which anthropogenic T can be released.

Tritium can also become biologically incorporated and migrate in environmental systems by processes like photosynthesis, respiration, and transpiration in the place of H—particularly when elevated levels of T are present.[2-4] Organic bound tritium (OBT) is found in different chemical forms in the environment, which in high levels, presents a health concern for humans and other biological life that live or consume food in these areas. These forms of OBT have been defined as exchangeable (E-OBT) and non-exchangeable OBT (NE-OBT). Typically, E-OBT bonds with O, N and S whereas NE-OBT bonds strongly with C.[4-8] The formation, behavior and persistence of OBT (as well as HTO) in the environment can be examined by chemically isolating these forms of OBT in materials. The definitions of OBT and HTO in living systems vary in the literature[6, 9-12] but for this presentation, we will utilize OBT as NE-OBT, E-OBT and HTO as tissue-bound tritiated water. Furthermore, HTO + E-OBT + NE-OBT is equal to total T, but each T species is measured independently of the total T measurement.

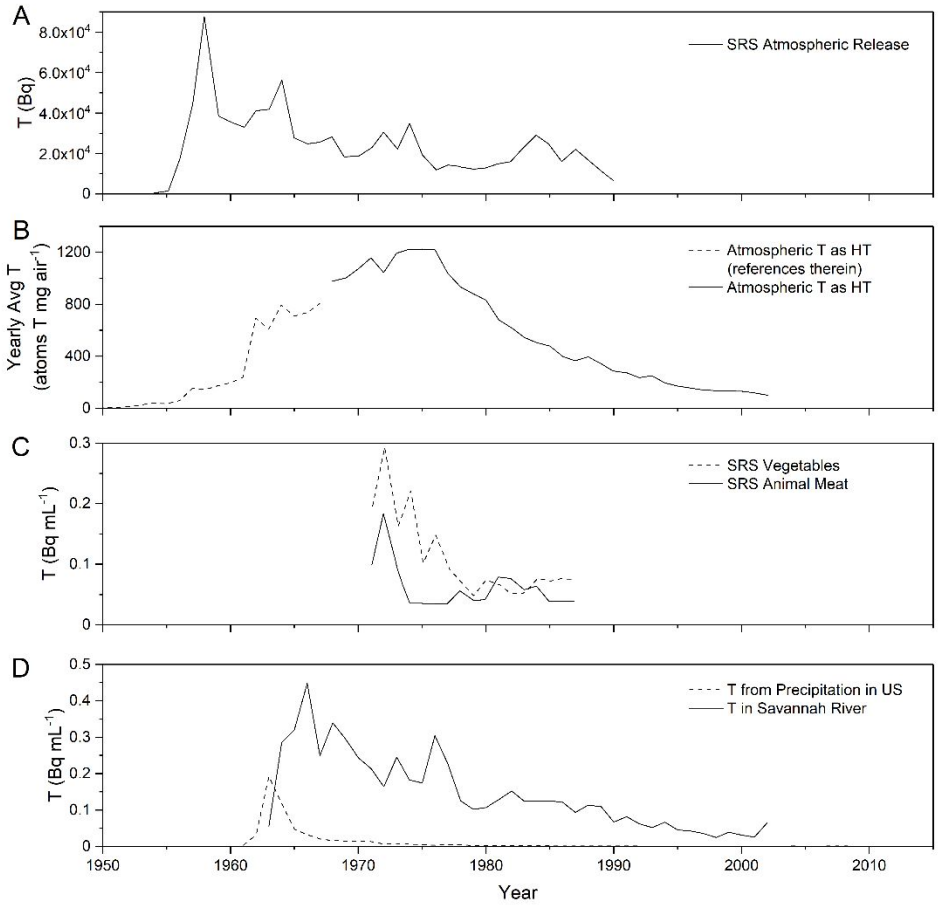

Figure 1. Compilation of various historic data for T in the environment. A) SRS atmospheric release[13] B) Solid line: Atmospheric HT[14]; dotted line: Atmopsheric HT (as cited)[14] C) Vegetables at SRS[13]; animal meat at SRS[13] D) T from precipitation in US[15] and T in the Savannah River.[16]

The Savannah River Site (SRS, in Aiken County, SC) is an ideal location to study T and OBT behavior in the environment due to its history of nuclear activities and associated legacy T contamination. These activities included at a minimum, nuclear fuel storage, spent fuel reprocessing, a T production facility and nuclear reactor operations. Most of the nuclear reactors were in operation by the 1950's; some of the reactors continued to operate until the late 1980's. Many of the activities that do not include reactor operations continue today but the release levels are diminished. A historical record of T at SRS and around the US is compiled in Figure 1 to include T atmospheric releases at SRS,[13] T in animal meat and vegetables at SRS,[13] HT in the atmosphere from Happell *et al.* (2004) and references therein,[14] T in US precipitation including

Washington, D.C. and 11 states,[15] and T in the lower Savannah River near Clyo, GA.[16] These records indicate that there were periodic peaks in SRS T releases and T incorporation into SRS biota that did not always coincide in time with atmospheric HT releases. This was because the SRS releases were localized whereas the atmospheric HT releases were country-to-global wide.

Previous work on tree cores from the SRS was published by Sanders (1976) and Duff *et al.* (2019).[17, 18] The former explored T levels at a range of distances from a central location at SRS.[17] Cellulose-based T from wood samples was extracted using combustion techniques and liquid scintillation counting (LSC) was used to measure the T. They found the levels of cellulose-T decreased with increasing sampling distance from the central portion of the SRS. The total T levels in extracted cellulose from a cord of dry pine wood ranged from 4.07×10^5 Bq to 6.96×10^6 Bq (or 0.29 to 5.03 Bq g^{-1} dry wood equivalent to 0.13 to 2.15 Bq g^{-1} wet wood) based on the distance from H Area, which is in the central portion of SRS.[17] Other prior work explored T contamination at a location at SRS called the Mixed Waste Management Facility (MWMF) over the ~20-year duration of a phyto-remediation project where forest stands have been irrigated with T-rich groundwater from a nearby burial ground.[18] They found that OBT levels were quite high relative to HTO levels in tree core samples from the last two decades indicating OBT was being retained in the tree tissues. The prior use of tedious cellulose-based T extraction techniques to assess T speciation and total T levels as SRS was fundamental[17] and provided helpful information. The recently-developed and rapidly-performed T extraction methods including automated oxidative pyrolytic combustion approaches (for HTO, NE-OBT and total T) and the wet chemical dead water exchange methods (for E-OBT extraction) to isolate and quantify NE-OBT, E-OBT and HTO behavior from tree core materials (without using cellulose-based methods) have their advantages.[18]

We focus our current investigation on more highly contaminated tree core samples from near the center of SRS for total T and T speciation to examine whether historical T release events can be recorded. This present study was performed to: 1) measure the total T levels in MWMF trees from additional MWMF locations to those sampled previously,[18] including trees from plots that were under consideration for disposition and replanting with younger stock, 2) determine how the T levels in the trees at the MWMF compared with other sampled trees from the SRS area as well as historic data for SRS and elsewhere, and 3) to make measurements of (decay

corrected) T levels (total T, HTO, E-OBT and NE-OBT) in segments of tree cores from shorter growth periods [three to five year segments instead of 16 to 20 year segments as in prior work.][18] It was anticipated that a closer examination of the T behavior in these MWMF trees would provide some historic information on T releases at the SRS and possibly show differences in the T speciation from before and after the MWMF was established.

Methods

Tree cores of pine and oak were collected in our current study from five locations in the SRS area (Figure 2; Table 1). The focus of this study was primarily on samples collected at the MWMF, which is a 25-hectare (~60-acre) area with old and new growth forest vegetation dominated by pine trees. Trees at the MWMF plots were irrigated with T-rich water for the last ~20 years as part of a T-based phytoremediation effort to slow the release and spread of T into the environment. The operations at the MWMF are managed by the U.S. Forest Service. Tritium-rich groundwater was collected in a holding pond and used to irrigate forest plots of old natural growth and as well as more recently planted trees since 2001. Figure 3 illustrates the T-rich groundwater plume migration from the burial ground complex, the MWMF pond, the sampling locations from previous work[18] (plots 28, 29, 30), and the sampling locations for this study, including plots 2, 4 and the Old Evaporator location. The Old Evaporator is located near the MWMF Pond and is the former location of a mechanical evaporator that was used, in addition to the irrigation efforts, to mobilize T from the pond into a vapor form during the MWMF operation.

Another sampling area was Tinker Creek which was ~12 km from any SRS nuclear facility and is an uncontaminated area relative to the other SRS areas. A third sampling location was R-Canal which is a narrow, heavily-wooded canal that received cooling waters from the former R-reactor, which ceased operations in the 1950's. The R-reactor facility was dismantled and decommissioned in 2011. The fourth sampling area was Par Pond, which is a large manmade reservoir that received reactor cooling waters from P- and R-reactors. The fifth location was an uncontaminated, offsite location in the greater Aiken County area about 16 km from the closest SRS border.

Tree core samples were collected at all these locations either along a shoreline area or within forest plots using a 5.15-mm diameter Haglöf Sweden 2-thread increment borer (Långsele, Sweden). Three cores were typically taken from each tree at breast height, placed in paper straws, and stored in a -80^{0}C freezer until time for analysis. Tree girth measurements were also taken at some of the field locations.

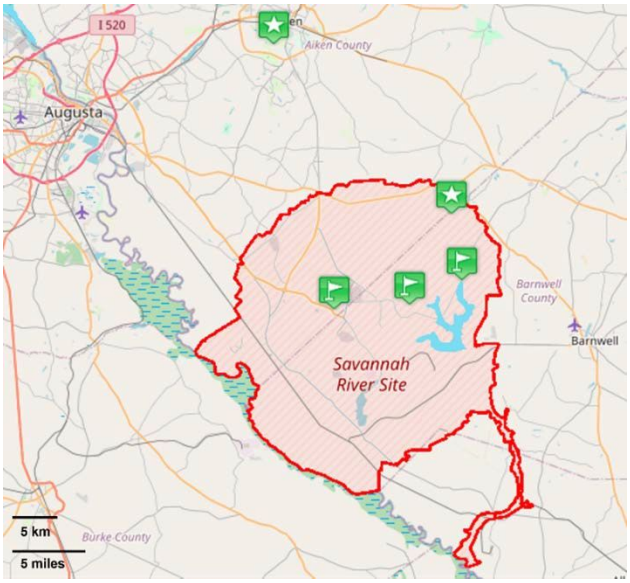

Figure 2. Map of the SRS and surrounding area marked with the sampling locations. Green stars: Tinker Creek, an uncontaminated area and an offsite, uncontaminated location in Aiken County, SC. Green flags: R-Canal and Par Pond, two radioactively-contaminated areas; MWMF, a T-contaminated area.

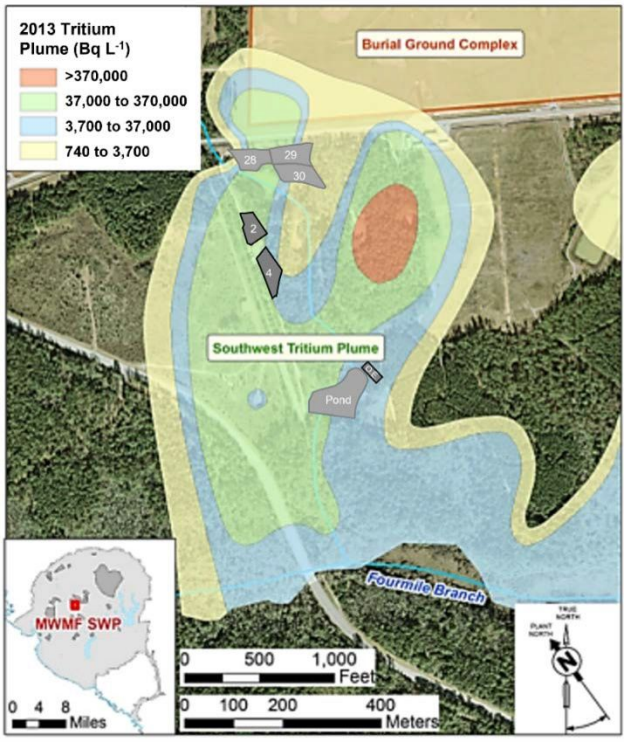

Figure 3. A map of the MWMF adapted from SRNS (2014) that shows the location of the T groundwater plume, the sampling sites (plots 28, 29, 30) from prior work,[18] the pond where the T-rich groundwater is collected, and the sampling sites for this study [plots 2, 4, and the Old Evaporator (O.E.)].[19]

Tree core samples were prepared for analysis by identifying the number of rings and cutting the cores into sections representing 3 to 5 year increments. The extraction of T from the tree cores was completed using a Raddec Pyrolyser-6 Trio combustion furnace (Southampton, UK). This furnace accommodates six different samples at one time. The tree core sample material (0.3 g to 1 g wet weight) was loaded into glass sample boats and were inserted into one of the six furnace work tubes. These work tubes were pre-loaded with 10 g of platinum (Pt)-coated alumina catalyst pellets to ensure the combustion and recovery of all the T in the attached T bubbler traps. The bubblers were each filled with 20 mL of 0.1 M trace metal grade nitric acid to capture the T released from the core samples. The Pt-alumina catalyst was changed out and pre-conditioned in an air stream after every 20 combustion furnace runs. The sample boats were cleaned after each run with DI water, Decon-90 soap (Decon Laboratories Limited, East Sussex, England), and ethanol wipes while the bubblers were rinsed with milliQ water.

Table 1. Summary of tree core samples collected from live trees and analyzed for total T and T speciation.

Sample Name	Sampling Date (m/yr)	Sampling Location	Tree Type	Estimated Age (years)	Growing Location	Number of Cores	Analyses Completed
MWMF Plot 2 Tree 2	May-21	SRS - MWMF	Oak	64	Plot 2	2	Total T
MWMF Plot 4 Tree 1	May-21	SRS - MWMF	Pine	82	Plot 4	3	Speciation
MWMF Plot 4 Tree 2	May-21	SRS - MWMF	Oak	63	Plot 4	2	Total T
MWMF Old Evap Tree 1	Jul-21	SRS - MWMF	Pine	> 64	Near Old Evaporator	3	Total T
R Canal Tree 1	Jun-21	SRS - R Canal	Pine	> 51	Near Edge of R Canal	3	Total T
Par Pond Tree 1	May-21	SRS - Par Pond	Pine	> 58	Near Edge of Par Pond	3	Total T
Tinker Creek (TC) Tree 2	Nov-21	SRS - TC	Pine	55	Along Roadside to TC	3	Total T
Aiken, SC Tree 1	Dec-21	Aiken County	Pine	92	Undisturbed woodland area	3	Total T

The total T and T speciation (HTO, E-OBT, NE-OBT) analyses were performed using the pyrolyser. The pyrolyser has three different furnace zones. Each zone has a different function during the furnace runs to release either all the T or to release certain T species. The total T, HTO and NE-OBT speciation methods are described in Tables 2 through 4. After the HTO pyrolyser run, the E-OBT was recovered by putting the run sample products in 15-mL centrifuge tubes with enough T-free or "dead" water to cover the sample (typically between 3 to 6 mL). The centrifuge tubes were then placed on a shaker table for 72 hours. After 72 hours, the water was decanted and saved for LSC analysis. The solid samples were placed in aluminum foil boats and oven heated at 150^{0}C for 15 minutes to dry. Dried samples were saved in a -80^{0}C freezer for subsequent NE-OBT pyrolyser runs.

Table 2. Total T pyrolyser method for tree core analysis.

ZONE 1			
Ramp Rate (^{0}C min.$^{-1}$)	**Target Temperature (^{0}C)**	**Dwell Time (min)**	**Purge Gas**
3	200	20	Air
3	300	20	Air
3	500	90	Oxygen
ZONE 2			
Ramp to 500^{0}C when Zone 1 reaches 500^{0}C			
ZONE 3			
Remain at 600^{0}C for run duration			

Table 3. HTO speciation pyrolyser method for tree core analysis.

ZONE 1			
Ramp Rate (^{0}C min.$^{-1}$)	**Target Temperature (^{0}C)**	**Dwell Time (min)**	**Purge Gas**
2.5	150	30	Air
ZONE 2			
No set temperature – intermediate zone between 150^{0}C and 600^{0}C			
ZONE 3			
Remain at 600^{0}C for entire run duration			

Table 4. NE-OBT speciation pyrolyser method for tree core analysis.

ZONE 1			
Ramp Rate (^{0}C min.$^{-1}$)	**Target Temperature (^{0}C)**	**Dwell Time (min)**	**Purge Gas**
5	600	60	Oxygen
ZONE 2			
Ramp to 500^{0}C when Zone 1 reaches 600^{0}C			

ZONE 3
Remain at 600^0C for run duration

After completion of total T, HTO or NE-OBT pyrolyser runs, 6 mL of the 0.1 M nitric acid bubbler solution was harvested and mixed with 14 mL of Perkin Elmer Ultima Gold LSC cocktail. For E-OBT measurements, 3 mL of sample water, collected after the 72-hour shaking period, was mixed with 3 mL of 0.1 M nitric acid, and 14 mL of Perkin Elmer Ultima Gold LSC cocktail. These samples were counted by LSC using a Perkin Elmer Tri-Carb Liquid Scintillation Analyzer (Quantulus ™ GCT 6220). The count times ranged from 50 to 450 minutes. The data were corrected based on the Ultima Gold quench curves and the Perkin Elmer ^{3}H standard (< 0.2 uCi, 281400 DPM, 10-Feb-2020, 89-TOL). The error on each LSC measurement was calculated using the formula for 2 Sigma % (%2σ) error (Eqn. 1) referred to in the Perkin Elmer LSC manual.

$$2\ Sigma\ \% = \frac{200}{\sqrt{accumulated\ counts}} \qquad \textbf{Equation 1}$$

This error represents the 95% confidence limit as a percent uncertainty of the total counts. This was applied to the Becquerel value of T gram^{-1} of sample (wet weight). The T activity calculations considered the dilution of T in the bubblers and a decay correction was applied to all the data to adjust for T decay; the oldest age of each core segment was used in this correction.

The reproducibility of the T concentration in tree cores could not be rigorously assessed because the measurement process is destructive, and no two tree cores were identical. There was also error in the year determinations for each core; some tree rings were easier to distinguish than others based on the environmental history of the area. The trees at the MWMF had tree rings that were extremely washed out and difficult to visually isolate due to ~20 years of irrigation. These features were noted in prior work.[18]

Results and Discussion

Figure 4 shows all the total T data from the various sampling locations around the SRS and surrounding area (Aiken County) along with the historical record of SRS

atmospheric T releases. Figure 4B shows the MWMF Old Evaporator samples plotted in comparison to other samples from around the SRS (Tinker Creek, R Canal, Par Pond and Aiken, SC) and Figure 4C shows data from MWMF plots 2 and 4 plotted in addition to irrigation amounts applied to plots 2 and 4 over the last ~20 years. The total T concentrations at all the locations sampled around the SRS increased with historic age and were marked by a peak in the 1960's – a time when nuclear releases of T were more prevalent at the SRS.[13] The trends in T levels in the tree cores did not correlate with other more global and country-wide trends in T inputs as shown in Figure 1; the peak in T for these samples is correlated with the T peak from SRS atmospheric releases. The samples with the greatest measured T concentrations were the ones collected at the MWMF during the last two decades. The MWMF is the sampling location that was nearest to the historical T releases (which were from mostly F and H area operations) and where, more recently, additional T contamination was introduced through T-rich groundwater irrigation. The T contamination that was found in the tree cores pre-2000 was due to the releases from F and H Areas whereas the T contamination post-2000 was dominated by the MWMF irrigation activities. Trees in the Old Evaporator location did not receive direct irrigation but the trees in plots 2 and 4 were irrigated. The MWMF Pond water used for irrigation contains on average 36.8 Bq mL^{-1} of T (with approximately 31% of the T being suspended OBT[18]). The water also contains low levels of RCRA- and CERCLA-listed contaminants with an average pH of 6 to 6.5, an average specific conductance of 30 to 40 μS cm^{-1}, and total $CaCO_3$ alkalinity of 3 to 9 mg L^{-1}. Additional MWMF pond characteristics are described in the supporting information of previously published work.[18]

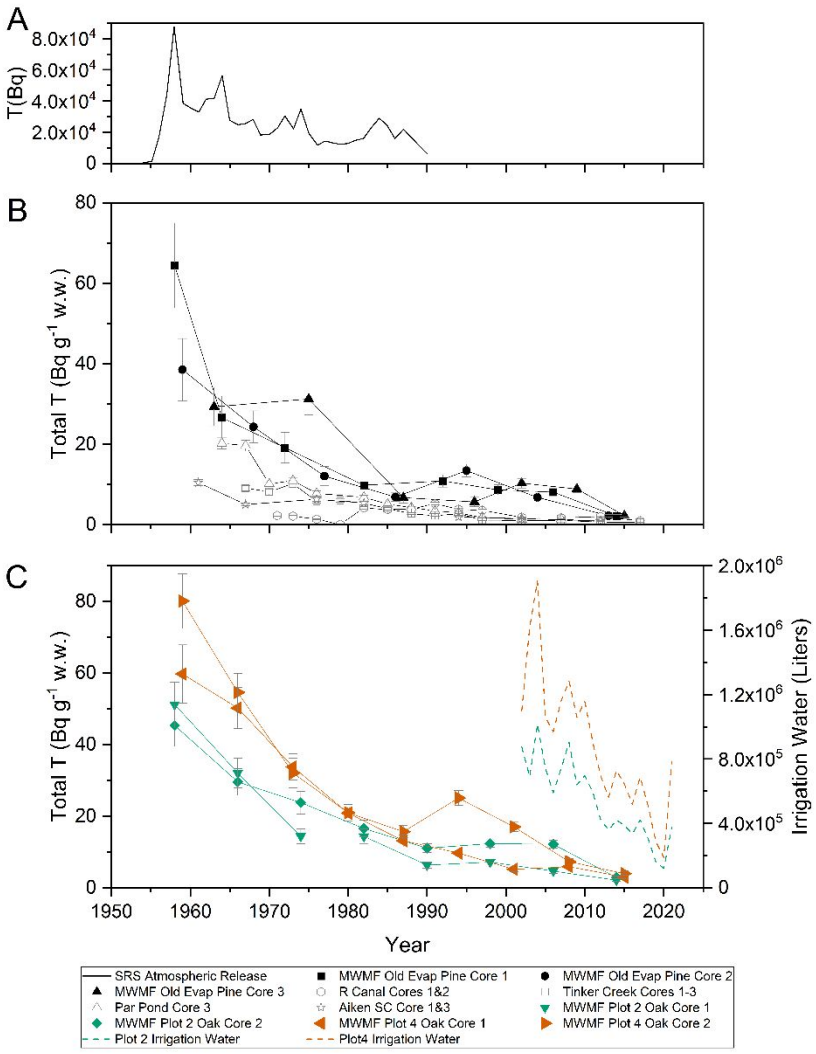

Figure 4. A) SRS atmospheric release of T over time.[13] B) Total T concentration in pine tree cores from around the SRS and surrounding area. C) Total T concentration in oak trees from the MWMF and the quantity of T-rich irrigation water supplied over the last ~20 years (personal communication from Andrew Thompson, U.S. Forest Service). Each data point plotted represents the oldest age of tree core segment.

The MWMF trees sampled from plots 2 and 4 for total T measurements were oak whereas the trees sampled from the Old Evaporator location were pine. This suggests that pine trees (also called a softwood) and oak can capture a historical record of T. The porosity of tree wood can define its ability to represent historic exposure to contaminants. Tree rings from a highly-porous wood do not preserve a reliable record of historic exposure while non-porous woods (all softwoods) can provide an ideal historic account of environmental exposure because the rings cannot exchange water or

other materials. Oak wood is ring-porous; other hardwoods can possess semi- or diffuse-porous structures and pine is non-porous.[20-22] Ring-porous hardwood trees have pores, and of all hardwoods, they should have the greatest propensity to preserve a historic account of environmental exposure. Figure 4B-C shows that the sampled oak and pine trees possess similar uptake behavior although the levels in the oak are considerably higher than that of the pine. Oak is generally a denser and slower-growing tree than pine; these two characteristics likely have facilitated its greater accumulation of T from atmospheric releases relative to that of pine.

The samples collected at other locations around the SRS (Tinker Creek, R Canal, Par Pond, and Aiken SC) have the lowest T concentrations and are the furthest away from H and F Areas. This is similar to the findings of the T from cellulose study[17] where the T concentration decreased with distance from H Area. There are other factors that could influence the T concentration at various distances away from the T source although we do not see a direct correlation of T with distance from H Area. This will be assessed in a future publication. The T concentrations reported in previous work[17] were also lower than those reported in this study. This was likely due to the different sample preparation techniques; wet chemistry techniques were used to extract cellulose from tree core material (comprising ~63% of the mass of a dry pine sample), followed by the combustion of the sample and measurement of the non-labile T and total T released by LSC. The method used in the current study is a more advanced technology that involved a small amount of wet chemistry, the ability to distinguish between E-OBT and NE-OBT, and the release of T from ~99% of the tree core sample mass by combustion.

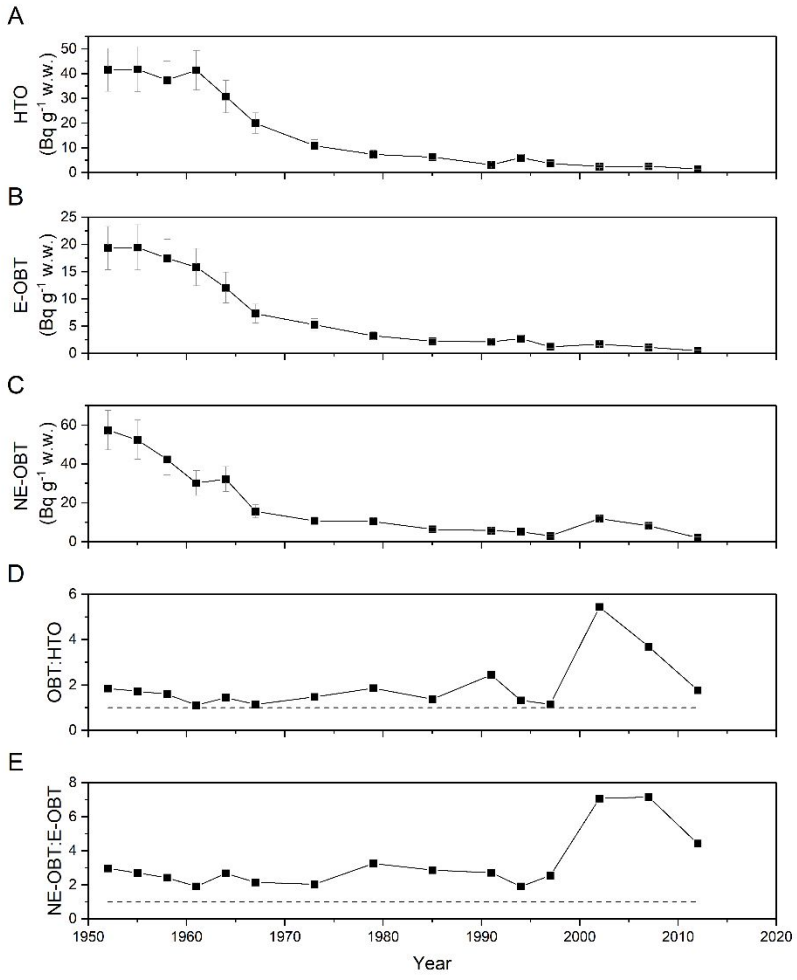

Figure 5. Tritium speciation data from MWMF plot 4 tree cores. A) HTO, B) E-OBT, C) NE-OBT, D and E) OBT:HTO and NE-OBT:E-OBT, respectively (dashed line denotes a 1:1 ratio). Each data point plotted represents the oldest age of tree core segment.

The T speciation data for a pine tree collected in plot 4 at the MWMF is shown in Figure 5. These data show similar behavior to the total T samples with a rise in T species with increasing time in history, especially in the 1950 to 1960's when nuclear activities at SRS were the greatest. The OBT:HTO ratio remain between 1 to 2 from the 1950's until the late 1990's. The data indicate that uptake and/or conversion of T in the form of OBT had occurred prior to 2000 in the MWMF trees (as shown in Figure 5) since the OBT:HTO levels generally exceeded 1.0 during these earlier years. After 2000, the OBT:HTO and NEOBT:EOBT ratios increase. This is during the time period when MWMF irrigation processes started and continue to date. Ratios of OBT:HTO as

high as 4.36 and NE-OBT:E-OBT ratios as high as 8.30 have been observed in MWMF tree cores in previous work and are corroborated here.[18]

The mechanism for OBT enrichment cannot be concluded in our study. Fievet *et al.* (2013) suggest a few reasons for a deviation from an OBT:HTO ratio close to 1, one of which is if a system under investigated has been perturbed, such as a T release event.[23] This suggests that the elevated anthropogenic T releases are the likely cause of the elevated T speciation ratios pre-2000, while the T in the irrigation water transpired by the trees as HTO and incorporated into the wood structure as OBT is the cause for T speciation ratios greater than 1 post-2000. It is clear from this data that the MWMF phytoremediation project goals of slowing T release into the environment have been successful, but some disadvantageous effects include the bioaccumulation of OBT in the MWMF trees. Elevated levels of OBT can be detrimental to the ecosystem and this concern will likely influence the selection of MWMF tree disposition approaches.

Conclusion

The SRS is an ideal location to study T recorded in tree cores due to the documented history of T releases over the last ~75 years as well as the on-going phyto-remediation efforts at the MWMF. Notable peaks in total T concentration were identified in the late 1960's through the 1980's, which was corroborated by the historical reports of T releases at SRS. The T speciation results indicate that OBT was retained in tree cores and accumulates over time especially when there is direct OBT and HTO addition to an ecosystem through irrigation. These findings are especially important when considering ecosystem effects from elevated T, disposition of trees and replanting with younger stock as well as understanding the historical events at SRS and around the world. Another data set is under development to provide a more complete historical record of tree T uptake at some of the lower level of contamination areas around SRS.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

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