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Influence of Tritium Exposure Route on Vegetation Types at the Savannah River Site

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Title: Influence of Tritium Exposure Route on Vegetation Types at the Savannah River Site

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Abstract

Plant, soil, water, and other media from various locations at the Savannah River Site were measured for total tritium (T) content and T speciation to characterize T in these areas, as well as investigate its uptake behavior and the transport of T species in these media. This characterization included the isolation and measurement of T in tritiated water (HTO), and (when possible) exchangeable organic bound T (E-OBT) and non-exchangeable organic bound T (NE-OBT). Two areas of interest were investigated: 1) a holding pond with T-contaminated water and 2) open basins or streams with low to background levels of T. Water in the holding pond is used to irrigate forest plots in the local area as a T remediation approach. This study compares the analytical data for water, soil/sediment, plants, and lichens from these locations. The results indicate that the behavior of T in plants from these areas can be a function of one or more of the following: seasonal precipitation, the plant's primary route of access to the T-contamination (such as water uptake through the root vs. shoot), plant physical location (relative to T-contaminated water sources), plant rooting depth, pond water level, and plant height above the ground. Total T concentrations were lowest in the un-irrigated forest plants, followed by irrigated forest plants, shallow rooting plants near the pond, deep rooting plants further from the pond, and then water-saturated plants. The OBT:HTO and NE-OBT:E-OBT ratios were always greater for plants from irrigated forest plots compared to those from the holding pond.

Environmental Significance Statement

Tritium (T) is an effluent from nuclear processes and anthropogenic activities and it is a biological hazard. Fusion reactors (once in operation) handle extremely high levels of T as HTO and there is some perceived risk of environmental contamination as a result. The findings provide information on impacts and environmental management options if an aqueous or atmospheric T release event from a fusion reactor occurs and reaches a water body. An improved understanding of how OBT and HTO move and are transformed in these locations will also provide information on biological risk.

Introduction

The anthropogenic production of tritium (T) presents some disposition challenges despite its short half-life of 12.3 years. Tritium is a biological concern to living organisms because it is an isotope of the essential element of hydrogen (H) and it is a beta radiation emitter. Environmental T is often defined as tritiated water (HTO), HT (gas), and organic bound tritium (OBT). These forms of T include HTO that is found in tissues and other matrices, tritiated methane gas (CH_3T), T-labeled drugs, amino acids, research chemicals, and OBT that is found in environmental media.[1] Tritium is a product of many nuclear processes that support electrical power, industrial needs, and anthropogenically mediated activities. It can be released from nuclear reactors, fuel storage and separation activities, nuclear weapons testing, nuclear waste sites, nuclear research, industrial T handling facility operations and potentially fusion power facilities.[2]

Fusion reactor facilities are under development. Fusion represents a “green” clean energy alternative to currently-used power sources, but they present a potential public health concern if they reach a level of maturity where they become widely used for global power production.[3] Tritium is the most abundant radionuclide released from fusion reactors.[4] It is not easily confined and it readily diffuses through materials. This is subject to inadvertent releases from handling, research, nuclear power and processing facilities.[2,3] Regulations restrict routine releases of airborne T to 3.7 to 7.4 x 10^{12} Becquerel (Bq) Ci of HTO day^{-1} for a boundary at 1 km from a fusion reactor.[5] An analysis of reference accidents has also been studied for the International Thermonuclear Experimental Reactor (ITER) that include primary source terms and environmental release guidelines.[6] In contrast to a base case estimate of T released from ITER (a ~500 Megawatt fusion reactor) during normal operations (1.8 x 10^{13} Bq Ci yr^{-1} as HTO)[7], potential accidents ranged from operational events (“Cat I” with 3.8 x 10^{14} Bq T as HTO $event^{-1}$) up to extremely unlikely sequences (“Cat IV” at 3.6 x 10^{16} Bq T as HTO $event^{-1}$).[6] Some T that is released will decay, while some T will accumulate and persist in the environment. It is conceivable that nearby surface water bodies, such as ponds or rivers will inadvertently or intentionally be contaminated from fusion and other T-related accidents.

Tritiated water is a biologically important form of T because water is common to all types of life. Water is found throughout the terrestrial and atmospheric environment. Tritiated water can move in the environment via wet/dry precipitation (with dry being precipitation that loses its water content before reaching the ground), in soil by diffusion, within biota, and within water bodies.[1,9] Tritium can isomorphically exchange with H in sediments containing kaolinite and montmorillonite clays as interlayer and outerlayer.[8] The exposure of biota to HTO-rich water sources also has considerable potential to allow exchange due to dilution of H_2O with HTO within the living and growing organism that are exposed when equilibrium conditions are met.[10] The microbial conversion of HT to HTO in soil is a process that allows for the re-entry of HTO into the atmosphere where more biological interactions can occur.[9,10] Organic-bound T can become bioaccumulated in HTO-rich environments, when in the case of plants (including algae, moss and higher plants), HTO can be converted to OBT through photosynthesis reactions.[11] Isotopic effects that favor the uptake of stable H_2O over HTO in the form of organic bound H should be noted.

Organic bound T is the sum of non-exchangeable OBT and exchangeable OBT in the present study. Non-exchangeable OBT includes T that is chemically bound to carbon (C), whereas exchangeable organic bound T (E-OBT) includes T that is weakly bound to oxygen (O), sulfur and/or nitrogen (N).[12] Exchangeable-OBT is considered to be more labile (i.e., exchangeable or more subject to displacement by other compounds) than NE-OBT in the environment. Exchangeable T in OBT is determined analytically by exchanging H from T-free “dead” water (i.e., groundwater that is geologically very old and nearly void of T due to radioactive decay) in a sample for 3 days after all forms of water (including HTO) have been liberated from the sample through heating of the sample to 150 deg C in a purge gas of air.[13] There is a type of OBT that is bound in an exchangeable form but it is not highly mobile because it is found in high molecular weight biomolecules that are present in dried matter. This form of E-OBT is often called “buried T” but it does not exchange with H in T-free “dead” water.[14] Boyet et al. (2009) and Diabate and Strack (1993) present an extended discussion about OBT forms and their incorporation and movement in biota and the environment.[11,15]

Tissue free water tritium (TFWT) in environmental material will be referred to in this manuscript as HTO; OBT will be delineated as E-OBT or NE-OBT when the analytical results support the assignment of NE-OBT (with a very small contribution of buried T) and/or E-OBT; otherwise, "OBT" will collectively denote all types of OBT. The behavior of OBT often impacts biological organisms when elevated levels of T are allowed to persist over time in the environment.[16,17,18] Microbial and other biological processes such as the deposition and absorption of T-containing bioaerosols on plants, can contribute to the uptake of T and conversion of HTO to OBT and these processes can influence the OBT:HTO ratio in biota.[19,20,21] The release of excreta which can be tritiated can be transferred and consumed by other living organisms that are part of the food chain in effluents from nuclear facilities.[11]

The Savannah River Site (SRS, Aiken County, SC) has a history of nuclear activities that involve T and its consequential legacy contamination in the environment. The presence of contamination at the SRS provides an opportunity to study the behavior of T and its speciation in the environment. Previous work on T releases and contaminant levels in SRS vegetation and other environmental media was published and reviewed by others.[22,23,24,25,26,27] Several of these works highlight the importance of OBT, as well as HTO, on T accumulation environment but more information is needed to explain the behavior of OBT and HTO in T-contaminated environmental systems. An improved understanding of how OBT and HTO move and are transformed in the environment will provide information on biological risk and support more informed T contamination response.

The primary focus of this study was on environmental samples collected at the Mixed Waste Management Facility (MWMF), which is a 25-hectare area within the SRS. It is managed by the U.S. Department of Agriculture's (USDA) Forest Service, with old and new growth forest vegetation that are 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. Tritium-rich seepage water has been collected in a holding pond and used to irrigate plots of old natural forest growth, as well as more recently-planted loblolly pine trees, since 2001. The T-rich water comes from a nuclear waste burial ground, which contains a variety of waste forms including T-rich absorber rods.[26] The intended phytoremediation path for T at the MWMF is to slow the release of environmental T via the irrigation of pine trees with T-contaminated water.[25,26,27]

This study was performed to: 1) measure the total T levels in materials from the highly contaminated (MWMF) pond and surrounding area including plants, lichens, water, and sediment, 2) make measurements of T speciation (HTO, E-OBT and NE-OBT) in the MWMF samples and a small selection of samples from three other SRS areas with considerably lower exposure to T contaminated waters, and 3) determine the likely reasons for the behavior, uptake and transport of T species in the plants and other sampled biological materials. We also examined how various routes of T exposure (via pond water irrigation vs. direct pond water exposure, for example) impacts the T speciation, as well as the OBT:HTO and NE-OBT:E-OBT ratios in the sampled materials. We anticipated that the MWMF pond and neighboring (unirrigated) vegetation would have elevated levels of OBT relative to HTO due to 20 years of consistent exposure to tritiated seepage water contamination as well as aerial inputs of T where irrigation was occurring nearby but not directly. This study identifies factors that influence T speciation and T accumulation from a nearby T-contaminated environment relative to an uncontaminated (mostly T-free) environment.

Methods

This investigation is focused primarily on the T-contaminated MWMF pond and to a more limited degree, three SRS areas with lower-level T contamination: Tinker Creek (TC), R-Canal, and the north arm of Par Pond (**Fig. 1**).[23] The source of T in the MWMF pond water is primarily ground water seepage from the Low-Level Radioactive Waste Burial Ground at SRS. This burial ground received an estimated 1.56 x 10^{16} Bq of T in 1988.[23] One of the low level contamination areas is TC, which receives water inputs from outside the SRS. Tinker Creek is considered to be a background area for water and biota comparisons with the MWMF due to the absence of T contamination. Tinker Creek is a fast-moving stream with water that comes from outside the SRS. It is fairly remote in terms of impact from nuclear facilities. The other two areas (R-Canal and the north arm of Par Pond) were subject to T inputs from SRS reactor operations that occurred several decades ago. The third sampling location was R-Canal which is a narrow, heavily-wooded canal that received cooling waters from the former R-reactor during operation from 1958 to 1964. It was dismantled and decommissioned in 2011. The fourth sampling area was Par Pond, which is a large manmade reservoir that has some floating marshes. This reservoir received reactor cooling waters from P- and R-reactors, which were in operation several decades ago.[24] Soil from an uncontaminated area that was 32 km from SRS in Aiken County, SC (**Fig. 1**) was also included in this study.

Environmental media were collected in plastic bags (for plants, lichens, soil and sediments) and plastic or glass bottles as noted (for water) from four locations in the SRS area (**Fig. 1**) in 2021 and 2022. Plant samples were taken of above ground portions unless noted. The plants that were available at these locations varied with season, proximity to the pond and the pond water level. It was not possible to sample the same plants throughout the year. This was due to changes in season (winter vs. summer), water levels, rain precipitation and/or other influences which impacted the dynamics of plant growth and prevalence throughout the year. A detailed description of the wetland and non-wetland plants that were sampled is provided in the **Supplementary Information (SI)**.

Soil and sediment samples were taken from the upper 5 cm of surface material. A few samples were taken from areas with low levels of known T exposure, but most of the samples were from various locations within the MWMF. Most samples were acquired in the mid-morning to early afternoon. The samples were stored in a -80^{o}C freezer until time of analysis. The **SI Figure 1** illustrates the T-rich groundwater plume migration from the burial ground complex to the MWMF sampling locations for this study, including: Plots 4, 33, and 43, Plot 43 ditch, the MWMF pond and its neighboring Old Evaporator area.[25,26] The Plot 43 ditch is a drainage area between Plots 4 and 43. Our sampling area within that ditch is noted on **SI Figure 1**. The Old Evaporator is the former location of a mechanical evaporator that was used for over a decade to mobilize T from the pond water into a vapor form during the MWMF operation. Soils at the SRS are predominantly well-drained, sandy, and have less than 2% organic matter. These soils have a high permeability which makes them ideal for growing timber and supporting the pine trees that dominate the area. These soils are members of the Fuquay-Blanton-Dothan Association.[28] The soil that was taken from northern Aiken County background location is closely related to the SRS soils that are part of the Dothan and Fuquay Series so it is related to the SRS soils.[29]

Unfiltered water samples from the MWMF pond and TC were collected, as well as waters filtered with 0.8- or 0.2-µm polyether sulfone membrane filters. Some waters, as noted in the reported data, were syringe-filtered with 0.45-µm cellulose acetate filters upon collection.

Filtering was completed to assess the impact of filtration on T activity. The storage of waters in plastic and glass was briefly investigated.

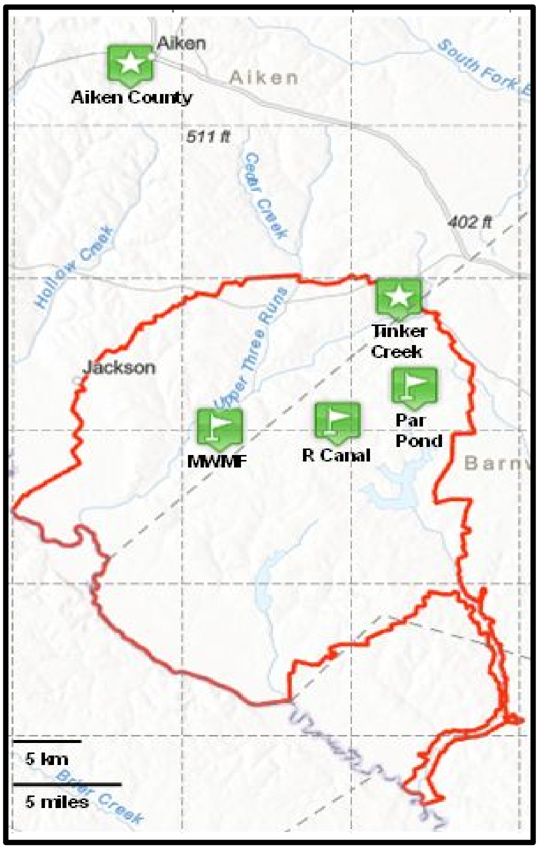

Fig. 1. A map of four SRS sampling locations and one offsite location. Green stars: Uppermost star is Aiken County and lower star is Tinker Creek (TC) and these are uncontaminated areas. Green flags (from left to right): the MWMF, R-Canal and Par Pond. R-Canal and Par Pond have low level T contamination, whereas the MWMF has some areas with high- and low-level T contamination. Please see SI Table 1 for latitude and longitude information for the sampling locations.

The extraction of T (HTO, E-OBT, NE-OBT) from the samples was completed using a Raddec Pyrolyser-6 Trio combustion furnace (Southampton, UK) equipped with three separate furnace zones and can accommodate six different samples at a time. Plant, lichen, surface organic matter, soil and sediment samples were prepared for analysis in triplicate as approximately 0.5 to 0.9 gram (g) samples. One milliliter (mL) volumes of the water samples were added to a 1-g mass of high purity silica sand support and analyzed in triplicate. The prepared samples were placed in glass boats that were inserted into the cold end of the furnace work tubes. These work tubes were pre-loaded with 10 g of platinum-coated alumina catalyst pellets (in the hot end) to ensure the combustion and recovery of all the T in the attached T bubbler traps. Each of the bubblers were filled with 20 mL of 0.1 M trace metal grade nitric acid to capture the T released from the plant, water, soil, and sediment samples. The catalyst was changed out and pre-conditioned in an air stream after every 20 oxidative combustion furnace runs. Sample boats were cleaned after each run with DI water, Decon-90 soap (Decon Laboratories Limited, East Sussex, UK), and ethanol wipes. The bubblers were rinsed with MilliQ water and allowed to dry in between use. The total T, HTO and NE-OBT speciation methods are described in Pettitt et al. (2022; 2024) and also shown in **SI Tables 2, 3** and 4.[25,27] After the HTO pyrolyser run, the E-OBT was recovered by extracting the T from the HTO run sample product (in T-depleted water).

Six mL of bubbler solution was added to 14 mL of Perkin Elmer (PE) Ultima Gold (UG) LSC cocktail—after completion of all of pyrolyser runs except for those where E-OBT was being measured. For those samples, three mL of 0.1 M nitric acid was added to 3 mL of sample water after a 72-hour period on an orbital shaker. A 14-mL amount of UG was then added to the 6-mL mixture for the E-OBT measurements. All sample were counted by LSC with Tri-Carb Liquid Scintillation Analyzer (Quantulus™ GCT 6220, PE). Count times were 50 to 450 minutes. Most MWMF pond biota, sediment and water samples required 50-minute count times due to their elevated T levels (roughly 10-fold more than the other SRS area samples) and the remaining samples were run for 450 minutes due to their relatively lower T levels. This approach allowed the measurements to achieve similar numbers of counts per minute. The LSC data were corrected based on the UG quench curves and the PE ^{3}H standard (<7400 Bq, 281,400 DPM, 10-Feb-2020, 89-TOL). Decay corrections were applied to the data. The UG and 6 M nitric acid blanks in 20-mL plastic scintillation vials had an average of 0.68 ± 0.01 Bq for a 450-minute count time and 0.602 Bq ± 0.12 Bq for a 50-minute count time.

The error on each LSC measurement was calculated using the formula for 2 Sigma % (%2σ) error (**Eqn. 1**) referred to in the PE LSC manual.[30]

$$2\,Sigma\,\% = \frac{200}{\sqrt{accumulated\ counts}}$$ **Equation 1**

This error represents the 95% confidence limit as a percent uncertainty of the total counts. This was applied to the Bq value of T g^{-1} of sample [wet weight (w.w.) or in the case of water, volume]. The T activity calculations considered the dilution of T in the bubblers.

Total dissolved C as well as organic and inorganic C in the MWMF pond and other SRS water samples were analyzed in triplicate with an XPERT C and N analyzer (Trace Elemental Instruments, Houston, TX USA). Standards of dissolved inorganic C (made from sodium carbonate) and organic C (made from potassium hydrogen phthalate) in water were used to calibrate the instrument.

Results and Discussion

Total T in Waters

Figure 2 shows all the total T data for various waters from the sampling locations as initially shown in **Figure 1**. Waters from TC had slightly lower levels of T than those of R Canal and Par Pond, whereas the water from all MWMF samplings had highly elevated levels of T. The levels of T in Par Pond and R Canal were probably higher historically, but considerable time has passed since there were sizable inputs of T and there has been enough time for the T to undergo several half-lives of radioactive decay. Some dilution of the T in these waters is also to be expected due to precipitation events in the sub-tropical SRS area.

The influence of water filtration on T activity was fairly minor; unfiltered (UF) TC and MWMF samples had approximately the same T levels as filtered samples (**Fig. 2**). This indicates the T in these waters exists primarily as a dissolved form as opposed to a particulate form–within the error of the triplicate sample measurements. Sampled waters that were taken directly from the laboratory MilliQ water purification system before processing had the lowest average levels of T as expected. The potential impact of glass (G) versus plastic (P) sampling bottles on the levels of T in the MWMF waters was also investigated with a small number of measurements. The results revealed little measurable differences in total T between the different storage medium that was used.

The irrigation sprinkler heads at the MWMF become intermittently fouled with black organic material called riser water. The sprinkler heads must be cleaned periodically to permit adequate function. Samples of this foulant material contained similar T levels to that of the MWMF pond, which was the irrigation water source (**Fig. 2**).

Levels of T in R-Canal water were slightly higher during spring relative to summer (**Fig. 2**). The amount of precipitation in the summer at the SRS can be quite high. The precipitation was more than 53 cm between June and August 2021 and down to 19 cm between October and December 2021, for example.[27] This elevated precipitation could result in the seasonal dilution of T water levels relative to months when precipitation and the temperatures are lower.

The MWMF pond waters have higher T in winter relative to other months (**Fig. 2**). The amount of precipitation is lower during the cooler months so the pond water is less subject to dilution from rain. The water levels had also dropped by more than 2 meters (m) from May 2021 to October 2021. Irrigation water use at the MWMF is lower in the winter due to smaller water deficits in the cooler months. This practice may keep the T levels higher in the pond in the winter months because less tritiated water is being removed for irrigation. Surface runoff from the MWMF forest (a particular problem due to road washout) was successfully diverted from entering the MWMF pond during the middle of our sampling program (in fall 2021) and this also was another contributing factor to the decreases in pond water level. The pond irrigation continued year-round throughout the majority of MWMF plots, with the exception of Plot 43 which was not watered between January 2020 through July 2021 (personal communication from Andrew Thompson, USDA Forest Service).

The MWMF pond water that is used for forest irrigation typically has 36.8 Bq mL^{-1} of T. This water also contains low levels of RCRA- and CERCLA-listed contaminants from more than 10 years of routine sampling, has 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}. These and other MWMF pond characteristics were described previously.[26]

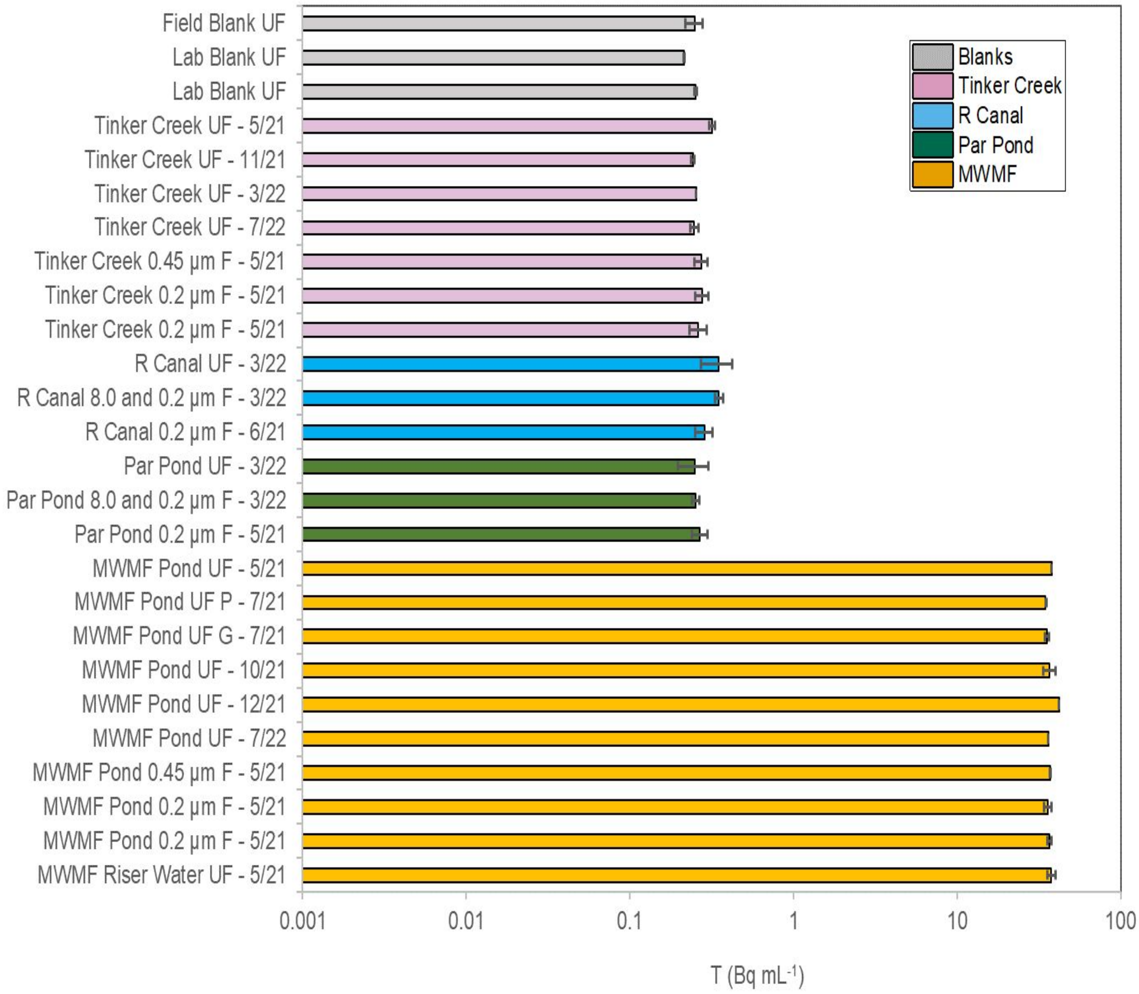

Fig. 2. A log plot of the total measured T from the total combustion of water samples. F: Filtered; UF: Unfiltered; P: Plastic; G: Glass. Sample names that are listed twice on the X-axis are those that were taken as two separate samples in the field or in the lab although they were analyzed in triplicate. Month and year of sampled collection are represented with a backslash. For example, 10/21 would represent October of 2021.

Total T in Sediment and Soil

SI Figure 2 shows a plot of the total measured T in soil, sediment, and organic matter from the sampling areas. The soils from Plots 33 and 43 at the MWMF had low levels of total T relative to the pond sediment. Plot 43 was not irrigated in 2020 through July 2021 due to the construction of a new building. Plot 4 has been in operation since the MWMF began irrigation and it is an old growth forest of oak and pine. Plot 33 has been under irrigation since 2011 (with trees planted in 2008), which is two years longer than that of Plot 43 (planted in 2013); but regardless of the irrigation schedule, the total soil T levels were quite similar. This suggests that the forest soils that have been irrigated for longer periods of time (like Plots 4 and 33) do not accumulate more T despite their multiple years of exposure. This may be due to the evaporative loss of added T (as HTO) to sandy soil and air into the atmosphere, the uptake and evaporative loss of HTO by tree transpiration, and the assimilation of OBT by the pine trees.[26] Trees are the dominant vegetation by mass in these plot areas, so they are likely to impact the behavior of the added T.

The soils from outside the SRS boundary had slightly lower T levels than that of the irrigated plots, and similar levels to Plot 43 ditch soils at the MWMF (**SI Fig. 2**). This is somewhat expected because these Plot 43 ditch soils have not had the direct exposure to T from MWMF pond water irrigation. It is possible that the Plot 43 ditch receives some HTO water vapor from other, nearby irrigated plots (which exist on both sides of the ditch) and this is the source of increased T contamination. These contributions are due to legacy contamination that causes the T levels in the MWMF soil to be above the background levels of the TC and Aiken County areas. All of the forest soils in this study have similar characteristics. They are sandy, well-drained, and are somewhat low in organic matter so differences in soil characteristics may not always contribute to differences in T contamination or T speciation. Isomorphic substitution of T in kaolinite and montmorillonite clays as interlayer and outerlayer H can occur. This form of clay-associated T is resistant to combustion at the temperatures that were used in this study.[8] It may have not been recovered at our combustion temperature of 600 ºC (instead of 800 ºC which is more optimal for clay-associated T combustion) and could be underestimated in the soil and sediments in this study. Additional studies would be needed to evaluate the magnitude of this possibility.
The sediments from the MWMF pond had very high levels of T (**SI Fig. 2**) compared to the T levels of the other sampled soils (a few 3.7 Bq g^{-1} relative to a less than 1 Bq g^{-1}). The sediment with the highest T levels was from the pond location that primarily receives T-contaminated seepage waters (USDA Forest Service, personal comm.). The other two areas sampled at the MWMF pond periphery also had high levels of sediment T, but not as much T as the area where seepage enters. Organic matter that was obtained from Plot 4 had elevated T relative to that of the MWMF plot soils, which is expected due to the ways T can be incorporated into organics and the abundance of sandy soils in the various MWMF plots.

Total T in Plants

Data for total T levels in the plants sampled are shown in **SI Fig. 3**. Most of the plants that were located on the upper elevation of the MWMF pond edge generally had low levels of T relative to that of the plants submerged in the pond or near the pond edge in water-saturated sediment. The plants that had higher levels of T were pond lily (*Nymphaea*), wild millet (*Echinochloa* spp, with a 1-m rooting depth), and moss (which grew in wet sediment on the edge of the pond), whereas other plants near the pond edge that had lower T levels were water hyssop (*Bacopa carolina*), *Juncus*, *Cyperus*, and *Vitus* (wild grape). *Bacopa*, *Juncus* and *Cyperus* are shallow-rooting plants (with rooting depths of 30 cm or less) and the grape plants were located several m away from the pond. Their levels of total T were low, and this is likely due to their shallow roots which give them limited physical access to T-rich MWMF pond water despite their proximity to the pond. Millet had fairly high levels of total T. This plant was not close to the pond water edge although its deep roots most likely provided it with pond water access.

Pond Lily, which is an aquatic plant at the MWMF, had particularly high levels of T that were almost equal to the levels of total T in the MWMF pond water. There were some possible seasonal influences on total T activity in the pond lily. The pond lilies that were sampled in May of 2021 had T activities that were more than twice that of the plants that were sampled in October 2021. The pond plants (*Bacopa* and *Juncus*) that were sampled in May 2021 also had higher T activities than those that were sampled in October 2021. The pond water during these two months in 2021 (**Fig. 2**) had similar T activities, but the pond water level was clearly more than 2 m lower in October through December relative to May in 2021.

Spanish moss, which is an aerial epiphyte that grows mostly on trees (at waist height or much higher), had measured total T levels that were slightly higher at the MWMF pond relative to TC (**SI Fig. 3**). This suggests that T water vapor in the MWMF pond air space probably contributes to the tritiated moisture in the aerial Spanish moss at the MWMF. It is also possible that the HTO from plant respiration also contributes to T levels in the Spanish moss. The TC vegetation had much lower levels of T than that of the MWMF areas.

Total T in Lichens

The **SI Figure 4** shows data for total levels of T in lichens. Lichens are a mixture of two species: an alga (or cyanobacterium) and a fungus. They can exist on a variety of living (on the bark of a tree, for example) and non-living media (such as metal, steel, rock and wood). Lichens were sampled from the dock (made of steel and wood) of the MWMF pond, as well as from surface soils around the SRS. Lichens at the MWMF forest areas had higher levels of T than those at Par Pond. Lichens that were collected from near the MWMF pond surface had the highest levels of T. The lichens from the MWMF pond dock and pond edge constantly receive T from moisture in the air above the pond, as well as from the air of the neighboring irrigated forest. The levels of total T in the lichens at the MWMF pond in May 2021 were much higher than that of similarly located lichens (in terms of sampling area) in November and December of 2021 when the water levels were more than 2 m lower (**Fig. 2**). These higher levels are probably due to the greater proximity of the T-rich pond water, which provide more potential for HTO exchange and interaction with lichen tissue. Daillant et al. (2004) review several processes by which lichens can remove T, minerals, and other radionuclides from their environment.[31]

The levels of total T in the lichens from the forest Plot 43, Plot 43 ditch and Plot 43 road showed a different seasonal trend than the lichens near the MWMF pond (**SI Fig. 4**). The lichens that were sampled in the Plot 43 ditch and road in the winter of 2021 had higher levels of T than the lichens that were sampled during July and May of 2021. These high T levels are probably due to the resumption of irrigation in plot 43 and its neighboring plots in August 2021. The levels of T in lichens from the Plot 43 ditch were higher in July 2022 than in July 2021.

The levels of T in the lichens were greater than that of Spanish moss (another aerial plant) from the MWMF pond area (compare **SI Fig. 3** with **SI Fig. 4**). The Spanish moss at the pond was sampled at a height of 0.5 m or more, unlike the lichens that were sampled from the ground or MWMF pond dock. The above ground elevation of the Spanish moss provides less exposure to MWMF pond water than that of the pond lichens that were found on the ground near the pond water. A concentration gradient for tritiated moisture in these areas and the rapid equilibration of HTO in these tissues[23] is expected and could cause these differences in T tissue levels. The concentration of T decreases with increasing distance from the ground surface.[23]

Total Dissolved Organic and Inorganic C in Pond Water

Total dissolved organic and inorganic C were measured in the MWMF pond waters to examine whether there were any changes in dissolved C speciation over time. The evaporation of the MWMF pond and the diversion of overflow water coincided with a substantial increase in soluble total organic C as shown in **Fig. 3.** This enrichment of organic C could favor the accumulation of organic C that is rich in T.

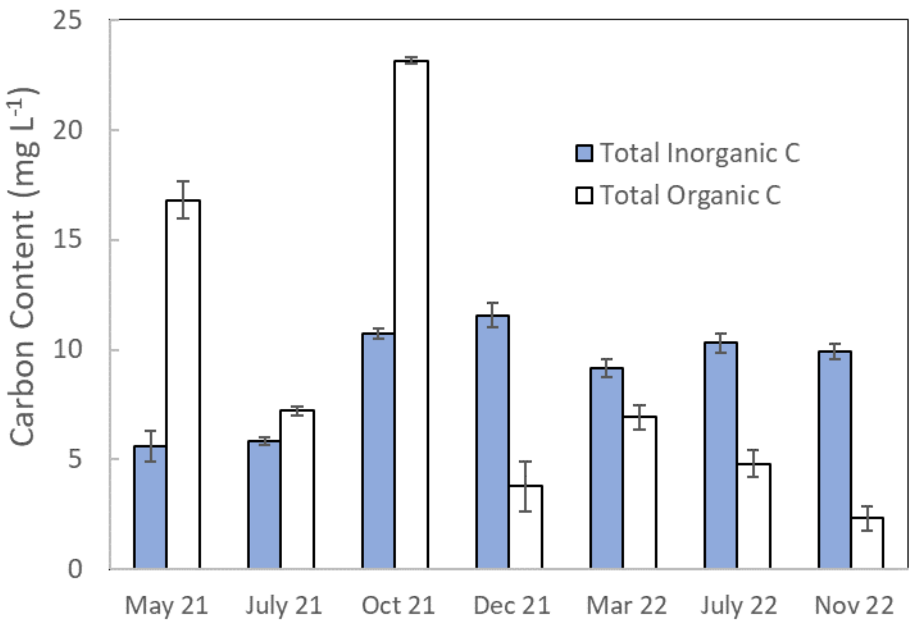

Fig. 3. A plot of the total inorganic and total organic C data for the unfiltered MWMF pond water samples from the dock. These waters were stored in plastic until analysis.

Tritium Chemical Speciation in Pond Water

The speciation of T was determined in several of the samples for which total T measurements were also made. Only two species of T in the pond water samples (total HTO and total OBT) were determined because NE-OBT and E-OBT could not be distinguished from one another with our method. The ratio of OBT to HTO (OBT:HTO) in the pond water (**Fig. 4**) appears to show a seasonal trend; the OBT:HTO ratio is greater in winter than in spring and summer. The March 2021 OBT:HTO ratio is also greater than that of July, which suggests that the high seasonal summer precipitation dilutes the pond water OBT:HTO ratio. There is less precipitation and more enrichment of OBT relative to HTO in the cooler winter month of October. The water level during March and July was typically at 2.3 to 2.4 m but in October, that level had dropped to less than 1.4 m. The USDA Forest Service diverted a large amount of surface runoff flow that was coming into the pond in the fall of 2021. This effort kept the pond water level lower than normal during late 2021 and into 2022 as well. This suggests that evaporation of HTO during these warmer months may have also caused some concentration of OBT.

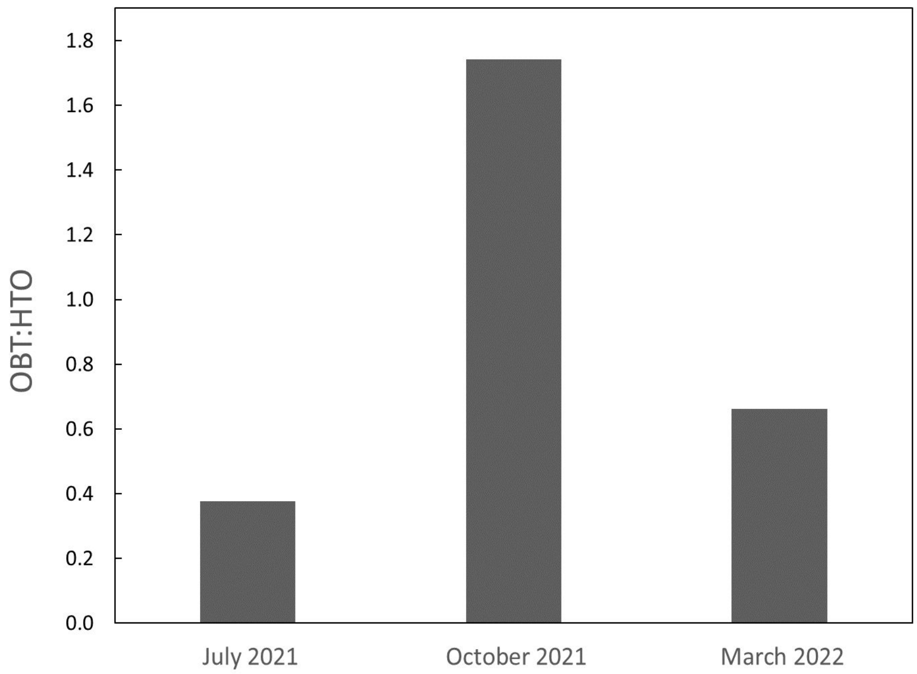

Fig. 4. A plot of the T speciation data for the unfiltered MWMF pond water samples from the dock. A 50 Bq T mL^{-1} pond water with an OBT:HTO ratio of ~0.4 would have 10 Bq T mL^{-1} as OBT. A pond water with an OBT:HTO ratio of 1.7 would have about 31.5 Bq T mL^{-1} as OBT.

The total T that was measured in the MWMF pond sediments was compared with the sum of T species that were obtained through separate HTO, E-OBT and NE-OBT measurements (**Table 4**). There are slight discrepancies between total measured T and the sum of the species; the sum of the analytically determined T species was consistently less than the measured total T. This could be due to sample heterogeneity or large differences in water content. We avoided homogenizing the samples because of the potential to lose T as HTO vapor to air. The OBT:HTO ratios in the July 2021 sediments were extremely low because HTO was the dominant T species in these sediments. This finding is rather consistent with low levels of pond water OBT:HTO that were observed in the summer when precipitation was greater than in the winter and early spring (**Fig. 4**).

One potential route of how NE-OBT, E-OBT and HTO enter and move through the MWMF pond could be proposed. It is known that the T-contaminated seepage enters the MWMF pond near the pond lilies and some seepage enters across the pond near the old evaporator. The total amount of incoming OBT is very low relative to that of HTO from the burial ground seepage (compare **SI Fig. 3** with **SI Table 5**). The NE-OBT:E-OBT ratios for the July MWMF pond sediment samples from these seepage areas are lower in NE-OBT relative to E-OBT. This small pond, in terms of physical mixing or boat activity, has been a fairly undisturbed water body throughout our sampling activities. There may be an impact of distance in the pond where NE-OBT has the opportunity to form over time and deposit in the sediments at greater distances from the T seepage source through biological activity. Another potential impact on this ratio could be that the pond intake for irrigation is nearer to the dock than the other two areas but no explanation can be provided (based on our current information) for the greater NE-OBT:E-OBT ratio in the sediments near the dock. More information about the groundwater seepage characteristics is needed to assess these potential explanations more adequately.

Tritium in Plants: E-OBT and HTO Relationships

The total T and T-based speciation data for the MWMF and TC plants are shown in **SI Table 6**. The total T obtained from complete combustion compared well with the total T obtained from the sum of the speciation in only a few cases. The standard deviation (SD) values for the sum of the T species in the plants were typically larger than the SD values from the total T determinations through combustion. The plants that were growing submerged in the MWMF pond (such as pond lily), growing on the MWMF pondwater edge, or with deep roots (like millet) but grew near the pond had much higher T than the other plants in this study. The T measurement data for these plants resembled that of the pond sediment total T data because they also have elevated total levels of T that are dominated by HTO relative to OBT (compare **SI Tables 5** and **6**). The results in **SI Table 6** present a somewhat unexpected case in which HTO is the dominant species of T in plants that are exposed to large amounts of (pond) water with OBT:HTO ratios from 0.4 to 1.7. This relationship is most easily observed in **Fig. 5** where the plants that are not in direct contact with MWMF pond water tend to have higher OBT:HTO ratios than those that are in pond water contact. This includes the aquatic plants in TC.

These observations suggest that the plants in direct physical contact with MWMF pond water do not have the capacity or preference to assimilate/retain the OBT that they are exposed to. This observation is in contrast to plants that bioaccumulate and retain more OBT relative to the HTO that they encounter—as in the wood of irrigated MWMF pine trees, in lichens (present study) and other plants.[11,26] The OBT in the pond water is not greatly impacted by post-collection filtration, so the OBT is in a dissolved and potentially bioavailable form. Further studies on the chemical behavior of organic compounds in the plants, MWMF pond, as well as the pond seepage water, could provide a more through explanation for these observations.

The plants that were sampled further away from the pond, such as those from the Plot 43 ditch, MWMF forest and the old evaporator area had mostly lower levels of total T than the plants in or at the pond edge (**SI Table 6)**. These plants also had OBT:HTO ratios that were near or greater than 1.0 and higher than those of the MWMF pond plants (**Fig. 5**). The irrigated MWMF forest plants had low OBT:HTO ratios (being equal or less than 0.5) which suggests that their repeated exposure to T from pond water irrigation results in above background levels of T accumulation and most of that T is present as HTO (**SI Table 6**). The TC plants, the MWMF Spanish moss (an aerial plant) and the Plot 43 ditch plants all had OBT:HTO ratios near or above 1.0 (**Fig. 5** and **SI Table 6**). The plants that were not irrigated and aerial plants that live above the irrigation zone, like Spanish moss, all had OBT:HTO ratios near or greater than 1.0. Plants that had more contact with the pond water through irrigation or direct immersion had OBT:HTO ratios that were 0.5 or less—with submerged aquatic plants having OBT:HTO ratios of 0.1 to 0.3.

Ota and colleagues (2012) concluded there should be greater assimilation and conversion of HTO to OBT in shallow soil rooting depths as opposed to deeper ones.[32] Their observations include HT deposition from the air, the oxidation of HT to HTO by H_2-oxidizing microbes, and the ultimate conversion of HTO (that is removed by plants) to OBT. This rooting relationship pertains to a T source that enters from above the soil as opposed to the current study with MWMF pond plants, which obtain their T from water saturated sediments or direct immersion with MWMF pond water.

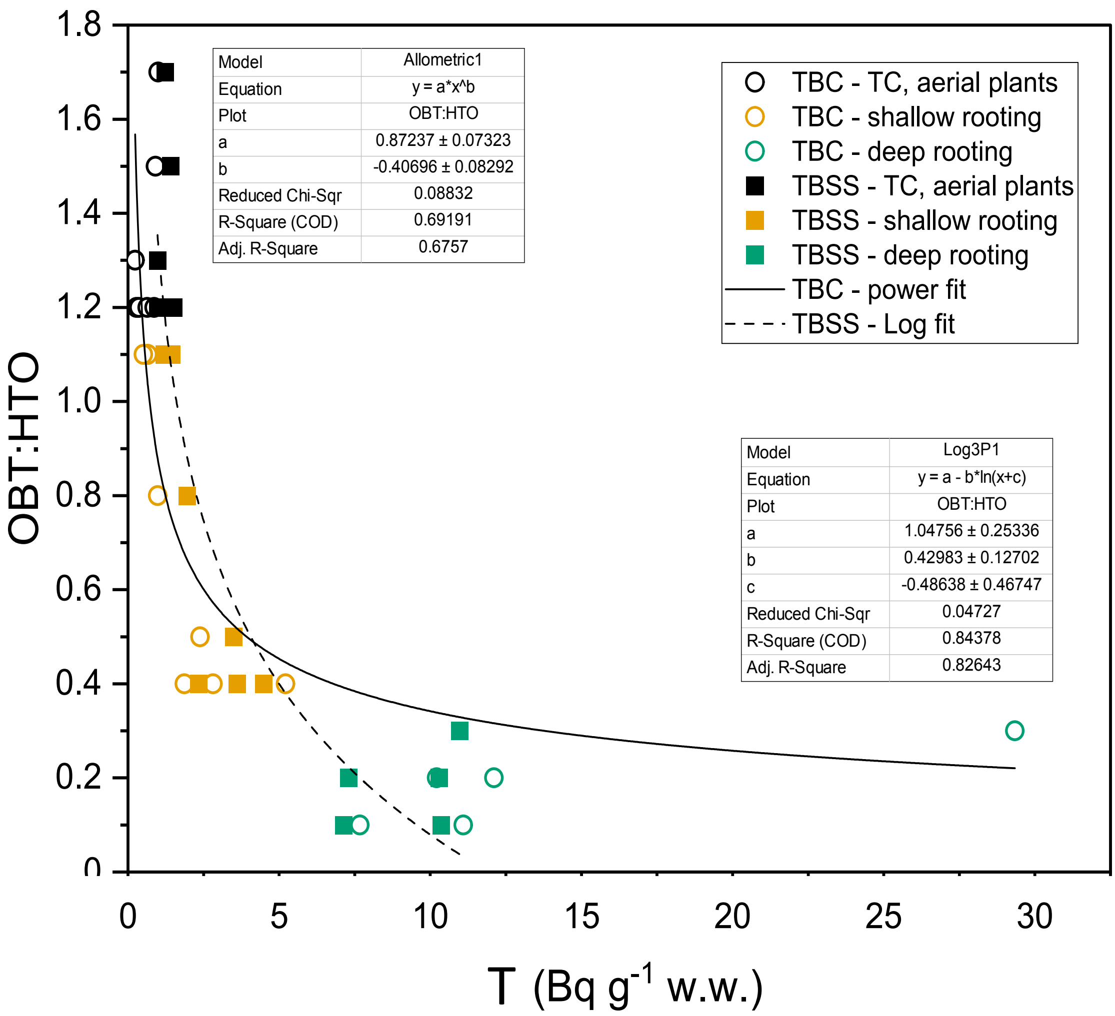

Fig. 5. Plot of OBT:HTO ratio vs. total T or sum of T species for SRS plants. The black filled and outlined data symbols (upper left) represent relatively uncontaminated plants from TC, aerial plants (Spanish moss) from multiple locations and the Plot 43 ditch. The orange data symbols represent the MWMF plants that were in the irrigated areas or found in areas near the MWMF pond and the green data symbols represent MWMF plants in direct contact or physical (i.e., deep root) access to the pond water. TBC: Total T by combustion; TBSS: Total T by sum of speciation. All plants are from the MWMF area unless noted in the legend as being from TC.

Baglan and colleagues (2013) reviewed published literature on OBT and HTO behavior in plants and several other T-analysis topics. They concluded that elevated levels of OBT:HTO (exceeding 1 and going as high as 4) are due to low levels of HTO in the soil root zone relative to the HTO levels in the air within the (plant) atmosphere above.[33] This may explain some of the observations that can be made for **Fig. 5**. More research could be conducted to better characterize this system and confirm the mechanism for these observations. It is evident that plants with root access to high levels of HTO (via pond water or irrigation) seem to have lower OBT:HTO ratios.

Measurement data for total T, HTO and OBT in vegetation were reviewed and plotted with respect to OBT:HTO versus total T—much like that in **Fig. 5**. Values from Svetlick et al. (2014)

for plants[34] were also evaluated (not shown) for comparison. There was little relationship between OBT:HTO and total T in these studies. The OBT:HTO ratios in this study were very similar to that of plants in Svetlick et al. (2014), but the total T levels spanned a narrow range. Strong correlations or trends were non-existent in that data set. The data for SRS plants showed some trends that are not captured in other published studies. This is likely because nearly every T-contaminated location is somewhat unique and it can be expected to have different dynamics than that of the MWMF. Areas that are managed in a similar manner to the MWMF are likely to have similarities in T uptake and speciation behavior. It is also possible that other studies have not yet reported similar information to ours at this time.

Some mechanisms for the enrichment of T and OBT relative to HTO are being revealed. Fievet *et al.* (2013) suggest the OBT:HTO ratio should be approximately one unless the system being investigated has been perturbed, such as by a T release event.[16] 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 one post-2000.

Tritium in Plants: NE-OBT and E-OBT Relationships

The OBT in the majority of the MWMF pond plants is almost entirely NE-OBT, which is consistent with the high NE-OBT:E-OBT levels in pond sediments (compare **SI Tables 5** and **6**). The levels of E-OBT were quite low in the Plot 43 ditch plants relative to NE-OBT as evident by the very high NE-OBT:E-OBT ratios. Another unexpected observation is that the NE-OBT:E-OBT ratios in the Plot 43 ditch plants were extremely high relative to all of the other plants that were analyzed. This may be because the OBT in the moist vapor space of the Plot 43 ditch plants during irrigation (of Plot 43 and other proximal irrigation plots) is more bioavailable than that of the other plants with direct physical contact to the MWMF pond water. It may also mean that there is uptake of the OBT in the moist T-rich air, but the total level of T exposure and uptake is not as high because there is little direct or continuous contact for these plants with MWMF pond water.

Tritium Chemical Speciation in Lichens

Data for the T speciation and corresponding total T by combustion for the lichen species *Cladina* are shown in **Table 1**. The lichens that were sampled from above the pond surface on the dock had the highest T levels (2.3 Bq g^{-1} w.w.). Most of the lichen samples that were found in un-irrigated areas like Par Pond, Plot 43 road and one of the two samples from the Plot 43 ditch had lower total levels of T (1.3 to 1.7 Bq g^{-1} w.w.).

The differences in T based on total sample combustion and T-based on speciation in the lichens (**Table 1**) can partially be explained by the fact that these two measurement approaches involve samples that are not homogenized prior to being put in the furnace. It was not desirable to subject the samples to excessive mechanical processing, which could alter the speciation or result in the loss of T as HTO vapor.

We observed that the lichens produce gases when stored at -80°C because the plastic containment was inflated when they were removed for processing. Gas generation of this magnitude was never observed for the other biota stored at -80°C. Lichens can release N_2O (nitrous oxide or laughing gas) and small amounts of CH_4 (methane)–even at very low temperatures and low levels of hydration.[35,36] Low levels of methane release may have an impact on the total T levels (through, for example, the conversion of T to CH_3T), but we do not know the extent of the impact of this gas-emitting behavior on T speciation in these biological materials. Our sample throughput was limited with the 6-tube furnace so the storage of samples at low temperatures was necessary and the lichens appeared to thrive well at very low temperatures.

The results indicate that there is always more OBT than HTO in the lichens—regardless of location or irrigation (**Table 1**). There was little trend in NE-OBT:E-OBT ratio with sampling location, time of year and irrigation. All but one of the samples (MWMF Plot 43 ditch Nov. 2021) had a NE-OBT:E-OBT ratio exceeding 2.2. The lichens contain more OBT than HTO and more NE-OBT than E-OBT, so this suggests the T is being bioaccumulated from the air as moisture (as HTO and potentially any aerosolized OBT from the pond water or the irrigation) which is being accumulated as mostly NE-OBT. Lichens are photosynthetic organisms so some concentration, conversion, and retention of OBT relative to HTO is expected.

The T speciation data for the lichens indicate that these aerial organisms tend to retain more OBT relative to the other plants in this study. Additionally, the exposure and the mechanism(s) for retaining OBT by the lichens may be different than that of the other plants in this study because the trends in T speciation are quite different. Par Pond water (**Fig. 2**) and plant and sediment biota from its surrounding areas are relatively uncontaminated with respect to T and this location can be considered similar to that of TC.[25] The Par Pond lichen data for total T and NE-OBT:E-OBT speciation data compared fairly well with most of the MWMF lichens.

Data for OBT:HTO ratios and total T from Vichot et al. (2008) were compared for lichens in the same manner as the plant values plotted in **Fig. 5**.[37] Lichen values from Vichot and researchers showed a large range in OBT:HTO values and total T but no trendlines or correlations could be discerned (data not shown). Similarly, the SRS lichen data (**Table 1**) shows no trend with respect to OBT:HTO vs. total T content (plot not shown). Daillant and co-workers determined that the exposure of lichens to high levels of T resulted in high levels of OBT.[31] This too can be concluded for the MWMF pond dock lichen which had more total T than the other lichens this study. It also had the highest OBT levels as can be observed from its high OBT:HTO ratio and high total T levels as shown in **Table 1**.

Table 1. Lichen data for total T and T-based on speciation measurements of HTO, NE-OBT and E-OBT.

Description for *Cladina rangiferina* Lichen Sampling (location – month/year)	Total T from Combustion		Total T from Speciation		OBT:HTO	NE-OBT:E-OBT
	Bq T g^{-1} (w.w.)	±SD	Bq T g^{-1} (w.w.)	±SD		
MWMF Pond Dock - 5/21	1.9	0.2	2.3	0.2	3.0	2.4
MWMF Plot 43 Ditch - 7/21	1.3	0.0	0.5	0.1	2.2	2.2
MWMF Plot 43 Ditch - 11/21	1.7	0.1	1.3	0.1	1.3	1.3
MWMF Near Pond - 12/21	1.3	0.1	0.8	0.1	1.8	2.5
MWMF Plot 43 - 12/21	1.2	0.0	0.8	0.1	1.6	2.2
MWMF Plot 43 Road - 7/22	1.2	0.1	0.7	0.1	2.4	2.3
Par Pond - 3/22	1.6	0.0	0.5	0.2	2.9	2.7

Similarities in OBT and Total T in Prior MWMF Studies with Plants

The OBT:HTO ratios for wood from MWMF pine tree that were irrigated with MWMF pond water ranged from 2 to nearly 6.[25,26,27] The MWMF pine trees transpire a considerable amount of the added HTO whereas the OBT from the pond water irrigation remains in the pine tissue. Similarly, the NE-OBT:E-OBT ratios in wood during the years that the pines were irrigated ranged from 4 to 8.3. Some transpiration of HTO by the plants is also expected, but only the lichens in our studies appear to approach the OBT:HTO and NE-OBT:E-OBT ratios that the pine wood exhibited after two decades of pond water irrigation. The Spanish moss at the MWMF did not have the same OBT:HTO ratios as the MWMF pine tree wood and lichens but they did have elevated NE-OBT:E-OBT ratios.

The influence pond water exposure proximity was observed in Pettit et al. (2024) in irrigated pine tree plots. The needles of pine trees on the perimeters of the plots had higher OBT:HTO ratios than needles from the inside canopy of the tree plot. A correlation coefficient of 0.54 was recorded for needles from these pine tree plots of 0.54 for their OBT:HTO vs. total T levels. The data ranged from ~0.6 to 1.5 for OBT:HTO and the total T for the needles ranged from 0.5 to 3 Bq T g^{-1}. These data if plotted on **Fig. 5** would compare well with the data on the upper left portion of **Fig. 5**.

Conclusion

This study provides a real world example of what could be observed for T behavior in and near a surface water body that received high inputs of T from a potential fusion source. The levels of T that are the source of contamination (in Bq L^{-1}) to the MWMF are comparable with that of projected fusion releases as previously noted. This manuscript highlights the importance of how physical location, method of T exposure, seasonal precipitation, plant height, plant rooting depth, and proximity to a tritiated water source influence the behavior and amount of T in plants.

These observations will prove helpful if other large bodies of T-contaminated water were to be released and managed in a similar way as in the MWMF, where natural attenuation and phytoremediation with local vegetation are being employed over the long term. These findings could be used to better evaluate and select future bioremediation strategies for T-contaminated areas. They also may help with defining the distances and/or adequate elevations at which proximal resource activities such as agricultural or human occupation could safely occur. Such evaluations would require additional information that were not identified in this study. Allowable levels of T exposure for the humans or biota (that will be frequenting the area), site specific information such as water table depth, water subsurface flow characteristics, biota selection, cost versus benefit analyses and other variables would need to careful consideration.

Conflicts of Interest

There are no conflicts to declare.

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References

[1] S. Okada and N. Momoshima. Overview of tritium: Characteristics, sources and problems, *Health Phys.,* 1993, **65:6**, 595-609.

[2] P. Calmon and J. Garnier-Laplace, Tritium and the Environment, Institut de Radioprotection et de Sureté Nucléaire, Saint Paul lez Durance Cédex, France, 2010.

[3] G. Larson and D. Babineau. An evaluation of the global effects of tritrium emissions from nuclear fusion power, *Fusion Engin. Design,* 2020, **158**, 111690.

[4] S. Sandri, G. M. Contessa, M. D'Arienzo, M. Guardati, M. Guarracino, C. Poggi and R. Villari. A review of radioactive wastes production and potential environmental releases at experimental nuclear fusion facilities, *Environments,* 2020, **7(6)**.

[5] J. P. Holdren, Safety and environmental aspects of fusion energy, *Ann. Rev. Energy Env*., 1991, **16:**235-258.

[6] H. W. Bartels, et al. ITER reference accidents, *Fusion Engin. Design,* 1998, **42(1-4):**13-19; https://doi.org/10.1016/S0920-3796(97)00148-8.

[7] I. R. Cristescu, et al. (2005). The fuel cycle of fusion power plants and experimental fusion reactors, presented at the First IAEA Technical Meeting on "First Generation of Fusion Power Plants- Design and Technology". Proc. Series (International Atomic Energy Agency. CD-ROM), IAEA, Vienna, Austria.

[8] A. López-Galindo, P. Fenoll Hach-Ali, A. V. Pushkarev, A. S. Lytovchenko, J. H. Baker and R. A. Pushkarova, Tritium redistribution between water and clay minerals, *Appl. Clay Sci.,* 2008, **39**, 151-159.

[9] C. E. Murphy Jr., Tritium transport and cycling in the environment, *Health Phys.,* 1993*,* **65:6**, 683-697.

[10] C. E. Murphy Jr., The relationship between tritiated water activities in air, vegetation and soil under steady state conditions, *Health Phys.,* 1984, **47:4,** 635-639.

[11] S. Diabate and S. Strack. Organically Bound Tritium, *Health Phys. Soc.,* 1993, **65:6** 698-712.

[12] P. Le Goff, M. Fromm, L. Vichot, P.-M. Badot and P. Gu´etat. Isotopic fractionation of tritium in biological systems, *Env. Int.*, 2014, **65,** 116-126.

[13] F. Pointurier, N. Baglan and G. Alanic. A method for the determination of low level organic bound tritium activities in the environmental samples, *Appl. Radiat. Isotopes,* 2004, **61,** 293-298.

[14] F. Baumgartner and W. Honhaerl. Non-exchangable organically-bound tritium (OBT): its real nature, *Anal. Bioanal. Chem.,* 2004, **379:2**, 204-209.

[15] C. Boyer, L. Vichot, M. Fromm, Y. Losseet, F. Tatin-Froux, P. Guétat and P.M. Badot. Tritium in plants: A review of current knowledge, *Env. Exper. Botany*, 2009, **67,** 34-51.

[16] B. Fi´evet, J. Pommier, C. Voiseux, P. Bailly du Bois, P. Laguionie, C. Conssonnet and L. Solier, Transfer of tritium released into the marine environment by French Nuclear Facilities bordering the English Channel, *Env. Sci. Technol.,* 2013, **47,** 6696-6703.

[17] S. B. Kim, N. Baglan and P. A. Davis, Current understanding of organically bound tritium (OBT) in the environment, *J. Env. Radioact.*, 2013, **126**, 83-91.

[18] A. Melintescu and D. Galeriu. Uncertainty of current understanding regarding OBT formation in plants, *J. Env. Radioact.,* 2017, **167,** 134-149.

[19] Q. Zhang, L. Du, Z. Dai, Y. Ma, L. Qin, K. Dong, Z. Ma, G. Yang, J. Liu and W. Liu. Studies of the particle size distribution of non-exchangeable organically-bound tritium activities in the soil around Quinshan Nuclear Power Plant, *J. Env. Radioact.,* 2018, **192,** 362-367.

[20] N. Momoshima, H. Kakiuchi, T. Okai, S. Hiramatsu and Y. Maeda. Tritium in a pine forest ecosystem: Relation between fresh pine needles, organic materials on a forest floor and atmosphere, *J. Radioanal. Nucl. Chem.,* 2000, **243:2**, 479-482.

[21] F. Eyrolle, L. Ducros, S. Le Dizès, K. Beaugelin-Seiller, S. Charmassona, P. Boyer and C. Cossonnet. An updated review on tritium in the environment, *J. Env. Radioact.,* 2018, **181**, 128-137.

[22] W. H. Carlton, et al. (1993). *Assessment of Tritium in the Savannah River Site Environment,* Westinghouse Savannah River Company, WSRC-TR-93-214, Aiken, SC, 1993.

[23] C. E. Murphy Jr., (1990). *The Transport, Dispersion and Cycling of Tritium in the Environment,* Westinghouse Savannah River Company, WSRC-RP-90-432, Aiken, SC, 1990.

[24] C. C. Ziegler, et al. (1989). *Radioactive Releases at the Savannah River Site 1954-1988.* Westinghouse Savannah River Company, WSRC-RP-89-737, Aiken, SC, 1990.

[25] E. A. Pettitt, M. C. Duff, and H. Vermeulen. Historical record of tritium from tree cores at the Savannah River Site, *Env. Sci.: Processes & Impacts,* 2022, **24**, 1144-1151.

[26] M. C. Duff, W. W. Kuhne, B. Viner, A. Swindle, A. L. Houk, S. Chiswell, D. B. Hunter and O. E. Rivera, Assimilation and transport of organic bound tritium in an irrigated pine forest, *Env. Sci.: Processes & Impacts,* 2019, **21**, 938-949.

[27] E. A. Pettitt, M. C. Duff and H. Vermeulen. Influence of irrigation approaches and spatial geolocation on tritium speciation, uptake and depuration, *Chemosphere,* 2024, **349**, 140921.

[28] United States Department of Agriculture, Soil Survey of Savannah River Plant Area, Parts of Aiken, Barnwell, and Allendale Counties South Carolina. National Cooperative Soil Survey. June p. 127, Aiken, SC, 1990.

[29] United States Natural Resources Conservation Service. Soil Survey of Aiken County Area South Carolina, 1985.

[30] QuantaSmart™ for the Tri-Carb® Liquid Scintillation Analyzer. Reference Manual. Rev. A, Printed in U.S.A. Copyright © 1998-2015, Manual Reorder No. 8860101, PE, Inc. U.S.A.

[31] O. Daillant, G. Kirchner, G. Pigrée and J. Porstendörfer. Lichens as indicators of tritium and radiocarbon contamination, *Sci. Total. Env.*, 2004, **323,** 253-262.

[32] M. Ota, H. Nagai and J. Koarshi, Importance of root HTO uptake in controlling land-surface tritium dynamics after an-acute HT deposition: a numerial experiment, *J. Env. Radioact.,* 2012, **109,** 94-102.

[33] N. Baglan, S. B. Kim, C. Cossonnet, I. W. Croudace, M. Fournier, D. Galeriu, P. E. Warwick, N. Momoshima and E. Ansoborlo, Organically bound tritium (OBT) behaviour and analysis: outcomes of the seminar held in Balaruc-les-Bains in May 2012. *Radioprotection*, 2013, **48:1**, 127-144, DOI: 10.1051/radiopro/2012051.

[34] I. Svetlik, M. Feigl, I. Malátová and L. Tomaskova, Enhanced activities of organically bound tritium in biota samples, *Appl. Radiat. Isot.*, 2014, **93**, 82-86.

[35] K. Lenhart, B. Weber, W. Elbert, J., Steinkamp, T. Clough, P. Crutzen, U. Pöschl and F. Keppler, Nitrous oxide and methane emissions from cryptogamic covers, *Glob. Change Biol.,* 2015, **21,** 3889-3900, doi:10.1111/gcb.12995.

[36] P. Porada, U. Pöschl, A. Kleidon, C. Beer and B. Weber, Estimating global nitrous oxide emissions by lichens and bryophytes with a process-based productivity model, *Biogeosci.,* 2017, **14,** 1593-1602.

[37] L. Vichot, C. Boyer, T. Boissieux, Y. Losset and D. Pierrat, Organically bound tritium (OBT) for various plants in the vicinity of a continuous atmospheric tritium release, *J. Env. Radioact.,* 2008, **99,** 1636-1643.

- The data supporting this article have been included as part of the Supplementary Information.