Activation of Organically-Bound Tritium by Tritiated Water in Soil

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Abstract

The fate of tritium in the environment is a target of interest in many studies. However reported concentrations of organically bound tritium (OBT) in soil are not well understood. In this study, a supplementary non-biological process of soil OBT activation in the environment was explored. The vicinity of SRB Technologies (Pembroke, Ontario) was chosen as the sampling location because of a significant airborne tritium release prior to 2001 which resulted in groundwater contamination. Soil cores were extracted from the ground near the tritium-releasing facility stack in 2017 and split into 10 cm subsamples for HTO/OBT, total carbon and hydrogen, particle size, thermogravimetric, radiocarbon and ^{3}He mass spectrometry analyses. Observed HTO profiles revealed elevated tritium concentrations still retained in the soil. The results indicated that clay bound tritium masks the OBT signal and cannot be easily distinguished. Multiple short-term sample rinses with tritium-free water have little effect on clay bound water removal. Therefore, clay bound tritium should to be addressed in any future research related to soil OBT.

Acknowledgement

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List of key acronyms

CNL – Canadian Nuclear Laboratories

CNSC – Canadian Nuclear Safety Commission

LLD – lower limit of detection

LSC – liquid scintillation counting

mbgs – meters below ground surface

MDA – minimum detectable activity

MS – mass spectrometry

OBT – organically bound tritium

SOM – soil organic matter

YBP – years before present

1. Introduction

Economical development and national security of any country is highly dependent on its' energy sector. Most countries try to diversify their energy portfolio to be less reliant on natural resource supply and demand fluctuations. The global push for decreasing the carbon footprint of industrial practices and power generating stations favours development of both renewable and nuclear energy sources. Renewable energy is still not considered a reliable source while nuclear presents an advantage of highly efficiency and a steady amount of energy generated per amount of fuel spent.

Canada was a pioneer of nuclear energy development for peaceful purposes. The availability of high quality uranium deposits steered the research towards advancing CANDU technology: **Can**adian **D**euterium **U**ranium (CANDU) reactors use natural uranium dioxide (UO_2) as a fuel and heavy water (D_2O) as a moderator. Meanwhile light water reactors require uranium-235 enriched fuel, which is achieved through additional processing of uranium ore. CANDU reactors are very versatile with capability of utilizing natural abundance uranium-based fuel, thorium-based fuel, or depleted uranium, which is often referred to as spent fuel.

CANDU reactors are inherently safe in their design and meet the standards of the International Atomic Energy Agency in terms of non-proliferation efforts. However, the use of heavy water as a moderator results in the generation of tritium which is considered an undesirable by-product. Routine and accidental releases of tritium into the environment are closely monitored and reported by the nuclear energy authority to the Canadian Nuclear Safety Commission (CNSC) in the role of regulator. The radiotoxicity of tritium is very low and poses little threat to human health and environment. However, tritium is the radioactive isotope that is the main contributor to the dose absorption of nuclear energy workers.

Tritium also has commercial applications outside of the nuclear industry such as self-luminescent exit signs, paint, watches, tritium batteries and radiolabelling in pharmaceuticals but the demand is still very low. The environmental risk assessment with tritium may change drastically if thermonuclear fusion technology becomes available in the near future. Then tritium will be in high demand and health risks will scale up with the large quantities required.

Increasing regulatory interest has sparked research to better understand the fate of tritium in the environment. However, data collected over the years suggests that some parameters used in the environmental transfer models approved for regulatory assessments should be revisited. In previous research the enrichment of organically bound tritium (OBT) was observed well above the associated pore water and tissue free water in the background locations (Thompson, Kwamena, Ilin, Wilk, & Clark, 2015). The behavior of tritiated water (HTO) and OBT are not fully understood in soil and modeled estimates (e.g., plant and soil OBT) are not appropriately conservative.

2. Study Objective

This study proposes a supplementary mechanistic concept of OBT activation (formation) by HTO in soil. The goal is to enhance the current knowledge of tritium pathways in the environment and fill the gap in understanding soil OBT enrichment. The concept is based on our hypothesis that an isotopic exchange reaction can take place between free water and organic molecules as a part of soil organic matter (SOM). This reaction is well-known in organic chemistry as a single step substitution reaction (Olah, 1971), but the concept has not been applied to environmental systems. The reaction is spontaneous, thermodynamically preferring heavier isotopes in organic phase.

$$\text{Organics-H}_{(s)} + \text{HTO}_{(l)} = \text{Organics-T}_{(s)} + \text{H}_2\text{O}_{(l)} \qquad (1)$$

Proving this concept in a controlled field experiment would be a challenging task due to various time and tritium related constraints. An existing environmental system with soil exposed to HTO was a preferred sampling location to meet the thesis objective.

SRB Technologies in Pembroke, Ontario, Canada is a unique tritium handling facility that has routine tritium releases into the environment (Mihok, et al., 2016). A major release in the year 2000 caused a tritium plume to develop that had traveled through the overburden for over 10 years. The soil exposure to the tritium plume was a perfect ongoing environmental experiment to support this study.

3. Background

3.1 Tritium

Tritium is the only radioactive isotope of hydrogen. It is a low-energy beta-emitter with a half-life of 4500 ± 8 days (12.32 ± 0.02 years) (Lucas & Unterweger, 2000). The maximum energy emitted from tritium decay is 18.6 keV with an average of 5.7 keV. With incredibly low abundances in the environment, tritium is considered to have similar physical and chemical properties as hydrogen despite of three-times bigger atomic mass of 3.01650492 au. The main difference in properties is revealed on atomic and subatomic levels where two extra neutrons in the nucleus affect the way tritium atom interacts with a neutron flux and other light atoms. On the macroscale fractionation of tritium also takes place in the environment indicating the differences between tritium and hydrogen (Kim & Baumgartner, 1997; Le Goff, Fromm, Vichot, Badot, & Guetat, 2014).

Although tritium was discovered in 1934, it only started drawing attention in 1950. Early work was mainly focused on detecting natural tritium, and then studying the global distribution of artificial tritium. Both cosmogenic and anthropogenic tritium are still of research interest, due to the increasing role of nuclear power plants in the global energy sector (Echávarri, 2007). The amount of tritium released to the environment may increase in the future because of increasing fuel reprocessing, spent fuel storage, routine and accidental emissions, and future development of nuclear fusion technology.

Tritium is present in different physical states and concentrations through environmental compartments. The choice of concentration units is based on applicability. Large inventories are usually described in kg or MCi while solutions tend to have units in Bq or Ci per unit of volume. Tritium units (TU) are generally used when concentrations are very low and compared to dilution from natural hydrogen. The relationship between different units are the following:

Specific Activity: 1 kg of ^{3}H = 9.65 MCi = $3.55 \cdot 10^{17}$ Bq

Atom Ratio: 1 TU = 1 ^{3}H atom per 10^{18} ^{1}H atoms = 0.119 Bq/L

Mixing Ratio: 1 ^{1}H atom/mg air = 0.0023 Bq/m^{3} air STP = $4.80 \cdot 10^{4}$ TU

The global inventory of tritium is comprised from both artificial and natural sources. Natural tritium is produced by the interaction of cosmic ray particles with nitrogen and oxygen molecules in the upper atmosphere and accretion of solar-produced tritons (Simpson, 1960). Tritium atoms recombine with oxygen and hydroxyl radicals/ions in the stratosphere entering the troposphere as predominantly HTO species and contributing from 5 to 20 TU (Clark, 2015).

3.2 Soil

Soils organic matter retains nutrients as well as pollutants and stores organic carbon as various organic compounds. Multiple transformations such as biological, physical and chemical, convert dead plants into organic products making soil studies very difficult. Currently three main soil organic matter models can be distinguished: classic humification, selective preservation and progressive decomposition. However, all models have been challenged with experimental data. A new "soil continuum model" was proposed as the way to reconcile existing theories (Lehmann & Klebber, 2015). It focuses on the ability of decomposer organisms to access soil organic matter and on the protection of organic matter from decomposition by soil minerals.

Organic matter can be divided into pools that have different turnover time. Carbon movement among pools and their decomposition rates are modified by temperature, texture, and moisture (Lehmann &

Klebber, 2015). Regardless of the SOM theory, the consensus is that polycyclic and polyaromatic compounds are very recalcitrant to decomposition thus more likely to be stored in soil over longer periods of time.

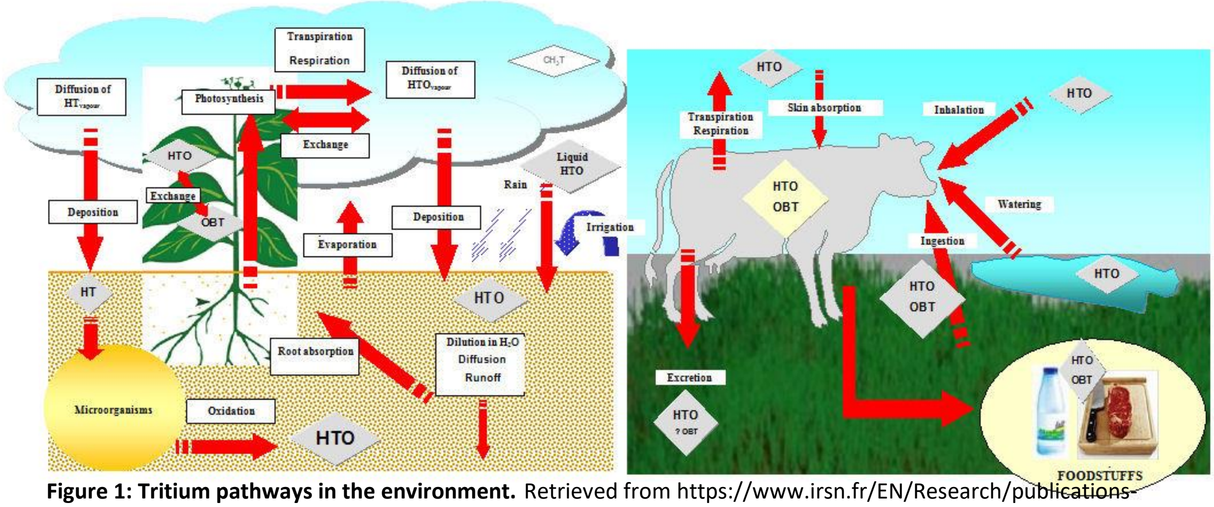

Figure 1: Tritium pathways in the environment. Retrieved from https://www.irsn.fr/EN/Research/publications-documentation/radionuclides-sheets/environment/Pages/Tritium-environment.aspx

Tritium can enter the soil through various pathways as HTO and/or OBT: with precipitation (CNSC, 2009), as the result of biological life cycles (Kim, Baglan, & Davis, 2013), by molecular tritium oxidation (Momoshima, Nagasato, & Takashima, 1990), or with contaminated groundwater (Kim, Workman, Davis, & Yankovich, 2008). A significant accumulation of tritium in both organic rich sediment and the food chain have been demonstrated (Turner, Millward, & Stemp, 2009; Kim, Workman, Davis, & Yankovich, 2008; Eyrolle-Boyer, Boyer, Claval, & Charmasson, 2014). The enrichment in sediments was attributed to isotopic exchange between clay minerals and HTO and adsorption of tritium to H-free minerals (Lopez-Galindo, et al., 2008). It was also discussed that exchangeable and non-exchangeable interaction between HTO and organic matter could be a factor (Turner, Millward, & Stemp, 2009) since preferential incorporation of tritium into biopolymers has been already documented (Baumgärtner, Kardinal, & Müllen, 2001; Baumgärtner F. , 2005).

The transport properties of tritium correlate to soil particle size (Zhang, et al., 2018). The higher the clay content, the slower tritium migrates through soil media (Fodor-Csányi, Kasza, Fehér, & Bérci, 1985). It was discovered that sorption on soils is small but noticeable (Teng, et al., 2011) despite the common acceptance of tritium as non-sorbing tracer. Distribution coefficients of tritium appear not only to be influenced by its affinity for organic matter (Turner, Millward, & Stemp, 2009) but also adsorption time, pH, water/soil ratio and higher contents of Al_2O_3 and Fe_2O_3 (Teng, et al., 2011).

3.3 Tritium reactions

Since the 1960s an assortment of one-step catalytic hydrogen isotope exchange reactions have been studied in order to tritiate organic compounds (Buncel & Jones, 1988). A range of catalysts is available for highly efficient substitution of hydrogen for deuterium or tritium. E.g. organic compounds have been tritiated via hydrogen isotope exchange reactions using polymer-supported acid catalysts (Brewer, Jones, Lawrie, Saunders, & Simmonds, 1993). A simple procedure for tritiating phenols was developed based on ion exchange resin modification (Tuck, Tan, & Hayball Peter J., 2000).

It has been demonstrated that the tritiation of toluene by HTO can be catalyzed by weak Lewis acid such as $FeCl_3$ or by strong Bronsted acids such as H_2SO_4 or $HClO_4$ (Oohashi, Mori, & Hirano, 1989). The yield would depend on both temperature and time of reaction. The yield of 2.9% was reported for 5°C reaction temperature and 2 min reactions time. By increasing the time of reaction to 180 min, the yield increased to 43%. Similarly, a 78% yield was achieved at 40°C after 60 min exposure time. Although tritium activities in that study were significantly higher than what would be expected in the environment, an effective tritiation has been demonstrated over relatively short laboratory experiments. With temperature ranges similar to environmental conditions tritiation of aromatics could take place in the environment provided there is enough time for HTO exposure.

Rapid deuteriation and tritiation (from 5 min to 1 week) was achieved by using organometallic and elemental halides as catalyst (Long, Garnett, & Vining, 1975). In that study derivatives of benzene and related compounds were successfully tritiated by HTO in the presence of $AlCl_3$.

Many catalysts used in tritiation reactions of organic molecules resemble clay minerals. Clay itself can promote hydrogen exchange reactions (Alexander, Kagi, & Larcher, 1982). The rapid tritiation appears to be a characteristic of benzene or phenol derivatives. Humic substances, which are part of SOM are described as conglomeration of polyaromatic macro molecules similar to benzenes and phenols (Stevenson, 1994). Therefore, activation of OBT by HTO in soil is highly probable under environmental conditions. The synergy of clay minerals to retain tritium and to catalyze isotopic exchange reactions would also favour OBT enrichment in SOM.

4. Site description

The sampling location was chosen near SRB Technology Inc in Pembroke, Canada. SRBT is one of a few tritium processing facilities in Ontario that releases tritium into the atmosphere during its routine operation procedures. The airborne emissions are predominantly in the form of HTO and HT. SRBT started its operation at the current location in 1990; a full record of actual air emissions is shown on Figure 2.

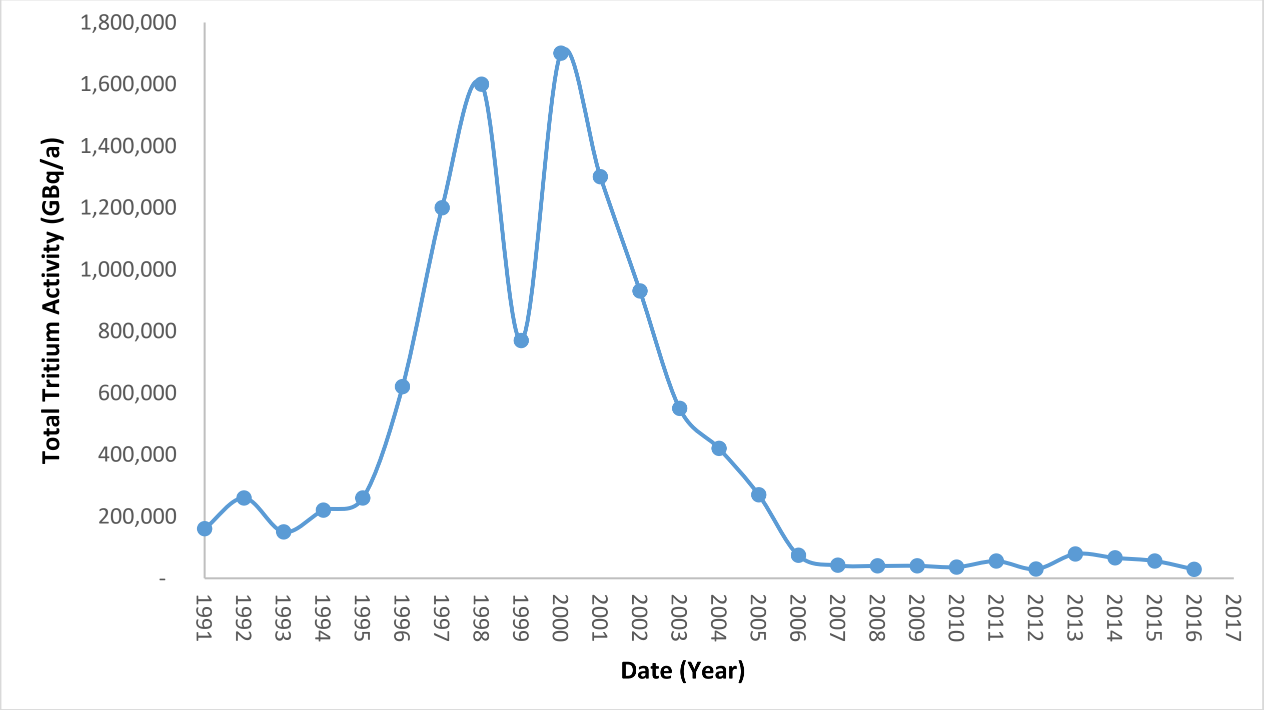

Figure 2: Historical Records of Air Emissions by SRBT (Pembroke, Ontario)

In 2005 the facility was temporally closed by CNSC due to exceedances of tritium concentrations in the surrounding monitoring wells and soil above the Ontario drinking water guideline of 7000 Bq/L. EcoMetrix Incorporated was invited to complete the groundwater investigation and to determine the source of elevated tritium levels. The report concluded that the stack emissions from SRBT facility were the only significant source of tritium in the surrounding environment (Ecometrix Incorporated, 2008).

Since then several research endeavors took place around SRBT (Mihok, et al., 2016; Dehay-Turner, 2016; Schmidt, 2017; Thompson, Kwamena, Ilin, Wilk, & Clark, 2015). The unique exposure of different environmental compartments to elevated tritium levels created an opportunity for scientists to study and understand the behavior of tritium in the environment. The site has been well characterized and described in multiple research papers and university thesis projects in terms of general geology and hydrogeology as well as distribution of tritium. SRBT also has an extensive monitoring program that keeps all tritium records updated and available for public viewing.

Consequently, the vicinity of the SRBT facility was an optimal sampling location to meet thesis objectives. It is situated at 320-140 Boundary Road within the industrial park zone in Pembroke, Ontario (figure 3). Overburden, the focus media of this study, is predominantly comprised from Champlain Sea deposits which were a marine clay-silt. The general overburden would include a layer of top soil followed by silty sand or gravel fill with underlying grey silty clay to a depth up to 6 m. The EcoMettrix report (Ecometrix Incorporated, 2008) listed the estimated values of hydraulic conductivities which were within the expected range for silty clay material (10^{-6} to 10^{-10} m/s). Such low conductivities suggest diffusive downward flow through silty-clay overburden until underlying media with higher hydraulic conductivity is encountered. In this case it could be a thin layer of till and sand above the bedrock surface or shallow bedrock.

Two sampling locations were selected around SRBT (figure 3). Soil Core 1 was extracted from the ground in the vicinity of the emission stack between monitoring wells MW07-17 and MW07-18 while soil Core 2 was approximately 60 m away from the stack near monitoring well MW07-26.

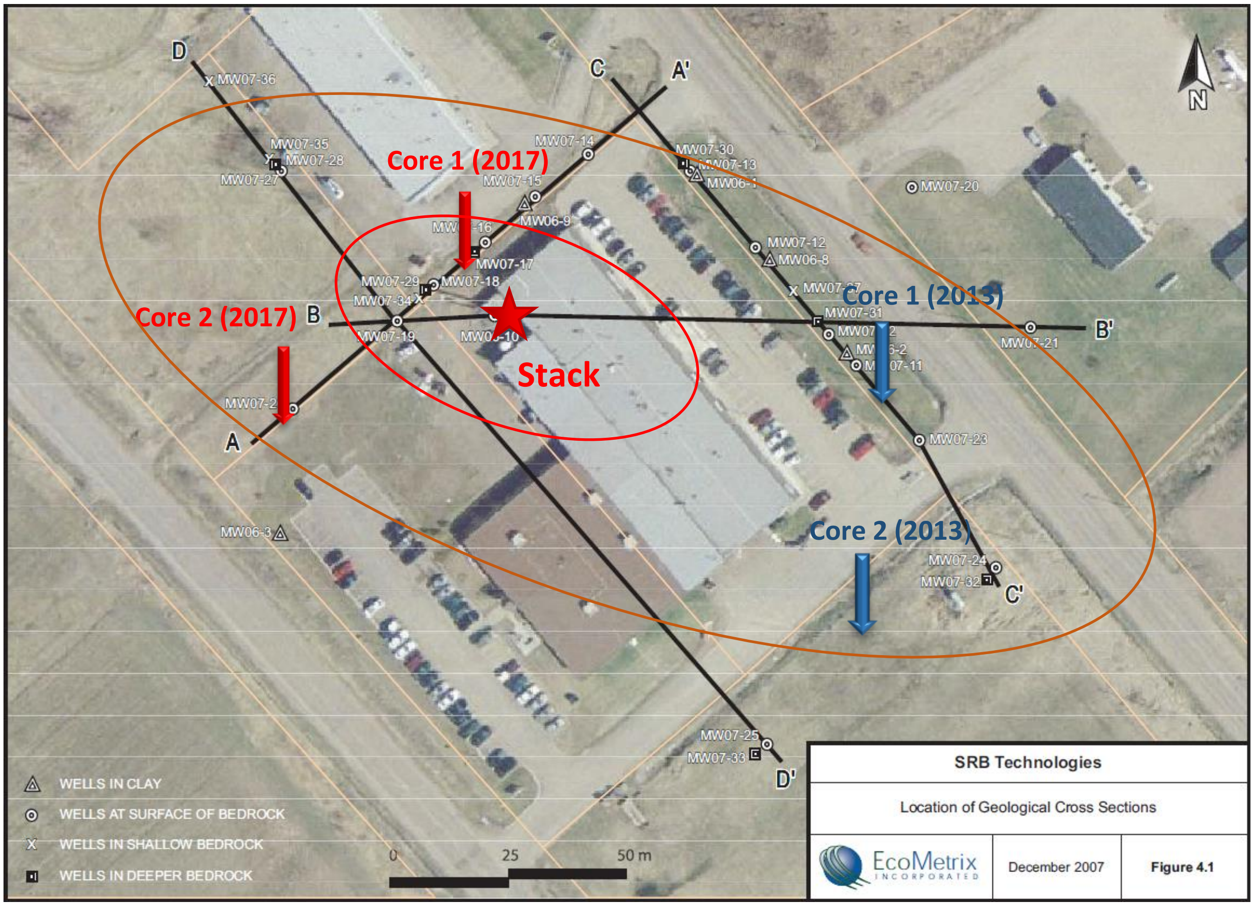

Figure 3: Sampling locations around SRBT, Pembroke, ON: in red – as part of this thesis, in blue – from (Dehay-Turner, 2016)

5. Methods and Materials

5.1 Soil Sampling

Soil sampling was performed on May 16th, 2017 at SRBT in Pembroke, Canada. A push rig model 54LT (Geoprobe) was used to extract the soil cores from the ground at two selected locations. The rig operation was based on the concept of hammering a sampling probe into the ground at constant speed (2 cm/second). The total length of 125 cm of soil core was extracted at once. Subsequent coring was achieved by using extensions that came

Figure 4: Push rig 54LT at core 1 sampling location (2017)

with the push rig. Since the soil material was mostly a compact silty clay, the hole did not collapse and stayed intact for further sampling.

The sampling probe was an essential part of Geoprobe tooling for 54LT which included a hollow 2” plastic casing for capturing the sampled material as the probe was descending through the overburden. After the probe was brought to the surface, the casing with soil was capped and labelled.

The sampling continued until the bedrock or a boulder was encountered. The accumulative length of the Core 1 was 491 cm (4 plastic tubes) and 625 cm for the Core 2 (5 plastic tubes). In both cases the very bottom sections of the cores consisted of gravel mixed with native material which was present above the bedrock surface or till. The sampling was stopped at that point.

Figure 5: Plastic tube with soil sample

The capped and labeled plastic tubes with the soil samples were brought indoors and placed in a freezer at -20°C until further processing. Time between extracting cores and freezing them was within 2 and 5 hours for the cores 2 and 1 respectively. The plastic tubes were kept horizontal for transportation purposes to minimize soil water movement and mixing along the plastic walls before they were frozen.

Frozen soil cores were cut into shorter sections with a hand saw while still inside the casings. Each core interval became an individual soil sample. The first 4 samples of the very top sections of Core 1 and 2 were 5 cm in length while other samples were 10 cm. The bottom 25 cm of each plastic casing was divided into 16 cm and 9 cm samples. That 9 cm sample was recovered from the sampling probe attachment which was part of the coring tool assembly. While still frozen, soil material was transferred to 500 ml mason jars and placed into the freezer again for storage.

5.2 Sample processing

All soil samples were freeze-dried in a vacuum for 20-24 hours and the released water was subsequently collected. The assembled freeze-drying system consisted of a vacuum pump, a chiller with 50% glycol in water by volume as a cooling liquid, a glass manifold, and multiple glass cold traps. The mason jars with the frozen samples were connected to individual cold traps using vacuum grade tygon tubing. The cold traps were also connected to the vacuum system through the manifold and placed into the chiller at -36°C. The vacuum seal integrity of the system was monitored with a vacuum gauge. The transfer of water from the frozen sample into the cold trap occurred by sublimation/deposition processes without going through the liquid phase.

Once the soil free water was extracted from the samples, the remaining samples were conditioned in a drying oven at 60°C for minimum 24 hours or until a constant weight was achieved. The final dry soil was mortar grinded and sieved through a coarse 2.00 mm mesh to remove any small stones and debris. The "Universal Mini-Splitter" was used to create representative subsamples for any future analysis that required dry soil material. All dry samples were stored in new sealed mason jars at room temperature.

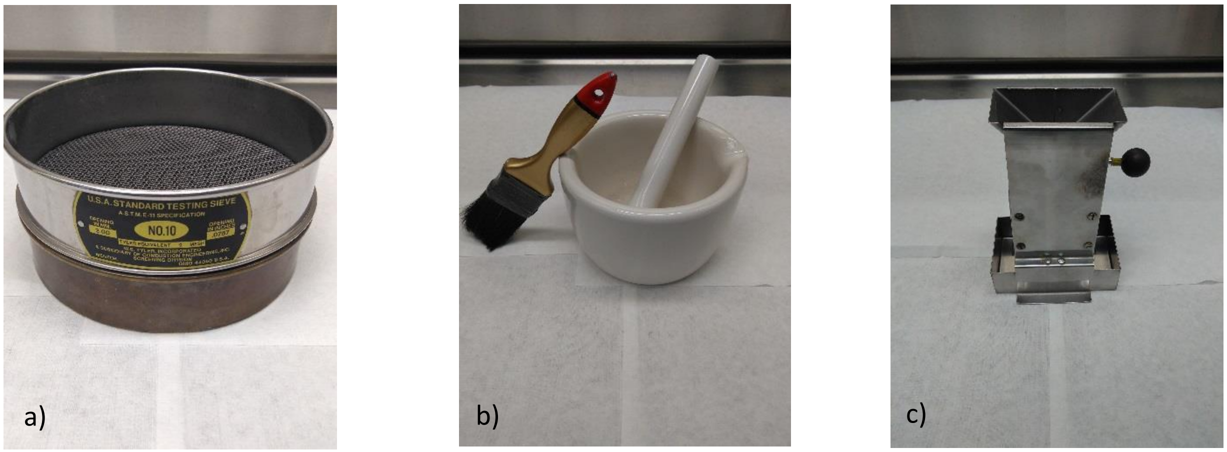

Figure 6: a) Testing Sieve; b) Mortar; c) Universal Mini-Splitter

5.3 HTO analysis

Water extracted from soil samples was analyzed by liquid scintillation counting (LSC) using an ultra low-level liquid scintillation spectrometer Quantulus 1220 (Perkin Elmer, USA). Polyethylene vials with 10 mL of water sample and 10 mL of Ultima Gold LLT scintillation cocktail were used in this procedure. Two blanks with tritium free water, spiked sample, and two standards with known tritium concentrations were analyzed for quality assurance purposes and further calculations. The counting protocol included default tritium counting window of 0 – 18.6 keV, 3 cycles with 60 min counting time per cycle. An external quench curve was used to calculate sample counting efficiency which was needed for converting counts per minute (cpm) to disintegration per minute (dpm) or tritium activity units (Bq/L). Quench curve was generated similarly to calibration curve using 10 standards with known tritium activity but different quench. All samples were cooled and dark adapted inside the Quantulus prior to counting.

5.4 OBT analysis

Combustions of dry soil samples, as part of OBT analysis procedure, was performed on the Sample Oxidizer 307 (Perkin Elmer, USA). The principle operation of the instrument was a flame combustion of the sample in an oxygen atmosphere followed by condensation of released water into a vial with scintillation cocktail. The instrument had a few major advantages over tube furnace combustions, namely it was a fully automated and fast system with small sample size requirements and an insignificant memory effect. The only disadvantage is a poor minimum detectable activity (MDA) of tritium due to limited sample size. Since high activity tritium samples were expected in the soil cores that disadvantage was considered inconsequential.

The sample size used in the Oxidizer was approximately 1 g. The sample was placed into a Combusto-Cone, a starch-based combustible boat, and spiked with 0.2 mL of Combustaid, a mixture of organic chemicals from Perkin Elmer for facilitating slow co-combustion. The combustion water was condensed into the glass vial with 15 mL of Monophase as scintillation cocktail. A few blanks combusted with the batch of samples consisted of 1g of Kimwipe paper tissue folded into Combusto-Cone and spiked with the 0.2 mL of Combustaid.

A new ultra low-level spectrometer Quantulus GCT 6220 (Perkin Elmer, USA) was used for counting vials with OBT samples. The counting protocol was similar to HTO analysis: solutions from glass vials were transferred to plastic vials, with a counting window from 0 to 12.0 keV; 3 cycles with 60 min counting time per cycle. A quench curve provided by the instrument manufacturer was used for counter efficiency calculations. All samples were cooled and dark adapted inside the Quantulus prior to counting. The resulting tritium activity was expressed in Bq per gram of dry soil. Only selected samples from Cores 1 and 2 were analyzed for OBT as part of time and cost optimization of all planned analyses performed in this thesis project.

5.5 Carbon and Hydrogen Elemental Analysis

An elemental CH Analyzer (Eltra) was employed for measuring total carbon and hydrogen in the soil samples. Approximately 3 g of soil sample in a ceramic boat was combusted at 1300°C in a continuous flow of dry oxygen. Two infrared cells in series served as the detector assembly. Total carbon and hydrogen contents were measured in units of weight percent of dry sample. The detectors were calibrated with calcium carbonate standard for Carbon and Sulfanilic acid standard for Hydrogen provided by the instrument manufacturer. The calibration was verified with the composite soil standards purchased from Alpha Resources LLC.

5.6 Thermogravimetric, Particle Size, Carbon Dating Analyses

Characterization of soil material from Cores 1 and 2 was done as part of an undergraduate thesis project by Jacob Harvey in 2017 (Harvey, 2018). Prior to analysis the selected samples were rinsed with tritium-free water three times to remove any non-bound forms of tritium. The rinsing procedure included soaking a sample in tritium-free water in 1:1 volumetric ratio for 24 hours followed by freeze-drying. A commercial freeze-drying system (Labconco FreeZone 6, USA) was used in the freeze-drying step since there was no requirement to analyze extracted water. An accumulative water sample was still collected for LSC to confirm that the third rinse did not yield any tritium activity in the rinse water thus samples were considered free from any non-bound form of tritium.

Three types of analyses were performed on representative rinsed samples: thermogravimetric analysis (TGA), particle size analysis (PSA), and carbon dating. The author of the undergraduate thesis followed established University of Ottawa procedures for those analyses which were described in his thesis report (Harvey, 2018). TGA and PSA were performed in the Physical Geography laboratory at the university of Ottawa, using a TGA701 and Microtrac s3500 laser particle size analyzer respectively. Radiocarbon analysis was performed at A.E Lalonde AMS Laboratory on a 3MV tandem accelerator mass spectrometer built by High Voltage Engineering.

5.7 Special investigation

A special sequence of sample processing and analyses was designed to measure the true OBT signal by ingrowth of ^{3}He, without interferences from the other forms of bound tritium. Three groups of 4 samples were selected from the Core 1 that would represent the distinctive features in terms of tritium concentrations. All samples were rinsed 3 times per procedure described in previous section. Two sets of copper tubes were crimped on one end and packed with approximately 5 g of rinsed and dried soil samples in the uOttawa laboratory for a helium ingrowth experiment. One set of copper tubes was prepared per regular helium ingrowth procedure, while a second set of tubes was initially conditioned at 350°C in vacuum. The procedure included keeping the tubes under high vacuum for 20-24 hours before crimping the other end. The day of crimping was considered the beginning of ingrowth duration. A total of 24 copper tubes (12 regular and 12 specially conditioned) were left for 72-77 days to accumulate helium as a tritium decay product.

The water extracted at 350°C in vacuum from the second set of copper tubes was collected, combined within the group, and analyzed according to HTO procedure. To satisfy the ratio requirement of 10 ml of water to 10 ml of scintillation cocktail, the extracted water was topped up with tritium-free water.

Helium isotope analysis was performed on a Helix SFT Noble Gas Mass Spectrometer, manufactured (Thermo Scientific). Internal standards using precise aliquots from a tank of clean dry atmospheric air were run each morning to measure instrument drift and sensitivity. Standards and samples were introduced into a vacuum preparation system, where bulk (N_2, O_2) and trace gases (CO_2, Ar) were removed using one liquid N_2 charcoal traps and two SAES getters. Following purification, He was separated from Ne using a He cooled cryo trap that cycles temperature down to 5K, before releasing He at 35K. Helium was then introduced into the Helix SFT operating under static vacuum. Each analysis underwent a mass peak center, followed by six separate 30-second integrations on each mass peak. These six integrations generated a linear regression used to calculate peak intensity at time zero (when the sample was released into the Mass Spectrometer).

The tritium activity, calculated from the helium ingrowth quantity, was expressed in Bq per gram of dry soil sample. To convert Bq/g to Bq/L the soil sample from each copper tube was analyzed for total H and C using the elemental analyzer as described above.

6. Results and Discussion

6.1 HTO results

Soil water was extracted from Core 1 and 2 discrete samples and analyzed for HTO. In total, 100 samples were processed and analyzed. The range of tritium concentrations was between 210 Bq/L and 20,200 Bq/L for Core 1 and 91 Bq/L and 1,348 Bq/L for Core 2. One sigma (±1 σ) was in the range from 8 to 49 Bq/L with the lower limit of detection (LLD) around 5 Bq/L. All measured tritium was above the background values that could be expected in Ontario (CNSC, 2013). Core 1 was sampled in the proximity of the stack and elevated tritium activity in soil water was expected. Core 2 was sampled at a distance and had lower tritium activity than Core 1. Observed tritium concentrations in both cores were in correlation with the fact that the airborne tritium from the stack was the only source of tritium in the surrounding environment (Ecometrix Incorporated, 2008), therefore, atmospheric dispersion would be responsible for decreasing tritium signal with the distance from the source.

Tritium activity in soil water obtained near SRBT in 2013 (Dehay-Turner, 2016) were similar to current results (Figure 7). Although these cores were extracted at different locations and 4 years earlier there were still within high deposition zone and in the dominant wind direction (Figure 3). The general profiles of tritium activity in soil water with depth match well in both studies.

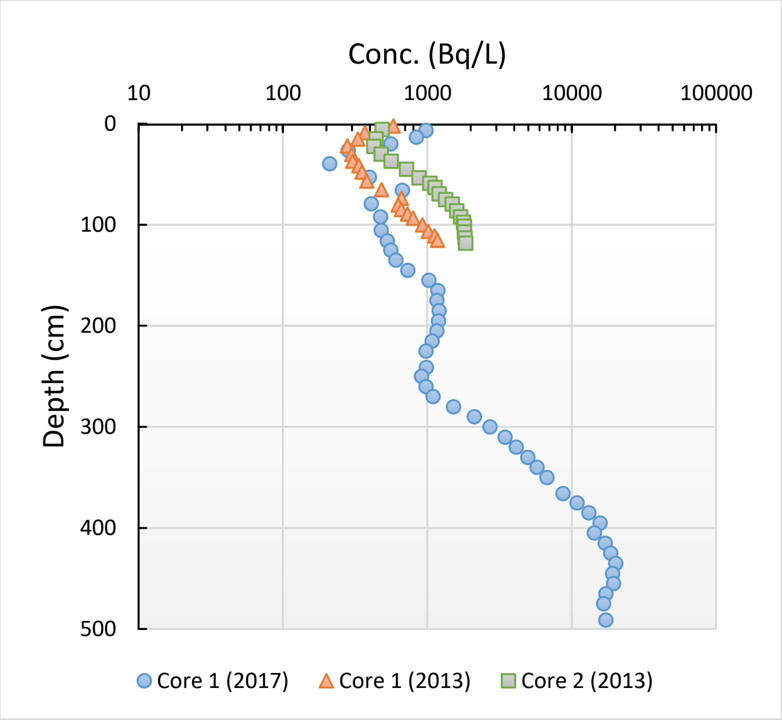

Figure 7: Tritium activity in soil water (SRBT, Pembroke, ON)

The similarity between three cores would become even more apparent if the 2013 data were corrected for tritium decay and vertical water movement through the overburden. Thus, if water movement through the silty-clay soil was assumed to be 0.25 m/a and tritium data was compensated for 4 years of decay, then the features of the 2013 profiles would shift downward by 1 m and towards slightly lower tritium activities, consequently exhibiting closer match to the presented results.

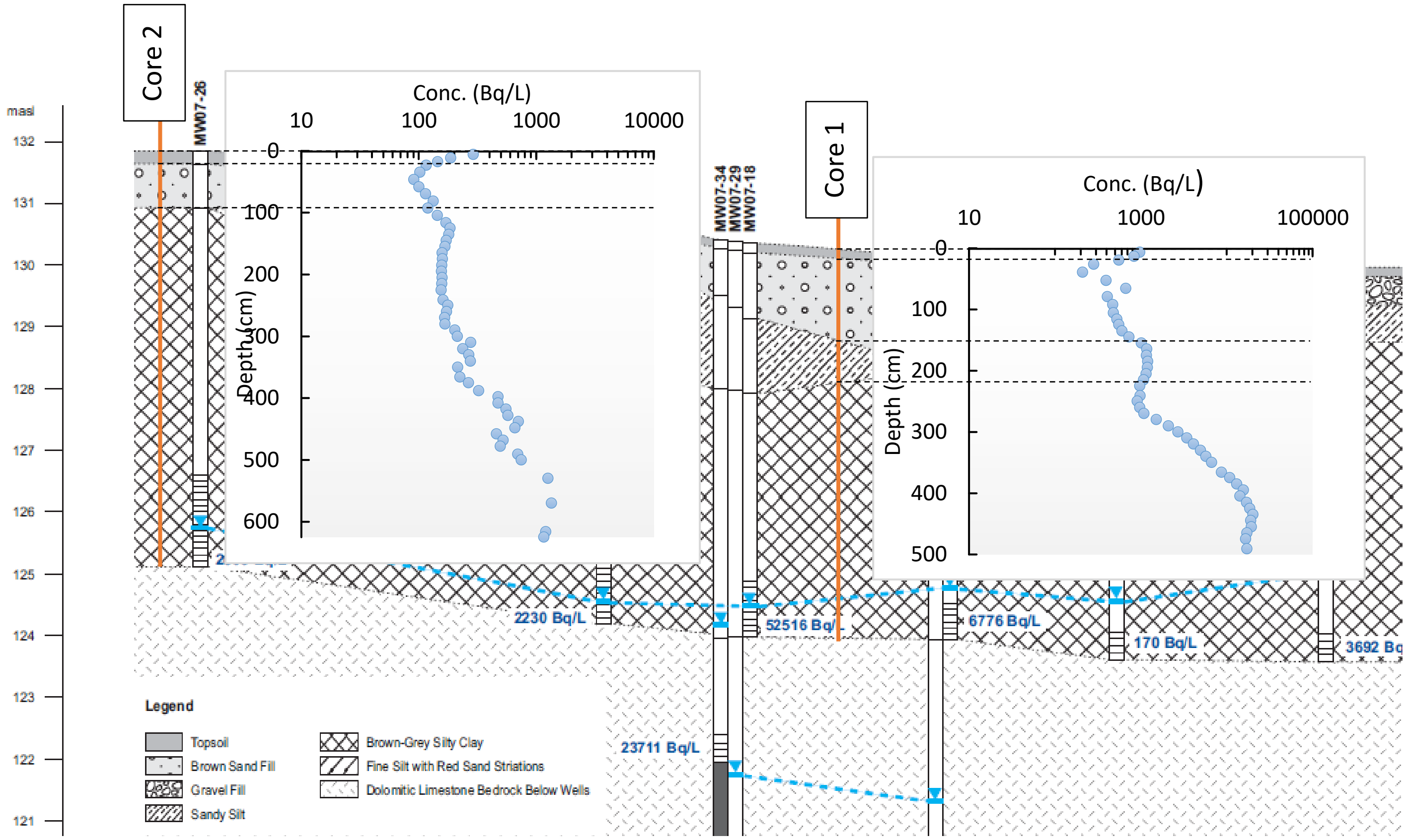

Figure 8: Core 1 and 2 HTO activity concentration profiles over geological cross-sections

The full HTO profile with depth overlaying an approximate geological cross-section provided by EcoMetrix is shown on figure 8. The change in tritium activity in the profile corresponds to variability in the overburden material. The thin top soil layer had relatively elevated tritium activity that rapidly dropped with depth. The trend continued while the soil type transitioned to brown sand fill. At some point the minimum of tritium concentration was reached followed by steady increase until next soil type. Such a parabolic characteristic of the soil tritium activity profile could be caused by different levels of saturation in the overburden material. The water in unsaturated soil would be able to exchange with the atmosphere, thus diluting or concentrating tritium in water. The top soil would be more responsive to immediate emissions from the stack while deeper unsaturated soil water would store attenuated tritium signal. Since the facility does not operate continuously, 24-hour average tritium signal would be less than transient atmospheric tritium concentration during operation. As saturation of soil increased, the exchange with the atmosphere would be hindered, and thus tritium concentration would represent an archive of past emissions. The increasing activity could be caused by infiltration water that would scavenge tritium from the atmosphere during precipitation events (Tokuyama & Oonishi, 1997).

To confirm that the discussed section of the Core 1 was within the unsaturated zone, water table levels were measured in the closest shallow wells on the day of sampling. The values were 1.49 and 1.60 mbgs for the wells MW07-16 and MW07-18 respectively. Therefore, the vadose zone at Core 1 location would stretch from the surface to the boundary between brown sand fill and sandy silt at around 1.5 m.

Core 2 did not have incursion of the sandy silt layer but still exhibited similar behavior until reaching layer of brown-grey silty clay at 1 m depth.

As an overall trend in the saturated zone, tritium concentration was increasing with depth, which could be the representation of historical atmospheric emissions. Although it is believed that the major tritium plume has passed through the overburden and reached the groundwater (Ecometrix Incorporated, 2008; Schmidt, 2017), the retention of tritium by silty clay material was not considered in those studies. Both Core 1 and Core 2 had a significant increase in tritium concentration to over 20,00 Bq/L and 1300 Bq/L, respectively, beyond the 4 m mark. However, the closest to Core 1 monitoring well MW07-18 had recorded tritium concentration in range of 2,000-3,000 Bq/L. The screen of that 6.36 m well was deeper than the length of Core 1, suggesting that the high tritium in the soil HTO is remnant from the peak emissions and has not fully migrated downward into the bedrock aquifer.

For the purpose of thesis objective, HTO profile demonstrated that the soil material at depth was exposed to an elevated concentration of tritium over extended period of time. Therefore, if organic carbon was still present in soil, the exchange reaction could take place, thus activating OBT.

6.2 OBT results

Measuring the bound form of tritium in soil and proving that it was organically bound was the essential part of this study. In total, 67 samples were processed on the Oxidizer and 49 samples on the CH Analyzer. The LLD of the OBT analysis varied from 300 to 700 Bq/L for most of the samples. Generally, the LLD depends on count time and sample quantity. Count time was kept constant at 60 min but the amount of water that was released from oxidizing 1 g of soil was specific to each sample. Most Core 1 samples were above LLD with a few exceptions (Table 1). On the contrary, bound tritium activity in core 2 was too small for the chosen method of analysis: only top soil and the very deep samples showed OBT values above LLD. Therefore, Core 2 could not be used in further investigation as it was deemed not suitable for achieving the objective.

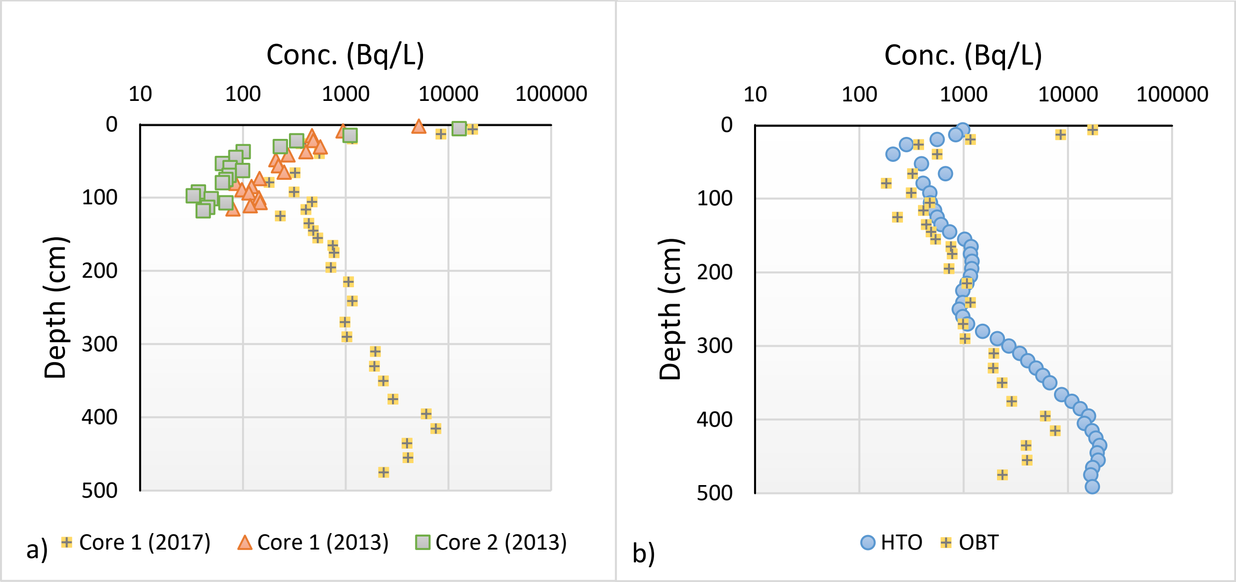

Figure 9: a) OBT activities measured in different years; b) HTO and OBT activities in core 1 (2017).

Figure 9a shows comparison of Core 1 OBT profile against the 2013 soil OBT profiles from thesis work (Dehay-Turner, 2016). The general trend and OBT scale were very similar. In both projects soil samples were not rinsed. The Core 1 data at depth 0.5-1.2 m was noisy because it was below or at LLD. Dehay-Turner (2016) also discussed reaching the detection limit for OBT analysis at 1 m depth, although the tube furnace soil combustion method he used had better LLD than Sample Oxidizer method.

With the change of soil moisture saturation and soil type at depth the OBT values started increasing following HTO profile as demonstrated on figure 9b. The OBT to HTO ratios were mostly below 1 except for the top soil which had a ratio significantly above 1. The high OBT values in deep soil could not be explained without full soil characterization e.g. particle size distribution, organic content, carbon age, etc. It can be argued that unrinsed soil samples would have a significant amount of surface adsorbed water that would have similar tritium concentration as surrounding pore water. As a result, OBT values would be overestimated. The work which involved rinsing soil samples was discussed later in section 6.6

Samples were also analyzed for total carbon and hydrogen content as part of OBT methodology using the elemental analyzer. Total hydrogen was needed for converting units from dpm/g to Bq/L where g is the weight of the soil and L is the volume of water released from combusted soil. It was also a good indication of total possible chemically and non-chemically bound water molecules stored in a complex mixture such as soil. Carbon content would indicate general quantity of soil organic matter. However, the carbon value could be skewed by carbonates since the processing temperature of 1300 °C was above the complete carbonate decomposition temperature of 850°C. Despite the fact that carbonates were not expected in silty-clay overburden, multiple samples were combusted at 650°C and 1300°C to test the possibility of carbonates interference. Both temperatures generated similar results

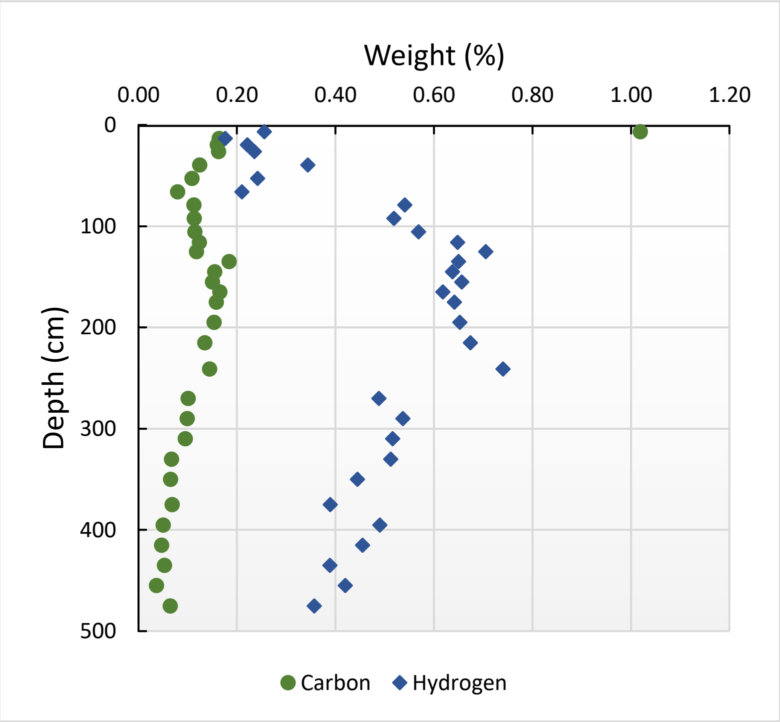

Figure 10: Total carbon and hydrogen contents in core 1 soil samples processed at 1300°C

within expected deviation. As a result, it was decided to use 1300°C as the processing temperature for the methodology to avoid incomplete decomposition of organics.

The total carbon and hydrogen profiles are shown on figure 10. The soil around SRBT was very carbon poor because it originated from Champlain Sea deposits (Catto, 1978). The top soil had the highest quantity of carbon, which was around 1% that rapidly dropped to 0.2%, decreasing to less than 0.1% at the maximum core 1 depth. A local maximum of 0.18% was observed at the soil type boundary at around 1.5 m that also corresponded to the water table level. Unlike carbon, total bound hydrogen was increasing with depth until reaching a plateau in 1.25-2.50 m range followed by steady decline. The range of hydrogen quantity in the samples was from 0.2 to 0.7%.

Measurable quantities of carbon as well as bound tritium throughout the extent of the overburden could imply that some of bound tritium could be organically bound. If carbon is organic and did not infiltrate the soil from the surface as already tritiated compounds, then the possible mechanism of OBT formation at such depth would be by HTO activation. To support this hypothesis radiocarbon analysis and TGA were performed.

6.3 Carbon dating results

Radiocarbon analysis was performed on 10 selected samples as part of undergraduate thesis project by Jacob Harvey (Harvey, 2018). All samples were rinsed with tritium-free water 3 times prior to proceeding with the treatment protocol for the accelerator mass spectrometer (AMS) analysis. The AMS methodology is fully described in Harvey, 2018. He concluded that the soil contained no modern carbon: all samples were Holocene in age with range from 4,193 YBP to 10,368 YBP (figure 11a) which approximate the age of these sediments. However, only 6 out of 10 samples had sufficient carbon yield for radiocarbon analysis. The fact that the deepest samples could not provide enough carbon for the analysis was consistent with carbon data from elemental analyzer. Harvey also observed that top soil carbon content was significantly disturbed by dead carbon from asphalt on the site. As the result the top soil carbon age was measured as 10,368 YBP.

Radiocarbon analysis confirmed that no measurable quantities of modern carbon infiltrated the soil therefore if tritium is organically bound it would not originate from the biological activity at the surface. Hence, any original plant OBT in decomposing soil organic matter would be negligible due to tritium decay.

6.4 Thermogravimetric Analysis results

Thermogravimetric analysis measures the weight loss of the sample as the function of temperature and time. The weight change at 110 °C, 550 °C, and 850 °C would be assigned to gravimetric water, organics, and carbonates quantities respectively. The results are summarized in the tables 1 and 2.

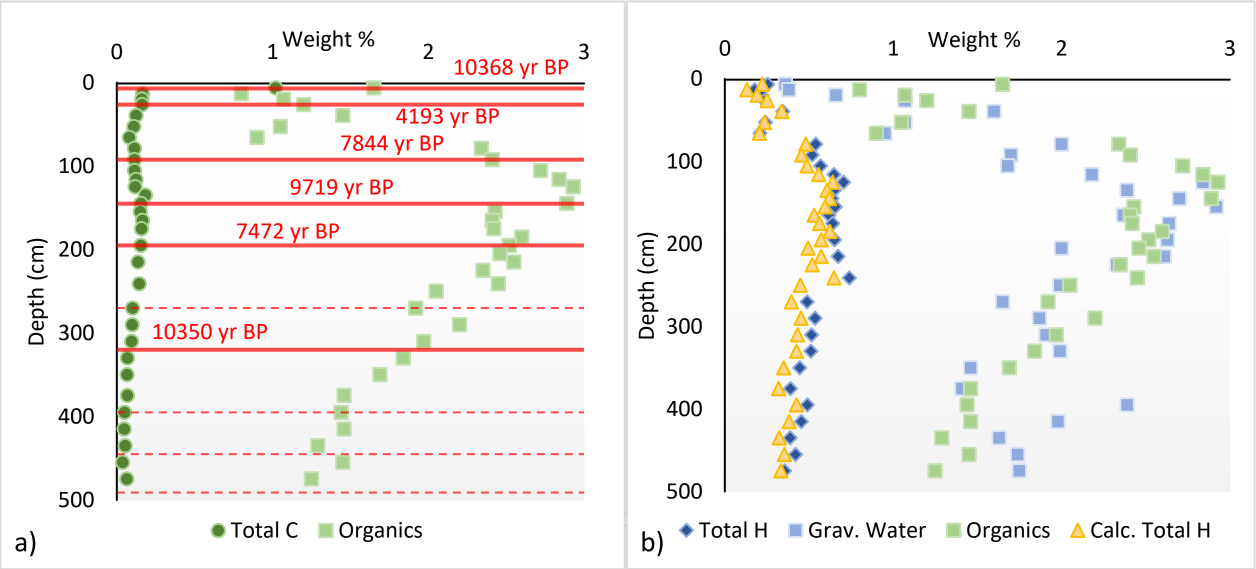

Figure 11: a) Comparison of total carbon, organics and carbon age in core 1 2017 soil; b) TGA results and calculated total hydrogen with assumption that organics is a bound form of water vs. total hydrogen measurement

The first inconsistency was observed while comparing total carbon and organic contents in soil samples (figure 11a). TGA predicted a significant amount of organics from 1 to 3% throughout the overburden material, however, the elemental analyzer results showed very small quantities of carbon, especially at greater depths (<0.1%). The noticeable organics peak at 125 cm did not correspond to such a magnitude change in total carbon. Also, top soil was expected to have the highest organic content that was confirmed by elemental analyzer results, but such trend was not observed in TGA results.

Gravimetric water from TGA had similar trend as total hydrogen from elemental analyzer (figure 11b). The results showed same magnitude global maximum around 125 cm as organics. The peak in both cases was more consistent with hydrogen data than with carbon data. From observed irregularities, it could be presumed that organics data set behaved more like water than carbon-based compound. To validate this hypothesis a simple conversion was performed: organics weight percent was assigned to water, combined with gravimetric water amount followed by total hydrogen calculation. As it can be seen on figure 11b, calculated total hydrogen from TGA results matched the elemental analyzer total hydrogen. Therefore, if bound water was present in the soil samples that would be released from 110 to 550 °C, the TGA would not be able to distinguish water from organics by simple weight change thus overestimating organics content.

Although TGA results could not provide precise information regarding amount of organics in the soil samples, they strongly indicated the presence of bound water. Such bound water could be the reason for high measured “OBT” values if equilibration with HTO took place.

6.5 Particle Size Analysis results

The presence of bound water in soil samples from SRBT could be attributed to clays. Particle size analysis was performed on both Core 1 and Core 2 to quantify clay occurrence in the overburden material. Figure 12 shows the distribution of clays throughout the extent of core 1 underlaying corresponding HTO and OBT profiles. Each soil layer had different type and quantity of clay that could be responsible for HTO retention.

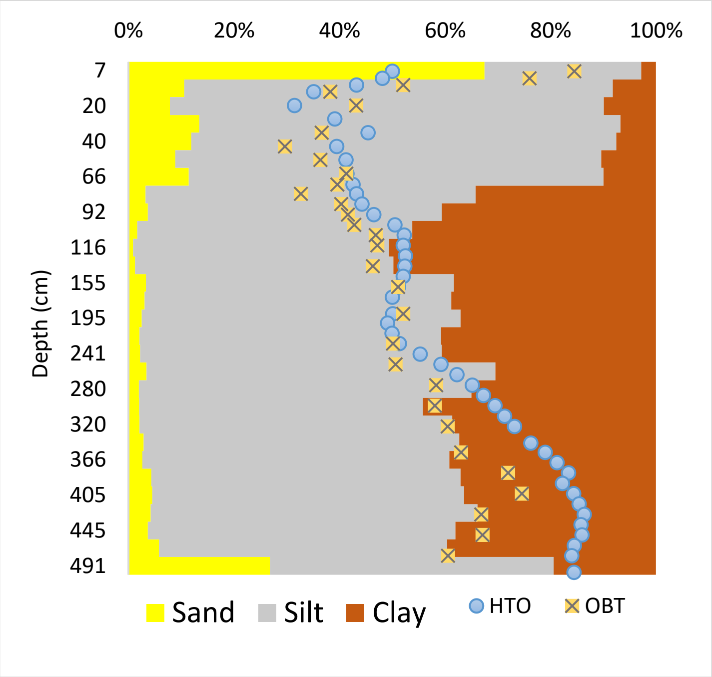

Figure 12: PSA results for core 1 in 2017 overlaying HTO and OBT profiles

Multiple publications (Kalinichenko, Pushkarova, Fenoll Hach-Ali, & Lopez-Galindo, 2002; Lopez-Galindo, et al., 2008) confirm the role of clay minerals (kaolinite and montmorillonite with some illite) in tritium sorption, redistribution, and accumulation. The data available on hydrogen stable isotope exchange in a “clay mineral–water” system suggests the principal ability of a heavier isotope to replace hydrogen in the hydroxyl group under standard thermodynamic conditions. Tritium can, therefore, enter into various structural positions in the clay particles. The strongest fixation of tritium is provided by hydrogen-isotope exchange at structural OH-group positions. That would explain possible long-term retention of tritium in soils around SRBT since the clays around the sampling site also contained illite, kaolinite, and montmorillonite (Catto, 1978).

Inconsistencies with TGA results and measured "OBT" values can also be clarified by inherit clay properties. The bound water that could exchange hydrogen for tritium would determine potential capacity for tritium accumulation. The total capacity can be expressed as the sum of individual bound water types: superficially adsorbed water, interlayer water, and structural OH-groups (Lopez-Galindo, et al., 2008). Each type of bound water would have its own temperature range at which that water would be released from the clay particles. E.g., clay adsorbed water would be completely desiccated around 200°C, followed by 200-300 °C for interlayer water and 400-750 °C for structural OH-groups. As presented on figure 13, clay water would interfere with both OBT and TGA analyses since different water fractions could be accounted for organics, carbonates or organically bound water depending on clay type.

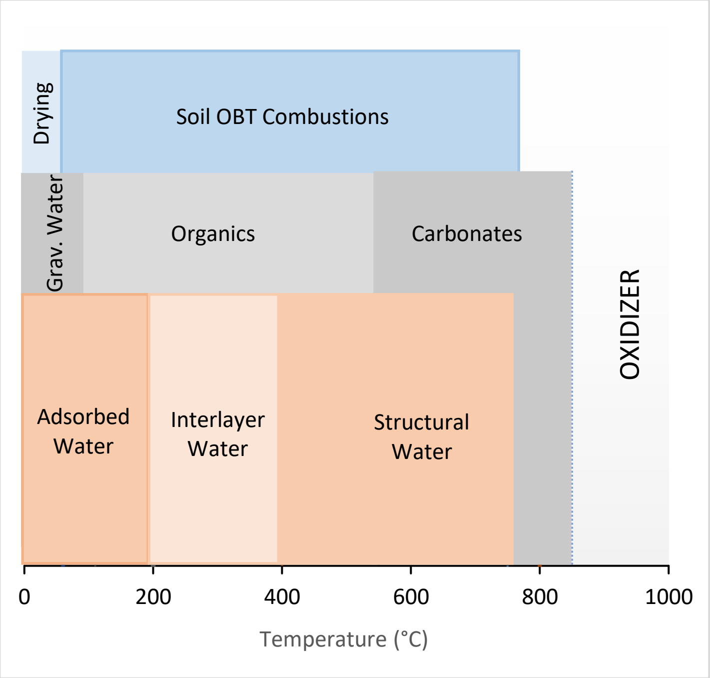

Figure 13: Analysis and water extraction temperatures in conventional soil OBT analysis, TGA, and clays (Lopez-Galindo, et al., 2008)

The discovery of a clay water interference with OBT analyses poses the major question whether true OBT can be measured by simple soil combustions. As seen on figure 12, clay particles are present at any depth interval, therefore potentially storing additional tritium in interlayer or structural clay water. Although the OBT activation by HTO in soil is still a valid hypothesis, it cannot be demonstrated in the presence of clay minerals using current OBT methods of analyses.

6.6 Special Investigation results

The idea behind the special investigation was to measure “OBT” signal in soil samples with and without an aggressive heat treatment in vacuum. Heat treatment would strip all bound water without carbon oxidation thus only true OBT could be measured.

Since special investigation included rinsing samples with tritium-free water, the measured tritium would not include exchangeable OBT (Kim & Korolevych, 2013). As shown on figure 14a rinsing clay containing soil samples did not have a detrimental effect on tritium levels: in the top soil layer and sandy silt incursion tritium levels were similar to OBT measured by Oxidizer, while in the region of brown-grey silty clay, helium mass spec measured slightly lower tritium activity.

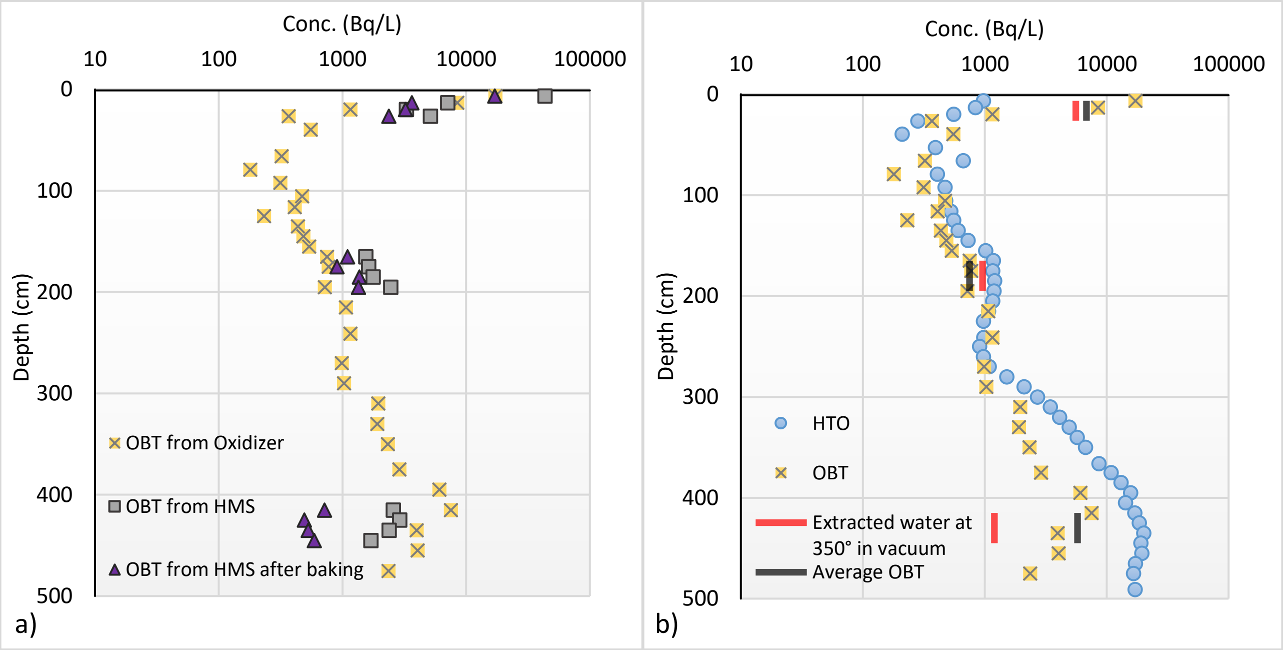

Figure 14: a) OBT measurements by Oxidizer (unrinsed), Helium Mass Spec (rinsed) and Helium Mass Spec (rinsed and pre-treated); b) correlation between tritium activity in extraction water from rinsed soil samples and OBT/HTO profiles of unrinsed soil samples

Baking the samples at 350 °C in vacuum had a general effect of “OBT” reduction but it was insignificant to make definite conclusion regarding domination of interlayer clay water over true OBT signal. The long exposure of soil to HTO would result in tritium as part of structural water, therefore, it would not be released at 350 °C (Lopez-Galindo, et al., 2008). The major decrease was only observed for brown-grey silty clay in the high activity soil samples. Also, both carbon and hydrogen contents decreased as shown in table 5 indicating that some organics could be affected.

The water released at 350 °C had activity similar to HTO and OBT values except for brown-grey silty clay samples. That would imply that short term rinsing of soil samples would not remove tritium from clay bound water. This was also observed in (Kalinichenko, Pushkarova, Fenoll Hach-Ali, & Lopez-Galindo, 2002) stating the equilibration with clay water is a slow process.

Special investigation confirmed that OBT and clay bound tritium are indistinguishable with conventional methods of analysis. Activation of OBT and clay bound tritium by HTO in soil would be parallel processes. Isolating true OBT could be very challenging in the samples with high percent of clay and low percent of organic carbon.

7. Conclusions

The current study sought to demonstrate OBT activation by HTO in soil which would imply a complimentary mechanism for tritium enrichment in soils that was observed in other OBT related studies. Instead, a greater insight into a clay-bound tritium was made, suggesting interference with OBT measurements. Since the term OBT excludes all but organically bound tritium from biological activity, it is not sufficient as an operational term. Matrix-bound tritium (MBT) would be a better term for describing total bound forms of tritium in soil including clay-bound tritium and OBT.

An environmental site was found which had an elevated tritium plume going through silty-clay overburden as a result of nearby nuclear facility operation. The HTO and “OBT” (MBT) profiles were remarkably similar and showed unexpected elevated concentrations of tritium at greater depths despite the groundwater monitoring data suggesting that the tritium peak had already occurred.

Further soil characterization quantified high clay content and carbon age in soil. It was concluded that clay water was responsible for tritium retention and redistribution thus masking the OBT signal. Short term rinses did not remove clay bound tritium which indicated long term tritium storage capability of that overburden material.

A new methodology is required for separating clay water and OBT without disturbing either of them for the purpose soil OBT quantification. Current methods of OBT analysis are insufficient to resolve the discovered issues. Although scientific hypothesis behind this thesis project is still valid, OBT activation by HTO in soil has not been demonstrated in the environment yet. The major outcome of this project is that the clay bound tritium has to be addressed in any future research related to soil OBT.

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Appendix A

Table 1: Core 1 data

Core Label	HTO (Bq/L)	±1 Sigma (Bq/L)	LLD (Bq/L)	Sample Interval (cm)	Sand %	Silt %	Clay %	Gravimetric Water %	Organics %	Carbonates %	Carbon % (at 1300°C)	Hydrogen % (at 1300°C)	OBT Activity (dpm/g)	OBT (Bq/L)
1-1-5 (0-5cm)	979	11	5	7	67.49	29.73	2.78	0.36	1.65	1.27	1.019	0.256	23.86	17284
1-1-10 (5-10cm)	840	10	5	13	10.55	81.23	8.22	0.38	0.80	0.46	0.164	0.177	8.12	8512
1-1-15 (10-15cm)	558	8	5	20	7.82	82.30	9.88	0.66	1.07	0.50	0.160	0.221	1.39	1161
1-1-20 (15-20cm)	283	6	5	26	13.43	79.81	6.76	1.07	1.20	0.51	0.162	0.235	0.47	370
1-1-30 (20-30cm)	210	5	5	40	11.88	80.58	7.54	1.60	1.45	0.61	0.124	0.344	1.03	556
1-1-40 (30-40cm)	395	7	5	53	8.87	80.76	10.37	1.07	1.05	0.50	0.109	0.242		
1-1-50 (40-50cm)	670	9	5	66	11.40	78.62	9.98	0.95	0.90	0.46	0.080	0.210	0.37	323
1-1-60 (50-60cm)	409	7	5	79	3.23	62.54	34.23	2.00	2.34	1.01	0.113	0.541	0.53	181
1-1-70 (60-70cm)	473	8	5	92	3.65	55.73	40.62	1.70	2.41	1.03	0.113	0.519	0.88	315
1-1-80 (70-80cm)	480	8	5	105	1.68	52.14	46.18	1.68	2.72	0.85	0.114	0.569	1.45	474
1-1-88 (80-88cm)	527	8	5	116	0.87	48.49	50.64	2.18	2.84	0.90	0.124	0.648	1.44	412
1-1 bottom 9cm	558	8	5	125			50.20	2.84	2.93	0.90	0.118	0.705	0.88	232
1-2-10 (0-10cm)	606	9	5	135	1.24	49.00	49.76	2.39	3.07	0.89	0.184	0.650	1.54	438
1-2-20 (10-20cm)	732	9	5	145			44.06	2.70	2.89	0.81	0.155	0.638	1.67	486
1-2-30 (20-30cm)	1021	11	5	155	3.31	58.34	38.35	2.92	2.43	1.10	0.151	0.657	1.91	538
1-2-40 (30-40cm)	1179	12	5	165			38.59	2.37	2.41	1.06	0.166	0.618	2.52	754
1-2-50 (40-50cm)	1163	12	5	175	3.03	58.15	38.82	2.64	2.42	1.09	0.158	0.642	2.68	775
1-2-60 (50-60cm)	1205	12	5	185			37.93	3.01	2.60	1.14			3.21	
1-2-70 (60-70cm)	1196	12	5	195	2.52	60.45	37.03	2.63	2.52	1.06	0.153	0.653	2.55	723
1-2-80 (70-80cm)	1162	12	5	205			38.90	2.00	2.46	1.05			2.89	
1-2-90 (80-90cm)	1077	11	5	215	2.07	57.17	40.76	2.61	2.55	1.09	0.135	0.674	3.90	1072
1-2-100 (90-100cm)	979	11	5	225			40.69	2.33	2.35	0.99			3.19	
1-2-116 (100-116cm)	983	11	5	241	2.23	57.15	40.62	3.38	2.45	1.02	0.144	0.740	4.64	1161

Core Label	HTO (Bq/L)	±1 Sigma (Bq/L)	LLD (Bq/L)	Sample Interval (cm)	Sand %	Silt %	Clay %	Gravimetric Water %	Organics %	Carbonates %	Carbon % (at 1300°C)	Hydrogen % (at 1300°C)	OBT Activity (dpm/g)	OBT (Bq/L)
1-2 bottom 9cm	910	10	5	250			35.53	1.99	2.05	0.88			1.92	
1-3-10 (0-10cm)	978	11	5	260	3.42	66.14	30.44						2.43	
1-3-20 (10-20cm)	1093	12	5	270			32.72	1.65	1.92	0.82	0.101	0.488	2.61	990
1-3-30 (20-30cm)	1520	14	5	280	1.97	63.03	35.00						1.87	
1-3-40 (30-40cm)	2108	16	5	290			39.59	1.87	2.20	0.92	0.099	0.537	2.99	1032
1-3-50 (40-50cm)	2718	18	5	300	2.03	53.79	44.18						4.94	
1-3-60 (50-60cm)	3450	21	5	310			41.41	1.91	1.97	0.85	0.095	0.516	5.44	1954
1-3-70 (60-70cm)	4127	22	5	320	2.08	59.29	38.63						4.340	
1-3-80 (70-80cm)	4952	24	5	330			37.97	1.99	1.84	0.84	0.067	0.513	5.30	1913
1-3-90 (80-90cm)	5747	26	5	340	2.86	59.84	37.30						5.82	
1-3-100 (90-100cm)	6718	29	6	350			38.24	1.46	1.69	0.78	0.065	0.445	5.62	2339
1-3-116 (100-116cm)	8686	33	6	366	2.66	58.17	39.17						13.20	
1-3 bottom 9cm	10888	36	6	375			38.12	1.41	1.46	0.72	0.069	0.390	6.11	2902
1-4-10 (0-10cm)	13150	39	5	385	4.32	58.61	37.07						7.05	
1-4-20 (10-20cm)	15734	43	5	395			36.74	2.39	1.44	0.89	0.050	0.490	16.11	6090
1-4-30 (20-30cm)	14341	40	5	405	4.53	59.07	36.40						12.51	
1-4-40 (30-40cm)	17037	44	5	415			35.14	1.98	1.46	0.93	0.047	0.455	18.57	7559
1-4-50 (40-50cm)	18582	46	5	425	4.22	61.91	33.87						5.82	
1-4-60 (50-60cm)	20200	49	5	435			35.95	1.63	1.29	0.79	0.053	0.389	8.35	3980
1-4-70 (60-70cm)	19131	47	5	445	3.64	58.33	38.03						7.20	
1-4-80 (70-80cm)	19430	47	5	455			38.81	1.74	1.45	1.02	0.037	0.420	9.19	4053
1-4-90 (80-90cm)	17247	45	5	465	5.77	54.64	39.59						12.21	
1-4-100 (90-100cm)	16608	44	5	475			29.51	1.75	1.25	0.83	0.064	0.357	4.54	2356
1-4-116 (100-116cm)	17185	44	5	491	26.82	53.72	19.43						1.17	
1-4 bottom 9cm								1.08	0.82	6.23				

Table 2: Core 2 data

Core Label	HTO (Bq/L)	±1 Sigma (Bq/L)	LLD (Bq/L)	Sample Interval (cm)	Sand %	Silt %	Clay %	Gravimetric Water %	Organics %	Carbonates %	Carbon % (at 1300°C)	Hydrogen % (at 1300°C)	OBT Activity (dpm/g)	OBT (Bq/L)
2-1-5 (1-5cm)	290	6	3	6	17.51	62.82	19.67	0.87	3.91	0.75	1.404	0.492	2.96	1116
2-1-10 (5-10cm)	187	5	3	12				0.74	3.67	0.79	1.248	0.448	1.48	610
2-1-15 (10-15cm)	145	4	3	17	12.17	66.74	21.09	0.73	3.34	0.73	0.936	0.425		
2-1-20 (15-20cm)	116	4	3	23	6.54	69.60	23.86	0.87	2.45	0.83	0.358	0.412	0.07	33
2-1-30 (20-30cm)	102	3	3	35										
2-1-40 (30-40cm)	91	3	2	46	1.65	50.59	47.76	1.91	3.14	0.87	0.206	0.633		
2-1-50 (40-50cm)	100	3	3	58										
2-1-60 (50-60cm)	114	4	3	70	2.77	53.19	44.04	1.48	3.11	0.87	0.191	0.592		
2-1-70 (60-70cm)	133	4	3	81										
2-1-80 (70-80cm)	120	4	3	93	1.36	49.94	48.70	1.38	2.97	0.83	0.189	0.557		
2-1-90 (80-90cm)	144	4	3	104										
2-1-100 (90-100cm)	171	5	3	116	1.49	57.98	40.53	1.29	2.77	0.77	0.143	0.530	1.39	485
2-1 bottom 9cm	184	5	3	125	16.29	63.79	19.92							
2-2-10 (0-10cm)	180	4	3	135										
2-2-20 (10-20cm)	172	4	3	145	2.10	59.15	38.75	1.40	2.72	0.77	0.155	0.548	0.14	49
2-2-30 (20-30cm)	167	4	3	155										
2-2-40 (30-40cm)	158	4	3	165										
2-2-50 (40-50cm)	159	4	3	175	2.28	61.05	36.67	1.64	2.60	0.75	0.132	0.544	0.04	15
2-2-60 (50-60cm)	157	4	3	185										
2-2-70 (60-70cm)	156	4	3	195										
2-2-80 (70-80cm)	158	4	3	205	2.47	61.14	36.39	1.84	2.86	0.75	0.255	0.573		
2-2-90 (80-90cm)	157	4	3	215										
2-2-100 (90-100cm)	155	4	3	225										
2-2-116 (100-116cm)	161	4	3	241	2.57	64.10	33.33	3.28	2.21	0.85	0.147	0.665		
2-2 bottom 9cm	177	4	3	250										

Core Label	HTO (Bq/L)	±1 Sigma (Bq/L)	LLD (Bq/L)	Sample Interval (cm)	Sand %	Silt %	Clay %	Gravimetric Water %	Organics %	Carbonates %	Carbon % (at 1300°C)	Hydrogen % (at 1300°C)	OBT Activity (dpm/g)	OBT (Bq/L)
2-3-10 (0-10cm)	173	4	3	260										
2-3-20 (10-20cm)	166	4	3	270	2.36	58.36	39.28							
2-3-30 (20-30cm)	167	4	3	280				1.20	2.20	0.7	0.139	0.443		
2-3-40 (30-40cm)	203	4	3	290										
2-3-50 (40-50cm)	213	4	3	300	3.96	59.06	36.98							
2-3-60 (50-60cm)	277	7	5	310										
2-3-70 (60-70cm)	237	6	3	320										
2-3-80 (70-80cm)	268	6	4	330	4.08	58.52	37.40	2.24	1.61	0.75	0.061	0.498		
2-3-90 (80-90cm)	276	6	4	340										
2-3-100 (90-100cm)	215	5	3	350										
2-3-116 (100-116cm)	224	5	3	366										
2-3 bottom 9cm	265	6	3	375	3.66	58.74	37.60							
2-4 top 7.5cm	323	7	3	388				0.91	1.52	1.01	0.046	0.381		
2-4-10 (0-10cm)	474	9	5	398										
2-4-20 (10-20cm)	472	9	4	408										
2-4-30 (20-30cm)	553	10	4	418	4.04	58.37	37.59							
2-4-40 (30-40cm)	575	10	4	428										
2-4-50 (40-50cm)	706	12	5	438				1.01	1.25	0.73	0.101	0.342	0.52	283
2-4-60 (50-60cm)	660	11	5	448	3.67	57.68	38.65							
2-4-70 (60-70cm)	460	7	3	458										
2-4-80 (70-80cm)	524	8	3	468										
2-4-90 (80-90cm)	494	7	3	478	4.29	56.93	38.78							
2-4-103 (90-103cm)	696	11	4	491				1.69	2.20	1.01	0.222	0.502	0.64	237
2-4- Bottom 9 cm	745	9	3	500										
2-5 (20-30cm)	1261	12	3	530	5.82	65.33	28.55							
2-5 (60-70cm)	1,348	12	3	570										
2-5 (106-116cm)	1209	11	3	616										
2-5 bottom 9 cm	1164	11	3	625	45.45	44.95	9.60	0.62	0.52	28.59	5.488	0.152	0.76	928

Appendix B

Table 3: Tritium in soil by helium ingrowth experiment

Sample ID	Bg/g	Bg/g error	Sample Crimped	Day of MS run	Weight of Sample (g)	Days of Ingrowth
SRBT_Soil_1-1-5	8.078E-01	1.022E-02	June-19-18	September-04-18	5.1	77
SRBT_Soil_1-1-10	1.115E-01	9.723E-03	June-19-18	September-04-18	5.07	77
SRBT_Soil_1-1-15	6.413E-02	5.773E-03	June-19-18	September-04-18	5.02	77
SRBT_Soil_1-1-20	1.072E-01	3.168E-03	June-19-18	September-04-18	4.98	77
SRBT_Soil_1-2-40	7.068E-02	8.462E-03	June-20-18	September-05-18	5.05	77
SRBT_Soil_1-2-50	7.421E-02	6.217E-03	June-20-18	September-05-18	5.04	77
SRBT_Soil_1-2-60	8.112E-02	4.144E-03	June-20-18	September-05-18	5.04	77
SRBT_Soil_1-2-70	9.073E-02	3.309E-03	June-20-18	September-05-18	5.06	77
SRBT_Soil_1-4-40	8.744E-02	6.405E-03	June-21-18	September-06-18	5.1	77
SRBT_Soil_1-4-50	8.680E-02	4.594E-03	June-21-18	September-06-18	5.05	77
SRBT_Soil_1-4-60	7.746E-02	4.947E-03	June-21-18	September-06-18	5.1	77
SRBT_Soil_1-4-70	7.894E-02	6.129E-03	June-21-18	September-06-18	5.06	77
SRBT_Soil_1-1-5b	1.966E-01	9.759E-03	June-27-18	September-07-18	5.05	72
SRBT_Soil_1-1-10b	3.542E-02	4.297E-03	June-27-18	September-07-18	4.94	72
SRBT_Soil_1-1-15b	3.630E-02	4.837E-03	June-27-18	September-07-18	5.00	72
SRBT_Soil_1-1-20b	2.541E-02	4.200E-03	June-27-18	September-07-18	5.03	72
SRBT_Soil_1-2-40b	2.068E-02	7.619E-04	June-28-18	September-10-18	5.12	74
SRBT_Soil_1-2-50b	1.842E-02	1.941E-03	June-28-18	September-10-18	5.15	74
SRBT_Soil_1-2-60b	2.646E-02	4.240E-03	June-28-18	September-10-18	5.07	74
SRBT_Soil_1-2-70b	2.714E-02	1.324E-03	June-28-18	September-10-18	5.06	74
SRBT_Soil_1-4-40b	1.053E-02	3.073E-03	June-29-18	September-11-18	5.00	74
SRBT_Soil_1-4-50b	6.415E-03	4.991E-04	June-29-18	September-11-18	5.16	74
SRBT_Soil_1-4-60b	7.083E-03	2.555E-03	June-29-18	September-11-18	5.11	74
SRBT_Soil_1-4-70b	9.250E-03	1.861E-03	June-29-18	September-11-18	4.93	74

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Table 4: Comparison of soil OBT by Oxidizer/LSC and Helium mass spectrometry analyses as part of special investigation

Sample ID	Depth (cm)	HTO (Bq/L)	**OBT Oxidizer** unrinsed (Bq/L)	**Av. OBT Oxidizer** unrinsed (Bq/L)	**OBT Helium** MS rinsed (Bq/L)	**Av. OBT Helium** MS rinsed (Bq/L)	**OBT Helium** MS rinsed **BAKED** (Bq/L)	**Av. OBT Helium** MS rinsed **BAKED** (Bq/L)	**Clay water** extracted during **BAKING** (Bq/L)
1-1-5	7	979	17284	6832	43384	14740	17107	6593	5585
1-1-10	13	840	8512		7122		3653		
1-1-15	20	558	1161		3290		3241		
1-1-20	26	283	370		5164		2370		
1-2-40	165	1179	754	751	1550	1856	1100	1184	960
1-2-50	175	1163	775		1633		905		
1-2-60	185	1205			1777		1378		
1-2-70	195	1196	723		2464		1351		
1-4-40	415	17037	7559	5769	2586	2402	718	584	1201
1-4-50	425	18582			2916		494		
1-4-60	435	20201	3980		2398		530		
1-4-70	445	19131			1707		592		

Table 5: Total carbon and hydrogen content in special investigation samples

Sample ID	Depth (cm)	Oxidizer	Helium MS	Helium MS	Oxidizer	Helium MS	Helium MS
		C in Unrinsed soil (%)	**C** in Rinsed soil (%)	**C** in Rinsed BAKED soil (%)	**H** in Unrinsed soil (%)	**H** in Rinsed soil (%)	**H** in Rinsed BAKED soil (%)
1-1-5	7	1.019	1.089	0.858	0.256	0.207	0.128
1-1-10	13	0.164	0.211	0.154	0.177	0.174	0.108
1-1-15	20	0.160	0.188	0.159	0.221	0.217	0.124
1-1-20	26	0.162	0.194	0.140	0.235	0.231	0.119
1-2-40	165	0.166	0.210	0.140	0.618	0.507	0.209
1-2-50	175	0.158	0.260	0.127	0.642	0.505	0.226
1-2-60	185		0.249	0.138		0.507	0.213
1-2-70	195	0.153	0.098	0.118	0.653	0.409	0.223
1-4-40	415	0.047	0.064	0.044	0.455	0.376	0.163
1-4-50	425		0.164	0.064		0.331	0.144
1-4-60	435	0.053	0.097	0.048	0.389	0.359	0.149
1-4-70	445		0.179	0.049		0.514	0.174