Validation of a long-term tritium dynamical model

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Abstract

This study addresses the issue of partitioning between organically bound and tissue free water tritium (OBT and TFWT consequently) and their modelling in plants subject to chronic releases, with major emphasis on this partitioning validation in field experiments. Under chronic releases, tritium level in plants oscillates between background environmental level and the elevated level when the atmospheric plume is present. Typical long term regulatory models are based on the quasi-equilibrium specific activity paradigm, which produces considerable uncertainty, making the model validation difficult. An alternative approach based on dynamical model describing the processes leading to tritium level oscillations is promising, as it allows for validation of process components and parameters while reducing uncertainty. New formulation of bi-directional tritium exchange under chronic releases is deployed for atmosphere-plant interactions modelling. The proposed robust and simple approach is sensitive to the accuracy of calculated evapotranspiration (ET). To minimize the uncertainty involved, the evapotranspiration and ground heat flux were accounted for using the temperature-based Reference Crop Penman-Monteith formulation (PM). The seasonal delay in the development of the summertime latent heat flux accounted via subsurface temperature in PM was found to be adequate for the Canadian Shield (CRL study site). Measurements of OBT (including OBT night-time formation) conducted in 2008 and 2009 at CRL were used for OBT model calibration. Published results dedicated to experimental quantification of OBT/HTO ratios and datasets collected at CRL in different years were used for OBT model validation. It is found, that notwithstanding enhanced predictive skill of the model (close proximity of model results to observations on a QQ plot), substantial difference from observations exist at high OBT/HTO ratios, which occur shortly after the plume departure. This suggests important contribution from fast-forming labile OBT currently ignored in the model.

1. Introduction

HTO and OBT have significantly different formation and clearance times in plants. An HTO measurement at a single point in time reflects the instantaneous HTO concentration at that time, but a single OBT measurement reflects an average over the previous month or weeks. In particular, the averaging time of OBT in plants is very important for predicting OBT doses, as well as OBT concentrations. The objective of this study was to determine the dynamical relationship between OBT and HTO in plants, to calibrate the corresponding dynamical model and finally perform the validation of dynamical model.

In experimental OBT measurements attention was paid to diurnal oscillations, so that they were not mistaken for intra-species or spatial variability. The dynamic process of the fast plant tritium uptake under acute release is relatively well understood and adequately modelled at short period following a release (Guenot and Raskob, 1993; Russell and Ogram, 1992). The longer term predictions however tend to deviate from observations significantly (EMRAS, 2008). Stationary long term models based on the specific activity equilibration paradigm also deviate from observations, especially when it comes to assessment of OBT and the OBT/HTO ratio – the ratio is observed to be different from the expected unit value most of the time. Two factors may be involved. Firstly, more adequate long term dynamical predictions occur simultaneously with significant over-prediction of tritium uptake in the initial phase (EMRAS, 2008). One of our experiments addresses this initial phase and allows for testing the hypothesis that elevated HTO uptake occurs immediately under the atmospheric load, with very rapid HTO conversion into to labile OBT (maintenance sugars). Secondly, the scattered OBT/HTO ratio converges to observations if enhanced re-emission via evapotranspiration is considered (Korolevych, 2008, 2009). Model enhancement has been performed accordingly:

$$dC_{leaf}/dt = \rho_w M_{leaf}^{-1}(V_{ex} (C_{atm} - C_{leaf}) + \boldsymbol{E}(C_{soil} - C_{leaf})) , \quad (1)$$

where:

C_{atm} is the HTO concentration in the atmospheric moisture (Bq/L),
C_{leaf} is the HTO concentration in the plant water in leaf (Bq/L),
M_{leaf} is the mass of a *leaf* part of the plant per surface area (kg/m^2),
V_{ex} is exchange velocity (m/s)
C_{soil} is the HTO concentration in the soil moisture (Bq/L),
$\boldsymbol{E}$ denotes ET measured in mm/s

This simple activity balance formulation can be found in many applications; the term $\boldsymbol{E}C_{soil}$ has been added here for consistency to capture prolonged bi-directional tritium exchange. In this study we keep Vex similar to dry deposition velocity and define the empirical constant α_1 using experimental data:

$$V_{ex} = \alpha_1 (r_b + r_c)^{-1} \quad (2)$$

Boundary layer resistance r_b and canopy resistance r_c are calculated using a standard algorithm (Wesely, 1989).

The rate of OBT ($\boldsymbol{C}_{OBT}$) accumulation simply follows the biomass (M) growth:

$$d(M\boldsymbol{C}_{OBT})/dt = ID_p \, dM/dt \, \boldsymbol{C}_{HTO,} \quad ID_p - \text{isotopic discrimination factor.} \quad (3)$$

We then address calibration of the OBT formation model using measurements of OBT concentrations in plants in the vicinity of a continuous atmospheric tritium release at Chalk River Laboratories (CRL).Our approach is targeted both at OBT accumulation processes in general and at fine-scale process modelling, including night-time processes. In the dedicated fine-scale experiment the scale of the analysed processes has been hourly

to diurnal, the air sampling therefore has been active (using bubbler) and the care has been taken that tritium transfer through the soil pathway was simplified; intra-species and ambient variability has been accounted for. Specifically, two plots were developed: one with imported and covered clean soil and the other (control) on the natural fertilized soil. Each sampling was performed from randomly selected, identically mature plants within a two-meter radius to minimize the soil moisture and intra-species variability.

Measurements of Tissue Free Water Tritium (TFWT) and organically bound tritium (OBT) in environmental samples are carried out routinely at CRL. Tritium measurements in environmental samples around CRL are required for environmental monitoring, dose assessments and general research and development programs. Tritium levels in the vicinity of the nuclear facilities are usually less than 1,000 Bq/L in environmental samples (Kim at al. 2008).

2. Materials and Methods

2.1. Experimental sites and Sampling method

AECL's Chalk River Laboratories (CRL) site is located in Ontario on the south shore of the Ottawa River, about 200 km northwest of Ottawa. Low amounts of radioactive airborne and liquid releases occur from CRL during normal operations. Tritium is released routinely by nuclear facilities, with HTO being the most abundant form of tritium (Kim et al., 2008).

The biological samples were collected within 1 km of the CRL nuclear facilities. Plant samples were collected from May to September in 2008. Two different plants (Dandelion, *Taraxacum officinale*; American Beech, *Fagus grandifolia*) were collected and stored in a freezer for tritium analysis. Figure 1a shows the two air samplers and an American Beech tree. Figure 1b shows a dandelion.

Fine-scale experiments were performed at the site 2.5 km NW from the reactor stack (Figures 1c and 1d), that was chosen for experimental garden plot. This direction coincides with the prevailing winds at CRL and therefore planning sampling campaigns by tracking the arrival and the departure of a plume was feasible. Experiments included overnight period, lasted several hours and samples were collected at sub-hourly intervals; in addition to this, one morning sample and one noon sample has been collected over the course of a growing season with a few days interval.

2.2. Analytical method

2.2.1. Atmospheric tritium

The HTO concentration in air moisture was sampled on a weekly basis using both passive and active samplers to cross check each measurement. The value obtained from an active sampler was used to determine the HTO concentration in air at the location from which the tree leaves were collected. An active bubbling sampler is a simple and reliable device

that can used to measure low levels of tritium activity in the environment. Only the active sampler was deployed in the fine-scale experimental site.

2.2.2. TFWT

Tissue Free Water Tritium (TFWT) was extracted using a freeze-drying method and completed by drying samples in an oven. They were collected and stored in a freezer at –20˚C. A specific apparatus (laboratory design) was used for cryogenic technique. The tissue-free water was extracted using a dry ice trap at vacuum pressure for 15 hrs or longer. When freeze drying produced incompletely dried samples, a drying oven at 55˚C was employed for 24 hours to complete the drying process. The total removal of TFWT was confirmed by weighing residual samples. Special attention was given to ensure no contamination occurred from ambient air.

2.2.3. Exchangeable and non-exchangeable OBT

Once the tissue-free water was removed completely, the dried sample (approximately 20g) was chopped and homogenized. The exchangeable tritium fraction was removed by isotopic exchange to mix the dehydrated samples with tritium free water. The dry matter was mixed with 30 to 50 mL of tritium-free water to remove exchangeable OBT. The rinsed samples were treated with the same freeze-drying system as the fresh ones in order to recover the rinse water.

Over 10g of the rinsed and dried sample were combusted using a Parr bomb system (Parr Instrument Company, U.S.A.) with pressurized oxygen (300 psi). Generally, less than 5 mL of the resulting combustion water was collected by a pasture pipette directly from the bomb and purified by azotropic distillation in a fume hood at B513.

2.2.4. Liquid scintillation counting

Tritium concentrations in water samples were determined by mixing 8 mL of the water sample with 10 mL of Ultima Gold XR scintillation cocktail and placing the solution in a 20 mL polyethylene Packard^{TM} scintillation vial. For the OBT measurements, the purified combustion water sample was placed into a 20 mL LSC vial, made up to 8 mL with tritium free water and mixed with 10 mL Ultima Gold XR (PerkinElmer). Both HTO and OBT activities were counted by LSC (Beckman 6500) for 100 minutes. The minimum detectable activity (MDA) was approximately 10 Bq/L at B513.

3. Experimental Results

3.1. Tree leaves

HTO concentrations in air and HTO and OBT concentrations in tree leaves collected weekly are shown in Figure 2a. Tree leaves were collected from May 1st (early growing stage) to October 19th (late deciduous stage), which covered the major growth period of the tree. In contrast, air moisture was measured from June 19th to October 2nd. HTO concentrations varied from 332 Bq/L to 2,306 Bq/L in tree leaves. OBT concentrations varied from 802 Bq/L to 2059 Bq/L in the same tree leaves. In the tree leaves, HTO

levels fluctuated much more than OBT concentrations. Soils collected from underneath the tree on June 19th and 26th had HTO concentrations of 782 and 755 Bq/L, respectively. The trend for tritium concentration in air is very similar to the trend for OBT concentrations in tree leaves. The results suggest that the tree uptakes the same source of water for both the leaves and root.

The specific activity ratio of HTO to OBT was observed to range from 0.72 to 6.2, with an average value of 1.9. The ratio fell mostly between 2 and 3. In this location, the OBT concentration present in the tree leaves was higher than TFWT. The HTO concentration of tree leaves as compared to OBT is consistently lower because lower tritium concentrations are present in the ground water at this location.

3.2. Dandelion

Figure 2b shows weekly collected HTO concentrations in air, as well as HTO and OBT concentrations in the dandelion plant. The plant samples were collected from May 1st (early growing stage) to September 11th (late matured stage). HTO concentrations varied from 270 Bq/L to 1772 Bq/L in plant. OBT concentrations also varied, from 706 Bq/L to 2397 Bq/L in the same plant. Unlike tree leaves, the OBT concentration of the plant showed a trend very similar to that of HTO concentration. The results suggest that plant water is being drawn from the air moisture.

Also HTO (TFWT) and OBT patterns in beech leaves and in dandelion leaves collected at CRL are only slightly different. Generally, beech leaves had higher concentrations of both HTO and OBT than those of the dandelion at the same time. Four samples of dandelion however had higher measured OBT concentrations as compared to tree leaves.

In this location, the ground water tritium is negligible. Therefore, the source of tritium for TFWT and OBT is mostly through air moisture. The specific activity ratio between OBT and HTO was observed to range from 0.75 to 11.34, with an average of 3.3.

3.3. Live and Dead leaves

In this study, we used the uppermost litter layer – dead leaves that had recently accumulated and still kept their original shapes. Figure 4 shows HTO and OBT concentrations between live leaves and dead leaves collected from the American Beech tree. There is no significant difference between the two types of leaves. The present results suggest that the collected dead leaves had enough of an opening of the stomata to allow for an enhanced exchange velocity of HTO due to wet conditions such as rain

3.4. Potato and Tomato

Figure 3 depicts the ratio of OBT to HTO in different plant compartments and in fruit/pod and is aligned with the simultaneous measurements of HTO in the air and with ambient gamma-radiation, taken ftrom the neighbouring stationary monitoring station (ARMMS 117). This picture allows us to test the working hypotheses about labile OBT, which is formed at much faster rates then structural OBT and as such, consumes the excess HTO rapidly entering the plant in the initial stage of contamination. This fast rate

explains the otherwise enigmatic exceedance of OBT over TFWT and the absence of evidence supporting elevated levels of HTO, needed to sustain this labile OBT. The hourly observations interval apparently appears too coarse to have this effect resolved. The only exception is seen in the left part of the Figure 3 – the singular evidence of elevated HTO level (square marker filled blue and connected with a dotted line), which does exceed its artefact – OBT (hollow red square markers, connected with a dotted line) before the rapid fixation.

Figure 5 also presents some new evidence – the preferential accumulation of OBT in potato collected from soil-covered L-plot (large round black markers filled red and having the prefix "L-" in their legend) as it exceeds OBT in potato from the exposed R-plot (round black markers filled blue, with the "R-" prefix in their legend). Otherwise, the effect of covered soil is not apparent.

Figure 1

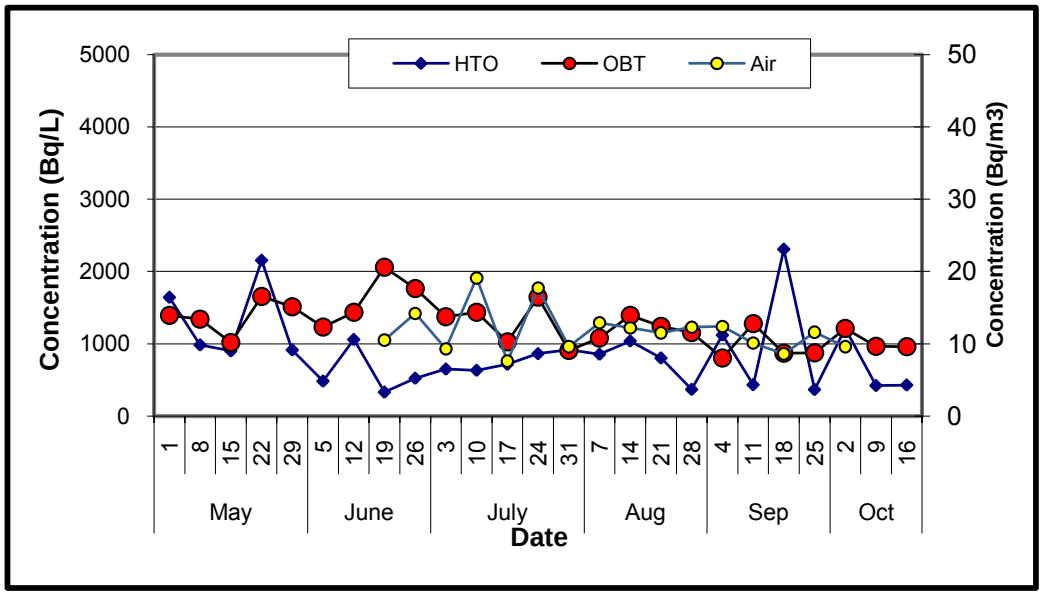
a) The continuous air sampling system and the Beech tree (*Fagus grandifolia*) that was sampled at CRL.

b) The dandelion (*Taraxacum officinale*) plant that was sampled at CRL. The plant is surrounded by the impervious pavement.

c) The experimental garden plot at CRL, Potato plants (*S. tuberosum, Russet Burbank*) at front and tomato plants (*S. lycopersicum, Beefsteak Slicing*) behind. Soil-atmosphere exchange is reduced as this portion of the plot had initially clean and protected soil.

d) The experimental garden plot at CRL, natural setting with exposed soil. Potato plants are to the left and tomato plants are to the right

a



b

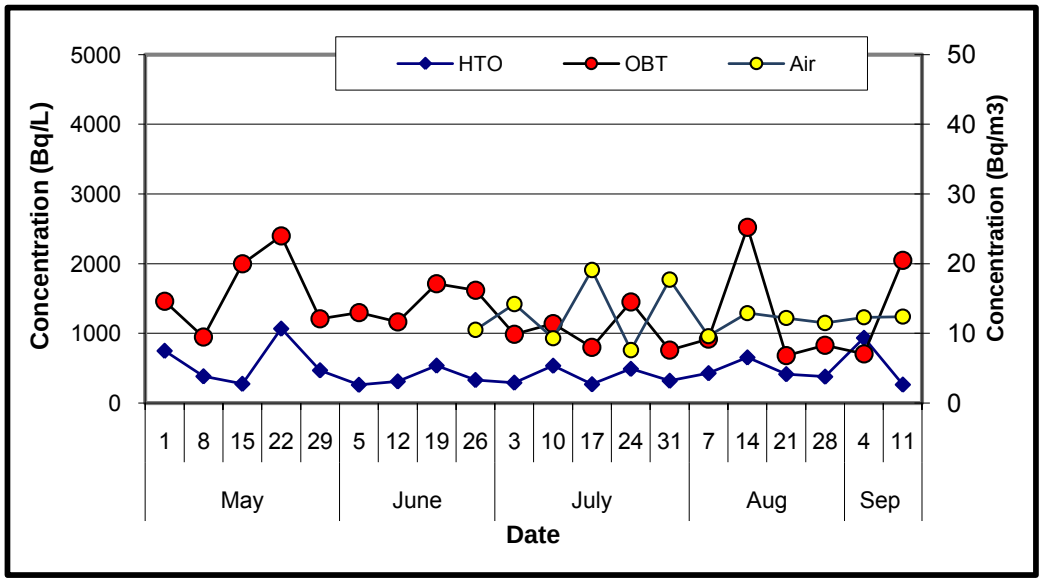


Figure 2. Weekly collected HTO in-air concentrations and HTO and OBT concentrations in:

a) tree leaves sampled at CRL
b) Weekly collected HTO in-air concentrations and HTO and OBT concentrations in dandelion sampled at CRL

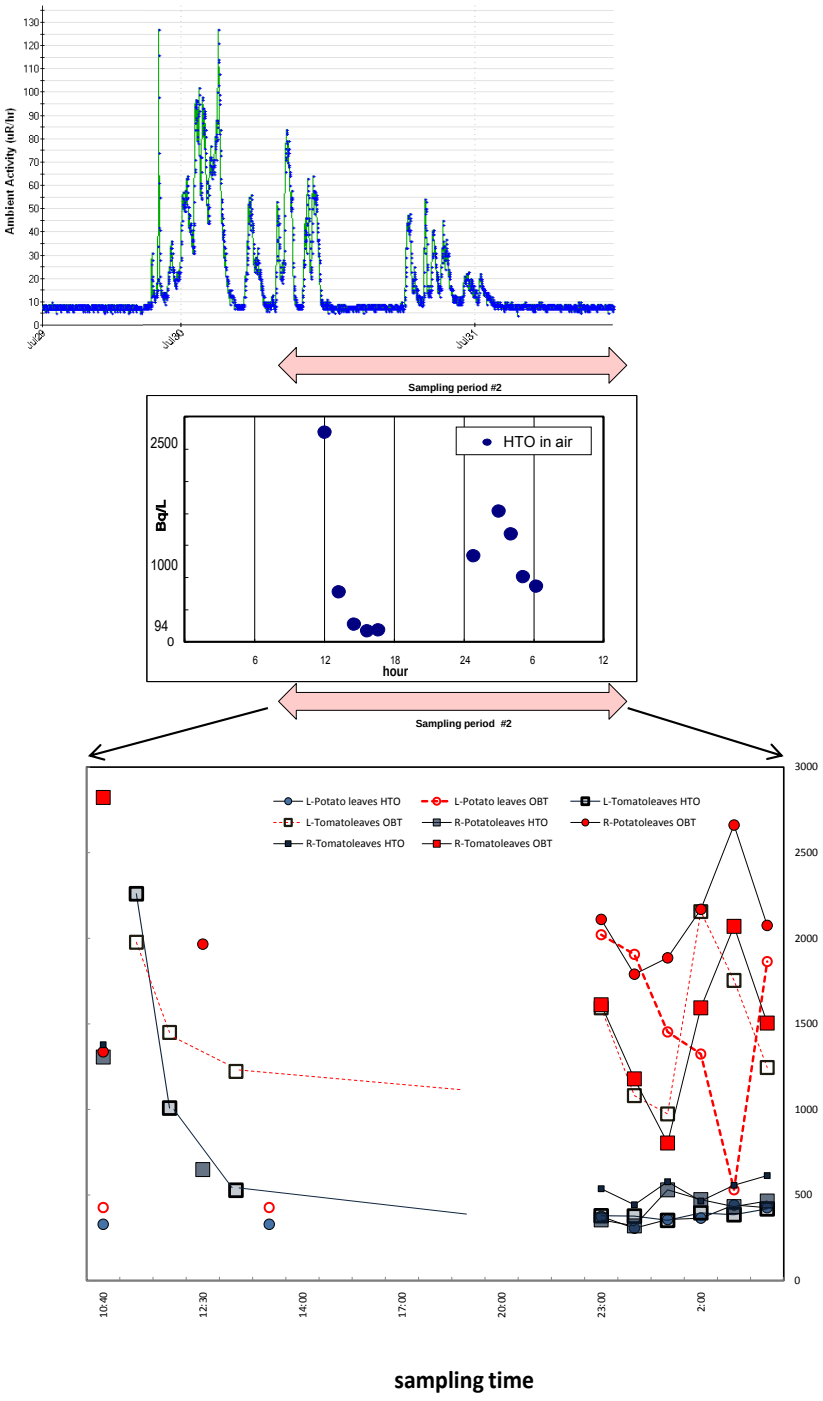


Figure 3. Ambient gamma-activity and tritium activity in the air and in different plant compartments at CRL Evidence of exceedance in OBT accumulation in plants (either red or hollow markers), as compared to plant HTO (filled blue markers).

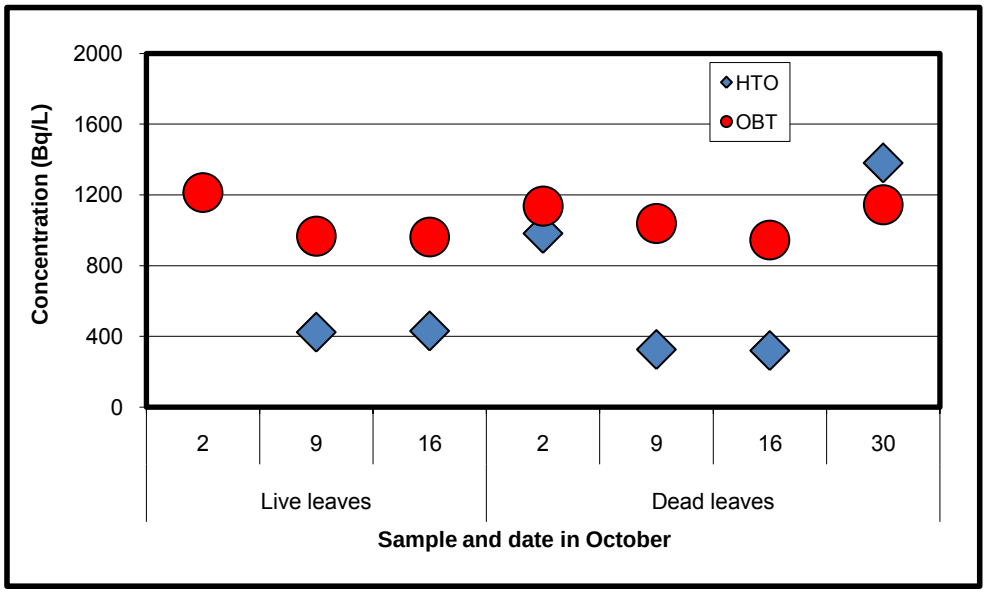


Figure 4. Comparison of HTO and OBT concentrations between live leaves and dead leaves collected from the Beech tree at B513.

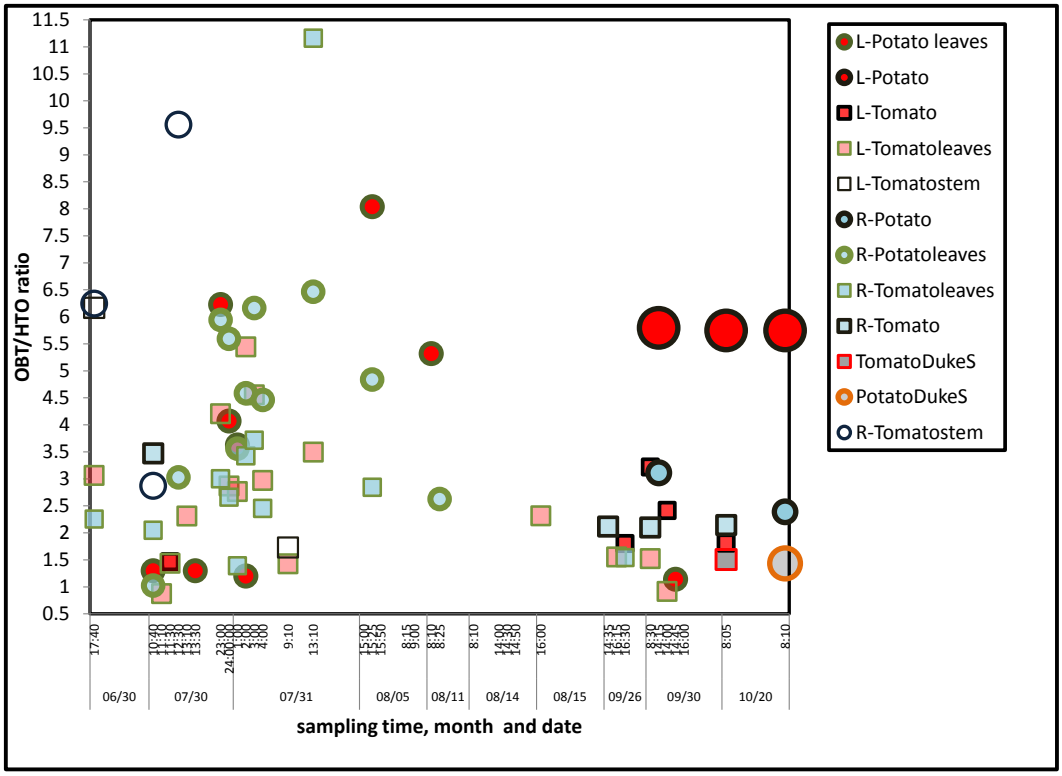


Figure 5. The ratio of OBT to HTO in different plant compartments and in fruit/pod measured at ARS plot. Preferential OBT accumulation in potato collected from the soil-covered L-plot (large red circles with the black border) as compared to OBT in potato from the exposed R-plot (smaller blue markers with the black border).

4. Model Calibration

The calibration of our model was performed using results of the field study presented in Section 3 with one exception – the labile OBT. In contrast to other measured quantities (like long-term HTO uptake rate V_{ex}), the evidence of extremely fast and efficient labile OBT formation was not incorporated into the model. First of all this evidence is still statistically insignificant. Second, it is difficult to measure the related HTO uptake rate and labile OBT formation. And third, without this additional sophistication the model remains much like its predecessors, and as such – more comparable in its predictive capability. This simplification however appeared at the cost of significant deviation of our model from observations when OBT/HTO ratios reached high values.

5. Model Validation

The validation exercise was performed using numerous published results pertaining to OBT/HTO experimental quantification. In this study the quartile-quartile plot, popular in air quality modelling (QQ-plot technique) has been implemented as an exploratory tool.

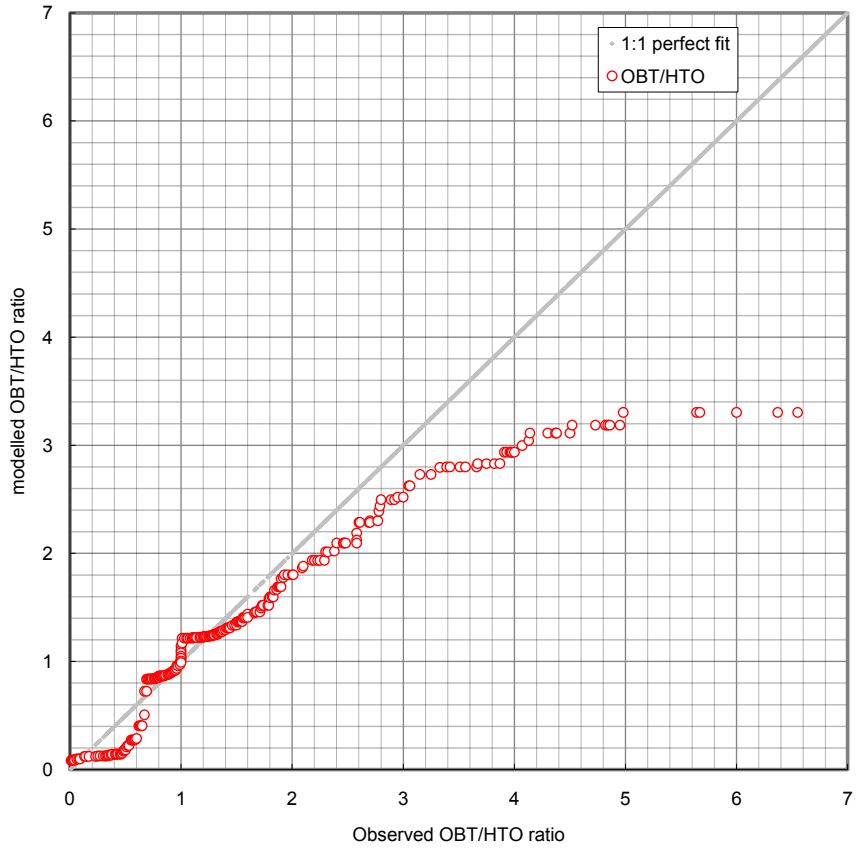


Figure 6. Plant OBT/HTO ratios: Standard tritium short-term model vs. observations reported as multiple individual ratios in different experiments from 1976-2005, QQ plot.

6. Results and Discussion

The model validation was satisfactory for two reasons. Firstly it showed that the model predictive skill (valid up to OBT/HTO ratio of 3.0) is sufficient as the model results appear quite close to observations on a QQ plot. Second, our deliberate simplification of the model (labile OBT has not been included) resulted in model under-prediction of OBT/HTO ratios during episodes of HTO depletion shortly after the plume departure, when observed OBT/HTO ratios were very large. This under-prediction fits our expectations and suggests the future direction of model development: the labile OBT formation rate should be quantified and included into consideration. Dedicated experiments should be designed to help with labile OBT quantification.

This study again confirmed, that the amount of produced OBT depends on a large number of environmental factors and plant parameters. It is difficult to obtain reliable estimates from infrequent field measurements of HTO and OBT concentrations. Useful values can be obtained only if the HTO concentration in the plant is monitored continuously over the period of OBT formation. In order to quantify the mismatched averaging times, HTO and OBT concentrations were measured weekly. The results suggest that weekly air and plant HTO sampling is definitely not sufficient to obtain an accurate estimate of processes underlying OBT formation and therefore they are not correlated well with the harvest time OBT measurements. These questions were partially resolved using an intermittent series of fine-scale (hourly) measurements from experiments of short duration. However experiments focussed at hourly scale also revealed insufficient temporal precision in some cases, e.g. in quantification of labile OBT. Future experimental campaigns should follow the chosen strategy and again consist of long term monitoring accompanied by a series of dedicated experiments on an hourly scale, with more focus made on labile OBT formation, since it is shown, that labile OBT could be a significant contributor to a total OBT concentration. Alignment of future experiment with sunrise and other key turning points may compensate for insufficient frequency of plant HTO measurements.

7. References

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