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Tritium in Bioassay Samples**

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liens organiques dans les échantillons biologiques**

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by

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**MESURES DES NIVEAUX ULTRA-FAIBLES DE TRITIUM FIXÉ
PAR DES LIENS ORGANIQUES DANS LES ÉCHANTILLONS BIOLOGIQUES**

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T. Kotzer†, A. Trivedi*, G. Waito† et W. Workman†

Résumé

Les auteurs ont effectué une étude de comparaisons corrélatives sur des échantillons d'urine présentant des niveaux élevés ($5 \text{ Bq}\cdot\text{L}^{-1}$) de tritium fixé par des liens organiques (OBT), conjointement à la méthode de comptage à scintillations du liquide de combustion d'oxygène (LSC) pour évaluer l'aptitude et la sensibilité de la technique de détection de l'OBT par spectrométrie de masse (SM) de la combinaison de ^3He dans les échantillons biologiques. L'étude a permis d'établir que la SM de la combinaison de ^3He offre la sensibilité nécessaire pour mesurer des niveaux ultra-faibles d'OBT dans l'urine ($\sim 0,1 \text{ Bq}\cdot\text{L}^{-1}$).

Des échantillons cumulatifs d'urine prélevés pendant 24 h chez quelques personnes de l'ensemble de la population vivant au voisinage du réacteur de recherche à eau lourde des Laboratoires de Chalk River (LCR) à Chalk River ont été analysés pour y déterminer la quantité d'eau tritiée (HTO) et d'OBT. Les participants étaient d'Ottawa (à 200 km à l'est), de Deep River (à 10 km à l'ouest) et un travailleur professionnellement exposé par intermittence à l'HTO aux LCR. Les valeurs de l'HTO dans l'urine étaient de $6,5 \text{ Bq}\cdot\text{L}^{-1}$ pour le résident d'Ottawa, $15,8 \text{ Bq}\cdot\text{L}^{-1}$ pour celui de Deep River et $1\,260 \text{ Bq}\cdot\text{L}^{-1}$ pour le travailleur exposé. Les concentrations d'OBT dans l'urine de ces mêmes personnes étaient de $0,06 \text{ Bq}\cdot\text{L}^{-1}$ (Ottawa), de $0,29 \text{ Bq}\cdot\text{L}^{-1}$ (Deep River) et de $2,2 \text{ Bq}\cdot\text{L}^{-1}$ (travailleur exposé). Grâce à un modèle élaboré pour calculer la fraction de dose d'OBT du rapport HTO-OBT mesuré dans l'urine, les auteurs ont estimé que la dose provenant de l'OBT dans l'organisme correspondait à 26 % de la dose totale de tritium dans le cas du résident d'Ottawa et à 50 % dans celui du résident de Deep River. Dans le cas du travailleur des LCR, la contribution de dose de l'OBT était de 5 %, mais sa dose globale de tritium était plus élevée en raison de fréquentes absorptions d'HTO. Cette étude indique que la majeure partie de la dose de tritium reçue par la population provient des absorptions d'HTO et ne sont pas dues à l'absorption alimentaire d'OBT.

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T. Kotzer†, A. Trivedi*, G. Waito† and W. Workman†

Abstract

An intercomparison study of urine samples having high levels ($5 \text{ Bq}\cdot\text{L}^{-1}$) of organically-bound tritium (OBT) was conducted, in conjunction with the oxygen combustion-liquid scintillation counting (LSC) method, to evaluate the suitability and sensitivity of the ^3He -ingrowth mass spectrometry (MS) technique for OBT in bioassay samples. The study established that ^3He ingrowth-MS has the required sensitivity to measure ultralow levels of OBT-in-urine ($\sim 0.1 \text{ Bq}\cdot\text{L}^{-1}$).

Cumulative 24 h urine samples from a few members of the general population, living in the vicinity of the heavy-water research reactor facility at Chalk River Laboratories (CRL) at Chalk River, were collected and analyzed for tritiated water (HTO) and OBT. The participants were from Ottawa (200 km east), Deep River (10 km west) and an occasionally occupationally HTO-exposed worker at CRL. HTO-in-urine values were $6.5 \text{ Bq}\cdot\text{L}^{-1}$ for the Ottawa resident, $15.8 \text{ Bq}\cdot\text{L}^{-1}$ for the Deep River resident, and $1260 \text{ Bq}\cdot\text{L}^{-1}$ for the exposed worker. OBT-in-urine levels from these same individuals were $0.06 \text{ Bq}\cdot\text{L}^{-1}$ (Ottawa), $0.29 \text{ Bq}\cdot\text{L}^{-1}$ (Deep River), and $2.2 \text{ Bq}\cdot\text{L}^{-1}$ (exposed worker). With a model developed for calculating OBT dose fraction from the measured ratio of HTO to OBT in urine, we estimated that the dose arising from OBT in the body was about 26% of the total tritium dose for the Ottawa resident and 50% for the Deep River resident. The CRL individual had a 5% dose contribution from OBT, but had higher overall tritium dose due to frequent intakes of HTO. The study indicates that the bulk of the tritium dose to the population is the result of HTO intakes and not due to dietary intake of OBT.

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1. INTRODUCTION

Exposures to tritiated water (HTO) and, to a lesser extent, the dietary intakes of organically-bound tritium (OBT) are important concerns among the public living around CANDU* nuclear power generating stations. The dose to an individual from environmental levels of tritium depends upon the proportions of HTO and OBT entering the body through all routes of intake (Brown, 1989). HTO enters the body through ingestion, inhalation and skin absorption, whereas OBT entry is primarily through ingestion (Bogen et al., 1975). An earlier study on a population living near a heavy-water research reactor facility at Chalk River Laboratories (CRL) indicated that the dose arising from the dietary intake of OBT would be small (<20% of total tritium dose) and the predicted OBT-in-urine levels are on the order of $0.1 \text{ Bq}\cdot\text{L}^{-1}$ (Trivedi et al., 1997). No OBT-in-urine measurements were performed, because of the higher limit of detection ($0.3 \text{ Bq}\cdot\text{L}^{-1}$) for available bioassay methods (e.g., low-level oxygen-combustion liquid scintillation counting (LSC)) (Trivedi et al., 1993). The methods were also subject to the increasing possibility of cross-contamination of tritium from HTO to OBT, and color- and chemical-quenching. In addition, larger quantities of sample required for OBT measurement were not easy to obtain from members of the public.

The ^3He -ingrowth mass spectrometry (MS) technique is a better alternative than low-level oxygen-combustion LSC. The determination of tritium (^3H) by the ^3He -ingrowth-MS technique indirectly measures ^3H ($t_{1/2} = 12.43 \text{ a}$) by determining the abundance of the decay daughter product, ^3He . Over the last two decades, this technique has been developed and used for routine measurements of ultralow levels of tritium in waters ($\leq 0.1 \text{ Bq}\cdot\text{L}^{-1}$; Clarke et al., 1976; Bayer et al., 1989), and occasionally to measure tritium in organic matrices (Brown, 1995). This technique: i) has typically much lower detection limits ($\leq 0.1 \text{ Bq}\cdot\text{L}^{-1}$), ii) is less susceptible to cross-contamination, iii) after sufficient ^3He -ingrowth has relatively short analysis times ($\sim 30 \text{ min}$), and iv) is readily adaptable to a wide variety of sample matrices because when a ^3H atom decays in a liquid or solid environmental sample, the resultant ^3He is sparingly soluble and chemically inert, and readily enters the gas phase (Clarke et al., 1976; Bayer et al., 1989; Kotzer et al., 1994). The technique is non-destructive in that the matrix of the sample is largely undisturbed throughout the entire sample processing and measurement procedure. This fact offers an additional advantage if repeated measurements are required on the same archived samples. The technique has been used at CRL for the measurement of ultralow level tritium concentrations in environmental samples to understand the dynamics of ^3H in the environment and to trace natural groundwater movement (Kotzer et al., 1994, 1998; Spencer et al., 1996).

Here, we report the use of ^3He -ingrowth MS to measure the ultralow levels of OBT-in-urine samples from a few members of the general population, and compare the measurement data with the model-predicted OBT concentration in urine (Trivedi et al., 1997). We have estimated the dose arising from OBT in the body due to environmental levels of tritium intake. However, first the following experiments were designed and carried out to evaluate the suitability of ^3He -ingrowth MS to measure OBT concentrations in dry residues of urine:

* CANDU: CANada Deuterium Uranium; registered trademark of AECL

- i) An OBT-in-urine intercomparison study using ^3He -ingrowth MS and oxygen combustion-LSC measurement techniques was carried out on 1 g dry residues of the urine obtained from the bioassay samples of chronically HTO-exposed workers at CRL.
- ii) Additionally, smaller portions (10-100 mg dry residue of the same urine sample) were used to investigate the sensitivity of ^3He -ingrowth MS for OBT-in-urine.

2. METHODS

2.1 Sample Preparation

2.1.1 Phase I -OBT-in-Urine Intercomparison Study

The dried urine from the bioassay samples of occupationally exposed workers were used for the intercomparison. The free-water tritium (as HTO) was removed from the urine samples and measured according to an established procedure (Trivedi et al., 1993). A portion of the dry residue (~ 1 g) of urine was processed for OBT measurement using the oxygen combustion-LSC method (Trivedi et al., 1993). Similarly, about 1 g of the dry residue was stored for ^3He ingrowth and analyzed for OBT using ^3He -ingrowth MS analysis.

The dried samples supplied for ^3He -ingrowth MS analysis were transferred into vessels constructed of Al-Si glassware (Dow-Corning 1724; Suckow et al., 1990), weighed and allowed to re-equilibrate with 20 mL of tritium-depleted water ($<0.1 \text{ Bq}\cdot\text{L}^{-1}$) for at least 24 h. The equilibration water was removed from the samples by drying in-vacuo using liquid N_2 and vacuum pressures of $\leq 10^{-4}$ torr for at least 48-72 h. The samples were then flame-sealed into the Al-Si glass vessel to isolate them from the atmosphere, and stored for about one month to allow for ^3He -ingrowth and measurement of tritium by ^3He -ingrowth MS (Table 1).

2.1.2 Phase II -OBT in Urine Samples

Healthy, middle-aged adults from communities in the vicinity of CRL participated in the study. The participants were from Ottawa (200 km east), Deep River (10 km west), and a worker occasionally occupationally exposed to HTO at CRL (Figure 1). Three participants, from the same family, from Ottawa submitted a bulk urine sample. After obtaining their consent, they were given procedures for collecting and submitting urine samples. Participants were requested to submit cumulative 24 h urine samples. Urine samples were collected in plastic, wide-mouthed *Nalgene* bottles and stored in a freezer (-20°C) to prevent microbial contamination and metabolic conversion of HTO to OBT in the samples before processing. Tritium in free water was removed from the urine samples and measured by the direct LSC as described elsewhere (Trivedi et al., 1993). The dried residue of the urine was washed several times with tritium-depleted waters to remove exchangeable OBT and adsorbed HTO. The OBT in dried urine residues were measured by ^3He -ingrowth MS as described in Appendix 1 (see also Table 1).

Table 1. Summary of Sample Preparation Methods for Tritium Measurements

Sample Type	Sample Size	HTO Separation and Measurement	Sample Preparation for OBT Measurements
Urine	Cumulative 24 h sample (0.5-3 L)	a) HTO removed by low-temperature distillation ($\sim 40^{\circ}\text{C}$) under vacuum using rotary evaporator. b) Sample washed with tritium-depleted water during processing to remove labile OBT. c) HTO measured by direct LSC method (Trivedi et al., 1993).	a) Dry residue vacuum-dried with liquid N_2 in Al-Si glassware to remove equilibration water and bring the sample to constant weight. b) Dried material sealed in Al-Si vessels and stored for a sufficient time period to measure ^3He -ingrowth using the MS technique.

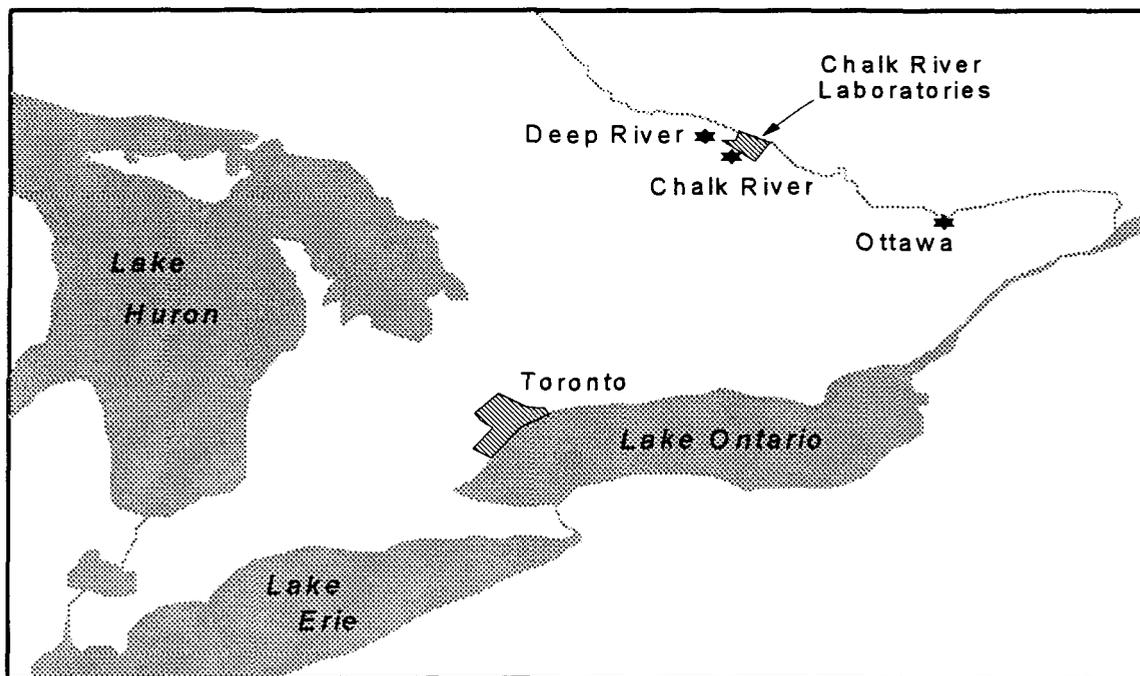


Figure 1. Location of communities in the vicinity of Chalk River Laboratories, Ontario, Canada, where urine samples from a few members of the general population were collected for this study (solid stars). Also shown are the locations of several of the Great Lakes and Toronto, Ontario.

3. RESULTS AND DISCUSSION

3.1 Intercomparison of OBT-in-Urine Measurements

Table 2 lists the measurement results of the oxygen-combustion LSC and the He-ingrowth MS techniques. Both methods provided comparable OBT-in-urine concentrations ($5.0 \pm 0.5 \text{ Bq}\cdot\text{g}^{-1}$) in dry residue of urine for sample sizes between 1 to 2 g dry weight. An earlier intercomparison exercise for measuring OBT in vegetation samples ($\sim 25 \text{ Bq}\cdot\text{g}^{-1}$ dry weight; technique adapted from Brown, 1995) from the CRL - HT release experiment (Amano et al., 1995; Davis et al., 1995) yielded comparable measurement results when comparing ^3He -ingrowth MS techniques at CRL with combustion-LSC techniques from several other laboratories. The estimated error in the measurements was on the order of $\pm 10\%$ (Spencer et al., 1996).

Table 2. OBT Measurements on the Dry Residue of a Urine Sample Using Oxygen-Combustion LSC and ^3He -Ingrowth MS Techniques

Oxygen-Combustion LSC		^3He -Ingrowth MS	
Urine Sample Size (g)	OBT ($\text{Bq}\cdot\text{g}^{-1}$)	Urine Sample Size (g)	OBT ($\text{Bq}\cdot\text{g}^{-1}$)
1.01	5.55	1.80	5.13
1.00	5.07	1.62	5.23
1.05	5.44	0.18	4.65
1.00	5.35	0.02	4.23

The sensitivity of the ^3He -ingrowth MS technique for OBT-in-urine was evaluated by reducing the size of the same dried urine sample by factors of 10- to 100-times, and storing them for the same length of time as for the 1 to 2 g samples (~ 1 month). This was done in an effort to simulate the ultralow levels of OBT in the urine samples ($\sim 0.05 \text{ Bq}\cdot\text{g}^{-1}$ dry residue or $0.1 \text{ Bq}\cdot\text{L}^{-1}$) predicted for adult residents living in Deep River (Trivedi et al., 1997). The oxygen-combustion LSC method has a lower limit of detection of $0.3 \text{ Bq}\cdot\text{L}^{-1}$ for OBT-in-urine (Trivedi et al., 1993), which is well above the expected level of OBT-in-urine.

The dilution experiment yielded comparable OBT concentrations of ~ 4.3 to $4.6 \text{ Bq}\cdot\text{g}^{-1}$ in the dry urine residues (Table 2), even though the total tritium activity was significantly reduced in each sample. Since the measurement results agree within experimental error for the measurement data from the 1-2 g sample size, it was concluded that the ^3He -ingrowth MS technique has sufficient sensitivity to measure ultralow levels of OBT activity in urine.

3.2 Urine Samples from Members of the Public

Urine samples were measured for both HTO and OBT for three individuals (Table 3). The concentrations of HTO-in-urine were $6.5 \text{ Bq}\cdot\text{L}^{-1}$ for the Ottawa resident, $15.8 \text{ Bq}\cdot\text{L}^{-1}$ for the Deep River resident, and $1260 \text{ Bq}\cdot\text{L}^{-1}$ for the occasionally occupationally exposed Atomic Radiation Worker (ARW) at CRL (Table 3). The HTO-in-urine values appear to be in equilibrium with the ambient background tritium levels for these three locations.

Table 3. Tritium Measurements in Urine Samples of Individuals and OBT Dose Fraction

Location of Participant	Sample Volume (L)	HTO ($\text{Bq}\cdot\text{L}^{-1}$)	OBT ($\text{Bq}\cdot\text{L}^{-1}$)	Ratio of HTO to OBT	OBT dose fraction (Δ)*	Remarks
Ottawa	5.0	6.5	0.06	105	0.26	Regional background levels of tritium in the environment. Ambient levels of tritium in precipitation ranged between 2.5 to $4 \text{ Bq}\cdot\text{L}^{-1}$. Three individuals participated in the study.
Deep River	1.7	15.8	0.29	54	0.51	Elevated environmental levels of tritium due to routine atmospheric releases of tritium from Chalk River Laboratories. Ambient levels of tritium in precipitation ranged between 10 and $20 \text{ Bq}\cdot\text{L}^{-1}$.
Chalk River Laboratories	0.5	1260	2.2	572	0.05	Occasionally occupationally exposed to low levels of tritium in the workplace. Ambient levels of tritium-in-air on the order of $1000 \text{ Bq}\cdot\text{L}^{-1}$.

*Eqn (1); $\Delta = 27.7 \times (\text{HTO}/\text{OBT})^{-1}$

OBT-in-urine levels from these same individuals were measured using ^3He ingrowth MS techniques. Times required for sufficient ^3He -ingrowth for measurement were on the order of six months to one year. The concentration of OBT-in-urine was $0.06 \text{ Bq}\cdot\text{L}^{-1}$ for the Ottawa resident, $0.29 \text{ Bq}\cdot\text{L}^{-1}$ for the Deep River resident, and $2.2 \text{ Bq}\cdot\text{L}^{-1}$ for the CRL worker (Table 3). As the predicted OBT concentration in urine was about $0.1 \text{ Bq}\cdot\text{L}^{-1}$ for an adult Deep River resident, the measured concentration of $0.29 \text{ Bq}\cdot\text{L}^{-1}$ may indicate that, within physiological variation among individuals, model uncertainty (factor of 2) and analytical errors (up to 20%), there appears to be agreement between the measured and predicted values (Figure 2). Based on the ambient HTO-in-air levels to which the

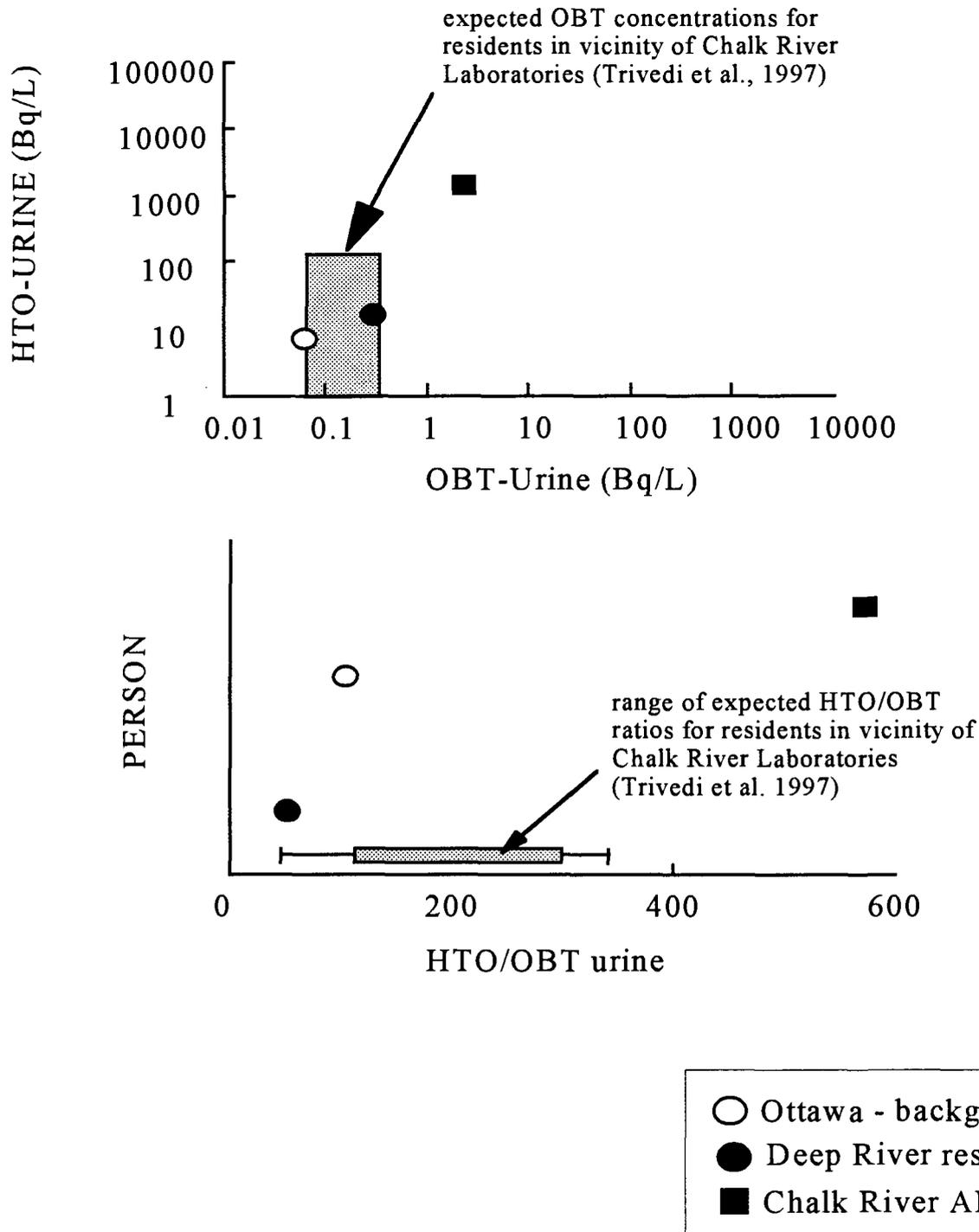


Figure 2. Measured concentrations of tritiated water (HTO-in-urine) and organically-bound tritium (OBT-in-urine) and HTO/OBT ratios in urine samples from study individuals. Shaded areas represent the predicted OBT-in-urine concentrations and HTO/OBT ratios for residents living near Chalk River Laboratories (Trivedi et al., 1997). Data from Table 3.

individuals were regularly exposed, a relatively high and low concentration of OBT-in-urine from the CRL worker and Ottawa resident, respectively, was expected.

At steady-state conditions, the ratio of HTO- to OBT-in-urine can provide an indication of the relative contributions of HTO and OBT to the daily intake of tritium (Trivedi et al., 1997). Individuals living in Deep River and in Ottawa had HTO/OBT ratios between 54 and 103, respectively, whereas the CRL worker had an HTO/OBT ratio of 572 (Table 3). The HTO/OBT ratio for a CRL worker was significantly high because of the elevated levels of daily HTO intakes.

The ratio of HTO- to OBT-in-urine has been used for calculating the OBT dose fraction from tritium intakes. The mathematical model developed to derive the relationship between the estimated ratio of HTO to OBT urine and OBT dose fraction was discussed elsewhere by Trivedi et al. (1997). The following relationship is used in computing the OBT dose fraction (Δ):

$$\Delta = 27.7 \times (\text{HTO/OBT})^{-1} \quad (1)$$

Using Eqn. 1 and the observed empirical values for HTO- and OBT-in-urine, the OBT dose contribution for individuals living considerable distances from CRL (i.e., Ottawa) would be on the order of 26% of the total body water dose. For the Deep River resident, the OBT dose contribution is on the order of 50%, which is comparable to the conservative value (20%) predicted by Trivedi et al. (1997), as they indicated that the OBT dose fraction from tritium intakes can range within a factor of 2. Conversely, the CRL individual had a 5% dose contribution from OBT, but had higher overall tritium dose due to frequent intakes of HTO. The fraction of dose from the tritium in the organic constituents to the dose from the tritium body water varies among individuals due to the nature and level of daily tritium intakes. From the limited data set here, however, the high HTO/OBT ratios among the individuals suggest that the bulk of the tritium dose is the result of HTO intakes, and not due to dietary intakes of OBT.

4. CONCLUSIONS

This study has led to the following conclusions:

- i) The ^3He -ingrowth MS technique yields OBT-in-urine concentrations that are comparable to those using the oxygen-combustion LSC method.
- ii) The ^3He -ingrowth MS technique has sufficient sensitivity to measure the low levels of OBT expected in members of the general population, which cannot be measured using the oxygen-combustion LSC technique.
- iii) OBT-in-urine measurements on a few individuals proximal and distal to CRL have yielded OBT concentrations that are comparable to the predicted concentration using a metabolic model.
- iv) The bulk of the tritium dose is the result of HTO intake and not due to dietary intake of OBT. The OBT dose contribution is between 5% and 50% of the total body water dose, depending on the nature and level of the tritium intake.

5. ACKNOWLEDGEMENT

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APPENDIX 1

³He-Ingrowth MS for Tritium Measurement

The mass spectrometric method used at CRL to determine the isotopic compositions of He (³He, ⁴He) in environmental samples utilizes a highly sensitive, double collector, static source, noble gas mass spectrometer system (*MAPL 215-50* noble gas mass spectrometer) operated in conjunction with a stainless steel gas inlet/cryogenic gas separation system (Bayer et al., 1989; Kotzer et al., 1994, 1998).

Measurement of ³H by the ³He-ingrowth technique requires that the sample be adequately degassed in a vacuum system (<10⁻⁴ torr) and sealed in specialized glassware having low He permeabilities (Al-Si glassware; Dow Corning 1724; Suckow et al., 1990). The samples are stored for a specified period of time determined by the minimum amount of ingrowth ³He (~ 10⁵ atoms ³He) required for instrumental analysis. The length of storage time (generally three to six months) is dependent upon a number of factors, mainly the amount of ³H in the sample and the detection limits and blank levels of the particular mass spectrometer system. Process blank levels were determined by measuring ³He in empty evacuated Al-Si vessels. Measurement blanks were determined by multiplying the measured levels of ⁴He in the samples, which could only result from diffusion of atmospheric helium during storage, by the measured ³He/⁴He ratio in the air standards (1.384x10⁻⁶). For low levels of tritium in waters, Kotzer et al. (1998) estimated the total blank to be on the order of <0.1 Bq·L⁻¹. A typical helium analysis consists of an HD⁺ peak centering routine from which the ³He and ⁴He peak center is established. This is followed by a series of ten 10 second ³He analyses (channel electron multiplier in ion counting mode), a 4-second measurement of ⁴He (Faraday cup), and background measurements for ³He and ⁴He. This is repeated for six consecutive cycles. Precisely aliquotted repeat air standards measured using this method yielded results of 1.0%, 0.5% and 1.0% for ³He ion counting, ⁴He volts and ³He/⁴He ratios, respectively. This is done for the unknown samples, reference samples and air standards containing known concentrations of ³He.

Determination of the concentrations of the ³He due to decay of ³H in the samples was done by peak height comparisons to standard temperature and pressure corrected He concentrations from precisely aliquotted air standards. Helium-3 measured in the samples is corrected for blank contributions (<10%), and then quantified by integration with He calibration lines derived from sequential addition of aliquots of the air standards (Eqn. (1)). Here, the mass spectrometric data was converted to Bq·g⁻¹ dry weight or Bq·L⁻¹ by taking the measured ³He signal that was converted to ³He atoms using Eqn. (1) and dividing by the total storage time (s) to get becquerels (Eqn. (2)). This was subsequently divided by the dry sample weight of urine or total volume of urine (L) processed to get Bq per unit volume or weight (Eqn. (3)):

$${}^3\text{He}_{\text{corrected}} \text{ (atoms)} = \frac{\text{total } {}^3\text{He}_{\text{counts measured}} - ({}^3\text{He}_{\text{counts in blanks}} + (\text{total } {}^4\text{He}_{\text{volts measured}} \times {}^3\text{He}/{}^4\text{He}_{\text{air}}))}{{}^3\text{He (atoms)}/{}^3\text{He}_{\text{calibration line counts}}} \times \quad (1)$$

$$\text{Bq (\#}^3\text{H decays/s)} = {}^3\text{He}_{\text{corr}} \text{ (atoms)} / \text{total storage time (s)} \quad (2)$$

$$\text{Bq (\#}^3\text{H decays/s)/unit volume or mass} = \text{Bq (\#}^3\text{H decays/s)/L or g} \quad (3)$$

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