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Measurements of Tritium (HTO, TFWT, OBT) in Environmental Samples at Varying Distances from a Nuclear Generating Station

Mesures du tritium dans les échantillons prélevés dans l'environnement à diverses distances d'une centrale nucléaire

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MESURES DU TRITIUM DANS LES ÉCHANTILLONS PRÉLEVÉS DANS L'ENVIRONNEMENT À DIVERSES DISTANCES D'UNE CENTRALE NUCLÉAIRE

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Résumé

On a mesuré les concentrations de tritium dans des échantillons prélevés dans l'environnement (végétation, eau, sol, air) de sites éloignés et proches d'une centrale nucléaire CANDU du sud de l'Ontario (OPG-Pickering). Les niveaux du tritium dans l'eau exempt de tissu et de tritium lié organiquement dans la végétation peuvent atteindre 24 000 UT immédiatement à côté de la centrale nucléaire et décroissent rapidement à des niveaux comparables aux concentrations du fond naturel pour le tritium dans l'environnement (environ ≤ 60 UT). Les concentrations de tritium ont également été mesurées dans des échantillons de végétation et des cernes d'arbres poussant à des distances considérables des centrales nucléaires, et correspondent à un facteur de 1 à 2 des niveaux ambiants du tritium mesuré dans les précipitations, en divers endroits du Canada (environ ≤30 UT).

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Abstract

Concentrations of tritium have been measured in environmental samples (vegetation, water, soil, air) from sites distal and proximal to a CANDU nuclear generating station in Southern Ontario (OPG-Pickering). Levels of tissue-free water tritium (TFWT) and organically bound tritium (OBT) in vegetation are as high as 24,000 TU immediately adjacent to the nuclear generating station and rapidly decrease to levels of tritium which are comparable to natural ambient concentrations for tritium in the environment (approximately ≤ 60 TU). Tritium concentrations (OBT, TFTW) have also been measured in samples of vegetation and tree rings growing substantial distances away from nuclear generating stations and are within a factor of 1 to 2 of the ambient levels of tritium measured in precipitation in several parts of Canada (approximately ≤30 TU).

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1. __INTRODUCTION__

Tritium is produced as a radioactive by-product in the heavy-water moderated CANDU (Canada Deuterium Uranium) reactors. A small percentage of the tritium inventory escapes during the routine operation of a CANDU reactor. Although tritium is not a particularly toxic radionuclide, its presence in the environment is a radiologic concern because it can become part of the hydrogen pool in environmental and biological reservoirs (Brown, 1989; Kotzer et al., 1999a); tritium has a propensity for assimilation into the biosphere when released as, or converted to, tritiated water (HTO), and metabolic conversion to organically-bound tritium (OBT).

In the environment, the local ambient concentrations of tritium can be measured in air, water and organic matrices, such as plant materials (Wood et al., 1993). Longer-term repositories for the historical deposition of tritium are ice cores (Kotzer et al., 1999b) and tree rings (Brown, 1979; Wallner, 1992). Tritium concentrations in air and water change in response to variations in the ambient concentrations of tritium in the atmosphere, although waters can be quite slow to re-equilibrate as a result of the mass dependencies of hydrogen in these reservoirs. Generally, the change in the tritium concentrations in air and air moisture are quite responsive to any variations in the atmospheric tritium source term, which in the vicinity of nuclear generating stations is dependent upon factors such as wind direction, wind velocity, temperature, relative humidity and the associated atmospheric dilution factor. Because of reservoir effects for hydrogen in the environment, changes in the concentrations of tritium in aquatic systems may lag behind changes in precipitation and tritium in water vapor, as has been shown for large inland water masses such as the Great Lakes drainage system. In these reservoirs, the tritium levels in regional precipitation were less than those measured for waters sampled from Lake Ontario (King and Workman, 1998). Such effects may also exist for soils that contain numerous organic and inorganic reservoirs for hydrogen, and actively oxidize hydrogen from the atmosphere.

Tritiated water vapor (HTO) may enter plants by root uptake and by direct entry via the stomata, which are predominantly located in a plants leaves. Relative contributions of tritium in a plant from these two sources (stomatal exchange and transpiration) are on the order of 4:1 (Raskob, 199). Two reservoirs for tritium exist in plants. Tissue-free water tritium (TFWT) represents the free-water cellular tritium that is influenced by daily plant-physiological processes such as respiration and exchange of water across the stomata, and approximates the local, ambient HTO-in-air values at the time of sampling. In the presence of HTO, the process of photosynthesis in green leaves produces organically bound tritium (OBT) wherein the tritium is bound organically either in exchange reactions or enzymatically-catalyzed reactions where it replaces hydrogen. Tritium is discriminated against hydrogen in photosynthetic processes involving tritiated water molecules. As a result, at equilibrium conditions the $^3H/H$ specific activity ratio in OBT may be 20 to 30% lower than the corresponding cellular water (Garland and Ameen, 1979).

Within the organically bound fraction, the tritium can be either "exchangeable OBT" which can quickly exchange tritium with extraneous HTO, or "non-exchangeable OBT" where the tritium is incorporated and fixed into stable bonds with carbon atoms as a result of enzymatically-catalyzed reactions (Diabate and Strack, 1993). Estimates on the proportions of tritium in these two reservoirs indicate that approximately 20 to 30% of OBT can exist as "exchangeable OBT"

(Guenot and Belot, 1984; Brown, 1989). OBT values reported here represent "non-exchangeable OBT" on the basis of the sample preparation techniques used (see Appendix).

In this study, the concentrations of tritium as: i) HTO-in-air and water, ii) HTO in soil pore waters, iii) TFWT in vegetation (leaves and berries) and iv) OBT in vegetation (leaves and berries) were measured. Samples were collected predominantly in Eastern Ontario and at varying distances (up to 400 km) from OPG-Pickering and Darlington Nuclear Generating Stations (NGS) in a northerly and easterly direction (Figure 1a and b). Some samples were collected from the OPG Provincial Background site at Lambton, Ontario (tree rings), near Sarnia, Ontario (from Sombra soybeans) and from Western Canada (cereal grains from Saskatchewan).

The main purpose of this study was to: i) compare and contrast the changes in tritium concentrations in the environment with increasing distance from a CANDU NGS, ii) provide information regarding the temporal changes in concentrations of tritium in plants and waters at natural background levels to provide baseline data for comparative and modelling purposes, and iii) evaluate the utility of the use of OBT in plants as a proxy record by which to calculate the co-existing tritium-in-air concentrations over the vegetative period through comparison with mathematical models of tritium in air (CSA-N288.1 (CSA, 1987)).

2.   ANALYTICAL TECHNIQUES

2.1   Sample Collection and Storage

Samples for this study were predominantly collected during September and October in 1997 and 1998. In this way, the measured OBT concentrations should reflect the average concentrations of tritium that existed in the environment throughout the growing season. For instance, samples collected distal to the CANDU NGS's should have TFWT and OBT concentrations that are constant and in equilibrium with the levels of tritium in precipitation, that is the dominant control over the concentrations of tritium-in-air moisture and soil pore waters. OBT concentrations have also been determined on vegetation samples collected in 1992 - 1993 and which had been previously dried and measured for their ^{14}C levels and archived in plastic Nalgene bottles (Milton et al., 1995).

In 1997 and 1998, vegetation samples were collected using plastic disposable gloves and stored in glass sealer-jars with leak-tight lids. These were packed in coolers filled with dry ice to keep the samples frozen, and transported to Chalk River Laboratories (CRL). This precluded the possibility of exchange between the TFWT and the ambient HTO-in-air during transport. Soil samples were sealed in plastic sampling tubes, bagged and stored in the coolers containing dry ice. At CRL, the vegetation and soil samples were put into freezers at the Low-Background Building (Building 560) and kept frozen until they were either: i) loaded into flasks for azeotropic distillation, ii) loaded into high-vacuum, Al-Si flasks for vacuum distillation and removal of free water, and subsequent preparation of the sample for OBT by ^3He-ingrowth mass spectrometry (MS), or iii) loaded into a Parr bomb for measurement of OBT by oxygen combustion techniques. Water samples from rivers and lakes and from passive HTO-in-air

samplers were collected directly in 20 mL polyethylene vials, and submitted for tritium measurements by direct liquid scintillation counting (LSC) techniques within a few days of sampling.

2.2   Measurement of HTO in Soils, Waters and TFWT in Plants

TFWT in vegetation and HTO in soil pore waters were removed from the samples using azeotropic distillation techniques (Brown and Workman, 1989; Revesz and Woods, 1990). Tritium concentrations in the distilled waters and HTO concentrations in the water samples were determined using direct LSC with polyethylene vials and approximately equal volumes (10 mL) of sample water and Ultima Gold XR scintillator on a Wallac 1220 Low-Level Counter. Total counting times on the order of 200 to 1200 min were used for each sample, depending upon the expected tritium levels.

For vegetation and soil samples collected at background sites where expected tritium concentrations were at natural atmospheric levels (10 to 20 tritium units (TU)), appropriately sized portions of the samples were loaded into flasks under N_2-glove-box conditions for azeotropic distillation, to prevent the possibility of exchange with the ambient HTO-in-air.

2.3   Measurement of HTO-in-Air

Concentrations of HTO-in-air were determined using passive diffusion samplers that sampled at a rate of 5 L air/day and direct LSC (as above). At background sites where the ambient tritium levels were expected to be at natural atmospheric levels, the passive samplers were placed under protective lids and remained out in the field for periods of up to one month (Wood and Workman, 1992).

2.4   OBT Tritium Determinations

OBT was measured on vegetation samples primarily using ^{3}He-ingrowth MS. For some samples, oxygen combustion LSC was also used. In a study on the levels of OBT in environmental samples in the vicinity of the Darlington NGS, it was demonstrated that both of the methods used at CRL yielded comparable results on samples with tritium concentrations of between 100 and 600 TU (Kotzer and Workman, 1999).

Because of the necessity to measure lower concentrations of tritium in this study, samples of plastic beads that were thoroughly rinsed with tritium-depleted waters were analyzed for their bound-tritium concentrations. Both ^{3}He-ingrowth MS and oxygen-combustion - LSC yielded almost identical tritium values of 16 TU. The water equivalent factors (WEF) listed in Brown (1995) were used for conversion of the tritium activities in the dry samples to Bq/L $_{water\ equivalents}$ (Bq/Lwe) and TU (where 1 TU = 0.1184 Bq/Lwe). Note that all data, with the exception of HTO-in-air, are reported as TU.

2.4.1 Oxygen-Combustion - LSC

For determination of OBT by oxygen combustion - LSC, about 5 to 10 g of the dried material was loaded into a Parr 1921 bomb and pressurized with oxygen to 20 atmospheres. After complete combustion, the bomb was depressurized by discharging the combustion products through methanol-dry ice traps (between -50°C and -70°C). The bomb and cold traps were then attached to a common vacuum source and evacuated to about 200 mtorr. At that point, liquid nitrogen was substituted for methanol-dry ice on the cold traps, and they were further evacuated to approximately 10 mtorr. During this process, the body of the bomb was heated to about 80°C to facilitate complete transfer of the water into the traps. After collection, a standard azeotropic distillation was performed on the combustion waters to eliminate various dissolved organic components that interfered with the LSC. Tritium concentrations in the treated water were then determined using direct LSC techniques (Brown and Workman, 1989). Using the above procedures, two dried organic samples can be processed on a daily basis.

2.4.2 ³He-Ingrowth MS

Helium-3-ingrowth MS was carried out on samples of approximately 1 to 10 g. The samples were loaded either as previously dried samples or wet samples, in a glove box, into Al-Si glassware, and attached to a vacuum line ($<10^{-5}$ torr) at LN_2 temperatures (-196°C), to completely freeze-dry the samples and remove any adsorbed or cellular water. The samples were also rinsed with approximately 80 mL of tritium-depleted water, each time bringing them to constant dryness to completely remove any effects of the exchangeable OBT component. Following this, the dry samples were vacuum sealed into the Al-Si flasks and stored for ³He-ingrowth for approximately 6 to 12 months, whereupon they were analyzed using a noble-gas mass spectrometer (see Appendix and Kotzer et al. (1999a) for details of the OBT sample preparation and ³He-ingrowth MS analyses).

3. <u>SAMPLING SITES</u>

In 1997 and 1998, samples for this study were collected from several areas, namely:

i) At different geographic areas in Canada where the tritium concentrations in the samples reflect the natural levels of tritium in the environment on a continental scale (Figure 1a). For these, TFWT, OBT or HTO were determined, as applicable (Tables 1 and 2). Some of the samples from these areas, primarily tree rings, were measured for their ^{14}C levels to establish historical and present-day levels of atmospheric $^{14}CO_2$ proximal and distal to CANDU NGS's (Kotzer and Watson, 1999). Several samples of cereal grain crops grown in 1998 were collected and their TFWT and OBT concentrations were measured. As well, the tritium concentrations on precipitation samples collected from Saskatchewan in 1997 and 1998 were measured and included here.

ii) From areas within several hundred kilometers of OPG-Pickering NGS, and primarily in a north and north easterly direction (Figure 1b).

iii)   From sites that are within 20 km and less from OPG-Pickering NGS (Figure 2). These
        samples include some dried and archived vegetation samples previously collected in
        1992-1993 and reported by Milton et al. (1995).

4.   RESULTS

4.1   TFWT Concentrations in Annual Plants and HTO Concentrations in Soils, Waters and Air

TFWT concentrations in plants collected in 1997 and 1998 ranged between approximately 28
and 19,000 TU, with the highest levels occurring immediately proximal to the NGS's (Figure 3a;
Tables 1 and 2). For both 1997 and 1998, comparison of the TFWT levels in vegetation with
increasing distance indicates a very rapid decrease in the TFWT levels in a predominant wind
direction away from OPG-Pickering NGS (Figure 3a). Up to a distance of approximately 15 to
18 km from OPG-Pickering NGS, samples collected in a predominant wind direction (NE) have
TFWT levels that decrease from approximately 19,000 TU to as low as between 80 and 180 TU
(Figure 3b). This decrease can be attributed to the very rapid mixing processes for hydrogen in
the atmosphere, which result in a large dilution factor for atmospheric tritium (Ka = 3.2×10^{-7}
s/m^3; LaMarre, 1998). Similar decreases in TFWT levels in vegetation with distance and
resultant dispersion co-efficients have been observed at other CANDU sites (e.g. Pt. Lepreau
NGS - Milton et al., 1998).

When compared with vegetation growing more proximal to OPG-Pickering NGS, TFWT levels
in 1997 and 1998 vegetation samples collected at distances of up to 300 km appear to reach a
constant specific activity (Figure 3a). At distances of between 80 and 400 km from OPG-
Pickering NGS, the TFWT levels vary between 28 and 126 TU (Figure 3c), although TFWT
values of ≥70 TU have generally been measured on samples from background sites #1 and #8
(Lake Dore and Peterborough; Figures 1b, 3c), both of which are likely influenced by some other
source of industrial, anthropogenic tritium.

When the two anomalous background sites (site #1 and #8) are removed, the TFWT levels
indicate a 2-year average value of 45±14 TU (Figure 3c). These tritium levels are within a factor
of 1.5 to 2 of that expected for regional precipitation (approximately ≤30 TU; IAEA/WMO,
1998). Although the values for TFWT measured on plants are considered to be somewhat
transient, due to stomatal exchange of water vapor across the leaf/atmosphere boundary,
calculation of an average tritium concentration in the cellular water of the plants from the TFWT
data and comparison with the ambient precipitation levels is valid, considering the distance of
these sampling sites from any anthropogenic source of tritium. The data indicate that the average
TFWT concentrations on vegetation in Eastern Ontario are slightly higher than the tritium levels
of approximately 20 to 30 TU measured in precipitation for the Ottawa area up to 1993, and in
Northern-Hemispheric sites at similar latitudes (#4 - Figure 3c; IAEA/WMO, 1998). In this
study, the TFWT concentrations in vegetation are more comparable to the measured
concentrations of tritium in rivers and lakes in Eastern Ontario (#5 - Figure 3c). In comparison,
samples of cereal grains and oilseeds grown in Eastern Saskatchewan in 1998 have TFWT
concentrations that are comparable to the tritium concentrations in precipitation from Central

Saskatchewan in 1997 and 1998 (~12.5 TU; Figure 4 and Table 1). That the TFWT concentrations on vegetation sampled from areas in Eastern Ontario are elevated slightly above the values for precipitation is expected, due to the operation of NGS's and the effects that has had on the tritium concentrations in the local watersheds (e.g. Lake Ontario - King and Workman, 1998), although the cumulative dose effects of the addition of these levels of anthropogenic tritium to the environment are inconsequential.

An interesting aspect of the study was that HTO values measured on soil pore-waters from shallow (0 to 20 cm depth) soil cores collected at several background sites in 1998 were up to two times higher than the corresponding TFWT values at those same sites (sample #1, 2 and 3 - Figure 3c; Table 1). It would be expected that, at considerable distances from any anthropogenic tritium source, the soil pore waters may have tritium levels similar to tritium in ambient precipitation. At present, because of the limited number of soil samples collected, it is not entirely clear why the levels of tritium in soil pore-waters are higher (~70 TU) relative to that of continental precipitation ($\leq$30 TU). It is possible that the higher tritium values in the pore waters relative to the ambient precipitation levels: i) are the result of oxidation of HT to HTO in soils that have very little pore water, or ii) represent a mixture between an earlier-formed reservoir of OBT in the soils that is being oxidized and decomposed, thereby releasing tritium to the pore waters. Research on the systematics of free-water tritium (FWT) and OBT in vegetation and soil indicates higher FWT in soils and litter relative to corresponding vegetation (pine needles), and documents OBT/FWT ratios in soils that are greater than unity (Bogen and Welford, 1976; Hisamatsu et al., 1998), supporting the observations made here.

Because of transpiration and stomatal exchange in plants, TFWT values in samples of vegetation located significant distances from anthropogenic sources should reflect both the tritium concentrations in soil porewaters and in atmospheric water vapor. HTO concentrations in the free water in vegetation (C_p) are given by the relationship:

$$C_p = 1.1 \, RH \, C_{am} + (1 - RH)C_s \qquad\qquad (1)$$

where RH is the relative humidity, C_{am} is the concentration of tritium-in-air moisture, and C_s is the concentration of tritium in soil pore waters (Raskob, 1994).

Using an average relative humidity of 50%, and assuming that tritium concentrations in soil pore waters (C_s) are on the order of 80 TU and that levels of tritium-in-air moisture (C_{am}) approximate that of regional precipitation (~20 TU), Equation (1) provides calculated TFWT values in plants (C_p) of around 51 TU, which are similar to the average of the TFWT concentrations measured in this study (45$\pm$14 TU). Although it is unlikely that the few soil pore waters that have been measured here adequately define the temporal and geographic tritium dynamics in the soil system for this large study area, it is interesting that using the approximate values measured for the precipitation and soil reservoirs provides similar TFWT values to those measured in samples of vegetation at the various background sites.

4.2 OBT Concentrations in Annual Vegetation Samples

OBT concentrations measured in annual vegetation samples vary between 37 and 24,000 TU with the highest OBT occurring immediately proximal to the NGS (Table 2). In general, OBT concentrations are slightly lower than their corresponding TFWT values, which is expected based on isotopic discrimination of tritium relative to hydrogen and deuterium during formation of OBT. Similar to the TFWT levels measured in vegetation, OBT levels in vegetation rapidly decrease with increasing distance in a predominant, north easterly wind direction from OPG-Pickering NGS (Figure 5a). Up to distances of approximately 18 km, OBT concentrations decrease from approximately 24,000 TU to as low as 140 TU (Figure 5b).

The non-exchangeable OBT component in a dried plant residue will remain fixed through time. As a result, OBT concentrations were measured on a limited suite of vegetation samples collected in the fall of 1992 and 1993 and integrated with the OBT concentrations measured in samples collected at similar sites in 1997 and 1998. A comparison of the decay-corrected OBT values for all of the samples indicates very similar levels for tritium in the environment at distances between 3 and 20 km from OPG-Pickering NGS (Figure 5b), suggesting that processes of dispersion have kept the average, atmospheric tritium values in the vicinity of the NGS at a relatively constant level for several years.

To date, the concentrations of OBT have been measured on a number of samples collected at background sites at distances up to 400 km from OPG-Pickering NGS (Table 2 and Figure 5c). The range of OBT levels on samples collected between 1992 and 1998 is between 33 and 62 TU and, more realistically, between 33 and 55 TU if the sample sites that are possibly influenced by other anthropogenic sources (background sites #1 and #8) are discounted. An average for these samples is 44±14 TU, which is slightly lower but comparable to the average TFWT values measured on these same samples. OBT concentrations in vegetation are similar to the concentrations of tritium in rivers and lakes in Eastern Ontario, although they are approximately two to three times higher than OBT measured in wheat samples from Western Canada (WC 1 - Table 2), where there are no anthropogenic sources of tritium.

4.3 Historical OBT Concentrations in Tree Rings

OBT concentrations have been determined on dendrochronologically-characterized samples of whole wood (Table 2) from trees collected from a few areas in Canada (Figure 1). As discussed in the Appendix, the OBT concentrations were determined on whole-wood samples of annual or multiple-year accumulations of individual tree rings that were previously measured for their ^{14}C levels (Kotzer and Watson, 1999). A comparison of the measured OBT levels in the tree rings indicates that: i) the temporal trend of OBT in tree rings from the Lambton, Ontario, site and the ambient levels of tritium in precipitation in the general geographic area (Ottawa and Chicago) are comparable (Figure 6a), and ii) elevated concentrations of OBT are observed for tree rings between 1975 and 1995 collected from Saskatchewan and Ottawa (100 to 200 TU; Figure 6a and Table 2). The reasons for the elevated OBT values in tree rings from two of the three sampling areas is unclear, as these areas, especially Saskatchewan, are significantly removed from any source of anthropogenic tritium other than fallout tritium from earlier periods of thermonuclear testing between 1952 and 1964. Possible reasons for the elevated OBT concentrations in these

samples could include: i) measurement of wood in tree rings having substantially different cellulose/lignin ratios ("reaction wood" - Fengel and Wegener, 1989; Wallner, 1992), ii) in-situ exchange of tritium amongst lignin formed at different time periods when the tritium levels were substantially different (Brown, 1979; Yamada et al., 1992), or iii) tree growth in an area where the tritium concentrations in the groundwater are substantially higher than the corresponding precipitation. For the samples from this study, it is impossible to decide which of the above processes may have affected the OBT measured in the tree rings. For the Saskatchewan sample there was considerable "reaction wood" in this sample, as a result of damage to the tree during its growth, which may be the cause of the anomalous tritium concentrations.

The tree sample from the Lambton, Ontario, site had concentric tree rings of uniform width with negligible resins apparent. Overall, the concentrations of OBT in the tree rings are comparable with the values for tritium in precipitation over the entire period of growth (Figure 6a and Table 1). Between 1975 and 1995, OBT values in tree rings from Lambton display decreasing tritium values, from 73±5 to 32±7 TU, which are comparable to the temporal trends of tritium measured in ambient precipitation in Ottawa (Figure 6b) and with OBT measured in recent samples of vegetation from the same area (Figure 6b). OBT values for tree rings grown between 1947 to 1952 are 36±15 TU, which are comparable with the tritium levels measured in 1953 precipitation (Figure 6a).

4.4   OBT/TFWT Ratios in Samples

OBT/TFWT ratios have been calculated for all samples distal and proximal to the OPG-Pickering NGS. The calculated OBT/TFWT ratios vary between approximately 0.3 to 1.5 (Figure 7a), with the most variation occurring in samples proximal to the NGS where higher concentrations of OBT were measured (Figure 7b). This is expected, since the TFWT values for vegetation are transient and reflect the ambient levels of tritium-in-water vapor at the time of sampling only. The variation of tritium-in-water vapor near the NGS's is dependent upon factors such as temporal variations in the amounts of anthropogenic reactor tritium released, temperature, relative humidity, and the sampling locations relative to the predominant wind directions, whereas the OBT values represent the time-integrated concentrations of tritium that existed throughout the vegetative period for the particular sampling location.

Vegetation collected distal (>80 km) to the NGS shows less variation in the OBT/TFWT ratios. With one exception (OBT/TFWT = 1.4), the OBT/TFWT ratios are between 0.6 and 1 (average = 0.87±0.15), although if all samples are used the OBT/TFWT is 0.95±0.25 (Figure 7a).

The range of OBT/TFWT ratios measured on foodstuffs and in the natural environment is quite large (e.g. 0.3 to 4.2 - Brown, 1995; 1.2 to 8 - Bogen and Welford, 1976; 0.56 to 2.68 - Hisamatsu et al., 1998; 0.57 to 1.3; McFarlane, 1976; Garland and Ameen, 1979; Hisamatsu et al. 1987, 1989; Inoue and Iwakura, 1990). The systematics of isotopic fraction dictates discrimination of ^{3}H relative to H and D during photosynthesis, which should result in OBT/TFWT ratios of less than 1 if the tritium in atmospheric, terrestrial and hydrologic reservoirs is in equilibrium. This is largely in agreement with the range of OBT/TFWT ratios on samples collected distal to anthropogenic tritium sources, where the reservoirs of tritium in atmospheric, terrestrial and hydrologic reservoirs should largely be in dynamic equilibrium. A

sample of wheat from Western Canada (*a* in Figure 7a), where no sources of modern anthropogenic tritium exist, yielded an OBT/TFWT ratio of 1.1. Given the degree of uncertainty in the TFWT and OBT measurements in this sample (WC1 - Table 2), the OBT/TFWT ratio could be slightly less than 1, in accordance with theory.

4.5.   HTO-in-Air

4.5.1   Measured HTO-in-Air at Distal Locations

No HTO-in-air measurements were taken proximal to OPG-Pickering NGS, as those measurements are routinely taken by their own personnel. HTO-in-air measurements were taken at several of the background sites located distal to OPG-Pickering NGS. At those locations, values for the HTO-in-air were variable, between 0.07 to 0.22 Bq/m^3, although with large errors (Table 1). The range for the HTO-in-air values is comparable with that reported for HTO-in-air from OPG Provincial Background Sites in 1997 (0.05 to 0.11; LaMarre, 1998).

4.5.2   Empirical Calculations of HTO-in-Air

Values for HTO-in-air (Bq/m^3) within 20 km of OPG-Pickering NGS were calculated using the measured OBT values for vegetation samples collected over the past several years, assuming that they reflect the average tritium-in-air moisture over the entire growing season (Table 4). Note that for these calculations the tritium concentrations were converted from tritium units (TU) to Bq/Lwe, as indicated in Section 2.4.

Tritium-in-air (Ca) values have been calculated on the basis of daily temperature (T) and relative humidity (Rh) records and established mathematical relationships relating the temperature and relative humidity to the absolute humidity (Q) in air, as follows:

$$Es = e^{[21.33 - 5327/(T+273)]} \tag{2}$$
$$Q = (217 \times Rh \times Es)/(T + 273) \tag{3}$$

where Es = saturation vapor pressure, Q = absolute humidity (g H$_2$O/m^3 air), e = 2.718 and T and Rh represent the year-specific daily temperatures (°C) and relative humidity values, respectively, which have been averaged over a 5-month growing period (May to September) for the individual sample-collection years.

Assuming that the OBT values measured in the plants are in equilibrium with the average tritium-in-air moisture (C$_{am}$) over the entire growing season, the tritium-in-air values have been calculated according to the relationship:

$$C_a = C_{am} \times Q \tag{4}$$

where C$_a$ = tritium-in-air, C$_{am}$ = concentrations of tritium in air moisture (assumed to be in approximate equilibrium with OBT in plants), and Q = absolute humidity (g H$_2$O/m^3 air).

From Equation 4 and on the basis of OBT concentrations in vegetation, the concentrations of tritium-in-air for the specific years vary between 0.18 to 31.8 Bq/m³, and decrease with increasing distance from the NGS (Figure 8a and Table 3). The total uncertainty in the calculated tritium-in-air values is on the order of ±70%, hence it is realized that these values are useful only for approximating the tritium-in-air within a factor of 1 to 2. For instance, a calculated tritium-in-air value using the OBT concentration for a 1997 vegetation sample proximal to the OPG Pickering NGS results in a concentration of 21.2 Bq/m³ (1997- Pickering NGS 5; Table 3), which is comparable to the measured tritium-in-air concentration of 18.9 Bq/m³ (LaMarre, 1998) near the same site, suggesting that the empirical values calculated using the OBT concentrations in vegetation are reasonable.

5.   COMPARISON OF OBT DATA WITH CSA-N288.1 MODEL PREDICTIONS

The empirical calculated tritium-in-air concentrations have been compared to the modelled tritium-in-air values using CSA-N288.1. Here the modelled tritium-in-air concentrations are based on the meteorological conditions and tritium-release data from OPG-Pickering NGS for the years 1991 to 1996 (Table 4), and using the distances and wind-sector direction from OPG-Pickering NGS for each of the vegetation collection sites where OBT and associated empirical tritium-in-air concentrations have been calculated. There is a fair degree of agreement between the empirically calculated tritium-in-air and the model-derived tritium-in-air concentrations (Figure 8b, c), taking into account the degree of uncertainty of approximately a factor of 2 for both the empirically calculated results using OBT on vegetation and CSA-N288.1.

Several deficiencies are realized with this approach. The model-calculated tritium-in-air values are only for the period between 1991 and 1996, whereas empirically calculated values using OBT data from 1997 and 1998 have been included. This may not introduce a large degree of uncertainty, as the concentrations of OBT measured on vegetation samples from several years appear to be quite similar (Figure 5b). Further, it is assumed that the OBT concentrations equate with those of the tritium-in-water vapor, which may not be entirely correct as tritium is discriminated against during formation of OBT from cellular water. On the basis of the range of OBT/TFWT ratios for the vegetation samples collected proximal to the NGS, (0.3 to 1.5 - Figure 7a), this uncertainty could be large, although it must be kept in mind that in these areas the OBT/TFWT ratio is quite dynamic and, over the vegetative period, may be more similar to the average OBT/TFWT ratio of 0.8 to 0.9 calculated on samples distal to the NGS (Figure 7a).

Even with these uncertainties, the agreement between the empirically calculated tritium-in-air values using OBT and the tritium-in-air values calculated using CSA N288.1 suggests that OBT can be used as a proxy to estimate the longer-term tritium-in-air in situations where other tritium data are unavailable.

6.   CONCLUSIONS

The results of this study show the following:

i)   The concentrations of atmospheric tritium released in the immediate vicinity of the NGS at OPG-Pickering NGS, although elevated with respect to the present day concentrations of tritium in precipitation and air at background sites, are relatively low (LaMarre, 1998). Within a short distance from the NGS, the tritium values are approximately equal to or less than the tritium-in-precipitation concentrations measured during peak periods of anthropogenic nuclear-fusion bomb-test fallout in atmospheric precipitation in the early to mid 1960's (~3000 TU or 355 Bq/L, where 1TU = 0.1184 Bq/L; IAEA/WMO, 1998).

ii)   At considerable distances from the NGS, the concentrations of tritium in vegetation are only slightly elevated (within a factor of 2 or less) above the tritium levels in large-scale precipitation, and are comparable with the values of tritium in rivers and lakes. This suggests that the operation of the NGS's has negligible effects on the balance of tritium in the environment.

iii)   The concentrations of OBT in vegetation can be used as a proxy to calculate the levels of tritium-in-air where appropriate tritium-in-air samples are not available.

8.   ACKNOWLEDGEMENTS

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Table 1 : Compilation of TFWT and HTO values for vegetation, soils, air and waters collected distal to OPG-Pickering in 1997 and 1998

Sample#	Year sampled	Sample Type	Distance from reactors (kms)	tritium-in-air (1) (Bq/m3)	TFWT (2) (TU)	HTO (2) (TU)
TFWT in Background Samples						
Backgnd#1 -(HWY41+DORE LK)	1997	berries	275		93+/-25	
	1997	berries	275		142+/-30	
	1998	large tree/small leaves	275		79+/-18	
	1998	small tree/large leaves	275		126+/-14	
Eganville (June 98)	1998	alder leaves	275		54+/-8	
Backgnd#2- (Haggarty Twnshp Rd #14)	1997	leaves	230		41+/-12	
	1997	berries	230		38+/-12	
	1998	white pine needles	230		59+/-14	
	1998	red pine needles	230		83+/-16	
	1998	soil (0-20 cm)	230		84+/-16	
Wilno (Oct 98)	1998	apple	220		44+/-18	
Bckgnd#3- (0.5 kms from Bancroft)	1997	leaves	175		61+/-16	
	1998	white pine	175		36+/-8	
	1998	berries (fruit)	175		37+/-10	
Bckgnd#4-(N of intxn620+28S - Apsley)	1997	leaves	135		52+/-9	
	1998	white pine needles	135		40+/-10	
Bckgnd#5-(Cornwall)	1997	berries	390		37+/-10	
Bckgnd#6 - (Brockville)	1997	apples	285		39+/-12	
Bckgnd#7 - (between Belleville+Trenton)	1997	apples	135		28+/-12	
Bckgnd#8 - (Peterborough)	1997	apples	80		140+/-30	
	1998	tree leaves (#115+lansdowne)	80		115+/-18	
	1998	oak leaves (#115+35)			31+/-10	
	1998	soil (0-20 cm)			55+/-10	
Kingston (June 98)	1998	Alder leaves	193		45+/-12	
	1998	soil (0-20 cm)	193		82+/-18	
Cloyne (June 98)	1998	Alder leaves	270		31+/-8	
Sombra (30 kms south of Sarnia -Oct 98)	1998	Rose leaves	300		40+/-12	
	1998	Rose hips	300		34+/-10	
	1998	Soya beans	300			
Yorkton, Saskatchewan (WC 1)	1998	wheat	2400		13+/-5	
(WC 2)	1998	canola	2400		13+/-3	

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Table 1, continued

Sample#	Year sampled	Sample Type	Distance from reactors (kms)	tritium-in-air (1) (Bq/m3)	TFWT (2) (TU)	HTO (2) (TU)
Rivers and Lakes						
Kamaniskeg Lake (Cobermere - Background #	1997	lakewater	200			29
Kamaniskeg Lake (Cobermere - Background #	1997	lakewater	200			21
Bonnechere River	1997	riverwater	275			36
York River (Bancroft - Background #3)	1997	riverwater	175			24
Lake Dore (Eganville - Background #1)	1998	riverwater	275			51+/-8
York River (Bancroft - Background #3)	1998	riverwater	175			31+/-16
Air samples						
Backgnd#1 -(HWY41+DORE LK)	1997	passive sampler	275	0.2+/-0.28		
	1998	passive sampler	275	0.223+/-.037		
Backgnd#2- (Haggarty Twnshp Rd #14)	1997	passive sampler	230	0.07+/-0.27		
	1998	passive sampler	230	0.098+/-.037		
Bckgnd#3- (0.5 kms from Bancroft)	1997	passive sampler	175	0.22+/-0.28		
	1998	passive sampler	175	0.147+/-.031		
Bckgnd#4-(N of intxn620+28S - Apsley)	1997	passive sampler	135	0.2+/-0.28		
	1998	passive sampler	135	0.166+/-.035		
Bckgnd#8 - (Peterborough)	1998	active air sample	80	0.9+/-0.2		

Remarks
1) Units = Bq/m3
2) Tritium values are given as TU, where 1 TU = 0.1184 Bq/Lwe

Table 2: TFWT, OBT and OBT/TFWT ratios for select vegetation samples collected distal and proximal to OPG-Pickering and tree rings from several areas in Canada

Sample#	Wind sector (1)	Year Collected	Sample	Distance from reactors (km)	TFWT (2) (TU)	OBT (2) (TU)	OBT/TFWT (5)	Remarks
1992, 1993 ARCHIVED SAMPLES - Proximal to OPG-Pickering								
PNGS 15 -(Upper Airport Conservation Area)	NE18	1993	grass	18		197+/-22		
PNGS 10 - (Ajax Oak)	ENE3	1993	oak leaves	2		1533+/-76		
Mt Albian - (Thorn Tree site)		1993	maple leaves	100		62+/-13		PICKED IN HAMILTON
PNGS 5 - (Montgomery Park Road)	N 0.7	1993	apple	0.1		10181+/-509		
Bckgnd#2 (Olin's Rd)		1993	leaves	240		41+/-10		
Bckgnd#6 (Hwy28 Nof Apsley)		1993	leaves	135		50+/-10		
PNGS4 - (Firehall - Bayly Rd)	N 0.7	1992	alder	0.5		524+/-25		
PNGS9 - (Brock-Pickering Parkway)		1992	maple basswood leaves	4		516+/-27		
PNGS16 (Lakeview Park Ave - Oshawa)		1993	maple leaves	19		141+/-13		
1997-1998 Vegetation - Proximal to OPG-Pickering								
PNGS#5 - (Montgomery Park Road)	N 0.7	1997	cranberries	0.7	18962+/-850	18318+/-549	0.96	
" " " " " " " " " " "		1997	apples	0 7	14860+/-743			
" " " " " " " " " " "	N 0.7	1998	spruce needles	0 7		24172+/-846		
" " " " " " " " " " "	N 0.7	1998	small apples	0 7	13674+/-738	15789+/-458	1.1	
PNGS#12 - Particl PK	NE 4	1997	berries	4	944+/-60	1342+/-67	1.42	
PNGS#13 - south Ajax (near waterfront)	ENE 3	1997	milkweed	3	1041+/-40	818+/-41	0.79	
" " " " " " " "		1997	milkweed berries	3	1287+/-40			
" " " " " " " (Lions Club Park)		1998	berries	3	2712+/-114			
" " " " " " " (Lions Club Park)		1998	soil (0-12 cm)	3	887+/-50			
PNGS#14	NE 10	1997	berries	10	335+/-30	498+/-24	1.49	
" " "		1998	tree leaves	10	134+/-24			
PNGS#15 - (Upper Airport Conservation Area)	NE 18	1997	apples	18	177+/-27	164+/-15	0.93	
PNGS#15a (South of PNGS 15)	NE 15	1998	pine needles	15	84+/-24	622+/-28	7.4	
			soil (0-20 cm)	15	109+/-14			
PNGS-W1 (Petticoat Conservation Area)		1998	red pine needles	5	8091+/-485	2032+/-102	0.25	
		1998	soil (0-20 cm)	5	954+/-44			

Table 2, continued

1997, 1998 BACKGROUND VEGETATION SAMPLES - Distal to OPG-Pickering

Sample#	Wind sector (1)	Year Collected	Sample	Distance from reactors (km)	TFWT (2) (TU)	OBT (2) (TU)	OBT/TFWT (5)	Remarks
Backgnd#1 -(HWY41+DORE LK)		1997	berries	275	93+/-25	58+/-7	0.62	
Backgnd#2- (Haggarty Twnshp Rd #14)		1997	leaves	230	41+/-12	41+/-5	1	
Bckgnd#3- (0.5 kms from Bancroft)		1997	leaves	175	61+/-16	51+/-5	0.84	
Bckgnd#4-(N of intxn620+28S - Apsley)		1997	leaves	135	52+/-9	49+/-5	0.94	
Bckgnd#5-(Cornwall)		1997	berries	390	37+/-10	55+/-8	1.4	
Bckgnd#6 - (Brockville)		1997	apples	285	39+/-12	37+/-9	0.95	
Sombra, Ontario		1998	soybeans	300		33+/-10		
WC1 - Western Canada		1998	wheat	2400	13+/-5	14+/-7	1.1	
WC2 - Western Canada		1998	canola	2400	13+/-3			

Tree Rings

Location (3)	Dendrochronology	Tree Type	OBT (2,4)
Langenburg, Saskatchewan	1965-1971	apple	1243+/-250
" " "	1975	"	246+/-25
" " "	1990	"	92+/-14
" " "	1995	"	123+/-15
Ottawa, Ontario	1980	pine	205+/-22
" "	1985	"	139+/-14
" "	1990	"	156+/-17
Lambton, Ontario	1947-1952	black oak	36+/-11
" "	1958	"	194+/-29
" "	1962	"	513+/-50
" "	1965	"	710+/-75
" "	1970	"	169+/-27
" "	1975	"	55+/-10
" "	1980	"	73+/-11
" "	1985	"	32+/-7
" "	1990	"	33+/-6
" "	1995	"	34+/-5

REMARKS

1) Wind sector locations taken from LaMarre, 1998
2) Tritium values are in units of TU, where 1TU = 0.1184 Bq/Lwe
3) Details of trees sampled given in Kotzer and Watson (1999)
4) OBT concentrations measured on whole-wood samples and decay-corrected to 1997
5) Uncertainty on OBT/TFWT ratios is +/- 15%

Table 3: Concentrations of Tritium-in-Air proximal to OPG-Pickering calculated using empirical OBT measurements on vegetation and with CSA N288.1

Sample location	Distance from OPG-Pickering (km)	Model (2) HTO-in-air	Absolute (3) Humidity	OBT (4)	Empirical (5) HTO-in-air
Windsector and Distance used in CSA N288.1 (1)					
N - 0.7	0.7	26.8			
NE - 4	4	3.96			
ENE-3	3	5.68			
NE-10	10	1.013			
NE-15	15	0.561			
NE-18	18	0.432			
Vegetation Samples compared with CSA N288.1					
Sample # (Location) (6)					
1993-PNGS5 (N - 0.7)	0.7		10.83	1205.4	13.05
1997-PNGS5 (N - 0.7)	0.7		9.78	2168	21.20
1998-PNGS5 (N - 0.7)	0.7		11.1	2861	31.76
1998-PNGS5 (N -0.7)	0.7		11.1	1787	19.84
1992-PNGS4 (N - 0.7)	1.2		9.77	62.016	0.61
1993-PNGS10 (ENE-3)	3		10.83	181.5	1.97
1997-PNGS12 (NE - 4)	4		9.78	158.9	1.55
1997 - PNGS13 (ENE-3)	3		9.78	96.9	0.95
1997 - PNGS14 (NE - 10)	10		9.78	58.9	0.58
1998-PNGS15A (NE - 15)	15		11.1	73.6	0.82
1993 - PNGS15 (NE - 18)	18		10.83	23.32	0.25
1997-PNGS15 (NE -18)	18		9.78	19.42	0.19

Remarks:

1) Windsector and distance for model sampling sites
2) Average HTO-in-air calculated using tritium release data and meterological conditions for 1991 to 1996 and CSA N288.1; Bq/m3
3) Value for Absolute Humidity (Q) calculated using equations 2 and 3 (g H2O/m3)
4) OBT value taken from Table 2 and converted to Bq/Lwe
5) Empirical HTO-in-air calculated using equation 4; Bq/m3
6) Location of sample also indicated in Table 2 and on Figure 2
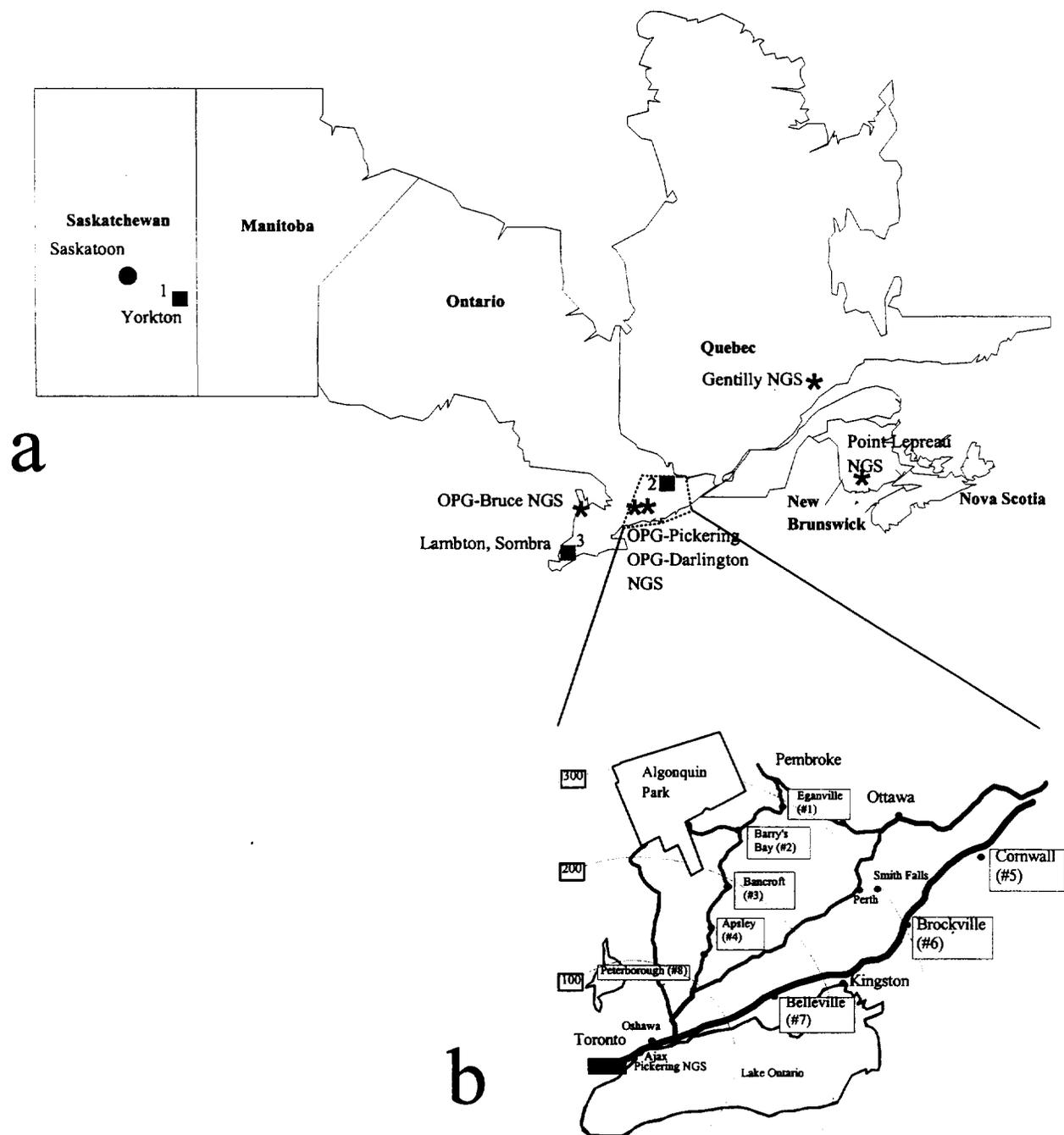
Figure 1. Map of Central and Eastern Canada showing locations of a) sampling sites for determining tritium in tree rings and agricultural crops (closed squares) from several areas in Canada, namely, i) Yorkton, Saskatchewan, ii) Ottawa, Ontario, iii) Lambton and Sombra, Ontario, and location where 1997-1998 precipitation samples from Saskatoon, Saskatchewan, were collected for HTO measurements (closed circle). Currently operating NGS's are shown with asterisks (*). Inset shown in b) indicates the locations in Eastern Ontario where environmental samples were sampled for their levels of tritium in background areas.
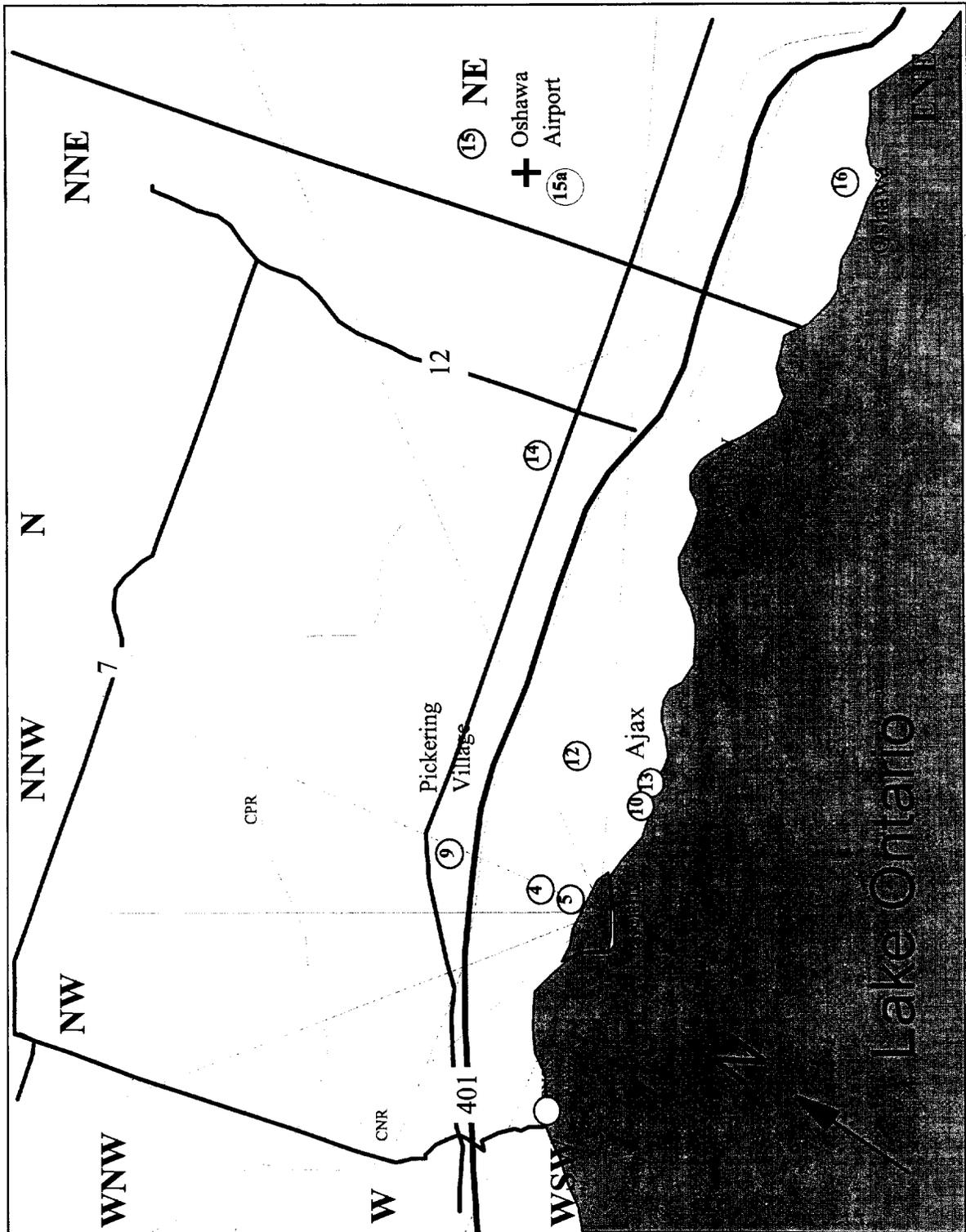
Figure 2. Map of area within approximately 20 km of OPG-Pickering NGS showing locations where vegetation samples were collected in 1992-1993, 1997, and 1998, and measured for their FWT and OBT concentrations.
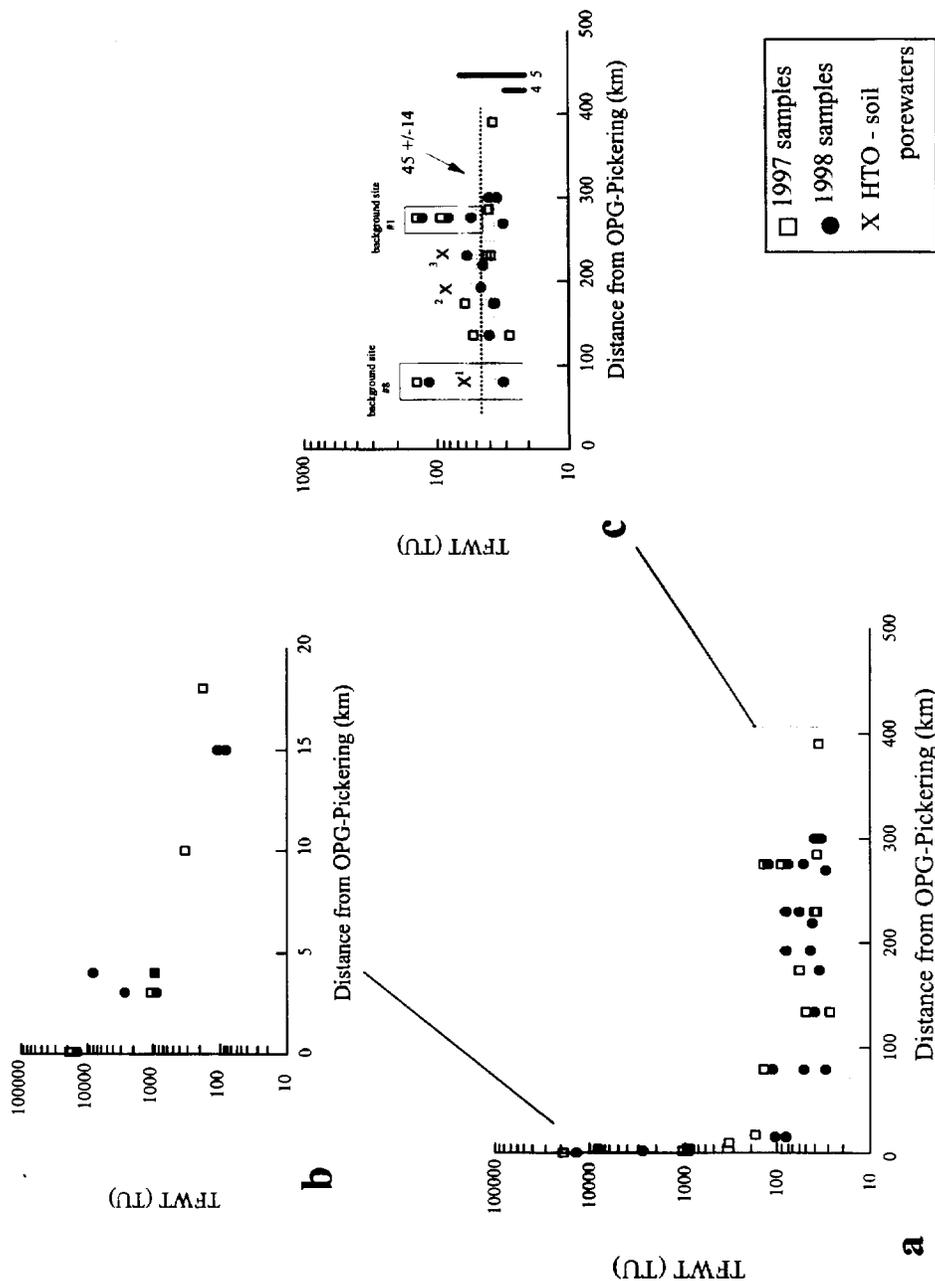
Figure 3. **a)** TFWT concentrations measured in vegetation samples collected in 1997 and 1998 at distances of up to 400 km from the NGS's. Insets are shown in **b)** vegetation collected within 20 km and less from OPG-Pickering NGS, and **c)** vegetation collected at background sites between 80 and 400 km from OH-Pickering NGS. Also indicated in **c)** are HTO values in soil pore waters (*small x's labelled 1, 2, 3*), along with ranges of tritium measured in regional precipitation to 1993 (*#4*) and in major lakes and rivers in Eastern Ontario (*#5*). The dashed line and shaded grey area in **c)** represents the mean and standard deviation (45±14 TU) on the TFWT values for samples from background sites, excluding site #1 and site #8. Data listed in Tables 1 and 2.
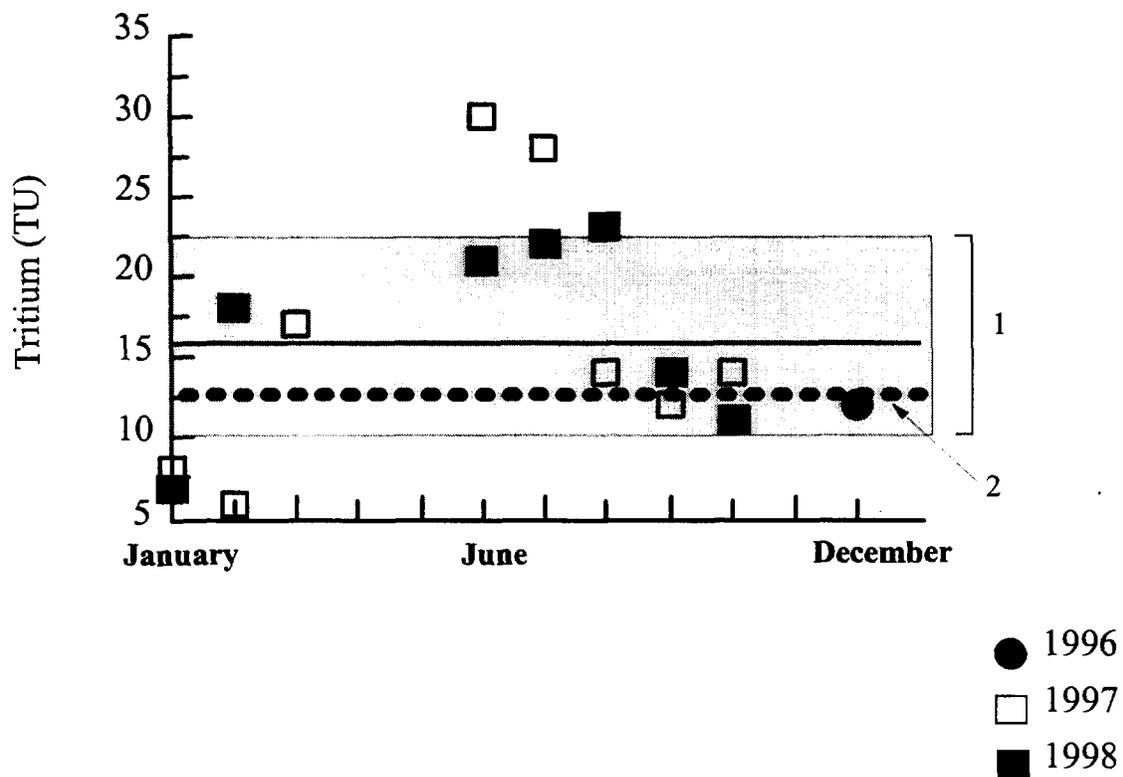
Figure 4. Tritium concentrations measured in precipitation samples (1996 to 1998) from Saskatoon, Saskatchewan. The solid line and shaded grey area (*#1*) represents the mean and standard deviation (16.1±6.9) for the precipitation samples, whereas the thicker dashed line (*#2*) represents the average TFWT concentrations (~12.5 TU) measured on agricultural samples (wheat and canola; Table 1) grown in Saskatchewan in 1998.
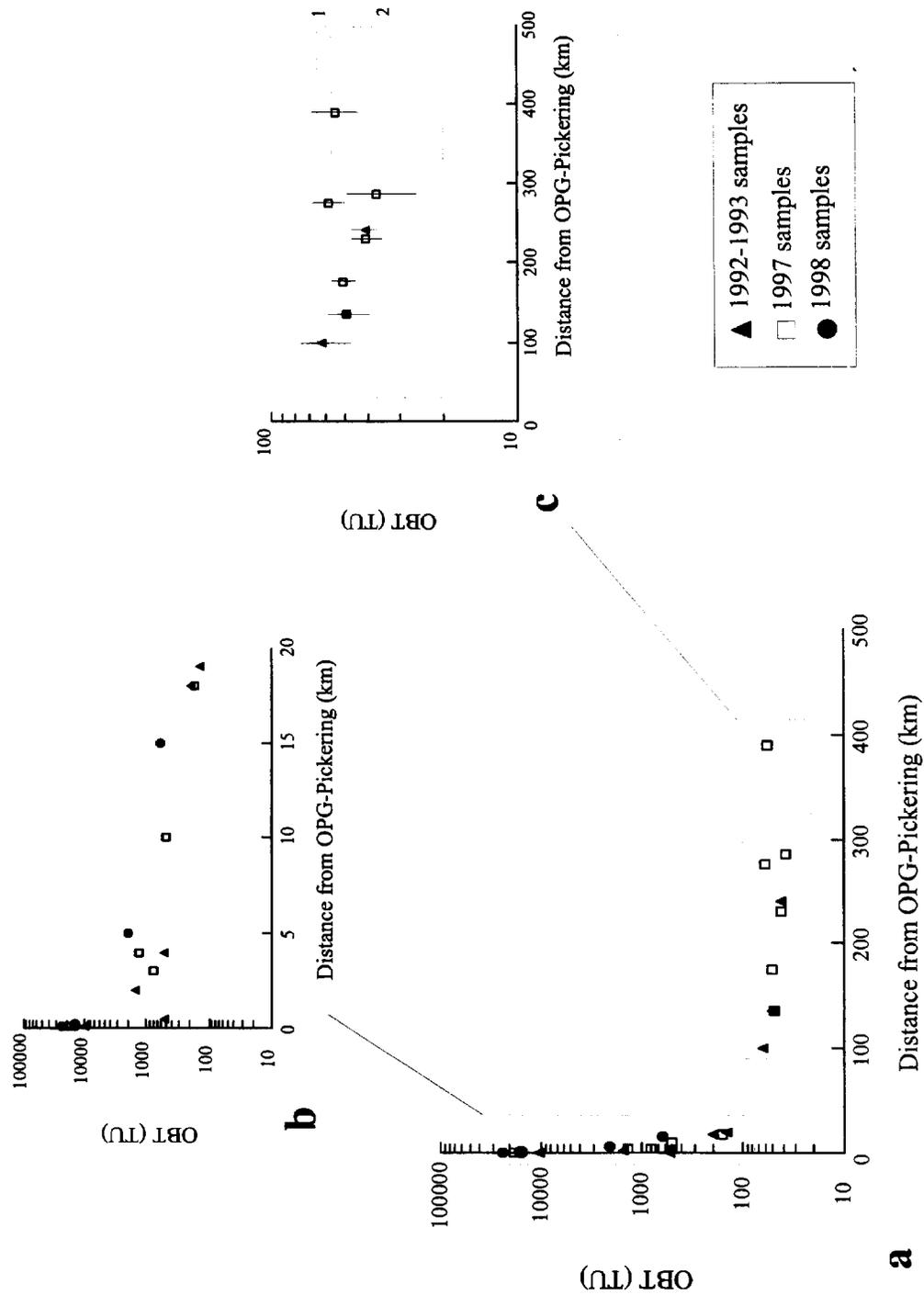
Figure 5. a) OBT concentrations measured in vegetation samples collected in 1992-1993, 1997, and 1998 at distances of up to 400 km from the NGS's. Insets are shown in b) vegetation collected within 20 km and less from OPG-Pickering NGS, and c) vegetation collected at background sites between 80 and 400 km from OPG-Pickering NGS. In c), fields labelled *1* and *2* represent the average tritium values measured in Lake Ontario (King and Workman, 1998) and in major lakes and rivers in Eastern Ontario, respectively. Data listed in Table 2.
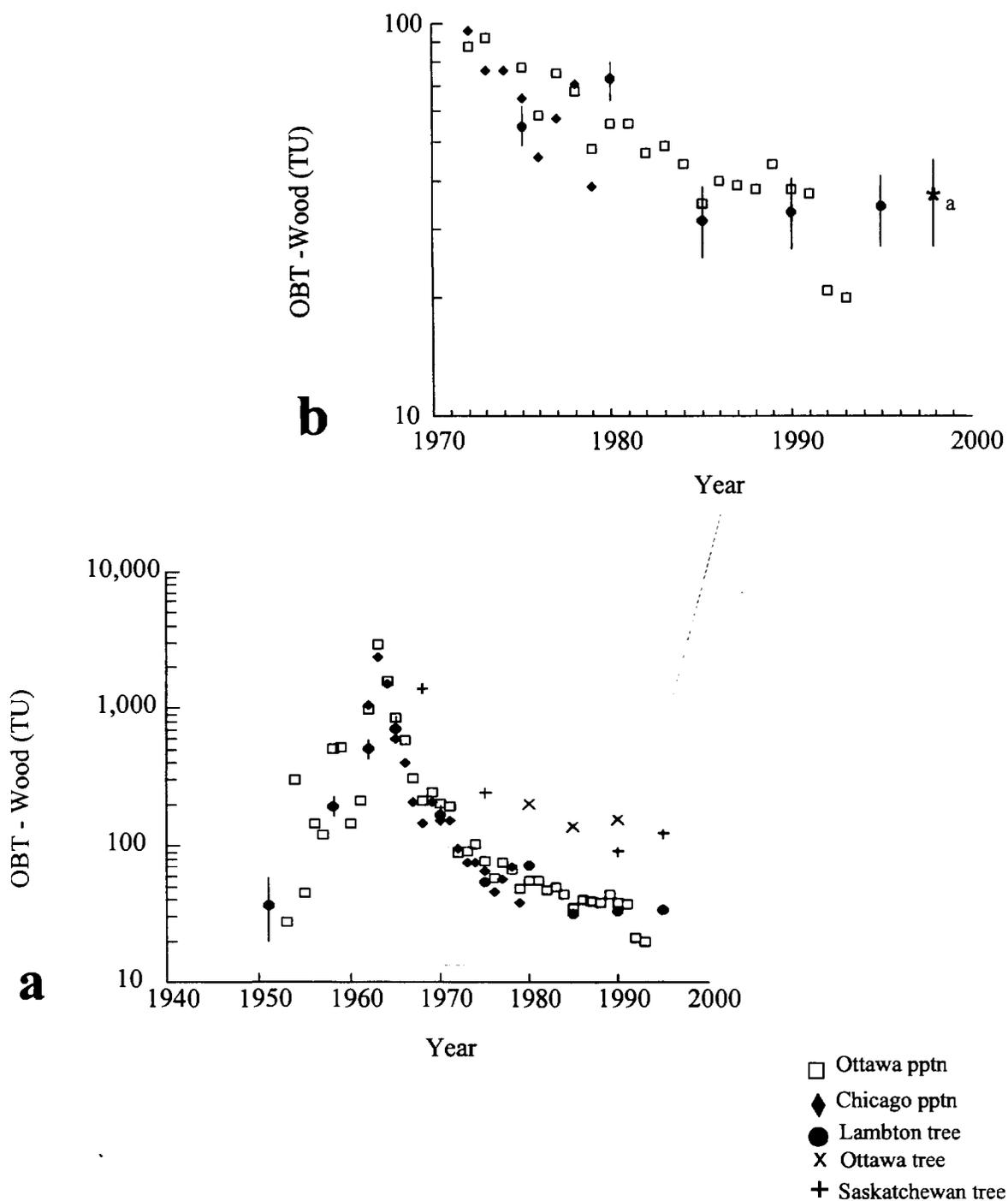
Figure 6. OBT concentrations measured in whole-wood samples from Saskatchewan (+) and Ontario (x, closed circles), and compared with the levels of tritium measured in large-scale precipitation between the years of **a)** 1950 to 1995 for all locations, and **b)** 1970 to 1995 for a tree from Lambton, Ontario. In **b)** asterisk labelled *a* represents the OBT concentration (33±10 TU) measured in soybeans from nearby Sombra, Ontario. Data in Table 2.
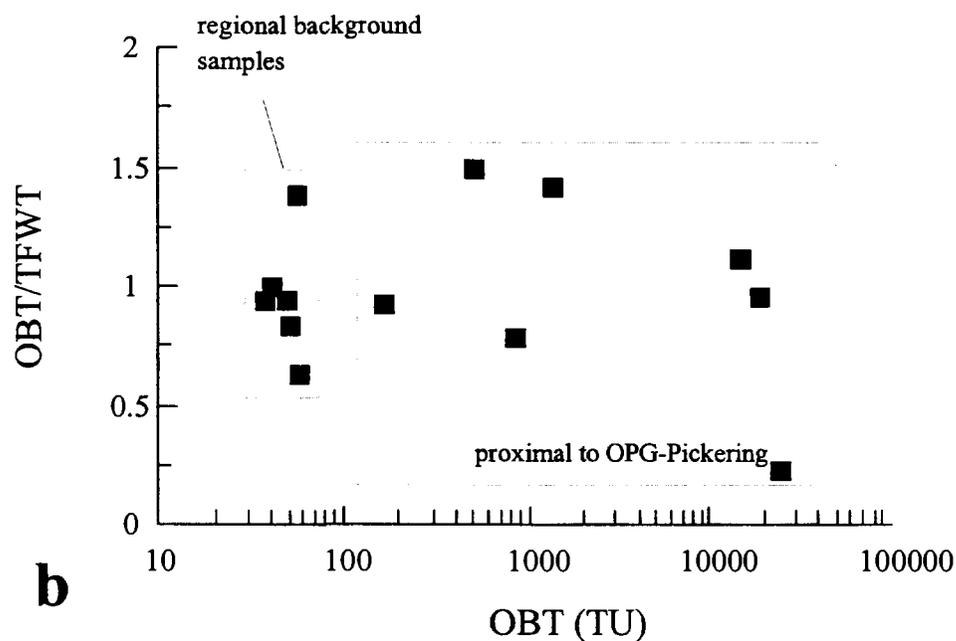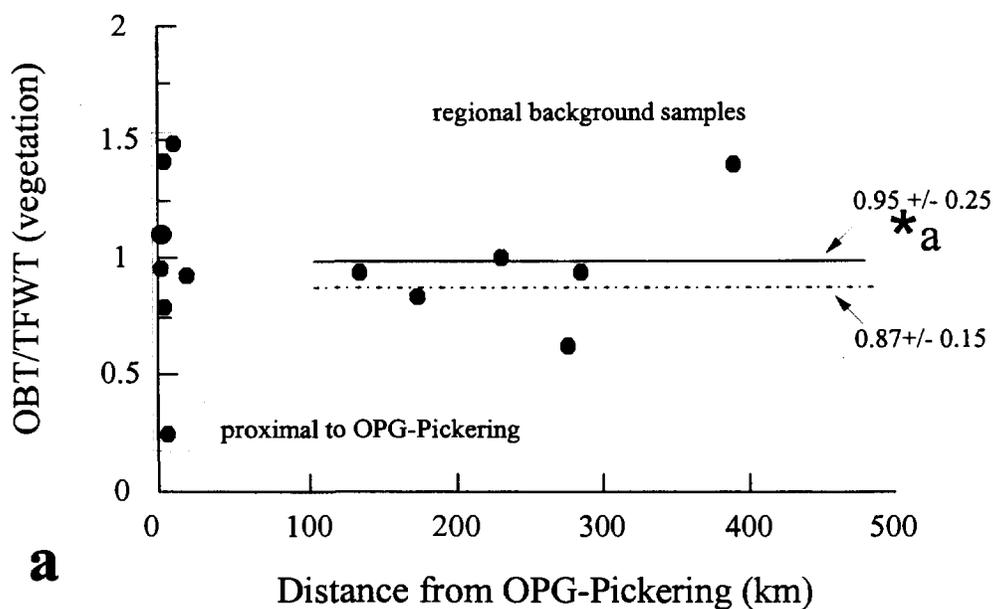
Figure 7. Comparison of OBT/TFWT ratios with **a)** distance and **b)** OBT concentrations for vegetation samples collected both distal and proximal to the OPG-Pickering NGS. In **a)** The dashed line represents the average OBT/TFWT value (0.87±0.15) for all regional background samples (except OBT/TFWT = 1.4), whereas the solid line represents the OBT/TFWT ratio (0.95±0.25) for all regional background samples. The asterisk labelled *a* indicates the OBT/TFWT ratio for a sample of cereal grains (WC1 - wheat) from Western Canada. Data in Table 2.
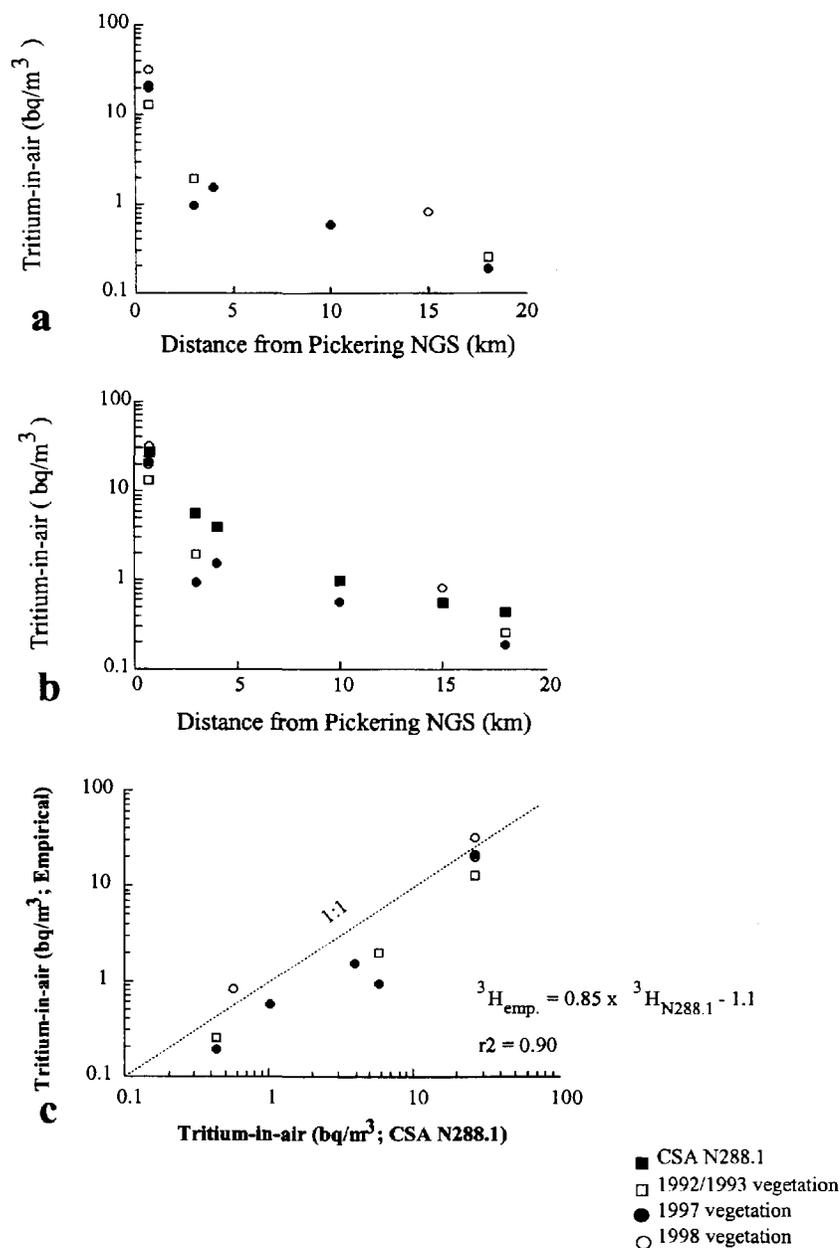
Figure 8. Comparison of concentrations of tritium-in-air with distance from OPG-Pickering NGS. **a)** Empirical tritium-in-air concentrations calculated using Equations (2) to (4) and measured OBT concentrations in vegetation samples. **b)** Variation of tritium-in-air concentrations with distance from OPG-Pickering for empirical data from **a)** and data derived using tritium-release data and CSA-N288.1. **c)** Comparison of the tritium-in-air values for empirical calculations from **a)** and data derived using tritium-release information and CSA-N288.1. The thin solid line represents 1:1 agreement between data. Regression analyses of the data indicates a good correlation (r2 = 0.90) between the data sets, although the data is biased high with respect to the modelled tritium-in-air data using CSA-N288.1. Data in Table 3.

APPENDIX

Sample Preparation Techniques

OBT in Vegetation: Previously at CRL, fresh vegetation samples (10 to 20 g) comprising tomatoes, radishes and Komatsuna (Japanese lettuce) from vegetation plots at Chalk River Laboratories (CRL) were collected and kept frozen in sealed glass jars until they were processed. The vegetation samples were collected during a controlled HT-release experiment wherein several types of plants were grown under conditions of chronically high tritium-in-air. OBT concentrations were measured in these samples using the ^{3}He-ingrowth MS techniques with the techniques used and results obtained reported in Spencer et al. (1996).

The same techniques for preparing the plant samples for measurement of OBT by ^{3}He-ingrowth MS have were used in this study. The procedures used were adopted and modified as necessary from Brown (1995). In summary, the TFWT and exchangeable-OBT components in the plants were removed while preparing the sample for measurement of OBT. To accomplish this, the plant samples, in Al-Si vessels, were either air-dried at low temperature (150°C) or subjected to vacuum-distillation techniques to remove their TFWT component. The tritium concentrations in this component can be measured using direct LSC techniques. The exchangeable OBT component was then removed by successively hydrating the dried-plant samples, in-vacuo, with tritium-depleted waters (<1 TU), and drying to remove the equilibration waters. Volumes on the order of 80 mL of tritium-depleted water were required for this, with the tritium-concentrations determined on the rinse waters by LSC. The completely dried and exchanged plant samples were then vacuum-sealed in the AL-Si glassware, reweighed and stored at low temperatures (~-20°C) to allow for sufficient ingrowth of ^{3}He for measurement (Kotzer et al., 1999a).

OBT in Tree Rings: A number of dendrochronologically-characterized tree-ring samples, collected from several species of trees in different areas in Canada and spanning the years between 1947 to 1995, were prepared for OBT analyses by ^{3}He-ingrowth mass spectrometry (Table 2). These samples are a subset of the tree rings that were measured for ^{14}C (Kotzer and Watson, 1999). The procedures used were based on the results of a study in Europe (Wallner, 1992), wherein OBT was measured on: i) dried, natural wood, ii) wood after resin extraction, and iii) cellulose from several splits of separated annual accumulations of tree rings. The results of the study essentially saw no difference in the OBT concentrations among the various fractions, and concluded that in trees with constant cellulose/lignin ratios and small amounts of resin, the time-consuming and tedious process of separating the cellulose for tritium measurement is not warranted. On this basis, we adopted the simplest and least intrusive method of measuring the OBT on dried, dendrochronologially characterized samples of tree rings. Evaporation of the cellular water in the tree-ring samples during storage precluded measurement of the TFWT component; hence the samples were dried in an oven at temperatures of 150°C for at least 24 h to remove adsorbed HTO. The dried samples were then loaded into 200 to 300 mL volume Al-Si vessels and attached to a high-vacuum system (~10^{-4} torr). A combination of several (approximately 5 to 6) equilibration flushes with tritium-free water (20 to 30 mL of <1 TU water) and lysophillization of this water, in vacuo at LN$_2$ (-196°C) temperatures was used to remove any of the remaining tritium-free water and establish a constant dry weight on the wood samples.

Tritium concentrations for each of the rinse waters were determined by LSC. For two of the three sampling sites (Saskatchewan and Lambton, Ontario - Figure 1), this procedure was considered complete when the results of LSC analyses were at analytical background for direct LSC ($\leq$10 TU). The final dried wood residue was then flame sealed into the AL-Si vessels at vacuum pressures of $\sim$10^{-4} torr, reweighed and stored in a freezer at temperatures of -20°C until analyses of ingrowth ^{3}He by mass spectrometry.

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