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ENVIRONMENTAL TRITIUM IN TREES

R.M. BROWN
Atomic Energy of Canada Limited,
Chalk River Nuclear Laboratories,
Chalk River,
Ontario.
Canada

Abstract

ENVIRONMENTAL TRITIUM IN TREES.

The distribution of environmental tritium in the free water and organically bound hydrogen of trees growing in the vicinity of the Chalk River Nuclear Laboratories (CRNL) has been studied. The regional dispersal of HTO in the atmosphere has been observed by surveying the tritium content of leaf moisture. Measurement of the distribution of organically bound tritium in the wood of tree ring sequences has given information on past concentrations of HTO taken up by trees growing in the CRNL Liquid Waste Disposal Area. For samples at background environmental levels, cellulose separation and analysis was done. The pattern of bomb tritium in precipitation of 1955-68 was observed to be preserved in the organically bound tritium of a tree ring sequence. Reactor tritium was discernible in a tree growing at a distance of 10 km from CRNL. These techniques provide convenient means of monitoring dispersal of HTO from nuclear facilities.

Trees present a convenient means of monitoring the dispersal of tritiated water in an area. Current levels of HTO in atmospheric and soil moisture are reflected in the tritium content of the leaf moisture. A dated record of the past concentrations of tritium in an area is preserved in the organically bound tritium of individual annual growth rings of the local trees.

Several workers have measured the tritium content of pine needles to study the dispersal of tritium in the environment. Stewart, Wyerman, Sherman and Schneider [1] found the tritium content of moisture extracted from pine needles collected at various sites across the United States correlated with the geographical distribution of tritium in precipitation resulting from thermonuclear tests or proximity to nuclear industrial facilities. Murphy and Corey [2] studied the uptake of HTO vapour by pine needles of branches enclosed in plastic bags. The appearance of HTO in pine needles, as well as other vegetation and soil, following passage of a cloud of molecular HT has been reported by Murphy, Watts and Corey [3].

Little work has been reported on the tritium content of individual tree rings. Kigoshi and Tomikura [4] measured the

concentration of tritium in dried wood of 1953-1960 rings and found a distribution corresponding to the known releases of thermonuclear tritium during the period.

We have been studying tritium distribution in tree components in the vicinity of Chalk River Nuclear Laboratories (CRNL). The CRNL Liquid Waste Disposal Area provides a useful site for studying tritium dispersal in the natural environment. In some areas, surface and ground waters have an elevated tritium content as the result of the controlled release of reactor-produced tritium. These concentrations are not high enough to constitute a health hazard, but provide convenient spikes which may be measured more easily than the tritium in the general environment. Studies have been extended to off-site locations to demonstrate potential applications of the techniques in the general environment.

EXPERIMENTAL PROCEDURES

This work has involved a wide range of tritium activity levels. To avoid contamination problems, low-level samples (<5000 TU¹ originally, <2000 TU more recently) have been analyzed in a separate low-level laboratory by personnel not involved with high-level samples.

Water Extraction

Water was recovered from soil, leaves, wood chips and cellulose by azeotropic distillation with toluene using a Dean-Stark receiver.

Ring Separation

(i) To obtain water from specific rings, separation was done manually with a sharp knife or chisel as soon as possible after the tree was cut.

(ii) When there was no requirement for isolation of free water from the wood, and cellulose separation was to be done, separation was greatly facilitated by extraction of an intact sector (2 cm thick) with refluxing monoethanolamine vapour for about three hours. This treatment softened the wood at ring boundaries making possible clean separations with a spatula blade.

¹ Tritium Unit (TU) = 1 T atom per 10¹⁸ H atoms
= 0.12 Bq per litre water
= 3.25 pCi per litre water.

TABLE I. HTO DISTRIBUTION IN MAPLE TREES IN PERCH LAKE BASIN, CRNL (CONCENTRATION IN TRITIUM UNITS)

Free water from:	Tree 1	Tree 2
Atmosphere	~5000	
Leaves	3700 - 4300	9200
Leaf stalks	1400 - 1500	
Twig wood	1200 - 1350	
Trunk wood	1200	
Trunk bark	1175	
Root wood	1400	
Soil	770	75200
Ground water	750	

Tree 1. Located on the east shore of Perch Lake where the atmospheric HTO level is raised by influx of reactor HTO evaporated from the lake, but the soil and ground waters are relatively low in tritium.

Tree 2. Located in a drainage path from the Liquid Waste Disposal Pit where the concentration of atmospheric HTO is low compared to the concentrations of soil and ground water HTO.

Cellulose Separation

For low activity samples, 40 g wood chips were boiled in two litres monoethanolamine with vigorous stirring for about eight hours (Wise [5]). The pulp was filtered hot and washed free of solvent with hot water. Coniferous woods required additional treatment with hypochlorous acid and sodium sulphite to complete removal of lignin.

Hydroxyl Equilibration

The cellulose pulp was boiled one hour in 0.4N HCl solution prepared with tritium-free water (<2 TU). The pulp was washed free of acid with tritium-free water and stored wet until combusted. This treatment was repeated just before drying for combustion.

Drying

(i) Ground or chipped wood was dried overnight in an air oven at 130°C prior to combustion.

(ii) To avoid exchange with atmospheric HTO during and after drying, low activity cellulose was sealed in the combustion apparatus while still damp with tritium-free water. It was dried overnight by heating to 170°C in vacuo, the water being collected in liquid nitrogen cooled traps.

Combustion

Wood or cellulose samples were burned completely in a flow of dried oxygen and nitrogen and the water collected in a trap cooled to -80°C .

Tritium Measurement

Samples were measured by liquid scintillation counting or gas counting, in some cases after isotopic enrichment by electrolysis.

HTO IN THE FREE WATER OF TREES

Pickup of Atmospheric HTO by a Tree

The concentrations of HTO in various parts of two trees growing in the CRNL Liquid Waste Disposal Area are shown in Table I. Tree 1 was located on the east shore of a small lake where the soil and ground waters are relatively uncontaminated but the atmospheric HTO level is elevated due to the influx of evaporate from the lake where the tritium concentration is 40 000 TU. It is seen that the HTO concentration in the leaves of the tree is much closer to that of the atmosphere than to that of the soil and ground waters which contribute the transpirational stream of the tree. Evidently the leaf moisture equilibrates with the surrounding atmospheric moisture. HTO diffuses back into the tree and the water of the woody parts of the tree appears surprisingly well-mixed at a concentration intermediate between those of the soil and atmospheric moisture.

Tree 2 was growing in a drainage path from the Disposal Pit where the soil and ground waters HTO concentration was high compared to the HTO content of the atmospheric moisture. In this reverse situation, the leaf water HTO was found to be much lower than the soil water as a result of exchange loss to the atmosphere.

This evidence that the HTO content of tree leaf moisture is strongly affected by the HTO content of the surrounding atmospheric moisture suggests the use of tree leaves as a sampling device for monitoring of atmospheric HTO in the general environment.

Regional Pattern of Leaf HTO Around an Industrial Source

As a result of reactor operations, HTO vapour is released from CRNL and the nearby Nuclear Power Demonstration (NPD) plant. A survey of the HTO content of poplar (*Populus L.*) leaves has delineated the overlapping plumes resulting

from these releases as shown in figure 1. Concentration contours are similar in geographic pattern and level of activity to those observed for HTO in snow cores (Brown and Fraser [6]). Reactor tritium is discernible above a background level of 150 TU (natural and bomb-test tritium) over an area 70 km long by 20 km wide oriented along the Ottawa River similar to the local wind pattern. The maximum concentration at the NPD site boundary was about 5000 TU, at the boundary of the larger CRNL site about 1000 TU. These concentrations were established by a release rate of about 7200 curies per year (270 TBq a^{-1}) from CRNL and roughly twice that from NPD. A concentration of 5000 TU in atmospheric moisture is 0.1% of MPC_a for general population.

It should be pointed out that operations at these two stations are experimental in nature and releases per unit power at full-scale commercial power stations are much lower. Furthermore, methods are under development for the removal of tritium from reactor fluids to limit the exposure of station personnel as well as the general population.

HTO Content of a Sequence of Tree Rings

Only the outer few rings of a tree conduct its transpirational stream. Resins and lipids are deposited in the conducting passages of older rings which become heartwood and no longer take part in the active life of the tree. It is of interest to see how isolated the inner wood is in terms of water exchange.

The distribution of HTO in a sequence of growth rings of a tree grown in the CRNL Liquid Waste Disposal Area is shown in Figure 2. The rings of 1971 to 1977 show a uniform HTO concentration. Evidently these are the active rings conducting present-day water up the tree. In earlier rings the HTO concentrations are higher indicating that water of higher tritium content came into the tree at some time in the past. Resistance to water exchange is evident since there has not been equilibration with the water of the outer rings. However, there certainly is significant diffusion of HTO into older rings since tritium is observed right to the centre of the tree, ring year 1938, in spite of the fact that there was no reactor tritium in this area prior to 1948 and very little prior to 1958.

ORGANICALLY BOUND TRITIUM IN TREE RINGS

Disposal Area Trees

The concentration of tritium found in the combustion water of dried wood of the tree discussed in the previous section is also shown in Figure 2. It is of note that the wood of pre-1958 rings has less than 5% of the tritium content of

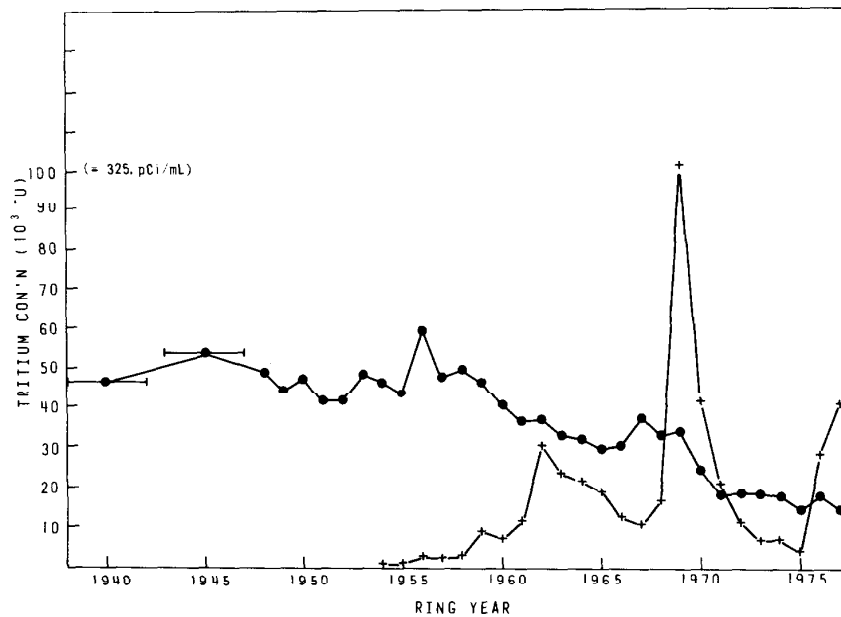


FIG. 2. Present-day concentrations of tritium in individual growth rings of a balsam fir, CRNL Disposal Area, cut May 1978.

- Free water of wood.
- + Combustion water of dried wood.

water permeating that wood. In another tree in which the concentrations were 100 times higher, this value was about 2%. This is rather surprising in view of the reported exchangeability of the hydroxyl hydrogen of cellulose (Lang and Mason [7], Sepall and Mason [8]). Presumably it indicates steric protection of these groups in the intact wood structure. In any case, it means that a reasonable estimate of the original tritium content of a tree ring can be obtained simply from the dried wood without serious interference by exchange of hydroxyl hydrogens or deposition of non-cellulosic materials after the original ring formation. This greatly facilitates the use of tree ring studies to learn the history of tritium dispersal within the Disposal Area.

The results from the analysis of several trees from the Disposal Area are shown in Figure 3 together with the concentration of tritium for recent years in the small stream draining the area. Concentrations are adjusted for radioactive decay back to the year of ring growth. The initial tree was cut and analyzed in 1964. It grew in the middle of the stream and had a tritium concentration in its outer ring similar to the

BROWN

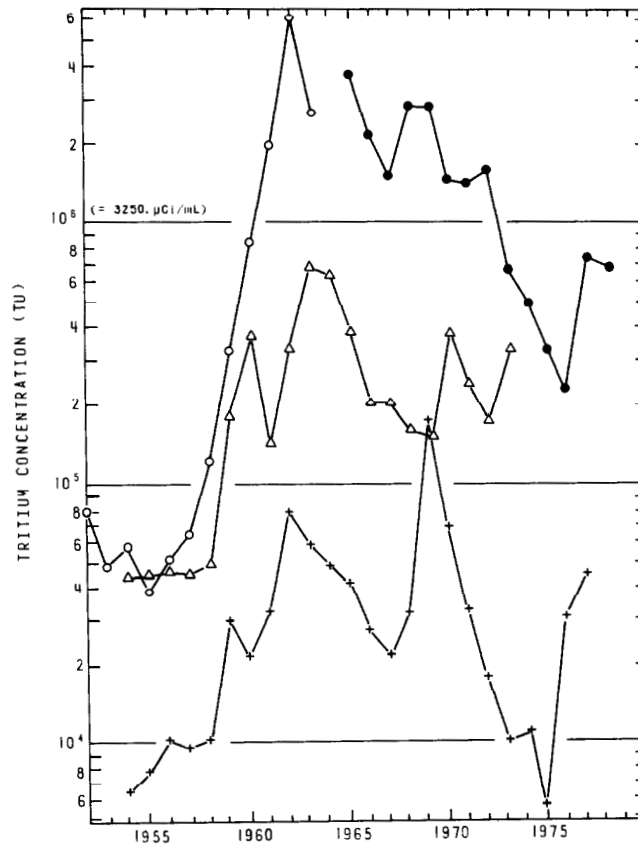


FIG. 3. Tritium concentrations in:

- Small stream draining area near the Liquid Waste Disposal Pit, CRNL; mean May to August values.
- Combustion water of dried wood from white spruce, cut 1964.
- △ Combustion water of dried wood from white spruce, cut 1974.
- + Combustion water of dried wood from balsam fir, cut 1978.

stream water. Subsequent concentrations in the stream look like a continuation of the pattern observed in the tree. The other trees were attempts to duplicate the original results at later dates and demonstrate preservation of the 1962 peak in trees that continued growing. The differences in concentration levels are attributed to siting differences. The area is close to the Disposal Pit and the appearance of tritium in specific trees is very dependent on the microhydrology of the area which is probably complex with narrow and variable sub-surface drainage paths influenced by discharges to the Pit.

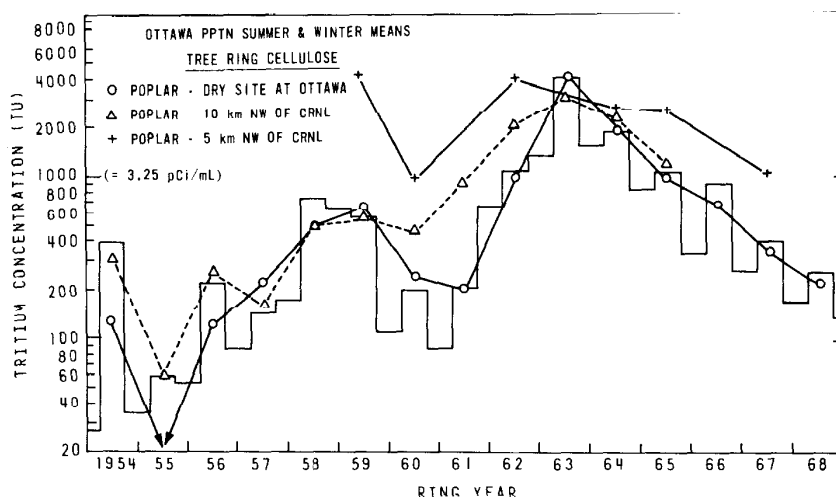


FIG. 4. Comparison of the distribution of tritium in tree ring cellulose from trees grown at Ottawa and near Chalk River Nuclear Laboratories with summer and winter mean concentrations in Ottawa precipitation.

In all trees, the pre-1957 values reflect the contamination level inherent in the whole dried wood samples. They are higher in Figure 3 than in Figure 2 because of the decay adjustment in the former. Pre-1955 cellulose separated from the 1964 tree and hydroxyl-equilibrated with tritium-free water in the low-level laboratory gave a value of 800 TU, <0.1% of the concentration of the water permeating this wood when it was cut. Thus, it is certain that there was no reactor tritium in the waters feeding these trees prior to 1957.

Concentration started to rise in the 1964 tree in 1958, one year ahead of the other trees. The 1974 tree seems to be one year out of phase relative to the other two trees, suggesting an error in ring year assignment. If this is the case, the 1962 peak is common to all three and the 1974 and 1978 trees have coincident peaks in 1959 and 1969 as well.

The patterns observed are consistent with the known history of tritium release in this area. NRU reactor, the chief source of tritium for liquid disposal, started operation in late 1957. It was plagued with heavy water leaks in its early years but these were remedied by 1962. Heavy water management was steadily improved through the mid-1960's. The reactor was out of operation 1972-74 for vessel change and as shown by the recorded stream concentrations and the 1978 tree, tritium levels in the area dropped accordingly. The cause of the 1969 peak in the 1978 tree is unknown but it does reflect a rise in the stream concentration for 1968-69.

BROWN

TABLE II. TRITIUM IN CELLULOSE OF OTTAWA POPLAR - DRY SITE
(CONCENTRATIONS IN TRITIUM UNITS)

Ring Year	Concentration as of June 1969 ^a	Adjusted for Blank and OH ^b	Concentration at Year of Growth	Concentration in Precipitation Average April-September ^a	Tree/Precipitation
1968	201	230	243 ± 17	262	0.93
1967	272	331	371 ± 26	410	0.90
1966	438	568	672 ± 38	903	0.74
1965	605	807	1010 ± 54	1070	0.94
1964	1126	1551	2057 ± 106	1886	1.09
1963	2213	3104	4353 ± 316	4107	1.06
1962	516	680	1010 ± 55	1080	0.94
1961	139	141	222 ± 20	204	1.09
1960	156	165	275 ± 22	198	1.39
1959	315	393	692 ± 42	550	1.26
1958	246	291	542 ± 37	730	0.74
1957	133	133	262 ± 26	142	1.85
1956	92	74	154 ± 21	222	0.69
1955	47	10	22 ± 20	59	0.37
1954	90	71	166 ± 23	393	0.42
1953	35	-	-	20	-
1949-52	44	-	-	20	-

^a±5% analytical uncertainty

^bAdjusting for blank (40 ± 5 TU) and 30% loss of original tritium by hydroxyl group exchange:

$$\text{Adjusted value} = \frac{\text{Measured concentration} (\pm 5\%) - 40 (\pm 5) \text{ TU}}{0.70}$$

Off Site Trees

On extending tree ring analysis for tritium to the level of bomb-test tritium in the general environment it was found advisable to prepare separated cellulose to reduce contamination problems. This eliminates material deposited subsequent to ring formation and provides a material of definite chemical composition from which all hydroxyl tritium can be eliminated in case it has been incorporated by exchange subsequent to ring formation. Various treatments were tried to achieve complete exchange of the hydroxyl groups of cellulose with water in a manner that would be practical with tritium-free reagents. Finally this was accomplished by boiling cellulose for one hour in 0.4N HCl prepared with tritium-free water (<2 TU). Experiments using tracer levels of tritium (10^6 TU) showed 28 to 32% exchange of cellulose hydrogens. After replacement of the original hydroxyl hydrogen with tritium-free hydrogen, the cellulose has 70% of its original tritium content and its measured T/H ratio needs to be corrected by the factor 10/7 to obtain the original tritium concentration.

This hydrolytic treatment did not eliminate contamination problems completely. No source of contamination could be identified but a consistent background level of about 50 TU was obtained on old cellulose. While this precluded any measurement of the pre-1953 tritium level, significant measurement of the distribution of thermonuclear tritium in post-1953 rings was possible. Values obtained for pre-1953 rings were accepted as a blank to be subtracted from all values for that tree.

In Figure 4, results obtained on poplar trees grown at well-drained sites at Ottawa and in the Chalk River vicinity are compared with the record of tritium concentration in Ottawa precipitation (Brown [9]). Data for the Ottawa tree is presented in Table II to show the levels of activity measured and the magnitude of the adjustments for blank, loss of hydroxyl tritium and radioactive decay. Concentrations observed in the Ottawa tree show good correlation with the mean concentrations of tritium in precipitation over the summer growth interval of each year back to 1960.

Reactor tritium is clearly evident in the rings of the trees growing 5 and 10 km northwest of the CRNL stack. Concentrations in the pre-1960 rings of the tree at 10 km correlate well with the record of thermonuclear tritium at Ottawa. This demonstrates the potential utility of such measurements for establishing environment levels before and after installation of a nuclear power plant.

CONCLUSIONS

Analysis of the tritium content of tree leaf moisture has been found to provide a convenient means of observing regional atmospheric dispersal of HTO from an industrial source.

Concentrations established in such vegetation by a given release are particularly relevant to population exposure considerations since they combine contributions from atmospheric moisture, precipitation and soil water averaged over a few weeks time.

Tree ring analysis has proved to be a practical means of investigating the history of tritium release in an area. Although recent water penetrates older rings, retention by the older wood components of tritium in the permeating water is <5%. When a contamination level of this order is acceptable, the tree ring tritium distribution can be obtained using dried whole wood samples. If HTO levels in the free water of the wood are much higher than the organically bound tritium levels, e.g. in old wood, separated cellulose samples must be used. Purified cellulose containing <0.1% contribution from the water that permeated it in the tree can be prepared. This demonstrates that the original isotopic composition of the carbon-bonded hydrogen as laid down in ring formation is preserved in the cellulose and can be determined.

In general, the pattern of tritium concentrations in tree ring sequences has correlated with the known history of tritium dispersal at the elevated levels of the CRNL Liquid Waste Disposal Area and at the level of bomb-test tritium in the general environment. However, it must be borne in mind that a tree ring tritium record simply reflects past concentrations in a specific tree's water supply and must be interpreted in light of knowledge of the origin of that water.

ACKNOWLEDGEMENTS

Much of this work was done by a succession of university students during their summer employment periods. These include the former Misses M.L. Church and A.R. Robertson, Eric Lloyd and Joan Yaraskavitch. Mrs. E. Robertson performed the cellulose analyses on off-site trees in the low-level laboratory. The leaf sampling and analysis was done by C.D. Fraser.

The author acknowledges with gratitude the able technical assistance of all the foregoing in carefully performing the numerous analyses involved.

REFERENCES

- [1] STEWART, G.L., WYERMAN, T.A., SHERMAN, M., SCHNEIDER, R., Tritium in Pine Trees from Selected Locations in the United States, including Areas near Nuclear Facilities, U.S. Geol. Survey Prof. Paper 800B (1972) B265.
- [2] MURPHY, C.E., Jr., COREY, J.C., "Absorption of tritiated water vapour from the atmosphere by the needles of pine trees", Radioecology and Energy Resources, Ecol. Soc. Am. Special Publ. No.1, Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pa. (1976) 108.

- [3] MURPHY, C.E., Jr., WATTS, J.R., COREY, J.C., Environmental tritium transport from atmospheric release of molecular tritium, *Health Phys.* **33** (1977) 325.
- [4] KIGOSHI, K., TOMIKURA, Y., Tritium and carbon-14 in the tree rings, *Bull. Chem. Soc. Jpn.* **34** 11 (1961) 1739.
- [5] WISE, L.E., (Ed.), *Wood Chemistry*, Reinhold Publishing Corp., New York (1946) 595.
- [6] BROWN, R.M., FRASER, C.D., Atmospheric dispersion of HTO from CRNL and NPD, Progress Report of Biology and Health Physics Division, CRNL, April-June 1976, AECL-5602, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, 39.
- [7] LANG, A.R.G., MASON, S.G., Tritium exchange between cellulose and water, *Can. J. Chem.* **38** (1960) 373.
- [8] SEPALL, O., MASON, S.G., Hydrogen exchange between cellulose and water: I. Measurement of accessibility, *Can. J. Chem.* **39** (1961) 1934; II. Interconversion of accessible and inaccessible regions, *Can. J. Chem.* **39** (1961) 1944.
- [9] BROWN, R.M., "Distribution of hydrogen isotopes in Canadian waters", *Isotope Hydrology 1970 (Proc. Symp. Vienna, 1970)*, IAEA, Vienna (1970) 3.

DISCUSSION

A.S. MASON: Was the source of HTO to which the trees were exposed at the Chalk River site evaporation or direct input from the effluent pond?

R.M. BROWN: In the study of tree ring tritium in trees growing in the Liquid Waste Disposal Area, the source of tritium was the surface and ground-water draining from the Disposal Pit. In the other studies, involving the leaf-moisture HTO distribution pattern and tree ring tritium in off-site trees, the source of tritium was atmospheric HTO vapour of bomb-test and local reactor origin.

F. BOVARD: Has the relative humidity of the air been fairly constant over your sampling period? Also, does the relative humidity have any effect on the ratio between the tritium in the atmosphere and in the leaf?

R.M. BROWN: The humidity was relatively constant during our sampling operations, and so we did not see effects that we would attribute to humidity fluctuations. The finite time for equilibration of leaf HTO and atmospheric HTO would serve to smooth out such effects. We have not studied the effect of air humidity on leaf HTO specifically.

L.A. KÖNIG: In the forests surrounding the Karlsruhe Nuclear Research Centre we measured the tritium concentration simultaneously in air and soil humidity as well as in leaves and pine needles. The tritium concentration in the air humidity was found to have a marked effect on that of the leaves and needles. However, rapid changes in the tritium concentration in the air humidity were observed.

W. ROETHER: Some years ago we made a study of tritium concentrations in wine and we looked into the relationship in tritium concentration between air humidity and water in, e.g. the leaves. I think it is quite obvious that there

has to be a dependence on humidity. In a case where the air humidity is 100% no water will be sucked up the stem, but the stomata of the leaves will be open and the water in the leaves will approach the tritium concentration of the air moisture, whereas at 0% humidity the leaves will only contain water drawn up from the soil. Therefore, the higher the humidity, the more will the tritium concentration in the leaves represent that of the atmospheric moisture.