METHODICAL PECULIARITIES OF TRITIUM AND RADIOCARBON RECOVERING FROM ANNUAL TREE RINGS

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Abstract

The paper summarizes main results of radioisotope tritium (H-3) and radiocarbon (C-14) investigation in the annual tree rings. The authors retrospectively reconstructed variations of H-3 and C-14 concentration in the period since 1950 to 1995 in pine-tree rings. Three objects were selected in the territory of Lithuania at the distance 200, 30 and 0.5 km from Ignalina NPP. Evaluated real influence of INPP upon radioactivity of tree rings near the station. The significant methodical work was carried out to reach sufficient sensitivity and precision of measurements. Concentration of H-3 and C-14 detected by the liquid scintillation spectrometer Quantulus-1220, LKB Wallac.

Keywords: tritium, radiocarbon, annual tree rings, model, retrospective reconstruction, Ignalina NPP, detection, experimental error

INTRODUCTION

Radioactive nuclides tritium (H-3) and radiocarbon (C-14) are widespread beta emitters produced naturally (in reactions by neutrons generated from cosmic rays) and artificially (nuclear weapons tests, nuclear industry and energetics). H-3 and C-14 may be used as a highly sensitive tracers for environment studies from ecologic (radioecologic) standpoint. Investigations of H-3 and C-14 involve different natural objects: precipitation, terrestrial plants, surface and ground water, aquatic plants and recently - tree radial growth rings (Kovaliukh and Skripkin, 1992).

The main purpose of this work was a retrospective evaluation of tritium and radiocarbon variations in atmosphere under the influence of Ignalina NPP. Taking it into consideration the H-3 and C-14 have been studied in pine-tree radial growth rings (Pinus sylvestris L.). An observation network involved some characteristic points in the territory of Lithuania (Fig.1) It corresponds to three different models: 1) Minciagire forest, model L-14-95 presented by J. Karpavicius and J. Kairaitis (33 km south-westwards from IIgnalina NPP); 2) Birstonas forest, the background model L-15-95 presented by J. Karpavicius and J. Kairaitis (30 km southwards from Kaunas, 200 km south-west from Ignalina NPP); 3) forest near INPP, selected by J. Mazeika with co-workers (Mazeika et. al., 1998).

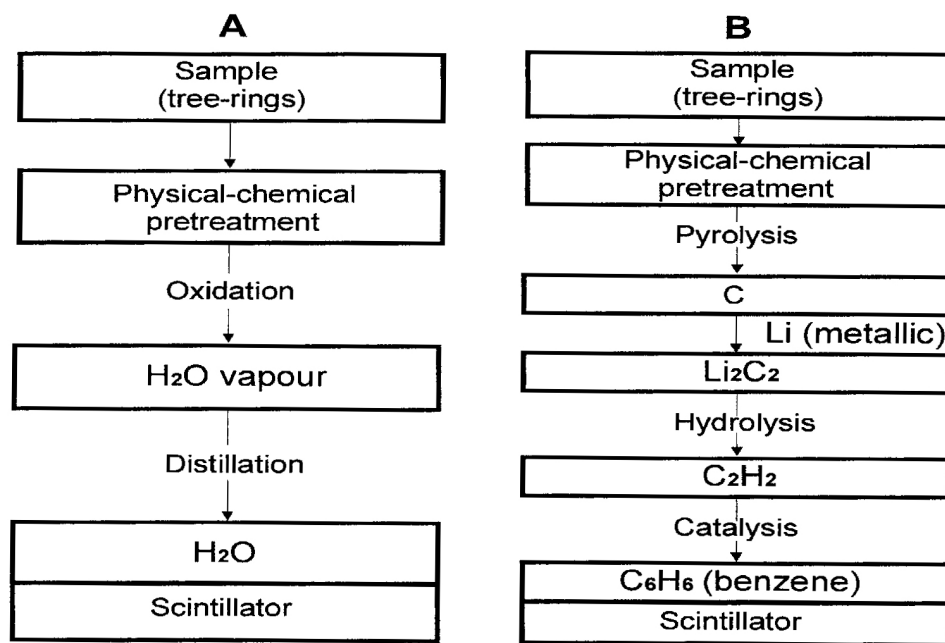**Figure 1.** Locations of sampling points

MATERIAL AND METHODS

Wood samples were collected from three above mentioned locations. The primary preparation of tree rings was performed by J. Karpavicius and J. Kairaitis in the Botany Garden of Kaunas University. The further treatment of samples was fulfiled by G. Davainis in Institute of Geology using special methods, described in literature (Skripkin and Kovaliukh, 1994). Figure 2 illustrates the main stages of sample preparation for H-3 and C-14 analysis.

Preparation of water sample for H-3 detection (Fig. 2A) is based on the well known property of the manganese dioxide to evolve oxygen during heating in a wide range of temperatures, from 530 to 940⁰C, using the special reactor, developed by V. Skripkin and N. Kovalyukh in the Ukrainian Academy of Sciences.

The main stages are:

1. Drying in the temperature150-200⁰C during 4-6 hours with the purpose to release

accumulated moisture from wood sample.

A	B
Sample (tree-rings)	**Sample (tree-rings)**
↓	↓
Physical-chemical pretreatment	**Physical-chemical pretreatment**
Oxidation	Pyrolysis
↓	↓
H₂O vapour	**C**
	↓ Li (metallic)
Distillation	**Li₂C₂**
↓	Hydrolysis
H₂O	**C₂H₂**
Scintillator	Catalysis
	C₆H₆ (benzene)
	Scintillator

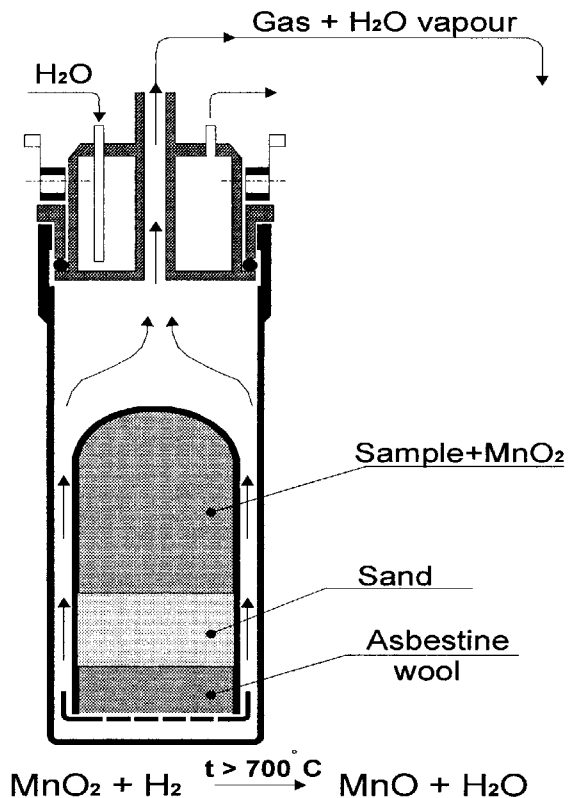**Figure 2.** The scheme of H-3 (A) and C-14 (B) sample preparation

2. Oxidation of released hydrogen in the reactor (Fig. 3). The sample to be combusted is mixed with MnO_2, covered by chemically passive medium (quartz sand) and asbestine wool. The ingredients in appropriate combination of layers are placed in a reactor tube made of stainless steel. The tube is reversed and inserted into the reactor. The whole volume is tightly closed with the special designed cap supplied with excentric mechanism. The cap is connected with module for trapping and purification of combustion products. The main stage of reaction occurs in the temperature about 800^0C when linkages between cellulose chains break and cellulose decomposes to free carbon (C) and hydrogen (H_2). Hydrogen gas reacts with oxygen (gas phase) faster then carbon (solid phase).

3. Condensation of H_2O vapour in the trap with the liquid nitrogen.

4. Distillation. Extracted water contains some organic admixtures. There is added $KMnO_4$ till full stopping of gas releasing process, then distillated to the last drop. Preparation of scintillation coctail. After purification water sample is mixed with the liquid scintillator (OptiPhase HiSafe 3, TriSafe).

Preparation of wood sample for C-14 detection (Fig. 2B) is based on routine metodics, described in literature (Arslanov, 1985). The final form for liquid-scintillation detection is benzene. Primary stages of preparation are the same as in the H-3 sample preparation. Carbon, remained after oxidation process of hydrogen, further is used for synthesis of benzene. Stages

of synthesis are following: 1) reaction of C with Li receiving Li_2C_2; 2) hydrolysis of Li_2C_2, receiving C_2H_2; 3) synthesis of benzene from C_2H_2 by catalysis; 4) adding of scintillate materials PPO and POPOP.

Gas + H₂O vapour

H₂O

Sample+MnO₂

Sand

Asbestine wool

$MnO_2 + H_2 \xrightarrow[\quad]{t > 700\ ^\circ C} MnO + H_2O$

Figure 3. The universal reactor

Detection of H-3 and C-14 activity in the specially prepared samples (water for H-3 and benzene for C-14) was fulfilled by liquid scintillation radiometry. Precision of this method depends on these main factors: 1) high count efficiency; 2) low background count; 3) high stability during long time measurement (weeks and months). To reach these aims the modern spectrometer Quantulus-1220, LKB Wallac used in the laboratory of Botany garden of Kaunas University. The Quantulus (Gupta and Polach, 1985) is a complete liquid scintillation counting system based on multiparameter, multichannel analysis. It is applied for micro-quantitative measurement of C-14, H-3 and for monitoring extremely low levels of beta- and alpha-emmiters present in the environment. With both passive and active shielding, the Quantulus employs an universal (passive and active) background reduction system. Complete analysis of the background and sample signals by two multichannel analyzers, optimization of electronic noises, photo-multiplier tube with high quantum efficiency , low inherent background and spectral stability, specially designed teflon copper vials and the special spectrum analysis program allow

to reduce background while maintaining high counting efficiency.

Concentration of C-14 (per cent from modern C, pmC) calculated by:

$$K = \frac{N_t - N_f}{N_0 - N_f} \cdot \frac{k_d}{k_q} \cdot \frac{M_0}{M_t} \cdot 100\% ,\qquad(1)$$

where N_t, N_0, N_f - count rate, cpm of sample, standard and background; k_d - sample dilution factor; k_q - sample quenching factor; M_0, M_t - mass of standard and sample.

Concentration of H-3 (tritium units, TU) calculated by:

$$C_{TU} = 141 \cdot \frac{n - n_f}{EmK} ,\qquad(2)$$

where n, n_f - count rate of sample and background, cpm; m - mass of sample, g; K=exp[-l(t_0-t_s)]; l = 0.055764 years^{-1} - decay constant of tritium; t_0 - t_s - time interval between sampling and measuring; E - count efficiency, E=N_0/A_0, where N_0 - count rate, counts per minute, cpm of standard sample, A_0 - activity of standard.

The special standards were used: 1) modern radiocarbon (C-14) standard prepared by L. Sulerzhitskyj in the Institute of Geology (GIN) Moscow, Russia. Its specific activity (1.129+-0.015 Bq/g = 500 pmC) is five times higher than the activity of modern wood before 1950; 2) tritium (H-3) water standard prepared by M. Groening in IAEA, Vienna, 1996.10.05, specific activity 2.221 Bq/g = 18824 TU.

Background count rate was minimized by to ways: 1) using special prepared standard samples: "old"- not containing C-14 - benzene, made from coal and "old"-   not containing H-3 - water from deep aquifers; 2) using special Teflon-copper vials of the volume 3 ml and 7 ml for C-14 measurements and special plastic vials of volume 20 ml for H-3 measurements.

Additional experiments related to calibration of Teflon-copper vials were performed before beginning of precision measurement of C-14. A goal of the first experiment was the estimation and comparison of background and standard sample count values deviations for each vial of volume 7 and 3 ml (Table 1). The second experiment - comparison of radiometric errors and standard deviation caused by different 7 ml vials - was fulfilled by measurement of special control wood sample (Table2) .

Results of test (Table 1, 2) indicate that all vials of volume 7 ml are suitable for precision measurement with the exception of vial No. 16 (standard deviation more then average). The goal of the third experiment was to evaluate experimental error arising under the influence of sample (benzene) mass decreasing under evaporation from the vial during measurement of long duration (several weeks). The minimal influence of evaporation effect was indicated comparing it with radiometric error (Table 3). Teflon-copper vials were sufficiently

hermetic.

Table 1. Results of control background-standard test for different Teflon-copper vials

Vial No	Background N_f, cpm	Standard deviation $\Box N_f$, cpm	Standard N_0, Cpm	Standard deviation $\Box N_0$, cpm
1	0.548	0.00	307.472	-2.31
2	0.585	0.04	307.979	-1.81
3	0.571	0.02	309.514	-0.27
4	0.534	-0.01	308.125	-1.66
5	0.575	0.03	311.071	1.29
6	0.540	-0.01	312.206	2.42
7	0.541	-0.01	308.241	-1.54
8	0.531	-0.02	311.531	1.75
9	0.585	0.04	308.559	-1.23
10	0.565	0.02	311.182	1.40
11	0.565	0.02	310.576	0.79
12	0.557	0.01	311.754	1.97
13	0.531	-0.02	312.786	3.00
14	0.582	0.03	311.926	2.14
15	0.561	0.01	311.157	1.37
16	0.498	-0.05	306.874	-2.91
17	0.543	0.00	310.219	0.43
18	0.540	-0.01	308.035	-1.75
19	0.483	-0.06	309.368	-0.42
20	0.522	-0.03	307.128	-2.66
Average	0.548		309.785	
Stdev		±0.03		±1.83

Sometimes significant errors appear when sample count efficiency decreases due to scintillation quenching effect (contamination by remains of organic admixtures).

To avoid this error, the quench calibration method was used. The special experiment (adding little by little the artificial pollutant CCl_4 into the sample) was performed with purpose to build up quenching calibration curve for estimation of quench factor k_q. Results of radiometry with further calculations of tritium and radiocarbon concentration including estimation of errors partially are presented in the Table 4 (H-3) and Table 5 (C-14). There are displayed main parameters (sampling date; mass of sample; detection time; count rate of sample, background and standard; radioactive decay factor) necessary for calculation of H-3 and C-14 concentration.

Table 2. Comparison of radiometric error and standard deviation after detection of the same control sample in the different Teflon-copper vials

Vial No	Background, N_f, cpm	Sample, N_t, cpm	Standard, N_0, cpm	Concentration of C-14, pmC	Radiometric Error ($\pm \sigma_{rad}$), pmC	Standard deviation($\pm \sigma$), pmC
3	0.571	47.733	61.838	77.190	0.59	0.15
4	0.534	47.770	61.567	77.590	0.59	0.55
5	0.575	47.729	62.149	76.798	0.59	-0.24
6	0.540	47.764	62.383	76.566	0.59	-0.47
7	0.541	47.763	61.589	77.551	0.59	0.51
8	0.531	47.773	62.250	76.744	0.59	-0.30
9	0.585	47.719	61.644	77.410	0.59	0.37
10	0.565	47.739	62.173	76.784	0.59	-0.26
11	0.565	47.739	62.052	76.934	0.59	-0.11
12	0.557	47.747	62.289	76.654	0.59	-0.39
13	0.531	47.773	62.501	76.436	0.59	-0.60
14	0.582	47.722	62.319	76.577	0.59	-0.46
15	0.561	47.743	62.169	76.796	0.59	-0.24

Table 3. Comparison of radiometric error and error caused by the evaporation losses of benzene in Teflon-copper vial of volume 7 ml

Date	Days	Mass, g	Sample, cpm	C-14, pmc	Radiometric error ($\pm \sigma_{rad}$ pmC)	Evaporation error, pmC
1996.11.14	0	5.901	47.777	76.377	0.30	0.00
1996.11.27	13	5.896	47.737	76.312	0.29	-0.06
1996.12.03	19	5.895	47.728	76.299	0.29	-0.08
1997.01.09	56	5.893	47.712	76.274	0.29	-0.10

RESULTS AND DISCUSSION

The three series of annual pine-tree ring samples were analyzed: 1) model L-14-95 - 16 rings for H-3 analysis; 2) model L-15-95 - 46 rings for H-3 and C-14 analysis; 3) 7 rings from the forest near INPP for H-3 and C-14 analysis.

Retrospective reconstruction of tritium and radiocarbon concentration variations in annual tree rings during the last 46 years (1950-1995) was realized from background model L-15-95 (Fig. 4). Global variations of these isotopes in the atmosphere, investigated by different authors (Fig. 5) are very similar to our experimental data in tree rings. The bomb produced peak of H-3 and C-14 concentration in the period about 1962-1966 represent the main tests of nuclear weapon carried out by USSR, USA and other countries up to 1962. Model L-14-95 (Fig. 4) demonstrates H-3

Table 4. Calculation of tritium (H-3) concentration in annual tree rings

| Date of radiometry	1996.10.25			n_f = 1.046 cpm			E=34.0 %
No	Object	Sampling date	m, g	Detection time, min	Count, n-n_f, cpm	Decay factor	Concentration of tritium, TU
3	L-15-95 1980-V	80-09-01	6.00	1200	0.51	0.406	84.4 ± 3.3
4	L-15-95 1981-A	81-03-01	6.00	1200	0.42	0.418	68.8 ± 3.2
5	L-15-95 1981-V	81-09-01	6.00	1200	0.51	0.429	80.7 ± 6.6
6	L-15-95 1982-V	82-09-01	6.00	1100	0.38	0.454	57.0 ± 4.9
7	L-15-95 1985-V	85-09-01	6.00	1100	0.48	0.537	60.2 ± 6.8
8	L-15-95 1987-V	87-09-01	6.00	1100	0.39	0.600	43.8 ± 3.3
9	L-15-95 1988-V	88-09-01	6.00	1100	0.43	0.635	46.1 ± 3.3
10	L-15-95 1994-V	94-09-01	6.00	1100	0.36	0.887	27.6 ± 4.2
11	L-15-95 1995-A	95-03-01	6.00	1100	0.32	0.912	24.0 ± 3.2
12	L-15-95 1995-V	95-09-01	6.00	1100	0.38	0.938	27.4 ± 3.3
13	INPP, ring 6	91-07-01	6.00	1100	0.82	0.743	74.9 ± 7.6
14	INPP, ring 7	92-07-01	5.00	1100	3.18	0.786	329 ± 8.8
15	INPP, ring 8	93-07-01	6.00	1100	0.95	0.831	77.5 ± 5.9
16	INPP, ring 9	94-07-01	6.00	1100	1.93	0.879	149 ± 9.6
17	INPP, ring 10	95-07-01	6.00	1100	0.50	0.929	36.3 ± 5.4

Table 5. Calculation of radiocarbon (C-14) concentration in annual tree rings

| Date of radiometry	1997.08.22		N_f = 1.637 cpm	N_0 = 55.139 cpm
No	Object	Sampling Date	Volume of benzene, ml	Count rate N_t, Cpm	Concentration of radiocarbon, pmC
1	L-15-95, 1950	1996	7.00	57.063	103.489 ± 1.97
2	L-15-95, 1951	1996	7.00	54.323	98.520 ± 1.58
3	L-15-95, 1958	1996	7.00	63.700	115.525 ± 1.78
4	L-15-95, 1959	1996	7.00	66.913	121.353 ± 1.85
5	L-15-95, 1963	1996	6.70	96.910	183.624 ± 2.59
6	L-15-95, 1964	1996	6.60	97.180	194.714 ± 3.57
7	L-15-95, 1966	1996	7.00	93.687	169.909 ± 2.41
8	L-15-95, 1967	1996	7.00	89.580	162.461 ± 4.65
9	L-15-95, 1968	1996	7.00	90.343	163.845 ± 4.22
10	L-15-95, 1969	1996	7.00	86.830	157.473 ± 3.86
11	L-15-95, 1970	1996	7.00	85.593	155.231 ± 2.24
12	L-15-95, 1971	1996	7.00	83.293	151.059 ± 3.29
13	L-15-95, 1972	1996	7.00	80.920	146.755 ± 3.43
14	L-15-95, 1975	1996	7.00	76.203	138.201 ± 3.68
15	L-15-95, 1976	1996	7.00	73.130	132.627 ± 1.98
16	L-15-95, 1977	1996	7.00	73.843	135.001 ± 3.22

and C-14 variations in the environs of Ignalina NPP during the last 16 years (1980-1995). Comparison of its curve with background curve allows to observe the imperceptible influence of INPP in the respect the H-3 and C-14. However, the experimental results in 5 rings sampled at the distance of 0.5 km from INPP during the last 5 years (1988-1992) indicate real contribution of H-3 produced by this nuclear plant.
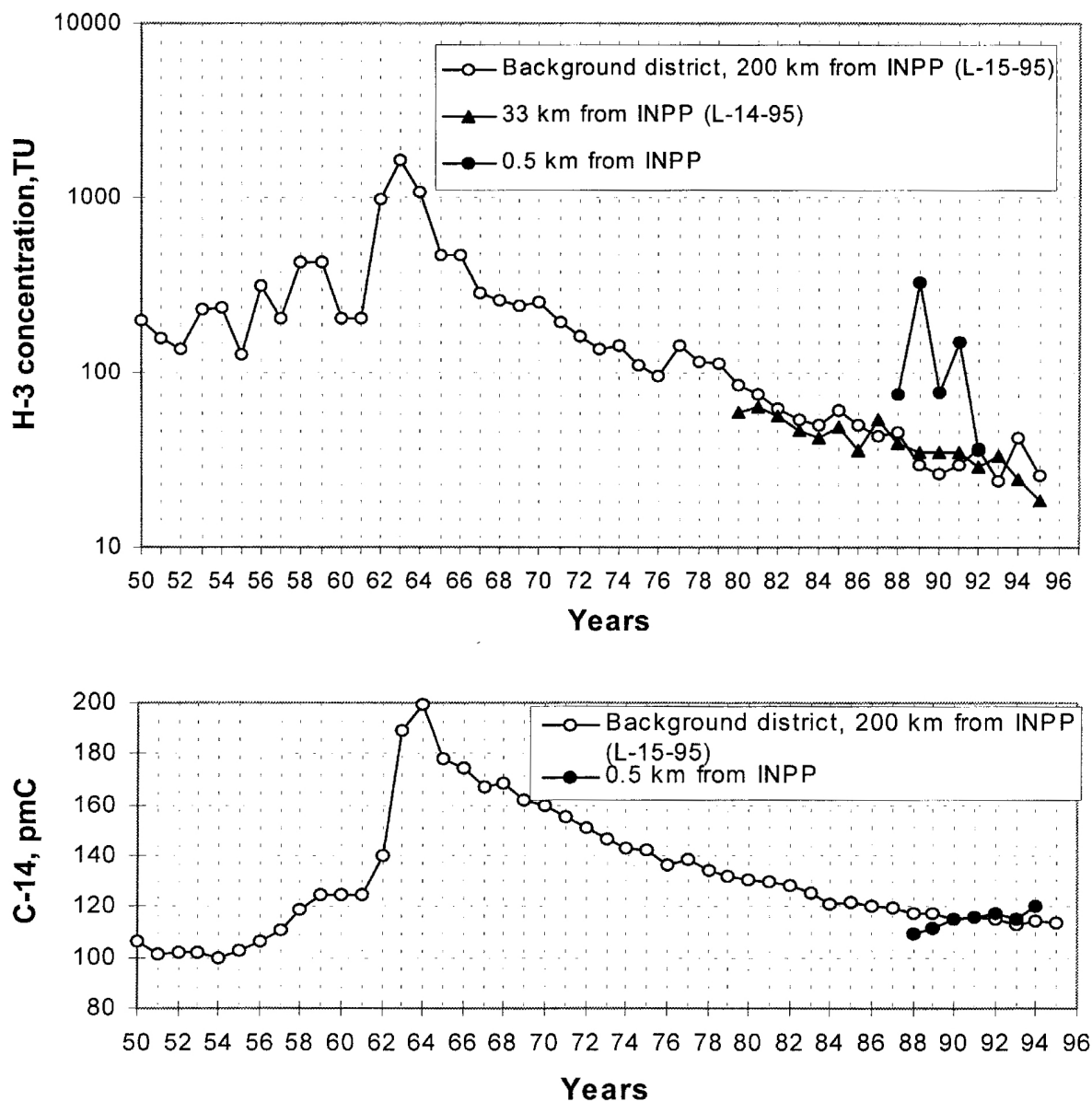
Figure 4. Variations of tritium (H-3) and radiocarbon (C-14) concentration in annual (1950-1995) growth pine-tree rings (experimental data performed in 1996-1997)
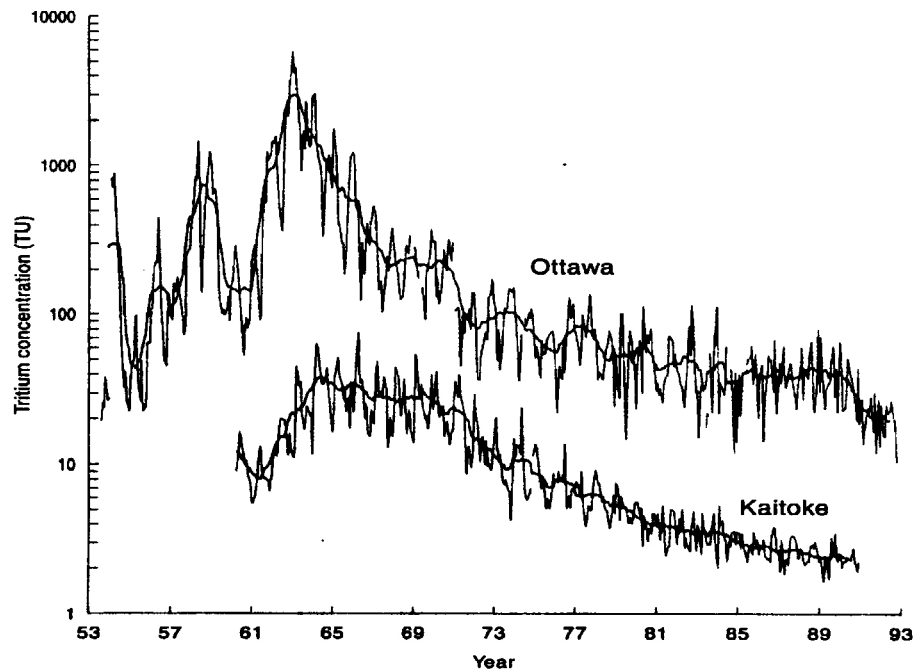
Figure 5. Tritium levels in the atmosphere increased between 1953 to 1962 due to atmospheric nuclear weapon tests (Isotopes in water...,1997)
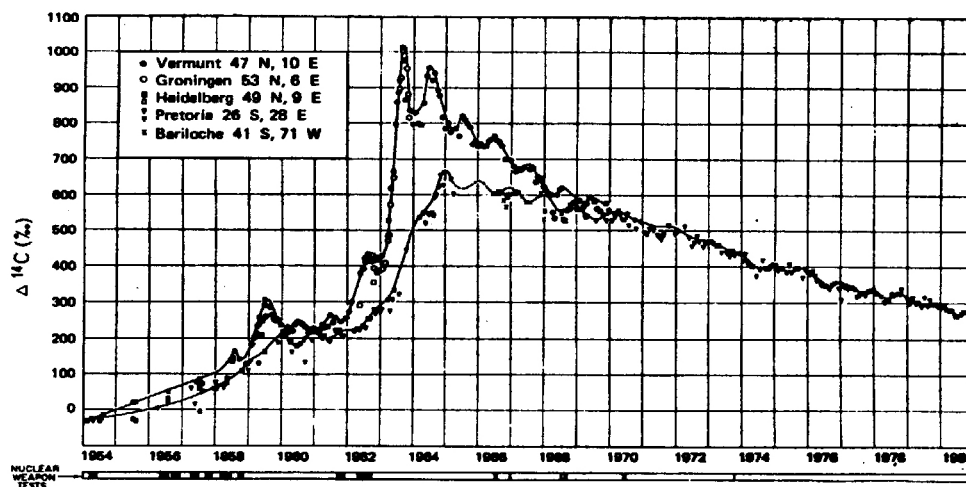
Figure 6. Bomb induced C-14 concentration variation in the global atmosphere (Gupta and Polach, 1985)

CONCLUSIONS

An accurate recover of tritium and radiocarbon from the annual tree rings in principle was possible thanks to special methodic and equipment for precise sample chemical

pretreatment and detection of very low activities (reactor developed by V. Skripkin and N. Kovalyukh, spectrometer Quantulus-1220, LKB Wallac).

The sufficiently high precision of H-3 and C-14 detection ensured additional methodical experiments including Teflon-copper vials calibration, quench calibration, estimation of benzene evaporation from vials.

Retrospectively reconstructed variations of tritium and radiocarbon in annual pine-tree rings since 1950 to 1995 in Birstonas forest (background model L-15-95) are very similar to global variations of these isotopes in the atmosphere including "bomb" peak about 1962-1966, investigated by different authors.

Retrospectively reconstructed variations of tritium and radiocarbon in annual pine-tree rings since 1980 to 1995 in Minciagire forest (model L-14-95) are similar to the background model L-15-95 with tendency of imperceptible influence of Ignalina NPP.

The more significant increase of H-3 (influence of NPP) in annual pine-tree rings (1988-1992) was observed at the distance of 0.5 km from the Ignalina NPP.

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