

¹⁴C RELEASE IN VARIOUS CHEMICAL FORMS WITH GASEOUS EFFLUENTS FROM THE PAKS NUCLEAR POWER PLANT

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ABSTRACT. We present results of airborne ¹⁴C emission measurements from the Paks PWR nuclear power plant. Long-term release of ¹⁴C in the form of carbon dioxide or carbon monoxide and hydrocarbons were simultaneously measured. The results of internal gas-proportional and liquid scintillation counting agree well with theoretical assessments of ¹⁴C releases from pressurized water reactors. The mean value of the ¹⁴C concentration in discharged air is 130Bqm⁻³ and the normalized release is equal to 740GBq/GW_e · yr. > 95% of ¹⁴C released is in the form of hydrocarbons, ca 4% is apportioned to CO₂, and <1% to CO. Tree-ring measurements were also made and indicated a minute increase of ¹⁴C content in the vicinity of the nuclear power plant.

INTRODUCTION

There are three anthropogenic sources that influence the environmental ¹⁴C level. The Suess effect reduces the ¹⁴C concentration (Suess, 1955); the decrease amounted to ca 3% from 1850 to 1950 (Oeschger *et al*, 1975). Atmospheric nuclear weapon tests produced 2.2·10¹⁷Bq excess to the atmospheric inventory between 1945 and 1980 (UNSCEAR, 1982). However, such tests increased the total ¹⁴C content of the earth only by ca 3% (Fairhall & Young, 1970); the tropospheric ¹⁴C concentration in the Northern Hemisphere was doubled in 1963 (Levin, Münnich & Weiss, 1980; Csongor & Hertelendi, 1981). Relatively little ¹⁴C is released by the nuclear industry. According to Hayes and MacMurdo (1977, p 215), the estimated global inventory of ¹⁴C produced by the nuclear power industry for the period 1975-2000 will be 10% of that from weapons testing and only 0.3% of the natural ¹⁴C inventory. ¹⁴C is produced in light-water reactors by neutron activation by ¹⁷O(n,α)¹⁴C reaction with ¹⁷O isotopes in oxides of fuels, moderators and coolants; by ¹⁴N(n,p)¹⁴C reaction with ¹⁴N in fuels, moderators and coolants where ¹⁴N exists as an impurity (Davis, 1979). The mean values of production rates of ¹⁴C of PWRs are 0.57TBq/GW_e · yr, 0.97TBq/GW_e · yr, and 0.19TBq/GW_e · yr in fuel, structural materials and coolant, respectively, when a concentration of 5ppm N is assumed in the coolant. If 50ppm of nitrogen is present in the coolant, the amount of ¹⁴C produced from dissolved ¹⁴N would be approximately equal to that from activation of ¹⁷O in the coolant water, *ie*, 0.36TBq/GW_e·yr (Kunz, 1985). The ¹⁴C that is produced will be released to the environment mainly via the stack except for that in fuel. Kunz (1985) reported that the quantity of ¹⁴C discharged with liquid and solid wastes is <5% of the gaseous release.

Table 1 shows a limited compilation on ¹⁴C release data for PWR type NPPs. Rather high release rates were reported on Soviet-designed PWRs, *ie*, 7.5-30TBq/GW_e · yr. This is apparently due to the use of nitrogen gas for

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TABLE 1
¹⁴C activity and distribution in effluents from pressurized water reactors

Nuclear power plant	Maximum output capacity (MW _e)	Date of discharge	Discharge rate (TBq/GW _e ·yr)	Chemical ¹⁴ CO ₂	form Hydrocarbons (%)	Reference
Biblis "A" (FRG)	1200	1976-77	0.04	6	94	1. Schwibach <i>et al</i> (1977)
		1978	0.07	30	70	2. Winkelmann <i>et al</i> (1984)
Biblis "B" (FRG)	1300	1976-77	0.41	1	99	3. Ref 1
		1978	0.13	10	90	4. Ref 2
Orbigheim (FRG)	328	1976-77	0.12	30	70	5. Ref 1
Stade (FRG)	630	1976-77	0.15	40	60	6. <i>Ibid</i>
Neckarwestheim (FRG)	805	1976-77	0.07	10	90	7. <i>Ibid</i>
FRG average	-	1978-81	0.21	ND*	ND	8. Ref 2
5 FRG PWRs average	-	ND	0.22	20	80	9. Ref 1
R E Ginna (US)	490	1980-81	0.43	10	90	10. Kunz (1985)
Indiana Point 3 (US)	1000	1980-81	0.36	26	74	11. <i>Ibid</i>
PWR "A" (US)	ND	ND	0.37	10	90	12. Wahlen & Kunz (1978)
European PWRs average	-	ND	0.22	ND	ND	13. UNSCEAR (1982)
"USSR PWRs"	ND	ND	7.5-30	ND	ND	14. Davis (1977)

*ND - no data

pressurization and ammonium hydroxide in the primary coolant (Davis, 1977). The chemical forms of released ¹⁴C are mainly hydrocarbons and, to a lesser degree, CO₂. The radiobiological impact is directly related to ¹⁴C release in CO₂. Thus, it is very important to determine the chemical form of ¹⁴C.

The Hungarian nuclear power plant at Paks, which uses Soviet-designed pressurized water reactors (WWER-440), consists of four power units each with a capacity of 440MW_e. Detailed experimental data published on ¹⁴C sources and releases of such PWR reactors are rare or non-existent. Although there is no national regulation relating to ¹⁴C discharge into the environment, we initiated a program in 1987 to determine ¹⁴C in gaseous discharge. The objectives of this study are to 1) develop and run a reliable sampling system for measuring ¹⁴C in various chemical species on a routine basis, 2) investigate the sources of ¹⁴C, 3) determine the annual emission of ¹⁴C in gaseous form, 4) study possible correlations between ¹⁴C levels and the operational parameters of the reactor, and 5) follow local contamination due to ¹⁴C release by means of tree-ring and leaf analysis.

DIFFERENTIAL RADIOCARBON SAMPLER

Two independent stack samplers for reactor units 1+2 and 3+4 were developed and continuously operated to obtain integrated samples for measurement of ^{14}C in all carbon chemical species, such as CO , CO_2 , CH_4 and other hydrocarbons. The main requirements of the sampler are set to be $0.2\text{Bq}\cdot\text{m}^{-3}$ as the lowest detectable concentration if the liquid scintillation counting (LSC) technique is used for activity measurement, a discrimination factor higher than 10^3 between the concentration of ^{14}C in different chemical forms, continuous work under operational conditions. The layout of the sampler is shown in Figure 1.

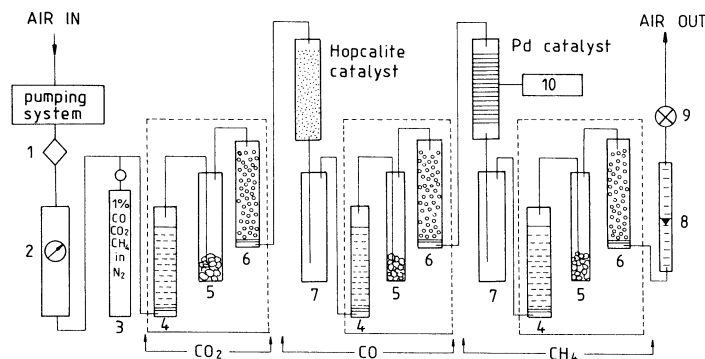


Fig 1. Layout of the differential ^{14}C sampler

The sampled air is passed through an aerosol filter (1); its volume is then measured by a gas meter (2); carrier gas (3) containing 1% of CO_2 , CO and CH_4 in purified N_2 is used to avoid difficulties that may originate from the minute amount of sample to be collected for CO and hydrocarbons. ^{14}C is collected in the form of CO_2 for all chemical species since carbon monoxide is converted into CO_2 using a Hopcalite catalyst at ambient temperature while CH_4 or other hydrocarbons are oxidized by a Pd catalyst kept at 600°C . A specially designed bubbler (4) containing 400ml 3M NaOH solution is used to absorb CO_2 . Drop catchers (5), drying columns filled with silica gel (6) and buffer flasks (7) prevent the catalyst from sodium hydroxide contamination and from getting wet in case of failure. The air flow is measured by a flow-rate meter (8) and can be adjusted by a regulating valve (9). The palladium catalyst is kept at 600°C by a regulated heater (10). Due to the varying air resistance of the sampler during the sampling period, a pneumatically operated pump system has been developed. Different parts of the sampler have been tested for performance; some features are summarized in Table 2.

TABLE 2
Main features of differential radiocarbon sampler

Flow rate of air sampling L.h ⁻¹	25–30
Flow rate of carrier gas, L.h ⁻¹	1
Sampling period	1 week
Absorption efficiency of CO ₂	99.9% in 3M NaOH solution
Conversion efficiency of CO into CO ₂	99.8% on Hopcalite bed at ambient temp
Conversion efficiency of CH ₄ into CO ₂	99.7% on Pd catalyst at 600°C
Discrimination ratio between CO and CO ₂	10 ³
CO ₂ and CH ₄	10 ⁵
Lowest detection limit mBq.m ⁻³	10 using LSC technique 0.3 using proportional counting

For the first experimental period, low-level gas-proportional counting and LSC measurement techniques were both used for the activity determination. The details of the low-level gas-proportional counting system are reported by Hertelendi *et al* (1989). The lowest detectable concentration of this technique, taking into account the sampling parameters, is ca 0.3mBq.m⁻³. Various sample preparation techniques for LSC were tested, such as absorption in Carbo-Sorb or ethanolamine systems, direct measurement in a special aerosol-type scintillation cocktail, and Instagel + CaCO₃ precipitate gel system and BaCO₃ with Cab-O-Sil. The last method was chosen for routine measurements using ca 2g BaCO₃ precipitate in one sample.

The lowest detectable concentration of these techniques varies from 10mBq.m⁻³ for the CaCO₃ gel system to 0.6Bq.m⁻³ for the aerosol scintillation cocktail. The sensitivities were calculated with the assumptions: 50mM CO₂ collected in a weekly sample with a sampling rate of 20L.h⁻¹, 10cpm background, 200min counting time. Even the simplest aerosol scintillator in which 3ml of 3M NaOH solution can be mixed directly with the cocktail may offer acceptable sensitivity for routine monitoring purpose.

RESULTS AND DISCUSSION

The production of electricity at Paks NPP commenced at the end of 1982 when the first unit went into industrial operation. The 2nd, 3rd and 4th units were commissioned in 1984, 1986 and 1987, respectively. Paks NPP was constructed on a twin-unit basis, *ie*, its ventilation stack serves for two energy units. The air throughput of a stack is 5.10⁵m³.h⁻¹. Two independent ¹⁴C differential samplers were installed in 1987. The experience gained during the test period of ca 6 months was used to overcome technical difficulties of routine measurements by modifying parts of the sampler and the techniques. Data of the last quarter of the year, when the samplers operated

TABLE 3
¹⁴C release with gaseous effluents from reactor units 1+2

Sampling date Month, day		¹⁴ C concentration, Bq.m ⁻³				Ratio to the total %	
		¹⁴ C _n H _m	¹⁴ CO ₂	¹⁴ CO	Total	¹⁴ CO ₂	¹⁴ C _n H _m
2/24-3/02	(1)*	123	5.9	0.32	129.2	4.6	95.0
3/02-3/09	(2)	147	6.2	0.39	153.6	4.0	95.7
3/09-3/17	(3)	122	8.0	0.26	130.3	6.1	93.7
3/17-3/24	(4)	142	4.4	0.35	146.8	3.0	96.8
3/24-3/31	(5)	299	12.5	0.30	311.8	4.0	95.9
3/31-4/07	(6)	115	3.5	1.5	120.0	2.9	95.8
4/07-4/14	(7)	117	4.3	-	121.3	3.5	96.5
4/14-4/21	(8)	134	5.3	-	139.3	3.8	96.2
4/21-4/28	(9)	136	2.9	-	138.9	2.1	97.9
4/28-5/05	(10)	103	3.6	-	106.6	3.4	96.6
5/05-5/12	(11)	106	5.8	-	111.8	5.2	94.8
5/12-5/19	(12)	77	2.9	-	79.9	3.6	96.4
5/19-5/27	(13)	68	3.0	-	71.0	4.2	95.8
5/27-6/01	(14)	55	5.6	-	60.6	9.2	90.8
Range		55-299	2.9-12.5	0.26-1.5	60.6-311.8	2.1-9.2	90.8-97.2
Mean		125	5.3	0.52	130.1	4.1	95.8
Reactor units 3+4							
3/10-3/17	(1)	132	6.5	0.30	138.8	4.7	95.1
3/17-3/24	(2)	131	3.9	1.90	136.8	2.9	95.8
3/24-3/31	(3)	115	12.2	0.29	127.5	9.6	90.2
4/07-4/14	(4)	126	2.5	0.13	128.6	1.9	98.0
4/14-4/21	(5)	134	3.0	-	137.0	2.2	97.8
4/21-4/28	(6)	118	3.8	-	121.8	3.1	96.9
4/28-5/05	(7)	140	5.3	-	145.3	3.6	96.4
5/05-5/12	(8)	147	5.3	-	152.3	3.5	96.5
5/12-5/19	(9)	130	4.9	-	134.9	3.6	96.4
5/19-5/27	(10)	147	5.8	-	152.8	3.8	96.2
5/27-6/01	(11)	110	6.9	-	116.9	5.9	94.1
Range		110-147	2.5-12.2	0.13-1.9	116.9-152.3	1.9-9.6	90.2-98.0
Mean		130	5.5	0.66	135.7	4.1	95.8

*Figures in parantheses indicate sampling intervals (see Fig 2).

continuously, are presented. For results of weekly samples for reactor units 1-2, 3-4, see Table 3 and Figure 2.

The concentration of ¹⁴C in the discharged air varies slightly around its mean value except for one case when the measured concentration was twice the average. A continuous decrease of release rate was observed at units 1 and 2 from 28 April-1 June when the first unit was shut down for refueling and maintenance. After two weeks from the start of the outage, a steady-

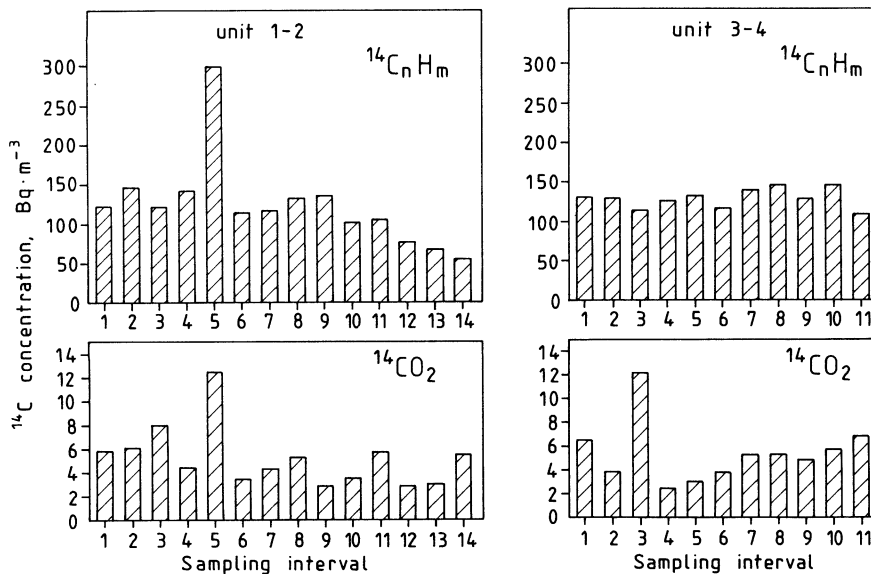


Fig 2. Weekly average ^{14}C concentrations of discharged air in $^{14}\text{CO}_2$ and $^{14}\text{C}_n\text{H}_m$ chemical forms

state release rate was reached, ca $60\text{Bq}\cdot\text{m}^{-3}$, which corresponds to the emission of the other operating unit. The ratio of $^{14}\text{CO}_2$ activity to the total is exactly the same, 4.1%, for both twin units. The contributions of CO on average is $<0.5\%$. This form of ^{14}C was measured only for a short time because of technical difficulties.

The discharged ^{14}C activity for the given period from units 1 and 2 was 150GBq in the form of hydrocarbons and 6.4GBq in $^{14}\text{CO}_2$ form. Similar values were obtained for reactors 3 and 4, *ie*, 117GBq for hydrocarbons and 5GBq for CO_2 . The extrapolated normalized ^{14}C releases using the relevant data of electricity production for units 1-2 and 3-4 were $0.79\text{TBq}/\text{GW}_e\cdot\text{yr}$ and $0.68\text{TBq}/\text{GW}_e\cdot\text{yr}$, respectively. The average emission rate of ^{14}C in gaseous form by Paks NPP is equal to $0.74\text{TBq}/\text{GW}_e\cdot\text{yr}$. Excess ^{14}C in the vicinity of Paks NPP has also been measured by tree-ring analysis. A *Robina pseudoacacia* tree was harvested from the site where the highest ^{14}C level was expected on the basis of relevant meteorologic and release data. The site is ca 1.7km from the 100m stack in the SSE direction and the dispersion factor is calculated to be $1.5\cdot 10^{-7}\text{s}\cdot\text{m}^{-3}$. For comparison, a tree of the same species was harvested near Debrecen, Hungary, 240km from the Paks NPP and analyzed for ^{14}C excess. For results of tree-ring analysis, see Table 4 and Figure 3.

The electricity produced by Paks NPP for the period 1983 to 1987 was $3.75\text{GW}_e\cdot\text{yr}$, which corresponds to an extrapolated discharge value of 2.63TBq ^{14}C in gaseous effluents. ^{14}C excess in the area may be estimated on the basis of release data. For the year 1987, when $1.25\text{GW}_e\cdot\text{yr}$ electricity was produced, a $0.18\text{mBq}\cdot\text{m}^{-3}$ excess in $^{14}\text{CO}_2$ concentration can be calculated as a maximum; this is ca 3.5% increase of the present, $50.9\text{mBq}\cdot\text{m}^{-3}$

TABLE 4

^{14}C excess in tree-rings in the vicinity of Paks NPP and at a reference point, Debrecen, Hungary

Tree-ring formation	Paks NPP		Reference point	
	$\delta^{13}\text{C}$ $\pm 0.05(\text{‰})$	$\Delta^{14}\text{C}$ $\pm 4(\text{‰})$	$\delta^{13}\text{C}$ $\pm 0.05(\text{‰})$	$\Delta^{14}\text{C}$ $\pm 4(\text{‰})$
1982	-22.50	253	-22.26	249
1983	-22.43	239	-22.84	231
1984	-21.56	228	-23.24	224
1985	-22.19	211	-23.46	208
1986	-22.53	212	-23.76	203

(STP), ^{14}C level in the atmosphere. The maximum annual effective dose equivalent to individuals living ca 1.7km from the NPP in a SSE direction is $6.10^{-2}\mu\text{Sv}$ due to the release of $^{14}\text{CO}_2$. The global impact of ^{14}C release is usually estimated on short- and long-term dose implications to the global population (Levin, Münnich & Weiss, 1980; McCartney *et al*, 1986).

In the long term, the collective dose equivalent commitment is conservatively estimated at $140\text{manSv} \cdot \text{TBq}^{-1}$ corresponding to $460\text{manSv}/\text{GW}_e \cdot \text{yr}$. The long-term global impact from the release of ^{14}C from Paks NPP is estimated at $115 \pm 25\text{manSv}$ if 1987 is considered and $345 \pm 75\text{manSv}$ based on the total length of the NPP operation. These collective dose commitments will be delivered if the sum is taken to infinity and 8, 24 and 75% of the total dose is delivered in 100, 1000 and 10,000 yr, respectively. In this calculation we assume that ^{14}C released in other chemical form than $^{14}\text{CO}_2$ will be oxidized to this form.

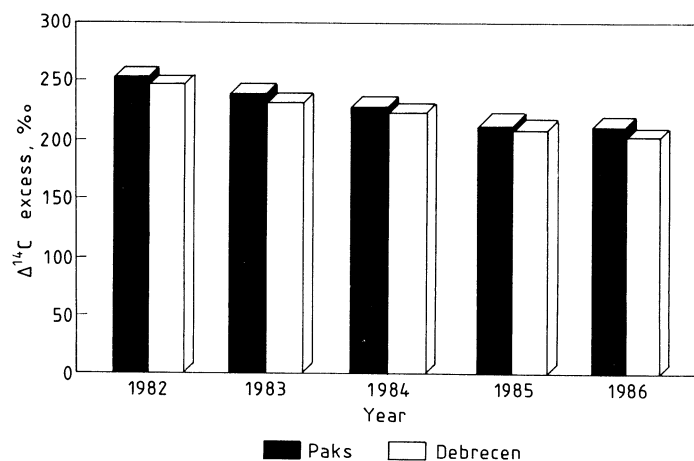


Fig 3. $\Delta^{14}\text{C}$ excess in tree rings at Paks NPP and at a reference point, Debrecen, Hungary

CONCLUSIONS

Our results on atmospheric ¹⁴C discharge from the Paks NPP agree with the literature, but we observed about three times higher release rate than the average value of PWRs (Table 1). The distribution of ¹⁴C activity between CO₂ and hydrocarbons is ca 4% and 95%, respectively. Thus the local impact of ¹⁴C release is small. The global impact of ¹⁴C release is by no means negligible but the impact of ¹⁴C in chemical forms other than CO₂ should be considered further.

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