^{14}C MEASUREMENTS AT PWR-TYPE NUCLEAR POWER PLANTS IN THREE MIDDLE EUROPEAN COUNTRIES

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ABSTRACT. Regular ^{14}C sampling of discharged air began in 1988 at Paks Nuclear Power Plant (NPP), Hungary, and in 1991 at NPPs in Krsko, Slovenia and Bohunice, Slovakia. Monitoring of ^{14}C discharges is carried out at all NPPs with similar differential samplers continuously collecting ^{14}C in the form of $^{14}CO_2$ and $^{14}C_nH_m$. The main results of airborne discharge monitoring are as follows: ^{14}C activity concentration varied roughly within a factor of two around their mean values, 125 Bq m^{-3} and 90 Bq m^{-3} for Paks and for Krsko NPP, respectively. The pattern of discharge for Bohunice NPP is slightly different from that at the other two stations. At Bohunice, there has been a continuous increase in the discharge rate at power unit V1, starting with 70 Bq m^{-3} in 1991 and reaching a value of 190 Bq m^{-3} in 1995. The values for power unit V2 are 50 Bq m^{-3} and 82 Bq m^{-3}. The average normalized yearly discharge rates are 0.887 ($TBqGW_e^{-1}yr^{-1}$) for Paks, 0.815 (V1) and 0.500 (V2) for Bohunice, and 0.219 for Krsko. Most of the discharged ^{14}C is in hydrocarbon form, 95% for Paks and Bohunice V2, but the CO_2 fraction may reach 25% or 43% at Bohunice V1 and Krsko, respectively. At Bohunice V1, not only the discharge rate increased but the $^{14}CO_2$ ratio to the total changed from 30% to 13%. The local radiological impact is estimated to be 1.5 μSv a^{-1} for Paks, 1.7 μSv a^{-1} for Bohunice, and 0.12 μSv a^{-1} for Krsko. The ^{14}C excess in the environment has been measured at Paks NPP since 1989. Based on the monitoring data, the long-term average ^{14}C excess from the Paks NPP was $D^{14}C$=50‰ for hydrocarbons. Tree-ring analysis has shown a slight excess around Krsko NPP: $D^{14}C$ is equal to 199.9‰ for a tree at 1 km from the NPP compared with a "reference" one for which $D^{14}C$ was equal to 111.6‰ (in 1994).

INTRODUCTION

The rapid disappearance of nuclear explosion-produced radiocarbon from the biosphere due to the oceanic sink is partly balanced by the ^{14}C produced and released by the nuclear industry. The emission rate and chemical composition of the released ^{14}C depends on the type and capacity of a given reactor. Several publications discuss various aspects of ^{14}C production rates of nuclear installations (Levin *et al.* 1988; Kunz 1985; Otlet, Longley and Walker 1989; McCartney *et al.* 1988a; Loosli and Oeschger 1989; Hertelendi, Uchrin and Ormai 1989; Otlet, Walker and Fulker 1990; Stenström *et al.* 1995; Milton *et al.* 1995). Uchrin *et al.* (1992) compiled ^{14}C discharge data for pressurized water reactor (PWR-type) nuclear power plants (NPP). The chemical forms of ^{14}C released into the environment influence the radiological impact, and in the case of PWR-type reactors, low CO_2/total carbon ratios lead to significant lowering of the local doses.

METHODS

A differential ^{14}C sampler, developed by Hungary's Institute of Isotopes together with the Institute of Nuclear Research, has been used at each NPP to obtain integrated samples for measuring ^{14}C in chemical forms such as CO_2, CH_4 and other hydrocarbons. The sampler makes use of two lines: in the first line, CO_2 is absorbed in a trapping column filled with a 3 M NaOH solution; in the second one, CO_2 plus hydrocarbons converted into CO_2 by a palladium catalyst held at 600°C are absorbed together. The methane fraction is deduced by substracting the CO_2 collected in the first line from the total collected in the second. For details on the sampler, see Uchrin and Hertelendi (1992).

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Proceedings of the 16th International ^{14}C Conference, edited by W. G. Mook and J. van der Plicht
RADIOCARBON, Vol. 40, No. 1, 1998, P. 439–446

The activity of the samples was determined in most cases by liquid scintillation counting (LSC) after precipitation of CO_2 in the form of $BaCO_3$, 4 g of which was mixed with 0.8 g Cab-O-Sil®[6] and a 20-mL toluene-based LS cocktail (5 g PPO+0.5 g dimethyl POPOP). The mass of sampled air was determined by weighing the mass of barium carbonate. The sample flow rate was set and stabilized at *ca.* 10 L h^{-1}. The discrimination factor between the $^{14}CO_2$ and $^{14}C_nH_m$ fractions was close to 100, and the absorption of CO_2 in the 3 M NaOH solution was 99.9% when a specially designed spiral bubbler-type trap was used. The typical sensitivity of LSC activity measurement was 10 mBq m^{-3}.

The samples of lower activities were analyzed using the low-level proportional counting method (Hertelendi *et al.* 1989). To extract the CO_2 from the samples, concentrated sulfuric acid was added to the NaOH solution. Prior to measurement, the liberated CO_2 gas was purified over charcoal. The standard deviation of a single ^{14}C measurement is $\sigma = \pm 0.17$ mBq m^{-3}, which may be higher (0.5 mBq m^{-3}), due to the uncertainties of sampling. High sensitivity proportional counting was used to determine the activity of environmental air and tree-ring samples.

Some relevant parameters of the investigated NPPs:

1. Paks NPP in Hungary uses Soviet-designed PWRs of type V213; the NPP has four power units each of 440 MW_e capacity. The first reactor block was put into operation in 1983, the fourth in 1988. Through the end of 1996, the electricity produced was equal to 17.79 GW_ey. The air throughput of the two ventilation stacks, each of which carried the effluents from a twin reactor unit, was 5.5×10^5 m^3hr^{-1}.
2. Bohunice NPP in Slovakia uses Soviet-designed PWRs similar to the Hungarian NPP (type V213) and a slightly different type V230. The units of reactor type V230 were put into operation in 1978 and 1980; those of reactor type V213 started operating in 1984 and 1985. Up until the end of 1996, the electricity generated was 11.3 GW_ey and 7.77 GW_ey for reactors type V230 and V213, respectively. The air throughput was 5.5×10^5 m^3hr^{-1} for reactors type V213 and 4.7×10^5 m^3hr^{-1} for V230.
3. Krsko NPP in Slovenia is a two-loop PWR supplied and constructed by Westinghouse Electrical Corp. with a capacity of 632 MW_e. The NPP started its commercial operation in January 1983. Until the end of 1996, the electricity generated was 6.62 GW_ey. The gaseous effluents are released by a stack in which the air throughput is 1.5×10^5 m^3hr^{-1}.

Results

Regular ^{14}C sampling of discharged air began in 1988 at Paks NPP (Hungary) and in 1991 at Bohunice (Slovakia) and Krsko (Slovenia) NPPs. The sampling period at Paks NPP is two weeks, whereas Bohunice and Krsko NPPs collect monthly samples. These discharge patterns are representative for the given reactor unit. The most important results are: 1) the concentrations of ^{14}C vary slightly around their mean values except for Krsko NPP where the variation is much more pronounced; 2) the outage and maintenance periods yield significantly lower concentrations; 3) most of the ^{14}C is released in the form of hydrocarbon and the ratio of hydrocarbon form to the total is *ca.* 95% at Paks NPP and at Bohunice reactor type V213, *ca.* 80% at Bohunice reactor type V230, and the lowest (*ca.* 57%) is at Krsko NPP. According to data in the literature, the ratio of C_nH_m to CO_2 varies between 99 and 1% (Uchrin *et al.* 1992) but in most cases it is close to 90%; 4) the ratio of chemical forms to which ^{14}C may be apportioned tends to be constant for reactor units type V213, but there is a distinct change at reactor V230 where, in 1994, this value dropped to half and remained at that level until the end of 1995 (Fig. 1B). Figure 1(A–D) and Table 1 summarize the data on ^{14}C discharges.

[6]Cab-O-Sil®, Packard Instruments Co., Ulgersmaweg 47, 9731 NL-9731 BK Groningen, The Netherlands

https://doi.org/10.1017/S0033822200018324 Published online by Cambridge University Press

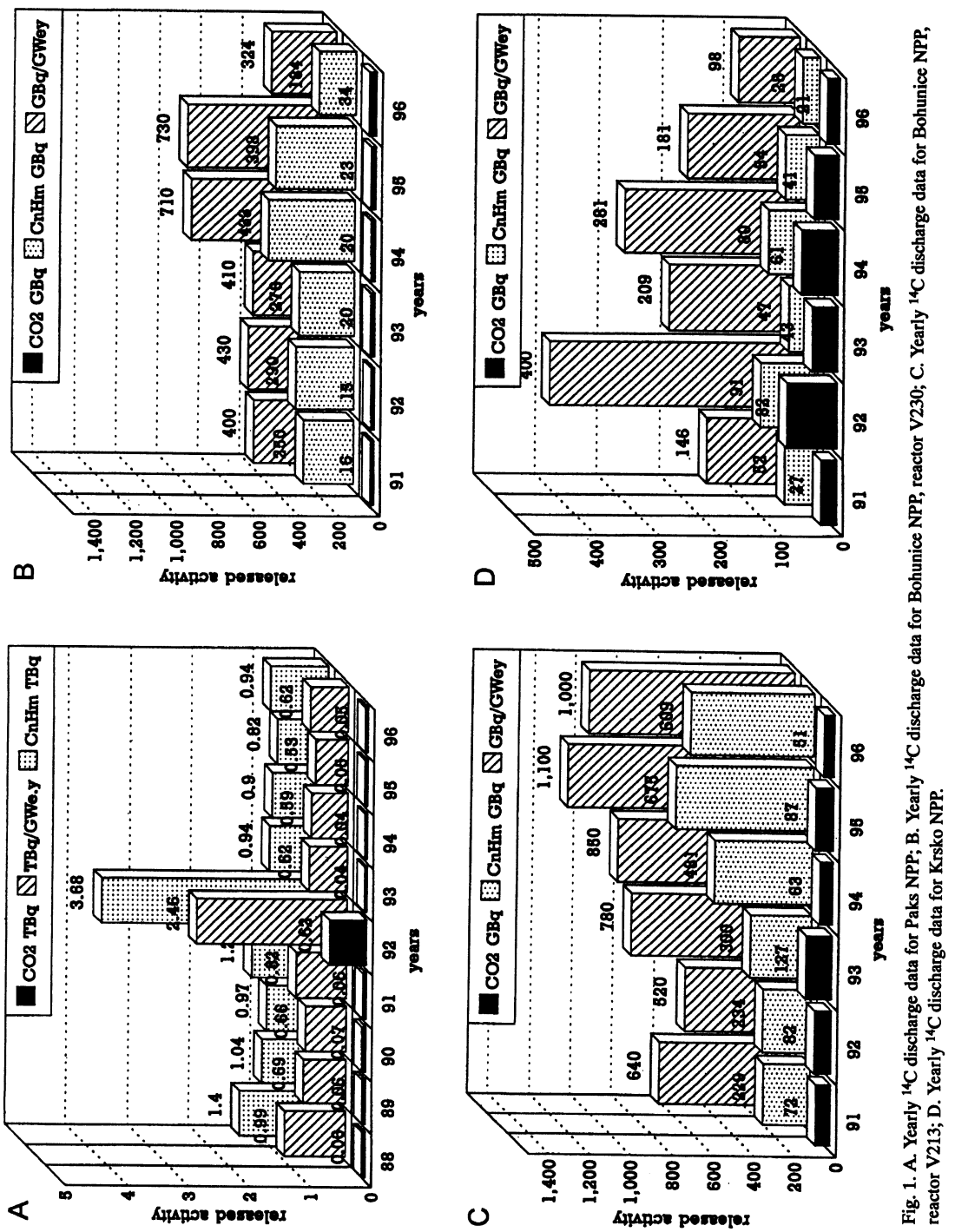

Fig. 1. A. Yearly ^{14}C discharge data for Paks NPP; B. Yearly ^{14}C discharge data for Bohunice NPP, reactor V230; C. Yearly ^{14}C discharge data for Bohunice NPP, reactor V213; D. Yearly ^{14}C discharge data for Krsko NPP.

https://doi.org/10.1017/S0033822200018324 Published online by Cambridge University Press

TABLE 1. NPP ^{14}C Gaseous Release Data: Paks (Hungary), Bohunice (Slovakia) and Krsko (Slovenia)

Discharge	Paks NPP reactors	Bohunice reactor block		Krsko
		V230	V213	
Average annual emission (TBq a^{-1})	1.44 (1.19)*	0.35	0.50	0.104
Mean CO_2/C_nH_m ratio (%)	8.9 (6)*	23.7	7.9	75
Normalized rate (TBq GWe^{-1} a^{-1})	0.887 (0.690)*	0.500	0.815	0.219
Total energy generated	17.79	11.3	7.8	6.62
Total released ^{14}C activity (TBq)	15.8 (12.3)*	6.3	5.7	1.45
Radiological impact				
Local† (nSV a^{-1})	90 (1600)†	200 (1600)†		50 (120)†
Global (man Sv)	2228 (1734)*	1685		204

*Estimates from one unusual year, 1992, are discarded.
†Values in parenthesis correspond to a conservative estimate.

The chemical composition of discharged ^{14}C at various light water reactors has been found (Kuntz 1985) to be *ca.* 75% methane while the remaining 25% consists of higher hydrocarbons. The data listed in Table 1 are based on monitoring results collected in 1988–1996 for Paks, and 1991–1996 for Bohunice and Krsko. Total released ^{14}C data were extrapolated and the corresponding radiological impact calculated on the assumption that NPPs did not change very much regarding their ^{14}C production and discharge. The local radiological impact of ^{14}C releases is calculated by a conversion factor derived from the 15 μSv a^{-1} annual dose due to the natural ^{14}C level and from *ca.* 45 $mBqm^{-3}$ concentration of the atmospheric air corresponding to that dose.

Dispersion models and monitoring ^{14}C of the environmental air around the NPP at Paks give *ca.* 5 mBq m^{-3} increase in ^{14}C concentration as a maximum. The estimate of annual effective dose equivalent is a conservative one because all hydrocarbons are taken as CO_2, which is an obvious overestimation. Although the local radiological impact due to ^{14}C releases is negligibly low, if compared with other gaseous releases (at Paks NPP it is estimated to be 0.2–0.4 μSv a^{-1}), it can be stated that ^{14}C may be responsible for one half of the dose caused by all airborne effluent releases.

The long-term effect of ^{14}C discharges is estimated on the basis of collective effective dose equivalent commitment (CEDEC) from a nominal unit release (1 TBq) of ^{14}C from the nuclear industry. For our calculation, the conservative value of 141 manSv per TBq (McCartney, Baxter and Scott 1988b) was used, although a more recent publication (UNSCEAR 1993) gives lower values of 59–67 manSv per TBq release. For our calculations, we assumed that ^{14}C released other than in CO_2 will be oxidized to this form. For the methane fraction, which is the highest among the hydrocarbons released, this process is quick because its lifetime is 7.5 yr in the environment (Khalil and Rasmussen 1985). In the long-term radiological calculation, the full length operation of NPPs was considered.

The estimated total release of ^{14}C from all nuclear power operations up to the year 1990 is *ca.* 9 PBq (NCRP 1985), yielding a dose of 180 nSv a^{-1}. It is estimated that by the year 2050, the individual dose due to reactor-derived ^{14}C will reach 1.8 μSv a^{-1} (McCartney, Baxter and Scott 1988b). The excess of ^{14}C in the environmental air sampled around the Paks NPP was determined at five sampling sites using similar samplers to those used in the stacks. Sampling sites A1, A4, A6 and A8 are *ca.* 2 km from the 100-m-high stack. For reference, a sampler was operated at station B24 *ca.* 20 km from the NPP. Since 1992, monthly air samples have been taken at these five stations. The yearly average ^{14}C excess data are given in Table 2 and illustrated in Figures 2 and 3.

TABLE 2. Annual Average $D^{14}C$ Excess in the Environmental Air at Sampling Stations A_1, A_4, A_6 and A_8 and at Reference Station B_{24} at Paks NPP, Hungary

Station	A_1		A_4		A_6		A_8		B_{24}	
Sampling period (mo–mo, yr)	CO_2	CO_2 + C_nH_m	CO_2	CO_2+ C_nH_m	CO_2	CO_2+ C_nH_m	CO_2	CO_2 + C_nH_m	CO_2	CO_2+ C_nH_m
03–11, 1992	147.3	188.4	148.9	197	143.6	181	146	179.6	140	151.4
02–12, 1993	127.1	143.3	136	202.9	139.3	155.9	132.5	169.7	139.7	--
01–10, 1994	122.2	132.1	131.6	207.8	114.6	133.1	123.3	149.6	--	--
01–12, 1995	123.7	148.7	117.5	171.3	116.7	150.5	114.4	153.8	110.2	130.0
01–09, 1996	112.2	157.6	121.5	186.1	109.6	152.6	110.8	149.9	109.8	115.3

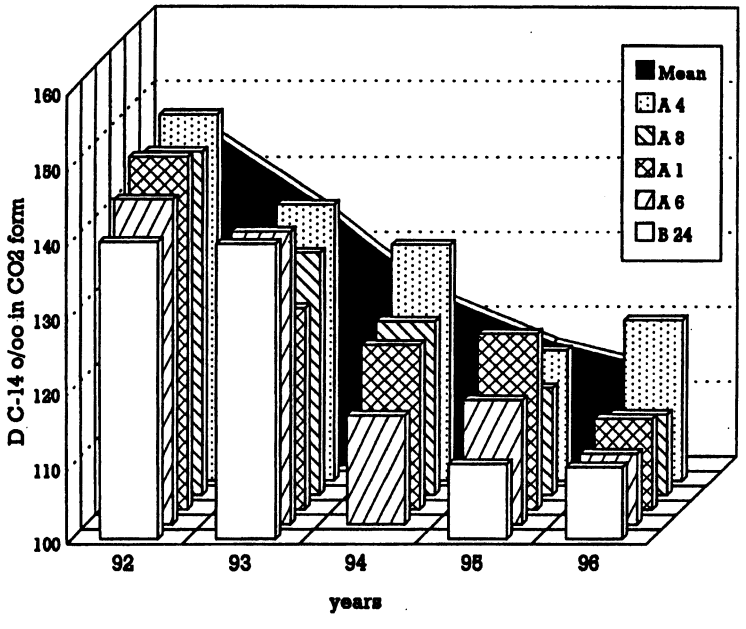

Fig. 2. Yearly average ^{14}C excess in CO_2 from environmental air at stations A1, A4, A6 and A8, and reference station B24 at Paks NPP

When CO_2 + hydrocarbons were analyzed, the excess ^{14}C varied from 130 to 200‰, thus slightly reflecting the location of the sampling site related to the prevailing wind direction. The maximum enhanced concentration of ^{14}C in the environmental air may reach 5 mBq m^{-3}, *ca.* 10% increase of the "natural" level, 45 mBq m^{-3} in 1996. The stable carbon ratio, $\delta^{13}C$‰, of atmospheric air varied between –8% and –10% , the mean being –9%. The CO_2 fraction of the samples showed no increase due to NPP operation, which is obvious considering the low ^{14}C concentration apportioned to this form. If one averages the data collected at five sampling stations, the "natural" ^{14}C variation can be followed for the years of monitoring (Fig. 2). The "natural" ^{14}C level declined at a rate of 6.4% a^{-1} and by a simple extrapolation this yields a half-life of 11.3 yr, which is in good agreement with the findings of Otlet *et al.*, T=13.0 yr and T=10.3 yr (1997).

Rings of a *Robinia pseudoacacia* tree were analyzed. The trees were harvested from the vicinity of the Paks and Krsko NPPs, 1.7 km and *ca.* 1 km from the release point in the prevailing wind direction at Paks and Krsko, respectively. For reference, trees taken from "clean" areas far from the NPPs were

https://doi.org/10.1017/S0033822200018324 Published online by Cambridge University Press

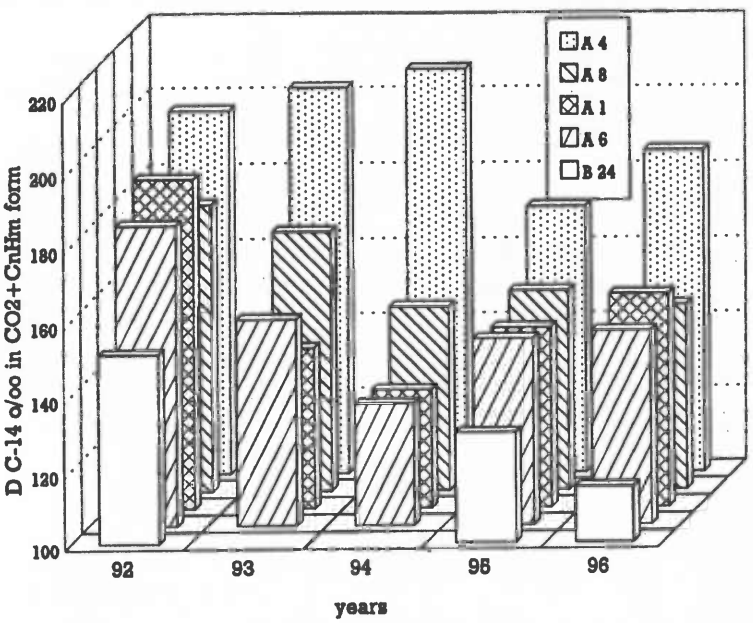

Fig. 3. Yearly average ^{14}C excess in $CO_2+C_nH_m$ from environmental air at stations A1, A4, A6 and A8 and reference station B24 at Paks NPP

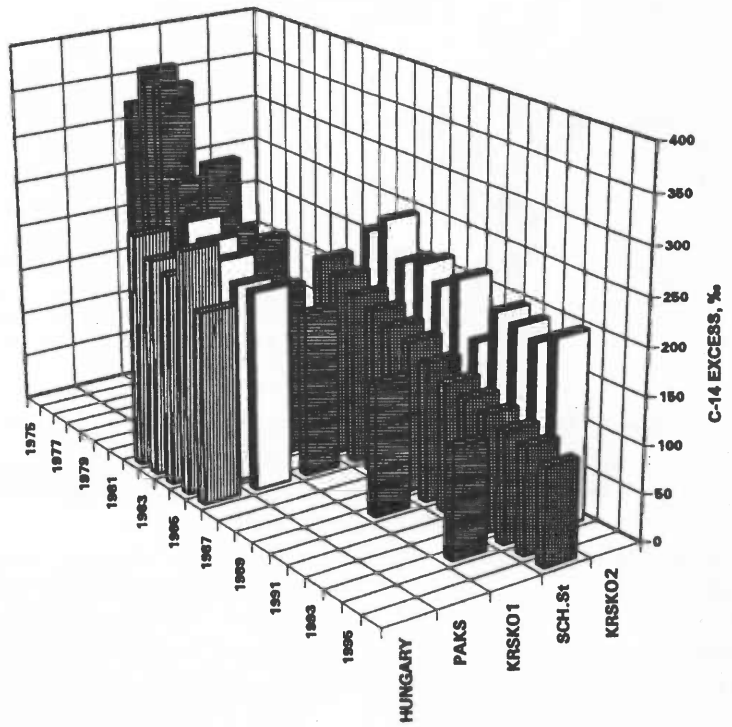

Fig. 4. ^{14}C excess in tree rings and atmospheric $^{14}CO_2$ at Schauinsland station. Krsko 1: tree from the opposite direction as the Krsko 2 tree. Krsko 2: tree from the direction of prevailing wind.

also collected and analyzed. Figure 4 shows the results of the tree-ring analysis. It can be seen that at Krsko NPP, the decline of the ^{14}C level from 1986 is balanced by uptake due NPP releases. There is no similar observation for Paks NPP because, in addition to the low amount of $^{14}CO_2$ discharges, the tree-ring analysis was carried out in the early years of NPP operation. The half-life of the "natural"

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^{14}C level, based on reference to tree-ring analysis, is T=14.5 yr (Hungary 1982–1986), T=15.7 yr (Slovenia 1976–1994) and T=13.7 yr (Slovenia 1982–1994). The half-life derived from the Schauinsland station data is 11.6 yr for 1984–1991 and 14.7 yr for 1993–1996 (Levin and Kromer 1997).

Conclusion

The ^{14}C discharge rates from Paks and Bohunice are about four times higher than the typical Western European PWR NPP data. These higher rates may be apportioned to the higher level of nitrogen impurities in the primary coolant. The need for regular monitoring of ^{14}C discharge is underlined by the fact that significant variation may occur, even at a given NPP, especially in the ratio of the chemical forms in which ^{14}C is released.

Acknowledgments

The authors thank Eszter Csaba for her valuable assistance in measurements and technical help. Barbara Vokal would like to thank MOBITEL d.d. (Slovenia) for financial support that allowed her to participate at the 16th International ^{14}C Conference in Groningen, The Netherlands.

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