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RADIOCARBON RELEASES AT THE KRŠKO NUCLEAR POWER PLANT

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ABSTRACT. Since 1991, radiocarbon analyses of exhaust air have been part of the regular radioactivity monitoring program at the Krško Nuclear Power Plant (NPP), a Westinghouse 632 MWe pressurized water reactor (PWR). Activity of CO_2 and hydrocarbons has been identified; the former contributes *ca.* 43%. A normalized release of total ^{14}C of 0.219 TBqGWe^{-1}a^{-1} was obtained. Indoor air ^{14}C concentrations in selected rooms inside the plant have generally been <5 Bq m^{-3}, although rare peaks of >1000 Bq m^{-3} may be reached. Tree rings have shown slight enhanced ^{14}C activity due to the operation of the plant.

INTRODUCTION

The presence of radiocarbon (half-life 5730 ± 40 yr, maximum beta energy of 162 keV) in our environment is due to three production pathways (Raaen, Ropp and Raaen 1968): nuclear reactions induced by cosmic rays in the upper atmosphere, nuclear weapons testing, and the nuclear fuel cycle including nuclear power plants. The total ^{14}C activity on the Earth is estimated to amount to 83×10^8 GBq (Fairhall and Young 1970) and is distributed among the hydrosphere, biosphere and atmosphere, the latter contribution being 1.6×10^8 GBq in the CO_2 form, resulting in an air concentration of 42.4 mBq m^{-3}. This is only 1.9% of the total ^{14}C as compared with 94.3% in the oceans.

The changes in ^{14}C content in the environment result from two opposing anthropogenic activities: 1) The Suess effect (Fairhall and Young 1970), caused by combustion of fossil fuel low in ^{14}C, and 2) an enhancement due to nuclear reactors and nuclear weapons testing. Thus, the industrial revolution first decreased its content and then nuclear weapons testing increased it. After weapons testing ceased, the content started to decrease (Levin, Münnich and Weiss 1980; Csongor and Hertelendi 1982; Levin *et al.* 1988; Hertelendi and Csongor 1982). The Suess effect may also explain the periodic ^{14}C depletions in the air of heavily industrialized urban areas during warm seasons (Csongor and Hertelendi 1982; Segl *et al.* 1983; Belan *et al.* 1990). According to some estimates, the total ^{14}C enhancement due to the nuclear industry in the years 1975–2000 will be 10% of that from nuclear weapons testing and only 0.3% of the natural inventory (Hayes and MacMurdo 1977). On the other hand, the "pessimistic" scenario predicts that releases from the nuclear fuel cycle will exceed natural production after 2000 (Otlet, Fulker and Walker 1992). Because of their ease of incorporation into the global carbon cycle and their long half-life, these releases should be considered very carefully in estimating their local and global effect on the collective dose commitments (McCartney, Baxter and McKay 1986; McCartney, Baxter and Scott 1988a; McCartney, Baxter and Scott 1988b).

In a light-water nuclear reactor, ^{14}C is produced by neutron activation according to the reactions $^{17}O(n,\alpha)^{14}C$ with oxygen in oxides of fuel, moderator and coolant, and $^{14}N(n,p)^{14}C$ with nitrogen as impurities in fuel, moderator and coolant (Wallace 1979). For the pressurized water reactor (PWR) type reactors, the ^{14}C production rates of 0.57, 0.97, and 0.19 TBq GWe^{-1}a^{-1} in the fuel, construction material, and coolant, respectively, are estimated (Wallace 1979; Hertelendi *et al.* 1989). More than 95% of the ^{14}C produced is released in a gaseous form through the stack of a nuclear power plant (NPP) (Kunz 1985), mainly in CO_2 form (Wahlen and Kunz 1978; Winkelmann, Gesewsky and Schwibach 1984), though the CO_2/hydrocarbons ratio may substantially differ for PWR reactors (Hertelendi, Uchrin and Ormai 1989; Uchrin *et al.* 1992).

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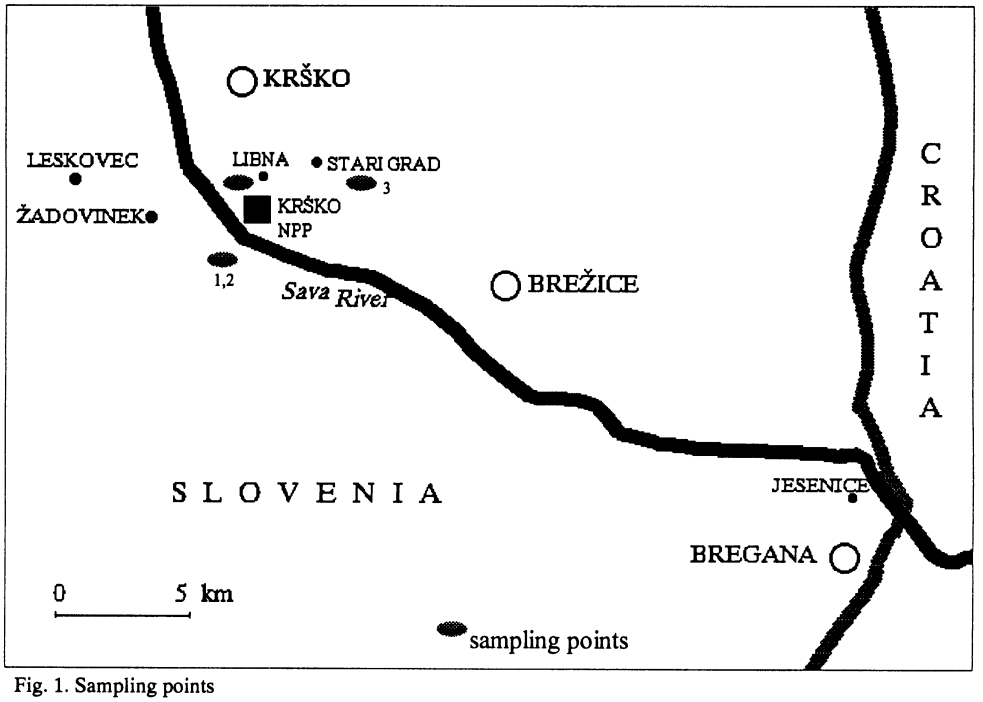

Fig. 1. Sampling points

The Krško Nuclear Power Plant is a PWR Westinghouse 632 MWe reactor, situated (Fig. 1) on the left bank of the Sava River (45°45′15″N, 15°31′14″E), close to the border between Slovenia and Croatia, *ca.* 100 km downstream from the Slovenian capital Ljubljana with 370,000 inhabitants, and about 30 km upstream from the Croatian capital Zagreb with about a million inhabitants. Its operation started in 1983.

The first ^{14}C measurements in air, water and plants sampled in the surroundings of the Krško NPP were already being performed in 1984 and continued until 1986 (Obelić *et al.* 1986, 1988). However, ^{14}C analyses were included in the regular radioactivity survey program in 1991. Air is continuously sampled at the stack and ^{14}C in the form of CO_2 and hydrocarbons is determined biweekly. In addition, air in several rooms in the plant was analyzed and ^{14}C from several trees was obtained.

Sampling and analytical procedure

Air is continuously sampled in a bypass of the main exhaust air stream in the stack at 115 m elevation by a differential CO_2/CH_4 sampler manufactured at the Institute of Isotopes at the Hungarian Academy of Science, Budapest (Hertelendi, Uchrin and Ormai 1989; Uchrin *et al.* 1992; Uchrin, Ormai and Hertelendi 1989; Veres *et al.* 1995). It consists of two parallel lines for air sampling. A single membrane pump maintains a continuous air flow at a rate of 2.5×10^{-4} m^{3}min^{-1} through each of the lines. The air in the first line passes through a potassium hydroxide trap where CO_2 is absorbed. In the second line, hydrocarbons are converted to CO_2 on a Pd catalyst at 873K and are passed through a second potassium hydroxide trap to absorb CO_2 originating from hydrocarbons. Every two weeks the traps are replaced with new ones.

Absorbed CO_2 was precipitated as $BaCO_3$ by adding $BaCl_2$ solution (Uchrin *et al.* 1993). We mixed 2 g of precipitate with 0.80 g of Cabosil M-5, and added 20 cm^3 of Instagel scintillation cocktail to

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the scintillation vial. Beta activity was measured with a liquid scintillation analyzer (Packard Tricarb® 2550TR A/B).

An identical sampler to that mentioned above was used and the same procedure followed also for ^{14}C analyses of air in selected rooms in the plant as requested by the Slovenian Nuclear Safety Administration in order to identify potential activities enhancing ^{14}C releases. Altogether, 18 analyses of two-week composite samples were made for the period April 1, 1994–January 3, 1995. Every two weeks, the sampler was moved to another place where elevated ^{14}C levels were expected. In some rooms the measurement was repeated. Among the places selected were the fuel handling building (FHB)—3 analyses, and the reactor containment at four elevations—3 analyses at 94 m above sea level (asl) (EL-94), 6 analyses at 100 m asl (EL-100), 2 analyses at 107 m asl (EL-107), and 4 analyses at 115 m asl (EL-115).

Three acacia trees (*Robina sp.*) were felled in a radius of a few kilometers from the plant stack at two locations. Based on the mean monthly dilution factors for individual directions and on the gamma dose rates as obtained by thermoluminiscent dosimeters, we determined the critical transport path for gas emissions to be in the east-northeastern (*Sp. Stari grad*) and northern directions (*Vrbina*) (2–3 μSv compared to 0.1–0.6 μSv at other directions). Trees were selected with ages that covered the period since 1975. Samples were first combusted to CO_2. The sample for $\delta^{13}C$ mass spectrometric measurements was collected at this stage. CO_2 was then reacted with hot lithium to form Li_2C_2. The addition of ^3H-free water to the cooled lithium carbide produced acetylene, and then the acetylene was catalytically trimerized to benzene. A scintillator compound (butyl-PBD) was dissolved in benzene and the solution was then counted in a low-level liquid scintillator counter (LSC) (Quantulus LKB-Wallac) for 1000 min, 10 times for each sample. Measurements were carried out at the Institute for Hydrology, GSF, Neuherberg, Germany.

Results and Discussion

Exhaust Air

Figure 2 shows (A) biweekly averages of ^{14}C activity concentrations of CO_2 in the exhaust air of the plant, (B) biweekly averages of ^{14}C activity concentrations of CO_2 and hydrocarbons in the exhaust air of the plant and (C) electrical energy generation of Krško NPP. We see that our CO_2/hydrocarbons ratio is among the highest for the PWR-type plants (Kunz 1985; Winkelmann, Gesewsky and Schwibach 1984; Obelić *et al.* 1988; Trampuž 1989). We obtained the normalized release of 0.219 TBq $GWe^{-1}a^{-1}$.

Indoor Air

Figure 3 presents the results of two-week average ^{14}C activity concentrations as CO_2 and hydrocarbons in the selected rooms inside the Krško NPP. Generally, the values are below 5 Bq m^{-3} in the fuel handling building (FHB) and below 3.5 Bq m^{-3} in the reactor containment at elevation 94 m (EL-94). Values more than ten times as high were obtained in the containment at 107 m (EL-107) for June 1–July 1, 1994, and at 115 m (EL-115) for May 17–June 1, 1994 and December 1, 1994–January 3, 1995. Substantially higher ^{14}C levels of 1900 Bq m^{-3} were found in the containment at 100 m (EL-100) during July 1–16, 1994, and 190 Bq m^{-3} at 115 m (EL-115) for November 16–December 1, 1994. Unfortunately, the sampler failed in August, and since then only CO_2 ^{14}C has been measured. However, before that, the majority of ^{14}C activity in the rooms appeared as CO_2.

Occasionally high indoor ^{14}C concentrations may be attributed to maintenance and other repair work in the plant. However, during the regular refit of the reactor in the period August 20–October

5, 1994, when the reactor was shut down, no increased levels were observed. It should be pointed out that even the highest value of 1900 Bq m^{-3} is far below the limit for occupational exposure in Slovenia of 40,000 Bq m^{-3} (Trampuž 1989).

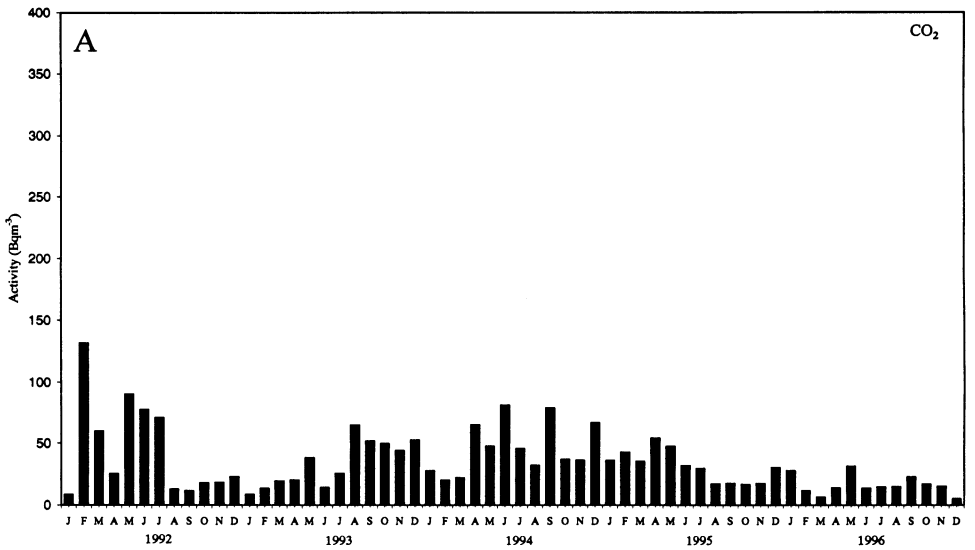

Fig. 2A. Biweekly averages of ^{14}C activity concentrations of CO_2 in the exhaust air of the NPP

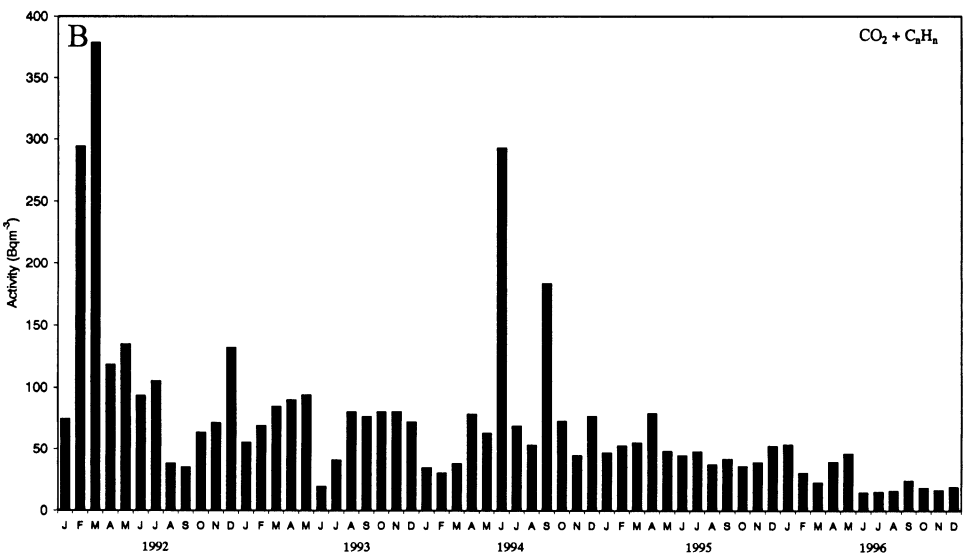

Fig. 2B. Biweekly averages of ^{14}C activity concentrations of CO_2 and hydrocarbons in the exhaust air of the NPP

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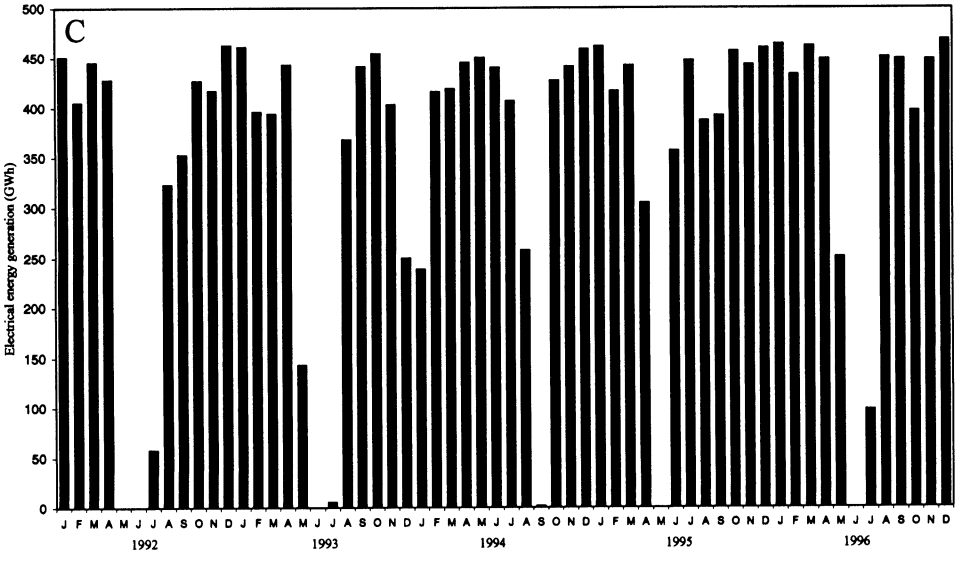

Fig. 2C. Electrical energy generation of Krško NPP

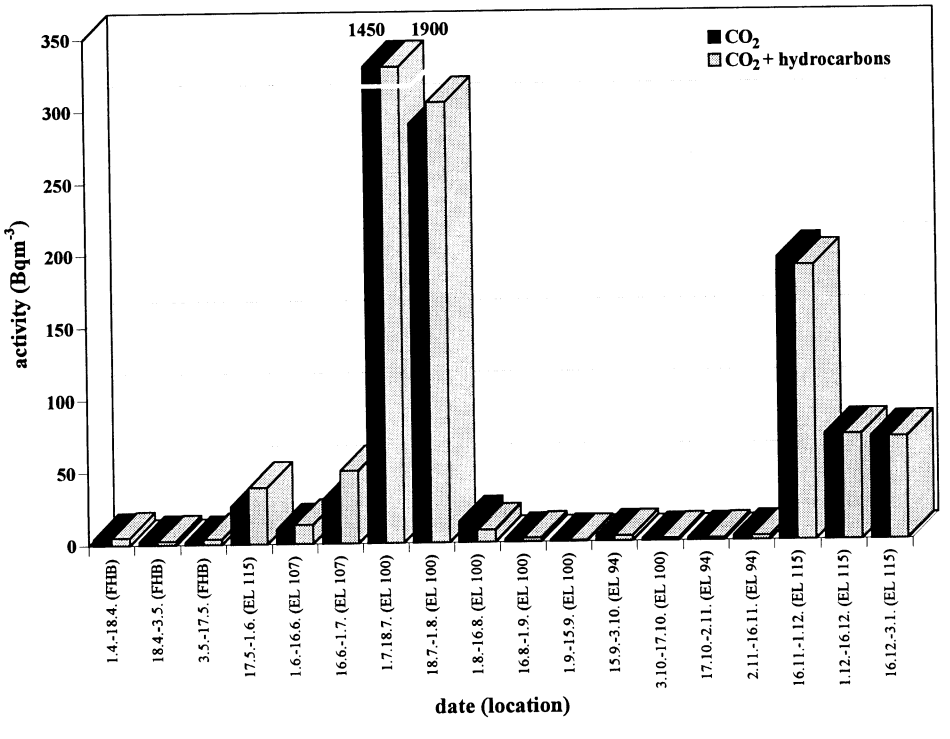

Fig. 3. Two-week average ^{14}C concentrations inside the Krško NPP

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Tree Rings

The results of ^{14}C activity in tree rings, expressed as a percentage of the modern standard (95% of the National Institute of Standards and Technology (NIST) oxalic acid standard), are collected together with the $\delta^{13}C$ values in Table 1. In Figure 4, the results are presented and compared with the previous results. The full line presents the mean clean air activity obtained (Levin and Kromer 1997). The mean atmospheric ^{14}C activity in Zagreb, according to Krajcar-Bronić (1998), is lower than the mean clean air activity for the Northern Hemisphere. Our results reflect slight enhancement only for sample 3, which may be attributed to the plant operation, which was expected (Uchrin *et al.* 1992). In the previous study mentioned above (Obelić *et al.* 1986, 1988), linden trees at Libna, 1.5 km away from the stack, and at Plitvice, *ca.* 150 km away from the plant, were analyzed.

TABLE 1. $\Delta^{14}C$ Activity and $\delta^{13}C$ Values in Tree Rings*

	Sample 1		Sample 2		Sample 3	
Year	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)
1975			320	−25.66		
1976			364	−25.81		
1977			351	−25.95		
1978			252	−25.72		
1979	253	−26.16	230	−25.94		
1980			288	−25.92		
1981			222	−25.72		
1982			209	−25.86		
1983			230	−25.92		
1984			185	−25.77	225	−26.11
1985					245	−27.05
1986			177	−25.68	207	−27.06
1987					214	−26.04
1988					199	−25.88
1989					215	−25.95
1990			140	−24.64	157	−25.32
1991					198	−25.19
1992					192	−24.72
1993					185	−24.04
1994	100	−25.94	116	−25.40	180	−25.88

*All $\Delta^{14}C$ data ± 6‰ error. All $\delta^{13}C$ data ± 0.05‰.

Conclusion

Within the regular radioactivity monitoring program at the Krško NPP, ^{14}C activity in the form of CO_2 and hydrocarbons was determined in two-week air composite samples of the gaseous effluents. On average, CO_2 contributes *ca.* 43% to the total ^{14}C activity. The normalized ^{14}C release for the period 1991–1996 was 0.219 $TBqGWe^{-1}a^{-1}$, placing this plant below the world mean value for PWR.

Generally, in the rooms of the plant where elevated ^{14}C air concentrations might be expected, the values measured fell below 5 Bq m^{-3}, with a few exceptions when they reached almost 2000 Bq m^{-3}. But these high values are also far below the allowed levels for occupational exposure.

The analyses of tree rings showed considerable enhanced ^{14}C activity due to the plant operation at a distance of 1.5 km from either stack.

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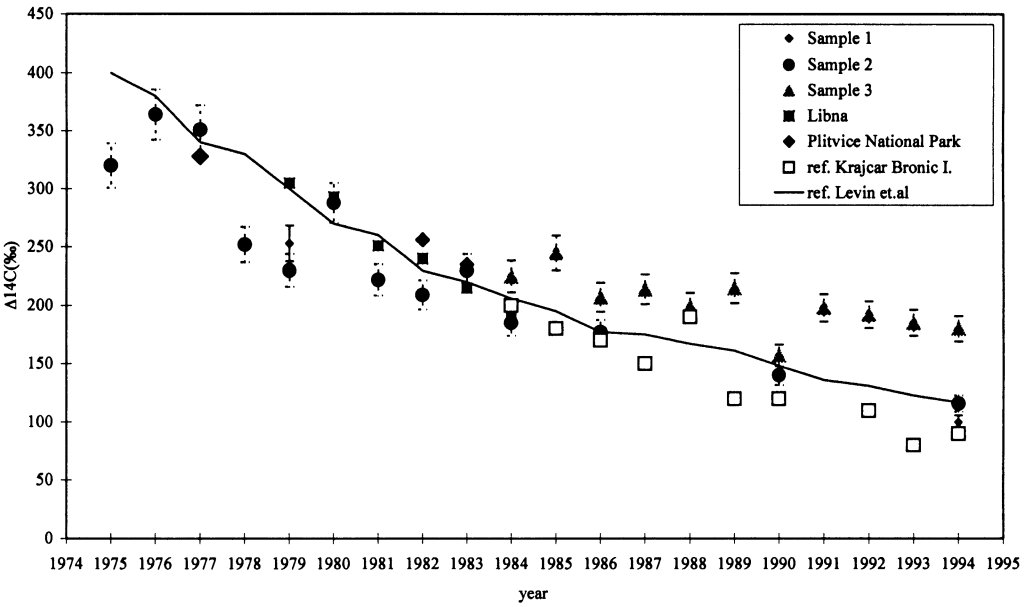

Fig. 4. $\Delta^{14}C$ activity (‰) of acacia tree rings, 1975–1994, compared with ^{14}C activity of linden tree rings from Libna, the mean atmospheric ^{14}C activity in Zagreb according to Krajcar-Bronić (1998), and clean air activities obtained by Levin and Kromer (1997).

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