RADIOCARBON, Vol 54, Nr 2, 2012, p 195–202

^{14}C LEVELS IN TREE RINGS LOCATED NEAR QINSHAN NUCLEAR POWER PLANT, CHINA

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ABSTRACT. Specific activities of radiocarbon in annual tree rings corresponding to 1980–2009 are reported for a pine tree located 2 km from the Qinshan Nuclear Power Plant (Qinshan NPP), China. While a negligible enhanced ^{14}C activity due to operation of the Qinshan NPP Plant I is evident, a relative increase (1.8–62.6 Bq/kg C) was observed in the specific activity after operation of the Qinshan NPP Plant II in 2002 and Plant III in 2003. The enhanced values were primarily affected by the ^{14}C discharged from Plant III (CANDU-type reactor), and a good correlation was found between the ^{14}C discharged from Plant III in the growing season and the ^{14}C excess value. The excess ^{14}C activities peaked in 2005 (at 302.0 Bq/kg C, which is 62.6 Bq/kg C above the "clean air" ^{14}C level), and then declined due to the improvement in ^{14}C discharge management of Plant III. In 2009, the ^{14}C-specific activity was near the background level.

INTRODUCTION

Carbon-14 is a radioactive isotope that decays to ^{14}N by emitting low-energy beta radiation. There are 3 production pathways of ^{14}C in our environment (IAEA 2004): natural production in the atmosphere from the reaction ^{14}N(n, p)^{14}C by cosmic-ray neutrons; production resulting from nuclear explosions; and production in and release from nuclear facilities. ^{14}C in the nuclear fuel cycle is produced by neutron interaction with ^{13}C, ^{14}N, ^{15}N, ^{16}O, and ^{17}O, which may be present in the nuclear fuels and the moderator and primary coolant systems of nuclear reactors. ^{14}C is radiologically important due to its ease of incorporation into the global carbon cycle and long half-life (5730 yr). Indeed, many studies have shown that ^{14}C discharged from nuclear facilities contributes a significant fraction of the radiation dose delivered to both local and global populations (Hertelendi et al. 1989; Veres et al. 1995; Isogai et al. 2002; Roussel-Debet et al. 2006; Mazeika et al. 2008; Povinec et al. 2009).

It is well documented that the chemical composition of the ^{14}C gaseous waste derived from the nuclear facilities is mainly $^{14}CO_2$ and ^{14}C hydrocarbons (Hertelendi et al. 1989; Vokal and Kobal 1997; Uchrin et al. 1998; Molnár et al. 2007; Yang et al. 2010). The ^{14}C effluents discharged from the nuclear power reactor diffuse into the atmosphere after emission. The radius affected by nuclear facilities' ^{14}C discharge is several tens of km, depending on the type of nuclear systems and the meteorological and geographical conditions of the sites (Kim et al. 2000; Magnusson et al. 2007; Molnár et al. 2007; Dias et al. 2008; Koarashi et al. 2008; Mazeika et al. 2008). $^{14}CO_2$ can be captured directly by plants through photosynthesis, while ^{14}C hydrocarbon plays a minor part in the ^{14}C enrichment of environmental samples around nuclear facilities. Owing to their growth characteristics, tree rings are widely used to study the ^{14}C discharge of nuclear facilities. The α-cellulose in tree rings remains fixed after formation, so tree rings can be used to indicate the average atmospheric ^{14}C activity during the growing season in different years (McNamara and McCartney 1998; Stenström et al. 1998; Kim et al. 2000; Isogai et al. 2002). Thus, for monitoring ^{14}C discharges from the nuclear facilities in previous years, tree rings are an appropriate environmental indicator.

For the Qinshan Nuclear Power Plant (Qinshan NPP), the first nuclear power plant in China, 2 types of reactors (PWR and CANDU) are in commercial operation. There exist no data on ^{14}C levels and their variation on the surrounding environments; therefore, to understand the temporal variation of ^{14}C-specific activity in terrestrial samples, measurements of the ^{14}C in tree rings representing the period 1980–2009 were carried out for this work. We discuss the results below.

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MATERIALS AND METHODS

Site Descriptions and Environmental Settings

The Qinshan NPP is located in Haiyan County, Zhejiang Province, China, ~100 km from Shanghai and consists of 3 plants: I, II, and III (Figure 1). Qinshan NPP Plant I is the first Chinese nuclear power plant with a 300-MW_e pressurized water reactor (PWR), and has been in operation since April 1994. The routine airborne release of Qinshan NPP Plant I is discharged from a 102-m-high stack. Plant II has 3 units that began operation in April 2002, May 2004, and August 2010, respectively. Each of their 600-MW_e pressurized water reactors has a 62.5-m-high stack. Qinshan NPP Plant III is China's first heavy-water reactor (HWR) nuclear power plant with 2 CANDU-6 reactors whose maximum electrical output is 728 MW_e. The CANDU-6 reactor is fueled with natural uranium and uses heavy water as a coolant and moderator. These reactors began operation in December 2002 and June 2003. The height of the 2 venting stacks is 55 m.

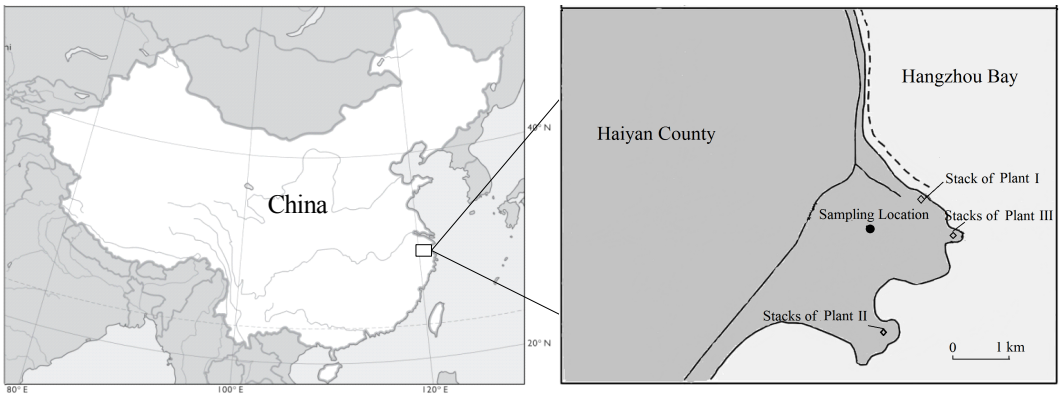

Figure 1 Qinshan NPP site map and sampling location

Wind direction data obtained from a monitoring station close to Qinshan NPP showed that the dominating wind direction (16.4%) is from the east (Figure 2). In 2006, ~12,100,000 people lived within an 80-km radius of the power plant. Within a radius of 10 and 5 km, referred to as "directly influenced areas," the populations decrease to 74,000 and 18,000, respectively.

Sampling

In March 2010, a section was obtained from a 40-yr-old pine tree found near Qinshan NPP (30°26′5.6″N, 120°56′28.2″E). The tree was downwind of the Plant III stacks (HWR), in the area considered as most directly affected by ^{14}C airborne release from the Qinshan NPP. The sampling location was chosen on a hill without other chemical or heavy industry, which could influence the ^{14}C concentration in the air (Figure 1). After whittling and polishing this 4-cm-thick section, the rings corresponding to the period 1980–2009 were used for ^{14}C analysis. Each ring was sliced into very thin sections and subjected to sample pretreatment.

Pretreatment Procedure

Alpha-cellulose in tree rings is the most reliable fraction of wood for determining the average atmospheric ^{14}C concentration at the time of growth (Hoper et al. 1998; Isogai et al. 2002). Other organic materials (e.g. lignin, waxes, resins) in the rings should be removed by pretreatment to leave pure

https://doi.org/10.2458/azu_js_rc.v54i2.15869 Published online by Cambridge University Press

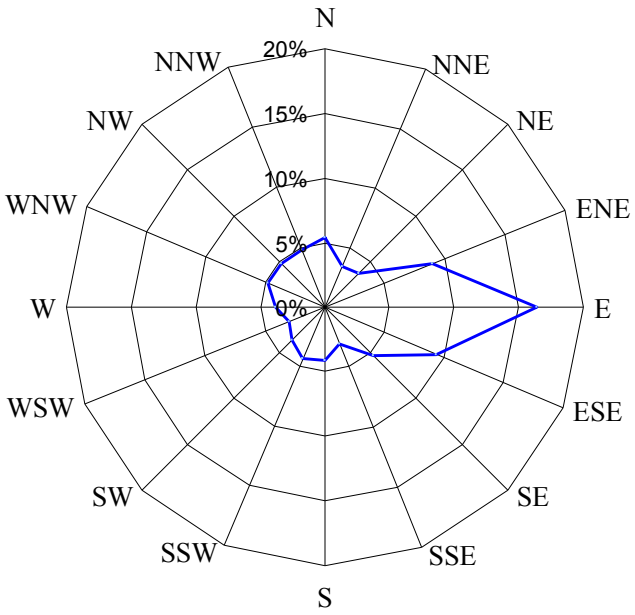

Figure 2 Rose diagram of average wind conditions at the Qinshan site (2003–2009)

cellulose. The samples were reduced to α-cellulose following the method described by Hoper et al. (1998). The α-cellulose extraction procedure consists of a 3-step Soxhlet extraction process; the solvents are a 300-mL ethanol/chloroform mixture (1:2 by volume), 300 mL of ethanol, and 300 mL of Milli-Q™ water, respectively. This process removes resins, fats, oils, waxes, and other mobile contaminants. It is followed by bleaching the sample with a $NaClO_2$/HCl mixture to remove most of the lignin. The samples were then stirred in 5% NaOH with bubbling N_2 for 1 hr, followed by washing with Milli-Q water until neutral. The last stage is stirring in 5% HCl for 10 min, followed by washing with Milli-Q water until neutral. The remaining insoluble material was α-cellulose; the remnant lignin and hemicelluloses were removed by the last 2 steps. About 10 g of the tree-ring sample was pretreated, and it was observed that the sample yielded, on average, 30% α-cellulose by dry weight.

The α-cellulose samples were graphitized as described by Xu et al. (2007), where a typical yield of 85–90% was obtained for high precision (2–3‰). After each sample was evaporated to dryness, about 4.5 mg of α-cellulose was removed to a combustion tube where copper oxide (~200 mg) was added. The combustion tube was then evacuated to 10^{-4} Torr using a vacuum pump and flame-sealed with a liquefied petroleum gas torch. The flame-sealed combustion tubes were baked at 900 °C for 3 hr in an oven, while the organic carbon was oxidized to CO_2. Carbon dioxide was purified and transferred to a septa-sealed vial where zinc dust, iron powder, and TiH_2 were placed for graphite generation. This was done by connecting the break-end combustion tube to a gas transferring apparatus. The septa-sealed vial containing CO_2 was placed in an oven at 540 °C for 8 hr. Finally, the CO_2 was reduced to graphite that coats the iron catalyst.

Measurement

Accelerator mass spectrometry (AMS) ^{14}C measurement was conducted at Peking University (Liu et al. 2007a). The measurement precision of the AMS system is 0.3%, and backgrounds ($^{14}C/^{12}C$) of less than 4×10^{-16} are achievable. Peking University AMS laboratories took part in the Fifth Inter-

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national Radiocarbon Intercomparison from September 2004 to May 2005. The measurement results of 3 kinds of standard samples (OXI, OXII, and ANU sucrose) were in good agreement with the average values, which are statistically calculated by the International Atomic Energy Agency (IAEA) based on the data from many laboratories in the world (Liu et al. 2007b). Our results were within 1 standard deviation.

The graphite-coated iron was poured into an AMS sample holder and pressed into the hole for analysis. During AMS measurement, carbon isotopes ^{12}C, ^{13}C, and ^{14}C were charged and accelerated in the AMS system. The beam intensities of these charged carbon isotopes were measured respectively, and the ratios $^{14}C/^{12}C$ and $^{13}C/^{12}C$ together with their uncertainties were calculated. Standard oxalic acid samples (NIST oxalic acid standard, SRM-4990C) and blank coal samples were also measured.

The $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios of samples were measured with the AMS system and normalized against the measured $^{14}C/^{12}C$ and $^{13}C/^{12}C$ of the oxalic acid standard. The sample $^{13}C/^{12}C$ ratio is given as the $\delta^{13}C_{sample}$ value, defined in Equation 1, where PDB indicates a reference material made from carbonate (Hoefs 1987). The ^{14}C results, presented as normalized specific activities A_{SN} (in Bq/kg C), are calculated according to Equation 3. A_s is the uncorrected specific activity of the sample, which can be calculated according to Equation 2, where λ is the decay constant for ^{14}C (3.84×10^{-12} s^{-1} = 1/8267 in yr^{-1}), N_A is the Avogadro constant, and 83.26 represents the number of moles contained in 1 kg of carbon.

$$\delta^{13}C_{sample} = \left[\frac{^{13}C/^{12}C}{^{13}C/^{12}C_{PDB}} - 1\right] \times 1000\,‰ \quad (1)$$

$$A_S = 83.26\lambda \times N_A \times {}^{14}C/^{12}C_{sample} \quad (2)$$

$$A_{SN} = A_S\left\{1 - \frac{2(25 + \delta^{13}C_{sample})}{1000}\right\} \quad (3)$$

RESULTS AND DISCUSSION

^{14}C Results of the Tree Rings

Specific ^{14}C results are given for individual rings (1980–2009), calculated using the equation below, from the Qinshan NPP pine sample, and compared with the ^{14}C in air of the Northern Hemisphere data of Levin and Kromer (2004) (Table 1, Figure 3).

$$\sigma^2_{A_{SN}} = \left(\frac{\delta A_{SN}}{\delta^{14}C/^{12}C_{sample}}\right)^2 \sigma^2_{^{14}C/^{12}C_{sample}} + \left(\frac{\delta A_{SN}}{\delta^{13}C/^{14}C_{sample}}\right)^2 \sigma^2_{^{13}C/^{12}C_{sample}} + \left(\frac{\delta A_{SN}}{\delta^{13}C/^{12}C_{PDB}}\right)^2 \sigma^2_{^{13}C/^{12}C_{PDB}}$$

The results in Table 1 show that the ^{14}C-specific activities decrease from 291.9 Bq/kg C (1980) to 251.9 Bq/kg C (1994) before Qinshan NPP's operation. The "bomb" ^{14}C induced by atmospheric nuclear explosions has decreased due to CO_2 uptake by the oceans and the biosphere (Levin and Kromer 1997; Dias et al. 2008). The results of the present study are compared with the ^{14}C activities in air of the Northern Hemisphere over the timespan 1987–1994 (Figure 3). The figure shows good correlation between these 2 data sets, allowing us to use the latter as the background activities.

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Table 1 ^{14}C activities in tree rings from the Qinshan NPP and $^{14}CO_2$ background from the Jungfraujoch site (46°33′N, 7°42′E).

Year	Tree-ring activity (Bq/kg C)	Error ±1σ (Bq/kg C)	Jungfraujoch $^{14}CO_2$ (Bq/kg C)[a]	Year
1980	291.9	1.1		1980
1981	287.9	0.8		1981
1982	282.2	1.4		1982
1983	280.6	0.8		1983
1984	275.5	1.1		1984
1985	274.2	1.0		1985
1986	271.3	1.1		1986
1987	268.7	0.8	267.5	1987
1988	264.1	1.1	264.5	1988
1989	263.2	0.9	263.1	1989
1990	261.2	1.5	260.4	1990
1991	259.1	1.0	258.1	1991
1992	255.9	1.0	256.6	1992
1993	254.9	0.8	254.8	1993
1994	251.9	0.8	253.5	1994
1995	250.4	0.8	252.2	1995
1996	250.7	0.7	250.5	1996
1997	248.5	0.7	249.0	1997
1998	248.7	1.0	248.9	1998
1999	250.9	0.8	247.6	1999
2000	244.7	0.8	246.1	2000
2001	242.2	0.9	244.4	2001
2002	241.6	0.7	243.7	2002
2003	246.4	0.9	242.2[b]	2003
2004	262.1	1.2		2004
2005	302.0	0.8		2005
2006	259.6	1.4		2006
2007	246.6	0.8		2007
2008	243.1	0.9		2008
2009	235.9	0.7		2009

[a]The average ^{14}C-specific activity from April to September (Levin and Kromer 2004).
[b]The average ^{14}C-specific activity from April to July (August and September's data is absent).

As indicated by Figure 3, no obvious difference is observed between ^{14}C activities in tree rings and the background values after Qinshan NPP Plant I began operation in 1994. This leads to the conclusion that the ^{14}C discharged from the 300-MW_e PWR reactor in Qinshan NPP Plant I has an insignificant influence on the ^{14}C-specific activities in the sample tree. In Figure 3, the ^{14}C activity in 1999 is 3.3 Bq/kg C higher than the background. According to the operation record, Plant I was shut down for refueling and maintenance from July 1998 to August 1999. Therefore, this peak was likely caused by the accumulated $^{14}CO_2$ release from the reactor.

Discussion of the Peak around 2005

An obvious increase of ^{14}C-specific activities in tree rings can be observed after Qinshan NPP plants II and III began operation in 2002. The range of ^{14}C excess activities in tree rings is 1.8–62.6 Bq/kg C for the period 2003–2009. It reaches a climax of 302.0 Bq/kg C in 2005, which is 26% higher than the background. However, the ^{14}C excess value decreases gradually after 2005.

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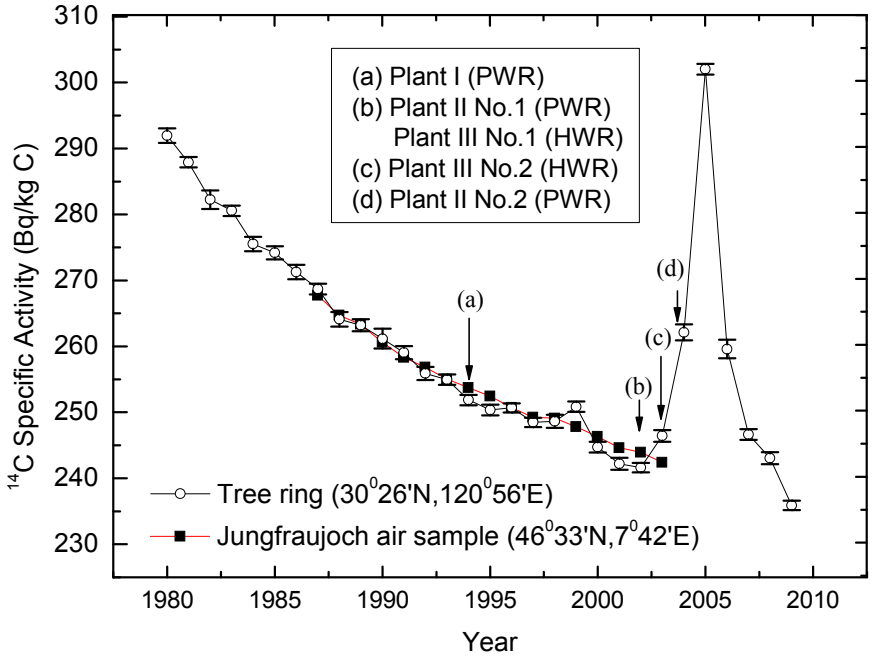

Figure 3 The ^{14}C-specific activity of pine tree rings near Qinshan NPP, compared with ^{14}C activity in the air of the Northern Hemisphere (April to September).

For a clear explanation of the peak, Figure 4 plots the net ^{14}C-specific activities in Qinshan pine rings and the ^{14}C discharge data of Qinshan NPP during the growing season from April to September, considering the climate of the temperate zone. The net ^{14}C specific activities are calculated by subtracting the estimated background values (based on the ^{14}C activities in air of the Northern Hemisphere in 1980–2003) from the gross activities. According to Figure 4, the total ^{14}C discharge of Plant III from April to September is 1~2 orders larger than that of Plant II, owing to the large quantity of heavy water (with ^{17}O) in the heavy-water reactor's moderator system. In addition, the chemical composition of the ^{14}C effluents discharged from the heavy-water reactors in Plant III is mainly $^{14}CO_2$, which can be assimilated directly through photosynthesis by plants. Meanwhile, the main component in the ^{14}C effluents derived from the pressurized water reactors in Plant II is ^{14}C hydrocarbon, which cannot be absorbed by plants. Furthermore, the sample tree was located in the prevailing wind direction of Plant III's stack. Thus, we believe that the ^{14}C enrichment in the tree rings from 2003 to 2009 is mainly attributed to the heavy-water reactors in Plant III.

In Figure 4, the excess ^{14}C values show good correlation with the total ^{14}C discharges from Qinshan NPP Plant III in the growing season. We thus can say the ^{14}C discharge from the heavy-water reactors is the leading reason for the excess ^{14}C in tree rings. Meteorological conditions and electric power production play a minor part in the tree rings' ^{14}C enrichment, for both the electric generation and meteorological conditions remain steady from 2003 to 2009.

It is clear that the ^{14}C discharge in 2005 is abnormally high. This is probably results from a problem with the ^{14}C pollutant management. Amelioration in ^{14}C clearance and discharge have been enforced since 2005. The amount of ^{14}C in gaseous waste was reduced by decreasing the venting rate of the tanks that contain spent ion-exchange resins. The airborne influent was selectively discharged according to the external meteorological conditions. Therefore, most of the influent was

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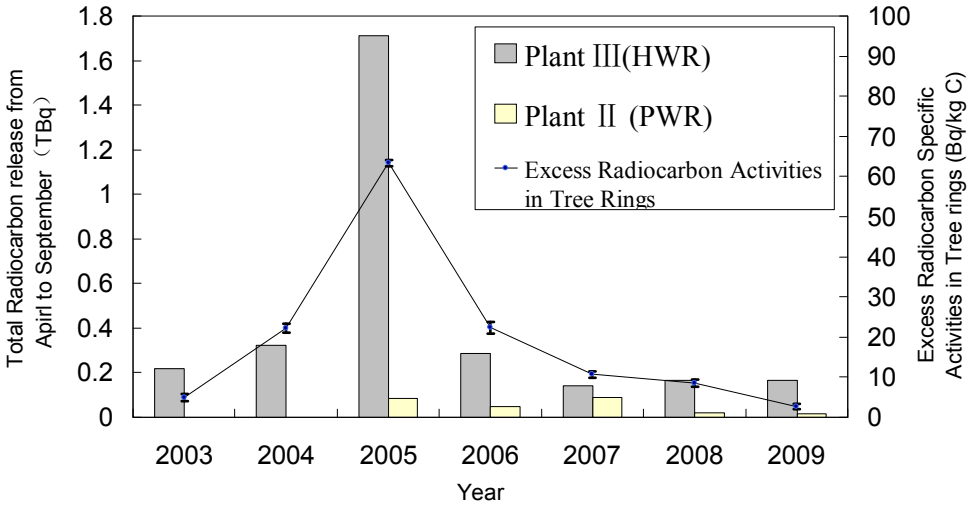

Figure 4 Comparison of excess ^{14}C in tree rings with ^{14}C discharges from Qinshan NPP (unpublished data provided by the nuclear power plant's operator). The ^{14}C discharge data of Plant II before 2004 and Plant I is absent.

blown over the sea, and a decrease in inland ^{14}C concentration was achieved. The ^{14}C-specific activities recorded in tree rings decreased gradually with each passing year, and by 2009 had approached the background level.

CONCLUSION

^{14}C activity near the Qinshan NPP was studied by analyzing annual tree-ring samples (1980–2009) measured by AMS. A comparison between the ^{14}C-specific activities in the tree rings and the atmospheric ^{14}C background in the time period 1994–2002 showed that the ^{14}C discharged from Plant I had a negligible influence on the ^{14}C-specific activities in tree rings under normal operation. The range of ^{14}C excess activity from 2003 to 2009 after Plant II and Plant III's operation was 1.8–62.6 Bq/kg C, and is mainly attributed to Plant III's ^{14}C discharge. The maximal excess value of ^{14}C concentration was found in 2005, and a good correlation was found between the ^{14}C discharge of Plant III in the growing season and the ^{14}C excess value. This study illustrates the effectiveness of using tree rings to trace previous discharge and to monitor the operating conditions of nuclear facilities.

ACKNOWLEDGMENTS

We thank the AMS group of the Institute of Heavy Ion Physics, Peking University, China, for performing all the AMS measurements. This work was supported by the Environmental Protection Department of Zhejiang Province, China. We are grateful to Xuemei Shao for dating the tree rings. All the ^{14}C sample pretreatments were carried out at the MOE Laboratory for Earth Surface Process, College of Urban and Environmental Sciences, Peking University, China.

REFERENCES

Dias CM, Santos RV, Stenström K, Nícoli IG, Corrêa RS, Skög G. 2008. ^{14}C content in vegetation in the vicinities of Brazilian nuclear power reactors. *Journal of Environmental Radioactivity* 99(7):1095–101.

Hertelendi E, Uchrin G, Ormai P. 1989. ^{14}C release in various chemical forms with gaseous effluents from Paks Nuclear Power Plant. *Radiocarbon* 31(3):754–61.

Hoefs J. 1987. *Stable Isotope Geochemistry.* Berlin: Springer-Verlag.

Hoper ST, McCormac FG, Hogg AG, Higham TFG, Head MJ. 1998. Evaluation of wood pretreatments on oak and cedar. *Radiocarbon* 40(1):45–50.

IAEA. 2004. Management of waste containing tritium and carbon-14. Technical Report Series No. 421. Vienna: International Atomic Energy Agency.

Isogai K, Cook GT, Anderson R. 2002. Reconstructing the history of ^{14}C discharges from Sellafield: part 1-atmospheric discharges. *Journal of Environmental Radioactivity* 59(2):207–22.

Kim CK, Lee SK, Rho BH, Lee YG. 2000. Environmental distribution and behavior of ^{3}H and ^{14}C around Wolsong Nuclear Power Plant. *Health Physics* 78(6): 693–9.

Koarashi J, Davis PA, Galeriu D, Melintescu A, Saito M, Siclet F, Uchida S. 2008. Carbon-14 transfer into rice plants from a continuous atmospheric source: observations and model predictions. *Journal of Environmental Radioactivity* 99(10):1671–9.

Levin I, Kromer B. 1997. Twenty years of atmospheric $^{14}CO_2$ observations at Schauinsland station, Germany. *Radiocarbon* 39(2):205–18.

Levin I, Kromer B. 2004. The tropospheric $^{14}CO_2$ level in mid-latitudes of the Northern Hemisphere (1959–2003). *Radiocarbon* 46(3):1261–72.

Liu KX, Ding XF, Fu DP, Pan Y, Wu XH, Guo ZY, Zhou LP. 2007a. A new compact AMS system at Peking University. *Nuclear Instruments and Methods in Physics Research B* 259(1):23–6.

Liu KX, Ding XF, Fu DP, Pan Y, Wu XH, Guo ZY, Zhou LP. 2007b. The AMS measurement of VIRI samples at Peking University. *Quaternary Sciences* 27(3):469–73. In Chinese.

Magnusson Å, Stenström K, Adliene D, Adlys G, Dias C, Rääf C, Skog G, Zakaria M, Mattsson S. 2007. Carbon-14 levels in the vicinity of the Lithuanian nuclear power plant Ignalina. *Nuclear Instruments and Methods in Physics Research B* 259(1):530–5.

Mazeika J, Petrosius R, Pukiene R. 2008. Carbon-14 in tree rings and other terrestrial samples in the vicinity of Ignalina nuclear power plant, Lithuania. *Journal of Environmental Radioactivity* 99(2):238–47.

McNamara N, McCartney M. 1998. A new estimate of atmospheric ^{14}C discharges from Sellafield. *Journal of Environmental Radioactivity* 41:1–10.

Molnár M, Bujtás T, Svingor E, Futó I, Svetlík I. 2007. Monitoring of atmospheric excess ^{14}C around Paks Nuclear Power Plant, Hungary. *Radiocarbon* 49(2): 1031–43.

Povinec PP, Chudý M, Šivo A, Šimon J, Holý K, Richtáriková M. 2009. Forty years of atmospheric radiocarbon monitoring around Bohunice nuclear power plant, Slovakia. *Journal of Environmental Radioactivity* 100(2):125–30.

Roussel-Debet S, Gontier G, Siclet F, Fournier M. 2006. Distribution of carbon 14 in the terrestrial environment close to French nuclear power plants. *Journal of Environmental Radioactivity* 87(3):246–59.

Stenström K, Skog G, Thornberg C, Erlandsson B, Hellborg R, Mattsson S, Persson P. 1998. ^{14}C levels in the vicinity of two Swedish nuclear power plants and at two "clean air" sites in Sweden. *Radiocarbon* 40(1): 433–8.

Uchrin G, Hertelendi E, Volent G, Slavik O, Morávek J, Kobal I, Vokal B. 1998. ^{14}C measurements at PWR-type nuclear power plants in 3 middle European countries. *Radiocarbon* 40(1):439–46.

Veres M, Hertelendi E, Uchrin G, Csaba E, Barnabás I, Ormai P, Volent G, Futó I. 1995. Concentration of radiocarbon and its chemical forms in gaseous effluents, environmental air, nuclear waste and primary water of a pressurized water reactor power plant in Hungary. *Radiocarbon* 37(2):497–504.

Vokal B, Kobal I. 1997. Radiocarbon releases at the Krško nuclear power plant. *Radiocarbon* 39(3):285–92.

Xu XM, Trumbore SE, Zheng SH, Southon JR, McDuffee KE, Luttgen M, Liu JC. 2007. Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: reducing background and attaining high precision. *Nuclear Instruments and Methods in Physics Research B* 259(1):320–9.

Yang YH, Kang DW, Lee GB. 2010. Evaluation of ^{14}C release characteristics in Korean standard pressurized water reactor. *Nuclear Engineering and Design* 240(10):3611–5.