Radiocarbon, Vol 56, Nr 3, 2014, p 1107–1114 DOI: 10.2458/56.17914

^{14}C DISTRIBUTION IN ATMOSPHERIC AND AQUATIC ENVIRONMENTS AROUND QINSHAN NUCLEAR POWER PLANT, CHINA

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ABSTRACT. Atmospheric CO_2 and aquatic water samples were analyzed to evaluate the environmental ^{14}C enrichment due to operation of the Qinshan nuclear power plant (NPP), where two heavy-water reactors and five pressurized-water reactors are employed. Elevated ^{14}C-specific activities (2–26.7 Bq/kg C) were observed in the short-term air samples collected within a 5-km radius, while samples over 5 km were close to background levels. The ^{14}C-specific activities of dissolved inorganic carbon (DIC) in the surface seawater samples ranged from 196.8 to 206.5 Bq/kg C (average 203.4 Bq/kg C), which are close to the background value. No elevated ^{14}C level in surface seawater was found after 20 years of operation of Qinshan NPP, indicating that the ^{14}C discharged was well diffused. The results of the freshwater samples show that excess ^{14}C-specific activity (average 17.1 Bq/kg C) was found in surface water and well water samples, while no obvious ^{14}C increase was found in drinking water (groundwater and tap water) compared to the background level.

INTRODUCTION

Radiocarbon is produced not only naturally by neutron interaction with nitrogen in the atmosphere, but also by anthropogenic activities: atmospheric nuclear weapon tests and the nuclear power industry. A series of bomb tests, which happened mainly in the 1950s and 1960s, released 220 PBq ^{14}C to the environment (IAEA 2004). After the nuclear moratorium on atmospheric nuclear bomb tests signed in 1963, the enhanced ^{14}C level has been declining to the natural level (Kim et al. 2000). ^{14}C is produced in nuclear power reactors by $^{14}N(n, p)^{14}C$ reactions with nitrogen in fuels, moderators, and coolants as a primary impurity; by $^{17}O(n, \alpha)^{14}C$ reactions in oxide fuels, moderators, and coolants; and by $^{13}C(n, \gamma)^{14}C$ reactions in graphite moderators (Yim and Caron 2006; Povinec et al. 2008). The mean ^{14}C production rates for pressurized-water reactors (PWRs) and heavy-water reactors (HWRs) are 1.48 and 10.13 TBq GW_e^{-1} yr^{-1}, respectively (IAEA 2004).

^{14}C produced in nuclear power reactors is mainly disposed in the solid radioactive waste, but still a small quantity of ^{14}C is released in gaseous and liquid effluents. Previous studies have shown that nearly all ^{14}C is emitted in the form of $^{14}CO_2$, except in PWRs where ^{14}C is mainly released as $^{14}CH_4$ (Hertelendi et al. 1989; Yim and Caron 2006). ^{14}C in aqueous liquid waste is usually in chemical forms of carbonate and bicarbonate, depending on the solution pH (IAEA 2004). Investigations of ^{14}C activity around nuclear power stations have found that elevated ^{14}C concentrations were observed in environmental samples (Magnusson et al. 2004; Molnár et al. 2007; Varlam et al. 2007; Povinec et al. 2009).

The Qinshan nuclear power plant (NPP), with an electrical output of 4156 MW_e, consists of five PWRs and two HWRs. The two HWRs were expected to be the main contributor of ^{14}C enrichment in the surrounding area (Wang et al. 2013). In previous studies, ^{14}C spatial and temporal distribution in the terrestrial environment was investigated by analyzing vegetation samples, and the internal dose of ^{14}C by ingestion of foodstuffs was evaluated (Wang et al. 2012, 2013). The aim of the present investigation was to study a spatial distribution of ^{14}C in the atmospheric and aquatic environment where ^{14}C gaseous and liquid waste was directly released. This study includes the ^{14}C measurements of CO_2 in air, as well as the ^{14}C of dissolved inorganic carbon (DIC) in water.

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MATERIAL AND METHODS

Site Description

Qinshan NPP, located in Haiyan County, Zhejiang Province, in southeast China, comprises three power plants, referred to as Plant I, Plant II, and Plant III. The 300-MW_e PWR reactor of Plant I began operation in April 1994. Furthermore, four PWR reactors (600 MW_e) of Plant II began commercial operation in April 2002, May 2004, August 2010, and April 2012. Plant III, which used two HWRs (CANDU type) of 728 MW_e, started to operate in December 2002 and June 2003. The ^{14}C released from Qinshan NPP was through airborne and liquid discharge. The positions of the venting stacks and outlets of each plant are shown in Figures 1 and 2. The active liquid waste of Qinshan NPP was discharged discontinuously, depending on the running condition of the plant.

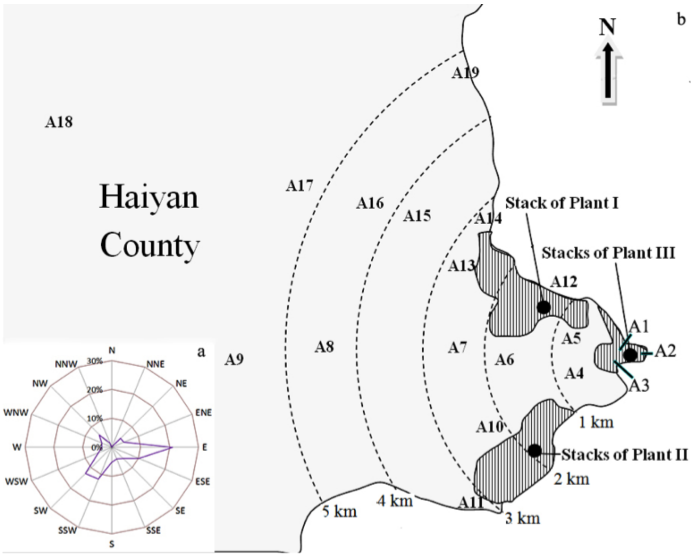

Figure 1 (a) Wind frequency at the Qinshan site in the period of air sampling (from 5 to 12 August 2011). (b) Sites of collection of the air samples at the Qinshan NPP.

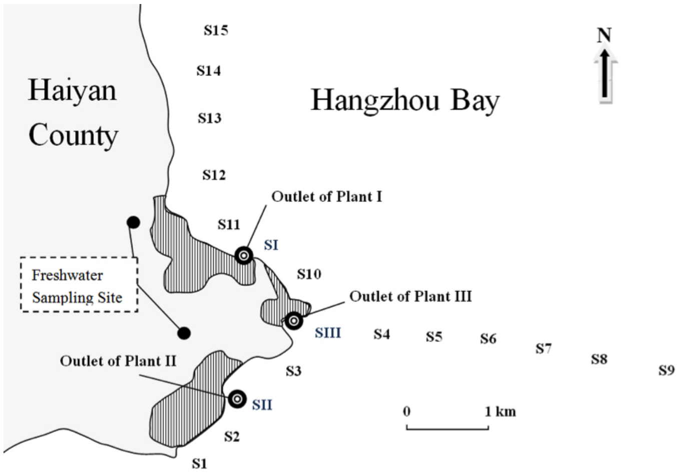

Figure 2 Locations of the sampling sites where seawater samples were collected on 28 May 2013.

The terrain around Qinshan NPP is basically flat, except for the small hill (170 m high) named Qinshan that lies to the west of the Plant III stacks (samples A4 and A5 in Figure 1 were located on the hill). Meteorological data were obtained from three meteorological monitoring stations within the Qinshan site.

Sample Collection

To determine the ^{14}C spatial distribution in local air, sampling was done at a flow rate of 1.5 L/min for 3 hr using CO_2 collection equipment, in which CO_2 was absorbed in two bubbling bottles with 500 mL of NaOH solution (2 mol/L) with the collection efficiency better than 98% (Yang et al. 1997). During 5–12 August 2011, 19 atmospheric CO_2 samples were collected in the vicinity of Qinshan NPP (Figure 1b), taking into account wind direction, the distance to the stacks of Plant III, and the availability of sample collection. During the 1-week sampling period, ^{14}C was continuously discharged from three plants under steady meteorological conditions, where seven reactors were all in operation. Two reference samples were collected at a site 20 km from Qinshan NPP, an area outside of the plant's ^{14}C contamination. Reference sampling points were situated in areas with an estimated similar density of buildup and with similar intensity of local road transport.

In May 2013, surface seawater samples were collected from the Qinshan site for DIC ^{14}C analyses using two 1-L glass bottles, following the sampling procedure described by Hinger et al. (2010). In order to evaluate the DIC ^{14}C concentrations in the outlets of Qinshan NPP, possible ^{14}C enrichment near the shore, and ^{14}C diffusion in seawater, 18 surface seawater samples were distributed around Qinshan NPP (Figure 2). Freshwater samples, including underground water, surface water (river water and pool water), and tap water, were collected in a village next to Qinshan NPP (Figure 2). The reference samples of water, whose ^{14}C concentrations were used as background, were collected at Jiading in Shanghai (100 km away). Both sampled rivers do not cross the karst area.

PRETREATMENT

Air Sample

^{14}C in the NaOH solution was recovered as $BaCO_3$ precipitate by adding $BaCl_2$ and NH_4Cl according to the method of Yang et al. (2010). After filtrating and drying, about 20 mg of $BaCO_3$ was decomposed with H_3PO_4 to re-evolve CO_2, which was then transferred to a vacuum system for purification and quantification. This was followed by transferring CO_2 (approximately 1 mg C) to a reaction tube containing zinc (Aldrich, #324930), titanium hydride (Alfa Aesar, #12857), and Fe catalyst (Alfa Aesar, 350 mesh, #39813). The reaction tube was sealed and heated at 540°C in a furnace for 8 hr, and graphite formed at the surface of the catalyst (Xu et al. 2007).

Water Sample

As shown in Figure 3, an apparatus extracting DIC from water was set up and applied to pretreat the water samples. The extracting device was connected to a vacuum system; the pressure of the entire system can reach 2 Pa. The extraction procedure comprised the following. About 300 mL of water sample and appropriate phosphoric acid were introduced into the bunsen flask and separating funnel (4 and 5 in Figure 3) in a glove box. After sealing the valves, the vessel was then connected to the extracting system, followed by pumping the vacuum system up to the valve of the glass vessel. In the next step, the valve of the nitrogen cylinder was opened and the flow rate of N_2 was controlled at 450 mL/min. The water sample was acidified and heated (at 80°C) to release CO_2, which was then transferred to the water trap by purified N_2 gas. The last stage was needed to convert CO_2 to graphite, similar to the pretreatment of the air samples described above.

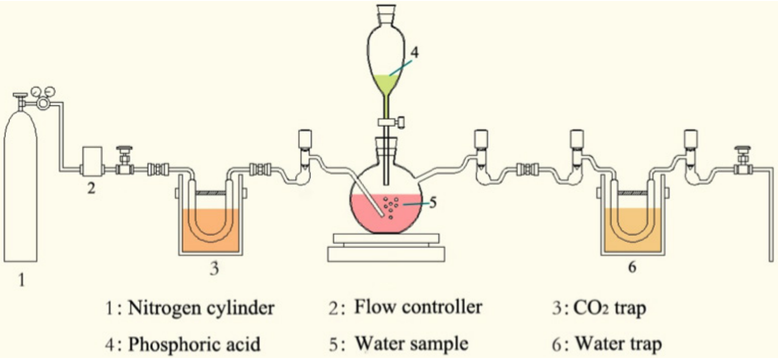

Figure 3 Diagram of the DIC extraction device for water samples

Measurement

^{14}C analysis was performed at the 0.6MV accelerator mass spectrometry (AMS) facility of Peking University, with a measurement accuracy better than 0.4% and a machine background lower than 0.03 pMC (Liu et al. 2007). Blank coal samples and NIST oxalic acid standard (SRM-4990C) samples were also graphitized and measured at the same time. After isotopic fractionation correction (Stuiver and Polach 1977), the final results are presented as normalized specific activities (Bq/kg C) (Wang et al. 2012) and Δ^{14}C (‰) (Roussel-Debet et al. 2006).

RESULTS AND DISCUSSION

Air Sample

As shown in Table 1, the average ^{14}C value of two reference air samples is 231.2 Bq/kg C (15.2‰ in Δ^{14}C), which is lower than the western Europe ^{14}C background (237.0 Bq/kg C in specific activity, 40.1‰ in Δ^{14}C) measured at Schauinsland station (47°55′N, 7°54′E) in August 2011 (Levin et al. 2013). The disagreement of these two values is probably due to the disturbance of regional ^{14}C-free fossil fuel CO_2 emission. To eliminate the regional CO_2 influence, the ^{14}C value of the reference samples was used as the background in the present study.

The ^{14}C results of the air samples (Table 1) show that the specific activity ranges from 231.2 to 257.9 Bq/kg C (average 239.5 Bq/kg C). Compared to the background, excess or equal levels of ^{14}C were found in all sampling sites. The maximum excess ^{14}C-specific activity of 26.7 Bq/kg C (11.5% above the background) was observed in A3, which was located in the prevailing wind direction of the 55-m-high stack of Plant III.

In a previous study of vegetation samples (Wang et al. 2013), it was well demonstrated that the diffusion of ^{14}C discharged from Qinshan NPP was predominantly affected by meteorological conditions. This conclusion is further validated by this study. In the region mainly contaminated by Plant III–derived ^{14}C (radius <3 km), samples located downwind in the eastern direction have higher ^{14}C concentrations than those of other directions, though the distances to Plant III stack were almost the same (A5>A4>A12, A7>A13>A10 in specific activity). As shown in Table 1, ^{14}C values of the samples collected beyond 5 km (A9, A17, and A18) are close to the background, indicating that the ^{14}C-influenced zone of Qinshan NPP was limited to a 5-km radius in this investigation.

In contrast to the atmospheric CO_2, data of vegetation samples collected at Qinshan in 2010 show a higher maximum excess value (18.1% above the background) and larger range of influence (6.5 km radius) (Wang et al. 2013). The discrepancy is probably attributable to different sampling periods of these two kinds of sample. While atmospheric CO_2 samples represent a 1-week sampling period, the plant moss represents a 1-yr assimilation period. Since both ^{14}C emission and meteorological conditions do not remain steady in a year, the annual average concentrations should be different from 1-week average concentrations. Similar discrepancies between short-term air and vegetation data were observed in studies of other countries (Milton et al. 1995; Dias et al. 2009).

Table 1 ^{14}C concentrations in air samples collected at Qinshan site (from 5 to 12 August 2011).

Sample ID	^{14}C-specific activity (Bq/kg C)	1σ error	Δ^{14}C (‰)	1σ error
A1	242.8	0.7	66.2	3.1
A2	237.7	0.9	43.8	4.0
A3	257.9	0.7	132.5	3.1
A4	243.1	0.8	78.5	3.5
A5	245.6	0.8	67.5	3.5
A6	249.8	1.0	96.9	4.4
A7	241.6	0.7	60.9	3.1
A8	233.2	0.8	24.0	3.5
A9	232.2	0.7	19.6	3.1
A10	236.5	1.0	38.5	4.4
A11	238.1	0.7	45.5	3.1
A12	243.0	0.8	67.1	3.5
A13	239.6	0.8	52.1	3.5
A14	242.2	0.7	63.5	3.1
A15	235.9	0.8	35.9	3.5
A16	233.3	0.7	24.5	3.1
A17	231.2	0.9	15.2	4.0
A18	232.3	0.7	20.1	3.1
A19	233.7	1.1	34.6	3.5
Background[a]	231.2	0.9	15.2	4.0

a: average ^{14}C values of two air samples collected at reference site.

Water Sample

Tables 2 and 3 show the ^{14}C concentrations in surface seawater and freshwater samples, respectively. The ^{14}C-specific activities in the seawater samples were in the range of 196.8–206.5 Bq/kg C (average 203.4 Bq/kg C). Compared to the background value (205.9 ± 1.8 Bq/kg C) measured from two reference samples, no obvious difference was observed.

As indicated by Figure 4, the ^{14}C values of the samples collected near the coast were close to the background, while samples whose sites were not adjacent to the coast had lower ^{14}C values. Considering that the reference samples were collected near the coast, it can be concluded that coastal surface seawater samples had higher ^{14}C concentrations, in comparison with the samples collected far away from the coast. A possible explanation is that the ^{14}C concentrations in coastal surface seawater samples could be influenced by terrestrial freshwater samples whose ^{14}C levels were higher (Table 3) (Shen et al. 2004).

Table 2 ^{14}C concentrations in seawater samples collected in May 2013 in the vicinity of Qinshan NPP.

Sample ID	^{14}C-specific activity (Bq/kg C)	1σ error	$\Delta^{14}C$ (‰)	1σ error
S1	204.7	1.5	–101.1	6.6
S2	205.9	1.4	–95.9	6.1
S3	206.5	1.3	–93.2	5.7
S4	204.4	1.4	–102.4	6.1
S5	198.8	1.0	–127.0	4.4
S6	199.5	1.2	–124.0	5.3
S7	196.8	1.7	–135.8	7.5
S8	198.2	1.6	–129.7	7.0
S9	201.7	1.3	–114.3	5.7
S10	204.2	1.5	–103.3	6.6
S11	206.0	1.4	–95.4	6.1
S12	203.8	1.3	–105.1	5.7
S13	206.1	1.2	–95.0	5.3
S14	205.7	1.0	–96.7	4.4
S15	205.5	1.1	–97.6	4.8
SI	205.9	1.2	–95.9	5.3
SII	202.2	1.3	–112.1	5.7
SIII	206.1	1.2	–95.0	5.3
Background[a]	205.9	1.3	–95.9	5.7

a: average ^{14}C values of two seawater samples collected at reference site.

Table 3 Results of freshwater samples around Qinshan NPP collected in May 2013.

	Qinshan site		Reference site[a]	
Sample	^{14}C-specific activity (Bq/kg C)	$\Delta^{14}C$ (‰)	^{14}C-specific activity (Bq/kg C)	$\Delta^{14}C$ (‰)
Surface water1	225.1 ± 1.2	–11.5 ± 5.3	207.3 ± 1.5	–89.7 ± 6.6
Surface water2	232.0 ± 1.4	18.8 ± 6.1	210.1 ± 0.8	–77.4 ± 3.5
Well water	220.6 ± 1.2	31.3 ± 5.3	208.9 ± 1.1	–82.7 ± 4.8
Groundwater	235.3 ± 1.8	33.2 ± 7.9	236.9 ± 2.1	40.3 ± 9.2
Tap water	204.6 ± 1.3	–101.6 ± 5.7	194.2 ± 1.5	–147.2 ± 6.6

[a] Located 100 km from the Qinshan site.

The liquid waste of Qinshan NPP was discharged discontinuously, but unfortunately we failed to obtain the accurate discharge time, leading to the fact that no liquid waste was released during the sampling period. As a consequence, the results of samples SI, SII, and SIII, which were collected to evaluate the ^{14}C levels in the outlets of Qinshan NPP, show no increase in ^{14}C concentration. It can be concluded from the results that the ^{14}C discharged previously was diluted and diffused well, resulting in no ^{14}C enrichment in seawater observed.

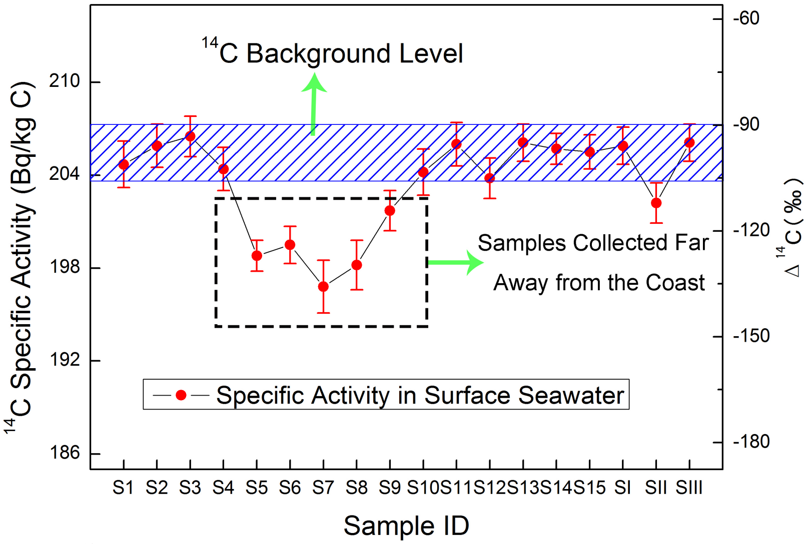

Figure 4 ^{14}C concentration distribution in surface seawater samples

For the freshwater samples collected at Qinshan, elevated ^{14}C concentrations were found in the surface water and well water, compared to the values of reference samples. The excess values are probably caused by the atmosphere-water gas exchange process (Shen et al. 2004), through which the $^{14}CO_2$ released from Qinshan NPP finds its way into water. The ^{14}C levels in underground water and tap water samples are similar to those collected at the reference site, resulting in no obvious increase in ^{14}C concentration at the Qinshan site.

CONCLUSION

The ^{14}C concentrations in the vicinity of Qinshan NPP have been studied by analyzing air and water samples using AMS. Enhanced ^{14}C values were observed in the air samples, which were collected within a 5-km radius in this short-term air investigation. The maximum ^{14}C excess value was 26.7 Bq/kg C, 11.5% higher than the background. The results of surface seawater samples show no enhanced activity, indicating that the ^{14}C discharged previously diffused well and no enrichment in the seawater existed after 20 yr of Qinshan NPP operation. In comparison with the reference site, an average of 17.1 Bq/kg C excess ^{14}C-specific activity was observed in the surface water and well water collected at Qinshan, which is probably attributed to the atmosphere-water gas exchange. No obvious enhanced ^{14}C activity in drinking water (underground water and tap water) was found in this study.

ACKNOWLEDGMENTS

All ^{14}C analyses were carried out by the AMS group of the Institute of Heavy Ion Physics, Peking University. We are grateful to Professor Kexin Liu and Xingfang Ding for their help. All the water samples were pretreated at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. The authors would like to thank Wei Liu and Guanghua Wang for their cooperation on this project.

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