Radioactivity of seawater nearby Daya Bay Nuclear Power Station

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Abstract. The radioactivity of seawater nearby Daya Bay NPPs was introduced in this paper. The average annual concentrations of 90Sr and 137Cs ranged from 0.55~2.38 and 0.81~4.68 Bq m⁻³ respectively during 1993~2015. The average annual concentration range of 3H is 0.8~7 Bq L⁻¹. The concentration range of 14C is 7.6~8.6 Bq m⁻³, and the concentration of 3H and 14C is higher than that of the reference location or the background, but with no cumulative effect. The concentrations of 90Sr and 137Cs in seawater have no obvious relationship with the nuclear liquid effluent discharging. The average concentrations of 238U and 232Th were 24.6±10.6 and 18.1±7.5 Bq m⁻³ respectively during 2000~2008.

1. Introduction
Natural nuclides 40K, U, Th and their decay products, cosmogenic nuclides 14C and 3H, released nuclides 90Sr and 137Cs due to nuclear test or accident in last century; moreover, these radionuclides appear in the seawater if without the influence of artificial radionuclides sources.

Dayawan Nuclear Power Station (GNPS), Lingao Nuclear Power Station I (LNPS I) and Lingao Nuclear Power Station II (LNPS II) co-locate in the Daya Bay, 6 REP NPPs started to generate electricity in 1994, 2002 and 2010 respectively. In normal operating state, liquid effluent rarely contains 90Sr, 137Cs, 124Sb, 58Co and 54Mn, and the activity concentrations of 124Sb, 58Co and 54Mn are usually below the detection limit in West Daya Bay. 110mAg is rarely detected since 2009 when silver flange was replaced by other materials, while because of the influence of nuclear explosion test and accident such as chernobyl, 90Sr, 137Cs could still be detected. 3H and 14C are accounted for a great proportion in liquid effluent, in the same time they naturally present in the environment.

In order to evaluate the effect of liquid effluent from nuclear power plants, 90Sr, 3H, 14C, γ nuclides (such as 137Cs, 124Sb, 56Co, 58Co, 54Mn, 110mAg) and 238U, 232Th were monitored in seawater in Daya Bay.

In this paper, the activity concentrations of 90Sr and 137Cs are accounted and analyzed during different stages of 6 REP reactors in Daya Bay from 1993 to 2015. Also, the activity concentration of 3H in 1993-2014, the concentration of U and Th, the activity of 14C in 2015 were presented.

2. Experimental part

2.1. Monitoring scheme
The radioactivity of seawater in West Daya Bay has been surveyed since 1993. The emission location was moved towards the east for about 1 km in order to reduce the liquid effluent discharge influence in 2000. So the sampling point location amount varied from the original 18 to 10 for better optimizing...
monitoring of seawater in West Daya Bay, which also strengthened the monitoring of Dapeng’ao area which has the weakest ability of dilution.

Before 2002, we set 18 sampling point locations which numbered from W1 to W18. The sampling frequency was 3~4 times per year. $^3$H was analyzed in all samples, while $^{90}$Sr and $\gamma$ nuclides were only analyzed in the locations of W2, W4, W9, W11, W12, W13 and W14. The distribution of the monitoring point diagram is shown in the left panel of figure 1.

We optimized the sampling point location amount to 10 in 2002, which were marked as L1~L10. Every year we took samples 2 or 4 times. $^3$H was analyzed in all samples. But $^{90}$Sr and $\gamma$ nuclides were only analyzed in L1, L4, L9 and L10. The right panel of figure 1 gives the distribution of the monitoring point location diagram.

The monitoring of $^{14}$C began at 2015, for which the monitoring points locate in L1, L4, L10 and the liquid effluent discharge channel.

![Figure 1](image)

Figure 1. Sampling point locations for tritium monitoring nearby NPPs before 2001 (left panel) and after 2002 (right panel).

2.2. Analysis method

In this paper, $^3$H, $^{14}$C, $^{90}$Sr, $^{137}$Cs, U and Th have been monitored using different methods follow state standard or method published in paper. Table 1 showed the methods used in this paper.

| Radionuclide | Method | Reference          |
|--------------|--------|--------------------|
| $^3$H        | analytical method of tritium in water | GB12375-90          |
| $^{14}$C     | liquid scintillation               | Guo Guiyin’s approach [1] |
| $^{90}$Sr    | Extraction chromatography by di-(2-ethylhexyl) phosphoric acid | GB6764-86           |
| $^{137}$Cs, U and Th | adsorption-coprecipitation method | Den Fei’s approach [2] |

GB12375-90 analytical method of tritium in water was used to detect $^3$H. The samples used for $^3$H measurement are not concentrated by electrolysis. For monitoring $^3$H, the low background liquid scintillation equipment Quantulus 1220 was used. For this equipment, the background turns to be lower than 0.7 cpm and the detection efficiency is greater than 60%. The detection limit was about 1.2 Bq L$^{-1}$ if the measurement time was set 24 h.

The monitoring method for $^{14}$C followed Guo Guiyin’s approach [1]: take 20 L pellucid samples to the four neck flask, stirring with magnetic stirrer when adding sulfuric acid. CO$_2$ origins from inorganic carbon were carried into the collecting bottle by N$_2$; K$_2$S$_2$O$_8$, FeSO$_4$ and H$_2$O$_2$ were added respectively and then collect CO$_2$ from organic carbon. Finally, the sample was measured by method of liquid scintillation with Carb-Sorb E absorption CO$_2$.

Radiochemical analysis of strontium-90 in water precipitation by fuming nitric acid GB6764-86 and Radiochemical analysis of strontium-90 in water extraction chromatography by di-(2-ethylhexyl) phosphoric acid GB6766-86 were used for the detect of $^{90}$Sr, "GB6764-86" and "GB6766-86" were
updated by "HJ815-2016" Radiochemical analysis of strontium-90 in water and ash of biological samples.

MnO₂, produced by chemical reaction between H₂O₂ and KMnO₄, along with K₂CoFe(CN)₅, were used for the precessing of γ radionuclides like ¹³⁷Cs, U and Th in seawater samples by adsorption-coprecipitation method [2].

When processing statistical analysis, sample activity is taken into consideration by 1/2 of the detection limit in case where activity is smaller than detection limit. The number of calculating samples is m/n, while n represents total number of samples and m refers to the amount of the samples which possess an activity higher than detection limit. The activity would be provided in the form of A±X, where A is means activity and X represents to the uncertainty caused by the counting error of the instrument during the measuring process.

3. Results and discussions

3.1. Artificial radionuclides ⁹⁰Sr, ¹³⁷Cs, et al

The activity concentration of ⁹⁰Sr and ¹³⁷Cs in the seawater of West Daya Bay among 1993~2016 is illustrated in table 2, which gives a value varies between 0.55~2.38, 0.81~4.68 Bq·m⁻³ respectively, while the maximum value in one sample turns out to be 4.70 and 7.05 Bq·m⁻³ respectively. These maximums appeared between 1993~1996 when NPPs was in pilot run. According to the NPP operation record, abnormal emissions took place during 1995~1997 which were mainly caused by maintenance and other activities. During this period, in some patches of seawater a trace of ¹²⁴Sb,
\(^{110}\text{m}\text{Ag}\) and \(^{58}\text{Co}\) was detected. As for example, the activity of \(^{124}\text{Sb}\) and \(^{58}\text{Co}\) in four samples in July 1994 ranged 0.55–2.38 and 0.81–4.68 respectively, the \(^{110}\text{m}\text{Ag}\) activity of four water samples in April 1995 and three samples in 1997 varied between 1.1–23.3 and 1.52–1.67 respectively [3], while for the rest samples, all the activities were below detection limit. In conclusion, the phenomenon that \(^{137}\text{Cs}\) activity turned out to be much higher during this period may relate to the abnormal emissions of NPPs. Also, the liquid effluent emissions of NPPs show no significant influence in \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\) concentrations through figure 2, which well satisfied the natural decay law, in West Daya Bay.

![Figure 2. Annual average concentration of \(^{137}\text{Cs}\) and \(^{90}\text{Sr}\) in seawater nearby Daya Bay NPPs.](image)

Table 3 and figure 3 give the \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\) activities for the effluent that has not been well diluted. The results in tables 3 and 2 do not tell much difference, which indicates that \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\) give a trace amount in the NPPs liquid effluent. Figure 4 showed the relationship between annual emission and specific activity of \(^{137}\text{Cs}\) in West Daya Bay seawater samples. When comparing data between tables 2 and 3 a conclusion could be made that the operation of LNPS I and LNPS II does not emit a detectable amount of \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\).

**Table 3. Activity of \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\) in the effluent of NPPs.**

| Date (year) | \(^{90}\text{Sr}\) (Bq m\(^{-3}\)) samples | range | average | \(^{137}\text{Cs}\) (Bq m\(^{-3}\)) samples | range | average |
|------------|--------------------------------|-------|---------|--------------------------------|-------|---------|
| 1999       | 3/3 | 1.00-1.80 | 1.40±0.40 | 3/3 | 1.59-3.36 | 2.54±0.89 |
| 2000       | 3/3 | 0.98-1.70 | 1.39±0.37 | 3/3 | 2.14-2.53 | 2.37±0.20 |
| 2001       | 3/3 | 0.46-2.82 | 1.46±1.22 | 3/3 | 1.92-3.60 | 2.48±0.97 |
| 2002       | 1/1 | 1.2 | 1.2 | 3/3 | 1.29-2.90 | 2.23±0.84 |
| 2003       | 2/2 | 0.92-1.41 | 1.17±0.35 | 2/3 | <1.6-2.08 | 1.60±0.70 |
| 2007       | 3/3 | 0.87-1.20 | 1.01±0.17 | 0/3 | <1.6 | <1.6 |
| 2008       | 3/3 | 0.66-0.88 | 0.80±0.12 | 3/4 | <1.0-1.87 | 1.26±0.54 |
Figure 3. Annual average concentration of $^{137}$Cs and $^{90}$Sr in the effluent of NPPs.

Figure 4. Annual emission and specific activity of $^{137}$Cs in West Daya Bay seawater sample.

3.2. $^3$H and $^{14}$C in West Daya Bay seawater
Due to the lack of relevant method and standard, the $^{14}$C activity monitoring in the seawater nearby Daya Bay Nuclear Power Station was launched until 2015. The result shows that the activity concentrations of $^{14}$C were 15.6, 7.6, 8.5, 8.6 Bq·m$^{-3}$ for seawater monitoring point locations discharge channel, L1, L4, L10 respectively, as a comparison, the value turns to be 5.5 Bq·m$^{-3}$ for seawater in
reference location Maoming, which locates several hundred kilometers from Daya Bay [internal information]. The \(^{14}\text{C}\) activity is higher in no well diluted discharge channel and in L4/L10 which have a weak dilution capacity, than in L1 which possesses a strong dilution capacity. Activity concentration of \(^{14}\text{C}\) in West Daya Bay seawater is more than 50% higher than that in the reference location Maoming.

The activity of \(^{3}\text{H}\) in West Daya Bay seawater ranges from a value below 0.6 to 70.7 Bq \(\text{L}^{-1}\), while the annual average value ranges 0.8–7 Bq \(\text{L}^{-1}\). The annual average activities of \(^{3}\text{H}\) are three to ten times higher than the background activities, which might be caused by the emission of liquid effluent from NPPs, the difference between sampling time and discharge time. No concentration effect of \(^{3}\text{H}\) appears facing the operations of the 6 NPPs [4], which indicates that the dilution-exchange capacity of West Daya Bay seawater satisfies the requirements on the discharge of liquid effluent.

3.3. Concentrations of \(^{238}\text{U}\) and \(^{232}\text{Th}\)

The method used to monitor \(^{238}\text{U}\) and \(^{232}\text{Th}\) is introduced in the literature [2]. The average value of \(^{238}\text{U}\) and \(^{232}\text{Th}\) were 24.6±10.6, 18.1±7.5 Bq \(\text{m}^{-3}\) in 177 samples sampled in West Daya Bay during 2000-2008 respectively. Convert to mass concentration of U and Th were 2.0±0.86, 4.47±1.85μg \(\text{L}^{-1}\) respectively (The activity of \(^{238}\text{U}\) in natural uranium is 12.35 kBq \(\text{g}^{-1}\), the activity of \(^{232}\text{Th}\) in natural thorium is 4.046 kBq \(\text{g}^{-1}\).The concentration of U is 3.1-3.9 g \(\text{L}^{-1}\) reported in the literature [5, 6], which is higher than the previous values. The main reason is that the samples were monitored before the decay balance between \(^{238}\text{U}\) and its progeny \(^{234}\text{Th}\), but take the activities of \(^{238}\text{U}\) deduced from \(^{234}\text{Th}\). The concentration of U was 2.82 μg \(\text{L}^{-1}\) in seawater from West Daya Bay detected by using sodium polyphosphate as fluorescence enhancement agent while the verified value was 2.83 μg \(\text{L}^{-1}\) by ICP-MS [7]. This value was a little lower than that in the literature [6].

4. Conclusion

The average annual concentration of \(^{86}\text{Sr}, ^{137}\text{Cs}\) and \(^{3}\text{H}\) ranged 0.55–2.38, 0.81–4.68 and 0.8–7 Bq \(\text{L}^{-1}\) respectively during 1993–2015, the concentration ranges of \(^{14}\text{C}\) was 7.6–8.6 Bq \(\text{m}^{-3}\) in 2015 in seawater nearby Daya Bay Nuclear Power Station. The concentrations of \(^{3}\text{H}\) and \(^{14}\text{C}\) were higher than that in the background or in the reference location, but with no cumulative effect. The trend of \(^{86}\text{Sr}\) and \(^{137}\text{Cs}\) concentrations was consistent with the natural decay law, with no relationship when comparing the discharging of liquid effluent from the NPPs. The Average concentration of \(^{238}\text{U}\) and \(^{232}\text{Th}\) were 24.6±10.6 and 18.1±7.5 Bq \(\text{m}^{-3}\) respectively during 2000 – 2008.

Artificial radionuclides could not be detected except for part of the samples sampled during 1995-1997 during which there was abnormal emission or nuclear power accident. Trace amounts of \(^{124}\text{Sb}, ^{60}\text{Co}\) and \(^{110m}\text{Ag}\) were detected in seawater from West Daya Bay.

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