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Tritium concentrations in precipitation in Shanghai

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Abstract Tritium concentrations in precipitation can be used as a criterion to evaluate the tritium baseline of the environment. The tritium concentration in precipitation in Shanghai during 2014–2015 was determined. Values ranged from 0.68 ± 0.04 to 4.11 ± 0.39 Bq/L, and it showed a decreasing trend compared with historical data; however, the values were slightly higher than the natural background tritium level. Additionally, the tritium concentration shows a seasonal variation: It was higher in autumn and winter and lower in summer and spring. A comparison of concentrations in precipitation in Shanghai and around the Qinshan Nuclear Power Plant reveals no correlation, implying that the nuclear power plant operations may not affect the environment of Shanghai. Thus, the raised tritium concentrations in Shanghai might be due to the effects of monsoons, spring leak, raindrop, or other activities that generate tritium there. Those activities may include chemistry research that uses tritium as a tracer.

Keywords Tritium · Precipitation · Seasonality · Origin

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1 Introduction

Tritium (^{3}H) is a radioisotope of hydrogen with a half-life of 12.3 years. It originates from natural and anthropogenic sources. Natural tritium is produced by the reaction of fast neutrons from cosmic rays with atmospheric nitrogen; i.e., $^{14}N(n,^3H)^{12}C$, or by the direct ejection of ^{3}H from cosmic rays in the stratosphere and upper troposphere [1, 2]. Anthropogenic tritium is produced by nuclear weapons tests, weapons manufacturing, nuclear power plants operations, and the reprocessing of nuclear fuels [3, 4]. Once tritium is released, it is rapidly oxidized into tritiated water (HTO) and deposited on the land surface through precipitation. The HTO can then enter the environment through absorption into plants or microorganisms in soils, and it is absorbed into the human body through ingestion, causing an internal radiation hazard.

Historical studies have shown that peak tritium activity concentrations in precipitation occurred in 1963, at around several thousand TU (tritium units), due to weapons testing between 1953 and 1963. One tritium unit is equivalent to one tritium atom per 10^{18} hydrogen atoms, corresponding to 120 mBq/L [5]. A global model of the distribution of bomb tritium in precipitation suggests that the tritium activity concentration in precipitation in the Northern Hemisphere has now reached the values that prevailed during the pre-bomb era: around 1.2–2.4 Bq/L [6, 7]. In order to carry out an impact assessment of HTO on the environment and human health, the tritium activity concentration in precipitation can be used.

Shanghai is an international metropolis, and hence, its environment is of concern for everyone. In this study, tritium activity concentrations in precipitation sampled from 2014 to 2015 in Shanghai were measured to show their

temporal variations. In order to identify their origin, they were compared with samples from a nearby nuclear power plant.

The Qinshan Nuclear Power Plant is situated southwest of Shanghai, and the distance between Qinshan Nuclear Power Plant and Shanghai city is about 120 km. It has three nuclear reactors, including two pressurized water reactors and one CANDU6 heavy-water reactor. The heavy-water reactor started to operate in 2003, and its capacity is about 1500 MW. This power plant generates a considerable amount of wastewater and exhaust gases containing tritium, which is discharged into the environment every year.

2 Experimental

2.1 Sites and sampling

The sampling site was located in the Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences, Jiading District of Shanghai, in the eastern coastal region of China (31°14′N 121°29′E, 4 m above sea level). Shanghai is influenced by the East Asian monsoon, which is characterized by dominant warm, wet southeasterlies in spring and summer and dry, cold northwesterlies in autumn and winter. High-pressure systems that develop in the Pacific Ocean trigger southeasterly winds in summer and spring, bringing maritime air masses from over the ocean. Northwesterly winds associated with monsoons from the Asian continent blow in autumn and winter. Therefore, southeasterly and northwesterly winds prevail throughout the year, aside from a short period in winter when northern winds dominate. The annual average of liquid precipitation is 1158.9 mm, mainly concentrated in the period from May to October, when 75.2% of the annual precipitation falls. Between November and April, the average precipitation is 287.4 mm, accounting for 24.8% of the annual precipitation. In summer, the rain is often associated with monsoons. In winter, the average precipitation is 25 mm, with a minimum of 0.5 mm occurring in December.

Rain samples were collected from February 2014 to October 2015 using rain collectors made from galvanized steel with a surface area of 0.16 m^2. They were placed in open areas on a rooftop at least 1 m above ground level to avoid splash contamination. About 1 L of rainwater could be collected during each rainfall event. After each rainfall event, the rainwater samples were collected, and the collector was replaced and cleaned for the next collection.

From the total amount of water collected in the rain collector, a 500mL sample was extracted. The rainwater samples were filtered and transferred to plastic bottles. Then, all of the rain samples were subjected to pretreatment and further measurements.

2.2 Sample pretreatment and measurement

The cryogenic distillation process, a routine method for the determination of low-level tritium activity concentrations in natural rain samples, was applied as the pretreatment step to prevent contamination from other impurities, and thereby minimize quenching [8, 9]. This process was performed by adding 10 mg of $KMnO_4$ to 250 mL of each water sample. The whole distillation process was conducted in a fume cupboard to prevent pollution of the samples from tritium in the atmosphere of the laboratory.

After the cryogenic distillation process, 8 mL of distilled water was mixed with 12 mL of scintillation cocktail in a 20mL polytetrafluoroethylene plastic bottle [10]. The tritium activity concentration in the bottle was measured by a liquid scintillation counter (LSC-LB7, Japan). The liquid scintillation cocktail used was PerkinElmer UltimaGold LLT. The background count rate was 1–2 counts per minute, and the counting efficiency was about 27.5%. The detection limit of the device is 1.4 Bq/L, which was obtained directly from the manual based on the counting time. The counting time was 100 min with 10 repetitions for each sample. For each rainfall event, three parallel samples were prepared from the sample collector. Therefore, each tritium activity concentration value is the average of 30 measurements.

3 Results and Discussions

3.1 Tritium activity concentration

The tritium activity concentration in precipitation is an important indicator of environmental quality. Figure 1 shows the tritium activity concentration in precipitation alongside the precipitation rates in the Jiading District of Shanghai from February 2014 to October 2015. The tritium activity concentration in precipitation varied from 0.68 ± 0.04 to 4.11 ± 0.39 Bq/L, with an annual average of 2.71 ± 0.13 Bq/L. This value is slightly higher than that of the pre-bomb era, 1.2–2.4 Bq/L, but it is within the range of average tritium activity concentration in Suzhou [11] (measured at an observation station in Suzhou, near Shanghai). According to the data obtained from the IAEA GNIP database, the tritium level in Shanghai was higher than that in many cities around the world, including Hong Kong (0.15–0.52 Bq/L), Ocala, Florida (0.1–0.45 Bq/L), and Miami (0.09–0.43 Bq/L). Figure 2 also shows the variation in the amount of precipitation at the sampling site. The two heaviest rainfall events were observed on August 24, 2015, and June 16, 2015. Interestingly, the two lowest tritium activity concentrations also occurred on these two days. This result agrees with those reported by

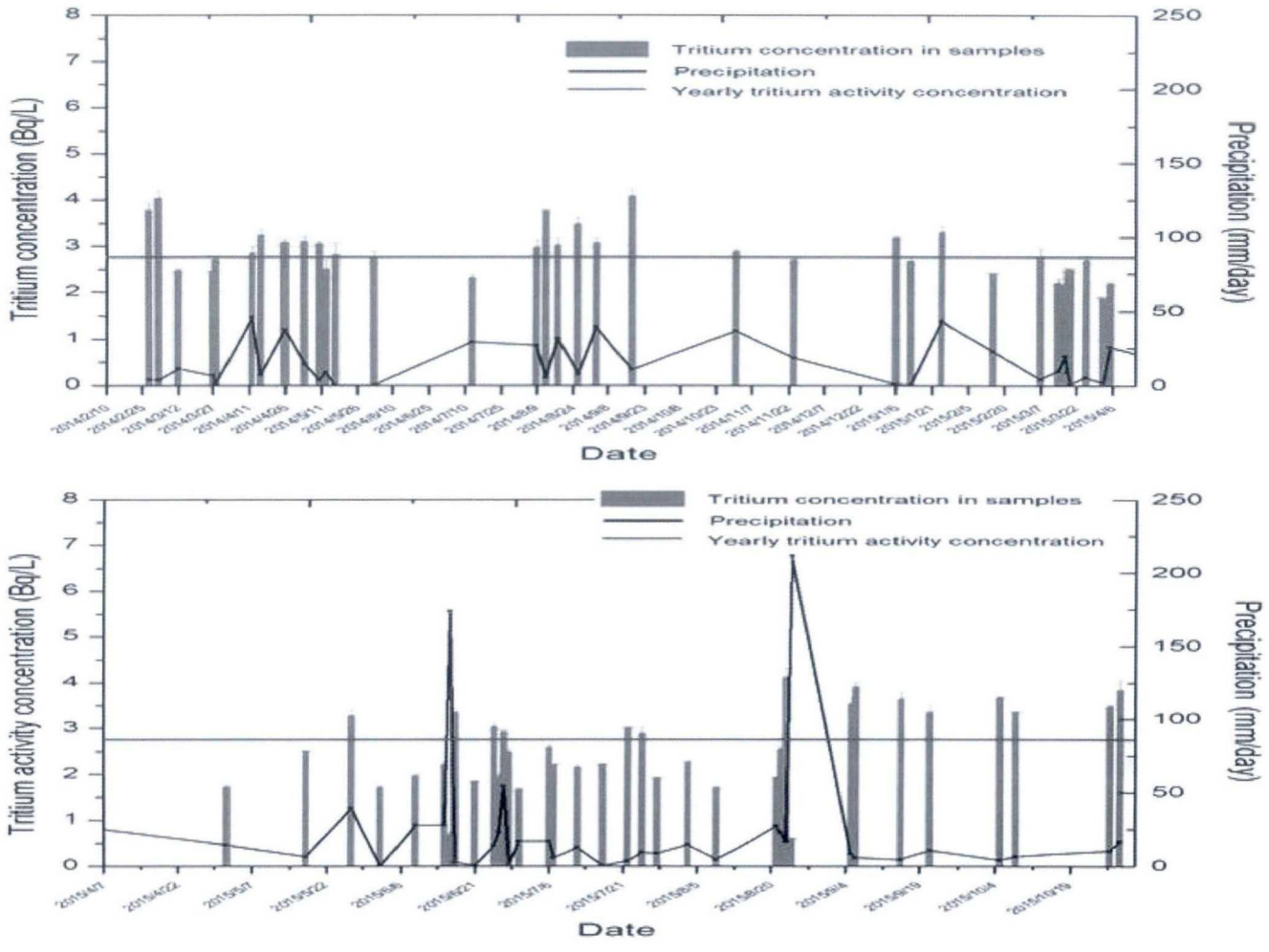

Fig. 1 Precipitation and tritium activity concentration in the rain samples collected after each rainfall event at SINAP from February 2014 to October 2015

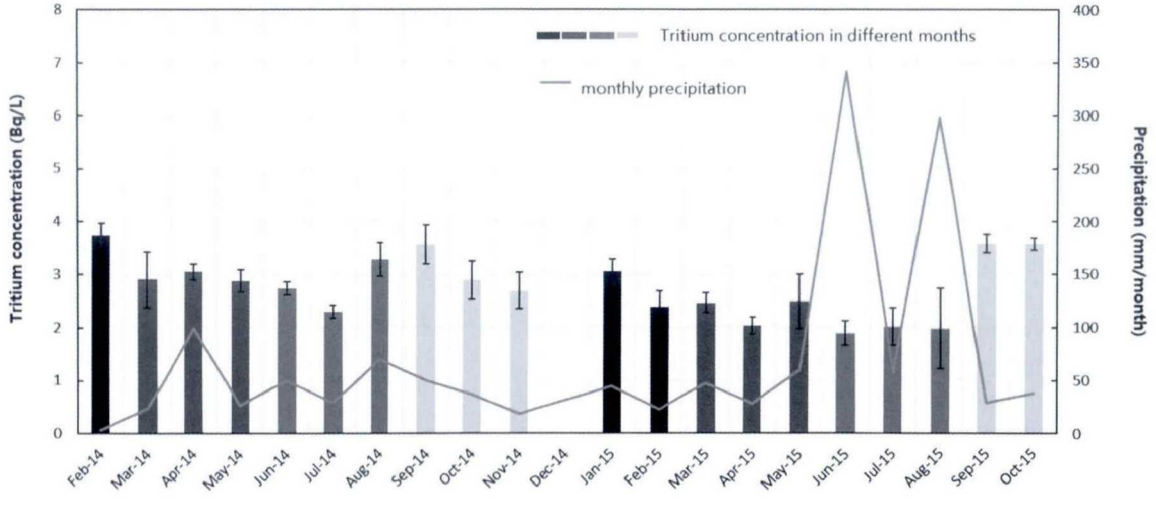

Fig. 2 (Color online) Monthly tritium activity concentrations in precipitation in Shanghai

Zhu et al. [12], who indicated that tritium activity concentrations were generally lower when there were more precipitation and higher humidity.

Monthly tritium activity concentrations were also obtained from the data in Fig. 1, which are shown in Fig. 2. Significant seasonal variations are observed. Values are higher in autumn (September to November) and winter (January to February) than in spring (March to May) and summer (June to August). The same trends were also reported by Zhu et al. [12, 13].

Figure 2 shows that the tritium activity concentration decreases as the amount of precipitation increases. Precipitation is heavier in both spring and summer than in autumn and winter; however, the tritium activity concentrations are lower in the former two seasons than the latter two seasons. The heaviest precipitation occurred in summer (June 15, July 15, and August 15) in 2015, and the lowest tritium activity concentrations appeared in the same periods. Thus, the results indicate that precipitation can dilute the tritium activity concentrations, which is consistent with the results reported in other papers [12, 13].

The continental and monsoon effects may explain the seasonal variation of tritium activity concentrations in precipitation in Shanghai. The continental effect makes the tritium activity concentrations higher in the interior of the continent compared to those in coastal sites [14]. In autumn and winter, Shanghai is affected by the northwest monsoon from Mongolia, which is associated with higher atmospheric pressure. The northwest monsoon brings more tritium from the continent and less rainfall to Shanghai, which results in elevated tritium activity concentrations in precipitation during autumn and winter. In summer, Shanghai is affected by the southeast monsoon, which develops in the Pacific Ocean and carries air with low tritium concentrations from the ocean. This is because water vapor over the ocean is depleted in tritium due to the transfer of HTO by the vapor exchange into the ocean [15]. Furthermore, there is a lot of rainfall in summer, meaning that precipitation is diluted by the molecular exchange of tritium between the rain droplets and ocean water vapor. However, maximum tritium activity concentrations in precipitation have been reported to appear in spring due to the effect of "spring leak," where the stratosphere-to-troposphere exchange causes the injection of tritium into the troposphere, and hence, the hydrological cycle [16, 17]. The tritium activity concentration in precipitation in Shanghai during spring was therefore higher than that in summer (Fig. 2). Furthermore, the amount of rainfall in spring was much higher than that in autumn and winter, and the dilution effect of rainfall and monsoon effects was much larger than that of "spring leak," which means that the tritium activity concentration in spring was lower than that in autumn and winter. This indicates that the rainfall amount is one of the major factors affecting the tritium concentration in precipitation in different seasons.

3.2 Impact of nuclear power plants

In order to know whether the tritium that escapes from the Qinshan Nuclear Power Plant affects the environment in Shanghai, the tritium activity concentrations in precipitation in Shanghai were compared with those in both precipitation and atmospheric water vapor around the Qinshan Nuclear Power Plant. Figure 3 shows the mean monthly tritium activity concentrations in atmospheric water vapor and precipitation around the Qinshan Nuclear Power Plant from 2014 to 2015, as well as the mean monthly tritium activity concentrations in precipitation in Shanghai. The Qinshan values were much greater than the Shanghai values.

Due to the operation of the nuclear power plant, the tritium activity concentration in Qinshan did not show similar seasonal variations as in Shanghai. The monthly precipitation in the Qinshan area was plotted in Fig. 4. Compared to the precipitation in Shanghai plotted in Fig. 2, the precipitation in Qinshan shows a clear seasonal variation, with precipitation peaks observed in August. Moreover, according to the tritium activity concentration and precipitation in Qinshan that are plotted in Figs. 3 and 4, respectively, precipitation peaks appeared in August, while a low tritium activity concentration was observed in September 2014 and March 2015. Hence, the influence of the nuclear plant operations exceeds the raindrop dilution effect.

Figure 5 shows the correlation of HTO activity concentrations in precipitation in Shanghai with those in the atmosphere around the Qinshan Nuclear Power Plant. As is well known, the correlation is dependent on the calculated P value. When the P value is less than 0.05, it indicates that the correlation is statistically significant at the 95% confidence level [18]. Figure 4 shows that the P value was > 0.05, implying that there was no obvious relation between them.

4 Conclusion

Tritium activity concentrations in precipitation from February 2014 to November 2015 were measured. Values ranged from 0.68 ± 0.04 to 4.11 ± 0.39 Bq/L and were higher in autumn and winter and lower in summer and spring. The tritium concentration in Shanghai was a little higher than that of the pre-bomb era and had no correlation with activity concentrations in precipitation and water vapor in the atmosphere around the Qinshan Nuclear Power Plant. This indicates that the tritium released from the

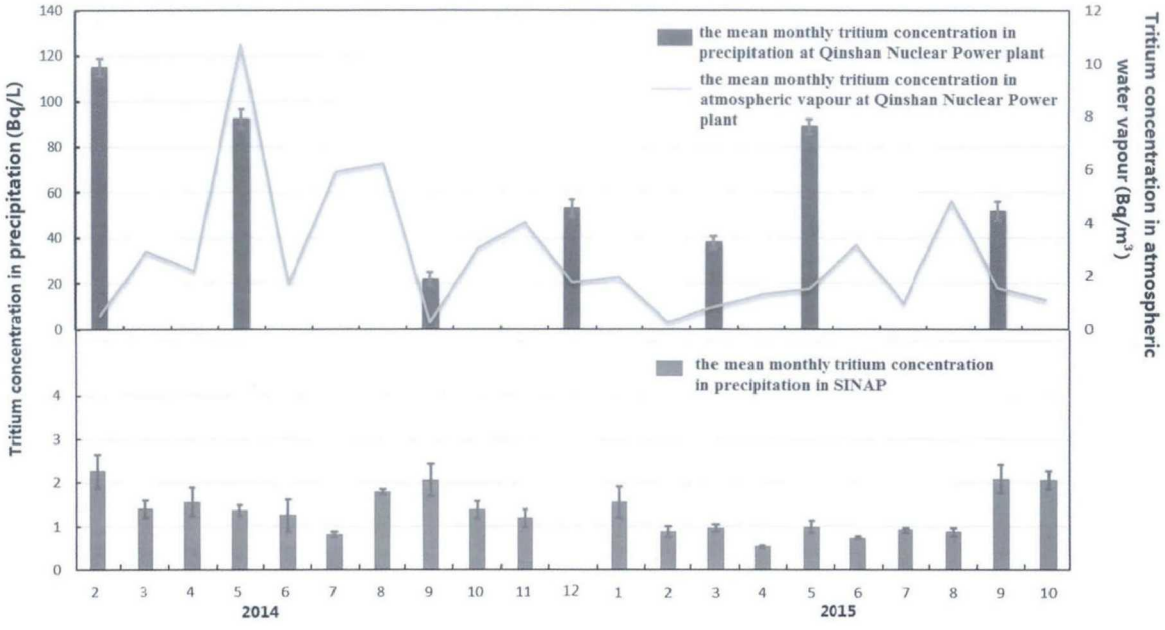

Fig. 3 (Color online) Mean monthly tritium activity concentrations in atmospheric water vapor and precipitation at the Qinshan Nuclear Power Plant (top panel) and the mean monthly tritium activity concentrations in precipitation in Shanghai (bottom panel) from 2014 to 2015

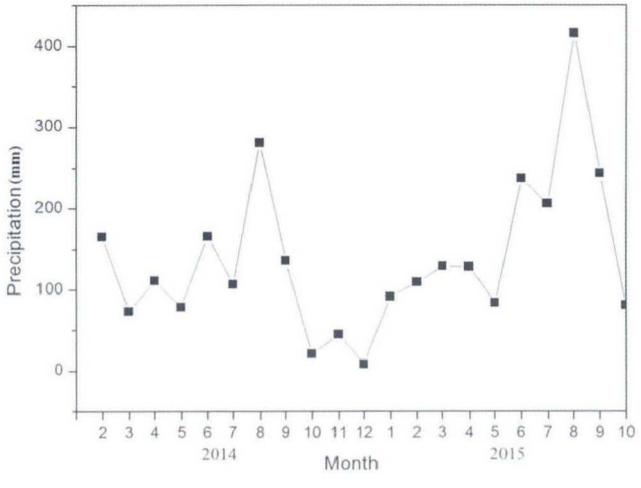

Fig. 4 Monthly precipitation in Qinshan

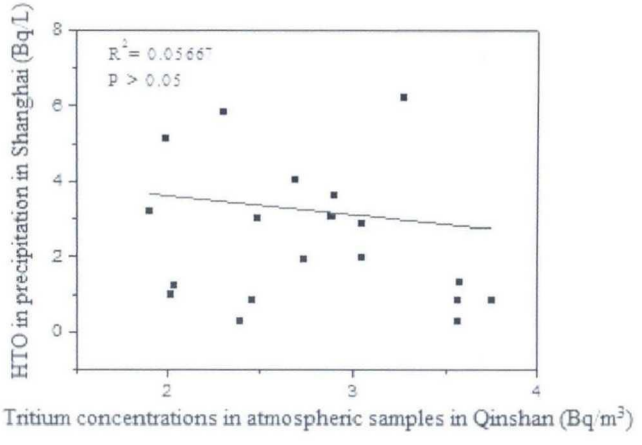

Fig. 5 Correlation analysis of the mean monthly HTO in precipitation in Shanghai and the HTO in the atmosphere around the Qinshan Nuclear Power Plant

Qinshan Nuclear Power Plant does not affect the environment of Shanghai. The variation in tritium activity concentration could be due to the combined effects of monsoon, spring leak, raindrop, and other activities that generate tritium.

More rain samples are now being collected. Moreover, due to the lack of historical data, we plan to reconstruct the tritium time series using the trend surface analysis method combined with the correlation method, based on the study carried out by Zhai et al. [19]. Hence, by analyzing more samples, the effects of monsoon and spring leak due to the tritium activity concentration will be further justified.

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