Tritium in the Atmospheric Environment

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Three chemical forms of atmospheric tritium, i.e., tritiated water vapor (HTO), hydrogen gas (HT), and hydrocarbons (CH_3T), were measured at Kumamoto, Japan during the period between 2003 and 2005. The average concentrations were in the order of HT, CH_3T, and HTO. The yearly average HT concentrations were not so different in each year, while that of CH_3T showed a large variation. The concentrations of all chemical species have decreased compared to those measured during the period between 1984 and 1995 at Fukuoka, about 100 km north of the present sampling location, suggesting a decrease in emissions of HT and CH_3T from their sources for these 8–10 years. The decrease in HTO concentration would be attributed to the decrease of the bomb-produced tritium and to a regional characteristic of the sampling locations; Kumamoto showed lower tritium concentrations in rain than Fukuoka.

1. Introduction

The production rate of natural tritium, produced constantly in the upper atmosphere by nuclear reactions between secondary cosmic rays and nitrogen or oxygen atoms, is estimated to be 0.2 to 0.25 tritium atom cm^{-2} s^{-1} which yields 1–1.3 EBq tritium inventory in the world.[1] The naturally occurring tritium has been found in various environmental materials which contain hydrogen atom as a constituent element. The concentration of tritium in the environment had increased by nuclear tests in 1950s–1960s that had released a large amount of artificial tritium to the environment. The amount of tritium emitted from the nuclear tests would be 240 EBq[1] and we can still detect the bomb tritium in environmental samples such as underground water more than 40 years after the test ban treaty in 1963. Peaceful use of nuclear energy has also increased environmental tritium concentrations such as around nuclear power stations and nuclear fuel reprocessing plants due to controlled release of tritium as airborne and liquid effluents. Tritium is found in the atmosphere as 3 different chemical forms[2] that are water vapor, hydrogen, and hydrocarbon. We report atmospheric tritium concentrations of 3 chemical species measured in the general environment of Japan.

2. Experimental

2.1. Sampling apparatus. Although three chemical species of tritium are found in the atmosphere, it should be noted that our measurement technique does not distinguish between the isotopic configurations of each chemical species.[3] The chemical species, "HTO" includes DTO and T_2O, "HT" includes DT and T_2, and "CH_3T" all volatile gaseous hydrocarbons. The sampling apparatus of atmospheric tritium is designed to collect successively 3 different chemical forms: in the order of HTO, HT, and CH_3T. The block diagram of the atmospheric tritium sampling apparatus is illustrated in Figure 1. Air is introduced to the sampling system with a diaphragm pump located at the last position of the system. An air filter removes dust in the air and then the volume of air and the flow rate is measured by a mass flow meter. Water vapor is at first collected on molecular sieve 3A (MS-3A) in an HTO column made of glass, 50 cm in length and 5 cm in diameter, and filled with 500 g of MS-3A. The water vapor content in air varies with season; in summer it sometimes exceeds the MS-3A adsorption capacity packed in the HTO column. Then an HTO cold trap, being made of glass and cooled at 2 °C, is placed just before the HTO column to avoid breakthrough of the HTO column.
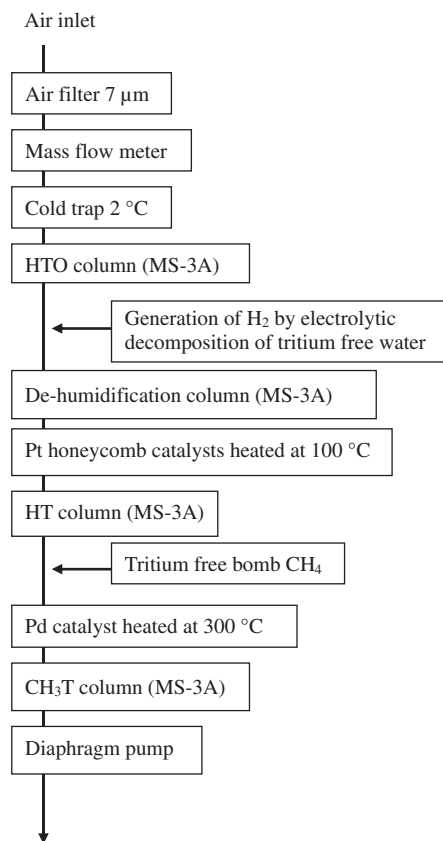

Air inlet

Air filter 7 µm

Mass flow meter

Cold trap 2 °C

HTO column (MS-3A)

Generation of H_2 by electrolytic decomposition of tritium free water

De-humidification column (MS-3A)

Pt honeycomb catalysts heated at 100 °C

HT column (MS-3A)

Tritium free bomb CH_4

Pd catalyst heated at 300 °C

CH_3T column (MS-3A)

Diaphragm pump

Figure 1. A block diagram of atmospheric tritium sampling apparatus.

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Hydrogen gas is converted to water by catalytic oxidation and collected as water on MS-3A in an HT column. The design of the HT column is the same as that of the HTO column and 500 g of MS-3A is packed in the column. The hydrogen concentration in air is about 0.5 ppm which would yield a quite small amount of water and it makes difficult to quantitatively recover water from the MS-3A and to measure tritium concentration by the liquid scintillation counting. To increase the amount of water available, tritium free H_2 that was generated by electrolytic decomposition of deep well water is added to the sampling air after the HTO column. Water vapor accompanied with the generated H_2 is removed with a de-humidification column which is the same as the HTO column and packed with 500 g of MS-3A. The H_2 generation rate is controlled to yield about 15 mL of water with oxidation of H_2. The original sampling apparatus adopted Pd coated MS catalyst for H_2 oxidation which is prepared by vigorous shaking of $PdCl_3$ solution and MS-4A followed by baking in H_2 atmosphere.[4] The Pd coated MS catalyst undergoes H_2 oxidation and collection of produced water on the MS-4A simultaneously. To maintain the oxidation capacity of the Pd coated MS catalyst, reactivation is carried out regularly by which H_2 is flowed under heating the catalyst. To reduce the task of this reactivation process, we prepared Pt honeycomb catalysts for H_2 oxidation, in which 0.12 g of Pt is dispersed on the surface of the honeycomb base metal (25 mm in diameter, 40 mm in length). The apparatus uses 3 pieces of the Pt honeycomb catalysts and is operated at 100 °C. Hydrocarbons are oxidized to water with the Pd catalyst (DASH-220D, 0.24 wt.% Pd, 3mm in diameter, NECHEMCAT Co. Ltd.) at 300 °C. Tritium free bomb CH_4 is added to the sampling air through a mass flow controller before the Pd catalyst column. The Pd catalyst column is made of quartz and packed with the 150 cm^3 Pd catalysts. The flow rate of CH_4 is controlled to yield about 15 mL of water by the sampling. The water yielded is collected on 500 g of MS-3A in a CH_3T column as the case for the water vapor and hydrogen. Teflon tubes (8 mm in outer diameter and 6 mm in inner diameter) and metal conjunctions (Swagelok Co. Ltd.) are used for connecting the columns and other units. The performance of the catalyst has been reported elsewhere.[3]

2.2. Sampling and measurement. We collected air at a flow rate of 1.2 L min^{-1} which requires the 69.4 h sampling time for the total of 5000 L air. The samplings were carried out at Kumamoto, Japan (130°43'E, 32°48'N) at about 25 m above the ground. Water adsorbed on the MS-3A is desorbed by heating the MS-3A in the column at 400 °C with flowing N_2 gas. The desorbed water is recovered on a cold trap cooled at –9 °C with taking care to avoid contamination of the sample water with ambient water vapor. About 15 mL of water is expected to be recovered from each HT and CH_3T column. The water recovered from the HTO column is combined with that collected on the HTO cold trap. Tritium radioactivity is measured by the low background liquid scintillation counting after mixing the water with the liquid scintillation cocktail (Ultima GOLD™ LLT, Packard). For the preparation of the HTO counting sample, the 50 mL HTO water and 50 mL scintillation cocktail is mixed in a polyethylene vial (Aloka Polyvial 145) of which internal wall is coated with Teflon. 10 mL water recovered from the HT and CH_3T columns are mixed with the 10 mL scintillation cocktail in the Teflon vials to prepare counting samples. The background counting samples are prepared as the same way for either HTO or HT/CH_3T using tritium free deep ground water. No tritium in the ground water was confirmed by an electronic enrichment technique. Each sample is measured for 1300 min with a low background counter (Aloka, LB-III). The typical background count rate for the HTO samples was about 3.5 cpm and that for the HT/CH_3T samples was about 2.8 cpm. Counting efficiencies were determined using standard tritium water (Nycomed Amersham),

showing 18.5% for HTO samples and 22.5 % for the HT/CH_3T samples.

3. Results and Discussion

The atmospheric concentrations of HTO, HT, and CH_3T are shown in Figures 2, 3, and 4, respectively. The samplings were carried out 24 times in the period from June 2003 to June 2005. The atmospheric concentrations of HTO, HT, and CH_3T are distributed from a few to a few tens mBq m^{-3} and the differences in concentrations among species are not so large. Average concentrations of HTO, HT, and CH_3T in the experimental period are summarized in Table 1 and the order of the average concentration is HT > CH_3T > HTO. The present tritium concentrations are lower than those of other gaseous radionuclides in the general environment such as ^{222}Rn which shows in the order of a few tens Bq m^{-3} (References 5–8), ^{85}Kr the order of a few Bq m^{-3} (Reference 9) and ^{14}C the order of a few tens mBq m^{-3} (Reference 10).

The distribution of HTO concentrations (Bq L^{-1}) is shown in Figure 5. The change of atmospheric concentrations in Figure 2 will be related to the amount of water vapor in the atmosphere and the HTO concentration. In general the water vapor content in the atmosphere is high in summer and low in winter because water vapor saturation is controlled by temperature. The atmospheric concentration of HTO in Figure 5 showed a seasonal variation; the highest value was observed in August 2004 and the lowest one in December 2003 though the HTO concentrations distributed widely from 0.1 to 1.3 Bq L^{-1}. This result suggests that the atmospheric concentration of HTO is mostly determined by water vapor content rather than its concentration (Bq L^{-1}). The average HTO concentration was 0.69 ± 0.35 Bq L^{-1} as shown in Table 1 that is significantly higher than the average HTO concentration of rain, 0.30 ± 0.13 Bq L^{-1} observed at the same sampling location during the corresponding period of the present atmospheric samples.[11] The higher HTO concentration of water vapor than the rain would be attributed to the upward flux of HTO to the atmosphere from the soil surface where HTO concentration is elevated by microbial oxidation of the atmospheric HT and CH_3T (Reference 12) and to the downward flux of naturally occurring HTO from the stratosphere to the troposphere.[13]

The atmospheric concentrations of HT and CH_3T in Figures 3 and 4 are lower than those measured in 1980s–1990s at Fukuoka, Japan,[2,14] which is located about 100 km north from the present sampling location. The present data revealed a large variation in the concentrations, ranging from 3.6 to 33.5 mBq m^{-3} for HT and from 0.7 to 32.3 mBq m^{-3} for CH_3T. A degree of scatter of the data strongly depends on duration of sampling; daily basis sampling gives larger scattering than such as weekly basis sampling. We collected the samples for about 3 days basis sampling, the samples collected in 1980s–1990s at Fukuoka also had showed large scatter for the HT and CH_3T concentration, though they were taken by weekly basis sampling. Neither seasonal variation nor change in yearly average concentration was observed in the present HT data: 12.6 for 2003, 12.9 for 2004, and 11.4 mBq m^{-3} for 2005. On the other hand, yearly averages of CH_3T concentrations were 14.1 for 2003, 6.7 for 2004, and 3.0 mBq m^{-3} for 2005. The present yearly average HT concentration, 11.4–12.9 mBq m^{-3} (2003–2005) was about half of that measured in 1995 at Fukuoka[2] and almost comparable to that measured in 2002 at Miami, USA (10.2 mBq m^{-3}).[15] The yearly average CH_3T concentration measured in 1995 at Fukuoka[2] was 12 mBq m^{-3} which was almost equal to the present data of 2003.

The concentration order of the present data shown in Table 1 is HT > CH_3T > HTO, which was different from that observed at Fukuoka during the period between 1984 and 1995.[2] In the 1984–1995 period, the order was HT > HTO > CH_3T; the CH_3T
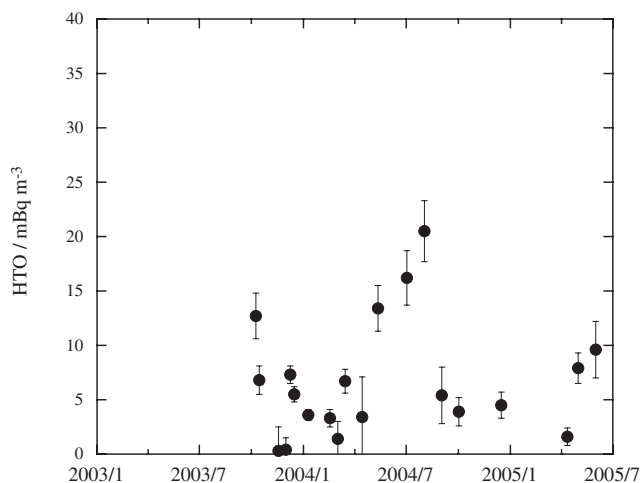
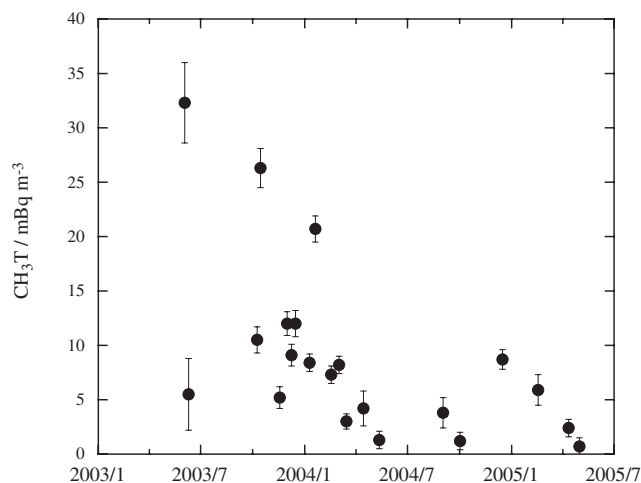**Figure 2.** HTO concentrations in the atmosphere.

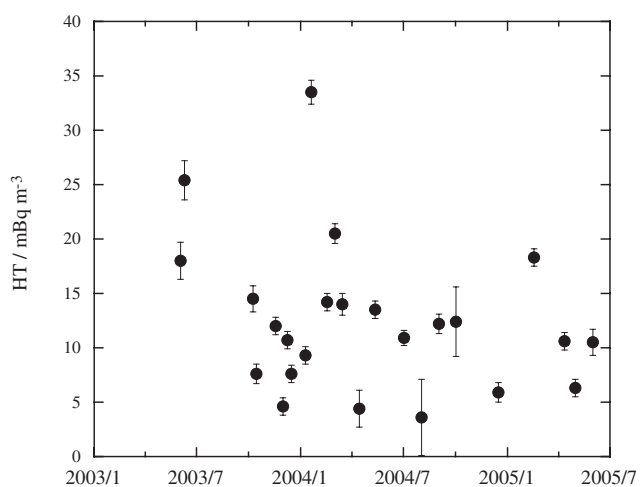**Figure 4.** CH₃T concentrations in the atmosphere.

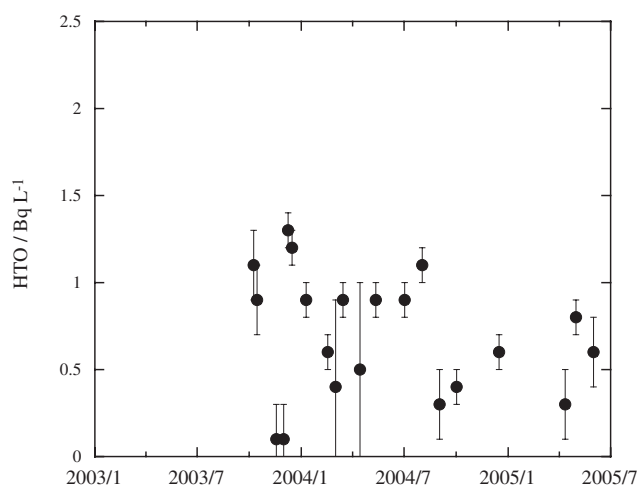**Figure 3.** HT concentrations in the atmosphere.

Figure 5. HTO concentrations of atmospheric water vapor.

concentration was lowest among them. As mentioned above, the yearly average CH_3T concentrations of the present data showed marked variation, probably suggesting a change of a CH_3T source intensity. Although the sources of CH_3T are not identified, emissions associated with activities of nuclear facilities would be involved. A regional characteristic, the present data were taken at Kumamoto while the data between 1984 and 1995 were taken at Fukuoka, would be one of the reasons for the low HTO concentrations because tritium concentration in rain at Kumamoto were lower than that at Fukuoka.[16] It has been shown that very marked peaks in the HT concentrations at Fairbanks, Alaska in 1973 are clearly correlated with large underground events at the Novaya Zemlya test site, in the former USSR.[17] One HT source from the late 1950s to the early 1990s was the testing of nuclear devices conducted underground.[15] Tritium can escape from underground to the atmosphere as HT through natural and bomb-produced faults and fractures because low O_2 environment would limit the formation of HTO. A coincident increase in yearly average HT concentration was observed at Fukuoka and Miami in 1988 and the underground nuclear tests yield in 1988 was high; the fact would be an indication that underground nuclear test is one of the major sources in atmospheric HT. The UNSCEAR[18] estimated HT emission from the nuclear power industry (Fuel rod reprocessing, power plants) and the emission has been increased. The HT observed in the present data would result from the release from such nuclear industry.

TABLE 1: Concentrations of atmospheric tritium

Chemical species	Concentration
HT	12.5 ± 6.9 mBq m⁻³
CH₃T	9.0 ± 8.2 mBq m⁻³
HTO	6.7 ± 5.4 mBq m⁻³
HTO	0.69 ± 0.35 Bq L⁻¹

References

(1) S. Okada and N. Momoshima, Health Phys. **65**, 595 (1993).
(2) T. Okai, N. Momoshima, and Y. Takashima, J. Radioanal. Nucl. Chem. **239**, 527 (1999).
(3) N. Momoshima, M. Takamura, Y. Nagao, T. Toyoshima, T. Okai, and T. Uda, *Radioecology and Environmental Dosimetry*, Eds. J. Inaba, H. Tsukada, and A. Takeda, Institute for Environmental Sciences, Rokkasho (2004), p 416.
(4) T. Okai and Y. Takashima, J. Radioanal. Nucl. Chem. **130**, 399 (1989).

(5) *Technical support document for the 1992 citizen's guide to radon*, U. S. Environmental, Protection, and Agency, Washington D. C., EPA 400-R-92-011 (1992).

(6) L. S. Quindos, P. L. Fernandes, and J. Soto, Environ. Inter. **17**, 449 (1991).

(7) J. C. H. Miles, B. M. R. Green, P. R. Lomas, and K. D. Cliff, Radiation Protection Dosimetry **36**, 117 (1991).

(8) T. Sanada, K. Fujimoto, K. Miyano, M. Doi, S. Tokonami, M. Uesugi, and Y. Takata, J. Environ. Radioactivity **45**, 129 (1999).

(9) Y. Igarashi, H. Sartorius, T. Miyao, W. Weiss, K. Fushimi, M. Aoyama, K. Hirose, and H. Y. Inoue, J. Environ. Radioactivity **48**, 191 (2000).

(10) N. Momoshima, H. Kawamura, and Y. Takashima, J. Radioanal. Nucl. Chem. **173**, 323 (1993).

(11) N. Momoshima, Y. Nagao, and T. Toyoshima, Fusion Sci. Tech. **48**, 520 (2005).

(12) N. Momoshima, H. Kakiuchi, T. Okai, and Y. Maeda, J. Radioanal. Nucl. Chem. **242**, 173 (1999).

(13) H. Kakiuchi, N. Momoshima, T. Okai, and Y. Maeda, J. Radioanal. Nucl. Chem. **239**, 523 (1999).

(14) T. Okai and Y. Takashima, Appl. Radiat. Isot. **42**, 389 (1991).

(15) J. D. Happell, G. Östlund, and A. S. Mason, Tellus **56B**, 183 (2004).

(16) Y. Hayashi, N. Momoshima, H. Kakiuchi, and Y. Maeda, J. Radioanal. Nucl. Chem. **239**, 517 (1999).

(17) A. S. Mason and H. G. Östlund, Geophys. Res. Lett. **1**, 247 (1973).

(18) UNSCEAR, *Sources and Effects of Ionizing Radiation, Sources*, United Nations Scientific Committee on the Effect of Atomic Radiation, New York (2000).