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A Case Study on the Effect of Storage of Advanced Treated Water in a Building's Plumbing System on Trihalomethane Levels

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Abstract Variations in trihalomethane (THM) levels during two-day period in the advanced treated water which had passed through a building's plumbing system (stored water) were compared with those in the advanced treated water delivered directly by the distribution system. THM levels in both the water were relatively uniform. The water quality deterioration measured by the increased THMs was apparently observed during the storage of the water in the plumbing system, even though the advanced treatment could produce high-quality water. Annual changes in THM in the stored water were also examined. Increasing air temperature increased THMs levels except for bromoform.

Keywords Trihalomethane · Building's plumbing system · Advanced treated water

The water purification treatment commonly being used in Japan consists of coagulation, sedimentation, intermediate chlorination, rapid sand filtration, and post-chlorination, called "conventional treatment". In 2001, a new and more sophisticated water treatment process was introduced into 20% of the Japanese water supplies (Terashima 2002). In all the water utilities of Osaka City, a conventional treatment modified by the introduction of ozonation followed by granular activated carbon filtration has been in operation since March 2000, called "advanced treatment". Total trihalomethane (THM) levels in advanced treated water leaving these utilities have dropped dramatically, to about 20% of the level in conventionally treated water (Terashima et al. 2003), and the THM problem therefore appears to be resolved.

However, many people in urban areas drink water that had passed through a building's plumbing system (i.e. a water-receiving tank, elevated tank, pumps and service pipes connected to the distribution system) rather than water delivered directly by the distribution system (Takahashi et al. 2003; Yamamura et al. 2006). Here, the former is referred to as "stored water" and the latter is "distributed water". Several studies have reported increased THM levels (Smith et al. 1980; Shikada et al. 1993; Takahashi et al. 2003) and loss of free residual chlorine (Yamamoto et al. 1981) in stored water. Less attention has however been paid to changes in THM concentrations between the time the water enters the receiving tank and the time it is drunk. It is important to understand the water quality deterioration of advanced treated water during storage in a building's plumbing system. As it is used to store water for fire-fighting as well as water supply, our receiving tank has a much larger volume than usual and therefore provides a good case for the study examining how storage of advanced treated water affects THM levels. We reported here on a set of two-day studies of the variations in THM levels in stored water and distributed water and a one-year survey of THM levels in stored water.

Materials and Methods

Figure 1 shows the sampling sites and the plumbing system of the building of Osaka City Institute of Public Health and Environmental Sciences. The distributed water is stored first in the receiving tank (350 m^3) and then is intermittently pumped up to an elevated tank (30 m^3) from where it is supplied under gravity to faucets on each floor. The

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available volume of the receiving tank is 44% of its total volume and the rest of the water is always stored. To calculate the residence time of water in our plumbing system, the available volume of both tanks (154 m^3 + 30 m^3) was divided by the daily water consumption (ranged from 59 m^3/d (April) to 108 m^3/d (August) with an average of 80 m^3/d). Our institute accommodates a staff of approximately 100 during working hours (i.e. from 9:00 a.m. to 5:30 p.m.) and is minimally staffed at night and on weekends. The actual residence time was therefore calculated using the following steps: the integer of the quotient obtained above was multiplied by 24 h/d and the decimal fraction was multiplied by the working hours of 8.5 h. The resulting values ranged from 30 h to 73 h, with an average of 51 h (i.e. the equations that give the average are: $(154\ m^3 + 30\ m^3)/80\ m^3/d = 2.3$ d and $2 \times 24\ h + 0.3 \times 8.5\ h = 51\ h$). A two-day sampling period was chosen because it corresponds closely to the actual residence time of the receiving tank.

The distributed water and the stored water were collected to 40 mL Teflon-lined screw-cap vials with about 25 mg of sodium thiosulfate. Samples for THM measurement were analyzed according to the U.S. EPA. Method 524.2 Rev. 4.1 (U.S. EPA 1995) using a gas chromatograph (Agilent 6890)/mass spectrometer (Agilent 5973GC/MSD) interfaced with a purge and trap system (O·I·Analytical Model 4560 Sample Concentrator, Model 4551-A Vial multi-sampler and standard addition module). A J&W DB-624 column (30 m × 0.32 mm i.d., 1.8 μm film thickness) was used. Analytical protocols ensured detection limits of 0.56 μg/L for chloroform, 0.50 μg/L for bromodichloromethane (BDCM), 0.47 μg/L for dibromochloromethane (DBCM) and 0.45 μg/L for bromoform. Free chlorine was measured at the time of water sampling by the DPD (*N*,*N*-diethyl-*p*-phenylene-diamine) colorimetric method using a Pack test (Kyoritsu Chemical Check Lab. Corp., Tokyo, Japan).

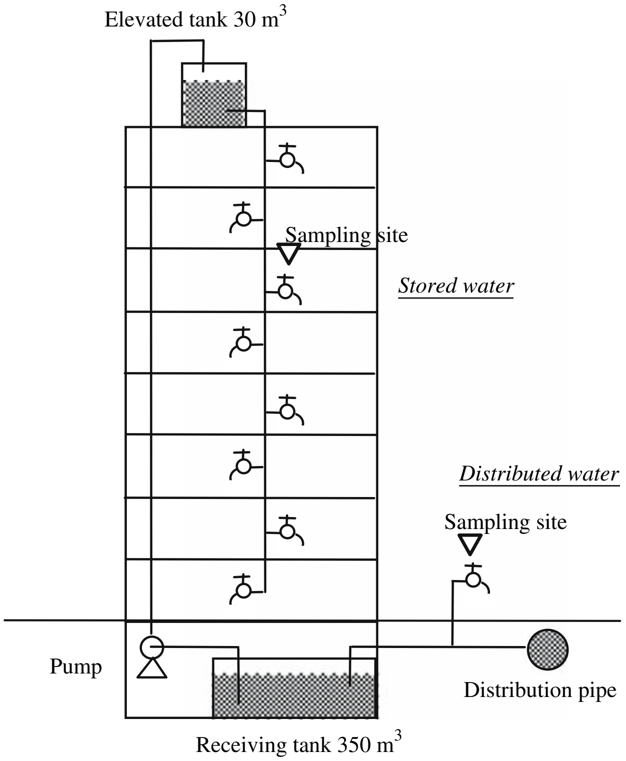


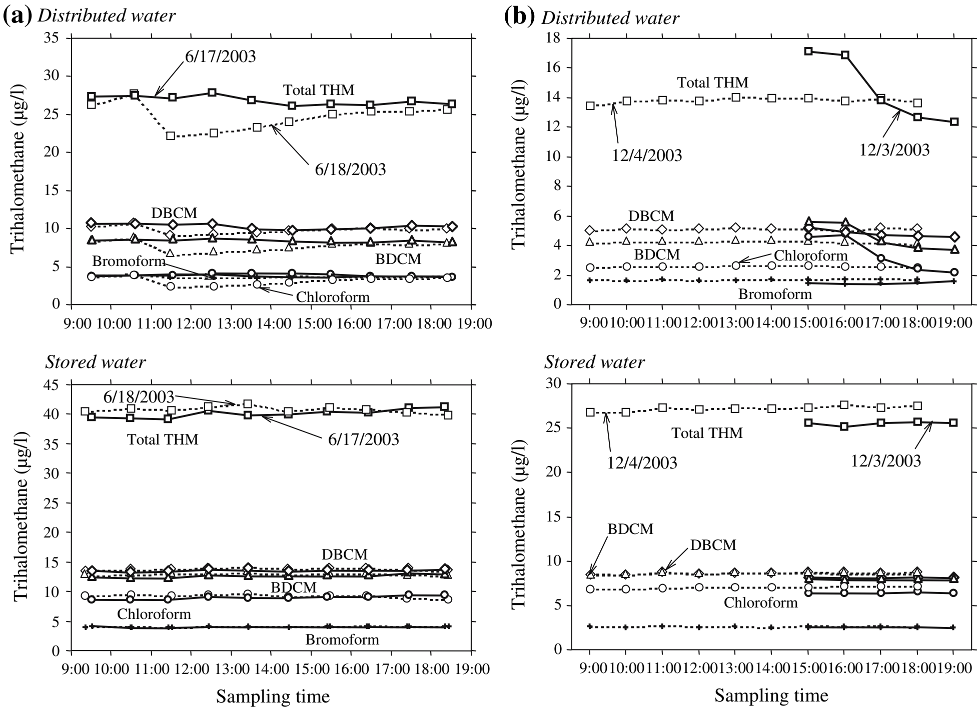
Fig. 1 Schematic representation of plumbing system of building of Osaka City Institute of Public Health and Environmental Sciences and sampling sites

Results and Discussion

Figure 2a show changes in THM concentrations in the distributed water and in the stored water by the hour between 9:30 a.m. and 6:30 p.m. on 17 and 18 June 2003, respectively. On 18 June, the total THM concentration in the distributed water showed a sudden dip from 27.9 μg/L to 22.2 μg/L at 11:30 a.m., and then slowly increased with time. A high-value for free chlorine was observed at 12:30 p.m. (0.6 mg/L); values at other times were 0.4 mg/L. Two faucets had been turned on for a half-day before the start of sampling and for the two-day sampling period. The probable explanation is that lower THM concentrations result after heavy use that flushes out the local distribution system. Total THM concentrations were relatively uniform, ranging from 22.2 μg/L to 28.0 μg/L, with an average of 25.9 μg/L and a coefficient of variation of 6.6%. The average values for chloroform, BDCM, DBCM and bromoform were 3.65, 8.29, 10.2 and 3.79 μg/L, respectively. Water temperatures ranged from 22.1°C to 22.4°C. We regarded the average THM level of the distributed water as the THM level of the water entering the receiving tank. Total THM concentrations in the stored water were consistent, ranging from 39.4 μg/L to 41.8 μg/L, with an average of 40.5 μg/L and a coefficient of variation of 1.7%. Free chlorine was not detected in any sample of stored water. This indicated that THM formation had already ceased by the time the water reached the extremity of plumbing system. Average levels of chloroform, BDCM, DBCM and bromoform were 9.28, 13.1, 13.9 and 4.29 μg/L, respectively. The water temperature ranged from 22.2°C to 22.8°C. Total THM concentration in the stored water was 1.6-fold higher than in the distributed water.

An experiment was designed to examine the THM levels formed by free chlorine in the water entering the receiving tank (Fig. 3). Several screw-cap vials of 40 mL capacity were filled with unquenched distributed water and stored water, both collected on 18 June 2003. These vials were placed upside down in the dark at room temperature. Total

Fig. 2 Two-day variations in THM levels in distributed water and stored water in June (**a**) and December (**b**) 2003



THM levels in the distributed water sample increased from 26.4 µg/L to 46.7 µg/L until free chlorine was depleted. THMs found in the distributed water sample were: DBCM > BDCM >> bromoform > chloroform. At the end of the incubation period (55 h), the order of THMs was the same as in the stored water sample: DBCM ≥ BDCM > chloroform > bromoform. Increases in brominated THMs during the storage of advanced treated water are possibly of health concern as data suggest that BDCM is the THM of greatest toxicological significance (U.S. EPA, Integrated Risk Information System). By contrast, there was no increase of THM levels in the stored water sample (40.5–42.5 µg/L, average 41.4 µg/L) as there was no free chlorine left to react with THM precursors.

As illustrated in Fig. 2b, total THM levels in the distributed water on 3 December decreased from 17.2 µg/L at 3:00 p.m. to 12.4 µg/L at 7:00 p.m. while free chlorine increased from 0.15 mg/L to 0.6 mg/L. Two faucets had been turned on at 1:50 p.m. and the water left running. The water temperature was 15.7–15.8°C. On 4 December, THM and free chlorine levels were stable (13.8 ± 0.18 µg/L, n = 10 and 0.8–1.0 mg/L). Average values for chloroform, BDCM, DBCM, and bromoform were 2.63, 4.33, 5.16 and 1.72 µg/L, respectively. The water temperatures ranged from 15.4°C to 15.7°C. By contrast, THM concentration in the stored water was stabilized by leaving the water running for a few minutes. With decreasing free chlorine from 0.2 mg/L to 0.1 mg/L, total THM levels increased significantly from 25.6 ± 0.19 µg/L (n = 5) on 3 December to 27.3 ± 0.27 µg/L (n = 10) on 4 December ($\alpha = 0.05$, degree of freedom: $df = 13$, tabulated t value = 2.16 < calculated t value = −12.1). THM formation had been proceeding in the extremity of plumbing system. The water temperature varied from 16.7°C to 17.3°C. Total THM in the stored water was 2-fold higher than in the distributed water.

If the water in the receiving tank is completely mixed, THM concentrations in the stored water will increase with increasing storage time as in Fig. 3a. There was a little fluctuation in THM and free chlorine concentrations in the stored water. A simplifying assumption can therefore be made: the plumbing system (receiving tank and elevated tank) has poor mixing characteristics and behaves in the manner of a plug-flow (tubular) reactor. The stored water appears to have the same residence time.

The water temperature and THMs levels varied slightly in the two-day sampling period. Total THM levels in the stored water in December were a half in June. To examine in detail the effect of seasonal temperature change on THM levels in the stored water, THM concentrations in the stored water were measured from March 2003 to February 2004 with a total of 37 sampling dates. The stored water was sampled from a faucet left running first for about 5 min. As shown in Fig. 4, THM levels in the stored water described a convex curve, ranging from 13.1 µg/L to 51.0 µg/L for total THM, 1.75 µg/L to 17.5 µg/L for chloroform, 4.08 µg/L to 16.8 µg/L for BDCM, 5.61 µg/L to 16.3 µg/L for DBCM, and 1.68 µg/L to 8.20 µg/L for bromoform. The daily average air temperature on the sampling date (Ta) is suggested as a factor influencing annual fluctuations in THM

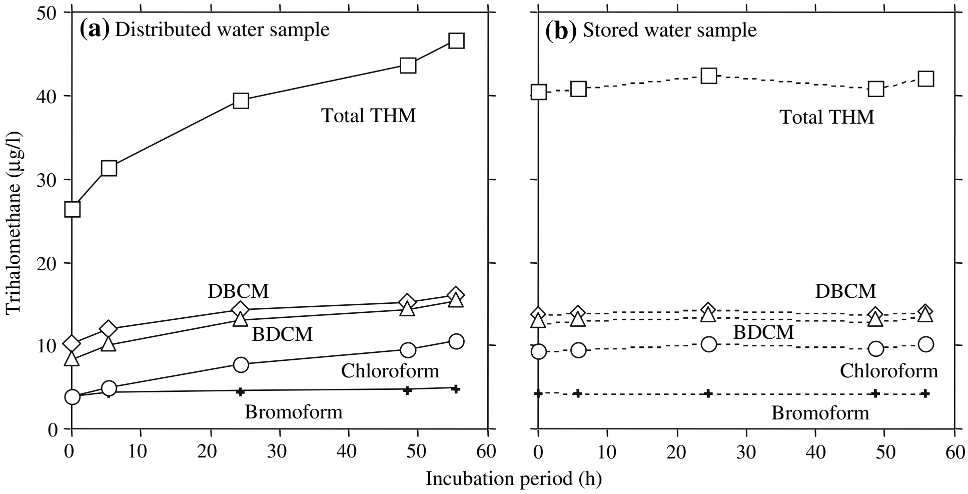


Fig. 3 Formation of THMs during incubation period in distributed water (**a**) and stored water samples (**b**) collected on 18 June 2003

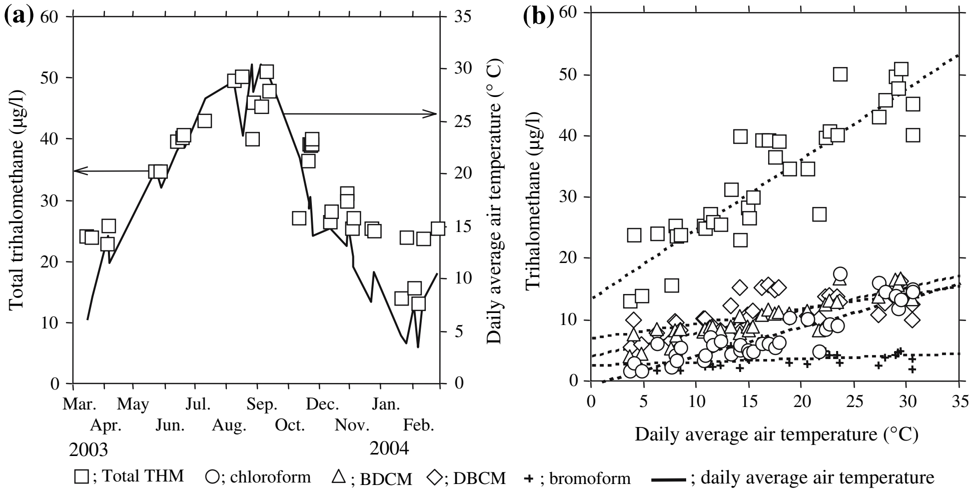


Fig. 4 (**a**) Annual changes in total THM in stored water and in daily average air temperature, and (**b**) relationship between concentration of different THMs and daily average air temperature on the sampling date

levels: total THM = 1.14*T*a + 13.8 (number of sample: n = 37, correlation coefficient: $r = 0.894$), chloroform = 0.47*T*a − 0.36 ($r = 0.877$), BDCM = 0.37*T*a + 4.18 ($r = 0.906$), DBCM = 0.24*T*a + 7.24 ($r = 0.656$), bromoform = 0.05*T*a + 2.79 ($r = 0.265$). Here, when THM levels were measured several times on the same day, the average value was adopted. Daily average air temperatures in Osaka City were cited from Japan Meteorological Agency records. Total THM, chloroform, and BDCM correlated well with *T*a. DCBM correlated less well, and bromoform showed no correlation. For n = 37, the correlations would be significant if $|r| \geq 0.325$ ($\alpha = 0.05$). Even though high correlation coefficients are reported, demonstrating that the vast majority of variation in THM is explained by air temperature, some scatter can still be observed. This is due to the wide variation in actual residence times from 30 h to more than 2-fold.

Variations in THM in the stored water were observed in a study undertaken on 22 and 23 June 1999, when the conventional treatment was in operation (data not shown). THM concentrations were relatively uniform, ranging from 58.0 μg/L to 70.1 μg/L, with an average of 65.7 μg/L and a coefficient of variation of 4.9%. Chloroform was found to be the predominant THM (38.1 μg/L), followed by BDCM (19.7 μg/L) and DBCM (7.30 μg/L), and contributed most to the variability in total THM concentration. Traces of bromoform (0.55 μg/L) were found. Total THM levels in stored water subjected to conventional treatment were 2.5-fold higher than in stored water subjected to advanced treatment. The water temperature varied from 23.1°C to 24.4°C.

Kajino (1982) reported annual changes in total THM at a faucet in Osaka City two decades earlier when the conventional treatment, in which breakpoint chlorination was used instead of intermediate chlorination, was in operation. Total THM varied from 16 μg/L to 54 μg/L while the water temperature ranged from 7.0°C to 29°C. Surprisingly, Student's *t*-test showed that his data were not significantly different from ours ($\alpha = 0.05$, $df = 45$, tabulated t value = 2.01 > calculated t value = −0.97).

The water quality deterioration measured by the increased THMs was apparently observed during the storage of the water in the plumbing system, even though the advanced treatment could produce high-quality water. The number of high-rise and large-scale buildings, which use a large amount of drinking water and require a storage tank system for stable water supply, has been increasing in urban areas. Our results are site-specific and further study is therefore needed.

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