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Episodic Trihalomethane Species and Levels in Tap Water at a Start of Operation of Advanced Treatment in Osaka Prefectural Water Supplies

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Abstract Dramatic changes in trihalomethanes of tap water caused by decreasing the chlorine dose from to break-point to zero at a pre-chlorination could be found during several years from starting the advanced treatment in Osaka Prefectural water utilities (from 1998 to 2002). In 1998 (break-point chlorination), chloroform was predominant (an average of 14.3 μg/L) and bromodichloromethane (5.96 μg/L), dibromochloromethane (4.19 μg/L) and bromoform (1.06 μg/L) were in the decreasing order. In contrast, in 1999 (chloramination), dibromochloromethane and bromodichloromethane were abundant trihalomethanes (6.61 and 5.72 μg/L) and followed by chloroform (4.14 μg/L) and bromoform (1.41 μg/L). Trihalomethane distribution in 2002 (non-chlorination) was almost the same as that in 1999.

Keywords Trihalomethane · Advanced water treatment · Trihalometane distribution · Pre-chlorination

Usually, in Japan, treatment processes of water utilities consist of pre-chlorination, coagulation, sedimentation, rapid sand filtration, and post-chlorination (called a "conventional treatment"). Today a new more sophisticated and an advanced water treatment (e.g., ozone-granular activated carbon filtration, membrane filtration) is in operation (about 25% of Japanese water supplies in 2002) (Japan Water Works Association 2009). Terashima et al. (2003) reported that, by operating the "advanced treatment" which is installed the ozone-granular activated carbon filtration into after the rapid sand filtration in the conventional treatment, total trihalomethane (THM) in the finished water in utilities of Osaka City was drastically decreased and THM speciation was shifted to brominated ones. The shifts in THM speciation to brominated THMs may induce little or no cancer risk reduction, if the carcinogenicities of brominated ones are high relative to chloroform.

To clarify the degree of shifting to the brominated THMs in THM speciation by starting the advanced treatment, THMs levels in tap water from Osaka Prefectural water utilities in 1998, 1999 and 2002 were examined. Moreover, cancer risks due to THMs were compared among each observation, using the US EPA unit cancer risk for each THM.

Materials and Methods

Advanced treated water samples were collected at thirteen well-flushed taps in the homes of students enrolled at Osaka City Nutrition College in ten cities of Osaka Prefecture on July 30, August 25, 27 and 28, 1998. Samplings on July 21, 26 and 27, 1999 were carried out at the same taps in 1998. Twenty-six samples were collected at different household taps in twelve cities of Osaka Prefecture on July 24, 25, 30 and 31, and September 26, 2002. In addition, sixteen conventionally treated water samples were also collected from Osaka City on July 27, 30, August 10 and 25, 1998. We used the student's address to determine their residential utilities, and gained information of type of source water and treatment processes from each municipal waterworks website (the water quality examination program, as stipulated in the Japanese Water Supply Law). All of water utilities in Osaka Prefecture and Osaka City take raw water from the same source (Yodo River).

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As the water contained residual chlorine, about 25 mg of sodium thiosulfate per 40 mL of sample was added to a screw cap vial equipped with a Teflon-faced silicone septum before filling with sample. Samples for THMs were analyzed according to US EPA Method 524.2 Rev.4.1 (US EPA 1995) using a gas chromatograph (Varian 3400)/mass spectrometer (Finnigan Magnum) interfaced with a purge and trap system (Tekmer Model LSC-2000 and ALS-2016 automatic sampler). A J&W DB-624 column (75 m × 0.53 mm i.d., 3 μm film thickness) was used. The mass scan range was m/z 47–260. Standard solutions were prepared by diluting the 16 VOC Mixture Standard Solution including THMs (Wako Pure Chemical Co., Tokyo, Japan) with methanol (Sigma-Aldrich, purge and trap grade). For this work, THMs were the only compounds, which could be detected in tap water samples. The method detection limits of chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform were 0.15, 0.07, 0.05 and 0.14 μg/L, respectively.

Results and Discussion

Figure 1 shows a box plot of individual THMs and total THM concentrations in tap water of Osaka Prefecture in 1998, 1999 and 2002. Here, a scatter of observed data may be caused by traveling long distance in the distribution system or passing through a building's plumbing system (Yamamoto et al. 2007). THM species and levels in 1998 could be directly compared to those in 1999, because tap water were collected at the same tap in the same season. Chloroform was the most abundant THM (average ± standard deviation: 14.3 ± 3.99 μg/L, number of samples: $n = 13$) in 1998, and BDCM (5.96 ± 2.04 μg/L), DBCM (4.19 ± 1.59 μg/L) and bromoform (1.06 ± 0.538 μg/L) were in the decreasing order. In contrast, in 1999, DBCM and BDCM were abundant THMs (6.61 ± 2.23 μg/L, 5.72 ± 1.67 μg/L, $n = 13$) and followed by chloroform (4.14 ± 2.50 μg/L) and bromoform (1.41 ± 0.674 μg/L). The distribution of THMs in 1999 was similar to those in 2002 (7.30 ± 1.56 μg/L for DBCM, 7.23 ± 1.87 μg/L for BDCM, 5.47 ± 2.12 μg/L for chloroform and 2.40 ± 0.597 μg/L for bromoform, $n = 26$). Using a paired student's t-test, the average total THM in 1998 (25.5 ± 6.29 μg/L) was significantly higher than that in 1999 (17.9 ± 5.12 μg/L) [degree of freedom: $df = 12$, tabulated t value ($p = 0.05$) = 2.18 < calculated t value = 4.12]. In contrast, a student's t-test showed no difference between the average total THM in 1998 and in 2002 (22.4 ± 5.47 μg/L) ($df = 37$, tabulated t value ($p = 0.05$) = 2.03 > calculated t value = 1.59). The advanced treatment has already been started, and therefore, the difference among THMs composition in the advanced treated water in 1998, 1999 and 2002 may be due to a difference in operation conditions.

Unfortunately, we did not have a scenario for monitoring THM levels before change to advanced treatment in Osaka Prefectural water utilities. In this study, we

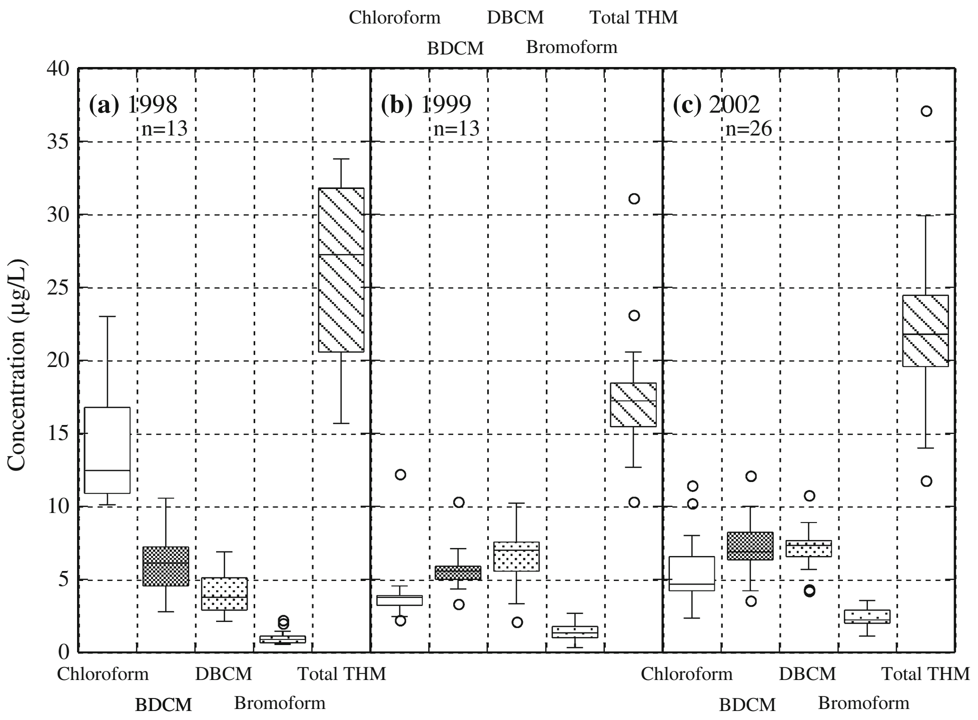

Fig. 1 Levels of individual THMs and total THM in advanced treated tap water of Osaka Prefecture in 1998, 1999 and 2002. The *rectangular boxes* cover the middle 50 percent of the data values, between the lower and upper quartiles. The *boxes* were divided by a *line* at the median value. The *whisker lines* extend to at most 1.5 times the *box* width from either or both ends of the *box*. They must end at an observed value, thus connecting all the values outside the *box* that are not more than 1.5 times the *box* width away from the *box*. *Open dots* showed mild outliers

examined THM levels in conventionally treated water of Osaka City in 1998 (total THM = 66.0 ± 11.8 µg/L and ranged of 43.9–83.4 µg/L). Chloroform was the predominant species (37.3 ± 8.59 µg/L) and followed by BCDM (20.7 ± 3.35 µg/L), DBCM (7.49 ± 0.62 µg/L) and bromoform (0.50 ± 0.08 µg/L). The decreasing order of THMs found in advanced treated water in 1998 was similar to that of conventionally treated water, although average of total THM was a half.

Starting July 22 1998, Osaka Prefectural water utilities changed their treatment processes by installing the ozone-granular activated carbon filtration after the rapid sand filtration of the conventional treatment processes (daily water supply = 2.23×10^6 m^3/day). Then, in order to control algae growth, a pre-chlorination step (to break-point, chlorine dose = 2–5 mg/L) was continued during the first warmer months (from July 1 1998 to August 24). Thereafter, chloramines were the primary disinfectant up to September 1999 (chlorine dose = 0.5–1.0 mg/L from August 24 to December 7 1998, and chlorine dose = 0.3 mg/L from December 8 1998), and after October 30 1999, pre-chlorination was quitted (The Water Quality Control Center, Osaka Prefectural Government 1998). US EPA (1999) showed that a number of options are available for controlling disinfection by-products (DBP) concentrations, i.e., the removal of DBP after formation, the use of alternative disinfectants to reduce formation or the removal of precursor organics prior to the addition of disinfectants. Here, the removal of precursor organics prior to disinfection represents the best option for DBP reduction and new technologies aimed at improving the effectiveness of this process would be well received by the water industry internationally. To our knowledge, our study was among the first results of THM data obtained from the actual advanced treatment processes with respect to US EPA's three basic methods for control DBP.

Cancer risks due to THMs were compared among the advanced treatment with and without pre-chlorination and with chloramines. Chloroform, BDCM and bromofrom are classified as Group B2, probable human carcinogens. Drinking water unit risks are 1.8×10^{-6} $(\mu g/L)^{-1}$ for BDCM and 2.3×10^{-7} $(\mu g/L)^{-1}$ for bromoform. Currently, the US EPA is proposing Maximum Contaminant Level Goal (MCLG) for chloroform of 70 µg/L (US EPA Integrated Risk Information System 2001). The cancer risk due to each THM was calculated from its concentrations by applying the unit risk, and total risk was the sum of risks associated with the BDCM and bromoform. A paired student's *t*-test showed that total risk in 1998 (average of 1.10×10^{-5}, ranged from 0.51×10^{-5} to 1.91×10^{-5}) were not significantly different with those in 1999 (average of 1.06×10^{-5}, ranged from 0.61×10^{-5} to 1.89×10^{-5}) ($df = 12$, tabulated t value ($p = 0.05$) = 2.18 < calculated t value = 0.432), although total THM concentrations in 1999 were three-fourths of those in 1998. Total risk in 2002 (average of 1.37×10^{-5}, ranged from 0.65×10^{-5} to 2.52×10^{-5}) were significantly higher those in 1998 ($df = 37$, tabulated t value ($p = 0.05$) = 2.03 < calculated t value = 2.18) and in 1999 ($df = 37$, tabulated t value ($p = 0.05$) = 2.03 < calculated t value = 2.63).

Although THMs levels in each sampling event were "snapshot" measurements, a difference in THM distribution could be found. Our findings suggested that the removal of precursor organics prior to disinfection was not the best option for THM reduction. Surprisingly, as a result of the comparison of concentrations and cancer risks, the advanced treatment with chloramines was the most effective measures. Actually, in Chiba Prefectural water utilities, the advanced treatment with pre-chlorination is in operation (e.g., annual water supply = 4.1×10^7 m^3/year and chlorine dose = 8.6 mg/L in Kashiwai water utilities in 1987) (Kuwahara 1989).

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