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Is Advanced Treated Water Truly High Quality?: the Answer from a Viewpoint of Cancer Risk Induced by Trihalomethane Class

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Abstract Before and after switching to the advanced treatment, a total of 48 trihalomethanes measurements was made at household taps in the specific distribution area in Osaka City, Japan. An average of total trihalomethanes concentrations in advanced treated water was three-fifths of that in conventionally treated water. The average lifetime cancer risks for total trihalomethanes were 48.5×10^{-6} in conventionally treated water and 44.8×10^{-6} in advanced treated water, which were higher than 10^{-6}, the negligible risk level. Surprisingly, the average lifetime cancer risk of conventionally treated water was not significantly different from that of advanced treated water. The highest value of hazard index found was an order of magnitude lower than unity.

Keywords Trihalomethane · Advanced treated water · Cancer risk · Hazard index

Chlorine is the most widely used drinking water disinfectant (White 1986). Despite the benefits of chlorine, halogenated disinfection byproducts (DBPs) of health concern, including trihalomethanes (THMs) and haloacetic acids are produced. Regular consumption of small amounts of DBPs may have adverse health effects, with much of the emphasis in the past on carcinogenicity (USEPA Integrated Risk Information System; IRIS 2005).

New more sophisticated and advanced water treatments, e.g., ozone-granular activated carbon filtration and membrane filtration, have been in operation of about 26% of water supplies in Japan in 2007 (Japan Water Works Association 2009). Total THMs concentrations in the finished water have drastically decreased and its speciation has be shifted to brominated ones after switching to the advanced treatment in the water utilities of Osaka City, Japan (Terashima et al. 2003). Simple comparative method for health effects associated with THMs determines whether the measured concentrations exceed to their water quality standards. However, this method is not appropriate for the comparison among drinking water with extremely different speciation, because the brominated THMs have high carcinogenicity relative to chloroform (IRIS 2005). Carcinogenic and noncarcinogenic risk assessment studies of THMs exposure for tap water had been carried out by many researchers (Lee et al. 2004; Uyak 2006; Viana et al. 2009; Basu et al. 2010). The resulting risk profiles were concentration profiles weighted by the relative risk of each species, and then the relative contribution to total risk by each species displayed important trends not readily apparent from the concentration profiles.

In this study serial sampling campaigns of water at household taps in the specific distribution systems in Osaka City before and after switching to the advanced treatment provided an opportunity to directly compare THMs levels between conventionally treated water (CTW) and advanced treated water (ATW). Evaluation of THMs speciation between CTW and ATW was carried out by using cancer risks and hazard indexes.

Materials and Methods

In all three water utilities in Osaka City, Japan (population supplied: about 2.6 million, daily water supply: ca.$1.2 \times 10^6 m^3$/day), a conventional treatment, consisting

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of coagulation, sedimentation, intermediate chlorination (breakpoint), sand filtration and post chlorination, had sequentially switched on March 30, 1998, March 30, 1999 and March 30, 2000 to an advanced treatment, which intermediate ozone is installed before sand filtration and post ozone and granular activated carbon filtration are located after it. Locations of sampling taps in the distribution area of Toyono utility switched to the advanced treatment on March 30, 2000 (daily water supply: ca. $2.5 \times 10^5 m^3$/day) were chosen by using the addresses of residences of students enrolled at Osaka City Nutrition College, as shown in Fig. 1. Five sampling campaigns were serially carried out: July–August 1998 (sampling point: Nos. 1–6 in Fig. 1), July–August 1999 (Nos. 1, 2, 4 and 7–14), July–September 2002 (Nos. 15–23), July–September 2003 (Nos. 16 and 18–31) and July–August 2004 (Nos. 24–27 and 29–31). Several taps could be sampled in two successive years (3 of 17 samples in 1998 and 1999; 7 of 24 samples in 2002 and 2003; 7 of 22 samples in 2003 and 2004), and as a result, a total of 48 measurements was made. But, both of CTW and ATW could not be collected from the same tap. Date of summer and early autumn seasons were selected as higher THMs concentrations were reported to be found in these periods of time (Yamamoto et al. 2007).

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. Duplicate water samples were obtained from each household tap after at least 30 s of flushing. Samples for THMs were analyzed according to USEPA Method 524.2 Rev.4.1 (USEPA 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 (30m × 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, respectively.

Results and Discussion

THMs concentrations in CTW at household taps (CTW_h) in the 1998–1999 campaigns were summarized in Table 1. Chloroform showed the highest concentration (58.5%), with marked decrease in order of BDCM (29.4%), DBCM (11.3%) and bromoform (0.8%). THMs in ATW at household taps (ATW_h) in the 2002–2004 campaigns were also listed. DBCM (33.9%) was the predominant species,

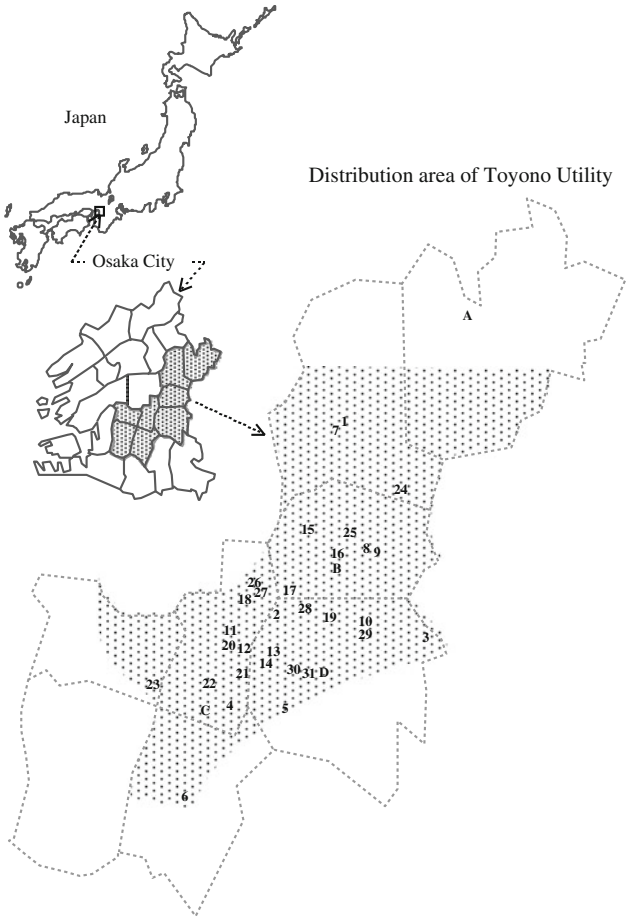

Fig. 1 Sampling locations of household taps (Nos.1–31) and the Toyono utility's four points at the extremities of distribution systems (A–D)

and followed by BDCM (31.9%), chloroform (22.5%) and bromoform (11.6%). An average of total THMs concentration in ATW_h (31.0 μg/L) was three-fifths of that in CTW_h (54.1 μg/L). All THMs measurements were below the water quality standards in Japan (60 μg/L for chloroform, 30 μg/L for BDCM, 100 μg/L for DBCM, 90 μg/L for bromoform, and 100 μg/L for total THMs).

Routinely monitored THMs concentrations at the fixed extremities of distribution systems by water utilities have been considered as representatives because THMs are found in highest concentration in these points. However, sometimes even more has been found at the consumer points. Lynberg et al. (2001) made comparisons among concentrations of THMs in water treatment plants, in water distribution system and in tap water, and showed that all intersystem differences were statistically significant. To know amounts of THMs which people actually drink, comparison of THMs concentrations at household taps with at the fixed extremities of distribution systems was carried out. The 1998–1999 and 2001–2003 THMs data at the fixed extremities of distribution systems of the Toyono

utility were abstracted from the records of Water Examination Laboratory of Osaka Municipal Waterworks Bureau. THMs concentrations in CTW were monitored nine times a year in 1998–1999 at the four points of extremities of distribution systems (CTW_e; A–D in Fig. 1), and these in ATW in 2001–2003 were measured six times a year at the three points (ATW_e; A–C). The records only listed the minimum, maximum and average of individual and total THMs. The minimum, maximum and average of total THMs in 1998–1999 were zero (below the minimum reporting level: <10 μg/L), 40, and 21.5 μg/L. For chloroform the values were zero (<6 μg/L), 26 and 12.5 μg/L, respectively. For BDCM the values were zero (<3 μg/L), 15 and 8.75 μg/L, respectively. DBCM (<10 μg/L) and bromoform (<9 μg/L) were below the respective minimum reporting levels in all cases. In 2001–2003, the minimum, maximum and average were 2, 23 and 11.2 μg/L for total THMs; zero (<1 μg/L), 4 and 1.6 μg/L for chloroform; 1, 8 and 3.9 μg/L for BDCM; zero (<1 μg/L), 9 and 4.8 μg/L for DBCM; zero (<1 μg/L), 3 and 1.3 μg/L for bromoform. Figure 2 shows the histograms of THMs concentrations at household taps, and the horizontal lines of ranges of data (minima, averages and maxima) at the fixed extremities of distribution systems. From the disparity in the sampling seasons between summer in this study and all seasons in the records, the THMs at household taps were corresponding to the maxima at the fixed extremities of distribution systems. Sixteen of 17 measurements of total THMs in CTW_h in 1998–1999 were larger than the maximum in CTW_e, and 25 of 31 ATW_h measurements in 2002–2004 were larger than the maximum in ATW_e in 2001–2003. The maximum of total THMs in CTW_e was three-fourths of the average in CTW_h. A similar ratio of the maximum in ATW_e and the average in ATW_h was also obtained. Therefore, THMs concentrations in household water represent the worst case that may happen.

A deterministic approach to human health risk assessment was used based on USEPA IRIS (2005) and recently adopted by many researchers (Lee et al. 2004; Uyak 2006; Viana et al. 2009; Basu et al. 2010). The cancer potency factors and the chronic reference doses (RfD) for four THMs are listed in Table 1. The chronic daily exposures were that four THMs concentrations were multiplied by an average drinking water consumption of 2 L/day and divided by an average weight per person of 70 kg. Each chronic daily exposure was multiplied by cancer potency factor and then yielded the lifetime cancer risk. Today, chloroform is classified as Group B2, probable human carcinogens, but cancer potency factor is not applicable. To take into consideration extremely different speciation between CTW_h and ATW_h, formerly applied chloroform factor was used (USEPA 1994). The average lifetime cancer risks for total THMs were 48.5×10^{-6} for CTW_h

Table 1 Lifetime cancer risks and hazard indexes of trihalomethanes in conventionally and advanced treated water at household taps

Trihalomethane	Cancer potency factor $((mg/kg)/day)^{-1}$	Chronic reference dose (RfD) (mg/kg-day)	Conventionally treated water			
			Concentration (μg/L)	Chronic daily exposure (mg/kg-day)	Lifetime cancer risk	Hazard index
Chloroform	6.1×10^{-3}	1×10^{-2}	31.6 ± 7.26	$9.03 \times 10^{-4} \pm 2.07 \times 10^{-4}$	$5.51 \times 10^{-6} \pm 1.27 \times 10^{-6}$	$9.03 \times 10^{-2} \pm 2.07 \times 10^{-2}$
Bromodichloromethane	6.2×10^{-2}	2×10^{-2}	15.9 ± 4.35	$4.55 \times 10^{-4} \pm 1.24 \times 10^{-4}$	$28.2 \times 10^{-6} \pm 7.71 \times 10^{-6}$	$2.27 \times 10^{-2} \pm 0.621 \times 10^{-2}$
Dibromochloromethane	8.4×10^{-2}	2×10^{-2}	6.12 ± 2.04	$1.75 \times 10^{-4} \pm 0.582 \times 10^{-4}$	$14.7 \times 10^{-6} \pm 4.89 \times 10^{-6}$	$0.874 \times 10^{-2} \pm 0.291 \times 10^{-2}$
Bromoform	7.9×10^{-3}	2×10^{-2}	0.428 ± 0.377	$0.122 \times 10^{-4} \pm 0.108 \times 10^{-4}$	$0.097 \times 10^{-6} \pm 0.085 \times 10^{-6}$	$0.061 \times 10^{-2} \pm 0.054 \times 10^{-2}$
Total trihalomethanes			54.1 ± 11.5		$48.5 \times 10^{-6} \pm 12.1 \times 10^{-6}$	$12.2 \times 10^{-2} \pm 2.61 \times 10^{-2}$
Trihalomethane	Cancer potency factor $((mg/kg)/day)^{-1}$	Chronic reference dose (RfD) (mg/kg-day)	Advanced treated water			
			Concentration (μg/L)	Chronic daily exposure (mg/kg/day)	Lifetime cancer risk	Hazard index
Chloroform	6.1×10^{-3}	1×10^{-2}	6.98 ± 3.08	$2.00 \times 10^{-4} \pm 0.880 \times 10^{-4}$	$1.22 \times 10^{-6} \pm 0.537 \times 10^{-6}$	$2.00 \times 10^{-2} \pm 0.880 \times 10^{-2}$
Bromodichloromethane	6.2×10^{-2}	2×10^{-2}	9.89 ± 3.35	$2.83 \times 10^{-4} \pm 0.956 \times 10^{-4}$	$17.5 \times 10^{-6} \pm 5.93 \times 10^{-6}$	$1.41 \times 10^{-2} \pm 0.478 \times 10^{-2}$
Dibromochloromethane	8.4×10^{-2}	2×10^{-2}	10.5 ± 2.78	$3.01 \times 10^{-4} \pm 0.793 \times 10^{-4}$	$25.3 \times 10^{-6} \pm 6.66 \times 10^{-6}$	$1.50 \times 10^{-2} \pm 0.396 \times 10^{-2}$
Bromoform	7.9×10^{-3}	2×10^{-2}	3.59 ± 0.606	$1.02 \times 10^{-4} \pm 0.173 \times 10^{-4}$	$0.809 \times 10^{-6} \pm 0.137 \times 10^{-6}$	$0.512 \times 10^{-2} \pm 0.087 \times 10^{-2}$
Total trihalomethanes			31.0 ± 9.32		$44.8 \times 10^{-6} \pm 13.0 \times 10^{-6}$	$5.42 \times 10^{-2} \pm 1.75 \times 10^{-2}$

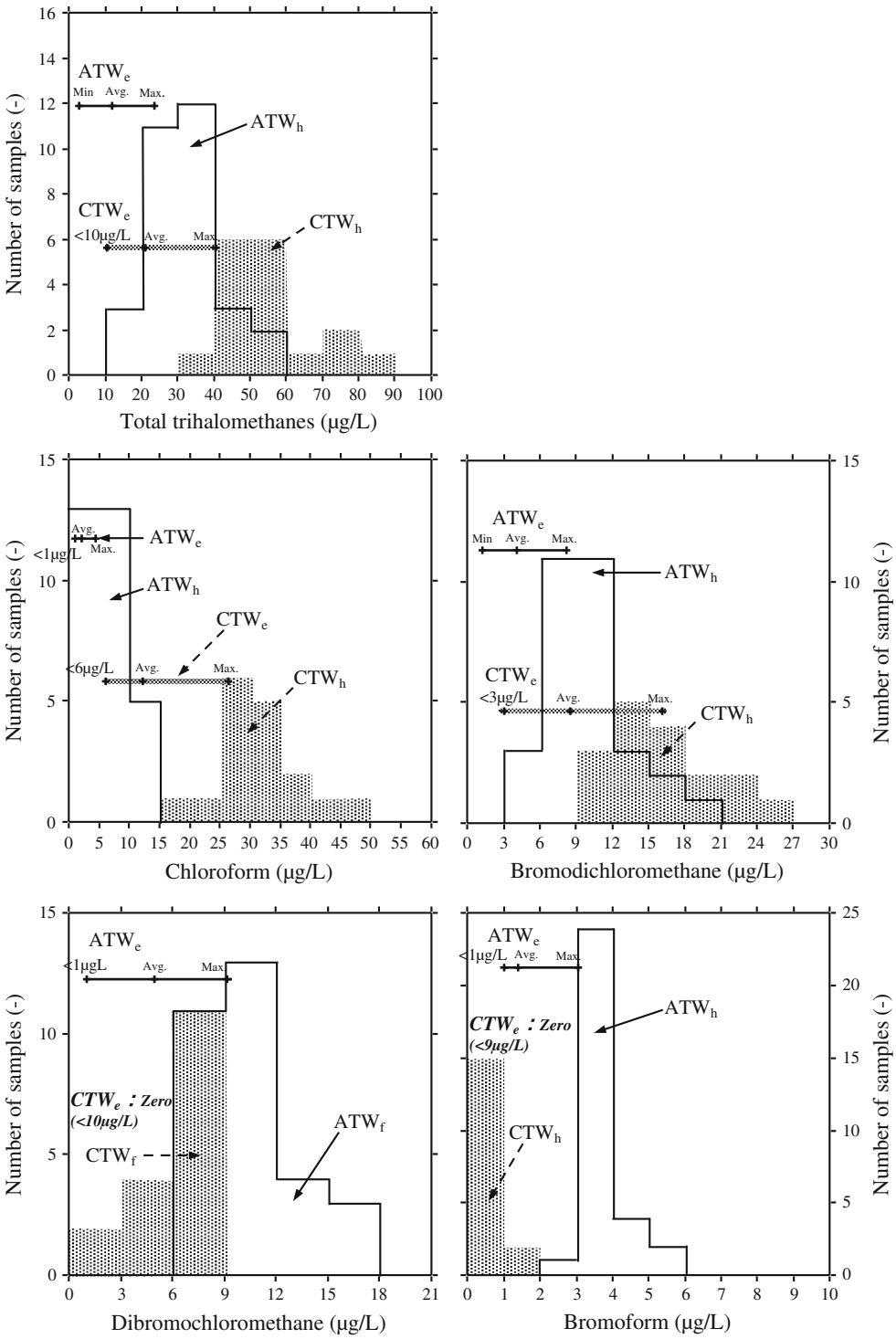

Fig. 2 Histograms of THMs concentrations in the water at household taps, and ranges of routinely monitored concentrations at the fixed extremities of distribution systems by the Toyono utility (minimum, average and maximum). CTW_h: Conventionally treated water (CTW) at household taps in 1998–1999; CTW_e: CTW at the extremities of distribution systems in 1998–1999; ATW_h: advanced treated water (ATW) at household taps in 2002–2004; ATW_e: ATW at the extremities of distribution systems in 2001–2003

and 44.8×10^{-6} for ATW_h, which were above the allowable limit, 10^{-6}, by a factor of about 50. THM individually contributed to the lifetime cancer risk for total THMs in CTW_h in the decreasing order: BDCM (58%), DBCM (30%) and chloroform (12%). ATW_h presented the highest contribution of DBCM (57%), followed by BDCM (39%) and chloroform (3%).

Two studies of risk assessment on drinking water at the same level as total THMs in CTW_h could be found. Lee et al. (2004) examined THMs concentrations in tap water in 19 districts in Hong Kong and found 60.7 μg/L for total THMs. Chloroform was the predominant species (78%), followed by BDCM (18%) and DBCM (4%). The average lifetime cancer risk for total THMs was 7.55×10^{-5} (an

average drinking water consumption of 4.48 L/day), and for BDCM made the highest percentage contribution (58%) to total risks, followed by chloroform (25%), DBCM (17%), and bromoform (0%). Here, total risk recalculated by using total ingestion of 2 L/day was 3.37×10^{-5}. An average of total THMs in tap water of the 15 districts in Istanbul was 65.7 μg/L. Chloroform (37%), BDCM (32%) and DBCM (25%) were similar levels. The lifetime cancer risk for total THMs was 8.79×10^{-5} (an average body weight of 65 kg). Both BDCM (46%) and DBCM (48%) were found to be significant contributors to total risks (Uyak 2006). These are very different each other. Cancer potency factors for BDCM and DBCM are one order of magnitude greater than those of chloroform and bromoform. Therefore, total risks are largely depended on the presence of BDCM and DBCM.

Surprisingly, the average lifetime cancer risk of CTW_h was not significantly different from that of ATW_h ($df = 46$, tabulated t value ($p = 0.05$) = 2.01 > calculated t value = 0.961). Although THMs measurements were "snapshots", the result in this study clearly showed that the water quality of ATW is not superior to that of CTW in relation to the cancer risk induced by THMs. Nobody has noticed that the same result is obtained by comparing lifetime cancer risks calculated from the abovementioned maximum of each THM between CTW_e (31.1×10^{-6}) and ATW_e (37.2×10^{-6}). This evidence supported the above findings. In addition, the hazard index associated to THMs exposure was calculated by using the chronic daily exposure to RfD, as shown in Table 1. The average hazard indexes for total THMs were 12.2×10^{-2} for CTW_h and 5.42×10^{-2} for ATW_h, respectively. The average hazard index of CTW_h was significantly different from that of ATW_h ($df = 46$, tabulated t value ($p = 0.05$) = 2.01 > calculated t value = 10.8). This is reasonable because CTW_h had higher total THMs than ATW_h. It shows that the highest value found in this study is about ten times lower than unity, not indicating non-cancer effects. Although other benefits, such as the removal of tastes, odors, or synthetic organic chemicals, should be considered, the findings in this study will strongly encourage continued evaluation of bromine substituted DBPs toxicity in ATW_h.

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