Simulating Distribution of Trihalomethane in Tap Water in the Area Receiving a Combination of Advanced Treated Water and Conventionally Treated Different Source Water: 1998, 1999 and 2002 Data on Osaka Prefecture and Its Surrounding Cities, Japan

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Abstract Empirical equations for explaining trihalomethane (THM) distribution were established based on data on tap water in Osaka City before and after starting the advanced treatment and were represented by the following equations for bromodichloromethane (S_1), dibromochloromethane (S_2) and bromoform distribution factors (S_3) as a function of chloroform distribution factor (S_0), respectively: $S_1 = -0.97S_0^2 + 0.75S_0 + 0.19$ (regression coefficient: $r = 0.71$), $S_2 = 0.13S_0^2 - 0.76S_0 + 0.51$ ($r = 0.98$) and $S_3 = 0.83S_0^2 - 0.99S_0 + 0.30$ ($r = 0.97$). Further, the derived equations were verified by THMs data of Osaka Prefecture and its surrounding cities (except for Osaka City), receiving a combination of advanced treated water and conventionally treated different source water.

Keywords Trihalomethane · Advanced treatment · Trihalomethane distribution factor

Occurrence and distribution of trihalomethanes (THMs) in tap water vary from place to place due to different source water quality and diverse water treatment processes with different waterworks. 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) showed that, by starting the advanced treatment, concentrations of total THM were drastically decreased and THM speciation shifted to brominated ones in the finished water of the water utilities of Osaka City. However, from a toxicological point of view, a shift in the distribution of THMs to brominated ones by starting the advanced treatment will continue to gain considerable attention. Empirical equations for explaining changes in THM species and concentrations in tap water in Osaka City before and after starting the advanced treatment were established, and then the derived equations were verified by data from Osaka Prefecture and its surrounding cities, receiving a combination of advanced treated water and conventionally treated different source water.

Materials and Methods

Water utilities in Osaka City switched step by step to the advanced treatment on March 30, 1998 (be equal to 16% of the population supplied of Osaka City), March 30, 1999 (59%) and March 30, 2000 (100%). "Advanced treatment processes" are that ozone-granular activated carbon filtration are installed into after rapid sand filtration instead of pre-chlorination in "conventional treatment processes" consisting of pre-chlorination, coagulation, sedimentation, rapid sand filtration and post-chlorination. About 75% of water supply in 41 cities in Osaka Prefecture except for Osaka City is purchased from Osaka Prefectural waterworks that the advanced treatment is operating since July 1998. The most part of water supply in the cities of Kobe, Nishinomiya, Ashiya and Amagasaki are purchased from the utilities of Hanshin Water Supply Authority who had changed to the advanced treatment between July 1993 and 2000. Those utilities take raw surface water from the Yodo River. The water supply in our study area together covers about 15% of Japanese population.

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Tap water samples of Osaka City were collected from well flushed taps (at least 30 s) in the homes of students enrolled at Osaka City Nutrition College on July and August 1998 (numbers of sample: n = 17), July and August 1999 (n = 23), and July and September 2002 (n = 21), respectively. Tap water of Osaka Prefecture and its surrounding cities (except for Osaka City) were also collected on July and August 1999 (from 25 cities) and July, August, and September 2002 (from 26 cities). 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).

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 (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

The observations of tap water in Osaka City in 1998, 1999, and 2002 are very beneficial for the purpose of evaluating the effect of changeover of treatment processes on the distribution of THMs in tap water. Average concentrations of total THM in conventionally treated surface water (CTSW) were 66.0 in 1998 (n = 16), 48.3 μg/L in 1999 (n = 15) and no data in 2002, and those in advanced treated surface water (ATSW) were 18.3 in 1998 (n = 1), 15.2 in 1999 (n = 8) and 24.9 μg/L in 2002 (n = 21). Chloroform was the most abundant THM in CTSW samples (an average of 33.4 μg/L and a range of 19.6–53.2 μg/L). Meanwhile, BDCM and DBCM were the dominant THMs in ATSW samples (averages of 6.81 and 7.79 μg/L, and ranges of 3.01–11.1 and 3.84–11.3 μg/L, respectively).

Hutton and Chung (1992) assumed the third-order polynomials for bromine distribution factors in terms of bromine incorporation factor. To derive coefficients for the equations, they performed regression analyses with the data obtained by the THM formation potential test based on

samples collected from the Sacramento-San Joaquin Delta of the US. Their study areas were a part of a tidal estuary and thereby could be encountered with a wide range of bromide levels. Meanwhile, ours had low levels (30–50 μg/L; Yamada 1997). Therefore, we did not use the bromine incorporation factor and focused on the interrelation among THMs distribution factors. Weight fractions of individual THM species existing in total THM are depicted as a function of chloroform distribution factor (S_0) that is the proportion of chloroform existing in total THM in Fig. 1a–c. Data points were divided into two groups in the range of S_0 that were $0.13 < S_0 \leq 0.32$ for ATSW and $0.49 < S_0 \leq 0.72$ for CTSW, but intuitively fitted to a quadratic. Regression equations by a least squares are as follows:

$$S_1 = -0.97S_0^2 + 0.75S_0 + 0.19 \text{ (regression coefficient: } r = 0.71, \ n = 61) \tag{1}$$

$$S_2 = 0.13S_0^2 - 0.76S_0 + 0.51 \ (r = 0.98) \tag{2}$$

$$S_3 = 0.83S_0^2 - 0.99S_0 + 0.30 \ (r = 0.97) \tag{3}$$

where S_1, BDCM distribution factor; S_2, DBCM distribution factor; and S_3, bromoform distribution factor. Here, of course it is $S_0 = S_0$, and the sum of THM distribution factors is one. With increasing S_0, predicted S_1 reached the maximum at $S_0 = 0.39$ and then decreased. Predicted S_2 and S_3 monotonically decreased. However, the observed S_3 deviated from the predicted values in the range of $0.60 \leq S_0$. Further, chloroform yields ($[CHCl_3]$) are plotted against S_0 on a log-log graph in Fig. 1d. With increasing $\log S_0$, $\log [CHCl_3]$ increased and the following equation is obtained:

$$[CHCl_3] = 91 \, S_0^{1.9} \quad (r = 0.96). \tag{4}$$

Here, predicted $[CHCl_3]$ had 91 μg/L at $S_0 = 1$. This means that total THM levels in all samples were lower than the 100 μg/L limit of the Japanese drinking water quality standard.

Total THM in Osaka Prefecture and its surrounding cities (except for Osaka City) were, on average, 27.9 μg/L in 1999 (ranged from 5.75 to 65.1 μg/L, n = 42) and 33.6 μg/L in 2002 (11.8–89.3 μg/L, n = 47), respectively. Smooth curves were obtained as illustrated in Fig. 1a–d even though these data represent combinations of various treatment processes and source water locations. Observed data (S_1, S_2, S_3, and $[CHCl_3]$) in Kobe City, where a mixture of its own CTSW and the purchased ATSW from Hanshin Water Supply Authority was received, were scattered between the data on ATSW and CTSW of Osaka City ($0.36 < S_0 \leq 0.55$). Generally, with the conventional treatment, "surface water source" has the highest chloroform concentrations and higher total THM, and "groundwater source" has higher brominated THMs and lower total THM. With increasing S_0, types of tap water were arrayed in

Fig. 1 **a–c** Bromine distribution factors versus chloroform distribution factor and **d** chloroform formation versus chloroform distribution factor. +, Data obtained from Osaka City in 1998, 1999, and 2002, ○, data obtained from cities of Osaka Prefecture and its surrounding in 1999 and 2000
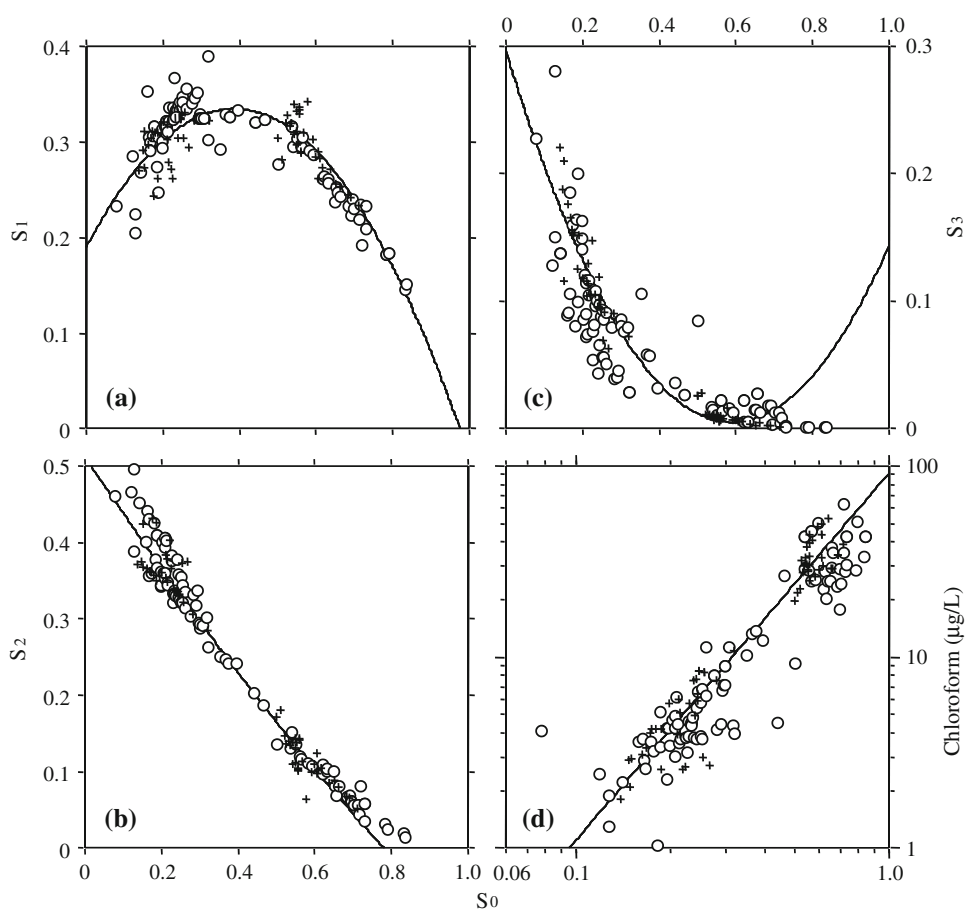
following order; conventionally treated groundwater (CTGW), ATSW, a mixture of ATSW and CTSW, a mixture of CTSW and CTGW, and CTSW.

To evaluate the agreement of predicted with observed values, a linear regression was conducted. Here, the intercept was always set equal to zero. The individual slopes of best-fit lines of S_1, S_2, S_3, and [$CHCl_3$] that obtained from Osaka Prefecture and its surrounding cities were 0.98 ($r = 0.83$), 0.96 (0.99), 1.06 (0.83), and 1.17 (0.87). Further, we verified applicability of the Eqs. (1)–(4) by using THM data on the findings of the National Organics Reconnaissance Survey (NORS) summarized by Symons et al. (1975). The NORS data set included THMs in finished water collected from late January to end of April 1975 from 80 locations geographically distributed in the US, and were chosen to represent a wide variety of raw-water sources and treatment techniques. Observed [$CHCl_3$] of the NORS data were scattered in a wide range (average of 46 μg/L, ranges of 0.2–311 μg/L, numbers of positive data: $n_p = 78$). With only positive THM data on the NORS, the best-fit line for S_1 had the slope of 0.91 and the r of 0.88 ($n_p = 77$). S_2 had 0.84 and 0.88 ($n_p = 61$). Predicted S_1 and S_2 were strongly correlated with observed ones. Prediction for S_3 was the least important, as this was

when bromoform was often not detectable. The predicted [$CHCl_3$] did not fit to the NORS data.

Thus, our empirical equations can predict the distribution of THM in any tap water, but not actual concentrations. Hence, for each study area, the correlation between S_0 and [$CHCl_3$] should be established before beginning to make a quantitative estimate.

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