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Use of a Home Water Filter in the Reduction of Trihalomethanes and Total Organic Halogen in Tap Water: Forty-One Samples from Osaka City and Surrounding Cities of Japan in 1999, 2000, and 2004

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According to the 1999 National Consumer Water Quality Survey, prepared for the Water Quality Association, 38% of respondents used a household water treatment device (Lisle, 1999). In Japan, the Asahi Newspaper conducted a cross-sectional questionnaire survey of home water filter use for randomly selected 3000 families in the spring of 2001. The result showed that 29% of the families used the filter, and in particular, Tokyo Metropolis and twelve cities with more than a million people reached 45%. The high prevalence of home water filter use will have the impact on human exposure of disinfection byproducts (DBPs) at a population level.

In Japan, with respect to removal efficiencies of DBPs by a home water filter, total trihalomethanes (THMs) is the only measurement item listed in certification. It is mandatory to list specifications for a filter on the accumulated volume of water filtrated which 20% of total THMs in tap water is found. Testing is carried out by filtering tap water fortified with THMs continuously according to Japanese Industrial Standards S3201 "Testing methods for household water purifiers" (2004). Takahashi and Morita (1998) showed that THMs concentrations in filtrates under the abovementioned test clearly differed from those in the experiment simulating use conditions of water filter at home. In the former THMs were completely removed until 2000*l* were continuously filtrated, while in the latter, 70% of THMs in tap water was found in the filtrate after which 30*l* were filtrated daily over a period of one month (900*l*). This suggests that there is no method of estimating THMs concentrations in filtrates except for the method that is directly measured at each home.

Two previous studies examined the removal efficiencies of THMs from tap water using water filters actually at home. Toyama's tests of forty-nine home water filters in the homes of staffs of Department of Urban Engineering, the University of Tokyo, demonstrated on average 45% removal of total THMs and 52% for total organic halogen (TOX) (1991). Takahashi and Morita (1998) tested six home water filters (activated carbon/hollow fiber membrane) used with various time and showed 53% removal of total THMs.

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Purification treatment commonly operated in Japan consists of coagulation, sedimentation, intermediate chlorination, rapid sand filtration and post chlorination and is called "conventional treatment". Today a new more sophisticated water treatment has been introduced into 20% of water supplies in Japan, 2001 (Terashima, 2002). At all water utilities of Osaka City, the conventional treatment installed ozonation followed by granular activated carbon filtration has been in operation for some years and is referred to as "advanced treatment". Terashima *et al.* (2003) showed that the advanced treatment could have had direct effect on decreasing [about 20% of conventionally treated tap water (CTTW)] and stabilizing the THMs concentrations. Reporting was considered satisfactory lower levels as regards THMs concentrations in advanced treated tap water (ATTW) at tap compared with filtrated CTTW by a home water filter. Osaka Municipal Waterworks Bureau conducted a questionnaire survey for 6,366 persons who drank ATTW during 1998-2000 and 39% of the persons have been still using a home water filter (Terashima, 2002). Our study area, namely Osaka City (population: two million and six hundred thousand) and its surrounding cities, provide a good case for the study examining whether a home water filter is effective for the removal of DBPs in ATTW similarly to CTTW or not.

In this study, to estimate how halogenated DBPs in tap water were actually removed by a home water filter at home, we examined THMs and TOX levels in tap water and their filtrates. Here, we regarded THMs as a representative of halogenated DBPs and looked upon TOX as a total of them, respectively. Comparing cancer risk due to THMs in filtrated ATTW with filtrated CTTW using the U.S. EPA unit cancer risk for each THM, we discussed whether a home water filter was useful for the reduction of cancer risks of ATTW or not.

MATERIALS AND METHODS

Tap water and their filtrates were collected from the homes of students enrolled at Osaka City Nutrition College in Osaka City and its surrounding cities to 40ml Teflon-lined screw cap vials with 25mg of sodium thiosulfate from 23 to 25 August 1999, 4 to 30 August 2000, 23 to 28 July and 27 September 2004. Most of home water filters were faucet mounted activated carbon/hollow fiber membrane type. Sixteen halogenated hydrocarbons (Wako Pure Chemical Co., Tokyo, Japan), which constitute measurement items under Japanese drinking water standards, were analyzed according to 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-1 column (60mx0.25mm i.d., 1μm film thickness) (Agilent Technologies, Wilmington, DE) was used (initial temperature 40°C and held for 1min, increased at a rate of 10°C/min to 180°C, at rate of 15°C/min to 200°C). Helium was used as a carrier gas at 1ml/min, and the split ratio was 10:1. None of these compounds appeared in any of the samples studied except the four THMs, for which the detection limits were 0.43$\mu g/l$ for

chloroform, 0.36μg/l for bromodichloromethane (BDCM), 0.35μg/l for dibromochloromethane (DBCM) and 0.37μg/l for bromoform. The concentration of TOX was measured according to Standard methods for the examination of water and wastewater "5320B. Adsorption-Pyrolysis-Titrimetric method" (APHA, AWWA, WEF, 1998) using an organic halogen analyzer TOX-10 (Mitsubishi Chem. Ind.).

RESULTS AND DISCUSSION

Brief question concerning the use of home water filters was concurrently asked to students of the Osaka City Nutrition College at the sampling of water. Proportion of families who used home water filters was 32% of 65 in 1999, 34% of 68 in 2000 and 34% of 68, respectively. Our sample size is small, but there are consistent with the previous results (The Asahi Shimbun, 2001: Terashima, 2002). Figure 1 (a) and (b) shows levels of THMs in tap water and their filtrates in 1999 and 2004, respectively. A set of bars was cumulative concentration of each THM in tap water (left side) and their filtrates (right side). The bar's numbers from 1 to 5 and 13-15 represented water supplies of Osaka City. Here, in 1999, CTTW was partly supplied. The numbers from 6 to 11 and 16-20 represented tap water in the other cities of Osaka Prefecture. Osaka Prefecture's water supplies (ATTW) are wholesaler. Almost all water supplies of municipalities in Osaka Prefecture purchase a wholesale ATTW and then a blend of their own CTTW or ATTW is supplied to the homes. The remaining bars represented surrounding Prefectures (Nos. 12, 21 and 22 for Hyogo, No.23 for Kyoto, No. 24 for Nara and Nos. 25 and 26 for Mie Prefecture). No breakdown of data by type or age of filter was provided.

Total THMs level in filtrated ATTW [range; not detected (N.D.)-48.2μg/l, mean±standard deviation; 10.4±12.8μg/l, number of sample; n=13] was, on average, a one-third of that in ATTW (11.6-55.6μg/l, 30.5±15.4μg/l). Filtrated CTTW (0.94-110μg/l, 41.1±38.1μg/l, n=7) was a four-fifth of CTTW (32.1-93.9μg/l, 51.3±19.8μg/l). Filtrate (N.D.-55.6μg/l, 32.3±20.5μg/l, n=6) was a four-fifth of blending tap water (11.7-61.2μg/l, 39.5±17.1μg/l). Concentrations of total THMs and chloroform in the filtrate (No.26) exceeded each quality standards for drinking water in Japan (100μg/l for total THMs and 60μg/l for chloroform). The remaining samples were well below the standards. Student's t-test showed that total THMs in ATTW was not significantly different with that in filtrated CTTW [degrees of freedom (df); 18, tabulated t value (p=0.05); 2.10, calculated t value; -0.893]. Chloroform was the dominant THM species in CTTW (62% of total THMs). The shift in speciation from chloroform to brominated THMs was observed in ATTW. DBCM was the THM species found at the highest concentration; BDCM was the second most abundant THM species. Chloroform constituted less than 25% of total THMs concentration and was the second lowest abundant species. Speciation of THMs in a blend of ATTW and CTTW was according to each blending ratio. Removal efficiency of THM in ATTW was, in descending order, bromoform (78%), DBCM (73%), BDCM (64%) and chloroform (45%). THM incorporated into more bromine had higher

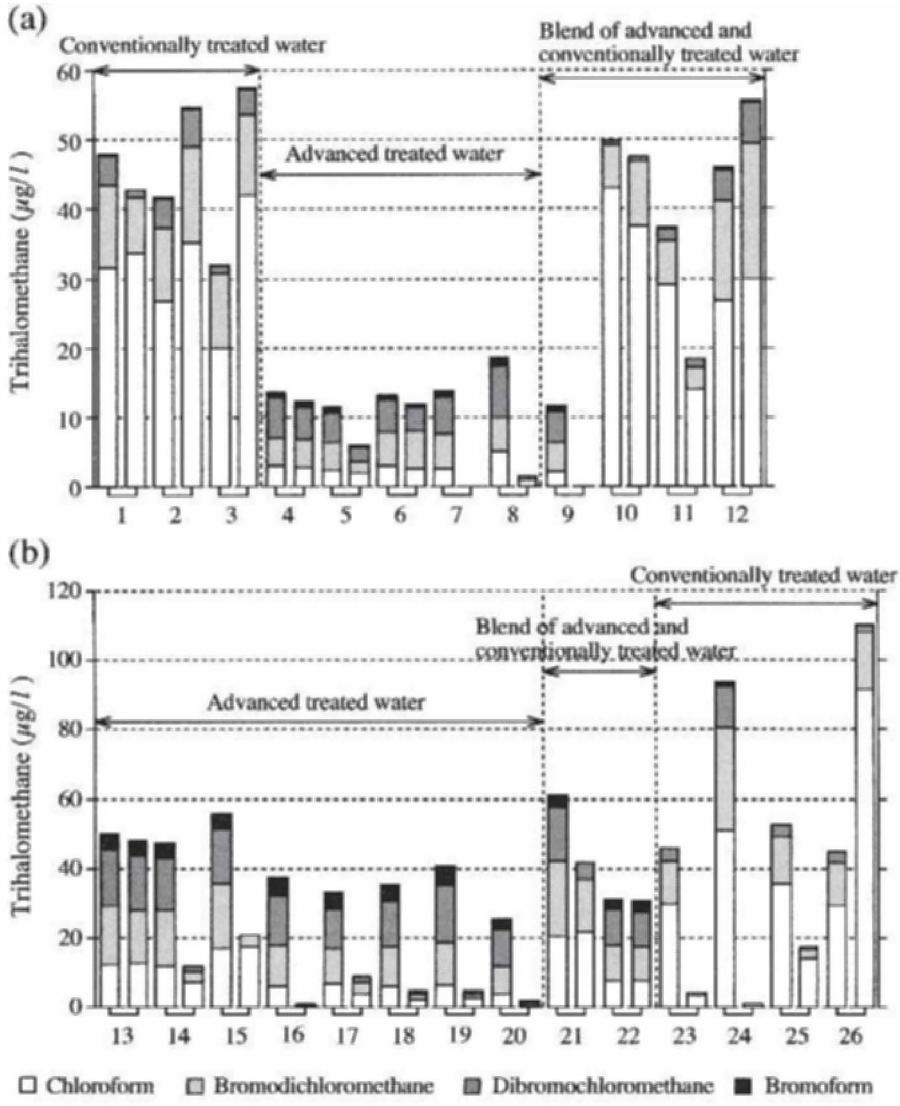

Figure 1. Levels of THM in tap water and their filtrates in 1999 (a) and 2004 (b).

affinity to cartridge. The similar tendency can be found in Takahashi and Morita's study (1998) of CTTW (-14% for chloroform, 68% for BDCM, 84% for DBCM and 89% for bromoform). Filtrated CTTW showed practically low removal of THMs. Chloroform in the filtrated CTTW was higher than the corresponding CTTW. Therefore, a home water filter appears to change the proportion of total THMs comprised by four THMs. Contrary, Savitz *et al.* (2005) showed that there was negligible difference in the removal efficiency between individual THM species in the laboratory study.

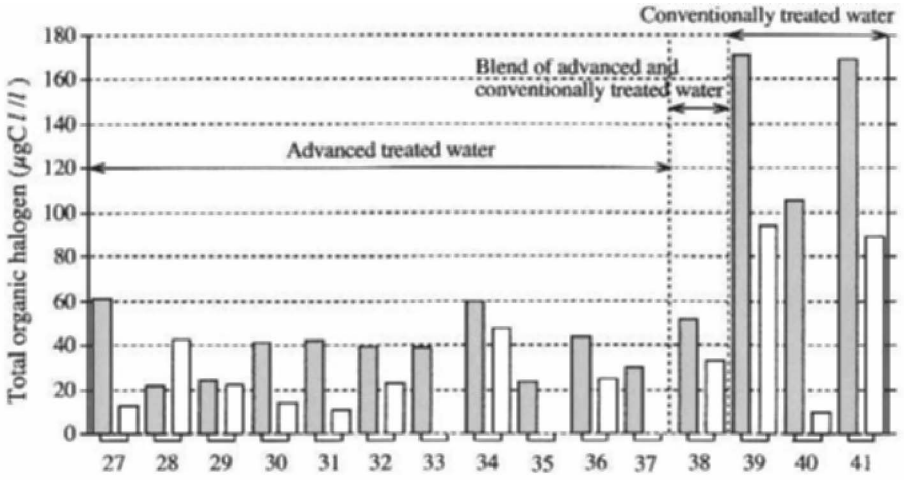

Figure 2. Levels of TOX in tap water and their filtrates in 2000.

Figure 2 shows levels of TOX in tap water and their filtrates in 2000. A set of bars was TOX concentration in tap water (left side) and their filtrates (right side). The bar's numbers from 27 to 32 represented water supplies of Osaka City and from 33 to 38 were tap water in the other cities of Osaka Prefecture. The remaining bars represented its surrounding Prefectures (No. 39 for Hyogo and Nos. 40 and 41 for Nara Prefecture). TOX in filtrated ATTW (N.D.-48.2μgCl/l, 19.3±15.2μgCl/l, n=11) was, on average, a half of that in ATTW (21.9-61.0μgCl/l, 39.0±13.4μgCl/l). Filtrated CTTW (9.6-94.3μgCl/l, 64.5±47.6μgCl/l, n=3) was also a half of CTTW (106-171μgCl/l, 149±37.0μgCl/l). Blending water and its filtrate were 52.0 and 33.4μgCl/l, respectively. TOX in ATTW was not significantly different with that in filtrated CTTW [df; 12, tabulated t value (p=0.05); 2.18, calculated t value; -1.70].

Total THMs concentrations in 4 of the 26 filtrates (Nos. 2, 3, 12 and 26 in Fig. 1) were higher than their corresponding concentrations in tap water, and six filtrates were almost equal to their paired tap water (Nos. 1, 4, 6, 10, 13 and 22). In contrast, only two out of 15 data regarding TOX showed filtrates higher than equal to tap water (Nos. 28 and 29 in Fig. 2). THMs and TOX in tap water are removed by adsorption on activated carbon in the cartridge. Some simplifying assumption can be made. Regardless of the large difference in characteristics of tap water, THMs or TOX concentrations in filtrates are equal to those in tap water when the capacity of cartridge is expired. Thereafter, replacement of adsorbed THMs to other TOX which have higher affinity to activated carbon will occur and THMs in filtrates will be higher than those in tap water. Average removal efficiencies were calculated using all measurements and were 39% for total THMs and 48% for TOX, respectively. These findings lead to support to the similar removals of THMs and TOX reported by Toyama (1991) and Takahashi and Morita (1998).

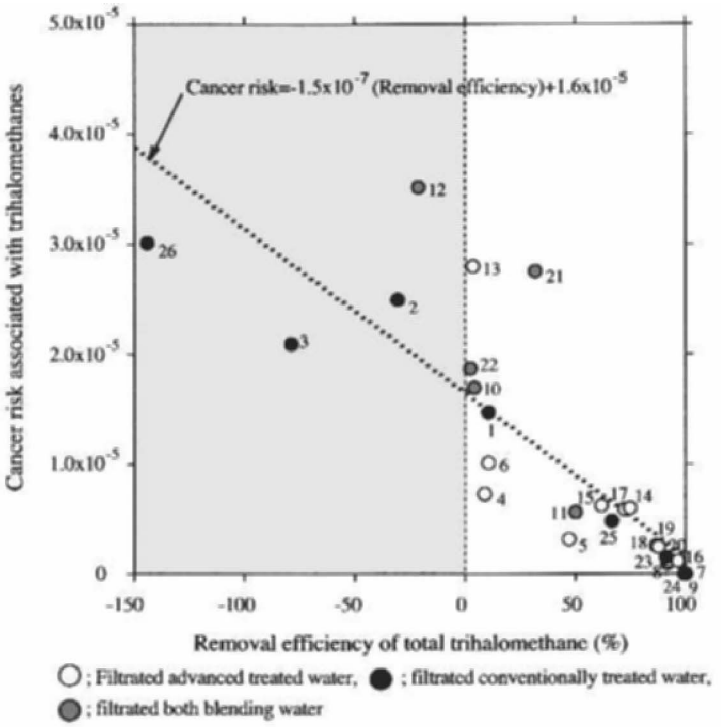

Figure 3. Relationship between cancer risks due to total THMs in filtrates and removal efficiencies of total THMs. Numbers are the same as Figure 1.

Chloroform, BDCM, and bromoform are classified as Group B2, probable human carcinogens. Currently, the U.S. EPA is proposing a Maximum Contaminant Level Goal (MCLG) for chloroform of 70$\mu g/l$. The MCLG is proposed at a level at which no adverse effects on the health of persons are anticipated and with an adequate margin of safety. The MCLG for DBCM, which is classified as a possible human carcinogen (Group C), is 60$\mu g/l$. Chloroform level in one measurement of filtrate in the present study was higher than MCLG level (No.26). Needless to say, snapshot measurement of THM on a given day may not be representative of THM in filtrates over a long period of time. Drinking water unit risks are $1.8\times10^{-6}(\mu g/l)^{-1}$ for BDCM and $2.3\times10^{-7}(\mu g/l)^{-1}$ for bromoform (U.S. EPA, Integrated Risk Information System).

Using the U.S. EPA unit cancer risk for each THM, we evaluated the reduction of risk by a home water filter. The cancer risks calculated for THMs in ATTW and filtrated ATTW ranged from 0.738×10^{-5} to 3.43×10^{-5} ($1.85\times10^{-5}\pm9.63\times10^{-6}$, n=13) and from zero to 2.80×10^{-5} ($0.579\times10^{-5}\pm7.31\times10^{-6}$). While the corresponding values for CTTW and filtrated CTTW were 1.92×10^{-5}-5.33×10^{-5} ($2.61\times10^{-5}\pm1.21\times10^{-5}$, n=7) and zero-$3.01\times10^{-5}$ ($1.39\times10^{-5}\pm1.20\times10^{-5}$), respectively.

A paired student's t-test showed that cancer risk for filtrated CTTW was not significantly different with that for CTTW [df; 6, tabulated t value (p=0.05); 2.45, calculated t value; 1.52], whereas cancer risk for filtrated ATTW was significantly lower than that for ATTW [df; 12, tabulated t value (p=0.05); 2.18, calculated t value; 4.82].

We should give attention to the occurrence of brominated THMs in ATTW, because they have greater toxicity than chloroform and their levels are equal to CTTW. Student's t-test showed that cancer risk for ATTW was not significant different with that for CTTW [df; 18, tabulated t value (p=0.05): 2.10, calculated t value; -1.55].

Figure 3 shows that the total risks due to THMs in the filtrates decrease to zero as the removal efficiency of total THMs increase to 100%, despite characteristics of tap water. The following equation was obtained:

$$\text{Cancer risk} = -1.5 \times 10^{-7} (\text{removal efficiency}) + 1.6 \times 10^{-5} \quad (r=0.83, n=26).$$

Any changes in absolute total THMs concentrations would not lead to changes in the risk arising from THMs. The plot was primarily controlled by the rise and fall in the concentrations of BDCM.

High concentrations of THMs that occurred some years ago were lowered by the introduction of advanced treatment and it looks like home water filter is unnecessary. However, with respect to the cancer risks due to THMs, a home water filter is a useful device for the reduction of risks of ATTW as well as CTTW. Consequently, further work concerning removal of other classes of halogenated disinfection byproducts, i.e., brominated haloacetic acids, in ATTW by a home water filter will be needed.

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