報　文

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Graphical Interpretation of Differences or Similarities in Trihalomethanes Speciation and Their Induced Cancer Risk in Various Tap Water

Kohji Yamamoto

Abstract

Graphical tool displaying differences or similarities in trihalomethanes (THMs) speciation and their induced cancer risk in a variety of tap water was proposed: tetra diagram with the upper side of chloroform and bromoform concentrations and the lower side of bromodichloromethane and dibromochloromethane concentrations. Its applicability was discussed by thirty two pairs of 2002 summer and winter THMs measurements in a variety of tap water in Osaka City and its surrounding cities, Japan. Trapezoids were drawn by THMs concentrations in advanced treated river water in both seasons, but their areas in summer were larger than these in winter. In summer, conventionally treated river water (CTRW) and reservoir water (CTReW) were warped trapezoids with a long tail at the chloroform vertex, while in winter, CTRW were parallelograms and CTReW were trapezoids. Further, the length of lower side of tetra diagram was considered as a promising index of magnitude of the lifetime cancer risk induced by THM class. Surprisingly, a little dependence of cancer risks on changes in treatment processes, a variety of raw water, and combination of blending of finished water could be found.

Key words: trihalomethanes speciation, cancer risk, tetra diagram, advanced treated water, conventionally treated water

I　INTRODUCTION

Today, a new more sophisticated and advanced water treatment (e.g., ozone-granular activated carbon filtration, membrane filtration) has been in operation (about 25 % of Japanese water supplies in 2002) [1]. Even though drinking water treatment processes are more sophisticated and advanced, chlorine disinfection is inevitable for maintaining safety to biological contamination in supplied water [2]. As a result, halogenated disinfection byproducts (DBPs) of health concern are formed. Trihalomethanes (THMs) are the predominant group of DBPs, and therefore, can be deemed as one of the most burdensome ones.

In Kansai area, Japan, the advanced treatment has widely been in operation. The comprehensive studies, corresponding to THMs speciation in conventionally treated and advanced treated river water (CTRW, ATRW), were aimed at: (i) investigating total organic halogen (TOX) concentrations in 68 tap water in 28 cities in Osaka Prefecture and its surrounding cities [3]; (ii) examining the changes in trihalomethane (THM) and TOX due to heating or boiling [4]; (iii) estimating how halogenated disinfection byproducts in tap water were actually removed by a home water filter [5]; (iv) examining how storage of ATRW in a building's plumbing system effects THM levels and speciation [6]; (v) elucidating effect of a little difference in trains of chlorination, ozonation and granular activated carbon filtration in the advanced treatment on THMs speciation and levels [7]; (vi) deriving empirical equations for explaining changes in THMs speciation [8]; (vii) comparing quality of CTRW and ATRW by using cancer risk and hazard indexes of THMs [9]. However, to cope with practical problems, a simple graphical display tool summarizing raw data and showing many different aspects of a phenomenon is lacking.

In this study, a simple graphical tool displaying differences or similarities in THMs speciation and their induced cancer risk in various tap water was proposed, and its applicability was discussed by 2002 summer and winter THMs concentrations in various tap water from Osaka Prefecture and its surrounding cities, Japan.

Osaka City Institute of Public Health and Environmental Sciences
8-34 Tojo-cho, Tennoji-ku, Osaka 543-0026, Japan

Ⅱ MATERIALS and METHODS

Thirty two pairs of water samples were collected from well flushed faucets in the homes of students enrolled at Osaka City Nutrition College in nineteen municipalities of Osaka Prefecture and its surrounding, Japan on July 24-30 and December 19-26, 2002. The student's addresses were used to determine their supply utilities, and gained information on raw water, treatment technologies and blends from each municipal or prefectural waterworks website (the water quality examination program as stipulated in the Japanese Water Supply Law).

Conventional treatment usually consists of pre-chlorination, coagulation, sedimentation, rapid sand filtration and post-chlorination. Advanced treatment in Osaka prefectural waterworks, adding an ozone-granular activated carbon filtration after the rapid sand filtration in conventional treatment, has been in operation, and ATRW has been wholesaled to almost all municipalities in Osaka Prefecture. The advanced treatment in Osaka municipal waterworks, adding intermediate ozone before the rapid sand filtration in the Osaka prefectural waterworks, has been in operation. The advanced treatment in Hanshin Water Supply Authority, adding an ozone-granular activated carbon filtration before the sedimentation in the conventional treatment, has been in operation and ATRW has been wholesaled to the cities of Kobe, Nishinomiya, Ashiya and Amagasaki in Hyogo Prefecture. The treatment in Hirakata municipal waterworks in Osaka Pref. is also the same. Here, the pre-chlorination is not operated in the advanced treatment.

As the water contained residual chlorine, about 25mg of sodium thiosulfate per 40mL 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 U.S.EPA Method 524.2 Rev.4.1 [10] 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 mx0.32 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.

Ⅲ RESULTS and DISCUSSION

THMs measurements in thirty two pairs of a variety of tap water in 2002 summer and winter were summarized in Figure 1 by using stacked column charts commonly used for representing the differences or similarities in THMs speciation and concentrations at the same time. In a stacked column chart, all of the columns in THM speciation are stacked on top of each other. The resulting stacked column represents the sum of all of the data items in the respective THM. Each data item is represented as a segment in the stacked column. At the vertical axis, the bar's numbers were the sample number.

A Stiff diagram is a graphical representation of the major ion composition of a water sample and can be used to help visualize ionically related water from which a flow path can be determined, or to show how the ionic composition of a water body changes over space and/or time if the flow path is known [11]. On the basis of concept of Stiff diagram, tetra diagram drawn by four THMs was proposed. Tetra diagram is created from two parallel horizontal axes extending on either side of a vertical zero axis. Chloroform and BDCM are plotted in μg/L on the left side of the zero axis, and bromoform and DBCM are plotted on the right side. Therefore, shape and size of tetra diagram represent THMs speciation and concentrations, and the area is equal to a half of total THMs concentration if the height is unity.

Figure 2 shows tetra diagrams drawn by THMs concentrations in various tap water in summer and winter. In summer, shapes of tetra diagrams could be roughly classified to three types. Firstly, trapezoids with short upper side (chloroform and bromoform concentrations) and long lower side (BDCM and DBCM ones) were found in ATRW of Osaka City, ATRW of Osaka prefectural waterworks, ATRW of Hanshin Water Supply Authority in Amagasaki City, and the blended water of ATRW of Osaka prefectural waterworks and ATRW of Hirakata City in Osaka Pref. (Nos.1-21 in Fig. 1). Although there is a variation in THMs concentrations by the differences in sampling faucets, tap water having the same raw water source and almost the same treatment processes are regarded as the same group. The shape and size of tetra diagram drawn by an average of THMs of the same group of tap water was compared. Trapezoid drawn by an average of each THM in ATRW of Osaka City (Nos. 1-7) was visually larger than that of Osaka prefectural waterworks (Nos. 8-19). Here, an average of each THM

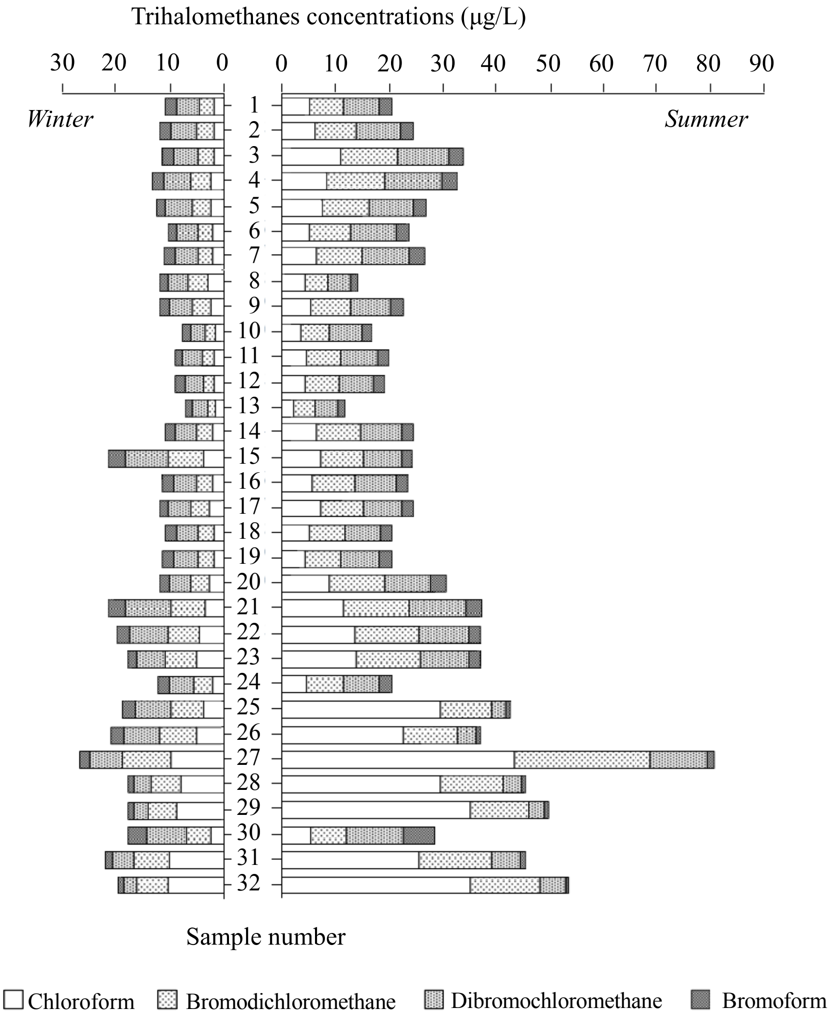

Figure 1 Stacked column charts for four trihalomethanes formation in various tap water in 2002 summer and winter.

1-7: Advanced treated river water (ATRW) of Osaka City; 8-19: ATRW of Osaka prefectural waterworks in eight cities (8: Mino City; 9: Takatsuki City; 10: Hirakata City; 11: Higashiosaka City; 12, 13: Daito City; 14-17: Sakai City; 18: Matsubara City; 19: Habikino City); 20: ATRW of Hanshin Water Supply Authority in Amagasaki City in Hyogo Pref.; 21: blended water of ATRW of prefectural waterworks and ATRW of Hirakata City in Osaka Pref.; 22, 23: blended water of ATRW of Hanshin Water Supply Authority and conventionally treated reservoir water (CTReW) of Kobe City in Hyogo Pref.; 24: blended water of ATRW of Osaka prefectural waterworks and conventionally treated groundwater (CTGW) of Sennan City in Osaka Pref.; 25, 26: CTReW of Kawachinagano City in Osaka Pref.; 27: conventionally treated river water (CTRW) of Itami City in Hyogo Pref.; 28, 29: CTRW of the cities of Wakayama and Hashimoto in Wakayama Pref.; 30-32: blended water of CTRW of prefectural waterworks and CTGW of municipal waterworks (30: Kyotanabe City in Kyoto Pref.; 31: Yahata City in Kyoto Pref.; 32: Yamatokoriyama City in Nara Pref.).

in seven samples of ATRW of Osaka City in summer was 7.00 μg/L for chloroform, 8.64 μg/L for BDCM, 8.59 μg/L for DBCM, 2.58 μg/L for bromoform and 26.8μg/L for total THMs: averages in winter were 2.08, 3.23, 4.49, 1.99 and 11.8 μg/L. An average of each THM in twelve samples of ATRW of Osaka prefectural waterworks in summer was 5.03μg/L for chloroform, 6.55μg/L for BDCM, 6.52 μg/L for DBCM, 2.00μg/L for bromoform and 20.1 μg/L for total THMs: averages in winter were 2.21, 3.25, 4.10, 1.86 and 11.4 μg/L. An average of total THMs in ATRW of Osaka City was significantly higher than that of Osaka prefectural waterworks (df = 17, tabulated t value ($p = 0.05$) = 2.11 < calculated t value = 3.25). Visually, trapezoids drawn by THMs in ATRW of Hanshin Water Supply Authority (No. 20) and the blended water of Hirakata City (No. 21) were slightly larger than the trapezoid of ATRW of Osaka City. Secondly, a warped trapezoid

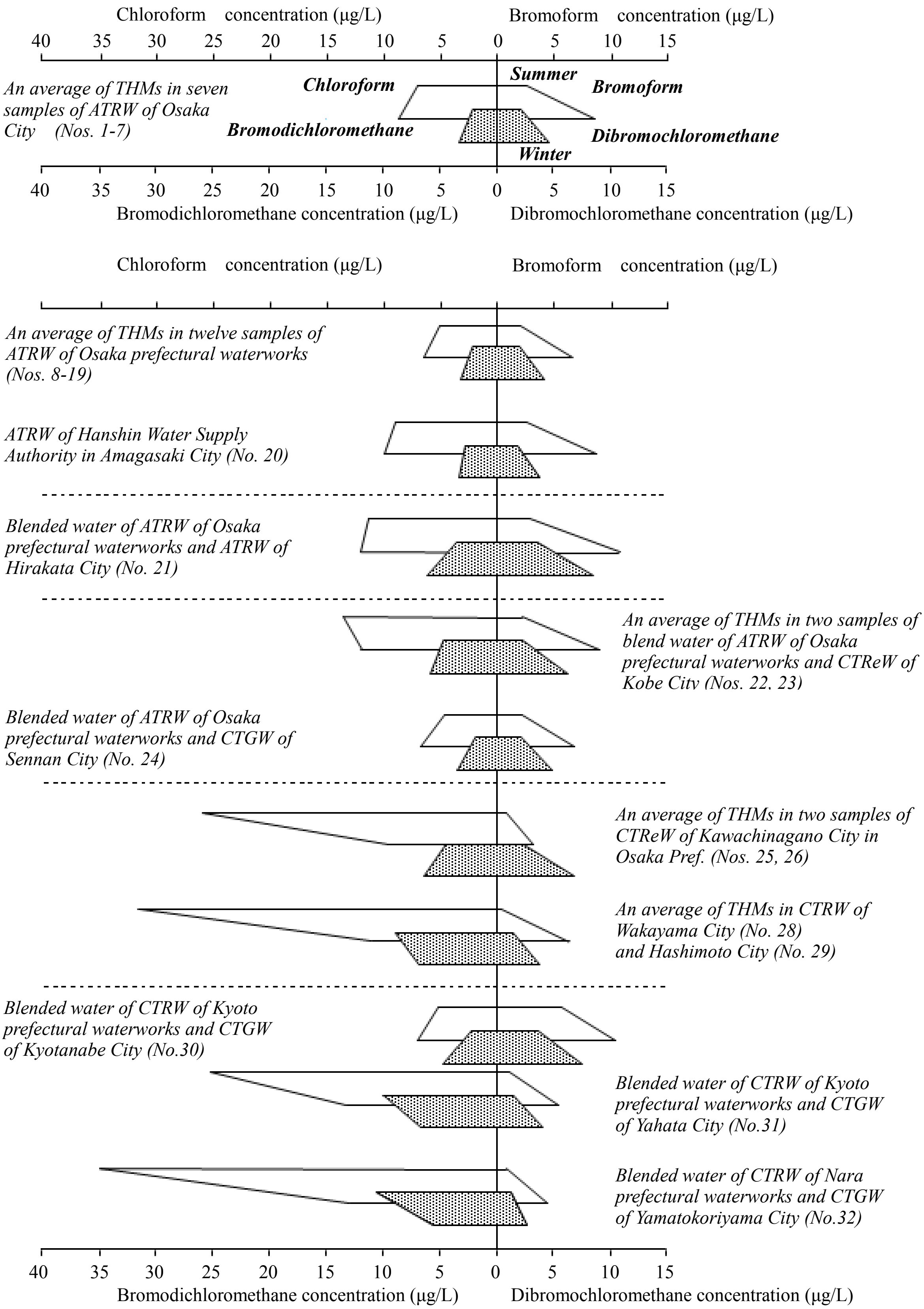

Figure 2 Tetra diagrams drawn by four trihalomethanes concentrations in various tap water in 2002 summer and winter.

Sample numbers were the same as Fig. 1.

with a long tail at chloroform vertex was drawn by an average of each THM in two samples of conventionally treated reservoir water (CTReW) of Kawachinagano City in Osaka Pref. (Nos. 25, 26). THMs in CTRW of Itami City in Hyogo Pref. (No.27; not shown in Fig. 2) and an average of THMs in CTRW of Wakayama City (No.28) and Hashimoto City in Wakayama Pref. (No. 29) drew a similar warped trapezoid. Here, CTRW of both cities in Wakayama Pref. have been drawn from the same raw water source. Thirdly, a parallelogram, being an intermediate shape between trapezoid and warped trapezoid, was found in an average of THMs in two samples of the blended water of ATRW of Hanshin Water Supply Authority and CTReW of Kobe City in Hyogo Pref. (Nos. 22, 23). These data are consistent with the result of study by Kawamoto and Makihata [12], in which THMs levels in a mixture of water that was purified using a combined slow sand filtration method and an advanced water treatment process with a ratio of 1:5.8 in Kobe City: 6.95μg/L for chloroform, 5.93μg/L for BDCM, 4.20μg/L for DBCM and 0.68μg/L for bromofrom. Compared with the trapezoid of ATRW of Hanshin Water Supply Authority in Amagasaki City (No. 20), water quality of the blended water of Kobe City in Hyogo Pref. was obviously deteriorated by blending with some CTReW.

Tetra diagram drawn by THMs in the blended water of ATRW of Osaka prefectural waterworks and conventionally treated groundwater (CTGW) of Sennan City in Osaka Pref. (No. 24) was almost similar to the trapezoid of ATRW of Osaka prefectural waterworks. A trapezoid, having a larger left side of the zero axis than the trapezoid of ATRW, was found in the blended water of CTRW of Kyoto prefectural waterworks and CTGW of Kyotanabe City in Kyoto Pref. (No. 30). Warped trapezoids with a long tail at chloroform vertex were drawn by THMs in the blended water of CTRW of Kyoto prefectural waterworks and CTGW of Yahata City (No.31), and of CTRW of Nara prefectural waterworks and CTGW of Yamatokoriyama City, respectively (No. 32).

All trapezoids in winter of ATRW, the blended water of ATRW and CTGW (No. 24) and the blended water of CTRW and CTGW (No. 30) were smaller size than these in summer. Tails at the chloroform vertex of warped trapezoids of CTRW, CTReW and blended water of CTRW and CTGW in winter were shortened by reflecting the kinetic disadvantage of chlorine relative to bromine in substitution reactions at a low temperature in winter. Here, THMs in CTRW (Nos. 28. 29) and in the blended water of CTRW and CTGW (Nos. 31, 32) drew slightly warped parallelograms, but THMs in CTReW (Nos. 25. 26) was a trapezoid. It is likely to be caused by subtle differences in the bromine ion of raw water.

The lifetime cancer risk is calculated by the sum of chronic daily exposure for each THM multiplied by each cancer potency factor. Here, chronic daily exposures are that four THMs concentrations (mg/L) are multiplied by an average drinking water consumption of 2L/day and divided by an average weight per person of 70kg. Cancer potency factors are $6.1x10^{-3}((mg/kg)/day)^{-1}$ for chloroform, $6.2x10^{-2}((mg/kg)/day)^{-1}$ for BDCM, $8.4x10^{-2}((mg/kg)/day)^{-1}$ for DBCM, and $7.9x10^{-3}((mg/kg)/day)^{-1}$ for bromoform, respectively [9]. THMs speciation is important factor to determine the magnitude of lifetime cancer risk induced by THM class. Cancer potency factors for BDCM are almost the same as DBCM, and both are one order of magnitude larger than these for chloroform and bromoform. Even in CTRW of Itami City (No. 27) with the highest total THMs, chloroform concentration had only twice BDCM and was several times higher than DBCM. Therefore, the length of lower side of tetra diagram, i.e., the sum of BDCM and DBCM concentrations, is considered as a promising index for displaying the cancer risk due to THM class.

Visually, the length of lower side of trapezoid of ATRW of Osaka City was longer than that of Osaka prefectural waterworks in summer, but in winter both were almost the same. Statistically, the average of calculated cancer risks by THMs in ATRW of Osaka City in summer ($3.77x10^{-5}$) was significantly higher than that in ATRW of Osaka prefectural waterworks ($2.86x10^{-5}$) (df=17, tabulated t value ($p= 0.05$) = 2.11<calculated t value = 3.34), but both were not significantly different in winter ($1.73x10^{-5}$ for ATRWs in Osaka City, $1.64x10^{-5}$ for ATRWs from Osaka prefectural waterworks; df=17, tabulated t value ($p=0.05$)=2.11>calculated t value=0.423). Trapezoids of Osaka prefectural waterworks (Nos. 8-19) and the blended water of Sennan City (No.24) had the shortest length of lower side, and these of the blended water of Kobe City (Nos. 22, 23) and of Hirakata City (No. 21) had the longest one. The remainder had the same length of the lower side. However, the lower sides look almost the same length. If the differences in cancer risks among ATRW are mainly due to the variability between samples, i.e., residence time in distribution system and plumbing system, cancer risks are not varied with changes in treatment processes, a variety of raw water and combination of blending of finished water, and are only varied with seasons. It poses a new problem. Further research into the estimation of cancer risks due to halogenated disinfection byproducts in various tap water is needed to better address this issue.

Tetra diagram provides a good overview of the differences or similarities in THMs speciation, levels and the magnitude of cancer risk, and therefore is more superior than stacked column chart. Further, it will be useful tool for visually explaining changes in water quality passing through distribution or plumbing systems.

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REFERENCES

1) Japan Water Works Association. Treated water quantity by water treatment system. Japan water supply data report 2003.
Available: http://www.jwwa.or.jp/
2) White GC. The handbook of chlorination. Second edition, Van Nostrand Reinhold Company, New York. 1986.
3) Yamamoto K, Kakutani N, Mori Y, Tsuruho K. Levels of total organic halogen (TOX) of tap waters in the area supplied advanced treated water from July to August in 2000: Osaka Prefecture and its surrounding cities. Jour. Environ. Chem. 2004: 14: 91-97. (in Japanese)
4) Yamamoto K, Kakutani N, Yamamoto A, Tsuruho K, Mori Y. Reduction of trihalomethanes and total organic halogen of advanced treated drinking water due to heating and boiling. Jour. Environ. Chem. 2005: 15: 137-144. (in Japanese)
5) Yamamoto K, Kakutani N, Yamamoto A, Tsuruho K, Mori Y. 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. Bull. Environ. Contam. Toxicol. 2006: 77 (3): 323-330.
6) Yamamoto K, Kakutani N, Yamamoto A, Mori Y. A case study on the effect of storage of advanced treated water in a building's plumbing system on trihalomethane levels. Bull. Environ. Contam. Toxicol. 2007:79 (6): 665-669.
7) Yamamoto K, Mori Y. Episodic trihalomethane species and levels in tap Water at a start of operation of advanced treatment in Osaka prefectural water supplies. Bull. Environ. Contam. Toxicol 2009: 83 (5): 674-676.
8) Yamamoto K, Mori Y. 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. Bull. Environ. Contam. Toxicol 2009: 83 (5): 677-680.
9) Yamamoto K. Is advanced treated water truly high quality?: the answer from a viewpoint of cancer risk induced by trihalomethane class. Bull. Environ. Contam. Toxicol. 2011: 87 (2): 101-105.
10) USEPA. Method 524.2 Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. Revision 4.1, Edited by J.W. Munch. 1995
11) Zaporozec A. Graphical interpretation of water-quality data. Ground Water. 1972: 10 (2): 32-43.
12) Kawamoto T, Makihata N. Distribution of bromine /chlorine-containing disinfection by-products in tap water from different water sources in the Hyogo Prefecture. Journal of Health Science. 2004: 50: 235-247.

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処理工程、原水、給水のブレンドの異なる水道水のトリハロメタン組成と発がんリスクの相違性あるいは類似性の視覚的評価

山本耕司

要旨

処理工程、原水、給水のブレンドの異なる水道水のトリハロメタン（THMs）の種形成とそれによる発がんリスクの相違性または類似性を視覚的・直観的に示すテトラ図を提案した。テトラ図は上辺をクロロホルムとブロモホルム濃度、下辺をブロモジクロロメタンとジブロモクロロメタン濃度からなる。その適用性を、大阪市とその周囲の市町村の家庭の蛇口から 2002 年の夏と冬に採水した 32 組の THMs 測定値によって議論した。高度処理水は夏冬ともに台形を描いたが、総トリハロメタンを示すその面積は夏が冬より大きかった。従来処理水では夏に河川水（CTRW）と貯水池水（CTReW）が原水ではクロロホルムの頂点が長い歪んだ台形を、冬に CTRW は平行四辺形を、CTReW は台形を描いた。さらに、テトラ図の下辺の長さは、THM 類による発がんリスクの大きさを示した。発がんリスクは季節によって変化するが、処理工程、原水、給水のブレンドによって影響されない可能性が示唆された。

キーワード: トリハロメタン種形成，発がんリスク，テトラ図，高度処理水，従来処理水