

Control of disinfection byproduct (DBP) precursors by soil aquifer treatment (SAT): what length of hydraulic retention time (HRT) is necessary?

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ABSTRACT

The study attempted to determine the hydraulic retention time (HRT) required for soil aquifer treatment (SAT) to reclaim water as potable water in an aspect of controlling disinfection byproduct (DBP) precursors. In order to evaluate the removal of DBP precursors, the uniform formation condition was used to estimate the formations of trihalomethanes (THMs) and haloacetic acids (HAAs). Effluent water from anaerobic-anoxic-oxic processes (A2O water) was fed through soil columns at different HRTs. Sand with low organic content and less specific surface area was selected to represent the 'worst available case' of subsurface environment in Japan. Overall, annual data ($n \geq 14$) indicated that the average concentrations of THMs and HAAs for water passed through SAT with HRT less than 7 days were below the standard of drinking water. However, risks of exposure to THMs and HAAs were observed. Increasing HRT to 30 days resulted in the concentrations of regulated THM and HAA species lower than the 10% of the drinking water standard values, except for dichlorobromoform. Therefore, a treatment unit for bromide ion removal (e.g., anion exchanger) prior to chlorination is recommended to lower the risk levels of exposure to dichlorobromoform.

Key words | haloacetic acids, hydraulic retention time, reclaimed water, soil aquifer treatment, trihalomethanes

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INTRODUCTION

Disinfection is a significant treatment for the direct (or indirect) reuse of reclaimed water to ensure public health protection. However, disinfection byproducts (DBPs) are a major concern for potable water quality. Trihalomethanes (THMs) and haloacetic acids (HAAs) are two major DBPs, which potentially cause human carcinogens (Richardson *et al.* 2007 and references therein). Therefore, their maximum allowable concentrations have been regulated in several countries (US.EPA 2006; WHO 2011; MHLW 2016). Formations of THMs and HAAs depend on both water matrix (e.g., dissolved organic carbon (DOC) concentrations, characteristics of organic compounds, bromide

ions) and chlorination condition (e.g., disinfectants, contact time, pH) (Sadiq & Rodriguez 2004; Chowdhury *et al.* 2009). To study the formations of THMs and HAAs, the formation potential approach is generally used under the standard reaction conditions (5710B): reaction time of 7 days with an excessive free chlorine of 3–5 mg/L (Xue *et al.* 2009; APHA *et al.* 2012). However, the uniform formation condition (UFC) for chlorination likely fits to the formations of THMs and HAAs in the water distribution system, compared with the formation potential protocol that mainly indicates the maximum DBP formation (Summers *et al.* 1996).

Several studies attempted to remove precursors of THMs and HAAs (e.g. natural organic matter, effluent organic matter) prior to chlorination (Toor & Mohseni 2007; Chu *et al.* 2011). Adsorption using an activated carbon is known to be a promising technology for removal of natural organic matter (Cheng *et al.* 2005), while vague effects on THM and HAA reductions are observed via chemical oxidation (e.g., ozonation, advance oxidation process (AOP) (Toor & Mohseni 2007; Hua & Reckhow 2013). Activated carbon adsorption combined with the chemical oxidation (e.g., ozonation, UV/H₂O₂) showed a significant improvement on the reduction of THMs, HAAs, and DOC, with the standalone activated carbon (Toor & Mohseni 2007; Yan *et al.* 2010). However, further treatment for solid waste (i.e., used activated carbon) is necessary. Therefore, a cleaner technology to control THM and HAA precursors is needed.

Soil aquifer treatment (SAT) is a natural treatment process that utilizes both sorption and biodegradation to remove organic pollutants in reclaimed water (Xu *et al.* 2009). It can be considered as a practical and clean solution to remove organic compounds because of no waste production and low operating cost. It is commonly known that characteristics of soil affect the organic removal performance of SAT. Increase in clay content and soil organic matter enhances the SAT sorption capability on the organic compounds (Juhna *et al.* 2003; Xu *et al.* 2009). Quanrud *et al.* (1996a) found that the sandy loam was more effective in DOC removal than sand. Thus, a small-grained soil with high soil organic content is preferred for SAT as long as infiltrability is adequate. However, some countries (e.g., Japan) have low availability on land selection. This may cause limitation on organic removal. To set the criteria for design of SAT with an adequate hydraulic retention time (HRT) to control THM and HAA precursors, the test with an undesired soil for organic removal (i.e., less organic content and specific surface area) under various HRT conditions should be carried out.

Quality of reclaimed water also depends on a hydraulic pattern in SAT systems, in particular to HRT. Increase in HRT enhances the DOC removal, leading to the higher reduction of THM and HAA formation potentials (Drewes & Fox 1999; Pavelic *et al.* 2005; Drewes *et al.* 2006; Xue *et al.* 2009). The HRT of 180 days has been provisionally recommended for groundwater recharge (Asano & Cotruvo

2004). This is only the economical practice when land is unlimited. In addition, requiring long HRT likely disagrees due to the fact that only a few meters of subsurface environment are effective to remove pollutants, while a limited removal is observed in a saturated zone (Quanrud *et al.* 1996b; Drewes & Fox 1999; Pi & Wang 2006; Rauch-Williams & Drewes 2006; Essandoh *et al.* 2013). This leads to the question of what length of HRT is necessary in practice to control the precursors of THMs and HAAs.

This research aims to evaluate the SAT with various HRTs to control the precursors of THMs and HAAs. The experimental condition was designed based on a 'worst-case' soil quality (i.e., low organic content and less specific surface area) to remove organic compounds. To avoid underestimation of risk exposure to THMs and HAAs, the formation potentials of THMs (THMFPs) and HAAs (HAAFPs) under the UFC protocol were determined, and compared with the standard of drinking water.

METHODOLOGY

Experimental conditions

Water was collected from the effluent of anaerobic-anoxic-oxic processes (A2O water) prior to chlorination. Then, A2O water was filtrated through 11- μ m cellulose-membrane filters, and stored in a refrigerator at 4 °C. The A2O water was fed into a laboratory-scale SAT column at room temperature (20 °C). It should be noted that water temperature at the end of inlet tube was 20 ± 2 °C. No THM and HAA formations were observed in unchlorinated A2O water. Two sands were used in this study. Sand, taken from Shiga prefecture, imitates the 'worst availability' of subsurface conditions in Japan, whereas Toyoura sand (Toyouura Co. Ltd), Japanese standard sand, represents the extreme characteristics of soil in terms of treatability. Both Shiga sand and Toyoura sand were used as media in SAT columns. Their properties are shown in Table 1. For laboratory-scale experiments, four acrylic columns (each with area: 0.018 m²; length, 1.5 m) were filled with 2-mm sieved media (three columns with sieved Shiga sand and one column with sieved Toyoura sand). To study the effect of vadose zone, one Shiga sand column with a vadose zone of 20 cm depth (Sa7) and the other without the

Table 1 | Characteristics of Shiga sand and Toyoura sand

Type	pH	CEC (meq/100 mg)	AEC (meq/100 mg)	TOC (%)	Porosity	Sand contents (%)	N ₂ /BET-specific soil surface (m ² /g)
Shiga sand	6.6	2.4	1.5	0.01	0.435	>99 (texture:sand)	2.397
Toyouira sand	6.9	0.2	2.3	0.01	0.425	100 (texture:sand)	0.812

vadose zone (Sat-Sa) were operated at the same HRT (7 days). The last Shiga sand column with vadose zone of 20 cm was operated with HRT of 3.5 days (Sa3.5). The Toyoura sand column with 20 cm vadose zone (named as TS) was operated with HRT of 7 days. Sa3.5, Sa7, and Sat-Sa columns were packed with 60 cm, 110 cm and 110 cm height of sand, respectively. TS columns were packed with 110 cm height of Toyoura sand. All columns were covered with aluminum foil for avoiding algae growth. All materials for tubes and valves were Teflon (TFPE). A2O water was continuously fed to all columns with the flowrate of 1.0 mL/min. In order to control the thickness of vadose zone, the inlet tubes were set at the top of all columns, while the outlet tubes were placed at 20 cm below the top media surface (i.e., Shiga sand and Toyoura sand), except for Sat-Sa columns for which the outlet tube was lifted 5 cm above the sand surface. Furthermore, the pilot-scale metal column (area: 2.25 m²; height: 3 m) packed with Shiga sand was installed at the wastewater treatment plant, and continuously operated with the A2O water. The HRT of the pilot scale column was 30 days (named as Sa30). Other details can be seen in [Takabe *et al.* \(2014\)](#). The operating conditions of SAT are summarized in [Table 2](#). Hydraulic characteristics of all columns were confirmed by using bromide ion as a tracer (data were not shown). All columns were continuously operated for 5 months until their DOC removal was stable. Then, water samples (i.e., before and after SAT columns) were collected and chlorinated prior to the determination of THMFPs and HAAFPs. To

include seasonal effects on changes in organic contents, THMFPs and HAAFPs concentrations were examined every season (i.e., summer, spring, autumn, and winter). The number of total samples was 15 ($n = 15$), except for the pilot scale ($n = 14$). Each analysis was duplicated.

Analytical methods

Stock chemical solutions were prepared using ultrapure water (Milli-Q water) produced by a Millipore Academic-A10 purification system (Tokyo, Japan). Four THMs (i.e., chloroform (CHCl₃), dichlorobromoform (CHBrCl₂), dibromochloroform (CHBr₂Cl), and bromoform (CHBr₃)) and nine HAAs (i.e., monochloroacetic acid (MCA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), monobromoacetic acid (MBA), bromochloroacetic acid (BCA), dibromoacetic acid (DBA), bromodichloroacetic acid (BDCA), tribromoacetic acid (TBA), chlorodibromoacetic acid (CDBA)) were purchased from Wako Pure Chemical Industries (Osaka, Japan).

To determine THMs and HAAs, the samples were chlorinated with sodium hypochlorite (NaOCl) under the modified UFC: free chlorine residual of 1.0 ± 0.4 mg/L with 24 hours' reaction time at neutral pH (pH 7.0 ± 0.5). This protocol is similar to the chlorination condition applied in the distribution system in Japan (i.e., contact time ≤ 1 day). Concentrations of residual chlorine after 24 hours' contact time were determined, and only the samples with free chlorine residual concentration

Table 2 | Operating conditions for both laboratory-scale and pilot-scale experiments

Experiment	Condition code	Media	HRT (days)	Vadose zone (20 cm)	Temperature
Laboratory-scale	Sa3.5	Shiga Sand	3.5	Include	20 °C
	Sa7	Shiga Sand	7	Include	
	Sat-Sa	Shiga Sand	7	Exclude	
	TS	Toyouira sand	7	Include	
Pilot-scale ^a	Sa30	Sand	30	Include	Ambience

^aVadose zone for the pilot-scale column was 17 cm.

equivalent to 1.0 ± 0.4 mg/L were used for DBP analysis. Chlorinated samples were analyzed for THMs and HAAs by gas chromatography with electron capture detector. The analytical procedure was explained elsewhere in US EPA 551.1 and US EPA 552.3 for THMs and HAAs, respectively. Limitations for quantification and detection are shown in SI-1 (available with the online version of this paper).

Chlorine concentrations were determined by the *N,N*-diethyl-*p*-phenylenediamine (DPD) titration method. Concentrations of bromide ion were determined by using high performance liquid chromatography (HPLC) (Shimadzu, Japan). DOC of the water samples was regularly analyzed using a TOC-L analyzer (Shimadzu). UV absorbance of each sample was measured at 254 nm wavelength as an indicator of unsaturated bonds (aromatic and unsaturated aliphatic compounds). The specific UV-absorbance (SUVA), an indicator of aromatic content, was calculated as the ratio of the UV_{254} to DOC.

The analysis of variance (ANOVA) test with multiple comparisons was used to confirm a significant difference between each two data sets. A significance level of 0.05 was applied for all tests.

The maximum concentrations of THMs and HAAs were used for risk assessment. The method was originated and explained elsewhere in Schriks *et al.* (2010). In brief, the maximum concentration of a targeted compound was divided by the acceptable value of drinking water quality (known as risk quotient). If the risk quotient is in the range of 0.1 to 1.0, a monitoring of suspected compounds is necessary. The risk quotient above 1.0 means the observed data is higher than the guideline value. The risk quotient lower than 0.1 means the potential exposure to the compounds is low.

RESULTS AND DISCUSSION

The concentrations of DOC in the A2O water were in the range of 3.03–4.61 mg/L, and the median (and average) was 3.90 mg/L as shown in the statistical DOC concentrations in Figure 1(a). SAT columns were operated over a four-fold HRT before treated water samples were collected and analyzed. After SAT columns, the fluctuation of DOC concentrations decreased, indicated by likely stable concentrations of DOC. Similarly, the observed concentrations of

four THM species (THM4) and nine HAA species (HAA9) in the treated water samples were not much different for every season, compared with the A2O waters (SI-2, available with the online version of this paper). Variations in observed THM4 and HAA9 formations for the A2O water implied that seasonal changes in characteristics of DOC (or THM and HAA precursors) were present. Ates *et al.* (2007) reported that different seasons caused an alternation of DOC characteristics, resulting in dissimilar formations of THMs and HAAs. The average DOC concentrations for TS, Sa3.5, Sa7, Sat-Sa, and Sa30 columns were 1.83, 1.18, 1.01, 1.05, and 0.57 mg/L, respectively. The Sa3.5 column significantly decreased DOC concentrations by 71%, compared with the A2O waters ($p < 0.05$). For the HRT of 7 days (i.e., Sa7 and Sat-Sa), the DOC removal was slightly improved by 3%, compared with the Sa3.5 column ($p > 0.05$). The Sa30 column enhanced the DOC reduction to 86% ($p < 0.05$). The SAT systems greatly reduced DOC concentrations. The effluent DOC concentrations for all columns were quite constant. This resulted in low fluctuation occurring in THM4 and HAA9 formations. Thus, the SAT system was capable of removing DOC in terms of both quantity and quality, indicated by consistent trends of DOC concentrations, THM4 and HAA9 formations. Several studies showed the strong positive correlation between organic carbon reduction and mass of microorganisms in groundwater recharge (Rauch-Williams & Drewes 2006; Kolehmainen *et al.* 2007), indicated that biodegradation took a major part on the DOC removals (Xue *et al.* 2009). Combined with our results, it implied that most of organic compounds in A2O waters were highly biodegradable since over 70% removal was found at the initial period (within 3.5 days). One of our research groups reported that an increase in microbial growth occurred through Sa30 column, particularly in the top layer of sand (0–5 cm) (Takabe *et al.* 2014). At the same HRT (7 days), significant difference in DOC removal was observed for TS and Sa7 columns ($p < 0.05$). The DOC removal for TS columns was 57%, whereas it was 74% for Sa7 columns. Thus, SAT columns packed with Shiga sand were better than that with Toyoura sand in terms of DOC removal. This could be resulted from different specific surface area. The specific surface area of sand was almost four times greater than Toyoura sand. Larger specific surface area provides more

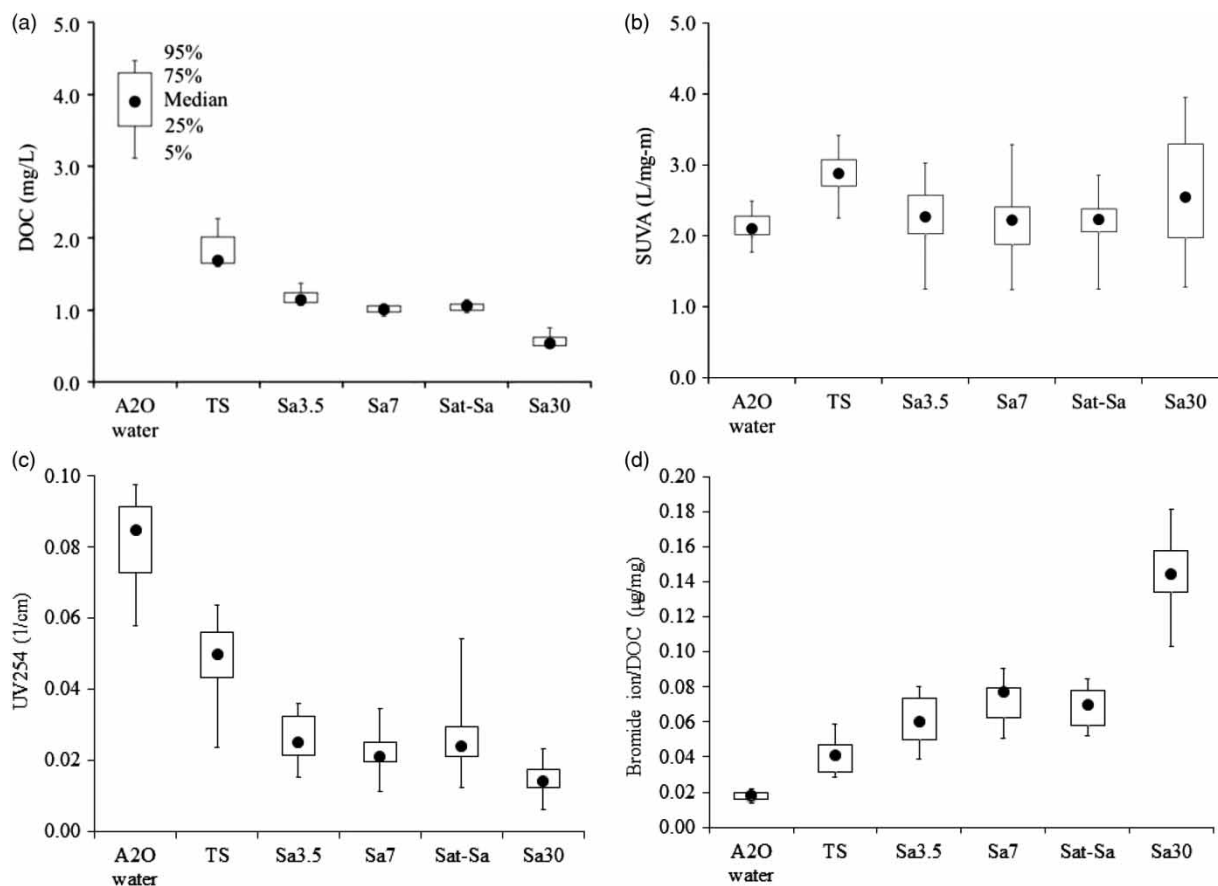


Figure 1 | Characteristics of inlet and outlet of SAT: (a) DOC, (b) SUVA, (c) UV₂₅₄, and (d) bromide ion/DOC.

space for not only sorption, but also biological accumulation. DOC removal by Sat-Sa columns were originally expected to be lower than that from Sa7 columns because the presence of anaerobic/anoxic degradation in saturated zone could lower the biological reactivity (Grunheid *et al.* 2005; Pi & Wang 2006). However, similar DOC concentrations were found for both cases (i.e., Sat-Sa and Sa7 columns). These may result from the availability of dissolved oxygen (DO) in pore spaces of Sat-Sa columns (effluent DO concentrations = 2–4 mg/L).

UV₂₅₄ for A2O waters ranged from 0.06 to 0.10 cm⁻¹ with an average of 0.09 cm⁻¹ (Figure 1(c)). Decrease in UV₂₅₄ by TS columns was 41%. Insignificant differences in UV₂₅₄ reduction were found between Sa3.5, Sa7 and Sat-Sa columns ($p > 0.05$). For Sa3.5 columns, the UV₂₅₄ reduction was 70–80%. Longer HRT of 7 and 30 days slightly increased the UV₂₅₄ reduction by 10%, compared with Sa3.5 columns ($p > 0.05$). This implied that the

characteristics of soil were more important than the HRT for the removal of unsaturated and aromatic compounds. This is in agreement with several reports (Drewes & Fox 1999; Drewes *et al.* 2006). However, their studies were conducted with soil collected at the field sites in which organic contents were expected to be present. The presence of organic content in soil tends to induce soil sorption of DOC, particularly for unsaturated and aromatic compounds (Chua *et al.* 2009; Wei *et al.* 2009; Xue *et al.* 2009). Our results indicated that the media with extremely low organic content (i.e., Toyoura sand) was still able to remove unsaturated aromatic compounds. This could result from indirect accumulation of organic content (i.e., regrowth of aquatic microorganisms on media) or biodegradation rather than sorption. This was supported by the previous study which reported that soil microbes could utilize organic compounds from the hydrophobic acid fraction, mainly composed of humic and fulvic acids (Rauch-Williams & Drewes 2006).

Also, biodegradation was believed to be the major mechanism for DOC removal during the top soil layer (Takabe *et al.* 2014). Changes in SUVA for all cases were minor ($p > 0.05$). However, SUVA slightly increased for the treated waters. The mean values of SUVA for RSF, TS, Sa3.5, Sa7, and Sa30 were 2.120, 2.853, 2.226, 2.160, 2.139, and 2.550 L/mg-m, respectively (Figure 1(b)), implying that the removal of aliphatic substances was likely favored than that of aromatic compounds.

Average summations for THM4 and HAA9 in the A2O waters were 84 and 95 $\mu\text{g/L}$, respectively. Although the average of THM4 was lower than the standard of drinking water in Japan (100 $\mu\text{g/L}$) (MHLW 2016), approximately 30% of the total data exhibited that the concentrations of THM4 were occasionally higher, leading to uncertainty in THM4 exposure (Figure 2). The potential exposure to specific species of THMs are discussed later. After the A2O waters passed through SAT processes, the average concentrations of THM4 for TS, Sa3.5, Sa7, Sat-Sa, and Sa30 remained 60, 23, 18, 18, and 8 $\mu\text{g/L}$, respectively. The average concentrations of HAA9 for TS, Sa3.5, Sa7, Sat-Sa, and Sa30 were 45, 17, 12, 13, and 10 $\mu\text{g/L}$, respectively. The lowest reduction of THM4 and HAA9 was obtained in the TS columns with 29 and 52% removal, respectively. Decrease in THMs and HAA9 for Sa3.5 was likely similar to the reduction by Sa7 and Sat-Sa ($p > 0.05$). Removal efficiencies were in the range of 73–78% for THM4 and 81–87% for HAA9 when sand columns with the HRT below 7 days were used. Thus, the precursors of THM4 and HAA9 were

mainly susceptible to the SAT with HRT over than 1 week. Longer HRT of 30 days increased the removal of THM4 and HAA9 up to 91 and 90%, respectively.

When speciation of THMs was considered, CHCl_3 and CHBrCl_2 were predominant in A2O waters after chlorination (Figure 3). After SAT, removal of two predominant THM precursors (i.e., CHCl_3 and CHBrCl_2) were observed. Decrease in CHCl_3 was greater than that in CHBrCl_2 at the same condition. For TS columns, CHCl_3 decreased by 63%, whereas the reduction of CHBrCl_2 was 24%. When Sa3.5 was used, the reductions of CHCl_3 and CHBrCl_2 were above 88 and 66%, respectively. Longer HRT of 7 days (i.e., Sa7 and Sat-Sa) did not significantly improve the reductions of CHCl_3 and CHBrCl_2 ($p > 0.05$). The Sa30 columns highly suppressed CHCl_3 and CHBrCl_2 by 97 and 93%, respectively. Thus, control of CHCl_3 precursors was likely easier than that of CHBrCl_2 . Negative effect on THM reductions was found for CHBr_2Cl and CHBr_3 . The concentrations of bromide-containing THMs (i.e., CHBr_2Cl and CHBr_3) increased when SAT columns were introduced. Several studies found that the addition of bromide ion before chlorination influenced the formation of brominated DBPs (Chang *et al.* 2001; Chang *et al.* 2011). In a similar manner to our results, no significant reductions of bromide ions in all columns were observed ($p > 0.05$), leading to the higher ratio between bromide ion and DOC concentrations at the outlet of SAT (Figure 1(d)). Therefore, bromination of organic compounds was possibly a predominant reaction rather than chlorination, inducing the formation of brominated THMs.

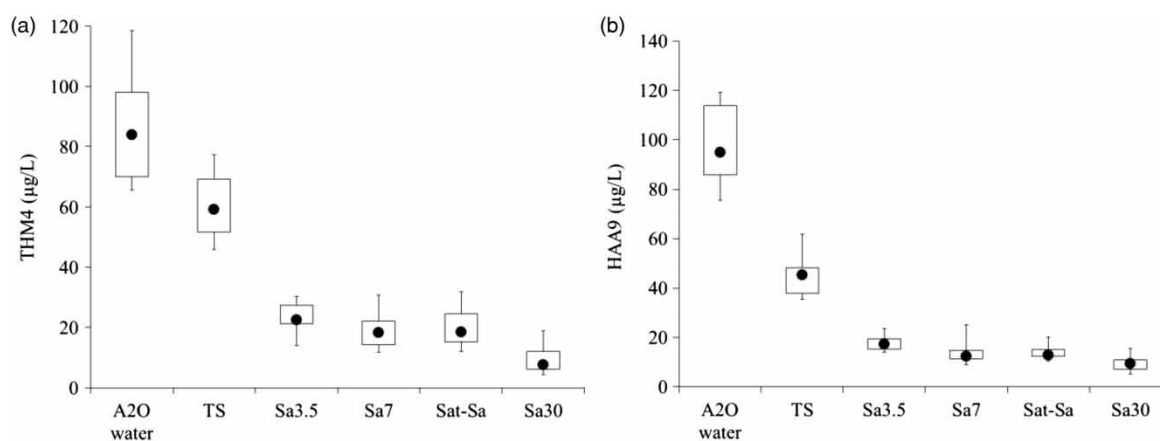


Figure 2 | Effect of SAT on formations of THM4 (a) and HAA9 (b).

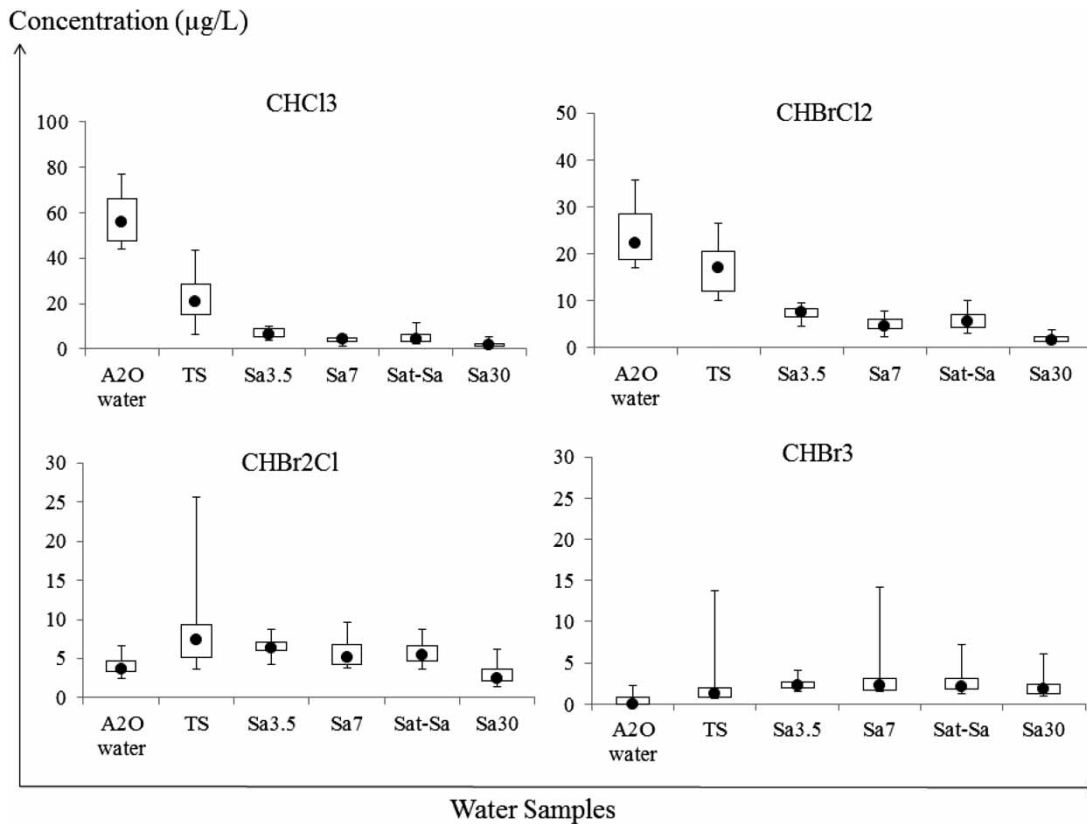


Figure 3 | Concentrations of THMs for inlet and outlet of SAT.

Figure 4 shows the formation of nine HAA species (HAA9) at the inlet and outlet of SAT columns. The average concentration of five HAA species (HAA5 = MCA + DCA + TCA + MBA + DBA) for the A2O water was 82 µg/L, which was 37% higher than the guideline value of US EPA (60 µg/L). Among nine HAAs, two major species formed in chlorination of the A2O waters were DCA and TCA, accounting for 34 and 45%, respectively. After SAT (i.e., TS, Sa3.5, Sa7, Sat-Sa, and Sa30), HAA5 decreased by 62–95% responsible for the concentrations in the range of 4–31 µg/L. Removals of predominant HAA precursors (i.e., DCA and TCA) were greatly achieved by SAT columns. Generally, the precursors of DCA and TCA were removed in the range of 60–99%. On the other hand, the removals of brominated HAAs were ambiguous. Most of brominated HAA precursors were reduced after passing through SAT, except for DBA. About 35–94% reduction of BCA and BDCA was achieved for all columns packed with Shiga sand. The TS column reduced BDCA by 35%, while it increased BCA by

10%. Decrease in CDCA was relatively low, with only 1–46% removal. Several studies found that bromination was preferred to aliphatic structures rather than aromatic substances (Heller-Grossman *et al.* 2001; Liang & Singer 2003). Consequently, a decrease in aliphatic contents (indicated by higher SUVA) at the outlet of SAT tended to suppress bromide-based byproducts. However, this is in contrast to our finding for the case of DBA. The high formation of DBA was observed for the columns packed with Shiga sand. It increased by one-to-two fold of the A2O water, which made DBA one of the two major HAAs found at the outlet of SAT ranging between 15 and 30%. The other one was BCA that contributed to 21–48%. Analogous explanation to the formation of THMs, HAAs species shifted from chlorinated species to brominated species due to the effects of higher ratio of bromide ion to DOC concentrations. Therefore, the standalone treatment process for removal of organic compounds (like SAT) may not be the promising process to control brominated byproducts.

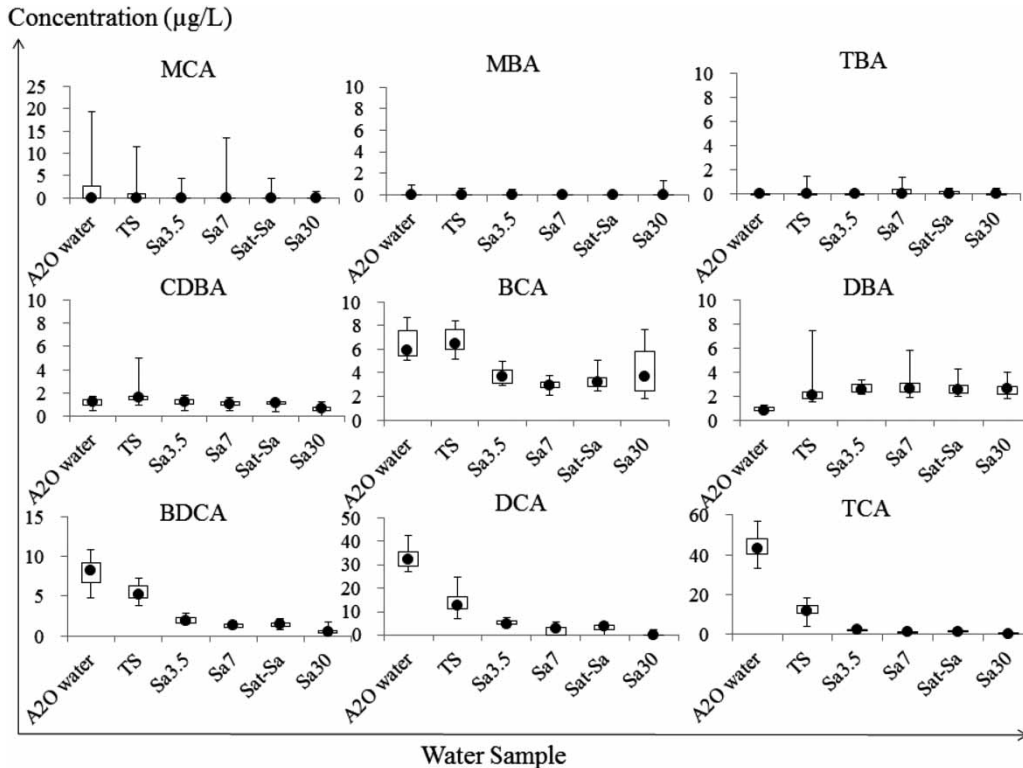


Figure 4 | Concentrations of HAAs for the inlet and outlet of SAT.

To compare the formations of THM4 and HAA9, their concentrations were normalized by a unit of DOC (Figure 5). A summation of four THM species was divided by DOC concentrations, and HAA9 were used to calculate the ratio of HAA9 to DOC. The yield of HAA9 (25.58 µg/mgDOC) for the A2O water was slightly higher than that of THM4

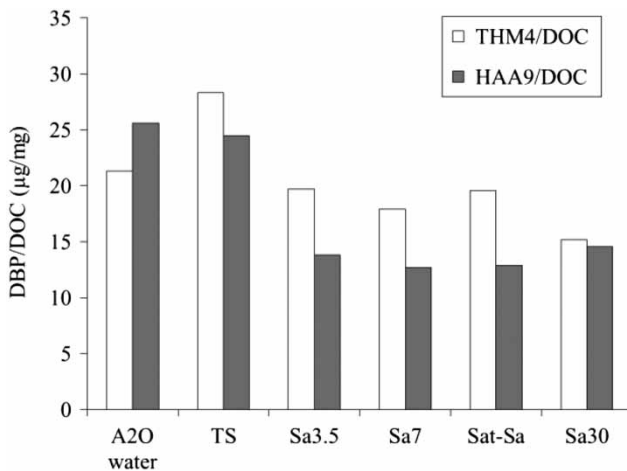


Figure 5 | The ratio of THM4 and HAA9 to DOC concentrations for inlet and outlet of SAT.

(22.35 µg/mgDOC). This indicated that DBP precursors in the A2O water was originally preferred to support the formations of HAA9, in particular for DCA and TCA (Figure 4). The columns packed with Shiga sand (i.e., Sa3.5, Sa7, Sat-Sa, and Sa30) significantly decreased both yields for THM4 and HAA9 ($p < 0.05$). The TS columns slightly decreased yields of HAA9, while an increase in THM4 yields was observed. Yields of THM4 for TS, Sa3.5, Sa7, Sat-Sa, and Sa30 were 38.36, 19.69, 17.93, 19.57, and 15.20 µg/mgDOC, respectively. Yields of HAA9 for TS, Sa3.5, Sa7, Sat-Sa, and Sa30 were 24.52, 13.83, 12.74, 12.87, and 14.56 µg/mgDOC, respectively. The yields of THM4 were higher than that of HAA9 for all treated waters. Thus, HAA precursors were preferentially removed by SAT rather than THM precursors. Kim & Yu (2005) reported that organic compounds with high aromatic contents (i.e., hydrophobic substances) highly supported the formation of THMs, while organic substances with aliphatic structures (i.e., hydrophilic ones) preferably promoted the HAA formation. Therefore, the preference in removals of aliphatic contents by SAT columns possibly resulted in the great reduction of HAA9 yields.

Based on the stringent drinking water standard (SI-3, available with the online version of this paper), the risk level for reclamation of water as potable water was evaluated (Figure 6). The values of risk quotients for four THM species and three HAA species in the A2O waters were higher than 0.1. Especially, the risk quotients for CHCl_3 , CHBrCl_2 and DCA were more than 1.0. Thus, direct consumption of chlorinated A2O waters was not recommended because of high risk exposures of regulated THM and HAA species. Similar results were found for TS, Sa3.5, Sa7 and Sat-Sa columns. The risk quotients for water passed through the SAT with HRT of less than 1 week (i.e., TS, Sa3.5, Sa7, Sat-Sa) were in the range of 0.1–1.0, showing the undesired level of risk exposure. When HRT increased to 30 days, the risk quotient was reduced to an acceptable level, except for CHBrCl_2 which was slightly higher than the risk quotient of 0.1. This is in

agreement with the above explanation that the removal of THM4 were more difficult than that of HAA9, particularly for bromide-containing byproducts. Therefore, although SAT systems with HRT of 30 days were able to suppress the precursors of regulated THM and HAA species, a water treatment unit for removal of bromide ions (i.e., anion exchanger) prior to chlorination is recommended in order to lower the risk level. In addition, the risk of exposures to other unregulated species of DBPs (e.g., BCA, DBA, haloacetonitriles and NDMA) should be taken into consideration, especially for brominated byproducts.

CONCLUSIONS

The major findings are highlighted below:

- Under the ‘worst-case’ of soil properties for organic removal in this study, SAT columns with short HRT (i.e., lower than 7 days) suppressed concentrations of THMFPs and HAAFPs below the drinking water standard.
- SAT columns preferably removed organic precursors of HAAs than that of THMs.
- Based on risk assessment in this study, the SAT column with HRT of 30 days was reliable for the control of THMs and HAAs to be lower than the drinking water standards. However, concentrations of CHBrCl_2 should be monitored.
- The control of bromide-containing byproducts was more difficult than for chlorine-containing byproducts. To lower the risk exposure levels of CHBrCl_2 , the removal of bromide-containing byproduct precursors (e.g., bromide ion) are further recommended before chlorination.

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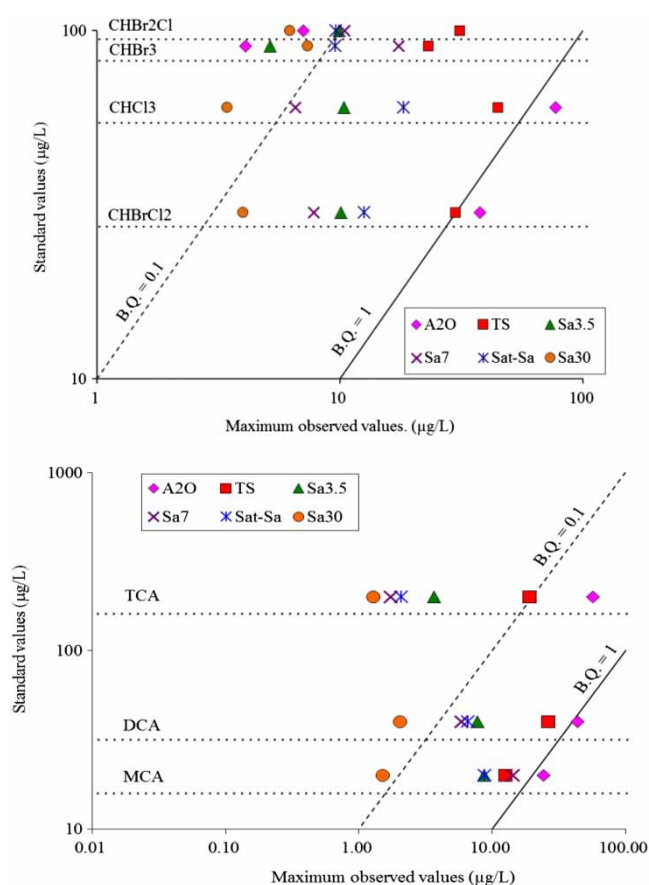


Figure 6 | The risk assessment of THMs and HAAs for inlet and outlet of SAT.

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