

## Impact of groundwater surface storage on chlorination and disinfection by-product formation

R. K. Padhi, K. K. Satpathy and S. Subramanian

### ABSTRACT

The change in water quality arising from the open storage of groundwater (GW) and its impact on chlorination and chlorination by-product formation were investigated. Water quality descriptors, such as temperature, pH, chlorophyll, and dissolved oxygen contents of GW undergo substantial alteration when stored in a reservoir. Dissolved organic content (DOC) measured in the two water sources studied, i.e., GW and open reservoir water (RW), varied from 0.41 mg/L to 0.95 mg/L and 0.93 mg/L to 2.53 mg/L, respectively. Although DOC demonstrated wide variation, UV absorbance at 254 nm ( $UVA_{254}$ ) values for GW (0.022–0.067) and RW (0.037–0.077) did not display reciprocal variations. The chlorine demand (CD) of RW was always higher than that of GW for the corresponding sampling period. Average trihalomethane (THM) formation for RW was 50–80% higher compared to GW and thus poses an enhanced health risk. Appreciable amounts of bromide present in these water sources (0.15–0.26 mg/L in GW and 0.17–0.65 mg/L in RW) have resulted in the non-selective distribution of the four THM species. The formation of more toxic brominated THM due to chlorination of these near-coast drinking water sources must be regarded as a decisive factor for the choice of water disinfection regime.

**Key words** | chlorination, chlorination by-product, chlorine demand, dissolved organic content, trihalomethanes

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### INTRODUCTION

Reservoirs are manmade lakes, primarily used for storing water for different purposes such as uninterrupted drinking water supply, industrial water requirements, hydroelectric power generation and irrigation. Flowing water when stilled in reservoirs undergoes physical, chemical, and biological changes requiring a totally different water treatment regime from that of the original source water, particularly when the water is to be used for drinking. For example, the temperature of stream water which is generally dynamic in nature, varies only a couple of degrees throughout the year, whereas it varies widely in a reservoir depending on the climatic condition of the area (Satpathy 1996). The same is true for nutrients, chlorophyll (Chl), dissolved oxygen (DO) and other associated chemical and biological parameters (Satpathy 1996).

Owing to the stagnant nature of the water in the reservoir, we can assume that a certain amount of contamination or deterioration in the water quality will occur compared to the subsoil river water. Of course, the extent of deterioration in water quality depends upon the residence time of the water decided by the storage capacity, amount and sources of the water flowing into it.

Chlorination is a widely used drinking water treatment process that inactivates many waterborne pathogens and combats biofouling in industrial cooling water systems. However, in addition to its intended function, chlorine reacts with organic compounds in the water to produce halogenated by-products including trihalomethanes (THMs), haloacetic acids, haloacetonitriles, and haloketones (Hu *et al.* 2010; Padhi *et al.* 2012a). Among these, THMs are the most

commonly found chlorination by-products (CBPs). Exposure to these disinfection by-products (DBPs) has been associated with adverse effects on human health including bladder cancer (Cantor *et al.* 1987; Freedman *et al.* 1997). After the emergence of pressing issues such as carcinogenic cell reproduction, genetic mutation and tissue damage, the US Environmental Protection Agency (EPA) instituted the stage-I disinfection by-product regulation (DBPR) during the late 1990s, and the stage-II DBPR was issued in 2006 limiting the total THMs to  $\leq 0.08$  mg/L. The types and yields of DBPs such as THMs vary with the type of disinfectant used and the nature of the source water (Whitaker *et al.* 2003). The DBPs' concentration and speciation are also affected by many water quality determinants (type and quantity of dissolved organic matter (DOM), pH, bromide, ammonia, nitrite concentration, and water temperature) and operational parameters (disinfectant dose and type, reaction time, etc.). Generally, THM formation increases with an increase in chlorine dose and DOM concentration (Xie 2004; Song *et al.* 2010).

In India, traditional open reservoirs for water fed by rain water or river water are important sources of drinking water supply both in rural and urban areas. In open reservoir storage facilities, water degradation has been a recognized concern for many decades (EPA 815-R-99-01 1999). Since the volume of water in a storage facility is normally large compared to the amount of exposed surface area, the effect of the wall and floor on disinfectant decay are normally not significant. Thus, disinfectant decay and by-product formation in storage facilities normally can be attributed to bulk decay, which mainly depends on the source water physico-chemical characteristics rather than to wall effects. Covering an open reservoir or replacing it with a covered storage facility can reduce or eliminate the potential for direct entry of contaminants and deterioration in the water quality (Kirmeyer *et al.* 1999). However, most reservoirs remain uncovered due to the capital cost involved in covering them and the difficulty in clearly quantifying the public health benefits accrued from covering. Direct input by runoff or internal growth of algae increases the organic material load in the open storage facilities. In addition, micro-organisms can enter from outside sources such as poorly constructed or inadequately maintained storage facilities, and can also be introduced into open reservoirs

from windblown dust and debris. In addition, groundwater (GW) having good nutrient content when stagnated and exposed to sunlight in an open reservoir is subject to eutrophication, which allows the proliferation of algae due to photosynthesis. Extracellular matter from the decay of these algae increases the organic load of the water, which serves as THM precursors (Hoehn *et al.* 1980). Organic matter, such as leaves and pollen also append to it and are a concern in open reservoirs. It should be noted, however, that DBP levels do not necessarily increase in all open reservoirs. High trihalomethane formation potential (THMFP) values were not correlated with peak algal levels in studies conducted in Seattle at Los Angeles Department of Water and Power's (LADWP's) Silver Lake reservoir (EPA 815-R-99-01 1999), which indicated that algae were not reactive causative agents contributing to DBP formation. Other types of organic substrate also have the potential to affect DBP formation. Some utilities have observed no significant changes and some have actually experienced decreases in DBP levels across their open reservoirs (AWWA 1983). One utility has conjectured that DBP levels may decrease through volatilization or through oxidation of precursors by heterotrophic bacteria (AWWA 1983). A study on inter-river comparison on the per unit algal contribution toward yield of THM by Jack *et al.* (2002) revealed that the potential of carbon fluxes arising from the algal senescence were much higher than the carbon required to account for TTHM formation. Much of the algal carbon is labile and therefore likely to be respired. Owing to different source water quality and diverse water treatment processes within different waterworks, the key parameters controlling DBP formation may vary from place to place.

Identification of the impact of storage facilities on water quality and strategies to minimize adverse effects are required to ensure that the water quality meets the regulatory guidelines and does not degrade in the distribution system. As there are many potential variables involved, investigation into the impact of storage facilities on water quality and strategies to minimize adverse effects are required to ensure that they meet the regulatory guidelines to deliver safe water. The present study focused on the total trihalomethanes formation potential (TTHMFP) of two different water types, mainly, upon open storage of subsoil water: (1) how primary water quality determinants, such as pH, temperature, Chl, dissolved

organic content (DOC) undergo changes; (2) how these parameters influence TTHMFP of both the water types; (3) whether DOC and UV<sub>254</sub> can be correlated with chlorine demand (CD) and THM formation; and (4) the role of bromide in the distribution of THM species.

## MATERIALS AND METHODS

### Sampling and storage

The Palar River, located in the district of Kancheepuram, Tamil Nadu, India, having GW, is the main source for the drinking water supply to the neighborhood. GW samples from a covered, concrete-lined infiltration well located inside the Palar River bed were collected monthly during January 2012 to December 2013. The depth of the well is around 20–25 feet and the water level varied from 2 to 10 feet during different seasons. Water samples from an open reservoir 20 km away from the river bed, located at Kalpakkam, were also collected. The reservoir has a storage capacity of 30,000 m<sup>3</sup>, and is spread over an area of about 2 ha and has a maximum depth of 3 m. The reservoir receives GW from the above-described infiltration well, transported through a 60 cm diameter cast iron pipe. Other than rain water, there is no external linkage to this reservoir. The reservoir caters for the raw water needs of various laboratories of the Indira Gandhi Centre for Atomic Research (IGCAR) as well as the demineralization plants of both the Madras Atomic Power Station (MAPS), and the Fast Breeder Test Reactor (FBTR). Moreover, it also serves as a drinking water source for IGCAR and MAPS. One liter (L) of water samples were collected in a pre-cleaned, air-tight high-density polyethylene (HDPE) bottle at about 11.30 hours every month from GW and open reservoir water (RW) and were brought to the laboratory within 30 minutes. Samples were filtered immediately after reaching the laboratory through a Millipore 0.45 µm nylon membrane filter. Filtered samples were kept separately in 20-mL screw cap glass vials with a pre-fitted septum for DOC analysis and 250-mL polytetrafluoroethylene (PTFE)-lined screw cap glass bottle for chlorination experiments. All samples were stored in the dark at 4 °C until further analysis and/or experiments and all the analyses were completed within 3 days of sample collection.

### Chemicals and reagent

The chemicals and standards used were acetone (AR, ACS), methanol (HPLC grade), pentane (HPLC, Spectrochem), and sodium thiosulfate (AR, ACS). Chloroform (CHCl<sub>3</sub>), bromodichloromethane (BDCM) (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl), and bromoform (CHBr<sub>3</sub>) were obtained from Sigma Aldrich (assay ≥98%, GC grade). Four percent of sodium hypochlorite solution was appropriately diluted in milli-Q water, standardized using standard sodium thiosulfate solution and used for chlorination experiments. Dibromochloropropane was used as internal standard for THM determination.

### Analytical methods

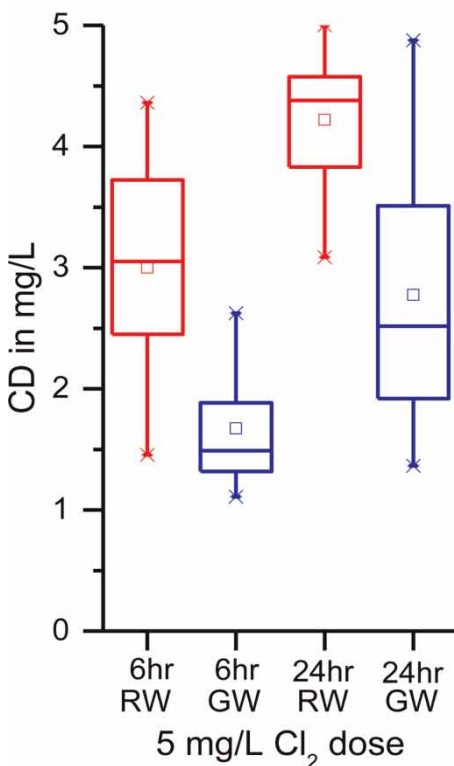
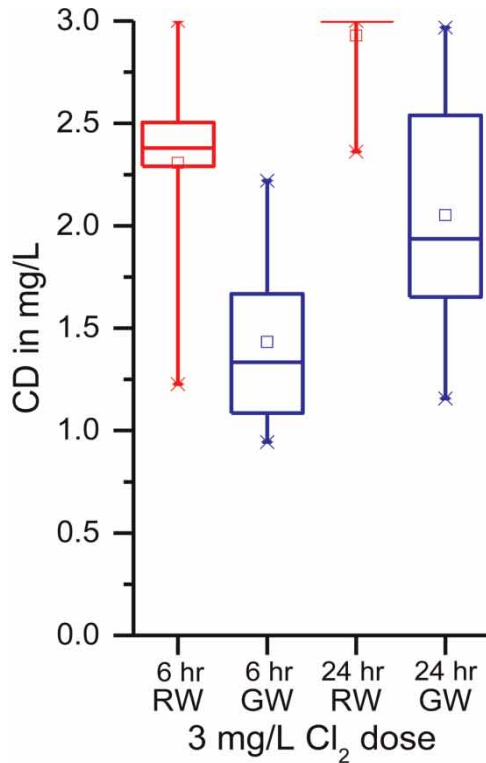
One hundred mL of water samples collected from GW and RW were chlorinated in PTFE-lined screw cap glass bottles with intermediate chlorine working standard prepared from 4% sodium hypochlorite solution. The initial chlorine dose was maintained at 3 and 5 ppm. Residual chlorine concentrations were measured at different time intervals ranging from 5 minutes to 24 hours by the DPD colorimetric method using a Lovibond chlorine analyzer. pH and temperature of the water samples were measured *in situ* by a hand-held portable pH meter (Lovibond Senso-Direct 100) with an accuracy of ±0.1 and a temperature probe with an accuracy of ±0.1 °C. Chl-a was measured using a standard colorimetric method (Parsons *et al.* 1984). The water samples chlorinated with different doses were drawn after 6 and 24 hours contact time and analyzed for THMs. Time intervals of 6 and 24 hours for THM analysis were chosen based on the assumption that maximum residence time of the treated water before use would be around the same. THM separation and analysis was carried out with a gas chromatography instrument (Chemito GC 1000) equipped with an electron capture detector. EPA method 551.1 was followed with some modifications for THM determination. Briefly, 5 mL of chlorinated samples at the end of the desired reaction time were de-chlorinated with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and THMs were extracted with 1 mL of pentane with the help of a circular mechanical shaker (Rotospin, Tarson) rotating at 50 rpm, after 10 minutes of shaking. A volume of 1 µL of pentane extract was injected

into the GC injector maintained at 150 °C. Separation of four THM species was carried out with the help of a DB-5 column in a temperature-programmed oven. The ECD detector was maintained at 290 °C. Reporting limits were set at  $\geq 1$   $\mu\text{g/L}$  for all THM species. Unchlorinated water samples were analyzed each time for blanks and were spiked with different concentrations of THM standards and extracted with pentane to test the recovery. Percentage recoveries of standard aqueous solution of  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$  amounted to 94.9, 93.7, 96.3, and 97.7, respectively. The limit of detection for the present instrumental condition was in the following order:  $\text{CHCl}_2\text{Br}$  (0.01  $\mu\text{g/L}$ ) >  $\text{CHClBr}_2$  (0.01  $\mu\text{g/L}$ ) >  $\text{CHBr}_3$  (0.05  $\mu\text{g/L}$ ) >  $\text{CHCl}_3$  (0.07  $\mu\text{g/L}$ ). Data acquisition was carried out by IRIS32 chromatography software. UV absorbance at 254 nm ( $\text{UVA}_{254}$ ) was measured for the fresh, untreated, 0.45  $\mu\text{m}$ -filtered sample with a UV spectrophotometer (Chemito Spectroscan UV 2600) without any pH adjustment. Owing to the lower UV absorbance values, all  $\text{UV}_{254}$  were measured with a 5 cm path length. Specific UV absorbance ( $\text{SUVA}_{254}$ ) values for the samples were calculated using the formula:  $\text{SUVA} (\text{L}/\text{mg}\cdot\text{m}) = (\text{UVA}_{254} (\text{cm}^{-1}) * 100 / [\text{DOC}] \text{ mg/L})$ . Non-purgeable organic carbon content was determined using a Shimadzu TOC auto analyzer by high-temperature combustion oxidation and non-destructive infrared absorption method. Bromide content was determined by ion chromatography-suppressed conductivity detection using Dionex ICS-2500 IC system. For chromatographic separation and quantification of bromide ion, Dionex analytical column AS-22 and guard column AG-22 were used with carbonate-bicarbonate as eluent.

## RESULTS AND DISCUSSION

The main factors that influence the formation of DBPs include contact time, CD, temperature, pH, concentration of precursors, and bromide ions. There were considerable differences in these parameters between GW and RW. In general, both RW and GW had moderate DOC with an average of 1.68 mg/L and 0.82 mg/L and  $\text{UVA}_{254}$  with an average of 0.057 and 0.049, respectively. The wide variation in DOC values of both the water types were not quantitatively reciprocated in the respective  $\text{UVA}_{254}$  variation.

Among the three main categories of problems, i.e., chemical, microbiological, and physical, that occur in the storage facilities, loss of disinfectant residual or CD and formation of DBPs are the most common chemical problems. For the same source water, CD is a function of both time and initial chlorine dose. CD values for both the source water types at different initial chlorine concentrations and time intervals during the 2 year sampling period are presented in Figure 1. It was observed that chlorine decay was faster and hence demands were lower in the case of GW with values ranging from 1.11 to 2.63 mg/L compared to 1.46–4.36 mg/L for RW for 5 ppm  $\text{Cl}_2$  dose, 6 hours contact time. It was obvious from the comparative higher Chl-a content in the open RW (Table 1) that, as expected, high biological activities in the reservoir led to the increase in organic content in the water and thus caused higher CD than GW. Therefore, higher amounts of chlorine will be required for RW to achieve the same desired residual compared to GW. However, the extent of compensation for the organic content in both the water types was different owing to the differences in their chlorine reactivity. Temporal variation of TTHMF at different chlorination conditions (Figure 2) showed that THM formation was always higher for RW than for GW for all chlorination conditions. Although higher THM formation was always observed for RW, magnitude of THM formation was not quantitatively reciprocated with the increase in CD, indicating the presence of non-THM-forming precursor constituents in the algal organic content in RW. Multi-parameter dependence of THM formation might result in a net facilitating effect or opposing effect when simultaneous temporal changes occur in these parameters. This factor was attributed to the random temporal behavior of TTHMF of both the water types and no seasonal trend could be established. On increasing residence time from 6 to 24 hours, both RW and GW exhibited an increase in TTHMF irrespective of the initial chlorine concentration of 3 or 5 mg/L. However, the monthly time course increment profile was arbitrary, for example RW displayed only an increase of  $\sim 10\%$  (11.58  $\mu\text{g/L}$ ) in the month of June 2012, whereas a nearly 62% increase was observed in July 2012 for a 3 mg/L  $\text{Cl}_2$  dose. Similar results were observed for higher chlorine doses and for Palar subsoil water also.

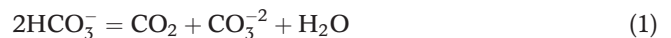


**Figure 1** | Comparison of CD values for RW and GW at different chlorination doses and contact times.

**Table 1** | Summary of water quality parameters (min–max) of GW and RW collected during the 2-year study period ( $n = 21$ )

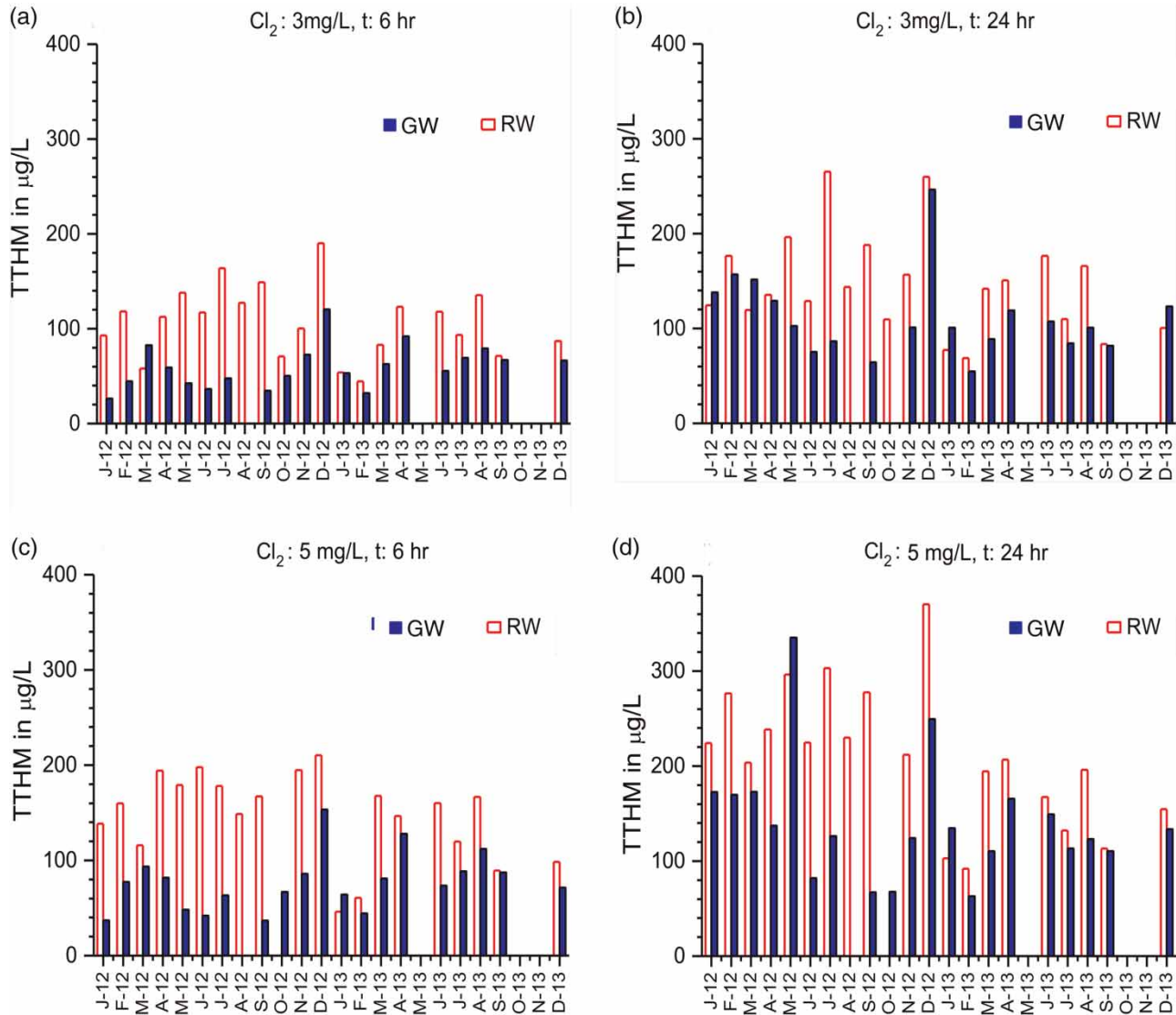
Water quality parameters	Palar subsoil water (min–max)	Open RW (min–max)
Temp ( $^{\circ}$ C)	27.0–32.8	27.5–34.7
pH	7.1–7.6	8.1–9.0
Chl <sup>a</sup> (mg/m <sup>3</sup> )	0.91–1.93	2.84–20.55
Br (mg/L)	0.09–0.26	0.15–0.65
DOC (mg/L)	0.41–0.95	0.93–2.56
UVA <sub>254</sub>	0.022–0.067	0.037–0.077
SUVA <sub>254</sub> (L/mg·m)	5.37–7.05	3.08–3.98
CD <sub>6Hr/3</sub> ppm (mg/L)	0.94–2.22	1.23–> 3.00
CD <sub>6Hr/5</sub> ppm (mg/L)	1.11–2.62	1.46–4.36
TTHMF <sub>6Hr/3</sub> ppm ( $\mu$ g/L)	26.3–120.3	44.2–190.2
TTHMF <sub>24Hr/3</sub> ppm ( $\mu$ g/L)	54.7–246.5	68.9–265.2
TTHMF <sub>6Hr/5</sub> ppm ( $\mu$ g/L)	36.3–153.4	40.1–210.4
TTHMF <sub>24Hr/5</sub> ppm ( $\mu$ g/L)	62.9–335.3	91.82–370.4

As expected, temperature and pH values for RW were always observed to be distinctly higher than the GW (Table 1). Higher pH observed in the RW as compared to the Palar water is apparently due to the photosynthetic activity by phytoplankton and macrophytes as per the following reactions (Boyd & Pillai 1985). Continuous uptake of carbon dioxide generated due to the dissociation of  $\text{HCO}_3^-$  by the phytoplankton and macrophytes drives the net reaction (Equation (1)) toward the right and  $\text{CO}_3^{2-}$  hydrolyses in water to produce hydroxyl ions (Equation (2)) which gradually assimilate in the RW to increase the pH.



Leaching of hydroxides and carbonates from concrete surfaces of the storage facilities also cause the pH level to increase to some extent. pH affects the ionization equilibrium of oxidants, which alter the species composition, i.e., among HOCl,  $\text{OCl}^-$ , HOBr, and  $\text{OBr}^-$ . These oxidant species have varying degrees of reactivity and can induce structural modification of organic precursors, thereby changing their propensity for THM production. In general, the rate of THM production increases with pH (Abdullah et al. 2003).





**Figure 2** | Temporal variation and comparison of TTHM formation potential of GW and RW at different chlorination conditions.

A three-fold increase in the reaction rate per unit increase in pH was reported by *Kavanaugh et al. (1980)*. Formation of THMs mainly depends on the last step base catalysis reaction favored at higher pH as in the haloform reaction. A decrease in THM formation as a result of lowering pH has been noted by many researchers (*Peters et al. 1980*; *Garcia-Villanova et al. 1997*). At lower pH, organic matter is condensed and at higher pH it undergoes structural expansion exposing the chromophoric sites (*Pace et al. 2011*). This change in configuration might also result in more natural organic matter (NOM) sites coming into contact with chlorine favoring THM

formation. The algal biochemical composition also plays an important role in determining the TTHM yield (*Hong et al. 2008*). This is supported by the previous study showing higher TTHMFPP for diatoms than green algae under the same chlorination conditions (*Plummer & Edzwald 2001*). Aquatic humic acids contain more aromatic carbon than algal-derived carbon, and therefore have higher TTHMFPP (*Reckhow et al. 1990*; *Nguyen et al. 2005*). These are possibly the reasons the higher CD of RW was not proportionally reflected in the magnitude of THM formation in GW under the same chlorination conditions. However, the CD and the

THMFP of RW were always observed to be higher than in GW.

Temporal variations in  $UVA_{254}$  are presented in Figure 3, which shows that its magnitude and temporal trend are similar for both RW and GW. As discussed previously, these two water sources exhibited low  $UVA_{254}$  absorption. In water with high  $UVA_{254}$ , such as those containing humic fractions, it is often observed that UV absorbance at 254 nm is strongly correlated to DOC content and THM formation (Chow et al. 2005). Such a trend was not found in our study possibly due to the fact that most of the NOM in these waters comprises non-UV absorbing fractions. Water samples having a DOC concentration of 0.1–0.8 mg/L generally exhibited a low and narrow range of  $UVA_{254}$  ( $<0.010 \text{ cm}^{-1}$ ), indicating that  $UVA_{254}$  is almost independent of TOC (Kitis et al. 2001). Figures 4 and 5 demonstrate the comparative  $UVA_{254}$  with respect to TTHMFP and CD (5 ppm, 24 hours) for both the water types.  $UV_{254}$  absorbing groups usually contain free electrons in the oxygen and sulfur atoms, conjugated C=C bonds, and aromatic carbons

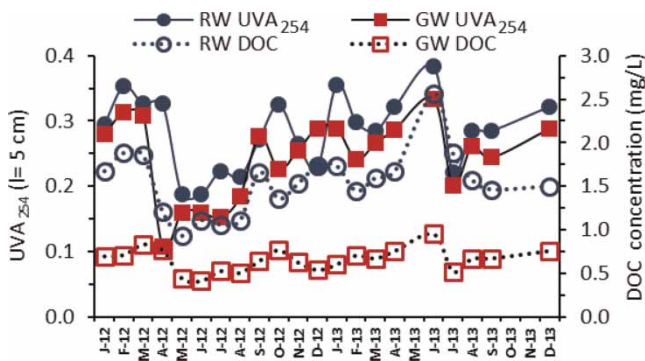


Figure 3 | Temporal variation and comparison of  $UVA_{254}$  with DOC in both water types.

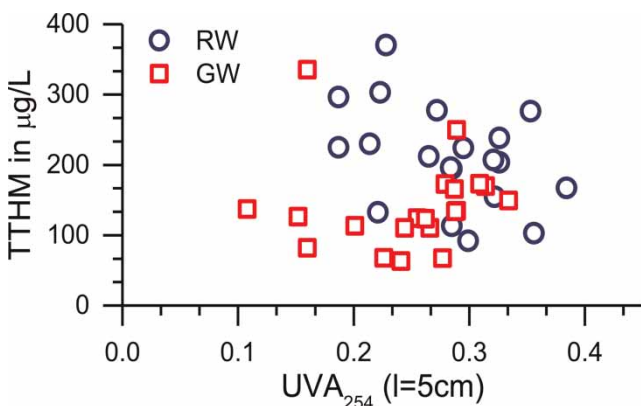


Figure 4 | Correlation of  $UVA_{254}$  with TTHM formation at 5 ppm  $Cl_2$  after 24 hours.

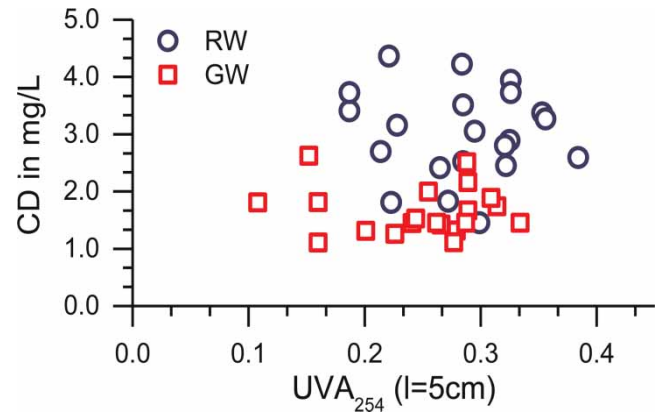
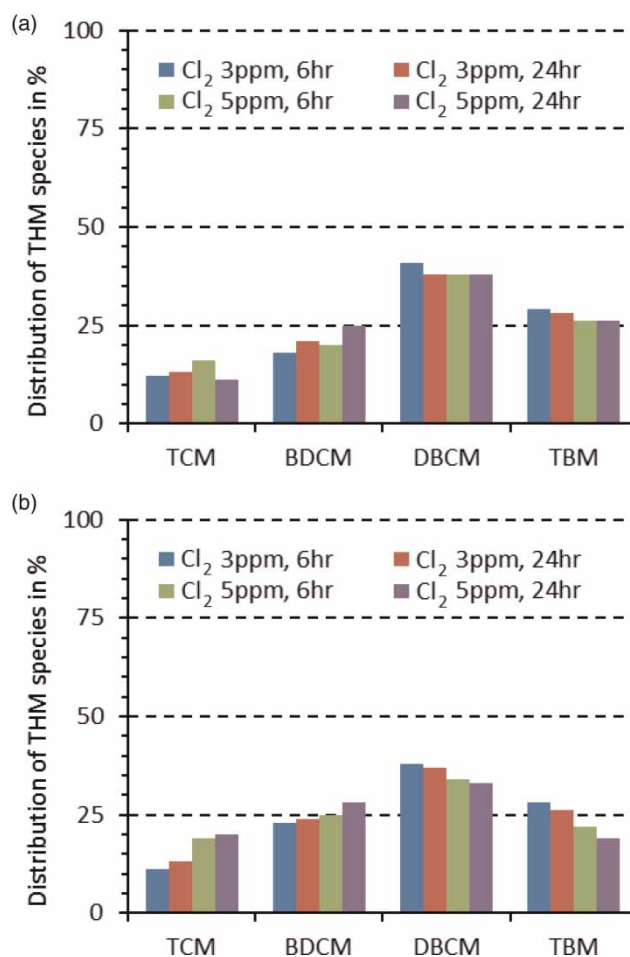


Figure 5 | Correlation of  $UVA_{254}$  with 6 hours, CD at 5 ppm  $Cl_2$ .

(Chow et al. 2008). Owing to easy measurement,  $UVA_{254}$  serves as a proxy for aromatic contents in the DOM and is correlated with THM formation in many studies (Fram et al. 1999). NOM has distinct characteristics associated with its origin, viz. vegetation, soil, wastewater, etc. For example, DOC from aquatic algae have relatively large nitrogen content, low aromatic carbon, and low phenolic contents. On the other hand, terrestrially derived DOC is relatively low in nitrogen content but rich in aromatic and phenolic components. Thus, the aromatic content, which is believed to be the major reactive content, varies with the source of generation (Fabris et al. 2008). When freshwater is impounded in reservoirs, the longer hydrologic residence time (typically in the order of months to years compared to a few hours to weeks in riverine systems) may be long enough to allow transformation of allochthonous carbon input (Mash et al. 2004). In addition, NOM is formed by autochthonous production from algal and microbial activity. Autochthonous organic materials derived from algal or microbiological productivity tend to be more aliphatic with much higher nutrient inclusion. Phytoplankton, in particular, are the major producers of autochthonous DOC in reservoirs (Imai et al. 2002). The relative influence of each end-member class determines the bulk chemical properties of the DOC, including hydrophobicity and hence oxidant reactivity (Malcolm et al. 1994; Westerhoff & Mash 2002). Many studies that have correlated  $UV_{254}$  and  $SUVA_{254}$  with the TTHM of the water have suggested that, with low to moderate value of  $UV_{254}$ , the usefulness of these surrogate parameters for prediction of TTHM formation is limited (Weishaar et al. 2003;

Ates *et al.* 2007). In our study, we did not observe any correlation of  $UVA_{254}$  with TTHMFP and CD in either source of water (Figures 4 and 5). Water having SUVA values  $<1.5$ – $2.0$  L/mg-M generally contains hydrophilic, non-humic, and smaller molecular weight NOM moieties (Kitis *et al.* 2010). The SUVA values for RW and GW were higher than this value which ranged between 3.09–3.98 L/mg-M and 5.37–7.05 L/mg-M, respectively. Thus, it appears that some special NOM moieties, most probably of non-humic, non-UV absorbing, and hydrophilic nature, are responsible for the THM formation in these source waters. In addition, these moieties possibly comprised only a small portion of all NOM and therefore DOC also showed no correlation with THMs.

Among the number of determinants that affect the DBPs' formation and speciation, the bromide level in raw water influences the species distribution to a great extent (Dore *et al.* 1988). The effects of bromide presence on the THM formation potential for both the waters were also investigated. Bromide content of the Palar subsoil water ranged between 0.15 and 0.26 mg/L, and relatively high values were observed for RW (0.17–0.65 mg/L). At different chlorine doses and reaction times, speciations of THMs for both the water types are depicted in Figure 6(a) and 6(b). Generally, chloroform is the major contributor of THMs with relatively low amounts of other species in freshwater chlorination; in contrast, bromoform constitutes more than 95% of THMs during seawater chlorination (Abdel-Wahab *et al.* 2010; Padhi *et al.* 2012b) owing to its higher bromide content (~65 mg/L). However, located near the coast, the appreciable amount of bromide present in these waters may be derived from the seawater aerosol. The coexistence of HOCl and HOBr formed due to oxidation of  $Br^-$  by HOCl during chlorination has resulted in THM species being non-selectively distributed among all the four species and no preferential formation of any particular species was observed. The abundant formation of partial brominated THM in these source waters associated with a higher level of toxicity can be a concern for adopting chlorination as a pathogen control measure. Previous studies have reported that the presence of bromide shifts the species distribution toward bromine-containing THMs as well as increasing total THM yield (Hua *et al.* 2006; Hua & Reckhow 2008). Furthermore, the bromine-containing DBPs are known to be more toxic



**Figure 6** | Percentage distribution of four THM species in chlorinated RW for: (i) Cl<sub>2</sub> 3 ppm, 6 hours; (ii) Cl<sub>2</sub> 3 ppm, 24 hours; (iii) Cl<sub>2</sub> 5 ppm, 6 hours; (iv) Cl<sub>2</sub> 5 ppm, 24 hours (a); and in chlorinated GW for (i) Cl<sub>2</sub> 3 ppm, 6 hours; (ii) Cl<sub>2</sub> 3 ppm, 24 hours; (iii) Cl<sub>2</sub> 5 ppm, 6 hours; (iv) Cl<sub>2</sub> 5 ppm, 24 hours (b).

than their chlorine counterparts. Bromide present in the water gets oxidized by HOCl forming hypobromous acid (HOBr) which is a better halogenating species at natural water pH. The instantaneous oxidation of bromide to HOBr and the easier formation of the Br-C bond than the Cl-C bond results in enhanced overall TTHM yield and greatly alters the species composition of THMs (Hansen *et al.* 2012), as was observed in the present case. No distinct difference in the species distribution character was observed between RW and GW. At a chlorine dose of 3 mg/L, the species pattern remained almost constant irrespective of the water type, i.e., RW or GW and reaction time. However, at the higher chlorine dose of 5 mg/L, the allocation of species shifted more towards the brominated analog in RW



compared to GW. Another important observation with respect to the THM formation mechanism, details of which are not included in the scope of this study, was that on increasing chlorine dose and contact time the contribution of BDCM toward overall TTHM increased irrespective of water type.

## CONCLUSION

DBPs were higher in RW compared to GW, suggesting that chlorination of open storage water carries a higher health risk due to exposure to THMs. The presence of THM-forming precursor constituents in the algal-derived organic content of RW is insignificant. Thus, increase in THM formation was not quantitatively reciprocated with the extent of difference in CD of RW and GW, suggesting different organic matter chemical composition. Temperature and pH values for open RW were observed to be higher than the original source GW and these were generally associated with high CD and TTHMF. DOC content and UVA<sub>254</sub> did not correlate well with THM formation for both water types and thus could not be taken as surrogate parameters for prediction of THM formation potential of the studied water. The distribution pattern of THM species was not selective for chloroform unlike that generally observed for freshwater chlorination. Appreciable amounts of bromide present in these water sources (0.15–0.26 mg/L in GW and 0.17–0.65 mg/L in RW) have resulted in non-selective distribution of the four THM species. The extent of bromide present must be taken into consideration if chlorine has to be used for disinfection and more so if the water source is near the coast. The profuse formation of partially brominated THMs associated with higher levels of toxicity in both water types could be a decisive factor in the choice of chemical for pathogen control.

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