THE IMPACT OF NATURALLY OCCURRING BROMIDE ON WATER QUALITY

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INTRODUCTION

Drinking water quality is of utmost importance to both the water utility and consumer alike. Of primary concern is the microbiological safety, but also of importance are the chemical safety and aesthetic characteristics of drinking water. The organoleptic properties are often the only way that a consumer may judge the quality of water, and may influence the customer's perception of the safety of the drinking water. Organic and inorganic constituents, including natural organic matter (NOM), inorganic ions and disinfection by-products (DBPs) formed from the reaction of a disinfectant with both organic and inorganic compounds, can impact water quality.

Bromide is a natural constituent of rainfall, cloud water, stream water or groundwater, and in Western Australian surface and groundwater drinking water sources, bromide concentrations are often relatively high and can range from not detected to 2 mg L^{-1}. Bromide is typically difficult to remove with conventional water treatment practices, and can readily undergo oxidation during disinfection with chlorine to form bromine. The formation of bromine has a number of implications for the quality of drinking water. Our previous studies have shown that bromine can contribute to chlorinous odours in Western Australian distributed waters. Also of concern is the formation of brominated DBPs, which are potentially more carcinogenic than their chlorinated analogues. The objectives of this research were to investigate the role that bromide has on drinking water quality, focussing on one water source in North-Western Australia. Increased understanding of the role of bromide in drinking water quality can allow improved management strategies.

METHODOLOGY/ PROCESS

Monthly Sampling

Harding Dam water was sampled on a monthly basis from the surface (epilimnion) and the bottom (hypolimnion) of the dam from October 2005 to January 2008. The analyses conducted on these water samples included dissolved organic carbon (DOC) and bromide concentrations. Water from distribution system supplied by water from Harding Dam was also sampled on a monthly basis over the same time period. The chlorine equivalent residual in each sample was quenched and the samples analysed for total trihalomethanes (THMs).

NOM Concentration and Fractionation

Water was collected from Harding Dam (1000 L), and concentrated to approximately 1.0 L using reverse osmosis (RO). The NOM concentrate was fractionated into five fractions using preparative-scale high performance size exclusion chromatography.

Disinfection of the Harding Dam Fractions

Laboratory-scale disinfection was conducted using the collected fractions. Bromide (0.5 mg L^{-1}) was added to the fractions, the DOC concentrations were adjusted to 2.0 mg C L^{-1}, and the fractions were dosed with 8.0 mg L^{-1} chlorine as Cl_2. THM formation potential experiments (THMs measured using solid-phase microextraction followed by gas chromatography- mass spectrometry (SPME/GC-MS)) and odour analysis (by a modified flavour profile analysis technique) were conducted on the disinfected fractions. Bromine incorporation factors for the disinfected fractions were also calculated.

RESULTS / OUTCOMES

NOM Characteristics

The NOM contained in the RO concentrate was fractionated into five fractions (Figure 1). The specific ultraviolet (UV) absorbance at 254 nm, weight average molecular weight, number average molecular weight, and polydispersity of Harding Dam raw water, NOM concentrate, and fractions are given in Table 1. Fractions were collected from higher apparent molecular weight and polydispersity through to lower apparent molecular weight and polydispersity.

Trihalomethane Formation

DOC had a positive correlation with bromide concentration ($p < 0.05$, Spearman's Rho correlation), and only total THM concentration in the epilimnion, during the monthly sampling of Harding Dam. Interestingly, bromide concentration exhibited a positive correlation with total THM concentration ($p < 0.05$, Spearman's Rho correlation). As bromide concentrations increased in the dam, total THM concentrations in the distribution system sample also increased (Figure 2). The results from the disinfection experiments using the fractions obtained from the concentration and fractionation of the Harding Dam water showed that, fraction 1, having the higher molecular weight moieties, produced mostly brominated THMs, with chlorodibromomethane being the dominant THM formed, followed by bromodichloromethane, bromoform, and chloroform. Other NOM fractions, however, displayed different THM species distributions. Overall, bromine was found to be incorporated more readily into THMs formed from the reaction between chlorine and the higher molecular weight fractions (Table 2).

Odour characteristics

We have recently proposed that bromine plays an important role in chlorinous off-flavours in distribution systems, with some waters containing relatively high concentrations of bromine exhibiting a chlorinous odour when the free chlorine residual has decreased to below measurable concentrations. Harding Dam water exhibited chlorinous off-flavours even when the free chlorine residual decreased to below measurable concentrations. Odour analysis was also conducted on fractions with and without bromide to investigate the impact of bromine on the chlorinous off-flavours.

CONCLUSION

Bromine was proposed to play an important role in the aesthetic quality of drinking water. Additionally, bromine may be incorporated into THMs upon disinfection with chlorine and reaction with NOM. Bromine incorporation was greater for higher apparent molecular weight NOM than lower molecular weight NOM. Our current research is focussed on developing novel treatment processes for selective removal of bromide from potable source waters.

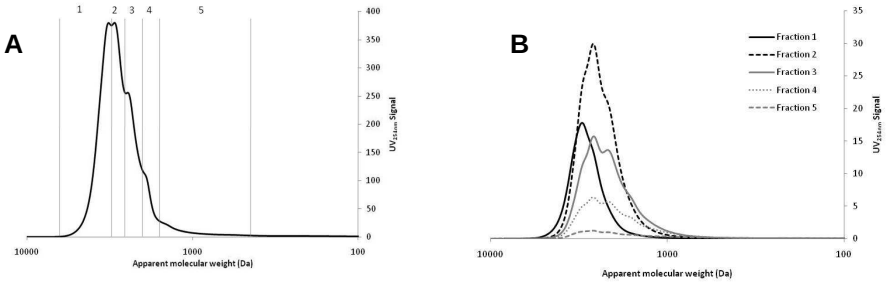

Figure 1. Molecular weight distribution of UV_{254}-active DOC in Harding Dam NOM concentrate (A) and preparative-scale size exclusion chromatography fractions (B)

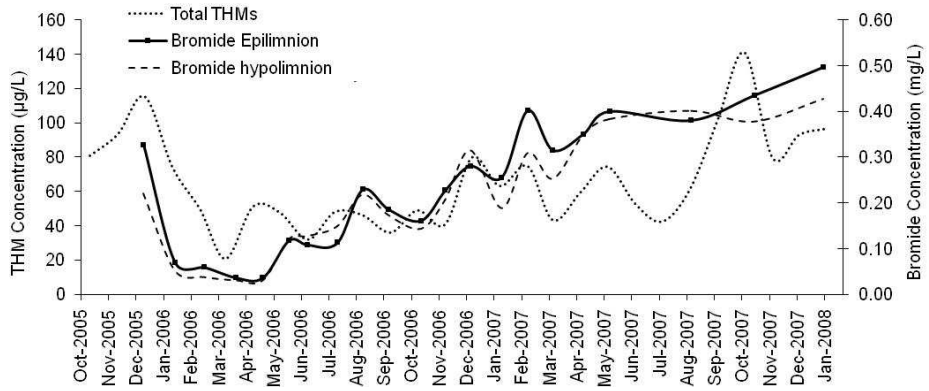

Figure 2. Concentration of total THMs in Harding Dam distribution system samples and bromide in Harding Dam from October 2005 to January 2008.

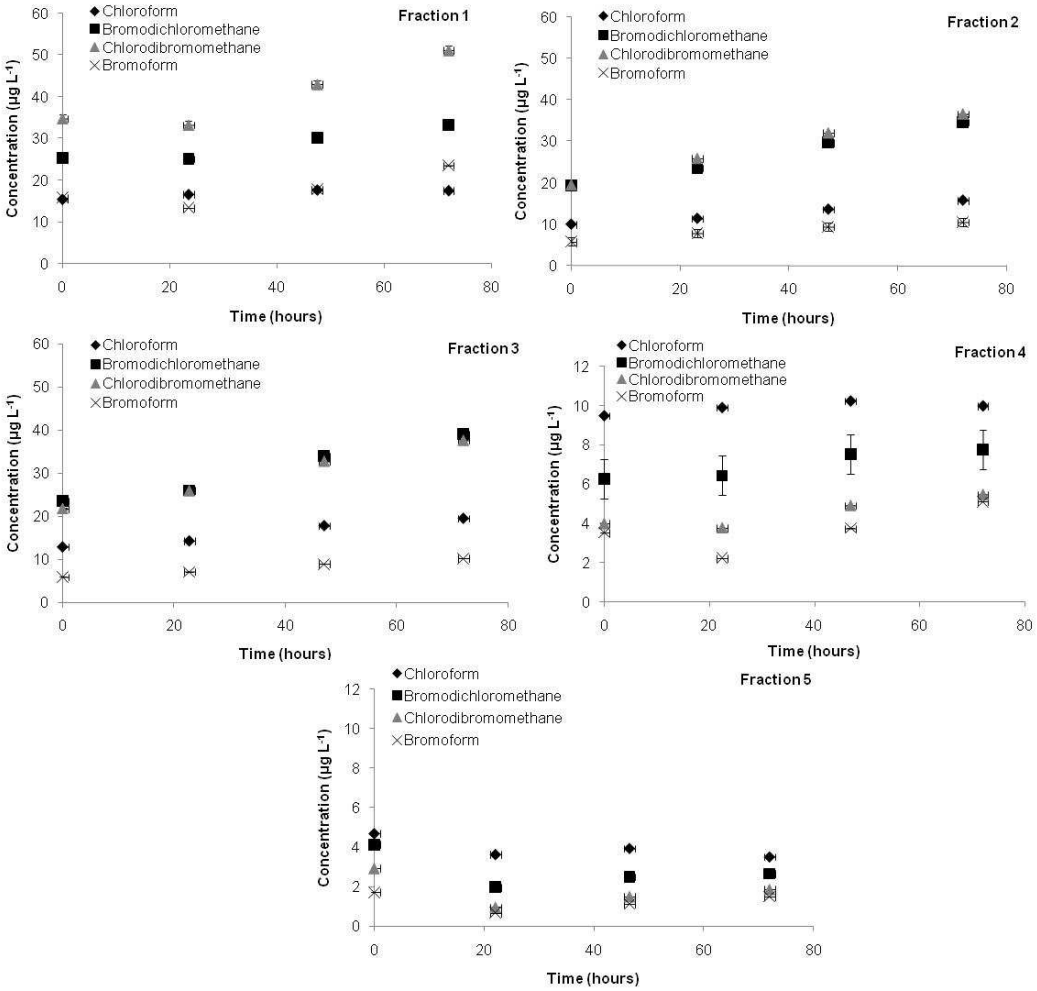

Figure 3. THM Formation Potentials for Harding Dam NOM fractions.

Table 1. Specific ultraviolet absorbance ($SUVA_{254}$), Weight average molecular weight (M_w), Number average molecular weight (M_n) and polydispersity of Harding Dam fractions, NOM concentrate and raw water.

Sample	**$SUVA_{254}$ (L/mg.m)**	**M_w**	**M_n**	**ρ**
Fraction 1	2.10	2946	2812	1.05
Fraction 2	1.55	2525	2379	1.06
Fraction 3	1.68	2305	2080	1.11
Fraction 4	1.75	2192	1840	1.19
Fraction 5	1.44	1910	798	2.39
NOM concentrate	1.77	2276	1953	1.17
Raw water	1.30	2545	2102	1.21

Table 2. Bromine incorporation factors for three day THM formation potentials for Harding Dam raw water and fractions.

Sample	**Bromine incorporation factor**
Fraction 1	0.472
Fraction 2	0.409
Fraction 3	0.386
Fraction 4	0.302
Fraction 5	0.287
Raw water	0.467