# IMPACT OF OPERATIONAL STRATEGY ON DBP FORMATION

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## ABSTRACT

The overall benefits of disinfection are well established; however a consequential concern is the formation and control of disinfection by-products (DBPs) that may result in adverse health effects. The vast majority of these compounds do not have limit values in the Australian Drinking Water Guidelines (ADWG) and therefore are not monitored by water utilities, regardless of their potential contribution to the risks associated with long term chlorinated water consumption. Therefore, to obtain a better understanding of the impacts of treatment on overall risk, this project measured DBP formation (including THMs and HAAs) and applied a cell-based bioassay. The key components controlling formation of DBPs are natural organic matter (NOM), bromide concentration, chlorine dose, pH and temperature. The most common treatment process utilised to remove NOM is conventional treatment. This project determined the impact of changing water treatment plant operational strategy on disinfection by-product formation.

## 1.0 INTRODUCTION

The primary purpose of disinfection of water supplies is to reduce the risk of infection by microorganisms. Chlorination is the most common form of disinfection used in Australia as it provides a residual which prevents microbial re-growth within the distribution network (Uber et al., 2003, Mancini et al., 2005). While chlorine's disinfection ability has provided substantial public health benefits, its interaction with natural organic matter and inorganic precursors can generate hundreds of DBPs (Wang et al., 2010, Agus and Sedlak, 2010) that can also result in adverse health effects (Richardson et al., 2007).

Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common and investigated halogenated DBPs found in drinking water (Mancini et al., 2005). In most developed countries, including Australia, total THMs (sum of chemical species: chloroform, dichlorobromomethane, dibromochloromethane and bromoform) are regulated (Rodriguez and Serodes, 2005). The concentration and speciation of THM and HAA formation is influenced by multiple physico-chemical factors, including disinfectant dose, pH, temperature and the concentration and character of precursors present, especially dissolved organic carbon (DOC) concentration. DOC is the analytical measure of dissolved NOM. To ensure DBPs are below Australian Drinking Water Guidelines (ADWG, National Health and Medical Research Council, 2011) or other licensing or regulatory limits, water utilities undertake treatment to reduce NOM and, consequently, the chlorine dose required for disinfection. The most common process employed by utilities to remove NOM is conventional treatment comprising coagulation, sedimentation and filtration.

This project measured total DBP formation and cytotoxicity (to assess possible toxic effects) in addition to the DBPs within the ADWG to obtain a better understanding of the impacts of treatment on overall risk with the aim to evaluate the extent that the formation of DBPs could be reduced by optimising both the conventional treatment and disinfection processes. Some of the outcomes of this work are presented here.

## 2.0 DISCUSSION

### 2.1 Methodology

Two water sources were selected, a dam (labelled 'D') from Western Australia with high DOC (13.8 mg/L) and high bromide (0.60 mg/L) and a location along the River Murray (labelled 'R'), South Australia, with moderate DOC (7.2 mg/L) and low bromide (0.07 mg/L). Each was characterised for basic water quality parameters, organic characterisation, as well as DBP formation potential and associated toxicity formation.

Coagulation/filtration jar testing using aluminium sulphate (alum) was conducted to produce waters of differing levels of treatment, from low dose clarification to enhanced coagulation for greater NOM removal. Aluminium sulphate (as $Al_2(SO_4)_3.18H_2O$) was used as this is the most commonly applied inorganic coagulant in Australia. The alum dose range for disinfection studies were determined by initial broad range jar tests. A PB-900 6-paddle gang stirrer (Phipps & Bird, USA) was used which allowed the evaluation of different conditions simultaneously. DBP formation was determined using simulated distribution system (SDS) tests over 72 hours at 2 temperatures representing summer (25°C) and winter conditions (15°C). Chlorine dose was determined as the demand over 72 hours plus 0.5 mg/L.

An additional test was completed to compare DBP formation using single and split chlorination dosing strategies. Treated water produced using optimum coagulation conditions (for removal of colour, turbidity and DOC) was used for the comparison. The split chlorination consisted of an initial chlorine dose to achieve a residual of 0.5 mg/L after 48 hours followed by an additional ('booster') chlorine dose of 1.0 mg/L and further contact time of 24 hours. The same total chlorine dose was used for both disinfection strategies. DBP formation was determined after 48 hours, prior to the addition of the second chlorine dose, and after 72 hours.

The impact of the kinetics of formation and detention times on total THM and HAA concentration and speciation were investigated by periodic sub-sampling. Analysed parameters also included bromide. Selected samples were concentrated to make responses detectable and evaluated using cell-based bioassays to determine the cytotoxicity, expressed as a percentage of cell inactivation - % cytotoxicity (Sawade et al., 2014).

### 2.2 Results

The results from both water sources showed that coagulation was an effective means of reducing DBP formation following chlorination, with treatment at 50 mg/L and 60 mg/L alum for the dam and river waters, respectively, able to meet typical water quality targets for turbidity (<0.1 NTU) and colour (<10 HU). No exceedance of ADWG limits for either THMs or HAA3 (three regulated HAAs) was observed for the river water after coagulation. In comparison, the dam water contained higher concentrations of DOC and bromide and produced higher concentrations of DBPs (Figure 1), in particular THMs.

Although coagulation reduced DBP formation, no dose was found to reduce the THMs to below the ADWG of 250µg/L at the higher temperature. Comparison within the optimum range of alum coagulation showed increased THM and HAA formation at the warmer (25°C) summer temperature (Figure 2). This indicates that coagulation with a focus on optimised removal of DOC is a beneficial means of reducing THMs and HAAs, with optimisation of coagulation more critical in summer, particularly in waters with higher DOC and bromide.

HAA3 (ADWG) significantly under represented the extent of total HAA formation (HAA9), particularly in the higher bromide water (dam) 27-54% compared to the lower bromide water (river) 54-83%. This is attributed to the increased formation of brominated species in the dam water.

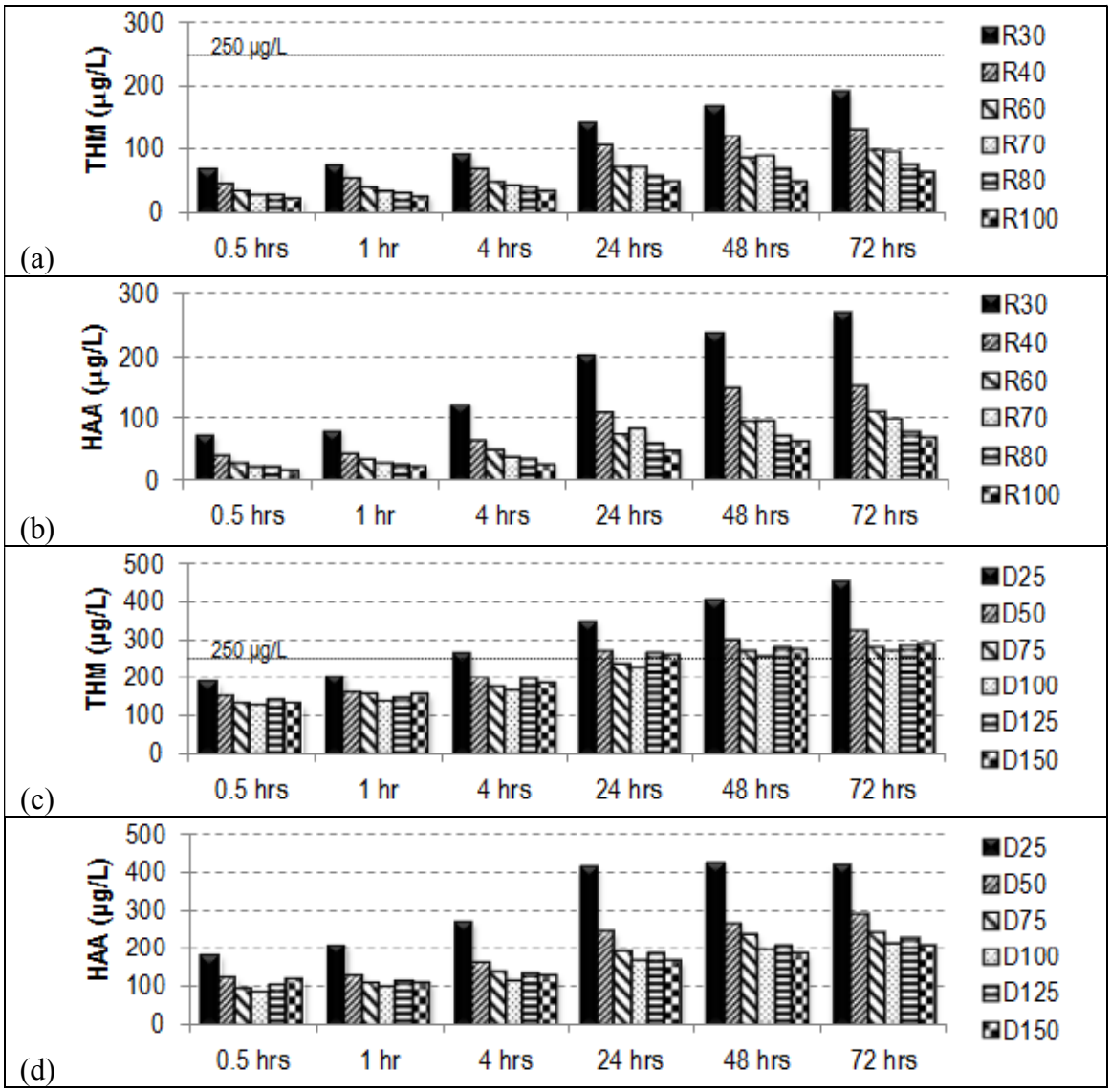


**Figure 1:** ***DBP formation for coagulation jar test series at summer temperature (25°C). Series (a) THM and (b) HAA9 for river water treated, where R30 = river water with 30mg/L alum. Series (c) THM and (d) HAA9 for dam water, where D25 = dam water treated with 25mg/L alum.***

Cell-based bioassays confirmed that despite pre-concentration, the treated and disinfected waters at natural bromide concentrations had low potential for acute health effects and the results could not be directly correlated to any of the measured DBPs. Chlorination of the untreated waters produced 76% and 65% cytotoxicity in the dam and river water respectively, while all treatments reduced cytotoxicity (Figure 3). These results indicate that coagulation is effective at reducing DBP formation potential through removal of organic precursors and highlights the importance of even minimal coagulation as a means of reducing overall cytotoxicity.

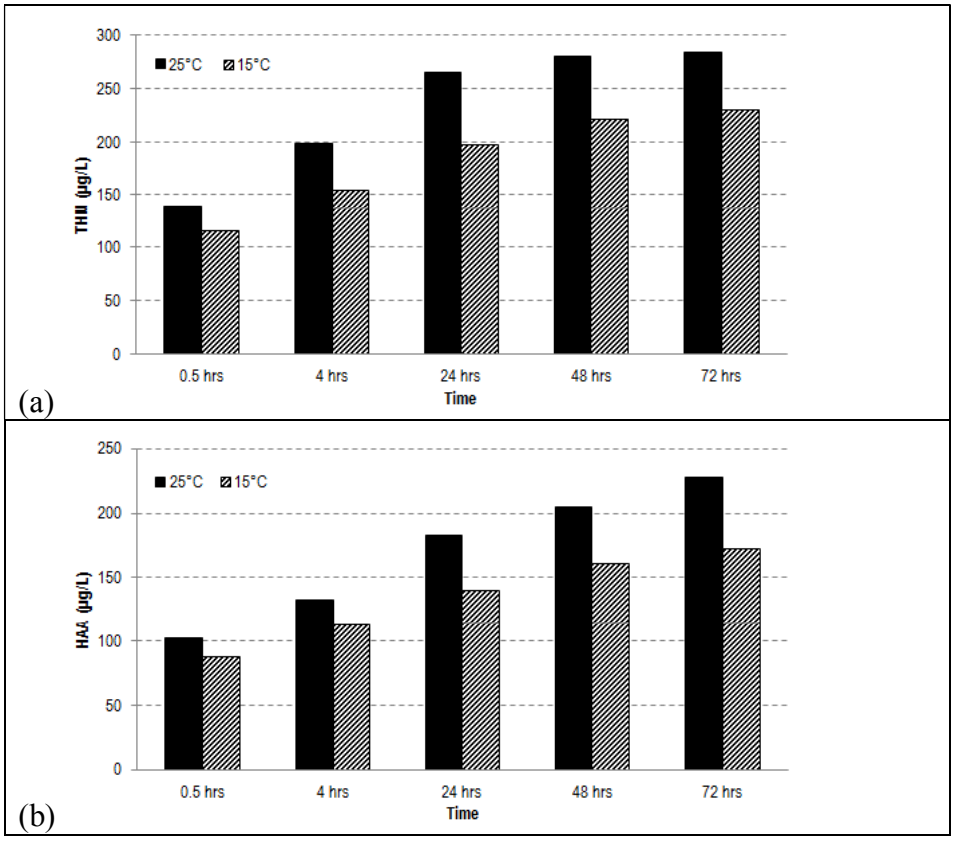


**Figure 2:** ***Comparison of temperature effect for dam water for (a) THM and (b) HAA9 formation over time for 125 mg/L alum.***

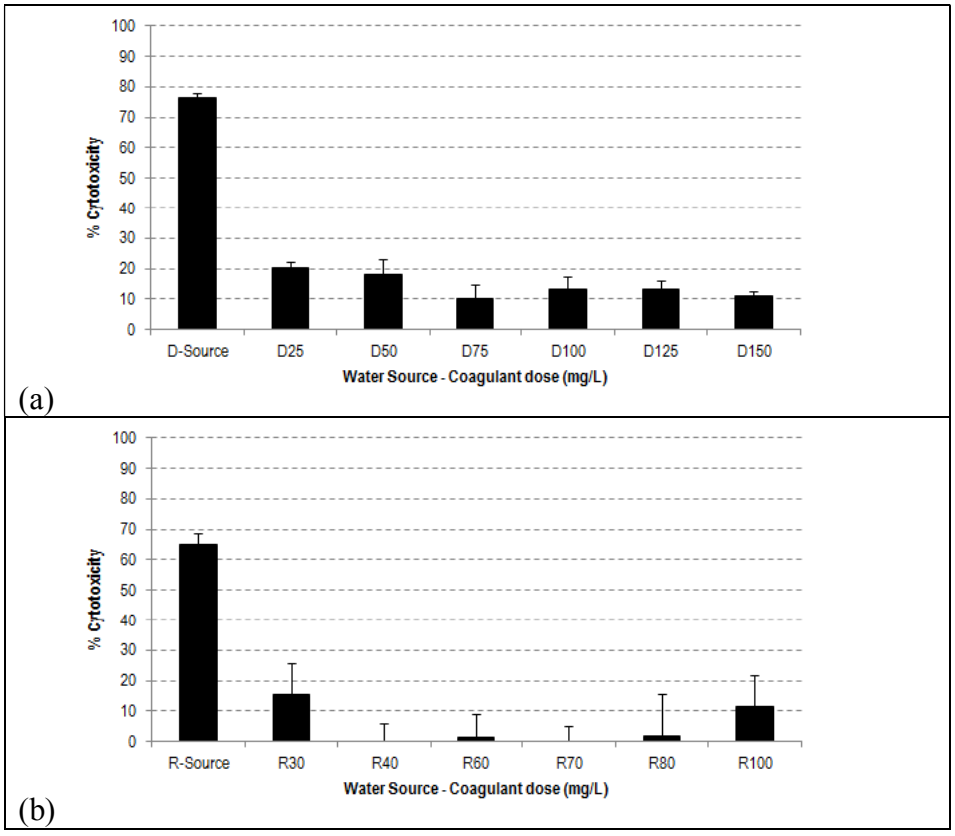


**Figure 3:** ***Cell assay toxicity of chlorinated coagulation series at 72 hours, (a) dam water, (b) river water. 'Source' represents the chlorinated, untreated water as a positive control.***

Split chlorination was compared with single dose tests while maintaining the total chlorine added. After 72 hours it was apparent that the addition of two lower doses of chlorine reduced both THM and HAA formation at the two temperatures in both water sources. Although there was a reduction in THM and HAA formation for the River Murray water source (moderate DOC/low bromide) using the split chlorination, the overall THM and HAA concentrations were below the ADWG for both strategies. In the dam water source (higher DOC and bromide), split chlorination facilitated sufficient change in the DBP formation mechanism to reduce the THM concentration to below the ADWG (250 µg/L) at the summer temperature (Figure 4). The link between the success of this strategy and the concentration of bromide in the source water or bromide to DOC ratio has yet to be established. Cell assay toxicity was also reduced with this chlorination strategy suggesting a possible link with decrease in formation of harmful DBPs.

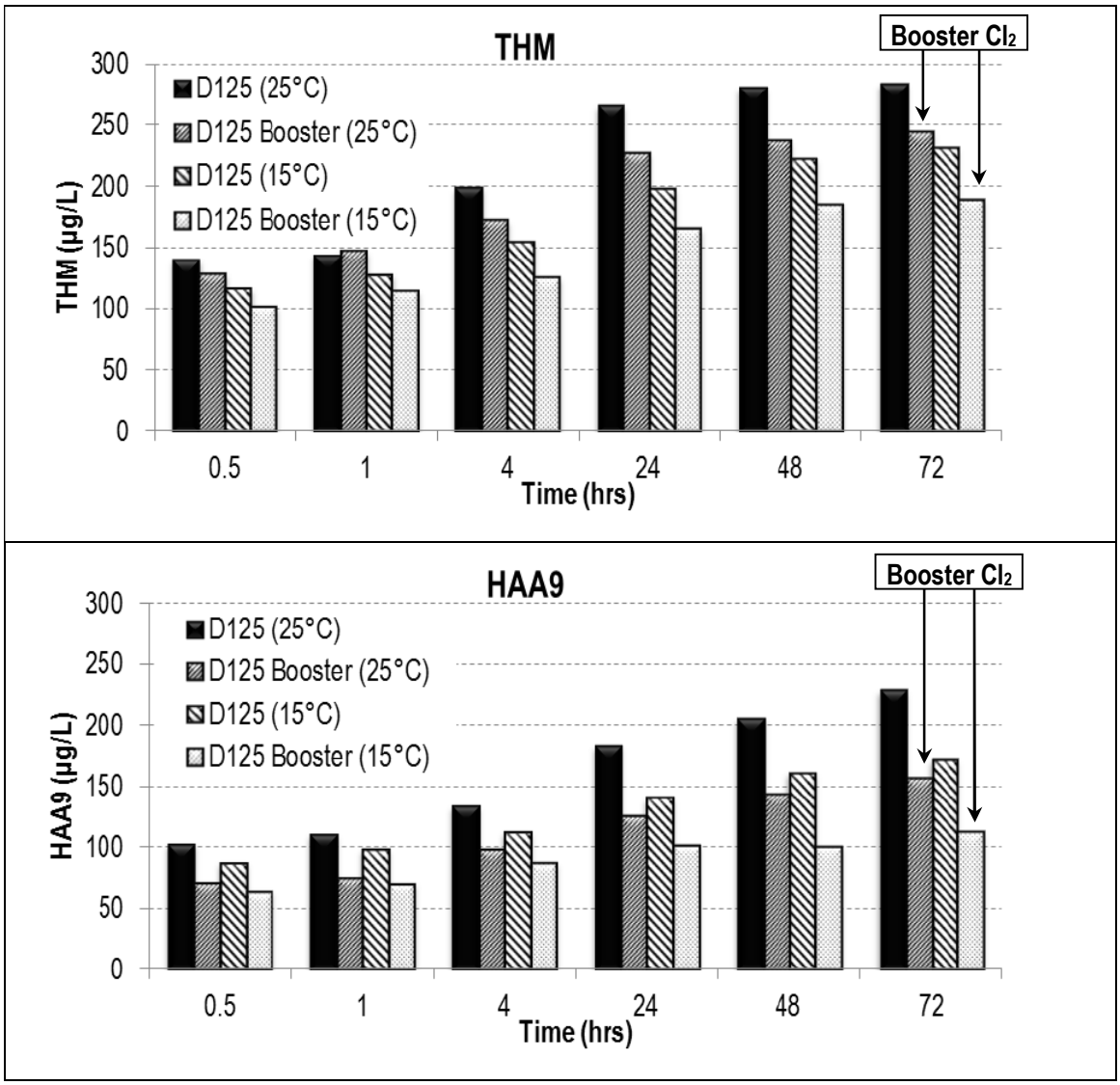


**Figure 4:** ***THM and HAA9 formation in treated dam water at summer and winter temperatures comparing single and split ('booster') chlorination over 72 hours. 'D125'= dam water treated with 125mg/L alum.***

## 3.0 CONCLUSION

The optimisation of coagulation to maximise DOC removal remains the most effective strategy to reduce DBP formation and the resulting bioassay responses in conventional treatment plants; therefore the adoption of enhanced coagulation philosophy may assist in the minimisation of seasonal DBP issues. Where distribution system detention times are long, requiring considerable chlorine doses, a reduction of final THM and HAA concentrations may be achievable by application of lower primary disinfectant doses after treatment, with booster chlorination at strategic points to ensure a residual is maintained. The outcomes from this project may assist water utilities to manage their existing treatment to minimise DBP formation before additional infrastructure changes are considered.

## 4.0 ACKNOWLEDGEMENTS

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