

The destruction of cyanobacterial toxins with oxidants used in drinking water treatment

Samuel J.L. Brooke

B.Sc. Flinders University 1997

B.Sc. (Hons.) Flinders University 1998

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Abstract

Saxitoxins were extracted from a bloom of toxic *Anabaena circinalis* and used to spike treated water from Hope Valley Reservoir (HVTW) and Milli-Q water. The waters were treated with ozone using the batch method and saxitoxin levels were measured in the samples using HPLC. The results for oxidation of saxitoxins in Milli-Q water versus HVTW show that despite the presence of natural organic matter (NOM) and the production of vastly different ozone residuals, there was a similar removal of all saxitoxins in both waters. The results show that high concentrations of saxitoxins were present in solution after ozonation with doses and contact times typically used in water treatment. Relating the toxin destruction to ozone residual showed that even with a residual ozone concentration of 0.8 mg/L after 10 minutes contact in HVTW, over 60% of the initial saxitoxin content was still present in the samples. The presence of an ozone residual in the water could not be related to saxitoxin destruction and it appeared that saxitoxin removal occurred more rapidly when ozone was consumed rather than stabilised in solution. The results indicate that the mechanism for toxin removal is probably based on the reaction with a hydroxyl radical species as the oxidant rather than molecular ozone. The results obtained during these experiments indicate that ozone is not an effective oxidant for this class of compound.

A range of ozone doses were applied to two different treated reservoir waters that had been spiked with microcystins LA (mLA) and LR (mLR). At the ozone dose where a residual was first measured in the sample after 5 minutes exposure time, no microcystins were detected by HPLC in either water. The removal of mLA and mLR was identical in all samples. The absence of mLA and mLR by HPLC was supported by a loss of toxicity using a highly sensitive and specific bioassay (PP2A) and by *in vivo* studies in mice. In both waters microcystins were removed with an ozone dose typical of that used in drinking water treatment. The results indicate that conventional ozone treatment was effective in removing hepatotoxicity at microcystin levels greater than those likely to be found in drinking water.

Two waters were sampled from reservoirs in South Australia. One was collected directly from Happy Valley Reservoir (HVRW) and the other from Myponga Reservoir after treatment but before chlorination (MFCW). They were spiked with mLA and mLR and chlorinated to measure toxin removal and chlorine consumption using the

CT concept. In MFCW at pH 7 there was a better removal of both mLA and mLR than in HVRW at pH 8.1. There was also a lesser effect from water temperature upon toxin removal in MFCW. Microcystin LA was less easily removed than mLR at both temperatures in both waters. For HVRW, at the higher pH, this required an initial dose of 7 mg/L of chlorine which corresponded to a CT of around 70 min.mg/L. If the water temperature was reduced to 6°C then under these conditions there would still be 40% of the initial concentration of mLA and mLR present in this water. At this temperature a final chlorine residual of 3.5 mg/L after 30 minutes, requiring a chlorine dose of 8 mg/L and corresponding to a CT of about 95 min.mg/L, was required to reduce microcystin levels below the WHO guidelines. This implies that in colder climates the application of chlorine for microcystin removal may require elevated chlorine doses and CT values. Arrhenius activation energies were calculated for mLA and mLR in both waters, revealing different E_a values for both toxins. Due to the complexity of the reactions and the possible effects of pH in solution, this system was considered too complicated to be described by the Arrhenius equation.

NOM was collected from Myponga Reservoir in South Australia using magnetic ion exchange (MIEX®) resin. The collected NOM was desorbed and separated into fractions of different molecular weight and character using ultrafiltration and mixed resin ion exchange. At approximately 5 mg/L dissolved organic carbon (DOC) the measured apparent second order rate constant (k_{app}) for mLA and mLR removal was fairly similar in both the high molecular weight fraction (designated F3), and the intermediate high molecular weight fraction (designated F2). The low molecular weight fraction (designated EN) had slightly higher k_{app} values as would be expected due to the less reactive nature of the NOM in this fraction. This meant more chlorine was available to react with microcystins in this fraction. Fractions F3 and F2 produced similar k_{app} values to those from the parent water source following treatment, indicating the similar reactivity of these NOM fractions at comparable DOC levels. Increasing the DOC concentration in the F2 fraction increased k_{app} for both mLA and mLR due to the additional chlorine needed to react with the additional NOM present. The results showed that pH, temperature and DOC concentration have a higher impact upon chlorination rates, and the efficiency of toxin removal, than NOM character alone. In general it is assumed that chlorine will be more effective at removing toxins in water with a low SUVA and low specific colour as these indicate less 'reactive' NOM in the water. The results of this study show that toxin removal was more effective in the EN fraction as indicated by the higher k_{app} . This fraction also had the lowest SUVA and lowest specific colour which supports the generally held view in water treatment. Relating the toxin removal to chlorine residual in these reconstituted fractionated NOM samples, indicated that a residual of around 1.5 mg/L after 30 minutes contact was generally adequate to remove all toxins in water with a DOC level of around 5 mg/L. This is consistent with the results obtained in real waters, where at 20°C a chlorine residual of 2 mg/L was found to be sufficient for removal of both mLA and mLR.