

Chlorate in Drinking Water

Defra WT2209

Executive Summary

Chlorate is a disinfection by–product (DBP) that can arise where sodium hypochlorite, calcium hypochlorite, chlorine dioxide or onsite electrolytic chlorination (OSEC) are used for disinfection. Although there is a legal requirement for water companies to minimise DBP formation, there is no current prescribed concentration or value for chlorate in drinking water in the EU, although a future drinking water standard of 0.25 mg / L has been proposed. The chlorate concentration data held by the DWI is limited.

Controls on chlorate in drinking water are in place through national conditions of use for OSEC and chlorine dioxide and purity requirements under the British Standard for sodium hypochlorite. These controls should ensure that the World Health Organisation (WHO) provisional guideline value for chlorate (0.7 mg / L) is not exceeded. A recent joint report of the Food and Agriculture Organisation of the UN and the WHO Expert Committee on Food Additives has proposed an acceptable daily intake of 10 µg / kg body weight (BW) for chlorate due to its acute toxicity. Using standard assumptions, this would correspond to a health-based value of ~ 0.3 mg / L for chlorate, which is below the current WHO provisional guideline of 0.7 mg / L (WHO, 2011). In addition the European Food Safety Authority (EFSA) has recently reviewed whether the default MRL of 0.01 mg / kg that applies to all food and feed commodities is achievable for chlorate at the current time (EFSA Draft Act, 2019). It has concluded that the level corresponding to the 95th percentile of the occurrence data reflecting levels that are realistically achievable when good manufacturing practices are used should be used as a temporary MRL. This may impact the value for drinking water determined by the EU.

A programme of investigation was carried out in England and Wales to determine the chlorate and chlorite concentrations in final waters and the impact of disinfectant storage conditions on their formation. Historic chlorate concentrations from 379 water treatment works (WTW) were obtained from water companies. In addition, 129 WTW were sampled comprising the following types of disinfection: 56 sodium hypochlorite, 43 OSEC, 12 chlorine gas (primary disinfectant) with UV (secondary), 7 chlorine gas, 10 with UV primary treatment with sodium hypochlorite (residual) and one calcium hypochlorite. Of

these, the OSEC and sodium hypochlorite constitute a greater risk of producing waters containing significant chlorate concentrations.

Of the WTW tested the source water for each WTW comprised 55 % groundwater, 36 % surface water and 8 % with mixed inlet sources. The chlorate and chlorite concentrations in final water and stored disinfectant solutions was determined by an accredited laboratory. Chlorite was not found above the detection limit of 1.0 μ g / L in any final water samples.

In this survey, which targeted high risk sites, no samples exceeded the WHO provisional guideline value of 700 μg / L chlorate. However, 23.5 % of final water samples exceeded the proposed value of 250 μg / L. These were at 60 % of the water companies surveyed. In contrast, when a locational average value was used, only 9.3 % final water sample points exceeded this value. The disinfectant types which most frequently exceeded 250 μg / L were OSEC (N = 77) and sodium hypochlorite (N = 65) for the 2018 data. The data collected from water companies from 2012-2017 was also considered in terms of complying with the proposed value of 250 μg / L. Assuming 126, 43 and 166 WTW use chlorine gas, OSEC and sodium hypochlorite disinfection respectively in England and Wales, it is therefore estimated that the national "compliance" to the 250 μg / L is 100 % of samples for chlorine gas, 97.15 % for OSEC and 95.1 % for sodium hypochlorite disinfection. Overall "compliance" is calculated as 96.34 %. Most of the exceedances in 2018 within these disinfectant types was linked to treatment of surface waters and the corresponding higher disinfectant doses which were used at these WTW. Multiple chlorine dosing points (e.g. additional points for manganese or zebra mussel control) contributed to elevated chlorate levels at some WTW.

Chlorate concentrations were higher in summer (June-September) as opposed to winter months (October-February). WTW which were using sodium hypochlorite had greater average chlorate values in summer compared to OSEC WTW, suggesting chlorate production is dependent on concentration of stored solutions and temperature during storage. In sodium hypochlorite solutions, chlorate formation is dependent on the sodium hypochlorite concentration. OSEC hypochlorite solutions are weak (1-2% sodium hypochlorite) and so do not decay significantly to chlorate over short periods of time (about 1 day). There was an association between the long storage residence time of bulk sodium hypochlorite and chlorate formation.

In addition to the WTW sampling, 10 large buildings that use chlorine dioxide for *Legionella* control were sampled. Levels of chlorate in chlorine dioxide treated water ranged from < 2 to 3736 μg / L with a median of 157 μg / L while chlorite levels ranged from < 1 to 597.3 μg / L with a median of < 1 μg / L. Samples were also taken prior to chlorine dioxide disinfection and it was clear that this disinfectant could increase the chlorate and chlorite concentrations significantly. The formation of chlorate and chlorite was site specific and optimisation of the dosing of chlorine dioxide could be used to decrease levels at those sites that had higher levels.

Ultimately, it is suggested that research is required to develop and calibrate kinetic models to determine the chlorate formation potential where new hypochlorite solutions are added to old when tanks are continually "topped up".

The extent of compliance with any chlorate standard will depend on the disinfection type used, the storage time, storage temperature and concentration of hypochlorite solutions used. Utilities in warmer regions and in remote areas with smaller works and those using sodium hypochlorite are most at risk should a low maximum contaminant level be introduced. Those sites which have booster chlorination, or large buildings which contain secondary disinfection using chlorine dioxide, represent an additional risk factor. This is because of the additive effect of chlorate concentrations from the secondary chlorination step. Additional monitoring of secondary disinfection units is recommended.

The implications of this study are that water companies would need to take action if a health based value for chlorate is implemented. In order to demonstrate compliance with national conditions of use companies should be monitoring at all OSEC sites. Additional monitoring to monitor at sites where sodium hypochlorite is used would also be prudent.