Salmon & Trout Conservation

The impact of chlorine and chlorinated compounds in freshwater systems

Literature Review

I. Summary

Many of the concentrations of chlorine and chlorinated compounds lethal to freshwater organisms have been quantified. However, a lack of standardised toxicity testing across earlier scientific literature lessens the confidence that can be had in these values. There is also a wide range of unknowns in terms of sublethal effects and how insufficient knowledge exists regarding the effectiveness of dechlorination processes and the quality of the effluent after treatment.

Determining precisely what is being released from disinfectant effluents is not typically feasible; residual chlorine content of water rapidly changes following sampling and collection. Rising temperatures and the presence of organic matter encourages loss of free and combined chlorine (Environment Agency, 2008). This volatility combined with sporadic sampling effort hinders obtaining an accurate picture of effluent chlorine discharges. Unfortunately, there is no "ideal" method for chlorine analysis that is specific and selective for free chlorine and chloramine species.

Until these insufficiencies are accounted for and knowledge gaps are filled a precautionary approach should be adopted by industries discharging effluents containing chlorine.

II. Introduction

Elemental chlorine (Cl_2) and other chlorine compounds have been used as disinfectants in water purification and wastewater treatment for many years because they are effective, relatively inexpensive, and remain active within systems for a considerable length of time (Lee & Westerhoff, 2009). Although chlorine is too reactive to persist in the aquatic environment for long, large quantities of chlorine constituents being repeatedly released into receiving waters are likely to have a considerable impact on riverine ecosystems (Heath, 1977).

In water at pH values above 5, elemental chlorine reacts rapidly. This reaction results in the formation of hypochlorous acid (HOCl) in equilibrium with hypochlorite ions (OCl-), known as 'free chlorine' (Camargo, 1991). At pH 7 and a temperature of 25°C, 70% of chlorine will be present as HOCl and at pH 8, 80% of chlorine will be present as OCl- (Sorokin *et al*. 2007). Hypochlorous acid is more toxic than the hypochlorite ion; HOCl can penetrate cells and react with cell enzymes. It is this property that makes chlorine particularly toxic to aquatic organisms (Moore, 1951). Therefore, across the pH range typically found in freshwaters (6.5–7.2), chlorine is likely to be present in its most damaging form. Temperature also plays a role in the speciation of chlorine, although it has a less pronounced impact than pH. Aquatic organisms tend to be more sensitive to chlorine at higher temperatures and so added care may be warranted when chlorine is present in heated water discharges (Sorokin *et al*. 2007).

Another major form of chlorine available to aquatic life is monochloramine (NH_2Cl), commonly referred to as 'combined chlorine'. This is the portion of chlorine injected into the water that remains combined with ammonia or nitrogenous compounds after the chlorine demand has been satisfied (Cooke & Schreer, 2001). Farrell *et al*. (2001) discussed the likelihood of chloraminated wastewater is to create a zone of biological damage near discharge pipes. Unfortunately, the biological consequences of releases of inorganic chloramines to the aquatic environment are still not fully understood.

Total residual chlorine (TRC) refers to the sum of the free and combined chlorine concentrations. The relative proportion of free and combined chlorine present following a chlorination dose depends primarily on the concentration of ammonia present in the receiving water to combine with the chlorine (Heath, 1977). The toxicity of chlorine wastes to aquatic life depends not on the amount of chlorine added but on the concentration of residual chlorine remaining and on the relative amounts of free chlorine and chloramines (Brungs, 1973).

Monitoring of chlorine is challenging as it often causes sublethal ecological damage in concentrations too low to be picked up by conventional methods. The iodometric titration method can only be used to detect chlorine concentrations greater than 1 mg/L and does not distinguish between free and combined available chlorine (Environment Agency, 2008). Titrimetric and colourimetric procedures using diethyl-p-phenylenediamine (DPD) are more specific with a higher limit of detection, but take longer amounts of time to complete and are subject to monochloramine interference (Harp, 2002). Some studies have indicated that free chlorine results are subject to 2.6-6.0% interference, depending on temperature and monochloramine concentration (Gordon *et al.* 1988).

Generally, all the accepted methods for chlorine are subject to potential interferences from particles, colour, inorganic and organic compounds, and buffer capacity in the sample. Unfortunately, there is no “ideal” method for chlorine analysis that is specific and selective for free chlorine and chloramine species (Harp, 2002).

III. Impacts on invertebrates

Very little is known about the toxicity of chlorine on aquatic macroinvertebrate communities. There is evidence showing that low levels of chlorinated effluent may adversely affect the survival of some invertebrates (Ward & DeGraeve, 1978), although sublethal effects have been largely neglected. Degradation of freshwater invertebrate communities has effects that are felt throughout the ecosystem; potential food supplies for species higher up the food chain, such as fish, are lost and detrital processing mechanisms become inhibited.

Lethal effects

Mortality

The majority of literature focuses on the acute toxicity of chlorine and chlorinated compounds to crustaceans in the family Daphniidae. Ward & DeGraeve (1978) found that *Daphnia magna* was the most sensitive to residual chlorine toxicity out of a wide range of aquatic organisms tested. TRC concentrations as small as 0.070 mg/L were lethal to three-day-old *D. magna* after exposure for only 10.5 hours. In a 48-hour acute test with *D. magna* less than one day old, the LC_{50} (concentration that produces 50% mortality in the population) was 0.017 mg/L TRC. The toxicity of chloramines to daphnids has also been explored. Farrell *et al.* (2001)

established that the LC_{50} of *Ceriodaphnia dubia* to monochloramine over 24 hours was 0.248 mg/L. For *D. magna*, Wan *et al*. (2000) found that 50% mortality in the population was caused by 0.017 mg/L exposure to inorganic chloramines over 48 hours.

However, despite the availability of LC_{50} values for macroinvertebrate chlorine toxicity, Williams & Gordon (2003) emphasised the discrepancies between older and newer studies. This was attributed to a lack of standardisation in acute toxicity testing. For example, the 48-hour LC_{50} of 6.5 µg/l for *Baetis harrisoni* found in their study is considerably lower than the 48-hour LC_{50} of 357 µg/l for mayfly larvae of the genus *Hexagenia* found by Ward & DeGraeve (1980). The difference between these values seems absurd, but in much of the preceding literature it is unclear what forms of chlorine were being tested. As toxicities of free chlorine and combined chlorine are different, comparisons of LC_{50} may be misleading. This highlights the demand for new standardised toxicity testing on chlorine concentrations lethal to freshwater macroinvertebrates.

Sublethal effects

Community changes

Palmer *et al*. (2003) compared benthic macroinvertebrate community structure between sites exposed to chlorinated and unchlorinated sewage in two rivers. In both rivers invertebrate abundance and number of taxa were substantially reduced (sometimes to zero) immediately downstream of the chlorinated effluent discharge. However, unchlorinated effluent caused very little change in community structure. For example, the mayfly *Baetis harrisoni* was completely absent at sites downstream of chlorinated sewage outflows, yet was present and appeared relatively unaffected by unchlorinated effluent exposure. This suggests that chlorine, rather than the effluent was responsible for its absence.

Gills

Camargo (1991) explored sublethal effects on the caddisfly larvae of *Hydropsyche pellucidula* generated by municipal chlorinated waters. Compared to control animals, 100% of larvae had damaged tracheal gills on their thoracic and abdominal segments. Other studies have also described corrosive injury to tracheal gills caused by residual chlorine (Simpson, 1980) Destruction of tracheal gills may inhibit life cycle completion, as immature animals may not obtain sufficient oxygen for development to adulthood.

Reproduction

Arthur & Eaton (1971) demonstrated sublethal effects of chloramines on the freshwater amphipod *Gammarus pseudolimnaeus*. The most significant effect was on reproduction, with exposed animals showing a reduction in the number of young produced. The authors also identified in the long-term study (15 weeks) that the lowest measured total chloramine concentration the amphipod could be exposed to without any significant effect was <0.0034 mg/L.

IV. Impacts on fish

Lethal effects

Mortality

The lethal concentrations of chlorine to freshwater fish are more widely available than values for invertebrates. Chlorinated effluent was acutely toxic to all species of fish tested by Ward & DeGraeve (1978), with LC_{50} values for fish ranging from 0.045 - 0.278 mg/L TRC. In this experiment salmonids and shiners exhibited the lowest tolerance to chlorine. For rainbow trout, it was found that 0.023 mg/L caused LC_{50} over a 96 hour period (Michigan Department of Natural Resources, 1971). A review by Brungs (1973) on the intermittent exposure of freshwater fish to chlorine recommended that TRC should not exceed 0.2 mg/L for 2 hours per day for the more resistant species of fish or 0.04 mg/L for 2 hours per day for trout and salmon.

A laboratory study by Dickson *et al*. (1977) identified the relationship between frequency of exposure, concentration, duration of exposure, and the expression of lethality in fish. The results showed that total time of exposure to chlorine (product of frequency and duration) was the most important parameter in predicting lethality. Rosenberger (1971) found that free chlorine was the most toxic form of chlorine to coho salmon, through the action of attacking gill tissue. It was observed that larger individuals died faster than smaller ones; this was attributed to larger fish having less gill surface area per unit body. Brooks & Bartos (1984) exposed three freshwater fish species to different forms of chlorine for a variety of different time periods. LC_{50} values indicated that solutions containing hypochlorous acid were the most toxic, closely followed by solutions with dichloramine. Monochloramine and hypochlorite ion solutions had a third to a quarter the toxicity of the previous two. They observed that fish were most tolerant of chlorine during short-term pulse exposures and least tolerant during the continuous exposures. Variation in the sensitivity to chlorine between the fish species also occurred. This work emphasised the importance of not only considering TRC when establishing chlorination regimes and regulations, as substantial differences in toxicity among the different chlorine forms do exist. Additionally, it shows that one size does not fit all when it comes to setting tolerable chlorine discharge levels for fish.

Sublethal effects

Behaviour

In the early 1970's it was proposed that low fish densities below chlorinated municipal outfalls were evidence of fish avoidance behaviour rather than lethality (Zillich, 1972). Where TRC exceeded 0.1 mg/L Tsai (1970) found a reduction in fish density of 50% and where TRC exceeded 0.37 mg/L no fish were present. Osborne *et al*. (1981) found that even where high TRC concentrations occurred, juvenile rainbow trout would move into the chlorinated plume but move out before they were adversely affected. The authors attributed this effect to inability of the fish to detect the boundary of the chlorinated plume or ignorance of the boundary due to other overriding stimuli. Fish exposed to sublethal levels of chlorine also become lethargic and often gulp air (Cooke & Schreer, 2001). In turn, suffering increased predation pressures from birds and other fish. Such disruptions to normal behaviour may inhibit natural foraging and migration processes.

Gills

Similar to invertebrates, chlorine is widely recognised to harm gill tissue in fish. In 1976 the National Research Council in Canada listed corrosive injury of exposed surfaces as one of the acute effects of chlorine to living organisms (Simpson, 1980). Bass & Heath (1977) demonstrated that exposure to sublethal pulses of free chlorine (0.4 and 0.5 mg/L) caused acute hypertrophy and hyperplasia of rainbow trout branchial epithelium, as well as extensive mucus secretion. The same fish also showed reduced arterial PO_2, marked bradycardia, and hyperventilation. Similar symptoms of changes in ventilation and heavy mucus secretion had previously been observed by Dandy (1972) in brook trout *Salvelinus fontinalis* exposed to 0.08 and 0.35 mg/L of chlorine.

V. Removal (Dechlorination)

To avoid the associated environmental consequences caused by chlorine, many industries treat disinfectant effluents through dechlorination. Dechlorination describes processes that reduce the oxidative Cl+ found in HOCl/OCl− and chlorination by-products such as organic and inorganic chloramines to aqueous Cl- (Bedner *et al*. 2004). Although dechlorination of effluents is generally advantageous to the environment, impacts associated with dechlorination processes are not well studied. Sulphur compounds, including sodium thiosulphate ($Na_2S_2O_3$) and sodium bisulphite ($NaHSO_3$), are widely used for dechlorination and can have unintended consequences when released to receiving waters.

Arthur *et al*. (1975) warned that one disadvantage of sulphur-based dechlorination was the need for accurate dose calculation to avoid excess chlorine or the creation of excess sulphite in the receiving waters. Operators can be lulled into overdosing effluents to ensure complete removal of residual chlorine. Ryon *et al.* (2002) highlighted that users of sulphur-based dechlorinators may be unaware of the potential impacts caused by overdosing. Overfeed situations can adversely affect fish in receiving streams through the depression of pH and dissolved oxygen. Bedner *et al.* (2004) also warned that the lengthy time required for effective reduction of organic chloramines by sulphite makes it difficult for treatment plants to meet effluent chlorine targets for freshwater, unless costly tank reactors are provided to increase reaction time. This means due to logistical difficulties effluents may be released prematurely with incomplete removal of chloramines.

For further information please contact Lauren Mattingley (Scientific Assistant for S&TC) at:

lauren@salmon-trout.org

VI. References

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