

Behaviour and regulation of chlorine in waters associated with the AGL Gas Import Jetty Project

Technical Report A - Annexure A

Behaviour and regulation of chlorine in waters associated with the AGL Gas Import Jetty Project

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Executive summary

AGL Wholesale Gas Limited (AGL) is proposing to develop a liquefied natural gas (LNG) import facility at Crib Point in Western Port, Victoria. The facility will receive LNG carriers, store the LNG and re-gasify it as required to meet demand for high pressure pipeline gas. Re-gasification involves the heating of cold LNG via heat exchangers using the ambient heat of seawater from Western Port. Biofouling of the heat exchanger pipes can occur from a range of marine biota and propagules that can attach to the pipes and grow into larger individuals.

The proposed use of chlorine as a biocide in heat exchanger pipes and the subsequent discharge of chlorine-containing seawater to a high conservation value ecosystem requires a range of regulatory considerations, including comparing predicted chlorine concentrations in the discharge with accepted guideline values that protect marine ecosystem values. Unlike most other toxicants, chlorine and the hypochlorite ion synthesised by the electrolysis of seawater are highly reactive, first reacting with natural bromide in seawater to form hypobromite ion that further reacts with organic matter such that, within hours, the original oxidants have chemically reacted and the toxic concentration is significantly reduced. This has consequences for the potential impacts of chlorine and other chlorine produced oxidants (CPOs) as toxicants on aquatic biota.

Regulation of persistent toxicants in seawater is typically based on chronic toxicity data used in a species sensitivity distribution (SSD) to derive a default guideline value (DGV) that is considered to be protective of a given percentage of species. The constant exposure durations for these toxicity tests range from 3 to 7 days. This duration is inappropriate for testing of a toxicant which has significantly decomposed within this period, so to account for effects over shorter durations, short-term GVs are more appropriate. These use acute toxicity data with endpoints based on lethality to 50% of the test species (LC50 values).

Canada derived a short-term GV of 0.5 µg Cl/L by applying an 'application factor' to the lowest toxicity data. In the UK, a short-term predicted no-effect concentration of 0.05 µg/L was derived also using the low reliability assessment factor approach. In Australia and New Zealand, in the absence of sufficient chlorine toxicity data for marine species, a low reliability environmental concern value of 3 µg Cl/L was adopted in 2000.

A review of available toxicity data for chlorine indicated a large database (24 points) of acute toxicity data and very few chronic data. The majority of the tests used flow-through systems to avoid the reduction in chlorine concentration due to its reaction, while a limited number of tests used static exposure conditions, with solution renewal, usually every 24 h. Using all of the acute LC50 data in an SSD, short-term toxicity values of 3.0 and 11 µg Cl/L were derived for 99 and 95% species protection respectively. Because this is based on LC50 data, and the preferred ANZG (2018) approach is to use LC10 data, a factor of 1.5 (experimentally derived) was used to convert these to short-term toxicity values of 2.0 and 7.3 µg Cl/L respectively, based on LC10 values. These are termed very high reliability compared to the lesser reliability of the Canadian and UK GVs.

We recommend that:

- 99 and 95% species protection short-term GVs of 2.0 and 7.3 µg Cl/L apply to CPO concentrations at and beyond the boundary of a mixing zone in situations where the concentration at the boundary of a mixing zone is relatively consistent over time.

- 99% species protection short-term GV of 6.0 Cl/L apply to CPO concentration at and beyond the boundary of a mixing zone where concentration at the boundary of a mixing zone is intermittent or variable over time such as North Arm of Western Port.
- These water quality objectives may not be met within a mixing zone.

Analytical methods for CPOs were reviewed and the two most sensitive were an amperometric and an iodometric method. Both of these will require some effort to reliably detect compliance with the 2 µg/L value.

1 Introduction

AGL Wholesale Gas Limited (AGL) is proposing to develop a liquefied natural gas (LNG) import facility at Crib Point in Western Port, Victoria. The facility will use a Floating Storage and Regasification Unit (FSRU) that will be continuously moored at the existing Crib Point Jetty and will receive LNG carriers of approximately 300 m in length. The FSRU will receive LNG cargos from visiting carriers, store the LNG and re-gasify it as required to meet demand for high pressure pipeline gas. Re-gasification involves the heating of the cold LNG via heat exchangers using the ambient heat of seawater from Western Port. Biofouling of the heat exchanger pipes can occur from the range of marine biota and propagules that can attach to the pipes and grow into larger individuals. Chlorine is an effective biocide that has been used to prevent biofouling (Nguyen et al., 2012; Rajagopal, 2012). It is easily generated by seawater electrolysis and introduced at the intake to the heat exchanger system (Apetroaei et al., 2018). A consequence of this is the potential, after discharge, for residual chlorine to affect the health of the receiving water ecosystem (Khalanski and Jenner, 2012).

AGL has been required to prepare an Environment Effects Statement (EES) under the Victorian Environment Effects Act. This is being managed by AECOM, who have contracted CEE Pty Ltd to assist with marine environmental matters. CEE Pty Ltd has asked CSIRO to provide a technical assessment of the recommended safe guideline values (GVs) for chlorine in the marine environment.

The study was to specifically investigate:

1. The behaviour of chlorine including its likely reactions and transformations as it is generated by electrolysis and as it travels from the intake, as it cools through the heat exchanger to the point of discharge and in the seawater as the discharged water mixes with seawater and disperses;
2. The processes and conservatism in establishing a GV for chlorine in the marine environment;
3. The present status and GV for chlorine (total residual chlorine (TRC) or total residual oxidants (TRO)) in the marine environment that is likely to be suitable for North Arm of Western Port, a Ramsar-listed Wetland of International Importance classified as an “Area of high conservation value” in Schedule 5 of Victoria’s State Environment Protection Policy Waters, 2018. The Policy also classifies the ecosystems of the management segment as “largely unmodified”. Consequently, the Policy requires 99% species protection with respect to environmental indicators and objectives including ANZECC/ARMCANZ (2000) guidelines (ANZG, 2018a).
4. The practicality of monitoring chlorine concentrations in the marine environment and likely detection limits.

2 Behaviour of chlorine in seawater

2.1 Chlorine chemistry

Chlorination remains one of the most effective approaches for the control of biofouling organisms in seawater. It can be undertaken by the addition of sodium hypochlorite (NaOCl) or more usually by electrolysis of seawater. Electrolysis produces chlorine and hydrogen according to the reaction:



Chlorine is soluble in seawater and rapidly hydrolyses to produce hypochlorous acid (HOCl) and its dissociation product, the hypochlorite ion (OCl⁻). At the pH of seawater, HOCl is 80% dissociated to hypochlorite (pK_a = 7.54). The term *free chlorine* refers to Cl₂, HOCl and hypochlorite ion OCl⁻ in equilibrium.



Both chlorine and the hypochlorite ion are powerful oxidants. *Residual chlorine* is the term given to the concentration of chlorine and its reaction product (hypochlorite ion) that remain in solution.

Bromide ion, present in seawater at a high concentration near 65 mg/L, is rapidly oxidised by hypochlorite to form hypobromous acid (pK_a = 8.6) which is only some 20% dissociated to hypobromite ion at the pH of seawater (8.1). This reaction is 99% complete in 10 s (Jenner et al., 1997).



Hypobromous acid is still a good oxidant, although a weaker oxidant than hypochlorite. The antifouling and oxidative capacity of electrolysed seawater is therefore largely due to hypobromite rather than hypochlorite. Total residual chlorine (TRC) in seawater is commonly taken as comprising all chlorine-produced oxidants in seawater and expressed as mg Cl/L (ANZECC/ARMCANZ, 2000). This would include hypobromous acid and would in fact be mostly bromine-based. The use of TRC is more usually used in reference to fresh waters, whereas in marine waters, the equivalent term is chlorine-produced oxidants (CPO).

In waters where ammonia is present at elevated concentrations, the formation of chloramines (and bromamines) is also a possibility:



It was estimated that for these to be significant, ammonia concentrations would need to exceed 10 µg/L for chlorination at 1 mg/L (Sugam and Helz, 1977). Ammonia concentrations in Western Port seawater are typically <10 µg/L, so there is negligible potential for formation of significant quantities of chloramines or bromamines as chlorination reaction products (Chidgey, 2018), and measured concentrations in Western Port seawater are reportedly below this value (Chidgey, 2018).

Because the majority of hypochlorous and hypobromous acids are consumed by reaction with organic compounds, the main products are a diverse range of halogenated organics, in particular trihalomethanes. Jenner et al. (1997) found that bromoform was the major product in a power station seawater cooling water discharge at 16 µg/L for a mean chlorine dosage of 0.5-1.5 mg/L as Cl₂. The high volatility of such compounds means that they are reasonably rapidly lost. The half-life of bromoform varies from 16.9 h at 1 m depth to

85 h at 5 m (Abarnou and Miossec, 1992), considerably longer than the half-life for chloroform of near 30 minutes.

2.2 Rates of reaction

In assessing the ecological impacts of residual chlorine resulting from cooling seawater discharges, the rates at which chlorine and hypochlorite species react initially to form hypobromite species and further with other receiving water constituents such as ammonia or natural dissolved organic matter (DOM), will be critical. Very few studies have examined this in any detail. Zeng et al. (2009) showed that at 15°C, an initial residual chlorine concentration of 2.35 mg Cl/L reduced to around 0.8 mg Cl/L in less than 1 minute. This reduction resulted from the oxidation of bromide to hypobromous acid (Equation 3) which is literally too fast to measure. This is followed by a slower first-order decomposition over 15 minutes to 0.5 mg/L and almost to completion in 30-40 minutes. The higher the water temperature, the faster the reactions and the reduction in chlorine concentration. They noted that in summer, the CPO had fully decayed before discharge, whereas in winter, the CPO decomposition was slower and might be incomplete. In Western Port, seawater temperatures (inlet cooling water) are in the range 11-22°C and the temperature of the discharge water after giving up heat in the heat exchanger, is typically a further 7°C lower than the inlet water (i.e. 4-15°C range). No studies have published useful CPO decay rate data for temperatures lower than 10°C, but the rates of decomposition of CPO appear similar at 10 and 15°C, and likely to be not too dissimilar at 5°C.

At Cribb Point, conservative estimates of the decomposition of CPO can be obtained using water temperatures of 10°C within the heat exchanger and discharge environment. Based on CPO decomposition data and models from the literature (Wang et al., 2008; Saeed et al., 2015), a CPO concentration of 100 µg Cl/L is predicted to decay to 50 µg/L within 2 h (~50%), and 25 µg/L within 24 h (~75%) in a 5-15°C receiving seawater environment. In a 24-h trial of CPO decomposition using Crib Point seawater at 12°C (Chidgey, 2018), an initial CPO concentration of 500 µg Cl/L decayed to approximately 400 µg/L within 0.5 h (~20%), 300 µg/L within 4 h (~40%), and 160 µg/L within 24 h (~68%). For an initial CPO concentration of 1000 µg/L the decay was ~7% in 0.5 h, ~19% within 4 h, and ~42% within 24 h, potentially indicating faster CPO decay at lower concentrations. The Cribb Point test results indicate a slower CPO decomposition rate over the first several hours, but, over 24 h, is similar to that of the literature models.

The CPO decomposition is slower at salinities lower than 35‰. The rate of reaction with DOM is slower than the reaction with bromide and increases with increasing DOM concentrations (Wang et al., 2008). Similar findings were obtained by Saeed et al. (2015).

The above findings are relevant to how the toxicity testing data might be interpreted and applied in order to protect the receiving environment. In tests using continuous flow hypochlorite addition, reaction with bromide would be presumed to have occurred (available bromide reacts rapidly), whereas in static tests, depending on the duration, further oxidative reactions might have progressed (slower reactions with DOM). Applying toxicity data derived in this way will need to take into account the time of exposure required to elicit either acute or chronic toxicity to determine the nature of the impact, if any.

3 Toxicity of chlorine and its reaction products

3.1 Toxicity testing

Because the half-lives of chlorine and its toxic reaction products are short in marine waters, it is usual for toxicity tests to be flow-through, resulting in continuous renewal of the test water and maintenance of a near-constant chlorine exposure to the test organisms. Concentrations of chlorine-produced oxidants (CPOs) must be measured frequently to demonstrate that substantial reduction in concentration is not occurring. The analytical method must measure all CPOs and not only one or more of the components.

Table 1 is a composite of the available toxicity data from Chariton and Stauber (2008), CCME (1999), USEPA (1985) and more recent literature data that have been quality assessed to meet the latest ANZG (2018) criteria as documented by Warne et al. (2018). Application of the revised quality assessment method led to the elimination of many data in estuarine waters where the salinity was below the 25‰ criterion.

As expected, the majority of the tests used flow-through systems containing continually added hypochlorite in seawater, rather than static tests where the test hypochlorite-containing seawater was replaced regularly (usually daily). The latter resulted in the test organisms being exposed to fluctuating concentrations. In static laboratory tests, it was usual to renew the test solutions regularly (usually every 24 h), but as a consequence, the exposure was to rapidly decaying hypochlorite concentrations. Not surprisingly the LC50 values (50% lethal effect concentration) from such tests were generally higher than those for flow-through tests. For example, a 0.5 h flow-through test with the rotifer *Brachionus plicatilis* had an LC50 of 90 µg Cl/L (Capuzzo et al., 1976) compared to a 24-h static test LC50 of 586 µg Cl/L (Lopez-Galindo et al., 2010). The flow-through test value only was used in the species sensitivity distribution (SSD) used to derive a guideline value (GV).

Nearly all of the reported bioassays were classified as acute tests, where a lethal or adverse sub-lethal effect occurs after exposure to a chemical for a short period relative to the organism's life span (acute test durations are organism specific as defined by Warne et al. (2019)). Chronic tests by comparison are ones where a lethal or adverse sub-lethal effect occurs after exposure to a chemical for a period of time that is a substantial portion of the organism's life span or an adverse effect on a sensitive early life stage. The only chronic data reported were for 72-h algal bioassays which by definition are considered as chronic tests (Warne et al., 2018), and for one 8-day fish test (Alderson, 1970).

The most sensitive species were sea urchins, with impacts on fertilisation being seen at near 6 µg Cl/L as CPO. Sperm were pre-exposed to the hypochlorite in seawater for 15 min with no effect on viability, while a time from 1 to 60 min of pre-exposure of eggs before adding sperm did not affect the result, for the sand dollar, *Dendraster excentricus*. LC50 values for 15-min sperm plus egg exposures following a 1, 1, 1, 5, 6, and 60 min pre-exposure, were 2, 10, 13, 7, 6 and 8 µg/L respectively, so the geometric mean of the three 1 min pre-exposures, 6.4 µg Cl/L, was used. For the sea urchin, *Strongylocentrotus droebachiensis*, an experiment where the hypochlorite and seawater were pre-mixed for 24 or 48 h before exposure did not affect the toxicity to sperm fertilisation, suggesting that reaction products other than CPOs were causing toxicity. As the exposure time of sperm and eggs was only 15 min in these fertilisation experiments, the tests are classified as acute (Warne et al., 2018); chronic tests with this species require ≥1 h exposure (Dinnel et al., 1981).

The next most sensitive species were fish, with plaice (*Pleuronectes platessa*) having an LC50 of 24 µg/L (Alderson, 1970), although data for water of salinity <25‰ indicate LC50 values as low as 5 µg CPO/L for copepods and oyster and clam larvae (Bellanca and Bailey, 1977).

There were results for only two algal species, *Isochrysis galbana* and *Dunaliella salina* (Lopez-Galindo et al., 2010), and these were not particularly sensitive, with chronic EC10 values for two species of 119 and 381 µg Cl/L respectively. These were, however, based on 96-h static exposures, and that might explain the lower sensitivity. Their respective EC50 values of 2910 and 1730 µg Cl/L were the highest of any tests reported (Table 1).

There have been few studies that have examined the toxicity of reaction products. The oxidation products from bromine were found to be less toxic than those from chlorine (Dinnel et al., 1981), while the toxicity of chloroform and bromoform produced by reactions with organics has been described as 'moderate to high', although a recent review showed that, at least for chloroform, effects on algae and fish are typically seen at mg/L concentrations, orders of magnitude above those for hypochlorite toxicity (UK Marine SAC, 2019).

Table 1. Toxicity data for CPOs in seawater with salinity $\geq 25\text{‰}$

| Species | Life stage | Exposure duration (h) | Acute / Chronic | Test type | Toxicity measure | Test medium | Temp (°C) | Conc. ($\mu\text{g/L}$) | Reference | Comments |
|---|--------------------|-----------------------|-----------------|--------------|----------------------|--------------------|-----------|--|--|--|
| Algae (Chronic) | | | | | | | | | | |
| Alga (<i>Isochrysis galbana</i>) | | 96 | Chronic | Static | Growth (EC10) | Synthetic seawater | 20 | 119 | Lopez-Galindo et al. (2010) | CPO every 30 min. IC50 2910 $\mu\text{g/L}$ |
| Alga (<i>Dunaliella salina</i>) | | 96 | Chronic | Static | Growth (EC10) | Synthetic seawater | 20 | 381 | Lopez-Galindo et al. (2010) | Daily biomass measurements. IC50 1730 $\mu\text{g/L}$ |
| Invertebrates (Acute) | | | | | | | | | | |
| American oyster (<i>Crassostrea virginica</i>) | Larvae | 0.5 | Acute | Flow through | Mortality (LC50) | Seawater | 25 | 80 | Capuzzo, 1979 | Acceptable quality |
| Copepod (<i>Acartia tonsa</i>) | | 0.5 | Acute | Flow through | Mortality (LC50) | Seawater | 20 | 820 | Capuzzo, 1979 | Acceptable quality |
| Rotifer (<i>Brachionus plicatilis</i>) | | 0.5 | Acute | Flow through | Mortality (LC50) | Seawater | 25 | 90 | Capuzzo, 1979 | Acceptable quality |
| Rotifer (<i>Brachionus plicatilis</i>) | 0.5 h old | 24 | Acute | Static | Mortality (LC50) | Synthetic seawater | 20 | 586 (LC50), 438 (LC10) | Lopez-Galindo et al., 2010 | Measured in 0.3 mL well plates |
| Amphipod (<i>Hyale barbicornis</i>) | Juveniles | 96 | Acute | 24-h renewal | Mortality (LC50) | Seawater | 20 | 2200 | Anasco et al., 2008 | Conc decayed rapidly Nominal for 24-h, measured for others |
| Amphipod (<i>Hyale barbicornis</i>) | Juveniles | 96 | Acute | 24-h renewal | Body length (EC50) | Seawater | 20 | 1100 | Anasco et al., 2008 | Conc decayed rapidly Nominal for 24-h, measured for others |
| Coon stripe shrimp (<i>Pandalus danae</i>) | Juvenile and adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater | 15 | 178 | Gibson et al., 1975 and Thatcher, 1978 | Acceptable quality |
| Sea urchin (<i>Strongylocentrotus droebachiensis</i>) | Sperm | 15 min | Acute | Static | Fertilisation (EC50) | Seawater | 14 | <5, <6 | Dinnel et al., 1981 | Sperm exposed for 15 mins, eggs exposed pre-test for 24 or 48 h. |
| Sand dollar (<i>Dendraster excentricus</i>) | Sperm | 15 min | Acute | Static | Fertilisation (EC50) | Seawater | 14 | 6.4 (geomean of 3 shortest pre-exposure times) | Dinnel et al., 1981 | Sperm exposed 15 min before adding to eggs. Pre-exposure of eggs for 1-60 min did not affect toxicity. |

Table 1. Toxicity data for CPOs in seawater with salinity $\geq 25\%$ (continued)

| Species | Life stage | Exposure duration (h) | Acute / Chronic | Test type | Toxicity measure | Test medium | Temp (°C) | Conc. ($\mu\text{g Cl/L}$ as CPO) | Reference | Comments |
|---|--------------------|-----------------------|-----------------|--------------|------------------|----------------|-----------|------------------------------------|----------------------|---|
| Lobster (<i>Homarus americanus</i>) | Larvae | 1 | Acute | Flow through | Mortality (LC50) | Seawater | na | 2890 | Capuzzo et al., 1976 | Seawater and toxicant mixed for 14 h before larvae addition. Flow through system. After 60 min exposure LC50 was 16300 based on applied conc and 2890 $\mu\text{g Cl/L}$ (calculated from a decay equation) based on the residual. Used ACR of 4.5 for crustaceans. |
| Mysid (<i>Neomysis</i> sp) | Adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 162 | Thatcher, 1978 | Acceptable quality |
| Amphipod (<i>Pontogeneia</i> sp) | Adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 687 | Thatcher, 1978 | Acceptable quality |
| Amphipod (<i>Anonyx</i> sp) | Adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 145 | Thatcher, 1978 | Acceptable quality |
| Shrimp (<i>Pandalus goniurus</i>) | Adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 90 | Thatcher, 1978 | Acceptable quality |
| Shrimp (<i>Crangon nigricauda</i>) | Adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 134 | Thatcher, 1978 | Acceptable quality |
| Shore crab (<i>Hemigrapsus nudus</i> and <i>H. oregonensis</i>) | Juvenile and adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 1418 | Thatcher, 1978 | Acceptable quality |

Fish (Acute)

| | | | | | | | | | | |
|---|--------|----|-------|--------------|------------------|-------------------|----|-----|----------------------|---|
| Tidewater silverside juvenile (<i>Menidia peninsulae</i>) | Fry | 96 | Acute | Flow through | Mortality (LC50) | Seawater (22-27‰) | 25 | 54 | Goodman et al., 1983 | Acceptable quality |
| Fish (<i>Oryzias javanicus</i>) | Larvae | 96 | Acute | 24-h renewal | Mortality (LC50) | Seawater | 26 | 190 | Anasco et al., 2008 | Conc decayed rapidly. Nominal for 24-h, measured for others |
| Fish (<i>Oryzias javanicus</i>) | Larvae | 24 | Acute | 24-h renewal | Mortality (LC50) | Seawater | 26 | 320 | Anasco et al., 2008 | Fish died immediately after exposure. To 50 $\mu\text{g Cl/L}$ based on averages of measured initial concentration. |

Table 1. Toxicity data for CPOs in seawater with salinity $\geq 25\%$ (continued)

| Species | Life stage | Exposure duration (h) | Acute / Chronic | Test type | Toxicity measure | Test medium | Temp (°C) | Conc. ($\mu\text{g/L}$) | Reference | Comments |
|--|--------------------|-----------------------|-----------------|--------------|------------------|----------------|-----------|---------------------------|-----------------------|--------------------|
| Plaice (<i>Pleuronectes platessa</i>) | Larvae | 96 | Acute | Flow through | Mortality (LC50) | Seawater | 8 | 24 | Alderson et al., 1970 | Low temperature |
| Coho salmon (<i>Oncorhynchus kisutch</i>) | Juvenile | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 32 | Thatcher, 1978 | Acceptable quality |
| Pacific herring (<i>Clupea harengus pallasii</i>) | Juvenile | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 65 | Thatcher, 1978 | Acceptable quality |
| Threespine stickleback (<i>Gasterosteus aculeatus</i>) | Juvenile and adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 167 | Thatcher, 1978 | Acceptable quality |
| Shiner perch (<i>Cymatogaster aggregata</i>) | Juvenile and adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 71 | Thatcher, 1978 | Acceptable quality |
| Pacific sand lance (<i>Ammodytes hexapterus</i>) | Juvenile and adult | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 82 | Thatcher, 1978 | Acceptable quality |
| English sole (<i>Parophrys vetulus</i>) | Juvenile | 96 | Acute | Flow through | Mortality (LC50) | Seawater (28‰) | 15 | 73 | Thatcher, 1978 | Acceptable quality |
| Fish (Chronic) | | | | | | | | | | |
| Plaice (<i>Pleuronectes platessa</i>) | Eggs | 8 days | Chronic | Flow through | Mortality (LC50) | Seawater | 8 | 120 | Alderson, 1970 | Low temperature |

3.2 Water quality guideline values for chlorine in marine waters

The derivation of guideline values (GVs) for chlorine and its reaction products has been dealt with by a number of jurisdictions (USEPA, 1985; CCME, 1999; ANZECC/ARMCANZ, 2000; Sorokin et al., 2007). The USEPA (1985) recommended that, “except possibly where a locally important species is very sensitive, saltwater aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration of chlorine-produced oxidants does not exceed 7.5 µg/L more than once every three years on the average and if the one-hour average concentration does not exceed 13 µg/L more than once every three years on the average”.

Environment Canada (CCME, 1999) noted that the four most sensitive species endpoints in their database were reduced egg fertilisation successes for sand dollars and green sea urchins at 2 and 5 µg Cl/L as CPO, respectively (Dinnel et al., 1981), the 48-h LC50 for the eastern oyster larvae of 5 µg/L and the 48-h EC50 for hard clam larvae of 6 µg/L (Roberts et al., 1975), were not considered acceptable due to reservations with respect to the analytical methodologies and testing protocols. Their default acute GV, termed a short-term GV, was derived by applying an ‘application factor’ of 0.05 to the 10 µg/L LC50 for the next most sensitive species, blue crabs (Patrick and McLean 1971), American oysters (Capuzzo, 1979), the rotifer *Brachionus plicatilis* (Capuzzo, 1976), and phytoplankton (Eppley et al., 1976), giving a value of 0.5 µg/L.

A risk assessment report for the UK Environment Agency (Sorokin et al., 2007) identified the lowest reliable short-term toxicity data point as a 24-h LC50 of 5 µg Cl/L as free available chlorine for a freshwater species, the crustacean *Ceriodaphnia dubia*. A standard assessment factor of 100 was applied resulting in a predicted no-effect concentration (PNEC) in saltwater of 0.05 µg Cl/L. This was recommended as a replacement for the existing environment quality standard (EQS) as part of the European Water Framework Directive. The existing EQS (Lewis et al., 1994) was based on an assessment factor of ~2 applied to an acute LC50 value of 28 µg/L for both plaice and sole for total residual oxidants (TRO). This resulted in an EQS of 10 µg/L, substantially higher than the proposed PNEC in saltwater.

In Australia and New Zealand, the absence of sufficient toxicity data for marine species, led to the adoption in 2000 of a moderate reliability freshwater chronic GV of 3 µg Cl/L as a low reliability environmental concern value for marine waters (ANZECC/ARMCANZ, 2000). It was noted that although the chlorine figure for 95% species protection was relatively close to the acute toxicity value for the most sensitive species, this was considered sufficiently protective, due to its decomposition rate in seawater, the narrow difference between acute and chronic toxicity and the lesser sensitivity of other data for this species (ANZECC/ARMCANZ, 2000).

A revision of the marine chlorine default GV (DGV) for Australia and New Zealand was identified as a priority as part of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018).

3.3 Process for developing an Australian marine chlorine default GV (DGV) for chlorine

An initial draft DGV for chlorine for the ANZG was prepared under contract in 2016. The resulting draft technical report and unpublished chronic DGV for 95% species protection was 0.9 µg/L (the 99% protection value was 0.03 µg C/L). Closer scrutiny of the draft report by independent specialist reviewers, showed that many of the data used in the 2016 analysis did not meet the acceptance criteria as discussed below. It was concluded that a more comprehensive analysis was required using the most recent data acceptance criteria and procedures (Warne et al., 2018; Batley et al., 2018).

The most recently accepted method for deriving GVs for toxicants in water provides the following advice on the use of short-term (acute) toxicity data in deriving GVs for particular chemicals where there are sound test data that show that effects over short times are environmentally relevant: “Such tests usually (but not necessarily) measure lethality and might be appropriate in cases of a spill event, or pulse exposures as can occur with pesticides in rivers, or where contaminants are short-lived and non-persistent due to dispersion, volatilisation or degradation. The minimum exposure period is generally 96 h, but there might be circumstances where a lesser exposure time is relevant. The types of tests considered to measure acute responses are detailed in Table 1” (Batley et al., 2018).

“If a short-term GV is required for a site-specific application, it can be derived using a species sensitivity distribution (SSD) applied to acute toxicity data. The preferred data order is: acute NEC, EC/IC/LC10, BEC10, EC/IC/LC15-20, and lastly NOEC data. However, if there are insufficient of those data then acute LC50/IC50/EC50, LOEC and MATC values should be divided by 5, 2.5 and 2, respectively, and used to estimate acute EC/IC/LC10 or NOEC values. If short-term GVs are to be used for non-guideline purposes such as setting licence conditions or in prosecutions, then the data preferences may change to reflect the purpose of the GV. No acute to chronic ratio (ACR) or default assessment factors (AFs) are applied to the acute data to derive short-term GVs, except for those used to convert the acute data to EC/IC/LC10 data. Apart from the use of acute toxicity data, the derivation process should follow the GV derivation method described in Warne et al. (2018)” (Batley et al., 2018).

On the basis of the above, it was clear that the behaviour of chlorine in seawater justified the derivation of a short-term GV. For this purpose, the Chariton and Stauber (2008) data were first re-evaluated using the latest Australian and New Zealand method for GV derivation (Warne et al., 2018). They had used 32 acute marine invertebrate and fish data in an SSD, and with the original Burrlioz 1.0 software derived an acute GV of 13 µg/L for 95% species protection and 5.6 µg/L for 99% species protection. Using an acute to chronic ratio of 2.4 (the geometric mean of the ACRs of 3.71 and 1.5 found by Fisher et al. (1999)), gave chronic GVs of 2.3 and 5.4 µg/L, respectively, for 99 and 95% species protection.

The 2018 screening procedure eliminated some 23 data points from the Chariton and Stauber list, the majority on the basis that the salinity was below 25‰, including the studies of Roberts et al. (1975) and Patrick and McLean (1971) that were used by Canada, as discussed above. The data were supplemented with other more recent literature data and the data referred to in the USEPA, Canadian and UK guidance. The final database was selected from Table 1. Only acute toxicity data from this table, from both flow-through and static tests were used to derive GVs using a species sensitivity distribution (SSD) according to the revised derivation method (Warne et al., 2018). The resulting SSD is shown in Figure 1. This first derivation of short-term toxicity values gave 3, 11 and 20 µg Cl/L respectively for 99, 95 and 90% species protection in Column 2, Table 2.

Table 2. Summary of short-term toxicity values derived from different data combinations

| Level of protection (% species) | All acute LC50 data (flow-through and static) | All acute LC50 data plus algal EC50s | Flow-through acute LC50 data only | All flow-through LC50 data plus only 15 min static LC50 data | All acute LC50 data converted to LC10s RECOMMENDED DGV |
|---------------------------------|---|--------------------------------------|-----------------------------------|--|--|
| µg Cl/L as CPO | | | | | |
| 99 | 3.0 | 3.2 | 19 | 2.2 | 2.0 |
| 95 | 11 | 12 | 31 | 8.5 | 7.3 |
| 90 | 20 | 21 | 41 | 16 | 13 |
| Reliability | Very high | | | | |

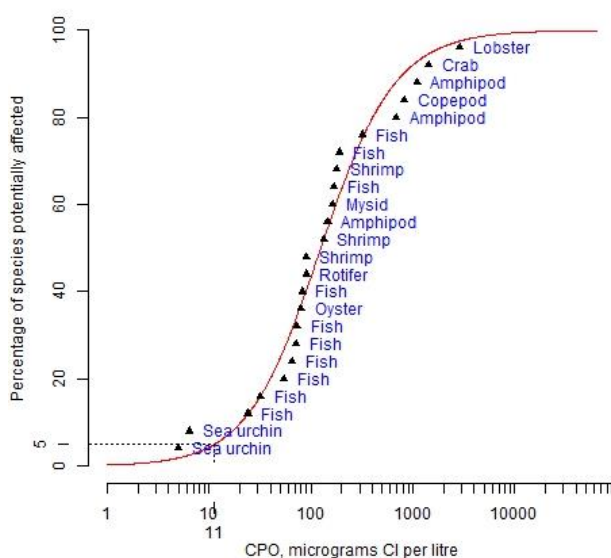


Figure 1. Species sensitivity distribution of all acute toxicity test data (flow-through plus static) from Table 1

Note that there were no data for toxicity to algae in this derivation. The European Chemicals Bureau (2002) recommend using the 72-h (or longer) algal EC50 values as equivalent to a short-term result, with the EC10 being the long-term result. Using these EC50 values from static tests that were very insensitive, the second derivation of protection levels were only marginally altered to 3.2, 12 and 21 µg Cl/L respectively (Column 5, Table 2).

Because of the high reactivity of chlorine, and with the lifetime of the reaction products being of the order of several hours at most, it would be appropriate for management purposes to apply guidelines that are

protective against short-term effects. Any toxicity tests that use flow-through systems in an attempt to prolong the exposure period will result in greater effects than tests undertaken with exposure conditions that mimic the field situation, and so the GV derived using such data will be overly conservative. For static tests, it is the renewal frequency in the context of reaction rate that is important, hence 1-15 min static exposures cannot be treated as analogous to 24+ h static tests. If all data from non-flow-through tests were omitted, the values for 99 and 95% species protection increased to 19 and 31 $\mu\text{g Cl/L}$ respectively for this third derivation (Column 3, Table 3), largely due to the removal of the most sensitive endpoints, which were static tests, although the minimum reaction time was only 15 min before each test plus 1-10 mins during fertilisation, which is a lot shorter than the other static tests. Leaving these data in gave the fourth derivation of 2.2 and 8.5 $\mu\text{g Cl/L}$ respectively (Column 4, Table 3) (see Figure 2).

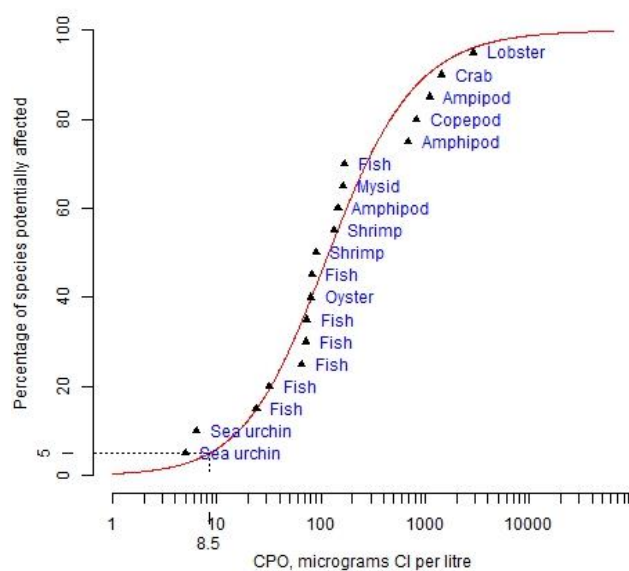


Figure 2. Species sensitivity distribution of all flow-through LC50 data plus only 15-min static toxicity test data from Table 1

It could be argued that chronic tests that last longer than 6 h to show an effect, should not be included in the derivation, assuming that the products of the reactions are less toxic than the starting materials. That this is the case for chloroform and bromoform has been shown by Stewart et al. (1979). LC50 values for larval survival for the oyster, *Crassostrea virginica*, estimated from the published dose-response curves, of 2, 1 and 0.1 mg/L respectively for chloroform, bromoform and bromate. They noted that chloroform and bromoform are both lost from solution by volatilisation. Not considered was the toxicity of chloramine and bromamine products only formed where ammonia concentrations are elevated in the seawater.

From a regulatory context, the application of a short-term GV makes sense, however, not necessarily one based on effects to 50% of the test population, i.e. LC50 values, but rather one based on a 10% effect, i.e. LC10, as we apply to chronic tests that use EC10 values. In some instances, however, regulations have stipulated an acute LC50/EC50-based GV not to be exceeded in mixing zones.

Unfortunately, very few papers either report LC10 values or publish dose-response curves from which the values could be estimated. For example, Lopez-Galindo et al. (2011) reported an LC50/LC10 ratio of 1.33 for NaOCl toxicity to *Brachionus plicatilis* and ratios in excess of 5 for the algae *Isochrysis galana* and *Dunaliella salina*. The normally accepted default ratio would be 5 (Warne et al., 2018), but based on the lower

observed value above, a value of 1.5 is suggested. On this basis, the recommended values for 99 and 95% species protection would be 2.0 and 7.3 $\mu\text{g Cl/L}$ (Column 6, Table 3) obtained by dividing the values in Column 2 of Table 2 by 1.5. The values are additionally conservative because the concentrations are decaying in the field whereas they were not in the flow-through laboratory tests. Note that this value has yet to be proposed and adopted as an official GV.

Northwestern and eastern Western Port is a Ramsar listed Wetland of International Significance, hence, the Waters State Environment Protection Policy Legal lists the Ramsar part of Western Port, which includes the Crib Point in North Arm, as an area of high conservation value with 99% species protection. It might be argued that areas within Port limits and in the planning regulations as a Port Zone around Crib Point jetty could be altered to requiring only 95% species protection. Noting, however, that since two apparently sensitive northern Pacific Ocean sea urchin species used in the SSD would not be protected by the 95% protection value (Figure 1), it would be additionally appropriate to recommend the 99% protection value.

4 Application of chlorine GVs to marine mixing zones

The regulation of contaminants being released to a water body from a point source requires consideration of a mixing zone. This is discussed in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG, 2018) (<http://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/mixing-zones>):

“We can define a mixing zone as an explicitly defined area around an effluent discharge where some, or all, water quality objectives may not be met.

Under some circumstances, it is an accepted practice to apply the concept of a mixing zone. As a consequence, some community values of the water body may not be protected.

The size of a mixing zone — and the environmental conditions within it — are important concerns, particularly because degraded areas around effluent discharges compromise community values.

How to apply a mixing zone

If mixing zones are to be applied, then they should be as small as practicable. Water quality management should ensure that the agreed and designated community values and management goals of the broader waterway outside the mixing zone are not compromised.

If a mixing zone is applied to a river or estuarine waterway, then it is essential to ensure it does not extend across the entire width of the waterway and impact on biota migration pathways.

Mixing zones are regulated at the state or territory level in Australia and the regional council level in New Zealand. You should seek specific guidance on mixing zones from your relevant local jurisdiction.”

In the case of the discharge of seawater containing chlorine-produced oxidants (CPOs), the species protection GV would apply at and beyond the boundary of a mixing zone.

The above discussion shows that the recommended GVs for 99 and 95% species protection for chlorine in the marine environment is 2.0 µg Cl/L and 7.3 µg Cl/L, respectively. These values were derived from experiments designed to maintain constant concentration over the period of exposure of the test biota. Hence, the derived GVs would apply where CPO concentration was relatively constant at the boundary of a mixing zone at some point along the dispersion pathway. However, dispersal of discharges to the marine environment are seldom consistently in a single direction and therefore concentration of a released constituent at a particular distance and direction from the release point will vary over time. Reversals in tidal currents every 6 h will result in variable ‘exposure’ to fixed benthic species close to the discharge, while planktonic species will have short exposure as they may be carried into the area affected and carried out as the chlorine concentration reduces by dilution and chemical reaction. This creates a complex exposure scenario, which is usual for the marine environment and fits the above discussion of pulses. The present approach has been to estimate a ‘worst case scenario’, which is the area over which the chlorine concentration calculated by dilution alone exceeds the GV at any time. This is a very conservative starting point and applies lines of logic (chemical decomposition, variable exposure, etc) to provide a more realistic estimate of the area of effect. In other cases, it has been suggested that the regulatory mixing zones for toxicity, nutrient effect, suspended solids or organic general enrichment be set at the worst-case boundary and be monitored to refine the dimensions over periods of licence review.

In considering the fact that this CPOs chemically decompose, our recent work (Angel et al., 2015) (and that of others) on pulsed exposures indicates that, while there might be an impact from the initial exposure, the use of a time-averaged concentration over the exposure period better reflects the exposure concentration. On that basis, a time-averaged concentration could be estimated from some of the published reaction rate data to estimate exposure in a tidal situation and compared to the time-averaged exposure concentration in a flow-through test, over the time interval for the dispersion and decay post discharge. Using this ratio, the GV could be accordingly increased. In a strongly tidal situation like North Arm of Western Port, this might add a factor of 2 to 3 to the recommended GV, making a value of near 6 µg Cl/L for 99% species protection more reasonable for assessing potential impacts in situations of intermittent exposure in situations of strong tidal reversals in dispersion.

4.1 GVs for marine mixing zone boundaries

From the above discussion it is apparent that the recommended values for 99 and 95% species protection of 2.0 and 7.3 µg Cl/L as short-term GVs would apply to CPO concentration at the boundary of a mixing zone where concentration was relatively consistent over time. We recommend that time-averaged or time-averaged GVs apply at the boundary of a mixing zone in areas affected by tidal reversals, where concentration varies between a maximum and near background over periods of minutes to hours. This would add a factor of 2 to 3 to the recommended GV exposure in such situations.

Hence, we recommend:

- 99 and 95% species protection short-term GVs of 2.0 and 7.3 µg Cl/L apply to CPO concentration at and beyond the boundary of a mixing zone where concentration is relatively consistent over time.
- 99% species protection short-term GVs of 6.0 Cl/L apply to CPO concentration at and beyond the boundary of a mixing zone where concentration is intermittent or variable over time such as North Arm of Western Port.
- These water quality objectives may not be met within a mixing zone

The 99 and 95% species protection short-term GVs of 2.0 and 7.3 µg Cl/L will be proposed for inclusion in the Australia New Zealand Water Quality Guidelines (ANZG, 2018) for situations of constant exposure with a recommendation that time-averaged concentrations measured at and beyond the mixing zone boundary be used in situations of variable exposure to assess GV compliance.

5 Monitoring of chlorine

A number of methods are available for the analysis of CPO (or TRC) in seawater as shown in Table 3, however, few have detection limits suitable for assessing compliance with a 2 to 6 µg/L GV. Three methods come close to these limits: (i) using amperometric titration, (ii) using an ion selective electrode to detect iodide, and (iii) an iodine colorimetric method.

Table 3. Analytical methods for chlorine produced oxidants

| Analytical method | Detection limit (µg Cl/L as CPO) | Reference |
|--|----------------------------------|---|
| Iodometric 4500-Cl B and 4500-Cl C | 100 | APHA, 2017; |
| Amperometric titration 4500-Cl D | 15 | APHA, 2017; Fisher et al., 1999; |
| Low-level amperometric titration 4500-Cl E | 1 | APHA, 2017; Dinnel et al., 1981 |
| DPD ^a ferrous titrimetric 4500-Cl F | 18 | APHA, 2017 |
| DPD colorimetric 4500-Cl G | 10 | APHA, 2017; Lopez-Galindo et al., 2010; Anasco et al., 2008 |
| Syringaldazine (FACTS) 4500-Cl H | 100 | APHA, 2017 |
| Iodine colorimetric method | 4 | Wang et al., 2008; Sugita et al., 1992 |
| Iodometric electrode 4500-Cl I | 1 | APHA, 2017, Jenkins and Baird, 1979; Rigdon et al., 1978; Dimmock and Midgely, 1982 |

^a DPD = N, N-diethyl-p-phenylenediamine

Dinnel et al. (1981) used a commercial amperometric titrator and the amperometric detection iodometric method to achieve a lower limit of detection in sewage of 50 µg Cl/L mg/L as CPO, however, using a dual platinum electrode amperometric titrator (Andrew and Glass, 1974) with addition of the titrant with a microburette, enabled detection of 1µg/L.

The iodometric electrode method described in APHA (2017) appears to offer the best detection limits. Dimmock and Midgely (1982) investigated the use of an Orion Residual Chlorine electrode for chlorine oxidants in cooling waters. This electrode consists of an iodide electrode and a platinum electrode mounted together. Iodide is added to the test solutions which reacts with the chlorine oxidants to form iodine. The electrode senses the difference in iodide concentrations, so for low CPO concentrations it will be important to use low concentrations of added potassium iodide. Reaction is fastest at pH 4, so the seawater pH first needs to be adjusted by the addition of acetate.

Wang et al. (2008) used an iodine colorimetric method, where potassium iodide is added to the test where it reacts with oxidants to form the triiodide ion, which can be determined spectrophotometrically at 352 nm. Unlike the DPD colorimetric method, which needs to be undertaken rapidly, with the iodine method, samples can be spiked with iodine reagent in the field (or laboratory) and safely analysed at a later time (Wang et al., 2008). The method is detailed in a paper by Sugita et al. (1992). The detection limit is, however, only 4 µg Cl/L.

This iodometric electrode method appears to be one of the best, however, for all three methods, detecting compliance against GVs will be pushing the method to its lower limits. Considerable effort will be required to master whatever method is applied and to get it to perform at low $\mu\text{g/L}$ concentrations.

6 Conclusions

The use of chlorine as a biocide in heat exchanger pipes and the subsequent discharge of chlorine-containing seawater to a high conservation value ecosystem presents a range of regulatory considerations. Unlike most other toxicants, chlorine and the hypochlorite ion formed in seawater are highly reactive, first reacting with natural bromide in seawater to form hypobromite ion that further reacts with organic matter such that, within hours, the original concentration is significantly reduced. This has consequences for the potential impacts of chlorine and other chlorine produced oxidants (CPOs) on aquatic biota.

Regulation of persistent toxicants in seawater uses chronic toxicity data in an SSD to derive a DGV that is protective of a given percentage of species. The exposure durations for these toxicity tests range from 3 to 7 days. This duration is inappropriate for testing of a toxicant where the concentration has significantly decayed within this period, so to account for effects over shorter durations, short-term GVs are more appropriate.

We recommend that:

- 99 and 95% species protection short-term GVs of 2.0 and 7.3 $\mu\text{g Cl/L}$ apply to CPO concentrations at and beyond the boundary of a mixing zone in situations where the concentration at the boundary of a mixing zone is relatively consistent over time.
- 99% species protection short-term GV of 6.0 Cl/L apply to CPO concentration at and beyond the boundary of a mixing zone where concentration at the boundary of a mixing zone is intermittent or variable over time such as North Arm of Western Port.
- These water quality objectives may not be met within a mixing zone.
- The 99 and 95% species protection short-term GVs of 2.0 and 7.3 $\mu\text{g Cl/L}$ will be proposed for inclusion in the Australia New Zealand Water Quality Guidelines (ANZG, 2018a) for situations of constant exposure with a recommendation that time-averaged concentrations measured at and beyond the mixing zone boundary be used in situations of variable exposure to assess GV compliance.

Analytical detection at this concentration will require either an amperometric or an iodometric method whose detection limits have been reported as 1 $\mu\text{g Cl/L}$.

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