GAS IMPORT JETTY AND PIPELINE PROJECT
ENVIRONMENT EFFECTS STATEMENT
INQUIRY AND ADVISORY COMMITTEE

TECHNICAL NOTE

TECHNICAL NOTE NUMBER:	TN 035
DATE:	19 October 2020
LOCATION:	Gas Import Jetty Works
EES/MAP BOOK REFERENCE:	Technical Report A and Attachment VIII - Appendix C and Annexure A-A
SUBJECT:	Response to RFIs 16, 17, 18, and 19 - Section 2.5 Chlorine and temperature discharge conditions
SUMMARY	Responses relate to subsection: Chlorine and temperature discharge conditions
REQUEST:	This technical note has been prepared in response to the Request for Further Information 16, 17, 18, and 19 provided to the proponents by the Crib Point Inquiry and Advisory Committee dated 16 September 2020.

NOTE:

[RFI 16] Provide information on the feasibility of alternative discharge options during the discharge of wastewater to manage chlorine and temperature such as:

- **discharging wastewater on an ebb tide**
- **moderating discharge based on tide and currents**
- **holding water to allow for adequate de-chlorination and temperature stabilisation prior to discharge**
- **alternative biocides to chlorine**

1. Limiting discharge to the ebb tide may be technically feasible but is not practical for the operation of the FSRU and has the potential to disrupt supply according to tidal conditions. This would effectively limit the times of day or duration for which the FSRU could be operated.

2. If the storage of waste water for regasification was to occur during periods of flood tide, or for the purposes of holding water to allow for de-chlorination and temperature stabilisation, large onshore holding tanks would be required, as the FSRU would not have sufficient storage capacity onboard. This solution would not be feasible due to the high storage tank capacity requirements as well as the complex connections that would be required between the FSRU and jetty. A storage tank or multiple storage tanks with a storage capacity of approximately 234,000 tonnes would be required for 12-hours of

regasification. This is over 78 times the storage capacity of the proposed 3,000 tonne nitrogen storage tank at the Crib Point Receiving Facility.

3. The preferred approach, supported by the proposed EPRs is to minimise the impact area for chlorine impacts and demonstrate that even this minimised area assumes the slack tide. The strength of tidal currents is such that any residual chlorine is effectively dispersed with tidal movement.

4. See also TN15. The marine growth prevention system proposed for the FSRU is an electro-chlorination growth protection system, which produces hypochlorite from the naturally occurring salt (NaCl) already existing in the sea water, through electrolysis. This system, which is also commonly used by most ships for the treatment of their engine cooling water systems, is the globally preferred method to prevent marine fouling as it introduces no chemicals from outside sources and decays rapidly. Alternate systems used for marine growth protection systems, such as a copper-based systems, require external biocides to be added to the local seawater and may accumulate in the local environment.

[RFI 17] Explain how the concentration of 100 parts per billion (ppb) discharged from the FSRU has been qualified and provide evidence of 100 ppb being the maximum discharge concentration.

5. After chlorination at the seawater intake, the chlorine rapidly dissipates and is absorbed by the seawater back to its natural state during the exposure time in the internal piping and heat exchangers. It is recommended an initial chlorine dosing of 500 parts per billion (ppb) by mass to prevent marine fouling in the system. It is understood that this would result in an upper limit of 100ppb (0.1mg/l) at the point of discharge, and would continue to rapidly decay away.

6. The FSRU proposed for the Crib Point LNG import facility is similar to other FSRUs and LNG carriers around the world, being equipped with an electro-chlorination system for protection of the onboard seawater systems against excessive marine growth. For this system, a free chlorine discharge concentration of no more than 100 ppb is presented as the project specific requirement for the FSRU operations at Crib Point. This concentration has been used in the assessment of an area of impact and this has in turn been minimised by operational and or design requirements under EPR MM01A.

7. While it may be possible to impose a lesser limit for residual free chlorine discharge concentration, this would be a matter for ultimate consideration in final detailed approval. However, a lesser residual concentration would be expected to require design modifications or more frequent shutdowns for maintenance. At Crib Point the tidal conditions provide for a minimised area of impact without a requirement for a lower residual concentration.

8. International examples involving discharges of chlorine from industrial premises vary. More recently, the Port Kembla approval appears to require a lower residual discharge for chlorine of 0.02 mg/l (20 ppb) but that FSRU is not operational, is yet to receive any wastewater discharge approval, has a single discharge port and is located within a harbour with significantly less tidal influence.

[RFI 18] Explain why 500 ppb is the suggested chlorine dosing concentration when efficacy as an antifoulant is implied as low as 200 ppb. Explain the dosing scenarios that would result in 0 ppb at the discharge point.

9. The initial dosing rate allows for the natural degradation of the chlorine concentration as the water is transported throughout the various sea water systems onboard the vessel.

As much of the hypochlorite decays whilst still in the internal piping, the initial dosing rate is selected to ensure chlorine levels are sufficient at the most distant part of the ship that require antifouling protection.

10. When referring to chlorine concentrations it is therefore important to distinguish between the following main locations of the onboard seawater system:

    (a) The initial dosing point (typically in relation to the seawater intake points)

    (b) The most distant part of the process where a certain concentration must be maintained in order to maintain sufficient antifouling efficacy

    (c) The discharge point(s) where the treated water is returned to sea (which is normally the reference point in environmental permitting)

11. The chlorine concentration starts to decay once generated, and decays rapidly within the time the sea water passes through the piping onboard the vessel. The sea water intake on the vessel, where the growth prevention system is installed, is in the engine room. The pipe run length, from the sea water intake to the regas system is above 100 meters, and due to the rapid decay rate the dosing concentration at the inlet point needs to be higher to allow for the degeneration as the water flows through the piping.

12. It is also important to note that the initial dosing will be flow dependent. If a low flow is transferred through the same piping system as a higher flow, the lower flow will have a longer retention time in the system than the larger flow. Consequently, the initial dosing level needs to be higher concentration for a low flow compared to a high flow, if the same residual chlorine level is targeted at the given discharge point(s).

13. The 500 ppb dosing concentration is the marine growth protection system maker's typical recommendation for the initial dosing point to ensure proper protection of the onboard sea water piping and equipment.

14. The 200 ppb is commonly used as a reference level for the concentration that provides adequate biofouling protection at the local process component (i.e. equipment or piping element).

15. Dosing rates that resulted in a guaranteed 0 ppb concentration at the discharge points of the ship would not provide adequate levels biofouling protection within the equipment.

16. Subject to the results of post commissioning monitoring and operational experience, it may be possible to further reduce dosing rates.

[RFI 19] Provide details of the optional chlorine reduction system referenced in Appendix C (Technical Specifications and Drawings) and explain why this has not been factored into the Project.

17. The project is still working with the FSRU supplier on design options to reduce chlorine levels while asking that the EES assesses the project on the assumption of 0.1mg/l (100ppb).

18. The options that AGL are reviewing to reduce the residual chlorine levels below 0.1mg/l (100ppb), include;

    (a) Modification of the location(s) of the marine growth protection systems to enable better control of chlorine levels

(b) Increased maintenance frequency to allow for increased levels of fouling

(c) Utilising new alternative technologies (UV and/or ultrasonic)

19. An increase in manual cleaning may result in frequent gas export disruptions impacting market supply security, intensive manual labour and the risk of damage to the ships system.

Guideline Values for Chlorine in Marine Waters

20. A copy of the following journal article is provided at Attachment 1 of this technical note:

(a) Batley, G E and Simpson, S L (2020). Short-Term Guideline Values for Chlorine in Marine Waters. *Environmental Toxicology and Chemistry*, 39(4), 754–764.

CORRESPONDENCE: N/A

ATTACHMENTS: 1 Attachment:

1. Batley, G E and Simpson, S L (2020). Short-Term Guideline Values for Chlorine in Marine Waters. *Environmental Toxicology and Chemistry*, 39(4), 754–764.

Attachment 1

Batley, G E and Simpson, S L (2020). Short-Term Guideline Values for Chlorine in Marine Waters. *Environmental Toxicology and Chemistry*, 39(4), 754–764.

Environmental Toxicology and Chemistry—Volume 39, Number 4—pp. 754–764, 2020
Received: 23 October 2019 | Revised: 21 November 2019 | Accepted: 3 January 2020

Environmental Chemistry

Short-Term Guideline Values for Chlorine in Marine Waters

Graeme E. Batley* and Stuart L. Simpson

Centre for Environmental Contaminants Research, Commonwealth Scientific and Industrial Research Organisation Land and Water, Lucas Heights, New South Wales, Australia

Abstract: Chlorination is commonly used to control biofouling organisms, but chlorine rapidly hydrolyzes in seawater to hypochlorite, which undergoes further reaction with bromide, and then with organic matter. These reaction products, collectively termed chlorine-produced oxidants (CPOs), can be toxic to marine biota. Because the lifetime of the most toxic forms is limited to several days, appropriate guideline values need to be based on short-term (acute) toxicity tests, rather than chronic tests. Flow-through toxicity tests that provide continuous CPO exposure are the most appropriate, whereas static-renewal tests generate variable exposure and effects depending on the renewal rate. There are literature data for acute CPO toxicity from flow-through tests, together with values from 2 sensitive 15-min static tests on 30 species from 9 taxonomic groups. These values were used in a species sensitivity distribution (SSD) to derive guideline values that were protective of 99, 95, and 90% of species at 2.2, 7.2, and 13 μg CPO/L respectively. These are the first marine guideline values for chlorine to be derived using SSDs, with all other international guideline values based on the use of assessment factors applied to data for the most sensitive species. In applying these conservative guideline values in field situations, it would need to be demonstrated that concentrations of CPOs would be reduced to below the guideline value within an acceptable mixing zone through both dilution and dissociation. *Environ Toxicol Chem* 2020;39:754–764. © 2020 SETAC

Keywords: Environmental chemistry; Ecotoxicology; Water quality guidelines; Chlorine; Chlorine-produced oxidants

INTRODUCTION

Chlorination, either by the addition of sodium hypochlorite (NaOCl) or electrolysis of seawater, remains one of the most effective approaches for the control of biofouling organisms in seawater (Nguyen et al. 2012; Rajagopal 2012). When chlorine-treated waters are discharged, there are concerns for the impacts of chlorine and its decomposition products on the health of nontarget aquatic biota.

The derivation of a water quality guideline value for chlorine is complicated by the fact that chlorine is highly reactive in seawater, first hydrolyzing and then rapidly oxidizing bromide. Because these reactions are rapid, chlorine or hypochlorite are not expected to pose a direct toxicity threat; however, a potential toxicity remains from their reaction products that can be assessed in the laboratory. On that basis, it is possible to generate a guideline value that relates to the original chlorine or hypochlorite concentration.

The derivation of guideline values for chlorine and its reaction products has already been dealt with by a number of jurisdictions (US Environmental Protection Agency 1985; Canadian Council of Ministers of the Environment 1999; Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand 2000; Sorokin et al. 2007), however, with improvements in methods for guideline value derivation (e.g., Batley et al. 2018), and the availability of newer toxicity data, there is an opportunity to potentially derive a more robust guideline value. In evaluating the toxicity data from experiments with reactive chemicals, there is the option to use the results of static tests (to simulate one-off discharges), of static-renewal tests where the test solution is typically renewed every 24 h, or of flow-through tests that model continuous discharges and avoid decay of toxic reaction products where tests continue for several days. The latter are more appropriate for the derivation of guideline values for ecosystem protection. Furthermore, given that toxicity will be time dependent, it becomes appropriate to derive a short-term guideline value rather than one based on longer term chronic effects.

A key application of the guideline value would be the use of chlorine in the biocidal treatment of heat-exchanger pipes or other systems. This treatment is often continuous, but where the discharge is into the marine environment, the impacts of the discharge are also influenced by varying rates of dilution of

* Address correspondence to graeme.batley@csiro.au
Published online 6 January 2020 in Wiley Online Library (wileyonlinelibrary.com).
DOI: 10.1002/etc.4661

chlorine-produced oxidants (CPOs) due to tidal currents and wave action. The guideline value we have derived is conservative because it is based on toxicity testing where the toxicant is continuously renewed, and not on static-renewal or static tests. The guideline value can thus be applied to all discharges, both continuous and intermittent. The risk assessment of intermittent scenarios would further consider the influence of exposure dynamics (duration and frequency; Angel et al. 2015).

Reactivity of chlorine in seawater

The rapid hydrolysis of chlorine leads to the formation of hypochlorous acid (HOCl) and its dissociation product, the hypochlorite ion (OCl^-). At the pH of seawater, HOCl is 80% dissociated to hypochlorite (dissociation constant [$pK_a = 7.54$). The term "free chlorine" is used to refer to the mixture of Cl_2, HOCl, and the hypochlorite ion, OCl^-, in equilibrium.

Both chlorine and the hypochlorite ion are powerful oxidants. In particular, the bromide ion, present in seawater at a high concentration near 65 mg/L, is rapidly oxidized by hypochlorite to form hypobromous acid ($pK_a = 8.6$), which is only some 20% dissociated to the 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. The term "residual chlorine" is given to the concentration of chlorine and its reaction product (hypochlorite ion) that remain in solution. The term "total residual chlorine" in seawater is commonly taken as comprising all CPOs in seawater and is expressed as mg Cl/L (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand 2000). This would include hypobromous acid and would in fact be mostly bromine based. The use of total residual chlorine is commonly a reference to freshwaters, whereas in marine waters, the equivalent term is CPOs.

In addition, in waters where ammonia is present at elevated concentrations, the formation of chloramines (NH_2Cl; 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), but values of this order are uncommon in seawater. 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 to 1.5 mg/L as Cl_2. 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 min. Measured total residual chlorine (and CPO) includes free chlorine and combined chlorine (as chloramines).

In assessing the ecological impacts of residual chlorine 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 factor in any detail. Zeng et al. (2009) showed that at 15 °C, an initial residual chlorine concentration of 2.35 mg/L reduced to approximately 0.8 mg/L in less than 1 min. This reduction resulted from the oxidation of bromide to hypobromous acid, which is literally too fast to measure. This was followed by a slower first order decomposition over 15 min to 0.5 mg/L and almost to completion in 30 to 40 min. The higher the water temperature, the faster the reactions and the reduction in chlorine concentration. Zeng et al. (2009) also noted that in summer, the CPO had fully decayed before discharge, whereas in winter, the CPO decomposition was slower and might be incomplete.

Using CPO decomposition data and models from the literature (Wang et al. 2008; Saeed et al. 2015), a CPO concentration of 100 μg/L is predicted to decay to 50 μg/L within 2 h (~50%), and to 25 μg/L within 24 h (~75%) in a 5 to 15 °C receiving seawater environment. 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 to derive guideline values to protect aquatic organisms in the receiving environment. In tests using continuous flow hypochlorite addition, reaction with bromide would be presumed to have occurred (available bromide reacts rapidly), and in seawater there is a large excess of bromide over the typical CPO concentration, whereas in static tests, depending on the duration, further oxidative reactions might have progressed (slower reactions with DOM). Application of 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.

Existing water quality guideline values for chlorine in marine waters

The oldest guideline value is that of the US Environmental Protection Agency (1985), which 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 4-day average concentration of CPOs does not exceed 7.5 μg/L more than once every 3 years on the average and if the one-hour average concentration does not exceed 13 μg/L more than once every 3 years on the average."

The Canadian Council of Ministers of the Environment (1999) noted that the 4 most sensitive species endpoints in their database were reduced egg fertilization successes for sand dollars and green sea urchins at 2 and 5 μg Cl/L, respectively (Dinnel et al. 1981), the 48-h median lethal concentration (LC50) for the eastern oyster larvae of 5 μg/L, and the 48-h median effect concentration (EC50) for hard clam larvae of 6 μg/L (Roberts et al. 1975). These were not considered acceptable due to reservations with respect to the analytical methodologies and testing protocols. Their default acute guideline value, termed a short-term guideline value, 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 et al. 1976), and phytoplankton (Eppley et al. 1976), giving a guideline 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 environmental quality standard (EQS) as part of the European Water Framework Directive. The existing EQS for total residual oxidants (TROs; Lewis et al. 1994) was based on an assessment factor of approximately 2 applied to an acute LC50 value of 28 μg/L for both plaice and sole for TROs. 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 guideline value of 3 μg Cl/L as a low-reliability environmental concern value for marine waters (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand 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 (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand 2000).

A revision of the marine chlorine default guideline value 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 (Australian and New Zealand Governments 2018).

MATERIALS AND METHODS

A thorough review of the literature was undertaken for all toxicity data, both acute and chronic, pertaining to CPOs in seawater. Data were quality assessed following the procedure outlined by Warne et al. (2018). Only data for salinities of 25‰ or higher were included. The results for both flow-though and static tests were recorded. The full dataset is shown in Table 1.

A species sensitivity distribution (SSD) of the toxicity dataset was plotted with the Burrlioz 2.0 software (Commonwealth Scientific and Industrial Research Organisation 2019) and used to derive guideline values that were protective of 99, 95, 90, and 80% of species with 50% confidence.

RESULTS AND DISCUSSION

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 (hypochlorite) exposure to the test organisms. Concentrations of CPOs must be measured frequently to demonstrate that substantial reduction in concentration is not occurring. Static-renewal tests in which the test hypochlorite-containing seawater was replaced regularly (usually daily) were used in some instances. In static laboratory tests, the exposure is to rapidly decaying hypochlorite concentrations, and not surprisingly the LC50 values from such tests were generally higher (i.e., toxicity was lower) than those for flow-through tests.

Table 1 is a composite of the available toxicity data from Chariton and Stauber (2008), Canadian Council of Ministers of the Environment (1999), US Environmental Protection Agency (1985), and additional recent literature data, all of which have been quality assessed in the present study to meet the latest Australian and New Zealand Governments (2018) criteria (score of more than 50%) as documented by Warne et al. (2018). As already noted, the revised guideline value derivation approach in Australia and New Zealand recommends not using data for estuarine waters in which the salinity is below 25‰. There were a number of tests conducted at salinities just outside this range (15–25‰), and these are shown in Table 2.

Nearly all the reported bioassays were classified as acute tests, in which a lethal or adverse sublethal effect occurred 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. 2018). Chronic tests by comparison are ones in which a lethal or adverse sublethal 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 is seen on a sensitive early life stage. The only chronic data reported were for 72-h algal bioassays (Lopez-Galindo et al. 2010), which, by definition, are considered chronic tests (Warne et al. 2018), and for one 8-d fish test (Alderson 1972).

Data from short-term tests are most appropriate for the development of guideline values when contaminants are short-lived and nonpersistent due to dispersion, volatilization, or degradation, as is the case with chlorine in marine waters. The minimum exposure period is generally 96 h, but there might be circumstances in which a lesser exposure time is relevant (Batley et al. 2018). For acute effects, usually only LC50 data are recorded, but given that this represents a 50% effect on

TABLE 1: Toxicity data for chlorine-produced oxidants (CPOs) in seawater with salinity ≥25‰

Species	Life stage	Exposure duration (h)	Acute/chronic	Test type	Toxicity measure	Test medium	Temp (°C)	Concentration (μg/L)[a]	Reference	Comments
Algae (chronic)										
Alga (*Isochrysis galbana*)		96	Chronic	Static	Growth (EC15)	Synthetic seawater	20	172	Lopez-Galindo et al. 2010	CPO measured every 30 min, IC50 1390 μg/L
Alga (*Dunaliella salina*)		96	Chronic	Static	Growth (EC15)	Synthetic seawater	20	481	Lopez-Galindo et al. 2010	Daily biomass (optical density) measurements, IC50 824 μg/L
Invertebrates (acute)										
American oyster (*Crassostrea virginica*)	Larvae	0.5	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	25	**80**	Capuzzo 1979	Acceptable quality
Copepod (*Acartia tonsa*)		0.5	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	20	**820**	Capuzzo 1979	Acceptable quality
Rotifer (*Brachionus plicatilis*)		0.5	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	25	**90**	Capuzzo 1979	Acceptable quality
Rotifer (*Brachionus plicatilis*)	0.5 h old	24	Acute	Static	Mortality (LC50)	Synthetic seawater	20	586 (LC50), 438 (LC10)	Lopez-Galindo et al. 2010	Measured concentrations in 0.3-mL well plates
Amphipod (*Hyale barbicornis*)	Juveniles	96	Acute	24-h renewal	Mortality (LC50)	Seawater (34‰)	20	1050	Anasco et al. 2008	Measured concentration decayed rapidly. Nominal concentration used for 24-h exposure, measured concentrations for other exposure times.
Amphipod (*Hyale barbicornis*)	Juveniles	96	Acute	24-h renewal	Body length (EC50)	Seawater (34‰)	20	524	Anasco et al. 2008	Measured concentrations decayed rapidly. Nominal concentration used for 24-h exposure, measured concentrations for other exposure times.
Amphipod (*Pontogeneia* sp.)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**687**	Thatcher 1978	Acceptable quality
Amphipod (*Anonyx* sp.)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**145**	Thatcher 1978	Acceptable quality
Coon stripe shrimp (*Pandalus danae*)	Juvenile and adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**178**	Gibson et al. 1975 and Thatcher 1978	Acceptable quality
Sea urchin (*Strongylocentrotus droebachiensis*)	Sperm	15 min	Acute	Static	Fertilization (EC50)	Seawater (28‰)	14	<5, <6	Dinnel et al. 1981	Sperm exposed for 15 min, eggs exposed pre-test for 24 or 48 h.
								5	Value selected	
Sand dollar (*Dendrastur excentricus*)	Sperm	15 min	Acute	Static	Fertilization (EC50)	Seawater (28‰)	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.

(*Continued*)

TABLE 1: (*Continued*)

Species	Life stage	Exposure duration (h)	Acute/ chronic	Test type	Toxicity measure	Test medium	Temp (°C)	Concentration (µg/L)[a]	Reference	Comments
Lobster (*Homarus americanus*)	Larvae	1	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	nr	**2890**	Capuzzo et al. 1976	Seawater and toxicant mixed for 14 h before larvae addition. Flow-through system. After 60 min exposure LC50 was 16 300 based on applied conc. and 2890 µg Cl/L (calculated from a decay equation) based on the residual; used ACR of 4.5 for crustaceans.
Mysid (*Neomysis* sp.)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**162**	Thatcher 1978	Acceptable quality
Shrimp (*Pandalus goniurus*)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**90**	Thatcher 1978	Acceptable quality
Shrimp (*Crangon nigricauda*)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**134**	Thatcher 1978	Acceptable quality
Shore crab (*Hemigrapsus nudus* and *H. oregonensis*	Juvenile and adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**1420**	Thatcher 1978	Acceptable quality
Fish (acute)										
Tidewater silverside juvenile (*Menidia peninsulae*)	Fry	96	Acute	Flow-through	Mortality (LC50)	Seawater (22–27‰)	25	**54**	Goodman et al. 1983	Acceptable quality
Fish (*Oryzias javanicus*)	Larvae	96	Acute	24-h renewal	Mortality (LC50)	Seawater (34‰)	26	91	Anasco et al. 2008	Conc. decayed rapidly; nominal for 24-h, measured for others.
Fish (*Oryzias javanicus*)	Larvae	24	Acute	24-h renewal	Mortality (LC50)	Seawater (34‰)	26	152	Anasco et al. 2008	
Plaice (*Pleuronectes platessa*)	Larvae	96	Acute	Flow-through	Mortality (LC50)	Seawater (35‰)	8	**24**	Alderson 1972, 1974	Low temperature
Coho salmon (*Oncorhynchus kisutch*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**32**	Thatcher 1978	Acceptable quality
Pacific herring (*Clupea harengus pailasi*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**65**	Thatcher 1978	Acceptable quality
Threespine stickleback (*Gasterosteus aculeatus*)	Juvenile and adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**167**	Thatcher 1978	Acceptable quality
Shiner perch (*Cymatogaster aggregata*)	Juvenile and adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**71**	Thatcher 1978	Acceptable quality

(*Continued*)

TABLE 1: (*Continued*)

Species	Life stage	Exposure duration (h)	Acute/chronic	Test type	Toxicity measure	Test medium	Temp (°C)	Concentration (µg/L)[a]	Reference	Comments
Pacific sand lance (*Ammodytes hexapterus*)	Juvenile and adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**82**	Thatcher 1978	Acceptable quality
English sole (*Parophrys vetulus*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (28‰)	15	**73**	Thatcher 1978	Acceptable quality
Fish (chronic)										
Plaice (*Pleuronectes platessa*)	Eggs	8 d	Chronic	Flow-through	Mortality (LC50)	Seawater (35‰)	8	120	Alderson 1972, 1974	Low temperature

[a]Values in bold type used in the species sensitivity distribution (SSD).
nr = not reported; EC10 = effect concentration, 10%; IC50 = median inhibitory concentration; LC50 = median lethal concentration; LC10 = 10% lethal concentration; ACR = acute-to-chronic ratio.

species survival, it is more reasonable to use acute LC or EC10 values in deriving a default guideline value, because this represents a point of incipient toxicity, not 50% mortality.

The most sensitive species were sea urchins, with impacts on fertilization being seen at near 5 µg Cl/L as CPO (Dinnel et al. 1981). Although these were static tests, the exposure duration was sufficiently short to warrant their inclusion. In these tests, sperm were pre-exposed to hypochlorite in seawater for 15 min with no effect on viability, whereas 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*. The 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 3 1-min pre-exposures, 6.4 µg CPO/L, was used. For the sea urchin *Strongylocentrotus droebachiensis*, an experiment in which the hypochlorite and seawater were premixed for 24 or 48 h before exposure did not affect the toxicity to sperm fertilization, suggesting that reaction products other than CPOs were causing toxicity (Dinnel et al. 1981). Because the exposure time of sperm and eggs was only 15 min in these fertilization experiments, the tests are considered to be acute (Warne et al. 2018); chronic tests with this species require 1 h or more of exposure. The next most sensitive species were fish, with plaice (*Pleuronectes platessa*) having a 96-h LC50 of 24 µg CPO/L (Alderson 1972).

There were results for only 2 algal species, *Isochrysis galbana* and *Dunaliella salina* (Lopez-Galindo et al. 2010), and these were not particularly sensitive, with chronic EC15 values for 2 species of 172 and 481 µg Cl/L respectively. These values were, however, based on 96-h static exposures, which might explain the lower sensitivity. Their respective EC50 values of 1390 and 824 µg Cl/L were the highest of any tests reported (Table 1). Flow-through tests with algae are difficult to undertake and are therefore rarely reported.

A few studies 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), whereas 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 Special Areas of Conservation 2019). The LC50 values for larval survival for the oyster *Crassostrea virginica* estimated from the published dose–response curves (Stewart et al. 1979) were 2, 1, and 0.1 mg/L, respectively, for chloroform, bromoform, and bromate. These authors noted that chloroform and bromoform were both lost from solution by volatilization. Not considered was the toxicity of chloramine and bromamine products only formed when ammonia concentrations are elevated in the seawater.

There are several general observations that can be made with respect to the toxicity data. First, static tests with regular renewal (24 h) show lower toxicity (higher LC50 values) than continuous flow-through tests because of the reactivity of chlorine (hypochlorite). For example, a 0.5-h flow-through test with the rotifer *Brachionus plicatilis* had an LC50 of 90 µg CPO/L

TABLE 2: Toxicity data for chlorine-produced oxidants (CPOs) in seawater with salinity ≥15 and <25‰

Species	Life stage	Exposure duration (h)	Acute/ chronic	Test type	Toxicity measure	Test medium	Temp (°C)	Concentration (μg/L)	Reference	Comments
Invertebrates										
American oyster (*Crassostrea virginica*)	Larvae	48	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	19–28	26	Roberts and Gleeson 1978	Acceptable quality
American oyster (*Crassostrea virginica*)	Larvae	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	19–28	23	Roberts et al. 1975	Acceptable quality
								25	**Geometric mean**	
Copepod (*Acartia tonsa)*		96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	20	**29**	Roberts and Gleeson 1978	Acceptable quality
Glass shrimp (*Palaemonetes pugio*)	Adult	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	19–28	**220**	Roberts and Gleeson 1978	Acceptable quality
Mysid (*Mysidopsis bahia*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20.5‰)	20	73	Fisher et al. 1994	Acceptable quality
Mysid (*Mysidopsis bahia*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	20	62	Fisher et al. 1999	Acceptable quality
								68	**Geometric mean**	
Atlantic marine amphipod (*Amphiporeia virginiana*)	Juvenile	48	Acute	Static	Mortality (LC50)	Seawater (21‰)	10	626	Wan et al. 2000	Acceptable quality
Pacific marine amphipod (*Eohaustorius washingtonianus*)	Juvenile	48	Acute	Static	Mortality (LC50)	Seawater (21‰)	15	567	Wan et al. 2000	Acceptable quality
Fish										
Atlantic silverside (*Menidia menidia*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	19–28	**37**	Roberts and Gleeson 1978	Used lower value (most sensitive life stage)
Atlantic silverside (*Menidia menidia*)	Eggs	48	Acute	Flow-through	Mortality (LC50)	Seawater (15‰)	8–12	300	Morgan and Prince 1977	Acceptable quality
Inland silverside (*Menidia beryllina*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20.5‰)	20	128	Fisher et al. 1994	Acceptable quality
Inland silverside (*Menidia beryllina*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	20	143	Fisher et al. 1999	Acceptable quality
								135	**Geometric mean**	Used lower 2 values
Inland silverside (*Menidia beryllina*)	Eggs	48	Acute	Flow-through	Mortality (LC50)	Seawater (15‰)	8–12	210	Morgan and Prince 1977	Acceptable quality
Northern pipefish (*Synnathus focus*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	17–28	**270**	Roberts et al. 1975	Acceptable quality
Naked gobi (*Gobiosoma bosci*)	Juvenile	96	Acute	Flow-through	Mortality (LC50)	Seawater (20‰)	17–28	**80**	Roberts et al. 1975	Acceptable quality
White perch (*Morone americana)*	Eggs	76	Acute	Flow-through	Mortality (LC50)	Seawater (15‰)	8–12	**270**	Morgan and Prince 1977	Acceptable quality
Striped bass *(Morone saxatilis)*	Eggs	48	Acute	Flow-through	Mortality (LC50)	Seawater (15‰)	8–12	**200**	Morgan and Prince 1977	Acceptable quality
Blueback herring *(Alosa aestivalis)*	Eggs	48	Acute	Flow-through	Mortality (LC50)	Seawater (15‰)	8–12	**240**	Morgan and Prince 1977	Acceptable quality

LC50 = median lethal concentration.

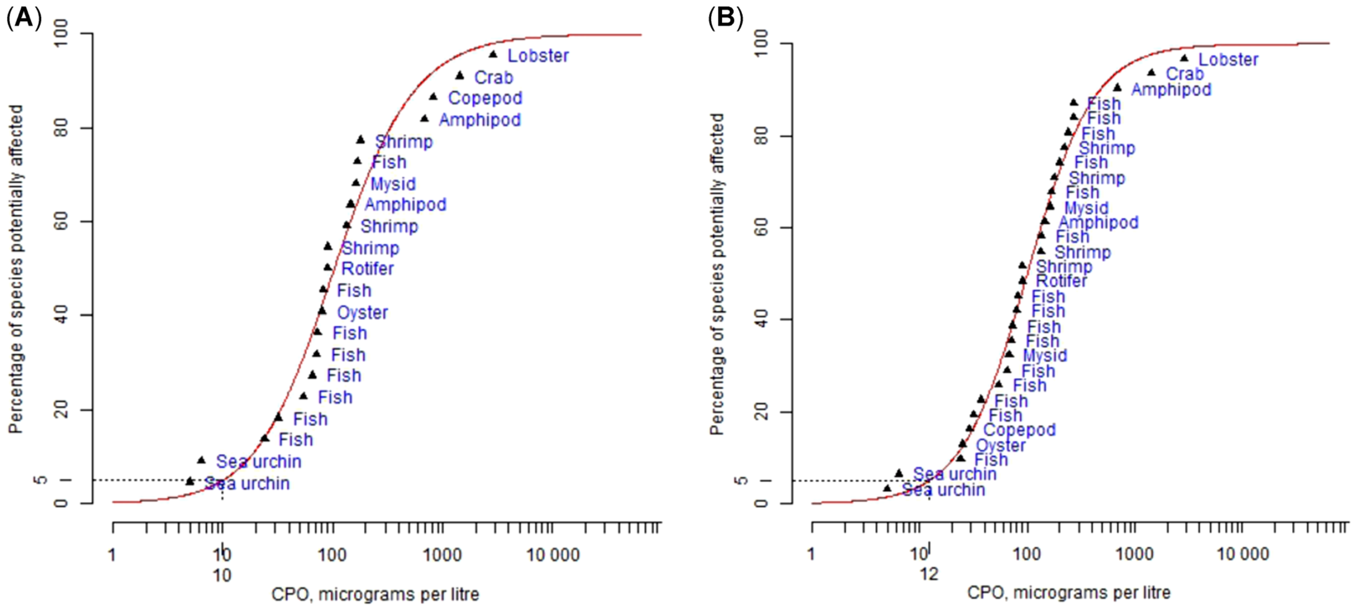

FIGURE 1: Species sensitivity distribution of selected (in bold) acute toxicity test data (flow-through plus static [15 min]). (**A**) ≥25‰ salinity data from Table 1, and (**B**) (**A**) plus <25‰ data from Table 2, showing the 95% species protection (PC95) value as an *x*-axis intercept. CPO = chlorine-produced oxidants.

(Capuzzo et al. 1976) compared with a 24-h static test LC50 of 586 µg CPO/L (Lopez-Galindo et al. 2010; Table 1).

Second, in flow-through systems, short-term exposures (0.5 h) generally show lower toxicity than 96-h exposures for the same species. The former may better reflect discharge conditions and the high reactivity of chlorine and its reaction products in seawater. For some species in flow-through tests, LC50 values decreased significantly as exposure duration increased from 24 to 96 h, as shown by Wan et al. (2000) for 2 marine amphipods, although for studies on *M. beryllina* fish embryos, Fisher et al. (1994) found little difference between 24- and 48-h LC50 values (i.e., a steep toxicity curve).

Guideline value derivation

The derivation of guideline values for CPOs in marine waters followed the procedures outlined by Warne et al. (2018) as used in Australia and New Zealand. Because of the high reactivity of chlorine, and with the lifetime of the reaction products being on the order of several hours at most, it was appropriate for management purposes to develop and apply guideline values 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, where the discharged CPOs are decreasing in concentration due both to reactions (e.g., with bromide) and to dilution caused by dispersion through wave and tidal action, and so the guideline values derived using such data will be quite conservative. For static tests, it is the renewal frequency in the context of reaction rate that is important, and hence 1- 15-min static exposures cannot be treated as analogous to 24+-h static tests.

Using only the highlighted more than 25‰ acute toxicity data from flow-through or very short-term static tests (i.e., less than 15 min) from Table 1, an SSD was plotted (Figure 1A) and used to derive guideline values. Values of 2.9, 10, and 18 µg CPO/L, respectively, were obtained for 99, 95, and 90% species protection (Table 3, column 2). If all data from non-flow-through tests were omitted, the values for 99 and 95% species protection increased

TABLE 3: Summary of short-term toxicity values derived from different data combinations (µg CPO/L, with 95% confidence limits in parentheses)

Level of protection (% of species)	All flow-through LC50 data plus 15-min static LC50 data salinity ≥25‰ ($n = 21$)	All flow-through LC50 data, plus 15-min static LC50 data, plus low salinity data ($n = 30$)	Column 3 acute LC50 data converted to LC10 values by multiplying by 0.6[a] Recommended default guideline value
99	2.9 (0.6–26)	3.7 (0.8–21)	2.2 (0.5–13)
95	10 (3.8–38)	12 (5.1–32)	7.2 (3.1–19)
90	18 (7.5–48)	21 (11–41)	13 (6.6–25)
80	33 (16–66)	37 (22–62)	22 (13–37)
Reliability	Very high	Very high	Very high

[a]See text for justification.
LC50 = median lethal concentration; LC10 = 10% lethal concentration; CPO = chlorine-produced oxidant.

to 19 and 31 μg CPO/L, respectively, largely due to the removal of the most sensitive endpoints, which were static tests using sea urchin species, although the minimum reaction time was only 15 min before each test plus 1 to 10 min during fertilization, which is a lot shorter than the other static tests.

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. The values were, however, from static tests lasting longer than 15 min, which we had decided against including because of the decay in concentration that would occur, even with 24-h renewal.

Given the small difference in salinity between the 25‰ or higher and the less than 25‰ datasets (Tables 1 and 2), the possibility of combining the datasets was considered, assuming that the lowered salinity did not result in greater toxicity. Data for 2 species were common to both sets, namely, for the oyster *Crassostrea virginica* and the copepod *Acartia tonsa*. For the oyster, Capuzzo (1979) found an LC50 of 80 μg/L after only a 30-min exposure in seawater, but in estuarine water of 20‰ salinity, Roberts and Gleeson (1978) obtained a 48-h LC50 of 26 μg/L, both in flow-through systems. Although the shorter exposure was possibly more appropriate for a chlorine discharge, for consistency with other data, the 48-h value was used in the combined data SSD.

For the copepod, the difference was more dramatic, with an LC50 of 820 μg/L after 30 min compared with 29 μg/L after 96 h in 20‰ water. The reasons for this difference were unclear. Again, in a combined dataset, the lower value was used in the combined data SSD.

A second SSD plot (Figure 1B) was obtained using the more than 25‰ data just mentioned supplemented by all the acute flow-through less than 25‰ salinity data from Table 2 (values highlighted in bold). The results are shown in column 3 of Table 3. As already noted, in this combined dataset, for the oyster *C. virginica* and the copepod *A. tonsa*, only the lower (less than 25‰) results were used. The results for the 2 datasets were effectively the same within the error of the determination.

Within a regulatory context, the application of a short-term guideline value makes sense, not necessarily one based on effects to 50% of the test population (i.e., LC50 values), but rather one based on a no or low effect (e.g., LC10), as we apply to chronic tests that use no or low effect values (Warne et al. 2018). In some instances, however, regulations have stipulated an acute LC50/EC50-based guideline value not to be exceeded in mixing zones, and in such cases the raw LC50 values would be applicable. Determining an appropriate LC10 value from the literature requires a published dose–response curve, and in almost all cases these were absent. In some instances, however, there were published LC10 or LC5 values.

Morgan and Prince (1977) reported LC values for flow-through tests on eggs and larvae of 5 estuarine fish species. Ratios of LC10/LC50 were 0.55, 0.50, 0.66, 0.53, and 0.76 (mean = 0.6). In static tests on the rotifer *B. plicatilis,* Lopez-Galindo et al. (2010) found an LC10/LC50 ratio of 0.75. Given the uncertainties in measurement of LC5 and LC10 values, as well as uncertainties in the effects of salinity and temperature, and in flow-through versus static tests, this difference is probably not that significant. Adopting an alternative and more conservative default ratio of 0.2, which is used to convert chronic EC50 values to EC10s (Warne et al. 2018), cannot be justified. Thus, for chlorine, the recommended guideline value used an LC10/LC50 factor of 0.6 applied to the combined dataset SSD (Figure 1B), as shown in Table 3. This dataset comprised results from 30 toxicity tests including 9 different taxonomic groups. There was an excellent fit of the data in the SSD such that the derived guideline values were classified as of very high reliability (Warne et al. 2018).

These guideline values for chlorine in marine waters are the first to be derived using SSDs, with all other international guideline values being based on smaller datasets and using assessment factors applied to data for the most sensitive species. Note that, owing to the large variation in bioassay durations, but limited overall toxicity data, it is not feasible to develop guideline values for specific durations that are protective of percentages of species.

It was notable that the majority of the data were derived from studies in the 1970s, 1980s, and 1990s, and although their quality was acceptable, newer data that looked more closely at the effects of exposure time, salinity, and temperature, as well as reporting both LC10 and LC50 values and showing the dose–response curves, would allow refinement of some of the existing data and construction of laboratory studies that more closely represent the field situation. Consideration should be given to deriving median time to lethality (LT50) and LT10, in which effects after a fixed time such as the lifetime of the CPOs in the field could underpin a guideline value derivation.

In applying these conservative guideline values in field situations, it would need to be demonstrated that concentrations would be reduced to below these values within an acceptable mixing zone both through dilution and dissociation.

Having decided that a short-term guideline value is the most appropriate way to manage the impacts of chlorine in marine waters, it is worth considering what the longer term impacts on biota might be. In terms of defining a chronic exposure guideline value, one option is to apply an acute-to-chronic ratio (ACR) to the guideline value based on LC50 values (column 3 in Table 3). Fisher et al. (1994) reported ACRs for continuous flow tests of 3.7 for the mysid *Mysidopsis bahia* and 1.5 for the silverside *M. beryllina*. Using the geometric mean of these values, 2.4 (multiplying an LC50-based guideline value by 0.42), yielded chronic guideline values of 1.5 and 5.0 μg CPO/L. However, these are also highly conservative, because we know that the most toxic CPOs are gone within 1 to 2 d, leaving products that are less toxic by at least 1 order of magnitude. The implication then is that compliance with the conservative short-term guideline values is likely to also be protective against chronic effects on biota downstream of any discharge.

CONCLUSIONS

A dataset of 30 species from 9 taxonomic groups was obtained by combining literature data for acute CPO toxicity in flow-through tests in ≥25‰ salinity seawater with those from more than 15 to less than 25‰ salinity flow-through tests. Included were the values from 2 very sensitive 15-min static tests with sea urchin species for tests in waters of less than 25‰ salinity. Using these values in an SSD resulted in guideline values of 2.2, 7.2, 13, and 24 µg CPO/L that were protective of 99, 95, 90, and 80% of species, respectively. Adding the less than 25‰ salinity data did not significantly affect the derived guideline values. These are the first marine guideline values for chlorine to be derived using SSDs, with all other international guideline values being based on the use of assessment factors applied to data for the most sensitive species. In applying these conservative guideline values in field situations, it would need to be demonstrated that concentrations of CPOs would be reduced to below the guideline value within an acceptable mixing zone through both dilution and dissociation.

Acknowledgment—The authors are grateful to Scott Chidgey, for bringing the topic of chlorine in marine waters to their attention. This study was funded in part by CEE Pty Ltd, Cheltenham, Vic (Australia) and the Australian Government Department of Agriculture.

Data Availability Statement—All data are in the main text. Data, associated metadata, and calculation tools are available from the corresponding author (graeme.batley@csiro.au).

REFERENCES

Abarnou A, Miossec L. 1992. Chlorinated waters discharged to the marine environment chemistry and environmental impact: An overview. *Sci Total Environ* 126:173–197.

Alderson R. 1972. Effects of low concentrations of free chlorine on eggs and larvae of plaice (*Pleuronectes platessa* L.). In Riuvo M, ed, *Marine Pollution and Sea Life*. Fishing News (Books), Surrey, England.

Alderson R. 1974. Sea-water chlorination and the survival of the early development stages of plaice, *Pleuronectes platessa* (L). *Aquaculture* 4:41–53.

Anasco N, Koyama J, Imai S, Nakamura K. 2008. Toxicity of residual chlorines from hypochlorite treated seawater to marine amphipod *Hyale barbicornis* and estuarine fish *Oryzias javanicus*. *Water Air Soil Pollut* 195:129–136.

Angel BM, Simpson SL, Chariton AA, Stauber JL, Jolley DF. 2015. Time-averaged concentrations of copper from continuous exposures conservatively predict pulsed exposure toxicity to the marine diatom, *Phaeodactylum tricornutum*: Importance of uptake and elimination. *Aquat Toxicol* 164:1–9.

Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Canberra, ACT, Australia.

Australian and New Zealand Governments. 2018. Australian and New Zealand guidelines for fresh and marine water quality. Canberra ACT, Australia. [cited 2019 September 20]. Available from: www.waterquality.gov.au/anz-guidelines

Batley GE, van Dam RA, Warne MStJ, Chapman JC, Fox DR, Hickey CW, Stauber JL. 2018. Technical rationale for changes to the method for deriving Australian and New Zealand water quality guideline values for toxicants—Update of 2014 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia.

Canadian Council of Ministers of the Environment. 1999. Canadian water quality guidelines for the protection of aquatic life: Reactive chlorine. In *Canadian Environmental Quality Guidelines*. Winnipeg, MN, Canada.

Capuzzo JM. 1979. The effect of temperature on the toxicity of chlorinated cooling waters to marine animals—A preliminary review. *Mar Pollut Bull* 10:45–47.

Capuzzo JM, Lawrence SA, Davidson JA. 1976. Combined toxicity of free chlorine, chloramine and temperature to stage I larvae of the American lobster *Homarus americanus*. *Water Res* 10:1093–1099.

Chariton AA, Stauber JL. 2008. Toxicity of chlorine and its major by-products in seawater: A literature review. Report No. 54/08, CSIRO Land and Water Science Lucas Heights, NSW, Australia.

Commonwealth Scientific and Industrial Research Organisation. 2019. Burrlioz 2.0 software. Canberra, ACT, Australia. [cited 2019 September 12]. Available from: https://research.csiro.au/software/burrlioz/

Dinnel PA, Stober QJ, DiJulio DH. 1981. Sea urchin sperm bioassay for sewage and chlorinated seawater and its relation to fish bioassays. *Mar Environ Res* 5:29–39.

Eppley RW, Renger EH, Williams PM. 1976. Chlorine reactions with seawater constituents and the inhibition of photosynthesis of natural marine phytoplankton. *Estuar Coastal Mar Sci* 4:147–161.

European Chemicals Bureau. 2002. Technical guidance document on risk assessment. Part II. Report No. EUR 20418 EN/2. Helsinki, Finland. [cited 2019 April 17]. Available from: http://publications.jrc.ec.europa.eu/repository/bitstream/JRC23785/EUR%2020418%20EN-2.pdf

Fisher DJ, Burton DT, Yonkos LT, Turley SD, Turley BS, Ziegler GP, Zillioux EJ. 1994. Acute and short-term chronic effects of continuous and intermittent chlorination on *Mysidopsis bahia* and *Menidia beryllina*. *Environ Toxicol Chem* 13:1525–1534.

Fisher DJ, Burton DJ, Yonkos LT, Turley SD, Ziegler GP. 1999. The relative acute toxicity of continuous and intermittent exposures of chlorine and bromine to aquatic organisms in the presence and absence of ammonia. *Water Res* 33:760–779.

Gibson CI, Thatcher TO, Apts CW. 1975. Some effects of temperature, chlorine and copper on the survival and growth of the coon stripe shrimp, *Pandalus danae*. Report No. BNWL-SA-5344. Battelle Northwest, Richland, WA, USA.

Goodman L, Douglas P, Middaugh DJ, Hansen PJ, Higdon PK, Cripe GM. 1983. Early life-stage toxicity test with tidewater silversides (*Menidia peninsulae*) and chlorine-produced oxidants. *Environ Toxicol Chem* 2:337–342.

Jenner HA, Taylor CJL, van Donk M, Khalanski M. 1997. Chlorination by-products in chlorinated cooling water of some European coastal power stations. *Mar Environ Res* 43:279–293.

Lewis S, Cartwright NG, Jerman E, Tynan P, Sims IR, Wellstein N. 1994. Proposed environmental quality standards for chlorine in fresh and marine waters. Water Research Centre, Medmenham, UK.

Lopez-Galindo C, Garrido MC, Casanueva JF, Nebot E. 2010. Degradation models and ecotoxicity in marine waters of two antifouling compounds: Sodium hypochlorite and an alkylamine surfactant. *Sci Total Environ* 408:1779–1785.

Morgan RP, Prince RD. 1977. Chlorine toxicity to eggs and larvae of five Chesapeake Bay fishes. *Trans Am Fish Soc* 106:380–385.

Nguyen T, Roddick FA, Fan L. 2012. Biofouling of water treatment membranes: A review of the underlying causes, monitoring techniques and control measures. *Membranes* 2:804–840.

Patrick R, McLean R. 1971. Entrainment simulation studies on some estuarine organisms for the Potomac Electric Power Company. Academy of Natural Sciences, Philadelphia, Department of Limnology, Philadelphia, PA, USA.

Rajagopal S. 2012. Chlorination and biofouling control in industrial cooling water systems. In Rajagopal S, Jenner HA, Venugopalan VP, eds, *Operational and Environmental Consequences of Large Industrial Cooling Water Systems*. Springer, New York, NY, USA, pp 163–182.

Roberts MH, Diaz RJ, Bender ME, Huggett RJ. 1975. Acute toxicity of chlorine to selected estuarine species. *J Fish Res Board Can* 32: 2525–2528.

Roberts MH, Gleeson RA. 1978. Acute toxicity of bromochlorinated seawater to selected estuarine species with a comparison to chlorinated seawater toxicity. *Mar Environ Res* 1:19–30.

Saeed S, Prakash S, Deb N, Campbell R, Kolluru V, Febbo E, Dupont J. 2015. Development of a site-specific kinetic model for chlorine decay and the formation of chlorination by-products in seawater. *J Mar Sci Eng* 3:772–792.

Sorokin N, Atkinson C, Aldous E, Rule K, Comber S. 2007. Proposed EQS for Water Framework Directive Annex VIII substances: Chlorine (free available). Science Report No. SC040038/SR4. Environment Agency, Bristol, UK.

Stewart ME, Blogoslawski WJ, Hsu RY, Helz GR. 1979. By-products of oxidative biocides: Toxicity to oyster larvae. *Mar Pollut Bull* 10:166–169.

Sugam R, Helz GR. 1977. Speciation of chlorine produced oxidants in marine waters. *Chesapeake Sci* 18:113–115.

Thatcher TO. 1978. The relative sensitivity of Pacific Northwest fishes and invertebrates to chlorinated sea water. In Jolley RL, Gorchev H, Hamilton DH, eds, *Water Chlorination: Environmental Impact and Health Effects*, Vol 2. Ann Arbor Science, Ann Arbor, MI, USA.

UK Marine Special Areas of Conservation. 2019. Biocides used in cooling water disinfection. [cited 2019 April 15]. Available from: http://www.ukmarinesac.org.uk/activities/water-quality/wq8_28.htm

US Environmental Protection Agency. 1985. Ambient water quality criteria for chlorine. EPA 440/5-84-030. Office of Water, Washington, DC.

Wan MT, Van Aggelen G, Cheng W, Watts RG. 2000. Acute toxicity of chlorine-produced oxidants (CPO) to the marine invertebrates *Amphiporeia virgiiana* and *Eohaustorius washingtonianus*. *Bull Environ Contam Toxicol* 64:205–212.

Wang J-T, Chen M-H, Lee H-J, Chang W-B, Chen C-C, Pai S-C, Meng P-J. 2008. A model to predict total chlorine residue in the cooling seawater of a power plant using iodine colorimetric method. *Intern J Mol Sci* 9:542–553.

Warne M, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW, Stauber JL. 2018. Revised method for deriving Australian and New Zealand water quality guideline values for toxicants—Update of 2015 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia.

Zeng J, Jiang Z, Chen Q, Zheng P, Huang Y. 2009. The decay kinetics of residual chlorine in cooling seawater simulation experiments. *Acta Oceanol Sin* 28:54–59.