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16 March 2021

AGL WHOLESALE GAS LIMITED

WORKS APPROVAL APPLICATION 1003907

RESPONSE TO SECTION 22(1) NOTICE TO SUPPLY FURTHER INFORMATION – QUESTION 13

Question 13 - Clarify what has been considered in selecting anti-fouling technologies and what could be other alternatives. Provide comparisons and feasibility analysis of alternative anti-fouling technologies

The use of electro-chlorination to prevent marine growth is the standard treatment method on Floating Storage and Regasification Units (**FSRUs**) for the prevention of biofouling.

In Technical Note 53, in response to the IAC's request for additional information, AGL provided a high-level discussion on alternative technologies to the FSRU water systems to limit or prevent chlorine discharges. Technical Note 53 is appended to this response, and identified alternative technologies (in considering the management of chlorination):

> *a. Ultrasonic growth prevention system: This system would require ultrasonic transmitters to be fitted to the seawater piping. The ultrasound prevents biofilm and micro-organisms from adhering to the equipment surfaces. This technology has not been tested for use in a regasification system or with large seawater volumes. As such, use of this system would require verification that installing ultrasonic transmitters on the regasification sea water heat exchanger will not impact the equipment or the performance or safety of the regasification system.*
>
> *b. Ultraviolet growth prevention system: This system uses ultraviolet (UV) radiation to prevent fouling of the regas systems. UV systems are large and have limited capacity to handle large volumes of water. For an FSRU using large seawater volumes, multiple UV systems would be required. Retrofitting multiple UV systems into an FSRU is complex due to space constraints.*
>
> *c. Dedicated electro-chlorination injection for the regasification system: This proposes the installation of a dedicated electro-chlorination Marine Growth Prevention System (MGPS) for the regasification system or relocation of the MGPS, to enable more tailored control of chlorine levels for different equipment. This would only reduce the chlorine discharge rate, not result in zero chlorine discharge.* [1]

AGL considered these technologies on a preliminary feasibility basis and determined that Ultrasonic and Ultraviolet growth prevention systems are not proven for the scale of water treatment required for the FSRU operation, and that there was no operational data that would allow a comparative assessment of the effectiveness of these technologies. In addition, AGL determined in consultation with Hoegh that there would be significant technical feasibility issues in retrofitting these alternative technologies within a FSRU given its complex systems within constrained space. AGL is unaware of any of these alternative technologies having been implemented within an FSRU or within any vessel of comparable size and functionality. They remain unproven in the context of vessels of this type and cannot be considered feasible alternatives to electro-chlorination at this time.

[1] AGL notes that the MGPS uses the same technology as the currently proposed electro-chlorination unit so that it does not require further technical assessment.

In Technical Note 35, in response to the IAC's request for additional information, AGL provided a high level discussion of alternative biocides that could be used in the MGPS. Technical Note 35, appended to this response, noted that alternate systems used for MGPS, such as copper-based systems, require external biocides to be added to the local seawater which may accumulate in the local environment. AGL considered that these alternate biocides would not result in acceptable environmental impacts, and so did not further evaluate these biocides.

In addition to considering alternative anti-fouling technologies, AGL has investigated alternative ways of operating the electro-chlorination system installed on the FSRU to achieve a minimised area of impact including varying the chlorination rate at the point of discharge to correspond with periods of greater and lesser mixing (dilution).

EPR-ME02 in the version 4 Environmental Performance Requirements (**EPRs**) is proposed by AGL to minimise potential impacts associated with chlorine discharges when operating in open loop by varying the chlorination rate at the point of discharge. Option 1 under EPR-ME02 is the most effective measure to achieve acceptable impacts for beneficial uses and the ecological character of the area associated with seawater discharge in open loop operation.

EPR-ME02 Seawater discharge

> *Option 1 – Varying chlorination rate at point of discharge*
>
> *Except as approved or required by the EPA, the OEMP must include requirements that seawater discharges from the regasification system must:*
>
> *(a) have a chlorine residual concentration of up to 0.1mg/L other than at Slack Tide;*
>
> *(b) have a chlorine residual concentration of 0mg/L during Slack Tide;*
>
> *(c) not exceed a tidally averaged chlorine residual concentration of 0.0022mg/L beyond a distance of 100 metres from the FSRU; and*
>
> *(d) not exceed a temperature variation of 7°C from ambient*
>
> *Note: The time of Slack Tide is half an hour either side of high tide or low tide at Crib Point. High tide and low tide at Crib Point are to be calculated by reference to the BOM Victorian Tide Tables or other source to the satisfaction of the EPA.*

Under Option 1 of EPR-ME02, operation of the FSRU will ensure residual chlorine concentration in the wastewater discharge is 0mg/L for half an hour either side of Slack Tide, when tidal currents are weak and there is less dilution. This will avoid pooling of chlorinated seawater beside and under the FSRU during Slack Tide. At times other than Slack Tide, in ebb tides and flood tides, there is considerable dilution of chlorine plumes (reducing the chlorine concentration from 100 µg/L to less than 5 µg/L within about 40 metres from the point of discharge).

Consistent with the materials before the EPA, AGL contends that Option 1 of EPR-ME02 will ensure that the operation of the FSRU protects beneficial uses and will not result in any material impacts on the ecological character or values of the area. Option 1 of EPR-ME02 is a bespoke response to the characteristics of Crib Point and the tidal influences in Western Port Bay.

ANNEXURE 1

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

TECHNICAL NOTE

TECHNICAL NOTE NUMBER:	TN 053
DATE:	7 December 2020
LOCATION:	Crib Point Jetty Works - FSRU
EES/MAP BOOK REFERENCE:	N/A
SUBJECT:	Response to IAC further RFI in relation to chlorine discharge from the FSRU
REQUEST:	On 1 December 2020, the IAC asked the Proponent to advise if it is technically feasible to operate the proposed FSRU, or any other FSRU, in such a way to achieve a zero chlorine discharge rate, or an absolute maximum of 0.02mg/L (20µg/L), at the point of discharge.

NOTE:

1. On 1 December 2020 the IAC posed the following question seeking a response on behalf of the Proponents:

   advise if it is technically feasible to operate the proposed FSRU, or any other FSRU, in such a way to achieve a zero chlorine discharge rate, or an absolute maximum of 0.02mg/L (20µg/L), at the point of discharge.

2. This question concerns the discharge of seawater from the regasification system which is proposed to be the subject of EPR ME01A.

Is it technically feasible to operate the proposed FSRU regasification in such a way as to achieve a chlorine discharge rate of 0 mg/L, or an absolute maximum of 0.02 mg/L, at the point of discharge?

3. While it is possible to operate the FSRU to achieve a chlorine discharge of zero by avoiding electrolysis altogether, this is not practicable at all times when the FSRU is operating.

4. A reduction in chlorine discharge to 0.02mg/L is technically feasible, and has consequences for maintenance and operation including:

   a. no biofouling prevention, or very limited biofouling prevention, will require an increased maintenance and cleaning regime;

   b. inefficiency including cost, shut down and onshore waste disposal; and

   c. potential for shut down of one train co-inciding with periods of high gas demand.

Is it technically feasible to operate a different FSRU regasification system in such a way as to achieve a chlorine discharge rate of 0mg/L, or an absolute maximum of 0.02mg/L, at the point of discharge?

5. Possibly. AGL understand this question to be whether there are alternative technologies for biofouling prevention other than electrolysis. As explained in Technical Note 035[1], AGL has been working with the FSRU supplier on possible design options to reduce chlorine levels, including utilising alternative technologies. Through Hoegh LNG, the Proponents are not aware of any operating FSRU or comparable land based facility using seawater that is operated to achieve a chlorine discharge of 0mg/L.

6. Some potential alternative technologies include (limited to the question of chlorination):

    a. Ultrasonic growth prevention system: This system would require ultrasonic transmitters to be fitted to the seawater piping. The ultrasound prevents biofilm and micro-organisms from adhering to the equipment surfaces. This technology has not been tested for use in a regasification system or with large seawater volumes. As such, use of this system would require verification that installing ultrasonic transmitters on the regasification sea water heat exchanger will not impact the equipment or the performance or safety of the regasification system.

    b. Ultraviolet growth prevention system: This system uses ultraviolet (**UV**) radiation to prevent fouling of the regas systems. UV systems are large and have limited capacity to handle large volumes of water. For an FSRU using large seawater volumes, multiple UV systems would be required. Retrofitting multiple UV systems into an FSRU is complex due to space constraints.

    c. Dedicated electro-chlorination injection for the regasification system: This proposes the installation of a dedicated electro-chlorination Marine Growth Prevention System (**MGPS**) for the regasification system or relocation of the MGPS, to enable more tailored control of chlorine levels for different equipment. This would only reduce the chlorine discharge rate, not result in zero chlorine discharge.

7. The proponents understand that:

    a. The Port Kembla approval includes a residual limit of 0.02 mg/L having applied for a limit of 0.2 mg/L within one discharge point. The Port Kembla approval has not proceeded to date and is not yet subject to detailed operational requirements or approval.

    b. The Croatian FSRU approval requires no chlorine discharge. The Croatian FSRU is not operational and the available information indicates that it will rely on mechanical cleaning.

Revised EPR ME01A

8. AGL has proposed the revised EPR-ME01A in the version 3 EPRs (Document 531). EPR-ME01A contains two options, and is set out below:

    Option 1 – Varying chlorination rate at point of discharge

    Except as approved or required by the EPA, the OEMP must include requirements that seawater discharges from the regasification system must not :

[1] Document 273

a. *have a chlorine residual concentration range of between 0.05mg/L and 0.1mg/L other than at Slack Tide;*

b. *have a chlorine residual concentration of 0mg/L during Slack Tide;*

c. *not exceed a tidally averaged chlorine residual concentration of 0.0022mg/L beyond a distance of 100 metres from the FSRU; and*

d. *not exceed a temperature variation of 7°C from ambient*

Note: The time of Slack Tide is half an hour either side of high tide or low tide at Crib Point. High tide and low tide at Crib Point are to be calculated by reference to the BOM Victorian Tide Tables or other source to the satisfaction of the EPA.

Option 2 – Constant chlorination rate at point of discharge

Except as approved or required by the EPA, the OEMP must include requirements that seawater discharges from the regasification system must:

a. *have a chlorine residual concentration of 0.02mg/L ;*

b. *not exceed a tidally averaged chlorine residual concentration of 0.0022 mg/L beyond a distance of 100 metres from the FSRU; and*

c. *not exceed a temperature variation of 7°C from ambient.*

9. AGL contends for Option 1 of EPR-ME01A, on the basis that this is supported by the evidence, and has acceptable impacts for beneficial uses and the ecological character of the area. Option 1 of EPR-ME01A is a bespoke response to the particular characteristics of Crib Point and the tidal influences in Western Port Bay

10. Option 2 of the EPR-ME01A is also technically feasible. However, it will result in greater inefficiencies listed in paragraph 4 above.

11. Both Options 1 and 2 would be supported by a dedicated maintenance and management plan. A memo from the FSRU supplier, Hoegh LNG, is provided at Attachment 1 to the Technical Note, and details the additional requirements for mechanical cleaning that is required in order to ensure compliance with revised ME01A, and Option 2 in particular.

CORRESPONDENCE: N/A

ATTACHMENTS: 1 Attachment:

1. Hoegh LNG, Mechanical Cleaning of Sea Water Systems dated 4 December 2020.

ATTACHMENT 1

Hoegh LNG, Mechanical Cleaning of Sea Water Systems dated 4 December 2020.

HÖEGH LNG

Memo

Project AGL Gas Import Jetty Project	
Subject Mechanical Cleaning of Sea Water Systems	Doc. No HLNG-AGL-09093-04 Rev 02
Author HLNG / VIA, BJH	Date 04 Dec 2020
To [Name]	
cc [Name]	

Mechanical Cleaning of Sea Water Systems

The memo elaborates on mechanical cleaning of the sea water systems onboard the Crib Point FSRU and is prepared in a response to the proposed ERP ME01A, as requested by AGL.

This results from the ongoing Environmental Effects Statement (EES) process, which may see a changed acceptance level for residual chlorine concentrations of the Marine Growth Prevention System (MGPS) for the sea water discharges from the FSRU, either in terms of a lower accepted residual chlorine concentration than the 0.1ppm initially envisaged, or alternatively a regime where the 0.1ppm concentration level is maintained and the MGPS is switched off at slack tides. Please also see the proposed ERP ME01A.

A changed acceptance level of residual chlorine concentration in the discharged sea water may impact how well the MGPS is able to protect key elements of the onboard sea water systems on the FSRU. To mitigate this, cleaning operations of the vital parts, such as for instance the regas sea water heat exchangers will be initiated if it is observed in operation that the fouling cannot be sufficiently controlled with the changed chlorine residuals acceptance level, affecting the regas performance of the FSRU.

The Cleaning Operation

The majority of heat exchangers in seawater service are gasketed plate type units, which are designed for easy dismantling and cleaning when required. The units in the regas module are also plate type heat exchangers, although these units in contrast to the conventional plate heat exchangers in the engine room are of the semi-welded type where two and two plates are welded together to cassettes in order to minimize the risk for leaks but also to improve the robustness of the heat exchangers for managing the higher design pressures on the propane side. The cassettes can be cleaned on the outside like for a normal plate heat exchanger, but this will leave the propane loop open, meaning that if one heat exchanger in a train shall be cleaned, the entire train's propane loop will need to be emptied and gas free. It will therefore be natural to clean all heat exchangers in one train whenever one of the units in a train shows symptoms of increasing pressure drops or deviating temperatures that could be

Höegh LNG AS
Drammensveien 134, P.O. Box 4 Skøyen, 0212 Oslo, Norway. Tel: +47 97 55 74 00, Fax: +47 97 55 74 01
Org.no: NO 989 837 877 MVA

resulting from excessive marine growth. Once the cassettes/plates have been dismantled, the plates will be subject to cleaning by pressure wash and physical scraping/removal of any remaining elements fixed to the surfaces. In relation to such cleaning the accessible associated seawater piping and valves would also be inspected and cleaned to the extent possible.

The main seawater headers are common for the regas train, and designed for the maximum installed capacity of 750 MMSCFD in open service, based on a differential seawater temperature not exceeding 7°C. The main sea water headers will be inspected on regular intervals, and cleaned if required. The headers will typically be cleaned by means of physical scraping after having drained and opened the concerned segments.

The sea water cooling systems for the engine room consumers are protected against marine growth by the MGPS as well, and will also be inspected and cleaned as required if a change in acceptance level for residual chlorine concentrations will leave these systems more exposed to fouling. The cleaning of the engine room sea water systems is further discussed in the following section.

Impact and Duration of the Cleaning Operations

The most cumbersome and time-consuming components to clean are the sea water heat exchangers in the regas module. This does not relate solely to the cleaning part, but involves the whole operation of isolating, emptying and gas freeing the individual regas train subject for cleaning, the cleaning of the three sea water heat exchangers on the train, and then the process of drying the heat exchangers, refilling propane from the onboard storage tank, and bringing the train online again. This operation is expected to take in excess of one week for each train at first, and then be reduced to a (short) week when the crew onboard the FSRU have performed the cleaning operation a few times and have familiarised themselves with the process. HLNG may also assess whether there are modifications that can be implemented on the regas trains to ease the cleaning operation and potentially shorten the duration.

While one train is being mechanically cleaned, the other two trains will be available for regas operations.

The condition of the sea water header to the regas module, and the sea water crossover between the sea chests in the engine room will be inspected, and cleaned as required. Regas sendout will be unavailable during this cleaning operation, which may be expected to take a couple of days.

The sea water cooling systems for the engine room consumers, including the engine cooling water system and the auxiliary machinery cooling water system will also be monitored and cleaned if required. The engine room cooling water systems have redundant sea water to fresh water heat exchangers in a 2 x 100% configuration, which implies that the time it takes to isolate and clean one set of heat exchangers should not impact the performance of the vessel.

Inspection and potential cleaning (to the extent possible) of the piping for the sea water cooling systems in the engine room is expected to be carried out at the same time as for the sea water header to the regas module and the engine room crossover, i.e. for the same number of days.

Waste Management and Propane Emissions

The solid marine waste from the cleaning operation, such as e.g. mud or seaweed will be collected and sent to shore for disposal at an appropriate facility.

Pressure washers are typically used for cleaning of the sea water heat exchangers, and a dialogue should be held with the Environmental Protection Authority (EPA) and other relevant regulators in Victoria to establish whether this wash water can be drained to sea, or if it will have to be collected and sent to shore for disposal. If the latter will be required from the regulators, trays will be put in place for collecting the wash water, and the scuppers in the area will be closed as well to ensure that the wash water does not drain overboard. The collected wash water can then be pumped to portable tanks and sent to shore for disposal, or pumped to the FSRU bilge holding tank if this should have sufficient spare capacity to contain the wash water. Due to the relatively large water volumes it should however be discussed with the regulators whether the “clean” wash water may be drained to sea

In this context it should also be mentioned that if any cleaning agent or detergent is being applied in the washing process, then the wash water will be collected and disposed of through a shore facility (unless the agent would be considered “green” and allowed to be flushed to sea). The same applies if CIP cleaning of the regas sea water heat exchangers is applied as a marine growth mitigating measure.

Mechanical Cleaning Risk Management

Dedicated procedures for the cleaning operations will be developed and implemented as activities in the AMOS maintenance management database. This in particular relates to the cleaning of the regas sea water heat exchangers which involves isolation of a regas train, draining, gas freeing, drying of cleaned heat exchangers and refill of propane, in addition to the cleaning itself.

Before a cleaning operation commence a Safe Job Analysis (SJA) will be carried out by the involved crew and others potentially participating in the process, such as e.g. service engineers, to ensure that the operation will be carried out in accordance with the established procedures and the governing HSE requirements on the vessel. Trays, buckets and required equipment for collecting the waste from the washing operation, such as for instance shovels and brooms will be put in place before the cleaning is started, to limit the risk of waste spills to the environment. Spill prevention will also be a dedicated item in the cleaning operations procedure.

The SJA will also cover the human risks, and for more exposed operations, such as for instance entering the sea water headers for cleaning, a more comprehensive risk assessment may be performed prior to the operation. It could also be mentioned that the components subject to the cleaning operation are of a size that allows the crew to handle them without the aid of a lifting device

Performance risks related to the cleaning operations will be addressed in the specific cleaning operation procedures, and maintenance management plans.

Frequency of Cleaning

The cleaning of the regas SW heat exchangers and the associated sea water piping and valves is condition / performance based, and will be carried out if the regas performance is degraded from fouling in the system, caused by insufficient protection by the MGPS.

The common sea water headers are (initially) expected to be inspected, and cleaned if required on an annual basis. Regas sendout will be unavailable during this operation.

When the FSRU is in operation at Crib Point, experience will be gained on the local marine climate and how the regas performance might be affected over time due to fouling. This will further aid to tailor a cleaning regime specific to the given location.

ANNEXURE 2

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.

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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
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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.
Sand dollar (*Dendrastur excentricus*)	Sperm	15 min	Acute	Static	Fertilization (EC50)	Seawater (28‰)	14	**5** **6.4** (geomean of 3 shortest pre-exposure times)	Value selected 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.

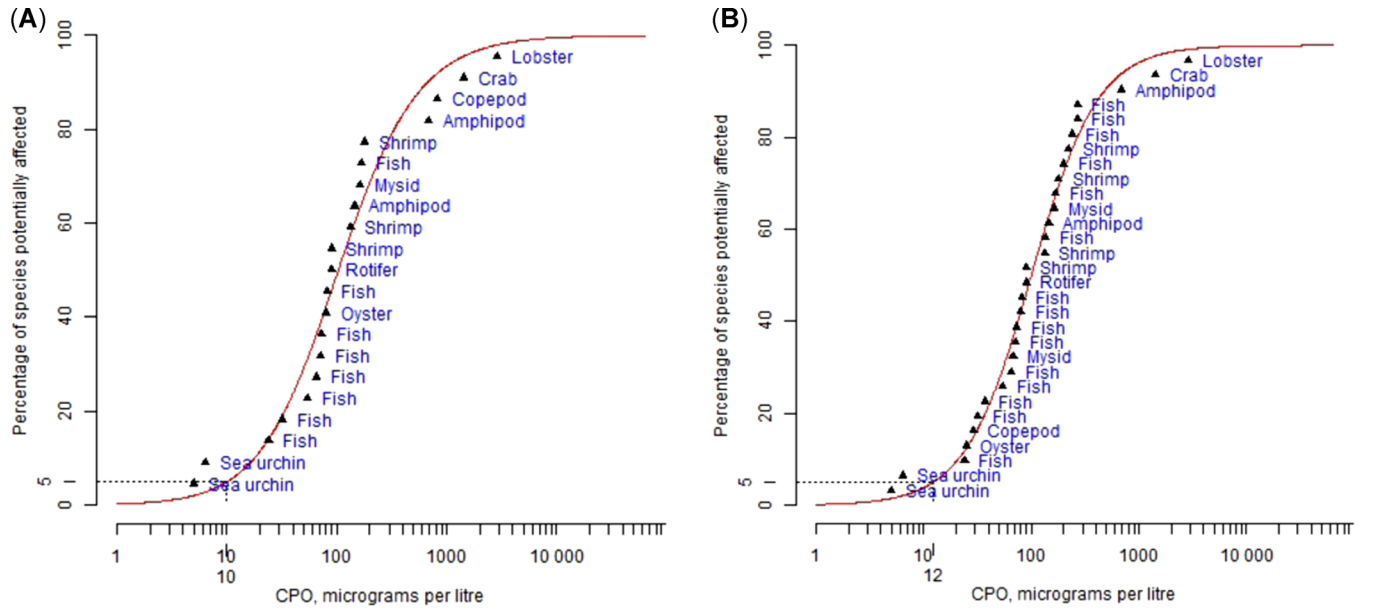

FIGURE 1: Species sensitivity distribution of selected (in bold) acute toxicity test data (flow-through plus static [15 min]). (**A**) ≥25‰ salinity data from Table 1, and (**B**) (**A**) plus <25‰ data from Table 2, showing the 95% species protection (PC95) value as an *x*-axis intercept. CPO = chlorine-produced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

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