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Effect of cooling water chlorination on entrained selected copepods species

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ABSTRACT

Laboratory experiments were conducted to assess the effects of chlorine on copepods. Three copepod groups (Calanoida, Cyclopoida and Harpacticoida) and copepod naupliar stages were collected from coastal water to assess their tolerance to chlorine. Percentage mortality of the different groups of copepods and the naupliar stages were assessed after 5, 15, 30, 45 and 60 min of exposure to chlorine residuals of 0.2, 0.5, 0.8 and 1.0 mg/l. Mortality increased with increase in exposure time and concentration of the biocide. Calanoids were relatively more tolerant to chlorine compared to the other groups. Chlorine toxicity may be classified in chronological order as calanoids > cyclopoids > harpacticoids > naupliar stages. Continuous chlorination (with total chlorine residuals of 0.1 − 0.3 mg/l at the discharge) is the general practices adopted in desalination and power stations. Considering this, results of the present study indicate expected percentage mortality of the different groups as: Calanoids 7.9%, cyclopoids 11.1%, harpacticoids 10.2% and naupliar stages − 21.6%. Therefore, mortalities of copepods in cooling water circuits are not only due to physical entrapment and entrainment processes but also due to cooling water circulation. As copepods play a vital role in marine food chains, further studies will evaluate the effect of copepods mortalities on coastal communities.

1. Introduction

Coastal desalination and power plants use large quantities of seawater for water treatment and condenser cooling purposes, which result in a large amount of heat being rejected into the environment (Huan Li et al., 2018). In addition, biocides (e.g. chlorine) are dosed for fouling control (Vinitha, Jang-seu, 2014), which is known to affect non target species like zooplankton present in the abstracted water. Once-through seawater cooled systems may use cooling water to the extent of 35 m^3 s^{-1} for a 500 MW (e) power station. The abstracted water is subjected to changes in temperature and hydrostatic pressure, in addition to biocidal dosing practiced for biofouling control. Small organisms in the abstracted water pass through the cooling water circuit in a process known as entrainment. Entrained organisms include both holoplankton (copepods, diatoms and bacteria) and meroplankton (larvae of invertebrates, fishes, juvenile shrimps) (Choi et al., 2012). Copepods are the second largest crustacean taxa and approximately 24,000 species of copepods have been described (Boxshall and Halsey, 2004). They are dominant taxa in zooplankton communities, representing 70% of oceans biomass. They also form the essential link between phytoplankton and higher trophic levels. In addition, they are ecologically important as invertebrate toxicity testing models (Raisuddin et al., 2007).

Entrainment effects can be measured either as direct effects on the entrained organisms or indirect effects on the receiving biota. Conventionally, entrainment effects on planktonic organisms have been studied at power stations looking at the survival of those organisms available or detectable (Abdul Azis et al., 2003; Vinitha et al., 2010). These studies have brought out the synergistic deleterious effects caused by physical (temperature, pressure); mechanical (velocity, passage through equipments) and chemical (biocides) stress factors on planktonic organisms. However the differential effects of various entrainment stresses can also be quantified under controlled laboratory conditions (Bamber and Seaby, 2004) for example, by the use of specialized apparatus like Entrainment Mimic Unit (EMU) (Bamber et al., 1994). In general, concentrations of residual chlorine in power plant discharges are in the range 0.1–0.2 mg/l (Allonier et al., 1999). Laboratory ecotoxicological assays on copepods, using antifouling biocides like chlorine are scant compared to other stress factors such as salinity and temperature. In addition, effects of stress factors on reproduction, oxygen consumption, sex ratio, osmoregulation and sodium regulation have been studied. Indirect effects of entrainment on the receiving water body have also been studied (Mayhew et al., 2000).

In once-through cooling water systems, entrained organisms are returned to the natural water body, where they experience rapidly decreasing temperature and biocidal concentrations, as the discharged

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water is mixed with the receiving water (Mayhew et al., 2000). The studies in the late 1970's and early 1980's with advances in sampling techniques revealed that many entrained organisms actually survived (Mayhew et al., 2000). However, in a majority of the studies carried out, effects of physical and mechanical factors were of prime importance. There were not many studies on the effects of biocides. Studies using the EMU on shrimp larvae (*Homarus gammarus*) and adult copepod (*Acartia tonsa*) subjected to mechanical, thermal, chlorine and pressure stresses synergistically and individually showed that mechanical stresses affected mostly lobster larvae and pressure changes affected mostly copepod adults. Residual chlorine caused significant mortality in the copepod and shrimp larvae, but no effect was observed on lobster larvae even at 1.0 mg/l (Bamber and Seaby, 2004). However, generalizations based on the responses of one species are not valid for other species (Bamber and Seaby, 2004) and site specific and species specific data on the response to different stress factors need to be generated. The objective of the present study was to understand the regimes of Jubail desalination and power plant electrolysis chlorination and their effect on Arabian Gulf aquatic organisms in laboratory condition by assessing the group-specific response of entrained copepods to varying concentrations of chlorine typically employed by the desalination and power stations.

2. Materials and methods

2.1. Cooling water system

The Saline Water Conversion Corporation's (SWCC) Jubail desalination and power plants (26°52'N and 49°52'E) are sourced from the Arabian Gulf and includes Multi Stage Flash (MSF) and Seawater Reverse Osmosis (SWRO) plants. The desalination and power plants produce 1.37 Mm^3 of portable water and generate 2000 MW electricity per day. Approximately 12.5 Mm^3 of feed water per day is pumped through five intakes (Fig. 1). The chlorination effects of copepods was assessed in the cooling water system of the SWCC of Desalination and Power station-Intake 11. The cooling water system at intake 11 comprises of a Trash Rack Screen (TRS) 5.44 m width, 7.1 m and Travelling Band Screens (TBS) are used where water must is screened to remove floating and suspended materials, which might damage downstream pumps and equipment. The screen mesh is attached to basket frames arranged in an endless link chain system. As the water flows through the baskets, debris is retained within the baskets, allowing the clean water to flow through the screens. The trapped screenings are carried over to the top by the revolving band screen where jets of water discharge the debris into a refuse trench for disposal. The spray header pipe is fitted with highly efficient spray nozzles to effectively backwash the screening baskets. The abstracted copepods are subjected to predation within the TRS and TBS, mechanical and biocidal stresses. To distinguish the effect of chlorine from other stressors, controlled bioassay toxicity tests must be carried out separately and this was done by exposing copepods specimens to varying chlorine concentrations.

2.2. Sampling copepods for bioassays

Copepods constituted the major fraction of zooplankton biomass at the study site and were used for the ecotoxicity assays. Copepod samples were collected from the coastal waters adjoining the SWCC station by towing a 100 µm (mesh) conical net from a boat. Samples were taken to the laboratory for analysis following protocols outlined in the International Council for the Exploration of the Sea (ICES) manual of zooplankton (Harris et al., 2000). The copepods in the samples were predominantly consisting of *Paracalanus aculeatus* (Calanoida), *Oithona rigida* (Cyclopoida) and *Euterpina acutifrons* (Harpacticoida). After collection, the copepods were manually transferred to fresh seawater prior to commencement of experiments. Dead and moribund plankton in the sample arising due to collection damage and found to settle at the bottom were manually removed and only actively swimming forms were separated out and used for experiments. Aliquots were drawn from the primary stock (density 4 Plankton mL^{-1}) of copepod and transferred into the experimental vessels (two litre separating funnels) to arrive at a final concentration of two plankton per mL.

2.3. Chlorination and residual chlorine estimation

Chlorine residuals at dosing points in the cooling water circuit of one of the intake systems (Intake 11) were measured on daily basis over

Fig. 1. Satellite view of the coastal area of the Jubail desalination and power plants showing: intake bay, outfall and mixing zone. (https://earth.google.com/web/).

12-month period (May 2017 to April 2018). The data were used to arrive at the experimental doses of chlorination to be employed. All the experiments were conducted using aged (7-day old) filtered (0.2 µm) seawater. Prior to chlorination, the chlorine demand of the seawater was ascertained and chlorine dose adjusted (after neutralizing the initial demand) to get initial concentrations of 0.2, 0.5, 0.8 and 1.0 mg/l as total residual. Residual chlorine in experimental vessels was estimated by the diethyl-r-phenylene-diamine (DPD) colorimetric method (APHA, 1998) using a HACH pocket colorimeter at the end of 5, 15, 30, 45 and 60-min exposure time.

2.4. Ecotoxicity assay by live: dead differentiation of zooplankton

The experimental duration and concentration of chlorine in the short term toxicity test were based on residual chlorine levels which are likely to be encountered or higher than to be encountered by the biota in a typical operating plant. Mortality assessment was carried out in two litre separating funnels mounted on a stand. An aliquot of natural copepod was introduced into the separating funnel containing 0.2 – 1.0 mg/l concentration of chlorine (0.2, 0.5, 0.8 and 1.0 mg/l). The organisms were incubated for one hour. At the end of 5, 15, 30, 45 and 60 min, dead and morbid plankton settling down at the bottom of the funnel were drained out. The collected plankton were immediately fixed in 4% buffered formalin for subsequent identification. The experiment was terminated after 60 min of exposure and the total plankton surviving after 60 min were preserved and counted separately to estimate percentage mortality (group-wise) after different time intervals. Identification of species within the respective groups of copepods was carried out using the methodology outlined in Conway et al. (2003).

2.5. Statistical analysis

All experiments were carried in triplicate and results presented as mean with standard deviations. Mortality in control versus treated samples was compared using Dunnet's multiple comparison tests. Tukey-Kramer multiple comparison tests were used to test differences between treatments (Sokal and Rohlf, 1979).

3. Results

3.1. Chlorine residuals

For biofouling control, the SWCC's Jubail desalination and power plants employ continuous chlorinating mode from on-line electrochemical generation of chlorine from seawater. Residual chlorine concentrations are normally in the range of 0.2–0.58 mg/l (Fig. 2). For experimental purpose, residuals of 0.2, 0.5, 0.8 and 1.0 mg/l were used after negating the chlorine demand of seawater. Since the demand was met before introduction of the test organisms, not much variation was observed in the experimental vessels.

3.2. Mortality of copepods in response to chlorine doses

Higher percent mortality of *P. aculeatus* (Calanoida) with increase in chlorine concentration and exposure time was observed (Fig. 3a). However, significant difference ($P < 0.05$) in percent mortality was observed only between controls and treatment at concentration of 1.0 mg/l. The mortality data for *O. rigida* (Cyclopoida) and *E. acutifrons* (Harpacticoida) are given in Figs. 3b and 3c, where increase in percent mortality was observed with increase in concentration of chlorine. Comparison of control with treatments at 1.0 mg/l showed significant difference only for *P. aculeatus* whereas comparisons between treatments were not significant ($P > 0.05$) for both. Results of mortality of naupliar stages of copepods were mixed. Percentage mortality increased with increase of exposure time in controls as well as in treatments (Fig. 3d). However, with respect to increasing concentrations of biocide, corresponding increase in mortality was not observed. Maximum mortality was observed at 1.0 mg/l, followed by 0.8 mg/l; mortality at 0.2 mg/l and 0.5 mg/l concentration were similar for all the three groups of copepods tested.

3.3. Differential sensitivity in response between copepod groups

In general, *P. aculeatus* was more tolerant to chlorine doses compared to *O. rigida* and naupliar stages. Both *P. aculeatus* and *E. acutifrons* were found to be equally susceptible at higher concentrations of 1.0 mg/l. However, *P. aculeatus* was more tolerant compared to *E. acutifrons* at concentration range of $0.2 - 0.8$ mg/l. There was no difference in mortality of *O. rigida* compared with *E. acutifrons* and both were found to be equally susceptible (Table 1). However, comparison of mortality of *O. rigida* with that of naupliar stages showed that the former were more tolerant to concentration ranges of $0.2 - 0.8$ mg/l, but were equally susceptible to 1.0 mg/l concentration. Comparison of mortality of *E. acutifrons* with that of naupliar stages showed that the former were more tolerant to biocidal treatments, as compared to naupliar stages.

4. Discussion

Marine planktonic, upon entering cooling water systems, are subjected to entrainment effects for a brief time period, usually ranging from less than a minute to about five minutes, depending on various factors, wherein they are exposed to extremes of temperature, hydrostatic pressure, biocides and mechanical stress factors. Field and laboratory studies on mortality of zooplankton resulting from passage through cooling water systems of power stations have been carried out to assess the environmental impact of such discharges (Bamber and Seaby, 2004). However, these studies do not throw light on the impact of the individual factors on entrained organisms. To assess the individual effects, laboratory assays using specific plankton groups are required. Furthermore, the concentration of the biocide encountered by these organisms at different season in the cooling system would vary. Data on the distribution of biocide levels at intake 11 in the cooling water system of the Jubail desalination and power plants showed instability in the residual chlorine concentration from day to day. However, residual chlorine levels were found to range from 0.20 to 0.35 mg/l (Fig. 2). The residence time of seawater in the cooling system usually ranges from 5 to 10 min, during which the planktonic forms are initially subjected to high chlorine levels at the dosing point. As copepods travel through the cooling system, they are subjected to decreasing biocide levels are as a result of interaction of chlorine with organic and inorganic matter present in cooling water (Sriyutha Murthy et al., 2011).

In the present study, three groups of copepods belonging to the classes by Calanoida (*P. aculeatus*), Cyclopoida (*O. rigida*), Harpacticoida (*E. acutifrons*) and their naupliar stages were chosen based on their abundance in the study area. All the four groups of copepods studied suffered mortalities on exposure to chlorine. Literature reports a mixed response by copepods to entrainment effects. One such study by Heinle (1976), carried out at three American Power plants, reported that copepods (including *Acartia tonsa*) were not affected by mechanical or temperature effects after passage through circuits, but suffered "extensive mortalities" due to exposure to chlorine. Bamber and Seaby (2004) summarized that 20% mortality of the copepod *A. tonsa* would be expected under standard power plant operating conditions. This figure of 20% mortality was observed when hydrodynamic forces, biocides, temperature and pressure were all in play. Another study (El-din, 2004), carried out in coastal waters receiving industrial discharges, showed that Copepoda, Mollusca, Polychaeta and to some extent Chaetognatha were able to adapt to stress factors. They showed resistance to chlorine at 0.1 mg/l and temperatures up to 36.0 °C. Entrainment effects in all the above mentioned studies were quantified in

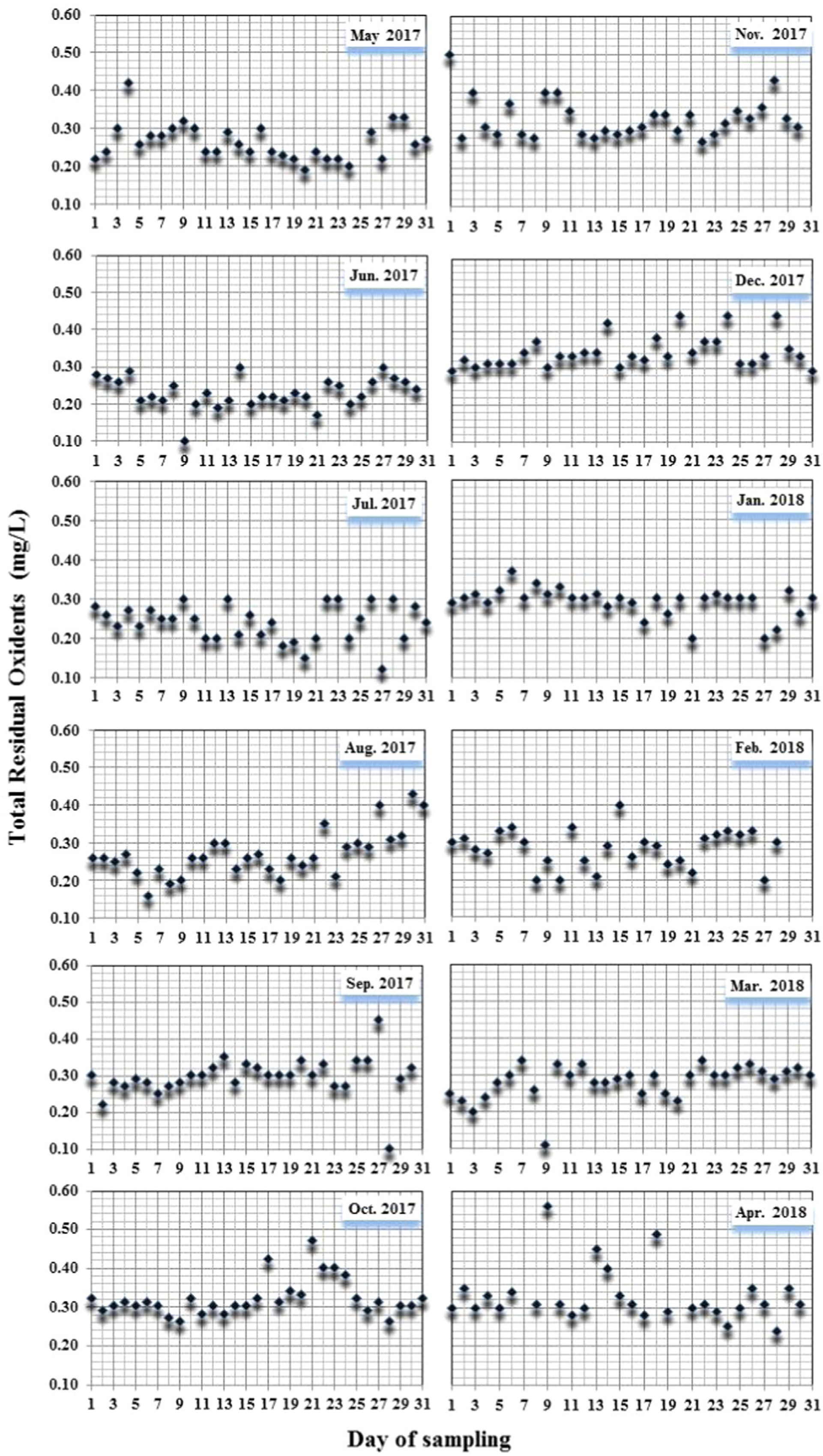

Fig. 2. Residual chlorine in cooling water of SWCC Jubail desalination and power plants during May 17- April 18.

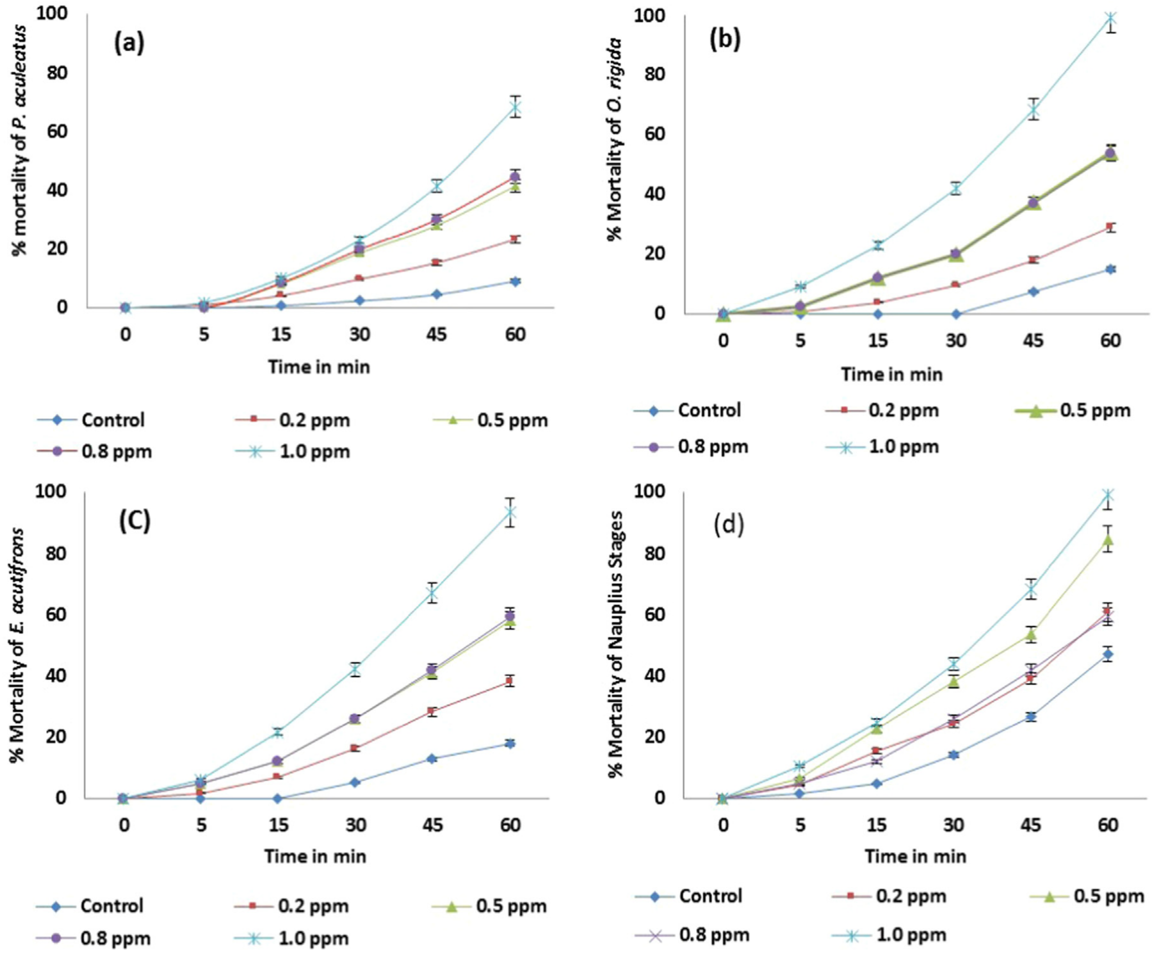

Fig. 3. Response of different groups of copepods to varying chlorine doses a) Calanoid species b) Cyclopoid species c) Harpacticoid species and d) Naupliar stages of copepods.

Table 1
Mortalities between groups of copepods tested after 60-min exposure to chlorine compared to natural mortality (control).

Groups	Control[a]	0.2 mg/l	0.5 mg/l	0.8 mg/l	1.0 mg/l
Calanoid Vs Cyclopoid	1.6	3.0	2.8	2.7	2.7
Calanoid Vs Harpacticoid	1.1	2.3	2.4	2.3	2.1
Calanoid Vs Nauplius	4.5	7.2	6.8	6.7	5.6
Cyclopoid Vs Harpacticoid	1.0	2.0	2.0	2.0	2.0
Cyclopoid Vs Nauplius	2.7	4.8	4.5	4.6	3.7
Harpacticoid Vs Nauplius	4.0	6.1	5.7	5.8	5.2

[a] Natural mortality.

power station cooling water systems, where environmental conditions vary at different points and replication of results to check for validity is limited. The observed percentage mortality for *P. aculeatus* in the present study were marginally higher compared to those reported for *Limonocalanus macrurus* (5%) and *Cyclops bicuspidatus* (5%) at a residual concentration of 0.9 mg/l (Davies et al., 1974). However, results of the present study are in accordance with studies by Coughlan and Davis (1981), who recorded mortalities between 4% and 10% after 1 h of chlorination. A limitation pointed out by Coughlan and Davis (1981) was differentiation of effects between species. In their study, 22% mortality of copepods was observed after 48 h of exposure at 0.24 mg/l residual chlorine. The samples included calanoids and harpacticoids and it was difficult to differentiate mortality percentages between these two groups. Comparison of percent mortality between groups of copepods showed that calanoids were more resistant than cyclopoids and harpacticoids to chlorination. However, as per Evans et al. (1986), under field conditions, calanoid copepods (*Diapgtomus sp., Eurytemora* sp. and *Limnocalanus* sp.) were more sensitive to plant passage compared to cyclopoids. Similar responses of differential sensitivity among zooplankton taxa to plant passage have been reported by Davies et al. (1974) and Wetzel (1975). Spatial distribution of copepods in the vicinity of an industrial outfall in the Gulf waters near Qatar showed that Harpacticoida (*E. acutifrons*) were abundant in the immediate vicinity, followed by Calanoida (*P. aculeatus*) and Cyclopoida (*O. rigida*) far away from the outfall (EL-Din, 2004). Compared to adult copepods, naupliar stages of all three groups (Calanoida, Cyclopoida and Harpacticoida) were found to be more susceptible to chlorination. Such effects were difficult to assess in field observations (Hoffmeyer et al., 2005).

5. Conclusions

Results of the present study revealed that adult and larval copepods are relatively tolerant to the level of chlorine in cooling water system. And, it is not anticipated that a shift in the copepod population would occur in receiving coastal waters. Copepods mortalities should be insignificant within a time frame of cooling water passage through the plant. The study ascertained the toxic effects of chlorine on representative copepods. To quantify the effect of entrainment and hydrodynamic stressors on copepods, field studies on the survival of copepods in the cooling water system should be an initiate.

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