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Decay of peracetic acid in seawater and implications for its chemotherapeutic potential in aquaculture

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ABSTRACT: Peracetic acid (PAA) is a widely applied disinfectant in aquaculture. Knowledge on PAA decay in seawater (SW) is crucial for its successful implementation in SW aquaculture systems. We investigated the decay dynamics of PAA in SW under controlled conditions to assess the potential effect of temperature, salinity and light. We also applied PAA to 22 tanks with post-smolt Atlantic salmon Salmo salar in full-strength SW (33‰) over a realistic range of therapeutic concentrations (0.15−4.8 mg l−1) to simulate relevant treatment scenarios. The study showed that PAA degrades rapidly in SW. The degradation follows exponential first-order decay with half-lives on the order of minutes to hours. Salinity and temperature significantly affected the decay of PAA, showing a 4-fold faster decay rate in full-strength SW compared to freshwater. The decay of PAA was not significantly related to the nominal concentration of PAA in the concentration range tested. The other 2 active ingredients in PAA products, hydrogen peroxide (H2O2) and acetic acid, were found to degrade at a much slower rate. H2O2 half-lives in SW were found to range from 15 to 70 h, and minimal acetate was found to be degraded when added to SW. Finally, we compiled published data on PAA decay in relevant water matrices and discussed the potential environmental impacts, mitigation options and future research.

KEY WORDS: Acetate · Amoebic gill disease · Decay kinetics · Half-life · Hydrogen peroxide · Peracetic acid

1. INTRODUCTION

Peracetic acid (PAA) or peroxyacetic acid, a biocidal peroxygen compound, constitutes the main active component in PAA-containing trade products (cf. excellent reviews by Kitis 2004 and Luukkonen & Pehkonen 2017). PAA is considered easily degradable and forms harmless residues (i.e. acetate and eventually CO2). PAA cannot persist in its pure form and is purchased solely as an acidified mixture of acetate and hydrogen peroxide:

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 & \rightarrow \text{CH}_3\text{COOOH} + \text{H}_2\text{O} \\
(\text{Acetic acid} + \text{hydrogen peroxide}) & \rightarrow \text{Peracetic acid} + \text{water}
\end{align*}
\]

Trade solutions contain PAA from 5−40 w/w% (typically between 10 and 15%), H2O2 and acetate (both ranging from 15−30%) (Kitis 2004, Muñio & Poyatos 2010, Liu et al. 2015).

PAA products have been used for over 60 yr (Greenspan & MacKellar 1951), and a number of studies have documented high disinfection efficiency against viruses, bacteria, fungi, protozoa, spores and cysts (Baldry 1983, Baldry et al. 1991, Liberti & Notar nicola 1999, Kitis 2004, Muñio & Poyatos 2010). PAA has powerful biocidal and biostatic effects, as it forms free radicals such as hydroxyl (cf. mode of action by Wessels & Ingmer 2013), is effective at low tempera-
and water upon decay (Jančula & Maršálek 2011). H$_2$O$_2$ is currently applied as a chemotherapeutant against salmon sea lice (Overton et al. 2019). However, the practice including large volumes used has recently been questioned due to treatment-related mortality and adverse environmental effects (Holan et al. 2017, Bechmann et al. 2019).

The prevalence of amoebic gill disease (AGD), caused by infestation with gill amoeba Paramoeba perurans (Adams et al. 2012), has increased markedly in Norway, with recorded cases in several different geographic locations. Currently, freshwater and H$_2$O$_2$ bathing are the most commonly practiced treatments for AGD in Norwegian salmon farming. However, neither treatment appears to be 100% effective, and the treatment resolution between laboratory trials and field practice does not always correspond well. Nonetheless, treatment with freshwater is more gentle for salmonids and seems to be more effective against amoeba than treatment with H$_2$O$_2$ (Powell et al. 2015, Hjeltnes et al. 2019).

The anti-parasitic function of PAA against AGD is currently being investigated, and there are recent studies of PAA on fish physiology and stress response (Gestro et al. 2018, Soleng et al. 2019, Liu et al. 2020). The development of new water disinfection routines and chemotherapeutants with water as a delivery matrix requires knowledge of the decay kinetics and fate of active residues to ensure safe and effective treatment regimens and to evaluate the potential adverse environmental impact on the receiving water bodies. The present study aimed to investigate central aspects of the chemical behaviour of PAA when exposed to SW at realistic treatment concentrations. To address this objective, a series of controlled in situ tests and pilot-scale trials with post-smolt salmon were conducted to identify the magnitude of PAA decay and the factors affecting decay kinetics. The discussion on the implications of the results has been contextualized for salmon sea cage production, although the information provided may still be relevant to other farmed marine fish.

2. MATERIALS AND METHODS

The study was divided into small-scale, controlled batch experiments in beakers (Section 2.1), followed by pilot-scale trials with Atlantic salmon post-smolts in full-strength SW mimicking aquaculture conditions (Section 2.2). The trials that involved fish were performed in accordance with national and EU legislation (2010/63/EU) on animal experimentation.
2.1. *In situ* beaker trials

2.1.1. Temperature effect on PAA

The temperature effect on PAA and $\text{H}_2\text{O}_2$ degradation was investigated by controlled PAA and $\text{H}_2\text{O}_2$ spiking and subsequent analysis of either PAA or $\text{H}_2\text{O}_2$ residues over time. Briefly, 34‰ SW (piped water supply from the Skagerrak) was divided into 1000 ml beakers with temperature control and with magnetic stirring and incubated at 4 different temperatures (5, 10, 15 and 20°C). A nominal PAA concentration equivalent to 1.00 mg l$^{-1}$ PAA (fresh stock solution of 1000 mg l$^{-1}$ made with Divosan Forte in Milli-Q water) was added and water samples were analysed after 0, 10, 20, 30, 45, 60, 120, 180 and 240 min. These experiments were made as true triplicates.

2.1.2. Salinity effect on PAA and $\text{H}_2\text{O}_2$ decay

The salinity effect on PAA and $\text{H}_2\text{O}_2$ degradation was investigated in 1000 ml beakers with magnetic stirring at 20°C. Water salinity matrices (0, 5, 10, 15, 20, 25, 30, 33‰) were made by mixing SW (33‰ piped water supply from the Skagerrak) with non-chlorinated municipal tap water (<0.1‰). A nominal PAA concentration equivalent to 1.00 mg l$^{-1}$ (1.6 mg l$^{-1}$ $\text{H}_2\text{O}_2$) was added to each beaker (n = 3), and water samples were analysed after 0, 15, 30, 60, 120, 180 and 240 min.

2.1.3. Light effect on PAA decay

The effect of light on PAA degradation was investigated in a similar set-up as described above. Three beakers were placed outdoors in direct sunlight and 3 beakers were placed next to these, but shielded by aluminum foil. Ambient temperature changes were monitored during the trial. A nominal PAA concentration equivalent to 1.00 mg l$^{-1}$ was added to each beaker, and water samples were analysed after 0, 5, 15, 30, 60, 120, 180 and 240 min (n = 3).

2.1.4. Decay of acetate and $\text{H}_2\text{O}_2$ at elevated nominal concentrations

$\text{H}_2\text{O}_2$ degradation was determined from 2 sets of experiments: (1) by measuring residual $\text{H}_2\text{O}_2$ over a period of 4 h (sampling at 0.25, 0.5, 1.0, 2, 3 and 4 h.) at different salinities (see Section 2.1.2) and (2) by adding $\text{H}_2\text{O}_2$ at increasing nominal concentrations (6.25, 12.5, 25, 50, 100 and 200 mg $\text{H}_2\text{O}_2$ l$^{-1}$) into SW and then measuring subsequent $\text{H}_2\text{O}_2$ residues over a period of 4 h. Decay kinetics of acetate was similarly determined as in the *in situ* beaker experiments, by adding either pure acetate (initial concentration $[\text{C}_0] = 10$ mg l$^{-1}$) to full-strength SW and taking samples for residual analysis at 0, 1, 4 and 24 h after addition. These experiments were conducted at 22°C and with the use of magnetic stirring.

2.2. Tank trials with SW and Atlantic salmon post-smolts

Fish were obtained as smolts from a neighbouring commercial recirculating aquaculture system (RAS). After the transfer to full-strength SW (33–34‰) in an experimental RAS, the fish were fed commercial diets with a daily ration equivalent to 1.5% body-weight. The fish were reared under stable and constant conditions for 3 wk prior to experiments, and no mortality was recorded during the period.

2.2.1. Fish density

The effect of fish density on PAA degradation was investigated in 8 tanks each holding 300 l of full-strength SW (33.5 ± 0.5‰, 15.2 ± 0.4°C). The tanks were stocked with 3 densities (ca. 8.2, 16.5 and 33 kg m$^{-3}$) in duplicates as well as 2 control tanks without fish. Just prior to and during the PAA exposure trial, water inlets to each tank were stopped to avoid any loss of PAA due to dilution. Pressurized air was delivered via air diffusers at the bottom of each tank to ensure sufficient oxygen and facilitate swift mixing of PAA. A quantity of 1.6 ml Divosan Forte, equivalent to a nominal PAA concentration of 1.0 mg l$^{-1}$, was added to a 500 ml beaker with tap water and immediately distributed at several locations of each tank. Water samples were collected at fixed times after PAA spiking (0, 10, 20, 30, 40, 50 and 60 min) and immediately analysed for PAA.

2.2.2. Nominal PAA concentration exposed to fish

PAA decay kinetics were investigated during simulated water disinfection trials in 10 tanks with 300 l full-strength SW as described by Soleng et al. (2019) in 3 trials. In the first 2 trials, PAA at 5 nominal con-
concentrations \( C_0 = 0.15, 0.30, 0.60, 1.20 \) and \( 2.4 \text{ mg l}^{-1} \) PAA) was added, and water samples were collected after 2, 4, 6, 15, 40 and 58 min and immediately analysed for PAA residues. The first trial included transfer of 50 post-smolts (~150 g each) to tanks with flow-through systems (15.4 ± 0.5°C, pH = 7.8−7.95, oxygen saturation 85−95%). After 25 min following transfer, water exchange was stopped and 5 min later, PAA was added to each of the closed, static tanks. The fish were exposed to PAA for 5 min and were then swiftly netted and returned to recovery tanks while water sampling continued for another 55 min. The second trial was run 2 wk after the first trial and was slightly modified, with fewer fish (i.e. 20 post-smolts of ~160 g) and an extended exposure period (30 min) before return to recovery tanks; all other procedures were as described for the first trial.

Three months later, a slightly modified third trial was conducted with the addition of PAA at a nominal concentration of 4.8 mg l\(^{-1}\). The PAA quantity was added to 2 full-strength SW tanks (500 l each) holding post-smolts and sampled and analysed as above (Soleng et al. 2019).

### 2.3. Chemical analysis

The concentration of PAA and \( \text{H}_2\text{O}_2 \) in the commercial PAA trade product (Divosan Forte\textsuperscript{®}, Lilleborg) was analysed by 2 consecutive autotitrations (0.1 M ceriumsulphate and sulphuric acid reaching transition at 960 mV to determine \( \text{H}_2\text{O}_2 \) concentration, followed by titration with 0.1 M sodiumthiosulphate to determine PAA concentration) according to the manufacturer’s protocol.

Residual PAA in SW samples was immediately analysed by the DPD method according to Falsanisi et al. (2006) and Pedersen et al. (2013) by adding 250 µl N,N-diethyl-phenylene-diamine-sulphate salt (reagent 1) into a 2.5 ml water sample. Thereafter, 250 µl of potassium iodide buffer solution (reagent 2) were added, gently mixed and allowed to react for 30 s, before the colour intensity was measured on a Hach Lange 2800D spectrophotometer at 550 nm. The absorbance values were used to calculate exact PAA concentration based on a standard curve made from a 1000 mg l\(^{-1}\) PAA stock solution with Milli-Q to vials with SW (33‰), and the absorbance was immediately measured to prevent in-vial decay.

\( \text{H}_2\text{O}_2 \) was measured according to the method of Tanner & Wong (1998) and modified as described by Arvin & Pedersen (2015) based on salinity-specific standard curves. Acetate was measured by ion chromatography (Metrohm), salinity was measured by use of a refractometer, and oxygen concentration, pH and water temperature were measured with a HQ40 multimeter (Hach).

### 2.4. Data analysis of PAA and \( \text{H}_2\text{O}_2 \) kinetics

Both PAA and \( \text{H}_2\text{O}_2 \) degradation exhibited exponential decay (Newman 1995), and the first-order decay rate constant \( (k, \text{ h}^{-1}) \) was therefore calculated using the equation:

\[
C_t = C_0 \times e^{-kt}
\]

where \( C_t \) is the concentration of PAA or \( \text{H}_2\text{O}_2 \) at time \( t \) (h), and \( C_0 \) represents the initial concentration. \( k \) was deducted from exponential regression analysis using concentrations above 0.1 mg l\(^{-1}\) only and/or calculated as the regression coefficient of ln-transformed concentration values versus time using the same set of data. The half-life \( (T_{\frac{1}{2}}) \) was calculated as:

\[
T_{\frac{1}{2}} = \frac{\ln 2}{k}
\]

### 2.5. Statistics

Statistical analyses were performed in Sigmaplot 13.0 Statistical Software (Systat). The calculated reaction rate constants and half-lives were subjected to 1-way ANOVA to test the effect of individual fixed factors. Pairwise multiple comparisons were made following the Holm-Sidak method to test for differences between groups. Data are presented as means ± SD. All tests were considered statistically significant at \( p < 0.05 \).

### 3. RESULTS

#### 3.1. In situ beaker trials

##### 3.1.1. Temperature

PAA decay in all temperature experiments was exponential (all \( R^2 > 0.997 \), \( N = 12 \)) and showed minimal variation within replicates. Temperature had a highly significantly positive effect on the decay of PAA in full-strength SW, with decay rate constants at 0.087 ± 0.001 h\(^{-1}\) at 5°C and 0.35 ± 0.012 h\(^{-1}\) at 20°C (Fig. 1). Corresponding \( T_{\frac{1}{2}} \) values were significantly inversely related to temperature, ranging from 8.1 h at 5°C to 1.9 h at 20°C (\( p < 0.001 \); Fig. 2).
3.1.2. Salinity

At all tested salinities, the PAA concentration declined exponentially over time (N = 24). Salinity significantly increased the decay rate of PAA. The decay rate constants increased linearly from 0.099 h⁻¹ in freshwater to 0.390 h⁻¹ in 33‰ SW (Fig. 3). Corresponding T½ values ranged from 6.7 h in freshwater to 1.7 h in full-strength SW. The relationship between PAA decay rate constants (y, h⁻¹) and salinity (x, ‰ or ppt) was highly significant; linear regression analysis: y = 0.0094x + 0.1084 (R² = 0.9827, p < 0.01).

3.1.3. Light

The exposure to light increased the decay rate of PAA in SW compared to under dark conditions. Four hours after addition of PAA equivalent to 1.0 mg l⁻¹, PAA was measured and ranged from 0.275–0.29 mg l⁻¹ and from 0.105–0.112 mg l⁻¹ PAA under dark and light conditions, respectively. The decay rate constant under direct light was 0.58 ± 0.03 h⁻¹ compared to 0.33 ± 0.01 h⁻¹ in the dark. Corresponding T½ values were 1.2 ± 0.06 and 2.1 ± 0.05 h, under light and dark conditions, respectively. The presence of light caused a temperature increase of 5.2°C after 4 h compared to the systems under darkness (see Section 4).

3.2. Tank trials with SW

3.2.1. Fish stocking density

Fish biomass increased the degradation of PAA to a minor degree, though not significantly (p = 0.16) at the densities tested (Fig. 4). The decay rate constants from the tanks with 33 kg m⁻³ were ca. 30% higher compared to the tanks without fish (0.332 vs. 0.249 h⁻¹), corresponding to half-lives of 2.1 and 2.8 h, respectively.

3.2.2. Nominal PAA concentration exposed to fish

PAA concentration decreased exponentially in all 22 tanks. At low PAA concentrations (0.15 and 0.30 mg l⁻¹ PAA) and at 4.8 mg l⁻¹, some variation was observed within the same treatments (Fig. 5).
The decay rates were generally higher in trial 2, although no significant effects of nominal PAA concentration were found. Over the entire nominal concentration range from 0.15 to 4.8 mg l\(^{-1}\) PAA, the decay value ranged from 0.17 to 0.39 h\(^{-1}\) with corresponding \(T_{\frac{1}{2}}\) values from 1.8 to 3.9 h.

### 3.3. Degradation of H\(_2\)O\(_2\) and acetate

H\(_2\)O\(_2\) degradation rate constants calculated from the Divosan Forte addition to different salinities ranged from 0.013 h\(^{-1}\) in freshwater to 0.05 h\(^{-1}\) at full strength SW at 20°C (Fig. 6A). There was some variation within and between salinities, and the degradation was generally positively correlated with salinity, albeit not statistically significantly. The associated \(T_{\frac{1}{2}}\) of H\(_2\)O\(_2\) ranged from 15 to 69 h.

Beaker trials with full-strength SW spiked with H\(_2\)O\(_2\) from 5 to 200 mg l\(^{-1}\) showed that the decay rates declined with increasing H\(_2\)O\(_2\) start \(C_0\) (Fig. 6B). Decay rates ranged from 0.010 to 0.036 h\(^{-1}\) corresponding to \(T_{\frac{1}{2}}\) up to 3 d.

Acetate concentration in the beakers with SW was 11.0 ± 0.1 mg l\(^{-1}\) immediately after addition and 10.8 mg l\(^{-1}\) after 4 h, and further decreased to 9.8 mg l\(^{-1}\) after 24 h. Degradation rate constants were not calculated due to the low number of samples.
4. DISCUSSION

4.1. Factors affecting PAA degradation

Generally, PAA degradation is considered a chemical oxidation process, in contrast to H$_2$O$_2$ where microbial-related enzymatic activity is the main route of degradation (Arvin & Pedersen 2015). This difference and its implications are discussed below.

4.1.1. Salinity

The in situ beaker trials conducted with different dilutions of SW showed an apparent effect of salinity on the degradation of PAA. Compared to freshwater, SW accelerated the PAA degradation 4-fold, with $T_{1/2}$ values in SW below 2 h. As bioavailable organic matter (BOD$_5$ < 1 mg O$_2$ l$^{-1}$), pH (7.8−7.95) and temperature (20°C) were similar in all trials, ion content was the only difference. PAA degradation is accelerated by the presence of transition metals (Yuan et al. 1997). Liu et al. (2014) observed significant PAA degradation in 10 and 30‰ SW but not in 10 and 30‰ saltwater made with NaCl only (Table 1). Howarth (2003) reported $T_{1/2}$ values of PAA in SW as short as 0.5 and 0.3 h when spiked with 1 and 20 mg l$^{-1}$ PAA, respectively (Table 1). All previous studies have shown that the $T_{1/2}$ values of PAA in saline water are on the order of 1–5 h, with the exception reported by de Lafontaine et al. (2009) showing a much lower decay; they demonstrated that 20 mg l$^{-1}$ PAA at 0.1–0.5°C took 3–5 d to degrade. The low $T_{1/2}$ are a significant advantage from an environmental point of view, as the active compound will only remain for a limited period of time, reducing the likelihood of spreading outside the area of operation (i.e. sea-cage production).

The chemical reactions of PAA in saline waters include formation of secondary oxidants during reaction with halide ions (Shah et al. 2015). The inorganic ion composition affects the initial PAA consumption and decay, and the addition of transition metals, i.e. Fe$_2$Cl$_3$ or KMnO$_4$ or addition of reducing compounds such as sodiumthiosulphate may be potential mitigation options to accelerate PAA decay (Henao et al. 2018b).

4.1.2. Temperature

The disinfection efficacy of PAA is positively correlated with temperature (Stampi et al. 2001); however, little information is available about temperature

Table 1. Overview of studies on peracetic acid (PAA) decomposition in seawater. Supplementary studies of PAA decomposition in other water matrices can be found in Luukkonen & Pehkonen (2017). RAS: recirculating aquaculture system

| Water source | Trade product | Nominal conc. | Degradation kinetics | Half-lives | Remarks | Reference |
|--------------|---------------|---------------|----------------------|------------|---------|-----------|
| 10 and 30‰ seawater | Lspez; E250; E400 | 1 mg l$^{-1}$ | Exponential decay | 0.8 h | Product specific degradation | Liu et al. (2014) |
| 10 and 30‰ NaCl solution | Lspez E250; E400 | 1 mg l$^{-1}$ | Linear decay | >>5 h | Room temp. | Liu et al. (2014) |
| Seawater | AQUA DES | 5 mg l$^{-1}$ | Exponential decay | 1.3 h | Data according to Table 1 | Massey (2005) |
| Seawater | AQUA DES | 50 & 100 mg l$^{-1}$ | Exponential decay | 1.9 and 5 h | Data according to Table 1 | Massey (2005) |
| Seawater | Peraclean | 15–20 mg l$^{-1}$ | Linear decay | 3–5 d | Ice-cold seawater | De Lafontaine et al. (2009) |
| Seawater | Peraclean | 20 mg l$^{-1}$ | Exponential decay | 1–2 d | 6–7°C | De Lafontaine et al. (2009) |
| Seawater (~20‰) | Sigma Aldrich | 2 mg l$^{-1}$ | Linear decay | 2–3 h | Zero-order | Chhetri et al. (2014) |
| Seawater | PERASAN | 1 mg l$^{-1}$ | Exponential decay | 0.5 h | H$_2$O$_2$ measured | Howarth (2003) |
| Seawater | PERASAN | 20 mg l$^{-1}$ | Exponential decay | 0.3 h | H$_2$O$_2$ measured | Howarth (2003) |
| Seawater | Divosan Forte | 1 mg l$^{-1}$ | Exponential decay | 1.7–8.1 h | 5–20°C | This study |
| Seawater | Divosan Forte | 0.2–4.8 mg l$^{-1}$ | Exponential decay | 1.8–3.9 h | 15°C | This study |
| Seawater | Aqua Oxides | 0.75 mg l$^{-1}$ | Exponential decay | 0.2 h | 15°C, commercial RAS with high organic matter content | L. F. Pedersen unpubl. |
impacts on PAA decay. In this study, we demonstrated that temperature had a pronounced effect on the degradation of PAA, with an estimated 9.5% increase in the decay rate constant per 1°C. This corresponds to a 4-fold increase in the temperature range tested (5–20°C).

Linear regression on the decay rate constants ($y, h^{-1}$) vs. temperature ($x, °C$) showed $y = 0.017x$ ($R^2 = 0.954$). By applying this equation for very low-temperature conditions, i.e. 0.5°C as in the case reported by de Lafontaine et al. (2009), the decay rate constant is registered at 0.009 $h^{-1}$, corresponding to a significantly low $T_{1/2}$ of more than 3 d as reported by the authors.

The temperature effect found in this study is more marked compared to that reported by Pedersen et al. (2013), who found the effect of organic matter on PAA degradation was exceedingly predominant and thereby masked the sole effect of temperature on PAA decay.

Temperature fluctuations are common in open-sea farming, and these environmental alterations may influence the kinetics of degradation when PAA is applied in sea cages or well boats. Knowledge of the effects of temperature on the degradation of PAA may provide important information that must be taken into account in its application in the field and may serve as a correction factor in using PAA at different times of the year and under varying environmental thermal conditions.

4.1.3. Light

The effect of light on PAA degradation demonstrated in the present study indicates potential involvement of photodegradation or photocatalysis. The presence of light (i.e. from sunlight) caused an approximately 20% increase in the degradation of PAA after 4 h compared to under dark conditions, with the model corrected for temperature effect. The effect of light may not have any particular consequences for the treatment efficacy of PAA or impacts on the environment but indicates a potential additional decomposition pathway (Block 1991, Zhao et al. 2008). Higashi et al. (2005) noted that PAA decomposed when exposed to UV irradiation at 182 nm. After 30 s of irradiation, they found that all PAA (0.02 wt% solution) decomposed within a short period of 3 min. There is increasing awareness about the risk of discharges from the use of chemotherapeutants in sea cage aquaculture; hence, ways of how to increase the rate of decay in SW must be explored. The effects of light on the degradation of PAA in SW provide implications on how to manage the discharge after treatment in sea cages, potentially by applying UV irradiation.

4.1.4. Fish density and organic matter

As PAA reacts with organic matter (suspended or by direct contact with surfaces), the presence of fish is expected to influence the degradation of PAA. In the current study, we found a positive correlation between PAA decay and fish density, but with some variation and with a modest impact. In freshwater, Pedersen et al. (2009) found that the $T_{1/2}$ of PAA dropped by around 40% at 35 kg m$^{-3}$ compared to tanks without fish, which was more pronounced than the reduction of 23% observed in the present study with SW under similar laboratory conditions. Information on fish density effects on PAA decay is useful and relevant in treatment water planning, emphasizing the adjustments needed to take biomass into account both from treatment and environmental perspectives.

The main factor affecting PAA consumption is the presence of organic matter (Koivunen & Heinonen-Tanski 2005, Muñío & Poyatos 2010, Henao et al. 2018a). The presence of large amounts of organic matter may lead to an instantaneous consumption of PAA (Pedersen et al. 2013, Henao et al. 2018b). This initial oxidative demand can be substantial, and the initial PAA consumption can be used as a parameter for a modified kinetic model (Haas & Finch 2001; and described by Chhetri et al. 2018 and Henao et al. 2018b). Zero to limited initial PAA consumption was observed in the present study and a simple first-order decay model was applied.

In open net-pen operations, organic matter content is expected to be low and of minor importance, whereas in land-based RASs with high feed loading, elevated organic matter content can be the main driving factor affecting PAA degradation. For example, PAA degradation was measured in a commercial brackish water RAS during water treatment with PAA (5 ml aqua oxides m$^{-3}$; $C_0 \approx 0.75$ mg l$^{-1}$ PAA); here the degradation rate was found to be 4.26 h$^{-1}$, corresponding to a $T_{1/2}$ of PAA below 10 min (L. F. Pedersen unpubl. data). From a practical point of view, contact with organic matter and/or biofilm on colonized surfaces could be a technical solution to further facilitate rapid PAA degradation and thereby reduce the discharge of PAA. A potential solution could be application of a floating wood chip compartment where PAA-enriched water could be directed.
hence facilitating rapid degradation when exposed to large surface areas (von Ahnen & Pedersen 2019). De Lafontaine et al. (2008) documented a significant effect of the presence of sediments on PAA degradation in SW, and this finding can potentially also be applied.

4.1.5. Concentration of PAA

The PAA concentrations applied in this study reflect a realistic concentration range where PAA has proven treatment efficacy against a number of pathogens (Pedersen et al. 2013, Soleng et al. 2019). Furthermore, since PAA is biocidal and very potent, the threshold level for being toxic to fish species begins at a relatively low concentration range below 5 mg l⁻¹ PAA (Straus et al. 2018).

Based on the tank trials with full-strength SW, PAA C₀ did not affect the PAA decay rate constants. A proportionally higher net removal of PAA was observed when PAA dosing increased, but the decay rates and T₁/₂ values were fairly consistent (Table 1), and an inherent consequence of the exponential decay kinetics.

The implication of PAA decay kinetics can be relevant when planning PAA water treatment regimes, recalling that treatment efficacy is a combination of de facto PAA concentration and exposure time (Rach et al. 1997). In situations dealing with readily degradable disinfectants, successful treatment requires knowledge of ‘unintended’ PAA consumption and ideally includes analytical verification on site.

4.2. H₂O₂ and acetate degradation

While PAA degradation is primarily governed by chemical oxidation processes, both H₂O₂ and acetate rely on microbial activity (Rojas-Tirado et al. 2019). When applying PAA products, H₂O₂ and acetate are directly introduced and formed during PAA degradation, eventually to become O₂ and CO₂. H₂O₂ degradation is controlled by enzymatic activity (Anderson & Miller 2001, Mishra & Imlay 2012, Arvin & Pedersen 2015), but photo-induced degradation and chemical oxidation have also been reported (Cooper et al. 1994). The concentration of H₂O₂ and hence the PAA:H₂O₂ ratio can differ substantially from product to product range-wide (Liu et al. 2015); however, common PAA and H₂O₂ concentrations are within the same order of magnitude. Recalling the low dose of PAA applied, the associated H₂O₂ is often on the order of a few mg H₂O₂ l⁻¹. These H₂O₂ concentration levels are orders of magnitudes below applied anti-parasitic treatment concentrations of H₂O₂ and hence are non-toxic (Wessels & Ingmer 2013).

Addition of Divosan Forte (nominal concentration of H₂O₂ equivalent to 1.6 mg l⁻¹) to water samples with different salinities showed that H₂O₂ degraded at low rates, with T₁/₂ of up to 3 d. The degradation of H₂O₂ increased with salinity, but to a far less extent than compared to PAA, and more than 1 d was required to consume the small amount of H₂O₂. Addition of technical-grade H₂O₂ (from 6.3 to 200 mg l⁻¹ H₂O₂) to full-strength SW showed degradation rate constants from 0.01 to 0.05 h⁻¹ (half-life from 15–70 h) with decreasing half-lives at increasing H₂O₂ concentrations. Substantial variation in H₂O₂ degradation was found in both experiments. The experiments were performed in July and subsequent similar analysis of H₂O₂ degradation in SW samples from October showed degradation rates of H₂O₂ below 0.001 h⁻¹ at 5 and 50 mg l⁻¹ H₂O₂ added. In both cases, H₂O₂ degradation was tested in SW samples (incubated to 22°C) without isolating or quantifying the potential abundance of bacteria and microalgae and their effect on H₂O₂ degradation (Pedersen et al. 2019). Future studies are therefore needed to investigate to which degree H₂O₂ degradation rates are affected by light and/or seasonal abundance of microorganisms in SW samples. A study by de Lafontaine et al. (2008) showed that presence of sediment increased H₂O₂ degradation initially, but after 1–2 d, no further H₂O₂ degradation occurred, probably due to bacterial inactivation (Arvin & Pedersen 2015).

Acetate is an energy-rich and readily biodegradable carbon source for many bacteria and other microorganisms (Ricoa Canelhas et al. 2017). Acetate is directly transferred to the water during application of peracetic acid, given the composition of all PAA products. The addition of 10 mg l⁻¹ acetate to SW at 20°C also showed also a marginal decrease in acetate concentration of 1.1 mg l⁻¹ after 24 h corresponding to a decay rate of 0.004 h⁻¹ and a half-life of ~7 d.

The cause of H₂O₂ degradation is primarily related to bacterial activity, and in this particular case, impeded by lack of nutrients and low bacterial activity present at the start. More research is needed to evaluate the degradation of acetate in relation to practical PAA application and to assess bacterial regrowth issues (Zhang et al. 2019) and the potential environmental implications (see Section 4.3.). PAA including acetate abatement by bioaugmentation is an unexplored option to date, but could potentially be applied as a measure to neutralize residual compounds.
4.3. Environmental aspects and management perspectives using PAA

The rapid decay of PAA may complicate correct dosing but reduces the exposure risk to the surrounding environment and hence is favourable from an environmental point of view. The existing antiparasitic treatment with H₂O₂ requires a substantially higher concentration (500- to 1000-fold), and with a much lower rate of decay, it has recently been found to be environmentally inexpedient (i.e. effects on non-target organisms).

There are both differences and similarities between use of PAA for ballast water disinfection and aquaculture disinfection/treatment in open net pens at sea. In both cases, a certain treatment efficacy is required; for ballast water disinfection, overdosing is not as critical compared to aquaculture disinfection, where the dose to be used must not compromise fish health and welfare. It is inherent that in identifying the effective treatment dose, these 3 arbitrary criteria must be taken into consideration: (1) low environmental risk (e.g. degrades rapidly, poses no challenges to non-target organisms); (2) no substantial impact to fish health and welfare; (3) effective against the target causative agents.

The potential environmental impact of both types of application is similar; ballast water operates at a far higher PAA concentration but deals with smaller water volumes (LaCarbona et al. 2010, Hess-Erga et al. 2019). In case of excess residues of PAA during de-ballasting, different mitigating options are available, such as addition of catalase or the reducing agent thiosulphate (Luukkonen & Pehkonen 2017). It remains to be investigated whether additional harmless salts/compounds containing transition metals (i.e. KMnO₄) can be applied or whether UV has any potential to accelerate degradation of PAA, especially in the field. The environmental impact of the H₂O₂ related to PAA application is considered negligible considering the diminishing small amount of H₂O₂ applied compared to commercial sea lice operation procedures (Adams et al. 2012).

PAA products are often highlighted as degradable via the rapidly biodegradable acetate. Acetate release is not critical from a toxicological point of view, but attention has been given to potential bacterial regrowth (Kitis 2004, Zhang et al. 2019). Sánchez-Ruiz et al. (1995) confirmed longevity of coliforms after PAA treatment compared to untreated controls, which was earlier stressed by Lefevre et al. (1992). More recently, Stehouwer et al. (2013) documented acetate consumption and regrowth associated with ballast water disinfection. Biofilm growth in freshwater tanks with continuous PAA addition have been observed (Liu et al. 2017), and even the mode of acetate addition has been found to affect microbial communities (Ricâo Canelhas et al. 2018). An important benefit of PAA compared to other chemicals is that PAA does not cause formation of toxic disinfection by-products. Henao et al. (2018) recently published a comprehensive review of the potential ecotoxicological effects of PAA, in which disinfection by-products were compiled and a toxicity overview of various aquatic species was provided. They concluded that PAA does not form genotoxic or persistent disinfection by-products (see Shah et al. 2015, for protective effect of H₂O₂ on secondary oxidants), that bioaccumulation of PAA is unlikely and that environmental impacts of PAA disinfection will be minimal and transient, and that prolonged exposure to PAA is toxic mainly against bacteria and algae (Henao et al. 2018).

5. CONCLUSION

The degradation of PAA is rapid (T₁/₂ values on the order of 1–2 h), and T₁/₂ values are lower in saline water compared to freshwater. PAA degrades via acetate to CO₂ and water and does not form toxic by-products. Moreover, its degradation profile is affected by several factors including light, salinity, temperature, stocking density and nominal dose. PAA is far more environmentally advantageous to use than existing chemical treatments, especially targeting ectoparasitic infections in fish. Future research is needed to optimize the full-scale application of PAA products including measures to reduce PAA and acetate residues. The results presented and discussed are essential in the eventual use of PAA as a chemotherapeutant against diseases affecting salmon during the SW stage of production. The factors identified here must be included in risk analyses that are conducted for the application of PAA to salmon at sea.

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