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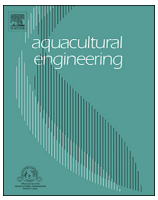

Fish survival in groundwater-desalination concentrate

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ABSTRACT

The number of groundwater brackish water desalination plants has been increasing in recent years. The concentrate streams produced by these plants are an attractive new source of water for aquaculture, but risk fish mortality associated with water composition and $CaCO_3$ precipitation. In the present work, fish survival in raw and calcium-reduced concentrate has been studied in a nearly closed system. All of the fish survived in all water types during the entire three months experiment. Nitrate, however, rapidly accumulated and mineral precipitates clogged the biofilter. These phenomena may complicate operation for longer duration, especially when high densities are employed.

1. Introduction

About 50 % of Israel's potable water supply in 2017, 670 million cubic meters (MCM), originated from desalination plants of seawater (90 %) and of brackish groundwater (10 %) (IWA, 2018). Globally, around 95 MCM of desalinated water are produced daily, 21 % of which originates from brackish groundwater, another 8 % from river water, and the rest mostly from seawater (61 %) and wastewater (6 %) (Jones et al., 2019). Typical groundwater desalination plants in Israel operate at recovery ratios of 80–90 %, which produce typical flowrates and TDS concentrations of 0.5–1.5 MCM y^{-1} and 10–15 g L^{-1}, respectively. These relatively high flowrates and salinities make these concentrates an attractive potential water source for inland aquaculture in Israel and elsewhere. Other advantages include essentially zero water costs, potential cultivation of valuable marine species, year round convenient temperature of around 22 °C and very low pathogenic risk. On the other hand, the concentrates usually contain food grade anti-scalants such as H_2SO_4 and phosphate-based polymers (McCool et al., 2013) to prevent membrane fouling, but which may affect fish health. Information regarding fish cultivation in such concentrates is currently very limited. Koina tilapia (*Oreochromis sp.*), native to Malaysia, was cultivated for nearly half a year at survival rates of 80 % and 94.7 % and normal growth rates in concentrates of two small scale desalination plants, at conductivity of 9.82–13.38 mS·cm^{-1} and low density rearing systems in Brazil (Sánchez et al., 2015). Survival rate of 95 % was reported for ocellaris clownfish (*Amphiprion Ocellaris*), grown in 25 ppt concentrate obtained after prolonged evaporation of the original 2 ppt desalination concentrate, although reduced growth rates and necrotic myositis was observed (Helvin et al., 2011). In another unpublished and uncontrolled trial, conducted nearly 10 years ago in Israel, gilthead seabream (*Sparus Aurata*) fingerlings in a flow-through system, fed by desalination concentrate, were heavily covered by mineral scale that prohibited further cultivation. The authors believe that this phenomenon occurred due to high supersaturation of the water with respect to $CaCO_3(s)$, induced by CO_2 release to the atmosphere during aeration of the rearing system (Zhang and Grattoni, 1998; Lisitsin et al., 2008), according to Eq (1).

$$Ca^{+2}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + CO_2(g) + H_2O(l) \quad (1)$$

Due to limited and contradictory data, the present work was aimed at a controlled study of fish survival in desalination concentrate. The premise was that in fish culture systems that use concentrates as growth media, substantial $CaCO_3$ will precipitate on available surfaces, including fish organs, resulting in fish mortality. It was also postulated that preliminary intense aeration of the concentrate, before its introduction into the cultivation system, would reduce $CaCO_3$ precipitation on the fish and its adverse health effects. Fish survival in aerated ("softened") and diluted concentrate, as well as in raw concentrate, was investigated in the current study.

2. Materials and methods

2.1. Procedures

The fish species chosen for the experiment was European Seabass (*Dicentrarchus labrax*) which is currently cultivated in the Kfar-Masaryk

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fish farm, Israel, where a new groundwater desalination plant recently began operation. In order to attain optimal growth conditions, the fish were grown in an air-conditioned wet-lab building, and water temperature was maintained at 25–27 °C throughout the experiment. The experiment was conducted in 15 tanks initially filled with 40 L of underground water ("control"), currently used for European seabass cultivation in the Kfar-Masaryk fish farm. Each tank contained a gravel biofilter and two 4 mm open air hoses, one of which located at the bottom of the biofilter. Air diffusers were not used to avoid clogging by mineral precipitates. External air was supplied in order to prevent CO_2 accumulation inside the lab, which could affect $CaCO_3$ precipitation. 15 European seabass fingerlings, weighing approximately 10 g each, were added to each tank at the beginning of the experiment. Each tank was fed 5 days a week throughout the experiment by 5.5 g Zemach 4992 pellets for seabream, containing 52 % and 18 % protein and fat, respectively. The fish were acclimatized for one week in the control water and then 50 % of the water was exchanged by 5 different water types (3 repetitions for each water type). The water types were as follows: A. Control, B. Raw concentrate, C. Softened concentrate, D. 50 % raw concentrate + 50 % control water, E. 50 % softened concentrate + 50 % control water. The conductivities of the raw concentrate, of the softened concentrate and of the control brackish water were 14.85, 12 and 4.4 mS/cm, respectively. Raw concentrate was obtained from the Kfar-Masarik desalination plant and transferred weekly in sealed tanks to prevent unintended CO_2 release. Softened concentrate was prepared in the wet-lab by subjecting the raw concentrate to intense aeration for 24 h, followed by precipitate settling and removal. Water exchange was conducted once a week, by reducing the water volume to 30 L in each tank, and adding fresh 10 L of the appropriate water type. The variability in water evaporation among the tanks was under 5 %. The experiment was conducted for 3 months during which survival was monitored. Fish weight was not measured, as growth rates in small tanks are not expected to be comparable to growth rates in commercial ponds. Water quality parameters were regularly monitored and included pH (pH 450, EUTECH), oxygen (OxyGuard Polaris), TDS (OAKTON SaltTester), conductivity (REF-211, Index Instruments), ammonium (Ammonium-Test, MQuant, 11117, Merck), nitrite (Nitrite-Test, MQuant, 10022, Merck), and nitrate (Nitrate-Test MQuant 10020, Merck). Calcium hardness was measured by EDTA titration (APHA, 1998) before and after water exchange. At the end of the experiment, one fish from each tank was subjected to pathological and histological examination at the central fish health laboratory, Nir David, Ministry of Agriculture, Israel.

2.2. Analyses

Ionic composition of the raw concentrate and of 1 g of re-dissolved precipitates in 1 L distilled-water, was determined by inductively coupled plasma - optical emission spectrometry (ICP-OES, Optima 3000 DV, Perkin Elmer). Mineral identification was determined by X-ray diffraction (XRD, Rikagu SmartLab 9 kV) operated at 150 mA and 45 kV at scanning rate of 1.5 degrees per minute and 0.01 ° steps. Precipitate mass of the settled slurry was determined after extraction and drying at 90 0C for 24 h.

3. Results and discussion

3.1. Concentrate softening

The composition of the raw concentrate is given in Table 1, together with some key components in the softened concentrate.

Table 1 shows, as expected, high solute concentrations, particularly calcium and inorganic carbon species. Table 1 also shows that the concentrate contains a high concentration of nitrate, which may be harmful to certain fish species (Camargo et al., 2005). Such high nitrate concentrations can be expected in concentrates originating from groundwater located beneath fertilized arable land. Table 1 shows that pH increased during aeration softening, presumably due to CO_2 release to the atmosphere, while calcium concentration and TDS decreased by 66 %–73 % and 15 %, respectively. According to this calcium removal, it was estimated that approximately 1.5 g of $CaCO_3$ were precipitated per liter of concentrate. In practice, around 1.8 g of dry precipitate per liter of concentrate was weighed. The surplus was attributed to salt crystallization during the drying of the unwashed precipitates. The elemental content of the precipitates were 339, 32, 89, 16, 6 and 54 mg g dry solids for Ca, Mg, Na, S, P, and K, respectively. These results asserted that the major cation in the solids was calcium, assumed to be in the form of $CacO_3$, while the other elements were associated with crystallization of dissolved salts during sample drying. XRD analysis of these precipitates is depicted in Fig. 1, which shows that the sample predominantly contained $CaCO_3$, with no sign of gypsum or other minerals.

Table 1
Composition of the raw and softened concentrate (mg L^{-1}). Raw and softened concentrate samples are from different batches.

Compound	Raw concentrate	Softened concentrate
Ca	827	220 - 275
Mg	485	519
Na	2,106	
K	54	
Sr	5	
S	204	
P	1	< 0.4
F	1.8[a]	
Cl	4975[a]	
NO_3^-	183[a]	
HCO_3^-	2,262[a]	189
CO_3^{2-}	30[a]	
B	0.5[a]	
SiO_2	93[a]	
TDS	11,985[a]	10,150
pH	7.0 – 7.4	8.0 – 8.5

[a] Data from desalination plant (with permission).

3.2. Fish cultivation

Fish were cultivated in 5 water types: A. underground brackish water ("Control"), B. Raw concentrate ("100 % brine"), C. Softened concentrate ("100 % softened"), D. 50 % raw concentrate + 50 % control ("50 % brine") and E. 50 % softened concentrate + 50 % control ("50 % softened"). The reason for testing growth in mixed water types was to evaluate the potential alternative of water mixing on fish health. It was presumed that fish survival in raw concentrate would be low due to CaCO3 precipitation on fish organs. However, unexpectedly, 100 % survival was observed in all water types during the entire 3 months experiment (except one mortality in a control tank). No build-up of precipitates on the fish was observed. Nevertheless, substantial mineral precipitation was observed inside the biofilters of the tanks fed with raw concentrate and some precipitation in the tanks fed by 50 % raw concentrate. These precipitates had to be washed out in order to avoid biofilter clogging. This observation led to the conclusion that the biofilter in the raw concentrate tanks adventitiously served as a softening reactor. The effectiveness of the biofilter in removing calcium from the water was attributed to three factors. A. high surface area of the gravel, B. air bubbling inside the filter, and C. low rate of concentrate addition, of about 25 % of the tank's volume once a week, whereas the time needed to reach equilibrium in terms of calcium precipitation was around 6–8 h (data not shown). The fact that CaCO3 precipitation was not observed at all in the other tanks was attributed to the lower concentrations of calcium in the feed water, as well as to the lower pH levels in these tanks, as shown in Fig. 2.

The relatively constant pH levels in the tanks fed by raw concentrate

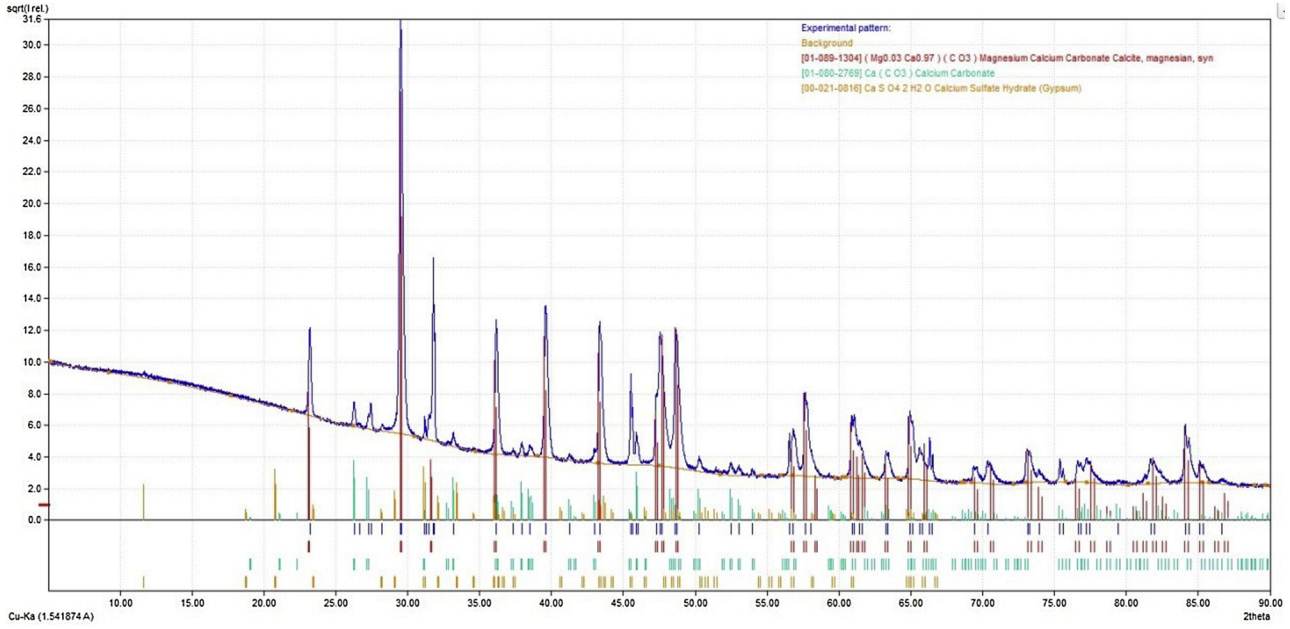

Fig. 1. XRD pattern of precipitates originated during concentrate aeration.

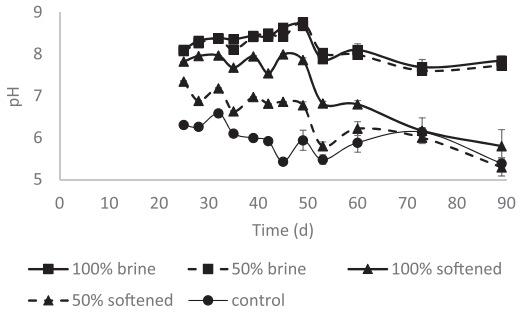

Fig. 2. pH during the experiment.

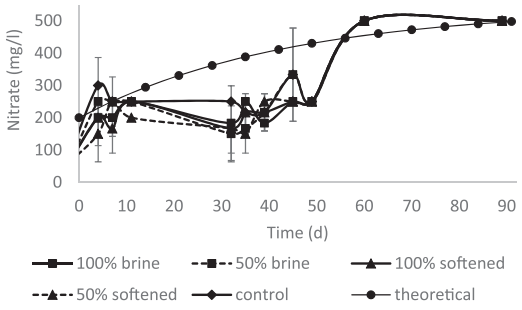

Fig. 3. Nitrate concentrations during the experiment.

and by 50 % raw concentrate, was attributed to the high concentration of the carbonic system, which provided high buffer capacity. During softening, the carbonic system concentration decreased dramatically, as both CO2 and CO32- were removed by stripping and by CaCO3 precipitation, respectively. The softened concentrate, therefore, had a much lower buffer capacity than the raw concentrate. The pH decrease in the tanks fed by softened concentrate and by control water was attributed to acidity release by nitrification. This acidity had little effect in the tanks fed by raw concentrate due to the aforementioned high buffer capacity. The presence of nitrification was appreciated by nitrate accumulation up to a concentration of 500 mg L-1 (113 mg L-1 as N) in all of the fish tanks, as depicted in Fig. 3. Fig. 3 also depicts the theoretical accumulation of nitrate, assuming complete ammonia conversion to nitrate, 4.5 % of NH3-N release per g feed (Summerfelt and Penne, 2007), and extraction of 5 liters of tank water before fresh water addition and during a weekly water exchange routine.

The relatively high difference between the theoretical and empirical nitrate concentrations, shown in Fig. 3, was attributed to the low accuracy of the nitrate determination method. Interestingly, differences in the dissolved calcium concentration in the tanks were not very high, as depicted in Fig. 4.

Fig. 4 shows that the dissolved calcium concentration increased in all tanks as expected. In the control and softened concentrate tanks, calcium was not expected to precipitate, as pH levels in these tanks were low. In the raw concentrate tanks, however, pH levels were relatively high, and calcium concentrations were stabilized toward the end of the experiment, probably due to precipitation of $CaCO_3$ in the biofilter. These findings suggested that fish survival in raw and diluted concentrate water depended not only on feed water composition, but also on operational parameters such as water exchange rate, presence of a nitrification biofilter and fish density. It was further postulated that in flow-through fish cultivation systems, $CaCO_3$ precipitation on the fish is likely, because of the high load of calcium and absence of nitrification. On the other hand, in closed systems, low calcium load and acidity addition due to nitrification are expected to hinder $CaCO_3$ precipitation on the fish or elsewhere.

Oxygen concentration in the fish tanks was sufficient, but decreased over time, as depicted in Fig. 5, probably as result of fish growth and organic solids and ammonium oxidation in the biofilter.

The conductivity of the culture water after replacing 50 % of the

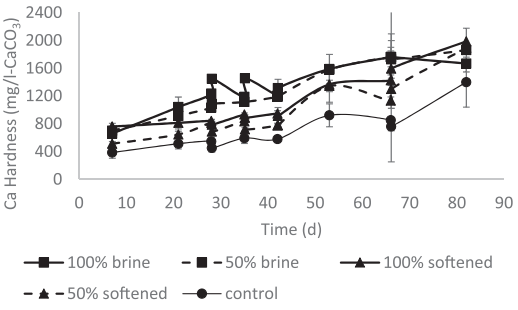

Fig. 4. Calcium concentrations during the experiment.

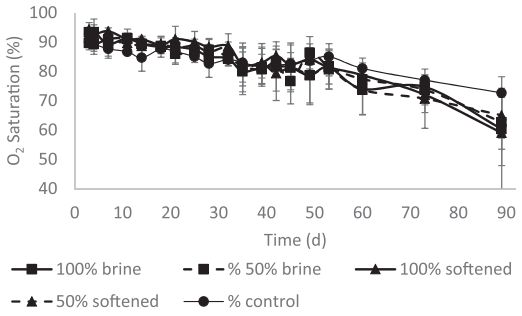

Fig. 5. Oxygen saturation levels during the experiment.

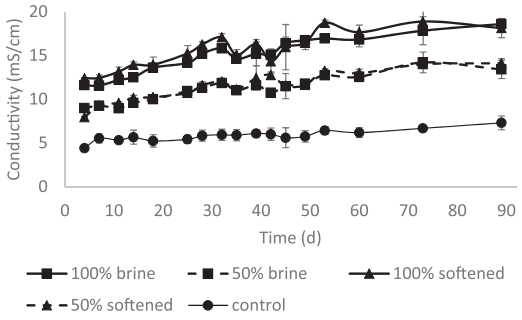

Fig. 6. Conductivity levels during the experiment.

initial brackish water (control water used of acclimatization) is depicted in Fig. 6, which shows that conductivity increased in all tanks during the experiment. These values corresponded well with the initial levels, and reflected the exchange of water and evaporation.

Ammonia and nitrite concentrations were below the detection levels during the entire experiment, except at the last week, when low levels of nitrite and ammonia were detected in the softened concentrate, 50 % softened concentrate and control tanks. The presence of these N species was attributed to the low pH in these tanks at the end of the experiment, which may have hindered nitrification.

According to pathological and histological examination of one fish from each tank at the end of the experiment, all fish were in relatively good health but showed signs of low to mild stress, that is not uncommon in fish cultivated in aquaculture facilities. Except for one fish (in 50 % softened brine), the external visual and microscopic appearance of all fish was good. Microscopic examination of liver, kidney and gut of all of the examined fish also revealed no pathological symptoms. In fish grown in raw concentrate, mild gills hyperplasia and high melanomacrophage center (MMC) increase in the spleen were observed. In fish grown in 50 % raw concentrate, mild hyperplasia in the gills of one fish and mild MMC increase in the spleen of two fish were observed. In fish grown in softened concentrate, low and high MMC increase in the spleen was observed. In fish grown in 50 % softened concentrate, high and mild visceral granuloma in the spleen was observed in two fish. In fish grown in the control water (underground brackish water), mild and high MMC increase in the spleen was observed.

4. Conclusions

The present work showed that fish survived for 3 months in raw, softened and diluted concentrate originating from brackish-groundwater desalination plant. This finding encourages further research in using such water for commercial fish cultivation. In order to achieve high survival rates of fish grown in desalination concentrate, control of $CaCO_3$ saturation level is required. This can be achieved by low exchange rate together with nitrification, by mixing the concentrate with water containing low Ca concentrations, or by preliminary removing calcium by aeration. When using low exchange rate, clogging of the biofilter by $CaCO_3$ precipitates may add to operational complexity and adds risk of ammonia and nitrite accumulation due to lower space available to nitrification bacteria. Extra attention must be given to nitrate concentrations, as the raw concentrate may contain high nitrate concentrations, as in the current case (150–180 mg L^{-1}). In the current experiment, nitrate concentration in the fish tanks exceeded 500 mg L^{-1} in just 3 months of cultivation under an average daily exchange rate of around 3.5 %. In intensive fish farms, where fish density may be 10 times higher than in the present work, nitrate will accumulate at a much faster rate and will have to be removed either by denitrification or by increasing the water exchange rate. The former option adds complexity to the system, while the latter may lead to precipitation of $CaCO_3$ on the fish. Mixing the concentrate with fresh water has the disadvantage that fresh water is normally limited in semi-arid or highly populated areas, while calcium removal from the concentrate has the disadvantage of increasing the concentrate treatment costs. A pilot plant that aims to study the aforementioned options is currently under consideration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgments

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