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Direct and continuous dissolved CO_2 monitoring in shallow raceway systems: From laboratory to commercial-scale applications

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ABSTRACT

Direct and continuous measurement of dissolved CO_2 (dCO_2) is crucial for intensive aquaculture, especially in shallow raceway systems (SRS). In this work the performance of a portable dissolved CO_2 probe analyzer was tested for the effects of different aqueous solutions, pure oxygen injection and agitation. Laboratory results showed significant ($p < 0.05$) solution effects on probe performance for low (10–20 mg L^{-1}) and high (30–50 mg L^{-1}) dCO_2 concentrations. Globally performance was better in deionized water, followed by marine fish farm water and artificial seawater. Accuracy and response time were the parameters most affected by the type of solution tested. Linearity was always observed ($R^2 = 0.995$–0.999). The probe was sensitive to 1 mg L^{-1} dCO_2 increments for concentrations <6 mg L^{-1} in artificial seawater. Pure oxygen injection did not affect probe readouts, and agitation was needed for better accuracy and response time. In real marine SRS with tanks in series dCO_2 dynamics was revealed using the probe coupled to a developed flow cell. A prototype SRS was built and used to study dCO_2 dynamics without endangering cultivated fish. Generally, results obtained indicate that the probe tested although precise, is better suited for discrete, single-point dCO_2 monitoring, being a limited resource for the special needs of shallow raceway systems. As SRS represent a paradigm change in aquaculture, new water quality monitoring strategies and instrumentation are needed, especially for dCO_2. Fiber optic sensors can be a solution for continuous, multipoint monitoring, thus contributing to the understanding of water quality dynamics in hyperintensive aquaculture systems.

1. Introduction

The current environmental concerns put high pressure on the aquaculture industry forcing the development of cleaner production processes. Recirculating aquaculture systems (RAS) and shallow raceway systems (SRS) are two recent developments aiming at achieving greener production coupled with better natural resources management, which is both economic and environmental beneficial. It is consensual that RAS enables the re-use of water multiple times before discharge, using different water treatment options (e.g. filters and biofilters), while SRS reduces water usage by lowering tank water column, maximizing at the same time fish density and productivity (Øiestad, 1999; Timmons et al., 2002). However, increases in fish density and water recirculation lead to increasing concentrations of metabolites in the water, which negatively affect fish performance and the environment. Dissolved CO_2 (herein named dCO_2) is one of the metabolites whose concentration increases, not only due to fish respiration but also to bacterial activity in piping systems and biofilters (Summerfelt and Sharrer, 2004). Additionally, salinity negatively affects CO_2 removal from water, a fact that can further increase dissolved CO_2 concentrations in marine aquaculture systems (Moran, 2010). Managing dCO_2 concentration is an important issue in aquaculture. The requirement for controlling dissolved CO_2 concentration, so that it is not too low for the nitrification processes (Azam et al., 2005) and hence for the quality of recirculated water, or too high, risking to induce negative effects in fish (Gil Martens et al., 2006), makes continuous, multipoint, dissolved CO_2 monitoring a clear necessity. This is of particular importance in shallow raceways, considered hyperintensive culture systems, where the very high fish densities used, combined with multiple tanks with small water volumes, result in working "on the edge", without much time for corrective measures in case of system failure (Øiestad, 1999). Recently, under the scope of the EU funded Raceways project, real-time water quality monitoring (including dCO_2) in a commercial SRS fish farm was addressed, and the importance and difficulties of this task

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recommended further research (Borges, unpublished data). It became also evident that there is not much published work documenting important SRS aspects like design and operation (besides Øiestad, 1999 and Labatut and Olivares, 2004) and on the effects that changes in hydrodynamic characteristics may have in water quality, as pointed out by Cripps and Poxton (1993) for other fish culture tanks. Defining a SRS prototype and studying dCO_2 behavior in it can be very useful for the aquaculture industry. However, assessing dCO_2 concentration is difficult. The standard APHA procedures (Clesceri et al., 1992) are very limited, having a large margin of error when applied to saline water (Pfeiffer et al., 2011) and not enabling direct and continuous monitoring. A commercially available solution for direct dCO_2 evaluation, specified for use in aquaculture, is the OxyGuard Portable CO_2 Analyzer®. Some important features of this instrument were evaluated at laboratory scale by Moran et al. (2010) and a comparison with other dCO_2 measuring methods can be found in Pfeiffer et al. (2011). However, considering the present uniqueness of this market solution, the importance of dCO_2 evaluation in aquaculture and more specifically in shallow raceways operation, further research with this instrument is needed, covering situations closer to or in real aquaculture environments.

The present study intends to extend knowledge on the dCO_2 probe recommended for aquaculture, testing parameters like type of aqueous solution, pure O_2 injection and agitation, and to give insights on the utilization of this probe for in situ continuous operation, especially in shallow raceway systems, either in a laboratory prototype or in real aquaculture scenarios.

2. Materials and methods

2.1. Dissolved CO_2 probe characteristics and operation

All the tests described in this work were performed using an OxyGuard Portable Dissolved CO_2 Analyzer® with built-in data logging capability. This instrument is based in infrared gas absorption and was purchased with a CO_2 gas pressure sensitive probe with a thermostat for temperature compensation (referred as dCO_2 probe in this work), a battery powered transmitter with display, a battery charger and calibration accessories (beaker, stirrer and appropriate chemicals). Calibration was performed in the calibration beaker according to manufacturer instructions, using calibration fluid and stirring. In brief, calibration steps include checking calibration water for CO_2 content, generating a known amount of CO_2 by a chemical reaction and adjusting the instrument accordingly for 0 and slope. General operation instructions refer the need of a non-specified flow under the probe, an accuracy dependent on calibration, with expected "practical accuracy up to $\pm 1\,mg\,L^{-1}$" (OxyGuard, 2007), maximum battery operating time of 72 h, 15,000 values of recording capacity and output for connection to a PC (G02C2PLOG). It is also advised to calibrate for sample salinity and values close to the maximum dCO_2 expected. During this work the manufacturer recommendations were followed with some modifications, consisting in preparing standard solutions of known dCO_2 based on the reaction of sodium carbonate (Na_2CO_3, Merck®, p.a.) with citric acid ($C_6H_8O_7$, Merck®, p.a.) plus dilutions with Millipore water, and addition of solutions with a micropipette for better accuracy. This procedure was repeated for the different aqueous solutions tested, using these solutions as solvents for all the standards.

2.2. Assessment of dCO_2 probe performance

2.2.1. Experimental set-up for small scale laboratory tests

Small scale tests were done using either the OxyGuard calibration beaker (100 mL useful volume) or a laboratory glass vessel (300 mL working volume) and stirring. Further laboratory tests were conducted in a rectangular tank 32 cm long, 60 cm wide, and 5 cm water depth, kept uncovered to simulate typical SRS conditions. For discrete evaluations known concentrations of dCO_2 were obtained adding sodium carbonate and citric acid until pH < 4.5. For dynamic studies, compressed CO_2 aquarium bottles were employed (Dupla CO_2 Set Delta 400, 500 g bottles) and a flow cell was specially constructed to hold the dCO_2 probe.

2.2.2. Probe calibration

Calibrations for 20 and $50\,mg\,L^{-1}$ dCO_2 in deionized water or saline water (NaCl in deionized water, according to the manufacturer) were tested. These concentrations were chosen as they correspond to the maximum advisable for fish cultivation (Timmons et al., 2002) and the maximum range of the instrument, respectively.

2.2.3. Precision, accuracy and response time in different aqueous solutions

A series of tests was carried out in the calibration beaker with stirring, at room temperature, to evaluate precision (coefficient of variation of measurements, CV (%) = SD/mean × 100, after stabilization), accuracy (difference between known and measured values, $mg\,L^{-1}$), response time (time required to achieve a stable reading) and linearity, in the following solutions: deionized water, artificial seawater (after Aminot and Chaussepied, 1983, 3.4% salinity, without $NaHCO_3$) and marine SRS fish farm water (2.2% salinity, after elimination of the carbonate system by acidification, N_2 flushing and pH restoration). Known dCO_2 concentrations tested varied from 5 to $50\,mg\,L^{-1}$, with 3 independent runs for each concentration, and data acquisition was made every second for up to 15 min. The time to achieve 80, 95 and 99% of dCO_2 value obtained after stabilization was also calculated. The dCO_2 results obtained with the OxyGuard probe were also checked for accuracy using a Gas Sensing Electrode (GSE) from Mettler-Toledo. These measurements are based in the electrode internal pH changes due to CO_2 diffusion through the electrode membrane and it was calibrated and operated following manufacturer procedures. A specific experiment was done to compare the simultaneous response of the two instruments for dCO_2 concentrations from 5 to $35\,mg\,L^{-1}$ in deionized water.

2.2.4. Probe sensitivity to small dCO_2 increments

Sensitivity of the dCO_2 probe, defined as the ability to detect small variations in dCO_2 concentrations, was tested in artificial seawater (formulated as referred above), using the calibration beaker and stirring. Concentrations were varied by the incremental addition of $1\,mg\,L^{-1}$ dCO_2 every 5 min up to $6\,mg\,L^{-1}$ dCO_2, using a known standard solution of sodium carbonate and citric acid. The probe was calibrated to $20\,mg\,L^{-1}$ dCO_2 in NaCl solution (3.5%) and measurements were logged at 1 s intervals for 30 min.

2.2.5. Effect of pure oxygen injection

In intensive aquaculture systems, like SRS, dissolved O_2 is kept at super saturation using pure O_2 injection, which can lead to a change in dissolved gas pressures. To assess the possible effect of high dissolved oxygen concentrations in the quality of the probe measurements, small volume tests were conducted in deionized water with stirring, at room temperature, by simultaneously injecting compressed O_2 and CO_2. Dissolved CO_2 (dCO_2 probe, calibrated for $20\,mg\,L^{-1}$) and pH (pH electrode SenTix 41, WTW multi 340i)