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# Dissolved ozone destruction using ultraviolet irradiation in a recirculating salmonid culture system

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#### Abstract

The objective of this research was to determine the ultraviolet (UV) irradiation dosages required to destroy dissolved ozone in a commercial-scale recirculating salmonid culture system operated at a constant 13-15 °C. Research was conducted in the recirculating system located at the Conservation Fund Freshwater Institute (Shepherdstown, West Virginia), which contains a UV channel unit to treat 100% of the 4750 L/min recirculating water flow with an approximately 90 mW s/cm<sup>2</sup> UV irradiation dose. However, the majority of ozone destruction data was collected using a second UV irradiation unit that was used to treat a side-stream flow of water pumped from the commercial-scale recirculating system's LHO sump. The water flow in this side-stream was adjusted to 85, 170, 255, and 330 L/min (i.e., approximately 1.8–7.4% of the entire recirculating flow) so as to produce a range of different water retention times within the UV irradiation unit (i.e., 6.7, 3.3, 2.2, and 1.7 s, respectively) and thus produced UV irradiation doses of  $153.3 \pm 2.1$  mW s/cm<sup>2</sup>,  $80.4 \pm 2.6$  mW s/  $cm^2$ , 49.3  $\pm$  0.6 mW s/cm<sup>2</sup>, and 35.6  $\pm$  0.3 mW s/cm<sup>2</sup>, respectively. The results show that dissolved O3 removal across the UV irradiation unit could be modeled using first order kinetics and was dependent upon the inlet O<sub>3</sub> concentration and the retention time within the irradiation chamber. At a temperature of 13–15 °C, UV irradiation doses of 80.4  $\pm$  2.6 mW s/cm<sup>2</sup> and 153.3  $\pm$  2.1 mW s/cm<sup>2</sup> consistently removed 100% of the dissolved  $O_3$  when the inlet  $O_3$  concentration was <0.30 mg/L. A UV irradiation dose of  $49.3 \pm 0.6 \text{ mW}$  s/cm<sup>2</sup> consistently removed 100% of the dissolved O<sub>3</sub> when the inlet O<sub>3</sub> concentration was <0.10 mg/L. A UV irradiation dose of  $35.6 \pm 0.3$  mW s/cm<sup>2</sup> could not

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remove 100% of the dissolved  $O_3$  even at inlet  $O_3$  concentration of  $\leq 0.10 \text{ mg/L}$ . When dissolved  $O_3$  data was averaged for each UV dosage applied, then approximately  $91 \pm 2\%$ ,  $81 \pm 5\%$ ,  $77 \pm 1\%$ , and  $58 \pm 5\%$  of the dissolved  $O_3$  was removed when passed through UV dosages of 153.3  $\pm$  2.1 mW s/cm<sup>2</sup>,  $80.4 \pm 2.6 \text{ mW s/cm}^2$ ,  $49.3 \pm 0.6 \text{ mW s/cm}^2$ , and  $35.6 \pm 0.3 \text{ mW s/cm}^2$ , respectively. Note that the mean dissolved  $O_3$  concentrations entering the UV unit were  $0.64 \pm 0.09 \text{ mg/L}$ ,  $0.51 \pm 0.10 \text{ mg/L}$ ,  $0.41 \pm 0.06 \text{ mg/L}$ ,  $0.43 \pm 0.07 \text{ mg/L}$ , respectively, for the conditions just described.

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## 1. Introduction

Recirculating systems for salmonids can require exceptional water quality and tight biosecurity to reduce the likelihood of restricted fish growth and increased mortality (Noble and Summerfelt, 1996). To optimize water quality, recirculating systems will use water treatment processes that effectively and rapidly remove fecal matter and waste feed, because rapid removal of organic matter can minimize the amount of fine particulates, soluble organic compounds, and ammonia that they would release if given the opportunity to degrade within the recirculating system (Blancheton and Canaguier, 1995; Blancheton, 2000; Leonard et al., 2000, 2002; Summerfelt et al., 1997, 2004b; Summerfelt and Vinci, 2003). However, the organic solids that are smaller than approximately 20 µm are harder to remove using conventional settling and mechanical filtration processes, so they can accumulate within recirculating systems, especially those systems with low water exchange (Chen et al., 1993; Patterson et al., 1999; McMillan et al., 2003; Patterson and Watts, 2003a, 2003b).

Refractory organic compounds can also accumulate within recirculating systems, because these compounds are not readily biodegradable due to their size or chemical nature and because daily replacement of water is low (Hirayama et al., 1988; Schuster, 1994). There is also concern that elevated concentrations of refractory organics may restrict fish growth and eventually increase mortality rates.

Large populations of bacteria, protozoa, and micrometazoa are also supported within recirculating systems, because these microorganisms metabolize waste organic matter, ammonia, nitrite, and nitrate (Bullock et al., 1993, 1997; Blancheton and Canaguier, 1995; Hagopian and Riley, 1998; Blancheton, 2000; Leonard et al., 2000, 2002; Nam et al., 2000). Recirculating systems support large populations of microorganisms within biofilters, but microorganisms are also found within the water column and on other biofilm coated surfaces within the system (Bullock et al., 1993; Blancheton and Canaguier, 1995; Hagopian and Riley, 1998; Blancheton, 2000; Leonard et al., 2000, 2002; Nam et al., 2000). Pathogenic microorganisms may also be present within recirculating systems. Controlling these pathogens can pose difficult challenges in recirculating systems that must maintain large populations of microorganisms within their biofilter. When chemotherapeutants are used to control pathogens in recirculating systems, these compounds can kill the necessary microorganisms in the biofilter and also return to the fish culture tank (Heinen et al., 1995; Noble and Summerfelt, 1996;

Schwartz et al., 2000; Bebak-Williams et al., 2002). Also, increasing makeup water flow rates to flush chemotherapeutants from recirculating systems is typically limited by the relatively small volume of makeup water supply in comparison to the total volume of flow under recirculation.

Ozone  $(O_3)$  can be added to recirculating systems to support water treatment and improve water quality by: breaking relatively non-biodegradable refractory organic compounds into smaller and more biodegradable compounds; directly oxidizing nitrite to nitrate; and precipitating dissolved organic molecules and microflocculating colloidal organic matter, which improves their removal via settling, filtration or foam fractionation (Colberg and Lingg, 1978; Otte and Rosenthal, 1979; Rosenthal and Otte, 1980; Williams et al., 1982; Paller and Lewis, 1988; Rosenthal and Black, 1993; Brazil, 1996; Bullock et al., 1997; Summerfelt and Hochheimer, 1997; Summerfelt et al., 1997; Christensen et al., 2000; Krumins et al., 2001a, 2001b; Tango and Gagnon, 2003). Ozonation can reduce fish disease simply by improving water quality (Brazil, 1996; Bullock et al., 1997). Ozonation can improve both water quality and fish health when approximately 7-24 g ozone are added for every 1.0 kg of feed fed to a recirculating system (Brazil, 1996; Bullock et al., 1997; Summerfelt et al., 1997; Christensen et al., 2000).  $O_3$  can also be added to inactivate microorganisms. However, disinfecting the water requires maintaining a specific dissolved  $O_3$  concentration for a given contact time, which can require more  $O_3$  than is required for achieving water quality improvements (Bullock et al., 1997). Microorganism inactivation is proportional to the product of the  $O_3$  residual concentration (C) at the end of the contact vessel multiplied by the hydraulic residence time (t) of the contact tank, i.e.,  $C \times t$ . Disinfecting water can require maintaining a residual  $O_3$  concentration of 0.1–2.0 mg/L for periods of 1–30 min, depending upon the target microorganism (Wedemeyer, 1996; Liltved, 2001; Summerfelt et al., in press). Many, but not all, fish pathogens are inactivated when exposed to  $O_3$  $C \times t$  dosages of 0.5–5.0 min mg/L (Wedemeyer, 1996; Liltved, 2001; Summerfelt et al., in press).

The O<sub>3</sub> residual exiting the contact chamber must be removed before the water reaches the fish culture tanks. Supplying extended water retention times can allow normal  $O_3$ decay to eliminate residual ozone concentrations, where colder water temperatures decrease the rate that dissolved O<sub>3</sub> decomposes (Langlais et al., 1991; Cryer, 1992; Summerfelt et al., in press). Passage through a forced-ventilation packed aeration column can also remove  $O_3$  from water (Cryer, 1992; Summerfelt et al., in press), yet, air stripping will also remove dissolved  $O_2$  concentrations that are in excess of saturation, which may not be desirable in a recirculating system. Dissolved  $O_3$  is also destroyed by high intensity ultraviolet (UV) irradiation, which catalyzes the conversion of  $O_3$  to  $O_2$ (Rodriguez and Gagnon, 1991; Cryer, 1992; Hunter et al., 1998) and the combination also provides synergistic advanced oxidation effects for achieving enhanced microbial reductions or destruction of dissolved organic carbon compounds (Langlais et al., 1991). Cryer (1992) reports data on the UV irradiation dosage required to destroy low levels of dissolved O<sub>3</sub> in a case study from the Cold Lake Northern Fish Hatchery (Cold Lake, Alberta), where UV irradiation dosages as high as approximately 112,500 mW s/cm<sup>2</sup> (at end of lamp life) were required to eliminate dissolved  $O_3$  from a surface water supply when temperatures dropped to 1-4 °C. In commercial recirculating systems used to culture salmonids, water temperatures can range from approximately 10–17 °C and UV irradiation units are currently being used to ensure that all dissolved O<sub>3</sub> residuals are destroyed before the water returns to the fish culture tanks and to inactivate microorganisms within the recirculating flow (Summerfelt, 2003; Sharrer et al., 2003). However, data describing the UV irradiation dose required to destroy dissolved O<sub>3</sub> in these salmonid recirculating systems, whose water contains constituents (e.g., dissolved organic compounds and nitrite) that exert an O<sub>3</sub> demand, has yet to be provided. Therefore, the objective of this research was to use controlled experiments to determine the UV irradiation dosages necessary to achieve a given level of dissolved O<sub>3</sub> destruction within a coldwater recirculating system operated at a constant 13–15 °C.

## 2. Materials and methods

### 2.1. System details

The UV irradiation dosages required to destroy dissolved O<sub>3</sub> were determined during controlled studies conducted in the fully-recirculating system used for Arctic char growout (Fig. 1) at the Conservation Fund Freshwater Institute (Shepherdstown, West Virginia). The recirculating system has been described elsewhere (Summerfelt et al., 2004b). In summary, the recirculating system pumped 4750 L/min of water from its lowest elevation in the system, i.e., the pump sump, to its highest elevation within the system, which was at to the top of a 2.7 m diameter  $\times$  6.1 m tall fluidized-sand biofilter. Water flowed by gravity out of the top of the fluidized-sand biofilter and then cascaded and channel flowed down through a forced-ventilated aeration column, a low head oxygenation unit, and UV channel unit (all placed in series) before the water entered the 150 m<sup>3</sup> fish 'Cornell-type' double-drain circular culture tank. Approximately 7% and 93% of the total flow through the circular culture tanks was discharged through its bottom-center drain and its side-wall drain, respectively. Flow discharged through the bottom-center drain was first treated within a swirl separator before it was recombined with the flow exiting the side-wall drain. This recombined water then flowed by gravity through a microscreen drum filter before returning to the pump sump where the water recirculation process repeats itself.

The custom UV channel unit – a product jointly supplied by PRAqua Technologies LLC (Nanaimo, British Columbia, Canada) and Emperor Aquatics Inc. (Pottstown, Pennsylvania) – was installed to irradiate 100% of the 4750 L/min recirculating water flow (Fig. 1). The UV channel unit supplied a total UV dose of approximately 90 mW s/cm<sup>2</sup>. However, a second UV irradiation unit (UVLogic, model no. 02AM15, Trojan Technologies Inc., London, Ont., Canada) was used to treat a side-stream flow of water pumped from the recirculating system's LHO sump (Fig. 2) and this was the flow used to study UV destruction of ozone.

Various concentrations of ozone were generated in a pure oxygen feed gas using a corona discharge machine (model GSO40, PCI-Wedeco Environmental Technologies, West Caldwell, NJ) capable of generating 4 kg ozone per day in a purified oxygen feed



Fig. 1. The 4,800 L/min recirculating system at the Freshwater Institute (from Summerfelt et al., 2004). Drawing courtesy of Marine Biotech Inc. (Beverly, MA).

gas. The ozonated feed gas was added to the pumped side-stream water flow using the suction side of a venturi injector (5 cm diameter, Mazzei Injector Corporation, Bakersfield, CA) that was located after each pump (Figs. 2 and 3). Immediately after the venturi injector, water flowed through an inline static mixer to improve gas–liquid contacting (Figs. 2 and 3). The water flowing from each of the two pump/injector/mixer lines was combined and piped to a down flow bubble contactor (Marine Biotech Inc., Beverly, MA) where any off-gas was removed from the flow and vented out of the building (Figs. 2 and 4). The water was then directed through the UVLogic unit (Fig. 2).

The water flow in this side-stream was adjusted to 85, 170, 255, and 330 L/min (i.e., approximately 1.8–7.4% of the entire recirculating flow) so as to produce a range of different water retention times within the UV irradiation unit (i.e., 6.7, 3.3, 2.2, and 1.7 s, respectively) and thus produced UV irradiation doses of 153.3  $\pm$  2.1 mW s/cm<sup>2</sup>, 80.4  $\pm$  2.6 mW s/cm<sup>2</sup>, 49.3  $\pm$  0.6 mW s/cm<sup>2</sup>, and 35.6  $\pm$  0.3 mW s/ cm<sup>2</sup>, respectively.



Fig. 2. An ozonated feed gas was added to the pumped side-stream water flow using the suction side of a venturi injector that was located after each pump. Immediately after the venturi injector, water flowed through an inline static mixer to improve gas–liquid contacting. The water flowing from each of the two pump/injector/mixer lines was combined and sent to a down flow bubble contactor where off-gas was removed from the flow and vented out of the building. The water was then directed through the UVLogic unit and was returned to the far side of the LHO sump.

## 2.2. Determinations of UV dosages, dissolved $O_3$ concentrations, and water quality

UV irradiation doses of approximately 35, 50, 80, and 150 mW s/cm<sup>2</sup> were applied to determine the dose necessary to destroy different levels of dissolved  $O_3$ . The UV irradiation dosages applied were calculated using the following equation:

$$UV \text{ dose} = (UV \text{ intensity})(\text{exposure time})(\text{transmittance factor})$$
$$= (UV \text{ intensity}) \left(\frac{V_{\text{vessel}}}{Q}\right)(\text{transmittance factor}) = mW \text{ s/cm}^2$$
(1)

where UV intensity is the average UV irradiation intensity  $(mW/cm^2)$  that was detected in the irradiation chamber,  $V_{vessel}$  the volume of the UV irradiation chamber (i.e., 9.4 L), and *Q* the water flow rate (L/min) through the irradiation chamber. Transmittance factor was calculated using a proprietary spreadsheet provided by the supplier of the UV irradiation unit, but this calculation was based on the percentage of 254 nm UV irradiation transmitted across a 1 cm path length (%UVT) and a correlation for lamp spacing.

A magnetic flow meter (model IFS/020F, Krohne Inc., Peabody, MA) was used to measure water flow rates. Percentage of 254 nm UV irradiation transmitted across a 1 cm path length (%UVT) was measured by placing water samples into a clean cuvette with a 1 cm path length and then placing the cuvette into a spectrophotometer (model DR/4000U, Hach Chemical Company, Loveland, CO) set to display transmittance at a wavelength of 254 nm.

Dissolved ozone concentrations were measured in the water immediately before and immediately after the side-stream UV irradiation unit using Hach Chemical Company



Fig. 3. Water pumped through a venturi injector (where ozone gas was suctioned into the flow) was then passed through an inline static mixer before being piped to the down flow bubble contactor.

Ozone AccuVac Reagent Ampuls (low, medium, and high range) and a spectrophotometer (model DR/4000U, Hach Chemical Company). Water samples were collected in conjunction with the ozone sampling events and these water samples were assayed for total suspended solids, total ammonia nitrogen, nitrite-nitrogen, dissolved CO<sub>2</sub>, and alkalinity concentrations, along with the water's pH, turbidity, and true color according to methods reported previously (Summerfelt et al., 1997; Summerfelt and Sharrer, in press).

The efficiency of dissolved  $O_3$  removal across the UV irradiation unit was calculated from the concentrations of dissolved ozone at the vessel inlet ( $C_0$ ) and outlet (C) using the following equation:

percent O<sub>3</sub> removal = 
$$100 \times \frac{C_0 - C}{C_0}$$
 (2)

#### 2.3. Kinetics of ozone destruction

Ozone destruction across the UV irradiation unit was at first modeled by assuming power law kinetics:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -kC^n \tag{3}$$



Fig. 4. A down flow bubble contactor was used to remove off-gas from the side-stream flow before it entered the UV irradiation chamber.

where *C* is the concentration of dissolved  $O_3$  exiting the UV irradiation unit, *t* the mean hydraulic residence time within the UV irradiation unit, *n* the power law kinetic coefficient for ozone decay under UV irradiation, and *k* the rate constant.

To integrate Eq. (3), it can be rearranged to the following form:

$$\int \frac{\mathrm{d}C}{C^n} = -\int k \,\mathrm{d}t \tag{4}$$

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After integration, Eq. (4) for  $n \neq 1$  becomes

$$\frac{C^{(1-n)}}{1-n} = A - kt$$
(5)

where A is a constant which can be found by using initial conditions.

Eq. (5) can be rearranged to solve for C:

$$C = [k(1-n)t + A]^{1/(1-n)}$$
(6)

Then at time zero (t = 0), Eq. (6) can be rearranged to define the integration "constant" as a function of the concentration of ozone entering the UV unit ( $C_0$ ):

$$A = C_0^{(1-n)} \tag{7}$$

To develop a numerical solution, we assumed that the rate constant (k) is a power law function of the irradiation intensity:

$$k = a + bI^m \tag{8}$$

The constant factor *a* is present because ozone decays even without UV radiation. A numerical solution was developed in Microsoft Excel to find the best fit for coefficients *a*, *b*, *n*, and *m* using experimental data on  $C_0$ , *C*, *t*, and *I*. The best fit of the data was found by identifying coefficients that minimized the standard deviation between *C* measured experimentally and *C* calculated using Eq. (6):

S.D. =  $\left[\frac{\sum_{i=1}^{n} (C_{\exp} - C_{calc})^2}{n}\right]^{1/2}$  (9)

Under the power law model, results indicated that UV destruction of dissolved ozone approximately followed 1st order kinetics (i.e., n = 1.0122). Therefore, a more simple 1st order kinetic decay model was developed:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -kC\tag{10}$$

After integration, Eq. (10) becomes

$$C = C_0 e^{-kt} \tag{11}$$

where k is as defined in Eq. (8).

Under 1st order decay kinetics (Eq. (11)), the minimum S.D. (i.e., 0.07729) was produced with the following coefficients:

 $a = 0.0343, \quad b = 6.34 \text{E}\{-4\}, \quad m = 2$ 

We note that there was little difference between an m = 2 and an m = 1, but an m = 2 produced a slightly lower S.D. than m = 1.

Therefore, under the assumption of 1st order kinetics, the following numerical solution provided the best fit to the experimental data:

$$C = C_0 e^{-(0.0343 + 6.34 \times 10^{-4} \times I^2)t}$$
(12)

Alternatively, this equation can be rearranged to estimate the UV irradiation exposure time, t, required to achieve a given reduction in dissolved O<sub>3</sub>:

$$t = \frac{\ln(C/C_0)}{-0.0343 - 6.34 \times 10^{-4} \times I^2}$$
(13)

#### 3. Results and discussion

## 3.1. Experimental findings

The water temperature was 13–15 °C during these tests, while the mean quality supplied to the ozone/UV side-stream system was approximately constant (Table 1).

The results demonstrate that dissolved  $O_3$  removal across the UV irradiation unit was dependent upon the inlet  $O_3$  concentration and the retention time within the irradiation chamber (Fig. 4, Table 2). UV irradiation doses of  $80.4 \pm 2.6 \text{ mW s/cm}^2$  and  $153.3 \pm 2.1 \text{ mW s/cm}^2$  consistently removed 100% of the dissolved  $O_3$  when the inlet  $O_3$  concentration was  $\leq 0.30 \text{ mg/L}$  (Fig. 4). A UV irradiation dose of  $49.3 \pm 0.6 \text{ mW s/cm}^2$  consistently removed 100% of the dissolved  $O_3$  when the inlet  $O_3$  concentration was  $\leq 0.10 \text{ mg/L}$  (Fig. 4). A UV irradiation dose of  $35.6 \pm 0.3 \text{ mW s/cm}^2$  could not remove 100% of the dissolved  $O_3$  even at inlet  $O_3$  concentration of  $\leq 0.10 \text{ mg/L}$ .

Cryer (1992) reports that the effectiveness of dissolved  $O_3$  destruction using UV irradiation decreases proportionally with decreasing temperature. A minimum UV irradiation dose of 112,500 mW s/cm<sup>2</sup> was required to eliminate low levels of dissolved  $O_3$  when water temperatures approach 1–4 °C (Cryer, 1992). In contrast, the research published here found that a UV irradiation dose of 49.3  $\pm$  0.6 mW s/cm<sup>2</sup> was all that was required to consistently remove 100% of the dissolved  $O_3$  at 13–15 °C, when inlet  $O_3$  concentration was  $\leq 0.10$  mg/L.

The dissolved O<sub>3</sub> removal efficiency declined with increasing dissolved O<sub>3</sub> concentration (Fig. 4). When dissolved O<sub>3</sub> data was averaged for each UV dosage applied, then approximately  $91 \pm 2\%$ ,  $81 \pm 5\%$ ,  $77 \pm 1\%$ , and  $58 \pm 5\%$  of the dissolved O<sub>3</sub> was removed when passed through UV dosages of  $153.3 \pm 2.1 \text{ mW s/cm}^2$ ,  $80.4 \pm 2.6 \text{ mW s/cm}^2$ ,  $49.3 \pm 0.6 \text{ mW s/cm}^2$ , and  $35.6 \pm 0.3 \text{ mW s/cm}^2$ , respectively. Note that for the

Table 1 Mean (±S.E.) water quality supplied to the ozonation/UV irradiation side-stream flow during this study

TAN	Nitrite-N	CO <sub>2</sub>	Alkalinity	рН	Turbidity	UV	Color	TSS
(mg/L)	(mg/L)	(mg/L)	(mg/L) as		(ntu)	transmittance	(Co units)	(mg/L)
$0.4 \pm 0.1$	$0.2\pm0.0$	12.1 ± 0.5	$233 \pm 5$	7.6 ± 0.0	$1.6\pm0.2$	$90.0 \pm 0.7$	6.7 ± 1.3	$4.0 \pm 0.7$

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Table 2

Mean water flow rate, hydraulic retention time, number of samples collected for each condition, UV dose applied ( $\pm$ S.E.), inlet dissolved O<sub>3</sub> concentration ( $\pm$ S.E.), outlet dissolved ozone concentration ( $\pm$ S.E.), measured removal efficiency ( $\pm$ S.E.), and model predicted removal efficiency

Flow (L/min)	Hydraulic retention time (s)	Number of samples	UV dose (mW s/cm <sup>2</sup> )	Inlet O <sub>3</sub> concentration (mg/L)	Outlet O <sub>3</sub> concentration (mg/L)	Measured O <sub>3</sub> removal efficiency <sup>a</sup> (%)	Predicted O <sub>3</sub> removal efficiency <sup>a</sup> (%)
UV 'on'							
85	6.7	18	$153 \pm 2$	$0.64\pm0.09$	$0.08\pm0.02$	$91 \pm 2$	91
170	3.3	11	$80.4\pm2.6$	$0.51\pm0.10$	$0.13\pm0.04$	$81 \pm 5$	74
255	2.2	24	$49.3\pm0.6$	$0.41\pm0.06$	$0.15\pm0.04$	$77 \pm 1$	54
330	1.7	24	$35.6\pm0.3$	$0.43 \pm 0.07$	$0.21\pm0.05$	$58\pm5$	41
UV 'off' (co	ontrol)						
85	6.7	4	0	$0.33\pm0.07$	$0.28 \pm 0.06$	$14 \pm 2$	20
330	1.7	5	0	$0.50\pm0.06$	$0.42\pm0.06$	$16 \pm 3$	6

<sup>a</sup> Mean removal efficiencies were calculated from all of the data from each treatment, which provides higher removal efficiencies than if they were calculated from the mean inlet and outlet concentrations shown above.

conditions just described, the mean dissolved O<sub>3</sub> concentrations entering the UV unit were, respectively,  $0.64 \pm 0.09 \text{ mg/L}$ ,  $0.51 \pm 0.10 \text{ mg/L}$ ,  $0.41 \pm 0.06 \text{ mg/L}$ ,  $0.43 \pm 0.07 \text{ mg/L}$ .

Some  $O_3$  decay also occurs even without UV irradiation (see 'control' data in Fig. 4), as dissolved  $O_3$  reacts with nitrite and dissolved organic carbon. The rate of natural ozone decay has been shown to increase with increasing water temperature (Langlais et al., 1991; Summerfelt et al., in press). Therefore, UV irradiation application to ensure dissolved  $O_3$  destruction may be less critical at higher water temperatures, e.g., at 25–30 °C, but is very critical at water temperatures approaching freezing (Cryer, 1992).

It is also worth noting that the water in the recirculating system was very hard at approximately 290 mg/L (as calcium carbonate), but that surprisingly little or no lime-scale formation was observed on the quartz sleeves surrounding the UV lamps, which were manually wiped at least weekly. In general, little or no lime-scale formation has been observed within the Freshwater Institute's fully recirculating system after its biofilter has become established, possibly because the system is operated at a lower none-scale forming pH (i.e., 7.6) and possibly also due to nitrifying bacteria that consume alkalinity. In contrast, heavy lime-scale formation in the Freshwater Institute's hard water has been encountered within all flow-through systems and within the partial-reuse system if dissolved  $CO_2$  stripping is not properly balanced against  $CO_2$  production to maintain a stable water pH (Summerfelt et al., 2004a).

### 3.2. Fit of 1st order decay model with experimental findings

Although water flows were adjusted to produce exact HRTs within the UV units, the UV dosage applied during each test were approximately  $35.6 \pm 0.3 \text{ mW s/cm}^2$ ,  $49.3 \pm 0.6 \text{ mW s/cm}^2$ ,  $80.4 \pm 2.6 \text{ mW s/cm}^2$ , and  $153.3 \pm 2.1 \text{ mW s/cm}^2$ , with the variations created by changes in %UVT and irradiation recorded between replicated tests. Therefore, the exact UV dosages that corresponded with each HRT, inlet O<sub>3</sub> concentration, and outlet



Fig. 5. Dissolved  $O_3$  removal across the UV irradiation unit was dependent upon the inlet  $O_3$  concentration, retention time within the irradiation chamber, and whether the UV unit was turned on. Note that some ozone decay occurred even without UV irradiation (listed as 'control' data).

$$C = C_0 e^{-(0.0343 + 6.34 \times 10^{-4} \times I^2)t}$$
(12)

According to Eq. (12), dissolved  $O_3$  destruction follows 1st order kinetics, i.e., a given UV irradiation intensity destroys the most dissolved  $O_3$  at the longest HRT within the irradiation chamber and destroys the least dissolved  $O_3$  at the shortest HRT, which also matched the experimental findings (Fig. 5). However, the 1st order kinetics model predicts a constant dissolved  $O_3$  removal efficiency for each UV dose. The data (Fig. 5), however, indicates that dissolved  $O_3$  removal efficiency actually declines as the inlet dissolved  $O_3$  concentrations increased. Therefore, when using Eq. (12) to predict dissolved  $O_3$  concentration exiting the UV irradiation unit at a temperature of 13–15 °C, note that the predicted effluent  $O_3$  concentrations are greater than 0.4–0.6 mg/L and an underestimate when inlet  $O_3$  concentrations are greater than 0.4–0.6 mg/L.

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