

## Ozone Application and Brominated By-Products: Monitoring, Formation, and Destruction in Water Recirculating Systems for Fish Culture

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### **Abstract**

Preventing bromine and bromate from accumulating within recirculating aquaculture system (RAS) waters that contain bromide is one of the greatest challenges facing the use of ozone in RAS. This study evaluated methods for real-time monitoring of ozone and bromine in synthetic seawater and bromide containing freshwater. Dissolved ozone probes were found to effectively measure ozone in freshwater and high salinity solutions that do not contain bromide. However, a dissolved ozone probe could not detect ozone in waters that contain bromide due to the nearly instantaneous conversion of dissolved ozone to brominated compounds. An ORP probe could detect an increase in total residual oxidant (TRO = bromine) in ozonated water containing bromide. However, the ORP probe only provided a crude approximation of TRO due to large variations in the measured TRO for a given ORP. This study also examined chemical and photochemical processes that can be used to convert bromine back to the non-toxic bromide ion. UV irradiation at 100-250 mJ/cm<sup>2</sup> was effective at removing TRO concentrations of < 0.15 mg/L as Br<sub>2</sub>, but only removed an average of 32-50% at inlet TRO concentrations > 1 mg/L as Br<sub>2</sub>. Under normal conditions, i.e., without UV irradiation, bromine decay was found to depend on the ratio of bromine: ammonia and the amount of phosphate in the water. The reaction of hypobromous acid with ammonia increased the rate of bromine decay back to bromide via breakpoint bromination; this reaction was not increased by elevated phosphate concentrations. We

conclude that bromine problems can be avoided by using bromide-free salt mixes to prepare synthetic seawater. When water does contain bromide, bromine production can be minimized by applying limited ozone doses to achieve water quality improvement in RAS, using high dosages of UV irradiation or reducing agent (i.e., sulfur dioxide or thiosulfite), or treating the water using granulated activated carbon filters.

**Keywords:** Ozone; Ultraviolet irradiation; Advanced oxidation; Bromine; Total residual oxidant; Water reuse; Aquaculture; Oxidative reduction potential (ORP); Break-point bromination

## **Introduction**

Recirculating aquaculture systems (RAS) use flowing water to intensively culture fish and, by definition, they treat and reuse a high percentage of the water to maintain favorable water quality in the fish culture units. RAS are finding wider acceptance in aquaculture because they allow for greater control of the rearing environment, especially water temperature, than is possible in conventional flow-through, pond, or net pen applications (Summerfelt et al, 2001). RAS also minimize water use and place the wastes into a concentrated and relatively small volume effluent. In addition, recirculating aquaculture systems are more amenable to implementation of biosecurity measures than outdoor systems because of a smaller facility footprint, smaller makeup water supplies (preferably from either ground water or disinfected surface water), and higher level of management (Summerfelt et al, 2001). When obligate pathogens are excluded, RAS can be operated with little or no chemotherapeutic or antibiotic

use. Thus, RAS are arguably one of the more environmentally sustainable production systems for aquatic organisms.

Both obligate and opportunistic fish pathogens can accumulate in the recirculating water or in the biofilm and sediments due to the prolonged water retention times and increased substrate concentrations in RAS. As the pathogen concentration is amplified in the recirculating water, the risk of disease and potentially catastrophic loss increases. However, an internal disinfection process can be used to prevent the accumulation of fish pathogens in recirculating systems. Although disinfection of recycled process water adds to the fixed and variable costs of these systems, mitigation of potential disease occurrence has been reported with ozonation by itself (Bullock et al., 1997; Ritar et al., 2006) and with ultraviolet (UV) irradiation by itself (Farkas et al., 1986; Blancheton, 2000; Sharrer et al., 2005) or a combination of the two (Sharrer and Summerfelt, 2007; Summerfelt et al., 2009). In addition, adding ozone to the recirculating water can significantly improve water quality by removing color, oxidizing nitrite to nitrate, micro-flocculating fine particulates to improve their removal via sedimentation or filtration, and enhanced biological processing of dissolved organic molecules to reduce carbonaceous biochemical oxygen demand (Brazil, 1996; Summerfelt and Hochheimer, 1997; Summerfelt et al., 1997; Christensen et al., 2000; Krumins et al., 2001a, 2001b; Summerfelt, 2003; Summerfelt et al., 2004; Tango and Gagnon, 2003; Sharrer et al., 2005; Sharrer and Summerfelt, 2007; Summerfelt et al., 2009). In addition, the overall improvement in water quality, especially the reduction in carbonaceous biochemical oxygen demand (cBOD) and total suspended (TSS), can substantially reduce bacterial loads even though the ozone dose does not disinfect. In North America, commercial fish farms have used ozonation of recirculating water to improve water

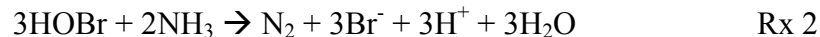
quality while culturing species that include: tilapia, rainbow trout, hybrid striped bass, Arctic char, Atlantic salmon, yellow perch, sturgeon, barramundi, and cobia. However, it is unlikely that many of these commercial fish farms provided ozone at levels sufficient to achieve significant micro-biological disinfection.

### *Bromine Formation from Ozone*

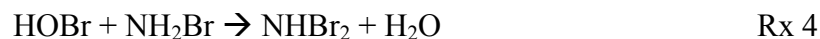
Preventing bromine and bromate from accumulating within RAS waters that contain bromide is one of the greatest challenges facing the use of ozone in such RAS. Ozone has a rapid reaction rate and forms dissolved oxygen as a reaction end product when bromide ( $\text{Br}^-$ ) is not present (Summerfelt and Hocheimer, 1997; Summerfelt, 2003). Bromide is not toxic under normal concentrations encountered. However, if sufficient bromide is present, as it is in some ground waters and natural seawater, then ozone ( $\text{O}_3$ ) can react with bromide to produce hypobromous acid ( $\text{HOBr} = \text{H}^+ + \text{OBr}^-$ ) and hypobromite ion ( $\text{OBr}^-$ ), i.e.,

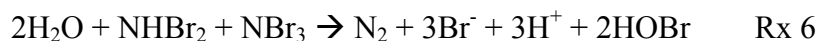


In turn, hypobromous acid can react with ammonia ( $\text{NH}_3$ ) to produce nitrogen gas ( $\text{N}_2$ ) while producing free acid ( $\text{H}^+$ ) that consumes alkalinity in a process called break-point bromination (Haag and Hoigne, 1984; Hofmann and Andrews, 2001; Tanaka and Matsumura, 2002; Tango and Gagnon, 2003; Whangchai et al., 2004), i.e.,



However, break-point bromination requires at least four sub-reactions to reach completion, i.e.,





Break-point bromination could be very useful, because the bromine produced during ozonation of seawater or other bromide containing solutions could be used to rapidly convert ammonia into nitrogen gas while it (i.e., bromine) reacts back to non-toxic bromide ions. In addition, break-point bromination could lead to the rapid decay of bromine, which is acutely toxic to fish, with an LC50 of 0.068 mg/L BrO<sup>-</sup> for rainbow trout (Fisher et al., 1999). However, when reactions 2-5 do not go to completion, then various bromamines and hypobromous acid remain and could create toxicity problems.

Phosphate enhances NH<sub>2</sub>Br disassociation into NHBr<sub>2</sub>, i.e., reaction 4 (Inman and Johnson, 1984), which could increase the overall rate of break-point bromination (Rx 2), i.e., bromine decay back to bromide, and the extent of the reaction, e.g., how much of the various bromamines and hypobromous acid remain after a reasonable reaction time.

Some saltwater RAS have reported controlling ozone addition at the foam fractionator process (Tal et al., 2009) or low head oxygenator (Wolters et al., 2009) to prevent ORP from exceeding a set-point of 250-350 mV, which provides a relatively low ozone dose that appears insufficient to create a bromine residual.

#### *Bromate Formation from Ozone*

Bromate (BrO<sub>3</sub><sup>-</sup>) is acutely toxic to non-larval fish only when concentrations exceed approximately 100 mg/l (Hutchinson et al., 1997), which is much less toxic to fish than bromine.

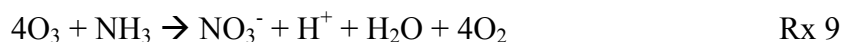
However, bromate is a known animal carcinogen (Kurokawa et al., 1986) and it can also be formed by ozonation:



However, according to Hofmann and Andrews (2001) and Tanaka and Matsumura (2002), bromate will not be formed as long as ammonia is still present in the water, because the conversion of hypobromous acid to bromamines blocks the pathway for bromate formation.

#### *Nitrate Formation from Ozone*

In addition, there are two other minor pathways that can theoretically produce nitrate ( $\text{NO}_3^-$ ) upon ozone addition (Tanaka and Matsumura, 2002):



In practice, little to no nitrate is produced via reactions 8 or 9. Additionally, nitrate is of little concern with regard to fish health until higher concentrations accumulate.

#### *Objectives*

We conducted two different studies to evaluate the effectiveness of chemical and photo-chemical reaction processes to remove ozone disinfection by-products from water containing bromide. The first study examined the formation, measurement, and decay of bromine during ozonation and UV irradiation of synthetic seawater in a RAS. The second study, (a bench top study), examined the extent, kinetics, and treatment efficiency of the reaction of bromine with ammonia at different concentrations of phosphorus.

#### **Materials and methods**

*Study #1 - Recirculating system details*

An ozonation and UV irradiation system (Fig. 1) was installed to pump and treat a side-stream flow within a large water recirculating system at The Conservation Fund's Freshwater Institute in Shepherdstown, West Virginia (Fig. 2). This side-stream system has been described elsewhere (Sharrer and Summerfelt, 2007). In summary, the side-stream system withdrew water from the head tank of the low head oxygenation unit and pumped this water through a 5-cm diameter venturi injector (Mazzei Injector Corporation, Bakersfield, CA), which entrained the ozonated oxygen feed gas into solution. The ozone in the oxygen feed gas was supplied using a PCI-Wedeco Model GSO40 (West Caldwell, NJ). Ozonated water exited the venturi injector and was passed through a 5-cm diameter inline static mixer and then a down flow bubble contactor (Marine Biotech Inc., Beverly, MA), which was used to capture and vent any off-gas from the building. Water exiting the down flow bubble contactor was piped to the inlet of the plug-flow contact chamber i.e., a U-tube contactor. Water then flowed through a UV Logic model 02AM15 UV irradiation unit (Trojan Technologies Inc., London, Ontario, Canada). UV doses ( $\text{mJ}/\text{cm}^2$ ) were determined utilizing a proprietary spreadsheet supplied by the UV unit manufacturer and the following inputs: water flow rate, UV dose measured in the unit, and % UV transmittance. The concentration of ozone generated within the oxygen feed gas was manually adjusted from 0 and 10% ozone and the oxygen feed gas was adjusted from 0 to 40 L/min until the desired ORP was achieved and stable.

The side-loop system was operated to produce flow rates of approximately 40 and 380 L/min. Water flows were measured using a Krohne Inc. (Peabody, MA) model IFS/020F magnetic flow meter.

*Study #1 - Synthetic seawater*

Synthetic seawater was created following the recipe for salt solution I and salt solution II provided by Berges et al. (2001). Natural spring water was added to the salts obtained from industrial suppliers (Tilley Chemical Company, Baltimore, MD; Barium and Chemicals, Steubenville, OH; Cargill Salt Company, Minneapolis, MN), and mixed in a 227 m<sup>3</sup> (60,000 gal) recirculating aquaculture system. Following the creation of a synthetic seawater solution, water samples were collected to determine actual concentrations of major ions and general chemistry parameters. Ionic concentrations were determined by Test America Analytical Testing Corporation (Nashville, TN).

Additional measurements were made at The Freshwater Institute to identify correctness in solution preparation and to categorize potential interferences with subsequent methods. Of critical importance to this study was bromide concentration, which was measured at 123 mg/L in the synthetic seawater. Other mean water quality values were as follows: salinity was 32 ppt; total hardness was 5,700 mg/L as CaCO<sub>3</sub>; phosphorus was 0.29 mg/L, and total alkalinity was 332 mg/L as CaCO<sub>3</sub>. Water temperature was maintained at 15±0.5°C, and pH ranged between 7.00-7.65 units during experiments.

*Study #1 - Oxidant determination*

Dissolved ozone concentrations were measured with a 9185sc Ozone Analyzer (Hach Company, Loveland, CO). Sample ports along the water stream, installed after ozone addition and after UV irradiation, supplied the necessary 300 mL/min flow rate to the Analyzer's flow through cell.

The Ozone Analyzer was designed for the drinking water industry, but was appealing for this study because of its alleged lack of interference by other oxidants, namely bromine. The ability to distinguish oxidant concentrations, i.e. bromine and ozone, from one another in work involving ozonation of seawater was critical to this study. Before system treatments were examined, the effects of other oxidants (i.e. bromine) and high salinity on the Ozone Analyzer were investigated. To accomplish the pretrial investigation, ozone concentrations were compared between Hach Method 8311- Indigo Method and the Ozone Analyzer using ozonated solutions consisting of (1) deionized water (DIW), (2) synthetic seawater without potassium bromide (KBr), (3) synthetic seawater, and (4) KBr in DIW. Each test solution was ozonated with 5% ozone gas at 5 L/min for 30 min. Following ozonation, samples were concurrently collected from the ozonated test solutions for immediate determination of dissolved ozone per each method. Analyses for the Indigo Method utilized a Hach DR4000U Spectrophotometer. Observations of dissolved ozone from the Ozone Analyzer were made from a Hach sc100 controller.

The concentration of Total Residual Oxidants (TRO) as bromine ( $\text{Br}_2$ ) produced during pretrial and system treatments was measured by Hach 8016 – DPD Method. Buchan et al. (2005) suggest that the DPD methods is an effective technique for measuring total residual oxidants in ozonated seawater. Synthetic seawater samples were analyzed following a 1:7 dilution with DIW to counteract the influences from high alkalinity and hardness. Samples were collected in 40 mL glass septum vials to prevent constituent loss. Accuracy checks were performed for this method using standard additions with a 20-30 mg/L  $\text{Cl}_2$  solution. In DIW, KBr solution, and synthetic seawater, the average bromine recovery was 82%, 90%, and 76%, respectively.

Oxidation reduction potential (ORP) was measured with a differential ORP electrode (Hach) at both sample locations, after ozonation and after UV irradiation.

During studies of UV irradiation of the entire 4,800 L/min recirculating flow, ozone generation was stopped after peak ORP was achieved. A UV irradiation dose of approximately 100 mJ/cm<sup>2</sup> was applied throughout the procedure. At the start of a trial and approximately every hour thereafter during normal working hours, samples were collected before and after UV irradiation (within 20 minutes of each other to allow for ORP reading stabilization) for ORP, ozone, and TRO (i.e., bromine) determination. During one trial, bromate and bromoform concentration were tested to depict the changes in their concentrations during and after ozonation of seawater. Samples were collected from each side of the UV channel before ozonation, at peak ORP, and at falling ORP and were sent to West Coast Analytical Services, Inc. (Santa Fe Springs, CA) for analysis of bromate and bromoform.

During studies of UV irradiation within the side-loop system, ozone was added continuously to maintain relatively stable TRO concentrations. Water flow rates through the side-loop UV irradiation unit were adjusted to approximately 40 and 380 L/min, which corresponded to UV irradiation doses of 206 to 260 mJ/cm<sup>2</sup> at the low flow and 28-30 mJ/cm<sup>2</sup> at the high water flow, respectively. Measurements of ORP were collected before and after UV irradiation (within 20 minutes of each other to allow for ORP reading stabilization). Samples of water were collected before and after UV irradiation for TRO (i.e., bromine) determination.

*Study #2 - Bromine Reaction with TAN as Catalyzed by Phosphate*

Bench top studies were conducted to determine how concentrations of phosphate (0, 1.0, 10.0 mg/L as P) and TAN (0.3, 1.0, and 3.0 mg/L) affect the rate and extent of bromine decay. For the bench top studies, elemental bromine (Br<sub>2</sub>) was added to solutions of with known concentrations of TAN and phosphate, instead of adding ozone to a bromide solution to generate bromine. Elemental bromine is a dark, reddish-brown liquid that dissolves well in water (White, 1992). When added to water, elemental bromine hydrolyzes to form hypobromous acid:



According to the overall break-point bromination reaction (Rx 2), 1.5 moles of HOBr are required to convert 1 mole of NH<sub>3</sub>-N into nitrogen gas. The molecular weights of HOBr (as Br<sub>2</sub>) and ammonia (as N) are 159.8 and 14.0 g/mole, respectively. Therefore, the mass of HOBr (as Br<sub>2</sub>) required to react with ammonia (as N) was estimated to be (1.5)\*(159.8): (1.0)\*(14.0) = 17.1:1. Thus, 17.1 mg/L of HOBr (as Br<sub>2</sub>) is the estimated stoichiometric requirement for converting 1 mg/L of NH<sub>3</sub> (as N) into nitrogen gas. In contrast, Tanaka and Matsumura (2002) only used 0.2 moles of bromide for 1 mole ammonia (as N), assuming that ozone would continuously regenerate the bromide into bromine. Thus, (0.2)\*(159.8):(1.0)\*(14.0) = 2.3 mg/L bromide (as Br<sub>2</sub>) for every 1 mg/L of ammonia (as N). However, the ozonation continuously regenerates bromine from spent bromide.

For this experiment, exact quantities of sodium bicarbonate (NaHCO<sub>3</sub>), ammonium chloride (NH<sub>4</sub>Cl), and potassium phosphate (K<sub>2</sub>HPO<sub>4</sub>) were added to DIW to create solutions with TAN concentrations of 0.3, 1.0, and 3.0 mg/L, an alkalinity concentration of 100 mg/L as CaCO<sub>3</sub>, and phosphorous concentrations of 0, 1, and 10 mg/L. To begin the study, bromine (100% HOBr and

hypobromite) was mixed with the TAN/phosphate solutions to create bromine concentrations of 17.1 mg/L (as Br<sub>2</sub>).

A 9184sc Chlorine Analyzer (Hach Chemical Company) was plugged into a Hach sc100 Universal Controller (Hach Chemical Company) for data display and logging of the concentration of bromine in the water. The pH probe and the chlorine probes were calibrated according to the Chlorine Analyzer User Manual. The chlorine probe was calibrated with a process calibration and a zero chemical calibration. The process calibration used standards of 5, 10, 15 , and 20 ppm chlorine solutions made from DIW and bleach in 1 L Nalgene bottles. The zero chemical calibration was performed by running DI water through the analyzer. A Digital Differential pH/Oxidation Reduction Potential (ORP) Sensor (Hach Chemical Company) was also attached to the sc100 and calibrated according to the manual using a 200 mV ORP Solution according to the Digital Differential pH/ORP Sensors User Manual. The sc100 was set to log the data every minute.

A Masterflex L/S Economy Pump (Cole-Parmer) was used to deliver water to the analyzer. Masterflex L/S 15 opaque tubing (Cole-Parmer) was used with the pump. A pulse dampener was used before the water entered the analyzer. Prior to use, the pump was calibrated to deliver approximately 300 mL/min to the analyzer.

A Bromide Combination Ion Selective Electrode (Accumet Research) was used to measure bromide concentrations throughout the experiment. It was attached to an AR15 pH/mV/°C Meter (Accumet Research) that was set in the mV mode. Bromide concentrations of 1 ppm, 10

ppm, and 100 mg/L were made using a stock solution of 0.1M sodium bromide and 100 mL of each solution was used to calibrate the Bromide Ion Selective Electrode. Two mL of Bromide Ionic Strength Adjuster Buffer (ISA) was added to 100 mL of each standard. The standards were stirred at a mid-level speed and the Bromide Ion Selective Electrode was placed into each standard, beginning with the lowest concentration and increasing. The absolute millivolt (mV) reading was recorded. These readings were plotted against the  $\log_{10}$  of the concentration. The data was best fit to a linear equation, which was then used to find the mg/L for each subsequent mV reading that day.

After all equipment was calibrated, the solution to be studied was prepared. A 10 L Nalgene carboy was filled with 10 L DIW. Sodium bicarbonate ( $\text{NaHCO}_3$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), and potassium phosphate ( $\text{K}_2\text{HPO}_4$ ) were used to achieve the desired levels of alkalinity, ammonia, and phosphorous, respectively. These chemicals were weighed using a Mettler Toledo AB54-S Analytical Balance. The correct amounts of the chemicals were added to the carboy. The water in the carboy was stirred at a mid-level speed. The tube removing water from the carboy was lowered halfway through the water depth. The tube coming from the analyzer was placed in the carboy and returned the already analyzed water to the carboy.

Prior to the addition of elemental bromine, three samples were taken from the tube returning water to the carboy at approximately five-minute intervals. A Spectrophotometer (Hach DR/2500) was used to measure the concentration of total ammonia nitrogen (TAN) and bromine. Bromine was measured with Hach's DPD Method 8016 for Bromine and TAN was measured using Hach's Ammonia Nitrogen Salicylate Method 8155. The mV readings from the Bromide

Ion Selective Electrode were also recorded. After the three initial readings were recorded, elemental bromine was added to the water within the carboy to raise the bromine level to 17.1 mg/L. The time of the elemental bromine addition was recorded, and the first samples were taken approximately three to five minutes after spiking the water. DPD Bromine tests, Salicylate Method TAN tests, and mV readings were performed. Samples were taken, and tests were performed at 10-minute intervals for approximately six hours. After the last tests of the day were performed, the logged data were downloaded. The solution was left running through the analyzer overnight. The next morning the Bromide Ion Selective Electrode was recalibrated, and three samples and the corresponding tests (DPD Bromine, Salicylate TAN, and mV readings) were performed. This was usually around 24-hours after the initial tests. All remaining data (since the download the day before) would be downloaded after the tests were finished.

The downloaded and recorded data were entered into a template that had been created in Microsoft Excel. The recorded times were corrected for the downloaded times, using the time of the bromine spike. The mV readings were converted to mg/L of Br<sub>2</sub> using the best fit linear equation from the Bromide Ion Selective Electrode calibration. The template included two graphs with the first showing the first eight hours and the next going to 24 hours.

After the experiment had finished, the tubing was removed from the carboy and emptied of the solution. The analyzer was also drained. Then tap water was run through the pump and the analyzer for at least 10 minutes. The analyzer was allowed to sit in tap water until the next experiment was to be performed. The carboy was washed thoroughly, rinsed with DIW, and allowed to dry.

## Results

### *Study #1 – Formation & Decay of Bromine During Ozonation & UV Irradiation*

Initial testing to compare ozone measurement methods and to determine the effectiveness of the 9185sc Ozone Analyzer in ozonated test solutions of (1) DIW, (2) seawater without KBr, (3) seawater, and (4) KBr in DIW (Fig. 3) indicated that all ozone applied to solutions containing bromide is consumed in the conversion of bromide ions to brominated compounds. Both methods, Indigo and Analyzer, produced similar results when introduced to ozonated DIW. Only the Indigo method detected a measurable amount of dissolved ozone in the other solutions. Measurable amounts of TRO as Br<sub>2</sub> were also detected in the seawater and KBr-containing solutions, supporting oxidant interferences in the DPD and Indigo methods, and not in the Analyzer method. The high salinity (31 ppt) of the seawater solution without KBr did not inhibit the Analyzer from measuring a dissolved ozone concentration, demonstrating that its ability to detect dissolved ozone is not limited by high salinity solutions, but by the conversion of dissolved ozone to brominated compounds in the presence of bromide.

A plot of ozone-generated ORP versus TRO (Fig. 4) in synthetic seawater indicates that ORP can only be used as a crude approximation of the TRO. We found that as ORP goes up, TRO will also generally rise, but with a huge variation in the amount of TRO detected at a given ORP (Fig. 4). For example, TRO concentrations above 0.1 mg/L were measured even at ORP levels of 230-300 mV (Fig. 4), which suggests that use of an ORP controller with a setpoint of  $\geq 230$  mV could still allow for some bromine production. Thus, ORP can only be used as a crude approximation of the bromine (TRO) in heavily ozonated waters containing bromide. Variation

among replicate measurements of ORP versus TRO suggests the complex nature of the bromine chemistry. W

With respect to monitoring dissolved ozone, our results suggest that an ozone probe can be used to effectively measure dissolved ozone in high salinity solutions that are bromide free (Fig. 3). However, the ozone probe cannot detect the presence of dissolved ozone or oxidizer (bromine) in heavily ozonated water containing bromide, as the oxidants produced are all brominated compounds that are undetectable to the probe.

UV irradiation of synthetic seawater was found to remove some TRO each pass through the irradiation, but this depended on UV dose (Table 1). The 206 to 260 mJ/cm<sup>2</sup> UV dosages provided the greatest removal (38 – 50%) of TRO during a controlled study on the sidestream UV irradiation unit. Additional data from over 90 bromine sampling events (data not tabulated) across the inlet and outlet of the UV irradiation unit treating the entire 4,800 L/min recirculating flow removed 32% of the TRO on average at a mean inlet TRO concentration of 1.2 mg/L as Br<sub>2</sub> and a UV dose of approximately 100 mg/cm<sup>2</sup>. However, when TRO concentrations were < 0.15 mg/L, this same UV dose achieved 100% bromine destruction. When TRO concentrations were between 0.15 to 0.35 mg/L, mean TRO removal across the UV unit was only 0.12 mg/L as Br<sub>2</sub>, causing mean TRO removal efficiency to drop to 42%. A lower dose of UV irradiation, i.e., 28-30 mJ/cm<sup>2</sup>, only removed 3-19% of the TRO in a single pass across the sidestream UV irradiation unit (Table 1). In comparison, ozone residual in freshwater is almost completely removed at dosages of 50-100 mJ/cm<sup>2</sup> (Summerfelt et al., 2004) when practically no bromide (< 0.02 mg/L) is present. Likewise, ultra-high dosages of UV irradiation is also effective at removing chlorine residuals (Seegert and Books, 1978; Watts and Linden, 2007).

TRO concentration was found to increase sharply when ozone was applied, but when ozonation ceased, it did not decay as quickly as it had formed, even with UV irradiation. Fig. 5 illustrates an example of bromine formation and decay. After 24 hours of ozonation, the TRO level reached a maximum concentration of 2.70 mg/L as Br<sub>2</sub> at an ORP of 846 mV. The average concentration of TRO that remained approximately 24 hrs after ozone generation was stopped was still toxic, at 0.51 mg/L as Br<sub>2</sub>.

A UV irradiation dose of approximately 100 mJ/cm<sup>2</sup> was not found to effectively remove bromate, but it was found to remove 34-41% of the bromoform each pass (Table 2). Liltved et al. (2006) also detected bromoform in ozonated seawater and found that it could be removed using granular activated carbon. In the present study, only three data sets were collected to measure the concentration of bromate and bromoform entering and exiting a UV irradiation unit; further research is required to better characterize bromoform removal via UV irradiation.

#### *Study #2 - Bromine Reaction with TAN as Catalyzed by Phosphate*

Bench top studies indicate that bromine did react with TAN via break-point bromination reactions and that the rate of reaction was not influenced by phosphate concentration. As an example, when elemental bromine was added to the solution, the concentrations of free bromine and total bromine nearly instantaneously increased and then decayed over the next 24 hrs while TAN concentrations fell and bromide was formed (Fig. 6). However, only 30-60% of the total bromine had decayed during the first 50 minutes within the 0.3 mg/L TAN treatment (Fig. 7). After approximately 24 hours, only approximately 30-70% of the total bromine had decayed within the 0.3 mg/L TAN treatment, but 98-100% of the bromine had decayed within the 1 mg/L

TAN and 3 mg/L TAN treatments. Within the first 3 minutes of the reaction of bromine with the 1 mg/L TAN and 3 mg/L TAN treatments, approximately 55-75% of the total bromine (including free bromine plus bromamines) had decayed (Fig. 7). After 52 minutes, approximately 90% and 83% of the total bromine had decayed within the 1 mg/L TAN and 3 mg/L TAN treatments, respectively. Likewise, free bromine (representing hypobromous acid plus hypobromite) was removed very rapidly during the first few minutes of the study within the 1 mg/L TAN and 3 mg/L TAN treatments (Fig. 8). These results indicate that if sufficient TAN was present, it would increase both the rate and extent of bromine decay. In particular, a TAN concentration of 1 mg/L increased the rate and extent of bromine decay, when compared to the other treatments. A bromine:TAN mass ratio of 17.1:1 (i.e., at 1 mg/L TAN concentration with the 17.1 mg/L of bromine as Br<sub>2</sub>) provided the highest rate of bromine removal, even slightly better than at TAN concentration of 3 mg/L (bromine:TAN of 5.7:1). The slowest rate and least extent of bromine decay occurred at a TAN:bromine mass ratio of 57:1. The optimal bromine:TAN mass ratio of 17.1:1 corresponds to the stoichiometric requirement for break-point bromination reaction (Rx 2), i.e., where 1.5 moles of HOBr are required to convert 1 mole of NH<sub>3</sub>-N into nitrogen gas. Hoffman and Andrews (2001) also report that the rate of break-point bromination is most rapid at these same stoichiometric ratios. Thus, bromine decay was not as pronounced if too much or too little TAN was provided for the amount of bromine present.

Because the decay rates of total bromine (Fig. 7) and free bromine (Fig. 8) were similar during the 1 mg/L TAN and 3 mg/L TAN treatments, this suggests that free bromine made up a large fraction of the total bromine. This also suggests that bromamines were never a large fraction of the total bromine concentration (which is supported by the bromamine concentration data),

because bromamine was rapidly converted into nitrogen gas. However, bromamine production could be optimized using bromine:TAN of 17.1:1, which appears to enhance the rate and extent of bromine decay to bromide.

Phosphate did not increase bromine removal at any of the TAN concentrations tested.

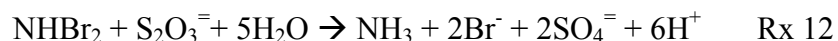
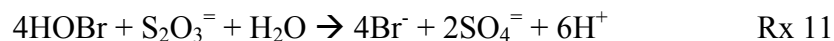
TAN removal was lowest at the highest initial TAN concentration, i.e., 3 mg/L (Fig. 9), because this treatment contained 2 mg/L more than the stoichiometric requirement of 1.5 moles of HOBr for every 1 mole of NH<sub>3</sub>-N converted into nitrogen gas. TAN removal for the 0.3 and 1 mg/L treatments ranged from about 60% to 95% (Fig. 9). Phosphate appeared to increase the percentage of TAN removal initially, but after approximately 1 hour, TAN removal was not impacted by phosphate concentration.

Bromide concentration provides a strong indication of how far the break-point bromination reaction has moved towards completion. Initially, bromide concentrations were all 0.0 mg/L, but bromide concentration increased immediately after elemental bromine was added to the solutions (Fig. 10). Bromide concentrations were highest (9-14 mg/L) at a TAN concentration of 1 mg/L, i.e., where the exact stoichiometric requirement for bromine to convert ammonia to nitrogen gas were attained. Bromide concentrations were lowest (3-7 mg/L) at the lowest TAN concentration, i.e., 0.3 mg/L TAN (Fig. 10), probably because there was inadequate TAN to provide for break-point bromination of more than a small fraction of the bromine present. These findings suggest that bromine is converted back to bromide as the break-point bromination reaction proceeds to completion.

Finally, according to Hoffman and Andrews (2001) and Tanaka and Matsumura (2002), little or no bromate will be produced from hypobromous acid when ammonia is also present, because the TAN ties up the hypobromous acid in reactions that form bromamine (see reactions 2-6). Study #1 did not examine bromate production when TAN was present, but it did find that large amounts of bromate could be produced when high bromine concentrations were produced. During study #2, no samples were sent to a third party laboratory for bromate analysis. Unfortunately, we did not collect the data to test for bromate formation.

### *Future Research*

Sodium thiosulfate ( $\text{NaS}_2\text{O}_3$ ) and sulfur dioxide ( $\text{SO}_2$ ) are used for dechlorination (Seegert and Books, 1978; Bedner et al., 2004; MacCrehan et al., 2005). These reducing agents should be tested to determine their efficacy at destroying residual bromine and to determine if bromamine reduction back to bromide will release ammonia or nitrogen gas, i.e., whether reaction 11 or 12 is valid:



In addition, further research is necessary to determine the effects of UV irradiation on removal of low concentrations of bromine (< 0.1-0.2 mg/L) in the presence of different concentrations of TAN and phosphate. Ideally, UV dosage could be identified that consistently provide complete removal of bromine at these more typical concentrations.

## Conclusions

Real time technologies for monitoring ozone and bromine are commercially available. An ozone probe detects dissolved ozone in freshwater and high salinity solutions that do not contain bromide, but cannot detect ozone in waters that contain bromide due to the nearly instantaneous conversion of dissolved ozone to brominated compounds. An ORP probe detects an increase in TRO (i.e., bromine) in ozonated water containing bromide, but can only be used as a crude approximation due to large variations in the measured TRO for a given ORP. Thus, we suggest extreme caution and careful experimentation when applying ORP to control ozone addition when bromide is present.

Bromine and bromate must be prevented from accumulating within ozonated waters that contain bromide, including freshwater and seawater, in RAS. Adding ozone to a bromide containing water will produce bromine, which must be avoided or removed because it is toxic to fish.

Chemical and photochemical processes were identified to convert bromine back to the non-toxic bromide ion. In particular, UV irradiation at dosages of 100-250 mJ/cm<sup>2</sup> effectively removed some bromine, but did not always eliminate bromine, depending on the inlet TRO concentration.

Bromine decay also depends on the break-point bromination reaction with TAN to produce bromamines. Bromine decay and ammonia removal via break-point bromination were both found to depend on both the ratio of bromine: ammonia and the amount of phosphorus in the water. The optimal bromine: TAN mass ratio of 17.1:1 corresponds to the stoichiometric requirement for break-point bromination reaction (reaction 2), i.e., where 1.5 moles of HOBr are required to convert 1 mole of NH<sub>3</sub>-N into nitrogen gas. Reaction of free bromine with TAN increases the rate of total bromine decay. Phosphate also increases the rate of bromine decay due

to break-point bromination. Although not tested in the present trial, reducing agents can also remove bromine, similar to chlorine.

Thus, bromine problems can be eliminated by preparing saltwater mixes that contain no bromide. And, in RAS with bromide containing water, bromine problems can be reduced by applying limited ozone doses, using high dosages of UV irradiation or reducing agent (i.e., sulfur dioxide or thiosulfite), or treating the water using granulated activated carbon filters.

### **Acknowledgements**

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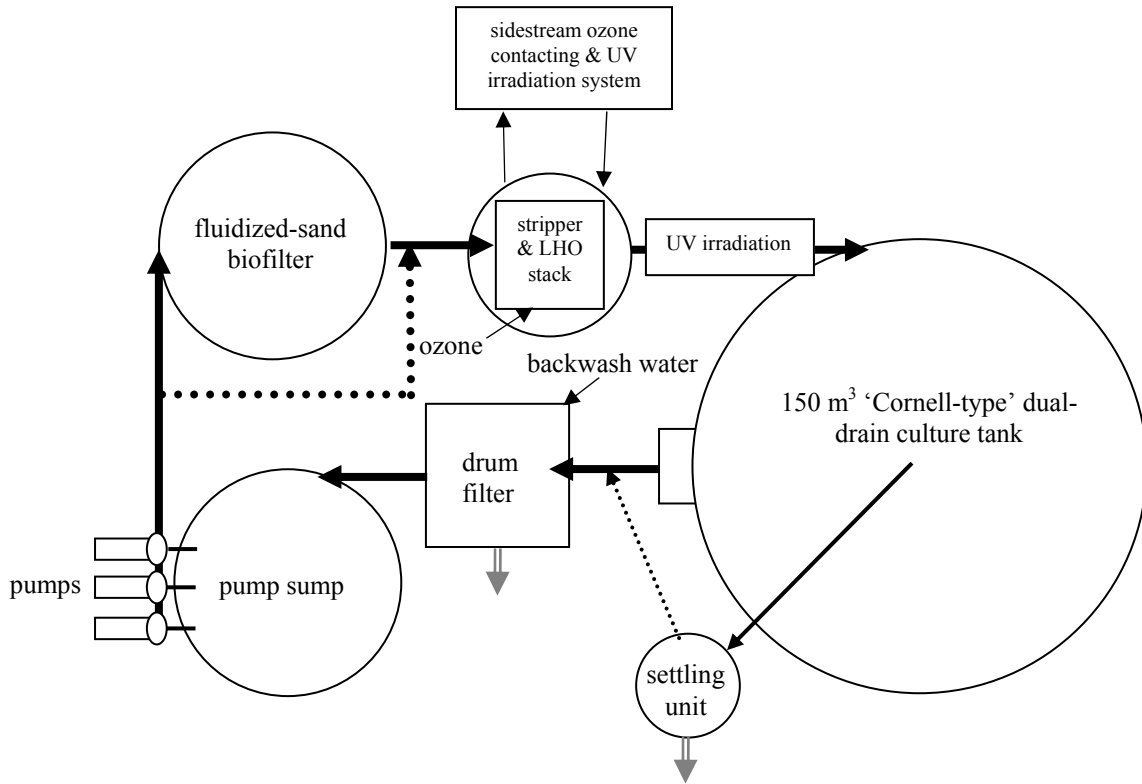
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Table 1. Total residual oxidant removal (TRO) by side-loop UV irradiation of ozonated synthetic seawater.

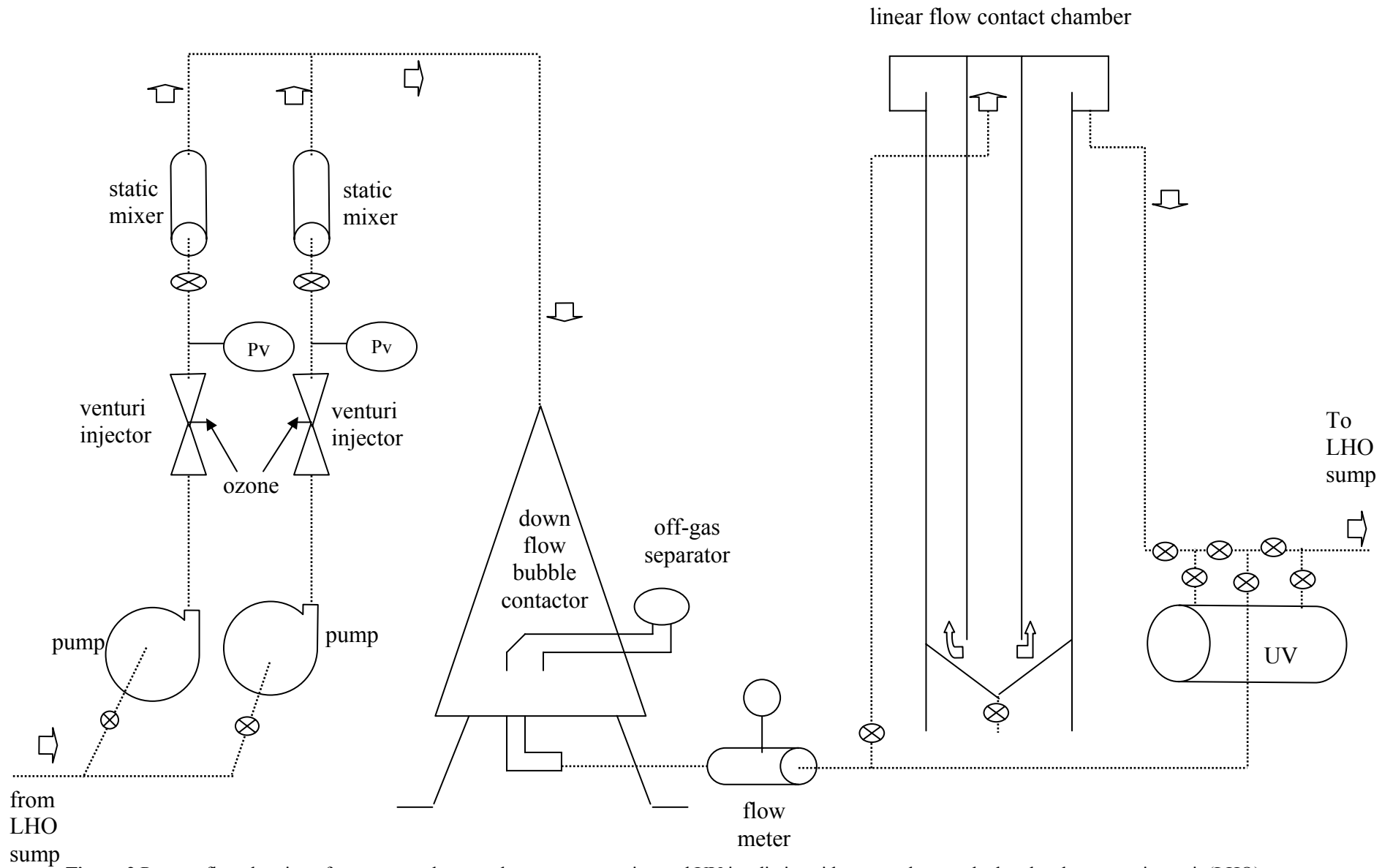
Max ORP (mV)	Ozone (mg/L)	UV Dose (mJ/cm <sup>2</sup> )	$\Delta$ ORP across UV (mV)	TRO before UV (mg/L as Br <sub>2</sub> )	TRO after UV (mg/L as Br <sub>2</sub> )	UV Removal of TRO (%/pass)
808	0	28	0	7.59	6.67	19
537	0	30	-3	1.75	1.2	3
801	0	206	-19	2.10	0.91	50
748	0	228	-6	3.02	2.10	38
846	0	260	-18	4.27	2.70	45

Table 2. ORP, bromate, and bromoform concentrations of synthetic seawater immediately before and after UV irradiation of the full recirculating flow; data was collected before addition of ozone, at peak ORP achieved by ozonation, and during the falling ORP after ozonation had been terminated.

Condition	ORP (mV)		Bromate by EPA 317 (mg/L)		Bromoform by GCMS ( $\mu$ g/L)	
	before UV	after UV	before UV	after UV	before UV	after UV
Before Ozone	269	268	54	47	1	ND
Peak ORP	748	742	61	71	77	51
Falling ORP	341	332	71	68	69	41



**Figure 1.** Process flow drawing of the 4,800 L/min recirculating system located at The Conservation Fund's Freshwater Institute, Shepherdstown, WV (after Davidson and Summerfelt, 2005).



**Figure 2.** Process flow drawing of water treated across the ozone contacting and UV irradiation side-stream loop at the low head oxygenation unit (LHO) sump.

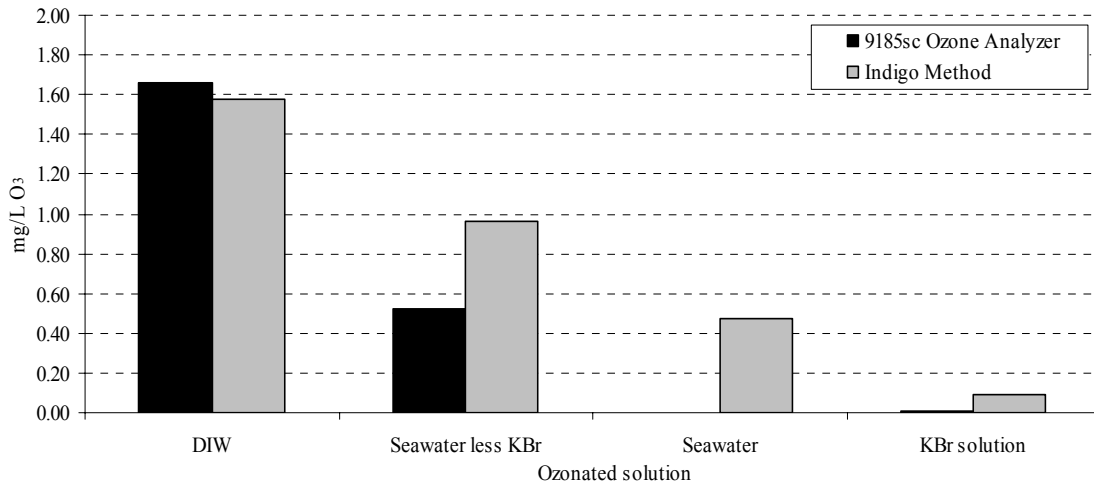


Figure 3. Comparison of ozone measurement methods in various ozonated test solutions.

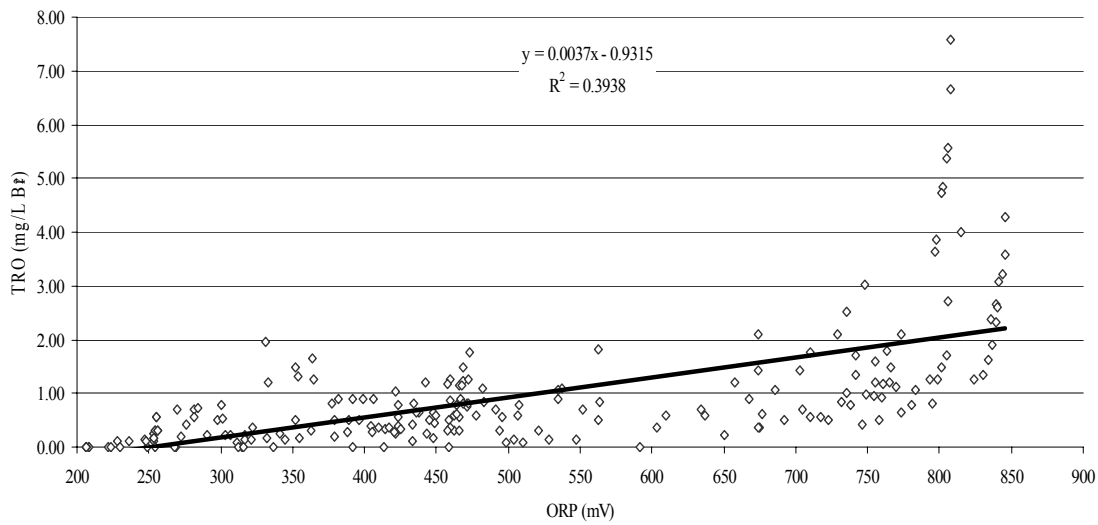


Figure 4. ORP versus mg/L TRO as Br<sub>2</sub> following ozonation of synthetic seawater. No residual ozone was detected with the 9185sc Ozone Analyzer.

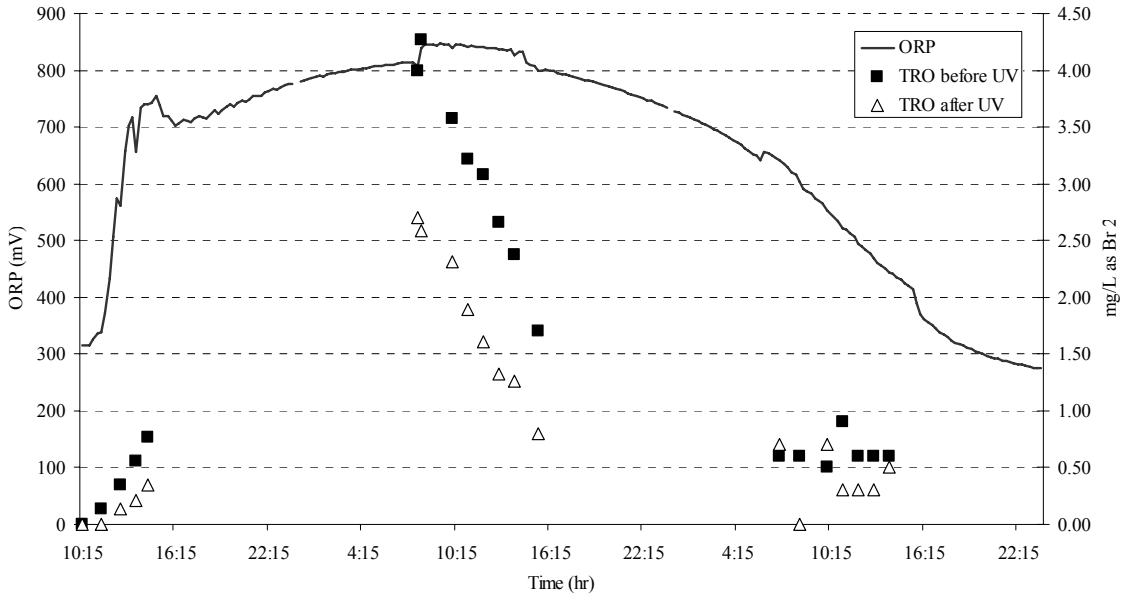


Fig. 5. Total residual oxidant formation and decay in ozonated synthetic seawater where the maximum ORP reached 846 mV, TRO reached 4.27 mg/L as Br<sub>2</sub>, UV was dosed at 260 mJ/cm<sup>2</sup>, and no residual ozone was detected with the 9185sc Ozone Analyzer.

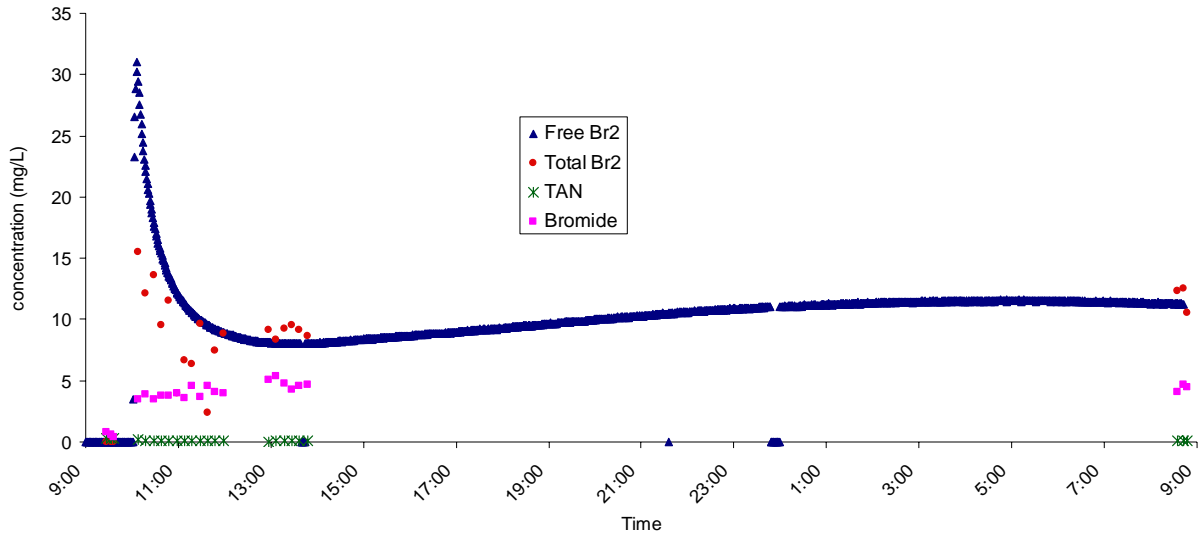


Fig. 6. Free bromine (as Br<sub>2</sub>), total bromine (as Br<sub>2</sub>), TAN, and bromide concentrations measured just before and for 24 hours after 17.1 mg/L (as Br<sub>2</sub>) of elemental bromine was added in the treatment containing 10 mg/L phosphate and 0.3 mg/L TAN, shown as an example of all such treatments.

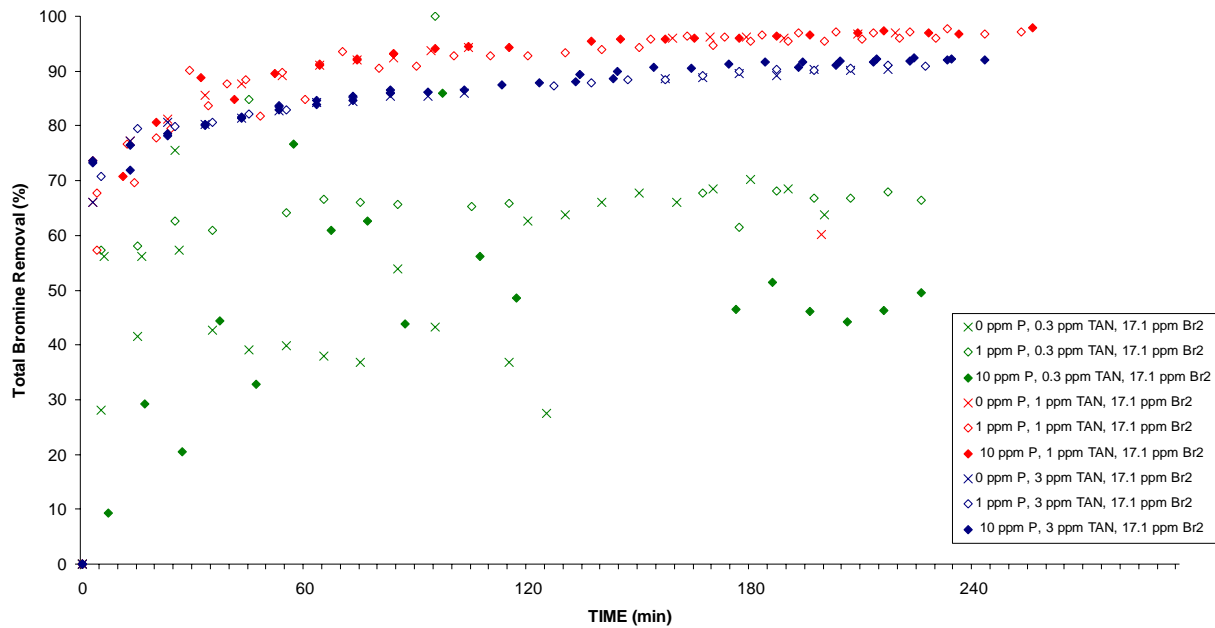


Fig. 7. Percentage of total bromine removed within the first four hours after elemental bromine addition during all treatments.

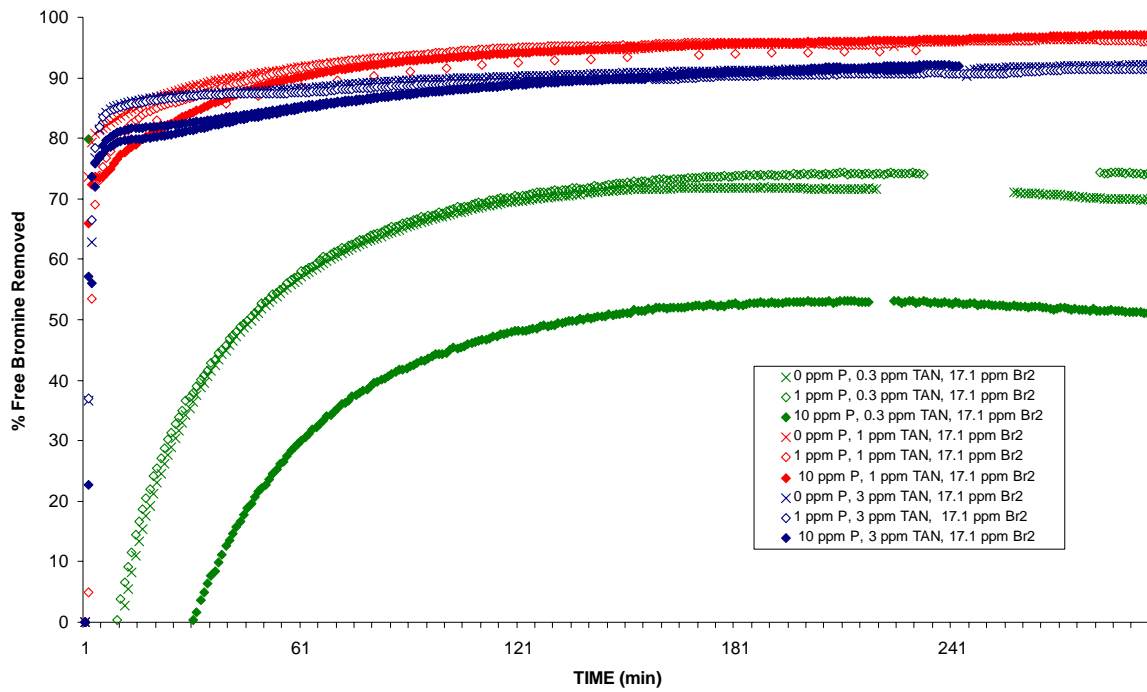


Fig. 8. Percentage of free bromine removed within the first four hours after elemental bromine addition during all treatments.

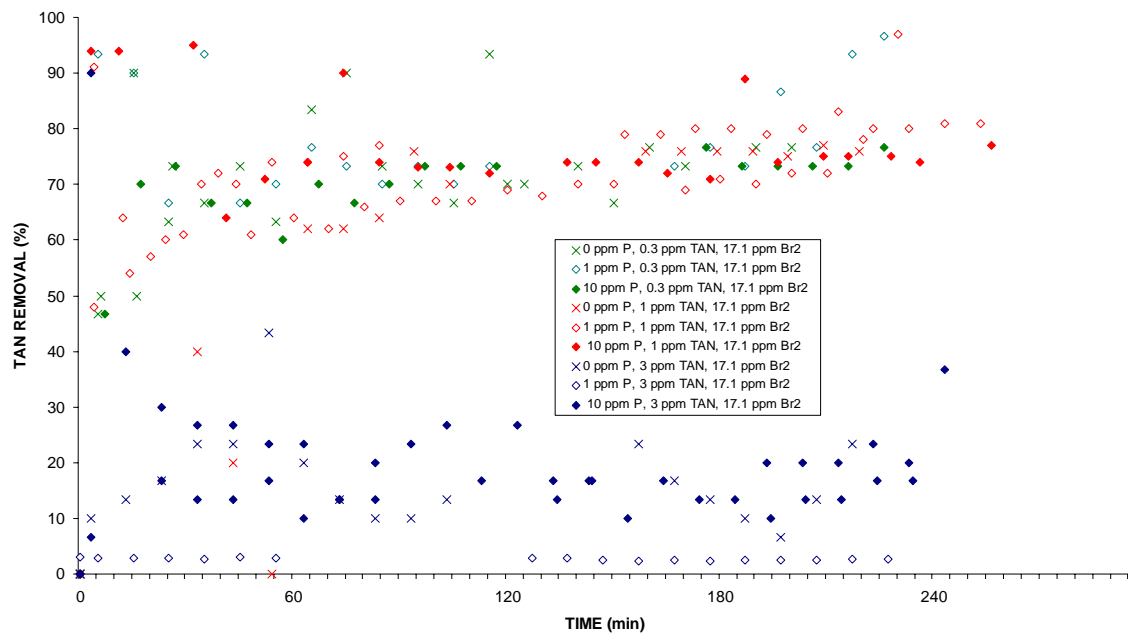


Fig. 9. Percentage of TAN removed within the first four hours after elemental bromine addition during all treatments.

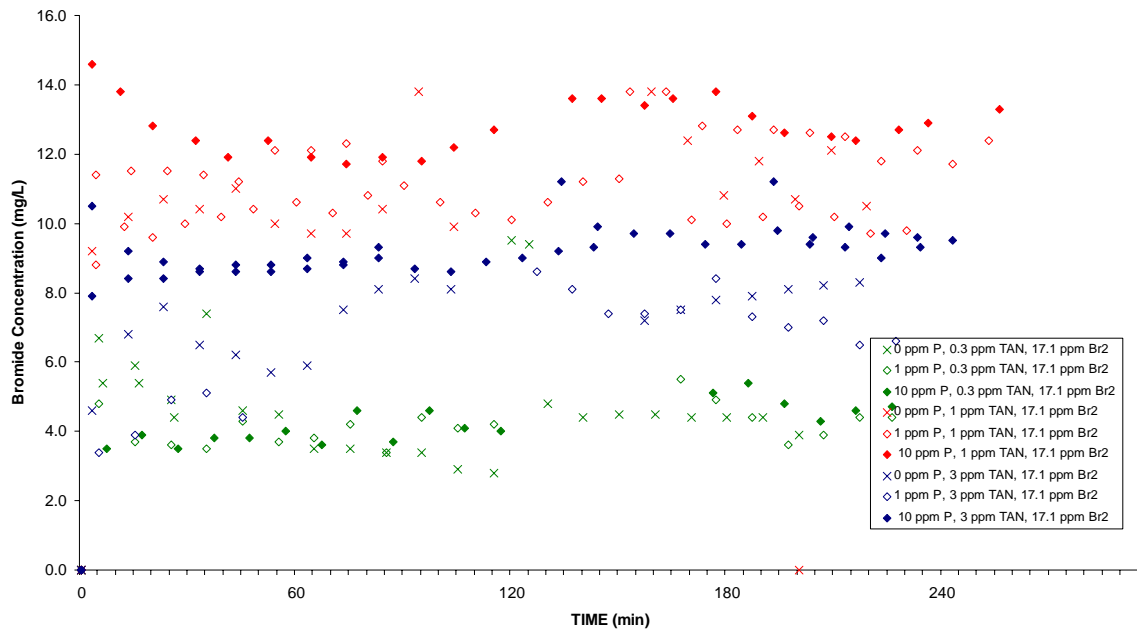


Fig. 10. Bromide concentration measured within the first four hours after elemental bromine addition during all treatments.