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Ozonation of seawater from different locations: Formation and decay of total residual oxidant—implications for ballast water treatment

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Abstract

Ballast water is a likely cause for worldwide transfer of non-indigenous aquatic species because of the large volumes and frequency of possible inoculations. Ozone is one treatment option being considered for eliminating non-indigenous species in ballast water. When ozone is applied to seawater, secondary disinfectants are formed, commonly measured and expressed as total residual oxidant (TRO). The goal of this study was to determine those variables most likely to affect the rate of TRO increase during ozonation and the subsequent TRO decline that occurs over time. These parameters strongly influence the efficacy of ozone treatments aimed to eliminate organisms present in ballast water. Seawater was obtained from Puget Sound, Washington; Cape Fear, North Carolina; and San Francisco Bay. Results indicated that seawater characteristics, including the organic content and ammonia, affect the amount of ozone required to achieve a desired TRO level and rate of TRO decay, and therefore need to be considered in determining ozone requirements for ballast water treatment.

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1. Introduction

Non-indigenous aquatic organisms are a threat to marine resources around the world and new introductions are occurring in many ports and on every coast. After habitat destruction, non-indigenous species are considered the greatest cause for loss of biological diversity (Vitousek et al., 1997). The best way to reduce species introduction is prevention and management of introduction pathways (Carlton, 2001). Due to the large volumes and regularity of potentially contaminated discharges, ballast water is currently the most frequently cited cause for the worldwide transfer of non-indigenous species. The US receives more than 79 million metric tons of ballast water from overseas each year, and over 10 billion metric tons of ballast are

transferred annually across the world (Ruiz et al., 2000; Niimi, 2004). National and international initiatives are developing methods for treating ballast water that hopefully will stem the influx of invasive species. One treatment method under consideration is ozonation.

Ozone has been used as a disinfectant in drinking water since the late 1800s. Ozone is an excellent biocide and is unstable in water (Langlais et al., 1991). It is widely used in Europe in drinking water treatment and to a lesser extent in the US (Hoigné, 1998). Recent reviews discuss various aspects of ozone chemistry in drinking water and consider the effect of bromide ion in source waters on reaction products (von Gunten, 2003a,b). Ozone is also applied in wastewater treatment as an oxidant and disinfectant and its use is increasing (van Leeuwen, 1996; van Leeuwen et al., 2003).

The use of ozone for ballast water treatment was investigated on a laboratory scale (Oemcke and van Leeuwen,

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1998, 2004, 2005; Herwig et al., 2004). The chemistry of ozone in seawater is considerably different than that in freshwater. This difference in chemistry has a profound effect on disinfection. The most important difference with ozone chemistry in seawater compared to freshwater is due to the presence of bromide, Br^- , in seawater (Oemcke and van Leeuwen, 1998). Bromide is oxidized by ozone to bromine, i.e., HOBr and OBr^- , hypobromous acid and hypobromite ion, (von Gunten and Hoigné, 1992; von Gunten and Oliveras, 1997; von Gunten and Pinkernell, 2000; Pinkernell and von Gunten, 2001). Bromine has disinfectant properties and is quantified as total residual oxidant (TRO), usually in units of $\text{mg Br}_2 \text{ l}^{-1}$ or $\text{mg Cl}_2 \text{ l}^{-1}$ (White, 1999).

Seawater has a salinity of approximately 35 practical salinity units (PSU) equivalent to parts per thousand on a mass basis, while the concentration of Br^- is approximately 67 mg l^{-1} (e.g., Millero, 1996; Pilson, 1998). Previous studies established the reaction mechanism and the reaction kinetics of the ozone-bromide ion system (Haag and Hoigné, 1983; von Gunten and Hoigné, 1992; von Gunten et al., 1996; Croué et al., 1996; Westerhoff et al., 1998). The half-life of ozone in water that has high concentrations of Br^- , such as seawater, is five seconds with the initial step being quantitative conversion to bromine (HOBr/OBr^-). Because ozone decomposition is essentially quantitative at high Br^- concentrations, a second important difference between freshwater and seawater is that there is no hydroxyl radical formation in seawater (von Gunten, 2003b). Therefore, ozone treatment of marine ballast water involves the initial unstable oxidant, ozone, and a secondary more stable oxidant, bromine (HOBr/OBr^-). The pK_a of HOBr/OBr^- is approximately 9.0 so that in most marine waters where open ocean water $\text{pH} = 8.1$ (Millero, 1996; Pilson, 1998), HOBr will be the dominant bromine form.

Bromine is removed from seawater by several mechanisms. HOBr/OBr^- will react with natural organic matter to form bromoform (CHBr_3) by the haloform reaction (e.g., Amy et al., 1985; Cooper et al., 1986; Shukairy and Summers, 1996; Richardson, 2003). In fact, a number of disinfection products (Richardson et al., 2000; Richardson, 2003) and other halogen containing compounds (Haag, 1980) are reported when ozone and bromide are present in natural waters. Therefore, organic matter in ballast water could lead to the disappearance of the TRO, thereby the loss of disinfection properties, through similar reactions.

Sunlight can reduce HOBr/OBr^- to Br^- through a complex series of photochemical reactions (Treinin, 1970; Macalady et al., 1977; Subhani and Lodhi, 1980; Klaning and Wolff, 1985; Amichai et al., 1989). In some cases, where high concentrations of Cl^- are present, it may be that sunlight-mediated photolysis of HOBr/OBr^- leads to the formation of bromate ion (Macalady, 2005). Therefore, photolysis may also lead to the loss of TRO; however, in the ballast tanks, where there is no light, this would not account for loss.

In the presence of ammonia, HOBr/OBr^- will react rapidly to form monobromamine (Johnson and Overby, 1971; Haag et al., 1984; Yang et al., 1999; Lei et al., 2004). Monobromamine can disproportionate to NHBr_2 and NH_3 (e.g., Lei et al., 2004) or with excess HOBr/OBr^- it can react further to form N_2 and bromide (e.g., Brunetto et al., 1989; Hofman and Andrews, 2001). Therefore, in waters with high ammonia/ammonium ion, there are several pathways for the loss of TRO, once formed, over time.

Richardson et al. (1981) determined that TRO decay rates in synthetic seawater were dependent on numerous variables including light and salinity concentration. These authors concluded that the use of natural seawater, instead of synthetic seawater, for the measurement of TRO decay rates would be influenced by even more factors due to the complexity and variability of natural seawaters.

The chemistry and toxicity of ozonation of seawater is strongly affected by the chemistry of the water. Measuring TRO serves as an indirect measure of ozone toxicity (Sugita et al., 1992; Liltved et al., 1995). A potential problem and alternatively an attractive feature of ozone treatment of ballast water is that the concentration of TRO in seawater declines over time. When it declines below a certain level, toxicity associated with the treated water is removed (Jones et al., in press; Perrins and Herwig, 2003).

Acceptable ballast treatment for the prevention of non-indigenous species must be able to remove viable organisms from the ballast water and upon discharge be non-toxic to the receiving waters. Due to these treatment requirements and to minimize the economic cost of ballast treatment, a goal when using biocides, such as ozone, is to use a minimum concentration for the removal of organisms in the ballast tank and to have the toxicity decay to a minimum level during the voyage before ballast is discharged. Applying a dose of ozone that is greater than necessary for effective treatment increases the treatment cost, such as those associated with the ozone generator installed or amount of electricity that needs to be produced on the ship. If the TRO concentration and its associated toxicity decline during a voyage then the ship may be able to discharge the treated ballast water without the addition of a chemical reductant that would be required to neutralize the remaining TRO.

In the study described here, we examined the formation and decay of TRO formed by the ozonation of seawater from different regions of the United States since these characteristics must be understood before effective ozone treatment systems can be operated on ships. Different ports around the world vary greatly in terms of their marine water chemistries. Differences between the marine water chemistries will determine the ozone concentration necessary for effective ballast treatment for invasive species control.

The goal of our bench-scale study was to determine the chemical variables that are most likely to affect ballast treatment with ozone onboard ships. Previous research suggests that ballast treatment with ozone would form an oxidant residual of bromine that will persist over time (Richardson et al., 1981). The specific objectives of our

study were: (1) to treat seawater from different locations with ozone using a slow dissolution system and observe the increase of TRO with time, and (2) to determine the effect of salinity, initial TRO concentration, and source water characteristics on the rate of TRO decay. Understanding these parameters is important since they directly impact the concentration of ozone necessary for an effective treatment of ballast water.

2. Methods

2.1. Sources of seawater

Synthetic seawater was prepared by adding Red Sea Salt[®], a commercially available coral reef salt produced from the Red Sea (Red Sea, Houston, Texas) to deionized water to final salinities of 15 and 30 PSU as measured with a conductivity meter (Hach sensION-5 meter). A salinity of 30 PSU was slightly less than oceanic water, but contained approximately 60 mg l⁻¹ of bromide. For each salinity, a volume of 20 l was prepared and filtered through a 0.45- μ m membrane filter into two sterile 10-liter Nalgene polypropylene containers.

Natural waters included water collected from the Puget Sound, Washington; Vallejo, California; Sausalito, California; and the Cape Fear River, North Carolina. Puget Sound seawater was collected from the Seattle Aquarium (Seattle, Washington) after it had been drawn into the pump lines, prior to any filtration process. The Vallejo water was collected from a pier at the California Maritime Academy in Morrow Cove of San Francisco Bay. The Sausalito water was obtained from rip-rap extending into the water just north of the Golden Gate Bridge in San Francisco Bay. Cape Fear River water was collected within the Cape Fear Estuary near Southport, North Carolina. Vallejo, Sausalito, and Cape Fear water was shipped to the University of Washington by overnight express. All water samples were stored at 8 °C in a dark incubator until ozonation experiments began.

2.2. Characterization of seawater

Chemical characteristics of each synthetic and natural seawater were measured, including: pH (HACH sensISE-1 meter), conductivity/salinity (HACH sensION-5 meter); nutrients, i.e., phosphates, silicates, nitrates, nitrites,

ammonia (analyzed with a Technicon Model AAI); and total organic carbon (determined using a Shimadzu TOC5000) (Table 1). The University of Washington School of Oceanography performed nutrient and total organic carbon analyses.

2.3. Ozone system design

Ozone was produced using a UV-275 ozone generator (ClearWater Tech), which could nominally produce 100 mg O₃ h⁻¹. Ozone production measurements were performed using the iodometric method (APHA et al., 1992) with a modified potassium iodide absorbent: 0.1 M H₃BO₃/1% KI, to verify the ozone production of the generator (Flamm, 1977). The production of the ozone generator averaged 84.2 mg O₃ h⁻¹.

The ozone distribution system design was similar to that of Driedger et al. (2000), where ozone entered a stirred equalization container that was a flow equalizer. The ozone then entered the water column through an air stone diffuser at the bottom of the water column. The water treatment column consisted of a 2-l acid washed glass container covered in tinfoil to prevent light penetration. The container was set on a stir plate and stirred vigorously to ensure optimal ozone dissolution (Hsu et al., 2002).

2.4. Oxidant (TRO) concentration with ozonation

Seawaters were ozonated for the time required to obtain a TRO concentration of 4 mg l⁻¹ as Br₂. Three replicate 1.8-l volumes of source waters were placed in the ozone treatment chamber and analyzed every 5 min for the TRO concentration. TRO was determined by the DPD (*N,N*-diethyl-*p*-phenylenediamine) spectrophotometric method (US EPA Method 8016) for bromine with a Hach 2010 spectrophotometer. Ozone was introduced into 1.8-l samples at a rate of 0.78 mg l⁻¹ min⁻¹. The system used to ozonate the water was not optimized for total ozone dissolution and some ozone was noticed in the off-gas. The data was used to determine the time necessary to reach the target TRO of 1 to 4 mg l⁻¹ as Br₂ in source waters for later TRO decay experiments.

2.5. TRO decay analysis

Four replicate 1.8-l volumes of seawater were placed in the ozone treatment chamber. Each set of replicates were

Table 1

Chemical analysis of the seawaters used in TRO decay experiments: synthetic seawater prepared at two salinities, PSU 15 and PSU 30; Puget Sound, Washington; Cape Fear River, North Carolina; San Francisco Bay at Sausalito, California; and San Francisco Bay at Vallejo, California

Source	pH	PSU	PO ₄ ³⁻ (mg l ⁻¹)	Si(OH) ₄ (mg l ⁻¹)	NO ₃ ⁻ (mg l ⁻¹)	NO ₂ ⁻ (mg l ⁻¹)	NH ₄ ⁺ (mg l ⁻¹)	TOC (mg l ⁻¹)
PSU 15	7.98	15.3	0.0014	0.034	0.002	0.0000	0.0069	0.66
PSU 30	7.93	29.8	0.0043	0.090	0.009	0.0012	0.0024	0.71
Puget Sound	7.80	29.9	0.0760	1.766	0.428	0.0012	0.0023	0.92
Cape Fear	7.82	31.0	0.0087	0.494	0.008	0.0011	0.0043	2.88
Sausalito	7.70	30.8	0.0734	1.464	0.176	0.0153	0.0760	1.34
Vallejo	7.58	19.8	0.0975	3.047	0.343	0.0168	0.1122	6.60

ozonated to the desired TRO, ranging from 1 to 4 mg l⁻¹ as Br₂, mixed by inverting 2 to 3 times, and TRO was measured to determine the initial TRO. The water was then stored in a dark incubator at 8 ± 1 °C, to simulate ballast conditions. TRO decay was determined by periodically measuring the TRO during the first 24 h and every 24 h thereafter for a minimum of 72 h or until the TRO was below the detection limit of 0.1 mg l⁻¹ as Br₂. Due to a limited amount of water, TRO decay in the Cape Fear River water was only performed at an initial TRO concentration of 2 mg l⁻¹ as Br₂.

2.6. Statistical methods

Data analysis was performed using repeated measures, which analyzes groups of related dependent variables that represent different measurements of the same attribute (Zar, 1996). Repeated Measures analysis was used to com-

pare the variance of different sample groups and their TRO over time. Tukey's post hoc testing was used for the statistical analysis when appropriate. The statistical analyses were performed using SPSS version 12.0 (SPSS Inc.). Using statistical analysis, it was possible to determine which variable(s) tested exhibited an effect on the rate of ozone dissolution and TRO decay. Comparisons were made to determine if salinity, initial TRO levels, and seawater characteristics affected the rate of TRO decay.

3. Results and discussion

3.1. TRO increase during ozonation

3.1.1. Response in seawater from different locations

TRO concentration increased in the seawater samples with increasing time of ozonation (Fig. 1). The rate of TRO increase was dependent on the source of the

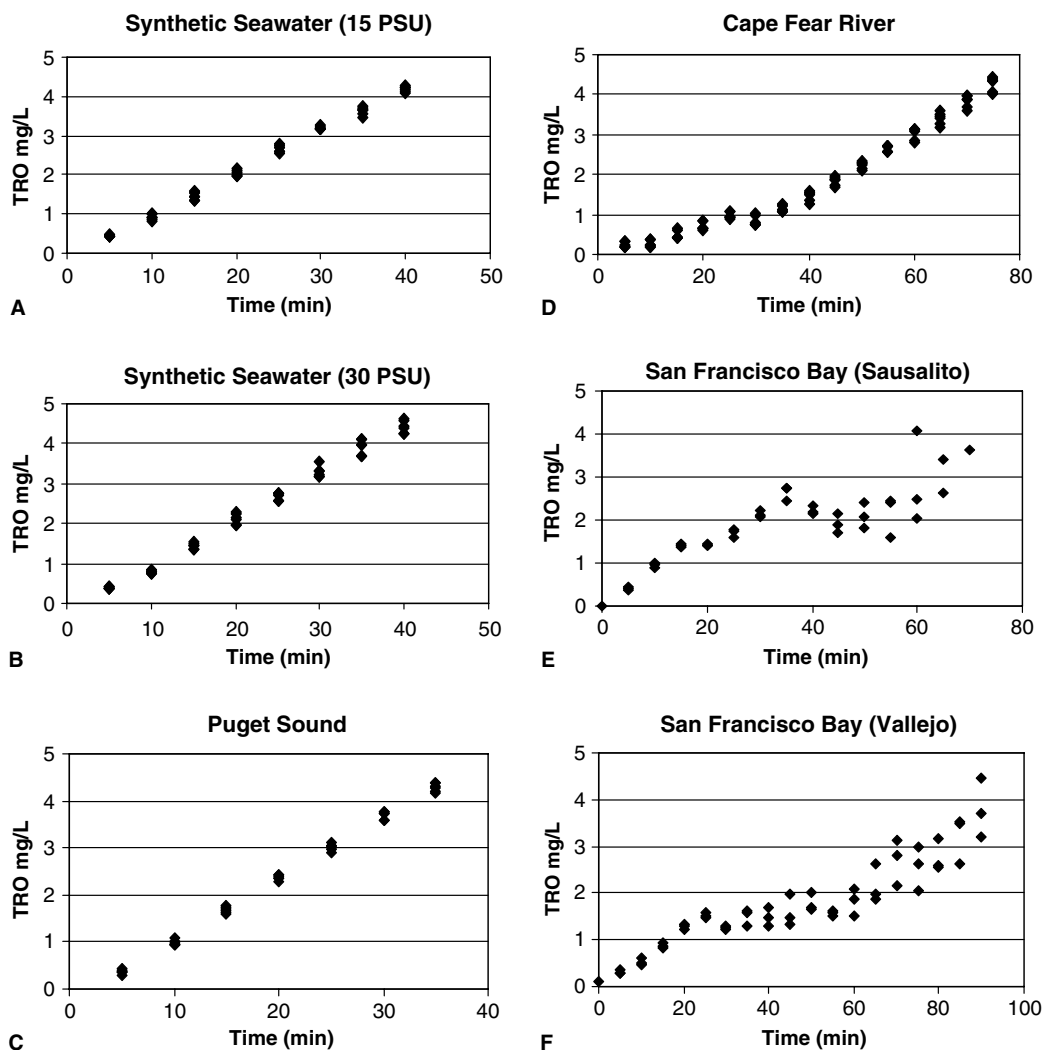


Fig. 1. Total residual oxidant (TRO) concentration (mg l⁻¹ as Br₂) with increasing ozonation time in synthetic seawater prepared at 15 PSU (A) and 30 PSU (B); and seawater obtained from Puget Sound, Washington (C); Cape Fear River, North Carolina (D); two sites in San Francisco Bay, Sausalito (E) and Vallejo (F).

water. Synthetic seawaters prepared at two salinities and Puget Sound water resulted in a TRO increase of $0.12 \text{ mg l}^{-1} \text{ min}^{-1}$ and $0.13 \text{ mg l}^{-1} \text{ min}^{-1}$, nearly linear with time (Fig. 1A, B, C). An initial ozone demand with no increase of TRO was observed in all of the waters. That is, during the first minutes the TRO build-up lagged with the addition of ozone. Cape Fear River water showed two distinct time responses in the TRO build-up rate, an initial rate of $0.033 \text{ mg l}^{-1} \text{ min}^{-1}$ over the first 30 min of ozonation and $0.075 \text{ mg l}^{-1} \text{ min}^{-1}$ thereafter (Fig. 1D). This was thought to be the result of a reaction of TRO with a component in the water, presumably organic material. The waters collected in San Francisco Bay at Sausalito and Vallejo had a linear TRO increase during the first 20 min of ozonation, followed by an irregular TRO increase upon further ozonation (Fig. 1E and F). The initial rate of increase for the Sausalito water was about $0.1 \text{ mg l}^{-1} \text{ min}^{-1}$ and the Vallejo water about $0.065 \text{ mg l}^{-1} \text{ min}^{-1}$. Subsequent ozonation led to an actual decrease in TRO in the Sausalito water and no further increase over a 30-min period of ozonation in the Vallejo water.

3.1.2. Explanations for the differences

One possible explanation for the different TRO response between the San Francisco Bay samples and the other waters tested could be the differences in the composition of the organic matter present in the water. There may have been an anthropogenic source (e.g., wastewater discharge) nearby, which exerted an influence on the source water different from the natural organic matter dominating the Cape Fear River.

The geochemical compositions of the different waters varied (Table 1). Not surprisingly, the lowest levels of phosphate, silicate, and TOC were found in the synthetic seawater. The highest levels of phosphate, silicate, nitrate, ammonia and TOC were found in Vallejo. The chemical signatures may suggest why the TRO responded as observed with ozonation. von Gunten (2003b) observed that ozone stability in natural waters was variable due to natural organic matter and it is impossible to estimate the fraction of organic matter that promotes or inhibits oxidant reactions.

Higher organic concentrations would explain the slower increase of TRO in both the San Francisco and Cape Fear waters. However, the decrease or no increase in TRO during periods of ozonation must be associated with nitrogenous oxidation reactions. The ammonium values were more than 10-fold greater in the San Francisco Bay samples compared to the Cape Fear sample. A reasonable explanation would be a breakpoint reaction in which monobromamine was oxidized to nitrogen gas (N_2) and the bromine reduced to bromide. Towards the end of the ozonation, the TRO build-up resumed in both these waters, again akin to a classical breakpoint phenomenon. The phenomena seen in the TRO curve fit a breakpoint phenomenon more or less quantitatively.

The slope of increasing TRO was determined for the water samples, and multiple slopes were determined for those source waters with more complex TRO versus time curves. There was no significant difference in the slope of TRO increase between the synthetic seawaters prepared at 15 and 30 PSU ($P \leq 0.222$). The slope of the TRO curve for the Puget Sound seawater appeared to be very similar. The slopes from the figures from all other waters were shown to be significantly different from the synthetic seawater and the sample from Puget Sound ($P \leq 0.001$).

Ozonation of seawater results in the formation of bromine compounds that react with natural organic compounds. For example, Jaworske and Helz (1985) suggested that natural waters containing organic matter consumed all of the bromine at low oxidant concentrations. They calculated that only 2% of the DOC sites served as reaction sites for this rapid oxidant demand in a Patuxent River water sample. Dotson and Helz (1984) indicated that oxidation reactions operated over a wide range of time scales with oxidant being consumed by certain nitrogen and aromatic heterocyclic rings within seconds, and oxidation reactions of inorganic and organic amines have been shown to occur over periods ranging from seconds to hours. Phenol, a compound consisting of a single aromatic ring, has relatively fast reaction kinetics with ozone (Grguric et al., 1994). Another possible explanation for the differences in TRO versus time curves is that the reaction byproducts (of the initial oxidation process) react with TRO (Sugita et al., 1996; Lazarova et al., 1998).

Andrews and Huck (1996) examined the effect of size fraction of natural organic matter on ozone demand in which smaller organic compounds would imply a surface-type phenomenon where an increase of easily accessible sites on the molecule could react with the oxidant compared to the original larger molecule. It is possible that this result could be extended to reactions of HOBr/OBr^- with natural organic matter. Huang et al. (2004) examined the effect of size fractions of natural organic material on the formation of organic bromine compounds. They showed that different organic compounds were formed from the different fractions of the natural organic matter. Although time studies were not reported, it is reasonable to assume that the formation of these different compounds, i.e., the rate of reactions, was different and therefore could explain the variation in rates that we observed in the TRO loss curves.

Ozonation of seawater results in the formation of bromine (HOBr and OBr^-), which is toxic to a wide variety of aquatic organisms. Ozone and bromine react with a variety of constituents present in seawater, whose concentration varies in different ports. Applying our results towards ozone ballast water treatment indicate that different ports and ballasting locations will require different doses of ozone to achieve the same initial TRO concentration. For example, to achieve a TRO of 3 mg l^{-1} as Br_2 would require 1.5 to 3 times the ozone dosage for water from San Francisco Bay compared to Puget Sound.

3.2. TRO decay

3.2.1. Measured TRO decay

Seawater from different locations was ozonated to specific initial TRO concentrations. Ozonation was then ceased and TRO decay was observed over time. The rate of TRO decay was shown to be dependent on the source water during the first 72 h of sampling (Fig. 2), where the synthetic seawater (Fig. 2A and B) showed the lowest rate of decay and the Cape Fear sample (Fig. 2D) showed the highest rate of decay at the greatest initial TRO. The San Francisco waters were shown to be different from one another with similar initial TRO concentrations (Fig. 2E and F).

3.2.2. TRO decay rates—salinity effect

To better understand the decay rates in the same water or different waters, when the initial TRO concentration was different, the concentration of TRO at time = t , C_t , was normalized by dividing by the initial concentration, C_0 . The natural logarithms of these normalized values were

then plotted as a function of time. If the decay processes were first order or pseudo-first order with respect to TRO, the resulting line would be straight, and the rate of decay would be the slope of that line. Fig. 3 shows a significant difference in the rate of TRO decay at the two TRO concentrations of 4.0 and 2.0 mg l⁻¹ as Br₂ for experiments prepared with synthetic seawater at 15 and 30 PSU. The higher TRO (4.0 mg l⁻¹ as Br₂) was shown to decay slower than the lower TRO (2 mg l⁻¹ as Br₂). Fig. 4 compares the decay of the two TRO concentrations relative to the salinity of the waters. There appears to be no difference in the rate of decay with a TRO of 2.0 mg l⁻¹ as Br₂ (Fig. 4A) while a clear difference was observed for the decay of the TRO of 4.0 mg l⁻¹ as Br₂ (Fig. 4B). Using a confidence interval of 90%, there was a significant difference in the TRO decay rate at the two salinities ($P \leq 0.005$) and the initial TRO of 2.0 mg l⁻¹ as Br₂ ($P \leq 0.061$), and 4.0 mg l⁻¹ as Br₂ ($P \leq 0.003$). Both phenomena were indicative of the demand for the TRO and a higher ozone dose would remove more of this demand, leading to a more stable TRO.

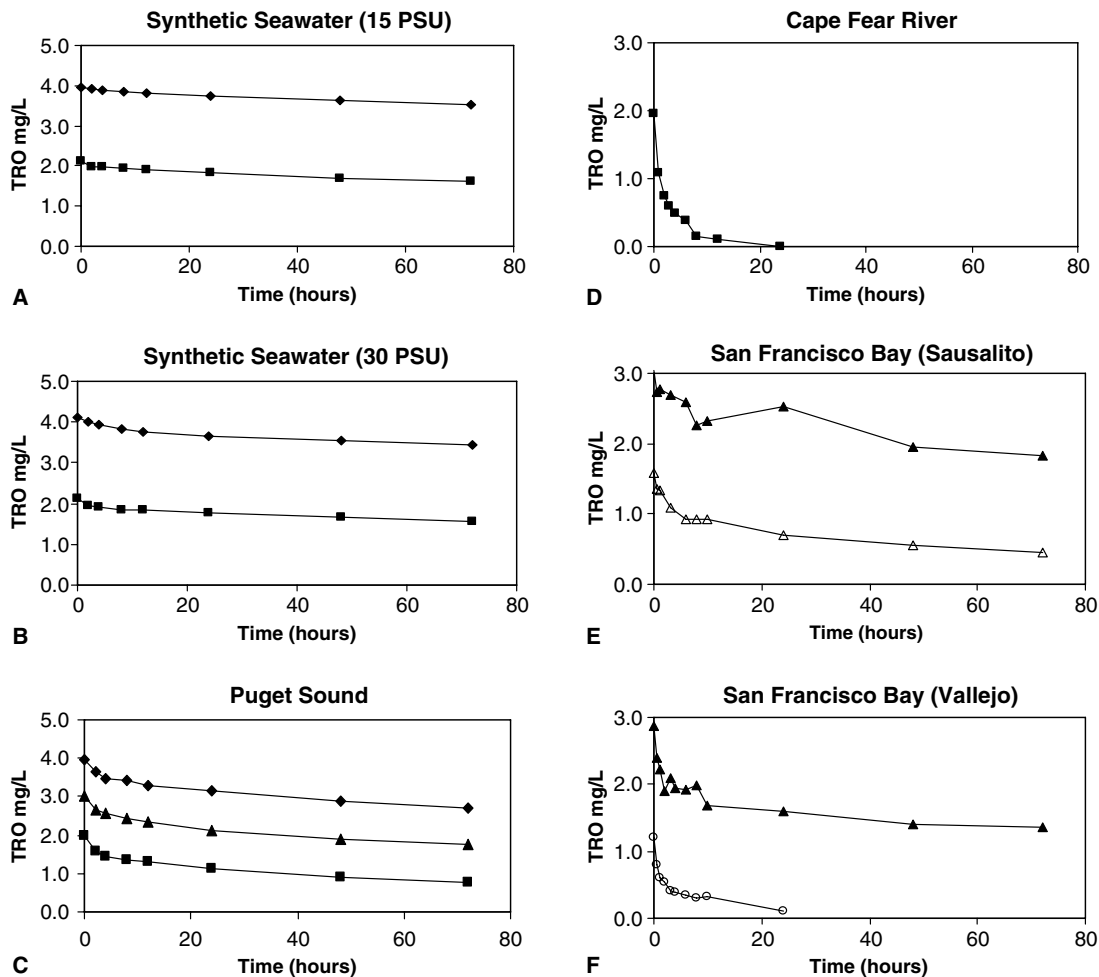


Fig. 2. Decay of total residual oxidant (TRO) in synthetic seawater prepared at 15 PSU (A) and 30 PSU (B); and seawater obtained from Puget Sound, Washington (C); Cape Fear River, North Carolina (D); two sites in San Francisco Bay, Sausalito (E) and Vallejo (F). Initial TRO concentrations measured in mg l⁻¹ as Br₂ were 4.0 (diamonds), 3.0 (triangles), 2.0 (squares), 1.5 (open triangles), and 1.0 (open circles).

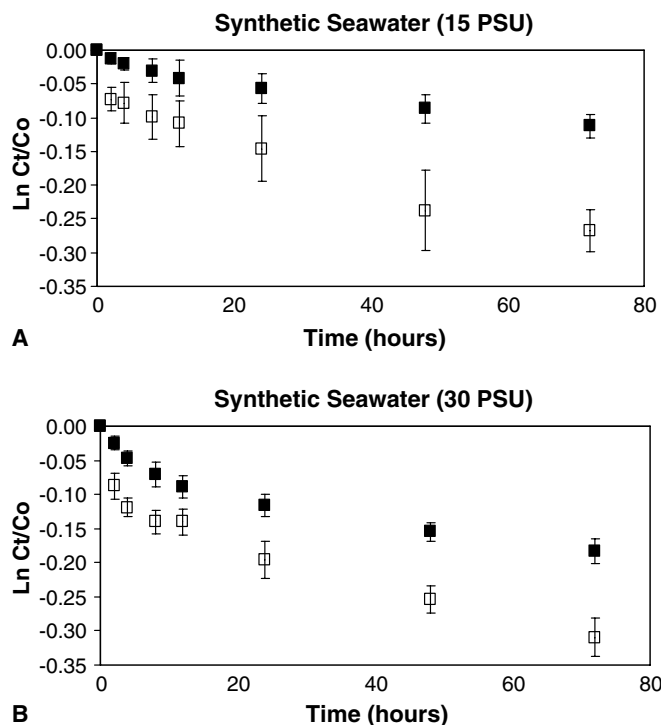


Fig. 3. Total residual oxidant, TRO (mg l⁻¹ as Br₂), decay in synthetic seawater at 15 PSU (A) and 30 PSU (B), and ozonated at two different TRO concentrations, 4.0 mg l⁻¹ as Br₂ (closed squares) and 2.0 mg l⁻¹ as Br₂ (open squares). Data is displayed as the natural logarithms (Ln) of the ratio of TRO value at time t (C_t) divided by the initial TRO (C_0). Error bars = 1 SD.

Similar to the Richardson et al. (1981) study, results presented here indicated that the rate of TRO decay seems dependant on salinity. However, it was not clear what the mechanism for this decay is in the synthetic seawater. The two obvious effects would arise from differences in the organic carbon and/or ammonium concentrations and these are not sufficiently different to account for the difference in decay rate (Table 1). Another reason for the differences in the decay rates at different salinity concentrations could be due to our manipulation of the TRO decay as a first order process. By assessing its likelihood as a first order decay rate amplifies small differences between the two salinities when ratios of TRO:TRO₀ are near 1 as our data represents.

Our results have practical implications for the installation of ozone systems on ships for inactivating organisms present in ballast water. The rate of TRO decay will determine the length of time that ballast water treated with ozone will be toxic to organisms residing within the ballast tank. The length of time that the ballast water remains toxic will also determine the initial TRO concentration necessary for the inactivation of organisms when considering that disinfection is the product of disinfectant concentration and exposure time (i.e., the $C * T$ concept) (Jones et al., in press). Our results suggested that vessels ballasting at locations with high salinity will have a slightly greater rate of TRO decay compared to vessels that collect ballast

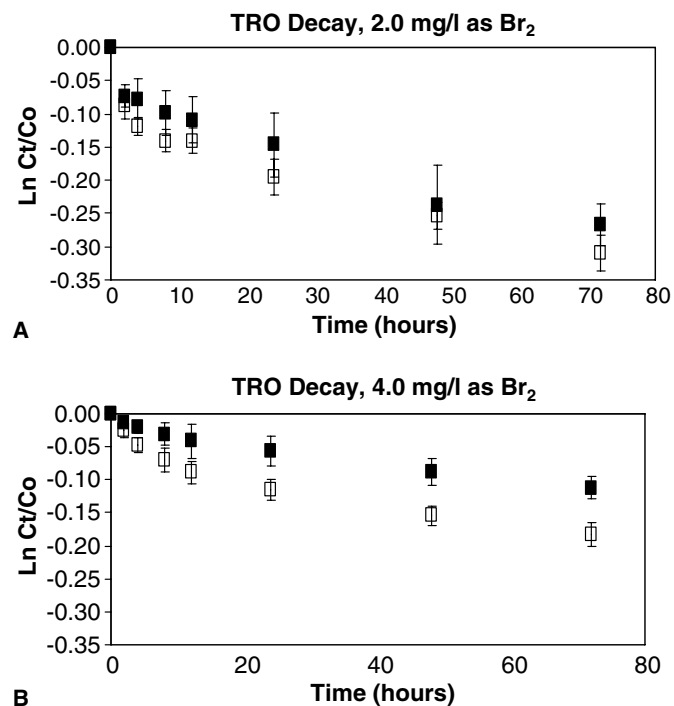


Fig. 4. Total residual oxidant decay starting at 2.0 mg l⁻¹ as Br₂ (A) and 4.0 mg l⁻¹ as Br₂ (B) in synthetic seawater prepared at two different salinities, 15 PSU (closed squares) and 30 PSU (open squares). Data is displayed as the natural logarithms (Ln) of the ratio of TRO value at time t (C_t) divided by the initial TRO (C_0). Error bars = 1 SD.

from locations that have a lower salinity. The resulting difference in TRO between the two salinities is, however, only 0.10 mg l⁻¹ as Br₂ after 72 h. This small difference would have a limited impact towards ballast treatment efficacy.

3.2.3. Rate of TRO decay in natural seawater

Four natural seawaters were ozonated to different TRO concentrations (Fig. 5). Of the three for which there are more than one final TRO, they showed a lower rate of decay as the concentration of the TRO increased. The rate of TRO decay in all of the natural waters was not linear, suggesting a complex mechanism(s). Also, the greater ozone dose would likely have lowered the TRO demand.

Water samples from Puget Sound were ozonated to three different initial TRO concentrations (Fig. 5A). There was a significant difference between the rate of decay and the starting oxidant level ($P \leq 0.003$). Puget Sound water with the initial TRO levels of 2 and 4 mg l⁻¹ as Br₂ were statistically compared to the synthetic seawaters of 15 and 30 PSU with the same initial TRO concentrations. The rates of decay for the three different sample waters with the same initial TRO concentration were found to be significantly different ($P \leq 0.0001$). The concentration of ammonium in Puget Sound water was low and similar to that of the synthetic seawater at 30 PSU (Table 1). The organic carbon concentration was slightly higher than the synthetic seawater, but not high enough to account for the differences observed. The phosphate ion concentration

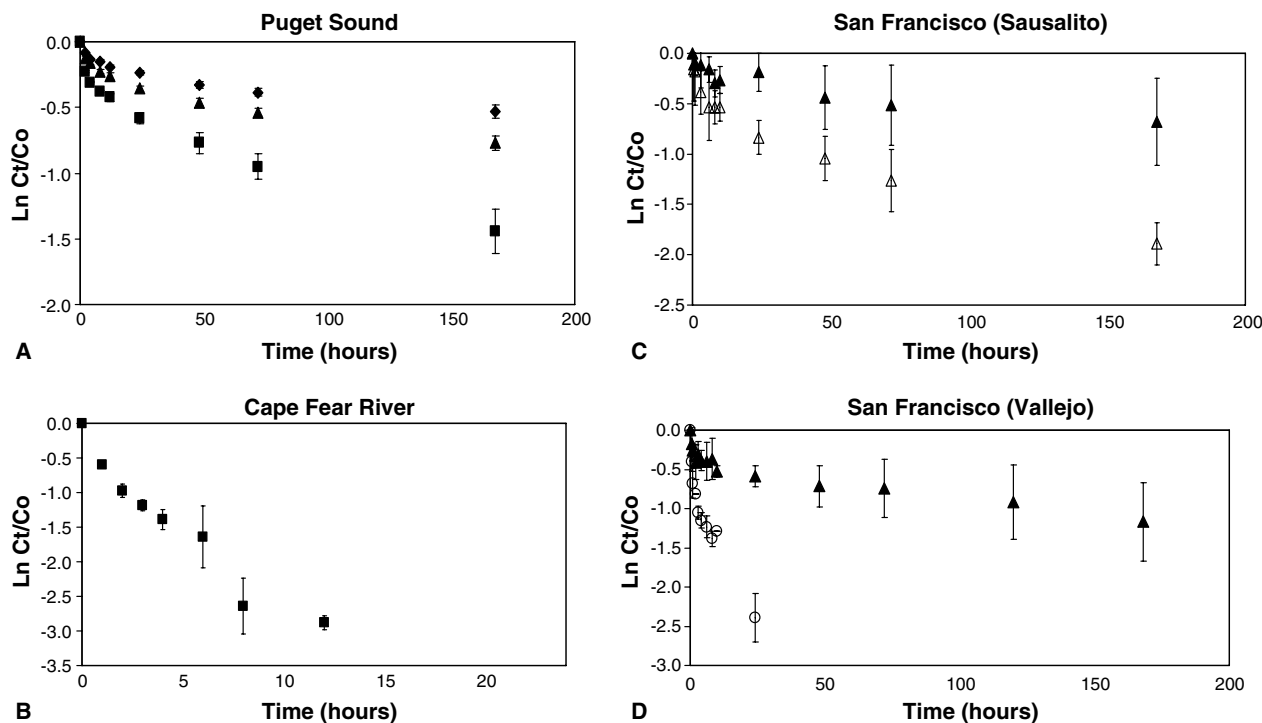


Fig. 5. Decay of total residual oxidant (TRO) in seawater obtained from Puget Sound, Washington (C); Cape Fear River, North Carolina (D); two sites in San Francisco Bay, Sausalito (E) and Vallejo (F). Initial TRO concentrations measured in mg l^{-1} as Br_2 were 4.0 (diamonds), 3.0 (triangles), 2.0 (squares), 1.5 (open triangles), and 1.0 (open circles). Data is displayed as the natural logarithms (\ln) of the ratio of TRO value at time t (C_t) divided by the initial TRO (C_0). Error bars = 1 SD.

was higher (approximately twofold) than the synthetic seawater with a PSU of 30, which could be the cause of the different rates of decay between the synthetic seawater and Puget Sound samples. However, the phosphate ion concentration and salinity would have been similar for three TRO concentrations of the Puget Sound samples and it is not obvious what accounts for the difference in the rate of TRO decay with increasing oxidant concentration.

Only one TRO concentration was studied in the Cape Fear River sample and that appeared to decay linearly over 12 h (Fig. 5B). The Cape Fear River sample was also compared with the previous samples from Puget Sound and the synthetic seawater at 30 PSU. The decay rate was found to be significantly different from the other water sources ($P \leq 0.0001$). From the limited data set, the rapid disappearance of TRO was most likely due to reaction of the TRO with the natural organic matter in the Cape Fear River.

Water samples from San Francisco Bay at Sausalito and Vallejo (Fig. 5C and D) mirrored the Puget Sound data in that at the higher TRO, the rate of decay was lower than at the lower oxidant concentration. This result would support either decay caused by breakpoint bromination or reaction with organic matter. Although both the Sausalito and Vallejo samples were from San Francisco Bay, there were differences in chemical characteristics between the two sources, including salinity, ammonium, and organic carbon concentrations (Table 1). A comparison of TRO decay rates from an initial TRO of 3 mg l^{-1} as Br_2 indicated that, when using a 90% confidence interval, there was a signifi-

cant difference between the two locations ($P \leq 0.056$). Both San Francisco Bay waters, when treated with the larger ozone dosage of 3 mg l^{-1} as Br_2 , demonstrated greater variability in TRO concentration over time, which would influence the statistical measurement of significance. Fig. 5C and D showed the rates of TRO decay for both of these sites were similar to the results of the other water samples, where the lower initial TRO concentrations were found to be significantly different from the larger initial TRO concentrations ($P \leq 0.005$). Similar to the Cape Fear River water, the Vallejo water, with an initial TRO of 1 mg l^{-1} as Br_2 , rapidly decreased below 0.1 mg l^{-1} within 24 h (Fig. 5D). The reason for its greater reduction could be due to one or more of the reactions described above.

Vessels using ozone for ballast water treatment need to reach an ozone concentration sufficient to produce a residual toxicity or TRO to inactivate organisms, but also need to know how quickly that TRO will disappear. Our results indicated that seawater from different sources have different concentrations of chemical compounds that affect TRO decay rates, thereby affecting the toxicity associated with the treatment over time. Knowledge of the rate of TRO decay can be used to determine an initial TRO concentration necessary for an effective reduction of organisms over the time that the TRO would remain in the ballast tank.

Our results indicated that the rate of TRO decay was dependent on the chemistry of the ballast water. For different source waters to maintain similar TRO concentrations over time, a greater amount of ozone will be required for

those waters that have greater organic carbon and ammonia concentrations. Puget Sound has relatively low organic carbon and ammonia concentrations comparable to both the San Francisco Bay and Cape Fear waters (Table 1). This suggests that a given ozone concentration would achieve a higher TRO and slower TRO decay within the Puget Sound than if the same ozone concentration was applied to any of the other natural waters tested in our study. For San Francisco Bay and Cape Fear waters, greater concentrations of ozone would be required compared to Puget Sound seawater if they are to achieve a similar TRO concentration that would remain over time. Any vessel using ozone for ballast treatment will need to determine how much ozone is necessary to maintain an effective TRO for ballast water collected from different ports having different chemical characteristics.

A ship may be able to take advantage of TRO decay in how it manages its ballast water discharge. At discharge, ballast water should ideally be non-toxic to the receiving ecosystem. As shown above, ozonation of seawater results in a TRO and therefore toxicity that decays over time. If necessary, remaining TRO could be neutralized before discharge by adding a reductant, such as sulfite (Jones et al., in press). Alternatively, if the TRO in the ballast water decays to near 0 mg l^{-1} during a voyage, then it could be discharged without performing a reduction step.

3.2.4. Other contributors to TRO decay

Residual oxidant decay rates are also dependent on relatively non-selective oxidation of organic matter (Dotson and Helz, 1984; Bichsel and von Gunten, 1999). Inorganic compounds, such as iron, and other source water impurities are also suggested to affect residual oxidant decay (Lawson, 1995; Oemcke and van Leeuwen, 2004).

The effects of microorganisms are generally considered part of the organic concentration. Their growth, decay, and byproducts may affect the rate of residual oxidant decay (Liltved et al., 1995; Kureshy et al., 1999). Seasonal changes in the water, such as biological production rates and temperature, may affect both the dissolution and decay rates of an oxidant for ballast treatment. The rate of residual oxidant decay could also depend on the type of organic compounds found. A review by von Gunten (2003a) indicated that not all organics promote oxidant reactions, and that the degree of protonation and complexation of amines in ligands leads to a decrease in their oxidation reactivity. Another study, in which the residual oxidant concentrations in the presence of two organic compounds, humic acid and bovine serum albumin (BSA) were measured over a period of 5 days, indicated that BSA had a greater oxidant demand than humic acid (Ayotte and Gray, 1984).

3.3. Biological implications for ballast water treatment with ozone

Previous studies measuring ozone's ability as a biocide in marine water were limited to specific organisms, but

these studies provide insights as to the effective dose necessary for the treatment of ballast water. Others found that microorganisms are eliminated at TRO concentrations less than 1 mg l^{-1} . Bacterial fish pathogens *Enterococcus seriolicida*, *Vibrio anguillarum*, and *Pasteurella piscicida* abundances decrease at relatively low TRO concentrations, ranging from 0.04 to 0.06 mg l^{-1} (Sugita et al., 1992). Ito et al. (1997) determined that a TRO of 0.1 mg l^{-1} reduced by more than three orders of magnitude the bacterial species *Vibrio anguillarum*, *Aeromonas salmonicida*, *Aeromonas caviae*, *Aeromonas hydrophila*, and *Escherichia coli* after 2 min. Kureshy et al. (1999) found that a TRO level of 0.92 mg l^{-1} reduced the cell counts of algal species for over four days.

Larger organisms may require higher TRO concentrations or longer exposures to a minimum TRO level to become inactivated. A study involving several marine invertebrate and fish species (*Americamysis bahia*, larval *Atherinops affinis*, juvenile *Cyprinodon variegatus*, and *Rhepoxynius abronius*) demonstrated that these organisms were "effectively eliminated following short term (i.e., less than 5 h) ozonation at less than 1 mg l^{-1} as Br_2 " (Jones et al., in press). These results and other data suggest that TRO concentrations greater than $1 \text{ mg Br}_2 \text{ l}^{-1}$ are required for rapid removal of some planktonic larvae and mesozooplankton (Cooper et al., 2002; Perrins and Herwig, 2003; Herwig et al., 2004).

Previously described experiments showed that a TRO of $1 \text{ mg Br}_2 \text{ l}^{-1}$ is sufficient for rapid removal of single celled organisms and some multicellular organisms. We recommend that to remove the large diversity of organisms that are present in seawater, a minimum TRO concentration of $1 \text{ mg Br}_2 \text{ l}^{-1}$ be maintained in a ballast tank for an extended period of time, ideally throughout the length of the voyage. Our results indicated that an initial TRO of $3.0 \text{ mg Br}_2 \text{ l}^{-1}$ created in Puget Sound and San Francisco Bay waters would provide a TRO of at least $1 \text{ mg Br}_2 \text{ l}^{-1}$ for 72 h. The most rapid decline in oxidant concentration occurs during the few hours followed by a much slower decay thereafter. Due to the limited testing with the Cape Fear water, the level of initial TRO needed to maintain a TRO of $1 \text{ mg Br}_2 \text{ l}^{-1}$ could not be determined, but was greater than $2 \text{ mg Br}_2 \text{ l}^{-1}$. Additional biological studies are needed to determine if ballast treatment will require a minimum TRO of $1 \text{ mg Br}_2 \text{ l}^{-1}$ for a period greater than 72 h for the removal of species in ballast water.

4. Summary and conclusions

We examined the formation of TRO during ozonation and the decay of TRO in synthetic seawater and in water samples collected from Puget Sound, Washington; Cape Fear, North Carolina; and San Francisco Bay. Ballast water treatment with ozone produces a residual disinfectant that slowly decays in the dark. This residual toxicity can increase the effectiveness of the ballast treatment by extending the time that organisms must survive in a toxic

environment. Assuming that the organism's response to treatment is linearly dependent on the disinfectant concentration and exposure time, this would imply that a lower disinfectant dose could be used to treat ballast water if there is a sufficient time of exposure during a voyage.

Our results also suggested that a higher initial TRO concentration in ballast water would decay slower than a lower initial TRO concentration. Therefore, increasing the initial TRO would provide the disinfectant effect over a longer time. This increased disinfection period will not only be able to increase the effectiveness of treatment on those organisms that are more resistant to oxidation, but will also inhibit the regrowth of organisms with rapid reproductive rates, such as bacteria. If the TRO declines below a certain level, toxicity associated with the treated water is removed. Therefore, if heterotrophic microorganisms are initially reduced in number, but not totally eliminated, their populations will increase once the TRO is removed from the water (Perrins and Herwig, 2003; Herwig et al., 2004). With knowledge of the type of source water and its TRO decay rate, it should be possible to determine the initial TRO concentration necessary to maintain a desired residual toxicant concentration for a specific time, such as the voyage of a ship from one port to another.

In experiments described here, ozone was introduced through diffusion into a water column. These results may not be totally applicable when using rapid dissolution ozonation technology, such as in-line ozonation through a venturi. This technology will result in the very rapid establishment of a residual disinfectant or TRO. However, since less oxidant demand will be satisfied over the short ozonation time, it is to be expected that the TRO decay rate will be more rapid. Our research team will be involved in evaluating the introduction of ozone through a venturi in future experiments.

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