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Evaluation of approaches to quantify total residual oxidants
in ballast water management systems employing chlorine for disinfection

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Abstract

With the maturation and certification of several ballast water management systems that employ chlorine as biocide to prevent the spread of invasive species, there is a clear need for accurate and reliable total residual oxidant (TRO) technology to monitor treatment dose and assure the environmental safety of treated water discharged from ship. In this study, instruments used to measure TRO in wastewater and drinking water applications were evaluated for their performance in scenarios mimicking a ballast water treatment application (e.g., diverse hold times, temperatures and salinities). Parameters chosen for testing these technologies in the past do not reflect conditions expected during ballast water treatment. Salinity, temperature, and oxidant concentration all influenced the response of amperometric sensors. Oxidation reduction potential (ORP) sensors performed more consistently than amperometric sensors under different conditions but it may be difficult to correlate ORP and TRO measurements for the multitude of biogeochemical conditions found naturally in ballast water. N,N-diethyl-p-phenylenediamine (DPD) analyzers and amperometric sensors were also tested under intermittent sampling conditions mimicking a ballasting scenario, with cyclical dosage and discharge operations. When sampling was intermittent, amperometric sensors required excessive response and conditioning times, whereas DPD analyzers provided reasonable estimates of TRO under the ballasting scenario.

Keywords: Ballast water, Online analyzers, Oxidation reduction potential, Total residual oxidants

Introduction

Invasions by non-native aquatic species are increasingly common in coastal habitats worldwide (Cohen and Carlton, 1998) and can decrease the abundance or cause local extinction of native species (Byers, 1999), alter habitat structure (Daehler and Strong, 1996), and result in large economic costs due to biofouling or fisheries losses (Johnson and Carlton, 1996). Shipping, which moves over 90% of the world's commodities and is fundamental to international trade (King and Tamburri, 2010), inadvertently transports aquatic organisms in ballast water (see review by National Research Council, 1996). To help minimize the risk of transporting invasive species through ballast water, the International Maritime Organization (IMO) drafted the Convention for the Control and Management of Ships' Ballast Water and Sediments (IMO, 2004). More recently, the United States Coast Guard (USCG) issued a similar set of federal regulations that require vessels to treat their ballast water in order to meet discharge limits for various size classes or taxa of live organisms (USCG, 2012), and the U.S. Environmental Protection Agency (EPA) established a Vessel General Permit (EPA VGP, 2013) that regulates 27 specific vessel discharge categories including ballast water. In response to these regulations, a variety of onboard Ballast Water Management Systems (BWMS) are now available or under development to remove, kill or inactivate organisms found in ships' ballast water.

Many current BWMSs have been adapted from industrial or municipal water treatment applications and several that incorporate chemical treatment have received Type Approval Certification based on extensive land-based and shipboard testing (e.g., EPA, 2011). Approximately 40% of BWMSs evaluated for the IMO so far incorporate chlorination and almost all use neutralization to reduce TRO prior to discharge (Bowmer and Linders, 2010), making ballast water chlorination one of the primary disinfection methods applied in BWMS to date. However, there are difficulties associated with chlorination of ballast water. Discharge of ballast water after oxidative treatment and neutralization can lead to potential ecotoxicity (Delacroix et al. 2013, Gregg et al. 2009). In particular, current ballast water treatment can lead to formation of residual TRO and disinfection by-products (DBPs), including trihalomethanes and halo-acetic acids, among others (Bowmer and Linders, 2013; Werschkun et al., 2013). It is for these reasons that the EPA VGP also includes requirements for self-monitoring of a variety of parameters, including periodic measures of ballast water TRO on discharge (using EPA approved methods) for vessels having BWMSs that utilize chlorine. Therefore, accurate measures of TRO are critical not only for efficient and effective dosing and process control for BWMSs but also to ensure that regulatory/permit requirements are met.

A broad range of effective technologies is desirable considering the varied environmental and technical conditions encountered by BWMS and the difficulties associated with effective process control. Traditional disinfection applications of TRO measurement methods often deal with consistent water and flow conditions when compared to ballast water treatment applications, which can vary significantly in salinities (ranging from fresh to brackish and ocean waters), levels of dissolved and particulate organics, temperatures (from near freezing to over 30°C), and flow rates (from 0 ft/sec to significant flow). Unlike the continuous monitoring that takes place in wastewater or drinking water treatment, TRO measurements are also focused on periods during uptake (treatment dose) and discharge (residual concentrations) during ballast water treatment, which occur intermittently and are dependent on vessel cargo operations. Additionally, to be effective within this new application, it is essential that TRO measurement approaches be

easily operated and have minimal maintenance requirements since little, if any, technical support is available during voyages.

Current BWMS use a combination of DPD (N,N-diethyl-p-phenylenediamine) analyzers, DPD field testing kits, amperometric sensor, and/or oxidation reduction potential (ORP) sensors to measure TRO. Amperometric sensors are electrochemical in nature, producing a current proportional to the chlorine concentration of the sample. Amperometric sensors are reagentless, unlike DPD analyzers, which employ colorimetric assays that utilize chemical reagents. These reagents react with oxidants in the sample water, producing a color proportional to the total oxidant concentration. DPD analyzers have been found to perform more consistently than amperometric sensors under certain conditions, including fluctuating temperature and pH (Badalyn et al., 2009; Malcov et al., 2009). However, the DPD analyzer requires periodic replacement of reagents, generates a wastestream, requires approximately 2.5 minutes between measurements, and incorporates cycling of reagents and sample through a flow-dependent sampling system. Finally, ORP sensors have also been demonstrated to provide reasonable estimates of TRO (Ryder, 2002; Goncharuk et al., 2010). ORP sensors produce a measurable potential that is proportional to the oxidant concentration of the sample water. On-line monitoring systems commonly use amperometric and DPD colorimetric technology to determine total residual oxidants in wastewater treatment and drinking water applications and these technologies have been tested for traditional applications (e.g. Badalyn et al., 2009; Malkov et al., 2009). However, recommendations gleaned during these studies cannot be directly applied to BW applications due to the lack of testing of BWMS-specific parameters such as varied salinity and flow-rate.

Although the DPD analyzer, amperometric sensor, and ORP sensor performance characteristics are generally known, the current understanding does not directly apply to BWMS application, and differences in application can significantly affect TRO sensor performance (Bender, 1978; Nutt et al., 1985; Badalyn et al., 2009; Malcov et al. 2009). Therefore, systematic efforts designed to test technologies under conditions specifically designed for application to BWMS are needed. The goal of this study is to evaluate the effects of several ballast water specific parameters and shipboard monitoring logistics on the performance of traditional TRO measurement approaches. Amperometric and ORP sensor responses were tested under a variety of conditions that reflect a range of water parameters likely to be encountered during ballast water treatment, including salinity, temperature, and treatment dose. In addition, the application of on-line analyzers (DPD and amperometric) was evaluated through simulated ballast water trials, testing the ability of these sensors to tolerate changes in flow and dosing without appreciable changes in sensor output.

Methods

Study Approach

While other disinfectant species may be present, this work is focused on instruments or methods that quantify total residual oxidants, which is required for chlorine-based BWMSs. Two phases of testing were conducted. In Phase 1, the performance of three different (distinct manufacturer and/or model) amperometric sensors and an ORP probe was evaluated in treatments testing water parameters likely to fluctuate during ballast water treatment onboard active ships. In Phase 2, the performance of three different DPD analyzers and the same three amperometric sensors was evaluated using conditions that mimic a ship's ballast cycle.

In both phases of testing, two EPA-certified DPD handheld colorimeters were used to take reference TRO measurements: the Hach Free and Total DPD pocket photometer (5870023, Hach Company, Loveland, Colorado) and the HF Scientific Chlorine Pocket Colorimeter (EW-99561-30, HF Scientific, Fort Meyers, FL). Handheld colorimetric methods are USEPA-approved for grab sample reference in conjunction with an approved online method (USEPA Method 334). Grab sample analyses were carried out according to American Public Health Association Standard Method 4500- Cl G, which allows for application of handheld DPD measurement to water, wastewater, estuary, and seawater samples (APHA et al. 1998).

Phase 1: Amperometric and ORP Sensor and Sodium Hypochlorite

Nine 54-hour trials were conducted, testing variability of sensor performance. Three different amperometric sensors were immersed directly in a well-mixed 325 L water bath with consistent flow and temperature fluctuating $\pm 1^{\circ}\text{C}$ during each 54-hour trial. Standard conditions applied were 25°C , 15 psu, and 9 ppm dosage concentration. These conditions were manipulated during the different trials to test sensor performance at different salinities (0, 15, and 30 psu), temperatures (7, 15, and 25°C) and doses of sodium hypochlorite (2, 5, and 9 ppm). Test water baths were prepared by collecting natural, unfiltered brackish water from Solomons, Maryland (all 15 psu trials), freshwater from Lake Lariat, Maryland (0 psu trial), and oceanic water from Virginia Beach, Virginia (30 psu trial). During each trial, residual chlorine levels were achieved by adding sodium hypochlorite (commercial grade 6% active NaOCl). After initial dosage, sensor performance was monitored every hour for the first 12 hours and every six hours thereafter. Sodium hypochlorite volatilized over 53 hours to a residual of between 1 and 2 ppm and to between 3 and 4 ppm during the 7°C and 15°C trials (chlorine volatilization slows as temperature declines). At 53 hours, residual TRO was then quenched through the additions of sodium thiosulfate. During the 4 and 2 ppm dosage trials, residual TRO quenching was not necessary because chlorine was effectively reduced below 0.1 ppm within the 54-hour trial period. Amperometric sensors were equilibrated for several days upon initial installation and equilibrated overnight in chlorinated water (12-hour run-in period) before each trial.

Phase 2: Amperometric Sensors, DPD Analyzers and Intermittent Use

Three DPD analyzers and three amperometric sensors were subjected to a laboratory-based simulated ballast cycle. Each test cycle included a 12-hour simulated sampling period followed by a 60-hour simulated hold/storage period. This was repeated once for consistency within each trial; each trial represented two hypothetical voyages. The water bath was initially dosed at either five (Treatment A, Trial 1) or nine ppm (Treatment A, Trial 2) followed by the 60-hour simulated hold time. After a 12-hour sampling period following dosage, sensors were turned off simulating a 60-hr hold/storage period. After 60 hours, sensors were turned back on and response was analyzed at a lower concentration (held between 0.4 ppm and 0.7 ppm), reflecting ballast water conditions with significant hold times prior to quenching of TRO residual and discharge.

An additional treatment, Treatment B, tested whether sensor performance can be improved by leaving sensors on during the 60-hour hold time. During Treatment B, one trial was completed, dosed at 5 ppm (Treatment B, Trial 1), sensors were left on during the 60-hour simulated hold time and flow to the reservoir and to the sensors was turned off. Amperometric sensors require an extensive run in period; therefore, amperometric sensor performance may show improvement if sensors are left on. DPD analyzers take independent samples; thus, this alternate application method is not expected to affect DPD analyzer response.

Testing was conducted using two 210 L water reservoirs. One reservoir was used for batching high and low concentration solutions and one reservoir contained the experimental apparatus. Water from the batching reservoir was added under controlled flow to the experimental reservoir as needed to maintain water level and concentration (approximately every two hours during sampling). Instruments were allowed to equilibrate to the test water according to manufacturers' guidelines prior to each trial.

Seawater was collected offshore of Long Beach, California, filtered and stored at the University of California, Los Angeles, in a 25,000 L reservoir and used to replenish the batching reservoir prior to each sampling period. Temperature, salinity and pH were held constant, at an average pH of 8.2, salinity of 30 psu and temperature of 22°C throughout testing.

Table 1 | Treatment details.

Test Water Chemistry

Chemical analyses of total suspended solids (TSS), dissolved organic carbon (DOC), and particulate organic carbon (POC) were carried out once per trial according to standard methods: USEPA Method 160.2 (TSS) and USEPA Method 415.1 (POC and DOC). Salinity and pH were measured every six hours during Phase 1 sampling and once every 12-hour sampling period during Phase 2 via grab sample collection. A Thermo Orion gel-filled triode pH probe was used for pH analysis and an Extech RF10 hand-held refractometer was used for analysis of salinity. Temperature was measured every two hours with a Fisher Scientific digital temperature probe secured in the water bath. For water chemistry results see Supplementary Material S1. For Phase 2 testing, temperature, salinity and pH were held constant, at an average pH of 8.2, salinity of 30 psu and temperature of 22°C.

Data Collection and Statistical Analysis

During Phase 1 testing, data from each test instrument and the DPD reference analysis were recorded every two hours during the first 12 hours and every six hours thereafter. Multivariate linear regression analysis was applied to analyze the effect of sensor type, salinity, dosage and TRO concentration on the difference between sensor and reference TRO measurements. Residuals (sensor measurement minus reference TRO measurement) were regressed on sensor type, salinity, dosage and TRO concentration. Salinity (0, 15, or 30 psu), sensor type (1, 2, or 3) and chlorine dose (10 ppm, 4 ppm, or 2 ppm) were included in the model as categorical covariates where standard conditions of 15 psu, sensor 1, and dose 10 ppm were applied as the referent category for analysis. White's heteroskedastic-consistent, robust standard errors were used.

Performance during the temperature trials was analyzed separately due to the differences in TRO concentration. A one-way ANOVA analysis was applied to see if sensor performance differed

significantly between the three temperature trials. All statistical analyses were carried out with STATA Version 11 software.

During Phase 2 testing, sensor performance data was recorded on-line. Sensor performance of four of the six analyzers was logged with a 4-channel U12 Hobo datalogger (Onset Computers). The two remaining sensors did not require external datalogging: one of the amperometric probes had internal logging capacity and one of the DPD analyzers was equipped with a sensor-specific data logger (SC 2000 controller). Grab samples were taken every two hours and TRO was measured with two handheld DPD colorimeters (applied as the reference method). To evaluate accuracy of the test instruments, Malcov et al. (2009) considered sensor performance to be acceptable if average sensor response fell within 10% of the reference method. For consistency, this study uses the same classification of an acceptable measured value as within 10% of the corresponding reference value. 90% confidence intervals (CIs) of average sensor response and reference method were compared in order to allow for some fluctuation in the chlorine concentration over the course of the twelve-hour sampling period, providing a narrower and more precise estimate of average sensor response. Instrument-measured means and confidence intervals were calculated and compared for each twelve-hour sampling period.

Results and Discussion

Phase 1: Amperometric and ORP sensor and Sodium Hypochlorite Results

Amperometric sensors are not commonly used in BWMS, but offer some potential advantages over other instruments. Amperometric sensors are reagentless and if applied to ballast water management systems would allow for the direct immersion of the sensor in a sampling inlet, eliminating the need for sampling pumps and reagents associated with DPD online analyzers. However, analysis of instrument performance reveals several limitations of the amperometric sensors evaluated for ballast water applications.

The regression analysis identified the effect of treatment differences on sensor performance (Figure 1, open symbols, $R=0.60$, $F = 81.21$, $P=0.00$); equation one (below) refers to the linear regression equation. Sensor performance significantly declined with increasing salinity (0 psu to 15 or 30 psu), and increasing chlorine concentration ($P=0.00$). Raising the salinity from 15 psu to 30 psu had a minimal effect on sensor measurements (Eqn.1, $\beta_{0 \text{ psu}} = 0.191$; $\beta_{30 \text{ psu}} = 0.009$). Lower initial treatment dosages of chlorine (4 ppm or 2 ppm) led to more accurate measurements of TRO by amperometric sensors. There was no significant difference between the effects of a dosage of 4 ppm versus 2 ppm on sensor performance ($P=0.19$). Significant differences in performance at different dosages (9 ppm versus 4 and 2 ppm) were likely a result of calibration limitations of the sensors. Previous analyses found amperometric sensors to have difficulty holding calibration for more than a ± 1 ppm TRO range (Ryder, 2002; Malcov et al. 2009). During lower dosage trials, TRO concentrations fluctuated within a much smaller range (between ± 2 ppm); thus, increased performance during the lower dosage trials is likely a result of the decreased concentration testing range.


Eqn.1: 

Figure | TRO concentrations of amperometric sensor (TRO ppm) and ORP sensor (ORP RmV) versus DPD reference (TRO ppm) over the sampling period for Phase 1 testing. Open symbols = amperometric sensor performance (results are an average of amperometric sensors 1-3). Closed symbols = ORP sensor results. Dashed line was fit to average ORP response.

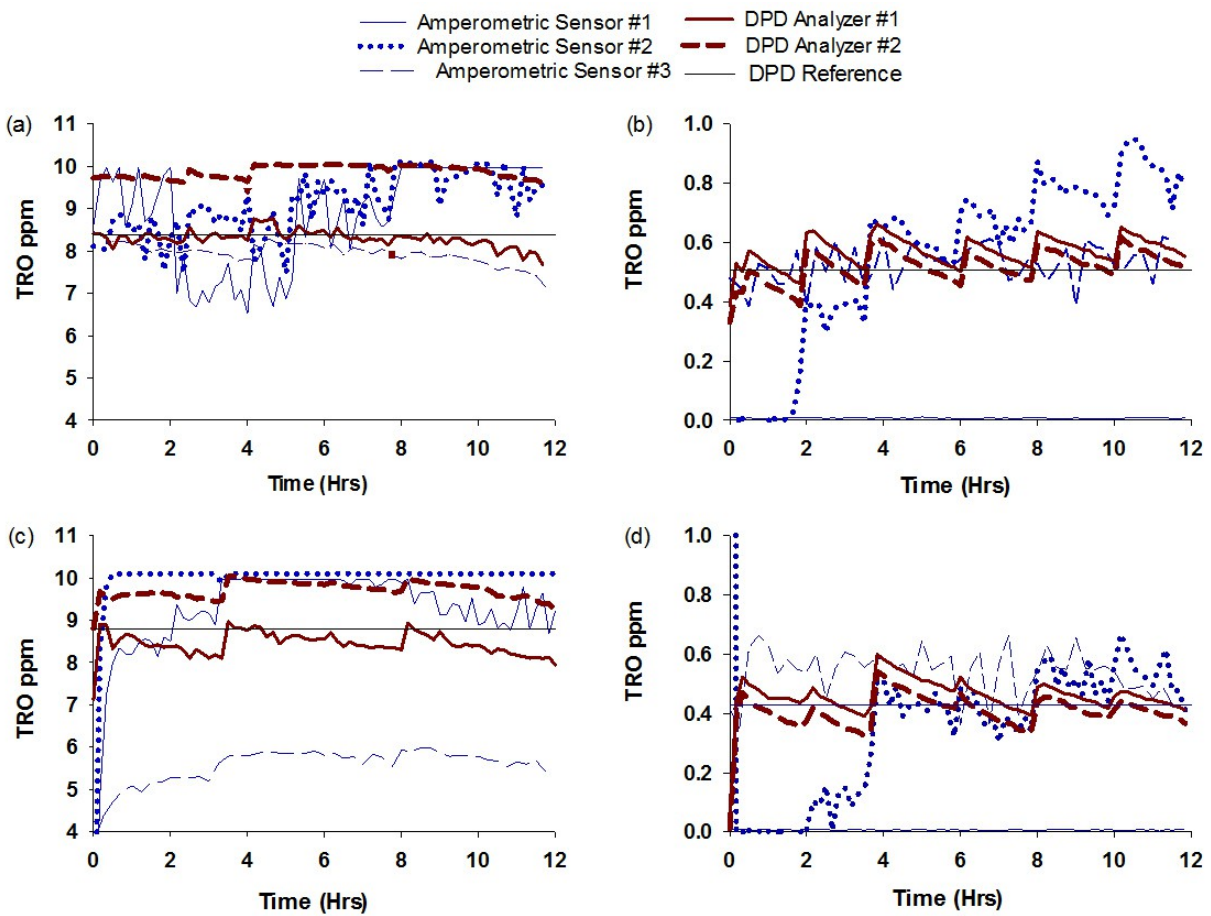
Analysis of the three temperature trials showed a decline in amperometric sensor performance with decreasing temperature (one-way ANOVA, $F_{df = 2, 378} = 15.67$, $p = 0.00$), as previously reported by Malcov et al. (2009) and Nutt (1985). There was no significant difference in sensor performance between the 15°C trial and the 25°C trial ($p=0.6221$), but average sensor response was significantly different between the 7°C trial and both the 25°C and 15°C trials (pairwise comparisons, $P < 0.01$). Since an effective and reliable TRO sensor would be required to perform consistently and accurately under diverse and unpredictable environmental conditions, including fluctuating salinity and temperature, there appears to be significant limitations associated with the application of current amperometric sensors to BWMS.

ORP sensors have been applied to BWMS. However, because of fluctuations in baseline mV measurements and the insensitivity of the mV reading at higher concentrations, it may be difficult to correlate ORP mV measurements to TRO concentration for varying BWMS applications. During Phase 1 testing, an ORP probe measured TRO via grab sample analysis. With the exception of the freshwater trial, mean RmV responded logarithmically to declining TRO concentration ($R^2=0.84$) (Figure 1, dashed line). The difference in ORP sensor response exhibited during the freshwater trial is likely a result of increased NOM (Table S2). Water properties, including organics, can affect ORP measurements (Charpentier et al., 1998), resulting in a reduction in sensitivity of ORP measurements, as seen in this study. The logarithmic response of the ORP sensor also results in decreased sensitivity of the sensor at higher TRO concentrations. For example, there was no substantial change in ORP mV when TRO concentration was reduced from 9 ppm to 4 ppm. Similarly, Bergendahl and Stevens (2005) found ORP instrument sensitivity in wastewater treatment application to decline at higher concentrations. It is not uncommon for BWMS to dose with 10 ppm or more of chlorine on

uptake of ballast water, requiring measurements beyond the linear range of mV readings. The logarithmic relationship between TRO concentration and mV results in increased sensitivity of the ORP mV measurement at lower TRO concentrations (White, 2010). However, substantial differences in ORP baseline measurements, near a zero chlorine residual, have been noted (Kim and Hensley, 1997; World Health Organization, 2006), making comparison between different water samples difficult.

Phase 2: Amperometric Sensors, DPD Analyzer and Intermittent Use Results

In the context of this study, response time reflects the warm-up time required by an instrument for a TRO measurement to be recorded after a period of non-use, which is important for the effective use of chemical treatments within BWMS.



B
D
Figure 2| Datalogged TRO concentrations (TRO ppm) measured by online analyzers (continuous measure) and reference TRO concentration measured by grab sample every two hours over each sampling period (12 hrs) for Phase 2, Trial 1A. a) Instrument response during initial dosage phase. b) Instrument response during initial discharge phase. c) Instrument response during secondary dosage phase. d) Instrument response during secondary discharge phase.

For the simulated ballast cycle testing (Phase 2), amperometric sensors exhibited delayed response after the simulated hold time. Two out of the three amperometric sensors evaluated exhibited excessive delayed response during initial warm up time (Figure 2). The delay in response time varied from a delay of 15 minutes to three hours, depending on sensor type. Amperometric sensor 1 responded with acceptable measurements during the dosage phases and

with no response to the lower concentrations during the discharge phases. Amperometric sensor 2 and amperometric sensor 3 provided measurements that fell outside $\pm 10\%$ of the reference measure on several occasions during both discharge and dosage phases of Treatment A (Table 1). Although response was more rapid for the third amperometric sensor, this instrument consistently underestimated TRO concentrations (Table 1). During Treatment B, the delay in response time (seen during Trial 1 and Trial 2 of Treatment A) of amperometric sensor 2 was minimized, decreasing from an average delay of 3 hours to 15 minutes after flow was regained.

Table 2 | Average analyzer and reference response (TRO ppm) for phase 2 testing. Average sensor/analyzer response results are included only for trial statistics that fell outside of the $\pm 10\%$ average reference measurement threshold applied. DPD analyzer #1 measurements remained within the 10% threshold throughout the study, so its average response is not included below.

DPD online analyzers operated effectively with accurate and rapid response during the intermittent sampling application testing. Response time was minimal, and readings corresponded closely with reference measurements for DPD analyzer 1 and 3 (Figure 2, bold lines). Response time was delayed 95 minutes for DPD analyzer 2 during the initial dosage phase of Treatment B. It is unclear what caused the delayed response during this trial; however, online DPD analyzers are fully automated and additional run-in time for reagents to cycle through the analyzer may have been necessary. Further, during Treatment A, Trial 2 (10 ppm dose), DPD analyzer 2 was outside $\pm 10\%$ of the reference method for the initial dosage phase. Accuracy of this analyzer declined with the higher dosage level applied in Treatment A, Trial 2. DPD analyzer 3 was not used during Treatment A, Trial 2 due to limitations of its performance requirements: the recommended measurement range of DPD analyzer 3 is between 0 and 5 ppm TRO.

Reference Method

Two EPA-certified DPD handheld colorimeters were used as the reference standard and as an alternative way to monitor TRO. Both handheld colorimeters were used effectively throughout testing without mechanical error and without additional calibration requirements. Trained technicians, engineers, or other qualified individuals would be required to collect grab samples and perform bench DPD analysis if handheld DPD was used to monitor TRO in BWMS application. Furthermore, because large volumes of water are treated or discharged over several

hours, collecting appropriate and representative samples from the entire discharge would be challenging (Miller et al., 2011).

Recommendations for Application

Our results support previous work that evaluated the performance of amperometric and colorimetric technologies for more traditional applications. Badalyn et al. (2009) evaluated performance of various amperometric, polarographic, and colorimetric online analyzers under laboratory test conditions. Three of the six amperometric analyzers tested illustrated poor response linearity, likely a result of failed calibration after three days of testing (Badalyn et al., 2009). As in our study, Malcov et al. (2009) found amperometric sensor performance to be a function of environment, with changing pH, temperature, and chlorine concentration affecting amperometric sensor response. Although amperometric sensors may be useful for continuous measurements under more traditional water treatment scenarios, the performance of current amperometric sensors, under cyclical conditions consistent with application to BWMS, declined resulting in inaccurate measurements and delayed response times.

DPD appears to be much better suited for BWMS application. The DPD colorimetric method has been shown to be independent of environmental conditions including pH and temperature changes (Malcov et al. 2009), and DPD analyzers tested in this study performed well and consistently in saline water under challenging cyclical dosage conditions. The automated nature of DPD analyzers means there are additional considerations, including generation of a wastestream, reagent consumption, and mechanical failures. Generation of a wastestream will require additional disposal and storage onboard vessels, but it does not affect instrument performance. While reagent replacement may not be difficult, most manufacturers recommend a monthly replacement cycle, and reagents can also become contaminated, both of which may present logistical challenges for vessel operators or crew. With several automated parts, mechanical failures (e.g., pump malfunctions, tubing leaks, flow obstructions) are also possible, and instrument redundancy will need to be considered (servicing was required to replace a faulty colorimeter on one instrument during this study). Flow delivered to the system should be routinely monitored, ensuring constant delivery of sample and reagents to the sampling inlet in order to limit error associated with reagent supply and sample flow. Verification and redundancy of online analyzer TRO measurements with grab sample analysis could provide a valuable backup method, considering the mechanical constraints associated with automated instruments.

Conclusions

Treatment of ballast water with chemical oxidants represents a complex and potentially hazardous process. Previous studies illuminate the challenges associated with quantifying residual chlorine levels in natural waters (e.g. Bender, 1978; Malcov et al., 2009). Further, the amount of DMPs and corresponding ecotoxicity of chlorinated ballast water is dependent on oxidant dosage (Gregg et al. 2009) as well as residual TRO and discharge concentration (Delacroix et al. 2013), making appropriate and effective measurement of TRO vital. Applying automated systems to BWMS application would allow for variability in the disinfection process to be monitored effectively, as well as the retrieval of continuous information describing the residual concentration of the ballast water. In this study, DPD analyzers were the most accurate, applicable, and the least sensitive to various interferences. However, TRO sensor performance was altered and in several instances degraded when sensors were applied to a simulated ballasting cycle. Although the amperometric sensors tested in this study had several significant

shortcomings that may limit their use in ballast water applications, recently both DPD analyzers and amperometric sensors have been ruggedized for specific maritime application to BWMS. These new ballast water specific TRO analyzers may potentially allow for improved application to BWMS. However, application specific technologies for measurement of TRO are not required and not always incorporated within BWMS. Ultimately for the safe and effective use of BWMS utilizing chemical treatment, there is a need for technologies that can be applied with minimal maintenance requirements under diverse environmental parameters and application processes and that have been performance tested under BWMS-specific conditions.

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References

- American Public Health Association; American Water Works Association; Water Environment Federation. 1998. Standard Methods for the Examination of Water and Wastewater. 20th ed.; Washington, D.C.
- Badalyn, A., Buff, J., Holmes, M., Chow, C.W.K., Vintage, D. 2009 On-line free-chlorine/total-chlorine monitors' evaluation – a step towards a correct choice of residual disinfectant monitoring. *Journal of Water Supply*, **58**(3), 181-190.
- Bender, D. F. 1978 Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices. *Environmental Monitoring Series*. USEPA Report No. 600/478019.
- Bergendahl, J. A., Stevens, L. 2005 Oxidation Reduction Potential as a Measure of Disinfection Effectiveness for Chlorination of Wastewater. *Environmental Progress*, **24**(2), 214-222.
- Charpentier, J., Martin, G., Wacheux, H., Gilles, P. 1998 ORP regulation and activated sludge: 15 years of experience. *Water Science and Technology*, **38**, 197–208.
- Bowmer, T., Liners, J. 2010. A summary of findings from the first 25 Ballast Water Treatment Systems evaluated by GESAMP. *WMU Journal of Marine Affairs*, **9**(2), 223-230.
- Brungs, W. A. 1973 Effects of residual chlorine on aquatic life. *Water Environmental Federation*, **45**(10), 2180-2193.
- Byers, J. 1999 The distribution of an introduced mollusc and its role in the long-term demise of a native congeneric species. *Biological Invasions* **1**, 339–353.
- Cohen, A.N., Carlton, J.T. 1998 Accelerating invasion rate in a highly invaded estuary. *Science*, **279**(5350), 555–558.
- Daehler, C.C., Strong, D.R. 1996 Status, prediction and prevention of introduced cordgrass *Spartina* spp. invasions in Pacific estuaries, USA. *Biological Conservation*, **78**(1/2), 51–58.
- Delacroix, S., Vogelsang, C., Tobiesen, A., & Liltved, H. 2013 Disinfection by-products and ecotoxicity of ballast water after oxidative treatment—Results and experiences from seven years of full-scale testing of ballast water management systems. *Marine pollution bulletin*, **73**(1), 24-36.
- Goncharuk, V.V., Bagrii, V. A., Mel'nik, L.A., Chebotareva, R. D., Bashton, S. Yu. 2010 The use of redox potential in water treatment processes. *Journal of Water Chemistry and Technology*, **32**(1), 1-9.

Gregg, M., Rigby, G., & Hallegraeff, G. M. 2009 Review of two decades of progress in the development of management options for reducing or eradicating phytoplankton, zooplankton and bacteria in ship's ballast water. *Aquatic Invasions*, **4**(3), 521-565.

International Maritime Organization (IMO), 2004. *Convention for the control and management of ships' ballast water and sediments*; Convention BWM/CONF/36 International: London, U.K.; [www.imo.org/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Control-and-Management-of-Ships'-Ballast-Water-and-Sediments-\(BWM\).aspx](http://www.imo.org/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Control-and-Management-of-Ships'-Ballast-Water-and-Sediments-(BWM).aspx).

Johnson, L.E., Carlton, J.T. 1996 Post-establishment spread in largescale invasions: dispersal mechanisms of the zebra mussel *Dreissena polymorpha*. *Ecology*, **77**(6), 1686–1690.

Kim, Y.H., Hensley, R. 1997 Effective control of chlorination and dechlorination at wastewater treatment plants using redox potential. *Water Environment Research*, **69**(5), 1008-1014.

King, D. M., Tamburri, M. N. 2010 Verifying compliance in ballast water discharge regulations. *Ocean. Dev. Int. Law*. **41**, 1-14.

Malcov, V.B., Zachman, B., Scribner, T. 2009 Comparison of on-line chlorine analysis methods and instrumentation on amperometric and colorimetric technologies. *American Water Works Association*.

Miller, W.A., Frazier, M., Smith, G. E., Perry, E. S., Ruiz, M.R., Tamburri, M. N. **2011** Enumerating sparse organisms in ship's ballast water: Why counting to 10 is not so easy. *Environmental Science and Technology*, **45**(8), 3539-3546.

National Research Council. 1996 *Understanding Risk: Informing Decisions in a Democratic Society*. National Academy Press, Washington, DC, USA.

Nutt, S.G., Jeffers, E.L., Vachon, D.T., Schuk, W. W. 1985 Bench Testing of On-Line Total Residual Chlorine Analyzers. *Water Pollution Control Federation Conference Issue* **57**(9), 948-954.

Ryder, R. A. 2002 The necessity of absolute reliability in chlorine disinfection and dechlorination systems. *Proceedings of the Water Environment Federation, Disinfection* **22**, 132-153.

U.S. Coast Guard. 2012 Standards for living organisms in ships' ballast water discharged in US waters. USCG-2001-10486.

U.S. Environmental Protection Agency. 2011 Efficacy of Ballast Water Treatment Systems: a Report by the EPA Science Advisory Board. EPA-SAB-11-009.

U. S. Environmental Protection Agency. 2013 Vessel General Permit. 33 USC 1251.

Werschkun, B., Sommer, Y., Nanerji, S. 2012 Disinfection by-products in ballast water treatment: An evaluation of regulatory data. *Water Research* **46**, 4884-4901.

White, G.C. 2010 Handbook of Chlorination and Alternative Disinfectants, fourth ed. John Wiley and Sons, INC, Hoboken, NJ, USA.

World Health Organization. 2006 Guidelines for Safe Recreation Water Environments Volume 2. New York, NY.