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Efficacy and residual toxicity of a sodium hydroxide based ballast water treatment system for freshwater bulk freighters

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ABSTRACT

The efficacy and residual toxicity of a sodium hydroxide (NaOH) based ballast water treatment system (BWTS) were tested aboard the Great Lakes carrier M/V *American Spirit* in 1000 L mesocosms containing water from the ship's ballast tanks. NaOH was added to elevate the pH to 11.5 or 11.7 for 48 h, after which pH was reduced to <9 before discharge by sparging with carbon dioxide to form sodium bicarbonate. In 4 trials, pH 11.7 NaOH BW was highly effective in reducing the densities of organisms relative to uptake water and met the ballast water discharge standards of the US Coast Guard (USCG), the US Environmental Protection Agency vessel general permit (USEPA VGP) and the International Maritime Organization (IMO) G8 for the classes of regulated organisms: ≥50 μm, ≥10 μm to <50 μm and indicator bacteria <10 μm. In addition, densities of heterotrophic bacteria were reduced >96% in pH 11.7 treated discharge water relative to uptake densities. Seven day whole effluent toxicity tests indicated pH 11.7 NaOH BW met the USEPA VGP daily maximum criteria for residual toxicity. Organism densities in uptake water did not meet the minimum densities for IMO G8 shipboard test validity in 2 of 4 trials for organisms ≥10 μm to <50 μm or in any trials for the <10 μm size class. The high efficacy and low residual toxicity observed indicates that a NaOH BWTS has great potential for successfully treating large volumes of ballast water released into freshwater systems.

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Introduction

The spread of non-indigenous species can have severe effects on local economies and ecosystems (Briski et al., 2013; Werschkun et al., 2014). Ballast water uptake and discharge by non-seagoing bulk freighters ('Lakers') is an important vector for the secondary transport of non-indigenous species in the Great Lakes (Adebayo et al., 2014; Rup et al., 2010). Treatment to reduce the discharge of live organisms in ballast water (BW) is required for seagoing ships, but non-seagoing vessels operating on the Great Lakes and known as Lakers, are currently exempt from such requirements if built before 2009 (United States Coast Guard, 2015; United States Environmental Protection Agency, 2013a). Various ballast water treatment systems (BWTS) are available for use in freshwater (American Bureau of Shipping, 2014), however the rapid rates of BW uptake and discharge (~40 m^3/min), large BW volumes (up to ~68,000 m^3), uncoated BW tanks (susceptible to oxidants), and other characteristics of Lakers 'render (present) treatment technologies or other strategies to meet the limits currently unavailable and economically unachievable' for these bulk freighters (United States Environmental Protection Agency, 2013b). This study examined the suitability of a novel NaOH based BWTS of promise for Lakers.

Ocean-going ships that treat their ballast with a BWTS must meet regulatory discharge standards for organism density and residual toxicity. Although the majority of Lakers in current service are exempt from meeting BW discharge standards, for the purposes of the present study the current regulatory standards were used to assess the capacity of a BWTS specifically designed for Lakers. Organism densities in BW discharge cannot exceed densities set by the USCG (United States Coast Guard, 2016a), the IMO G8 (International Maritime Organization, 2008a) and the USEPA VGP (United States Environmental Protection Agency, 2013a) based on size class: ≥50 μm (nominally zooplankton), ≥10 μm to <50 μm (nominally phytoplankton and heterotrophic protists), and certain <10 μm organisms (potential pathogenic indicator

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bacteria) (see Electronic Supplementary Material (ESM) Tables S1 to S3 for density criteria). Additionally, approval of a BWTS under USCG regulations requires that system developers demonstrate minimal residual toxicity to organisms in waters receiving the treated BW (United States Coast Guard, 2016c) in accordance with the December 2008 USEPA VGP (United States Environmental Protection Agency, 2009) and IMO G9 (International Maritime Organization, 2008c). Treated BW must meet effluent limits on residual biocides and residual toxicity under the 2013 USEPA VGP (United States Environmental Protection Agency, 2013a).

Elevating pH through the addition of NaOH holds great promise as an economical and efficacious biocide for freshwater ballast treatment. Laboratory-based efficacy tests of a NaOH-based BWTS indicate that exposure to pH 11.5 reduced the survival of zooplankton by 100% in 4 h (*Daphnia magna*, *Eucyclops* sp., *Branchionus calyciflorus*), of total coliforms and *Escherichia coli* by >92% in 2 h, of *Enterococci* by >96% in 24 h and of heterotrophic bacteria by >95% in 48 h (TenEyck and Cangelosi, 2009). An 18 h exposure to pH 11.7 resulted in 100% mortality of zooplankton in ballast water trials conducted aboard the M/V *Ranger III* (Moffitt et al., 2015b). A 48 h laboratory-based exposure to pH 12.5 was 100% lethal to green algae (*Selenastrum* sp.) and rotifer cysts (*B. calciflorus*) (TenEyck and Cangelosi, 2009) while a 30 min exposure to pH 12 resulted in 100% mortality of quagga mussel veligers (Moffitt et al., 2015a). A pH of 12 was also lethal to Gram-negative and Gram-positive bacteria after ≤72 h exposure (Starliper and Watten, 2013; Starliper et al., 2015).

Following treatment, the elevated pH of NaOH-treated water can be neutralized by sparging with carbon dioxide (Cangelosi et al., 2013), even for the large volumes of ballast water carried by Great Lakes freighters (e.g. ~68,000 m^3 for the M/V *Indiana Harbor* (The Glosten Associates, 2012)), resulting in the production of sodium bicarbonate. Moreover, NaOH-treated water can be neutralized using the CO_2 available from scrubbed diesel exhaust (Elskus et al., 2015; Moffitt et al., 2015b), simultaneously decreasing carbon emissions and eliminating the need for freighters to carry compressed gas. Tests using laboratory water, instead of ballast water, indicate that scrubbed exhaust is not likely to introduce residual toxicity to treated ballast water (Elskus et al., 2015). Treatment and neutralization can occur quickly making the current version of the NaOH BWTS well suited to the typical 24 to 96 h port-to-port transport time of Lakers (Waterhouse et al., 2014). Moreover, the industry uses NaOH in closed-loop exhaust gas scrubbing systems currently installed on some Lakers and thus has established supply chains, bunkering and storage procedures, and safety precautions for NaOH use on its ships. A further benefit of the NaOH BWTS is that, unlike the oxidant-based BWTS used on ocean-going freighters, which can be corrosive to the uncoated tanks of freshwater bulk carriers (Liu et al., 2010), elevating pH (pH 11 to pH 12) with NaOH retards the corrosion of uncoated steel (Uhlig and Revie, 1985). However, NaOH cannot be used to treat BW in ocean-going vessels because of the high amounts of calcium and magnesium precipitates formed when NaOH is added to saltwater.

In addition to high efficacy for protecting the receiving water from non-indigenous species, a BWTS should produce minimal residual toxicity to organisms in receiving waters upon release of treated BW. A pilot study aboard the American Steamship Company's M/V *Indiana Harbor* indicated that discharge water treated with NaOH, and then neutralized, retained little to no residual toxicity when diluted by 50% with untreated water (Elskus et al., 2015). Such dilution can be easily achieved during regular ship discharge (e.g. dyed ballast water discharged to a small, enclosed harbor was diluted by a factor of 10^3 after 1 d (Wells et al., 2011)) and it is likely that the residual toxicity standard would be met without dilution prior to discharge.

The present study expands significantly upon previous work. Previous studies examined the efficacy of elevated pH in land-based, bench-scale experiments with standard test organisms (Elskus et al., 2015; TenEyck and Cangelosi, 2009), invasive species (Moffitt et al., 2015a) or single classes of organisms (Starliper and Watten, 2013; Starliper et al., 2015) that were exposed to NaOH added to laboratory water or to filtered harbor water, not to ballasted water. The one previous shipboard study conducted with ballasted water collected preliminary data from only a single trial, and due to cross-contamination of some samples, the results were not conclusive or determinative (Cangelosi et al., 2013). In the present study, 4 independent efficacy trials using ballasted water were carried out in July and September of 2015 aboard the American Steamship Company's bulk carrier, M/V *American Spirit*, during the ship's usual loading and unloading of cargo. In these 4 temporally distinct trials BW uptake occurred at 3 different locations along the usual trade pathways for American Steamship Company (ASC) carriers (i.e. Detroit and Chicago areas in Lakes Michigan and Erie and the Detroit River). Tests gauged the ability of the NaOH BWTS to meet USEPA, IMO G8 and USCG ballast water discharge standards for organisms in all 3 size classes. In addition to these standard analyses, various other efficacy measurements were also undertaken, using corroborative methods and un-regulated organisms. To evaluate residual toxicity following the NaOH BW treatment, 2 tests were performed. A USCG compliant test, the 7 d whole effluent toxicity (WET) test (United States Coast Guard, 2015), was conducted on BWTS water from trial 4. An additional, corroborative assay of residual toxicity, the 24 h QwikLite Biosensor System test based on light output by a bioluminescent dinoflagellate, was used in all 4 trials.

The present study was designed to provide information relevant for research on and development of a NaOH BWTS for Lakers. As the BWTS tests were conducted shipboard in mesocosms using water from the ship's ballast tanks, they were neither shipboard tests (in which source water organisms are exposed to treatments added directly to the ships' ballast tanks) nor land-based tests (in which the size composition and density of organisms in the test water are controlled by the experimenter), but contained aspects of both. For this reason, the present study followed regulations set by the IMO G8 (International Maritime Organization, 2008a), the USCG (United States Coast Guard, 2016a), the USEPA VGP (United States Environmental Protection Agency, 2013a) and the USEPA Environmental Technology Verification (ETV) program (United States Environmental Protection Agency, 2010) and used protocols outlined by the USEPA-ETV to analyze organism densities. It is important to note that although consideration was given to the USEPA ETV regulations for BWTS testing, the present study does not constitute a type-approval land-based test.

Methods

Trial description

Four independent shipboard trials were conducted in 2015 aboard the American Steamship Company's M/V *American Spirit*, a 306 m long bulk freighter that carries approximately 45,793 metric tons of ballast water. Each trial was designed within the context of a single port-to-port journey (1 ballasting operation, 1 retention period, 1 de-ballasting operation). The dates, destination ports and source water for the trials are provided (ESM Table S4). Water for these trials was taken from ballast tank 7P as soon as it was filled and placed into 12 experimental mesocosm tanks (1000 L; 1 m^3) located in the conveyor tunnel of the ship. Mesocosms were pre-rinsed multiple times before and after each trial using water from the location where the ship took on ballast (trial 1, Zug Island; trial 2, Gary Harbor; trials 3 and 4 Indiana Harbor, ESM Table S4). The pre-rinse was followed by a final rinse with water from ballast tank 7P. For the efficacy tests, there were 3 replicate mesocosms for each of 3 treatments: control BW (untreated: C1, C2, C3), low NaOH BW (pH 11.5: L1, L2, L3), high NaOH BW (pH 11.7: H1, H2, H3). To minimize manipulation of the experimental mesocosms during the trials, a fourth set of 3 mesocosm tanks ('engineering mesocosms' ENG: CENG, LENG, HENG) was used to determine the initial density of the organisms in the uptake water, to monitor water quality,