RESEARCH ARTICLE

Characterizing shipboard bilgewater effluent before and after treatment

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Abstract Operational discharges from oceangoing vessels, including discharges of bilgewater, release oil into marine ecosystems that can potentially damage marine life, terrestrial life, human health, and the environment. Bilgewater is a mix of oily fluids and other pollutants from a variety of sources onboard a vessel. If bilgewater cannot be retained onboard, it must be treated by an oily water separator before discharge for larger ocean-going vessels. We evaluated the effectiveness of bilgewater treatment systems by analyzing land-based type approval data, collecting and analyzing shipboard bilgewater effluent data, assessing bilgewater effluent concentrations compared to regulatory standards, evaluating the accuracy of shipboard oil content monitors relative to analytical results, and assessing additional pollution reduction benefits of treatment systems. Land-based type approval data were gathered for 20 treatment systems. Additionally, multiple samples of influent and effluent from operational bilgewater treatment systems onboard three vessels were collected and analyzed, and compared to the land-based type approval data. Based on type approval data, 15 treatment systems were performing below 5 ppm oil. Shipboard performance measurements verified land-based type approval data for the three systems that were sampled. However, oil content monitor readings were more variable than actual oil concentration measurements from effluent samples, resulting in false negatives and positives. The treatment systems sampled onboard for this study generally reduced the majority of other potentially harmful pollutants, which are not currently regulated, with the exception of some heavy metal analytes.

Keywords Bilgewater · Oily water separator · Vessel discharges · Marine pollution · Oil content monitor · MARPOL

Introduction

Ocean-going vessels generate millions of tons of oily wastes annually (GESAMP 2007). Vessel-related operational discharges, including discharge of bilgewater, represent one of the largest anthropogenic inputs of oil into the marine environment and are estimated to be even higher than accidental oil spills [National Research Council (NRC) 2003; Pavlakis et al. 2001; GESAMP 2007; Etkin 2010]. Although oil enters the marine environment through both spills and chronic releases, greater effort and treatment can reduce frequent small releases whereas catastrophic and accidental oil spills are less easy to prevent. Less work has been done to understand the threat posed by these chronic releases that are suspected of causing notable environmental impacts (Wiese and Ryan 2003). The toxicological effects of oil in the environment are a function of not only the volume of oil released but also other factors such as the nature of the oil released and the physical and biological ecosystem exposed. Oil in the marine environment can cause damage to marine life, terrestrial life, human health, and natural resources (Kennicutt et al. 1992; Camphuysen and Heubeck 2001; NRC 2003; Radovic et al. 2012).

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Bilgewater, one chronic oil pollution source, has been estimated to account for 20 % of the oily water released by vessels into the oceans worldwide (Tomaszewska et al. 2005). Bilgewater is a mixture of a complex suite of compounds including oily fluids and other pollutants such as metals, detergents, and solvents, which come from a variety of sources (e.g., engines, piping, and mechanical sources found in the machinery space of a vessel) and accumulate in shipboard bilges [U.S. Environmental Protection Agency (EPA) 1999, 2008a, b, 2010]. Large vessels predominantly burn bunker oil and use petroleum-based lubricating oils and hydraulic fluids, and the likely source of most oil in bilgewater is leaks of motor oil, hydraulic fluids, and fuel lines (Krozer et al. 2003). These oil sources most likely contain relatively heavy components with higher boiling points compared to those expected of gasoline-fueled vessels (Albaiges et al. 2013). Oil in bilgewater appears in several forms based primarily on the size of oil droplets: free, dispersed, and emulsified (Cheryan and Rajagopalan 1998). Emulsified oil (i.e., oil droplets smaller than 20 μm) is the hardest to treat because its neutral buoyancy makes it difficult to separate by gravity alone (Coca et al. 2011; EPA 2011). Since bilgewater cannot always be retained onboard, many vessels must treat it with an oily water separator (OWS) prior to discharge.

In addition to oil and hydrocarbons, bilgewater contains a mixture of other contaminants, and the amount of contaminants varies based on a ship's operations, equipment performance, and repairs, among other things. For example, bilgewater samples collected from a variety of ships contained multiple EPA priority pollutants (40 Code of Federal Regulation CFR §§ 423 2005) including metals, conventional pollutants and nutrients (e.g., nitrogen and phosphorous-containing compounds, suspended solids), and organics along with significant concentrations of detergents, solvents, and polyaromatic hydrocarbons (PAHs) (Chang et al. 1997; EPA 1999, 2010). The presence of these other compounds in bilgewater results in multiple interactions among pollutants and between pollutants and surfaces, complicating the treatment processes (Chang et al. 1997). Additionally, the behavior of these compounds if released into the environment differs and their toxic potential depends on their bioavailability in a given aquatic environment and the characteristic of the environment itself (e.g., the species of fish present, the ambient concentrations, temperature, pH, salinity, etc.). Potential affects could include impairment of organ function or reproduction in aquatic life, bioaccumulation in the aquatic food chains, acute mortality, oxygen depletion, and eutrophication (nutrient enrichment).

Regulating bodies have restricted the extent of allowable discharges and treatment requirements in an effort to reduce or eliminate the discharge of oil into the sea [International Convention for the Prevention of Pollution from Ships (MARPOL 1973/1978); Clean Water Act (United States Code (U.S.C.) §§ 1251 et seq. 1987); Act to Prevent Pollution from Ships (33 U.S.C. §§ 1901, et seq. 2000)].

Among other things, the International Maritime Organization (IMO) set the standard for developing regulations regarding treatment and disposal of oily bilgewater. Annex I of MARPOL (73/78) requires all ships over 400 gross tons to only discharge treated oil or oily mixtures while en route and if equipment limits the discharge concentration of oil into the ocean to 15 ppm. The U.S. Coast Guard (USCG) implements the requirements of MARPOL through the Act to Prevent Pollution from Ships (33 U.S.C. §§ 1901, et seq. 2000) in U.S. waters. Additionally, EPA's Vessel General Permit for Discharges Incidental to the Normal Operation of Vessels (VGP) also establishes limitations for bilgewater discharges in U.S. waters (EPA 2008a, 2013). Bilgewater is one of the 27 specific permitted discharges regulated by the VGP, and the discharge standards are generally consistent with the IMO requirements (15-ppm oil content discharge limitation for ocean-going vessels) with some additional management practices and nearshore discharge location limitations. In contrast, the Canada Shipping Act (2001) has a more stringent discharge limitation and stipulates Canadian domestic vessels must comply with a 5-ppm oil content limit for bilgewater discharges for Canadian inland waters.

Traditionally, bilgewater was treated by gravity OWSs, which use the different specific gravities of oil and water and their immiscibility to separate them. While gravity OWSs can effectively separate discrete phases of oil and water (Koss 1996), they do not separate emulsified oil because the buoyancy differences are too small. Additionally, gravity OWSs are ineffective at removing colloidal metals and soluble compounds (Caplan et al. 2000; Penny and Suominen-Yeh 2006). Finally, gravity OWSs work less effectively in a shipboard environment where the motion of the vessel may agitate the oil–water mixture. Centrifugal OWSs also utilize the difference in density between oil and water to separate oil from bilgewater, but the centrifugal force imposed on the bilgewater being treated causes the immiscible liquids or solids to separate more effectively than by gravity alone. These traditional OWSs have been shown not to reliably meet the 15-ppm oil requirement without subsequent polishers or other treatments in some cases (Haupt 1989; Smookler and Alig 1992; Cheryan and Rajagopalan 1998). Physical methods typically have low removal efficacy for separating emulsion oil droplets of less than 20 μm in diameter (Caplan et al. 2000). Polishing treatments include absorption and adsorption, biological treatment, coagulation and flocculation, flotation, electrochemical demulsification and purification, or ultrafiltration. Adding such polishing units has been shown to effectively treat bilgewater to very low effluent oil concentrations although the influence of operating parameters may differ among treatment technologies (Ghidossi et al. 2009; Korbahti and Artut 2010, 2013). Furthermore, the addition of chemicals or microorganisms, which help to reduce oil concentrations, may influence the effluent quality in regards to other pollutants.

Although OWSs are optimized for removing oil, some can also remove other pollutants. For example, ultrafiltration and electrocoagulation has been shown to effectively remove turbidity, suspended solids, organic carbon, and several trace metals (Woytowich et al. 1993; Tomaszewska et al. 2005; Asselin et al. 2008). Conversely, an air-stripping and photocatalysis system showed increases in volatile organic compound (VOC) emissions, a gaseous pollutant (Cazoir et al. 2012), and biological treatments require an additional clarifier to remove the bacteria used to degrade the oil (Yu et al. 2013; EPA 2011). Because of the interactions among these other pollutants, developing a better understanding of the chemistry of both the influent and effluent of these bilgewater treatment systems should be considered to optimize the efficacy of the OWSs and prevent the discharge of these pollutants into the environment.

The effectiveness of a given OWS is usually demonstrated by the results of laboratory experiments and land-based type approval tests of effluent oil concentrations achieved by that OWS treating either synthetic oily bilgewater or wastewater resulting from bilge washing (e.g., Asselin et al. 2008; Cazoir et al. 2012; Korbahti and Artut 2013). Type approval is a third-party certification that is designed to be an impartial method for determining and attesting to a product's conformity with specific standards [e.g., MEPC 2003; Det Norske Veritas (DNV) 2011; 46 CFR 162.050 2012]. Certificates of approval are provided by various governments and delegated organizations (e.g., vessel classification societies). Historically, flag administrations and delegated organizations granted type approval certificates for bilgewater treatment systems to treat and measure to at least a 15-ppm oil content limit. More recently, some delegated organizations have begun granting type approval certificates for bilgewater treatment systems to treat and measure to at least a 5-ppm oil content limit (DNV 2011; EPA 2011). In the United States, the USCG issues type approval certifications. To receive USCG approval, equipment must demonstrate compliance with relevant requirements, complete specific tests, and be enrolled in a follow-up program as required (46 CFR 162.050 2012). These approvals allow for enforcement of regulations without requiring continuous analytical monitoring. However, to meet requirements under MARPOL and other U.S. domestic regulations, a vessel must continuously monitor its bilgewater discharges using an approved OWS and oil content monitor (OCM).

Laboratory-based type approval tests demonstrate how certain OWSs perform under controlled conditions. However, the short duration of certification tests, the use of a test fluid with a constant composition, and the stationary condition of the OWSs do not always simulate the conditions aboard vessels (TANKEROperator 2009; EPA 2011). Additional considerations such as installation and operating costs, corrosion potential, and the long-term efficacy of certain components are important for determining the suitability for onboard operations

(Asselin et al. 2008). Therefore, shipboard testing could complement land-based testing to determine if these OWSs are meeting regulatory and practicability requirements (Ghidossi et al. 2009).

Vessel operators measure compliance with regulatory limits by utilizing a continuous OCM with a bilge alarm to detect whether the discharge from the OWS meets requirements. When an OCM reading exceeds the defined regulatory threshold (e.g., 15 ppm oil, 5 ppm oil), a bilge alarm shuts off the discharge and recirculates the effluent back into the bilge or OWS for additional treatment. OCMs and bilge alarms are also required to be certified, and regulations cover acceptance of laboratories that examine these types of pollution prevention equipment, certification procedures for equipment, and requirements for vessels to install such equipment (e.g., 46 CFR 162.050). Because the OCM is so important in preventing the discharge of oil from vessels when the bilgewater separator fails to meet requirements, the OCM's accuracy and reliability are critical factors to consider when evaluating the effectiveness of an OWS.

We evaluated the effectiveness of bilgewater OWSs based on analyzing type approval data and measurements of oil concentrations in samples of treated bilgewater effluent collected from onboard OWSs treating actual bilgewater. The overall goals of this study were (1) to evaluate certification test data conducted by independent laboratories under controlled conditions and compare them to shipboard measurements where feasible, (2) to assess the ability of different current bilgewater OWS treatment technologies to meet current IMO standards and more stringent discharge standards, (3) to assess the accuracy of current OCMs at low oil concentrations, and (4) to evaluate whether some OWSs offer additional pollution reduction benefits other than merely reducing oil concentrations in bilgewater discharges.

Methods

Land-based type approval testing

We gathered and evaluated performance data from laboratory testing for USCG type approvals for 20 OWS systems. Tests were performed using the USCG defined grades of Test Fluids: A—a marine residual fuel oil; B—a marine distillate fuel oil; and C—a mixture of oil-in-fresh water emulsion that included a mixture of Test Fluids A and B, a surfactant, and iron oxide (46 CFR 162.050 2012). Because Test Fluid C contained a surfactant chemical, emulsified oil, and fine particulates, it is considered a more realistic synthetic bilgewater. Treated effluent was analyzed for oil using ISO method 9377-2:20005.

Shipboard testing

To examine the shipboard performance of different OWS treatment technologies, we collected multiple samples from three vessels with operational OWSs. We were specifically interested in vessels that had OWSs believed to be among the best technologies available and representative of different treatment technologies. Vessels were selected based on the type of OWS, the expected performance of the OWS, ship schedule and/or logistics, and ease of sampling (e.g., availability of sample taps or willingness of operators to install them). The three ships selected included two container ships and one bulk carrier (Table 1).

Ship #1, a container ship that services ports in the United States, Middle East, Northern Europe, and Asia, was sampled in September 2012 in Norfolk, VA. The OWS on this vessel (OWS 1) was a continuous-flow dual-stage treatment system. To remove free oil, bilgewater was first separated by a differential specific gravity stage with coalescence plates. The emulsified oil was removed by a subsequent filtration stage.

Ship #2, the other container ship, was sampled in Los Angeles, CA, in October 2012. The treatment system (OWS 2) consisted of the following components: a gravimetric oil separator; a reactor combining coagulation, flocculation, and flotation; an Aqualite (volcanic rock) granular media filter; and an activated carbon polishing filter.

The bulk carrier, Ship #3, services the Great Lakes carrying salt or coal between the United States and Canada, and was sampled in Chicago, IL in November 2012. The OWS consisted of a strainer and preheater followed by a high-speed centrifugal separator.

Shipboard bilgewater samples were collected while the selected vessels were in port. The vessels collected untreated bilgewater generated while underway in a holding tank prior to the sampling day. Sample taps from the bilgewater OWSs were used to collect grab samples and were first flushed with approximately one sample volume prior to sample collection. The hydraulic residence time of the OWS was calculated by dividing the hydraulic volume of the OWS by the average flow rate. Four to five sets of paired grab samples of influent to and effluent from the OWSs were collected; for each set, samplers waited one hydraulic residence time between collecting the influent and effluent samples. Samplers also

waited a minimum of one hydraulic residence time between collecting each set of paired samples to avoid statistical auto-correlation of the results. The OCM reading for each effluent sample was also recorded.

Sample containers and bottles were purchased precleaned, and appropriate preservation agent(s) added. Except for VOC samples, which were collected with zero headspace, bottles were filled to the shoulder. All samples were cooled immediately in an ice-water bath. For water with temperatures greater than 35 °C, samples for analysis of VOCs were collected using a 15- to 25-ft-long Teflon® tube connected to the sampling tap and coiled in ice water to cool the sample to at least 35 °C before filling the vials. Vials were filled to overflowing from the bottom, and the tube was slowly withdrawn leaving a convex sample meniscus before sealing with the appropriate septum. After collection, samples were stored in ice maintaining a temperature of 6 °C (±2 °C) and sent overnight to analytical laboratories.

Laboratory analyses

Land-based type approval test results were assembled from third-party testers (i.e., regulatory agencies, vendors). Land-based testing of OWSs was conducted according to the specifications of the USCG [46 CFR 162.050, generally consistent with IMO Res. MEPC 107(49)]. These tests were performed at the maximum throughput and pressure for which the OWS was designed to operate. For Test Fluid A, five different approval tests were conducted simulating different operational conditions (e.g., operating times between 15 min and 3 h and using an influent with water, a mixture of Test Fluid A in water, and 100 % Test Fluid A). Two tests were repeated using Test Fluid B. One test was conducted using Test Fluid C, during which the OWS was fed with a mixture of 6 % Test Fluid C in water for 3 h. Concentrations of oil in these samples were characterized by the oil index (Method ISO 9377-2), and all measurements were made by different independent laboratories.

Shipboard samples were collected and analyzed from OWSs onboard three vessels. All shipboard samples were analyzed for target analytes representing five pollutant groups: (1) oil and hydrocarbons, (2) metals, (3) VOCs and semivolatile organic compounds (SVOCs which are less volatile than VOCs with higher boiling points), (4) surfactants, and (5) conventional pollutants and nutrients (Table 2). The analytical methods used to determine the concentration of these target analytes were chosen because of comparability with type approval testing or because they are the common methods used and required by the National Pollution Discharge Elimination System to assess regulatory compliance by point sources that discharge pollutants into waters of the United States.

The oil content of each shipboard sample was characterized by four measurements including the oil index (method ISO 9377-2, used for typed approval testing), hexane extractable

Table 1 Descriptive data for the three vessels that were sampled to determine the effectiveness of bilgewater oily water separators (OWSs) onboard ships

Ship	Build year	Gross tons	Twenty-foot equivalent unit	Length (m)
1	1996	49,985	4,296	292
2	1995	49,995	4,065	273
3	1983	22,881		223

Table 2 List of analytes measured in shipboard bilgewater samples, the method used for the measurements, and any onboard preservation used

Analyte	Method	Onboard preservation
Oil index	ISO 9377-2	Cool, ≤6 °C
HEM	EPA 1664A/SOP C-126	Cool, ≤6 °C, HCl or H_2SO_4 to pH <2
SGT-HEM	EPA 1664A/SOP C-126	Cool, ≤6 °C, HCl or H_2SO_4 to pH <2
Metals	EPA 200.8	Total: HNO_3 to pH<2; dissolved: 0.45 μm filter and HNO_3 to pH<2
VOCs	EPA 624	Cool, ≤6 °C, 10 mg $Na_2S_2O_3$ per vial if chlorine present, 2 drops HCl per vial

4-Methyl-2-pentanone, acetone, benzene, bromobenzene[a], bromoform[a], butylbenzene, butylbenzene, sec-, butylbenzene, *tert*-[a], carbon disulfide, carbon tetrachloride[a], chlorobenzene, chlorobromomethane[a], chloroethane[a], chloroform, chlorotoluene, chlorotoluene-*p*, cyclohexane, DBCP[a], dibromochloromethane[a], dibromoethane-1,2[a], dibromomethane[a], dichlorobenzene-1,2[a], dichlorobenzene-1,3[a], dichlorobenzene-1,4[a], dichlorobromomethane[a], dichlorodifluoromethane[a], dichloroethane-1,1[a], dichloroethane-1,2[a], dichloroethene-1,2 trans[a], dichloroethylene-1,1[a], dichloroethylene-1,2 *cis*[a], dichloropropane, 1,2-[a], dichloropropane, 1,3-[a], dichloropropane, 2,2-[a], dichloropropene, 1,1-[a], dichloropropene, 1,3 *cis*-[a], dichloropropene, 1,3 *trans*-[a], ethylbenzene, freon 113[a], hexachlorobutadiene[a], hexanone, 2-, isopropylbenzene, isopropylbenzene-4,methyl-1, M,P-xylene (sum of isomers), methyl acetate, methyl bromide, methyl chloride[a], methyl cyclohexane, methyl ethyl ketone, methyl tertiary butyl ether (MTBE), methylene chloride[a], propylbenzene-*n*, styrene[a], tetrachloroethane, 1,1,1,2-[a], tetrachloroethane, 1,1,2,2-[a], tetrachloroethylene[a], toluene, trichlorobenzene-1,2,3[a], trichlorobenzene-1,2,4[a], trichloroethane-1,1,1[a], trichloroethane-1,1,2[a], trichloroethylene[a], trichlorofluoromethane[a], trichloropropane-1,2,3[a], trimethylbenzene-1,2,4, trimethylbenzene-1,3,5, vinyl acetate[a], vinyl chloride[a], xylene-*o*

SVOCs	EPA 625	Cool, ≤6 °C, 80 mg/L $Na_2S_2O_3$ if chlorine present

Acenaphthene, acenaphthylene, acetophenone[a], anthracene[a], atrazine[a], benzaldehyde, benzo(*a*)anthracene[a], benzo(*a*)pyrene[a], biphenyl, bromophenyl-4 phenyl ether[a], butylbenzyl phthalate[a], caprolactam[a], carbazole[a], chlorobenzenamine-4[a], chloronaphthalene-2[a], chlorophenol-2[a], chlorophenyl-4 phenyl ether[a], chrysene[a], cresol, parachloro *meta*-[a], cresol-4,6-dinitro-*ortho*[a], cresol-*o*[a], cresol-*p*[a], dibenz(*a,h*)anthracene[a], dibenzofuran[a], dichlorobenzidine-3,3'[a], dichlorophenol-2,4[a], dimethylphenol, 2,4-[a], dinitrophenol-2,4[a], dinitrotoluene-2,4[a], dinitrotoluene-2,6[a], ether, bis(2-chloroethyl)[a], ether-bis(2-chloroisopropyl)[a], fluoranthene benzo(*k*)[a], fluoranthene[a], fluoranthene-benzo(*b*)[a], fluorene, hexachlorobenzene[a], hexachlorocyclopentadiene[a], hexachloroethane[a], isophorone[a], methane, bis(2-chloroethoxy)[a], methylnaphthalene-2, naphthalene, nitroaniline, ortho[a], nitroaniline-3[a], nitrobenzenamine-4[a], nitrobenzene[a], nitrophenol-2[a], nitrophenol-4[a], nitrosodimethylamine-*n*[a], nitrosodiphenylamine-*n*[a], pentachlorophenol[a], perylene-benzo(*ghi*)[a], phenanthrene, phenol[a], phthalate, bis(2-ethylhexyl) (DEHP), phthalate, dimethyl[a], phthalate, di-*n*-butyl-, phthalate, di-*n*-octyl[a], phthalate-diethyl[a], propylamine,*n*-nitroso di-*n*-[a], pyrene, pyrene-indeno(1,2,3-*cd*)[a], tetrachlorobenzene, 1,2,4,5-[a], tetrachlorophenol, 2,3,4,6-[a], trichlorophenol-2,4,5-[a], trichlorophenol-2,4,6[a]

Surfactants	SM 5540 C/SOP C-61	Cool, ≤4 °C, H_2SO_4 to pH <2
Conventional pollutants and nutrients		
COD	EPA 410.4/SOP C-53	Cool, ≤6 °C, H_2SO_4 to pH <2
NH_4–N	EPA 350.1/SOP C-80	Cool, ≤6 °C, H_2SO_4 to pH <2
TKN	EPA 351.2/SOP C-40	Cool, ≤6 °C, H_2SO_4 to pH <2
NO_3 and NO_2–N	EPA 353.2/SOP C-79	Cool, ≤6 °C, H_2SO_4 to pH <2
Phosphorus	EPA 365.4/SOP C-68	Cool, ≤6 °C, H_2SO_4 to pH <2
TSS	SM 2540 D/SOP C-33	
BOD	SM 5210B/SOP C-21	Cool, ≤6 °C
Organic carbon	SM 5310/SOP C-83	Cool, ≤6 °C, H_2SO_4 to pH <2

[a] Analyte was not detected in any sample and therefore not included in dataset

material (HEM, method EPA 1664A/SOP C-126), silica gel treated hexane extractable material (SGT-HEM, method EPA 1664A/SOP C-126), and OCM readings. Oil in water was measured using empirical methods that yielded method-defined parameters; consequently, the different method-defined parameters were not expected to be equivalent. To measure the oil index, samples were extracted and analyzed according to procedures outlined in method ISO 9377-2. The analysis was performed using a Restek RXi-5MS 30-m×0.32-mm id capillary column on a Hewlett Packard HP-5890 Series II gas chromatograph equipped with a flame ionization detector (reporting limit ranged from 0.55 to 28 ppm depending on sample dilution). The sum of all the responses within the hydrocarbon index range of C_{10} to C_{40} was reported. HEM and SGT-HEM concentrations were measured according to the procedures outlined by EPA Method 1664A. Samples were acidified to pH of less than 2, extracted using *n*-hexane, distilled at 85 °C, and the residual oil dried and weighed. For SGT-HEM samples, the hexane extract underwent an additional silica gel treatment process to remove polar material, and therefore, measurements include only nonpolar material. The HEM and SGT-HEM methods most likely do not capture the lighter components of fuel that the oil index method is able to detect, but the HEM and SGT-HEM methods do capture certain heavier weight components that are not captured by the oil index method. Of the three OWSs tested, all had light-scattering-based OCMs. This technology involves passing visible light through a sample and measuring the amount of transmitted light together with the amount of light that is scattered at different angles to determine the oil concentration (Yang 2011).

The additional analytes were selected to provide a screening-level analysis of the presence or absence of almost all priority pollutants (40 CFR Appendix A to Part 423 2005), conventional pollutants [CWA 1987 Section 304 (a)(4)], and toxic pollutants [EPA's 2006 National Recommended Water Quality Criteria (NRWQC)]. Table 2 lists the method used for each analysis. The EPA Region 1 Office of Environmental Measurement and Evaluation in North Chelmsford, MA, conducted oil index measurements. Measurements for HEM, SGT-HEM, surfactants, and all of the conventional pollutants and nutrients were conducted at the EPA Region 2 Facility in Edison, NJ. The USEPA Region 3 Office of Analytical Services and Quality Assurance in Fort Meade, MD, conducted the analyses for metals, VOCs, and SVOCs. All samples were preserved onboard.

Statistics

Land-based type approval test data were used to assess the ability of different technologies to achieve current and potentially more stringent discharge standards. Mean (±standard error) was reported for each grade of test fluid as well as for each OWS. A one-tailed Z test was used to compare the mean of the land-based type approval test data for each OWS to the current regulatory standard (15 ppm oil) and to a more stringent potential regulatory standard (5 ppm oil). For the purposes of the statistical analyses, the null hypothesis was that the systems cannot reliably achieve either a 15-ppm or a 5-ppm oil limit. Rejecting the null hypothesis ($p<0.05$) indicates there is statistical evidence that systems are performing below the regulatory standard of 15 ppm oil and/or a 5-ppm oil limit.

An analysis of variance (ANOVA) was conducted to examine the differences between the oil index concentrations from land-based type approval tests using each of the synthetic fluids and the concentrations measured in shipboard bilgewater effluent. Tukey post hoc analysis was then performed to test all possible pairwise comparisons among means. Land-based type approval data were not available for OWS 3, and therefore, type approval data for a functionally similar system was used for comparing type approval and shipboard measurements. Because the only differences between the shipboard system sampled and the system for which type approval data were available were the use of different automation and not based on the separation technology being utilized, we feel this comparison was valid.

The shipboard performance of the three OWSs was analyzed by comparing paired effluent and influent concentrations for each system and by comparing the average percent removal among systems. Shipboard effluent and influent concentrations for each system were plotted against each other and evaluated for a potential linear relationship using Pearson correlation. A linear relationship between these data indicates that the effluent quality depends on the concentration of the influent with higher slopes illustrating lower performance, while a nonlinear relationship may indicate that a system can achieve a level of effluent quality regardless of influent characteristics. Paired T tests were conducted to further evaluate any differences between shipboard influent and effluent concentrations for each system and data from all systems combined. For each paired sample and each of the three oil analytes, a percent removal was calculated. A one-way ANOVA followed by Tukey post hoc analysis was used to determine differences in the influent and effluent concentrations and percent removal among the three OWS. Additionally, a one-tailed T test was used for each OWS and each oil analyte measured in shipboard samples to evaluate the null hypothesis that effluent concentrations were greater than 15 ppm and 5 ppm oil. Pearson's correlation coefficients were computed to assess the relationships between OCM readings and each of the three oil analytes measured in shipboard effluent samples and to evaluate the accuracy of the shipboard OCMs.

To determine if the shipboard OWS systems provided any additional pollution reduction benefits, we compared the influent and effluent concentrations for each analyte and calculated percent removal for each paired set of samples. To provide a context for these concentrations as to potential environmental significance, we compared shipboard effluent concentrations to the NRWQC as benchmarks. Table 3 presents the NRWQC chosen for this purpose, which generally represent the most water quality protective concentration for each analyte. We also calculated potential hazard quotients (PHQs) by dividing the analyte concentrations in shipboard effluent samples by their corresponding water quality criterion. If the concentration in the shipboard discharge is less than the screening criterion (<1), it is unlikely that the discharge concentration would exceed water quality standards. If the PHQ value is significantly greater than one, there could be a potential for ecological or human health risk, depending on several factors including discharge volume, receiving water characteristics, and how the given pollutant is assimilated, stored, or degraded by the aquatic environment.

Results and discussion

Land-based type approval data

Land-based type approval data for the 20 systems ranged from below detection to 14.7 ppm oil (Fig. 1). Despite the substantial variation in performance of individual OWSs, 100 % of the measurements were below the 15-ppm oil standard (as would be expected as these data were submitted for type approval below a 15-ppm oil limit), and there was statistical evidence that all systems are performing below the 15-ppm oil standard in the land-based setting ($p<0.001$). Of the 20 OWSs, 15 systems appear to reliably perform below a 5-ppm oil standard

Table 3 Water quality benchmark concentration used to screen the effluent concentrations from bilgewater oily water separators (OWSs)

Pollutant	Priority/nonpriority	Benchmark	Units	Source[a, b]
Total aluminum	N	87	µg/L	EPA 2006 FW CCC
Total antimony	P	5.6	µg/L	EPA 2006 HH W+O
Dissolved arsenic	P	36	µg/L	EPA 2006 SW CCC
Total arsenic	P	0.018	µg/L	EPA 2006 HH W+O
Total barium	N	1,000	µg/L	EPA 2006 HH W+O
Dissolved chromium	P	11	µg/L	EPA 2006 FW CCC
Dissolved copper	P	3.1	µg/L	EPA 2006 SW CCC
Total copper	P	1,300	µg/L	EPA 2006 HH W+O
Total iron	N	300	µg/L	EPA 2006 HH W+O
Dissolved lead	P	2.5	µg/L	EPA 2006 FW CCC
Manganese	N	50	µg/L	EPA 2006 HH W+O
Dissolved nickel	P	8.2	µg/L	EPA 2006 SW CCC
Total nickel	P	610	µg/L	EPA 2006 HH W+O
Dissolved selenium	P	5	µg/L	EPA 2006 FW CCC
Total selenium	P	170	µg/L	EPA 2006 HH W+O
Dissolved zinc	P	81	µg/L	EPA 2006 SW CCC
Total zinc	P	7,400	µg/L	EPA 2006 HH W+O
VOCs				
Benzene	P	2.2	µg/L	EPA 2006 HH W+O
Chlorobenzene	P	130	µg/L	FR 2003 HH W+O
Chloroform	P	57	µg/L	EPA 2006 HH W+O
Ethylbenzene	P	530	µg/L	EPA 2006 HH W+O
Methyl bromide	P	47	µg/L	EPA 2002 HH W+O
Toluene	P	1,300	µg/L	EPA 2006 HH W+O
SVOCs				
Acenaphthene	P	670	µg/L	EPA 2006 HH W+O
Bis(2-ethylhexyl) phthalate	P	1.2	µg/L	EPA 2006 HH W+O
Di-*n*-butyl-phthalate	P	2,000	µg/L	EPA 2006 HH W+O
Pyrene	P	830	µg/L	EPA 2006 HH W+O
Fluorene	P	1,100	µg/L	EPA 2006 HH W+O
Ammonia [As N]	N	1.2	mg/L	EPA 2006 SW CCC
BOD	P	30	mg/L	FR 1984
Nitrate+nitrite [As N]	N	10	µg/L	EPA 2006 HH W+O
Phosphorus	N	0.1	mg/L	EPA 1986

[a] 49 Federal Register (FR) 27006 (1984) Secondary Treatment Effluent Limits

68 FR 250 (2003) National Recommended Water Quality Criteria for the Protection of Human Health

EPA (1986) Quality Criteria for Water (The Gold Book) Office of Water. EPA-440/5-86-001

EPA (2002) National Recommended Water Quality Criteria. Office of Water, Office of Science and Technology. Washington, D.C. EPA-822-R-02-047

EPA (2006) National Recommended Water Quality Criteria. Office of Water, Office of Science and Technology. Washington, D.C., Available Online at: http://epa.gov/waterscience/criteria/wqcriteria.html

[b] FW CCC: freshwater chronic

SW CCC: salt water chronic

HH W+O: human health for the consumption of water+organism

Fig. 1 Box plots illustrating the range of effluent concentrations (including all data from tests conducted with Test Fluids A, B, and C) measured during land-based type approval testing of 20 oily water separators (OWSs) approved by the USCG. *Dotted lines* indicate current discharge standard (15 ppm) and more stringent potential standard (5 ppm). **a** OWSs included in the shipboard sampling, and **b** datasets that include at least one nondetect value
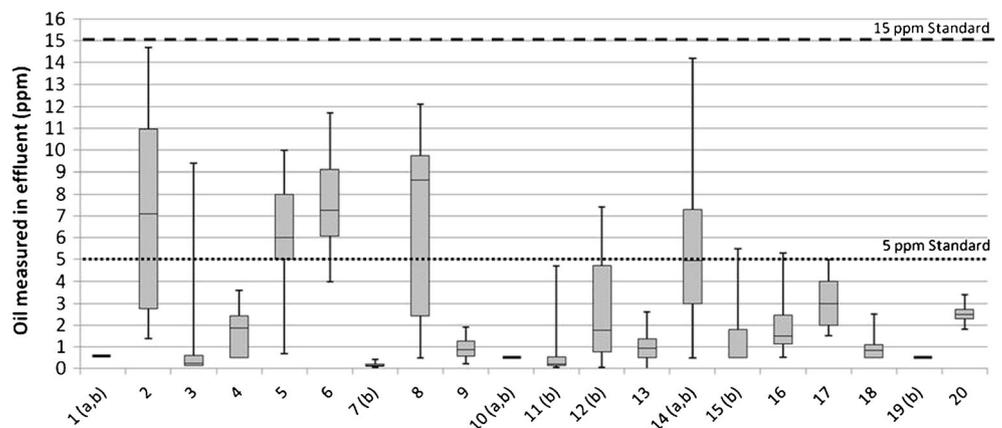
in a land-based setting. Of the 15, there was statistical evidence that 12 systems performed on average below a 5-ppm oil standard ($p < 0.001$). The other three systems all reported effluent oil concentrations below 1 ppm ($n = 18, 36, 19$), indicating their ability to perform well below the 5-ppm oil standard (as measured concentrations are all below those for which there is statistical evidence that systems perform below a 5-ppm oil standard); however, the datasets for these systems were not statistically tested due to all of the measurements being below the reporting limit. The mean effluent concentration (±standard error) for the five systems that were not statistically below the 5-ppm oil standard ($p > 0.05$) ranged from 4.93 ± 0.53 to 7.40 ± 0.33 ppm oil. These results illustrate that OWSs based on different technologies can meet or do better than meet compliance limits with the current oil discharge standards when properly operated and maintained.

Only synthetic bilgewater is used in land-based testing, whereas real bilgewater is a mixture containing many chemicals that often interact in complex ways. Different synthetic bilgewater test fluids are used to better simulate the potential fluids OWS might actually receive. Across all OWSs, tests conducted with Test Fluid B had the lowest mean effluent oil concentration of 3.01 ± 0.15 ppm, whereas Test Fluids A and C had higher mean effluent oil concentrations at 3.47 ± 0.15 ppm and 3.70 ± 0.26 ppm, respectively. There was not a significant difference in mean effluent oil concentrations among the three test fluids, indicating that, in a land-based setting, the systems are able to perform regardless of the bilgewater characteristics. Although land-based testing provides reproducible results useful for the type approval process, these tests have been criticized for not simulating real-world conditions (TANKEROperator 2009).

Type approval testing requirements were designed to ensure that system performance will be consistent with type approval testing data once installed onboard vessels. However, we cannot speculate as to whether all newer systems are in fact performing as intended once installed and operated onboard a given vessel. Mean oil index concentrations in effluent from the three shipboard OWSs were lower than the corresponding type approval test data reported for the same systems (Fig. 2). For OWS 1, both land-based oil index data ($n = 17$) and shipboard ($n = 4$) oil index measurements of effluent were below the reporting limit (1 and 0.55 ppm, respectively). Similarly, all land-based oil index data ($n = 18$) for OWS 2 were reported as 1 ppm, and shipboard ($n = 5$) oil index measurements of effluent were below the reporting limit (0.55 ppm) for all but one sample (1.3 ppm). Additionally, the shipboard measurement for OWS 2 were significantly less than the land-based data [ANOVA, $F_{(3,22)} = 7.97$, $p = 0.001$; Tukey's test $p < 0.01$], but there was no significant difference among land-based tests (Tukey's test $p > 0.05$). For OWS 3, the land-based oil index data had the greatest variability ($n = 18$, 1 to 14.2 ppm, CV = 94.0 %). The mean shipboard oil index
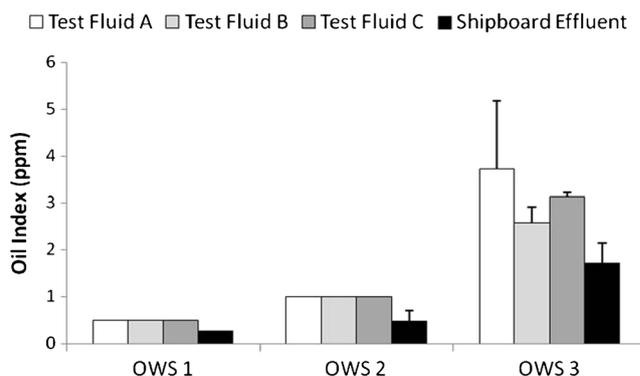
Fig. 2 Mean oil index concentrations in effluent from the three shipboard oily water separators (OWSs) compared to land-based type approval data for Test Fluids A, B, and C reported to the USCG for the same or similar systems

concentration ($n = 5$) for effluent from OWS 3 was lower than the mean land-based effluent concentration for each of the test fluids but not significant different [ANOVA, $F_{(3,22)} = 0.57$, $p = 0.64$]. Therefore, in the case of the three OWSs tested onboard ships for this study, the efficiency was similar to the land-based type approval tests and results indicate that these systems are performing equally as well or better than the land-based testing would suggest.

Shipboard oil treatment data

All shipboard samples were analyzed for oil concentrations using the three generally accepted laboratory methods used by EPA in compliance monitoring. Generally, HEM and SGT-HEM concentrations (oil and grease measured via EPA Method 1664A) measured in shipboard samples were greater than oil index concentrations (measured via IS0 9377-2) which is reasonable considering vessel generated oil sources have heavier petroleum fractions that are detected by EPA Method 1664A but not by ISO 9377-2 (Table 4). All of these methods involve a solvent extraction that separates the organic phase and is followed by some measurement of the oil and grease. EPA Method 1664A measures the weight of extracted oil and grease after the solvent is evaporated (reported as HEM and SGT-HEM). Alternatively, ISO Method 9377-2 runs a portion of the dried solvent extract through a gas chromatography instrument (reported as oil index). In general, the oil index method has the potential to provide detailed information on composition but requires sophisticated instruments. HEM and SGT-HEM methods are relatively simple and inexpensive but do not provide detailed compositional information. These types of reference methods are important since the data obtained from various sources and different laboratories can be compared. However, different methods will produce different results, and consequently, the magnitude and concentration of the different oil analytes may not be directly comparable (Yang 2011). The higher HEM and SGT-

Table 4 Summary data for shipboard sampling of three oily water separators (OWSs) including mean concentrations (±SE) of influent and effluent (ppm) and mean percent removal (±SE)

		Oil index	HEM	SGT-HEM
OWS 1	Influent (ppm)	8.22±2.87[a]	37.5±1.29	38.03±0.87
n=4	Effluent (ppm)	0.28±0.0[b]	1.0±0.0[b]	1.0±0.0[b]
	Removal efficiency (%)	97.37±0.34 %[c]	97.32±0.09 %	95.53±0.18 %
OWS 2	Influent (ppm)	129.56±55.53	180.8±44.84	118.6±26.37
n=5	Effluent (ppm)	0.48±0.21[a]	1.0±0.0[b]	1.0±0.0[b]
	Removal efficiency (%)	96.47±2.95 %	99.29±0.16 %	98.98±0.21 %
OWS 3	Influent (ppm)	39.6±9.99	90.4±16.36	51.6±9.29
n=5	Effluent (ppm)	1.71±0.42	19.4±1.57	10.28±0.96
	Removal efficiency (%)	95.54±0.61 %	75.77±4.33 %	75.25±8.06 %

For those data below minimum detection limit (MDL) or minimum reporting limit (MRL), calculations were made using MRL/2

[a] Mean contains at least one measurement below the minimum reporting limit (MRL). MRL_{ISO}=0.55 ppm; MRL_{HEM} & $_{SGT-HEM}$=2 ppm

[b] All measurements were below the MRL

[c] Grab 4 was not used in this calculation because both the influent and effluent concentrations were below MRL

HEM concentrations are likely due to the detection and measurement of waxes, soaps, greases, and other related material in the bilgewater whereas the oil index measurement only includes hydrocarbons with a retention time between $C_{10}H_{22}$ and $C_{40}H_{82}$. For these reasons, we treated these measurements as three separate analytes.

Each of the three systems had significant oil removal during shipboard treatment (varying between oil measurement methods and ranging from a mean of 75.3±8.1 % to 99.3±0.2 %; see Table 4). There was a significant difference in the oil index, HEM, and SGT-HEM concentrations between influent and effluent for all systems (p<0.05, except OWS 2, oil index p=0.08). There was no significant difference among OWSs for the oil index percent removal, but OWS 3 had significantly higher effluent concentrations compared to the other systems [$ANOVA_{ISO}$ $F_{(2,13)}$=7.28, p=0.01; Tukey's test p<0.05]. OWS 3 had significantly lower percent removal of HEM and SGT-HEM compared to OWSs 1 and 2 [$ANOVA_{HEM}$ $F_{(2,13)}$= 24, p<0.01; $ANOVA_{SGT\_HEM}$ $F_{(2,13)}$=6.80, p=0.01; Tukey's test p<0.05] along with significantly higher effluent concentrations [$ANOVA_{HEM}$ $F_{(2, 13)}$=122, p<0.01; $ANOVA_{SGT-HEM}$ $F_{(2,13)}$=82, p<0.01, Tukey's test p<0.01]. OWS 2 had the highest influent concentrations and therefore removed greater total amounts of oil. Regardless, treatment by all three OWSs reduced the oil concentration significantly between influent and effluent, resulting in high removal percentages.

Bilgewater influent varies among vessels, and the removal efficacy of oil and grease partially depends on the water quality of the bilgewater being treated (including the concentration and physical nature of the oil present). The influent concentrations of HEM and SGT-HEM differed significantly among systems [$ANOVA_{HEM}$ $F_{(2,13)}$=5.78, p=0.02; $ANOVA_{SGT-HEM}$ $F_{(2,13)}$=7.88, p=0.01]; OWS 2 had the highest mean influent concentration (Table 4). There was also

more than an order of magnitude difference among the influent oil index concentrations from the three OWSs sampled and among the replicate samples collected from OWS 1 and 2. Oil concentrations in shipboard influent were within the ranges measured by others (EPA 1999; Ghidossi et al. 2009). This large range in concentration measured in shipboard influent samples means that the challenge conditions for each OWSs was different. However, OWS technologies should be effective enough to treat this large range of influent concentrations and not rely on clean influent water.

Despite the significant difference between the oil concentrations in the influent for OWS 1 and 2, there was no significant difference between their effluent oil concentrations, indicating that the efficiency of these OWSs was consistent across the range of influent oil concentrations they received. Both systems appeared effective at removing oil below regulatory limits and a 5-ppm limit irrespective of influent concentrations. Additionally, there was no linear relationship for OWS 1 and 2 between the influent and effluent concentrations for all three oil analytes (Fig. 3a, b), indicating that the treatment efficiency was not dependent on low influent concentrations. Similarly, SGT-HEM concentrations measured in the influent and effluent of OWS 3 had no relationship (Fig. 3c). However, there was a strong but not significant relationship between the influent and effluent oil index and HEM concentrations for OWS 3 (Fig. 3c, oil index r^2=0.64, p=0.11; HEM r^2=0.39, p=0.26), suggesting that the effluent quality and the efficiency of the OWS depends on the influent water quality.

OCM readings

OCM readings on effluent samples from the three shipboard OWSs ranged from 0 to 8 ppm. In contrast, the concentrations measured in effluent samples ranged from below the reporting
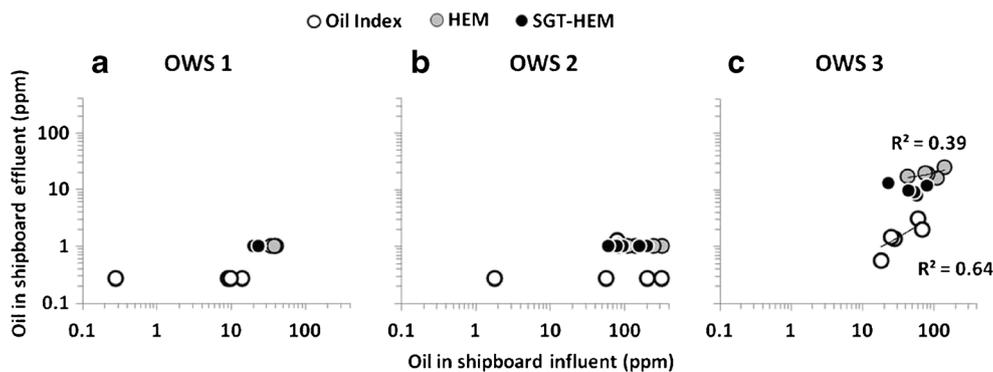
Fig. 3 Log-scale plot of paired influent and effluent oil concentrations for three shipboard oily water separators (OWSs). Oil content was characterized by three method-defined parameters: oil index, hexane extractable material (HEM), and silica gel treated hexane extractable material (SGT-HEM). Data were evaluated for linear relationships, and a lack of a linear relationship indicates a system capable of achieving high-quality effluent regardless of influent concentrations

limit (0.55 ppm) to 3.1 ppm for oil index, below the reporting limit (2 ppm) to 25 ppm for HEM, and below the reporting limit (2 ppm) to 13 ppm for SGT-HEM. For the samples that were below the reporting limit for the three oil analytes, OCM readings ranged from 2 to 8 ppm, which is a false-positive reading. For the two samples with OCM readings of zero, the measured laboratory concentrations ranged from an oil index concentration of 0.56 ppm to a HEM concentration of 19 ppm. These samples are examples of false-negative readings. For the effluent samples that were above the HEM method's reporting limit (which happen to be also above 15 ppm), there was a strong linear but not significant relationship between the OCM readings and the laboratory-measured HEM concentrations (Fig. 4, $r^2=0.73$, $n=5$, $p=0.16$). However, though there was a linear relationship, the correlation resulted in a slope of 0.92 an intercept of 17.0, and the actual OCM readings and

HEM readings for each sample differed notably. For those samples above the oil index and SGT-HEM methods' reporting limits, there was a weak relationship between the OCM readings and the oil index (Fig. 4, $r^2=0.50$, $n=6$, $p=0.31$), but no observable relationship between OCM readings and SGT-HEM concentrations (Fig. 4, $r^2=0.04$, $n=5$, $p=0.95$).

These onboard OCMs are used to detect whether OWSs are properly functioning on a daily basis. However, the OCM readings from the three vessels sampled included both false negatives and false positives, indicating that they were not accurately measuring actual oil discharge at low concentrations. Using traditional turbidity OCMs to measure oil concentrations in the 5- to 15-ppm range is complicated because most OCMs detect other bilgewater contaminants and detergents, resulting in false-positive readings (EPA 2008b), and the inability to detect clear emulsions would yield false negatives (EPA 2011).
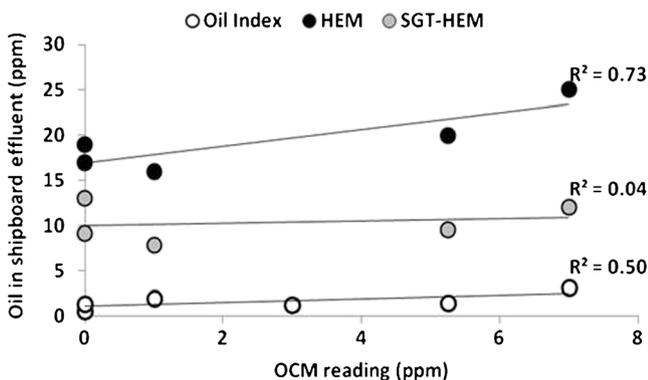
Other pollutant data

The three OWSs treated metals differently (Fig. 5). OWS 3 reduced the concentration of 17 analytes between influent and effluent whereas OWS 1 and OWS 2 reduced the concentration of only eight and 11 metals, respectively. However, OWS 1 and 2 achieved greater mean percent reduction of some metal analytes. OWS 1 reduced concentrations of three priority metal pollutants (dissolved chromium, total copper, and total lead) by more than 80 % and four other metal analytes (dissolved and total iron, dissolved and total manganese) by more than 50 %. OWS 2 reduced concentrations of priority metal pollutants (total chromium, total copper, total lead, and total zinc) by more than 80 % and those of four other metal analytes (total aluminum, total cobalt, dissolved and total vanadium) by more than 50 %. All three OWSs reduced the concentrations of total copper (66.6±8.2 %), total lead (62.5± 8.0 %), and total chromium (46.5±10.3 %) between influent and effluent. The effluent concentrations of all three OWSs had PHQ values of greater than 1 for total antimony (mean
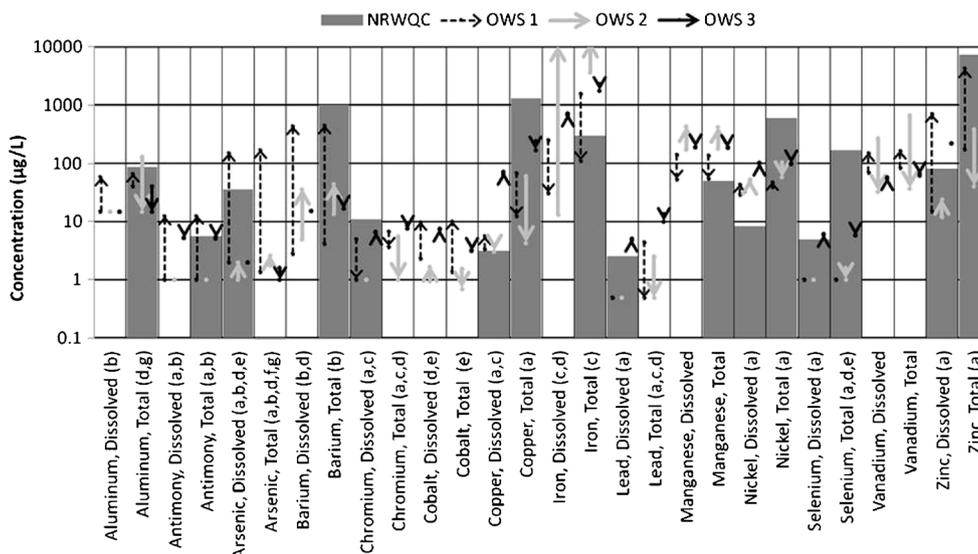

Fig. 4 A comparison of oil content measured from shipboard oily water separator (OWS) effluent and oil content monitor (OCM) readings to evaluate the accuracy of OCMs. Oil content was characterized by three method-defined parameters: oil index, hexane extractable material (HEM), and silica gel treated hexane extractable material (SGT-HEM). Only effluent samples with measurements above the reporting limit are shown. Data that line up on the y-axis indicate false negatives in which OCMs read zero but laboratory methods measured higher concentrations of oil in samples. Nine additional samples not shown on graph were false positives with no detectable concentrations in laboratory methods but OCM readings ranging from 2 to 8 ppm

Fig. 5 *Arrows* indicating the difference and magnitude of change between the mean influent and effluent concentrations of metal analytes measured from three shipboard oily water separators (OWSs) using EPA method 200.8. Concentrations on the *y*-axis are on a log scale. The lack of an *arrow* indicates no change between the mean influent and effluent concentrations. Concentrations are also compared to National Recommended Water Quality Criteria (NRWQC), when available. **a** Priority pollutant, **b** OWS 1 influent dataset includes at least one value below the reporting limit (MRL), **c** OWS 1 effluent dataset includes at least one value below MRL, **d** OWS 2 influent dataset includes at least one value below the MRL, **e** OWS 2 effluent dataset includes at least one value below MRL, **f** OWS 3 influent dataset includes at least one value below MRL, and **g** OWS 3 effluent dataset includes at least one value below MRL

PHQ=1.51, *n*=9), dissolved arsenic (1.88, *n*=9), dissolved copper (9.21, *n*=14), total iron (17.17, *n*=14), dissolved lead (2.06, *n*=5), total manganese (4.66, *n*=14), dissolved nickel (8.29, *n*=14), dissolved selenium (1.23, *n*=5), and dissolved zinc (3.57, *n*=14). The PHQ value for total arsenic was substantially above 1 (2,794, *n*=14); however, that result is because the benchmark used is based on human health criteria for consumption and overly conservative for use in evaluating wastewater effluent.

Samples were analyzed for 69 VOCs and 67 SVOCs, but only 26 VOCs (including six priority pollutants) and 11 SVOCs (including five PAH priority pollutants) analytes were measured above the reporting limit in at least one influent or effluent sample. An additional 61 VOCs and 91 SVOCs were tentatively identified in at least one sample. Overall, the OWSs substantially reduced the concentrations of VOCs and SVOCs between the influent and effluent, and there was no detectable effluent concentration in 68 % of VOC and 57 % of SVOC paired samples with detectable influent concentrations. The solubility and volatility of these compounds are dependent on Henry's Law constant and the concentrations of other chemicals in the samples which affect the water solubility. It is possible that the low VOCs and SVOCs concentrations are a result of gases being purged from the aqueous phase during treatment or bilgewater storage. All of the effluent VOC sample results and most of the effluent SVOC sample results [except bis(2-ethylhexyl) phthalate] were below the NRWQC benchmark concentration resulting in PHQ values of less than 1. The PHQ values for bis(2-ethylhexyl)

phthalate [also known as di(2-ethylhexyl) phthalate or DEHP] ranged from 1.17 to 4.43.

The majority of paired VOC samples (72 %) had no detectable concentrations measured in both the influent and effluent. Of the 26 VOC analytes, 16 (two priority pollutants) were detected in influent samples from all OWSs (Fig. 6). The majority of influent samples with detectable VOC concentrations had no detectable VOC concentration in the paired effluent sample. OWS 1 had no detectable VOC concentration in all effluent samples for 14 of these analytes (94 % of all paired samples) and minimal concentrations of the other two analytes, acetone (1.2 µg/L, *n*=1) and carbon disulfide (0.08± 0.0 µg/L), despite having higher influent concentrations compared to the other OWSs (158.0±4.9 and 10.4±0.4 µg/L, respectively). OWS 2 also had a large number of influent samples with detectable VOC but no detectable effluent concentrations (86 % of all paired samples). OWS 2 also had detectable effluent concentrations of acetone (27.2±4.7 µg/L) and carbon disulfide (0.1±0.0 µg/L), but lower influent concentrations than OWS 1 (84.2±3.7 and 8.6±0.3 µg/L, respectively). Additionally, OWS 2 had the highest average influent concentration of methyl ethyl ketone (33.4±1.2 µg/L) but the lowest effluent concentration (1.6±0.1 µg/L). Calculations using one half the quantification limit for samples that were below detection resulted in a perceived increase in VOC concentrations for some analytes from OWS 1 and OWS 2 because of differences in the quantification limits for influent and effluent samples. All 16 VOC analytes were detected in at least three effluent samples from OWS 3 with concentrations
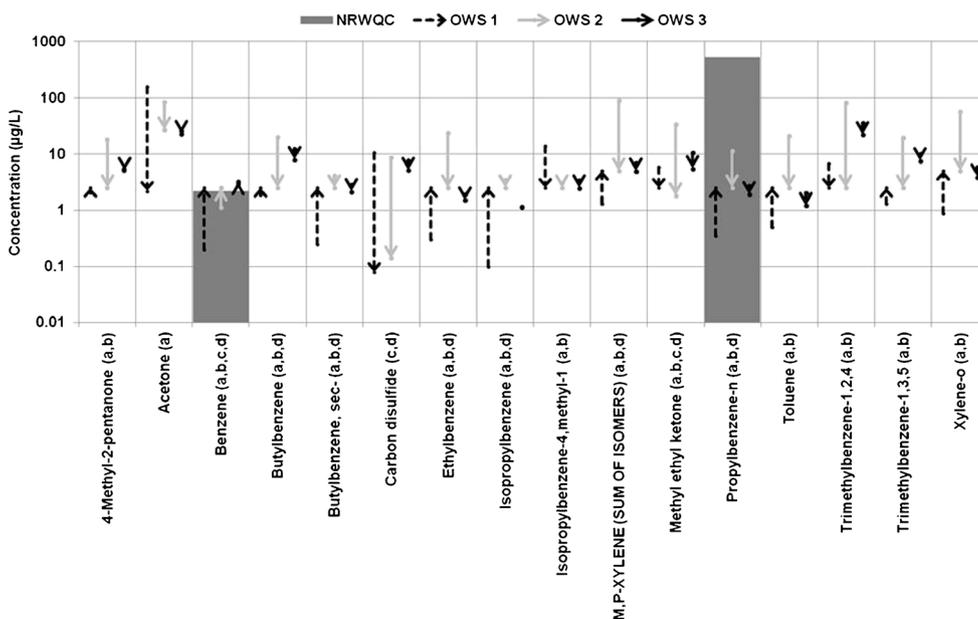
Fig. 6 *Arrows* indicating the difference and magnitude of change between the mean influent and effluent concentrations of volatile organic compounds (VOCs) measured from three shipboard oily water separators (OWSs). Concentrations on the *y*-axis are on a log scale. The lack of an *arrow* indicates no change between the mean influent and effluent concentrations. Concentrations are also compared to National Recommended Water Quality Criteria (NRWQC), when available. **a** OWS 1 effluent dataset includes at least one value below the reporting limit (MRL), **b** OWS 2 effluent dataset includes at least one value below MRL, **c** OWS 3 influent dataset includes at least one value below MRL, and **d** OWS 3 effluent dataset includes at least one value below MRL

ranging from 0.05 to 36.7 μg/L and percent removals ranging from actual increases (acetone, 4-methyl-2pentanone, and *n*-propylbenzene) in concentrations to up to 95 % removal.

Of the remaining 10 VOC analytes measured above detection, seven (chlorobenzene, chlorotoluene, chlorotoluene-*p*, cyclohexane, 2-hexanone, methyl cyclohexane, and methyl tertiary butyl ether) were detected in the influent from OWSs 1 and 2 but were not detected in any effluent sample. The concentrations of these VOC analytes were low in the influent samples for OWS 1 and OWS 2, ranging from 0.06 to 3.6 μg/L and below detection for 43 % of the samples. Of the remaining three, chloroform was found only in small concentrations in two influent and two effluent samples from OWS 3 (0.2 to 0.3 μg/L). Methyl bromide (0.4 to 0.5 μg/L) was measured only in effluent samples with no detectable concentration in the influent samples from both OWSs 1 and 3. Finally, OWS 1 reduced concentrations of methyl acetate (influent concentration ranged from 1.3 to 2.5 μg/L; effluent concentration was below detection), but OWS 2 marginally increased concentrations in the effluent from no detectable concentration to 0.5 to 1.4 μg/L.

The majority of paired SVOC samples (89 %) had no detectable concentrations in both the influent and the effluent. Of the influent samples with detectable SVOC concentrations, 55 % had no detectable concentration in the paired effluent sample. Of the 11 SVOC analytes detected in influent, five analytes (benzaldehyde, biphenyl, fluorene, methylnaphthalene-2, and naphthalene) were not detected in

effluent samples from any of the OWSs with 33 % of the influent samples also below detection. All of the OWSs reduced the concentrations of three of the SVOC analytes [phenanthrene, bis-(2-ethylhexyl) phthalate, and pyrene] by varying extents ranging from 46.0 to 100 % (Fig. 7). There were contrasting results for concentrations of di-*n*-butyl-phthalate, acenaphthene, and acenaphthylene among the three OWSs (Fig. 7). OWSs 1 and 2 had no detectable influent concentrations of di-*n*-butyl-phthalate, but small concentrations were detected in effluent (0.64 to 1.81 μg/L). However, OWS 3 reduced the concentration of di-*n*-butyl-phthalate by 80.6 to 100 %. Acenaphthene and acenaphthylene were not detected in any influent or effluent samples for OWS 1 and OWS 2, but small concentrations were detected in the effluent from OWS 3 (3.86±0.6 μg/L and 3.10±0.2 μg/L, respectively). Calculations using one half the quantification limit for samples that were below detection resulted in a perceived increase in SVOC concentrations for samples from OWS 3 because of differences in the quantification limits for influent and effluent samples. Only four effluent samples from OWS 3 truly had greater concentrations of DEHP, acenaphthene, and naphthalene than influent samples with increases ranging from 11 to 58 %. Overall, OWS 3 had the lowest percent removals (29–90 %) and OWS 1 had the highest percent removals (92–97 %).

There were dissimilarities in the treatment of surfactants by the different OWSs. OWS 1 had the lowest influent concentrations (1.8 to 3 mg/L) and effluent sample concentrations
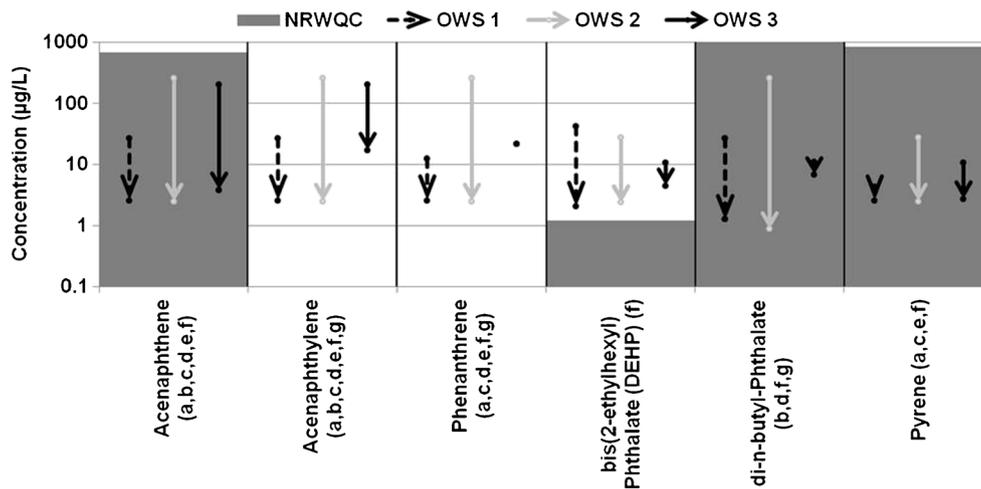
Fig. 7 *Arrows* indicating the difference and magnitude of change between the mean influent and effluent concentrations of semivolatile organic compounds (SVOCs) measured from three shipboard oily water separators (OWSs). Concentrations on the *y*-axis are on a log scale. The lack of an *arrow* indicates no change between the mean influent and effluent concentrations. Concentrations are also compared to National Recommended Water Quality Criteria (NRWQC), when available. **a** Priority pollutant, **b** OWS 1 influent dataset includes at least one value below the reporting limit (MRL), **c** OWS 1 effluent dataset includes at least one value below MRL, **d** OWS 2 influent dataset includes at least one value below MRL, **e** OWS 2 effluent dataset includes at least one value below MRL, **f** OWS 3 influent dataset includes at least one value below MRL, and **g** OWS 3 effluent dataset includes at least one value below MRL

that were all below detection. OWS 2 had the highest influent sample concentrations (3.7 to 4.1 mg/L) but still reduced the concentrations of surfactants by up to 82 %. There was no difference in the surfactant concentrations between the influent (1.9 to 2.2 mg/L) and the effluent (2.0 to 2.6 mg/L) of OWS 3, indicating that system did not remove surfactants.

The concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), organic carbon, and phosphorus were reduced between the influent and effluent of all three OWSs (Fig. 8). OWS 1 had the highest percent reduction (76 to 100 %), OWS 2 the second highest (42 to 69 %), and OWS 3 the lowest (10 to 43 %). Regarding nitrogen analytes (Fig. 8), OWS 1 showed reductions in ammonia (mean percent removal=63.1 %), total Kjeldahl nitrogen (TKN) (78.5 %), and nitrate+nitrite (100.0 %). Conversely, OWS 2 had no notable changes in total nitrogen loading, showing minimal increases in ammonia between influent (2.4±0.03 mg/L) and effluent (4.2±0.6 mg/L), minimal reductions in TKN (17.2±0.5 and 14.2±0.4 mg/L, respectively), and no measureable concentration of nitrate+nitrite in both influent and effluent samples. OWS 3 showed no significant reduction in ammonia (7.2 %) and TKN (1.1 %) and no measureable concentration of nitrate+nitrite. The inorganic ion composition of the bilgewater was generally similar to that of seawater, except for nitrate and ammonia concentrations. Nitrate concentrations were lower than sea water and ammonia concentrations were higher, consistent with both the low oxygen concentrations of bilgewater measured in this study (0 to 3.7 ppm) and reported by Cazoir et al. (2012). Each system performed differently for total suspended solids (TSS) as well, with OWS 1 showing an increase between influent

and effluent, OWS 2 showing a reduction (57.4 %), and OWS 3 having no measureable concentrations (Fig. 8).

Conclusions

Based on both the land-based certification test results and our shipboard sampling, OWSs currently on the market can achieve and exceed compliance with a 15-ppm oil standard when properly maintained and operated. However, we are also aware that many vessel operators and crews have described poor performance from OWSs installed onboard vessels, and if type approved OWSs underperform at sea even though they passed land-based tests and are unable to meet regulatory limits, ship owners face operational, financial, and legal consequences. In some cases, vessel operators and/or crews circumvent the OWS, tamper with the OCM, or otherwise illicitly discharge because the OWS equipment does not properly function or has not been properly maintained. In fact, there have been several prosecutions of vessel companies and crew members for such illegal activities, including criminal sanctions (see, e.g., among others, US v. Kun Yun Jho 2008; US v. Dalnave Navigation, Inc et al. 2009; US v. Ilios Shipping Company 2011). However, we were also able to show that land-based certification test results for three OWSs are comparable to the shipboard performance and that at least these systems appear capable of achieving a discharge oil standard of 5 ppm both in a land-based and shipboard setting.

It is also apparent from our data that there are notable differences in results between methods used to measure oil and oil and grease, and these differences might complicate
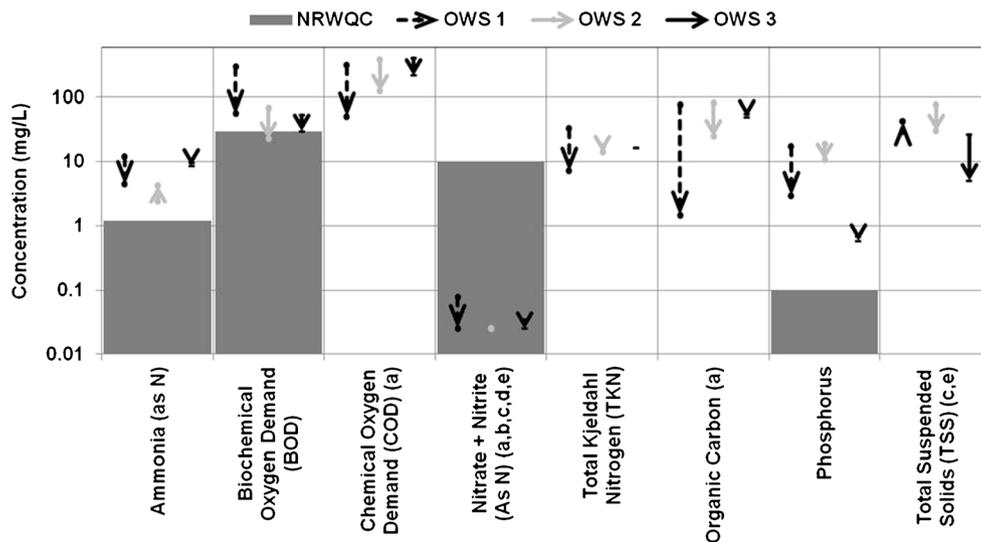
Fig. 8 *Arrows* indicating the difference and magnitude of change between the mean influent and effluent concentrations of conventional pollutant and nutrient analytes measured from three shipboard oily water separators (OWSs). Concentrations on the *y*-axis are on a log scale. The lack of an *arrow* indicates no change between the mean influent and effluent concentrations. Concentrations are also compared to National Recommended Water Quality Criteria (NRWQC), when available. **a** OWS 1 effluent dataset includes at least one value below the reporting limit (MRL), **b** OWS 2 influent dataset includes at least one value below MRL, **c** OWS 2 effluent dataset includes at least one value below MRL, **d** OWS 3 influent dataset includes at least one value below MRL, and **e** OWS 3 effluent dataset includes at least one value below MRL

analyses of future bilgewater data collected by vessel operators where different methods are utilized. Though we do not find these results concerning, they do indicate that some greases and other materials are being discharged for which the systems are not being tested in type approval testing. Additionally, some new-build vessels operating in U.S. waters will have to annually monitor their bilgewater discharges as required by EPA's 2013 VGP (EPA 2013). Those vessels that elect to use EPA Method 1664A may have different (and possibly elevated) results than those that utilize ISO 9377-2 since they will be measuring a wider range of constituents.

Additionally, our data illustrate that shipboard oil concentration measurements through standard turbidity OCMs are unreliable at low detection levels. It is generally believed that UV fluorescence OCMs are more accurate (EPA 2011; Yang 2011). The effectiveness of a given OWS to prevent the discharge of oil from vessels depends on the OCM triggering the discharge-stopping device when the OWS fails to meet discharge limits. Therefore, if an OCM produces a false negative when an OWS is not adequately treating the bilgewater effluent, elevated levels of oil may be discharged into the aquatic environment. Likewise, an OCM that is giving a false positive may prevent the vessel operator from discharging bilgewater that would otherwise meet regulatory limits, thereby increasing cost and frustration for the vessel owner and operator. As such, the accuracy and reliability of the OCM is critical, and using OCMs with reduced accuracy at low levels compromises vessel operators' ability to effectively manage bilgewater. Therefore, the use of more sophisticated OCM technology (e.g., UV fluorescence) should be considered for

all new OWSs due to the importance of OCM in managing the discharge of oil from vessels.

Despite being designed specifically to remove oil from bilgewater, OWSs have the potential to provide additional pollution reduction benefits since bilgewater contains a mixture of other pollutants (Andrade 2009; EPA 2011). Variations in bilgewater influent composition are not unexpected as it will vary depending on differences in vessels, shipboard equipment, and the operations and procedures used to maintain the engine room. Although these analytes are not currently regulated, another main advantage to improving OWS and bilgewater treatment processes (e.g., using OWS with afterpolishers or other advanced features) is the possibility of removing more of these other potentially harmful pollutants. Generally, the OWSs that were sampled reduced or eliminated the majority of pollutants measured, except for about half of the heavy metals analytes, for which concentrations increased. The increase in some metals could be the result of adding coagulants (e.g., $FeSO_4$) or inorganic species such as acids or salts (e.g., ferric salts) used to reduce the surface charge of the oil droplets and increase coagulation (Coca et al. 2011). These additional pollution reduction benefits are noteworthy, and OWS manufacturers should take them into consideration as technology improves and evolves in the future.

Due to the different treatment technologies utilized by the three shipboard OWSs, it is not surprising the effluent concentration and removal efficiencies varied, and these results are consistent with other examinations of onboard OWSs (see, e.g., Navy 2003; EPA 2008b; EPA 2011). OWS 1 used coalescence plates to which oil droplets attach, form larger

droplets (coalesce), and then break free rising to the surface of the tank. When oil is detected in the top of the tank, it is automatically pumped to a waste oil tank. Because OWS 1 used filtration as an additional treatment, it is not surprising that it had high removal efficiencies for most analytes. However, the reason for increases in some metal concentrations from OWS 1 is unknown. The treatment processes for OWS 2 were based on coagulation and flocculation, which are typically facilitated by adding separating agents to the bilgewater. Both coagulation and flocculation bring suspended material together into larger agglomerates that are then removed through floatation and filtration. Theoretically, this technology should remove metals, phosphates, TSS, in addition to oil and grease; consistent with expectations, our results indicated reduction in approximately half of the metals and 58.3 to 87.5 % reductions in TSS. However, the addition of coagulant or flocculant chemicals that might include metallic salts could potentially explain the increase in some of the other metal concentrations. OWS 3 utilized a centrifugal separator, which mechanically separates oil from the bilgewater. As previously discussed, this treatment approach relies on density differential between water and pollutants, and where there is no differential (e.g., dissolved metals), one would expect lower removal efficiencies without additional polishing units. While OWS 3 had reasonable oil removal, consistent with expectations, it had the lowest removal efficiency for oil of the three units and least reductions of other pollutants such as metals of the three OWS units. An afterpolisher unit (e.g., ultrafiltration) would be expected to improve the performance of this system. Despite differences in these system designs, as discussed above, all 20 systems for which there are land-based data and the three systems we sampled onboard ships appear to substantially outperform a 15-ppm oil discharge compliance limit utilizing most oil analytical methods, with most samples from the land-based testing and shipboard testing meeting a 5-ppm oil discharge compliance limit.

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