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Exploring the limits of dissolved organic matter fluorescence for determining seawater sources and ballast water exchange on the US Pacific coast

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ABSTRACT

To minimize the risk of biological invasions associated with commercial shipping, vessels are required to conduct ballast water exchange (BWE) ≥ 200 nautical miles offshore when arriving in the US from foreign ports, and some states require coastal BWE ≥ 50 miles offshore along domestic routes. Previous research suggests that the intensity of fluorescent dissolved organic matter (fDOM) can be used to verify whether BWE was implemented. This study examined seasonal and spatial variability of fDOM in Pacific rim ports and the adjacent seas, using the North American coast as a model system to test whether regional fluorescence intensity thresholds consistently distinguish port sites from coastal and oceanic sites at increasing distances from shore. Over 2000 samples from major port systems on the US Pacific coast and along offshore (perpendicular) and alongshore (parallel) transects were analyzed. Overall, humic fDOM fluorescence intensity ($C3^* = 370/494$ nm) effectively discriminated port versus oceanic sites located further than 100 miles from shore, but discriminated only a subset of coastal versus oceanic sources within the northeastern Pacific. Data from additional global ports are needed to predict the frequency of false positive or false negative ballast source determinations using fDOM for foreign vessel traffic.

1. Introduction

The role played by ships' ballast water in spreading non-native organisms between ports is well-documented (Carlton and Geller, 1993; Hulme et al., 2008; Ruiz et al., 2000). To reduce the risk that foreign organisms are imported via ballast water at densities sufficient to establish reproductive populations, the US requires that ships arriving from overseas, together with some domestic vessels, treat their ballast water prior to discharging in port (EPA, 2010; USCG, 2004a). Currently, ballast water exchange (BWE) is the only approved treatment that is readily available to nearly all vessels and meets regulations for mandatory ballast water treatment.

To conduct BWE, tanks that were originally filled in port or coastal waters are flushed out in the ocean during transit, creating a treatment to reduce the concentrations of coastal organisms which can pose a risk of biological invasion upon discharge in other ports or coastal areas (Gray et al., 2007; Minton et al., 2005). In the US, current federal regulations require that ships arriving from overseas conduct BWE at 200 nautical miles (nmi) from shore with at least 95% exchange efficiency, prior to ballast discharge in coastal waters (USCG, 2004a). In addition, vessels on domestic coastwise routes in California, Oregon, and Washington (across particular regional boundaries) are required to conduct BWE at distances exceeding 50 nmi from shore before discharging into state waters (CSLC, 2006; DEQ, 2001; EPA, 2010; WDFW, 2007).

Ships arriving in US ports are required to submit advance notice of their intent to discharge ballast (USCG, 2004b), reporting the ballast source, volume, and details (type, degree and location) of BWE for each ballast tank being discharged. However, these data are self-reported, and there is currently no independent verification of compliance with BWE regulations. Direct measurement of naturally-occurring tracers in the ballast water offers a scientifically defensible and tractable solution to this problem.

It is possible to deduce whether a tank was ballasted in a port or oceanic location based upon concentrations of chemical constituents that are known to differ between these sources. Although salinity is a useful tracer of coastal waters influenced by river discharge, many high salinity ports also exist with salinities indistinguishable from the open ocean (Doblin et al., 2010). Chromophoric dissolved organic matter (CDOM) fluorescence is an alternative tracer with several attractive characteristics. These include high sensitivity, with concentrations varying up to two

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orders of magnitude between rivers and the open sea (Murphy et al., 2008; Opsahl and Benner, 1997), straightforward measurement of its fluorescent fraction (fDOM) via fluorescence spectroscopy, the potential for delivering information about both fDOM quantity (i.e. fluorescence intensity) and quality (composition) by varying the excitation and emission wavelengths measured (Coble, 1996), and the growing functionality of handheld fluorometers available for in-situ data collection.

Earlier research assessed the effect of BWE on fDOM in ships' ballast via experiments conducted on commercial vessels, determining that fDOM in ballast water was reduced dramatically by mid-ocean BWE, even in cases where accompanying salinity changes were negligible (Doblin et al., 2010; Murphy et al., 2004, 2006, 2009b); these studies also included limited ocean sampling in the North Pacific (4 transects), North Atlantic (2 transects) and South Pacific (4 transects). Murphy et al. (2006) further examined full excitation–emission matrices with parallel factor analysis (PARAFAC) to identify independent fluorescent components and determine which wavelengths were most informative about ballast water sources. Two excitation/emission wavelength pairs (C2*: 320/414 nm and C3*: 370/494 nm) were found to track separate humic-like fluorescent components (responsible for the "M" and "C" peaks, respectively (Coble, 1996)) and afford sensitive discrimination of coastal origins. C3* appeared to track a breakdown product of terrestrial organic matter, while C2* represented material recently produced by microbes from substrates that were abundant in terrestrial environments (Murphy et al., 2008). Apparent thresholds bounding the maximum fluorescence of exchanged ballast water, in units of ppb quinine sulfate equivalents (QSE), were identified at 1.7 QSE and 0.7 QSE for C2* and C3*, respectively (Murphy et al., 2006).

Most of the CDOM in coastal environments has allochthonous origins, being derived from the breakdown of plant matter in soils and transported to the coast via rivers, runoff and groundwater (Blough and Del Vecchio, 2002; Yamashita et al., 2008). In contrast, CDOM in the surface open ocean appears to be a comparably dilute combination of recently produced autochthonous organic matter against low background levels of highly degraded terrestrial material (Blough and Del Vecchio, 2002; Jørgensen et al., 2011; Yamashita and Tanoue, 2009). Nevertheless, elevated fluorescence can also occur in surface ocean regions subject to persistent, large scale upwelling in which higher-CDOM deep water is brought to the surface through the actions of wind or deflection of currents by coastal boundaries or seamounts (Siegel et al., 2002). For example, along the US west coast, the ocean is the dominant source of nutrients and biomass, with seawater properties controlled primarily by seasonal, decadal and short-term variability in the California Current System that is driven by large-scale atmospheric systems (Hickey, 1979; Hickey and Banas, 2003). Wind-driven coastal upwelling brings nutrients to the sea surface adjacent to shore for much of the year, resulting in a productive coastal zone (Huyer, 1983). Other than the Columbia River outflow which is observable far from the river mouth and the Fraser River outflow via the Straits of Juan de Fuca, most estuaries in the region have only localized influences on seawater properties (Hickey, 1979).

The observed natural variability in the oceans (and especially along coasts) represents a significant challenge to predicting fDOM quantities in ballast water. Importantly, the success of fDOM as a tracer of BWE rests upon there being measurable differences in and near ports versus in areas of the ocean where BWE is allowed to take place. In a regulatory application, ballast water sources may be reported inaccurately, so any fluorescence thresholds applied to determine compliance must be robust to spatial and temporal variability within broad geographic regions.

The purpose of this study was to identify whether fDOM exhibits consistent and detectably large differences between intensities in port, coastal and oceanic waters, using the North American Pacific coast as a model system. Herein, the distribution of humic fDOM was examined in ports and at varying distances from shore in order to assess its sensitivity for deducing the coastal versus oceanic sources of seawater samples.

2. Methods

2.1. Experimental design

Sampling of surface waters in the Eastern Pacific, west of North America, was focused in estuaries with major ports and in the adjacent coastal waters. Port sampling involved intensive surveys of four port systems in 2006–2008: Los Angeles/Long Beach (LALB), San Francisco Bay (SFB), Puget Sound (PS), and the Strait of Georgia (SG) (for details, see the Supplementary files). Surveys at the first three ports were replicated on a quarterly basis throughout a year, and those at SG were replicated in summer and winter, to examine seasonal and spatial variation across 14 different survey events (across all bays). During each port survey, replicate samples were collected (as below) from 12 to 24 sites. Detailed descriptions and analyses of these data are provided elsewhere (Boehme et al., 2008); in the current study, data from samples collected in ports were simply pooled by region to estimate terrestrial end-member concentrations mixing with the coastal ocean.

In coastal waters, sampling occurred perpendicular to shore along transects extending to approximately 60–80 nmi (offshore transects) and parallel to shore at varying distances from the coast (coastwise transects) (see the Supplementary files for details). Offshore transects provided data on the rate that terrestrial signals decline with distance from specific areas of the coast, whereas coastwise transects evaluated latitudinal variability in tracer penetration from the coast. Samples were collected for a total of 22 offshore transects and 10 coastwise transects between 2006 and 2008. Offshore transects were oriented approximately perpendicular offshore from: San Diego, Los Angeles, Bodega Bay, Monterey Bay, and San Francisco Bay (CA); Gray's Harbor and Newport (OR); the Columbia River and the Strait of Juan de Fuca west of Puget Sound (WA); and Seward (AK) (Fig. 1). Up to 13 sites were sampled per transect, attempting to sample at specific distances from land (80, 70, 60, 50, 40, 30, 20, 15, 10, 5, 2, 1, and 0 nmi), defined as the distance to the closest point on mainland excluding islands (except for Vancouver Island, which was treated like mainland due to its large size).

Coastwise transects generally tracked within 25–40 nmi of shore except during a single transect between California and Alaska, with sites spaced 3 to 10 nmi apart outbound and inbound from port, and up to 100 nmi apart elsewhere. The coastwise transects ranged from 134 to 1804 nmi, and included 14–62 sites sampled (see the Supplementary files). On some of these transects, samples were also collected at distances over 100 nmi from land and were considered oceanic (versus coastal). Such oceanic samples were collected from a total 51 sites ($n = 130$ total), of which 88 were in the Eastern North Pacific off the US west coast and 42 were in the Western North Pacific off Asia.

In total, across all port and transect surveys, 1026 sites were sampled generating nearly 2400 samples that were used in this study. This sampling effort was concentrated near-shore, where steeper concentration gradients were anticipated, and included multiple seasons (Fig. 1, see also the Supplementary data). At each site, 2–3 replicate samples for fDOM analyses were obtained at 2–5 m depth, and water quality parameters (salinity, temperature, conductivity, dissolved oxygen, and pH) were recorded.

2.2. Sample collection and analysis for fDOM

During port surveys and offshore transects, seawater was sampled over the side of chartered boats and research vessels using a precleaned, purpose-built peristaltic pumping assembly. Samples for coastwise transects were collected on commercial vessels via engine cooling seawater intake pipes (shipside source of 3–7 m depth) and upstream of the engine, as previously described (Murphy et al., 2004, 2006) or on research vessels via circulating seawater intake systems. All samples were filtered via a high-capacity inline 0.45 μm capsule filter (GE Memtrex MP), frozen and analyzed within 3 months.

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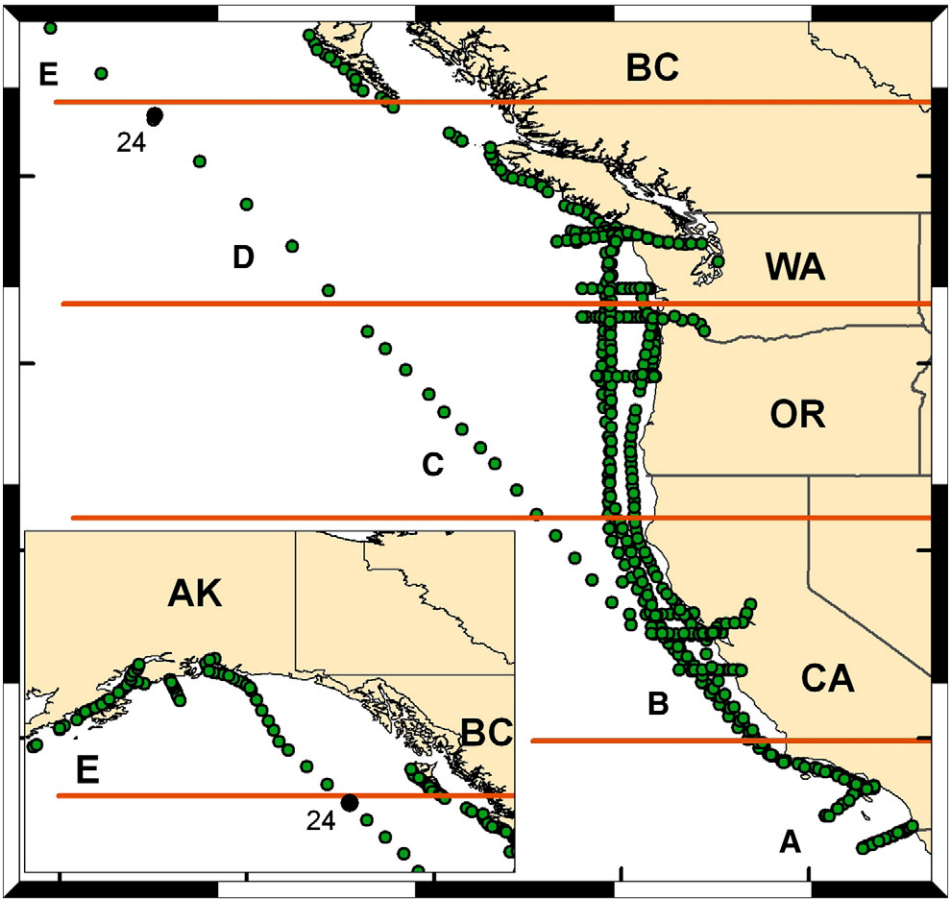

Fig. 1. Sampling zones (labeled A–E) and sites (circles) along the US Pacific coast west of California (CA), Oregon (OR) and Washington State (WA). Map shows 31°–54° N and 117–141° W with 60 nmi intervals indicated by alternating black/white bars. Northern zone boundaries are located at 34.5, 41.5, 46.5, and 51° N. Inset shows sites north of 46° N adjacent to Alaska (AK) and British Columbia, Canada (BC).

The freezing of 1.2-μm filtered freshwater samples with high organic matter concentrations and reactivity has been implicated in decreasing fluorescence measurement precision without overall increases or decreases in fluorescence intensity (Spencer et al., 2007). However, other studies have observed no freezing effects on high-CDOM (i.e. humic peak intensities at 340 nm excitation exceeding 100 ppb QSE), 0.45-μm filtered extracted estuarine pore waters (Otero et al., 2007) or on low-CDOM (humic peak intensities below 1.5 ppb QSE), 0.22-μm filtered oceanic samples (Yamashita et al., 2010). The freeze/thawing of 0.45-μm filtered seawater samples was also examined in controlled experiments in our laboratory, using replicate samples from four sources (two ports and two ballast tanks) for which humic peak (350/450 nm) intensities ranged between 1.2 and 5.2 ppb QSE (Murphy, 2007). In these experiments, freezing introduced no measurement bias or additional inter-replicate variability in humic peak measurements after 3 months relative to analyzing samples following a week of refrigeration. Overall, these studies suggest that if freezing artifacts had occurred, this was most likely at a minority of port sites where humic fluorescence was relatively high (up to 30 ppb QSE). Also, while freezing artifacts could potentially decrease measurement precision for individual replicates, there is no indication that this would bias site-averaged data or the statistical analyses in the remainder of this paper.

Fluorescence was measured at 20 °C in a 1 cm quartz cell with a SPEX Fluorolog-3 from Horiba Jobin Yvon (Edison, New Jersey, USA) using a 450 W xenon lamp as the light source. Measurements were performed in ratio mode with 0.5 s integration times and 5-nm slit widths on the excitation and emission monochromators. To track changes in instrument response over the analytical period, repeated measurements of freshly prepared 100 ppb quinine sulfate were made every two weeks over the period of fluorometer operation. After correcting for instrument response and lamp variability, the percent relative standard deviation (RSD) of these measurements was 5.8%. Instrument intensities were corrected for instrumental bias and scaled to quinine-sulfate equivalent units, QSE (Coble et al., 1993). An approximate conversion (±15%) to Raman units (R.U., i.e. signal normalized to the area of the water Raman peak excited at 350 nm in a clean water blank) was calculated for this instrument using the FDOMcorr toolbox for Matlab (Murphy et al., 2010), giving $QSE = 100 \times R.U.$

This study focused analyses upon data collected for two wavelength pairs: C2*: 320/414 nm and C3*: 370/494 nm, which have been previously determined to be sensitive tracers of coastal seawater (Murphy et al., 2006). In this dataset, the fluorescence intensities of C2* and C3* in coastal waters were highly correlated ($C2^* = 1.72 \times C3^*$, $r^2 = 0.99$) and displayed nearly identical trends. This is likely to reflect the identical effects of dilution upon high initial concentrations of both tracers at the coasts, rather than an indication of a common terrestrial source (Murphy et al., 2008; Yamashita and Tanoue, 2008). To avoid repetition, only the results for C3* are reported here.

Inner filter effect (IFE) corrections were calculated from absorbance collected on a Cary 4E UV–Visible spectrophotometer (1-cm cell) using the method described by Lakowicz (2006). Correction factors were applied to the relatively concentrated samples from the Columbia River, Vancouver, and San Francisco and exceeded 5% only in a handful of samples from the Strait of Georgia/Puget Sound and San Francisco Bay. IFE correction factors for C3* were always below 3%. Salinity, measured with YSI-85 CTD probes (YSI Inc.), was accurate to ±2 (±8% at oceanic salinities).

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2.3. Statistical analysis

The effects on fluorescence intensity of season, latitude and distance from shore outside ports were examined in linear mixed models ('PROC MIXED', in SAS), using log-transformed fluorescence intensity and distance from shore. Models examined latitude, season, and distance from shore as fixed effects, and whether additional random effects applied to the intercepts or slopes for season and latitude. Since the main effect of season and all its interactions were significant, further models were developed to examine the effects of latitude and distance from shore for each seasonal dataset independently.

In order to graphically depict spatial variability and model fluorescence at different distances from land, fluorescence measurements were averaged by site then grouped into one of five geographical zones bounded above by 34.5° N (zone A), 41.5° N (zone B), 46.5° N (zone C), 51° N (zone D), and 62° N (zone E) (Fig. 1) and six distance from shore bins (i.e. <0.2, 0.2–5, 5–25, 25–50, 50–100, and >100 nmi from the nearest point on land, excluding minor islands). For each distance from shore category, a cumulative distribution function (CDF) for C3* and salinity was obtained by sorting the data from lowest to highest and assigning it to evenly spaced percentile values according to the number of data points in the set, then plotting as lognormal cumulative distribution functions on a probability scaled x-axis.

Probability density functions (PDF) were fitted to port and ocean datasets using the distribution fitting tools in the Matlab statistics toolbox (Mathworks Inc.). Individual datasets examined were (1) all sites in the US west coast ports (Ports), (2) low-fDOM sites in west coast ports ($Port_{low}$), defined as only sites for which fluorescence was less than 6× the lowest fluorescence measured in port, (3) sites 50–100 miles from the west coast ($Ocean_{50}$), (4) sites > 100 miles from land in the Eastern Pacific ($Ocean_{100}$), and (5) sites > 200 miles from land ($Ocean_{200}$). To facilitate examination of open ocean sources > 200 miles from land despite a limited oceanic dataset, open ocean data from an additional 23 sites sampled in the North Pacific between 2000 and 2001 were incorporated in this analysis (Murphy et al., 2006, cruises LF, AS, K1 and K2).

Lognormal PDFs were fitted to each dataset and provided adequate representations ($p > 0.05$ on Jarque–Bera goodness-of-fit test) except in the case of the full ports dataset, which was not modeled well by any single distribution due to bimodality (i.e. distinct populations of high and low-fDOM sites). Representations of the fitted PDFs were generated using a Monte-Carlo simulation in Matlab with 10,000 iterations and used to derive a PDF for the ratio of C3* in port to oceanic seawater. PDFs of port:ocean fluorescence ratios were developed considering (a) all port sites, and (b) low-fDOM port sites. The former was used to estimate the median ratio of port to oceanic fluorescence, while the latter was used to estimate the lower tail (i.e. 5th percentile) of the PDF distribution. This approach is justified on three grounds: (1) the low-fDOM sites were more accurately represented by a separate lognormal distribution, (2) if discrimination between oceans and low-fDOM sites is demonstrated, it is implicit that high-fDOM sites can be discriminated, and (3) calculated 5th percentiles were relatively insensitive to the threshold chosen to divide high- and low-fDOM sites, differing from values reported herein by less than 5% for thresholds ranging between 3–10× the minimum fluorescence measured in port.

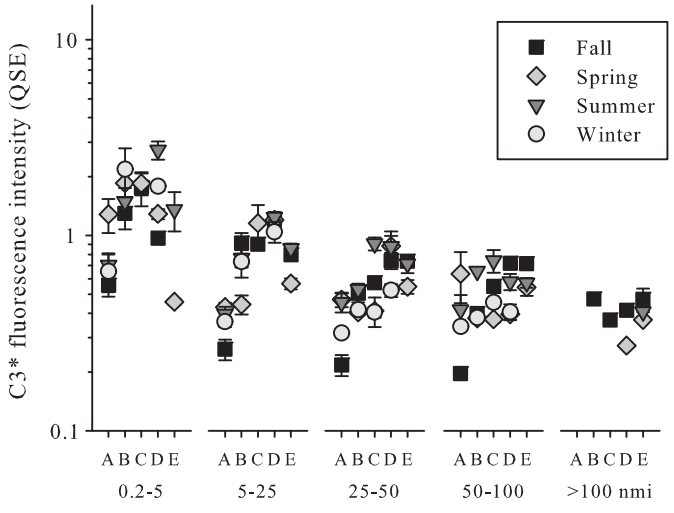

Fig. 2. C3* ($\lambda_{ex}/\lambda_{em}$ = 370/494 nm) fluorescence intensity (mean ± standard error) by season and geographic zone (A–E) for sites at increasing distances (in nautical miles, nmi) from the US Pacific coast.

3. Results

3.1. Sources of variability in fDOM

Statistical models indicated significant effects of latitude, season and distance from shore on C3* fluorescence. In the overall model ($n = 1693$ samples collected outside of ports), all main effects and interactions involving season were highly significant ($p < 0.0001$), whereas latitude × distance interactions were not ($F_{1,1674} = 0.54$, $p = 0.46$). Individual seasonal models indicated geographical variability in the rate at which fluorescence decreased with distance from shore, especially in spring and summer (significant latitude × distance interactions). Seasonally averaged data (Fig. 2) showed seasonal differences particularly off southern California (zone A). The zone × season interaction was also clearly observed 25–50 and 50–100 nmi offshore, where fall lows in southern California increased to fall highs at higher latitudes, and in the absence of latitudinal trends in spring relative to other times of year.

Samples sizes for Figs. 1 and 2 are indicated in Table 1, which also summarizes how the surveyed sites were distributed in relation to the ballast water threshold $t_c = 0.7$ QSE for C3* (Murphy et al., 2006). From Table 1 it can be seen that sites with mean fluorescence below $t_c = 0.7$ QSE were surveyed nearshore in southern zones but further from shore in northern zones. At sites 50–100 nmi where coastal BWE would normally take place, intensities at 98% of sites south of Oregon state were below t_c, while a minority of northerly sites had intensities up to $2t_c$. Similar results are seen at sites 25–50 nmi from land, although with an increasing proportion of sites in the higher intensity range. At sites less than 25 nmi from land, sites were widely distributed across intensities ranging from below t_c to more than $8t_c$.

For oceanic samples > 100 nmi from land, the mean C3* fluorescence intensities were consistently below 0.5 QSE for (a) all latitudinal zones in the eastern Pacific, (b) the western Pacific, and (c) all samples together (Table 2). Within a geographical zone, coefficients of variation (SD/mean) were 17–19%, whereas in the Western Pacific and North Pacific as a whole, they were 24–26%.

Fig. 3 depicts the overall geographical variability along a north–south gradient, when combining data across all seasons. In and near ports (Fig. 3i), C3* ranged approximately 20 fold between 0.8 and 15 QSE, with the highest mean fluorescence intensities (exceeding 5 QSE) observed in northern California (zone B) and coastal Oregon (zone C) and lower mean intensities (below 2.5 QSE) observed in southern California (zone A), coastal Canada and Alaska (zone E). Off the coast (Fig. 3ii–vi), fDOM decreased with distance from land in all five regions at rates that varied regionally. Oceanic levels (0.3 to 0.6 QSE) were typically reached within 25–50 miles from the mainland (zones A, B, C) or 50 to 100 nmi (zones D and E).

Comparison of these data with the C3* fluorescence threshold determined for ships' ballast water (Murphy et al., 2006) is aided by the vertical line ($t_c = 0.7$ QSE) in Fig. 3, corresponding to the upper threshold of fluorescence measured previously in exchanged ballast tanks. In all samples collected from port and most samples within 5 nm of land in zones B–D, fDOM exceeded t_c (Fig. 3i–ii). Off southern California and Alaska in contrast, a substantial proportion of samples collected

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Table 1
The seasonal and geographical distribution of C3* ($\lambda_{ex}/\lambda_{em}$ = 370/494) intensities in the eastern north Pacific off the US west coast. Data shown are numbers of sites (of 996 surveyed sites) in each range of fluorescence intensity categories, depicted as multiples of the threshold t = 0.7 QSE. Sites are divided by season (su = summer, sp = spring, f = fall, w = winter), distance from land (in nautical miles) and geographical zone (A–E, as classified in Fig. 1). Intensities at each site were determined by averaging data for 2–3 replicate samples.

Distance	Zone	0–1t				1–2t				2–3t				3–4t				4–8t			>8t				n (sites)
		sp	su	f	w	sp	su	f	w	sp	su	f	w	sp	su	f	w	su	f	w	sp	su	f	w	
<0.2	A					1	8	10	7	11	7	2	8	1			1				1				57
	B															6		15	9	1	13	10	8	24	86
	C																		3						3
	D						1	1	3	8	6	10	10	4	19	1	12	4	1	4	1			2	87
	E							6																	6
0.2–5	A	1	4	4	5	2	4	3	3	3															29
	B		3	2	1	1	3	5			3	3		2	3	1	2		1	1					31
	C					1		11		1		5		1					3						22
	D					10	5	13	11	3	5	1	14		7		9	8		1		1			88
	E	5					2				2														9
5–25	A	10	19	7	8		1																		45
	B	7	9	19	5		7	11	3		1	1				4									67
	C	1		17		1		24		2		5													50
	D				3	26	8	7	7	5	2	5	1	1											65
	E	27	4	1		7	11	6			1														57
25–50	A	2	8	6	2																				18
	B	24	21	6	23		4	1																	79
	C	7		9	7	1	5																		29
	D	3	4	4	7	5	3	3			1														30
	E	9	3			1	2	2																	17
50–100	A	1	5	5	2	1																			14
	B	2	1	7	1																				11
	C	14	5	8	6		6	1																	40
	D	3	3	1	3			2																	12
	E	8	3			1		1																	13
>100	B			4																					4
	C			9																					9
	D	3		4																					7
	E	1	1	9																					11
n (sites)		128	93	122	73	58	70	107	34	33	28	32	33	9	29	12	24	27	17	7	15	11	8	26	996

0.2–5 nmi from land were below threshold. The vast majority of samples obtained greater than 50–100 nmi from any point on the coast were below t_c (Fig. 3v), as were all sites sampled from >100 nmi (Fig. 3vi).

3.2. Probabilistic assessment of fDOM as a distance from shore tracer

3.2.1. Cumulative distribution functions (CDFs)

A preliminary assessment of whether there may be a threshold that distinguishes between different seawater sources can be made by examining the overlap between CDFs corresponding to different source locations (Fig. 4). Each point (x_i, y_i) shows the proportion (x_i) of measurements equal to or below the corresponding fluorescence (y_i) on the y-axis. An 'exclusive' threshold that completely separates samples from two different source locations will divide their CDFs without intersecting either of them.

Salinity was not an exclusive tracer at any distance from shore, as evidenced by the large overlap between salinities in ports and the ocean (Fig. 4A). Conversely for C3*, a straight line drawn through the CDF graph at 0.7 QSE (horizontal dashed line) completely divided the port and nearshore (<0.2 nmi) sites versus oceanic sites >100 nmi offshore, indicating that fDOM concentrations in the two sources were exclusive (Fig. 4B). This suggests that a similar threshold may divide unexchanged port waters and ballast water exchanged more than 100 miles from land along international vessel routes. Sites that were 50–100 nmi from land fall within regions where coastal BWE is authorized. In this case, 8 oceanic sites located north of Oregon state and sampled between spring and fall (Table 1) overlapped with around 15% of port sites (Fig. 4A). This indicates that some areas where coastal ballast water exchange may occur would be indistinguishable from low-fDOM ports on the basis of C3* alone.

In coastal waters, fluorescence at approximately 15% of sites 0.2–5 nmi offshore overlapped with the range for oceanic sites (i.e. fell below t_c Fig. 4A), as did about half of sites 5–25 nmi, increasing to 90% at 25–50 nmi. This indicates that while it is may be possible to determine that a ship is not carrying ballast water from a port on the basis of a C3* threshold, it would be difficult to verify whether BWE took place in coastal or oceanic waters without introducing additional information to the analysis.

Table 2
Mean fluorescence intensity (C3*: $\lambda_{ex}/\lambda_{em}$ = 370/494) in oceanic samples collected >100 nautical miles from the US west coast in this study. Units are quinine sulfate equivalents (QSE).

Location	Mean	Standard deviation	n
Eastern Pacific			
Zone A			0
Zone B	0.47	0.08	12
Zone C	0.37	0.07	27
Zone D	0.37	0.07	18
Zone E	0.46	0.08	29
Western Pacific	0.33	0.08	44
Overall	0.39	0.10	130

3.2.2. Probability density function (PDF)

Fitted PDFs for C3* fluorescence in ports and the ocean are shown in Fig. 5. The probability of successfully distinguishing sources using C3* can be estimated by the PDF of the ratio of fluorescence in port compared to oceanic seawater. When the ratio exceeds 1.0 at the level of the 5th percentile, fluorescence is greater at the port site in at least 95% of comparisons of one port and one oceanic site. Ratios of fDOM in port to oceanic seawater when all port data are included (Port) compared to when high-fDOM sites are excluded ($Port_{low}$) are summarized in Table 3, with the former estimating overall differences between port

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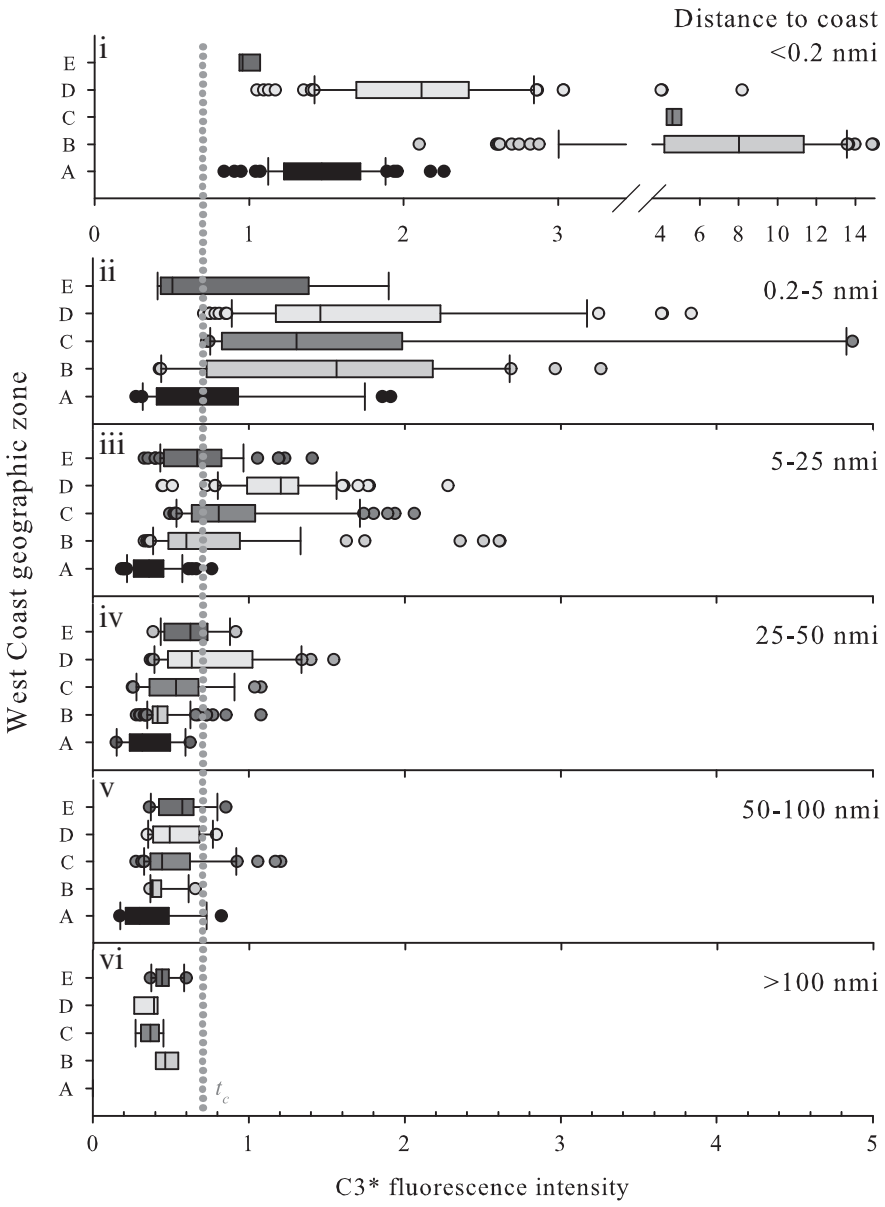

Fig. 3. Stem and whisker plots of C3* fluorescence intensity in seawater pooled by geographic zone (A–E) and distance from shore categories (panels i–vi) on the US west coast. The vertical dotted line t_c indicates the upper limit of fluorescence observed previously in exchanged ballast water (Murphy et al., 2006).

and oceanic sites, and the latter specifically addressing the most challenging situation of distinguishing low-fDOM port sites from ocean sites.

In Table 3, the PDF ratios increase as the near-shore boundary of the oceanic dataset moves progressively offshore from 50 to 100 nmi to >100 nmi and then >200 nmi from land. Median ratios suggest that C3* intensity at a random port site would be typically 6.5× or 7.4× greater than at a random ocean site 50–100 or 100–200 nmi from land respectively, compared to 11× times greater than at a random site >200 nmi from land. In comparisons of $Port_{low}$:Ocean seawater, the PDF ratios predicted that in 95% of comparisons, fluorescence intensities would be at least 2.5× greater for the port site than an oceanic site located >200 nmi from land, 2.3× greater than an oceanic site >100 nmi offshore, and at least 1.7× greater than an oceanic site 50–100 nmi offshore.

4. Discussion

In 2005–2008, the observed fDOM distribution along the US Pacific coast was consistent with seasonal shifts in the positions of oceanic water masses and in the delivery of terrestrial sources to the coast within the sampling regions. Intensities of fDOM were highest in ports and within 5 nautical miles of the coast, where water properties are most strongly influenced by coastal upwelling and river sources, particularly in the Pacific North West (PNW), due to the Columbia River and Fraser River via the Straits of Juan de Fuca (Hickey, 1979; Hickey and Banas, 2003; Mertes and Warrick, 2001). In the southern California Bight south of the Point Conception break, where maximal coastal upwelling occurs in spring but is still relatively low all year round (Bray et al., 1999; Huyer, 1983), fluorescence was relatively high when close to the port of Los Angeles in spring. However, during summer to fall near-shore, and year-round off the coast, fluorescence in this region was noticeably less than in the PNW, especially during the fall survey.

High fluorescence observed off Washington and Oregon in summer probably reflects the convergence of bottom topography, strongly upwelling-favorable winds and snow-melt enhanced Columbia River outflow (Hickey and Banas, 2003, 2008). In the mid-coastal zone 25–50 nmi (~45–90 km) offshore, north south variation in average

fluorescence was observed in all seasons except spring. Although seasonal measurements at oceanic sites were limited in this study, satellite observations of colored dissolved material absorbance and fluorescence indicate seasonal variability in the oceanic distribution of CDOM in the North Pacific within the latitudes sampled (Siegel et al., 2002; Yamashita and Tanoue, 2009).

4.1. Chemical tracers of distance from shore

Predicting concentration changes with distance from shore is critical to successfully using chemical tracers to verify ballast water exchange. Since those who would ultimately be charged with verifying BWE are enforcement agencies (inspectors) rather than oceanographers, a rapid and relatively naïve interpretation of the data without regard to seasonal or geographical factors would ideally form the basis of a satisfactory judgment. In order for fDOM to perform reliably for verification of BWE in this fashion, there can be no significant overlap between fluorescence intensities at port sources versus at authorized exchange locations, regardless of the specific sites involved, or the time of year that sampling occurs. The original legal requirements for BWE required exchange in the open ocean (>200 nmi from shore) (USCG, 2004a), where fluorescence intensities are often a fraction of those observed at the coast. However, the International Maritime Organization (IMO) and several states within the US have advanced an additional 50 nmi limit for BWE for some vessel traffic on coastwise routes that do not extend into the open ocean (CSLC, 2006; DEQ, 2001; WDFW, 2007), creating a need to evaluate the chemical differences between oceanic and coastal waters at a finer spatial resolution.

4.1.1. Ports (<0.2 nmi) vs ocean (>50, 100, and 200 nmi)

A minimum condition for successful application of chemical tracers for verifying BWE is a year-round ability to reliably discriminate between samples obtained from ports versus samples obtained from the ocean at sites where BWE may legally be conducted. If the primary goal is to verify that a ballast tank does not contain unexchanged ballast water originating from within a port, then the results of this study indicate that verification could very often succeed on the basis of a simple C3* threshold. Thus, despite significant seasonal and spatial variability in the north eastern Pacific, there was no overlap between fluorescence intensities measured in ports (>0.8 QSE) versus in the open ocean more than 100 nmi from land (<0.6 QSE). Current federal regulations for ships arriving from overseas ports require BWE to be performed at least 200 nmi from land. Statistical models of the ratio of port to oceanic seawater fluorescence predicted that for a pair of random samples representing one oceanic (>200 nmi) and one port site, C3* fluorescence would be typically around 11× greater at the port site, and would be at least 2.5× greater for the port site in more than 95% of comparisons.

Verifying compliance with state ballast water management regulations that require BWE at any distance beyond the 50 nmi coastal boundary for selected coastwise traffic (CSLC, 2006; DEQ, 2001; WDFW, 2007), necessitates the more difficult task of distinguishing between port and offshore sites>50 nmi from the coast. The results of this study indicate that a higher threshold would be needed to verify coastal BWE, due to elevated fluorescence offshore from the Pacific Northwest relative to the zone west of California. Observed intensities at sites beyond 50 nmi from land were always below 1.3 ppb QSE, however, so were approximately 15% of port sites. It is apparent that any threshold exceeding the full range of intensities at sites where coastal BWE may take place would also exceed intensities at some port and embayment sites, resulting in loss in sensitivity (i.e. false negative determinations). Some sensitivity could potentially be recovered by taking into account additional parameters when verifying BWE compliance, such as geographical, and potentially, seasonal data corresponding to the reported location of BWE. However, it appears unavoidable that some ports will be indistinguishable from the open ocean on the basis of fDOM at some locations or times of year. Ports located in open embayments and seasonally lacking significant riverine inputs are likely to be especially difficult, e.g. Botany Bay in Australia (Doblin et al., 2010) and Busan in Korea (Murphy et al., 2009a).

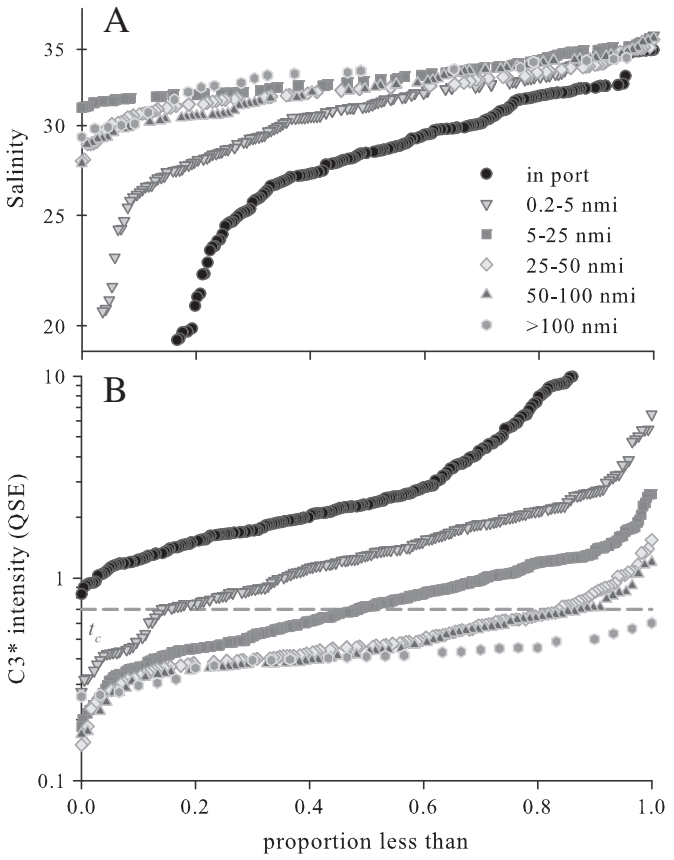

Fig. 4. Cumulative distribution functions for A) salinity at various distances from shore in the Pacific Ocean; B) fDOM tracer C3*. The horizontal line t_c indicates the oceanic ballast water threshold for C3* reported previously (Murphy et al., 2006).

4.1.2. Near-shore (<50 nmi) vs ocean

Identifying when ballast water has been exchanged unacceptably close to shore relies on the ability to distinguish between coastal versus oceanic sites. In this study, seasonal and geographical variability in the rates that fluorescence decreased with distance from land resulted in a wide range of fluorescence intensities observed near the coast. Approximately four-fifths of sites located 25–100 miles from land, together with half of sites 5–25 miles offshore, and an eighth of sites 0.2–5 miles offshore, had fDOM within the range of oceanic sites>100 miles offshore. Thus, while some ships that conducted BWE just off the coast would have significantly elevated fDOM, many would not, with the rate of successfully detecting noncompliant BWE expected to decrease rapidly the farther offshore that BWE was performed. Again, this suggests that consideration of geographical and seasonal conditions would be needed to reliably evaluate whether a foreign vessel executed BWE in compliance with the 200 nmi distance-from-shore requirements, or whether coastal BWE was performed at least 50 nmi offshore by a vessel completing a coastwise route.

4.2. Fluorescence thresholds for BWE verification

Alterations in fDOM within ballast tanks is a potential confounding factor for BWE verification, since ballast water could potentially be contained in tanks for days or months prior to sampling. Repeated measurements of fluorescence in ballast tanks over a two-week voyage found C3* intensities to be stable, at the same time as C2* increased

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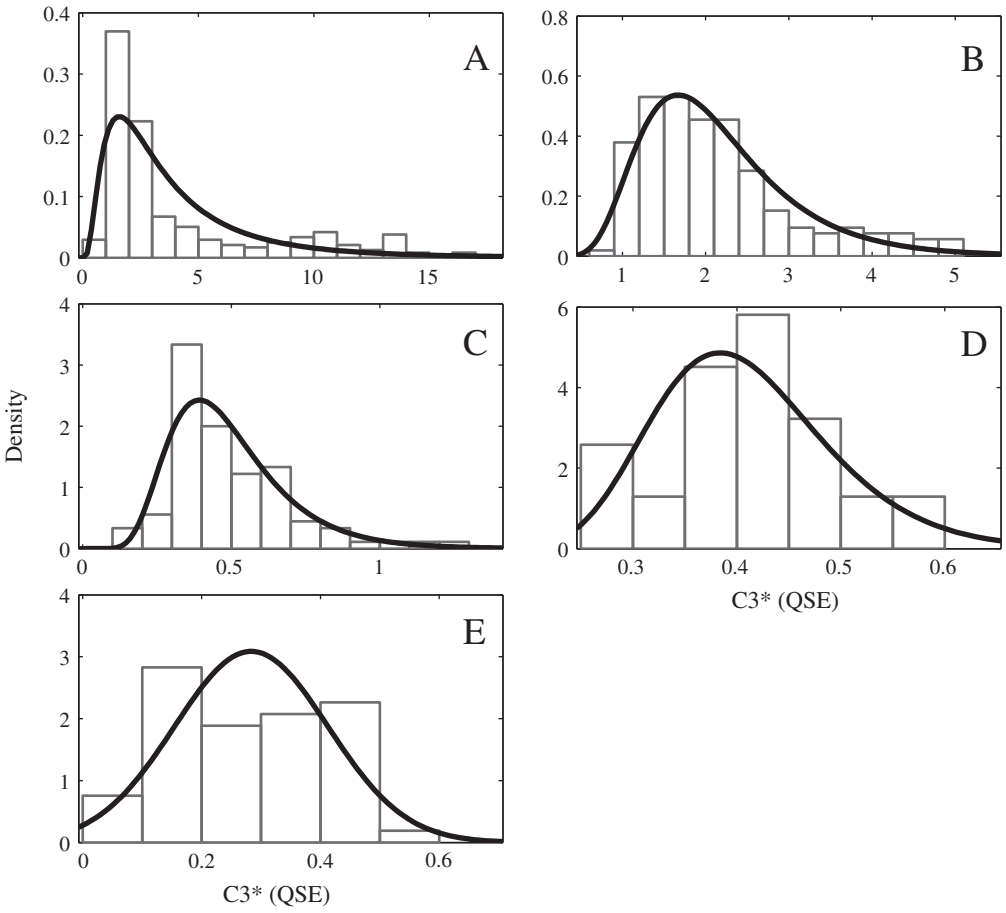

Fig. 5. Probability densities (bars) and fitted PDFs (lines) for C3* fluorescence in (A) ports and coasts<0.2 nmi from land; (B) low-fDOM port sites less than 6× the minimum fluorescence in port; (C) coastal samples, obtained 50–100 nmi offshore; (D) oceanic samples, obtained >100 nmi offshore; (E) oceanic samples, obtained >200 nmi offshore.

(Murphy et al., 2004). This behavior is consistent with the interpretation of C3* as a tracer of refractory humic material (Coble, 1996; Murphy et al., 2008; Stedmon and Markager, 2005) and of C2* as having a microbial origin (Murphy et al., 2008; Yamashita et al., 2010). Another potential confounding factor in ballast tanks is the likely presence of oils and other fluorescent contaminants found in ports and on ships. Again, C3* appears to be a reliable tracer since contamination at C3* wavelengths has not been reported, whereas it is suspected that pyrene-like fluorescence in ballast water could interfere with the measurement of C2* (Murphy et al., 2006).

In earlier work, a C3* threshold of 0.7 QSE discriminated exchanged and unexchanged ballast water samples collected on commercial ships trading in the North Pacific and North Atlantic oceans (Murphy et al., 2006). In the current study of over 2000 seawater samples collected from nearly 1000 different sites in the North Pacific, this simple fluorescence intensity threshold provided sufficient resolution for discriminating between port sources and open ocean sources, supporting a first order determination of compliance with open ocean BWE (>100 nmi from land) by foreign vessels. Estimates in this study of the expected differences between port and oceanic samples indicated no significant overlap between fluorescence intensities in port compared to in the open ocean far from land. Clearly, these could improve in accuracy with the inclusion of more data, sampled over a longer period of time.

Despite a relatively small ocean dataset (n=86 samples from 31 sites), observations are consistent with earlier datasets from the same region. Yamashita and Tanoue (2008) observed humic fluorescence ($\lambda_{ex}/\lambda_{em}$=320/420 nm) along two north–south transects through the central Pacific between 55° N to 65° S. South of 45° N, fluorescence intensities in the surface mixed later were low and relatively uniform (i.e. below approx. 1 ppb QSE at C2*, equating to below approx. 0.6 QSE at C3*). Swan et al. (2009) observed CDOM absorbance in surface (ca 5 m) samples along a longitudinal (150° W) transect between 71° S to 55° N (Kodiak Island, Alaska). In those studies as in the current one, surface fluorescence was significantly elevated in the subarctic Pacific north of 40° N relative to southern latitudes.

Although it was increasingly difficult to discriminate port from coastal water sources with decreasing distance from land, it is also the case that high fDOM would indicate a lack of compliance with BWE at the appropriate locations (Fig. 4). Uncertainty would exist when low fDOM is encountered, as to whether vessels exchanged too close to land or whether coastwise arrivals carried ballast water from ports with low

Table 3
The ratio of fDOM at C3*=370/494 nm in port to oceanic seawater in the North Pacific derived from probability density functions, indicating medians, 5th (P_5) and 95th (P_{95}) percentiles. Ocean sources were $Ocean_{50}$ (90 sites 50–100 miles from the west coast), $Ocean_{100}$ (31 sites>100 miles from land in the Eastern Pacific), and $Ocean_{200}$ (53 sites>200 miles from land anywhere in the North Pacific, incorporating 23 sites sampled in previous studies (Murphy et al., 2008)). Ratio data are shown separately for all 238 sites in US west coast ports (Port), and the subset of low fDOM ($Port_{low}$) sites (n=176).

Sources	$Port_{low}$			Port		
	Median	P_5	P_{95}	Median	P_5	P_{95}
$Ocean_{50}$	4.3	1.7	11.1	6.5	1.5	28
$Ocean_{100}$	4.9	2.3	10.3	7.4	1.9	28.9
$Ocean_{200}$	7.2	2.5	26.8	11.0	2.2	62.6

fDOM. Nonetheless, PDF models indicate that a proportion of vessels would be reliably detected as non-compliant in either category in the case of gross exceedance.

To improve upon this first order verification of BWE, it would be necessary to make use of data provided by the ship on the date and location of BWE. The predictable north–south variability in surface chromophoric DOM in particular suggests that it would be possible to refine the BWE threshold by considering the ship's latitude at the time of BWE. Potentially, seasonal and geographical trends in surface ocean chromophoric DOM as inferred from ocean satellite data (Nelson et al., 2010; Siegel et al., 2002) could be used to develop a matrix of geographical and seasonal correction factors that would be used to adjust the BWE threshold. The ship is also a potential (although not necessarily reliable) source of information regarding pre-BWE ballast water sources, which may constitute up to 5% of the water mass in an exchanged ballast tank. Such information could be difficult to incorporate into analyses, however, because (1) fDOM distributions are currently unknown for most of the worlds' ports, especially in Asia where most ballast water destined for western USA originates; also, fDOM near the coast is spatially variable within short distances and can show strong seasonal variability (Blough and Del Vecchio, 2002; Murphy et al., 2009a); (2) highly-resolved coastal chromophoric DOM conditions cannot be accurately inferred from satellite measurements (Siegel et al., 2002); and (3) ballast water source information is frequently confounded by the operational reality that ballast tanks may contain water from a variety of sources collected over a long period of time.

Differences between ballast water and seawater must also be considered when interpreting the results in this study. Studies have shown fDOM to be elevated relative to external sources due to inefficiencies in the BWE process (Murphy et al., 2006, 2009b), which is a reason why current regulations permit up to 5% retention of coastal seawater following BWE. Incomplete ballast water exchange introduces further complexity into the determination of ballast water origin. Specifically, if fDOM in unexchanged ballast is extremely high, it may still be above threshold even when diluted with 95% ocean water (creating a false positive). Future work should formally examine the potential for ambiguity arising from partially exchanged ballast water, via a sensitivity analysis, especially for foreign arrivals involving open-ocean BWE where the performance of fDOM is best. The foreign ports contributing the overwhelming majority of ballast to the US west coast are in Asia with lesser amounts from Mexico, Central America, and the Hawaiian Islands (Miller et al., 2011). Ideally, a sensitivity analysis would include fDOM measures from each of the major port sources, weighted by the relative contribution from each port. This process would be valuable for estimating the frequency with which ships load and exchange ballast in high and low fDOM sites, and hence predicting the potential frequency of false positive or false negative determinations for any assumed threshold.

DOM fluorescence intensity can be measured using handheld fluorometers, potentially allowing for rapid assessments in the field, an essential element in the real-time enforcement of BWE regulations. A range of hand-held instruments employing various optical configurations and intended for in-situ fDOM measurement have entered the market in recent years, but are yet to be adequately tested in this application. For the data in this study to be transferrable to an in situ instrument, it must be sufficiently sensitive and specific in targeting the humic fluorescence region that a predictable relationship with C3* can be established across a wide range of fDOM intensities. Studies using parallel factor analysis to identify independently varying fluorescent components in EEMs suggest that fluorescence intensities within ~30 nm of the C3* pair are largely due to either a single component or to two highly correlated components (Jørgensen et al., 2011; Murphy et al., 2008; Stedmon and Markager, 2005), indicating that it would be possible to track C3* in situ using instruments with broad emission band-passes targeting the long-wavelength (>450 nm) humic region.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jmarsys.2012.10.010.

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