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**Chemical Parameters in Ships' Ballast Water: Non-Indigenous Species
Investigations in the Columbia River**



**FINAL REPORT
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16. Abstract Mid-ocean ballast water exchange (BWE) is mandatory for many ships discharging ballast water in the U.S. and other countries in order to reduce the risk of biological invasions. However, a reliable tool for determining whether the procedure took place is still lacking. The Columbia River receives ballast water from ships from Asian trade partners and worldwide ports, thus BWE is important in protecting the river from biological invasions. The current study was conducted as part of the Columbia River Aquatic Nuisance Species Initiative and investigated naturally occurring chemical tracers in coastal and open ocean waters. Several trace elements (Mn, P, U, V, Mo, Ba), chromophoric dissolved organic matter (CDOM) fluorescence and an isotope of radium (^{223}Ra) were investigated as tracers of mid-ocean exchange on five research cruises out of Asia, Europe and the USA, focusing on especially high-salinity source conditions. Several tracers, particularly CDOM, were successful indicators of BWE on multiple cruises although it was not possible to set thresholds that could be unambiguously applied to verify BWE across all cruises. In offshore transects, a large range of decay functions was seen suggesting that in many cases it will be difficult to determine if BWE was performed 200 nmi or 50 nmi from shore.			
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Executive Summary

Ships unintentionally transport organisms associated with their cargo, ballast tanks and outer hulls. Billions of tons of ballast water are moved around the world each year, from one port or coastline to another, transferring diverse collections of organisms which can result in the establishment of non-native populations (invasions) that can have significant economic and ecological impacts.

Mid-ocean ballast water exchange (BWE) has been advanced as a means to reduce the risk of biological invasions through ballast water discharge. BWE reduces the delivery of coastal organisms by replacing them with oceanic organisms considered unlikely to colonize coastal habitats. There is national and international support for mandatory BWE while treatment technologies are developed and phased in over approximately the next decade. In the United States (U.S.), the U.S. Coast Guard (CG) implemented mandatory rules in 2004 specifying that exchange must take place outside of the nation's 200 nautical mile (nmi) Exclusive Economic Zone (EEZ) and in water depths exceeding 2000 meters.

Enforcement of BWE regulations requires a technique for discriminating between ballast water originating in coastal waters and that from oceanic environments. Currently the CG uses salinity to verify exchange since oceanic (exchanged) salinities are typically high while coastal (unexchanged) salinities are often lower due to freshwater run-off. Under the salinity criterion, water with salinity below 30 parts per thousand is assumed to be predominantly coastal in origin. The utility of this approach is limited because many ports have high salinities indistinguishable from the open ocean for all or part of the year. Thus, alternative tracers are required that are applicable to a wider range of port systems and seasons.

In a recent proof-of-concept study for BWE verification, naturally-occurring trace elements, radioactive isotopes and chromophoric dissolved organic matter (CDOM) were found to be useful tracers of exchange during four experimental cruises in the Atlantic and Pacific Oceans in 2001-2002. This study builds upon the scope of that research by presenting measurements from ballast tanks and from surface water along ocean tracks during five additional cruises in the Pacific and Atlantic Oceans in 2003-2004. Four voyages were conducted in the North Pacific

Ocean to provide data on trade partners of particular relevance to the Columbia River region, and the cruise in the Atlantic Ocean increased the scope of the study to wider geographical relevance. CDOM, six trace elements, radium and salinity were measured in samples of ballast water and the ambient water collected throughout the cruises. Ballast tanks were sampled at minimum before and after mid-ocean ballast water exchange and more regularly when time allowed.

Several tracers were successful indicators of BWE on each cruise, but none could be unambiguously applied across all cruises. This was due to a) the imperfect efficiency of BWE, resulting in the incomplete dilution of the original port water, and b) a wide range of tracer concentrations in the port environments, some of which included high salinity, low nutrient port water with characteristics similar to open ocean waters. Although many tracers were successful indicators on the Atlantic cruise, most were relatively poor at discriminating between tanks ballasted in coastal Hawaii versus tanks exchanged in the Pacific Ocean more than 200 nautical miles offshore.

As seen in the earlier study, CDOM was a generally reliable indicator of exchange. Trace elements provided varying results. Whereas the previous study found barium to be a consistent indicator of BWE, in this study it was found to be an unreliable tracer of ballast water loaded in Japanese ports and exchanged in the northeastern Pacific. Conversely, this study confirmed the previous observation that magnesium and phosphorus could provide high discrimination between port and ocean water but are less stable in ballast tanks over time. Magnesium in particular decreased in ballast tanks over time; it would not be useful for detecting unexchanged ballast if port water were held in the tank for more than one week.

Radium was a consistent indicator of BWE on each cruise, although as for CDOM and trace elements, no single threshold could be found that applied to all cruises. In addition, radium data were time-consuming to collect and by necessity infrequent, particularly on ocean transects.

Tracer concentrations measured in ambient (shipside) samples on the cruises allowed characterization of the decay function of terrestrial signals with distance from shore. Rarely did tracer decay functions extend close to the full 200 nmi to the boundary of the EEZ. The large range of decay functions seen in this study suggests that in many cases it will be difficult or impossible to determine if BWE was performed 200 nmi or 50 nmi from shore. Future work

should examine the degree to which a wider range of factors, including ocean bathymetry and circulation, can be used to predict the decay functions of BWE tracers and facilitate the identification of ships that performed BWE in coastal waters.

While this and previous studies indicate that naturally occurring chemical elements can be used to verify that BWE has been performed, additional research is required. Two primary areas of concern are tracer decay with increasing distance from shore and the spatial and temporal variations of tracers within and among ports. The next steps for developing a chemical tracer method for BWE verification include a) conducting a multivariate analysis of existing cruise data to determine the advantages of sampling for multiple parameters, b) obtaining tracer measurements in major ports and nearby coastal waters, and c) obtaining tracer measurements in exchanged and unexchanged ballast tanks in ships arriving to U.S. ports.

Based on current analysis techniques, the CG should focus on CDOM, barium, and phosphorus as potential tracers. Results of a multivariate analysis of existing data should provide insight as to whether any other tracers should be pursued. The CG should research the decay of CDOM, barium, and phosphorus with distance from shore and use this information to define a specific offshore limit for BWE. The CG should complete the development of the field verification tool based on CDOM and select an initial CDOM value as a BWE verification limit. It is recommended that the value of one quinine sulfate equivalent (1 QSE) be selected, and this value should be revised after a broad range of ships from various cruise routes have been examined.

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Acronyms

Cruises		
LF	Cruise 1: Haramachi, Japan – Vancouver, Canada	
AS	Cruise 2: Yokkaichi, Japan – Portland, Oregon	
K1	Cruise 3: Oakland/San Francisco – Honolulu	
K2	Cruise 4: Honolulu – Seattle	
K	Cruises 3 & 4, as above.	
BN	Cruise 5: Rotterdam, Netherlands – Sao Luis, Brazil	
Treatments, tanks and sample identifiers		
C	Control (unexchanged) ballast tank	
ER	Empty-Refill ballast water exchange	
FT	Flow-Through ballast water exchange	
SS	Shipside	
c	Center ballast tank, e.g. Tank 1c	
p	Port side ballast tank, e.g. Tank 1p	
s	Starboard side ballast tank, e.g. Tank 1s	
Tracers		Units
CDOM	Chromophoric (Colored) Dissolved Organic Matter	QSE
A1	CDOM peak A1 ($\lambda_{ex} / \lambda_{em} = 250/450$ nm)	QSE
A2	CDOM peak A2 ($\lambda_{ex} / \lambda_{em} = 260/470$ nm)	QSE
C3	CDOM peak C3 ($\lambda_{ex} / \lambda_{em} = 325/420$ nm)	QSE
C4	CDOM peak C4 ($\lambda_{ex} / \lambda_{em} = 370/450$ nm)	QSE
$\lambda_{ex}, \lambda_{em}$	Wavelengths of excitation, emission	nm
Ag	Total dissolved silver	ppb
Ba	Total dissolved barium	ppb
Mn	Total dissolved manganese	ppb
Mo	Total dissolved molybdenum	ppb
P	Total dissolved phosphorus	ppb
U	Total dissolved uranium	ppb
V	Total dissolved vanadium	ppb
Ra	Radium	dpm/100 L
Rn	Radon	Dpm/100 L
Th	Thorium	dpm/100 L
Countries and US States		
BC	British Columbia	
BR	Brazil	
CA	California	
HI	Hawai'i	
JPN	Japan	
NL	Netherlands	
OR	Oregon	
US	United States	
USA	United States of America	
WA	Washington	

Measures and Units	
°C	Degrees Celsius
cm	Centimeter
dpm	Disintegrations per minute
L	Liter
m	Meter
min	Minute
MT	Metric tons
nm	Nanometers (10^{-9} m)
nmi	Nautical miles (= 1852 m precisely)
NTU	Nephelometric turbidity unit
ppb	Parts per billion
ppt	Parts per thousand
QSE	Quinine-sulfate equivalent units
<i>t</i>	Time, storage in days
µm	Micron (10^{-6} m)
Computational Symbols	
<i>E</i>	Extraction efficiency of Radium onto Mn-fibers
<i>ln</i>	natural logarithm
<i>q</i>	Quenching
$\bar{x}$	Mean
<i>SE</i>	Standard Error
<i>y</i>	Measured fluorescence intensity
<i>y_{pred}</i>	Predicted fluorescence intensity
Other acronyms	
BP	Part of a company name: BP Amoco PLC
BWE	Mid-ocean ballast water exchange
CG	U.S. Coast Guard
CRANSI	Columbia River Aquatic Nuisance Species Initiative
CTD	Conductivity / Temperature / Depth meter
d.y ASA.	Part of a company name: Bergesen d.y. ASA
EEM	Excitation – emission matrix
EEZ	Exclusive economic zone
EST	USA Eastern States Time
GMT	Greenwich Mean Time
GmbH	Limited liability company (German language translation)
GPS	Global Positioning System
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LD(T)	Local ship's date (and time)
Ltd	Limited
MV	Motor Vessel
NOAA	National Ocean and Atmospheric Administration
PLC	Part of a company name: BP Amoco PLC
Pty	Proprietary
SERC	Smithsonian Environmental Research Center

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This document presents the final report on Task II of the study “ANS Investigations in the Columbia River,” conducted as a component of the Columbia River Aquatic Nuisance Species Initiative for the U.S. Coast Guard Research and Development Center. More specifically, Task II investigates the potential use of naturally occurring chemical tracers for verifying whether a ship has performed ballast water exchange (BWE) in the open ocean.

1. Introduction

Ships unintentionally transport organisms associated with their cargo, ballast tanks and outer hulls (Carlton, 1985). To reduce the risk of biological invasions through ballast water discharge (Carlton & Geller, 1993), mid-ocean ballast water exchange (BWE) has been advanced at both national and international levels. During BWE, a vessel replaces its original ballast water (taken on board while the vessel had been in coastal waters, at or near a port) with water from the open ocean. BWE reduces the delivery of coastal organisms, replacing them with oceanic organisms considered unlikely to colonize coastal habitats (Minton, Verling, Miller & Ruiz, 2005). This reduction results from the physical removal of organisms during exchange or, in some cases, from increasing the salinity of residual ballast water to levels above the tolerance of organisms that originate in fresh and brackish water environments.

At the time this research was initiated, ballast water management regulations by the U.S. Coast Guard (CG) requested voluntary BWE in waters outside the 200 nautical mile (nmi) exclusive economic zone (EEZ) and in depths greater than 2000 meters. In 2004, mandatory rules replaced voluntary compliance (69 FR 44952, July 28 2004a). Failure to comply with mandatory ballast water management requirements is now a Class C felony subject to fines of up to \$27,500 per day (69 FR 32864, June 14 2004b). Further modifications to distance and depth requirements have been advanced by the International Maritime Organization (IMO) (International Maritime Organization, 2004) and are being considered at the federal and state levels.

Despite advances in developing ballast water treatment technologies, BWE is currently the process used most frequently by ships and is likely to remain in use for several years. A general framework has emerged nationally and internationally that includes mandatory BWE as treatment technologies are developed and phased in over approximately the next decade (Hunt, Tanis, Stevens, O. Russell Bullock, Frederick & Everett, 2005). Under the current or future requirements, verification of BWE requires a technique for distinguishing between coastal and oceanic ballast water that is both reliable and suitable for implementation by existing regulatory agencies.

As a first step to development of verification methods, a previous study examined the use of naturally-occurring chemical characteristics or tracers, providing a proof of concept (Murphy, Ruiz, Coble, Boehme, Field, Cullen, Perry & Moore, 2004b). This initial study identified several promising tracers that provided discrimination between exchanged and unexchanged ballast water. These tracers were salinity, trace elements (total dissolved barium (Ba), manganese (Mn), molybdenum (Mo), phosphorus (P), uranium (U) and vanadium (V)), radium (^{223}Ra) and colored (or chromophoric) dissolved organic matter (CDOM). The verification method pursued relies on the ability to detect differences between oceanic and coastal (port) sources, based upon a combination of chemical characteristics. Establishing the generality of this method for verification of BWE requires further data on tracer concentrations associated with additional geographic locations (ports and the mid-ocean), seasons, vessels or vessel types, as well as data on the stability of these tracers within ballast tanks.

The current study sought to further test the generality of using chemical tracers to verify BWE by expanding the scope of available data to additional geographic regions and vessels. Five experiments were conducted on four commercial ships transiting the Pacific and Atlantic Oceans in 2003-2004. For each cruise, tanks were sampled at a minimum before and following mid-ocean ballast water exchange, or more regularly when time allowed. CDOM, trace element, radium and salinity samples were collected from the ballast tanks and from the ambient water (shipside) throughout the cruises.

The first four cruises were selected to provide data from international ports of particular importance to shipping in the Columbia River region. These were as follows:

- The 1st cruise (LF) between Haramachi, Japan (JPN) and Vancouver, British Columbia (BC) took place in June 2003 on the *MV Lily Fortune*, a coal carrier owned by NYK Bulkship (USA) Inc. Ballast water in all eight tanks sampled originated in the port of Haramachi, Japan.
- The 2nd cruise (AS) between Yokkaichi, JPN and Portland, Oregon (OR) took place in August 2003 on the *MV Asahi Sunrise*, a bulk carrier owned by Gateway Maritime Corporation (Japan). Five pairs of ballast tanks were sampled; they

contained water from Korea (ports of Incheon and Kunsan) and from Yokkaichi, Japan.

- The 3rd (K1) and 4th (K2) cruises took place on the *MV Kauai*, a container ship owned and operated by Matson Pty Ltd, during a typical cycle between two ports on the U.S. West Coast (Seattle, WA and Oakland, CA), and Honolulu, HI. Three ballast tanks were sampled in two sequential experiments (Oakland – Honolulu, Honolulu – Seattle) involving port water from Oakland and Honolulu. The K1 and K2 voyages are collectively referred to as Cruise K.
- The 5th and final cruise (BN) for this project took place in the Atlantic Ocean on the bulker *MV Berge Nord*, which sailed between Rotterdam, Netherlands (NL) and Sao Luis, Brazil (BR) in September 2004. All six ballast tanks sampled were sourced from the port of Rotterdam. The selection of an Atlantic voyage for the final experiment allowed us to increase the scope of the study to wider geographical relevance, and it will allow us to assess the robustness of verification tracers to a greater range of environmental variables.

The extensive dataset and experience from these five cruises is being used to test the robustness of the trends identified in the pilot study; refine ballast water sampling protocols; further define the distribution of target tracers in and among ships' ballast tanks, the coastal ocean and the open ocean; and develop better models for predicting the origin of ships' ballast water.

This report presents an initial summary of the results, including the tracer measurements and comparisons among voyages, locations, and ballast tanks. Each group of tracers (salinity, CDOM, trace elements and Radium) was examined with respect to three qualities that underpin an assessment of their value as BWE verification tools. These qualities are: 1) stability in ballast tanks and in archived samples, 2) ability to predict BWE, and 3) behavior in offshore transects.

Understanding the stability of tracers in ballast tanks and in archived samples is of critical importance to verifying ballast water exchange and successfully defending penalties for

non-compliance in a court of law. In general, suitable tracers will behave conservatively in that they will be neither produced in, nor removed from, the ballast tanks over time. Non-conservative behavior can lead to two undesirable outcomes. In the first case, where tracer signals are produced in ballast tanks over time, exchanged ballast water will appear progressively more ‘coastal’ the longer it is held. In the second case, where tracers are depleted in ballast tanks over time, unexchanged ballast water will appear progressively more oceanic. In the first case, there is a risk of penalizing complying vessels and in the second a risk of failing to detect vessels in non-compliance.

Achieving a predictable signature following BWE is clearly an essential quality of a successful verification tracer. For most of the tracers examined, concentrations were highest in port and near the coast and decreased in response to BWE. As long as the signature of exchanged ballast tanks is predictable, the direction and degree to which it varies in ports and unexchanged ballast is less important, providing it is established that the range of expected concentrations within exchanged and unexchanged tanks are largely non-overlapping.

Finally, understanding how far terrestrial signals penetrate offshore is an important issue for BWE verification, since ships may exchange water at distances less than 200 nautical miles from the coast. This may occur by default in several geographic regions, including for example, ship traffic to the eastern seaboard via the Caribbean basin, as well as for a large number of domestic trade routes around the U.S. Similarly, it is important to understand any differences that may exist in the decay function (rate of decline of tracer concentrations) among regions. Signal strength may vary strongly as a function of land mass size, rainfall, population, land use, anthropogenic sources and river inputs, among numerous other factors.

Several comprehensive analyses that combine this dataset with that from the previous study, employing novel statistical approaches, are still underway and will result in subsequent publications.

2. Methods

2.1. Sample Collection

Sampling methods were based on a published protocol (Murphy, Ruiz & Sytsma, 2003). Revisions to the protocol are maintained by the Smithsonian Environmental Research Center and are available to the public via their website. For this study, methods that deviated from Revision III of the published protocol (Murphy, Ruiz & Sytsma, 2005) are documented in the following sections.

2.1.1. Ballast Water Sampling

Ballast water samples for trace element and CDOM analysis were collected using an air driven diaphragm pump (Wilden Pumps Inc., P.025 Pro-Flo). In a modification to the original protocols, the pump outflow was directed through an inline capsule filter (Osmonics Inc., Memtrex™ CMMP, 0.45 micron (μm)) (Murphy et al., 2005). The filter was stored in the refrigerator when not in use to retard bacterial activity that could potentially affect measurements.

Ballast water samples for radium (^{223}Ra) isotope quantification were collected using a larger diaphragm pump (Wilden Pumps Inc., P.5 Pro-Flo) to fill large volume containers with ballast water. The smaller pumps were then deployed to drain the containers over the next 2-3 hours through columns containing material to adsorb the ^{223}Ra .

When sampling within a ballast tank, the pump inlet hose was lowered into the aft manhole or quick-connected to pre-installed hoses. On the first two cruises, the inlet hose was lowered to a randomly determined depth of 1, 2 or 3 meters. On the 3rd and 4th cruises, sampling was from approximately 80-centimeter (cm) depth in the shallow double-bottom tanks. On the final cruise, samples were collected from 1 meter (m) and 12 m deep via pre-installed lines.

Trace Metal and CDOM Protocols

Prior to sample collection, the pump was first flushed with a minimum of 4 liters (L) of ballast water. At least 1 L of this was diverted through the membrane filter. Following

flushing, filtered ballast water was collected in plastic centrifuge tubes (trace elements) or glass bottles (CDOM).

On the second cruise, additional CDOM fluorescence readings were taken by pumping ballast water through a field fluorometer (Turner Designs Inc., 10AU-005-CE). The fluorometer experienced numerous technical difficulties apparently due to infiltration of the power supply cables by rain and ballast water. The field fluorometer was deployed on subsequent cruises with greater success. These data were used for comparisons internal to our laboratory and are not presented here.

To aid comparison with data from previous cruises, a subset of trace element samples collected on the first two cruises were obtained with a syringe sampler instead of the pump and capsule filter system. Syringe samples were filtered through individual acid-cleaned 45 μm supor membranes (Fisher Scientific, 09-731-124). Following collection, samples were stored in the ship's freezer (temperature -10 to -20 $^{\circ}\text{C}$), then shipped frozen to the laboratory, where they were analyzed along with the pumped samples over the ensuing 2-6 months.

Radium Sampling Protocol

Radium sample volumes were standardized by filling 300-L plastic bladders with filtered ballast water (0.5 μm , nominal pore size). The filtered ballast water was then passed through up to two sequentially connected plastic columns, each containing a single manganese-impregnated fiber (Mn-fiber: Moore, 1976). On the first cruise, the bladders were drained under pressure through two columns. Since the flow rates using this method were very low ($< 0.5 \text{ L per minute (min}^{-1}\text{)}$) and the pressurized bladders proved susceptible to leaks and tears, the protocol was modified prior to the second cruise. On the second cruise, water from the bladders was pumped through the columns and fibers. This was quicker (good results were obtained up to 2 L min^{-1}), more reliable and resulted in many fewer bladder breakages. Consequently, the pumping method was used to obtain radium samples on all subsequent cruises.

On the first cruise, most samples consisted of a single column containing a single Mn-fiber (Fiber A). For the remaining samples, and on all subsequent cruises, two columns each containing Mn-fibers were connected in series and both fibers were analyzed. Theoretically, the first fiber in a series should extract over 80 percent of the radium in the water at flow rates up to 1 L min⁻¹ (Moore, W.S., pers. com.). If a second fiber is appended at the outflow (Fiber B), it will theoretically extract the same proportion of the remaining radium in the sample water. The ratio of radium extracted onto Fibers A and B is used to calculate extraction efficiency, and by extrapolation, estimate the actual (corrected) concentration of radium in the sample, i.e.,

$$\text{Extraction efficiency (E)} = (1 - [\text{Fiber B}]/[\text{Fiber A}])$$

$$\text{Concentration (corrected)} = ([\text{Fiber B}] + [\text{Fiber A}]) * 1/E$$

Where:

[Fiber A] = quantity of radium extracted onto Fiber A

[Fiber B] = quantity of radium extracted onto Fiber B

Salinity Measurement Protocols

Salinity was measured using a conductivity-temperature-depth (CTD) sensor (Hydrolab Incorp., Minisonde®) in tanks amenable to profiling instruments (Cruises 1-2) or else a salinometer (Hydrolab Incorp., YSI-85) in tanks that were not (Cruises 3-5). The Minisonde® was used both to collect profiles from ballast tanks and to take point readings from the engine room while collecting shipside CDOM and trace element samples. Instruments were calibrated with a National Institute of Standards and Technology (NIST) -traceable seawater conductivity standard (Yellow Springs Instruments (YSI) 3169, 50 000 µS cm⁻¹ [microsiemens per centimeter]) prior to each cruise. During the first cruise, the Minisonde® experienced a technical failure which caused measurements to decrease over time. The instrument was serviced and the CTD used successfully on the second cruise. The YSI-85 was used without difficulties on the subsequent cruises.

2.1.2. Shipside Sampling

Shipside CDOM and trace element samples were collected in the ships' engine rooms. First, a short length of plastic tubing was attached to a small sampling pipe at the sea chest. The tubing remained in the engine room for the entire cruise and was sealed with Parafilm™ when not in use.

Before sampling, the tubing was flushed with at least 4 L of water. Next, the Memtrex™ inline filter was connected to the tubing and flushed with 1 L of water. Sampling was initiated after completion of flushing.

Shipside radium samples were collected on deck after filling plastic bladders with water using the fire hose (first cruise), or via a line to the engine room cooling water (second and subsequent cruises). The hoses were flushed for at least ten minutes before bladders were filled, except on Cruises K1 and K2. On these cruises sampling was performed inside the engine room and flushing was eliminated so as to reduce the amount of water that would need to be processed via the oil-water separator system.

2.2. Global Positioning System Locations and Distance to Shore

In general, it is impossible to record a ship's precise location during shipside (SS) sampling because Global Positioning System (GPS) satellites and communications equipment will not function in the depths of the ship where sampling from the sea chest takes place. However, GPS positions can be back-calculated by interpolating data recorded in the ships' logs, waypoints logged by an assistant on deck using a handheld GPS and knowledge of the time of sampling. Ship's personnel are required to record GPS location and ship speed at least every 60 minutes, yielding regular data on the ship's bearing and average speed. To obtain more precise estimates of position, intermediate waypoints were recorded on deck using a handheld GPS, or by a GPS with an auto-logging capability. Typically, waypoints were recorded within 5-20 minutes of shipside sampling. The expected time error in estimated GPS coordinates using an interpolative method is approximately 10 minutes, or 2-3 nautical miles for a ship traveling at full speed.

Distance from shore is defined as the minimum distance between the GPS position of sampling and the nearest land location. Coastal boundaries were obtained from the coastline extractor website of the National Oceanographic and Atmospheric Administration (NOAA) and represent mean location at mean tide (National Oceanographic and Atmospheric Administration, 2000). The minimum distance between these boundaries and sampling locations was determined in Matlab (Mathworks Inc., Version 6.5) using the seawater toolbox of the Commonwealth Scientific and Industrial Research Organization, Australia (CSIRO, Version 1.4).

2.3. Sample Analysis

All samples were collected by the Smithsonian Environmental Research Center (SERC) and analyzed at one of three collaborating specialist laboratories in the U.S.

2.3.1. Trace Elements

Trace element samples were analyzed at Rutgers Inorganic Analytical Laboratory, Institute of Marine and Coastal Sciences, Rutgers the State University of New Jersey. Concentrations of six trace elements (total dissolved barium, manganese, molybdenum, phosphorus, uranium, vanadium) were determined by mass spectrometry. Samples were analyzed on a sector field inductively coupled plasma mass spectrometer (ICP-MS) with high-resolution capability (ELEMENT, Finnigan MAT, Bremen, Germany). The sensitivity of this method was too low to collect meaningful measurements of silver [Ag]. Sample concentrations were determined according to published methods (Field, Cullen & Sherrell, 1999).

2.3.2. CDOM

CDOM analysis by excitation-emission matrix (EEM) spectroscopy [Excitation: 240-600 nanometers (nm) in 5-nm intervals; Emission: 300-600 nm in 2-nm intervals (generally written as $\lambda_{\text{ex}}/\lambda_{\text{em}}$)] was performed by spectrofluorometer at one of three analytical laboratories: 1. The University of South Florida, using a SPEX FluoroLog-2 (Cruises LF and AS) (Coble, 1996); 2. The University of Maine, using a SPEX FluoroMax-2 (Cruises K1 and K2); or 3. The National Environmental Research Institute, Denmark, using a

Varian Cary Eclipse (Cruise BN) (Stedmon, Markager & Bro, 2003). EEMs were corrected for instrumental differences with user-generated excitation, emission and lamp intensity correction factors and blank subtraction, and normalized to Quinine Sulfate Equivalent units (QSE) using standard methods (Coble, Mopper & Schultz, 1993, Mobed, Hemmingsen, Autry & McGown, 1996). Intercalibration of fluorometers, using specifically supplied standard reference materials, was conducted in October 2004 and confirmed the existence of only minor differences between spectra from different instruments and from the technical emission spectrum as determined by Velapoldi and Mielenz (Velapoldi & Mielenz, 1980, Murphy, Ruiz, Dunsmuir & Waite, submitted).

Reabsorption of emitted radiation in concentrated samples can affect the linearity of the fluorescence response and estimation of CDOM concentrations (inner filter effect). Inner filter effects cause a flattening of the linear response between concentration and fluorescence, so that above some point, additional CDOM in the water accounts for a proportionally smaller amount of additional fluorescence, thus leading to the underestimation of CDOM levels at higher concentrations. The published literature often uses UV-vis absorbance criteria to delineate the likely onset of inner filtering effects [e.g. A_{300} (absorbance at 300 nm) < 0.02 in a 1 cm cell (Green & Blough, 1994) or A_{350} < 0.02 in a 1 cm cell (Moran, Sheldon & Zepp, 2000)]. In the Tampa Bay estuary, Boehme (J. Boehme, pers. com.) found the onset of inner filter effects to occur at around 16-20 parts per billion (ppb) QSE which roughly corresponded to A_{300} < 0.02.

Due to the focus on high salinity environments, samples from this study were relatively dilute with 350/450 ($\lambda_{ex}/\lambda_{em}$) intensities below 8 ppb QSE in more than 97 percent of samples; the remainder were below 10.5 ppb QSE. Absorbance (A_{350}) measurements corresponding to ~ 8 ppb fluorescence were below 0.045 (Shimadzu UV-2401PC spectrophotometer, 10 cm cell; Cruise BN). Inner filter effects may have caused slight underestimation of concentrations of the most concentrated samples in our dataset. However, since these were nearly an order of magnitude more concentrated than exchanged ballast water samples, inner filter effects are considered unlikely to affect the diagnosis of concentration thresholds for BWE.

2.3.3. Radium

Radium samples were analyzed at the Department of Geological Sciences of the University of South Carolina. Measurements of ^{223}Ra and ^{224}Ra were made by partially drying the Mn-fiber, and placing it in an air circulation system, described by Moore and Arnold (Moore & Arnold, 1996). Short-lived gaseous radon isotopes (^{219}Rn and ^{220}Rn) formed by the decay of ^{223}Ra and ^{224}Ra were flushed from the Mn-fiber into a scintillation cell where alpha particles from the decay of radon and its daughters were detected by a photomultiplier tube, and identified using a delayed coincidence system. Isotope concentrations are presented in units of disintegrations per minute per 100 L (dpm/100 L).

In this report we present only the data for ^{223}Ra , which has a half life of approximately 11.4 days. ^{224}Ra was considered an unreliable tracer due to its short half life of 3.7 days and the presence of its parent, ^{228}Th (Thorium 228).

2.4. **Experimental Design**

2.4.1. Experimental Cruises

Five research cruises were conducted in 2003-2004. On each cruise, we collected water samples for analysis of tracers (CDOM, trace metals, and radium) in port side (p), starboard side (s) or center (c) ballast tanks and at shipside (SS) along the cruise track. Samples were collected from ballast tanks before and after BWE, and multiple pairs of tanks were involved in our analyses on these cruises. These ships differed not only in route but also design and method of BWE, two using the empty-refill (ER) method and two using the flow-through (FT) method. An overview of each experimental cruise is provided below (see also Table 1). Supporting information for the five cruises (LF, AS, K1, K2, BN) are provided in Appendices B-E, respectively. Within each Appendix, details are provided of (i) ballasting and exchange dates and locations; (ii) source locations and descriptions of radium samples; (iii) source locations and descriptions of CDOM / trace element samples; (iv) sampling design. Sampling design includes number of samples taken, dates, and indications of BWE events.

Table 1. Experimental design and characteristics of five voyages completed for Columbia River Aquatic Nuisance Species Initiative (CRANSI) in 2003-2004. Ballast tanks were assigned to three treatments: Unexchanged / control (C), Empty-Refill (ER) exchange or Flow-Through (FT) exchange. Salinity is in parts per thousand (ppt).

	Voyage 1: "Cruise LF"	Voyage 2: "Cruise AS"	Voyage 3-4: "Cruise K"	Voyage 5: "Cruise BN"
Voyage Characteristics				
Vessel Name	<i>MV Lily Fortune</i>	<i>MV Asahi Sunrise</i>	<i>MV Kauai</i>	<i>MV Berge Nord</i>
Owner (/Operator)	NYK Bulkship (USA) LTD.	Gateway Maritime Corp. / Sincere Industrial Corp.	Matson Navigation Company	Bergesen DY ASA.
Departure port	Haramachi (JPN)	Yokkaichi (JPN)	K1: Oakland, CA K2: Honolulu, HI	Rotterdam (NL)
Destination port	Vancouver (BC)	Portland, OR	K1: Honolulu, HI K2: Seattle, WA	Sao Luis (BR)
Date	Jun. 5-16, 2003	Aug. 5-17, 2003	Jun. 19 - Jul. 6, 2004	Sep. 10-23, 2004
Cruise length (days)	12	13	K1. 3 K2. 4	14
Vessel Type	Bulk Carrier	Bulk Carrier	Container Ship	Bulk Carrier
Cargo	Coal	Soda Ash	Containers	Iron Ore
Source salinity (ppt)	32.9-33.6	26.1-28.0	K1: 31, K2: 35.5-37	32.3-32.8
Experiment Characteristics				
Treatments	C, ER	C, FT	C, ER	C, FT
No. ballast tanks	4 per treatment	5 per treatment	3 per experiment	3 per treatment
No. times sampled	2-6 per tank	2-7 per tank	2-3 per tank/experiment	4 per tank
Sample Characteristics				
Depth (m)	1, 2 or 3 m	1, 2 or 3 m	< 1 m	1, 12 m
Profile depth (m):	0-3.5	0-3.5	-	-
Replication (per tank & time):				
CDOM	2-3	2-3	2-4	2-4
Trace Elements	2-5	2-5	2-4	2-4
Radium	1-2	2	1-2	1-2
Salinity	2	2	2	2
Tracer Characteristics				
Ballast water tracers	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity
Mid-ocean tracers	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity	CDOM, trace elements, radium, salinity

Voyage 1: Cruise LF

The first cruise (Cruise LF) between Haramachi, JPN and Vancouver, BC took place in June 2003 on the *MV Lily Fortune*, a coal carrier owned by NYK Bulkship (USA) Inc. CDOM, metals and radium samples were collected from eight ballast tanks and from the ambient ocean (shipside) throughout the cruise. Figure 1 shows the cruise track and location of shipside sample collections.

Initial ballasting of six tanks (Tanks 1-3, p & s) took place in Haramachi, JPN on June 4th. Tanks 4 p & s were ballasted on June 6th shortly after departure. Prior to ballasting, the Tank 4 pair were already partially loaded with ballast water brought from Korea. This ship undertook empty-refill BWE. Details on sampling and experimental design for Cruise LF are provided in Table 1 and Appendix B.

Voyage 2: Cruise AS

The second cruise (Cruise AS) between Yokkaichi, JPN and Portland, OR took place in August 2003 on the *MV Asahi Sunrise*, a bulk carrier owned by Gateway Maritime Corporation (Japan) and operated by the Sincere Industrial Corporation (Taiwan). CDOM, metals and radium samples were collected from ten ballast tanks and from the ambient ocean throughout the cruise.

Initial ballasting took place in two Korean ports (Inchon: Tank 1, Kunsan: Tanks 2 and 4, p & s) and Yokkaichi, JPN (Tank 3 p & s) between July 26 and August 3, 2003 (Table 1). Figure 1 shows the cruise track and location of shipside sample collections. This ship undertook flow-through ballast water exchange. Details on sampling and experimental design for Cruise AS are provided in Table 1 and Appendix C.

Voyages 3-4: Cruise K (Cruises K1 and K2)

The third and fourth cruises between Oakland – Honolulu (Cruise K1) and Honolulu – Seattle (Cruise K2) took place in June/July 2004 on the *MV Kauai*, a container ship owned by the Matson Navigation Company. CDOM, metals and radium samples were collected from three shallow (< 1.2 m) double-bottom ballast tanks and from the ambient

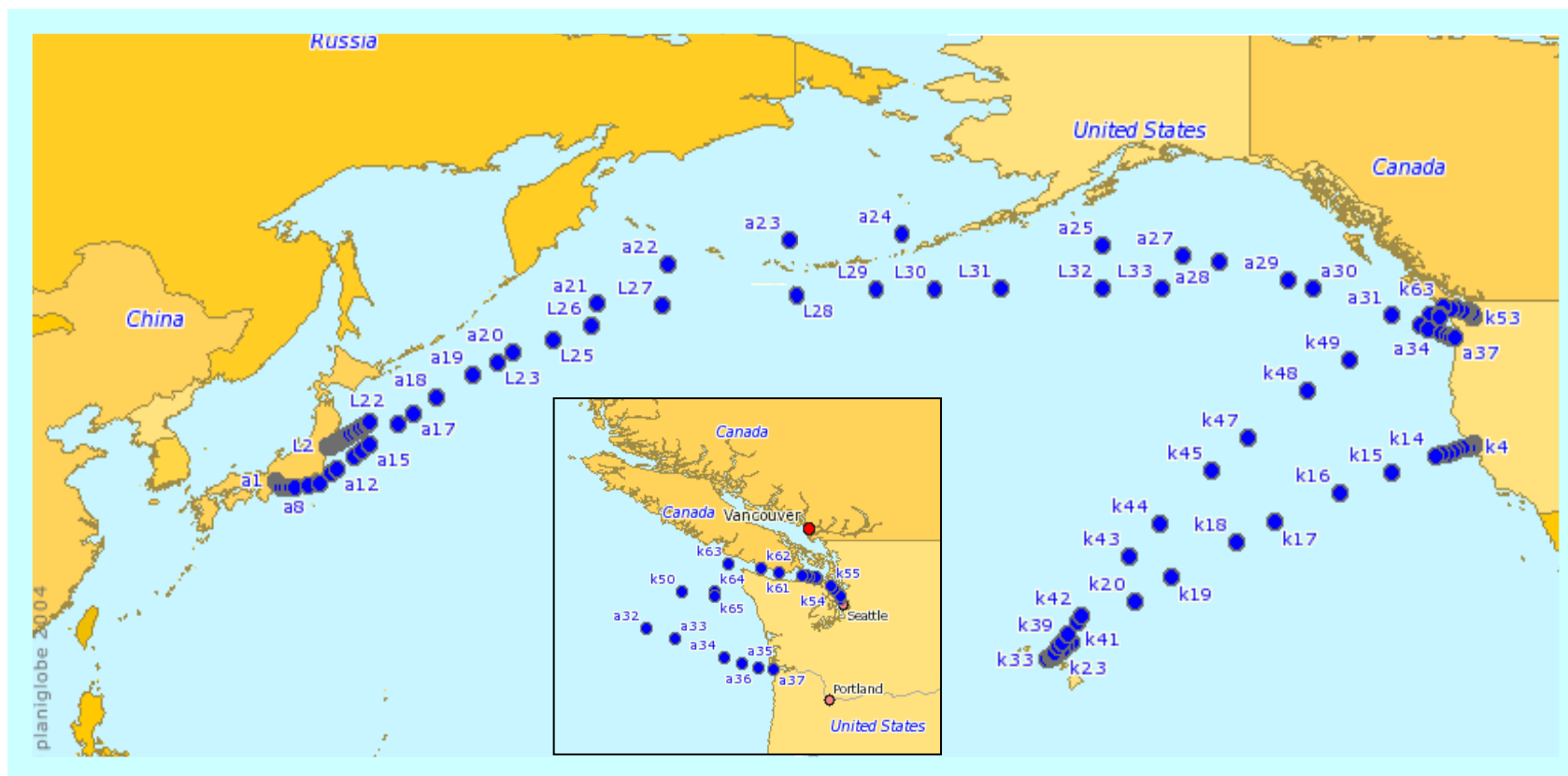


Figure 1. Tracks taken during CRANSI cruises in the Pacific Ocean, showing positions where shipside CDOM and trace element samples were collected. Sampling positions are indicated by circles labeled “L”, “a” or “k”, corresponding to Cruises LF, AS and K respectively. Inset shows detail of U.S. West Coast sampling. See Appendices for position coordinates.

ocean (shipside) throughout the cruise.

Two sequential experiments were conducted on this vessel, corresponding to Cruises K1 and K2 and referred to collectively as Cruise K. Initial ballasting of three double-bottom tanks took place in Oakland on June 21st (Tank 2 p & s, Tank 1c). These tanks were exchanged, using the empty-refill method, and later discharged *en route* to Honolulu, prior to the second experiment. On June 27 in the port of Honolulu, Tank 2 p & s were ballasted with port water, while on the following morning the Tank 1c was ballasted. A second exchange experiment was then conducted between Honolulu and Seattle.

Figure 1 shows the cruise track and location of shipside sample collections. Details on sampling and experimental design for Cruise K are provided in Table 1 and Appendix D.

Voyage 5: Cruise BN

The final cruise (Cruise BN) between Rotterdam, Netherlands and Sao Luis, Brazil took place in September 2004 on the *MV Berge Nord*, a bulk carrier owned by Bergesen d.y. ASA. CDOM, metals and radium samples were collected from six wing ballast tanks and from the ambient ocean throughout the cruise.

Initial ballasting of all six ballast tanks took place in Rotterdam (Tanks 3, 5, 7, p & s). These tanks were exchanged by the flow-through method and later discharged *en route* to Sao Luis. Figure 2 shows the cruise track and location of shipside sample collections. Details on sampling and experimental design for Cruise BN are provided in Table 1 and Appendix E.

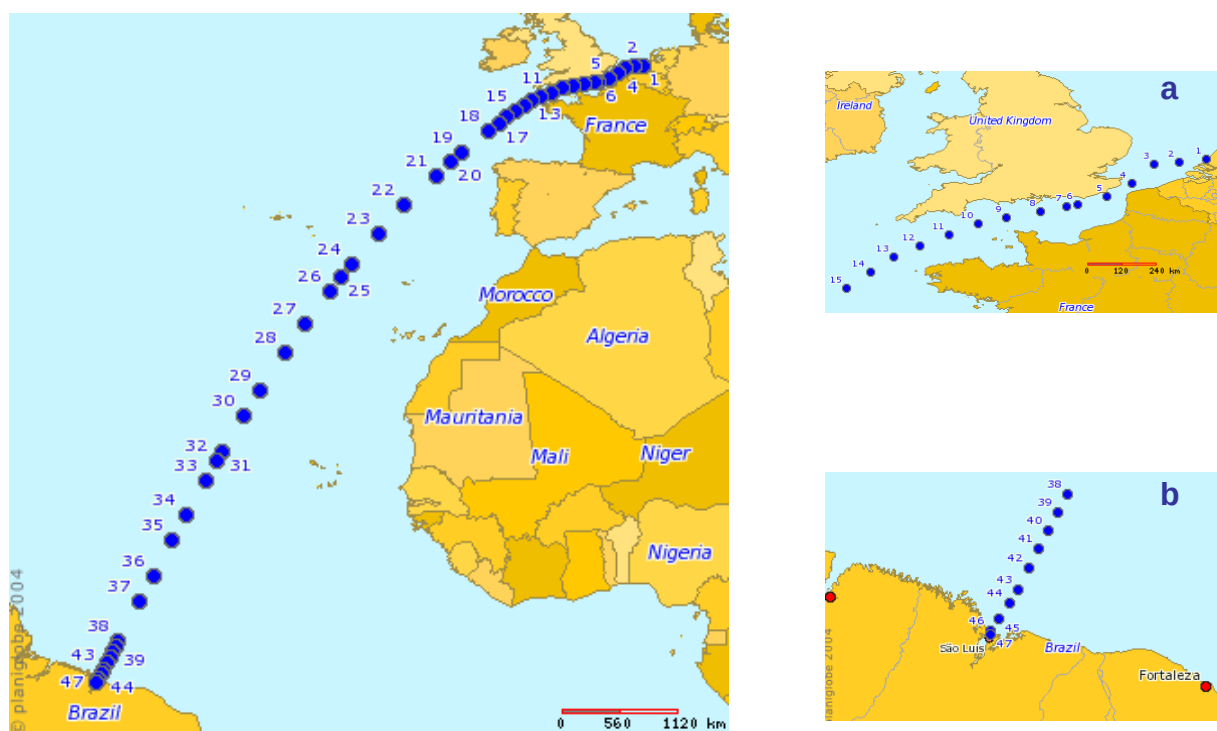


Figure 2. Cruise track through the Atlantic Ocean taken by the *MV Berge Nord* (Cruise BN) in September 2004, showing locations (1-47) where shipside CDOM and trace element samples were collected. Insets show detail of sampling in a) the English Channel and b) the approach to Brazil. See Appendices for position coordinates.

3. Results

3.1. Salinity

3.1.1. Tracer Stability

Tank Holding Effects

Since salinity is conservative over time in a fully mixed and closed system, salinity in unexchanged ballast tanks should be constant over time. Deviations from this condition are likely to result only from sensor drift or mixing of depth-stratified layers of differing salt content.

On Cruise LF, a faulty depth board on the CTD resulted in a strong instrument drift that manifested itself in decreasing measurements over time, beginning around the third day of sampling. Since salinity in unexchanged tanks was close to full strength, significant depth stratification was unlikely. Under the assumption that salinity in the tanks remained constant over time, a correction factor was calculated for each day of sampling. The factors were applied to the measurements each day to estimate the true salinities of the samples. Corrected data are considered accurate to within 0.5 parts per thousand (ppt) until the eighth day of sampling and are questionable thereafter.

On Cruise AS, with a new CTD depth board, salinity increased in all tanks by ~ 0.5 ppt over the course of the cruise. Although this could be due to mixing of slightly stratified ballast water (salinity ~ 27 ppt), the fact that the tanks were shallow, and that most were ballasted in Korea several days earlier, suggested that a slight instrument drift caused these changes also.

On Cruise BN, salinity measurements were stable over time in Tanks 3 and 5 p & s, and increased over time by ~ 1.4 ppt in Tank 7 p & s. The increase is attributable to mixing of stratified ballast water in the deep ballast tanks (> 20 m). Due to obstructions in this tank, it was possible to measure only at the surface (1 m) of the Tank 7 pair. Stratification probably resulted from tidal conditions during ballasting, which also resulted in elevated salinity in this tank pair compared to other tank pairs.

Cruises K1 and K2 were of insufficient duration for meaningful examination of salinity behavior over time.

Storage Time Effects

Salinity measurements were performed in situ and storage time effects were not assessed. If samples are kept sealed, it is generally accepted that salinity should be conserved.

3.1.2. Effect of Ballast Water Exchange

On all cruises except AS, salinity in unexchanged ballast tanks exceeded 31 ppt and consequently exceeded the current CG's salinity-based criterion (< 30 ppt) for unexchanged ballast water (Figure 3). This means that for four of five cruises, any diagnosis of ballast water origin based solely on the salinity criterion would have been incorrect.

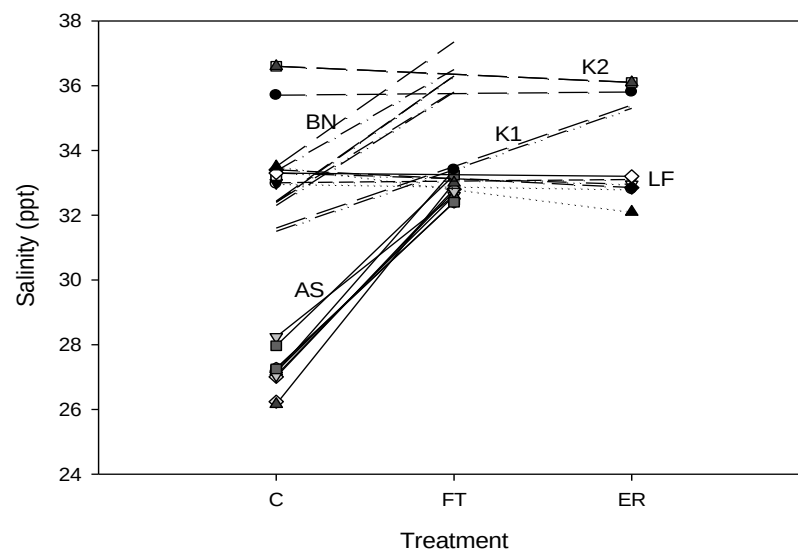


Figure 3. Effect of ballast water exchange on salinity in ballast tanks during the five CRANSI research cruises (Cruises LF, AS, K1, K2 and BN). Treatments are unexchanged ballast (C), ballast exchanged using the Flow-Through (FT) method and ballast exchanged using the Empty-Refill (ER) method. Various symbols and lines join mean values for independent ballast tanks.

Across all cruises, salinity increased or remained stable following ballast water exchange. The largest increases of approximately 25 percent were on Cruise AS, where tanks contained ballast water from Tokyo Bay, Japan and Inchon or Kunsan, Korea. Salinity also increased by

approximately 15 percent on Cruise BN out of Rotterdam, the Netherlands and by approximately 10 percent on Cruise K1 out of Oakland, California.

Salinity remained stable ± 5 percent on Cruises LF and K2. Salinity appeared to decrease in one tank on this cruise, but this effect is probably spurious and due to the CTD drift described previously.

3.1.3. Ocean Transects

Salinity in the offshore Pacific Ocean ranged between 31-37 ppt. Salinities generally increased in a southerly direction (Figure 4).

Salinities were higher overall (> 35 ppt) in the Atlantic Ocean (Figure 5). The highest salinities (> 37.5 ppt) were measured west of North Africa.

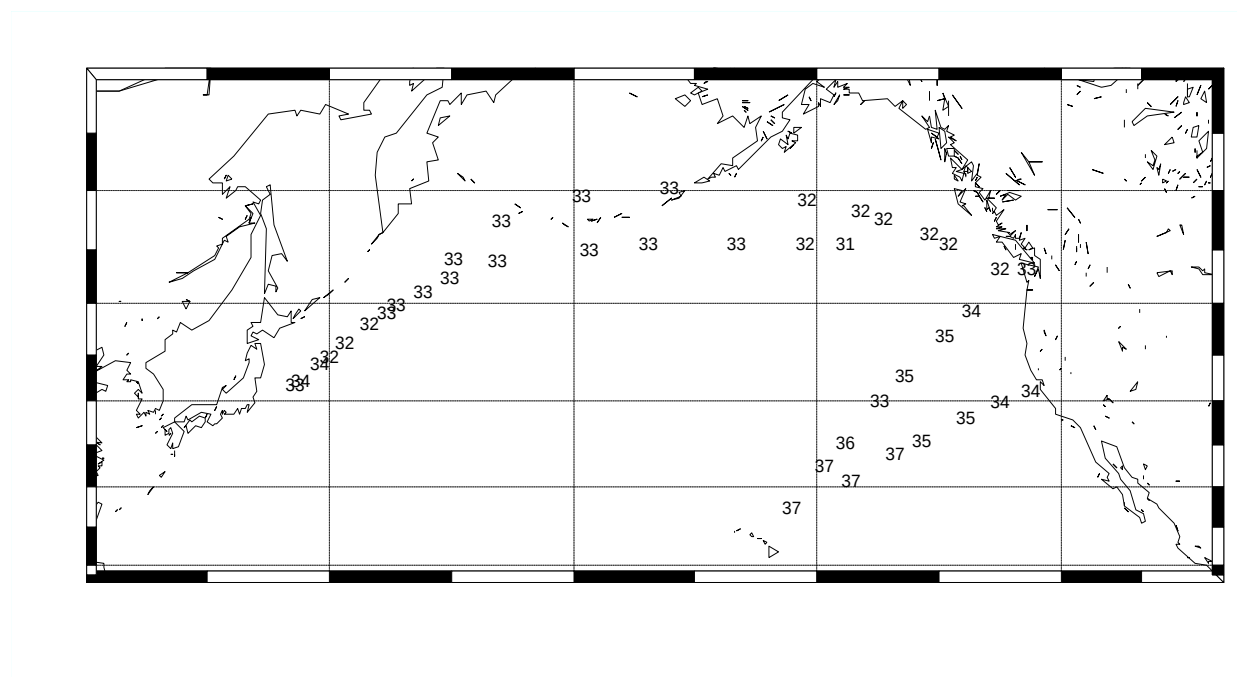


Figure 4. Salinity (± 0.5 parts per thousand) in the offshore ocean during four cruises in the North Pacific for the CRANSI study (Cruises LF, AS, K1 and K2).

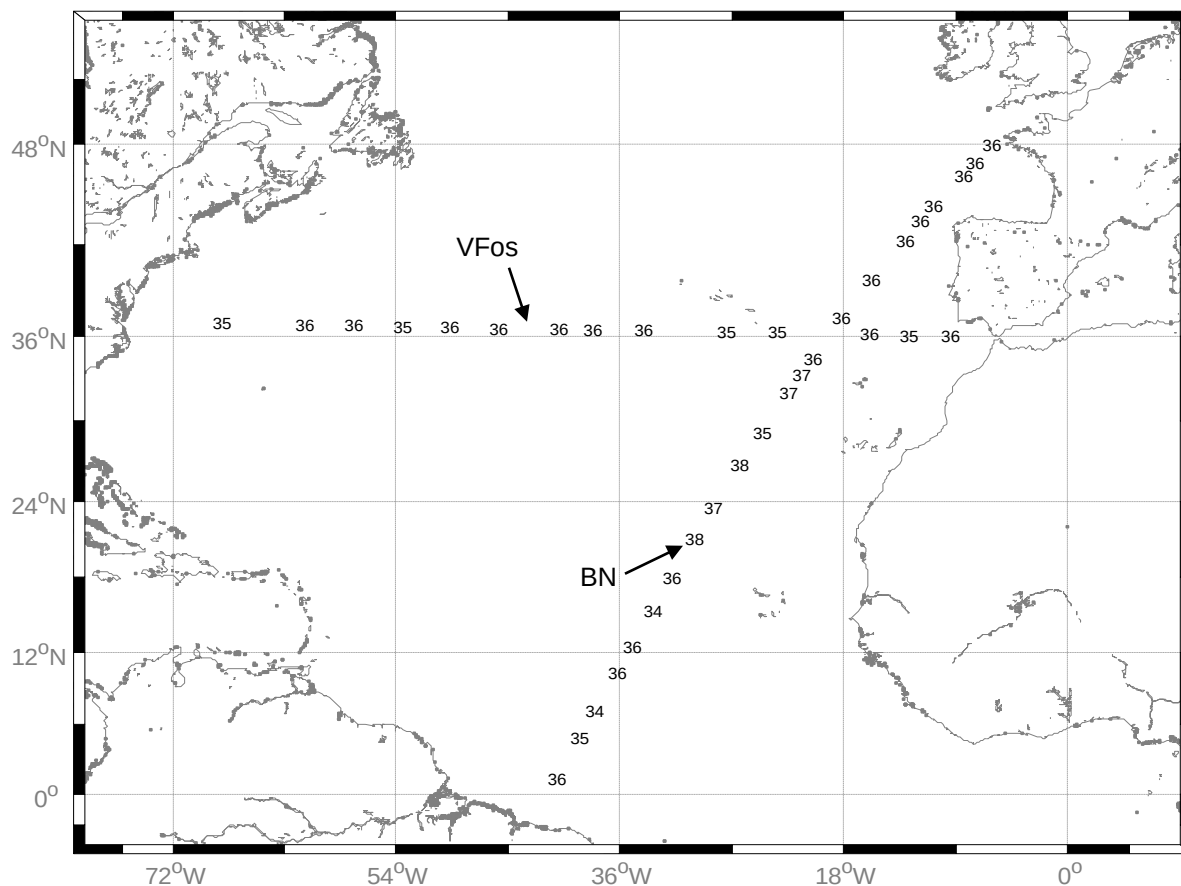


Figure 5. Salinity (± 0.5 parts per thousand) in the offshore ocean during the Atlantic cruise (BN) of the CRANSI study. Data from Cruise VFos, conducted during a previous cruise conducted in 2000 (Murphy et al., 2004a) are shown for comparison.

3.2. CDOM

Analysis of CDOM samples by Excitation-Emission Matrix (EEM) spectroscopy resulted in three-dimensional plots of excitation wavelength x emission wavelength x intensity (Figure 6). In the figure, Peaks A and C arise from the fluorescence of humic material. The protein fluorescence (P) identified in the same figure was similar to that of tyrosine, with primary (1' - 230 nm) and secondary (2' - 270 nm) excitation peaks; on Cruise K these were intense enough to cause apparent secondary emission peaks to appear at twice the primary emission wavelengths. Diagonal lines through the EEMs are attributed to Rayleigh and Raman scatter; data in this region should be disregarded.

Fluorescence is reported throughout this report in terms of intensity in parts per billion quinine sulfate equivalent units (ppb QSE) at fixed excitation (λ_{ex}) and emission (λ_{em}) wavelengths (in nanometers, nm), written as wavelength pairs, i.e. $\lambda_{\text{ex}}/\lambda_{\text{em}}$. Results are summarized by reporting fluorescence at two wavelength pairs in the A-peak region (A1: $\lambda_{\text{ex}}/\lambda_{\text{em}} = 250/450$; A2: $\lambda_{\text{ex}}/\lambda_{\text{em}} = 260/470$) and two in the C-peak region (C3: $\lambda_{\text{ex}}/\lambda_{\text{em}} = 325/420$; C4: $\lambda_{\text{ex}}/\lambda_{\text{em}} = 370/450$). Peaks A1, A2 and C3 were selected to enable comparison with previous efforts (Murphy et al., 2004a). C4 is included to facilitate the prediction of fluorescence intensities in the wavelength regions measured by the Ballast Exchange Assurance Meter (BEAM, Dakota Technology Inc., $\lambda_{\text{ex}} = 375 \pm 10$ nm, $\lambda_{\text{em}} = 460 \pm 10$ nm).

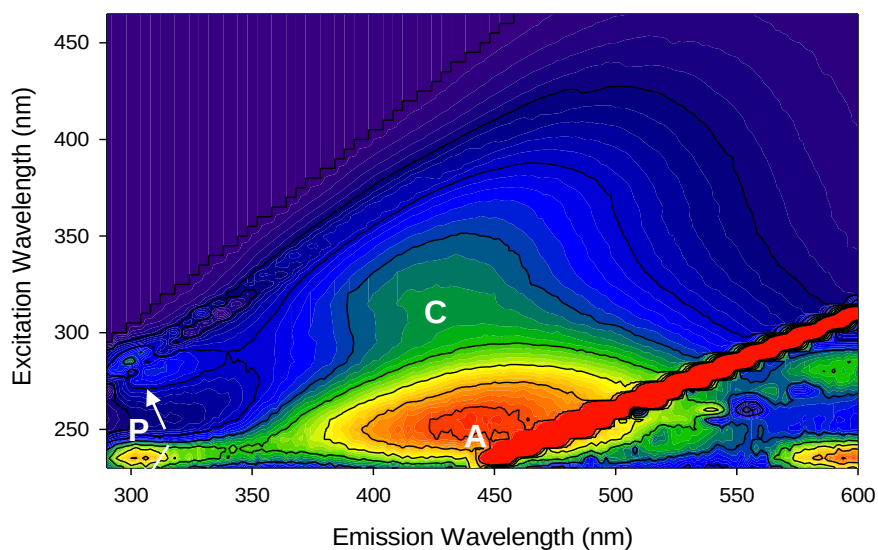


Figure 6. Example Excitation Emission Matrix (EEM) from a CDOM sample on Cruise K, illustrating peaks typically attributed to CDOM fluorescence. Obvious diagonal band is due to scatter. Peaks A and C are discussed in text. Peak P is a protein fluorescence peak.

3.2.1. Tracer Stability

Tank Holding Effects

There was some evidence that fluorescence intensity increased slightly in ballast tanks over time. While not statistically significant on any single voyage, the trend was noticeable on multiple voyages and in both exchanged and unexchanged ballast tanks (Figure 7). The slight increase is not expected to introduce significant error decisions on BWE verification.

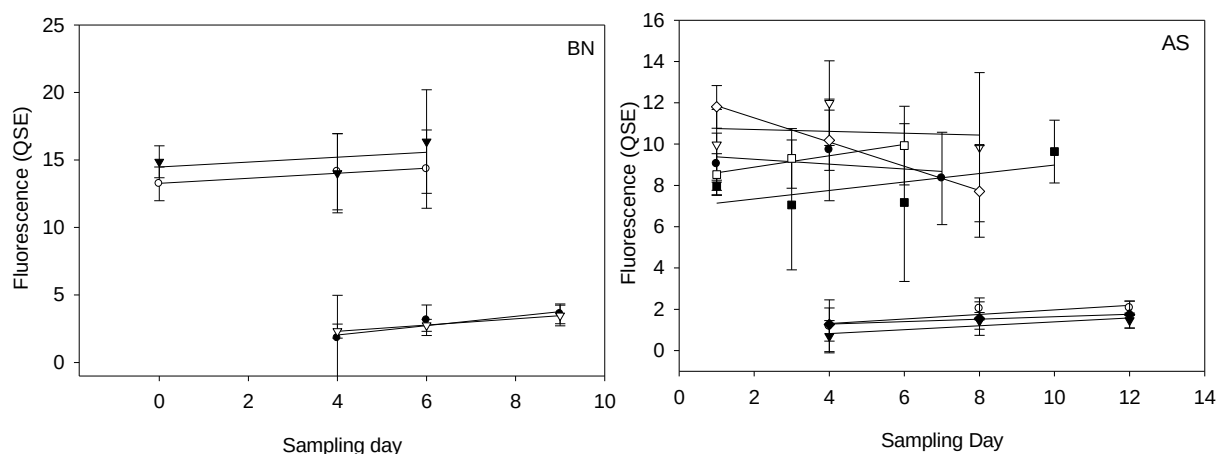


Figure 7. Peak A1 fluorescence intensities increased in ballast tanks over time ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 250/450$ nm). Points linked by regression lines represent measurements from the same ballast tank.

Storage Time Effects

Results for two cruises conducted in 2003 (LF, AS) featured high variation between fluorescence intensities measured on replicate samples at similar excitation and emission wavelengths. This inter-replicate error (up to 50 percent) greatly exceeded the expected (sampling + analytical) error of less than 15 percent (Murphy, unpublished data) and the error (< 10 percent) usually seen for replicate samples from 2004 cruises (Cruises K1, K2 and BN). The fluorescence loss is a subject of ongoing investigation in our laboratory and results reported here are preliminary at this time.

Fluorescence loss (quenching) was found to be strongly correlated with the number of days between collection of the sample and its analysis in the laboratory. For all wavelength pairs examined, fluorescence decreased as an exponential function of storage time (Figure 8), suggesting that chemical processes occurred that altered the optical properties of the samples during storage. Although the earliest analyses were run nearly three weeks after collection, the onset of quenching appeared to be immediate. It was not possible to correlate analysis date with fluorescence intensities for cruises in the earlier project because samples were analyzed sequentially, so storage time and treatment were confounded factors. Consequently, it is unclear how much of the variability seen in the earlier project was attributable to storage issues.

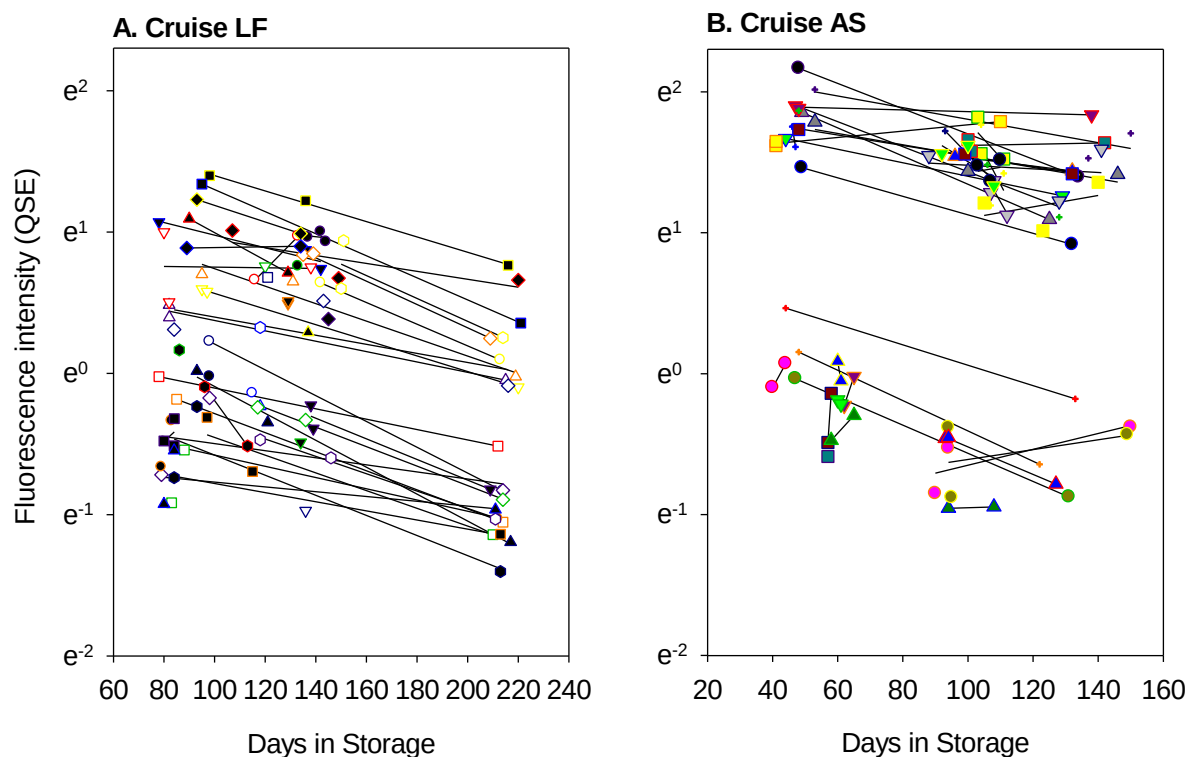


Figure 8. Loss of CDOM fluorescence ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 300/390$ nm) in freezer-stored samples collected on a) *MV Lily Fortune*; b) *MV Asahi Sunrise*, in 2003. Straight lines show linear regression upon the logarithm of fluorescence intensity from replicate samples analyzed on different dates.

For the 2003 cruises, statistical analyses showed that quenching rates of CDOM fluorescence depended upon the measurement wavelengths, but not upon the ship or the ballast water source.

Original fluorescence (y_{pred}) could be estimated using an exponential relationship:

$$y_{\text{pred}} = e^{(y - qt)} \quad \text{Equation 1}$$

where q is the quenching rate in parts per billion QSE day⁻¹, t is the storage time in days, y is the measured fluorescence, y_{pred} is the corrected (predicted) fluorescence and e is the exponential function.

Quenching rates for various regions within EEMs were typically between ~ 0.004 - 0.006 ppb per day, equating to approximately 50 percent loss of fluorescence after 4 months in storage (Figure 9). Equation 1 was used to correct data from Cruises AS and LF to account for fluorescence losses during storage. Correction increased fluorescence in every sample, with the amount of the

increase proportional to the length of time that the sample was in storage prior to analysis. Correcting the data in this manner greatly reduced differences in intensity (and hence standard deviations) for replicate samples that were analyzed several months apart.

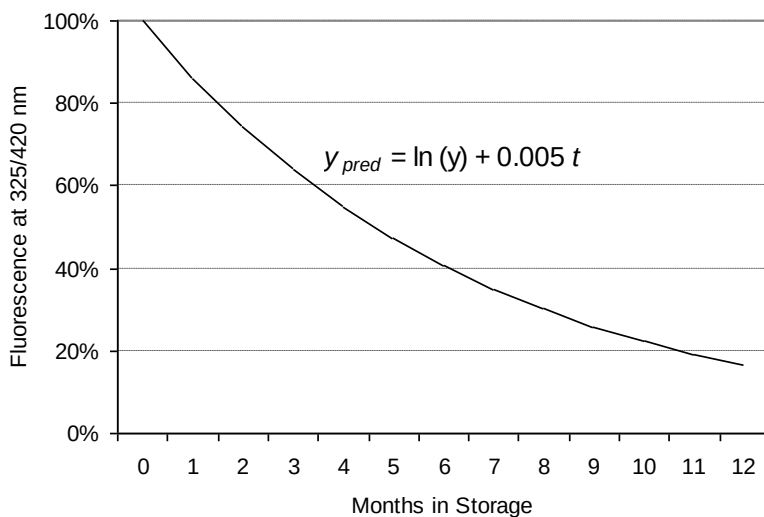


Figure 9. Modeled CDOM fluorescence loss ($\lambda_{ex}/\lambda_{em} = 325/420$ nm) in freezer-stored samples. Predicted fluorescence (y_{pred}) is a function of measured fluorescence (y) and days in storage (t).

3.2.2. Effect of Ballast Water Exchange

CDOM fluorescence intensity in unexchanged ballast water varied among source regions and was inversely correlated with salinity. Intensities always decreased following ballast water exchange (Figures 10 and 11). These results are consistent with findings from the first four verification experiments (Murphy et al., 2004a). For a fuller examination of the effect of ballast water exchange on CDOM fluorescence in all nine verification experiments conducted to date, the reader is referred to Murphy et al. (submitted; see Appendix F for further information).

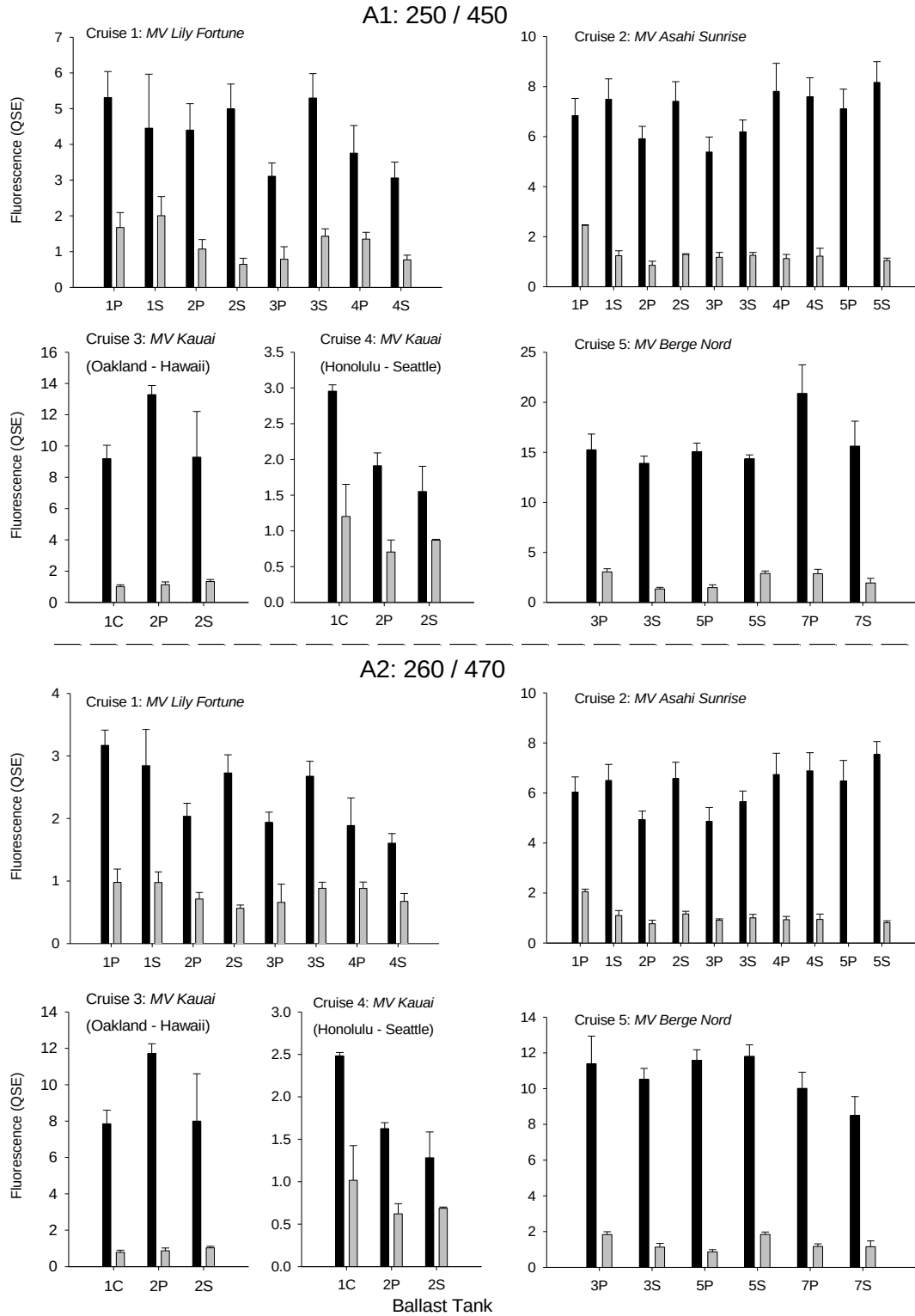


Figure 10. Effect of ballast water exchange (BWE) on CDOM fluorescence intensities in the A-peak EEM region, illustrated by wavelength pairs A1 (250/450 nm) and A2 (260/470 nm). Concentrations in ballast tanks (P = port tank, S = starboard tank, C = center tank) in units of ppb QSE ($\bar{x}$ + SE) are shown before (■) and after BWE (▒).

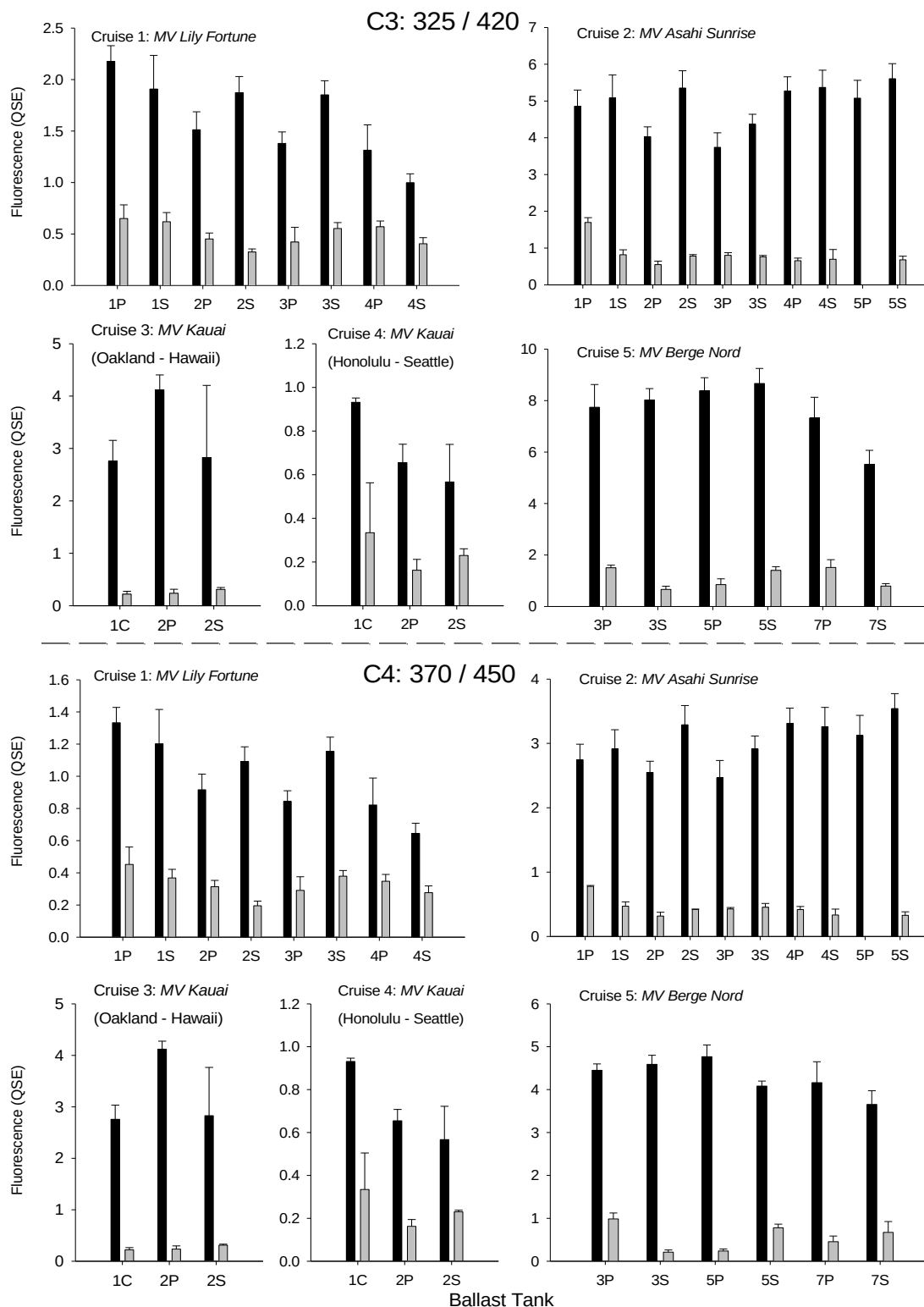


Figure 11. Effect of ballast water exchange (BWE) on CDOM fluorescence intensities in the C-peak EEM region, illustrated by wavelength pairs C3 (325/420 nm) and C4 (370/450 nm). Concentrations in ballast tanks (P = port tank, S = starboard tank, C = center tank) in units of ppb QSE ($\bar{x} + SE$) are shown before (■) and after BWE (■).

3.2.3. Ocean Transects

With exceptions described below, surface ocean fluorescence of CDOM showed a general trend of decreasing concentration with increasing distance from shore (Figures 12 - 15). In the figures, tracer concentrations are plotted against distance from shore (i.e. the nearest position on the shore as indicated by the symbols and legend). The rate of this decline was rapid, with baseline ('blue water') water usually encountered within 10 nmi of the coast. For the most part results for the A1, A2, C3 and C4 peak positions were similar except for a scaling factor.

On Cruise LF, factors other than distance from shore were clearly responsible for the observed trends in fluorescence intensity. This was most obvious for peak A2, which exhibited three cyclical maxima while the ship passed through different water masses in the western Pacific (Figure 12).

On Cruise AS (Figure 13), blue water fluorescence was encountered 10 nmi from Japan, then remained at low levels until picking up again approximately 50 nmi from the coast of North America.

On Cruise K1 (Figure 14), fluorescence intensities declined exponentially in the first 10 nmi from shore, then persisted at slightly elevated levels until the ship neared Hawaii. On Cruise K2, elevated fluorescence intensities were seen in samples from the Honolulu Harbor, but fluorescence decreased to baseline levels in the first few miles of the voyage. Two samples collected in the Seattle harbor were of similar intensity to samples from Honolulu.

On Cruise BN (Figure 15), all fluorescence of peak C3 was more variable than peaks C4, A1 and A2. For the latter peaks, fluorescence declined exponentially until reaching baseline ~ 60 nmi from Europe where it persisted throughout the Atlantic Ocean transit until ~ 60 nmi from Brazil, where it increased again.

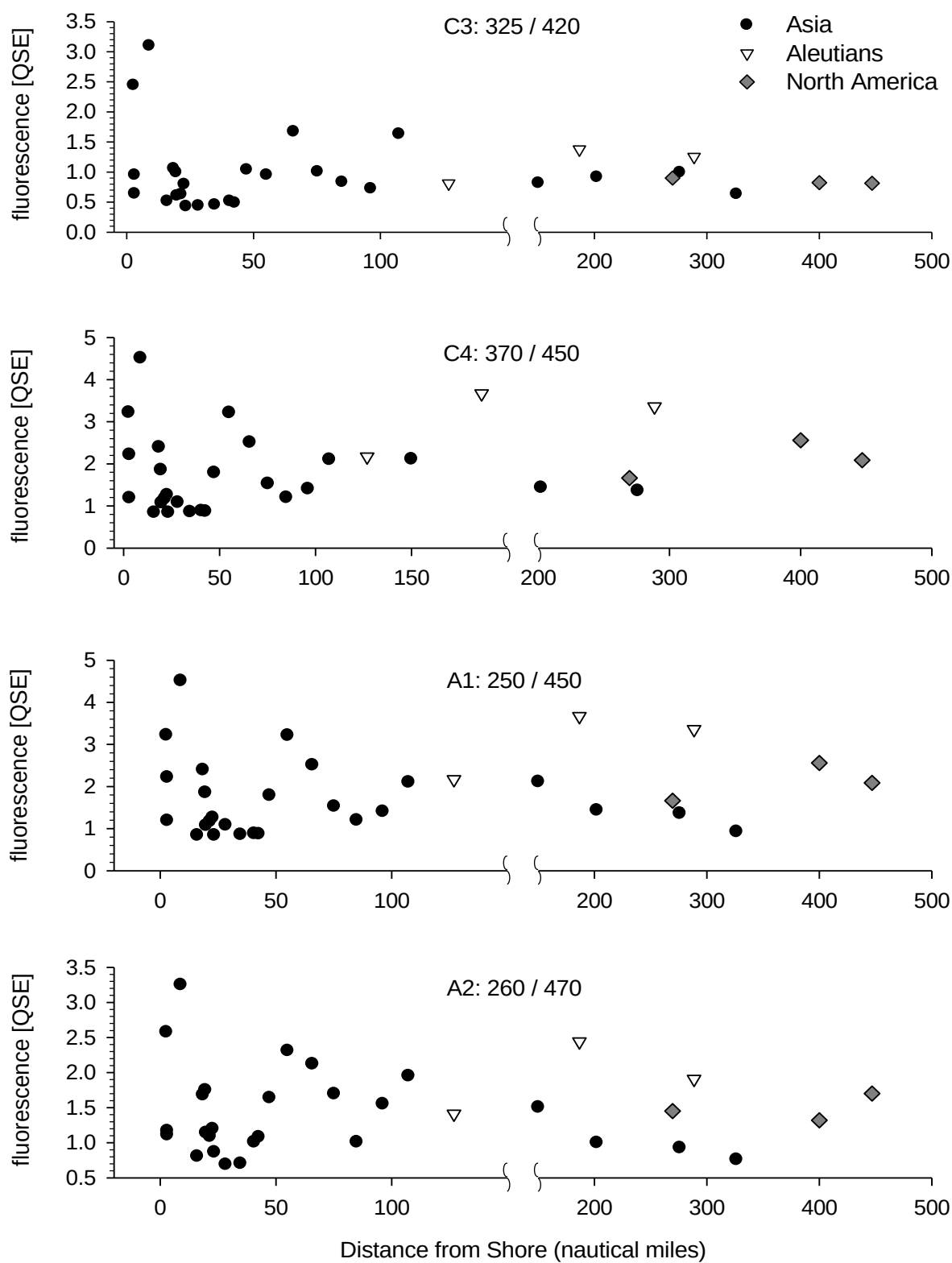


Figure 12. Surface ocean CDOM fluorescence at fixed wavelength pairs in samples collected while departing Japan and sailing to North America via the Aleutian Islands on Cruise LF.

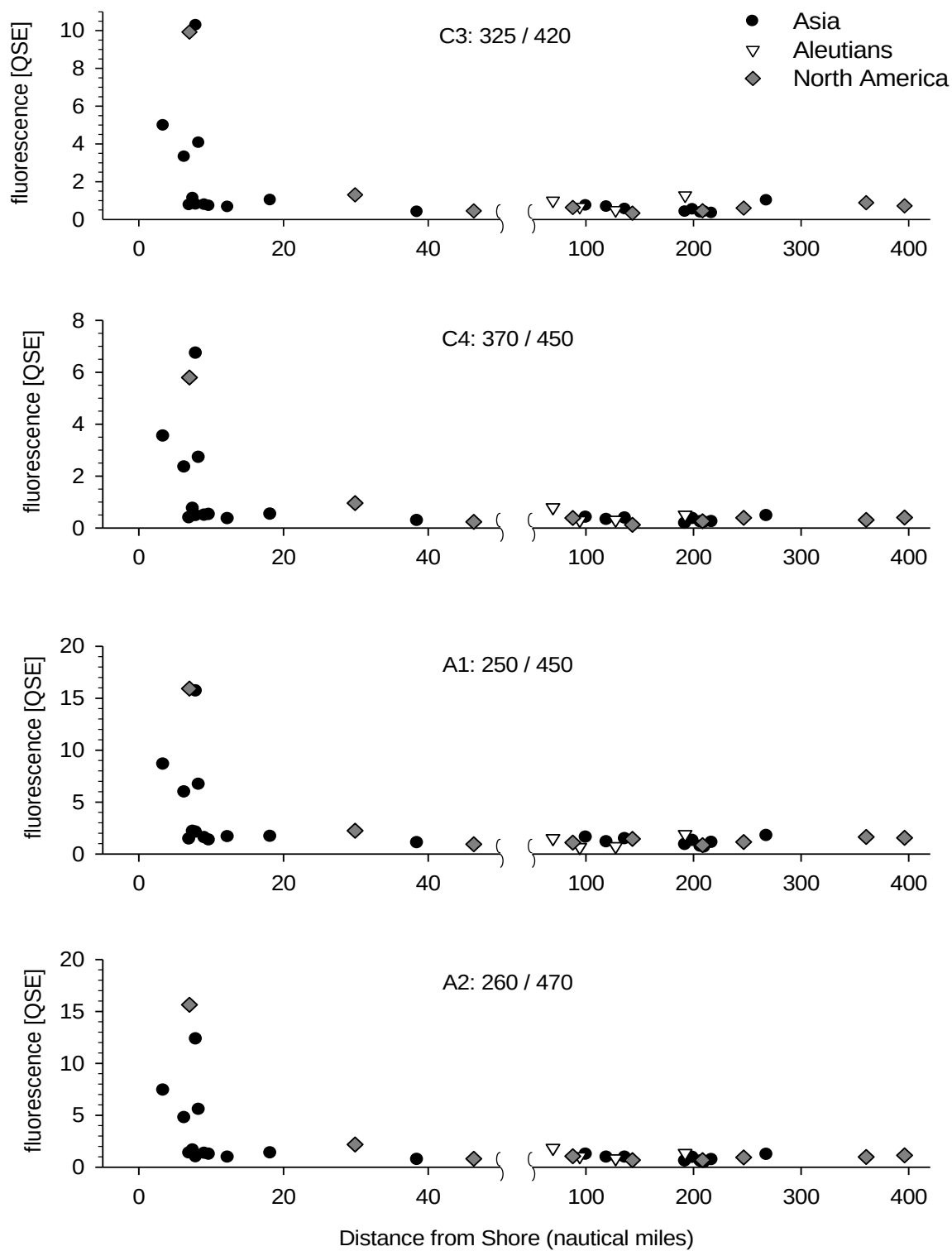


Figure 13. Surface ocean CDOM fluorescence at fixed wavelength pairs in samples collected while departing Japan and sailing to North America via the Aleutian Islands on Cruise AS.

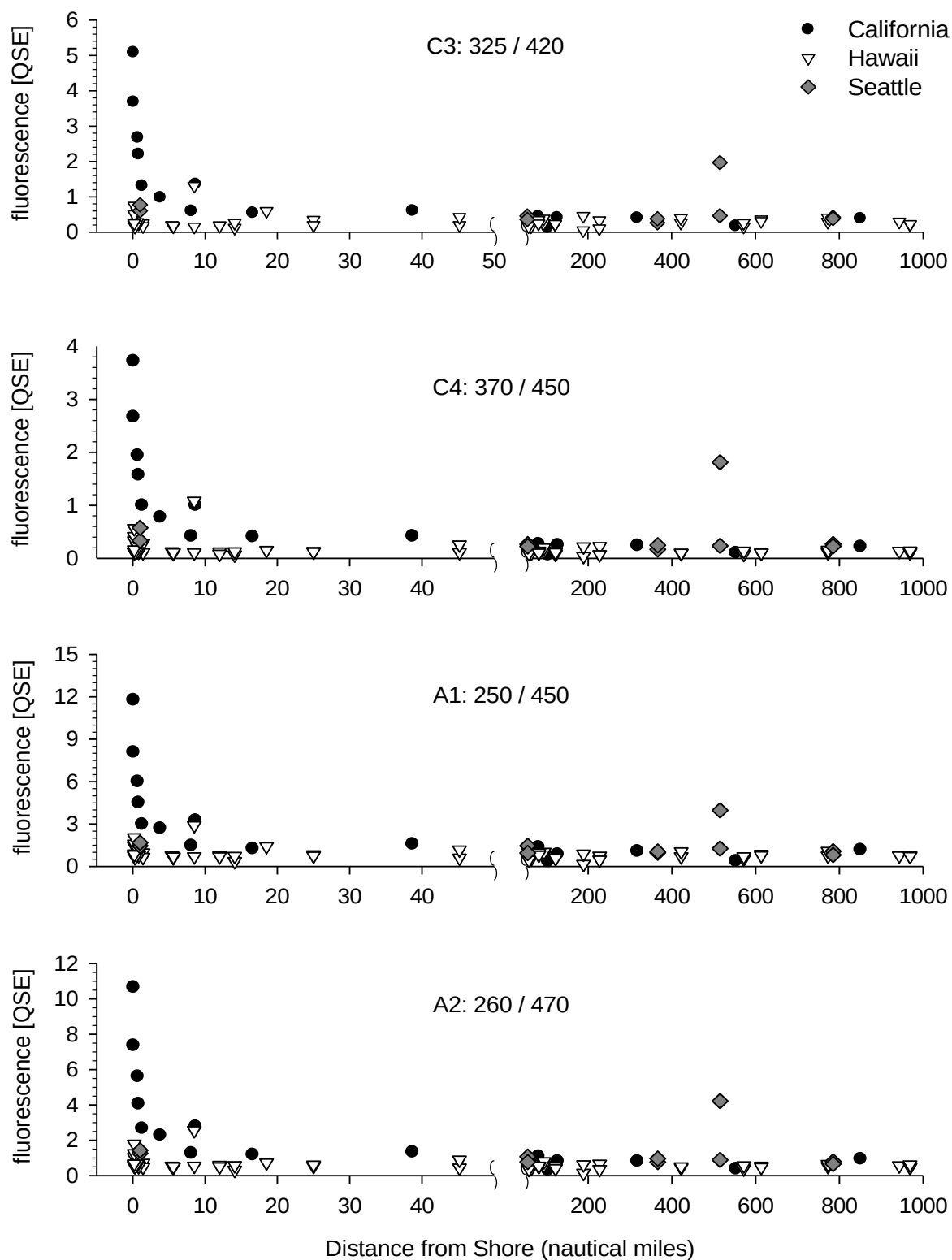


Figure 14. Surface ocean CDOM fluorescence at fixed wavelength pairs in samples collected while departing California and approaching Hawaii on Cruise K1 and while departing Hawaii and approaching Seattle on Cruise K2.

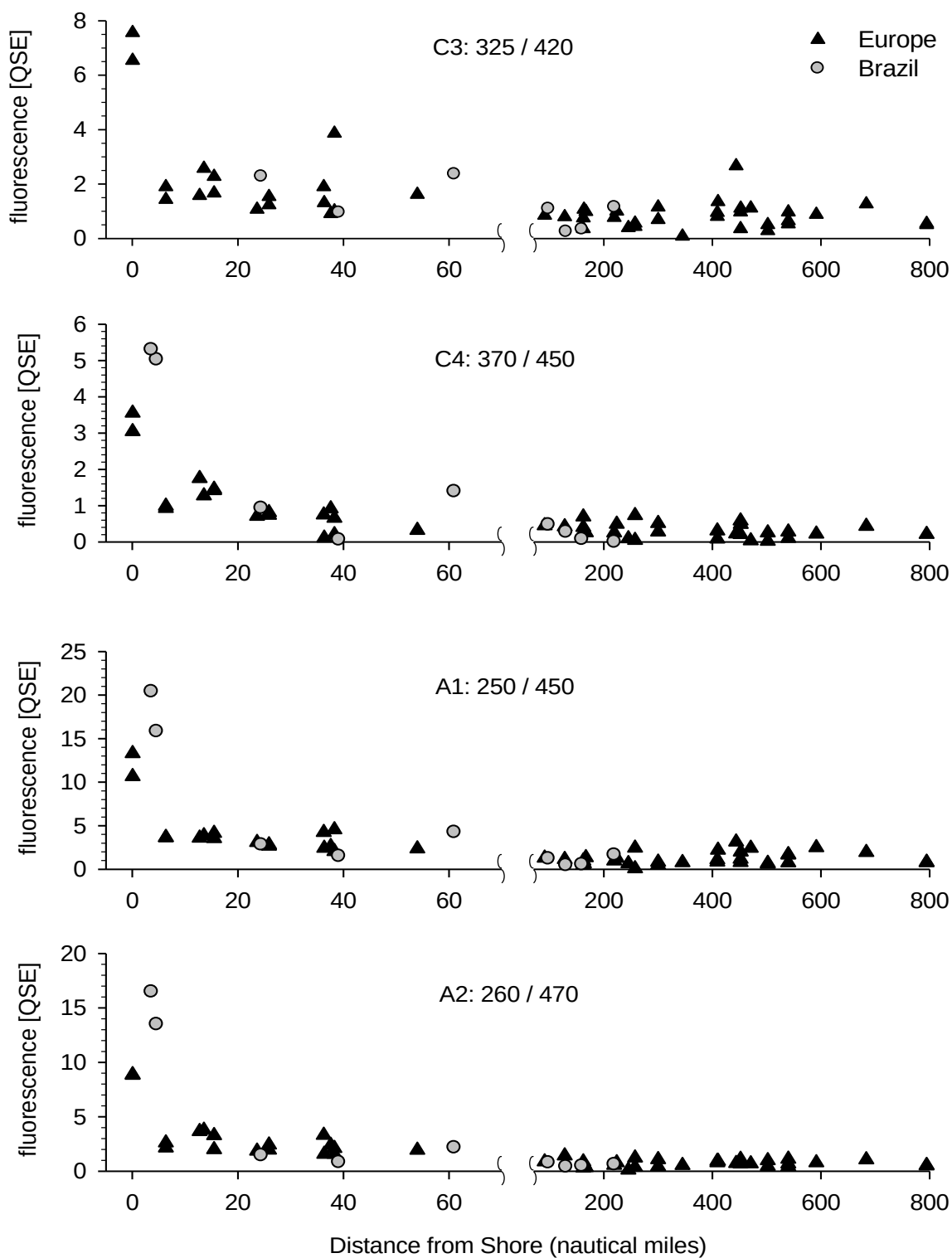


Figure 15. Surface ocean CDOM fluorescence at fixed wavelength pairs in samples collected while departing Europe and approaching Brazil on Cruise BN.

3.3. Trace Elements

3.3.1. Molybdenum / Salinity Relationship

Molybdenum is conservative with salinity; consequently, trends for this tracer should reflect trends for salinity. A linear relationship between Mo and salinity was confirmed for Cruises LF and AS, but it broke down for a number of samples from Cruises K and BN (Figure 16). For Cruise BN, analytical irregularities are the likely source of error. When first analyzed, data for a high portion of samples from these cruises were anomalous, as indicated by inconsistent data within groups of replicates and/or treatments. To address this problem, we reanalyzed the majority of samples from Cruise BN and a subset of samples from Cruise K.

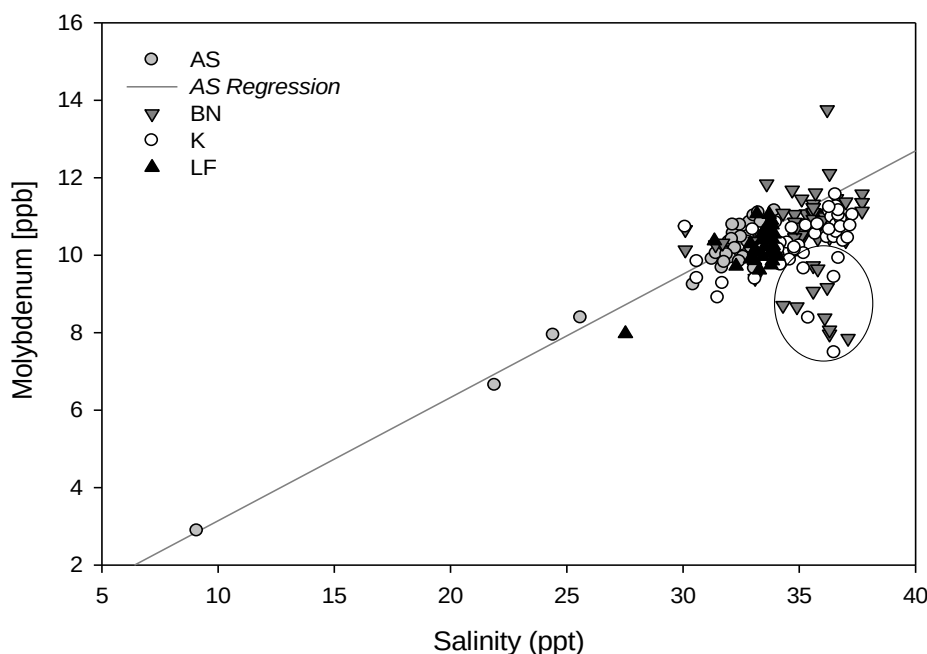


Figure 16. Relationship between salinity and Molybdenum on the CRANSI cruises. The expected linear relationship broke down for a number of samples from Cruises K and BN (circled).

Although reanalysis corrected most irregularities, a subset of samples remained anomalous. Since it is highly unlikely that samples were contaminated with Mo, it appears likely that sporadic analytical errors may affect some data that remain in the dataset. Consequently, Mo data from Cruises K and BN may be less reliable than data from Cruises LF and AS. This is a finding that could extend to data for other trace elements. In most cases, however, values

presented in this report represent averages of multiple replicate samples and thus are less sensitive to occasional anomalous data.

3.3.2. Tracer Stability

Tank Holding Effects

Stability was assessed on three cruises (Cruises LF, AS and BN) in tanks that were sampled on at least two separate occasions. While some trace elements behaved conservatively in ballast tanks, others did not.

Barium was stable over time in ballast tanks on Cruises LF and AS (Figure 17). On Cruise BN, Ba decreased over time in Tanks 7 p & s, fluctuated over time in Tank 3s, and stayed approximately stable in Tank 5s. The decrease in concentrations seen in Tank 7 surface samples was further indication that the tank was not fully mixed until several days into the cruise (see also the salinity data from this cruise, Section 3.1.1). Incomplete mixing may also have been responsible for the smaller Ba fluctuations in other ballast tanks on the same cruise.

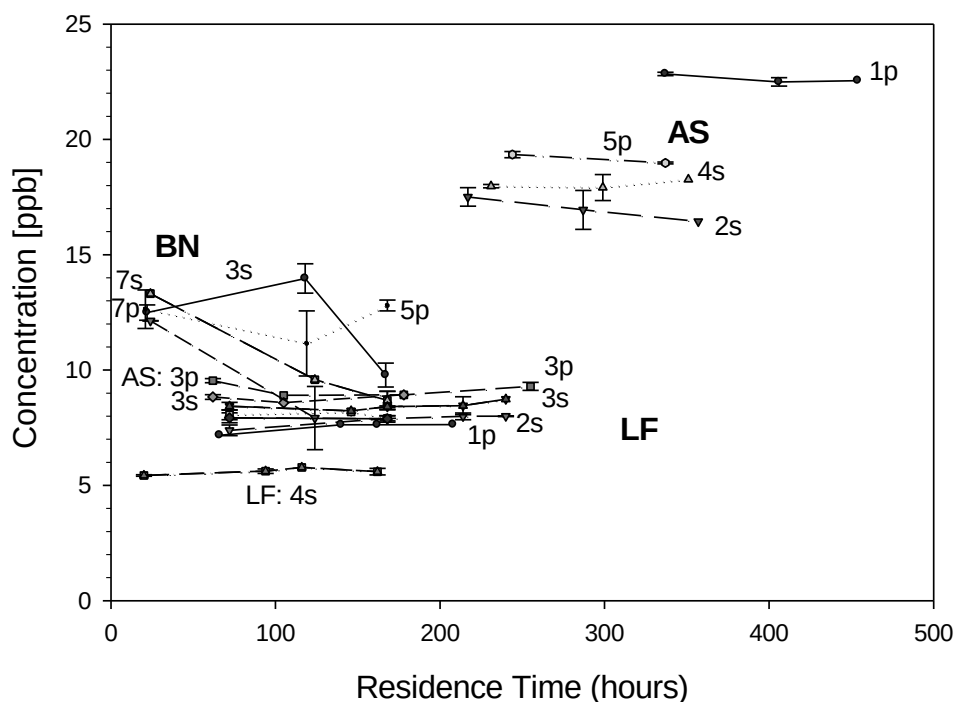


Figure 17. Ba in unexchanged ballast tanks (p = port, s = starboard) sampled repeatedly over time on Cruises LF, AS and BN.

Concentrations of manganese decreased over time in ballast tanks on all cruises probably due to the element adsorbing to particulates that were settling from the water column in a process known as scavenging (Figure 18). The rate of depletion of Mn varied among and within cruises and between tanks sourced from different locations. Depletion rates were greatest on Cruise BN, high on Cruise AS, and lowest (although still significant) on Cruise LF. It is not possible to entirely separate the effect of mixing from scavenging in Tank 7 on Cruise BN. However, as a result of these combined processes, Mn in unexchanged tanks held for 5 days showed similar levels to Mn in exchanged ballast tanks.

Phosphorus concentrations were somewhat variable in all tanks and on cruises but did not increase or decrease in a predictable manner (Figure 19). For this tracer also, mixing effects in Tank 7 on BN are likely responsible for most of the loss of phosphorus from the water column. Otherwise, concentrations of this reactive element probably reflect variable chemical and biological activity in individual ballast tanks.

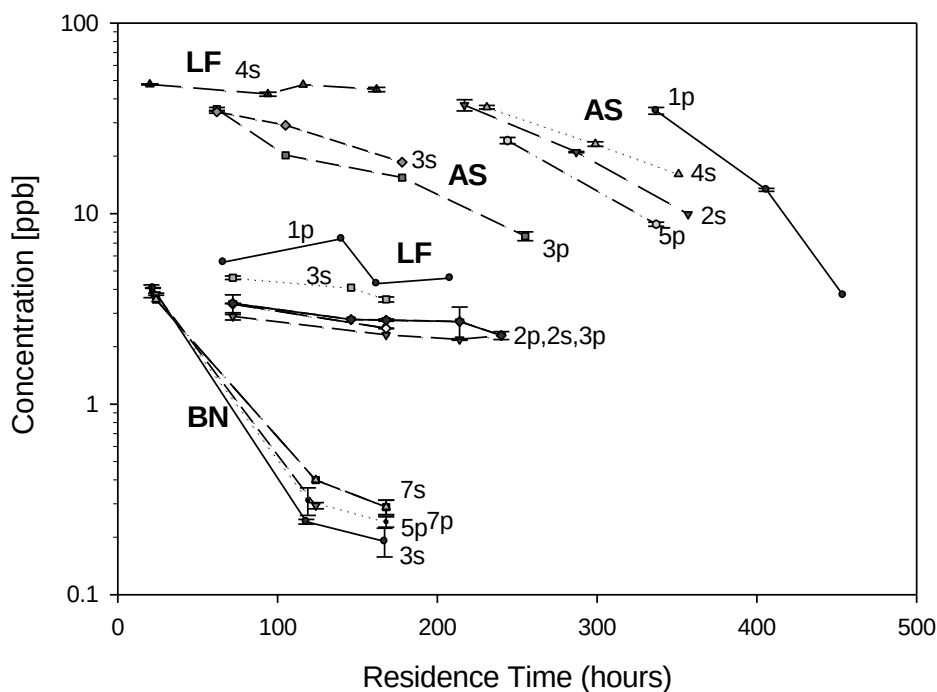


Figure 18. Mn in unexchanged ballast tanks (p = port, s = starboard) sampled repeatedly over time on Cruises LF, AS and BN.

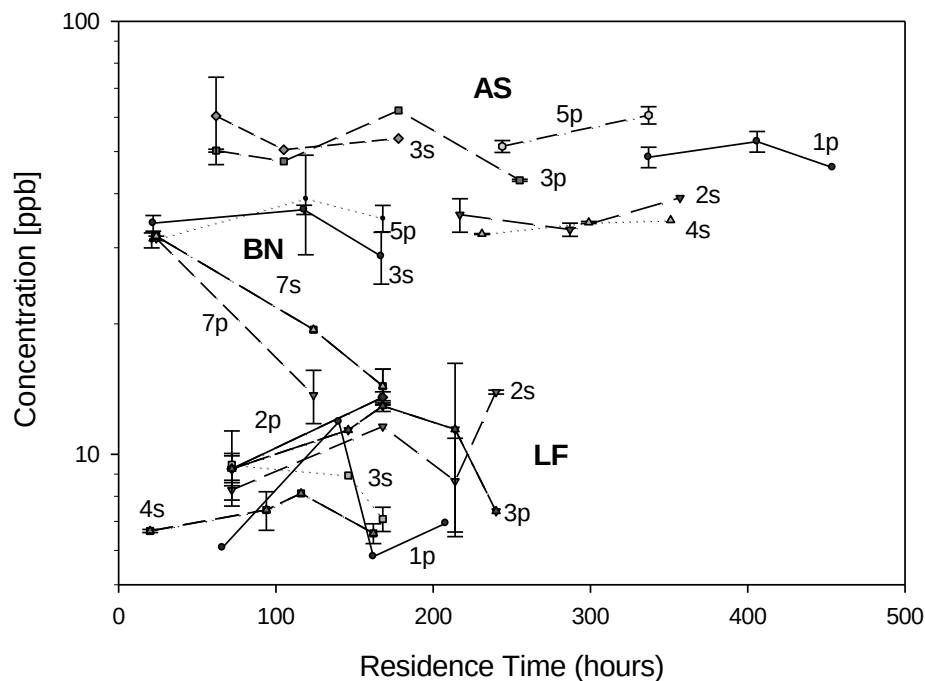


Figure 19. P in unexchanged ballast tanks (p = port, s = starboard) sampled repeatedly over time on Cruises LF, AS and BN.

Storage Time Effects

There was no evidence to suggest that trace element concentrations were affected by sample storage time. For a number of samples, replicate aliquots were run in different batches up to 6 months apart. These samples were usually chosen for reanalysis because data from the original analysis appeared to be anomalous. In all but a few cases, reanalysis brought these samples in line with the remaining data. Otherwise, reanalysis generally confirmed the original results to within 5 percent measurement error.

3.3.3. Effect of Ballast Water Exchange

In the majority of cases, trace element concentrations in ballast tanks were similar to concentrations in shipside samples collected in either the source port or within the region of ballast water exchange. This suggested a high degree of fidelity between concentrations of tracers in ballast tanks and in the ocean during ballasting. The exceptions to this rule involved

Mn and were time dependent, thus probably resulting from processes within the tanks that occurred subsequent to ballasting.

Barium

With few exceptions, levels of Ba on all cruises were higher in unexchanged than in exchanged ballast tanks (Figure 20). On Cruise LF, initial concentrations in the port and starboard tanks of a pair were similar. This is to be expected since pairs of tanks were ballasted simultaneously. Conversely, levels of Ba were lower in Tanks 4 p & s, reflecting their different port water sources. Following BWE, port and starboard tanks diverged according to location of BWE. For example, concentrations following BWE in 2s and 3p, which were exchanged together, were slightly lower than in 2p and 3s, which were also exchanged together but in a different region of the North Pacific Ocean.

Three different ballast water signatures were clearly distinguishable in Ba data from Cruise AS. These corresponded to different source concentrations in the ports of Inchon, Korea (~ 23 ppb), Kunsan (Tanks 2, 4 and 5) (~ 18 ppb) and Yokkaichi, Japan (Tank 3) (~ 9 ppb). Following BWE, concentrations decreased to 4-7 ppb depending on the location of BWE. In exchanged tanks, concentrations corresponded closely with shipside samples collected during BWE.

On Cruise K1 out of California, concentrations of Ba were high initially (~ 15 ppb) and decreased to ~ 4-7 ppb after exchange depending on the tank pair. Levels were higher in the Tank 2 pair after exchange than in shipside samples collected during exchange, suggesting that BWE may have been less efficient than on previous cruises. On Cruise K2 out of Hawaii, levels of Ba were significantly higher in the 1c (center) tank (~ 9 ppb) than in Tank 2 p & s (~ 6 ppb), suggesting either that a chemically different parcel of water was ballasted in this tank (the tank was ballasted approx. 12 hours after Tank 2 p & s; see Appendices), or that residual oceanic water in Tank 2 significantly lowered mean levels of Ba. Given the levels of Ba measured in shipside samples (~ 5.5 ppb) in Honolulu, the first explanation seems most likely.

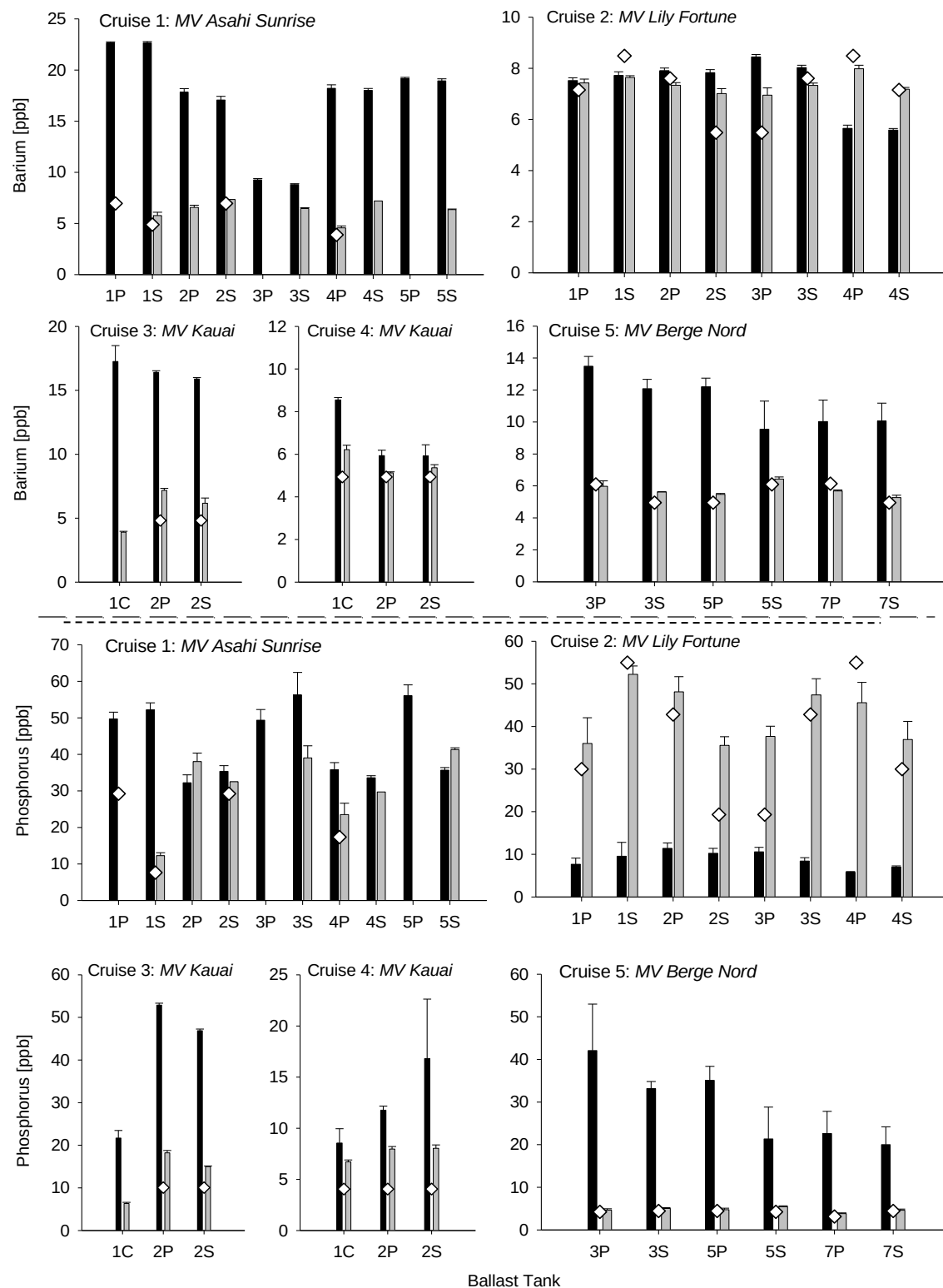


Figure 20. Effect of BWE on total dissolved Barium and Phosphorus in ships' ballast tanks (P = port tank, S = starboard tank, C = center tank). Concentrations in ppb ($\bar{x} + SE$) are shown before BWE (■), after BWE (■) and in shipside samples when collected during BWE (◇).

On Cruise BN in the North Atlantic, Ba levels in unexchanged tanks were more variable than on the other cruises where tanks were ballasted in the same location. The explanation for this probably lies in the size of the ballast tanks. On Cruise BN, tanks were 1-2 orders of magnitude larger than the ballast tanks on the other cruises. Thus tanks were ballasted over a greater range of depths and encountered more variable conditions. This may have resulted in depth-stratified tracer concentrations, particularly in Tank 7 p & s. Concentrations of Ba in exchanged ballast tanks, despite the BWE process taking over 36 hours during which time the ship sailed more than 500 nmi, reflected concentrations in twice-daily shipside samples collected during BWE (approximately 5.5 - 6.5 ppb).

Phosphorus

Phosphorus in ballast tanks increased or decreased as a result of BWE in a manner that reflected both variable starting conditions among cruises and variable oceanic levels of P among the regions where BWE took place (Figure 20). On Cruise LF, levels of P were below 14 ppb in all tanks at the start of the cruise and increased to 35 - 55 ppb following exchange, depending on the location where exchange took place. A similar trend was seen for Cruise AS, although overlaid with this behavior were anomalously elevated levels of P in some tanks. For example, P is the only tracer showing significantly elevated levels in Tank 5p despite having been ballasted in the same location as Tank 5s and Tanks 2 p & s and 4 p & s. In tanks for which shipside samples were taken during exchange, P levels in samples from exchanged tanks were consistent with samples from the ocean.

On Cruise K1 out of California, levels of P were very high in Tank 2 p & s (> 45 ppb) and considerably lower in Tank 1c (~ 20 ppb) despite all three tanks having been ballasted in the same location at almost the same time of day. Following BWE, levels of P in Tank 2 p & s (> 15 ppb) remained high relative to Tank 1c (< 8 ppb). The latter result echoed differences in oceanic concentrations in the respective regions of BWE (see also section 3.2.3). On Cruise K2, levels of P were slightly lower in Tank 1c than Tank 2 p & s, a difference that was still noticeable following BWE although exchange was conducted simultaneously for all three tanks.

On Cruise BN in the North Atlantic, levels of P were high (> 20 ppb) but variable in unexchanged ballast and uniformly low in exchanged tanks (~ 5 ppb). The high standard errors

on P concentrations in unexchanged tanks were probably due to time and depth-dependent distributions of P in port during ballasting. Conversely, levels of P in the open ocean were relatively invariable over longer periods of time and large geographical distances (> 500 nmi).

Manganese

Manganese showed the greatest differences between exchanged and unexchanged tanks on all cruises (Figure 21). However, as previously discussed, its utility as a tracer of BWE was severely compromised by the fact that concentrations of Mn in ballast tanks decreased over time, often precipitously.

On all cruises, Mn was on average significantly higher in unexchanged than in exchanged ballast tanks. Concentrations of Mn in samples from unexchanged tanks ranged from approximately 1 ppb to 50 ppb, depending upon both the source region and the time that had elapsed since ballasting. Levels in exchanged ballast tanks were invariably below 1 ppb. These conformed to levels in shipside samples, except on Cruises K1 and K2, where tank levels were significantly lower. Data from these cruises suggest that while levels of Mn in the surface ocean may have been relatively high (~ 5 ppb, see section 3.3.4), Mn was quickly scavenged from the water column while in the ballast tanks.

Molybdenum

Molybdenum concentrations on Cruises LF and AS were consistent across ballast tanks (Figure 21), which is in keeping with their consistent initial salinities. Salinity generally decreased due to BWE on Cruise LF, and K1 and increased due to BWE on other cruises. Although salinities never changed by more than 15 percent as a result of BWE, Mo in exchanged ballast tanks was often inconsistent with levels in shipside data collected during BWE, even on cruises that were unaffected by anomalous Mo measurements (see section 3.3.1). This indicated that the distribution of Mo in the ocean was more patchy than were some other tracers, and that Mo (and consequently salinity) were relatively insensitive tracers of BWE.

Other trace elements

Uranium and vanadium were less reliable indicators of BWE than Ba, although all three elements are not reactive and behave conservatively with salinity. Results for uranium and

vanadium were similar to each other. For other elements the effect of BWE was usually significant, but overall levels of U and V were similar in exchanged and unexchanged ballast tanks across all cruises (Figure 22).

Concentrations of U were around 2.9 ± 0.4 ppb before and after BWE. Vanadium in unexchanged ballast water varied by an order of magnitude (0.3 – 2.5 ppb), but in most tanks before and after BWE concentrations were around 1.5 ± 0.2 ppb. Exceptions were Cruises K1 and K2, where concentrations in exchanged tanks were approx. 0.7 ± 1 ppb, despite higher concentrations (1.2 - 1.4 ppb) measured in the ocean during BWE.

3.3.4. Ocean Transects

With exceptions described below, surface ocean concentrations of trace elements (Mn, P, Ba) showed a general trend of decreasing concentration with increasing distance from shore. However, the rate of this decline was variable both between cruises, between shores on the same cruise and, in the case of the *MV Kauai*, between the same shore (Hawaii) on two consecutive cruises. Throughout this section, concentrations of Mn, P, and Ba are displayed together for each cruise: LF, AS, K, and BN (Figure 23 - Figure 26 respectively). In the figures, samples are classified broadly according to the coastline that was closest to the vessel at the time of sampling, since this is the coastline considered most likely to define the distribution of the tracers. In practice, however, coastlines with strong salinity signals are likely to affect tracer distributions farther offshore than other coastlines, an effect that is demonstrated clearly on some cruises.

Manganese

Concentrations of Mn were variable among Pacific cruises. On Cruise LF, surface concentrations of Mn dropped dramatically in the first 20 miles from shore. No port samples were obtained during this cruise and the highest concentrations of Mn measured (~ 2.5 ppb) were from the first shipside station located 3.1 nmi from shore. Since initial concentrations in ballast tanks were approximately 7.5 ppb, this suggests that Mn declined by up to two-thirds in the first 3 nmi from shore. By the time the vessel had traveled to approximately 20 nmi offshore, concentrations of Mn were indistinguishable from those in the open ocean ($\sim 1 - 3$ ppb).

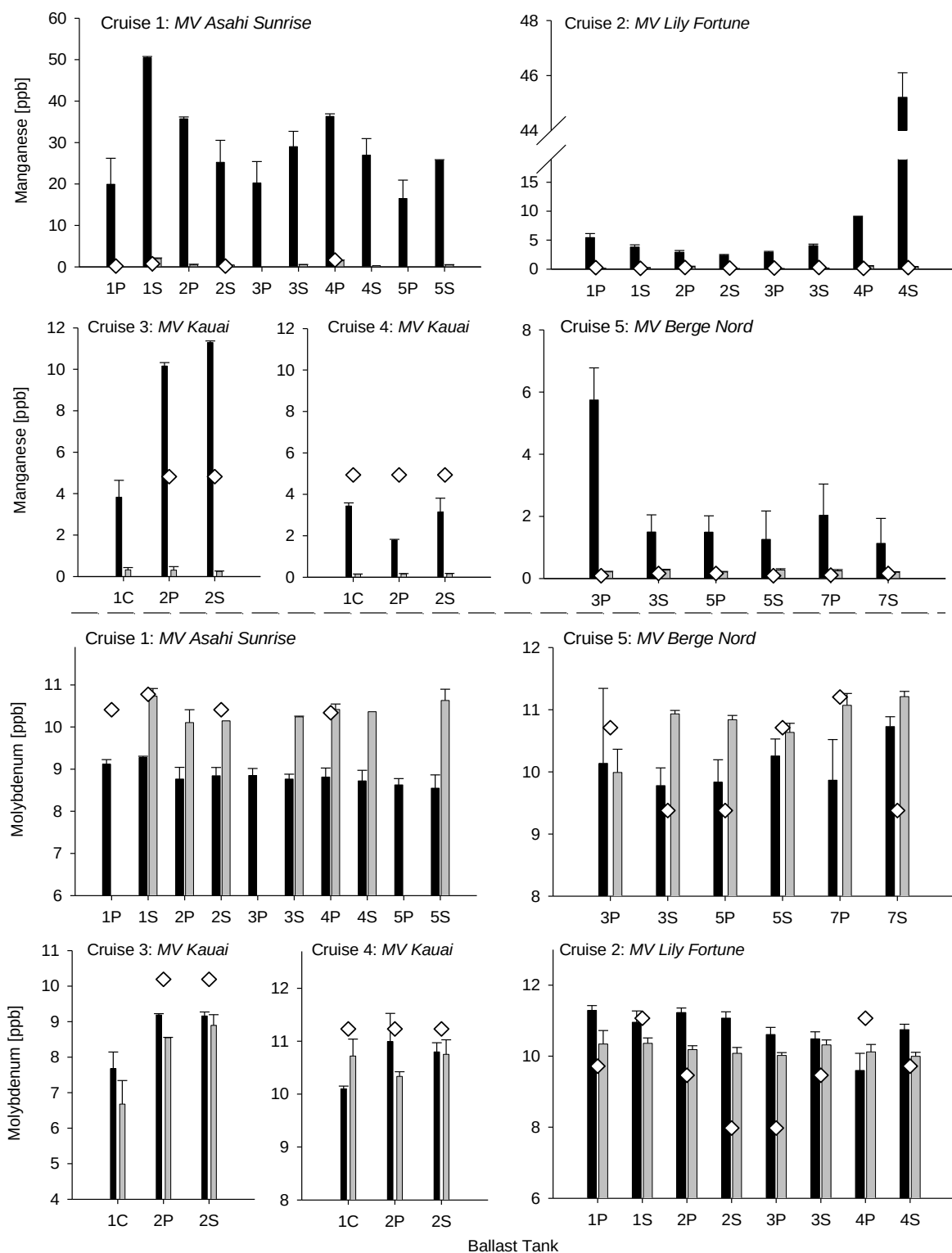


Figure 21. Effect of BWE on total dissolved Manganese and Molybdenum in ships' ballast tanks (P = port tank, S = starboard tank, C = center tank). Concentrations in ppb ($\bar{x} + SE$) are shown before BWE (■), after BWE (■) and in shipside samples when collected during BWE (◇).

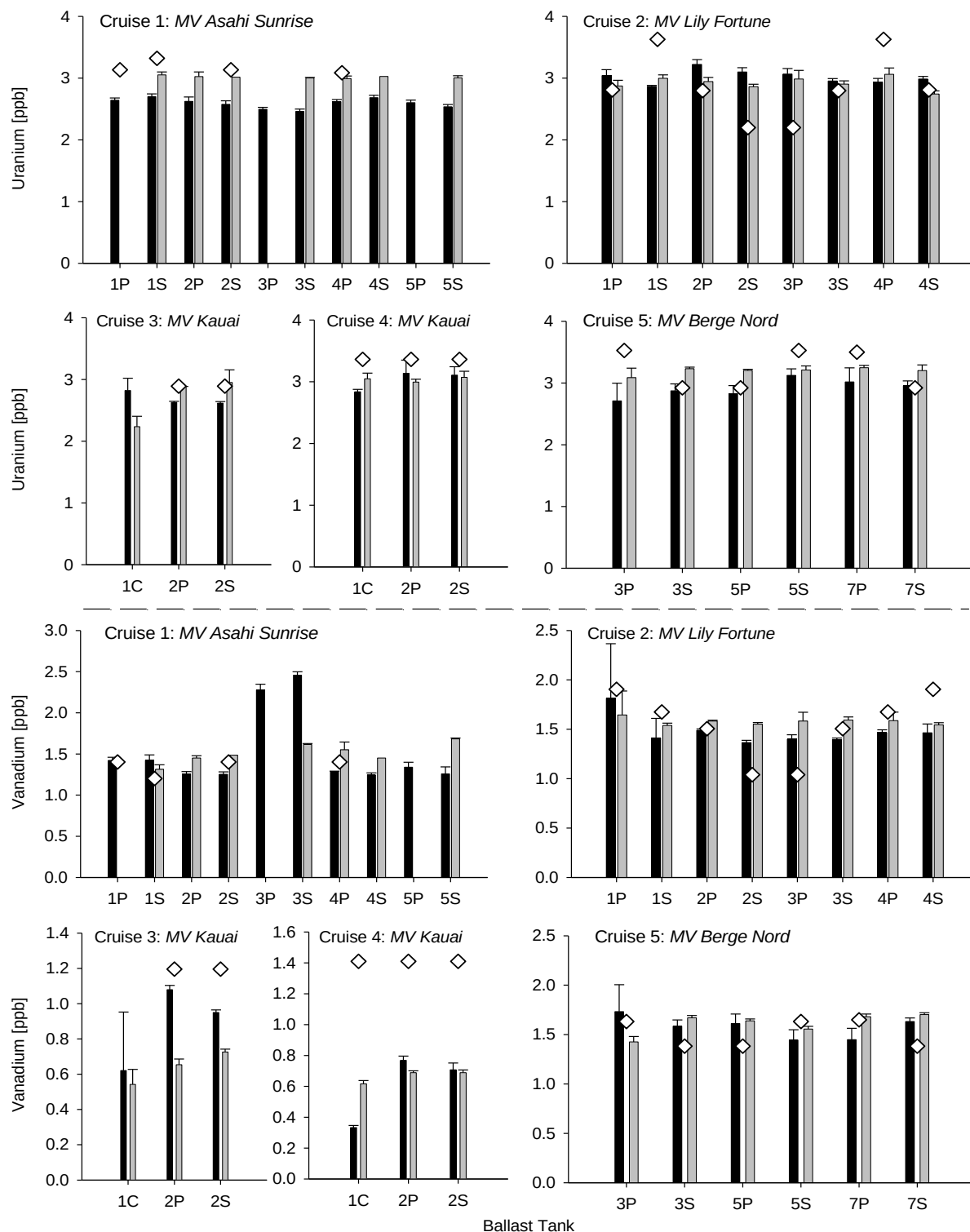


Figure 22. Effect of BWE on total dissolved Uranium and Vanadium in ships' ballast tanks (P = port tank, S = starboard tank, C = center tank). Concentrations in ppb ($\bar{x} + SE$) are shown before BWE (■), after BWE (■) and in shipside samples when collected during BWE (◇).

On Cruise AS, nearshore concentrations of Mn of 7-28 ppb decreased to baseline ocean levels (< 2 ppb) by the time the ship traveled 10 nmi offshore. Spikes of up to 6 ppb were seen in four consecutive samples beginning around 200 nmi offshore and are of unknown origin. On Cruise K1 out of California, Mn concentrations dropped precipitously from greater than 20 ppb to less than 3 ppb within 10 nmi of the coast. In the vicinity of Hawaii, Mn concentrations displayed two separate trends as the vessel approached and departed Honolulu. While approaching Hawaii, tracer levels barely increased above background ocean levels right up to docking in Honolulu. When the vessel departed two days later, Mn concentrations were high (12 ppb) and followed a gradual decline to ocean concentrations (~ 5 ppb) over about 80 nmi. The interpretation of these data is unclear and suggests that surface Mn levels were spatially and temporally variable. A possible explanation is that the ship's draft, and hence sampling depth, changed as a result of offloading cargo in Honolulu. Alternatively, the data may be unreliable for a reason as yet unexplained. Certainly, baseline levels of Mn in shipside samples on this cruise (~ 5 ppb) significantly exceed levels from all other cruises (< 1 ppb). Levels of Mn increased from the baseline as the vessel approached Seattle, peaking at ~ 6 ppb.

In the North Atlantic on Cruise BN, levels of Mn were lower than on Pacific cruises. With the single exception of samples collected while ballasting in port (7.5 ppb), all samples had Mn concentrations lower than 0.8 ppb. Since the first shipside samples were collected almost 20 nmi from the coast, the only thing known for certain in regard to the rate of decline of Mn as a function of distance from shore on this cruise is that oceanic levels of Mn were achieved before the vessel was 20 nmi offshore.

Phosphorus

Concentrations of P in shipside samples were also variable among Pacific cruises. Counter to trends seen on previous cruises, concentrations of P on Cruise LF increased with distance from shore, such that concentrations in the Eastern North Pacific (particularly in the Gulf of Alaska) were higher than in the Western region. This trend was independently corroborated by data from exchanged ballast tanks on this and other cruises, thus accounting for temporal variation and suggesting that open-ocean levels of P in the North Pacific are geographically variable. On Cruise AS also in the North Pacific, elevated P is seen both close to the North American and Asian (Japan, China) coastlines and far from either in the North Pacific Ocean. A more

traditional distribution was seen on Cruise K1 departing California, with levels of P declining exponentially over the first 100 nmi of the cruise. Thereafter, concentrations of P near the island of Hawaii were indistinguishable from oceanic levels (< 6 ppb) until gradually increasing as the vessel headed Northeast, beginning more than 800 nmi from Seattle. In the North Atlantic on Cruise BN, levels of P in shipside samples decreased from 30 ppb to ~ 5 ppb in the first ~ 40 nmi offshore (including the English channel), and were similar to levels off the Californian coast for most of the Atlantic Ocean, until beginning to increase again within 20 nmi of Brazil.

Barium

There was no clear trend relating Ba with distance from shore on Cruise LF. Similarly, the relationship on Cruise AS was complex and indicated that geographical factors other than distance from shore were controlling the distribution of Ba (e.g., the presence of upwelling regions). On Cruise K1 out of California, Ba concentrations declined precipitously from approximately 16 to 7 ppb within 2 miles of San Francisco Bay, and then gradually declined from approximately 6 ppb to 4 ppb as the vessel sailed west to Hawaii. These low levels of Ba persisted during Cruise K2 until samples were collected after the vessel had arrived in Puget Sound.

In the North Atlantic on Cruise BN, Ba declined approximately linearly from around 14 ppb over approximately the first 60 nmi of the cruise. Mid-ocean levels were consistent at around 6 ppb, and did not increase again until the vessel was less than 20 nmi from Brazil.

Other Trace Elements

The remaining trace elements measured in shipside samples during this project (U, V) showed no discernable geographical trends.

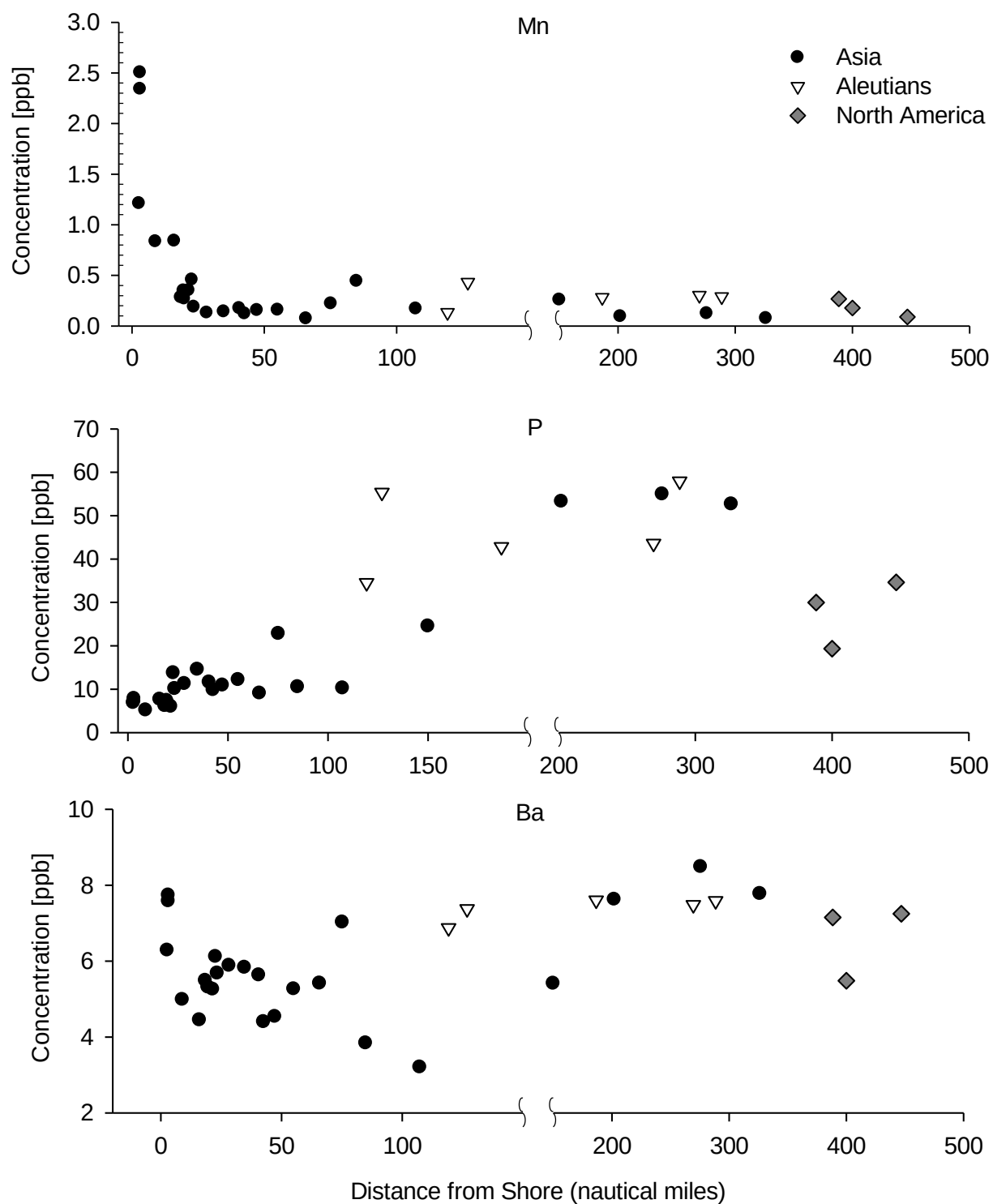


Figure 23. Trace elements on Cruise LF. Surface ocean total dissolved concentrations of trace elements (Mn, P, Ba) while departing Japan and sailing to North America via the Aleutian Islands.

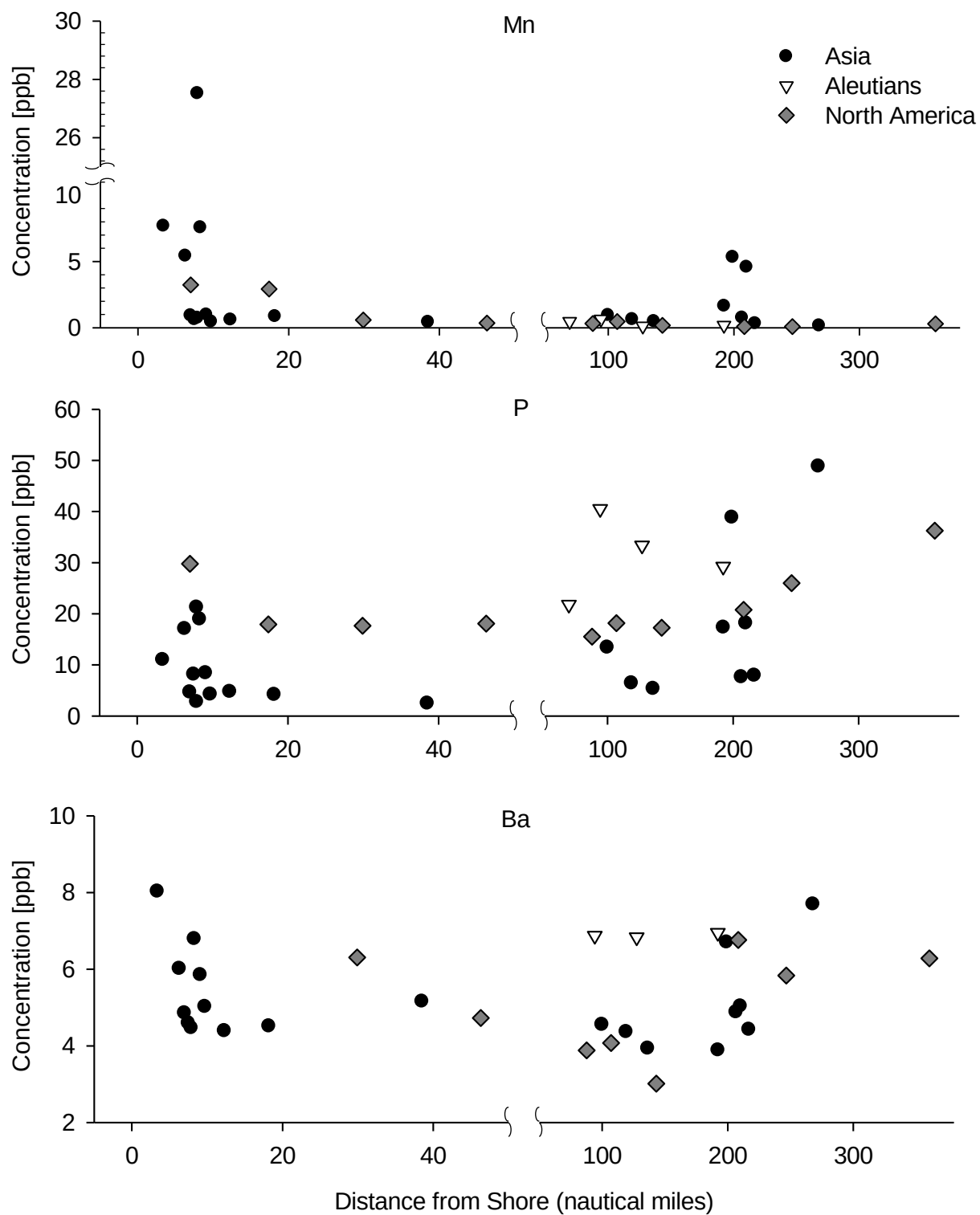


Figure 24. Trace elements on Cruise AS. Surface ocean total dissolved concentrations of trace elements (Mn, P, Ba) while departing Japan and sailing to North America via the Aleutian Islands.

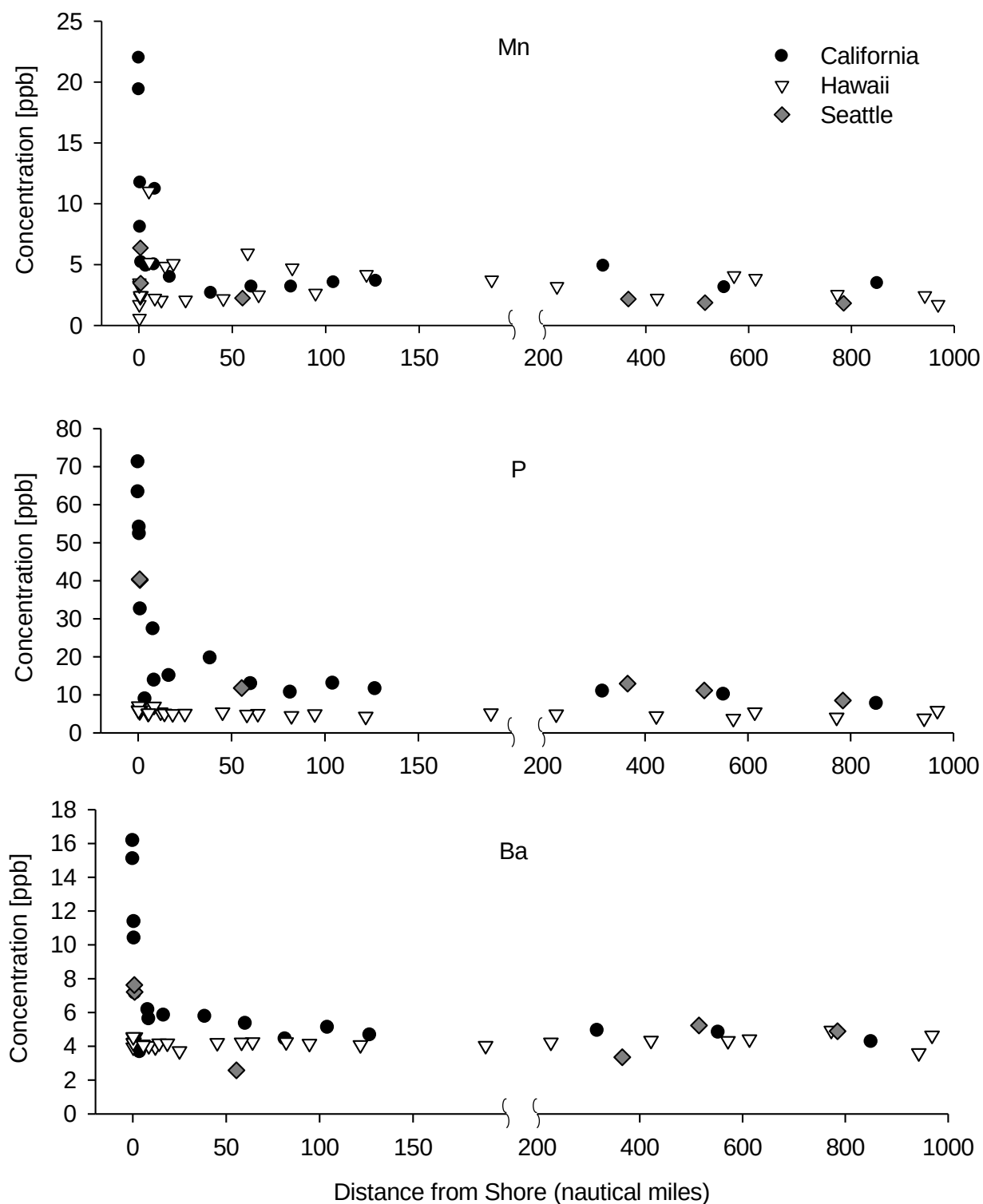


Figure 25. Trace elements on Cruise K1 and K2. Surface ocean total dissolved concentrations of trace elements (Mn, P, Ba) while departing California and approaching Hawaii on Cruise K1 and while departing Hawaii and approaching Seattle on Cruise K2.

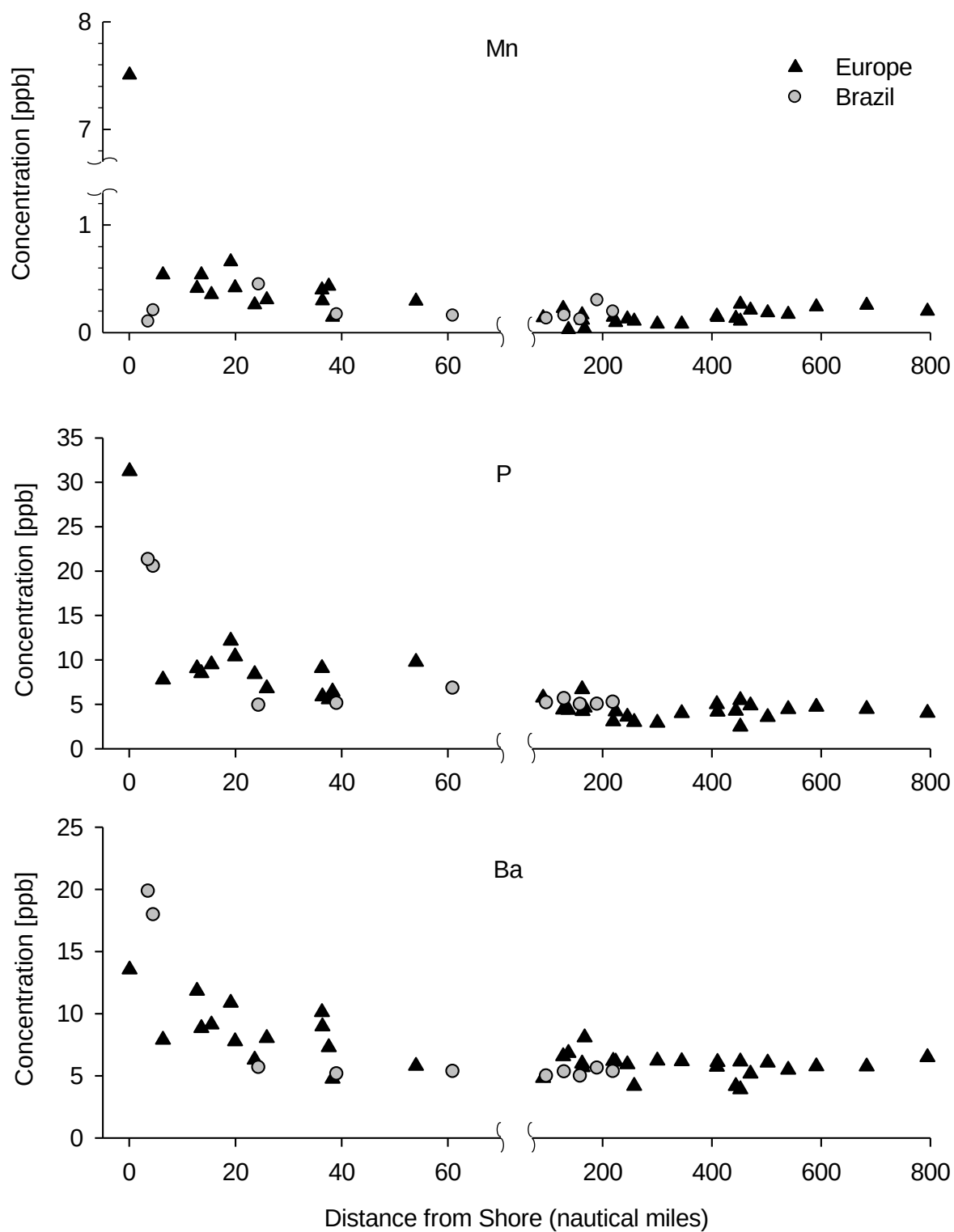


Figure 26. Trace elements on Cruise BN. Surface ocean total dissolved concentrations of trace elements (Mn, P, Ba) while departing Europe and approaching Brazil.

3.4. Radium

Radium was a consistent indicator of BWE, with higher concentrations prior to BWE on all cruises. However, the precision and accuracy of most measurements were constrained by inaccuracies in measurement of sample volumes on listing vessels and by technical/equipment constraints upon controlling flow rates through the Mn-filters (thus affecting extraction efficiency and ultimately the estimation of ^{223}Ra concentrations). Additionally, ^{223}Ra undergoes exponential radioactive decay with a half life (time until disappearance of half its original amount) of approximately 11.4 days (274 hours). Decay times (time between collection and analysis of sample) exceeded 300 hours for most samples, which led to decreased measurement sensitivity, particularly at low concentrations.

Problems with sampling precision were clearly evident from the large error bars associated with replicate ^{223}Ra measurements on Cruise LF (seen later in Figure 28). The subsequent cruises used a modified sampling protocol (Section 2.1.1) with a double fiber system, which allowed extraction efficiencies to be calculated and measurements to be adjusted to account for variable efficiencies. Extraction efficiencies for these cruises were AS: 94.8 ± 0.01 percent; K: 80.6 ± 0.03 percent and BN: 84.7 ± 0.03 percent. While we could not measure extraction efficiencies on Cruise LF, the very slow flow rates (less than all other cruises) that resulted from the sampling method used on Cruise LF probably resulted in high extraction efficiencies relative to other cruises, and consequently, the corrected and uncorrected ^{223}Ra concentrations would likely have been similar. The high inter-replicate variability seen on this cruise may thus have resulted predominantly from failures in standardizing sample volumes.

3.4.1. Tracer Stability

Tank Holding Effects

It was difficult to determine the effect of tank residence time on ^{223}Ra concentrations because of low replication and sampling frequency on most cruises. Sampling frequency was highest on Cruises AS and BN and for most unexchanged tanks, sampling was repeated over time. For these tanks, ^{223}Ra concentrations were approximately stable over time (Figure 27).

Storage Time Effects

Since ^{223}Ra undergoes exponential radioactive decay, all measurements of ^{223}Ra must be corrected to account for the period of time that elapsed between isolating the ^{223}Ra in the sample from its source and measuring it in the laboratory. Providing that no sources of ^{223}Ra exist within the ballast tanks, the date of isolation will correspond to the date that the ballast water entered a tank. However, given that the objective of this study was to identify a verification method that can be applied independent of any information on a tank's ballasting history, decay times were calculated with reference to the date that the sample was collected.

3.4.2. Effect of Ballast Water Exchange

On all cruises, concentrations of ^{223}Ra decreased following BWE. This is evident in comparisons of the effect of BWE on ^{223}Ra measured in single fibers (Cruise LF) or the first fiber in series (all other cruises) (Figure 28). It is similarly evident when data are corrected for extraction efficiency (Figure 29), which reduced overall sample variability. In unexchanged ballast water, mean ^{223}Ra concentrations corrected for extraction efficiency were 0.86 ± 0.11 dpm/100 L (range: 0.25 – 2.1 dpm/100 L).

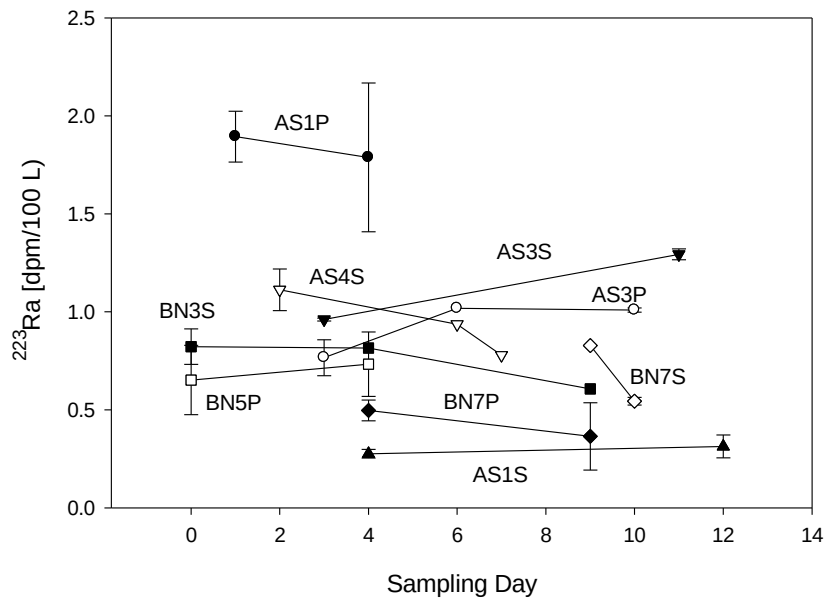


Figure 27. Effect of tank residence time upon ^{223}Ra (corrected for extraction efficiency), in port (P) and starboard (S) ballast tanks on two cruises (Cruises AS, BN).

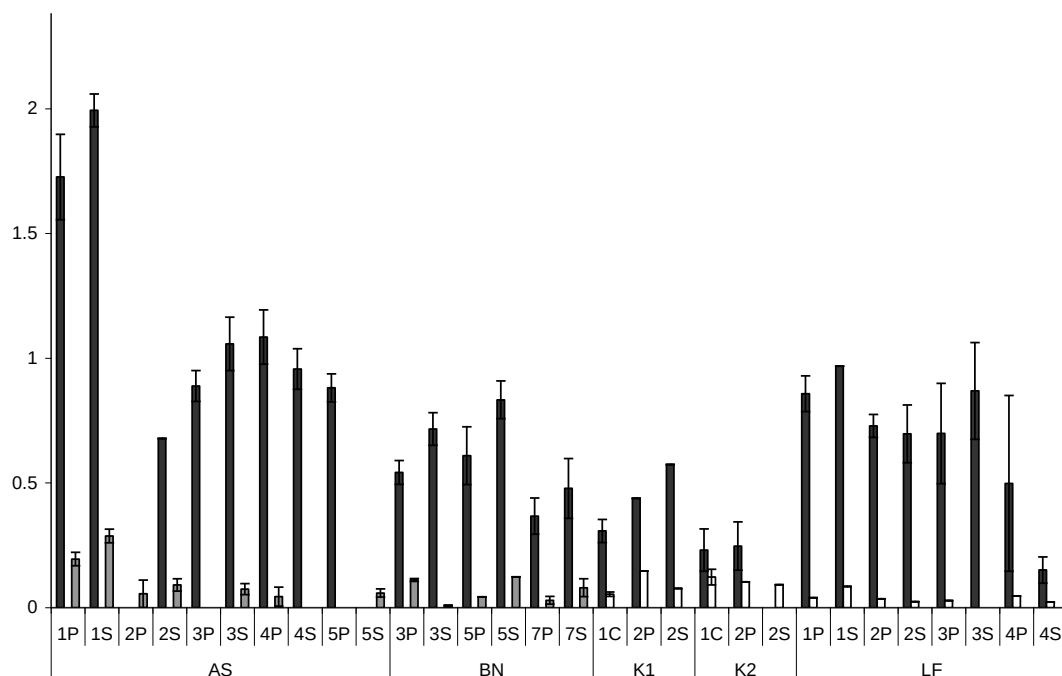


Figure 28. The effect of BWE on ^{223}Ra [dpm/100 L] in ballast tanks (P = port wing, S = starboard wing, C = center) on five cruises (AS, BN, K1, K2, LF). To enable comparison across all cruises, measurements are shown for single Mn-fibers and thus are not corrected for extraction efficiency. Treatments were control (■), FT (■) or ER (□). Samples without visible error bars (± 1 SE) were not replicated.

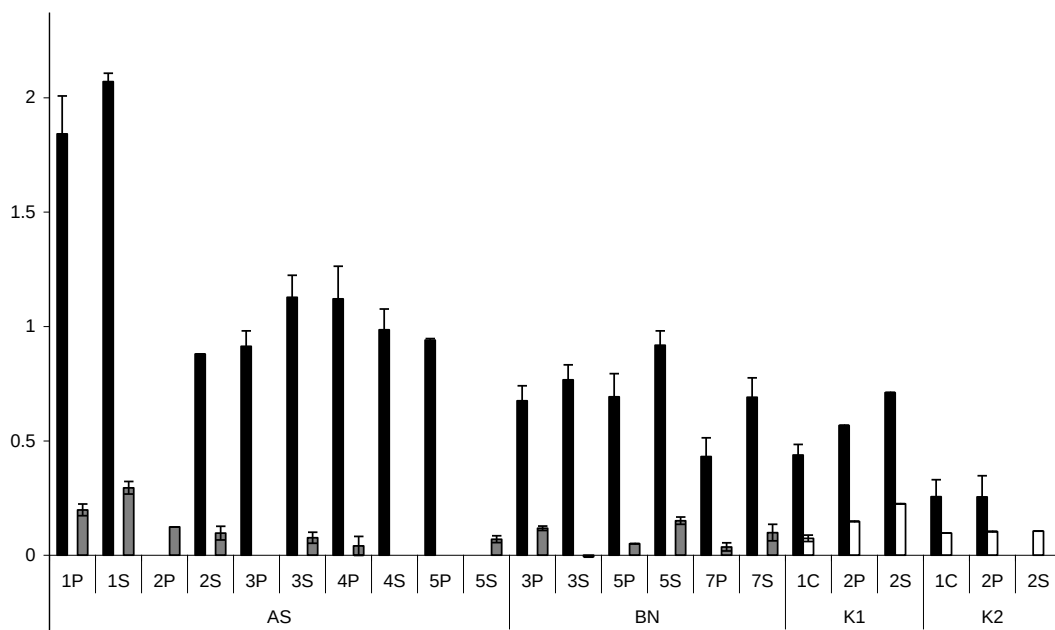


Figure 29. The effect of BWE on ^{223}Ra [dpm/100 L] in ballast tanks (P = port wing, S = starboard wing, C = center) on four cruises (Cruises AS, BN, K1, K2). Measurements are corrected for extraction efficiency; samples for which this is unknown are missing data. Treatments were control (■), FT (■) or ER (□). Samples without visible error bars (± 1 SE) were not replicated.

In samples from unexchanged tanks, concentrations exceeded 0.5 dpm/100 L with two exceptions: (1) tanks ballasted in Honolulu on Cruise K2 where concentrations were approximately 0.25 dpm/100 L; and (2) tank 4S on Cruise LF, which was mixed with older ballast water from Korea and where concentrations were approximately 0.49 dpm/100 L. These tanks were also outliers for other tracers, e.g. Mn. In exchanged ballast tanks, concentrations of ^{223}Ra were less than 0.3 dpm/100 L in all samples, with mean concentrations 0.13 ± 0.02 and 0.11 ± 0.02 dpm/100 L in ER and FT tanks respectively.

3.4.3. Ocean Transects

Concentrations of ^{223}Ra in shipside samples were, with few exceptions, less than 0.1 dpm/100 L. The exceptions were samples collected in port or close to the coast. In some cases, coastal samples had levels below detection limits. This may have been partially attributable to the error introduced by relatively long decay times - up to three weeks elapsed before all samples could be processed in the laboratory.

In the Pacific Ocean, concentrations in samples collected close to Hawaii were not measurably higher than in samples collected far offshore (Figure 30). Elevated concentrations were seen for one sample collected in San Francisco Bay (0.7 dpm/100 L) and one sample collected near Japan (1.0 dpm/100 L). On Cruise BN in the Atlantic, elevated levels of ^{223}Ra were measured in the English Channel (Figure 31). There was a further suggestion that concentrations in the Atlantic Ocean may have increased in a southerly direction, however, data are too few to make definitive conclusions in this regard.

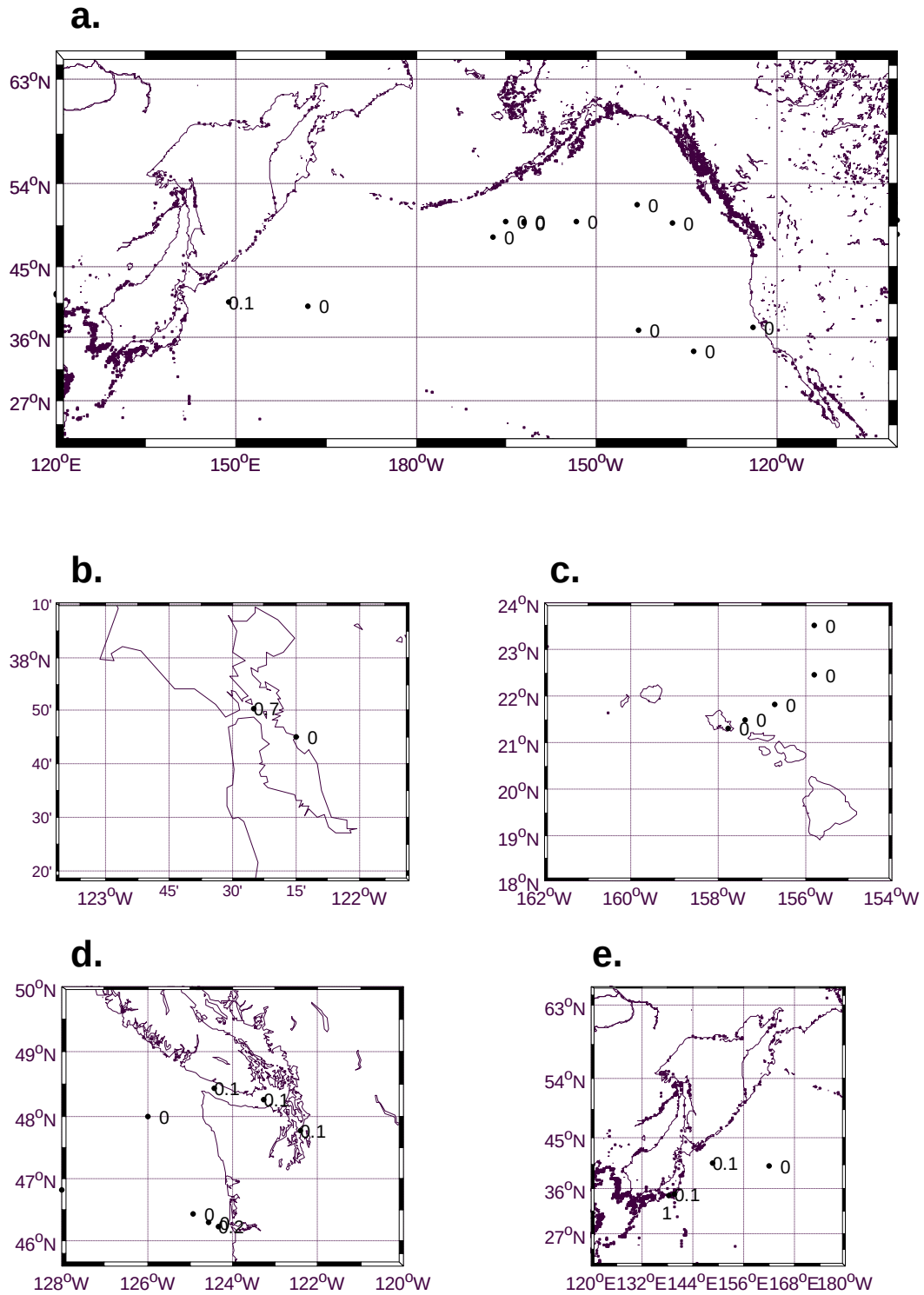


Figure 30. ^{223}Ra in the Pacific Ocean. Maps show concentrations [dpm/100 L] measured in (a) the offshore Pacific Ocean, or in coastal locations near (b) San Francisco/Oakland; (c) Hawaii; (d) Seattle; (e) Japan.

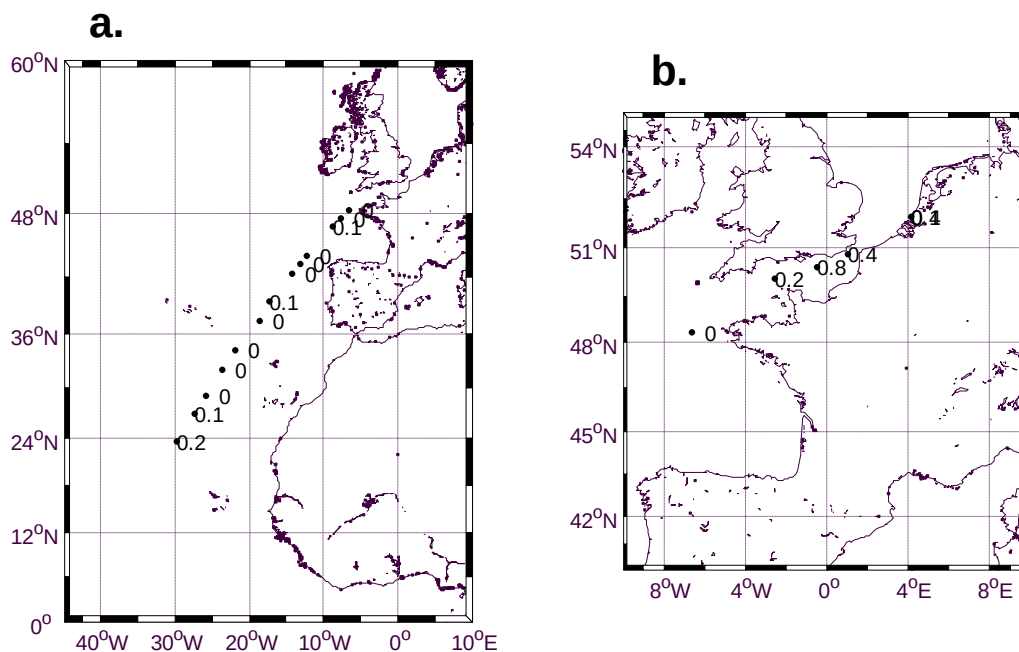


Figure 31. ^{223}Ra in the Atlantic Ocean. Maps show concentrations [dpm/100 L] measured in (a) the offshore Atlantic Ocean; (b) near Rotterdam and throughout the English Channel.

4. Conclusions

The goal of this study was to build upon initial research on the utility of CDOM, radium and trace metals for verifying BWE. While preliminary research indicated that all three approaches held promise, it was unclear whether the results were robust or could be extended into new ocean regions. Additionally, since questions remained regarding the stability of tracers in ballast tanks, it was considered critical to gather more data on the behavior of those tracers in ballast tanks. Finally, with the possible future designation of acceptable locations of BWE within 200 nmi of shore, understanding the rate at which tracer signal strength changes in the transition between ports (onshore) and open ocean (offshore) was clearly an important issue for verification of BWE.

Overall, while a few tracers were successful indicators of BWE on every cruise, none were unambiguous indicators across all cruises. Most tracers were successful indicators on the

Atlantic cruise. Conversely, concentrations in samples sourced from Honolulu Harbor, coastal Hawaii and the Northeast Pacific Ocean were quite similar for most tracers.

For several tracers examined in this study, concentrations were highest in port and near the coast, and decreased in response to BWE. This is the classic response expected from a terrestrially-sourced tracer. This trend was seen consistently for CDOM, ^{223}Ra and Mn. For most other trace elements (Ba, P, Mo, U and V), this trend was reversed on some, or all, cruises and in some, or all, of the ballast tanks. Generally, this reversal was due to elevated background levels in the northeastern Pacific Ocean (west of Seattle), where many BWE events took place. The inclusion of this geographic region in this study thus brought into doubt the effectiveness of trace elements as indicators of BWE.

CDOM was a reliable indicator of BWE on each cruise, with fluorescence intensities always indicating higher concentrations in port water and unexchanged ballast tanks relative to offshore water and tanks subject to BWE. Trends for the A- and C-peak regions were similar. At wavelengths within the region measured by DTI's Ballast Exchange Assurance Meter, a threshold of approximately 1 ppb QSE delineated exchanged from unexchanged ballast water in four of five cruises. Cruise K2 was the exception to this rule; tanks ballasted in Honolulu had levels of CDOM similar to tanks exchanged in the open ocean on previous cruises.

Radium was also a consistent indicator of BWE on each cruise, although as for CDOM and trace elements, no single threshold could be found that applied to all cruises. Additionally, radium data were time-consuming to collect and by necessity infrequent, relative to trace elements and CDOM. This is a substantial disincentive for devoting further efforts to this tracer, at least until sampling protocols progress to the point that samples can be collected with much greater ease than is currently possible.

Results for trace elements were mixed. The earlier BWE verification study found Ba to be a consistent indicator of BWE, with initial concentrations in unexchanged ballast tanks typically above 10 ppb and concentrations following BWE below 7 ppb. Whereas data from Cruises BN and K1 in this study support these results, data from other cruises do not. In this study, all tanks with Japanese ballast water (i.e. Tanks 3s, 3p on Cruise AS; all tanks on Cruise LF) had relatively low initial concentrations of Ba (~ 8 ppb). At the same time, concentrations in ballast

tanks exchanged in the northeastern Pacific and in shipside samples from the same region were also around 8 ppb, resulting in no noticeable effect of BWE. On Cruise K2 out of Honolulu, initial levels of Ba were low (~ 6 ppb) in two of three tanks and thus indistinguishable from oceanic water.

The earlier study also found Mn and P to be potential indicators of BWE, despite questions about their stability in tanks over time. Both qualities were confirmed in this study. Mn was unstable over time, with a net loss (scavenging) from the water column. Since Mn is highly reactive, it adsorbs to particulate matter and gradually settles from the water column. The highest rate of loss of Mn was seen on Cruise BN, which had the deepest ballast tanks and therefore the least potential for replenishment of the upper water column by release of Mn from the sediments. The behavior of P was more complex, with measurable but smaller fluctuations seen in either direction, possibly due to biological activity.

Despite the rapid depletion of Mn from ballast water, Mn was a consistent indicator of BWE across all cruises, with Mn in exchanged ballast water always less than 1 ppb. However, due to scavenging, Mn would not have been useful for detecting unexchanged ballast on Cruise BN if the port water had been held in the tank for more than one week. P was a useful tracer on the Atlantic cruise, but its utility in the Pacific was dependent on the location of BWE. Similar to Ba, concentrations of Mn in the eastern Pacific were elevated relative to other Pacific Ocean regions and in some cases also relative to coastal waters.

Tracer concentrations were measured in ambient (shipside) samples on the cruises to aid characterization of the decay function for terrestrial signals with distance from shore. In few cases, if any, did decay functions extend the full 200 nautical miles to the boundary of the EEZ. This result is not unexpected, since the EEZ boundary is a political boundary and is not derived from relevant biogeographical processes. The large range of decay functions seen in this study suggest that in many cases it will be difficult or impossible to determine whether BWE was performed 50 or 200 nmi from shore. On the other hand, since there appears to be a range of possible decay functions that vessel operators are unlikely to know how to predict, this uncertainty provides an incentive to conduct BWE far from shore.

For most tracers, terrestrial signatures disappeared between 5 and 100 nmi from the coast. Elevated trace element signals often extended farther offshore than elevated CDOM signals, which usually penetrated no further than 10 nmi. The frequency of radium sampling was too low to reliably determine the persistence of ^{223}Ra on an offshore transect. In many cases, factors other than distance from shore appeared to drive offshore concentration profiles. Future work should examine the degree to which a wider range of factors, including ocean bathymetry and circulation, can be used to predict the observed patterns.

5. Recommendations

The next steps in development and implementation of the chemical tracer method for BWE verification require (a) multivariate analysis of tracer performance across all cruises conducted to date (nine in total), (b) measurement of tracer concentrations in several global regions at higher spatial and temporal resolution, (c) determination of concentration thresholds expected to discriminate exchanged and unexchanged ballast water in a high proportion of vessel types, routes and trading activities, and (d) demonstration of BWE verification for ships arriving to U.S. ports.

Recommendations for further research

Future priorities for BWE verification research thus include the following elements:

- ❖ Determine whether overall discrimination between port and mid-ocean water can be improved by combining data from multiple tracers. This is particularly relevant for the most difficult cases, e.g. the cruise from Honolulu, which featured highly saline, oligotrophic ballast water.
- ❖ Determine the magnitude of spatial and temporal variation within ports (bay and estuaries). These data are necessary to test for consistent differences between ports (unexchanged) from ocean (exchanged) water, regardless of season and specific location.
- ❖ Understand the drivers for changing tracer signal strengths with increasing distance from shore. In this study, we have found the shape of the offshore ‘decay’ function to vary among tracers and regions. Since it is not feasible to measure the function for all regions in all seasons, we wish to identify the drivers of change, and use these to predict the

function. Possible drivers include ocean bathymetry, circulation and sea-surface temperature, among others.

- ❖ Determine thresholds for single tracers or combinations of tracers that give the best results for a high proportion of vessel types, routes and trading activities. It is clear that any thresholds set for exchanged ballast water must take into account spatial and temporal variability in tracer concentrations in potential source ports and the imperfect efficiency of BWE. Thus thresholds must be sufficient to prevent false positives due to residual port water, even if this reduces the likelihood of detecting unexchanged ballast water sourced from a small number of highly saline, oligotrophic ports.
- ❖ Test and refine the application of concentration thresholds on a broad range of ships upon arrival to U.S. West Coast ports, including those arriving from ports that have been well characterized. Measurements on a broad range of ships will help prioritize tracer performance based upon dominant source regions and route characteristics.

Recommendations for Coast Guard BWE verification

As discussed in this report, no tracer tested proved to be capable of discriminating open ocean from coastal water or exchanged from unexchanged ballast water for all tanks on all cruises or all routes. Some, such as CDOM, were very consistent with only a few exceptions. Others, such as Mo, have patchy distributions or are otherwise unreliable. For the purposes of Coast Guard BWE verification efforts, the following recommendations are made.

- ❖ CDOM can be a viable tracer for BWE verification.
 - Concentrations are nearly an order of magnitude greater in ports than in the open ocean. (Exceptions: High salinity, oligotrophic waters such as around Hawaii).
 - Samples are easy to take and relatively easy to analyze.
 - A and C peaks form in similar regions (Similar wavelength pairs) for all samples taken.
 - Problems such as inner filter effects (tendency for elevated concentrations to not increase readings) are unlikely to affect BWE determinations.

- Portable instruments measuring fluorescence at appropriate wavelengths can be used (i.e., DTI BEAM).
 - Cutoff values for inshore/open ocean can be determined. Based on this study, the recommended cutoff value for the DTI BEAM is 1 QSE except for rare instances described above.
 - Recommend CDOM be pursued as tracer for BWE verification.
- ❖ Ra^{223} is not currently suitable as a tracer for BWE.
- Concentration distribution is classic – high near shore and low in open ocean waters.
 - Samples are difficult to obtain, i.e., very large volumes of ballast water are required.
 - Rapid analysis of samples is required due to short half-life (~11.4 days).
 - Short half-life means coastal ballast water stored in ballast tanks for several weeks will resemble open ocean water.
 - Recommend Ra^{223} not be pursued further for routine BWE verification.
- ❖ Mn is not a viable tracer of BWE.
- Like CDOM and Ra^{223} , Mn distribution is classic – high nearshore and very low in open ocean.
 - Concentrations in ballast tanks decrease rapidly due to adsorption. Within five days, unexchanged ballast tanks resemble open ocean concentrations.
 - Recommend Mn not be pursued further for routine BWE verification.

- ❖ Ba is an inconsistent tracer of BWE.
 - Concentrations from shore to open ocean were highly variable and had no consistent trend.
 - Low, open ocean concentrations could occur within five miles of the coast.
 - Data from earlier research cruises indicated Ba is potentially a suitable tracer.
 - More research could better define Ba as a tracer.
 - Recommend Ba be pursued further to determine value for BWE verification.
- ❖ Other trace elements are inconsistent or not suitable as tracers for BWE.
 - Mo distribution in the open ocean is patchy.
 - U and V have no discernable geographic trends.
 - U and V concentrations were similar in exchanged and unexchanged tanks.
 - P distribution was highly variable in ports but relatively invariable over large areas and long periods of time in the open ocean. Eastern Pacific concentrations were higher than western Pacific concentrations.
 - Recommend U, V, and Mo not be pursued further for routine BWE verification.
 - Recommend P be pursued further to determine value for BWE verification.

Based on the results of this and previous research, it is recommended that CG:

- ❖ Continue research by looking closely at the decay functions of CDOM, Ba, and P with distance from shore.
- ❖ Define offshore limit for BWE that can be supported by verification techniques.
- ❖ Conduct multi-variate analysis of data collected by researchers thus far.

- ❖ Continue to develop a CDOM probe for practical, shipboard use.
- ❖ Select a CDOM cutoff limit for BWE evaluations. The 1QSE value provided here is recommended as a starting point.

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7. Acronyms Used in Appendices A – E

A number of common terms and acronyms are used in Appendices A – E. Terms have previously been described within the report but are listed here for ready reference.

Cruises

LF	Cruise 1: Haramachi, Japan – Vancouver, Canada
AS	Cruise 2: Yokkaichi, Japan – Portland, Oregon
K1	Cruise 3: Oakland/San Francisco – Honolulu
K2	Cruise 4: Honolulu – Seattle
K	Cruises 3 & 4, as above.
BN	Cruise 5: Rotterdam, Netherlands – Sao Luis, Brazil

Treatments, tanks and sample identifiers

ExchID	Exchange event identification
C	Control (unexchanged) ballast tank
ER	Empty-Refill ballast water exchange
FT	Flow-Through ballast water exchange
SS	Shipside
c	Center ballast tank, e.g. Tank 1c
p	Port side ballast tank, e.g. Tank 1p
s	Starboard side ballast tank, e.g. Tank 1s
w	Wing tank
x_i	Exchange initiation
x_f	Exchange completion
A1 – A13	Turner fluorometer measurements
Rad A, Rad B	Radium sample columns
λ_{ex} , λ_{em}	Wavelengths of excitation, emission
CDOM	Colored Dissolved Organic Matter

Other

BWE	Mid-ocean ballast water exchange
EEM	Excitation – emission matrix
GMT	Greenwich Mean Time
GPS	Global Positioning System
$^{\circ}\text{N}$, $^{\circ}\text{S}$	North latitude, South latitude (South shown as negative)
$^{\circ}\text{E}$, $^{\circ}\text{W}$	East longitude, West longitude (West shown as negative)
am, pm	Before noon, after noon
Dates	Provided as day/month/year

Measures and Units

MT	Metric tons
nm	Nanometers (10^{-9} m)
nmi	Nautical miles (= 1852 m precisely)
ppb	Parts per billion
ppt	Parts per thousand
QSE	Quinine-sulfate equivalent units

APPENDIX A - Spectral comparisons for CDOM fluorometers

To detect if there were systematic differences between spectra collected by different laboratories, intercalibration of the three fluorometers used during this study was performed during a two week period in October 2004 using Quinine Sulfate Standard Reference Material (SRM 936) (50 ppb).

Laboratories that participated in the study included the University of South Florida using a SPEX FluoroLog-2; University of Maine using a SPEX FluoroMax-2; National Environmental Research Institute, Denmark, using a Varian Cary Eclipse. Each laboratory used their standard EEMs collection and correction protocols and produced fully corrected EEMs from scans at 20 °C.

When normalized to peak height, emission scans for the reference material at $\lambda_{\text{ex}} = 350$ nm corresponded closely to the relative technical emission spectrum for Quinine Sulfate dehydrate of Velapoldi and Mielenz (1980) (Figure A-1), referred to hereafter as the technical emission spectrum. For all three instruments, deviations from the technical emission spectrum were less than ± 10 percent of peak height (data lying within horizontal grey lines) across most of the wavelength range. The Varian was operated at a low sensitivity setting and displayed relatively high scatter.

All three instrument curves displayed similar slight shoulders at emission wavelengths 380-430 nm, due to incomplete correction for Raman interference scatter ($\lambda_{\text{ex}} = 398\text{-}428$ nm at $\lambda_{\text{ex}} = 350$ nm). The FluoroMax-2 has a single monochromator on the emission side, allowing the detection of scatter peaks at wavelengths corresponding to secondary Rayleigh and Raman scatter (i.e., $\lambda_{\text{ex}} \sim 500, 545 \pm 15$ nm at $\lambda_{\text{ex}} = 250$ nm). The interpretation of CDOM data in this study focuses on regions of EEMs that are unaffected by scatter processes.

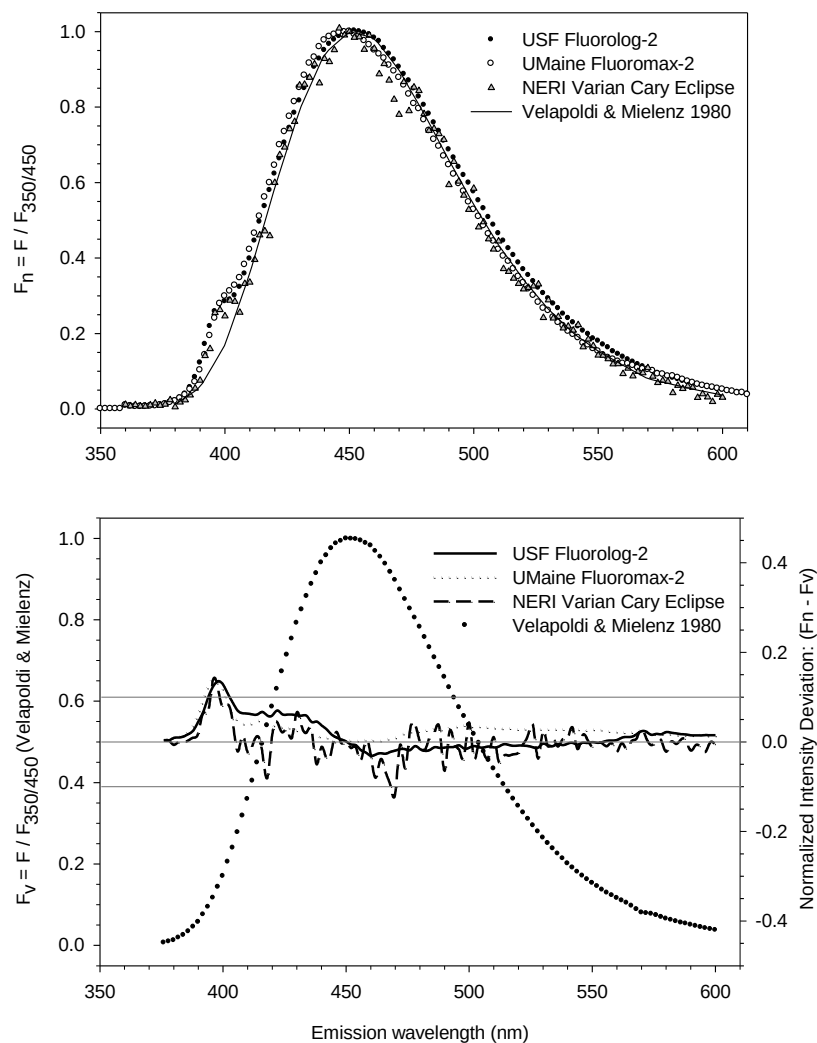


Figure A-1. Normalized emission scans from fluorometers in this study, compared with the relative technical emission spectrum of Velapoldi & Mielenz (1980). A) Emission scan at $\lambda_{\text{ex}} = 350$ nm of Quinine Sulfate dehydrate standard (50 ppb); B) Deviations relative to the Velapoldi curve at $\lambda_{\text{ex}} = 350$ nm. For wavelengths unaffected by Raman scatter, deviations are less than ± 10 percent of peak height (data lying within horizontal grey lines).

APPENDIX B - Cruise LF experimental design and sampling

Table B-1. Ballasting and exchange details on Cruise LF.

Ballasting at the port of Haramachi was performed episodically over several days; times and locations are given as a volume-weighted mean. Time and location of ER exchanges are also provided as means.

ExchID	Tank	Local Date/Time	GMT Date/Time	Latitude (°N)	Longitude (°E / -°W)	Process	Location	BWE %	Vol. (MT)
1	1p	4/06/03 18:50	4/06/03 10:50	37.67	141.02	Ballast	Haramachi	100	3767
2	1s	4/06/03 18:50	4/06/03 10:50	37.67	141.02	Ballast	Haramachi	100	3767
3	2p	4/06/03 12:34	4/06/03 4:34	37.67	141.02	Ballast	Haramachi	100	9388
4	2s	4/06/03 12:34	4/06/03 4:34	37.67	141.02	Ballast	Haramachi	100	9388
5	3p	4/06/03 12:31	4/06/03 4:31	37.67	141.02	Ballast	Haramachi	100	9625
6	3s	4/06/03 12:31	4/06/03 4:31	37.67	141.02	Ballast	Haramachi	100	9625
7	4p	6/06/03 16:10	6/06/03 7:10	37.67	141.02	Ballast	Haramachi	100	3817
8	4s	6/06/03 16:10	6/06/03 7:10	37.67	141.02	Ballast	Haramachi	100	3817
9	1s	9/06/03 9:30	8/06/03 23:30	46.03	159.83	ER	Ocean	100	3767
10	4p	11/06/03 0:15	10/06/03 14:15	46.03	159.83	ER	Ocean	100	3817
11	2p	12/06/03 11:22	12/06/03 22:22	49.99	-165.14	ER	Ocean	100	9388
12	3s	13/06/03 1:45	13/06/03 12:45	49.99	-165.14	ER	Ocean	100	9625
13	1p	13/06/03 16:07	14/06/03 2:07	54.99	-154.34	ER	Ocean	100	3767
14	4s	14/06/03 4:45	14/06/03 14:45	54.99	-154.34	ER	Ocean	100	3817
15	2s	14/06/03 17:30	15/06/03 2:30	50.00	-145.01	ER	Ocean	100	9388
16	3p	12/06/03 4:45	12/06/03 13:45	49.99	-145.01	ER	Ocean	100	9625

Table B-2. Sources of shipside radium samples on Cruise LF.

GPS positions are presented as means, with error shown as distance along the cruise track.

Set	Collection Date & Time (GMT)	Latitude (°N)	Longitude (°E / -°W)	LF-Rad A	LF-Rad B	Error (distance in nmi)
1	9/06/2003 11:30	49.81	-161.88	1231	-	7
2	10/06/2003 8:54	48.34	-167.20	1232	-	7
3	12/06/2003 10:00	50.00	-164.99	1233	-	7
4	12/06/2003 19:42	49.98	-161.88	1234	-	7
5	13/06/2003 19:15	50.00	-153.20	1235	-	7
6	15/06/2003 12:00	49.83	-137.32	1236	-	7

Table B-3. Sources for shipside CDOM/trace element samples on Cruise LF

No.	Collection Date/Time	Source Location		LF-	LF-
	(GMT)	Latitude (°N)	Longitude (°E /-°W)	CDOM	Trace Element
1	05-JUN-03 09:37	37.67	141.02	1171	1121
2	05-JUN-03 09:37	37.67	141.02	1172	1122
3	06-JUN-03 05:00	37.66	141.14	1173	1123
4	06-JUN-03 05:30	37.73	141.26	1174	1124
5	06-JUN-03 06:00	37.80	141.38	1175	1125
6	06-JUN-03 06:29	37.87	141.50	1176	1126
7	06-JUN-03 07:00	37.94	141.62	1177	1127
8	06-JUN-03 07:29	38.00	141.74	1178	1128
9	06-JUN-03 08:00	38.07	141.86	1179	1129
10	06-JUN-03 08:31	38.14	141.99	1180	1130
11	06-JUN-03 09:02	38.22	142.11	1181	1131
12	06-JUN-03 09:31	38.29	142.23	1182	1132
13	06-JUN-03 10:06	38.38	142.38	1183	1133
14	06-JUN-03 10:32	38.44	142.50	1184	1134
15	06-JUN-03 11:00	38.50	142.62	1185	1135
16	06-Jun-03 12:00	38.65	142.90	1186	1136
17	06-Jun-03 13:00	38.80	143.17	1187	1137
18	06-Jun-03 14:00	38.96	143.47	1188	1138
19	06-Jun-03 15:00	39.10	143.73	1189	1139
20	06-Jun-03 16:00	39.23	143.96	1190	1140
21	06-Jun-03 17:00	39.37	144.23	1191	1141
22	06-Jun-03 18:00	39.51	144.47	1192	1142
23	08-JUN-03 08:02	44.24	155.07	1193	1143
24	.	.	.	1194	1144
25	08-JUN-03 22:59	46.00	159.64	1195	1145
26	09-JUN-03 09:00	47.12	162.84	1196	1146
27	10-JUN-03 02:14	48.66	168.73	1197	1147
28	11-Jun-03 08:30	49.48	-179.80	1198	1148
29	12-JUN-03 03:32	50.00	-172.53	1199	1149
30	12-JUN-03 17:32	49.99	-167.12	1200	1150
31	13-JUN-03 07:09	49.98	-161.71	1201	1151
32	14-JUN-03 05:08	50.01	-153.20	.	1152
33	14-JUN-03 17:35	49.99	-148.33	1203	1153

Table B-4. Sampling design on Cruise LF.

Numbers in italics are a tally of samples collected for A) radium, and B) CDOM/trace elements. (If two numbers appear, e.g., 3/5, the first is CDOM samples and the second is trace element samples.) Numbers in bold represent exchange event identification numbers (ExchID). Note that dates June 11a, 11b result from crossing International Date Line.

A: Radium

			Local Date: JUN												
			DAY: 0 1 2 3 4 5 6 7 8 m 8 a 9 10 11												
<i>Tank:</i>															
ER	W1	S	2		<i>1</i>	9				<i>1</i>					
ER	W2	P	3		<i>1</i>				<i>1</i>	11		<i>1</i>			
ER	W3	S	6	<i>2</i>					<i>1</i>	12		<i>1</i>			
ER	W4	P	7	<i>2</i>		10		<i>1</i>				<i>1</i>			
C	W1	P	1		<i>1</i>				<i>1</i>		13		<i>1</i>		
C	W2	S	4		<i>1</i>				<i>1</i>		<i>1</i>			15	<i>1</i>
C	W3	P	5	<i>2</i>					<i>1</i>			<i>1</i>		16	<i>1</i>
C	W4	S	8	<i>2</i>				<i>1</i>			<i>1</i>	14		<i>1</i>	
Shipside Samples:				<i>2</i>		<i>1</i>		<i>1</i>		<i>1</i>				<i>1</i>	

B: CDOM/trace elements

			Local Date: JUN												
			DAY: 0 1 2 3 4 5 6 7 8 m 8 a 9 10 11												
<i>Tank:</i>															
ER	W1	S	2	<i>3</i>		9	<i>3</i>		<i>1</i>		<i>1</i>		<i>1</i>	<i>3/5</i>	
ER	W2	P	3	<i>3</i>					<i>2</i>	11	<i>3/5</i>		<i>1</i>	<i>3</i>	
ER	W3	S	6	<i>3</i>			<i>1</i>		<i>2</i>	12	<i>3/5</i>		<i>1</i>	<i>3/5</i>	
ER	W4	P	7	<i>3</i>		10	<i>3</i>		<i>1</i>		<i>1</i>		<i>1</i>	<i>3</i>	
C	W1	P	1	<i>3</i>			<i>3</i>		<i>1</i>		<i>3</i>	13	<i>3</i>	<i>3</i>	
C	W2	S	4	<i>3</i>					<i>2</i>		<i>3/5</i>		<i>2</i>	15,3/5	
C	W3	P	5	<i>3</i>			<i>1</i>		<i>2</i>		<i>3/5</i>		<i>2</i>	16,3	
C	W4	S	8	<i>3</i>			<i>3</i>		<i>1</i>		<i>3</i>	14	<i>3</i>	<i>3/5</i>	
Shipside Samples:			<i>18</i>	<i>5</i>	<i>1</i>	<i>2</i>	<i>1</i>	<i>1</i>	<i>1</i>	<i>2</i>			<i>1</i>		

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APPENDIX C - Cruise AS experimental design and sampling

Table C-1. Ballasting and exchange details on Cruise AS.

Ballasting times in Korea are +/- 10 hours. Ballasting and exchange locations are presented as means.

ExchID	Tank	Date/Time (LDT)	Date/Time (GMT)	Latitude (°N)	Longitude (°E / °W)	Process	Location	BWE %	Vol. (MT)
1	1S	22-07-03 12:00	7-22-03 3:00	37.47	126.60	Ballast	Inchon	100	276
2	1P	22-07-03 12:00	7-22-03 3:00	37.47	126.60	Ballast	Inchon	100	276
3	2S	27-07-03 12:00	7-27-03 3:00	36.00	126.72	Ballast	Kunsan	100	448
4	2P	26-07-03 23:59	7-26-03 14:59	36.00	126.72	Ballast	Kunsan	100	448
5	3S	03-08-03 0:01	8-2-03 15:01	53.96	136.64	Ballast	Yokkaichi	100	447
6	3P	03-08-03 0:01	8-2-03 15:01	53.96	136.64	Ballast	Yokkaichi	100	447
7	4S	27-07-03 0:01	7-26-03 15:01	36.00	126.72	Ballast	Kunsan	100	447
8	4P	27-07-03 0:01	7-26-03 15:01	36.00	126.72	Ballast	Kunsan	100	447
9	5S	26-07-03 12:00	7-26-03 3:00	36.00	126.72	Ballast	Kunsan	100	419
10	5P	26-07-03 12:00	7-26-03 3:00	36.00	126.72	Ballast	Kunsan	100	419
11	1S	06-08-03 16:15	8-6-03 7:15	40.73	148.79	FT	Ocean	317	276
12	4P	06-08-03 19:30	8-6-03 10:30	41.24	149.61	FT	Ocean	313	447
13	2P	08-08-03 4:30	8-7-03 20:30	46.22	158.55	FT	Ocean	313	448
14	5S	08-08-03 4:30	8-7-03 20:30	46.22	158.55	FT	Ocean	334	419
15	1P	12-08-03 17:30	8-13-03 4:30	53.38	-153.53	FT	Ocean	380	276
16	2S	12-08-03 21:00	8-13-03 8:00	53.26	-152.11	FT	Ocean	312	448
17	5P	13-08-03 13:30	8-14-03 0:30	53.11	-150.50	FT	Ocean	334	419
18	3S	13-08-03 6:00	8-13-03 17:00	52.91	-148.96	FT	Ocean	313	447
19	3P	13-08-03 18:00	8-14-03 5:00	52.12	-144.47	FT	Ocean	313	447
20	4S	13-08-03 21:59	8-14-03 8:59	51.85	-142.92	FT	Ocean	313	447

Table C-2. Sources of shipside radium samples on Cruise AS

GPS positions are presented as means, with error shown as distance along the cruise track.

Sample ID	Collection Date & Time (GMT)	Latitude (°N)	Longitude (°E / °W)	Volume (L)	Error (nmi)
1071	5-08-03 05:20	53.9561	136.6444	300	5
1072	5-08-03 10:31	34.7450	139.8342	300	5
1073	7-08-03 06:57	40.6850	148.7267	300	5
1074	9-08-03 06:10	40.1370	162.0760	300	5
1075	15-08-03 08:32	51.8813	-143.0793	300	5
1076	17-08-03 14:04	46.4372	-124.9406	300	5
1077	17-08-03 15:10	46.3135	-124.5699	300	5
1078	17-08-03 15:59	46.2367	-124.3305	250	5

Table C-3. Sources and salinity of shipside CDOM/trace element samples on Cruise AS.

Set	Collection Date, Time	Source Location		Salinity	AS-	AS-
	(GMT)	Latitude (°N)	Longitude (°E /-°W)	(ppt)	CDOM	Trace Element
1	5/08/03 6:45	34.95	136.68	21.9	1011	961
2	5/08/03 7:45	34.75	136.78	25.6	1012	962
3	5/08/03 8:35	34.60	136.96	30.44	1013	963
4	5/08/03 9:25	34.51	137.10	31.25	1014	964
5	5/08/03 10:20	34.48	137.38	32.87	1015	965
6	5/08/03 11:30	34.46	137.75	33.39	1016	966
7	5/08/03 12:15	34.46	137.99	32.69	1017	967
8	5/08/03 13:15	34.44	138.28	32.94	1018	968
9	5/08/03 17:15	34.61	139.42	33.51	1019	969
10	5/08/03 20:10	34.88	140.25	33.28	1020	970
11	6/08/03 0:15	35.59	141.28	33.05	1021	971
12	6/08/03 2:00	35.87	141.68	33.25	1022	972
13	6/08/03 8:20	36.94	143.25	32.16	1023	973
14	6/08/03 11:00	37.41	143.87	33.36	1024	974
15	6/08/03 13:30	37.83	144.48	33.63	1025	975
16	6/08/03 23:25	39.43	146.84	33.94	1025	976
17	7/08/03 4:27	40.25	148.07	32.46	1026	977
18	7/08/03 12:20	41.53	150.07	31.98	1027	978
19	7/08/03 23:10	43.18	152.98	32.16	1028	979
20	8/08/03 11:00	44.95	156.32	32.79	1030	980
21	9/08/03 4:41	48.80	163.34	32.79	1031	981
22	10/08/03 6:02	51.85	169.24	32.5	1032	982
23	11/08/03 7:51	53.61	179.26	33.07	1033	983
24	12/08/03 8:36	54.20	-170.09	32.6	1034	984
25	14/08/03 4:25	53.34	-153.17	32.11	1036	985
27	14/08/03 21:44	52.48	-146.48	32.14	1037	987
28	15/08/03 5:18	51.97	-143.58	32.02	1038	988
29	15/08/03 20:57	50.68	-137.89	32.04	1039	988
30	16/08/03 3:23	50.01	-135.75	32.24	1040	989
31	16/08/03 22:26	47.91	-129.20	32.42	1041	990
32	17/08/03 5:53	47.12	-126.92	31.43	1042	991
33	17/08/03 7:59	46.87	-126.26	31.68	1043	992
34	17/08/03 11:33	46.49	-125.12	31.88	1044	993
35	17/08/03 12:48	46.36	-124.71	31.78	1045	994
36	17/08/03 14:00	46.23	-124.32	24.42	1046	995
37	17/08/03 15:29	46.23	-123.97	9.09	1047	996

Table C-4. Sampling design on Cruise AS.

Numbers in italics are a tally of samples collected for A) radium, and B) CDOM/trace elements. (If two numbers appear, e.g., 3/5, the first is CDOM samples and the second is trace element samples.) Numbers in bold represent exchange event identification numbers (ExchID). Note that dates August 11a, 11b result from crossing International Date Line.

A: Radium

			Local Date: AUG														
			DAY: -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13														
Tank:																	
FT	W1	S	1	2	11		2										2
FT	W2	P	4			13				2							
FT	W3	S	5			2			2			18		2			
FT	W4	P	8		2, 12				1	1							
FT	W5	S	9			14		2									
C	W1	P	2	2			2					15		2			
C	W2	S	3							1	16				2		
C	W3	P	6			2			1			2		19			
C	W4	S	7		2				1	1				20			
C	W5	P	10					2				17					
Shipside Samples:				2		1		1		1				1			3

B: CDOM/trace elements

			Local Date: AUG														
			DAY: -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13														
Tank:																	
FT	W1	S	1	3	11		3		2								2
FT	W2	P	4	3/5		13	3			2						2/3	
FT	W3	S	5	3/5		3			3			18		2/4			
FT	W4	P	8	2	12		3		2			2/5				2/3	
FT	W5	S	9	2		14		3									
C	W1	P	2	3			2		2			15				2	
C	W2	S	3	3/5			3			2	16					2/3	
C	W3	P	6	3/5		3			3					19		2	
C	W4	S	7	2			3		2					20		2/3	
C	W5	P	10	2				3				17					
Shipside Samples:			10	5	3	2	1	1	1	1	1	1	2	1	2	2	

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APPENDIX D - Cruise K experimental design and sampling

Table D-1. Ballasting and exchange details on Cruise K.

Locations of mid-ocean Empty/Refill (ER) exchange initiation (Xi) and completion (Xf) are +/- 5 nautical miles along the cruise track.

Exchange ID	Tank	Date & Time (GMT)	Lat (°N)	Lon (-°W)	Process	Location	Vol (MT)	% Replaced
1	2P	6/22/2004 5:30	37.75	-122.25	Ballast	Oakland	264	100
2	2P	6/24/2004 2:00	34.18	-133.08	Xi	Ocean	264	100
2	2P	6/24/2004 5:18	33.49	-134.27	Xf	Ocean	264	100
3	2P	6/27/2004 23:00	21.18	-157.52	Ballast	Honolulu	264	100
4	2P	6/30/2004 2:30	31.31	-148.41	Xi	Ocean	264	100
4	2P	6/30/2004 15:39	35.11	-144.52	Xf	Ocean	264	100
5	2P	7/1/2004 2:00	38.05	-141.3	Xi	Ocean	264	100
5	2P	7/1/2004 5:48	39.07	-140.14	Xf	Ocean	264	100
6	2S	6/22/2004 5:30	37.75	-122.25	Ballast	Oakland	264	100
7	2S	6/24/2004 2:00	34.18	-133.08	Xi	Ocean	264	100
7	2S	6/24/2004 5:18	33.49	-134.27	Xf	Ocean	264	100
8	2S	6/27/2004 23:00	21.18	-157.52	Ballast	Honolulu	264	100
9	2S	6/30/2004 2:30	31.31	148.41	Xi	Ocean	264	100
9	2S	6/30/2004 15:39	35.11	-144.52	Xf	Ocean	264	100
10	2S	7/1/2004 2:00	38.05	-141.3	Xi	Ocean	264	100
10	2S	7/1/2004 5:48	39.07	-140.14	Xf	Ocean	264	100
11	1C	6/22/2004 5:15	37.75	-122.25	Ballast	Oakland	286	100
12	1C	6/25/2004 21:35	26.12	-149.51	Xi	Ocean	286	100
12	1C	6/25/2004 23:12	26	-150.1	Xf	Ocean	286	100
13	1C	6/28/2004 13:00	21.18	-157.52	Ballast	Honolulu	286	100
14	1C	6/30/2004 2:30	31.31	-148.41	Xi	Ocean	286	100
14	1C	6/30/2004 15:39	35.11	-144.52	Xf	Ocean	286	100
15	1C	7/1/2004 2:00	38.05	-141.3	Xi	Ocean	286	100
15	1C	7/1/2004 5:48	39.07	-140.14	Xf	Ocean	286	100

Table D-2. Sources of shipside radium samples on Cruise K.

GPS positions are presented as means, with error shown as distance along the cruise track.

Set	Collection Date & Time (GMT)	Latitude (°N)	Longitude (°W)	K- Rad A	K- Rad B	Error (distance in nmi)
1	6/20/2004 23:25	37.75	-122.25	1437	1443	0
2	6/22/2004 23:25	37.84	-122.42	1438	1444	2
3	6/23/2004 3:30	37.37	-123.95	1439	1445	3
4	6/24/2004 3:20	34.12	-133.66	1440	1446	3
5	6/26/2004 18:40	22.46	-155.78	1441	1447	3
6	6/26/2004 21:35	21.84	-156.69	1442	1448	3
7	6/27/2004 1:00	21.3	-157.76	198	200	3
8	6/27/2004 18:40	21.18	-157.52	188	190	0
9	6/27/2004 21:35	21.18	-157.52	197	199	0
10	6/28/2004 16:35	21.51	-157.38	207	209	3
11	6/28/2004 23:20	23.5	-155.79	208	210	3
12	6/30/2004 22:10	37	-142.84	107	109	3
13	7/1/2004 17:05	42.11	-136.14	218	220	3
14	7/2/2004 17:55	47.99	-125.99	217	219	3
15	7/4/2004 18:40	47.77	-122.42	1431	1432	2
16	7/4/2004 22:00	48.25	-123.29	1433	1434	3
17	7/5/2004 0:10	48.44	-124.44	1435	1436	3

Table D-3. Sources and salinity of shipside CDOM/trace element samples collected on Cruise K.

K-CDOM numbers refer to EEMs + Turner fluorometer measurements, with the exception of Sample ID numbers A1-A13, which refer to Turner fluorometer measurements only.

Set	Collection Date & Time (GMT)	Latitude (°N/°S)	Longitude (°W)	Salinity (ppt)	K- CDOM	K- Trace Element
1	6/22/2004 23:05	37.83	-122.38	30.6	354	294
2	6/22/2004 23:07	37.83	-122.38	30.6	355	295
3	6/22/2004 23:22	37.85	-122.41	33.4	356	296
4	6/22/2004 23:37	37.82	-122.46	33.7	357	297
5	6/22/2004 23:52	37.80	-122.54	34.5	358	298
6	6/23/2004 0:28	37.74	-122.69	34.9	359	299
7	6/23/2004 1:05	37.65	-122.94	35	360	300
8	6/23/2004 1:32	37.60	-123.14	35.2	361	301
9	6/23/2004 1:58	37.55	-123.32	34.8	362	302
10	6/23/2004 3:03	37.42	-123.79	34.7	363	303
11	6/23/2004 4:03	37.30	-124.23	34.2	364	304
12	6/23/2004 5:05	37.18	-124.65	34.1	365	305
13	6/23/2004 6:05	37.05	-125.10	34	366	306
14	6/23/2004 7:05	36.92	-125.55	34.1	368	307
15	6/23/2004 16:03	35.76	-129.22	34.2	367	308
16	6/24/2004 3:07	34.15	-133.59	34.8	369	309

Table D-4. (Cont'd). Sources and salinity of shipside CDOM/trace element samples collected on Cruise K.

Set	Collection Date & Time (GMT)	Latitude (°N/-°S)	Longitude (-°W)	Salinity (ppt)	K- CDOM	K- Trace Element
17	6/24/2004 17:05	31.93	-138.87	35.4	370	310
18	6/25/2004 2:03	30.37	-142.17	36.5	371	311
19	6/25/2004 17:27	27.52	-147.56	36.5	372, 373	312
20	6/26/2004 2:33	25.75	-150.56	37.3	374, 375	313, 314
21	6/26/2004 18:37	22.47	-155.77	36.3	376, 377	315, 316
22	6/26/2004 20:10	22.14	-156.25	35.7	378, 379	317, 318
23	6/26/2004 21:14	21.92	-156.59	36.4	380, 381	320, 319
24	6/26/2004 22:32	21.64	-157.01	36.7	385, 386	321, 322
25	6/26/2004 23:27	21.44	-157.28	36.6	382, 383	323, 324
26	6/27/2004 0:03	21.33	-157.47	36.6	387, 388	325, 326
27	6/27/2004 0:33	21.31	-157.65	36.2	389, 390	327, 328
28	6/27/2004 0:48	21.31	-157.74	36.6	392, 393	329, 332
29	6/27/2004 1:01	21.30	-157.84	35.3	394, 395	331, 334
30	6/27/2004 1:16	21.30	-157.85	36.6	391, 396	333, 336
31	6/27/2004 1:32	21.30	-157.86	36.6	397	335, 338
32	6/27/2004 1:44	21.30	-157.87	36.5	384, 398	337, 340
33	6/27/2004 3:16	21.31	-157.88	36.6	400, 402	339, 341
34	6/28/2004 16:10	21.38	-157.47	35.8	401, 403	342, 343
35	6/28/2004 16:32	21.49	-157.39	36.3	399, 404	344, 345
36	6/28/2004 16:58	21.62	-157.30	36.8	405, 406	346, 347
37	6/28/2004 17:08	21.68	-157.24	36.9	407	348, 349
38	6/28/2004 18:58	22.22	-156.83	36.8	408, 409	350, 351
39	6/28/2004 20:03	22.54	-156.56	37.2	410, 411	352, 353
40	6/28/2004 22:03	23.12	-156.09	36.7	412, 413	415, 416
41	6/29/2004 1:10	24.05	-155.35	30.1	1400, 1401	417, 418
42	6/29/2004 2:58	24.58	-154.93	37.1	1402, 1403	419, 420
43	6/29/2004 18:33	29.17	-150.94	36.7	1406, 1407	1421, 1422
44	6/30/2004 3:37	31.77	-148.46	36.3	1408, 1409	1423, 1424
45	6/30/2004 18:07	35.88	-144.12	33	1404, 1405	605, 606
47	7/1/2004 3:13	38.40	-141.14	35.4	600, 601	607, 608
48	7/1/2004 17:00	42.09	-136.16	35.2	602, 603	609, 610
49	7/2/2004 2:17	44.39	-132.73	34.6	604, 613	611, 614
50	7/2/2004 17:32	47.91	-126.11	34.2	616, 617	615, 620
51	7/3/2004 2:00	47.91	122.50	33.1	618, 619	621, 622
52	7/4/2004 18:31	47.75	-122.41	31.7	A1	
53	7/4/2004 18:47	47.79	-122.43	30.9	A2	
54	7/4/2004 19:47	48.03	-122.63	31.3		623, 624
55	7/4/2004 20:01	48.03	-122.63	31.5	A3	
56	7/4/2004 20:48	48.20	-122.94	31.3	A4	
57	7/4/2004 21:00	48.21	-123.00	32.4	A5	
58	7/4/2004 21:30	48.23	-123.14	33	A6	
59	7/4/2004 21:45	48.24	-123.21	33.8	A7	
60	7/4/2004 22:04	48.25	-123.31	33.5	A8	
61	7/4/2004 23:04	48.31	-123.85	33.1	A9	
62	7/4/2004 23:52	48.40	-124.25	33.9	A10	
63	7/5/2004 1:18	48.50	-125.01	33.6	A11	
64	7/5/2004 3:05	47.91	-125.32	34.4	A12	
65	7/5/2004 3:20	47.81	-125.33	33.9	A13	

Table D-5. Sampling design on Cruise K.

Numbers in italics are a tally of samples collected for A) radium, and B) CDOM/trace elements. (If two numbers appear, e.g., 3/5, the first is CDOM samples and the second is trace element samples.) Numbers in bold represent exchange event identification numbers (ExchID).

A: Radium

		SEAT. OAKL.						HON.						SEAT.		OAK.	
June	Day	19	20	21	22	23	24	25	26	27	28	29	30	1	2	3	4
	Tank			am pm	am pm	pm pm	am pm	am pm pm	am pm	am pm	am pm	am pm	am pm	am pm			
	No. 2 Port			1	1	2	1			3		1	4	1	5		
	No. 2 Starboard			6		1	7	1		8		1	9	1	10		
	No. 1 Center			11				2	12	2		13	2		2	14	2
Shipside Samples:		1		2		1			3		2		1	1	2	3	

B: CDOM/trace elements

		SEAT. OAKL.						HON.						SEAT.		OAK.	
June	19	20	21	22	23	24	25	26	27	28	29	30	1	2	3	4	
			am pm	am pm	pm pm	am pm	am pm pm	am pm	am pm	am pm	am pm	am pm	am pm				
				1	2	3	4	5	6	7	8	9					
Day																	
Tank																	
No. 2 Port			1		3-4 2	3			3		3-4 4	3-4 5					
No. 2 Starboard			6		3-4 7	3			8		3-4 9	3-4 10					
No. 1 Center			11			3-4	2-3 12 2-3			13 3-4		14 3-4 15	0-2				
Shipside Samples:				14	3	2	2	13	0	9	2	3	2	2	0	14	

APPENDIX E - Cruise BN experimental design and sampling

Table E-1. Ballasting and exchange details on Cruise BN.

Ballasting times in Rotterdam are +/- 8 hours. Locations of mid-ocean Flow-Through (FT) exchange initiation (Xi) and completion (Xf) are +/- 5 nautical miles.

Exchange ID	Tank	Date & Time (GMT)	Process	Location	Lat (°N/-°S)	Lon (E /-°W)	Vol (MT)	% Replaced
1	3P	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	11665	100
2	3P	9/12/04 12:00	Xi	Ocean	47.58	-7.58	11665	302
2	3P	9/13/04 20:00	Xf	Ocean	41.70	-14.93	11665	302
3	3S	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	11665	100
4	3S	9/18/04 8:00	Xi	Ocean	18.66	-32.57	11665	307
4	3S	9/19/04 14:00	Xf	Ocean	11.65	-36.67	11665	307
5	5P	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	11648	100
6	5P	9/18/04 8:00	Xi	Ocean	18.66	-32.57	11648	301
6	5P	9/19/04 14:00	Xf	Ocean	11.65	-36.67	11648	301
7	5S	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	11648	100
8	5S	9/12/04 12:00	Xi	Ocean	47.58	-7.58	11648	302
8	5S	9/13/04 20:00	Xf	Ocean	41.70	-14.93	11648	302
9	7P	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	8763	100
10	7P	9/15/04 6:00	Xi	Ocean	34.90	-20.95	8763	301
10	7P	9/16/04 8:23	Xf	Ocean	29.08	-25.88	8763	301
11	7S	9/9/04 10:00	Ballast	Rotterdam	51.97	4.11	8763	100
12	7S	9/18/04 8:00	Xi	Ocean	18.66	-32.57	8763	302
12	7S	9/19/04 1:30	Xf	Ocean	15.02	-34.80	8763	302

Table E-2. Sources of shipside radium samples on Cruise BN.

GPS positions are presented as means, with error shown as distance along the cruise track.

Set	Collection Date & Time (GMT)	Latitude (°N)	Longitude (°E / -°W)	BN- Rad A	BN- Rad B	Error (distance in nmi)
1	9/9/2004 15:00	51.97	4.11	461	462	0
2	9/9/2004 15:18	51.97	4.11	463	464	0
3	9/11/2004 7:05	50.82	1.00	465	466	2
4	9/11/2004 11:43	50.43	-0.50	467	468	2
5	9/11/2004 17:08	50.07	-2.56	469	470	2
6	9/12/2004 7:33	48.35	-6.61	471	472	3
7	9/12/2004 11:40	47.64	-7.65	473	474	3
8	9/12/2004 16:38	46.80	-8.79	475	476	3
9	9/13/2004 8:06	44.12	-12.19	477	478	2
10	9/13/2004 12:34	43.30	-13.12	479	480	2
11	9/13/2004 17:42	42.35	-14.22	481	482	3
12	9/14/2004 8:06	39.45	-17.20	483	484	3
13	9/14/2004 17:33	37.52	-18.65	485	486	2
14	9/15/2004 8:45	34.26	-21.87	487	488	3
15	9/15/2004 18:30	32.16	-23.57	489	490	2
16	9/16/2004 8:24	29.10	-25.86	491	492	2
17	9/16/2004 18:39	26.84	-27.44	493	494	2
18	9/17/2004 8:41	23.48	-29.68	495	496	2

Table E- 3. Sources of shipside CDOM/trace element samples on Cruise BN and associated sample identity numbers.

Set	Collection Date & Time (GMT)	Latitude (°N/ -°S)	Longitude (E/ -°W)	Salinity (ppt)	BN- CDOM	BN- Trace Element
1	9/9/2004 12:10	51.97	4.11	30.1	321, 322	391, 392
2	9/10/2004 21:45	52.04	3.79	33.1		393
3	9/11/2004 1:30	51.82	2.46	34.9	324, 325	394, 395
4	9/11/2004 4:38	51.21	1.74	31.4	326	396
5	9/11/2004 7:15	50.80	0.97	35.2	327, 328	397, 398
6	9/11/2004 10:05	50.53	0.04	35.1	329	399
7	9/11/2004 11:02	50.47	-0.32	35.2		400
8	9/11/2004 13:00	50.33	-1.13	35.2	331, 332	401, 402
9	9/11/2004 16:20	50.11	-2.29	35.3	333	403
10	9/11/2004 19:00	49.96	-3.11	35.1	334, 335	404, 405
11	9/11/2004 22:08	49.58	-4.06	34.9	336	406
12	9/12/2004 1:05	49.22	-4.95	35.6	337, 338	407, 408
13	9/12/2004 4:09	48.87	-5.79	34.8	339	409
14	9/12/2004 7:00	48.42	-6.50	35.6	340	410
15	9/12/2004 10:00	47.92	-7.27	35.8	341	411, 412
16	9/12/2004 13:04	47.40	-7.96	35.9	343	413
17	9/12/2004 16:11	46.87	-8.68	35.8	344	414
18	9/12/2004 20:15	46.18	-9.63	36.2	345, 346	415, 416
19	9/13/2004 7:15	44.28	-11.98	36.3	347	417
20	9/13/2004 12:00	43.43	-13.00	35.9	348	418
21	9/13/2004 17:57	42.29	-14.28	35.6	350	419, 420
22	9/14/2004 7:05	39.68	-17.01	35.6	351	421
23	9/14/2004 18:55	37.24	-19.26	36.3	352, 353	422, 423
24	9/15/2004 8:03	34.42	-21.74	35.7	354	424
25	9/15/2004 13:02	33.34	-22.63	36.6	355	425
26	9/15/2004 19:01	32.05	-23.65	37	356, 357	426, 427
27	9/16/2004 8:02	29.18	-25.80	34.7	358	428
28	9/16/2004 19:00	26.75	-27.52	37.7	359, 360	429, 430
29	9/17/2004 10:00	23.41	-29.73	37.1	361	431
30	9/17/2004 20:00	21.12	-31.17	37.7	362, 363	432, 433
31	9/18/2004 11:00	17.99	-33.06	36.1	364	434
32	9/18/2004 15:00	17.12	-33.57	36.3	365	435
33	9/18/2004 23:00	15.39	-34.57	34.3	366, 367	436, 437
34	9/19/2004 11:00	12.45	-36.22	35.6	368	438
35	9/19/2004 21:00	10.17	-37.49	35.6	369, 370	439, 440
36	9/20/2004 12:00	6.99	-39.20	33.8	371	441
37	9/20/2004 22:00	4.76	-40.39	34.8	372, 373	442, 443
38	9/21/2004 12:05	1.25	-42.25	36.3	374	444
39	9/21/2004 14:00	0.80	-42.49	36.2		445
40	9/21/2004 16:04	0.30	-42.75	36.4	376	446
41	9/21/2004 18:00	-0.17	-43.00	34.9	377	447
42	9/21/2004 20:00	-0.66	-43.26	36.1	378	448
43	9/21/2004 22:30	-1.23	-43.55	36.4		449
44	9/22/2004 0:05	-1.61	-43.75	33.6	380	450
45	9/22/2004 2:05	-1.99	-44.05	36	381	451
46	9/22/2004 4:02	-2.34	-44.29	33.1	382	452
47	9/22/2004 12:03	-2.43	-44.28	31.7	383	453

Table E-4. Sampling design on Cruise BN.

Numbers in italics are a tally of samples collected for A) radium, and B) CDOM/trace elements. Numbers in bold represent exchange event identification numbers (ExchID).

A: Radium

		Rotterdam												Sao Luis	
		9	10	11	12	13	14	15	16	17	18	19	20	21	22
		-1	0	1	2	3	4	5	6	7	8	9	10	11	12
<i>Tank</i>															
No. 3	<i>Port</i>	1	2		2		2		2			2			
No. 3	<i>Stbd</i>	3	2				2		2		4	2			
No. 5	<i>Port</i>	5	2				2		2		6	2			
No. 5	<i>Stbd</i>	7	2		8		2		2			2			
No. 7	<i>Port</i>	9	2				2	10	2			2			
No. 7	<i>Stbd</i>	11	2				2		2		12	2			
Shipsides		2	1	12	11	4	3	4	3	3	4	3	3	8	2

B: CDOM/trace elements

		Rotterdam												Sao Luis	
		9	10	11	12	13	14	15	16	17	18	19	20	21	22
		-1	0	1	2	3	4	5	6	7	8	9	10	11	12
<i>Tank</i>															
No. 3	<i>Port</i>	1	4		2		4		4			4			
No. 3	<i>Stbd</i>	3	4				4		4		4	4			
No. 5	<i>Port</i>	5	4				4		4		6	4			
No. 5	<i>Stbd</i>	7	4		8		4		4			4			
No. 7	<i>Port</i>	9	2				2	10	2			2			
No. 7	<i>Stbd</i>	11	2				2		2		12	2			
Shipsides		2		3	3	3	2	2	2	1					

APPENDIX F - Further reading

For a fuller examination of the effect of ballast water exchange on CDOM fluorescence in all nine verification experiments conducted to date, the reader is referred to Murphy, K. R., Ruiz, G. M., Dunsmuir, W. T. M., Waite, T. D. (in press) Optimized parameters for fluorescence-based verification of ballast water exchange by ships. *Environmental Science and Technology* (40). A brief overview of the paper is provided below.

Overview:

Chromophoric dissolved organic matter (CDOM) fluorescence was investigated as a tracer of mid-ocean exchange on nine research cruises out of Asia, Europe and the USA. Using parallel factor analysis (PARAFAC), nine independent fluorescent components were identified at varying concentrations in the ocean and in ballast water. Two humic-like components were considered to be particularly useful for verifying exchange, although one component was sufficient for predicting the coastal vs. oceanic source of most ballast water samples. It was found that by setting thresholds (1.7 ppb and 0.7 ppb QSE) at two fixed wavelength pairs ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 320/414$ and $370/496$ nm, respectively), it was possible to discriminate coastal from oceanic ballast water in over 95 percent of samples ($N = 514$). These results suggested that it would be possible to optimize simple single and dual channel fluorometers for verifying ballast water exchange.