

U.S. Coast Guard Research and Development Center

1082 Shennecossett Road, Groton, CT 06340-6048

Report No. CG-D-02-04

Mid-Ocean Ballast Water Exchange: Approach & Methods for Verification



**FINAL REPORT
AUGUST 2004**



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Prepared for:

U.S. Department of Homeland Security
United States Coast Guard
Marine Safety and Environmental Protection (G-M)
Washington, DC 20593-0001

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Marc B. Mandler, Ph.D.
Technical Director
United States Coast Guard
Research & Development Center
1082 Shennecossett Road
Groton, CT 06340-6048

Technical Report Documentation Page

1. Report No. CG-D-02-04		2. Government Accession Number		3. Recipient's Catalog No.	
4. Title and Subtitle Mid-Ocean Ballast Water Exchange: Approach & Methods for Verification				5. Report Date AUGUST 2004	
				6. Performing Organization Code Project No. 4121.2/4126	
7. Author(s) Kate Murphy, Greg Ruiz, Paula Coble, Jen Boehme, Paul Field, Jay Cullen, Elgin Perry & Willard Moore				8. Performing Organization Report No. R&DC 454	
9. Performing Organization Name and Address: Kate Murphy & Greg Ruiz, Smithsonian Environmental Research Center, P.O. Box 28, Edgewater, Maryland 21037		U.S. Coast Guard Research and Development Center 1082 Shennecossett Road Groton, CT 06340-6048		10. Work Unit No. (TR AIS)	
				11. Contract or Grant No. DTCG23-00-X-E0012	
12. Sponsoring Organization Name and Address U.S. Department of Homeland Security United States Coast Guard Marine Safety and Environmental Protection (G-M) Washington, DC 20593-0001				13. Type of Report & Period Covered Final	
				14. Sponsoring Agency Code Commandant (G-MSO-4) U.S. Coast Guard Headquarters Washington, DC 20593-0001	
15. Supplementary Notes The R&D Center's technical point of contact is Ms. Penny Herring, 860-441-2868, email: pherring@rdc.uscg.mil.					
12. Abstract (MAXIMUM 200 WORDS) Ballast water management of ships entering the United States is a key component in stopping invasions of non-indigenous aquatic species. Ballast water exchange (BWE) is currently the most common method of ballast water management and it is likely to remain an approved management technique for the foreseeable future. The United States Coast Guard's present salinity based BWE verification procedure is ineffective when ships' tanks are ballasted in high salinity ports. In an attempt to improve this procedure, a suite of parameters was sought to better discriminate between open ocean and coastal waters. Analyses indicated that salinity, colored dissolved organic matter (CDOM), certain trace metals, and radium isotopes provided good discrimination power. Univariate and multivariate analyses conducted on the separate and combined data sets indicated that radium was the best single discriminator and that salinity coupled with six trace metals (barium, manganese, phosphorus, molybdenum, uranium, and vanadium) was the most successful suite for discriminating open ocean from coastal water. CDOM combined with salinity proved to be a successful discriminator. Water clarity and phytoplankton salinity tolerance proved unsuitable. Sampling and analysis procedures are included in the report.					
17. Key Words ballast water, exchange, verification, CDOM, trace metals, radium			18. Distribution Statement This document is available to the U.S. public through the National Technical Information Service, Springfield, VA 22161		
19. Security Class (This Report) UNCLASSIFIED		20. Security Class (This Page) UNCLASSIFIED		21. No of Pages	22. Price

Form DOT F 1700.7 (8/72) Reproduction of form and completed page is authorized.

Acknowledgements

This project would not have been possible without the cooperation of four shipping companies who provided the experimental platforms for the research cruises described herein. In each case they accommodated up to three scientists on their vessels for the duration of an experiment. Our thanks go to Phil Eichenberger of Sea River Maritime, Houston TX, for assistance in scheduling the first experiment on the S/R BENICIA. Tom Colby helped arrange a second experiment with the Alaska Tanker Company on the OVERSEAS BOSTON. Samples for our third cruise were taken on the BP Amoco PLC oil tanker, TONSINA. Our fourth cruise was conducted aboard the MOSEL ORE of Krupp Seeschiffahrt GmbH. We are greatly indebted to each of these companies, as well as to each ship's officers and crew, who provided invaluable assistance throughout the experiments.

Many people contributed ideas to this project during an initial workshop session. These included Dr. Larry Brand, Dr. Fred Dobbs, Mark Geiger, Dr. Chad Hewitt, Dr. Patrick Louchouart, Jae Ryoung Oh, Dr. Patricia Tester, Dr. Whitman Miller, Dr. Robert Hiltabrand, LT Mary Pat McKeown, Penny Herring and Dr. Rich Everett.

Sampling on the vessels was conducted with assistance from Brian Steves, Alan Burdick, Andy Chang, George Smith and Esther Collinetti.

Executive Summary

United States Coast Guard (USCG) regulations will soon be in place that require all ships entering United States waters from outside the Exclusive Economic Zone to a) hold ballast on board, b) treat ballast to a standard currently being finalized, c) discharge ballast water to a shore-based treatment facility, or d) conduct a mid-ocean ballast water exchange (BWE). BWE is currently the most common method of ballast water management, and although its actual efficacy is not known, it is likely to remain an approved management technique for the foreseeable future. In order to enforce its regulations, USCG must have a means of verifying that BWE has taken place in mid-ocean. Compliance is currently based on the salinity of the ballast water; salinity of more than 30 parts per thousand (ppt) is considered to have been exchanged, while salinity less than 30 ppt is considered un-exchanged. While this practice has been in use for several years, it is recognized that it cannot discriminate between ballast water exchanged in mid-ocean and that taken aboard in a high salinity port.

In an attempt to improve the USCG's salinity-based method, a suite of parameters with better discriminatory capabilities was sought. Based on the recommendations from a workshop convened to discuss potential tracers, six parameters, along with salinity, were selected for testing on commercial ships. Experimental exchange and control ballast tanks, as well as shipside surface water, were sampled during three Pacific voyages along the west coast of North America and during one trans-Atlantic cruise. Initial ports where ballasting took place were selected to encompass a low salinity to high salinity range.

Parameters measured during the initial Pacific cruises included salinity, salinity tolerance of phytoplankton, colored dissolved organic matter (CDOM), trace metals, radium (Ra) isotopes, lignin, and turbidity. Rhodamine dye was added to the tanks before ballasting and was used as a tracer of volumetric exchange during these voyages. Protocols for sampling and handling were refined. Evaluation of the first two cruises revealed that trace metals, radium isotopes, and CDOM Excitation-Emission Matrix (EEM) fluorescence held promise as potential verification indicators. Turbidity and in-situ CDOM fluorescence were inconclusive, and phytoplankton salinity tolerance could not distinguish exchanged from un-exchanged tanks. Furthermore, rhodamine dye appeared to interfere with CDOM fluorescence peaks. As a result, the remaining experiments omitted rhodamine dye and phytoplankton salinity tolerance completely, and efforts concentrated on the remaining suite. The final two voyages also included more over-the-side samples in an attempt to better characterize open ocean and coastal waters.

Statistical analyses of the data included both univariate and multi-variate analysis. Univariate analysis indicated CDOM could sometimes be used to discriminate between exchanged and un-exchanged tanks. The trace metals barium (Ba), manganese (Mn), and phosphorus (P) could likewise discriminate between tanks. Salinity was a good discriminator except when water from the initial port was high. Of the radium isotopes, ^{223}Ra and ^{228}Th (thorium) were powerful discriminators. Multi-variate analysis showed the combination of salinity and six trace metals (Ba, Mn, P, molybdenum, uranium, and vanadium) was the most successful combination for discriminating open ocean from coastal water. Fortunately, a single trace metal analysis can provide values for all six of these metals at one time. The combination of salinity and CDOM measurements did not provide quite as much discrimination capability. Due to the short half-lives of some of the radium isotopes, radium could not be sampled and evaluated in the same manner as the other parameters.

The study concludes that several of the parameters initially suggested at the workshop do have strong potential to discriminate between exchanged and un-exchanged ballast tanks. Trace metals, particularly Ba, P, and Mn, were successful as indicators of BWE. CDOM showed a high potential for discrimination when it was coupled with salinity or other parameters. Based on long-lived isotopes, radium was the most successful indicator of the ballast water source. There are significant drawbacks to using radium, however. These include large volume of sample required, very specialized filter cartridges, high cost of analysis and equipment, and short life of samples. Overall, the experimental voyages indicated that multi-variate analysis of selected parameters is a viable method of determining compliance to BWE regulations.

From a discriminatory point of view, salinity and radium are the best parameters to use in verifying BWE. From a practical application point of view, salinity, trace metals, and CDOM are the recommended parameters for the Coast Guard to use to improve the current use of salinity only. Radium is omitted from this list due to the drawbacks already cited. Operational protocols and analysis arrangements will need to be developed before this technique can be implemented into Coast Guard procedures.

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List of Acronyms

A Emx	Peak A emission maximum	T0,T1,T2,T3	Sampling Times
A Exx	Peak A excitation maximum	USCG	U.S. Coast Guard
A QSE	Peak A intensity in quinine sulfate equivalents (QSE)	VFos	Cruise 4: Fos Sur Mer - Norfolk
a(280)	Absorption coefficient at 280 nm	VLA	Cruise 2: Los Angeles - Valdez
a(312)	Absorption coefficient at 312 nm	VPS	Cruise 3: Puget Sound - Valdez
a(412)	Absorption coefficient at 412 nm	VSF	Cruise 1: San Francisco - Valdez
A.R.	Activity ratio	wt/wt	weight to weight
BWE	Ballast Water Exchange		
C	Control		
C Emx	Peak C emission maximum		
C Exx	Peak C excitation maximum		
C QSE	Peak C intensity in quinine sulfate equivalents (QSE)		
CDOM	Colored Dissolved Organic Matter		
CTD	Conductivity / Temperature / Depth Meter		
D.I.	Deionized/distilled water		
dpm	Disintegrations per minute		
EEM	Excitation – Emission Matrix		
EEZ	Exclusive Economic Zone		
EI	Electron ionization		
ER	Empty-Refill		
fIS	Flashlamp CDOM fluorescence units		
FT	Flow-Through		
GC	Gas chromatograph		
GC/MS	Gas chromatograph/Mass spectrophotometer		
HCl	Hydrochloric acid		
ICP-MS	Inductively Coupled Plasma Mass Spectrometry		
MilliQ	High purity deionized water		
MT	Metric tons		
NIS	Nonindigenous species		
NTU	Nephelometric turbidity unit		
PAH	Polyaromatic hydrocarbon		
PMT	Photomultiplier tube		
ppb	Part per billion		
ppt	Part per thousand		
QSE, qse	Quinine-sulfate equivalent units		
SE	Standard Error		
SERC	Smithsonian Environmental Research Center		
SPE	Solid Phase Extraction		
SS	Shipside		

Ba	Barium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Mn	Manganese
Mo	Molybdenum
Ni	Nickel
P	Phosphorus
Pa	Protactinium
Pb	Lead
Po	Polonium
Ra	Radium
Rn	Radon
Sb	Antimony
Th	Thorium
U	Uranium
V	Vanadium
Zn	Zinc

1. Introduction

Successful invasions of nonindigenous species (NIS) result in many unwanted ecological, economic and human health impacts. For example, recent studies have estimated the impact of NIS to exceed \$100 billion dollars annually in the U.S. alone. Furthermore, many analyses suggest that the rate of invasions has increased in recent years, causing great public concern and resulting in many state, national, and international efforts to reduce the risk of future invasions.

Invasions, or the transfer of species outside of their historical range, result most often from human activities. In coastal marine ecosystems, ships are considered the transfer mechanism (or vector) responsible for most historical invasions and are responsible for a dramatic increase in the number of new invasions detected in recent decades. Species are transferred unintentionally in the ballast and on the hulls of ships, and a portion of these organisms are able to colonize upon arrival to a new port. Today, ballast water is considered to be the largest single vector in that organisms are entrained in ballast tanks and released at subsequent ports of call.

In an effort to reduce the risk of invasions associated with ships, Congress passed P.L. 101-646, the Nonindigenous Aquatic Nuisance Prevention and Control Act (NANPCA) of 1990. The Act contains specific language and directly addresses the challenges of ballast water as a vector for exotic species. Included in the Act was a mandate that the U.S. Coast Guard (USCG) promulgate regulations to prevent further ballast water introductions into the Great Lakes and upper Hudson River.

The International Maritime Organization (IMO) established voluntary guidelines aimed at minimizing such introductions, requesting that ships perform mid-ocean ballast water exchange (BWE). This is now the primary method for reducing the risk of species transfer and invasion into coastal water of the United States and elsewhere. During exchange, a vessel replaces its original ballast water (taken on board while the vessel was in port or near to the coast) with water from the open ocean. Ballast exchange reduces NIS by 1) discharging a percentage of them into the inhospitable environment of the ocean, and in some cases, 2) by increasing the salinity level within the ballast tank to a level such that many species of freshwater or brackish water origins cannot survive.

On May 10, 1993, the USCG's ballast water management regulations became effective for vessels traveling to the Great Lakes and also operating beyond the Canadian or U.S. exclusive economic zones (EEZ).

These regulations mandate BWE as the current procedure to control the introduction of NIS. Exchange is to take place in water outside the 200 mile EEZ and in depths greater than 2000 meters.

On October 26, 1996, Congress enacted the National Invasive Species Act of 1996 (NISA) (P.L. 104-332), which amended and reauthorized NANPCA. NISA provides for ballast water management to prevent introductions and spread of NIS. It expands the scope of USCG regulations to include all waters of the United States.

In compliance with NISA, the USCG's regulatory guidelines would become mandatory after three years unless the maritime industry showed a high rate of compliance under a self-policing system. Therefore, the interim rule established a ballast management reporting provision to assist the USCG in assessing compliance for the first two years. Compliance was significantly less than 50 percent leading to recommendations for mandatory treatment, exchange, or management of ballast water.

The USCG currently uses salinity to verify ballast water exchange. In some cases, the presence of low salinity ballast water (< 30 ppt) is sufficient to show that the water was not exchanged in mid-ocean. However, the technique fails when the source of the ballast water is a high-salinity coastal port. The quest to identify better verification techniques to determine the origin of the ballast water is the basis of the USCG Research and Development Center's Ballast Water Exchange Verification Program.

As part of this BWE verification program, the Smithsonian Environmental Research Center (SERC) implemented research to test whether a suite of characteristics (chemical, biological, physical or a combination of these) can be used to discriminate between coastal and oceanic water, regardless of salinity. These analyses were intended as a "proof of concept" for an approach and for particular methods to verify ballast water exchange. An exhaustive analysis to test the full resolution of these measures, across all ocean basins and seasons, was clearly beyond the scope of this study. Instead, the aim was to demonstrate the potential of particular measures, which could then be tested more fully and for which appropriate instrumentation could be advanced simultaneously.

This report discusses the sampling efforts and resulting data from the three Pacific coastwise cruises and the trans-Atlantic voyage. Sampling, handling, and analytical methods are described. Parameters for each cruise are discussed individually and numerous graphs and EEM figures are provided. Analysis of the individual parameters indicated that salinity, CDOM, trace metals, and radium isotopes had the most

potential to be used as successful indicators of exchange in the open ocean. While the clarity of the open ocean is significantly greater than that of coastal waters, experimental results indicated more turbidity variations between ballast tanks than between open ocean and coastal waters thus making water clarity an inappropriate tool for verification of exchange. Lignin proved to be difficult to analyze and was dropped from consideration.

The report is organized to first provide a description of the approach and experimental methods for sample collection and analytical analysis for each parameter investigated. Each voyage is then discussed in terms of experimental design and methods used and the results found for each parameter. Summary results for both the Pacific cruises and the trans-Atlantic voyage are provided. Following the discussion of the individual voyages and results, the univariate and multi-variate statistical analyses are discussed. The tables provided in this discussion are excerpts from full statistical results tables found in the appendices. The conclusion section discusses each of the recommended parameters and recommends compiling a multi-variate database and developing in-situ or rapid analysis techniques for those parameters. A stepwise approach to sample analysis is also suggested. The first five appendices included with this report provide a report describing the initial workshop, detailed methodologies, a description of radium decay products, a table of univariate statistical results from all voyages, and a similar table of multi-variate results. Instrument specifications, locations and depths of ballast exchanges, locations of shipside samples during the Atlantic cruise, and data from in-situ and laboratory measurements are provided in the remaining appendices.

2. Methods

2.1. Planning and Methods Development

In August 2000, a panel of representatives from SERC, USCG and invited oceanographic scientists were brought together to discuss and evaluate techniques that could be used to verify whether a vessel has undertaken mid-ocean exchange in accordance with current Ballast Water Exchange Guidelines or, potentially, in accordance with future mandatory exchange laws. The results of the workshop were presented in the Phase 1 report to the USCG (Appendix A). Sampling, handling, and analysis information is provided in the appendix for each parameter.

The recommendation of the panel was to investigate a subset of potential techniques discussed at the workshop:

- Salinity
- Salinity Tolerance of Phytoplankton
- Colored Dissolved Organic Matter (CDOM) fluorescence (in-situ and excitation - emission matrix (EEM))
- Trace Metal Isotopes
- Radium Isotopes
- Lignin
- Turbidity

Potential verification techniques recommended in Phase 1 of this project were tested on four commercial voyages in the North Pacific and North Atlantic Oceans. On each voyage, ships filled ballast tanks at the port of departure (source port), designating at least one for ballast water exchange and another as an unexchanged control. Ballast water samples were collected from each tank at the beginning of the voyage, again following exchange events, and at the end of the voyage. In addition, shipside samples were collected periodically during each voyage. Samples were collected and analyzed following a methodology specific to each parameter.

Voyages were selected to depart from ports such that the salinities of the ballast water would encompass a range of salinity conditions likely to be encountered by persons monitoring compliance. On three of the

voyages, source water salinities were close enough to full oceanic salinities to render the USCG current verification criterion (salinity >30 ppt) unreliable.

Work was implemented in two stages. The first stage focused on experiments in the northern Pacific and involved three separate voyages parallel to the coast of North America. One pair of tanks was sampled on each Pacific voyage, and shipside samples were limited (in part due to the coastwise voyage route). These voyages were used to refine many of the sampling protocols and to streamline measures for subsequent voyages. The second component comprised experiments aboard one trans-Atlantic voyage involving four pairs of ballast tanks. In addition to ballast tank samples, extensive shipside sampling took place throughout this voyage.

A summary of the voyages, including port of departure and arrival as well as dates, is as follows:

Voyage Identifier	Ports	Dates
A. Pacific Ocean		
• VSF -	San Francisco (CA) to Valdez (AK)	Nov. 6-Nov. 11 2000
• VLA -	Los Angeles (CA) to Valdez (AK)	Dec. 8-Dec. 14 2000
• VPS -	Puget Sound (WA) to Valdez (AK)	May 20-May 24 2001
B. Atlantic Ocean		
• VFos -	Fos Sur Mer (France) to Norfolk (VA)	June 11-June 25 2001

An intermediate evaluation of the data was performed in March 2001 after the first results of the VSF and VLA voyages became available. Conclusions of that evaluation were as follows:

- Trace metal isotopes, radium isotopes and CDOM Excitation-Emission Matrix (EEMs) fluorescence all held promise as potential verification techniques.
- Results for turbidity and in-situ CDOM fluorescence were inconclusive.
- Phytoplankton Salinity Tolerance could not distinguish reliably between exchanged and unexchanged ballast tanks.
- Rhodamine dye may interfere with determination of CDOM fluorescence peaks.
- In-situ measurements were particularly susceptible to failures in field instruments.

Consequent to the evaluation, sampling protocols on subsequent voyages were amended as follows:

- Rhodamine dye was omitted from subsequent experiments.
- Investigations of Phytoplankton Salinity Tolerance were discontinued.
- In-situ fluorescence measurements were discontinued until laboratory CDOM measurements could determine appropriate parameters for in-situ equipment.

A summary of techniques investigated on a per-voyage basis is provided in Table 1. In addition to the intentional omission of techniques on latter voyages as described above, time constraints and equipment failure occasionally reduced the subset of techniques tested on a given voyage.

Although lignin was sampled, data from lignin analyses were unavailable for this report. Lignin analysis is not a common procedure. Analysis of lignin requires the reduction of a large volume of water (10L), isolation of lignin by Solid Phase Extraction (SPE), and finally analysis. Difficulties encountered by laboratories involved in analyzing lignin samples compromised the availability of lignin data for this report.

Table 1. Verification techniques investigated on individual voyages.

Tracer / Technique	VSF	VLA	VPS	VFos
Salinity	x	x	x	x
Salinity Tolerance of Phytoplankton	x	x	-	-
Turbidity	x*	x	na	x
CDOM fluorescence (in-situ)	x	x	na	na
CDOM fluorescence (EEMs)	x	x	x	x
Radium Isotopes	x	x	na	x
Metal Isotopes	x	x	x _f	x _f
Lignin	p	p	na	p

(x) data are presented in this report; (x*) data were lost due to equipment failure; (-) technique considered obsolete; (na) data were not collected; (p) data were unavailable at the time of publication, (x_f) metals samples in later voyages were filtered.

2.2. Sample Collection Methods

A brief overview of general methods for sample collection are provided in this section. Methodologies specific to particular cruises are reported in the methods sections for those cruises, as are experimental design issues including the numbers and positions (depth and location) of replicate samples.

Sampling apparatus

Ballast water sampling

Ballast water samples for trace metal, CDOM, lignin, radium, rhodamine and phytoplankton analyses were collected using an air driven diaphragm pump (Wilden Pro-Flo Models P.025 or P0.5). All internal parts of the pump, tubing, and fittings were made of plastic.

Sampling was initiated by attaching the pump fittings to lengths of 0.25" tubing which were installed in the tanks at the beginning of the experiment. The depths and locations of these tubes varied by cruise. Pumps were flushed for several minutes to clear stale water before collecting samples.

Shipside sampling

Methods used to collect shipside samples varied across cruises and are reported in the relevant cruise sections.

Salinity and Turbidity

The protocol for measuring salinity and turbidity differed depending on the availability of in-situ instruments. Procedures used on individual cruises are described at the beginning of each cruise chapter (Sections 3.2 through 4.1).

CDOM

Samples of approximately 120 mL of filtered ballast water were collected in sterile, amber glass bottles with Teflon® caps (Fisher Scientific). Filtration was accomplished using a 47 mm polycarbonate in-line filter holder fitted with GF/F filters to extract particles > 0.7 µm. Amber bottles and GF/F filters were pre-baked at 450 °C for 8-24 hours and 5-12 hours at 400 °C, respectively. Filter papers were stored individually in baked aluminum foil envelopes, then placed in batches in zip-lock bags.

Filtration of the CDOM samples was performed on deck by attaching the filtration apparatus to the pump outlet. Since allowing all of the discharge to enter the filter holder would have ruptured the filter, most of the pump discharge was bled on to the deck. Only a small trickle of ballast water (ca. 20 mL/min) was allowed to pass through the filter and into the sample bottle. While sampling, care was taken not to touch the inside of the sample bottle or lid and to protect the sample from air-borne contaminants as much as possible.

Samples were stored frozen (-15 °C) and shipped (FedEx 1-2 day) in insulated containers to the laboratory of Dr. Paula Coble (University of South Florida) for analysis. Samples that thawed during transit were not refrozen and were analyzed within a two week window.

Trace Metals

Ballast water (10-40 mL) was collected via pump in acid-cleaned 50 mL plastic centrifuge tubes (Fisher Scientific). Acid cleaning of sample tubes, pump tubing, syringes and filters was performed prior to the cruises. Acid cleaning involved leaching in 1 molar hydrochloric acid (HCl) for 1-2 days at room temperature (or for at least 4 hours at 60 °C), then rinsing in high purity deionized water (MilliQ water). Pump tubing was sealed prior to transporting to the ship. Sample tubes, syringes and filters were stored in small batches in zip-lock bags.

Trace metal samples were not filtered on the first two voyages (VSF and VLA). Samples collected during the last two voyages (VPS and VFos) were filtered through 20 mL polypropylene syringes fitted with 25 mm syringe filters with 45 µm supor membranes (Fisher Scientific). Filtration was performed by slowly pushing the water through the syringe and filter, since excess pressure can rupture filters. While sampling, care was taken not to contaminate the inside of the vial or lid and to protect the sample from air-borne contaminants as much as possible.

Samples were stored frozen and shipped (FedEx 2 day) in insulated containers to the Institute of Marine and Coastal Sciences (Rutgers University) for analysis.

Radium

Radium samples were collected at the beginning and end of the voyage. For each sample, a known volume of ballast water in excess of 180 liters was pumped at 1-2 L min⁻¹ via a filter (5 µm) through a plastic column containing a manganese dioxide coated fiber (Mn fiber, Moore 1976). Pump rates and sample volumes were monitored using a digital flow meter/accumulator (Cole Parmer). Excess water was squeezed from each Mn-fiber and the fibers placed in an individual "zipper locked" plastic bag.

Samples were shipped (FedEx® overnight) at ambient temperature to the laboratory of Dr. Willard Moore (University of South Carolina) immediately upon arrival in port.

Rhodamine Dye

On cruises which included rhodamine dye measurement (i.e. VSF, VLA), a gallon of undiluted Rhodamine WT dye was added to each ballast tank prior to ballasting. Rhodamine WT (Brightdyes, OH) comes as a 20 percent solution in water (meaning it is 20 percent active ingredient). The dye has a specific gravity at standard pressure and temperature of 1.03 ± 0.05 and maximum wavelength of excitation/emission of 550/588 nm. Unfiltered water samples were pumped directly into clean amber glass bottles. Samples were refrigerated on the ship and again at SERC prior to analysis.

Salinity Tolerance

Ballast water was pumped through a 40 µm mesh (to remove most predatory zooplankton) and collected in clean 250 mL plastic containers.

Samples were kept cool and in ambient light on the vessel, then shipped (FedEx® 2 day) to the laboratory of Dr. Larry Brand (University of Miami) immediately upon arrival in port.

Lignin

Unfiltered water samples were pumped directly into clean amber-tinted collapsible 4-liter PolyPac® containers (Fisher Scientific). Three containers full of seawater (totaling approximately 12 L) were collected for each sample time and location. Untreated ballast water samples were kept in cold storage (4 °C) until analysis. SERC and the Tiburon Research Center performed filtration and Solid Phase Extraction. Following extraction, sample cartridges were shipped to the laboratory of Patrick Louchouart

(Texas) for elution and thereafter to the laboratory of Marc Lucotte (Montreal, Canada) for quantification of terrigenous dissolved organic matter.

2.3 Analytical Methods

The following sections outline the analytical procedures used to process samples collected on each of the verification voyages. The protocols described below are valid for all cruises, with minor variations which are noted in the methods sections of individual cruises.

CDOM

CDOM samples were analyzed between January - October 2001. It was necessary to re-filter around 10 percent of the samples before analysis, since appreciable levels of particulates remained in the sample (possibly due to filter papers rupturing under excessive discharge pressure).

Absorbance scans were run over wavelengths of 220-700 nm. Excitation-emission matrices (EEMs) were generated across excitation wavelengths of 220-455 nm and emission wavelengths of 250-710 nm. Readings were corrected for instrument variability and normalized to the standard quinine sulfate dihydrate, (presented in QSE or quinine sulfate equivalents). Further details of methodologies, peak designation and significance are available in published references (Coble et al. 1998, Coble 1996) and Appendix B.

Trace Metals

All apparatus used for sample digestion and preparation were acid cleaned and rinsed with deionized/distilled (D.I.) water according to standard trace metal procedures. Samples were acidified to 0.2 percent with optima grade HCl for 24 hours and then centrifuged. The supernatant was removed and diluted 10 times with three percent optima grade HNO₃ acid for analysis. All samples were spiked with a known concentration of Indium to monitor and correct for any variations in instrument sensitivity throughout the run.

Samples were analyzed on the ELEMENT (Finnigan MAT, Bremen, Germany), a sector field inductively coupled plasma mass spectrometer with high resolution capability (Field *et al.* 1999). Instrument precision is approximately ± 10 percent (1-sigma).

Sample concentrations in solution, expressed in parts per billion, were calculated using the average slopes determined from three point standard additions to ten replicates. Any potential contamination of trace metals introduced during sample preparation was corrected using the mean values of diluted clean open ocean seawater or three percent HNO₃ where appropriate. For example, Molybdenum [Mo], Phosphorus [P], Vanadium [V] and Chromium [Cr] are "high" in the open ocean and therefore the three percent HNO₃ blank was used.

For VSF and VLA, samples were analyzed for the presence of thirteen metal elements (Molybdenum [Mo], Cadmium [Cd], Antimony [Sb], Barium [Ba], Lead [Pb], Phosphorus [P], Vanadium [V], Chromium [Cr], Manganese [Mn], Iron [Fe], Cobalt [Co], Nickel [Ni] and Copper [Cu]).

For VPS and VFos, samples were analyzed for the presence of eight metal elements tested on previous voyages (Mo, Ba, P, V, Mn, Cd, Fe, Cu) as well as two elements not previously tested (Uranium [U], Zinc [Zn]).

Radium

At the conclusion of each voyage, samples were immediately shipped to the laboratory of Willard Moore at the University of South Carolina. The Mn fibers were washed with D.I. water and partially dried in a stream of high pressure air. They were then placed in a closed loop air circulation system described by Moore and Arnold (1996). Helium was circulated over the Mn fiber to sweep the Radon isotopes ²¹⁹Rn and ²²⁰Rn generated by ²²³Ra and ²²⁴Ra (Radium) decay through a 1.1 liter scintillation cell where alpha particles from the decay of radon and daughters were recorded by a photomultiplier tube (PMT) attached to the scintillation cell. Signals from the PMT were routed to a delayed coincidence system pioneered by Giffin et al. (1963) and adapted for Ra measurements by Moore and Arnold (1996). The delayed coincidence system utilizes the difference in decay constants of the short-lived polonium daughters (²¹⁵Po and ²¹⁶Po) of ²¹⁹Rn and ²²⁰Rn to identify alpha particles derived from ²¹⁹Rn or ²²⁰Rn decay and hence to determine activities of ²²³Ra and ²²⁴Ra on the Mn fiber. The expected error of the short-lived Ra measurements is 10 percent.

Following completion of the ²²³Ra and ²²⁴Ra measurements, the Mn fiber samples were aged for 2-6 weeks to allow initial excess ²²⁴Ra to equilibrate with natural ²²⁸Th (Thorium) adsorbed to the Mn fiber. The samples were measured again to determine ²²⁸Th and thus to correct for supported ²²⁴Ra.

Long-lived Ra isotopes were measured for a subset of the samples (VFos final time point samples only). Mn fibers were leached with HCl in a Soxhlet extraction apparatus to quantitatively remove the long lived Ra isotopes. The Ra was coprecipitated with BaSO₄. The precipitant was aged for three weeks to allow ²²²Rn and its daughters to equilibrate with ²²⁶Ra. The samples were measured in a gamma ray spectrometer to assess the activities of ²²⁶Ra and ²²⁸Ra (Moore, 1984). The expected error of the long-lived Ra measurements is seven percent.

Rhodamine Dye

Rhodamine dye concentrations in ballast water samples were measured at SERC by fluorometer (model 10-005R, Excitation / Emission = 550 nm/580 nm, Turner Designs).

Salinity Tolerance

In order to determine salinity tolerance, phytoplankton samples were first split into three equal subsamples. Each subsample was further split into three subsamples each of which was randomly assigned to one of three salinities (0 parts per thousand (ppt), 15 ppt and 35 ppt). Algal growth was measured daily by fluorometry for two weeks. Salinity tolerance ratios were determined on the final sampling day as the ratio of fluorescence at 15 ppt / 35 ppt. The results of the three comparisons were averaged to give a single ratio for each ballast water sample.

According to Brand's Salinity Tolerance hypothesis (Larry Brand, pers.comm.) phytoplankton which are truly oceanic are relatively intolerant to lower than oceanic salinities (< 32 ppt). Conversely, phytoplankton originating in high salinity coastal regions flourish under a wider range of salinities. The ratio of growth rates (measured as fluorescence at 15 ppt/35 ppt) of coastal versus oceanic species incubated over a range of salinities reflects the origin of the sample. Low ratios are indicative of predominantly oceanic species, and high ratios are indicative of predominantly coastal species.

Lignin

Processing was performed in three stages. As indicated earlier, untreated ballast water samples were stored in a cold room at SERC (VFos) and in cold rooms at the Tiburon Research Center and a second cold storage facility in San Francisco (VLA and VSF).

The first processing phase for these samples (filtration and Solid Phase Extraction (SPE)) was performed at SERC (VFos) and Tiburon, CA (VLA, VSF). In the first stage, the raw seawater samples were filtered

through a 15 micron prefilter followed by a 0.2 micron high performance pleated polypropylene filter cartridge (Cole Parmer). Filtered water samples were acidified to pH 2 using reagent-grade concentrated HCl prior to SPE. SPE of dissolved organic matter was performed on pre-packed columns containing 10 g of sorption material composed of octadecyl carbon moieties (C_{18}) chemically bonded to a silica support (C_{18} - SPE Mega-Bond Elut; Varian). Cartridges were pretreated with methanol (60 mL) followed by acidified (pH 2) Milli-Q water (60 mL), making sure the sorbent remained wet with water prior to extraction. Filtered, acidified water samples were pumped through the SPE cartridge with a peristaltic pump (mounted with two pump heads to process two samples simultaneously) and silicone tubing (Cole Parmer). The pumping line ran through a silicone stopper that was inserted in the top of the syringe-like SPE cartridge. By this method, the water (10-14 liters) was delivered directly into the headspace of the SPE cartridge and forced by pressure through the sorbent at a flow rate of $100 \pm 3 \text{ mL min}^{-1}$. After the samples were extracted, each C_{18} - SPE cartridge was rinsed with one liter of acidified (pH 2) Milli-Q to remove residual salts. The cartridges were stored in the freezer until they were shipped to the laboratory of Dr. Patrick Louchouart for second stage processing.

In the second stage of processing, cartridges were allowed to warm to room temperature and the retained CDOM was eluted from the column in one fraction using 50 mL of methanol. The eluent was collected into a muffled glass flask and evaporated to dryness under N_2 flow using a TurboVap II Concentration Workstation (Zymark Corporation, Hopkinton, MA).

The quantification of lignin-derived phenols in SPE eluents was performed in Dr. Marc Lucotte's laboratory (Montréal, Québec) using a modified version of the CuO oxidation and extraction scheme of Hedges and Ertel (1982) as presented in Louchouart et al. (2000). The dry eluates (isolated CDOM and residues adhered to the vials) were dissolved into a previously N_2 -sparged NaOH solution (eight percent weight to weight (wt/wt)) and then loaded along with reagents into the microwave Teflon® vessels. These were then closed under a N_2 stream to purge the head space. The oxidation of samples was performed at a temperature of $150 \text{ }^\circ\text{C}$ and a reaction time of 90 minutes. Upon completion of the oxidation reaction, the reaction vessels were allowed to cool, then opened to introduce known amounts of internal/recovery standards (ethyl vanillin and *trans*-cinnamic acid). The alkaline solutions were then acidified to pH 1 and liquid-liquid extraction of the compounds of interest was performed using known volumes (6-8 mL) of ethyl acetate; samples were then blown to dryness under constant N_2 pressure. Once the organic solvent had been completely dried, the samples were redissolved in pyridine and a subsample of each was

derivatized with BSTFA [N,O-Bis(trimethylsilyl)trifluoroacetamide] + one percent TMCS [Trimethylchlorosilane].

Trimethylsilyl ether and ester derivatives of CuO oxidation products were quantified using selected ion monitoring (SIM) on a Varian gas chromatograph/mass spectrophotometer (GC/MS) fitted with a DB-5MS capillary column (30 m, 0.25 mm ID; J&W Sci., #122-5532). The GC oven was temperature programmed from 100 °C, with no initial delay, to 270 °C at 4 °C min⁻¹ and held at the upper temperature for 16 minutes. The GC injector was maintained at 300 °C whereas the GC/MS interface was maintained at 280 °C. The mass spectrometer was operated in the electron ionization (EI) mode (70 eV) and three ion masses were monitored for each lignin-derived phenol during the GC run. Positive identification was performed using retention times and by comparing the relative abundance of the three ions in each sample to those produced by standards.

Despite the processing just described, no data from lignin analyses were available for this report. Difficulties encountered when implementing this procedure at one of the laboratories significantly delayed final analysis.

3. Pacific Cruises

3.1. Introduction

Ballast exchange experiments were conducted on three different voyages along the western coast of North America. The experimental voyages began in either California (San Francisco Bay or Los Angeles) or Washington (Puget Sound) and ended in Valdez, Alaska. In each case, ballast water was taken aboard at port of origin, and ballast water exchange was conducted along a coastwise route more than 200 miles offshore. Thus, all samples originated in the eastern margin of the Pacific Ocean between California and Alaska.

While the goal was to take parallel measures across all voyages, some modifications to the experimental design were made based upon initial results. This strategy was intended to streamline sampling effort over time by removing techniques that proved unproductive, and by refining techniques for those that appeared promising. Consequently, tracers measured later in the Atlantic Ocean (see below) were a subset of those initially measured in the Pacific Ocean.

Shipside sampling was less extensive in the Pacific voyages compared to the Atlantic voyage. This was due both to the limited distance and time associated with the Pacific coastwise transits and to a conceptual shift about the relative importance of ballast water versus shipside samples that occurred as the project progressed.

3.2. VSF : San Francisco to Valdez

3.2.1. Overview

Samples were collected from three ballast tanks (Control (C), Empty-Refill (ER) and Flow-Through (FT)) on the oil tanker "S/R BENICIA" (Table 2) during a commercial voyage between San Francisco, CA and Valdez, AK during November 2000. This cruise is hereafter identified by the abbreviation "VSF."

Table 2. VSF vessel specifications.

Name (Call Sign)	S/R BENICIA (KPKL)
Owner	Sea River Maritime, Inc.
Length x Breadth x Draft	266.6 m x 52.76 m x 23.2 m
Cargo	Oil
Experimental ballast tanks: (i.d. / volume / max. depth)	#2 port / 11381 MT / 23 m #4 port and starboard / 11486 MT / 23 m

3.2.2. Experimental Design

Initial ballasting of the three experimental tanks took place in San Francisco Bay on November 5, 2000 between the hours of 1400 and 1700. Rhodamine dye was added to each of the tanks prior to ballasting. After ballasting was completed, one tank was designated the control (C) and remained untouched for the length of the experiment. Of the remaining two tanks, one was subjected to a single Empty-Refill (ER) exchange while the other underwent three single-volume Flow-Through (FT) exchanges. The sample measurements for VSF voyage included the following:

- in-situ determination of salinity, turbidity and CDOM fluorescence
- laboratory determination of trace metal isotopes, radium isotopes, Phytoplankton Salinity Tolerance, rhodamine and CDOM fluorescence (Emission-Excitation Matrix Spectroscopy)

All exchanges were conducted in oceanic water beyond the 200 mile limit off the coasts of California and Oregon (Table 3).

Table 3. Timing and location of mid-ocean exchanges (FT = Flow-Through; ER = Empty-Refill) during the VSF cruise.

Exchange	Date (2000)	Volume (%)	Start Location	Stop Location
FT (100%)	8 Nov: 1000-1500	100% (FT)	42°13' N, 129°39' W	42°52' N, 130°10' W
FT (200%)	10 Nov: 1000-1500	100% (FT)	48°05' N, 134°33' W	49°06' N, 135°24' W
FT (300%)	10 Nov: 1730-2200	100% (FT)	49°43' N, 135°58' W	50°36' N, 136°44' W
ER (100%)	9 Nov: 1200-1930	100% (ER)	44°47' N, 131°54' W	45°26' N, 132°52' W

3.2.3. Methods

Tank sampling

In-situ instruments

In-situ profiles (salinity, CDOM fluorescence and turbidity) were obtained by lowering a Conductivity/Temperature/Depth Sensor (CTD) (Seabird Electronics, Inc.) fitted with a Light Back Scattering Sensor and a Flash Lamp Fluorometer (Wetlabs Inc.) through a single manhole into each tank. The Light Scattering Sensor was later discovered to have been incorrectly mounted on the CTD and consequently to have collected no useful turbidity data during the cruise.

Ballast water samples

General sample collection procedures for different types of samples are provided in Section 0. Methodologies specific to this cruise are described below.

Samples for laboratory analysis (CDOM, metals, radium, rhodamine, salinity tolerance) were obtained by pumping ballast water through tubing installed at two access points (fore and aft) and two depths (1 m, 12 m) in each tank.

For trace metals and rhodamine, one replicate was collected at the fore and aft locations from 1 m and 12 m depths in the Control and Flow-Through tanks during four sampling sessions (2 tanks * 2 locations * 2 depths * 4 days = 32 samples). The same applied to the Empty-Refill tank with the following exceptions: i) One post-exchange sampling session (T₂) was omitted; ii) The water level in the tank after the exchange dropped below the depth of the 1 m tubing, preventing the collection of samples from 1 m depth and changing the deeper samples to 11 m. Salinity tolerance samples were collected from the tanks only after ballast water exchanges had been completed. CDOM samples were collected in the same manner at the beginning and end of the voyage (T₀ and T₃), while samples for the intermediate time points were collected only at T₁ from the ER tank and at T₂ from the FT tank. In the CDOM figures that follow, T₁ FT and T₂ ER values are linear interpolations of the prior and subsequent data points.

Numerous technical difficulties were encountered in establishing the correct flow rate for pumping radium samples and with the flowmeter/accumulators used to record sample volumes. Consequently, collection of

these samples was extremely time consuming and it was possible to collect only a single radium sample from the surface of each tank per time point.

Ocean water (Shipside) sampling

CDOM, metals and salinity tolerance samples from the ambient ocean (SS) were collected via the ship's fire hose. Two replicate samples of each type were collected during each ballast water exchange. The fire hose was supplied with untreated seawater from the side of the vessel at a depth of approximately 5 m. Prior to collecting samples, the fire hose was left running at full blast over the side of the ship for at least half an hour. For radium samples, the fire hose was used to fill 55 gallon plastic drums. Water was then pumped from the barrels through the Mn fibers according to the standard protocol.

3.2.4. Results

Exchange efficiency

Ballast water samples from different depths in the Control, Flow-Through and Empty-Refill tanks contained similar concentrations of rhodamine, indicating that the tanks were well mixed at the times of sampling (Figure 1). This result was used to justify the averaging of data from different depths in the same tank in this and subsequent analyses. Note that in Figure 1 and all following graphs, T0-T3 indicate initial through final sampling times.

A single ER exchange was sufficient to remove 98 percent of the original tracer and port water, while a series of three single-volume FT exchanges achieved slightly less than the theoretical (95 percent) exchange efficiency.

The composition of the ballast in each tank at any time can be inferred from relative concentrations of rhodamine. The proportion of port- and ocean- water in each tank per sampling time are summarized in Table 4.

Table 4. Composition of ballast water in experimental tanks during the VSF cruise.

Sample Time	Control (C)		Flow-Through (FT)		Empty-Refill (ER)	
	Port (%)	Ocean (%)	Port (%)	Ocean (%)	Port (%)	Ocean (%)
T0	100	0	100	0	100	0
T1	100	0	45	55	2	98
T2	100	0	17	83	2	98
T3	100	0	7	93	2	98

Salinity

Salinities in the three tanks varied slightly (20-22.5 ppt) at the beginning of the experiment, possibly as a result of an interaction between the vessel's draft and stratification of the port water while ballasting (Figure 2). During the voyage, salinity measurements described the inverse pattern to the rhodamine data, i.e. the salinity increased in the treatment tanks as progressively more exchanges were performed. At the end of the experiment, the salinity in the exchanged tanks was close to that of the surrounding ocean water (31.5-32.6 ppt).

In-situ CDOM Fluorescence

Peak CDOM fluorescence intensity (fIS) in the Control Tank was stable during the voyage (Figure 3). CDOM fluorescence in the Empty-Refill and Flow-Through tanks was almost perfectly correlated with rhodamine fluorescence intensity ($R^2 > 0.999$) and salinity ($R^2 > 0.99$). Fluorescence dropped to 6 – 13 percent of initial values by the end of the voyage.

The in-situ CDOM fluorescence intensity is treated here and throughout the report as an independent measure. In-situ readings in fIS have not been correlated to EEM measurements.

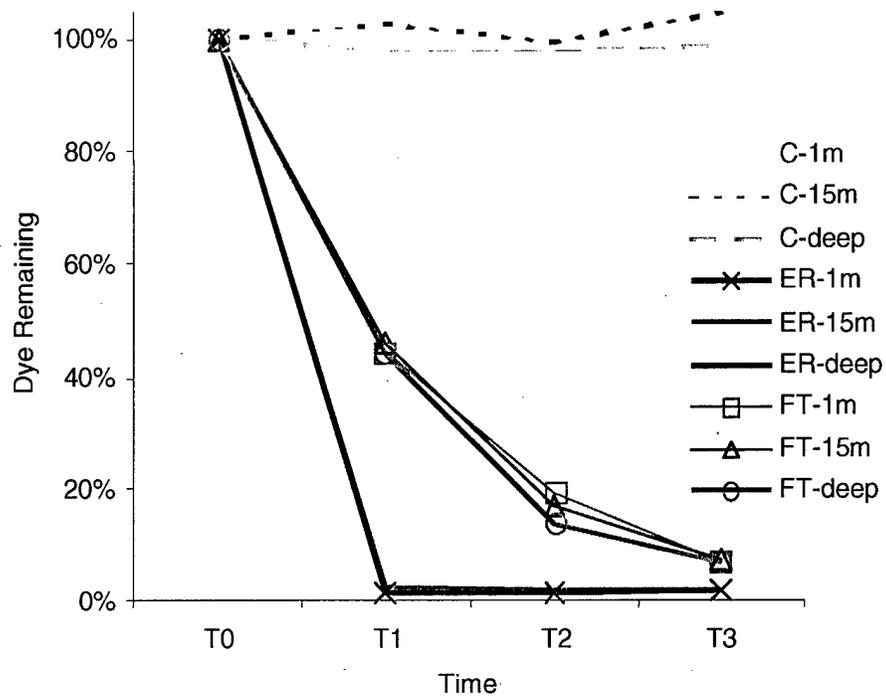


Figure 1. Rhodamine dye displacement at three depths (1 m, 15 m and 1m from tank bottom) in three tank treatments (C, ER, FT) during the VSF cruise.

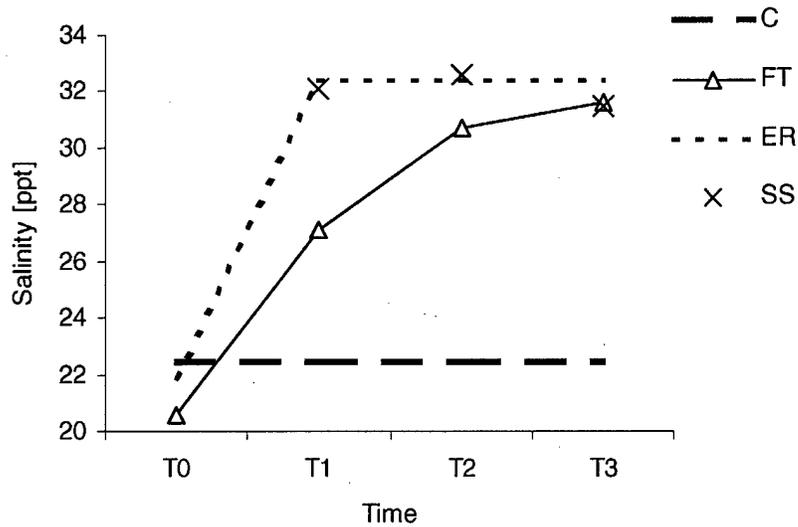


Figure 2. Salinity variation in ballast tanks (C, FT, ER) and shipside (SS) during the VSF cruise.

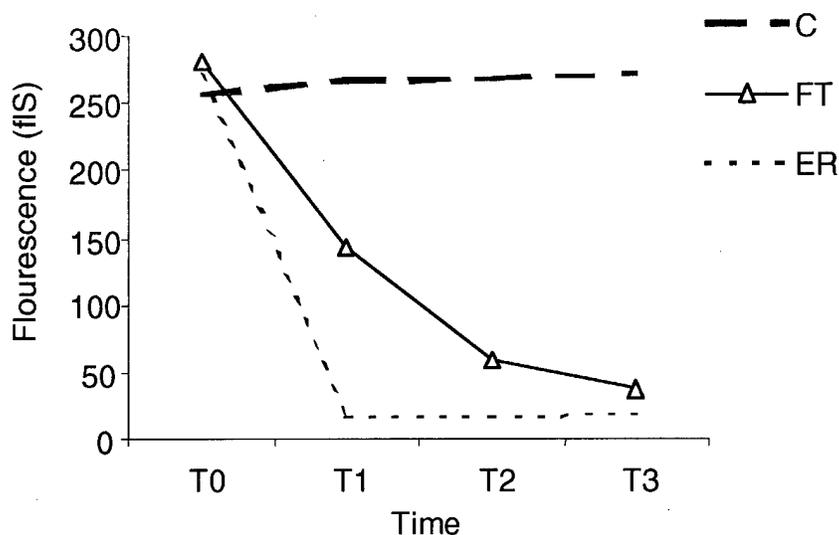


Figure 3. In-situ Peak CDOM fluorescence during the VSF cruise.

CDOM EEMs

Several fluorescent peaks were observed in the EEM plots of CDOM samples analyzed in the laboratory. Peaks A and C of Figure 4 arise from the fluorescence of humic material. CDOM fluorescence intensities are quantified in quinine sulfate equivalent units (QSE). (Here and throughout this report, "CDOM EEM" and "CDOM EEM Fluorescence" are used interchangeably. Likewise, "qse" in the figures is equivalent to "QSE" in the text). Peak A was more intense than Peak C for all samples and represented the dominant natural peak during this cruise. The protein fluorescence identified in the same figure was similar to that of tyrosine, with primary (1'-230 nm) and secondary (2'-270 nm) excitation peaks.

The fluorescence peaks due to rhodamine can be clearly identified from Figure 4. It is apparent that rhodamine excites throughout the entire range of CDOM excitation wavelengths. Since the excitation spectrum for rhodamine also reflects its absorption spectrum, this indicates that the absorption data were contaminated by rhodamine across the entire spectrum. Consequently, these absorption data are unusable and will not be discussed further in the context of this data set.

The characteristics of humic peaks A and C and the tyrosine-like fluorescence (excitation, emission, intensity) were examined with reference to different tanks sampled and along the sampling time line and are discussed in detail below.

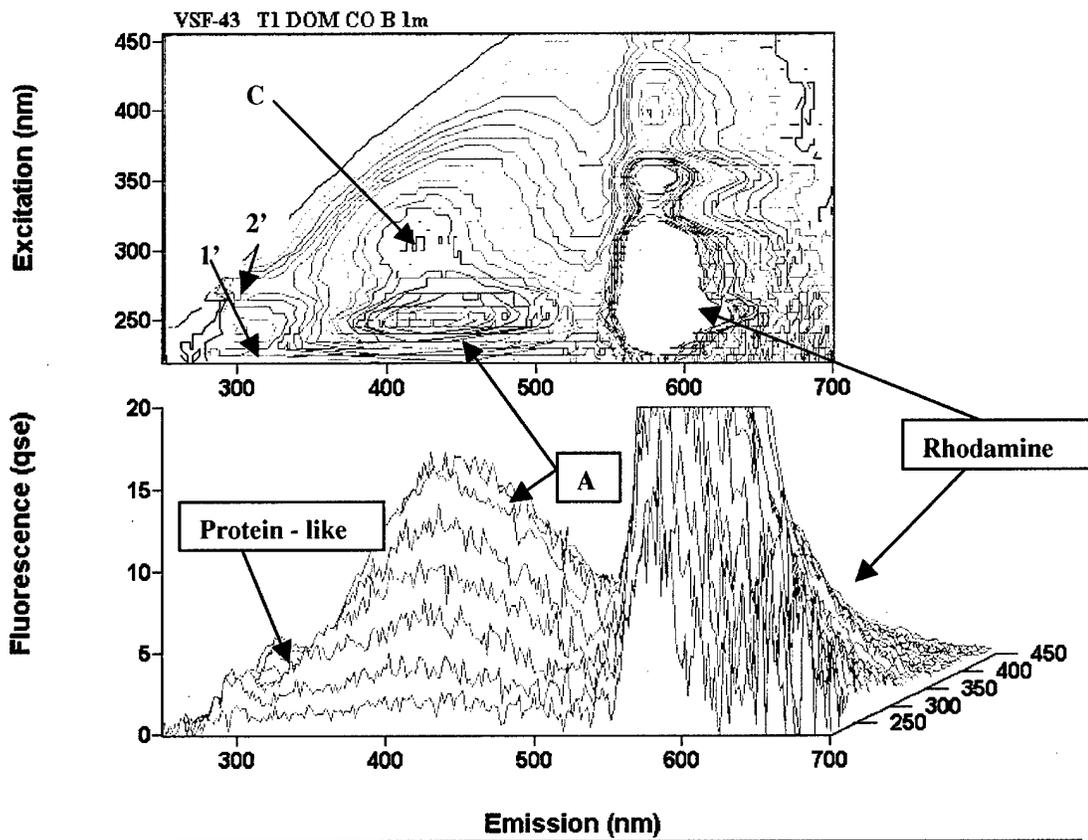


Figure 4. Example EEM from the VSF cruise data (T1 Control, 1 m depth).

Fluorescence Peak Intensity

The intensities of each of the natural fluorescence peaks (averaged across tank) are plotted against time in Figures 5-8. Here and in subsequent figures, error bars represent "1 standard error." Note that samples were not collected from the FT tank at T1 nor from the ER tank at T2. Thus points at these sampling times are interpolations of the data on either side of the time line.

Fluorescence A and C data were consistent across locations and depths in the same tank, indicating the water was well mixed. Peak intensities again mirrored the behavior of the in-situ CDOM and rhodamine data (Figures 5 and 6).

Tyrosine-like peaks were both variable within tanks and displayed inconsistent trends over time (Figures 7 and 8). This may indicate the biological production of tyrosine-like signals during the experiment.

Alternatively, the samples are much more likely to become contaminated in this region of the EEM than in the humic region.

Fluorescence Peak Position

The wavelength of the humic fluorescence peaks did not vary consistently with degree of ballast water exchange (or salinity) in this study.

The position of the humic "A" peak in control samples varied between 432-436 nm over the course of the voyage (Figure 9). There was a slight trend in the data toward the peak intensity occurring at decreasing wavelengths (i.e. blue-shifting) following exchange of the FT tank. Three of the four exchanged ER samples also had relatively short wavelengths, however, the other did not and there was no overall trend.

There was also some evidence for 'blue-shifting' of the C peak in the exchanged tanks (Figure 10). However, once again the high variability within tanks masked any statistical differences between the tanks at the end of the voyage ($F = 1.74$, 9 df, $p > 0.24$).

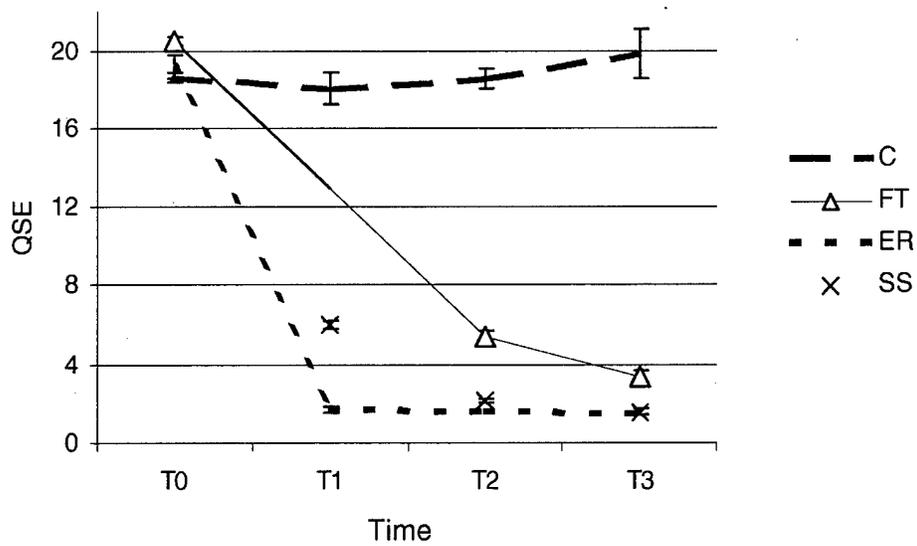


Figure 5. Humic Peak "A" intensities in the control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shippide samples (SS) during the VSF cruise. Error bars are indicated.

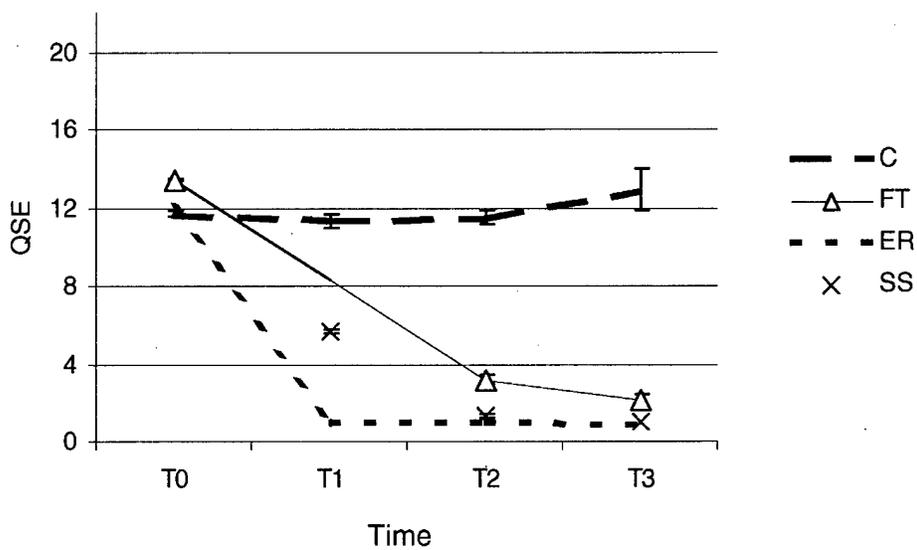


Figure 6. Humic Peak "C" intensities in the control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shippide samples (SS) during the VSF cruise. Error bars are indicated.

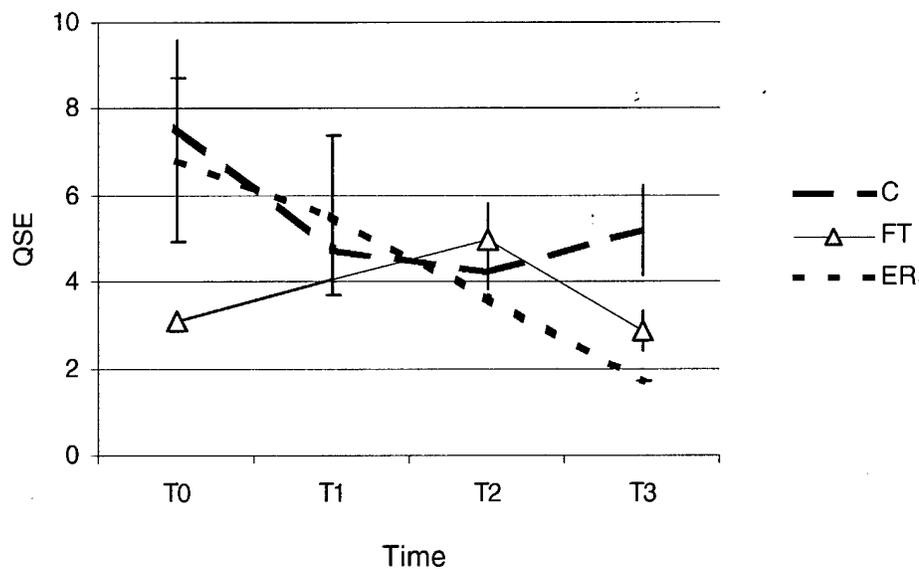


Figure 7. Tyrosine – like 1' peak intensities in the control (C), Flow-Through (FT) and Empty-Refill (ER) tanks during the VSF cruise.

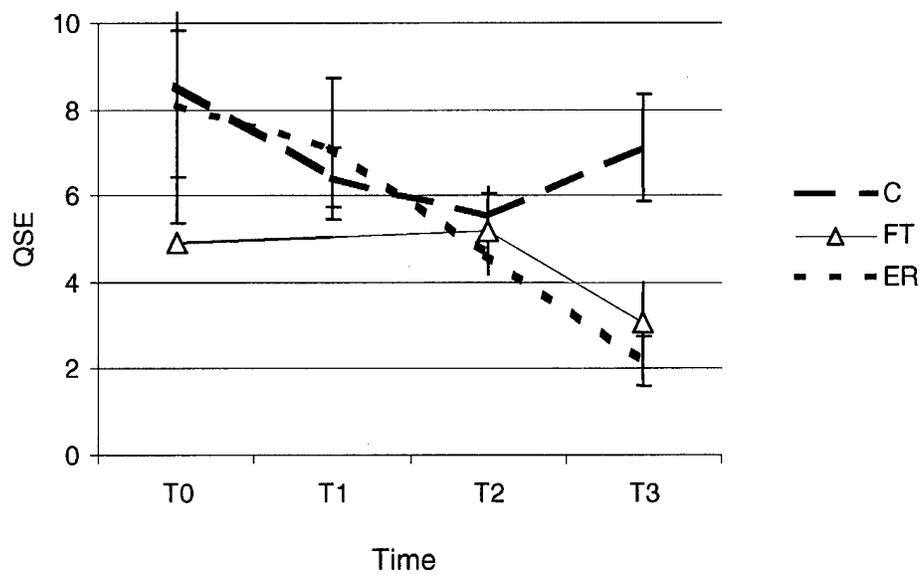


Figure 8. Tyrosine – like 2' peak intensities in the control (C), Flow-Through (FT) and Empty-Refill (ER) tanks during the VSF cruise.

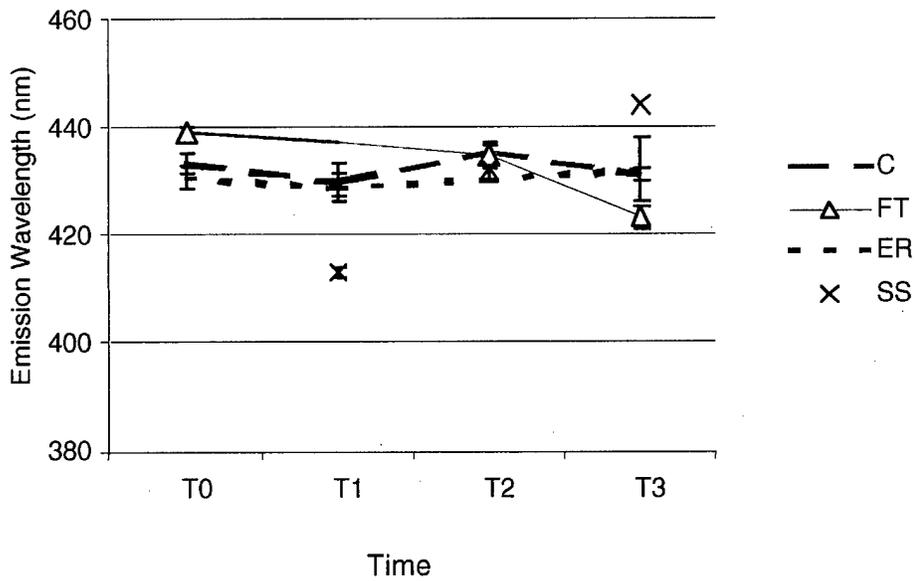


Figure 9. Position of "A" emission peak maximum in the control (C), Flow-Through (FT) and Empty Refill (ER) tanks and in shipside samples (SS) during the VSF cruise.

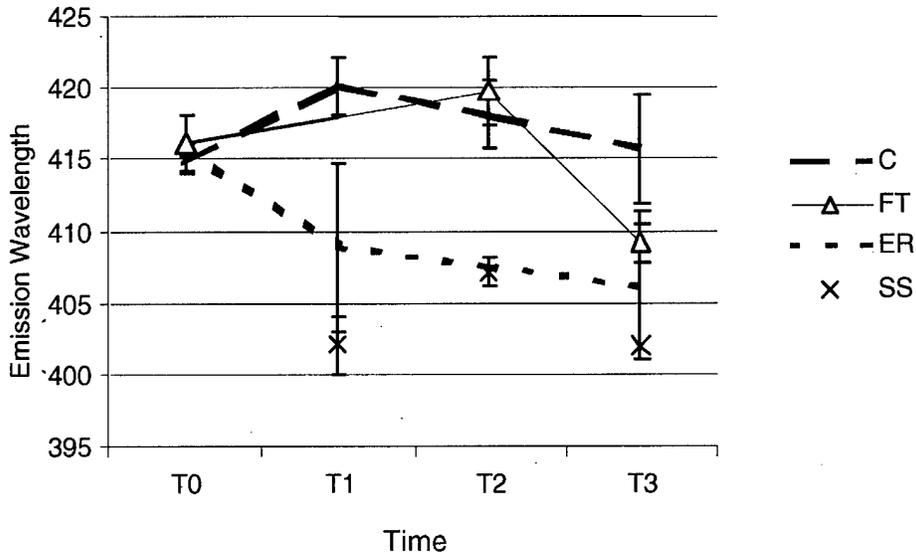


Figure 10. Position of "C" emission peak maximum in the control (C), Flow-Through (FT) and Empty Refill (ER) tanks and in shipside samples (SS) during the VSF cruise. Note high variability indicated by error bars.

Radium

Radium Isotopes ^{223}Ra ($t_{1/2} = 11$ days) and ^{224}Ra ($t_{1/2} = 3.7$ days) were both recovered in measurable levels from the manganese fibers. Only one ocean sample (T1) contained appreciable quantities of either isotope. ^{223}Ra (Figure 11) levels in the tanks were an order of magnitude lower than ^{224}Ra levels (Figure 12). ^{223}Ra and ^{224}Ra in control samples varied considerably over the course of the voyage. Both isotopes decreased following the Empty-Refill and first Flow-Through exchanges. ^{223}Ra continued to decrease after subsequent exchanges, while ^{224}Ra concentrations recovered slightly. Comparing the samples at the final time point only (T3), the concentrations of ^{223}Ra in the ER and FT samples were 13 percent and 18 percent of the Control sample concentration, while the concentrations of ^{224}Ra in the ER and FT samples were 30 percent and 27 percent of Control respectively.

The variability of both isotopes within control samples could be attributable to one or more of the following i) within-tank patchiness, ii) sediment-water exchange of radium during the voyage, iii) biological activity altering sediment/water exchange rates, or iv) procedural problems during sampling (particularly the incomplete filtration of sediment particles). Because of the lack of replication of samples (N=1), no statistical conclusions can be drawn from these data.

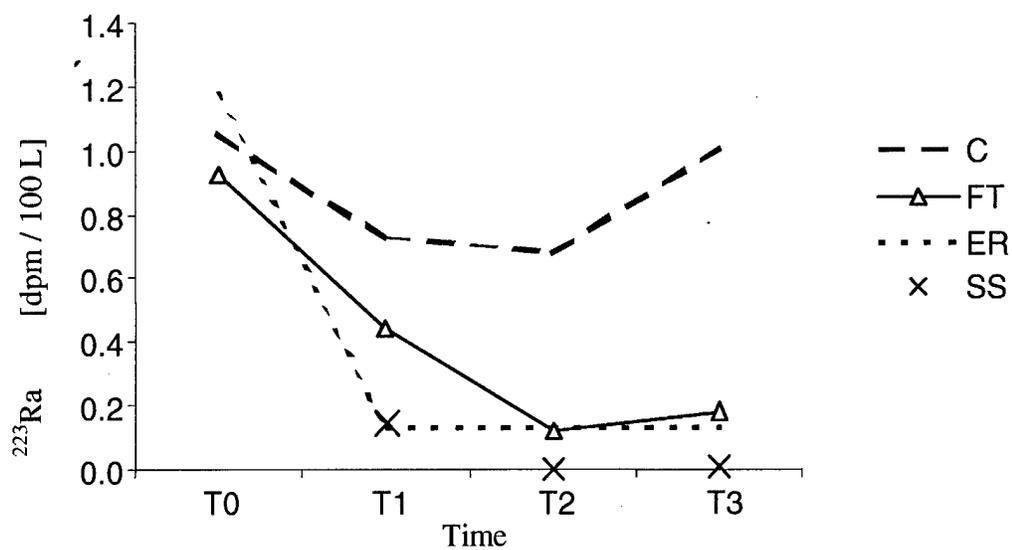


Figure 11. ^{223}Ra variation in control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shipside samples (SS) during the VSF cruise.

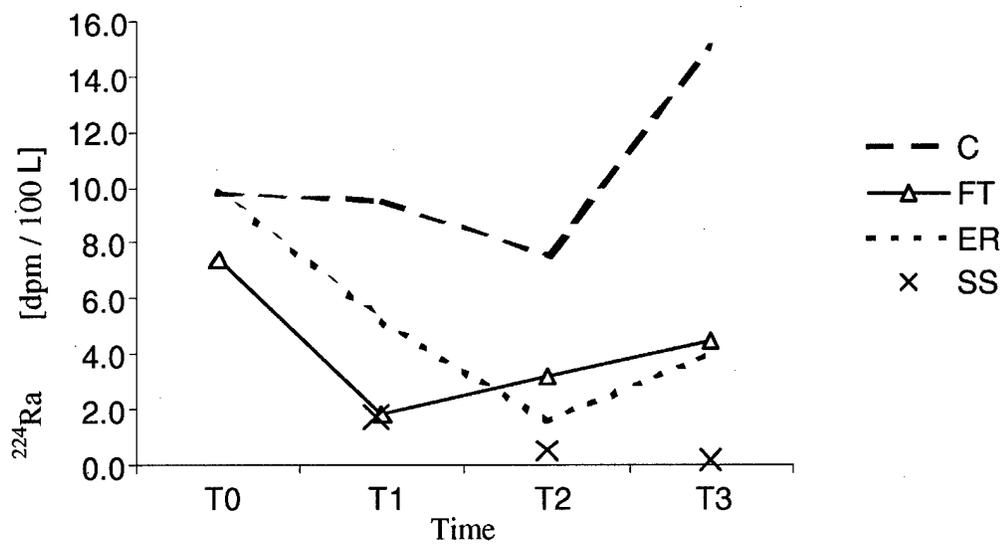


Figure 12. ^{224}Ra variation in control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shipside samples (SS) during the VSF cruise.

Trace Metals

The results for 13 elements (Mo, Cd, Sb, Ba, Pb, P, V, Cr, Mn, Fe, Co, Ni, Cu) are presented as three groups which share important characteristics. Group A [Mo, Ba, P, V, Mn] contains metals which demonstrated the highest potential as tracers of ballast water exchange for two reasons: i) they were not clearly contaminated by the tanks or procedure; ii) they demonstrated trends consistent with data obtained using other techniques (salinity, rhodamine, CDOM) (Figure 13) (Sohrin 1987, Monnin *et al.* 1999, Collier 1984, Johnson *et al.* 1996, Donat and Bruland 1995). With the exception of Mo which increased or decreased in a manner conservative with salinity ($R^2 > 0.99$), concentrations of these tracers declined as a result of exchange with ocean water.

Group B [Fe, Co, Ni] consists of metals which demonstrated similar trends but exhibited concentrations several orders of magnitude above those expected for estuarine and Pacific ocean water and were certainly contaminated by the ship (Figure 14) (Martin and Gordon, 1988; Martin *et al.*, 1989, Donat and Bruland 1995, Esser and Volpe, 2002). Metals which demonstrated the least potential as tracers, due to their low concentrations in seawater and resulting susceptibility to contamination, as indicated by high variability in our samples, are in Group C [Sb, Cd, Pb, Cr, Cu] (Figure 15) (Donat and Bruland 1995).

In all tanks, data obtained from both depths and locations demonstrated good agreement and were averaged for the analysis. The generally small standard error bars apparent on group A and B plots indicate reliability of the complete procedure. The large error bars seen for most metals at T2 (Control Tank) are due to the contamination of a single replicate sample; it is notable, however, that this contamination did not appear to affect Mo or Ba. Otherwise, concentrations of group A and B metals did not vary significantly in the Control Tank over depth or time.

The Flow-Through tank demonstrated a gradual change from initial concentrations similar to those of the Control Tank, to final concentrations approaching ocean levels, with statistically significant changes in group A and B metal concentrations following partial exchanges. A similar result was seen after a single exchange in the ER tank. These results are interpreted as a simple dilution effect of the original ballast water with offshore water. In the FT and ER tanks, concentrations of Ba, Mn and P varied by as much as ten times over the voyage, whereas Mo varied by approximately 30 percent. Since Mo is conservative with salinity, these results indicate that the Ba, Mn and P concentrations were more sensitive indicators than salinity on this voyage.

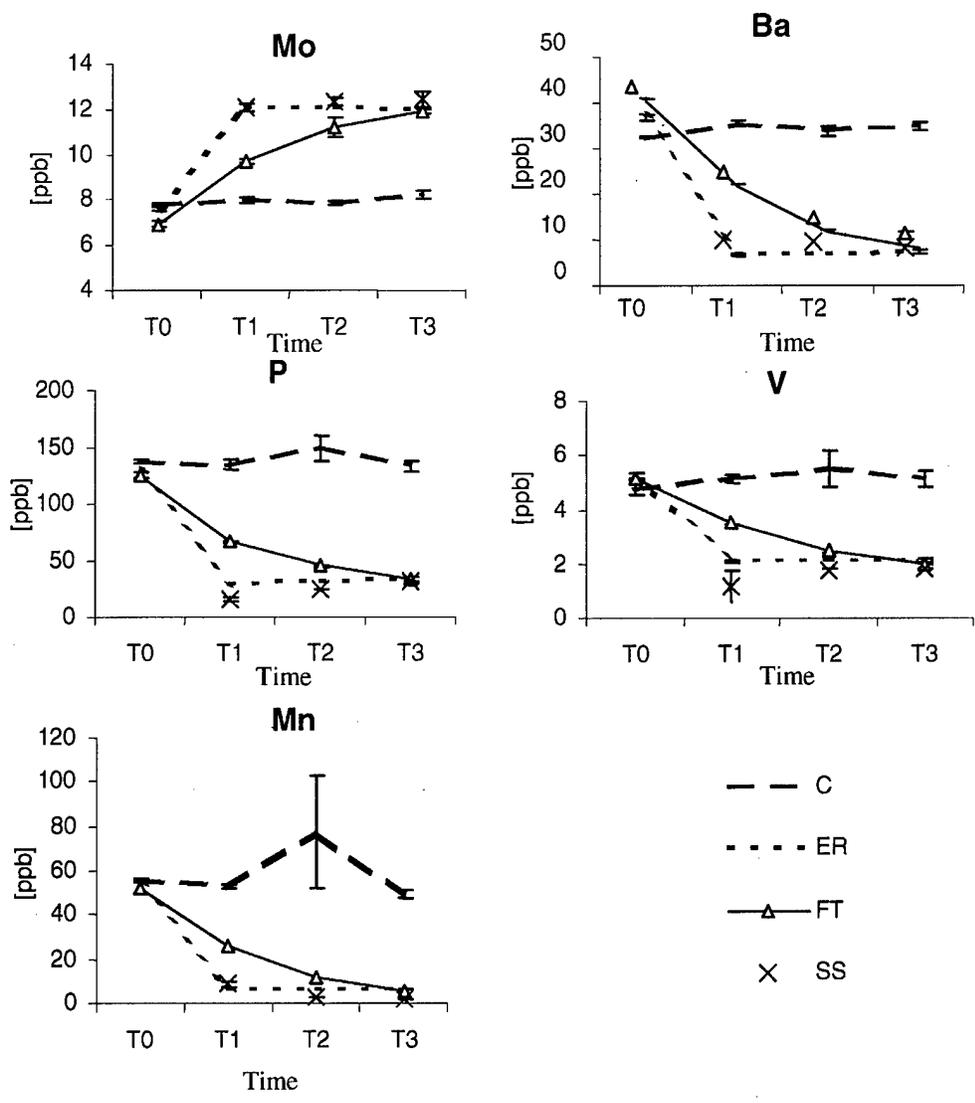


Figure 13. Variation of Group A Metal concentrations in Control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shippside samples (SS) during the VSF cruise. Note contamination of one replicate in Control Tank at T2.

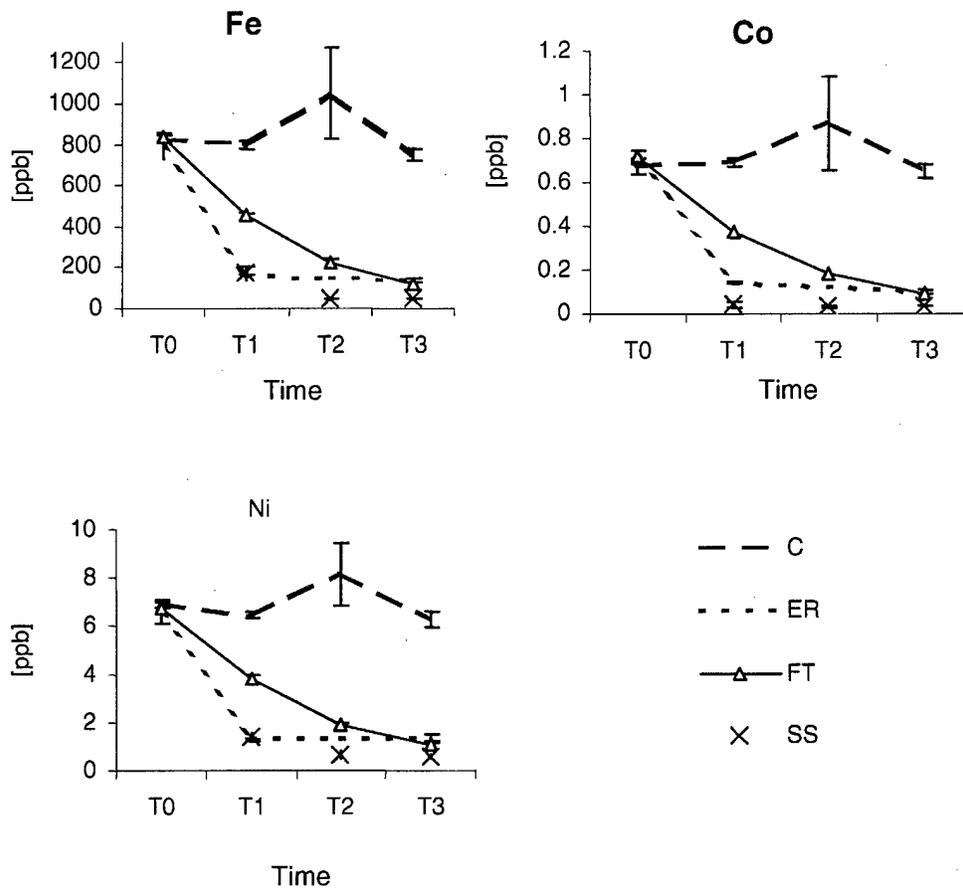


Figure 14. Variation of Group B Metal concentrations in Control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shipside samples (SS) during the VSF cruise. Note contamination of one replicate in Control Tank at T2.

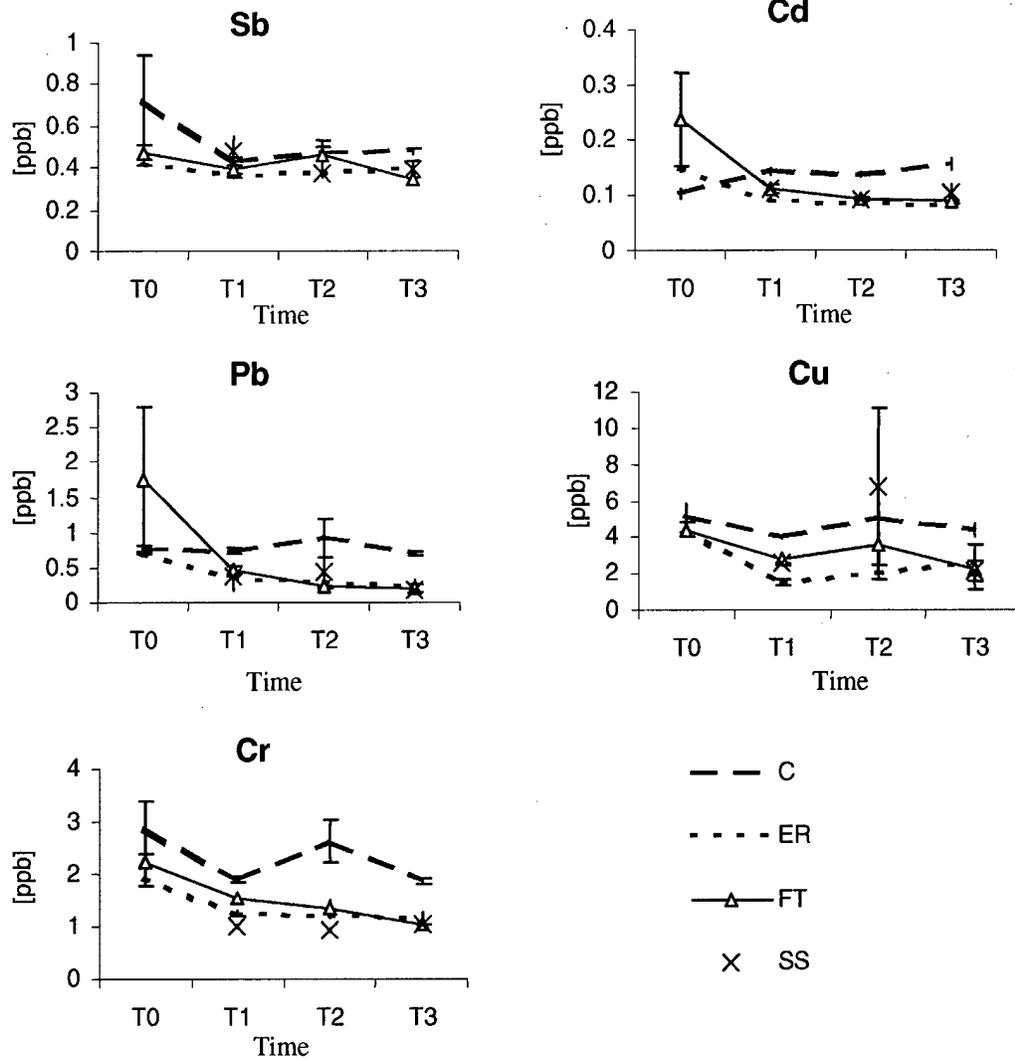


Figure 15. Variation of Group C Metal concentrations in control (C), Flow-Through (FT) and Empty-Refill (ER) tanks and in shipside samples (SS) during the VSF cruise. Note: Control Tank value at T2 reflects contamination of one replicate sample.

Phytoplankton Salinity Tolerance

Phytoplankton fluorescence ratios were higher for the exchanged samples (FT and ER) than for the control samples (Figure 16). A comparison of the tank samples indicated significantly different means (ANOVA: $F = 4.78$, 10 df, $p < 0.05$). These results are the reverse of Brand's "salinity tolerance hypothesis," which supposes that high ratios indicate the predominance of coastal phytoplankton. However, contrary to expectation, the shipside samples had highly variable ratios. This may have been due in part due to low replication of these samples ($N=2$). The large variation among the shipside samples makes the overall effectiveness of this method difficult to judge.

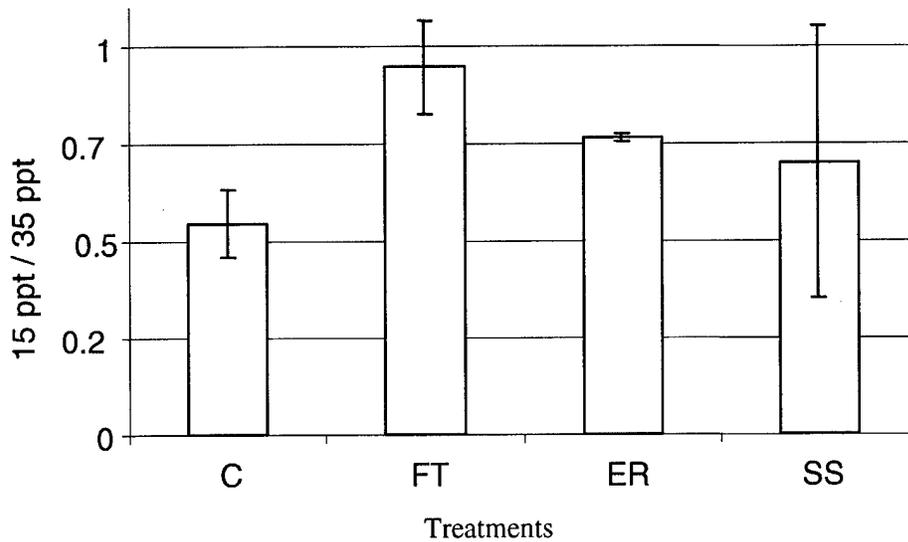


Figure 16. Phytoplankton fluorescence ratios in final samples [control (C), Flow-Through (FT), Empty-Refill (ER), shipside (SS)] from the VSF cruise (Mean \pm SE).

3.3. VLA : Los Angeles to Valdez

3.3.1. Overview

Samples were taken from two ballast tanks on the oil tanker "M/V OVERSEAS BOSTON" during a commercial voyage between Los Angeles, CA and Valdez, AK during December 2000. Specifications for this cruise (referred to hereafter as "VLA") are provided in Table 5.

Table 5. VLA cruise vessel specifications.

Name (Call Sign)	M/V OVERSEAS BOSTON (KRDB)
Charterer	Alaska Tanker Company
Length x Breadth x Draft	260.5 m x 40.6 m x 23 m
Cargo	Oil
Experimental ballast tanks: (i.d. / volume / max. depth)	# 3 port and starboard / 6740 m ³ / 22.5 m

3.3.2. Experimental Design

Initial ballasting of two experimental tanks took place in Los Angeles Bay on December 7, 2000 between the hours of 0215 and 0730. Rhodamine dye was added to each of the tanks prior to ballasting. After ballasting was completed, one tank was designated the control (C) and remained untouched for the length of the experiment. The other tank was subject to three single-volume Flow-Through exchanges. There was no Empty-Refill treatment during this voyage. Because of limitations imposed by the short voyage duration, the first two exchanges were conducted consecutively with no opportunity to take samples between these exchanges. Furthermore, the collection date for "final" CDOM samples from the FT tank (T3) was the day following the final collection date for the other sample types (T2). Overall, samples were collected from the two tanks prior to the first exchange (T0), after two exchanges of the FT tank (T1) and after a third exchange of the FT tank (T2 or T3). All exchanges were conducted beyond the 200 mile limit off the Pacific Coast (Table 6).

Table 6. Timing and location of mid-ocean Flow-Through exchanges during the VLA cruise.

Event	Date	Vol.	Start Exchange	Stop Exchange
FT-1	10 Dec 0900-1130	100 %	39°21' N, 127°24.2' W	39°30' N, 128°15' W
FT-2	10 Dec 1130-1400	100 %	39°30' N, 128°15' W	39°36.7' N, 128°59.8' W
FT-3	11 Dec 1400-1700	100 %	45°00' N, 132°19.4' W	45°30.5' N, 132°19.4' W

3.3.3. Methods

Tank Sampling

In-situ instruments

In-situ profiles (salinity, CDOM fluorescence) were obtained by lowering a CTD (Seabird Electronics, Inc.) fitted with a Light Back Scattering Sensor and a Flash Lamp Fluorometer (Wetlabs Inc.) through a single manhole into each tank. Profiles were taken once per sampling session (T0, T1 and T2), with an additional profile taken at T0.5 immediately prior to the first exchange.

The pressure sensor on the CTD failed at the beginning of the cruise. The remaining in-situ instruments functioned normally; however, their measurements could not be related to depth.

Ballast water samples

Trace metal, salinity tolerance, CDOM, rhodamine and radium samples were obtained by pumping ballast water through plastic tubing pre-installed at two access points (fore and aft) and two depths (1 m, 12 m) in each tank.

For trace metals, salinity tolerance, CDOM and rhodamine, one replicate was collected at each location and depth during three sampling sessions in each of the Control and Flow-Through tanks (2 tanks * 2 locations * 2 depths * 3 days = 24 samples). Radium was collected from 1 m depth at the beginning and end of the voyage (2 tanks * 2 locations * 2 days = 8 samples). Salinity tolerance samples were only collected subsequent to exchange of the FT tanks.

Ocean water (Shipside) sampling

CDOM, metals and Salinity Tolerance samples from the ambient ocean were collected via the ship's fire hose. The fire hose was supplied with untreated seawater from the side of the vessel (depth approximately 5 m). Prior to collecting samples, the fire hose was left running at full blast over the side of the ship for at least half an hour. Two replicate samples of each type were collected during each ballast water exchange. For radium samples, the fire hose was used to fill 55-gallon plastic drums. Water was then pumped from the barrels through the Mn fibers according to the standard protocol.

3.3.4. Results

Exchange efficiency

Ballast water samples from different depths in the same tank contained similar concentrations of rhodamine, indicating that both tanks were well mixed (Figure 17). The exception was the Control Tank at T1, which had slightly more rhodamine dye in the lower part of the tank.

The first two Flow-Through exchanges removed 60 percent of the rhodamine tracer, indicating that 40 percent of the original coastal water remained at the first sampling session (T1). The final exchange removed a further 15 percent of the tracer. On this voyage, the three-volume Flow-Through exchange achieved significantly less than the theoretical 95 percent exchange efficiency with 25 percent coastal water remaining in the tank at the end of the experiment.

The composition of the ballast in each tank at any time can be inferred from the rhodamine data. Proportions of port- and ocean- water in the tanks per sampling time are summarized in Table 7.

Table 7. Composition of ballast water in experimental tanks during VLA.

Sample Time	Control		Flow-Through	
	Port (%)	Ocean (%)	Port (%)	Ocean (%)
T0	100	0	100	0
T0.5	100	0	100	0
T1	100	0	40	60
T2	100	0	25	75

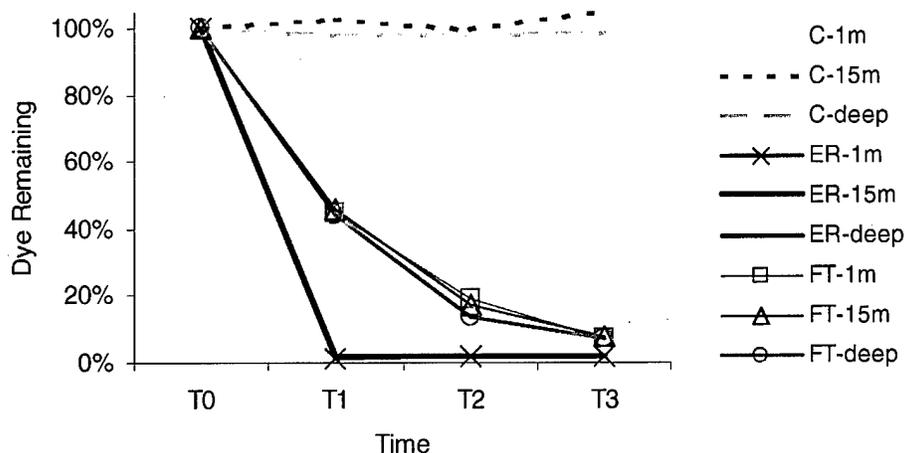


Figure 17. Rhodamine dye displacement at three depths (1 m, 15 m, 1m off the tank bottom) in three tank treatments (C, ER, FT) during the VLA cruise.

Salinity

Salinity in both tanks was approximately 33.3 ppt at the beginning of the experiment (Figure 18). This was slightly higher than the ocean water salinity where the exchanges were performed. Salinity in the exchanged tank declined slightly as a result of the addition of ocean water but varied by less than 0.7 ppt over the entire experiment. A salinity criterion of > 30 ppt could not have been used to verify the exchange on this voyage.

Turbidity

Turbidity in the Control Tank varied between 2.5 and 4.3 Nephelometric Turbidity Units (NTU) over the course of the voyage (Figure 19). Within each tank, turbidity varied negligibly with depth (SE < 0.02 NTU). Turbidity was slightly lower in the Flow-Through tank at all times, however, this was no more pronounced after the first exchanges (T1) than immediately before them (T0.5). Turbidity was not measured in shipside samples because the pumping process was presumed to introduce substantial artifacts to turbidity readings. Turbidity at the end of the experiment was significantly greater in the Control Tank than the exchanged tank. The increase in turbidity in both tanks at T1 probably reflects the stormy weather conditions (high winds and rocking) experienced on that day. Overall, turbidity varied more over time than across tanks and was an unreliable verification tool on this voyage.

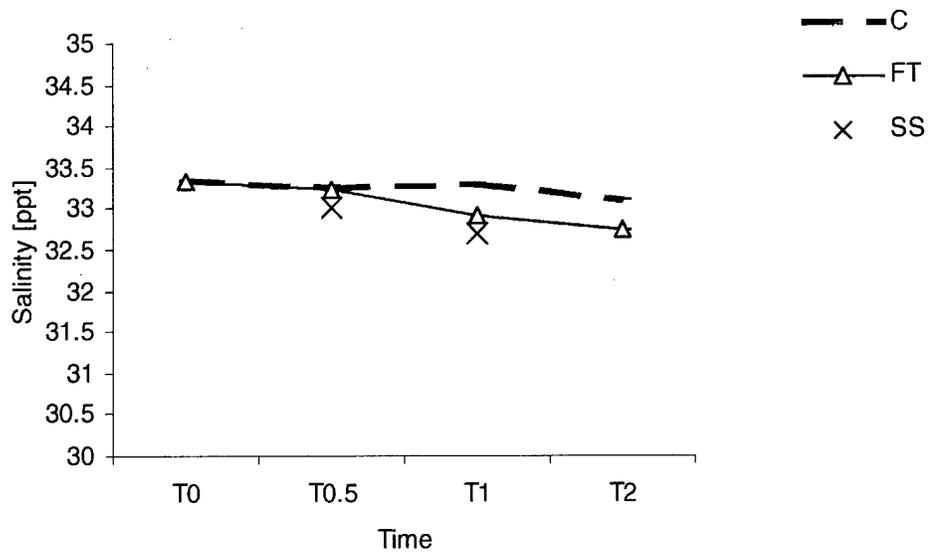


Figure 18. Salinity in the control (C) and Flow-Through (FT) tanks and shippside (SS) during VLA.

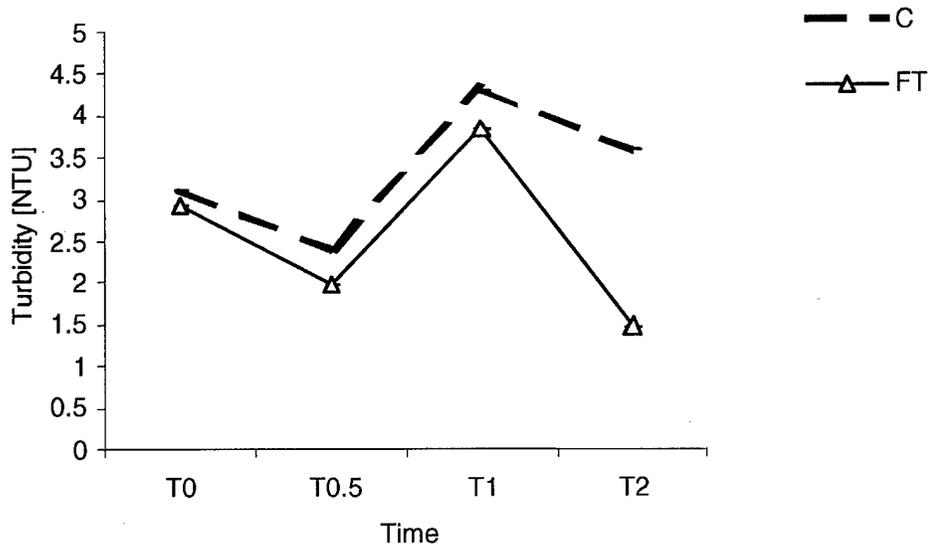


Figure 19. Turbidity in the control (C) and Flow-Through (FT) tanks during the VLA cruise.

In-situ CDOM fluorescence

Peak CDOM fluorescence intensity (fIS) in the Control Tank was stable over the length of the voyage (Figure 20). CDOM Fluorescence in the Flow-Through tanks was almost perfectly correlated with rhodamine fluorescence intensity ($R^2 > 0.999$) but less strongly correlated with salinity ($R^2 = 0.82$). CDOM and rhodamine intensities both decreased by nearly 75 percent following three exchanges of the FT tanks.

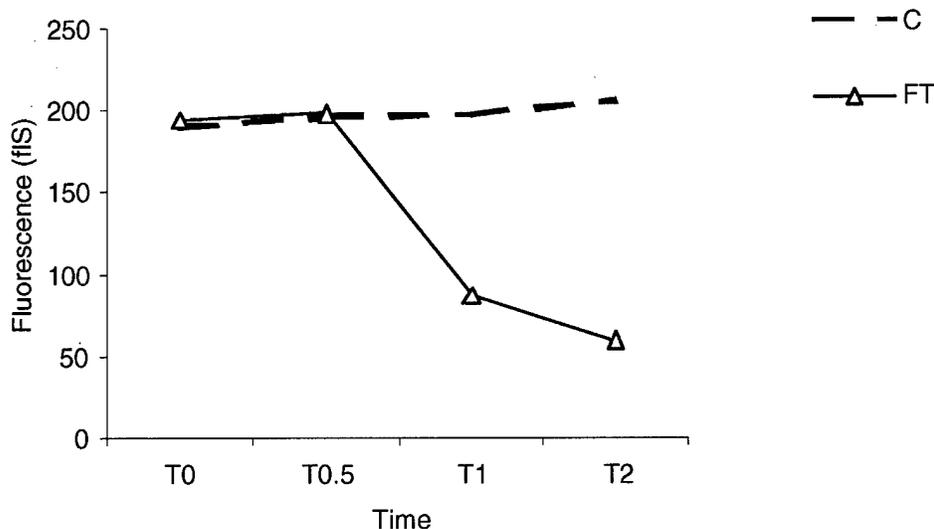


Figure 20. In-situ Peak CDOM fluorescence in control (C) and Flow-Through (FT) tanks during VLA.

CDOM EEMs

Fluorescence Peak Intensity

Tank-averaged intensities were determined for the natural fluorescence peaks humic "A," humic "C," Tyrosine 1' and Tyrosine 2', and plotted against time. Note that final CDOM samples were collected from the Control Tank at T2 and from the Flow-Through tank at T3. Ocean samples were highly variable, possibly due to low replication combined with contamination of one or more samples. For clarity, large standard errors for ocean samples are omitted from these graphs.

Humic "A" fluorescence exhibited a peak at T1 in the Control Tank, otherwise it was consistent across locations and depths (Figure 21). In the Flow-Through tank, fluorescence "A" decreased after the first two exchanges. The high mean and standard error at T3 (3.0 ± 1.0 QSE) is a result of a single anomalous sample

collected from 12 m depth. When this sample is removed, the mean drops 2 ± 0.0 (This is designated as FT* in Figures 21 and 22). Humic "C" fluorescence (Figure 22) varied in a similar manner to Humic "A" fluorescence. Primary (Figure 23) and secondary (Figure 24) Tyrosine-like peaks were variable within tanks (note large error bars) and displayed no noticeable trend over time.

Fluorescence Peak Position

The positions of the humic fluorescence peaks show an overall but non-significant trend toward shorter wavelengths (blue-shifting). The position of the humic "A" peak in control samples varied between 406-440 nm over the course of the voyage (Figure 25). The Flow-Through samples were indistinguishable from the control samples at the end of the experiment.

The position of the humic "C" peak in control samples varied between 396-418 nm over the course of the voyage, peaking at T1 (Figure 26). This variability is not significant (within measurement error). There was convincing evidence for 'blue-shifting' of the C peak in the exchanged tank between the initial and final sampling times ($t = 4.71$, 5 df, $p < 0.005$). However, the end point samples from the control and exchanged tanks are not significantly different. Note also that the final control samples were taken a day prior to the final exchanged samples.

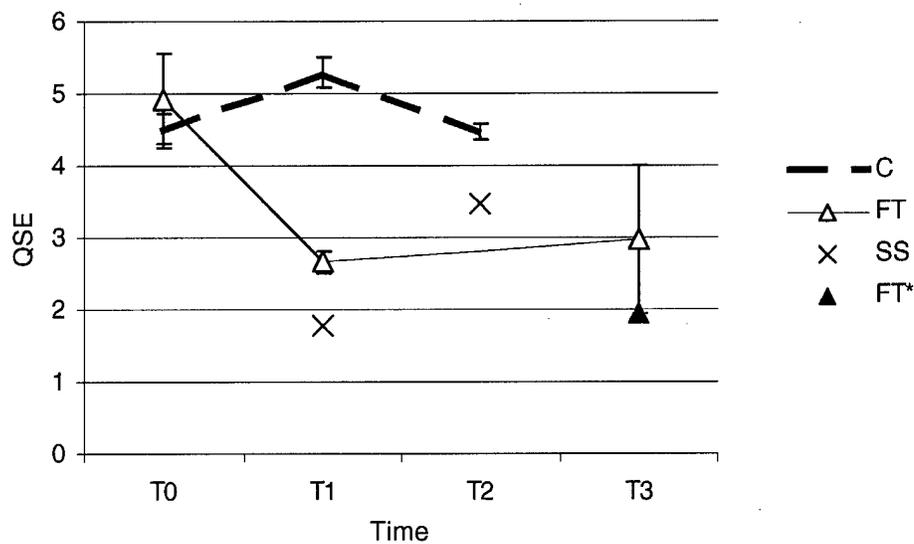


Figure 21. Humic Peak "A" fluorescence intensities in control (C), Flow-Through (FT) and shipperside (SS) samples during VLA. FT* is the intensity value of the Flow-Through tank at T3 after the removal of apparently contaminated data.

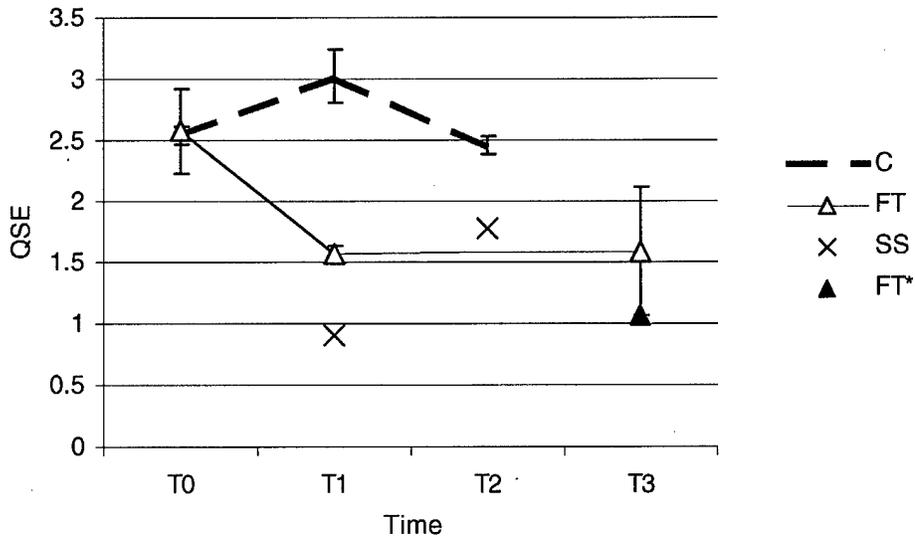


Figure 22. Humic Peak "C" fluorescence intensities in control (C), Flow-Through (FT) and shipperside (SS) samples during the VLA cruise. FT* is the intensity value of the Flow-Through tank at T3 after the removal of apparently contaminated data.

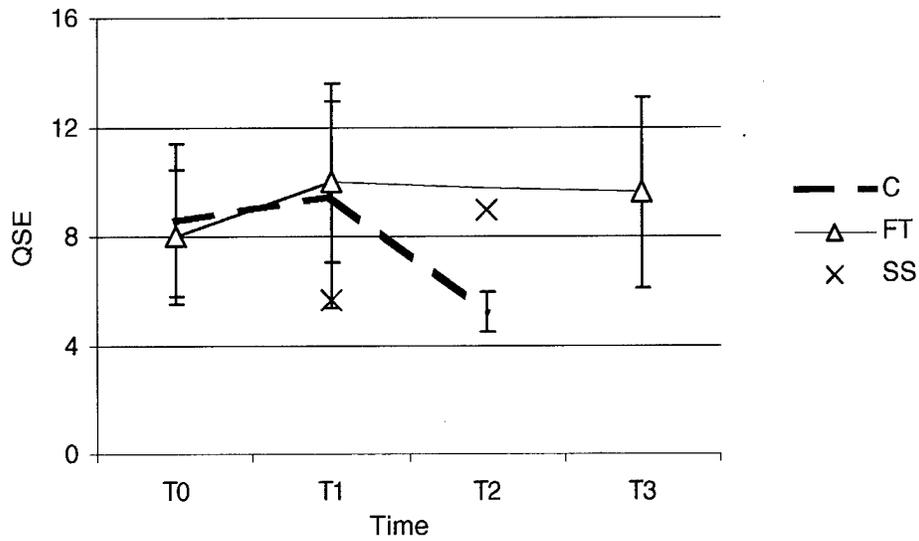


Figure 23. Tyrosine-like primary (1') peak fluorescence intensities in control (C), Flow-Through (FT) and shippside (SS) samples during the VLA cruise.

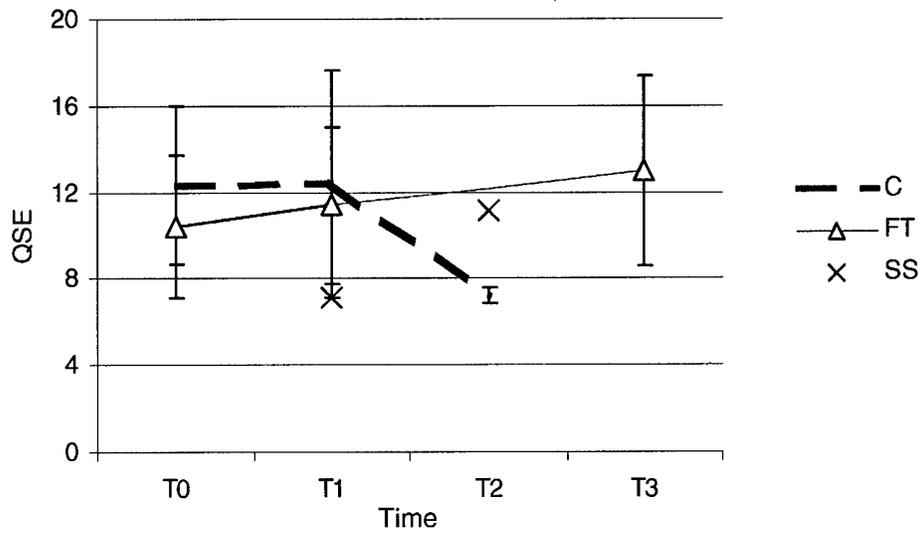


Figure 24. Tyrosine-like secondary (2') peak fluorescence intensities in control (C), Flow-Through (FT) and shippside (SS) samples during VLA.

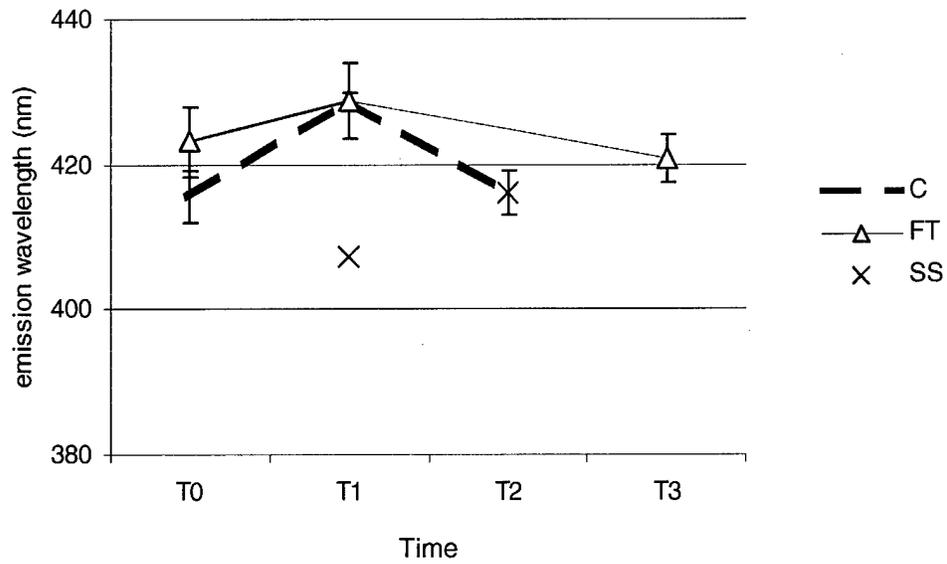


Figure 25. Position of humic "A" emission peak in control (C), Flow-Through (FT) and shipside (SS) samples during VLA.

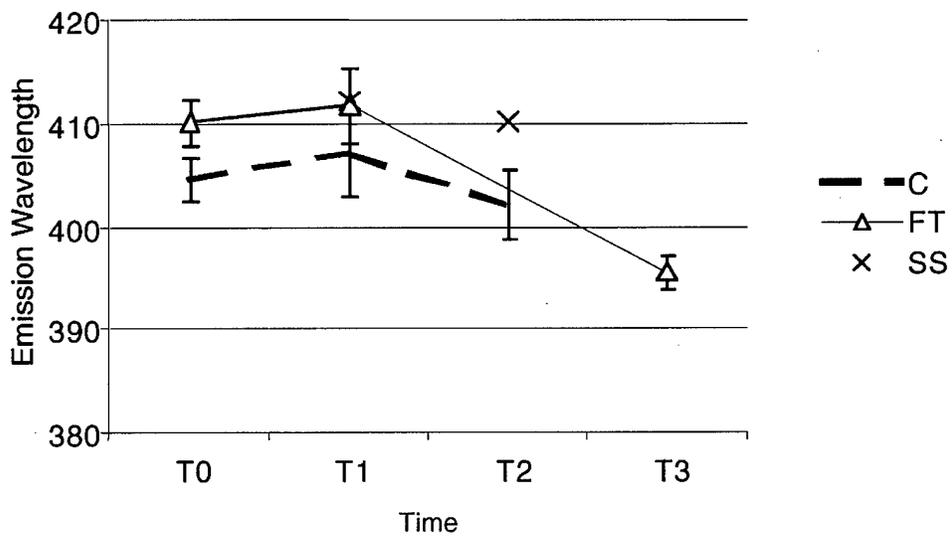


Figure 26. Position of humic "C" emission peak in control (C), Flow-Through (FT) and shipside (SS) samples during VLA.

Radium

Radium Isotopes ^{223}Ra ($t_{1/2} = 11$ days) and ^{224}Ra ($t_{1/2} = 3.7$ days) were both recovered in measurable levels from tank samples. Ocean samples contained extremely low quantities of both isotopes. Low replication ($N=2$) is at least partly responsible for the relatively high standard errors for this voyage.

^{223}Ra (Figure 27) levels in the tanks were nearly an order of magnitude lower than ^{224}Ra levels (Figure 28). At the beginning of the experiment, ^{223}Ra and ^{224}Ra were both significantly higher in the control samples than in FT samples. This may reflect real differences in the source waters of the two tanks. More likely, there may have been a systematic bias introduced during sample collection, (for example, one of the flow accumulators may have underestimated the actual volume of water pumped).

Concentrations of ^{223}Ra in samples from both tanks decreased during the voyage - the control samples by approximately 30 percent and the Flow-Through samples by approximately 75 percent. Concentrations of ^{224}Ra in samples from the Control Tank decreased after the first pair of exchanges then recovered to initial concentrations in the final samples. Between the beginning and the end of the voyage, control ^{224}Ra increased by approximately five percent while Flow-Through ^{224}Ra decreased by approximately 70 percent.

The variability of both isotopes within control samples could be attributable to one or more of the following: i) within-tank patchiness, ii) sediment-water exchange of radium during the voyage, iii) procedural problems during sampling. It is considered that the latter was a significant contributor of error to these data, since there were indications that the flow meter accumulator did not always reliably calculate volumes at the low flow rates necessary for extraction of the Ra isotopes onto the Mn-fibers.

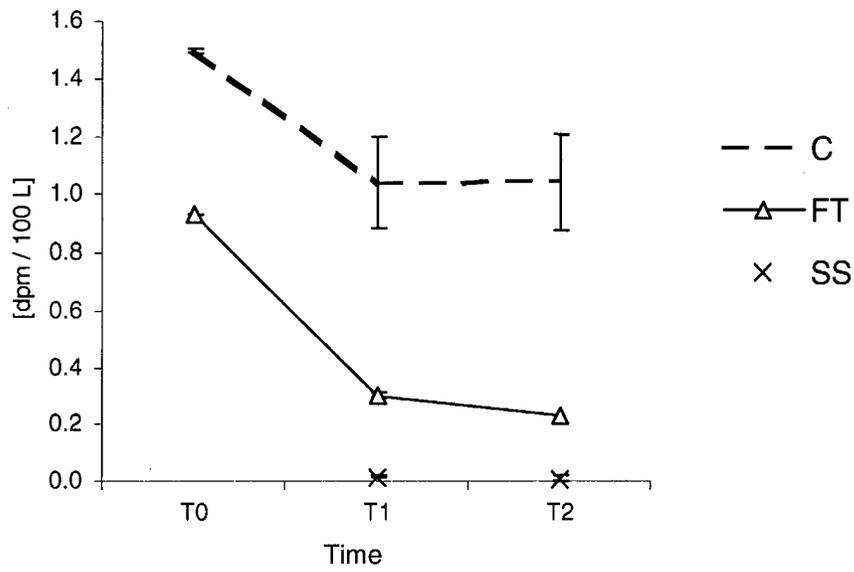


Figure 27. ^{223}Ra variation in control (C), Flow-Through (FT) and shipline (SS) samples during VLA.

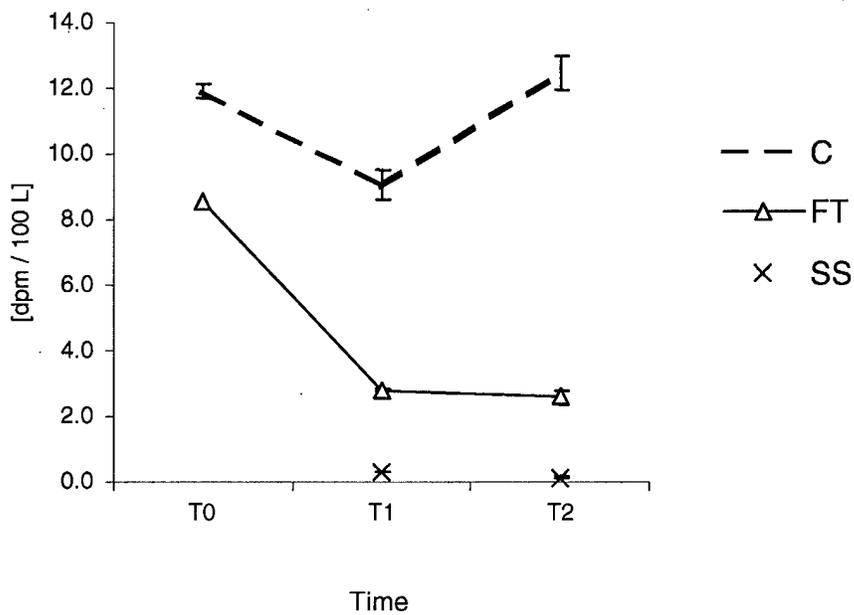


Figure 28. ^{224}Ra variation control (C), Flow-Through (FT) and shipline (SS) samples during VLA.

Trace Metals

The results for thirteen elements (Mo, Cd, Sb, Ba, Pb, P, V, Cr, Mn, Fe, Co, Ni, Cu) are presented in three groups (A, B, C) as discussed in Section 0. Group A [Mo, Ba, P, V, Mn] contains metals which demonstrated the highest potential as tracers on VSF (Figure 29) (Section 0). These metals exhibit stable concentrations in unexchanged ballast tanks whereas in exchanged tanks, their concentrations approach levels measured in shipside samples.

Group B [Fe, Co, Ni] consists of metals which demonstrate similar trends but exhibit concentrations well above that expected for the California coast (Martin and Gordon, 1988; Martin et al., 1989, Donat and Bruland 1995, Esser and Volpe, 2002) and are probably contaminated by the ship structure (Figure 30). Metals demonstrating little potential as tracers due to high variability and susceptibility to contamination are in Group C [Sb, Cd, Pb, Cd, Cr] (Figure 31) (Donat and Bruland 1995).

Control samples demonstrated good agreement between locations and depths, except at T1. The high variability at this time is due to elevated concentrations in the 12 m samples relative to the 1 m samples ($t = -8.6$, 1 df, $p = 0.07$, 2 tailed). Concentrations of all Group A metals were higher in samples from the control than the exchanged tanks, with the exception of Mo, which is conservative with salinity. Barium measurements were most precise but varied by less than 50 percent over the entire voyage.

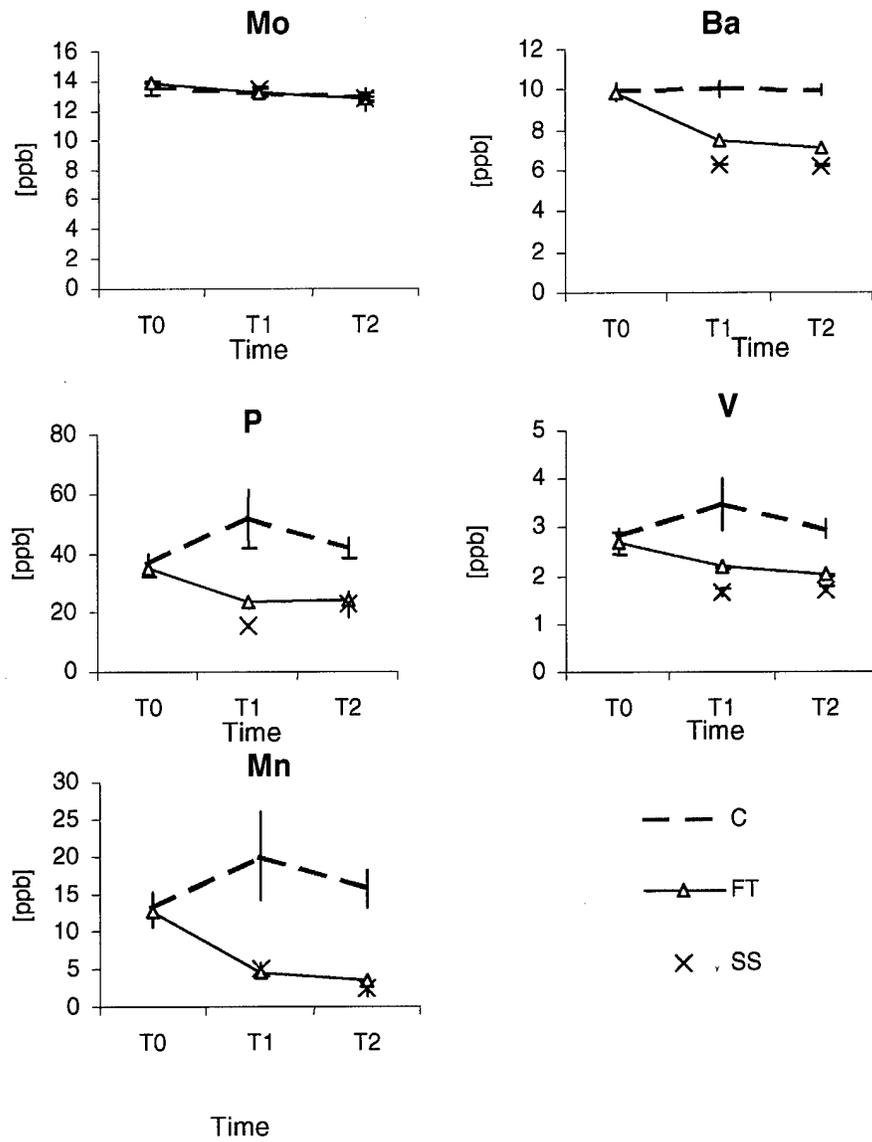


Figure 29. Variation of Group A metal concentrations in control (C), Flow-Through (FT) and shippside (SS) samples during the VLA cruise.

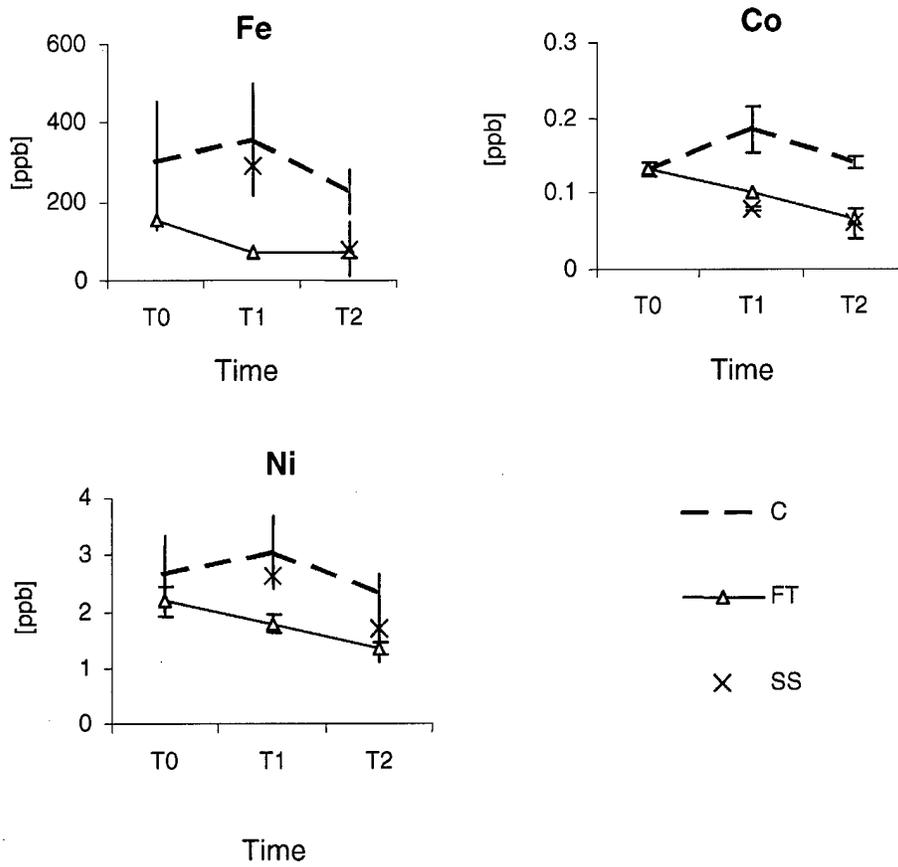


Figure 30. Variation of Group B metal concentrations in control (C), Flow-Through (FT) and shipside (SS) samples during the VLA cruise.

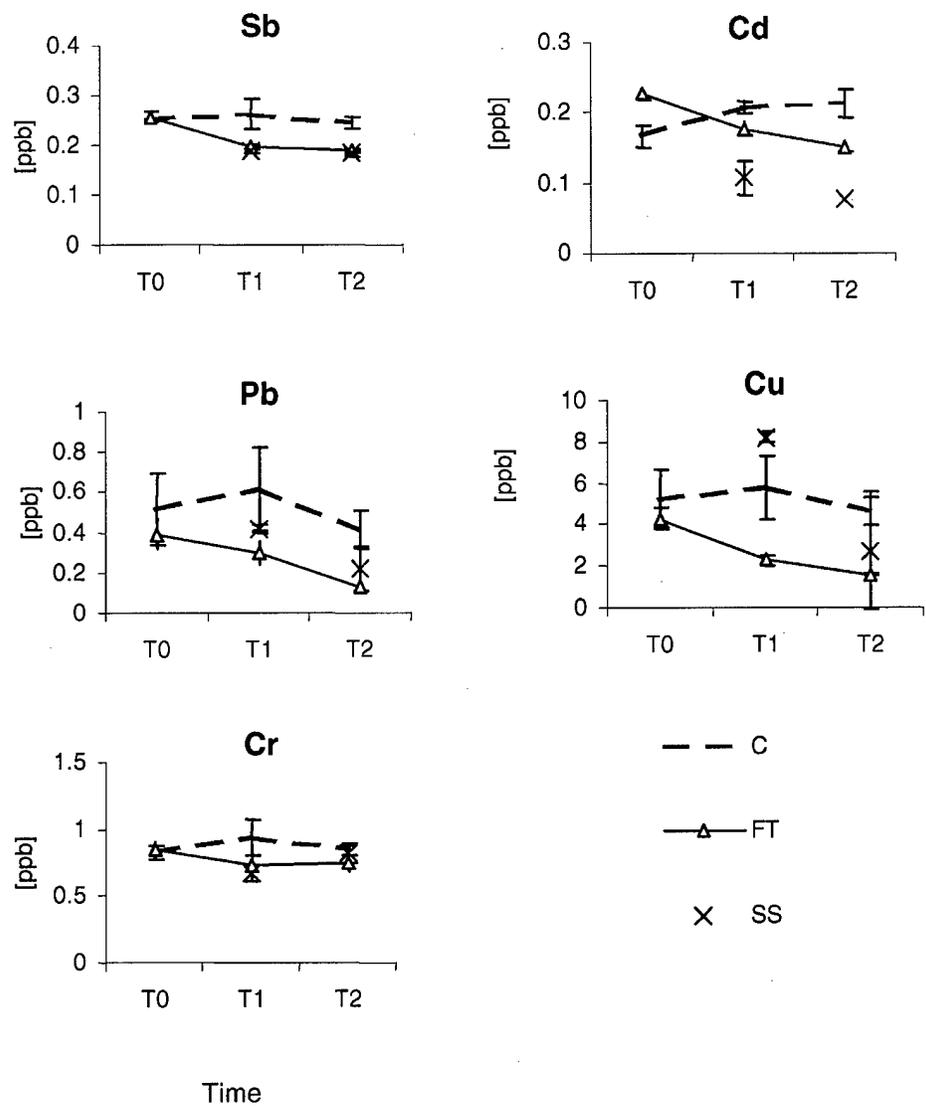


Figure 31. Variation of Group C metal concentrations in control (C), Flow-Through (FT) and shipside (SS) samples during the VLA cruise.

Phytoplankton Salinity Tolerance

Phytoplankton fluorescence ratios (15 ppt / 35 ppt) were often variable in samples collected at the same time from the same tank (Figure 32). Ratios were significantly higher for the control samples than both the exchanged samples and the shipside samples. This result is in line with to the salinity tolerance hypothesis which supposes that high phytoplankton fluorescence ratios indicate a more “coastal” phytoplankton character, and by extension, that a tank with a high phytoplankton fluorescence ratio contains coastal water.

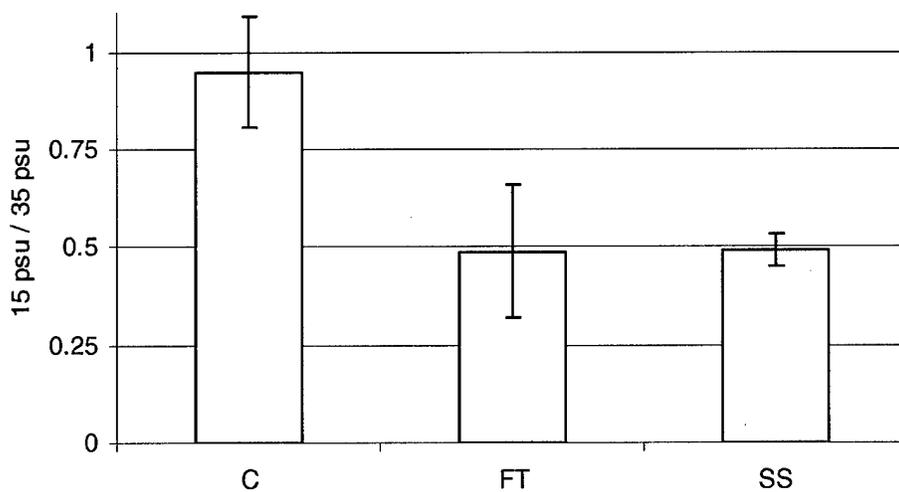


Figure 32. Phytoplankton fluorescence ratios in final samples [control (C), Flow-Through (FT), shipside (SS)] from the VLA cruise (Mean \pm SE).

3.4. VPS: Puget Sound to Valdez

3.4.1. Overview

SERC was able to obtain a small number of ballast water samples (filtered trace metals and CDOM only) from two ballast tanks on the *M.V. TONSINA* during an unrelated research experiment. Samples were collected at the beginning and the end of a short voyage between Puget Sound (WA) and Valdez (AK) in May 2001. Vessel specifications for this cruise (referred to hereafter as "VPS") are summarized in Table 8.

Despite the limited data set, the VPS cruise was of particular interest because the port water salinity (29.9 ppt) was comparable to the suggested minimum salinity for compliance according to the USCG salinity verification criterion (30 ppt).

Table 8. VPS vessel specifications.

Name (Call Sign)	M/V TONSINA (KJDG)
Charterer	British Petroleum
Length x Breadth x Draft	264.88 m x 41.51 m x 16.76 m
Cargo	Oil
Experimental ballast tanks: (i.d. / volume / max. depth)	#4 port and starboard / 2123 MT / 20 m

3.4.2. Experimental Design

Two wing ballast tanks (4-Port and 4-Starboard) were sampled during the experiment. Both tanks were ballasted at Cherry Point in Puget Sound on May 20, 2001. The port tank was designated the control (C) and was not touched during the experiment except to obtain samples. The starboard tank was subjected to two consecutive Empty-Refill (ER) exchanges in the open ocean more than 200 miles from the nearest coast in water exceeding 2000 m depth¹ (Figure 33).

¹ Estimated from Smith and Sandwell (1997).

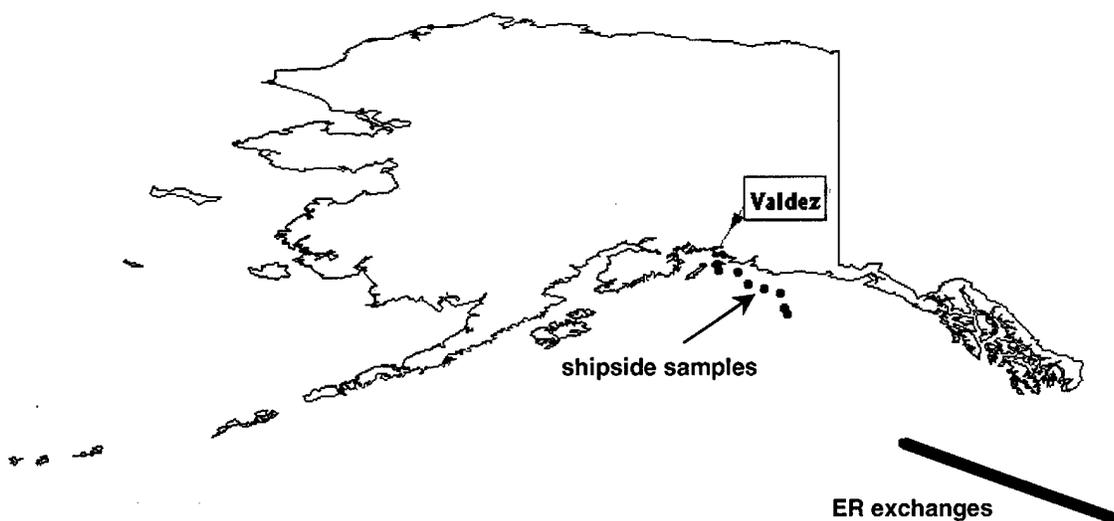


Figure 33. Location of Empty-Refill (ER) exchanges and shipperside samples during VPS.

CDOM and trace metal samples were taken from the two tanks immediately prior to exchange (day T0) and on the day following consecutive Empty-Refill exchanges of the experimental tank (day T1). Additionally, during the final 12 hours of the voyage, sixteen shipperside samples of each CDOM and metals were collected to obtain data on the near shore variability of tracers in the North Eastern Pacific. With the exception of salinity, no in-situ data were collected on this cruise.

The protocol on the VPS cruise included the following:

- in-situ determination of salinity
- laboratory determination of trace metal concentrations and CDOM fluorescence

3.4.3. Sampling Design

Tank Sampling

In-situ samples

In-situ measurements of salinity at three depths (1 m, 12 m, 20 m) were obtained by lowering a salinometer (YSI) through a single manhole into each tank.

Laboratory samples

Replicate samples (CDOM, metals) were obtained by pumping water through plastic tubing pre-installed at two depths (1 m, 12 m) in two locations (A, B) in each tank (2 days * 2 tanks * 2 locations * 2 depths * 2 replicates = 32 samples). The protocol for CDOM sampling was similar to previous voyages. The trace metal protocol differed in that ballast water was first filtered on deck through a 45 μm supor membrane.

Procedural “blanks” were collected at the end of the voyage by pumping high purity water (Milli-Q) through two of the tubes to estimate residual tracer concentrations in the tubing and pump. Unfortunately, all but two of the procedural blanks broke during freezing or shipment to the laboratory.

Shipside sampling

CDOM, metals and salinity samples were obtained from the engine room by tapping the engine-cooling water pipe at its inlet end. This pipe constantly circulates water from the side of the ship (depth ca. 7 m) past the engine and out again. Sixteen shipside samples of each CDOM and metals, with corresponding GPS position, were collected from continental shelf waters as the vessel approached Valdez. (Figure 33). Shipside samples were not collected in the open ocean.

3.4.4. Results

Salinity

Initial tank salinities were 29.2 ± 0.20 ppt in the Control Tank and 29.7 ± 0.03 ppt in the ER tank.

Following exchange, salinity in the Control Tank had increased to 30 ± 0.0 ppt. The slight increase in the Control Tank salinity may have been caused by the redistribution of an initially stratified water column or instrument drift. In the exchanged tank, salinity increased to 32 ± 0.0 ppt due to the input of higher-salinity ocean water.

Trace Metals

Concentrations of six elements (Mo, Ba, P, V, Mn, U) in ballast tanks during VPS are presented in Figure 34. While concentrations were also determined for Cd, Fe, Cu and Zn, values for these elements were many times above typical ocean values (less than 0.1 ppb) and demonstrated pronounced inter-sample variability. Given the nature of the sampling environment (rusting hull and decks), values for these elements reflect sample contamination during collection and subsequent handling on board ship and were dropped from the analysis (Bruland 1980, 1983; Bruland & Franks 1983; Martin et al. 1993; Martin et al. 1989). However, these measurements were used to flag samples grossly compromised by material from the vessel.

Compared to the unfiltered trace metals samples collected on the earlier voyages, there was more variation on this cruise in Group A trace metal concentrations within and between tanks, as evidenced by relatively large standard error bars, particularly for Mn. An examination of the raw data indicates that the non-significant results for this metal are driven by four ER (samples 6105, 6108, 6110, 6113) that were clearly contaminated across a range of metals, particularly Fe, Cu, Zn, P and Mn. However, data from these and other anomalous samples were not removed prior to analysis since their inclusion gives an indication of the robustness of different metals to contamination episodes.

Analyses of variance (ANOVAs) indicated no significant effects of depth or within-tank sampling location on trace metal concentrations. Ballast water exchange had no significant effect on the concentrations of Mo, V, Mn or U. Mean concentrations of Ba and P were stable in the Control Tanks but decreased significantly in the exchanged tanks, with Ba decreasing by 31 percent (from 9.8 ppb to 6.8 ppb) and P by 46 percent (from 70 ppb to 38.1 ppb).

Onshore profiles for the same set of elements are presented in Figures 35 and 36. Concentrations of Mo, V, Mn, and U undulated gently, neither increasing nor decreasing with proximity to Valdez. Barium increased steadily from an initial 7.6 ppb approximately 100 miles from the coast and peaked at 9.5 ppb in the channel. The extremely low levels of barium (2.3 ppb) of the final pair of shipside samples are attributed to an analytical error during measurement and should be disregarded.

Phosphorus levels started around 52 ppb offshore, decreased gradually at first and then more rapidly to finish at 11 ppb. Salinity was initially 32.2 ppt, decreased very slowly as the vessel approached Valdez,

then dropped briefly in response to ice melt in the Sound, and recovered to 29.7 ppt when the last sample was taken in the channel approximately one hour prior to arrival at the Valdez terminal.

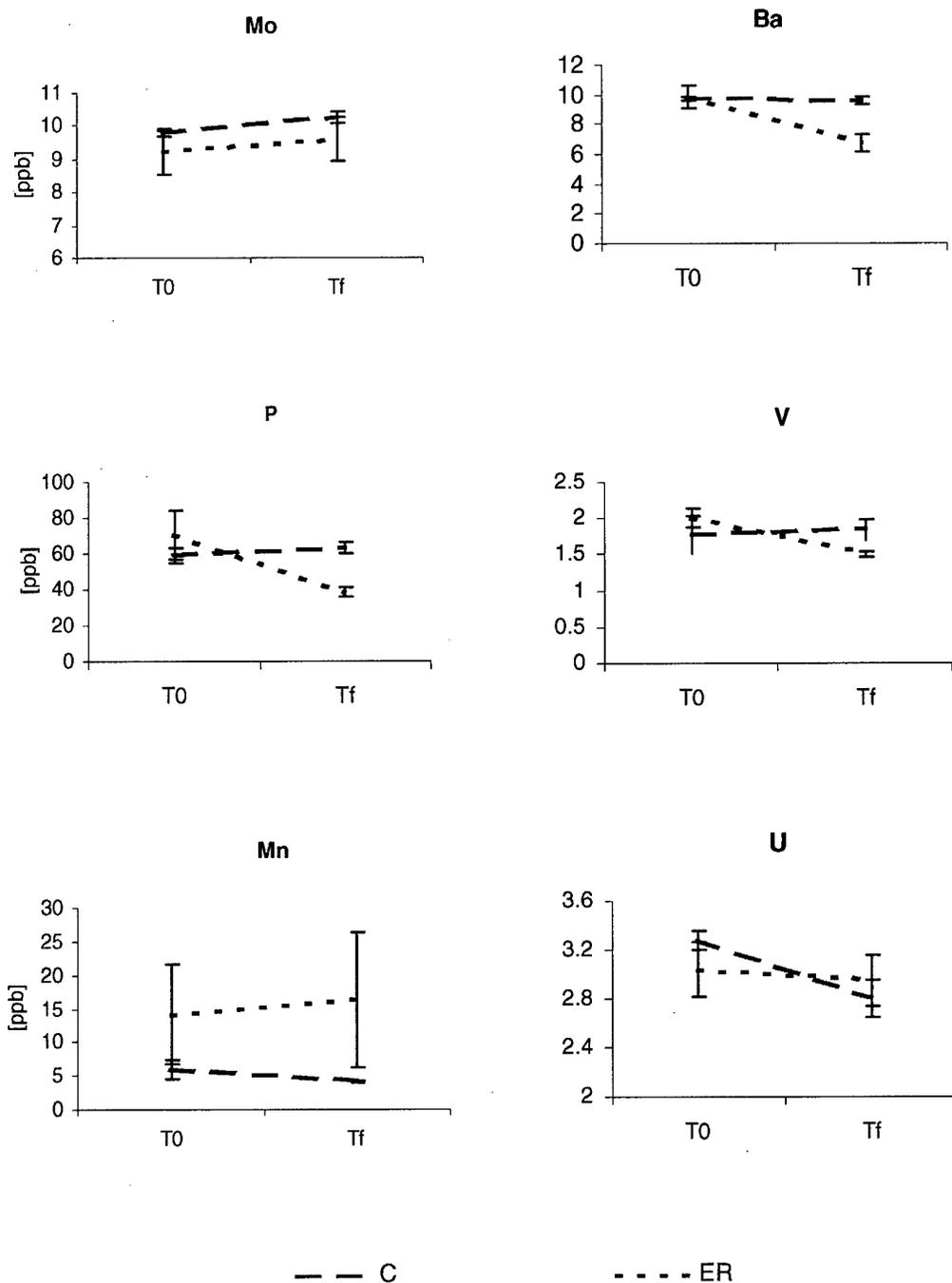


Figure 34. Concentrations of six trace metals before and after two consecutive Empty-Refill exchanges on VPS. Concentrations are in parts per billion (ppb). Samples were filtered.

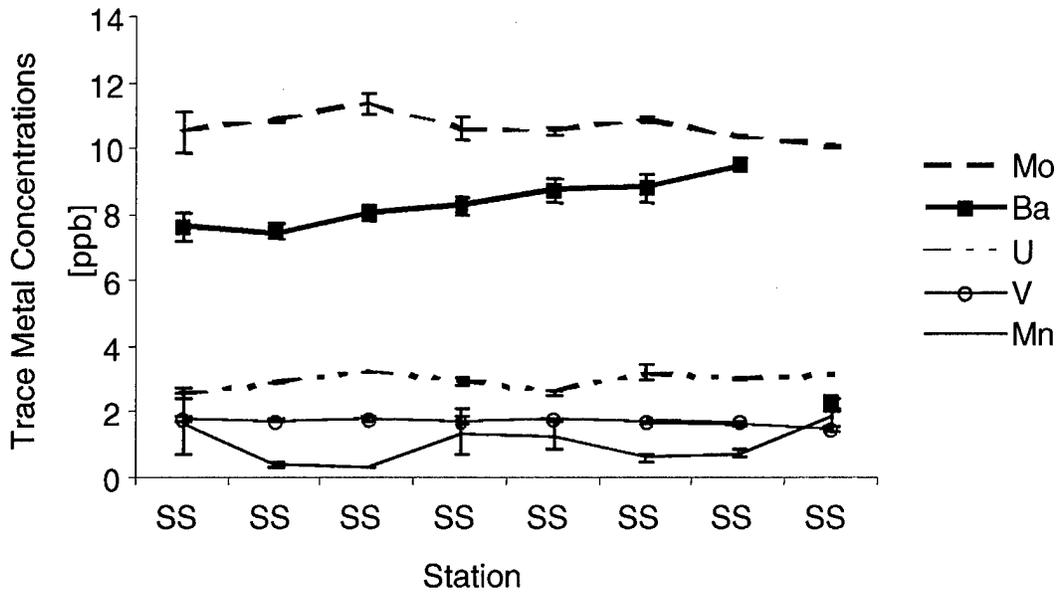


Figure 35. Offshore (SS8) to Onshore (SS1) profile of five trace metals approaching Valdez, AK. The low levels of Ba measured at SS1 are attributed to an analytical error and should be disregarded.

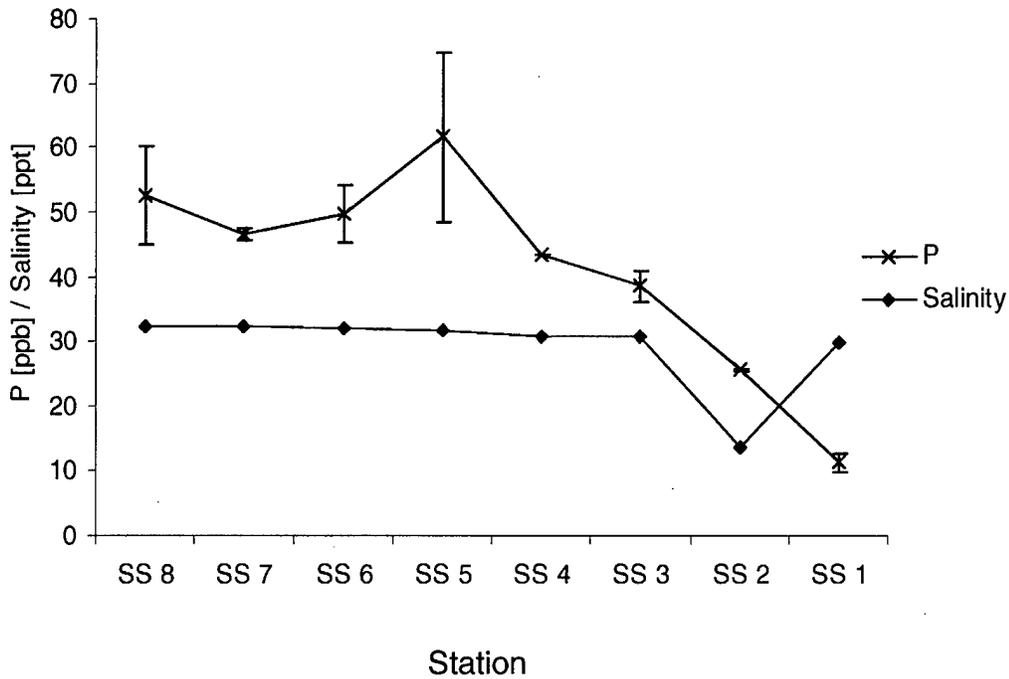


Figure 36. Offshore (SS8) to Onshore (SS1) profile of Phosphorus and Salinity approaching Valdez, AK. The salinity drop at SS2 may result from localized ice-melt.

CDOM EEMs

Fluorescence peaks observed in the EEMs from the VPS cruise samples were similar to those found in the previous cruises. Peaks A and C arise from the fluorescence of humic material, with peak A dominating peak C in all samples (see Figure 37). The protein fluorescence identified in the same figure is similar to that of tyrosine, with primary (1'- 230 nm) and secondary (2'- 270 nm) excitation peaks. A second pair of protein peaks (tryptophan-like) which excited in the UV (1'- 230 nm; 2'-280 nm) and emitted at longer wavelengths was also evident in some samples. The characteristics of humic peaks A and C and the tyrosine and tryptophan-like fluorescence (excitation, emission, intensity) were examined with reference to control and treatment tanks before and after ballast water exchange. ANOVAs on CDOM excitation, emission and intensity indicated no effect of sample depth or location, thus all subsequent plots show averages across locations and depths within a single tank.

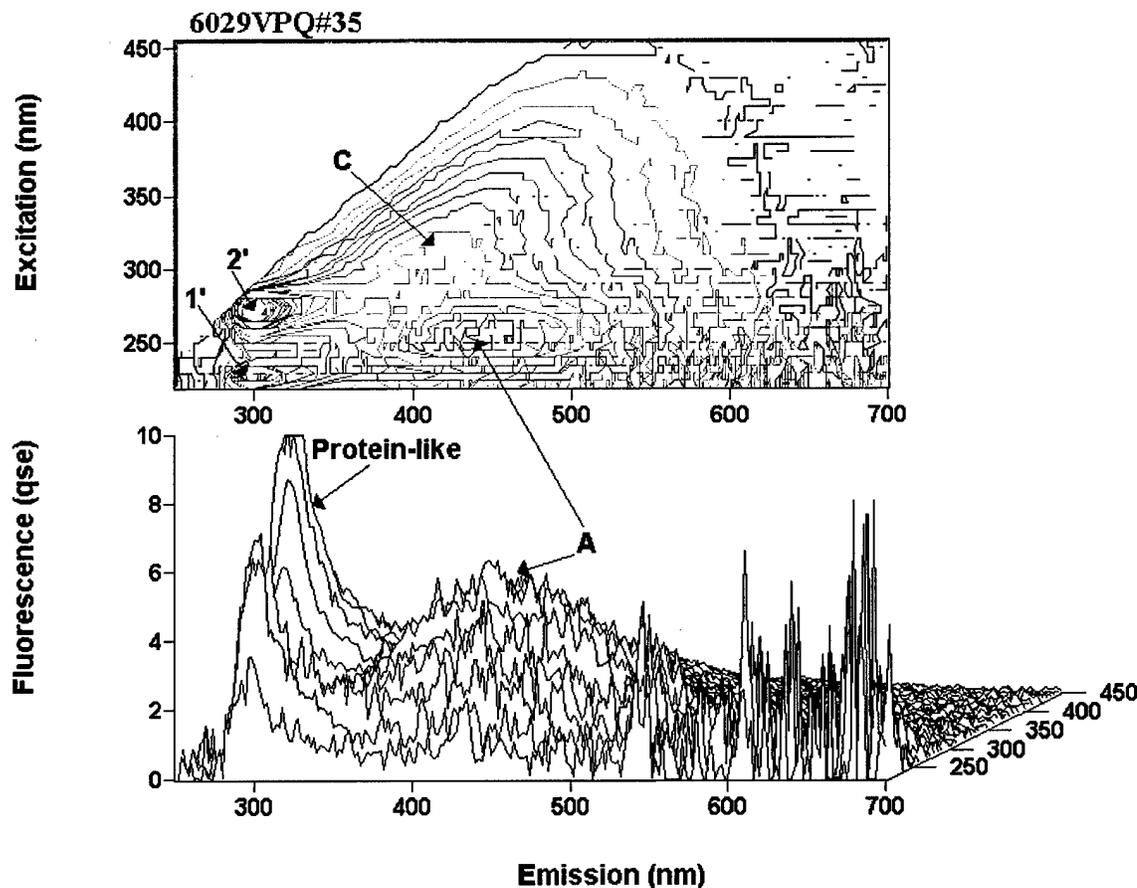


Figure 37. EEM of ballast water from the VPS data set.

The pre-exchange water endmember for the VPS cruise displayed an intensity of 6.01 QSE for humic-like peak A in the Control Tank at T1 (Figure 38). Fluorescence intensity of peaks A and C decreased very slightly in the Control Tank over the voyage. The position of the excitation maximum in the control samples did not change significantly over time, although mean values decreased for peak A and increased for peak C. The positions of the emission maxima for both A and C peak fluorescence showed small, inconsistent variability over time.

The ER tank showed a marked decrease in humic-like peaks A and C fluorescence intensity following exchange. Results from all sampling sites within these tanks were in good agreement. Changes in the position of the excitation and emission maxima in the ER tank were not statistically significant due to high inter-replicate variation. The emission maximum for peak A remained relatively stable, with a very slight blue shift. The emission at peak C was more variable.

Absorption coefficients in initial samples at 280, 312, and 412 nm were lower in the Control Tank than in the ER tank (Figure 39). This may have been due to small differences in the fluorescence efficiencies of the humic material in the two tanks. Fluorescence efficiency, or the number of photons emitted per quanta of light absorbed, is associated with fluorescence intensity. CDOM fluorescence expressed quantitatively as fluorescence efficiency provides additional information directly related to the chemical structure of CDOM.

In the Control Tank, absorption coefficients decreased slightly over the sampling period. In the ER tank, these coefficients decreased markedly following exchange. Results from all sampling sites within these tanks were in good agreement. The 280 nm and 312 nm wavelengths correspond generally to the regions that excite the fluorescence of peaks A and C. The 412 nm wavelength corresponds to the shortest waveband available from SeaWiFS satellite data, which could provide another source of comparison data.

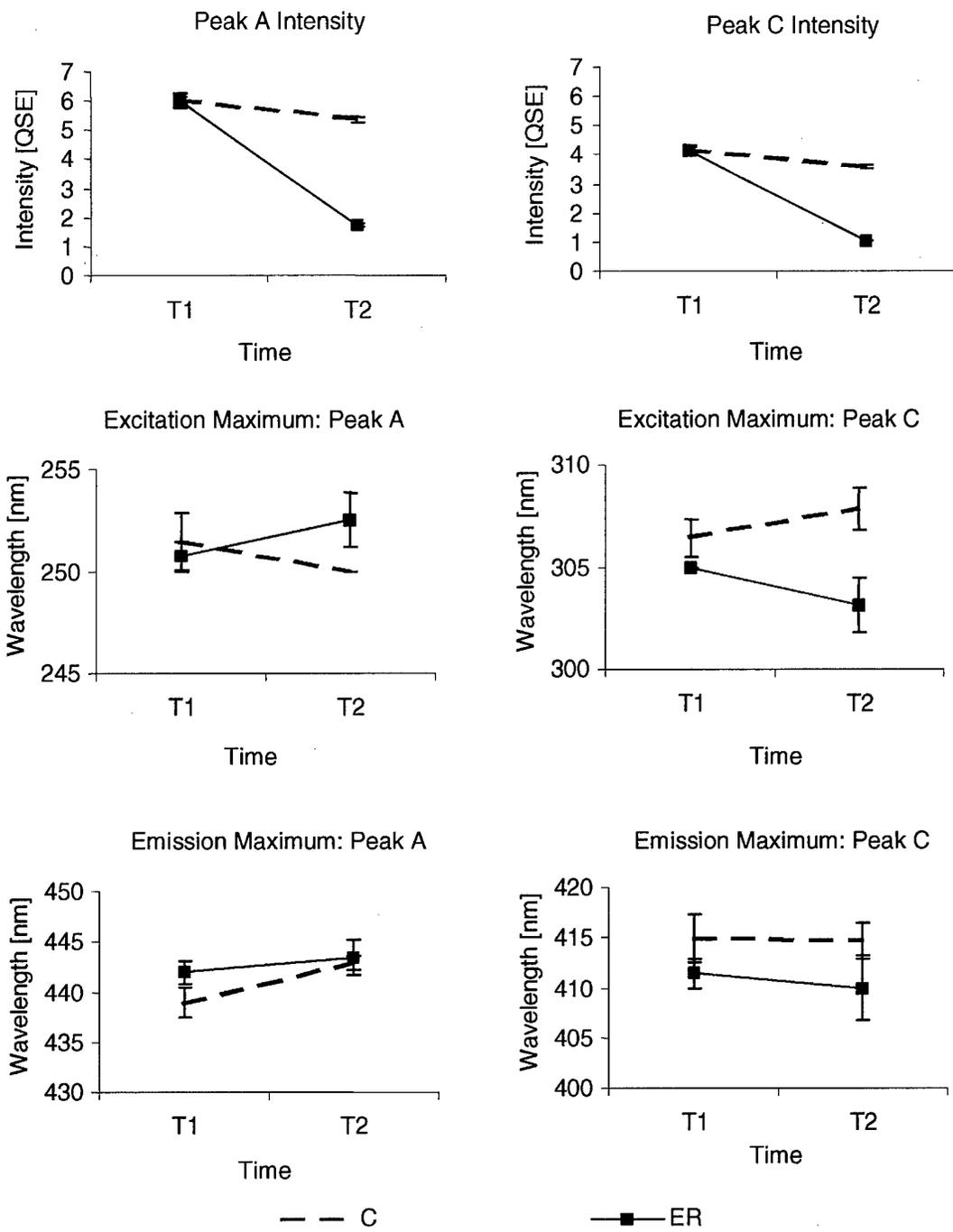


Figure 38. Variation in CDOM fluorescence peak A and C properties during VPS (mean \pm SE).

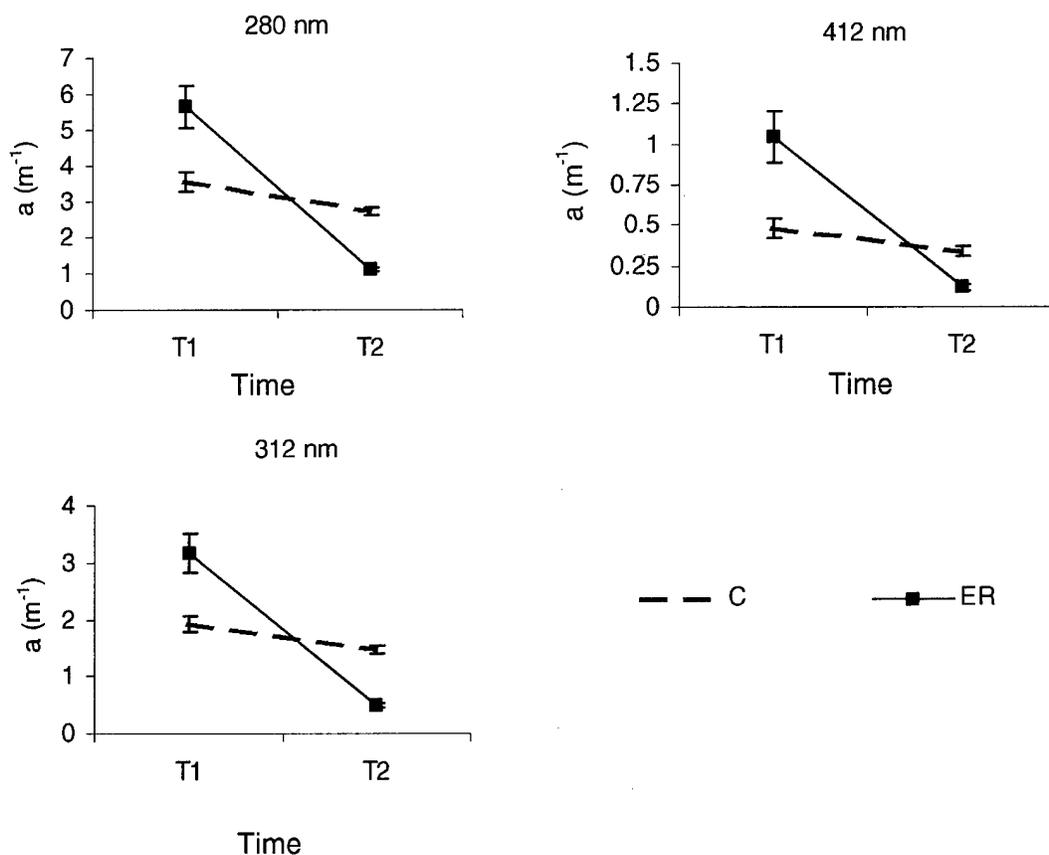


Figure 39. Variation in CDOM absorbance coefficients during VPS (mean \pm SE).

Shipside samples were collected within 200 miles of the coast instead of during the ballast exchange and consequently do not correlate directly with the ocean water in the ER tank following the exchange (Figure 33). As expected, all ship-side samples show peak intensities comparable to those measured in the ER tank after the exchange event (Figure 40). The positions of the emission maxima for the two humic peaks were more variable in the shipside samples than in either tank (Figure 41). These fluctuations serve to highlight the changing water masses encountered by the vessel on its way into port.

The high variability at station SS3 is due to a single sample which had abnormally high fluorescence intensity at the position of both peaks A and C as well as excitation and emission peaks that corresponded neither to humic nor protein-like fluorescence. The fact that peak C for this sample was higher than peak A also indicates that the fluorescence measured in this sample was not from CDOM.

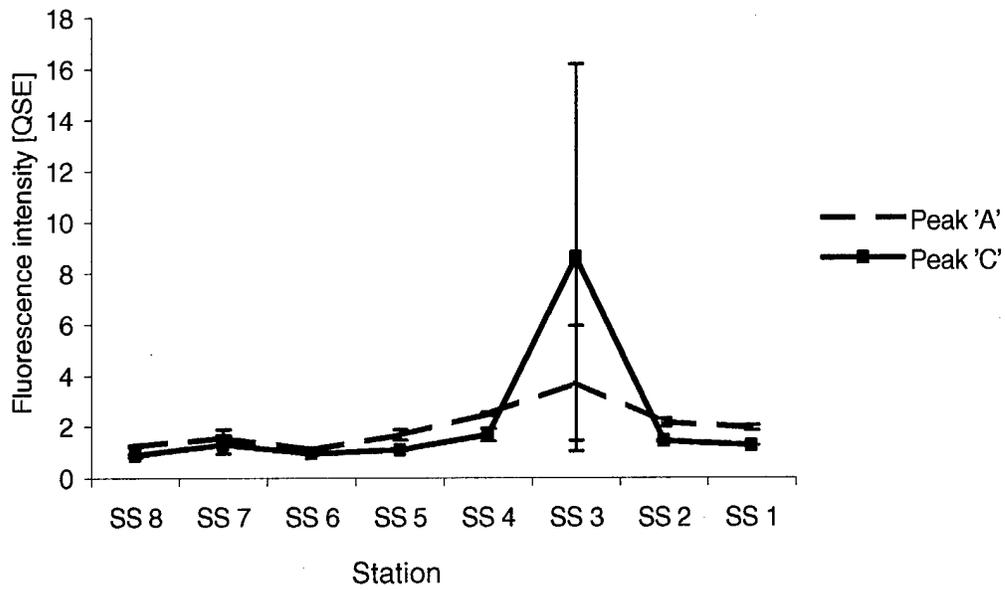


Figure 40. CDOM fluorescence intensities (N=2) in shipside samples (SS) taken as the vessel approached Valdez, AK during VPS. The anomalous reading at SS3 is due to a non-CDOM contaminant.

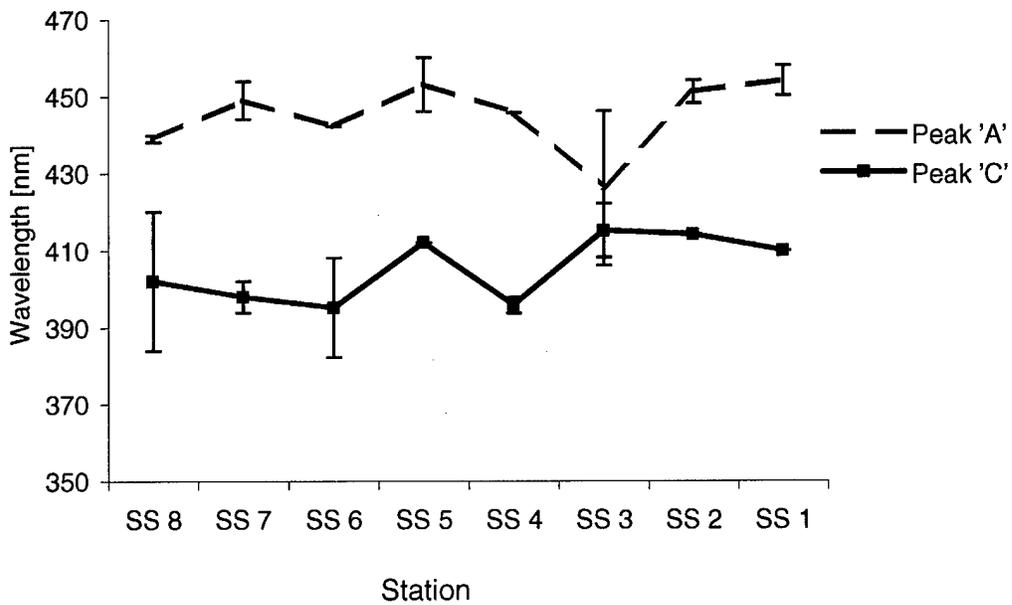


Figure 41. CDOM peak emission wavelengths (N=2) in shipside samples taken as the vessel approached Valdez, AK during VPS.

Protein-like fluorescence was examined in an attempt to characterize biological production in the C and ER tanks. In samples from both tanks, tyrosine-like and tryptophan-like fluorescence were highly variable in incidence and intensity, which is taken as evidence of contamination at those wavelengths. Not all replicates exhibited the same levels of protein-like fluorescence, nor were trends consistent among treatments. Examination of the procedural sample blanks showed a very similar set of protein-like peaks at similar intensities to those found in some samples, however, the procedural blanks showed little or no fluorescence contamination in the humic region (Figure 42). Given the high variability within the samples and the condition of the sample blanks, examination of potential biological production of protein-like fluorescence in the tanks was impossible, and will not be discussed further in the context of the data set.

Contamination of procedural blanks is problematic for any analyses, especially those used in a regulatory capacity. Protein-like fluorescence occurs in a wavelength region that is easily contaminated by a variety of sources, including but not limited to hand lotion, perfume, and sunscreen. Contact of the sample with any type of plastic (from latex and vinyl gloves, tubing, fittings, and o-rings), adhesives (used to hold Teflon® liners to the insides of bottle caps), marine paints or epoxies (used commonly aboard ship) can also give rise to this type of fluorescence. As a result, analysis at the protein-like fluorescence wavelengths requires extremely stringent sample collection, handling and shipping in order to achieve reliable results. This would make it difficult or impossible to use those wavelengths for any type of routine forensic determination. However, the short emission wavelengths typical of this type of contamination do not affect the utility of CDOM humic fluorescence peaks in determining ballast exchange, since the fluorometer for this experiment uses gratings capable of fine scale wavelength resolution (± 0.2 nm).

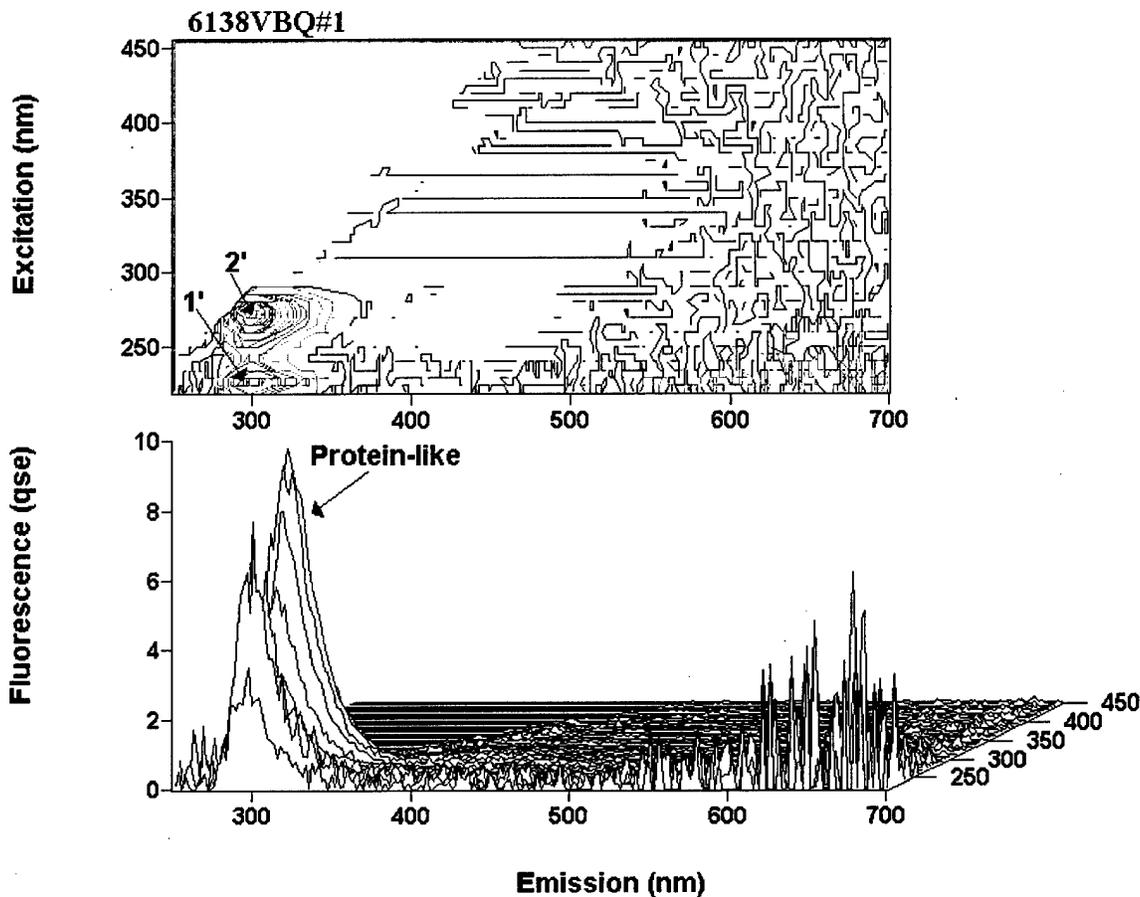


Figure 42. EEM of procedural blank showing contamination in the protein-like fluorescence region.

3.5. Summary: Pacific Ocean Voyages

3.5.1. Exchange efficiency

Ballast water exchange efficiency and the degree of vertical mixing was assessed for the VSF and VLA cruises by comparing rhodamine dye samples from different depths in the ballast tanks over time. On the VSF cruise, a single ER exchange was sufficient to remove 98 percent of the original tracer and port water, while a series of three single-volume FT exchanges achieved slightly less than the theoretical (95 percent) exchange efficiency. On the VLA cruise, three FT exchanges removed only 75 percent of the rhodamine dye, suggesting that the mate had underestimated the amount of time required to perform a 300 percent volumetric exchange operation. On both cruises, ballast water appeared to be well mixed by depth.

3.5.2. Salinity

Initial ballast tank salinities varied according to cruise although ocean salinities at the position of exchanges were between 30 - 33 ppt for all three cruises. VSF was a relatively low salinity port, such that initial tank salinities (20-21.5 ppt) were clearly below that which would be expected from exchanged ballast tanks. In contrast, VLA initial salinities (33.3 ppt) and VPS salinities (around 29.9 ppt) were within a range that overlaps with exchanged ballast water. Salinity behaved in a conservative manner during ballast exchange and consequently was a sufficient tracer of exchange only for the low salinity (VSF) port.

3.5.3. Turbidity

Turbidity was measured successfully on the VLA cruise only. Turbidity at the end of the VLA experiment was significantly greater in the Control Tank than the exchanged tank, but varied more over time in a single tank than between the control and exchanged tanks. Consequently, turbidity was considered an unreliable verification tool on this voyage.

3.5.4. CDOM Fluorescence

Peak CDOM fluorescence intensity, as measured in-situ by the FlashLamp (Wetlabs Inc.), was almost perfectly correlated with rhodamine dye and recorded up to an 87 percent reduction following ballast exchange on VSF and a 75 percent reduction on VLA. There are two possible interpretations to this result: 1. CDOM was as useful an indicator of ballast exchange efficiency as a dye tracer introduced to the tank, or 2. the FlashLamp measured intensities at the tail end of the rhodamine spectrum rather than the CDOM peak. While trying to reach a decision about which conclusion was most likely, it was discovered that wrong equations had been programmed into the Seabird instrument used to log these data, thwarting attempts to convert the instrument's fluorescence units (fIS) to quinine sulfate equivalents (QSE). Consequently, it was not possible to determine conclusively which interpretation was the correct one. For the same reason, direct comparisons of the results of the EEMs and the in-situ CDOM measurements have been avoided. However, the in-situ measurements can be considered to be internally consistent along the factory-specified scale, making comparisons between the two voyages and across treatments useful.

3.5.5. CDOM EEMs

Several fluorescent peaks were observed in the EEM plots of CDOM samples analyzed in the laboratory. Peaks A and C were the dominant natural peaks arising from the fluorescence of humic material, with Peak A dominating during all cruises. In addition to the humic peaks, protein fluorescence similar to tyrosine was present in all samples. These peaks may result from biological production within the tanks or from contamination of samples during collection. On all cruises, tyrosine-like peaks were too variable to enable their use as a tracer of ballast water exchange. Similarly, the wavelengths of the humic fluorescence peaks (excitation and emission) did not vary consistently with salinity on VSF nor could they be used as tracers of exchange on the latter cruises.

Because of interference by rhodamine dye on the first two cruises, CDOM absorbance was determined only on the VPS cruise. While absorbances at 280 nm, 312 nm and 412 nm were significantly affected by ballast water exchange on this cruise, the latter two wavelengths appeared most useful as tracers.

3.5.6. Radium

Radium Isotopes ^{223}Ra and ^{224}Ra were recovered in measurable levels from the two cruises for which samples were taken (VSF, VLA). Only one ocean sample contained appreciable quantities of either isotope. ^{223}Ra levels in the tanks were typically an order of magnitude lower than ^{224}Ra levels. ^{223}Ra and ^{224}Ra in control samples varied considerably over the two voyages, however, some of this variation may be due to low replication and sampling difficulties rather than to real differences over time. The same reasons might also be responsible for the large differences observed between initial concentrations of these isotopes in the control vs. FT tank on the VLA cruise.

On both cruises, concentrations of ^{223}Ra and ^{224}Ra decreased following ballast water exchanges, although there may have been some recovery of ^{224}Ra concentrations on VSF, possibly from a source within the ballast tanks. At the end of the VSF cruise, the concentrations of ^{223}Ra in the ER and FT samples were 13 percent and 18 percent of the control sample concentration, while the concentrations of ^{224}Ra in the ER and FT samples were 30 percent and 27 percent respectively. On the VLA cruise, concentrations of ^{223}Ra in FT samples decreased by approximately 75 percent over the course of the voyage, whereas ^{224}Ra decreased by approximately 70 percent relative to initial values.

3.5.7. Trace Metals

Of the suite of trace metals measured on the three Pacific cruises, only Mo, Ba, P, U, V and Mn demonstrated potential as tracers. These metals were least often contaminated by the tanks or procedure and demonstrated trends consistent with data obtained using other techniques (salinity, rhodamine, CDOM). With the exception of Mo, which behaved in a manner conservative to salinity, and U, which did not vary significantly following exchange on the one cruise in which it was measured (VPS), concentrations of these metals decreased in ballast tanks following exchange.

The extremely high concentrations of Fe, Ni, Cu (and other metals that are abundant in ships' structures) which were observed during the VSF and VLA cruises indicated that the sampling protocol needed to be altered to remove the influence of particles on the dissolved concentrations of these tracers. As a result of the protocol modification, concentrations of most metals were greatly reduced on the VPS voyage. However, of the five potential metals tracers tested on all voyages (Mo, Ba, P, V and Mn), only Mn and V were at their lowest levels on the VPS cruise, suggesting that the remaining tracers may be less sensitive to particulates in unfiltered samples.

While Fe and Cu concentrations were lower on VPS than on the two previous cruises, many VPS samples were observed to contain excessive concentrations of these and other elements despite filtration. Furthermore, the VPS data showed higher variability among replicate samples than earlier cruises, particularly for Mn and U. This suggests that the filtration process removed significant contaminants, yet was not always applied successfully. This may have been a question of technique; alternatively, it may indicate that these elements are likely to be contaminated in ballast water samples and hence are unreliable tracers.

Across all voyages, Ba was the most reliable indicator of ballast water exchange and rarely appeared to be contaminated, even in unfiltered samples. Ba concentrations in oceanic shipside samples were consistently lower than 7 ppb. Initial Ba levels on the two high salinity cruises (VLA, VPS) were much lower (approximately 10 ppb) than on the low salinity cruise (approximately 35 ppb), which suggests that Ba may be a less powerful discriminator of exchanged and unexchanged tanks on high salinity cruises from oligotrophic ports.

3.5.8 Phytoplankton Salinity Tolerance

Salinity tolerance ratios were significantly higher for the exchanged samples than the control samples on VSF, suggesting a more "coastal" phytoplankton character. On the same voyage, shipside samples encompassed the full range of the exchanged and unexchanged ballast tanks, making it difficult to draw conclusions from the data. On VLA, the pattern seen in the ballast tanks was opposite, suggesting that the exchanged tanks were more oceanic than the unexchanged tanks. The contradictory nature of these results, coupled with the high variability among replicate samples, suggests that this method cannot be used reliably to verify ballast water exchange.

4. Atlantic Cruise

4.1. VFos : France to U.S. East Coast

4.1.1. Overview

Samples were collected from the M/V MOSEL ORE (Table 9), the Mediterranean Sea and the Atlantic Ocean during a fourteen day voyage between Fos Sur Mer (France) and Norfolk (VA) in June 2001 (Figure 43).

The long duration of the voyage enabled thorough sampling of four tank pairs (Port and Starboard) exchanged in a range of locations, collection of shipside samples every 12 hours and intensive onshore/offshore profiling of ambient seawater at the beginning (Figure 44) and end (Figure 45) of the voyage. This cruise has been designated VFos.

Table 9. VFos vessel specifications.

Name (Call Sign)	M/V MOSEL ORE (D5GS)
Owner	Seekrupp Seeschiffsfahrt
Length x Breadth x Draft	253.02 m x 40.06 m x 15.13 m
Cargo	Coal
Experimental ballast tanks: (i.d. / volume / max. depth)	W1: 1 port and starboard / 613.9 m ³ / 6.4 m W2: 2 port and starboard / 1759 m ³ / 6.4 m W3: 3 port and starboard / 1765 m ³ / 6.4 m W4: 5 port and starboard / 705.9 m ³ / 6.4 m

A transatlantic route was selected for the final cruise of this project because it provided the opportunity to examine data from a completely different region to previous cruises. The Mediterranean is a semi-contained basin that encloses some of the most oligotrophic waters on the planet (Dugdale and Wilkerson, 1988; Turley, 1999). This oligotrophic state is maintained by the constant inflow of warm, already nutrient-poor Atlantic surface water through the Strait of Gibraltar. With a residence time on the order of 10² yr, these waters become increasingly depleted of phosphorous and other nutrients through phytoplankton growth as they circulate through the basin (Bethoux et al., 1998). In addition, salinity in

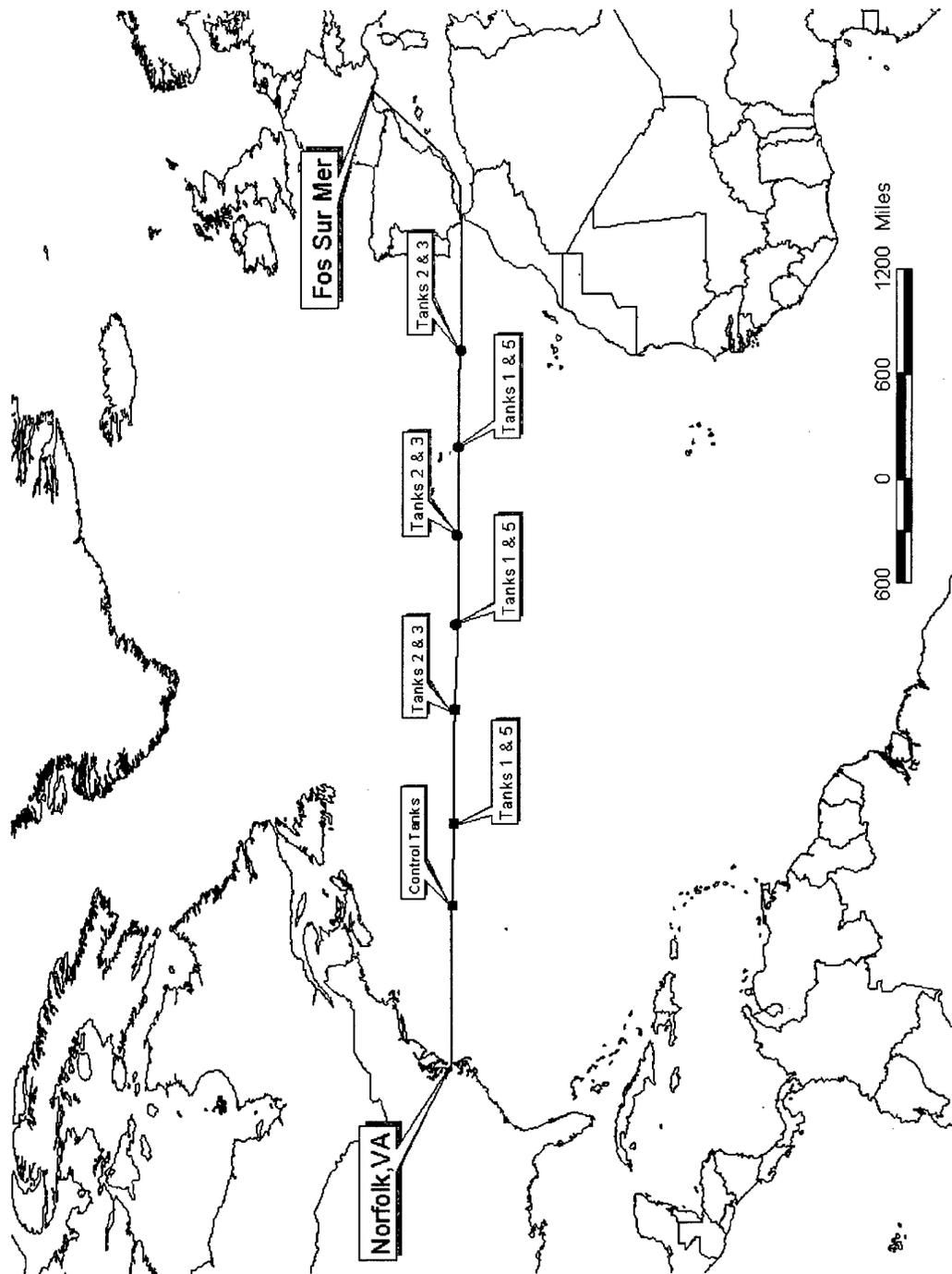


Figure 43. Track of the M/V MOSEL ORE during VFos, showing positions of exchange events. Flow-Through (●) and Empty/Refill (■) exchanges were performed in pairs (W2 port with W3 starboard and W1 starboard with W4 port).

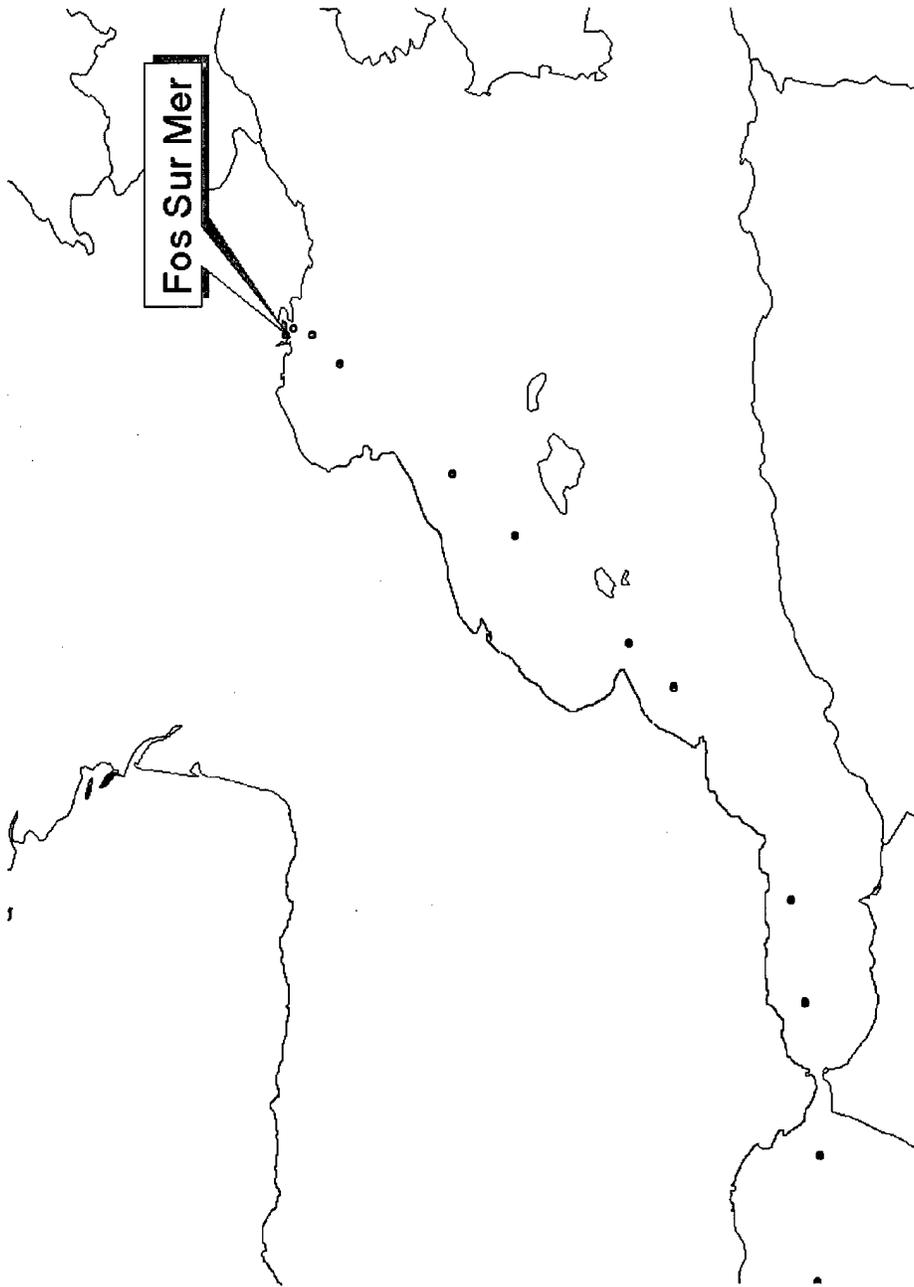


Figure 44. Offshore Profile Sampling Points: CDOM and Trace Metal samples of ambient seawater were taken as the M/V MOSEL ORE left the Mediterranean Sea and entered the Atlantic Ocean.

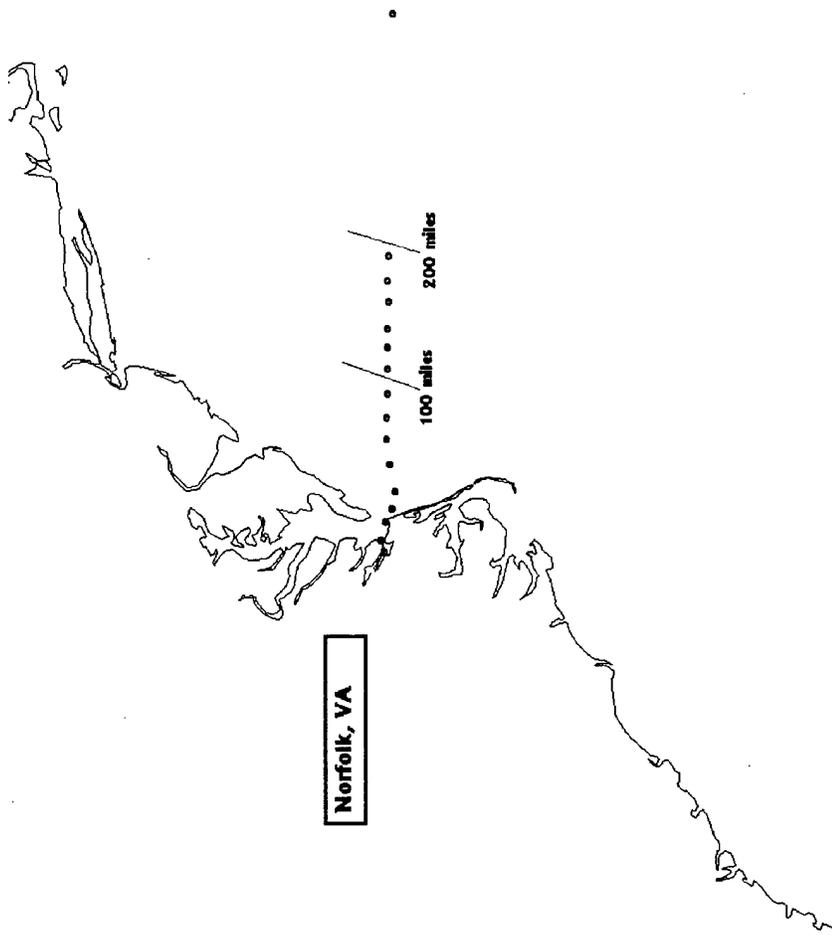


Figure 45. Onshore Profile Sampling Points: CDOM and trace metal samples of ambient seawater were taken every hour as the M/V MOSEL ORE approached the U.S. Coast.

the basin increases by roughly 10 percent eastward owing to climatic factors that make the basin evaporative. Its high salinity (over 36 ppt), extremely low nutrient levels, and low productivity make the Mediterranean a difficult and valuable test case for ballast water exchange compliance determination.

4.1.2. Experimental Design

Eight top-side wing ballast tanks were sampled over the course of the experiment. All eight tanks were ballasted in the port of Fos Sur Mer on June 13 2001 (Figure 46). Half of the tanks (1P, 2S, 3P, 5S) were designated "Control Tanks" and were not touched other than to obtain samples until they underwent a single Empty-Refill exchange on June 23 prior to arrival in U.S. waters. The other four tanks (1S, 2P, 3S, 5P) were designated "treatment tanks," split into pairs of similar capacity (i.e. Tanks 1 & 5; Tanks 2 & 3), and subjected to a series of three exchanges on alternating schedules. The first two of these were 100 percent Flow-Through exchanges, and the last was a 100 percent Empty-Refill exchange. Exchanges were initiated in full ocean water more than 500 miles from the nearest European coast and concluded at least 400 miles from the U.S. coastline.

The sampling protocol on the VFos voyage included the following:

- in-situ determination of salinity in ballast tanks and shipside samples
- in-situ determination of turbidity in ballast tanks
- laboratory determination of trace metal concentrations and CDOM fluorescence/absorbance in ballast and shipside samples
- laboratory determination of radium isotopes and dissolved lignin in ballast and shipside samples

4.1.3. Sampling Design

Tank Sampling

In-situ samples

In-situ profiles of salinity and turbidity were obtained by lowering a CTD (Hydrolab: Minisonde) through a single manhole into each tank. Because of the triangular shape of the wing tanks and the positions of unobstructed access to the tanks, the maximum profiling depth did not exceed 2.2 m. The CTD recorded data every 10 seconds over a 2.5 minute period.

Laboratory samples

Tank samples of CDOM, trace metals, radium and lignin were obtained by pumping water through nylon tubing pre-installed at two locations in each tank. One tube gave access to a location close to the discharge hole at the bottom aft region of the tank (5 m depth); the other to a point approximately 1.5 m below the surface at the forward end of the tank.

CDOM and metals were collected during four sampling days per tank (4 days * 8 tanks * 2 locations * 2 replicates = 128 samples). In addition, the Control Tanks were sampled subsequent to a single exchange at the end of the voyage (4 Control Tanks * 2 locations * 2 replicates = 16 samples).

Radium samples were collected at the beginning and at the end of the voyage. For each sample, a known volume of ballast water (exceeding 180 liters) was pumped at 1-2 L min⁻¹ via a filter (5 µm) through a column containing a manganese dioxide coated fiber. Initial (T0) and final (T3) samples were collected for tanks W1, W2 and W4 (1 replicate at 2 locations per tank). Time did not allow collection of initial samples from tank W3, but final samples were collected for this tank.

At the end of the voyage, all lengths of tubing were removed from the tanks, sealed with parafilm, labelled and retained for subsequent determination of procedural blanks. Procedural blanks for CDOM and trace metals only were obtained by pumping high purity water (Milli-Q) through the tubing and relevant sample apparatus (including the pump, hoses and and filter apparatus) to estimate the contribution of the sampling procedure to the tracer levels measured throughout the experiment.

Shipside sampling

CDOM, metals and salinity samples were obtained from the engine room by tapping the engine-cooling water pipe at its inlet end. This pipe constantly circulates ocean water from the side of the ship (depth ca. 5 m) past the engine and out again. A total of 54 shipside samples of each type, with corresponding GPS positions, were collected during the voyage.

	13-Jun	14-Jun	15-Jun	16-Jun	17-Jun	18-Jun	19-Jun	20-Jun	21-Jun	22-Jun	23-Jun	24-Jun
Tank 2 P	load	T0	100% FT	T1	100% FT	T1	100% FT	T2	ER	T3		
Tank 5 P	load		T0	100% FT	T1	100% FT	T1	100% FT	T2	ER	T3	
Tank 2 S	load		T0			T1		T2		T3	ER	T4
Tank 5 S	load		T0				T1		T2	T3	ER	T4

T0-T4 = Sample collection

P, S = Port side, Starboard side

100% FT = single volume Flow-Through exchange

ER = full volume empty/refill exchange

Figure 46. Sampling and Exchange schedule of eight experimental tanks on VFos.

4.1.4. Results

Salinity

Salinity did not vary consistently with depth in any tank at any time on the VFos cruise, hence all salinity data presented in this section represent averages over the accessible portion (ca. top 2 m) of the ballast tanks. Standard deviations were typically less than 0.05 ppt and consequently are too small to be visible on the figures. Initial tank salinities were around 37.6 ppt in all tanks except W1 (P & S), which was approximately 0.5 ppt lower than in the other tanks (Figure 47). Control Tank salinities increased slightly in all tanks until T3, after which salinities dropped as a result of exchange with ocean water. The slight increasing trend in the Control Tanks from T0 to T3 may be a result of instrument drift or a mixing phenomenon. A drift of similar magnitude is noticeable for the FT tanks between T3 and T4.

Salinity of shipside samples differed slightly from salinities measured in the FT tanks (Figures 47 and 48). Ocean and FT salinities did not agree as closely at T3 (following the complete empty-refill exchange of the FT tanks) as might be expected given the high efficiency of this type of exchange. The reason for this discrepancy is thought to be two-fold. First, shipside salinity data were derived from discrete (ca. 300 mL) samples and will naturally encompass less variation than depth profiles; second, there was some indication that the CTD did not measure salinity from discrete samples as accurately as depth profiles, as evidenced by readings differing by as much as 0.4 ppt depending on whether or not the flow circulator was turned on. Ocean salinity was initially measured at 37.0 ppt in the eastern Atlantic. Salinity decreased to around 35.5 ppt at the locations of the exchanges of the treatment tanks and then increased slightly at the time of the final exchange (performed on Control Tanks prior to arrival at Norfolk).

Turbidity

Due to equipment difficulties, turbidity data are missing at the beginning of the voyage (T0) and for two tanks at T3. However, remaining data clearly indicate that turbidity is highly variable both between tanks at any given time and within a single Control Tank over the course of the voyage (Figure 47). Tanks exchanged at the same time (e.g. W1 and W4) are more similar to each other than to the others (W2 and W3) and vice versa, indicating that measurements are sensitive to either the location of the exchange or, more likely, to the conditions on the day of sampling. Furthermore, end point turbidities differed by less than 1 NTU between exchanged and unexchanged treatments.

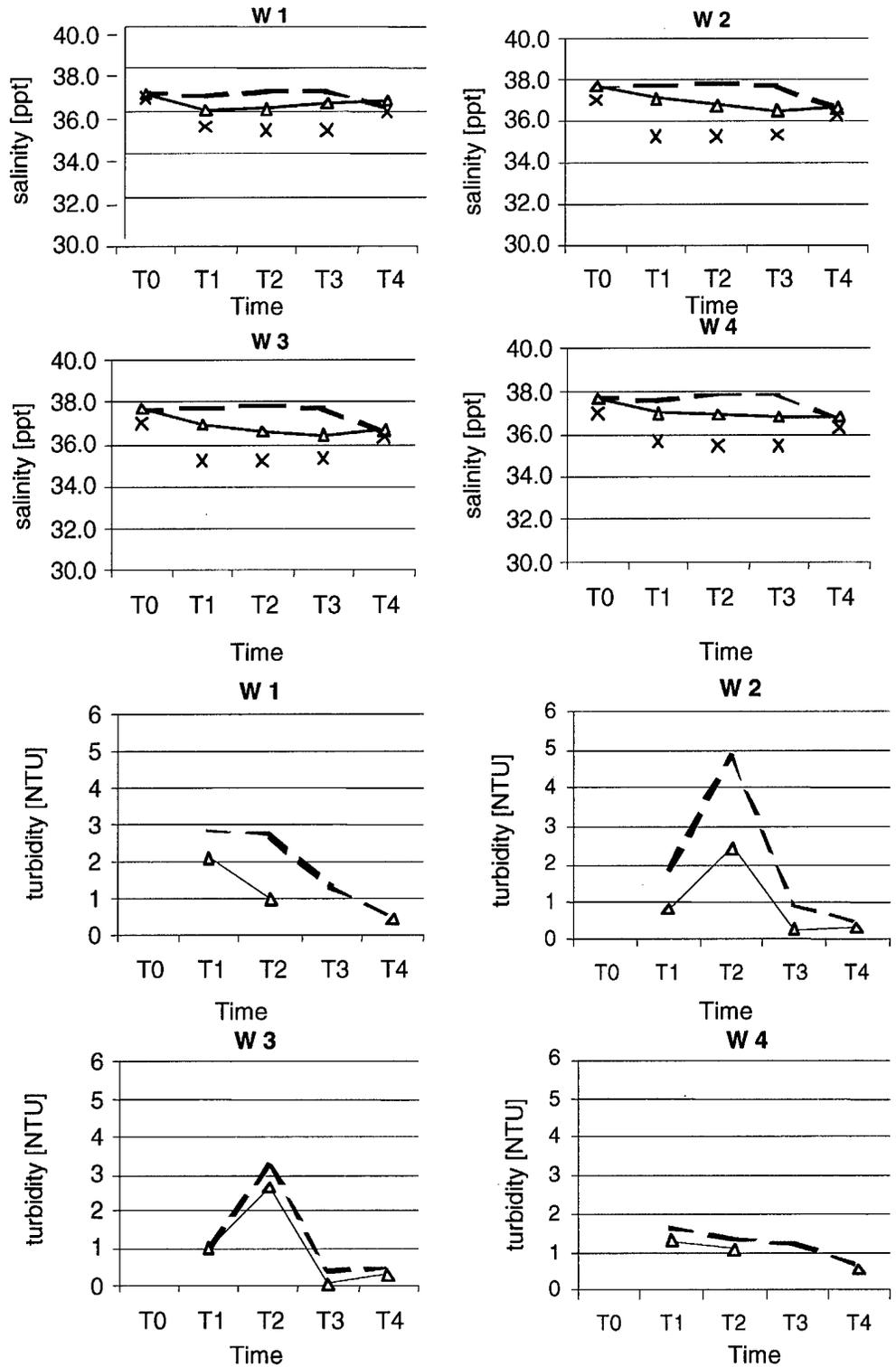


Figure 47. Depth-averaged salinity (top four plots) and turbidity in ballast tanks during VFos. Control Tank (---), Flow-Through Tank (-Δ-), Shippside (X).

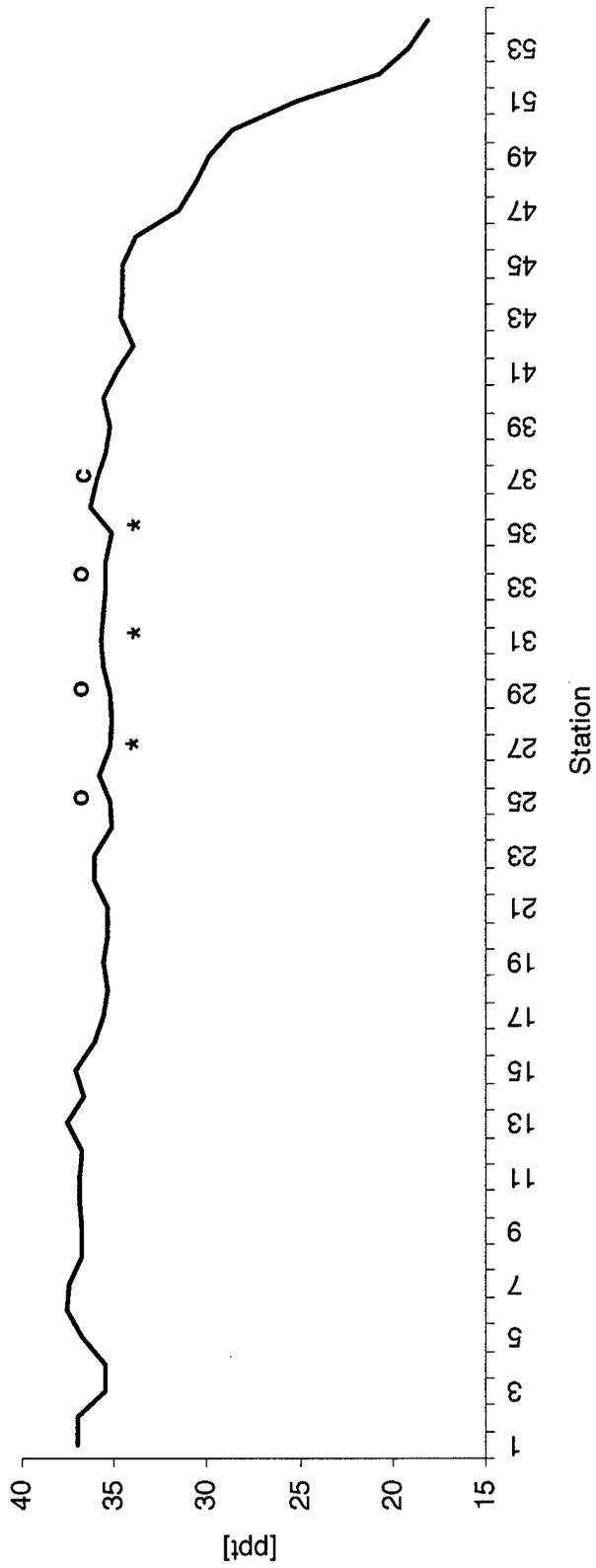


Figure 48. Salinity of shipside samples as the vessel moved from the Mediterranean Sea to Norfolk, VA during VFos. Relative locations of ballast water exchanges indicated by symbols o (W2 & W3), * (W1 & W4) and c (all Control Tanks).

Trace Metals

Trace metal concentrations in samples collected from the port of Fos Sur Mer, as well as samples from unexchanged ballast tanks on VFos, were comparable to levels measured in the VPS cruise, with the exception of phosphorus, which was recorded at substantially lower concentrations. Concentrations of six elements (Mo, Ba, P, Mn, U, V) in ballast tanks during VFos are presented in Figure 49 - Figure 51.

As in the other cruises from high salinity ports (i.e. VLA, VPS), Mo levels in exchanged and unexchanged tanks were measured at similar concentrations throughout the voyage. Although at low concentrations in initial and control samples, Ba levels decreased noticeably as the treatment tanks were progressively flushed with ocean water during exchange. Levels of Mn and P exhibited a similar decline in the exchanged tanks, however considerably more variation at all levels (within tanks, between tanks and among unexchanged Control Tanks) was measured for these elements. Levels of U and V were not significantly affected by ballast water exchange on this voyage.

The data for P are consistent with the unique nutrient chemistry of the Mediterranean. Phosphorus concentrations in initial ballast water samples were considerably higher (ca. 7 ppb) than in the shipside samples taken while the ship was in port (ca. 2-3 ppb). Levels of P were also observed to increase with time in the Control Tanks. These findings suggest that a source of P existed within the ballast tanks. A possible source is P efflux from mildly reducing sediments on the tank bottom as has been observed for continental slope/shelf sediments (Schenau and De Lange, 2001).

For the other elements, data from shipside samples mostly corroborates the trends seen in the ballast tanks (Figure 52). Concentrations of Mo U, and V in Mediterranean samples were barely distinguishable from concentrations in samples from 200 miles offshore. Ba levels exhibited a gradual decline from around 10 ppb to 6 ppb within the Mediterranean and persisted at around this level until the ship began to approach the U.S. east coast. Initial Mn levels were relatively high (ca. 3-4 ppb), but decreased rapidly while still in the Mediterranean, and further decreased to levels below 0.5 ppb in the open ocean. The Mn spike observed at station 22 (63 miles southwest of the Cape of St Vincent) may result from an unknown point source originating in Spain or Portugal or else it may be an anomaly. However, this station did not exhibit noticeably elevated levels of Fe and other metals, such as was usually seen with contaminated trace metal samples during this project.

At the opposite side of the Atlantic, the increase of trace metal concentrations with increasing proximity of the U.S. coastline was more marked than the Mediterranean case. Previous work has shown that trace metal and nutrient concentrations in seawater are much higher in coastal waters which receive elevated inputs from riverine, eolian and terrestrial sources (Bruland, 1983; Donat and Bruland, 1995; Shiller, 1997). Mn levels were the first to rise beginning around 150-200 miles offshore, followed by P (100 - 150 miles) and Ba (50 - 100 miles). Levels of the predominantly conservative elements Mo (Paulsen and List, 1997) and U (Andersson et al., 2001) began declining around 50-100 miles offshore in concert with decreasing salinity.

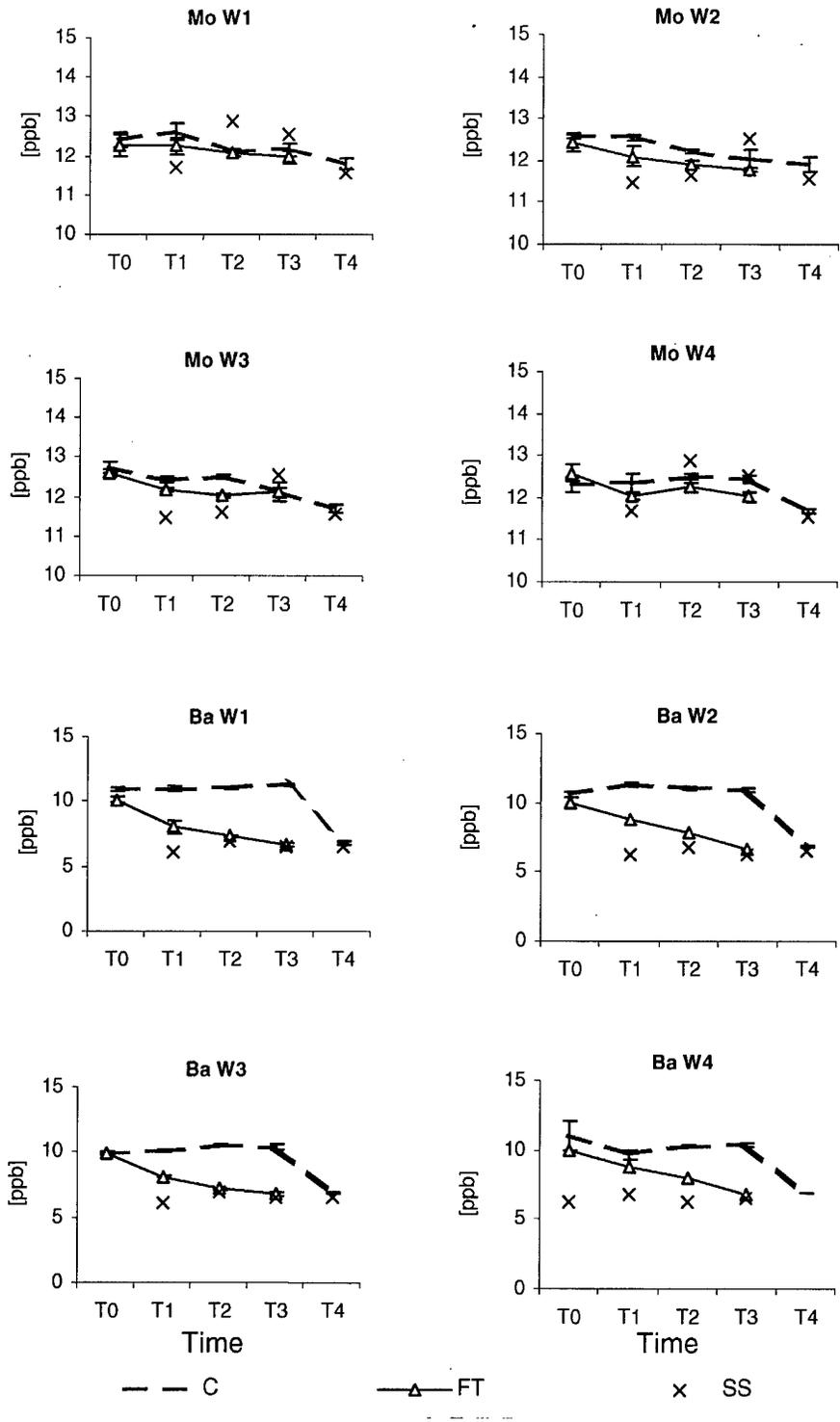


Figure 49. Concentrations of Mo and Ba in replicate tanks (W1-W4) on the VFos cruise, plotted against corresponding shipside samples.

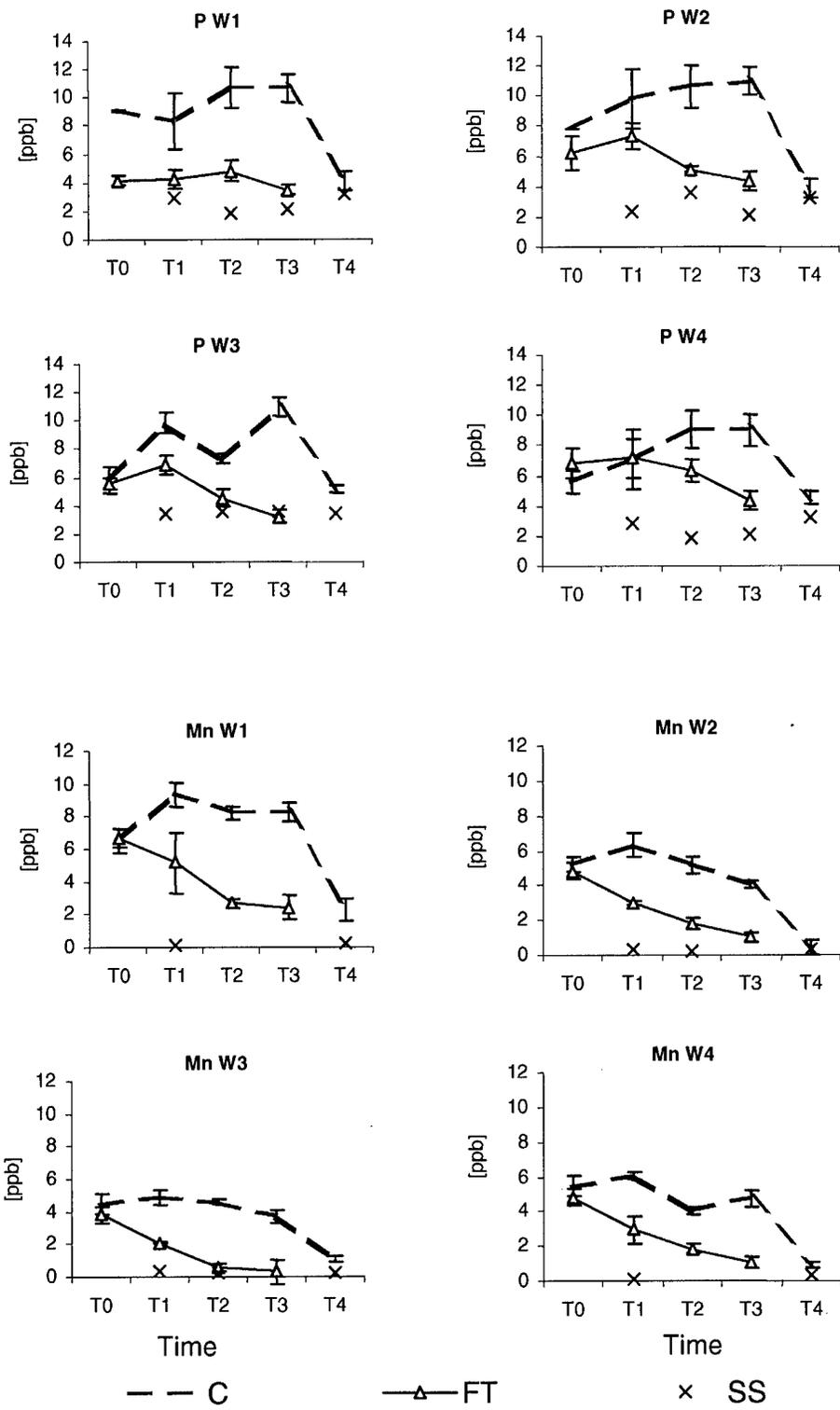


Figure 50. Concentrations of P and Mn in replicate tanks (W1-W4) on the VFos cruise, plotted against corresponding shipside samples.

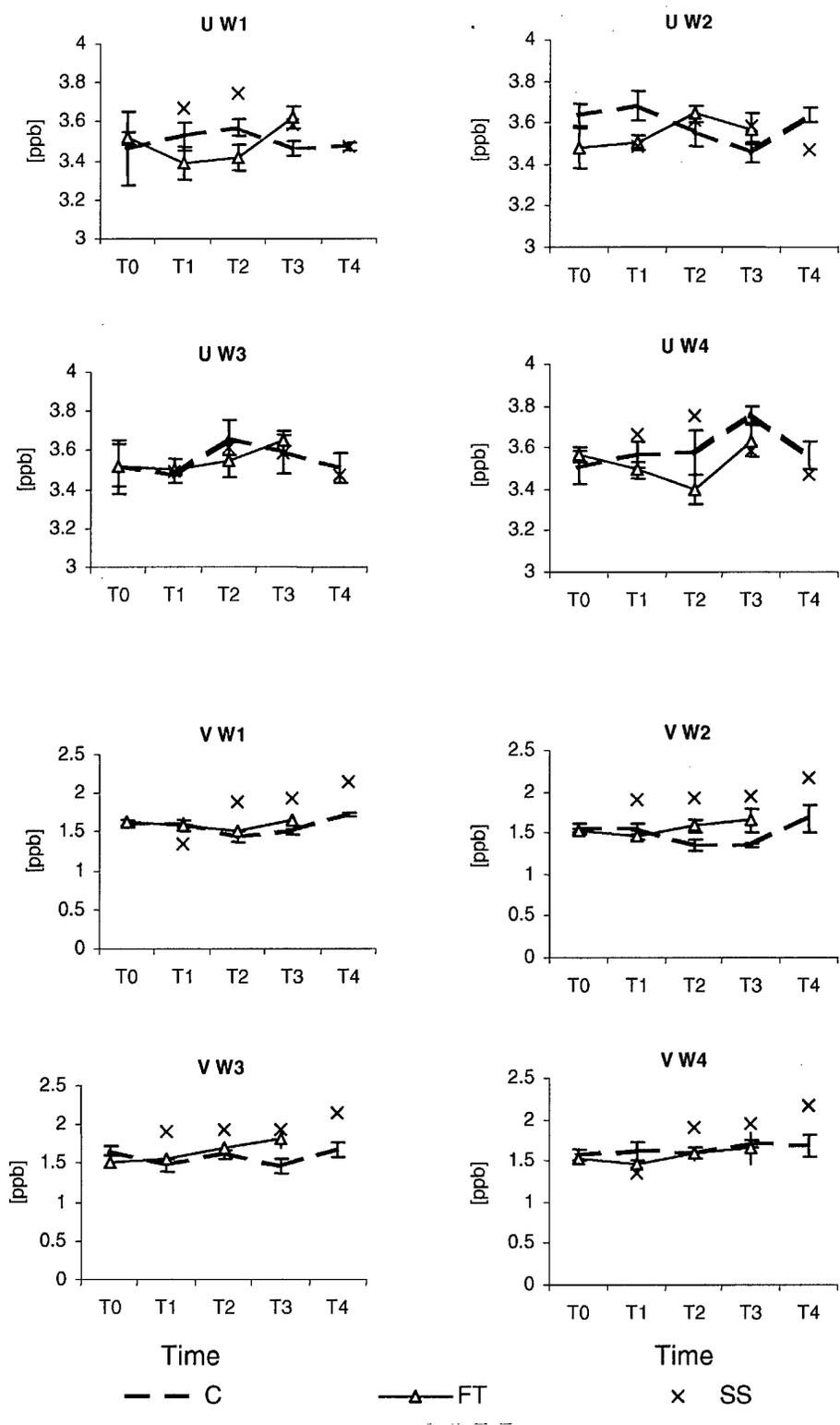


Figure 51. Concentrations of U and V in replicate tanks (W1-W4) on the VFos cruise, plotted against corresponding shipside samples.

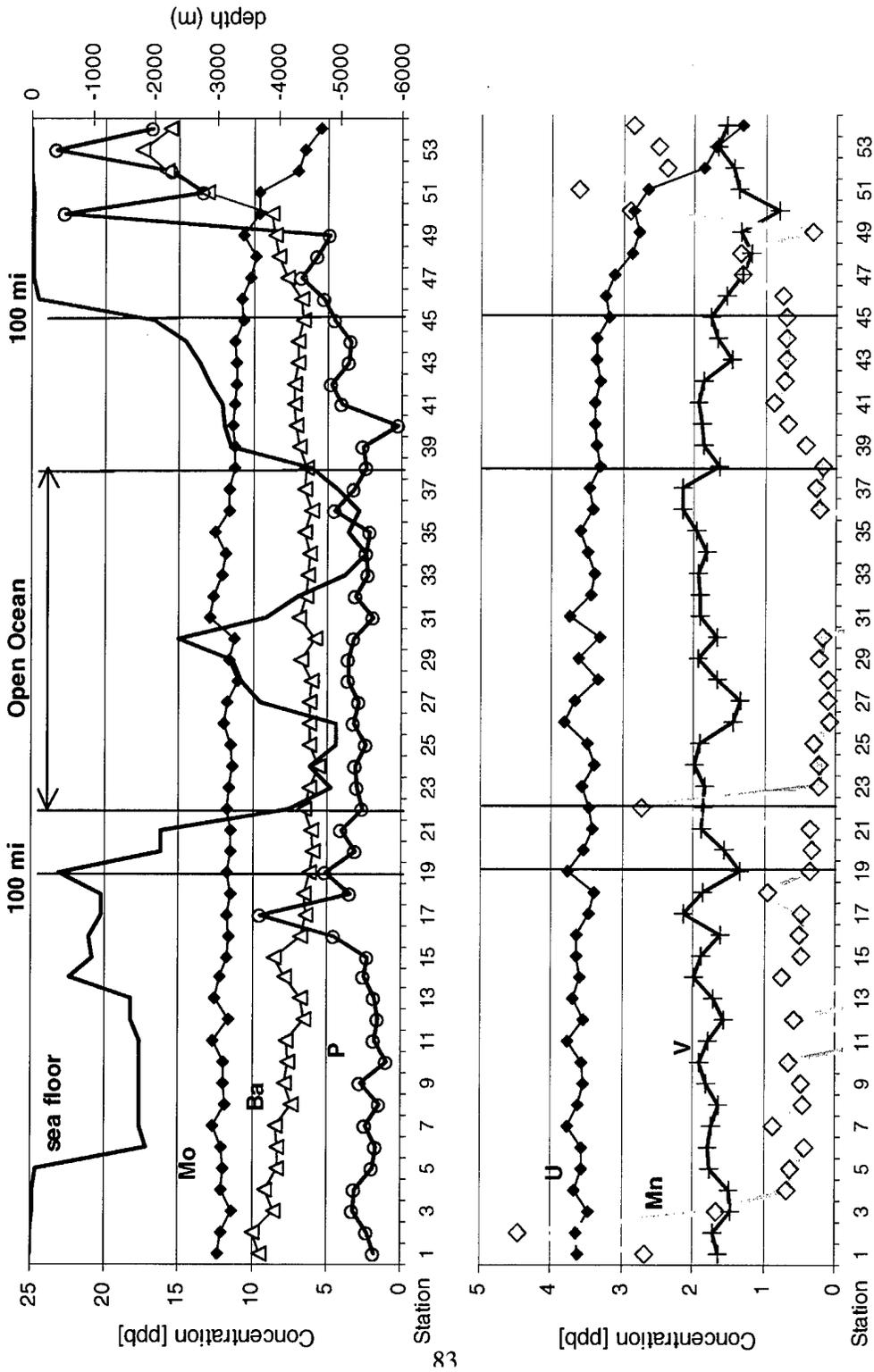


Figure 52. Trace metals (Mo, Ba, P, U, Mn, V) in shipside samples during VFos. Bathymetry plotted for comparison. Vertical lines indicate "open ocean" (>200 mi offshore, >2000 m depth) and 100 mi offshore boundaries. Station 1 is Fos Sur Mer, FR; Station 54 is Port of Norfolk, VA

CDOM EEMs

The VFos data set showed smooth rounded peaks from fluorescence of natural colored dissolved organic matter (CDOM) (Figure 53). A fluorescence component with sharp peaks at multiple excitation and multiple emission wavelengths was also observed (Figure 54). There was some wavelength overlap between these sharp peaks and CDOM fluorescence peaks. The sharp multiple peaks can arise from components possessing multiple aromatic rings, such as polycyclic aromatic hydrocarbons (PAHs). PAHs are common constituents in a variety of fuel oils and are thus a likely source of these peaks. Some peaks in the VFos samples correspond closely to that of the PAH pyrene (Figure 55) (Frimmel 2000). PAH fluorescence peaks were more intense than CDOM peaks in all of the control samples as well as in the pre-exchange (T0) samples of the treatment (FT) tanks.

The presence of PAH-like fluorescence in all tanks supports the source of this fluorescence being the original port water as opposed to contamination in the tanks. Fuel oil contamination could be problematic for a verification method based on CDOM fluorescence if it persists within the tanks and does not flush efficiently. In this data set, the fluorescence intensity of PAH peaks decreases in the exchanged tanks along with decreasing CDOM fluorescence, indicating concurrent dilution of the two constituents.

The presence of PAH fluorescence had a strong influence on the positions of the excitation and emission peak maxima throughout the VFos data set. Humic peak A generally displayed its maximum fluorescence at one of the PAH peaks in both the control samples and FT tank samples. The peak C region falls in an area of minimal pyrene fluorescence and was less influenced by PAHs. This variability in contamination between peaks indicates the importance of using multiple wavelength channels in a diagnostic method.

In addition to the PAH fluorescence, most of the excitation emission matrices (EEMs) showed strong protein-like fluorescence in the tryptophan and/or tyrosine-like region and evidence of contamination. The three types of contamination observed in this cruise each exhibited a pair of excitation wavelengths with a single emission peak. An example of all three pairs of contamination peaks were observed in one of the procedural blanks, as seen in Figure 56 and identified arbitrarily as P1, P2 and P3.

The presence of these peaks can influence the ultimate position of the fluorescence emission maxima, or in the worst case, completely overwhelm the seawater fluorescence. P1 fluorescence occurs at very short wavelengths similar to tyrosine-like protein fluorescence and is not likely to cause difficulties in data analysis. P2 and P3 however are much more problematic, since they exhibit longer emission wavelengths

that could interfere with CDOM fluorescence determinations. The chemical identities of the contaminants are unknown.

Generally, the sample blanks and pre-blanks analyzed show evidence of at least one contaminant peak, P1, to varying degrees. Contamination of some of the procedural blanks by P2 and P3 may be in part attributed to bottle breakage during freezing, especially since the cruise data do not show evidence of chronic fluorescence contamination by P2 or P3.

P1 was observed at varying intensities in most of the ballast tanks samples but did not interfere with CDOM fluorescence measurement. P2 appeared sporadically in ballast tank samples, but there was no evidence of a trend. Sample replicates did not show identical levels of contamination, and overall the presence P1 and P2 did not interfere with the diagnostic use of CDOM fluorescence. P1, P2 and P3 were also observed in varying combinations in shipside samples.

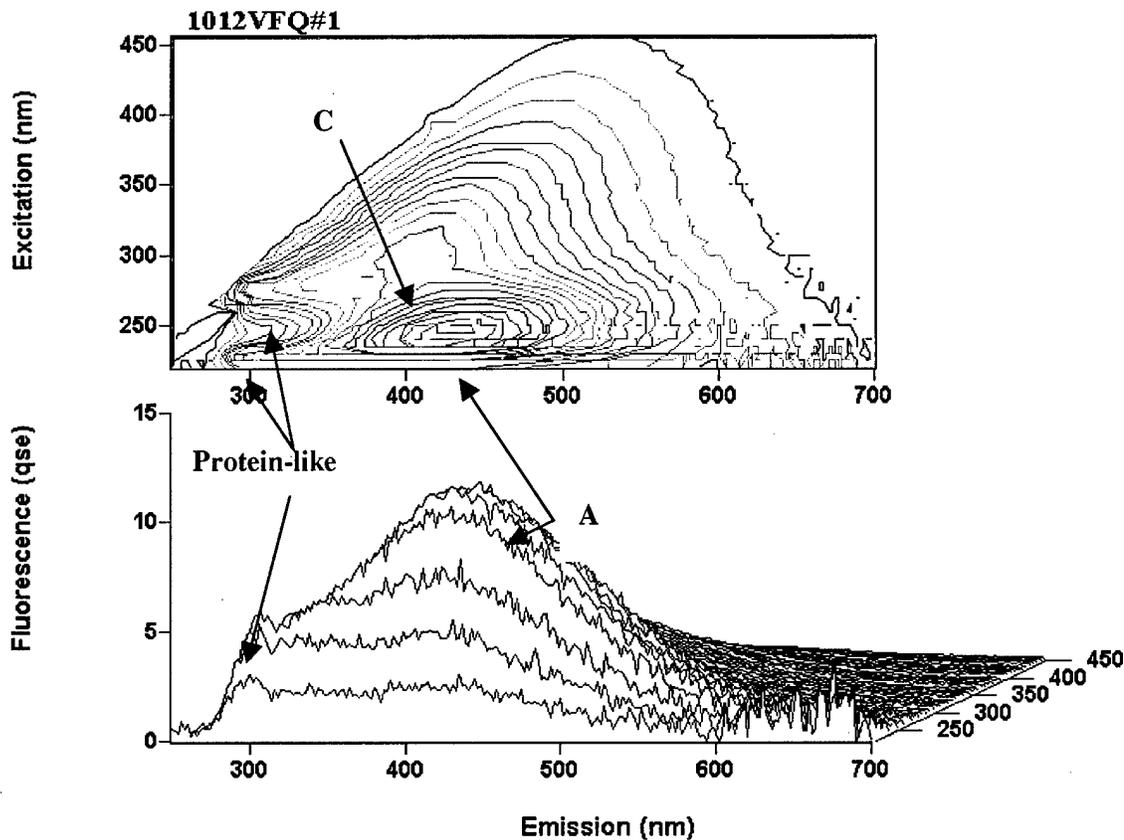


Figure 53. EEM from the VFos data set (shipside sample, station 52).

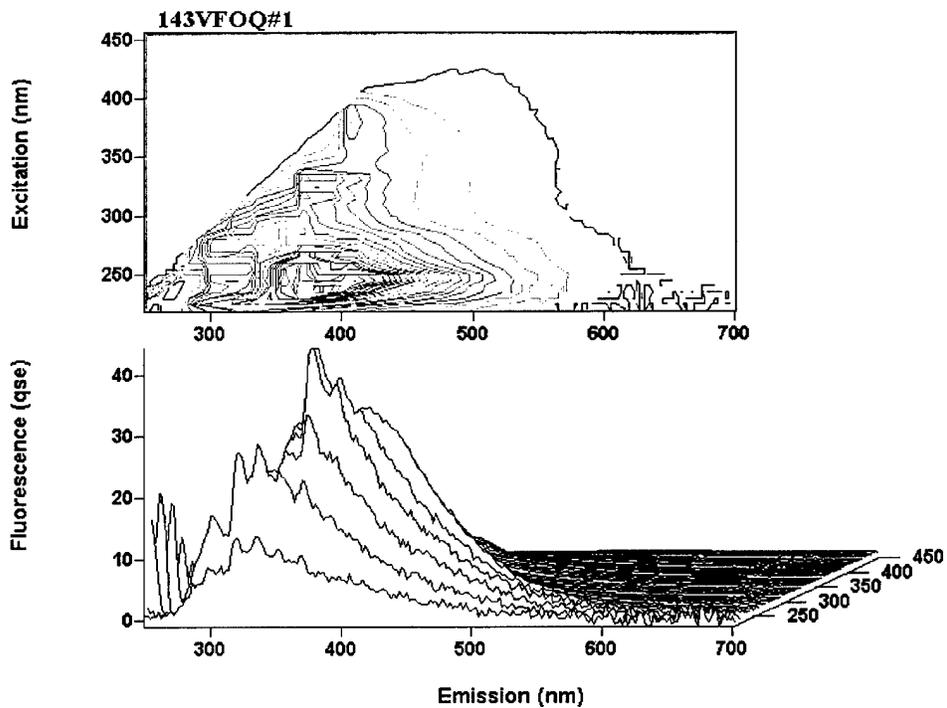


Figure 54. EEM of ballast water showing presence of PAH fluorescence.

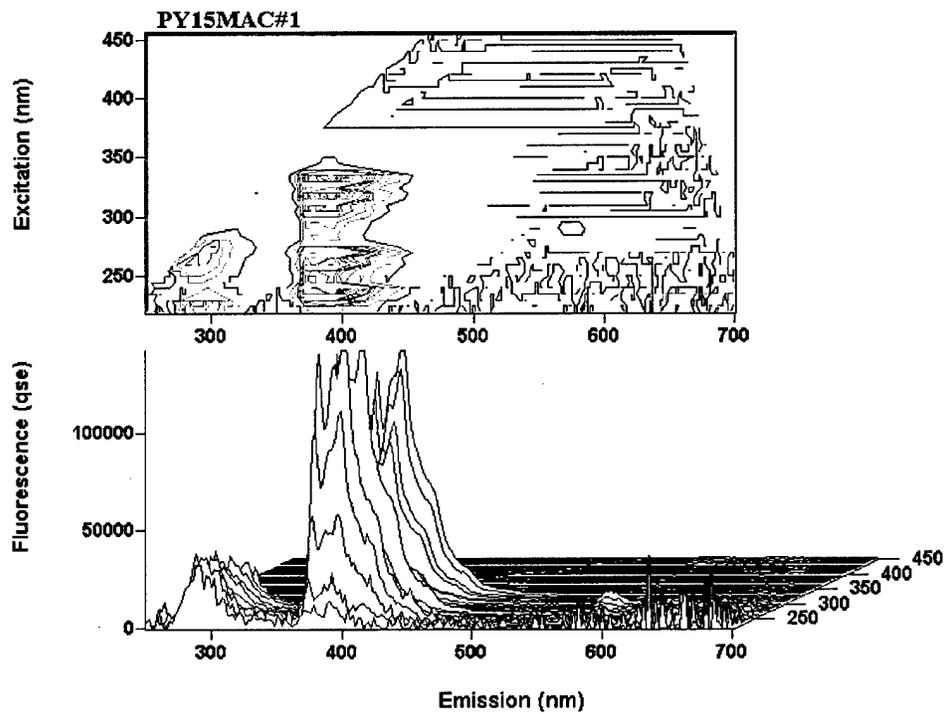


Figure 55. EEM of the PAH pyrene.

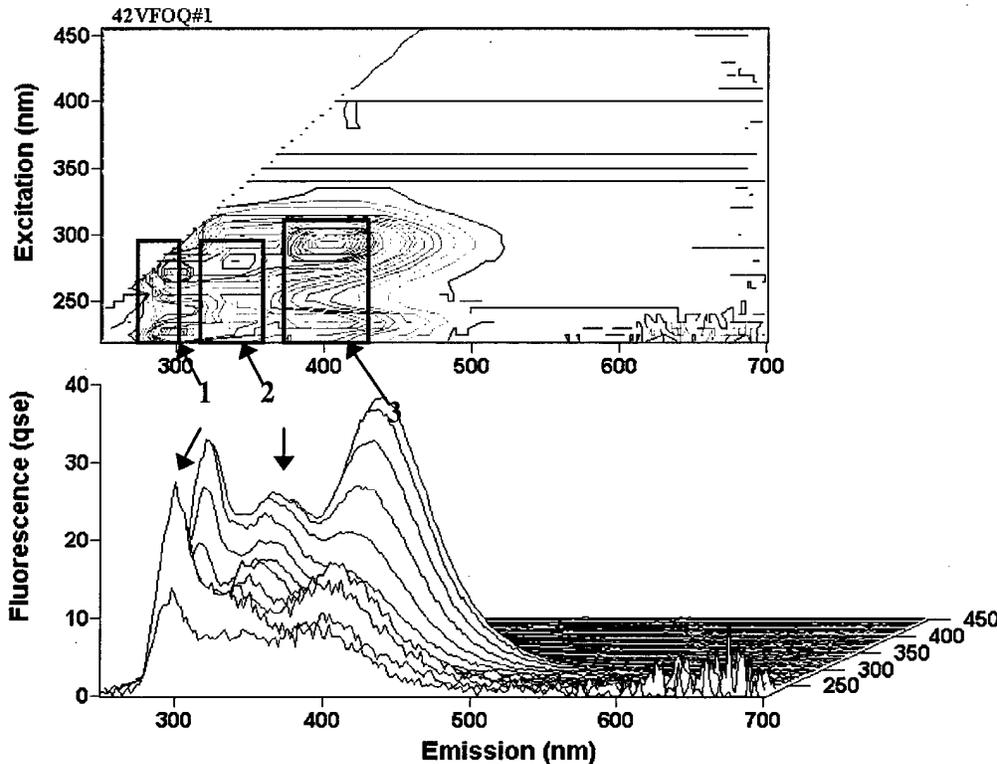


Figure 56. EEM of a 2procedural blank (Control Tank, W1) showing the different fluorescence contaminants observed during the VFos cruise.

Average fluorescence characteristics of humic-like peaks A and C (emission, intensity) are presented in Figure 57. As for previous cruises, peak A was more intense than peak C in all samples. Peak A intensity tended to increase slightly over time in the Control Tanks, then decrease markedly after the exchange at the end of the experiment. Peak C followed a similar trend. Shiptside fluorescence intensities were lower than or comparable to water in the exchange tanks, except during the Control Tank exchange at T4.

Fluorescence peak A intensity among FT tank samples ranged from 4.98-9.28 ppb QSE prior to exchange and from 0.622-5.37 ppb QSE after the third exchange of these tanks (T3). There was an overall decrease in humic-like peaks A and C fluorescence intensity in all exchanged tanks, despite the presence of PAH fluorescence. Although initial samples were taken over a 3-day period, no trend relating intensity variability to length of time in the ballast tank could be discerned.

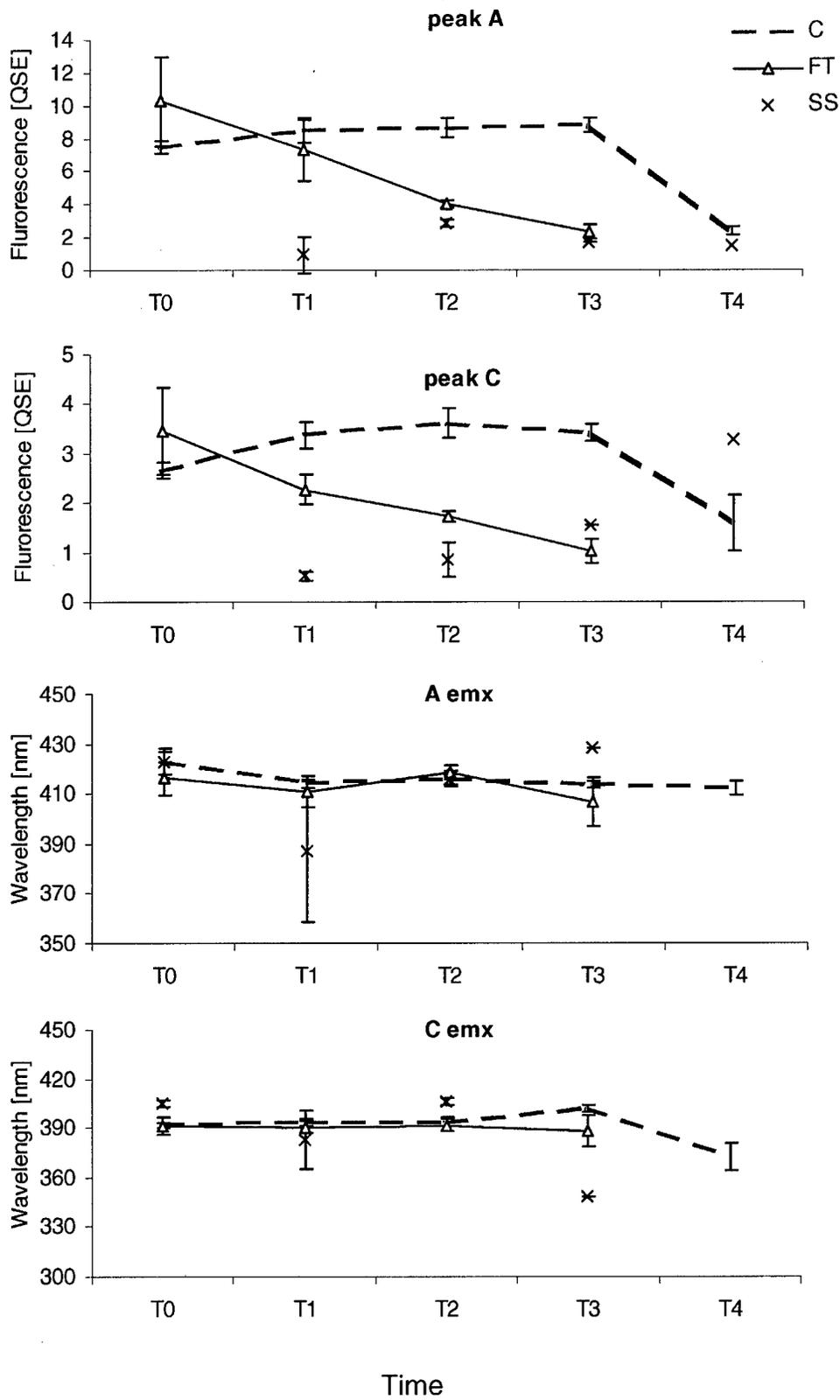


Figure 57. Fluorescence peak A and C intensities (peak), and wavelength of maximum emission (emx) averaged across all tanks and replicates during VFos (N=16 [C, FT], N=2 [SS]).

Variability among tanks in peak A and C intensity (Figure 58), fluorescence emission maxima (Figure 59) and absorbance at 312 and 412 nm (Figure 60) are evident upon comparing them visually.

Tank W1 showed very high variability in initial FT samples, due to high A and C peak fluorescence intensities in samples collected at the aft position of this tank. This variability is attributed to PAHs in the port water, rather than contamination from P1, P2 or P3 which would have caused emission wavelength maxima to shift to considerably shorter wavelengths. The trends in emission wavelength positions for this tank indicate that either PAH fluorescence influenced the wavelength position of tank samples even after several exchanges or that the exchanged open ocean water showed fluorescence emission maxima close to that of the PAH emission wavelengths. The P2 contaminant was present in one or more samples from all tanks at some point along the cruise. This contaminant tended to increase the intensity of the fluorescence while shifting the maximum emission wavelengths of those samples to shorter wavelengths relative to the other samples.

All of the tanks exhibited approximately stable or slightly increasing fluorescence intensities in the Control Tanks which contrasted with successive decreases in the FT tanks (Figure 58). The positions of emission maxima for the humic-like A and C peaks were highly variable among tanks (Figure 59). Between-tank variability may be partly due to differences in location of ballast exchange between the W1/W4 pair compared with the W2/W3 pair, although in some cases is clearly influenced by sample contamination. In all but the W3 tank, absorption coefficients at both wavelengths decreased as a result of exchange (Figure 60). However, the high variability among tanks illustrates the limitations of using these to determine ballast exchange. Since the absorbance method measures total absorbance at a given wavelength, it is more susceptible to contaminants than is a fluorescence sample (which may still yield useful information, depending on the fluorescence wavelengths of the contaminant).

Shipside samples are plotted sequentially by sample number and reflect the progression of the vessel from the Mediterranean Sea westward toward Norfolk (Figure 61). Fluorescence intensities and wavelengths are similar to those found in FT and Control Tanks subsequent to exchange.

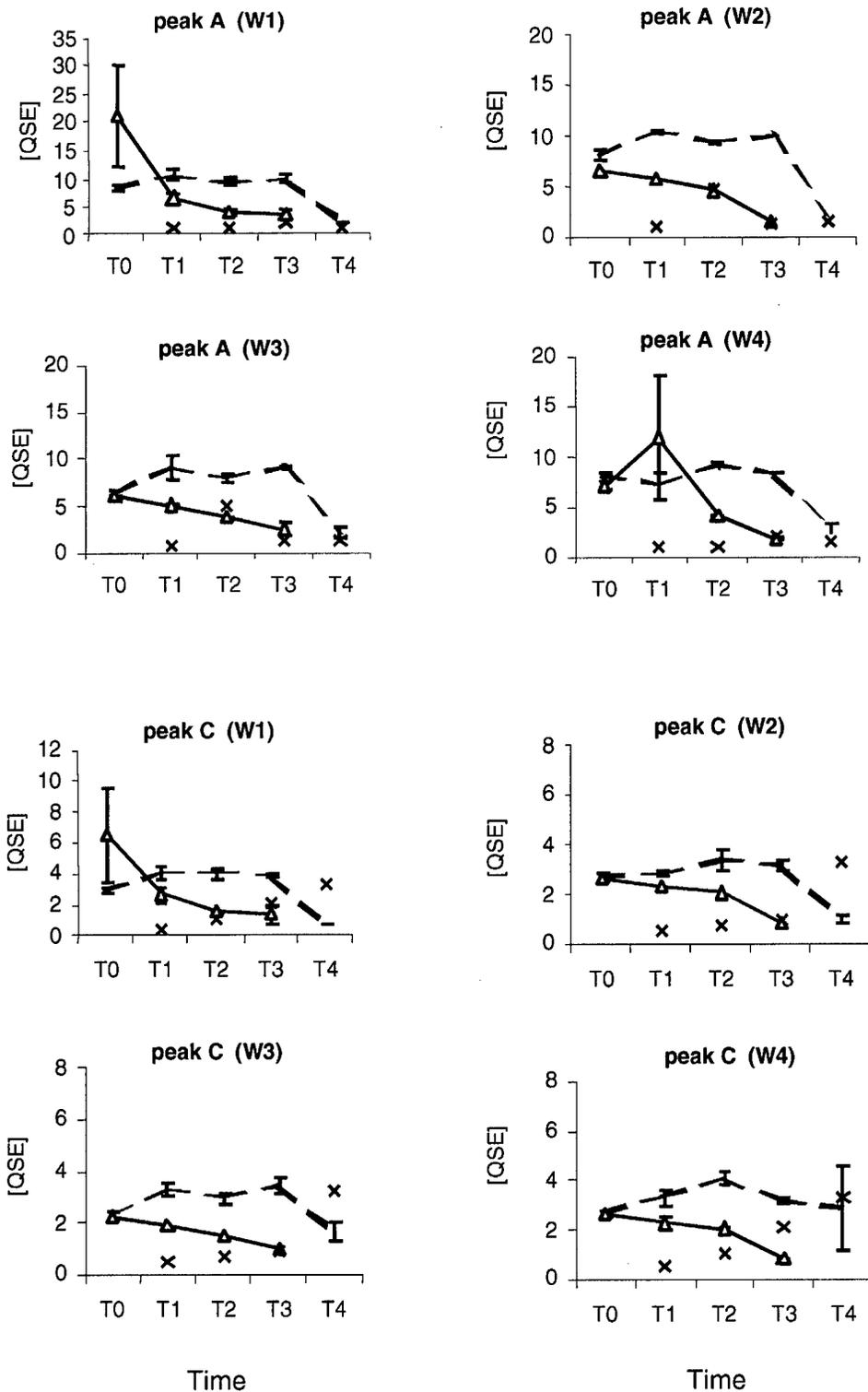


Figure 58. Fluorescence intensities of humic-like peak A and C in replicate ballast tanks (W1-W4) on the VFos cruise. Control Tank (---), Flow-Through Tank (-Δ-), Shiptside (X).

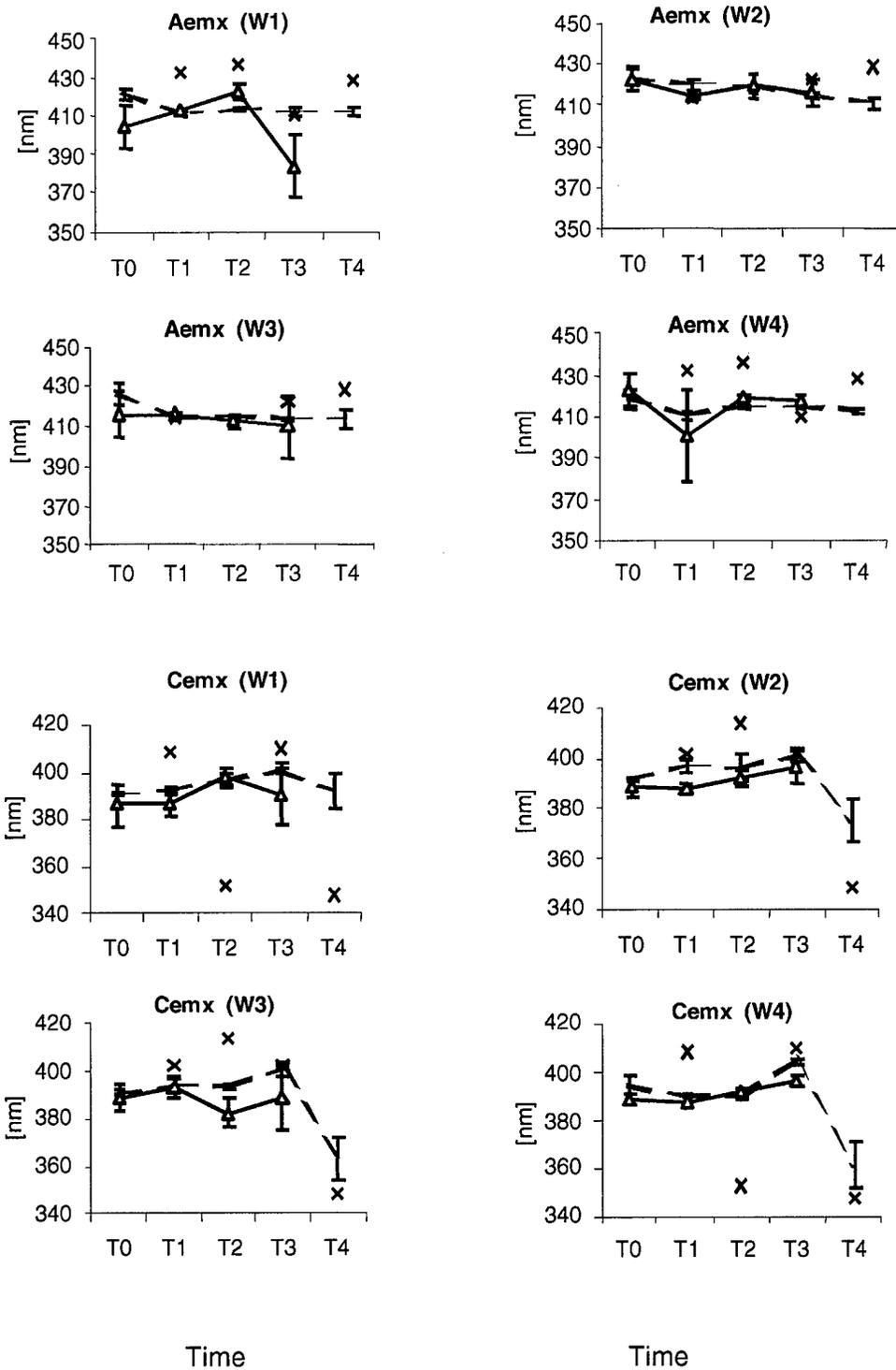


Figure 59. Emission wavelengths corresponding to humic peak A and C maxima in replicate tanks (W1-W4) on the VFos cruise. Control Tank (---), Flow-Through Tank (-Δ-), Shipside (X).

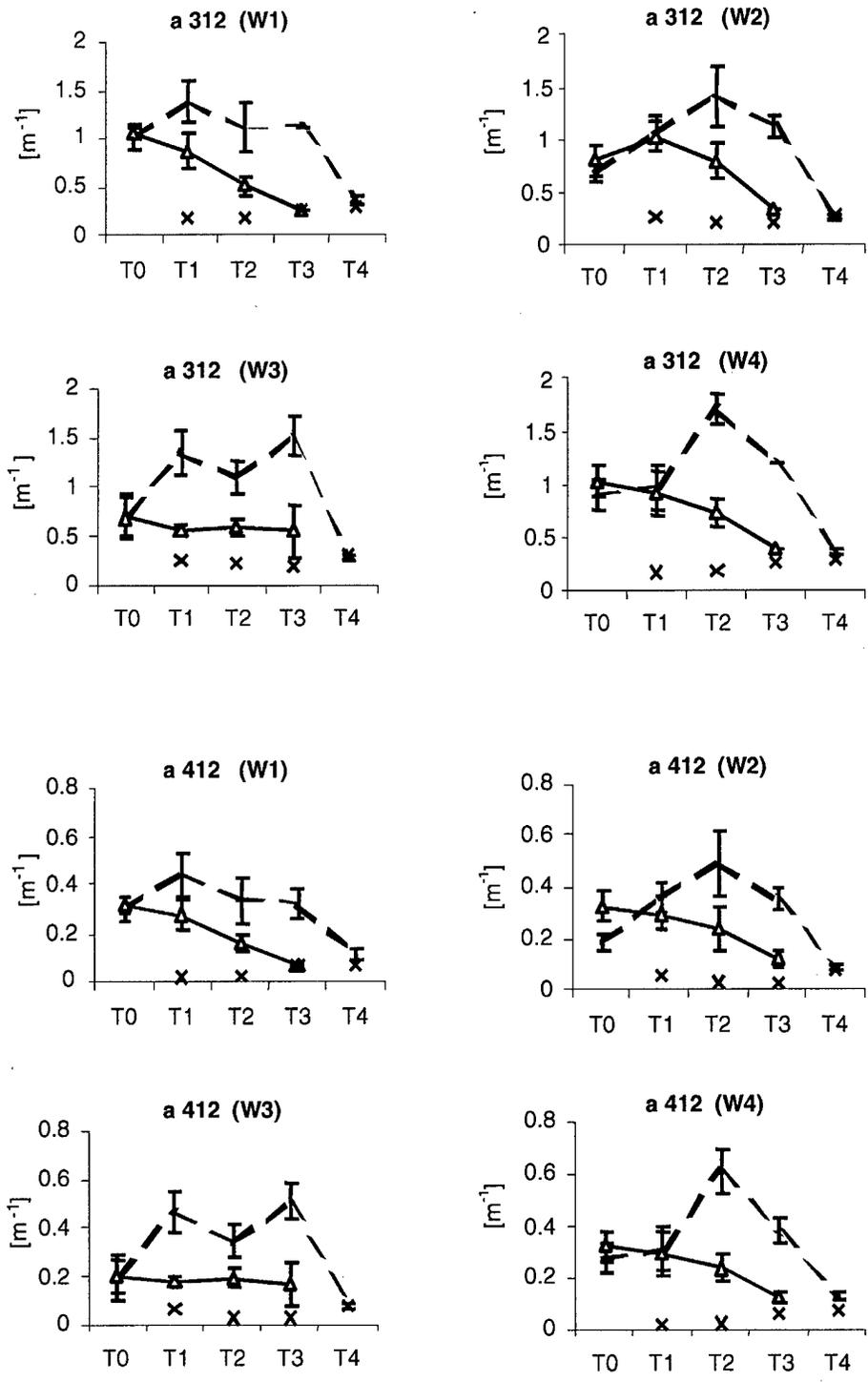


Figure 60. CDOM absorption coefficients at 312 nm and 412 nm in replicate ballast tanks (W1-W4) on the VFos cruise. Control Tank (---), Flow-Through Tank (Δ), Shippside (X).

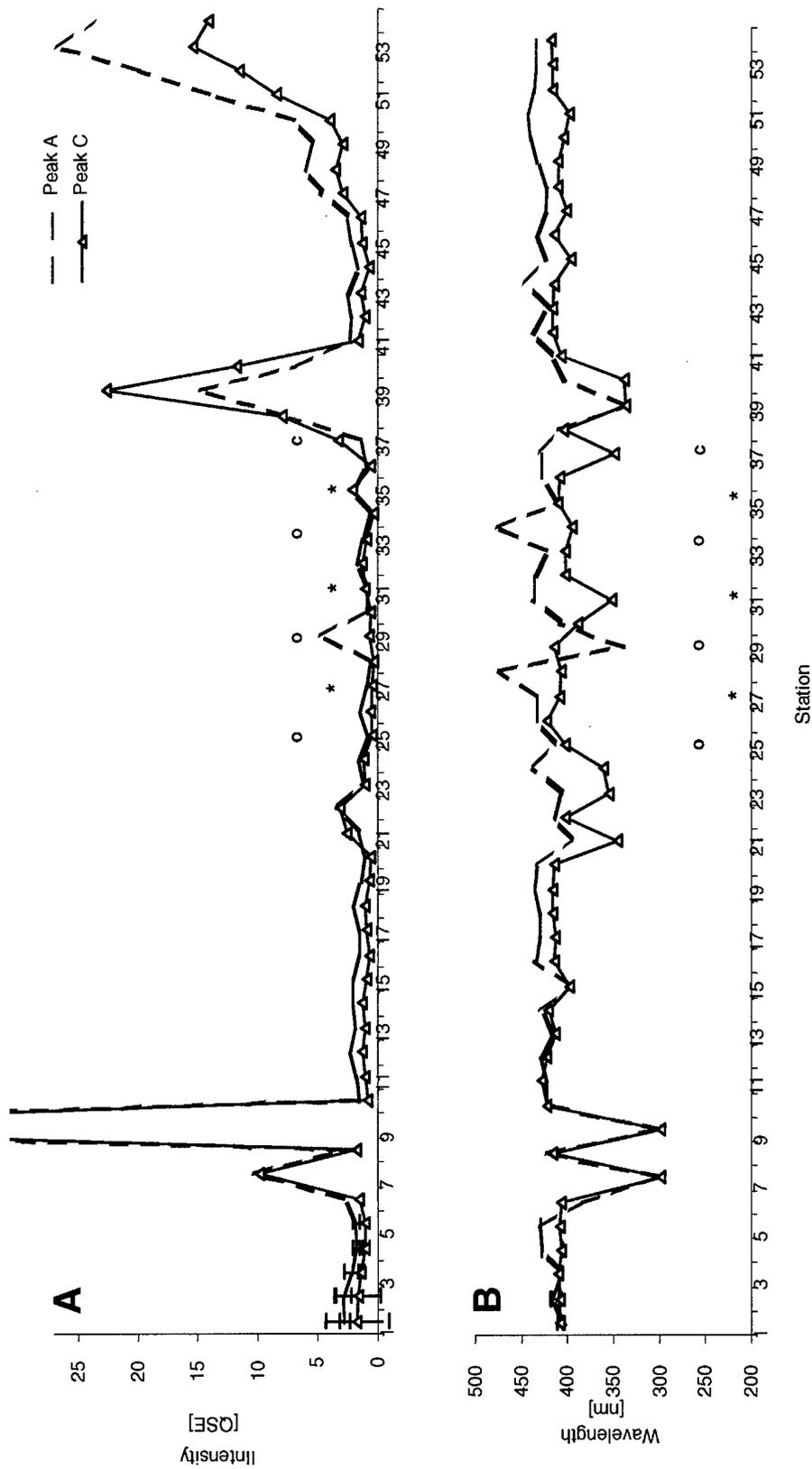


Figure 61. Fluorescence properties of shipside samples during VFos. Station 1 is Port of Fos Sur Mer. Station 54 is Port of Norfolk, V.A. **A.** Peak A and C intensity **B.** Emission maxima. Relative locations of ballast water exchanges indicated by symbols o (W2 & W3), * (W1 & W4) and c (all Control Tanks).

Several shipside samples (stations 7, 9, 21, 23, 24, 29, 31, 37, 39, 40) were contaminated in the region of the spectrum where CDOM fluorescence was expected. In contrast, the increase in peak A and C intensities observed in stations 46–54 reflect an increase in natural CDOM fluorescence as the ship moved closer to the eastern U.S. coast. Contaminated samples are indicated by anomalously high peak A and/or peak C intensities (Figure 61-A) coupled with short emission maxima wavelengths (Figure 61-B). For example, the high intensities assigned to humic peaks A and C for stations 37-40 are due to the interference of a combination of contaminants introduced previously. The EEMS for these stations indicate that the samples were affected by high levels of P1 and P2 (Station 37); P1 and P3 (Station 38); P2 (Station 39); P1, P2 and P3 (Station 40). While CDOM was almost certainly present in these samples, the CDOM peaks were overwhelmed by the portion of various contaminant peaks which overlapped their defined ranges. The vessel's cargo, coal, is one possible source of this contamination. Coal dust covered the deck at the beginning of the cruise until hosing down of the vessel was completed several days into the voyage. Unfortunately, little is known about the EEM spectral properties of coal. Since the same contamination peaks were observed occasionally in procedural blanks and in ballast water samples, a seawater source of the contaminant fluorescence peaks seems unlikely, unless lumps of coal became trapped in the sea-chest (water intake) or pipes. Instead, the source of the contamination may be the ship itself and/or the sampling apparatus/filter system.

To improve the interpretation of the CDOM peaks A and C in this data set, it would be necessary to revise their definitions to exclude excitation and emission wavelengths that overlap with contaminant excitation and emission wavelengths. In the VFos data set, the incidence of erroneous CDOM identifications would have been reduced by rejecting excitation wavelengths lower than 280 nm and emission wavelengths lower than 400 nm. Data at these higher excitation and emission wavelengths still displayed high initial intensities which decreased with successive ballast exchanges.

Since the source of the contaminants of the VFos cruise is uncertain, it is unclear whether this wavelength restriction is absolutely necessary for in-situ measurements. Depending on whether the contaminants originate from oils and other fluorophores released from the ship or are introduced by the sample collection/shipping/analysis process, in-situ devices may not encounter the same problem. That said, not all of the contaminants seen in in the VFos samples are likely to be artifacts of the sampling procedure; furthermore, it is expected that many ports and vessels are contaminated with a variety of fluorophores. The question of contaminants should be revisited before finalizing CDOM criteria for ballast exchange verification.

Radium

^{223}Ra in the Control Tanks increased by (40 or 50 percent) between the beginning and end of the voyage (Figure 62). In the exchanged tanks, ^{223}Ra decreased by approximately 87 percent following the final mid-ocean exchange. In initial samples, ^{223}Ra levels were more variable between tanks than between replicates within a tank (Figure 63).

Due to the length of the trip coupled with the short half-life of ^{224}Ra (3.7 days), only 5-6 percent of the source concentration of isotope ^{224}Ra remained at the end of the voyage. The very low final activity of ^{224}Ra and the presence of its parent, ^{228}Th , renders it an unreliable tracer on this voyage; consequently, these data will not be considered further.

For the final time-point samples, the concentrations of ^{226}Ra and ^{228}Ra were significantly lower in the exchanged tanks than in the unexchanged tanks (Figure 64). The same was true for both the $^{223}\text{Ra}/^{226}\text{Ra}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (A.R.) (Figure 65). Conversely, there was no difference between concentrations of $^{228}\text{thorium}$ in the exchanged and unexchanged tanks.

The significant increase over time of ^{223}Ra in the Control Tanks and its finite concentration in the exchanged tanks following a complete (i.e. Empty-Refill) mid-ocean exchange indicates the presence of a ^{223}Ra source within the tanks. This source is probably particulate matter having the parents of ^{223}Ra adsorbed to the surface. As the vessel was transporting coal, coal dust was certainly present in the ballast tanks. Coal is normally rich in uranium (U) and ^{223}Ra is produced in the decay chain of ^{235}U (Appendix C). It is likely that the coal dust was a source of ^{223}Ra on this voyage. Because the decay chain is broken at ^{231}Pa , U in seawater does not account for the presence of ^{223}Ra .

Since thorium (Th) is largely particle-bound in seawater, we had hoped to use ^{228}Th as a proxy of marine particulate matter that would produce ^{223}Ra . We expected the particulate matter and hence ^{228}Th to be higher in the tanks containing coastal water. The lack of variation in ^{228}Th between control and exchanged tanks is surprising. One would expect the Control Tanks containing coastal waters to have higher particulate and therefore higher ^{228}Th levels. The lack of variation in ^{228}Th is considered to be due to the cancellation of two effects: (1) the dissolved $^{228}\text{Th}/^{228}\text{Ra}$ A.R. in the coastal water was a factor of 2 lower than the A.R. in the open ocean, and (2) ^{228}Ra was a factor of 2 higher in the coastal water than in the open ocean. This means that ^{228}Th retained on the Mn fibers is not a reliable measure of ^{223}Ra production from particulates. Because coal does not contain high levels of thorium, ^{228}Th would not identify that source.

While there may have been real differences between initial ^{223}Ra levels in the different tanks despite their contents being sourced from the same location, some of this variation may also be attributable to flow meter inaccuracies. The flow meters employed for this experiment were operating at speeds within, but at the lower end, of their design specification range. From observations made while taking the initial samples, it was suspected that the flow meters might introduce as much as a 20 percent error in volume calculation. To eliminate this source of error, all of the final samples were taken after first standardizing the sample volumes using a plastic 55 gallon drum. This appeared to eliminate much of the between-tank variation evident in Figure 64.

With one exception, measurements from all of the samples were in good agreement. Sample #665 was the only sample which did not satisfy all of the 'oceanic' criteria defined in the model. This sample is considered an outlier (Dixon test: $r_{11} > r_{\text{crit}}$; $p < 0.06$) and was excluded from the analysis. It is suspected that a leak in the system while taking this sample may have caused significantly less than 200 liters of water to be filtered through the Mn fiber. This explanation is supported by the fact that although ^{228}Ra and ^{226}Ra were much lower than expected, the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio was similar to the other control samples. It should also be noted that the inclusion of data from this sample would have had no effect on the overall conclusions presented in this section.

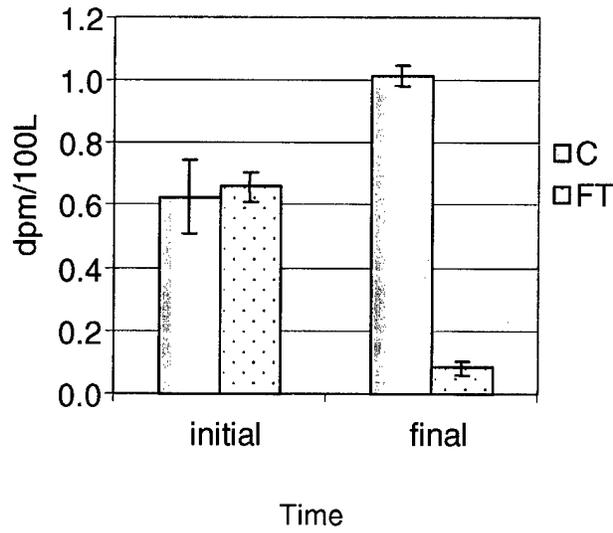


Figure 62. ²²³Ra concentrations in initial vs. final control (C) and Flow-Through (FT) samples, averaged across tanks (N=4) on the VFos cruise.

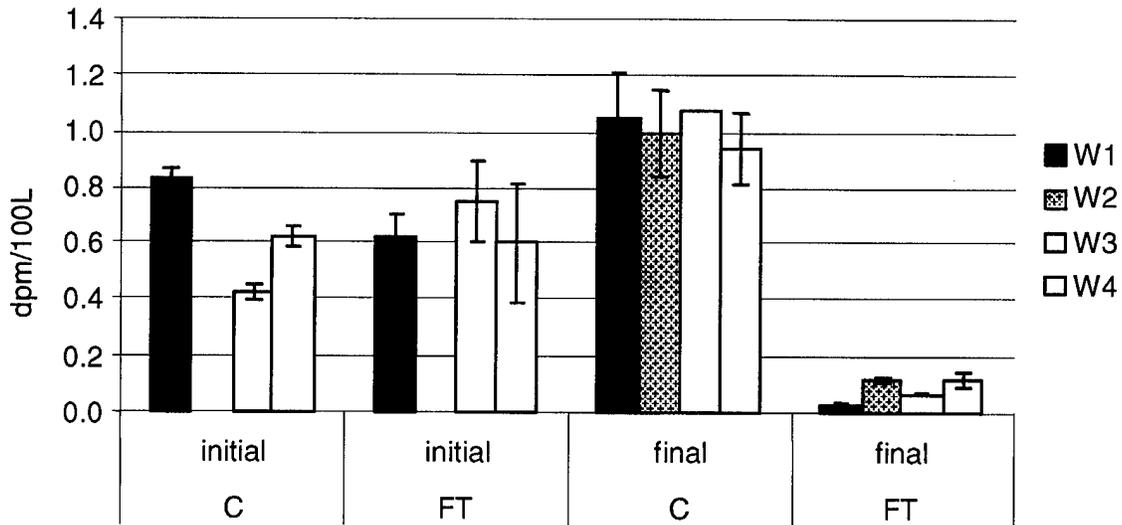


Figure 63. ²²³Ra concentrations in control (C) and Flow-Through (FT) samples from the beginning and end of the VFos cruise, averaged by tank (W1-W4, N=2). Initial (pre-exchange) samples were not collected from tank W2.

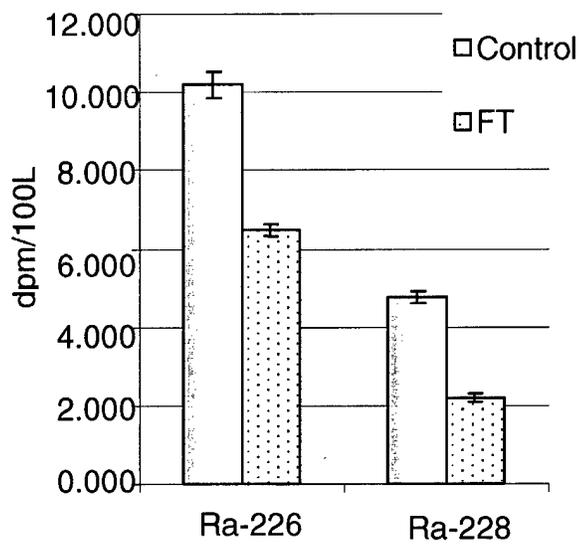


Figure 64. ²²⁶Ra and ²²⁸Ra concentrations in Control and Flow-Through (FT) final samples, averaged across tanks (N=4), following three exchanges of the FT tanks on the VFos cruise.

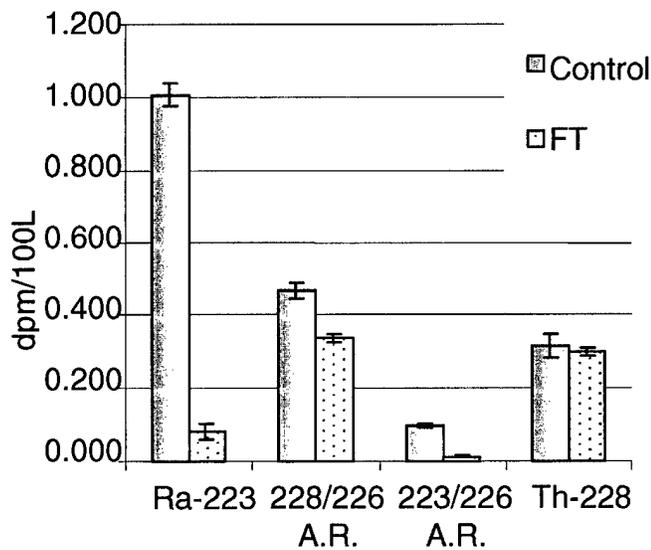


Figure 65. ²²³Ra, ²²⁸Th and activity ratios in Control and Flow-Through (FT) final samples, averaged across tanks (N=4), following three exchanges of the FT tanks on the VFos cruise.

4.1.5. Summary: Atlantic Voyage

Several tracers appeared useful for verifying ballast water exchange on the Atlantic voyage. These were trace metals, CDOM and radium. Turbidities differed by less than 1 NTU between exchanged and unexchanged tanks and appeared to depend as much on the timing of sampling as on whether an exchange had been performed. As a result, turbidity was not a useful verification tool on this voyage.

The trace metals P and Mn showed the greatest discrimination between exchanged and unexchanged tanks, although they were less stable in the Control Tanks than Ba, possibly as a result of release of these elements from sediments in the ballast tanks (p 78). Once again, Ba was the most reliable tracer on this voyage in terms of stability in the Control Tanks and resistance to contamination. This in part reflects the fact that Ba is a highly soluble element and tends to exist in solution rather than bound to sediments. Mo and U tracked salinity and consequently varied little between exchanged and unexchanged tanks and much of the shipside data set. V did not vary consistently between tanks nor between regions of the shipside data set.

The CDOM data for this cruise indicated that fluorescence intensity, and to a lesser extent absorbance, may be useful and sensitive tracers of ballast exchange. However, sample contamination was a problem in this and previous cruises and has serious implications for a fluorescence-based verification technique. In many cases, the presence of contaminants was clear upon reconciling peak excitation and emission wavelengths with fluorescence intensity information.

Despite high levels of PAH-like fluorescence in the original port water, possibly due to fuel oil or coal contamination, ballast water exchange was able to greatly reduce the fluorescence signal in the humic region of the fluorescence spectrum. Data from this cruise displayed a difference factor of roughly 3 between fluorescence intensities prior to and subsequent to full (300 percent FT or 100 percent ER) exchange. The absorbance data also showed an appreciable difference between pre-exchange samples versus those taken after the final exchange. Although the data were examined closely for any consistent migration of the position of the humic A and C emission maxima toward shorter wavelengths (i.e. "blue-shifting") in exchanged ballast tanks, this was not discerned even when obvious contamination outliers were removed. This may in part reflect that the CDOM signature of the highly oligotrophic Mediterranean Sea is already relatively blue-shifted relative to other coastal environments.

Radium was a strong tracer on the VFos cruise. ^{223}Ra levels were quite variable between tanks, possibly as a result of differing sediment loads (which continuously released ^{223}Ra into the surrounding water). Despite this variation, there was a more than tenfold difference in concentration of ^{223}Ra and a twelvefold difference in the $^{223}\text{Ra}/^{226}\text{Ra}$ Activity Ratio in the control vs. exchanged tanks at the end of the voyage.

5. Statistical Analyses

5.1. Overview

In the preceding sections of this report, a suite of potential tracers of ballast water exchange were analyzed independently for four experimental cruises. In this section, an attempt is made to draw together trends which emerged from all four cruises. In the first section of this chapter univariate analyses is used to summarize the performance of individual tracers in the Pacific and Atlantic data sets. In the second section, multivariate analyses is employed to investigate the degree to which information from different tracers can be combined to yield a robust set of parameters that together can discriminate between exchanged and unexchanged ballast water for each ocean and for the combined oceans.

In the absence of data which define end-member concentrations (i.e. samples from the original port water during ballasting and the ocean water at the position where ballast exchange occurred), two potential approaches to a ballast water exchange verification model were considered:

- Port-referenced: Ballast water samples taken from a vessel to assess compliance are compared with data from the original source water, and
- Ocean-referenced: Ballast water samples taken from a vessel to assess compliance are compared with data characterizing the ocean in which the alleged exchange was performed.

A model in the second category is preferred for two reasons. First, in comparison to coastal water, the deep ocean is a relatively stable environment within which less temporal and spatial variation in physical and chemical parameters would be expected. Second, reliably determining the source water of a ballasted tank may be very difficult, especially since in some cases the water may have been drawn from multiple ports over a long period of time.

For the statistical analyses, two questions need to be examined with reference to one or more potential tracers.

- Does the tracer set accurately discriminate between unexchanged, partially exchanged and fully exchanged ballast water?
- Can the tracers(s) be used to detect a vessel which exchanged ballast water in non-compliance with a > 200 mile/ > 2000 m depth ballast exchange requirement? In other words, if a complete ballast water exchange were performed less than 200 miles from the nearest coast, how close to

the coast might it be performed before it is possible to tell that it did not occur in fully oceanic water?

5.2. Univariate Analysis

A simple univariate model was used to assess the performance of individual tracers across all four cruises. Given a single variate Y_1 , it is possible to determine whether it differs from a reference ocean set with mean μ_0 . If the variance of the ocean set is σ , and if the variable is distributed normally, the test is:

$$Y_1 - \mu_0 / \sigma \quad \text{- Equation 1}$$

In this instance: Null Hypothesis, H_0 = No difference between ballast water sample and open ocean samples. Degrees of freedom, df = number of ocean observations - 1 (2 tailed)

Since a MANOVER test indicated the oceans were significantly different ($p < 0.001$), all cruises conducted in the Pacific were tested against the Pacific Ocean reference set, and the cruise conducted in the Atlantic was tested against the Atlantic Ocean reference set. Since each tracer is tested against a reference set, any tracer which does not have a reference (because shipside sample data do not exist in one or both oceans) cannot be tested. The following tracers have Pacific and Atlantic reference sets and are available for testing in both oceans: Salinity, peak A intensity (Aqse), peak A excitation maximum (Aexx), peak A emission maximum (Aemx), peak C intensity (Cqse), peak C excitation maximum (Cexx), peak C emission maximum (Cemx), Ba, Mn, Mo, P, V. In the Pacific Ocean, additional tests could be performed for ^{223}Ra and ^{228}Th . In the Atlantic Ocean, additional tests were performed for absorbance at 280 nm (a280), 312 nm (a312) and 412 nm (a412). Summary results of the univariate tests are tabulated in Appendix D.

For demonstration purposes, a portion of Appendix D is reproduced in Table 10; the remainder of the appendix can be interpreted in a similar manner. Consider the results for the FT tanks on Pacific voyages. Each tank from a particular cruise on a particular day is considered a single test case. The numbers in the table are a tally of the number of test results which correspond with a particular tracer at a specified probability level. If the mean value of a tracer from a tank is found to be significantly different from the ocean set, this occurrence is tallied next to the corresponding probability statistic (either $p < 0.05$, $p < 0.01$ or $p < 0.001$). If the mean value of a tracer from a tank is found to be not significantly different to the ocean set, this occurrence is indicated next to the abbreviation "nsd."

For tanks containing untreated port water (i.e. all Control Tanks and all treatment tanks at time T0), a successful tracer will show a **highly significant** result ($p < 0.01$). A tracer which does not show a significant result has allowed a Type II error; in other words, acceptance of the false null hypothesis of no difference between open ocean water and unexchanged ballast water. For VSF in Table 10, CDOM peak A intensity, all trace metals (Ba, Mn, Mo, P, V), salinity, Ra and Th each successfully discriminated untreated port water from ocean water. Conversely, Type II errors occurred at T0 for CDOM peaks A and C excitation and emission maxima and peak C intensity.

For tanks which have undergone a complete exchange (i.e. three FT exchanges or 1 or more ER exchanges), a successful tracer will show a **nonsignificant** result ($p > 0.05$). A tracer which shows a significant result has allowed a Type I error; in other words, rejection of the true null hypothesis of no difference between ocean water and exchanged ballast water. On VLA, all tracers tested show nonsignificant results after three FT exchanges (T2). A Type I error occurs for Ba after three FT exchanges on VSF (T3), indicating that even a "fully" exchanged ballast tank retained a significantly coastal character.

For tanks which have undergone partial exchange (i.e. less than three FT exchanges), a sensitive tracer will show a **moderately significant** result ($p < 0.05$). As progressively more ocean water is added to a tank, samples from the tank should look progressively less different from the ocean. This progression is seen most clearly for Barium on VSF. The p-statistic increases from $p < 0.001$ to $p < 0.01$ to $p < 0.05$ after successive FT exchanges.

Overall on the Pacific voyages, most CDOM measures were unable to distinguish unexchanged or exchanged ballast water from oceanic water, with the occasional exception of peak A intensity. However, the small number of viable oceanic samples comprising the ocean reference set certainly contributed to this result. The trace metals Ba, Mn and P most often discriminated unexchanged treatments from the ocean set, and on some occasions (particularly for VSF), also discriminated partially exchanged tanks. Salinity was a good discriminator on the VSF and VPS cruises, but not on VLA. On the cruises where Radium samples were collected (VSF, VLA), ^{223}Ra and ^{228}Th were powerful univariate tracers, despite low sample replication.

Overall on the Atlantic voyage, CDOM peak A and C intensities were useful measures for identifying unexchanged but not partially exchanged ballast tanks. Salinity, Ba, Mn and P were good univariate

discriminators for unexchanged and partially exchanged tanks, although even fully exchanged ballast tanks sometimes appeared significantly different from the ocean set when using these tracers.

Table 10. Summary of univariate analyses for all FT tanks on Pacific Ocean cruises.

Treat	FT	Time	Probability	A _{qse}	A _{exx}	A _{emx}	C _{qse}	C _{exx}	C _{emx}	Ba	Mn	Mo	P	V	Salinity	²²⁸ Ra	²²⁸ Th	Total	
VLA	T0		0.001													1		1	
			0.01							1									1
			0.05								1				1			1	3
		nsd	1	1	1	1	1	1	1			1	1					9	
	T1		0.05														1		1
			nsd	1	1	1	1	1	1	1	1	1	1	1	1	1			13
			nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	14
	VSF	T0		0.001															8
				0.05	1														
			nsd		1	1	1	1	1	1									5
T1			0.001																1
			0.01								1	1	1	1	1	1	1	1	7
			0.01								1								1
T2			0.05																4
			nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	9
			0.05																1
T3		nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	13	
		nsd																	

5.3. Multivariate Analysis

A model is proposed which compares the multivariate distribution of discriminating tracers in a ballast tank with the multivariate distribution of the same tracers in the open ocean using the Mahalanobis distance statistic (Johnson and Wichern, 1982). The method assumes that the constituents of seawater have a multivariate normal distribution. For any individual sample (whether from a ship's ballast tank or from the ambient water along its journey), the likelihood that it falls within the usual range of ocean water is estimated by calculating the distance statistic for a defined vector of tracers. If the likelihood is small, then one must infer that the ballast tank contents were not derived from ocean water.

Implementation of this method entails a sequence of steps:

- Formulate a list of q potentially discriminating tracers.
- For this list of tracers, compile a data base of measurements from ocean water.
- Using this data base, estimate the mean and variance-covariance structure of these tracers in ocean water.
- For each tracer used in the method, verify that it is reasonable to use the multivariate normal distribution to approximate the frequency distribution of this tracer. If the tracer as measured does not appear normal in distribution, some transformation of the raw data may yield an approximately normal distribution.
- For a vector of tracer measurements taken from a ballast water tank, compute the Mahalanobis distance statistic, D , between the observed tracer vector and the mean tracer vector for ocean water. The square of Mahalanobis distance follows a chi-square distribution with q degrees of freedom which allows for the computation of the likelihood that the ballast water tracers come from ocean water.

This multivariate test has the potential to be much more powerful than a sequence of univariate tests when the tracers are correlated. Consider a two dimensional example (Figure 66). Let the abscissa and ordinate of the graph represent two correlated tracers. Let "o" represent ocean water observations and "X" represent a test observation. The "+" symbols define an ellipsoid that contains all of the ocean water observations "o". The box outlined by the dots is formed by the maximum and minimum tracer coordinates of all the points. Clearly when their coordinates are projected onto the two axes, each observation falls within the box.

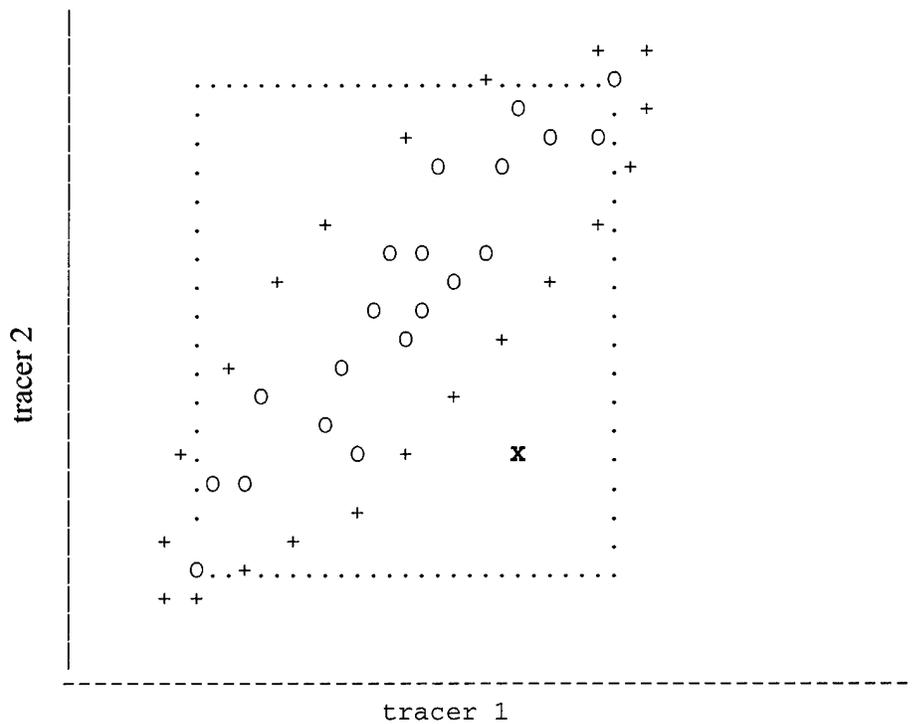


Figure 66. Multivariate model example.

In the example, it is clear that \mathbf{X} is well within the normal range of tracer 1 and tracer 2, as would be any observation within the box formed by the dots. However, when viewed in two dimensions, \mathbf{X} falls outside of the ellipsoid bounding the ocean observations.

The square of the Mahalanobis distance statistic between the sample tracer vector and the mean oceanic tracer vector is computed as

$$(\mathbf{x}_i - \mathbf{x})' \mathbf{S}^{-1} (\mathbf{x}_i - \mathbf{x})$$

- Equation 2

where \mathbf{x}_i is a column vector of tracers that are being tested, \mathbf{x} is the column vector of the mean level of tracers in ocean water, and \mathbf{S}^{-1} is the inverse of the variance-covariance matrix for the tracers in ocean water.

While multivariate analysis can be more powerful than a series of univariate hypothesis tests, the opposite can also be true if some of the tracers are not informative about differentiating ocean water from coastal water. A noninformative tracer would add more noise than signal to the Mahalanobis distance measure and thus would weaken the signal to noise ratio. One of the challenges of using this technique will be to define the best possible minimum tracer set, i.e. the set which contributes the maximum amount of information and minimum amount of noise to the analysis.

As was done for the univariate analysis, the Mahalanobis tests were performed only on tracers for which there is an ocean reference set (see page 102 for a list of available tracers). Note that contaminated CDOM stations (stations 7, 9, 21, 23, 24, 29, 31, 37, 39, 40) were removed from the data set prior to analysis (the justification for this is discussed in detail in section 4.1.4). Summary results of the Mahalanobis tests are tabulated in Appendix E.

For demonstration purposes, the summary tables for the shipside samples on the Atlantic cruise are reproduced in Table 11. These results directly address the question of whether it would be possible to detect that a ballast water exchange was performed less than 200 miles from a coastline. Each shipside station is considered a single test case. The numbers in the table represent the Mahalanobis distance probability (either $p = 1$, $p < 0.1$, $p < 0.05$, $p < 0.01$ or $p < 0.001$) that the samples from the station were drawn from water which was significantly different from the open ocean. For clarity, all results greater than $p = 0.1$ are indicated by '1's (indicating a non-significant distance statistic). The second last column represents the distance (in nautical miles) between the station and the nearest coastal reference point (the Cape of St Vincent in Spain for the eastern Atlantic stations, and the port of Norfolk for the western Atlantic stations). The last column shows ocean depth in meters.

For "coastal" shipside samples, that is, samples collected within 200 miles of the Mediterranean or US coast (all stations that are not highlighted in the table), a successful tracer will show a **significant** result. A tracer which does not show a significant result has allowed a Type II error, in other words, acceptance of the false null hypothesis of no difference between open ocean water and the "coastal" water from that station.

For "oceanic" shipside samples, that is, samples collected beyond 200 miles from the Mediterranean or US coast (all highlighted stations in the table), a successful tracer will show a **non-significant** result. A

tracer which shows a significant result has allowed a Type I error, in other words, rejection of the true null hypothesis of no difference between open ocean water and the "oceanic" water from that station.

Table 11. Mahalanobis distance probabilities for the Atlantic shipside samples.

SS	Sal	SalBa	SalBaMn	SalMoBaMn	SalMoBaPMn	SalMoBaUP VMn	SalAqseCqse a312a412	distance offshore (miles)	ocean depth (m)
1	0.05	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-1
2	0.05	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-1
3	1	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-16
4	1	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-16
5	0.05	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-92
6	0.001	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-1866
7	0.001	0.001	0.001	0.001	0.001	0.001	nd	< 60	-1764
8	0.05	0.05	0.001	0.001	0.001	0.001	0.001	< 60	-1764
9	0.05	0.001	0.001	0.001	0.001	0.001	nd	< 60	-1764
10	0.05	0.01	0.001	0.001	0.001	0.001	0.001	< 60	-1764
11	0.05	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-1764
12	0.05	0.05	0.001	0.001	0.001	0.001	0.001	< 60	-1610
13	0.001	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-1610
14	0.05	0.01	0.001	0.001	0.001	0.001	0.001	< 60	-613
15	0.05	0.001	0.001	0.001	0.001	0.001	0.001	< 60	-990
16	0.1	1	0.05	0.05	0.01	0.001	0.01	< 60	-929
17	1	1	0.05	0.05	0.001	0.001	0.1	< 60	-1139
18	1	1	0.001	0.001	0.001	0.001	0.001	< 60	-1139
19	1	1	1	0.1	0.05	0.001	0.1	< 60	-455
20	1	1	1	0.1	1	0.05	1	70.8	-2106
21	1	1	1	0.1	0.1	0.05	nd	70.8	-2106
22	0.1	1	0.001	0.001	0.001	0.001	0.001	63.2	-4175
23	1	1	1	1	1	1	nd	100.5	-4853
24	1	0.1	1	1	1	1	nd	244.5	-4521
25	1	1	1	1	1	1	1	395.9	-4959
26	1	1	1	1	1	1	1	> 400	-4959
27	1	1	1	1	1	1	1	> 400	-3715
28	1	1	1	1	1	1	1	> 400	-3406
29	1	1	1	1	1	1	nd	> 400	-3258
30	1	1	1	1	1	1	1	> 400	-2385
31	1	1	1	1	1	1	nd	> 400	-3805
32	1	1	1	1	1	1	1	> 400	-4318
33	1	1	1	1	1	1	1	> 400	-5081
34	1	1	1	1	1	1	1	> 400	-5430
35	1	1	1	1	1	1	1	> 400	-5156
36	0.05	0.05	0.1	1	1	1	1	> 400	-5312
37	1	1	1	1	1	1	nd	> 400	-4986
38	1	1	1	1	1	1	1	343.9	-4536
39	1	1	0.05	0.05	0.05	0.01	nd	188.8	-3239
40	1	0.1	0.001	0.001	0.001	0.001	nd	173.0	-3120
41	1	0.05	0.001	0.001	0.001	0.001	0.001	159.5	-3098
42	0.05	0.001	0.001	0.001	0.001	0.001	0.001	142.1	-2897
43	0.05	0.05	0.001	0.001	0.001	0.001	0.001	130.8	-2722
44	0.05	0.05	0.001	0.001	0.001	0.001	0.001	116.4	-2497
45	0.05	0.05	0.001	0.001	0.001	0.001	0.001	100.6	-2001
46	0.05	0.01	0.001	0.001	0.001	0.001	0.001	85.6	-101
47	0.001	0.001	0.001	0.001	0.001	0.001	0.001	71.6	-42
48	0.001	0.001	0.001	0.001	0.001	0.001	0.001	56.0	-39
49	0.001	0.001	0.001	0.001	0.001	0.001	0.001	39.3	-23
50	0.001	0.001	0.001	0.001	0.001	0.001	0.001	27.8	-15
51	0.001	0.001	0.001	0.001	0.001	0.001	0.001	19.7	-19
52	0.001	0.001	0.001	0.001	0.001	0.001	0.001	8.5	-5
53	0.001	0.001	0.001	0.001	0.001	0.001	0.001	1.1	-1
54	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.0	-1

nd = no data for one or more tracers in test set

The power of the multivariate analysis is demonstrated by comparing the effect of adding tracers to a base reference set which uses only salinity. Whereas salinity is an effective tracer only sporadically in the Mediterranean and eastern Atlantic, adding to the set increases the geographic discrimination for the Mediterranean and U.S. coasts and reduces the likelihood of Type II errors (by reducing the probability statistics in the table). Addition of Mn to the reference set further improves the resolution, and eliminates the Type I error for the Salinity / Ba combination at station 36. The most successful combination combines salinity with all six trace metals (Mo, Ba, Mn, U, P, V). This set correctly identifies the coastal vs. noncoastal origin of all but one station (station 39). It is not possible to fully assess the efficacy of combinations involving CDOM, due to the absence of test data at the ten stations which were contaminated. However, the combination shown of salinity with peak A and C intensity and absorbance at 312 nm and 412 nm can be seen to begin losing sensitivity around station 16 while still in the Mediterranean Sea and generates type 2 errors at for stations 17, 19 and 20, all of which are within 71 miles of the coast of Spain. Overall, combining salinity with all six trace metals provides the most discrimination.

Tables 12 and 13 address the question of whether it is possible to discriminate between exchanged and unexchanged ballast tanks. The effect of exchange is illustrated by comparing the probability statistic of tanks which have not undergone exchange with tanks which have. The highlighted rows represent fully compliant (i.e. 300 percent FT or 100 percent ER exchanged) ballast tanks. The first thing to note is that even tanks that have undergone complete ballast water exchange are usually significantly different from the ocean. In the case of VFos (Table 12), all of the tracer combinations in the table detected significant differences for all tanks at all times. However, the higher p-values for the exchanged tanks (highlighted) indicate that they are less different from the ocean than the unexchanged tanks. In the case of VSF (Table 13), the tracer set of salinity, Ba and Mn indicates the tank which underwent three FT exchanges was still significantly different from the ocean (a Type I error), whereas the tank subjected to a single ER exchange was not.

The high rate of Type I errors in Tables 12 and 13 is not a failing of the statistical technique but a reflection of its high sensitivity. This raises two important points: First, ballast water exchange will never remove all coastal elements, consequently, there will be a greater number of Type I errors than would be based on theory.

Table 12. Mahalanobis distance probabilities for Atlantic tank samples.

Cruise	Tank	Time	Treatment	Sal	SalBa	SalBaMn	SalBaMn Aqse	SalMoBa PMn	SalMoBaP MnAqse	SalMoBaUPV MnAqse Cqse
VFos	W1	T0	C	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T0	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T0	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T0	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T1	C	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T1	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T1	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T1	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T2	C	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T2	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T2	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T2	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T3	C	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T3	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T3	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T3	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T4	E	0.05	0.05	0.001	0.001	0.001	0.001	0.001
VFos	W2	T4	E	0.05	0.05	0.05	0.05	0.05	0.05	0.01
VFos	W3	T4	E	0.05	0.05	0.05	0.05	0.01	0.01	0.001
VFos	W4	T4	E	0.05	0.05	0.05	0.05	0.05	0.05	0.001
VFos	W1	T0	FT	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T0	FT	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T0	FT	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T0	FT	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T1	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W2	T1	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W3	T1	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W4	T1	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T2	FT	0.05	0.05	0.001	0.001	0.001	0.001	0.001
VFos	W2	T2	FT	0.05	0.01	0.001	0.001	0.001	0.001	0.001
VFos	W3	T2	FT	0.05	0.05	0.05	0.05	0.05	0.05	0.001
VFos	W4	T2	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VFos	W1	T3	FT	0.05	0.05	0.001	0.001	0.001	0.001	0.001
VFos	W2	T3	FT	0.05	0.05	0.05	0.05	0.05	0.05	0.001
VFos	W3	T3	FT	0.05	0.05	0.05	0.05	0.05	0.05	0.01
VFos	W4	T3	FT	0.05	0.05	0.05	0.01	0.01	0.01	0.001

Table 13. Mahalanobis distance probabilities for Pacific tank samples, Voyage VSF.

Cruise	Time	Treatment	Sal	SalBa	SalBaMn	SalMoBaMn	SalMoBaPMn	SalMoBaUP VMn	SalCemxCqse
VSF	T0	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T1	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T2	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T3	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T0	FT	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T1	FT	0.001	0.001	0.001	0.001	0.001	0.001	nd
VSF	T2	FT	0.05	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T3	FT	0.1	0.001	0.001	0.001	0.001	0.001	0.01
VSF	T0	ER	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VSF	T1	ER	1	1	1	0.05	0.05	0.05	0.1
VSF	T3	ER	1	1	1	0.01	0.001	0.001	1
VLA	T0	C	1	0.001	0.001	0.001	0.001	0.001	1
VLA	T1	C	1	0.001	0.001	0.001	0.001	0.001	1
VLA	T2	C	1	0.001	0.001	0.001	0.001	0.001	nd
VLA	T0	FT	1	0.001	0.001	0.001	0.001	0.001	1
VLA	T1	FT	1	0.1	0.05	0.05	0.01	0.01	0.05
VLA	T2	FT	1	1	0.1	1	0.1	0.1	0.01
VPS	T0	C	0.001	0.001	0.001	0.001	0.001	0.001	0.001
VPS	T1	C	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VPS	T0	ER	0.01	0.001	0.001	0.001	0.001	0.001	0.001
VPS	T1	ER	1	1	0.01	0.001	0.001	0.001	0.05

nd = no data for one or more tracers in test set

Second, a ballast tank itself may potentially alter the chemistry of certain tracers in a way which sets them apart from water which has not entered a ballast tank. The occurrence of Type 1 errors was lower for the Pacific cruises (Table 13) because we tested against a smaller and more temporally variable ocean reference set.

Fortunately, it is fairly simple to decrease the rate of Type 1 errors in the statistical tests. If the variability of the ocean reference set is artificially increased, more exchanged tanks will fall within the expanded ocean range. The most simple way to accomplish this would be to increase the size of the variance-covariance matrix (S) in Equation 1, by multiplying it by an expansion constant, k , with $k > 1$.

The square of the Mahalanobis distance statistic is then computed as:

$$(\mathbf{x}_i - \mathbf{x})' (\mathbf{kS})^{-1} (\mathbf{x}_i - \mathbf{x})$$

- Equation 3

where \mathbf{x}_i is a column vector of tracers that is being tested, \mathbf{x} is the column vector of the mean level of tracers in ocean water, \mathbf{S} is the variance-covariance matrix for the tracers in ocean water and \mathbf{k} is an expansion constant accounting for incomplete ballast exchange and tank effects.

The appropriate value for \mathbf{k} cannot be determined at this time, since it ultimately must depend on a performance criterion (e.g. a water quality standard) rather than a process requirement (e.g. 300 percent Flow-Through exchange). In the absence of such a standard, comparing the statistical results for a range of \mathbf{k} may help move toward a performance criterion by indicating what degree of ballast exchange efficiency should be considered to be in compliance with ballast exchange regulations. Tests for normality performed on the tracer data are inconclusive because of the small sample size ($N \leq 15$ for the Atlantic, $N \leq 10$ for the Pacific). However, it is considered that most or all of the tracers targeted in this study behave in a conservative manner and are normally distributed in the ocean. Expansion of the ocean reference sets with additional data from the Pacific and Atlantic Oceans will resolve this question.

It is anticipated that the addition of new data to the ocean reference sets will have two opposite effects on the statistical analyses. The first effect is an increase in the variance of the ocean set, leading to less sensitive statistical tests (i.e. a increase in the rate of Type II errors and a decrease in the rate of Type I errors). The second effect, likely to dominate only after N becomes sufficiently large (> 100) to reliably characterize the ocean is a reduction in the overall ocean variance, leading to more sensitive statistical tests (decreasing the rate of Type II errors and increasing the rate of Type I errors). A reliable verification program would need to respond to these shifts as more data become available.

5.4. Classification Trees

An alternative framework for a ballast water verification program from one based on simultaneous measurement of multiple tracers is to conduct the analyses sequentially and flexibly according to a classification tree system (Breiman *et al.* 1984). Classification trees are widely used in applied fields including medicine (diagnosis), computer science (data structures), botany (classification), and psychology (decision theory) to explain responses on a categorical dependent variable.

The radium analysis scheme in Figure 67 conceptually illustrates a classification tree for BWE verification. Based on the results of a salinity test, a decision is made about appropriate subsequent tests. If a ballast tank is found to fail the salinity criterion of > 30 ppt, it is automatically deemed to fail the entire test, precluding the need for further more expensive testing. If, however, it passes this test, compliance is undetermined until further results are examined.

Based upon the data currently available, it appears likely that radium in combination with salinity could be used to determine compliance using a decision tree system as was presented in the Workshop Report (Appendix A, Figure A-1). Several revisions to the original radium verification model are proposed (Figure 67).

- To accommodate the event that coal dust will increase ^{223}Ra levels, the lower limit of ^{223}Ra should be raised to 0.3 dpm/100 liters.
- To accommodate the lower than expected activity of ^{228}Ra in ports of the Mediterranean Sea, the coastal ^{228}Ra threshold should be lowered to 4 dpm/100 liters and the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio lowered to 0.4. This introduces a slight overlap in the acceptable ranges of the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios for coastal and oceanic water.

If the verification scheme of Figure 67 were applied to the VSF, VLA or VFos cruise data, the exchange process would be verified on the second tier of the scheme, precluding the necessity for analysis of long-lived radium isotopes. For VFos, with the exception of the $^{228}\text{Ra}/^{226}\text{Ra}$ A.R. which was relatively low for the control samples, each of the third tier criteria would also have unambiguously distinguished between the unexchanged and exchanged ballast tanks during this cruise.

Although additional data are clearly needed to test the robustness of radium (as well as other variables) as a diagnostic measure of oceanic ballast water, this provides a useful example of how a classification tree based upon this data may quickly resolve whether BWE has occurred. One of the advantages of a

classification tree is that the hierarchical scheme readily lends itself to graphical display, making it more intuitive and easier to interpret than a strictly numerical process. It is also possible to hybridize between a numerical classification tree framework and a numerical framework, so that, for example, a more costly multivariate analysis is performed only on the second or third tier of the tree after cheaper and/or in-situ options are exhausted.

While it may be appropriate to apply a pure decision tree framework to a verification scheme, data available at this time are insufficient for determining how such a tree should be structured to maximize discrimination. However, it may be worth re-exploring this avenue as more data become available.

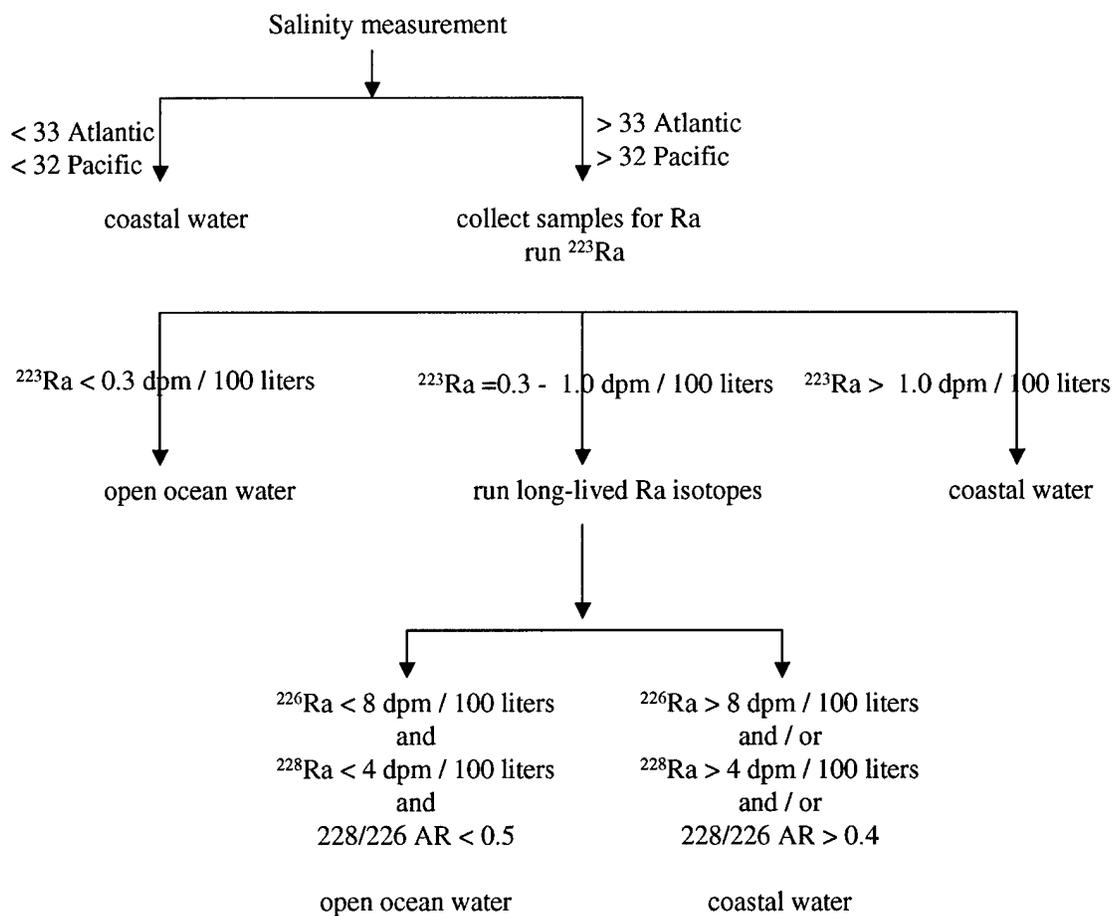


Figure 67. Proposed Radium Verification Scheme. This figure is based on figure A-1 in Appendix A but has been modified in light of Ra data from Mediterranean Sea samples from this study. (dpm=disintegrations per minute; AR=activity ratio).

6. Summary

The overall goal of this research was to test the potential of various chemical and biological attributes to be used, singly or in combination, to discriminate (a) whether ships exchange their ballast water in open ocean and (b) the extent to which ships' ballast water was exchanged. Since ships are asked to conduct exchange in the open ocean (> 200 miles from shore and > 2000 m depth), a suite of characteristics was tested to determine whether coastal water could be discerned from oceanic water within actual ballast tanks (which may include contaminants that decrease such resolution).

The analyses were intended as a proof of concept for an approach to verification of ballast water exchange. An exhaustive analysis to test the full resolution of these measures, across all ocean basins and seasons, was clearly beyond the scope of this study. The study sought to demonstrate the potential of particular measures, which should be tested more fully and for which appropriate instrumentation could be advanced simultaneously.

Experiments conducted on four commercial vessels in two oceans indicated that several tracers can be used in conjunction with salinity to discriminate between exchanged and unexchanged ballast tanks. These included:

1. Concentrations of up to six metallic elements (Ba, P, Mn, Mo, U, V);
2. The intensity of two CDOM fluorescence peaks (humic substances "A" and "C") and absorbance at 280 nm, 312 nm and 412 nm;
3. Concentration of a short-lived isotope of Radium (^{223}Ra) combined where necessary with measurements of two long-lived isotopes (^{226}Ra , ^{228}Ra).

Conversely, the data indicated that neither turbidity nor phytoplankton salinity tolerance was successful at verifying ballast water exchange.

Details associated with each of the tracers that showed particular promise in verification of ballast water exchange are discussed below. Additionally, some issues that deserve attention are highlighted and specific recommendations for future research in this area are provided.

Trace Metals

Trace metals (particularly Ba, P, and Mn) were highly successful as quantitative measures to verify ballast water exchange. This result was counter to the a priori expectation expressed by some researchers, who considered contamination of trace metals from the ships would compromise all such measures. Instead, a limited number of metals performed remarkably well in both univariate and multivariate analyses. Furthermore, since analysis of a single sample can simultaneously provide concentrations of many different trace metals, sample collection and analysis is relatively simple.

A potential drawback with trace metals, at least in the current analysis, is that concentrations were not measured in-situ. Samples were collected and sent to the laboratory for analyses. The capacity for in-situ measures or whether an alternate strategy exists to expedite metals analyses has not been explored.

CDOM

The results of the experiments and statistical analyses for cruises from high salinity ports (VLA, VPS and VFos) in this study indicate that CDOM contributes significant information to the description of ballast water. It is as yet unclear whether CDOM measures alone will be powerful enough to consistently discriminate between open ocean water and oligotrophic high salinity coastal water.

Although CDOM has the potential for in-situ measurement, the in-situ devices (salinity, turbidity and CDOM fluorescence) tested in the VLA, VSF and VFos experiments presented a number of technical and interpretive hurdles during this study. The CDOM fluorescence intensities measured by the CDOM Flash Lamp could not be compared directly with the CDOM EEMs measurements due to incorrect factory specifications coupled with the presence of rhodamine dye in the ballast tanks during deployment.

The experiments of this project suggest two possible avenues for in-situ CDOM fluorometers. CDOM fluorometers on the market today, including the Wetlabs FlashLamp used in this study, tend to use relatively broad band CDOM filters and record maximum fluorescence intensity on a single channel. If the contamination events seen in the multispectral CDOM analyses during this project (which generally occurred at low UV excitation [230 - 280 nm] and emission [275 - 400 nm]) are not purely due to the sample collection process, this would suggest that an in-situ fluorometer suited to verification should use multiple channels (> 5) to monitor selected excitation and emission wavelength pairs above 400 nm.

Since the use of multiple channels would greatly increase the complexity and cost of the instrument, an alternative would be to modify an existing single channel instrument so that it monitors only in the region of the humic C peak, which although less intense than the humic A peak, was much less subject to contamination interference during this study.

Radium

^{223}Ra was the most sensitive indicator of the source of ballast water on all voyages where it was measured (VSF, VLA and VFos). The long-lived isotopes ^{226}Ra and ^{228}Ra were sensitive indicators, as were the ratios of various isotopes, in particular the $^{223}\text{Ra} / ^{228}\text{Ra}$ Activity Ratio. ^{224}Ra was unreliable due to its rapid decay.

The main drawbacks for applying Radium as a verification technology are 1) high cost of analysis and sampling equipment; 2) extended sample collection time; and 3) sample expiry after 2-3 weeks.

Sample and equipment costs (up to \$150 /sample), while high at this time, can be expected to decrease as better techniques are developed and in response to increased usage. Sample collection of ^{226}Ra may be improved by a procedure currently being developed that will allow measurement of this isotope using ICP-MS. The new procedure for collecting samples of ^{226}Ra is likely to be similar to the trace metals protocol.

Sample collection times of remaining isotopes could be greatly reduced compared to the present sampling protocol by developing a specialized pump system capable of taking complimentary samples simultaneously. The pump system would divert water from a high volume (200 L), high flow (5-15 L min⁻¹) main stream to allow filtration of a smaller volume of water (20 L) at a slower rate (1-2 L min⁻¹). The former sample would be for activity ratio determination and the latter for quantitative determination of radium isotopes.

The dual system described above would need to be fitted with a pair of precise flow accumulators suited to the flow rates involved. In order to achieve flow rates of close to 15 L min⁻¹, a pump would probably require a hose inlet of around 0.75 inch internal diameter (under minimal suction head). Sounding pipes of diameter exceeding one inch could theoretically be used as tank access locations. Use of sounding pipes for sampling is not recommended, however, unless it can be ascertained that the water in the pipes fairly represents the ballast water in the rest of the tank. If the described flow rates could be achieved by a

dual system, radium sampling could then be accomplished in around 30 minutes. Note that if time is limited, replicate samples would need to be taken by two or more pump systems operating at once.

If radium is to be a useful verification tool, it is necessary to ensure that systems are in place to allow extremely rapid processing of the samples to prevent the sample from 'expiring' – that is, producing unreliable concentrations for short-lived isotopes (^{223}Ra and ^{224}Ra). Furthermore, the longer the voyage, the harder it will become to use short-lived isotopes to distinguish between water ballasted near the coast several weeks earlier and water exchanged in mid-ocean in the more recent past.

Conclusions

Although some variables show promise individually, the Mahalanobis multivariate analysis technique introduced in this report provides even greater resolution and confidence in the source of ballast water, and thus provides a potential framework for a USCG compliance monitoring program. By comparing with an oceanic reference database, the probability that any ballast tank contains water that is not derived from an oceanic source can be estimated. Judgements of non-compliance can therefore be tailored according to what is deemed an acceptable risk of false determination.

Despite the apparent sensitivity and capacity of these methods to detect BWE, significant gaps presently exist in the quality and quantity of data that limit the development and implementation of verification by Coast Guard or others. Some data exist for each of these measures at various coastal or ocean locations, however these existing data sets rarely include a full suite of variables considered relevant to BWE verification. Further, since a multivariate approach has the most power to test for BWE, it is critical to collect data simultaneously for each measure, since multivariate analyses rely on covariance among measures. Regardless of the tracer set used for verification, it is obvious that additional reference data will be necessary from both oceanic and coastal regions. Furthermore, it is often not clear how the tracer concentrations of interest vary with distance from shore. The current analysis indicates that clear differences exist between coastal and oceanic water but does not indicate how tracer concentrations change within the first few hundred miles of most coastlines. Multivariate measures along transects could be of great importance in assessing a distance-based requirement for exchange.

Thus, to successfully implement either a univariate or multivariate scheme for BWE verification, it is necessary to expand the reference databases constructed in this study to (1) test the robustness of these results and (2) properly characterize the regions in which ballast exchange may occur. This could be done

rapidly, given the relative ease of collection and analysis for the most promising measures. Importantly, with expanded reference data, the current research indicates the multivariate approach can verify exchange with high confidence.

Recommendations

Based upon the current research, it is believed that ballast water verification is feasible and can be implemented in a 18-24 month time frame if funding is available. The following steps are suggested to develop and implement a functional system for ballast water verification:

1. Develop a multivariate database of key measures for coastal and oceanic water. This should include (a) "transect sampling," whereby water samples for analysis are drawn frequently (< 25 mi intervals near coastlines and <100 mi intervals in open ocean), (b) comparison samples, which are samples drawn from exchanged versus unexchanged tanks, and (c) geo-temporal samples, which are samples obtained from regions or seasons of expected complexities (e.g., Gulf Stream). This could be completed within a 12-18 month time frame by using many on-going ballast water exchange experiments, international collaborations, and the same analytical laboratories as in the current research.
2. Explore further the capacity for in-situ or rapid analysis for those measures that effectively discriminate ballast water exchange. It is recognized that the specific methods used in this study currently have significant limitations (e.g., radium and perhaps trace metals). Options to streamline such measurements were not fully explored in this study. Such exploration should include both a review of existing methods and the rapid development of alternate methods (or equipment) that may promote rapid (in-situ) field measures.
3. Define the framework for verification requirements by Coast Guard. This should include: the volumetric extent (%) of ballast water exchange that needs to be detected; the confidence limits (probability) required; the time limits necessary for verification; the need for high-quality archival samples; and possible strategies available to meet Coast Guard requirements in this area. This should outline the extent to which Coast Guard requires in-situ (or real time) measures for enforcement as well as less time-sensitive measures to assess compliance. The latter could be the focus of a research assessment or education outreach. The two objectives have very different goals and constraints.

4. Develop a classification tree approach to verification testing. This approach makes use of multivariate data to implement a stepwise set of tests to verify exchange. A classification (or decision) tree system should be developed for an expanded set of reference data (as in #1), using those measures to be included in verification. This serves to minimize the number of tests required to test for verification.

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Appendices

Definitions and Acronyms

The appendices contain a number of tables, seven of which use common abbreviations and acronyms within the headings or within the tables. The definitions below are arranged by groups for the common table headings found in appendices G-M. Other miscellaneous abbreviations and symbols used in all appendices follow.

Ship:	VSF - Cruise 1: San Francisco – Valdez VLA - Cruise 2: Los Angeles – Valdez VPS - Cruise 3: Puget Sound – Valdez VFos - Cruise 4: Fos Sur Mer – Norfolk
ID #:	Sample identification number
Tank:	W1 – W4, Wing Tanks 1 – 4
Time:	Time of sampling; T0, T1, T2, T3, T4 = Before Exchange, After 100%, 200%, 300%, 300% Volume Exchange; Tf = Final Sample Time Regardless of Treatment S0 – S54 = Shiptside Sample Time/Location
Treatment:	Empty-Refill (ER) Flow-Through (FT) Control (C)
Location:	Locations within ballast tank (A, B) or along ship's route (0 – 54)
Depth:	Depth in meters; single point sample Profile; in-situ readings over depth
Replicate:	Replicate sample number

Parameters Measured:

Longitude:	Longitude in decimal degrees; + = °E, - = °W
Latitude:	Latitude in decimal degrees; + = °N
Temperature:	Temperature in degrees Celsius (°C)
Salinity:	Salinity in parts per thousand (ppt)
CDOM:	Colored Dissolved Organic Matter fluorescence intensity as measured in-situ; units reported as "fIS" readings
Turbidity:	Turbidity in Nephelometric Turbidity Units (NTU)
Oxygen:	Dissolved oxygen content in milligram-atoms O ₂ per liter (mg-at O ₂ /L)
A _{exx} :	Peak A Excitation Maximum
A _{emx} :	Peak A Emission Maximum
A _{qse} :	Peak A Intensity; Quinine Sulfate Equivalentents (qse)
C _{exx} :	Peak C Excitation Maximum
C _{emx} :	Peak C Emission Maximum
C _{qse} :	Peak C Intensity; Quinine Sulfate Equivalentents (qse)
a(280):	Absorption Coefficient at 280 nanometers (nm)
a(312):	Absorption Coefficient at 312 nanometers (nm)
a(412):	Absorption Coefficient at 412 nanometers (nm)
Volume:	Volume Filtered for Radium Measurements in Liters (L)
Ra223:	Radium Ion
Ra224:	Radium Ion
Ra226:	Radium Ion
Ra228:	Radium Ion
Th228:	Thorium Ion
A.R. 223/226:	Activity Ratio of Ra223 to Ra226; dimensionless
A.R. 228/226:	Activity Ratio of Ra228 to Ra226; dimensionless
Salinity Tolerance:	Relative growth rates of phytoplankton incubated at 15 ppt and 35 ppt

Other Abbreviations:

A.R.	Activity Ratio
bl	Blank – aliquot of “clean water” passed through sample apparatus
CTD	Conductivity-Temperature-Depth
dpm	Disintegrations per minute
EEM	Excitation Emission Matrix
fIS	Flashlamp CDOM Fluorescence Units
Hg	Mercury
km	Kilometers
L	Liters
m	Meters
MT	Metric Tons
nd	No data taken
preb	Pre-blank – aliquot of “clean water” not passed through sample apparatus
ppb	Parts per billion
QSE	Quinine Sulfate Equivalents (also qse)
SS	Shipside Samples
VDC	Voltage, direct current

Trace metals sampled included the following:

Ba	Barium [ppb]	P	Phosphorus [ppb]
Cu	Copper [ppb]	Pb	Lead [ppb]
Cd	Cadmium [ppb]	Ra	Radium [dpm / 100 l]
Cr	Chromium [ppb]	Th	Thorium [ppb]
Fe	Iron [ppb]	U	Uranium [ppb]
Mn	Manganese [ppb]	V	Vanadium [ppb]
Mo	Molybdenum [ppb]	Zn	Zinc [ppb]
Ni	Nickel [ppb]		

Appendix A

Methods for Verifying Mid-Ocean Ballast Water Exchange:

Ballast Water Exchange Verification Workshop

Edgewater, MD

August 3-4, 2000

Report by:

Kate Murphy & Greg Ruiz

With contributions from:

Larry Brand	(University of Miami)
Paula Coble	(University of Southern Florida)
Jay Cullen	(Rutgers University)
Fred Dobbs	(Old Dominion University)
Mark Geiger	(Naval Oceanographic Office)
Chad Hewitt	(CSIRO Australia)
Patrick Louchouart	(University of Corpus Christi)
Willard Moore	(University of South Carolina)
Jae Ryoung Oh	(KORDI, Korea)
Patricia Tester	(National Ocean Service, NOAA)

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1. Verification Workshop

1.1. Goals and Scope

The aim of the Ballast Water Exchange (BWE) Verification workshop was to identify, discuss and evaluate techniques that may be used to verify that a vessel has undertaken mid-ocean ballast exchange in accordance with current Ballast Water Exchange Guidelines or, potentially, in accordance with future mandatory exchange laws.

Panel members at the BWE Workshop were selected after discussions with a large number of marine scientists. Once a potential verification technique had been identified, experts were contacted for preliminary discussions on the applicability of the technique to the verification issue. Practical constraints and cost issues associated with applying techniques in an investigative or regulatory environment were frequently addressed in discussions and played a secondary role in the final selection of the workshop panel. The highest priority was to consider all techniques capable of discriminating oceanic and coastal water samples in order to have a comprehensive scientific basis from which selections based on non-scientific factors (e.g. cost, practicality) could be made. Thus, the goal was to test the capacity of currently available analytical methods, individually or in combination, to discriminate exchanged from unexchanged coastal water. A second step may be to determine which methods can be applied readily to maximize discrimination while minimizing cost and inconvenience to the operator.

The BWE Workshop agenda and a complete listing of workshop participants are provided in Sections 4 and 5 of this document. Cost, practicality and legal issues were discussed in detail during presentations by panel members as well as on the final (evaluation) day of the workshop. These issues will play a prominent role in the design of Phase 2 of the program and in the final recommendations by SERC to the USCG.

1.2. Presentations by invited panel members

Panel members gave a short informal presentation describing at least one technique which could potentially be used to verify ballast water exchange.

The panel was asked to identify the tracer(s) or properties used to verify exchange and the techniques used to measure them, considering only existing technology. Panelists were asked to provide an outline of:

- Each of the steps (e.g. collection, processing, analysis) involved in applying the technique, and corresponding requirements in terms of personnel, equipment and time

- Sources of uncertainty, and their potential impact on the use of the technique in a regulatory environment
- Approximate cost per sample (collection, processing, analysis)
- Potential pitfalls for people collecting samples
- Potential pitfalls for people processing samples
- Potential pitfalls for regulators
- Other advantages and disadvantages of the technique
- Existing data that could be drawn upon when applying the technique to BWE verification
- The likelihood that the technique will be significantly improved upon in the short term (1-3 years) for any reason, for example, imminent advances in technology
- People and/or organizations who could conduct the described analysis

The following section of this document is a synopsis of the techniques presented in the workshop.

2. Synopses of potential verification techniques

2.1. Trace Metal Isotopes

Contributor: Jay Cullen, Rutgers University

2.1.1. Background

Many metals exhibit pronounced onshore-offshore concentration gradients which reflect their terrestrial origin. Metals enter waterways after leaching naturally from rocks and soil, or in elevated concentrations associated with industrial sources. Particularly common in nearshore waters are the constituents of steel, brass and bronze (iron (Fe), nickel (Ni), zinc (Zn), copper (Cu), and aluminum (Al)). In localized regions, high concentrations of silver (Ag) in seawater are found in association with sewage outfalls and the jewelry industry. Main coastal sources for Manganese (Mn), Barium (Ba) and Thorium (Th) are riverine inputs (desorption from minerals), groundwater input (seepage through sediments) and atmospheric deposition of dust.

Although metal concentrations vary considerably along coastlines in response to geographic boundaries and point sources, existing data suggest that trace metal concentrations in coastal waters are 4 – 25 times higher than they are 100-200 miles offshore. Moving away from the shoreline, metals are rapidly scavenged through biological uptake or adsorption to sediments, resulting in decreasing concentrations in the water column with increasing distance from the shore line.

Because of the wide range of metals used in ship construction, contamination from the vessel itself is a serious obstacle to using trace metal analyses to verify ballast water exchange. While the trace metal composition of exchanged and unexchanged ballast water has never been studied, three metals known to exhibit strong coast to open ocean gradients (Mn, Ba, Ag) may be among the least likely to be compromised by cross-contamination from the vessel.

Trace metal analysis is performed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In the United States (U.S.), there are currently around seven to eight machines capable of performing ICP-MS analyses on trace metals, although the procedure is currently performed routinely only at Rutgers University, PA. Processing requires only a few mL of water and takes approx. 5-10 min per sample (minimum ca. 10 samples per day) to quantify all metal peaks simultaneously.

2.1.2. Procedure

On vessel

- 10-50 mL ballast water samples are collected in trace metal clean containers
- Containers are frozen (to prevent microbial alteration of the sample).
- Frozen samples are shipped directly to the laboratory.

In laboratory

- Sample is diluted, acidified and filtered (0.45 µm)
- Analysis for a suite of trace metals is performed using ICP-MS.

2.1.3. Costs:

Collection costs are low. Shipping costs range from \$8 to \$30 per ship, depending on whether special arrangements are necessary to keep the sample frozen during transit. ICP-MS analysis at Rutgers University costs ~\$50 /sample with a minimum of 10 processed per occasion. Table A-1 summarizes time and cost requirements for analysis.

Table A-1. Time and cost requirements for metal isotope analyses.

Stage	Time required	Cost
Preparation (lab)	3 hr	Operator time
Sample Collection	10 min	\$1 per sample
Shipping to laboratory	overnight	\$8-30
Sample analysis	1 day (min. 10 /day)	\$50 per sample for multiple elements
Data interpretation	2 hr / sample	Operator time

2.1.4. Advantages

- Trace metals analyses using ICP-MS allow complete metal characterization of samples relatively quickly and economically.
- All of the complexities in the methodology are first encountered after the sample leaves the hands of the Coast Guard boarding team and enters a controlled laboratory environment.
- ICP-MS instrumentation is highly sensitive (i.e. able to detect concentrations as low as 1 nano-molar/kg), works well in seawater and is subject to low blank (noise) interference. The

quantification of metal concentrations is considered accurate to approximately 5 percent for common elements (e.g. Mn, Ba) and 10 percent for rare elements.

2.1.5. Disadvantages

- Not in-situ (real time)
- Potential metal contamination by the ship structure or cargo
- Uncertainty in the effect of alterations in the physical (e.g. temperature), chemical (oxygen, sediments) and biological (e.g. bacteria, plankton) environment on trace metal concentrations
- Many metals cannot be detected 100-200 mi. offshore making it impossible to distinguish between water exchanged beyond the Exclusive Economic Zone (EEZ) and water exchanged in metal-depleted waters closer to the coastline.

2.2. Radium Isotopes

Contributor: Willard S. Moore, University of South Carolina

2.2.1. Background

The radium (Ra) budget of the ocean is controlled by input from sedimentary sources and loss by radioactive decay and biological removal. The biological loss term is only thought to be important for the long-lived ^{226}Ra (half-life = 1600 years) as the Ra residence time in the ocean is of the order of 400 years. Because the residence time far exceeds the mixing time of the surface ocean, activities of ^{226}Ra are rather constant in open ocean surface water and differ little in the surface Atlantic and Pacific Oceans. However, near the continents where new additions of ^{226}Ra occur, activities may exceed open ocean values by factors of 1.3 to 4. The budget of the other long-lived Ra isotope, ^{228}Ra (half-life = 5.7 year), is strongly affected by radioactive decay in the surface ocean. Significant variations occur between the Atlantic and Pacific Oceans and within the surface waters of each ocean. Although it is not possible to define a unique value for the ^{228}Ra activity in the open ocean, it is known that activities in coastal waters exceed open ocean activities by factors of 5-20. It is also known that the activity ratio $^{228}\text{Ra}/^{226}\text{Ra}$ is much higher in coastal waters than in the open ocean. In addition to these long-lived isotopes, there are also two short-lived Ra isotopes that only occur in coastal waters, ^{223}Ra (half-life = 11 day) and ^{224}Ra (half-life = 3.7 day). Because of their rapid rates of radioactive decay, these isotopes are only measurable within 50-200 km of the coast. The presence of these short-lived isotopes in a sample is a clear indicator of its origin near the coast.

2.2.2. Procedure

On vessel

Two types of samples (Activity ratio, Quantitative) are used to fully characterize Radium Isotopes in seawater. Because of the large volume of water required for the first type of sample, extraction of Radium onto filters is easiest performed on deck using a pump. In the interests of efficiency, the pumping system should be organized such that the two types of samples are collected simultaneously:

1. Activity ratio (AR): 200 L of water is pumped through a manganese dioxide coated fiber cartridge at a flow rate of 5 -10 L/m. This process extracts 50-80 percent of the Ra.
2. Quantitative: Radium is extracted from a 20 L sample at flow rates of 1-2 L/m

It is not necessary for an operator to be present during the entire pumping process provided that the pump is appropriately secured and automated. Once the pumping is complete, the cartridges can be placed into plastic bags and mailed directly to the laboratory.

In laboratory

At least four laboratories in the U.S. are currently set up to analyze Radium isotopes. Because radioactive isotope concentrations decay over time, samples should be processed as soon as possible after collection.

A multistage analysis was proposed in which progressively more intensive (and costly) analyses are performed depending on the results of earlier stage analyses (Figure A-1). Upon arriving at the laboratory, the large volume sample is measured immediately for ^{223}Ra at a cost of approximately \$30. If the concentration of ^{223}Ra is intermediate to coastal and oceanic water, the large volume sample is used to calculate the Activity Ratio ($^{228}\text{Ra} / ^{226}\text{Ra}$) at an additional cost of \$80 (this process takes two weeks for high priority samples). At the same time, the small volume sample is analyzed for ^{226}Ra at a cost of \$40.

2.2.3. Cost

Once a pump has been purchased and custom-fitted, radium samples are inexpensive both to collect (about \$10) and to transport to the laboratory (about \$8). Laboratory costs are comparatively high. Unless the initial ^{223}Ra analysis indicates the sample is clearly oceanic or clearly coastal, a complete analysis is required at a cost of around \$150 per sample. Table A-2 summarizes time and cost requirements.

Table A-2. Time and cost requirements for Radium analyses.

Stage	Time required	Cost
Preparation (lab)	2 hr.	Operator time
Sample Collection	45 min.	\$10
Shipping to laboratory	2-3 day	\$8
Sample analysis	4 hr – 2 weeks	\$30 - \$150
Data interpretation	1 hr / sample	Operator time

2.2.4. Advantages

- Radium concentrations in the oceans are well studied, enabling a substantial reference database to be drawn upon
- Radium quantification techniques are accurate and highly sensitive

2.2.5. Disadvantages

Sediments are a source of Radium and are likely to confound analyses on tanks which have accumulated sediments that are not removed on deballasting. Although potentially a significant refuge for exotic species, there is presently no requirement (external to the vessel's own policies) for ships to remove sediments from their ballast tanks. Consequently, it would be inappropriate to regulate exchange using a verification technique which is sensitive to ballast sediment loads. However, the potential accuracy of Radium techniques for verifying exchange of tanks which do not contain sediments suggests this method is useful as a benchmark against which other techniques could be assessed.

Further disadvantages include

- Relatively costly
- Potentially time consuming
- Expiry of radioactive isotopes (particularly short-lived isotopes) after 2 –3 weeks

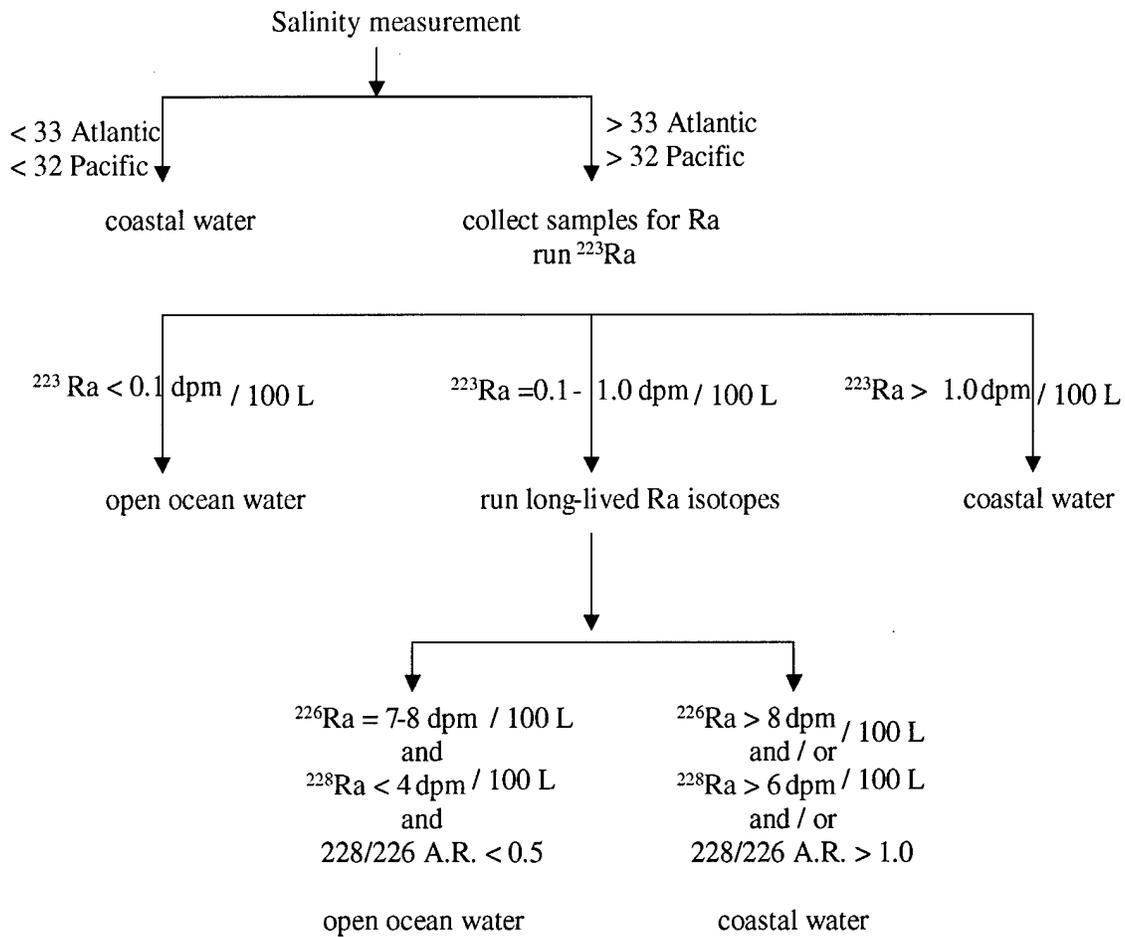


Figure A-1. Radium Analysis Flow Chart.

2.3. Salinity Responses of Phytoplankton

Contributor: Larry Brand, University of Miami

2.3.1. Background

The presence or absence of different phytoplankton species in different environments reflects their specific growth requirements and tolerances. Ballast tanks that have been exchanged in mid ocean will contain low concentrations of coastal species relative to oceanic species. One technique for determining the origin of phytoplankton relies on the observation of Brand (1984) that most (possibly all) coastal phytoplankton species are adapted to low salinity environments (ie. they are euryhaline) even when not subject to low salinities in their present day habitat. Such adaptations may have arisen during past ice ages when the continental shelves were dry land and estuaries were the refuge for coastal species, and/or because the gene flow between populations in estuaries and the continental shelves is much larger than between coastal and oceanic waters.

In line with this observation, a qualitative indication of the success with which coastal water was removed by mid-ocean exchange may be inferred from the growth of ballast water phytoplankton incubated under a range of salinity conditions. Phytoplankton which are truly oceanic are relatively intolerant to lower than oceanic salinities (< 32 - 34 ppt). Conversely, phytoplankton originating in high salinity coastal regions flourish under a wider range of salinities. The ratio of growth rates (measured as fluorescence) of coastal versus oceanic species incubated over a range of salinities reflects the origin of the sample, with low ratios indicative of predominantly oceanic species and high ratios indicative of predominantly coastal species. Relative proportions of oceanic and coastal species could be inferred by the slopes of population growth curves; if only a few live cells of a particular type are present, the initial rate of increase in the population curve will be slow.

2.3.2. Procedure

On vessel

- Sterilize sampling apparatus with bleach
- Fill a 100 mL sample jar with ballast water filtered through a 40 μ m mesh to remove grazing zooplankton.
- Send sample via Fed-Ex[®] to laboratory

In laboratory

- Split the sample into equal portions and incubate each portion at different salinities for 2 weeks.
- Monitor samples every 2-3 days for algal growth (by fluorometry)
- Calculate the ratio of phytoplankton fluorescence under low salinity (15 ppt) versus high salinity (35 ppt).
- Low fluorescence ratios correspond to rapid growth of phytoplankton species under low salinity conditions relative to growth under high salinity conditions, indicating a dominance of coastal water in the sample. Table A-3 summarizes time and cost requirements.

2.3.3. Costs

Table A-3. Time and cost requirements for salinity tolerance analyses.

Stage	Time required	Cost
Preparation (lab)	3 hr	Operator time
Sample Collection	10 min	\$1 per sample
Shipping to laboratory	overnight	\$20 per ship
Sample analysis	1 hr for 5 days	Operator time
Data interpretation	3 hr / sample	Operator time

2.3.4. Advantages

- Small sample volumes are sufficient (ca. 100 ml)
- Incubation procedure is straightforward and does not require expensive instrumentation or highly trained personnel.
- Since tolerance responses at different salinities effectively control for each other, the method is not sensitive to environmental abuse (darkness, heavy metals, oils, other toxins) or ballast water history.
- Since the method relies only on the presence of a small number of viable plankton cells to begin the culture, the method should work regardless of the original salinity of the ballast water or conditions in the ballast tank between ballasting and sampling.
- Research to date indicates salinity responses are independent of watershed characteristics, local salinity and species composition

- Interpretation is based on differences between, not absolute values of, growth rates under different salinity conditions. Critical manipulations and measurements are made under controlled conditions (the laboratory) rather than in the field.

If it is indeed possible to distinguish oceanic and coastal phytoplankton solely on the basis of their salinity responses, salinity tolerance may be a more biologically relevant criterion for distinguishing 'safe' from 'unsafe' phytoplankton than is an arbitrary distance from a coast line. Conversely, if the rule is to exchange ballast water at least 200 miles offshore, this method will not be able to distinguish between ships that have performed some type of exchange closer to the coast but still in a region occupied by oceanic phytoplankton species.

2.3.5. Disadvantages

- Qualitative, or semi-quantitative
- Relatively time consuming (around 2 weeks)
- Dependence on living phytoplankton to seed the incubated populations
- Mid-ocean exchange will always leave a seed population of coastal species, although this may be small.
- The use of plankton density as a tracer for exchange volume will be inappropriate if there are large unpredictable disparities between coastal and oceanic cell densities. These would be expected to vary in response to season, location, bloom events and nutrient delivery. Thus a tank containing only 20% coastal water could contain more than 50% coastal phytoplankton cells, by virtue of much higher initial concentrations of coastal plankton cells.
- Oceanic plankton are accustomed to a more stable environment and may experience higher mortality rates than coastal species in ballast water. The method requires that rates of oceanic and coastal phytoplankton mortality in ballast water are similar or otherwise predictable so that relative densities of coastal versus oceanic phytoplankton cells at the time of the exchange may be estimated. This may lead to difficulty in distinguishing a low (acceptable) coastal signal and a low (unacceptable) oceanic phytoplankton signal.
- Disparities in generation times between coastal and oceanic species, if they exist, will affect the interpretation of lag times (used to estimate the initial densities of oceanic vs. coastal phytoplankton).

2.4. Dissolved Organic Matter

Contributor: Paula Coble, University of Southern Florida

2.4.1. Background

Fluorescence of dissolved organic matter (DOM) has been used as a sensitive and specific tracer of natural and anthropogenic compounds in the environment for many years. Rivers are the major source of natural DOM to the oceans; in association with rivers, concentrations of DOM can vary two orders of magnitude along a 0 to 35 ppt salinity gradient. In addition to large changes in intensity, spectral properties also vary with DOM source and type. Riverine and marine samples can be distinguished on the basis of DOM as can contributions from petroleum hydrocarbons, microbial growth, and other specific sources. Although a global data base of measurements on discrete water samples is lacking, the good correlation between DOM fluorescence and ocean color at 412 nm in areas studied to date make DOM in conjunction with satellite remote sensing a potentially useful tool in ballast water exchange verification strategies.

Parameters used to characterize colored DOM (CDOM) signatures include fluorescence intensity, positions of excitation and emission maxima, quantum efficiency, life time and peak width. The first three of these parameters are considered sufficient to characterize the origin of ballast water. Fluorescence intensity in rivers and on coasts is normally much higher than in the open ocean. The spectral position of blue excitation and emission maxima for surface oceanic samples occurs at lower wavelengths than for surface coastal or riverine samples causing oceanic and coastal samples to plot in separate regions of a spectral graph.

Fluorescence can be measured in situ using field fluorometers or with more complex lab-based instrumentation. Both methods allow calculation of emission spectra at multiple excitation wavelengths; however, lab-based analyses allow much finer resolution of the data (allowing the representation of the data as 3 dimensional plots of excitation, emission and intensity) and provide additional information such as the position of wavelength-independent fluorescence maxima. Laboratory instrumentation is also capable of greater sensitivity at low concentrations by roughly a factor of ten.

2.4.2. Procedure

In situ instrumentation:

- Calibrate and optimize field instrument for detection of DOMs
- Measure DOM profile of tank
- Determine compliance by comparison of output with pre-determined standards

EEM data

- Collect replicate 100 ml ballast water samples in clean containers
- Protect samples from light at all times
- Using a hand pump, pass through 0.45 μm filter
- Store samples in light-proof Styrofoam[®] boxes, freeze, ship to laboratory
- Use clean DOM techniques to minimize contamination by organics

EEM (laboratory) analysis

- Run emission scans (48 per sample; ex/em = 220-455 / 250-700 nm)
- Adjust output: normalize, subtract blank, apply spectral corrections, calibrate

2.4.3. Costs

In situ instrumentation:

Ballast tank profiling by a skilled operator would take approximately 20 min/tank. Discrete fluorescence measurements could be taken more rapidly. Submersible fluorometers range in price according to complexity, but start at around \$3000.

EEM (laboratory) analysis

The majority of time is absorbed in the laboratory while preparing, calibrating, analysing and interpreting the samples. The estimated breakdown of DOM analysis time demands and per sample cost is provided in Table A-4. In the future, instantaneous fingerprinting using close coupled device (CCD) detectors would greatly reduce collection and analysis time.

Table A-4. Time and cost requirements for laboratory based DOM analyses.

Stage	Time required	Cost
Preparation	4 hr. (for 20 samples)	Operator time
Sample Collection	10 min. per sample	\$2 / sample
Shipping to laboratory	overnight	\$10 / ship
Calibration	4 hr. (for 20 samples)	Operator time
Sample analysis	2 hr / sample	Operator time
Data interpretation	1 hr / sample	Operator time

2.4.4. Advantages

In situ instrumentation:

- In situ analysis (no sample collection or storage)
- Can take profiles of the water column
- Potential rapid determination of compliance
- Running costs low

EEM (laboratory) analysis

- Sample collection rapid, no pre-concentration is required
- Capable of distinguishing between specific water types and contaminants
- No interference from plant pigments or particles
- Potential to link DOM verification with the global distribution of CDOM obtained by satellite
- Samples may be stored for approx. 1 year if frozen (or 2 weeks if unfrozen)

2.4.5. Disadvantages

In situ instrumentation:

- Field instrumentation is costly and susceptible to damage / loss in the field
- Analysis is less comprehensive than could be obtained from EEM spectroscopy of DOM

EEM (laboratory) analysis

- Filtration of sample required prior to shipping to the laboratory

- In most surface waters DOM is negatively correlated with salinity. Coastal areas that do not receive significant river inputs have high salinity and low DOM, hence DOM may be a poor tracer of high salinity coastal water.
- There is an absence of a detailed global dataset of DOM concentrations in soils, porewaters, rivers and surface waters. Particularly lacking are baseline data for the western Indo - Pacific region, a significant source of traffic to the Pacific Coast USA. However, DOM data are usually well correlated with ocean color which can be determined via existing satellite imagery.
- Crude oil, wood pulp, soils, pAH and organic contaminants would contribute their own peaks to spectral analysis. It would be necessary to develop a library of contaminant peaks to assist in interpretation of spectral peaks.
- Interaction between microbial/phytoplankton growth and spectral results is uncertain
- Considerable expertise is necessary to run analyses correctly and interpret the spectral fluorescence graphs.

2.5. Water Clarity

Contributor: Mark Geiger, Naval Oceanographic Office

2.5.1. Background

Turbidity measurements can be taken rapidly and may offer a convenient method of identifying ballast tanks which contain coastal water. In general, coastal waters are turbid in comparison to oceanic waters due to high biological productivity and high suspended sediment loads. Terrestrial inputs and coastal processes contribute high nutrient loads to the water column which support plankton and neritic communities. In shallow waters, shear stresses caused by waves, tides and currents cause sediments to be lifted from the seafloor and transported in the water column. All of these suspended particles contribute to an increase in turbidity and corresponding reduction in water clarity.

2.5.2. Procedure

On vessel

- A turbidity meter is lowered into the open manhole or sounding pipe
- Turbidity profile is obtained for entire (accessible) water column
- Low turbidity readings in addition to “above threshold” salinity indicates vessel is in compliance with exchange guidelines / regulations.

2.5.3. Costs

Hand held turbidity meters cost upwards of \$900 off the shelf. They need to be interfaced with a readout or internal data logger in order to obtain data in workable format. Several companies are able to make turbidity meters and other sensors to required specifications. Large orders would presumably reduce the cost of individual units. Table A-5 summarizes time and cost requirements.

Table A-5. Time and cost requirements for water clarity analyses.

Stage	Time required	Cost
In situ measurements	20 min	Operator time
Data interpretation	10 min	Operator time

2.5.4. Advantages

- In situ
- No sample handling or processing costs
- Potentially instantaneous determination of compliance by the USCG

2.5.5. Disadvantages

Coastal water which is isolated in a ballast tank and is not well mixed by the movement of the vessel will become less turbid over time as a result of the following processes:

- Depletion of nutrients in the tank
- Mortality and sinking of phytoplankton and zooplankton
- Sinking of sediment particles

These processes will make coastal water appear progressively more oceanic as it ages.

The pumping of water in and out of the ballast tanks during exchange will cause resuspension of settled particles, particularly in the case of sequential (Empty-Refill) exchange. If particles which were resuspended during exchange do not settle by the time verification is performed, water of oceanic origin may be confused with turbid coastal water.

Particle sinking rates in still water can be estimated by Van Rijns (1990) or Stokes's equations (Table A-6). Many live phytoplankton can regulate their buoyancy and sink only a few meters per day. Dead plankton and sediments sink more rapidly such that all but the smallest particles would disappear from the water column in a matter of hours. On the other hand, only small shear stresses would be necessary to resuspend small particles from sediment pools in the ballast tanks. The minimum bed shear stress which can displace a 100 micron silt particle is approx. 0.15 N/m^2 .

Table A-6. Approximate sinking rates for a range of particle sizes.

Grain size (μm)	Sinking rate (mday^{-1})	Example
1	0.1	'Neutrally' buoyant beads
10	7	Dead phytoplankton
50	150	Large phytoplankton, diatom, silt
100	500	Fine sand
200	2500	Coarse sand

2.6. Lignin

Contributor: Patrick Louchouart Texas A&M University – Corpus Christi

2.6.1. Background

Lignin is a major and unique structural component of vascular plants, and as such is an important component of terrigenous dissolved organic matter (TDOM) exported from land to the coastal ocean. The presence of dissolved lignin in seawater thus indicates, and in some cases helps quantify, unambiguous inputs of TDOM to the sea. The unique biochemical signature of lignin provides the added advantage that it helps characterize the source and diagenetic state of vascular plant material and thus “fingerprint” riverine DOM. Such “fingerprinting” can provide drainage basin-specific distinctions of sources of fresh waters to the coastal ocean.

Solid-phase extraction (SPE) allows for a fast and accurate isolation of dissolved lignin from diverse natural waters (fresh, estuarine and marine) in preparation for CuO oxidation. Capillary gas chromatography (GC) coupled to selected-ion monitoring mass spectrometry (SIM-MS) of CuO oxidation products provides the high sensitivity and precision required for the identification and quantification of trace levels of lignin in seawater. The low blanks and quick clean up of C18 cartridges support SPE for processing such samples.

Comparison of SPE with other isolation procedures (direct dry-down and ultrafiltration) has shown that this method quantitatively recovers dissolved lignin and preserves its compositional parameters. Extraction efficiencies are independent of flow rate within a range of five to fifteen bed volumes per minute (50-150 ml min⁻¹), and both refrigeration and freezing are appropriate long-term storage methods for processed cartridges prior to elution of retained dissolved lignin.

Existing data suggest that lignin concentrations in rivers [10-100 µg L⁻¹] are orders of magnitude higher than in the open ocean [10-50 ng L⁻¹]. In coastal waters, lignin concentrations are highly dependent on riverine inputs and consequently can be strongly seasonally variable.

2.6.2. Procedure

On vessel

- Obtain replicate 10 L samples of water from ballast tank
- Store sample in a cool light-proof drum
- Transport to laboratory

In laboratory

- Sample is filtered at 50-150 ml min⁻¹ (1-2 hr / sample)
- Lignin is isolated by SPE

2.6.3. Costs

- 10 l black plastic carton (reusable) \$10
- 1-5 day Fed Ex[®] sample to laboratory (\$8.86-\$43 per 26 pound (10 l) drum, depending on sample origin and destination). More expensive if sample is to be kept cold.
- SPE Analysis incl. Cartridge ~\$80 per sample

Table A-7 summarizes time requirements and per sample cost.

Table A-7. Time and cost requirements for lignin analyses.

Stage	Time required	Cost
Preparation (lab)	3 hr	Operator time
Sample Collection	15 min	\$2 /sample
Shipping to laboratory	1-5 day	\$9-\$43 /sample
Sample analysis	1 day	\$80
Data interpretation	1 hr / sample	Operator time

2.6.4. Advantages

- High resolution is possible due to large differences in lignin concentrations in riverine and marine environments.
- Lignin does not readily adsorb to sediments, thus sediments retained in the tank following reballasting are not expected to affect the analysis.

2.6.5. Disadvantages

- Not in-situ
- Relatively costly to process
- Large sample volume is difficult to transport from the ship to the laboratory. Shipping costs are high on a per sample basis
- There is a high correlation of coastal lignin concentrations with rainfall and season (a problem particularly for high salinity ports)

2.7. Phytoplankton

Contributor: Pat Tester, NOAA

2.7.1. Background

Marine phytoplankton have specific growth requirements and consequently their presence within a habitat (water type) will reflect certain conditions of salinity, temperature, macro and micronutrients, including trace metals. While some species are strictly oceanic, others are found in coastal or estuarine waters. Knowledge of the environmental preferences of different phytoplankton species can be used to infer the water type of their origin.

2.7.2. Procedure

On ship

- Obtain replicate 100-500 ml samples of ballast water from a range of depths
- Obtain sediment samples if possible
- Add preservative to samples (e.g. Utermohl's solution)
- Transport to laboratory

In laboratory

- Concentrate sample by allowing cells to settle in a column overnight
- Examine under 200-400 x magnification
- Record presence/absence of marine and coastal species, or
- Quantify coastal and oceanic phytoplankton

2.7.3. Costs

- Leak-proof sample jars (ca. \$1 ea)
- Preservative (ca. \$1 per sample)
- Transportation of sample to laboratory (US: about \$5 per ship, international rates variable)
- Salary time (consultant rates ca. \$40-\$80 per sample)

Table A-8 provides time requirements and per sample costs.

Table A-8. Time and cost requirements phytoplankton analyses.

Stage	Time required	Cost
Preparation (lab)	3 hr	Operator time
Sample Collection	15 min	\$2 per sample
Shipping to laboratory	2-3 day, hazardous	\$30 +
Sample analysis	2 hr / sample	\$80-150
Data interpretation	1 hr / sample	Operator time

2.7.4. Advantages

- Rapid sample collection
- Samples are relatively long lived (expiry is approx. 6 months if sample is unrefrigerated or 1-1.5 year if sample is refrigerated)

2.7.5. Disadvantages

- Not in-situ
- Analysis is labor intensive, not automated
- Potentially long time lag between collection and processing
- Preservative is a hazardous chemical
- Delicate cells can be destroyed during preservation
- Difficult to obtain sediment samples
- Can be very difficult to locate suitably skilled experts to identify plankton
- May be difficult to distinguish cells which were alive during collection from cysts and dead cells resuspended from the sediments
- Patchiness of phytoplankton densities in the ocean and extrusion of coastal species beyond EEZ boundary compounds coastal/open ocean determination
- As with any coastal organism, we expect a residual concentration of phytoplankton to be present after exchange. Given the large range of concentrations of organisms in natural waters, interpreting the extent of exchange from plankton densities is problematic, although ratios of coastal oceanic species may be a useful indicator.

2.8. Bacteria

Contributor: Fred Dobbs, Old Dominion University

2.8.1. Background

Pattern analysis of carbon-source utilization has been proposed as a simple and rapid method to characterize heterotrophic microbial communities. In particular, the microtiter plates developed by Biolog, Inc. have been used extensively in this regard. The Biolog plates consist of multiple carbon substrates, each contained in a separate well to which a minimal growth medium and tetrazolium violet are added. The redox dye turns purple in the presence of electron transfer, indicating the substrate has been utilized by the inoculated microbes.

The Biolog plates originally were designed to identify bacterial isolates. In addition to that role, however, the plates have been found useful in microbial community studies and have been widely used to characterize bacterial communities from various environments, including freshwater, seawater, sediments, and ships' ballast water. Biolog data are well suited for multivariate statistical analyses such as principal component analysis and cluster analysis, tools which can distinguish among bacterial communities from various environments and can be used to describe temporal changes in physiological characteristics.

In the context of this workshop, Dobbs is conducting Sea Grant funded research to characterize—using Biolog sole substrate utilization patterns—heterotrophic bacteria in ballast water of ships arriving in lower Chesapeake Bay. He has reported a wide range of responses among the ships sampled; clearly the bacterial assemblages of ballast waters vary considerably. In more than half the cases, however, there are commonalities in response that may be influenced by duration of voyage, source water, and exchange history.

2.8.2. Procedure

On vessel

- Collect 1 liter water in a light-proof, sterile container
- Ship immediately to laboratory

In laboratory

- Transfer water from sample to biolog plates (minimum 2 plates per sample)
- Take daily readings of each plate with the biolog reader for five days
- Interpret results after 5 days using PCA or cluster techniques

2.8.3. Costs

Costs of collecting biolog samples are trivial; the major expenses are incurred in the laboratory. A biolog reader can be purchased for ca. \$4500. The other significant cost is salary time for sample preparation and operation of the reader during processing. Time and cost requirements are provided in Table A-9.

Table A-9. Time and cost requirements for bacteria analyses.

Stage	Time required	Cost
Preparation (lab)	1 hr	Operator time
Sample Collection	5 min	\$6
Shipping to laboratory	Fedex [®] overnight	\$20
Sample analysis	1 minute per plate for 5 days	Operator time
Data interpretation	2 hr / sample	Operator time

2.8.4. Advantages

- sample collection is simple and rapid

2.8.5. Disadvantages

- Time consuming (approximately 8 day lag time between sample collection and results)
- Short expiry time (48-72 hr) necessitates immediate sample processing
- Limited reference database available (lower Chesapeake bay)
- High levels of DOM or other particles may contaminate the samples. The control well provides a correction for this.
- Interpretation involves specialized data analysis techniques

2.9. Coprostanol

Contributor: Jae Ryoung Oh, KORDI

2.9.1. Background

Coprostanols are chemical compounds produced in the digestive tracts of many terrestrial animals. Rats, primates and sea lions have shown to produce coprostanol (5β -cholestan- 3β -ol) whereas fish and invertebrates do not. Coprostanols do not appear to occur naturally in fresh or marine waters and consequently may be used as a tracer of terrestrially sourced water.

2.9.2. Procedure

On vessel

- Obtain representative 5 L samples of ballast water
- Add preservative
- Filter sample through glass fiber filters
- Ship filter papers to laboratory

In laboratory

Laboratory processing of coprostanol samples necessitates a multi-stage procedure of extraction, saponification, silylation and GC analysis. Under this method, the sterols are converted to their corresponding trimethylsilyl ethers (O-TMSi) and analyzed using gas chromatography.

2.9.3. Costs

- Leak-proof sample jars (ca. \$1 ea)
- Preservative (ca. \$1 per sample)
- Transportation of sample to laboratory (US: ca. \$5 per ship, international rates variable)
- Salary time (consultant rates ca. \$40-\$80 per sample)

Time and cost requirements are provided in Table A-10.

2.9.4. Advantages

- No contamination issues

2.9.5. Disadvantages

- Relatively large sample volume required

- Filtration of sample required prior to shipping
- Expensive to process
- Few baseline data exist on the distribution of sterols in natural waters
- Stability of Coprostanols in ballast water is unknown

Table A-10. Time and cost requirements for coprostanol analyses.

Stage	Time required	Cost
Preparation (lab)	3 hr	Operator time
Sample Collection	15 min	\$2 per sample
Shipping to laboratory	2-3 day, hazardous	\$30 +
Sample analysis	2 hr / sample	\$80-150
Data interpretation	1 hr / sample	Operator time

2.10. Conclusions and recommendations

All of the verification techniques proposed at the workshop had drawbacks in terms of cost, ease of application and/or scientific rigour; consequently, no single technique stood apart from the others as being the only one worth examining in detail. With the exceptions of salinity, turbidity and fluorescence, all of the proposed techniques involved laboratory processing time precluding in situ determination of compliance.

A preliminary comparison of the anticipated strengths and weaknesses of the presented techniques is summarized in Table A-11. Each technique is rated on a 1 to 3 scale according to a number of variables, listed in the first column of the table. An entry of '1' indicates high performance under a particular variable (e.g. cheap or quick) while at the other end of the spectrum, a value of '3' indicates poor performance (e.g. expensive or time consuming). The table is still incomplete with respect to variables falling in the category 'interpretation' since it is generally not possible to say in advance of formal tests (ie. Phase II of this program) whether a given technique can alone or in combination reliably discriminate between exchanged and unexchanged ballast water.

In addition to the techniques represented by panel members (metal isotopes, radium isotopes, salinity tolerance, DOM fluorescence, water clarity, lignin, phytoplankton, bacteria, coprostanol) the panel discussed briefly, and discounted for further investigation, the use as tracers of plankton pigments, bioluminescence, chlorophyll fluorescence or stable isotopes.

Table A-11. Ballast Water Exchange Verification Assessment Matrix.

	Trace Metals	Radium	Salinity Tolerance	DOM Fluorescence	In situ Fluorescence	Water Clarity	Lignin	Phytoplankton	Bacteria	Coprostanol
Collection										
# Personnel	1	2	1	1	1	1	1	1	1	1
-Training	1	3	1	1	3	3	1	1	1	2
-Safety	1	2	1	1	2	1	1	1	1	2
-Sample Volume	1	3	1	1	1	1	2	1	1	2
-Equipment	1	3	1	2	3	3	2	2	1	2
-Time	1	3	1	2	2	2	2	2	1	2
-Cost	1	3	1	1	3	3	1	1	1	1
-Special handling	2	3	2	2	3	3	1	3	1	2
Preservation										
-Delivery	2	1	2	2	1	1	1	2	2	1
-Expiry	2	2	2	2	1	1	1	2	2	1
-Transportation	1	1	1	2	1	1	1	2	2	1
-Cost	2	1	2	2	1	1	3	2	2	1
Processing										
-In situ?	3	3	3	3	1	1	3	3	3	3
-Difficulty	3	3	2	3	1	1	3	3	3	3
-Time	1	3	3	3	1	1	2	3	3	2
-Facilities	3	2	2	2	1	1	2	3	3	2
-Cost	2	3	2	2	1	1	3	2	2	3
Interpretation										
-Accuracy	1	1	3	1	1	1	1	2	?	2
-Precision	1	1	3	1	1	1	1	2	?	2
-Robustness	?	?	?	?	?	?	?	?	?	?
-Uncertainty	?	?	?	?	?	?	?	?	?	?
-Contaminants	3	2	1	2	1	?	?	?	2	1
Existing Database	2	1	2	2	3	?	?	?	2	2
Sediments (cont.)	2	3	1	2	2	3	1	2	?	?
(sequent.)	2	3	1	2	2	3	1	2	?	?

1 = ideal, 2 = tolerable, 3 = problematic

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4. Agenda

Aug 3, 2000

8:30	Opening Remarks	Kate Murphy
8:35	Overview	Greg Ruiz
8:50	USCG Programme Needs	Penny Herring
9:00	Assessment Process	Kate Murphy
9:10	Metals, isotopes	Jay Cullen
9:40	Radium isotopes	Willard Moore
10:10	<i>Break</i>	
10:30	Pigments, Salinity responses	Larry Brand
11:00	DOM fluorescence	Paula Coble
11:30	Water clarity	Mark Geiger
12:00	<i>Lunch</i>	
1:00	Lignin	Patrick Louchouart
1:30	Fecal-derived sterols	Jae Ryoung Oh
2:00	Phytoplankton	Pat Tester
2:30	<i>Break</i>	
2:50	Bacteria	Fred Dobbs
3:20	Summary and Conclusions	SERC
3:50	Closing Remarks	Greg Ruiz / Kate Murphy

Aug 4, 2000

8:30	Opening Remarks	Kate Murphy / Greg Ruiz
8:45	The Australian Experience	Chad Hewitt
9:15	Evaluation session	open discussion
10:10	<i>Break</i>	
10:30	Evaluation session	open discussion
12:00	<i>Lunch</i>	
1:00	Evaluation session	open discussion
2:30	Evaluation session	close

5. Workshop Participant List

Larry Brand
University of Miami
RSMAS
4600 Rickenbacker Cswy.
Miami, FL 33149
Ph. 305-361-4138
FAX 305-361-4600
lbrand@rsmas.miami.edu

Richard A. Everett
Commandant (G-MSO-4)
U. S. Coast Guard
2100 Second Street, SW
Washington, DC 20593
Ph. 202-267-2243
FAX 202-267-4690
REverett@comdt.uscg.mil

Paula Coble
University of South Florida
Department of Marine Science
140 Seventh Ave. S
St. Petersburg, FL 33705
Ph. 727-553-1631
FAX 727-553-1189
pcoble@marine.usf.edu

Mark Geiger
Naval Oceanographic Office
Laboratory Branch, Code N931
Stennis Space Center, MS 39522.5001
Ph. 228-688-5645
FAX 228-688-4632
geigerm@navont3.navy.navy.mil

Jay T. Cullen
Rutgers University
Institute of Marine and Coastal Sciences
71 Dudley Road
New Brunswick, NJ 08901
Ph. 732-932-6555 x222
FAX 732-932-8578
cullen@imcs.rutgers.edu

Penny Herring
USCG Research and Development Center
1082 Shennecossett Rd
Avery Point
Groton CT 06340
Ph. 860-441-2868
PHerring@rdc.uscg.mil

Fred C. Dobbs
Old Dominion University
Department of Ocean, Earth and
Atmospheric Sciences
4600 Elkhorn Avenue
Norfolk, VA 23529-0276
Ph. 757-683-5329
FAX 757-683-5303
fdobbs@odu.edu

Chad L. Hewitt
Centre for Research on Introduced Marine
Pests, CSIRO
GPO Box 1538
Hobart, Tasmania 7001
AUSTRALIA
Ph. +61(3) 6232 5102
FAX +61(3) 6232 5485
Chad.Hewitt@marine.csiro.au

Robert R. Hiltabrand
USCG Research and Development Center
1082 Shennecossett Rd
Avery Point
Groton CT 06340
Ph. 860-441-2701
rhiltabrand@rdc.uscg.mil

Kate Murphy
Smithsonian Environmental Research Center
PO Box 28
Edgewater, MD 21037-0028
Ph. 410-798-4424 x 361
FAX 301-261-7954
murphy@serc.si.edu

Patrick Louchouart
Conrad Blucher Institute for Surveying and
Science
Department of Environmental Sciences
Texas A&M University-Corpus Christi
6300 Ocean Drive
Corpus Christi, Texas 78412-5503
Ph. 361-825-3254
FAX 361-825-2715
loup@cbi.tamucc.edu

Jae Ryoung OH
KORDI, Chemical Oceanography Div.
Ansan P.O.Box 29
Seoul 425-600
Kyunggido
Korea
Ph. +82-31-400-6162
FAX +82-31-406-4250
jroh@sari.kordi.re.kr

Whitman Miller
Smithsonian Environmental Research Center
PO Box 28
Edgewater, MD 21037-0028
Ph. 410-798-4424 x 439
FAX 301-261-7954
miller@serc.si.edu

Gregory Ruiz
Smithsonian Environmental Research Center
PO Box 28
Edgewater, MD 21037-0028
Ph. 410-798-4424 x 227
FAX 301-261-7954
ruiz@serc.si.edu

LT Mary Pat McKeown
Commandant (G-MSO-4)
2100 Second St. SW
Washington, DC 20593
Ph. 202-267-0500
FAX 202-267-4690
mmckeown@comdt.uscg.mil

Patricia A. Tester
National Ocean Service, NOAA
101 Pivers Island Rd., Beaufort, NC 28516
Ph. 252-728-8792
FAX 252-728-8784
pat.testler@noaa.gov

Willard S. Moore
University of South Carolina
Department of Geological Sciences
Columbia, SC 29208
Ph. 803-777-2262
moore@geol.sc.edu

Appendix B

CDOM (EEMs) Fluorescence Analysis and Data Correction

Instrumentation

Excitation-emission matrices (EEMs) were generated on a SPEX Fluorolog-2 Spectrofluorometer (JY-SPEX, Edison, NJ). Experiments were run in ratio mode with a 0.5 second integration time and a 5 nm bandwidth for both excitation and emission. Analyses covered the UV-visible region of the spectrum (Table B-1), with forty-eight emission scans collected at an excitation range covering 220-455 nm in 5 nm increments and an emission range of 250-700 nm collected every 2 nm. The Fluorolog-2 is equipped with a 450-Watt Xenon arc lamp, a single excitation monochromator (1200 grooves/mm) blazed at 250 nm and a double emission monochromator (1200 grooves/mm) blazed at 330 nm. The detector is a red-sensitive photomultiplier tube (Hamamatsu type R928) that is cooled by a thermocouple device and a mixture of water:ethylene glycol coolant held at 19 °C.

All post-collection data manipulation used GRAMS Version 5.2 software (Galactic Industries, Salem, NH). Excitation emission matrices (EEMs) were generated by concatenating the 48 individual emission spectra.

Data correction

All data were normalized to the intensity of the water Raman scatter peak at Ex/Em 275/303, which was determined daily. The water Raman peak was also used to calibrate fluorescence versus that of a standard, quinine sulfate dihydrate. A MilliQ water blank was subtracted to eliminate water Raman scatter peaks and correct for instrument baseline.

Spectra were corrected for effects due to wavelength dependent efficiencies of the instrumental components (gratings, mirror, lamps, etc.) on both excitation emission intensities. Emission correction factors were generated by scanning the emission of a standardized 200-watt quartz-halogen tungsten coiled filament lamp (Optronic Laboratory Model 220M) operated at 6.50 amp at a distance of 50 cm. Values obtained were then divided into the known irradiance values of the lamp at each wavelength and normalized to produce correction factors. This procedure was done once only and should remain constant as long as none of the optical components are changed.

Excitation correction was used to account for the differences in optical path between the reference quantum counter and the sample. An identical solution of Rhodamine B (8 g/L laser grade quality in ethylene glycol) was placed in both reference and sample cuvettes and an excitation spectrum was

collected between 200 and 600 nm with emission at 630 nm. The spectrum was inverted and normalized to produce excitation correction factors.

Standard curves were run using quinine sulfate dihydrate in 0.05 M H₂SO₄. Quinine sulfate fluorescence was corrected as described above, and the fluorescence intensity at Ex/Em 350/450 was used to generate a regression line. The slope of the regression line was used to normalize all corrected EEMs to quinine sulfate equivalents (QSE).

Determination of Peaks A and C

The peaks referred to in this report are areas of maximum fluorescence intensity that have been identified in the corrected EEMs. Peak A represents the area of highest CDOM fluorescence intensity observed in the EEM due to excitation at UV-C wavelengths used in this experiment (220-280 nm). Peak C represents the area of maximum CDOM fluorescence intensity observed in the EEM due to excitation at UV-B and UV-A wavelengths (280-390 nm). Table B-1 provides the complete range of wavelength classifications used in these experiments. Peak A generally shows the total maximum fluorescence intensity for the entire matrix. In the case of peak C, the intensity maximum is actually a local peak, a shoulder next to peak A.

Table B-1. Spectrum classifications for the wavelengths used in this work.

Spectrum Region	Wavelength Range (nm)
UV-C	200-280
UV-B	280-320
UV-A	320-390
Visible	390-800

Specifically, the single maximum intensity value and the wavelength pair responsible for each peak, A and C, is determined as follows:

A corrected EEM is opened in GRAMS (or any compatible software) and viewed as a Contour plot (Figure B-1, also seen in the upper portion of the EEM plots in the cruise data appendices). A contour plot displays all the excitation/emission wavelength pairs as a 2D intensity map that allows focus on the areas of maximum intensity in each peak region. For Peak A, this intensity maximum generally occurs between Excitation 230-265 nm and Emission 380-460 nm. In the case of Figure B-1, the maximum intensity in the Peak A region is seen in shades of yellow and gray between Ex: 245-265 nm and Em: 410-460 nm. The maximum intensity in the Peak C region is seen in shades of bright blue between Ex:

290-315 nm and Em: 390-430 nm. The maximum intensity point occurs in the center of the spherical peak regions observed in the contour plot, and the excitation/emission wavelength pair exhibiting maximum fluorescence intensity in each peak region can be determined.

In selecting the actual maximum wavelength pair, GRAMS allows the display of each individual emission scan within the EEM, along with its corresponding wavelength and intensity data. Figure B-2 shows the Peak A information for the contour map in Figure B-1. By paging through emission scans sequentially, the area of maximum fluorescence indicated in the contour map can be reached. The excitation wavelength used to collect the scan, the emission wavelength of maximum fluorescence, and the intensity at that wavelength are then recorded as Peak A (or C, depending on the wavelength region being examined).

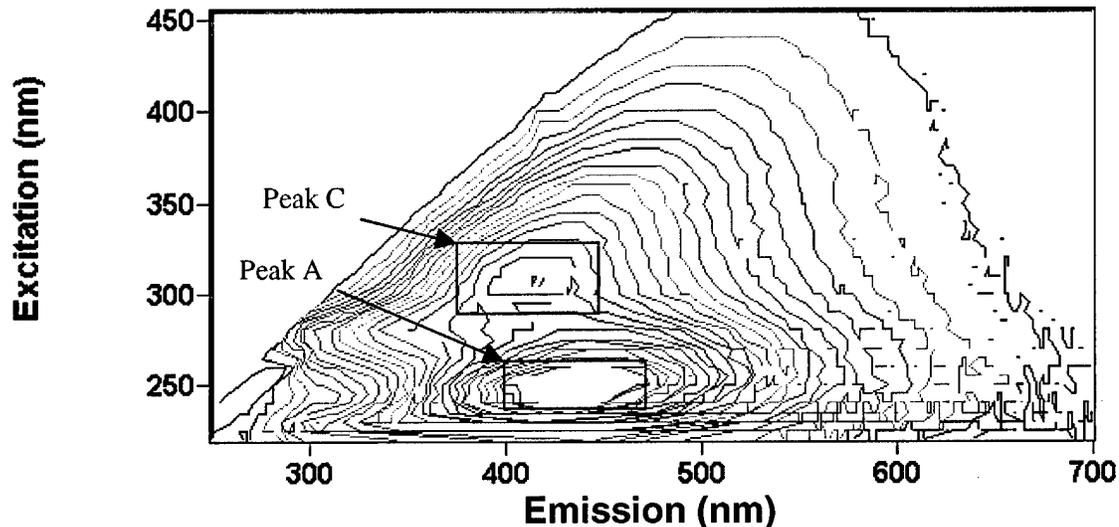
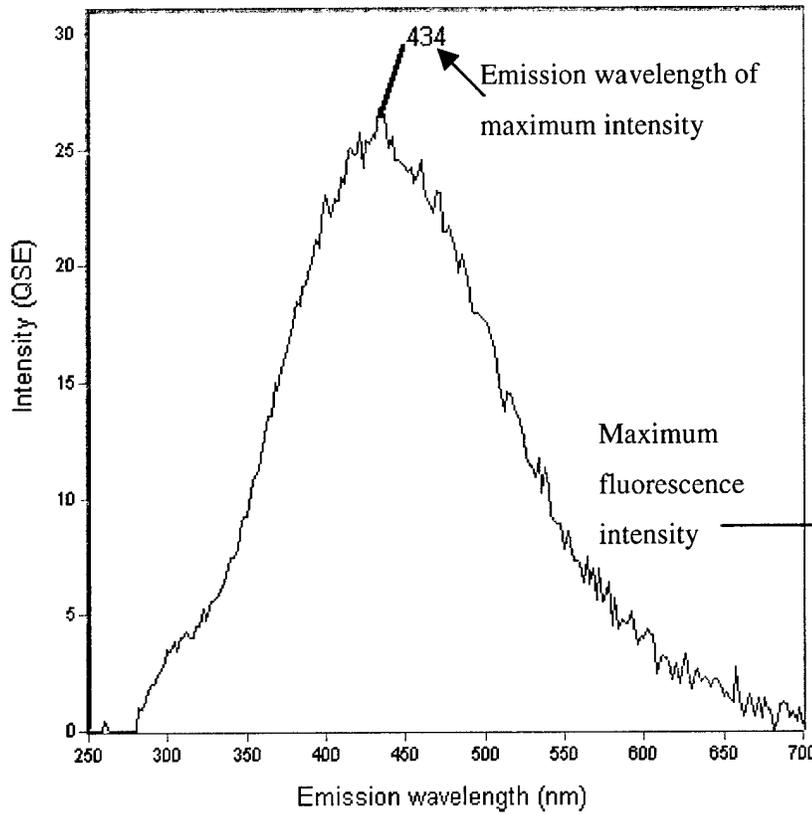


Figure B-1. Contour plot of VFos sample 1013.



Wavelength / Intensity

X Value	Y Value
394	21.0714035
396	20.74874306
398	21.95319557
400	23.00328636
402	22.35056877
404	22.10975838
406	22.90922165
408	22.77115822
410	23.77395439
412	23.5451889
414	24.92440987
416	25.04971695
418	24.82857704
420	24.87388992
422	25.68590927
424	24.24373627
426	25.41862869
428	25.20962334
430	25.64602335
432	25.43431664
434	26.70630455
436	26.40699959
438	26.46484947
440	25.00804138
442	25.56742668
444	24.5471859
446	24.57055283
448	24.35103416
450	24.25667572
452	24.07215881
454	24.22377205
456	23.50122452
458	23.96574402
460	24.51965141
462	23.36192131
464	22.74716949
466	22.46548058
468	22.28117371
470	23.19114685

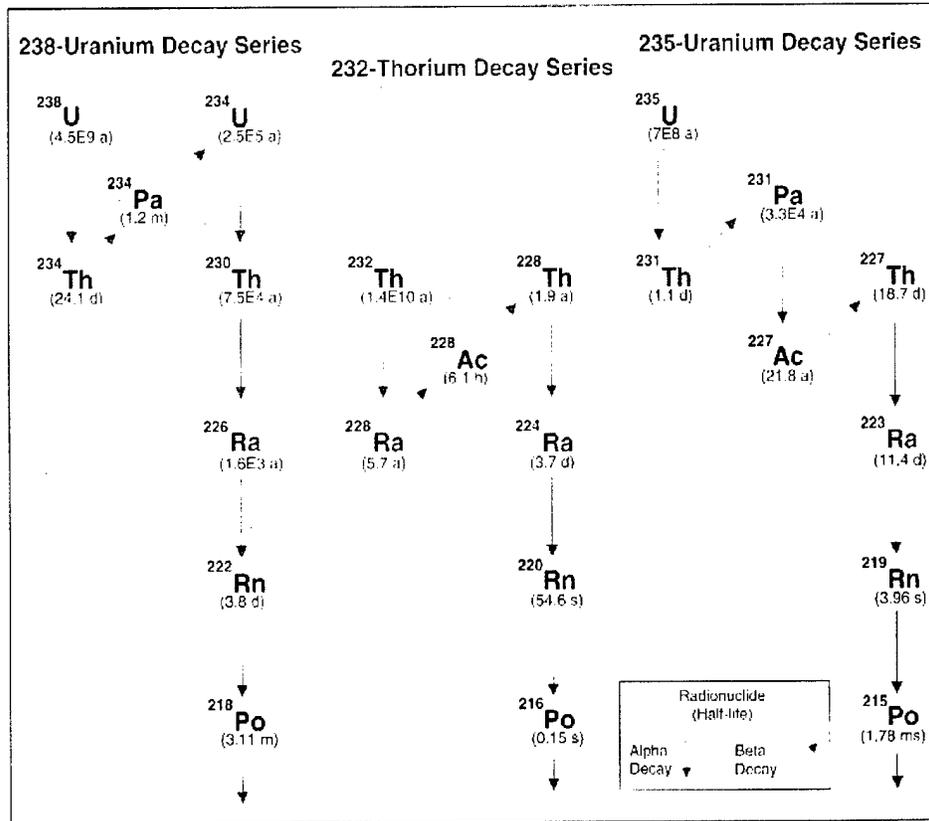
File # 1 : 1013VFQ#7 @250 Nanometers

Excitation wavelength

Figure B-2. Emission scan from center of Peak A contour.

Appendix C

Isotopes of the U and Th Decay Series



Source: Table of Radioactive Isotopes by E. Browne and R.B. Firestone, John Wiley & Sons, NY, 1986 as presented in <http://sofia.usgs.gov/publications/fs/65-99/index.html>.

Appendix D

Univariate Analyses of Pacific and Atlantic Ballast Water Exchange Experiments

This table tallies the statistical results of univariate comparisons between tracer levels in 4 pairs of ballast tanks on VFos and oceanic values from the Atlantic ocean reference sets. Significant differences are tallied next to the corresponding probability statistic (either $p < 0.05$, $p < 0.01$, $p < 0.001$ or “nsd” (not significantly different)).

I. Atlantic Experiment

Cruise	Treat	Time	probability	Aqse	Cqse	Aemx	Ba	Mh	Mo	P	U	V	salinity	Total	
VFos	FT	T0	0.001	1			4	4		2			4	31	
			0.01	2	1					1				1	
		T1	0.05	1	3	4				4	1	4	4		3
			nsd	1	3	4									21
		T2	0.001	1				4	4	3				2	29
			0.01	1										1	2
	T3	0.05	1						4	1	4	4	1	2	
		nsd	2	4	4								4	23	
		0.001	4	4	4			2	3	1				19	
		0.01	1				1	1		1				8	
	ER	T3	0.05	1				1	1		2			1	5
			nsd	4	4	4				4	4	4	4		24
0.001									4					4	
0.01														3	
0.05			4	4	4			4	4	4	4	4	2	7	
nsd			4	4	4									42	
C	T0-T3	0.001	1				1							5	
		0.01	3				3	3	1			1		9	
		0.05	1				1	3	3			3		8	
		nsd	4	4	4					4	4	4	4	34	
		0.001	16				16	16	15				16	128	
		0.01	11						1					12	
		0.05	4						16		16	16		4	
			nsd	16	16	16							80		

This table tallies the statistical results of univariate comparisons between tracer levels in ballast tanks on VSF, VLA and VPS and oceanic values from the Pacific ocean reference sets. Significant differences are tallied next to the corresponding probability statistic (either $p < 0.05$, $p < 0.01$, $p < 0.001$) or "nsd" (not significantly different).

II. Pacific Experiments

a. Control Tanks

Cruise	Time	probability	Aqse	Aexx	Aemx	Cqse	Cexx	Cemx	Ba	Mn	Mo	P	V	Salinity	Ra-223	Th-228	Total	
VSF	T0-T3	0.001							4	4		4	4	4	3	1	24	
		0.01									4				1	2	7	
		0.05	4				1									1		6
		nsd		4	4	4	4	3										19
VLA	T0-T2	0.001							3	1			1		3	3	3	
		0.01								2		2	2				8	
		0.05																6
		nsd	3	3	3	3	3				3	1			3			25
VPS	T0-T1	0.01							2		1	2		1			6	
		0.05									1			1			2	
		nsd	2	2	2	2	2	2		2								16

b. Empty-Refill Tanks

VPS	T0	0.01							1		1	1					3	
		0.05								1				1				2
	T1	nsd	1	1	1	1	1						1					7
		0.01									1							1
VSF	T0	0.05								1		1	1	1			1	1
		nsd	1	1	1	1	1						1	1				10
		0.001								1	1	1	1	1	1	1	1	
	T1	0.01										1						1
		0.05																1
		nsd																1
		0.05	1															1
T3	nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		14
	nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		14
	nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		14

c. Flow-Through Tanks

Cruise	Time	probability	Aqse	Aexx	Aemx	Cqse	Cexx	Cemx	Ba	Mn	Mo	P	V	Salinity	Ra -223	Th-228	Total
VLA	T0	0.001													1		1
		0.01							1								1
		0.05								1				1		1	3
		nsd	1	1	1	1	1	1			1	1					9
	T1	0.05													1		1
		nsd	1	1	1	1	1	1	1	1	1	1	1	1		1	13
VSF	T2	nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	14
	T0	0.001													1		8
		0.05	1														1
		nsd	1	1	1	1	1	1									5
	T1	0.001							1								1
		0.01								1	1	1	1	1	1	1	7
	T2	0.01															1
		0.05						1				1	1	1			4
		nsd	1	1	1	1	1	1		1	1				1	1	9
	T3	0.05							1								1
	nsd	1	1	1	1	1	1	1	1	1	1	1	1	1	1	13	

Abbreviations used in Appendix D tables:

Cruises 1-4: VSF, VLA, VPS, VFos

Treatments: Control (C), Empty-Refill (ER), Flow-Through (FT)

Replicate tank pairs 1-4 : W1, W2, W3, W4

Sampling Time Points: T0, T1, T2, T3

Tracers: CDOM - A and C Peak Intensity (qse), Excitation Maximum (exx), Emission Maximum (emx); Trace Metals - Barium (Ba), Manganese (Mn), Molybdenum (Mo), Phosphorus (P), Vanadium (V); Other - Radium (Ra-223), Thorium (Th-228)

Appendix E

Mahalanobis Distance Tests for Tracers in Ballast Water

a. Trace Metals

Cruise	Tank	Time	Treatment	Sal	SalBa	SalBaMn	SalBaPMn	SalMoBaPMn
VSF	-	0	C	0.001	0.001	0.001	0.001	0.001
VSF	-	1	C	0.001	0.001	0.001	0.001	0.001
VSF	-	2	C	0.001	0.001	0.001	0.001	0.001
VSF	-	3	C	0.001	0.001	0.001	0.001	0.001
VSF	-	0	FT	0.001	0.001	0.001	0.001	0.001
VSF	-	1	FT	0.001	0.001	0.001	0.001	0.001
VSF	-	2	FT	0.05	0.001	0.001	0.001	0.001
VSF	-	3	FT	0.1	0.001	0.001	0.001	0.001
VSF	-	0	ER	0.001	0.001	0.001	0.001	0.001
VSF	-	1	ER	1	1	1	0.05	0.05
VSF	-	3	ER	1	1	1	0.01	0.001
VLA	-	0	C	1	0.001	0.001	0.001	0.001
VLA	-	1	C	1	0.001	0.001	0.001	0.001
VLA	-	2	C	1	0.001	0.001	0.001	0.001
VLA	-	0	FT	1	0.001	0.001	0.001	0.001
VLA	-	1	FT	1	0.1	0.05	0.05	0.01
VLA	-	2	FT	1	1	0.1	1	0.1
VPS	-	0	C	0.001	0.001	0.001	0.001	0.001
VPS	-	1	C	0.01	0.001	0.001	0.001	0.001
VPS	-	0	ER	0.01	0.001	0.001	0.001	0.001
VPS	-	1	ER	1	1	0.01	0.001	0.001
VFos	W1	0	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	1	C	0.05	0.001	0.001	0.001	0.001
VFos	W2	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	2	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	3	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	4	ER	0.05	0.05	0.001	0.001	0.001
VFos	W2	4	ER	0.05	0.05	0.001	0.001	0.001
VFos	W3	4	ER	0.05	0.05	0.001	0.001	0.001
VFos	W4	4	ER	0.05	0.05	0.001	0.001	0.001
VFos	W1	0	FT	0.01	0.001	0.001	0.001	0.001
VFos	W2	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W3	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W4	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W1	1	FT	0.05	0.001	0.001	0.001	0.001
VFos	W2	1	FT	0.05	0.001	0.001	0.001	0.001
VFos	W3	1	FT	0.05	0.001	0.001	0.001	0.001
VFos	W4	1	FT	0.05	0.001	0.001	0.001	0.001
VFos	W1	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W2	2	FT	0.05	0.01	0.001	0.001	0.001
VFos	W3	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W4	2	FT	0.05	0.001	0.001	0.001	0.001
VFos	W1	3	FT	0.05	0.05	0.001	0.001	0.001
VFos	W2	3	FT	0.05	0.05	0.001	0.001	0.001
VFos	W3	3	FT	0.05	0.05	0.001	0.001	0.001
VFos	W4	3	FT	0.05	0.05	0.001	0.001	0.001

b. CDOM EEMs

Ship	Tank	Time	Treatment	Sal	SalAqse	SalCqse	SalAqseCqse	SalCemaxCqse
VSF	-	0	C	0.001	0.001	0.001	0.001	0.001
VSF	-	1	C	0.001	0.001	0.001	0.001	0.001
VSF	-	2	C	0.001	0.001	0.001	0.001	0.001
VSF	-	3	C	0.001	0.001	0.001	0.001	0.001
VSF	-	0	FT	0.001	0.001	0.001	0.001	0.001
VSF	-	1	FT	0.001	nd	nd	nd	nd
VSF	-	2	FT	0.05	0.05	0.05	0.001	0.001
VSF	-	3	FT	0.1	1	1	0.001	0.01
VSF	-	0	ER	0.001	0.001	0.001	0.001	0.001
VSF	-	1	ER	1	1	1	1	0.1
VSF	-	3	ER	1	1	1	1	1
VLA	-	0	C	1	1	1	0.001	1
VLA	-	1	C	1	1	1	0.001	1
VLA	-	2	C	1	nd	nd	nd	nd
VLA	-	0	FT	1	1	1	0.001	1
VLA	-	1	FT	1	1	1	0.05	0.05
VLA	-	2	FT	1	1	1	0.001	0.01
VPS	-	0	C	0.001	0.001	0.001	0.001	0.001
VPS	-	1	C	0.01	0.01	0.01	0.001	0.001
VPS	-	0	ER	0.01	0.01	0.01	0.001	0.001
VPS	-	1	ER	1	1	1	1	0.05
VFos	W1	0	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	0	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	1	C	0.05	0.001	0.001	0.001	0.001
VFos	W2	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	1	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	2	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	2	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	3	C	0.01	0.001	0.001	0.001	0.001
VFos	W2	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W3	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W4	3	C	0.001	0.001	0.001	0.001	0.001
VFos	W1	4	ER	0.05	0.05	0.01	0.001	0.01
VFos	W2	4	ER	0.05	0.05	0.05	0.001	0.05
VFos	W3	4	ER	0.05	0.05	0.05	0.05	0.05
VFos	W4	4	ER	0.05	0.05	0.05	0.001	0.001
VFos	W1	0	FT	0.01	0.001	0.001	0.001	0.001
VFos	W2	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W3	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W4	0	FT	0.001	0.001	0.001	0.001	0.001
VFos	W1	1	FT	0.05	0.05	0.001	0.001	0.001
VFos	W2	1	FT	0.05	0.01	0.001	0.001	0.001
VFos	W3	1	FT	0.05	0.05	0.001	0.001	0.001
VFos	W4	1	FT	0.05	0.001	0.001	0.001	0.001
VFos	W1	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W2	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W3	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W4	2	FT	0.05	0.05	0.001	0.001	0.001
VFos	W1	3	FT	0.05	0.05	0.001	0.001	0.05
VFos	W2	3	FT	0.05	0.05	0.05	0.01	0.01
VFos	W3	3	FT	0.05	0.05	0.001	0.001	0.001
VFos	W4	3	FT	0.05	0.05	0.05	0.001	0.001

nd = missing data

This table provides the statistical results from multivariate analysis comparisons between tracer levels in four pairs of ballast tanks on VFos and oceanic values from the Atlantic Ocean. The Mahalanobis distance statistic is significant at either $p < .05$, $p < .01$, $p < .001$. All distance statistics greater than 0.5 are designated as equal to 1. *nd* means missing data. The combinations of variables analyzed include salinity with trace minerals and salinity with CDOM EEMS.

Appendix F

Instrument Specifications

SBE 19 CTD

Manufacturer: SeaBird Electronics

The Sea-Bird SBE 19 was used on VPS and VLA cruises to collect salinity, temperature and depth data and to digitize and log data collected by the Wetlabs instruments (FLF and LSS). The instrument was succeeded on later cruises by the Minisonde CTD (see below).

Retail price ca. \$10,000

Flash Lamp Fluorometer

Manufacturer: Wetlabs Inc.

The Flash Lamp Fluorometer is designed to perform in-situ measurement of fluorescence in aquatic environments. The optical filters used in the fluorometer were selected for measurement of Colored Dissolved Organic Matter (CDOM) in water. The instrument must be used in conjunction with a data logger or Conductivity-Temperature-Depth meter (CTD).

Description: CDOM fluorometer

Signal output: 0–5 VDC

Optical filters:

Excitation—330 nm peak, 80 nm FWHM

Emission—450 nm peak, 65 nm FWHM

Power supply:

Voltage—12 VDC

Power—2 Watts

Material:

Housing—Celcon

Windows—acrylic

Weight:

in air—13 lbs (5.9 kg)

in water—7.1 lbs (3.2 kg)

Diameter: 4.75 in (12.1 cm)

Length: 15.5 in (39.4 cm)

Rated depth: 500 meters

Retail Price: \$4999 (Data logger additional, e.g. MPak III \$5150 or SBE 19 \$10,000)

Light Backscattering Sensor (LSS)

Manufacturer: Wetlabs Inc.

The Light Scattering Sensor (LSS) measures turbidity of suspended solids concentration ranging 2.5 to 750 Nephelometric Turbidity Units (NTU) and provides high resolution profiles of total suspended mass (> 0.002 NTU). It is capable of two remotely controlled measurement ranges — 0-7.5 and 0-25 NTU.

Users can specify either. The LSS is easily interfaced with current meters, CTDs, and recorders in the lab or field. Applications for the LSS include measuring visibility, microbial biomass, sediment transport, optical sediment traps, particle profiles, and microstructure mapping of plumes and fronts. This instrument must be used in conjunction with a data logger or CTD.

Specifications

Measured Parameters: Turbidity and suspended solids

Power: 9–18 VDC +/- 20 mA

Signal Output: 0–5 VDC

Temperature Stability: +/- 0.5 %, 0–50 °C

Power Supply: 9–18 VDC @ 24 mA

Power Consumption: ~200 mW

Sensor Output: 0–5 VDC

Mechanical

Length: 5 in (12.7 cm)

Diameter: 1.25 in (3.2 cm)

Weight in air: 0.57 lbs (0.26 kg) in water: 0.29 lbs (0.13 kg)

Housing material: ABS plastic housing filled with epoxy

Window material: clear epoxy optical

Rated Depth: 6000 meters

Optical

Resolution: < 0.03 % full scale

Measurement Range: ~ 2.25 NTU on high gain; ~ 7.5 NTU on low gain

Sample Volume Varies. Large for clean water; small for turbid water

Retail Price: \$ 899 (Data logger additional)

Minsonde 4a Multiprobe

Manufacturer: Hydrolab Inc.

This is a multi-sensor probe consisting of Conductivity / Temperature / Depth sensors with turbidity probe. Specifications for various parameters are provided in the table.

Mechanical:

Length: 24.5" (62.2 cm)

Diameter 1.75" (4.44 cm)

Weight: 2.46 lbs. (1.11 kg)

Maximum immersion depth: 200 meters

Operating temperature range: -5° to 50° C

Specifications

Parameter	Range	Accuracy	Resolution
Temperature	-5° to 50 °C	± 0.10 °C	0.01 °C
Specific Conductance	0 to 100 mS/cm	± 1 % of reading ± 0.001 mS/cm	4 digits
Dissolved Oxygen	0 to 50 mg/L	± 0.2 mg/L	0.01 mg/L
Depth / 0-25 m	0 to 25 m	± 0.08 m	0.01 m
Salinity	0 to 70 ppt	± 0.2 ppt	0.01 ppt
Turbidity	0 to 100 or 0-1000 NTU	± 5% of range	0.1 or 1 NTU
Barometric Pressure	500 to 850 mm mercury (Hg)	± 10 mm Hg	0.1 mm Hg

Retail price: \$4000

YSI Model 85 Dissolved Oxygen and Conductivity Meter

Manufacturer: YSI

This handheld instrument takes simultaneous measurements (in-situ) of dissolved oxygen (DO), conductivity, salinity and temperature. There is automatic salinity compensation for DO.

Power : Battery

Other Features : Handheld, backlit display, automatic temperature compensation

Specifications

Parameter	Range	Accuracy	Resolution
Specific Conductance	0 to 200 mS	$\pm 0.5 \%$	0.1 μ S
Salinity	0 to 80 ppt	$\pm 2 \%$ or ± 0.1 ppt	0.1 ppt
Temperature	-5 to 65 °C	$\pm 0.1^\circ\text{C}$	0.1 °C
Dissolved Oxygen	0-20 mg/L	± 0.3 mg/L	0.01 mg/L

Retail price (50 ft cable): \$1575

Appendix G

Ballast Exchange Position and Depth

Ballast exchange position and estimated water depth during exchange are provided below. 'Error' refers to the distance (km) between the position of the exchange and the closest position in the database of Smith & Sandwell (1997) from which depth estimates were obtained.

Cruise	Tank	Treatment	No.	(Commence Exchange)				(Conclude Exchange)			
				Longitude (° W)	Latitude (° N)	Depth (m)	Error (km)	Longitude (° W)	Latitude (° N)	Depth (m)	Error (km)
VLA		FT	1	127.40	39.35	4303	2.0				
		FT	2	128.25	39.50	4234	1.0				
		FT	3	132.20	45.00	3663	1.8				
VSF		FT	1	129.65	42.22	3246	0.3	132.87	45.43	3630	1.3
		FT	2	134.55	48.08	3729	0.0	135.40	49.10	3874	1.2
		FT	3	135.97	49.72	3628	1.6	136.73	50.60	3635	1.2
		ER	1	131.90	44.78	3642	1.5	130.17	42.87	3414	1.8
VPS		ER	1&2	128.42	49.10	2479	0.4	138.06	52.49	3350	0.7
VFos	1 & 5	FT	1	24.58	36.23	3458	0.3				
	1 & 5	FT	2	39.38	36.43	3828	1.5				
	1 & 5	ER	1	55.90	36.65	5391	1.7				
	2 & 3	FT	1	16.60	36.08	4569	2.0				
	2 & 3	FT	2	31.93	36.32	2919	1.7				
	2 & 3	ER	1	46.43	36.53	5042	1.4				
	Controls	(ER)	1	62.70	36.77	4954	1.6				

Appendix H

Coordinates of Shiptside Samples on the VFos Cruise.

SS Shiptside Samples	Longitude (°E, °W)	Latitude (°N)	Date
1	4.87	43.43	12-Jun-01
2	4.87	43.43	12-Jun-01
3	4.98	43.33	12-Jun-01
4	4.98	43.33	12-Jun-01
5	4.88	43.06	13-Jun-01
6	4.48	42.68	13-Jun-01
7	2.95	41.11	14-Jun-01
8	2.95	41.11	14-Jun-01
9	2.95	41.11	14-Jun-01
10	2.95	41.11	14-Jun-01
11	2.95	41.11	14-Jun-01
12	2.10	40.23	14-Jun-01
13	2.10	40.23	14-Jun-01
14	0.59	38.64	14-Jun-01
15	0.01	38.02	14-Jun-01
16	-2.96	36.37	15-Jun-01
17	-4.38	36.16	15-Jun-01
18	-4.39	36.16	15-Jun-01
19	-6.51	35.96	15-Jun-01
20	-8.27	35.99	16-Jun-01
21	-8.27	35.99	16-Jun-01
22	-9.36	36.01	16-Jun-01
23	-10.67	36.02	16-Jun-01
24	-13.92	36.07	16-Jun-01
25	-17.13	36.12	17-Jun-01
26	-17.13	36.12	17-Jun-01
27	-24.56	36.22	18-Jun-01
28	-28.67	36.28	18-Jun-01
29	-28.67	36.28	19-Jun-01
30	-35.37	36.36	19-Jun-01
31	-39.32	36.43	20-Jun-01
32	-42.18	36.47	20-Jun-01
33	-46.97	36.54	21-Jun-01

SS Shiptside Samples	Longitude (°E, °W)	Latitude (°N)	Date
34	-50.90	36.59	21-Jun-01
35	-54.72	36.65	22-Jun-01
36	-58.54	36.70	22-Jun-01
37	-62.52	36.76	23-Jun-01
38	-69.26	36.86	24-Jun-01
39	-72.49	36.91	24-Jun-01
40	-72.82	36.91	24-Jun-01
41	-73.10	36.90	25-Jun-01
42	-73.46	36.91	25-Jun-01
43	-73.70	36.91	25-Jun-01
44	-74.00	36.92	25-Jun-01
45	-74.33	36.92	25-Jun-01
46	-74.64	36.93	25-Jun-01
47	-74.93	36.93	25-Jun-01
48	-75.26	36.89	25-Jun-01
49	-75.62	36.83	25-Jun-01
50	-75.85	36.88	25-Jun-01
51	-76.01	36.95	25-Jun-01
52	-76.26	37.01	25-Jun-01
53	-76.40	36.95	25-Jun-01
54	-76.42	36.96	25-Jun-01

Appendix I

Raw Data: In-situ Measurements of Temperature, Salinity, CDOM Fluorescence and Turbidity in Ballast Water and Shipside Samples

VSF cruise data

Cruise	Time	Treatment	Location	Depth	Replicate	Temperature (°C)	Salinity (ppt)	CDOM (fls)	Turbidity (NTU)
VSF	T0	C	A	profile	1	14.65	22.5	256.51	nd
VSF	T1	C	A	profile	1	14.51	22.46	267.15	nd
VSF	T2	C	A	profile	1	13.59	22.46	268.11	nd
VSF	Tf	C	A	profile	1	12.4	22.46	271.12	nd
VSF	T0	ER	A	profile	1	14.62	21.83	269.65	nd
VSF	T1	ER	A	profile	1	12.7	32.41	16.9	nd
VSF	T1	FT	A	profile	1	14.81	27.09	142.54	nd
VSF	T2	FT	A	profile	1	12.22	30.68	60.26	nd
VSF	Tf	FT	A	profile	1	10.92	31.64	36.76	nd
VSF	T0	C	B	profile	1	14.65	22.5	256.51	nd
VSF	T1	C	B	profile	1	14.51	22.46	267.15	nd
VSF	T2	C	B	profile	1	13.59	22.46	268.11	nd
VSF	Tf	C	B	profile	1	12.4	22.46	271.12	nd
VSF	T0	ER	B	profile	1	14.62	21.83	269.65	nd
VSF	T1	ER	B	profile	1	12.7	32.41	16.9	nd
VSF	Tf	ER	B	profile	1	11.65	32.41	17.31	nd
VSF	T1	FT	B	profile	1	14.81	27.09	142.54	nd
VSF	T2	FT	B	profile	1	12.22	30.68	60.26	nd
VSF	S0	SS	0	5m	1	nd	32.4	nd	nd
VSF	S0	SS	0	5m	2	nd	32.4	nd	nd
VSF	S1	SS	1	5m	1	nd	33	nd	nd
VSF	S1	SS	1	5m	2	nd	33	nd	nd
VSF	S2	SS	2	5m	1	nd	31.8	nd	nd
VSF	S2	SS	2	5m	2	nd	31.8	nd	nd

VLA cruise data

Cruise	Time	Treatment	Location	Depth	Replicate	Temperature (°C)	Salinity (ppt)	CDOM (fls)	Turbidity (NTU)
VLA	T0	C	A	profile	1	15.20	33.36	189.95	3.12
VLA	T1	C	A	profile	1	14.28	33.31	197.94	4.32
VLA	T2	C	A	profile	1	12.64	33.10	206.82	3.59
VLA	T0	C	B	profile	1	15.20	33.36	189.95	3.12
VLA	T1	C	B	profile	1	14.28	33.31	197.94	4.32
VLA	T2	C	B	profile	1	12.64	33.10	206.82	3.59
VLA	T0	FT	A	profile	1	15.14	33.31	193.64	2.92
VLA	T1	FT	A	profile	1	13.83	32.92	85.77	3.83
VLA	T2	FT	A	profile	1	12.08	32.75	58.96	1.47
VLA	T0	FT	B	profile	1	15.14	33.31	193.64	2.92
VLA	T1	FT	B	profile	1	13.83	32.92	85.77	3.83
VLA	T2	FT	B	profile	1	12.08	32.75	58.96	1.47
VLA	T0.5	C	A	profile	1	14.75	33.26	196.65	2.41
VLA	T0.5	FT	A	profile	1	14.77	33.24	197.61	1.97
VLA	S1	SS	1	5m	1	nd	33.30	nd	nd
VLA	S2	SS	2	5m	1	nd	33.00	nd	nd

VPS cruise data

Cruise	Time	Treatment	Location	Depth	Replicate	Temperature (°C)	Salinity (ppt)	CDOM (fIS)	Turbidity (NTU)
VPS	T0	C	A	15m	1	nd	29	nd	nd
VPS	T0	ER	A	15m	1	nd	29.7	nd	nd
VPS	T1	C	A	15m	1	nd	29.9	nd	nd
VPS	T1	ER	A	15m	1	nd	32	nd	nd
VPS	T0	C	A	1m	1	nd	29.6	nd	nd
VPS	T0	ER	A	1m	1	nd	29.7	nd	nd
VPS	T1	C	A	1m	1	nd	29.9	nd	nd
VPS	T1	ER	A	1m	1	nd	32	nd	nd
VPS	S0	SS	1	5m	1	nd	32.2	nd	nd
VPS	S1	SS	1	5m	2	nd	32.2	nd	nd
VPS	S2	SS	2	5m	1	nd	32.3	nd	nd
VPS	S3	SS	2	5m	2	nd	32.3	nd	nd
VPS	S4	SS	3	5m	1	nd	31.9	nd	nd
VPS	S5	SS	3	5m	2	nd	31.9	nd	nd
VPS	S6	SS	4	5m	1	nd	31.6	nd	nd
VPS	S7	SS	4	5m	2	nd	31.6	nd	nd
VPS	S8	SS	5	5m	1	nd	30.8	nd	nd
VPS	S9	SS	5	5m	2	nd	30.8	nd	nd
VPS	S10	SS	6	5m	1	nd	30.8	nd	nd
VPS	S11	SS	6	5m	2	nd	30.8	nd	nd
VPS	S12	SS	7	5m	1	nd	13.7	nd	nd
VPS	S13	SS	7	5m	2	nd	30.8	nd	nd
VPS	S14	SS	8	5m	1	nd	29.7	nd	nd
VPS	S15	SS	8	5m	2	nd	29.7	nd	nd

VFos cruise Data

Ship	Tank*	Time	Treatment	Location	Depth	Replicate	Salinity (ppt)	Oxygen mg-at/L	Temperature (°C)	Turbidity (NTU)
VFos	-	S1	SS	1	5m	1	36.97	nd	nd	nd
VFos	-	S2	SS	2	5m	1	36.97	nd	nd	nd
VFos	-	S3	SS	3	5m	1	35.53	nd	nd	nd
VFos	-	S4	SS	4	5m	1	35.53	nd	nd	nd
VFos	-	S5	SS	5	5m	1	36.76	nd	nd	nd
VFos	-	S6	SS	6	5m	1	37.57	nd	nd	nd
VFos	-	S7	SS	7	5m	1	37.49	nd	nd	nd
VFos	-	S8	SS	8	5m	1	36.77	nd	nd	nd
VFos	-	S9	SS	9	5m	1	36.77	nd	nd	nd
VFos	-	S10	SS	10	5m	1	36.93	nd	nd	nd
VFos	-	S11	SS	11	5m	1	36.93	nd	nd	nd
VFos	-	S12	SS	12	5m	1	36.72	nd	nd	nd
VFos	-	S13	SS	13	5m	1	37.55	nd	nd	nd
VFos	-	S14	SS	14	5m	1	36.6	nd	nd	nd
VFos	-	S15	SS	15	5m	1	37.11	nd	nd	nd
VFos	-	S16	SS	16	5m	1	36.1	nd	nd	nd
VFos	-	S17	SS	17	5m	1	35.58	nd	nd	nd
VFos	-	S18	SS	18	5m	1	35.41	nd	nd	nd
VFos	-	S19	SS	19	5m	1	35.55	nd	nd	nd
VFos	-	S20	SS	20	5m	1	35.42	nd	nd	nd
VFos	-	S21	SS	21	5m	1	35.42	nd	nd	nd
VFos	-	S22	SS	22	5m	1	36.1	nd	nd	nd
VFos	-	S23	SS	23	5m	1	36.01	nd	nd	nd
VFos	-	S24	SS	24	5m	1	35.18	nd	nd	nd
VFos	-	S25	SS	25	5m	1	35.2	nd	nd	nd
VFos	-	S26	SS	26	5m	1	35.83	nd	nd	nd
VFos	-	S27	SS	27	5m	1	35.21	nd	nd	nd
VFos	-	S28	SS	28	5m	1	35.1	nd	nd	nd
VFos	-	S29	SS	29	5m	1	35.31	nd	nd	nd
VFos	-	S30	SS	30	5m	1	35.65	nd	nd	nd
VFos	-	S31	SS	31	5m	1	35.66	nd	nd	nd

VFos cruise data (continued).

Ship	Tank*	Time	Treatment	Location	Depth	Replicate	Salinity	Oxygen	Temperature	Turbidity
VFos	-	S32	SS	32	5m	1	35.65	nd	nd	nd
VFos	-	S33	SS	33	5m	1	35.53	nd	nd	nd
VFos	-	S34	SS	34	5m	1	35.5	nd	nd	nd
VFos	-	S35	SS	35	5m	1	35.12	nd	nd	nd
VFos	-	S36	SS	36	5m	1	36.3	nd	nd	nd
VFos	-	S37	SS	37	5m	1	35.9	nd	nd	nd
VFos	-	S38	SS	38	5m	1	35.49	nd	nd	nd
VFos	-	S39	SS	39	5m	1	35.3	nd	nd	nd
VFos	-	S40	SS	40	5m	1	35.56	nd	nd	nd
VFos	-	S41	SS	41	5m	1	34.96	nd	nd	nd
VFos	-	S42	SS	42	5m	1	33.98	nd	nd	nd
VFos	-	S43	SS	43	5m	1	34.73	nd	nd	nd
VFos	-	S44	SS	44	5m	1	34.6	nd	nd	nd
VFos	-	S45	SS	45	5m	1	34.61	nd	nd	nd
VFos	-	S46	SS	46	5m	1	33.91	nd	nd	nd
VFos	-	S47	SS	47	5m	1	31.56	nd	nd	nd
VFos	-	S48	SS	48	5m	1	30.64	nd	nd	nd
VFos	-	S49	SS	49	5m	1	29.88	nd	nd	nd
VFos	-	S50	SS	50	5m	1	28.64	nd	nd	nd
VFos	-	S51	SS	51	5m	1	25.15	nd	nd	nd
VFos	-	S52	SS	52	5m	1	20.76	nd	nd	nd
VFos	-	S53	SS	53	5m	1	19.2	nd	nd	nd
VFos	-	S54	SS	54	5m	1	18.16	nd	nd	nd
VFos	W1	T0	C	A	profile	1	37.2	7	19.4	nd
VFos	W1	T0	FT	A	profile	1	37.2	7	19.2	nd
VFos	W1	T1	C	A	profile	1	37.1	6.6	37.1	2.8
VFos	W1	T1	FT	A	profile	1	36.4	6.9	36.4	2.1
VFos	W1	T2	C	A	profile	1	37.3	6.4	22	2.7
VFos	W1	T2	FT	A	profile	1	36.5	6.7	21.5	1
VFos	W1	T3	C	A	profile	1	37.3	6.4	22.8	1.3
VFos	W1	T3	FT	A	profile	1	36.8	6.5	23.6	nd
VFos	W1	T4	C	A	profile	1	36.5	6.2	25.7	0.5
VFos	W2	T0	C	A	profile	1	37.6	6.9	18.7	nd
VFos	W2	T0	FT	A	profile	1	37.6	7.2	18.9	nd
VFos	W2	T1	C	A	profile	1	37.6	6.8	20.5	1.9
VFos	W2	T1	FT	A	profile	1	37.1	6.7	21.3	0.8
VFos	W2	T2	C	A	profile	1	37.7	6.7	20.8	4.8
VFos	W2	T2	FT	A	profile	1	36.7	6.8	21.4	2.4
VFos	W2	T3	C	A	profile	1	37.7	6.5	22.3	0.9
VFos	W2	T3	FT	A	profile	1	36.5	6.7	22.2	0.3
VFos	W2	T4	C	A	profile	1	36.5	6.1	26	0.5
VFos	W3	T0	C	A	profile	1	37.6	7	19.3	nd
VFos	W3	T0	FT	A	profile	1	37.6	7	19.1	nd
VFos	W3	T1	C	A	profile	1	37.7	6.8	20.8	1.1
VFos	W3	T1	FT	A	profile	1	36.9	6.8	21.2	1
VFos	W3	T2	C	A	profile	1	37.8	6.6	21.3	3.2
VFos	W3	T2	FT	A	profile	1	36.6	6.7	21.2	2.6
VFos	W3	T3	C	A	profile	1	37.7	6.5	22.7	0.4
VFos	W3	T3	FT	A	profile	1	36.5	6.7	22.1	0
VFos	W3	T4	C	A	profile	1	36.5	6.2	25.8	0.5
VFos	W4	T0	C	A	profile	1	37.7	7	19.7	nd
VFos	W4	T0	FT	A	profile	1	37.7	7.1	19.9	nd
VFos	W4	T1	C	A	profile	1	37.6	6.8	21.3	1.6
VFos	W4	T1	FT	A	profile	1	37	6.9	37	1.3
VFos	W4	T2	C	A	profile	1	37.8	6.5	21.7	1.4
VFos	W4	T2	FT	A	profile	1	36.9	6.7	22.3	1.1
VFos	W4	T3	C	A	profile	1	37.8	6.6	22.6	1.2
VFos	W4	T3	FT	A	profile	1	36.8	6.6	23.7	nd
VFos	W4	T4	C	A	profile	1	36.6	6.1	26.4	0.6

* Note that "-" indicates a shipside sample.

Appendix J

Raw Data: CDOM EEMs

VSF cruise data

Ship	Id #	Time	Treatment	Location	Depth	Replicate	A _{exx}	A _{emx}	A _{qse}	C _{exx}	C _{emx}	C _{qse}
VSF	517	S0	SS	0	5m	1	245	414.135	5.821	325	404.135	5.573
VSF	518	S0	SS	0	5m	2	245	412.144	6.163	325	400.144	5.771
VSF	519	S1	SS	1	5m	1	245	434.168	2.237	310	408.168	1.446
VSF	520	S1	SS	1	5m	2	250	430.183	2.001	300	406.183	1.214
VSF	522	S2	SS	2	5m	2	245	444	1.502	300	402	1.03
VSF	1	T0	C	A	1m	1	250	434.131	18.284	310	414.131	11.434
VSF	37	T0	C	B	1m	1	250	430.066	18.452	300	414.066	11.655
VSF	38	T0	C	B	15m	1	250	436.105	19.133	300	416.105	11.937
VSF	3	T0	ER	A	1m	1	245	424.144	18.688	300	414.144	11.766
VSF	4	T0	ER	A	15m	1	250	434.107	20.607	295	416.107	12.489
VSF	39	T0	ER	B	1m	1	250	432.125	17.628	300	416.125	11.448
VSF	40	T0	ER	B	15m	1	250	432.086	19.661	300	416.086	12.177
VSF	6	T0	FT	A	15m	1	250	438.183	20.662	310	414.183	13.365
VSF	42	T0	FT	B	15m	1	255	440.077	20.289	305	418.077	13.462
VSF	7	T1	C	A	1m	1	250	434.175	19.017	300	422.175	11.952
VSF	43	T1	C	B	1m	1	250	432.147	16.406	310	422.147	10.657
VSF	44	T1	C	B	15m	1	250	424.129	18.696	310	416.129	11.32
VSF	9	T1	ER	A	1m	1	250	430.166	1.899	295	406.166	1.292
VSF	10	T1	ER	A	15m	1	250	432.354	1.754	300	400.354	0.904
VSF	45	T1	ER	B	15m	1	250	424.212	1.441	300	420.212	0.82
VSF	14	T2	C	A	15m	1	250	438.252	17.765	295	422.252	10.782
VSF	49	T2	C	B	1m	1	250	436.067	18.284	310	414.067	11.628
VSF	50	T2	C	B	15m	1	250	432.145	19.534	310	418.145	12.044
VSF	17	T2	FT	A	1m	1	245	430.178	5.171	300	424.178	3.147
VSF	18	T2	FT	A	15m	1	245	436.237	4.994	315	420.237	2.912
VSF	53	T2	FT	B	1m	1	250	434.209	5.14	310	414.209	2.855
VSF	54	T2	FT	B	15m	1	245	438.461	6.159	305	420.461	3.765
VSF	31	Tf	C	A	1m	1	250	428.283	18.103	305	422.283	12.021
VSF	32	Tf	C	A	15m	1	250	430.155	18.471	300	410.155	11.155
VSF	67	Tf	C	B	1m	1	250	434.137	23.565	300	408.137	15.907
VSF	68	Tf	C	B	15m	1	250	432.226	19.231	310	422.226	12.562
VSF	34	Tf	ER	A	15m	1	250	426.133	1.755	300	396.133	1.011
VSF	69	Tf	ER	B	1m	1	245	444.253	1.255	305	412.253	0.86
VSF	70	Tf	ER	B	15m	1	250	426.207	1.671	305	410.207	0.941
VSF	35	Tf	FT	A	1m	1	245	422.371	3.081	300	410.371	2.203
VSF	36	Tf	FT	A	15m	1	250	428.004	4.271	300	408.004	2.833
VSF	71	Tf	FT	B	1m	1	250	418.167	2.971	310	412.167	1.538
VSF	72	Tf	FT	B	15m	1	250	424.255	3.106	300	406.255	1.977

VLA cruise data

Ship	Id #	Time	Treatment	Location	Depth	Replicate	Aexmax	Aemax	Aqse	Cexmax	Cemax	Cqse
VLA	517	S1	SS	1	5m	1	245	376.11	1.66	300	396.11	0.80
VLA	518	S1	SS	1	5m	2	250	438.11	1.91	320	428.11	1.00
VLA	519	S2	SS	2	5m	1	245	410.25	2.36	310	416.25	1.10
VLA	520	S2	SS	2	5m	2	250	422.11	4.59	305	404.11	2.46
VLA	37	T0	C	B	1m	1	245	406.00	4.54	305	400.00	2.43
VLA	38	T0	C	B	15m	1	245	414.19	5.04	305	402.19	2.74
VLA	2	T0	C	A	15m	1	250	422.00	4.38	305	408.00	2.53
VLA	41	T0	FT	B	1m	1	245	412.08	3.86	310	414.08	2.05
VLA	42	T0	FT	B	15m	1	250	418.20	5.02	310	406.20	2.65
VLA	5	T0	FT	A	1m	1	245	434.08	4.06	310	414.08	2.08
VLA	6	T0	FT	A	15m	1	250	428.00	6.72	310	406.00	3.53
VLA	1	T0	C	A	1m	1	245	420.12	4.08	310	408.12	2.46
VLA	43	T1	C	B	1m	1	245	416.20	5.22	315	418.20	2.76
VLA	44	T1	C	B	15m	1	250	424.33	5.87	320	410.33	3.56
VLA	7	T1	C	A	1m	1	250	434.17	4.97	320	402.17	2.60
VLA	8	T1	C	A	15m	1	260	440.14	5.08	315	398.14	3.16
VLA	47	T1	FT	B	1m	1	250	430.25	2.32	310	410.25	1.43
VLA	48	T1	FT	B	15m	1	250	428.31	2.86	310	416.31	1.72
VLA	11	T1	FT	A	1m	1	250	426.00	2.93	320	418.00	1.62
VLA	12	T1	FT	A	15m	1	250	430.21	2.51	310	402.21	1.51
VLA	54	T2	FT	B	15m	1	245	424.10	1.94	300	392.10	1.09
VLA	17	T2	FT	A	1m	1	245	424.10	1.94	305	398.10	1.04
VLA	18	T2	FT	A	15m	1	245	414.19	5.02	305	396.19	2.64

VPS cruise data

Ship	Id #	Time	Treatment	Location	Depth	Rep.	Aexx	Aemx	Aqse	Cexx	Cemx	Cqse	a(280)	a(312)	a(412)
VPS	6001	S0	SS	1	5m	1	255	438.20	1.20	300	420.20	0.81	1.13	0.48	0.15
VPS	6002	S1	SS	1	5m	2	250	440.00	1.28	300	384.00	0.94	1.16	0.51	0.18
VPS	6003	S2	SS	2	5m	1	255	444.16	1.23	300	402.16	0.93	1.11	0.48	0.12
VPS	6004	S3	SS	2	5m	2	250	454.00	1.87	305	394.00	1.64	2.69	1.38	0.54
VPS	6005	S4	SS	3	5m	1	260	442.18	1.14	300	408.18	1.00	1.01	0.42	0.11
VPS	6006	S5	SS	3	5m	2	260	442.26	1.05	300	382.26	0.88	0.92	0.39	0.12
VPS	6007	S6	SS	4	5m	1	250	446.15	1.87	305	412.15	1.05	2.34	1.19	0.39
VPS	6008	S7	SS	4	5m	2	260	460.17	1.45	300	412.17	1.12	1.40	0.67	0.18
VPS	6009	S8	SS	5	5m	1	250	445.94	2.55	315	397.94	1.91	4.50	2.47	1.00
VPS	6010	S9	SS	5	5m	2	250	445.82	2.42	305	393.82	1.42	4.26	2.27	0.88
VPS	6011	S10	SS	6	5m	1	235	406.26	5.95	295	408.26	16.19	1.26	0.58	0.13
VPS	6012	S11	SS	6	5m	2	250	446.25	1.44	305	422.25	1.03	1.55	0.73	0.19
VPS	6013	S12	SS	7	5m	1	260	448.20	2.31	310	414.20	1.39	3.20	1.83	0.68
VPS	6014	S13	SS	7	5m	2	255	454.21	1.99	305	414.21	1.47	1.95	0.96	0.26
VPS	6016	S14	SS	8	5m	1	255	458.00	1.84	305	410.00	1.25	1.58	0.74	0.18
VPS	6017	S15	SS	8	5m	2	250	450.20	2.04	305	410.20	1.25	1.78	0.84	0.22
VPS	6029	T0	C	A	1m	1	250	434.09	5.99	305	408.09	4.02	3.97	2.17	0.60
VPS	6030	T0	C	A	1m	2	250	436.19	6.02	310	422.19	4.20	3.84	1.94	0.51
VPS	6031	T0	C	A	15m	1	250	440.12	5.64	305	414.12	3.83	2.83	1.53	0.33
VPS	6032	T0	C	A	15m	2	250	444.00	5.55	305	422.00	3.66	2.72	1.45	0.29
VPS	6033	T0	C	B	1m	1	250	438.11	6.15	310	416.11	4.00	3.05	1.67	0.40
VPS	6034	T0	C	B	1m	2	260	443.86	6.16	305	415.86	4.45	4.75	2.55	0.73
VPS	6036	T0	C	B	15m	2	250	436.00	6.59	305	406.00	4.68	3.67	2.01	0.52
VPS	6037	T1	C	A	1m	1	250	446.21	4.96	305	422.21	3.48	2.71	1.48	0.36
VPS	6038	T1	C	A	1m	2	250	440.13	5.57	310	416.13	3.76	2.73	1.50	0.37
VPS	6039	T1	C	A	15m	1	250	442.26	5.61	310	408.26	3.62	2.68	1.44	0.33
VPS	6040	T1	C	A	15m	2	250	442.00	5.38	310	416.00	3.61	2.66	1.42	0.31
VPS	6041	T1	C	B	1m	1	250	444.00	5.45	310	414.00	3.52	2.51	1.33	0.26
VPS	6043	T1	C	B	15m	1	250	444.00	5.41	305	410.00	3.47	3.29	1.84	0.47
VPS	6044	T1	C	B	15m	2	250	442.00	5.20	305	416.00	3.74	2.47	1.31	0.25
VPS	6054	T0	ER	A	1m	2	250	440.00	5.91	305	406.00	4.42	4.63	2.43	0.70
VPS	6055	T0	ER	A	15m	1	250	440.00	5.45	305	416.00	3.92	7.62	4.57	1.74
VPS	6056	T0	ER	A	15m	2	250	440.00	5.63	305	414.00	3.82	6.13	3.43	1.15
VPS	6057	T0	ER	B	1m	1	250	441.94	5.80	305	413.94	3.80	4.70	2.59	0.81
VPS	6058	T0	ER	B	1m	2	255	448.15	5.76	305	414.15	3.93	3.28	1.79	0.42
VPS	6059	T0	ER	B	15m	1	250	440.00	6.27	305	408.00	4.32	6.25	3.44	1.19
VPS	6060	T0	ER	B	15m	2	250	443.85	7.28	305	407.85	4.93	6.92	3.86	1.30
VPS	6061	T1	ER	A	1m	1	260	446.18	1.52	300	392.18	1.06	1.14	0.47	0.10
VPS	6062	T1	ER	A	1m	2	250	440.27	1.86	305	414.27	1.16	1.13	0.49	0.11
VPS	6063	T1	ER	A	15m	1	250	438.30	1.66	300	414.30	0.96	1.20	0.57	0.16
VPS	6064	T1	ER	A	15m	2	255	450.21	1.55	305	418.21	0.98	1.25	0.56	0.16
VPS	6065	T1	ER	B	1m	1	255	444.21	1.53	305	408.21	1.08	1.21	0.56	0.14
VPS	6066	T1	ER	B	1m	2	250	448.16	1.89	300	400.16	1.09	1.31	0.62	0.18
VPS	6067	T1	ER	B	15m	1	250	436.00	1.95	310	416.00	1.14	0.93	0.37	0.08
VPS	6068	T1	ER	B	15m	2	250	444.17	1.84	300	416.17	1.00	0.77	0.24	0.04
VPS	6138	preb	C	A	-	2	250	450.25	0.17	300	402.25	0.31	0.11	0.03	0.00
VPS	6156	bl	ER	A	-	2	250	450.24	0.39	310	414.24	0.45	nd	nd	nd

VFos cruise data

Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexx	Aemx	Aqse	Cexx	Cemx	Cqse	a(280)	a(312)	a(412)
VFos	121	W1	T1	C	A	1	245	422.13	8.92	315	392.13	3.02	1.61	0.8	0.2
VFos	122	W1	T1	C	A	2	250	421.94	7.6	315	391.94	2.9	1.66	0.85	0.23
VFos	123	W1	T1	C	B	1	245	426.13	8.83	315	390.13	3.17	2.51	1.34	0.42
VFos	124	W1	T1	C	B	2	250	415.89	7.17	315	389.89	2.66	1.95	1.06	0.33
VFos	125	W2	T1	C	A	1	250	438.06	6.18	315	392.06	2.19	1.28	0.6	0.15
VFos	126	W2	T1	C	A	2	250	414	7.73	315	390.00	2.99	1.15	0.47	0.12
VFos	127	W2	T1	C	B	1	245	426.1	8.24	315	392.10	2.88	1.7	0.87	0.24
VFos	128	W2	T1	C	B	2	250	413.92	7.16	320	393.92	2.77	1.68	0.79	0.23
VFos	129	W3	T1	C	A	1	245	420.14	6.9	315	392.14	2.61	1.4	0.63	0.14
VFos	130	W3	T1	C	A	2	250	413.98	5.46	310	389.98	1.87	0.98	0.36	0.07
VFos	131	W3	T1	C	B	1	250	433.96	6.9	315	387.96	2.65	2.41	1.36	0.47
VFos	132	W3	T1	C	B	2	250	437.95	5.97	315	391.95	2.06	1.14	0.44	0.1
VFos	137	W4	T1	C	A	1	245	430	8.57	315	390.00	2.77	2.19	1.17	0.37
VFos	138	W4	T1	C	A	2	250	417.98	7.35	315	389.98	2.49	1.48	0.66	0.19
VFos	139	W4	T1	C	B	1	245	414	8.45	315	392.00	3.01	2.08	1.13	0.36
VFos	140	W4	T1	C	B	2	250	413.95	7.87	325	405.95	2.32	1.4	0.62	0.17
VFos	141	W1	T1	FT	A	1	245	418.1	9.28	315	392.10	3.04	1.99	1.03	0.3
VFos	142	W1	T1	FT	A	2	250	414	5	310	408.00	1.86	2.19	1.2	0.4
VFos	143	W1	T1	FT	B	1	235	370	45.85	315	370.00	14.9	1.97	1	0.27
VFos	144	W1	T1	FT	B	2	250	413.92	24.63	315	373.92	6.31	1.87	0.98	0.28
VFos	145	W2	T1	FT	A	1	245	414.06	6.78	310	406.06	2.35	1.5	0.74	0.2
VFos	146	W2	T1	FT	A	2	250	415.97	5.05	310	403.97	1.8	1.09	0.51	0.12
VFos	147	W2	T1	FT	B	1	245	422.11	7.77	315	408.11	2.65	2.21	1.2	0.39
VFos	148	W2	T1	FT	B	2	250	435.93	7.13	310	391.93	2.55	1.5	0.75	0.2
VFos	149	W3	T1	FT	A	1	245	414.09	6.37	315	390.09	2.22	1.37	0.64	0.16
VFos	150	W3	T1	FT	A	2	250	419.93	5.38	315	391.93	2.02	0.99	0.37	0.07
VFos	151	W3	T1	FT	B	1	245	414	7.55	320	372.00	2.97	2.24	1.23	0.4
VFos	152	W3	T1	FT	B	2	250	415.9	4.99	310	401.90	1.97	1.23	0.5	0.14
VFos	157	W4	T1	FT	A	1	245	414	7.48	315	388.00	2.81	1.9	0.99	0.31
VFos	158	W4	T1	FT	A	2	250	439.9	6.4	320	391.90	2.38	1.52	0.78	0.24
VFos	160	W4	T1	FT	B	2	245	414	7.63	315	386.00	2.84	2.26	1.28	0.43
VFos	217	W1	T2	C	A	1	250	414.38	12.09	315	390.38	5.14	3.37	1.93	0.67
VFos	218	W1	T2	C	A	2	250	411.85	9.92	320	395.85	3.53	2.74	1.47	0.5
VFos	219	W1	T2	C	B	1	250	412.36	8.05	315	390.36	3.76	2.18	1.19	0.36
VFos	220	W1	T2	C	B	2	250	407.96	12	325	391.96	3.77	1.92	0.93	0.24
VFos	221	W2	T2	C	A	1	250	414.34	8.68	310	390.34	3.14	2.54	1.43	0.5
VFos	222	W2	T2	C	A	2	250	417.86	7.41	320	397.86	2.63	2.34	1.31	0.45
VFos	223	W2	T2	C	B	1	250	426.42	6.18	320	394.42	2.87	1.33	0.66	0.23
VFos	224	W2	T2	C	B	2	250	415.98	7.18	315	407.98	2.52	2.21	1.22	0.4
VFos	225	W3	T2	C	A	1	250	414.49	9.81	320	392.00	4.02	2.4	1.34	0.45
VFos	226	W3	T2	C	A	2	250	415.83	9.27	315	391.83	3.25	2.07	1.07	0.37
VFos	227	W3	T2	C	B	1	250	413.79	8.31	325	401.79	2.84	3.4	1.97	0.7
VFos	228	W3	T2	C	B	2	250	413.89	8.72	315	389.89	3.13	1.95	0.98	0.32

VFos cruise data (continued).

Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexx	Aemx	Aqse	Cexx	Cemx	Cqse	a(280)	a(312)	a(412)
VFos	233	W4	T2	C	A	1	250	413.21	9.7	325	389.21	3.93	2.44	1.37	0.45
VFos	234	W4	T2	C	A	2	250	407.97	5.23	320	391.97	2.7	1.3	0.55	0.14
VFos	235	W4	T2	C	B	1	250	415.13	8.3	315	389.13	3.88	2.38	1.31	0.45
VFos	236	W4	T2	C	B	2	250	405.97	5.52	315	389.97	2.75	1.52	0.7	0.2
VFos	237	W1	T2	FT	A	1	250	410.31	8.23	315	374.31	4.22	2.43	1.35	0.45
VFos	238	W1	T2	FT	A	2	250	411.96	7.51	315	393.96	2.61	1.4	0.64	0.17
VFos	239	W1	T2	FT	B	1	250	414.42	5.46	315	386.42	1.98	1.78	0.95	0.3
VFos	240	W1	T2	FT	B	2	250	413.86	4.9	315	389.86	1.82	1.24	0.52	0.18
VFos	241	W2	T2	FT	A	1	250	414.35	6.25	320	392.35	2.47	1.96	1.06	0.38
VFos	242	W2	T2	FT	A	2	250	413.91	5.29	310	399.91	1.81	1.35	0.62	0.18
VFos	243	W2	T2	FT	B	1	250	412.34	5.86	315	390.34	2.54	2.2	1.28	0.47
VFos	244	W2	T2	FT	B	2	250	415.84	5.6	315	395.84	2.21	1.98	1.11	0.4
VFos	245	W3	T2	FT	A	1	250	416.15	4.74	315	392.15	1.83	1.28	0.61	0.2
VFos	246	W3	T2	FT	A	2	250	417.96	5.09	315	387.96	1.58	1.03	0.46	0.11
VFos	247	W3	T2	FT	B	1	250	414.39	5.79	300	406.39	2.44	1.21	0.59	0.19
VFos	248	W3	T2	FT	B	2	250	413.95	4.91	315	385.95	1.69	1.32	0.62	0.19
VFos	253	W4	T2	FT	A	1	250	433.86	6.8	315	391.86	2.74	2.3	1.27	0.43
VFos	254	W4	T2	FT	A	2	250	413.93	6.41	320	391.93	2.76	2.22	1.19	0.42
VFos	255	W4	T2	FT	B	1	250	418.02	3.84	325	390.02	1.75	1.59	0.8	0.28
VFos	256	W4	T2	FT	B	2	240	337.96	30.49	325	379.96	1.85	0.92	0.33	0.06
VFos	313	W1	T3	C	A	1	250	412.35	10.02	320	400.35	3.7	1.9	1.05	0.31
VFos	314	W1	T3	C	A	2	250	413.96	7.46	325	403.96	3.19	1.41	0.61	0.14
VFos	315	W1	T3	C	B	1	250	412.38	10.74	320	392.38	4.84	3.19	1.8	0.61
VFos	316	W1	T3	C	B	2	250	413.92	9.32	320	389.92	4.11	1.92	0.97	0.28
VFos	317	W2	T3	C	A	1	250	435.19	8.77	320	407.19	3.41	2.28	1.24	0.4
VFos	318	W2	T3	C	A	2	250	413.96	6.87	315	401.96	2.65	1.68	0.8	0.23
VFos	319	W2	T3	C	B	1	250	411.98	9.57	320	385.98	4.62	3.68	2.18	0.84
VFos	320	W2	T3	C	B	2	250	413.85	7.28	315	389.85	2.9	2.66	1.41	0.49
VFos	321	W3	T3	C	A	1	250	415.23	7.8	320	391.23	2.7	1.48	0.78	0.22
VFos	322	W3	T3	C	A	2	250	417.97	6.51	320	397.97	2.64	1.61	0.85	0.24
VFos	323	W3	T3	C	B	1	250	415.17	8.86	320	391.17	3.2	2.28	1.26	0.41
VFos	324	W3	T3	C	B	2	250	411.84	8.41	320	391.84	3.33	2.67	1.52	0.49
VFos	329	W4	T3	C	A	1	250	416	10	315	390.00	4.7	2.48	1.41	0.46
VFos	330	W4	T3	C	A	2	250	415.86	8	315	389.86	3.51	3.04	1.71	0.57
VFos	331	W4	T3	C	B	1	250	412.24	9.5	320	388.24	4.31	3.34	2.09	0.84
VFos	332	W4	T3	C	B	2	250	415.83	8.92	315	389.83	3.89	2.81	1.62	0.55
VFos	333	W1	T3	FT	A	1	250	414.4	4.63	325	408.40	1.81	1.4	0.72	0.24
VFos	334	W1	T3	FT	A	2	250	422	2.98	320	390.00	1.15	0.72	0.21	0.05
VFos	335	W1	T3	FT	B	1	250	433.14	4.25	315	397.14	1.65	1.2	0.59	0.19
VFos	336	W1	T3	FT	B	2	250	421.87	3.77	320	395.87	1.44	1.15	0.49	0.15
VFos	337	W2	T3	FT	A	1	250	433.96	4.53	320	401.96	1.5	1.58	0.84	0.28
VFos	338	W2	T3	FT	A	2	250	413.94	4.22	315	387.94	1.66	1.02	0.45	0.11
VFos	339	W2	T3	FT	B	1	250	418	4.97	320	390.00	2	2.19	1.27	0.5

VFos cruise CDOM data (continued).

Cqse	Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexx	Aemx	Aqse	Cexx	Cemx	a(280)	a(312)	a(412)
1.86	VFos	340	W2	T3	FT	B	2	250	413.96	4.29	320	391.96	1.31	0.6	0.22
1.87	VFos	341	W3	T3	FT	A	1	250	415.24	3.84	315	373.24	1.47	0.8	0.28
1.46	VFos	342	W3	T3	FT	A	2	250	409.99	3.44	315	391.99	1.1	0.5	0.15
1.62	VFos	343	W3	T3	FT	B	1	250	410.39	4.26	315	394.39	1.27	0.63	0.23
1.36	VFos	344	W3	T3	FT	B	2	250	413.93	3.39	315	369.93	0.94	0.41	0.11
2.25	VFos	349	W4	T3	FT	A	1	250	419.07	4.37	315	389.07	1.04	0.5	0.15
2.02	VFos	350	W4	T3	FT	A	2	250	421.83	4.01	320	391.83	1.89	1.08	0.4
1.96	VFos	351	W4	T3	FT	B	1	250	413.92	4.36	315	393.92	1.18	0.6	0.19
1.93	VFos	352	W4	T3	FT	B	2	250	421.95	3.9	315	393.95	1.39	0.7	0.22
3.79	VFos	409	W1	T4	C	A	1	250	416	10.23	315	400.00	1.71	0.88	0.22
3.64	VFos	410	W1	T4	C	A	2	255	408	7.85	315	398.00	1.62	0.84	0.21
3.88	VFos	411	W1	T4	C	B	1	245	410	9.73	315	402.00	2.34	1.27	0.37
4.25	VFos	412	W1	T4	C	B	2	250	413.87	11.72	315	401.87	2.65	1.48	0.48
3.12	VFos	413	W2	T4	C	A	1	250	414	8.31	315	406.00	2.53	1.4	0.47
3.2	VFos	414	W2	T4	C	A	2	250	413.85	7.79	315	397.85	1.89	1.03	0.32
3.63	VFos	415	W2	T4	C	B	1	245	414	8.78	320	402.00	2.18	1.19	0.37
2.67	VFos	416	W2	T4	C	B	2	250	417.94	7.38	315	395.94	1.64	0.89	0.26
3.53	VFos	417	W3	T4	C	A	1	250	414.33	9.13	315	394.33	2.36	1.33	0.46
2.92	VFos	418	W3	T4	C	A	2	250	411.94	8.43	320	405.94	2.2	1.21	0.37
4.16	VFos	419	W3	T4	C	B	1	245	415.93	9.83	315	403.93	3.68	2.1	0.72
3.21	VFos	420	W3	T4	C	B	2	250	411.91	8.57	320	397.91	2.44	1.4	0.46
3.44	VFos	425	W4	T4	C	A	1	250	414	8.24	315	408.00	2.39	1.33	0.43
3.06	VFos	426	W4	T4	C	A	2	250	413.83	8.53	320	403.83	2.6	1.44	0.48
3.36	VFos	427	W4	T4	C	B	1	250	412	8.64	315	406.00	1.96	1.04	0.3
2.83	VFos	428	W4	T4	C	B	2	250	417.94	7.93	320	401.94	1.84	1	0.3
3.26	VFos	429	W1	T4	FT	A	1	240	372	4.24	300	352.00	0.81	0.31	0.07
0.66	VFos	430	W1	T4	FT	A	2	250	405.83	1.68	320	395.83	0.73	0.3	0.1
0.72	VFos	431	W1	T4	FT	B	1	240	344	5.37	325	404.00	0.68	0.23	0.06
1.04	VFos	432	W1	T4	FT	B	2	250	411.98	2.94	325	409.98	0.71	0.27	0.07
1.23	VFos	433	W2	T4	FT	A	1	245	414.06	1.5	330	390.00	0.64	0.22	0.05
0.65	VFos	434	W2	T4	FT	A	2	250	433.96	1.59	315	383.96	0.96	0.49	0.19
0.78	VFos	435	W2	T4	FT	B	1	245	410.05	1.46	300	356.05	0.69	0.25	0.06
0.81	VFos	436	W2	T4	FT	B	2	245	403.89	1.64	315	371.89	0.82	0.37	0.14
1.36	VFos	437	W3	T4	FT	A	1	235	372.08	4.29	325	390.00	0.88	0.38	0.11
1.16	VFos	438	W3	T4	FT	A	2	245	433.94	1.58	300	349.94	0.48	0.07	0
0.63	VFos	439	W3	T4	FT	B	1	245	414.05	1.89	325	406.05	2.39	1.33	0.43
0.73	VFos	440	W3	T4	FT	B	2	245	419.96	2.19	325	409.96	0.85	0.37	0.12
0.99	VFos	445	W4	T4	FT	A	1	240	416.05	2.15	320	400.05	1.06	0.5	0.17
0.62	VFos	446	W4	T4	FT	A	2	250	411.87	1.49	320	395.87	0.72	0.31	0.08
0.79	VFos	447	W4	T4	FT	B	1	245	428	1.81	320	390.00	0.82	0.33	0.1
0.72	VFos	448	W4	T4	FT	B	2	250	413.27	1.78	325	401.27	0.95	0.39	0.14
0.91	VFos	505	W1	T5	C	A	1	250	411.25	2.36	325	409.25	1.02	0.51	0.18
0.85	VFos	506	W1	T5	C	A	2	250	407.95	2.26	325	395.95	0.85	0.35	0.1

VFos cruise CDOM data (continued).

Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexx	Aemx	Aqse	Cexx	Cemx	Cqse	a(280)	a(312)	a(412)
VFos	507	W1	T5	C	B	1	250	411.33	2.08	320	375.33	0.8	0.77	0.31	0.1
VFos	508	W1	T5	C	B	2	250	417.92	1.96	325	387.92	0.67	0.79	0.3	0.09
VFos	509	W2	T5	C	A	1	250	406	2.13	330	390.00	0.78	0.69	0.27	0.09
VFos	510	W2	T5	C	A	2	250	418.02	1.93	310	386.02	1.04	0.91	0.35	0.11
VFos	511	W2	T5	C	B	1	250	409.9	2.86	300	351.90	1.32	0.57	0.19	0.06
VFos	512	W2	T5	C	B	2	250	407.92	2.36	300	371.92	0.92	0.69	0.26	0.08
VFos	513	W3	T5	C	A	1	250	409.98	2.5	300	355.98	1.67	0.71	0.28	0.09
VFos	514	W3	T5	C	A	2	250	407.92	2.1	325	389.92	0.71	0.82	0.33	0.1
VFos	515	W3	T5	C	B	1	250	408	2.32	300	352.00	2.35	0.7	0.27	0.08
VFos	516	W3	T5	C	B	2	250	427.93	1.77	300	351.93	1.78	0.68	0.22	0.04
VFos	521	W4	T5	C	A	1	250	416	2.37	300	350.00	1.29	0.94	0.42	0.15
VFos	522	W4	T5	C	A	2	250	409.91	1.66	300	351.91	1.22	0.77	0.3	0.09
VFos	523	W4	T5	C	B	1	250	411.99	4.27	300	351.99	8.03	0.85	0.39	0.14
VFos	524	W4	T5	C	B	2	250	411.95	2.92	315	389.95	1.08	0.87	0.38	0.13
VFos	853	W4	preb	C	A	1	235	366.17	0.84	300	350.17	0.25	-0.09	-0.1	-0.02
VFos	877	-	S1	SS	1	1	250	403.95	2.76	305	407.95	1.71	1.6	0.75	0.14
VFos	878	-	S2	SS	2	1	240	418	2.9	305	408.00	1.64	1.82	0.86	0.19
VFos	879	-	S3	SS	3	1	245	405.95	2.23	305	409.95	1.35	1.58	0.71	0.12
VFos	880	-	S4	SS	4	1	240	428	1.72	300	406.00	1.08	1.6	0.72	0.15
VFos	881	-	S5	SS	5	1	245	430	1.83	310	408.00	1.05	1.52	0.62	0.07
VFos	882	-	S6	SS	6	1	240	384.13	2.8	300	406.13	1.53	2.19	0.9	0.17
VFos	883	-	S7	SS	7	1	225	300.02	10.34	270	298.02	9.81	1.53	0.63	0.07
VFos	884	-	S8	SS	8	1	240	422.28	2.79	305	416.28	1.72	1.35	0.54	0.14
VFos	885	-	S9	SS	9	1	220	298.34	72.89	270	298.34	66.2	1.33	0.46	0.09
VFos	886	-	S10	SS	10	1	240	422.05	1.56	320	422.05	0.78	1.56	0.63	0.08
VFos	887	-	S11	SS	11	1	245	422.09	1.79	320	428.09	1.11	1.79	0.69	0.06
VFos	888	-	S12	SS	12	1	240	430	2.4	315	422.00	1.26	1.03	0.34	0.07
VFos	889	-	S13	SS	13	1	245	416.08	1.94	325	412.08	1.02	2.09	0.85	0.07
VFos	890	-	S14	SS	14	1	245	428	2.15	310	420.00	1.27	1.14	0.39	0.07
VFos	891	-	S15	SS	15	1	240	396	2.09	310	398.00	0.99	0.96	0.36	0.07
VFos	892	-	S16	SS	16	1	245	434.06	1.52	325	414.06	0.75	0.95	0.38	0.08
VFos	893	-	S17	SS	17	1	245	430.05	1.53	310	412.05	0.92	0.85	0.3	0.04
VFos	894	-	S18	SS	18	1	245	430	2.12	325	416.00	1.01	0.97	0.35	0.06
VFos	895	-	S19	SS	19	1	240	436.08	1.46	320	416.08	0.73	0.85	0.29	0.04
VFos	896	-	S20	SS	20	1	245	432	1.03	320	414.00	0.59	0.93	0.33	0.08
VFos	897	-	S21	SS	21	1	240	396	1.67	300	346.00	2.59	0.96	0.36	0.06
VFos	898	-	S22	SS	22	1	235	414	3.23	295	402.00	3.16	1.12	0.43	0.1
VFos	899	-	S23	SS	23	1	240	406.08	1.17	300	354.08	1.07	0.71	0.21	0.02
VFos	900	-	S24	SS	24	1	245	436.08	1.62	300	360.08	1.15	0.82	0.3	0.07
VFos	901	-	S25	SS	25	1	245	413.97	0.87	300	401.97	0.51	0.73	0.25	0.06
VFos	902	-	S26	SS	26	1	240	432.13	1.5	325	422.13	0.63	0.52	0.11	0.02
VFos	903	-	S27	SS	27	1	250	432.08	0.94	300	408.08	0.52	0.6	0.17	0.01
VFos	904	-	S28	SS	28	1	245	474.11	0.55	330	406.11	0.35	0.75	0.3	0.04

VFos cruise data (continued).

Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexmax	Aemax	Aqse	Cxmax	Cemax	Cqse	a(280)	a(312)	a(412)
VFos	905	-	S29	SS	29	1	235	338.01	4.81	325	414.01	0.7	0.67	0.21	0.03
VFos	906	-	S30	SS	30	1	240	408.14	0.91	300	388.14	0.57	0.76	0.28	0.07
VFos	907	-	S31	SS	31	1	245	436.05	0.86	300	352.05	1	0.62	0.18	0.02
VFos	908	-	S32	SS	32	1	245	436.19	1.79	300	402.19	1.31	0.84	0.31	0.06
VFos	909	-	S33	SS	33	1	245	422.06	1.27	295	402.06	0.93	0.65	0.2	0.02
VFos	910	-	S34	SS	34	1	245	476.15	0.74	330	394.15	0.38	0.63	0.19	0.02
VFos	911	-	S35	SS	35	1	240	410.08	2.06	295	410.08	2.16	0.77	0.26	0.06
VFos	912	-	S36	SS	36	1	245	428.23	0.95	300	408.23	0.62	0.58	0.12	0.03
VFos	913	-	S37	SS	37	1	245	428.03	1.47	300	348.03	3.29	0.85	0.29	0.07
VFos	914	-	S38	SS	38	1	235	410.15	7.7	300	404.15	7.99	0.63	0.14	0.02
VFos	915	-	S39	SS	39	1	240	336	14.79	300	336.00	22.64	0.92	0.33	0.06
VFos	916	-	S40	SS	40	1	235	404.16	6.83	300	338.16	11.69	0.98	0.31	0.05
VFos	917	-	S41	SS	41	1	245	418.02	2.39	310	406.02	1.59	1.23	0.45	0.08
VFos	918	-	S42	SS	42	1	245	438.2	2.19	320	416.20	1.03	1.02	0.27	0.03
VFos	919	-	S43	SS	43	1	245	422.09	2.63	320	416.09	1.38	1.31	0.48	0.09
VFos	920	-	S44	SS	44	1	250	444.14	1.59	325	414.14	0.66	0.95	0.24	0.03
VFos	921	-	S45	SS	45	1	240	424.11	2.18	300	396.11	1.25	1.01	0.34	0.06
VFos	922	-	S46	SS	46	1	240	434	2.53	300	414.00	1.45	1.21	0.37	0.05
VFos	923	-	S47	SS	47	1	240	424.04	4.73	305	400.04	2.89	2.54	1.12	0.22
VFos	924	-	S48	SS	48	1	240	422.2	6.1	300	410.20	3.58	3.02	1.24	0.19
VFos	925	-	S49	SS	49	1	255	432.02	5.47	325	410.02	2.92	3	1.36	0.28
VFos	926	-	S50	SS	50	1	245	440.12	6.93	300	404.12	3.98	3.43	1.52	0.26
VFos	1011	-	S51	SS	51	1	250	444.02	13.92	305	398.02	8.46	6.22	3.3	0.78
VFos	1012	-	S52	SS	52	1	245	436	19.81	305	416.00	11.49	8.21	4.05	0.79
VFos	1013	-	S53	SS	53	1	250	434	26.71	305	416.00	15.36	9.02	4.67	0.96
VFos	1014	-	S54	SS	54	1	250	434	23.77	300	418.00	14.14	9.47	4.92	0.94
VFos	41	W1	bl	C	A	1	240	338	40.73	300	338.00	63.37	1.06	0.58	0.17
VFos	42	W1	bl	C	A	2	235	398.15	16.47	295	404.15	35.22	3.21	0.71	0.08
VFos	51	W1	bl	C	B	1	230	296.01	11.77	270	294.01	21.65	1.11	0.5	0.14
VFos	52	W1	bl	C	B	2	225	294.01	6.02	270	288.01	16.73	0.8	0.35	0.09
VFos	55	W3	bl	C	B	1	225	298.1	7.86	270	294.10	7.9	0.12	0.07	0.03
VFos	56	W3	bl	C	B	2	240	336.19	39.77	300	338.19	60.84	2.16	0.61	0.13
VFos	61	W1	bl	FT	A	1	240	338.17	10.85	300	16.07	16.07	0.82	0.34	0.13
VFos	62	W1	bl	FT	A	2	240	338	55.67	300	338.00	87.39	3.55	1.47	0.28
VFos	63	W2	bl	FT	B	1	225	296.15	26.43	270	298.15	26.14	0.55	0.32	0.17
VFos	64	W2	bl	FT	B	2	225	298.14	22.98	270	298.14	24.56	0.54	0.32	0.18
VFos	65	W3	bl	FT	A	1	230	302.17	15.12	270	302.17	15.4	0.48	0.29	0.11
VFos	66	W3	bl	FT	A	2	225	296.27	32.48	270	300.27	37.47	1.76	0.45	0.08
VFos	69	W4	bl	FT	A	1	240	336.16	31.39	300	338.16	51.98	0.64	0.27	0.07
VFos	70	W4	bl	FT	A	2	225	298.07	3.86	270	290.07	5.71	0.24	0.14	0.06
VFos	71	W1	bl	FT	B	1	225	298.06	4.53	270	294.06	4.63	0.18	0.09	0.03
VFos	72	W1	bl	FT	B	2	225	300.11	6.42	270	298.11	7.76	0.35	0.19	0.08
VFos	851	W3	preb	C	B	1	225	300.11	7.77	275	298.11	7.23	0.06	0.02	0.01

VFos cruise data (continued).

Ship	Id #	Tank	Time	Treat.	Loc.	Rep.	Aexmax	Aemax	Aqse	Cxmax	Cemax	Cqse	a(280)	a(312)	a(412)
VFos	859	W2	preb	FT	B	1	225	302.04	5.61	275	298.04	4.87	0.24	0.17	0.08
VFos	861	W3	preb	FT	A	1	230	297.99	1.02	280	303.99	1.02	0.03	0.02	0.02
VFos	865	W4	preb	FT	A	1	225	296.05	8.08	275	298.05	8.27	0.12	0.04	0.02
VFos	866	W4	preb	FT	A	2	240	335.99	19.57	300	331.99	25.53	0.29	0.11	0.02
VFos	-	W1	bl	C	A	1	225	302.13	15.85	270	298.13	15.95	0.23	0.11	0.04
VFos	-	W1	bl	C	A	2	225	298.08	4.35	270	300.08	4.26	0.26	0.17	0.09

Appendix K

Raw Data: Trace Metals

VLA cruise data (unfiltered samples)

Ship	id	Time	Treatment	Location	Depth	Rep.	Mo	Cd	Sb	Ba	Pb	P	V	Cr	Mn	Fe	Co	Ni	Cu
VLA	181	T0	C	A	1m	1	12.40	0.13	0.25	9.47	0.42	37.90	2.83	0.75	13.20	749.00	0.14	4.53	4.38
VLA	182	T0	C	A	15m	1	14.10	0.18	0.25	9.96	0.28	30.50	2.53	0.77	9.92	84.40	0.13	1.57	3.49
VLA	187	T1	C	A	1m	1	12.60	0.20	0.35	11.10	1.09	64.70	4.65	1.30	34.10	688.00	0.27	4.65	9.27
VLA	188	T1	C	A	15m	1	13.40	0.20	0.22	9.37	0.26	35.10	2.55	0.75	10.50	117.00	0.13	1.71	3.15
VLA	193	T2	C	A	1m	1	13.80	0.27	0.25	10.20	0.41	44.70	3.14	0.80	15.40	197.00	0.15	2.74	4.70
VLA	194	T2	C	A	15m	1	12.40	0.20	0.22	9.32	0.19	34.10	2.42	0.76	9.46	88.00	0.12	1.42	3.00
VLA	217	T0	C	B	1m	1	13.60	0.19	0.26	11.00	1.04	46.30	3.19	0.98	18.90	260.00	0.15	2.68	9.30
VLA	218	T0	C	B	15m	1	13.80	0.16	0.25	9.48	0.33	29.90	2.73	0.81	10.50	100.00	0.11	1.89	3.77
VLA	223	T1	C	B	1m	1	13.80	0.23	0.23	9.43	0.27	34.50	2.57	0.71	10.10	114.00	0.15	2.31	3.32
VLA	224	T1	C	B	15m	1	12.90	0.20	0.25	10.20	0.85	71.80	4.09	0.96	25.50	502.00	0.19	3.50	7.46
VLA	229	T2	C	B	1m	1	13.10	0.18	0.27	10.00	0.38	39.30	2.95	0.89	16.60	243.00	0.14	2.55	4.66
VLA	230	T2	C	B	15m	1	12.10	0.20	0.23	10.40	0.66	49.40	3.27	0.92	21.40	362.00	0.16	2.69	6.20
VLA	532	S1	SS	1	5m	1	13.30	0.10	0.19	6.27	0.39	16.00	1.58	0.73	5.87	356.00	0.08	2.79	7.94
VLA	533	S2	SS	2	5m	1	13.60	0.11	0.19	6.31	0.44	14.90	1.73	0.62	4.34	221.00	0.08	2.43	8.42
VLA	534	S1	SS	1	5m	2	12.10	0.06	0.18	6.17	0.22	23.70	1.62	0.77	2.40	81.70	0.04	1.22	2.80
VLA	535	S2	SS	2	5m	2	13.40	0.09	0.19	6.31	0.22	21.80	1.80	0.87	2.27	74.40	0.08	2.18	2.67
VLA	185	T0	FT	A	1m	1	14.30	0.21	0.27	10.20	0.50	40.40	2.93	1.02	15.50	192.00	0.13	2.36	5.21
VLA	186	T0	FT	A	15m	1	13.30	0.23	0.23	9.23	0.28	30.70	2.26	0.77	9.06	97.30	0.12	1.43	3.21
VLA	191	T1	FT	A	1m	1	13.80	0.20	0.21	7.67	0.33	24.70	2.22	0.65	4.64	82.10	0.10	2.16	2.87
VLA	192	T1	FT	A	15m	1	13.60	0.18	0.19	7.45	0.21	24.30	2.23	0.67	4.28	56.90	0.10	1.78	1.98
VLA	197	T2	FT	A	1m	1	12.70	0.14	0.19	6.82	0.11	23.10	2.04	0.70	3.10	53.00	0.04	1.07	1.55
VLA	198	T2	FT	A	15m	1	12.50	0.14	0.18	7.48	0.12	25.10	1.96	0.66	3.36	75.30	0.08	1.47	1.47
VLA	221	T0	FT	B	1m	1	14.10	0.21	0.28	10.60	0.55	39.80	3.14	0.88	16.80	198.00	0.14	2.43	5.24
VLA	222	T0	FT	B	15m	1	13.40	0.25	0.25	9.09	0.24	30.20	2.95	0.70	8.75	123.00	0.15	2.50	3.43
VLA	227	T1	FT	B	1m	1	13.30	0.16	0.19	7.54	0.19	23.20	2.16	0.67	4.16	93.00	0.10	1.37	1.97
VLA	228	T1	FT	B	15m	1	12.20	0.17	0.20	7.40	0.45	23.20	2.09	0.91	4.45	54.80	0.11	1.80	2.29
VLA	233	T2	FT	B	1m	1	12.90	0.16	0.20	6.98	0.13	25.80	2.02	0.92	3.26	62.50	0.08	1.42	1.62
VLA	234	T2	FT	B	15m	1	13.00	0.16	0.19	6.95	0.13	22.80	2.03	0.70	3.46	85.90	0.07	1.44	1.66

VSF cruise data (unfiltered samples)

Ship	id	Time	Treatment	Location	Depth	Rep.	Mo	Cd	Sb	Ba	Pb	P	V	Cr	Mn	Fe	Co	Ni	Cu
VSF	181	T0	C	A	1m	1	7.76	0.10	0.56	32.40	0.65	134.00	4.42	2.00	52.80	761.00	0.58	6.60	4.16
VSF	182	T0	C	A	15m	1	7.95	0.13	0.49	32.60	0.71	135.00	5.55	2.02	55.90	834.00	0.75	6.82	4.06
VSF	187	T1	C	A	1m	1	8.39	0.15	0.48	33.70	0.71	142.00	5.46	2.08	54.90	848.00	0.74	6.82	4.21
VSF	188	T1	C	A	15m	1	8.06	0.15	0.42	35.10	0.65	127.00	4.87	1.90	51.10	783.00	0.66	6.51	3.93
VSF	193	T2	C	A	1m	1	8.11	0.14	0.49	32.90	0.63	134.00	5.31	2.07	50.70	836.00	0.71	6.91	3.80
VSF	194	T2	C	A	15m	1	7.57	0.15	0.39	36.90	1.76	182.00	7.27	2.72	154.00	1700.00	1.49	12.00	7.86
VSF	211	Tf	C	A	1m	1	8.02	0.19	0.44	34.80	0.65	120.00	4.29	1.71	43.00	671.00	0.56	5.39	3.71
VSF	212	Tf	C	A	15m	1	7.91	0.15	0.62	33.20	0.67	135.00	5.47	2.44	51.70	755.00	0.80	6.66	4.24
VSF	217	T0	C	B	1m	1	7.81	0.09	0.51	31.50	0.72	144.00	4.69	3.87	57.00	855.00	0.67	7.17	5.63
VSF	218	T0	C	B	15m	1	7.73	0.10	1.36	32.70	0.92	134.00	4.47	3.59	56.70	855.00	0.71	7.28	6.87
VSF	223	T1	C	B	1m	1	7.95	0.15	0.43	36.00	0.78	127.00	4.87	1.80	52.10	772.00	0.66	6.13	3.92
VSF	224	T1	C	B	15m	1	7.59	0.13	0.41	36.50	0.81	140.00	5.32	1.83	53.90	781.00	0.70	6.44	3.89
VSF	229	T2	C	B	1m	1	7.74	0.13	0.49	33.00	0.65	139.00	4.11	1.95	48.70	735.00	0.51	6.37	4.15
VSF	230	T2	C	B	15m	1	8.02	0.13	0.51	32.40	0.68	139.00	5.40	3.78	56.10	908.00	0.77	7.27	4.19
VSF	247	Tf	C	B	1m	1	8.73	0.15	0.51	35.00	0.74	137.00	5.44	2.04	52.50	792.00	0.66	6.79	5.10
VSF	248	Tf	C	B	15m	1	8.10	0.15	0.47	36.50	0.74	140.00	5.29	1.82	50.50	766.00	0.71	6.31	4.62
VSF	183	T0	ER	A	1m	1	7.32	0.13	0.39	37.40	0.65	125.00	5.02	1.54	47.70	653.00	0.63	5.61	3.65
VSF	184	T0	ER	A	15m	1	7.63	0.15	0.45	35.90	0.72	130.00	5.62	2.28	58.00	846.00	0.78	7.08	4.30
VSF	189	T1	ER	A	1m	1	12.40	0.09	0.37	6.89	0.16	31.60	2.22	1.19	6.63	154.00	0.14	1.30	1.36
VSF	190	T1	ER	A	15m	1	12.00	0.09	0.39	6.82	0.16	28.00	1.98	1.43	6.32	148.00	0.14	1.19	1.43
VSF	214	Tf	ER	A	15m	1	12.00	0.07	0.51	6.39	0.30	33.40	2.15	1.47	6.88	163.00	0.12	1.67	1.91
VSF	219	T0	ER	B	1m	1	7.70	0.15	0.44	36.00	0.69	129.00	5.17	1.98	53.50	795.00	0.73	6.91	5.48
VSF	220	T0	ER	B	15m	1	7.74	0.16	0.41	37.90	0.77	127.00	5.24	1.86	54.70	797.00	0.72	6.26	4.44
VSF	225	T1	ER	B	1m	1	11.60	0.10	0.35	6.58	0.92	30.30	2.07	1.12	6.90	161.00	0.14	1.35	1.12
VSF	226	T1	ER	B	15m	1	12.20	0.09	0.34	6.71	0.21	28.40	2.10	1.22	6.61	165.00	0.14	1.30	2.04
VSF	249	Tf	ER	B	1m	1	12.20	0.09	0.36	7.21	0.40	31.60	2.26	1.11	5.92	142.00	0.09	1.11	2.11
VSF	250	Tf	ER	B	15m	1	12.10	0.08	0.33	6.94	0.13	30.80	1.98	0.98	6.50	141.00	0.11	1.30	3.13
VSF	186	T0	FT	A	15m	1	7.05	0.15	0.42	40.90	0.72	127.00	5.20	1.99	50.80	819.00	0.70	6.47	4.22
VSF	191	T1	FT	A	1m	1	9.72	0.10	0.42	21.30	0.60	68.40	3.66	1.54	26.80	468.00	0.44	4.11	3.02
VSF	192	T1	FT	A	15m	1	9.86	0.11	0.38	21.90	0.37	65.50	3.41	1.42	24.90	428.00	0.36	3.45	2.34
VSF	197	T2	FT	A	1m	1	11.80	0.10	0.39	13.00	0.22	48.30	2.68	1.31	13.80	268.00	0.22	2.22	9.07
VSF	198	T2	FT	A	15m	1	11.80	0.10	0.38	10.80	0.19	44.00	2.45	1.13	9.77	201.00	0.13	1.70	1.58
VSF	215	Tf	FT	A	1m	1	11.90	0.09	0.36	8.72	0.11	36.10	2.14	1.03	5.85	115.00	0.08	1.00	0.92

VSF cruise data (continued).

Ship	id	Time	Treatment	Location	Depth	Rep.	Mo	Cd	Sb	Ba	Pb	P	V	Cr	Mn	Fe	Co	Ni	Cu
VSF	216	Tf	FT	A	15m	1	11.80	0.08	0.38	8.88	0.29	32.50	2.03	1.08	5.54	116.00	0.10	1.07	1.62
VSF	222	T0	FT	B	15m	1	6.78	0.32	0.51	39.80	2.80	123.00	5.04	2.45	53.30	851.00	0.74	7.04	4.44
VSF	227	T1	FT	B	1m	1	9.78	0.13	0.42	22.00	0.41	67.20	3.62	1.86	26.60	469.00	0.35	3.79	2.79
VSF	228	T1	FT	B	15m	1	9.50	0.12	0.37	22.40	0.52	62.50	3.33	1.42	24.80	465.00	0.36	3.83	2.95
VSF	233	T2	FT	B	1m	1	11.20	0.09	0.38	11.80	0.26	44.50	2.37	1.07	11.00	211.00	0.16	1.67	1.75
VSF	234	T2	FT	B	15m	1	9.92	0.09	0.67	11.40	0.23	44.00	2.41	1.84	11.30	222.00	0.20	1.91	1.82
VSF	252	Tf	FT	B	15m	1	11.60	0.08	0.33	8.67	0.19	33.70	1.93	1.09	5.13	99.30	0.09	0.86	0.94
VSF	532	S0	SS	0	5m	1	11.90	0.12	0.55	7.01	0.40	14.70	0.55	1.04	7.61	139.00	0.03	1.20	2.62
VSF	533	S0	SS	0	5m	2	12.30	0.10	0.41	6.82	0.36	17.10	1.73	0.96	9.88	201.00	0.06	1.54	2.42
VSF	534	S1	SS	1	5m	1	12.50	0.10	0.35	6.67	0.65	24.80	1.74	0.88	2.63	47.40	0.03	0.81	11.10
VSF	535	S1	SS	1	5m	2	12.20	0.08	0.38	6.60	0.22	24.10	1.83	0.95	2.73	45.60	0.03	0.53	2.41
VSF	536	S2	SS	2	5m	1	12.70	0.09	0.36	5.45	0.13	32.40	1.86	0.97	2.16	51.10	0.04	0.62	1.58
VSF	537	S2	SS	2	5m	2	12.10	0.12	0.43	5.09	0.22	30.60	1.76	1.10	2.14	51.40	0.04	0.53	2.66

VPS cruise data (filtered samples)

Ship	id	Time	Treatment	Location	Depth	Replicate	Mo	Cd	Ba	Pb	U	P	V	Mn	Fe	Cu	Zn
VPS	6077	T0	C	A	1m	1	9.94	0.02	9.75	-0.92	3.53	52.44	1.72	4.72	0.52	2.16	266.98
VPS	6078	T0	C	A	1m	2	10.24	0.02	9.95	1.51	2.80	86.44	1.95	5.31	10.74	1.80	369.51
VPS	6079	T0	C	A	15m	1	9.43	0.01	9.44	-0.91	3.42	50.60	1.61	3.94	13.64	1.01	328.18
VPS	6080	T0	C	A	15m	2	9.47	0.00	9.11	-0.85	3.23	52.98	1.62	4.04	2.86	0.98	336.83
VPS	6081	T0	C	B	1m	1	9.77	-0.01	9.30	-0.73	3.31	52.21	1.72	4.54	1.21	1.06	257.64
VPS	6082	T0	C	B	1m	2	9.54	0.04	10.10	-0.05	3.21	54.74	1.84	4.83	32.17	1.78	271.79
VPS	6083	T0	C	B	15m	1	10.03	0.05	10.49	0.62	3.33	67.63	1.95	15.50	600.34	4.80	334.54
VPS	6084	T0	C	B	15m	2	9.75	-0.02	9.37	-0.94	3.41	54.43	1.69	4.12	2.36	1.60	319.99
VPS	6085	T1	C	A	1m	1	9.54	0.07	9.40	-0.55	3.44	50.31	1.52	3.35	3.68	1.37	497.70
VPS	6086	T1	C	A	1m	2	10.27	0.00	9.12	0.22	2.45	68.67	1.90	4.11	5.77	2.25	612.35
VPS	6087	T1	C	A	15m	1	9.71	0.30	11.08	1.07	3.55	52.05	1.72	3.54	13.88	2.26	524.77
VPS	6088	T1	C	A	15m	2	10.63	-0.01	9.25	0.54	2.60	67.88	1.95	3.91	4.28	1.28	621.91
VPS	6089	T1	C	B	1m	1	10.33	0.04	9.79	-0.76	2.67	60.56	1.84	5.32	4.65	1.46	562.08
VPS	6090	T1	C	B	1m	2	9.83	0.06	9.14	-0.64	2.36	67.70	1.88	4.23	12.57	1.63	627.64
VPS	6091	T1	C	B	15m	1	10.53	0.01	9.43	-0.89	2.72	64.16	1.91	3.87	2.73	1.34	624.99
VPS	6092	T1	C	B	15m	2	11.21	0.07	9.49	1.73	2.63	72.83	1.98	4.64	129.88	1.57	632.03
VPS	6101	T0	ER	A	1m	1	9.75	-0.04	9.51	-0.76	3.26	50.04	1.74	3.92	1.67	1.01	194.93
VPS	6102	T0	ER	A	1m	2	9.19	-0.01	9.04	-0.64	3.08	51.70	1.64	3.72	7.03	1.28	210.79

VPS cruise data (continued).

Ship	Id	Time	Treatment	Location	Depth	Replicate	Mo	Cd	Ba	Pb	U	P	V	Mn	Fe	Cu	Zn
VPS	6103	T0	ER	A	15m	1	9.69	-0.02	9.08	-0.84	3.30	51.59	1.70	3.46	3.06	1.05	206.29
VPS	6104	T0	ER	A	15m	2	9.72	-0.04	9.50	0.03	3.11	54.07	1.87	4.02	30.23	5.68	230.53
VPS	6105	T0	ER	B	1m	1	12.47	0.25	15.06	4.04	4.06	112.62	3.05	29.32	564.79	8.37	270.44
VPS	6106	T0	ER	B	1m	2	7.41	-0.04	7.41	-0.89	2.38	41.83	1.34	3.17	0.67	1.27	174.80
VPS	6107	T0	ER	B	15m	1	9.81	-0.13	9.61	-0.10	3.18	57.14	1.80	3.74	8.58	3.53	237.17
VPS	6108	T0	ER	B	15m	2	5.83	0.17	9.18	9.47	1.95	146.71	2.94	61.87	1488.24	10.95	180.91
VPS	6109	T1	ER	A	1m	1	5.30	-0.22	2.91	-0.69	1.67	19.39	0.88	0.42	6.49	0.86	55.45
VPS	6110	T1	ER	A	1m	2	9.30	-0.03	6.81	-0.14	3.27	37.59	1.43	57.62	3.00	5.39	112.91
VPS	6111	T1	ER	A	15m	1	11.04	-0.04	7.80	-0.59	3.38	40.69	1.69	1.66	3.36	0.68	98.91
VPS	6112	T1	ER	A	15m	2	9.66	0.02	6.99	88.67	2.51	47.08	1.60	1.00	55.52	5.14	112.99
VPS	6113	T1	ER	B	1m	1	9.41	-0.01	6.70	0.31	2.87	39.52	1.43	67.63	21.16	6.37	120.87
VPS	6114	T1	ER	B	1m	2	10.69	-0.04	7.81	-0.91	3.40	38.91	1.62	0.89	2.75	0.83	105.30
VPS	6115	T1	ER	B	15m	1	10.55	-0.02	7.34	-0.95	3.22	41.18	1.64	0.64	4.80	0.55	101.23
VPS	6116	T1	ER	B	15m	2	10.69	-0.03	7.66	-1.01	3.26	40.73	1.69	0.60	3.55	0.54	100.51
VPS	6117	S0	SS	1	5m	1	11.11	2.06	8.07	2.15	2.77	60.04	1.86	0.71	11.59	3.11	30.99
VPS	6118	S1	SS	1	5m	2	9.86	-0.05	7.18	-0.70	2.40	44.78	1.70	2.56	32.62	2.86	19.58
VPS	6119	S2	SS	2	5m	1	10.90	-0.02	7.70	-0.70	2.89	47.32	1.77	0.46	11.03	1.90	60.86
VPS	6120	S3	SS	2	5m	2	10.82	-0.06	7.27	-0.82	2.89	45.61	1.71	0.33	5.88	1.39	28.53
VPS	6121	S4	SS	3	5m	1	11.05	-0.02	7.84	29.46	3.24	45.07	1.71	0.32	7.58	1.20	43.41
VPS	6122	S5	SS	3	5m	2	11.70	0.02	8.34	7.26	3.26	54.22	1.83	0.31	6.95	1.36	47.78
VPS	6123	S6	SS	4	5m	1	10.22	-0.05	8.00	-0.75	2.79	74.77	1.65	2.06	126.30	2.12	136.13
VPS	6124	S7	SS	4	5m	2	10.92	-0.04	8.52	2.78	3.04	48.40	1.82	0.67	51.35	1.38	11.64
VPS	6125	S8	SS	5	5m	1	10.40	-0.03	9.13	-0.55	2.68	43.40	1.75	1.70	21.21	4.23	189.23
VPS	6126	S9	SS	5	5m	2	10.63	-0.08	8.39	-0.82	2.53	43.45	1.75	0.86	6.98	1.40	10.30
VPS	6127	S10	SS	6	5m	1	10.92	-0.02	9.21	-0.32	2.95	40.94	1.74	0.71	11.67	2.20	115.08
VPS	6128	S11	SS	6	5m	2	10.81	-0.02	8.39	-0.95	3.41	36.11	1.63	0.47	3.55	0.95	12.02
VPS	6129	S12	SS	7	5m	1	10.34	-0.05	9.31	-0.86	3.00	25.35	1.73	0.87	11.20	1.66	11.50
VPS	6130	S13	SS	7	5m	2	10.38	-0.04	9.65	-0.89	3.03	25.58	1.55	0.64	5.97	2.61	7.30
VPS	6131	S14	SS	8	5m	1	10.11	-0.02	2.47	-0.86	3.02	12.67	1.50	2.00	25.77	1.67	11.11
VPS	6132	S15	SS	8	5m	2	10.04	-0.05	2.14	-1.05	3.18	9.78	1.39	1.61	1.40	0.83	5.48

VFos cruise data (filtered samples)

Ship	Id #	Tank*	Time	Treatment	Location	Replicate	Mo	Cd	Ba	Re	U	P	V	Mn	Fe	Cu	Zn
VFos	82	W1	T1	C	A	2	12.08	0.07	10.68	0.01	3.69	8.97	1.65	6.86	1.29	3.22	8.39
VFos	83	W1	T1	C	B	1	12.73	0.01	11.04	0.01	3.09	9.12	1.5	5.1	0	2.55	7.83
VFos	84	W1	T1	C	B	2	12.35	0.07	10.88	0.01	3.61	9.06	1.67	7.6	0.26	2.97	8.65
VFos	85	W2	T1	C	A	1	12.52	0.09	10.12	0.01	3.74	6.46	1.62	4.36	0.18	2.07	18.65
VFos	86	W2	T1	C	A	2	12.49	0.06	10.48	0.01	3.67	7.72	1.4	4.78	1.48	2.27	6.51
VFos	87	W2	T1	C	B	1	12.52	0.07	10.76	0.01	3.49	10.43	1.61	6.02	0	2.22	5.94
VFos	88	W2	T1	C	B	2	12.68	0.06	11.02	0.01	3.65	6.63	1.57	5.7	0.48	2.01	5.12
VFos	89	W3	T1	C	A	1	12.67	0.02	9.68	0.01	3.13	7.64	1.65	3.11	0	1.36	4.74
VFos	90	W3	T1	C	A	2	13.11	0.09	9.57	0.01	3.57	4.48	1.8	3.87	14.82	1461.1	189.2
VFos	91	W3	T1	C	B	1	12.75	0.08	9.9	0.01	3.73	4.01	1.69	5.48	1.98	1.96	3.34
VFos	92	W3	T1	C	B	2	12.41	0.08	10.43	0.01	3.63	7.2	1.51	5.38	3.67	2.21	5.11
VFos	97	W4	T1	C	A	1	12.18	0.16	9.74	0.01	3.66	4.11	1.61	6.55	0.07	1.7	32.7
VFos	98	W4	T1	C	A	2	12.6	0.11	10.04	0.01	3.55	6.32	1.42	4.79	0	1.7	15.9
VFos	99	W4	T1	C	B	1	12.58	0.03	10.2	0.01	3.28	7.22	1.54	4.11	0	1.65	15.31
VFos	100	W4	T1	C	B	2	11.82	0.1	14.12	0.01	3.53	4.63	1.71	6.41	6.65	1.92	39.38
VFos	101	W1	T1	FT	A	1	12.74	0.07	10.43	0.01	3.48	3.99	1.64	5.96	2.18	3.03	12.39
VFos	102	W1	T1	FT	A	2	12	0.16	9.72	0.01	3.61	3.31	1.55	7.81	0.64	2.66	10.76
VFos	103	W1	T1	FT	B	1	11.56	0.12	9.71	0.01	3.47	4.72	1.57	7.37	3.84	2.32	15.55
VFos	104	W1	T1	FT	B	2	12.74	0.08	10.38	0.01	3.5	4.49	1.72	5.51	0.84	2.63	7.92
VFos	105	W2	T1	FT	A	1	12.84	0.02	10.09	0.01	3.19	7.37	1.35	3.23	0	2.22	7.73
VFos	106	W2	T1	FT	A	2	11.83	0.14	9.13	0.01	3.57	2.86	1.47	4.68	0	1.67	11.54
VFos	107	W2	T1	FT	B	1	12.57	0.07	10.21	0.01	3.62	7.13	1.37	5.11	0	1.99	4.32
VFos	108	W2	T1	FT	B	2	12.53	0.07	10.28	0.01	3.54	7.3	1.44	4.98	1.53	2.37	5.92
VFos	109	W3	T1	FT	A	1	12.48	0.03	9.94	0.01	3.32	5.37	1.35	2.91	1.94	1.35	7.97
VFos	110	W3	T1	FT	A	2	12.73	0.03	9.72	0.01	3.35	5.45	1.6	2.96	0.11	1.54	7.89
VFos	111	W3	T1	FT	B	1	12.75	0.08	9.98	0.01	3.65	6.73	1.57	4.88	0	1.91	3.89
VFos	112	W3	T1	FT	B	2	12.43	0.12	10.1	0.01	3.77	4.68	1.52	4.44	0.67	1.96	3.68
VFos	117	W4	T1	FT	A	1	12.93	0.08	10.17	0.01	3.65	7.52	1.58	5.45	0.06	2.01	11.85
VFos	118	W4	T1	FT	A	2	11.96	0.11	9.58	0.01	3.6	4.12	1.65	5.64	3.06	1.55	12.55
VFos	119	W4	T1	FT	B	1	12.8	0.04	10.24	0.01	3.48	8.63	1.41	3.54	0	1.5	9.87
VFos	120	W4	T1	FT	B	2	12.64	0.09	10.03	0.01	3.53	6.9	1.43	4.69	0	1.79	10.03
VFos	177	W1	T2	C	A	1	12.44	0.09	11.33	0.01	3.5	9.47	1.63	10.42	0.33	1.66	11.07
VFos	178	W1	T2	C	A	2	12.3	0.09	10.87	0.01	3.72	4.48	1.63	10.57	2.37	2.78	10.14
VFos	179	W1	T2	C	B	1	12.48	0.04	11.08	0.01	3.42	13.4	1.46	7.44	0	1.41	10.75
VFos	180	W1	T2	C	B	2	13.2	0.08	10.46	0.01	3.46	5.94	1.67	9.06	3.13	2.94	10.52
VFos	181	W2	T2	C	A	1	12.84	0.05	11.11	0.01	3.58	12.45	1.55	5.25	0.47	1.72	7.86
VFos	182	W2	T2	C	A	2	12.49	0.09	11.42	0.01	3.73	8.68	1.36	5.66	0.16	1.81	8.49
VFos	183	W2	T2	C	B	1	12.54	0.1	11.26	0.01	3.82	8.61	1.67	7.9	0.07	2.61	12.31
VFos	183	W2	T2	C	B	1	12.41	0.12	11.63	0.01	3.83	9.41	1.72	7.93	0.34	2.61	10.79
VFos	184	W2	T2	C	B	2	12.5	0.05	10.87	0.01	3.46	9.67	1.45	4.78	0	1.37	5.78

VFos cruise data (continued).

Ship	Id #	Tank*	Time	Treatment	Location	Replicate	Mo	Cd	Ba	Re	U	P	V	Mn	Fe	Cu	Zn
VFos	185	W3	T2	C	A	1	12.32	0.06	10.3	0.01	3.46	9.66	1.52	4.14	0	1.04	4.96
VFos	186	W3	T2	C	A	2	12.33	0.07	9.86	0.01	3.47	9.38	1.29	4.6	0	1.19	5.68
VFos	187	W3	T2	C	B	1	12.59	0.06	9.95	0.01	3.48	9.64	1.69	6.15	0	1.6	6.86
VFos	188	W3	T2	C	B	2	12.41	0.04	10.32	0.01	3.47	10.57	1.42	4.4	0	1.29	5.21
VFos	193	W4	T2	C	A	1	12.13	0.16	9.4	0.01	3.59	5.59	1.51	6.44	0	1.35	21.12
VFos	194	W4	T2	C	A	2	12.18	0.15	9.35	0.01	3.65	4.42	1.57	6.21	0	1.24	31.37
VFos	195	W4	T2	C	B	1	12	0.17	9.3	0.01	3.63	5.25	1.45	6.04	0.56	3.75	42.23
VFos	196	W4	T2	C	B	2	13.03	0.03	10.46	0.01	3.4	12.86	1.92	5.47	0	1.97	24.2
VFos	197	W1	T2	FT	A	1	12.76	0.08	8.93	0.01	3.95	3.71	1.69	7.22	3.55	2.28	10.66
VFos	198	W1	T2	FT	A	2	12.02	0.15	8.54	0.01	3.63	3.91	1.55	9.4	0	1.41	13.28
VFos	199	W1	T2	FT	B	1	12.43	0.07	6.87	0.01	3.28	3.08	1.74	1.71	0	2.13	4.89
VFos	200	W1	T2	FT	B	2	11.81	0.03	7.75	0.01	3.28	6.19	1.39	2.44	7.09	0.83	6.23
VFos	201	W2	T2	FT	A	1	12.3	0.05	8.81	0.01	3.46	8.69	1.45	3.01	21.11	2.46	9.1
VFos	202	W2	T2	FT	A	2	12.45	0.06	8.73	0.01	3.51	7.44	1.39	2.76	0.1	1.73	6.41
VFos	203	W2	T2	FT	B	1	11.33	0.06	9.01	0.01	3.61	4.72	1.65	27.05	1466.11	2.1	8.16
VFos	204	W2	T2	FT	B	2	12.31	0.05	8.6	0.01	3.44	8.33	1.59	3.03	0	0.99	5.44
VFos	205	W3	T2	FT	A	1	12.06	0.11	8.29	0.01	3.65	5.14	1.63	2.32	1.79	1.12	5.44
VFos	206	W3	T2	FT	A	2	12.16	0.06	7.86	0.01	3.42	7.67	1.52	2.07	0.1	0.75	5.69
VFos	207	W3	T2	FT	B	1	12.2	0.04	8.23	0.01	3.39	8.12	1.63	1.95	0	0.83	4.6
VFos	208	W3	T2	FT	B	2	12.26	0.04	8.14	0.01	3.52	6.42	1.42	2	0	0.67	4.9
VFos	213	W4	T2	FT	A	1	11.84	0.16	8.88	0.01	3.6	4.17	1.49	4.95	0	1.32	13.78
VFos	214	W4	T2	FT	A	2	12.26	0.07	9.8	0.01	3.48	9.97	1.31	3.48	0	1.15	12.77
VFos	215	W4	T2	FT	B	1	11.97	0.06	8.12	0.01	3.44	8.54	1.53	1.67	0	0.91	5.34
VFos	216	W4	T2	FT	B	2	12.05	0.07	8.07	0.01	3.44	5.82	1.54	1.68	0	0.79	5.14
VFos	285	W1	T3	C	A	1	12.23	0.09	10.96	0.01	3.52	13.02	1.39	7.69	0.17	1.26	11.58
VFos	286	W1	T3	C	A	2	12	0.09	10.92	0.01	3.49	11.49	1.31	8.02	0.12	1.1	11.18
VFos	287	W1	T3	C	B	1	12.15	0.1	11.07	0.01	3.68	6.43	1.63	9.43	0	1.6	61.33
VFos	288	W1	T3	C	B	2	12.09	0.1	11	0.01	3.59	11.82	1.42	7.87	0	1.11	10.54
VFos	277	W2	T3	C	A	1	12.19	0.11	11.17	0.01	3.71	9.91	1.49	6.08	2.41	1.92	7.42
VFos	279	W2	T3	C	B	1	12.18	0.07	11.16	0.01	3.45	11.1	1.34	4.78	0	1.37	6.41
VFos	280	W2	T3	C	B	2	12.26	0.09	10.68	0.01	3.52	10.85	1.23	4.67	0	1.29	6.46
VFos	281	W3	T3	C	A	1	12.43	0.08	10.46	0.01	3.4	10.42	1.46	4.91	1.86	1.26	8.06
VFos	282	W3	T3	C	A	2	12.59	0.12	10.65	0.01	3.79	6.62	1.62	4.68	1.34	1.83	7.64
VFos	283	W3	T3	C	B	1	12.47	0.11	10.65	0.01	3.76	6.56	1.68	4.39	6.56	3.13	9.04
VFos	284	W3	T3	C	B	2	12.48	0.1	10.38	0.01	3.7	5.69	1.7	4.18	0	1.38	14.67
VFos	289	W4	T3	C	A	1	12.52	0.08	10.2	0.01	3.4	10.36	1.51	4.67	0	1.76	25.91
VFos	290	W4	T3	C	A	2	12.27	0.11	10.3	0.01	3.74	6.86	1.68	3.6	2.11	2.71	26.29
VFos	291	W4	T3	C	B	1	12.57	0.09	10.14	0.01	3.77	7.09	1.75	3.79	0	1.64	27.55
VFos	292	W4	T3	C	B	2	12.6	0.07	10.4	0.01	3.39	12	1.45	4.19	0	1.59	24.54
VFos	209	W1	T3	FT	A	1	12.06	0.06	7.4	0.01	3.4	5.92	1.55	2.65	0	1.65	5.44
VFos	210	W1	T3	FT	A	2	12.18	1.57	7.17	0.04	3.59	2.62	1.56	3.37	0.81	0.98	8.08

VFos cruise data (continued).

Ship	Id #	Tank*	Time	Treatment	Location	Replicate	Mo	Cd	Ba	Re	U	P	V	Mn	Fe	Cu	Zn
VFos	211	W1	T3	FT	B	1	12.2	0.07	7.48	0.01	3.26	5.36	1.56	2.66	0.49	1.74	7.62
VFos	212	W1	T3	FT	B	2	11.8	0.05	7.29	0.01	3.4	5.2	1.34	2.02	0	0.56	4.86
VFos	297	W2	T3	FT	A	1	11.88	0.11	7.79	0.01	3.68	5.1	1.56	1.83	1.9	0.97	4.44
VFos	298	W2	T3	FT	A	2	12.06	0.09	8.01	0.01	3.66	5.57	1.65	3.03	0.08	1.3	4.75
VFos	299	W2	T3	FT	B	1	11.68	0.11	7.53	0.01	3.53	4.63	1.75	2.77	0.03	0.79	4.6
VFos	300	W2	T3	FT	B	2	12	0.11	7.79	0.01	3.7	5.08	1.39	1.88	2.29	0.94	3.05
VFos	301	W3	T3	FT	A	1	12.07	0.05	7.3	0.01	3.28	6.27	1.56	1.32	0	0.96	5.12
VFos	302	W3	T3	FT	A	2	12.2	0.1	7.05	0.01	3.66	3.57	1.73	0.25	2.88	1.11	5.07
VFos	303	W3	T3	FT	B	1	11.95	0.1	7.26	0.01	3.63	3.75	1.72	0.32	0	1.04	4.31
VFos	304	W3	T3	FT	B	2	11.91	0.1	7.11	0.01	3.62	4.48	1.78	0.43	0	1.03	6.77
VFos	309	W4	T3	FT	A	1	12.42	0.05	8.12	0.01	3.34	7.42	1.62	2.1	0.11	1.18	8.74
VFos	310	W4	T3	FT	A	2	11.91	0.1	7.89	0.01	3.61	4.39	1.66	1.05	6.39	1.44	10.72
VFos	311	W4	T3	FT	B	1	12.26	0.05	7.94	0.01	3.3	7.24	1.37	1.97	0	1.54	8.53
VFos	312	W4	T3	FT	B	2	12.38	0.04	7.89	0.01	3.34	6.23	1.69	2.15	0	1.13	8.69
VFos	369	W1	T4	C	A	1	12.39	0.05	11.42	0.01	3.35	11.75	1.55	7.64	1.07	1.48	11.84
VFos	370	W1	T4	C	A	2	12.45	0.09	11.28	0.01	3.45	11.68	1.5	8.64	0	1.61	12.47
VFos	371	W1	T4	C	B	1	11.98	0.11	11.13	0.01	3.49	11.4	1.36	7.21	0	1.07	9.86
VFos	372	W1	T4	C	B	2	11.81	0.1	11.18	0.01	3.55	7.73	1.58	9.59	0.4	1.47	13.6
VFos	373	W2	T4	C	A	1	12.12	0.08	11.22	0.01	3.49	11.91	1.28	4.59	0	3.62	20.79
VFos	374	W2	T4	C	A	2	12.64	0.08	10.82	0.01	3.58	10.89	1.35	3.55	0	1.54	8.15
VFos	375	W2	T4	C	B	1	11.63	0.11	10.62	0.01	3.36	11.87	1.34	3.92	0	1.52	8.29
VFos	376	W2	T4	C	B	2	11.77	0.09	11	0.01	3.4	9.16	1.4	4.19	0	1.14	7.56
VFos	377	W3	T4	C	A	1	12.38	0.08	10.38	0.01	3.63	12.82	1.58	4.93	0	1.5	9.51
VFos	378	W3	T4	C	A	2	11.53	0.09	9.78	0.01	3.33	11.27	1.23	3.09	0.07	0.78	6.33
VFos	379	W3	T4	C	B	1	12.55	0.12	10.72	0.01	3.85	8.88	1.65	3.34	0	1.53	8.4
VFos	380	W3	T4	C	B	2	12.05	0.1	10.59	0.01	3.55	10.97	1.35	3.48	0	1.03	6.18
VFos	385	W4	T4	C	A	1	12.51	0.1	10.48	0.01	3.81	9.97	1.75	5.01	0.5	1.84	26.98
VFos	386	W4	T4	C	A	2	12.56	0.12	10.75	0.01	3.78	9.2	1.7	5.34	1.2	1.74	27.23
VFos	387	W4	T4	C	B	1	12.19	0.09	9.99	0.01	3.64	6.01	1.56	3.23	3.47	1.58	24.78
VFos	388	W4	T4	C	B	2	12.55	0.1	10.29	0.01	3.81	10.9	1.79	5.38	0	1.89	27.74
VFos	389	W1	T4	FT	A	1	11.5	0.13	6.41	0.01	3.48	2.78	1.71	3.48	0.53	0.81	11.62
VFos	390	W1	T4	FT	A	2	12.08	0.08	6.89	0.01	3.64	4.46	1.76	3.96	0	1.17	3.19
VFos	391	W1	T4	FT	B	1	12.19	0.12	6.92	0.01	3.76	3.77	1.5	1.33	0	0.8	1.53
VFos	392	W1	T4	FT	B	2	12.08	0.1	6.46	0.01	3.6	2.97	1.62	0.92	2.96	1.14	4.24
VFos	393	W2	T4	FT	A	1	11.83	0.12	6.66	0.01	3.74	3.49	1.55	0.53	0	0.78	1.06
VFos	394	W2	T4	FT	A	2	11.85	0.1	6.92	0.01	3.61	6.13	2.06	1.2	0.65	1.39	5.1
VFos	395	W2	T4	FT	B	1	11.66	0.08	6.59	0.01	3.37	3.22	1.46	0.49	0	0.51	0.36
VFos	396	W2	T4	FT	B	2	11.79	0.09	6.63	0.01	3.56	4.55	1.98	1.52	0.44	2.38	11.65
VFos	397	W3	T4	FT	A	1	12.42	0.09	6.7	0.01	3.65	2.54	1.79	0	1.26	0.7	2.14
VFos	398	W3	T4	FT	A	2	11.97	0.08	6.89	0.01	3.6	4.45	2.11	2.26	34.7	1.56	6.37
VFos	399	W3	T4	FT	B	1	12.13	0.08	6.57	0.01	3.63	2.69	1.8	0	0	0.85	3.78

VFos cruise data (continued).

Ship	Id #	Tank*	Time	Treatment	Location	Replicate	Mo	Cd	Ba	Re	U	P	V	Mn	Fe	Cu	Zn
VFos	400	W3	T4	FT	B	2	11.88	0.11	6.97	0.01	3.73	3.19	1.57	0.45	0	0.57	1.88
VFos	405	W4	T4	FT	A	1	12.1	0.1	6.63	0.01	3.72	3.77	1.61	0.52	0	0.78	2.07
VFos	406	W4	T4	FT	A	2	12.23	0.09	6.9	0.01	3.61	6.08	2.2	1.94	0.38	1.58	4.57
VFos	407	W4	T4	FT	B	1	11.78	0.12	7.16	0.01	3.77	3.3	1.37	0.84	0	0.99	2.18
VFos	408	W4	T4	FT	B	2	11.95	0.09	6.65	0.01	3.43	4.02	1.42	0.85	0	0.71	0.57
VFos	465	W1	T5	C	A	1	11.61	0.13	6.69	0.01	3.45	2.53	1.74	4.08	1.81	4.38	13.54
VFos	466	W1	T5	C	A	2	12.13	0.09	6.67	0.01	3.46	4.17	1.71	2.58	0.8	1.12	2.13
VFos	467	W1	T5	C	B	1	11.98	0.09	6.52	0.01	3.52	3.92	1.68	0.94	0.32	1.41	1.32
VFos	468	W1	T5	C	B	2	11.53	0.1	7.31	0.01	3.44	5.66	1.77	1.62	0.73	0.61	1.34
VFos	469	W2	T5	C	A	1	12.4	0.09	6.72	0.01	3.58	3.26	1.98	0	0.87	1.36	13.01
VFos	470	W2	T5	C	A	2	11.58	0.13	6.88	0.01	3.7	4.2	1.2	0.23	0	1.07	1.68
VFos	471	W2	T5	C	B	1	11.81	0.11	6.91	0.01	3.7	4.43	1.69	1.06	0.02	1.36	4.19
VFos	472	W2	T5	C	B	2	11.87	0.11	6.93	0.01	3.57	3.54	1.82	1.19	0.53	1.24	3.98
VFos	473	W3	T5	C	A	1	11.83	0.15	6.77	0.01	3.73	4.28	1.42	0.58	0	0.37	2.14
VFos	474	W3	T5	C	A	2	11.84	0.12	7.07	0.01	3.43	6.77	1.75	1.07	7.01	2.62	7.7
VFos	475	W3	T5	C	B	1	11.57	0.11	6.99	0.01	3.43	5.4	1.86	1.22	0.7	0.84	1.8
VFos	476	W3	T5	C	B	2	11.5	0.1	6.89	0.01	3.45	4.05	1.68	1.28	1.49	1.08	18.15
VFos	481	W4	T5	C	A	1	11.71	0.12	6.92	0.01	3.65	4.67	1.59	0.78	0.68	0.81	4.5
VFos	482	W4	T5	C	A	2	11.78	0.12	6.93	0.01	3.71	3.76	1.37	0.68	0	0.64	5.57
VFos	483	W4	T5	C	B	1	11.57	0.13	6.83	0.01	3.45	3.82	1.82	1.32	0.7	2.64	10.18
VFos	484	W4	T5	C	B	2	11.72	0.1	6.82	0.01	3.44	5.63	1.96	0.84	0.26	0.75	4.07
VFos	803	W4	preb	C	B	1	0.01	0	-0.03	0	0	0.1	0	0.07	0	0.12	6.67
VFos	804	W4	preb	C	B	2	0.01	0	-0.06	0	0	0.03	0	0.14	3.21	0.2	13.5
VFos	927	-	S1	SS	1	1	12.31	0.08	9.5	0.01	3.61	1.75	1.64	2.69	9.13	13.57	19.55
VFos	928	-	S2	SS	2	1	12.07	0.1	9.98	0.01	3.63	2.31	1.7	4.46	8.02	14.41	22.34
VFos	929	-	S3	SS	3	1	11.43	0.15	8.56	0.01	3.47	3.23	1.46	1.65	6.91	16.71	26.97
VFos	930	-	S4	SS	4	1	12.06	0.1	9.09	0.01	3.68	3.06	1.5	0.67	9.18	11.45	12.66
VFos	931	-	S5	SS	5	1	12.01	0.11	8.28	0.01	3.57	1.84	1.75	0.62	7	14.75	6.99
VFos	932	-	S6	SS	6	1	12.1	0.1	8.34	0.01	3.57	1.7	1.79	0.43	6.18	21.59	12.35
VFos	933	-	S7	SS	7	1	12.64	0.08	8.38	0.01	3.77	2.37	1.74	0.87	11.14	25.48	19.59
VFos	934	-	S8	SS	8	1	11.85	0.14	7.34	0.01	3.61	1.4	1.63	0.45	5.98	2.98	7.49
VFos	935	-	S9	SS	9	1	11.98	0.1	7.86	0.01	3.55	2.76	1.8	0.48	7.97	3.51	5.06
VFos	936	-	S10	SS	10	1	11.92	0.1	7.55	0.01	3.56	0.99	1.91	0.66	7.83	26.51	14.29
VFos	937	-	S11	SS	11	1	12.7	0.09	7.73	0.01	3.77	1.83	1.79	0	6.75	23.68	19.3
VFos	938	-	S12	SS	12	1	11.56	0.13	6.57	0.01	3.53	1.57	1.56	0.58	7.72	5.26	16.37
VFos	939	-	S13	SS	13	1	12.55	0.08	6.74	0.01	3.7	1.81	1.72	0	6.16	23.47	9.94
VFos	940	-	S14	SS	14	1	12.15	0.1	7.79	0.01	3.59	2.48	1.99	0.75	8.03	4.16	5.97
VFos	941	-	S15	SS	15	1	11.72	0.08	8.48	0.01	3.64	2.21	1.89	0.46	5.94	5.62	22.43
VFos	942	-	S16	SS	16	1	11.6	0.1	6.7	0.01	3.63	4.48	1.61	0.5	6.6	4.99	25.8
VFos	943	-	S17	SS	17	1	11.71	0.12	6.34	0.01	3.46	9.52	2.13	0.47	7.81	9	34.34
VFos	944	-	S18	SS	18	1	11.52	0.11	6.52	0.01	3.4	3.44	1.85	0.95	7.21	5.56	15.57

VFos cruise data (continued).

Ship	Id #	Tank	Time*	Treatment	Location	Replicate	Mo	Cd	Ba	Re	U	P	V	Mn	Fe	Cu	Zn
VFos	945	-	S19	SS	19	1	11.68	0.12	6.21	0.01	3.76	5.04	1.33	0.35	6.34	4.49	9.8
VFos	946	-	S20	SS	20	1	11.5	0.13	5.93	0.01	3.55	3.13	1.57	0.33	5.34	3.74	6.25
VFos	947	-	S21	SS	21	1	11.55	0.11	6.06	0.01	3.42	4	1.89	0.34	7.25	3.88	6.33
VFos	948	-	S22	SS	22	1	11.71	0.13	6.5	0.01	3.48	2.63	1.85	2.71	8.97	5.42	3.67
VFos	949	-	S23	SS	23	1	11.66	0.09	6.19	0.01	3.56	2.95	1.83	0.23	8.09	2.71	17.51
VFos	950	-	S24	SS	24	1	11.35	0.11	5.51	0.01	3.38	3.13	1.97	0.21	8.86	8.1	28.59
VFos	951	-	S25	SS	25	1	11.45	0.12	6.19	0.01	3.49	2.34	1.9	0.3	8.62	7.01	31.08
VFos	952	-	S26	SS	26	1	11.93	0.13	6.19	0.01	3.8	3.14	1.44	0.07	6.24	3.86	5.08
VFos	953	-	S27	SS	27	1	11.68	0.12	6.11	0.01	3.67	2.89	1.34	0.11	4.36	2.35	5.36
VFos	954	-	S28	SS	28	1	11.04	0.13	6	0.01	3.33	3.57	1.67	0.1	6.61	0.81	27.3
VFos	955	-	S29	SS	29	1	11.63	0.06	6.75	0.01	3.61	3.57	1.93	0.23	7.31	1.11	10.31
VFos	956	-	S30	SS	30	1	11.21	0.13	5.84	0.01	3.32	3.19	1.67	0.17	8.53	5.14	22.14
VFos	957	-	S31	SS	31	1	12.87	0.07	6.9	0.01	3.75	1.87	1.89	0	6.48	3.74	6.66
VFos	958	-	S32	SS	32	1	12.74	0.07	6.39	0.01	3.44	3.03	1.91	0	5.54	4.61	11.53
VFos	959	-	S33	SS	33	1	12.12	0.07	6.28	0.01	3.4	2.25	1.94	0	4.96	4.47	3.8
VFos	960	-	S34	SS	34	1	11.81	0.08	6.16	0.01	3.49	2.36	1.81	0	7.55	4.58	7.38
VFos	961	-	S35	SS	35	1	12.54	0.08	6.57	0.01	3.59	2.13	1.94	0	5.56	4.11	3.9
VFos	962	-	S36	SS	36	1	11.58	0.11	6.08	0.01	3.4	4.45	2.16	0.22	19.98	5.06	6.9
VFos	963	-	S37	SS	37	1	11.56	0.11	6.5	0.01	3.47	3.21	2.16	0.27	8.7	0.72	3.65
VFos	964	-	S38	SS	38	1	11.28	0.12	6.36	0.01	3.33	2.38	1.64	0.18	6.59	3.43	5.11
VFos	965	-	S39	SS	39	1	11.28	0.11	6.89	0.01	3.36	2.59	1.87	0.43	10.49	3.99	5.32
VFos	966	-	S40	SS	40	1	11.39	0.11	7.09	0.01	3.39	0.23	1.88	0.68	8.83	5.19	12.86
VFos	967	-	S41	SS	41	1	11.2	0.1	7.27	0.01	3.39	4	1.92	0.87	8.61	5.56	10.96
VFos	968	-	S42	SS	42	1	11.08	0.13	7.2	0.01	3.32	4.76	1.85	0.71	8.81	4.27	6.72
VFos	969	-	S43	SS	43	1	11.09	0.14	6.99	0.01	3.35	3.52	1.46	0.7	7.49	3.61	10.82
VFos	970	-	S44	SS	44	1	11.23	0.09	7.02	0.01	3.36	3.44	1.66	0.71	8.27	3.95	23.92
VFos	971	-	S45	SS	45	1	10.65	0.11	6.65	0.01	3.19	4.51	1.75	0.69	9.38	3.51	12.69
VFos	972	-	S46	SS	46	1	10.79	0.13	6.71	0.01	3.23	5.24	1.53	0.73	6.62	3.46	8.94
VFos	973	-	S47	SS	47	1	10.24	0.06	7.66	0.01	3.11	6.77	1.3	1.31	6.08	3.84	5.93
VFos	974	-	S48	SS	48	1	9.81	0.12	8.31	0.01	2.88	5.64	1.18	1.34	7.46	3.9	7.64
VFos	975	-	S49	SS	49	1	10.64	0.07	8.54	0.01	2.77	4.82	1.34	0.31	4.49	4.78	9.5
VFos	976	-	S50	SS	50	1	9.64	0.12	8.8	0.01	2.85	22.79	0.78	2.9	9.59	8.05	17.96
VFos	1001	-	S51	SS	51	1	9.54	0.07	13.14	0.01	2.66	13.39	1.35	3.61	4.78	4.88	10.21
VFos	1002	-	S52	SS	52	1	7.01	0.05	15.85	0.01	1.86	15.58	1.44	2.38	6.13	5.14	19.12
VFos	1003	-	S53	SS	53	1	6.57	0.07	17.51	0.08	1.68	23.33	1.67	2.5	4.46	5.36	16.51
VFos	1004	-	S54	SS	54	1	5.4	0.04	15.64	0	1.32	16.81	1.53	2.85	7.42	5.82	33.73

* Note that "-" indicates a shipside sample.

Appendix L

Raw Data: Radium

VSF cruise data

Cruise	Id #	Time	Treatment	Location	Depth	Rep.	Volume	Ra223	Th228	Ra224	date	clock
VSF	362	T0	C	B	1m	1	189	1.05	0.66	9.78	4-Nov	1200
VSF	331	T1	C	A	1m	1	253	0.73	0.45	9.51	4-Nov	1200
VSF	373	T2	C	B	1m	1	229	0.68	0.23	7.56	4-Nov	1200
VSF	392	T3	C	A	1m	1	238	1.01	0.37	14.97	4-Nov	1200
VSF	552	S0	SS	0	5m	1	189	0.17	0.15	1.75	7-Nov	1200
VSF	553	S1	SS	1	5m	1	189	0	0.05	0.53	9-Nov	1200
VSF	374	S2	SS	2	5m	2	197	0.01	0.04	0.14	9-Nov	2030
VSF	363	T0	ER	B	1m	1	201	1.17	0.69	7.45	4-Nov	1200
VSF	333	T1	ER	A	1m	1	216	0.13	0.1	1.83	4-Nov	1200
VSF	357	T3	ER	A	1m	1	262	0.13	0.07	4.53	4-Nov	1200
VSF	329	T0	FT	B	1m	1	205	0.92	0.65	9.92	4-Nov	1200
VSF	335	T1	FT	A	1m	1	237	0.44	0.39	5.21	4-Nov	1200
VSF	x	T2	FT	A	1m	1	266	0.12	0.11	1.56	4-Nov	1200
VSF	360	T3	FT	A	1m	1	231	0.18	0.17	3.98	4-Nov	1200

VLA cruise data

Cruise	Id #	Time	Treatment	Location	Depth	Rep.	Volume	Ra223	Th228	Ra224	date	clock
VLA	325	T0	C	A	1m	1	227	1.5	0.59	12.12	6-Dec	1500
VLA	331	T1	C	A	1m	1	302	1.19	0.39	9.51	6-Dec	1500
VLA	337	T2	C	A	1m	1	227	1.2	0.37	11.93	6-Dec	1500
VLA	361	T0	C	B	1m	1	249	1.49	0.45	11.67	6-Dec	1500
VLA	367	T1	C	B	1m	1	263	0.88	0.44	8.6	6-Dec	1500
VLA	373	T2	C	B	1m	1	285	0.88	0.44	12.99	6-Dec	1500
VLA	552	S1	SS	1	5m	1	227	0.02	0.04	0.32	8-Dec	1030
VLA	553	S2	SS	2	5m	1	177	0.02	0.06	0.16	9-Dec	1030
VLA	-	S1	SS	1	5m	2	219	0.01	0.05	0.28	8-Dec	1300
VLA	-	S2	SS	2	5m	2	204	0	0.14	0.11	9-Dec	1300
VLA	330	T0	FT	B	1m	1	195	0.93	0.35	8.52	6-Dec	1500
VLA	329	T0	FT	A	1m	1	241	0.55	0.17	4.83	6-Dec	1500
VLA	-	T1	FT	A	1m	1	201	0.3	0.11	2.76	6-Dec	1500
VLA	341	T2	FT	A	1m	1	264	0.22	0.08	2.39	6-Dec	1500
VLA	371	T1	FT	B	1m	1	220	0.3	0.12	2.86	6-Dec	1500
VLA	377	T2	FT	B	1m	1	234	0.24	0.11	2.79	6-Dec	1500

VFos cruise data

Ship	Id #	Tank	Time	Treatment	Location	Depth	Rep.	Volume	Ra-223	Ra-224	Ra-226	Ra-228	A.R. 228/226	A.R. 223/226	Th-228
VFos	717	W1	T0	C	A	1m	1	217.28	0.8	18.52	nd	nd	nd	nd	nd
VFos	719	W1	T0	C	B	1m	1	193.2	0.86	18.09	nd	nd	nd	nd	nd
VFos	725	W3	T0	C	A	1m	1	215.33	0.45	14.85	nd	nd	nd	nd	nd
VFos	727	W3	T0	C	B	1m	1	267.71	0.39	8.68	nd	nd	nd	nd	nd
VFos	734	W4	T0	C	A	1m	1	280.13	0.59	16.23	nd	nd	nd	nd	nd
VFos	735	W4	T0	C	B	1m	1	227.03	0.66	13.55	nd	nd	nd	nd	nd
VFos	657	W1	Tf	C	A	1m	1	217	0.89	32.49	9.1	4.4	0.48	0.098	0.38
VFos	658	W1	Tf	C	B	1m	1	217	1.21	39.6	10.17	5.79	0.57	0.119	0.31
VFos	661	W2	Tf	C	A	1m	1	217	1.15	43.15	10.93	4.74	0.43	0.105	0.43
VFos	662	W2	Tf	C	B	1m	1	217	0.84	40.87	11.08	4.97	0.45	0.076	0.27
VFos	665	W3	Tf	C	A	1m	1	217	0.56	21.94	6.59	2.99	0.45	0.085	0.25
VFos	666	W3	Tf	C	B	1m	1	217	1.08	36.22	9.63	4.41	0.46	0.112	0.36
VFos	673	W4	Tf	C	A	1m	1	217	1.06	34.76	10.21	4.18	0.41	0.104	0.23
VFos	674	W4	Tf	C	B	1m	1	217	0.82	30.34	10.29	4.73	0.46	0.079	0.22
VFos	737	W1	T0	FT	A	1m	1	262.73	0.54	14.38	nd	nd	nd	nd	nd
VFos	739	W1	T0	FT	B	1m	1	272	0.71	15.44	nd	nd	nd	nd	nd
VFos	745	W3	T0	FT	A	1m	1	194	0.89	19.27	nd	nd	nd	nd	nd
VFos	747	W3	T0	FT	B	1m	1	261.53	0.61	15.65	nd	nd	nd	nd	nd
VFos	753	W4	T0	FT	A	1m	1	244.13	0.39	7.57	nd	nd	nd	nd	nd
VFos	755	W4	T0	FT	B	1m	1	219.04	0.82	15.7	nd	nd	nd	nd	nd
VFos	677	W1	Tf	FT	A	1m	1	217	0.04	2.79	6.57	2.37	0.36	0.006	0.33
VFos	678	W1	Tf	FT	B	1m	1	217	0.02	2.54	6.85	2.35	0.34	0.003	0.21
VFos	681	W2	Tf	FT	A	1m	1	217	0.1	4.66	5.69	1.96	0.34	0.018	0.26
VFos	682	W2	Tf	FT	B	1m	1	217	0.13	5.48	6.52	2.25	0.35	0.02	0.33
VFos	687	W3	Tf	FT	A	1m	1	217	0.07	3.96	6.33	1.97	0.31	0.011	0.34
VFos	688	W3	Tf	FT	B	1m	1	217	0.06	3.84	6.53	1.97	0.3	0.009	0.27
VFos	693	W4	Tf	FT	A	1m	1	217	0.14	4.6	6.73	2.42	0.36	0.021	0.28
VFos	694	W4	Tf	FT	B	1m	1	217	0.09	4.66	6.81	2.21	0.33	0.014	0.36

Appendix M

Raw Data: Phytoplankton Salinity Tolerance

VSF cruise data

Ship	Id #	Time	Treatment	Location	Depth	Replicate	Salinity Tolerance†
VSF	-	S0	SS	-	5m	1	1.05
VSF	-	S0	SS	-	5m	2	0.35
VSF	505	Tf	C	A	1m	1	0.62
VSF	511	Tf	C	B	1m	1	0.45
VSF	506	Tf	C	A	15m	1	0.75
VSF	512	Tf	C	B	15m	1	0.36
VSF	509	Tf	FT	A	1m	1	1.26
VSF	515	Tf	FT	B	1m	1	0.78
VSF	510	Tf	FT	A	15m	1	0.73
VSF	516	Tf	FT	B	15m	1	1.01
VSF	513	Tf	FT	B	1m	1	0.78
VSF	508	Tf	FT	A	15m	1	0.75
VSF	514	Tf	FT	B	15m	1	0.76

VLA cruise data

Ship	Id #	Time	Treatment	Location	Depth	Replicate	Salinity Tolerance†
VLA	X3	S0	SS	-	5m	1	0.53
VLA	X4	S0	SS	-	5m	2	0.45
VLA	511	Tf	C	B	1m	1	1.16
VLA	L6	Tf	C	C	1m	2	1.12
VLA	506	Tf	C	A	15m	1	0.97
VLA	512	Tf	C	B	15m	2	0.54
VLA	L3	Tf	C	C	profile	1	0.48
VLA	L4	Tf	C	C	profile	2	0.44
VLA	509	Tf	FT	A	1m	1	0.21
VLA	515	Tf	FT	B	1m	2	0.49
VLA	L5	Tf	FT	C	1m	3	0.24
VLA	L1	Tf	FT	C	profile	1	0.55
VLA	L2	Tf	FT	C	profile	2	0.19
VLA	510	Tf	FT	A	15m	1	0.36
VLA	516	Tf	FT	B	15m	2	1.14

† Salinity Tolerance refers to the relative growth rates of phytoplankton incubated at 15 ppt and 35 ppt.
See main report for full details.