

Disclaimer

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CHAPTER 3

ANALYSIS OF DISCHARGES AND POTENTIAL IMPACT TO HUMAN HEALTH AND THE ENVIRONMENT

This chapter summarizes the results of the wastewater characterization data for the nine types of vessel discharges sampled from the 61 vessels identified in Chapter 2. It includes the characterization of the nature, type, and composition of discharges for each class of vessel, as well as other relevant information collected regarding shipboard processes, equipment, materials, and operations that might contribute to the level or explain the presence of pollutants in these discharges.

This chapter begins with a description of the approach used for the analyses of contaminants in the various discharges of the vessel classes of interest in this sampling program, and the specific procedures used to reduce, present, and interpret these data. Each section in the chapter presents and discusses in detail the results found for each discharge type selected for evaluation in the vessel classes of interest and summarizes the major findings for the discharges associated with each major vessel type. The final section discusses anti-foulant hull coating, which warrants discussion based on the results of other studies conducted on this discharge type even though EPA did not sample this discharge in this study.

3.1 APPROACH TO ANALYSES

EPA's approach was designed to ensure that the analyses conducted under this study would be as comprehensive as possible and provide results that would represent the different vessels and discharges to the greatest extent possible. EPA included the discharge data collected from the vessels selected for this study (primary data) and any relevant data collected from other studies (secondary data) (e.g., engine effluent from small Armed Forces vessels covered under EPA's sampling program for the Uniform National Discharge Standards (UNDS) rulemaking). Where appropriate, EPA also assessed ambient (harbor) and potable waters at each geographic location where vessels were sampled.

EPA's analysis attempted to make full use of the primary and secondary data collected for this study, including data collected from ambient (harbor) and source (vessel service¹ or city water supply) waters. However, EPA recognizes that the analyses are based on a limited number of samples; in some cases, on a sample size of fewer than five. These results should be regarded as preliminary in nature due to statistical considerations related to small sample sizes.

¹ Service water here means the vessel potable water supply. For study vessels, vessel service water generally originates from municipal water supply rather than produced on board.

EPA also attempted to identify where the analyses and results from this study could be reasonably extrapolated to vessels other than those vessels sampled in this study. Many of the discharges are not unique to vessels subject to the P.L. 110-299 moratorium in terms of the expected pollutants or volumes and may also be found on larger nonrecreational vessels or recreational vessels.

3.1.1 Data Reduction and Presentation

EPA compiled the data collected for the nine vessel discharges sampled from the 61 vessels into a Microsoft (MS) Access database developed specifically for this study as described in Chapter 2, Section 2.2.5.3 of this report. For each discharge type, EPA reduced the data for summary according to the following procedure.

First, data were retrieved from MS Access by discharge group, using a query developed specifically for this task. The queried data included the analytical result with the corresponding screening benchmark (defined in Section 3.1.3) and ambient and source water concentrations. For each discharge group, the queried data were exported to MS Excel, and then resaved as tab-delimited ASCII text (*.txt) files. Record counts were compared between the discharge group-filtered MS Access query and the MS Excel and ASCII files to ensure that data were not lost.

The ASCII data for each discharge group were read into an Interactive Data Language (IDL) (Research Systems Inc., 2003) program that carried out a series of calculations for each analyte, based on the following algorithm:

1. Identify and average concentrations measured for field replicate samples, including replacing below-detection concentrations with $1/2$ of the reporting limit² when at least one replicate was detected.
2. Identify and average concentrations measured for laboratory replicate samples, including replacing below-detection concentrations with $1/2$ of the reporting limit when at least one replicate was detected.
3. Identify and average concentrations measured for vessel replicate samples (e.g., multiple deck wash, graywater, engine effluent samples from a single vessel), including replacing below-detection concentrations with $1/2$ of the reporting limit when at least one replicate was detected.
4. Calculate potential hazard quotients (PHQs) by dividing the vessel average concentration by the corresponding screening benchmark, if one was available (see further details provided in Section 3.1.3).

² Laboratory analyses for low concentration pollutants report a detection limit (the presence or absence of a pollutant) and a reporting limit (the level at which the concentration of a pollutant can be quantified with appropriate certainty). Statistical methods often require replacement of values that are below the detection and reporting limits of an analytical method (especially for zero values). EPA has established conventions on how to conduct this replacement. In this study, certain labs were able to provide a reporting limit for only certain analytes, which is not uncommon. For consistency, EPA chose to use a convention of replacing the nondetects with a value of $1/2$ of the reporting limit.

5. Output vessel-average results to a comma-separated value (CSV) text file.
6. Calculate nonparametric percentiles of the distribution of vessel-average analyte concentrations using the algorithm of Hyndman and Fan (2003). Note that below-detection vessel average concentrations were not replaced at this step.
7. Replace below-detection vessel average concentrations for those analytes where at least one concentration was detected with 1/2 of the reporting limit. Calculate detected proportion of vessel concentrations for each analyte.
8. Output vessel-average results to a CSV text file.
9. Calculate average discharge group analyte concentrations from the vessel average concentrations, including replacement values.
10. Output statistics for each analyte (number of samples, number and proportion detected, average, and nonparametric percentiles) to a CSV text file.
11. Read vessel-average results (including replacement) into SYSTAT Version 6.1 (SPSS, 1996) to generate box and density plots for each analyte class (see Section 3.2.1 below).
12. Read these results into MS Excel and then reassemble into a workbook with the database query exported from MS Access. Generate summary data tables from these workbooks.
13. For each discharge category, reproduce by hand the data reduction and statistical calculations identified above for two or more randomly selected analytes as a QA procedure.

All discharge-specific analytes summarized in subsequent sections of this chapter are organized into the following major groups: classical pollutants³, metals, nonylphenols, nutrients, pathogen indicators, semivolatile organic compounds, and volatile organic compounds. For each discharge type, the analyte groups are generally presented according to the order of highest expected significance or risk in that specific discharge (e.g., the graywater section begins with pathogen indicators). The specific list of target analytes by group is provided in Appendix D. EPA did not analyze all vessel discharges for all selected analyte groups; see Table 2.2 for target analyte groups by discharge type.

3.1.2 Summary Statistics and Box Plots

This section includes, for each analyte group within a specific discharge type (e.g., bilgewater, deck washdown water), tables that summarize the number of samples analyzed, the number of times a specific analyte within an analyte group was detected, the average concentration (when only one sample was analyzed, the average is equal to the measurement), and additional standard summary statistics related to the measured analyte concentrations (median, min, max and selected (10th, 25th, 75th, and 90th) percentiles). These additional statistics were only calculated when a sufficient number of samples had detected values for any given

³ The classical pollutants group of analytes combines several standard water quality parameters such as conductivity, salinity, temperature, etc. with other parameters EPA defines as conventional pollutants (biochemical oxygen demand (BOD), total suspended solids (TSS), pH, fecal coliform, and oil and grease). For convenience, this group also includes other common analytes such as total residual chlorine, or TRC. For simplicity, these conventional and other common analytes and water quality parameters have all been grouped under the term "classical pollutants."

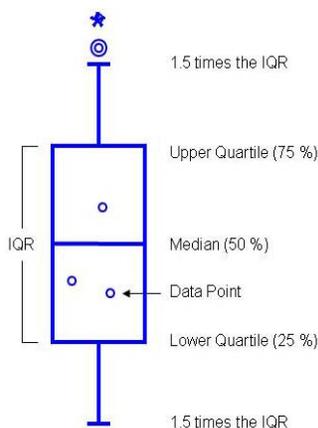
analyte (usually five detected values or greater). In cases where some of the concentrations of an analyte were reported as nondetect (censored), the concentration of that sample was estimated as $\frac{1}{2}$ of the reporting limit for purposes of calculating average concentrations⁴.

In addition to the summary tables, this section includes figures that graphically present the analyte-specific concentrations that were detected (as well as any replacement values for nondetects) for each analyte group within a discharge to better identify data trends related to analytes of potential concern. These figures are shown as box and dot plots, with the names of the analytes along the x (independent)-axis and their associated measured concentrations along with y(dependent)-axis.

For box plots, the bottom and top of the box displays the 25th and 75th percentile concentrations defined as the interquartile range or IQR (i.e., the “box” contains 50 percent of the data values), respectively. The median is displayed as the horizontal line within the box. The “whiskers” show the relative distribution of data points outside of the IQR and represent 1.5 times the IQR. Superimposed over each box plot are the actual data points, shown as small open circles. Circles surrounded by large circles are outliers greater or less than 1.5 times the IQR. Circles covered by asterisks are outliers greater or less than three times the IQR.

What is a Box Plot?

A box plot is a useful, simple statistical tool used to show basic characteristics of a data set. A box plot can show the approximate center of a data set and how those data are spread over a range in values – in this case, a range of concentrations. Below is an example box plot indicative of the type of graphical data display used throughout this chapter.



3.1.3 Calculation of Potential Hazard Quotients

To provide a context for the level of contaminant concentrations presented, EPA used National Recommended Water Quality Criteria (NRWQC)⁵ and several other benchmarks as a

⁴ See footnote 2.

⁵ National Recommended Water Quality Criteria (NRWQC) include acute (short-term) and chronic (long-term) criteria (toxicity threshold values) for the protection of aquatic life, as well as Human Health criteria for protection of humans from consumption of contaminated water or contaminated water and aquatic organisms. EPA's most recent compilation of NRWQC (2006) is presented as a summary table containing recommended water quality criteria for the protection of aquatic life and human health in surface water for approximately 150 pollutants. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA) and provide guidance for states and

preliminary screen for all discharge data with the potential to cause or contribute to the nonattainment of a water quality standard in a given receiving water body. The “screening-level” benchmarks chosen for this purpose are shown in Table 3.1 at the end of this subsection, and generally represent EPA’s most conservative (protective) concentration available for the specific analyte of interest. Several “legacy” standards (for BOD, TSS and total phosphorus) are also included with the screening benchmarks. For BOD and TSS, these benchmarks are EPA’s secondary treatment effluent limits for sewage treatment plants⁶. For total phosphorus, the benchmark of 0.1 mg/L is from EPA’s Gold Book (USEPA, 1986b) and represents a concentration recommended to prevent nuisance algal blooms resulting from eutrophication in flowing waters. EPA did not consider it appropriate to apply ecoregional nutrient criteria for this project.

EPA’s NRWQC are recommended concentrations of analytes in a water body that are intended to protect human health, aquatic organisms and the water body uses from unacceptable effects from exposures to these pollutants. The NRWQC are not directly related to analyte concentrations in a discharge for a number of reasons. First, NRWQC not only have a concentration component, but also a duration and frequency component. Second, it is not always necessary to meet all water quality criteria within the discharge pipe to protect the integrity of a water body (USEPA, 1991). Under EPA’s regulations at 40 CFR 122.44(d)(1)(ii), when determining whether a discharge causes, has the reasonable potential to cause, or contributes to an in-stream excursion above a narrative or numeric criteria within a state water quality standard, the permitting authority will use procedures that account for, where appropriate, the dilution of the effluent in the receiving water. A mixing zone allows for ambient concentrations above the criteria in small areas near outfalls while dilution occurs. To ensure mixing zones do not impair the integrity of the water body, the permitting authority will determine the mixing zone such that it does not cause lethality to passing organisms and, considering likely pathways of exposure, significant human health risks.

tribes to use in adopting water quality standards. EPA’s 2006 NRWQC are available at:

<http://www.epa.gov/waterscience/criteria/wqctable/>, hereafter referred to as EPA’s 2006 NRWQC.

⁶ Secondary treatment standards for sewage treatment plants were technology-based limits developed in the late 1970s and early 1980s, and are not the same as the water-quality-based criteria in the 2006 NRWQC. Thus, the PHQs for BOD and TSS calculated as described below are not directly comparable to the PHQs based on criteria designed to protect aquatic life or human health but, by design, such standards are imposed to limit ecological impacts.

Nevertheless, comparing analyte concentrations in vessel discharges to NRWQC (or other equivalent screening benchmark) provides a conservative screen of whether these discharges cause, have the reasonable potential to cause, or contribute to nonattainment of the water quality standards in a water body. EPA calculated hazard quotients (HQs) by dividing the concentration of a particular analyte⁷ by its corresponding water quality criterion or other benchmark as an initial screen for the discharge-specific water sample data. If the concentration of a given analyte in vessel discharge is less than the applicable screening criterion or benchmark

Mitigating Conditions/Circumstances in a Water Body

Compared to the volume of a typical harbor, the effluent volume of any particular vessel discharge is small (see Chapter 4). Therefore, even when pollutant concentrations of a particular effluent are high, the total loading of that pollutant on the receiving water of the harbor can be relatively small. Furthermore, most harbors are continually flushed by freshwater and tidal activity. These dilution factors, in addition to the mitigating capacity of saltwater cations and organic matter, may reduce the toxicity of many of these pollutants.

values (HQ<1), the discharge would likely not cause, have the reasonable potential to cause, or contribute to nonattainment of a water quality standard based on that value, particularly after considering assimilation and/or dilution by the receiving water. If the HQ value is greater than one, then there is the possibility of ecological or human health risk as the concentration of a

given analyte in vessel discharge is greater than the applicable screening criterion or benchmark values (USEPA, 1997). However, because discharges in this study are measured at the “end of pipe” before being released into a harbor where they are subsequently diluted, HQ values of greater than one do not necessarily indicate that a discharge poses a significant risk or would be likely to cause or contribute to a water quality standard exceedance. Further, the presence of additional environmental factors such as dissolved organic carbon can reduce the toxicity of certain pollutants (e.g., metals and many organic pollutants) and reduce the likelihood of ecological or health risk. Because of these additional considerations, EPA uses the term potential hazard quotients (PHQs) instead to indicate this difference, as the PHQs are only intended to indicate that a screening benchmark was exceeded and the discharge thus warrants further consideration regarding the potential to cause or contribute to nonattainment of water quality standards⁸.

Mobile sources such as vessels complicate the analysis because they discharge to many different water bodies, but in general, greater mixing and dilution would be expected for discharges from vessels than from stationary sources when they are in motion while discharging. EPA acknowledges that vessel discharges to areas with high vessel traffic, areas with a low degree of flushing, or impaired water bodies could reduce mixing and dilution. With these

⁷ HQs were also calculated using replacement values for nondetected concentrations, so that such results would be represented in the box and scatter plots.

⁸ EPA does not consider a PHQ that exceeds 1 to signal that these discharges pose a potential risk to cause or contribute to the non-attainment of a water quality standard when the PHQ is based on replacement values for nondetected concentrations.

factors in mind and assuming the data from this study are representative of the class of vessels as a whole, a PHQ marginally above a value of 1 is most likely not of significant concern. On the other hand, a PHQ value substantially above 1 (e.g., 10 or 100) may be more likely to be of concern, particularly if the discharge is of significant volume, is in an area of low flushing, is in an area where there is a high degree of vessel traffic, or is in a waterbody that is already impaired or under other stress.

EPA recognizes that one of the key factors in evaluating metal toxicity is the bioavailability of the metal to an organism. Exposure to metals at toxic levels can cause a variety of changes in biochemical, physiological, morphological, and behavioral patterns in aquatic organisms. In the aquatic environment, elevated concentrations of dissolved metals can be toxic to many species of algae, crustaceans, and fish. Some metals have a strong tendency to adsorb to suspended organic matter and clay minerals or to precipitate out of solution, thus removing the metal from the water column. The tendency of a given metal to adsorb to suspended particles is typically controlled by the pH and salinity of the water body, as well as the organic carbon content of the suspended particles. If the metal is highly sorbed to particulate matter, then it is not likely to be in a dissolved form that aquatic organisms can process (i.e., bioavailable)⁹.

Accordingly, NRWQC for the protection of aquatic life for metals are typically expressed in the dissolved form. Therefore, a high concentration of a metal measured in its total form (dissolved and particulate) may not be an accurate representation of its toxic potential to aquatic organisms. In contrast, human health criteria (for the consumption of organisms) for metals are commonly expressed in the total metal form because human exposure to pollutants is assumed to be through the consumption of organisms, where the digestive process is assumed to transform all forms of metals to the dissolved phase, thus increasing the amount of biologically available metals. EPA was mindful of this distinction between aquatic life and human health criteria for metals when comparing the dissolved and total metals concentration data in the various discharges to NRWQC and when calculating PHQs using the screening benchmarks. In particular, in considering the potential for vessel discharges to pose a risk to human health, EPA also noted the likelihood of human exposure to such discharges (e.g., potential for receiving water to be used as drinking water source).

EPA chose to include the major cations calcium, magnesium, potassium and sodium in the metals analysis to further characterize the vessel discharges. As common ions in surface

⁹ Note that the bioavailability of metals is a relative term and depends on many factors. For example, particulate metals complexed to suspended organic matter or clay minerals may be recycled into the water column and become bioavailable due to physical resuspension (dredging activities) of bed sediments or bioturbation (the stirring or mixing of sediment particles by benthic animals). Depending on conditions in the water column and microbiological activity within the surficial sediment and overlying water surface layers, these physical and biological actions might remobilize the metals in the dissolved bioavailable form for potential uptake by aquatic organisms. Likewise, certain benthic organisms called deposit feeders might consume particulate-bound metals and re-release metals via digestion and excretion or introduce metals into the food chain when consumed by predators.

waters, the concentrations of these ions are indicative of the sample matrix (i.e., freshwater, saltwater, brackish water) rather than pollutant loadings. Accordingly, major cation concentrations are typically elevated (up to three orders of magnitude higher) relative to other metals included in the metals analysis (e.g., copper, lead, and zinc). For example, the typical concentrations of major cations in full and partial (brackish) strength seawater and in freshwater of various total water hardness levels are listed in Tables 3.2 and 3.3 below. Major cations are not toxic except at extreme, uncommon levels.

For convenience, data tables for metals in this chapter segregate the presentation of major cation concentration data from that of the other metals to clearly distinguish between the naturally occurring cations and other metals of potential concern in vessel discharges.

Table 3.1. Water Quality and Other Benchmark Values Used to Screen the Vessel Discharge Data

Analyte	Screening Benchmarks	Units	Source ¹
1,1,2,2-Tetrachloroethane	0.17	µg/L	2006 NRWQC HH W+O
1,1,2-Trichloroethane	0.59	µg/L	2006 NRWQC HH W+O
1,1-Dichloroethene	330	µg/L	2006 NRWQC HH W+O
1,2,4,5-Tetrachlorobenzene	0.97	µg/L	2006 NRWQC HH W+O
1,2,4-Trichlorobenzene	35	µg/L	2006 NRWQC HH W+O
1,2-Dichlorobenzene	420	µg/L	2006 NRWQC HH W+O
1,2-Dichloroethane	0.38	µg/L	2006 NRWQC HH W+O
1,2-Dichloropropane	0.5	µg/L	2006 NRWQC HH W+O
1,2-Diphenyl hydrazine	0.036	µg/L	2006 NRWQC HH W+O
1,3-Dichlorobenzene	320	µg/L	2006 NRWQC HH W+O
1,3-Dichloropropane	0.34	µg/L	2006 NRWQC HH W+O
1,4-Dichlorobenzene	63	µg/L	2006 NRWQC HH W+O
2,3,7,8-TCDD (Dioxin)	5.0E-09	µg/L	2006 NRWQC HH W+O
2,4,5-Trichlorophenol	1800	µg/L	2006 NRWQC HH W+O
2,4,6-Trichlorophenol	1.4	µg/L	2006 NRWQC HH W+O
2,4-Dichlorophenol	77	µg/L	2006 NRWQC HH W+O
2,4-Dimethylphenol	380	µg/L	2006 NRWQC HH W+O
2,4-Dinitrophenol	69	µg/L	2006 NRWQC HH W+O
2,4-Dinitrotoluene	0.11	µg/L	2006 NRWQC HH W+O
2-Chloronaphthalene	1000	µg/L	2006 NRWQC HH W+O
2-Chlorophenol	81	µg/L	2006 NRWQC HH W+O
2-Methyl-4,6-Dinitrophenol	13	µg/L	2006 NRWQC HH W+O
3,3'-Dichlorobenzidine	0.021	µg/L	2006 NRWQC HH W+O
4,4'-DDD	0.00031	µg/L	2006 NRWQC HH Org Only
4,4'-DDE	0.00022	µg/L	2006 NRWQC HH Org Only
4,4'-DDT	0.0010	µg/L	2006 NRWQC CCC
4,6-Dinitro-2-methylphenol	13	µg/L	2006 NRWQC HH W+O
Asbestos	7000000	fibers/L	2006 NRWQC HH W+O
Acenaphthene	670	µg/L	2006 NRWQC HH W+O
Acrolein	6.0	µg/L	2006 NRWQC HH W+O
Acrylonitrile	0.051	µg/L	2006 NRWQC HH W+O
Aldrin	1.3	µg/L	2006 NRWQC SW CMC
Alkalinity	20000	µg/L	2006 NRWQC FW CCC
alpha-BHC	0.0026	µg/L	2006 NRWQC HH W+O
alpha-Endosulfan	0.0087	µg/L	2006 NRWQC SW CCC
Aluminum, Total	87	µg/L	2006 NRWQC FW CCC
Ammonia As Nitrogen (NH ₃ -N)	1.2	mg/L	2006 NRWQC SW CCC
Anthracene	8300	µg/L	2006 NRWQC HH W+O
Antimony, Total	5.6	µg/L	2006 NRWQC HH W+O
Arsenic, Total	0.018	µg/L	2006 NRWQC HH W+O
Arsenic, Dissolved	36	µg/L	2006 NRWQC SW CCC
Barium, Total	1000	µg/L	2006 NRWQC HH W+O
Benzene	2.2	µg/L	2006 NRWQC HH W+O
Benzidine	0.000086	µg/L	2006 NRWQC HH W+O
Benzo(a)Anthracene	0.0038	µg/L	2006 NRWQC HH W+O

Analyte	Screening Benchmarks	Units	Source ¹
Benzo(a)Fluoranthene	0.0038	µg/L	2006 NRWQC HH W+O
Benzo(a)pyrene	0.0038	µg/L	2006 NRWQC HH W+O
Benzo(b)fluoranthene	0.0038	µg/L	2006 NRWQC HH W+O
Benzo(k)Fluoranthene	0.0038	µg/L	2006 NRWQC HH W+O
beta-BHC	0.0091	µg/L	2006 NRWQC HH W+O
beta-Endosulfan	0.0087	µg/L	2006 NRWQC SW CCC
Biochemical Oxygen Demand (BOD)	30	mg/L	1984 Secondary Treatment Effluent Limits
Bis (2-Chloroethyl) ether	0.030	µg/L	2006 NRWQC HH W+O
Bis (2-chloroisopropyl)ether	1400	µg/L	2006 NRWQC HH W+O
Bis(2-Chloroethyl)ether	0.030	µg/L	2006 NRWQC HH W+O
Bis(2-Ethylhexyl) phthalate	1.2	µg/L	2006 NRWQC HH W+O
Bromodichloromethane	0.55	µg/L	2006 NRWQC HH W+O
Bromoform	4.3	µg/L	2006 NRWQC HH W+O
Bromomethane	47	µg/L	2006 NRWQC HH W+O
Butyl benzyl Phthalate	1500	µg/L	2006 NRWQC HH W+O
Cadmium, Dissolved	0.25	µg/L	2006 NRWQC FW CCC
Carbon tetrachloride	0.23	µg/L	2006 NRWQC HH W+O
Chlordane	0.0040	µg/L	2006 NRWQC SW CCC
Chloride	230000	µg/L	2006 NRWQC FW CCC
Chlorobenzene	130	µg/L	2006 NRWQC HH W+O
Dibromochloromethane	0.40	µg/L	2006 NRWQC HH W+O
Chloroform	5.7	µg/L	2006 NRWQC HH W+O
Chlorophenoxy Herbicide (2,4,5,-TP)	10	µg/L	2006 NRWQC HH W+O
Chlorophenoxy Herbicide (2,4-D)	100	µg/L	2006 NRWQC HH W+O
Chlorpyrifos	0.0056	µg/L	2006 NRWQC SW CCC
Chromium, Dissolved	11	µg/L	2006 NRWQC FW CCC
Chrysene	0.0038	µg/L	2006 NRWQC HH W+O
Copper, Dissolved	3.1	µg/L	2006 NRWQC SW CCC
Copper, Total	1300	µg/L	2006 NRWQC HH W+O
Cyanide	1.0	µg/L	2006 NRWQC SW CMC
Demeton	0.10	µg/L	2006 NRWQC FW and SW CCC
Diazinon	0.17	µg/L	2006 NRWQC FW CMC and CCC
Dibenz(a,h)Anthracene	0.0038	µg/L	2006 NRWQC HH W+O
Chlorodibromomethane	0.40	µg/L	2006 NRWQC HH W+O
Dichlorobromomethane	0.55	µg/L	2006 NRWQC HH W+O
Dieldrin	0.0019	µg/L	2006 NRWQC SW CCC
Diethyl Phthalate	17000	µg/L	2006 NRWQC HH W+O
Dimethyl phthalate	270000	µg/L	2006 NRWQC HH W+O
Di-n-butyl phthalate	2000	µg/L	2006 NRWQC HH W+O
Dinitrophenols	69	µg/L	2006 NRWQC HH W+O
E. Coli by MPN	126	MPN/100 ml	1986 NRWQC B FW
Endosulfan Sulfate	62	µg/L	2006 NRWQC HH W+O
Endrin	0.0023	µg/L	2006 NRWQC SW CCC
Endrin Aldehyde	0.29	µg/L	2006 NRWQC HH W+O
Enterococci by MPN	33	MPN/100 ml	1986 NRWQC B FW
Ether, Bis(Chloromethyl)	0.00010	µg/L	2006 NRWQC HH W+O
Ethylbenzene	530	µg/L	2006 NRWQC HH W+O
Fecal Coliform by MF	14	MPN/100 ml	1976 QCW SH

Analyte	Screening Benchmarks	Units	Source ¹
Fluoranthene	130	µg/L	2006 NRWQC HH W+O
Fluorene	1100	µg/L	2006 NRWQC HH W+O
Gamma-BHC (Lindane)	0.16	µg/L	2006 NRWQC SW CMC
Guthion	0.010	µg/L	2006 NRWQC FW and SW CCC
Heptachlor	0.0036	µg/L	2006 NRWQC SW CCC
Heptachlor Epoxide	0.0036	µg/L	2006 NRWQC SW CCC
Hexachlorobenzene	0.00028	µg/L	2006 NRWQC HH W+O
Hexachlorobutadiene	0.44	µg/L	2006 NRWQC HH W+O
Hexachlorocyclo-hexane-Technical	0.0123	µg/L	2006 NRWQC HH W+O
Hexachlorocyclopentadiene	40	µg/L	2006 NRWQC HH W+O
Hexachloroethane	1.4	µg/L	2006 NRWQC HH W+O
Hexane Extractable Material (HEM)	15	mg/L	MARPOL 73/78
Ideno(1,2,3-cd)Pyrene	0.0038	µg/L	2006 NRWQC HH W+O
Iron, Total	300	µg/L	2006 NRWQC HH W+O
Isophorone	35	µg/L	2006 NRWQC HH W+O
Lead, Dissolved	2.5	µg/L	2006 NRWQC FW CCC
Malathion	0.1	µg/L	2006 NRWQC FW and SW CCC
Manganese	50	µg/L	2006 NRWQC HH W+O
Mercury	0.77	µg/L	2006 NRWQC FW CCC
Methoxychlor	0.03	µg/L	2006 NRWQC SW CCC
Methylene chloride	4.6	µg/L	2006 NRWQC HH W+O
Mirex	0.001	µg/L	2006 NRWQC FW and SW CCC
Nickel, Dissolved	8.2	µg/L	2006 NRWQC SW CCC
Nickel, Total	610	µg/L	2006 NRWQC HH W+O
Nitrates	10000	µg/L	2006 NRWQC HH W+O
Nitrobenzene	17	µg/L	2006 NRWQC HH W+O
Nitrosamines	0.0008	µg/L	2006 NRWQC HH W+O
Nitrosodibutylamine,N	0.0063	µg/L	2006 NRWQC HH W+O
Nitrosodiethylamine,N	0.0008	µg/L	2006 NRWQC HH W+O
Nitrosopyrrolidine,N	0.016	µg/L	2006 NRWQC HH W+O
N-Nitroso Di-n-propylamine	0.005	µg/L	2006 NRWQC HH W+O
N-Nitrosodimethylamine	0.00069	µg/L	2006 NRWQC HH W+O
N-Nitrosodiphenylamine	3.3	µg/L	2006 NRWQC HH W+O
Parathion	0.013	µg/L	2006 NRWQC FW CCC
Pentachlorobenzene	1.4	µg/L	2006 NRWQC HH W+O
Pentachlorophenol	7.9	µg/L	2006 NRWQC SW CCC
Phenol	21000	µg/L	2006 NRWQC HH W+O
Phosphorus (as phosphate)	0.1	mg/L	EPA 1986 Goldbook
Polychlorinated Biphenyls (PCBs)	0.000064	µg/L	2006 NRWQC HH W+O
Pyrene	830	µg/L	2006 NRWQC HH W+O
Selenium, Dissolved	5	µg/L	2006 NRWQC FW CCC
Selenium, Total	170	µg/L	2006 NRWQC HH W+O
Silica Gel Treated HEM (SGT-HEM)	15	mg/L	MARPOL 73/78
Silver, Dissolved	1.9	µg/L	2006 NRWQC SW CMC
Solids Dissolved and Salinity	250000	µg/L	2006 NRWQC HH W+O
Sulfide-Hydrogen Sulfide	0.002	mg/L	2006 NRWQC FW and SW CCC
Tetrachloroethene	0.69	µg/L	2006 NRWQC HH W+O
Thallium, Total	0.24	µg/L	2006 NRWQC HH W+O

Analyte	Screening Benchmarks	Units	Source ¹
Toluene	1300	µg/L	2006 NRWQC HH W+O
Total Nonylphenols	1.7	µg/L	2006 NRWQC SW CCC
Total Phosphorus	0.1	mg/L	1986 NRWQC
Total Polychlorinated Biphenyls	0.000064	µg/L	2006 NRWQC HH Org Only
Total Suspended Solids (TSS)	30	mg/L	1984 Secondary Treatment Effluent Limits
Total Residual Chlorine (TRC)	0.0075	mg/L	2006 NRWQC SW CCC
Toxaphene	0.0002	µg/L	2006 NRWQC FW and SW CCC
trans-1,2-Dichloroethene	140	µg/L	2006 NRWQC HH W+O
Tributyltin (TBT)	0.0074	µg/L	2006 NRWQC SW CCC
Trichloroethene	2.5	µg/L	2006 NRWQC HH W+O
Vinyl chloride	0.025	µg/L	2006 NRWQC HH W+O
Zinc, Dissolved	81	µg/L	2006 NRWQC SW CCC
Zinc, Total	7400	µg/L	2006 NRWQC HH W+O

(1) Sources:

MARPOL 73/78: International Convention for the Prevention of Pollution From Ships, 1973 as modified by the Protocol of 1978 (MARPOL 73/88, 1978).

1976 QCW SH (shellfish harvesting): Note MPN is most probable number and approximates the unit of measure for fecal coliform in this study of CFU (colony forming units) (USEPA, 1976).

1984 Secondary Treatment Effluent Limits: 49 FR 37006, Sept. 20, 1984.

1986 NRWQC B FW (bathing (full body contact) recreational waters – fresh water): (USEPA, 1986).

Quality Criteria for Water 1986 (Goldbook) (USEPA, 1986b).

2006 NRWQC FW CCC (freshwater chronic): (USEPA, 2006).

2006 NRWQC SW CCC (saltwater chronic) (USEPA, 2006).

2006 NRWQC SW CMC (saltwater acute) (USEPA, 2006).

2006 NRWQC HH Org Only (human health for the consumption of organism only) (USEPA, 2006).

2006 NRWQC HH W+O (human health for the consumption of water + organism) (USEPA, 2006).

Table 3.2. Major Cation Concentrations in Seawater

Seawater Salinity Level	Calcium, mg/L	Magnesium, mg/L	Potassium, mg/L	Sodium, mg/L
Full Strength ¹ (35 ppt salinity)	400	1,350	380	10,500
Brackish ² (10 ppt salinity)	114	386	109	3,000

(1) Source: Mowka, 2009.

(2) Calculated from full strength seawater concentrations, assuming dilution by ion-free water.

Table 3.3. Major Cation Concentrations in Freshwater

Freshwater Hardness Level	Calcium, mg/L	Magnesium, mg/L	Potassium, mg/L	Sodium, mg/L
Soft (40-48 mg CaCO ₃ /L) ¹	6.99	6.06	1.05	13.1
Moderately Hard (80-100 mg CaCO ₃ /L) ¹	14.0	12.1	2.10	26.3
Hard (160-180 mg CaCO ₃ /L) ¹	27.9	24.2	4.20	52.5

(1) Source: USEPA, 2007.

3.2 CHARACTERIZATION OF DISCHARGES

Each subsection of Section 3.2 presents in detail the observed results for the discharge types selected for evaluation in the study vessels: bilgewater; stern tube packing gland effluent; deck runoff and/or washdown; fish hold effluent (both refrigerated seawater effluent and ice slurry) and effluent from the cleaning of fish holds; graywater; propulsion (inboard and outboard) and generator engine effluent; and discharges from firemain systems. Tables and figures are presented at the end of each subsection.

3.2.1 Bilgewater

Bilgewater can be found on board every vessel and describes the water that collects in the bottom of a vessel. This water may be from rough seas, rain, minor leaks in the hull or stuffing box, etc. Depending on the ship's design and function, bilgewater sometimes contains contaminants such as oil, fuel, graywater, detergents, solvents, chemicals, pitch, and particulates. For this study, EPA collected bilgewater samples from seven vessels: two tow/salvage vessels, two water taxis, one longline fishing vessel, one shrimping vessel, and one tour boat.

EPA estimated bilgewater discharge volumes based on data and field observations from EPA's vessel sampling program, as well as information from secondary data sources. Based on this information, EPA estimates many commercial vessels generate, on average, between 10 and 15 gallons per day (gpd) of bilgewater depending on the vessels' configuration and intended use; however, EPA noted that vessels might generate as little as 2 gallons of bilgewater or as much as 750 gallons of bilgewater per day. For vessels such as small tow/salvage vessels or water taxis with open bows, bilgewater pump-out can occur frequently throughout the day, resulting in small volumes during each pump-out cycle (1-2 gallons). Larger vessels such as commercial fishing boats are likely to pump less frequently due to larger storage capacity in the bilge; however, the bilgewater discharge volume can be hundreds of gallons. For example, EPA noted that a 26-foot, center console Boston Whaler being used as a tow/salvage vessel had accumulated only 2 gallons of bilgewater following a tow activity. However, a 62-foot shrimp boat sampled by EPA in the Gulf of Mexico discharged approximately 750 gallons of bilgewater during the daily pump-out.

In general, the volume of bilgewater generated by commercial fishing boats and commercial vessels depends on the following factors:

- Hull and deck construction
- Vessel size
- Precipitation
- Frequency of deck cleaning
- Amount of spray reaching the deck(s)
- Accidental spills
- Integrity of hull and below-deck piping systems
- Potential for condensate formation in below-deck areas.

Commercial vessels with open bow and stern areas (e.g., commercial fishing and tow/salvage vessels) have relatively large deck areas that are exposed to precipitation, spray, and cleaning water, which results in greater bilgewater volumes compared to vessels such as tour boats or water taxis that have less exposed deck. Other sources that contribute to bilgewater onboard commercial vessels include small leaks in potable water, graywater and sewage piping systems, and condensates from the interior of the hull or refrigeration systems. The volume of these additional bilgewater sources is also highly vessel-specific.

In this vessel sampling program, EPA collected single grab samples of bilgewater discharge from selected vessels for laboratory analysis. The results of the analysis were intended to be representative of bilgewater pollutant concentrations over the range of normal vessel operations. Collecting bilgewater samples proved difficult for EPA for a number of reasons including: (1) automatic bilge pumps would discharge insufficient volumes of bilgewater in a single operating cycle, (2) vessel operators were generally reluctant to discharge bilgewater for fear of exceeding existing CWA § 311 requirements (oily discharges), and (3) sampling was often impractical because bilgewater was typically discharged via thru-hull openings located at or near the vessel's waterline.

Bilgewater samples were analyzed for a wide range of pollutants including metals, classical pollutants, pathogen indicators, nutrients, semivolatile and volatile organic compounds, and nonylphenols. Results for each class of pollutant are presented and discussed in the following subsections.

3.2.1.1 Metals

Bilgewater samples were analyzed for dissolved¹⁰ and total (dissolved plus particulate) concentrations of metals. The analytical results are summarized in Table 3.1.1 for dissolved metals and in Table 3.1.2 for total metals that were detected in at least one bilgewater sample. The following metals were measured in all bilgewater samples:

- Total aluminum
- Total arsenic
- Dissolved and total barium
- Dissolved and total calcium
- Dissolved and total copper
- Dissolved and total magnesium
- Dissolved and total manganese
- Dissolved and total potassium
- Dissolved and total sodium
- Dissolved and total zinc.

¹⁰ Dissolved metals were obtained by filtering the water sample.

Concentrations of other metals were measured in 50 percent or more of the samples analyzed:

- Dissolved aluminum
- Dissolved arsenic
- Dissolved and total chromium
- Total iron
- Total lead
- Dissolved and total nickel
- Dissolved and total selenium.

Figure 3.1.1 presents the range of concentrations measured for dissolved metals in the bilgewater samples. The plots show that dissolved metals concentrations range over six orders of magnitude. Calcium, magnesium, potassium and sodium were the dissolved metals measured at the highest concentrations. As discussed in Chapter 1 and Section 3.1.3, these cations naturally occur in seawater and their levels in the discharges are similar to levels seen in ambient seawater. As many discharges use ambient water for onboard activities, and spray would contribute to other discharges, it was not unexpected to find these levels of cations in the bilgewater samples as most vessels were sampled in coastal areas. At these concentrations, these cations are generally not toxic to aquatic organisms, which is why there are no NRWQC for these metals, and therefore, no PHQs were calculated (see Section 3.1.3 for additional explanation). Dissolved aluminum, barium, copper, manganese, selenium and zinc were also measured at relatively high concentrations (tens to hundreds of $\mu\text{g/L}$) in most bilgewater samples; dissolved arsenic and iron were also measured at concentrations greater than $100 \mu\text{g/L}$ in individual samples. Among the vessels from which bilgewater was sampled, a tow/salvage boat had the highest concentrations of the most dissolved metals (seven analytes), while the water taxi had only one dissolved metal.

Dissolved versus Total Metals

EPA recommends using dissolved metal to set and measure compliance with water quality standards because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal (USEPA, 1993). EPA considers that the primary mechanism for toxicity to organisms that live in the water column to be adsorption to or uptake across the respiratory surfaces of aquatic organisms (i.e., the gills) as well as the carapace of certain invertebrates, and this physiological process requires metal to be in a dissolved form. This is not to suggest that particulate metals are nontoxic; rather, because toxicity of particulate metals are primarily restricted to direct ingestion via dietary exposure, they are less toxic overall compared to dissolved metal (USEPA, 1996). There are exceptions, however, particularly for bottom feeding organisms, and for metals that bioaccumulate (also see footnote in Section 3.1.3 regarding physical and biological recycling of particulate metals). Dissolved metal is *operationally defined* as that which passes through a $0.45\text{-}\mu\text{m}$ or a $0.40\text{-}\mu\text{m}$ filter and particulate metal is *operationally defined* as total recoverable metal minus dissolved metal. EPA typically uses the dissolved fraction, or f_d , to express the fraction of the total chemical concentration in water that is dissolved. To calculate f_d , divide the dissolved concentration by the total concentration. A chemical that is entirely in the dissolved phase has a f_d of 1, while a chemical that is entirely in the particulate phase has a f_d of 0.

Figure 3.1.2 shows the total metals concentrations in the bilgewater samples. The box plots show that the relative ranges of total metals concentrations are comparable to the concentrations of dissolved metals. Among the vessels from which bilgewater was sampled, the shrimper had the highest concentrations of the most total metals (11), while the longliner and the water taxi had the fewest (one each). In general, total concentrations for each metal are similar to or slightly higher than the dissolved concentrations. To explore this relationship further, EPA calculated the average dissolved fraction f_d of each metal in the bilgewater samples to better understand the potential for aquatic organism impacts. The metals with the highest average dissolved fractions ($f_d > 90$ percent) included barium, calcium, magnesium, potassium, selenium, and zinc. Metals having intermediate average dissolved fractions ($90 \text{ percent} > f_d > 50 \text{ percent}$) included antimony, arsenic, cadmium, chromium, cobalt, copper, iron, manganese, and nickel. Aluminum, lead, and vanadium had the lowest average dissolved fractions ($f_d < 50$ percent).

Figure 3.1.3 shows the distributions of PHQs based on the most conservative screening benchmark for each of the dissolved metals. Per Section 3.1.3 above, points on this plot above the dashed line (demarcating a PHQ of one) indicate a dissolved metal concentration exceeding the benchmark; three of the dissolved metals (cadmium, copper, and selenium) have PHQs that include values greater than 10, indicating that the measured concentrations were one (or more) order of magnitude greater than the screening benchmark. The highest PHQ (113) was for dissolved copper, measured in the bilgewater sample from the tour boat. EPA also found PHQs exceeding one for dissolved arsenic, chromium, lead, nickel, and zinc, bringing to eight the number of dissolved metals that exceeded the most stringent 2006 NRWQC in one or more bilgewater sample. Dissolved copper concentrations, ranging from 6.6 to 350 $\mu\text{g/L}$, exceeded the saltwater acute (4.8 $\mu\text{g/L}$) and chronic (3.1 $\mu\text{g/L}$) criteria in all seven bilgewater samples; concentrations in all but one bilgewater sample also exceeded the freshwater acute (13 $\mu\text{g/L}$) and chronic (9 $\mu\text{g/L}$) criteria. Each of the four detected dissolved selenium concentrations, ranging from 30 to 57 $\mu\text{g/L}$, exceeded the freshwater chronic criterion (5 $\mu\text{g/L}$). The single elevated dissolved cadmium concentration (10 $\mu\text{g/L}$) exceeded the freshwater acute (2.0 $\mu\text{g/L}$) and chronic (0.25 $\mu\text{g/L}$) criteria, and the saltwater chronic (8.8 $\mu\text{g/L}$) criterion. In addition, the highest dissolved arsenic concentration (230 $\mu\text{g/L}$) exceeded the 36 $\mu\text{g/L}$ saltwater chronic criterion. For the other dissolved metals (chromium, lead, nickel, and zinc), concentrations in one or more bilgewater samples exceeded saltwater and/or freshwater criteria, although in each of these cases the PHQs were less than five.

Three of the total metals (aluminum, arsenic, and iron) exceeded the most stringent 2006 NRWQC¹¹ in one or more bilgewater samples as shown in Figure 3.1.4. PHQs for total arsenic ranged from 72 to 1,790. All of the total arsenic concentrations exceeded the human health criterion for consumption of water plus organism of 0.018 $\mu\text{g/L}$, as well as the human health

¹¹ PHQs for total metals are based on NRWQC for human health and not aquatic life, as stated in Section 3.1.3.

criterion for organism consumption alone, 0.14 µg/L. PHQs for aluminum and iron did not exceed 11. Five of the seven total aluminum concentrations measured in bilgewater (at concentrations ranging from 332 to 940 µg/L) exceeded the freshwater chronic criterion (87 µg/L, expressed as total recoverable metal). For total iron, concentrations in two of three bilgewater samples exceeded the human health criterion for water plus organism consumption of 300 µg/L; PHQs for total iron ranged from 0.17 to 6.3.

To further evaluate the significance of the dissolved and total metals concentrations in the bilgewater samples, EPA compared them to ambient dissolved and total metal concentrations in surface water samples collected near the vessels. This was done because surface water might occasionally leak into certain vessel bilges, be used onboard the vessel, or splash onto the vessel and drain into the bilge. In these cases, the concentrations of metals (as well as other analytes) measured in the bilgewater samples might be similar to or significantly influenced by the ambient concentrations. Indeed, EPA found that the concentrations of many of the metals (including aluminum, barium, calcium, chromium, magnesium, manganese, nickel, potassium, selenium, and sodium) measured in multiple bilgewater samples were no more than double the ambient concentrations. The similarity in the concentrations of many of these metals in bilgewater and ambient samples suggests that some proportion of the water sampled in the vessel bilges may be from ambient water. It is less clear whether the significant background ambient metals concentrations in the sampled harbors reflect the loading from the cumulative discharges of the many vessels that operate there, or loadings from other point and/or nonpoint pollutant sources to these water bodies.

On the other hand, the highest concentrations of some of the dissolved and total metals measured in bilgewater were substantially elevated above the corresponding ambient concentrations. For dissolved copper, the ambient concentration that accompanied the highest bilgewater concentration (350 µg/L from a tour boat) was below the detection limit. The next two highest dissolved copper concentrations in bilgewater (119 and 120 µg/L) were from water taxis with a somewhat higher corresponding ambient concentration of 24 µg/L.

For dissolved selenium, the ambient concentration that accompanied the highest bilgewater concentration (57 µg/L from the shrimper) was 76 µg/L; in this case, and several others, even the highest concentration for a metal in bilgewater was exceeded by the ambient concentration.

The data for total metals also demonstrate considerable variability in the relationships between bilgewater and ambient concentrations. The highest total arsenic concentration in bilgewater (291 µg/L from a tow/salvage boat) exceeded the corresponding ambient concentration (12 µg/L) by a considerable margin. The ambient concentration that accompanied the next highest total arsenic concentration in bilgewater (32 µg/L from the shrimper) was a comparable 29 µg/L.

The results shown here illustrate that relationships between metals concentrations in bilgewater and ambient samples are quite variable, even for the highest concentrations of metals measured in bilgewater. EPA acknowledges that such variability could be due to type of bilgewater production and dilution onboard. For example, a shrimper might have used a substantial amount of ambient water for washdown as compared to a tow boat, and thus, dilute what might be a similar actual bilge sample absent the washdown. Clearly the potential for metals in bilgewater discharges to pollute receiving waters may be overestimated if the ambient metals concentrations and other considerations (type and dilution of bilgewater) are not appropriately considered.

In summary, metals were frequently detected in bilgewater samples. EPA found relatively high concentrations of a number of dissolved and total metals in these samples. Total arsenic and dissolved copper concentrations were consistently elevated above the most conservative screening benchmarks, with PHQ values from greater than 10 to over 1,000. Dissolved cadmium concentrations in a single bilgewater sample also generated PHQs in this range. For these and other metals (including total aluminum and iron and dissolved chromium, lead, nickel, selenium, and zinc), concentrations measured in one or several bilgewater samples exceeded saltwater and/or freshwater criteria. EPA found that the concentrations of many of the metals measured in bilgewater samples (except for dissolved copper and total arsenic) were comparable to the ambient receiving water concentrations.

Table 3.1.1. Results of Bilgewater Sample Analyses for Dissolved Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	7	6	86	150	37			9.7	420	520	520	NA
Antimony	µg/L	5	1	20	0.66					0.65	1.3	1.3	NA
Arsenic	µg/L	7	6	86	41	10			1.1	21	230	230	36
Barium	µg/L	5	5	100	49	43	38	38	39	62	64	64	NA
Cadmium	µg/L	7	1	14	1.9						10	10	0.25
Chromium	µg/L	7	5	71	12	1.6				17	56	56	11
Cobalt	µg/L	5	2	40	1.0					1.8	2.5	2.5	NA
Copper	µg/L	7	7	100	100	56	6.6	6.6	25	120	350	350	3.1
Iron	µg/L	5	1	20	75					87	170	170	NA
Lead	µg/L	7	3	43	2.3					4.2	7.2	7.2	2.5
Manganese	µg/L	7	7	100	34	28	3.9	3.9	13	50	79	79	NA
Nickel	µg/L	7	6	86	9.2	8.8			4.7	14	15	15	8.2
Selenium	µg/L	7	4	57	24	30				36	57	57	5
Vanadium	µg/L	5	1	20	0.62					0.55	1.1	1.1	NA
Zinc	µg/L	7	7	100	130	100	53	53	72	190	250	250	81
Cationic Metals													
Calcium	µg/L	7	7	100	76000	76000	33000	33000	47000	100000	140000	140000	NA
Magnesium	µg/L	7	7	100	180000	180000	8300	8300	14000	310000	420000	420000	NA
Potassium	µg/L	5	5	100	67000	65000	9800	9800	37000	98000	120000	120000	NA
Sodium	µg/L	5	5	100	1400000	1400000	120000	120000	730000	2000000	2700000	2700000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.1.2. Results of Bilgewater Sample Analyses for Total Metals¹

Analyte	Units	No. samples	No. detected	Detected proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	7	7	100	370	330	26	26	28	640	940	940	87
Antimony	µg/L	5	1	20	1.3					0.65	1.3	1.3	5.6
Arsenic	µg/L	7	7	100	53	12	1.3	1.3	5.5	32	290	290	0.018
Barium	µg/L	5	5	100	50	44	38	38	38	66	67	67	1000
Cadmium	µg/L	7	1	14	2.6						12	12	NA
Chromium	µg/L	7	6	86	25	3.5			2	37	96	96	NA
Cobalt	µg/L	5	1	20	1.3					0.7	1.4	1.4	NA
Copper	µg/L	7	7	100	150	130	8.5	8.5	50	210	430	430	1300
Iron	µg/L	5	3	60	520	250				1100	1900	1900	300
Lead	µg/L	7	6	86	9.6	7.5			2.3	18	26	26	NA
Manganese	µg/L	7	7	100	53	52	7.4	7.4	37	79	97	97	100
Nickel	µg/L	7	6	86	12	9.4			6.2	17	24	24	610
Selenium	µg/L	7	4	57	25	25				38	66	66	170
Vanadium	µg/L	5	2	40	2.6					1.4	1.7	1.7	NA
Zinc	µg/L	7	7	100	160	87	56	56	72	260	360	360	7400
Cationic Metals													
Calcium	µg/L	7	7	100	76000	77000	36000	36000	47000	110000	130000	130000	NA
Magnesium	µg/L	7	7	100	180000	180000	9200	9200	14000	310000	390000	390000	NA
Potassium	µg/L	5	5	100	68000	65000	9600	9600	37000	100000	130000	130000	NA
Sodium	µg/L	5	5	100	1400000	1400000	120000	120000	740000	2000000	2600000	2600000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

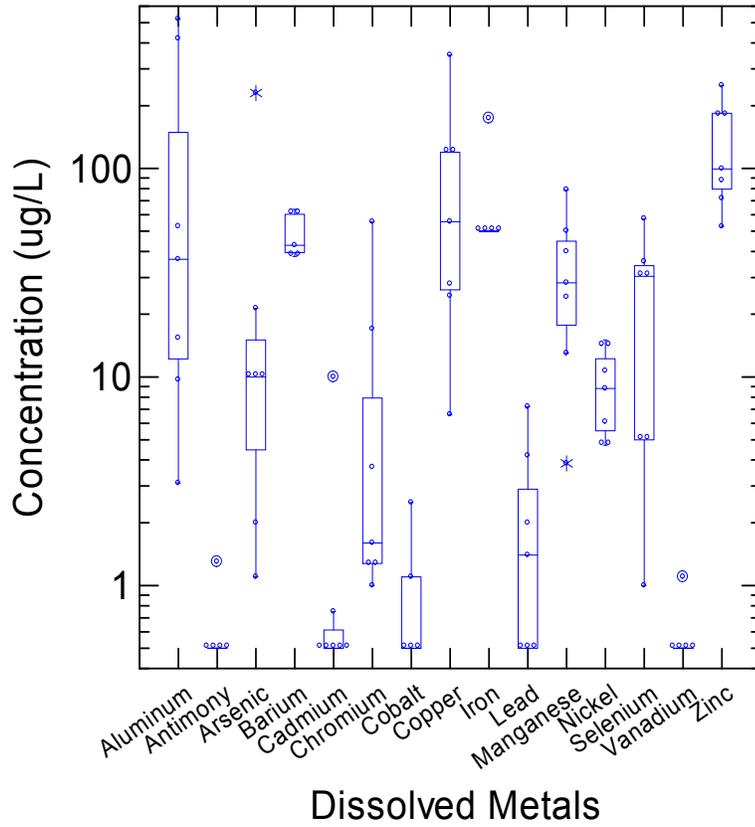


Figure 3.1.1. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Bilgewater

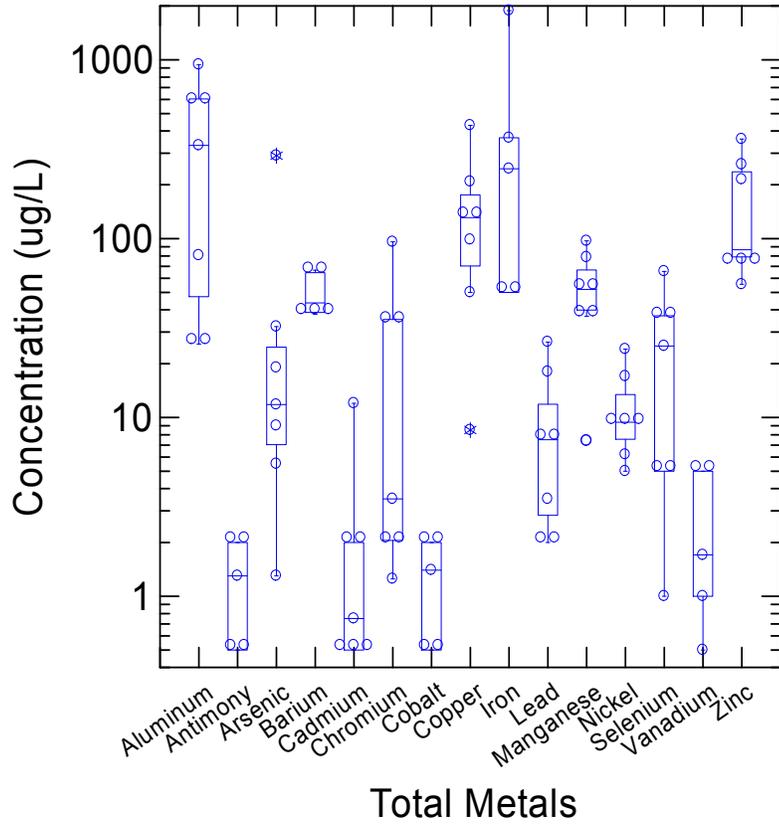


Figure 3.1.2. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Bilgewater

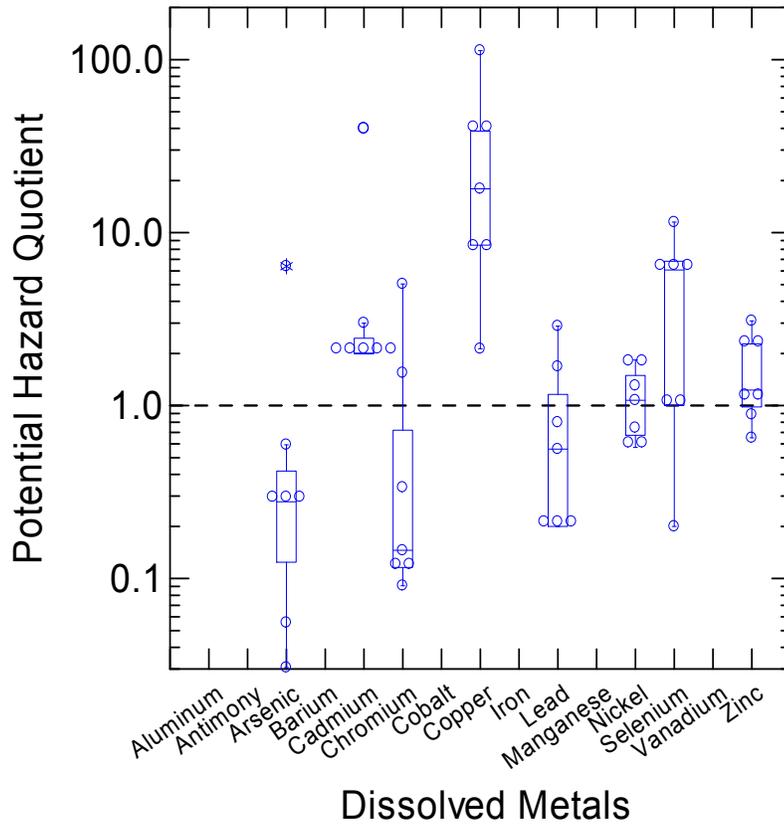


Figure 3.1.3. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Bilgewater

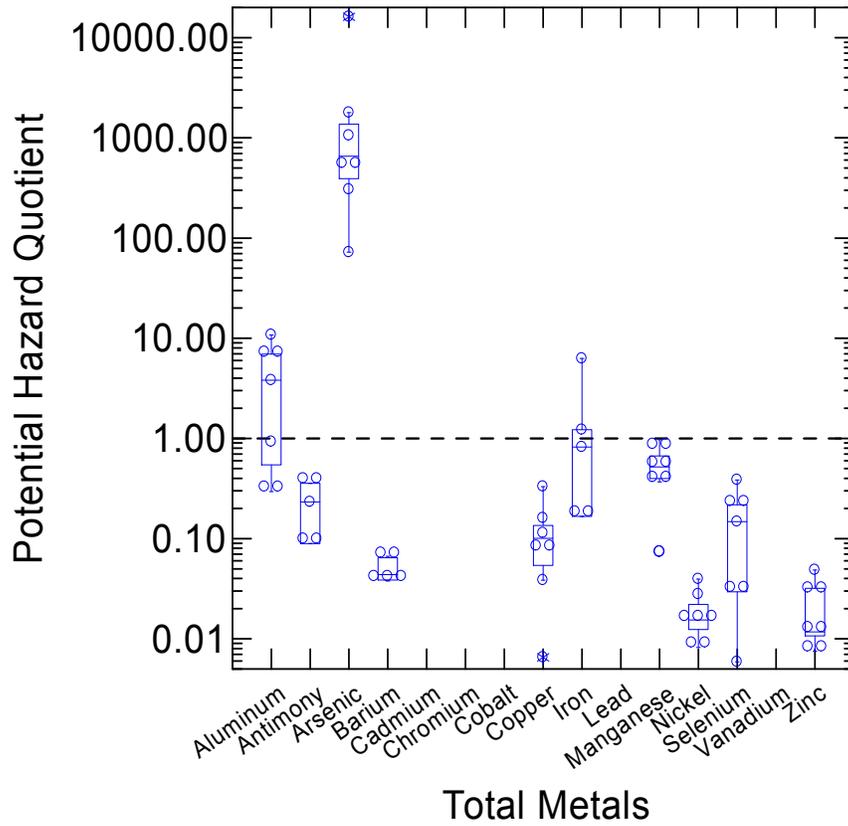


Figure 3.1.4. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Bilgewater

3.2.1.2 Classical Pollutants

Bilgewater samples were analyzed for 14 classical pollutants (see Table 3.1.3). These pollutants include measurements that are qualitatively quite different: physical properties (pH, temperature, conductivity, salinity, turbidity, TOC, TSS), oxygen consumption (BOD and COD), oil and grease (hexane extractable material (HEM) and silica-gel treated hexane extractable material (SGT-HEM)), as well as concentrations of several chemicals (sulfide, DO, TOC and TRC).¹² Figure 3.1.5 illustrates the variability of the concentrations/values measured for the classical pollutant in bilgewater. The highest concentrations of BOD, COD and TOC (770, 2970, and 732 mg/L, respectively), as well as HEM, SGT-HEM, and TRC, were measured in a single bilgewater sample from a tow/salvage boat. BOD and TOC concentrations were highly variable among the bilgewater samples, ranging from 2 to 770 mg/L for BOD and from 9 to 730 mg/L for TOC.

Oil and grease were measured as HEM and petroleum hydrocarbons were measured as SGT-HEM. HEM and SGT-HEM were detected in all of the bilgewater samples, with concentrations ranging from 1.1 to 43.6 mg/L (HEM) and 1.1 to 18.2 mg/L (SGT-HEM). These concentrations were compared to the existing international and U.S. regulatory limit of 15 mg/L of oil and grease that can be discharged from a moving ship when within 12 nautical miles from land¹³. Some type of oil collector (sorbent pad, rags, etc.) was used on four of the seven vessels sampled for bilgewater. A single value taken from the tow/salvage boat exceeded the 15-mg/L benchmark by threefold. Oil and grease discharges at this concentration are significant enough to cause a visible sheen. The tow/salvage boat had no equipment or management practices in place to remove oil or other pollutants prior to overboard discharge of bilgewater.

Sulfide was detected in two bilgewater samples, at concentrations of 0.015 and 0.2 mg/L. These concentrations exceeded the NRWQC of 2 µg/L (0.002 mg/L) by factors of 7.5 to 100. Sulfide (hydrogen sulfide) is a pollutant that is commonly elevated in water distribution systems as well as sewers. Sulfur-reducing bacteria, which use sulfur as an energy source, are believed to be the primary producers of large quantities of hydrogen sulfide in bilgewater. Ecologically, these bacteria are common in anaerobic environments (e.g., plumbing systems). Sulfur-reducing bacteria are apparently present in at least some of the vessels, because sulfide was not detected in the ambient water sampled at the vessel locations.

Figure 3.1.6 presents box and dot density plots of the PHQs for classical pollutants. PHQs were calculated for the six classical pollutants for which benchmarks were available. As this figure shows, all of the detected TRC concentrations exceeded the saltwater chronic

¹² See Section 3.1.1 this chapter for the rationale to use this term for this large group of conventional, nonconventional, and other physico-chemical factors.

¹³ International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL).

NRWQC benchmark of 0.0075 mg/L and yielded PHQs ranged from 6.7 to 21. The highest TRC concentration (0.16 mg/L) was measured in a bilgewater sample collected from a tour boat.

EPA compared classical pollutant concentrations in the bilgewater samples to ambient concentrations in surface water samples collected near the vessels. Concentrations of a number of the classical parameters (including conductivity, pH, salinity, temperature, and (to a varying degree) turbidity in bilgewater were comparable with ambient water. This was expected, considering the likelihood of ambient water leaking into vessel bilges. The concentration of DO measured in one bilgewater sample (1.8 mg/L in the longliner) was hypoxic (<2 mg/L), although the ambient DO value at this location (Sitka, Alaska) was also very low (1.0 mg/L). TRC concentrations were elevated at 0.1 mg/L in two of the seven bilge samples; for the remaining samples, TRC concentrations were comparable between bilgewater and ambient samples. For the remaining classical pollutants (BOD, COD, HEM, SGT-HEM, sulfide, TOC, and TSS) the concentrations measured in bilgewater greatly exceeded those measured in ambient samples. BOD concentrations in three of the bilgewater samples (189, 325, and 770 mg/L) were high enough to be comparable to values typical of raw domestic sewage (110 to 400 mg/L; Metcalf and Eddy, 1979). These three bilgewater samples also exceed EPA's secondary treatment effluent limit of 30 mg/L for BOD. COD concentrations in four of the bilgewater samples (430, 546, 780, and 2,970 mg/L) were again high enough to compare with values for raw domestic sewage (250 to 1,000 mg/L; Metcalf and Eddy, 1979). These high levels of BOD and COD in bilgewater discharges could potentially cause stress on a water body (e.g., where there are many sources of oxygen demand, where there may be limited circulation or flushing, or where the water body is under existing hypoxic or anoxic stress). Although TSS concentrations in bilgewater were not as high as values for raw sewage, four of the bilgewater samples exceeded the 30 mg/L effluent limit for TSS by factors ranging from 1.2 to 3. EPA realizes that these effluent limits are based upon the high removal efficiencies for BOD and TSS that are achievable by land-based sewage treatment plants, and may be overly conservative as benchmarks for vessel discharge. However, as discussed in Section 3.1.3, the benchmarks are still useful in a screening level analysis as a starting point for evaluating the potential of these pollutants to cause or contribute to ecological stress on a water body.

Table 3.1.3. Results of Bilgewater Sample Analyses for Classical Pollutants¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Biochemical Oxygen Demand (BOD)	mg/L	7	7	100	190	14	2.0	2.0	4.1	330	770	770	30
Chemical Oxygen Demand (COD)	mg/L	7	7	100	740	430	91	91	98	780	3000	3000	NA
Conductivity	mS/cm	6	6	100	5.0	6.9	0.017	0.017	0.56	9.3	14	14	NA
Dissolved Oxygen	mg/L	6	6	100	5.3	5.5	1.8	1.8	3.4	6.9	11	11	NA
Hexane Extractable Material (HEM)	mg/L	7	7	100	9.3	5.2	1.1	1.1	1.2	7.0	44	44	15
pH	SU	7	7	100	7.2	7.0	6.9	6.9	6.9	7.3	8.0	8.0	NA
Salinity	ppt	6	6	100	5.5	4.5	0.40	0.40	3.1	8.9	13	13	NA
Silica Gel Treated HEM (SGT-HEM)	mg/L	7	7	100	4.4	2.4	1.1	1.1	1.2	3.5	18	18	15
Sulfide	mg/L	7	2	29	0.034					0.015	0.20	0.20	0.0020
Temperature	C	7	7	100	20	21	9.0	9.0	14	27	28	28	NA
Total Organic Carbon (TOC)	mg/L	5	5	100	200	110	8.9	8.9	16	440	730	730	NA
Total Residual Chlorine	mg/L	7	3	43	0.077					0.13	0.16	0.16	0.0075
Total Suspended Solids (TSS)	mg/L	7	7	100	39	38	3.7	3.7	5.5	71	88	88	30
Turbidity	NTU	7	7	100	41	20	3.5	3.5	5.2	41	160	160	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

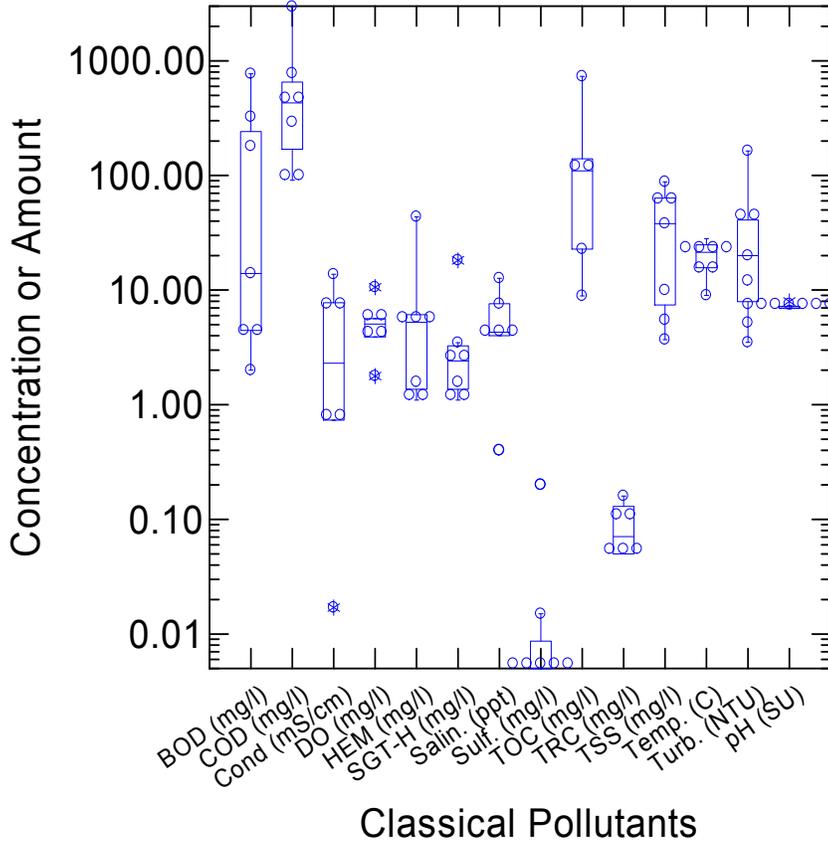


Figure 3.1.5. Box and Dot Density Plot of Classical Pollutant Concentrations Measured in Samples of Bilgewater

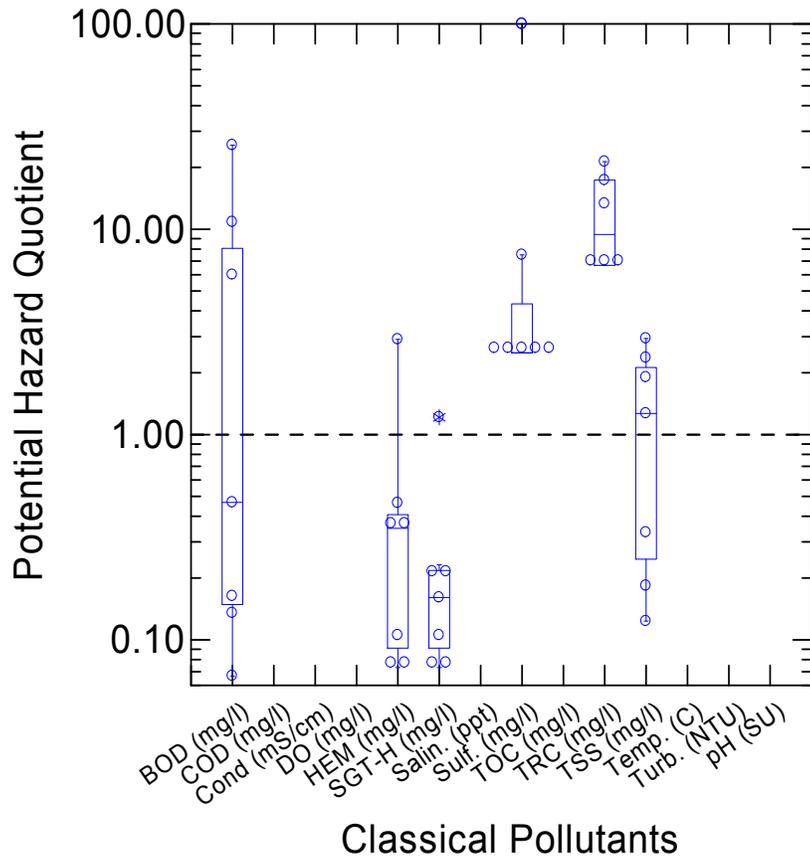


Figure 3.1.6. Box and Dot Density Plot of Potential Hazard Quotients for Classical Parameters in Samples of Bilgewater

3.2.1.3 Pathogen Indicators (Microbiologicals)

Bilgewater samples¹⁴ from two commercial fishing vessels were analyzed for the pathogen indicator bacteria *E. coli*, enterococci, and fecal coliform (commercial fishing vessels only) (see Table 3.1.4). *E. coli* and enterococci were detected in a bilgewater sample collected from a shrimping vessel, and fecal coliform were detected in bilgewater from two fishing vessels (a longliner and the shrimper).

The NRWQC for pathogen indicators references the bacteria standards in EPA's 1986 *Quality Criteria for Water*, commonly known as the Gold Book. NRWQC standards for bacteria are described in terms of three different water body use criteria: freshwater bathing, marine water bathing, and shellfish harvesting waters.

For each of the pathogen indicators, the lowest NRWQC was exceeded in one of the bilgewater samples. The *E. coli* value (393 MPN/100 mL) exceeds the freshwater bathing NRWQC of 126 MPN/100 mL. The enterococci value (4,100 MPN/100 mL) exceeds the bathing NRWQCs of 33 CFU/100 mL for fresh water and 35 CFU/100 mL for salt water. One of the two fecal coliform values (118 CFU/100 mL) exceeds the NRWQC of 14 MPN/100 mL for shellfish harvesting¹⁵.

Values of the pathogen indicators measured in these bilgewater samples exceed the values measured in nearby *ambient* surface water samples by factors ranging from 4 (for enterococci) to 15 (*E. coli*), suggesting that leakage or other entry of ambient water is not a significant source of these pathogen indicators in bilgewater. EPA is unsure as to the source of pathogen indicators in bilgewater.

¹⁴ Logistics prevented EPA from delivering all bilgewater samples to laboratories within allowable holding times.

¹⁵ MPN is most probable number and approximates the unit of measure for fecal coliform in this study of CFU (colony forming units).

Table 3.1. 4. Results of Bilgewater Sample Analyses for Pathogen Indicators¹

Analyte	Units ²	No. Samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ³
<i>E. Coli</i>	MPN/100 ml	1	1	100	390								130
Enterococci	MPN/100 ml	1	1	100	4100								33
Fecal Coliform	CFU/100 ml	2	2	100	61	120	4.0	4.0	4.0	120	120	120	14

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) MPN = Most Probable Number; CFU = Colony Forming Units.

(3) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

3.2.1.4 Nutrients

Bilgewater samples were analyzed for four nutrient-related parameters: ammonia nitrogen, nitrate/nitrite, total Kjeldahl nitrogen (TKN), and total phosphorus (see Table 3.1.5). The box and dot density plots in Figure 3.1.7 illustrate the variability of the nutrient concentrations measured in bilgewater. Ammonia, TKN and total phosphorus concentrations were elevated in a single bilgewater sample collected from a longliner fishing vessel. The elevated nutrient concentrations may be attributable to seepage from the/ice slurry in the fish hold of the longliner. Water containing biological material (e.g., fish waste tissues, excreta) might seep down into the bilge compartment, resulting in an increase in nutrient discharge.

Ammonia is the only nutrient for which there are currently numeric NRWQC. EPA established these numeric criteria based on chronic toxicity to aquatic life, not nutrient enrichment. An ammonia-nitrogen concentration of 7.6 mg/L, measured in the bilgewater sample from the longliner fishing vessel, exceeded the NRWQC chronic criteria in both salt water (1.2 mg/L) and fresh water (1.24 mg/L). Three of the five bilgewater samples for total phosphorus exceeded EPA's 0.1 mg/L 1986 Gold Book criterion. The highest total phosphorus concentration, 13 mg/L, exceeded the benchmark by a factor of 130. Figure 3.1.8 presents box and dot density plots of the PHQs calculated for the nutrient data.

EPA compared nutrient concentrations in the bilgewater samples to ambient concentrations in surface water samples collected near the vessels. Ammonia was detected in one of the ambient samples at a concentration of 0.11 mg/L, comparable (within a factor of two) to the concentration in the corresponding bilgewater sample, 0.13 mg/L. TKN was detected in three ambient samples; in one, the ambient concentration of 0.60 mg/L marginally exceeded the bilgewater concentration of 0.55 mg/L. However, ambient TKN concentrations were less than the bilgewater concentrations in the other two cases. For total phosphorus, the comparison showed the concentrations detected in two ambient samples were comparable to the corresponding bilgewater concentrations; however, total phosphorus was not detected in the ambient samples corresponding to the three bilgewater samples having the highest total phosphorus concentrations. Thus, although ambient nutrient concentrations appear to be comparable to the *lower* concentrations of nutrients in bilgewater and may be a partial source of these nutrients in some samples, they cannot explain the sources of the *higher* nutrient concentrations measured in other samples.

Table 3.1.5. Results of Bilgewater Sample Analyses for Nutrients¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Ammonia As Nitrogen (NH ₃ -N)	mg/L	5	4	80	1.7	0.24			0.064	4.0	7.6	7.6	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	7	5	71	0.38	0.18				0.36	1.9	1.9	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	5	5	100	16	2.5	0.55	0.55	1.0	39	73	73	NA
Total Phosphorus	mg/L	5	5	100	3.0	0.47	0.084	0.084	0.093	7.1	13	13	0.10

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

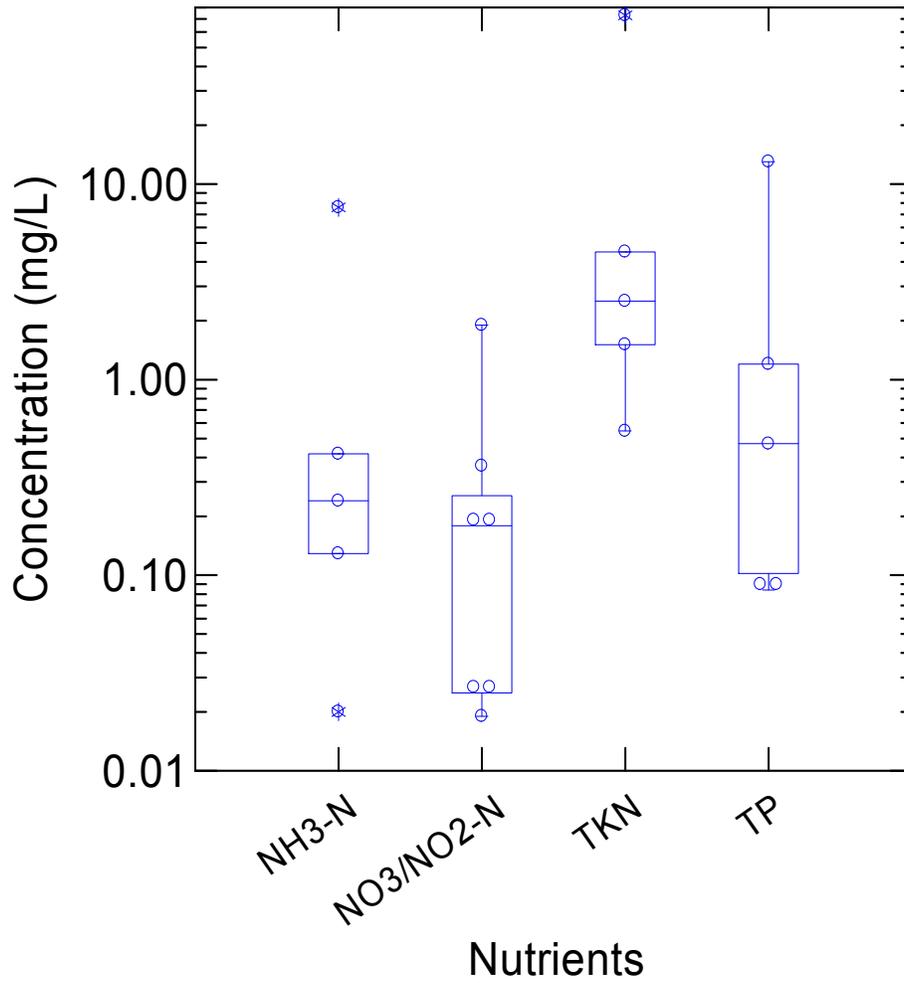


Figure 3.1.7. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Bilgewater

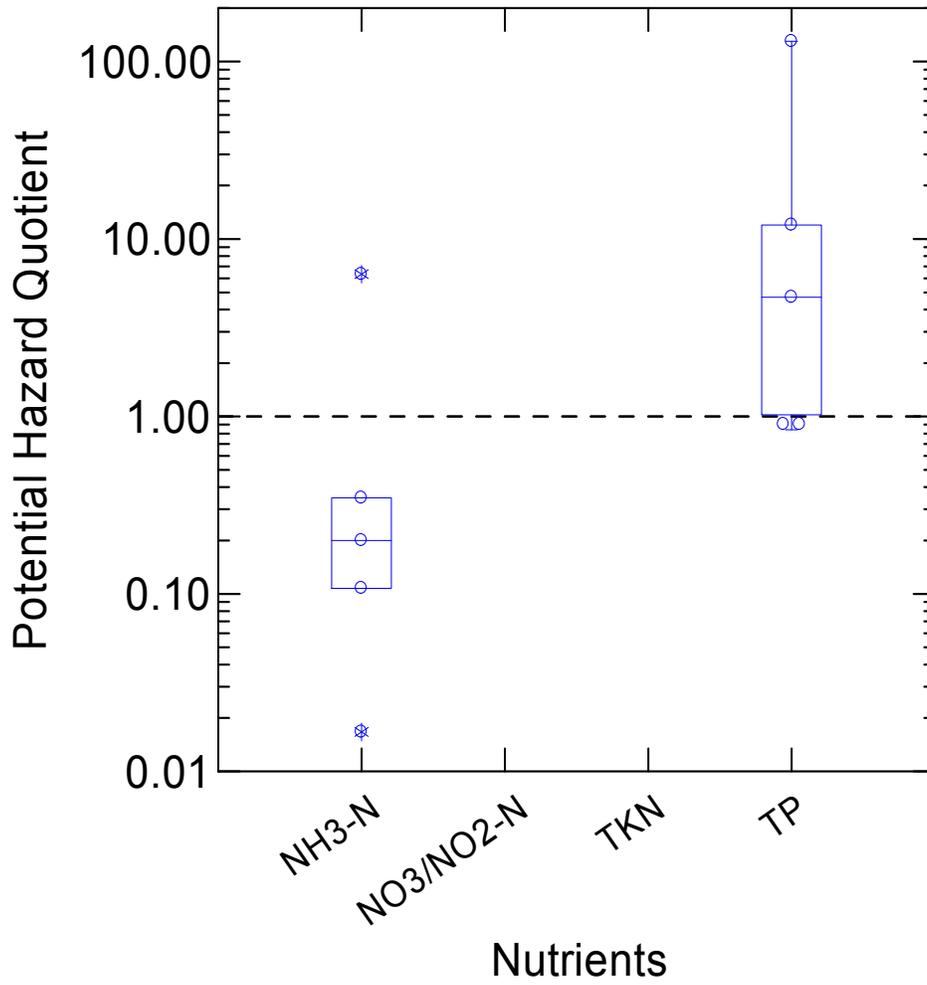


Figure 3.1.8. Box and Dot Density Plot of Potential Hazard Quotients for Nutrients in Samples of Bilgewater

3.2.1.5 Semivolatile Organic Compounds (SVOCs)

Bilgewater samples were analyzed for 79 SVOCs. Out of the 79 analytes, 56 were not detected in any of the bilgewater samples. Of the remaining 23 SVOCs, 18 were only detected in a single bilgewater sample and five were found in multiple samples (see Table 3.1.6). Of these, bis(2-ethylhexyl) phthalate was detected in more than 50 percent of the samples. This SVOC is a manufactured chemical that is commonly added to plastics to make them flexible and can be found in a variety of products used on vessels such as hoses, tubing, and gaskets. Di-n-butyl phthalate, di-n-octyl phthalate, naphthalene, and phenanthrene were also detected in more than one bilgewater sample. There was no obvious trend in the occurrence of SVOCs based on the type of vessel sampled.

Figure 3.1.9 presents the range of concentrations measured for SVOCs in the bilgewater samples. Concentrations of five SVOCs (2-butoxy ethanol, 2-methyl-naphthalene, dimethyl phthalate, indole, and naphthalene) exceeded 100 µg/L in single (but not the same) bilgewater samples. It was difficult for EPA to compare the concentration distributions between SVOCs because the majority were detected in a single sample. Bis(2-ethylhexyl) phthalate and phenanthrene concentrations ranged over nearly two orders of magnitude.

The distributions of PHQs, based on the most conservative screening benchmarks, are displayed for each SVOC in Figure 3.1.10. PHQs for two SVOCs, 2,4,6-trichlorophenol and bis(2-ethylhexyl) phthalate, exceeded the screening threshold of one. The 2,4,6-trichlorophenol concentration (24 µg/L) measured in a single bilgewater sample from a tour boat exceeded the 1.4 µg/L human health (water and organism consumption) criterion by a factor of 17¹⁶. Bis(2-ethylhexyl) phthalate was detected in four of the seven bilgewater samples, at concentrations that exceeded the 1.2 µg/L human health (water and organism consumption) criterion by factors that ranged from 1.1 to 59. As shown in Figure 3.1.10, the PHQs for four other SVOCs were orders of magnitude less than 1, and therefore, likely pose little risk as pollutants from bilgewater discharges.

SVOCs were detected in two ambient samples, and for these chemicals (bis(2-ethylhexyl) phthalate and Di-n-butyl phthalate) the ambient concentrations were only comparable to the lowest concentrations measured in bilgewater.

¹⁶ Because of elevated reporting limits for this SVOC in several samples, replacement values for the nondetected concentrations exceed the benchmark (e.g., PHQ >1). However, these values were not based on measured concentrations and are therefore uncertain.

Table 3.1.6. Results of Bilgewater Sample Analyses for SVOCs¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
2,4,6-Trichlorophenol	µg/L	7	1	14	7.0						24	24	1.4
2-Butoxy ethanol	µg/L	1	1	100	260								NA
2-Methylnaphthalene	µg/L	5	1	20	39					88	180	180	NA
3-Methyl-butanoic acid	µg/L	1	1	100	57								NA
4-Methyl-pentanoic acid	µg/L	1	1	100	38								NA
Benzeneacetic acid	µg/L	1	1	100	29								NA
Benzenepropanoic acid	µg/L	1	1	100	32								NA
Benzothiazole	µg/L	1	1	100	45								NA
Bis(2-ethylhexyl) phthalate	µg/L	7	4	57	15	1.4				21	71	71	1.2
Cholesterol	µg/L	1	1	100	88								NA
Dimethyl phthalate	µg/L	7	1	14	24						140	140	270000
Di-n-butyl phthalate	µg/L	7	2	29	4.0					1.4	4.9	4.9	2000
Di-n-octyl phthalate	µg/L	7	2	29	4.1					3.1	3.5	3.5	NA
Heptadecane	µg/L	1	1	100	56								NA
Indole	µg/L	1	1	100	160								NA
Naphthalene	µg/L	7	3	43	100					2.3	700	700	NA
n-Hexadecane	µg/L	1	1	100	39								NA
Nonadecane	µg/L	1	1	100	49								NA
p-Cresol	µg/L	5	1	20	7.7					8.7	17	17	NA
Phenanthrene	µg/L	7	2	29	12					1.3	69	69	NA
Phenol	µg/L	7	1	14	18						100	100	21000
Pyrene	µg/L	7	1	14	6.8						34	34	830
Triethyl Phosphate	µg/L	1	1	100	20								NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

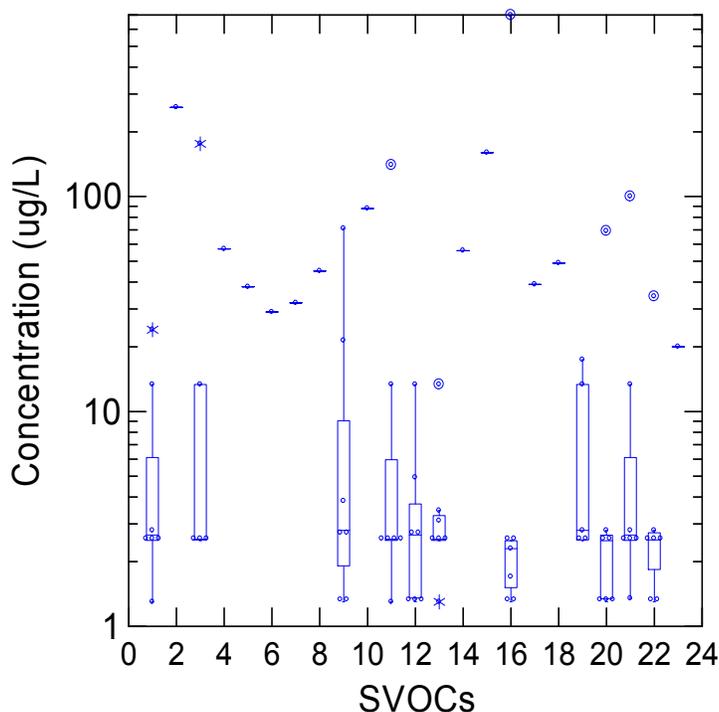


Figure 3.1.9. Box and Dot Density Plot of SVOC Concentrations Measured in Samples of Bilgewater. Nondetect (censored) concentrations were replaced with $\frac{1}{2}$ of the reporting limit for use in these plots. SVOCs are identified as follows:

- | | | |
|-----------------------------|---------------------------------|-------------------------|
| (1) 2,4,6-Trichlorophenol | (9) Bis(2-Ethylhexyl) Phthalate | (17) N-Hexadecane |
| (2) 2-Butoxy Ethanol | (10) Cholesterol | (18) Nonadecane |
| (3) 2-Methylnaphthalene | (11) Dimethyl Phthalate | (19) P-Cresol |
| (4) 3-Methyl-Butanoic Acid | (12) Di-N-Butyl Phthalate | (20) Phenanthrene |
| (5) 4-Methyl-Pentanoic Acid | (13) Di-N-Octyl Phthalate | (21) Phenol |
| (6) Benzeneacetic Acid | (14) Heptadecane | (22) Pyrene |
| (7) Benzenepropanoic Acid | (15) Indole | (23) Triethyl Phosphate |
| (8) Benzothiazole | (16) Naphthalene | |

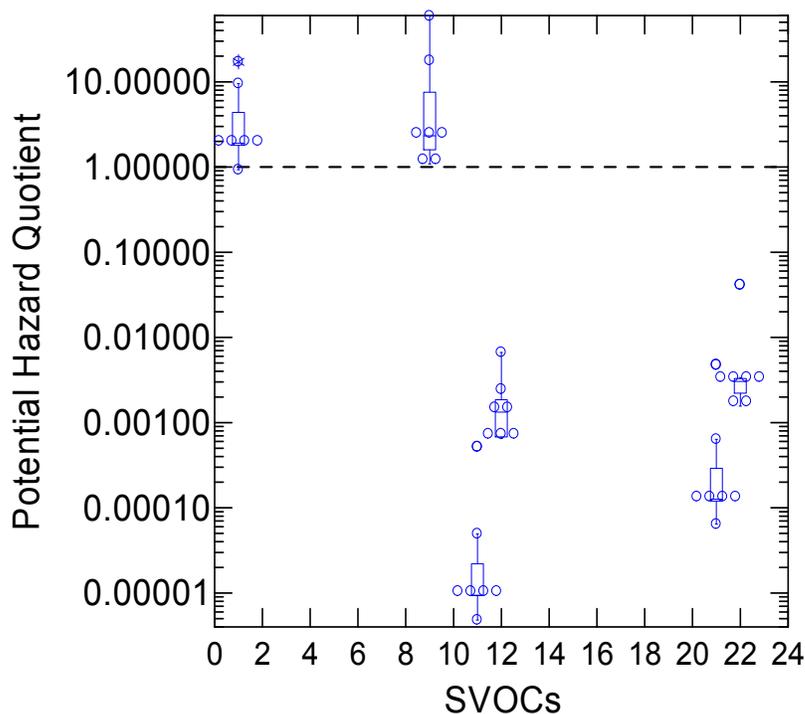


Figure 3.1.10. Box and Dot Density Plot of Potential Hazard Quotients for SVOCs in Samples of Bilgewater Nondetect (censored) concentrations were replaced with $\frac{1}{2}$ of the reporting limit for use in these plots. SVOCs are identified as follows:

- | | | |
|-----------------------------|---------------------------------|-------------------------|
| (1) 2,4,6-Trichlorophenol | (9) Bis(2-Ethylhexyl) Phthalate | (17) N-Hexadecane |
| (2) 2-Butoxy Ethanol | (10) Cholesterol | (18) Nonadecane |
| (3) 2-Methylnaphthalene | (11) Dimethyl Phthalate | (19) P-Cresol |
| (4) 3-Methyl-Butanoic Acid | (12) Di-N-Butyl Phthalate | (20) Phenanthrene |
| (5) 4-Methyl-Pentanoic Acid | (13) Di-N-Octyl Phthalate | (21) Phenol |
| (6) Benzeneacetic Acid | (14) Heptadecane | (22) Pyrene |
| (7) Benzenepropanoic Acid | (15) Indole | (23) Triethyl Phosphate |
| (8) Benzothiazole | (16) Naphthalene | |

3.2.1.6 Volatile Organic Compounds (VOCs)

Bilgewater samples were analyzed for 72 VOCs. Out of the 72 analytes, 46 VOCs were not detected in any of the bilgewater samples. Of the remaining 26 VOCs, 11 were detected in more than one bilgewater samples and 15 were detected only in one bilgewater sample (see Table 3.1.7). Of the 11 VOCs that were detected in more than one bilgewater sample, the following were detected in more than 50 percent of the samples:

- 1,2,4-Trimethylbenzene
- 1,3,5-Trimethylbenzene
- Acetone
- Benzene
- m-,p-Xylene (sum of isomers)
- Methylene chloride
- O-Xylene.

2-butanone, ethylbenzene, styrene, and toluene were also detected in more than one bilgewater sample.

Figure 3.1.11 presents the range of concentrations measured for VOCs in the bilgewater samples. The VOC concentrations measured in bilgewater samples varied widely, with concentrations of a half-dozen VOCs ranging over three orders of magnitude. The maximum concentrations of four VOCs (1,2,4-trimethylbenzene, m-,p-xylene, o-xylene and toluene) exceeded 1,000 µg/L (1 mg/L), while the maximum concentrations of four other VOCs (1,3,5-trimethylbenzene, benzene, ethylbenzene and n-propylbenzene) exceeded 100 µg/L. Each of these maximum VOC concentrations was measured in the bilgewater sampled from one tow/salvage boat. These VOCs are commonly constituents of petroleum products, refining by-products, and gasoline additives, and are used as solvents.

Figure 3.1.12 presents the distributions of PHQs for each VOC, based on the most conservative screening benchmarks. The maximum PHQ for benzene, based on the 2.2 µg/L human health (water plus organism consumption) criterion benchmark, was 187. The maximum PHQ for toluene was marginally higher than one; the highest concentration of toluene (1,700 µg/L) exceeded the human health (water and organism consumption) criterion of 1,300 µg/L. For two other VOCs (chloroform and tetrachloroethene), only one of seven sample concentrations were detected, and these detected concentrations were below the screening benchmark. However, because the method detection limits for these two compounds were more than double their respective screening benchmarks, the resulting PHQs for these compounds, as reported in Figure 3.1.12, are greater than one when concentrations equal to ½ of the detection limit are included. Because these PHQ values were not based on detected concentrations, EPA considers them highly uncertain.

Finally, two VOCs (acetone and methylene chloride) were measured in ambient samples at concentrations comparable to the corresponding bilgewater concentration. However, these ambient concentrations were only comparable to the lowest concentrations of these VOCs measured in some bilgewater samples. Therefore, it is unlikely that leakage or other entry of ambient water is a significant source of the elevated acetone and methylene chloride concentrations measured in bilgewater.

Table 3.1.7. Results of Bilgewater Sample Analyses for VOCs¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc. ³	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ³	Screening BM ²
1,2,4-Trimethylbenzene	µg/L	5	3	60	220	0.50				540	1100	1100	NA
1,3,5-Trimethylbenzene	µg/L	5	3	60	65	0.10				160	320	320	NA
2-Butanone	µg/L	5	2	40	2.6					2.8	3.7	3.7	NA
4-Isopropyltoluene	µg/L	5	1	20	3.3					3.3	6.5	6.5	NA
Acetone	µg/L	5	5	100	13	10	2.3	2.3	4.3	23	31	31	NA
Benzene	µg/L	7	4	57	61	0.10				1.3	410	410	2.2
Biphenyl	µg/L	5	1	20	4.5					0.87	1.7	1.7	NA
Carbon disulfide	µg/L	5	1	20	2.0					0.050	0.10	0.10	NA
Chloroform	µg/L	7	1	14	3.3						4.1	4.1	5.7
cis-1,2-Dichloroethene	µg/L	5	1	20	2.3					0.75	1.5	1.5	NA
Cyclohexane	µg/L	5	1	20	5.8					9.5	19	19	NA
Ethylbenzene	µg/L	7	3	43	68					1.3	460	460	530
Isopropylbenzene	µg/L	5	1	20	9.9					20	40	40	NA
m-,p-Xylene (sum of isomers)	µg/L	5	3	60	370	0.50				930	1900	1900	NA
Methyl tertiary butyl ether (MTBE)	µg/L	5	1	20	2.0					0.050	0.10	0.10	NA
Methylcyclohexane	µg/L	5	1	20	5.4					8.5	17	17	NA
Methylene chloride	µg/L	7	4	57	1.6	0.10				0.20	0.30	0.30	4.6
Nonanal	µg/L	1	1	100	3.1								NA
n-Pentadecane	µg/L	1	1	100	58								NA
n-Propylbenzene	µg/L	5	1	20	26					60	120	120	NA
O-Xylene	µg/L	5	3	60	240	0.20				590	1200	1200	NA
Styrene	µg/L	5	2	40	11					20	39	39	NA
Tetrachloroethene	µg/L	7	1	14	2.6						0.40	0.40	0.69
Toluene	µg/L	7	3	43	240					0.30	1700	1700	1300
Trichloroethene	µg/L	7	1	14	2.6						0.30	0.30	2.5
Trichlorofluoromethane	µg/L	7	1	14	3.5						5.5	5.5	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

(3) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

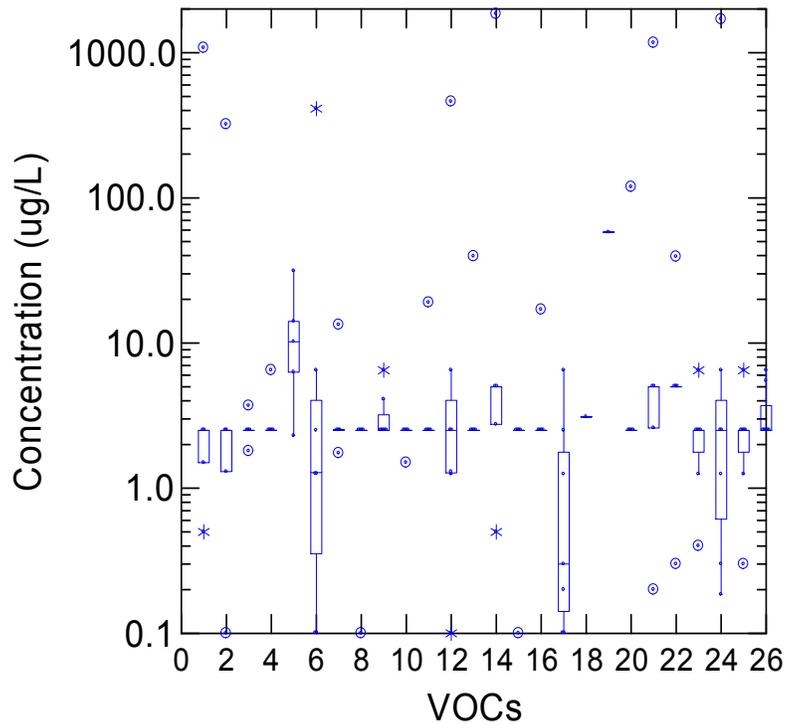


Figure 3.1.11. Box and Dot Density Plot of VOC Concentrations Measured in Samples of Bilgewater VOCs are identified as follows:

- | | | |
|----------------------------|---|-----------------------------|
| (1) 1,2,4-Trimethylbenzene | (10) Cis-1,2-Dichloroethene | (18) Nonanal |
| (2) 1,3,5-Trimethylbenzene | (11) Cyclohexane | (19) N-Pentadecane |
| (3) 2-Butanone | (12) Ethylbenzene | (20) N-Propylbenzene |
| (4) 4-Isopropyltoluene | (13) Isopropylbenzene | (21) O-Xylene |
| (5) Acetone | (14) M-,P-Xylene (sum of isomers) | (22) Styrene |
| (6) Benzene | (15) Methyl Tertiary Butyl Ether (Mtbe) | (23) Tetrachloroethene |
| (7) Biphenyl | (16) Methylcyclohexane | (24) Toluene |
| (8) Carbon Disulfide | (17) Methylene Chloride | (25) Trichloroethene |
| (9) Chloroform | | (26) Trichlorofluoromethane |

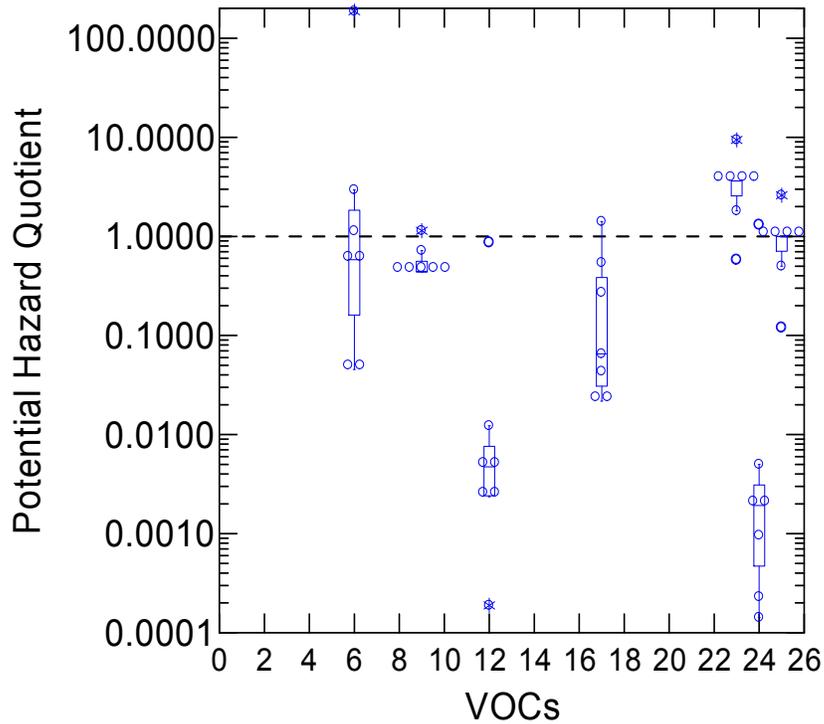


Figure 3.1.12. Box and Dot Density Plot of Potential Hazard Quotients for VOCs in Samples of Bilgewater VOCs are identified as follows:

- | | | |
|----------------------------|----------------------------------|-----------------------------|
| (1) 1,2,4-Trimethylbenzene | (10) Cis-1,2-Dichloroethene | (18) Nonanal |
| (2) 1,3,5-Trimethylbenzene | (11) Cyclohexane | (19) N-Pentadecane |
| (3) 2-Butanone | (12) Ethylbenzene | (20) N-Propylbenzene |
| (4) 4-Isopropyltoluene | (13) Isopropylbenzene | (21) O-Xylene |
| (5) Acetone | (14) M-,P-Xylene | (22) Styrene |
| (6) Benzene | (sum of isomers) | (23) Tetrachloroethene |
| (7) Biphenyl | (15) Methyl Tertiary Butyl Ether | (24) Toluene |
| (8) Carbon Disulfide | (Mtbe) | (25) Trichloroethene |
| (9) Chloroform | (16) Methylcyclohexane | (26) Trichlorofluoromethane |
| | (17) Methylene Chloride | |

3.2.1.7 Nonylphenols

Bilgewater samples were analyzed for 34 long- and short-chain nonylphenols. Of these analytes, 14 nonylphenols were not detected and 20 were detected in a single bilgewater sample (see Table 3.1.8). Of these 20 distinct nonylphenols, 16 were detected in the bilgewater from a tour boat, three were detected in the bilgewater from a tow/salvage boat, and one was detected in the bilgewater from a shrimper. Measured concentrations of nonylphenols in bilgewater ranged from less than 1 µg/L for three of the octylphenols (OP10EO, OP12EO, and OP11EO) to 1,050 µg/L for total nonylphenol polyethoxylates (sum of NPEOs – NP5EO through NP18EO). This latter maximum concentration was measured in the bilgewater sample from the tour boat. Although there is no NRWQC for nonylphenol polyethoxylates, they can degrade to nonylphenol, which does have a NRWQC, in fresh and salt water.

The one detected concentration for nonylphenol (NP, representative of the same concentration of nonylphenol isomers in the commercial mixture of isomers upon which EPA's NRWQC is based – CAS #84852-15-3) of 4.9 µg/L exceeded the saltwater chronic criterion of 1.7 µg/L by less than a factor of three. The operators of this vessel added “Dawn” dish soap to bilgewater prior to overboard discharge. However, this detergent is not necessarily the likely source of the detected nonylphenol. Lubricants also contain nonylphenol. The likelihood that “Dawn” detergent was not the source of the one detected concentration of nonylphenol is further corroborated by the fact that the operators of three of the other vessels where bilgewater was sampled also reported using commercial bilge cleaners, yet nonylphenol was not detected in these samples. Furthermore, the operator of the tour boat from which 16 of the long- and short-chain nonylphenols were detected made no comment about using bilge cleaners. Although the presence of long- and short- chain nonylphenols in bilgewater may reflect, in general, the use of detergents in various ship-board cleaning activities, using detergent as a bilge cleaning agent does not appear to be responsible for the one exceedance of a conservative screening benchmark for nonylphenols. Note, however, as previously discussed in Section 1.6.6, all long- and short-chain nonylphenols eventually degrade to nonylphenol.

Nonylphenol was not analyzed for in the ambient surface water sample collected at the location where the exceedance occurred (Pass Christian, Mississippi).

Table 3.1.8. Results of Bilgewater Sample Analyses for Nonylphenols¹

Analyte	Units	No. samples	No. Detected	Detected Proportion (%)	Average Conc. ³	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ³	Screening BM ²
Long-Chain Nonylphenols													
Total Nonylphenol Polyethoxylates	µg/L	5	1	20	260					530	1100	1100	NA
Nonylphenol octadecaethoxylate (NP18EO)	µg/L	5	1	20	0.78					1.8	3.6	3.6	NA
Nonylphenol heptadecaethoxylate (NP17EO)	µg/L	5	1	20	1.8					4.2	8.4	8.4	NA
Nonylphenol hexadecaethoxylate (NP16EO)	µg/L	5	1	20	3.6					8.2	16	16	NA
Nonylphenol pendeceethoxylate (NP15EO)	µg/L	5	1	20	6.8					16	31	31	NA
Nonylphenol tetradecaethoxylate (NP14EO)	µg/L	5	1	20	12					28	56	56	NA
Nonylphenol tridecaethoxylate (NP13EO)	µg/L	5	1	20	20					44	88	88	NA
Nonylphenol dodecaethoxylate (NP12EO)	µg/L	5	1	20	27					61	120	120	NA
Nonylphenol undecaethoxylate (NP11EO)	µg/L	5	1	20	35					77	150	150	NA
Nonylphenol decaethoxylate (NP10EO)	µg/L	5	1	20	35					77	150	150	NA
Nonylphenol nonaethoxylate (NP9EO)	µg/L	5	1	20	33					70	140	140	NA
Nonylphenol octaethoxylate (NP8EO)	µg/L	5	1	20	28					57	110	110	NA
Nonylphenol heptaethoxylate (NP7EO)	µg/L	5	1	20	22					42	83	83	NA
Nonylphenol hexaethoxylate (NP6EO)	µg/L	5	1	20	16					27	53	53	NA
Nonylphenol pentaethoxylate (NP5EO)	µg/L	5	1	20	9.7					14	27	27	NA
Octylphenol dodecaethoxylate (OP12EO)	µg/L	5	1	20	0.97					0.25	0.49	0.49	NA
Octylphenol undecaethoxylate (OP11EO)	µg/L	5	1	20	1.4					0.38	0.77	0.77	NA
Octylphenol decaethoxylate (OP10EO)	µg/L	5	1	20	3.2					0.39	0.78	0.78	NA
Short-Chain Nonylphenols													
Bisphenol A	µg/L	4	1	25	5.3					11	15	15	NA
Nonylphenols													
NP	µg/L	4	1	25	9.2					3.7	4.9	4.9	1.7

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

(3) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

3.2.1.8 Summary of the Characterization of Bilgewater Discharge

Table 3.1.9 summarizes the specific analytes within bilgewater effluent that may have the potential to pose risk to human health or the environment for these types of vessels based on these samples. EPA's interpretation of a realized risk likely posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

In summary, among the metals, dissolved copper, selenium, and zinc, as well as total arsenic, were consistently measured at concentrations exceeding the most stringent NRWQC in fishing vessels, tow/salvage vessels, water taxis, and tour vessels. The classical pollutants BOD, sulfide, TSS, and TRC exceeded at least one of the screening benchmarks in fishing vessels, tow/salvage vessels, water taxis, and tour vessels. Among the pathogen indicators, enterococcus was the only taxa present at concentrations exceeding NRWQC, and these samples were collected only from fishing boats. Total phosphorus was the only nutrient to exceed a screening benchmark. Concentrations of the SVOC bis(2-ethylhexyl) phthalate exceeded NRWQC in the bilgewater discharges of fishing vessels, tow/salvage vessels, water taxis, and tour vessels. Benzene sampled from tow/salvage vessels was the only VOC found at concentrations exceeding the most stringent NRWQC. The screening benchmark for nonylphenol was exceeded in a single sample collected from a fishing vessel.

Table 3.1.9. Characterization of Bilgewater Discharge and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Bilgewater Discharge and Vessel Sources ^{1, 2}												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Fishing (2)	Enterococcus			Cu, Se, Zn	As		x	x		Total P	BOD	x	TRC
Tow/Salvage (2)		Benzene	Bis(2-ethylhexyl)-phthalate	Cu, Se, Zn	As	x	x			Total P	BOD	x	TRC
Water Taxis (2)			Bis(2-ethylhexyl)-phthalate	Cu, Se, Zn	As					Total P	BOD	x	TRC
Tour (1)			Bis(2-ethylhexyl)-phthalate	Cu, Cd, Se, Zn	As					Total P	BOD	x	TRC

(1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), or, in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

(2) EPA notes that the conclusion of potential risk is drawn from a small sample size, in some cases a single vessel, for certain discharges sampled from some vessel classes. EPA included these results in the tables to provide a concise summary of the data collected in the study, but strongly cautions the reader that these conclusions, where there are only a few samples from a given vessel class, should be considered preliminary and might not necessarily represent pollutant concentrations from these discharges from other vessels in this class.

3.2.2 Stern Tube Packing Gland Effluent

The packing gland or stuffing box surrounds the propeller shaft at the point it exits a boat's hull underwater. Based on the vessels sampled for this analysis, using a packing gland is a common method for preventing water from entering the hull while still allowing the propeller shaft to turn. A stuffing box packed with greased flax rings is designed to leak a few drops per minute of ambient water to cool the gland when a vessel is underway. Stuffing boxes are also used to seal rudder stocks that penetrate the hull below the waterline. The packing gland effluent water is often collected in a segregated section of the bilge that generally contains an automatic bilge pump.

During this study, EPA observed this segregated discharge onboard tugboats but not on any other vessel classes. In most of the other vessels sampled, the packing gland effluent dripped directly into the bilge. Possible constituents of concern in the packing gland effluent include metals (from contact of the discharge with the drive shaft), hydraulic fluid, grease or lubricants found in the gland, and fuel constituents since the packing gland is located in the engine compartment.

Based on field observations from EPA's vessel sampling program, EPA estimated the drip rate into the stuffing box at approximately 10 drips per minute, which is consistent with the literature data (Casey, 2007; Chin, 2005). This equates to a stern tube effluent generation rate of between 2 and 4 gpd. Since most tugboats had dual propeller systems, these boats are expected to generate between 4 and 8 gpd of stern tube effluent.

For this study, EPA collected samples from the packing gland effluent from nine tugboats. Samples on these vessels were analyzed for metals (dissolved and total), classical pollutants, nutrients, VOCs, SVOCs, and nonylphenols. Packing gland effluent samples were collected by placing a glass transfer jar under the shaft to collect any water dripping and then compositing the sample in a Teflon-lined pail. In some cases, EPA dipped the transfer jar into the segregated bilge compartment. If the vessels had a dual propeller system, EPA collected samples from each for the composite. However, samples for analysis of oil and grease and VOCs are not appropriate to composite, so these samples were collected separately.

3.2.2.1 Metals

Packing gland effluent samples were analyzed for both total and dissolved concentrations of 22 metals. Of the 22 metals, 18 total metals and 15 dissolved metals were detected in the EPA sample set (see Table 3.2.1). Antimony, beryllium, silver, and cadmium were not detected in any samples in the total or dissolved form, while cobalt, iron, thallium, and vanadium were not detected in the dissolved form. Figures 3.2.1 and 3.2.2 present box and dot density plots of the detected results for dissolved and total metals, respectively. The box and density plots in Figures

3.2.3 and 3.2.4 present these same detected results for dissolved and total metals, respectively, normalized by the lowest NRWQC where applicable. Points on these plots above the dashed line (demarking a PHQ of 1) indicate metals concentrations exceeding the benchmark. With a few exceptions, the results were below the PHQs at the point of sampling.

Dissolved and total aluminum were found in all nine samples analyzed. Dissolved aluminum was detected at concentrations ranging from 7.8 to 150 $\mu\text{g/L}$ in the packing gland effluent; however, no screening benchmark is available for dissolved aluminum. Total aluminum was detected at concentrations ranging from 50.7 to 6,400 $\mu\text{g/L}$ and exceeded the screening benchmark of 87 $\mu\text{g/L}$ eight times. Arsenic, both total and dissolved, was detected in three of nine samples in the packing gland effluent. All three total arsenic values exceeded the screening benchmark of 0.018 $\mu\text{g/L}$ (based on the human health criterion for drinking water plus fish consumption) with values of 2.8, 4.4, and 15.3 $\mu\text{g/L}$. None of the three detected dissolved arsenic values (1.2, 1.4 and 14.7 $\mu\text{g/L}$) exceeded the screening benchmark of 36 $\mu\text{g/L}$ (based on the saltwater chronic criterion for the protection of aquatic life). Dissolved copper was detected in four of nine samples with values ranging from 16.2 to 92 $\mu\text{g/L}$. All four sample values exceeded the screening benchmark of 3.1 $\mu\text{g/L}$. Total copper was detected in seven of the nine sample from the packing gland effluent, with values ranging from 7 to 891 $\mu\text{g/L}$. None of the total copper values exceeded the screening benchmark of 1,300 $\mu\text{g/L}$.

Dissolved and total nickel was detected in six of nine and eight of nine packing gland effluent samples respectively. Two of the total nickel results (1,670 and 3230 $\mu\text{g/L}$) exceeded the screening benchmark of 610 $\mu\text{g/L}$, while all of the dissolved nickel values exceeded the screening benchmark of 8.2 $\mu\text{g/L}$. Zinc was found in seven of nine samples in the dissolved form and eight of nine samples in the total form. One sample value of 120 $\mu\text{g/L}$ for dissolved zinc exceeded the screening benchmark of 81 $\mu\text{g/L}$. Selenium was found in three of nine samples in the dissolved form and only one of nine samples in the total form. Dissolved chromium and lead were also detected in several samples. Chromium values exceeded the benchmark criteria of 11 $\mu\text{g/L}$ in four detected samples. Dissolved lead was detected at a concentration of 4.9 $\mu\text{g/L}$, which slightly exceeded the benchmark of 2.5 $\mu\text{g/L}$.

Total iron, manganese, and thallium were all detected at levels below the screening benchmarks, except for one sample for total thallium that was detected at the reporting level of 1 $\mu\text{g/L}$. This sample exceeded the benchmark of 0.24 $\mu\text{g/L}$ for thallium and has a PHQ of 4.17 as shown on Figure 3.2.4. Barium, sodium, and potassium, in both forms (total and dissolved) were detected in three of three samples, but did not exceed benchmark criteria. The metals magnesium and calcium, in both forms (total and dissolved); cobalt and vanadium (in total); and dissolved manganese were detected in one or more samples but no screening criteria exists for these compounds.

EPA analyzed ambient metal concentrations to determine if dissolved and total aluminum concentrations found in packing gland effluent were contributed primarily by the vessel or reflected contributions primarily by background ambient concentrations. For both dissolved and total aluminum, sample concentrations were moderately influenced by ambient background concentrations, with ambient concentrations as high as 130 µg/L (dissolved aluminum) and 3,950 µg/L (total aluminum). For both dissolved and total arsenic, sample concentrations from stern tube packing gland effluent were strongly influenced by ambient background concentrations. Ambient dissolved and total arsenic concentrations as high as 16.1 and 15.4 µg/L, respectively, were measured in water surrounding one of the three vessels sampled (a vessel sampled in Baltimore, Maryland). The source of the arsenic detected in the surrounding background water is unknown. Ambient background concentrations of both dissolved and total copper were comparatively low relative to the packing gland effluent sample concentrations and therefore of little influence (i.e., dissolved and total copper concentrations were largely from packing gland effluent). As in the case of copper, nickel was not found at high levels in the surrounding ambient water; thus, nickel is another metal that may have a significant source from the packing gland effluent. All of the selenium values were consistent with concentrations in the surrounding water. Neither chromium nor lead was strongly influenced by ambient concentrations in the surrounding water. The concentrations barium, sodium, potassium, magnesium, calcium cobalt, vanadium, and manganese generally reflect the concentrations in the surrounding water.

Table 3.2.1. Results of Packing Gland Effluent Sample Analyses for Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum, Dissolved ⁴	µg/L	9	9	100	88	110	7.8	7.8	31	140	150	150	NA
Aluminum, Total ⁴	µg/L	9	9	100	1200	300	51	51	170	1500	6400	6400	87
Arsenic, Dissolved ³	µg/L	9	3	33	3.3					1.3	15	15	36
Arsenic, Total ³	µg/L	9	3	33	3.8					3.6	15	15	0.018
Barium, Dissolved ³	µg/L	3	3	100	53	63	30	30	30	66	66	66	NA
Barium, Total ³	µg/L	3	3	100	88	98	32	32	32	140	140	140	1000
Chromium, Dissolved	µg/L	9	5	56	19	3.8				20	110	110	11
Chromium, Total	µg/L	9	8	89	230	130			9.7	440	760	760	NA
Cobalt, Total ⁴	µg/L	3	2	67	3.0	2.9				5.6	5.6	5.6	NA
Copper, Dissolved	µg/L	9	4	44	22					38	92	92	3.1
Copper, Total	µg/L	9	7	78	140	20			3.5	150	890	890	1300
Iron, Total ⁴	µg/L	3	3	100	3900	2700	710	710	710	8300	8300	8300	300
Lead, Dissolved ⁴	µg/L	9	1	11	1.8						4.9	4.9	2.5
Lead, Total	µg/L	9	3	33	7.9					8.9	43	43	NA
Manganese, Dissolved ⁴	µg/L	9	8	89	44	9.6			2.9	53	250	250	NA
Manganese, Total ⁴	µg/L	9	9	100	160	110	79	79	93	230	350	350	100
Nickel, Dissolved	µg/L	9	6	67	210	13				370	1000	1000	8.2
Nickel, Total	µg/L	9	8	89	610	45			12	970	3200	3200	610
Selenium, Dissolved ³	µg/L	9	3	33	8.1					1.2	41	41	5
Selenium, Total ³	µg/L	9	1	11	8.6							42	170
Thallium, Total ⁴	µg/L	3	1	33	0.67					1.0	1.0	1.0	0.24
Vanadium, Total ³	µg/L	3	1	33	4.6						13	13	NA
Zinc, Dissolved ⁴	µg/L	9	7	78	34	18			3.3	53	120	120	81
Zinc, Total	µg/L	9	8	89	70	73			113	120	180	180	7400
Cationic Metals													
42													
Calcium, Dissolved ³	µg/L	9	9	100	36000	24000	23000	23000	23000	35000	110000	110000	NA
Calcium, Total ³	µg/L	9	9	100	37000	24000	22000	22000	23000	39000	110000	110000	NA

Table 3.2.1. Results of Packing Gland Effluent Sample Analyses for Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Magnesium, Dissolved ³	µg/L	9	9	100	40000	7800	6200	6200	6500	11000	290000	290000	NA
Magnesium, Total ³	µg/L	9	9	100	39000	7900	6000	6000	6300	12000	280000	280000	NA
Potassium, Dissolved ³	µg/L	3	3	100	39000	4700	4000	4000	4000	110000	110000	110000	NA
Potassium, Total ³	µg/L	3	3	100	37000	4600	4600	4600	4600	100000	100000	100000	NA
Sodium, Dissolved ³	µg/L	3	3	100	810000	20000	18000	18000	18000	2400000	2400000	2400000	NA
Sodium, Total ³	µg/L	3	3	100	810000	20000	17000	17000	17000	2400000	2400000	2400000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

(3) Sample concentrations are strongly influenced by background concentrations in ambient water, accounting for greater than 90% of sample concentrations in the majority of samples.

(4) Sample concentrations are moderately influenced by background concentrations in ambient water, accounting for between 50 and 90% of sample concentrations in the majority of samples.

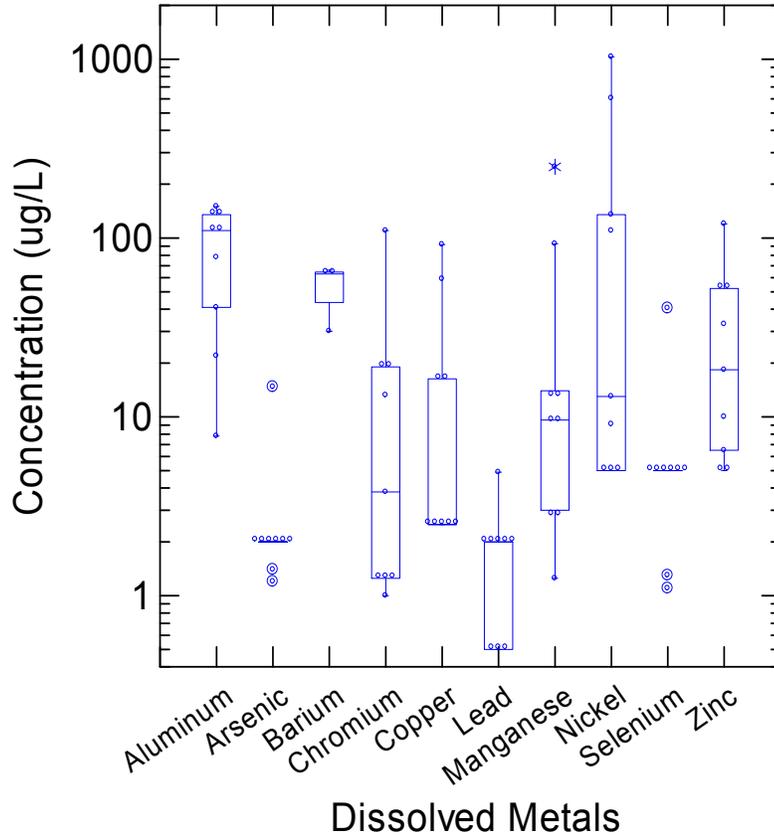


Figure 3.2.1. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Packing Gland Effluent

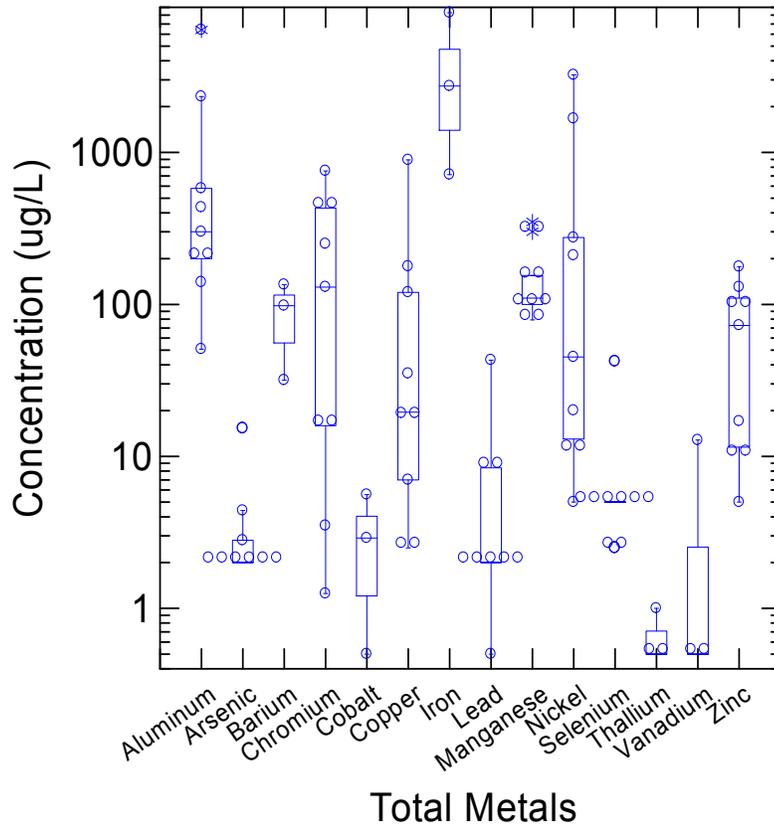


Figure 3.2.2. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Packing Gland Effluent

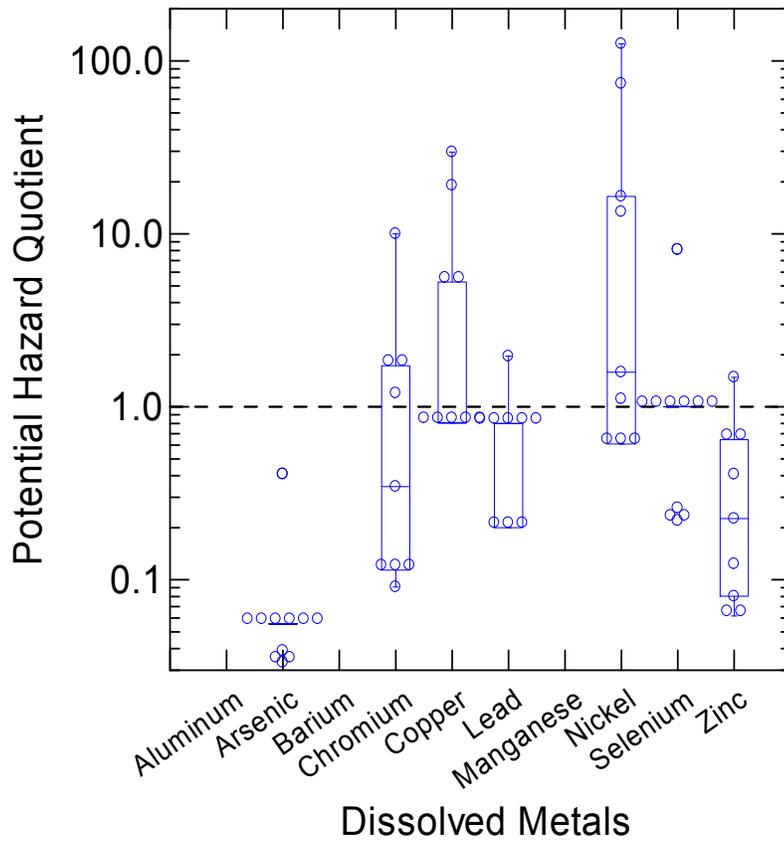


Figure 3.2.3. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Packing Gland Effluent

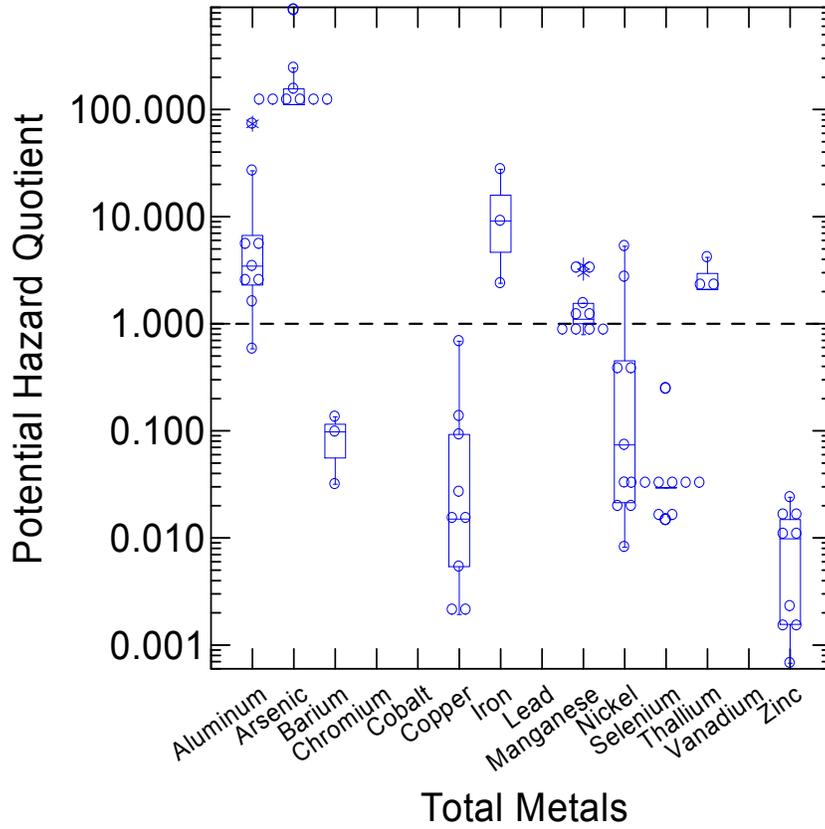


Figure 3.2.4. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Packing Gland Effluent

3.2.2.2 Classical Pollutants

EPA sampled the packing gland effluent for numerous classical pollutants to further characterize this discharge type for the tugboats sampled under this program. The classical pollutants include measurements that are physical properties (temperature, conductivity, salinity, turbidity, TSS), oxygen consumption (BOD, COD), oil and grease (HEM and SGT-HEM), as well as chemical concentrations (pH, sulfide, DO, and TRC). Table 3.2.2 presents the data for these parameters.

Figure 3.2.5 illustrates the varied concentrations of measured for these parameters in the packing gland effluent. Most of the concentrations and values reported reflect the concentrations and values in the ambient water surrounding the vessel, as this water is the source of the drive shaft water. Two parameters (sulfide and TRC) were not detected in any samples.

The PHQs were calculated for the classical pollutants for which they were available. Only two pollutants exceeded these PHQ screening benchmarks (see Figure 3.2.6): oil and grease and TSS. One of the vessel samples had values which exceeded the screening benchmark for oil and grease measured as both HEM and petroleum hydrocarbon (SGT-HEM). The concentrations detected were 66.7 mg/L for HEM and 55.8 mg/L for SGT-HEM, both of which exceeded the benchmark of 15 mg/L. EPA noted a visible oily sheen on the surface of this effluent and evidence of settled hydrocarbons on the bottom of the tank as this sample was collected. Based upon conversations with the vessel engineer, the likely source is an oil leak that was somehow making its way into this effluent. This seems a plausible explanation given that background concentrations of HEM and SGT-HEM in surrounding ambient water were very low (< 1.5 mg/L) relative to the measured sample concentrations.

Total suspended solids were detected in all nine samples collected from the packing gland effluent. Two samples with concentrations of 269 and 134 mg/L exceeded the screening benchmark of 98 mg/L.

Table 3.2.2. Results of Packing Gland Effluent Sample Analyses for Classical Pollutants¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Conductivity	mS/cm	9	9	100	1.6	0.30	0.22	0.22	0.22	0.55	12	12	NA
Dissolved Oxygen	mg/L	9	9	100	8.3	8.4	5.3	5.3	7.2	9.3	11	11	NA
Total Organic Carbon (TOC)	mg/L	7	7	100	3.5	3.5	2.2	2.2	2.6	4.8	4.9	4.9	NA
Biochemical Oxygen Demand (BOD)	mg/l	9	9	100	11	7.2	3.3	3.3	4.3	13	35	35	30
Chemical Oxygen Demand (COD)	mg/l	9	4	44	31					53	88	88	NA
Hexane Extractable Material (HEM)	mg/l	9	5	56	14	1.65				23	67	67	15
pH	SU	9	9	100	7.1	7.5	2.4	2.4	7.3	8.0	8.2	8.2	NA
Salinity	ppt	8	7	88	0.14	0.20			0.10	0.20	0.20	0.20	NA
Silica Gel Treated HEM (SGT-HEM)	mg/l	9	5	56	13	1.7				19	56	56	15
Temperature	C	9	9	100	20	20	9.3	9.3	18	23	26	26	NA
Total Suspended Solids (TSS)	mg/l	9	9	100	59	28	5.6	5.6	13	81	270	270	30
Turbidity	NTU	9	9	100	46	18	9.0	9.0	13	70	190	190	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

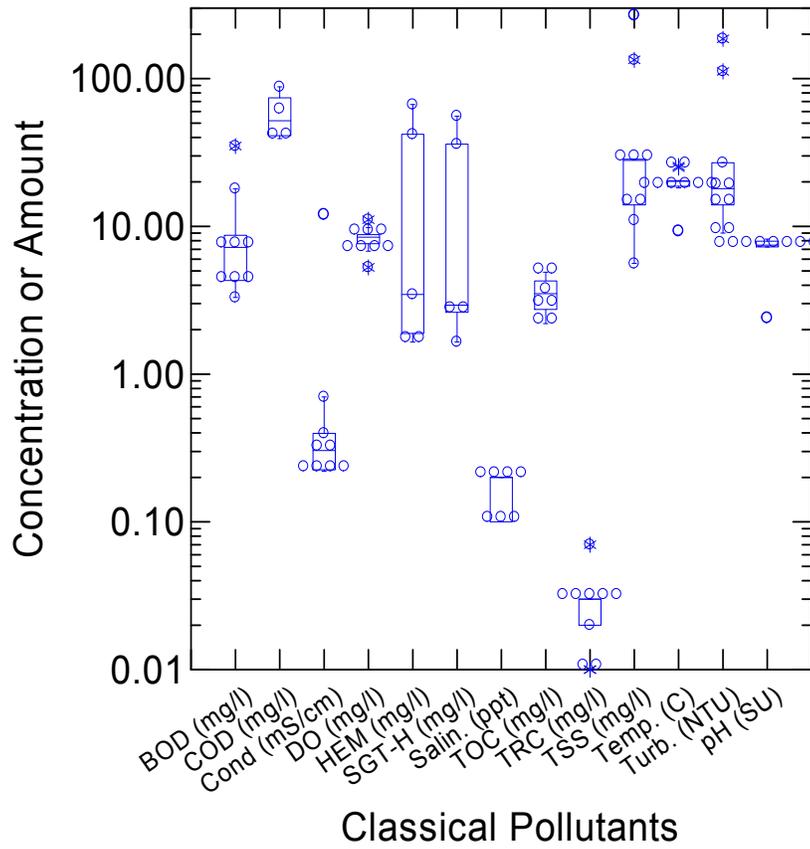


Figure 3.2.5. Box and Dot Density Plot of Classical Pollutants Measured in Samples of Packing Gland Effluent

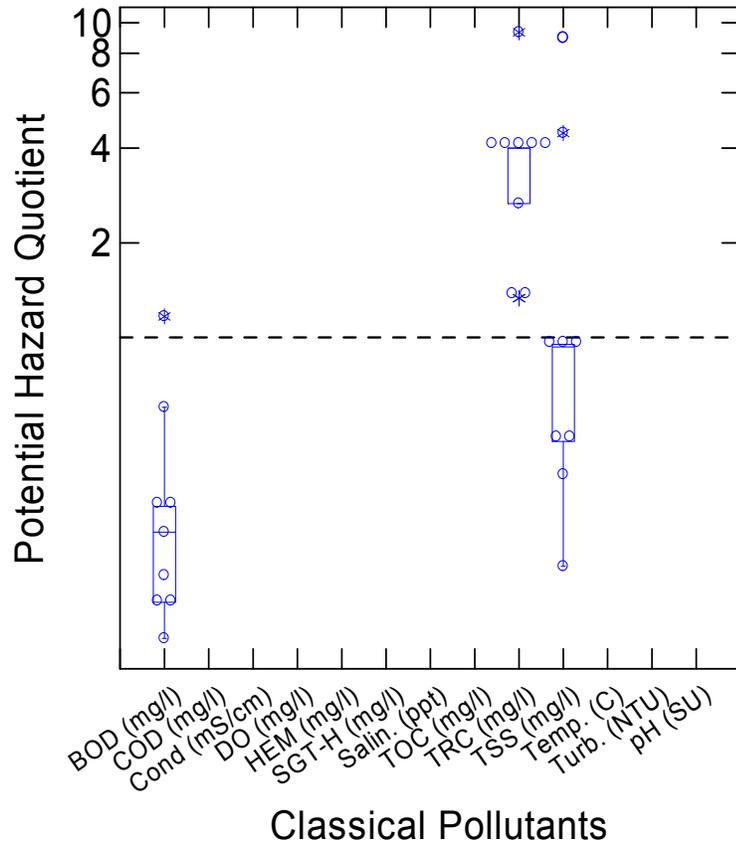


Figure 3.2.6. Box and Dot Density Plot of Potential Hazard Quotients for Classical Pollutants in Samples of Packing Gland Effluent

3.2.2.3 Nutrients

Packing gland effluent samples were analyzed for four nutrient-related parameters: ammonia nitrogen, nitrate/nitrite, TKN, and total phosphorus (see Table 3.2.3). Figures 3.2.7 and 3.2.8 illustrate the variability of the nutrients in the packing gland effluent. Ammonia, nitrate/nitrite, and TKN were detected in most of the samples analyzed, but in relatively low concentrations. Phosphorus was detected in seven of the nine tugboat samples collected.

Only ammonia has a current numeric NRWQC value. The results for ammonia detected in the packing gland effluent range from 0.07 to 0.23 mg/L, well below the benchmark of 1.2 mg/L. TKN and nitrate/nitrite were detected in all of the nine tugboat samples, with values ranging from 0.40 to 1.8 mg/L for TKN to 0.62 to 1.5 mg/L for nitrate/nitrite. Total phosphorus was detected in seven of the nine samples for packing gland effluent. The detected concentrations ranged from 0.06 to 0.25 mg/L and only two values, 0.19 and 0.25 mg/L, exceed the 0.1 mg/L benchmark.

Most of these values for ammonia, TKN, and nitrate/nitrite are consistent with ambient background results in each location. The background ambient for these total phosphorus samples reported values from 0.06 to 0.19 mg/L, indicating a moderate influence of surrounding ambient water on sample concentrations.

In general, it appears that nutrient concentrations from packing gland effluent are generally low and the wastestream does not appear to be adding significant nutrients to the surrounding waters. Nutrient addition from packing gland effluent was not considered a likely concern in this discharge relative to metals from contact of the discharge with the drive shaft, hydraulic fluid, grease or lubricants from the gland, and fuel constituents.

Table 3.2.3. Results of Packing Gland Effluent Sample Analyses for Nutrients¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Ammonia As Nitrogen (NH ₃ -N)	mg/L	9	7	78	0.10	0.10			0.034	0.14	0.23	0.23	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	9	9	100	0.69	0.62	0.085	0.085	0.58	0.80	1.5	1.5	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	9	9	100	1.1	1.4	0.41	0.41	0.69	1.4	1.8	1.8	NA
Total Phosphorus	mg/L	9	7	78	0.13	0.10			0.030	0.22	0.25	0.25	0.10

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

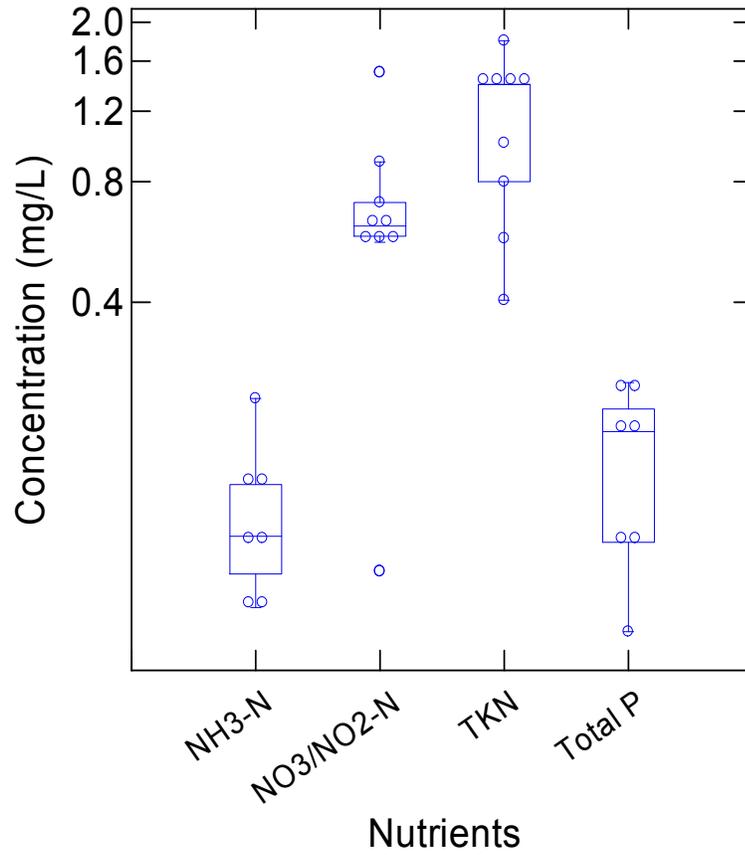


Figure 3.2.7. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Packing Gland Effluent

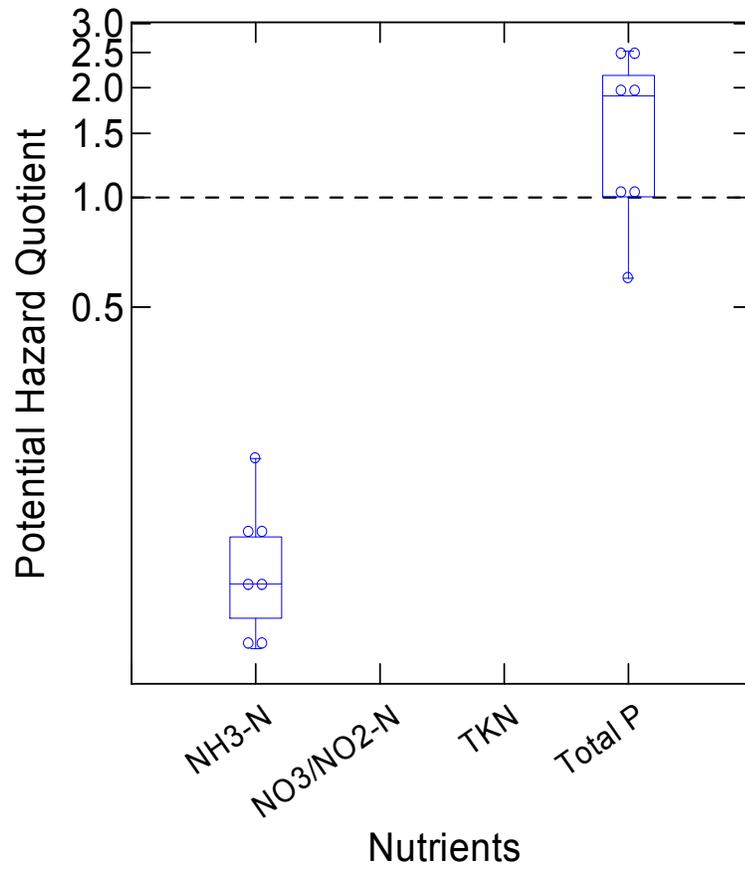


Figure 3.2.8. Box and Dot Density Plot of Potential Hazard Quotients for Nutrients in Packing Gland Effluent

3.2.2.4 Volatile and Semivolatile Organic Chemicals

Packing gland effluent samples were analyzed for 70 VOCs and 73 SVOCs in nine tugboats (see Table 3.2.4). Of the analytes tested, six VOC compounds and 10 SVOC compounds were detected in the samples. Figures 3.2.9 and 3.2.10 illustrate the range of concentrations measured for SVOCs and VOCs, respectively.

Three VOCs, m-p-xylene, acetone, and methylene chloride, were detected in more than one sample. Eight of the 10 SVOCs detected were found in one sample. Bis(2-ethylhexyl) phthalate was found in the effluent of three vessels sampled and n-hexadecane was found in the effluent of two of the vessels sampled. Bis(2-ethylhexyl) phthalate was detected at notably high (compared to ambient surrounding water) values of 2.8, 5.4, and 23.5 µg/L. The only other compound with a screening benchmark is di-n-butyl phthalate, which was detected in one sample with a concentration of 2.45 µg/L, which is well below the screening benchmark of 2,000 µg/L. These two phthalate compounds are used as plasticizers, and bis(2-ethylhexyl) phthalate is used as a hydraulic fluid and as a dielectric fluid in capacitors.

Figure 3.2.12 presents the distributions of PHQs, based on the most conservative screening benchmarks, for each VOC; none of the detected values exceed the screening threshold¹⁷. PQH was above one for all three samples of bis(2-ethylhexyl) phthalate, based on the screening benchmark of 1.2 µg/L (Figure 3.2.11).

Of the six VOC and 10 SVOC compounds detected in packing gland effluent samples, bis(2-ethylhexyl) phthalate was the only compound whose measured concentrations in the discharge was substantially higher than in ambient water; all other VOCs and SVOCs detected in packing gland effluent appear to reflect the similar concentrations found in surrounding water.

¹⁷ PHQs for benzene, methylene chloride and tetrachloroethene in multiple packing gland effluent samples were based on replacement values of ½ of the reporting limit for nondetected concentrations. In Figure 3.2.12 the PHQs based on replacement values for nondetected concentrations have been circled for identification. EPA does not consider PHQs that exceed 1 to signal that these discharges pose a potential risk to cause or contribute to the non-attainment of a water quality standard when the PHQs are based on replacement values for nondetected concentrations.

Table 3.2.4. Results of Packing Gland Water Sample Analyses for SVOCs and VOCs¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc. ³	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ³	Screening BM ²
SVOCs													
2,6,10,14-Tetramethyl Pentadecane	µg/L	1	1	100	12								NA
3,6-Dimethylundecane	µg/L	1	1	100	8.7								NA
5-Butyl-Hexadecane	µg/L	1	1	100	6.7								NA
Bis(2-ethylhexyl) phthalate	µg/L	9	3	33	4.7					4.1	24	24	1.2
Di-n-butyl phthalate	µg/L	9	1	11	1.7						2.5	2.5	2000
Dodecane	µg/L	1	1	100	5.0								NA
Eicosane	µg/L	1	1	100	5.4								NA
n-Hexadecane	µg/L	2	2	100	5.5	6.0	5.0	5.0	5.0	6.0	6.0	6.0	NA
Nonanoic Acid	µg/L	1	1	100	4.3								NA
VOCs													
Acetone	µg/L	3	3	100	2.9	2.7	2.7	2.7	2.7	3.2	3.2	3.2	NA
Benzene	µg/L	9	1	11	1.4						0.20	0.20	2.2
m-,p-Xylene (sum of isomers)	µg/L	3	2	67	1.7	0.10				0.10	0.10	0.10	NA
Methylene chloride	µg/L	9	2	22	1.2					0.10	0.20	0.20	4.6
n-Pentadecane	µg/L	1	1	100	11								NA
Sulfur dioxide	µg/L	1	1	100	13								NA
Tetrachloroethene	µg/L	9	1	11	1.4						0.20	0.20	0.69

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

(3) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

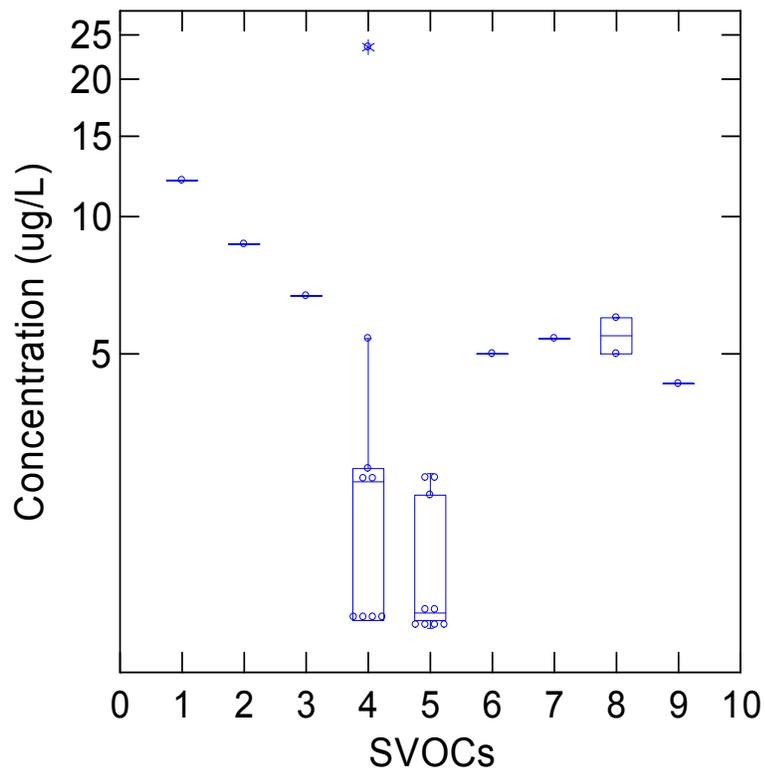


Figure 3.2.9. Box and Dot Density Plot of SVOC Concentrations Measured in Samples of Packing Gland Effluent Samples SVOCs are identified as follows:

- (1) 2,6,10,14-Tetramethyl Pentadecane
- (2) 3,6-Dimethylundecane
- (3) 5-Butyl-Hexadecane
- (4) Bis(2-ethylhexyl) phthalate
- (5) Di-n-butyl phthalate
- (6) Dodecane
- (7) Eicosane
- (8) n-Hexadecane
- (9) Nonanoic acid

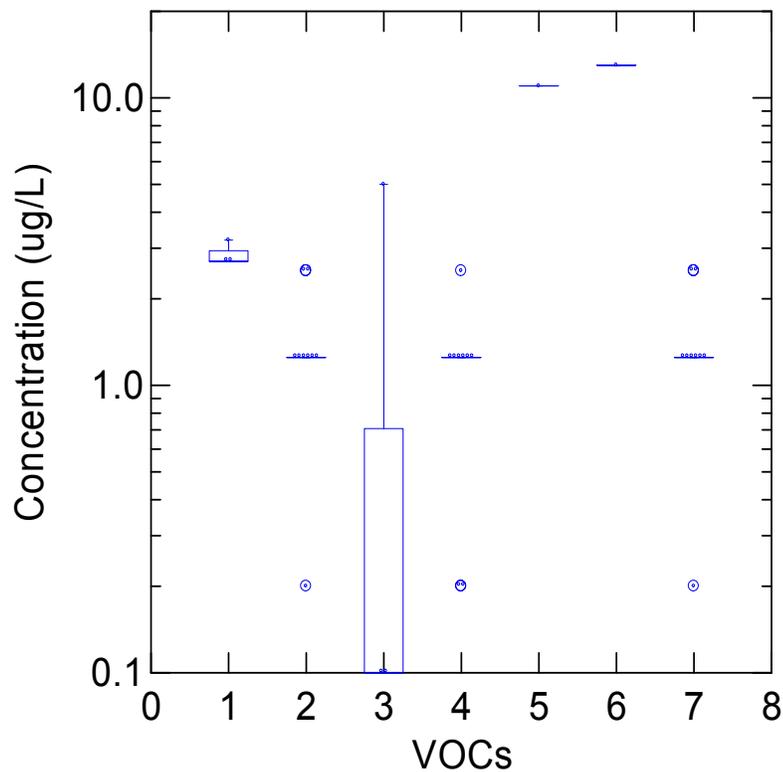


Figure 3.2.10. Box and Dot Density Plot of VOC Concentrations Measured in Samples of Packing Gland Effluent Samples VOCs are identified as follows:

- (1) Acetone
- (2) Benzene
- (3) m-,p-Xylene (sum of isomers)
- (4) Methylene chloride
- (5) n-Pentadecane
- (6) Sulfur dioxide
- (7) Tetrachloroethene

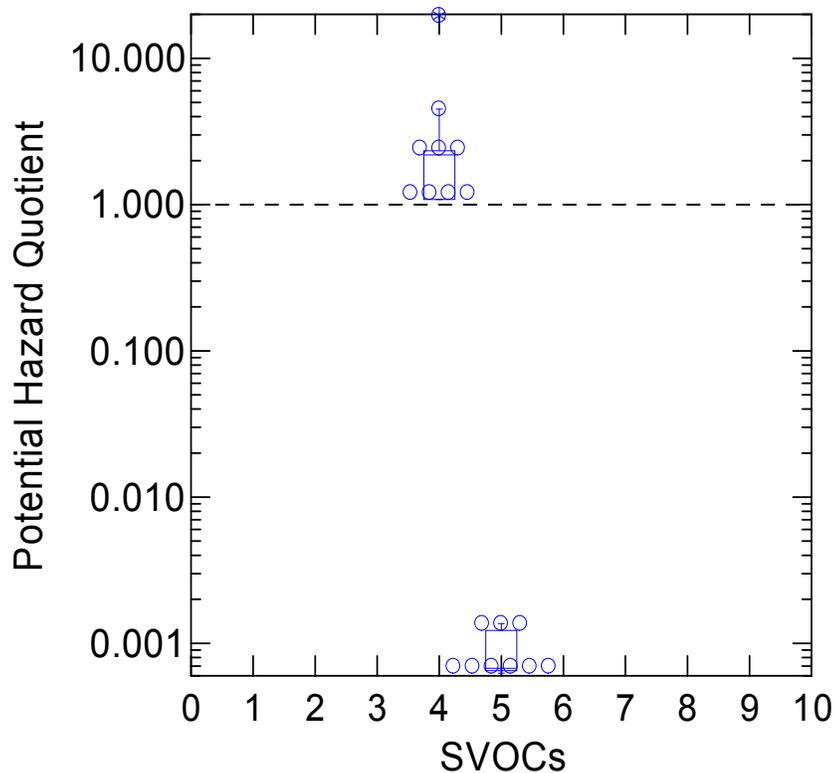


Figure 3.2.11. Box and Dot Density Plot of Potential Hazard Quotients for SVOCs in Samples of Packing Gland Effluent SVOCs are identified as follows:

- (1) 2,6,10,14-Tetramethyl Pentadecane
- (2) 3,6-Dimethylundecane
- (3) 5-Butyl-Hexadecane
- (4) Bis(2-ethylhexyl) phthalate
- (5) Di-n-butyl phthalate
- (6) Dodecane
- (7) Eicosane
- (8) n-Hexadecane
- (9) Nonanoic Acid

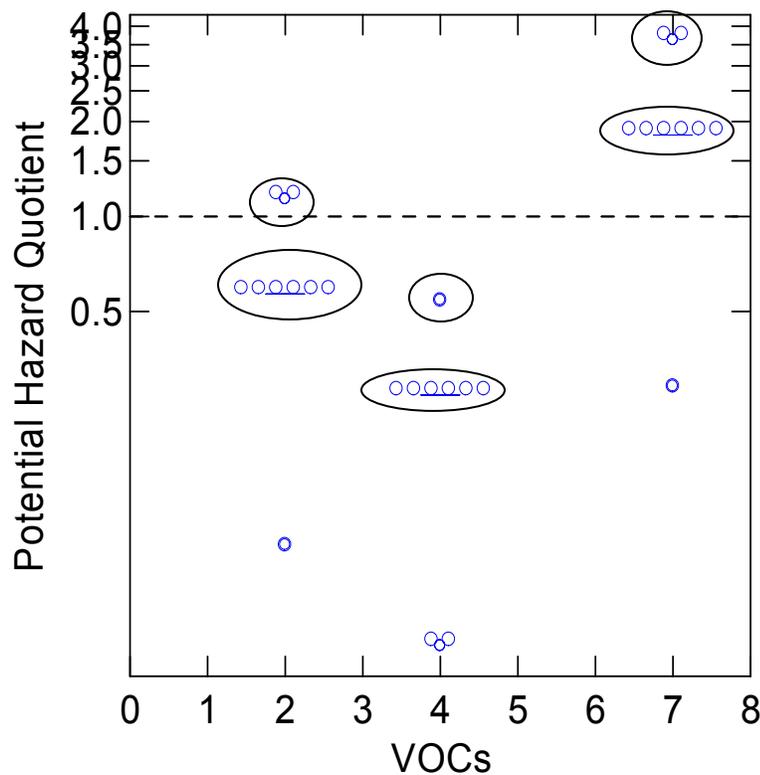


Figure 3.2.12. Box and Dot Density Plot of Potential Hazard Quotients for VOCs in Samples of Shaft Packing Gland Effluent. PHQs based on replacement values of $\frac{1}{2}$ of the reporting limit for nondetected concentrations are identified by ovals in this figure; refer to Section 3.3.2.4 for further discussion.

VOCs are identified as follows:

- (1) Acetone
- (2) Benzene
- (3) m-,p-Xylene (sum of isomers)
- (4) Methylene chloride
- (5) n-Pentadecane
- (6) Sulfur dioxide
- (7) Tetrachloroethene

3.2.2.5 Nonylphenols

EPA analyzed samples of shaft packing gland effluent for nonylphenols because of the possibility of nonylphenol-containing water from the bilge or other areas of the vessel leaking into the shaft packing gland effluent compartment. Table 3.2.5 presents the detected results.

Of the nine samples for which long- and short-chain nonylphenols were analyzed, only six long-chain nonylphenols of the octylphenol polyethoxylate (OPEO) type were detected: OP12EO, OP11EO, OP10EO, OP9EO, OP8EO, and OP7EO. All of the detected OPEOs are long-chain octylphenols and were found in one tugboat sampled. The OPEO with the longest ethoxylate chain (OP12EO) was detected at the lowest concentration (Figure 3.2.13). The OPEO isomers showed the trend of increasing concentrations as the size of the ethoxylate chain is reduced (from OP12EO to OP7EO), indicating moderately advanced degradation of the long-chain OPEOs in the packing gland.

Average concentrations of OPEOs with the longest ethoxylate chains (OP12EO through OP10EO) were similar to bilgewater effluent (see Table 3.1.8). In contrast to bilgewater effluent, however, NP was not detected in packing gland effluent.

None of the OPEOs detected in the packing gland effluent sample were detected in ambient water, indicating a probable source from onboard the vessel (tugboat) – possibly from seepage from the bilge. Another possible source of OPEOs in packing gland effluent could be from the use of lubricants for which octylphenol ethoxylates are common constituents.

Table 3.2.5. Results of Packing Gland Water Sample Analyses for Nonylphenols¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Octylphenol dodecaethoxylate (OP12EO)	µg/L	9	1	11	1.7						12	12	NA
Octylphenol undecaethoxylate (OP11EO)	µg/L	9	1	11	2.6						15	15	NA
Octylphenol decaethoxylate (OP10EO)	µg/L	9	1	11	4.8						22	22	NA
Octylphenol nonaethoxylate (OP9EO)	µg/L	9	1	11	5.3						26	26	NA
Octylphenol octaethoxylate (OP8EO)	µg/L	9	1	11	10						30	30	NA
Octylphenol heptaethoxylate (OP7EO)	µg/L	9	1	11	13						28	28	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

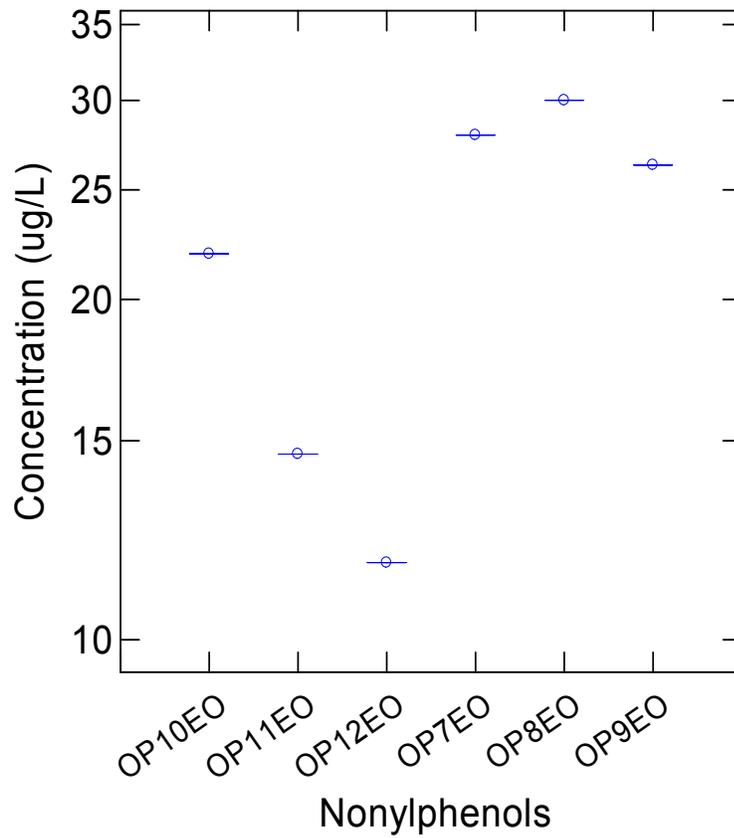


Figure 3.2.13. Box and Dot Density Plot of Nonylphenol Concentrations Measured in Samples of Packing Gland Effluent

3.2.2.6 Summary of the Characterization of Packing Gland Discharge

Table 3.2.6 summarizes the specific analytes within packing gland effluent that may have the potential to pose risk to human health or the environment for these types of vessels based upon these samples. EPA's interpretation of a realized risk likely posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

To summarize the results of packing gland discharge measured in the nine tugboats, metals were the constituents found most frequently and with the highest magnitudes of exceedance of their respective screening benchmarks. Among the dissolved forms of metals, concentrations of copper and nickel exceeded the most stringent NRWQC benchmarks. Among the total forms of metals, aluminum, arsenic, iron, and manganese exceeded the most stringent NRWQC benchmarks. However, concentrations of total iron and total manganese in surrounding (ambient) waters were similar to concentrations measured in packing gland discharge. Among the classical pollutants, most of the concentrations and values reported reflect the concentrations and values in the ambient water surrounding the vessel, as this water is the source of the drive shaft water. Two (of nine) total phosphorus samples exceeded the screening benchmark; however, these concentrations were similar to total phosphorus concentrations in the surrounding waters. Among the remaining contaminants, the SVOC bis(2-ethylhexyl) phthalate had a PHQ of >10 for one of the vessels sampled, and six of the relatively long-chained octylphenols were measured in one of the nine vessels sampled.

Table 3.2.6. Characterization of Packing Gland Effluent and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Packing Gland and Vessel Sources ¹												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Tugboats (9)			Bis(2-ethylhexyl)-phthalate	Cu, Ni	As, Al	x			x				

(1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2, or when concentrations of analytes are sufficiently high that they may have the potential to pose risks to local water bodies. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

3.2.3 Deck Washdown

Deck washdowns involve removing dirt, grit, or other materials that can impact the integrity of the deck surface (for aesthetic and safety reasons) and are a common vessel maintenance task. The process uses hoses and/or swabs (mops) to move the deck washdown water, debris, and cleaning agents (if any) to the scuppers, which then discharge the water overboard. EPA collected samples of deck water as it is drained through the scupper against the hull of the vessel (see Section 2.2.4 Sampling Methods). More than half the vessels sampled reported using detergents (dish soaps, ZEP™, Simple Green™) or other cleaners (chlorine bleach) during the washdown process. Depending on the vessel's design and function, deck washdown water sometimes contains contaminants such as detergents, metals, oil, particulates, and pathogens (the latter primarily from catch brought onboard fishing vessels).

Deck washdowns can occur at any time onboard these classes of vessels. Fishing vessels most often discharge while underway either into the nearshore (< 3 Nm from shore) or farshore (> 3 Nm from shore). Washdowns are usually performed on fishing vessels after nets are pulled, fish are brought onboard and cleaned, while returning to port, and after offloading the catch. EPA notes that the majority of deck washdown samples from fishing vessels were taken while the vessel was shoreside, and do not reflect constituents of deck washdown while the vessel is engaged in fishing operations. Decks are washed less frequently for other types of vessels such as water taxis, tour boats, and tow boats. Wash locations are generally pierside after excursions or within the harbor for these types of vessels.

The volume of deck washdown water generated by a vessel depends on the frequency of deck washdown, the flow rate from the hose, and the washdown time. Since most vessels use a common garden-hose for deck washdowns, EPA estimated the flow rate to be between 10 and 12 gallons per minute (gpm). The time required for deck washdown varies depending on the type of vessel and size. EPA observed during the vessel sampling program that most deck washdowns were generally 15 minutes or less.

To estimate the daily volume of deck washdown water generated from the different vessel classes, EPA assumed tour boats, water taxis, and tow boats washed their decks once every two weeks. For these types of vessels, the average deckwash water volume would range between 10 and 15 gpd. Deckwash water volumes for fishing boats varies depending on the type of boat. For example, trollers, trawlers, gill netters, and purse seiners sometimes wash their decks three to four times per day while fishing, plus one additional time after unloading seafood at the processing facility. For these vessels, deckwash volumes might range between 750 and 900 gpd.



Collecting Deck Washdown Samples from a Tow and Salvage Vessel



Deck Washdown Sample Collected in a Lined Bucket

For this study, EPA collected deck washdown samples from 32 vessels: 11 fishing vessels (gillnetter, trawlers, and trollers), nine tugboats, six tow/salvage vessels, two tour boats, a water taxi, a fire boat, a supply boat, and a recreational boat (see Table 2-1). EPA collected single grab samples from one or more scuppers (composited sample if more than one accessible scupper) on selected vessels for laboratory analysis in order to determine representative pollutant concentrations for deck washdown across the range of normal vessel operations.

EPA also sampled a deck runoff discharge during a rain event. Deck runoff differs from washdown in that the runoff discharge occurs because of precipitation or spray landing on the deck in sufficient quantities to mobilize pollutants on the deck surface rather than an intentional introduction of washdown water (often including detergents). However, deck runoff incorporates pollutants that would have been included in an eventual washdown so the samples are comparable. The deck runoff sample was collected from a fishing trawler that was being unloaded at a fish processing facility in the Northeastern United States.

EPA focused its sampling effort on the following analyte groups in deck washdown/runoff that were expected to be present in the discharge: metals, classical pollutants, pathogen indicators (commercial fishing vessels only), nutrients, nonylphenols, and semivolatile and volatile organic compounds (tow/salvage vessels only). Results for each class of pollutant are presented and discussed in the subsections below.

3.2.3.1 Metals

Deck washdown water samples were analyzed for dissolved and total metals. The analytical results are summarized in Table 3.3.1. The following metals were detected in 90 percent or more of the deck washdown water samples:

- Dissolved and total aluminum
- Dissolved and total barium
- Total chromium
- Total cobalt
- Dissolved and total copper
- Total iron
- Total lead
- Dissolved and total manganese
- Dissolved and total zinc.

Concentrations of a number of other metals were detected in 50 percent or more of the samples analyzed:

- Total antimony
- Dissolved arsenic¹⁸
- Dissolved chromium
- Dissolved cobalt
- Dissolved iron
- Dissolved and total nickel
- Dissolved selenium
- Dissolved and total vanadium.

Figure 3.3.1 presents the concentration ranges for dissolved metals detected in the samples. These plots show that dissolved metals concentrations span three orders of magnitude. Aside from the alkali and alkali earth metals that are major ions in seawater (Na, K, Ca, Mg), average dissolved concentrations of iron, aluminum, and zinc were highest, followed by dissolved barium, manganese, and copper. Concentrations of total metals are displayed in Figure 3.3.2, and follow the same general pattern, but are much higher than their corresponding dissolved metal concentrations (f_{ds} substantially <1.0), except for Na, K, Ca, and Mg, which exist almost entirely in their dissolved forms (see Table 3.3.1).

For all metals, the mean ratios of dissolved to total metal concentrations (f_{ds}) in a particular sample range from a low of 0.11 for aluminum to 0.89 for selenium (Table 3.3.2). The f_{ds} for the 13 (out of 14) metals for which corresponding data are available are approximately equal to or less than 50 percent, indicating that at least half of the total metal concentration in deck washdown water samples is in particulate form. Such results were expected from certain vessels (e.g., tugboats and supply boats) where particulate material was readily visible on deck surfaces. Particulate metal is less biologically available than dissolved metals, and therefore less likely to cause an immediate toxic effect in aquatic organisms.

Dissolved cadmium concentrations were detected in two of the 31 vessels sampled - a supply and tow/salvage boat. The concentrations were 1.2 (supply boat) and 22.4 $\mu\text{g/L}$ (tow/salvage boat), which exceeded the saltwater chronic aquatic life criterion (8.8 $\mu\text{g/L}$) in the case of the tow/salvage boat and the freshwater chronic aquatic life criterion (0.25 $\mu\text{g/L}$) in both cases.

Deck washdown water samples collected from 29 of the 31 vessels sampled contained dissolved copper concentrations that exceeded the saltwater chronic aquatic life criterion of 3.1 $\mu\text{g/L}$. Dissolved copper concentrations ranged from 2.5 $\mu\text{g/L}$ for a tug and fishing (trawler) boat

¹⁸ Even though a dissolved metal is detected in 50% of the samples, it does not mean that the total metal value (which includes dissolved and particulate metals) are considered to be detected in the laboratory analyses. All dissolved metal detections are not considered total metal detections because the detection limits differ for a given sample based on dissolved versus total recoverable metal analyses. For example, in the case of selenium, the detection limit for total recoverable selenium was 5 $\mu\text{g/L}$ for the analysis. In contrast, the detection limit for dissolved selenium in these analyses was as low as 1 $\mu\text{g/L}$.

to 204 µg/L for the supply boat. The dissolved copper concentrations in deck washdown samples from the tug and assorted fishing boats were evenly distributed across the entire range of measured dissolved copper concentrations, while the tow/salvage, fire, taxi, tour, and supply boats all had relatively high dissolved copper concentrations (above 30 µg/L).

Dissolved lead concentrations exceeding the freshwater chronic aquatic life criterion (2.5 µg/L) were limited to just three (of nine) tugboats, five (of six) tow/salvage boats, one of the two tour boats, and the fire and supply boats. Dissolved lead concentrations exceeding chronic aquatic life criterion concentrations ranged from 2.9 µg/L for one of the tugboats to 53.5 µg/L for the supply boat.

Similar to dissolved copper, dissolved zinc in deck washdown samples collected from the majority of vessels sampled (22 of 31) exceeded the most stringent 2006 NRWQC - the saltwater chronic aquatic life criterion of 81 µg/L. In contrast to dissolved copper, however, only the deck washdown samples from the various types of fishing boats appeared to be evenly distributed throughout the entire measured dissolved zinc concentration range, while dissolved zinc in deck washdown water samples collected from all the tugboats exceeded the criterion. Dissolved zinc concentrations in deck washdown water samples ranged from 16 µg/L for a fishing vessel (the gillnetter) to 1,200 µg/L for one of the tugboats. All but one of the tow/salvage boats produced dissolved zinc in deck washdown water samples exceeding the criterion, as did the tour, fire, and supply boats (the last with a measured dissolved zinc concentration of 465 µg/L).

For the other dissolved metals (chromium, nickel, and selenium) where measured concentrations exceeded the saltwater and/or freshwater criteria in one or more of the deck washdown water samples, the PHQs were generally less than two. For both chromium and nickel, the tow/salvage vessel type had the greatest number of dissolved metal concentration exceedances for their respective most stringent criteria. No information was available concerning the frequency of deck washdowns for the supply vessel, although this particular vessel is known to transport petroleum products, and its deck appeared visibly “soiled” to the samplers. According to the surveys, the tow/salvage boats generally undergo deck washdowns once to twice per week, about the same frequency as tugboats, but less frequent than the fishing and tour boats.

Four of the total metals (aluminum, arsenic, iron, and manganese) exceeded the most stringent 2006 NRWQC in approximately half (manganese) or all the deck washdown water samples (aluminum, arsenic, and iron), although sample concentrations of these metals appear to be greatly influenced by surrounding ambient water concentrations (see Table 3.3.3). This pattern was identical to the one observed for bilgewater discharge. In contrast to the bilgewater samples, about half the deck washdown water samples for a fifth metal (antimony) exceeded the most stringent 2006 NRWQC in the deck washdown water samples, as shown in Figure 3.3.4. PHQs for total arsenic ranged from 56 to 4,600. All of the total arsenic concentrations exceeded

the most stringent human health (water plus organism consumption) criterion of 0.018 µg/L, as well as the human health criterion for organism consumption alone, 0.14 µg/L. The protective human health criteria values for total arsenic are driven by the carcinogenic potential of this metalloid. However, when compared to the less stringent saltwater chronic aquatic life criterion for arsenic of 36 µg/L, only five of the 31 vessels produced total arsenic concentrations in deck washdown water samples that exceeded this less stringent criterion, and the corresponding PHQs ranged only from 1.0 to 2.3. These total arsenic exceedances were found on a fishing (shrimping) vessel, three (of the six) tow/salvage vessels, and the fire boat. In fact, the total arsenic concentrations in deck washdown water samples from all six of the tow/salvage boats were close to or within the upper quartile of samples.

Figure 3.3.3 displays the distribution of PHQs based on the most conservative (most protective) screening benchmark for each of the dissolved metals. PHQs for four of the dissolved metals (cadmium, copper, lead, and zinc) include values from greater than 10 to over 100, indicating that the measured concentrations were one or more orders of magnitude greater than the most conservative screening benchmark. In addition, although the mean dissolved selenium PHQ was less than one, there were two measured occurrences where PHQ exceeded 10. PHQs exceeding one were also observed for dissolved chromium and nickel, bringing to seven the number of dissolved metals that exceeded the most stringent 2006 NRWQC in one or more deck washdown water samples.

PHQs for total aluminum were also high, ranging from 7.5 to 150, followed closely by total iron, with PHQs ranging from 3.1 to 48. For both metals, the majority of tug and tow/salvage boats were consistently above the median (middle concentration of the range) of total metal concentrations (in addition to the fire and supply boats), while the fishing boats were below the respective median total metal concentrations. Conversely, only three of the PHQs for total manganese exceeded a value of 5 (a tugboat, the supply boat, and the water taxi).

The frequency of PHQ exceedances for antimony, like total arsenic, are driven by the low human health (water plus organism consumption) criterion of 5.6 µg/L (the human health criterion for organism consumption alone (640 µg/L) is much higher). Only five of the 19 vessels from which deck washdown water samples were obtained had PHQ below 1, and were collected from the supply, fire, recreational, and two of the salvage vessels. Among the PHQs for antimony that were greater than 1, the low PHQ of 5.2 corresponded with the supply boat, and the high PHQ of 47 corresponded with a tow/salvage vessel – a PHQ value three times higher than in the recreational vessel (PHQ = 15).

From the perspective of potential risk, the discharges of metals where dissolved and total concentrations exceed EPA's most stringent criteria correlate most strongly to utility, passenger, or general service vessels such as the supply boat, tow/salvage boats, tugboats, water taxi, and

fire boat. Commercial fishing vessels may not be a source of concern except for metals such as dissolved copper.

EPA tested the hypothesis that the utility, service, and passenger vessels (referred to as nonfishing vessels) discharged metals at higher concentrations than fishing vessels per discharge event using two approaches. For both approaches, 20 nonfishing vessels (the tow/salvage boats, tugboats, tour vessels, fire boat, water taxi, and supply vessels) were compared to the 10 fishing vessels (six shrimping vessels, two trawlers, one troller, and a gillnetter). For the analysis, when multiple minimum detection limits were reported for a particular metal, the minimum concentration was set to ½ of the highest reporting limit. This more conservative approach was chosen to reduce the likelihood of detecting a difference that was not a “true” difference (Type I error).

For the first approach, a subset of the metals with the highest frequencies of screening benchmark (NRWQC) exceedance from the nonfishing vessels were compared to those from the fishing vessels. Although there is no NRWQC for total lead, this metal was used in these analyses because of the high proportion of nondetects in the dissolved form. This analysis was performed using modified t-tests for unequal sample sizes and uneven variances (see Table 3.3.4). Concentrations of dissolved zinc and total lead were significantly higher in deck washdown discharges of non-fishing vessels (e.g., tug boats) than fishing vessels. Although concentrations of total arsenic were not significantly different between nonfishing and fishing vessels, when the six tow/salvage vessels were compared to the remaining 24 vessels, total arsenic concentrations in the tow/salvage vessels were significantly higher than in other vessels (Table 3.3.4). When this analysis was performed for dissolved lead despite the occurrence of nondetects, the results were the same (i.e., concentrations of dissolved lead in industrial vessels were higher than in fishing vessels).

For the second approach, mean concentrations for both dissolved and total forms of the heavy metals (cadmium, chromium, copper, lead, nickel, zinc) were compared using an exact binomial test. This approach assumes that, even if the difference in mean concentrations between nonfishing and fishing vessels for any given metal is not statistically significant, if the mean metal concentrations from a particular vessel class are always or nearly always lower than those of another class of vessels, then the overall trend may be statistically significant. Both dissolved and total metals concentrations of all six heavy metals were higher in nonfishing vessel discharges than in fishing vessel discharges (see Table 3.3.5). A binomial test was then performed to determine whether the overall pattern of lower mean metal concentrations in fishing vessel discharges could be attributed to chance, assuming an equal likelihood that concentrations in fishing vessels or industrial vessels would be lower. The probability that mean concentrations of all six metals (either dissolved or total) would be lower in fishing vessels compared to nonfishing vessels, given an equal likelihood of either outcome occurring, was statistically significant ($P = 0.016$). The probability of concentrations being lower in fishing

vessels for all 12 comparisons (six dissolved metals + six total metals) was also statistically significant ($P = 0.0002$). The mean concentrations of these heavy metals by vessel class are shown in Table 3.3.5. Results of this analysis support the assertion that metals from deck washdown discharges from nonfishing (utility, service, and passenger) vessels tend to be higher than metals from deck washdown discharges from fishing vessels for each discharge event.

One possible explanation for the higher metal concentrations in nonfishing vessels is that the frequent washing of fishing vessels' decks may prevent metal build-up and keep metal concentrations lower in each individual deck washdown discharge.

With regard to assessing potential risk, it is important to understand that, for most of the metals identified above as of potential concern in deck washdown water, maximum metal concentrations in the ambient or potable water used for deck washdown (see left half of Table 3.3.3) were higher than the median metal concentrations in deck washdown water samples (Table 3.3.1). The ambient receiving waters to which these deck washdown waters are being discharged have metal concentrations that often exceed the most stringent NRWQC (see right half of Table 3.3.3). The relatively high metals concentrations for the five dissolved metals (copper, manganese, nickel, selenium, zinc) in potable water and four total metals (aluminum, arsenic, iron, lead) in ambient water can at least partially account for the high concentrations of metals found in some of the deck wash discharges. Furthermore, based on corresponding concentrations of alkali and alkali earth metals (calcium, magnesium, sodium, and potassium) in the deck washdown water samples (see Table 3.3.1), few, if any, of the potentially toxic dissolved metal concentrations are likely to be bioavailable to biological organisms because of the high hardness values, which reduce metal bioavailability.

In summary, metals were frequently detected in deck washdown water samples, with certain metals occurring much more frequently at levels that may have potential for risk than others. EPA found high concentrations of a number of dissolved and total metals in these samples. Dissolved cadmium, copper, lead, and zinc were consistently elevated above the most conservative screening benchmarks, with all the PHQ values in the 1 to 100 range. However, dissolved cadmium concentrations measured in deck washdown water samples were only detected in two of 31 vessels. For these and other metals (total aluminum, arsenic, iron, and manganese), concentrations measured in most if not all of the water samples exceeded saltwater and/or freshwater criteria.

Table 3.3.1. Results of Deck Washdown/Runoff Sample Analyses for Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum, Dissolved	µg/L	31	28	90	420	260		1.7	31	570	1100	1900	NA
Aluminum, Total	µg/L	31	30	97	3400	1900		820	990	4700	8300	13000	87
Antimony, Dissolved	µg/L	19	9	47	7.3					4.2	13	91	NA
Antimony, Total	µg/L	19	13	68	26	1.9				29	86	260	5.6
Arsenic, Dissolved	µg/L	31	19	61	6.4	2.3				9.8	13	28	36
Arsenic, Total	µg/L	31	23	74	18	8.3				29	49	83	0.018
Barium, Dissolved	µg/L	19	19	100	63	42	23	27	33	69	96	280	NA
Barium, Total	µg/L	19	19	100	270	100	52	59	70	160	1300	1400	1000
Cadmium, Dissolved	µg/L	31	2	6	1.3							22	0.25
Cadmium, Total	µg/L	31	5	16	2.0						1.7	36	NA
Chromium, Dissolved	µg/L	31	17	55	5.1	2.3				9.1	16	18	11
Chromium, Total	µg/L	31	29	94	34	24			8.3	55	84	130	NA
Cobalt, Dissolved	µg/L	19	12	63	2.7	1.3				3.9	8.2	14	NA
Cobalt, Total	µg/L	19	18	95	6.0	4.1	3.1		2.0	6.7	20	26	NA
Copper, Dissolved	µg/L	31	29	94	42	23			7.2	59	120	200	3.1
Copper, Total	µg/L	31	31	100	130	110	6.4	12	47	160	340	530	1300
Iron, Dissolved	µg/L	19	12	63	520	190	5.6			1100	1100	3000	NA
Iron, Total	µg/L	19	18	95	4400	2300		950	1700	5300	13000	15000	300
Lead, Dissolved	µg/L	31	15	48	6.0					4.7	19	54	2.5
Lead, Total	µg/L	31	30	97	48	23			8.0	42	160	260	NA
Manganese, Dissolved	µg/L	31	29	94	60	35		2.7	11	91	200	240	NA
Manganese, Total	µg/L	31	28	90	210	98	3.6	4.3	55	300	540	1300	100
Nickel, Dissolved	µg/L	31	19	61	6.9	4.8				8.2	13	17	8.2
Nickel, Total	µg/L	31	25	81	16	12			6.2	18	27	100	610
Selenium, Dissolved	µg/L	31	17	55	8.9	1.1				2.1	25	82	5.0
Selenium, Total	µg/L	31	12	39	9.5					1.8	23	96	170
Thallium, Dissolved	µg/L	19	1	5	0.64							3.2	NA
Vanadium, Dissolved	µg/L	19	14	74	1.9	1.3				2.0	5.2	7.6	NA
Vanadium, Total	µg/L	19	16	84	9.8	6.2			2.9	9.8	20	58	NA

Table 3.3.1. Results of Deck Washdown/Runoff Sample Analyses for Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Zinc, Dissolved	µg/L	31	31	100	260	120	16	35	51	430	620	1200	81
Zinc, Total	µg/L	31	31	100	580	330	20	52	150	720	1400	4000	7400
Cationic Metals													
Calcium, Dissolved	µg/L	31	31	100	73000	34000	5900	25000	32000	83000	190000	320000	NA
Calcium, Total	µg/L	31	31	100	77000	39000	7300	27000	34000	88000	190000	310000	NA
Magnesium, Dissolved	µg/L	31	31	100	130000	14000	6600	7000	7900	59000	510000	1000000	NA
Magnesium, Total	µg/L	31	31	100	130000	19000	6800	7800	9200	59000	510000	1000000	NA
Potassium, Dissolved	µg/L	19	19	100	30000	8000	3300	4000	5400	24000	140000	180000	NA
Potassium, Total	µg/L	19	19	100	30000	8100	3600	3900	5600	25000	130000	180000	NA
Sodium, Dissolved	µg/L	19	19	100	510000	79000	26000	38000	45000	410000	2800000	3600000	NA
Sodium, Total	µg/L	19	19	100	510000	78000	24000	38100	45000	400000	2600000	3600000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.3.2. Dissolved-to-Total Metal Ratios (f_{ds}) in Paired Deck Washdown/Runoff Samples

Metal	Summary Statistics of Dissolved:Total Metal Ratios Calculated for Select Metals			
	Geomean	Median	Min	Max
Aluminum	0.10	0.12	0.010	1.00
Iron	0.12	0.090	0.050	0.33
Lead	0.14	0.18	0.030	0.62
Chromium	0.16	0.13	0.060	0.76
Vanadium	0.25	0.26	0.12	1.13
Manganese	0.25	0.28	0.010	0.93
Antimony	0.30	0.34	0.14	0.64
Copper	0.33	0.34	0.050	1.04
Arsenic	0.38	0.47	0.060	0.93
Cadmium	0.48	0.49	0.36	0.62
Nickel	0.50	0.53	0.17	0.93
Cobalt	0.53	0.52	0.26	1.25
Zinc	0.54	0.54	0.18	2.95
Selenium	0.89	0.89	0.61	1.30

Table 3.3.3. Minimum and Maximum Dissolved and Total Metal Concentrations in Vessel Source¹ and Ambient² (Harbor) Water Relative to Median Sample Concentrations and Most Stringent Screening Benchmarks

Metal	Source Water Conc. (min)	Source Water Conc. (max)	N	Median Conc. From Table 3.3.1	Ambient Conc. (min)	Ambient Conc. (max)	N	Most Stringent Screening BM
Aluminum, Dissolved	6.3	310	6	258	0	870	12	NA
Aluminum, Total	8.6	250	6	1900	44.5	3950	15	87
Arsenic, Dissolved	0	1.9	3	2.3	2	26	8	36
Arsenic, Total	0	1.8	3	8.3	2.9	28.9	8	0.018
Copper, Dissolved	2.4	36	5	23.1	0	24.2	10	3.1
Copper, Total	2.6	51	4	109	0	23.3	11	1300
Iron, Dissolved	0	0	1	189.5	226	259	2	NA
Iron, Total	0	801	4	2330	114	4180	8	300
Lead, Total	1.2	6	2	23	0	3.1	3	2.5**
Manganese, Dissolved	0	33	6	34.8	0	106	11	NA
Manganese, Total	3.6	37	6	97.8	8.3	165	13	100
Nickel, Dissolved	0	3	4	4.8	2.3	7.2	10	8.2
Nickel, Total	0	2.7	4	12	2.4	16.7	11	610
Selenium, Dissolved	0	1.6	3	1.1	1.7	75.5	8	5

Table 3.3.3. Minimum and Maximum Dissolved and Total Metal Concentrations in Vessel Source¹ and Ambient² (Harbor) Water Relative to Median Sample Concentrations and Most Stringent Screening Benchmarks

Metal	Source Water Conc. (min)	Source Water Conc. (max)	N	Median Conc. From Table 3.3.1	Ambient Conc. (min)	Ambient Conc. (max)	N	Most Stringent Screening BM
Selenium, Total	0	1.9	2	0	19.4	86.5	6	170
Zinc, Dissolved	4.1	1200	6	124	0	116	13	81
Zinc, Total	4.1	1100	6	331	0	23.9	15	7400

N = sample size.

(1) Ambient water was collected from background water surrounding the vessel sampled.

(2) Source water was collected from the city tap water supply while pierside, except for one tugboat in Havre De Grace, Maryland, where source water was collected from a potable water storage tank on the vessel (service water) that was filled with city water.

Table 3.3.4. Comparison of Metal Concentrations in Deck Washdown Discharge Between Fishing Vessels and Non-Fishing Vessels¹

Metal	Form	Average Metal Concentration (µg/L) by Vessel Type		Welch's Modified 2-Sample t-Test		
		Fishing	Non-Fishing	t	df	P< t _{α/2}
Copper	Dissolved	27.7	50.7	-1.68	18.2	0.110
Nickel	Dissolved	6.19	7.23	-1.05	20.7	0.306
Zinc	Dissolved	161	314	-2.15	14.9	0.049
Arsenic ²	Total	14.0	20.5	-0.49	19.8	0.629
Lead	Total	5.48	70.7	-3.76	19.1	0.001

Notes:

(1) Nonfishing vessels defined as tow/salvage vessels, tugboats, tour vessels, fire boat, water taxis, and supply vessels. The recreational vessel is not a study vessel and was excluded from these analyses.

(2) Total arsenic concentrations discharged from the six tow/salvage boats were significantly higher than for the other 24 vessels (Welch's Modified 2-Sample t-test, t=-5.26, P<0.001, on 16.7 df).

Table 3.3.5. Mean Concentrations of Dissolved and Total Heavy Metals from Deck Wash Discharges from Fishing Vessels and Nonfishing Vessels^{1,2}

Metal	Form	Conc. (µg/L) in			Conc. (µg/L) in		
		Fishing Vessels	n	Not Det. (%)	Non-Fishing Vessels	n	Not Det. (%)
Cadmium	Dissolved	0.750	10	100	1.86	20	90
Chromium	Dissolved	3.79	10	70	5.93	20	35
Copper	Dissolved	27.7	10	0	50.7	20	0
Lead	Dissolved	2.00	10	100	8.85	20	45
Nickel	Dissolved	6.19	10	40	7.23	20	40
Zinc	Dissolved	161	10	0	314	20	0
Cadmium	Total	2.00	10	100	3.77	20	90
Chromium	Total	15.7	10	20	42.3	20	0
Copper	Total	93.2	10	0	157	20	0
Lead	Total	5.48	10	10	70.7	20	0
Nickel	Total	8.65	10	40	19.4	20	10
Zinc	Total	207	10	0	791	20	0

Notes:

- (1) Nonfishing vessels defined as tow/salvage vessels, tugboats, tour vessels, fire boat, water taxis, and supply vessels. The recreational vessel is not a study vessel and was excluded from these analyses.
- (2) For these comparisons, minimum concentrations were set at ½ of the reporting limit of the highest minimum detection level, when multiple detection limits were present. Average concentrations of dissolved and total forms of all six heavy metals were lower in fishing vessels than in nonfishing vessels.

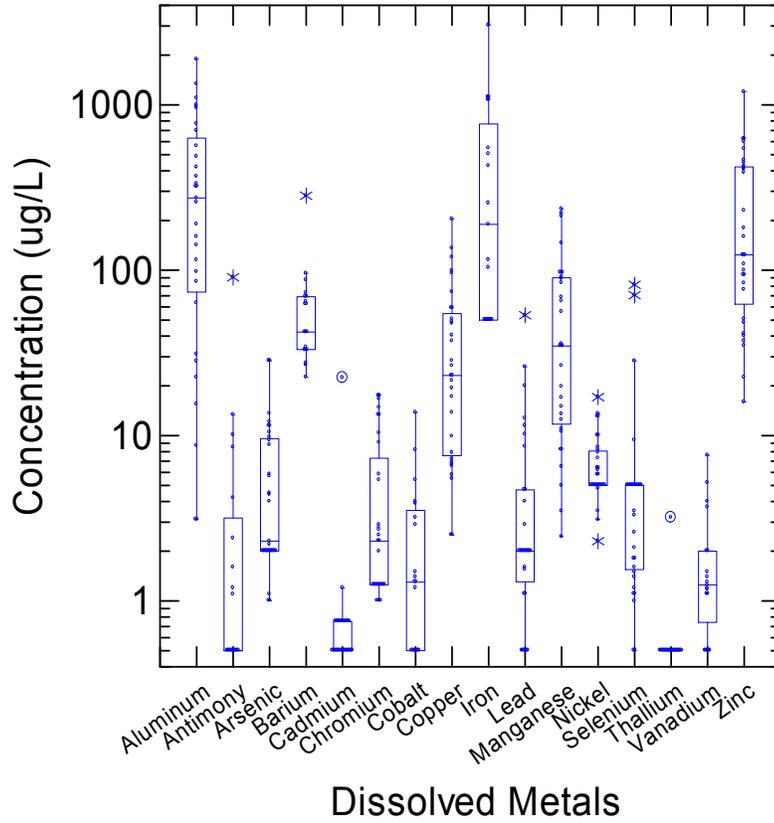


Figure 3.3.1. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Deck Washdown Water (Dissolved beryllium and silver were not detected in any of the deck washdown samples)

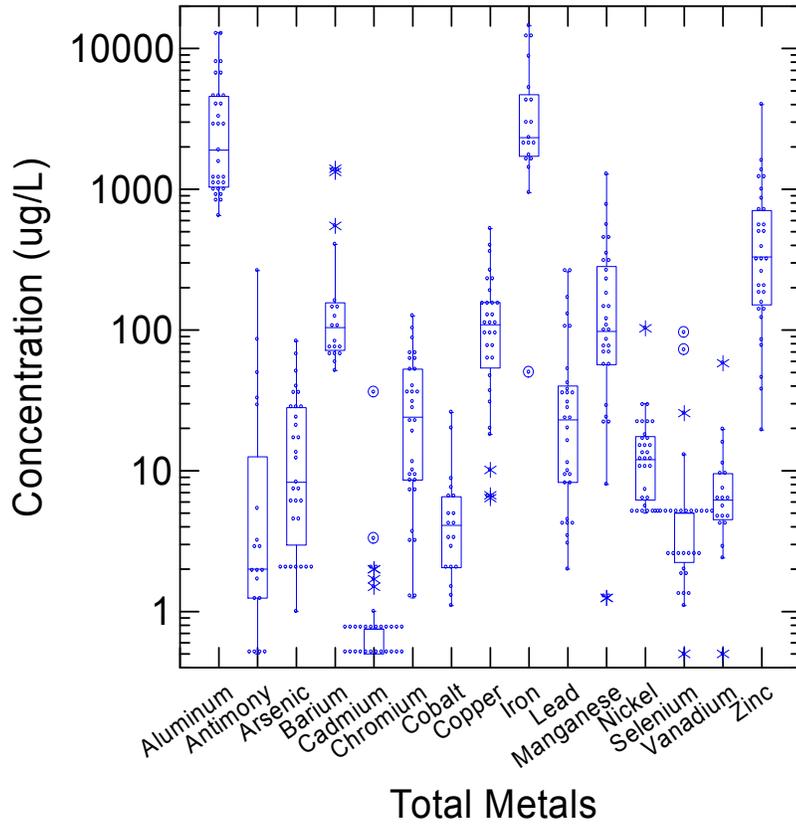


Figure 3.3.2. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Deck Washdown Water

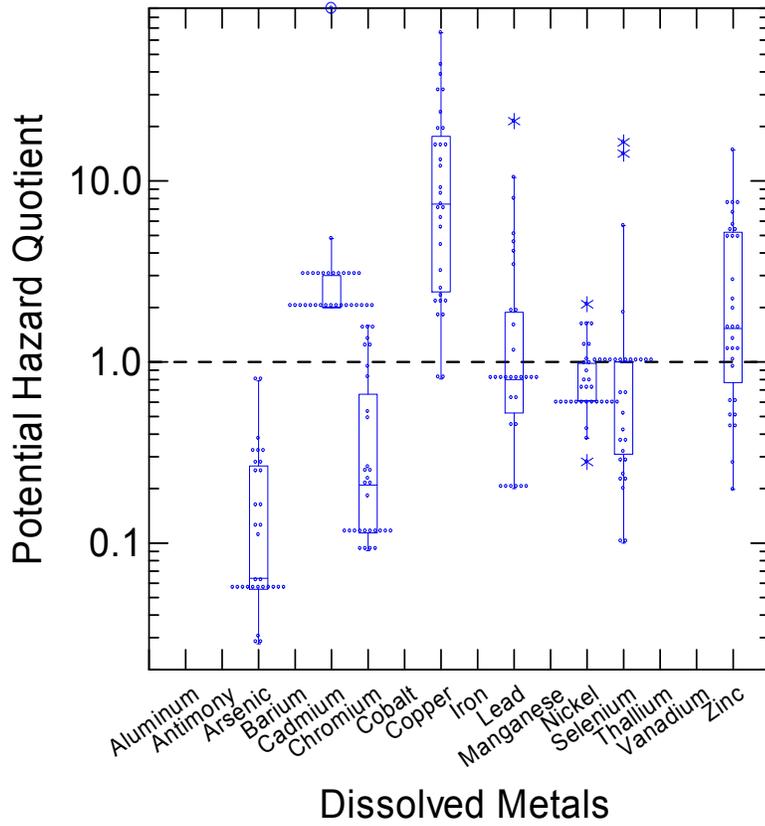


Figure 3.3.3. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Deck Washdown Water

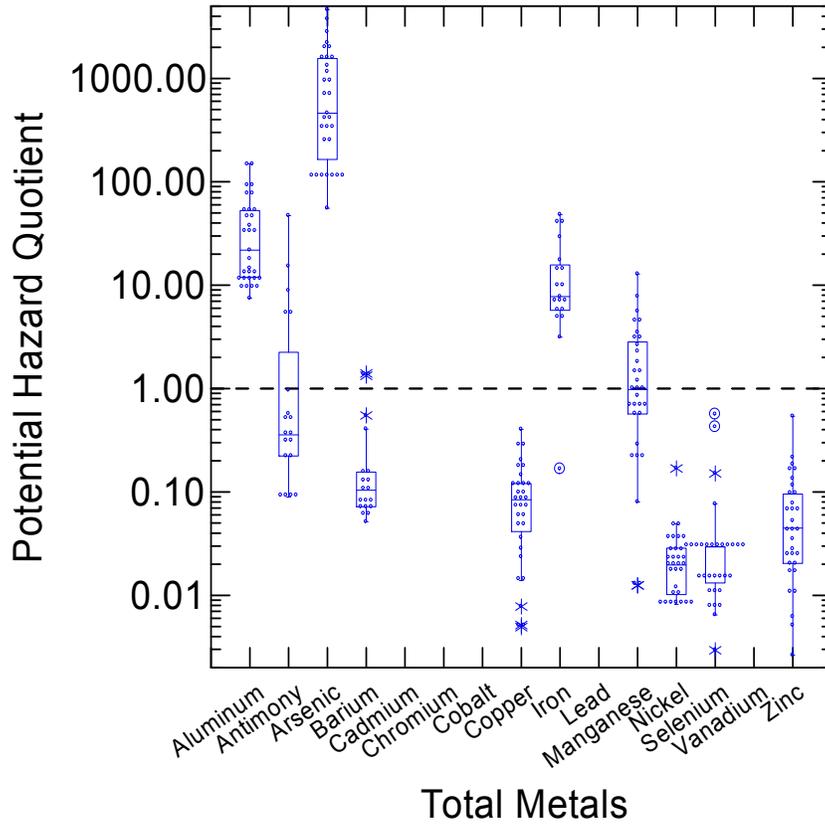


Figure 3.3.4. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Deck Washdown Water

3.2.3.2 Classical Pollutants

Deck washdown water samples from 32 vessels were analyzed for 14 classical pollutants (see Table 3.3.6). The classical pollutants include measurements that are physical properties (temperature, conductivity, salinity, turbidity, TSS), oxygen consumption (BOD, COD), oil and grease (HEM and SGT-HEM), as well as chemical concentrations (pH, sulfide, DO, and TRC).

Measured values of the physical properties of the discharge (conductivity, dissolved oxygen, pH, temperature, salinity) are unremarkable and appear to reflect conditions at the time (seasonality) and location (geographical) of sampling. For instance, conductivity and salinity in deck washdown water appear to reflect the type of source water used (ambient or potable service/city¹⁹ water), as shown by the measured values of these two parameters. Half the fishing vessels appear to have used ambient saltwater during normal operations (six of 11 vessels), while the remaining fishing boats and nearly all other vessel types (tugs, tow/salvage, tour, supply boats) used a freshwater source (aboard the vessel or pierside). Levels of pH were generally about neutral (between 7 and 8), with the only exceptions being two tugboats where the pH was 9.1 and 9.8 (relatively high). Temperature of the deck washdown water ranged from 7.5 to 32 °C and varied according to month (season) sampled and geographic location (warmer water samples in southern United States and colder in mid-Atlantic and northern states). Dissolved oxygen (DO) in deck washdown samples was sufficiently saturated (50 percent plus; DO ranged from 5.5 to 10.5 mg/L) in all samples, except for low DO concentrations from three fishing vessels participating in the north Pacific fishery, which ranged from 1.6 to 1.9 mg/L.

Figure 3.3.5 illustrates the variability of the values measured for the classical pollutants in deck washdown water. Turbidity (measure of water clarity) and TSS are clearly related and range from 4.1 to 460 NTU and 31 to 530 mg/L, respectively. Measured values above the median concentrations were dominated by the tug, tow/salvage, supply, fire, and water taxi boats for both parameters, while measured values below the median were largely from the fishing boats (with only a few exceptions). EPA notes that the majority of deck washdown samples from fishing vessels were taken while the vessel was shoreside, and do not reflect constituents of deck washdown while the vessel is engaged in fishing operations. Potable water measured during the study was low in turbidity (0 to 16 NTU) and TSS (0 mg/L), as was ambient (harbor) water, except for waters sampled in the Gulf Coast (Louisiana). Ambient turbidity and TSS were as high as 186 NTU and 98 mg/L, respectively, in a sample collected from one harbor in Louisiana.

Of the remaining parameters, BOD, COD, and TOC have quite high concentrations (see Figure 3.3.5). While the measured values for these parameters in deck washdown water samples were generally evenly distributed for the different vessel types across the entire concentration

¹⁹ Service water here means the vessel potable water supply. For study vessels, vessel service water generally originates from municipal water supply rather than produced on board. When deck washdown is performed pierside most vessels used city water as their source water. Many fishing vessels and at least one tugboat use ambient water as their water source when performing deck washdown offshore or underway.

range, a select few vessels were clear standouts: three tugboats, a fishing (shrimping) vessel, and the supply boat. The concentrations of all three parameters were highly variable and span two orders of magnitude. In contrast, measured sulfide concentrations from deck washdown water samples collected from two fishing boats and a tow/salvage boat were all relatively low, but, when compared to the most stringent NRWQC of 0.002 mg/L, had PHQs ranging from 2.5 to 8.5 (moderate exceedance - data not shown).

PHQs were calculated for three additional classical pollutants for which benchmarks were available and are shown in Figure 3.3.6. As the figure shows, the TRC concentrations where TRC was detected above the reporting limit of 0.10 mg/L greatly exceeded the benchmark (most stringent NRWQC of 0.0075 mg/L, the saltwater chronic aquatic life criterion) by factors that ranged from 23 (tow/salvage vessel) to 106 (exceedance by 2 orders of magnitude – a fishing vessel). These concentrations (ranging from 0.17 to 0.80 mg/L) were measured in deck washdown water samples collected from three (of the 11) fishing vessels, the two tour boats, a tugboat, and the tow/salvage boat. It is worth pointing out that in one instance (i.e., for a tugboat with a high TRC concentration of 0.39 mg/L), the measured TRC concentration in the source (potable) water was 0.70 mg/L. It is also worth noting that only one of 11 respondents (a fishing vessel) indicated using chlorine bleach while washing decks, and this particular vessel had a measured TRC concentration in the deck washdown sample of 0.38 mg/L and a PHQ of 51.

TSS in most of the deck washdown water samples collected exceeded the secondary treatment effluent limitation benchmark of 30 mg/L. However, 27 of 32 PHQs calculated for these samples were below 10 (Figure 3.3.6), and all five TSS samples with PHQs > 10 (max PHQ = 17.7) were associated with tugboats. As discussed above, in the one potable water sample for which TSS was measured, TSS was not detected.

BOD was measured in 22 deck washdown water samples that exceeded EPA's secondary treatment effluent limit of 30 mg/L (Figure 3.3.6). As indicated above, the vessels with the highest level of exceedance (PHQs > 5) were associated with three tugboats, a fishing (shrimping) vessel, and the supply boat.

EPA compared HEM and SGT-HEM concentrations measured in deck washdown samples to the existing international and U.S. regulatory limit of 15 ppm (15 mg/L) for oil and grease discharge. HEM and SGT-HEM were detected in all of the deck washdown water samples, with concentrations ranging from 1.2 to a very high 133 mg/L for HEM and 0.91 to a comparably high 84 mg/L for SGT-HEM. Based on the regulatory limit of 15 mg/L, PHQs exceeded one in only six of 29 vessels sampled for HEM and two in the 29 vessels sampled for SGT-HEM. The highest PHQs for both parameters corresponded with the supply boat and a tugboat, with PHQs of 4.7 and 8.9 for HEM and 1.2 and 5.6 for SGT-HEM, respectively. Note, oil and grease were not detected in the two potable water samples collected in this sampling program.

To summarize, just under a third of the vessels sampled had concentrations of TRC in deck washdown samples above the reporting limit of 0.10 mg/L. Of these seven samples, the measured TRC concentrations (as high as 0.80 mg/L) that exceeded the screening benchmark were not associated with any one particular class of vessel. For TSS, however, one vessel type (tugboats) had the highest number of exceedances. The elevated TSS in deck washdown water samples from tugboats may be caused by a less frequent washdown on these vessels compared with vessels such as fishing vessels. Just over two-thirds of vessels (22 out of 32) exceeded the most stringent screening benchmark for BOD; however, as in the case with TRC, no one particular class of vessels had a higher number of exceedances than other classes.

Oil and grease are generally not of concern for this type of discharge, nor are any of the other physical parameters that were measured (conductivity, dissolved oxygen, pH, temperature, salinity). TOC was detected in all samples ranging from 3.6 to a very high 350 mg/L (one of the tugboats with high HEM). Organic carbon strongly complexes metals in both freshwater and saltwater matrices, and like the competing cations such as calcium and magnesium, renders dissolved metals less bioavailable and less likely to be rapidly available for biological organisms.

Table 3.3.6. Results of Deck Washdown Water Sample Analyses for Classical Pollutants¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Biochemical Oxygen Demand (BOD)	mg/L	32	30	94	110	56		4.7	14	92	370	830	30
Chemical Oxygen Demand (COD)	mg/L	32	32	100	390	160	24	52	90	570	1200	1800	NA
Conductivity	mS/cm	26	26	100	7.7	1.0	0.24	0.37	0.50	13	30	47	NA
Dissolved Oxygen	mg/L	26	26	100	7.2	7.7	1.6	1.8	6.3	8.9	9.7	11	NA
Hexane Extractable Material (HEM)	mg/L	29	26	90	14	2.8			1.7	12	39	130	15
pH	SU	30	30	100	7.7	7.6	7.0	7.0	7.2	7.9	8.5	9.8	NA
Salinity	ppt	24	24	100	4.9	0.60	0.10	0.20	0.23	8.0	21	28	NA
Silica Gel Treated HEM (SGT-HEM)	mg/L	29	22	76	7.0	1.7			0.45	3.8	13	84	15
Sulfide	mg/L	3	2	67	0.011	0.011				0.017	0.017	0.017	NA
Temperature	C	31	31	100	21	21	7.5	9.0	13	29	31	32	NA
Total Organic Carbon (TOC)	mg/L	25	25	100	44	24	3.6	5.0	7.1	52	96	350	NA
Total Residual Chlorine	mg/L	31	7	23	0.12						0.37	0.80	0.0075
Total Suspended Solids (TSS)	mg/L	32	32	100	170	120	27	31	59	250	470	530	30
Turbidity	NTU	31	31	100	150	110	4.1	36	58	190	380	463	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

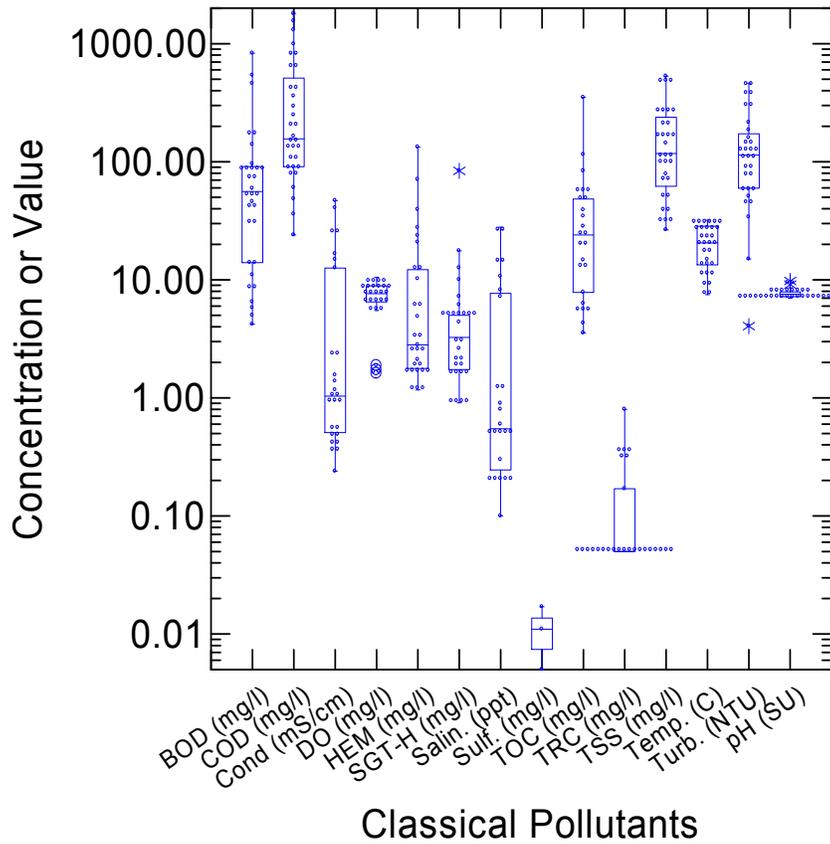


Figure 3.3.5. Box and Dot Density Plot of Classical Pollutants Measured in Samples of Deck Washdown Water

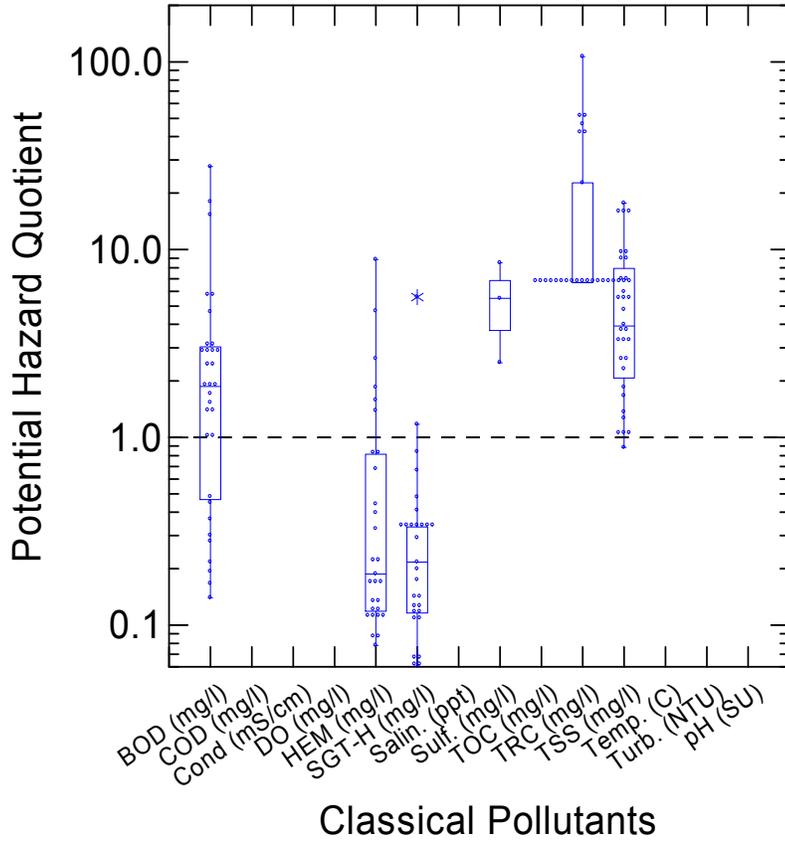


Figure 3.3.6. Box and Dot Density Plot of Potential Hazard Quotients for Classical Pollutants in Samples of Deck Washdown Water Note PHQs for sulfide are not shown in the figure, but are mentioned in the text.

3.2.3.3 Pathogen Indicators (Microbiologicals)

Selected deck washdown water samples were analyzed for the pathogen indicator bacteria *E. coli*, enterococci, and fecal coliform. Sampling for pathogens was limited to fishing vessels since EPA could not identify likely potential sources of pathogens in deck washdown discharges on other vessel types. EPA targeted select fishing vessels to attain the best cross-representation possible based on available funding and proximity to qualified subcontractor laboratories to meet sample hold times (< 6 hours). The types of fishing vessels sampled included three shrimping (trawler) boats in Louisiana, two ground fishery trawlers in Massachusetts, and a gillnetter boat in Alaska. All vessels indicated that their decks are washed frequently throughout the day (after or between catches, after unloading, etc.), and while pierside and underway (nearshore and farshore). Table 3.3.7 summarizes the analytical results. Concentrations were determined for each pathogen using the same (*E. coli*, enterococci) or comparable methods (fecal coliform).

Figure 3.3.7 shows the variability of the values measured for the pathogens in deck washdown water samples from the various fishing vessels. Measured concentrations of *E. coli* range from 20 MPN/100 ml for one of the shrimping trawlers to 8,336 MPN/100 ml for one of the ground fishery trawlers in Massachusetts. It should be noted, however, that the water the ground fishery trawler used for desk washing was ambient (harbor) water receiving stormwater and combined sewer overflow from a storm event. The measured concentration of *E. coli* in the ambient water at that location was 24,200 MPN/100 ml. Excluding this outlier, the concentration of *E. coli* from only one vessel (shrimper; concentration = 650 MPN/100 ml) exceeded EPA's most stringent freshwater bathing NRWQC of 126 MPN/100 ml by more than a factor of five (PHQ = 5.1), as illustrated in Figure 3.3.8. EPA collected multiple samples from another shrimping vessel in Louisiana to measure *E. coli* in pre-fishing deck washdown water, post-fishing water, without catch rinse water, and with catch rinse water. For this vessel, *E. coli* concentrations ranged from a low of 10 (pre-fishing sample) to a high of only 50 MPN/100 ml (without catch rinse). The concentrations of *E. coli* were largely unaffected by either the addition of catch to the vessel (as *E. coli* concentrations in pre-fishing and post-fishing deck washdown samples were similar) or the process of rinsing the catch while on deck.

The enterococci values measured in a deck washdown water samples ranged from 1.5 to 1,300 MPN/100 ml, and follow the same general pattern as *E. coli* (Figure 3.3.7). Excluding the previously described example of the trawler in Massachusetts, which was directly influenced by high levels of enterococci in the ambient water resulting from storm-related combined sewage overflow (5,100 MPN/100 ml), the deck washdown water samples from two vessels (both shrimpers; concentrations = 637 and 914 MPN/100 ml, respectively) exceeded EPA's most stringent bathing NRWQC for enterococci of 33 MPN/100 ml (freshwater) and 35 MPN/100 ml (saltwater) by factors of nearly 20 and 30 respectively (Figure 3.3.8). In contrast to *E. coli*, however, analysis of the multiple samples collected for enterococci in pre-fishing deck washdown

water (540 MPN/100 ml), postfishing water (8 MPN/100 ml), without catch rinse (1,200 MPN/100 ml), and with catch rinse (801 MPN/100 ml) for the shrimping vessel in Louisiana indicate that their deck washing process appeared to reduce the presence of the pathogen in deck washdown discharge.

The concentrations of fecal coliform bacteria measured in a deck washdown water samples are all substantial (ranging from 91 to 600 CFU/100 ml²⁰), except for the very low concentration of 0.75 CFU/100 ml for the gillnetting vessel in Alaska (Figure 3.3.7). The associated PHQs for fecal coliform range from 0.05 (gillnetter) to 43 (one of the shrimping boats), as illustrated in Figure 3.3.8. The PHQs for this pathogen are based on the NRWQC of 14 MPN/100 ml for shellfish harvesting. As with enterococci, the multiple samples measured for fecal coliform bacteria in prefishing deck washdown water (0 CFU/100 ml), postfishing water (6 CFU/100 ml), without catch rinse (1,630 CFU/100 ml), and with catch rinse (620 CFU/100 ml) for the shrimping vessel indicate that their deck washing process did not increase (and seemed to reduce) the presence of this pathogen in deck washdown discharge. The single potable water sample taken while onboard a shrimping vessel pierside in Louisiana was free of all pathogens.

The data collected for this study show that, while the three groups of pathogens are present in deck washdown discharge samples from commercial fishing vessels, concentrations are variable, and the source of the water used for deck washdown can greatly influence the background bacteria levels. Of the three pathogen groups, fecal coliform are present at concentrations exceeding EPA's most stringent criteria more often than enterococci and *E. coli*, in that order.

²⁰ Excluding the outlier value of 8,050 CFU/ml from the ground fishery trawler in Maine influenced by the storm event.

Table 3.3.7. Results of Deck Washdown Water Sample Analyses for Pathogen Indicators¹

Analyte ²	Units ³	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ⁴
<i>E. Coli</i> by MPN	MPN/100 ml	5	5	100	1900	160	20	20	62	4500	8300	8300	130
<i>Enterococci</i> by MPN	MPN/100 ml	5	5	100	580	640	1.5	1.5	27	1100	1300	1300	33
Fecal Coliform by MF	CFU/100 ml	6	6	100	1600	560	0.75	0.75	68	2500	8100	8100	14

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) MPN = Most Probable Number; MF = Membrane Filtration.

(3) CFU = Colony Forming Units.

(4) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

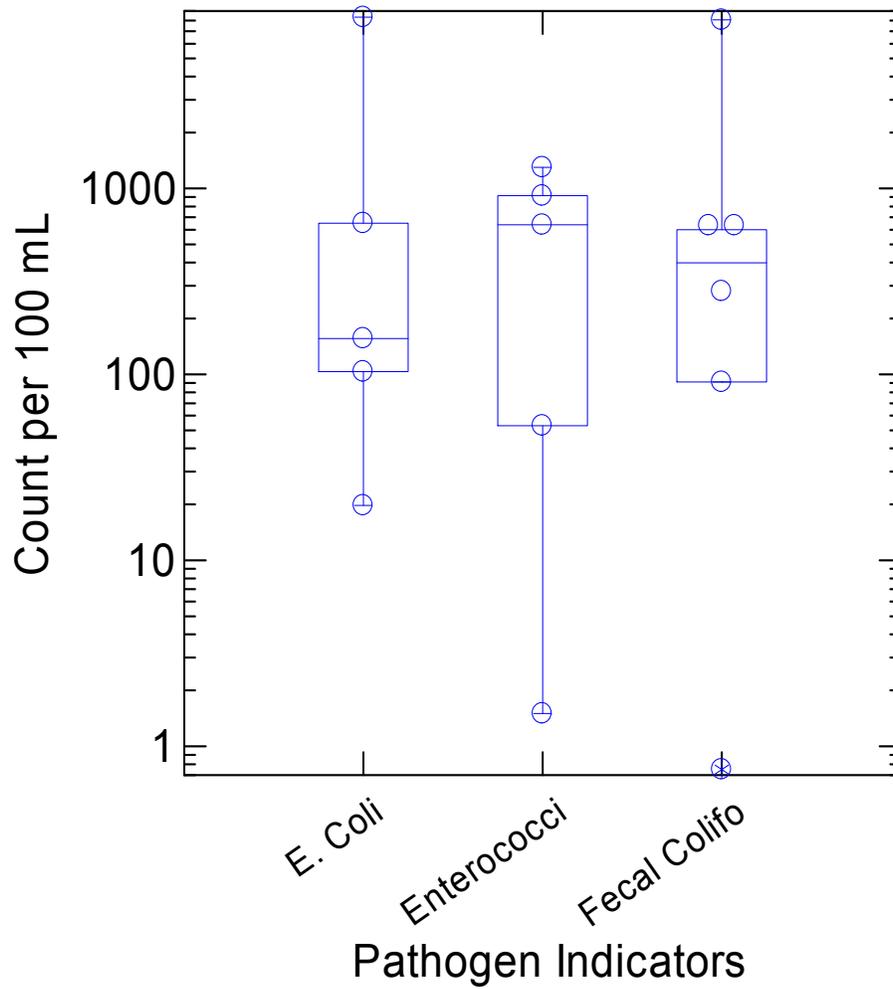


Figure 3.3.7 Box and Dot Density Plot of Pathogen Indicator Concentrations Measured in Samples of Deck Washdown Water Corresponding units are MPN/100 ml for *E. coli* and enterococci, and CFU/100 ml for fecal coliform

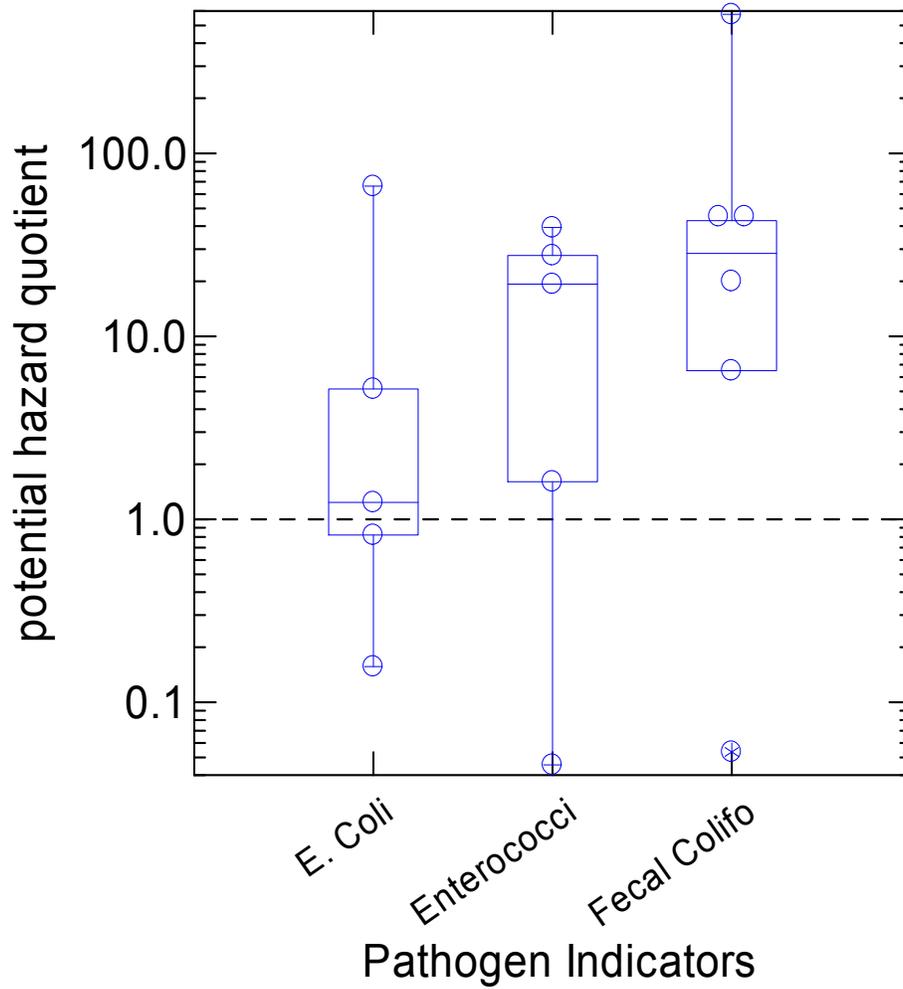


Figure 3.3.8. Box and Dot Density Plot of Potential Hazard Quotients for Pathogens in Samples of Deck Washdown Water

3.2.3.4 Nutrients

Deck washdown discharge was also characterized for nutrient levels. Nutrient pollution, including nitrogen, phosphorus, and numerous micronutrients, is a component of certain vessel discharges and a major source of water quality degradation throughout the United States (USGS, 1999). Deck washdown discharges from all vessel types were expected to contain potentially high levels of phosphorus because of the wide-spread use of detergents for deck cleansing. Deck washdown discharges from commercial fishing vessels were also expected to contain potentially elevated ammonia concentrations for the same reason, as well as from biological wastes from fish and shellfish catch. In addition to total phosphorus and total ammonia (as nitrogen), deck washdown water samples were also analyzed for nitrate/nitrite nitrogen (inorganic nitrogen) and TKN, the sum of organic nitrogen (including toxic ammonia nitrogen) (see Table 3.3.8).

Concentrations of nitrate/nitrite nitrogen in deckwash discharge samples range from 0.025 to 6.5 mg/L (see Figure 3.3.9). An interesting note is that the deck washdown water samples for commercial fishing vessels of all types did not exceed 0.50 mg/L while all other vessels exceeded this value. The five highest nitrate/nitrite concentrations (ranging from 2.5 to 6.5 mg/L) were analyzed in samples from three tugs and two tow/salvage vessels. It is important to note, however, that most samples of deck washdown on fishing vessels were collected onboard fishing vessels pierside and not when fishing activity was occurring. In the two cases where deck washdown samples were collected where fishing activities were taking place, the samples were collected towards the end of the deck washdown activity and may not have captured potentially higher levels of nitrate/nitrite from biological wastes.

The concentrations determined for TKN (sum of organic nitrogen) show the concentration range spans two orders of magnitude, from 0.05 to 40 mg/L (see Figure 3.3.9). In contrast to the nitrate/nitrite samples, the TKN concentrations from all vessels were evenly distributed across the entire concentration range. The two highest TKN concentrations (by more than a factor of two) correspond to a trolling vessel and a tugboat, with TKN concentrations of 28 and 40 mg/L, respectively.

Ammonia is the only nutrient form for which there are currently numeric NRWQC established to protect against its toxic effects. Only five of 31 vessels contained ammonia in deck washdown water samples slightly above (1.2 to 1.8 mg/L ammonia as nitrogen) the most stringent 2006 NRWQC of 1.2 mg/L, the freshwater chronic aquatic life criterion for total ammonia as nitrogen (see Figure 3.3.10). These values correspond with deck washdown water samples collected from two tow/salvage boats, two fishing vessels, and the recreational vessel.

The benchmark for total phosphorus of 0.1 mg/L from the 1986 EPA Gold Book was exceeded in samples collected from all but one of the 31 vessels. The highest total phosphorus concentration of 22 mg/L from a tugboat exceeded the benchmark by a factor of 220 (see Figure

3.3.10). This concentration was 6.5 times higher than the next highest measured concentration of 3.4 mg/L from a trolling vessel. The deck washdown water samples for phosphorus from all vessels were generally evenly distributed across the entire concentration range.

Total ammonia in ambient and service water ranged from below detection to 0.93 mg/L and from below detection to 0.73 mg/L, respectively (all below the most stringent 2006 NRWQC of 1.24 mg/L). Total phosphorus in ambient and service water ranged from below detection to 2.0 mg/L and from below detection to 0.52 mg/L, respectively (compared to 0.1 mg/L from the 1976 EPA Red Book).

In summary, out of the four nutrient parameters, only total phosphorus is of potential concern from deck washdown effluent. Twelve of the 19 respondents confirmed using standard liquid detergents aboard their vessels for deck washing, the expected source of total phosphorus in deck washdown discharges. However, ambient and domestic service water are also likely sources of phosphorus in a meaningful percentage of instances.

Table 3.3.8. Results of Deck Washdown Water Sample Analyses for Nutrients¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Ammonia As Nitrogen (NH ₃ -N)	mg/L	31	31	100	0.53	0.32	0.058	0.074	0.10	0.81	1.5	1.8	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	32	27	84	1.4	1.5			0.16	1.9	2.7	6.5	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	31	30	97	6.0	3.6		1.4	1.8	6.6	11	40	NA
Total Phosphorus	mg/L	31	31	100	1.7	0.79	0.060	0.15	0.44	1.6	2.9	22	0.10

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

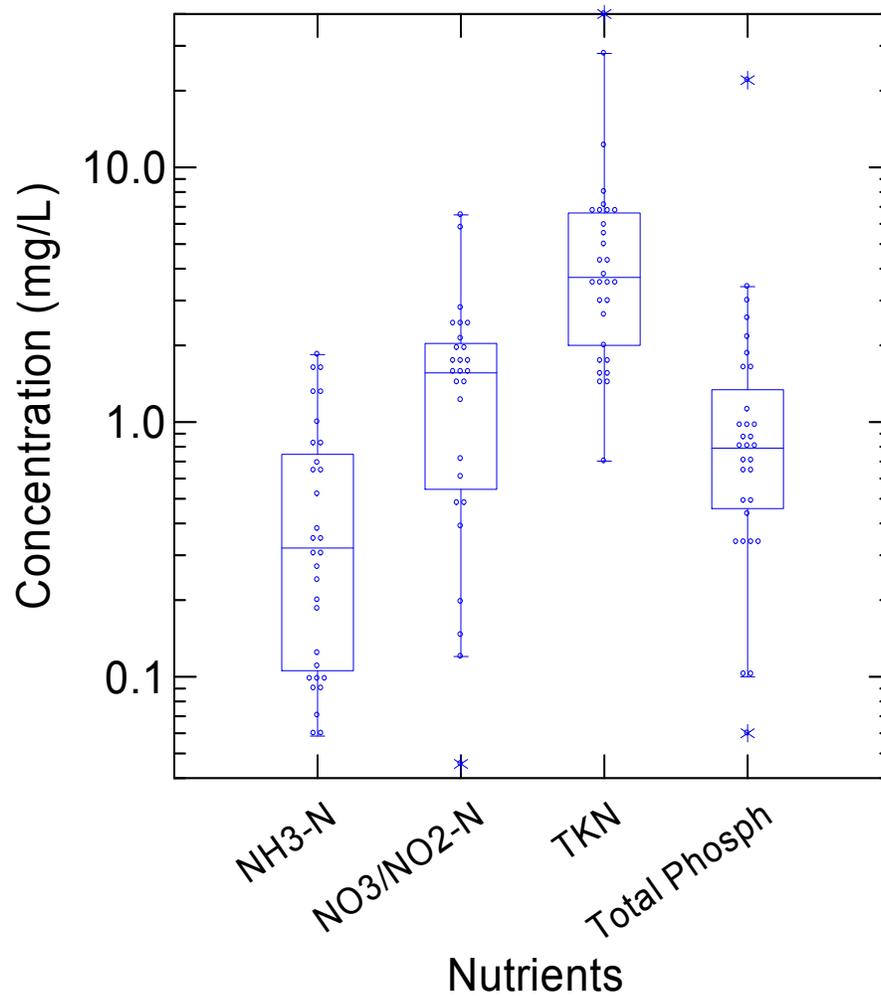


Figure 3.3.9. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Deck Washdown Water Note NH3-N=Ammonia as Nitrogen, NO3/NO2-N= Nitrate/Nitrite Nitrogen, TKN=Total Kjeldahl Nitrogen, and Total Phosph (truncated)=Total Phosphorus

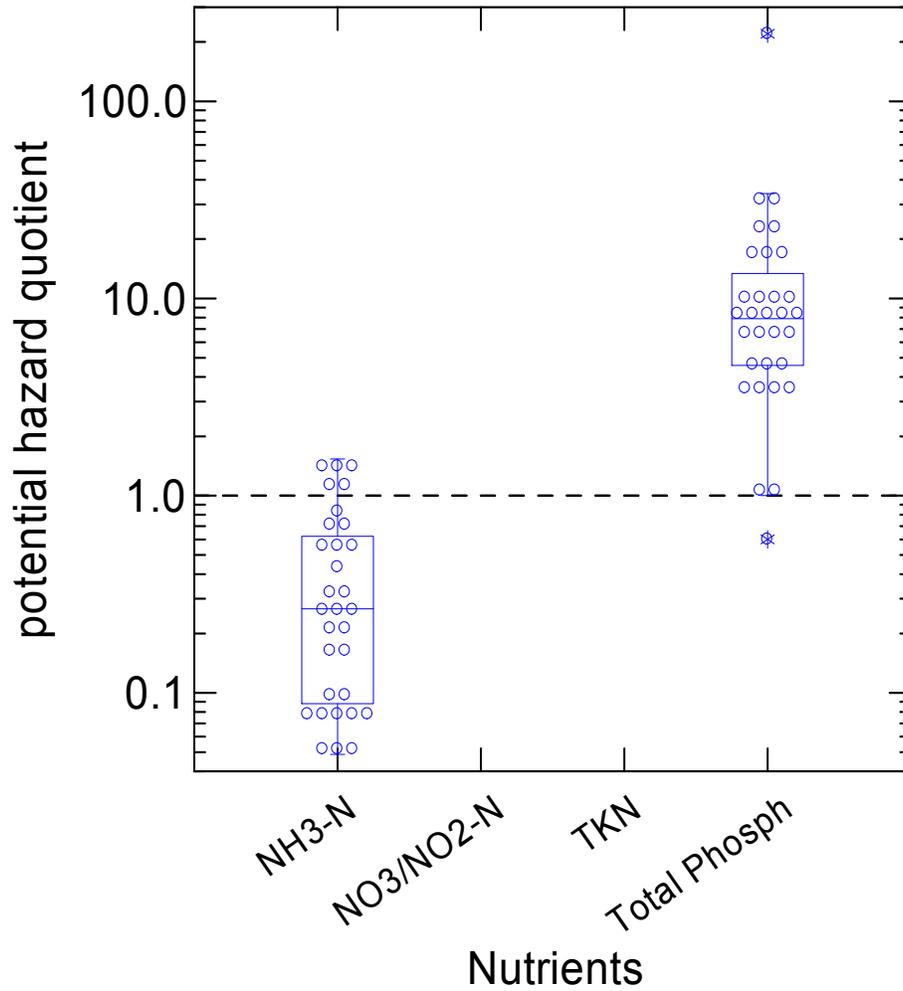


Figure 3.3.10. Box and Dot Density Plot of Potential Hazard Quotients for Nutrients in Samples of Deck Washdown Water See note above

3.2.3.5 Long-Chain Nonylphenols

Deck washdown water samples from 29 vessels were analyzed for 27 long-chain nonylphenols: 16 NPEOs and 5 OPEOs (see Table 3.3.9). The NPEOs with the longest ethoxylate chains (i.e., less degraded products (NP18EO through NP10EO)) were detected in slightly under a third of the vessels (nine of 29), with concentrations increasing as ethoxylate chain is reduced (i.e., concentrations increasing from NP18EO to NP10EO because the longer-chain products found in commercial formulations are quickly degraded). The OPEO with the longest ethoxylate chain (OP12EO) was also detected in about a third of the vessels (see Table 3.3.9). As with NPEOs, the OPEO concentrations generally increase as the ethoxylate chain is reduced, except that no OPEOs with ethoxylate chains smaller than OP7EO were detected (similar to the situation in packing gland effluent; see Section 3.3.2.5).

Of the several vessels where NPEOs were detected in the longer (NP18EO through NP10EO) ethoxylated compounds, only three of those vessels also had detectable concentrations of NPEOs of the shortest chain (NP3EO), albeit at very low concentrations ranging from 0.80 to 29 $\mu\text{g/L}$. These were tow/salvage vessels, one of which confirmed using liquid detergent (Palmolive™) for deck washing (NP3EO concentration of 29 $\mu\text{g/L}$ in deck washdown sample). A tugboat had the only measured concentration of OP8EO in its deck washdown water sample at a concentration of 19 $\mu\text{g/L}$.

Total NPEO concentrations could be calculated from summed concentrations of individual chain lengths for five of the 29 vessels: three tow/salvage vessels and two tour boats (see Figure 3.3.11). The concentrations of total NPEOs ranged from 30 to 8,330 $\mu\text{g/L}$.

As discussed in previous subsections (see Sections 3.2.1.7 (bilgewater) and 3.2.2.5 (packing gland effluents)), while there are no NRWQC for individual ethoxylate chains of NPEOs or OPEOs, these compounds will ultimately degrade to NP in fresh and salt water over time under all conditions. The NRWQC for NP in salt water based on chronic toxicity to aquatic organisms is 1.7 $\mu\text{g/L}$. EPA is uncertain as to exactly how much NP might be generated from the degradation of NPEO and OPEO isomers under a given harbor scenario and water quality condition (see Section 1.6.6 of this report). However, neither total NPEO or OPEO, nor any of the different isomers, were detected in ambient water at the locations where the vessels were sampled. Service water (generally city tapwater pierside) was not analyzed for long- or short-chain nonylphenols.

Table 3.3.9. Results of Deck Washdown Water Sample Analyses for Long-Chain Nonylphenols¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Total Nonylphenol Polyethoxylates	µg/L	29	5	17	540						1400	8300	NA
Nonylphenol octodecaethoxylate (NP18EO)	µg/L	29	12	41	1.5					0.15	5.0	21	NA
Nonylphenol heptadecaethoxylate (NP17EO)	µg/L	29	9	31	3.4					0.21	13	41	NA
Nonylphenol hexadecaethoxylate (NP16EO)	µg/L	29	10	34	7.4					0.89	27	87	NA
Nonylphenol pendeceethoxylate (NP15EO)	µg/L	29	9	31	14					0.91	55	160	NA
Nonylphenol tetradecaethoxylate (NP14EO)	µg/L	29	9	31	25					1.8	75	290	NA
Nonylphenol tridecaethoxylate (NP13EO)	µg/L	29	9	31	44					2.9	180	480	NA
Nonylphenol dodecaethoxylate (NP12EO)	µg/L	29	8	28	64					4.5	260	760	NA
Nonylphenol undecaethoxylate (NP11EO)	µg/L	29	9	31	86					6.1	350	1100	NA
Nonylphenol decaethoxylate (NP10EO)	µg/L	29	9	31	91					6.9	350	1300	NA
Nonylphenol nonaethoxylate (NP9EO)	µg/L	29	8	28	88					3.1	330	1300	NA
Nonylphenol octaethoxylate (NP8EO)	µg/L	29	8	28	75					3.2	280	1100	NA
Nonylphenol heptaethoxylate (NP7EO)	µg/L	29	7	24	61					0.99	220	950	NA
Nonylphenol hexaethoxylate (NP6EO)	µg/L	29	6	21	34						140	440	NA
Nonylphenol pentaethoxylate (NP5EO)	µg/L	29	6	21	19						40	270	NA
Nonylphenol tetraethoxylate (NP4EO)	µg/L	29	4	14	11						2.6	120	NA
Nonylphenol triethoxylate (NP3EO)	µg/L	29	3	10	4.9						0.80	30	NA
Octylphenol dodecaethoxylate (OP12EO)	µg/L	29	8	28	1.4					0.98	2.4	8.8	NA
Octylphenol undecaethoxylate (OP11EO)	µg/L	29	2	6.9	1.8							7.8	NA
Octylphenol decaethoxylate (OP10EO)	µg/L	29	4	14	3.6						1.8	2.1	NA
Octylphenol nonaethoxylate (OP9EO)	µg/L	29	5	17	3.8						1.3	9.6	NA
Octylphenol octaethoxylate (OP8EO)	µg/L	29	1	3.4	10							19	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

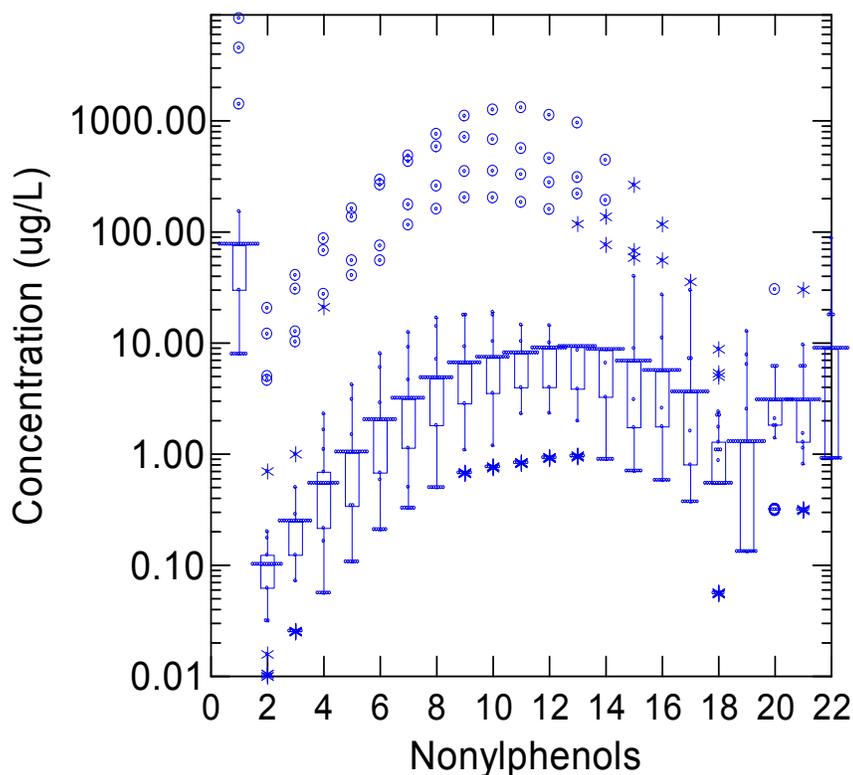


Figure 3.3.11. Box and Dot Density Plot of Nonylphenol Concentrations Measured in Samples of Deck Washdown Water Nonylphenol parameters are identified as follows:

- | | | |
|--|---|--|
| (1) Total Nonylphenol Polyethoxylates | (9) Nonylphenol undecaethoxylate (NP11EO) | (17) Nonylphenol triethoxylate (NP3EO) |
| (2) Nonylphenol octodecaethoxylate (NP18EO) | (10) Nonylphenol decaethoxylate (NP10EO) | (18) Octylphenol dodecaethoxylate (OP12EO) |
| (3) Nonylphenol heptadecaethoxylate (NP17EO) | (11) Nonylphenol nonaethoxylate (NP9EO) | (19) Octylphenol undecaethoxylate (OP11EO) |
| (4) Nonylphenol hexadecaethoxylate (NP16EO) | (12) Nonylphenol octaethoxylate (NP8EO) | (20) Octylphenol decaethoxylate (OP10EO) |
| (5) Nonylphenol pendeaethoxylate (NP15EO) | (13) Nonylphenol heptaethoxylate (NP7EO) | (21) Octylphenol nonaethoxylate (OP9EO) |
| (6) Nonylphenol tetradecaethoxylate (NP14EO) | (14) Nonylphenol hexaethoxylate (NP6EO) | (22) Octylphenol octaethoxylate (OP8EO). |
| (7) Nonylphenol tridecaethoxylate (NP13EO) | (15) Nonylphenol pentaethoxylate (NP5EO) | |
| (8) Nonylphenol dodecaethoxylate (NP12EO) | (16) Nonylphenol tetraethoxylate (NP4EO) | |

3.2.3.6 Volatile and Semivolatile Organic Chemicals

VOCs and SVOCs were not targeted for deck washdown water sample collection in this study because these compounds were not expected to be found in common deck washdown on most vessels²¹. In two cases during scheduled cleanings of the decks of two tow/salvage vessels, however, there was a noticeable oily sheen and where fuel was spilled at the fueling location while samplers were onboard the vessels. Samples of deck washdown water were taken in these instances and analyzed for VOCs and SVOCs (see Table 3.3.10).

Of the 70 VOCs that were analyzed for in the two deck washdown samples, only 12 were detected in one or more of the two samples. Of these 12 VOCs, only acetone, chloroform, and toluene were detected in both samples. In one sample from the vessel with the oily sheen; acetone was detected at 20 µg/L. Figure 3.3.12 contains all the samples that were detected, the other five samples were detected with very low values. Benzene, ethylbenzene, and xylene (compounds associated with fuel oil spills) were detected in one of the two samples at surprisingly low levels. The PHQ of 13 for the benzene sample that was below detection levels was an artifact of the relatively high reporting limit of 25µg/L compared to the screening benchmark of 2.2 µg/L. PHQs for only two VOCs, dibromochloromethane and bromodichloromethane exceeded the benchmark (see Figure 3.3.13), which were artifacts of the reporting limits which were as high as 25µg/L compared to the screening benchmarks of 0.4 µg/L and 0.55 µg/L, respectively. Both these were formerly used as flame retardants and as an intermediate in chemical manufacturing.

Similarly, of the 62 SVOCs that were analyzed for in the two deck washdown samples, only three were detected in one or more of the two samples: bis(2-ethylhexyl) phthalate, caprolactam, and di-n-butyl phthalate (data not shown due to so few analytes detected). Levels detected in the latter two SVOCs are unremarkable. The concentration of bis(2-ethylhexyl) phthalate in the one sample where it was detected (i.e., the tow/salvage vessel with the oily sheen), however, was sufficiently high (6.7 µg/L) such that the associated PHQ, based on the most conservative screening benchmark of 1.2 µg/L (human health criteria), was 5.6 (data not shown). As previously noted, bis(2-ethylhexyl) phthalate is a manufactured chemical that is commonly added to plastics to make them flexible. Phthalates in general are known to interfere with reproductive health and liver and kidney function in both animals and humans (Sekizawa et al., 2003; DiGangi et al., 2002). Bis(2-ethylhexyl) phthalate was not detected in the associated

²¹ It is worth noting that solvents in cleaning agents may be used for certain activities such as above-water-line hull cleaning. Samples associated with above-water-line hull cleaning were not collected during this study because none of the vessels engaged in such an activity while EPA's sampling crew was aboard the vessel. During a survey collected while onboard the vessels, however, 11 of 16 respondents confirmed that they do perform above-water-line hull cleaning occasionally on their vessels.

ambient water sample collected at the site corresponding with the two tow/salvage vessels, but di-n-butyl phthalate was (ambient concentration of 1.1 µg/L).

Di-n-butyl phthalate was the only SVOC detected in ambient water samples collected in association with the deck washdown samples collected in the study. No VOCs were detected in ambient samples.

Table 3.3.10. Results of Deck Washdown Water Sample Analyses for VOCs and SVOCs¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
VOCs													
1,2,4-Trimethylbenzene	µg/L	2	1	50	13	0.30				0.30	0.30	0.30	NA
1,3,5-Trimethylbenzene	µg/L	2	1	50	13	0.090				0.090	0.090	0.090	NA
Acetone	µg/L	2	2	100	13	20	5.5	5.5	5.5	20	20	20	NA
Benzene	µg/L	2	1	50	13	0.3				0.3	0.3	0.3	2.2
Bromodichloromethane	µg/L	2	1	50	13	1.2				1.2	1.2	1.2	0.55
Chloroform	µg/L	2	2	100	1.3	1.5	1.0	1.0	1.0	1.5	1.5	1.5	5.7
Dibromochloromethane	µg/L	2	1	50	13	0.7				0.70	0.70	0.70	0.4
Ethylbenzene	µg/L	2	1	50	13	0.10				0.10	0.10	0.10	530
m-,p-Xylene (sum of isomers)	µg/L	2	1	50	25	0.40				0.40	0.40	0.40	NA
O-Xylene	µg/L	2	1	50	25	0.20				0.20	0.20	0.20	NA
Toluene	µg/L	2	2	100	0.65	0.70	0.60	0.60	0.60	0.70	0.70	0.70	1300
SVOCs													
Bis(2-ethylhexyl) phthalate	µg/L	2	1	50	4.7	6.7				6.7	6.7	6.7	1.2
Caprolactam	µg/L	2	2	100	79	100	56	56	56	100	100	100	NA
Di-n-butyl phthalate	µg/L	2	1	50	2.5	2.4				2.4	2.4	2.4	2000
Naphthalene	µg/L	2	1	50	13	0.40				0.40	0.40	0.40	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

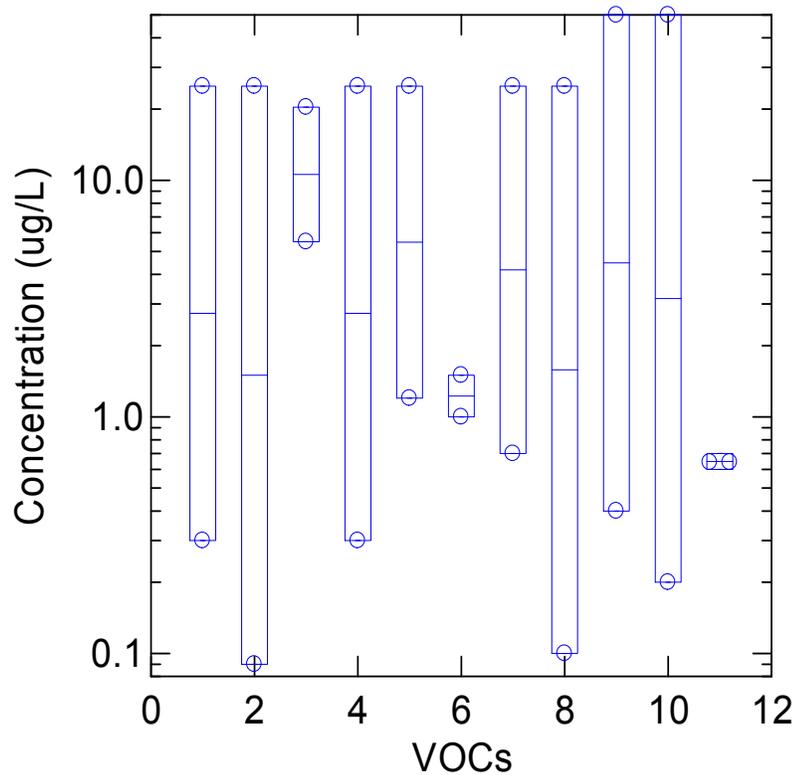


Figure 3.3.12. Box and Dot Density Plot of Volatile Organic Chemical Concentrations Measured in Samples of Deck Washdown Water VOCs are identified as follows:

- | | | |
|----------------------------|--------------------------|----------------------------------|
| (1) 1,2,4-Trimethylbenzene | (5) Bromodichloromethane | (9) m-,p-Xylene (sum of isomers) |
| (2) 1,3,5-Trimethylbenzene | (6) Chloroform | (10) O-Xylene |
| (3) Acetone | (7) Dibromochloromethane | (11) Toluene |
| (4) Benzene | (8) Ethylbenzene | |

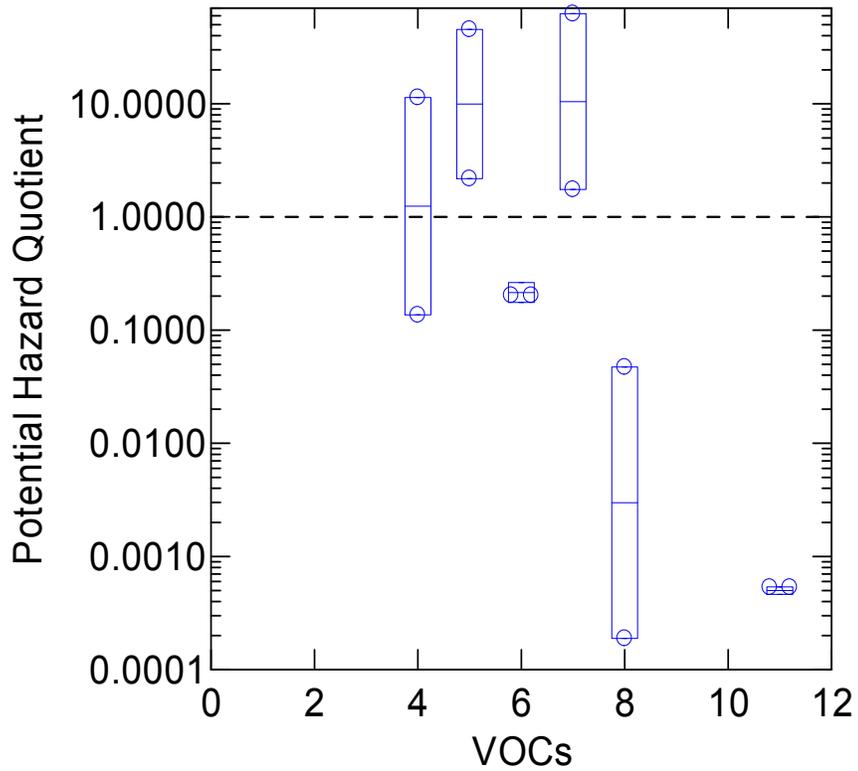


Figure 3.3.13. Box and Dot Density Plot of Potential Hazard Quotients for VOCs in Samples of Deck Washdown Water VOCs are identified as follows:

- | | | |
|----------------------------|--------------------------|----------------------------------|
| (1) 1,2,4-Trimethylbenzene | (5) Bromodichloromethane | (9) m-,p-Xylene (sum of isomers) |
| (2) 1,3,5-Trimethylbenzene | (6) Chloroform | (10) O-Xylene |
| (3) Acetone | (7) Dibromochloromethane | (11) Toluene |
| (4) Benzene | (8) Ethylbenzene | |

3.2.3.7 Summary of the Characterization of Deck Washdown Water

Table 3.3.11 summarizes the specific analytes within deck washdown and runoff water that may have the potential to pose risk to human health or the environment. EPA's interpretation of a realized risk likely posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

Metals were the class of pollutants found most frequently and at concentrations that exceeded national water quality criteria in samples of deck washdown discharge. Several dissolved metals were measured at PHQs > 10, relative to the most stringent benchmarks. Among the dissolved metals, copper was the most prevalent, and was measured at PHQ > 10 in tow/salvage, fire, taxi, tour, and supply vessels. Dissolved cadmium was rarely detected, but had the highest exceedance, in a tow/salvage vessel. Dissolved lead exceeded NRWQC benchmarks in five of six salvage vessels, three of nine tugboats, one of two tour vessels, the one fire vessel, and the one supply vessel. Dissolved zinc exceeded NRWQC benchmarks in five of six tow/salvage vessels, as well as in tug, tour, fire, and supply vessels. Among the total metals, arsenic and aluminum were the most prevalent, particularly in deck washdown discharges of tow/salvage boats (both metals), tugboats (aluminum), and fishing and fire vessels (arsenic). Total iron exceedances were relatively less common, and the highest PHQs for total iron were in tugboats and tow/salvage vessels. Finally, total antimony exceedances were rare, with PHQs in those instances distributed across vessel classes. In general, metal discharges were higher in industrial vessels compared to fishing vessels.

Among the conventional pollutants, TRC was the most prevalent, with regard to high concentrations and frequency of exceedance of the discharge. The highest PQHs for TRC were observed in three of the 11 fishing vessels, the two tour boats, a tow/salvage vessel, and a tugboat. TSS and turbidity were the next most important classical pollutants, with high occurrences distributed across all vessel classes, but particularly tugboats. The highest exceedances of BOD were found in three tugboats, one shrimp vessel, and the supply boat. COD and TOC concentrations were similar to BOD concentrations. Oil and grease and sulfide were high in only a select few samples (in tugboat, tow/salvage boat, and the supply boat).

Samples for pathogens were taken from only fishing vessels, with fecal coliform potentially having the highest concentrations. Levels were high in all vessels except for the gillnetting vessel in Alaska. Differences in pathogen loads could be related to location or method of fishing (gillnetting vs. trawling). Pathogen loads in deck wash declined after washing in all cases.

Total phosphorus was the only nutrient of potential concern, with high levels found in almost all samples, presumably due to the use of detergents in the deck wash practices. Long-chain nonylphenol polyethoxylates of the smallest chain (i.e., NP3EO, most degraded form) were

found in only three of the tow/salvage vessels, and total nonylphenol polyethoxylates were found at high concentrations in two tow vessels. Finally, a moderately high PHQ of 5.6 for bis(2-ethylhexyl) phthalate was found in the discharge of a tow/salvage vessel with a noticeably oily sheen.

Table 3.3.11. Characterization of Deck Washdown and Runoff Water and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential Risk to Pose Risk in Deck Washdown and Runoff Water and Vessel Sources ^{1,2,3,4,5}												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Fishing (11)	Fecal coliform Enterococci <i>E. coli</i>			Cu,Zn	Al,As					TP	BOD, COD	x	TRC
Tugboats (9)				Cu,Zn, Pb	Al, As,Fe	(one vessel PHQ=9)				TP (including one very high PHQ220)	BOD, COD	x	TRC
Tow/Salvage (6)			Bis(2-ethylhexyl) phthalate	Cu, Cd, Zn, Pb	Al, As, Fe		(one vessel PHQ=9)			TP	BOD, COD	x	TRC
Tour (2)				Cu, Zn,	As			x	x	TP	BOD, COD	x	TRC
Water Taxi (1)				Cu	Al, As							x	
Fire (1)				Cu, Pb	As,Al,Fe					TP	BOD, COD	x	
Supply (1)				Cu, Pb,Zn	Al, As, Fe	(PHQ<5)				TP	BOD, COD	x	TRC
Recreational (1)					Al, As					TP	BOD, COD	x	

Notes:

(1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), or, in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

(2) EPA notes that the conclusion of potential risk is drawn from a small sample size, in some cases a single vessel, for certain discharges sampled from some vessel classes. EPA included these results in the tables to provide a concise summary of the data collected in the study, but strongly cautions the reader that these conclusions, where there are only a few samples from a given vessel class, should be considered preliminary and might not necessarily represent pollutant concentrations from these discharges from other vessels in this class.

- (3) All dissolved metals identified as possible risks are potentially influenced by the dissolved metal concentrations measured in source water (generally city tap water; used by all vessel types), particularly dissolved Cu and Zn.
- (4) All total metals identified as possible risks are influenced by total metal concentrations measured in surrounding ambient water (relevant only for vessels where ambient water is used for deck washdown (i.e., many fishing vessels performing deck washdown while offshore, certain tug boats (as indicated in vessel survey)).
- (5) Elevated total phosphorus concentrations in deck washdown samples likely influenced by ambient and source water concentrations.

3.2.4 Fish Hold and Fish Hold Cleaning Effluent (Refrigerated Seawater and Ice Slurry)

Refrigerated seawater and ice/ice slurry are the two commonly used methods for preserving fish in the fish hold of many fishing vessels. EPA noted that some vessels (e.g., large shrimping vessels in the Gulf of Mexico) use dry freezers to preserve their catches; however, these vessels do not produce significant amounts of effluent from the hold that comes into contact with seafood product and that is later discharged. Lobster and crab boats have seawater flow-through tanks used to keep lobsters and crabs alive. Both the freezers and flow-through tanks might contain residual seafood material that sometimes are discharged when the vessels clean their holds.

The analytes and parameters detected in fish hold effluent come from the vessel, ambient water and potable/service water. Additionally, many of the constituents can come from the seafood product itself. If the seafood (e.g., fish, shrimp) are not frozen, but preserved in refrigerated seawater or ice slurry, small quantities of organic material from the fish (e.g., lipids, protein) will be released as the fish degrade, thereby increasing the concentration of those constituents in the discharge. Furthermore, different volumes of blood, mucus, and other matter can drain from the seafood into the hold, depending on how the fish is butchered or cleaned on deck. For example, salmon, when caught via gillnets on gillnetting vessels, are cut at the gills and bled and then placed into the refrigerated sea water tanks/on ice before being cleaned (resulting in their internal organs and some blood leaking into the water). In contrast, salmon caught on trollers are cleaned while the fishing vessel is still at sea and the internal organs are discharged into the surrounding waters. Hence, on the salmon trollers, the organs and most of the residual blood are not in contact with refrigerated water/ice, and consequently, lower quantities of these materials are discharged when the vessel empties its hold at the dock.

The volume of fish hold water generated by a fishing vessel depends on the size of the vessel and the method used for keeping the product fresh. Vessels such as small salmon trollers or long-liners that frequent Alaska waters have around 1,500 gallons of fish hold storage. EPA estimated this volume is occupied by approximately 50 percent fish and 35 to 40 percent ice when the vessel off-loads at the seafood processing facility. The ice, which is thrown overboard daily after the fish are unloaded, would result in a fish hold discharge of between 500 and 600 gpd for these types of fishing vessels.



Collecting Fish Hold Ice from a Long Liner



Fish Hold Ice from a Trawler

EPA estimated that mid-size fishing vessels, such as gill netters, and purse seiners found in Alaska, and shrimp boats in the Gulf of Mexico, have fish hold volumes of

between 3,000 and 5,000 gallons. Assuming these vessels have between 35 and 40 percent of ice/water slurry in the fish hold tanks, they likely discharge between 1,000 and 2,000 gallons of fish hold water every two to three days (333 to 1,000 gpd).

Larger fishing vessels such as off-shore trawlers found off the coast of New England and tenders found in Alaska can have refrigerated seawater holding tanks or ice hold tanks with capacities as large as 15,000 gallons. These tanks, which contain 30 to 40 percent refrigerated seawater or ice after the seafood is unloaded, result in a fish hold discharge of between 4,500 and 6,000 gallons. These vessels are expected to unload seafood and discharge the fish hold water every three to five days (900 to 2,000 gpd).



Two Examples of Full Fish Hold Tanks on a Tender Vessel

EPA collected effluent samples from 31 commercial fishing vessels for this study. Samples were collected from the fish holds that were in use on 26 of these vessels. EPA generally collected single grab samples from these vessels while the vessels were dockside. These samples were usually collected while the effluent was being discharged, but they were occasionally collected directly from the fish hold. EPA analyzed samples for both total and dissolved metals, classical pollutants, pathogens, and nutrients. EPA also analyzed three samples from fish holds for nonylphenols.

The fish hold tank is cleaned after the catch has been off-loaded at the seafood processing facility, so the frequency of fish hold cleaning depends on the type and amount of fish being caught. For example, off-shore trawlers in New England might only clean the fish hold tank every three to five days when they return to the fish processing facility. Small fishing vessels such as salmon trollers and long-liners in Alaska off-load the catch daily and therefore clean the fish hold tanks daily. Fish tenders and purse seiners with refrigerated seawater tanks might clean the tanks every couple of days when they return to the fish processing facility.

On small fishing boats such as trollers and long-liners, and mid-size fishing boats such as gill netters, fish holds are typically cleaned using a garden hose at a flow rate of between 10 and 12 gpm. Fish hold cleaning is completed in 15 minutes or less, resulting in a discharge of between 150 and 200 gallons per day. Larger vessels such as off-shore trawlers found in New England and large tenders in Alaska also use a garden hose to wash down the fish hold tanks; however, cleaning these tanks requires approximately 30 minutes. EPA estimated the volume of fish hold cleaning water discharge for these vessels ranges between 300 and 400 gallons per cleaning (60 to 200 gpd depending on frequency).

EPA was able to collect samples of the fish hold cleaning water discharge from nine vessels. These samples were analyzed for the same constituents as fish hold effluent plus nonylphenols. Nonylphenols are suspected pollutants associated with cleaning products.

3.2.4.1 Metals

Fish Hold Effluent

Samples of refrigerated cooling water and ice slurry from 26 fish holds were analyzed for dissolved and total concentrations of 22 metals. The analytical results are summarized in Table 3.4.1 (total metals data) and Table 3.4.2 (dissolved metals data) for the 19 metals that were detected in one or more fish hold effluent samples. Figures 3.4.1

and 3.4.2 present these same results for total and dissolved metals, respectively, normalized by the lowest NRWQC where applicable. The following metals were detected in all fish hold water samples:

- Total aluminum
- Dissolved and total barium
- Dissolved and total calcium
- Dissolved and total cobalt
- Dissolved and total iron
- Dissolved and total potassium
- Dissolved and total sodium
- Dissolved and total vanadium
- Dissolved and total zinc

Concentrations of a number of other metals were measured for 50 percent or more of the samples analyzed:

- Dissolved aluminum
- Total arsenic
- Dissolved and total copper
- Dissolved and total magnesium
- Dissolved and total manganese
- Dissolved and total potassium
- Total silver.

Several metals for which EPA tested had concentrations that were notable. These metals include dissolved and total arsenic, and dissolved copper, selenium, and zinc (see Figures 3.4.1 and 3.4.2). A small percentage of the samples contained all the metals which EPA regularly analyzes; however, metals such as lead, nickel, and selenium were, with a few notable exceptions, in concentrations below PHQs at the point of discharge (see Figures 3.4.3 and 3.4.4). EPA analyzed for and detected dissolved and total barium, cobalt, iron, potassium, silver, sodium, and vanadium in only two samples. All of the detected concentrations in the two samples were low, except for iron. EPA also analyzed for antimony, beryllium, and thallium in these two samples and did not detect any of these metals.

The concentrations of many of the metals that were detected in fish hold discharges are not unexpected as fish holds generally have numerous exposed metal surfaces. In addition, the pumps used to add water to the hold might also add low concentrations of metals. Finally, metallic fishing equipment, deck surfaces, and other materials sometimes come in contact with the fish or water that runs into the hold.

Some metal concentrations, particularly mineral salts, appear to be primarily a result of background concentrations in the ambient water. For example, aluminum, barium, calcium, iron, magnesium, sodium, and potassium appear to be primarily influenced by background concentrations. Other metals that had measurable concentrations (e.g., arsenic, copper, manganese, and zinc) appear to result largely from mechanically refrigerated water used to cool the sea water to preserve seafood catch, adding ice to do the same, or possibly, from the seafood catch itself, or from any combination of the three.

Several metals were detected in at least one sample of fish hold effluent with PHQ values of greater than 1 (see Figures 3.4.3 and 3.4.4). For total metals, this included aluminum, arsenic, copper, iron, and manganese. However, as discussed above, aluminum concentrations appear to be primarily influenced by ambient water background concentrations. Total copper concentrations exceeded the total copper benchmark based on human health (for consumption of water and aquatic organisms) of 1,300 µg/L by a small fraction in two samples (Table 3.4.1). These total concentrations, however, could pose potential risk to the aquatic environment because the human health criteria of 1,300 µg/L is significantly higher than the 3.1 µg/L benchmark used for dissolved copper based on the saltwater chronic ambient water quality criterion for the protection of aquatic life. When high levels of particulate copper are discharged, some of the particulate copper will likely convert to dissolved copper and be made bioavailable to aquatic life. EPA collected only two samples for analysis of total iron, one of which had a PHQ value of five and the other eight.

Another metal with high PHQ values is total arsenic. The PHQ values for total arsenic ranged from between more than 100 to more than 20,000 (Figure 3.4.3). One reason for these extreme PHQ values is the exceptionally low screening benchmark of 0.018 µg/L for total arsenic. Nonetheless, concentrations of total arsenic in the upper end ranges of these measurements are a possible environmental concern. These discharges may have the potential to cause or contribute to exceedances of water quality standards, particularly in areas where multiple fishing vessels discharge their holds into the same waters within the same time period.

Several dissolved metals, including arsenic, cadmium, copper, iron, nickel, and selenium, also had PHQs above 1 (see Figure 3.4.4). Dissolved arsenic samples resulted in PHQs of approximately 9-10 for two discharges; one was from a shrimping vessel from the Gulf Coast and the other from a ground fishery vessel in New England, while a third boat ground fishery vessel in New England had a PHQ value of just over 2. There was also only one sample which had a PHQ value for cadmium of approximately 5. Only four of the 26 values exceeded a PHQ value of 1 for dissolved nickel, and none exceeded a value of 2. Dissolved selenium had 6 samples exceed a PHQ value of 1 (the highest

value of which was approximately 12). Dissolved zinc had numerous PHQ values of greater than 1, but none greater than 10. Dissolved copper had numerous samples that exceeded the PHQ value of 1, with more than 25 percent of these samples having a PHQ value of greater than 10.

The high dissolved arsenic concentrations were observed exclusively from three vessels; a shrimping boat (345 µg/L) and two ground fishery trawlers (74 and 310 µg/L). Ambient water concentrations indicate that the arsenic likely did not come from the surrounding water, although dissolved arsenic was measured at a substantial level of 26 µg/L in the ambient water where the shrimping vessel was sampled. Another possible explanation is entrainment of arsenic contaminated sediments on nets. Each of the vessels with high arsenic values (trawlers and shrimp boats) use nets that drag the ocean floor. When nets are retrieved and emptied on the deck of the vessel, entrained sediments from the ocean floor could migrate into the fish holds along with the fish and shrimp. One other possible source includes organic arsenic compounds that are primarily found in organisms living in the sea. Based on the limited data collected, EPA cannot identify the specific source(s) of the high dissolved arsenic values at this time.

In summary, some samples of dissolved copper in fish hold effluent discharges were well above the PHQ screening benchmark of 3.1 µg/L based on the 2006 NRWQC saltwater chronic aquatic life criterion. Many of these concentrations resulted in PHQs of greater than 10, with some upwards of 200. The three elevated concentrations of dissolved arsenic could potentially pose an environmental concern, particularly if these arsenic concentrations are common in these vessel discharges. Finally, concentrations of total arsenic are also high relative to the benchmark, resulting in high PHQ values and may have the potential to pose risks to human health if discharged into drinking water sources, though almost all fishing vessels operate in marine or estuarine environments that are not used for drinking water.

Table 3.4.1. Results of Fish Hold Effluent Sample Analyses for Total Metals¹

Total Metal	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	26	26	100	827	840	89	180	420	900	1800	2400	87
Arsenic	µg/L	26	16	62	40	4.8				13	210	380	0.018
Barium	µg/L	2	2	100	98	110	83	83	83	110	110	110	1000
Cadmium	µg/L	26	3	12	0.99							3.3	NA
Chromium	µg/L	26	7	27	4.3					2.6	19	35	NA
Cobalt	µg/L	2	2	100	3.7	4.4	2.9	2.9	2.9	4.4	4.4	4.4	NA
Copper	µg/L	26	24	92	190	40		5.8	12	140g	710	1700	1300
Iron	µg/L	2	2	100	2000	2500	1600	1600	1600	2500	2500	2500	300
Lead	µg/L	26	9	35	7.1					5.6	31	42	NA
Manganese	µg/L	26	15	58	24	6.6				17	130	140	100
Nickel	µg/L	26	5	19	7.7							30	610
Selenium	µg/L	26	7	27	12					13	29	90	170
Silver	µg/L	2	1	50	2.4	2.7				2.7	2.7	2.7	NA
Vanadium	µg/L	2	2	100	9.2	10	8.1	8.1	8.1	10	10	10	NA
Zinc	µg/L	26	26	100	340	230	27	46	100	450	940	1700	7400
Cationic Metals													
Calcium	µg/L	26	26	100	150000	190000	1900	3000	15000	270000	300000	310000	NA
Magnesium	µg/L	26	25	96	450000	580000		1800	14000	840000	980000	1100000	NA
Potassium	µg/L	2	2	100	330000	480000	190000	190000	190000	480000	480000	480000	NA
Sodium	µg/L	2	2	100	1200000	1900000	370000	370000	370000	1900000	1900000	1900000	NA

Notes:

- (1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.
- (2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.4.2. Results of Fish Hold Effluent Sample Analyses for Dissolved Metals¹

Dissolved Metal	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	26	24	92	490	670		20	60	850	970	1000	NA
Arsenic	µg/L	26	10	38	31					5.7	150	350	36
Barium	µg/L	2	2	100	64	84	44	44	44	84	84	84	NA
Cadmium	µg/L	26	1	4	0.77								0.25
Chromium	µg/L	26	3	12	1.9						5.8	7.9	11
Cobalt	µg/L	2	2	100	1.8	2.0	1.6	1.6	1.6	2.0	2.0	2.0	NA
Copper	µg/L	26	23	88	96	15			6.0	38	390	920	3.1
Iron	µg/L	2	2	100	350	360	340	340	340	360	360	360	NA
Lead	µg/L	26	3	12	2.3						4.4	8.0	2.5
Manganese	µg/L	26	19	73	22	11				28	80	110	NA
Nickel	µg/L	26	4	15	6.1						13	17	8.2
Selenium	µg/L	26	6	23	9.2					2.5	20	61	5.0
Silver	µg/L	2	2	100	1.3	1.5	1.0	1.0	1.0	1.5	1.5	1.5	1.9
Vanadium	µg/L	2	2	100	3.4	3.5	3.2	3.2	3.2	3.5	3.5	3.5	NA
Zinc	µg/L	26	26	100	180	120	24	31	55	240	450	790	81
Cationic Metals													
Calcium	µg/L	26	26	100	160000	180000	1200	1900	9000	290000	300000	310000	NA
Magnesium	µg/L	26	25	96	480000	560000		770	11000	920000	990000	1100000	NA
Potassium	µg/L	2	2	100	330000	470000	180000	180000	180000	470000	470000	470000	NA
Sodium	µg/L	2	2	100	1200000	2000000	360000	360000	360000	2000000	2000000	2000000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

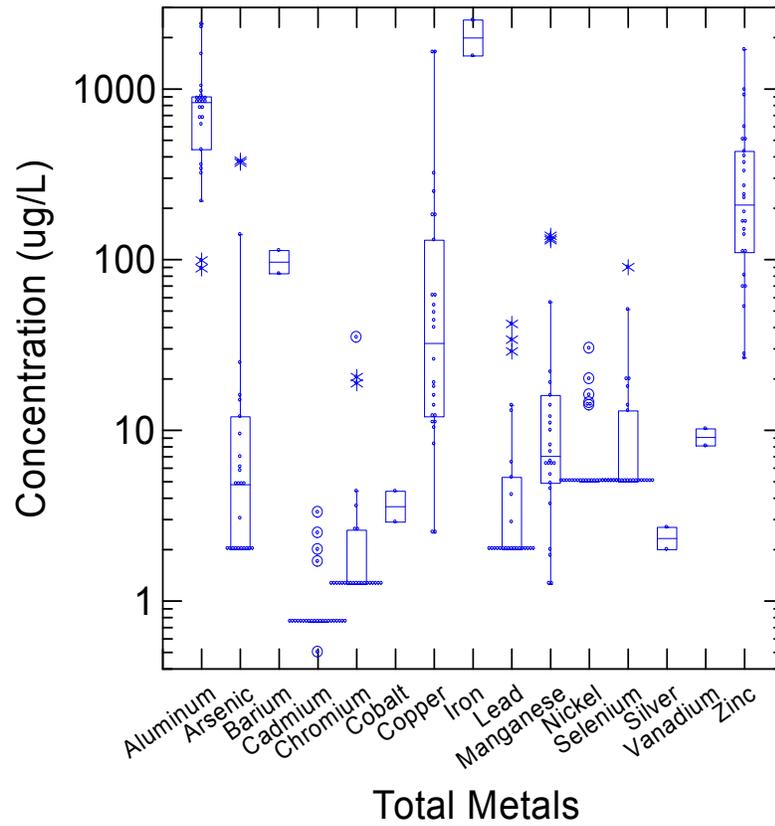


Figure 3.4.1. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Fish Hold Effluent

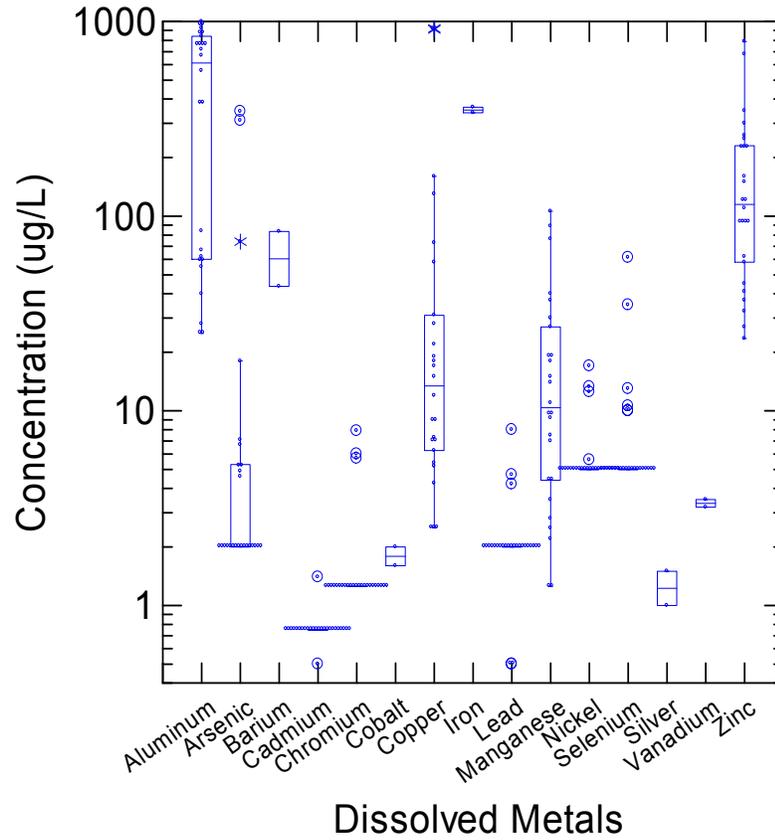


Figure 3.4.2. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Fish Hold Effluent

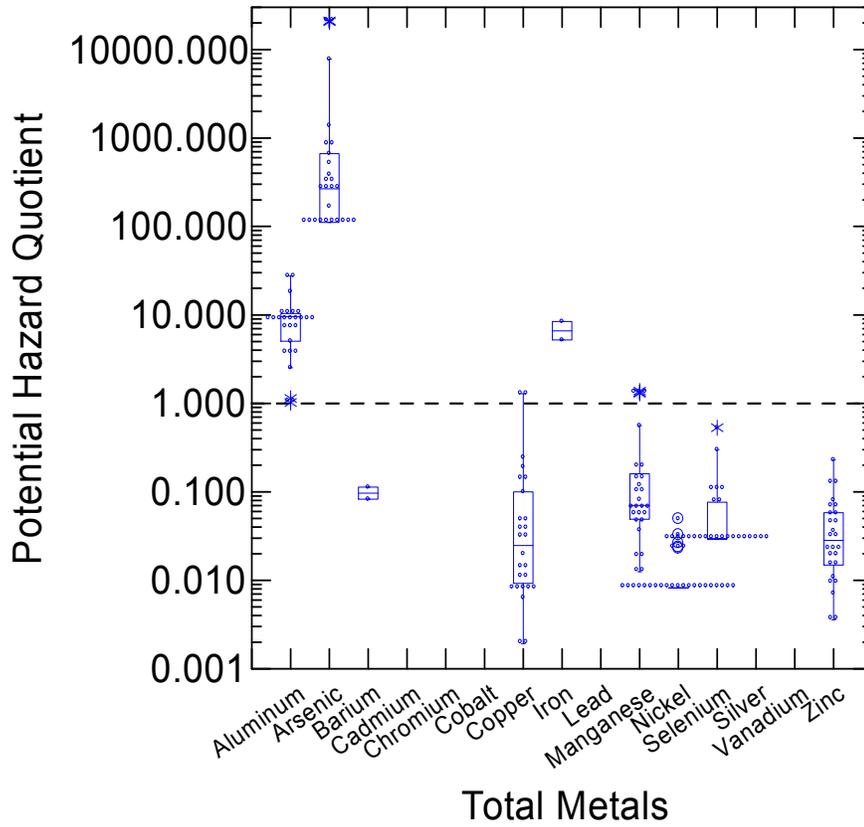


Figure 3.4.3. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Fish Hold Effluent Note: as discussed in the text above, total arsenic is a potential concern; however, the exceptionally high PHQ values are due in part to the low human health value for total arsenic used as a benchmark.

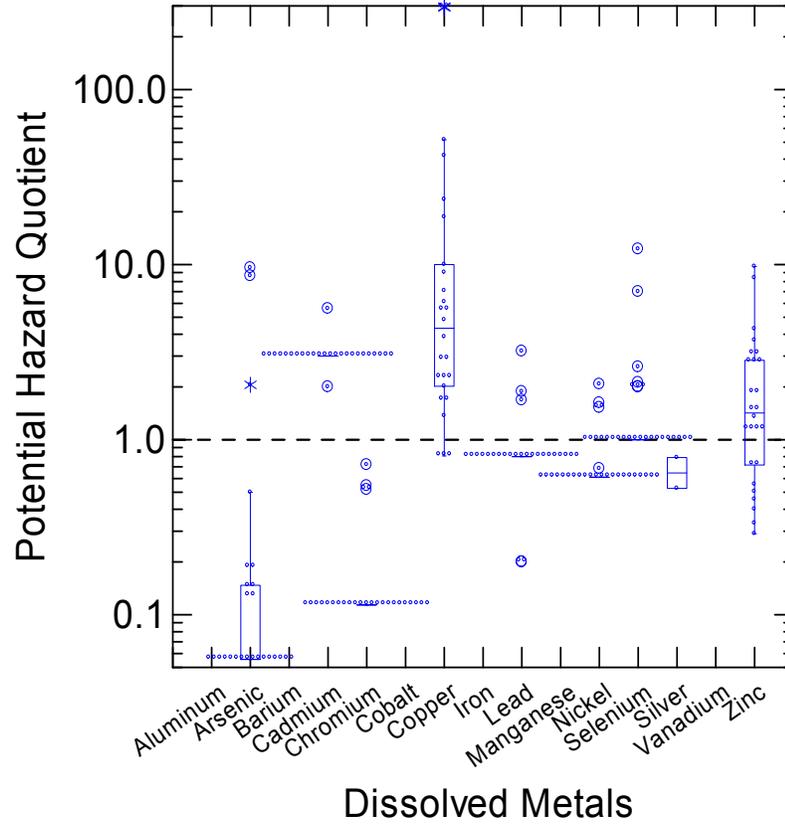


Figure 3.4.4. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Fish Hold Effluent

Fish Hold Cleaning Effluent

EPA expected effluent from the cleaning of fish holds to be fundamentally similar to fish hold effluent with two exceptions: 1) many vessels used a soap or disinfectant, which would not be expected to be present in the hold, and 2) cleaning fish holds brings in either potable water from the local municipality via a pierside hose (service water) or ambient water pumped from the surrounding waters. Table 3.4.3 presents summary statistics for fish hold cleaning effluent. Figures 3.4.6 and 3.4.7 show the detected results for total and dissolved metal concentrations, respectively, and Figures 3.4.8 and 3.4.9 shows the PHQ values for total and dissolved concentrations, respectively, where applicable.

Generally, average and maximum total and dissolved metals concentrations for fish hold cleaning were slightly lower than for fish hold effluent. These lower values could be due to any number of reasons: less contact time with the vessel for fish hold cleaning effluent, differences in source water (mechanically refrigerated and ice versus city tap water), less contact time (or none at all) with the seafood product or its residuals, etc.

The lower concentrations of metals for fish hold cleaning effluent resulted in lower overall PHQ values for both total and dissolved forms, as well as a lower percentage of samples that exceed a PHQ of 1. Not surprisingly, the metals (dissolved copper, dissolved and total arsenic) identified as having high PHQs for fish hold effluent also exhibited higher PHQ values in fish hold cleaning effluent. Likewise, dissolved copper occurs in fish hold cleaning effluent at concentrations mostly above a PHQ value of one, and dissolved arsenic was found in two samples with PHQ values above one. Dissolved zinc was also found in several samples with PHQ values above one, the maximum being a PHQ value just below 10 (Figure 3.4.8).

Table 3.4.3. Results of Fish Hold Cleaning Effluent Sample Analyses for Metals¹

Metal	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum, Dissolved	µg/L	9	9	100	780	880	74	74	760	950	1000	1000	NA
Aluminum, Total	µg/L	9	9	100	1100	930	850	850	860	1500	1700	1700	87
Arsenic, Dissolved	µg/L	9	5	56	22	5.3				38	97	97	36
Arsenic, Total	µg/L	9	5	56	35	8.7				64	150	150	0.018
Cadmium, Total	µg/L	9	1	11	1.0						3.0	3.0	NA
Chromium, Dissolved	µg/L	9	1	11	1.5						3.4	3.4	11
Chromium, Total	µg/L	9	3	33	4.6					5.4	23	23	NA
Copper, Dissolved	µg/L	9	8	89	34	12			8.6	32	180	180	3.1
Copper, Total	µg/L	9	9	100	57	25	6.4	6.4	11	61	290	290	1300
Lead, Dissolved	µg/L	9	1	11	2.7						8.7	8.7	2.5
Lead, Total	µg/L	9	4	44	19					37	79	79	NA
Manganese, Dissolved	µg/L	9	4	44	21					39	64	64	NA
Manganese, Total	µg/L	9	5	56	33	4.8				61	110	110	100
Selenium, Dissolved	µg/L	9	1	11	6.0						14	14	5.0
Selenium, Total	µg/L	9	2	22	7.4					7.0	18	18	170
Zinc, Dissolved	µg/L	9	8	89	190	53				420	640	640	81
Zinc, Total	µg/L	9	8	89	470	140			17	890	1800	1800	7400
Cationic Metals													
Calcium, Dissolved	µg/L	9	9	100	250000	270000	11000	11000	240000	300000	320000	320000	NA
Calcium, Total	µg/L	9	9	100	260000	280000	13000	13000	260000	310000	320000	320000	NA
Magnesium, Dissolved	µg/L	9	9	100	790000	860000	12000	12000	750000	990000	1000000	1000000	NA
Magnesium, Total	µg/L	9	9	100	780000	880000	13000	13000	710000	1000000	1000000	1000000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

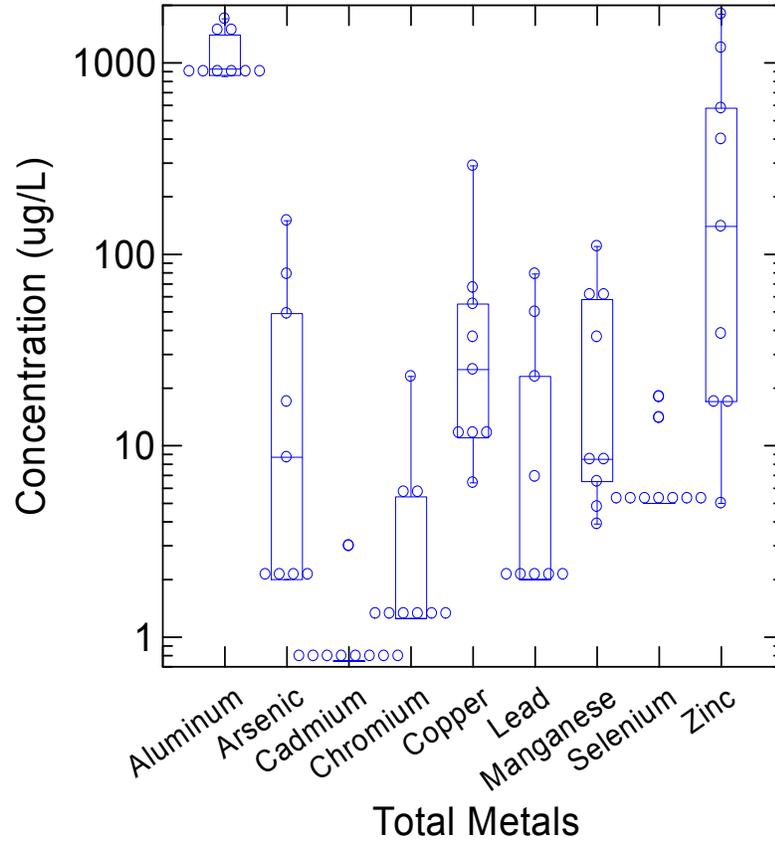


Figure 3.4.5. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Fish Hold Cleaning Effluent

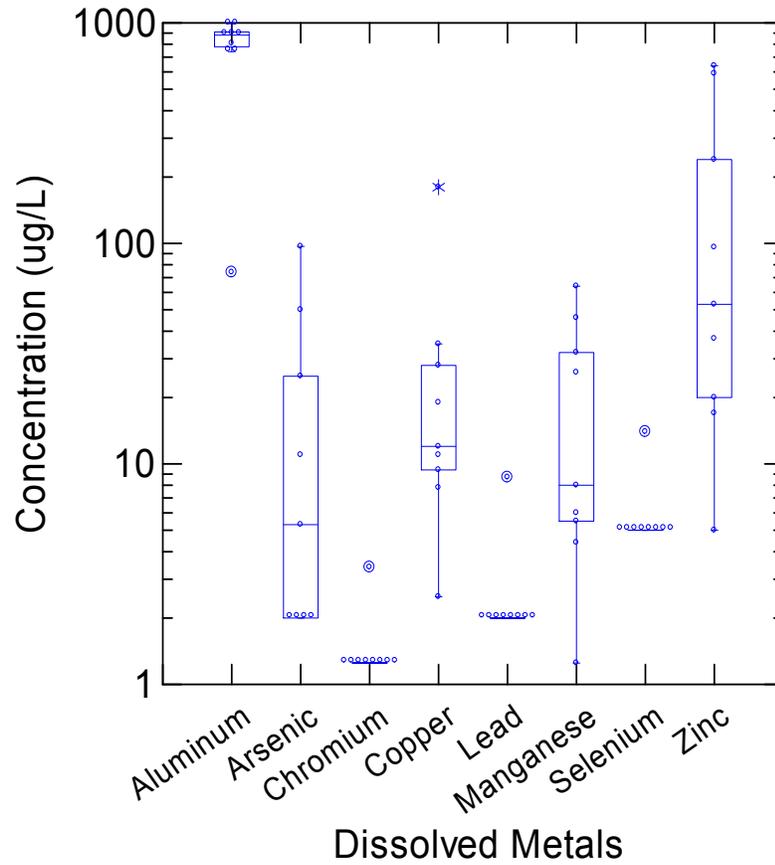


Figure 3.4.6. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Fish Hold Cleaning Effluent

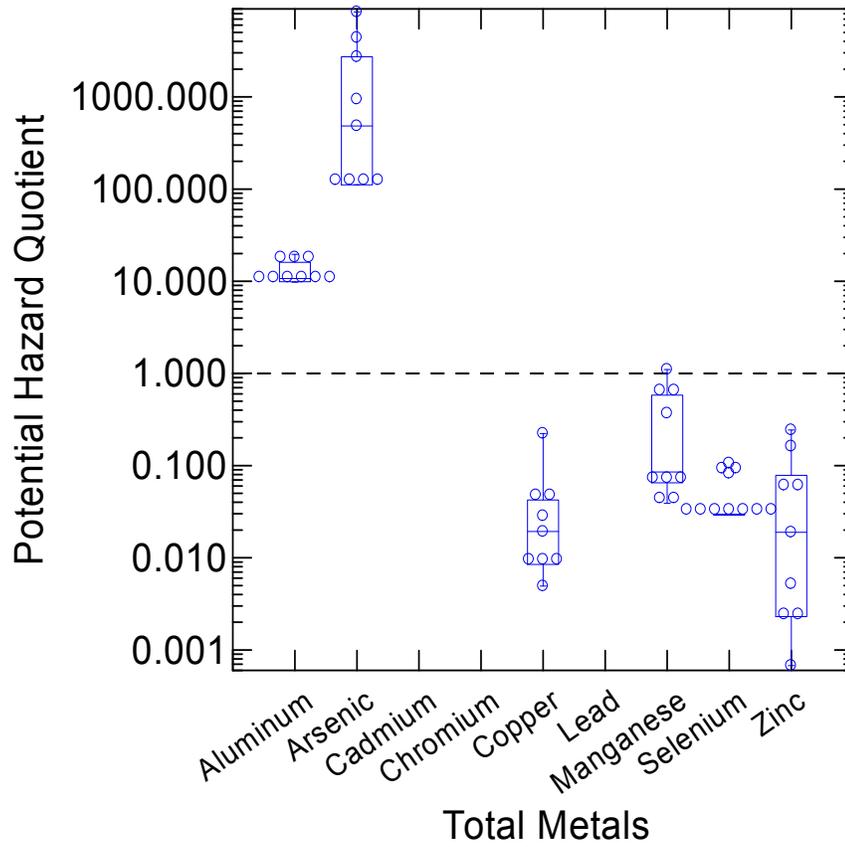


Figure 3.4.7. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Fish Hold Cleaning Effluent

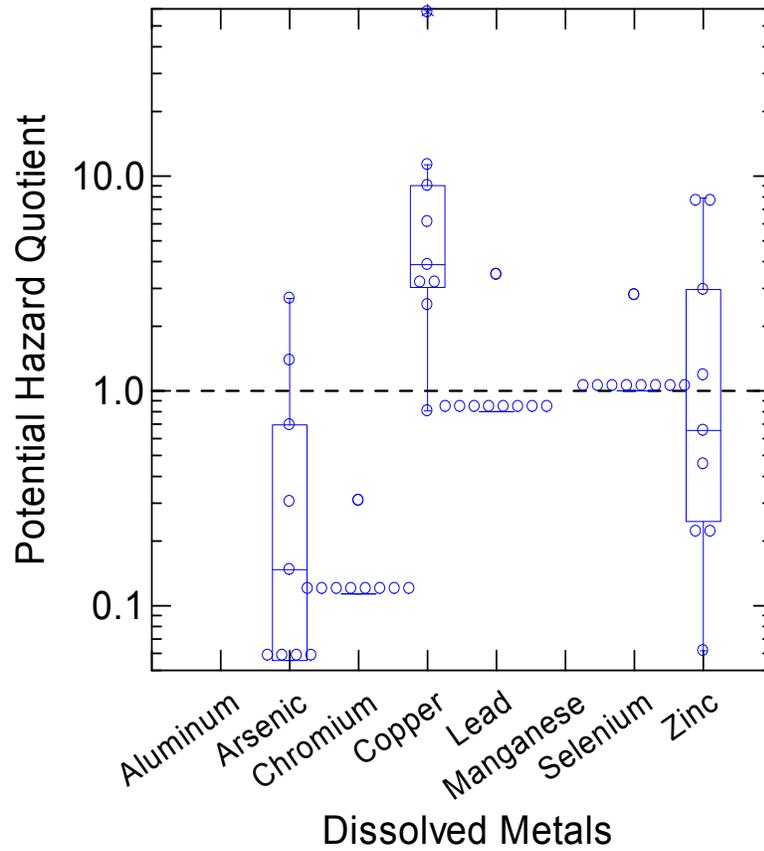


Figure 3.4.8. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Fish Hold Cleaning Effluent

3.2.4.2 Classical Pollutants

Table 3.4.4 presents analytical results for 14 classical pollutants detected in samples from fish hold effluent (all classical pollutants analyzed for in the study were detected). These detected results are also shown in Figure 3.4.9.

Except for dissolved oxygen, other physical parameters measured (conductivity, pH, salinity, and temperature) did not have results that were likely to result in any impact on receiving water quality. Dissolved oxygen concentrations were low in several samples of fish hold effluent: hypoxic (< 2 mg/L) in three cases and marginal (<5 mg/L) in 19 additional cases. These low oxygen conditions may be driven by the high BOD concentrations found in many of the fish holds. Effluent with low dissolved oxygen concentrations were also noted in the fish hold cleaning effluent, with six of nine samples (67 percent) having concentrations of less than 5 mg/L (see Table 3.4.5 and Figure 3.4.10).

EPA found BOD and COD to be highly elevated in fish hold effluent (Table 3.4.4). BOD was measured in several samples in concentrations in the thousands of mg/L. High levels of BOD are almost certainly caused by the decay of the organic material associated with the seafood product. As shown in Figure 3.4.9, the majority of these concentrations are generally higher than those of raw sewage (which can range up to a few hundred mg/L), and almost all are higher than a wastewater treatment plant's secondary treatment limit of 30 mg/L for BOD. The median value for BOD discharge was approximately 471 mg/L, indicating that BOD discharge from fish holds are abnormally elevated (see Figure 3.4.11). The highest BOD value of 5,130 mg/L approximates the concentrations found in sewage sludge (Metcalf and Eddy, 1979).

These high levels of BOD in discharges could potentially pose environmental problems in certain circumstances. For example, high BOD concentrations in fish hold effluents are potentially ubiquitous, and discharges could result in impacts to receiving waters where there are numerous fishing vessels, poor flushing, or high levels of existing hypoxic (low oxygen) stress in the water body. In stratified waters with hypoxic or anoxic (no oxygen) conditions, the risk associated with elevated BOD is most likely to occur in deeper waters under a thermocline or pycnocline. When using refrigerated seawater systems, fish hold effluent may be as saline (or more saline) than the surrounding water. Where it is also cooler than the surrounding water, the fish hold effluent would be more likely to sink to the bottom of the stratified water under the warmer water. This may deliver the BOD load to the deeper layers of the water body where oxygen levels are likely to be lower in eutrophic waters. In contrast, where ice is used to cool fish in the fish hold, the BOD load may be more likely to stay in the surface layers since fresh water is less dense than salt water. Thus, a low salinity fish hold

effluent discharge may prevent the BOD loading from having as significant an impact to aquatic organisms in the receiving waters.

The considerable variability in BOD concentrations from the 26 fish hold effluent samples may be due to how fish are kept. The average concentration of BOD is lowest for the lobster tank compared with the other fish hold types, which is logical since lobster tanks have continuously circulating ambient water with live seafood inside. Hence, the water is constantly being refreshed, while the seafood product generally has not begun the process of degrading or bleeding into the tank. There could be other differences in BOD concentrations based upon whether fish are kept on top of ice, in ice water slurry, or in refrigerated seawater. New England trawlers and Gulf Coast shrimp boats had several vessels with exceptionally high BOD concentrations.

Whereas BOD measures oxygen demand from biodegradable material, COD measures oxygen demand for both biodegradable material and nonbiodegradable oxidizable material. Like BOD, COD discharge is elevated in fish hold effluent and fish hold cleaning effluent (Tables 3.4.4 and 3.4.5). Occasionally, these values are exceptionally high, which could potentially cause stress on a water body where there are many discharges from fish holds and where there may be low circulation or flushing or existing hypoxic or anoxic stress in the water body.

Oil and grease as measured by HEM and SGT-HEM are generally discharged in low concentrations from fish hold effluent, with the vast majority of samples from both fish hold effluent and fish hold cleaning effluent having HEM and SGT-HEM being discharged in quantities below 5 mg/L. However, there are a few discharges where the concentrations exceed 15 mg/L. The highest of these values for either fish hold or fish hold cleaning effluent (the HEM concentration was approximately 28 mg/L - slightly less than twice the regulatory limit of 15 mg/L) are from the samples taken during a fish hold cleaning event while onboard a New England ground fishing vessel. These values demonstrate that while oil and grease discharges from fish holds sometimes occasionally occur at elevated concentrations, they were generally not observed at concentrations that are of particular concern.

The concentrations of the classical pollutants EPA measured that are associated with sediment or cloudiness (i.e., TSS and turbidity) were roughly equivalent to concentrations observed in raw sewage effluent, but considerably lower than stormwater runoff from construction sites or highly urbanized streams. TSS was elevated in both fish hold effluent and fish hold cleaning effluent; however, concentrations were generally not sufficiently elevated to alone exceed water quality standards. Just under 90 percent of samples exceed the secondary treatment concentration of 30 mg/L for TSS (the value used to establish the PHQ benchmark), with a maximum concentration of 1,100 mg/L in

a fish hold effluent sample. As with BOD, TSS appears to be more diluted in fish hold cleaning effluent than in fish hold effluent. While it did not test for volatile suspended solids (VSS) in this sampling program, EPA assumed that a significant percentage of the TSS concentration is directly caused by organic material related to the seafood product. Similar to TSS, turbidity concentrations were elevated in both fish hold effluent and fish hold cleaning effluent, and slightly more concentrated in fish hold effluent than in fish hold cleaning effluent.

The concentrations of sulfide in fish hold and fish hold cleaning effluent were low in most samples, with most values falling below a reporting limit value of 0.01 mg/L. Sulfide was detected in only seven of 25 samples where the parameter was tested, and in only four of seven fish hold cleaning samples. However, a few samples had significantly elevated sulfide concentrations, including a maximum fish hold concentration of 0.16 mg/L (PHQ value of 80) from fish hold discharges, and a maximum fish hold cleaning value of 0.48 mg/L (PHQ value of 240). These high sulfide values cannot be attributed to high background concentrations. A relatively higher percentage of detectable sulfide concentrations were noted in New England ground fishery trawlers compared with other areas (seven out of the 11 detections). EPA is unable to determine why the New England fishery vessels have higher concentrations of sulfide compared with vessels using other fishing platforms or from other areas; however, one possible explanation is that the New England fishery vessels are at sea for seven to 10 days, whereas Alaskan fishing vessels are off loaded once every one to two days.

TOC was detected in all of the 25 of the fish hold effluent samples for which it was tested and all nine fish hold cleaning samples. Concentrations ranged from a low of 1.8 mg/L to an extreme high of 2,200 mg/L (see Table 3.4.4). Background concentrations of TOC (i.e., from mechanically refrigerated water or ice) are much lower (in the range of 2 to 19 mg/L) and do not appear to be a significant cause of the high TOC loads in the effluent. TOC levels are likely elevated by decay and residuals from the seafood product.

Table 3.4.4. Results of Fish Hold Effluent Sample Analyses for Classical Pollutants¹

Parameter	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Biochemical Oxygen Demand (BOD)	mg/L	26	24	92	840	440		25	140	830	3100	5100	30
Chemical Oxygen Demand (COD)	mg/L	26	26	100	1500	940	52	340	660	1900	2600	8700	NA
Conductivity	mS/cm	26	26	100	25	30	0.20	0.35	3.3	43	46	61	NA
Dissolved Oxygen	mg/L	26	26	100	4.3	3.9	1.7	2.0	2.8	5.7	8.2	9.2	NA
Hexane Extractable Material (HEM)	mg/L	26	18	69	3.2	1.5				2.9	6.4	16	15
pH	SU	26	26	100	7.0	6.8	6.0	6.3	6.5	7.5	7.8	8.3	NA
Salinity	ppt	26	26	100	13	17	0.10	0.47	1.4	25	28	28	NA
Silica Gel Treated HEM (SGT-HEM)	mg/L	26	15	58	3.4	0.98				2.2	3.7	4.4	15
Sulfide	mg/L	25	7	28	0.017					0.011	0.045	0.16	0.0020
Temperature	C	26	26	100	7.0	6.9	-0.16	0.098	3.0	9.5	16	26	NA
Total Organic Carbon (TOC)	mg/L	25	25	100	290	140	1.8	8.3	48	260	970	2200	NA
Total Residual Chlorine	mg/L	26	10	38	0.096					0.13	0.22	0.30	0.0075
Total Suspended Solids (TSS)	mg/L	26	26	100	210	130	10	29	71	190	690	1100	30
Turbidity	NTU	26	26	100	96	63	9.0	16	25	120	310	450	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.4.5. Results of Fish Hold Cleaning Effluent Analyses for Classical Pollutants¹

Parameter	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Biochemical Oxygen Demand (BOD)	mg/L	9	6	67	470	300				770	1800	1800	30
Chemical Oxygen Demand (COD)	mg/L	9	9	100	1100	960	490	490	530	1600	2400	2400	NA
Conductivity	mS/cm	8	8	100	35	41	2.6	2.6	27	45	46	46	NA
Dissolved Oxygen	mg/L	9	9	100	5.6	2.9	1.4	1.4	1.6	9.6	15	15	NA
Hexane Extractable Material (HEM)	mg/L	9	6	67	5.4	1.4				4.2	28	28	15
pH	SU	9	9	100	7.6	7.6	6.9	6.9	7.2	8.1	8.6	8.6	NA
Salinity	ppt	9	9	100	48	24	1.3	1.3	19	27	260	260	NA
Silica Gel Treated HEM (SGT-HEM)	mg/L	9	4	44	4.9					2.8	12	12	15
Sulfide	mg/L	7	4	057	0.10	0.019				0.17	0.48	0.48	0.0020
Temperature	C	9	9	100	9.2	8.2	4.7	4.7	5.7	12	15	15	NA
Total Organic Carbon (TOC)	mg/L	9	9	100	210	74	1.9	1.9	5.1	430	730	730	NA
Total Residual Chlorine	mg/L	9	6	67	0.29	0.11				0.29	1.5	1.5	0.0075
Total Suspended Solids (TSS)	mg/L	9	9	100	190	84	16	16	26	400	460	460	30
Turbidity	NTU	9	9	100	100	59	0.20	0.20	1.0	210	330	330	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

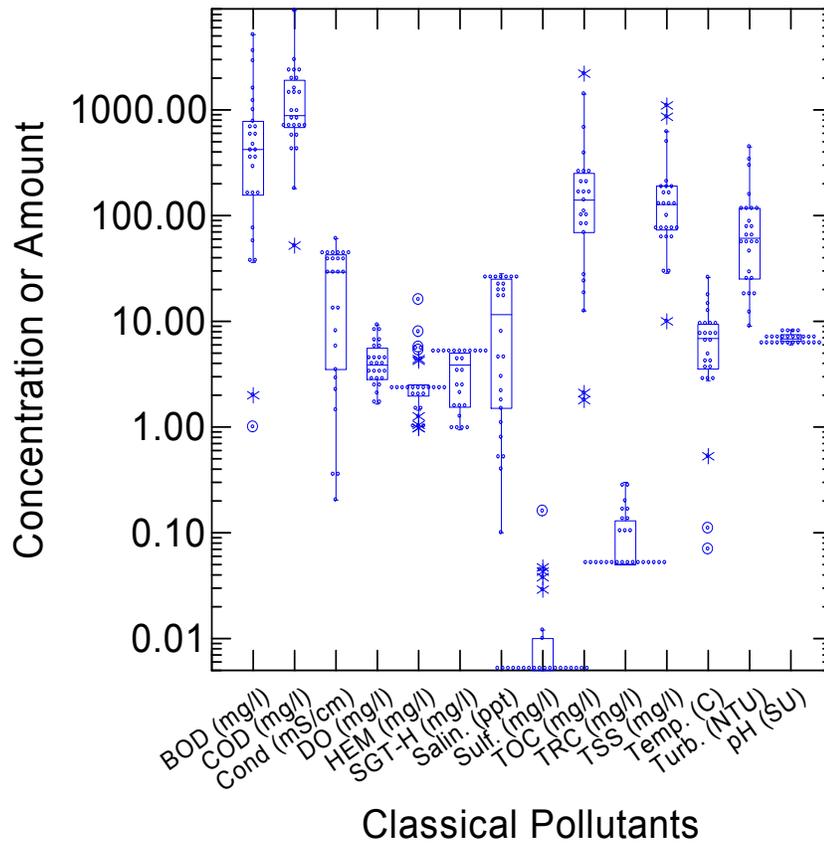


Figure 3.4.9. Box and Dot Density Plot of Classical Pollutant Concentrations/Values Measured in Samples of Fish Hold Effluent

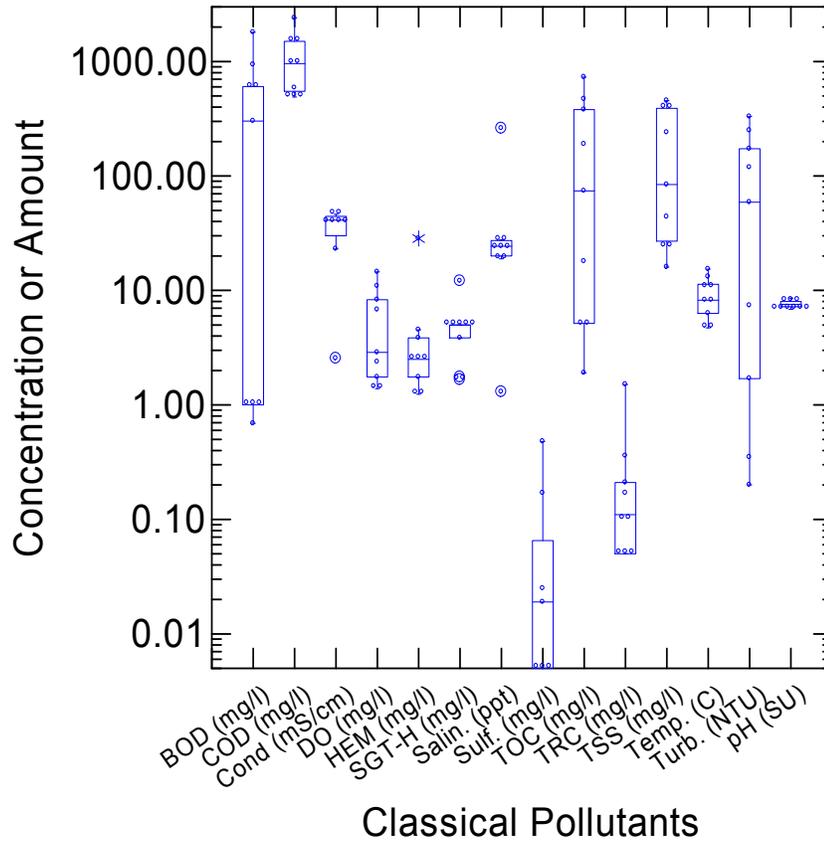


Figure 3.4.10. Box and Dot Density Plot of Classical Pollutant Concentrations/Values Measured in Samples of Fish Hold Cleaning Effluent

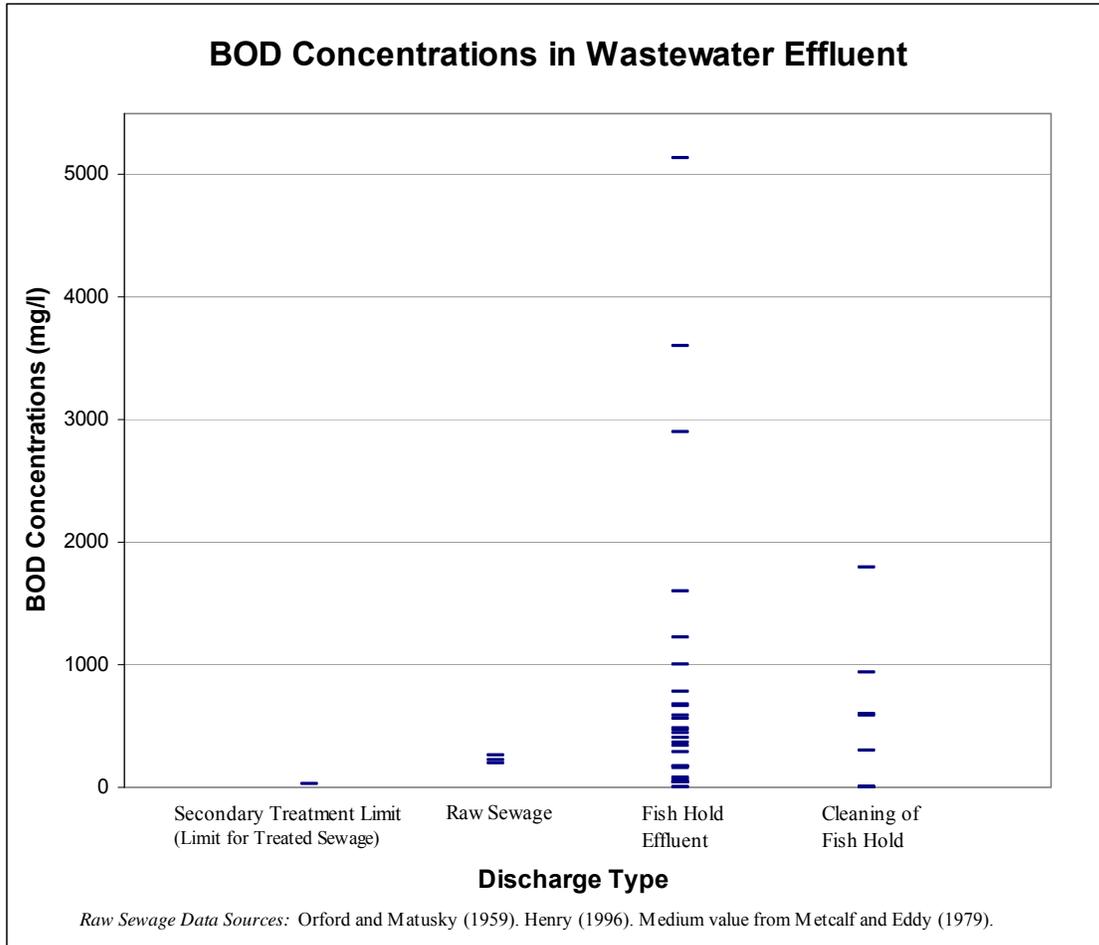


Figure 3.4.11. Comparison between the BOD secondary treatment limit from sewage treatment facilities (30 mg/L), average BOD raw sewage concentrations, and BOD concentrations from fish hold effluent and fish hold cleaning effluent

3.2.4.3 Pathogen Indicators (Microbiologicals)

Sampling pathogen indicators from fish holds presented logistical challenges for the EPA sampling team. Many fishing vessels were sampled in locations remote from laboratories and the holding times of tests for these three pathogens (< 6 hours) prevented EPA from analyzing these samples from many of the sampling events. Nonetheless, EPA was able to test for *E. coli* and enterococci in seven fish hold effluent samples and for fecal coliform in 11 fish hold effluent samples. The results are summarized in Table 3.4.6 (upper half of table) and shown graphically in Figure 3.4.12.

Of these fish hold effluent samples, EPA detected bacteria concentrations above the most stringent screening benchmarks for one (of the seven) *E. coli* sample, four (of the seven) enterococci samples, and three (of the 11) fecal coliform samples. However, EPA strongly suspects that all of these exceedances were due primarily or exclusively due to background concentrations. For example, the fish hold effluent from a fishing vessel sampled in Gloucester, Massachusetts, exceeded all three stringent screening benchmarks for *E. coli*, enterococci, and fecal coliform. However, ambient water concentrations collected earlier in the day exceeded the concentrations in the later sample taken from the fish hold. The likely source of the pathogenic bacteria in this case was a combined sewer overflow (CSO) a few hundred feet above the location of the fishing vessel.

The fishing vessel used ambient water to wash off its deck while unloading cargo (see section 3.2.3.3). Some of this water likely made its way into the fish hold before EPA sampled the fish hold effluent again at the later time period; hence, in this case, EPA strongly doubts that the vessel was the source of the extremely high

What are Combined Sewer Overflows (CSOs) and Sanitary Sewer Overflows (SSOs)?

Combined sewer systems are sewers that are designed to collect rainwater runoff, domestic sewage, and industrial wastewater in the same pipe. Most of the time, combined sewer systems transport all of their wastewater to a sewage treatment plant, where it is treated and then discharged to a water body. During periods of heavy rainfall or snowmelt, however, the wastewater volume in a combined sewer system can exceed the capacity of the sewer system or treatment plant. For this reason, combined sewer systems are designed to overflow occasionally and discharge excess wastewater directly to nearby streams, rivers, or other water bodies. These overflows, called combined sewer overflows (CSOs), contain not only stormwater but also untreated human and industrial waste, toxic materials, and debris.

Properly designed, operated, and maintained sanitary sewer systems are meant to collect and transport all of the sewage that flows into them to a publicly owned treatment works (POTW). However, occasional unintentional discharges of raw sewage from municipal sanitary sewers occur in almost every system. These types of discharges are called sanitary sewer overflows (SSOs). SSOs have a variety of causes, including but not limited to severe weather, improper system operation and maintenance, and vandalism. EPA estimates that there are at least 40,000 SSOs each year. The untreated sewage from these overflows can contaminate our waters, causing serious water quality problems.

pathogen levels.

EPA encountered a similar situation while sampling a commercial fishing vessel in New Bedford, Massachusetts. The samples from the fish hold exceeded water quality criteria for enterococci (127 MPN/ 100 ml) and fecal coliform (125,000 CFU/ 100 ml). However, this vessel was sampled immediately adjacent to an SSO that contained raw fish waste and human sewage: the ambient water had enterococci concentrations of 4,342 MPN/ 100 ml and fecal coliform concentrations of 6,500 CFU/ 100 ml. This vessel also used ambient water to hose off its deck, introducing the pathogenic bacteria to the fish hold. Note that for fecal coliform, this latter vessel's fish hold effluent did appear to add to the high fecal coliform count in the sample.

None of the concentrations of the three pathogens exceeded the most stringent NRWQC set for the pathogens in cases where the ambient concentrations were also below the stringent NRWQC. Although the results were based on this limited number of samples, EPA believes it is unlikely that there is an onboard source of these pathogenic bacteria in the fish hold.

EPA was able to test the effluent from three separate fish holds from three vessels while they were being cleaned (see Table 3.4.6, lower half of table). Two of the fish hold cleaning effluent samples were from those vessels discussed above, where ambient water pathogen concentrations were impacted by the discharge from a CSO and an SSO. The third sample was from a vessel sampled in Sitka, Alaska. Similar to the fish hold effluent results from Massachusetts, EPA found that the concentrations of the effluent from the fish hold cleaning exceeded the NRWQC in one out of the three samples for *E. coli*, two out of the three samples for enterococci, and two out of three samples for fecal coliform. All the samples exceeding the most stringent screening benchmarks for the pathogens were from the vessels located in Massachusetts. Pathogen concentrations were below the detection limit for all three pathogens for the fish hold cleaning effluent from the vessel in Sitka. In all cases, background concentrations in the ambient water exceeded the fish hold cleaning effluent. Similar to what EPA observed with the fish hold effluent data, pathogen contamination in fish hold cleaning effluent from fishing vessels is not a likely source of pathogen contamination to receiving waters. Instead, EPA suspects that the pathogen contamination in these effluents might come from the vessel pumping ambient water with high levels of bacteria onboard.

Table 3.4.6. Results of Fish Hold and Fish Hold Cleaning Effluent Sample Analyses for Pathogen Indicators¹

Analyte ²	Units ³	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ⁴
Fish Hold													
<i>E. coli</i> by MPN	MPN/100 ml	7	6	86	83	41			10	110	310	310	130
Enterococci by MPN	MPN/100 ml	7	5	71	380	41				250	2200	2200	33
Fecal Coliform by MF	CFU/100 ml	11	6	55	11000	10				270	100000	130000	14
Fish Hold Cleaning													
<i>E. Coli</i> by MPN	MPN/100 ml	3	2	67	200	52				550	550	550	130
Enterococci by MPN	MPN/100 ml	3	2	67	1000	150				2800	2800	2800	33
Fecal Coliform by MF	CFU/100 ml	3	2	67	1900	250				5300	5300	5300	14

Notes:

(1) Nondetect (censored) concentrations were replaced with 1/2 of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) MPN = Most Probable Number; MF = Membrane Filtration.

(3) CFU = Colony Forming Units.

(4) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

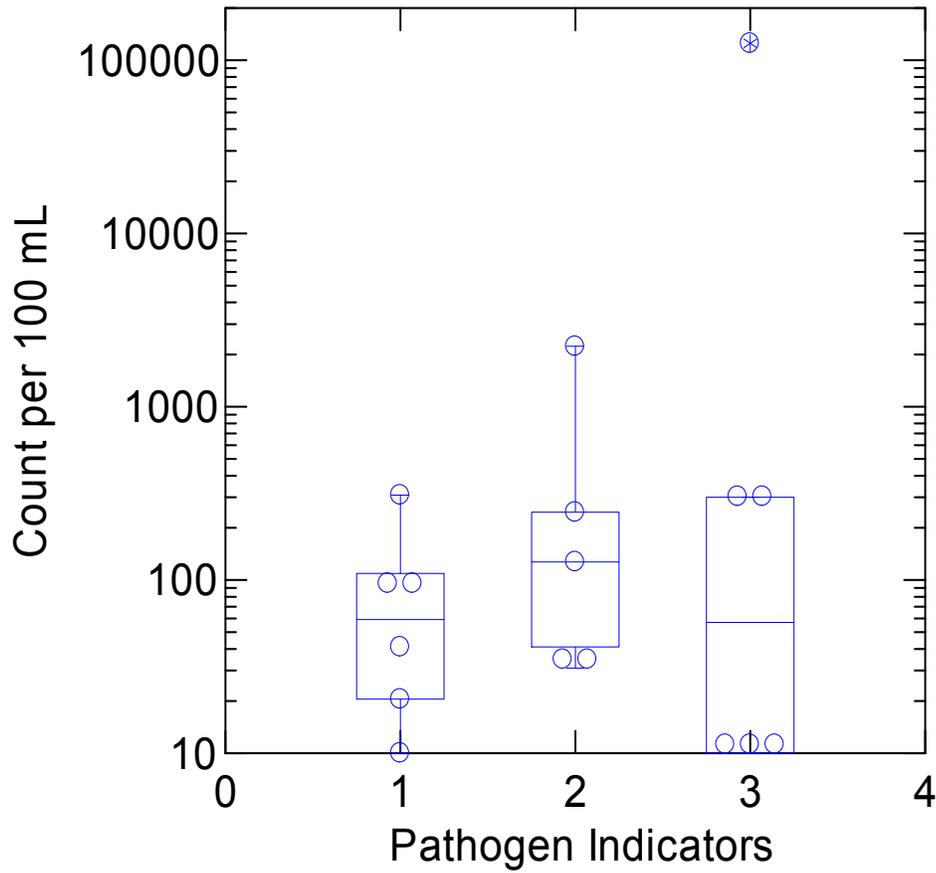


Figure 3.4.12. Box and Dot Density Plot of Measured Pathogen Concentrations in Samples of Fish Hold Effluent EPA notes that all values were substantially influenced by background concentrations in the ambient water, and that of the 25 sample results presented (seven results for *E. coli*, seven for enterococci, and 11 for fecal coliform), only two of the samples exceeded their background concentrations by more than 20 CFU/MPN 100 ml.

3.2.4.4 Nutrients

Samples of fish hold effluent and fish hold cleaning were analyzed for four nutrients or nutrient-related parameters: ammonia nitrogen, nitrate/nitrite, TKN, and total phosphorus (see Table 3.4.7). The corresponding nutrient concentrations detected in fish hold and fish hold cleaning effluent samples are shown in Figures 3.4.13 and 3.4.14, respectively.

Concentrations of total ammonia nitrogen (NH₃-N), nitrate/nitrite nitrogen (NO₃/NO₂-N), TKN, and total phosphorus roughly compare to values of untreated raw sewage (see values in Table 3.4.8). The fish hold effluent had average ammonia concentrations of approximately 12 mg/L and the fish hold cleaning effluent had average concentrations of 16 mg/L, which compares roughly to weak sewage as reported by Metcalf and Eddy (1979) (see Table 3.4.8). However, there were several discharges in which the ammonia concentration substantially exceeded these concentrations, and these discharges could potentially result in acute toxic effects in the receiving water at and near the point of discharge (see Figure 3.4.13). These high values increase the average considerably (the median values for fish hold and fish hold cleaning effluent are 2.1 and 4.8 mg/L, respectively). Most of the ammonia concentrations in samples collected from both fish hold and fish hold cleaning effluent exceed the PHQ screening benchmark of 1.2 mg/L based on the freshwater chronic aquatic life criterion of 1.2 mg N/L, with the highest concentration resulting in a PHQ value of over 130.

In contrast, average nitrate concentrations were near zero for both fish hold effluent (maximum concentration of 0.39 mg/L) and fish hold cleaning effluent (maximum concentration of max 0.53 mg/L). These concentrations are similar to those expected in raw sewage effluent no matter the strength of the sewage effluent (see Table 3.4.8). However, the average total phosphorus concentrations of 13 mg/L for the fish hold effluent and 8.5 mg/L for fish hold cleaning effluent were similar to concentrations in medium to strong raw sewage (see Tables 3.4.7 and 3.4.8).

TKN values averaged 110 mg/L for fish hold effluent and 59 mg/L for fish hold cleaning effluent. These TKN results²² can be roughly compared with total nitrogen results from Metcalf and Eddy (1979), showing that the nitrogen discharges are roughly equivalent to strong sewage.

Protein, free amino acids, and nucleotides from fish and fish by-products are all potential sources of nitrogen. Inorganic phosphorus in the form of phosphate is a key

²² TKN includes ammonia (NH₃) and ammonium (NH₄⁺), and organic nitrogen values. Total nitrogen includes ammonia (NH₃) and ammonium (NH₄⁺), organic nitrogen, and nitrate and nitrite values. Raw sewage tends to have very low nitrate and nitrite values.

element in DNA, RNA, and adenosine triphosphate (ATP) – key components present in the tissue and blood of any animal.

As shown in Figures 3.4.14 and 3.4.15, there is considerable variation exceeding two orders of magnitude in the concentrations of three of the four nutrient and nutrient-related parameters. EPA observed that nutrient concentrations showed some relationship to the geographical location where the vessels operated. As shown in Figure 3.4.15, concentrations of ammonia, TKN, and TP from the Gulf Coast shrimp boats and the New England ground fishery trawlers appear to be higher than those from the fishing vessels sampled in Alaska or the New England lobster tank. In addition, compared to the lobster tank, whose water source is primarily flow-through water, all fishing vessel platforms appear to add nutrients to the effluent.

Table 3.4.7. Results of Fish Hold (upper half) and Fish Hold Cleaning Effluent (lower half) Sample Analyses for Nutrients¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Fish Hold													
Ammonia As Nitrogen (NH ₃ -N)	mg/L	26	25	96	12	2.1		0.64	1.1	6.7	32	160	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	26	18	69	0.10	0.092				0.11	0.27	0.39	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	26	25	96	110	75		3.5	19	160	340	540	NA
Total Phosphorus	mg/L	26	25	96	13	9.7		0.43	3.2	17	28	76	0.10
Fish Hold Cleaning													
Ammonia As Nitrogen (NH ₃ -N)	mg/L	9	7	78	16	4.8			0.034	18	97	97	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	9	8	89	0.24	0.27			0.070	0.35	0.53	0.53	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	9	6	67	59	40				140	170	170	NA
Total Phosphorus	mg/L	9	7	78	8.5	11			0.025	17	20	20	0.10

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.4.8. Raw Sewage Concentrations of Nutrients

Constituent	Concentration (expressed as mg/L)		
	Strong Sewage	Medium Sewage	Weak Sewage
Ammonia as N	50	25	12
Nitrate as N	0	0	0
Total Nitrogen	85	40	20
Total Phosphorus	15	8	4

Source: Metcalf and Eddy, 1979.

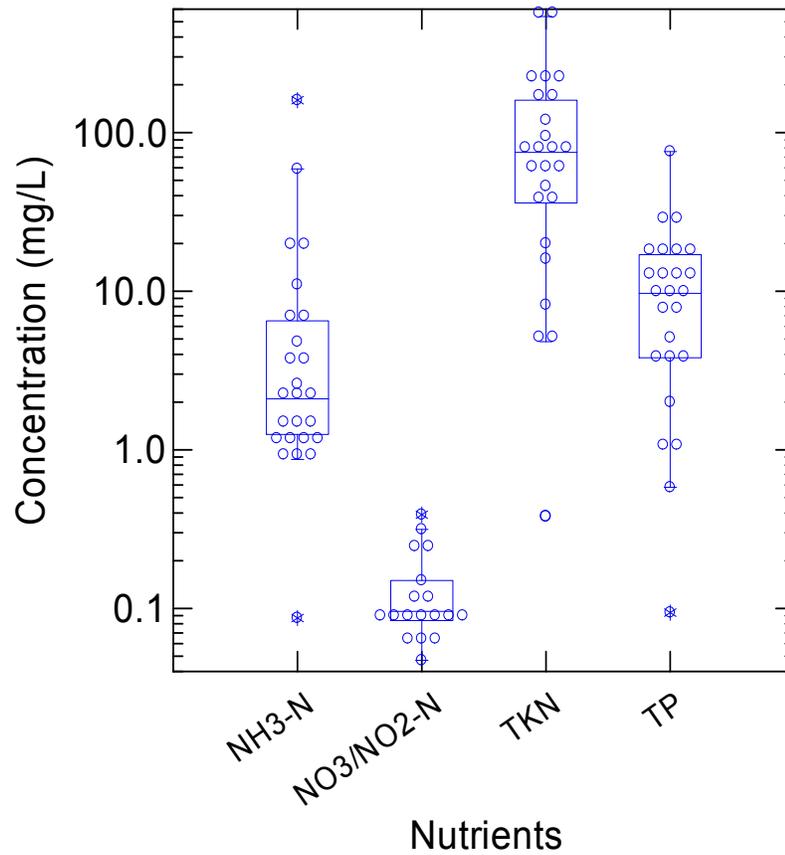


Figure 3.4.13. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Fish Hold Effluent Note the high maximum concentrations for certain samples for ammonia (160 mg N/L), total phosphorus (76 mg/L), and TKN (338 mg/L).

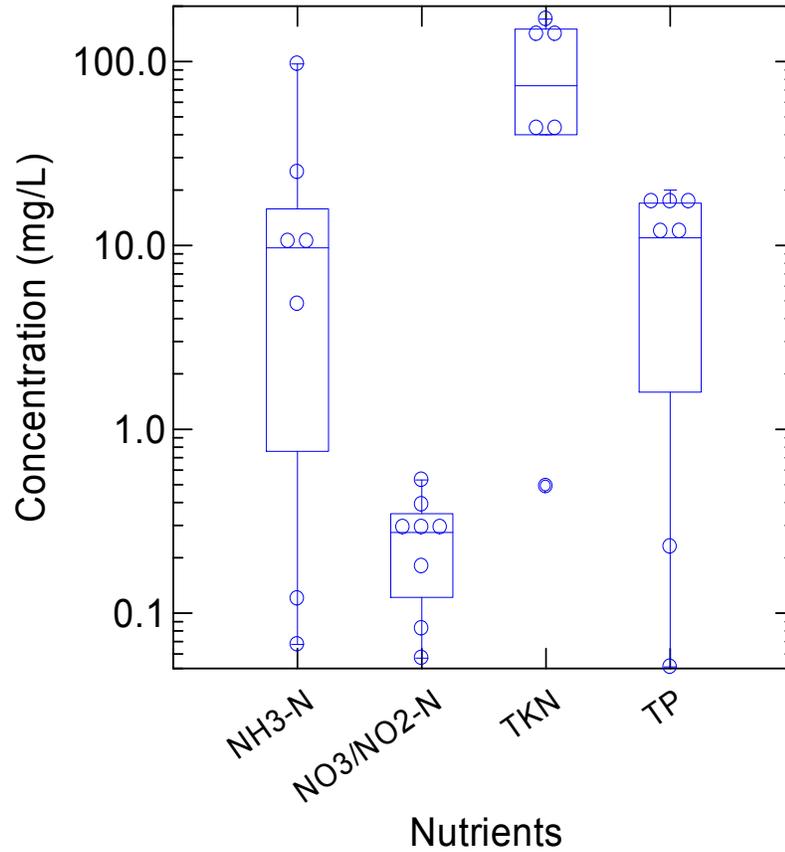


Figure 3.4.14. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Fish Hold Cleaning Effluent For all parameters except ammonia, nutrient concentrations tend to be lower for fish hold cleaning effluent.

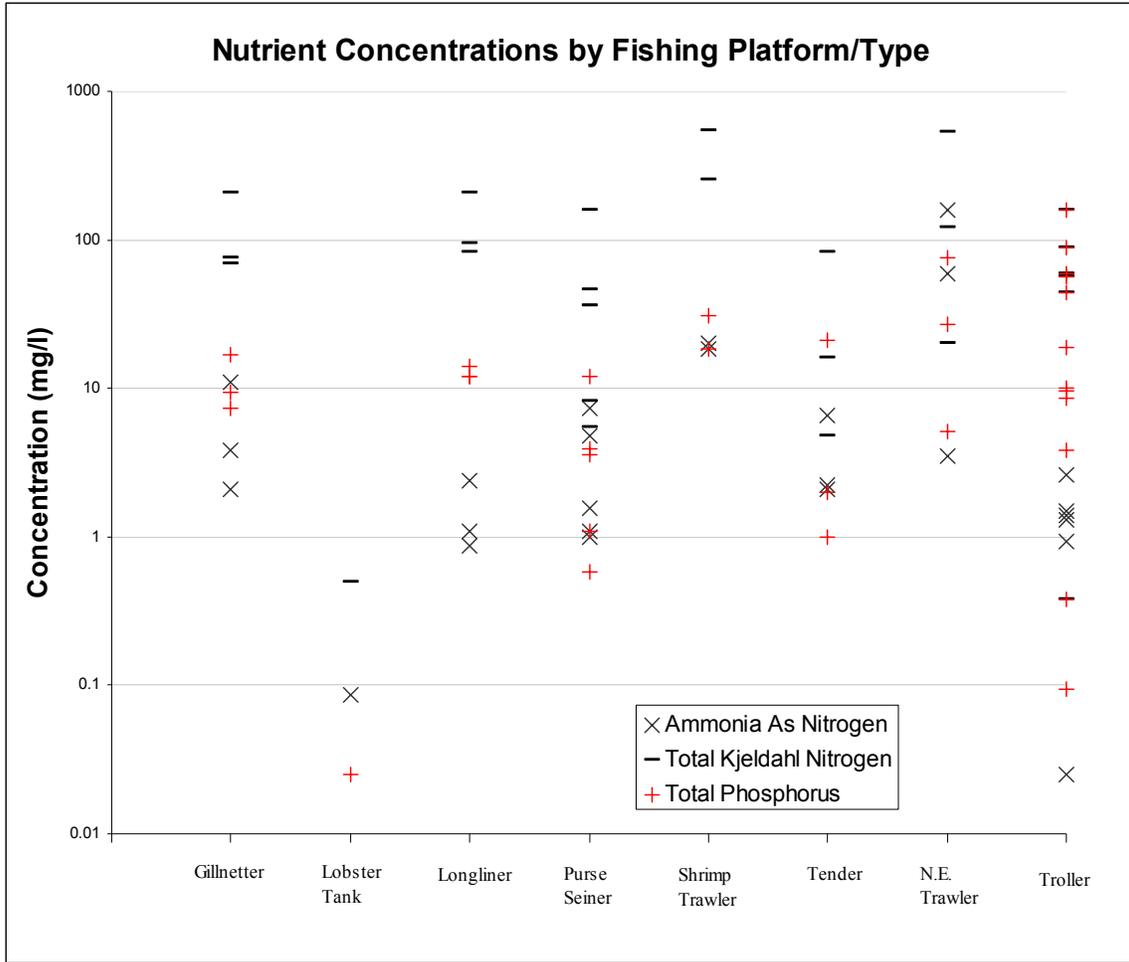


Figure 3.4.15. Comparison of Concentrations of Ammonia, TKN, and Total Phosphorus in Different Fishing Vessel Platforms to those in the Lobster Tank (which has a live catch and continuously circulating water)

3.2.4.5 Nonylphenols

EPA analyzed three fish hold samples for nonylphenols. Short-chain nonylphenols (e.g., NP2EO, NP1EO, bisphenol A, NP) were not detected in any of these samples. EPA expected this result because detergents should not be present when seafood catch is stored in the vessel's fish hold compartment except for residual amounts from poor rinsing after cleaning.

As expected, several NPEO and OPEOs (long-chain nonylphenols) were detected in the fish hold cleaning samples collected from eight vessels (see Table 3.4.9). As with deck washdown water, the NPEOs with the longest ethoxylate chains were detected in approximately a third of the vessels, with concentrations increasing as ethoxylate chain is reduced (i.e., concentrations increasing from NP18EO to NP10EO). Of the vessels where long ethoxylate chain NPEOs were detected, only one of the three vessels had detectable concentrations of NPEOs representing the shortest chains (NP3EO through NP5EO); measured concentrations were low in the range of 12 to 32 $\mu\text{g/L}$, respectively. The OPEO with the longest ethoxylate chain (OP12EO) was detected in only one vessel, as were the lower ethoxylate chain OPEOs. For OPEOs, the concentrations showed the same general trend as the NPEOs with concentrations increasing as ethoxylate chain is reduced, although the concentrations of the shorter chain OPEOs were much lower than the shorter chain NPEOs.

Total NPEO concentrations (from samples containing all 16 NPEO isomers) could be calculated for only two of the eight vessels whose fish hold cleaning effluent was sampled. The concentrations of total NPEOs ranged from 56 (a ground fishery trawler in Massachusetts) to 4,540 $\mu\text{g/L}$ (another ground fishery trawler in Massachusetts). These results are shown graphically in Figure 3.4.16.

While there is no NRWQC for NPEOs or OPEOs, as indicated in previous subsections, these compounds can degrade to NP in fresh and salt water (the saltwater chronic aquatic life criterion for NP is only 1.7 $\mu\text{g/L}$). EPA did not collect samples of background levels for analysis of total NPEOs, OPEOs, and NP from ambient or source water.

Table 3.4.9. Results of Fish Hold Cleaning Effluent Sample Analyses for Long-chain Nonylphenols¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Total Nonylphenol Polyethoxylates	µg/L	8	2	25	620					42	4500	4500	NA
Nonylphenol octodecaethoxylate (NP18EO)	µg/L	8	4	50	1.6	0.15				0.27	12	12	NA
Nonylphenol heptadecaethoxylate (NP17EO)	µg/L	8	3	38	3.1					0.49	23	23	NA
Nonylphenol hexadecaethoxylate (NP16EO)	µg/L	8	3	38	6.9					1.1	51	51	NA
Nonylphenol pendeaethoxylate (NP15EO)	µg/L	8	3	38	14					2.1	100	100	NA
Nonylphenol tetradecaethoxylate (NP14EO)	µg/L	8	2	25	25					2.9	180	180	NA
Nonylphenol tridecaethoxylate (NP13EO)	µg/L	8	2	25	39					3.9	290	290	NA
Nonylphenol dodecaethoxylate (NP12EO)	µg/L	8	2	25	56					5.5	420	420	NA
Nonylphenol undecaethoxylate (NP11EO)	µg/L	8	2	25	75					6.4	560	560	NA
Nonylphenol decaethoxylate (NP10EO)	µg/L	8	2	25	75					5.9	550	550	NA
Nonylphenol nonaethoxylate (NP9EO)	µg/L	8	2	25	73					4.7	530	530	NA
Nonylphenol octaethoxylate (NP8EO)	µg/L	8	2	25	74					4.3	540	540	NA
Nonylphenol heptaethoxylate (NP7EO)	µg/L	8	2	25	66					3.1	470	470	NA
Nonylphenol hexaethoxylate (NP6EO)	µg/L	8	2	25	51					1.9	360	360	NA
Nonylphenol pentaethoxylate (NP5EO)	µg/L	8	1	13	32						220	220	NA
Nonylphenol tetraethoxylate (NP4EO)	µg/L	8	1	13	21						140	140	NA
Nonylphenol triethoxylate (NP3EO)	µg/L	8	1	13	12						79	79	NA
Octylphenol dodecaethoxylate (OP12EO)	µg/L	8	1	13	2.8						11	11	NA
Octylphenol undecaethoxylate (OP11EO)	µg/L	8	1	13	2.7						15	15	NA
Octylphenol decaethoxylate (OP10EO)	µg/L	8	1	13	4.5						20	20	NA
Octylphenol nonaethoxylate (OP9EO)	µg/L	8	1	13	4.9						23	23	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

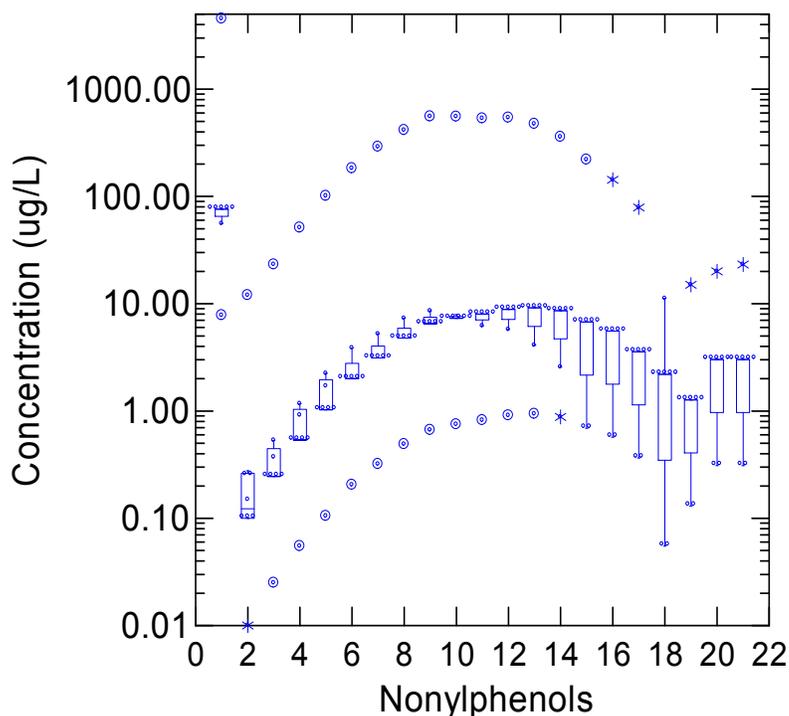


Figure 3.4.16. Box and Dot Density Plot of Nonylphenol Concentrations Measured in Samples of Fish Hold Cleaning Effluent (Note: Nonylphenols in Fish Hold Effluent Were Not Detected.)

Nonylphenol Parameters are Identified as Follows:

- | | | |
|--|---|--|
| (1) Total Nonylphenol Polyethoxylates | (8) Nonylphenol dodecaethoxylate (NP12EO) | (15) Nonylphenol pentaethoxylate (NP5EO) |
| (2) Nonylphenol octodecaethoxylate (NP18EO) | (9) Nonylphenol undecaethoxylate (NP11EO) | (16) Nonylphenol tetraethoxylate (NP4EO) |
| (3) Nonylphenol heptadecaethoxylate (NP17EO) | (10) Nonylphenol decaethoxylate (NP10EO) | (17) Nonylphenol triethoxylate (NP3EO) |
| (4) Nonylphenol hexadecaethoxylate (NP16EO) | (11) Nonylphenol nonaethoxylate (NP9EO) | (18) Octylphenol dodecaethoxylate (OP12EO) |
| (5) Nonylphenol pendeaethoxylate (NP15EO) | (12) Nonylphenol octaethoxylate (NP8EO) | (19) Octylphenol undecaethoxylate (OP11EO) |
| (6) Nonylphenol tetradecaethoxylate (NP14EO) | (13) Nonylphenol heptaethoxylate (NP7EO) | (20) Octylphenol decaethoxylate (OP10EO) |
| (7) Nonylphenol tridecaethoxylate (NP13EO), | (14) Nonylphenol hexaethoxylate (NP6EO) | (21) Octylphenol nonaethoxylate (OP9EO) |

3.2.4.6 Summary of the Characterization of Fish Hold Effluent and Fish Hold Cleaning Effluent

Table 3.4.10 summarizes the specific analytes within fish hold and fish hold cleaning effluent water that may have the potential to pose risk to human health or the environment. EPA's interpretation of a realized risk likely posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

Total iron was sampled for in only two vessels, but PHQs were between 5 and 10. Concentrations of dissolved copper exceeded NRWQC standards in all effluents sampled, with PHQs > 10 in four of the vessels sampled.

The concentrations of certain total and dissolved metals, as well as many of the other pollutants, measured in fish hold and fish hold cleaning effluent were elevated. Concentrations of total arsenic were detected in 16 of 26 samples, and when detected were measured at levels greatly exceeding its respective screening benchmark (i.e., NRWQC), resulting in PHQs of well over 100. Likewise, total copper concentrations, while only exceeding the NRWQC for human health of 1,300 µg/L in a few samples, were high in these few instances and might pose potential acute toxicity risk to aquatic life²³. To a large degree, total aluminum, iron, and manganese concentrations could be explained by the respective metal concentrations in the surrounding waters. Arsenic and copper, however, most likely originated from the fish hold effluent. Concentrations of dissolved copper exceeded NRWQC standards in all effluents sampled, with PHQs well above 10 in four of the vessels sampled. Samples with concentrations of dissolved arsenic resulting in PHQs above 10 were limited to just two fishing vessels (a shrimper and a ground fishing trawlers) with a third vessel having a PHQ of approximately 2. Approximately 2/3 of the concentrations of dissolved zinc in fish hold effluent exceeded NRWQC benchmarks, but no concentrations of dissolved zinc exceeded a PHQ of 10, and most concentrations were below a PHQ of 3. Selenium was sampled for in only six discharges with PHQs > 1 in all samples, and PHQs between 5 and 10 for two samples. Total and dissolved metals concentrations were qualitatively similar in fish hold cleaning effluents, but, in general, concentrations in cleaning effluent were lower than in corresponding fish hold effluents.

Several classical pollutants found in fish hold and fish hold cleaning effluent may have the potential to pose risk. A classical pollutant found in fish hold and fish hold cleaning effluent that poses one of the greatest potential risks to receiving waters is BOD, which was found at elevated concentrations in all sampled vessels and, in many instances, was higher than

²³ As discussed earlier in this chapter, total copper concentrations could pose potential risk to the aquatic environment because the human health criteria of 1,300 µg/L is significantly higher than the 3.1 µg/L benchmark used for dissolved copper based on the saltwater chronic ambient water quality criterion for the protection of aquatic life. When high levels of particulate copper are discharged, some of the particulate copper will likely convert to dissolved copper and be made bioavailable to aquatic life.

concentrations found in raw sewage (see Fig. 3.4.12). Concentrations of COD and TOC correlated with BOD concentrations and were similarly elevated in all fishing vessels. The high BOD in these samples likely contributed to the pervasively low dissolved oxygen levels in these samples. TSS and turbidity in fish hold and fish hold cleaning effluent are also equivalent to levels found in raw sewage, and concentrations of sulfide, particularly in samples from the New England ground fishery trawlers, exceeded the low PHQ screening benchmark (0.002 mg/L) for this classical pollutant.

The other pollutants of potential concern in fish hold and fish hold cleaning effluent were the nutrient and nutrient-related parameters, particularly NH₃-N, TKN, and TP, all of which were measured at concentrations similar to comparable concentrations typically measured in strong (raw) sewage samples. Again, mean concentrations of BOD, COD, TOC, NH₃-N, TKN, and TP were highest in shrimping and trawling vessels.

The high pathogen concentrations found in a select few fish hold and fish hold cleaning samples likely did not stem from the effluent itself, but rather, from the excessively high concentrations measured in ambient background water contaminating the fish holds from the deck washdown process.

Table 3.4.10. Characterization of Fish Hold Effluent and Fish Hold Cleaning Effluent and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Fish Hold and Fish Hold Cleaning Effluent ¹												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Fishing Vessels (31)				Cu, Zn	As, (Cu)²		x			NH3-N TKN Total P	BOD COD TOC	x	DO

(1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2, or when concentrations of analytes are sufficiently high that they may have the potential to pose risks to local water bodies. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

(2) Only a few PHQs near or slightly exceeding 1, but concentrations (in excess of 1,000 µg/L) potentially acutely toxic to aquatic life, particularly to organisms living in the benthos.

3.2.5 Graywater

EPA sampled graywater from eight vessels: five tugboats, a shrimper, a water taxi and a recreational powerboat. The samples included graywater from sinks, dishwashers, and showers, as well as graywater samples from several mixed or unspecified sources. Graywater samples were analyzed for a range of pollutants including pathogen indicators, classical pollutants, nonylphenols, metals, and nutrients. The analytical results were intended to provide representative graywater pollutant concentrations over the range of normal vessel operations.

Graywater volumes vary considerably depending on the class of vessel and its intended use, vessel size, the number of crew and passengers onboard, and the types of graywater-generating activities onboard (e.g., galleys, sinks, showers, wash machines). Based on observations made during the sampling program and from discussions with crew members, EPA estimated that tugboats, some of which provide living quarters for three to five crew members, generate approximately 130 gpd of graywater. Water taxis, which carry a significantly larger number of crew and passengers, but with fewer graywater-generating activities, generate approximately 75 gpd of graywater. Graywater generation on commercial fishing boats might range from a few gpd to hundreds of gpd, depending on the length of the trip and the size of the crew. Due to the highly variable graywater generation volumes possible within vessel classes, EPA was unable to further define graywater generation rates.



The Sink and Shower Facilities of a Tugboat

3.2.5.1 Pathogen Indicators (Microbiologicals)

Graywater is generated from personal bathing, food preparation, and dish and clothes washing, so EPA expected that this vessel discharge category could contain high levels of pathogens. The analytical data for the pathogen indicator bacteria *E. coli*, enterococci and fecal coliform confirm this expectation as the levels of pathogens measured in graywater were by far the highest values measured in any of the vessel discharges. However, it should also be noted that for each of the pathogen indicators, a wide range of values were measured in the graywater samples. EPA also noted that source water (generally municipal water transferred onto the vessel (service water)) does not appear to account for any of the pathogen concentrations.

The analytical results for pathogen indicators in the eight graywater samples are summarized in Table 3.5.1 and displayed in Figure 3.5.1. For each of these parameters, the highest levels (660,000 MPN/100 mL for *E. coli*, 240,000 MPN/100 mL for enterococci, and 570,000 CFU/100 mL for fecal coliform) were measured in the mixed graywater sample from a tugboat. For comparison, EPA measured average levels of 292,000 MPN/100 mL for *E. coli*, 8,920 MPN/100 mL for enterococci, and 36,000,000 CFU/100 mL for fecal coliform in untreated graywater, as reported in the 2008 Cruise Ship Discharge Assessment Report (USEPA, 2008). Typical fecal coliform concentrations in untreated domestic wastewater are 10,000 to 100,000 MPN/100 mL²⁴. The second highest concentration, of *E. coli*, was measured in a mixed (dish/shower) graywater sample, while the second highest concentrations, for enterococci and fecal coliform, were measured in a dishwashing sample. Samples of graywater from sinks and showers tended to have lower levels of the pathogen indicators. Pathogen indicators were not detected in graywater samples from the sink of one vessel, a water taxi.

Figure 3.5.2 presents in box/scatter plots the PHQs for the three pathogen indicators in graywater. As this figure shows, the majority of the values measured for each of the pathogen indicators exceeded the water quality screening benchmarks, by up to four orders of magnitude (or more, in the case of fecal coliform).

²⁴ Note, as indicated above in Table 3.1 and elsewhere, units of MPN/100 ml for fecal coliform approximate similar units of CFU/100 ml; therefore, the two units of expression are appropriate for comparison here.

Table 3.5.1. Results of Graywater Sample Analyses for Pathogen Indicators¹

Analyte	Units ²	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ³
<i>E. Coli</i>	MPN/100 ml	8	7	88	110000	16000			180	120000	660000	660000	130
Enterococci	MPN/100 ml	8	7	88	40000	500			70	57000	240000	240000	33
Fecal Coliform	CFU/100 ml	8	7	88	200000	270000			74	450000	570000	570000	14

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) MPN = Most Probable Number; CFU = Colony Forming Units.

(3) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

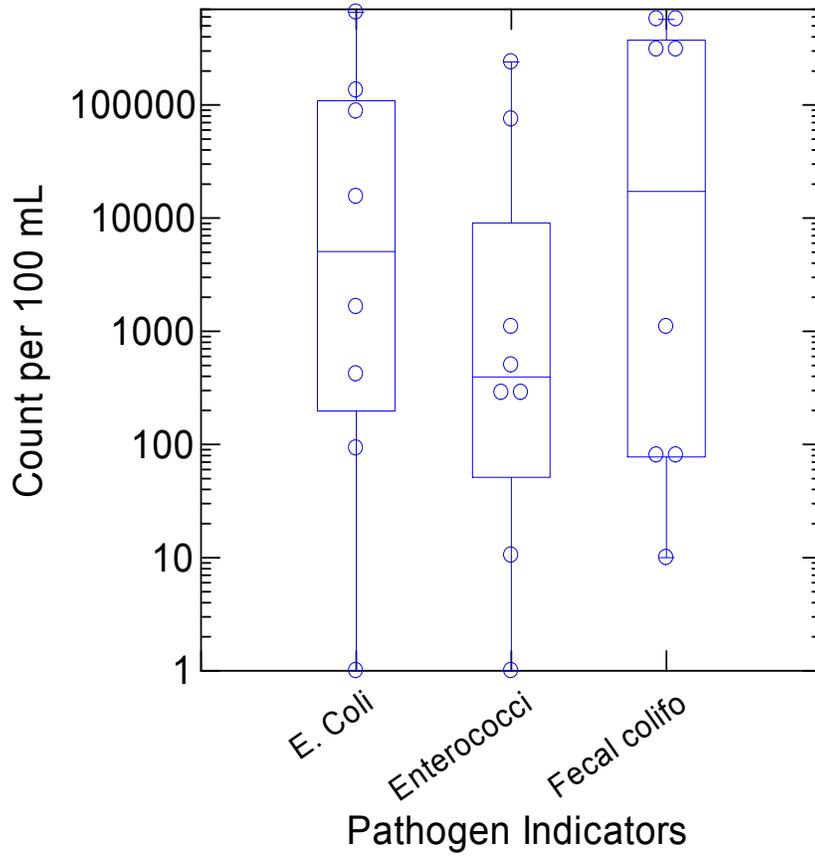


Figure 3.5.1. Box and Dot Density Plot of Pathogen Indicator Values Measured in Samples of Graywater

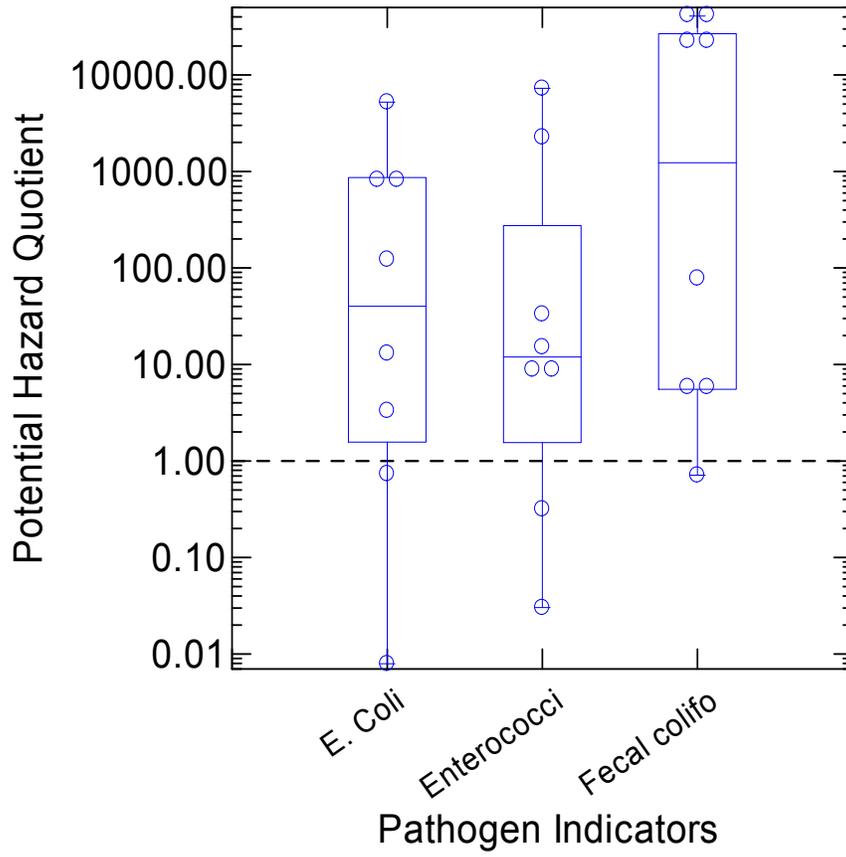


Figure 3.5.2. Box and Dot Density Plot of Potential Hazard Quotients for Pathogen Indicators Measured in Samples of Graywater

3.2.5.2 Classical Pollutants

Graywater samples were analyzed for 14 classical pollutants (see Table 3.5.2). Figure 3.5.3 illustrates the variability of the concentrations/values measured for the classical pollutants in graywater. There was no one vessel or graywater source that tended to have the highest level of a majority of the classical pollutants, unlike the case for the pathogen indicators. The highest concentrations of oil and grease (100 mg/L HEM and 35.3 mg/L SGT-HEM) were measured in the sample of mixed dish/shower graywater on one tugboat; EPA speculates that the source of the oil and grease are primarily oils from cooking and other food sources discharged with the sink water. The highest levels of TSS (99 mg/L) and turbidity (128 NTU) were measured in the dishwashing graywater from a second tugboat. The highest sulfide concentration (1.45 mg/L) was measured in a shower graywater sample from a third tugboat. The highest measured concentrations of BOD (1200 mg/L), COD (4,040 mg/L), and TOC (440 mg/L) were measured in the sample of shower graywater from the recreational powerboat.

Many of the classical pollutants that were elevated in the graywater samples likely reflect the washing and bathing activities that generate graywater discharges. For example, sulfide²⁵ is a parameter that is commonly elevated in water distribution systems, especially on the hot water side. Sulfur-reducing bacteria, which use sulfur as an energy source, are the primary producers of large quantities of hydrogen sulfide. Sulfur-reducing bacteria can live in plumbing systems and hot water heaters. A second example is the high concentration of BOD measured in graywater samples (mentioned above), which reflects the BOD generated onboard the vessels sampled and not from the service water used by that vessel.

Figure 3.5.4 presents the PHQs for classical pollutants in graywater in box/scatter plots. As this figure shows, the PHQ threshold of 1 was exceeded for sulfide, TRC (detected in only one sample (0.11 mg/L) above the reporting limit of 0.01 mg/L for a PHQ of 15), BOD, oil and grease, and TSS. The highest PHQs were calculated for sulfide at 367 and BOD at 40. All of the graywater samples exceeded the 30 mg/L benchmark for BOD, and all five of the detected concentrations of sulfide exceeded the 0.002 mg/L benchmark.

The source of water used on the sampled vessels was, in all cases, potable freshwater bunkered in port (service water). Therefore, EPA did not consider it appropriate to compare the

²⁵ Although sulfide (S^{2-}) is the analyte, hydrogen sulfide (H_2S) is the nonpriority pollutant for which a NRWQC has been established. Sulfides are commonly found as either hydrogen sulfide or hydrosulfide (HS^-). EPA conservatively assumes that all of the sulfide is in the form of hydrogen sulfide (H_2S) is the form that is toxic to fish). However, the proportion of each depends on the pH of the water. At pH 9 about 99 percent of the sulfide is in the form of HS^- ; at pH 7 the sulfide is equally divided between HS^- and H_2S ; and at pH 5 about 99 percent of the sulfide is present as H_2S . Unless heavily polluted, freshwater rivers typically tend have a pH which ranges from about 4.5 to about 7, marine environments have an average pH of around 8.1 (seawater is more basic freshwater), while estuaries may have a pH between that of freshwater and seawater (approximately 5 to 8) dependent upon salinity and other factors. Hence, the use of sulfide (S^{2-}) as the analyte to detect for the presence of hydrogen sulfide (H_2S) is more conservative in marine and estuarine environments than in freshwater ones, but is a reasonable analyte to use due to variation found in different aquatic ecosystems.

concentrations of classical pollutants in graywater to ambient water body concentrations; rather, EPA compared the concentrations of classical pollutants to those found in the service water. None of the conventional parameters discussed here were consistently detected in service water.

Table 3.5.2. Results of Graywater Sample Analyses for Classical Pollutants¹

Analyte	Units	No. samples	No. detected	Detected proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Biochemical Oxygen Demand (BOD)	mg/L	8	8	100	430	260	99	99	110	850	1200	1200	30
Chemical Oxygen Demand (COD)	mg/L	8	8	100	1000	440	180	180	270	1700	4000	4000	NA
Conductivity	mS/cm	7	7	100	0.43	0.41	0.22	0.22	0.30	0.50	0.79	0.79	NA
Dissolved Oxygen	mg/L	7	7	100	7.4	7.1	6.0	6.0	6.3	8.3	10	10	NA
Hexane Extractable Material (HEM)	mg/L	8	8	100	39	29	9.4	9.4	14	68	100	100	15
pH	SU	8	8	100	7.4	7.2	6.1	6.1	6.7	8.5	8.7	8.7	NA
Salinity	ppt	6	6	100	0.25	0.20	0.10	0.10	0.18	0.40	0.40	0.40	NA
Silica Gel Treated HEM (SGT-HEM)	mg/L	8	6	75	8.1	1.5			0.33	9.4	35	35	15
Sulfide	mg/L	8	5	63	0.11	0.017			0.0	0.035	0.73	0.73	0.0020
Temperature	C	8	8	100	27	27	21	21	24	29	36	36	NA
Total Organic Carbon (TOC)	mg/L	7	7	100	140	83	27	27	66	160	440	440	NA
Total Residual Chlorine	mg/L	8	6	75	0.12	0.020					0.11	0.11	0.0075
Total Suspended Solids (TSS)	mg/L	8	8	100	52	58	14	14	37	69	81	81	30
Turbidity	NTU	8	8	100	74	89	40	40	45	110	110	110	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

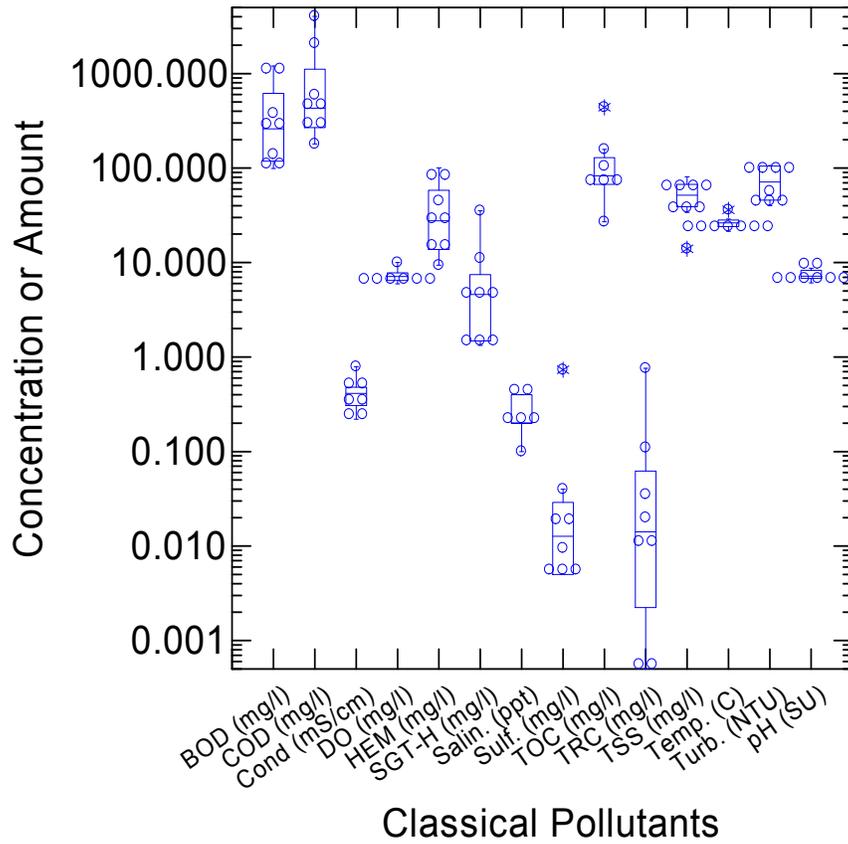


Figure 3.5.3. Box and Dot Density Plot of Classical Pollutant Concentrations/Values Measured in Samples of Graywater

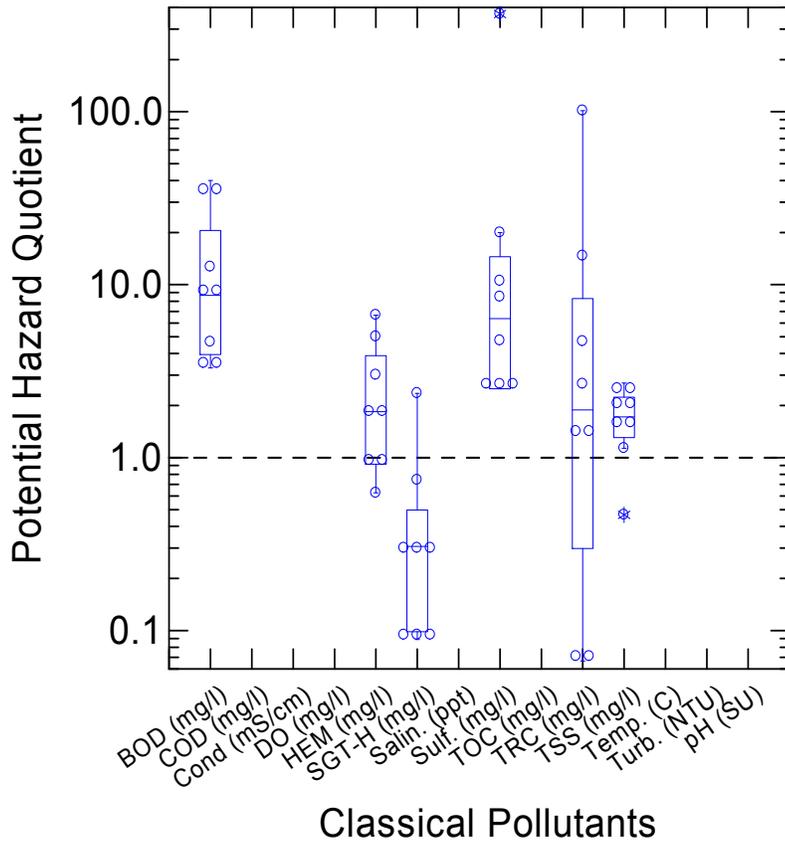


Figure 3.5.4. Box and Dot Density Plot of Potential Hazard Quotients for Classical Pollutants in Samples of Graywater

3.2.5.3 Nonylphenols

Long- and short-chain nonylphenols were expected in graywater discharges given their use in soaps for hand and body washing and in liquid detergents for dish washing. EPA anticipated that long-chain nonylphenols would be present in all graywater samples where detergents were used for cleaning, while short-chain nonylphenols would be present if detergents were used for cleaning and there was a graywater holding tank that provided the additional residence time necessary for biological activity to degrade the NPEOs and OPEOs.

Graywater samples were analyzed for 34 long- and short-chain nonylphenols, including 28 NPEOs and OPEOs, bisphenol A, and nonylphenol (NP). Of these parameters, 25 were detected in one or more samples (see Table 3.5.3). Average concentrations for NP18EO-NP3EO and OP12EO-OP6EO ranged from approximately 0.1 to 10 µg/L. The average concentrations of total nonylphenol polyethoxylates (sum of NPEO isomers) and total octylphenol polyethoxylates (sum of OPEO isomers) were 66 and 63 µg/L, respectively. All of the NPEOs were detected in the graywater sample from the sink of one of the tugboats and the graywater sampled from the shower on the recreational powerboat. All of the OPEOs were detected in the graywater sampled from the shower on the recreational powerboat. NPEOs and OPEOs were also occasionally detected in graywater samples from three of the other vessels.

EPA did not calculate any PHQs for the nonylphenol parameters measured in graywater. The only screening benchmark available was the saltwater chronic NRWQC for NP (a value = 1.7 µg/L). There were no analytical results for NP to compare to this screening benchmark, and no NRWQC exist for the other nonylphenol parameters (individual or total long- and short-chain NPEOs and OPEOs). None of the long- or short-chain nonylphenols or NP were detected in the ambient water surrounding these vessels.

Table 3.5.3. Results of Graywater Sample Analyses for Nonylphenols (only long-chain NPEOs and OPEOs were detected) ¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Total Nonylphenol Polyethoxylates	µg/L	8	2	25	66					15	53	53	NA
Nonylphenol octadecaethoxylate (NP18EO)	µg/L	8	2	25	0.084					0.023	0.041	0.041	NA
Nonylphenol heptadecaethoxylate (NP17EO)	µg/L	8	3	38	0.31					0.12	1.0	1.0	NA
Nonylphenol hexadecaethoxylate (NP16EO)	µg/L	8	3	38	0.59					0.23	1.6	1.6	NA
Nonylphenol pentadecaethoxylate (NP15EO)	µg/L	8	3	38	1.1					0.49	2.4	2.4	NA
Nonylphenol tetradecaethoxylate (NP14EO)	µg/L	8	3	38	2.2					0.95	5.8	5.8	NA
Nonylphenol tridecaethoxylate (NP13EO)	µg/L	8	3	38	3.5					1.9	9.3	9.3	NA
Nonylphenol dodecaethoxylate (NP12EO)	µg/L	8	3	38	5.4					3.2	14	14	NA
Nonylphenol undecaethoxylate (NP11EO)	µg/L	8	3	38	7.0					4.7	16	16	NA
Nonylphenol decaethoxylate (NP10EO)	µg/L	8	2	25	6.7					2.0	6.9	6.9	NA
Nonylphenol nonaethoxylate (NP9EO)	µg/L	8	2	25	7.3					2.5	7.3	7.3	NA
Nonylphenol octaethoxylate (NP8EO)	µg/L	8	2	25	7.9					1.5	7.6	7.6	NA
Nonylphenol heptaethoxylate (NP7EO)	µg/L	8	1	13	7.8						6.5	6.5	NA
Nonylphenol hexaethoxylate (NP6EO)	µg/L	8	1	13	7.3						5.5	5.5	NA
Nonylphenol pentaethoxylate (NP5EO)	µg/L	8	2	25	5.8					1.6	3.7	3.7	NA
Nonylphenol tetraethoxylate (NP4EO)	µg/L	8	2	25	4.7					1.1	2.7	2.7	NA
Nonylphenol triethoxylate (NP3EO)	µg/L	8	1	13	2.8						0.99	0.99	NA
Total Octylphenol Polyethoxylates	µg/L	8	1	13	63						37	37	NA
Octylphenol dodecaethoxylate (OP12EO)	µg/L	8	4	50	1.5	0.22				3.3	3.5	3.5	NA
Octylphenol undecaethoxylate (OP11EO)	µg/L	8	2	25	2.0					3.1	5.2	5.2	NA
Octylphenol decaethoxylate (OP10EO)	µg/L	8	2	25	3.5					4.1	7.2	7.2	NA
Octylphenol nonaethoxylate (OP9EO)	µg/L	8	1	13	3.3						7.8	7.8	NA
Octylphenol octaethoxylate (OP8EO)	µg/L	8	1	13	7.6						7.3	7.3	NA
Octylphenol heptaethoxylate (OP7EO)	µg/L	8	1	13	10						6.3	6.3	NA
Octylphenol hexaethoxylate (OP6EO)	µg/L	8	1	13	10						4.1	4.1	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

3.2.5.4 Metals

Graywater samples were analyzed for dissolved (filtered) and total concentrations of metals. The analytical results are summarized in Table 3.5.4 for the dissolved metals and Table 3.5.5 for the total metals that were detected in at least one graywater sample. The following metals were detected in all of the graywater samples:

- Dissolved and total aluminum
- Total barium
- Dissolved and total calcium
- Dissolved and total copper
- Dissolved and total manganese
- Dissolved and total potassium
- Dissolved and total sodium
- Dissolved and total zinc.

Concentrations of other metals were measured in 50 percent or more of the graywater samples:

- Dissolved barium
- Total chromium
- Total iron
- Total lead
- Dissolved and total magnesium
- Dissolved and total nickel
- Dissolved and total selenium
- Total vanadium.

Figures 3.5.5 and 3.5.6 present the ranges of concentrations measured for dissolved and total metals in the graywater samples. The plots show that dissolved and total metals concentrations range over five orders of magnitude. Calcium, magnesium, potassium and sodium, which are the major cations present in seawater, were the dissolved metals measured at the highest concentrations. Dissolved aluminum, copper, and zinc were also measured at relatively high concentrations (greater than 100 $\mu\text{g/L}$) in most graywater samples. For these dissolved metals, service water samples contained up to 80 percent of the graywater concentration for aluminum, up to 100 percent for copper, and up to 170 percent for zinc. Although the comparison of service water and graywater concentrations suggests that service water might be the source of these metals in some of the graywater samples, this was not always the case. In fact, service water concentrations tended to be low in the samples that corresponded to the highest metals concentrations in graywater.

Total concentrations for each metal were generally similar to or somewhat higher than the dissolved concentrations. Aside from the major seawater cations, concentrations of total metals in the graywater samples were highest for aluminum (912 $\mu\text{g/L}$), copper (440 $\mu\text{g/L}$), iron (458 $\mu\text{g/L}$), and zinc (3,470 $\mu\text{g/L}$). For these total metals, EPA found that service water samples contained up to 74 percent of the graywater concentration for aluminum, up to 115 percent for copper, up to 175 percent for iron, and up to 32 percent for zinc. As was the case for dissolved metals, comparing the service water and graywater concentrations suggests that service water might be the source of these total metals in some, but not all, of the graywater samples.

To quantify the relationship between dissolved and total metals concentrations, EPA calculated the average dissolved fraction (f_d) of each metal in the graywater samples. The metals in graywater discharges with the highest average dissolved fractions ($f_d > 90$ percent) included arsenic, calcium, magnesium, nickel, potassium, and sodium. For all of the other metals where dissolved fractions could be calculated (aluminum, barium, chromium, copper, iron, lead, manganese, selenium, vanadium, and zinc), the average values were in the intermediate (90 percent $> f_d > 50$ percent) range.

The plots in Figures 3.5.7 and 3.5.8 display the distribution of PHQs based on the screening benchmark for each of the dissolved and total metals. For dissolved metals, copper and zinc concentrations consistently exceed the screening benchmarks; the maximum PHQs for copper and zinc were 90 and 18.5, respectively. For total metals, the measured concentrations of arsenic and aluminum consistently exceeded the screening benchmarks. The PHQs based on measured concentrations of total arsenic were 160 and 110 (arsenic was detected in only two of eight graywater samples); these high values reflect the very low NRWQC (0.018 $\mu\text{g/L}$; human health for the consumption of water + organism) for this carcinogen. PHQs for total aluminum varied from 0.6 to 10.5.

Table 3.5.4. Results of Graywater Sample Analyses for Dissolved Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	7	7	100	190	160	24	24	86	300	460	460	NA
Arsenic	µg/L	8	2	25	1.9					1.1	4.5	4.5	36
Barium	µg/L	3	2	67	26	27				45	45	45	NA
Chromium	µg/L	8	2	25	1.4					1.4	2.2	2.2	11
Copper	µg/L	8	8	100	55	17	5.3	5.3	7.6	60	280	280	3.1
Iron	µg/L	3	1	33	83					150	150	150	NA
Lead	µg/L	8	4	50	2.5	1.1				4.2	6.0	6.0	2.5
Manganese	µg/L	8	8	100	17	8.8	4.7	4.7	6.4	35	42	42	NA
Nickel	µg/L	8	4	50	5.5	2.1				70	9.8	9.8	8.2
Selenium	µg/L	8	1	13	3.5						1.4	1.4	5.0
Thallium	µg/L	3	1	33	0.80					1.4	1.4	1.4	NA
Vanadium	µg/L	3	1	33	0.73					1.2	1.2	1.2	NA
Zinc	µg/L	8	8	100	400	240	70	70	80	610	1500	1500	81
Cationic Metals													
Calcium	µg/L	8	8	100	34000	33000	1800	1800	25000	36000	81000	81000	NA
Magnesium	µg/L	8	7	88	9400	11000			6600	13000	18000	18000	NA
Potassium	µg/L	3	3	100	5500	5700	4100	4100	4100	6700	6700	6700	NA
Sodium	µg/L	3	3	100	79000	48000	31000	31000	31000	160000	160000	160000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

Table 3.5.5. Results of Graywater Sample Analyses for Total Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Heavy and Other Metals													
Aluminum	µg/L	8	8	100	380	420	50	50	190	540	910	910	87
Arsenic	µg/L	8	2	25	2.0					1.5	2.9	2.9	0.018
Barium	µg/L	3	3	100	29	28	7.4	7.4	7.4	51	51	51	1000
Cadmium	µg/L	8	1	13	0.82						2.0	2.0	NA
Chromium	µg/L	8	4	50	2.5	2.2				4.2	4.9	4.9	NA
Copper	µg/L	8	8	100	100	71	10	10	14	140	440	440	1300
Iron	µg/L	3	2	67	220	150				460	460	460	300
Lead	µg/L	8	5	63	7.6	1.7				5.8	43	43	NA
Manganese	µg/L	8	8	100	22	13	7.3	7.3	8.9	41	51	51	100
Nickel	µg/L	8	4	50	5.9	2.6				8.6	10	10	610
Selenium	µg/L	8	1	13	3.8						1.7	1.7	170
Vanadium	µg/L	3	2	67	1.7	1.9				2.6	2.6	2.6	NA
Zinc	µg/L	8	8	100	890	270	54	54	130	2000	3500	3500	7400
Cationic Metals													
Calcium	µg/L	8	8	100	35000	36000	1900	1900	26000	37000	82000	82000	NA
Magnesium	µg/L	8	7	88	9700	11000			6500	13000	18000	18000	NA
Potassium	µg/L	3	3	100	5500	6400	3400	3400	340	6600	6600	6600	NA
Sodium	µg/L	3	3	100	81000	47000	36000	36000	36000	160000	160000	160000	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

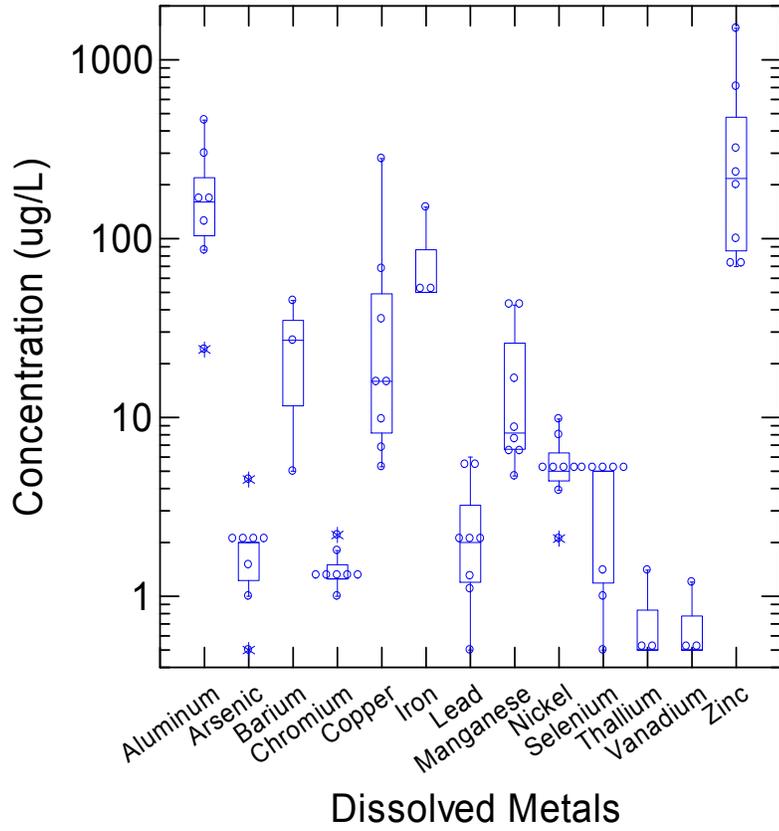


Figure 3.5.5. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Graywater

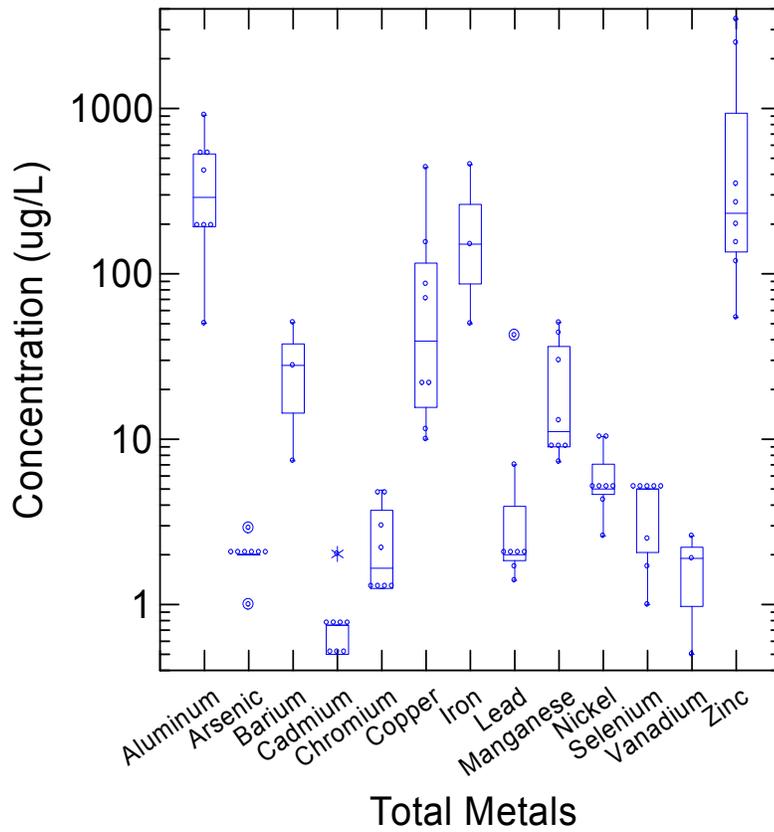


Figure 3.5.6. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Graywater

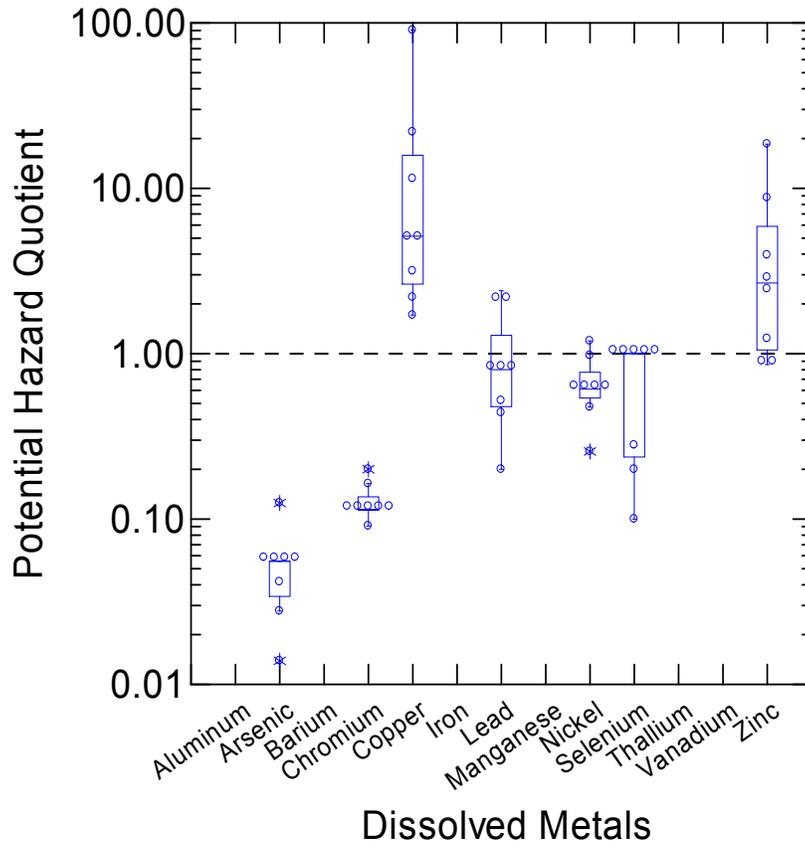


Figure 3.5.7. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Graywater

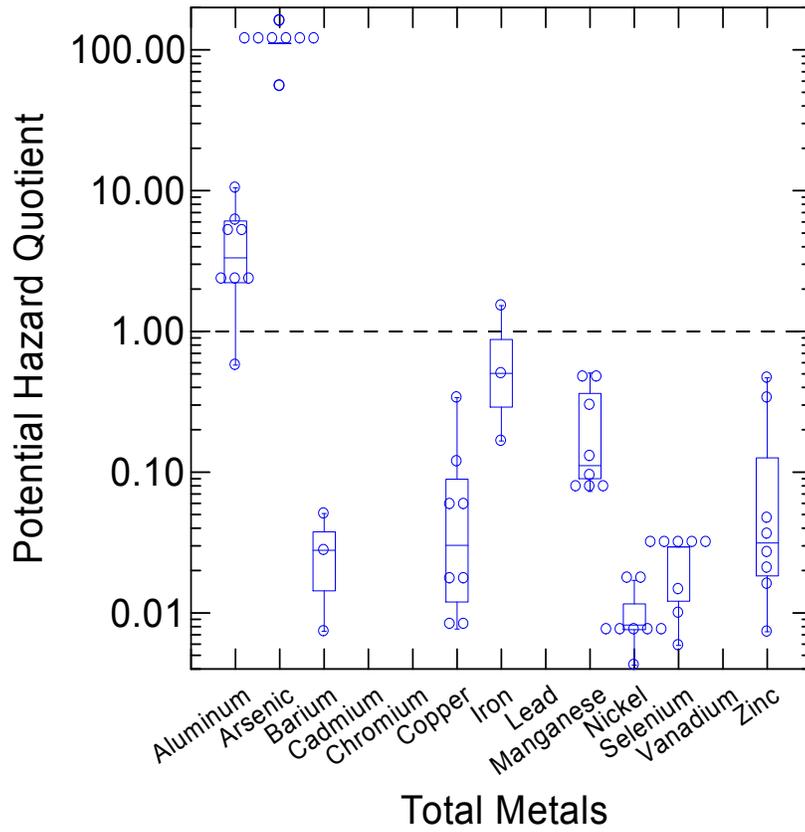


Figure 3.5.8. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Graywater

3.2.5.5 Nutrients

Graywater samples were analyzed for four nutrient and nutrient-related parameters: ammonia nitrogen, nitrate/nitrite, TKN, and total phosphorus (see Table 3.5.6). The nutrient concentrations measured in graywater samples are displayed in Figure 3.5.9. The highest nutrient concentrations measured in graywater were: 4.5 mg/L (ammonia nitrogen), 2.4 mg/L (nitrate/nitrite), 45 mg/L (TKN), and 3.4 mg/L (total phosphorus); all of these values were measured in a single sample of shower graywater from a tugboat. A likely source of the phosphorus in graywater could be phosphate detergents, although both phosphorus and nitrogen parameters also reflect food and possibly other wastes. Of these maximum nutrient concentrations, only TKN was high enough to fall within the range of concentrations typical of untreated domestic wastewater (20 to 85 mg/L; Metcalf and Eddy, 1979). Although each of these nutrients was occasionally detected in service water, only nitrate/nitrite was present in service water at concentrations high enough to be comparable with those in graywater.

Figure 3.5.10 presents the PHQs calculated for the nutrients. As shown in this figure, total phosphorus PHQs ranged from 4.2 to 34 because concentrations in graywater consistently exceeded the screening benchmark. Graywater samples from three tugboats also had PHQs of greater than 1 because the concentrations for ammonia nitrogen exceeded the screening benchmark.

Table 3.5.6. Results of Graywater Sample Analyses for Nutrients¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Ammonia As Nitrogen (NH ₃ -N)	mg/L	8	8	100	1.3	0.75	0.19	0.19	0.22	1.8	4.5	4.5	1.2
Nitrate/Nitrite (NO ₃ /NO ₂ -N)	mg/L	8	7	88	1.6	1.9			0.90	2.3	2.4	2.4	NA
Total Kjeldahl Nitrogen (TKN)	mg/L	8	8	100	10	6.7	2.2	2.2	3.8	7.7	45	45	NA
Total Phosphorus	mg/L	8	8	100	1.4	1.2	0.42	0.42	0.62	2.2	3.4	3.4	0.10

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

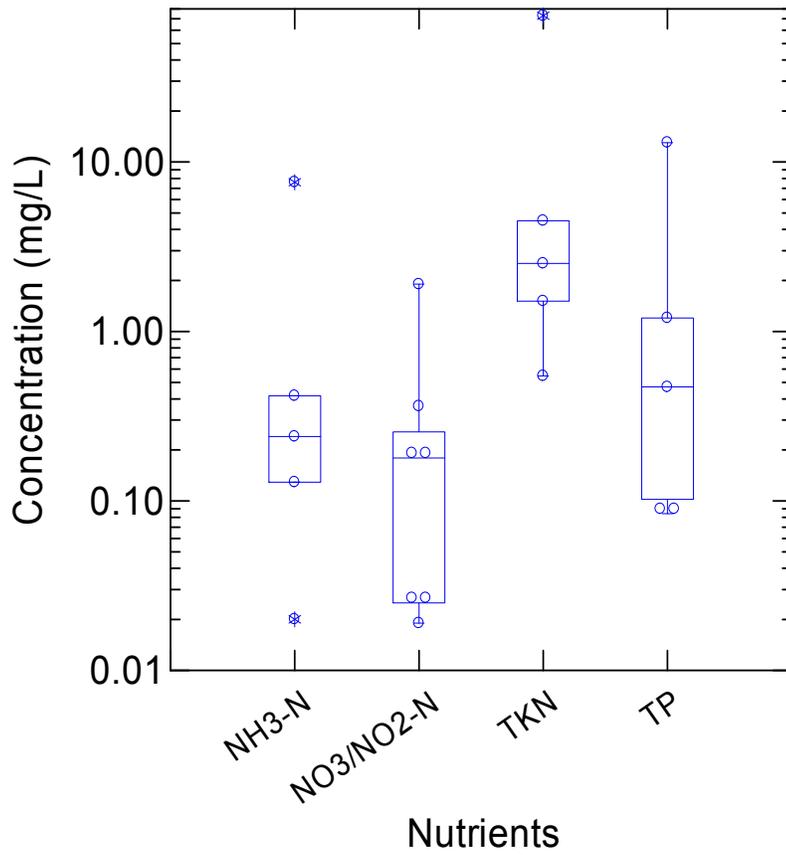


Figure 3.5.9. Box and Dot Density Plot of Nutrient Concentrations Measured in Samples of Graywater

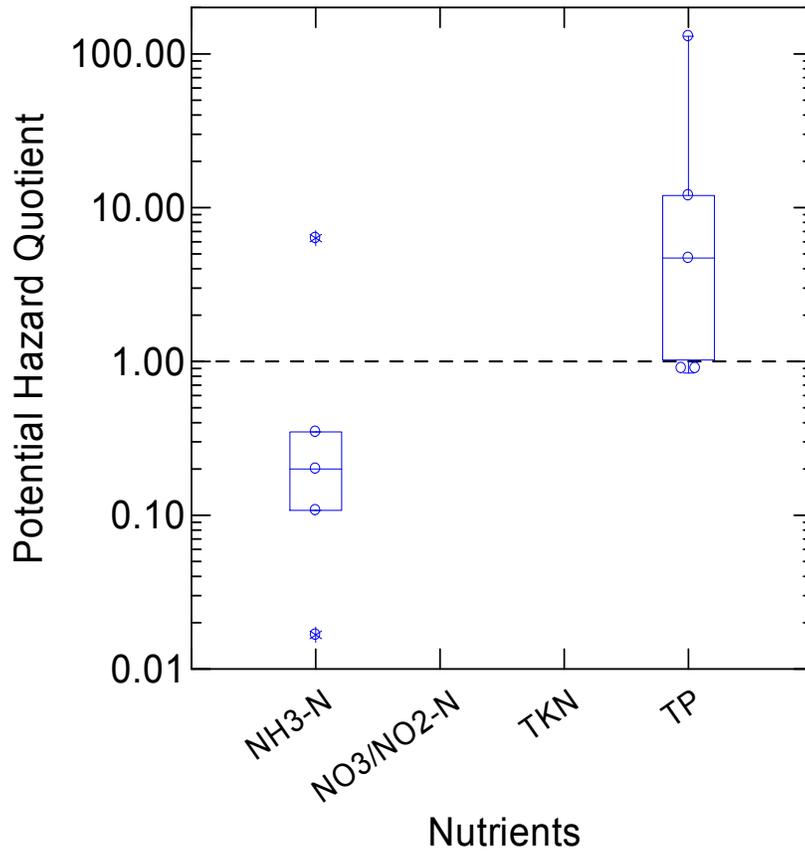


Figure 3.5.10. Box and Dot Density Plot of Potential Hazard Quotients for Nutrients in Samples of Graywater

3.2.5.6 Summary of the Characterization of Graywater Effluent Analyses

Table 3.5.7 summarizes the specific analytes in graywater effluent that may have the potential to pose risk to human health or the environment. EPA's interpretation of the realized risk that may be posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

Pathogens were found at higher concentrations in graywater effluent than in any other type of pollutant. The highest concentrations of all three pathogen groups (fecal coliforms, enterococci, and *E. coli*) were found in the effluent of one of the five tugboats sampled, but were found at high concentrations in all five sampled tugboats. For all eight vessels sampled, the majority of PHQs for all three pathogen groups were greater than 1 (PHQs for all fecal coliform samples were greater than 10), and, in many cases, were between 100 and 10,000. The fecal coliform concentrations most often exceeded the water quality benchmarks, followed by *E. coli* and enterococci concentrations, in that order. Pathogens were not detected in the one water taxi.

BOD was the pollutant with the next highest concentrations that exceeded water quality benchmarks, with PHQs > 1 in all eight vessels and PHQ values exceeding 9 for five of the vessels. The highest BOD concentrations were found from the recreational powerboat (PHQ = 40). Concentrations of COD and TOC were positively correlated to BOD concentrations and were found at high levels in all eight vessels. Sulfide was detected in five of the eight vessels and exceeded benchmark concentrations in all five instances (PHQs of up to 367). TSS and oil and grease (HEM) concentrations were also marginally elevated. Sulfides were detected in the five tugboat discharges, with PHQs ranging from 5-367.

Total nonylphenol polyethoxylates (sum of isomers from NP3EO to NP18EO) were notable only in one tugboat and the recreational boat. Total NPEOs was highest in the graywater sample collected from the recreational powerboat. No short-chain nonylphenols (bisphenol A or NP1EO or NP2EO) were detected in any of the graywater samples. Likewise, no NP was detected, so no comparisons could be made to the screening benchmark.

Among the nutrients sampled, total phosphorus concentrations exceeded the benchmark of 0.10 mg/L in all vessels sampled, with PHQs ranging from 4.2 to 34.

Concentrations of dissolved copper and zinc regularly exceeded NRWQC benchmarks, with a maximum PHQ of 90 for dissolved copper and 18 for dissolved zinc. Service water concentrations of dissolved aluminum, copper, and zinc were moderately influential, but only in the graywater samples with the lowest measured concentrations. The median concentration for dissolved aluminum was 160 µg/L, but no benchmark exists for dissolved aluminum. Total arsenic was detected in the shrimping and recreational vessel, and concentrations exceeded NRWQC benchmarks (PHQ values were 111 and 161 respectively). Total aluminum

concentrations exceeded NRWQC benchmarks in seven of the eight vessels, with one vessel exceeding a PHQ of 10.

HEM (oil and grease) were detected in all 8 samples, with PHQs in excess of 2 in four samples. Concentrations ranged from 9.4-100 mg/L, with the highest HEM concentrations observed in tugboat graywater discharges. SGT HEM were detected in six of eight vessels, but only one sample had a PHQ greater than 2.

Table 3.5.7. Characterization of Graywater Effluent and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Graywater Effluent and Vessel Sources ^{1,2}												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Tugboat (5)	fecal coliform Enterococci <i>E. coli</i>			Cu, Zn	As, Al	x	x	x		Total P	BOD COD TOC		
Shrimping Vessel (1)	fecal coliform Enterococci <i>E. coli</i>			Cu, Zn	As, Al	x				Total P	BOD COD TOC		
Water Taxi (1)	fecal coliform Enterococci <i>E. coli</i>			Cu, Zn	As, Al	x				Total P	BOD COD TOC		
Recreational (1)	fecal coliform Enterococci <i>E. coli</i>			Cu, Zn	As, Al	x		x	x	Total P	BOD COD TOC		

(1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2, or when concentrations of analytes are sufficiently high that they may have the potential to pose risks to local water bodies. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

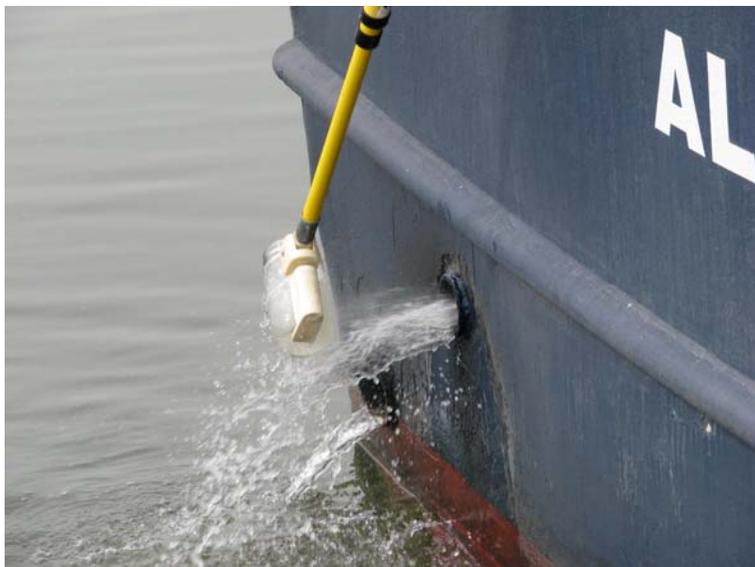
(2) EPA notes that the conclusion of potential risk is drawn from a small sample size, in some cases a single vessel, for certain discharges sampled from some vessel classes. EPA included these results in the tables to provide a concise summary of the data collected in the study, but strongly cautions the reader that these conclusions, where there are only a few samples from a given vessel class, should be considered preliminary and might not necessarily represent pollutant concentrations from these discharges from other vessels in this class.

3.2.6 Engine Effluent

Vessel engines are primarily used for two purposes: propulsion and electrical generation. Engines used for vessel propulsion can be either outboard or inboard engines. Vessels that require significant lighting or have electrical equipment such as appliances and/or electric motors are likely equipped with engines used for electrical generation.

Engine cooling systems include direct cooling, indirect cooling, and keel cooling. Direct and indirect cooling systems discharge wastewater, while keel cooling systems are zero discharge. Some engines with direct and indirect cooling systems also use water to cool and quiet their exhaust, referred to as engine wet exhaust. These engines inject spent cooling water from the engine into the exhaust stream, so that the cooling water directly contacts the engine exhaust. Possible constituents of concern in engine effluent include the following: thermal loading; metals from the discharge contacting the exhaust system, from erosion of moving engine components (e.g., pistons), or from trace constituents of the fuel; and oil and grease and organic compounds as constituents of fuel or possible products of incomplete fuel combustion.

The volume of engine cooling water discharged depends on the type of engine and power level of operation. Vessels with outboard propulsion engines discharge between 1 and 2 gpm of raw cooling water per engine based on observations made during the sampling program. The cooling water discharge rate from inboard marine diesel engines varies based on power levels, but typically averages around 20 gpm when engines operate between 1,500 and 2,000 rpm (Sherwood Pumps, 2009). Marine diesel generator sets require 5 to 6 gpm of cooling water for smaller units (9.5 kW) (Cummins, 2008), and up to 20 and 25 gpm of cooling water for larger marine generator sets (80 kW) (Cummins, 2004). Daily discharge rates for these engines are a function of daily operating time.



Collecting the Engine Effluent of a Water Taxi at Idle



Collecting the Engine Effluent of a Tow and Salvage Vessel at Full Speed

For this study, EPA collected engine cooling water discharge samples from a variety of vessel classes with different engine types, as summarized in Table 3.6.1. Note that two of the sampled vessels are recreational vessels and are not study vessels. In addition, both of the sampled research vessels and four of the six sampled tow/salvage vessels (those with outboard propulsion engines) were manufactured for pleasure and therefore are also recreational vessels and not study vessels. EPA sampled engine effluent from these vessels because all of the sampled engines can be installed on either recreational or nonrecreational vessels and are representative of engines on study vessels.

Samples were analyzed for classical pollutants, metals (dissolved and total), SVOCs, and VOCs. Engine discharge samples were typically collected from the discharge port using a sample transfer jar attached to a pole. The contents of the sample transfer jar were poured into a lined utility bucket. If the engines were operated at multiple engine levels (e.g., idle, half power, full power), then equal portions of sample were collected from each power level and composited for a single laboratory analysis. Ten of the 13 sampled vessels with inboard propulsion engines and all six sampled vessels with outboard propulsion engines were operated at multiple power levels. Similarly, if a vessel operated more than one engine, then equal portions of sample were collected from each engine and composited for a single laboratory analysis. However, samples for analysis of oil and grease and VOCs are not appropriate to composite. For these analytes, samples were collected and analyzed separately for each engine power level or were collected from only one of the multiple engines.

Table 3.6.1. Sampled Engine Characteristics

Fuel Type	Cooling Type	Engine Wet Exhaust?	Number of Vessels Sampled	Vessel Types
Inboard Propulsion Engines				
Diesel	Direct	Yes	3	Water Taxi (2), Fishing
Diesel	Indirect	Yes	5	Tour Boat (2), Water Taxi, Tow/Salvage, Fire Boat
Diesel	Unknown	Yes	3	Tour Boat, Water Taxi, Recreational
Diesel	Unknown	Unknown	1	Fishing
Gasoline	Indirect	Yes	1	Recreational
Outboard Propulsion Engines				
Gasoline	Direct	Yes	5	Tow/Salvage (4), Research
Gasoline	Unknown	Yes	1	Research
Generator Engines				
Diesel	Direct	Yes	1	Tour Boat
Diesel	Indirect	Yes	1	Fire Boat
Diesel	Unknown	Unknown	2	Fishing, Tour Boat
Unknown	Indirect	Yes	1	Water Taxi

EPA also observed a number of vessels, particularly tug boats and larger commercial fishing vessels, that use keel-cooled propulsion and generator engines. The vessels were not sampled as these closed-loop cooling systems do not have a discharge. Approximately two-thirds of the 61 vessels visited had keel cooled engine systems.

An additional source of relevant engine effluent data is EPA's sampling program for the Uniform National Discharge Standards (UNDS) rulemaking. In 2006, EPA sampled propulsion engine wet exhaust discharges from two small Armed Forces vessels with inboard diesel engines with engine wet exhaust: a 36-foot landing craft personnel large (LCPL) and a 7-meter rigid inflatable boat (RIB) (USEPA, 2008b). This sampling program was specifically designed to

characterize engine wet exhaust discharges by power level. While these Armed Forces vessels are not study vessels, the engines used on these vessels are comparable to those used on study vessels. Samples from both vessels were analyzed for eight classical pollutants and 92 volatile and semivolatile compounds. Samples from the LCPL were also analyzed for seven total metals. Grab samples of the engine discharge were collected from sample taps installed into the exhaust lines of the vessels. Three replicate engine discharge samples were collected at each of five different engine power levels: 0 percent (idle), 25 percent, 50 percent, 75 percent, and 100 percent (full power). Three replicate background seawater samples were also collected. Sampling was conducted in the open ocean.

3.2.6.1 Inboard Propulsion Engines

For this study, EPA collected cooling water discharge samples from inboard propulsion engines on 13 vessels: four water taxis, three tour boats, two fishing vessels, one tow/salvage vessel, one fire boat, and two recreational vessels (Table 3.6.1). These engines included both direct and indirect cooling discharges from both gasoline- and diesel-fueled engines. For the UNDS program, EPA sampled engine wet exhaust from inboard propulsion engines on two personnel craft. Results for each class of pollutant are presented and discussed in the following subsections.



The Inboard Propulsion Engine of a Fire Boat

3.2.6.1.1 Classical Pollutants

Table 3.6.2 presents analytical results for 11 classical pollutants detected in samples of discharges from inboard propulsion engines. All of the classical pollutants analyzed for were detected and the detected results are shown in Figure 3.6.1. Engine cooling water discharge differs from all other discharges in that the water used in the engines is drawn from surrounding waters and immediately discharged to the same waters. For this reason, EPA analyzed the sample results to determine which pollutant concentrations were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations (see footnotes on Table 3.6.2 and Figure 3.6.1). The remainder of this subsection discusses those pollutants found to be contributed primarily by engine operations.

Temperature increases in engine effluent above background were generally less than 5°C. However, on three vessels operated at higher power levels (recreational vessel, tow/salvage vessel, and fire boat), temperature increases were greater than 20°C. EPA's findings were similar for the UNDS sampling program, with temperature increases ranging from less than 3°C at idle to a maximum of 27°C at full power.

Oil and grease (measured as HEM) was detected in the majority of engine effluent samples; however, detected concentrations were low (most were less than 5 mg/L). All sample results were well below the 33 CFR § 151.10 and MARPOL prohibition of the discharge of oil and oily mixtures with an oil content greater than 15 ppm into seawater from vessels. HEM values exceeded 5 mg/L in only three grab samples, and all three were collected during engine operation at relatively high power levels. For the UNDS sampling program, HEM was not detected in any engine effluent samples, regardless of power level (≤ 4 mg/L).

Sulfide was detected in only two of 11 samples at concentrations of 0.013 and 0.016 mg/L. These measured concentrations are six to eight times greater than the most conservative PHQ screening benchmark of 0.002 mg/L. Sulfide might be present as a trace constituent in the fuel, as a product of incomplete combustion, or due to formation within the biofilm in the cooling system piping. For the UNDS sampling program, sulfide was not detected in any engine wet exhaust samples.

For this study, TSS concentrations in effluent discharge samples were contributed primarily by background ambient concentrations (i.e., sample concentrations ranged from <5 to 17 mg/L while ambient water concentrations ranged from 7.8 to 20 mg/L). For the UNDS sampling program, TSS was not detected in any of the samples from the LCPL; however, TSS was present in the RIB discharge samples at concentrations ranging from 6 to 14 mg/L, which were statistically greater than background for some power levels. UNDS TSS results correspond with the field observations for samples from the RIB at the highest power levels (i.e., the samples were observed to be cloudy and contained settleable materials (resembling soot)). In this

study, EPA observed that some effluent engine samples were also cloudy and contained settleable materials at higher power levels.

TRC was detected in only one engine effluent sample collected from a fishing vessel at a concentration of 0.17 mg/L. Fish hold effluent from this vessel, containing TRC at a concentration of 0.27 mg/L, was discharged into the water surrounding the vessel just prior to collection of engine effluent samples; the propulsion engine on this vessel utilizes the ambient water for cooling. EPA believes that the TRC value for the engine effluent sample was likely influenced by the fish hold effluent discharge.

Table 3.6.2. Results of Inboard Propulsion Engine Sample Analyses for Classical Pollutants¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Conductivity ²	mS/cm	10	6	100	11	6.1	0.22	0.22	0.22	17	44	44
Dissolved Oxygen ³	mg/L	10	6	100	6.8	7.4	1.7	2.0	4.0	9.3	13	14
Hexane Extractable Material (HEM)	mg/L	12	8	66	3.0	2.2				3.8	5.4	5.7
pH ²	SU	13	13	100	6.9	6.6	6.2	6.2	6.4	7.4	7.9	8.0
Salinity ²	ppt	10	10	100	6.9	3.3	0.10	0.10	0.10	9.9	28	28
Silica Gel Treated HEM (SGT-HEM)	mg/L	12	7	58	4.0	2.6				3.6	4.3	4.4
Sulfide	mg/L	11	2	18	0.0062						0.013	0.013
Temperature	C	13	13	100	22	21	6.5	9.9	17	26	36	39
Total Residual Chlorine ²	mg/L	13	1	7.7	0.048						0.10	0.17
Total Suspended Solids (TSS) ³	mg/L	11	8	73	11	13				16	17	17
Turbidity ³	NTU	13	13	100	32	29	1.2	2.7	18	45	69	80

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

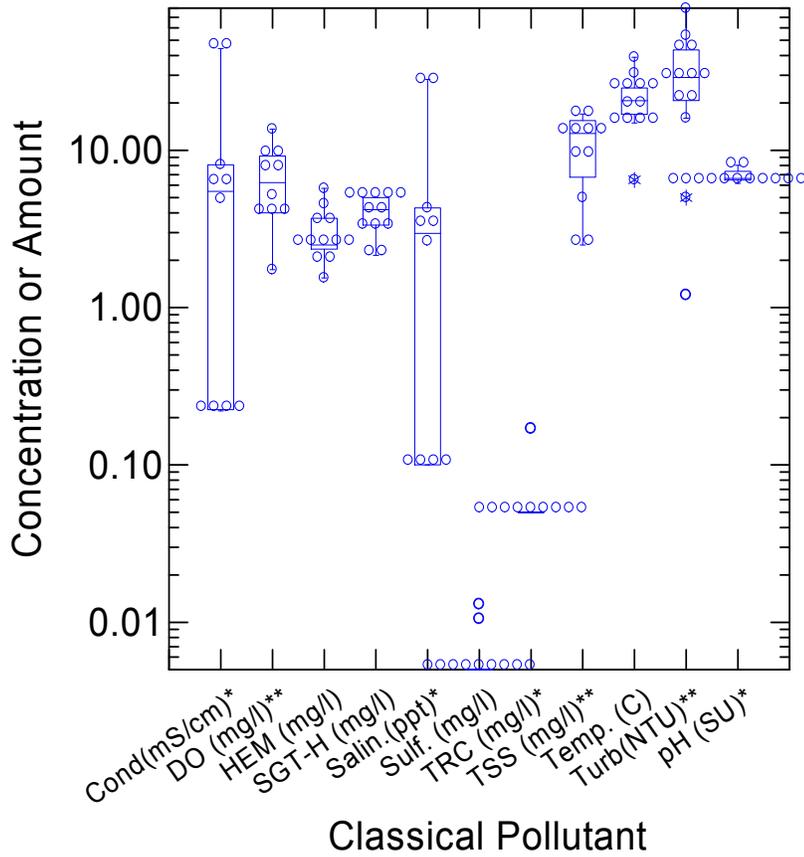


Figure 3.6.1. Box and Dot Density Plot of Classical Pollutant Values Measured in Samples of Inboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.1.2 Metals

Inboard propulsion engine effluent samples were analyzed for 22 dissolved and total metals. Table 3.6.3 presents analytical results for the 16 metals that were detected in one or more engine effluent samples. The detected results are also shown in Figures 3.6.2 and 3.6.3 for dissolved and total metals, respectively. Figures 3.6.4 and 3.6.5 display the distribution of PHQs based on the screening benchmark for each of the dissolved and total metals. EPA analyzed the sample results to determine which metals were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations. The remainder of this subsection discusses those metals found to be contributed primarily by engine operations.

For most metals, concentrations for the dissolved and total forms were similar, indicating that engine operations contribute metals in dissolved rather than particulate form. Two exceptions were iron and lead. A comparison of dissolved and total iron concentrations indicates that almost all iron was present in particulate form. One possible source of particulate iron in engine effluent is rust. Lead was detected in engine effluent samples from only four of the 13 vessels sampled (three water taxis and a tow/salvage vessel). Total lead concentrations (maximum measured concentration = 9.6 µg/L) exceeded dissolved lead concentrations by three to four times.

Dissolved and total copper were detected in almost all engine effluent samples at concentrations ranging from 3 to 53 µg/L and 5 to 66 µg/L, respectively. Dissolved copper concentrations exceeded the PHQ screening benchmark of 3.1 µg/L (saltwater chronic criterion) by one to 17 times (see Figure 3.6.4). In contrast, none of the total copper concentrations exceeded the PHQ screening benchmark of 1,300 µg/L (human health for consumption of water and aquatic organisms (see Figure 3.6.5)).

Dissolved and total zinc were also detected in a majority of engine effluent samples. Detected concentrations ranged from 12 to 120 µg/L and 11 to 95 µg/L for dissolved and total zinc, respectively (see Figures 3.6.2 and 3.6.3). However, only the two highest detected dissolved zinc concentrations (83 and 120 µg/L) exceeded the PHQ screening benchmark of 81 µg/L (saltwater chronic criterion). None of the detected total zinc concentrations exceeded the PHQ screening benchmark of 7,400 µg/L (human health for consumption of water and aquatic organisms).

Dissolved and total nickel were detected in approximately half of the engine effluent samples, and dissolved and total chromium and lead were each detected in fewer than half of the engine effluent samples. Detected concentrations were generally within five times the reporting limit and none exceeded the screening benchmarks for these analytes (see Figures 3.6.4 and 3.6.5). Note, however, that lead is a persistent bioaccumulative and toxic chemical (PBT) and the long-term mass loading is more important than the discharge concentrations.

Dissolved manganese was detected in 11 of 13 engine effluent samples. Manganese was predominantly in particulate form in background ambient water; therefore, EPA assumed dissolved manganese concentrations in engine effluent samples to be contributed by engine operations. NRWQCs or other PHQ screening benchmarks have not been determined for dissolved manganese.

Dissolved iron and dissolved and total vanadium were each detected in no more than three engine effluent samples at measured concentrations close to the reporting limit. NRWQCs or other PHQ screening benchmarks have not been determined for these analytes at this time.

Finally, the concentrations in engine effluent discharges that exceeded the PHQ screening benchmark concentrations for dissolved selenium, total aluminum, and total arsenic were caused by high background concentrations in ambient water (which exceeded benchmark concentrations) and not by engine operations. After subtracting the contribution of ambient water, none of the detected concentrations exceeded their PHQ screening benchmarks.

Comparing study sampling results with the metals data from the engine wet exhaust sampling conducted for the UNDS program affirms EPA's sampling results. For the UNDS program, EPA determined that five of the seven total metals analyzed for were present at concentrations statistically greater than background: cadmium, chromium, copper, lead, and nickel. Total mercury was not detected in any samples, and total arsenic concentrations did not exceed background concentrations. Table 3.6.4 compares the metals results from this study and the UNDS program.

EPA notes that there were some important differences between the UNDS sampling and the sampling conducted in this study to consider when comparing the results. The UNDS program used a different analytical method, as well as a different methodology to calculate mean concentrations. Also, background metals concentrations in harbors for this study are greater than those in the open ocean for the UNDS program.

Table 3.6.3. Results of Inboard Propulsion Engine Sample Analyses for Metals¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Heavy and Other Metals												
Aluminum, Dissolved ²	µg/L	13	12	92	200	100		3.8	23	180	880	940
Aluminum, Total ²	µg/L	13	13	100	340	300	59	61	120	410	920	940
Arsenic, Dissolved ³	µg/L	13	4	31	4.2					8.7	12	14
Arsenic, Total ³	µg/L	13	6	46	4.5					8.7	13	15
Barium, Dissolved ²	µg/L	7	7	100	35	32	23	23	29	34	63	63
Barium, Total ²	µg/L	7	7	100	36	34	24	24	28	35	63	63
Chromium, Dissolved	µg/L	13	3	23	1.2					0.75	1.9	2.1
Chromium, Total	µg/L	13	3	23	1.3					0.95	2.4	2.6
Copper, Dissolved	µg/L	13	12	92	16	6.6		1.6	5.5	23	51	53
Copper, Total	µg/L	13	11	85	18	9.3				25	62	66
Iron, Dissolved	µg/L	7	1	14	64						150	150
Iron, Total ³	µg/L	7	6	86	250	250				310	520	520
Lead, Dissolved	µg/L	13	3	23	1.5			5.6		0.60	2.1	2.3
Lead, Total	µg/L	13	4	31	3.0			150		4.1	8.5	9.6
Manganese, Dissolved	µg/L	13	11	85	43	44				55	82	91
Manganese, Total ²	µg/L	13	11	85	55	53				74	95	100
Nickel, Dissolved	µg/L	13	7	54	4.4	2.5				4.3	4.9	5.3
Nickel, Total ²	µg/L	13	7	54	4.6	3.1		30		4.3	5.5	5.6
Selenium, Dissolved ²	µg/L	13	4	31	11			40		21	32	34
Selenium, Total ³	µg/L	13	4	31	11					21	31	32
Vanadium, Dissolved	µg/L	7	3	43	0.90					1.4	1.7	1.7
Vanadium, Total	µg/L	7	2	29	1.4					1.1	1.6	1.6
Zinc, Dissolved	µg/L	13	9	69	38	23					110	120
Zinc, Total	µg/L	13	11	85	38	29				75	89	95
Cationic Metals												
Calcium, Dissolved ²	µg/L	13	13	100	80000	37000	24000	24000	74 26000	62000	310000	310000

Table 3.6.3. Results of Inboard Propulsion Engine Sample Analyses for Metals¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Calcium, Total ²	µg/L	13	13	100	81000	37000	26000	26000	29000	62000	310000	310000
Magnesium, Dissolved ²	µg/L	13	13	100	200000	12000	5200	5200	5900	160000	1000000	1100000
Magnesium, Total ²	µg/L	13	13	100	200000	12000	5800	5900	6500	160000	1000000	1100000
Potassium, Dissolved ²	µg/L	7	7	100	32000	39000	4000	4000	4100	58000	63000	63400
Potassium, Total ²	µg/L	7	7	100	32000	39000	3700	3700	3800	58000	65000	65000
Sodium, Dissolved ³	µg/L	7	7	100	770000	860000	36000	36000	40000	1600000	1600000	1600000
Sodium, Total ³	µg/L	7	7	100	860000	860000	35000	35000	39000	1600000	2000000	2000000

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

Table 3.6.4. Comparison of Metals Results for EPA P.L. 110-299 and UNDS Engine Wet Exhaust Sampling

Metal	Mean Inboard Propulsion Engine Effluent Concentration (µg/L)	
	EPA P.L. 110-299 Sampling	UNDS Engine Wet Exhaust Sampling
Arsenic, Total	4.5	2.2
Cadmium, Total	Not Detected (Reporting Limit = 1)	0.024
Chromium, Total	1.3	0.33
Copper, Total	18	24
Lead, Total	3.0	0.2
Nickel, Total	4.6	6.8

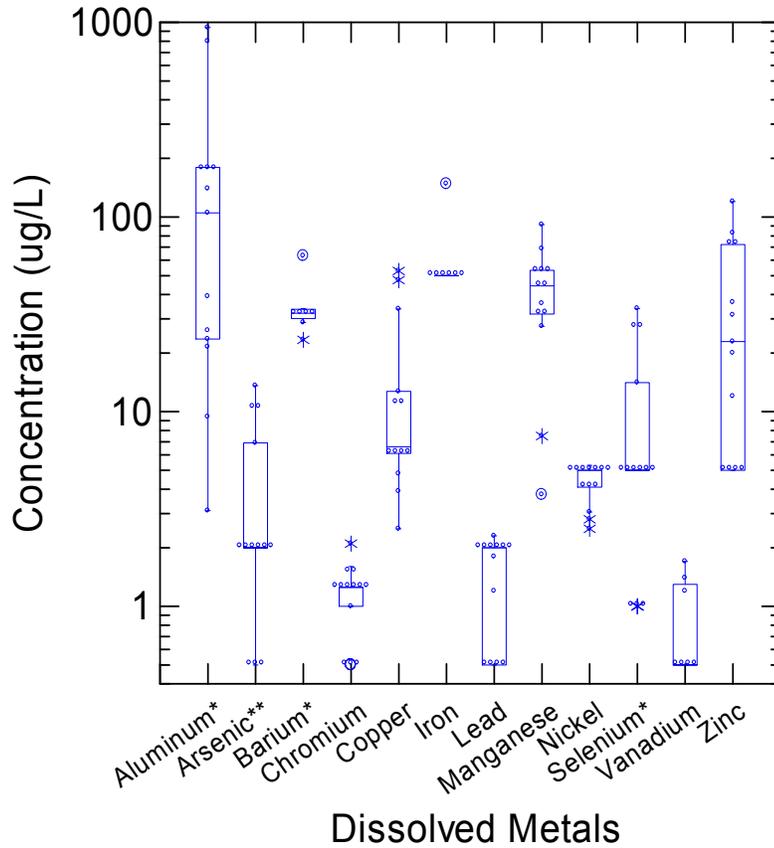


Figure 3.6.2. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Inboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

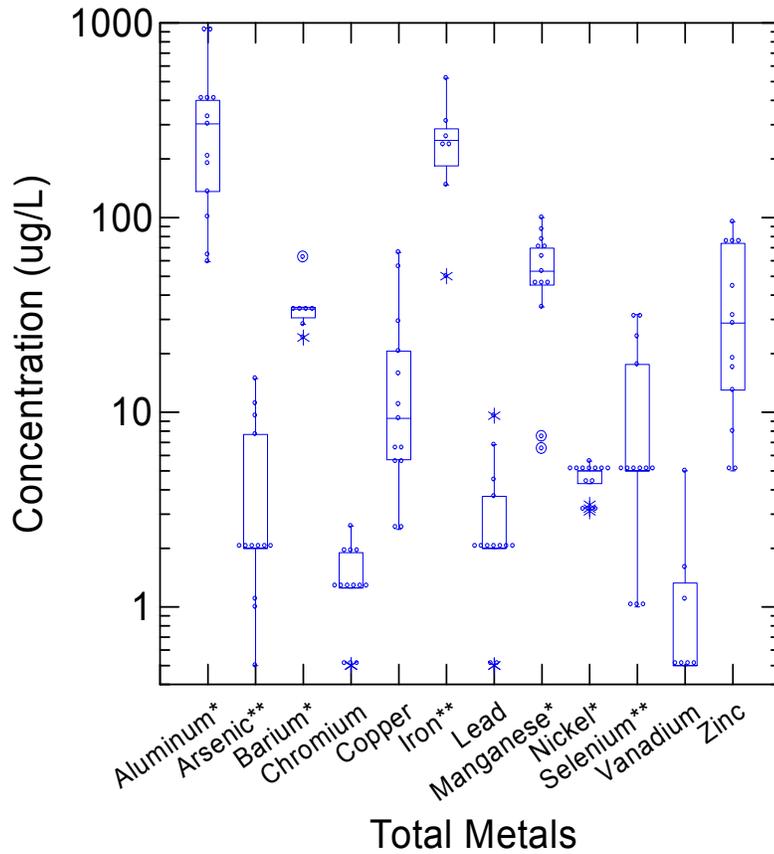


Figure 3.6.3. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Inboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and < 90 percent) by background concentrations in ambient water.

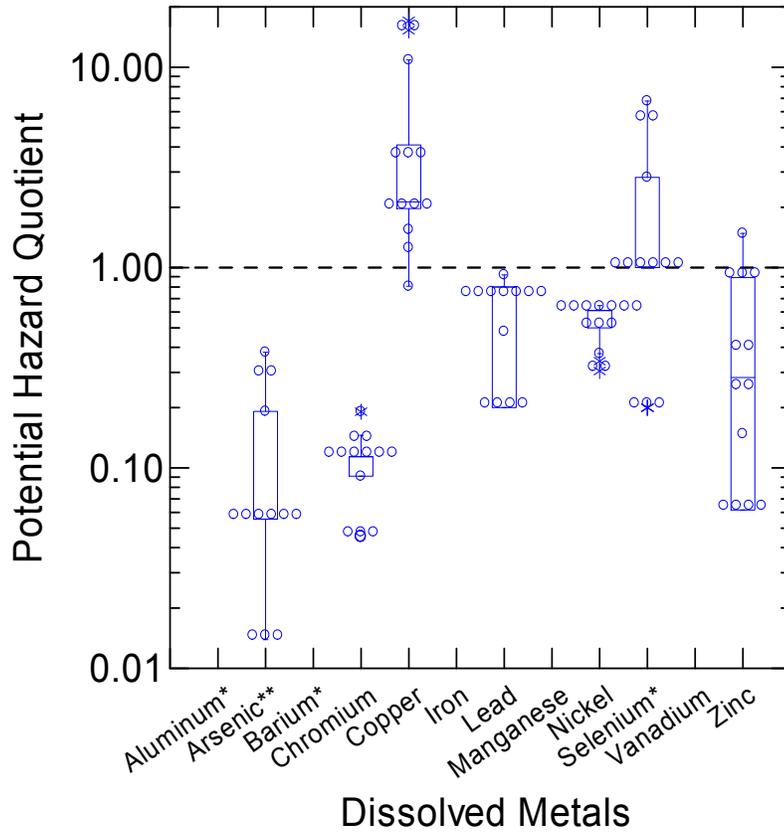


Figure 3.6.4. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Inboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and < 90 percent) by background concentrations in ambient water.

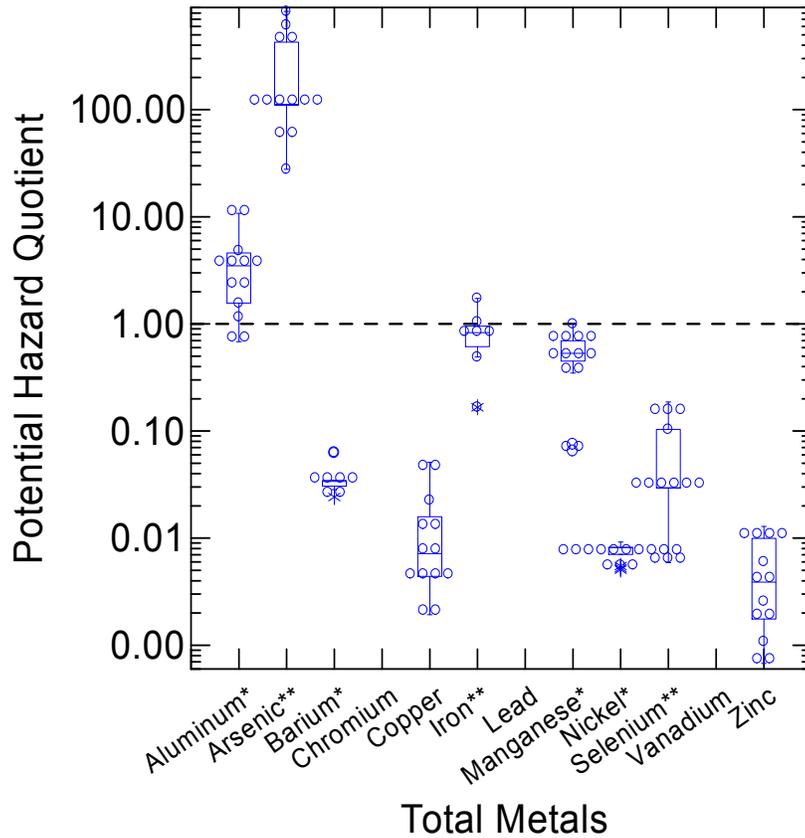


Figure 3.6.5. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Inboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.1.3 Semivolatile Organic Compounds

Inboard propulsion engine effluent samples were analyzed for 76 SVOCs for the sampling conducted as part of the P.L. 110-299 study. Table 3.6.5 presents analytical results for the 31 SVOCs that were detected in one or more engine effluent samples. The detected results are also shown in Figures 3.6.6 and 3.6.7 for analyte concentrations and for PHQs based on the lowest NRWQC or other PHQ screening benchmark where applicable, respectively. EPA analyzed the sample results to determine which SVOCs were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by engine operations.

Many of the detected SVOCs can be classified among the following pollutant classes: polycyclic aromatic hydrocarbons or PAHs (14 analytes), straight-chain hydrocarbons (five analytes), phenol and methyl phenols (five analytes), and phthalates (two analytes). These include all of the SVOCs detected most frequently and at the highest concentrations.

PAHs are present in fuel in small amounts and may be formed as products of incomplete combustion. EPA has identified seven PAHs as probable human carcinogens, six of which were detected in engine effluent: benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, and indeno(1,2,3-cd)pyrene. Most of these compounds exceed a PHQ of 1,000 as shown in Figure 3.6.7.

Phthalates are plasticizers (chemicals added to plastics to make them flexible) and are commonly detected in environmental samples (ATSDR, 2002). Bis(2-ethylhexyl) phthalate was detected at concentration just above the screening benchmark of 1.2 µg/L (human health for consumption of water and aquatic organisms).

Phenol and methyl phenols are present in petroleum products and may also be generated as products of incomplete combustion. Discharges of phenol and methyl phenols are assumed to not to cause any environmental impacts as detected concentrations did not exceed the PHQ screening benchmarks for these analytes. Straight-chain (alkane) hydrocarbons are also components of fuel; none of the straight-chain hydrocarbons detected in engine effluent have a NRWQC or other PHQ screening benchmark, and they are not PBT chemicals

It is important to note that 11 of the detected SVOCs were found only in one sample collected from a recreational vessel (recreational vessels are not study vessels). These included all six of the detected PAHs that are probable human carcinogens, as well as four additional PAHs. Engine effluent from this recreational vessel also contributed the maximum detected concentrations for six additional analytes, including several additional PAHs as well as four of the five detected phenol/methyl phenols. (Maximum sample concentrations for 2,4-dimethylphenol, straight-chain hydrocarbons, and phthalates were contributed by other vessels.) This recreational vessel was the only sampled vessel that used gasoline as fuel rather than diesel;

however, the lack of replication precludes any determination as to whether fuel type is a critical factor for engine effluent characteristics. In addition, the engines on this vessel were dewinterized immediately prior to sampling. The lack of engine operation for several months prior to sampling could have contributed to engine effluent characteristics.

Comparing study sampling results with the results from the engine wet exhaust sampling conducted for the UNDS program reveals some similarities. For the LCPL, phenol and bis(2-ethylhexyl)phthalate were the only detected SVOCs; however, the presence of bis(2-ethylhexyl)phthalate in LCPL effluent may be due to laboratory contamination and so data for the purpose of comparison are not shown in this report. For the RIB, phenol was the only detected SVOC. EPA determined that phenol was present at concentrations statistically greater than background. Table 3.6.6 compares the phenol results from this study to those from the UNDS program. Note that the UNDS program used a different methodology to calculate mean concentrations.

Table 3.6.5. Results of Inboard Propulsion Engine Sample Analyses for SVOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
1,2-Diethyl-Cyclobutane	µg/L	1	1	100	10							
1,6-Dimethyl naphthalene	µg/L	1	1	100	35							
1-Methylnaphthalene	µg/L	2	2	100	13	24	3.2	3.2	3.2	24	24	24
2,4-Dimethylphenol	µg/L	12	4	33	3.7					2.4	16	22
2-Methylnaphthalene	µg/L	8	6	75	17	13			0.90	36	46	46
Acenaphthene	µg/L	12	1	8.3	2.0						1.5	2.2
Acenaphthylene	µg/L	12	3	25	7.0					1.7	44	61
Anthracene	µg/L	12	1	8.3	3.3						12	18
Benzo(a)anthracene	µg/L	12	1	8.3	3.3						13	18
Benzo(a)pyrene	µg/L	12	1	8.3	3.2						11	16
Benzo(b)fluoranthene	µg/L	12	1	8.3	2.8						7.8	11
Benzo(g,h,i)perylene	µg/L	12	1	8.3	2.6						6.9	9.8
Benzo(k)fluoranthene	µg/L	12	1	8.3	3.1						11	15
Bis(2-ethylhexyl) phthalate	µg/L	12	4	33	1.7					1.2	1.8	20
Chrysene	µg/L	12	1	8.3	3.3						12	18
Di-n-butyl phthalate	µg/L	12	6	50	1.7	1.1					3.5	3.8
Eicosane	µg/L	2	2	100	19	28	10	10	10	28	28	28
Fluorene	µg/L	12	4	33	3.5					2.8	14	18
Heptadecane	µg/L	4	4	100	29	27	3.5	3.5	3.8 ⁶	67	80	80
Indeno(1,2,3-cd)pyrene	µg/L	12	1	8.3	2.5						5.6	8.0
m-Cresol	µg/L	4	1	25	13					34	45	45
Naphthalene	µg/L	12	10	8.3	30	6.6			1.9	34	160	210
n-Hexadecane	µg/L	3	3	100	26	17	3.1	3.1	3.1	57	57	57
Nonadecane	µg/L	2	2	100	27	38	15	15	15	38	38	38
Nonanoic Acid	µg/L	1	1	100	11							
o-Cresol	µg/L	3	3	100	6.6	5.8	5.7	5.7	5.7	8.4	8.4	8.4

Table 3.6.5. Results of Inboard Propulsion Engine Sample Analyses for SVOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Octadecane	µg/L	2	2	100	10	17	3.1	3.1	3.1	17	17	17
p-Cresol	µg/L	7	5	71	26	17				24	110	110
Phenanthrene	µg/L	12	3	25	6.1					1.3	35	48
Phenol	µg/L	12	8	67	27	3.7				37	140	170
Pyrene	µg/L	12	1	8.3	6.6						40	57

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

Table 3.6.6. Comparison of Phenol Results for EPA P.L. 110-299 and UNDS Engine Wet Exhaust Sampling

Analyte	Mean Inboard Propulsion Engine Effluent Concentration (µg/L)		
	EPA P.L. 110-299 Sampling	UNDS Small Boat Engine Wet Exhaust Sampling	
		LCPL	RIB
Phenol	27	13	14

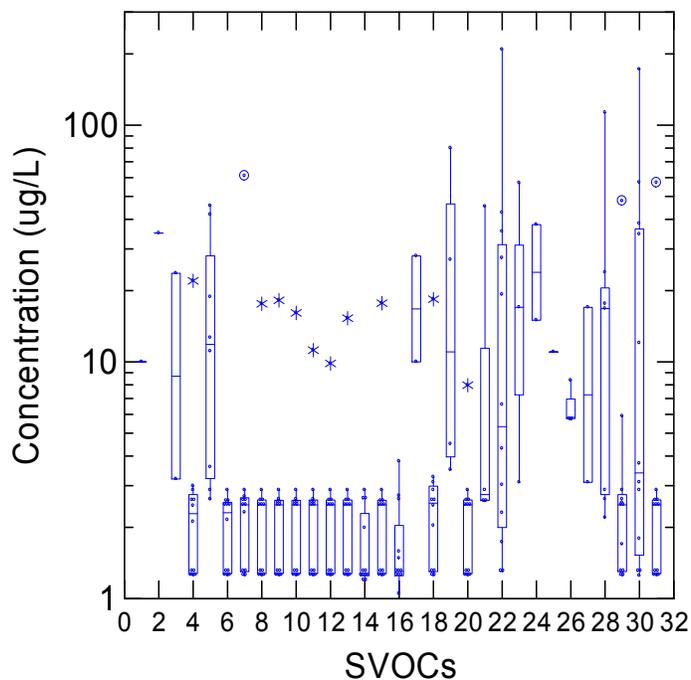


Figure 3.6.6. Box and Dot Density Plot of SVOC Concentrations Measured in P.L. 110-299 Study Samples of Inboard Propulsion Engine Effluent SVOCs are identified as follows:

- | | | |
|-----------------------------|----------------------------------|--------------------|
| (1) 1,2-Diethyl-Cyclobutane | (12) Benzo(g,h,i)perylene | (23) n-Hexadecane |
| (2) 1,6-dimethylnaphthalene | (13) Benzo(k)fluoranthene | (24) Nonadecane |
| (3) 1-methylnaphthalene | (14) Bis(2-ethylhexyl) phthalate | (25) Nonanoic Acid |
| (4) 2,4-Dimethylphenol | (15) Chrysene | (26) o-Cresol |
| (5) 2-Methylnaphthalene | (16) Di-n-butyl phthalate | (27) Octadecane |
| (6) Acenaphthene | (17) Eicosane | (28) p-Cresol |
| (7) Acenaphthylene | (18) Fluorene | (29) Phenanthrene |
| (8) Anthracene | (19) Heptadecane | (30) Phenol |
| (9) Benzo(a)anthracene | (20) Indeno(1,2,3-cd)pyrene | (31) Pyrene |
| (10) Benzo(a)pyrene | (21) m-Cresol | |
| (11) Benzo(b)fluoranthene | (22) Naphthalene | |

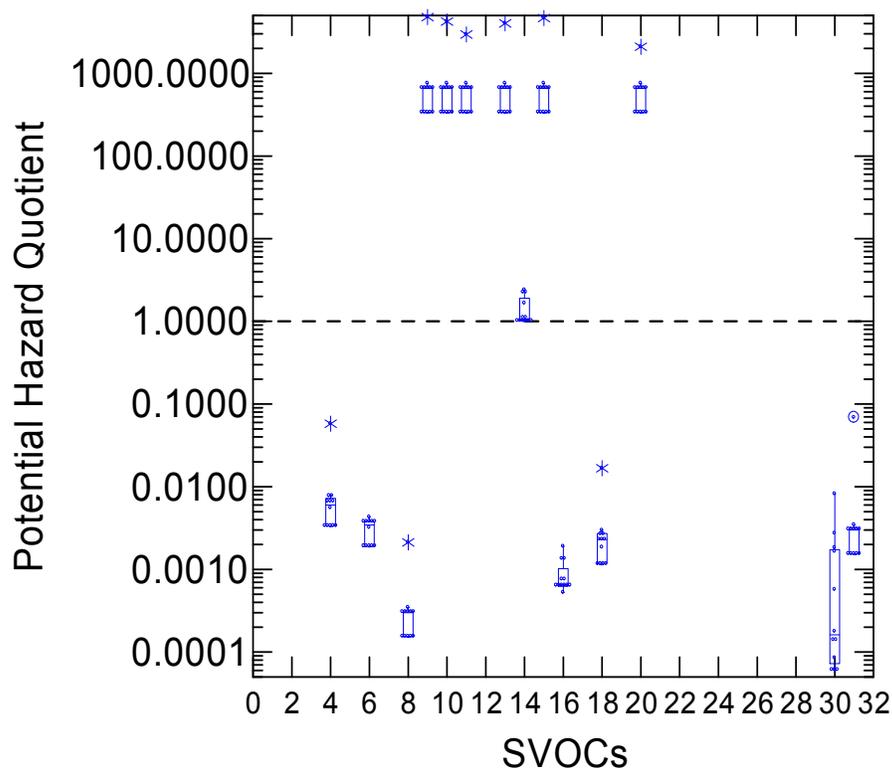


Figure 3.6.7. Box and Dot Density Plot of Potential Hazard Quotients for SVOCs in P.L. 110-299 Study Samples of Inboard Propulsion Engine Effluent SVOCs are identified as follows:

- | | | |
|-----------------------------|----------------------------------|--------------------|
| (1) 1,2-Diethyl-Cyclobutane | (12) Benzo(g,h,i)perylene | (23) n-Hexadecane |
| (2) 1,6-dimethylnaphthalene | (13) Benzo(k)fluoranthene | (24) Nonadecane |
| (3) 1-methylnaphthalene | (14) Bis(2-ethylhexyl) phthalate | (25) Nonanoic Acid |
| (4) 2,4-Dimethylphenol | (15) Chrysene | (26) o-Cresol |
| (5) 2-Methylnaphthalene | (16) Di-n-butyl phthalate | (27) Octadecane |
| (6) Acenaphthene | (17) Eicosane | (28) p-Cresol |
| (7) Acenaphthylene | (18) Fluorene | (29) Phenanthrene |
| (8) Anthracene | (19) Heptadecane | (30) Phenol |
| (9) Benzo(a)anthracene | (20) Indeno(1,2,3-cd)pyrene | (31) Pyrene |
| (10) Benzo(a)pyrene | (21) m-Cresol | |
| (11) Benzo(b)fluoranthene | (22) Naphthalene | |

3.2.6.1.4 Volatile Organic Compounds

Inboard propulsion engine effluent samples were analyzed for 84 VOCs. Table 3.6.7 presents analytical results for the 38 VOCs that were detected in one or more engine effluent samples. The detected results are also shown in Figures 3.6.8 and 3.6.9 for analyte concentrations and for PHQs based on the lowest NRWQC or other PHQ screening benchmark where applicable, respectively. EPA analyzed the sample results to determine which VOCs were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by engine operations.

Approximately one-third of the detected VOCs were frequently detected in engine effluent (i.e., greater than half of the sampled vessels). Some of these compounds are volatile constituents of fuel, specifically benzene, toluene, ethylbenzene, and xylene. Others are trimethylbenzenes, which are naturally present in fuel, and ketones, which may be formed as products of incomplete combustion. Among these compounds, only benzene and toluene have an NRWQC. Approximately half of the detected benzene concentrations exceeded the PHQ screening benchmark of 2.2 µg/L (human health for consumption of water and aquatic organisms), including discharges from one vessel that exceeded the benchmark by a factor of more than 50 (the next highest concentration that exceeded the benchmark was by less than a factor of 4) (see Figure 3.6.9). None of the detected toluene concentrations exceeded the PHQ screening benchmark of 1,300 µg/L (human health for consumption of water and aquatic organisms).

Approximately one-third of the detected VOCs were detected relatively infrequently (i.e., detected in fewer than half the sampled vessels). Among these compounds, only chloroform and methylene chloride have an NRWQC. However, none of the detected concentrations for these two analytes exceeded the PHQ screening benchmarks of 5.7 µg/L (human health for consumption of water and aquatic organisms) and 1,300 µg/L (human health for consumption of water and aquatic organisms), respectively.

The final third of detected VOCs were detected in engine effluent from only one or two vessels. None of these analytes have an NRWQC or are PBT chemicals, and are therefore not expected to have the potential to pose risk to human health or the environment.

It is important to note the maximum detected concentrations for 11 of the VOCs were found in samples collected from a recreational vessel (recreational vessels are not study vessels). These included benzene, toluene, ethylbenzene, xylene, and trimethylbenzenes (maximum sample concentrations for ketones were contributed by other vessels). As noted above, this recreational vessel was the only sampled vessel that used gasoline as fuel rather than diesel; however, this data set is too small to demonstrate whether fuel type is a critical factor for engine effluent characteristics. In addition, the engines on this vessel were dewinterized immediately

prior to sampling. The lack of engine operation for several months prior to sampling could have contributed to engine effluent characteristics.

Comparing these sampling results with the results from the engine wet exhaust sampling conducted for the UNDS program reveals some similarities. For the LCPL, no VOCs were detected. For the RIB, 1,2,3-trimethylbenzene, and 1,3,5-trimethylbenzene were the detected VOCs. However, EPA determined that the trimethylbenzenes were not present at concentrations statistically greater than background.

Table 3.6.7. Results of Inboard Propulsion Engine Sample Analyses for VOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ²	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ²
(2-Methyl-1-Propenyl)-Benzene	µg/L	1	1	1.00	3.2							
1,2,3,4-Tetrahydro-5-Methylnaphthalene	µg/L	1	1	1.00	24							
1,2,3,4-Tetrahydro-6-Methylnaphthalene	µg/L	2	2	1.00	19	33	4.6	4.6	4.6	33	33	33
1,2,3,4-Tetrahydro naphthalene	µg/L	2	2	1.00	12	22	3.2	3.2	3.2	22	22	22
1,2,4-Trimethylbenzene	µg/L	7	7	1.00	6.1	1.8	0.12	0.12	0.30	3.8	32	32
1,3,5-Trimethylbenzene	µg/L	7	5	0.71	2.1	0.70				0.92	7.2	7.2
1,3-Methylnaphthalene	µg/L	1	1	1.00	4.2							
1,7-Methylnaphthalene	µg/L	1	1	1.00	19							
2,3-Dihydro-4-Methyl-1H-Indene	µg/L	1	1	1.00	53							
2,6-Dimethylnaphthalene	µg/L	1	1	1.00	41							
2-Butanone	µg/L	7	7	1.00	17	7.8	2.6	2.6	3.0	32	40	40
2-Ethyl-1,3,5-Trimethyl-Benzene	µg/L	1	1	1.00	4.4							
2-Ethyl-1,4-Dimethyl-Benzene	µg/L	1	1	1.00	20							
2-Hexanone	µg/L	7	5	0.71	2.1	1.1					3.2	3.2
4-Isopropyltoluene	µg/L	7	3	0.43	1.8					1.3	1.4	1.4
4-Methyl-2-Pentanone	µg/L	7	3	0.43	1.9					0.80	1.6	1.6
Acetone	µg/L	8	8	1.00	58	34	6.0	6.0	15 ⁹	110	150	150
Benzene	µg/L	12	9	0.75	12	2.3			0.17	5.4	84	120
Benzocycloheptatriene	µg/L	1	1	1.00	39							
Biphenyl	µg/L	8	6	0.75	4.1	3.0			0.27	4.5	12	12
Chloroform	µg/L	12	4	0.33	1.7					1.0	2.1	2.1
Dimethoxymethane	µg/L	1	1	1.00	89							
Ethylbenzene	µg/L	12	6	0.50	2.3	0.10				0.83	12	16
Isopropylbenzene	µg/L	7	3	0.43	1.9					1.4	1.5	1.5

Table 3.6.7. Results of Inboard Propulsion Engine Sample Analyses for VOCs ¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ²	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ²
m-,p-Xylene (sum of isomers)	µg/L	7	7	1.00	11	1.8	0.30	0.30	0.90	2.0	70	70
Methyl acetate	µg/L	7	1	0.14	2.4						1.5	1.5
Methyl tertiary butyl ether (MTBE)	µg/L	7	1	0.14	2.4						1.9	1.9
Methylene chloride	µg/L	12	4	0.33	1.2					0.14	0.19	0.20
n-Butylbenzene	µg/L	7	3	0.43	1.8					1.0	1.1	1.1
n-Pentadecane	µg/L	2	2	100	24	31	16	16	16	31	31	31
n-Propylbenzene	µg/L	7	4	57	1.5	0.15				0.40	2.2	2.2
n-Tetradecane	µg/L	2	2	100	20	33	6.5	6.5	6.5	33	33	33
O-Xylene	µg/L	7	7	100	5.5	1.5	0.20	0.20	0.65	1.8	32	32
sec-Butylbenzene	µg/L	7	1	14	2.3						1.4	1.4
Styrene	µg/L	7	7	100	6.1	1.3	0.13	0.13	0.50	3.4	35	35
Toluene	µg/L	12	8	67	11	0.90				2.8	80	110
Trichlorofluoromethane	µg/L	12	1	8.3	2.1						1.9	2.7
Vinyl acetate	µg/L	7	1	14	2.4						1.9	1.9

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

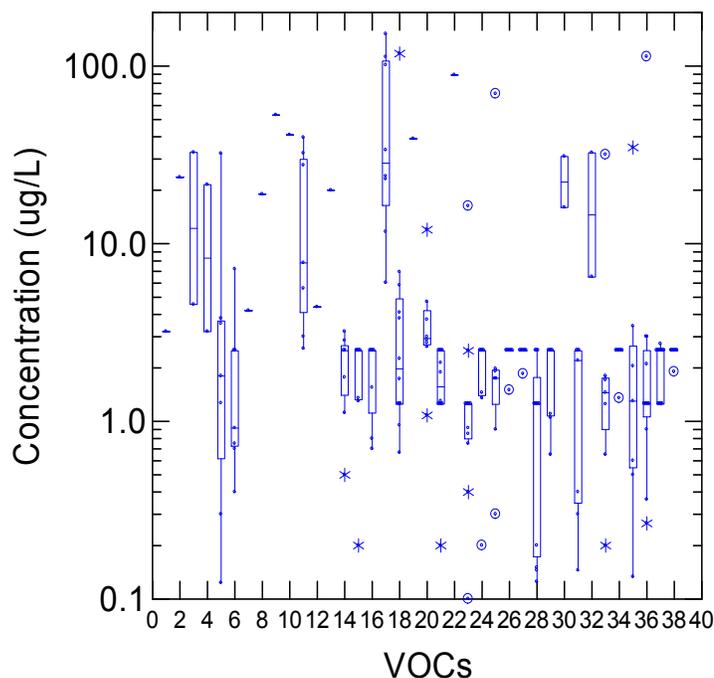


Figure 3.6.8. Box and Dot Density Plot of Volatile Organic Compounds Concentrations Measured in P.L. 110-299 Study Samples of Inboard Propulsion Engine Effluent VOCs are identified as follows:

- | | | |
|--|--------------------------------------|---|
| (1) (2-Methyl-1-Propenyl)-Benzene | (12) 2-Ethyl-1,3,5-Trimethyl-Benzene | (25) m-,p-Xylene (sum of isomers) |
| (2) 1,2,3,4-Tetrahydro-5-Methylnaphthalene | (13) 2-Ethyl-1,4-Dimethyl-Benzene | (26) Methyl acetate |
| (3) 1,2,3,4-Tetrahydro-6-Methylnaphthalene | (14) 2-Hexanone, | (27) Methyl tertiary butyl ether (MTBE) |
| (4) 1,2,3,4-Tetrahydronaphthalene | (15) 4-Isopropyltoluene | (28) Methylene chloride |
| (5) 1,2,4-Trimethylbenzene | (16) 4-Methyl-2-Pentanone | (29) n-Butylbenzene, |
| (6) 1,3,5-Trimethylbenzene | (17) Acetone | (30) n-Pentadecane |
| (7) 1,3-Methylnaphthalene | (18) Benzene | (31) n-Propylbenzene |
| (8) 1,7-Methylnaphthalene | (19) Benzocycloheptatriene | (32) n-Tetradecane |
| (9) 2,3-Dihydro-4-Methyl-1H-Indene | (20) Biphenyl | (33) O-Xylene |
| (10) 2,6-dimethylnaphthalene | (21) Chloroform | (34) sec-Butylbenzene |
| (11) 2-Butanone | (22) Dimethoxymethane | (35) Styrene |
| | (23) Ethylbenzene | (36) Toluene |
| | (24) Isopropylbenzene | (37) Trichlorofluoromethane |
| | | (38) Vinyl acetate |

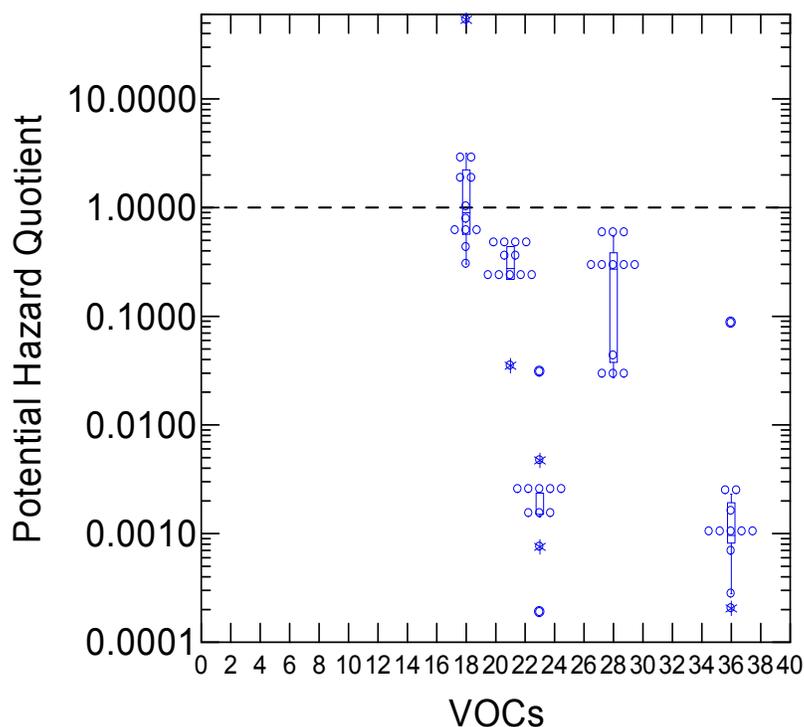


Figure 3.6.9. Box and Dot Density Plot of Potential Hazard Quotients for Volatile Organic Compounds in P.L. 110-299 Study Samples of Inboard Propulsion Engine Effluent VOCs are identified as follows:

- | | | |
|--|--------------------------------------|---|
| (1) (2-Methyl-1-Propenyl)-Benzene | (12) 2-Ethyl-1,3,5-Trimethyl-Benzene | (25) m-,p-Xylene (sum of isomers) |
| (2) 1,2,3,4-Tetrahydro-5-Methylnaphthalene | (13) 2-Ethyl-1,4-Dimethyl-Benzene | (26) Methyl acetate |
| (3) 1,2,3,4-Tetrahydro-6-Methylnaphthalene | (14) 2-Hexanone | (27) Methyl tertiary butyl ether (MTBE) |
| (4) 1,2,3,4-Tetrahydronaphthalene | (15) 4-Isopropyltoluene | (28) Methylene chloride |
| (5) 1,2,4-Trimethylbenzene | (16) 4-Methyl-2-Pentanone | (29) n-Butylbenzene |
| (6) 1,3,5-Trimethylbenzene | (17) Acetone | (30) n-Pentadecane |
| (7) 1,3-Methylnaphthalene | (18) Benzene | (31) n-Propylbenzene |
| (8) 1,7-Methylnaphthalene | (19) Benzocycloheptatriene | (32) n-Tetradecane |
| (9) 2,3-Dihydro-4-Methyl-1H-Indene | (20) Biphenyl | (33) O-Xylene |
| (10) 2,6-dimethylnaphthalene | (21) Chloroform | (34) sec-Butylbenzene |
| (11) 2-Butanone | (22) Dimethoxymethane | (35) Styrene |
| | (23) Ethylbenzene | (36) Toluene |
| | (24) Isopropylbenzene | (37) Trichlorofluoromethane |
| | | (38) Vinyl acetate |

3.2.6.2 Outboard Propulsion Engines

For this study, EPA collected samples of discharges from outboard propulsion engines on six vessels: four tow/salvage vessels and two research vessels (see Table 3.6.1 above). It is important to note that all six of these vessels were confirmed by the vessel owners/operators to be manufactured for pleasure. Vessels manufactured for pleasure are defined as recreational vessels under P.L. 110-288 and are not study vessels. Nonetheless, EPA has included the results here assuming they are representative of vessels with outboard propulsion engines, some of which may be study vessels. EPA also collected these results so that the Agency could later compare results between study vessels and recreational vessels if appropriate.



The Outboard Engine of a Tow and Salvage Vessel

3.2.6.2.1 Classical Pollutants

Outboard propulsion engine effluent samples were analyzed for 11 classical pollutants. Table 3.6.8 presents analytical results for the eight classical pollutants that were detected in one

or more engine effluent samples. The detected results are also shown in Figure 3.6.10. EPA analyzed the sample results to determine which pollutants concentrations were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations (see footnotes on table and figure). The remainder of this subsection discusses those pollutants found to be contributed primarily by engine operations.

Temperature increases in engine effluent above background were less than 5°C for all vessels. Engine effluent temperatures were only slightly higher (approximately 1°C) when vessels were operated at higher power levels as compared to idling.

Oil and grease (measured as HEM) was not detected in any of the engine effluent samples. SGT-HEM was detected in only two of 16 grab samples at concentrations significantly less than the reporting limit (sample concentrations of 0.86 mg/L and 0.94 mg/L, compared to reporting limit of 10 mg/L).

Table 3.6.8. Results of Outboard Propulsion Engine Sample Analyses for Classical Pollutants¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Conductivity ³	mS/cm	5	5	100	167	17	7.3	7.3	9.2	22	25	25
Dissolved Oxygen ²	mg/L	5	5	100	6.2	6.3	5.7	5.7	5.9	6.4	6.4	6.4
pH ²	SU	6	6	100	7.4	7.3	7.0	7.0	7.1	7.7	7.9	7.9
Salinity ³	ppt	5	5	100	11	12	3.9	3.9	7.3	14	16	16
Silica Gel Treated HEM (SGT-HEM)	mg/L	6	2	33	4.5					3.6	3.6	3.6
Temperature	C	6	6	100	28	31	14	14	25	31	32	32
Total Suspended Solids (TSS) ³	mg/L	6	2	33	8.1					13	17	17
Turbidity ²	NTU	6	6	100	13	10	6.5	6.5	8.0	21	25	25

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

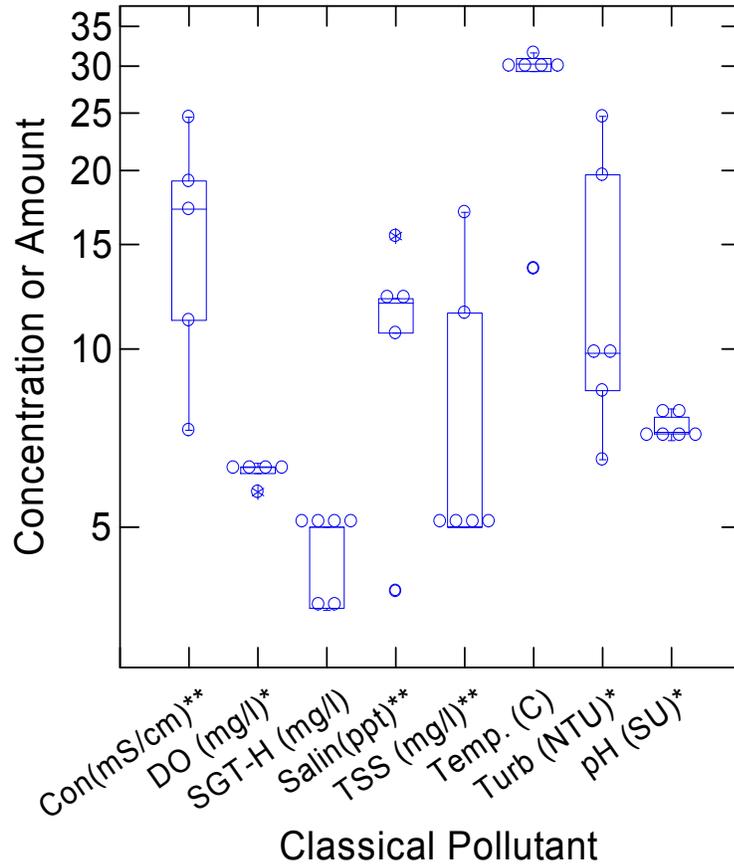


Figure 3.6.10. Box and Dot Density Plot of Classical Pollutant Values Measured in Samples of Outboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.2.2 Metals

Outboard propulsion engine effluent samples were analyzed for dissolved and total concentrations of 22 metals. Table 3.6.9 presents analytical results for the 14 metals that were detected in one or more engine effluent samples. The detected results are also shown in Figures 3.6.11 and 3.6.12 for dissolved and total metals, respectively. Figures 3.6.13 and 3.6.14 display the distribution of PHQs based on the screening benchmark for each of the dissolved and total metals. EPA analyzed the sample results to determine which metals were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations (see footnotes on table and figures). The remainder of this subsection discusses those metals found to be contributed primarily by engine operations.

Dissolved and total concentrations for both vanadium and zinc are similar, which indicates that engine operations contribute these metals in dissolved rather than particulate form. Dissolved zinc was detected in all engine effluent samples at concentrations two to five times the reporting limit; none of the concentrations exceed the PHQ screening benchmark (a value of 81 µg/L based on the chronic saltwater criterion for aquatic life). Dissolved vanadium was detected in engine effluent from four of the six sampled vessels at concentrations close to the reporting limit (<2 times reporting limit of 1 µg/L). Dissolved vanadium does not have an NRWQC or other PHQ screening benchmark.

Total arsenic was detected in engine effluent from five of the six sampled vessels at concentrations two to five times the reporting limit (reporting limit = 8 µg/L). Although total arsenic is contributed primarily by background ambient concentrations (an estimated one-third of total arsenic is contributed by engine operations and two-thirds by background ambient concentrations), detected concentrations exceed the very low PHQ screening benchmark (0.018 µg/L for protection of human health) even after subtracting the potential contribution from ambient waters.

Dissolved selenium was detected in all engine effluent samples at concentrations ranging from 2.4 to 100 µg/L. Although dissolved selenium is contributed primarily by background ambient concentrations (an estimated one-third of dissolved selenium is contributed by engine operations and two-thirds by background ambient concentrations), detected concentrations exceed the PHQ screening benchmark (5 µg/L for protection of chronic toxicity to freshwater aquatic life) even after subtracting the potential contribution from ambient waters.

Finally, concentrations in engine effluent discharges for dissolved arsenic, dissolved copper, total aluminum, total iron, and total manganese that exceed benchmark concentrations appear to be caused by background concentrations in ambient water and not by engine operations.

Table 3.6.9. Results of Outboard Propulsion Engine Sample Analyses for Metals¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Heavy and Other Metals												
Aluminum, Dissolved ²	µg/L	6	5	83	7.4	8.2			5.1	9.7	10	10
Aluminum, Total ²	µg/L	6	6	100	160	58	34	34	38	320	570	570
Arsenic, Dissolved ³	µg/L	6	5	83	25	32			8.6	37	41	41
Arsenic, Total ³	µg/L	6	5	83	24	30			9.9	34	41	41
Barium, Dissolved ²	µg/L	6	6	100	25	15	13	13	14	41	57	57
Barium, Total ²	µg/L	6	6	100	27	16	14	14	14	43	65	65
Copper, Dissolved ³	µg/L	6	6	100	3.3	3.4	2.8	2.8	3.1	3.5	3.5	3.5
Copper, Total ³	µg/L	6	5	83	3.6	3.4			2.4	3.8	3.9	3.9
Iron, Total ³	µg/L	6	2	33	200					460	560	560
Manganese, Dissolved ²	µg/L	6	6	100	6.0	5.4	1.0	1.0	1.2	10	18	18
Manganese, Total ³	µg/L	6	6	100	57	35	29	29	29	91	140	140
Nickel, Dissolved ³	µg/L	6	6	100	5.6	6.6	3.2	3.2	3.6	7.1	7.4	7.4
Nickel, Total ³	µg/L	6	6	100	11	7.7	3.3	3.3	5.6	14	33	33
Selenium, Dissolved ³	µg/L	6	6	100	76	97	2.4	2.4	24	110	130	130
Selenium, Total ³	µg/L	6	6	100	72	94	1.5	1.5	22	100	120	120
Vanadium, Dissolved	µg/L	6	2	33	0.87					1.5	1.8	1.8
Vanadium, Total	µg/L	6	3	50	1.7	1.2					1.5	1.5
Zinc, Dissolved ³	µg/L	6	6	100	11	11	3.5	3.5	7.1	14	19	19
Zinc, Total	µg/L	6	6	100	11	8.3	3.5	3.5	6.4	14	28	28
Cationic Metals												
Calcium, Dissolved ³	µg/L	6	6	100	130000	160000	43000	43000	50000	170000	200000	200000
Calcium, Total ³	µg/L	6	6	100	130000	160000	43000	43000	51000	170000	190000	190000
Magnesium, Dissolved ³	µg/L	6	6	100	380000	480000	31000	31000	120000	520000	630000	630000

Table 3.6.9. Results of Outboard Propulsion Engine Sample Analyses for Metals¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Magnesium, Total ³	µg/L	6	6	100	370000	480000	31000	31000	120000	520000	600000	600000
Potassium, Dissolved ³	µg/L	6	6	100	130000	160000	11000	11000	48000	190000	220000	220000
Potassium, Total ³	µg/L	6	6	100	130000	160000	11000	11000	48000	180000	210000	210000
Sodium, Dissolved ³	µg/L	6	6	100	2900000	3800000	220000	220000	1000000	4100000	4700000	4700000
Sodium, Total ³	µg/L	6	6	100	2900000	3700000	220000	220000	1100000	4000000	4700000	4700000

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

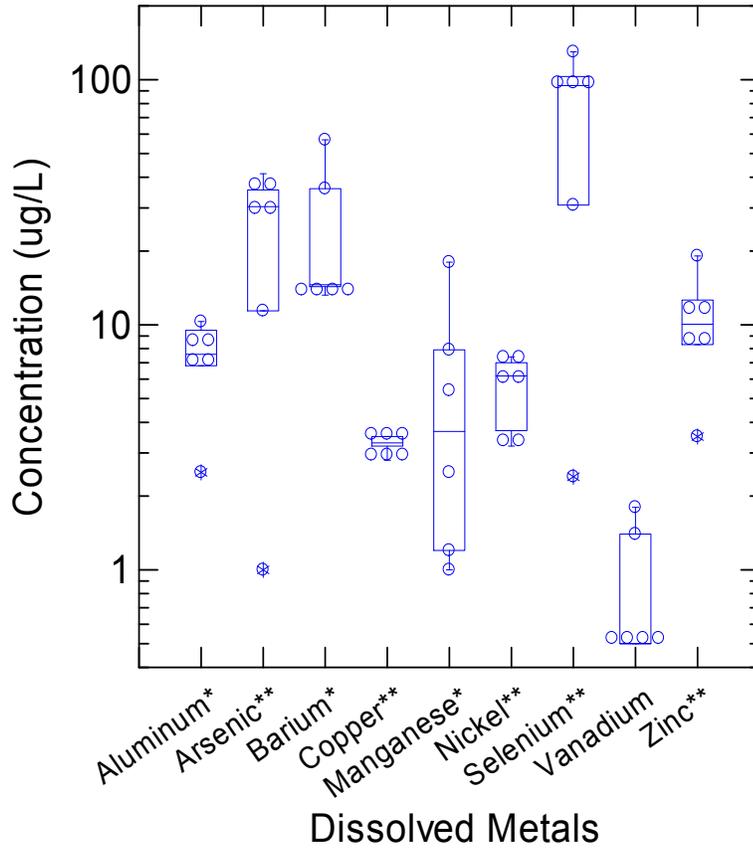


Figure 3.6.11. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Outboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and < 90 percent) by background concentrations in ambient water.

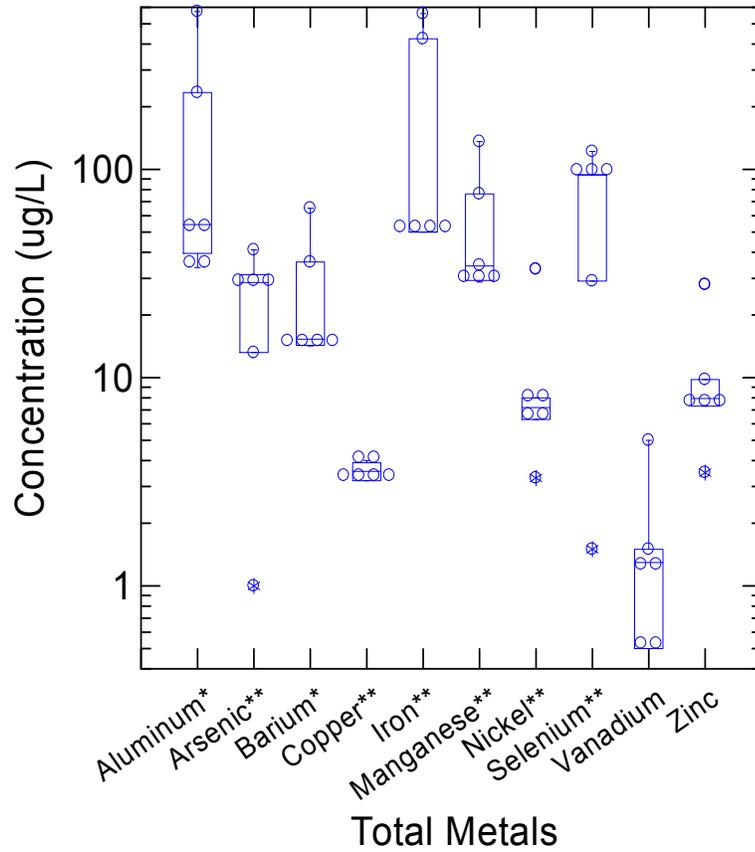


Figure 3.6.12. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Outboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and < 90 percent) by background concentrations in ambient water.

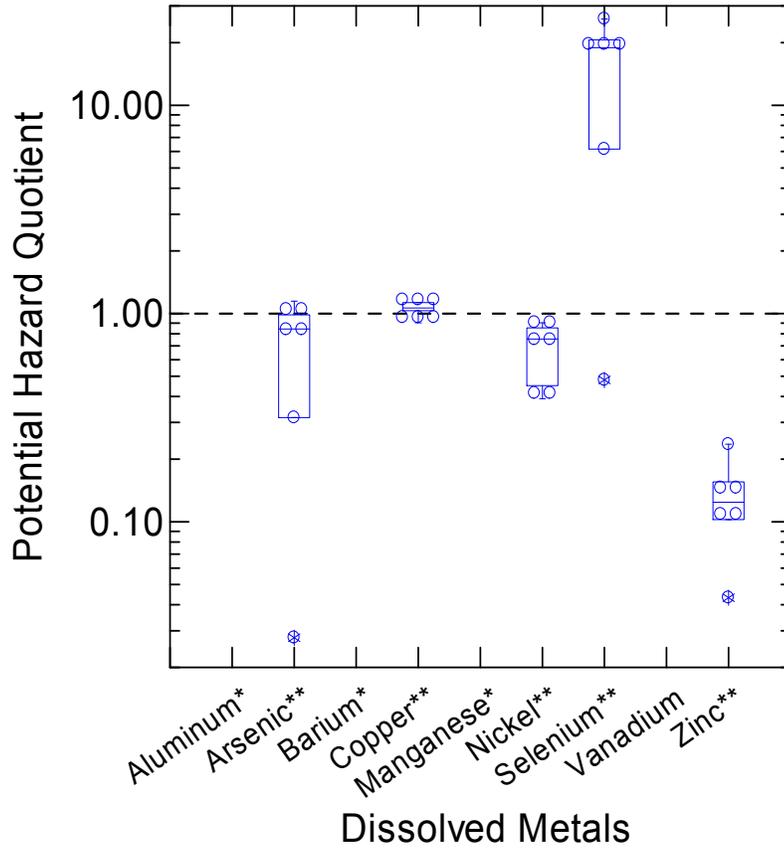


Figure 3.6.13. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Outboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

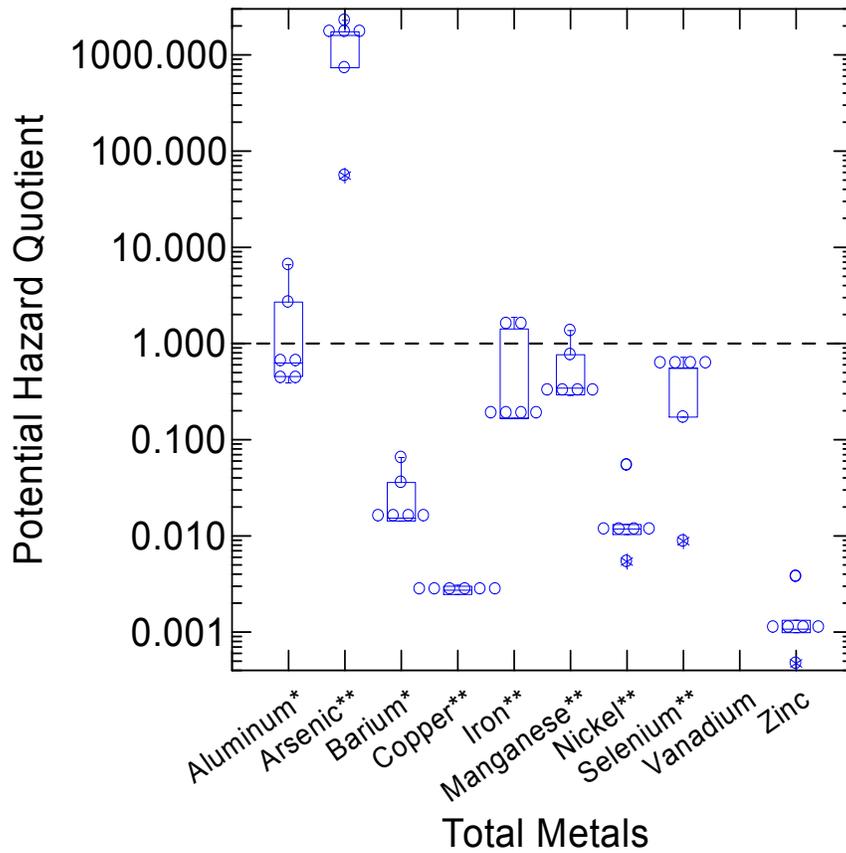


Figure 3.6.14. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Outboard Propulsion Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.2.3 Semivolatile Organic Compounds

Outboard propulsion engine effluent samples were analyzed for 62 SVOCs. Table 3.6.10 presents analytical results for the seven SVOCs that were detected in one or more engine effluent samples. The detected results are also shown in Figure 3.6.15. EPA analyzed the sample results to determine which SVOCs were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by engine operations.

The detected SVOCs can be classified among the following pollutant classes: polycyclic aromatic hydrocarbons (PAHs) (one analyte), phenol and methyl phenols (four analytes), phthalates (one analyte), and methylnaphthalenes (one analyte). All of these SVOCs were frequently detected in engine effluent (i.e., more than half of the sampled vessels). However, all of the detected SVOC concentrations are well below any applicable PHQ screening benchmarks. For example, the maximum PHQ for any of the detected SVOCs was 2,4-dimethylphenol with a PHQ of approximately 0.005. Therefore, SVOCs in engine effluent are highly unlikely to have the potential to pose risk to human health or the environment.

Table 3.6.10. Results of Outboard Propulsion Engine Sample Analyses for SVOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
2,4-Dimethylphenol	µg/L	6	1	17	2.5					0.49	2.0	2.0
2-Methylnaphthalene	µg/L	6	2	33	2.4					1.5	2.8	2.8
Di-n-butyl phthalate	µg/L	6	3	50	2.4	1.2					3.5	3.5
m-Cresol	µg/L	6	2	33	2.6					1.9	4.2	4.2
Naphthalene	µg/L	6	5	83	7.8	2.0			1.4	12	35	35
p-Cresol	µg/L	6	2	33	3.7				2.3	3.9	9.8	9.8
Phenol	µg/L	6	2	33	4.6					5.9	14	14

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

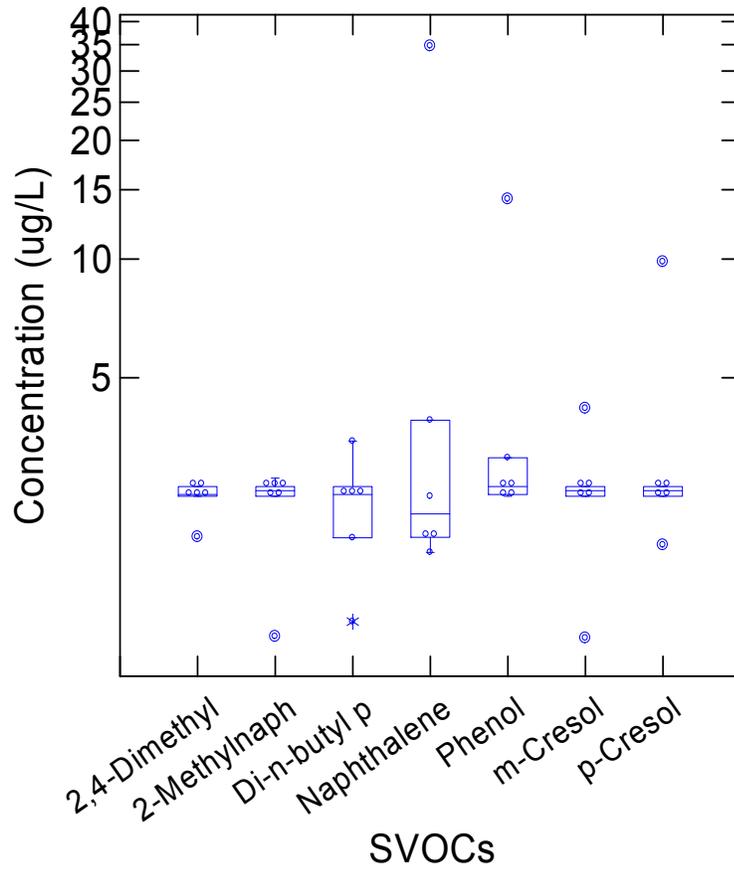


Figure 3.6.15. Box and Dot Density Plot of SVOC Concentrations Measured in Samples of Outboard Propulsion Engine Effluent Note: two analyte names were truncated: 2-Methylnaphalene and Di-n-butyl phthalate.

3.2.6.2.4 Volatile Organic Compounds

Outboard propulsion engine effluent samples were analyzed for 70 VOCs. Table 3.6.11 presents analytical results for the 18 VOCs that were detected in one or more engine effluent samples. The detected results are also shown in Figures 3.6.16 and 3.6.17 for analyte concentrations and for PHQs based on the lowest NRWQC or other PHQ screening benchmark where applicable, respectively. EPA analyzed the sample results to determine which VOCs were contributed primarily by engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by engine operations. Some of these compounds are volatile constituents of fuel, specifically benzene, toluene, ethylbenzene, and xylene. Others are trimethylbenzenes, which are naturally present in fuel, and one is a ketone, which may be formed as a product of incomplete combustion. Among these compounds, benzene, ethylbenzene, and toluene have an NRWQC. Most of the detected benzene concentrations exceeded the PHQ screening benchmark of 2.2 µg/L (human health for consumption of water and aquatic organisms), including discharges from the two research vessels that exceed the benchmark by factors of five and 28. None of the detected ethylbenzene and toluene concentrations exceeded the PHQ screening benchmarks.

The final one-third of the detected VOCs were detected relatively infrequently (i.e., detected in fewer than half the sampled vessels). Among these compounds, only methylene chloride has an NRWQC. However, none of the detected methylene chlorine concentrations exceeded the screening benchmark.

Table 3.6.11. Results of Outboard Propulsion Engine Sample Analyses for VOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ²	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ²
1,2,4-Trimethylbenzene	µg/L	6	6	100	13	2.3	0.30	0.30	0.53	24	63	63
1,3,5-Trimethylbenzene	µg/L	6	5	83	4.6	1.9			0.75	6.5	18	18
2-Butanone	µg/L	6	2	33	3.8					3.8	12	12
2-Hexanone	µg/L	6	1	17	2.5					0.56	2.3	2.3
4-Methyl-2-Pentanone	µg/L	6	1	17	2.3					0.35	1.4	1.4
Acetone	µg/L	6	5	83	7.8	2.5			1.4	11	34	34
Benzene	µg/L	6	6	100	13	2.4	0.13	0.13	0.76	24	62	62
Cyclohexane	µg/L	6	1	17	2.4					0.41	1.7	1.7
Ethylbenzene	µg/L	6	6	100	8.2	2.1	0.90	0.90	0.92	14	38	38
Isopropylbenzene	µg/L	6	2	33	2.4					1.3	3.8	3.8
m-,p-Xylene (sum of isomers)	µg/L	6	6	100	28	3.4	0.33	0.33	0.43	52	140	140
Methyl tertiary butyl ether (MTBE)	µg/L	6	1	17	2.3					0.34	1.4	1.4
Methylcyclohexane	µg/L	6	1	17	2.3					0.36	1.5	1.5
Methylene chloride	µg/L	6	5	83	0.58	0.20			0.15	0.20	0.20	0.20
n-Propylbenzene	µg/L	6	4	67	3.2	1.7					9.4	9.4
O-Xylene	µg/L	6	6	100	15	4.0	0.17	0.17	0.43	26	70	70
Styrene	µg/L	6	5	83	4.9	3.4			0.22	6.6	16	16
Toluene	µg/L	6	6	100	52	3.8	0.40	0.40	0.75 ^{3,6}	98	260	260

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

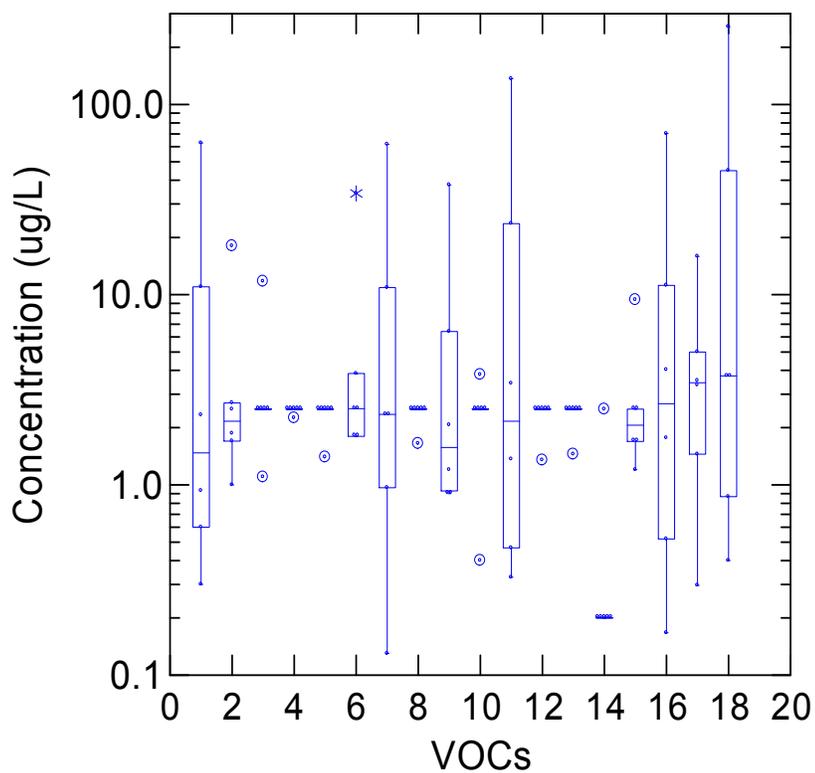


Figure 3.6.16. Box and Dot Density Plot of Volatile Organic Compounds Concentrations Measured in Samples of Outboard Propulsion Engine Effluent VOCs are identified as follows:

- | | | |
|----------------------------|---|-------------------------|
| (1) 1,2,4-Trimethylbenzene | (8) Cyclohexane | (13) Methylcyclohexane |
| (2) 1,3,5-Trimethylbenzene | (9) Ethylbenzene | (14) Methylene chloride |
| (3) 2-Butanone | (10) Isopropylbenzene | (15) n-Propylbenzene |
| (4) 2-Hexanone | (11) m-,p-Xylene (sum of isomers) | (16) O-Xylene |
| (5) 4-Methyl-2-Pentanone | (12) Methyl tertiary butyl ether (MTBE) | (17) Styrene |
| (6) Acetone | | (18) Toluene |
| (7) Benzene | | |

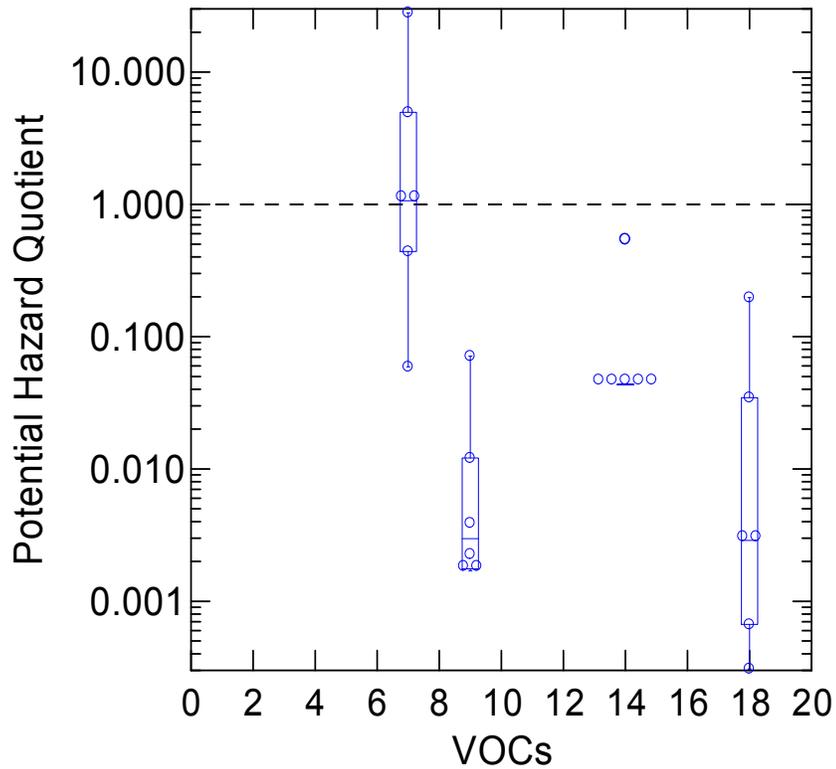


Figure 3.6.17. Box and Dot Density Plot of Potential Hazard Quotients for Volatile Organic Compounds in Samples of Outboard Propulsion Engine Effluent VOCs are identified as follows:

- | | | |
|----------------------------|---|-------------------------|
| (1) 1,2,4-Trimethylbenzene | (8) Cyclohexane | (13) Methylcyclohexane |
| (2) 1,3,5-Trimethylbenzene | (9) Ethylbenzene | (14) Methylene chloride |
| (3) 2-Butanone | (10) Isopropylbenzene | (15) n-Propylbenzene |
| (4) 2-Hexanone | (11) m-,p-Xylene (sum of isomers) | (16) O-Xylene |
| (5) 4-Methyl-2-Pentanone | (12) Methyl tertiary butyl ether (MTBE) | (17) Styrene |
| (6) Acetone | | (18) Toluene |
| (7) Benzene | | |

3.2.6.3 Generator Engines

For this study, EPA collected cooling water discharge samples from engines on generator sets onboard five vessels: a fishing vessel, a fire boat, two tour boats, and a water taxi (Table 3.6.1). These engines included both direct and indirect cooling discharges from both gasoline- and diesel-fueled engines.



The Generator on a Fire Boat

3.2.6.3.1 Classical Pollutants

Table 3.6.12 presents analytical results for 11 classical pollutants detected in samples of discharges from generator engines (all classical pollutants analyzed for were detected). The detected results are also shown in Figure 3.6.18. EPA analyzed the sample results to determine which pollutant concentrations were contributed primarily by generator engine operations and which were contributed primarily by background ambient concentrations (see footnotes on table and figure). The remainder of this subsection discusses those classical pollutants found to be contributed primarily by generator engine operations.

Temperature increases in generator engine effluent above background were approximately 5°C for the fishing vessel, fire boat, and water taxi. For the two tour boats, temperature increases were 9 and 13°C.

Oil and grease (measured as HEM) was detected in engine effluent from three of the five sampled generators; however, detected concentrations were low, ranging from less than the reporting limit to just above the reporting limit (reporting limit = 5 mg/L). All sample results were well below the 33 CFR Part 151.10 prohibition of the discharge of oil and oily mixtures with an oil content greater than 15 ppm into seawater from vessels.

Sulfide was detected in only one of five samples at a concentration of 0.012 mg/L, which is slightly above the reporting limit of 0.01 mg/L. This concentration is six times greater than the most conservative PHQ screening benchmark – a 2006 NRWQC value of 0.002 mg/L for the protection of aquatic life. Sulfide could be present due to entrainment in fuel, as a product of incomplete combustion, or due to formation within the biofilm in the cooling system piping.

TRC was detected in only one generator engine effluent sample collected from a water taxi at a concentration of 0.15 mg/L. This detected concentration is 20 times greater than the PHQ screening benchmark of 0.0075 mg/L. There is no known source of TRC for this vessel as background concentration of the ambient water at this location was below detection and the generator did not use service water that might contain TRC.

Table 3.6.12. Results of Generator Engine Sample Analyses for Classical Pollutants¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ⁴	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ⁴
Conductivity ²	mS/cm	4	4	100	11	0.31	0.23	0.23	0.23	32	43	43
Dissolved Oxygen ²	mg/L	4	4	100	5.3	6.2	1.9	1.9	2.6	7.7	8.2	8.2
Hexane Extractable Material (HEM)	mg/L	5	3	60	2.9	1.1					5.8	5.8
pH ²	SU	5	5	100	6.5	6.6	5.7	5.7	5.9	7.0	7.0	7.0
Salinity ³	ppt	4	4	100	6.5	0.20	0.10	0.10	0.10	19	25	25
Silica Gel Treated HEM (SGT-HEM)	mg/L	5	1	20	4.2				4.3	0.55	1.1	1.1
Sulfide	mg/L	4	1	25	0.0068					0.0090	0.012	0.012
Temperature	C	5	5	100	21	20	18	18	19	24	26	26
Total Residual Chlorine	mg/L	5	1	20	0.060					0.075	0.15	0.15
Total Suspended Solids (TSS) ³	mg/L	4	3	75	9.0	12			2.1	13	13	13
Turbidity ²	NTU	5	5	100	27	33	1.3	1.3	14	38	39	39

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

(3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

(4) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

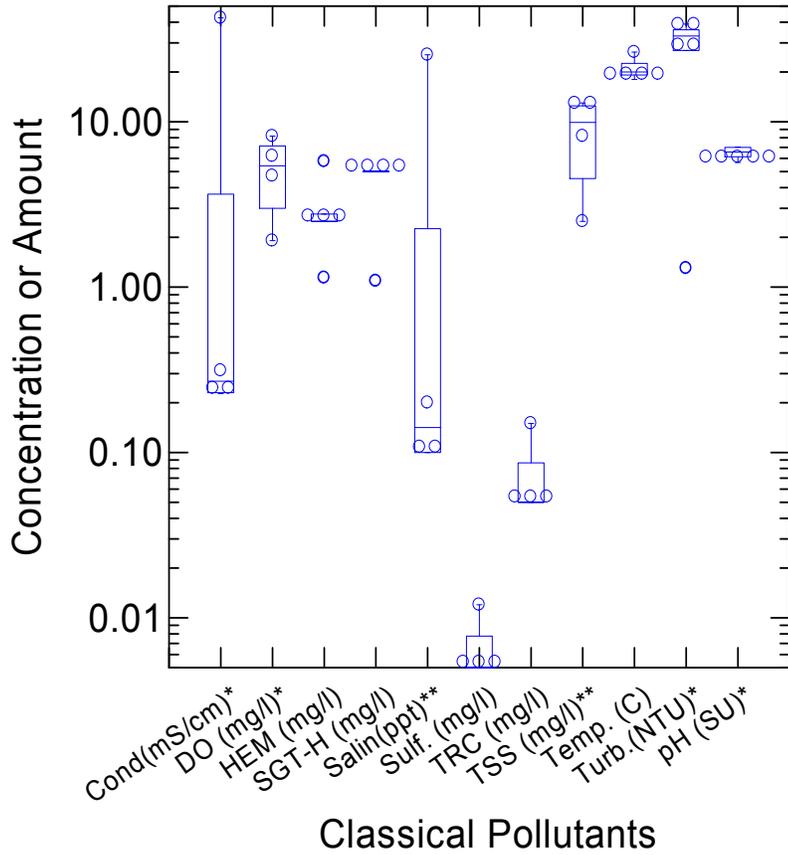


Figure 3.6.18. Box and Dot Density Plot of Classical Pollutant Values Measured in Samples of Generator Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.3.2 Metals

Generator engine effluent samples were analyzed for dissolved and total concentrations of 22 metals. Table 3.6.13 presents analytical results for the 11 metals that were detected. The detected results are also shown in Figures 3.6.19 and 3.6.20 for dissolved and total metals, respectively. Figures 3.6.21 and 3.6.22 display the distribution of PHQs based on the screening benchmark for each of the dissolved and total metals. EPA analyzed the sample results to determine which metals were contributed primarily by generator engine operations and which were contributed primarily by background ambient concentrations (see footnotes on table and figures). The remainder of this subsection discusses those metals found to be contributed primarily by generator engine operations.

Dissolved and total metals concentrations are similar, which indicates that engine operations contribute metals in dissolved rather than particulate form. Dissolved copper was detected in all five generator effluent samples at concentrations ranging from 2.4 to 13 µg/L. Total copper was detected in two of the five samples at concentrations of 2.4 and 11 µg/L (reporting limit = 5 µg/L). Dissolved copper concentrations exceeded the PHQ screening benchmark of 3.1 µg/L (2006 NRWQC saltwater chronic aquatic life criterion) by as much as five times. In contrast, none of the total copper concentrations exceeded the PHQ screening benchmark of 1,300 µg/L (human health criterion based on consumption of water and aquatic organisms).

Dissolved manganese was detected in four of the five generator engine effluent samples. Manganese was predominantly in particulate form in background ambient water; therefore, dissolved manganese concentrations in engine effluent samples are assumed to be contributed by engine operations. NRWQCs or other PHQ screening benchmarks have not been determined for dissolved manganese.

Dissolved zinc was detected in two of the five generator engine effluent samples. Detected concentrations were 21 to 29 µg/L, which are substantially lower than the screening benchmark of 81 µg/L (2006 NRWQC saltwater chronic aquatic life criterion).

Finally, concentrations in generator engine effluent discharges that exceed benchmark concentrations for total aluminum are likely caused or heavily influenced by higher concentrations in ambient water (which exceeded benchmark concentrations).

Table 3.6.13. Results of Generator Engine Sample Analyses for Metals¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ⁴	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ⁴
Heavy and Other Metals												
Aluminum, Dissolved ²	µg/L	5	5	100	280	160	11	11	86	540	870	870
Aluminum, Total ²	µg/L	5	5	100	420	390	120	120	220	640	890	890
Barium, Dissolved ²	µg/L	1	1	100	37							
Barium, Total ²	µg/L	1	1	100	37							
Copper, Dissolved	µg/L	5	5	100	6.5	5.6	2.4	2.4	3.9	9.5	13	13
Copper, Total	µg/L	5	2	40	4.2					6.7	11	11
Iron, Total ²	µg/L	1	1	100	200							
Manganese, Dissolved	µg/L	5	4	80	33	36			16	49	53	53
Manganese, Total ³	µg/L	5	4	80	40	43			17	59	63	63
Nickel, Dissolved ³	µg/L	5	1	20	4.5					1.4	2.7	2.7
Nickel, Total ³	µg/L	5	1	20	3.5					1.4	2.7	2.7
Zinc, Dissolved	µg/L	5	2	40	13					25	29	29
Zinc, Total ³	µg/L	5	3	60	11	12				15	19	19
Cationic Metals												
Calcium, Dissolved ²	µg/L	5	5	100	80000	26000	23000	23000	24000	160000	290000	290000
Calcium, Total ²	µg/L	5	5	100	82000	28000	27000	27000	27000	160000	290000	290000
Magnesium, Dissolved ²	µg/L	5	5	100	180000	5900	5200	5200	5200	440000	870000	870000
Magnesium, Total ²	µg/L	5	5	100	180000	6600	5900	5900	5950	450000	890000	890000
Potassium, Dissolved ²	µg/L	1	1	100	4000							
Potassium, Total ²	µg/L	1	1	100	3600							
Sodium, Dissolved ²	µg/L	1	1	100	37000							
Sodium, Total ²	µg/L	1	1	100	36000							

Notes:

- (1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.
- (2) Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.
- (3) Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.
- (4) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

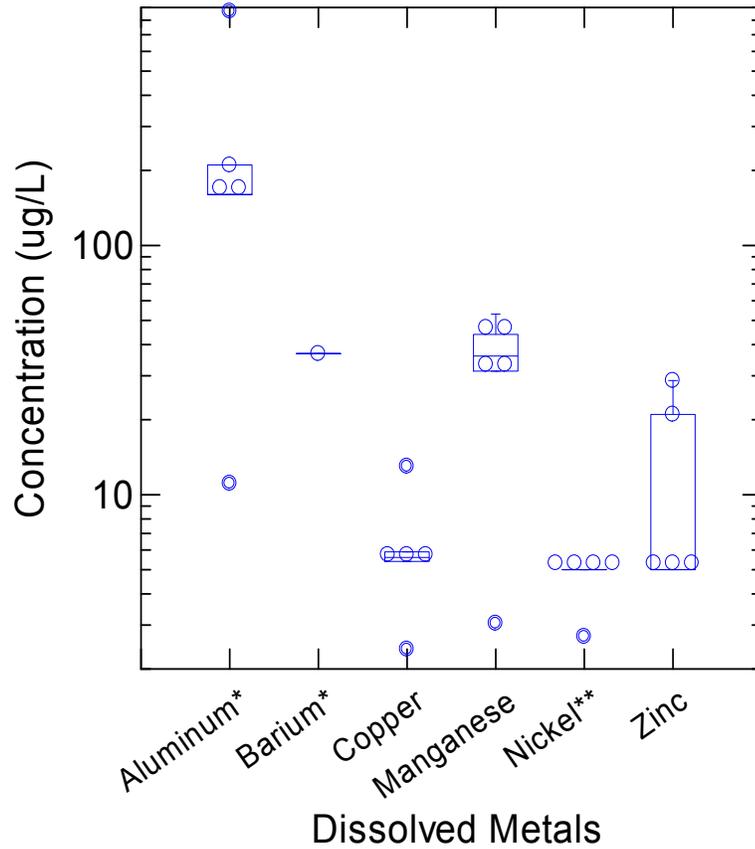


Figure 3.6.19. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Generator Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

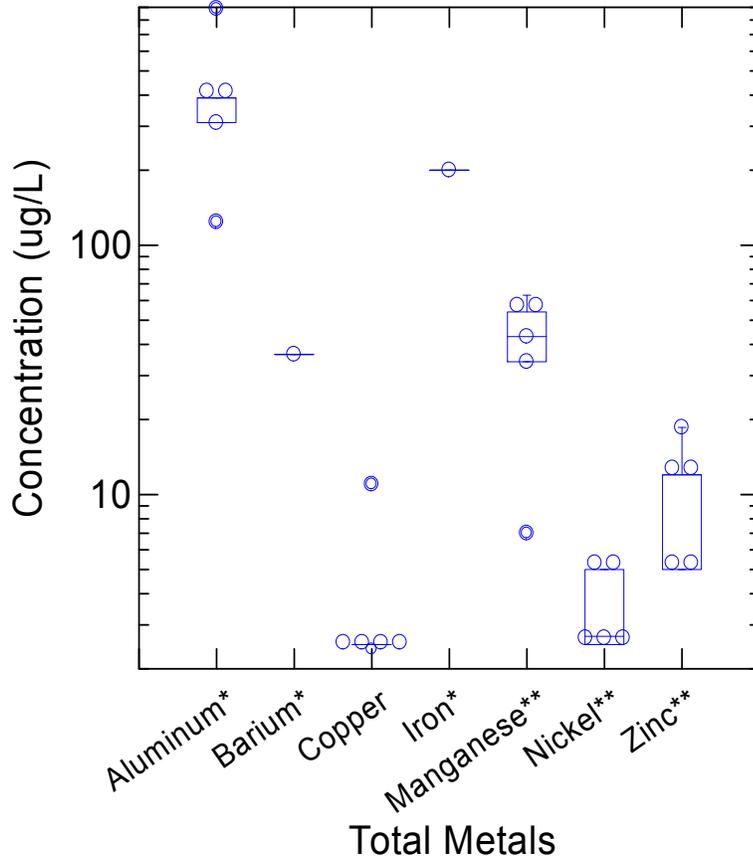


Figure 3.6.20. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Generator Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

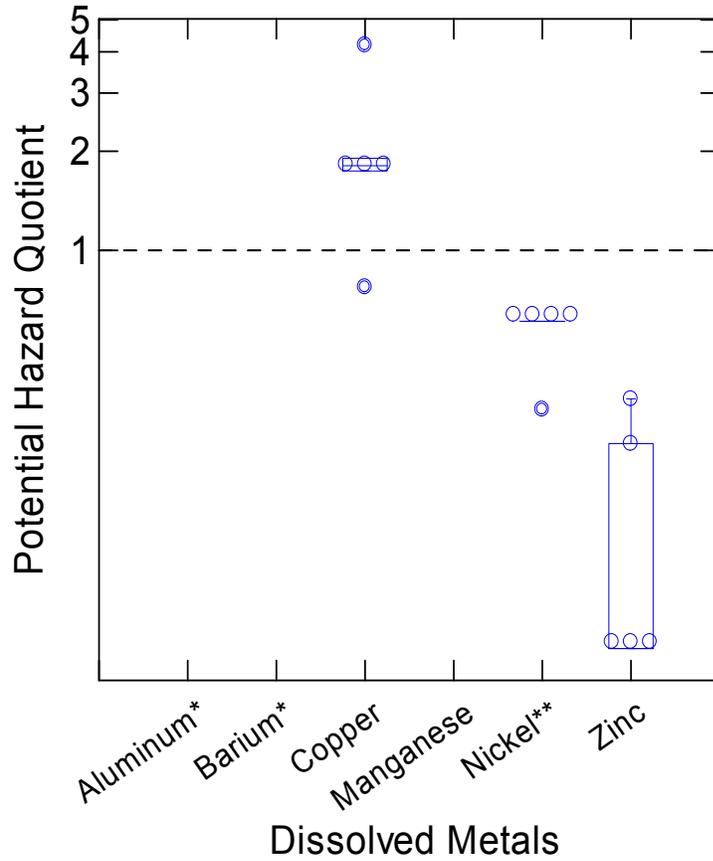


Figure 3.6.21. Box and Dot Density Plot of Potential Hazard Quotients for Dissolved Metals in Samples of Generator Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

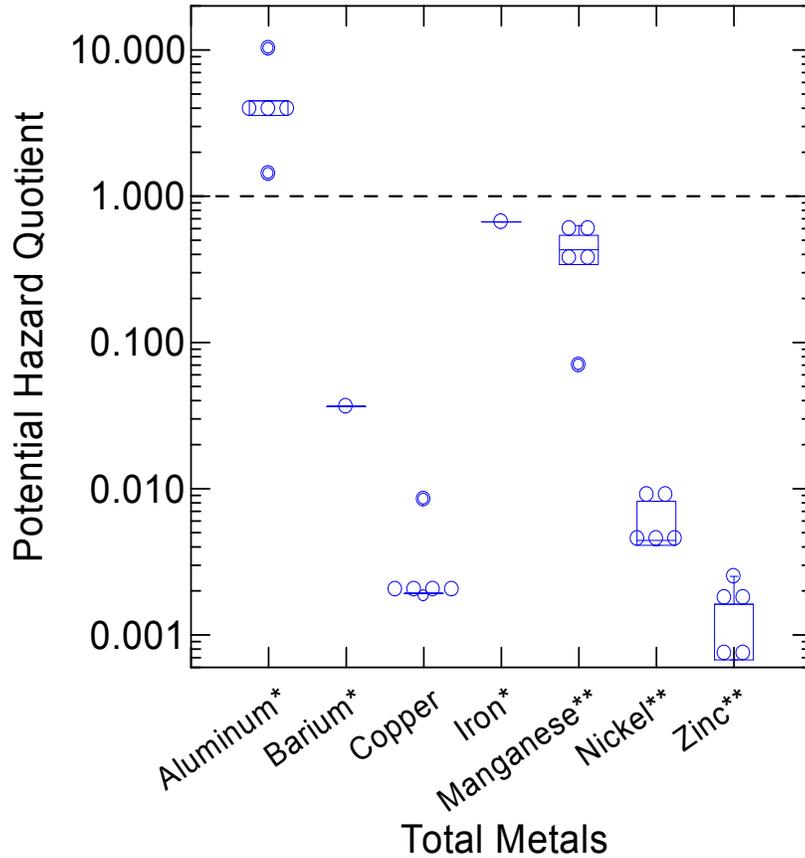


Figure 3.6.22. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Generator Engine Effluent

* Sample concentrations were almost completely accounted for (≥ 90 percent) by background concentrations in ambient water.

** Sample concentrations were predominantly accounted for (≥ 50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.3.3 Semivolatile Organic Compounds

Generator engine effluent samples were analyzed for 79 SVOCs. Table 3.6.14 presents analytical results for the 26 SVOCs that were detected in one or more engine effluent samples (14 of the detected SVOCs were analyzed for and detected in only one generator effluent sample). The detected results are shown in Figures 3.6.23 and 3.6.24 for analyte concentrations and PHQs based on the lowest applicable NRWQC or other PHQ screening benchmark. EPA analyzed the sample results to determine which SVOCs were contributed primarily by generator engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by generator engine operations.

Many of the detected SVOCs can be classified among the following pollutant classes: PAHs (five analytes), straight-chain hydrocarbons (six analytes), phenol and methyl phenols (five analytes), and phthalates (two analytes). These include all of the SVOCs analyzed for and detected most frequently and at the highest concentrations.

PAHs are present in fuels in small amounts and may be formed as products of incomplete combustion. However, none of the detected PAH concentrations exceeded the screening benchmarks for these analytes, indicating that they are unlikely to have the potential to pose risk to human health or the environment.

Straight-chain (alkane) hydrocarbons are also components of fuel. None of these analytes has an NRWQC or other PHQ screening benchmark, and they are not PBT chemicals. Therefore, the straight-chain hydrocarbons detected in engine effluent are unlikely to have the potential to pose risk to human health or the environment.

Phenol and methyl phenols are also present in petroleum products and may also be generated as products of incomplete combustion. Discharges of phenol and methyl phenols are assumed not to result in any environmental impacts as detected concentrations did not exceed the screening benchmarks for these analytes.

Phthalates are plasticizers (chemicals added to plastics to make them flexible) and are commonly detected in environmental samples (ATSDR, 2002). Bis(2-ethylhexyl) phthalate was detected at concentration just above the screening benchmark of 1.2 µg/L (human health for consumption of water and aquatic organisms).

The generator engine effluent sample from the fire boat contained the maximum concentration of 12 of the detected SVOCs. These include all five of the detected PAHs, four of the five detected phenols and methyl phenols, and both of the detected phthalates. The generator effluent sample from a tour boat contained the maximum concentration of all six of the detected straight-chain hydrocarbons.

Table 3.6.14. Results of Generator Engine Sample Analyses for SVOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ²	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ²
1-methylnaphthalene	µg/L	3	3	100	6.7	5.4	3.8	3.8	3.8	11	11	11
2,4-Dimethylphenol	µg/L	5	1	20	2.6					4.0	7.9	7.9
2-Cyclopenten1-one	µg/L	2	2	100	8.5	13	3.9	3.9	3.9	13	13	13
2-Hydroxy-Benzaldehyde	µg/L	2	2	100	11	17	4.3	4.3	4.3	17	17	17
2-Methylnaphthalene	µg/L	4	4	100	16	10	4.6	4.6	5.5	32	40	40
2-Naphthalene carboxaldehyde	µg/L	2	2	100	18	20	16	16	16	20	20	20
3-Methyl-Benzaldehyde	µg/L	1	1	100	18							
3-Methylphenol	µg/L	1	1	100	12							
3-Phenyl-2-Propenal	µg/L	1	1	100	8.1							
Acenaphthylene	µg/L	5	1	20	1.8					1.9	3.8	3.8
Acetophenone	µg/L	1	1	100	11							
Bis(2-ethylhexyl) phthalate	µg/L	5	1	20	1.3					0.63	1.3	1.3
Di-n-butyl phthalate	µg/L	5	1	20	1.3					0.59	1.2	1.2
Eicosane	µg/L	1	1	100	32							
Fluorene	µg/L	5	1	20	2.0					2.4	4.9	4.9
Heneicosane	µg/L	1	1	100	22							
Heptadecane	µg/L	3	3	100	30	8.9	4.1	4.1	4.1	76	76	76
m-Cresol	µg/L	1	1	100	18							
Naphthalene	µg/L	5	4	80	17	7.3			2.3	36	61	61
n-Hexadecane	µg/L	1	1	100	46							
Nonadecane	µg/L	1	1	100	40							
Octadecane	µg/L	1	1	100	44							
p-Cresol	µg/L	1	1	100	43							

Table 3.6.14. Results of Generator Engine Sample Analyses for SVOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc. ²	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ²
Phenanthrene	µg/L	5	3	60	3.9	3.2					9.7	9.7
Phenol	µg/L	5	4	80	23	13			2.1	48	75	75
Pyrene	µg/L	5	1	20	1.4				6.8	0.90	1.8	1.8

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

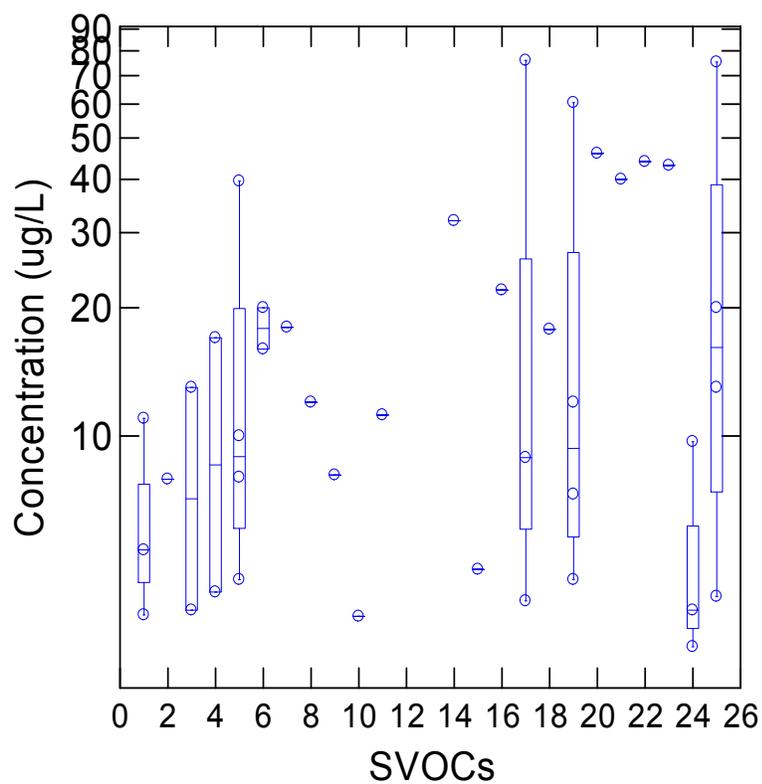


Figure 3.6.23. Box and Dot Density Plot of SVOC Concentrations Measured in Samples of Generator Engine Effluent SVOCs are identified as follows:

- | | | |
|---------------------------------|----------------------------------|-------------------|
| (1) 1-methylnaphthalene | (9) 3-Phenyl-2-Propenal | (18) m-Cresol |
| (2) 2,4-Dimethylphenol | (10) Acenaphthylene | (19) Naphthalene |
| (3) 2-Cyclopenten1-one | (11) Acetophenone | (20) n-Hexadecane |
| (4) 2-Hydroxy-Benzaldehyde | (12) Bis(2-ethylhexyl) phthalate | (21) Nonadecane |
| (5) 2-Methylnaphthalene | (13) Di-n-butyl phthalate | (22) Octadecane |
| (6) 2-Naphthalenecarboxaldehyde | (14) Eicosane | (23) p-Cresol |
| (7) 3-Methyl-Benzaldehyde | (15) Fluorene | (24) Phenanthrene |
| (8) 3-Methylphenol | (16) Heneicosane | (25) Phenol |
| | (17) Heptadecane | (26) Pyrene |

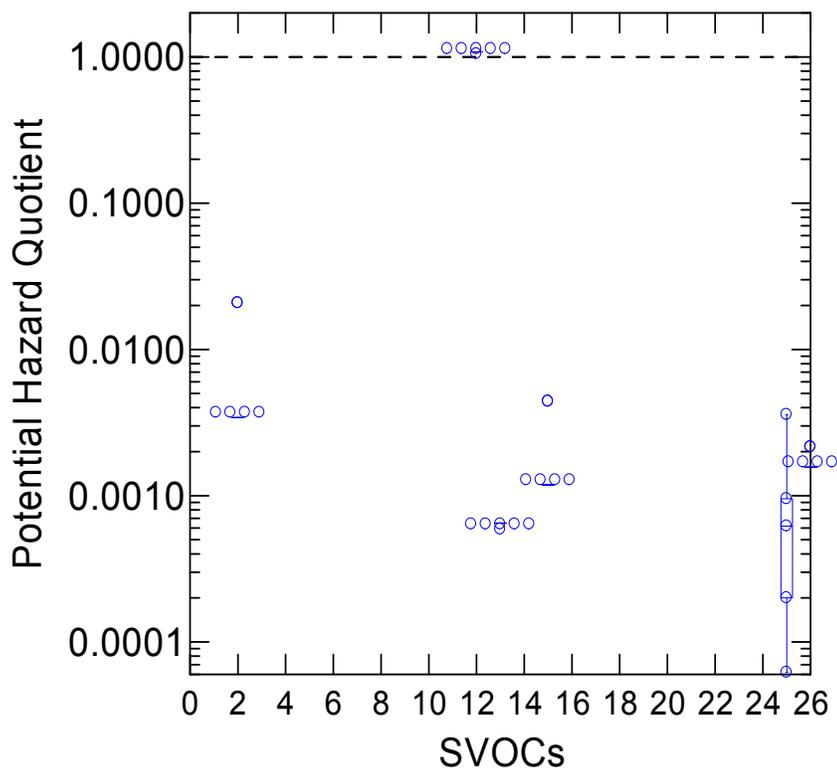


Figure 3.6.24. Box and Dot Density Plot of Potential Hazard Quotients for SVOCs in Samples of Generator Engine Effluent Nondetect (censored) concentrations were replaced with $\frac{1}{2}$ of the reporting limit for use in these plots. SVOCs are identified as follows:

- | | | |
|---------------------------------|----------------------------------|-------------------|
| (1) 1-methylnaphthalene | (9) 3-Phenyl-2-Propenal | (18) m-Cresol |
| (2) 2,4-Dimethylphenol | (10) Acenaphthylene | (19) Naphthalene |
| (3) 2-Cyclopenten1-one | (11) Acetophenone | (20) n-Hexadecane |
| (4) 2-Hydroxy-Benzaldehyde | (12) Bis(2-ethylhexyl) phthalate | (21) Nonadecane |
| (5) 2-Methylnaphthalene | (13) Di-n-butyl phthalate | (22) Octadecane |
| (6) 2-Naphthalenecarboxaldehyde | (14) Eicosane | (23) p-Cresol |
| (7) 3-Methyl-Benzaldehyde | (15) Fluorene | (24) Phenanthrene |
| (8) 3-Methylphenol | (16) Heneicosane | (25) Phenol |
| | (17) Heptadecane | (26) Pyrene |

3.2.6.3.4 Volatile Organic Compounds

Generator engine effluent samples were analyzed for 80 VOCs. Table 3.6.15 presents analytical results for the 28 VOCs that were detected. The detected results are also shown in Figures 3.6.25 and 3.6.26 for analyte concentrations and for PHQs based on the lowest NRWQC or other PHQ screening benchmark, where applicable, respectively. EPA analyzed the sample results to determine which VOCs were contributed primarily by generator engine operations and which were contributed primarily by background ambient concentrations. All were found to be contributed primarily by generator engine operations.

Twenty-two of the detected VOCs were analyzed for in only one sample. None of these compounds has an NRWQC or are PBT chemicals. Of the seven detected VOCs that were analyzed for in more than one sample, three have an NRWQC: benzene, ethylbenzene, and toluene. All of the detected benzene concentrations exceeded the PHQ screening benchmark of 2.2 µg/L by factors ranging from one to nine. The single detected concentration for each of ethylenebenzene and toluene did not exceed their respective PHQ screening benchmarks.

Note that the generator effluent sample from the fire boat contained the maximum concentration of 19 of the detected VOCs. These include benzene, toluene, ethylbenzene, xylene, trimethylbenzenes, and ketones.

Table 3.6.15. Results of Generator Engine Sample Analyses for VOCs¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
(E)-2-Butenal	µg/L	1	1	100	12							
1,2,3,4-Tetrahydro-5-Methylnaphthalene	µg/L	1	1	100	5.9							
1,2,3,4-Tetrahydro-6-Methylnaphthalene	µg/L	1	1	100	7.2							
1,2,4-Trimethylbenzene	µg/L	1	1	100	8.0							
1,3,5-Trimethylbenzene	µg/L	1	1	100	1.6							
2,6-Dimethylnaphthalene	µg/L	1	1	100	5.5							
2-Butanone	µg/L	1	1	100	83							
2-Butenal	µg/L	1	1	100	19							
2-Ethyl-1,4-Dimethyl-Benzene	µg/L	1	1	100	5.7							
4-Isopropyltoluene	µg/L	1	1	100	0.40							
4-Methyl-2-Pentanone	µg/L	1	1	100	1.7							
Acetone	µg/L	2	2	100	120	220	22	22	22	220	220	220
Benzaldehyde	µg/L	1	1	100	4.2							
Benzene	µg/L	5	3	60	5.9	3.1				12	21	21
Benzofuran	µg/L	1	1	100	6.9							
Biphenyl	µg/L	1	1	100	12							
Ethylbenzene	µg/L	5	1	20	1.4					1.0	2.0	2.0
Isopropylbenzene	µg/L	1	1	100	0.50							
m-,p-Xylene (sum of isomers)	µg/L	1	1	100	5.3							
Methyl acetate	µg/L	1	1	100	0.80							
n-Pentadecane	µg/L	1	1	100	40							
n-Propylbenzene	µg/L	1	1	100	0.90							
n-Tetradecane	µg/L	1	1	100	20							
O-Xylene	µg/L	1	1	100	3.4							
sec-Butylbenzene	µg/L	1	1	100	0.50							

Table 3.6.15. Results of Generator Engine Sample Analyses for VOCs ¹

Analyte	Units	No. Samples	No. Detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.
Styrene	µg/L	1	1	100	8.9							
Toluene	µg/L	5	1	20	3.5					6.2	12	12
Vinyl acetate	µg/L	1	1	100	1.5							

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

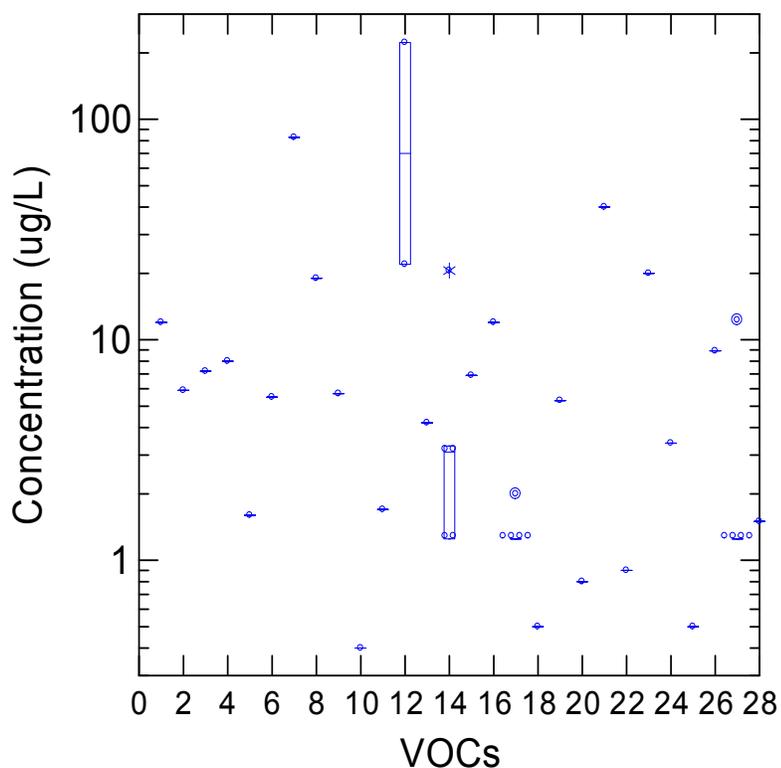


Figure 3.6.25. Box and Dot Density Plot of VOC Concentrations Measured in Samples of Generator Engine Effluent VOCs are identified as follows:

- | | | |
|--|----------------------------------|-----------------------------------|
| (1) (E)-2-Butenal | (9) 2-Ethyl-1,4-Dimethyl-Benzene | (19) m-,p-Xylene (sum of isomers) |
| (2) 1,2,3,4-Tetrahydro-5-Methylnaphthalene | (10) 4-Isopropyltoluene | (20) Methyl acetate |
| (3) 1,2,3,4-Tetrahydro-6-Methylnaphthalene | (11) 4-Methyl-2-Pentanone | (21) n-Pentadecane |
| (4) 1,2,4-Trimethylbenzene | (12) Acetone | (22) n-Propylbenzene |
| (5) 1,3,5-Trimethylbenzene | (13) Benzaldehyde | (23) n-Tetradecane |
| (6) 2,6-dimethylnaphthalene | (14) Benzene | (24) o-Xylene |
| (7) 2-Butanone | (15) Benzofuran | (25) sec-Butylbenzene |
| (8) 2-Butenal | (16) Biphenyl | (26) Styrene |
| | (17) Ethylbenzene | (27) Toluene |
| | (18) Isopropylbenzene | (28) Vinyl acetate |

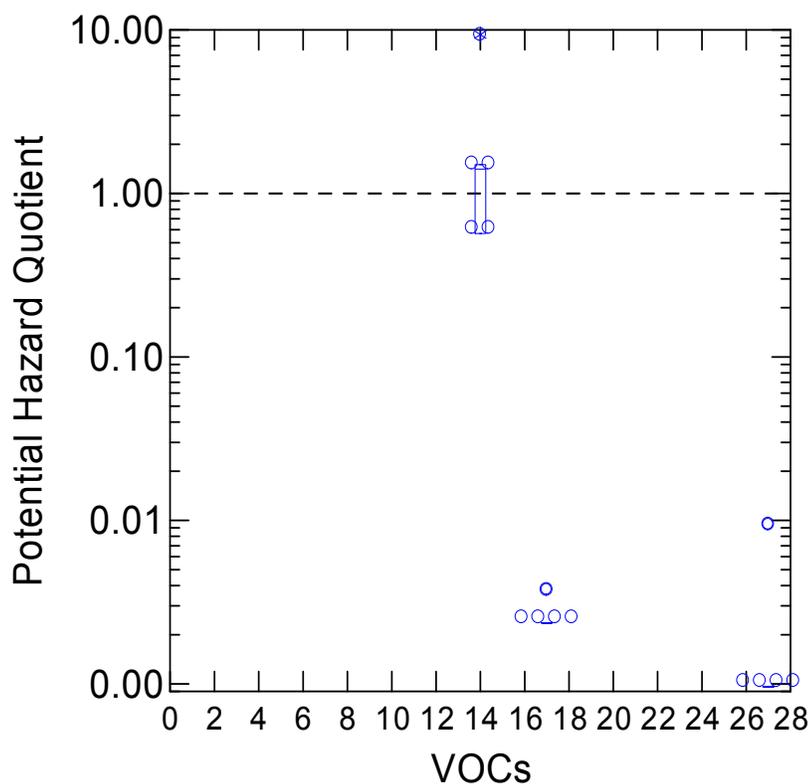


Figure 3.6.26. Box and Dot Density Plot of Potential Hazard Quotients for VOCs in Samples of Generator Engine Effluent VOCs are identified as follows:

- | | | |
|--|----------------------------------|-----------------------------------|
| (1) (E)-2-Butenal | (9) 2-Ethyl-1,4-Dimethyl-Benzene | (19) m-,p-Xylene (sum of isomers) |
| (2) 1,2,3,4-Tetrahydro-5-Methylnaphthalene | (10) 4-Isopropyltoluene | (20) Methyl acetate |
| (3) 1,2,3,4-Tetrahydro-6-Methylnaphthalene | (11) 4-Methyl-2-Pentanone | (21) n-Pentadecane |
| (4) 1,2,4-Trimethylbenzene | (12) Acetone | (22) n-Propylbenzene |
| (5) 1,3,5-Trimethylbenzene | (13) Benzaldehyde | (23) n-Tetradecane |
| (6) 2,6-dimethylnaphthalene | (14) Benzene | (25) sec-Butylbenzene |
| (7) 2-Butanone | (15) Benzofuran | (26) Styrene |
| (8) 2-Butenal | (16) Biphenyl | (27) Toluene |
| | (17) Ethylbenzene | (28) Vinyl acetate |
| | (18) Isopropylbenzene | |

3.2.6.4 Comparison of Effluent Generated at Different Propulsion Engine Power Levels

Although inboard and outboard propulsion engines were often sampled during operation at different power levels (e.g., idle, half power, full power), these samples were generally composited for a single analysis. Exceptions include samples for analysis of HEM/SGT-HEM and VOCs, which were collected and analyzed separately for each power level of engine operation (composite samples for these analytes are not appropriate). EPA reviewed the HEM/SGT-HEM and VOC data to determine whether there were any trends in the resulting data based on engine power level of operation.

HEM was detected in the majority of inboard engine effluent samples; however, detected concentrations were low (the majority were less than the reporting limit of 5 mg/L). Of the eight vessels with inboard engines with detected HEM concentrations that were sampled at different power levels, engine effluent samples from six had higher HEM concentrations at higher engine levels than at idle. Data for the remaining two vessels were inconclusive. Note, however, that differences in HEM concentrations among power levels were small, ranging from 0.1 to 5 mg/L. For outboard engines, HEM was not detected in any of the engine effluent samples.

Regarding VOC results for inboard engines, EPA reviewed benzene, toluene, ethylbenzene, and xylene concentrations as these compounds were the most frequently detected. Of the eight vessels with inboard engines with detected benzene concentrations that were sampled at different power levels, engine effluent samples from five contained higher benzene concentrations at higher engine levels than at idle. Data for the remaining three vessels showed the opposite pattern, with higher benzene concentrations at idle than at higher engine levels. For seven of these sampled vessels, differences in benzene concentrations among the power levels were small, ranging from 0.1 to 4.7 µg/L. In contrast, for the remaining vessel (a recreational vessel), the difference in benzene concentrations from idle to three-quarter speed was 89 µg/L, with the higher concentration detected at idle. As discussed previously, this recreational vessel was the only sampled vessel that used gasoline as fuel rather than diesel. In addition, the engines on this vessel were dewinterized immediately prior to sampling.

The differential among detected concentrations of ethylbenzene, xylene, and toluene at different power levels is too small to draw any conclusions, except for the engine effluent data for the recreational vessel. Differences in detected concentrations between idle and three-quarter power were 18 µg/L for ethylbenzene, 73 µg/L for m-,p-xylene, 31 µg/L for o-xylene, and 84 µg/L for toluene. The higher concentrations were found at idle for all four analytes.

The UNDS sampling program provides a useful comparison for this study as it was specifically designed to evaluate engine wet exhaust characteristics among power levels, including the separate collection and analysis of three replicate samples at each of five different

power levels. Tables 3.6.16 and 3.6.17 present sample results from the UNDS study by power level for the LCPL and RIB, respectively.

EPA made several conclusions for the LCPL based on a review of the engine effluent results. Chromium, copper, lead, and nickel were all detected at concentrations significantly greater than background concentrations for all five power levels. For copper and nickel, concentrations were highest at idle, second highest at 100 percent power, and then generally decreased with decreasing power levels (decreasing engine RPM). Chromium concentrations were highest at 100 percent power and then also decreased with decreasing power levels, with the lowest chromium concentrations found at idle. Lead concentrations were not significantly different at the various power levels. For TOC and phenol, only idle concentrations were significantly greater than background concentrations.

For the RIB, only TOC concentrations were significantly greater than background concentrations for all five power levels. TOC concentrations were highest at 100 power and then generally decreased with decreasing power levels; TOC concentrations were lowest at idle.

Table 3.6.16. Mean Concentration Results, UNDS Engine Wet Exhaust Discharge and Background Samples for the LCPL¹

Analyte	Mode 1 RPM 2050 (100% Power)	Mode 2 RPM 1850 (75% Power)	Mode 3 RPM 1650 (50% Power)	Mode 4 RPM 1300 (25% Power)	Mode 5 RPM 750 (0% Power)	Background Water	Units
	Mean	Mean	Mean	Mean	Mean	Mean	
Classical Parameters							
Nitrate/Nitrite (NO ₂ + NO ₃ -N)	ND (0.010)	0.011	0.011	ND (0.010)	0.012	ND (0.010)	mg/L
Total Organic Carbon (TOC)	1.15	1.03	0.933	0.858	1.73	0.992	mg/L
Metals							
Arsenic, Total	2.22	1.98	1.92	2.38	2.21	2.29	µg/L
Cadmium, Total	0.032	0.028	0.024	0.022	0.022	0.020	µg/L
Chromium, Total	0.574	0.431	0.313	0.310	0.260	ND (0.100)	µg/L
Copper, Total	21.7	26.0	17.2	13.5	40.1	0.780	µg/L
Lead, Total	0.369	0.188	0.145	0.118	0.127	0.030	µg/L
Nickel, Total	4.12	4.79	3.04	2.81	14.8	0.477	µg/L
SVOCs							
Bis(2-ethylhexyl)phthalate	ND (10.0)	ND (10.0)	ND (10.18)	ND (10.0)	20.4	ND (10.0)	µg/L
Phenol	ND (10.0)	ND (10.0)	ND (10.18)	ND (10.0)	19.7	ND (10.0)	µg/L

Source: USEPA, 2008b.

(1) Mean values were estimated based on the replicate concentrations for each mode or background sample using a lognormal or modified-delta lognormal distribution.

ND – Not detected (number in parentheses is reporting limit).

Table 3.6.17. Mean Concentration Results, UNDS Engine Wet Exhaust Discharge and Background Samples for the RIB¹

Analyte	Mode 1 RPM 2450 (100% Power)	Mode 2 RPM 2270 (75% Power)	Mode 3 RPM 1720 (50% Power)	Mode 4 RPM 1290 (25% Power)	Mode 5 RPM 400 (0% Power)	Background Water	Units
	Mean	Mean	Mean	Mean	Mean	Mean	
Classical Parameters							
Biochemical Oxygen Demand (BOD)	ND (2.00)	ND (2.00)	ND (2.00)	4.8	3.3	3.3	mg/L
Nitrate/Nitrite (NO ₂ + NO ₃ -N)	0.017	ND (0.010)	0.015	0.012	0.013	ND (0.010)	mg/L
Total Organic Carbon (TOC)	1.67	1.55	1.27	1.15	1.29	0.832	mg/L
Total Suspended Solids (TSS)	11.9	12.4	ND (5.00)	5.3	ND (5.00)	ND (5.00)	mg/L
SVOCs							
Phenol	32.4	24.6	ND (10.0)	ND (10.0)	ND (10.0)	ND (10.0)	µg/L
VOCs							
1,2,3-Trimethylbenzene	12.3	ND (10.0)	ND (10.0)	ND (10.0)	12.6	ND (10.0)	µg/L
1,3,5-Trimethylbenzene	12.3	ND (10.0)	ND (10.0)	ND (10.0)	12.6	ND (10.0)	µg/L

Source: USEPA, 2008b.

(1) Mean values were estimated based on the replicate concentrations for each mode or background sample using a lognormal or modified-delta lognormal distribution.

ND – Not detected (number in parentheses is reporting limit).

3.2.6.5 Engine Dewinterizing Effluent

Marine engines used in cold climates typically require maintenance prior to winter storage to prevent engine damage caused by freezing or corrosion. The indirect cooling systems in inboard engines are typically winterized by draining the water from the ambient water cooling system and refilling the system with approximately 5 gallons of antifreeze. Marine engine antifreeze contains propylene glycol²⁶, corrosion inhibitors, and other additives. In spring, the 5 gallons of antifreeze is emptied by starting the engine, which discharges the glycol solution and replaces it with ambient water. EPA sampled dewinterizing effluent from an inboard engine on a recreational vessel as it was converted from winter storage. This sample was collected in the same manner as that used for sampling other engine effluents. The sample was analyzed for select classical pollutants and metals.

Table 3.6.18 presents the collected dewinterizing effluent data, together with the mean inboard propulsion engine effluent concentrations from Tables 3.6.2 and 3.6.3. The source of the biochemical oxygen demand concentrations is the propylene glycol in the antifreeze. Elevated metals concentrations in dewinterizing effluent compared to those in inboard engine effluent could have been due to prolonged contact of the antifreeze with the engine cooling system and associated piping.

Outboard engines are winterized by spraying an oily aerosol, commonly referred to as “fog,” into the combustion air intake while the motor is running. Therefore, the engine dewinterizing effluent sample results in this subsection are not applicable to outboard engines.

Table 3.6.18. Comparison of Dewinterizing Effluent with Propulsion Effluent

Analyte	Units	Dewinterizing Effluent	Inboard Propulsion Engine Mean Concentration from Tables 3.6.2 and 3.6.3
Classical Parameters			
Biochemical Oxygen Demand (BOD)	mg/L	11	Not analyzed
Total Residual Chlorine	mg/L	2.8	0.048 ¹
Turbidity	NTU	350	32 ²
Metals			
Aluminum, Dissolved	µg/L	560	200 ¹
Aluminum, Total	µg/L	3,700	340 ¹
Antimony, Dissolved	µg/L	2.1	Not detected
Antimony, Total	µg/L	2.4	Not detected
Arsenic, Dissolved	µg/L	24	4.2 ²
Arsenic, Total	µg/L	32	4.5 ²
Barium, Dissolved	µg/L	43	35 ¹
Barium, Total	µg/L	59	36 ¹
Calcium, Dissolved	µg/L	21,000	80,000 ¹

²⁶ Ethylene glycol is not used for marine applications due to its higher toxicity as compared to propylene glycol.

Table 3.6.18. Comparison of Dewinterizing Effluent with Propulsion Effluent

Analyte	Units	Dewinterizing Effluent	Inboard Propulsion Engine Mean Concentration from Tables 3.6.2 and 3.6.3
Calcium, Total	µg/L	25,000	81,000 ¹
Chromium, Dissolved	µg/L	820	1.2
Chromium, Total	µg/L	720	1.3
Cobalt, Dissolved	µg/L	8.7	Not detected
Cobalt, Total	µg/L	12	Not detected
Copper, Dissolved	µg/L	370	16
Copper, Total	µg/L	820	18
Iron, Dissolved	µg/L	3,300	64
Iron, Total	µg/L	20,000	250 ²
Lead, Dissolved	µg/L	19	1.5
Lead, Total	µg/L	64	3.0
Magnesium, Dissolved	µg/L	5,200	200,000 ¹
Magnesium, Total	µg/L	6,400	200,000 ¹
Manganese, Dissolved	µg/L	160	43
Manganese, Total	µg/L	400	55 ¹
Nickel, Dissolved	µg/L	7.2	4.4
Nickel, Total	µg/L	18	4.6 ¹
Potassium, Dissolved	µg/L	23,000	32,000 ¹
Potassium, Total	µg/L	23,000	32,000 ¹
Selenium, Dissolved	µg/L	45	11 ¹
Selenium, Total	µg/L	54	11 ²
Sodium, Dissolved	µg/L	690,000	770,000 ²
Sodium, Total	µg/L	630,000	860,000 ²
Vanadium, Dissolved	µg/L	230	Not detected
Vanadium, Total	µg/L	190	Not detected
Zinc, Dissolved	µg/L	570	38
Zinc, Total	µg/L	900	38

(1) Sample concentrations were almost completely accounted for (≥90 percent) by background concentrations in ambient water.

(2) Sample concentrations were predominantly accounted for (≥50 percent and <90 percent) by background concentrations in ambient water.

3.2.6.6 Summary of the Characterization of Engine Effluent Analyses

Tables 3.6.19 and 3.6.20, and Table 3.6.21 at the end of this subsection, compare effluent characteristics for inboard and outboard propulsion engines and generator engines. Specifically, Table 3.6.19 compares the number of analytes detected in effluent from these engines, while Table 3.6.20 compares engine effluent analyte concentrations for those pollutants that may have the potential to lead to environmental impacts. Finally, Table 3.6.21 summarizes the specific analytes within each engine effluent type with the potential to pose risk to human health or the environment. The Table 3.6.21 is presented here to help interpret a realized risk likely posed by these analytes in engine effluent as summarized in Chapter 5.

Table 3.6.19. Comparison of Number of Detected Analytes in Engine Effluent

Analyte Class	Number of Analytes Detected in Engine Effluent		
	Inboard Propulsion	Outboard Propulsion	Generator
Classical Parameters	11	11	11
Metals	16	14	11
SVOCs	31	7	26
VOCs	38	18	28
Total	96	50	76

Table 3.6.20. Comparison of Results for Selected Analytes in Engine Effluent

Analyte	Units	Mean Concentration		
		Inboard Propulsion	Outboard Propulsion	Generator
Temperature Differential	°C	5 (low power levels) 20 (high power levels)	<5	<5 to 13
Oil and Grease (HEM)	mg/L	3.0	Not detected	2.9
Arsenic, Total	µg/L	4.5	24	Not detected
Copper, Dissolved	µg/L	16	3.3	6.5
Lead, Dissolved	µg/L	1.5	Not detected	Not detected
Lead, Total	µg/L	3.0	Not detected	Not detected
Selenium, Dissolved	µg/L	11	76	Not detected
Zinc, Dissolved	µg/L	38	11	13
PAHs	µg/L	14 total detected 6 carcinogens	1 detected 0 carcinogens	5 detected 0 carcinogens
Benzene	µg/L	12	13	5.9

Among all engine types, the SVOCs and VOCs were the most frequently detected pollutants (Table 3.6.19). Concentrations of PAHs were particularly high in inboard engine effluent. Fourteen PAHs were detected, including six of the seven PAHs classified as known carcinogens (Table 3.6.20), which were detected in all inboard engine effluents at concentrations several hundred to over 1,000 times greater than their associated benchmarks. PAHs were also detected in outboard engine and generator effluents, but at concentrations lower than their associated benchmarks. Furthermore, none of the probable human carcinogens were detected in generator or outboard propulsion engine effluent samples.

The plasticizer bis(2-ethylhexyl) phthalate was found in the effluents of all engine types, but PHQs were just above 1. The VOC benzene was also found at concentrations above PHQ screening benchmarks in all engine effluents. In addition, PHQs of toluene were greater than 1 in inboard engine effluents, but not in outboard engine or generator effluents. Trimethylbenzenes and ketones (VOCs) were frequently detected in the effluents of inboard engines, but no screening benchmarks exist for these compounds. Despite the high frequency of concentrations of benzene that exceeded screening benchmarks in engine effluent of all types, rarely were PHQs in excess of 5.

Among the classical pollutants, inboard propulsion engines increase cooling water temperatures by moderate amounts ($<5^{\circ}\text{C}$) at low power levels, but by as much as 20°C at higher power levels. In contrast, outboard propulsion engines increase cooling water temperatures by $<5^{\circ}\text{C}$, regardless of engine level. Most of the generator engine effluent samples increased cooling water temperature by $<5^{\circ}\text{C}$; however, two of the generator engine effluent samples had greater temperature differentials.

Oil and grease was not detected in effluent from outboard propulsion engines, but was detected at concentrations just above reporting limits in effluent from inboard propulsion and generator engines. Such concentrations were well below PHQ screening benchmarks for saltwater discharge. However, EPA did occasionally observe a sheen in receiving waters where marine engines were operating.

Table 3.6.21 lists those metals that were found to be contributed primarily by engine operations (elevated above ambient water concentrations) and were detected at concentrations that exceed a NRWQC, indicating that they may have the potential to cause environmental impacts. After accounting for background concentrations, dissolved concentrations of copper exceeded NRWQC in most inboard engine effluents. The highest PHQ for dissolved copper was 17. Several effluents from inboard and outboard engines had dissolved selenium at concentrations approximately two to seven times higher than NRWQC benchmarks; however, half of the selenium in these effluents was attributable to the surrounding waters. Among the total metals, PHQs for arsenic were much greater than 1 in both inboard and outboard engines. However, in the case of the inboard engines, after subtracting the contribution of ambient water, none of the detected total arsenic concentrations exceeded the very low PHQ screening benchmark ($0.018\ \mu\text{g}/\text{L}$ for protection of human health). In the case of outboard engines, detected total arsenic concentrations exceeded the PHQ screening benchmark even after subtracting the potential contribution from ambient waters. Total arsenic was not analyzed for in generator effluents.

Table 3.6.21. Characterization of Engine Effluent and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Engine Effluent Discharge and Vessel Sources ^{1,2}												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Inboard Engines													
Water Taxis (4)		Benzene	PAHs, Bis(2-ethylhexyl) phthalate	Cu									Temp ³
Tour Boats(3)		Benzene	PAHs,	Cu									Temp ³
Fishing Vessels (2)		Benzene	PAHs,	Cu									Temp ³
Tow/Salvage Vessel (1)		Benzene	PAHs,	Cu									Temp ³
Fire Boatl (1)		Benzene	PAHs, Bis(2-ethylhexyl) phthalate	Cu									Temp ³
Recreational Vessel (2) ⁴		Benzene	PAHs,	Cu									Temp ³
Outboard Engines													
Tow/Salvage Vessel (4)		Benzene		Se	As								
Research (2)		Benzene		Se	As								

Table 3.6.21. Characterization of Engine Effluent and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Engine Effluent Discharge and Vessel Sources ^{1,2}												
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (dissolved)	Metals (total)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Generator Engines (5)		Benzene (PHQ 9 for fire boat)	Bis(2-ethylhexyl) phthalate										

Notes:

- (1) Analytes are generally **bolded** when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), or, in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.
- (2) EPA notes that the conclusion of potential risk is drawn from a small sample size, in some cases a single vessel, for certain discharges sampled from some vessel classes. EPA included these results in the tables to provide a concise summary of the data collected in the study, but strongly cautions the reader that these conclusions, where there are only a few samples from a given vessel class, should be considered preliminary and might not necessarily represent pollutant concentrations from these discharges from other vessels in this class.
- (3) At full (100%) power.
- (4) For inboard engine effluent, higher measured concentrations and concentrations that exceeded the screening benchmarks were consistently from the recreational vessel, which was de-winterized immediately prior to sampling (see text). The recreational vessel was the only vessel sampled that used gasoline instead of diesel fuel. PHQs for the majority of samples were less than 5.

3.2.7 Firemain Discharges

The primary purpose of the firemain system is to supply water for fire fighting, although this system can also be used for other secondary purposes (deck washing, various maintenance and training activities, anchor chain washdown, or to create bypass flow from the firemain pumps to cool auxiliary machinery equipment) onboard the vessels of interest in this study. The firemain systems (see Section 1.5) sampled by EPA on three tour boats, two tug boats, and the single fire boat for this study are generally only used during emergencies and during biweekly testing. The firemain system intake water sampled on the vessels selected in this study was taken from the surrounding (ambient) water without addition of foam-forming agents such as aqueous film-forming foam (AFFF) or other chemical additions.



The Firemain Hose on a Tour Boat

It should be noted that AFFF agents could potentially be used on the vessels of interest in this study, although none of the vessels were outfitted with systems that used AFFF. AFFF agents are used for fire suppression and are a combination of fluoro-chemical surfactants, hydrocarbon surfactants, and solvents that are injected into the water stream of a fire hose. These film-forming agents can form water solution films on the surface of flammable liquids, separating the fuel from the air (oxygen).

EPA focused on analyzing the samples of firemain discharge water for metals, VOCs, and SVOCs. Metals were selected for analysis because water in the “wet type” firemain system passes through a significant amount of metal pipe onboard most vessels. EPA initially selected

VOCs and SVOCs to characterize the AFFF, which, as noted, none of the vessels sampled in the study used while testing their firemain systems. Despite the lack of AFFF use while testing firemain systems, EPA decided to analyze for VOCs and SVOCs in firemain system discharge water anyway.

3.2.7.1 Metals

Only half the total number of metals analyzed for in water samples from firemain systems were detected in the six vessels sampled.

Figure 3.7.1 presents the concentration ranges for dissolved metals detected in firemain water samples. The figure shows that dissolved metals concentrations span two orders of magnitude. Average dissolved concentrations of aluminum and zinc were highest, followed, in order of decreasing concentration, by barium, copper, manganese, nickel, and lead.

Figure 3.7.2 presents the concentration ranges of total metals detected in firemain water samples. Except for barium (dissolved:total metal ratio, or f_d , of 0.96), total metal concentrations were much higher than their corresponding dissolved metal concentrations, particularly for lead and copper. For the other total metal concentrations detected at higher levels, a disproportionate amount of the metals in ambient water is in the particulate form (i.e., aluminum, manganese and probably iron).

Arsenic, cadmium, selenium, antimony, beryllium, cobalt, silver, thallium, and vanadium were not detected in the firemain discharges.

Dissolved and total aluminum and total manganese were detected in the firemain effluent of all six of the vessels sampled. These metal concentrations are moderately to strongly influenced by ambient water concentrations. Dissolved zinc, also moderately influenced by ambient water, was detected in five of the samples. Dissolved and total copper, as well as dissolved manganese, were detected in four of the samples and were generally not affected by ambient water concentrations. Total lead was detected in three of the samples, and only one of the firemain systems had dissolved lead and chromium at detectable levels. Dissolved and total barium and total iron were also detected in one sample from a firemain system.

Disparities between dissolved:total metal concentrations sampled in firemain water versus ambient water suggest chromium, lead, and iron detected in firemain samples at least partially originated from the network of pipes within the firemain system. The dissolved:total metal ratio for copper was lower in the firemain water samples than in the ambient water samples (f_{ds} of 0.79), suggesting the possibility that some of the total copper detected in firemain samples originated from the network of pipes within the vessels that support the firemain system - most likely due to corrosion. Dissolved:total concentrations in firemain samples for the remaining metals (aluminum, barium, zinc, manganese, nickel) were similar to corresponding ambient

dissolved:total concentration ratios, suggesting most of these metals detected in firemain samples originated from the ambient water. Ambient harbor water data are not shown.

Figures 3.7.3 and 3.7.4 display the distribution of PHQs based on the most conservative (most protective) screening benchmark for each of the dissolved and total metals. PHQs for only one of the dissolved metals (copper) include a value of greater than 10 (one dissolved copper concentration from the firemain system analyzed from a tour boat resulted in a PHQ of 24). PHQs with values of slightly higher than 1 were found for two other dissolved metals (lead and zinc) when using the most conservative (most stringent 2006 NRWQC) screening benchmark. In contrast, all of the concentrations for total aluminum and the concentrations for the single detected total iron value exceeded the most stringent 2006 NRWQC; however, none of these PHQs exceeded 11.

In summary, the concentration of metals in firemain water was generally lower than some other discharges (e.g. bilgewater, deck washdown water). The water used in the vessel firemain systems analyzed in this study was ambient water, and the concentrations of most of the dissolved and total metals in firemain water reflect these surrounding ambient concentrations. Aluminum, manganese, and iron had high concentrations in the ambient water from which the firemain withdrew water and were generally higher or the same as other discharges. Dissolved and total copper, dissolved and total lead, and to a lesser degree, nickel and zinc, were found in concentrations higher than the ambient water. Of these metals, dissolved copper is the only metal also found at concentrations consistently above the most conservative screening benchmarks, albeit only with PHQ values in the 1 to 11 range, which is considerably lower than values found in most other discharge types discussed in this report.

Table 3.7.1. Results of Firemain System Sample Analyses for Metals¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc. ⁵	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc. ⁵	Screening BM ²
Heavy and Other Metals													
Aluminum, Dissolved ³	µg/L	6	6	100	110	140	15	15	72	150	160	160	NA
Aluminum, Total ⁴	µg/L	6	6	100	330	360	180	180	200	440	650	650	87
Barium, Dissolved ³	µg/L	1	1	100	36								NA
Barium, Total ³	µg/L	1	1	100	37								1000
Chromium, Total ⁴	µg/L	6	1	17	1.7					1.2	4.9	4.9	NA
Copper, Dissolved	µg/L	6	4	67	23	15				40	74	74	3.1
Copper, Total	µg/L	6	4	67	150	70				290	580	580	1300
Iron, Total	µg/L	1	1	100	3800								300
Lead, Dissolved	µg/L	6	1	17	2.1					1.1	4.3	4.3	2.5
Lead, Total	µg/L	6	3	50	50	7.6				81	270	270	NA
Manganese, Dissolved ⁴	µg/L	6	4	67	17	16				31	47	47	NA
Manganese, Total ⁴	µg/L	6	6	100	86	98	49	49	59	120	120	120	100
Nickel, Dissolved ⁴	µg/L	6	1	17	4.9					1.1	4.4	4.4	8.2
Nickel, Total ⁴	µg/L	6	2	033	7.0					11	11	11	610
Zinc, Dissolved ⁴	µg/L	6	5	83	120	58			5.3	270	370	370	81
Zinc, Total	µg/L	6	6	100	490	280	20	20	26	1200	1600	1600	7400
Cationic Metals													
Calcium, Dissolved ³	µg/L	6	6	100	27000	25000	23000	23000	24000	29000	37000	37000	NA
Calcium, Total ³	µg/L	6	6	100	30000	29000	23000	23000	23000	38000	40000	40000	NA
Magnesium, Dissolved ³	µg/L	6	6	100	6500	6500	5200	5200	5700	7200	9000	9000	NA
Magnesium, Total ³	µg/L	6	6	100	7300	6600	5500	5500	6200	9200	9800	9800	NA
Sodium, Dissolved ³	µg/L	1	1	100	38000								NA
Sodium, Total ³	µg/L	1	1	100	37000								NA
Potassium, Dissolved ³	µg/L	1	1	100	3800								NA
Potassium, Total ³	µg/L	1	1	100	3600								NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

(3) Sample concentrations were strongly influenced by background concentrations in ambient water, accounting for greater than 90% of sample concentrations in the majority of samples.

(4) Sample concentrations were moderately influenced by background concentrations in ambient water, accounting for between 50 and 90% of sample concentrations in the majority of samples.

(5) In some cases, the detected concentration(s) for an analyte could be lower than the replacement value (½ of the reporting limit) for a concentration that was nondetected. In an extreme (but possible) case, this could result in an average concentration for an analyte that is greater than the maximum detected concentration.

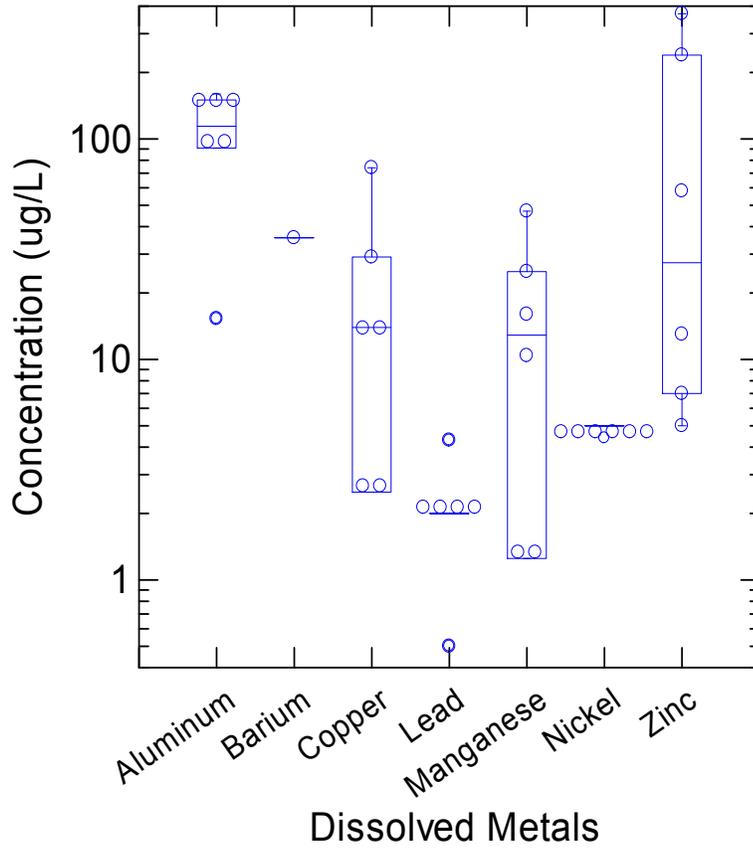


Figure 3.7.1. Box and Dot Density Plot of Dissolved Metals Concentrations Measured in Samples of Firemain Water Dissolved antimony, arsenic, beryllium, cadmium, chromium, cobalt, iron, selenium, silver, thallium, and vanadium were not detected in any of the firemain water samples.

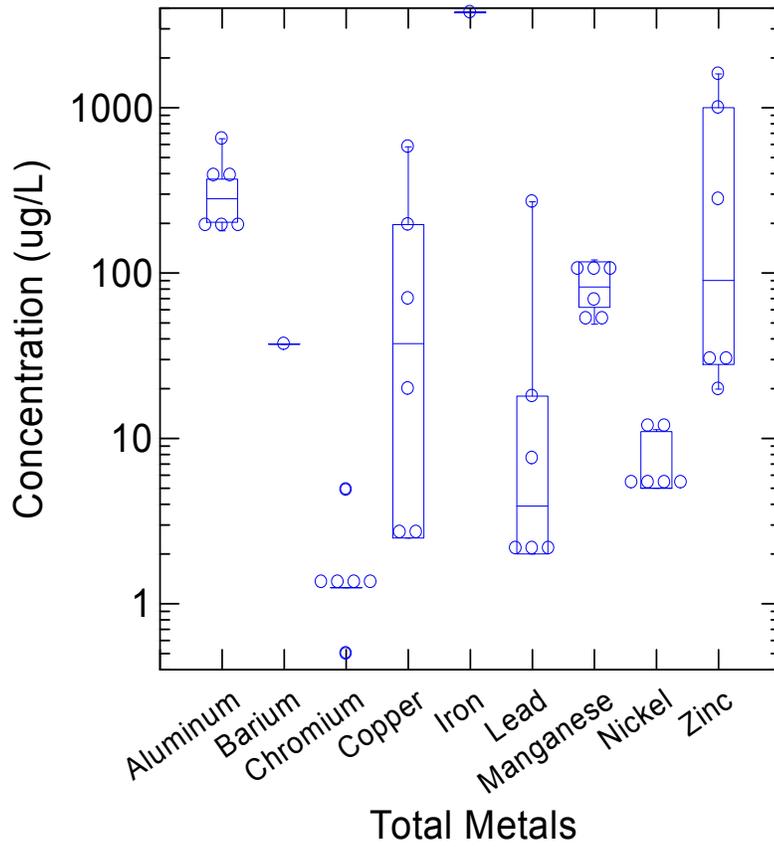


Figure 3.7.2. Box and Dot Density Plot of Total Metals Concentrations Measured in Samples of Firemain Water Total antimony, arsenic, beryllium, cadmium, cobalt, selenium, silver, thallium, and vanadium were not detected in any of the firemain water samples.

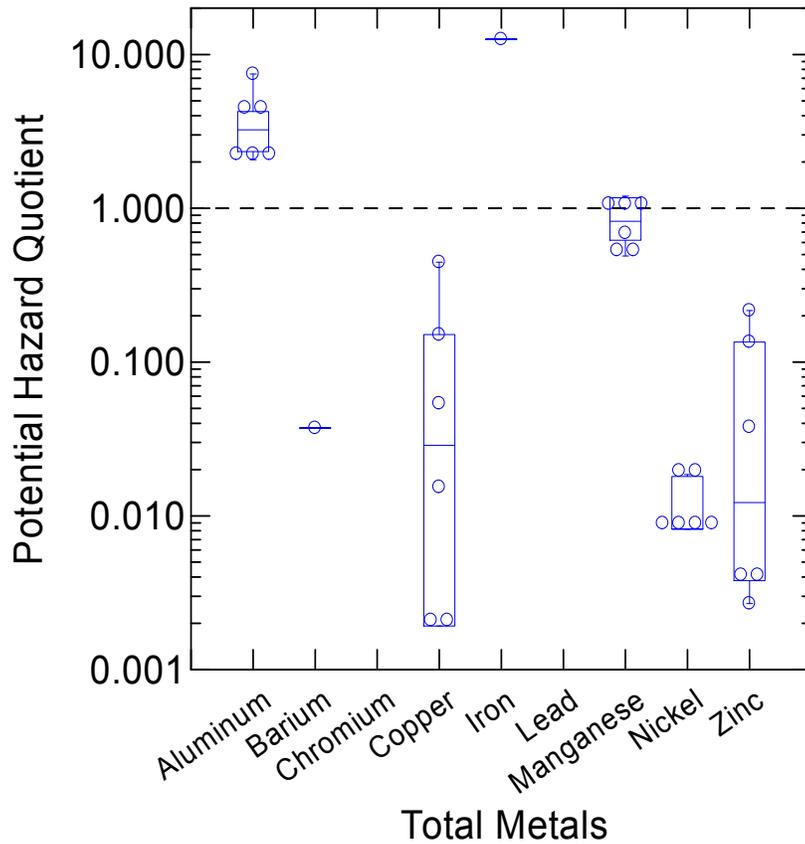


Figure 3.7.4. Box and Dot Density Plot of Potential Hazard Quotients for Total Metals in Samples of Firemain Water Total antimony, arsenic, beryllium, cadmium, cobalt, selenium, silver, thallium, and vanadium were not detected in any of the firemain water samples.

3.2.7.2 Classical pollutants

The firemain system water samples were analyzed for 10 classical pollutants (BOD, COD, TOC, and sulfide were not analyzed for as they were not expected in firemain system discharge (see Table 2.2)). Of the 10 classical pollutants analyzed for, oil and grease (measured as HEM and SGT-HEM) were not detected in any samples (Table 3.7.2). The concentrations of all other pollutants, with the possible exception of turbidity, were not elevated.

The conductivity, pH, and low salinity (ranging from 0.01 to 0.2 parts per thousand) in the firemain water samples are consistent with freshwater ambient water (all firemain samples were taken from vessels operating in fresh water). The pH of these waters was between 7 and 8, and turbidity and TSS was low, under 90 NTU and 20 mg/L, respectively. The firemain system effluent was sampled in the spring, and the temperature was in a seasonal range of 14 to 22°C and varied according to geographic location (warmer water samples in southern United States and colder in mid-Atlantic and northern states). Dissolved oxygen in firemain system water ranged from a low of 4.1 mg/L (slightly less than 50 percent saturation) to a high of 13 mg/L (super-saturated). All of these values were, to a large degree, consistent with concentrations of these parameters found in respective ambient water.

Figure 3.7.5 illustrates the variability of the values measured for the classical pollutants in firemain system water, which is relatively low given the relative similarities in ambient water quality (freshwater harbors sampled during springtime) for the three locations where vessels were sampled. The only other parameters detected in this category were TRC and turbidity. TRC was only detected in one of the six samples collected (measured at the reporting limit = 0.10 mg/L; PHQ = 13). All of the other TRC concentrations were below the reporting limit of 0.10 mg/L, which, when reported at half the reporting limit or 0.05 mg/L, still exceeds the most stringent 2006 NRWQC for TRC of 0.0075 mg/L. In contrast, turbidity ranged from a low of 4.6 to a high of 89 NTU, concentrations similar to the range of turbidities (3 to 180 NTU) observed in estuaries. In contrast, turbidity in raw sewage can be several hundred NTUs or more. There is no screening benchmark for turbidity from which to assess potential to cause or contribute to adverse effects on water quality.

To summarize, the concentrations of classical pollutants in firemain system water samples are within the normally expected ranges for the given season and geographical location where vessels were sampled. It appears that the classical pollutant concentrations primarily reflect concentrations found in the ambient water.

Table 3.7.2. Results of Firemain System Water Sample Analyses for Classical Pollutants¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc.	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
Conductivity	mS/cm	5	5	100	0.32	0.24	0.23	0.23	0.24	0.43	0.47	0.47	NA
Dissolved Oxygen	mg/L	5	5	100	7.7	6.8	4.1	4.1	4.9	11	13	13	NA
pH	SU	6	6	100	7.4	7.4	6.9	6.9	7.0	7.8	7.9	7.9	NA
Salinity	ppt	5	5	100	0.12	0.10	0.010	0.010	0.055	0.20	0.20	0.20	NA
Temperature	C	5	5	100	18	19	14	14	15	21	22	22	NA
Total Residual Chlorine	mg/L	6	1	17	0.05					0.025	0.10	0.10	0.0075
Total Suspended Solids (TSS)	mg/L	1	1	100	16								30
Turbidity	NTU	6	6	100	33	27	4.6	4.6	16	48	89	89	NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

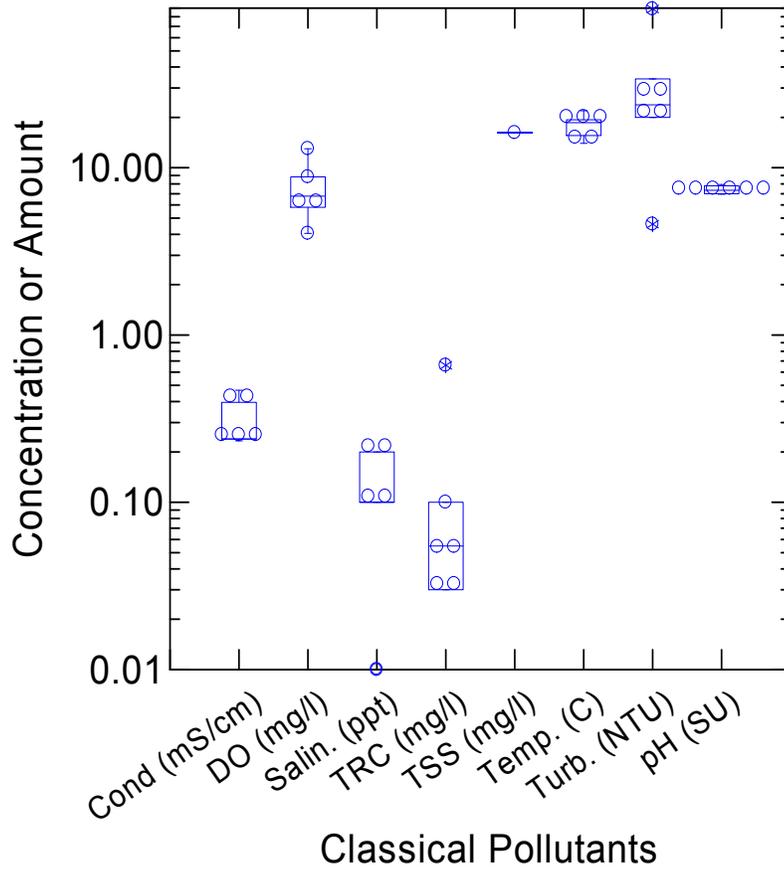


Figure 3.7.5. Box and Dot Density Plot of Classical Pollutants Measured in Samples of Firemain Water Concentrations reflect ambient water concentrations and values because ambient water was used as the source of water for all fireman systems in the vessels sampled in the study program.

3.2.7.3 Volatile and Semivolatile Organic Chemicals

VOC and SVOCs were targeted in firemain systems for this program because of the expectation that AFFF agents might be injected into the water stream of a fire hose to practice potential fire suppression scenarios. AFFF was not used, however, by any of the vessels sampled for this study.

Of the 57 SVOCs that were analyzed for in the six firemain system water samples, only six were detected, none of which were detected in more than one sample (Table 3.7.3 and Figure 3.7.6). Similarly, of 37 VOCs analyzed for, only five were detected, and as with the SVOCs, none were detected in more than one sample (Table 3.7.3). When SVOC and VOC concentrations were above detection levels, concentrations were relatively low. Of these, only bis(2-ethylhexyl) phthalate was measured at a sufficiently high concentration of 4.6 $\mu\text{g/L}$ that exceeded the associated PHQ of 3.8, based on the most conservative screening benchmark of 1.2 $\mu\text{g/L}$ (human health criterion). Bis(2-ethylhexyl) phthalate was also the only SVOC or VOC detected in ambient water, but interestingly, at a slightly higher concentration of 13 $\mu\text{g/L}$.

Table 3.7.3. Results of Firemain Water Sample Analyses for SVOCs¹

Analyte	Units	No. samples	No. detected	Detected Proportion (%)	Average Conc. ¹	Median Conc.	Minimum Conc.	10%	25%	75%	90%	Maximum Conc.	Screening BM ²
SVOCs													
2,6,10,14-Tetramethyl Pentadecane	µg/L	1	1	100	9.9								NA
2-Mercaptobenzothiazole	µg/L	1	1	100	4.1								NA
Benzothiazole	µg/L	1	1	100	7.2								NA
Bicyclo[2.2.1]heptane,1,7,7-Trimethyl-	µg/L	1	1	100	14								NA
Bis(2-ethylhexyl) phthalate	µg/L	4	1	25	2.1					3.4	4.6	4.6	1.2
Isopropylbenzene-4,methyl-1	µg/L	1	1	100	9.9								NA
VOCs													
1-Methyl-2-(1-Methylethyl)-Benzene	µg/L	1	1	100	97								NA
1-Methyl-4-(1-Methylidene)-Cyclohexane	µg/L	1	1	100	6.8								NA
Limonene	µg/L	1	1	100	9.5								NA
n-Pentadecane	µg/L	1	1	100	3.8								NA
n-Tetradecane	µg/L	1	1	100	3.5								NA

Notes:

(1) Nondetect (censored) concentrations were replaced with ½ of the reporting limit for calculating average concentrations. The remaining statistics in this table were only calculated when analytes were detected at a sufficient frequency. For example, if an analyte was detected in fewer than 50% of samples, then a median concentration was not calculated. A blank cell reflects a situation when a median or percentile could not be computed based on detected concentrations. The percentiles are the concentrations of each analyte below which at least that percentage of the values fall. So the 10th percentile is the concentration below which at least 10% of the observations were found.

(2) Screening BM represents the screening benchmark referred to in Section 3.1.3, and is the most stringent 2006 NRWQC or other conservative benchmark used to calculate PHQs.

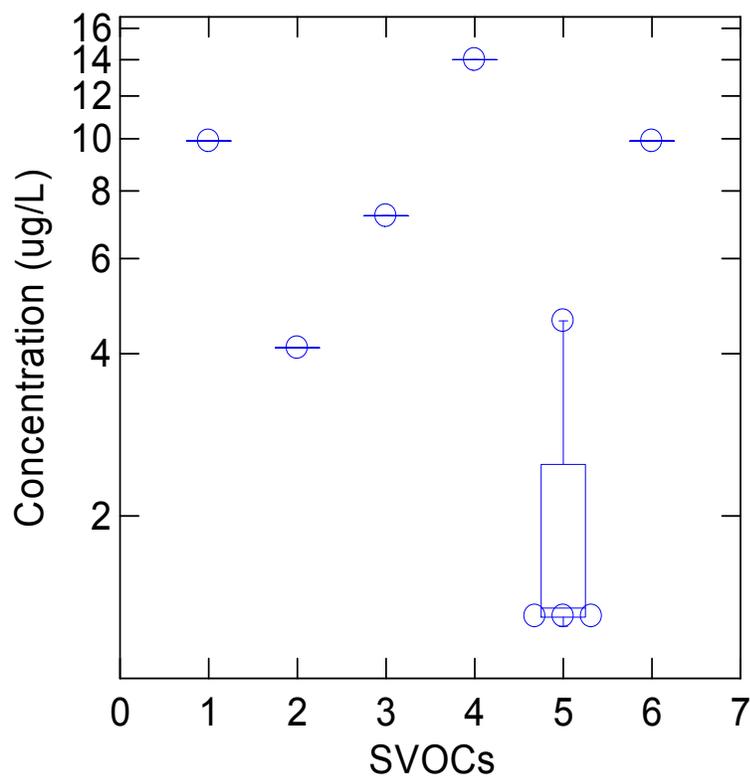


Figure 3.7.6. Box and Dot Density Plot of SVOC Concentrations Measured in Samples of Firemain Water SVOCs are identified as follows:

- | | | |
|---|---|--------------------------------------|
| (1) 2,6,10,14-Tetramethyl
Pentadecane, | (4) Bicyclo[2.2.1]Heptane,1,7,7-
Trimethyl-, | (5) Bis(2-Ethylhexyl) Phthalate, |
| (2) 2-Mercaptobenzothiazole, | | (6) Isopropylbenzene-4, Methyl-
1 |
| (3) Benzothiazole, | | |

3.2.7.4 Summary of the Characterization of Firemain System Water Analyses

Table 3.7.4 summarizes the specific analytes in firemain system effluent that may have the potential to pose risk to human health or the environment. EPA's interpretation of a realized risk likely posed by these analytes, relative to pollutant loadings, background ambient and source water contaminant levels and characteristics, and other relevant information useful for this assessment, is presented in Chapter 5.

The proportion of dissolved to total metals for firemain system discharge was low overall, relative to other discharge types. Among the dissolved metals, copper was detected in the highest concentrations and these both exceeded the most number of NRWQCs (four of six samples) and had the highest PHQs (ranging from approximately 4 to over 20). Dissolved lead and zinc had concentrations that exceeded one and three NRWQC, respectively, but none of the PHQs were above 10. Total aluminum concentrations exceeded NRWQC benchmarks in all samples, with PHQs ranging from 1-5. However, most of the aluminum in firemain discharge can be attributed to aluminum in the ambient waters. Overall, the concentrations of metals in firemain discharge were low compared to other discharge types.

Among the classical pollutants, TRC was the only pollutant of potential concern. However, TRC was detected right at the reporting limit of 0.10 mg/L in only one of six samples and the concentration likely reflects an elevated TRC concentration in the ambient water.

Finally, the concentration of bis(2-ethylhexyl) phthalate (an SVOC) exceeded the NRWQC (PHQ = 3.8) in one discharge sample; however, most SVOCs and VOCs sampled for were below detection limits, and when they were detected, occurred at very low concentrations. It is noteworthy to reiterate that bis(2-ethylhexyl) phthalate was also the only SVOC or VOC detected in ambient water, and at a slightly higher concentration (13 µg/L) than in the one firemain water sample.

Table 3.7.4. Characterization of Firemain Discharge and Summary of Analytes that May Have the Potential to Pose Risk

Vessel Type (no. vessels)	Analytes that May Have the Potential to Pose Risk in Firemain Discharge and Probable Source ^{1,2}											
	Microbiologicals	Volatile Organic Compounds	Semivolatile Organic Compounds	Metals (total and dissolved)	Oil and Grease	Sulfide	Short-Chain Nonylphenols	Long-Chain Nonylphenols	Nutrients	BOD, COD, and TOC	Total Suspended Solids	Other Physical/Chemical Parameters
Tour (3)				Cu (dissolved)								
Tug (2)				Cu (dissolved)								
Fireboat (1)				Cu (dissolved)								

Notes:

(1) EPA notes that the conclusion of potential risk is drawn from a small sample size, in some cases a single vessel, for certain discharges sampled from some vessel classes. EPA included these results in the tables to provide a concise summary of the data collected in the study, but strongly cautions the reader that these conclusions, where there are only a few samples from a given vessel class, should be considered preliminary and might not necessarily represent pollutant concentrations from these discharges from other vessels in this class.

(2) Analytes are generally bolded when a large proportion of the samples have concentrations exceeding the NRWQC (e.g., 25 to 50 percent), when several of the samples have PHQs > 10 (e.g., two or three of five), when a few samples result in PHQs greatly exceeding the screening benchmark (i.e., 100s to 1,000s), or, in the case of oil and grease and for nonylphenol, when one or more samples exceed an existing regulatory limit by more than a factor of 2. See text in Section 3.1.3 for a definition of PHQs and Table 3.1 for screening benchmarks used to calculate these values.

3.2.8 Antifouling Hull Coatings

Antifouling hull systems (AFSs) are specialized paints and other coatings intended to retard the growth of algae, weeds, and encrusting organisms such as barnacles and zebra mussels on the underwater portion of vessel hulls. These organisms may foul hulls and other underwater parts, increasing corrosion and drag, reducing safety and maneuverability, decreasing fuel efficiency and economy, and lengthening transit times (WHOI, 1952). Vessel hull fouling is often significant as vessels can move between a diverse range of aquatic environments and remain in the photic zone that is the most productive region of the water body (Chambers et al., 2006). Exposed to a variety of organisms, vessel hulls can transfer the organisms into other water bodies, where they can become invasive species.



Figure 3.8.1. Encrusting organisms (left) and weeds (right) growing on vessel hulls (figures from the Naval Surface Warfare Center’s Carderock Division, West Bethesda, Maryland, and the Boating Industry Association of Victoria, South Melbourne, Australia²⁷).

The development of AFSs has a long history, as mariners have tried for centuries to keep vessel bottoms free of barnacles and other fouling growth (Yebera et al., 2004; Readman, 2006). Ancient civilizations of the Greeks and the Romans coated their vessels with lead sheathing secured by copper nails. These heavy metals were early examples of using biocides to control fouling. Columbus’ ships are thought to have been coated with pitch and tallow. In the United Kingdom, lead sheathing was abandoned by the Navy in the late 1600s, and antifouling paints containing tar, grease, sulphur pitch and brimstone were developed (Carberry, 2006). One hundred years later, copper sheathing was used that prevented fouling through dissolution of the toxic metal ions (Readman, 2006). With the introduction of iron ships in the mid-1800s, different

What is a Biocide?

A **biocide** is a chemical substance capable of killing living organisms, usually in a selective way.

²⁷ See <http://www.dt.navy.mil/sur-str-mat/fun-mat/pai-pro-bra/fou-con-tec/images/fouling.jpg> and <http://www.biavic.com.au/files/weedunderhull.jpg>, respectively, for access to figures.

antifouling paints were needed because the copper sheathing reacted with the hull material to hasten corrosion of the iron. New paints were developed by adding toxic biocides such as copper oxide, arsenic, and mercury oxide to resin binders. Following the Second World War, the introduction of petroleum-based resins and health and safety concerns relating to arsenic- and mercury-containing paints meant that copper-based paints became most popular (Readman, 2006).

In the late 1950s and early 1960s, new antifouling paint formulations using tributyltin (TBT) proved to be excellent in preventing hull fouling. TBT, especially in “self-polishing” formulations, proved very efficient, and the application of TBT-based paints rapidly expanded. TBT was frequently formulated together with cuprous oxide to control a broader range of organisms. Not only was antifouling performance improved, but tin-based formulas (without copper components) are noncorrosive to aluminum, which was being used more in the construction of vessel hulls and propulsion systems. Unfortunately, the use of TBT also had severe and unexpected environmental consequences (Carberry, 2006). As the popularity of TBT grew, oyster producers in France reported shell malformations caused by paint leachate containing TBT that rendered their harvest worthless. Wild populations of other mollusc species were also affected at very low concentrations of TBT in the water and sediment (Evans et al., 1994). For example, female dog whelks (*Nucella* sp.) developed male characteristics (termed imposex) at these levels (Bryan et al., 1986). This masculinization of female gastropods was also reported in the open North Sea (Ten Hallers-Tjabbes et al., 1994). TBT use on small vessels was phased out in the late 1980s, when EPA and other regulatory agencies (including those in Canada, Australia, and many in Europe) restricted use of TBT-based AFSs to ships longer than 25 meters (see Section 6.2.3 of this report for further discussion about regulatory elimination of TBT).

Restrictions on the use of TBT-based AFSs opened the market for paint manufacturers and chemical companies developing new biocides for new antifouling paints to be used on vessels. Other metallic species, such as copper (copper hydroxide, copper thiocyanate) and zinc (zinc pyrithione), are currently used as substitutes for TBT. Copper oxide (in formulations without TBT) is by far the most common of the metallic biocides, used in more than 90 percent of the approximately 180 AFS products registered in California (Singhasemanon, 2008). A single AFS product might actually contain multiple biocides, with “booster biocides” incorporated to increase the duration and functionality of copper-based AFSs (Chambers et al., 2006). Irgarol is currently the organic biocide booster most frequently formulated into AFS products. As was the case for TBT, the biocides used in AFSs today can be toxic to a range of aquatic organisms, not just fouling organisms. In the subsections below, EPA discusses the literature on studies of adverse effects of these AFS biocides to aquatic resources as well as alternatives to using biocidal AFSs.

EPA did not sample antifouling systems as part of this study because of lack of time and resources available for this study. Assessing AFS discharge involves isolating a commercial vessel within a confined body of water (a “boat bag” or slip liner), and measuring the release, discharge, or leaching of the AFS biocide(s) over a period of time (weeks or months); the amount of time needed for the study would impose economic hardship on the vessel’s owners and operators. Rather, EPA elected to rely on the significant secondary data on antifouling systems available in the literature.

3.2.8.1 Copper Biocides

Copper is typically the biocide added to antifouling paints to prevent biofouling organisms from attaching to the hull. The most common form of copper used in AFSs is cuprous oxide, which acts as a preventative biocide by leaching into the water body. Cuprous oxide concentrations in marine antifouling paints range from 26 to 76 percent by weight, with most paints in the 40- to 70-percent range. Since cuprous oxide is 89 percent copper by weight, typical cuprous oxide marine antifouling paints are 36 to 62 percent copper by weight (TDC Environmental, 2004). Two additional copper biocides are occasionally used in AFSs: copper thiocyanate and copper hydroxide. These formulations are not as common, although copper thiocyanate has the advantage of being compatible with aluminum. The contribution of copper from these paints to receiving water is small relative to AFSs containing cuprous oxide (TDC Environmental, 2004).

Conventional copper-based AFSs fall into several general categories: copolymer or ablative paints and hard contact leaching paints (Conway and Locke, 1994). Copolymer paints release biocide at a constant rate, ablating (wearing away) much like a bar of soap, which is intended to reduce the need for cleaning. Hard contact leaching paints are usually modified epoxy paints that leach biocide upon contact with water, and, over time, the biocide is released at a decreasing rate. Each of these coating formulations can benefit from periodic hull cleaning to remove fouling growth, maintain a smooth surface, and improve the copper release on vessel hulls, but underwater hull cleaning can be a source of pollution or introduce non-native species if not done carefully. Cleaning frequencies and methods vary by paint type, area of vessel operation, frequency and conditions of operation, and vessel operator’s needs. Techniques that capture removed fouling growth and paint residue reduce negative impacts on the environment.

Passive leaching rates from antifouling paint, including those that are copper-based, depend on a number of factors, including the paint matrix (e.g., vinyl, epoxy), copper content, age of the paint, time since last hull cleaning, and frequency of painting. Leaching rates also vary with environmental conditions such as pH, temperature, salinity, and the existing slime “biofilm” layer (CRWQCB, 2005).

Rates of passive leaching of dissolved copper from AFSs on seven recreational vessels painted with epoxy copper antifouling paints were investigated in studies conducted in Southern

California by the U.S. Navy, under test conditions intended to represent realistic vessel conditions. Copper release rates were found to range from 2 to 14 $\mu\text{g}/\text{cm}^2/\text{day}$, with an average leaching rate of 8.2 $\mu\text{g}/\text{cm}^2/\text{day}$ ²⁸. In another study of copper-based AFSs on recreational vessels, researchers with the Southern California Coastal Water Research Project (SCCWRP) measured the mass emissions of dissolved copper from both passive leaching and underwater hull cleaning (Schiff et al., 2003). Fiberglass panels were painted with copper-based antifouling paints and immersed in seawater in a harbor environment. SCCWRP researchers determined the average flux rates for epoxy and hard vinyl copper antifouling paints to be approximately 4.3 and 3.7 $\mu\text{g}/\text{cm}^2/\text{day}$ over the course of a month, respectively. In the SCCWRP study, the authors also discussed the comparability of the results between the U.S. Navy and SCCWRP studies. According to the authors, the range of passive leaching measurements from the U.S. Navy study was within the range of measurements obtained in the SCCWRP study. By combining the results from the two studies, an average passive leaching rate for vessels at the Shelter Island Yacht Club (SIYB) was determined to be 6.5 $\mu\text{g}/\text{cm}^2/\text{day}$ (CRWQCB, 2005). In the United Kingdom, Thomas et al. (1999) found higher copper leaching rates for ablative copper antifouling paint ranging from 18.6 to 21.6 $\mu\text{g}/\text{cm}^2/\text{day}$ in 17 day experiments (Schiff et al., 2003). Table 3.8.1 summarizes the passive leaching rates for vessel AFSs found in the literature. The copper leaching rates summarized in this table were measured in experiments designed to simulate environmentally relevant conditions. However, more recently developed types of AFSs may leach at different rates, and the actual rates of copper leaching from many vessels and real-world environmental conditions may differ from those in Table 3.8.1.

Estimates of copper released from AFS leaching and underwater hull cleaning were calculated based upon the 6.5 $\mu\text{g}/\text{cm}^2/\text{day}$ average flux rate cited above, which was extrapolated to vessels using the underwater surface area of the hull²⁹, and then to marinas (or harbors) based on the number of vessels in the marinas. Despite the caveats and limitations discussed above, EPA uses these estimates in Chapter 4 to calculate loadings from vessel hull AFSs to attempt to understand the impacts of this source of copper discharge from certain vessels on large water bodies.

Even when an effective AFS is used, the biofouling could accumulate over time to unacceptable levels. If the AFS is still viable, this accumulated growth can be removed from vessel hulls by a number of methods, most frequently by underwater hull cleaning. Several studies have investigated the release of copper from copper-based AFSs into water bodies during underwater hull cleaning. The amount of copper released depends on cleaning frequency, method of cleaning, type of paint, and frequency of painting (SWRCB, 1996). Valkirs et al. (1994) found

²⁸ EPA notes that a calculated average for release rates will not reflect real-world conditions for many vessels and environmental conditions.

²⁹ Hull surface area can be estimated using the following equation: Hull Surface Area = VesselLength*Beam*0.85 (Interlux, 1999).

that underwater hull cleaning resulted in elevated total copper concentrations near the vicinity of the operation as dissolved copper was released during and shortly after hull cleaning. Smaller amounts of dissolved copper also leached from debris and sediments after cleaning. The particulate form of copper was rapidly incorporated into the bottom sediment, likely rendering it unavailable to aquatic organisms. The biologically active species of copper complexed rapidly, and dissolved copper levels returned to precleaning conditions within minutes to hours after the hull cleaning. Valkirs et al. (1994) concluded that potential adverse effects of hull cleaning on aquatic organisms from the increased dissolved copper concentrations were relatively short-term and pulsed in nature, while the potential adverse effects of increased particulate copper were probably long-term in nature, and dependent on resuspension or sediment uptake from benthic organisms.

McPherson and Peters (1995) also studied the effects of underwater hull cleaning on water body copper concentrations and toxicity to aquatic life. In the study, an underwater hull cleaning operation was performed in Shelter Island Yacht Basin using Best Management Practices (BMPs) that used less abrasive techniques to remove fouling growth (e.g., hand-wiping with a soft cloth). Most of the copper released during the cleaning was in the dissolved form. Researchers found that the plume of copper released by cleaning moved with the current, and that the degree of plume contamination depended on fouling extent and exertion by the diver. McPherson and Peters (1995) concluded that underwater hull cleaning elevates concentrations in the vicinity of the operation, which return to background levels within minutes. The researchers did not identify the type of antifouling paint (ablative or contact leaching paint), the age of the antifouling paint on the vessel, or the time since last hull cleaning. While the study provided important information regarding impacts of underwater hull cleaning on water quality, it did not provide copper emission rates associated with hull cleaning.

Schiff et al. also estimated dissolved copper emissions rates associated with underwater hull cleaning. Fiberglass panels were painted with copper antifoulants to simulate the hulls of recreational vessels. The study objective was to estimate the flux rates of dissolved copper from underwater hull cleaning of vessels painted with two commonly used types of copper-based antifouling paints in San Diego Bay. Schiff found that hull cleaning released between 3.8 to 17.4 $\mu\text{g}/\text{cm}^2$ per event (see Table 3.8.2), with an average release of 8.6 $\mu\text{g}/\text{cm}^2/\text{event}$. The researchers concluded that underwater hull cleaning results in a greater daily load of copper to the environment than passive leaching. In terms of mass loading, the authors concluded that approximately 95 percent of dissolved copper from antifouling paint enters the environment via passive leaching (CRWQCB, 2005). EPA notes, however, that this does not include loading rates from particulate copper, which may also impair the environment in the benthos due to biogeochemical cycling.

AFSs that are applied to vessel hulls are one of the most commonly identified major sources for copper in marinas. A number of studies have been carried out to estimate the loading

of copper from vessel AFSs. EPA estimated that copper loading from AFS use in California's Lower Newport Bay (LNB) area, which harbors approximately 10,000 boats, contributed more than 62,000 pounds of copper (via passive leaching and underwater hull cleaning) into LNB waters annually (USEPA, 2002). EPA believed that this load could account for as much as 80 percent of all copper input into LNB.

The U.S. Navy and private researchers conducted two copper source loading studies for the San Diego Bay in the late 1990s (Johnson et al., 1998; PRC, 1997). Both studies concluded that AFSs accounted for the majority of dissolved copper loading to the bay. The San Diego Regional Water Quality Control Board (SDRWQCB) estimated that passive leaching and underwater hull cleaning of the 2,400 boats berthed in the SIYB marina combine to contribute 98 percent of the copper load to the basin (Singhasemanon et al., 2009). Of the approximately 1.8 pounds of copper estimated released per boat per year (TDC Environmental, 2004), about 95 percent is believed to leach from AFS while boats are moored at the dock; the remaining 5 percent is believed to be released during monthly underwater hull cleaning activities.

The constant input of copper by leaching from the AFSs applied to pleasure, commercial, and military vessels has been cited as a likely primary source of copper in San Diego Bay. Sediment concentrations measured at the SIYB were relatively high (from 133 to 212 mg/kg) compared to other areas in San Diego Bay (Valkirs et al., 1994). Elevated copper concentrations (108 to 270 mg/kg) were found throughout San Diego Bay, with small boat harbors, commercial shipping berths, and military berths most affected. This distribution pattern is expected, considering the historical use of copper-based antifouling paints in the area.

Marinas in general tend to have elevated levels of pollutants in the water and sediments, including copper, as explained later in this subsection. For example, monitoring in the Southern California Bight demonstrated that sediment from marinas throughout southern California had consistently elevated copper levels compared to surrounding waters (Bay et al., 2000). The National Oceanic and Atmospheric Administration (NOAA, 1991) found the highest sediment concentrations, reaching over 104 mg copper/dry kg, in marinas, compared to other areas throughout the Southern California Bight. Sediment quality surveys around the United States routinely find high copper concentrations in marinas and harbors (USEPA, 1996; NOAA, 1994).

A recent study of AFS biocides in California marinas found dissolved copper concentrations ranging from 0.1–18.4 µg/L (Singhasemanon, 2008) in the water. Concentrations were significantly higher in salt- and brackish water marinas than in freshwater marinas. Dissolved copper concentrations in many of the salt- and brackish water marinas exceeded established water quality standards. Thus, there are ecological risks due to copper in many salt and brackish water marinas (Singhasemanon, 2008).

Copper contamination from vessel hulls is a water quality problem that is not unique to California. Within the United States, other areas of current concern to regulators include

Chesapeake Bay, Maryland; Port Canaveral and Indian River Lagoon, Florida; and various harbors in the state of Washington (Carson et al, 2009). Sweden, the Netherlands, and Denmark have recently banned copper-containing AFSs on recreational vessels in certain areas, and several European countries are now closely monitoring levels of dissolved copper in boat basins.

Elevated copper levels in marinas may be attributable to a number of factors. Marinas are home to high concentrations of recreational and commercial vessels. Since recreational vessels spend much of their time moored in marinas, most of the biocide from the antifouling paints on the vessel hulls is released in the marinas. Moreover, marinas are purposefully constructed to shelter boats from currents and waves, so they are not flushed well. Elevated trace metal concentrations in marinas are partly the result of the lack of mixing and dispersion. Thus, AFS pollution at these locations would represent some of the worst-case scenarios with regard to water quality (Singhasemanon et al., 2009; CRWQCB, 2005).

The biocides leached from AFSs can accumulate in the water of poorly flushed boat basins to levels that might harm marine life, especially mollusks, crustaceans, and echinoderms (Johnson and Gonzalez, 2006). At relatively low concentrations, copper is toxic to a wide range of aquatic organisms, not just fouling organisms (CRWQCB, 2005). Concentrations as low as 5 to 25 $\mu\text{g/L}$ can be lethal for marine invertebrates (Chambers et al., 2006). Elevated copper levels affect growth, development, feeding, reproduction, and survival at various life stages of fish, mussels, oysters, scallops, crustaceans, and sea urchins. High copper levels also change the types of phytoplankton that thrive in boat basins (Calabrese et al., 1984). Low levels of dissolved copper affect the olfactory capabilities in juvenile Coho salmon, which is critical for homing, foraging, and predator avoidance (Baldwin et al., 2004). The effect of copper on olfaction of juvenile salmonids suggests that copper might affect other fish species, too. Most effects on fish are sublethal (e.g., they may hinder metabolic processes, reproduction, development, activity levels and behavior). Thus, the damage is chronic and less noticeable than, for example, fish kills caused by sudden oxygen depletion (Evans et al., 1994).

In the California marina study, significant toxicity was measured in eight of 47 water samples; seven of the toxic samples came from Marina del Rey (MdR) in Los Angeles (Singhasemanon et al., 2009). The authors concluded that copper was the most likely cause of the toxicity in these samples. Two models of copper bioavailability and toxicity to aquatic organisms, the Biotic Ligand Model (BLM) and dissolved organic carbon (DOC) model, were used to confirm these findings. The BLM and DOC model predictions agreed favorably with the actual toxicity data, although both models tended to slightly overpredict toxicity, especially when close to the toxic effect concentration (i.e., EC_{50}) (Singhasemanon, 2008).

Rivera-Duarte et al. (2003) also investigated the bioavailability and toxicity of copper in San Diego Bay and found that toxicity was based on chemical speciation and followed the free ion activity model. The EC_{50} for mussel larval development was observed near 10^{-11} molar (i.e.,

0.64 ng/L) free copper ion. The toxic threshold concentration of free copper ion was independent of spatial and temporal effects, indicating the need to study chemical speciation of copper released from antifouling paints in order to determine its environmental effects (Rivera-Duarte et al., 2003).

Table 3.8.1. Rates of Passive Copper Leaching from Vessel AFSs

Study	Test Method	AFS	Leaching Rate ($\mu\text{g}/\text{cm}^2/\text{day}$)
UK (Thomas et al., 1999)	Not reported	Ablative copper antifouling paint	18.6 – 21.6
U.S. Navy (Zirino and Seligman, 2002)	Not reported	Ablative copper antifouling paint	Average = 3.9
U.S. Navy (Valkirs et al., 2003)	7 recreational vessels in recirculating dome system	Epoxy copper antifouling paint	2 - 14 (average = 8.2)
SCCWRP (Schiff et al., 2003)	Fiberglass panels in recirculating dome system	Epoxy copper antifouling paint	4.3
		Hard vinyl/Teflon copper antifouling paint	3.7
		Biocide-free coating	0.24

Table 3.8.2. Dissolved Copper Release from Vessel AFSs During an Underwater Hull Cleaning “Event”

AFS	Cleaning Method	Copper Release ($\mu\text{g}/\text{cm}^2/\text{event}$)
Epoxy copper antifouling paint	Less abrasive management practices	8.6
	No management practices	17.4
Hard vinyl/Teflon copper antifouling paint	Less abrasive management practices	3.8
	No management practices	4.2
Biocide-free coating	Less abrasive management practices	0.03
	No management practices	0.05

Source: Schiff et al., 2003

Table 3.8.3. Estimated Dissolved Copper Mass Emissions from a 9.1m (30ft) Powerboat

Source	Dissolved Copper Emission (grams/month)		
	Epoxy Copper Antifouling Paint	Hard Vinyl/Teflon Copper Antifouling Paint	Biocide-Free Coating
Passive leaching (min-max)	24.9 (23.3-27.8)	21.4 (15.7-24.5)	1.4 (0.9-1.8)
Underwater hull cleaning with BMPs (min-max)	1.8 (1.7-2.0)	0.8 (0.5-1.2)	<0.01 (0-0.01)
Total emissions (min-max)	26.7 (20.5-33.6)	22.2 (15.0-31.5)	1.4 (0.9-1.8)

Source: Schiff et al., 2003

3.2.8.2 Irgarol and Other Organic Biocide Boosters

Irgarol (Irgarol 1051, *N*-tert-butyl-*N'*-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine) is a highly effective biocide used in AFSs to prevent the growth of autotrophic (e.g., plants and algae) organisms on vessel hulls. After the ban of tributyltin (TBT) on vessels shorter than 25 meters, the use of TBT-free paints containing copper compounds and organic booster biocides such as Irgarol increased considerably and became more widespread (Mohr et al., 2009). Other organic biocides, including Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), dichlorofluanid (1,1-dichloro-*N*-(dimethylamino)sulfonyl)-1-fluoro-*N*-phenylmethanesulfenamide), and Sea-Nine (4,5-dichloro-2-*n*-octyl-4-isothiazolino-3-one) are also added to AFS preparations to boost performance (Thomas et al., 2001). The use of biocide boosters is in part a response to concerns about performance, environmental impacts, and, according to Chambers et al., (2006), a reported increasing tolerance of some macrophytes and algae to copper. Freshwater locations such as the Great Lakes are plagued primarily by algae (West Marine, 2008), and booster biocides such as Irgarol are used to restrict the growth of algae by blocking photosynthesis near the water surface. To date, however, most studies on Irgarol have focused on marine areas and toxicity tests with marine organisms (Mohr et al., 2009).

Irgarol has been detected with increasing frequency at ecologically sensitive levels in coastal waters worldwide, as reviewed by Konstantinou and Albanis (2004). In ports and marinas in coastal waters, it has been detected in relevant effect concentrations of up to 4.2 µg/L (Basheer et al., 2002). Levels of up to 1.4 and 2.4 µg/L have been reported from UK marinas and freshwater sites (Thomas et al., 2002). In the United States, Irgarol and its major metabolite M1 have been detected in the Chesapeake Bay and Florida (Hall and Gardinali, 2004). In the California marina study, Irgarol and M1 were detected in all 45 marina samples (Singhasemanon et al., 2009); Irgarol concentrations ranged from 12 to 712 ng/L, and M1 concentrations ranged from 1.6 to 217.1 ng/L. Higher concentrations of irgarol and M1 were found in salt water marinas.

Although Irgarol was predicted to easily dissipate under natural conditions (Hall et al., 2005), it is the most frequently detected antifouling biocide worldwide (Konstantinou and Albanis, 2004). Published values of the half-life of Irgarol in water are between 24 and 200 days (Mohr et al., 2009).

EPA has expressed concern over the potential toxic effects of Irgarol on aquatic plants and algae (USEPA, 2003a). Compared to other triazines like atrazine and simazine, Irgarol is a more potent inhibitor of algal photosynthesis, and is therefore highly toxic to macrophytes, phytoplankton, and periphyton (Mohr et al., 2008). Irgarol is likely to be much less toxic to animals than flora (Mohr et al., 2009). The main metabolite M1 is also toxic to aquatic plants and algae, but in many cases much more than 10 times less toxic than Irgarol.

Although Irgarol is formulated in AFSs to control periphyton on vessel hulls, the range of environmental concentrations measured in freshwater can be toxic to nontarget macrophytes. The results of the Mohr et al. (2009) study indicate that Irgarol is likely to have serious impacts on natural macrophyte communities at environmentally relevant concentrations. The fact that Irgarol accumulates in macrophytes, especially at lower concentrations, suggests the expected toxicity of Irgarol may be underestimated (Mohr et al., 2009).

Irgarol concentrations at many of the marinas in the California study were high enough to be toxic to some phytoplankton and aquatic plants (Singhasemanon et al., 2009). For example, the range of observed Irgarol concentrations (12 to 712 ng/L) exceed aquatic benchmark values that are protective of 90 percent of aquatic plant species. The Irgarol metabolite M1 never exceeded the aquatic benchmark value (Singhasemanon, 2008).

What are Macrophytes, Phytoplankton, and Periphyton?

A **macrophyte** is an aquatic plant that grows in or near water and is either emergent, submergent, or floating.

Phytoplankton are planktonic algae that live in water bodies.

Periphyton is a complex mixture of algae, cyanobacteria, heterotrophic microbes, and detritus that is attached to submerged surfaces in most aquatic ecosystems.

3.2.8.3 Zinc Biocides

In recent years, there has been an increase in the registration of AFS products with zinc pyrithione (bis(N-oxopyridine-2-thionato)zinc(II)), also commonly known as zinc omadine, as the primary biocide (Singhasemanon et al., 2009).

In a California marina study, dissolved zinc concentrations from paints containing zinc omadine ranged from 1.0–66.6 µg/L with a concentration distribution that was similar to dissolved copper (Singhasemanon, 2008). Dissolved zinc concentrations were much higher in saltwater marinas than brackish and freshwater marinas. Zinc concentrations did not exceed California Toxics Rule (CTR) fresh- and saltwater standards. If zinc pyrithione becomes more popular as an AFS biocide in the future (e.g., as a replacement for copper AFSs), the contributions of zinc AFSs to the marina zinc load will increase and potentially lead to zinc-related toxicity (Singhasemanon et al., 2009).

3.2.8.4 Emerging Biocides

As mentioned in the introduction to this subsection, AFSs using copper-containing biocides are the most common substitutes for TBT. However, paint manufacturers continue to search for new antifouling biocides. One promising development is ECONEA, a metal-free biocide developed by a pharmaceutical company. According to the paint manufacturers, ECONEA is rapidly biodegradable and does not accumulate in the marine environment, and is reported by the manufacturer to very effectively control a wide range of invertebrate fouling organisms in significantly less amounts compared to conventional biocides. However, AFSs formulated with ECONEA have not entered the market, and independent testing data are not currently available.

3.2.8.5 Biocide-Free (Nonbiocidal) AFSs

In recent years, biocide-free coatings designed to prevent fouling growth from adhering to boat hulls have entered the market. Biocide-free coatings are designed to produce a slick surface that prevents fouling organisms from firmly adhering to the hull. Currently available nonbiocidal bottom coatings may be silicone-based, epoxy-based, water (urethane)-based, or polymer-based. They do not include biocidal components. Epoxy coatings are durable, and are expected to last for many years, but require frequent and aggressive cleaning (Johnson and Miller, 2002). The most commonly used nonbiocidal coatings are silicone elastomeric coatings, which are rubbery and are more easily nicked or abraded than epoxy, although recent advances have improved their durability. They are sometimes called “fouling release” coatings, because fouling growth is sheared off the hull once the vessel exceeds a certain speed (e.g., 20 knots). Movement of a foul-release-coated vessel through the water dislodges organisms that do adhere. The utility of these coatings depends on vessel speeds and the proportion of time the vessel is underway (rather than at dock). Foul-release coatings are typically more expensive than biocidal AFSs. Because of their expense and operational requirements, foul-release systems generally are not used on recreational vessels at this time.

To date, nontoxic AFS alternatives have not been widely accepted in the boating industry, due to concerns about practicality and cost. If adopted, these alternatives would eliminate the leaching of biocides from marine antifouling paint, as well as biocide release during underwater hull cleaning.

A number of projects are underway to develop new biocide-free AFSs. The European Commission is collaborating with industry with the goal of developing a nonbiocidal antifouling coating that relies on nanostructuring to impede the adhesion of fouling organisms (Ambio, 2008). The U.S. Navy is sponsoring research by University of Florida engineers to develop a

biocide-free hull coating based on the geometry of shark skin scales. Chambers et al. (2006) provide a review of these and other biomimetic approaches to environmentally effective AFSs.

Because nonbiocidal coatings do not affect fouling growth, they may need more frequent cleaning than biocide-based AFSs, and can be more effective when used with other practices designed to increase the amount of shearing and decrease exposure to fouling organisms during times of inactivity: using the vessel more often and/or operating it at higher speeds; storing it on land or on a hoist at the slip when not in use; and, surrounding the vessel with a slip liner and adding 10 to 15 percent fresh water to reduce salinity (Johnson and Gonzalez, 2006).

3.2.8.6 BMPs

The most effective way to reduce biocide emissions from AFSs on recreational vessels is by carefully selecting the AFS. The owner/operator should match antifouling performance with how the vessel typically operates. Choosing a nonbiocidal AFS can eliminate emissions from vessels that, for example, operate at high speeds when they are underway. Slow-release formulations or formulations with lower biocide content may also reduce the release of biocides into the aquatic environment. As noted previously, passive leaching accounts for most of the biocide release from recreational vessels, but biocide also could leach into the water body during underwater hull cleaning and AFS application and removal.

In addition to AFS selection, other BMPs may be used to limit emissions of toxic components from AFSs. These BMPs include specifications for capturing and treating materials removed during underwater hull cleaning, properly managing wastes from AFS application processes, and capturing and appropriately disposing of old hull coating residue prior to repainting. When nonbiocidal coatings are used, companion strategies can be used to reduce fouling including slip liners, boat lifts, and frequent hull cleaning (Johnson and Gonzalez, 2006).

BMPs for underwater hull cleaning must also address the potential introduction of aquatic nuisance species (ANS). EPA notes that small vessels are strongly suspected of contributing to the spread of numerous invasive species including zebra and quagga mussels. Prohibitions on biocide-containing AFSs could potentially exacerbate the spread of ANS as the toxicity of vessel hull coatings declines and as water quality improves as a result. Conversely, improvements to water quality, including those associated with AFS restrictions and BMPs, may allow native ecosystems to recover from acute and chronic impacts and become more resistant to invasions of non-native species (Johnson and Gonzalez, 2006).

Pollutants from passive leaching and hull cleaning can be reduced by implementing other BMPs, such as using nontoxic (or less toxic) antifouling paints to replace copper-based paints. Switching to nontoxic and less toxic antifouling paints will reduce the loading from both passive leaching and underwater hull cleaning. For example, if all new boats entering the Shelter Island Yacht Basin use nontoxic or less toxic coatings and existing boats replace copper coatings with

nontoxic or less toxic coatings at the next routine hull-stripping (as assumed in their total maximum daily load), the basin's water quality is expected to dramatically improve (CRWQCB, 2005). Additionally, nontoxic or less toxic coatings will require companion strategies such as slip liners, boat lifts, and frequent hull cleaning to control fouling (Johnson and Gonzalez, 2006).

3.2.8.7 Conclusion

Antifouling systems currently used on the majority of recreational and commercial vessels are paints that prevent and retard fouling growth by leaching biocides, most frequently cuprous oxide, onto the hull. Biocides can enter a water body through passive leaching, underwater hull cleaning, hull painting, and AFS removal processes. Biocides leached from vessel AFSs can accumulate in the water of poorly flushed boat basins to levels that could harm marine life. Copper from vessel hulls in particular is a water quality concern in many near-coastal waters of the United States, including the waters of Southern California, the Chesapeake Bay, Port Canaveral and Indian River Lagoon in Florida, and in various harbors in the state of Washington. Copper leaching from vessel hulls has also been reported as a problem in several European countries, including Sweden, the Netherlands, and Denmark.

Concerns about impacts to aquatic ecosystems from both TBT and copper have led to the development of AFSs that use alternative biocides or are biocide-free. At this time, these alternatives are relatively costly and have not been widely accepted by boaters. Releases of biocidal components of AFS can be reduced by implementing BMPs, including the use of nontoxic (or less toxic) antifouling paints to replace copper-based paints.