

Removal of Copper and Zinc From Shipyard Waters

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ABSTRACT

Characterization of copper and zinc concentrations in shipyard wash waters and removal coincident with treatment operations that are targeting tributyltin removal is presented. Copper and zinc were observed to be major components of shipyard wash waters ranging in concentration from 250 to 140,000 ppb total copper and 600 to 72,000 ppb total zinc. High concentrations were associated with the large amount of particulate material in the waters generated through wash down and hydroblasting of ship hulls.

Batch coagulation/clarification in the laboratory was conducted from pH 6 to pH 10. Consistent with pH dependent solubility of a metal oxyhydroxide, copper and zinc removals were greater at higher pH with zinc more effectively removed than copper. Solubilization of organic matter from the particulate fraction that was observed at higher pH may include organo-copper complexes that increase solubility.

Removal of both metals was observed to substantially occur by treatment with granular activated carbon. Removal is likely related to both particulate and dissolved metals removal, possibly through removal of metal-organic complexes of zinc and copper.

Key Words: copper, zinc, treatment, activated carbon, coagulation, shipyards

INTRODUCTION

Copper and zinc are two of the most common trace metals found in stormwater runoff in urban regions (USEPA, 1983) and are also prevalent in runoff waters discharged from industrial sites (Line et al., 1997). Shipyards are sites of intense, industrial activity and contain many sources of these metals (Schafran et al., 1998). While many shipyards have had monitoring requirements for a number of years and requirements for implementation of best management practices (BMPs) to control metals mobilization, more shipyards are likely to be faced with collection and treatment requirements of metal-containing waters in the near future.

One specific shipyard water that has been undergoing evaluation for possible control is the water generated on shipyard dry docks associated with hull washing to remove biological growth/slime and hydroblasting to remove paint. During these operations, removal of paint on the hull occurs directly or indirectly and both particulate and dissolved metals can be transported with hull and dry dock runoff. In the past, little management of this water was required by regulatory agencies and much of it discharged directly to adjacent waterways. Recognition of the potentially significant loading of metals to receiving waters is contributing to regulatory actions that in some regions require collection and treatment before discharge. This action is

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likely to continue to more shipyards based on industry projections.

That copper and zinc might be prevalent at elevated concentration in shipyard wash waters is consistent with the amount of these metals found in marine paints. Primer coats applied to bare metal (steel) typically contain high concentrations of zinc due to the improved cutting and welding that is associated with high-zinc primer coatings. While using primers with lower zinc content might be one way to control zinc releases, the use of primers with lower zinc content has been observed to negatively impact production and quality (S. Lacoste, personal communication).

Copper is also found as a significant component of marine coatings/paints due to its biocidal properties that inhibit biological fouling on ship hulls. While there is a class of paints where copper is recognized as a significant component since it is the active biocidal ingredient, it is also found as a dominant ingredient in tributyltin (TBT) paints. Hence, paints that contain TBT and may be subject to a specific TBT discharge limit are also likely to need to meet a copper (and zinc) discharge limit also. Consequently, there will likely be multiple treatment objectives and removal goals for shipyard wash waters. The study reported here provides information that can help assess whether these multiple treatment objectives can be met with a “conventional” treatment process. This work specifically characterizes wash water copper and zinc concentrations and the observed removal trends under conditions where the treatment focus was TBT removal.

Study Methodology

Evaluation of copper and zinc removal by coagulation, and treatment with a laboratory

and full-scale treatment process train were investigated. Descriptions of the treatment conditions and many other facets of the study effort are provided in Schafran et al. (2001) found elsewhere in this volume. A brief description is provided here except for efforts (e.g. analytical methodology, sample handling) unique to the copper and zinc study effort.

Large volume wash water samples (typically 40 to 60 L) collected from southeastern Virginia, the Gulf Coast, and Pacific Northwest shipyards were used for the characterization of copper and zinc concentrations and for laboratory treatability studies. Samples were collected either from water draining directly from the hull, as runoff from a drydock surface, or after collection in storage vessel.

Samples were returned to the laboratory when collected locally or shipped by overnight mail when collected at remote locations. After receipt of samples at the laboratory, wash waters were held at 4 C and in the dark. Prior to removal of aliquots for analysis, sample containers were vigorously mixed, and quickly poured to prevent resettling of particulate material. Aliquots removed were analyzed for total and dissolved metals analysis, total suspended solids analysis, pH, conductivity, and dissolved organic carbon analysis.

Coagulation efforts to remove copper and zinc during this study examined the influence of coagulant dose, coagulant type, and coagulation pH using standard jar test procedures (AWWA, 1992). Samples were collected following the settling phase and were acidified to pH <2 and held for subsequent analysis. Dissolved metals were not determined during the coagulation studies.

A laboratory process train consisting of a sand filter and two granular activated carbon (GAC) columns was also used to assess copper and zinc removal by these unit processes. Samples were collected between each unit process and acidified and handled in the same manner as other samples used for total metals analysis.

The evaluation of copper and zinc removal in a full-scale treatment plant was also examined during this effort. The full-scale treatment plant provided coagulation, dissolved air flotation, sand filtration, and contact with two GAC contactor columns. The system was operated at 50 gallons per minute (190 liters per minute) during the study providing a GAC empty bed contact time (EBCT) of 36 minutes and an actual contact time (with GAC porosity of 0.44) of 16 minutes for the two contactors combined.

Total copper and zinc concentrations in the wash waters were analyzed from the same sample aliquot that was used for total and dissolved TBT. The procedure entailed a digestion phase that consisted of acidification of an aliquot of wash water to pH <2 with 2 mL of trace metal grade HCl followed by placement on a shaking table and agitation overnight (typically 17 hours). After digestion, the sample was filtered through a 0.45 µm filter and collected in a pre-washed polycarbonate bottle. Dissolved copper and zinc concentrations were determined on unacidified samples by filtration through a 0.45 µm filter followed by acidification with trace metal grade acid to pH<2. Samples collected during the coagulation studies, during operation of the laboratory process train, and from full-scale treatment efforts were similarly handled.

Analyses of copper and zinc were conducted utilizing flame and furnace atomic absorption spectroscopy (Perkin Elmer

Model 2100) deuterium arc background correction. All samples were initially analyzed by flame AAS and reanalyzed by furnace AAS if the measured copper concentration was < 50 ppb and the measured zinc concentration was < 100 ppb. Additional details on metals analyses including quality assurance and quality control procedures can be found elsewhere (Pommerenk, 1996).

Results

Wash water composition was determined for waters collected from southeastern Virginia, the Gulf Coast, and Pacific Northwest shipyards. Table 1 below summarizes the wash water characteristics of these waters including the total and dissolved copper and zinc. Dissolved copper and zinc are operationally defined and characterize solution concentrations on an aliquot of a sample passed through a 0.4 µm membrane filter. Consequently, some of the fraction considered dissolved may represent particulate copper and zinc below 0.4 µm in size.

Wash water total copper concentrations varied between 0.067 to 139 mg/L (median = 0.552 mg/L) while dissolved concentrations varied between 0.042 and 1.19 mg/L (median = 0.289 mg/L). For these samples, the proportion of copper in the dissolved fraction also varied between a minimum of 0.8% and a maximum of 63% (median = 29%). The fraction of copper in the dissolved fraction can be seen to be negatively correlated with total copper concentrations ($\%Cu_{diss} = -0.191 \cdot \log Cu_{total} + 0.341$; $r = -0.91$) indicating that waters with higher copper concentrations are dominated by particulate copper.

Wash water total zinc concentrations varied between 0.60 to 72 mg/L (median = 8.3 mg/L) while dissolved zinc concentrations varied between 0.5 and 6.6 mg/L (median = 3.3 mg/L). Total dissolved zinc concentrations comprised a greater fraction of the total zinc concentration than was seen with copper (median = 52%) and an even stronger (negative) correlation was observed between the %dissolved zinc fraction and

total zinc ($\%Zn_{diss} = -0.390 \cdot \log Zn_{total} + 0.772$; $r = -0.98$) than observed with copper. The greater amount of dissolved zinc (relative to dissolved copper) is consistent with the higher zinc concentrations predicted by chemical equilibrium calculations when the solubility of both metals is controlled by metal oxide/hydroxide solid phases (Stumm and Morgan, 1996).

Table 1. Characterization of Shipyard Wash Water Composition
(all values in mg/L).

Ship Designation	Cu _{total}	Cu _{diss.}	Zn _{total}	Zn _{diss.}	TSS	DOC ¹
CV5	0.552	0.289	8.3	4.3	14	3.4
CV6	139	1.19	72	3.5	4,340	24.8
CV7	0.067	0.042	0.60	0.50	17	3.0
CV8	15.3	0.61	34	6.6	540	10.2
CV9	13.5	1.04	23	3.3	-	13.4
CV10	0.25	0.12	1.1	0.80	17	7.4
CV11	0.27	0.074	1.5	1.1	15	4.3

¹ DOC – dissolved organic carbon; CV – commercial vessel

Total suspended solids exhibited substantial variability while variability in DOC was more moderate. The suspended solids contribute significantly to the total metal concentrations in solution since much of the solids are paint coatings containing copper and zinc. Very strong correlations have been previously observed for dry dock runoff associated with storm events as illustrated in Figure 1.

Organic matter present in the wash water is likely to originate in large part from the solids removed from a ships hull since fresh waters low in DOC are typically used for washing. For the events in Table 1, DOC was correlated to the TSS supporting this

supposition ($DOC = 7.23 \cdot \log TSS - 4.6$, $r^2 = 0.87$).

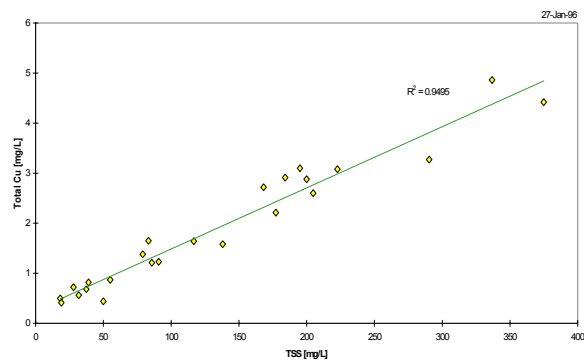


Figure 1. Relationship between total copper and TSS in dry dock runoff (Pommerenk, 1996).

From a treatment perspective, the DOC present in solution could potentially complex with copper and zinc increasing their solubility and mitigating their removal. This “inhibitory” effect would be most noticeable in any unit process where removal of the inorganic fraction of the metal (including a precipitate) is favored over the organic fraction. Coagulation and metal removal by chemical precipitation of a hydrous metal oxide are processes that could be negatively impacted by the presence of DOC. While certain unit processes may be negatively impacted, the formation of metal-organic complexes could prove to increase the removal of copper and zinc in other unit processes where sorption of the organic moiety of the metal-organic compound is favored (e.g. GAC).

Coagulation Studies

Coagulation is traditionally used to improve particle removal through destabilization or coprecipitation/enmeshment of particles with the precipitate formed from the addition of a hydrolyzing metal salt coagulant. Both alum and ferric sulfate were used as coagulants in this effort and were used to treat each wash water. Comparison of copper and zinc concentrations following coagulation revealed that metal removal was comparable using either coagulant. An example of this removal is illustrated for water CV8 treated at pH 6.5 (Figure 2).

The pH during coagulation typically plays an important role in particle removal due to the influence on the amount of precipitate formed and the electrical charge of the precipitate. pH is also important for the removal of copper and zinc since solution pH directly influences metal solubility. For copper removal, copper concentrations

decreased with increasing pH as expected based on solubility (Figure 3). Prediction of copper species and total solubility (total Cu line) were based on assuming $\text{Cu}(\text{OH})_2(\text{s})$ ($\text{pK}_{\text{so}} = 19.3$) as the solubility-controlling solid phase. The trend in measured total copper concentrations following coagulation suggests either a more soluble solid phase controls solubility, that particulate copper represented a significant component of the measured total copper, or organic complexation caused elevated copper concentrations.

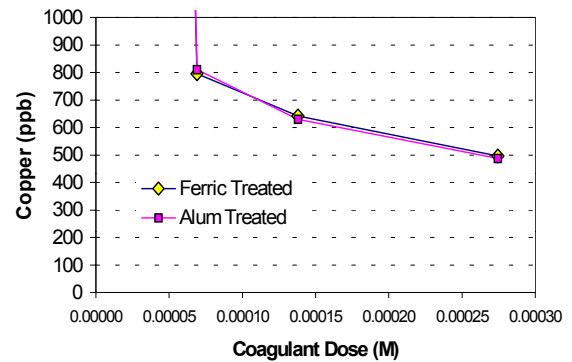


Figure 2. Comparison of total copper concentrations following coagulation of CV8 wash water.

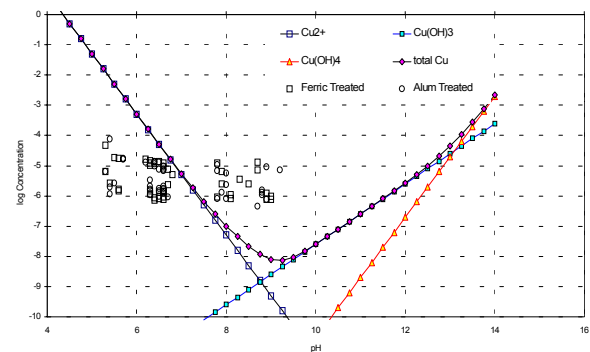


Figure 3. Log total copper concentrations (molar) for alum and ferric sulfate treatment as a function of pH.

Zinc concentrations were more significantly influenced by coagulation pH (Figure 4) compared to the trend observed with copper. The good fit between the data points and the total Zn solubility line suggest that the total zinc concentrations were dominated by inorganic, dissolved species and that the solid phase ($Zn(OH)_2(s)$, $pK_{so} = 17.1$) used for the equilibrium calculations well describes the controlling solid phase.

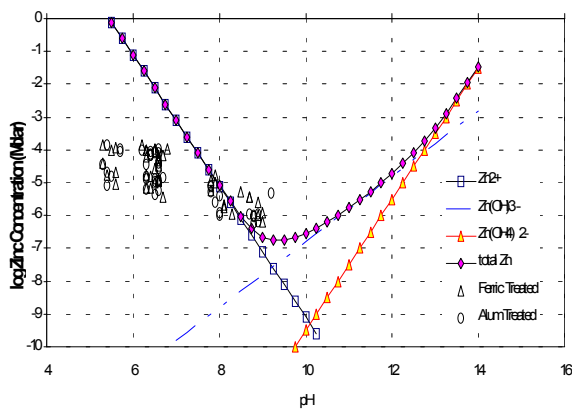


Figure 4. Log total zinc concentrations for alum and ferric sulfate treatment as a function of pH.

The trend in copper and zinc concentrations suggest that both metals are better removed at higher pH (>8) which contrasts with coagulation removal of TBT where the optimum pH range for TBT removal was observed at pH 6-7 (Schafran et al., 2001). These results suggest that coagulation can not be optimized for both copper and zinc removal and TBT.

Laboratory Process Train

A laboratory continuous-flow process train consisting of a sand filter and two columns of GAC was used in study efforts to treat the

waters listed in Table 1 after they were initially batch coagulated and clarified. This process train configuration was consistent with a full-scale treatment plant used to treat shipyard waters.

For each wash water, five samples were collected after each unit process and one sample was collected from the influent. (Missing influent values for CV5 and CV6 were due to loss of sample volume) Total copper concentrations for water treated with this process train illustrate the trend in removal and concentrations in the final effluent (Figure 5). Final effluent copper concentrations were typically below 50 ppb and removal varied with water and unit process. Waters CV8 and CV9 with influent concentrations over 400 and 600 ppb, respectively, illustrate the removal that occurred in the sand filter and the considerably higher removal that occurred in GAC1 (the first GAC column in series). While the removal in the filter is likely due to particle removal, the removal in GAC1 is either the removal of dissolved copper or removal of particulate copper that escaped the sand filter.

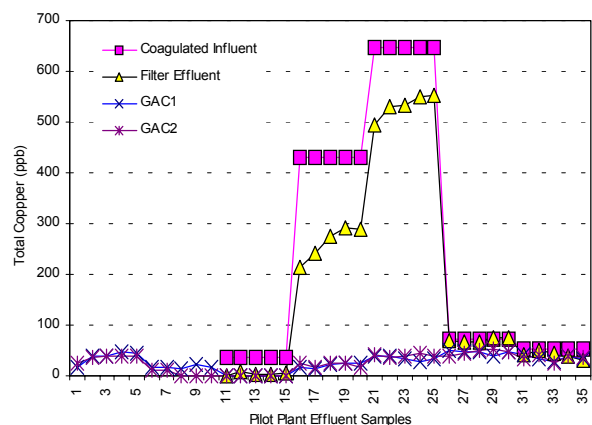


Figure 5. Variation in total copper concentrations in the laboratory process train treating CV5 – CV11 (Table 1.)

Total zinc concentrations in the laboratory process train are illustrated in Figure 6. Final effluent concentrations were generally considerably reduced from the coagulated influent concentration. Similar to trends with copper, substantial removal of zinc occurred in the activated carbon columns. Increasing concentrations with run time were observed for CV8 and CV9 and CV10 exhibited concentrations in GAC1 that exceeded copper concentrations in water entering GAC1. This trend may reflect remobilization of particulate material removed in GAC1 or solubilization of particulate TBT previously captured.

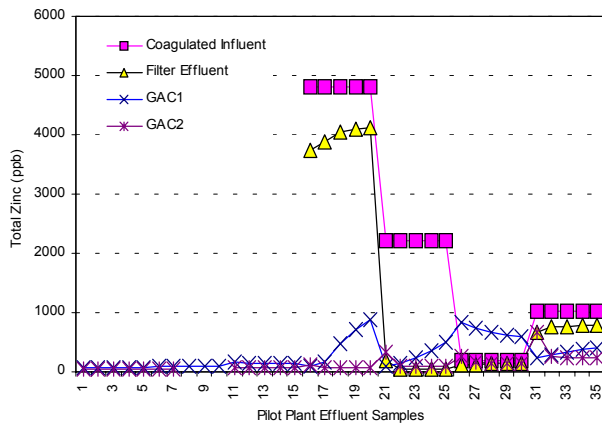


Figure 6. Variation in total zinc concentrations in the laboratory process train treating CV5 – CV11 (Table 1.)

Full-Scale Treatment Results

Treatment with the full-scale treatment process train commenced in December 1999 and through the end of March 2001, 2.2 million gallons had been processed with the treatment plant. During treatment plant operation, a minimum of one final effluent sample was collected per day with greater numbers (including after each unit process) during periods when operational conditions were changed to assess the effect on

treatment performance. Selected representations from this data set are illustrated.

The first full-scale treatment of a wash water occurred during April 26-28, 2000. During this period, coagulant and coagulation pH conditions were changed which allow assessment of the effect of these changes on copper and zinc removal. Two samples were collected from the influent and after each unit process on the 26th (pH 10, ferric sulfate) and the 27th (pH 9.5 and 8, alum) and a single sample was collected on the 28th (pH 7.3, alum).

Influent total copper concentrations during the three-day treatment event ranged between 400 and 700 ppb with concentrations generally increasing over time (Figure 7). The majority of the copper was removed in the clarification stage (DAF). Of the following stages, little change was observed after passage through the sand filter, additional removal was observed in GAC1, and no additional removal occurred after contact with GAC2. Higher copper concentrations for samples 4 and 5 occurred at lower pH values (8 and 7) compared to earlier samples. The higher concentrations may reflect higher solubility of dissolved copper at these pH values.

Total zinc concentrations in the full-scale treatment plant during this period were similar to copper concentrations with some noticeable differences (Figure 8). Influent concentrations were generally constant at 2,000 ppb with the majority of removal occurring in the DAF. Similar to copper but even more dramatic, zinc concentrations increased in the post DAF on the last two sampling occasions. Similar to copper, this increase is likely related to increased solubility at the lower pH.

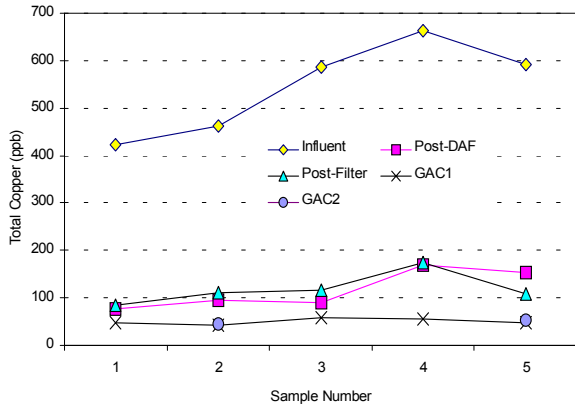


Figure 7. Total copper concentrations at the indicated location in the full-scale treatment plant. April 26-28, 2000.

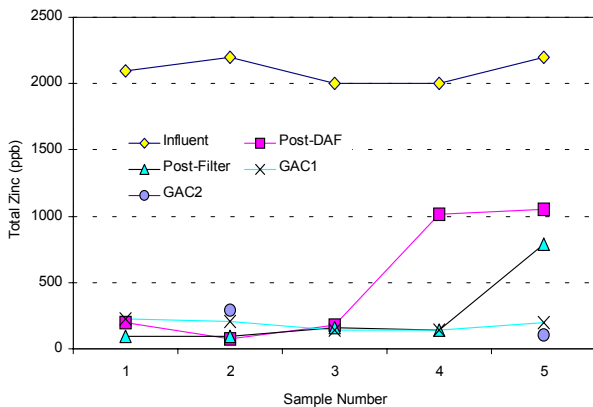


Figure 8. Total zinc concentrations at the indicated location in the full-scale treatment plant. April 26-28, 2000.

Treatment results for the full-scale plant are also presented for treatment that occurred in November–December, 2000. During this period, coagulation conditions included the use of ferric sulfate and operating at a coagulation pH of 10. Water exiting the DAF (prior to entering the sand filter) was also acidified to pH 6.5 to 7.5 to improve the removal of TBT on the GAC. Similar to observations concentrations analyzed for

this period illustrate that copper removal between the influent and post-sand stage varied widely. Noteworthy is the consistently low copper concentrations (<10 ppb) of the post GAC1 and Effluent (i.e. GAC2) from the full-scale plant. These data suggest that the process train tested has the capability to meet copper treatment requirements that shipyards may be faced with achieving sometime in the near future.

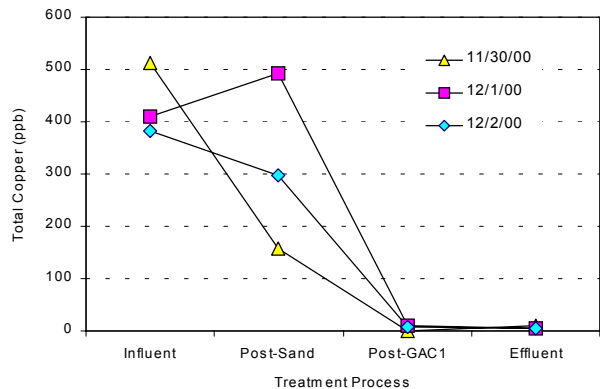


Figure 9. Total copper concentrations for the full-scale treatment plant for November 30 to December 2, 2000.

Summary

The laboratory and full-scale study results indicate that copper and zinc removal from shipyard wash waters can be accomplished to a substantial degree with a treatment process train designed and operated primarily for TBT removal. During the study efforts reported here, copper and zinc were removed to effluent concentrations that often approached levels that may be considered for regulation in the near future. Little fractionation of copper and zinc into the dissolved fraction was conducted and it

is not know what the fractionation is in the final effluent of the treatment plant. Better understanding the fractionation that exists in the final effluent will better serve determining what additional treatment processes would effectively target this copper and zinc for removal.

References

AWWA (1992). *Operational Control of Coagulation and Filtration Processes (M37)*. American Water Works Association, Denver, CO, 112 pp.

Eaton, A.D., Clesceri, L.S., and Greenberg, A.E, editors (1995). *Standard Methods for the Examination of Water and Wastewater*. 19th ed., American Public Health Association, Washington, D.C.

Line, D.E., Wu, J., Arnold, J.A., Jennings, G.D., and Rubin, R.A. (1997). Water quality of first flush runoff from 20 industrial sites. *Water Environment Research* 69(3): 305-310.

Pommerenk, P. (1996). *Characterization of Rainfall Runoff Quality from a Shipyard Drydock*. M.S. Thesis, Old Dominion University, Norfolk, VA.

Schafran, G.C., Winfield, J. and Akan, A.O., (1998). *Treatment, recycle, and reuse of stormwater runoff in shipyards*. Final Report to the National Shipbuilding Research Program. Project N

Schafran, G.C., T.Tekleab, R. Prasad, T. Fox, M.A. Champ, and D.A. Johnson, 2001. *Removal of tributyltin (TBT) from shipyard waters: Laboratory evaluations and one year of full-scale, shipyard-based treatment*, Proceedings of the Oceans International

2001 Special Session on Pollution Prevention in Ships and Shipyards. Miami, FL, April 4-6.

Stumm, W. and Morgan, J.M., (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd Edition, John Wiley & Sons, New York.

USEPA (1983). *Results of the National Urban Runoff Program*. Washington, D.C. Executive Summary, NTIS No. PB84-1855345.