CHARACTERIZATION AND TREATABILITY
OF HYDROBLAST WASTEWATER

by

KENNETH C. ALEXANDER

A thesis presented in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE IN ENGINEERING

UNIVERSITY OF WASHINGTON

1988

Approved by H David Stensel
H. David Stensel
Chairman of Supervisory Committee

Program Authorized
to Offer Degree Department of Civil Engineering

Date 8-19-1988

MASTER'S THESIS

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at the University of Washington, I agree that the Library shall make its copies freely available for inspection. I further agree that extensive copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U. S. Copyright Law. Any other reproduction for any purposes or by any means shall not be allowed without my written permission.

Signature Kenneth Alexander

Date 19 August 1988

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

TABLE OF CONTENTS
(continued)

LIST OF FIGURES

FIGURE PAGE

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

LIST OF TABLES

LIST OF TABLES
(continued)

ACKNOWLEDGMENTS

The author must acknowledge a number of individuals and groups who made the timely completion of this study possible.

First I wish to thank the taxpayers of the United States of America and the State of Washington for funding my salary/tuition and the research costs, respectively.

I wish to acknowledge the assistance and encouragement I received this past year from my advisor, Dr. Stensel as well as the other faculty in the Environmental Engineering and Science program.

For their invaluable assistance in the laboratory I want to recognize Ron Sletten, who performed the metals analysis and helped me with numerous other experimental procedures, Victoria Jelderks, who assisted me in the final hectic conclusion of the laboratory work, Dr. Richard Dobbs and associates of the Environmental Protection Agency, who graciously provided analysis for the tributytin and, of course, Lorna Goebel who provided me with needed equipment and materials in a consistently timely fashion.

Finally, I must acknowledge the many individuals with whom I had the pleasure of working during the gathering of water samples. I gratefully acknowledge Mr. Kris Lunde of Foss Maritime, Ken Anderson of Marco Seattle, and Mr. Rich Allen of Mercer Marine for their highly professional and invaluable assistance in procuring the hydroblast samples. These gentlemen as well as company officials from all four of the study sites, Marco, Foss, Union Bay and Mercer Marine, were unfailingly and exceptionally cooperative throughout the course of this study.

DEDICATION

This thesis is dedicated to the families of Michael and Helen Littwin and Richard and Jae-Sook Cohen. The active, prayerful and loving support these two families offered me, my wife and daughters during this past year has unequivocally made this the most memorable, enjoyable and successful experience of my life.

CHAPTER 1

INTRODUCTION AND GOALS OF THE STUDY

The practice of applying anti-foulant bottom paints to ship hulls has come under scrutiny in recent years with concerns that these paints contribute to significant degradation of water quality in areas with high water vessel traffic. Of particular interest has been the use of anti-foulant paints containing highly toxic organotin compounds.

Anti-foulant bottom paints come in a wide variety of formulations, but they can be segregated into two classes based upon their primary anti-fouling ingredient: (1) copper paints and (2) organotin paints. In the recreational and commercial sector both types of paints have been widely used, but the organotin products, normally containing tributyltin fluoride or tributyltin oxide, have outperformed the cuprous oxide paints leading to their more common use in recent years. Due to tributyltin's exceptional biocidal characteristics, the United States Navy is proposing using tributyltin paints on a fleet-wide basis. The Navy projects that considerable monetary savings will result from decreasing fuel requirements and ship drydocking periods due to reductions in hull friction and less frequent re-painting of hull surfaces. Current formulations for anti-foulant paints strive to provide consistent protection against marine growth on a ship's hull over the longest possible period of time. Thus the release of antifouling compounds into the environment is clearly designed to occur from the initial to the final phases of the paint's life. When the anti-foulant has lost its ability to protect the hull surface from new growth, several options are available to clean the hull surface and prepare for a new coat or coats of paint. One such method used by both commercial shipyard and recreational marina owners is the application of high pressure water jets, sometimes called hydroblasting. When applied at very high pressure over a long enough period of time, hydroblasting is capable of completely removing the paint from the hull surface, but normally it is used to merely clean the hull of scale and marine growth and leave the paint intact. Thus the question arises whether the hydroblasting waters are also contributing significantly to further releases of the anti-fouling chemicals into the environment.

At the present time, there are no effluent guidelines or treatment requirements for wastewater discharges resulting from the practice of hydroblasting, unless hydroblasting is performed in a graving dock. Little is known regarding actual quantities and components of hydroblasting wastewaters which could be used to determine whether regulation or treatment of this wastewater is feasible or desired.

This ~~study~~ thesis, ~~therefore~~, has two goals. The first is to characterize hydroblasting wastewaters in terms of standard water quality parameters (e.g., total suspended solids, chemical oxygen demand, turbidity) and the heavy metals and tributyltin they are likely to carry. The second objective is, based on the hydroblast water's characteristics, devise and investigate the feasibility of simple treatment processes that could be used to perform on-site wastewater treatment. Based on the results of this study, recommendations for treatment alternatives and future research in this area are suggested.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Marine Paint Characteristics

Marine anti-foulant paints come in many formulations and, with the exception of those formulations identified in standard military specifications, these mixtures are proprietary information carefully guarded by the paint manufacturers. For the purposes of this study, only the non-volatile paint components are of interest, since it is presumed that the toxic and carcinogenic solvents have essentially dissipated once the vessel's maintenance cycle requires re-painting the hull.

Research by Phillips (1976) into the toxic and carcinogenic components of paint reveals that all marine paints contain some type of non-volatile toxic compound, usually cuprous oxide or an organotin chemical, that is normally found in quantities between 7 and 75 percent (by "wet" weight). Such large quantities are not surprising because of the long term biocidal function desired of these products.

In addition to the biocidal agents, a number of other heavy metal constituents are present in marine paints that are potentially toxic or at least of concern from an environmental standpoint. Zinc compounds are found as pigments (ZnO) and flatting agents (zinc stearate). Barium compounds are used as extenders. Copper is found in pigments as cupric oxide (CuO) and as the biocide cuprous oxide (Cu_2O). Iron oxide (Fe_2O_3) is used for red pigmentation. Aluminum is used as an extender in the form of aluminum silicate. Lead, cobalt and manganese are contained in napthenate drying salts. Inorganic tin is not considered toxic, but some of its organic compounds are quite toxic. In addition to use as a biocide in the form of tributyltin (TBT), organotins are also used as paint stabilizers.

Comparing paint components and release rates of cuprous oxide anti-foulant paints with the newer copolymer TBT paints, the biocidal effectiveness of TBT paints becomes quite evident. Copper antifoulant paints contain between 40 to 75 percent by weight cuprous oxide and initial release rates (James, 1975) for a paint with 49 percent Cu_2O are as high as 250 $ug/cm^2/day$, decreasing to 50+ $ug/cm^2/day$ after 15 days. TBT anti-foulant copolymer paints with less than 25 percent TBT compounds experience high early TBT releases above 75 $ug/cm^2/day$, but bottom out to around 15 $ug/cm^2/day$ after about 3 days (USEPA, 1987b). Ship hulls painted with TBT paints are reported to have 5+ years of freedom from significant amounts of marine growth, while copper paints are normally effective for only 18 to 24 months (USEPA, 1987b). Thus the copper paints must carry a biocide with significantly higher quantities and release rates, yet they are less effective over the long term.

Biocide release rates are a key parameter being considered for federal regulation of the use of TBT paints on ship hulls. The U. S. House of Representatives has proposed a bill (HR 2210, 9-22-87) which limits TBT release rates to 5 $ug/cm^2/day$ while the Senate version (S 1788, 11-9-87) has a rate of 3 $ug/cm^2/day$. The state of Washington has enacted a law, adding new sections to 70.54 RCW, which echoes the release rate in the House of Representatives bill. The Senate version of the bill requires EPA to issue a water quality criteria document for TBT by 30 March 1989. Additionally, the Senate version will require the EPA and National Oceanic and Atmospheric Administration (NOAA) to monitor estuaries, with the U.S. Navy designated to monitor harbors, for a period of five years to determine the environmental impacts of this restriction (JWPCF, 1988).

2.2 Tributyltin and the Environment

Tributyltin (TBT) has been used as a marine anti-foulant paint component since the early 1960s. Recent new formulations have replaced the freely associating type TBT paint, where the $Sn(C_4H_9)_3^+$ species mixes freely among the paint components, with a copolymer in which the tributyltin is chemically bonded to the paint resin. This latter formulation provides for a more controlled, and hence economical, release of the TBT biocide through a process of chemical hydrolysis. The older mixture, on the other hand, released the TBT ion through a more random physical dissolution that resulted in rapid and early release of the biocide. In its recently issued Water Quality Advisories for Tributyltin (USEPA, 1987a), the Environmental Protection Agency (EPA) has reviewed results of over 120 studies from the United States, Canada and Europe reporting the biological effects of TBT in the environment. From this information, the EPA has concluded that acute toxicity to aquatic organisms exists in the lower parts per billion (ppb) range and for chronic toxicity the range is in the upper parts per trillion (ppt), depending upon the organism. Thus water quality advisories for TBT have been set very conservatively at 0.026 ug/L for fresh water and 0.01 ug/L for salt water.

The basis for selecting a smaller advisory level for saltwater is the current perception that TBT is not as serious an environmental threat in those waters as it is in shallow fresh water such as those found in small inlets and harbors where sensitive aquatic life resides (Cardwell, 1988 and JWPCF, 1988).

Regarding the fate of TBT in the environment, two recent reviews by Cardwell (1988) and Clark et al (1988) generally agree that the research to date points to aerobic biological degradation as the primary degradation pathway of TBT in the aquatic environment. Aerobic biological degradation is mediated by both microorganisms and algae at comparable rates: TBT half lives in the range of six to twelve days. By comparison, anaerobic degradation appears to be far slower, with TBT half lives generally being 200 days and greater. Abiotic degradation of TBT is also possible, but photolysis has been shown to be the sole abiotic degradation process of any importance and only at the water surface microlayer does it occur at a significant rate. Direct ultraviolet radiation can produce photolytic half-lives of less than one day, but TBT in direct sunlight has been reported to have a half life of up to three months.

Degradation products from TBT are the dibutyltin (DBT) and monobutyltin (MBT) species and ultimately inorganic tin, but disagreement exists as to whether DBT or MBT is the primary initial product. Some studies indicate that methyl-butyltin intermediates may actually be formed (Clark et al, 1988). The most important aspect of the degradation products from a water quality standpoint is that the products are far less toxic than their TBT parent species. For example, the toxicity of DBT is more than 300 times less than TBT but 4 times higher than MBT for certain species of algae (Wong et al, 1982).

One of the most significant characteristics of TBT's fate in the environment is related to its ability to sorb to solid matter, as measured by its octanol-water coefficient (Kow). Octanol water coefficients reported for TBT have ranged from 200 to 7000 in Laughlin's (1986) studies, but the Kow for TBT appears to have found a generally accepted value of around 2650 (Cardwell, 1988). Sediment-water coefficients are reported in the 3000+ ug/kg/mg/L range at low suspended solids concentrations (<10 mg/L) in the water column, but will be even lower with higher concentrations of suspended solids (USEPA, 1986). Thus TBT exhibits a strong tendency to sorb to solid matter in both sediment and suspended particulate matter. Yet some studies (Valkirs et al, 1986; Maguire, 1986) indicate that TBT is more highly associated with the dissolved phase in the water column than with the suspended particulate, so its soluble form cannot be ignored or discounted either.

The presence of tributyltin in aquatic environments in the United States, Canada and Europe has been reported to some extent. Maguire (1982) found waters at a marina in Toronto, Canada, had TBT concentrations as high as 2.91 ug/L (1.58 ug/L as Sn), which is one or two magnitudes higher than those found in other waterways in the same geographical proximity. The surface microlayer contained TBT at 50.9 ug/L (27.67 ug/L as Sn) in the same marina. By comparison, background levels of total tin have ranged from 0.009 to 0.8 ug/L in salt water and 0.004 ug/L in fresh water (NRCC, 1985). Valkirs and associates (1986) found TBT levels were increasing with time in surface waters at two marinas in San Diego Bay. One location, for example, went from 0.05 ug/L TBT in January 1983 to 0.93 ug/L TBT in September 1985, an 18 fold increase in two and a half years. In both the San Diego and Toronto studies, widespread use of anti-foulant TBT paints on boat hulls was documented.

2.3 Copper and the Environment

Implicit in the recent acceptance of TBT anti-foulant paints over the traditional copper-based anti-foulant paints is the fact that copper is less effective as a biocide, hence far less toxic compared to TBT. Nevertheless, copper is highly toxic to a wide range of aquatic organisms. By comparison, copper is acutely toxic to fish at concentrations of 200 to 7500 times higher than TBT, 15 to 90 times higher for crustaceans, and 50 to 100 times higher for bivalves (e.g. clams). Toxicity of algae to TBT has been observed for some species in the 0.1 - 5 ug/L range (USEPA, 1986) while copper exhibits toxicity to various species of algae at concentrations between 10 and 1000 times the aforementioned TBT levels (Hodson et al, 1979).

Another key difference between copper and TBT is that copper is a micronutrient in most plant and animal life. Most marine organisms have natural copper levels of approximately 1 mg-Cu/kg-body weight. So, trace amounts of copper are actually desirable in the aquatic environment. Background levels for copper in relatively unpolluted bodies of water are approximately 1 ug/L. Downstream of copper smelters, rivers and lakes have reported concentrations of 20 ug/L (Hodson, 1979). In

Puget Sound, copper concentrations of 0.1 - 1 ug/L were detected in the central basin, but concentrations between 10 and 370 times these levels were found in various inlets and bays, with the highest concentration being found in Commencement Bay, at Tacoma, the site of the now inoperative Asarco copper smelter (PSWQA, 1986). As a source of copper in the aquatic environment, copper anti-foulant paints are more of a footnote than a significant contributory factor because copper is introduced into the environment from a variety of industrial sources as well as copper drinking water pipes. The EPA has established drinking water regulations (USEPA, 1979a) for copper concentrations not to exceed 1 mg/L, but this criteria is based on undesirable taste more than for human health concerns. Since copper must be in its ionic form to exhibit toxicity, significant environmental or health hazards appear diminished by copper's strong complexing capability with various common aquatic chemical species such as hydroxyl and carbonate ions (Snoeyink and Jenkins, 1980). Additionally, the copper ion concentration decreases considerably with an increase in pH. For example, in equilibrium with the hydroxyl and carbonate systems, free copper ion is predominant when $pH < 6.5$. Seawater contains a number of positively charged ions (e.g., Ca^{+} and Mg^{+}) that electrically displace hydrogen ions and, therefore, has a tendency to be alkaline. Copper, then, may be a significantly greater hazard in fresh water bodies that have become acidified than in the ocean which has essentially "unlimited" alkalinity.

2.4 Hydroblast Water Treatment and Disposal

2.4.1 Institution of "Best Management Practices"

In the mid-1970s, the EPA undertook a study to determine the practicability of establishing numerical effluent guidelines for submerged and floating drydocks at shipyards. As stated in the Development Document for Proposed Best Management Practices or BMPs (EPA, 1979b), the EPA concluded "this industry is such that numerical effluent limitations are impractical and difficult to apply in a manner which could be monitored; therefore, guidance is provided for controlling wastewater pollutant discharges which require that best management practices be applied." With respect to the discharge of wastewater from water blasting operations used to prepare ship surfaces for re-painting, the BMPs only have guidelines for their discharge from submerged drydocks (also called a "graving dock") and not floating drydocks. This apparently is due to the submerged drydock's ability to temporarily hold the water for subsequent delivery into other holding containers for "removal and disposal or (to be) subjected to treatment to concentrate the solids for disposal and prepare the water for reuse or discharge." (USEPA, 1979b)

A review of the literature reveals little on the subject of hydroblasting, shipyard wastewaters or shipyard wastewater treatment methods. The EPA draft guidelines list several water treatment strategies for drydock discharges including (1) baffled drainage systems, (2) absorbents (sic) and wire meshes placed in discharge flow paths and (3) use of pontoons for settling solids. However, in practice, none of these methods had gained wide acceptance by the end of the 1970s and the literature does not indicate any research into the actual design and construction of such methods has taken place since the BMP guidance document was released.

2.4.2 Drydock Design and Operation

The BMP guidance document points out that difficulties in collecting and treating wastewaters from drydocks are presented by the drydock design itself. Floating drydocks (Figure 1) are large pontoons with two high side walls along the length of the pontoon deck and open ends along the deck's shorter dimension. The drydock is lowered and raised in and out of the water by means of flooding and flushing immense volumes of water in and out of hollow ballast compartments within the drydock. The ship is positioned to sit on keel and bilge blocks located down the platform's center and sides respectively. The keel and bilge blocks on a drydock are positioned on fixed tracks that are either raised above or constructed flush with the deck. Thus there are several problems inherent in the existing drydock construction that pose potential obstacles in collection and removal of wastewaters from drydocks:

(1) The drydock is designed to carry the weight of large ships, but not large volumes of water in the way a submerged graving dock can.

(2) The tracks for positioning the keel and bilge blocks can both hamper and aid the collection and removal of drydock wastewater, depending upon their locations respective to the deck level. Additionally, these tracks can serve to entrap solids that settle out from the wastewater.

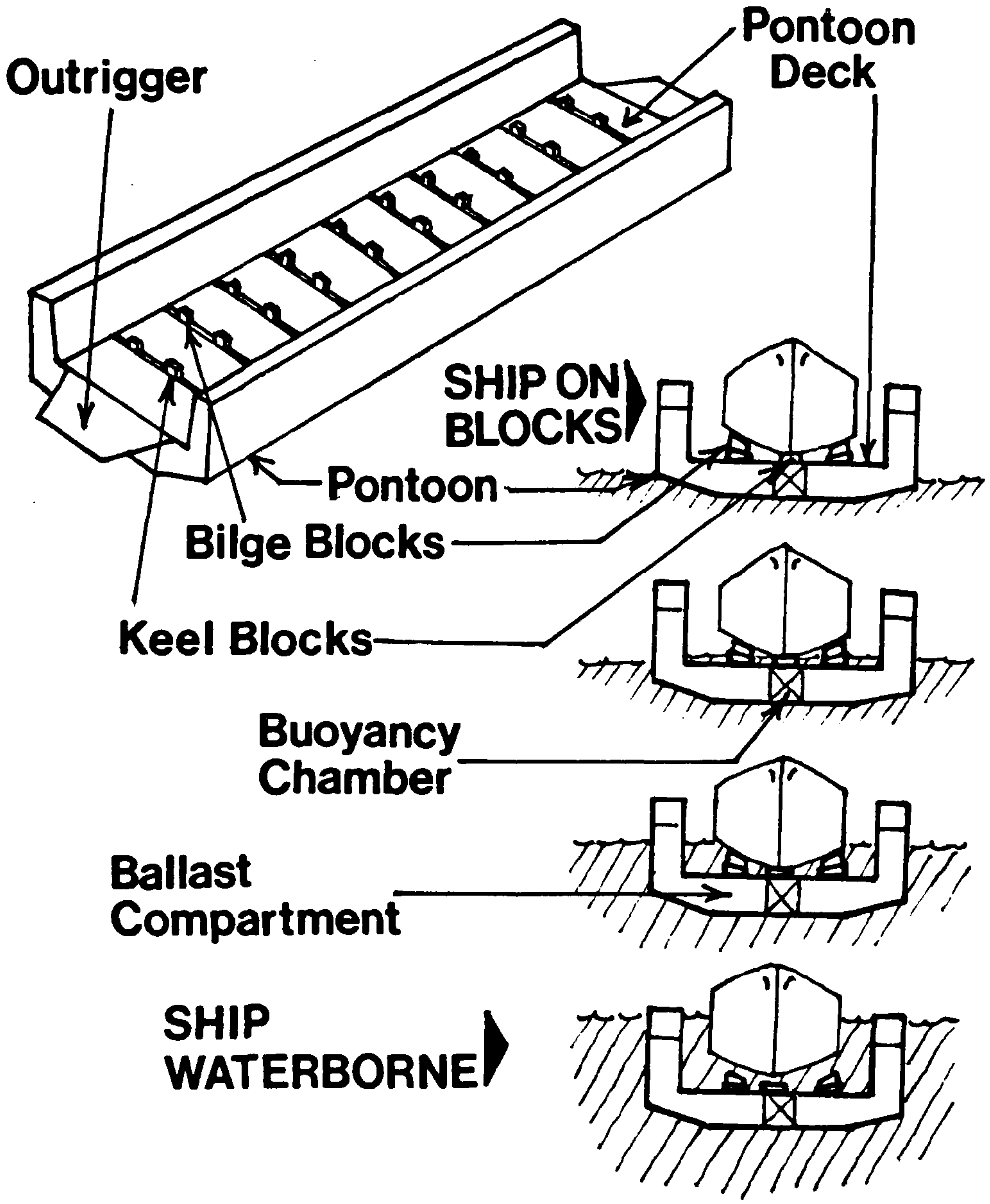


Figure 1 - Typical Floating Drydock Showing Basic Construction and Operation

(3) The large open deck area, coupled with the wide open ends of the drydock make transport of the water to a single ultimate collection point difficult. According to one Seattle shipyard operations manager, some floating drydock designs permit flushing a larger quantity of water from one side of the hollow ballast compartments. This makes it possible to tip the platform to allow the flow of water to favor one side of the platform over the other. However, this is an operational decision that must take into account the effect of tipping the platform on the stability of the ship sitting on the keel and bilge blocks, i.e. a ship with a high center of gravity could be in danger of shifting if the tilt is too great.

2.4.3 Drydock Wastewater Characteristics

Research by the EPA for the development of graving dock and drydock management guidelines involved sampling of wastewater discharges at three commercial shipyards. The sampling results reported parameters shown in Table 1. The samples analyzed for this study were discharges taken from graving docks that had been flooded and dewatered.

Table 1 - Wastewater Characteristics from Discharges at Three Commercial Shipyards (USEPA, 1979b)

Parameter	Drainage Water		Harbor Water	
	High	Low	High	Low
pH	8.8	6.8	9.3	6.7
TSS (mg/L)	19,312	2	200	6
Settleable Solids (mg/L)	200	<0.1	19	<0.1
Oil/Grease (mg/L)	61	0	8.2	1.2
METALS (all as mg/L), where (T) = Total, (S) = Soluble				
Aluminum(T)	1.6	<1.0	<1.0	<1.0
Aluminum(S)	<1.0	<1.0	<1.0	<1.0
Arsenic(T)	0.19	<0.01	0.05	<0.01
Arsenic(S)	0.15	<0.01	0.02	<0.01
Cadmium(T)	<0.1	<0.01	0.06	<0.01
Cadmium(S)	<0.1	<0.01	0.05	<0.01
Chromium(T)	1.0	<0.025	0.1	<0.1
Chromium(S)	0.79	<0.03	<0.1	<0.02
Copper(T)	60.0	<0.01	1.2	<0.05
Copper(S)	4.5	<0.04	<0.1	0.03
Iron(T)	1,250.0	0.02	0.39	<0.01
Iron(S)	2.1	<0.1	0.2	<0.1
Lead(T)	13	1.2	0.57	<0.05
Lead(S)	0.5	<0.01	0.57	<0.04
Mercury(T)	0.056	<0.0001	0.0035	0.0013
Mercury(S)	<0.0025	<0.0001	0.0031	0.0004
Nickel(T)	0.35	<0.2	0.36	<0.2
Nickel(S)	<0.2	<0.2	0.36	<0.2
Tin(T)	5.0	0.01	3.4	<0.4
Tin(S)	3.0	<0.1	2.1	<0.4
Zinc(T)	39.0	<0.02	1.6	<0.02
Zinc(S)	4.1	<0.02	0.45	<0.02

Due to the many operations that were taking place at these three sampling locations, the sampling results reported in Table 1 do not include a detailed description of the ship maintenance activities that contributed to the contamination of the "drainage water", but "hull cleaning waste" was a major component. At the time of this study, the EPA reports that 95 percent of all shipyards utilized dry abrasive blasting as a hull surface preparation method.

The U.S. Navy performed a characterization and treatability study of drydock discharges from Long Beach Naval Shipyard (Saam et al, 1977). The Navy does not perform hydroblasting as part of cyclic maintenance of its ships, therefore hydroblast wastewaters were not part of the waters analyzed in this study. Wastewater flows generated by "industrial" sources such as dry-grit hull blasting represented only 2.5 percent of the total discharge. Sewage, hydrostatic leakage and cooling water contributed the largest volume to the drydock waste stream. The industrial waste stream was high in zinc (2.01 mg/L) and copper (3.3 mg/L) and total suspended solids (433 mg/L). From separate analysis of the blasting grit and paint, the Navy determined that paint was the main contributor to the water's heavy metal content.

In the absence of actual reported data on hydroblasting water characteristics, the EPA and Navy results at least offer a preliminary clue to what hydroblasting wastewater is likely to contain. From these studies it is apparent that certain metals will figure more prominently in the water make-up than others. The EPA study demonstrates that the metals, in most cases, are not highly solubilized and, in fact, the soluble metals concentrations are often on the same order of magnitiude as the background concentrations in the harbor water: this is the case with aluminum, cadmium, lead, mercury, nickel and tin. It is also generally observed that metals such as copper, iron, lead and zinc in their insoluble form contribute significantly to the total metals concentration in these effluents. Yet, from saltwater leachate studies performed with the dry blasting/paint waste in the Navy study, it appears that metals from the spent paint chips are likely to be more soluble in seawater due to the formation of metal chloride complexes.

The upper range of total suspended solids (TSS) found in one EPA sample is over 19 grams per liter. The corresponding settleable solids concentration for this particular sample is only 200 mg per liter. A significant portion of this particular sample's total suspended solids, 1.2 g/L, is insoluble iron. It is surprising that so little, only 1 percent of the total solids, settled out. Unfortunately, the report does not offer any explanation for this apparent anomaly. The median value for total suspended solids in drainage water at the three locations is only 10, 36 and 17 mg/L respectively, with only trace amounts of settleable solids in each case. Thus these waters are generally quite diluted and are unlikely to be representative of the hydroblasting waters in terms of suspended solids concentrations.

Tin, in the EPA study, is also present in relatively high concentrations, but no attempt was made to distinguish the organotin species from the reported concentrations of total tin. Soluble tin is quite high, ranging anywhere from 60 to 100 percent of the total tin. If the soluble tin is TBT, it is present in the drainage water at 1000 times the acute toxicity level for many marine organisms. The implications for treatability of such a water are clear: some means of removing soluble organics from this water, such as activated carbon or biological treatment, would be necessary.

2.4.4 Related Treatment Studies for Wastewaters Contaminated with Marine Paints

In conjunction with its proposal to use organotin anti-foulant paints on a fleet-wide basis, the U. S. Navy initiated a number of studies to determine the treatability of water contaminated with TBT (Adema and Schatzberg, 1984). In order to comply with federal and local water quality criteria, the Navy also performed a a characterization and treatability study of drydock wastewaters (Saam et al, 1977).

2.4.4.1 Tributyltin's Effects on Activated Sludge

The first Navy sponsored study (Argaman et al, 1984) looked at the effects of tributyltin-laden waters on activated sludge treatment processes. The study used both Warburg respiration tests and a continuous flow activated sludge system. Tables 2 and 3 show characteristics of the activated sludge used in this study. The tributyltin species used was bis(tributyltin) oxide, or simply TBTO. This was the form of TBT to be used in military specification anti-foulant paints for the U. S. Navy.

Table 2 - Tributytin's Effects on Activated Sludge: Continuous Loading (Argaman et al, 1984)

CONTINUOUS TBTO LOADING

Parameter	Influent	Effluent					
TBTO dose (ug/L)		0	25	100	200	500	1000
BOD (mg/L)	72-108	9	12	9	11	17	14
Soluble BOD		4	5	2	2	4	4
COD (mg/L)	216-280	45	53	51	51	66	77
Soluble COD		28	43	26	36	37	34
TOC (mg/L)	49-78	10	10	8	11	15	18
Soluble TOC		10	10	9	7	10	10
TSS (mg/L)	100	14	31	13	9	17	14
MLSS (mg/L)	2300-3600	3179	3246	2790	2600	2355	2513
MLVSS	1800-2700	2516	2589	2228	2023	1822	1980
DO (mg/L)	3.0-6.5	4.0	4.6	4.8	4.0	6.2	5.1
OUR (g/g/day)	0.15-0.3	0.26	0.25	0.22	0.23	0.18	0.21
SVI (ml/g)	40-80	53	61	65	65	78	75
ZSV (m/hr)	3.0-9.0	5.5	4.7	4.9	4.2	3.6	3.2
F/M (g/g/ day)	0.1-0.18	0.14	0.13	0.13	0.14	0.17	0.16
Detention Time (hr)	6-8	7.2	7.4	5.8	6.0	6.5	6.2

Legend: TBTO = Bis(tribytyltin) oxide, $(C_4H_9)_3SnOSn(C_4H_9)_3$

OUR = Oxygen Uptake Rate

F/M expressed as g-BOD/g-BOD/day

Note: All reactors operated at 21 degrees Centigrade

Table 3 - Tributytin's Effects on Activated Sludge:
Transient Loading (Argaman et al, 1984)

----------------TRANSIENT TBTO LOADING------------------

Parameter	Influent	Effluent					
TBTO dose (ug/L)		0	500	500	0	1000	1000
Acclimated/Unacclimated		U	U	A	U	U	A
BOD (mg/L)	63-114	5	7	11	8	12	13
Soluble BOD		3	3	2	2	2	2
COD (mg/L)	179-438	36	34	45	23	39	42
Soluble COD		35	29	39	22	22	21
TOC (mg/L)	33-51	9	8	9	9	8	13
Soluble TOC		8	7	9	7	6	7
TSS (mg/L)	100	18	11	27	4	16	17
MLSS (mg/L)	2200-3000	2922	2816	2450	2893	2523	2279
MLVSS	1800-2300	2218	2140	1940	2214	1952	1815
DO (mg/L)	3.5-6.5	3.8	5.8	5.1	4.6	6.2	6.2
OUR (g/g/day)	0.1-0.3	0.30	0.18	0.21	0.19	0.14	0.16
SVI (ml/g)	50-81	54	63	73	69	82	81
ZSV (m/hr)	2.9-5.8	5.8	4.2	3.1	4.8	4.0	3.0
F/M (g/g/day)	0.1-0.25	0.18	0.19	0.22	0.11	0.11	0.13
Detention Time (hr)	6-7.5	6.2	6.2	6.0	6.0	7.2	6.2

Legend: TBTO = Bis(tribytyltin) oxide,
$(C_4H_9)_3SnOSn(C_4H_9)_3$

OUR = Oxygen Uptake Rate

F/M expressed as g-BOD/g-BOD/day

Note: All reactors operated at 19 degrees Centigrade

In 96-hour respirometer tests, percent oxygen consumption was significantly decreased (8 - 18 percent) in unacclimated activated sludges with doses as low as 25 ug/L TBTO. In equivalent tests, sludge acclimated with 25, 200 and 1000 ug/L TBTO respectively, a dose of 25 ug/L TBTO resulted in respective oxygen consumptions of 145, 105 and 101 percent of the non-dosed seed sludge oxygen consumptions.

For the 1000 ug/L TBTO-acclimated sludge, a dosage as high as 8,000 ug/L TBTO was observed to cause an insignificant (1-2 percent) decrease in oxygen consumption compared to the non-dosed sludge.

The activated sludge process was run with a continuous TBTO loading at concentrations varying between zero and 1000 ug/L. This was followed by a transient loading of both acclimated and unacclimated sludges at TBTO concentrations varying from zero to 1000 ug/L. Key results of continuous and transient experiments are found in Tables 2 and 3, respectively.

In the continuous flow reactor (Table 2), the highest concentrations of 1000 ug/L had little effect on effluent concentrations of soluble organic carbon and total suspended solids. However, at TBTO doses of 100 ug/L and greater, sludge settling and compaction characteristics were affected, although the change was not that pronounced and the detention time had also changed. Shock TBTO loadings of 500 and 1000 ug/L in the transient reactor (Table 3) had a significant effect on sludge settling characteristics, resulting in higher effluent suspended solids and total organic concentrations.

The Navy's second study of TBT's effects on activated sludge (Avendt et al, 1982) was a full scale treatability study conducted at a sewage treatment plant which used *primary sedimentation*, activated sludge, biological nitrification, pressure filters, chlorination and anaerobic digestion of sludge. The influent to the plant was subjected to initial doses ranging from 40 to 75 ug/L TBTO for periods of 2 to 4 days and the TBTO concentrations in the effluent streams (digester sludge, digester supernatant and filtered effluent) were monitored for periods ranging from 2 to 32 days.

In each of the three tests, effluent concentrations of TBTO were reported to be negligible. The digester sludge contained quantities of TBTO that were between zero and 23 percent of the cumulative mass of TBTO added to the system. The digester supernatant always carried

TBTO, but in quantities that were one or two orders of magnitiude less than the digested sludge. These results reflect the current knowledge of the fate of TBT compounds: (1) aerobic degradation of TBT is relatively fast and complete, (2) anaerobic degradation of TBT is far slower than aerobic degradation and (3) TBT has a strong tendency to associate with the solids in an aqueous mixture.

Both the bench-scale and full-scale studies indicate that the introduction of small quantities (< 100 ug/L) of TBT in the form of TBTO has no serious effects on activated sludge treatment systems. Still to be learned, however, are TBT's effects on other types of biological treatment systems such as aeration ponds and lagoons and trickling filters where oxygen transfer rates and mechanisms could significantly alter the rate of biodegradation of TBT. Because of the highly variable nature of shipyard work, shock loadings of TBT into a municipal sewage treatment system could be quite likely, therefore, a fuller understanding of transient loading effects in a full-scale treatment system is necessary.

2.4.4.2 Removal of Tributyltin by Adsorbents

Bhattacharyya et al (1981) studied the removal of aqueous organotin by activated carbon, polymeric adsorbents and synthetic carbon adsorbents. Inlet TBTO concentrations varied from 20,000 ug/L to as little as 100 ug/L. In terms of adsorptive capacity (gram TBTO/gram adsorbent), two activated carbon adsorbents outperformed both the polymeric adsorbent and the two synthetic carbon adsorbents, with the polymeric adsorbent working slightly better than the synthetic carbon. The best adsorptive capacity attained in the study was 0.358 (g-organtin adsorbed/g-adsorbent) at the breakpoint, i.e. the point at which less than 99 percent removal was first measured. Complete exhaustion of the adsorbent was not determined experimentally, but the authors of the study postulated theoretical adsorption capacity complete exhaustion could be as high as 0.518 for one of the activated carbon adsorbents. They also noted that because the adsorbents are not fully saturated at the breakthrough point, adsorbent columns in series would be desirable in an actual treatment system.

2.4.4.3 Removal of Heavy Metals from Drydock Wastewater

Saam et al (1977) concluded that treatment of wastewater generated from Navy drydocks was essentially a problem of removing dissolved heavy metals, most of which originate in the hull paint removed from dry blasting operations. In bench scale testing, three methods were studied:

(1) Sulfide Precipitation
(2) Resin Adsorption
(3) Chemical Fixation

The chemical fixation treatment involved mixing the waste with an alkali metal silicate and adding a settling agent that converts the mixture into a stable end-product. This was successful, but not recommended based on the high cost of the process as well as the vast volume of solids that would be generated.

The resin adsorption technique was found ineffective in removing 10 mg/L of zinc and lead to levels that would meet local discharge requirements.

Sulfide precipitation coupled with the addition of anionic polyelectrolytes to assist flocculation was determined to be the most effective method tested. This process removed copper, lead and zinc to desired effluent levels. The authors of the study also theorized that the chemistry of the sulfides of mercury, tin, silver, iron, nickel, and cadmium suggests that this is a viable treatment alternative and proposed a pilot scale facility for further investigation of this process (Figure 2). The Navy treatability study was particularly concerned with dissolved metals, as evidenced by the type of bench-scale studies that were performed. This concern appeared to be driven by the fact that saltwater was the primary component of the wastewater and that its high chloride ion concentration would cause a high proportion of the metals from the solids to leach out due to the high solubility of metal chlorides.

2.5 Potential Treatment Processes for Hydroblast Wastewater

On-site treatment of hydroblast wastewater must be a simple yet robust process. Simplicity is desirable due to the likelihood that the operators of any treatment system will have other primary assigned duties at the shipyard/marina and their interests and skills will generally be focused elsewhere. Robustness, on the other hand, is necessary due to the highly variable

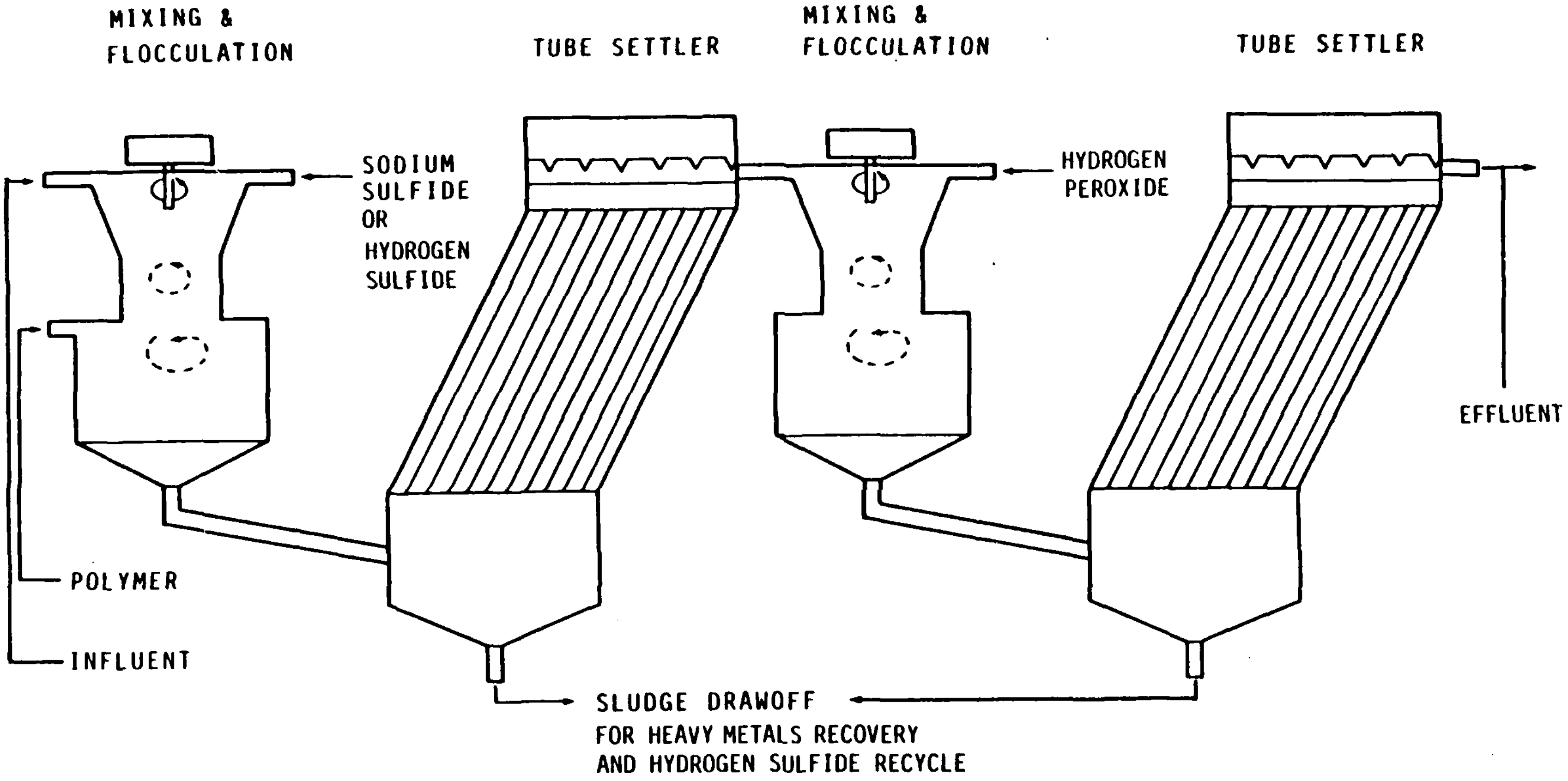


Figure 2 - Pilot Scale Heavy Metal Removal Unit (Proposed by U. S. Navy for treating drydock wastewater, from Saam et al, 1977)

timing, volume and characteristics probable for the wastewaters generated by hydroblasting.

The crude characterization of drydock wastewater discharges presented in Table 1 suggests that the selection of a water treatment system will essentially be based on some type of liquid-solid separation process. In contrast to the conclusions of the Navy drydock treatability study, the EPA study shows that heavy metal concentrations of any significance are normally found in the insoluble form. The possible exception to this may be tin, which could be either the highly toxic TBT or one of its less toxic degradation products, DBT, MBT or inorganic tin. Because of TBT's acute toxicity at concentrations in the low ug/L range, soluble tin might be of concern.

2.5.1 Treatment Process Selection Based on Particle Size

The use of particle size as the primary criteria for selecting and designing a wastewater treatment process has been proposed by a number of individuals (Kavanaugh, 1980; Levine et al, 1985; Lawler et al, 1980). This idea has as its basis the understanding that processes such as sedimentation, mass transfer, adsorption, diffusion and biochemical reactions are dependent almost wholly or in part by particle size.

Levine, Tchobanoglous and Asano (1985) have constructed three spectral charts to illustrate process selection based upon particle size (Figures 3(a), 3(b) and 3(c)). The first chart, Figure 3(a), correlates particle size with typical organic constituents in municipal wastewater. The second chart, Figure 3(b), matches wastewater treatment unit operations that achieve effective removal over a given particle size range. The last chart identifies analytical techniques for particle size measurement and the particle size range over which they can be applied (Figure 3(c)).

Kavanaugh (1980) has developed a diagram to assist in process selection based on mean particle size as well as the particle number and mass concentrations. A reproduction of this diagram is found in Figure 4. This figure uses a relationship between total particle number concentration, N_T, the mass concentration, M, number volume mean size, l_{NV}, as expressed by

$$M = (\rho)(C_3)(l_{NV})^3(N_T) \qquad (1)$$

where density, ρ, is the average particle density, selected as 1.02 g/cm^3 and the particle is assumed perfectly spherical in shape. The process boundaries are based on 90 percent particle removal in a 60 min period.

The two process selection models have their own set of assets and drawbacks.

Kavanaugh's model is more three dimensional in that it permits process selection based on particle and solids concentration, not just particle size. However, the Levine model has specific advantages in that wastewater components are identified by their size range and some basis for selecting analytical tools is provided as well.

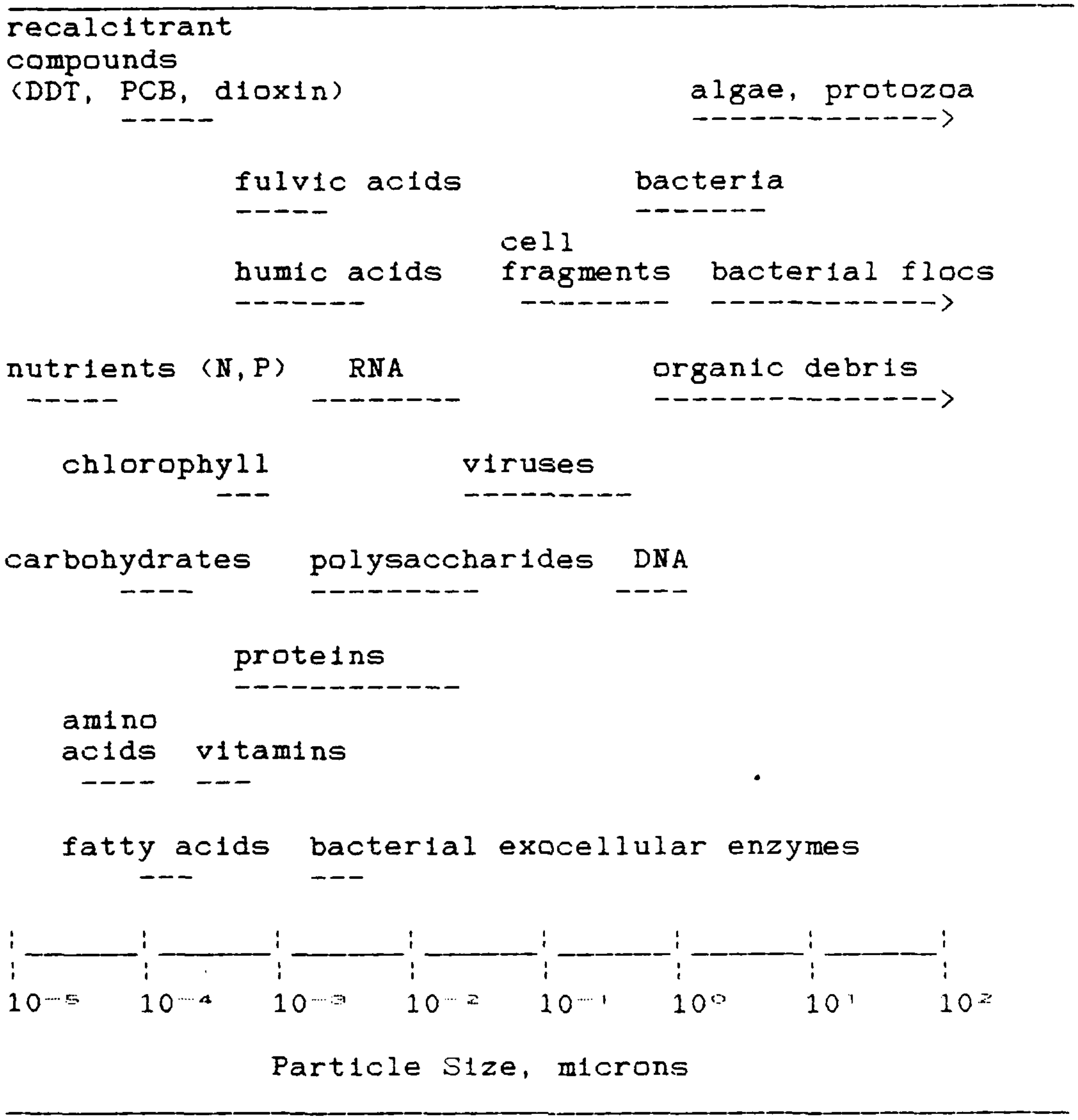


Figure 3(a) - Typical Organic Constituents in Settled Municipal Wastewater (Adapted from Levine et al, 1985)

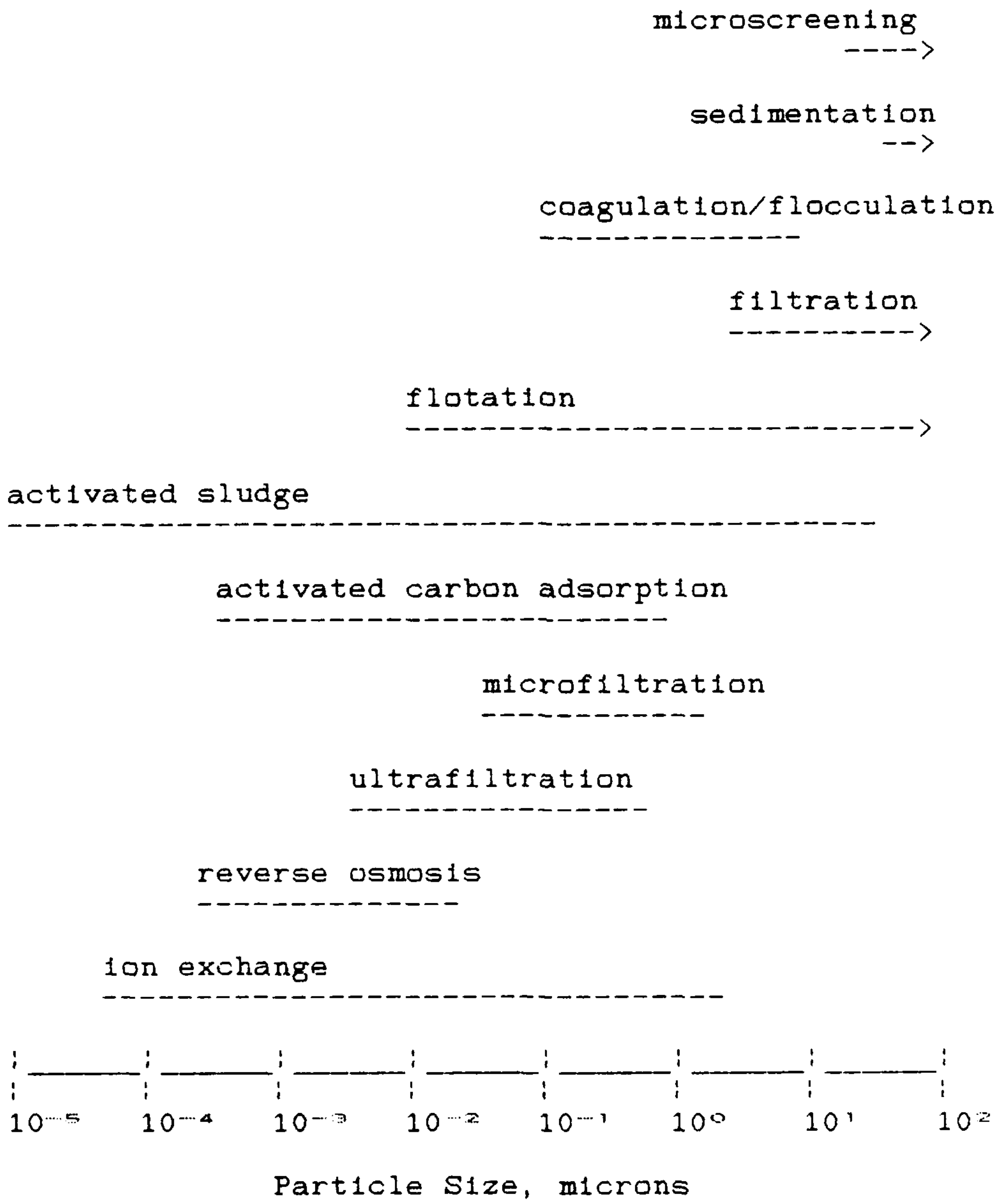


Figure 3(b) - Size Ranges Over Which Various Wastewater Treatment Unit Operations are Effective (Adapted from Levine et al, 1985)

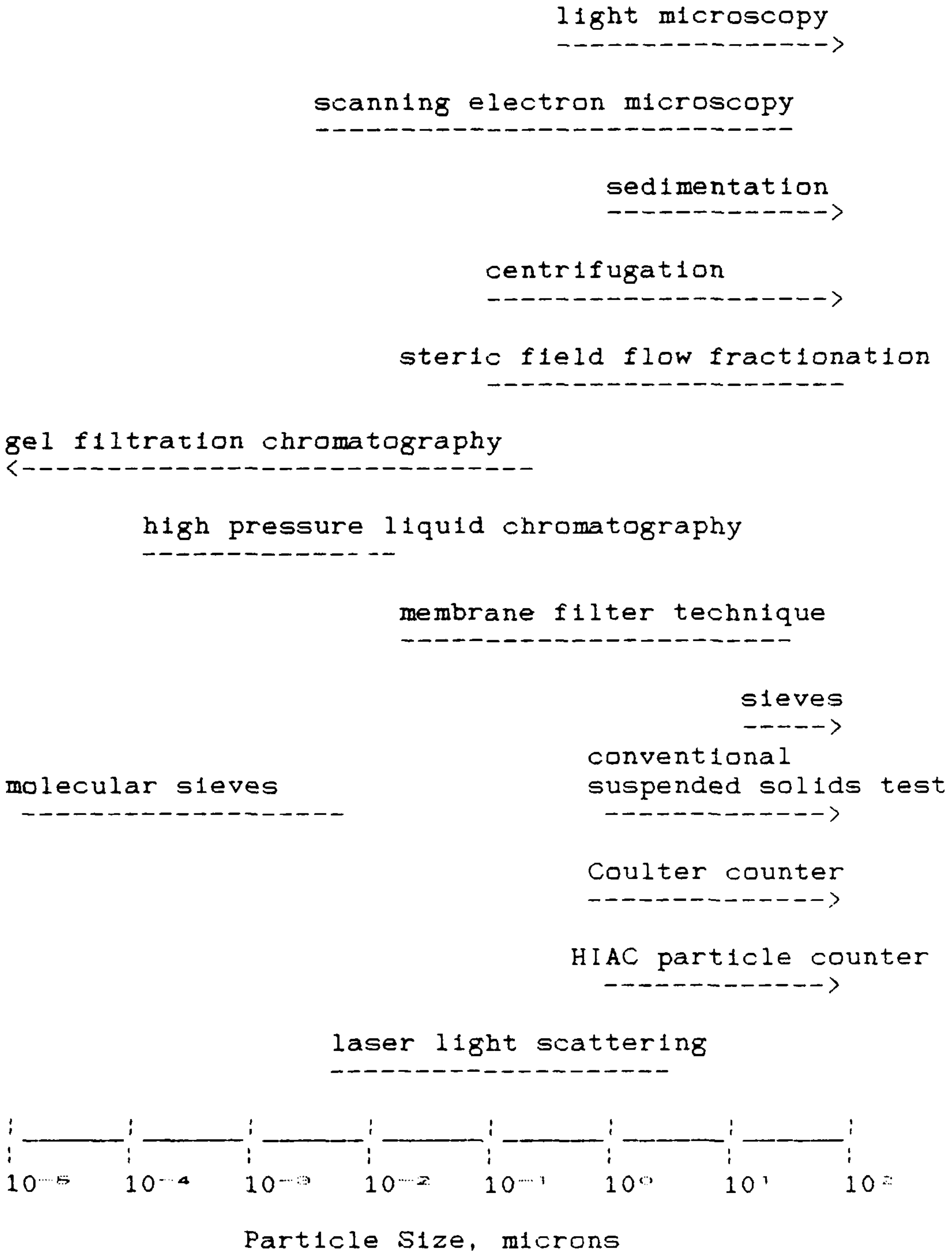


Figure 3(c) - Analytical Techniques for Identification of the Size of Wastewater Contaminants <100 microns (Adapted from Levine et al, 1985)

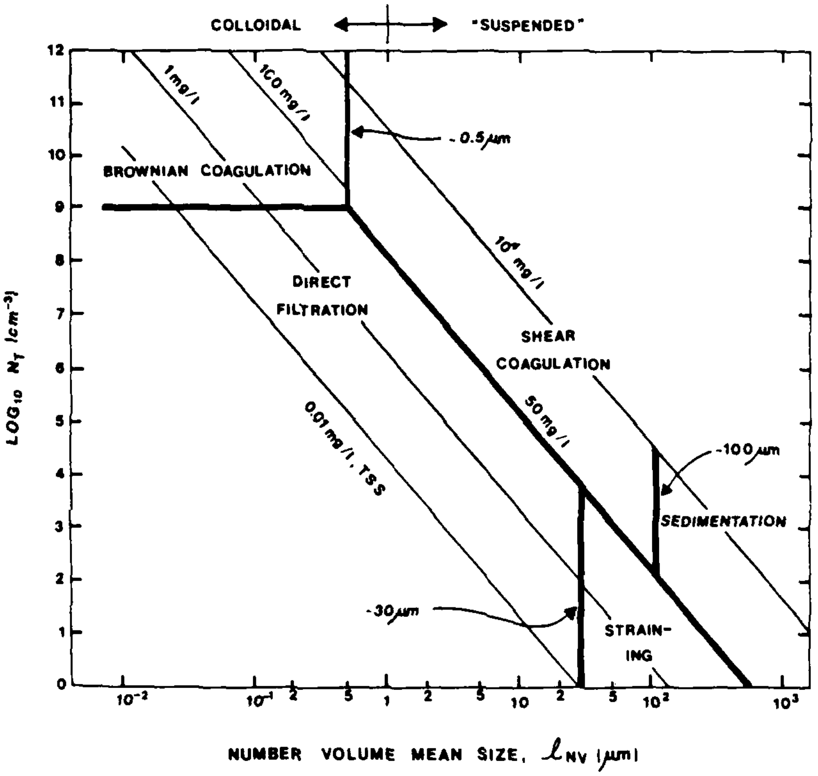


Figure 4 - Solids/Liquid Separation Process Selection Diagram. (Mass concentration isopleths computed assuming spherical particles with specific gravity of 1.02 g/cm^3 (Kavanaugh, 1980)

2.5.1.1 Sedimentation and Particle Size

Levine's chart shows sedimentation being effective for particle sizes in the range of 50 microns and greater. The Kavanaugh diagram, however, places the size range at 100 microns or greater. This difference is explained by a variation in assumed particle settling velocity (or overflow rate) as well as particle density. Levine's assumption is based on typical overflow rates between 32 - 48 m^3/m^2-day and a particle density of 1.2 g/cm^3. Kavanaugh uses a smaller particle density of 1.02 g/cm^3 but does not state an assumed settling velocity. Based on this density, a settling velocity of about 11 m^3/m^2-day is computed from Stoke's law for a particle 100 microns in diameter.

Since Stoke's law is based on the settling of discrete and non-flocculating particles it may not be valid at high particle concentrations (which is a likely assumption in Kavanaugh's model) where compressed and hindered settling are likely to occur in addition to flocculant and discrete settling (Metcalf and Eddy, 1979). Thus solids concentration and particle density will determine what the transition point will be for a particle to efficiently settle out. These factors must both be considered in using either Figure 3(b) or 4.

Typically only settling tests will determine the settling characteristics for water that is high in suspended solids (ibid).

2.5.1.2 Filtration and Particle Size

In Kavanaugh's diagram, "direct filtration" occurs in the region bounded by a particle size <30 microns, total suspended solids <50 mg/L and particle concentration that is $<10^3$ particles per cm^3. Levine's chart is actually more helpful in selecting a specific filtration process because it breaks filtration down into filtration of larger particles (> 3 microns), by such filtration mechanisms as granular media, and smaller particles (< 3 microns), by microfiltration and ultrafiltration. In Levine's chart there is no upper particle size limit for the use of filtration.

But Kavanaugh's model is a reminder that granular medium filtration will be most effective with lower total suspended solids concentrations. Increased filter clogging will occur under high TSS conditions (> 50 mg/L) unless a concomitant increase in shear strength (Montgomery, 1985) and particle density occurs.

2.5.1.3 Screening and Particle Size

Kavanaugh and Levine appear to agree that particle sizes greater than 30 microns are effectively removed by microscreening. Kavanaugh's model indicates that low total suspended solids (< 50 mg/L) are preferred for this process because of the high incidence of screen clogging at high TSS. Kavanaugh also states that microscreening removes particles with a dimension at least one size larger than than the minimum screen opening and that rigid particle structure is important for screening to be successful.

2.5.1.4 Coagulation/Flocculation and Particle Size

Levine indicates that coagulation and flocculation are effective in a particle size range from 0.1 to 10 microns. Kavanaugh distinguishes between two coagulation regions: (1) brownian, where particles are < 0.5 microns and (2) shear, where particles are generally above 0.5 microns. Again, Kavanaugh's model also accounts for particle concentration. For brownian coagulation to be effective alone, particle concentrations must be greater than $10^8/cm^3$. The shear coagulation region is bounded on the lower end by the 50 mg/L TSS isopleth, but Kavanaugh does not comment on an upper boundary for this region. This is most likely because chemical treatment of high TSS waters is normally not cost effective as sedimentation will serve as a more economic removal mechanism for high TSS wastewater. Montgomery (1985) agrees with Levine that 10 microns is an appropriate upper particle size for the selection of coagulation/flocculation as a treatment process.

2.5.2 Treatment Process Operational Characteristics

In addition to particle size as the basis of process selection, other parameters relevant to the four basic treatment processes discussed in the previous section must be considered. For hydroblast wastewaters, simple yet robust treatment operations are envisioned that would require a minimum of an operator's time and effort, minimize physical space requirements and possess uncomplicated, if any, electromechanical equipment.

With all treatment methods being considered, batch processes appear the most likely to be used, due to the non-continuous and fluctuating wastewater characteristics likely to be encountered with the hydroblasting discharges and limited available space for multiple wastewater holding tanks. Therefore, pertinent operational parameters that can be simulated and measured in bench-scale treatment units such as flow rates, media sizes and volumes, screen sizes, chemical doses and mixing requirements warrant discussion.

2.5.2.1 Sedimentation Operational Characteristics

For a simple batch sedimentation system, in addition to the particle size considerations already mentioned, the key operation parameters are settling velocity, solids loading and sludge characteristics (volume and density).

Settling velocity is best quantified by Stoke's law which is a function of particle diameter, density difference between the particle and the fluid and the fluid viscosity. However, Stoke's law strictly applies for only one of the four classifications of sedimentation termed "discrete particle" where particle interaction is not a factor. The other three types of settling, "flocculant", "hindered" and "compression" must be considered when larger concentrations of solids are encountered (Metcalf and Eddy, 1979). The only way to effectively analyze these last three settling types is with the use of some type of settling column or cone where changes in settled solids depth and volume can be measured after prescribed periods of time.

2.5.2.2 Filtration Operational Characteristics

Two types of granular media filters will be looked at in this study: (1) slow sand and (2) coal/sand dual media filters. For both types of filters, batch treatment processes are feasible if anticipated water volumes and filter space requirements can be matched. Key elements of a bench-scale treatment process for either filtration system will be filtration rates, media sizes and bed depth, and solids loading capacity and backwash requirements (Montgomery, 1985).

Table 4 shows typical parameters for slow sand and dual media filters. These operating parameters are reported from constant rate filtration studies. A batch process where a fixed volume of wastewater is pumped into a tank and allowed to flow through the filter media would be in the category of a declining rate filter. The key variables in granular media filtration have been found to be media size and depth, whereas the filtration rate has a far less important effect on particle removal

Table 4 - Typical Operating Characteristics of Granular Media Filters

Parameter [Reference]	Slow Sand [1]	Dual Media (Coal/Sand) [2]
Filtration Rate		
(gal/day-ft^2)	88.35	3976 - 9484
(m/hr)	0.15	6.6 - 16.1
Media Size (mm)	0.38	1.54/0.43
Filter Solids Capacity (kg-solids/m^3-media)	[3]	8.0 [4]
Influent Turbidity (ntu)	4.0	0.35 - 18.1
Effluent Turbidity (ntu)	0.65	0.13 - 1.68
Filter Depth (cm)	84	40/30
(in)	33	16/12
Water Depth (cm)	173	222
(in)	68	87

[1] Slezak and Sims (1984): Results of U.S.-wide survey of 27 operating slow sand filtration systems. All values are mean values. Parameters are in close agreement with those used in other recent studies (Bellamy et al, 1984; Cleasby et al, 1984; Paramasivan, 1984; Seelaus et al, 1984)

[2] Cleasby et al (1984): From a pilot plant study comparing slow sand filtration with dual media filtration over a one year period. Parameters are in general agreement with those found in earlier studies of coal/sand filters (Tchobanoglous et al, 1970; Baumann et al, 1974)

[3] No reported values. By comparison, Stensel et al (1988) reported loadings of 3.0 kg TSS/m^3-media in a biological aerated filter with media sizes of 2.8 to 3.4 mm (vitrified clay)

[4] Baumann et al (1974): Not a reported value. Calculated from TSS removal efficiencies and run length as a function of flow rate in as given in figures 8 and 13, respectively, in the reference, where initial TSS = 40 mg/L. Coal/sand filter is 12-in. of 1.84 mm anthracite on 12-in. 0.55 mm sand

(Baumann et al, 1974; Bellamy et al 1984). This is evident from the wide variations in hydraulic loading rates reported for slow sand filters (Seelaus et al, 1984; Slezak et al, 1984) that perform effectively.

2.5.2.3 Microscreening Operational Characteristics

Screening is used in both primary and secondary wastewater treatment. In primary treatment, screen sizes range from 10 to 1500 micron openings and are arranged in either inclined fashion or in a rotating mechanism such as a drum or centrifuge (Metcalf and Eddy, 1979). The term microscreening generally applies to screen sizes in the 10 to 35 micron opening category. In any screening process, particles are strained out by their inability to pass through the openings in the screen itself and, with the passage of time, the decreasing size and number of openings in a mat that develops on the screen face.

Screens lack the depth found in most types of filters, even relatively thin cloth types, and thus have limited removal capacity. Due to this limitation, they are primarily used as either a pretreatment or polishing step in addition to other treatment processes.

In Europe, microscreens have been used to remove algae from surface waters treated with granular media filters (Montgomery, 1985).

For a simple microscreening process involving nothing more than pumping wastewater through a fine mesh screen, key operational parameters will be those found below in Table 5.

Table 5 - Typical Operating Parameters in Microscreening
(Adapted from Metcalf and Eddy, 1979)

ITEM	TYPICAL VALUE	NOTES
Screen Size (microns)	20 - 35	Typically polyester or stainless steel construction
Hydraulic Loading (m^3/m^2-min) (gal/ft^2-min)	 $3 - 6 \times 10^{-3}$ 0.074 - 0.147	
Head Loss Through Screen (mm)	75 - 150	Head losses >200 mm should use bypass
Backwash Requirements	2% of throughput @ 50 psi 5% of throughput @ 14.5 psi	
Composition of Waste Solids (percent solids by weight)	0.05 - 0.2	
Suspended Solids Removal (%)	10 - 80	

From Table 5 it is evident that the effectiveness of microscreening is unpredictable, since TSS removal varies from 10 to 80 percent. In one study cited by Metcalf and Eddy (1979), removal of algae from a facultative lagoon using microscreens yielded a highly variable total suspended solids concentration in the effluent. One reason for this was the wide range of shapes and sizes of the algae species.

Also, the 10 - 35 micron screens manufactured for large scale drum and centrifuge devices are not standard mesh sizes that can be purchased in small cuts such as would be necessary for a bench-scale study. The smallest stainless steel screen fabric that is readily available is 325 mesh (an opening of 45 microns).

2.5.2.4 Chemical Treatment Operational Characteristics

A number of coagulants are available for chemical treatment of wastewater, including aluminum and iron salts and various synthetic polymers. For this study, aluminum in the form of aluminum sulfate (alum) was used. This selection was based on several considerations. First, aluminum sulfate is one of the cheapest and most widely available coagulants.

Secondly, much is known regarding the chemistry and behavior of alum treatment, making it amenable to designing treatment systems from bench-scale studies. Third, overdosing with synthetic polymers produces a poor effluent whereas alum is much less a problem when overdosing occurs. Finally, alum has more attractive properties from a storage and handling perspective than do some of the other common coagulants since it has less tendency to cake up, is less corrosive and does not require dilution prior to dosing (Montgomery, 1985).

Amirtharajah and Mills (1982) have developed a design and operation diagram for alum that is found in Figure 5. This diagram is an excellent guide for matching dosage and pH requirements as it summarizes much of the existing research that has taken place for alum wastewater treatment. The earlier work of Stumm and O'Melia (1968) looks at the stoichiometry of coagulation and is useful for predicting the effects of suspended solids concentrations on coagulant dosage (Figure 6), which is not covered by the Amirtharajah work.

From Amirtharajah's diagram, it is evident that lower alum doses find a smaller pH region in which they are effective. This is due to the very complex equilibrium that exists between the free aluminum ion, its three

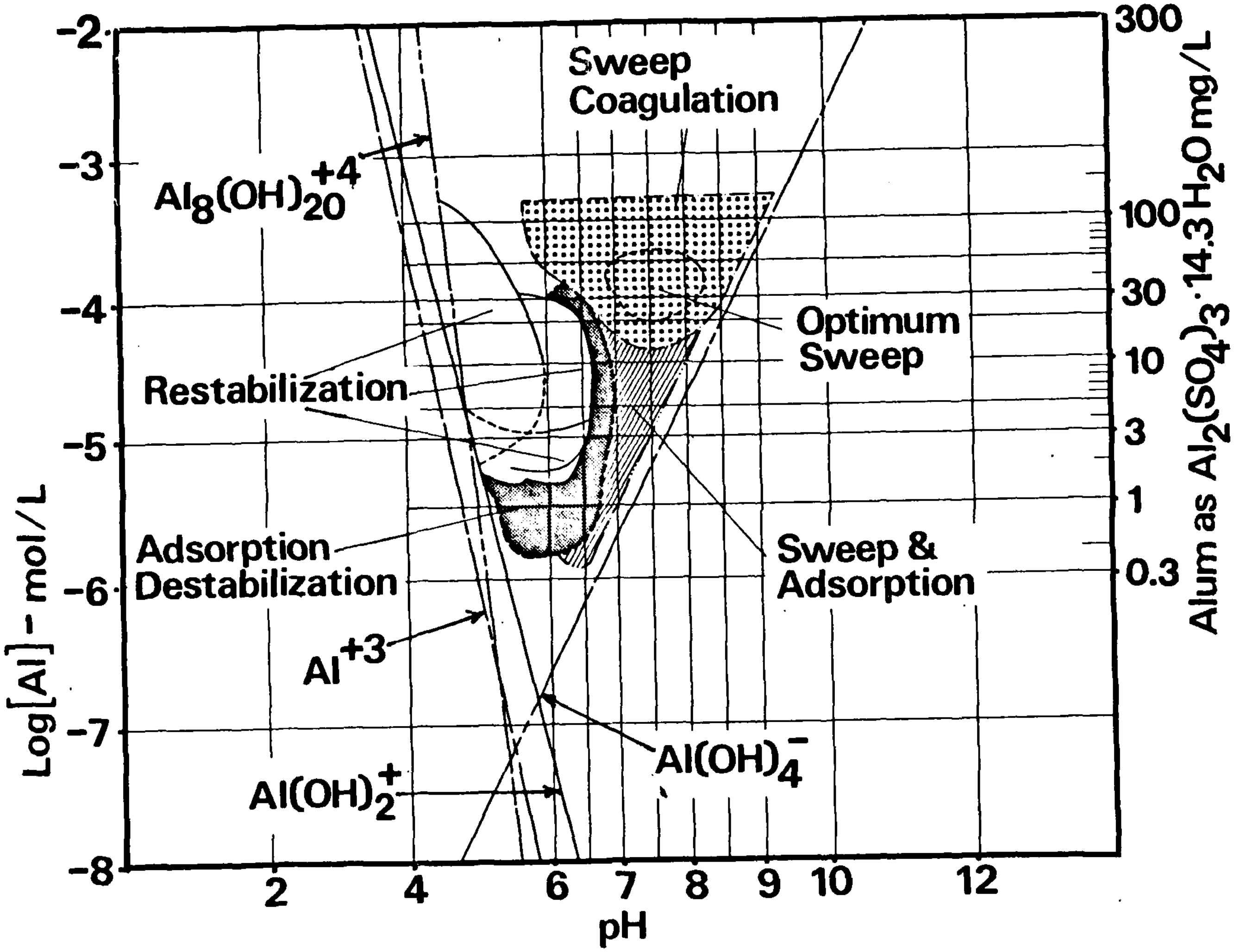


Figure 5 - Design and Operation Diagram for Alum Coagulation (Amirtharajah et al, 1982)

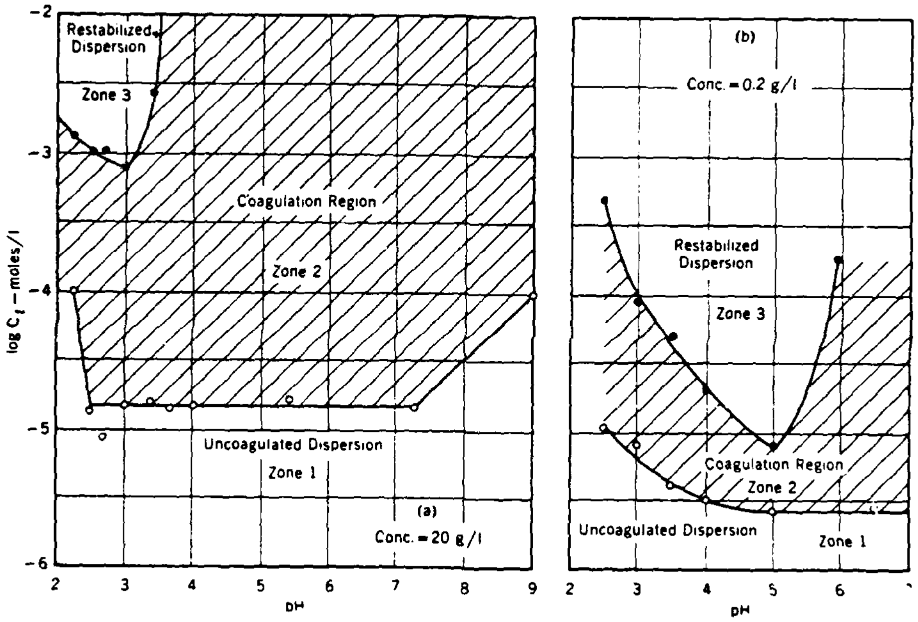


Figure 6 - Log Coagulant Concentration-pH Domains of Coagulation and Restabilization at Two Colloidal Silica Concentrations with Metal Hydroxide Coagulant (Stumm, O'Melia, 1968)

most common hydroxyl species, $Al(OH)_4^-$, $AlOH^{+2}$, and $Al(OH)_{20}^{+4}$ and solid aluminum hydroxide, $Al(OH)_3(s)$. The lower total aluminum concentrations are regions of alternating destabilization and restabilization of the suspended particulate matter by adsorption of positively charged aluminum hydroxide species (destabilization) and formation of aluminohydroxide species (restabilization). At higher alum doses, enough hydroxo-metal complexes form to effectively entrap all the suspended particles, even the very small ones (0.1 - 10 microns). Thus an area of optimum sweep coagulation, defined as the "area for best settling floc with the lowest coagulant dosages", is bounded in Amirtharajah's diagram between pH 6.8 to 8.2 and an alum concentration 20 to 50 mg/L (log of $[Al_T]$, mol/L = -4.17 to -3.77).

With increasing suspended solids concentration, the effective coagulation region spans a wider pH due to the increasing opportunities for particles to come into contact and aggregate. This is best illustrated by Stumm and O'Melia's figure comparing coagulation and destabilization regions for different colloidal concentrations, reproduced here as Figure 6. Also evident from Figure 6 is that the higher solids concentrations require a larger dose of coagulant, on the order of one magnitude increase in coagulant dosage per two magnitudes increase in solids concentration.

Adding alum to water causes the aluminum to hydrolyze and form aluminum hydroxide species. In water with little or no alkalinity, the net effect of these reactions is to release hydrogen ions and lower the pH. As Amirtharajah points out, it is not possible to accurately predict the pH reduction that occurs with a given alum dose due to the complexity and diversity of the aluminum-water chemistry involved. Nevertheless, some type of concurrent pH adjustment mechanism is needed to offset the reduced pH. If the pH becomes too low it will place the aqueous solution out of the region of effective coagulation. In the absence of existing buffer capacity, several chemicals can be added to the water to cause the release of hydroxyl ions, such as lime or sodium carbonate. A minimum dose requirement for a chemical such as sodium carbonate (soda ash) can be calculated based on the reaction stoichiometry:

$$Al_2(SO_4)3\ 14.3\ H_2O + 3\ Na_2CO_3 + 3\ H_2O \dashrightarrow$$
$$2\ Al(OH)_3(s) + 3\ Na_2SO_4 + 3\ CO_2 + 14.3\ H_2O$$

However, because the carbonate ion contributed by the base is also free to react with water, the equilibrium of the aqueous carbonate system will require a dosage of sodium carbonate in excess of the stoichiometric dose prescribed by the above reaction. Once again, the complexity of the aluminum chemistry does not permit one to accurately predict the pH reduction a system will experience with a given alum dose, hence prediction of an exact concurrent base dosage is not possible either. Only by performing a jar test will it be possible to determine the exact dosages.

Because the aluminum ions and their subsequent aluminum hydroxide species must come into contact with one another, to precipitate solid aluminum hydroxide, some understanding of the mixing requirements is also needed. Amirtharajah (1982) studied the effects of three different rates of mixing and discovered that for the higher alum dose area of optimum sweep coagulation, coagulation performance is not dependent on mixing rate. In the areas of low dosage/low pH, however, the slower paddle mixer is less effective because the adsorption-coagulation reactions occur much faster (on the order of microseconds) than those which form aluminum hydroxide species (on the order of 1 to 7 seconds). As can be seen by referring to Amirtharajah's figure, aluminum hydroxide species can be restabilized in regions of lower alum dose/pH and poor coagulation takes place because slow-mix conditions do not exploit the rapid kinetics of adsorption-coagulation. Nonetheless, a conventional paddle type mixer found on a jar testing apparatus is sufficient as long as the optimum pH and dosage ranges are used.

The use of chemical treatment prior to filtration is a common method used to improve filtration performance. Selecting an appropriate alum dose for this process appears to be a matter of choice. Jar tests are first run to determine coagulation performance alone. Habibian et al (1975) concluded that optimum coagulation dose corresponded to the optimum dose for filtration. Cleasby et al (1984) determined that alum dose selection was a trade-off between better filtrate quality in earlier runs and an early breakthrough of turbidity and rapid head loss. Certainly the latter conclusion requires consideration if large alum doses are used because significant quantities of sludge will result with large doses. The approach of Wagner et al (1982) was to intentionally limit alum dosing to very small amounts (< 25 mg/L) because they perceived that alum doses above 20 mg/L would result in uneconomical filter performance and an optimum dose would be around 6 to 7 mg/L.

CHAPTER 3

FIELD INVESTIGATIONS

3.1 Purpose of Field Investigations

On-site inspections and investigations were conducted of ship repair and maintenance facilities performing hydroblasting. The purpose of these visits was to become familiar with the operations and layouts of these facilities in order to develop a sampling strategy and a sense of the physical constraints that must be considered if on-site treatment processes are to be implemented.

An initial visit was held on 21 January 1988 at Marco's Seattle, a medium-size shipyard located on Union Canal (Lake Washington Ship Canal). A meeting with representatives from three other shipyards as well as the Washington State Department of Ecology was also conducted at this time. Two key pieces of information that came from this meeting were:

(1) Hydroblasting is used only when the existing hull paint is in good condition and the underlying paint surface can still bond effectively with a new coat of paint. Hydroblasting is not used to remove paint from a

ship hull, although this regularly occurs incidental to the blasting. Hydroblasting's main purpose is to remove marine growth (primarily algae) from the ship's hull.

(2) The facilities used to raise ships from the water and thereafter become the site of hydroblasting operations vary greatly between shipyards. In the Seattle area essentially two methods of raising large commercial ships out of water are employed: drydocks or marine railways. The configurations and sizes of these facilities differ considerably depending upon the type and size of vessels being serviced.

Because of the variations in shipyard facilities evident from this initial meeting, the need to visit other sites was clear. From such vists, a coherent sampling strategy could be developed and the appropriateness of water treatment methods could be evaluated.

3.2 Shipyard Operations and Physical Layouts

Figure 7 shows the four sites chosen for this investigation. Three of the locations are commercial shipyards and the fourth is a recreational boat marina.

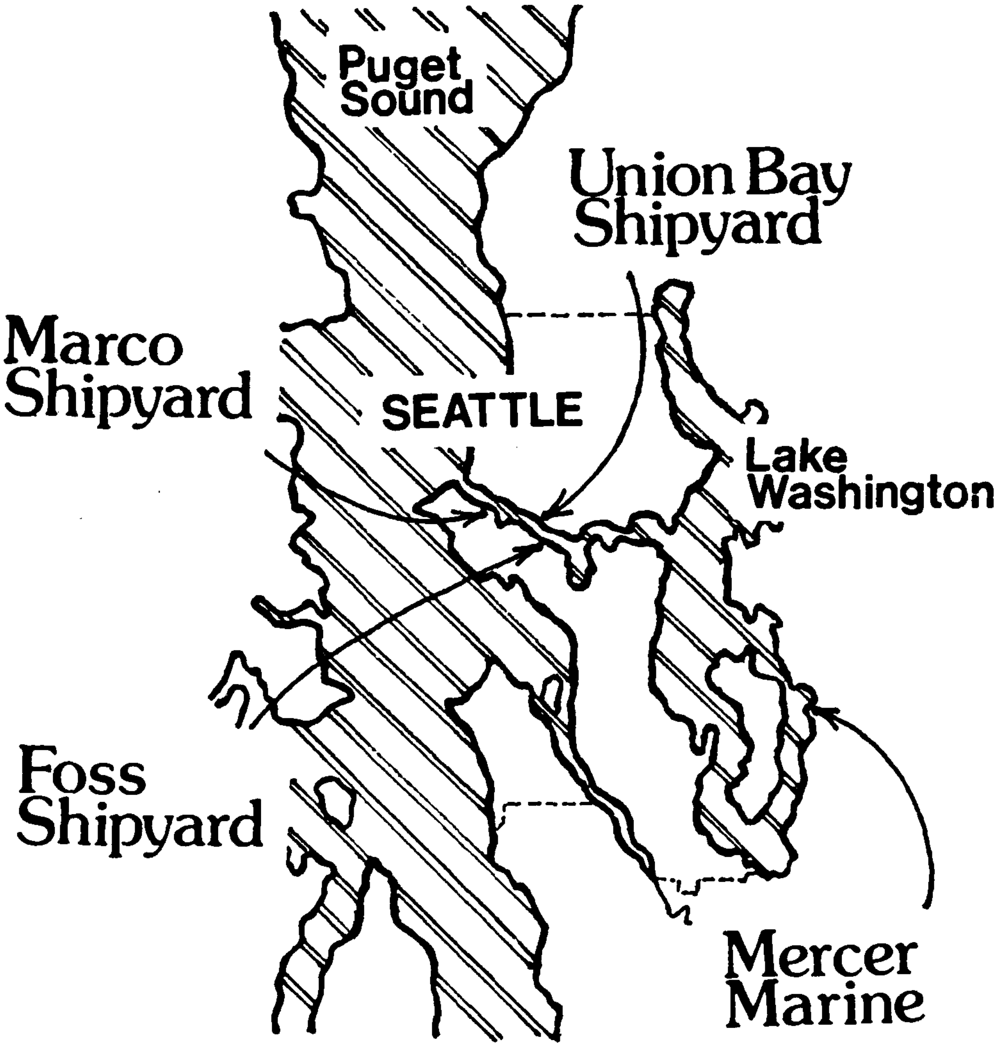


Figure 7 - Map of Seattle, Washington, and Vicinity.
Sites Shown were used in Hydroblasting Study
Scale: 1 inch = 3 miles

The three shipyards inspected were Marco Seattle, Foss Maritime and Union Bay Shipbuilding Corporation. All shipyards are located on Union Canal connecting Puget Sound and Lake Union in Seattle. The marina, Mercer Marine, is located at the Newport Yacht Basin on the east shore of Lake Washington in the city of Bellevue.

3.2.1 Marco Seattle

Marco Seattle is the largest of the four sites. It has three drydocks and a large marine railway. The smallest drydock has a wood surface deck while the two larger docks have concrete surfaces (Figures 8(a) and 8(b)).

The wood deck has a somewhat irregular surface while the concrete surfaces on the larger drydocks is relatively smooth, excepting the tracks used for the keel and bilge blocks. Marco's two concrete-decked drydocks have internal drains (Figures 8(c) and 8(d)) located at either end of the tracks on every other track. The ends of the drydocks are open (Figures 8(e) and 8(f)) on both ends. When relatively small water volumes, such as those from a hydroblasting operation (Figure 8(g)), flow off the drydock deck, the majority of the water is captured in the tracks (Figure 8(h)) and flows to

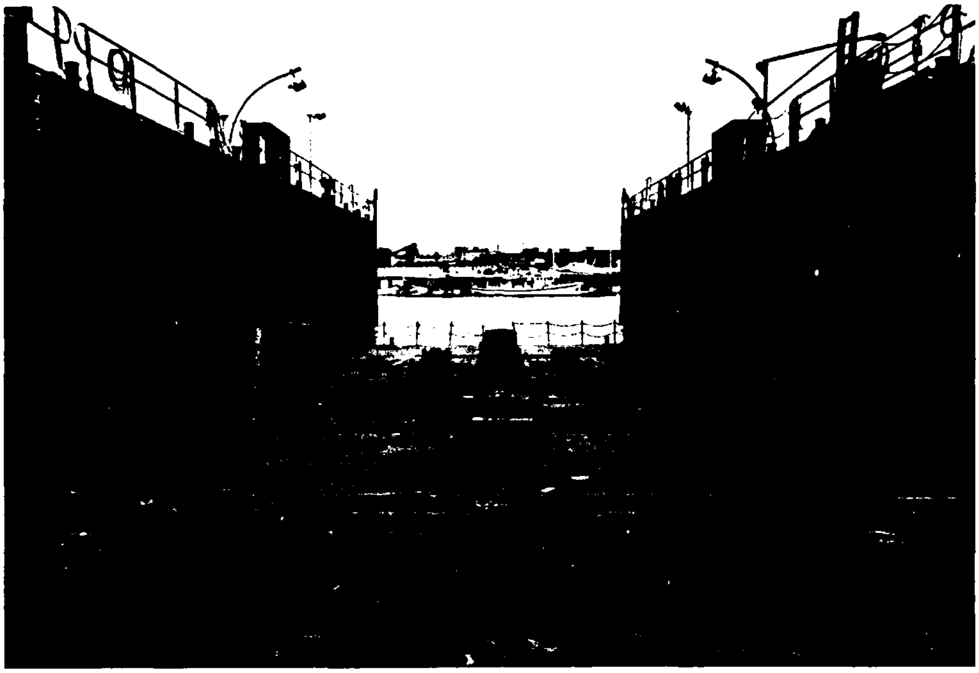


Figure 8(a) - (top) Small Concrete Deck Drydock-
Marco Shipyard
Figure 8(b) - (bottom) Large Concrete Deck Drydock-
Marco Shipyard

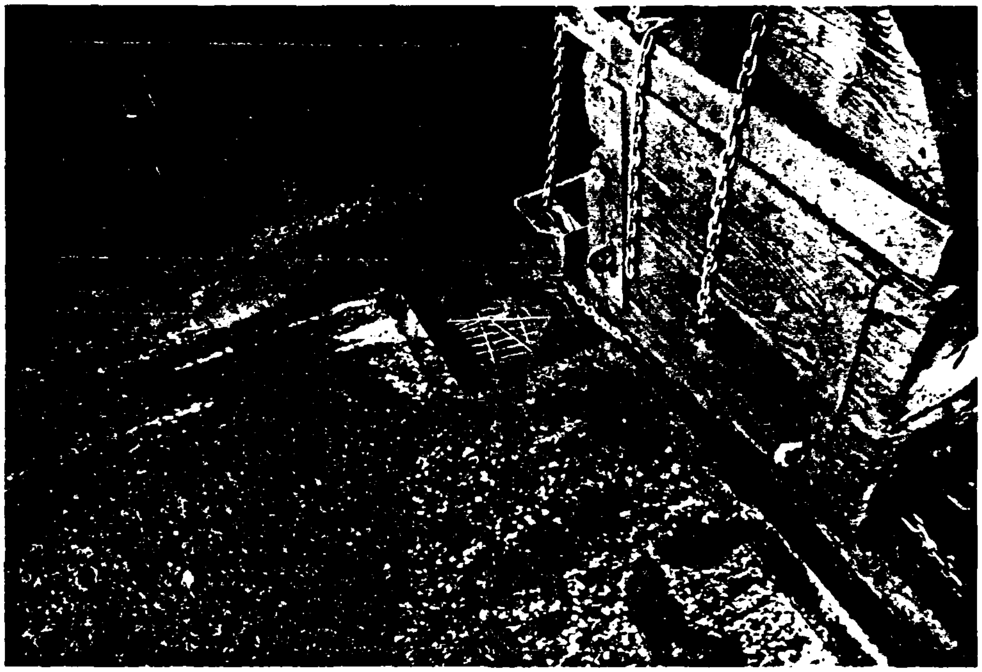


Figure 8(c) - (top) Internal (6-inch) Drain on Drydock Track next to Bilge Block-
Marco Shipyard

Figure 8(d) - (bottom) Internal Drain, Close Up-
Marco Shipyard

Figure 8(e) - (top) Drydock End, Towards Canal-
Marco Shipyard
Figure 8(f) - (bottom) Drydock End, Towards Shipyard-
Marco Shipyard

Figure 8(g) - (top) Hydroblasting at Marco Shipyard
Figure 8(h) - (bottom) Hydroblasting Water Captured in
Keel/Bilge Track-Marco Shipyard

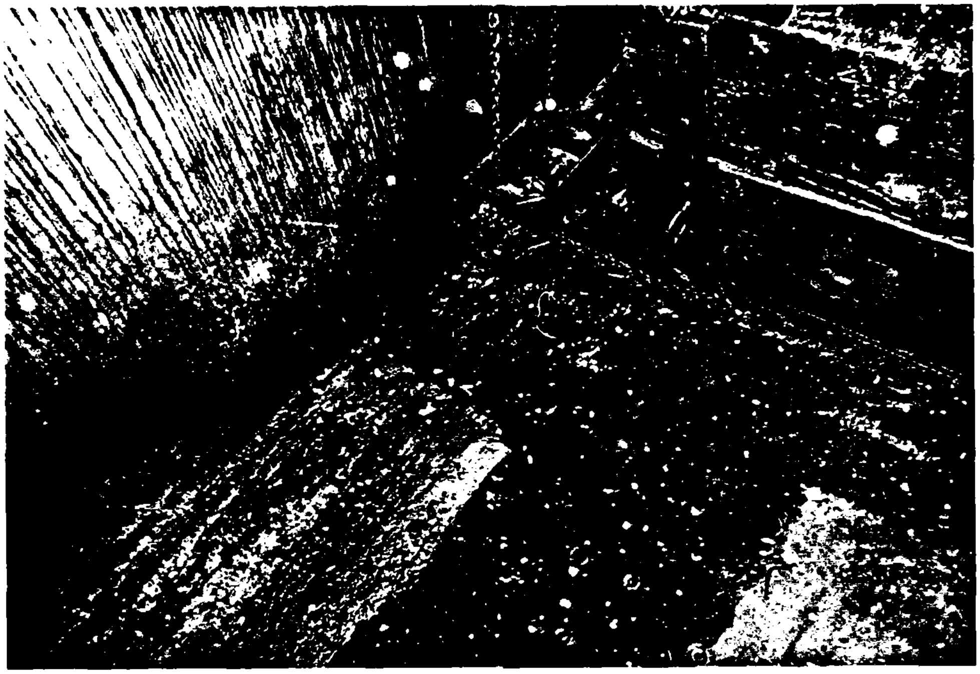
the drains (Figure 8(i)), although some water will escape via the open end (Figure 8(j)).

Marco keeps their deck surfaces clean of the solid blasting grit used for hull preparation (an alternative to hydroblasting when the hull paint is in need of removal). Water generated from hydroblasting at Marco is contaminated only with the solids removed from the ship hull. Figure 8(g) shows that dispersion of the hydroblasting water is quite random and when a large ship is being serviced, as in Figure 8(k), multiple sources of hydroblasting water are possible.

No hydroblasting was observed on ships brought out of water with the marine railway at Marco (Figures 8(l) and 8(m)). This area has no drains and even less containment capacity than the drydocks, but it has a sloped surface that allows gravitational flow of water.

3.2.2 Foss Maritime

Foss Shipyard, slightly smaller than Marco Shipyard, has two drydocks built by the U. S. Navy during World War II. The drydocks at Foss have a wood surface deck and are each 200 ft in length, slightly smaller than



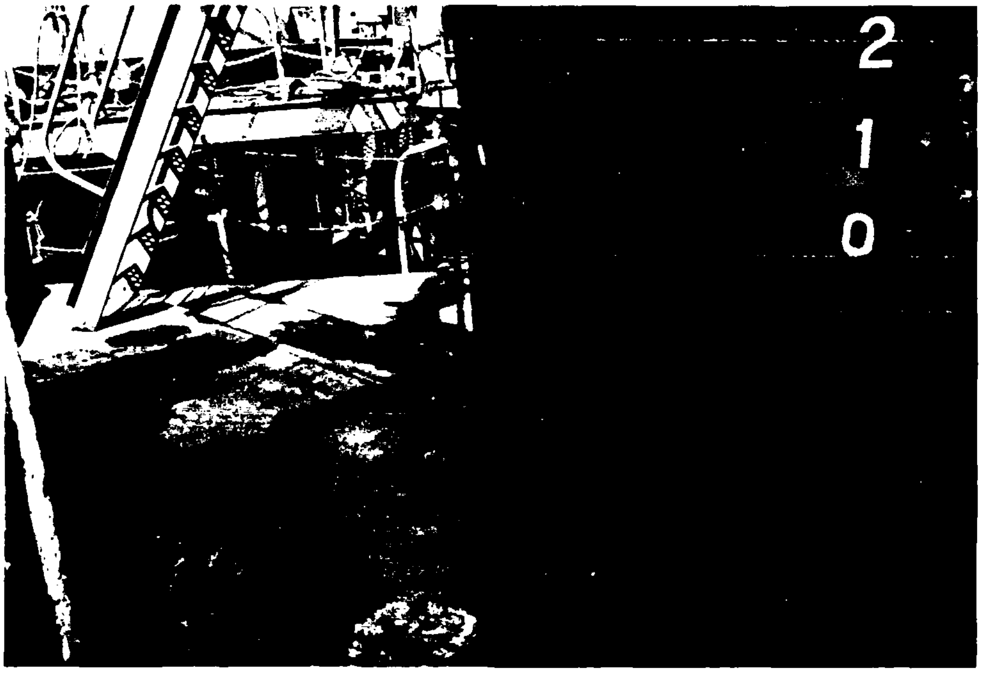


Figure 8(i) - (top) Hydroblast Water Flowing into Drain on Drydock-Marco Shipyard

Figure 8(j) - (bottom) Hydroblast Water Flowing off Open End of Drydock-Marco Shipyard

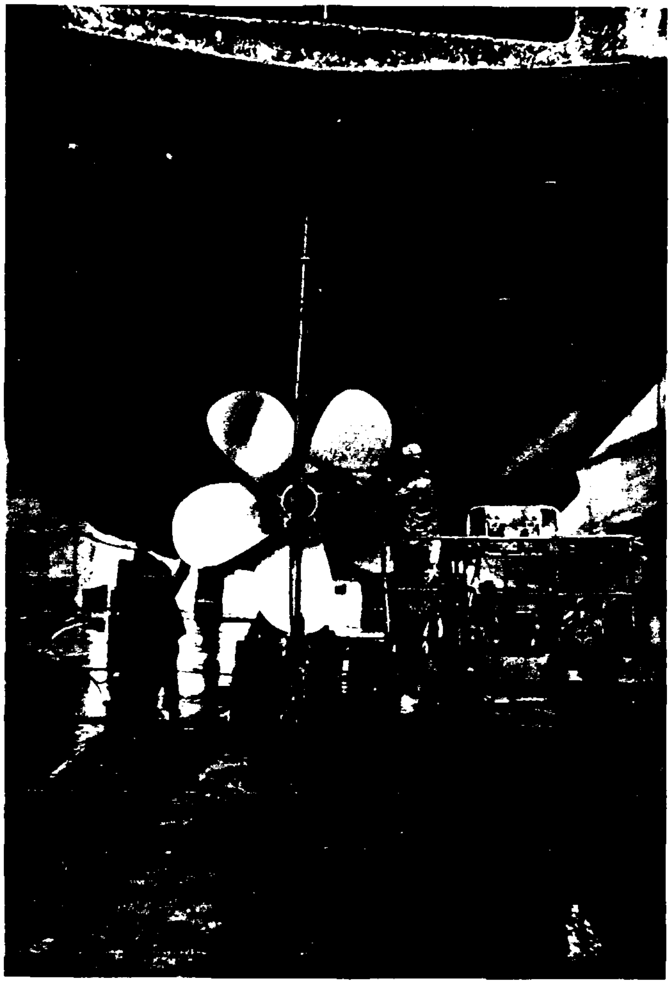


Figure 8(k) - Two Man Hydroblasting Operation on 120 ft Ship-Marco Shipyard

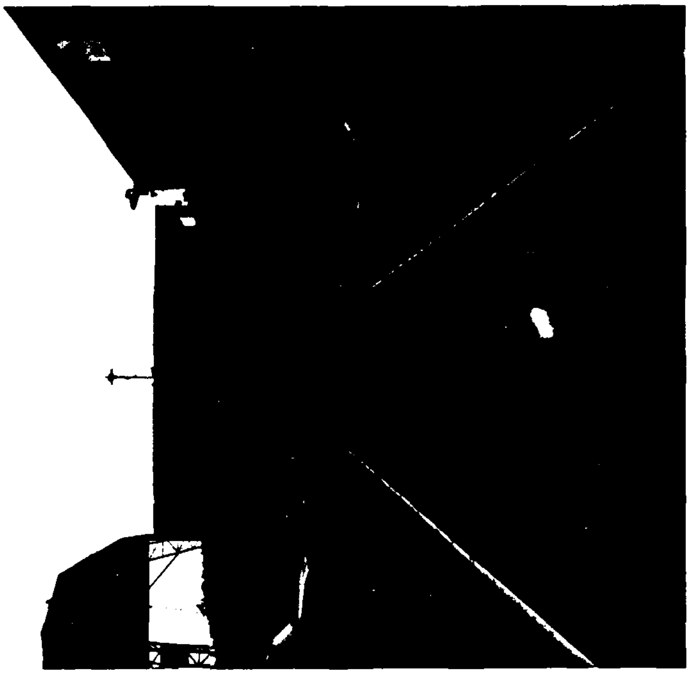
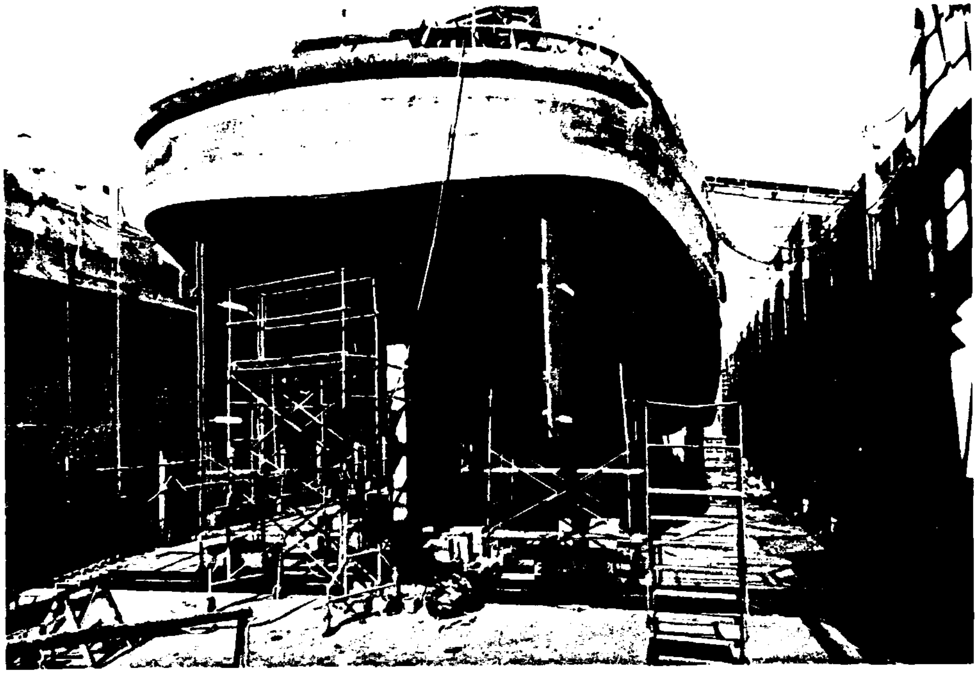


Figure 8(l) - Marine Railway at Marco Shipyard

Figure 8(m) - Ship on Marine Railway at Marco Shipyard

Marco's large 250 ft drydock. One Foss drydock has a 1200 ton capacity and the other a 1000 ton capacity. Figure 9(a) shows one of the Foss drydocks. Unlike Marco where bilge/keel block tracks are recessed, the tracks on the Foss drydocks are raised, allowing water to be captured (Figure 9(b)) and slowly drain into channels located on each side of the dock (Figure 9(c)). In an attempt to control the release of suspended solids in this drainage, the channels have been equipped with 7.5 inch high steel dams fitted with 5.5 inch drain pipes (Figure 9(d)). When hydroblasting is underway, the pipes are loosely stuffed with absorbent cloths which serve as crude but reasonably effective filter media. A grab sample of the water discharged through these filters was relatively free of settleable solids and far lighter in color than the hydroblast water itself.

Foss Shipyard is a good example of potential problems in siting a wastewater treatment system due to space limitations. A drydock is often filled completely with the vessel (Figure 9(a)) plus ship maintenance equipment such as scaffolding, welding gear, and a personnel lift. Space on shore is also severely limited. Figure 9(e) indicates the limited areal space available at Foss in the vicinity of the drydocks. The small road



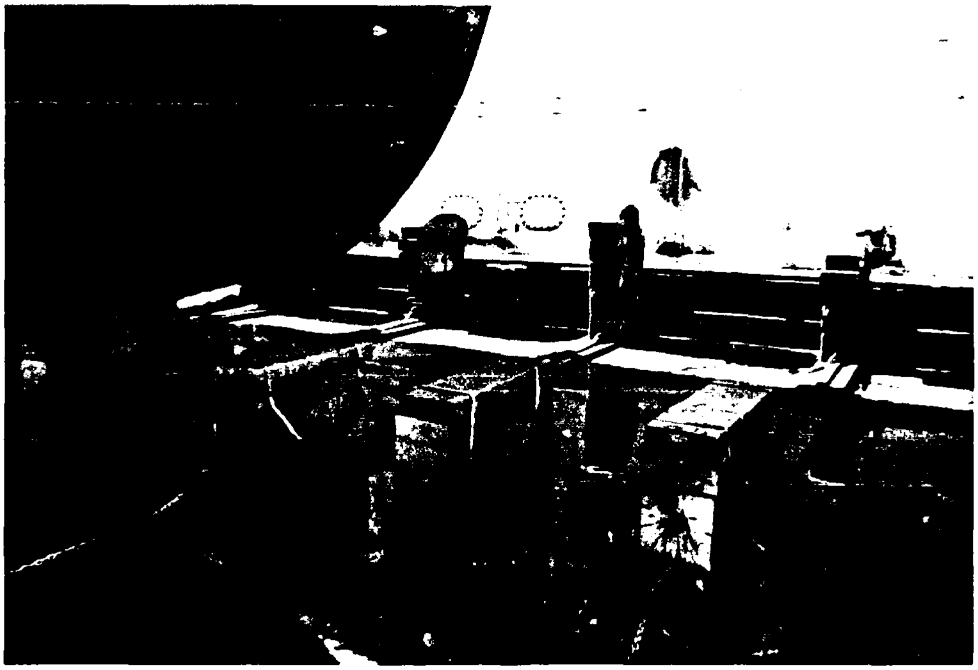


Figure 9(a) - (top) Boat in Drydock at Foss Shipyard

Figure 9(b) - (bottom) Drydock Deck at Foss Shipyard
[Note the raised keel/bilge
tracks and standing water]

Figure 9(c) - Drydock at Foss Shipyard
[Note the channel at the base of the wall- during drydock the water runs into this channel]

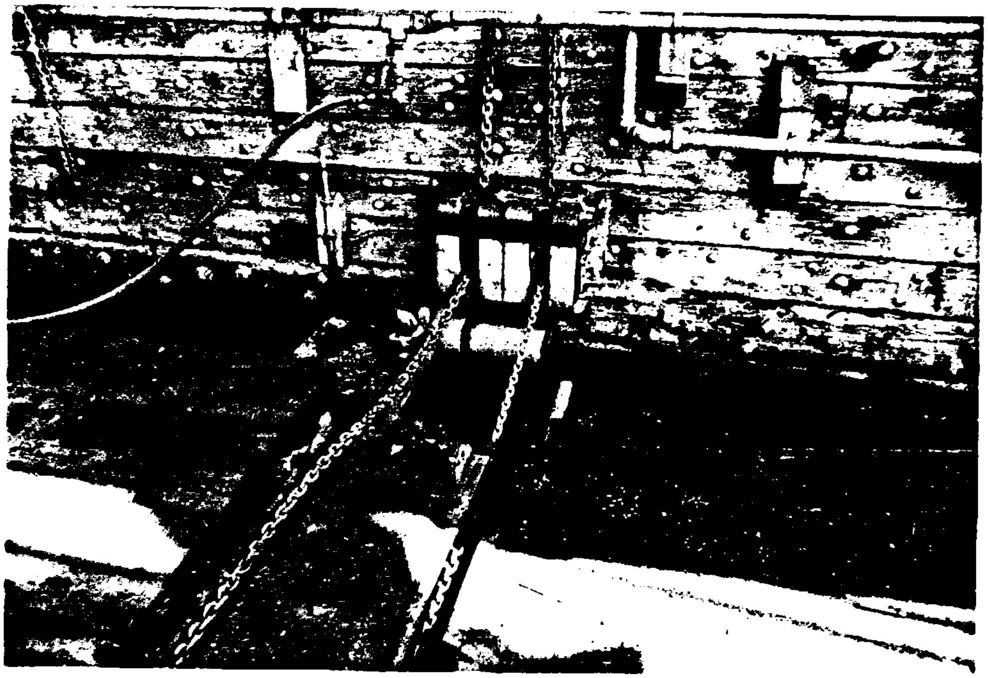


Figure 9(d) - Close-up of Drain Pipe at end of Drydock Channel at Foss Shipyard [Note the cloths stuffed into inlet side of drain pipe]

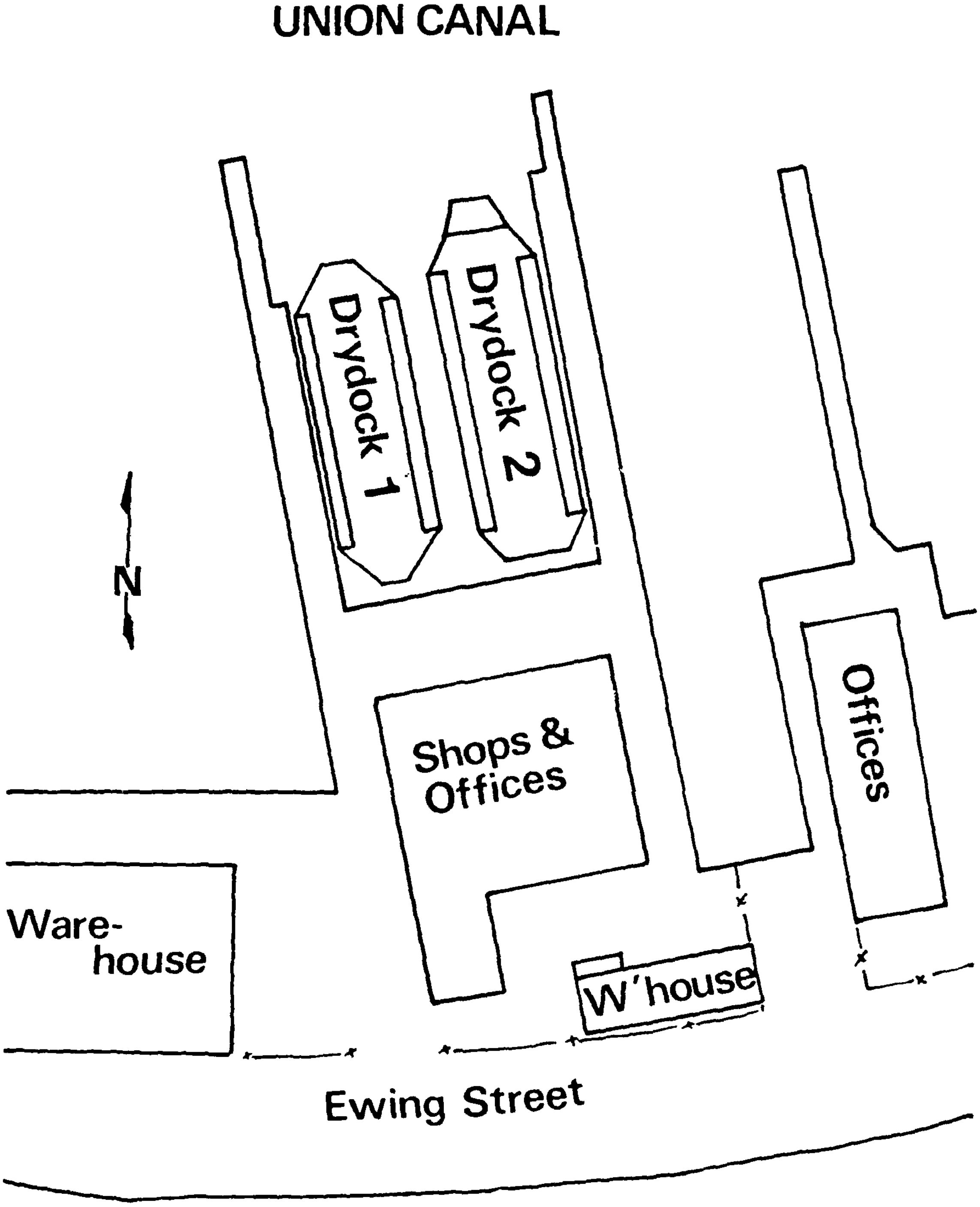


Figure 9(e) - Plan View of Foss Shipyard in Vicinity of Drydocks SCALE: 1 inch = 100 feet [Note, several permanent and semi-permanent facilities are located on the road between the drydocks and shops which are not indicated on drawing] immediately adjacent to the two drydocks has several semi-permanent and permanent facilities, including a storage shed and the hydroblasting equipment, none of which are indicated on Figure 9(e).

Foss also provides an example of how variations in shipyard operating practices effect the quality of the water discharged from the drydock. At Foss the solid blasting grit is cleaned and removed from the drydock deck at less frequent intervals than at Marco. Subsequently, water captured in between the bilge/keel tracks has the opportunity to intermingle with any blasting grit and paint chips that have not either been manually removed or washed out during the lowering of the drydock. This infrequent cleaning practice also diminishes the effects of the well intentioned filters shown in Figure 9(d) because the filters are only effective while the drydock is fully raised. Although it appears that a significant portion of the heavy grit stays with the drydock through successive lowering/raising cycles, whatever solids remain on the drydock deck have an opportunity to become suspended in the canal water.

3.2.3 Union Bay Shipbuilding Corporation

Union Bay is a smaller operation than Marco or Foss. At Union Bay, ships are raised from the water via a marine railway (Figure 10(a)) and, occasionally, are simply serviced from pierside.

The layout at Union Bay, however, is more amenable to containment of hydroblasting water because of a sea wall that is located at the bottom of the railway. Figure 10(b) shows the sea wall holding back water (on the lower right of photo) that has accumulated from hydroblasting as well as rainfall. Some means of closing off the rail slot in the wall (center of photo) would have to be devised to make full containment of hydroblast discharges possible.

3.2.4 Mercer Marine

Mercer Marine is one of the largest recreational marinas on Lake Washington. Here, boats are raised and lowered by means of a mobile hoist with straps (Figure 11(a)). Hydroblast water is much less dispersed during hull washings (Figure 11(b)) and it readily flows to an open storm drain located adjacent to the hydroblasting area.

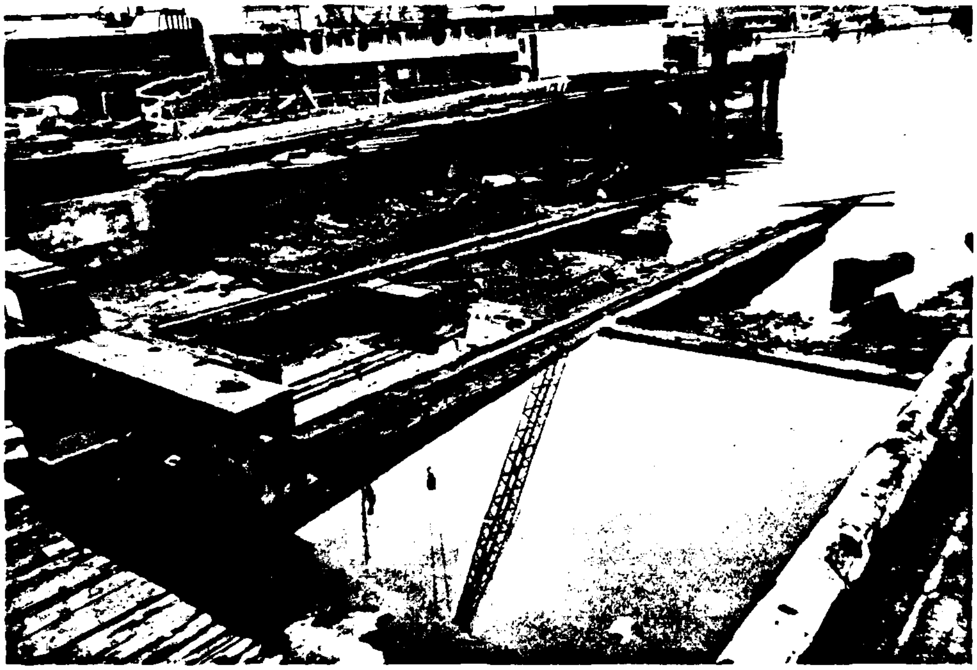


Figure 10(a) - (top) Marine Railway at Union Bay Shipyard
Figure 10(b) - (bottom) Sea Wall at Bottom of Marine Railway at Union Bay Shipyard

Figure 11(a) - Mobile Hoist at Mercer Marine
Newport Yacht Basin, Bellevue, Washington

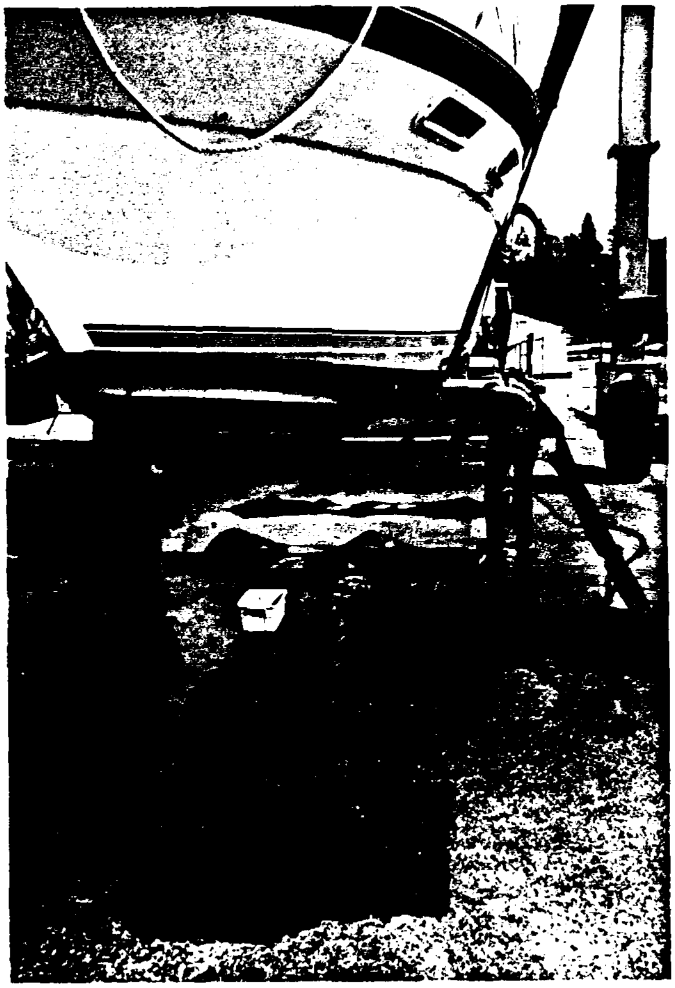


Figure 11(b) - Hydroblasting at Mercer Marine
[Note: Boat is typical size of those at this facility. Drain is an open storm drain, 18-in x 12-in]

3.3 Hydroblasting Equipment

Marco, Union Bay and Mercer Marine all use small, gas-fired, portable pressure washing units similar to the one shown in Figure 12(a). The water source is normally the municipal water supply, although water from the nearby canal or lake has been used during water shortages. The gear shown in Figure 12(a) is capable of producing a jet at 2,000-2,200 psi and is quite effective at removing marine growth on any type and size of vessel. Some machines are capable of heating the water, but this option is seldom used. The gun is similar in size and operation to those used at commercial do-it-yourself car washes. An on-off trigger activates the water and very little adjustment in the delivery rate is possible.

Foss has a much larger unit with a 10,000 psi capacity. This unit is relatively immobile due to its size and weight. It sits semi-permanently on a site adjacent to the drydock . Foss normally sets their hydroblasting unit to deliver a stronger jet of water at 3,500 psi. Water flows from the nozzle at all times since the trigger on the gun is designed only for restricting flow and creating a high pressure jet.

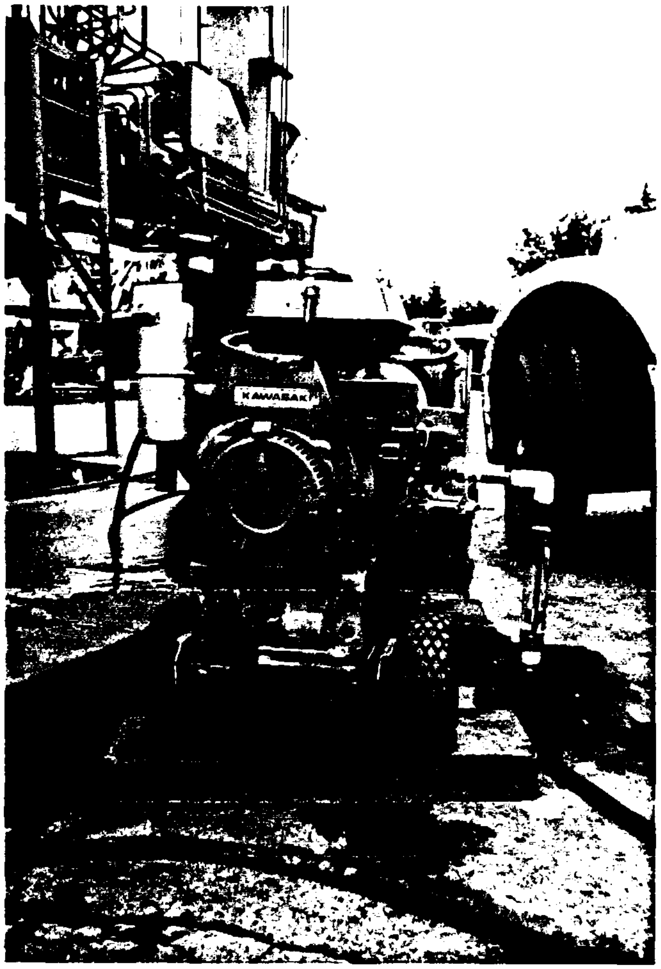


Figure 12(a) - Hydroblasting Equipment, Mercer Marine [Note: This unit is similar to those used at Union Bay and Marco. In-line flow meter is on inlet side of unit]

Figures 12(b) and 12(c) illustrate the difference between the high pressure (washing) delivery and the low pressure (idle) delivery of water from the Foss unit. With this feature, the hydroblast operation generates much larger quantities of water than the small units and the final effluent from the drydock is far more diluted than it would be at a facility using the smaller unit.

3.4 Anti-foulant Paint Use

Information gathered at the initial meeting with shipyard representatives and subsequent follow-on visits, indicates that the use of organotin paints at Seattle area commercial shipyards is minimal. None of the three commercial shipyards visited for this study used organotin anti-foulant paints. Shipyards in the Seattle area predominantly use copper based antifoulant paints. In the past, some Seattle shipyards used organotin anti-foulant paints, but concerns about future environmental regulations and perceptions of potential liability have discouraged their use. The three shipyards in this study use one particular brand of copper anti-foulant almost exlusively. This is Devran 216 AF Permanent Red manufactured by Devoe Marine Coatings Co.

Figure 12(b) -- (left) Hydroblasting at Foss Shipyard (5-9-88)

Figure 12(c) - (right) Idle De'ivery from Hydroblast Gun, Foss Shipyard

The material safety data sheet for Devran 216 is found in Appendix 1(a). This paint contains by weight 35 percent cuprous oxide, 10 percent zinc oxide and 10 percent iron oxide. Other non-volatile components include bentonite clay, fumed silica and sulfonamide salt, at less than 5 percent.

Just prior to the time of this study, Mercer Marine was using organotin paints almost exclusively. As of 1 April 1988, however, they were forced to remove these items from their retail shelves and discontinue their use to comply with Washington State law RCW 70.54. Mercer Marine sold and used the Trilux brand of organotin paint containing 13.8 percent tributyltin fluoride. Appendix 1(b) - 1(e) contains material safety data sheets for the various Trilux organotin paints. Trilux organotin paints contain lead and chromium drying salts, each contributing 1 - 5 percent by weight (as lead or as chromium) to the paint's initial wet composition. These drying agents were not found in the Devran 216 copper paint, which had organic sulfonamide salts for this purpose.

These two brands of paint were not expected to exclusively influence this study due to variations in past paint use. However, they certainly appeared to have predominance over all other anti-foulant paints.

3.5 Hydroblast Water Characteristics

From observing hydroblasting during initial site visits at Foss Shipyard and Mercer Marine, no easy method of sampling the hydroblast water was evident. Water was observed to ricochet off the hull surface in all directions, even when attempts were made to deflect the spray to a specific location. The larger the ship, the more widespread the dispersion of the spray.

However, it appeared that the largest volume of water ran down the hull to the lowest point, usually the keel, before falling off the boat. Another significant portion of water ran partially down the hull surface before dripping off at various intermediate locations between the point of application and the lowermost point on the hull. Spray was generated in all directions. These observations suggested a simple and consistent sampling strategy would involve capturing water from all three sources and determining their respective contributions to the effluent quality as well as well as quantity.

Small grab samples of the hydroblast water were taken and found to contain small paint chips and, primarily, algae. From the larger steel hulled vessels, occasional large paint chips, rust flakes and barnacles were found. Generally, whether the water was from a large commercial vessel or a recreational craft, the visible solid particles carried in the water were quite small (<< 1 mm) and well dispersed in the water. Normally no large chunks, long filaments and agglomerated masses were observed.

CHAPTER 4

MATERIALS AND METHODS

4.1 Hydroblast Wastewater Characterization

4.1.1 Hydroblast Water Sampling

A simple and reproducible method of sampling water was developed to adapt to the many variations in layout and operation at each site. Additionally, the sampling strategy was made flexible enough to permit sampling on a moment's notice because the decision of whether to hydroblast a ship hull (versus solid media blasting) was normally made only after a ship had been raised from the water and an appraisal of the paint's condition had been made.

Samples were collected in small stackable plastic trays. The trays were either 14-in. x 22-in. x 8-in. or 16-in. x 22-in. x 6-in., and held either 8 or 5 gallons of liquid, respectively.

The trays were set in one of the three areas identified in the field investigation as a distinct target under or around the ship hull. These areas were identified as "fall zone", "drip zone" and "spray zone". Figure 13

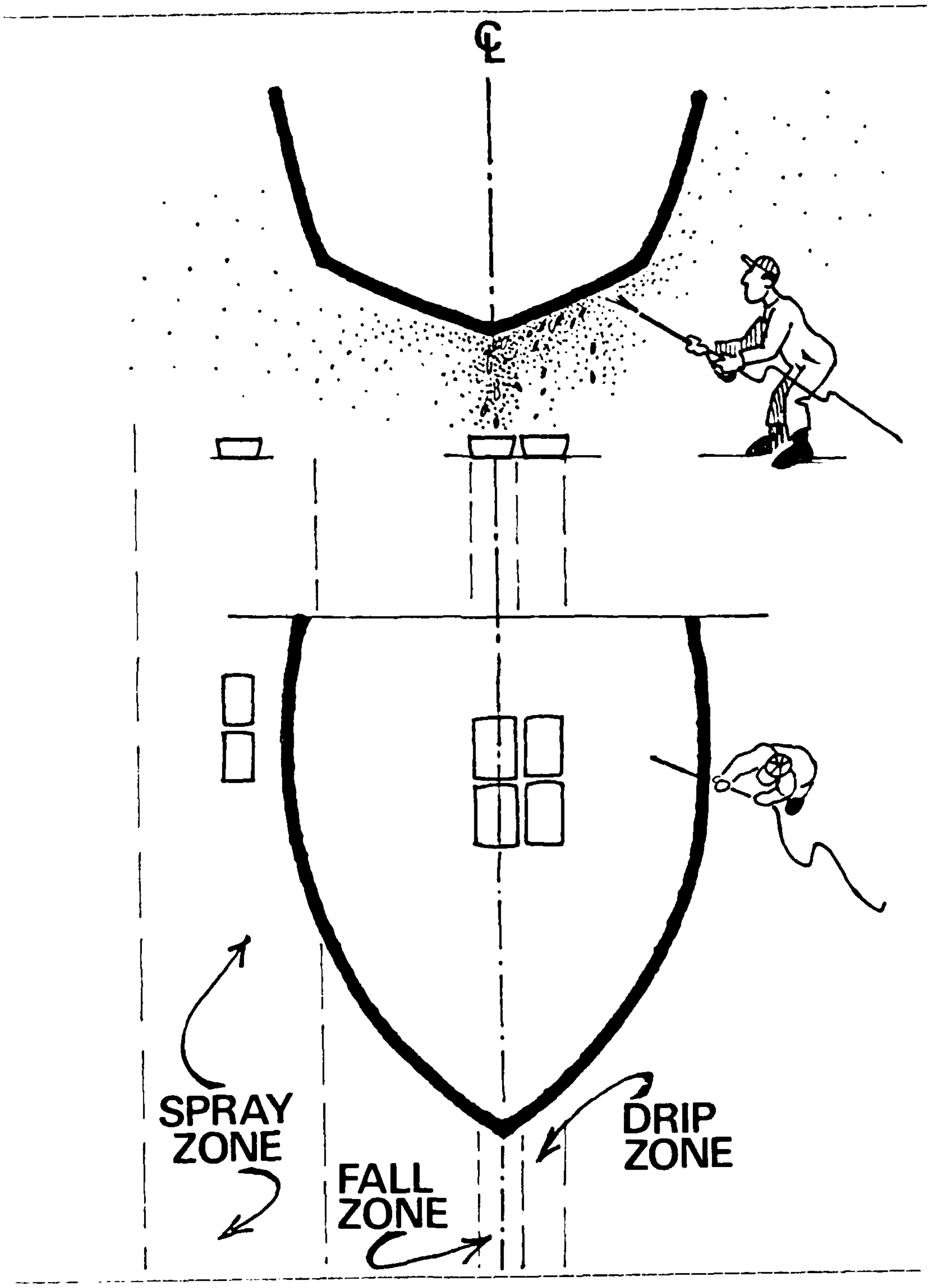


Figure 13 - Layout of Sampling Trays used to Collect Hydroblast Water and Designation of "Spray", "Drip" and "Fall" Zones Used in Hydroblast Water Characterization

shows the general locations of these zones with respect to the vessel and hydroblast application. Normally two trays were place side by side in each zone to maximize the capture.

The hydroblast operator followed his normal cleaning procedure. No attempt was made to apply the water differently than would have been done if sampling were not taking place. Efforts were made to make sure that sampling did not encourage prolonged application of water in one spot, which could have led to undesired removal of the "good" paint. This procedure also avoided generating more water than would be produced in a normal operation. The sampling trays were moved to follow the operator's path and maximize the volume of water captured in a given zone. At each site a small sample of the washwater directly from the hydroblast nozzle was taken for separate laboratory analysis.

When the hydroblasting was completed, the water was transferred to 5 gallon plastic buckets, covered and labeled to describe the water's origin. As soon as practicable, the buckets were returned to the laboratory and if not analyzed immediately, they were place in a 4° Celsius cooler. The sampling trays were washed off immediately with water, inside and out, and thoroughly wiped clean with paper towels at the end of each sampling. Later on, they were washed with soap and water, rinsed thoroughly and dried with cloth towels.

Information collected at the sampling site included the following:

(1) The name, type and size of the vessel, where the vessel had been since it was last painted and the date it was last painted.

(2) The exact type of paint if known, otherwise it was noted simply whether the anti-foulant paint was copper or organotin.

(3) The hull material (i.e. steel, wood, fiberglass).

(4) The time that hydroblasting began and ended as well as the actual sampling period (these two times were normally the same on smaller boats).

(5) The actual time of water application using a stopwatch.

(6) Quantities of water collected in each sampling zone.

(7) Volumetric flow rates from the hydroblast unit. Volumetric flow rate at Foss was estimated by filling a 5 gallon bucket and recording the time it took to fill the bucket as the water was delivered in its non-pressurized stream. At Marco Shipyard and Mercer Marine marina, an in line flow meter (30 GPM, 1-1/2 inch

O.D., Model K-72, In-Line Meter, manufactured by King Instrument Co.) was used to directly measure the volumetric flow rate. Figure 12(a) shows the installed flow meter.

(8) A small sketch of the boat hull was made, and the hull area represented in the collected washwater was estimated.

(9) Photographs of the hull were taken before and after washing. Photos were taken of a surface deemed representative of the type of growth covering the entire hull. Photographs were also taken of the hydroblast washing sequence, with particular emphasis given to the way the water was coming off the boat and falling into the sampling trays. The overall appearance of the boat hull was also noted.

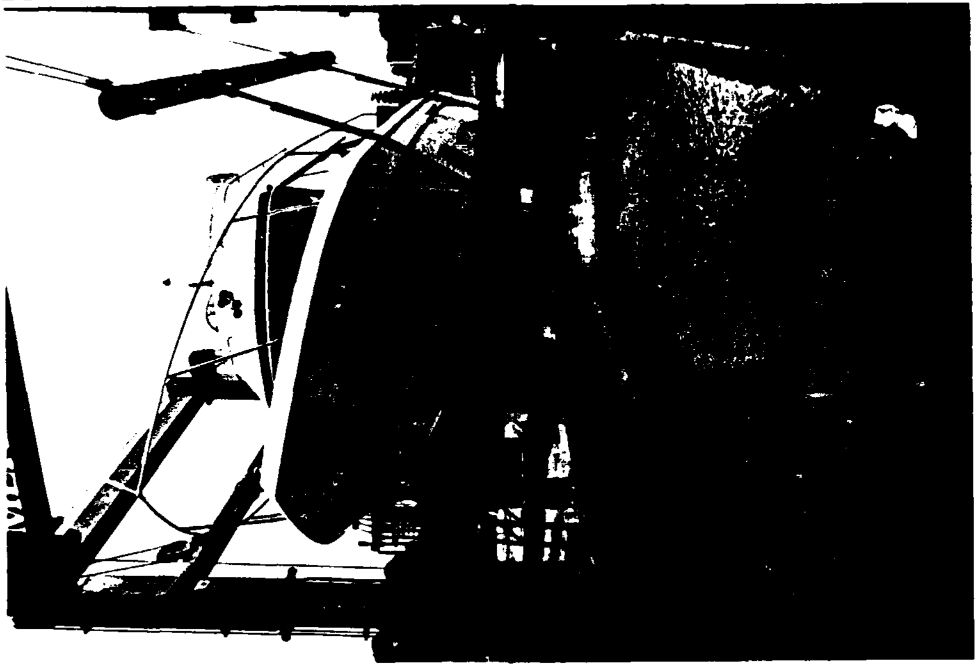
Although an attempt was made to make each sampling event similar to every other sampling event, certain variations occurred with every sample that affected the quality and quantity of water that was captured and subsequently analyzed. Therefore, a brief description follows for each of the six samples used in the water characterization phase of this study.

4.1.1.1 Sampling at Mercer Marine, 3 May 1988

Variations from the sampling sequence already described were minor. The operator elected to use a hot pressure wash to remove unusually thick growth. This boat had been immobile for the last six months and was covered with small living worm-like creatures that one marina employee thought might be crayfish larvae. Figures 14(a) through 14(d) show the boat being lifted with the hoist, the sampling technique and hull surface before and after the washing. Small red paint chips were observed in the otherwise dark green washwater, but overall the hull did not appear to have lost much paint.

4.1.1.2 Sampling at Mercer Marine, 5 May 1988

The hull surface was in good condition. This was a sailboat with large flat rudder and keel blades whose surface areas could be easily calculated. A sample was taken of the wash water from the rudder as part of an attempt to correlate the washed hull area with water volume and water quality parameters. Only the "fall zone" and "spray zone" were sampled. Figures 15(a) and 15(b) show the sampling technique used and Figures 15(c) and 15(d) show the hull before and after washing.



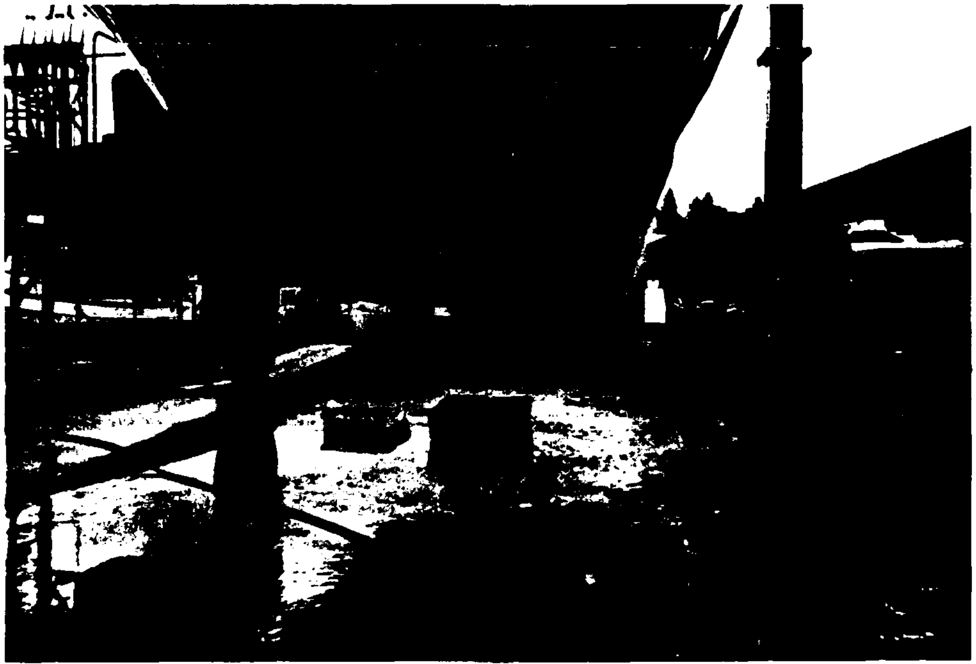
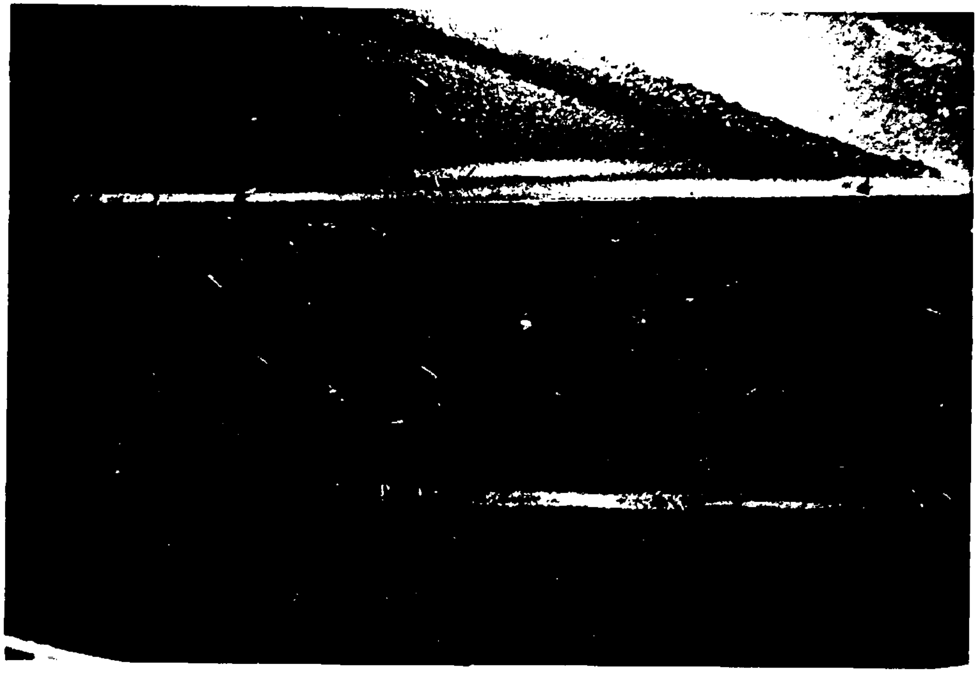


Figure 14(a) - (top) 5-3-88, 28-ft Bayliner with Red TBT Bottom Paint, Lifted from Water

Figure 14(b) - (bottom) Sampling of Hydroblasting Water 5-3-88



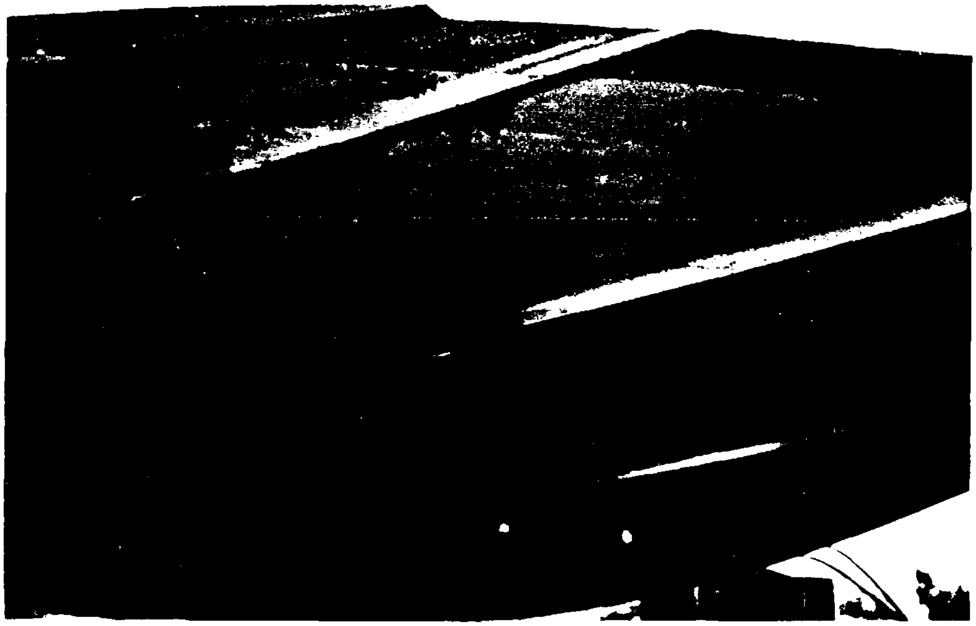


Figure 14(c) - (top) Two Years of Hull Growth on 28-ft Bayliner Painted with TBT Anti-foulant
Figure 14(d) - (bottom) Same Boat and Hull Area After Hydroblast Washing, 5-3-88

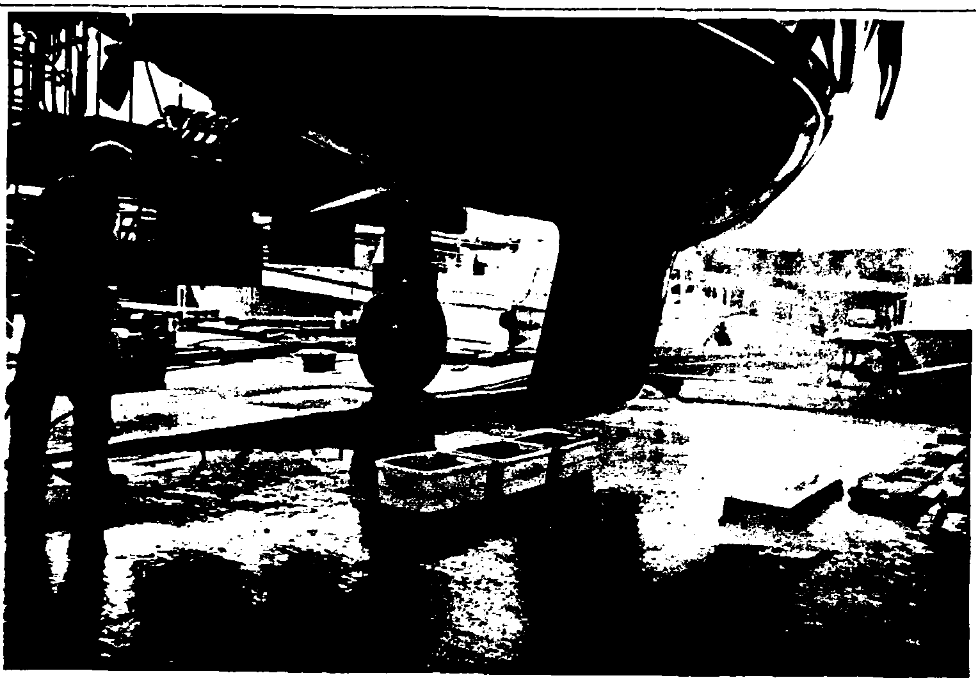


Figure 15(a) - (top) 5-5-88, Sampling Hydroblast Water
from 31-ft Sailboat
Figure 15(b) - (bottom) 5-5-88, Sampling Hydroblast
Water from Rudder Only

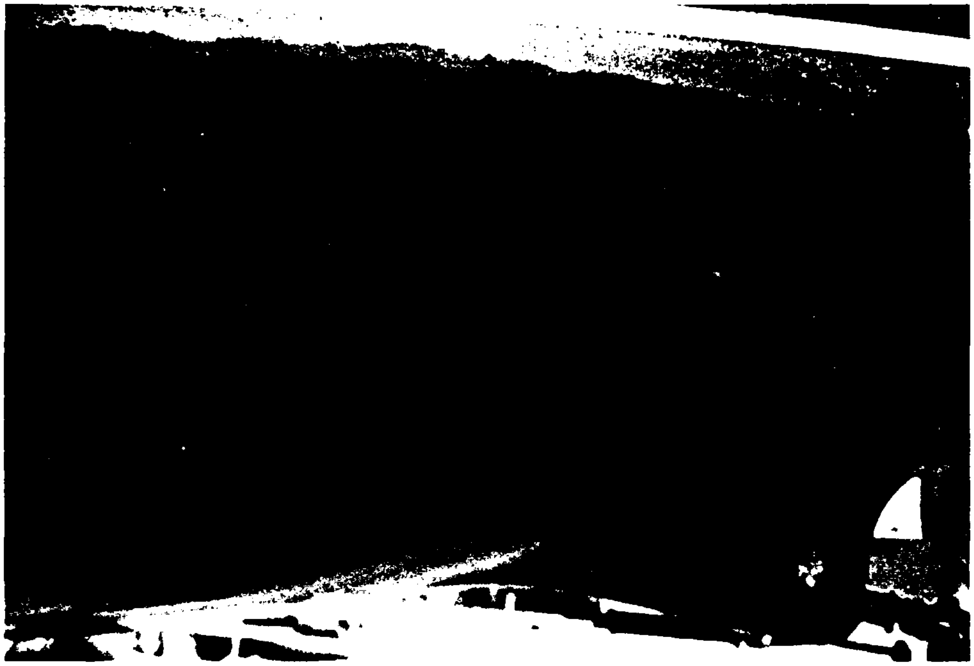


Figure 15(c) - (top) One Year's Growth on Sailboat Hull Painted with TBT Antifoulant

Figure 15(d) - (bottom) Same Boat and Hull Area after Hydroblasting Wash, 5-5-88

4.1.1.3 Sampling at Mercer Marine, 6 May 1988

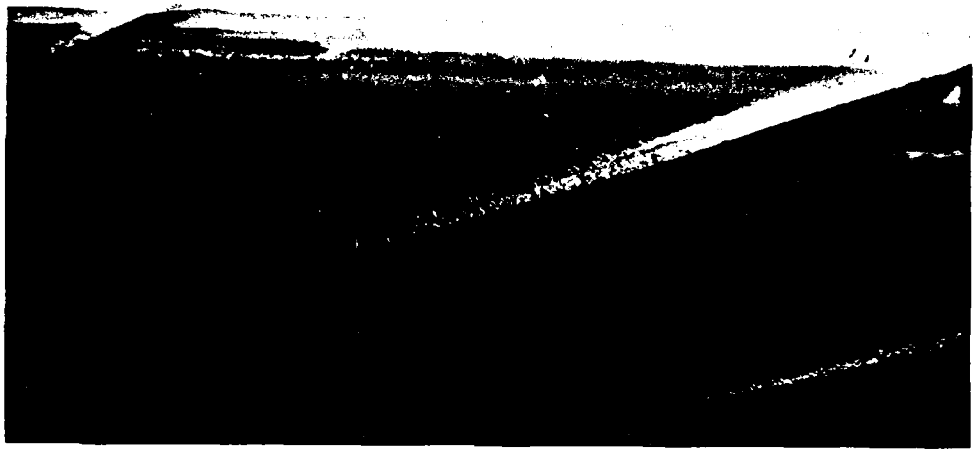
Hull growth on this boat was completely black. The boat's owners stated it had been painted only once, over two years ago. Some worm-like creatures like those noted on the 5-3-88 washing were observed but not in the same density. This boat took much longer to wash than that of 5-3-88 even though it was the same size and model. The reason for this is two-fold: first, the operator was less experienced with the work and, second, the growth on this vessel was quite hard and resistant to removal. The total washing period was 31 minutes, compared to an average of 20 minutes observed on other recreational boats, thus a more dilute sample was probably obtained compared to others. Additionally, less of the growth was removed from the boat, even though a hot water wash was used. Sampling techniques for this sample are shown in Figures 16(a) and 16(b) and the hull surface, before and after washing, is shown in Figures 16(c) and 16(d).

4.1.1.4 Sampling at Foss Shipyard, 11 April 1988

This was the first sample taken for a characterization

Figure 16(a) - (top) 5-6-88, Sampling Hydroblast Water from Washing of 28-ft Bayliner

Figure 16(b) - (bottom) 5-6-88, Sampling Hydroblast Water [Note "spray zone" tray placement]



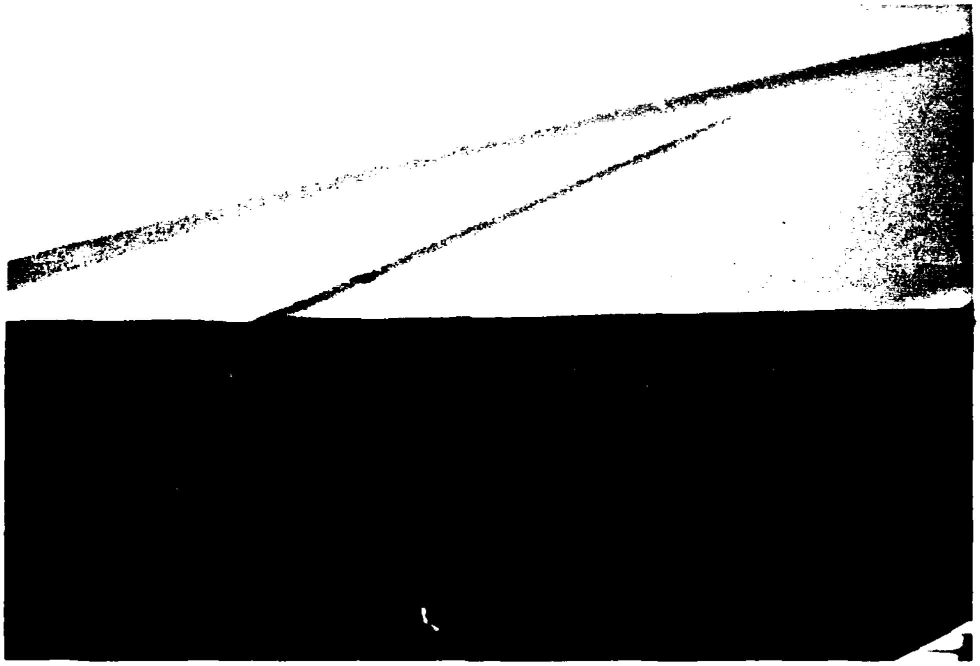


Figure 16(c) - (top) Two Years' Growth on Hull Coated with TBT Anti-foulant
Figure 16(d) - (bottom) Same Boat and Hull Area after Hydroblast Washing, 5-6-88

analysis. Only the "fall zone" was sampled. The water was completely opaque, almost black in color. No photographs were taken of this initial sampling. The rate of the water generated was visibly greater than that later observed at other sites due to the type of hydroblasting equipment used (refer to figure 12(b)).

4.1.1.5 Sampling at Foss Shipyard, 9 May 1988

Due to the shape of the ship hull, only "fall zone" and "spray zone" samplings were made. Figure 12(b) shows sampling tray placement. The hull surface being washed was perpendicular to the ground, so no intermediate dripping took place as it does on a round hull. The operator experienced several problems with his personnel lift as well as the hydroblasting equipment causing the sampling to stop sooner than anticipated. This sample was uncharacteristic of other commercial ship washings. The hull surface was relatively free of growth and the operator inadvertently directed the idle spray towards the sample trays in between high pressure applications (Figure 12(c)), resulting in a more dilute sample. The wash was stopped before completion because of an oil leak in the hydroblast pump. Nonetheless, the samples were considered to be representative of an actual discharge from this drydock and they were taken to the laboratory for analysis.

4.1.1.6 Sampling at Marco Shipyard, 11 May 1988

This was the last sampling done for the characterization phase of the study. Sampling proceeded in accordance with the methods already described (Figure 17(a)). The hull surface was covered with a consistent mat of algae, but the paint on the boat appeared to be intact at most locations. The hydroblast operator pointed out a common problem on painting work done on the large steel-hull commercial ships. When paint is applied to a partially wet surface these areas blister and actually retain some of the liquid solvents from the original paint. Blisters were not widespread on this hull, but at least a dozen quarter sized blisters were observed in an area of about 1,500 square feet and a few had popped open to release the liquid solvent. Figure 17(b) shows the hull surface before and after washing.

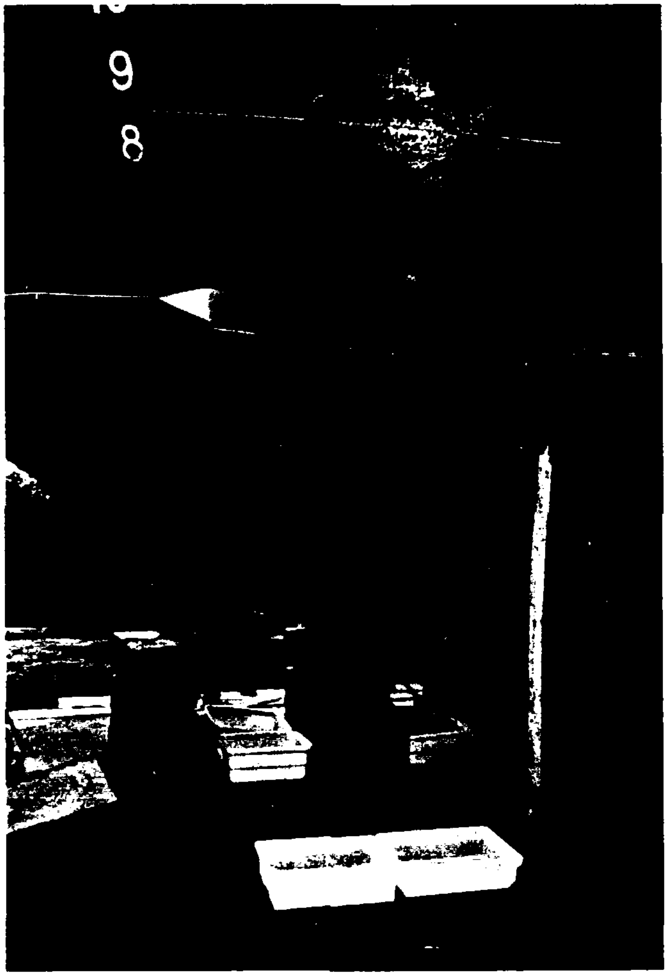


Figure 17(a) - 5-11-88, Sampling of Hydroblast Water from 58-ft Steel Hulled Ship

Figure 17(b) - Two Years' Growth Versus Just Washed Hull Surface, 5-11-88

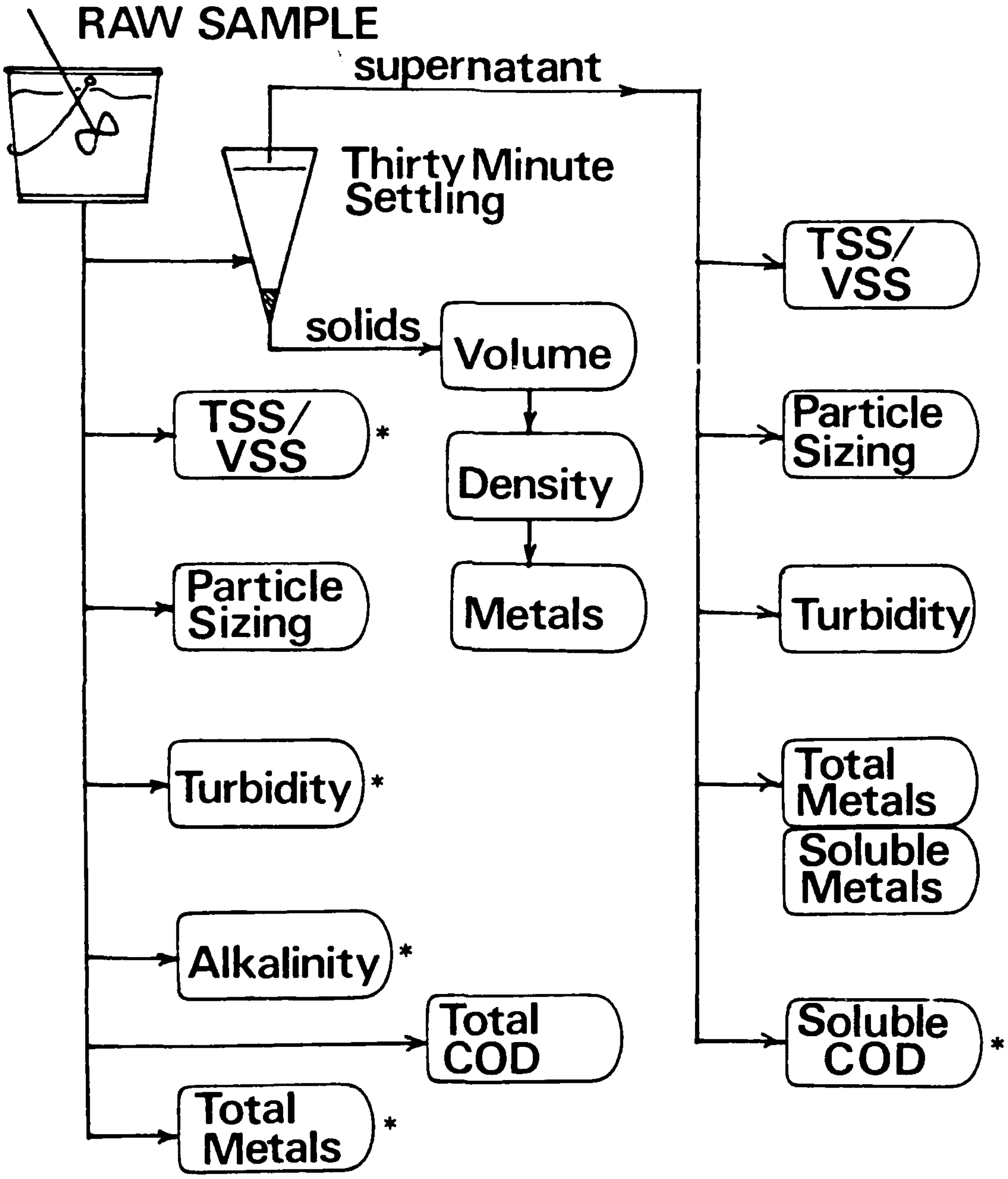
4.1.2 Analysis of the Water

Samples were analyzed as quickly as possible after being brought to the laboratory at the University of Washington. Analyses proceeded as shown in the flow diagram shown in Figure 18 and were performed in accordance with Standard Methods for the Examination of Water and Wastewater (APHA, 1988) except as described below.

Each sampling zone ("spray", "drip", "fall") was treated as a discrete sample and the same tests were performed on each zone's water. For total/volatile suspended solids, total/soluble chemical oxygen demand and particle sizing, a replicate analysis was made for each test. All other tests were performed once per sample.

4.1.2.1 Particle Size Analysis

Particle size analysis was performed with a HIAC/ROYCO Model 4100A Particle Counter. This instrument analyzes particles in the size range 1 - 100 microns (see Figure 3(c)). This range was deemed suitable for this study because an absence of dissolved particles (< 1 micron) appeared likely. From Figure 4, it is apparent that



Temperature and pH measured for Raw Sample and Supernatant

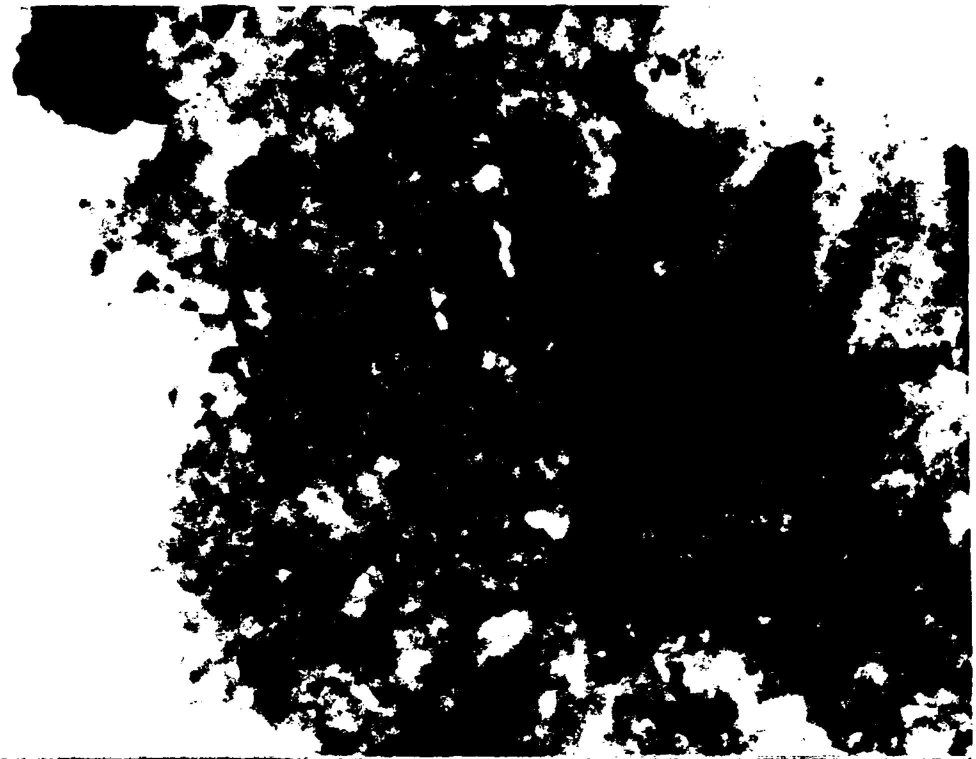
Figure 18 - Hydroblast Water Characterization - Analytical Flow Sheet
[* Indicates this test was also performed on raw water direct from hydroblast unit]

algae, which appeared to make the most significant contribution to solids in the water, was in the range of 1 - 100 microns. Paint chips larger than the algae appeared to be present in significant numbers. Figures 19(a) and 19(b) show microscopic views (magnification: 100x) of the paint chip sizes relative to the algae in a raw hydroblast sample. It was clear that the paint chips (the dark patches) were generally much larger than the algae particles. This trait was particularly evident in the recreational boat water, Figure 19(a). The particle counter has six channels, thus the six size ranges chosen for analysis throughout this study were:

1 - 5 microns
5 - 10 microns
10 - 40 microns
40 - 70 microns
70 - 100 microns
100+ microns

Criteria for these choices were based on Levine's diagram, Figure 3(b), and Kavanaugh's diagram, Figure 4, as well as characteristics of certain treatment processes selected for the study.

Five (5) microns was chosen as a cut-off for particles that would be less likely to be captured in a granular media filtration process. This was a somewhat arbitrary



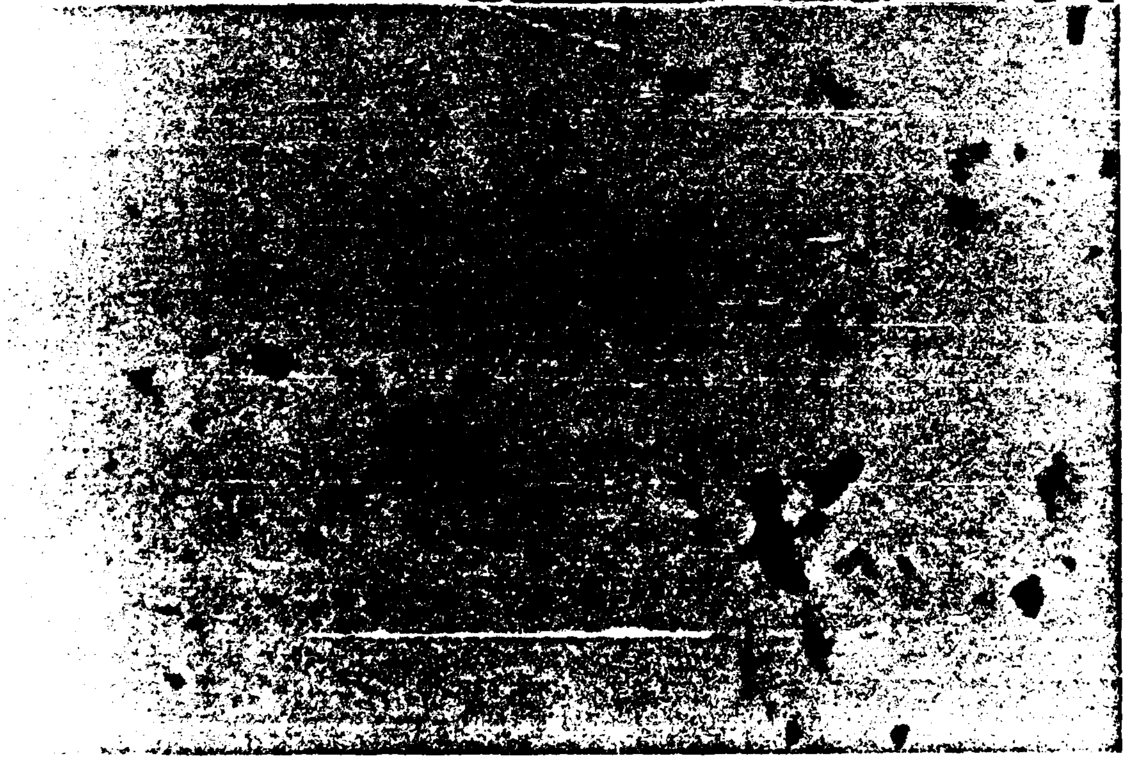


Figure 19(a) - Raw Hydroblast Water from TBT Painted Hull (Magnification 100x)

Figure 19(b) - Raw Hydroblast Water from Cu_2O Painted Hull (Magnification 100x) choice based on studies with slow sand and dual media (coal/sand) filters. A study by Slezak et al (1984) demonstrated that removal of 1 - 50 micron particles in a slow sand filter was least effective for 2.4 - 4 micron particles, although the removal rate was still near 99% in this range. From Levine (1985) it was apparent that 3 microns and larger would be effectively removed in granular medium filtration. It was clear from Kavanaugh's diagram, Figure 4, that filtration could remove particles less than even 1 micron in size if the particle concentration is high enough because brownian movement of the particles would be an efficient particle-media attachment mechanism when there are more particles to collide with. Yet with Kavanaugh, the middle range for direct filtration appeared to be between 2 and 5 microns. Thus 5 microns was determined to be a reasonable cut-off point for gauging the effectiveness of granular media filtration.

Ten (10) microns was selected as the next size plateau because 1 - 10 micron is a size range in which chemical coagulation performance is particularly good (Levine et al, 1985; Montogomery, 1985).

Microscreening ("straining" in Figure 4) was seen to be effective at 25+ microns, but the smallest commercially available screen size (325 mesh) had an opening of 44 microns. Figure 3(b) showed 50 microns as the lower limit for sedimentation to be effective. Thus, in order to judge the effectiveness of microscreening and sedimentation, 40 microns was conservatively selected as the next cut-off point for particle size analysis.

The next smallest screen size that was available, 200 mesh, had an opening of 74 microns. Therefore, the upper point of the next range was selected at 70 microns.

The last range, 100 microns and larger, was chosen to determine the number of exceptionally large suspended particles in the water. From visible and microscopic inspection, paint chips appeared to contribute the greatest number of particles in this size range. Analysis of this size range would also determine whether sedimentation was more effective with 100+ micron particles, as Figure 4 indicated, or with 50+ micron aprticles as indicated by Figure 3(b).

Clearly no finely drawn boundaries existed for process selection based on particle size. Rather, the effectiveness of each process might be based upon relative particle size and would also have to consider other factors, such as particle concentration and density.

Particle shape may also have some effect on particle size analysis. Microscopic examination (Figures 19(a) and 19(b)) revealed that the paint chips had a more uniform shape than the amorphous and filamentous algae masses. The HIAC/ROYCO particle counter employed a "photozone stream" method of counting particles. A beam of light was directed across a moving fluid stream carrying suspended particles. The power drop experienced by the beam of light correlated to known average particle sizes that had been used in calibrating the instrument. The particles used in the calibration were spherical, hence the introduction of non-spherical particles such as the paint chips and algae made for a relatively inexact measurement. Nevertheless, the HIAC/ROYCO particle counter was a quick and reliable method of establishing the distribution of particles by their relative number and sizes in the water.

In the characterization phase of the study, all samples, including supernatant from the thirty minute settling test, had to be diluted with deionized water prior to running them through the particle counter. Samples diluted 1:10 clogged the sampling tube in the particle counter. Therefore, all raw samples and supernatants from settling tests were diluted 1:100 before particle size analysis. Deionized water used for sample dilution was also analyzed to get a background particle count.

Initially a total of 5 particle counts were performed for each sample, but very good agreement was found in all 5 counts in all 6 size ranges so it was determined that two counts per sample would be sufficient. This decision was important for the treatability phase of the study because limited sample volumes would be available then. Particle counts were performed for 40 mL samples in accordance with the baseline settings for sample volume and flowrate on the instrument. Particle counts for diluted samples were calculated and recorded as the particle count multiplied by 100, to account for dilution. Between each sample the sampling tube was cleaned with approximately 100 mL of deionized water and periodic particle counts were made of the deionized water to determine if the background count was shifting.

4.1.2.2 Analysis for Metals

As seen in Figure 18, three samples were analyzed for metals in the characterization phase of the study: the raw sample as well as the supernatant and settled solids from a thirty minute settling test in an Imhoff cone. The samples were analyzed for metals using inductively coupled argon plasma atomic emission spectroscopy or ICP (Jarrel-Ash Model 96-955) with the detection limits as shown in Table 6. For comparison, primary and secondary drinking water standards are also given for the metal in question.

Table 6 - Metals Analyzed in Hydroblast Water and Their Detection Limits on the ICP

Metal	Known Marine Paint Constituent	Detection Limit (mg/L)	Primary [1] or Secondary [2] Drinking Water Standard (mg/L)	
Aluminum	X	0.015	none	
Barium	X	0.001	1.0	(p)
Cadmium		0.001	0.01	(p)
Chromium	X	0.001	0.05	(p)
Copper	X	0.001	1.0	(s)
Iron	X	0.005	0.3	(s)
Manganese	Possible	0.001	0.05	(s)
Nickel		0.005	none	
Lead	X	0.02	0.05	(p)
Vanadium		0.002	none	
Zinc	X	0.001	5.0	(s)

[1] USEPA, 1975
[2] USEPA, 1979a

Tin analysis was performed on an atomic absorption (AA) graphite furnace, (Instrumentation Laboratories, Model No. 655, Furnace Atomizer and Model AAS11, Spectrophotometer), but a detection limit of only 0.1 mg/L was achieved. This detection limit is comparable to those reported (Analytical Chemistry, 1986) for the flame AA and ICP, as well as the analytical resolution that appeared to have been achieved in the EPA drydock wastewater study (USEPA 1979b). The manuafacturer of the AA instrument had stated detection limits for tin of 0.005 mg/L. The cause of this problem was not discovered and considerable additional time would have been necessary for its resolution, so the 0.1 mg/L detection limit was accepted as an operating constraint in this study.

The ICP was viewed as an excellent means of analyzing a a single sample for a wide array of metals over a significant spectrum of concentrations because the ICP is relatively free of interelement interactions. This characteristic of the instrument is traced to the method of atomizing the sample in the ICP. The ionic plasma formed by the 5500+ degree Kelvin temperatures in the ICP, appears to be relatively unaffected by the fluid flow characteristics and does not form refractory products that are common in other atomic emission spectroscopy methods such as flame AA and graphite furnace AA (Fassel, 1978).

Soluble metals samples were prepared by filtering the supernatant sample with a glass syringe through a 0.22

micron Millipore 25 mm diameter disposable filter and acidified to < pH 2 with Ultrex nitric acid. Total metals samples were prepared by taking either a 5 or 10 mL sample and placing it in a 75 mL Taylor tube. Settled solids samples were prepared by weighing approximately 0.1 mg of sample that had been oven dried at 105° C and placing the dried solids in a Taylor tube for acid digest.

The nitric acid digest was performed by placing 5 mL of reagent grade nitric acid, plus a boiling chip, in the Taylor tube, placing a small glass funnel for refluxing on top of the Taylor tube and digesting for 3 hours at 150° C. The tubes were allowed to cool to 90° C and the reflux funnels were removed. The Taylor tubes were kept at 90° C until they evaporated to dryness, usually 2 - 3 days. Finally, the Taylor tubes were cooled and 1 M nitric acid was added to bring the final volume to 12.5 mL. All glassware was soaked in nitric acid and rinsed in distilled water prior to use.

ICP analysis was performed on the samples as well as standards made from ultrapure chemicals (SPEX Industries, Mutuchen, NJ). A multielement standard was prepared with metals at 1 or 10 mg/L. ICP values were corrected for background levels found in digest blanks.

Tin analysis was attempted on the ICP, but detection limits were not sufficient. Therefore, tin was analyzed on the graphite furnace atomic absorption. Background levels could not be established for the tin analysis due to the high detection limit already discussed. Thus the tin values gained from this analysis were valuable only for relative comparisons between samples.

4.2 Hydroblast Wastewater Treatability

For the treatability phase of the study, two samples were made. One was taken 6-2-88 at Mercer Marine marina from a fiberglass-hull recreational boat coated with a tributyltin anti-foulant paint. The other sample was taken from a steel-hull vessel with copper anti-foulant paint at Marco Shipyard on 6-24-88. Samples were taken only in what had been designated the "fall zone" in the characterization phase because this target area received the largest volumes of water. Sampling proceeded in the manner already described.

Analyses of the influent and effluent from the various treatment processes described below were performed aswas that particle counts could be done on un-diluted effluents. All analyses shown on Figure 18 were discussed in the previous sections. The only exception performed on influent and effluent samples, except that alkalinity measurements were only done on samples that involved chemical treatment. And, finally, analysis for tributyltin was made on the influent and various treated effluents from a single sample.

Analysis for tributyltin, TBT, was performed on one raw influent (6-2-88), raw influent filtered with a glass fiber filter, and one effluent each from a chemical treatment and dual media filter. Only the aqueous phase TBT extraction and derivitization was performed. The procedure is similar to that used by Matthias et al (1986). Simultaneous hydridization (formation of tributyltin hydride, TBTH) with sodium borohydride, $NaBH_4$, and extraction with dichloromethane, $CHCl_2$, was performed. This solution was analyzed using a gas chromatograph equipped with a flame photometric detector. Dipropyltin was utilized as the concentration standard.

The treatability study began with the most simple processes and worked towards more complicated treatments that could include combinations of the four main treatment steps studied. Figure 20 shows the treatment processes studied.

Process>	Sedimentation	Screening (SC)		Filtration		Chemical (CH)
Sequence \/		200m	325m	SF	DMF	(Alum)
Alone	X	X	X	X	X	X
+200m SC				X		
+325m SC				X	X	
+Alum CH					X	

SF = Sand Filter DMF = Dual Media Filter

Figure 20 - Treatment Processes used in Hydroblast Wastewater Treatability Study

4.2.1 Sedimentation

This process was tested on a total of sixteen (16) of the samples taken from the characterization phase of the study as well as the 6-2-88 sample from Mercer Marine taken for the treatability work. Well mixed, unrefrigerated raw samples directly from the field were measured for temperature and pH and placed in one liter glass Imhoff cones for a settling test. The Imhoff cones as well as all glassware used in this study had been washed in mild soap and water, followed by a 10% nitric acid wash, rinsed a minimum of three times in deionized water and air dried.

The sample was allowed to settle for 30 minutes. At the end of the settling period the supernatant was drawn off and saved for analysis in seven 125 mL polyethylene bottles that had been washed in the same manner described for the Imhoff cone.

The volume of settled solids was recorded at 10, 20 and 30 minutes during the settling period. If a sufficient volume of at least 15 mL of the settled solids was available after 30 minutes of settling, it was pipetted out and its density was measured by taking the filled pipette (capped at the tip with a clean rubber plug) directly to the balance for weighing. The tare weight of the clean and dry pipette and rubber tip plug had been measured beforehand. All pipettes used in the study had a small amount of their tips ground off to ensure the larger solids in the sample could be drawn into the pipette. If the settled solids' volume was smaller than 15 mL, it proved much too awkward and difficult to retrieve an adequate sample for a density measurement and leave enough for metals analysis. Hence not all sample densities were measured. Temperature and pH of the supernatant were recorded at the end of the 30 minute settling period.

4.2.2 Screening

Stainless steel fine mesh screening in 325 mesh and 200 mesh sizes were procured from Pacific Wire Works in Seattle. The wire fabric was cut to fit a Gelman stainless steel pressure filtration funnel (Model 4280,Gelman Sciences, Inc., Ann Arbor, MI) as shown in Figure 21. The Gelman filter apparatus, its related accessories and the 325 mesh and 200 mesh cut screens were all washed with mild soap and water, soaked in 20% nitric acid, rinsed numerous times with deionized water and air dried before use.

The filter barrel was filled with approximately 250 mL of raw sample (Mercer Marine, 6-2-88) taken directly from the 4° C cooler and well mixed. The filter barrel was pressurized with air using a small vacuum pump (Gast, Model 1022 P3 G272X, 3/4 hp, 1725 RPM). Effluent was emptied directly into a 1000 mL polyethylene sample bottle. This step was repeated until a minimum of 750 mL of effluent had been generated. With the 200 mesh screen no backflushing was necessary, but the 325 mesh screen required backflushing after every 250 mL of screening. The pump was rated at 9.8 psi (10 CFM) standard operating pressure and had a maximum rating of 13.2 psi. Both the influent and effluent temperature

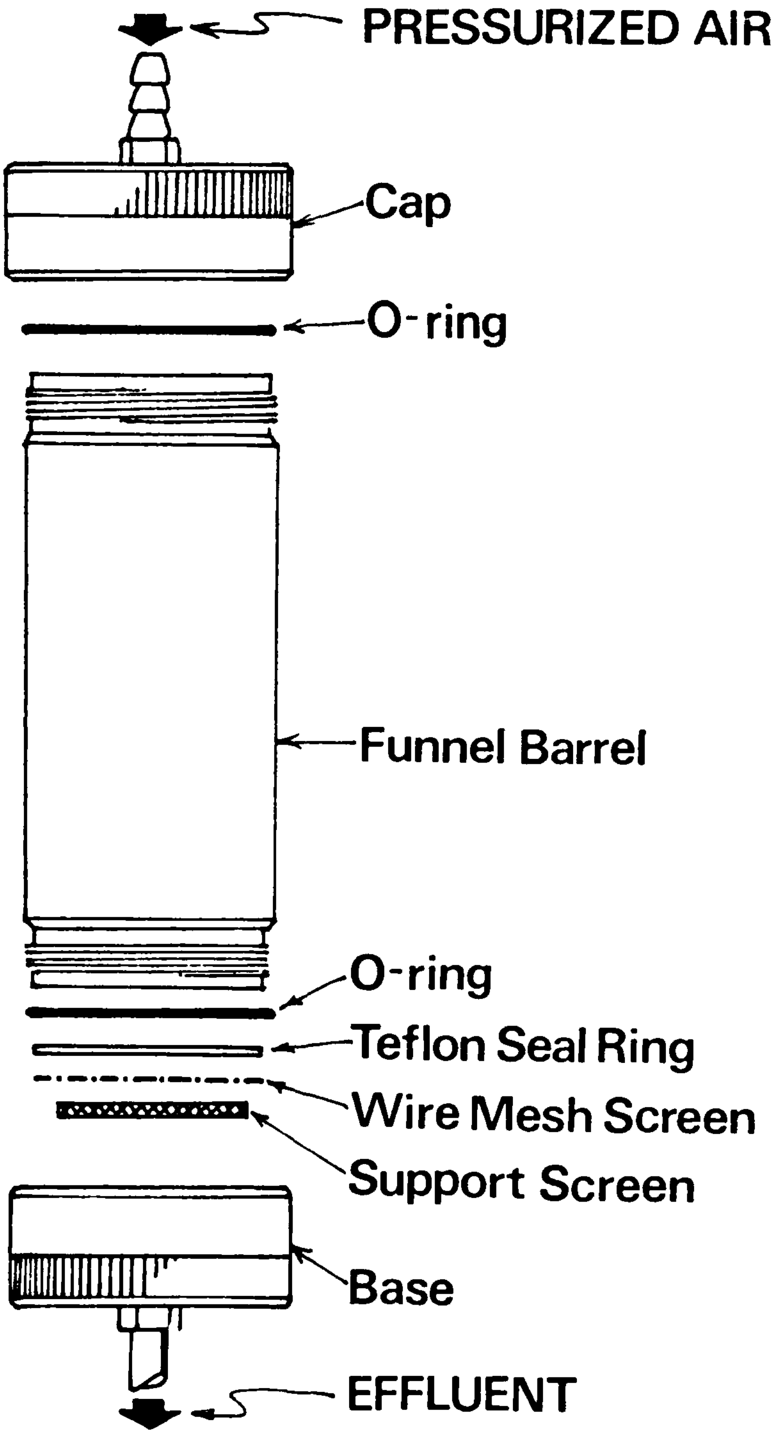


Figure 21 - Pressure Filtration Funnel used in Screening Process--SCALE: 1/2 inch = 1 inch

and pH were measured for each screening.

Initial blank runs were made with both screen sizes using deionized water. These effluents were analyzed for metals as well as particle size distribution.

4.2.3 Granular Media Filtration

Two types of filters were studied: sand and dual media (coal/sand). Both filters used one oi two identical columns constructed from 1-1/8 inch I.D. acrylic tubing. Figure 22 shows a column in its dual media mode. Both coal and sand columns had PVC rings placed every two inches to avoid wall effects. The 3-ft bottom section of the column was attached to the 6-ft top section with threaded PVC fittings for easy removal during cleaning. The outlet at the bottom of the tube was 100 mesh nylon fabric held in place by a threaded fitting, a design which facilitated easy removal of the filter media as well as allowing unimpeded water flow through the entire base of the column without the loss of sand.

The sand media was procured from the Emmett Company, Emmett, OH. It was pre-washed sand that was twice passed through 40 and 70 mesh sieves to get sand grains

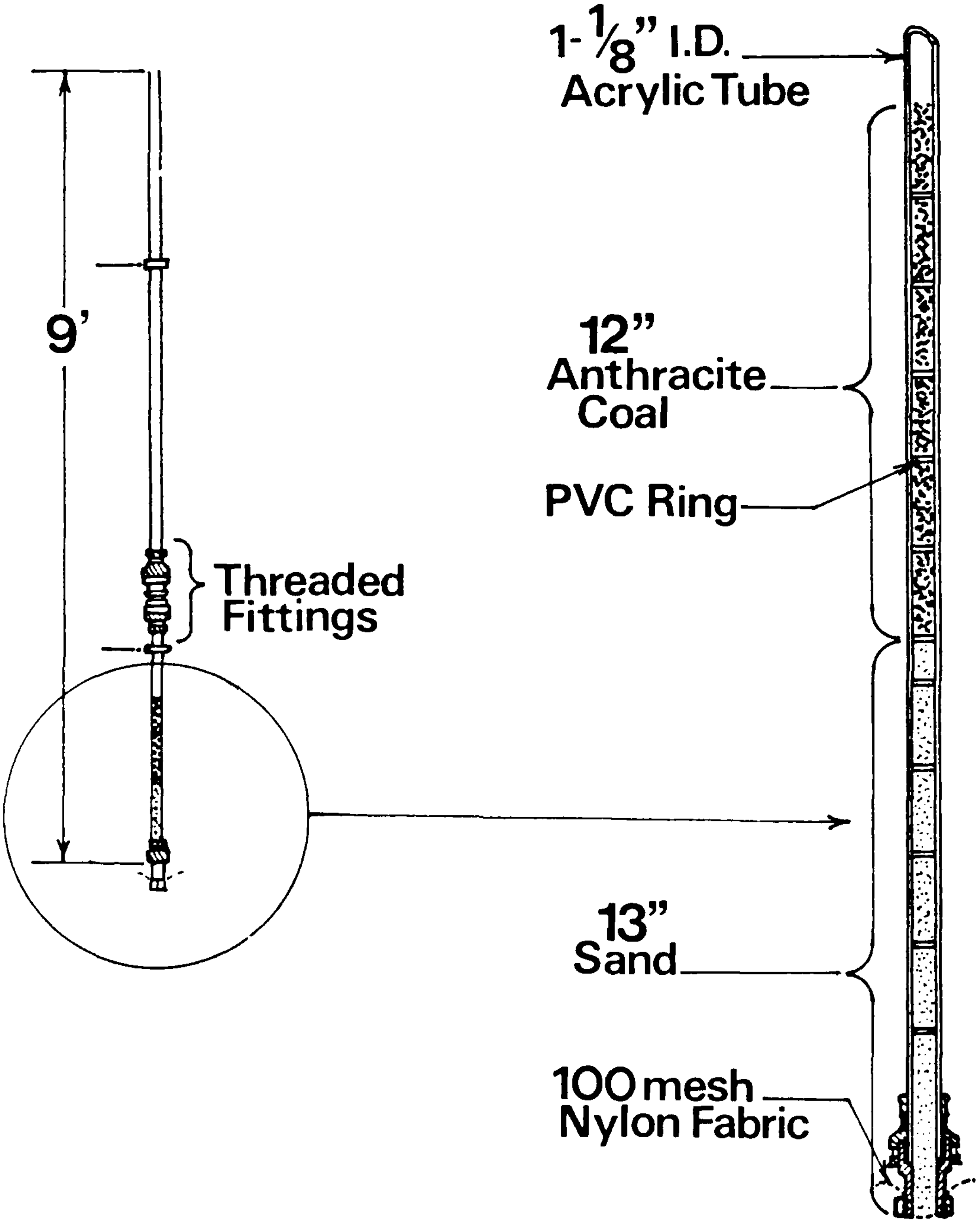


Figure 22 - Construction of Column used for Sand and Dual Media (Coal/Sand) Filtration Studies--Scale (Left): 1 inch = 2 feet
--Scale (Right): 1 inch = 2/3 feet

that were in the typical slow sand media size range of 0.2 to 0.4 mm. After sieving, the sand was washed with 10% nitric acid and then again with copious amounts of deionized water. The coal was anthracite coal procured from Northwest Filter Co. in Seattle, obtained courtesy of the Environmental Health Department, University of Washington. This media was 0.9 - 1.0 mm in size with a uniformity coefficient of 1.5. The coal was acid washed once with 10% nitric acid and was then washed over twenty-five (25) times with deionized water to remove the visible fines.

The height of the sand column was 13 inches in both the slow sand and dual media mode. The height of the dry coal column was 12 inches. These heights were chosen based on studies by Huang et al (1974) showing 12 inches to be the minimum depth necessary for effective operation of filters with either media. Media depths were comparable to those used in other dual media filter studies already summarized in Table 4. A typical slow sand filter media depth is 3 feet, however, it is common for actual slow sand filters to be reduced to depths of 12 inches during the course of scraping off the top layers of sand over time before being built back up (Seelaus et al, 1984). Thus for a bench scale batch filter operation, 13 inches of sand was determined to be an adequate depth.

Prior to operating either the sand or dual media filters, three 800 mL volumes of deionized water were passed through the filter to get the media saturated. On the last pass the water column height was recorded with the elapsed time and the effluent was collected as a "blank" for particle count and metals analysis.

For each filter run described below, temperature and pH were recorded on the influent and effluent. Normally, filtration times were limited to 24 hours per run since it was conceivable that actual systems would have to be able to drain overnight to make room for hydroblast wastewaters generated on successive days. In most cases the samples had been refrigerated at 4° C just prior to each run. After mixing the sample for about 5 minutes, and just prior to applying it on the filter, water temperature was typically 10 - 14° C, somewhat lower than the 14 - 20° C range measured at the wastewater's origin.

Initially, an attempt was made to filter raw hydroblast wastewater (collected 6-2-88 at Mercer Marine) with a sand filter. An eight foot column of raw sample, approximately 1500 mL, was poured on top of the column and a stopwatch was used to record the height of the water in the column as a function of elapsed time. The sand appeared to clog almost immediately. Even after being allowed to stand for 23 hours, a total drop of only six inches was observed. The column was emptied and the top one inch of sand was cleaned off and replaced with new dry sand taken from the batch prepared earlier. The same raw sample (6-2-88) was screened with a 325 mesh screen as described in the previous section. Only four feet of water was placed on the column, approximately 750 mL. The column drained more quickly than the first attempt. All but 7.5 inches of the water had drained after 24 hours and water was still draining, albeit very slowly. At this time the run was terminated, the top one inch of sand cleaned off and, as necessary, replaced. On the second run a slightly smaller sample volume, 600 mL, was screened with the 325 mesh screen and run through the column. This sample drained in less than 18 hours.

A second slow sand filter was set up identical to the first. Three 750 mL volumes of deionized water were run through the filter and column head was recorded as a function of elapsed time. Approximately 750 mL of raw sample (6-2-88) that had been passed through a 200 mesh screen was then placed on the filter. This sample drained in less than 17 hours. A second run was made with a slightly smaller volume of 600 mL sample (screened through 200 mesh) just as with the first column. All but five inches had drained in 21.5 hours. At this time the run was terminated. In both columns, the flow appeared to become impeded once a mat of solids had established itself on top of the sand.

In an attempt to prevent this mat from forming, four baffles were installed in the first column as shown in Figure 23 to capture the solids as they drifted down the water column. This arrangement effectively simulated sedimentation prior to sand filtration. A raw sample (6-2-88) volume of approximately 750 mL was placed in the column. This sample drained at about the same rate as the first run that had used a 325 mesh screened sample: after 24 hours approximately 6 inches of water remained. This column was allowed to continue draining until it was empty, which took 53 hours total elapsed time.

The baffle experiment indicated that the mat was not the only cause of obstructed flow. The baffled column developed a final mat depth of only 1/32 inch compared to an average 1/8 inch on the non-baffled runs. The fine pores in the sand column were observed filling up

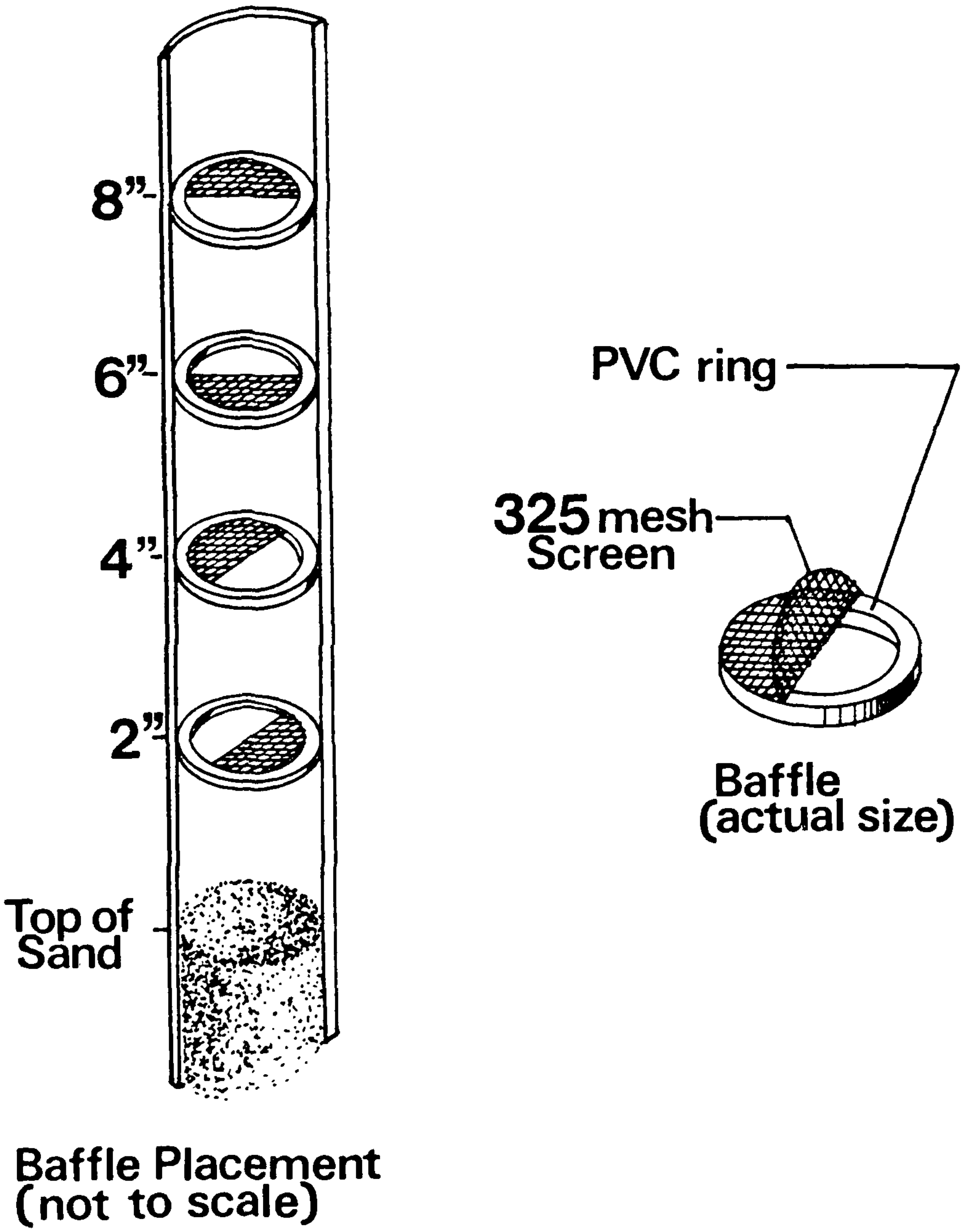


Figure 23 - Baffle Arrangement in Slow Sand Filter

more quickly on the baffled column than with previous runs. Thus in previous runs the mat was actually operating as a straining mechanism, keeping the small sand pores from clogging, during the mat's initial development.

These observations led to two conclusions. First, prior settling of the suspended solids does not aid this type of filter. Typical slow sand filter influents are low in turbidity (<10 ntu) and suspended solids (0 mg/L TSS) (Slezak, 1984). The supernatant from the settling tests were never less than 30 ntu and still high in TSS (around 400 mg/L). Therefore, sand filtration alone is not an appropriate treatment for this water. Second, a more effective means of trapping the solids prior to the slow sand column was needed, one that could remove large amounts of the fine particles that clogged the sand. Thus a coal/sand dual media filter was seen as a possible solution.

Both columns were completely cleaned out. The sand was removed, cleaned in an ultrasonic water bath, and oven dried for eventual re-use. The columns were disassembled, washed with soap and water, rinsed several times with weak nitric acid (5%) and rinsed three times with deionized water before being air dried.

Identical dual media filters were constructed as shown in Figure 22. Three deionized water washes were made in each column in the method already described. In one column, raw sample (6-2-88) was filtered and in the other column a sample previously screened with a 325 mesh screen was used. Three runs, each of approximately 750 mL volumes, were achieved with both columns. The accumulated depths of solids visible in the coal and sand columns were measured and recorded at the end of each run. The final run was completed in less than 3 hours for the screened sample and in a little over 7 hours for the raw non-screened sample. However, at the end of the third run, both columns appeared to have completely exhausted their ability to capture more solids because the mat atop the coal column was beginning to grow and solids were observed throughout the coal sections of both columns. On the basis of these observations, the decision was made to not attempt more filtration without flushing and cleaning the media.

Dual media filtration was also performed on samples taken from Marco Shipyard (6-24-88). A column was thoroughly cleaned out and fresh media was placed in the column in the manner already described. Four successive runs of approximately 750 mL each were achieved. Solids depths in the coal and sand portions of the column were recorded at the end of each run.

Dual media filtration of samples (6-2-88) dosed with alum was also performed. Two columns were completely cleaned and fresh media installed as described above. One column filtered raw sample, the other column filtered the same sample dosed with 34.5 mg/L of reagent grade alum ($Al_2(SO_4)_3 \cdot 18\ H_2O$) and 16.5 mg/L of reagent grade sodium carbonate (Na_2CO_3) that had been rapidly mixed for 2 minutes. (The choice of chemical doses is explained in the next section covering chemical treatment.) Two runs of 750 mL each were completed on the raw sample and three 750 mL runs were performed with the chemically treated sample. The reason only two runs were completed on the raw sample was that solids began building up on top of the coal column, clogging it completely, and the run had to be aborted. The second run on the raw sample was completed in less than 2 hours while the third run on the chemically treated sample was terminated after 27 hours with approximately 4 inches of water still remaining.

4.2.4 Chemical Treatment

Experimental protocol for the "jar test" procedure varied between references (Sanks, 1978; Eckenfelder, 1966). A procedure was established similar to those found in the literature that would simulate actual field conditions, i.e. where a moderate mixing speed and constant pH would be likely operational parameters. Individual samples were placed in a 1000 mL beaker that had been acid washed and thoroughly rinsed with deionized water. The solution was mixed at slow speed (70 RPM) for approximately 3 minutes on a Phipps and Bird Jar Testing apparatus (Model No. 5P36DA1A) to ensure the sample was initially well mixed. During this time, temperature and pH of the solution were recorded. A pre-weighed dose of chemicals was added and the mixing speed was increased to a maximum (100 RPM) setting for 2 minutes. At the end of the two minute rapid mix, pH was recorded and the sample was allowed to flocculate while being slow mixed (70 RPM). At the end of a 10 minute slow mix period, the mixer was turned off, the beaker set aside for settling and the pH again measured. At the end of a 15 minute settling period, supernatant was drawn off with a 50 mL pipette. Drawing off the mixture was a slow process, normally taking 10 minutes, so an average settling time of 20 minutes occurred. A final pH value was also recorded at the end of settling.

The target pH for the entire process was 7.0, but it varied between 6.8 and 7.2 at the end of settling. This pH was chosen because it is within the pH range of optimum sweep for alum treatment (see Figure 5), it coincides with the range of pH values measured in the raw samples and it requires the least amount of concomitant base dosing to adjust the pH to the optimum sweep coagulation range.

Alum doses were chosen using Figure 5 for the region most likely to given the best coagulation. Doses were also chosen just outside of the optimum range for good contrast in the effluents. For the first sequence of dosings the pH was adjusted by titrating the solution directly with 1.0 N NaOH during the rapid mix. The amount of NaOH used with each test was compared to the stoichiometric amount of (OH^-) combining with aluminum in the reaction:

$$Al_2(SO_4)3 \cdot 14.3\ H_2O + 3\ Na_2CO_3 + 3\ H_2O \text{ ------->}$$
$$2\ Al(OH)_3(s) + 3\ Na_2SO_4 + 3\ CO_2 + 14.3\ H_2O$$

For all doses, the NaOH used corresponded to the stoichiometric hydroxide requirement. This was expected since the raw samples analyzed in the characterization phase had very little alkalinity (less than 50 mg/L as $CaCO_3$, titration end point pH = 4.5).

Stoichiometric doses of sodium carbonate were calculated based on the reaction stoichiometry above. On the next sequence of jar tests, the alum dosages were similar to the previous run (slight adjustments were made to get exact correspondence to a specific log of total aluminum concentration) and the <u>initial</u> sodium carbonate dose was the stoichiometric dose. Because of the carbonate ion's ability to react with water, more than the stoichiometric amount of sodium carbonate was needed, so small increments of additional sodium carbonate were added during the two mixing phases mix to bring the pH to 7.

The alum/sodium carbonate dosing was performed on samples from a tributyltin-painted boat wash (6-2-88) and copper-painted boat wash (6-24-88). Table 7 summarizes the chemical doses used in the three jar tests performed.

To determine a suitable alum dose for filtration with a dual media filter, three considerations were involved: (1) sludge production, (2) particle size and (3) coagulation chemistry.

Sludge volumes were measured after 3 hours for each dose. These were compared with one liter of raw sample

Table 7 - Chemical Doses Used in Three Jar Tests

log [Al_T]	Alum* (mg/L)	1.0 N NaOH (mL)	Na_2CO_3(S) (mg/L)	Na_2CO_3(A) (mg/L)
-2.5	1073		503.4	803.3
	1029	8.7		
-2.75	604		283.3	485.6
	558	5.8		
-3.0	339		159.0	259.1
	311	2.5		
-3.25	191		89.6	138.5
	175	1.4		
-3.5	107	1.0	50.3	91.8
	99	0.8		
-3.75	60		28.3	46.4
-4.0	34		15.9	31.1
	21	2.8#		
-4.25	19		4.2	4.2
	11.3	2.1#		
-4.5	10.7			

* - Reagent grade aluminum sulfate ($Al_2(SO_4)_3 \cdot 18\ H_2O$)

- Represents titration with 0.1 N NaOH, all others in column are 1.0 N NaOH volumes

that was allowed to settle without chemical addition. The lowest dose, 8.6 mg/L alum was comparable to the non-dosed sample in terms of its 3-hour settling volume: each settled out 25 mL/L within that time. The next highest doses, 34.5 mg/L and 60.5 mg/L alum, produced 35 mL/L and 50 mL/L sludge respectively. This latter dose mearly doubled the volume of solids compared to the non-dosed sample. Such an increase in solids would have likely led to rapid clogging of the dual media filter. The purpose of the pre-treatment of the influent with alum was to help bring smaller particles (in the 1 - 10 micron range where granular media filtration is normally least effective) together to form larger particles and thereby increase the particles' chances of attaching to the filter media. Therefore, particle counts of the chemical treated effluent were compared with particle counts of samples from the same source (Mercer Marine, 6-2-88) through a dual media filter (Table 8).

Particle size analysis showed that a significant transition occured above the 35 mg/L alum dose in the coagulation of small particles. While the lower chemical dose of 10.7 mg/L (log $[Al_T]$ = -4.5) appeared slightly more effective in coagulating the 1 - 10 micron particles, it was judged that such a small dose might place the solution at risk of ending up in the poor-coagulation restabilization zone , where mixing is critical to achieve good coagulation (Figure 5). Thus a dose of 34.5 mg/L alum was used in conjunction with the dual media filtration process previously discussed.

Table 8 - Comparison of Particle Counts of Dual Media Filter (DMF) and Chemical (CH) Treatment Effluents

Sample*	Treatment	1 - 5 micron	5 - 10 micron
C	DMF Run #1	5,715	24,848
	DMF Run #2	2,105	5,394
	DMF Run #3	2,829	6,619
D	DMF Run #1	7,178	22,852
	DMF Run #2	2,521	6,384
	DMF Run #3	2,872	7,819
A	CH 60.5 mg/L	199,677	98,538
	CH 34.5 mg/L	2,627	5,331
	CH 10.7 mg/L	1,251	2,260

* - All samples are from the same boat washing, 6-2-88 Each sample varies somewhat in terms of total suspended solids, but are essentially similar in composition

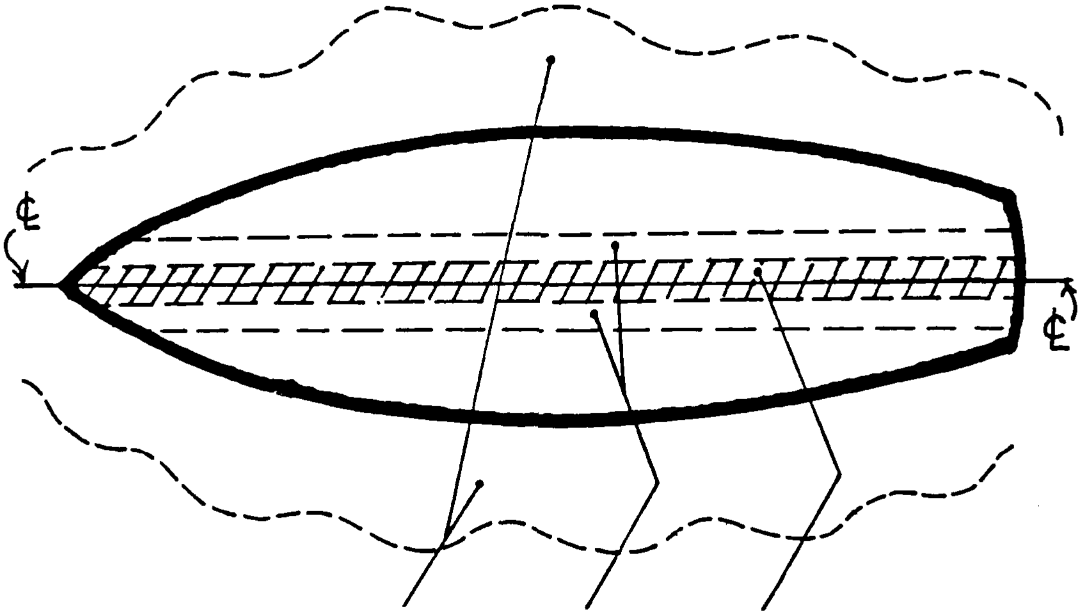
CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characterization of Hydroblast Wastewater

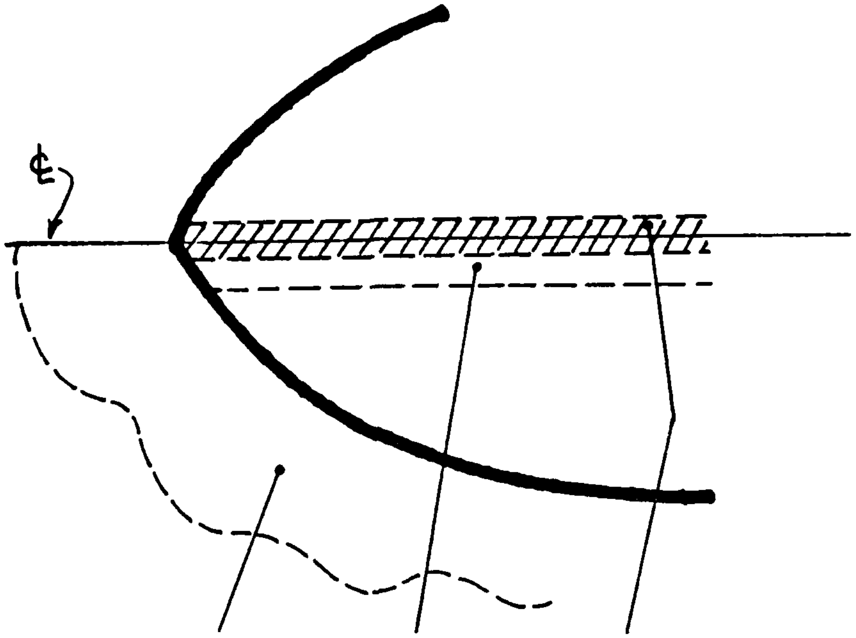
Two consistently distinct types of hydroblast wastewaters were sampled and analyzed: hull washings of fiberglass-hull boats coated with organotin anti-foulant paints and hull washings of steel-hull boats coated with copper anti-foulant paints. For the purposes of the following discussion, these two wastewaters will be designated by their origins which are recreational boats and commercial ships (on the graphs, "RCR" and "CML", respectively). This designation does not imply that all recreational boats are fiberglass-hull/organotin-paint or that all commercial ships are steel-hull/copper-paint combinations, because other hull material and paint combinations exist, rather it is used to simplify the discussion.

Figures 24(a) and 24(b) summarize hydroblast water characteristics from recreational boats and commercial boats, respectively. Variations in water characteristics within the sampling zones were significant in some cases, but not so in others. A discussion of key water quality parameters follows.



Sample Area	SPRAY	DRIP	FALL	WASHWATER
No. of Samples	3	2	3	1
% Vol of Total	9-16%	38-45%	43-86%	n/a
pH	6.1-6.5	6.4	6.3-6.6	6.5
Alkalinity (as mg $CaCO_3$/L)	25-37	24-41	27-43	n/a
Temperature (°C)	14-20	14-20	14-20	14
TSS (mg/L)	650-810	800-1690	570-1240	0
VSS (mg/L)	380-440	320- 810	290- 690	0
VSS/TSS	0.47-0.67	0.4-0.48	0.4- 0.8	n/a
Settled Solids (mL/L)	12- 75	18- 62	13- 50	n/a
Particles (no./L)				
1-5 micron	3-4 E8	3-4 E8	4-5 E8	n/a
5-40 micron	1-5 E8	4-6 E8	2-6 E8	n/a
40+ micron	3-24 E6	3-17 E6	2-25 E6	n/a
Total COD (mg/L)	430-608	104-608	530-698	36
Soluble COD	20- 36	25	10- 54	25
Turbidity (ntu)	38-55	40-48	45-58	2.2

Figure 24(a) - Hydroblast Water Characteristics: Recreational Boats



Sample Area	SPRAY	DRIP	FALL	WASHWATER
No. of Samples	2	1	3	2
% Vol of Total	2-9%	45%	45-94%	n/a
pH	6.3-6.4	6.2	6.2-6.4	6.5
Alkalinity (as mg $CaCO_3$/L)	17-53	43	18-47	14
Temperature (°C)	20	14-20	14-20	14
TSS (mg/L)	195-1500	975	350-1670	0
VSS (mg/L)	80- 850	690	20- 630	0
VSS/TSS	0.41-0.43	0.7	0.06- 0.43	
Settled Solids (mL/L)	1- 30	9.5	0.7- 14	n/a
Particles (no./L)				
1-5 micron	3-7 E8	2 E8	1-4 E8	n/a
5-40 micron	2-4 E8	4 E8	1-5 E8	n/a
40+ micron	1-2 E6	2 E6	1-8 E6	n/a
Total COD (mg/L)	160-1200	312	148-2520	4-48
Soluble COD	52- 104	48	68- 180	n/a
Turbidity (ntu)	75	no data	52-1000+	3.5

Figure 24(b) - Hydroblast Water Characteristics: Commercial Ships

5.1.1 Temperature, Turbidity, pH and Alkalinity

Hydroblast water temperatures at both shipyards and the marina were measured (upon completion of the washing) between 14 and 20° C. Normally, 14 - 16° C temperatures were observed. When the washwater was heated or had been exposed to warm ambient temperatures for a significant time, the water temperatures were higher.

Turbidity of raw samples was usually lower in the recreational boat waters than in the commercial ships. Turbidity appeared to be a function of the particle size distribution. Waters with more large particles actually had lower turbidities because the smaller particles tended to attach themselves to the larger particles and allow more light to pass through the sample. One commercial ship washwater (4-11-88) had a turbidity that was above 1000. This particular sample had mostly fine particles (< 40 micron) that were well dispersed in solution and blocked light completely.

When measuring pH for the samples, the solution was always well mixed. Thus the pH values reported were the apparent pH values, because the suspended solids may have effected the pH electrode's resistivity measurement and may not have been strictly measuring the hydrogen ion concentration. Whether samples were taken from the shipyard or marina, pH was in the same range of 6.1 to 6.6. However, it is noteworthy to report that the samples used in the treatability phase of this study had slightly higher pH readings, between 6.8 and 7.4. Constant re-calibration of the pH meter and repeated readings confirmed these measurments were accurate.

Alkalinity measurements were very low (< 50 mg/L as $CaCO_3$ to a titration endpoint of pH 4.5) for all the washwaters, regardless of their source. Although saltwater is naturally high in alkalinity, it appeared that the hydroblasting diluted whatever residual saltwater that may have been left, since alkalinity was no higher in the washings from boats that had been in seawater than those that had been in freshwater.

5.1.2 Total and Volatile Suspended Solids

Figure 25(a) shows total suspended solids (TSS) concentrations found in the six samples from the characterization study. Figure 25(b) shows volatile suspended solids (VSS) for the same samples. TSS in the three sampling zones from one of the recreational boats (5-3-88) varied as much as 1000 mg/L. Most samples,

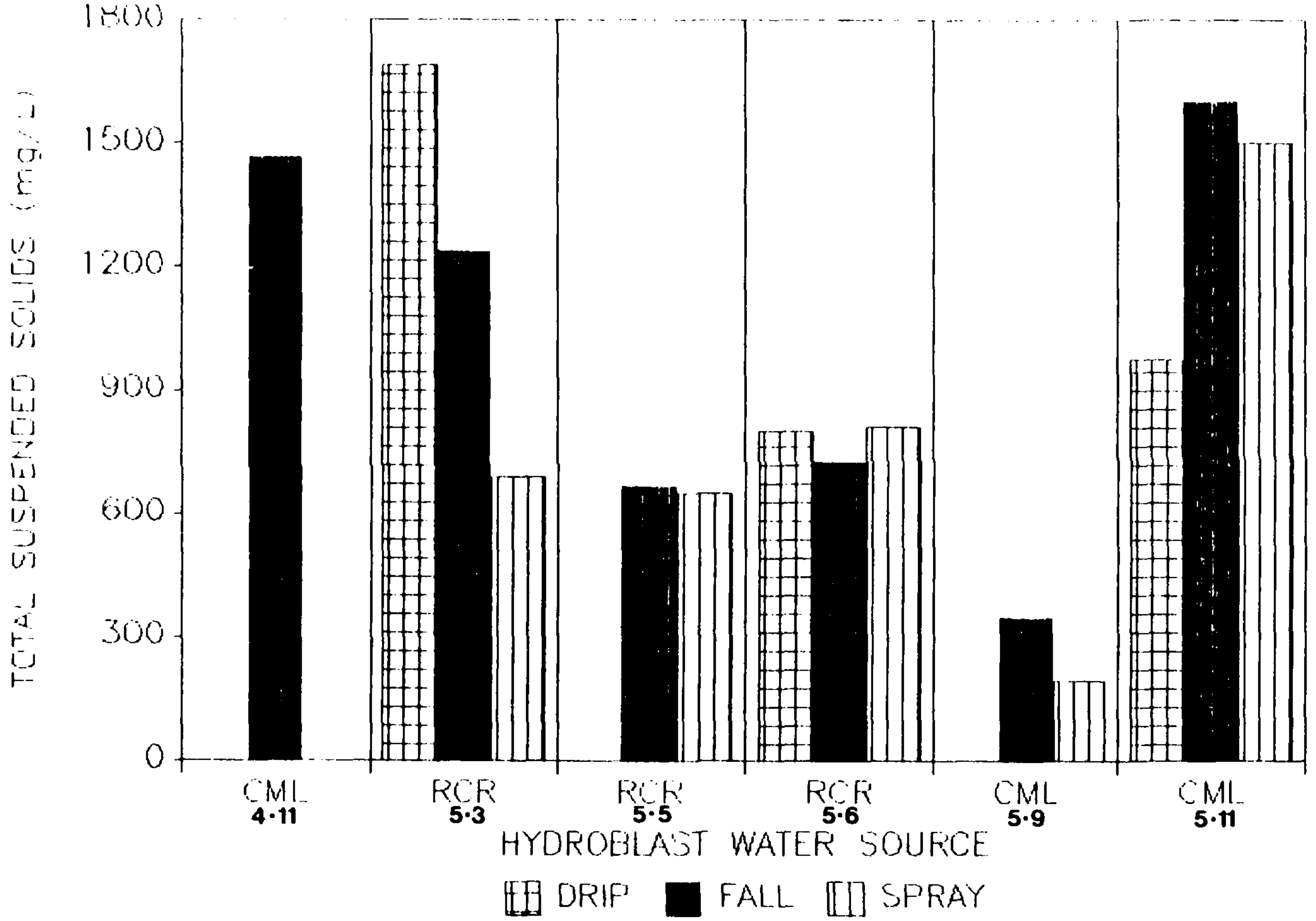


Figure 25(a) - Hydroblast Water Samples- Total Suspended Solids

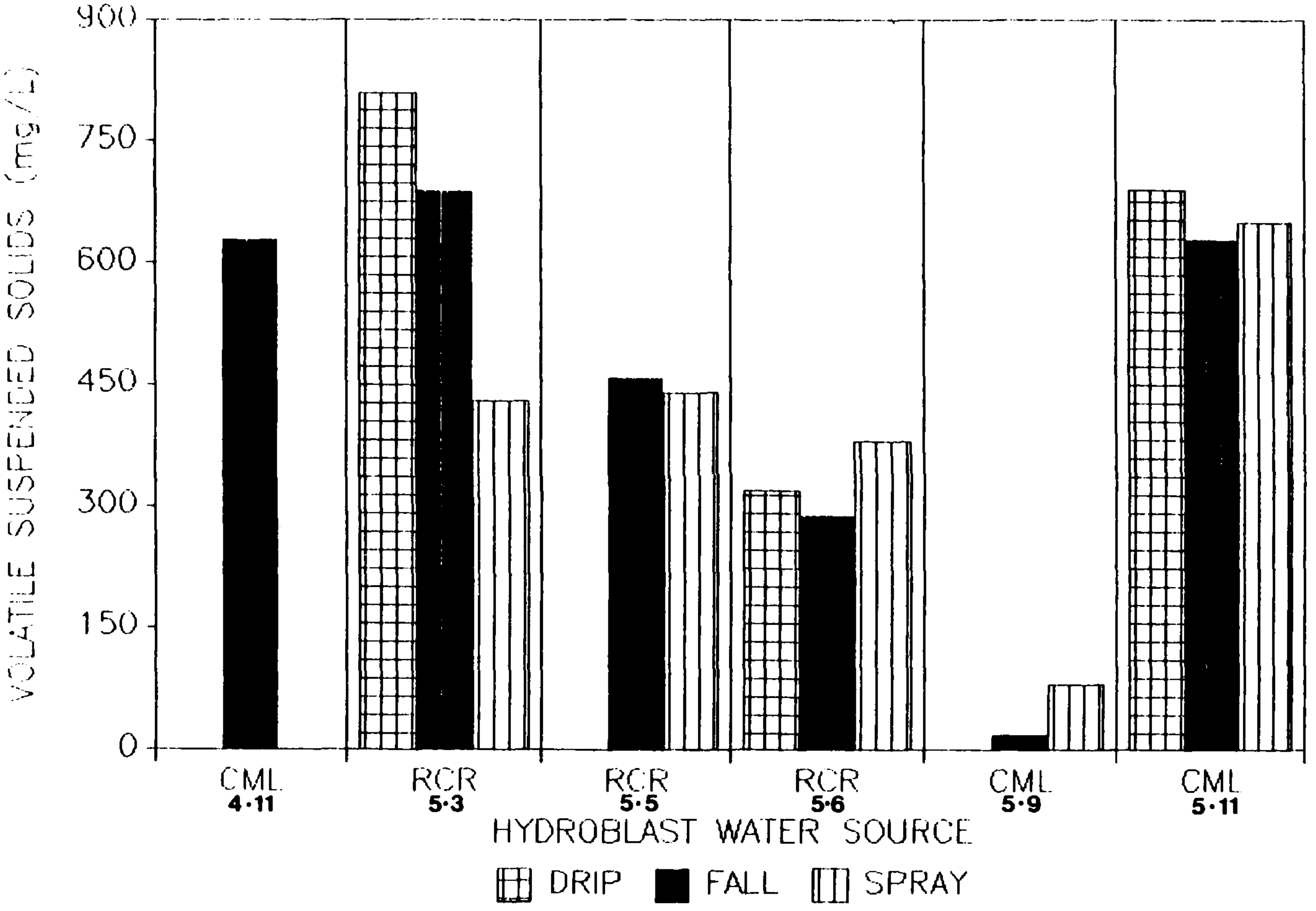


Figure 25(b) - Hydroblast Water Samples- Volatile Suspended Solids however, had comparable TSS concentrations within all the sampling zones, even the spray zone, where it was originally anticipated the water would be more dilute. Even better agreement was found between sample zones for VSS.

Generally, TSS was higher in the commercial ship hydroblast water (> 1400 mg/L in the fall zones of two of the three samples). The diluted sample of 5-9-88 was not characteristic of washings from the large ships. In the recreational boat hull washings, two of the three samples had only about 600 mg/L TSS, while the one boat that was heavily covered with some type of worm-like organism had TSS concentrations comparable to the commercial ships' wash water. Therefore, while the trend indicated higher TSS in the large boat washings, a wide range was possible for both types of washwater.

TSS consisted of between 6 and 80 percent VSS but averaged 50 percent for all samples. No significant overall differences were noted between the commercial and recreational vessels in this regard.

5.1.3 Total and Soluble Chemical Oxygen Demand

Figures 26(a) and 26(b) summarize total and soluble chemical oxygen demand (COD and SCOD) measured for the characterization samples.

The lowest COD was measured in a commercial ship washing. This sample was quite dilute due to the hydroblasting method (refer to Figures 12(b) and 12(c)) and minimal growth on the ship hull. Nonetheless, it appeared that COD in washwater from commercial boats was generally higher than recreational boats. Later hydroblast samples taken for the treatability phase of the study supported this conclusion: the recreational boat samples from 6-2-88 had an average COD of 1,320 mg/L compared to a COD of 2,070 for a sample taken from a commercial vessel on 6-24-88. However, as it was with TSS, a wide range of COD values were certainly possible with both types of boat washings.

Figure 26(b) indicates that SCOD was quite low for all samples. Higher values were found in the commercial ship washings (even the very dilute sample) than in the recreational boat washings. Except for one commercial boat sample (where SCOD was measured as 180 mg/L) SCOD for the wash water was near COD levels in the raw

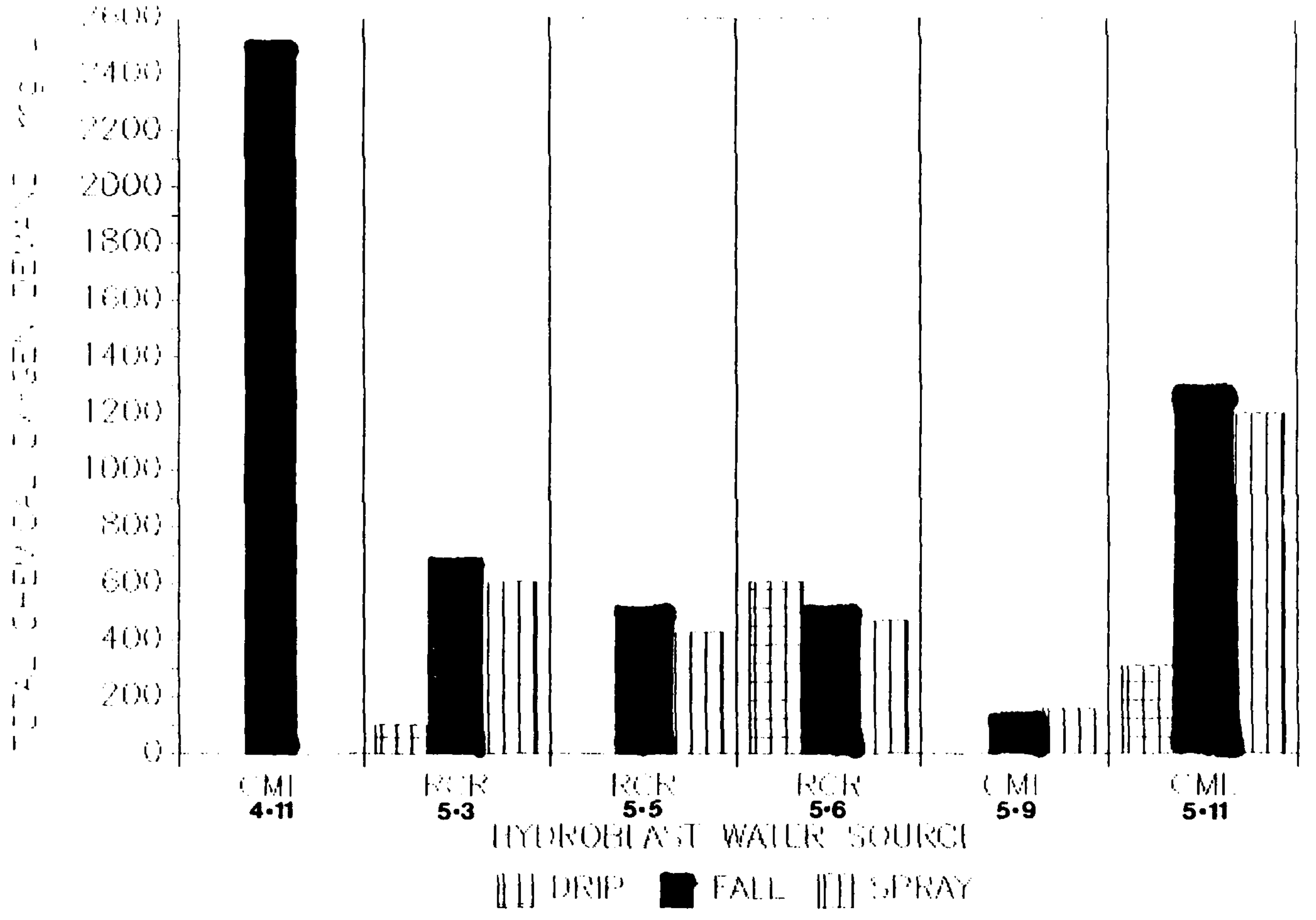


Figure 26(a) - Hydroblast Water Samples- Total Chemical Oxygen Demand

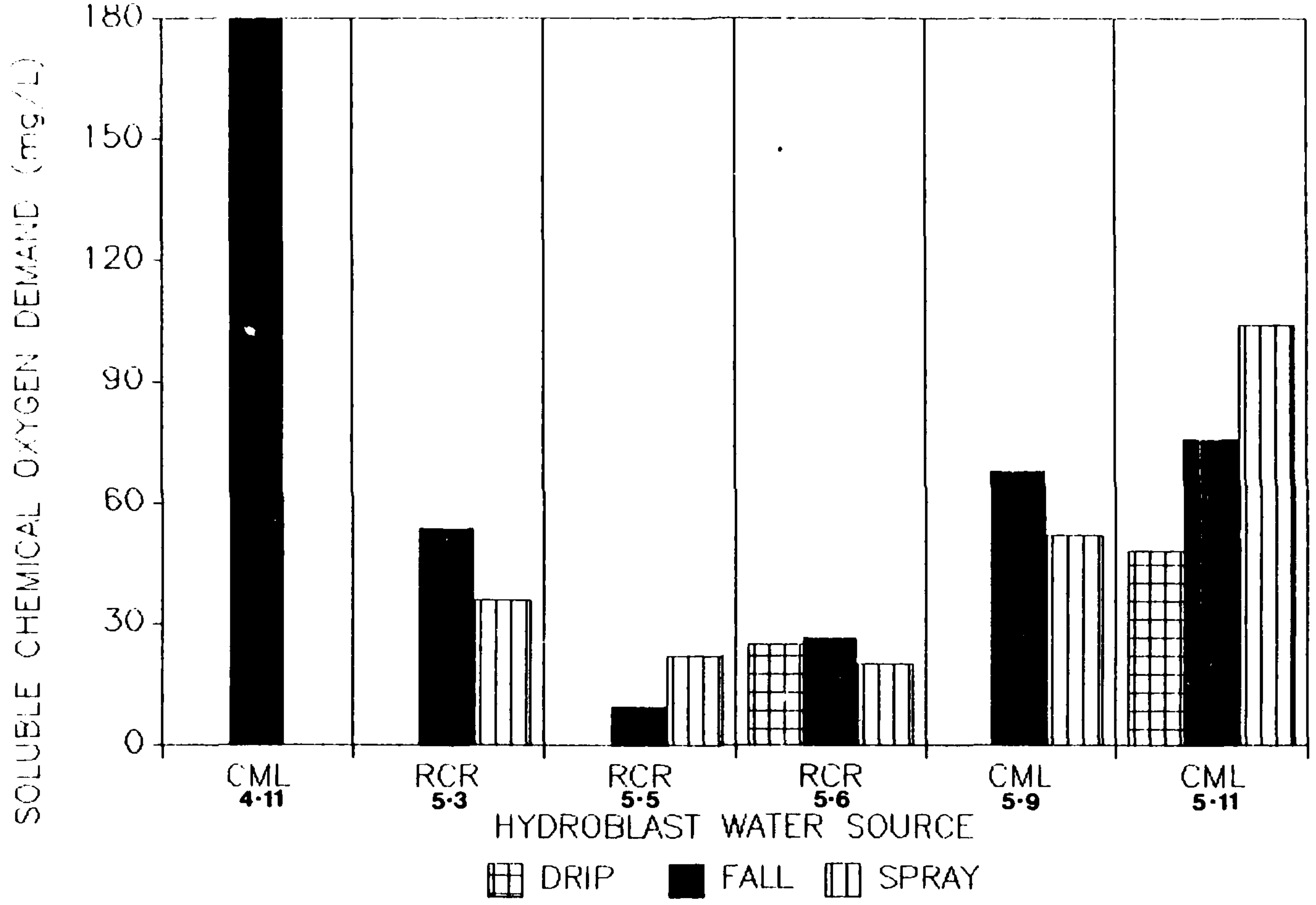


Figure 26(b) - Hydroblast Water Samples- Soluble Chemical Oxygen Demand washwater. SCOD was generally 5% or less of the total COD and in many cases was only 1% or less of the total COD. This observation supported the original hypothesis that little dissolved matter was present in the water. Furthermore, it suggested that tributyltin, if present, was unlikely to be in the soluble phase to a significant extent because of tributytin's high octanol-water partition coefficient and the presence of high TSS.

5.1.4 Particle Size Distribution

Table 9 gives particle counts for the samples analyzed in the characterization study. In the first three size ranges, average particle counts for the commercial ship samples are comparable to those of the recreational boat samples. However, in the three size ranges above 40 microns, the particle count averages for the recreational boat samples are 2 to 3 times those found in the commercial boat water. A similar trend was observed in hydroblast samples taken for the treatability phase: two samples with similar TSS (about 820 mg/L) had 1 - 40 micron particle counts that did not differ by more than 14 percent for any size range.

Table 9 - Particle Counts for Characterization Samples

Sample Zone/ Date	1-5 u	5-10 u	10-40 u	40-70 u	70-100 u	100+ u
	<------------No. Particles in 40 mL------------>					
[Commercial Ships]						
Fall/ 4-11	4.2 E6	6.6 E6	1.4 E7	3.0 E5	1.1 E4	3.0 E2
Fall/ 5-9	8.3 E6	8.8 E5	8.7 E5	4.8 E4	2.1 E3	1.0 E2
Spray/ 5-9	3.1 E7	8.9 E6	2.0 E6	2.1 E4	9.0 E2	0
Drip/ 5-11	1.7 E7	1.1 E7	9.8 E6	1.2 E5	1.0 E4	1.1 E3
Fall/ 5-11	9.2 E6	1.0 E7	1.2 E7	1.9 E5	1.7 E4	2.2 E3
Spray/ 5-11	1.1 E7	1.3 E7	1.1 E7	1.4 E5	1.4 E4	2.9 E3
[Recreational Boats]						
Drip/ 5-3	1.3 E7	1.0 E7	1.6 E7	2.9 E5	2.3 E4	2.4 E3
Fall/ 5-3	1.4 E7	1.0 E7	1.3 E7	3.1 E5	2.8 E4	3.4 E3
Spray 5-3	1.3 E7	6.3 E6	9.8 E6	3.3 E5	3.4 E4	5.3 E3
Fall/ 5-5	1.1 E7	1.5 E6	2.5 E6	5.5 E5	6.6 E4	5.7 E3
Spray 5-5	1.7 E7	3.3 E6	4.8 E6	1.5 E5	1.0 E4	1.3 E3
Drip/ 5-6	1.5 E7	6.9 E6	8.6 E6	1.4 E5	1.2 E4	1.8 E3
Fall/ 5-6	1.8 E7	8.4 E6	9.3 E6	9.0 E4	6.6 E4	4.0 E2
Spray 5-6	1.2 E7	4.2 E6	8.3 E6	1.5 E5	9.0 E3	1.0 E3

Above 40 microns the recreational boat sample had particles counts that were 2.7x (40 - 70 microns), 8.3x (70 - 100 microns), and 6.5x (100+ microns) those of the commercial boat sample. Looking at these two particular waters under the microscope (Figures 19(a) and 19(b)) provided an explanation for this difference. Larger paint chips and algae flocs were found in the recreational boat water than in the commercial boat water. This trend also indicated two other possibilities. First, because a higher percentage of particles in a water with comparable TSS fall in the size range that is easily strained or settled out, the recreational boat water would be more amenable to screening and sedimentation than the commercial ship washings. However, because the commercial ship washwater has fewer particles but the same TSS, the average particle in this water were more dense, making them likely to settle out as well.

5.1.5 Metals

Table 10 summarizes the analysis for total metals in the samples using the ICP. In terms of metal content, distinct differences were discovered between the recreational boat and the commercial ship washings.

Six metals were regularly found in concentrations greater than 1 mg/L in both types of washwaters. These six metals were aluminum, copper, iron, manganese, lead and zinc. The commercial ship washwater had

Table 10 - Total Metal Concentrations in Hydroblast Wastewater

COMMERCIAL SHIPS

(all concentrations in mg/L)

Metal	Spray Zone		Drip Zone		Fall Zone		Washwater	
	Low	High	Low	High	Low	High	Low	High
Al	2.1	20.0		13.3	2.1	16.7		0.38
Ba	0.22	0.23		0.04	0	0.24	0	
Cd	0.01	0.55		0.18	0.002	0.08		0.002
Cr	0.05	0.19		0.14	0.05	0.31		0.001
Cu	5.6	62.2		50.2	8.1	139.8		0.09
Fe	30.4	123.8		117.4	27.0	187.0		0.31
Mn	0.19	1.05		12.8	0.85	1.36		0.007
Ni	0.03	0.37		0.87	0.03	0.44		0.05
Pb	0.24	1.27		0.31	0.27	1.26	0	
Sn	0			0.25	0	1.0	0	
V	0.008	0.08		0.08	0.01	0.14	0	
Zn	2.6	84.8		26.2	3.3	26.8		0.06

Table 10 - (Continued from Previous Page)
Total Metals Concentrations in Hydroblast Wastewater

RECREATIONAL BOATS

(all concentrations in mg/L)

Metal	Spray Zone		Drip Zone		Fall Zone		Washwater	
	Low	High	Low	High	Low	High	Low	High
Al	8.0	20.0	14.1	39.6	9.5	26.9		0.03
Ba	0.12	0.42	0.35	0.39	0.04	0.34		0.003
Cd	0.01	0.02	0.01	0.02	0.001	0.01		0.001
Cr	0.05	0.17	0.06	0.13	0.05	0.24		0.001
Cu	2.1	4.5	4.6	6.6	0.4	6.4		0.005
Fe	9.8	36.9	19.3	43.8	10.6	39.4		0.06
Mn	3.2	30.9	22.2	28.0	1.8	25.8		0.006
Ni	0.02	0.05	0.04	0.11	0.03	0.06	0	
Pb	0.66	20.6	0.9	12.1	0.9	13.4	0	
Sn	0	1.0	0	1.0	0	1.25	0	
V	0.02	0.11	0.05	0.11	0.02	0.1		0.002
Zn	1.6	7.2	3.8	6.0	0.9	5.3		0.021

preponderate quantities of copper, iron and zinc. This indicated that the suspended solids contained hull paint, because these ships were coated with paint mixtures having oxides of all three of these metals.

Water from recreational boats had high quantities of manganese and generally had significantly higher amounts of lead and aluminum than the commercial boat washwaters. Lead is a known component of the organotin paints used at Mercer Marine. However, manganese was found in the TBT-painted hull washings in quantities far exceeding all other metal constituents in these paints. In both studies of drydock discharges by the EPA (1979b) and U.S. Navy (Saam et al, 1977), manganese was reported in concentrations of 1 mg/L or less, comparable to levels found in the washwaters from commercial ships in this study. Manganese is a common constituent in lead drying salt formulations (James, 1975) and manganese linoleate and manganese octoate are known paint driers used in industrial paints (Phillips, 1976). Although manganese was not listed on the material safety data sheets (Appendix 1(a) - 1(e)) for the paints used at either the marina or shipyards, it appeared to be an anti-foulant paint component. The use of manganese in the organotin paints in particular appeared likely.

Copper and iron also appeared in significant quantities in the recreational boat washings. Once again, neither metal was listed as a constituent in the particular TBT paints recently used at the marina. However, these metals could have been residual from prior use of copper based paints, because copper anti-foulant paints were sold and used in minor amounts at the marina. Also, there are organotin paints which contain cuprous oxide (USEPA, 1979b) which may have been applied to these boat hulls at one time.

The other six metals, barium, chromium, cadmium, nickel tin and vanadium were found in concentrations well under 1 mg/L, although in a few instances tin reached or exceeded 1 mg/L.

Tin was detected in only two of the six washings used for the characterization phase. Both waters had high TSS and high COD, suggesting the presence of organotin species which would likely be associated with organic solids. However, this sporadic appearance may also be a function of the graphite furnace AA detection limit that was achieved (0.1 mg/L) as well as sample dilution necessary to prepare it for analysis. Tin was present in the non-organotin painted hull washes as well as the washings from the known TBT-painted hulls. This pattern later repeated itself in the samples taken for the treatability study, where tin was actually found in equal concentrations, 0.25 mg/L, in both types of washwaters. Tin was found in concentrations that were far less than a companion metal constituent in TBT paint: lead. In the original paint mixture, Sn/Pb ratios were in the range of 0.8 to 5.8, while the washwater from a TBT-painted hull had Sn/Pb ratios between 0.05 to 0.09. This clearly indicated that tin leached from the paint much faster than the lead and strongly suggested that organotin had leached from the paint in significant quantities.

Chromium was listed in the material safety data sheet for the TBT paint used at Mercer Marine in concentrations equal to the lead constituent (most likely a drying agent). Yet chromium was found in concentrations that are 10 to 100 times less than total lead detected in waters from the TBT-painted hulls. This echoed the findings of the Navy study (Saam et al, 1977) that found high zinc concentrations but low amounts of chromium in residual paint chips whose original formulation included zinc chromate, $ZnCrO_4$. Thus, like tin, chromium was leached from the paint at a higher rate than other metals.

The trace metals barium, cadmium, nickel and vanadium were not found in quantities exceeding 0.5 mg/L, except for a single commercial ship washing that had 0.87 mg/L of nickel. The recreational boat washes were higher in barium and vanadium, while the commercial ship samples had higher cadmium and nickel.

In the recreational boat washings, soluble metals were measured in concentrations that were normally within an order of magnitude of the metal levels in the raw washwater, which themselves were near the ICP detection limits. However, certain soluble metal concentrations were quite high in several of the commercial boat samples. Figures 27(a) through 27(d) show soluble metal concentrations found in all samples for copper, iron, manganese and zinc.

Soluble copper was over 4 mg/L in one washing and soluble zinc exceeded 1 mg/L in all commercial ship washings and was as high as 11 mg/L in one sample. It was clear from these results that the commercial ship washings were more inclined to have high soluble metal concentrations. One cause of high metal solubility would have been low pH, but the washings from both the marina and shipyards were near neutral pH.

Saam et al (1977) summarized chemical equilibria for the copper, iron and zinc hydroxides and oxides in freshwater and various concentrations of seawater where chloride was assumed to be the only negatively charged ion in solution other than hydroxide (Appendix 2(a) -

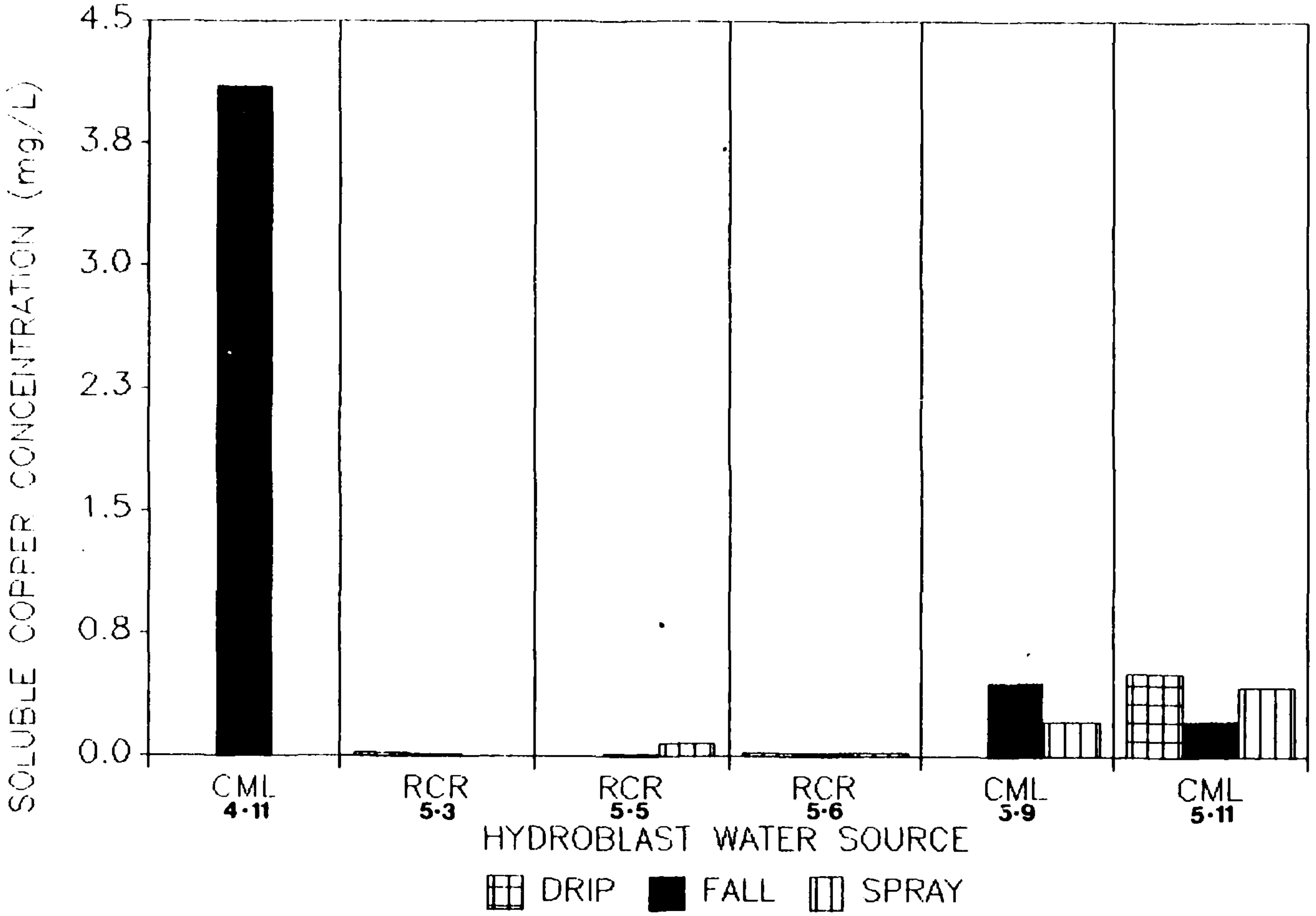


Figure 27(a) - Hydroblast Water Samples- Soluble Copper

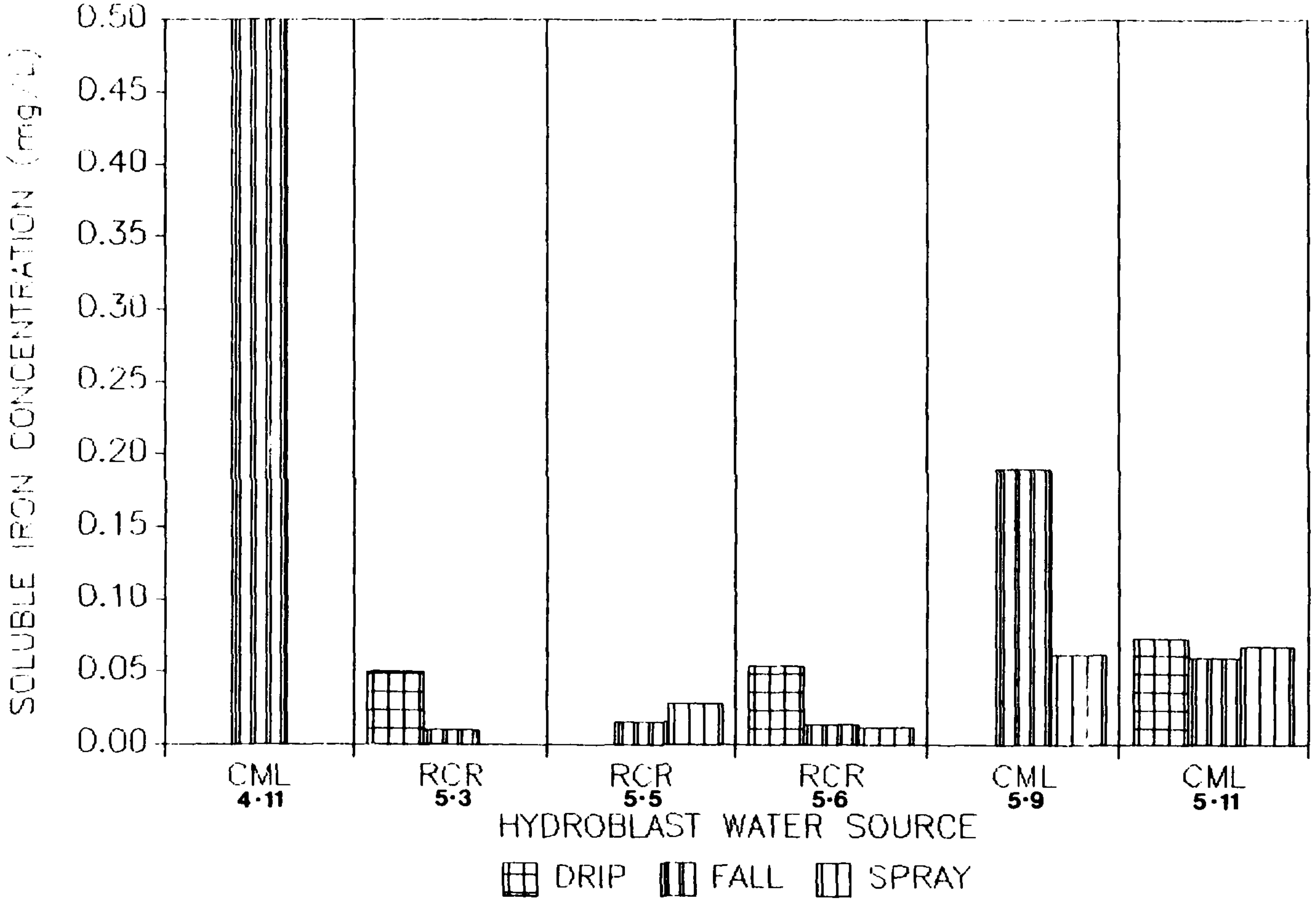


Figure 27(b) - Hydroblast Water Samples- Soluble Iron

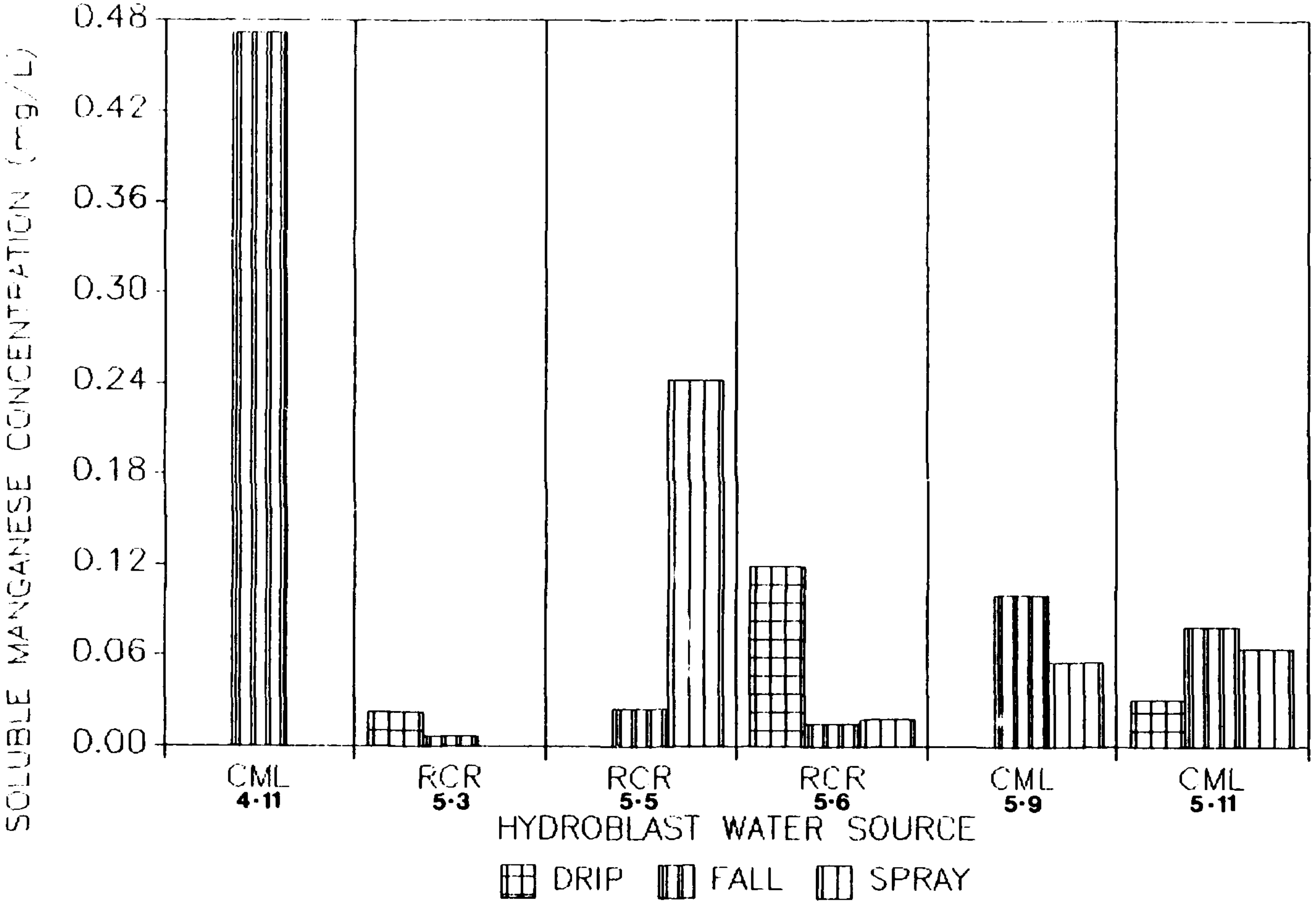


Figure 27(c) - Hydroblast Water Samples- Soluble Manganese

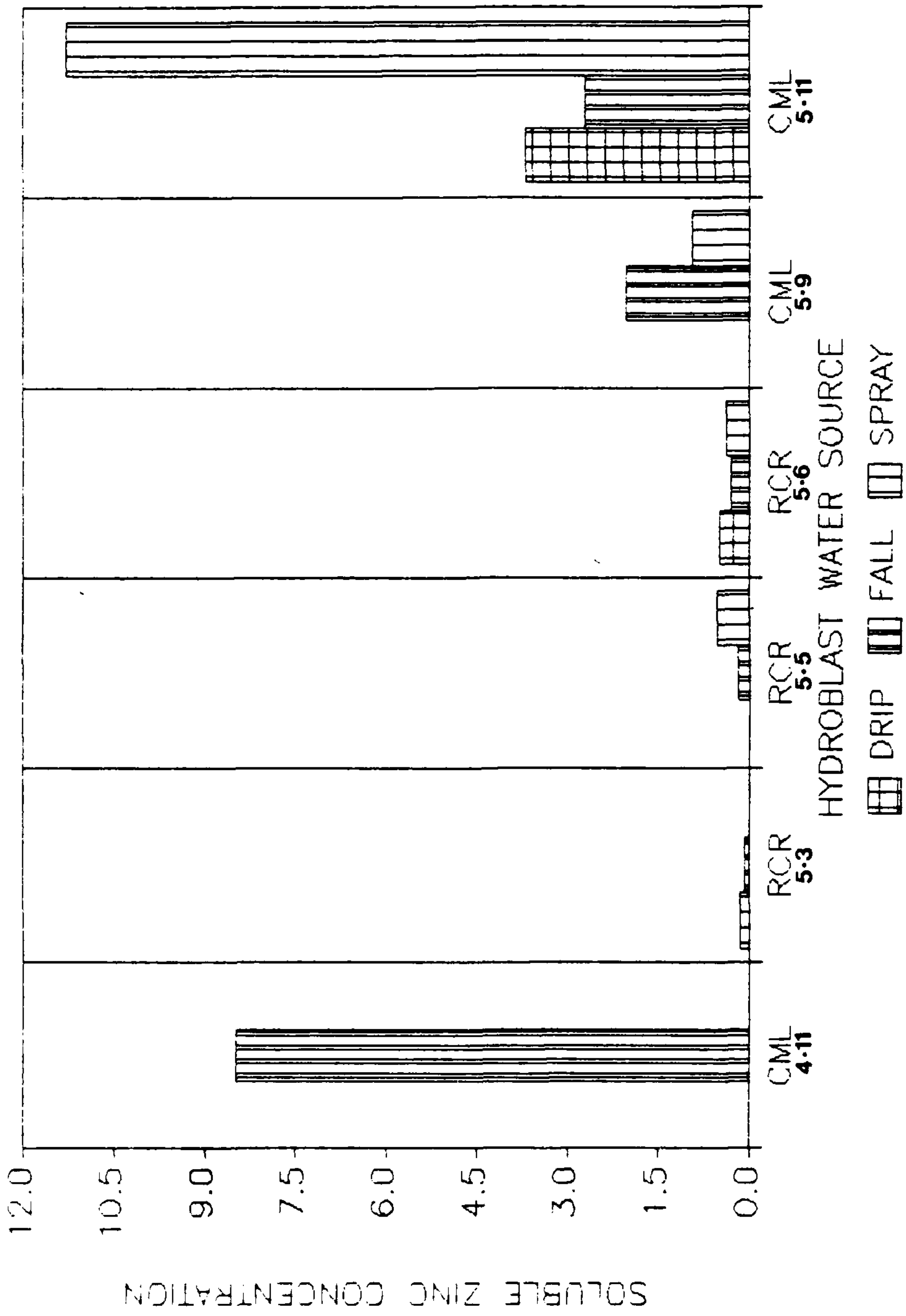


Figure 27(d) - Hydroblast Water Samples- Soluble Zinc

2(c)). These equilibria diagrams show $Cu(OH)_2$ solubility increases significantly in seawater; a slightly smaller increase is indicated for $Zn(OH)_2$ solubility and an even less marked increase with $Fe(OH)_2$ in seawater.

Because all of the commercial ships had spent considerable time (up to 2 years) in saltwater immediately prior to returning for drydocking, it appeared that soluble metals may have been a product of chemical equilibrium with a negatively charged species, such as chlorine, which was a residue of the seawater in the commercial boats had traveled. Snoeyink and Jenkins (1980) point out that large concentrations of chloride ions are present in seawater (0.56 M Cl^-), but even much smaller concentrations of chloride ion (0.001 M Cl^-) can have significant effects on the solubilities of metal hydroxides.

Yet another explanation for the presence of soluble metals would be the presence of a reduced environment near the hull surface due to anaerobic biological activity. Algae growth on the larger ships appeared to be in various stages of decay on the lower hull surfaces (where sunlight could not reach). Nonethless, the exact cause of the metal solubilization remains unclear.

Appendix 3(a) - 3(f) contains results of ICP analysis for total copper, iron, manganese, lead , tin, and zinc in the six samples used in the characterization study. Good agreement was generally seen between all three of the sampling zones. It was concluded, then, that settled solids compositions from any of the three sampling zones were reasonably representative of the overall settled solids. Figures 28(a) and 28(b) show metal compositions of solids from the 30 minute settling tests from the fall zone of each sampling.

Iron and copper contributed significantly to the total mass of solids from the commercial boat washings. In two samples, iron represented over 14% of the dry solids weight.

The most striking observation from these results, however, was the percentage of tin in the dry solids. Suspended solids from two of the three commercial boats were actually higher in tin on a dry weight basis than any of the recreational boat samples. Pinpointing the exact source of the tin was not possible due to the limited scope of this study, but it appeared most likely that the commercial boats were picking up residual tin from organotin paints. As already discussed in Chapter 2, naturally occuring levels of tin are low, because tin

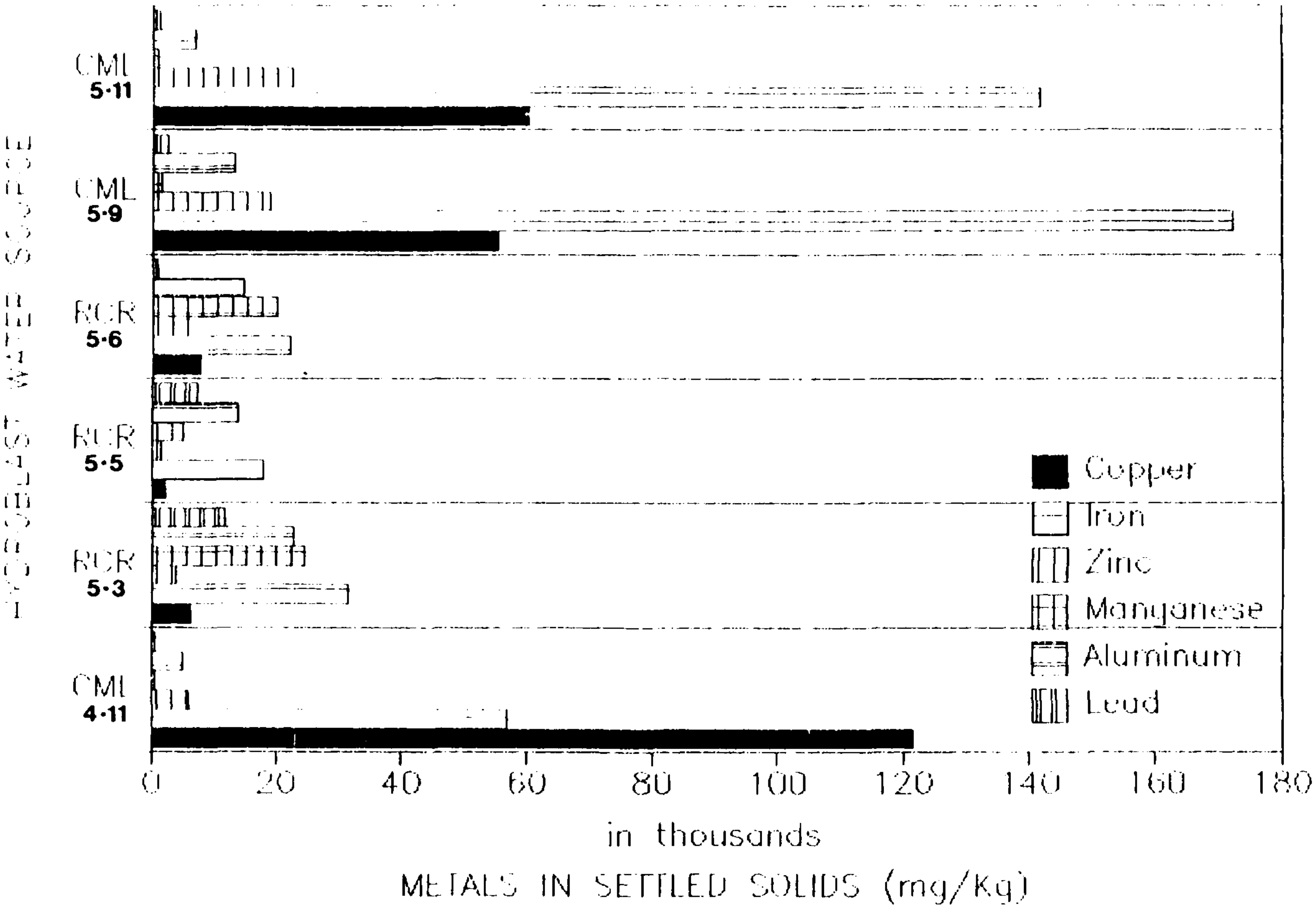


Figure 28(a) - Hydroblast Water Samples- Major Metals in Settled Solids

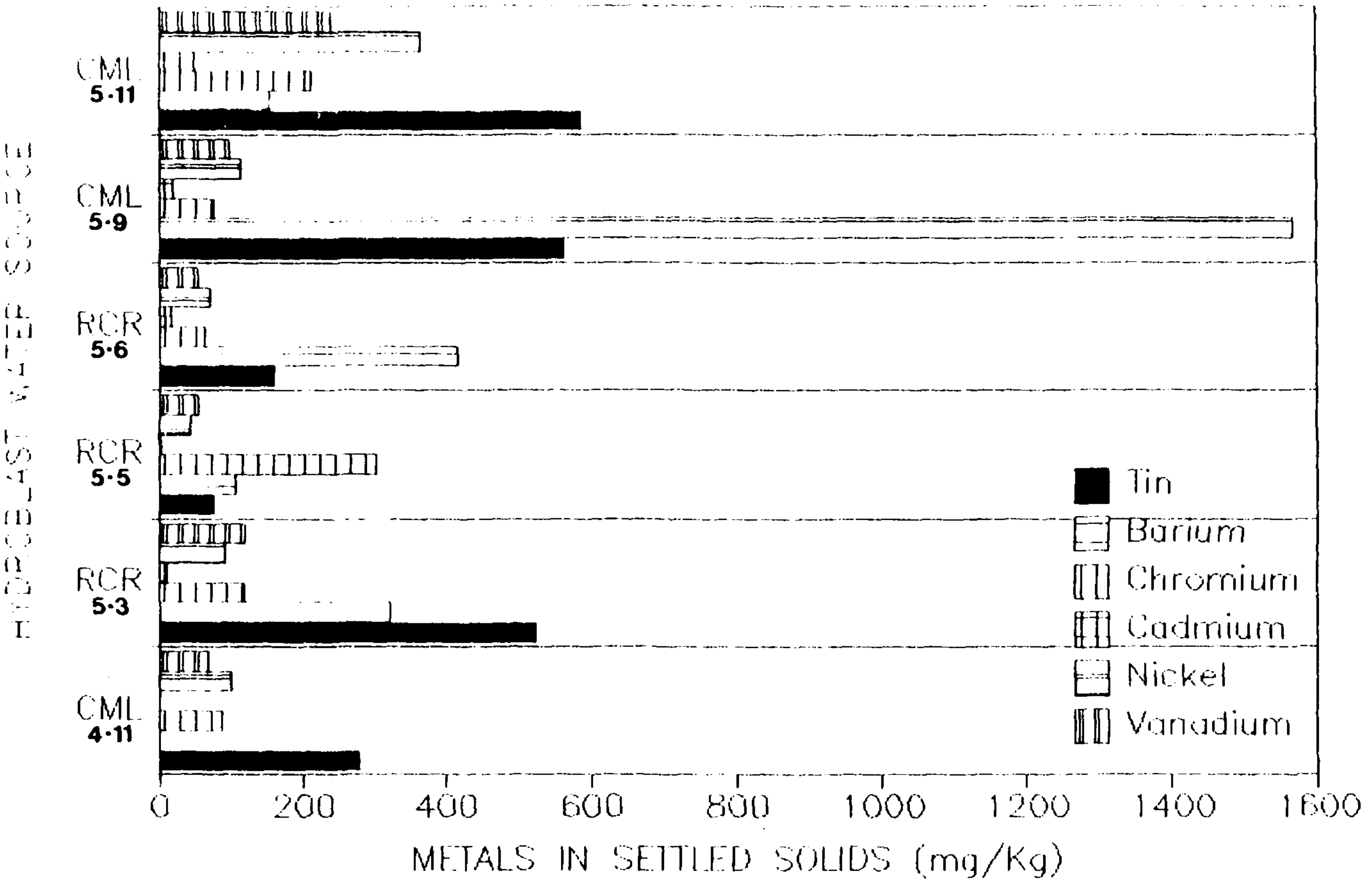


Figure 28(b) - Hydroblast Water Samples- Trace Metals in Settled Solids oxides and hydroxides have very low solubility. In water with pH between 6 and 7, SnO and $Sn(OH)_2$ solubilities are between 10^{-2} and 10^{-3} mg/L (Saam et al, 1977). Therefore, the opportunity for picking up this metal from the surrounding waters seemed highly unlikely. Rather, it was more probable that previous hull paintings with TBT paints left residual tin on the hull.

5.1.6 Tributyltin

The single analysis of a raw sample from a recreational boat washing found a TBT concentration of 75.2 ug/L (30.8 ug/L as Sn) of total TBT. The filtered sample contained 52.6 ug/L of TBT (21.6 ug/L as Sn). The raw sample had a total tin concentration of 250 ug/L. Appendix 4(a) and 4(c) contain the chromatographs for the raw and filtered samples.

The analytical method was limited to detection of TBT in the aqueous phase. Other tin species were apparent in the raw sample. The chromatograph (Appendix 4(a)) showed numerous peaks around the TBT peak, but these were not identified by species. These other peaks were likely to have represented degradation products of the tributyltin. However, they may have also been a product of the analytical method's inability to completely extract the TBT from the solid phase. Extraction and derivitization of TBT from the solid phase is a very involved procedure. Maguire (1984) developed such a procedure requiring double refluxing and extraction of the TBT to make a butyl-pentyltin derivative for analysis using gas chromatography with a flame photometric detector.

The inability to completely extract the TBT from the solids phase appears likely for two other reasons. (1) At 250 ug/L, total tin is an order of magnitude greater than TBT-tin. (2) TBT has a Kow of about 2650, indicating a strong tendency to sorb to solid organic matter. High total suspended solids (848 mg/L) as well as high COD (870 mg/L) indicated a significant amount of organic matter was present in this sample, yet the analysis showed over 72 percent of the TBT was in soluble form. Assuming all of the tin in the sample was TBT (highly unlikely, since some degradation was apparent), the soluble TBT would represent only 8.5 percent of the total TBT.

Therefore, TBT is quite likely to be present in similar hull washings from fiberglass-hull recreational boats operated in freshwater and painted with TBT anti-foulant paints within the past one or two years. This work did not establish presence of TBT in hull washings from commercial ships that have been operated and maintained in a much different fashion than the recreational craft. However, the high levels of tin in the settled solids from commercial ship washings (as much as 600 mg/kg, Figure 28(b)) has clearly established the presence of tin species in these waters. Further investigation into the quantities, speciation and partitioning of the tin species found in both recreational and commercial hull washings is still needed.

5.1.7 Quantifying Discharge Parameters

With few exceptions, water quality parameters were essentially the same within the sampling zones for a given sample. Yet between individual samples, wide variations were observed for suspended solids, chemical oxygen demand and metals. To quantify the drydock and marina discharges based upon just 3-4 samples would be difficult, therefore a range of possible quantities was calculated based upon the lower and upper ranges observed for each parameter (Figures 24(a) and 24(b) and Table 10). Water volumes generated were estimated based on a measured flow rate and an average wash time taken from sampling information on the eight washings observed (six from characterization phase, two from the treatability phase). Based on information provided by the maintenance scheduling personnel at Marco Shipyard and Mercer Marine, an estimate of annual discharges was also made. Tables 11(a) and 11(b) provide estimated hydroblast waste generation from a shipyard and marina, respectively.

From Tables 11(a)and 11(b), an active medium size commercial shipyard has the capacity to discharge between 3.5 to 400 times the quantity of solids in its hydroblast wastewater than does a large recreational marina in a year's time. Based on volatile suspended solids measurements, the majority of the solids are likely to be algae and, in the <u>extreme</u> case, up to 26 percent of the solids are heavy metals such as copper and iron.

Looking at quantities generated from a single vessel, it is valuable to compare the amount of metal constituents released to the environment in the hydroblast water with theoretical leaching rates. Tributyltin leaching rates are being proposed by the state of Washington not to exceed 5 ug/cm^2-day, down from a current rate estimated

Table 11(a) - Estimated Hydroblast Waste Generated from a Medium Size Shipyard (Marco Seattle)

Basis for Minimum: 1 hr application @ 7 gal/min, lower range of water quality parameters

Basis for Maximum: 6 hr application @ 7 gal/min, upper range of water quality parameters

PARAMETER	One Ship		150 Ships	
	Minimum	Maximum	Minimum	Maximum
Water Volume				
Liters	1,590	9,540	238,480	1,430,880
Gallons	420	2,520	63,000	378,000
Total Suspended Solids				
Kilograms	0.31	15.9	46.5	2,390
Pounds	0.68	35	102	5,258
Total Metals kg [lb]				
Aluminum	0.003	0.19	0.049 [0.11]	28.61 [62.94]
Barium	< 1 g	< 1 g	0.023 [0.05]	0.34 [0.75]
Cadmium	< 1 g	0.005	< 1 g	0.79 [1.74]
Chromium	< 1 g	0.003	0.012 [0.026]	0.44 [0.97]
Copper	0.009	1.33	1.33 [2.92]	200 [440]
Iron	0.042	1.78	6.43 [14.1]	267 [587]
Manganese	< 1 g	0.12	0.045 [0.1]	18.31 [40.3]
Nickel	< 1 g	0.008	0.007 [0.015]	1.24 [2.72]
Lead	< 1 g	0.012	0.057 [0.13]	1.82 [4.00]
Tin (based on settled solids)	< 1 g	0.002	0.067 [0.78]	1.72 [3.78]
Vanadium	< 1 g	< 1 g	0.002 [0.004]	0.20 [0.44]
Zinc	0.004	0.81	0.62 [1.36]	121 [266]
TOTALS	0.058	4.26	8.64	641

Table 11(b) - Estimated Hydroblast Waste Generated from a Recreational Marina (Mercer Marine)

Basis: 15 minute application @ 3.75 gal/min

Minimum based on lower range of parameter values
Maximum based on upper range of parameter values

PARAMETER	One Ship		50 Ships	
	Minimum	Maximum	Minimum	Maximum
Water Volume				
Liters	213	213	10,650	10,650
Gallons	56	56	2,800	2,800
Total Suspended Solids				
Kilograms	0.12	0.26	6.05	13.2
Pounds	0.27	0.58	13.35	29.1
Total Metals kg [lb]				
Aluminum	0.002	0.006	0.101 [0.22]	0.29 [0.63]
Barium	< 1 g	< 1 g	< 1 g	0.009 [0.02]
Cadmium	< 1 g	< 1 g	< 1 g	< 1 g
Chromium	< 1 g	< 1 g	0.001 [0.002]	0.003 [0.007]
Copper	< 1 g	0.001	0.004 [0.009]	0.068 [0.15]
Iron	0.004	0.018	0.113 [0.25]	0.42 [0.92]
Manganese	< 1 g	0.005	0.019 [0.042]	0.27 [0.60]
Nickel	< 1 g	< 1 g	< 1 g	0.001 [0.002]
Lead	< 1 g	0.003	0.010 [0.022]	0.143 [0.32]
Tin	< 1 g	< 1 g	0.0005 [0.001]	0.006 [0.013]
Vanadium	< 1 g	< 1 g	< 1 g	0.001 [0.002]
Zinc	< 1 g	0.001	0.009 [0.02]	0.056 [0.12]
TOTAL	0.006	0.034	0.26	1.27

by the EPA (1986) as 20 ug/cm^2-day. Copper anti-foulant paint leaching rates can vary considerably based in their formulation, but James (1975) has suggested the rate levels out to about 20 ug/cm^2-day after two months. Leaching rates for either tributyltin or copper will not be constant over a year's time, but for the purpose of this comparison (Table 12) the average rates proposed above will be used to make conservative estimates.

Table 12 - Comparison of Single Vessel Discharge of Tin and Copper into Aqueous Environment via Leaching and Hydroblasting - Annual Basis

Biocide	Average Release Rate (ug-Biocide/ cm^2-day)	Hull Area* (ft^2)	Leaching	Hydroblast (maximum/ minimum)
			(as kg-[Sn or Cu]/yr)	
TBT	5	215	0.15	2×10^{4}/ $1 \times 10^{[illegible]}$
Cu_2O	20	2,000	12.0	1.33 $1.0 \times 10^{[illegible]}$

* - Hull areas based on average of total hull areas washed on recreational boats and commercial boats as observed during sampling

From Table 12 it is evident from even the rough estimates shown that tin leached from the hull of a single recreational boat or commercial ship over a year's time is several magnitudes greater than an annual hull washing for a comparable vessel.

Other factors requiring consideration are the bioavailability and relative dispersion of the biocide in the aquatic environment. The biocide leached directly off the ship hull is much more likely to be in its toxic form than the paint chip that has already leached out a large portion of its biocide by the time it is washed off. It was clear from comparing Sn/Pb ratios in settled solids that tin was leached out at a much higher rate than other paint metals. It is not conclusive from the analysis of the raw sample what fraction of total tin is in the form of TBT, but the presence of a number of TBT degradation products (Appendix 4(a)) indicated that a significant amount of degradation of the original TBT compound had occurred.

A concern with hydroblasting is that it is a concentrated and localized discharge that repeatedly deposits biocide and heavy metals in one area over long periods of time whereas the deposition of the leaching biocide and metals will be fairly well dispersed over the vessel's course of travel. Relatively speaking, hydroblast wastes generated from the large commercial boats present a bigger problem because the biocides and metals can be deposited in significant quantities by a number of shipyards in the same close proximity (Figure 7).

From Table 10, minimum and maximum copper concentrations in the fall zone were 8 mg/L and 140 mg/L, respectively. A 100 ft vessel requires up to 10,000 liters of hydroblast water. On this basis, hull leaching discharges copper into the environment at a rate between 9 and 150 times that of an annual hull washing. By the same comparison, it would take between 750 to 15,000 washings to equal the tin leached from a single recreational boat in a year's time. As Cardwell (1988) has pointed out, the state and federal regulatory language for TBT paint appears to be appropriately targeted for the smaller vessels. Deposition of TBT by pleasure vessels that are densely moored together in a marina will be enormously significant and many orders of magnitiude larger than releases from hull washings.

5.2 Hydroblast Wastewater Treatability

5.2.1 Sedimentation

The large number of particles in the raw samples with sizes under 40 microns was a clue that sedimentation would not be an effective means of total suspended solids removal. Figure 29 shows that the best suspended solids removal achieved was 92 percent. However, the

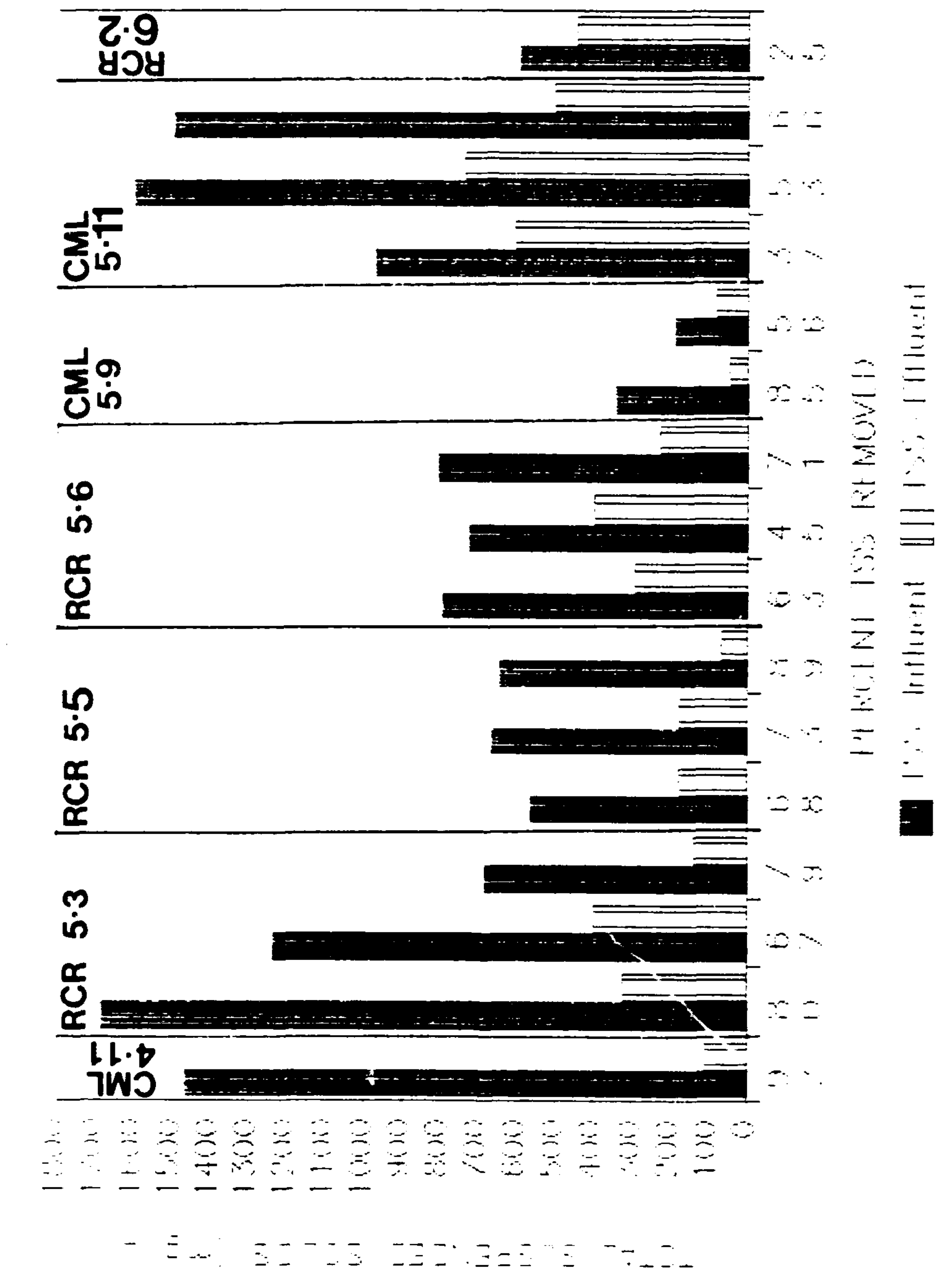


Figure 29 - 30-minute Settling Tests- Influent/Effluent TSS
[No effluent data for tests #2 - #4, 5-3-88]

average removal was 65.5 percent for the sixteen 30-minute settling tests performed. This removal efficiency was about the same for the commercial ship washings as it was with the recreational boat water. Although the recreational boat waters contained larger percentages of 40+ micron particles that would be the most likely particles to settle out, these particles did not have the density necessary to permit rapid settling. Specific gravity for sludges from these waters were never higher than 1.005 and in most cases were 1.000. Ironically, the best removals of 40+ micron particles occurred in the commercial ship waters where average removals were 72 percent (40-70 micron), 86 percent (70-100 micron) and 97 percent (100+ micron).

Furthermore, in the 40-70 micron size range, effluents from one recreational boat water actually had particle quantities 6 to 100 percent higher than the influent (refer to figures 30(a) through 30(c)). This phenomena resulted from smaller particles sticking together, which was evidenced by the significant decreases in particle numbers for the same sample in the two size ranges between 5 and 40 micron (Figures 30(d) and 30(e)). Thus in the recreational boat water, flocculation occurred naturally, but it did not aid settling significantly.

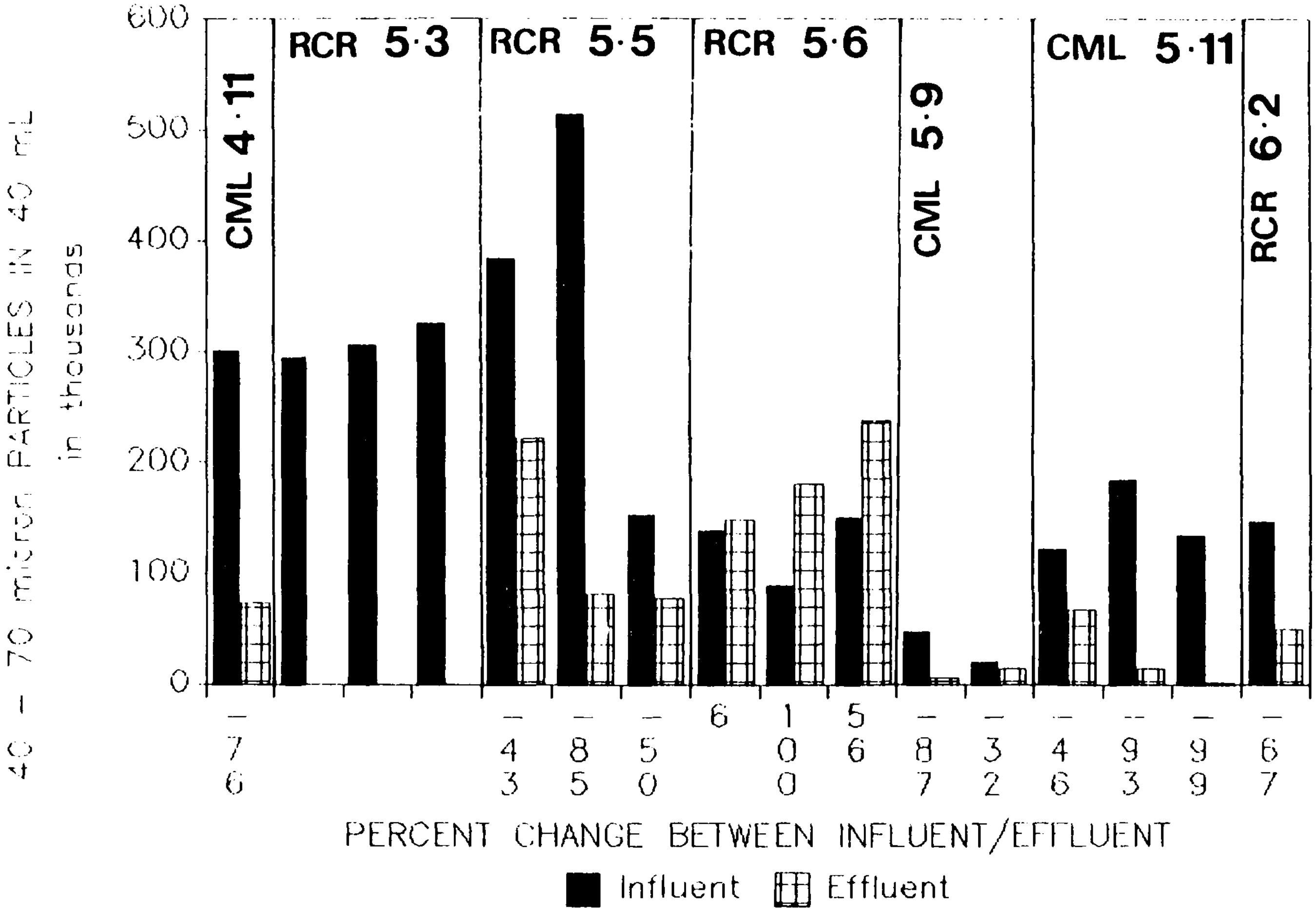


Figure 30(a) - 30-minute Settling Tests- Influent/Effluent 40-70 μ Particles
[No effluent data for tests #2 - #4, 5-3-88]

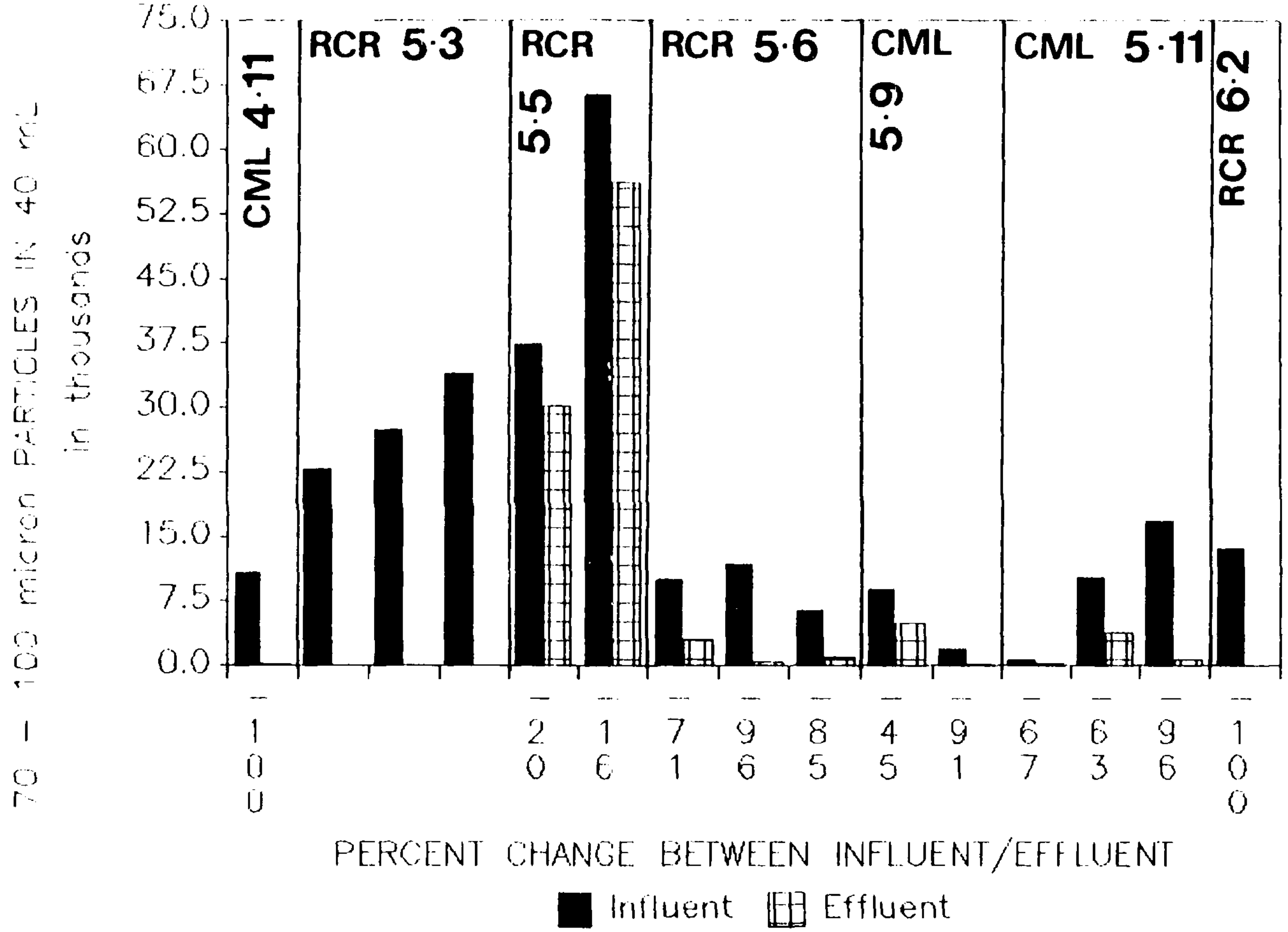


Figure 30(b) - 30-min. Settling Tests- Influent/Effluent 70-100 µ
[No effluent data for tests #2 - #4, 5-3-88] Particles

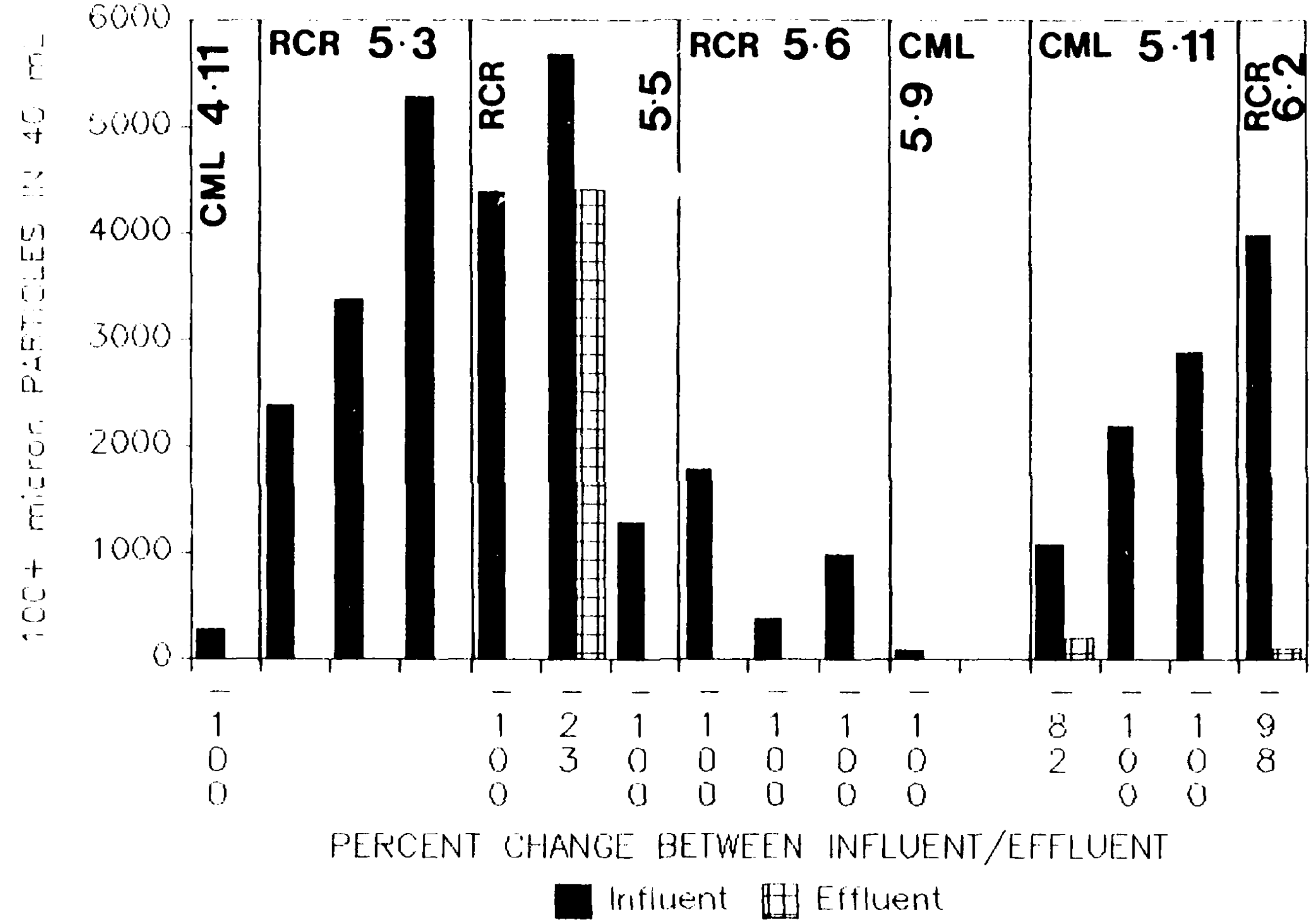


Figure 30(c) - 30-minute Settling Tests- Influent/Effluent 100+ μ Particles
[No effluent data for tests #2 - #4, 5-3-88]

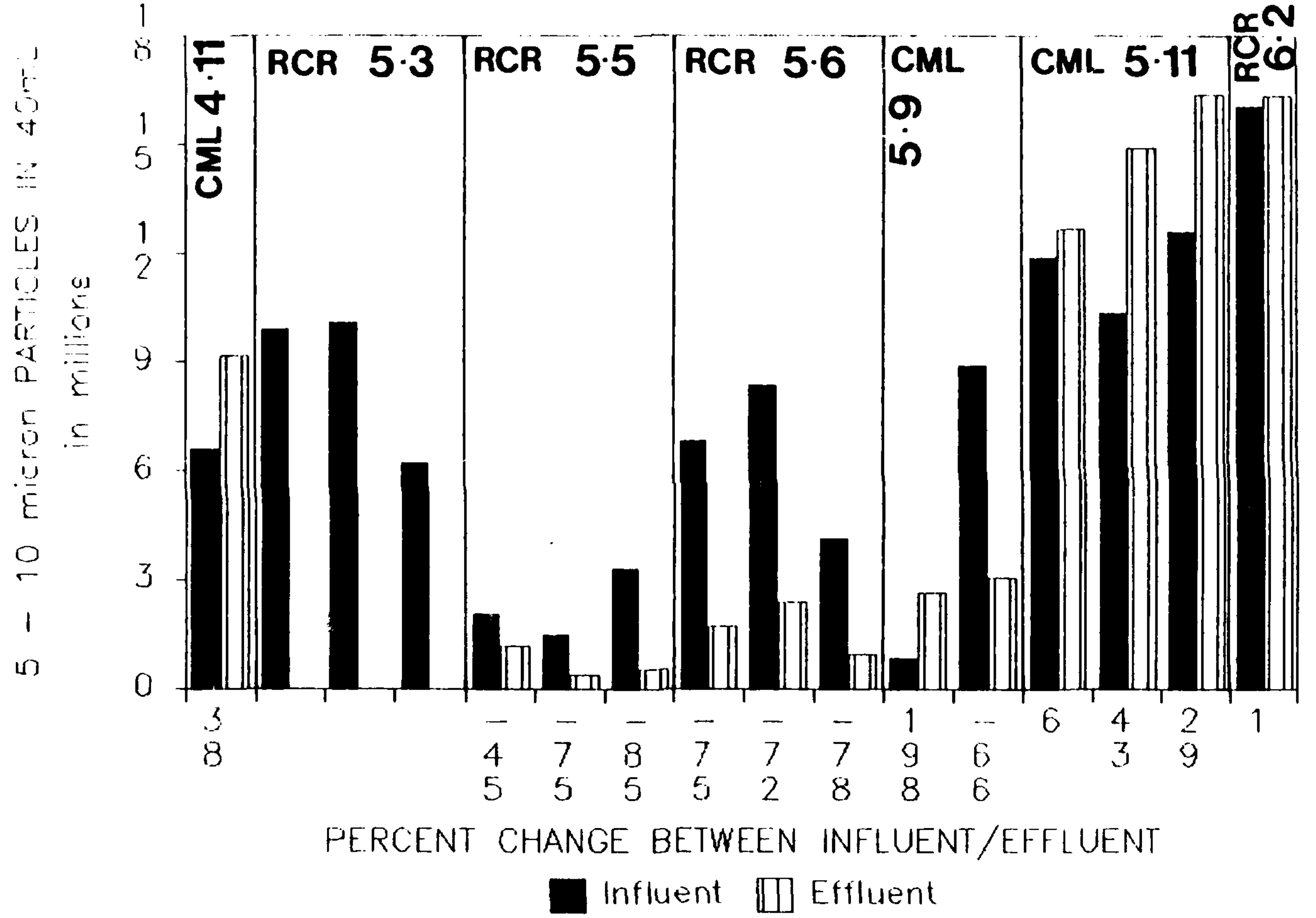


Figure 30(d) - 30-minute Settling Tests- Influent/Effluent 5-10 μ Particles
[No effluent data for tests #2 - #4, 5-3-88]

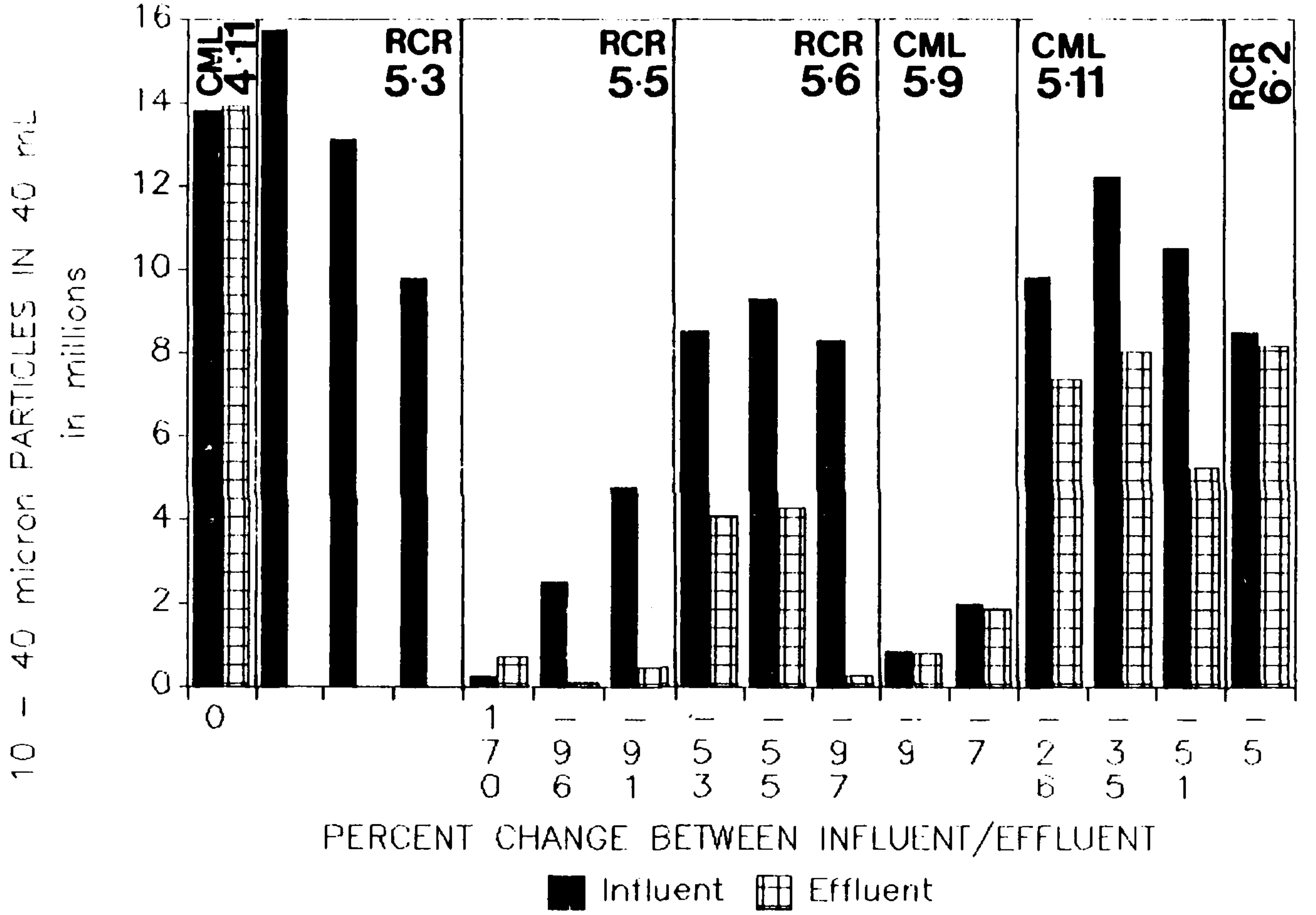


Figure 30(e) - 30-minute Settling Tests- Influent/Effluent 10-40 µ Particles
[No effluent data for tests #2 - #4, 5-3-88]

The recreational boat waters underwent hindered and compression settling. Sludge volume measured after the first 10 minutes elapsed time was consistently 30 percent greater than the final volume measured after 30 minutes. In one sample, where wriggling worm-like creatures were present in high numbers, the volume was between 44 and 81 percent higher at the 10 minute point than it was at the end of 30 minutes. This phenomena is characteristic of hindered and compressed settling as described by Metcalf and Eddy (1979).

In the commercial boat waters, all of the samples experienced gradual increases or no change at all in the settled solids volume between the 10 minute and 30 minute marks, a characteristic of discrete settling. In most of these waters it appeared that two zones were in the settled material. The bottom zone contained smaller, well defined and more dense particles that looked like paint and rust flakes while the upper zone was not as compacted and had larger, more amorphous solids. The smaller more compacted solids may have actually been dense enough that they behaved as discrete particles. But as previously discussed, density measurements on the settled solids in the commercial ship washings were not possible due to the small volumes of these solids and the difficulty in retrieving adequate amounts for density measurements as well as metal analysis.

Sedimentation was even less effective at removing the larger concentrations of metals than it was in removing suspended solids. While sedimentation removed 74 and 70 percent of the copper and iron, zinc and manganese experienced 59 percent removal, lead 65 percent and aluminum only 56 percent. Thus only copper and iron appeared to be associated with the more dense settleable material. All other metals appeared to be distributed relatively equally among the solids.

Finally, the supernatants from the settling tests had turbidities which were normally higher than the influent. The effect of settling out the large amount of solids in the raw sample was to give the smaller particles more room to disperse. In one of the most dramatic shifts, the influent had a turbidity of 56 ntu while the supernatant turbidity was 90 ntu.

5.2.2 Screening

Removal of suspended solids achieved with 200 mesh and 325 mesh screen sizes are presented in Figure 31. These

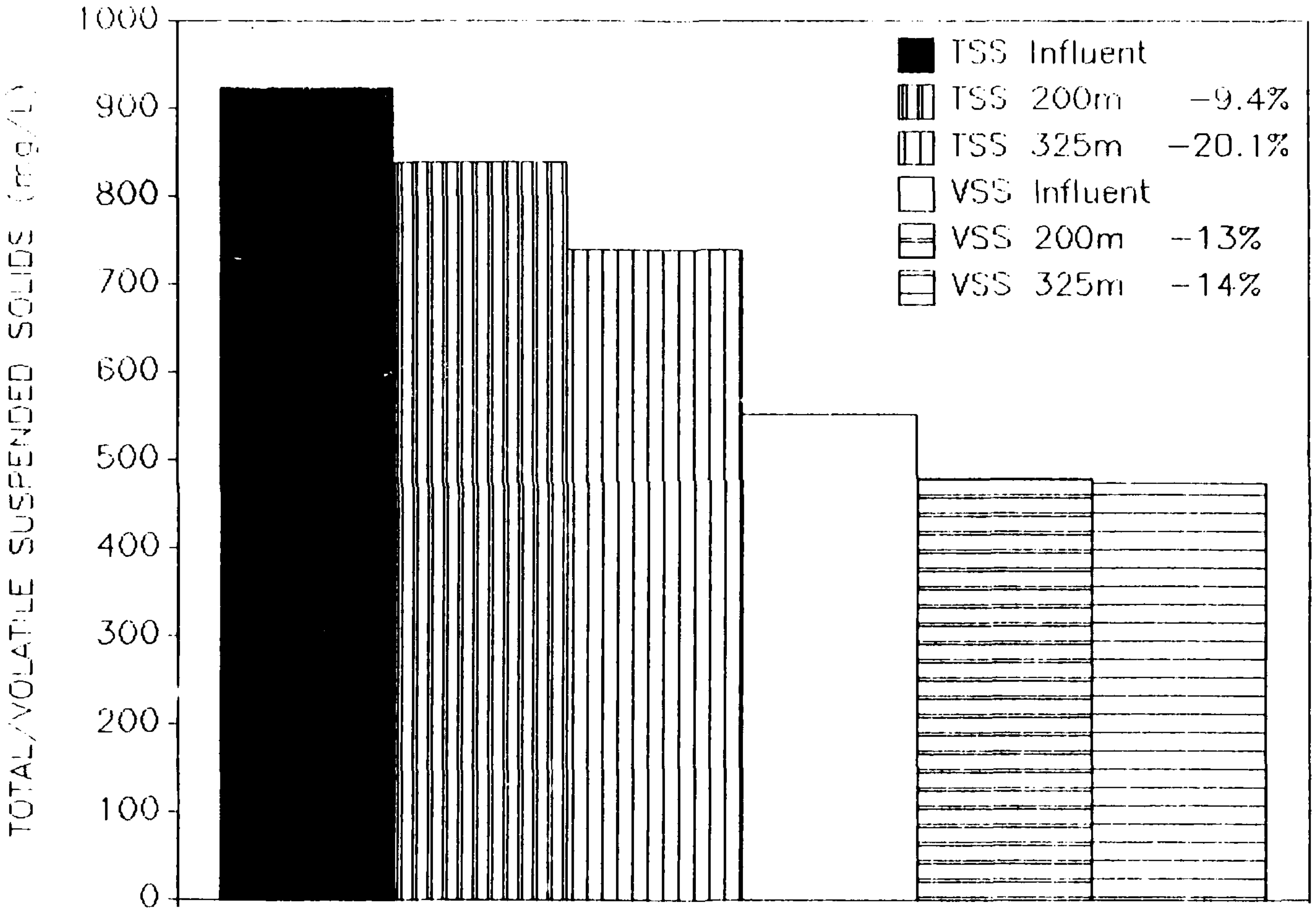


Figure 31 - Screening- Influent/Effluent Total/Volatile Suspended Solids

were not encouraging results because the removals were in the lower range of typical microscreening efficiencies (Table 5), but it was apparent that screening might at least remove a portion of the suspended solids which might prove critical in subsequent treatment steps such as filtration. The 325 mesh screen actually removed a fair portion of solids (187 mg/L), but it required frequent backflushing to remain operative. A very dense mat developed making it unlikely that higher pressure would result in greater screening efficiency.

Particle counts shown in Figure 32 indicate that particles above 40 microns in size were removed by both screens. Paradoxically, the 200 mesh screen worked better on 40 - 70 micron particles than the 325 mesh screen, but the 325 mesh screen was slightly more effective in the next size range of 70 - 100 micron. In the last size category, 100+ micron, there was essentially 100 percent removal.

The efficiency of the screening process appeared to be related to the ability of a mat to develop which would also allow water to pass through. The mat was composed of both paint chips and algae. When the filter chamber was initially pressurized, water freely passed through

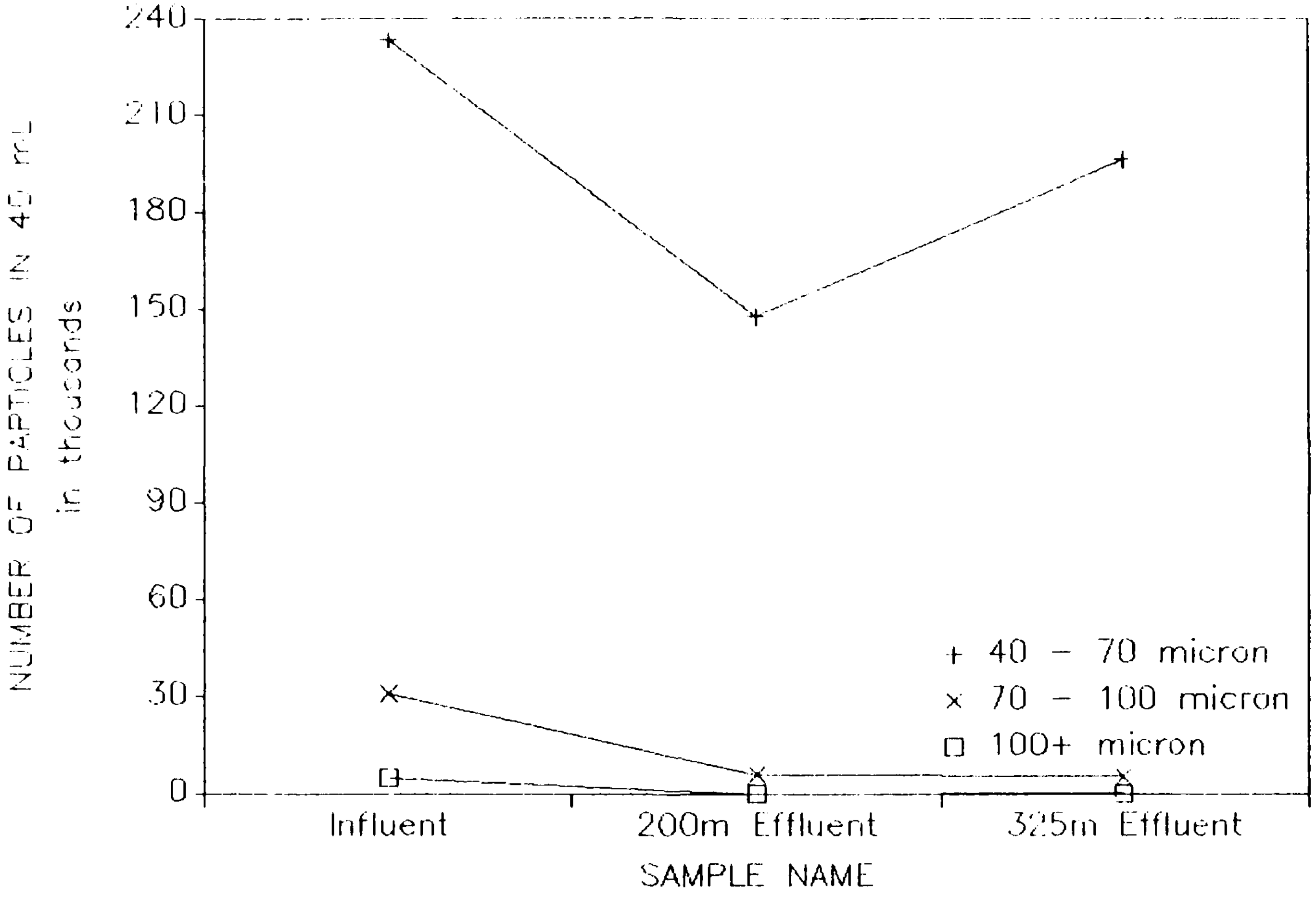


Figure 32 - Screening- Influent/Effluent 40+ µ Particles

the screen, but slowed down with the mat build-up.

The particle shape and rigidity also appeared to contribute to the effectiveness of screening. Based on visual observations of the influent and effluent, the visible paint particles were completely removed by both screens. The algae, being more amorphous and flexible could pass through the screen, particularly during the initial screening period prior to mat development. The flexibility of the algae particles serves to explain why so many particles larger than the screen opening were able to appear in the effluent.

Solids loading (based upon the available screen size in the filter funnel and suspended solids removal achieved for a given screen) are presented in Table 13.

Table 13 - Solids Loading Capacity of 200 mesh and 300 mesh Screens

Screen Mesh	Influent TSS (mg/L)	Effluent TSS (mg/L)	Terminal Head (psi)	Solids Loading until Backwash (kg/m^2)
200	927	840	9.8	0.068
325	927	740	9.8	0.049

On the basis of solids loading, the 200 mesh screen was actually 38 percent more efficient than the 325 mesh screen. The trade-off, obviously, is that the 325 mesh screen produced a better effluent.

For the six major metals, removal efficiencies were quite good compared to suspended solids removal (Figure 33). Compared to 9.4 percent TSS removed with the 200 mesh screen, aluminum removal was 17 percent, copper 35 percent, iron 15 percent, manganese 24 percent, lead 28 percent and zinc 48 percent. With the 325 mesh screen where TSS removal was over 20 percent, metal removals were nearly identical. These results strongly suggest two things. First, solids removed in screening are likely to contain a considerable amount of paint chips because a high percentage of metals are associated with them. Second, the 200 mesh screen appears just as adequate for removing the paint particles as the 325 mesh screen. As further proof of this, COD measured in both 200 mesh and 325 mesh effluents was only 8.3 and 7.4 percent less than influent COD, indicating that little of the algae had been caught by the screens. Thus in the case of the paint, rigid particle structure made it a good candidate for screening.

5.2.3 Granular Media Filtration

5.2.3.1 Sand Filtration

Filtration with sand filters was extremely effective at removing total suspended solids (Figure 34). The problem already discussed with this treatment method was rapid clogging. Even when passed through a 200 or 325 mesh screen before filtration, an initial 4 ft column of water began clogging in a matter of 5 to 10 minutes when the head was about 3 ft. Flow rate dropped below typical design rates within 60 minutes and even after 24 hours as much as 12 percent of the original volume remained to drain.

Figures 35(a) and 35(b) show average flow rates as a function of time for the two slow sand filter columns used in the study. It was immediately apparent from the blank runs that one column filtered slightly faster than the other. Although both columns were constructed exactly the same, it may have been that one column developed some short circuits around the PVC rings (see Figure 22) where sand had settled unevenly after the column was saturated with water. Nevertheless, both columns performed in a similar fashion.

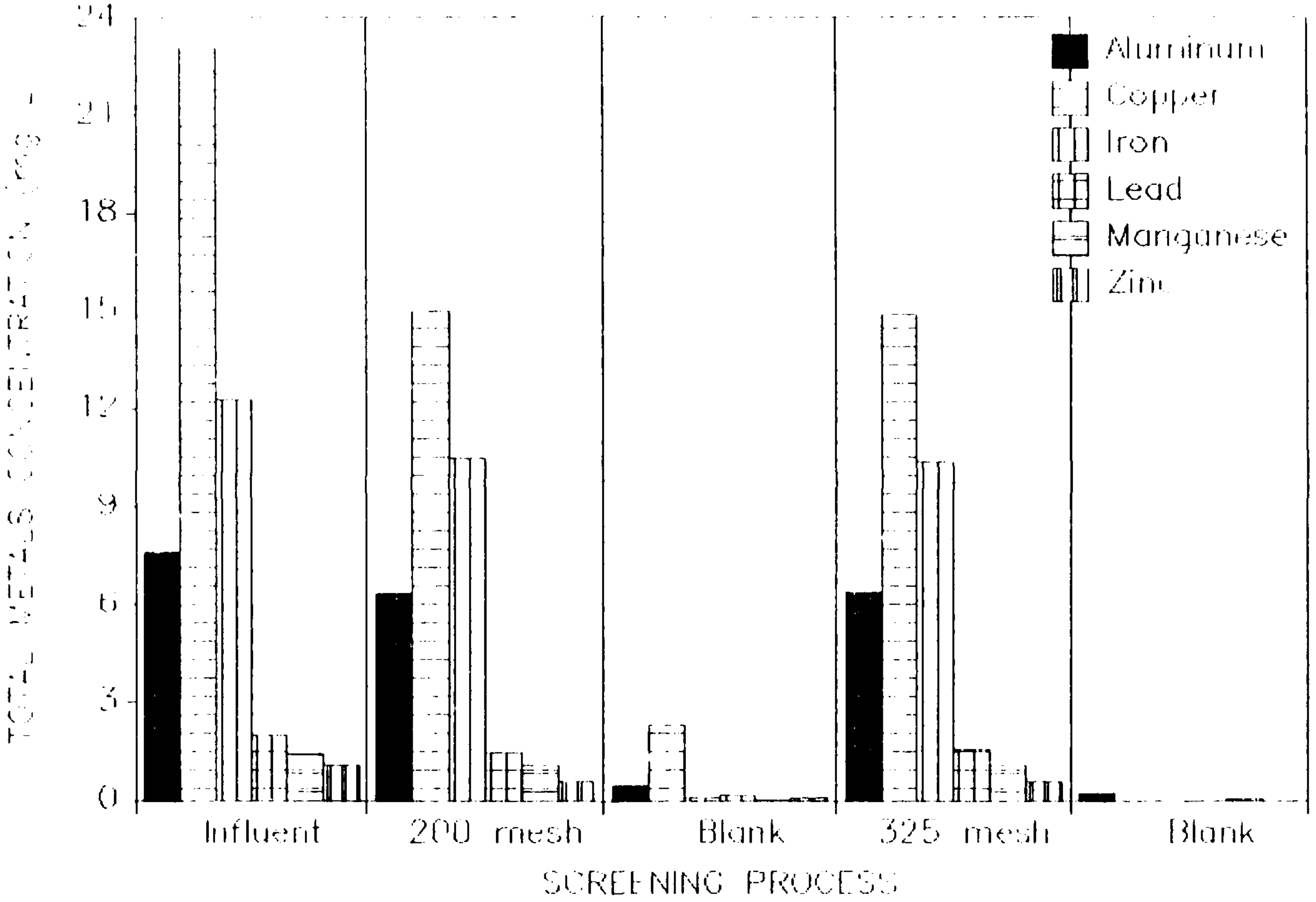


Figure 33 - Screening- Influent/Effluent Major Metals

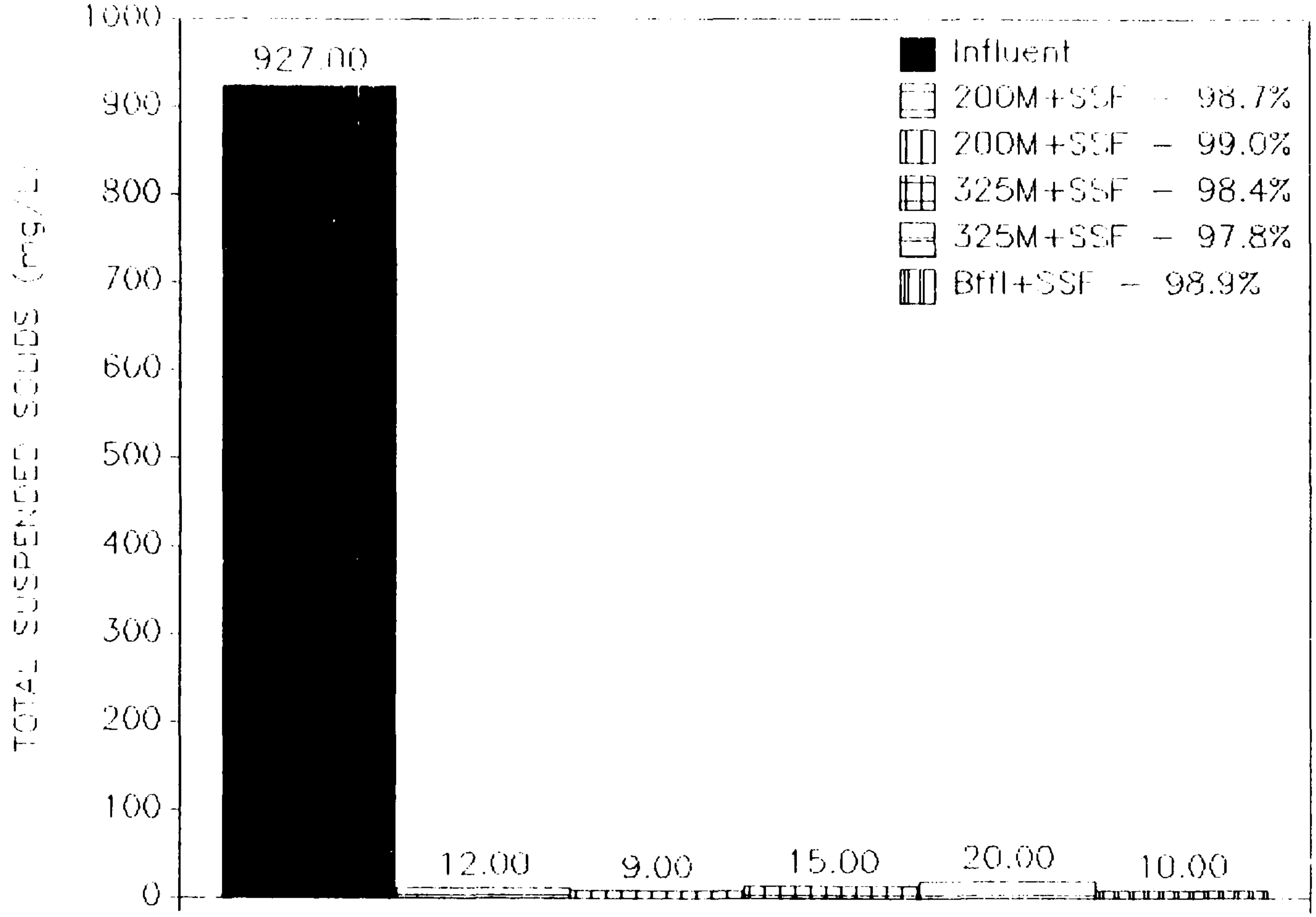


Figure 34 - Sand Filter- Influent/Effluent Total Suspended Solids

At the 60 minute mark the average flow rate had reached a typical slow sand filter flow rate of 88 gal/day-ft . This cross-over generally occurred after approximately two feet of water (half the intial volume) had been filtered.

Flow rate was proportional to time elapsed for the first 10 minutes as the inverse of the square root of elapsed time. However, the rate of decline in flow changed after 10 minutes. At this point flow was proportional to the inverse of time elapsed, a much more rapid decline in flow rate. This phenomenom occurred in both sand columns and indicated that the initial period (10 minutes) was a time of relatively unimpeded flow. After 10 minutes the mat of solids atop the sand column began acting as a form of resistance, so the flow rate declined more rapidly after that point. It was interesting to observe that this rate of decline was constant even near the end of the run, perhaps suggesting that resistance from the solids deposition was constant once the initial layer of solids had built up on top of the sand column.

In Figures 35(a) and 35(b), Run 1 filtered 750 mL and Run 2 filtered approximately 600 mL. Placing less water on the filter initially, it was hoped that less clogging

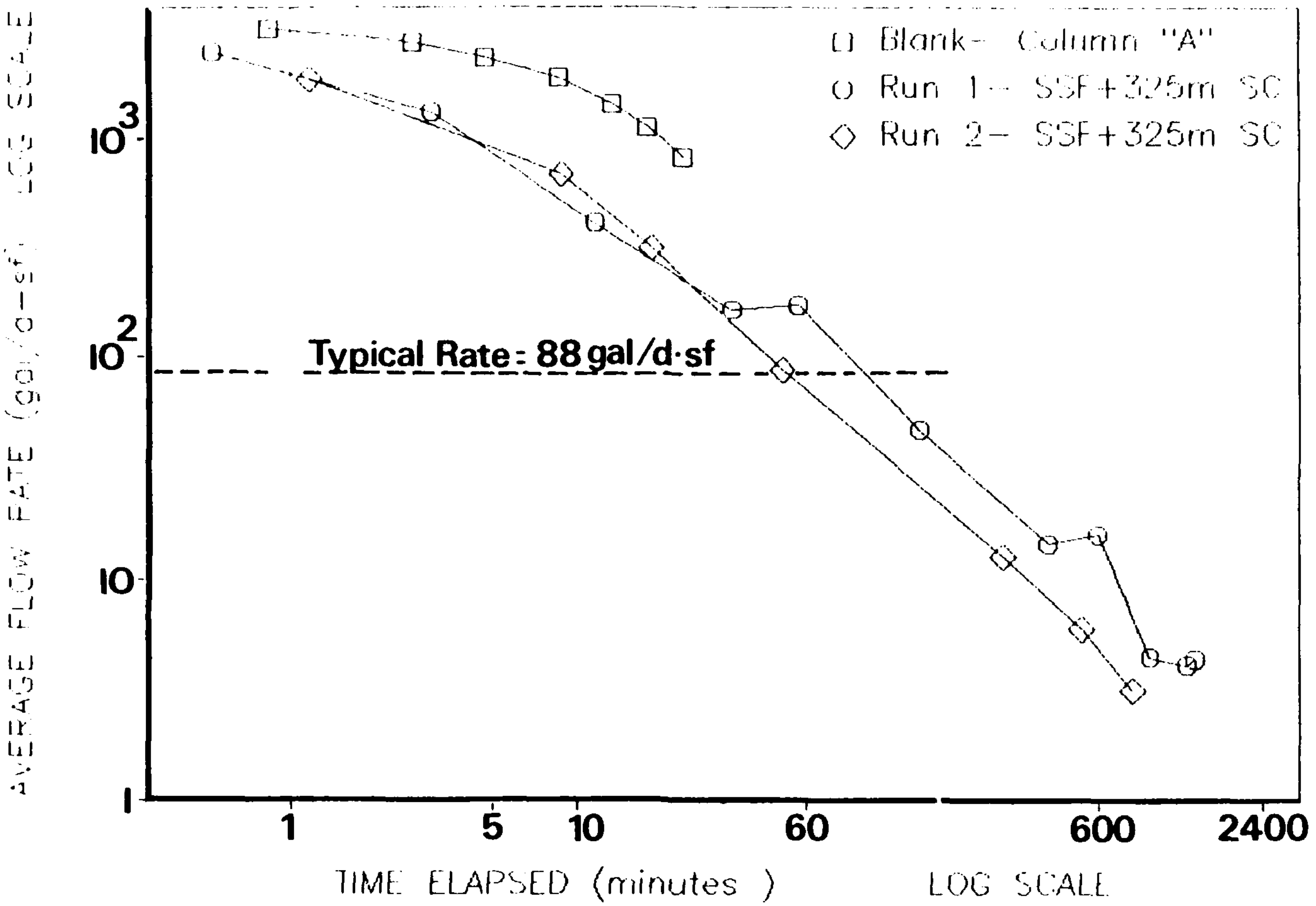


Figure 35(a) - Sand Filter- Flow Rate vs Elapsed Time (Column A)

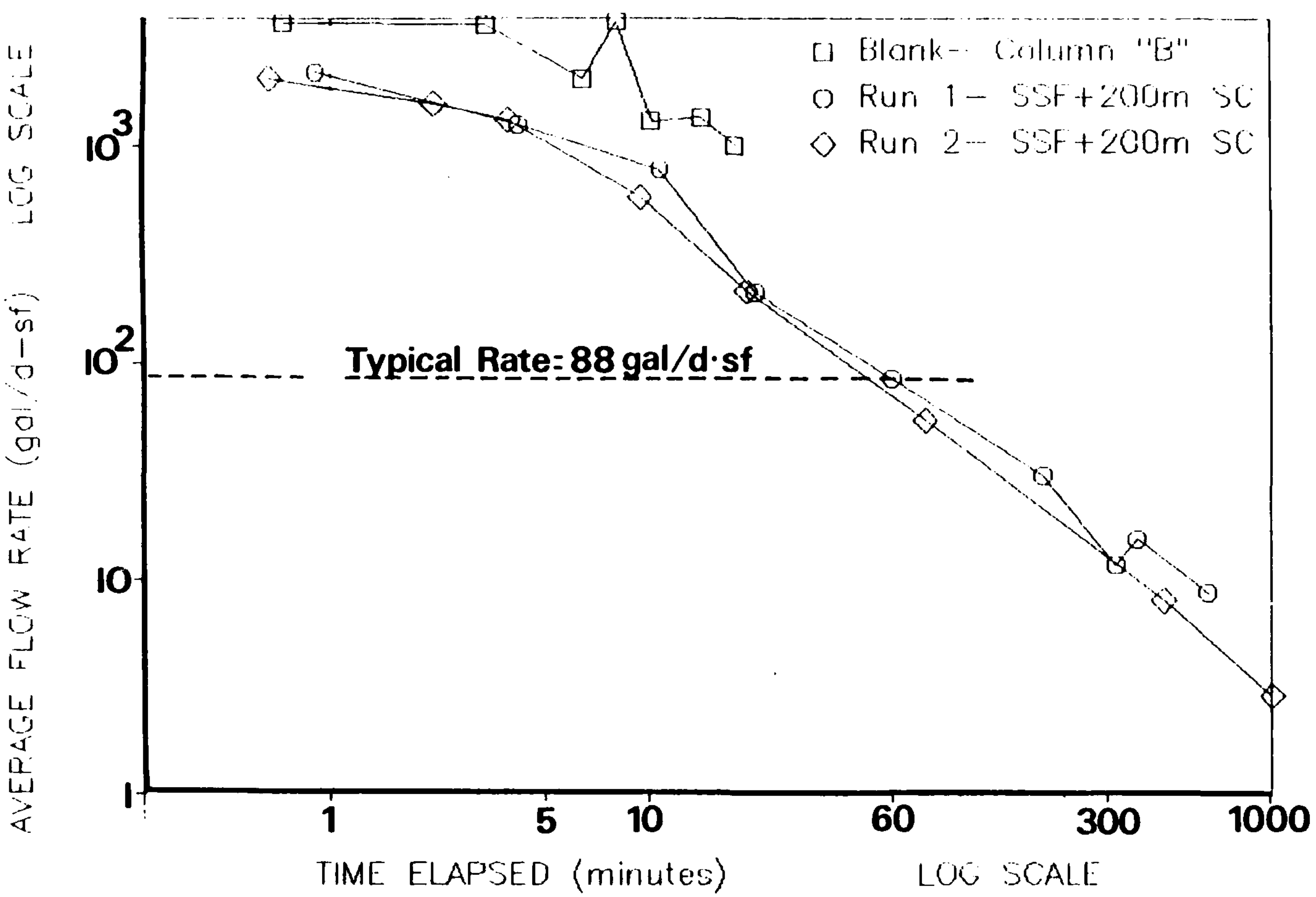


Figure 35(b) - Sand Filter- Flow Rate vs Elapsed Time (Column B) would occur and shorter filtration times would result. In column "A" the desired result was achieved, but in column "B" a greater initial volume drained in less time than the smaller volume. Also, the same pattern of clogging within 10 minutes was observed with the 3 ft initial head as it was with the 4 ft intial head indicating that the mat of solids was still the key factor in the filter's operation. Thus it was apparent that even smaller initial head (3 ft versus 4 ft) did not improve the sand filter's performance.

The development of a 3/8-inch mat of solids on the sand surface was observed at the termination of each run. As was already discussed, within the first ten minutes this mat had an observable effect on the flow rate. By placing baffles in the column (Figure 23) an attempt was made to limit this mat's effect on flow. In the baffled sand filter a non-screened raw influent was used, yet the baffles successfully prevented a build-up of solids on the top of the sand surface as evidenced by a final mat depth of less than 1/32-inch. However, it turned out from this test that the mat had actually played an important role in the the prior sand filtrations because it was keeping the upper layer of the sand column from being clogged by fine algae particles. Thus the baffled column did not drain at a faster rate than the previous runs on the same column. The baffles also contributed to a greater clean-up problem as a gluey and gelatinous mass of algae built up in the sand media and was quite difficult clean. This build up was much less pronounced on the non-baffled sand filtrations.

The baffle experiment also indicated that a separate pre-treatment to allow most of the solids to settle out prior to sand filtration was not feasible. The baffles captured what appeared to be 90 percent or more of the settleable solids (by volume), yet the sand media became badly clogged with the remaining particles in the water.

Sand filtration removed total COD in excess of 90 percent for each run (Figure 36(a)), which was less than the 98 percent removal of TSS. Sand filtration was not effective at removing soluble COD to any extent (Figure 36(b)). These facts, as well as the pale green color of the effluent indicated that a the smaller algae particles were able to get through the filter. Effluent turbidities ranged from 39 - 45 ntu for the screening+slow sand processes with a low of 23 ntu observed with the baffle+slow sand arrangement.

Better than 99 percent reduction of particles in the 1 - 40 micron range was observed in all sand filtered

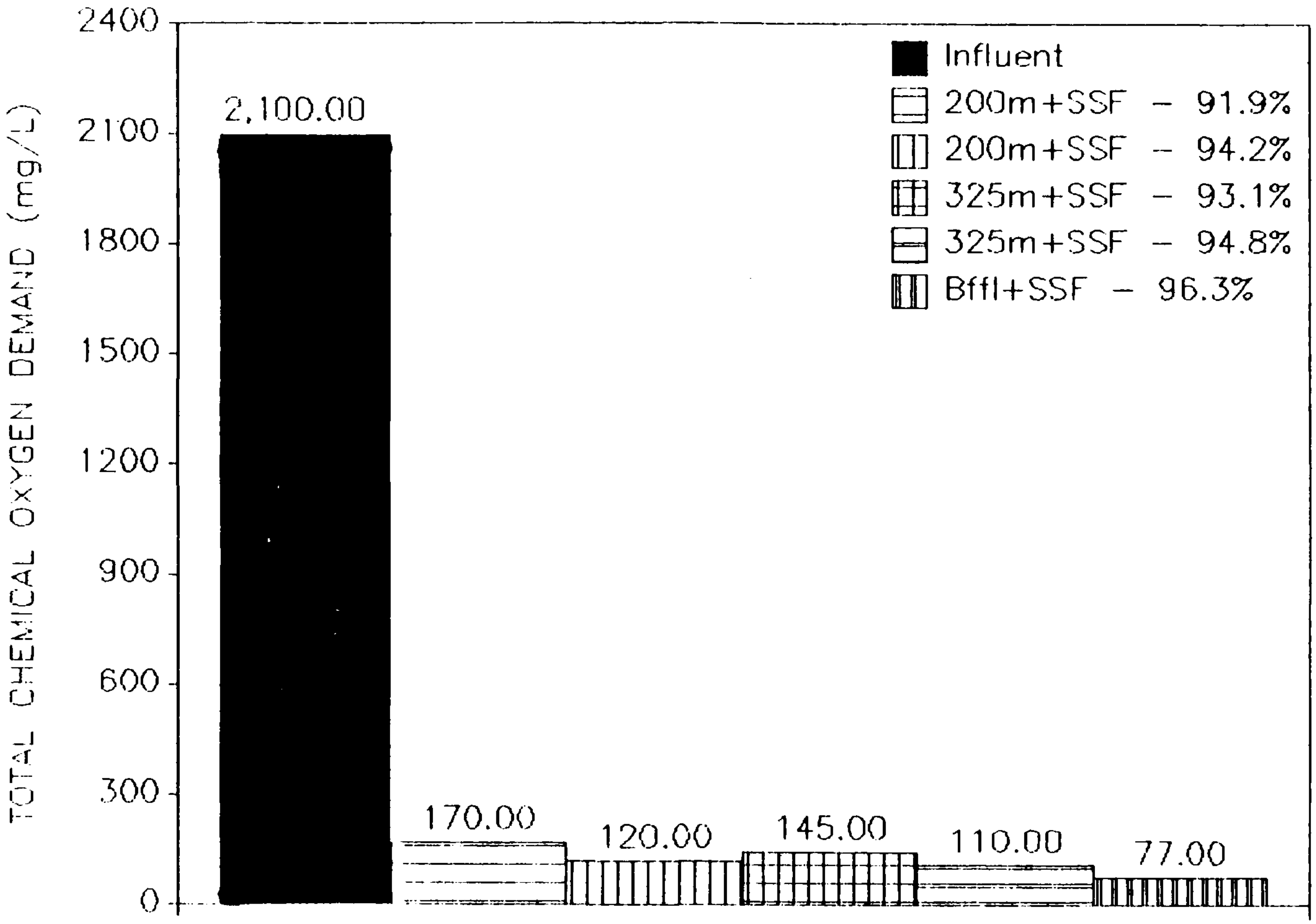


Figure 36(a) - Sand Filter- Influent/Effluent Total COD

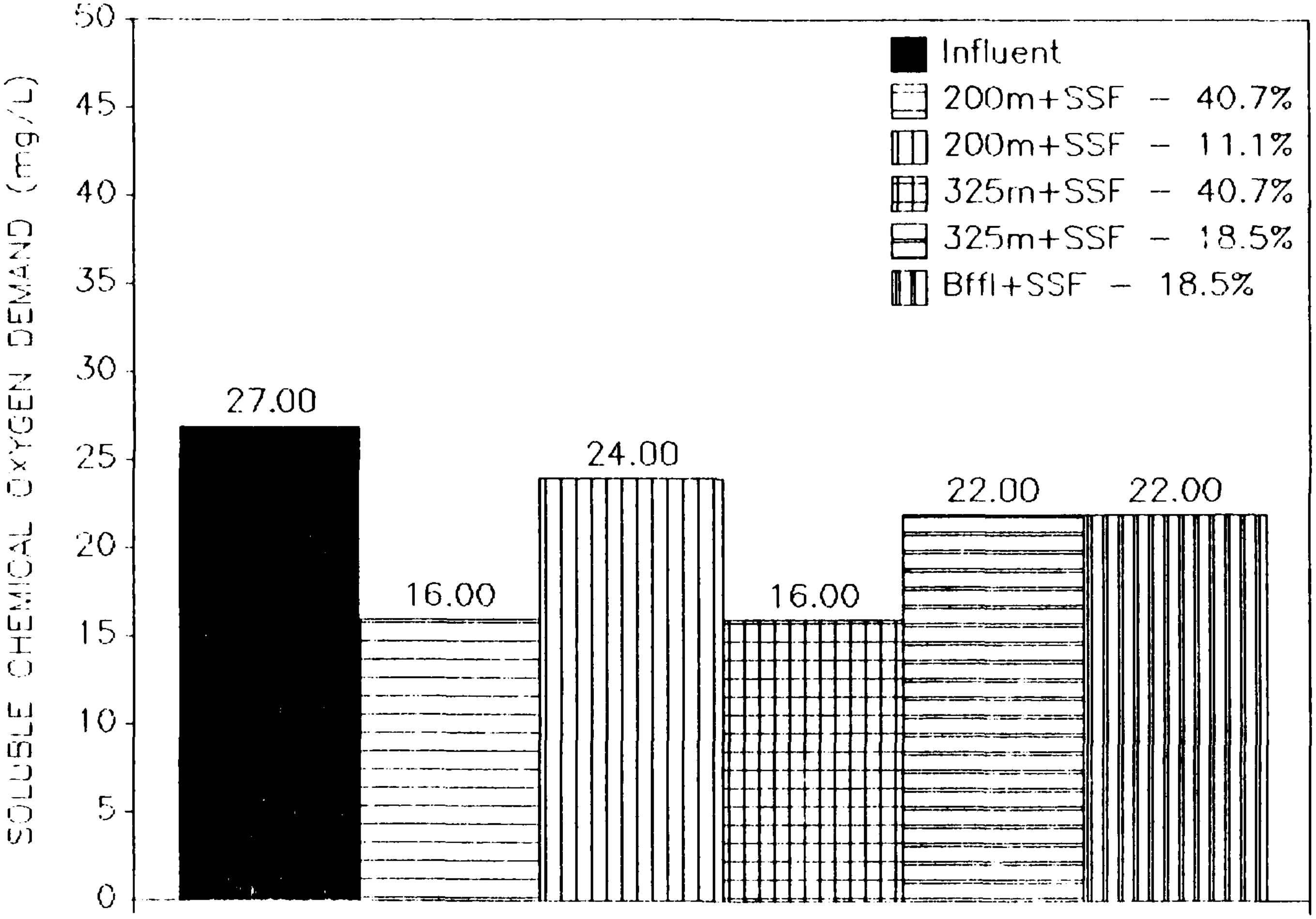


Figure 36(b) - Sand Filter- Influent/Effluent Soluble COD effluents. In the size range of 40 - 100 micron, 99.9 percent reduction was consistently achieved and 100 percent reduction was obtained in the 100+ micron particle sizes.

For the six major metals, slow sand filtered effluents were consistently below 1 mg/L, with the exception of one effluent that had over 2 mg/L of iron. Figure 37 compares effluent levels for aluminum, copper, iron, lead, manganese and zinc. For these same metals, levels were consistently below 0.1 mg/L, except that copper and aluminum were regularly 0.2 mg/L or greater in soluble form. With cadmium, chromium, nickel and vanadium, levels were at or below the ICP detection limits. Tin was only detected (0.25 mg/L) in the effluent of the initial slow sand filtration. This particular effluent, however, only represented a 100 mL volume because the filter had become clogged after a short period and the run was aborted. Barium was consistently found at levels in the range of 0.05 mg/L.

No significant differences were observed in effluent parameters or hydraulic bahavior for waters initially screened with 200 mesh and 325 mesh screens. As was already noted, both screens appeared to remove the larger paint chips at about the same rate and the

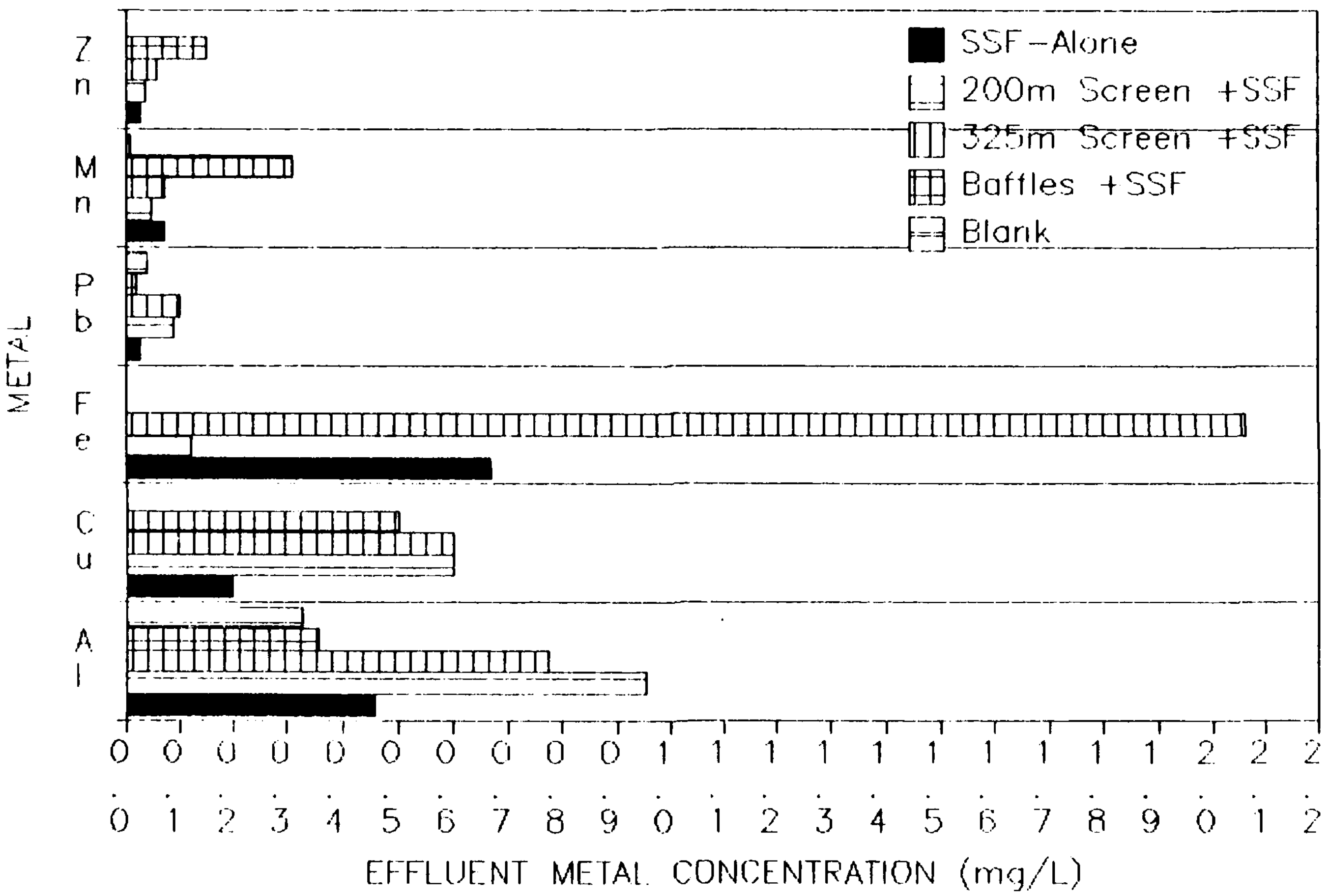


Figure 37 - Sand Filter- Major Metals in Effluent

additional solids removed by the finer screen (100mg/L) were not a factor in filter performance. Enough solids were present in both filter influents to create a top mat and clog the top 1/2-inch layer of sand.

5.2.3.2 Dual Media Filtration

The dual media filters were capable of filtering between two and four successive volumes of approximately 750 mL each, representing an initial loading of about 4 ft. The hydraulic behavior of these columns was much less consistent than the sand filters. Like the sand filters, the dual media filters experienced a shift in the rate of decline in flow rate at about the ten minute mark, but this change was not as distinct. It was apparent that very complex resistance patterns were developing in the coal column as the solids accumulation progressed. Figure 38(a) is typical of the flow pattern for all five filtration runs made with a dual media filter. This pattern was still evident after a fourth run with the one sample achieving that degree of efficiency (Figure 38(b).

Referring to Figure 39, total suspended solids removal for the dual media filters was consistently greater than

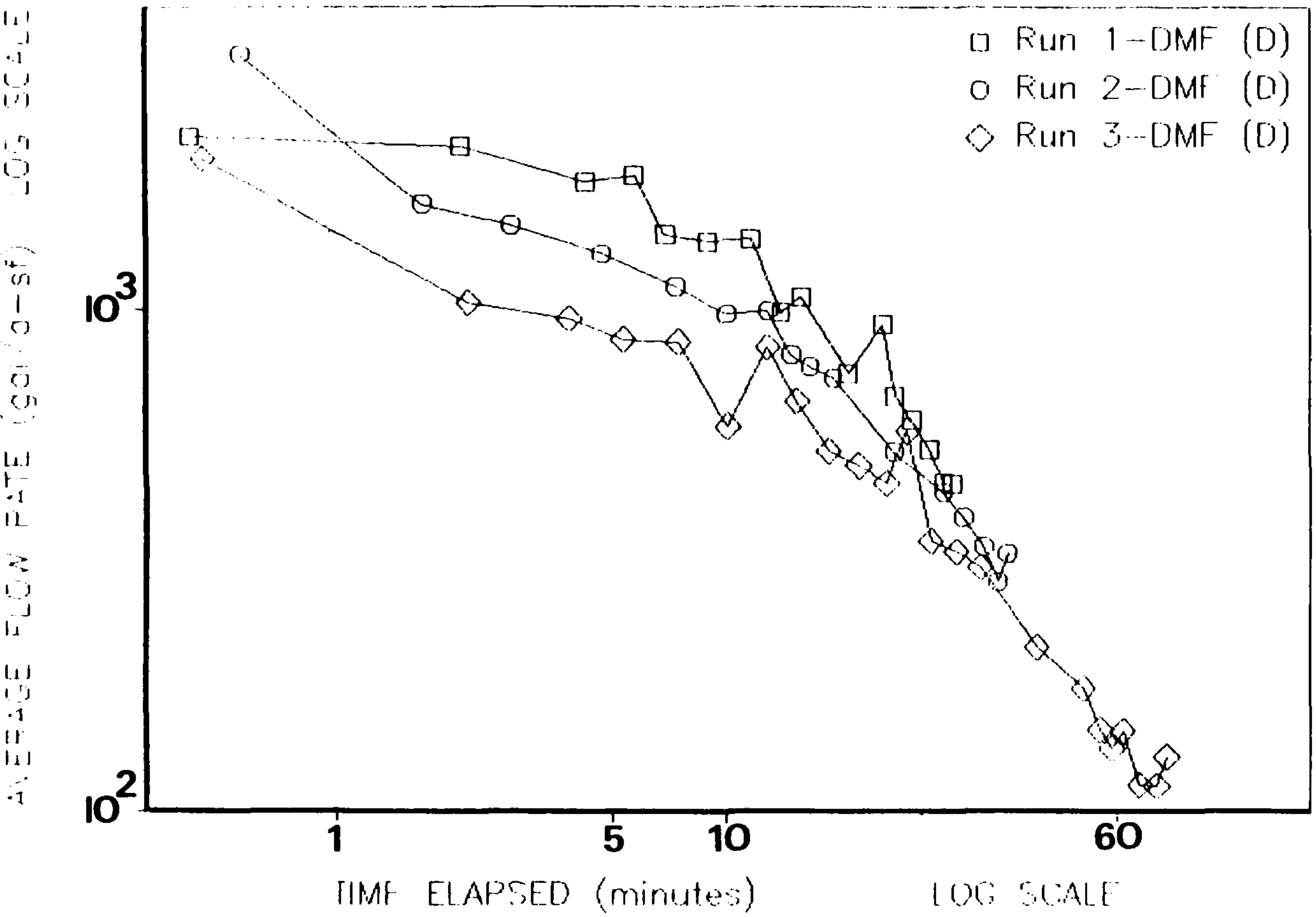


Figure 38(a) - Dual Media Filter- Flow Rate vs Elapsed Time (Sample D)

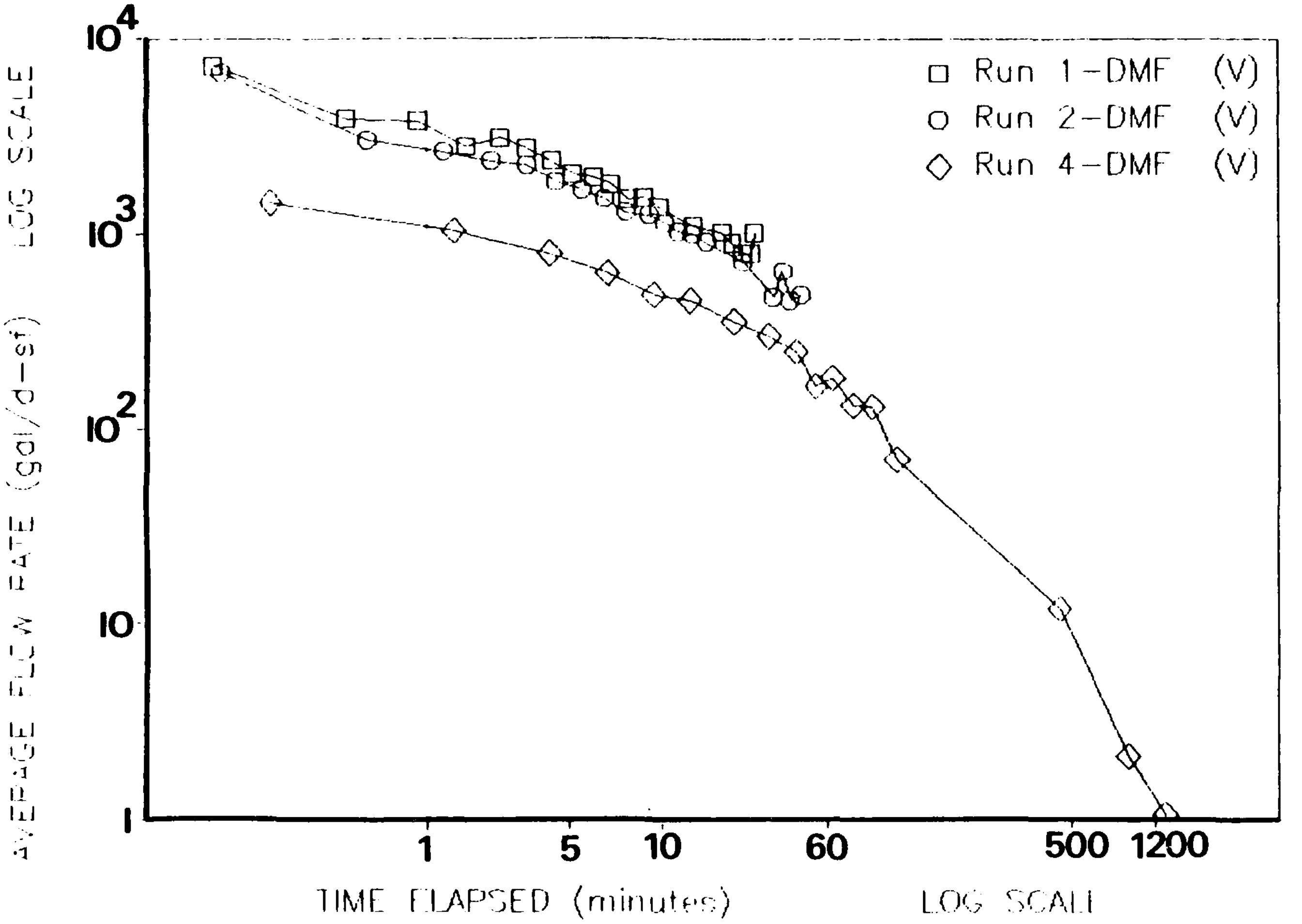


Figure 38(b) - Dual Media Filter- Flow Rate vs Elapsed Time (Sample V)

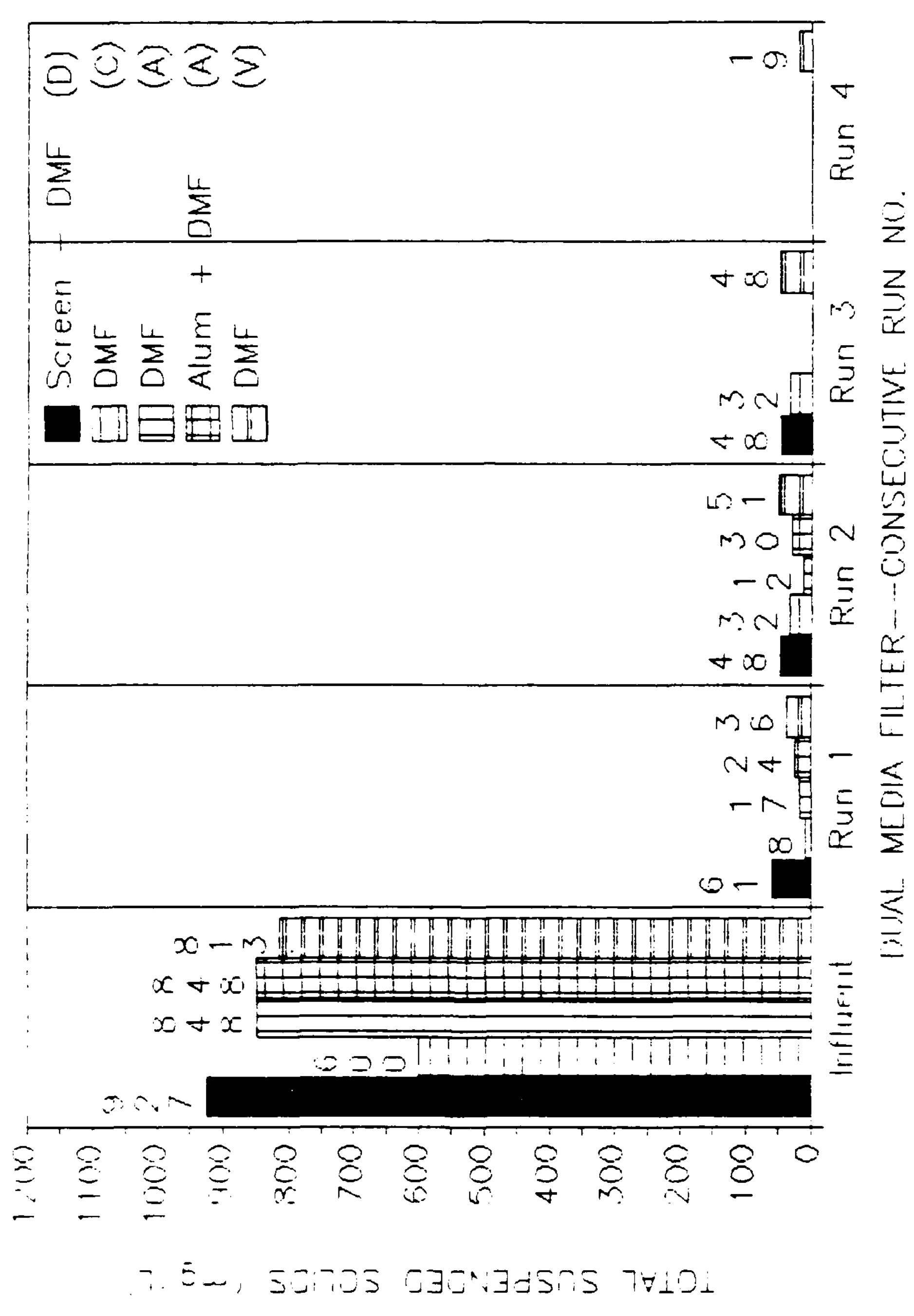


Figure 39 - Dual Media Filter- Influent/Effluent Total Suspended Solids

94 percent compared to 98 percent and better with sand alone. Effluent TSS levels were almost 4 times those of the slow sand filtered water from the same sample ("D"). Suspended solids removal for the recreational boat water (samples "D", "C", "A") was comparable to that of the commercial boat water (sample "V"). There were no consistent trends observed in effluent TSS between successive filtrations, i.e. no patterns of either decreasing or increasing TSS concentrations.

COD removal ranged anywhere from 82 to 95 percent (Figure 40(a)) and, like the slow sand filter effluents, COD removal was less percentage-wise than suspended solids removal. Soluble COD did not undergo significant removal (Figure 40(b). In a few cases, higher soluble COD was measured in the effluent than the influent, perhaps indicating that a small amount of the organic material had undergone dissolution as it traveled through the filter.

Particle counts of the effluent from dual media filters were similar to those from the slow sand filter. A comparison of particle counts is provided in Table 14.

As seen in Table 14, the dual media filter slightly outperformed the slow sand filter in terms of reducing

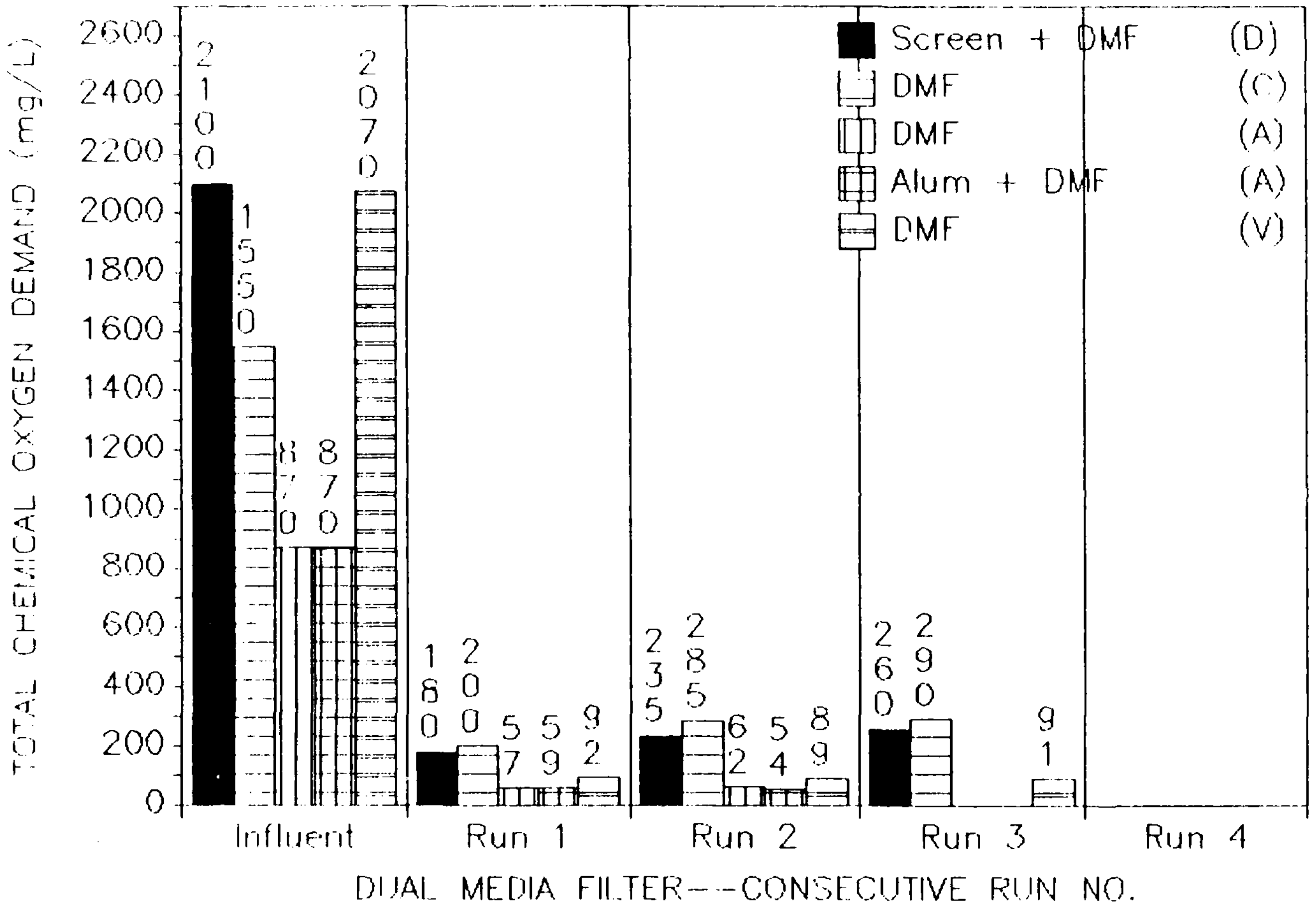


Figure 40(a) - Dual Media Filter- Influent/Effluent Total COD

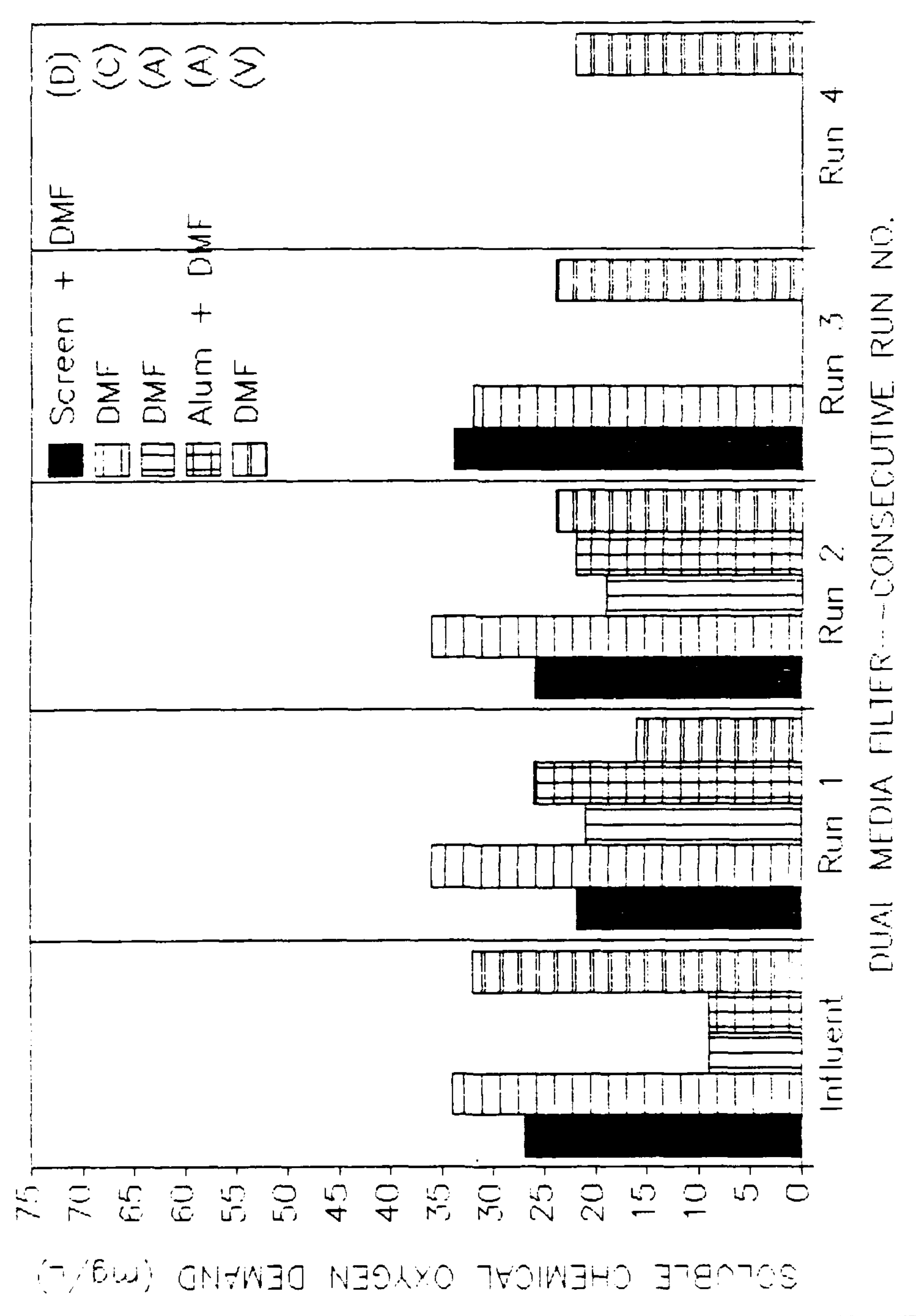


Figure 40(b) - Dual Media Filter- Influent/Effluent Soluble COD

Table 14 - Comparison of Average Particle Counts in Slow Sand and Dual Media Filter Effluents

Particle Size (microns)	Slow Sand		Dual Media	
	(Avg. No. of Particles Counted in 40 mL)			
		Minimum % Decrease		Minimum % Decrease
1 - 5	27,000	99	15,000	99.9
5 - 10	87,000	99	45,000	99
10 - 40	42,000	99	53,000	99
40 - 70	127	99.9	55	99.9
70 - 100	7	99.9	4	99.9
100+	0	100	0	100

the number of 1 - 5 micron particles, but on the whole, both filters had similar particle size distributions and the best performance for both filters was observed in 40+ micron range.

Table provides several interesting comparisons between the two filters and various pre-treatments used on the influent by comparing the capacity of the filters to accumulate solids between backwashes. As would be expected, the coal/sand filter had a higher capacity for solids than the slow sand filter by virtue of the greater interstitial space within the coal media.

Table 15 - Solids Loading Capacity Achieved with Sand and Dual Media Filters

Sample	No. Complete Runs	Solids Loading Capacity* (kg TSS/m^3 media)	Remarks
		SAND ALONE	
D	1	2.91	200m Screened
D	1	2.34	" "
D	1	2.55	325m Screened
D	1	2.02	" "
		COAL/SAND DUAL MEDIA	
D	3	3.76	325M Screened
C	3	3.16	Raw Influent
A	2	3.03	Raw Influent
A	3	4.50	34.5 mg/L Alum Dose in Influent
V	4	5.67	Raw Influent

* - Solids Loading Capacity is an expression of solids accumulation between backwashes

Media volumes: Sand = 213.0 cm^3 Coal = 196.6 cm^3

Screening the influent prior to filtration may have given the filter a greater capacity for accumulating solids. Raw influent "A" and screened influent "D" had similar TSS concentrations (848 and 740 mg/L respectively). Screened influent "D" was capable of depositing almost 25 percent more solids than "A" as well as achieve 50 percent higher volumetric throughput. Raw influent "C" achieved a greater number of runs than "A", but had a lower TSS concentration (600 mg/L), so based on solids loading capacity both raw influents experienced similar removal rates.

Raw influent "V" had a relatively high TSS concentration (813 mg/L) and resulted in the highests solids loading capacity. The reason this happened was likely related to several factors. First, this influent was from a commercial ship washing. The other influents, "A", "B" and "C" came from a recreational boat washing. Just as the screened influent (over 99.9 percent of 40+ micron particles removed) had fewer large particles, the same was true for the commercial ship influent. The larger particles contributed to different deposition patterns in the media whereby interstitial spaces were filled up more quickly, but less efficiently than with the smaller particles. This hypothesis is further supported by the studies cited in Table 4, in which much higher solids loadings (on the order of 8 kg TSS/m^3 media) were achieved with waters that had low influent concentrations and, presumably, small-particle suspended solids. It must be stated, however, that larger media sizes were used in the particular study cited (Baumann et al, 1974) which would increase solids loading capacity.

Another factor that appeared likely to influence solids loading, was the flocculating character of the particles. In the sedimentation studies, it was consistently observed that the recreational boat waters had a high degree of solids flocculation whereas this phenomena was less prevalent in the commercial ship waters. The solids from the commercial ships formed denser, less fluffy and less sticky sediments than the recreation boat washwaters. In the filter, solids from the commercial ship washwater formed a more compact and tractable mass that allowed for greater solids deposition within the interstitial areas.

Finally, the commercial ship water had particles that appeared to be more dense than those from the recreational boat. This higher density would account for a greater solids loading capacity as well.

Prior chemical treatment of the influent also appeared to benefit the solids loading capacity. Effluent TSS was only slightly higher in these filtrates compared to the non-dosed filtrate. COD was comparable for both the dosed and non-dosed filtrates as well. Effluent turbidities, however, were lower in the chemically-treated-filtration effluent, ranging from 22 to 39 ntu.

Effluent particles counts revealed a possible explanation for the better solids loading performance with the chemically treated water. In the 1 - 10 micron range, particle counts in the chemically treated filtrate were 3 times those found in the non-treated filtrate. However, in the next size range, 10 - 40 micron, effluent particle counts in the pre-treated filtrate were 8 times less in number than those in the non-treated water. The alum was evidently able to gather up these mid-size particles via sweep flocculation and cause them to be retained in the coal portion of the filter. The net effect was a more efficient use of the interstitial spaces in the media.

With both dosed and non-dosed influents the volume of solids that accumulated in the coal media appeared identical. This was an encouraging result because it indicated that the selected dose was not producing an undesirable volume of solids that could lead to premature media clogging and fewer runs between backwashing.

Effluent metal concentrations from the dual media filter were significantly higher than they were in the slow sand filtrate. Figure 41(a) shows that for the six major metals found in the influent, copper was regularly

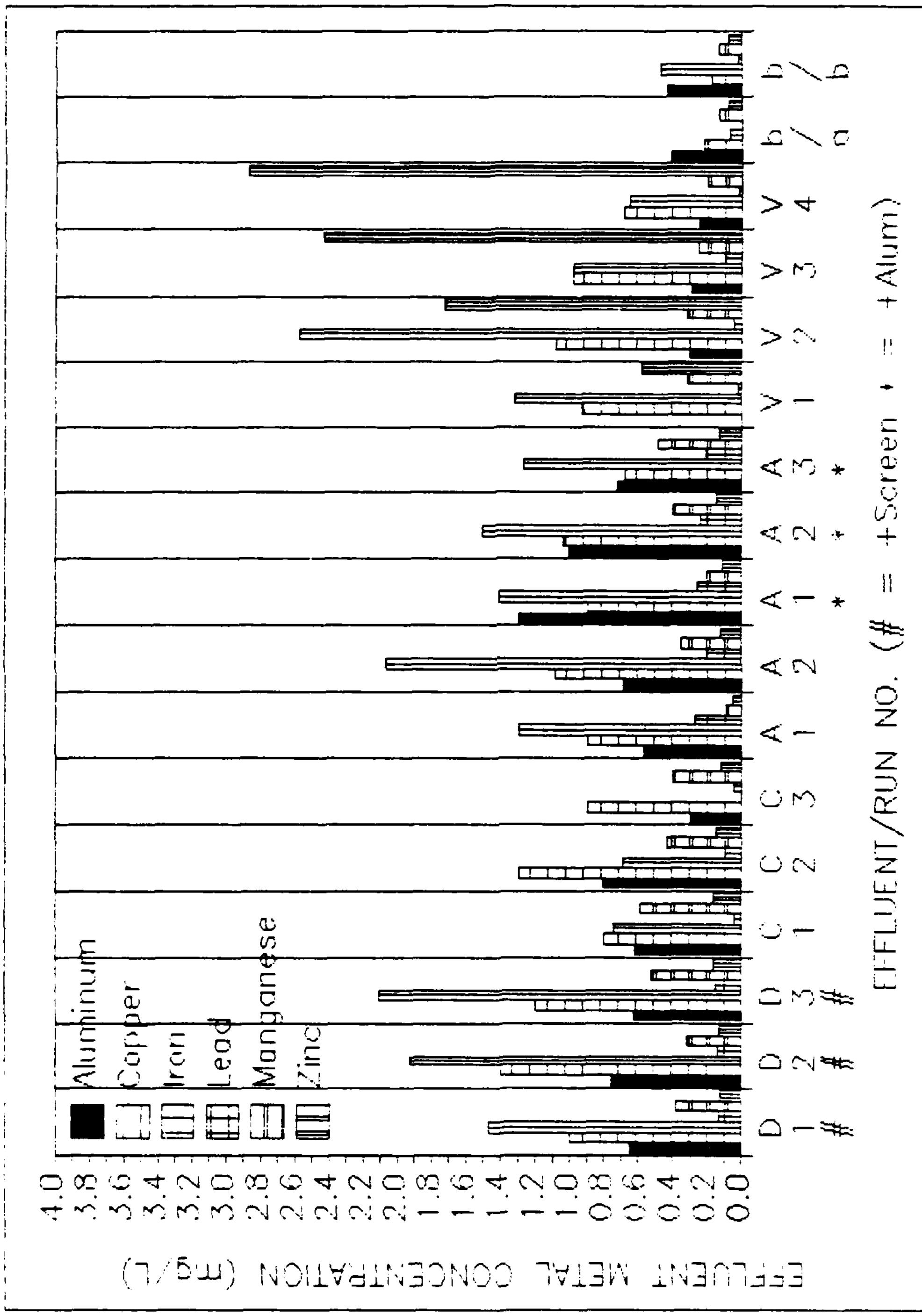


Figure 41(a) - Dual Media Filter- Major Metals in Effluent in the 1 mg/L range and iron was consistently muchhigher than copper, almost 3 mg/L in one case. Zinc was very high in the commercial ship washwater filtrate (designated V1 - V4), between 2 and 3 mg/L. Lead and manganese were generally less than 0.2 mg/L.

Tin was found in significant amounts in several dual media filter effluents between 0.25 and 0.5 mg/L (Figure 41(b). An attempt was made to correlate total tin with tributyltin in one dual media effluent. No TBT was detected in the effluent designated A3* on Figure 41(b) although some tin species were detected with chromatography below 0.1 mg/L (Appendix 4(a)). Yet Figure 41(b) gives some significant information when it is compared to the particle counts in the five effluents where tin was detected. In all five samples the majority of particles in these effluents were under 40 microns in size (fewer than 100 particles total in the 40+ micron sizes). Influent and filtered effluent levels of tin were the same order of magnitude (0.25 - 0.5 mg/L) thus the majority of the tin was associated with the finer particles. This observation was striking, because it indicated that the tin was not predominately associated with the significant number of large paint particles that were visible in the water. Also, soluble tin species were not detected in any of

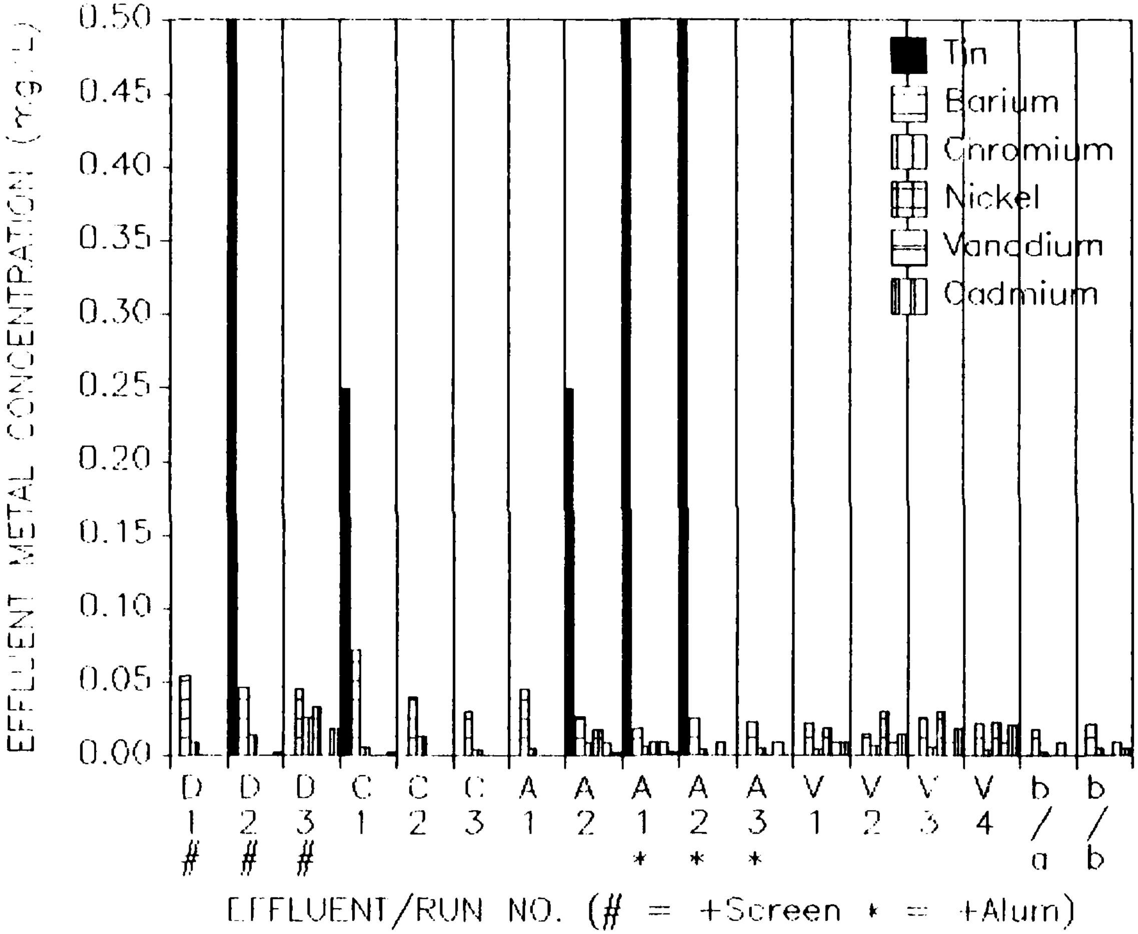


Figure 41(b) - Dual Media Filter- Trace Metals in Effluent the six characterization samples or any of the treated effluents, so tin appeared to be primarily associated with the 1 - 40 micron particle sizes.

Soluble metals in the dual media filter effluent were detected in the same levels as the slow sand effluents with the exception of copper. Soluble copper was measured as high as 0.6 mg/L in one filtrate from a recreational boat washwater. One interesting observation was that copper was present in the filtered effluent of both the commercial and recreational boat washings in comparable amounts regardless of the influent concentrations. It was also noteworthy that soluble copper was higher in the recreational boat washings in spite of having lower influent copper levels than the commercial ship washwater. These observations indicated that copper was generally in two different forms in the two waters. One possible explanation for this is that the algae in the recreational boat washes have solubilized the copper and taken it up in their cells to a significant extent, whereas the copper in the commercial ship washings is likely to still be in its oxidized state, much as it was when it was first added to the anti-foulant paint mixture.

5.2.4 Chemical Treatment

Comparing effluent characteristics with the other treatment methods, alum dosing was the most successful treatment method studied. Effluent turbidity, TSS, VSS, COD, soluble COD, and all major metals' concentrations were significantly lower (or at least comparable) with optimum-dose alum treated waters than the best results obtained with sedimentation, microscreening, slow sand filtration, dual media filtration and any combination thereof.

Results of the three jar tests are best illustrated by the effluent-turbidity-versus-alum-dose graph presented in Figure 42. A wide range of alum doses from 107 to 1073 mg/L resulted in effluent turbidities below 8 ntu, but an alum dose of 107 mg/L (log $[Al_T]$ = -3.5) was found to give consistently good results for all three samples. Referring to Figure 5, this dose is just outside what is called an optimum sweep range, but is safely within an area where the aluminum chemistry permitted good sweep coagulation. As expected from Figure 6, the region of coagulation has widened at the upper dosing range due to the high suspended solids in the influent.

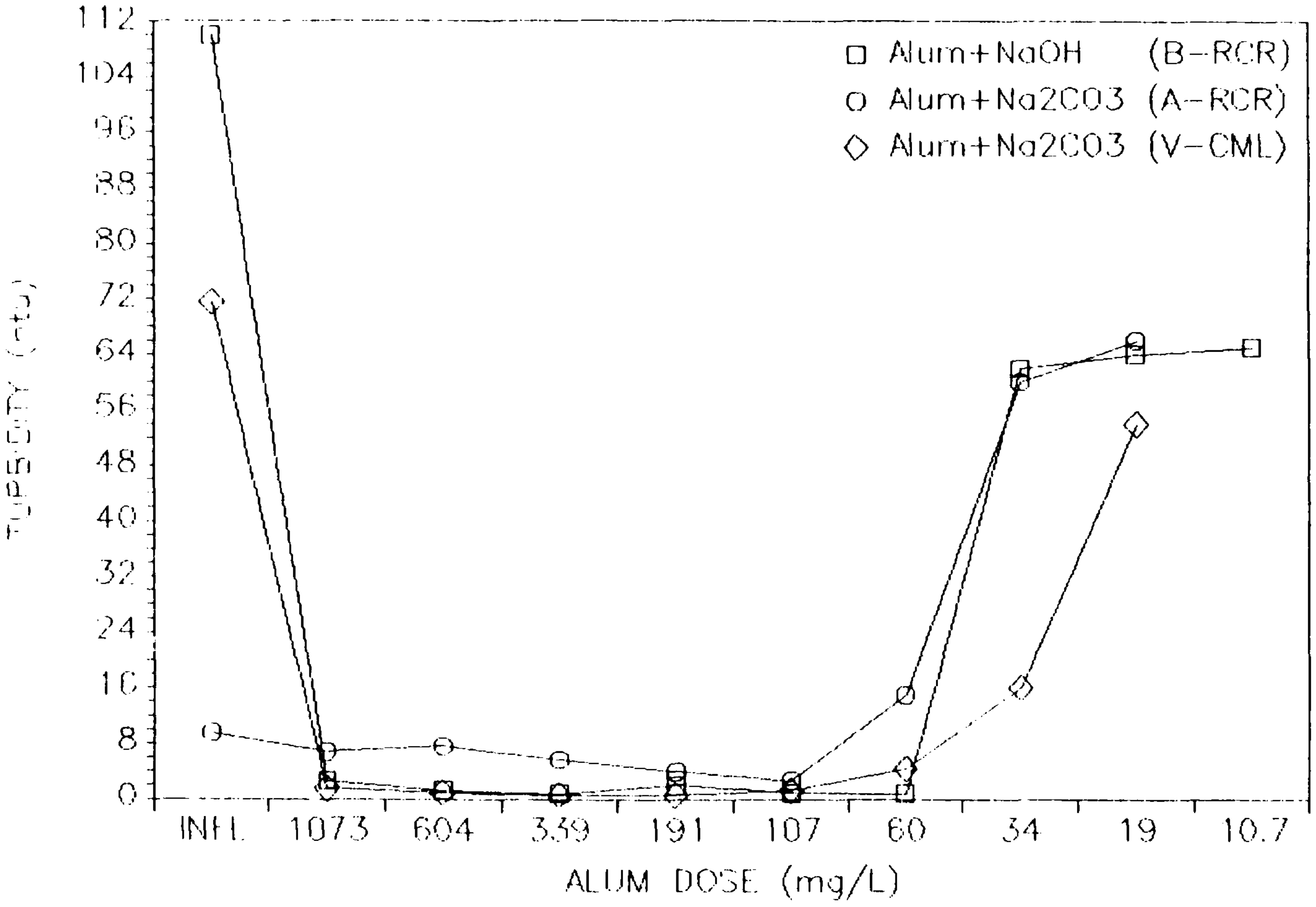


Figure 42 - Effluent Turbidity vs Alum Dose

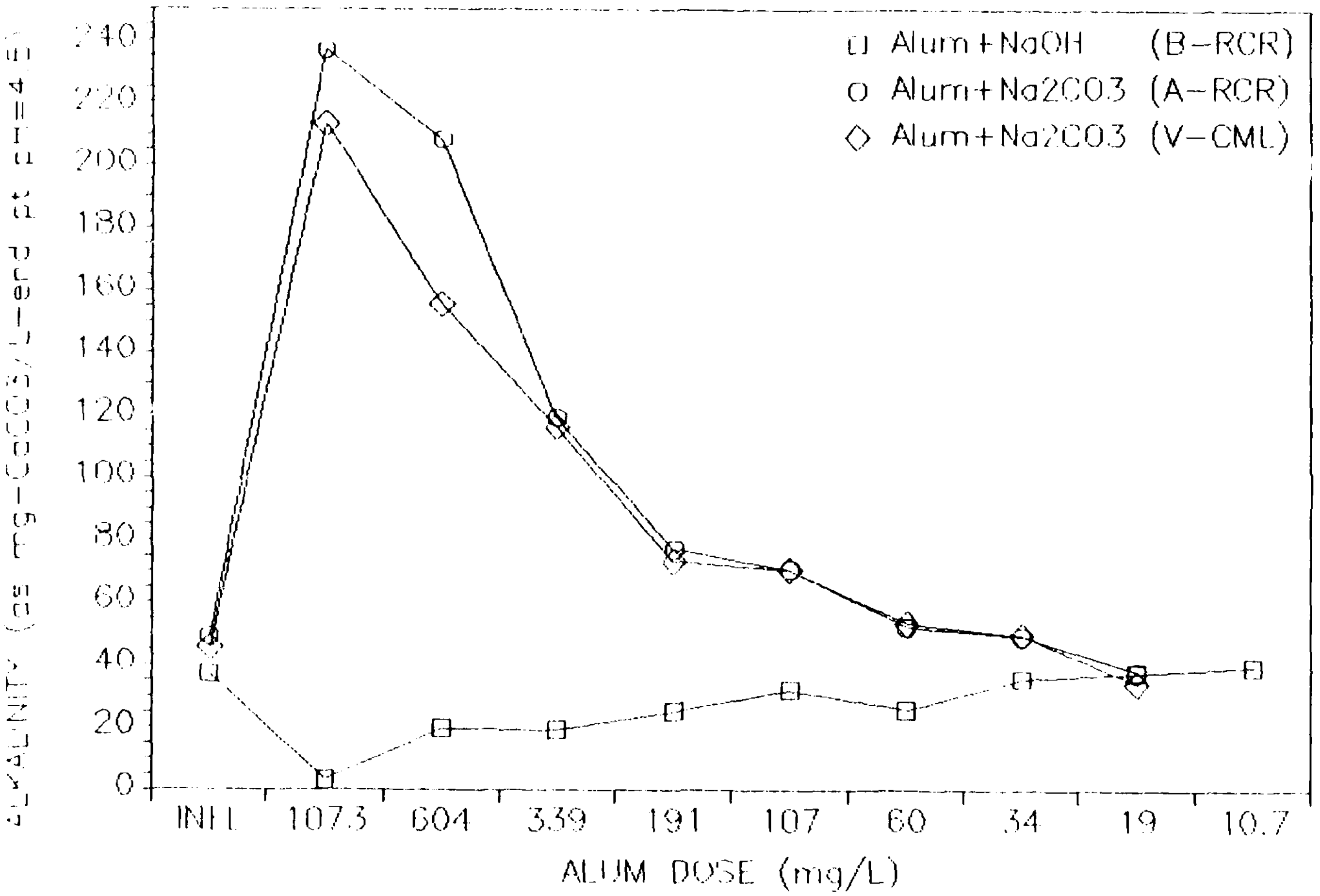


Figure 43 - Effluent Alkalinity vs Alum Dose

In addition to providing desirable turbidities, the 107 mg/L alum dose has the advantage of imparting minimal additional alkalinity in the effluent over what was in the influent (Figure 43). The companion doses of sodium carbonate (refer to Table 7) have the effect of contributing significant alkalinity to the effluent at the higher alum doses.

Generation of sludge is also minimized at lower alum doses (Figure 44). At a dose of 107 mg/L, the sludge volume is only 5 percent of the influent volume after 3 hours of settling. A single hydroblasting of a large commercial ship could generate a water volume as high as 2,500 gallons (Table 11(a)). Thus a dose of 107 mg/L of alum would produce 126 gallons of sludge. By comparison, sedimentation unaided by chemicals would produce 50 percent of that volume or about 62 gallons of solids for the same type of hydroblast wastewater.

As seen from Figures 45, 46(a) and 46(b), effluent TSS, COD and soluble COD were minimized at a dose between 60 and 191 mg/L. However, it was interesting to see that effluent metal concentrations did not necessarily follow this trend. The higher alum doses generally result in lower metal effluent concentrations even if effluent total suspended solids are lower in the low-dose

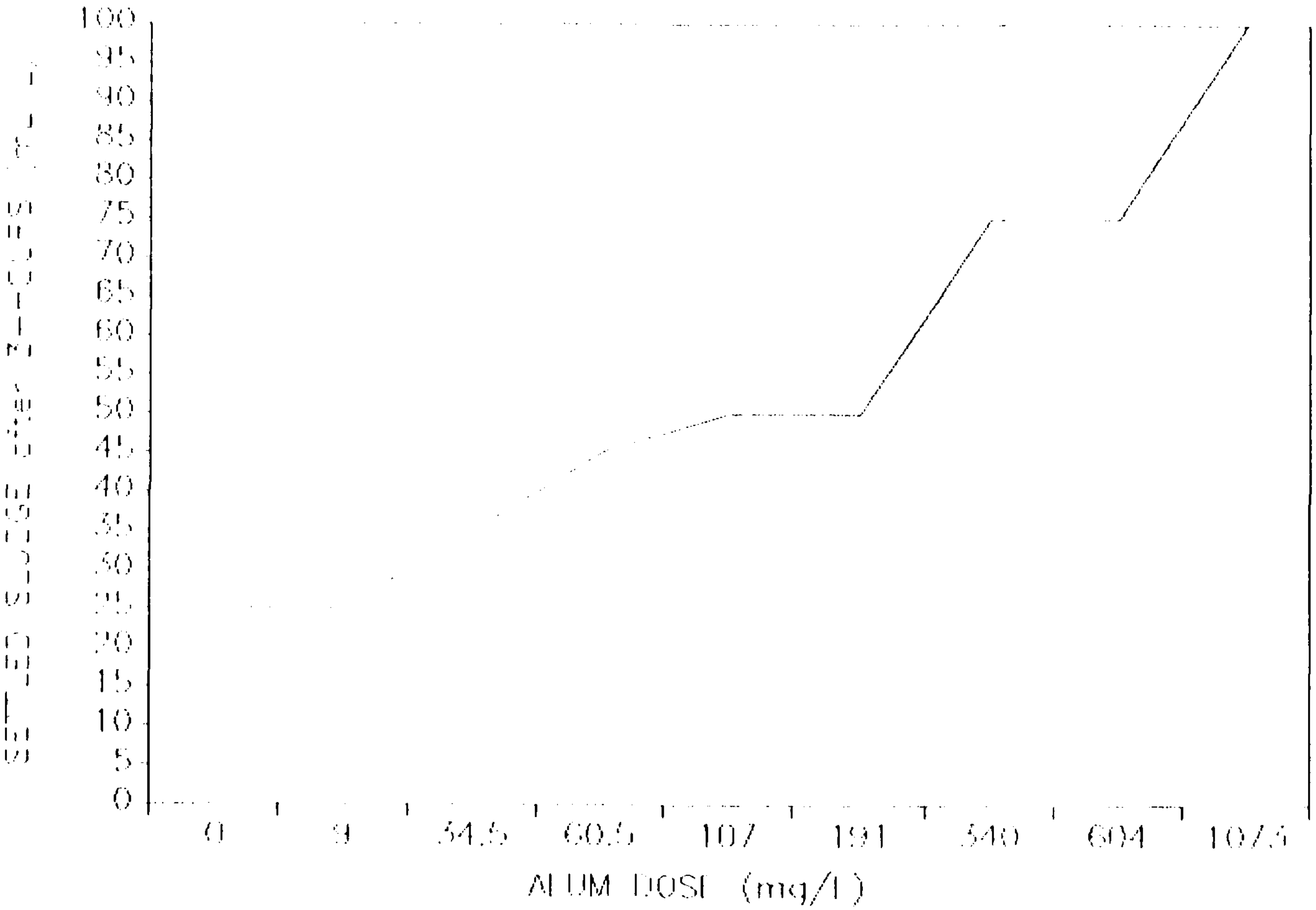


Figure 44 - Sludge Volume Generated vs Alum Dose

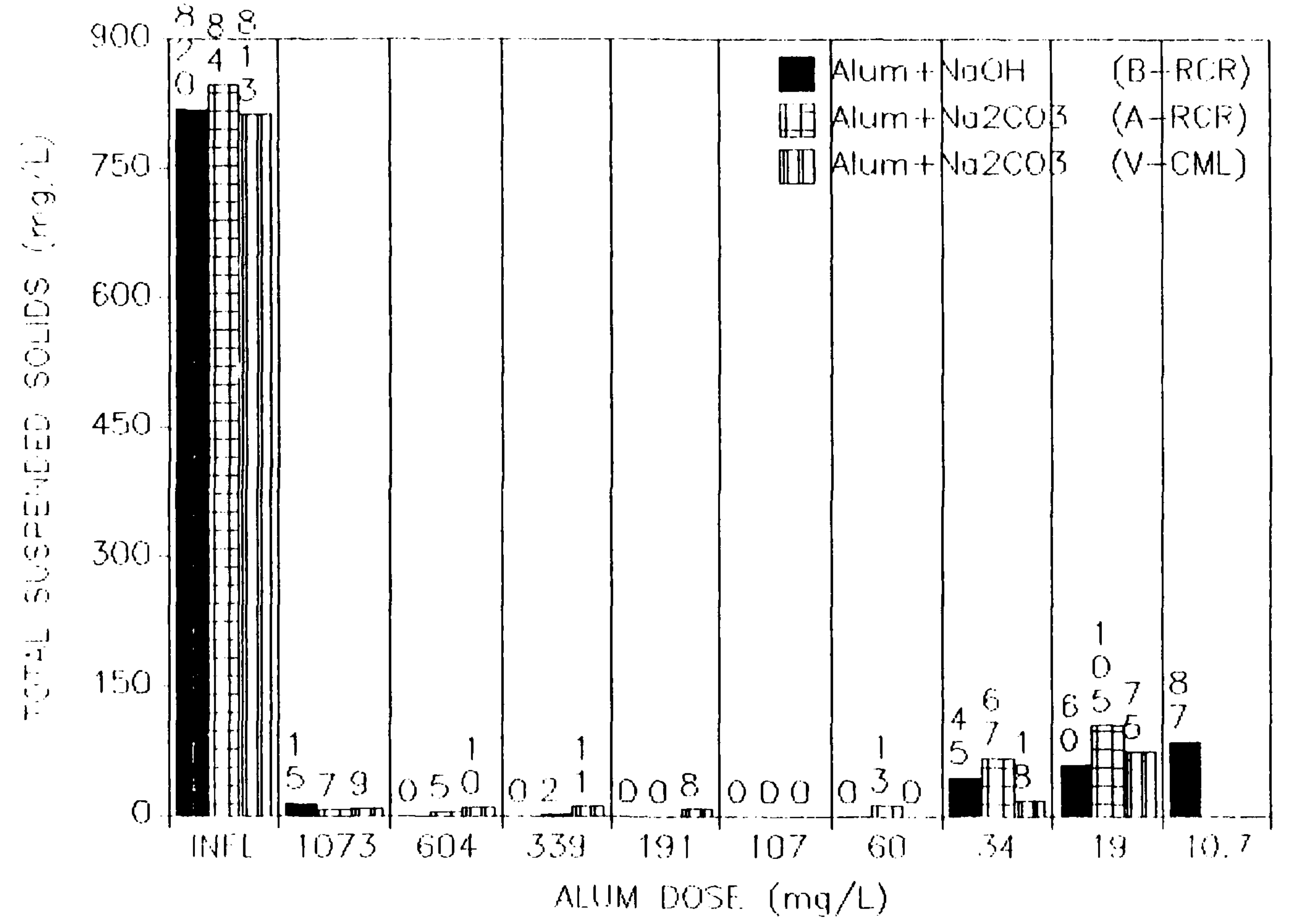


Figure 45 - Chemical Treatment- Influent/Effluent Total Suspended Solids

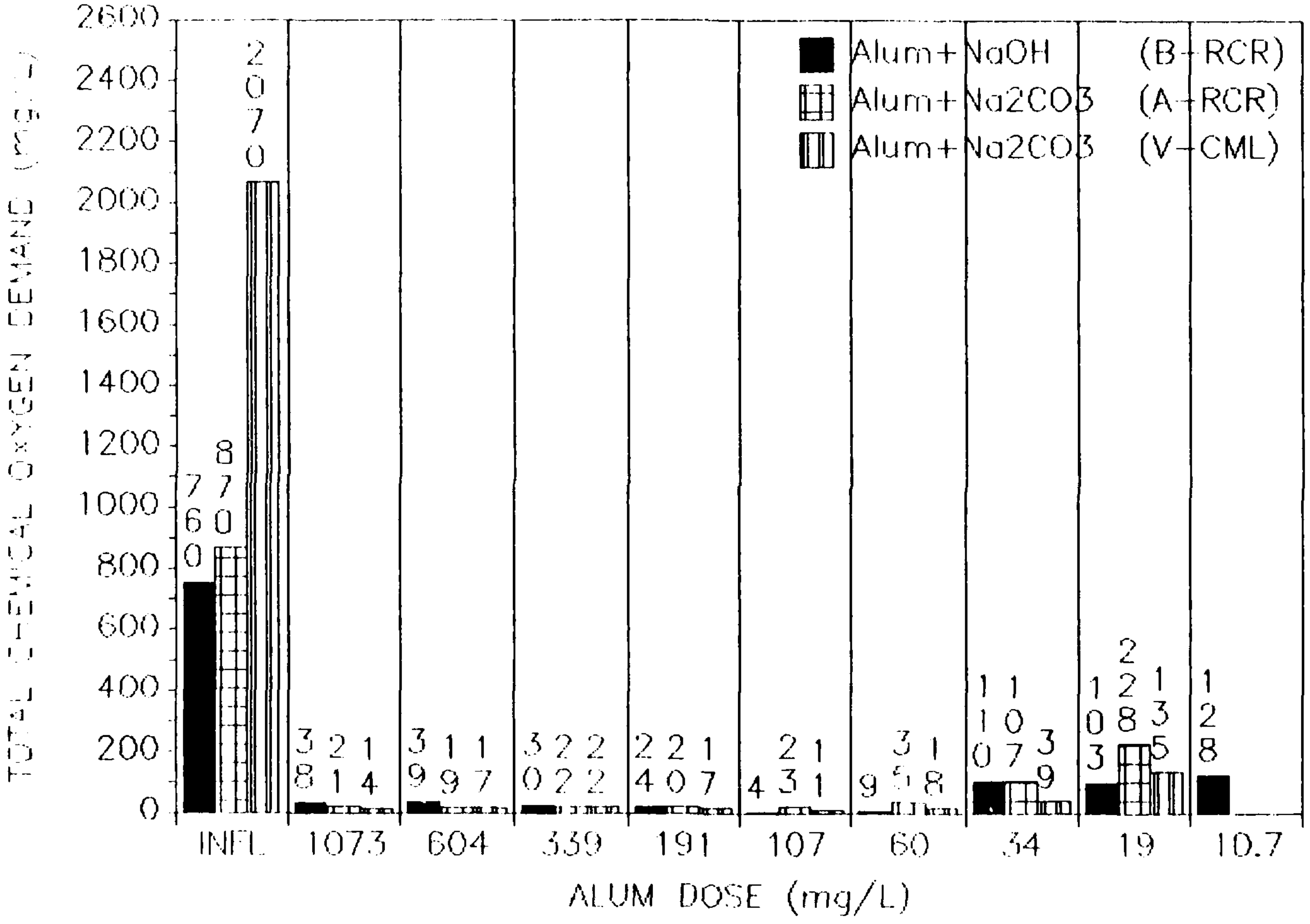


Figure 46(a) - Chemical Treatment- Influent/Effluent Total COD

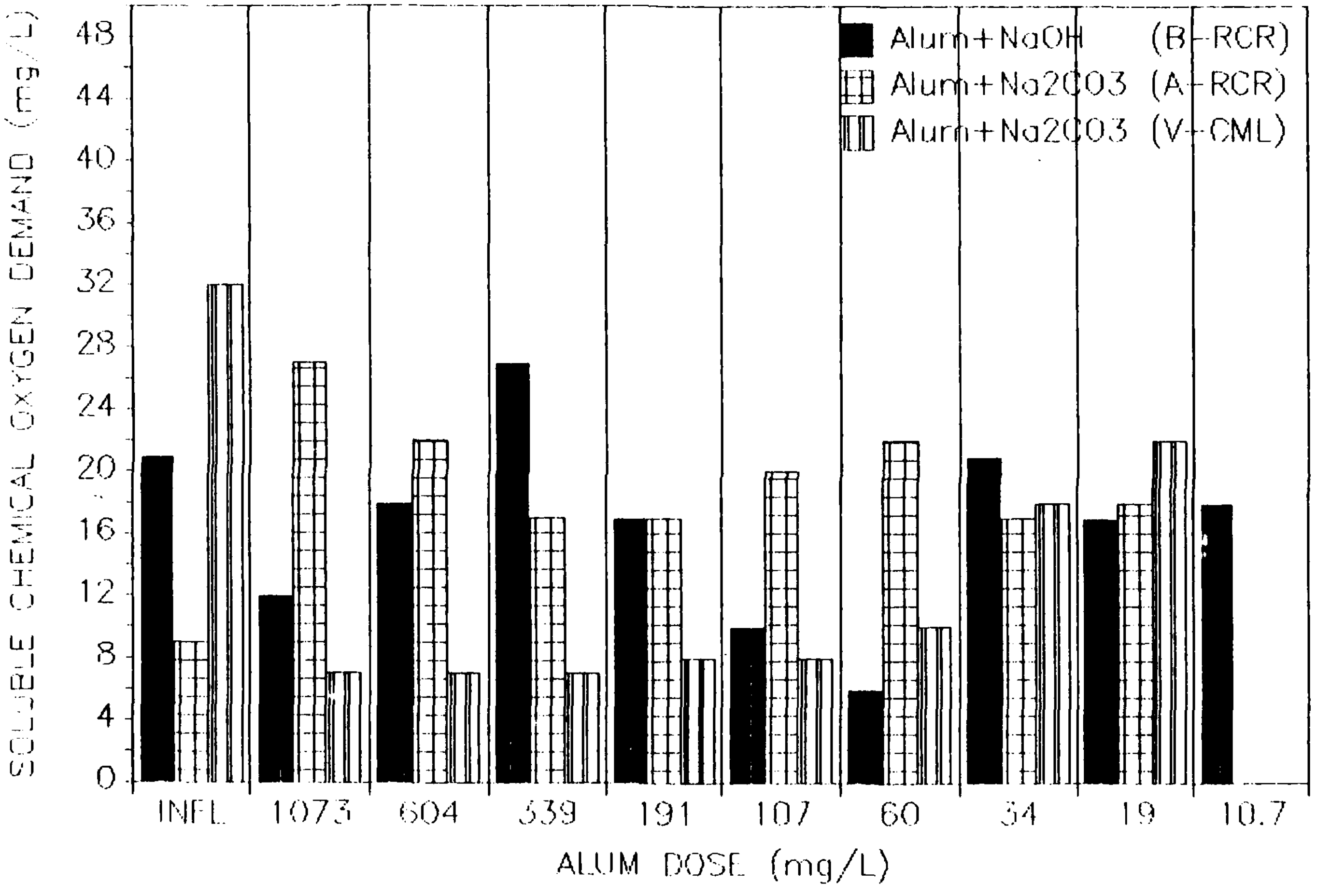


Figure 46(b) - Chemical Treatment- Influent/Effluent Soluble COD

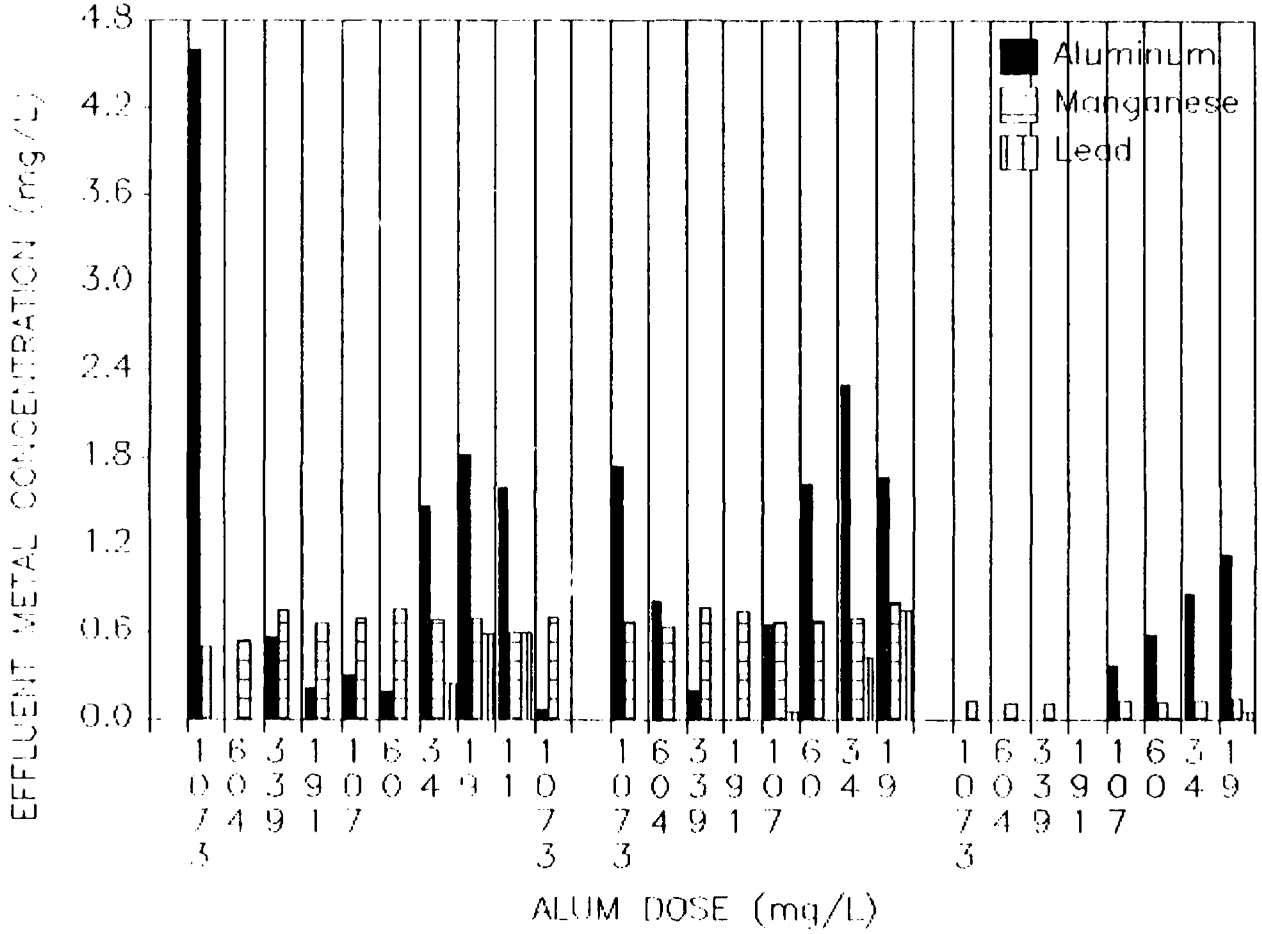


Figure 47(a) - Chemical Treatment- Al, Mn, Pb Levels in Effluent

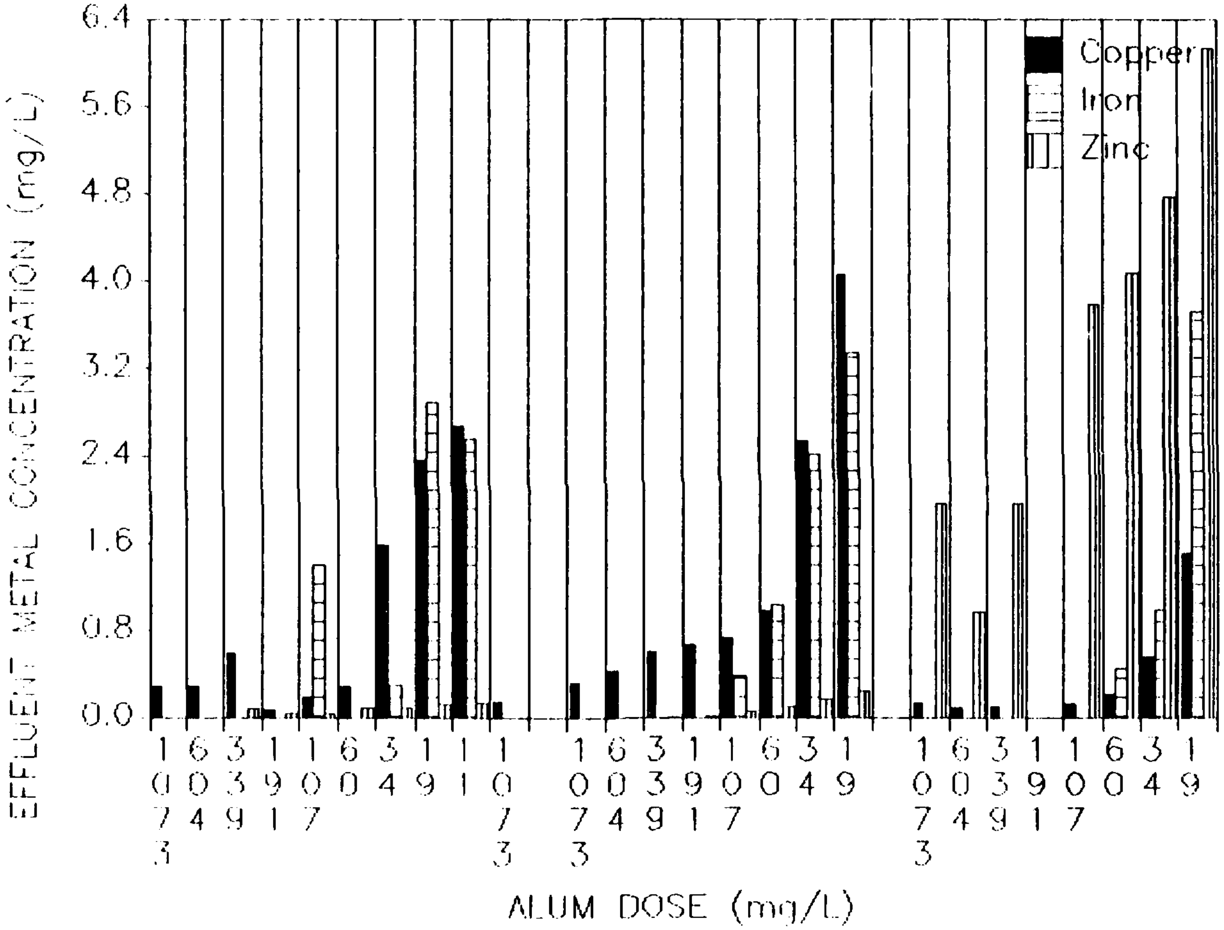


Figure 47(b) - Chemical Treatment- Cu, Fe, Zn Levels in Effluent

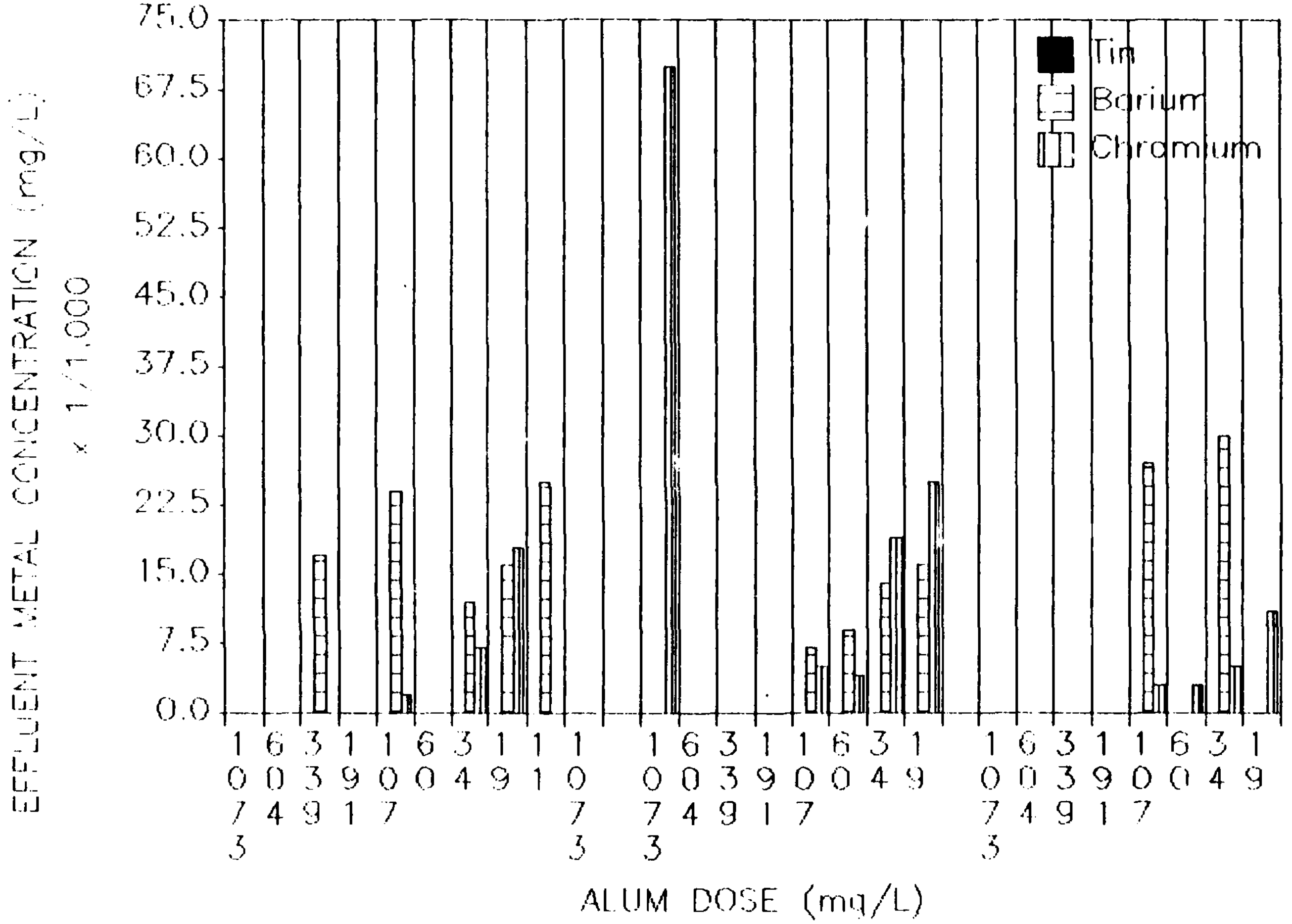


Figure 47(c) - Chemical Treatment- Sn, Ba, Cr Levels in Effluent

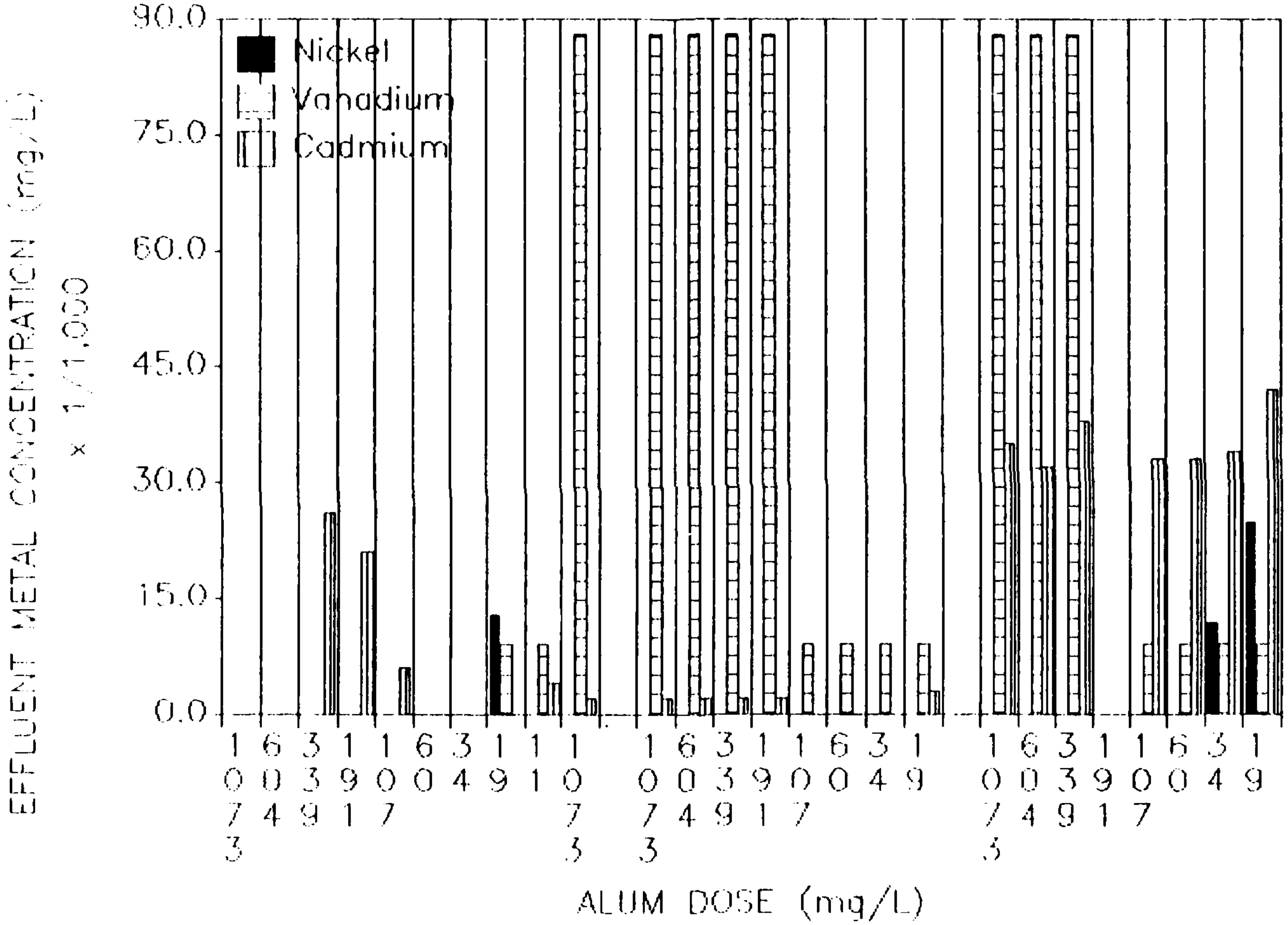


Figure 47(d) - Chemical Treatment- Ni, V, Cd Levels in Effluent spectrum. (This is not the case with the following metals: aluminum, manganese, vanadium, and cadmium.) It is evident from the metal levels in the alum-treated effluents (Figures 47(a) through 47(d)) that along with sweep flocculation, some type of chemical precipitation (likely in the form of metal hydroxides) has taken place for copper, iron, lead, zinc, chromium and nickel. Iron, for instance was not even detected in effluents with alum doses of 197 mg/L and higher. Lead was absent in all effluents in this dose range as well.

Obviously, the chemistry of the various competing reactions was quite complex. Managanese and cadmium are known to form highly insoluble hydroxide precipitates (Montgomery, 1987; Snoeyink and Jenkins, 1980), but both metals appeared in the same relative concentrations in each effluent regardless of the alum dose. Furthermore, how much of the metals were actually in a form that was amenable to chemical precipitation or if their removal was merely incidental to getting caught up in sweep flocculation is not completely clear from the results.

It was difficult to see any pattern emerging for effluent particle count purely as a function of dosage, particularly in the lower particle sizes (< 40 micron). It was clear, however, that all particles were being removed as efficiently as any of the other treatment methods. Particles in the 1 - 10 micron range were consistently 99 percent less than influent counts.

The 10 - 40 micron range, however, was where chemical treatment was more effective than any of the other treatment processes. In this size range, over 99.9 percent reductions were consistently achieved at alum doses greater than 107 mg/L. In fact, it was this size range that appeared to have the greatest effect on effluent turbidities.

A similiar trend had been observed in effluents from other treatment processes: increases in the number of 10 - 40 micron particles were accompanied by increases in effluent turbidity. Even substantial increases in the numbers of other particle sizes did not result in significant changes in turbidity. So it appeared that 10 - 40 micron was a key particle size range for gauging the effectiveness of a treatment method.

Filtration was able to produce effluents low in numbers of particles (e.g. < 10,000 in some cases) in the 1 - 10 micron range, but the lowest effluent turbidity acheived for all filtration processes was 22 ntu and average filtrate turbidities were around 40 ntu.

To illustrate this point, Table 16 compares particle sizes to turbidities for the particle size ranges 1-10, 10-40 and 40+ microns for chemical treatment and filtration effluents. It is clear that the 10 - 40 micron particle size controls the turbidity far more

Table 16 - Particle Size versus Effluent Turbidity

Effluent	Particle Size (microns)			Turbidity
	* 1 - 10	* 10 - 40	* 40+ *	(ntu)
	(no. of particles in 40 mL)			
Slow Sand Filter				
6-2-88	74,702	53,752	355	45
6-3-88	71,701	50,243	34	43
6-3-88	169,052	24,543	45	39
6-4-88	165,409	13,039	101	35
6-4-88	199,132	45,702	92	23
Dual Media Filter				
6-8-88	30,030	67,463	194	72
6-9-88	8,905	68,476	44	70
6-9-88	10,697	73,788	104	62
6-9-88	30,563	65,822	33	59
6-9-88	7,499	66,101	147	72
6-9-88	9,448	68,453	161	67
6-26-88	54,953	43,864	76	47
6-26-88	51,634	45,349	20	48
Chemical Treatment				
6-25-88	301,331	29,402	1,068	6.8
6-25-88	275,861	47,058	2,340	7.6
6-25-88	135,728	22,236	3,434	5.7
6-25-88	64,625	10,860	3,027	4.0
6-25-88	197,093	11,041	907	2.6
6-25-88	296,223	47,787	911	15
6-25-88	7,958	61,470	1,955	60
6-25-88	3,534	51,203	5,433	66
6-30-88	90,024	6,518	435	1.5
6-30-88	112,000	7,010	505	0.85
6-30-88	98,944	4,996	331	0.64
6-30-88	54,449	5,726	409	0.57
6-30-88	27,699	1,220	65	1.2
6-30-88	216,200	9,146	181	4.4
6-30-88	343,502	18,200	427	16
6-30-88	13,420	76,846	1,749	54

than any particle size group. Even 200,000 - 300,000 particles in the 1 - 10 micron range have a negligible effect on turbidity. The turbidity measurement is made by passing white light through the water and measuring the lack of transmittance. Theoretically, this lack of transmittance is proportional to the area of the particles perpendicular to the beam of light. Assuming a relatively uniform particle shape, turbidity, T, will be related to particle number, PN, as the square of the particle number:

$$PN^2 = k*T \qquad (2a)$$

$$\text{or } PN = k*T^{0.5}. \qquad (2b)$$

Figure 48 is a log-log plot of 10 - 40 micron particle counts versus turbidity. The theoretical relationship is plotted as a dashed line and the solid line is the fit of the actual data by linear regression. The theoretical fit is very close to the linear regression fit,

$$PN = (5076)*T^{0.57} \qquad (2c)$$

but there is significant data scatter and the correlation coefficient, r^2, for the curve fit is only 0.67 (r^2 = 1 indicates an exact linear relationship, r^2 = 0 indicates no correlation exists between data). Data scatter is probably attributable to factors such as non-uniform particle size. Nonetheless, Figure 48

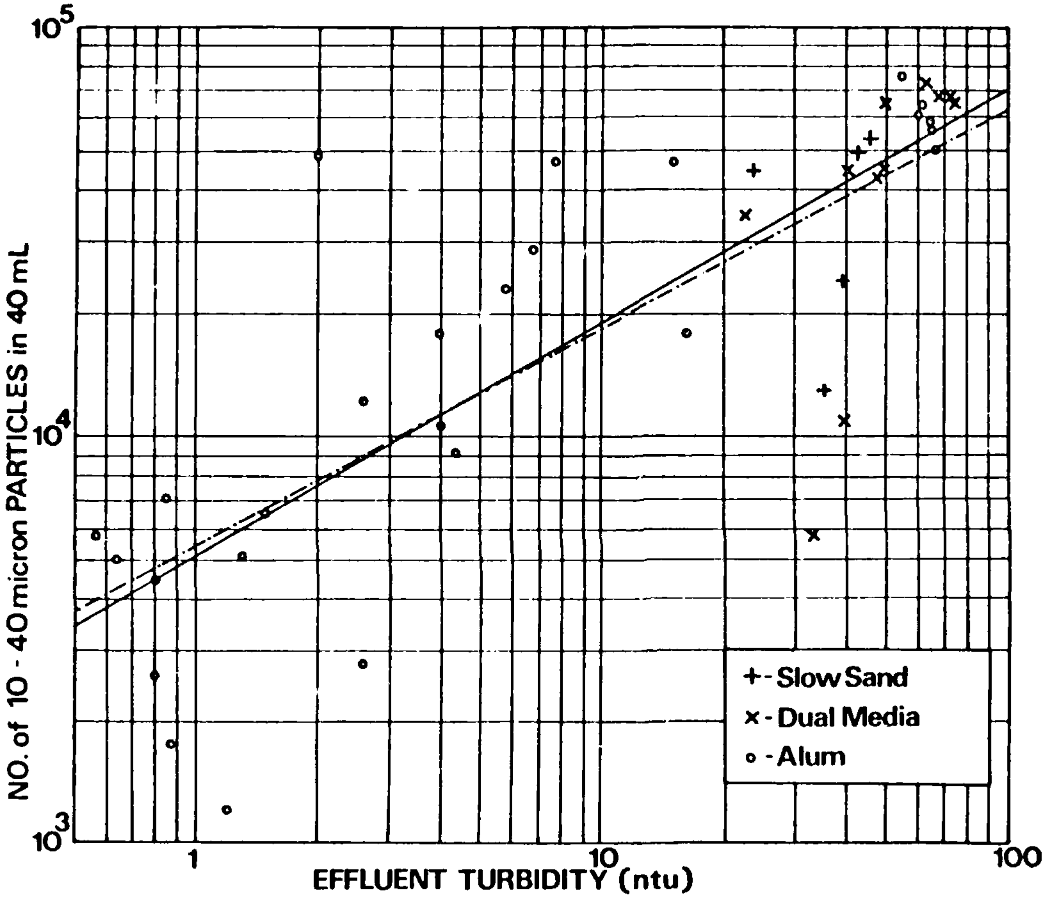


Figure 48 - Relationship Between Effluent Turbidity and Particle Number (10 - 40 micron) with Chemical Treatment and Filtration [Dashed line indicates theoretical relationship, $PN = k*T^{0.5}$, Solid line indicates curve fit by linear regression, $PN = (5076)*T^{0.57}$, correlation coefficient, $r^2 = 0.67$]

indicates that the turbidity and the water quality in general are strongly influenced by the particles in the 10 - 40 micron size range. A quick review of the data in Table 16 confirms that for a given turbidity, wide variations in particle counts are present in the 1 - 10 and 40+ particle size ranges and only the mid-size particle range correlates with turbidity.

5.3 Comparison of Treatment Alternatives

Tables 17(a) and 17(b) summarize the results of the treatability study.

Table 18 lists the advantages and disadvantages of each treatment method studied as well as other possible treatment/disposal alternatives as they pertain to actual implementation at a commercial shipyard or recreational marina. Table 18 does not address the more immediate problem of how to collect the hydroblast wastewater prior to treatment. Whatever method is employed, it will be costly and require considerable initiative on the part of the shipyard operators to operate effectively. The one marina that was studied would actually have the least problem installing a collection system.

Table 17(a) - Summary of Treatability Study: Removal Efficiencies

Treatment	<------Maximum/Minimum Percent Removal------>							
Method	TSS	COD	SCOD	Cu	Fe	Pb	Zn	TBT
	(Percent change, Influent/Effluent)							
SD	92/25	n/m	n/m	90/53	83/56	81/49	80/30	n/m
SC	20/9	8/7	26	36	16	28	48	n/m
SC+SF	99/98	96/92	41/11	98/97	100/84	98/95	97/83	n/m
DMF	99/93	93/81	50/0	97/94	99/88	97/95	93/86	n/m
SC+DMF	95	91	19	96	88	94	89	n/m
CH/DMF	97	94	0	97	93	96	88	100
CH*	100	99/97	71/0	98/97	100/91	100/95	97/89	33

Legend: SD = Sedimentation SC = Screening
SF = Sand Filter DMF = Dual Media Filter
CH = Chemical (Alum) Treatment, * 107 mg/L
n/m = not measured

Table 17(b) - Summary of Treatability Study: Effluent Quality

Treatment Method	TSS	Cu	Sn	TBT	Turbidity
	<------Maximum/Minimum Effluent Level------->				
	(All expressed as mg/L of the parameter- except turbidity expressed as ntu)				
SD	610/50	62/0.1	1.5/0	n/m	90/32
SC	840/740	15	0.25/0	n/m	66/45
SC+SF	20/9	0.6/0.2	0.25/0	n/m	45/23
DMF	61/8	1.3/0.7	0.50/0	n/m	72/36
SC+DMF	61/48	1.4/1.0	0.50/0	n/m	72/62
CH/DMF	30/24	1.0/0.7	0.50/0	0.000	39/22
CH*	0	0.6/0.1	0.0	0.050	2.0/0.8

Legend: SD = Sedimentation SC = Screening
SF = Sand Filter DMF = Dual Media Filter
CH = Chemical (Alum) Treatment, * 107 mg/L
n/m = not measured

Table 18 - Hydroblast Treatment/Disposal Alternatives

Alternative	Advantages	Disadvantages
Continue Current Best Management Practices	-No additional cost	-Possible long term water quality degradation, particularly at shipyards
Sedimentation	-Simplest operation -Least cost to construct/maintain batch settling unit	-Least desirable effluent quality: particularly metals, TSS and turbidity
Screening	-Simple operation -Easy to add to as pre-treatment step	-Can only be used in conjunction with other treatments -Frequent backwashing required- some electro-mechanical equipment needed
Sand Filter	-Simple operation (no moving parts) -Good TSS, metals removal -No requirement for intermediate storage of effluent	-High turbidity effluent -Frequent backwashing e.g. every run -High solids loading results in hard-to-clean media -Higher maintenance costs than settling unit alone -Backwash tank requirements might be significant
Dual Media Filter	-Simple operation (no moving parts) -Good metals removal -Less frequent backwashing than slow sand filter due to higher solids loading capacity of media -Easier to clean coal media	-High turbidity, moderate TSS in effluent -Higher maintenance costs than settling unit alone -Higher initial capital costs for media and columns -Less effective with recreational boat washwater

Table 18 - (Continued) Hydroblast Treatment/Disposal Alternatives

Alternative	Advantages	Disadvantages
Dual Media Filter	-Appears most effective in TBT removal	-Backwash water tank could be prohibitive in size -Harder to handle waste solids than sedimentation tank
Chemical (Alum)	-Best effluent quality: low turbidity low metals -Easier handling of sludge than filters -Influent quality has little effect on effluent; wider application possible between varying operations and sites	-Higher volume and mass of waste solids -Higher operator skill and interest needed -Electro-mechanical equipment required -Higher operation cost than settling unit alone -Storage requirements for chemicals -Monitoring of pH and mixing speed needed to get predictable results -May not be effective for TBT removal
Biological (disposal to municipal waste treatment facility)	-No on-site treatment required -One time cost of constructing drainage system -Good TBT removal in activated sludge for low influent concentrations (100 ug/L)	-Extensive re-piping of sanitary sewer drains may be needed -Possible problems with high metals and and TBT in waters-accumulation in waste sludges likely (Municipal treatment facility may request pre-treatment)

By virtue of the limited dispersal and small volumes of water generated at these facilities, it is judged that any marina servicing boats in the 30 - 40 ft class would be able to construct a collection system at minimal cost. With only 60 - 100 gallons of water generated by a single washing, it would be simple to construct a shallow concrete dike for the collection with a small pump to transport the water to a small batch treatment unit.

The U.S. Navy has considered the possibility of water reuse for possible future wet blasting operations (Adema et al, 1984). This method employs a special tool that blasts the hull and immediately retrieves the water for filtration and re-use. This would entail the purchase of new equipment and very likely would increase the labor costs for hull preparation, but it would eliminate the need for large settling tanks and filtration columns and only solid waste disposal would then be a consideration.

For the short term, it would be necessary for the drydocks to be fitted with small dikes (such as those now employed at Foss shipyard) to plug any existing drains or crevices that offer an escape route and install a number of pumps to remove the hydroblasting water at the many and various locations it naturally runs to. A portable water "sweeper" following behind the hydroblasting operator would be another alternative for consideration. In principle, this latter idea would not be much different from the Best Management Practice of sweeping up the dry blasting grit following each hull cleaning by that method.

Another alternative, which the U.S. Navy has employed, is to ban or limit the practice of hydroblasting. This, however, carries negative environmental consequences itself. Dry grit blasting would be the only alternative to hydroblasting and it is capable of generating considerable volumes of waste as well. As already pointed out, this dry grit contains paint waste that can easily become waterborne due to the infrequent cleaning of the drydock deck. Plus, dry grit blasting is a more immediate health hazard to the operator because of the dust and noise generation.

Any hydroblast water collection system would have to be designed on a case by case basis for each site. As pointed out in the field investigation, some sites would be more amenable to constructing collection systems than others. The possibility of co-locating a collection and treatment system such as screens and a settling tank appears possible in a case such as Union Bay (Figure 10(b)), but would be much more difficult and possibly undesirable at a drydock where the workers must walk in the area where the water would collect.

The volumes of water generated from each site would also have to be considered. At Marco, for example, it was estimated that one large ship washing might generate on the order of 2,500 gallons. Thus if the tank is dosed, mixed and discharged once a week, at a rate of three washings per week, a 8000 gallon tank would be sufficient to act as either a settling and/or chemical treatment tank. A 5-ft high tank of this size would have a footprint of approximately 14-ft x 15-ft, which is not unreasonable. However, at Foss, the same washing (approximately 6 hours) would generate 5,400 gallons. Based on the same scenario just described, a tank volume of approximately 18,000 gallons would be necessary and the tank would take up an area 22-ft x 22-ft. Additionally, with the larger tank more mixing units would be necessary to get the appropriate water-chemical-solids contact that is critical to the alum coagulation.

In the case of an operation like Foss Shipyard where the quantities of water are significantly greater, a rapid direct filtration offered by dual media filtration might be considered because no accumulation of hydroblasting water is necessary. Based on the 5,400 gallon water volume just mentioned, a filtration tank with 12-in of sand and 12-in of coal and a maximum hydraulic loading of 4 ft, would require an 8-ft high, 15-ft in diameter filter. However, the backwash water applied every third or fourth filtration could be significant. Assuming a backwash rate of 18 gal/min-ft^2 for 15 minutes, the necessary water volume would be 54,000 gallons, 10 times the initial influent volume. This water would require its own settling chamber to remove solids. Although this study did not really address backwash requirements, this illustration clearly serves notice of potential drawbacks to granular media filtration.

Finally, before any type of collection or treatment of hydroblast wastewater is considered, one should compare the effects of the hydroblast waste generation versus the direct leaching of the biocides and heavy metals (e.g. chromium) from the ship hull (refer to Table 12). Clearly the quantity of biocides and metals released from a ship hull by leaching is enormously greater than by hydroblasting. This comparison does not diminish the potential impact of hydroblasting on the environment, but is offered as a means of gauging hydroblasting's contribution to the overall problem posed by the use of anti-foulant paints on ship and boat hulls.

CHAPTER 6

CONCLUSIONS

6.1 Characterization of Hydroblast Wastewater

1. Two types of hydroblast waters were encountered and were defined based on theri origin: fiberglass-hull tributyltin-painted recreational boats and steel-hull cuprous-oxide-painted commercial ships.

2. Commercial ship hull washings were generally higher in total and volatile suspended solids, higher in total and soluble chemical oxygen demand and had higher turbidities than the recreational boat washings. Total suspended solids in both waters was generally above 700 mg/L. Chemical oxygen demand was normally above 800 mg/L. Soluble chemical oxygen demand was usually less than 50 mg/L.

3. Six major metals found in washwaters from both sources were aluminum, copper, iron, lead, manganese, and zinc. Total tin was found in both waters within the same order of magnitude, but generally was under 0.5 mg/L.. Aluminum, manganese and lead were higher in the recreational boat washings than in the commercial ships' washwaters. Conversely copper, iron and zinc were

higher in the commercial ship washings. The source of these metals appeared in all cases to be the anti-foulant hull paints.

4. Particle size distribution in the two waters was not distinctly different between 1 - 40 microns. Above 40 microns, the recreational boat waters had higher particle counts than the commercial boat waters. The larger numbers of 40+ micron particles in the recreational boat washings appeared to consist largely of paint chips.

5. Dissolved particles (< 1 micron) did not appear to contribute significantly to the water characteristics in either type of washwater. In a few cases, soluble metal concentrations for copper, iron and zinc exceeded 1 mg/L, but most soluble metals were at levels well under 0.1 mg/L. The consistently low soluble chemical oxygen demand indicated very little dissolved organic material was present in the waters as well.

6. Tributyltin is present in washings from the boat hulls painted with this type of anti-foulant paint. A total of 75.2 ug/L of TBT was detected in one wash sample, but the analytical method was designed only for detecting the soluble species. Total tin appeared to be

associated primarily with with the solid phase. Insufficient analytical resolution was available to track tin as carefully as other metals present in the waters. The single sample analyzed for tributyltin does not provide an adequate body of data to make clear conclusions regarding the fate of the TBT. Nonetheless, based on the ratios of Sn/Pb and TBT/Sn-total found in the washwaters, much of the original TBT appeared to have leached from the paint and a significant amount of degradation to other tin species appears to have occurred.

6.2 Treatability of Hydroblast Wastewater

1. Sedimentation does not appear to be an efficient treatment method for either type of wastewater. This is due to the large number of particles that are present in the size range of less tham 40 microns where settling is unlikely to occur. This is also affected by the low density of the majority of the solids.

2. Screening is only effective as a pre-treatment step because most of the particles are too small to be effectively screened out. However, screening does remove larger and more rigid particles where a higher

proportion of metals are found. This indicates that the paint chips are being screened out more efficiently than the other solids which appear to be primarily algae.

3. Sand filtration achieved 99 percent removal of total suspended solids, 98 percent removal of chemical oxygen demand and 97+ percent removal of major metals. However, effluent turbidities ranged from 23 to 45 and effluent suspended solids were about 15 mg/L. Undesirable operating features such as frequent media removal or backwashing due to rapid media clogging make it an ill-suited treatment method for these high TSS waters. Tests with baffles to capture settleable solids inside the filter column showed that pre-settling of the influent would still result in similar operational problems due to media clogging.

4. Dual media (anthracite coal/sand) filters produce an effluent comparable to the slow sand filter, although slightly higher in turbidity and suspended solids. They are more favorable than slow sand filtration from an operational standpoint because their solids loading capacity is significantly higher and their media are easier to clean during backwashing. Pre-treatment steps such as screening and chemical treatment with alum appear effective at increasing the dual media filter's

ability to accumulate solids and thereby operate more efficiently.

5. Chemical treatment with aluminum sulfate (alum) performs better than any treatment process that was studied. Reductions in total suspended solids approached 100 percent, chemical oxygen demand removal reached 99 percent and soluble chemical oxygen demand was as high as 71 percent within an an optimum dose range of 60 - 197 mg/L alum and a pH of 7, regardless of the influent water characteristics.

6. The critical particle size range that relates to treatments effective for these waters is 10 - 40 micron. This particle size range has a measurable effect on effluent turbidity. A relationship between effluent turbidity, T, and particle number of 10 - 40 micron particles, PN, was found similar to the theoretical relationship, $PN = k*T^{0.5}$, as

$$PN = (5076)*T^{0.57} \qquad (2c)$$

Thus the removal of 10 - 40 micron particles proved to be the critical feature of successful treatment of the hydroblasting waters.

6.3 Treatment Alternatives

1. Of all the methods included in this study, alum dosing in the range of 60 - 197 mg/L offers the highest level of treatment performance for on-site hydroblast wastewater treatment. A mixing and settling tank would be a straightforward design effort based on known water volumes and hull-washing schedules. However, this treatment has certain drawbacks including handling and disposal of a large sludge volume (compared to settling alone) and requires greater operator time, skill and interest to be effective. Because iron salts produce a smaller sludge volume than alum, they should be considered in a chemical treatment process.

2. More simplified treatment systems, such as a settling tank require less operator time and skill and would be less costly to construct and maintain, but a lower quality treated effluent will result from such a scheme.

3. High rate direct filtration such as a dual media granular filter may be a more desirable treatment option where lower TSS waters are generated in higher volumes and space limitations make large settling tanks impractical. However, backwash requirements for this

process could generate water volumes well in excess of the original influent volume. Backwash water would eventually require separation of suspended solids thus introducing another treatment step into the overall process. Backwash requirements must be well understood before this process is implemented.

4. Efficient collection of the often highly dispersed hydroblast wastewater may be the most significant obstacle to designing an effective treatment system at sites servicing larger vessels. Possible methods, involving water recycling, containment dikes, fixed or portable pumping arrangements would add to the cost and time involved in hydroblasting ship hulls and would have to be adapted to each site's space and operational constraints.

4. Disposing of the wastewater in the sanitary sewer system should be considered as a treatment alternative, particularly when small wastewater volumes such as those generated by a marina are involved. The soluble tributyltin concentrations evident in the marina hydroblast waters are significantly less than those successfully treated in a pilot study at an activated sludge treatment facility.

5. Prior to implementing any treatment system at any site, consideration must be made for hydroblasting's relative contribution to the environmental impact of anti-foulant hull paints. Hull washings from smaller recreational boats release tin into the aquatic environment in an amount conservatively estimated to be 15,000 less than the amount leached directly from the hull. A conservative estimate of the amount of copper released in a single washing of a large commercial vessel indicates that it would take up to 150 washings to equal one year's leaching of the paint from the hull.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORK

1. Further characterization of the hydroblast waters from both sites (shipyards and marina), as well as the treated effluents is needed to determine actual tin concentrations, speciation and partitioning.

(a) The amount of the tin in the shipyard washings which is the highly toxic tributyltin is unknown.

(b) The amount of tributyltin that has degraded into other species such as dibutyltin, monobutyltin and inorganic tin is not known.

Analytical procedures for both total tin and organotin species should be developed and fully operational prior to pursuing any future work. Separate procedures to analyze tributyltin associated with both the solid and aqueous phases must be used.

2. Because hydroblasting is a concentrated and localized discharge its impact should be felt predominantly in the waters and sediments surrounding the shipyards and marinas. It would be useful to have metal and tributyltin levels for these waters and

sediments to determine how the hydroblasting water compares and possibly contributes to these contaminant levels.

3. If state or federal regulatory agencies deem it necessary to treat the discharges from hydroblasting operations, a pilot study should be conducted to determine the following:

(a) The most efficient means of collecting the hydroblast water, particularly in the case of a drydock where large vessels, a large deck area, uneven deck surface and highly dispersed water present a particular challenge

(b) Whether reasonably sized tanks, say under 8,000 gallons (portable when empty), could effectively serve a medium size shipyard, either as sedimentation tanks or chemical treatment mixing/settling tanks. Floating tanks that will not exacerbate existing shipyard space problems should also be considered

(c) Whether the sludges generated from either a settling tank, granular media filter or chemical treatment unit would be treated as a hazardous waste or as solid waste suitable for landfill by performing EP toxicity tests on the sludge

(d) Whether further optimization is possible in terms of chemical doses for alum dosing/rapid mix processes or dual media filter and if iron salts could also be be used to reduce sludge volumes

(e) Whether simple post-treatment operations such as activated carbon after chemical treatment can further improve water quality, particularly in the removal of tributyltin and soluble metals

(f) What methods of separating and collecting the waste sludge would be most feasible given the highly variable nature of shipyard operations and the wide range of water volumes generated by hydroblasting

REFERENCES

Adema, C. M. and Schatzberg, P., (1984) **Naval Engineers Journal**, p. 209-217, May 1984

Amirtharajah, A. and Mills, K. M., (1982) **Journal of the American Water Works Association (JAWWA)**, p. 210-216, April 1982

Analytical Chemistry, (1986) 58:4, April 1986, p. 590A

Argaman, Y., Hucks, C. E., and Shelby, S. E., (1984) **Water Research**, 18:5, p. 535-542, 1984

Avendt, R. J. and Avendt, J. B., (1982) "Performance and Stability of Municipal Activated Sludge Facilities Treating Organotin-Contaminated Wastewater", David Taylor Naval Ship Research and Development Center Report SME-CR-29-82, December 1982

Battacharyya, D., Adema, C. and Jackson, D., (1981) **Separation Science and Technology**, 16:5, p. 495-503, 1984

Baumann, E. R. and Huang, J. Y. C., (1974) **Journal of the Water Pollution Control Federation (JWPCF)**, 46:8, p. 1958-1973, August 1974

Bellamy, W. D., Hendricks, D. W., and Logdson, G. S., (1985) **JAWWA**, December 1985, p. 62-66

Cardwell, R. D., (1988) "Water Quality Issues in the Shipbuilding and Ship Repair Industry 'Balancing the Economy with the Ecology', Seattle, Washington, 23 May 1988 (from Symposium Overview)

Clark, E. A., Sterritt, R. M., and Lester, J. N., (1988) **Environmental Science and Technology (EST)**, 22:6, p. 600-604, 1988

Cleasby, J. L., Hilmoe, D. J., and Dimitracopoulos, C. J., (1984) **JAWWA**, December, 1984, p. 44-55

Eckenfelder, W. W., (1966) Industrial Water Pollution Control, McGraw-Hill Publishing Co., 1966

Fassel, V. A., (1978) **Science**, 202:13, p. 183-191, October 1978

Habibian, M. T. and O'Melia, C. R., (1975) **Journal of the Environmental Engineering Division**, ASCE, 101:EE4, p. 567-583, August 1975

Hodson, P. V., Borgmann, U., and Shear, H., (1979) "Toxicity of Copper to Aquatic Biota", Copper in the Environment, Ed. J. O. Nriagu, John Wiley and Sons, Inc., 1979

James, D. M., (1975) "Marine Paints", Treatise on Coatings/Volume 4, Formulations, Part I, Eds. R. R. Myers and J. S. Long, Marcel Dekker, Inc., 1975

JWPCF, (1988) 60:3, p. 289-290, March 1988

Kavanaugh, M. C., Tate, C. H., Trussel, A. R., Trussel, R. R., and Treweek, G., (1980) "Use of Particle Size Distribution Measurements for Selection and Control of Solid/Liquid Separation Processes", Particulates in Water, Characterization, Fate, Effects and Removal, ACS Advances in Chemistry Series 189, 1980

Laughlin, R. B., Guard, H. E., and Coleman, W. M., **EST**, (1986) 20:2, p 201-204, 1986

Lawler, D. F., O'Melia, C. R., and Tobiason, J. E., (1980) "Integral Water Treatment Plant Design: From Particle Size to Plant Performance", Particulates in Water, Characterization, Fate, Effects and Removal, ACS Advances in Chemistry Series 189, 1980

Levine, A. D., Tchobanoglous, G., and Asano, T., (1985) **JWPCF**, 57:7, p. 805-816, July 1985

Maguire, R. J., Chau, Y. K., Bengert, G. A., and Hale, (1982) **EST**, 16:10, p. 698-702, 1982

Maguire, R. J., (1984) **EST**, 18:4, p. 291-294, 1984

Maguire, R. J., (1986) in "Proceedings of the Organotin Symposium, Oceans 86", Marine Technology Society, Washington, D. C., Vol. 4, p. 1252-1255

Matthias, C. L., Bellama, J. M., Olson, G. J., Brinckman, F. F. (1986) **EST**, 20:6, p. 609-615, 1986

Metcalf and Eddy, Inc., (1979) Wastewater Engineering Treatment/Disposal/Reuse, McGraw-Hill, Co., 1979

Montgomery (James M.) Consulting Engineers Inc., (1985) Water Treatment Principles and Design, John Wiley and Sons, Inc., 1985

National Research Council Canada (1985), "Organotin Compounds in the Environment: Scientific Criteria for Assessing their Effects on Environmental Quality, NRCC Subcommittee on Water, NRCC Report No. 22494, 1984

Paramisivam, P., Mhaisalkar, V. A., and Bertheouex, P. M., (1981) **JAWWA**, April 1981, p. 178-185

Phillips, L. W., (1975) "Literature Search on Toxic and Carcinogenic Components of Paint", NIOSH Contract No. 210-76-0108, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Robert A. Taft Laboratories, Cincinnati, OH, 1975

Puget Sound Water Quality Authority, (1986) "The State of the Sound 1986", July 1986

Saam, R. D., Hearst, P. J., Schwab, L. K., and Chan, D. B., (1977) "Drydock Waste Treatment Study", Report No. N-1490, Civil Engineering Laboratory, Naval Construction Battalion Center, Port Hueneme, CA, 1977

Sanks, R. L., (1978) Water Treatment Plant Design, Ann Arbor Science, 1978

Seelaus, T. J., Hendricks, D. W., and Janonis, B. A. (1984) **JAWWA**, December 1986, p. 35-41

Slezak, L. A. and Sims, R. C., (1984) **JAWWA**, December 1984, p. 38-43

Snoeyink, V. L., and Jenkins, D. J., (1980) Water Chemistry, John Wiley and Sons, Inc., 1980

Standard Methods for the Examination of Water and Wastewater (1988), American Public Health Association, Washington, D.C.

Stensel, H. D., Brenner, R. C., Lee, K. M., Melcer, H., and Rakness, K. (1988) **Journal of Environmental Engineering, ASCE**, 114:3, p 655-671, June 1988

Stumm, W., and O'Melia, C. R., (1968) **JAWWA**, May 1968, 514-539

Tchobanoglous, G. and Eliassen, R., (1970), **Journal of the Sanitary Engineering Division, ASCE**, 96:SA2, p. 243-265, April 1970

U. S. Environmental Protection Agency (USEPA), (1975) "National Interim Primary Drinking Water Regulations", Federal Register, 40:248, p. 59566-59587, 24 December 1975

USEPA, (1979a) "National Secondary Drinking Water Regulations", Federal Register, 44:153, p. 42195-42202, 19 July 1979

USEPA, (1979b) "Development Document for Proposed Best Management Practices for the Shipbuilding and Repair Industry: Drydocks Point Source Category", Effluent Guidelines Division, Office of Water and Hazardous Materials, USEPA, Washington, D.C., December 1979

USEPA, (1986) "Tributyltin Support Document", Office of Pesticide Programs, Office of Pesticides and Toxic Substances, USEPA, Washington, D.C.

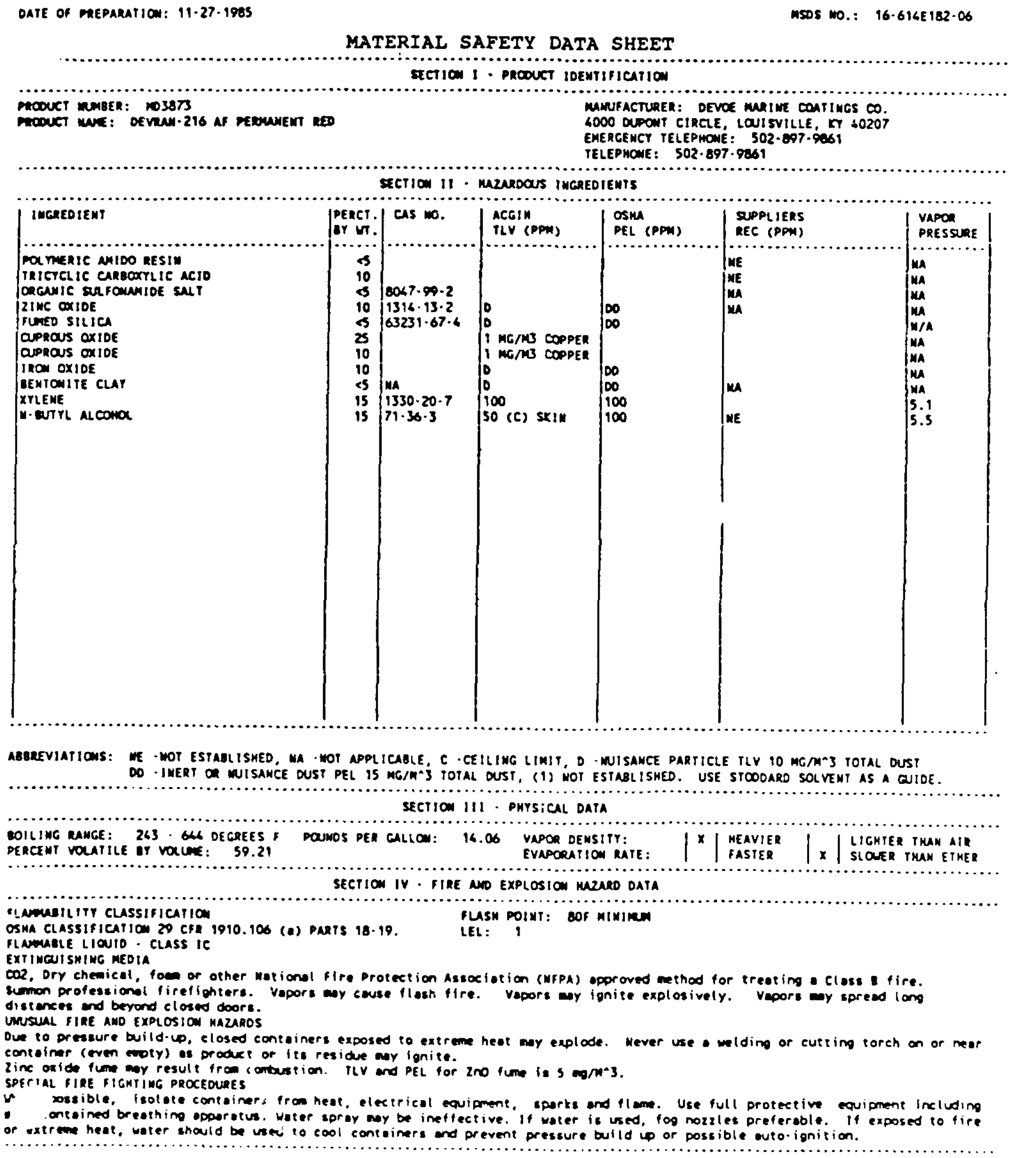
USEPA, (1987) "Ambient Aquatic Life Water Quality Advisories for Tributyltin", USEPA, Office of Research and Development, Environmental Research Laboratories, Duluth, MN and Narragansett, RI, 14 September 1987

Valkirs, A. O., Seligman, P. F., Stang, P. M., Homer, V., Lieberman, S. H., Giti, V., and Dooley, C. A., (1986) **Marine Pollution Bulletin**, 17:7, p. 319-324, 1986

Wagner, E. G. and Hudson, H. E., (1982) **JAWWA**, May 1982, p. 256-261

Wong, P. T. S., Chau, Y. K., Kramer, O., Bengert, G. H. (1982) **Canadian Journal of Fish. Aquat. Sci.** Vol. 39, p. 483-488

APPENDIX 1 MATERIAL SAFETY DATA SHEETS FOR ANTI-FOULANT PAINTS



DATE OF PREPARATION: 11-27-1985

MSDS NO.: 16-614E182-06

MATERIAL SAFETY DATA SHEET

SECTION I - PRODUCT IDENTIFICATION

PRODUCT NUMBER: MD3873
PRODUCT NAME: DEVRAN-216 AF PERMANENT RED

MANUFACTURER: DEVOE MARINE COATINGS CO.
4000 DUPONT CIRCLE, LOUISVILLE, KY 40207
EMERGENCY TELEPHONE: 502-897-9861
TELEPHONE: 502-897-9861

SECTION II - HAZARDOUS INGREDIENTS

INGREDIENT	PERCT. BY WT.	CAS NO.	ACGIH TLV (PPM)	OSHA PEL (PPM)	SUPPLIERS REC (PPM)	VAPOR PRESSURE
POLYMERIC AMIDO RESIN	<5				NE	NA
TRICYCLIC CARBOXYLIC ACID	10				NE	NA
ORGANIC SULFONAMIDE SALT	<5	8047-99-2			NA	NA
ZINC OXIDE	10	1314-13-2	D	DO	NA	NA
FUMED SILICA	<5	63231-67-4	D	DO		N/A
CUPROUS OXIDE	25		1 MG/M3 COPPER			NA
CUPROUS OXIDE	10		1 MG/M3 COPPER			NA
IRON OXIDE	10		D	DO		NA
BENTONITE CLAY	<5	NA	D	DO	NA	NA
XYLENE	15	1330-20-7	100	100		5.1
N-BUTYL ALCOHOL	15	71-36-3	50 (C) SKIN	100	NE	5.5

ABBREVIATIONS: NE -NOT ESTABLISHED, NA -NOT APPLICABLE, C -CEILING LIMIT, D -NUISANCE PARTICLE TLV 10 MG/M^3 TOTAL DUST
DO -INERT OR NUISANCE DUST PEL 15 MG/M^3 TOTAL DUST, (1) NOT ESTABLISHED. USE STODDARD SOLVENT AS A GUIDE.

SECTION III - PHYSICAL DATA

BOILING RANGE: 243 - 644 DEGREES F POUNDS PER GALLON: 14.06 VAPOR DENSITY: | X | HEAVIER | | LIGHTER THAN AIR
PERCENT VOLATILE BY VOLUME: 59.21 EVAPORATION RATE: | | FASTER | X | SLOWER THAN ETHER

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLAMMABILITY CLASSIFICATION
OSHA CLASSIFICATION 29 CFR 1910.106 (a) PARTS 18-19.
FLAMMABLE LIQUID - CLASS IC

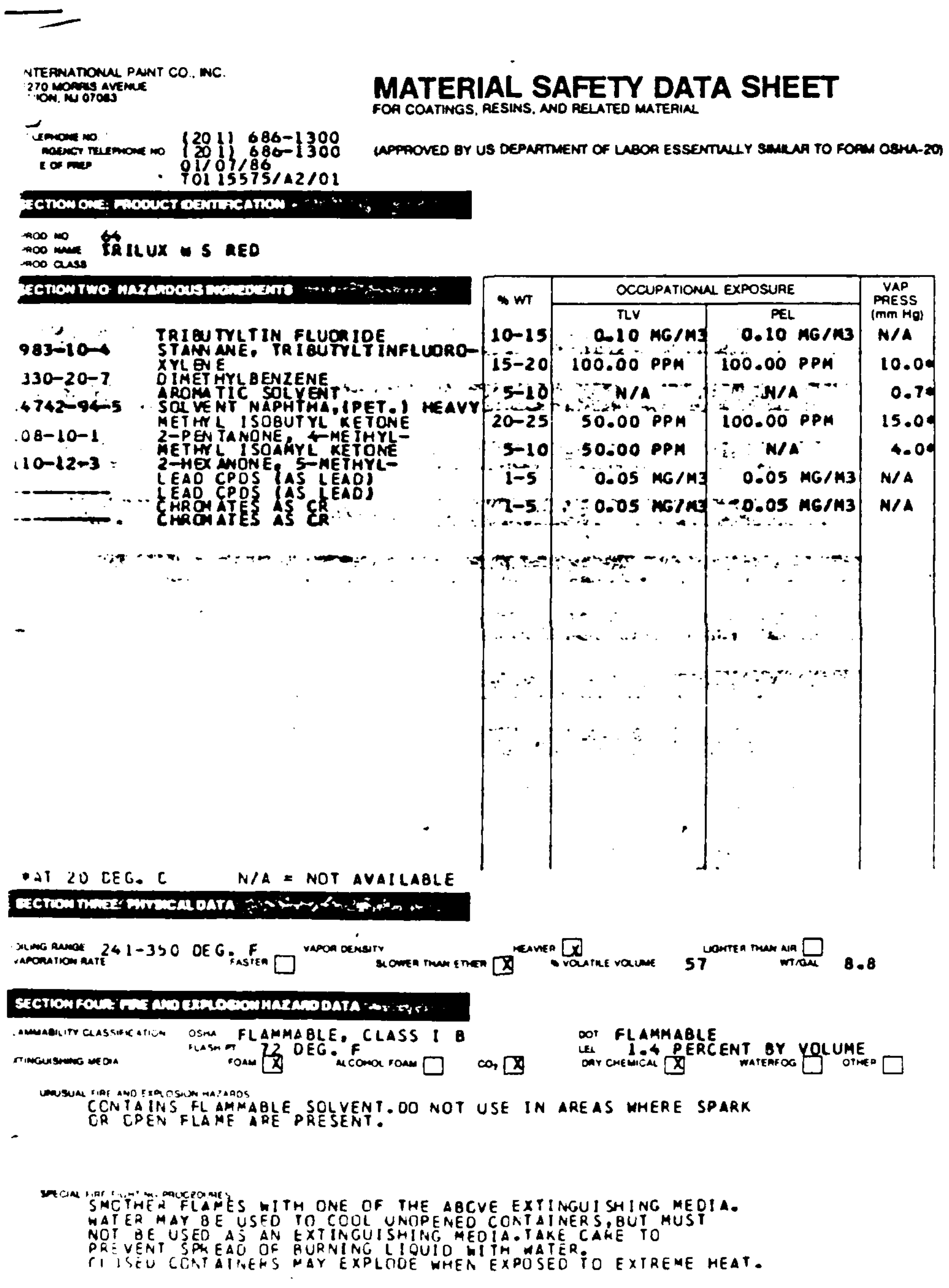
FLASH POINT: 80F MINIMUM
LEL: 1

EXTINGUISHING MEDIA
CO2, Dry chemical, foam or other National Fire Protection Association (NFPA) approved method for treating a Class B fire. Summon professional firefighters. Vapors may cause flash fire. Vapors may ignite explosively. Vapors may spread long distances and beyond closed doors.

UNUSUAL FIRE AND EXPLOSION HAZARDS
Due to pressure build-up, closed containers exposed to extreme heat may explode. Never use a welding or cutting torch on or near container (even empty) as product or its residue may ignite.
Zinc oxide fume may result from combustion. TLV and PEL for ZnO fume is 5 mg/M^3.

SPECIAL FIRE FIGHTING PROCEDURES
W[illegible] possible, isolate containers from heat, electrical equipment, sparks and flame. Use full protective equipment including s[illegible]contained breathing apparatus. Water spray may be ineffective. If water is used, fog nozzles preferable. If exposed to fire or extreme heat, water should be used to cool containers and prevent pressure build up or possible auto-ignition.

Figure 49(a) - Material Safety Data Sheet for Devran 216 Anti-Foulant Paint



NTERNATIONAL PAINT CO., INC.
270 MORRIS AVENUE
ION, NJ 07083

MATERIAL SAFETY DATA SHEET

FOR COATINGS, RESINS, AND RELATED MATERIAL

LEPHONE NO (201) 686-1300
RGENCY TELEPHONE NO (201) 686-1300
E OF PREP 01/07/86
T01 15575/A2/01

(APPROVED BY US DEPARTMENT OF LABOR ESSENTIALLY SIMILAR TO FORM OSHA-20)

ECTION ONE: PRODUCT IDENTIFICATION

ROD NO 64
ROD NAME TRILUX w S RED
ROD CLASS

ECTION TWO: HAZARDOUS INGREDIENTS

		% WT	OCCUPATIONAL EXPOSURE		VAP PRESS (mm Hg)
			TLV	PEL	
983-10-4	TRIBUTYLTIN FLUORIDE STANNANE, TRIBUTYLTINFLUORO-	10-15	0.10 MG/M3	0.10 MG/M3	N/A
330-20-7	XYLENE DIMETHYLBENZENE	15-20	100.00 PPM	100.00 PPM	10.0*
4742-94-5	AROMATIC SOLVENT SOLVENT NAPHTHA,(PET.) HEAVY	5-10	N/A	N/A	0.7*
08-10-1	METHYL ISOBUTYL KETONE 2-PENTANONE, 4-METHYL-	20-25	50.00 PPM	100.00 PPM	15.0*
10-12-3	METHYL ISOAMYL KETONE 2-HEXANONE, 5-METHYL-	5-10	50.00 PPM	N/A	4.0*
--------	LEAD CPDS (AS LEAD) LEAD CPDS (AS LEAD)	1-5	0.05 MG/M3	0.05 MG/M3	N/A
--------	CHROMATES AS CR CHROMATES AS CR	1-5	0.05 MG/M3	0.05 MG/M3	N/A

*AT 20 DEG. C   N/A = NOT AVAILABLE

SECTION THREE: PHYSICAL DATA

ILING RANGE 241-350 DEG. F   VAPOR DENSITY   HEAVIER ☒   LIGHTER THAN AIR ☐
APORATION RATE   FASTER ☐   SLOWER THAN ETHER ☒   % VOLATILE VOLUME 57   WT/GAL 8.8

SECTION FOUR: FIRE AND EXPLOSION HAZARD DATA

AMMABILITY CLASSIFICATION   OSHA FLAMMABLE, CLASS I B   DOT FLAMMABLE
FLASH PT 72 DEG. F   LEL 1.4 PERCENT BY VOLUME
TINGUISHING MEDIA   FOAM ☒   ALCOHOL FOAM ☐ CO_2 ☒   DRY CHEMICAL ☒   WATERFOG ☐   OTHER ☐

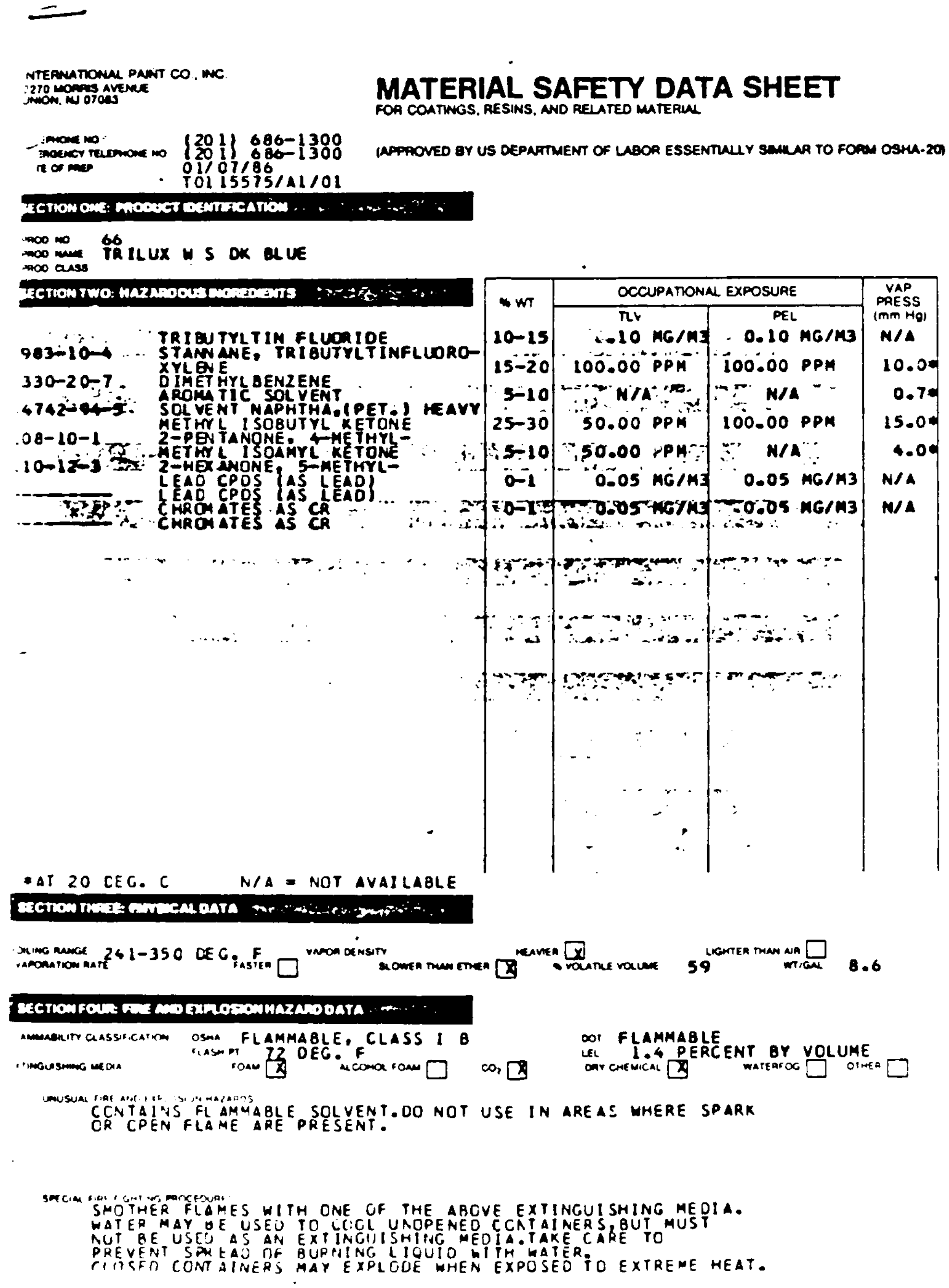
UNUSUAL FIRE AND EXPLOSION HAZARDS

CONTAINS FLAMMABLE SOLVENT.DO NOT USE IN AREAS WHERE SPARK OR OPEN FLAME ARE PRESENT.

SPECIAL FIRE FIGHTING PROCEDURES

SMOTHER FLAMES WITH ONE OF THE ABOVE EXTINGUISHING MEDIA.
WATER MAY BE USED TO COOL UNOPENED CONTAINERS,BUT MUST NOT BE USED AS AN EXTINGUISHING MEDIA.TAKE CARE TO PREVENT SPREAD OF BURNING LIQUID WITH WATER.
CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT.

Figure 49(b) - Material Safety Data Sheet for Trilux Red Anti-foulant Paint



NTERNATIONAL PAINT CO., INC.
270 MORRIS AVENUE
JNION, NJ 07083

MATERIAL SAFETY DATA SHEET

FOR COATINGS, RESINS, AND RELATED MATERIAL

(APPROVED BY US DEPARTMENT OF LABOR ESSENTIALLY SIMILAR TO FORM OSHA-20)

EPHONE NO (201) 686-1300
ERGENCY TELEPHONE NO (201) 686-1300
TE OF PREP 01/07/86
T01 15575/A1/01

ECTION ONE: PRODUCT IDENTIFICATION

ROD NO 66
ROD NAME TRILUX W S DK BLUE
ROD CLASS

ECTION TWO: HAZARDOUS INGREDIENTS

		% WT	OCCUPATIONAL EXPOSURE		VAP PRESS (mm Hg)
			TLV	PEL	
983-10-4	TRIBUTYLTIN FLUORIDE STANNANE, TRIBUTYLTINFLUORO-	10-15	0.10 MG/M3	0.10 MG/M3	N/A
330-20-7	XYLENE DIMETHYLBENZENE	15-20	100.00 PPM	100.00 PPM	10.0*
4742-94-5	AROMATIC SOLVENT SOLVENT NAPHTHA,(PET.) HEAVY	5-10	N/A	N/A	0.7*
08-10-1	METHYL ISOBUTYL KETONE 2-PENTANONE, 4-METHYL-	25-30	50.00 PPM	100.00 PPM	15.0*
10-12-3	METHYL ISOAMYL KETONE 2-HEXANONE, 5-METHYL-	5-10	50.00 PPM	N/A	4.0*
	LEAD CPDS (AS LEAD) LEAD CPDS (AS LEAD)	0-1	0.05 MG/M3	0.05 MG/M3	N/A
	CHROMATES AS CR CHROMATES AS CR	0-1	0.05 MG/M3	0.05 MG/M3	N/A

*AT 20 DEG. C N/A = NOT AVAILABLE

SECTION THREE: PHYSICAL DATA

OILING RANGE 241-350 DEG. F
VAPOR DENSITY HEAVIER ☒ LIGHTER THAN AIR ☐
VAPORATION RATE FASTER ☐ SLOWER THAN ETHER ☒
% VOLATILE VOLUME 59
WT/GAL 8.6

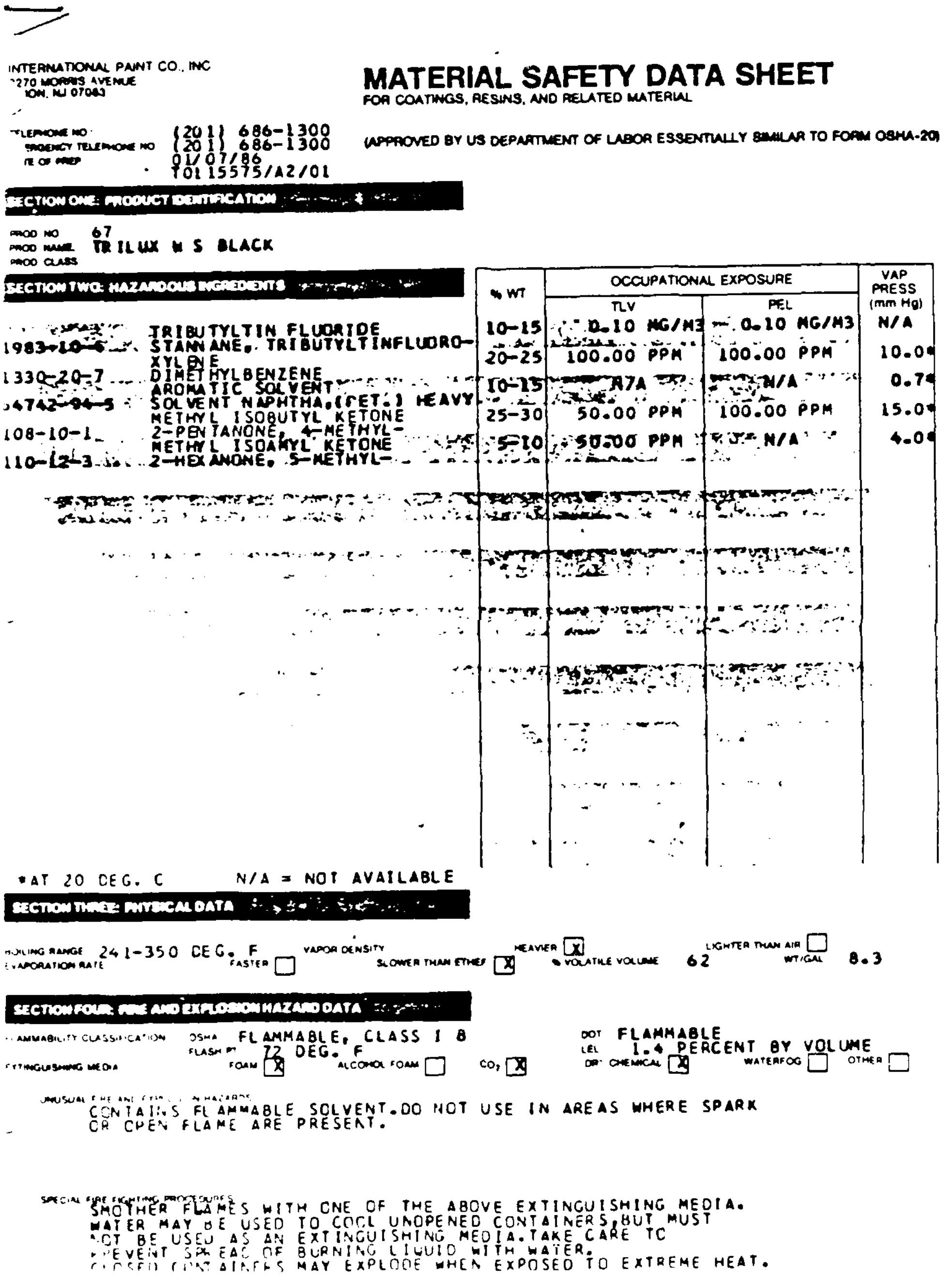
SECTION FOUR: FIRE AND EXPLOSION HAZARD DATA

AMMABILITY CLASSIFICATION OSHA FLAMMABLE, CLASS I B
DOT FLAMMABLE
FLASH PT 72 DEG. F
LEL 1.4 PERCENT BY VOLUME
TINGUISHING MEDIA FOAM ☒ ALCOHOL FOAM ☐ CO_2 ☒ DRY CHEMICAL ☒ WATERFOG ☐ OTHER ☐

UNUSUAL FIRE AND EXPLOSION HAZARDS
CONTAINS FLAMMABLE SOLVENT.DO NOT USE IN AREAS WHERE SPARK
OR OPEN FLAME ARE PRESENT.

SPECIAL FIRE FIGHTING PROCEDURES
SMOTHER FLAMES WITH ONE OF THE ABOVE EXTINGUISHING MEDIA.
WATER MAY BE USED TO COOL UNOPENED CONTAINERS,BUT MUST
NOT BE USED AS AN EXTINGUISHING MEDIA.TAKE CARE TO
PREVENT SPREAD OF BURNING LIQUID WITH WATER.
CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT.

Figure 49(c) - Material Safety Data Sheet for Trilux Dark Blue Anti-foulant Paint



INTERNATIONAL PAINT CO., INC
270 MORRIS AVENUE
ION, NJ 07083

MATERIAL SAFETY DATA SHEET

FOR COATINGS, RESINS, AND RELATED MATERIAL

(APPROVED BY US DEPARTMENT OF LABOR ESSENTIALLY SIMILAR TO FORM OSHA-20)

LEPHONE NO (201) 686-1300
ERGENCY TELEPHONE NO (201) 686-1300
TE OF PREP 01/07/86
T01 15575/A2/01

SECTION ONE: PRODUCT IDENTIFICATION

PROD NO 67
PROD NAME TRILUX W S BLACK
PROD CLASS

SECTION TWO: HAZARDOUS INGREDIENTS

		% WT	OCCUPATIONAL EXPOSURE		VAP PRESS (mm Hg)
			TLV	PEL	
1983-10-6	TRIBUTYLTIN FLUORIDE STANNANE, TRIBUTYLTINFLUORO-	10-15	0.10 MG/M3	0.10 MG/M3	N/A
1330-20-7	XYLENE DIMETHYLBENZENE	20-25	100.00 PPM	100.00 PPM	10.0*
64742-94-5	AROMATIC SOLVENT SOLVENT NAPHTHA,(PET.) HEAVY	10-15	N/A	N/A	0.7*
108-10-1	METHYL ISOBUTYL KETONE 2-PENTANONE, 4-METHYL-	25-30	50.00 PPM	100.00 PPM	15.0*
110-12-3	METHYL ISOAMYL KETONE 2-HEXANONE, 5-METHYL-	5-10	50.00 PPM	N/A	4.0*

*AT 20 DEG. C N/A = NOT AVAILABLE

SECTION THREE: PHYSICAL DATA

BOILING RANGE 241-350 DEG. F
EVAPORATION RATE FASTER ☐ SLOWER THAN ETHER ☒
VAPOR DENSITY HEAVIER ☒ LIGHTER THAN AIR ☐
% VOLATILE VOLUME 62 WT/GAL 8.3

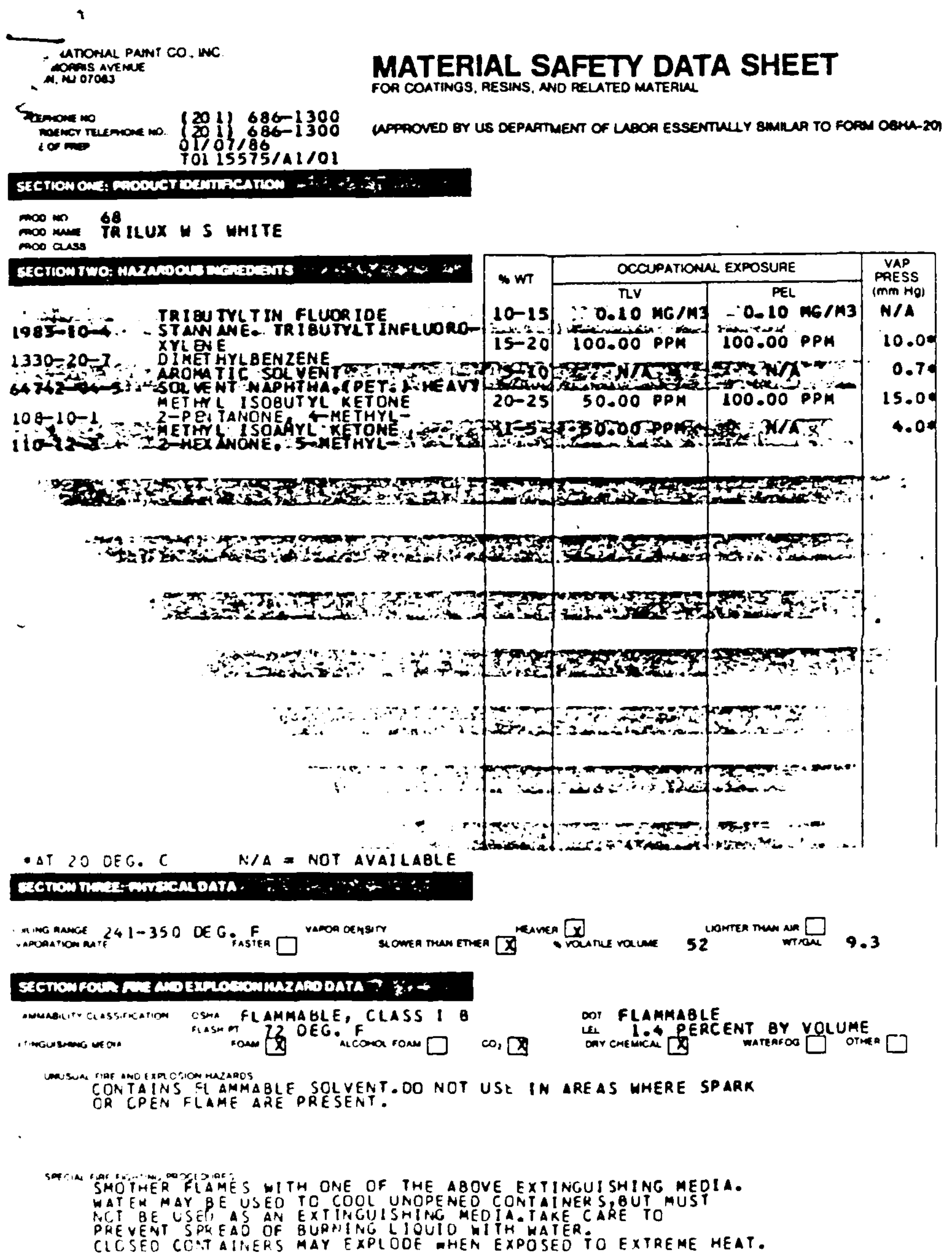
SECTION FOUR: FIRE AND EXPLOSION HAZARD DATA

FLAMMABILITY CLASSIFICATION OSHA FLAMMABLE, CLASS I B DOT FLAMMABLE
FLASH PT 72 DEG. F LEL 1.4 PERCENT BY VOLUME
EXTINGUISHING MEDIA FOAM ☒ ALCOHOL FOAM ☐ CO2 ☒ DRY CHEMICAL ☒ WATERFOG ☐ OTHER ☐

UNUSUAL FIRE AND EXPLOSION HAZARDS
CONTAINS FLAMMABLE SOLVENT.DO NOT USE IN AREAS WHERE SPARK OR OPEN FLAME ARE PRESENT.

SPECIAL FIRE FIGHTING PROCEDURES
SMOTHER FLAMES WITH ONE OF THE ABOVE EXTINGUISHING MEDIA. WATER MAY BE USED TO COOL UNOPENED CONTAINERS,BUT MUST NOT BE USED AS AN EXTINGUISHING MEDIA.TAKE CARE TO PREVENT SPREAD OF BURNING LIQUID WITH WATER. CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT.

Figure 49(d) - Material Safety Data Sheet for Trilux Black Anti-foulant Paint



ATIONAL PAINT CO., INC.
ORRIS AVENUE
N, NJ 07083

MATERIAL SAFETY DATA SHEET
FOR COATINGS, RESINS, AND RELATED MATERIAL

(APPROVED BY US DEPARTMENT OF LABOR ESSENTIALLY SIMILAR TO FORM OSHA-20)

EPHONE NO (201) 686-1300
RGENCY TELEPHONE NO. (201) 686-1300
OF PREP 01/07/86
T01 15575/A1/01

SECTION ONE: PRODUCT IDENTIFICATION

PROD NO 68
PROD NAME TRILUX W S WHITE
PROD CLASS

SECTION TWO: HAZARDOUS INGREDIENTS

		% WT	OCCUPATIONAL EXPOSURE		VAP PRESS (mm Hg)
			TLV	PEL	
[illegible]	TRIBUTYLTIN FLUORIDE	10-15	0.10 MG/M3	0.10 MG/M3	N/A
1983-10-4	STANNANE, TRIBUTYLTINFLUORO-				
	XYLENE	15-20	100.00 PPM	100.00 PPM	10.0*
1330-20-7	DIMETHYLBENZENE				
	AROMATIC SOLVENT	5-10	N/A	N/A	0.7*
64742-94-5	SOLVENT NAPHTHA,(PET.) HEAVY				
	METHYL ISOBUTYL KETONE	20-25	50.00 PPM	100.00 PPM	15.0*
108-10-1	2-PENTANONE, 4-METHYL-				
	METHYL ISOAMYL KETONE	1-5	50.00 PPM	N/A	4.0*
110-12-3	2-HEXANONE, 5-METHYL-				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

*AT 20 DEG. C N/A = NOT AVAILABLE

SECTION THREE: PHYSICAL DATA

ING RANGE 241-350 DEG. F VAPOR DENSITY HEAVIER ☒ LIGHTER THAN AIR ☐
APORATION RATE FASTER ☐ SLOWER THAN ETHER ☒ % VOLATILE VOLUME 52 WT/GAL 9.3

SECTION FOUR: FIRE AND EXPLOSION HAZARD DATA

AMMABILITY CLASSIFICATION OSHA FLAMMABLE, CLASS I B DOT FLAMMABLE
FLASH PT 72 DEG. F LEL 1.4 PERCENT BY VOLUME
TINGUISHING MEDIA FOAM ☒ ALCOHOL FOAM ☐ CO_2 ☒ DRY CHEMICAL ☒ WATERFOG ☐ OTHER ☐

UNUSUAL FIRE AND EXPLOSION HAZARDS
CONTAINS FLAMMABLE SOLVENT.DO NOT USE IN AREAS WHERE SPARK OR OPEN FLAME ARE PRESENT.

SPECIAL FIRE FIGHTING PROCEDURES
SMOTHER FLAMES WITH ONE OF THE ABOVE EXTINGUISHING MEDIA.
WATER MAY BE USED TO COOL UNOPENED CONTAINERS,BUT MUST NOT BE USED AS AN EXTINGUISHING MEDIA.TAKE CARE TO PREVENT SPREAD OF BURNING LIQUID WITH WATER.
CLOSED CONTAINERS MAY EXPLODE WHEN EXPOSED TO EXTREME HEAT.

Figure 49(e) - Material Safety Data Sheet for Trilux White Anti-foulant Paint

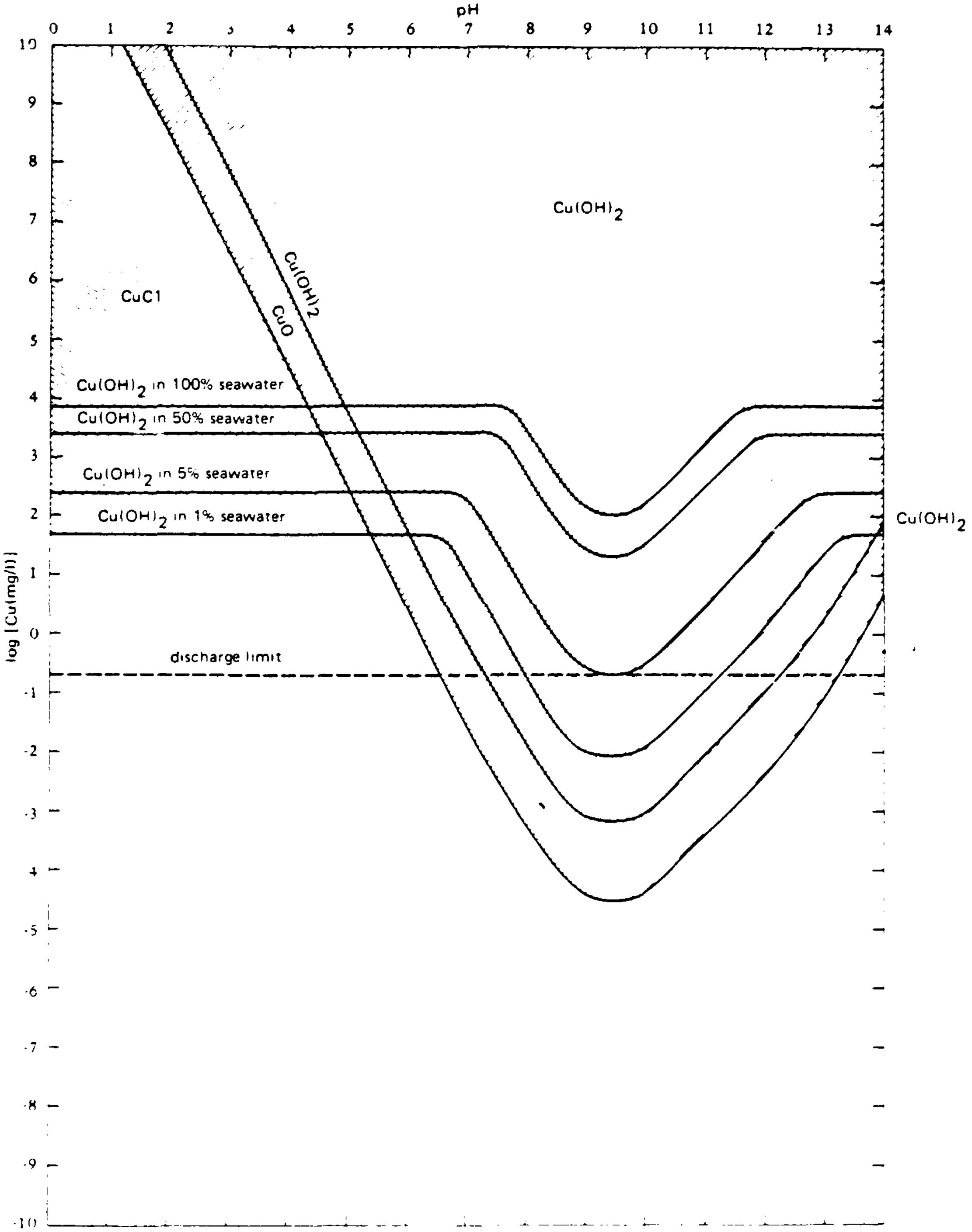


Figure 50(a) - Equilibrium Diagram for Copper in Freshwater and Seawater (Saam et al, 1977)

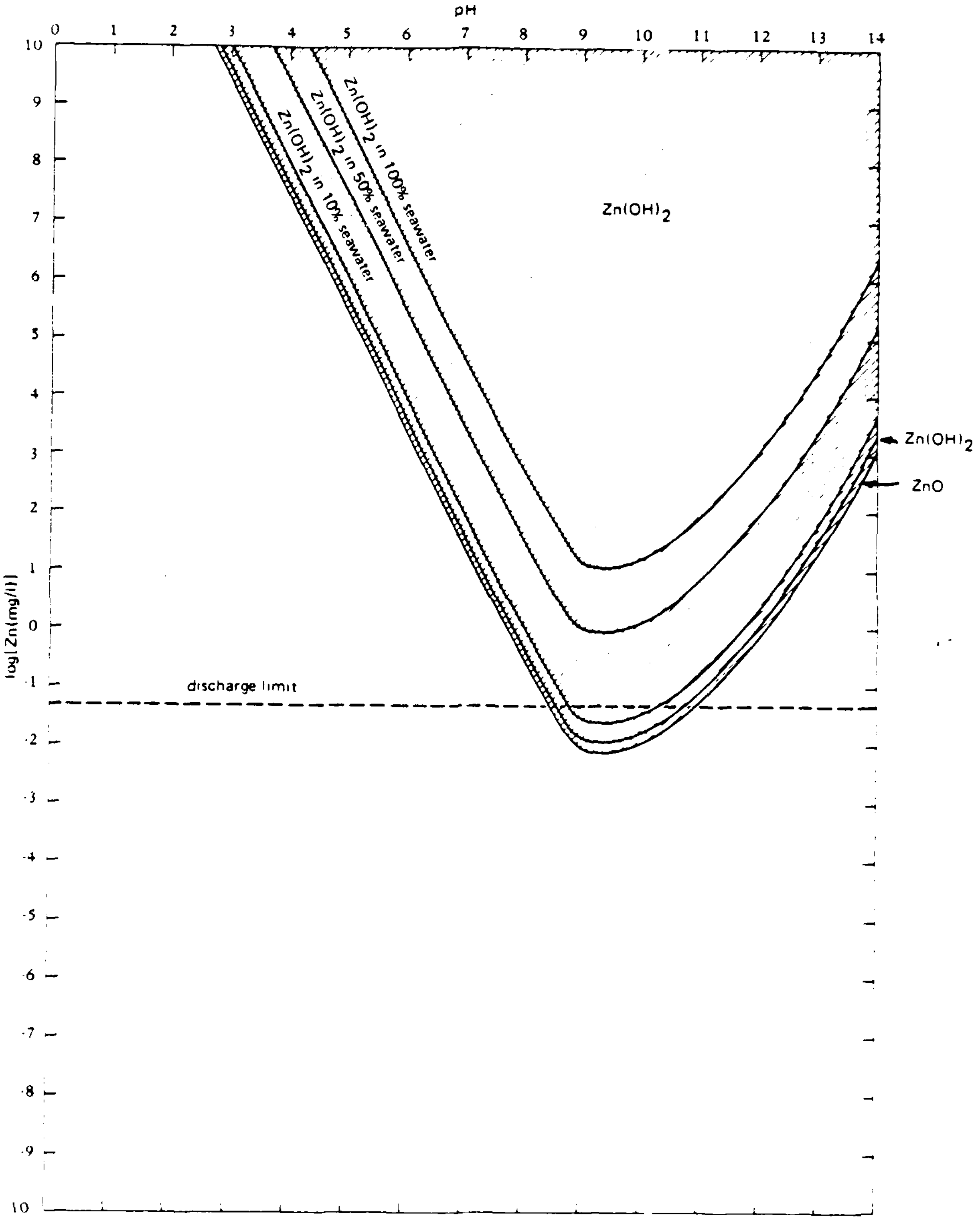


Figure 50(c) - Equilibrium Diagram for Iron in
Freshwater and Seawater
(Saam et al, 1977)

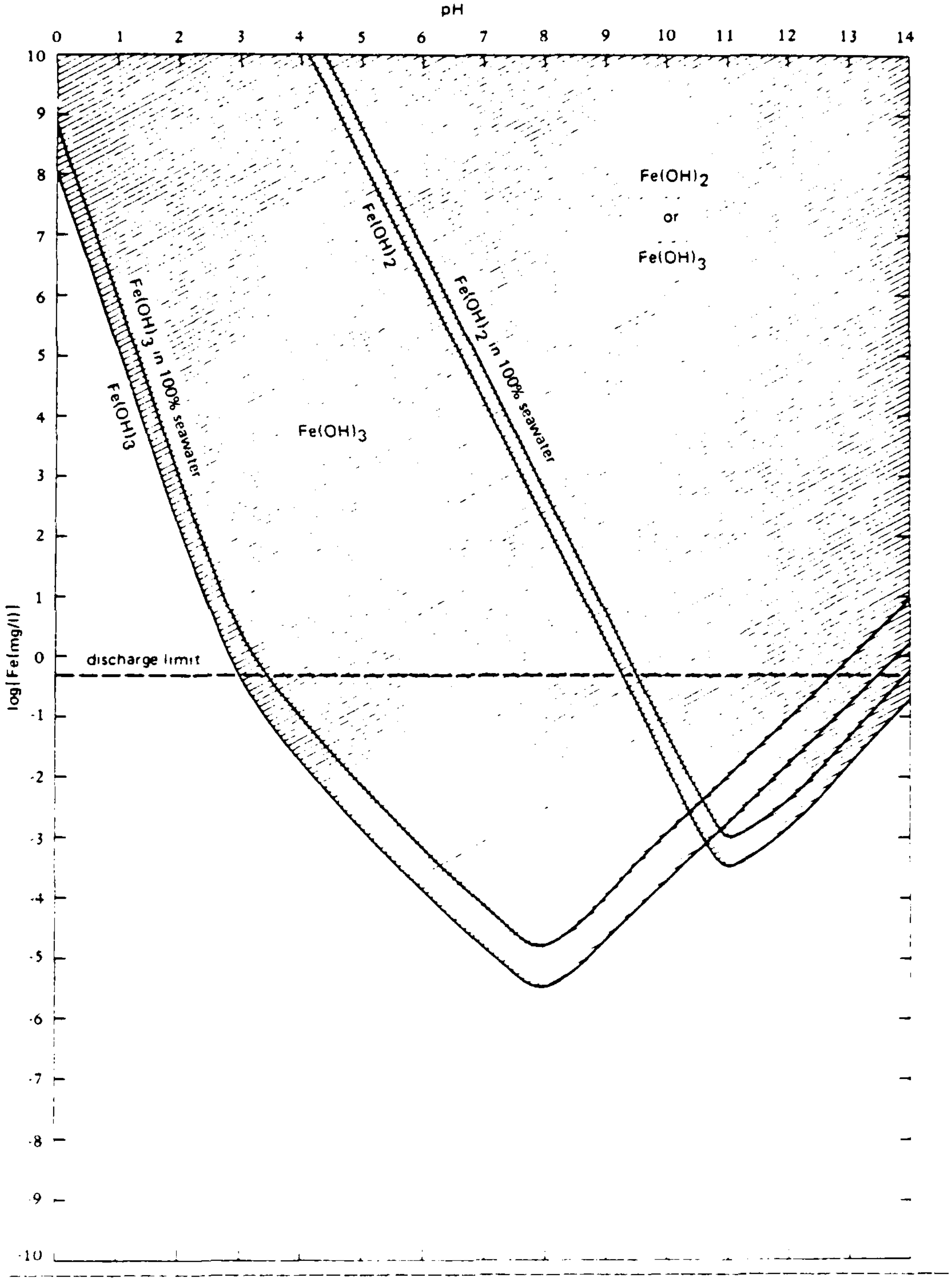


Figure 50(b) - Equilibrium Diagram for Zinc in Freshwater and Seawater (Saam et al, 1977)

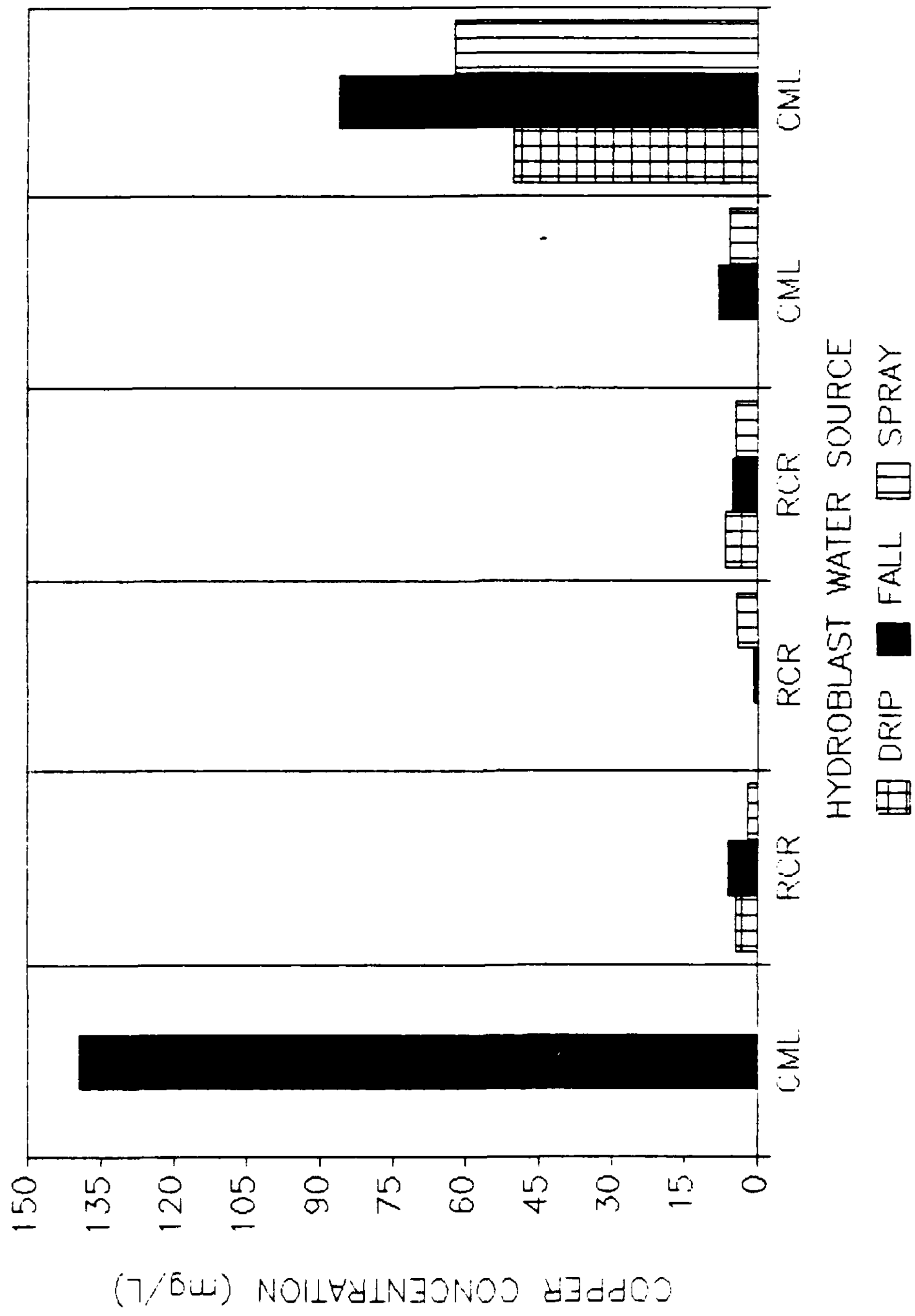


Figure 51(a) - Hydroblast Water Samples- Total Copper Levels

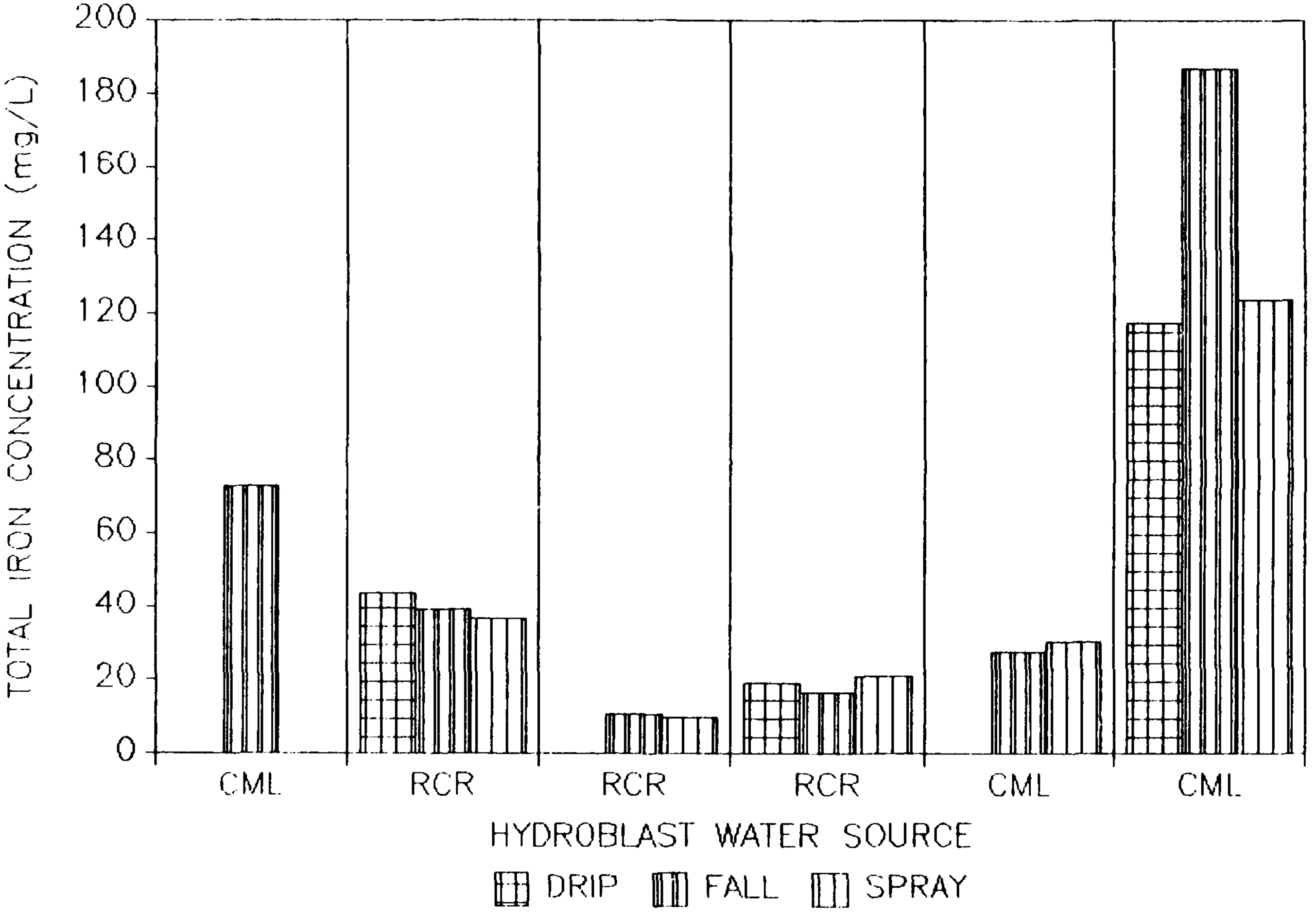


Figure 51(b) - Hydroblast Water Samples- Total Iron Levels

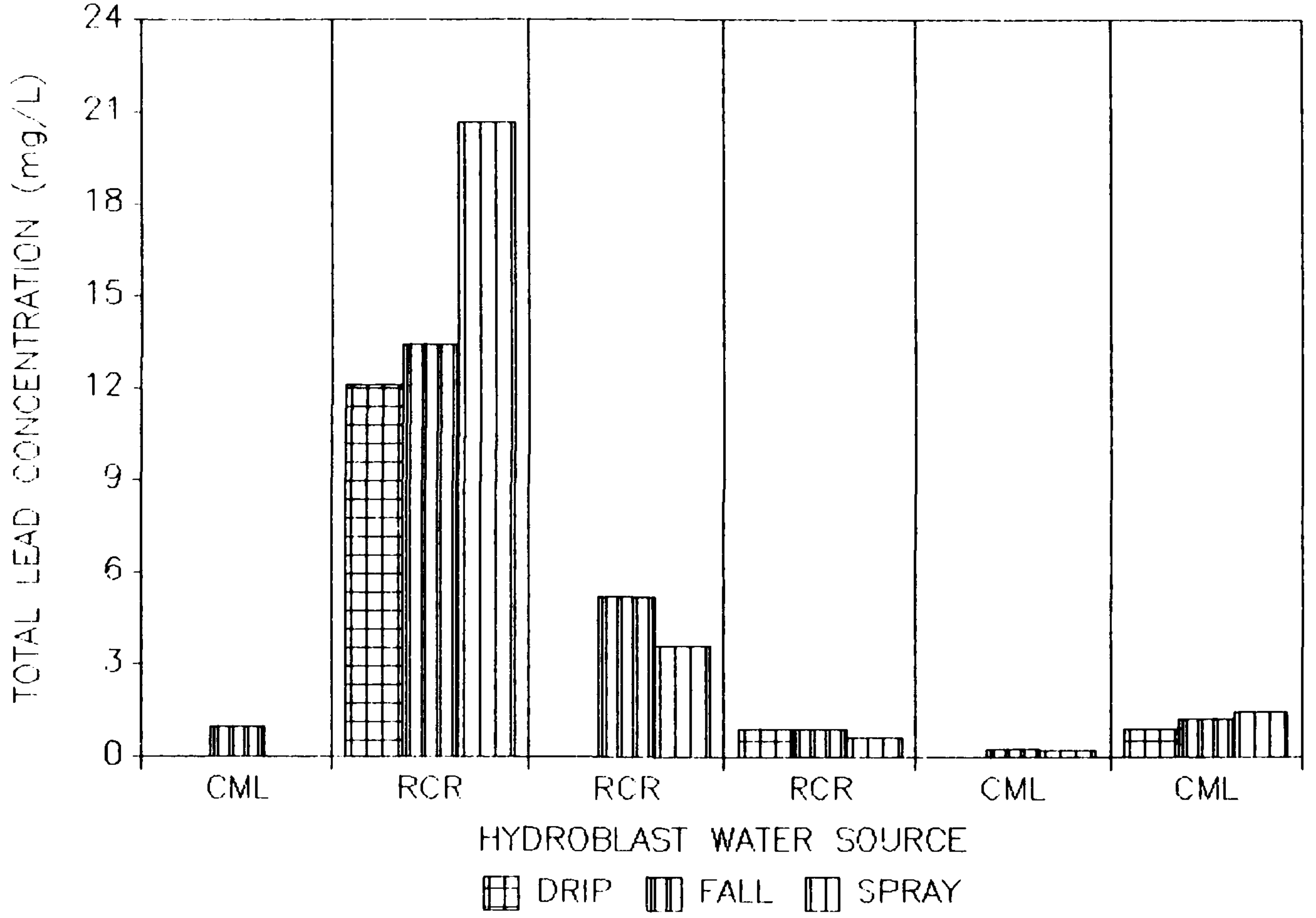


Figure 51(c) - Hydroblast Water Samples- Total Lead Levels

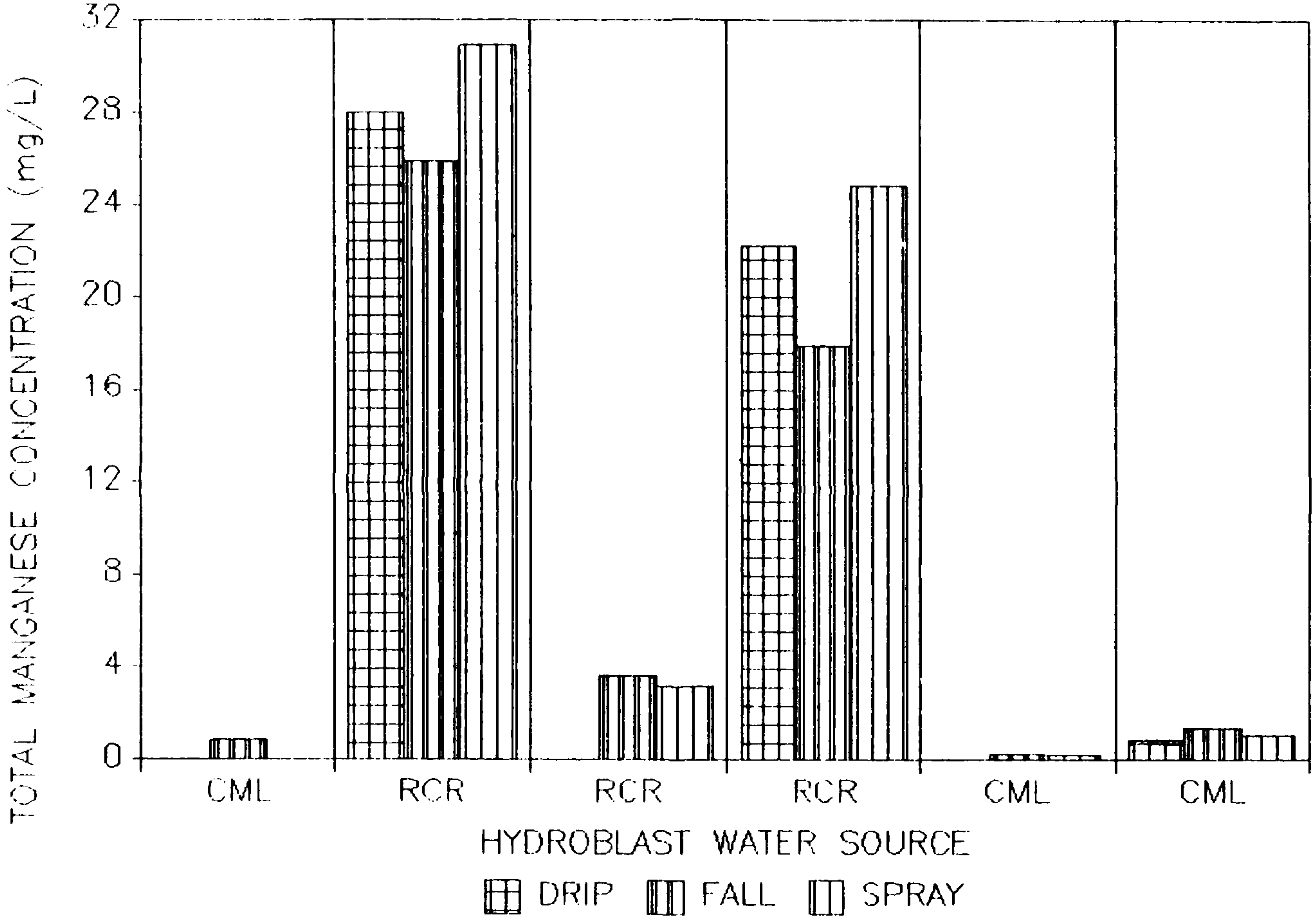


Figure 51(d) - Hydroblast Water Samples- Total Manganese Levels

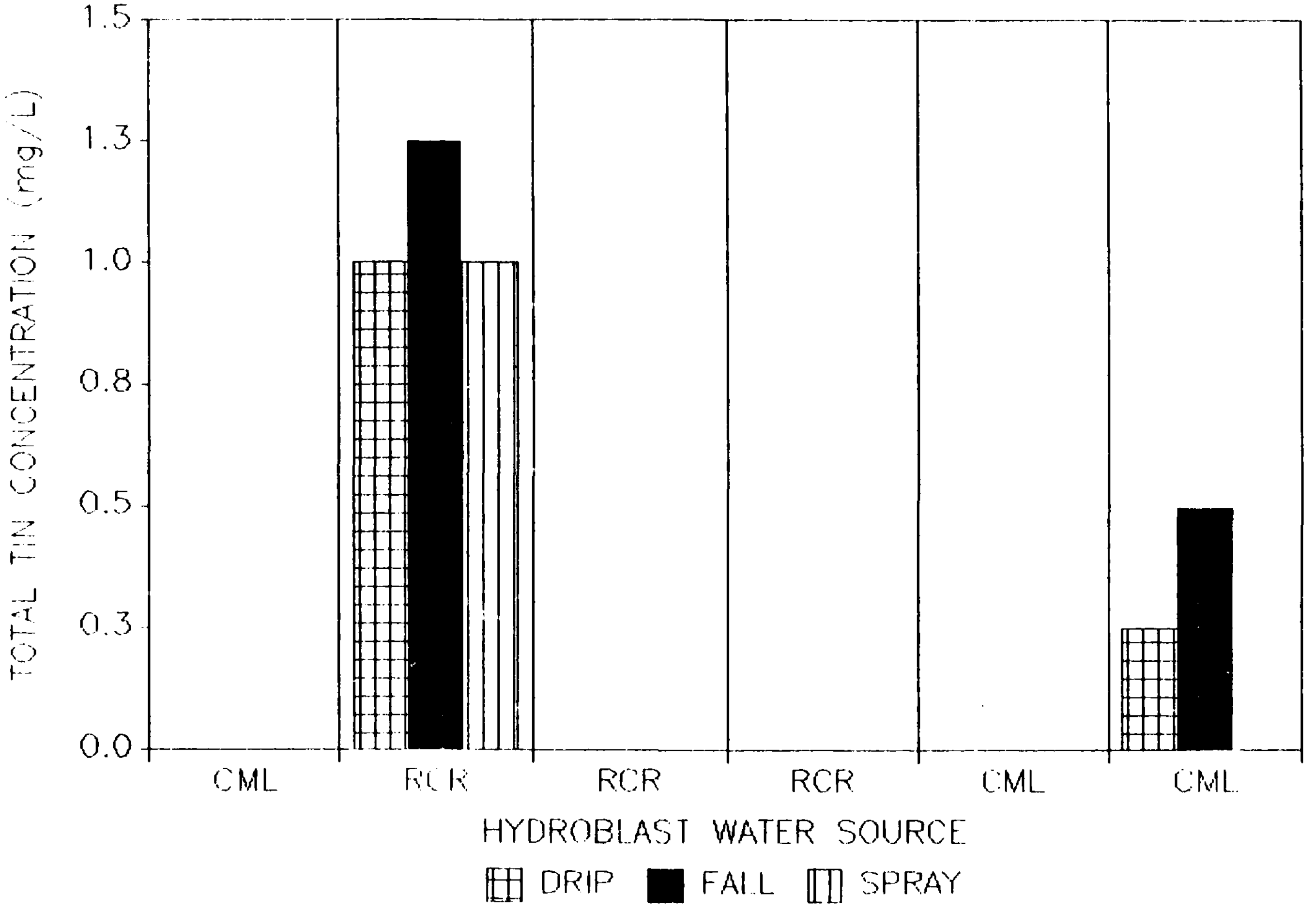


Figure 51(e) - Hydroblast Water Samples- Total Tin Levels

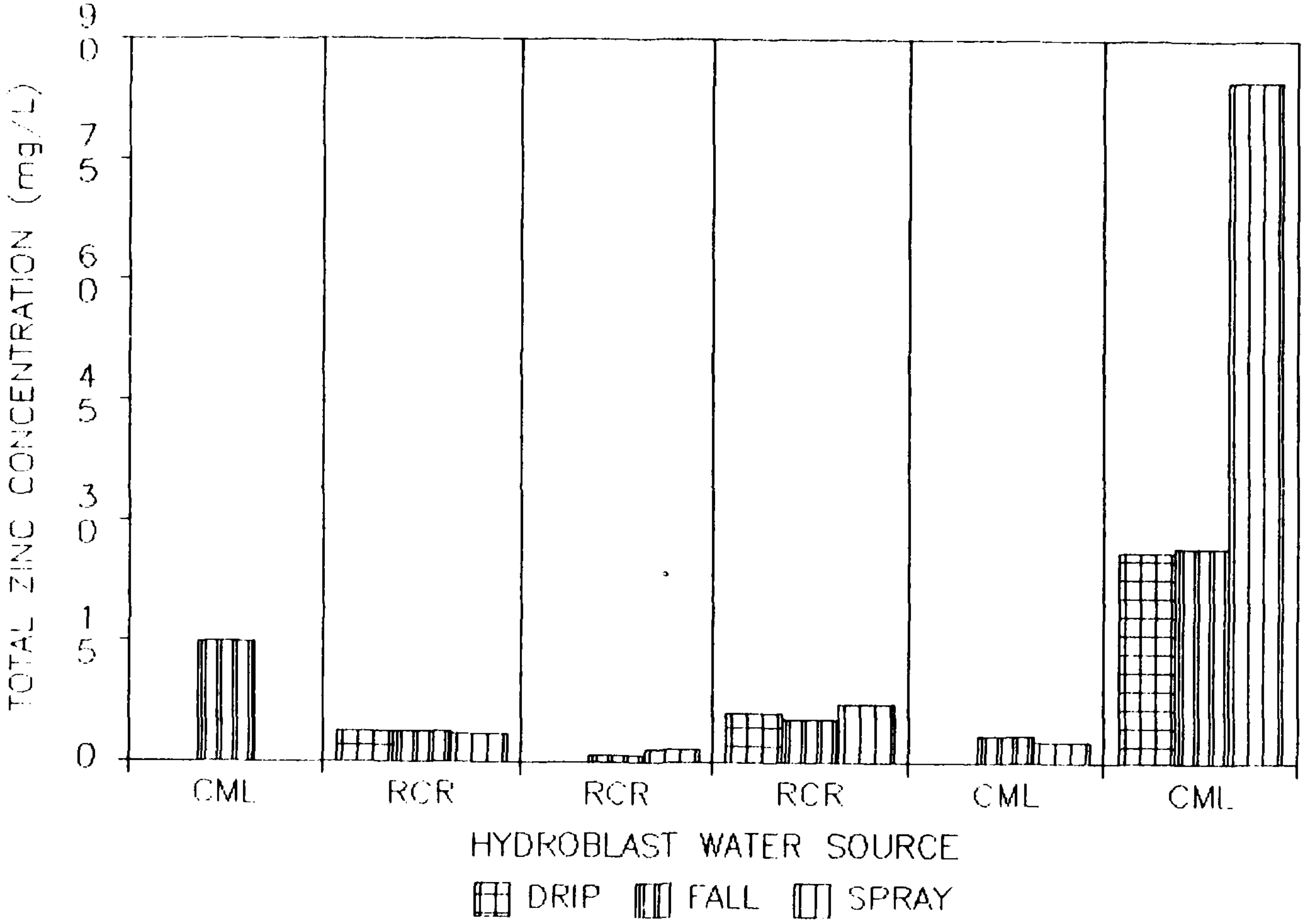


Figure 51(f) - Hydroblast Water Samples- Total Zinc Levels

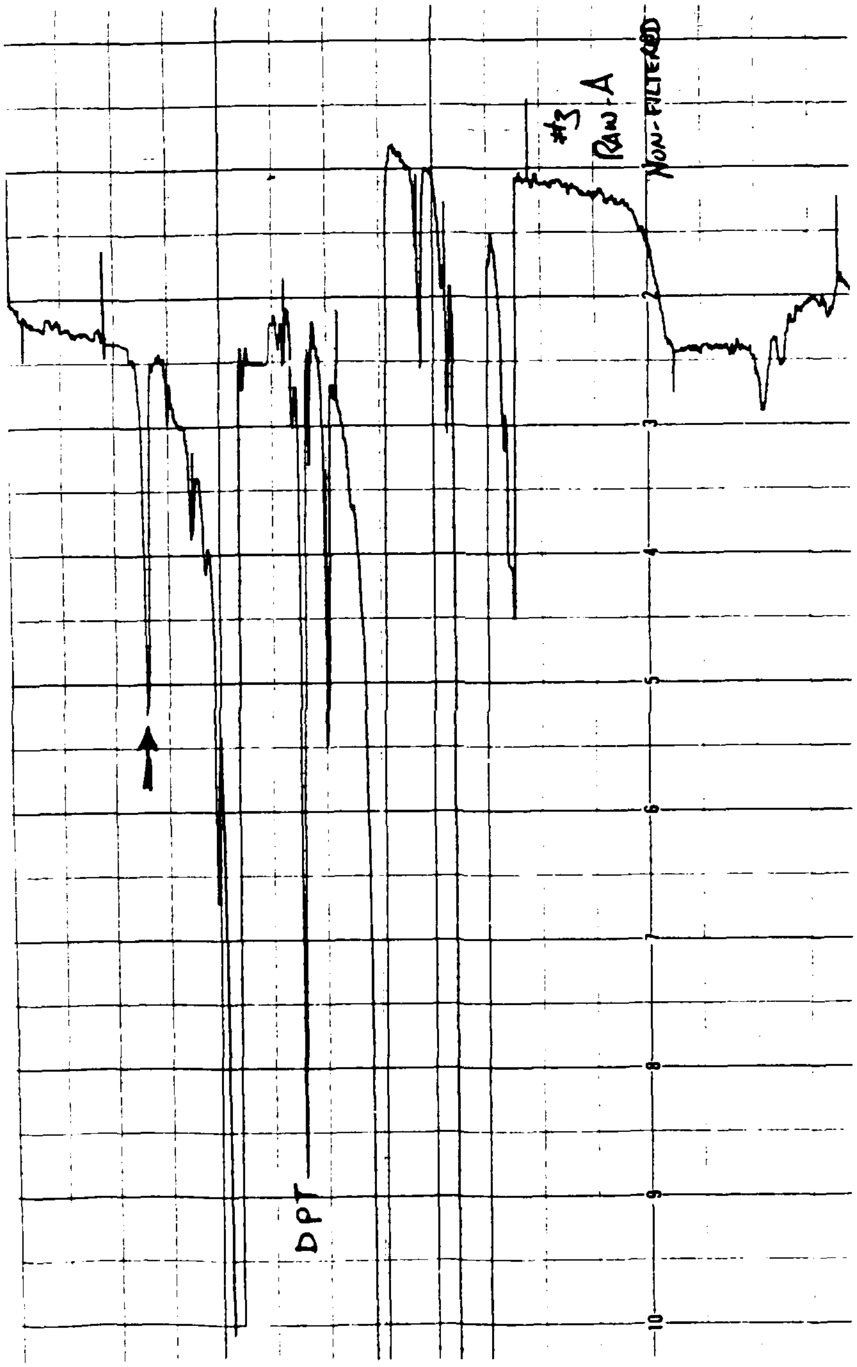


Figure 52(a) - Chromatograph for Raw Sample "A" taken from Mercer Marine, 6-2-88 (Arrow indicates peak for Tributyltin, Dipropyltin standard indicated as "DPT" Measured TBT = 75.2 ug/L)

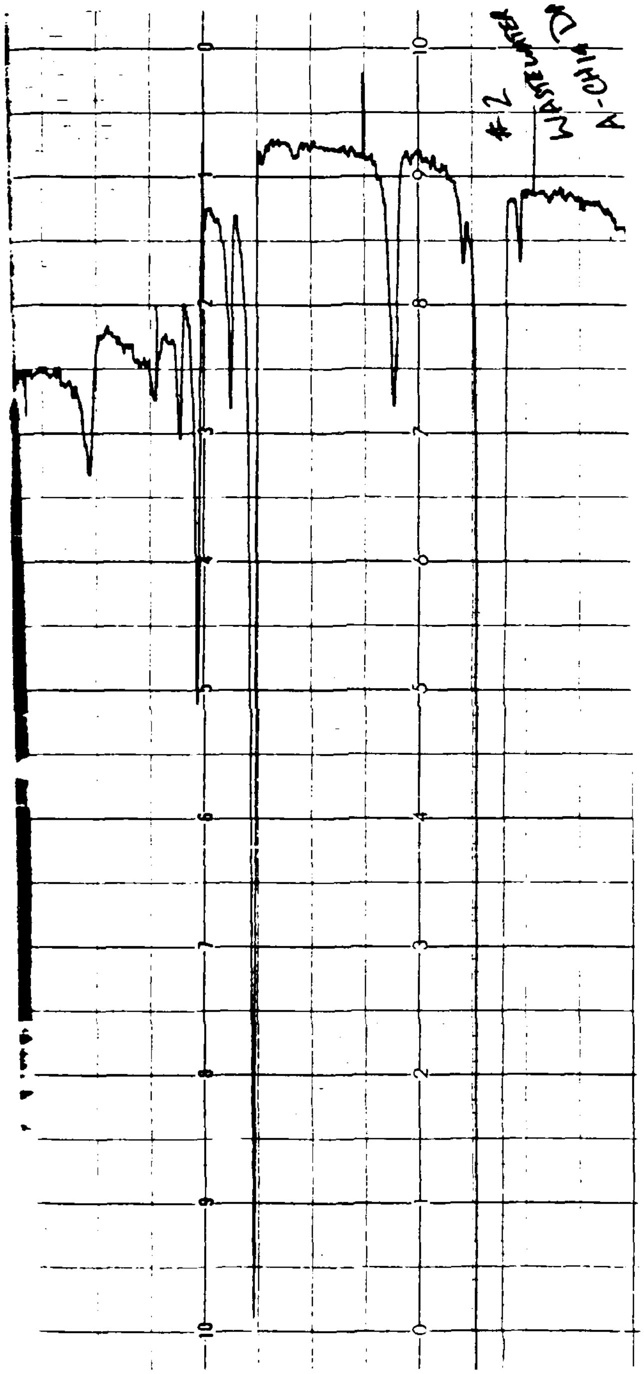


Figure 52(b) - Chromatograph for Effluent from Alum dosed Dual Media Filtration. No TBT was detected in this effluent

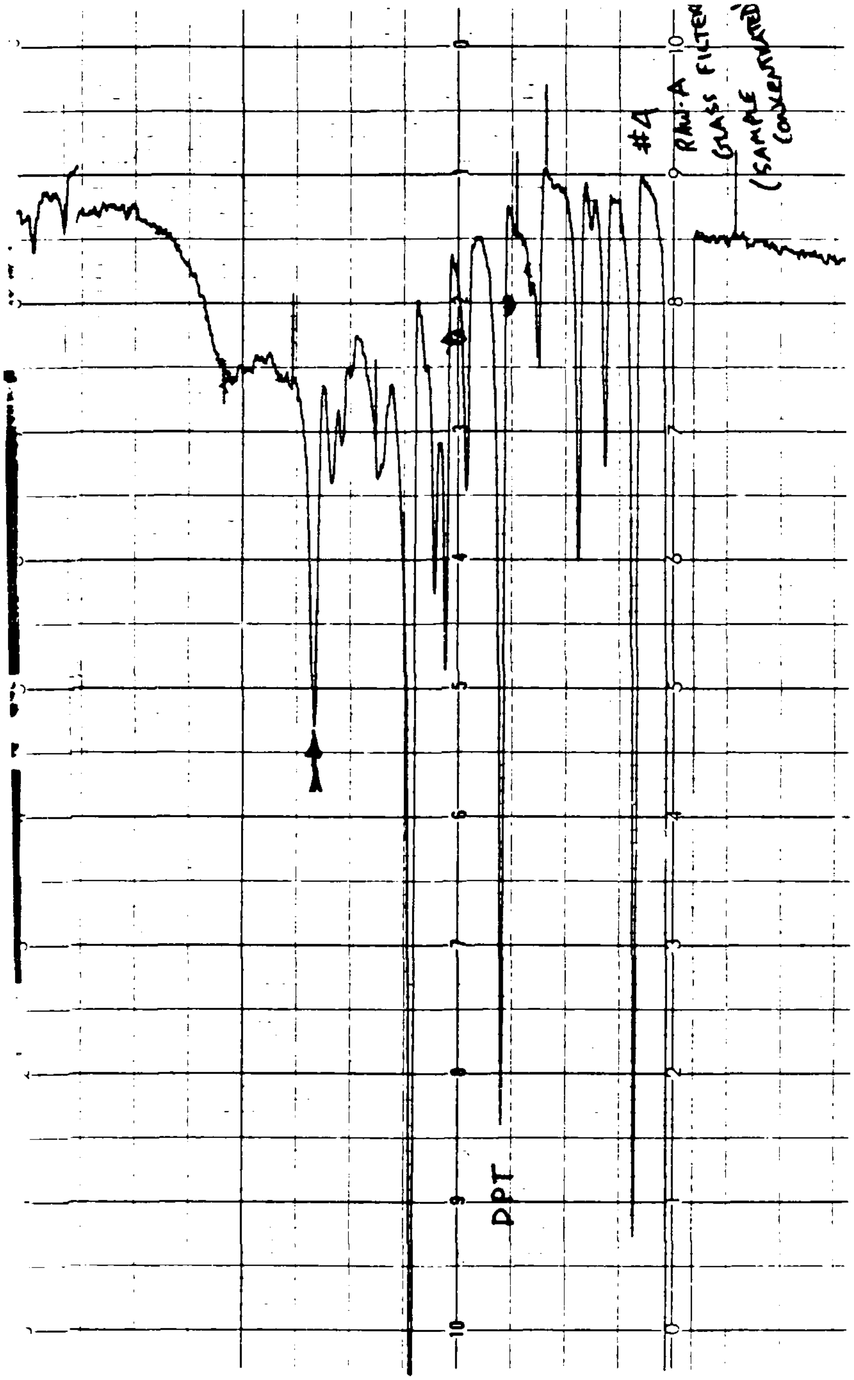


Figure 52(c) - Chromatograph for Filtered Raw Sample taken 6-2-88 at Mercer Marine (TBT, denoted by arrow, measured = 52.6 ug/L)

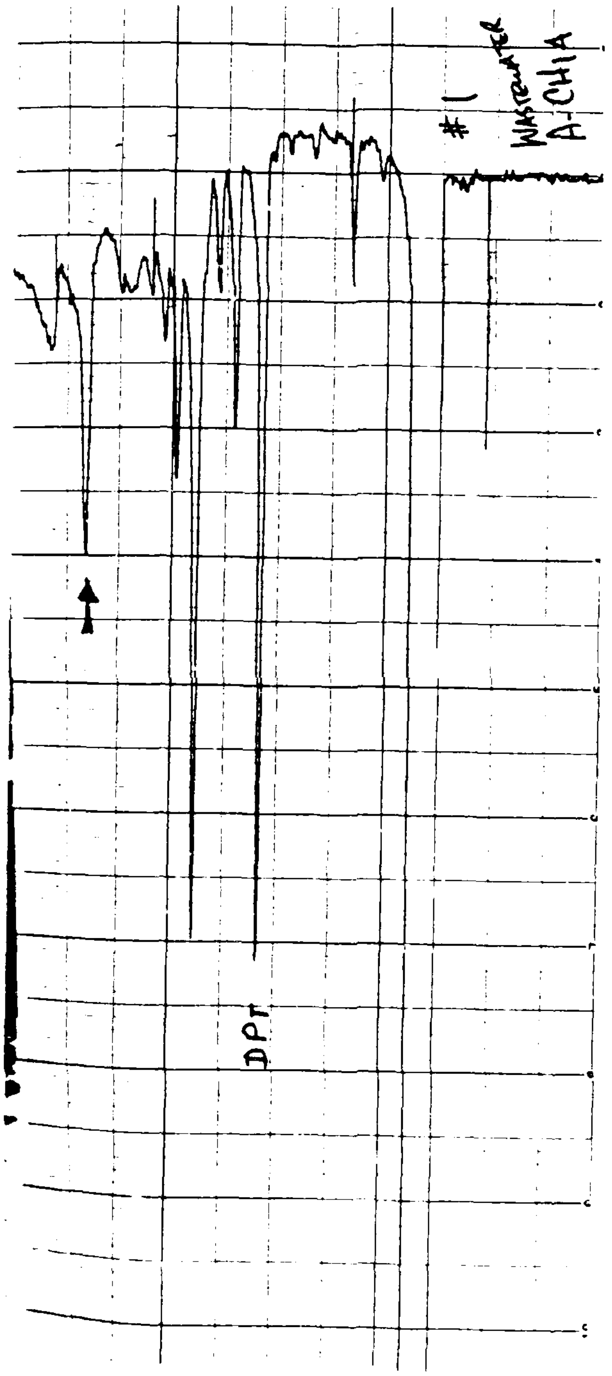


Figure 52(d) - Chromatograph for Effluent from Alum treated Water taken 6-2-88 at Mercer Marine (TBT, denoted by arrow, measured = 50.7 ug/L)