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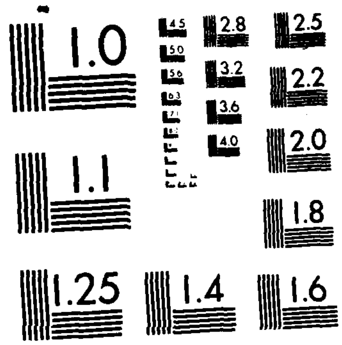

MICROCOPY RESOLUTION TEST CHART
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December 1985
By L.A. Karr
Sponsored By Naval Facilities
Engineering Command

NCEL
Technical Note

THE PHYSICAL, CHEMICAL, AND TOXICOLOGICAL PROPERTIES OF NAVY OILY SLUDGE

ABSTRACT **A research program was caried out to sample and characterize, in terms of physical, chemical, and toxicological properties, oily sludges generated by oily wastewater and waste oil treatment facilities at ten major Naval installations in the United States. The information generated under this program provides a basis for oily sludge classification and for developing design criteria for treatment and ultimate disposal technology for oily sludges produced at Naval installations.**

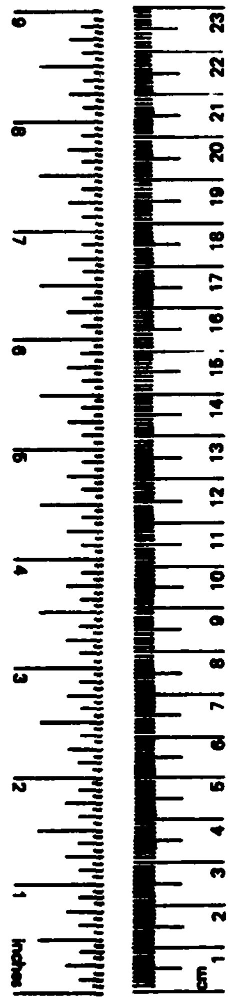
NAVAL CIVIL ENGINEERING LABORATORY PORT HUENEME, CALIFORNIA 93043

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

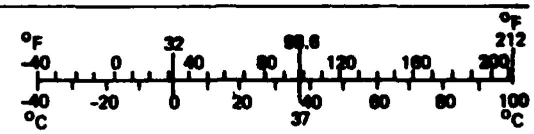
Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (weight)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2,000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (weight)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1,000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (exact)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A research program was carried out to sample and characterize, in terms of physical, chemical, and toxicological properties, oily sludges generated by oily wastewater and waste oil treatment facilities at ten major Naval installations in the United States. The information generated under this program provides a basis for oily sludge classification and for developing design criteria for treatment and ultimate disposal technology for oily sludges produced at Naval installations. The oily sludges analyzed indicate that a typical oily sludge is well-

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20. Continued

dispersed, fairly uniform in consistency, and is a stable mixture of oil, suspended and dissolved organic and inorganic solids, and water. It contains traces of volatile hydrocarbons (usually less than 50 ppm). In spite of the high water content (80 to 90% of the volume), separation of oil from water in sludges is difficult. Some of the collected samples have remained of uniform consistency for a number of months with no indication of phase separation.

Organic toxic substances found in the oily sludge include phenolic compounds and polynuclear aromatic hydrocarbons. Inorganic priority pollutants were also found and included: nickel, zinc, lead, copper, and chromium. In spite of low oil and solids content of the oily sludges examined, they do exhibit strong toxic properties. Typically, oily sludges exhibit (on a wet basis) toxicity levels comparable with those of benzene and phenol.

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1. Oily sludge characterization 2. Toxicity I. YO817-004-01-1214

A research program was carried out to sample and characterize, in terms of physical, chemical, and toxicological properties, oily sludges generated by oily wastewater and waste oil treatment facilities at ten major Naval installations in the United States. The information generated under this program provides a basis for oily sludge classification and for developing design criteria for treatment and ultimate disposal technology for oily sludges produced at Naval installations. The oily sludges analyzed indicate that a typical oily sludge is well-dispersed, fairly uniform in consistency, and is a stable mixture of oil, suspended and dissolved organic and inorganic solids, and water. It contains traces of volatile hydrocarbons (usually less than 50 ppm). In spite of the high water content (80 to 90% of the volume), separation of oil from water in sludges is difficult. Some of the collected samples have remained of uniform consistency for a number of months with no indication of phase separation.

Organic toxic substances found in the oily sludge include phenolic compounds and polynuclear aromatic hydrocarbons. Inorganic priority pollutants were also found and included: nickel, zinc, lead, copper, and chromium. In spite of low oil and solids content of the oily sludges examined, they do not exhibit strong toxic properties. Typically, oily sludges exhibit (on a wet basis) toxicity levels comparable with those of benzene and phenol.

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FOREWORD

This report is based upon the two volumes prepared by Rockwell International while under subcontract to Two-D Corporation. The prime contract number was N00123-81-D-0248 with the Civil Engineering Support Office (CESO), Port Hueneme, CA.

Field and laboratory studies dealing with the comprehensive characterization of oily sludges generated at Naval installations were carried out jointly by NCEL and Rockwell-EMSC personnel. The field studies were conducted primarily by Leslie A. Karr, NCEL, and Ihor Lysyj, Rockwell International. Assitance was also provided by the following NCEL personnel: Nicholas J. Olah, Charles Carpenter, and Will Pedersen.

The physical analysis of the oily sludge samples was carried out by Will Pedersen. The chemical analyses were performed by the following personnel: (1) HPLC - Will Pedersen, NCEL, (2) GC - Dan Zarate, NCEL, (3) AA - Gina Melendez, NCEL, and (4) GC-MS - Matthew Yoong, Rockwell. The toxicological studies were conducted by Carmen Lebron, NCEL, with assistance from Ana Chavez and Regina Guerrero for computer graphing of the results.

The results reported are derived from field observations and discussions with plant personnel, and from experimental efforts carried out in the field and in laboratories. Such experimental effort generated new information and data on the physical, chemical, and toxicological properties of oily sludges found at Naval installations and forms a foundation for the conclusions and recommendations presented here.

ACKNOWLEDGMENTS

The conduct of field investigations at the Naval installations in San Diego, CA; Craney Island, VA; Pearl Harbor, HI; Manchester, WA; Mayport, FL; Oakland, CA; and Charleston, SC, was greatly assisted by the following treatment/reclamation plant operating personnel. We wish to express our appreciation for their assistance to:

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Mr. Steve Asato, NSC, Pearl Harbor, HI

Mr. Dale Barker, NSC, Puget Sound, WA

Mr. Carlos Rosado, NAVSTA, Mayport, FL

Mr. Fred Lawrenz, NSC, Point Molate, CA

Mr. Luis Rosa, NSC, Point Molate, CA

Mr. Jake Nelms, NSC, Charleston, SC

LIST OF ACRONYMS

AA	Atomic Absorption
API	American Petroleum Institute
CPI	Corrugated Plate Interceptor
DAF	Dissolved Aeration Flotator
DONUT	Waste Oil Raft
EPA	Environmental Protection Agency
FACET	Oil-Water Separation System
GC	Gas Chromatography
GC/MS	Gas Chromatography - Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
NAS	Naval Air Station
NAVSTA	Naval Station
NCEL	Naval Civil Engineering Laboratory
NSC	Naval Supply Center
PAH	Polynuclear Aromatic Hydrocarbons
SLOP	General Waste Oil Receiving Barge/Tank
SWOB	Ship Waste Offloading Barge

CONTENTS

INTRODUCTION

The Naval Civil Engineering Laboratory (NCEL) was tasked by the Naval Facilities Engineering Command (NAVFAC) to develop sampling and analytical procedures for oily sludge characterization, and to subsequently characterize Naval generated oily sludges.

Oily sludges are complex, multi-phase compositions of matter and contain various chemical species in volatile, liquid, and solid physical states. Sludges are generated as the result of treatment of oily wastes and contain some toxic residues of the process. Legal and environmentally sound approaches to the ultimate disposal of oily sludge require a clear understanding of the nature and amount of this toxic residue.

The data requirements and the methods for acquiring the needed data for handling, treating, and disposing of oily sludges have not been available. A sampling and analytical protocol was developed to identify and quantify the relevant physical, chemical, and toxicological properties of oily sludge.

This report summarizes the sampling and analytical procedures used in the Oily Sludge Characterization Program, while giving a complete characterization of the physical, chemical, and toxicological properties of Navy generated oily sludges according to source.

BACKGROUND

Oily sludges are found at all stages of handling and treatment of oily wastes and oily wastewaters which result from operation of the Navy fleet and onshore installations. Deposits of oily sludges can be found onboard military vessels in bilge compartments, engine rooms, in SWOB barges used for transfer of bilgewater from vessels to onshore installations, in DONUTS used to contain oily wastes, in onshore storage tanks, and at all stages of onshore treatment operations. The principal repositories of oily sludges are in SWOB barges, bilge and ballast storage tanks, gravity separators, DAF sludge storage tanks, oil sumps, and oil recovery towers.

Onshore, oily sludges are a result of the treatment of bilge and ballast wastewaters, as well as from waters contaminated by oil in various onshore operations, such as surface water runoff from fuel storage facilities. In a normal mode of Naval operation, bilge and ballast waters are either delivered directly from docked ships to shore treatment installations through lift stations, or transferred from various Naval vessels into SWOB barges and then delivered to onshore oily waste treatment facilities. Typically, onshore oily wastewater treatment involves the separation of oil and heavier-than-water sludges from the water in the primary treatment operation, which usually consists of gravity settling tanks. The treatment of oily wastewaters under current Naval practices at the majority of shore installations results in, for the most part, its separation into three major fractions: recoverable oil, oily wastewater, and oily sludges. Partially treated oily wastewater is then transferred into and is treated by secondary unit processors, quite often of the dissolved aeration-flotation type. This treatment produces additional recoverable oil and treated effluent, which is disposed of by discharging into receiving waters or sewer lines.

Large quantities of oily sludge/scum are generated by dissolved aeration flotation units. Such sludges contain only small amounts of oil, but nevertheless form a stable oil-in-water dispersion as a result of chemical additives used in the process.

Recovered oil is often processed by heating and separation (settling) of residues (oily sludge) in recovery towers. The great bulk of oily sludges produced at Naval installations results from settling in gravity separators, treatment in DAF units, and in oil recovery units. The toxic organic and inorganic substances are, by and large, removed from the oily wastewaters during such treatment processes, and are concentrated in the oily sludge. Consequently, the oily sludge becomes the principal repository of toxic substances and priority pollutants derived from oily waste generating activities.

Oily sludges are a complex composition of matter, which is multiphase in a physical sense and varied in chemical content. In three states of matter (gas, liquid, and solids) that comprise typical oily sludges, we find water, petroleum, water-soluble organics, volatile organics, and organic and inorganic solids. In chemical terms we find an assortment of volatiles, water-soluble and water-insoluble petroleum-related compounds, as well as dissolved and particulate metallic substances, and soil and sand particles. In toxicological terms, oily sludges are the repository of principal organic and inorganic toxicants and priority pollutants that are separated from the water and oil during storage and treatment of oily wastewaters. In simple terms, oily wastewater treatment processes tend to separate toxic and environmentally hazardous substances from the oil/water mixture and store them in the sludge.

Until recently, oily sludges generated by industrial and government operations alike were not treated any further and were disposed of by commercial contractors in an unregulated manner. Such a mode of disposal in many instances amounted to the introduction of the separated toxic substances into the environment, negating to some extent the basis for treating oily wastewater in the first place.

Oily sludges produced by petroleum refining, including those generated in API and gravity separators and in DAF units, are designated under the law as hazardous waste, and can be disposed of only in regulated hazardous waste disposal sites. There is no reason to believe that oily sludges produced at Naval installations are any less hazardous than those produced at petroleum refineries. They also contain hazardous substances and priority pollutants of an organic and inorganic nature, including phenolic and polynuclear aromatic hydrocarbons and heavy metals (chromium, zinc, copper, lead, nickel). Consequently, similar disposal practices should be expected. The accredited disposal sites are few in number at this time and the costs associated with oily sludge disposal in a regulated manner are high. Because of this, new technological approaches to ultimate disposal of oily sludges are needed. Such technology can only be developed from a factual data base detailing the physical, chemical, and toxicological properties of oily sludges. The principal objective of this research effort is to develop such data.

EXPERIMENTAL DESIGN

GENERAL

The data requirements and the methods for acquiring the needed data for handling, treating, and disposing of oily sludges have not been available. An experimental program was implemented, involving both field and laboratory investigations, to establish the handling and treatability requirements for the ultimate disposal of oily sludges. A sampling and analytical protocol was developed to identify and quantify the relevant physical, chemical, and toxicological properties of oily sludge.

ANALYTICAL PROCEDURES

Physical State Characterization

Oily sludges are complex mixtures and/or dispersions of liquid, solid, and gaseous matter. The following classification specifies the physical components of oily sludge that must be considered for its disposal. Methods are required for determining the following physical components of oily sludge:

a. Solid Phase

- amount of organic solids
- amount of inorganic solids

b. Liquid Phase

- water content
- free oil content
- dissolved oil content

c. Volatile Phase

- concentration of volatile aromatic and aliphatic hydrocarbons

A flow diagram (Figure 1), and a list of calculations are presented herein describing the basic methodology in determining the above.

d. Calculations

Total suspended solids:

% concentration = weight of dry residue x 100/sample weight

Inorganic suspended solids:

% concentration = weight of ashed residue x 100/sample weight

Organic suspended solids:

% concentration = (weight of dry residue - weight of ashed residue) x 100/sample weight

Free oil:

% concentration = weight of oil residue (Freon 113 extraction) x 100/sample weight

Dissolved petroleum:

% concentration = weight of residue (methanol extraction) x 100/sample weight

Water:

% concentration = [weight of sample - (total suspended matter + free oil + dissolved petroleum + volatile compounds*)] x 100/weight of sample

Chemical Characterization

The chemical composition of oily sludges is highly complex and full analysis (compound by compound) for each and every chemical present is neither practical nor required as handling and treatability criteria. Of principal interest to this program are toxic chemicals that might be present in such sludges. Such toxicants associated with oily waste

*Determination of volatile organics is described in the Chemical Characterization section of "Manual for Physical, Chemical, and Toxicological Characterization of Oily Sludge." This value is not critical in determining the percentage of water since it constitutes such a small fraction of the total sample weight.

generally fall into two categories: (a) organic compounds of aromatic nature, including aromatic hydrocarbons and substituted aromatic compounds, and (b) inorganic compounds, mainly heavy metals.

Three separate determinations are performed as part of the chemical analysis for toxic organic and inorganic compounds of oily sludge samples.

HPLC. This method is used for the analysis of aromatic hydrocarbons and other toxic compounds of an aromatic nature. The analytical technique is that of reverse phase, high-pressure liquid chromatography. A methanol-water mixture is used as carrier solvent. The organic compounds elute in order of decreasing polarity in the following sequence: phenols, aromatic hydrocarbons, substituted aromatics, naphthalenes, and finally, polynuclear aromatic hydrocarbons. The HPLC system is calibrated for principal types of organic toxic compounds and average calibration constants are used for calculation of each class of organic compounds found.

A 5-ml aliquot of the methanol-water fraction and a 5-ml aliquot of the Freon 113 fraction are secured in appropriate vials and 10-microliter samples are injected into the HPLC system.

GC. This method covers the determination of principal classes of toxic organic compounds that are known to be present in oily wastewaters. The head space method is used for analysis of volatile hydrocarbons. In this method a known amount (2-3 grams) of oily sludge is placed into a 5-ml reaction vessel with Mininert Teflon caps. The vessel is heated to a temperature of 100°C for 1 hour, then brought down to room temperature and a sample of gas phase is withdrawn by means of a gas-tight syringe and injected into a gas chromatograph equipped with suitable column for separation of volatile hydrocarbons. The system is calibrated with known mixtures of standard gases and concentration of evolved hydrocarbons is calculated from the weight of the sample used and the volume of head space.

AA. This method is used for the determination of heavy metals concentration in the sludge. Ashed residue is dissolved in concentrated nitric acid with gentle heating, transferred quantitatively into 100-ml volumetric flasks, and diluted with distilled water to the mark. A description of procedures for determination of heavy metals is extracted from EPA Methods for Water and Wastewater, EPA 600-4-79-020, March 1979, EPA, Cincinnati, OH 45268. The analysis is based on atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in water samples.

Heavy metals represent the inorganic priority pollutants which are found in suspended form in the sludge. Analyses are performed for antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn).

Toxicological Examination

The toxicity of the sample is determined using Beckman Instruments Microtox Model 2055 precision photometer. This photometer measures the decrease in bioluminescence as the result of exposure of marine luminescent bacteria to toxic samples. Light production in these microorganisms is an expression of the cells of the total rate at which a complex set of energy-producing reactions is operating. Inhibition of any one of a multitude of enzymes involved in this process may cause a change in this rate. Thus, many different modes of action or types of toxicants can be accommodated by the Microtox system. A flow diagram is presented in Figure 2.

Microtox technique provides an extremely rapid, simple test of toxicity with a precision equal to, or greater than a traditional fish toxicity test (Carolanne Curtis et al, U.S. EPA, Duluth, Minn. publication No. 42, Center for Lake Superior Environmental Studies at the University of Wisconsin). Moreover, direct relationships exist between toxicity of organic chemicals to bacteria and the toxicity to fish and mammals as shown in Table 1. Using benzene and phenol as toxicity standards, it is possible to estimate toxic effects of any chemical composition for which EC_{50} value has been determined. The toxicity values reported in this document should be considered in relationship to the toxicity of benzene and phenol.

STATISTICAL METHODS

In the analysis of generated data under the Results section, four statistical expressions were used: average value (mean of sample); standard deviation of sample; correlation coefficient or factor; and test value of correlation factor.

a. Average value is calculated for number of samples analyzed.

b. Standard deviation of the sample is calculated as:

$$S_x = \sqrt{\frac{E_i(x_i - \bar{x})^2}{n - 1}}$$

c. Correlation coefficient is calculated using linear regression to indicate the degree of linearity between two sets of data. For instance, in one case, toxicity of sample was correlated with the PAH of the sludge. A value close to plus 1 indicates a high positive correlation, and a value close to minus 1 indicates a high negative correlation. A value of zero indicates that the two sets of data are not related. Zero correlation or correlation with small negative values were not reported.

d. Test value of calculated correlation factor reflects the validity of correlation value and depends on the number of samples examined. For the same correlation factor, the greater the number of samples examined the greater is the test value. The test values reported were obtained from statistical tables using the number of samples analyzed and the value of correlation factors. The test value (r_{test}) is calculated as follows:

$$r_{test} = \left(\frac{t^2}{t^2 + df} \right)^{1/2}$$

where df is degrees of freedom and t score is from a table of test scores for a given degree of freedom. (Refer to Calculator Decision-Making Sourcebook, Texas Instruments, Inc.)

For example, for the 18 samples analyzed from gravity separators (bottom), the correlation coefficient of 0.75 for the relationship between toxicity and PAH can be considered 99.9% valid (Table 2).

For more detailed information on the analytical procedures used in this study, refer to NCEL Technical Memorandum TM 54-83-18 CR "Manuals for Oily Sludge," Part 2, August 1983.

FIELD OPERATIONS

Sampling

The sample collection plan is designed individually for each facility whose sludge is being examined. Common to the majority of Naval installations are sludge accumulations in storage tanks and gravity separators, DAF unit processes, and oil recovery cookers. Sludges from those sources are always collected if available. Additionally, major sources of sludge collection are oil sumps, API separators, underground and surface fuel storage tanks, and surface oily wastewater impounds. Samples from such sources are also collected when appropriate. The sludge treatment and disposal facilities (such as land disposal farms, sludge drying beds, and others) are examined when available.

The overall scheme for field sampling is designed in such a manner as to provide a comprehensive picture of sludge generation and disposal at the individual Naval installations examined. Actual activities sampled are shown in Figure 3. The scheme also provides for development of an overall comprehensive picture of physical, chemical, and toxicological properties of oily sludges produced at a Naval facility.

Following are brief descriptions of sludge types and sampling equipment used in this study:

a. Low Viscosity. These sludges are often produced in gravity separators, settling tanks, and aeration-flotation cells; usually water based.

b. Medium Viscosity. These sludges accumulate in oily waste storage tanks/sumps and barges after prolonged containment; usually petroleum based.

c. Semi-solid. These sludges are a result of long storage periods in tanks, lagoons, or sludge drying beds; high solids content.

Following are the sampling equipment used in this study:

a. Bacon Bomb Sampler. A commercially available sampling device used for sampling oil and crude oils in storage containers (Figure 4). It is deployed to the bottom, or desired depth, by fishing rod and reel with a safety line. Excellent for low viscosity sludge; good to satisfactory for medium viscosity sludge; unsuitable for semi-solid sludge. (VWR Scientific Inc., #52145-061, ASTM #D117, D270 or D923 or equivalent of.)

b. Sediment Grab Sampler. A commercially available sampling device used for sampling unconsolidated sediments (Figure 5). The sampler is deployed by hydrowire* to the bottom of open storage containers or lagoons. Excellent for semi-solid sludge; marginal for medium viscosity sludge; unsuitable for low viscosity sludge. (Kahl Sci. Co. Box Sampler, #214WA172 or equivalent of.)

c. Hand-operated Bellows Pump. A commercially available sampling device used for sampling oily sludge in enclosed containers and hard-to-access locations (Figure 6). Excellent for low and medium viscosity sludge; unsuitable for semi-solid sludge. (Guzzler, Medium Flow Pump, Lab Safety Supplies Co., #B2140 or equivalent of.)

Sample Preservation and Transportation

Collected samples are secured in appropriately sized wide-mouth glass or plastic bottles and shipped in plastic coolers equipped with blocks of blue ice and secured in a styrofoam matrix (Figure 7). This provides for EPA-specified regulated temperature for the required period of time, 7 days, as well as a stable containment of sampling bottles in a dry environment. (Plastic bottles - VWR Scientific Inc., #16186112 (1000 ml) or equivalent of; Glass bottles - VWR Scientific Inc., #16188140 (1000 ml) or equivalent of; Blue Ice - a commercial mixture of liquids freezing below the freezing point of water, and cooler, may be purchased in a sporting goods store.)

For more information on oily sludge sampling, techniques for sample handling, containment, preservation and shipment refer to Manuals for Oily Sludge, Part 1, NCEL Technical Memorandum 54-83-18CR, August 1983.

*A wire or string needed for deployment of sampler in water.

Data Sources

Samples of various types of oily sludges were collected at ten Naval installations throughout the U.S. Physical, chemical, and toxicological characterizations of each sample were performed.

In San Diego, CA, field work was completed at (a) North Island Naval Air Station, (b) Point Loma Naval Supply Center, (c) 32nd Street Naval Station and (d) Miramar Naval Air Station. At Craney Island, VA, sampling was performed at the Naval Fuel Depot and at Pearl Harbor, HI, samples were collected at the Oily Wastewater Treatment and Reclamation Facility, Naval Supply Center, and at Red Hill underground storage facility. At Manchester, WA, the treatment facility operated by Puget Sound Naval Supply Center was examined. Treatment plants at the Naval Station in Mayport, FL, the Fuel Department in Oakland, CA (Point Molate), and NSC Charleston, were also studied. The results of NSC Charleston were not included in the statistical correlations due to late sampling.

Reporting Structure

The results of these field and laboratory investigations will not be presented according to location (this information; a brief description of each facility and a block diagram of each is presented along with details on each sample taken in 10 separate reports). The data presented here are by source only.

CHARACTERIZATION RESULTS BY SOURCE

As a result of the preceding characterization of oily sludges, ten distinct types of sludges were identified. These sludge types are:

(1) Gravity separator (bottom)

(2) Gravity separator (interface)

(3) DAF

(4) Oil recovery cooker

(5) Oil sump

(6) Dewatered

(7) Oily wastewater impoundments

(8) API and coalescer

(9) Oily waste transport

(10) Fuel tanks

The analytical approach to the examination of the data is based on relating toxicological properties to principal chemical parameters determined: free and dissolved oil, PAHs, phenols, inorganic and organic solids, heavy metals, and volatiles. Such examination permits pinpointing relative contributions of each chemical parameter to the overall toxicity of the sample in each category of oily sludge examined.

GRAVITY SEPARATOR (BOTTOM) SLUDGE

Sludges are produced as a result of settling of heavier than water components of oily wastewater in settling or gravity separation tanks. Such treatment of oily wastewater is most common in Naval shore installations. Gravity separation, by itself, or in combination with other unit processes is the backbone of Naval technology for treating oily wastes, and generates large portions of oily sludges. Composition of such sludges consists largely of heavier than water petroleum, including the bulk of PAHs and inorganic solids.

Chemical Considerations

Analyses were carried out for free and dissolved oil, inorganic and organic solids, and toxicologically important PAHs, phenols, volatiles, and heavy metals. As shown in Table 2, the average free oil content was found to be 23.6% with a standard deviation of 23.7% . The PAHs concentration in analyzed samples was found to average at 7,823 ppm with a standard deviation of 9,320 ppm. On the basis of collected data it appears that PAHs concentration in analyzed samples is proportional to free oil concentration. The PAHs constituted an average 2.8% of free oil content (with a standard deviation of 1.2%).

As can be seen from Table 3, the dissolved oil content of analyzed samples was considerably lower: 0.9% with a standard deviation of 0.6%. The phenolics content averaged 476 ppm with a standard deviation of 419 ppm. The concentration of phenols appears to be proportional to dissolved oil and constitutes 6.3% of the dissolved oil with a standard deviation of 3.2%.

As expected, relatively high concentrations of inorganic solids were found in this type of sludge sample: an average of 6.6% with a standard deviation of 15.6 (Table 4). Concentrations of organic solids were lower: an average of 2.1% with a standard deviation of 3.2% . The volatile hydrocarbon content of analyzed samples (Table 5) was found to be on an average 42 ppm with a standard deviation of 14 ppm. This value is relatively low in terms of total material balance. It is believed that the volatile content of such samples will not significantly effect any of the state-of-the-art treatment options or pose any air pollution problems in sludge disposal.

Heavy metals content of waste matter is of considerable toxicological importance and environmental consequence. Such chemical matter is designated by the EPA as priority pollutants and their release into the environment is regulated. For this reason all oily sludge samples were analyzed in terms of eleven (11) designated priority pollutants: Antimony (Sb), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead

(Pb), Nickel (Ni), Selenium (Se), Silver (Ag), Thallium (Tl), and Zinc (Zn). Consistently present in the analyzed samples were chromium, copper, lead, nickel, and zinc (Table 6). Such metals are widely used in equipment associated with ship and shore operations and their consistent presence in oily sludges generated at naval installations is not surprising. Zinc was found to be present in the highest concentrations: 204 ppm with a standard deviation of 351 ppm. Next was copper: 78 ppm with a standard deviation of 117 ppm, and lead: 70 ppm with a standard deviation of 145 ppm. Chromium and nickel were in a lower concentration range: chromium value averaged 37 ppm with a standard deviation of 64 ppm, and nickel was found at 12 ppm with a standard deviation of 16 ppm. This pattern of concentration relationship between various heavy metals appears to be consistent in all types of oily sludges examined under this program. The average total heavy metals content of gravity separator bottom sludges was found to be 400 ppm with a standard deviation of 679 ppm.

Toxicological Considerations

The average toxicity value of the 18 oily sludge samples in this category is EC_{50} (15 minutes) of 61.8. This value falls in the middle range between toxicity of phenol, [EC_{50} (15 minutes) of 28] and toxicity of benzene, [EC_{50} (5 minutes) of 173].*

The correlations between toxicity and various chemical parameters are depicted graphically in Figure 8. As can be seen from this figure the free oil content and PAHs content of sludge samples correlate rather well with toxicity. A correlation factor of 0.77 with a test value of 99.9% was calculated for toxicity to free oil relationship, and a correlation factor of 0.75 with a test value of 99.9% was calculated for toxicity to PAHs concentration relationship. A lower order of correlation is observed between toxicity and volatiles (a factor of 0.51 with a test value between 90 and 95%). Other chemical parameters correlated poorly, or not at all with toxicological properties: phenols 0.19, dissolved oil 0.09, and organic solids, inorganic solids and heavy metals have negative correlation factors. Examination of the composite data (Figure 8) reveals that free oil is the main chemical constituent of gravity separator bottom sludges (23.6%), and also contains high levels of PAHs (7,823 ppm). Based on this it can be concluded that in the case of gravity separator bottom sludges the main chemical components (free oil and PAH) are principal contributors to the toxicity of the sludge and their removal or destruction will significantly reduce any environmental hazards associated with disposal of such sludges.

Also shown in Figure 8 is the correlation between free oil and PAHs, which was found to be very high (0.98 with a test value of 99.9%) and the correlation between dissolved oil and phenols, which was found to be considerably lower (0.40 with a test value of 90%).

*Microtox Application Notes, Beckman Instruments, Carlsbad, Calif.

GRAVITY SEPARATOR (INTERFACE) SLUDGE

Two types of oily sludges are produced in gravity separators or settling tanks: bottom and interface. Bottom sludges contain organic and inorganic compositions heavier than water. Interface sludges contain a chemical composition which is heavier than oil but lighter than water. A typical gravity separator unit-process contains interface sludge layers several feet deep. Such sludge is composed largely of colloidal and emulsified petroleum as well as biologically degraded oil. It is an extremely stable mixture, and is very difficult to treat. Since interface sludges are generated in gravity separators which are widely used as the principal method of treatment of oily wastewaters, such sludges are important in terms of volume generated and wide geographic distribution.

Chemical Considerations

Collected samples were analyzed for free and dissolved oil, PAHs and phenols, inorganic and organic solids, heavy metals, and volatiles. Six individual samples comprise the data base on interface sludges.

Free oil content was found to average at 18.5% with a standard deviation of 6.9% (Table 7). The PAHs concentration was determined at 4,679 ppm and constituted 2.7% of free oil. The proportion of PAHs in free oil from bottom and interface sludges was almost identical.

Dissolved oil content as well as phenol content of interface sludges are also similar to gravity separator bottom sludges. It was found that average concentrations of dissolved oil (Table 8) were 0.8% with a standard deviation of 0.3%. Phenols were found at 575 ppm concentration with a standard deviation of 386 ppm. The concentrations of phenols and dissolved oil appear to be proportional. Phenols constitute 8.2% of the dissolved oil with a standard deviation of 5.8%. A similar relationship was also observed in gravity separator bottom sludges.

The inorganic solids content, as expected, is lower in interface sludge than in bottom sludge (Table 9). It averaged at 1.6% with a standard deviation of 0.7%. Organic solid concentrations on the other hand are higher: 2.9% with a standard deviation of 2.2%. The bacterial decomposition of petroleum is most intensive at the interface of oil and water and some of the organic solids in this case might be derived from the biological degradation of petroleum.

The volatile organic content (Table 10) averages at 49 ppm with a standard deviation of 7 ppm. This value was similar to the volatile organic content found in gravity separator bottom sludges.

The interface oily sludges were analyzed for eleven (11) priority pollutant metals, and five were found to be present: chromium, copper, lead, nickel, and zinc (Table 11). Zinc was found in the highest concentrations: 180 ppm with a standard deviation of 60 ppm. Next was copper: 107 ppm concentration with a standard deviation of 63. Chromium and lead were found in similar concentrations: chromium averaged 46 ppm with standard deviation of 66 ppm, and lead 52 ppm with a standard deviation of 62 ppm. Nickel was found in the lowest concentrations: 16 ppm with a standard deviation of 14 ppm. The total heavy metals content of the interface sludge averaged at 402 ppm with a standard deviation of 237 ppm. Both the total heavy metals concentration level, and the distribution between individual metals were very similar to those observed in gravity separation bottom sludges.

Comparing chemical compositions of bottom and interface sludges in gravity separators, we find similarities such as concentration and types of heavy metals found, and concentration levels of dissolved oil and volatiles. The principal differences are found in the inorganic solids content and PAH concentrations. These differences are sufficiently high to classify sludges from gravity separators into two distinct generic types: bottom and interface.

Toxicological Considerations

The average toxicity for six gravity separator interface sludges is EC_{50} (15 min) of 35 with a standard deviation of ±80%. These sludges are closer in toxicity to phenols [EC_{50} (15 min) of 28] than to benzene [EC_{50} (5 min) of 173].

The correlation between toxicity and various chemical parameters is depicted graphically in Figure 9. As can be seen from this figure there is no correlation between toxicity and free oil, PAHs, and dissolved oil, inorganic solids, and heavy metals. A low order of correlation was calculated for phenols (0.16), organic solids (0.22), and volatiles (0.39).

It must be kept in mind, however, that the number of samples analyzed in this category were rather small (6) and the concentration spread for individual parameters (expressed as standard deviation) was considerably narrower than for gravity separator bottom sludges. Combination of these two factors makes development of correlation factors more difficult. Additional sampling and analyzing of this type of oily sludge is recommended to form a more extensive basis for evaluations.

DISSOLVED AERATION FLOTATORS (DAF) SLUDGE

Second to gravity separators, DAF unit-processes are widely used for the treatment of oily wastewaters at Naval shore installations. Such units are commonly found in conjunction with gravity separators and function as a second means for treatment. In DAF treatment, air is dissolved under pressure in the side stream and this water stream becomes supersaturated with air. As the pressure is released, the excess air comes out of the solution in the form of minute bubbles. These bubbles collide with any suspended solids or oil globules in the stream and become attached. This changes the net specific gravity of the agglomerates, causing them to float. The floating particulate matter and oil are skimmed from the surface. The separation of oil from water by aeration flotation is aided by the addition of flocculating chemical agents (alum and polyelectrolytes).

Oily sludge produced in the operation of a DAF unit is initially lighter than water due to the presence of air bubbles in the oil agglomerate. After separation, surface scum/sludge is usually transferred into DAF sludge storage containers, where excess air is gradually lost and the agglomerate of oil and chemical additives becomes heavier than water. The dissolved aeration flotators produce large volumes of waste at Naval installations. Such sludge contains, in addition to separated oil, substantial amounts of chemicals (both organic and inorganic) added as a part of the process. Added chemicals in many instances become principal components of produced sludge and are found in this type of sludge in larger quantities than the separated oil due to the large volume produced. The disposal of DAF sludge poses serious problems in operation of some Naval shore installations.

Chemical Considerations

Samples of DAF sludges were collected, in some instances, from the DAF itself or from sludge storage tanks. Numerous samples were taken at various depths to account for spatial distribution in such tanks. In one instance (Manchester, WA) such samples were collected from the top surface of the operating unit. The collected samples were analyzed for free and dissolved oil, organic and inorganic solids, PAH and phenols, heavy metals, and volatile organics.

The free oil content of DAF sludges was found to be low: 2.4% with a standard deviation of 2.5% (Table 12). This value is approximately 10 times lower than the free oil content in gravity separator bottom sludges. Correspondingly, PAHs concentration was also low: 663 ppm with standard deviation of 661 ppm. The ratio of PAHs to free oil appears to be constant. On the average, PAHs contributed 3.1% to the concentration of free oil. This proportion is not unlike one that was observed in gravity separator (both bottom and interface) sludges.

As shown in Table 13, dissolved oil content as well as concentrations of phenols were also lower than those observed in gravity separator sludges. Dissolved oil averaged at 0.6% with a standard deviation of 0.5%, while phenols were found to be present in average concentrations of 336 ppm, with a standard deviation of 202 ppm. The ratio of phenols to dissolved oil was however, constant; at 8.4% concentration phenols in dissolved oil, it was not unlike values observed in samples of gravity separator sludges.

Suspended solids constituted the bulk of chemicals found in DAF oily sludge (Table 14). Organic solids were found at an average concentration of 4.9% with a standard deviation of 5.9%. The organic solids value was approximately twice the value for free oil. Inorganic solids constituted, on an average, 2% of the sludge with a standard deviation of 1.4%. It is believed that the bulk of suspended solids found in DAF sludges arise from chemical additives (alum and polyelectrolytes) used in the process treatment. The volatile organic content of DAF sludges was very low: 5.3 ppm with a standard deviation of 2.5 ppm (Table 15).

Out of eleven (11) priority pollutant metals, five were found in significant quantities: chromium, copper, lead, nickel, and zinc (Table 16). The concentrations, however, were considerably lower than those observed in gravity separator sludges: zinc was found at 71 ppm concentration with a standard deviation of 53 ppm, next to zinc was lead at 29 ppm concentration with a standard deviation at 28 ppm. Copper was found in concentrations of 22 ppm with a standard deviation of 18 ppm. Chromium and nickel were found in very low concentrations: chromium averaged at 6 ppm with a standard deviation of 8 ppm. Nickel concentration was found to be 4 ppm with a standard deviation of 3 ppm. The total heavy metal load in DAF sludges was found to be, on the average, 132 ppm with a standard deviation of 100 ppm.

The analysis of the chemical composition of DAF produced sludges indicates that such sludges form a distinct and generically different class of waste produced in treatment of oily wastes. The concentration of significant (from a toxicological point of view) parameters (free oil, PAHs, dissolved oil, phenols, volatiles, and heavy metals), is considerably lower than that observed in gravity separator sludges. The concentration of suspended solids, however, is high and is probably due to chemical additives in the process stream.

Toxicological Considerations

The average toxicity for 18 samples of DAF sludge is an EC_{50} (15 min) of 182 with a standard deviation of 257. A low order of toxicity in DAF sludges collected at Manchester contributed to the low average value for this type of sludge.

The correlation between toxicity and various chemical parameters is depicted graphically in Figure 10. The best correlation exists between suspended organic solids and toxicity (a correlation factor of 0.90 with a test value of 99.9%), and between phenols and toxicity (a correlation factor of 0.73 with a test value of 99.9%).

Lower orders of correlation were observed between toxicity and heavy metals (a correlation factor of 0.58 with a test value of 99%); between toxicity and inorganic solids (a correlation factor of 0.59 with a test value of 95%); and between toxicity and volatiles (a correlation factor of 0.31 with a test value <80%). No correlations were observed between toxicity and dissolved oil and a very low order of positive correlation (a factor of 0.11) was found between toxicity and PAHs.

It is interesting to note that DAF sludges, one of the major types produced by Naval operations, are of a relatively low order of toxicity, and that principal contributions to its toxicity are inorganic and organic solids, which are added to process streams to enhance oil water separation. In addition to chemical additives (alum and polyelectrolytes and lime) phenolic materials are also contributors to toxicity of this generic type of oily sludge.

Free oil, heavy metals, PAHs, and volatile organic compounds are present in much lower concentrations in this type of sludge than in the other sludges examined in this program and consequently do not contribute significantly to toxicity of DAF sludges. It can be postulated that elimination of alum and polyelectrolytes from the treatment process and substitution of separation aids with lower toxicity (such as DAFSORB, manufactured by RADECCA Inc.,) could further reduce toxicity of this type of waste, simplifying procedures for its disposal.

Considering that free oil, PAHs and heavy metals are found only in very low concentrations in this type of oily sludge, and that the overall toxicity of this waste is the lowest of all examined under this program, less stringent requirements for its treatment and disposal may be justified. Positive correlations were observed in the relationship between free oil and PAHs (a correlation factor of 0.59 with a test value of 99%) and between dissolved oil and phenols (a correlation factor of 0.89 with a test value of 99.9%).

OIL RECOVERY SLUDGE

Recovery of oil from oily wastewater is a common practice at Naval treatment operations. Normally, oily wastes which are separated from the wastewater are transferred into treatment towers (commonly called "cookers"). Treatment towers are usually heated and equipped with means for the addition of demulsification chemicals. With assistance of heat and chemicals, oily wastes are separated into an oil and water phase. Depending on the quality of recovered oil, it is either used as a fuel in marine operations or as a fuel in onshore power generation plants. Some of the Naval shore installations are equipped with two oil recovery units - one for producing specification fuel, the other for producing off-specs products.

The undesirable waste compounds, including heavy metals, suspended organic and inorganic solids, and water accumulate at the bottom of oil recovery towers and constitute oily sludge produced in oil recovery operations.

Chemical Considerations

In all instances oily sludges were collected at the bottom layer of oil recovery towers using a Bacon sampling bomb. Samples were analyzed for free and dissolved oil, inorganic and organic solids, PAHs and phenols, heavy metals and volatile organics. The free oil content of the sludges from the oil recovery towers was the highest of all the types of samples collected under this program from treatment plants, and only oily sludges from fuel tanks had higher concentrations of free oil.

As shown in Table 17, the average value for free oil in 16 sludge samples collected from the oil recovery towers was found to be 40.3% with a standard deviation of 33.6. Concentration of PAHs in this type of oily sludge was also high. An average value of 10,924 ppm with a standard deviation of 13,371 ppm was recorded. The concentration of PAHs correlated rather well with free oil; a correlation factor of 0.74 with a test value of 99% was calculated for 16 samples. Analyzed PAH constituted 2.6% of free oil, a value similar to others observed in this study.

The concentration of dissolved oil was also high, and at an average of 2.8% with a standard deviation of 4.8% it was the highest observed in this study (Table 18). The average level of phenols was recorded at 563 ppm with a standard deviation of 543 ppm. Phenols constituted 8.5% of the dissolved oil concentration and correlated well with this parameter. A correlation factor of 0.73 with a test value of 99.9% was recorded for phenols - dissolved oil relationship.

Suspended solids were present in moderate concentrations (Table 19). Organic solids were found at 2.9% concentration with a standard deviation of 2.6%. The inorganic solids content averaged at 1.3% with a standard deviation of 2.1.

As shown in Table 20, the volatile hydrocarbon content in this type of sludge was high, it averaged at 49 ppm with a standard deviation of 38 ppm.

Out of eleven (11) priority pollutant metals studied, five were present in significant quantities: chromium, copper, lead, nickel, and zinc (Table 21). The range of concentrations for individual metals in five (5) sources of sludges collected was quite wide. Zinc was found in the highest concentration of 152 ppm with a standard deviation of 200 ppm. Next was chromium in concentrations of 82 ppm with a standard deviation of 196 ppm. Copper was present in concentrations of 68 ppm with a standard deviation of 88 ppm. Concentrations of lead were found to be 52 ppm with a standard deviation of 78 ppm. Nickel was found in the lowest concentrations: 23 ppm with a standard deviation of 47 ppm. The total heavy metal content in the oil recovery sludges was found to be 379 ppm with a standard deviation of 532 ppm. The highest concentration of heavy metals was found in oily sludges collected from special oil treatment and recovery tanks (Nos. 115 and 116) at the Manchester facility. These tanks were used for reclamation of gravity separator sludges accumulated over a period of many years. The process of reclamation is by heat and emulsion breaking chemicals.

The analysis of oily sludges produced in oily recovery processes indicates that such sludges form a distinct and generically different class of waste produced at Naval facilities for treating oily wastewaters. Such sludges have the highest free oil content, approximately twice the average concentration for all oily sludges examined, and very high PAHs content, which is second only to PAH concentrations in sludges collected from fuel tanks. Higher than average concentrations of organic solids, and lower than average concentrations of inorganic solids are also characteristic of this type of oily sludge. Both free oil and PAHs, dissolved oil and phenol concentrations correlated well (correlation factors of 0.74 and 0.73, respectively).

Toxicological Considerations

It was found that oily sludges from oil recovery unit-processes exhibit the highest order of toxicity within all the types of oily sludges examined under this program. The average toxicity for 16 samples of oily sludges was found to be EC_{50} (15 min) of 19, with a standard deviation of 13. It must be kept in mind that this type of sludge has a very high free oil and PAH content, which is an important factor, as far as toxicity is concerned.

The correlation between toxicity and various chemical parameters is depicted in Figure 11. Good correlation exists between PAHs and toxicity; a correlation factor of 0.70 with a test value of 99.9% was established for these two parameters. The degree of correlation between free oil and toxicity is lower: a correlation factor of 0.49 with a test value of 95%. There is no correlation between toxicity and concentrations of dissolved oil, phenols, inorganic and organic solids. Some degree of correlation is observed between toxicity and volatile hydrocarbon content: a correlation factor of 0.32 was computed. Fair correlation exists between heavy metals and toxicity: a correlation factor of 0.50 with a test value of 95-99%.

On the basis of examination of this data, it may be concluded that the principal factors influencing the toxicity of oil recovery sludges are: PAHs, heavy metals, and free oil. Because this type of oily sludge is found to be extremely toxic, special protection of personnel conducting disposal operations is recommended. Respiratory and skin protection in this instance is advised.

OIL SUMP SLUDGE

Oil sumps are found at the majority of facilities used for treating or transporting oily wastewaters. They are normally below ground, cemented structures, of rectangular or circular design, 5 to 10 feet deep. The oil sumps function as a part of the wastewater flow system and as receivers for oily waste delivered by tanker-trucks or other means. Heavier than water components of oily wastewater tend to settle at the bottom of oil sumps and accumulate to depths of several feet. Periodically, such sumps are cleaned, usually by contractors, and recovered oily sludge is removed from Naval property. It is difficult to estimate, at this time, the volume of sludges produced at such sources, but it could be a significant source of specific waste generated by the Navy.

Chemical Considerations

Oily sludges from oil sumps were collected at three (3) Naval installations (Point Loma, CA , NSC; Pearl Harbor, HI, NSC; and Point Molate, CA, NSC.) and analyzed for free and dissolved oil, inorganic and organic solids, PAHs, phenols, volatiles, and heavy metals. It was found that the average free oil content of this sludge was 5.24% with a standard deviation of 3.8% (Table 22). The PAHs concentration was found to average at 1,004 ppm with a standard deviation of 705 ppm. Both free oil and PAHs concentrations in this class of oily sludge were relatively low. Concentrations of free oil correlated well to the concentration of PAHs (a correlation coefficient of 0.76 with a test value of 95%), and PAHs constituted on the average 2.2% of the free oil content.

Dissolved oil content was found to average 1.0% with a standard deviation of 1.1 (Table 23). Phenols were present at 423 ppm level with a standard deviation of 281 ppm. Both the dissolved oil content and the phenols concentrations in oily sludges from oil sumps were very close to the average values observed for all types of oily sludges analyzed under this program.

Inorganic solids were found to average at 7.1% with a standard deviation of 10 (Table 24). The organic solids were in lower concentrations of 4.8% with a standard deviation of 7.1.

The level of volatile hydrocarbons was similar to that of the other sludges analyzed under this program and averaged at 29 ppm with a standard deviation of 24 ppm (Table 25).

The heavy metal content, on the other hand, was relatively high, and the total value averaged at 1,076 ppm with a standard deviation of 1,668 ppm (Table 26). Zinc, similar to all the other sludges, was found in the highest concentrations - 418 ppm with a standard deviation of

639 ppm. Next in concentration was lead - 299 ppm with a standard deviation of 500 ppm, and copper - 285 ppm with a standard deviation of 417 ppm. Present in lower concentrations were nickel - 41 ppm with a standard deviation of 69 ppm, and chromium - 28 ppm with a standard deviation of 46 ppm. The heavy metal content of oily sludges was found to be quite high, and only dewatered (concentrated) sludges recorded higher values.

Toxicological Considerations

The average toxicity value of the 6 oily sludge samples in this category is EC_{50} (15 min) of 56, with a standard deviation of 42. This value is close to the average toxicity value of all sludges analyzed. Because of the low number of samples analyzed in this category, correlation between toxicity and various chemical parameters was more difficult to establish. Nevertheless, positive correlations were established between toxicity and free oil (a correlation factor of 0.80 with a test value of 95%) and between toxicity and PAHs (a correlation factor of 0.47) (Figure 12).

DEWATERED SLUDGE

Oily sludges contain large amounts of water, and dewatering is used as a method for volume reduction. Two methods for dewatering are normally used: open drying beds, and sludge presses. Air drying of oily sludges is practiced at North Island NAS, and in Mayport, FL, NAVSTA. The San Diego facility is equipped with two cemented beds, and leachates from the beds are prevented from entering ground waters, while the Mayport, FL facility has three unlined beds, where leachates may enter groundwater. Two facilities are equipped with oily sludge presses: Craney Island, VA, and Manchester, WA. The Manchester facility uses its presses in routine plant operations, while the facility in Craney Island does not.

Sludges produced by dewatering processes are concentrated and contain 30 to 40% of solid matter and oil. Heavy metal residues are concentrated in such sludges and constitute a principal source of toxicants. Organic matter, including PAHs undergo biodegradation in open air lagoons and as a result are chemically modified and differ from the original petroleum composition. Because of their concentrated nature, this type of oily sludge represents a distinct type and is generically different from other types of oily sludge.

Chemical Considerations

Samples of dewatered sludges were collected from three Naval installations: North Island NAS, San Diego, CA; Mayport NAVSTA, FL; and Manchester NSC, WA. A total of 12 samples were collected and analyzed for free and dissolved oil, inorganic and organic solids, PAHs and phenols, volatiles, and heavy metals.

As indicated in Table 27, the free oil content of dewatered oily sludge samples was quite high, it averaged at 10.8% with a standard deviation of 8.3. Biodegradation over a period of years (oily sludge concentrates were not removed from either lagooning facilities since they were established) probably contributes to some reduction in the concentration of free oil. The PAHs were found to be present in concentrations of 3,829 ppm with a standard deviation of 2,670 ppm. The concentration of PAHs in the free oil was quite high (3.6%) and correlated well (a factor of 0.86 with a test value of 99%).

The concentration of dissolved oil was rather average at 1.1% with a standard deviation of 0.6 (Table 28). The phenolic materials on the other hand were present in very high concentrations: 7,821 ppm with a standard deviation of 6,348 ppm. This value is almost five times greater than the average phenol content of all the samples analyzed. The high phenolic content in such sludges might be due to the oxidative nature of biodegradation processes during long periods of fermentation in drying beds. It is possible that the bulk of phenolic materials originates not in petroleum waste, but is formed during long storage periods in drying beds. Because of relatively low concentrations of dissolved oil and very high concentrations of phenols, accurate determination of phenol content in dissolved oil was not possible.

Both organic and inorganic solids were present, as expected, in high concentrations in this type of sludge (Table 29). The average value for inorganics was found to be 13% with a standard deviation of 7.6. The organic solids were present at 10.2% with a standard deviation of 6.1. Both organic and inorganic content of dewatered sludges were the highest of all oily sludge samples analyzed under this program.

The volatile organic content of dewatered sludges was very low: 5.7 ppm with a standard deviation of 2 ppm (Table 30). This low value might be explained by the fact that a long residence time of petroleum waste in open air beds leads to depletion and loss of volatile matter through evaporation.

Out of eleven (11) priority pollutant metals examined under this program, five were found in significant quantities: chromium, copper, lead, nickel, and zinc (Table 31). Zinc was found in the highest concentration, 1,072 ppm with a standard deviation of 1,195 ppm, next was copper at an average concentration of 176 ppm with a standard deviation of 131 ppm. Lead was present in 74 ppm concentration, with a standard deviation of 69 ppm; nickel was found at 49 ppm level, with a standard deviation of 42 ppm; and chromium was present at 45 ppm with a standard deviation of 30 ppm. The total heavy metal content of analyzed samples was found to be 1,410 ppm with a standard deviation of 1,297 ppm. The total heavy metal content of dewatered sludges was highest of all the types of sludges analyzed under this program. Cadmium was also present in some samples. Average concentration for cadmium was less than 1 ppm.

Toxicological Considerations

The average toxicity value for 12 samples of dewatered sludges is an EC_{50} (15 min) of 46, with a standard deviation of 42. This toxicity was close to the mean value for all the oily sludges tested under this program. Heavy metals correlated positively with toxicity, and a correlation factor of 0.74 with test values of 95-99% were computed for those parameters (Figure 13). Other chemical parameters did not correlate with toxicity. There are two possible explanations for these observations: (1) the very high heavy metal content is responsible for major contributions to the toxicity of the sludge, overshadowing contributions of other chemical parameters, and (2) biological modification of organic matter over long residence periods in drying beds results in chemical modification of compounds, leading to a lower order of toxicity than found in original petroleum compositions. In any case, it is apparent that the major source of toxicity in dewatered sludges is due to heavy metals content.

API AND COALESCER SEPARATORS SLUDGE

The preceding chapters dealt with major sources of oily sludge generation at Naval installations. There are additional specialized oily wastewater treatment units that are used at some Naval shore installations. These units will be discussed in this section.

API separators can be described as dynamic gravity separators. Oil separates from water as wastewater flows through open air channels that are approximately 60 feet long. Two of these channels are used at Pearl Harbor NSC, HI, for treating oily wastewaters after primary treatment in storage tanks.

Coalescer separators use physical means for separation of oil from water on fibrous filters. A unit of this kind is used for secondary separation of oil from water in Point Molate NSC, CA.

While those two types of treatment are different in nature they will be grouped in this chapter as specialty equipment of limited use at Naval installations.

Chemical Considerations

The free oil content of sludges in this category was the lowest of all sludge examined under this program: it averaged at 1.2% with a standard deviation of 0.4 (Table 32). In a similar way to free oil, the concentration of PAHs was also lowest of all values observed: it averaged at 224 ppm with a standard deviation of 92 ppm. The PAHs constituted 1.9% of free oil and a correlation factor of 0.45 with a test value of 80% was calculated for the relationship between PAHs and free oil.

As shown in Table 33, the dissolved oil concentration was found to be low also, it averaged 0.5% with a standard deviation of 0.5%. Phenols were present at 211 ppm average concentration, with a standard deviation of 159 ppm. This value was the lowest of all generated under this program. Phenols constituted 5.8% of dissolved oil, and correlated with it fairly well (an 0.69 correlation factor with a test value of 95%).

Inorganic solids were found at an average concentration of 2.5% with a standard deviation of 1.6 (Table 34). The organic solids were present in a similar concentration of 2.6% with a standard deviation of

2.4. The solids content in this type of sludge was low relative to the other types of sludges. Volatile organics were present at a 9.3 ppm average concentration level with a standard deviation of 3.8 ppm (Table 35).

Out of eleven (11) priority pollutant metals analyzed, five were present in significant quantities. The total heavy metal content was 146 ppm with a standard deviation of 106 ppm (Table 36). Zinc was found in the highest concentration; it averaged 83 ppm with a standard deviation of 54 ppm. Copper was present at 34 ppm with a standard deviation of 36 ppm. The average concentration of lead was found to be 18 ppm with a standard deviation of 17 ppm. Nickel had an average concentration of 5 ppm with a standard deviation of 5 ppm. The concentration of chromium was found to be 5 ppm with a standard deviation of 3 ppm. Generally speaking, the concentration of heavy metals in this type of sludge was low. It must be kept in mind that both API separators and coalescer separators are used as secondary treatment processes, and that the bulk of separatable oily sludge is removed from the process stream in primary gravity separators before the process stream ever reaches the second stage of treatment.

The analysis of the chemical composition of sludges produced in secondary treatment processes of specialized design reveals that the concentration of almost every chemical parameter analyzed was very low. This is due to the secondary nature of treatment, and the bulk of contaminants are removed prior to the process water entering the secondary unit-processes. The oily sludge from this type of processing is a distinct type or category.

Toxicological Considerations

The average toxicity for 8 samples is EC_{50} (15 min) of 109 with a standard deviation of 106. This toxicity level was the second lowest of all the types of sludges analyzed under this program. Only DAF sludges have a lower toxicity. The DAF, API, and coalescer separators are normally used as secondary treatment unit-processes, and the influent into such units has been previously treated in gravity separators. Data reported in this document indicate that primary treatment units are quite effective in separation of toxic substances from the process stream into the sludge, and that the process stream is detoxified to a large degree prior to its entry into secondary treatment unit-processes. For this reason oily sludges produced in DAF, API, and coalescer separators have lower concentrations of free oil, PAHs and heavy metals, than those produced from primary treatment, and consequently exhibit lower orders of toxicity.

The correlations between toxicity and various chemical parameters are depicted in Figure 14. As can be seen from this table some of the chemical parameters correlated quite well with toxicological properties of sludge while others did not.

Poor correlations exist between free and dissolved oil and toxicity. The correlation factor of 0.14 was recorded for free oil and a correlation factor of 0.17 was observed for dissolved oil. The PAH and phenol concentrations, on the other hand, correlated with toxicity rather well. For PAHs, a correlation factor of 0.54 with a test value of 90% was observed, while a correlation factor for phenols was 0.69 with a test value of 95%.

Inorganic solids correlated with toxicity rather well; a correlation factor of 0.64 with a test value of 90% was established. The correlation between organic solids and toxicity was, on the other hand, poorer; a factor of only 0.26 was established. The volatiles content of this sample did not correlate with toxicity at all (a negative factor was computed in this case). The correlation between heavy metals and toxicity was fairly good, a factor of 0.61 with a test value of 95% was computed.

It can be stated, in general terms, that secondary treatment units of API and coalescer type produce sludge that is lower in toxicity than sludges produced by other unit processes, and that the following chemical parameters: heavy metals, PAHs, and phenols correlate fairly well with observed toxicity of samples.

IMPOUND SLUDGE

Impounds of oily wastewaters in open air lagoons is practiced at two Naval installations. Red Hill fuel storage facility at Pearl Harbor, HI, uses this method for storage and treatment of fuel tank bottom residues, which are composed largely of water. This storage pond or lagoon is cemented and oily wastes separate into lighter than water surface scum and heavier than water sludges, which deposit at the bottom.

The Naval treatment facility at Mayport, FL, uses unlined lagoons for final storage of treated oily wastewater before discharging into the St. Johns River. In both instances oily wastewater is open to the air for extended periods of time.

Chemical Considerations

Samples of bottom sludges and surface scum were collected in Pearl Harbor, HI. No surface scum was observed in the holding pond for treated water in the Mayport, FL, facility, and only bottom sludges were collected there. A total of 8 samples of sludges from this source were collected and analyzed for free and dissolved oil, inorganic and organic solids, PAHs and phenols, heavy metals and volatile organics.

Free oil content (Table 37) of this type of sludge was found to be 7.3% with a standard deviation of 12.3. A large standard deviation is due to the dissimilar nature of sludges collected from the surface and bottom of a storage pond in Pearl Harbor. The surface layer in this case contained an average 28% free oil, while bottom sludge had only 0.6% of free oil. PAH concentration was found to average at 2,667 ppm with a similarly high standard deviation of 4,607 ppm. PAHs accounted for 2.7% of free oil and correlation between both parameters was good - a factor of 0.99% was computed.

Dissolved oil content in this type of oily sludge averaged at 1.0% with a standard deviation of 0.9 (Table 38). This concentration value is close to the average value obtained for oily sludges analyzed under this program. The phenolic content of analyzed sludges in this category, however, was high. It averaged at 2,850 ppm with a standard deviation of 4,182 ppm. Very high concentrations of phenols were observed in the top layer of oily scum collected at the Pearl Harbor facility - an average concentration of 9,500 ppm was recorded, inflating the average value of all samples collected in this category.

Concentrations of inorganic and organic solids in impound sludges were high: an average value of 8.6% with a standard deviation of 9.0% was determined for inorganic solids, and a 4.3% value with a standard deviation of 4.2 was recorded for organic solids (Table 39).

The concentration of volatile hydrocarbons was moderate and a value of 26 ppm with a standard deviation of 24 ppm was recorded (Table 40).

Heavy metals content of the samples was low: the total concentration averaged at 196 ppm with a standard deviation of 113 ppm (Table 41). Out of 11 substances analyzed, five were found to be present in significant concentrations: zinc at 80 ppm concentration, with a standard deviation of 45 ppm; copper at 32 ppm concentration, with a standard deviation of 17 ppm; chromium at 24 ppm concentration, with a standard deviation of 17 ppm; lead at 16 ppm concentration, with a standard deviation of 12 ppm; and nickel at 15 ppm concentration, with a standard deviation of 15 ppm.

Based on the information reported here, it can be concluded that surface scums and bottom sludges produced from oily wastewater in open air impoundments do form a distinct type of oily sludge. It is characterized by a high inorganic and organic solids content and a lower than average free oil and heavy metals content.

Toxicological Considerations

The average toxicity value for the 8 samples analyzed in this category is EC_{50} (15 min) of 102 with a standard deviation of 100.

Good correlation was established between toxicity and free oil, a factor of 0.98 with a test value of 99.9%; toxicity and PAHs, a factor of 0.99 with a test value of 99.9%; toxicity and phenols, a factor of 0.96 with a test value of 99.9%; and toxicity and volatile hydrocarbons, a factor of 0.79. No correlation was observed between toxicity and dissolved oil, inorganic and organic solids, and heavy metals. On the basis of this information it may be concluded that toxicological properties of impound type of scum and sludges are derived mainly from free oil, PAHs, and phenols (Figure 15).

FUEL TANK AND WASTEBARGE SLUDGE

Oily sludges accumulate in fuel storage tanks as a result of fuel aging. The aging process includes chemical and bio-oxidation of hydrocarbons resulting in the formation of oxygenated compounds that have a tendency to settle at the bottom of tanks. Water that might intrude into storage tanks also accumulates at the bottom. The sludges from fuel tanks are normally removed during periodic cleaning and disposed offsite by contractors. Oily sludges produced in such a manner represent a significant part of all waste material produced at Naval installations.

Oily sludges are also produced during wastewater transportion in DONUTS and SWOB barges. Under this program we had an opportunity to examine only one situation of this kind at the 32nd Street NAVSTA in San Diego, CA.

At this time we have only limited information on those two types of oily sludges, and the following discussion is indicative, rather than conclusive in character.

Chemical Considerations

The free oil content of sludges from fuel storage tanks was the highest of all observed in this study (Table 42). The average value was 48.5% with a standard deviation of 38.8. PAH content was also high: it averaged at 21,978 ppm with a standard deviation of 19,940 ppm. PAH a correlated well with free oil: a correlation factor was found to be 0.99 with a test value of 99%.

The dissolved oil content was 1.3% with a standard deviation of 1.2. Phenols were present in 1,098 ppm concentration with a standard deviation of 548 ppm (Table 43).

The inorganic solids content was low: 0.5% with a standard deviation of 0.1%, while organic solids content was high: 10.7% with a standard deviation of 8.0 (Table 44). The high organic solids content is probably due to hydrocarbon oxidation products formed during fuel storage. Volatile organic content was high at 97 ppm concentration, and was probably due to the generally high oil content of the sample (Table 45).

Heavy metals were almost absent from the fuel storage tank sludges, and only traces of copper and lead were found (Table 46).

The average composition of samples from transportation sources (SWOB and DONUTs) is reported in Tables 42 through 46. The amount of data generated is insufficient for statistical analysis. It appears, however, that toxicity of sludges from either source is fairly high and generally close to that of phenol.

Toxicological Considerations

The amount of toxicological data generated on samples of sludges from fuel tanks and transportation sources is insufficient for detailed statistical analysis.

DISCUSSION

GENERAL

Oily sludges found at Naval installations can be broadly classified into ten (10) generic types: (1) gravity separators - bottoms; (2) gravity separators - interface; (3) DAF units; (4) oil recovery cookers; (5) secondary unit-processes; API and coalescer separators; (6) dewatering unit-processes; (7) oil sumps; (8) oily wastewater impoundments; (9) oil waste barges; and (10) fuel tanks. Each generic type has specific and characteristic properties of a physical, chemical, and toxicological nature.

The data indicate that oily sludges produced in primary treatment operation (gravity separators) are generally more toxic than oily sludges produced during secondary treatment (DAF, API, and coalescer separators). This may be explained by the fact that heavier than oil toxic substances, including PAHs and heavy metals, are removed by settling in the gravity separators, and that process stream is substantially detoxified before it enters into secondary unit-processes. High toxicity levels were also observed in dewatered sludge, probably due to the concentration of heavy metals, and in oil sumps, oil waste barges, and fuel tanks. Since each of these units functions also as a gravity separator, it is reasonable to expect substantial concentrations of PAHs and heavy metals in its sludge. The highest order of toxicity was observed in oil recovery cooker sludges (EC_{50} (15 min) of 19); and the lowest order of toxicity was observed in DAF sludges (EC_{50} (15 min) of 182). Correlating to toxicity were high concentrations of PAHs and free oil in sludges from oil recovery cookers. Low concentrations of PAHs and free oil were recorded for DAF sludge.

It was established through correlation of chemical and toxicological data that principal contributors to oily sludge toxicity are: PAHs, a significant (in toxicological terms) component of free oil; phenols; and heavy metals. It was possible through correlation of chemical and toxicological data to determine the principal sources of toxicity in each type of oily sludge. Generally speaking, the predominant toxic chemical specie dominates the toxicological properties of a given type of oily sludge. Out of 8 metals regulated by federal standards for drinking water and hazardous waste (Table 47), four (chromium, copper, lead, and nickel) were found in all the sludge samples analyzed.

The study also disclosed that close correlation exists between free oil and PAHs in all the types of oily sludges analyzed, and that the concentration of PAHs is directly proportional to the concentration of free oil in all instances studied. On the average, PAHs constitute 2.5% of free oil. Concentrations of dissolved oil and phenols correlated well. Concentrations of phenols were directly proportional to concentrations of dissolved oil content. These findings suggest that the origin and source of toxicants in all types of oily sludges and at all Naval installations are probably the same.

FREE OIL AND PAH

Free oil and PAHs are found in all oily sludges, as shown in Table 48. The highest concentrations of free oil are observed in sludges from fuel tanks and oil recovery cookers, 48.5% and 40.3%, respectively. The lowest concentrations are in secondary treatment processes: API and coalescer separators, and DAF; 1.2% and 2.4%, respectively. Gravity separator sludges, both bottom and interface, are in the middle of the range; 23.6% and 18.5%, respectively. PAHs concentrations are generally proportional to concentrations of free oil and are highest in oily sludges from fuel tanks and oil recovery cookers, and lowest in oily sludges from secondary treatment processes (API, DAF, and coalescer). This observation may be explained by the fact that the bulk of oil and PAHs are removed by gravity separators and only smaller quantities of such are carried out into secondary unit-processes for treatment.

Examination of chemical/toxicological correlation reveals that free oil and PAHs contribute significantly to toxicologic properties of oily sludges from: gravity separators - bottoms, oil sumps, impounds of oily wastewaters, and oil recovery cookers. All those unit-processes are essentially gravity separators for sludge. Because of the limited data base, chemical/toxicological correlation could not be established for oily sludges from oily waste barges and fuel storage tanks.

In the case of secondary treatment processes, including DAF, API and coalescers, the contribution of free oil and PAHs to toxic properties is less significant, and other chemical components play a greater role.

No free oil or PAH/toxicological correlation was established for dewatered sludges and for oily sludges from gravity separator interface. It is believed that in the first case, a very high concentration of heavy metals overshadows toxic contributions from other sources. In the case of gravity separator interface sludges the small numbers of samples analyzed may have been insufficient to establish valid correlation.

DISSOLVED OIL AND PHENOLS

Dissolved oil and phenols are found in all the oily sludges analyzed, and are reported in Table 49. Both chemical parameters are interrelated, and phenols constitute on the average 8.6% of the dissolved oil content. The concentrations of dissolved oil in sludges are usually considerably lower (by factor of 20) than that of free oil. The highest level of dissolved oil was found in sludges from oil recovery cookers (2.8%) and the lowest level was found in secondary treatment sludges: API, coalescer, and DAF separators (∿0.5%). The average concentration for dissolved oil in all types of oily sludges is 1%.

Phenols are toxicologically important compounds and are present in significant concentrations in all the oily sludges analyzed, averaging at 1,746 ppm. The highest concentrations are found in dewatered sludges (9,255 ppm) and the lowest in secondary treatment unit-processes (API, coalescer, DAF).

There is very little correlation between dissolved oil and the toxicity of the sludges. This might be due to the relatively low concentration of dissolved oil in oily sludges. Other toxic substances such as free oil/PAH and heavy metals, which are present in high concentrations, overshadow toxic contributions of dissolved oil, which is present in considerably lower concentrations.

Phenols correlated fairly well with toxicity in oily sludges from impoundments of oily wastewater (a factor of 0.96) and in sludges from secondary treatment processes: API - coalescer a factor of 0.55, and a DAF factor of 0.73. There was little correlation between toxicity and phenols in oily sludges from oil recovery cookers, oil waste barges, gravity separators (bottom and interface) fuel tanks, dewatered sludges and oil sumps. Generally speaking, secondary treatment units produce oily sludge low in free oil, PAH and heavy metals. Because of low concentrations of those important types of toxic substances, they contribute to overall toxicity of sludges from secondary treatment to a lower degree than primary separators. Because of this shift in chemical composition, the correlation between phenols and toxicity is more apparent in secondary treated sludges than in sludges produced in primary treatment processes.

SOLIDS

Organic and inorganic solids are found in all oily sludges. Such materials are heavier than water and tend to settle to the bottom of storage containers and unit-processors. The highest concentrations of inorganic and organic solids are found in dewatered sludges: 13.0% inorganic solids and 10.2% organic solids (Table 50). Primary separators, as well as storage units (oil sumps and impoundments) generally have fairly high inorganic solid content. The inorganic and organic content of the rest of the oily sludges generally ranges between 2 and 5%.

No correlation between toxicity and inorganic content exists in primary treatment unit-processes, and it is reasonable to assume that such matter does not contribute significantly to the toxicity of such sludges.

Good correlation, however, was established between the toxicity and organic and inorganic content of DAF sludges (factors of 0.59 and 0.90, respectively). The inorganic and organic solids in this case derive from chemical additives used in the processes and it does appear that toxicity of DAF sludges is mainly due to such chemical additives (alum and polyelectrolytes) and phenols.

HEAVY METALS

Heavy metals are toxicologically important chemical compounds and release of such into the environment is closely regulated by the government. Principal types, including antimony (Sb), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), and thallium (Tl) are designated priority pollutants. Additional federal regulations dealing with heavy metals are in force for drinking water and hazardous wastes. Eight (8) metals have designated maximum limits in drinking water: arsenic (0.05 ppm), barium (1 ppm), cadmium (0.01 ppm), chromium (0.05 ppm), lead (0.05 ppm), mercury (0.002 ppm), selenium (0.01 ppm), and silver (0.05 ppm). Federal limits also exist for the same eight metals in hazardous wastes. Maximum concentration limits, as determined by extraction procedures (EP) for those metals in hazardous waste are: arsenic (5 ppm), barium (100 ppm), cadmium (1 ppm), chromium (5 ppm), lead (5 ppm), mercury (.02 ppm), selenium (1 ppm), and silver (5 ppm).

The results for the heavy metals reported here are comparable to federal limits for drinking water, since in both cases analysis is performed directly on collected samples. The federal limitations for hazardous waste, however, are based on a specially designed procedure (EP), which requires aqueous extraction prior to analysis.

Under this program all collected sludges were analyzed for 11 heavy metals: antimony, beryllium, cadmium, chromium, copper, lead, nickel, selenium, silver, thallium, and zinc. Consistently present in all the sludges analyzed were five metals: chromium, copper, lead, nickel, and zinc. Cadmium was found in some oily sludge samples less frequently. The average total concentration of heavy metals found in oil sludges was 470 ppm (Table 51). Zinc was present in the highest concentrations, an average of 260 ppm; next down the line was copper (98 ppm), lead (62 ppm), chromium (28 ppm), and nickel (18 ppm) (Table 51). When the above values are related to the maximum concentrations limit for drinking water, we find that they exceed the concentration limit for chromium by a factor of 560, and for lead by a factor of 1,240.

Considering the chemical nature and toxicological properties of ten types of oily sludges characterized in this study it can be concluded that heavy metals make significant contributions to toxicity of oily sludges produced in secondary treatment unit-processes, including the DAF separator with a correlation factor of 0.58, and API - coalescer separators with a correlation factor of 0.61. Good correlation also exists between heavy metals and toxicity in dewatered sludges (a factor of 0.74) and in sludges from oil recovery cookers (a factor of 0.50). Poor correlation between heavy metals and toxicity was found in oily sludges that are high in free oil and PAH content: gravity separators (bottom and interface). In this case, the impact of PAHs and free oil on overall toxicity of predominates.

VOLATILES

Volatile organic matter that is present in oily sludges consists largely of aliphatic and aromatic hydrocarbons including methane, ethane, ethylene, propane, propene, unsaturated and saturated C_4, C_5, C_6 hydrocarbons and benzene, toluene, ethylbenzene, and xylenes. Benzene, toluene, and ethylbenzene are designated by the EPA as priority pollutants.

The analysis of oily sludges carried out under this program revealed that all contained volatile hydrocarbons (Table 52). The average concentration level was found to be 35 ppm. Volatiles in this concentration range will not have a significant effect on treatment operation, nor pose air pollution problems when disposed of at waste sites. Fair correlation between toxicity and volatile hydrocarbons was observed in the case of gravity separator sludges (bottom 0.51, interface 0.39), oil recovery cookers (a factor of 0.32), and DAF sludges (a factor of 0.31). In other types of oily sludges toxicity and volatile organic content did not correlate.

SOURCES OF TOXICITY

The completed study and data base generated on the chemistry and toxicology of oily sludges permit identification of principal chemical contributors to toxicity of each type or class of oily sludge studied. Examination of data reveals the following:

Gravity Separator Sludges - Bottoms

Principal contributing factors to toxicity of this type of oily sludge are free oil and PAH. Dissolved oil and phenols, solids (organic and inorganic), and volatiles do not contribute significantly to toxicity of this type of waste.

Gravity Separator Sludges - Interface

Because of the small number of samples analyzed in this category no positive relationship between toxicity and chemical parameters can be established.

DAF Sludges

Principal contributing factors to toxicity of this type of oily sludge are organic and inorganic solids, free oil and phenols, and heavy metals. PAH and dissolved oil do not contribute significantly to this type of waste. The toxic organic and inorganic content of these sludges originates in chemical additives used in the treatment process.

Oil Recovery Cookers

Principal contributing factors to toxicity of this type of sludge are free oil, PAH, and heavy metals. Dissolved oil, phenols, and inorganic and organic solids do not contribute significantly to toxicity of this waste.

Oil Sumps

Principal contributing factors to toxicity of this type of sludge are free oil and PAHs. Dissolved oil and phenols, inorganic and organic solids, and heavy metals do not contribute significantly to this type of sludge.

Dewatered Sludges

The only significant contributors to toxicity of this type of oily sludge are heavy metals, which, due to a concentrated nature, are present in high concentrations. All other chemical parameters do not contribute significantly to this type of waste.

Impounds of Oily Wastewaters

Principal contributing factors to toxicity of this type of sludge are free oil, PAHs, and phenols. Dissolved oil, inorganic and organic solids, and heavy metals do not contribute significantly to toxicity of this type of waste.

API - Coalescer Separators

Principal contributing factors to toxicity of this type of sludge are heavy metals, inorganic solids, phenols, and PAHs. Free and dissolved oil, and organic solids do not contribute significantly to this type of waste.

Sludge Barges

Insufficient data to draw conclusions on source of toxicity in this type of oily sludge.

Fuel Tanks

Insufficient data to draw conclusions on source of toxicity in this type of oily sludge.

CONCLUSIONS

All oily sludge samples contain toxic chemical substances. Organic toxicants include PAHs and phenols. Inorganic toxicants include zinc, chromium, copper, lead, and nickel. High concentrations of free oil and PAHs were found in primary treaters, low concentrations were found in secondary treaters: DAF, API, and coalescer separators.

All oily sludges exhibit toxic properties. Generated data indicate that oily sludges produced in primary treatment operations (gravity separation) are generally more toxic than oily sludges produced during secondary treatment (DAF, API, and coalescer separators). This may be explained by the fact that heavier than oil toxic substances, including PAHs and heavy metals, are removed by settling in the gravity separators; the concentrations of principal toxicants are significantly reduced in the process stream prior to its entry into secondary treatment units. High toxicity levels were also observed in dewatered sludge, probably due to the concentration of heavy metals, and in oil sumps, waste barges, and fuel tanks.

Close correlation exists between free oil and PAHs in all the types of oily sludges analyzed, and the concentration of PAHs is directly proportional to the concentration of free oil in all the instances studied. On the average, PAHs constitute 2.5% of free oil. Good correlation exists between concentrations of dissolved oil and phenols. Concentrations of phenols were directly proportional to concentrations of dissolved oil content. Those findings suggest that the origin and source of toxicants in all types of oily sludges and at all Naval installations are probably the same.

It was established through correlation of chemical and toxicological data that principal contributors to oil sludge toxicity are: PAHs, a toxicologically significant component of free oil; phenols; and heavy metals. It was possible through correlation of chemical and toxicological data to determine principal sources of toxicity in each type of oily sludge. Generally speaking, the predominant toxic chemical specie dominates toxicological properties of a given type of oily sludge.

The oily sludges from different sources exhibit different physical, chemical, and toxicological properties. Using an accumulated information base it was possible to define the ten different types or classes of oily sludges produced at Naval installations. The most toxic sludge was generated in oil recovery cookers. The least toxic oily sludge was produced in the DAF unit.

Table 1. Relationship Between EC_{50} and LC_{50} (Fish) and LD_{50} (Mammal) Measurements

	EC_{50}/ppm[a]		LC_{50} Fish Toxicity[b] (mg/l)	LD_{50} (oral)[c] (mg/kg)
	5 Min	15 Min		
Benzene	173	--	50	5.7
Phenol	25	28	5	0.53
Ratio: Benzene/Phenol	7		10	11

[a]Microtox Application Notes, Beckman Instruments, Carlsbad, CA
[b]McKim et al., J. Water Poll. Control, 48, 1544 (1976)
[c]Merck Index, Merck and Co., Hohway, NJ

Table 2. Gravity Separator Bottom Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in oil	Comments
North Island NAS	56	55.0	1,336	2.4	
San Diego, CA	59	43.0	587	1.4	
Point Loma NSC	112	44.0	384	0.9	
San Diego, CA	287	29.0	329	1.1	
Miramar NAS	62	2.0	1,156	5.8	Aged oil
San Diego, CA	24	21.3	4,724	2.2	Aged oil
	23	52.9	16,588	3.1	Fresh oil
	7	50.1	16,578	3.3	Fresh oil
Craney Island, VA	132	11.3	2,749	2.4	
Fuel Depot	45	13.9	3,189	2.3	
Pearl Harbor, HI	11	37.8	15,912	4.2	
NSC	9	64.2	23,874	2.3	
Manchester, WA	6	29.9	7,104	2.3	
NSC	9	45.3	13,696	3.0	
Point Molate, CA	9	4.9	1,241	2.5	Waste oil waters
	5	70.3	30,355	4.3	Waste oil waters
	136	2.0	533	2.6	Run-off waters
	120	2.1	482	2.3	Run-off waters
Average value	61.8	23.6	7,823	2.8	
Standard deviation	73.0	23.7	9,320	1.2	
% Standard deviation	±118	±100	±119	±43	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.77	0.75	0.98
Test Value	99.9%	99.9%	99.9%

Table 3. Gravity Separator Bottom Sludges; Toxicity - Dissolved Oil - Phenols Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
North Island NAS	56	0.4	416	10.4	
San Diego, CA	59	0.4	257	6.4	
Point Loma NSC	112	1.7	216	1.3	
San Diego, CA	287	1.7	280	1.6	
Miramar NAS	62	1.1	1,300	11.8	Aged oil
San Diego, CA	24	1.5	1,456	9.7	Aged oil
	23	1.3	671	5.3	Fresh oil
	7	1.4	764	5.5	Fresh oil
Craney Island, VA	132	0.6	200	3.3	
Fuel Depot	45	0.6	82	1.4	
Pearl Harbor, HI	11	0.6	453	7.6	
NSC	9	0.5	240	4.8	
Manchester, WA	6	1.8	938	5.2	
NSC	9	1.4	739	5.2	
Point Molate, CA NSC	9	0.1	94	9.4	Waste oil water
	5	0.3	330	11.0	Waste oil water
	136	0.1	68	6.8	Run-off water
	120	0.1	69	6.9	Run-off water
Average value	61.8	0.9	476	6.3	
Standard deviation	73.0	0.6	419	3.2	
% Standard deviation	±118	±68	±88	±52	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol	Phenol to Dissolved Oil
Factor	0.06	0.19	0.40
Test Value	--	--	90%

Table 4. Gravity Separator Bottom Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comments
North Island NAS	56	53.2	11.6	
San Diego, CA	59	45.7	8.8	
Point Loma NSC	112	1.3	0.5	
San Diego, CA	287	1.3	0.6	
Miramar NAS	62	0.3	0.7	Aged oil
San Diego, CA	24	0.5	4.5	Aged oil
	23	0.2	0.4	Fresh oil
	7	0.2	0.5	Fresh oil
Craney Island, VA	132	3.0	0.7	
Fuel Depot	45	1.3	1.0	
Pearl Harbor, HI	11	0.9	1.9	
NSC	9	0.9	2.2	
Manchester, WA	6	2.5	1.9	
NSC	9	1.9	2.2	
Point Molate, CA NSC	9	0	0	Waste oil waters
	5	1.9	0.3	Waste oil waters
	136	2.6	0.4	Run-off waters
	120	1.4	0.3	Run-off waters
Average value	61.8	6.5	2.1	
Standard deviation	73	15.6	3.2	
% Standard deviation	±118	±236	±152	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	Negative	Negative
Test Value	--	--

Table 5. Gravity Separator Bottom Sludges;
Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comments
North Island NAS	56	--	
San Diego, CA	59	21.5	
Miramar NAS	62	25.1	Aged oil
San Diego, CA	24	41.2	Aged oil
	23	51.2	Fresh oil
	7	52.9	Fresh oil
Pearl Harbor, HI	11	55.5	
NSC	9	36.1	
Manchester, WA	6	55.8	
NSC	9	--	
Point Molate, CA	9	54.1	Oily waste waters
NSC	5	42.4	Oily waste waters
	136	52.5	Run-off waters
	120	15.5	Run-off waters
Average value	38	42	
Standard deviation	43	14	
% Standard deviation	±113	±33	

Correlation	Toxicity to Volatiles
Factor	0.51
Test Value	90-95%

Table 6. Gravity Separator Bottom Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)					
		Cr	Cu	Pb	Ni	Zn	Total
North Island NAS	56	218	407	486	57	1,444	2,612
San Diego, CA	59	148	331	436	45	714	1,674
Point Loma NSC	112	9	115	15	6	154	299
San Diego, CA	287	4	5	11	4	104	128
Miramar NAS	62	7	16	0	4	37	64
San Diego, CA	24	9	32	0	7	84	132
	23	4	12	0	4	61	83
	7	4	7	0	3	30	44
Craney Island, VA	132	13	39	40	7	138	237
Fuel Depot	45	5	25	0	4	49	83
Pearl Harbor, HI	11	5	67	57	8	142	279
NSC	9	7	53	47	7	138	252
Manchester, WA	6	119	159	86	30	>240	>634
NSC	9	100	133	62	24	>270	>589
Point Molate, CA	9	0	0.3	0	0	2	2
NSC	5	0	0.4	9	0	16	29
	136	2	3	5	0	18	28
	120	3	2	8	0	23	36
Average value	61.8	37	78	70	12	204	400
Standard deviation	73.0	64	117	145	16	351	679
% Standard deviation	±118	±173	±150	±207	±137	±171	±170

Correlation	Toxicity to Total Heavy Metals
Factor	Negative
Test Value	--

Table 7. Gravity Separator Interface Sludge; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil
Craney Island, VA	93	22.7	4,943	2.2
Fuel Depot	18	22.6	5,093	2.3
Pearl Harbor, HI	24	26.9	6,640	2.5
NSC	19	18.0	4,851	2.7
Manchester, WA	22	10.7	3,363	3.1
NSC	33	10.2	3,182	3.1
Average value	35	18.5	4,679	2.7
Standard deviation	28	6.9	1,272	0.4
% Standard deviation	±80	±37	±27	±14

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	Negative	0.11	0.96
Test Value	--	--	0.99%

Table 8. Gravity Separator Interface Sludge; Toxicity - Dissolved Oil - Phenol Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil
Craney Island, VA	93	0.9	109	1.2
Fuel Depot	19	0.9	142	1.6
Pearl Harbor, HI	24	0.5	765	15.3
NSC	19	0.4	508	12.7
Manchester, WA	22	1.2	985	8.2
NSC	33	0.9	938	10.4
Average value	35	0.8	575	8.2
Standard deviation	28	0.3	386	5.8
% Standard deviation	±80	±38	±67	±71

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol	Phenol to Dissolved Oil
Factor	Negative	0.16	0.71
Test Value	--	--	90%

Table 9. Gravity Separator Interface Sludge; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)
Craney Island, VA	93	1.3	1.2
Fuel Depot	18	1.4	0.9
Pearl Harbor, HI	24	0.9	1.5
NSC	19	0.9	6.2
Manchester, WA	22	2.4	2.8
NSC	33	2.6	4.8
Average value	35	1.6	2.9
Standard deviation	28	0.7	2.2
% Standard deviation	±80	±46	±74

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	Negative	0.22
Test Value	--	--

Table 10. Gravity Separator Interface Sludge; Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)
Pearl Harbor, HI	24	53.9
NSC	19	45.9
Manchester, WA	22	55.8
NSC	33	41.9
Average value	25	49
Standard deviation	6	7
% Standard deviation	±25	±14

Correlation	Toxicity to Volatiles
Factor	0.39
Test Value	--

Table 11. Gravity Separator Interface Sludge; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)						
		Cd	Cr	Cu	Pb	Ni	Zn	Total
Craney Island, VA	93	--	8	37	40	5	130	220
Fuel Depot	18	--	8	44	54	5	128	239
Pearl Harbor, HI	24	--	8	105	28	10	150	301
NSC	19	--	7	96	15	10	164	292
Manchester, WA	22	6	168	>200	>173	40	>240	>827
NSC	33	4	75	157	3	26	>270	>535
Average value	35	--	46	107	52	16	180	402
Standard deviation	28	--	66	63	62	14	60	237
% Standard deviation	±80	--	±143	±59	±119	±88	±33	±59

Correlation	Toxicity to Total Heavy Metals
Factor	0.12
Test Value	--

Table 12. DAF Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
North Island NAS	60	6.4	1,721	2.7	
San Diego, CA	56	7.1	1,708	2.4	
Point Loma NSC	446	0.1	16	1.6	
San Diego, CA	287	0.02	4	2.0	
Craney Island, VA	132	1.2	430	3.6	Top
Fuel Depot	156	0.7	355	5.1	Top
	20	2.7	217	0.8	Middle
	9	4.0	203	0.5	Middle
	20	7.0	667	0.9	Bottom
	22	5.5	681	1.2	Bottom
Pearl Harbor, HI	121	1.4	217	1.6	Top
NSC	172	0.8	202	2.5	Top
	49	1.3	667	5.1	Middle
	58	1.0	681	6.8	Middle
	54	2.4	1,535	6.4	Bottom
	24	2.5	2,023	8.1	Bottom
Manchester, WA	616	0.1	40	4.0	
NSC	980	0.1	20	2.0	
Average value	182	2.4	633	3.1	
Standard deviation	257	2.5	661	2.3	
% Standard deviation	±141	±103	±104	±68	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.51	0.11	0.59
Test Value	95%	--	99%

Table 13. DAF Sludges; Toxicity - Dissolved Oil - Phenol Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comment
North Island NAS	60	0.2	155	7.8	
San Diego, CA	56	0.2	185	9.3	
Point Loma NSC	446	1.5	89	0.6	
San Diego, CA	287	2.2	118	0.5	
Craney Island, VA	132	0.5	125	2.5	Top
Fuel Depot	156	0.5	116	2.3	Top
	20	0.4	475	11.9	Middle
	9	0.4	830	20.8	Middle
	20	0.5	326	6.5	Bottom
	22	0.3	387	12.9	Bottom
Pearl Harbor, HI	121	0.3	455	15.2	Top
NSC	172	0.4	331	8.3	Top
	49	0.5	438	8.8	Middle
	58	0.5	380	7.6	Middle
	54	0.5	662	13.2	Bottom
	24	0.5	492	9.8	Bottom
Manchester, WA	616	0.4	268	6.7	
NSC	980	0.3	219	7.3	
Average value	182	0.6	336	8.4	
Standard deviation	257	0.5	202	52	
% Standard deviation	±141	±83	±60	±62	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol	Phenol to Dissolved Oil
Factor	0.20	0.73	0.89
Test Value	--	99.9%	99.9%

Table 14. DAF Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comment
North Island NAS	60	0.1	0.5	
San Diego, CA	56	0.1	1.8	
Point Loma NSC	446	0.3	0.4	
San Diego, CA	287	0.5	2.0	
Craney Island, VA	132	0.7	1.2	Top
Fuel Depot	156	0.4	1.4	Top
	20	2.8	15.9	Middle
	9	3.4	19.9	Middle
	20	3.7	12.2	Bottom
	22	3.9	4.0	Bottom
Pearl Harbor, HI	121	2.1	2.3	Top
NSC	172	2.2	3.4	Top
	49	2.3	2.8	Middle
	58	2.3	1.5	Middle
	54	3.7	5.6	Bottom
	24	3.9	12.2	Bottom
Manchester, WA	616	2.3	1.2	
NSC	980	1.8	0.7	
Average value	182	2.0	4.9	
Standard deviation	257	1.4	5.9	
% Standard deviation	±141	±69	±121	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	0.59	0.90
Test Value	99%	99.9%

Table 15. DAF Sludges; Toxicity - Volatiles Relationships

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comment
North Island NAS	60	4.3	
San Diego, CA	56	3.2	
Pearl Harbor, HI	121	6.1	Top
NSC	172	4.3	Top
	49	10.9	Middle
	58	4.7	Middle
	54	--	Bottom
	24	--	Bottom
Manchester, WA	616	6.4	
NSC	980	3.1	
Average value	219	5.3	
Standard deviation	320	2.5	
% Standard deviation	±146	±47	

Correlation	Toxicity to Volatiles
Factor	0.31
Test Value	--

Table 16. DAF Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)						Comment
		Cr	Cu	Pb	Ni	Zn	Total	
North Island NAS	60	2	0	0	0	4	6	Bilge water
San Diego, CA	56	4	12	7	2	21	46	Oily water
Point Loma NSC	446	0.3	7	0	1	2	10	Bottom
San Diego, CA	287	0.3	21	2	2	10	35	Bottom
Craney Island, VA	132	5	11	17	0	42	75	Top
Fuel Depot	156	3	5	9	0	23	40	Top
	20	9	26	50	7	128	220	Middle
	9	9	27	53	6	120	215	Middle
	20	8	27	51	7	123	216	Bottom
	22	7	22	44	7	116	196	Bottom
Pearl Harbor, HI	121	4	25	32	4	25	90	Top
NSC	172	4	26	38	4	81	153	Top
	49	35	20	29	5	110	199	Middle
	58	5	26	29	5	110	175	Middle
	54	7	65	90	10	145	317	Bottom
	24	8	61	78	10	145	302	Bottom
Manchester, WA	616	4	7	0	0	42	53	Top
NSC	980	3	5	0	0	34	42	Top
Average value	182	6	22	29	4	71	132	
Standard deviation	257	8	18	28	3	53	100	
% Standard deviation	±141	±133	±81	±97	±75	±75	±76	

Correlation	Toxicity to Total Heavy Metals
Factor	0.58
Test Value	99%

Table 17. Oil Recovery Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
Point Loma NSC	31	85.4	5,628	0.7	
San Diego, CA	26	79.1	4,224	0.5	
Craney Island, VA	13	18.2	2,213	1.2	
Fuel Depot	35	14.3	2,289	1.6	
Pearl Harbor, HI	12	12.0	4,452	3.7	
NSC	29	8.9	2,211	2.4	
Manchester, WA	13	35.8	6,089	1.7	Off-spec tank
NSC	6	46.9	12,158	2.6	Off-spec tank
	10	80.8	27,646	3.1	Spec tank
	11	58.7	18,143	3.1	Spec tank
	26	13.7	5,176	3.8	Rec. tank 115, bottom
	48	7.8	1,974	2.5	Rec. tank 115, bottom
	5	78.5	39,922	5.1	Rec. tank 116, top
	1	93.1	40,006	4.3	Rec. tank 116, top
Point Molate, CA	15	6.1	1,440	2.3	
NSC	27	5.2	1,219	2.3	
Average value	19	40.3	10,924	2.6	
Standard deviation	13	33.6	13,371	1.3	
% Standard deviation	±68	±84	±112	±46	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.49	0.70	0.74
Test Value	95%	99.9%	99.4%

Table 18. Oil Recovery Sludges; Toxicity - Dissolved Oil - Phenols Relationships

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comment
Point Loma NSC	31	14.8	0	0	
San Diego, CA	26	10.1	0	0	
Craney Island, VA	13	0.7	127	1.8	
Fuel Depot	35	0.7	177	2.5	
Pearl Harbor, HI	12	0.3	768	25.6	
NSC	29	0.5	929	18.6	
Manchester, WA	13	1.2	273	2.3	Off-spec tank
NSC	6	1.6	417	2.6	Off-spec tank
	10	0.2	53	2.7	Spec tank
	11	12.1	93	0.1	Spec tank
	26	1.2	1,781	14.8	Rec. tank 115, bottom
	48	1.2	1,415	11.8	Rec. tank 115, bottom
	5	0.4	252	6.3	Rec. tank 116, top
	1	0.4	953	23.8	Rec. tank 116, top
Point Molate, CA	15	0.8	999	12.5	
NSC	27	0.7	767	11.0	
Average value	19	2.8	563	8.5	
Standard deviation	13	4.8	543	8.6	
% Standard deviation	±68	±172	±96	±101	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol	Phenol to Dissolved Oil
Factor	*Negative*	0.12	0.73
Test Value	--	--	99.9%

Table 19. Oil Recovery Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comment
Point Loma NSC	31	0.03	3.9	
San Diego, CA	26	0.04	6.9	
Craney Island, VA	13	1.4	4.1	
Fuel Depot	35	2.1	5.1	
Pearl Harbor, HI	12	0.1	2.4	
NSC	29	1.3	1.0	
Manchester, WA	13	0.6	2.8	Off-spec tank
NSC	6	0.3	0	Off-spec tank
	10	0	0	Spec tank
	11	0	0	Spec tank
	26	7.3	3.9	Rec. tank 115, bottom
	48	5.3	4.1	Rec. tank 115, bottom
	5	0.8	8.1	Rec tank 116, top
	1	0.8	3.7	Rec. tank 116, top
Point Molate, CA	15	0	0.1	
NSC	27	0	0.1	
Average value	19	1.3	2.9	
Standard deviation	13	2.1	2.6	
% Standard deviation	±68	±161	±90	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	0.08	0.09
Test Value	--	--

Table 20. Oil Recovery Sludges; Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comments
Pearl Harbor, HI	12	21.1	
NSC	29	53.0	
Manchester, WA	13	53.2	Off-spec tank
NSC	6	39.4	Off-spec tank
	10	128.2	Spec tank
	11	68.2	Spec tank
	26	--	Tank 115, bottom
	48	20.4	Tank 115, bottom
Point Molate, CA	15	--	
NSC	27	10.5	
Average value	20	49	
Standard deviation	13	38	
% Standard deviation	±65	±78	

Correlation	Toxicity to Volatiles
Factor	0.32
Test Value	--

Table 21. Oil Recovery Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)							Comments
		Cd	Cr	Cu	Pb	Ni	Zn	Total	
Point Loma NSC	31	1	2	2	0	1	2	7	
San Diego, CA	26	0	1	2	0	2	4	9	
Craney Island, VA	13	0	10	35	35	6	95	181	
Fuel Depot	35	0	14	47	52	8	128	249	
Pearl Harbor, HI	12	0	8	68	21	8	134	239	
NSC	29	0	14	117	63	13	169	376	
Manchester, WA	13	0	9	16	0	0	57	82	Off-spec oil
NSC	6	0	7	12	0	0	42	61	Off-spec oil
	10	0	0	0	0	0	1	1	Spec oil
	11	0	0	0	0	0	1	1	Spec oil
	26	3	230	280	240	188	>660	>1,500	Tank 115, bottom
	48	1	169	211	209	83	>510	>1,163	Tank 115, bottom
	5	3	82	158	144	17	>330	>734	Tank 116, top
	1	2	772	149	51	171	>300	>1,445	Tank 116, top
Point Molate, CA	15	0	0	0	4	0	0.2	4	
NSC	27	0	0	0	6	0	2.0	8	
Average value	19	--	82	68	52	23	152	379	
Standard deviation	13	--	196	88	78	47	200	532	
% Standard deviation	±68	--	±239	±130	±149	±102	±132	±140	

Correlation	Toxicity to Total Heavy Metals
Factor	0.50
Test Value	95-99%

Table 22. Oil Sump Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
Point Loma NSC	125	0.8	109	1.3	Ballast water
San Diego, CA	16	10.4	1,163	1.1	Waste oil water
Pearl Harbor, HI	32	8.0	1,535	1.9	
NSC	35	7.0	2,023	2.9	
Point Molate, CA	91	4.0	656	1.6	
NSC	37	1.1	539	4.9	
Average value	56	5.2	1,004	2.2	
Standard deviation	42	3.8	705	1.4	
% Standard deviation	±76	±75	±70	±65	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.80	0.47	0.76
Test Value	95%	80%	95%

Table 23. Oil Sump Sludges; Toxicity - Dissolved Oil - Phenol Relationships

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
Point Loma NSC	16	2.7	256	0.9	Waste oil water
San Diego, CA	125	2.1	56	0.3	Bilge water
Pearl Harbor, HI	32	0.5	857	17.1	
NSC	35	0.5	613	12.3	
Point Molate, CA	91	0.1	459	a	
NSC	37	<0.1	330	a	
Average value	56	1.0	423	--	
Standard deviation	42	1.1	281	--	
% Standard deviation	±76	±110	±66	--	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol
Factor	0.17	0.10
Test Value	--	--

[a] Concentration of dissolved oil to low to make reliable calculations.

Table 24. Oil Sump Sludges; Toxicity - Inorganic Solids - Organic Solids

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comments
Point Loma NSC	125	0.1	0.2	Bilge water
San Diego, CA	16	0.9	0.3	Waste oil water
Pearl Harbor, HI	32	25.0	10.5	
NSC	35	12.9	16.8	
Point Molate, CA	91	1.1	0.1	
NSC	37	2.6	1.0	
Average value	56	7.1	4.8	
Standard deviation	42	10.0	7.1	
% Standard deviation	±76	±141	±148	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	0.09	0.07
Test Value	--	--

Table 25. Sump Sludges; Toxicity - Volatiles

Location	Toxicity EC_{50} (15 min)	Volatiles Hydrocarbons (ppm)
Pearl Harbor, HI	32	55.8
NSC	35	6.6
Point Molate, CA	91	41.0
NSC	37	11.1
Average value	49	29
Standard deviation	28	24
% Standard deviation	±57	±83

Correlation	Toxicity to Volatiles
Factor	Negative
Test Value	--

Table 26. Oil Sump Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)							Comments
		Cd	Cr	Cu	Pb	Ni	Zn	Total	
Point Loma NSC	16	1	4	100	20	9	68	202	Waste oil
San Diego, CA	125	0.2	1	5	4	1	15	26	Bilge water
Pearl Harbor, HI	32	0	113	990	1,232	175	1,577	4,087	
NSC	35	0	51	609	521	60	773	2,014	
Point Molate, CA	91	0	0	3	10	0	25	38	
NSC	37	0	0	4	8	3	51	66	
Average value	56	--	28	285	299	41	418	1,072	
Standard deviation	42	--	46	417	500	69	639	1,668	
% Standard deviation	±76	--	±165	±147	±167	±169	±153	±156	

Correlation	Toxicity to Total Heavy Metals
Factor	0.12
Test Value	--

Table 27. Dewatered Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
		Drying Beds			
North Island NAS	40	27.8	9,623	3.5	Drying bed #1
San Diego, CA	63	25.4	5,539	2.2	Drying bed #1
	35	16.2	5,921	3.7	Drying bed #2
	59	9.0	2,263	2.5	Drying bed #2
Mayport, FL	170	5.7	1,147	2.0	Inlet lagoon #1
Naval Station	47	12.1	3,911	3.2	Inlet lagoon #1
	39	9.6	4,963	5.2	Opposite side lagoon #1
	28	7.9	5,170	6.5	Opposite side lagoon #1
	24	5.6	2,618	4.7	Lagoon #2 middle
	19	6.2	3,964	6.4	Lagoon #2 middle
		Sludge Presses			
Manchester, WA	16	2.4	336	1.4	Pressed cake
NSC	18	2.2	492	2.2	Pressed cake
Average value	46	10.8	3,829	3.6	
Standard deviation	42	8.3	2,670	1.7	
% Standard deviation	±91	±75	±70	±48	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	Negative	0.35	0.86
Test Value	--	--	99%

Table 28. Dewatered Sludges; Toxicity - Dissolved Oil - Phenols Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
Drying Beds					
North Island NAS	40	0.8	15,504	[a]	Bed #1
San Diego, CA	63	1.1	15,995	[a]	Bed #1
	35	0.3	4,693	[a]	Bed #2
	59	0.3	3,081	[a]	Bed #2
Mayport, FL	170	1.4	3,927	28.1	Lagoon #1 inlet
NAVSTA	47	2.3	9,024	39.2	Lagoon #1 inlet
	39	2.0	17,290	86.2	Lagoon #1 opposite inlet
	28	0.8	14,668	[a]	Lagoon #1 opposite inlet
	24	1.1	3,051	27.7	Lagoon #2 middle
	29	1.0	5,325	53.3	Lagoon #2 middle
Sludge Presses					
Manchester, WA	16	1.0	577	5.8	
NSC	18	0.9	732	8.1	
Average value	46	1.1	7,821	--	
Standard deviation	42	0.6	6,348	--	
% Standard deviation	±91	±54	±81	--	

[a] Concentration of dissolved oil is too low to make reliable calculations.

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol
Factor	Negative	Negative
Test Value	--	--

Table 29. Dewatered Sludges; Toxicity - Organic Solids - Inorganic Solids

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comments
North Island NAS	40	20.9	18.9	Drying bed #1
San Diego, CA	63	26.5	22.8	Drying bed #1
	35	1.5	4.5	Drying bed #2
	59	0.7	1.2	Drying bed #2
Mayport, FL	170	19.4	11.9	Lagoon #1 inlet
Naval Station	47	17.6	11.5	Lagoon #1 inlet
	39	8.3	11.8	Lagoon #1 opposite side
	28	12.6	13.2	Lagoon #1 opposite side
	24	10.1	7.3	Lagoon #2 middle
	19	9.9	6.3	Lagoon #2 middle
Manchester, WA	16	15.1	6.4	Sludge press
NSC	18	14.0	6.5	Sludge press
Average value	46	13.0	10.2	
Standard deviation	42	7.6	6.1	
% Standard deviation	±91	±58	±60	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	Negative	Negative
Test Value	--	--

Table 30. Dewatered Sludges; Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comment
North Island NAS	40	4.1	Drying bed #1
San Diego, CA	63	4.6	Drying bed #1
	35	4.4	Drying bed #2
	59	4.9	Drying bed #2
Manchester, WA	16	9.1	Sludge press
NSC	18	7.0	Sludge press
Average value	40	5.7	
Standard deviation	20	2.0	
% Standard deviation	±50	±35	

Correlation	Toxicity to Volatiles
Factor	Negative
Test Value	--

Table 31. Dewatered Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm) Cd	Cr	Cu	Pb	Ni	Zn	Total	Comments
North Island NAS	40	--	73	366	232	35	754	1,460	Drying bed #1
San Diego, CA	63	0	127	451	168	26	1,010	1,782	Drying bed #1
	35	0	51	125	64	9	158	407	Drying bed #2
	59	0	24	59	30	5	129	247	Drying bed #2
Mayport, FL	170	4	25	68	41	37	204	371	Lagoon #1 inlet
NAVSTA	47	2	41	173	45	59	485	805	Lagoon #1 inlet
	39	0	36	202	69	80	>670	>1,057	Lagoon #1 opposite side
	28	1	41	245	138	83	>3,380	>3,821	Lagoon #1 opposite side
	24	0.4	40	189	36	132	>2,910	>3,307	Lagoon #2 middle
	29	0.5	30	177	40	101	>2,650	>2,998	Lagoon #2 middle
Sludge Presses									
Manchester, WA	16	0	5	6	0	0	41	52	
NSC	18	0	41	51	26	22	469	608	
Average value	46	0.7	45	176	74	49	1,072	1,410	
Standard deviation	42	1.2	30	131	69	42	1,195	1,297	
% Standard deviation	±91	±179	±68	±74	±93	±86	±111	±92	

Correlation	Toxicity to Total Heavy Metals
Factor	0.74
Test Value	95-99%

Table 32. API and Coalescer Sludges; Toxicity - Free Oil - PAH Relationships

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
Pearl Harbor, HI	65	1.5	206	1.3	API #1 inlet
NSC	91	1.8	208	1.2	API #1 inlet
	69	0.9	135	1.5	API #1 outlet
	72	0.8	212	2.7	API #1 outlet
	63	1.1	247	2.2	API #2 inlet
	67	1.6	411	2.5	API #2 inlet
Point Molate, CA	370	0.9	108	1.2	Coalescer
NSC	75	0.9	262	2.9	Coalescer
Average value	109	1.2	224	1.9	
Standard deviation	106	0.4	92	0.7	
% Standard deviation	±97	±32	±42	±38	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.14	0.54	0.45
Test Value	--	90%	80%

Table 33. API and Coalescer Sludges; Toxicity - Dissolved Oil - Phenol Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
Pearl Harbor, HI	65	1.1	402	3.7	API #1 inlet
NSC	91	1.4	--	--	API #1 inlet
	69	0.3	432	14.4	API #1 outlet
	72	0.4	227	5.6	API #1 outlet
	63	0.3	153	5.1	API #2 inlet
	67	0.4	199	5.0	API #2 inlet
Point Molate, CA	370	0.1	30	3.0	Coalescer
NSC	75	0.1	36	3.6	Coalescer
Average value	109	0.5	211	5.8	
Standard deviation	106	0.5	159	3.9	
% Standard deviation	±97	±100	±76	±68	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol	Phenol to Dissolved Oil
Factor	0.17	0.55	0.69
Test Value	--	80%	95%

Table 34. API and Coalescer Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comment
Pearl Harbor, HI	65	3.6	4.7	API #1 inlet
NSC	91	3.5	7.2	API #1 inlet
	69	2.9	1.4	API #1 outlet
	72	2.7	1.8	API #1 outlet
	63	3.1	3.5	API #2 outlet
	67	4.3	1.6	API #2 outlet
Point Molate, CA	370	0.1	0.1	Coalescer
NSC	75	0.1	0.3	Coalescer
Average value	109	2.5	2.6	
Standard deviation	106	1.6	2.4	
% Standard deviation	±97	±63	±93	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	0.64	0.26
Test Value	90%	--

Table 35. API and Coalescer Sludges; Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comment
Pearl Harbor, HI	65	5.9	API #1 inlet
NSC	91	14.1	API #1 inlet
	69	7.9	API #1 outlet
	72	3.1	API #1 outlet
	63	11.5	API #2 inlet
	67	11.8	API #2 inlet
Point Molate, CA	370	--	Coalescer
NSC	75	--	Coalescer
Average value	109	9.3	
Standard deviation	106	3.8	
% Standard deviation	±97	±40	

Correlation	Toxicity to Volatiles
Factor	Negative
Test Value	--

Table 36. API and Coalescer Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)						Comments
		Cr	Cu	Pb	Ni	Zn	Total	
Pearl Harbor, HI	65	5	18	0	3	92	118	API #1 inlet
NSC	91	8	30	24	5	100	167	API #1 inlet
	69	8	21	8	6	106	149	API #1 outlet
	72	8	23	32	5	92	160	API #1 outlet
	63	5	81	30	10	131	257	API #2 inlet
	67	6	98	46	14	143	307	API #2 inlet
Point Molate, CA	370	0	0	0	0	2	2	Coalescer
NSC	75	0	0	0	0	1	6	Coalescer
Average value	109	5	34	18	5	83	146	
Standard deviation	106	3	36	17	5	54	106	
% Standard deviation	±97	±60	±107	±96	±100	±65	±73	

Correlation	Toxicity to Total Heavy Metals
Factor	0.61
Test Value	95%

Table 37. Impound Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
Mayport, FL	107	0.4	52	1.3	Inlet
Naval Station	73	1.1	377	3.4	Inlet
Settling pond	47	0.8	158	2.0	Outlet
	90	1.1	158	1.4	Outlet
Pearl Harbor, HI	14	30.1	10,134	3.4	Top layer
NSC	14	24.0	10,125	4.2	Top layer
Stilling basin	149	0.5	158	3.2	Bottom layer
	323	0.6	175	2.9	Bottom layer
Average value	102	7.3	2,667	2.7	
Standard deviation	100	12.3	4,607	1.0	
% Standard deviation	±98	±168	±173	±39	

Correlation	Toxicity to Free Oil	Toxicity to PAH	PAH to Free Oil
Factor	0.98	0.98	0.99
Test Value	99.9%	99.9%	99.9%

Table 38. Impound Sludges; Toxicity - Dissolved Oil - Phenol Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
Mayport, FL	107	1.2	508	4.2	Inlet
NS	73	1.2	177	1.5	Inlet
Leaching pond	47	3.0	146	0.5	Outlet
	90	1.1	153	1.4	Outlet
Pearl Harbor, HI	14	0.7	10,191	[a]	Top
NSC	14	0.5	8,836	[a]	Top
Stilling basin	149	0.1	1,327	[a]	Bottom
	323	0.1	1,094	[a]	Bottom
Average value	102	1.0	2,805	--	
Standard deviation	100	0.9	4,182	--	
% Standard deviation	±98	±90	±149	--	

Correlation	Toxicity to Dissolved Oil	Toxicity to Phenol
Factor	Negative	0.96
Test Value	--	99.9%

[a]Concentration of dissolved oil too low for reliable calculation.

Table 39. Impound Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comments
Mayport, FL	107	13.6	10.7	Inlet
NS	73	7.2	4.2	Inlet
Leaching Pond	47	20.9	10.5	Outlet
	90	21.7	4.9	Outlet
Pearl Harbor, HI	14	2.3	1.3	Top
NSC	14	2.3	1.4	Top
Stilling basin	149	0.2	1.4	Bottom
	323	0.5	1.6	Bottom
Average value	102	8.6	4.3	
Standard deviation	100	9.0	4.2	
% Standard deviation	±98	±105	±97	

Correlation	Toxicity to Inorganic Solids	Toxicity to Organic Solids
Factor	Negative	Negative
Test Value	--	--

Table 40. Impound Sludges; Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)	Comments
Pearl Harbor, HI	14	3.8	Top
NSC	14	5.9	Top
	149	50.8	Bottom
	323	41.9	Bottom
Average value	125	26	
Standard deviation	147	24	
% Standard deviation	±118	±92	

Table 41. Impound Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)							Comments
		Cd	Cr	Cu	Pb	Ni	Zn	Total	
Mayport, FL	107	1	45	38	28	32	81	225	Inlet
NS	73	1	11	50	11	23	128	224	Inlet
Leaching pond	47	3	20	29	32	30	43	157	Outlet
	90	2	38	36	25	28	55	390	Outlet
Pearl Harbor, HI	14	0	7	7	0	0	32	46	Top
NSC	14	0	5	8	0	0	34	47	Top
Stilling basin	149	0	46	38	16	3	127	230	Bottom
	323	0	41	50	18	3	139	251	Bottom
Average value	102	--	24	32	16	15	80	196	
Standard deviation	100	--	17	17	12	15	45	113	
% Standard deviation	±98	--	±72	±52	±76	±100	±56	±58	

Correlation	Toxicity to Total Heavy Metals
Factor	Negative
Test Value	--

Table 42. Fuel Tanks and Waste Barge Sludges; Toxicity - Free Oil - PAH Relationship

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
		Fuel Tanks			
Pearl Harbor, HI	[a]	17.3	6,349	3.6	Tank 11
NSC	[a]	12.6	3,257	2.6	Tank 11
	48	79.8	41,160	5.2	Tank 13
	44	84.2	37,147	4.4	Tank 13
Average value	46	48.5	21,978	4.0	
Standard deviation	--	38.8	19,940	1.0	
% Standard deviation	--	±80	±90	±28	

Correlation	PAH to Free Oil
Factor	0.99
Test Value	99%

Location	Toxicity EC_{50} (15 min)	Free Oil (%)	PAH (ppm)	% PAH in Oil	Comments
		Waste Barges			
32nd Street	39	11.6	1,100	0.9	SWOB barge
Naval Station	29	1.8	54	0.3	SWOB barge
San Diego, CA	28	96.2	2,932	0.5	Top of DONUT
Average value	32	36.5	2,029	0.6	

[a]Not determined.

Table 43. Fuel Tanks and Waste Barge Sludges; Toxicity - Dissolved Oil - Phenol Relationship

Location	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Phenol (ppm)	% Phenol in Dissolved Oil	Comments
		Fuel Tanks			
Pearl Harbor, HI	[a]	2.0	1,608	8.0	Tank 11
NSC	[a]	2.5	1,527	6.1	Tank 11
	48	0.3	716	23.8	Tank 13
	44	0.2	541	27.1	Tank 13
Average value	46	1.3	1,098	16.2	
Standard deviation	--	1.2	548	10.7	
% Standard deviation	--	±92	±50	±66	
		Waste Barges			
32nd Street	39	1.6	1,580	9.9	SWOB barge
Naval Station	29	3.0	3,576	11.9	SWOB barge
San Diego, CA	28	1.3	0	0	Top of DONUT
Average value	32	2.0	1,719	7.3	

[a]Not determined.

Table 44. Fuel Tank and Waste Barge Sludges; Toxicity - Inorganic Solids - Organic Solids Relationship

Location	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Organic Solids (%)	Comment
		Fuel Tanks		
Pearl Harbor, HI	[a]	0.6	5.4	Tank 11
NSC	[a]	0.3	2.4	Tank 11
	48	0.5	17.0	Tank 13
	44	0.5	18.0	Tank 13
Average value	46	0.5	10.7	
Standard deviation	--	0.1	8.0	
% Standard deviation	--	±20	±74	
		Waste Barges		
32nd Street	39	9.7	5.8	SWOB barge
Naval Station	29	1.2	0.4	SWOB barge
San Diego, CA	28	0	0	DONUT Top
Average value	32	3.6	2.1	

[a]Not determined.

Table 45. Fuel Tank Toxicity - Volatiles Relationship

Location	Toxicity EC_{50} (15 min)	Volatile Hydrocarbons (ppm)
Pearl Harbor, HI	48	125.8
NSC	44	67.3
Average value	46	97

Table 46. Fuel Tanks and Barge Sludges; Toxicity - Heavy Metals Relationship

Location	Toxicity EC_{50} (15 min)	Concentration (ppm)							Comments
		Cd	Cr	Cu	Pb	Ni	Zn	Total	
				Fuel Tanks					
Pearl Harbor, HI	a	0	0	0	0	0	0	0	Tank 11
NSC	a	0	0	0	0	0	0	0	Tank 11
	48	0	0	0	6	0	7	13	Tank 13
	44	0	0	12	11	0	0	23	Tank 13
Average value	46	0	0	3	4	0	2	9	
				Waste Barges					
32nd Street	39	6	1	423	8	29	991	1,458	SWOB barge
Naval Station	29	2	11	85	15	8	36	157	SWOB barge
San Diego, CA	28	0	1	4	0	0	19	24	Top DONUT
Average value	32	3	4	171	8	12	349	546	

Table 47. Federal Regulations for Drinking Water and Hazardous Waste

Substance	Maximum Concentration Limits: Drinking Water (mg/l)	Maximum Concentration Limits: Hazardous Waste (EP Toxicity)[a] (mg/l)
Arsenic	0.05	5.0
Barium	1.0	100.0
Cadmium	0.010	1.0
Chromium	0.05	5.0
Lead	0.05	5.0
Mercury	0.002	0.2
Nitrate (as NO_3)	45	--
Selenium	0.01	1.0
Silver	0.05	5.0
Endrin	0.002	0.02
Lindane	0.004	0.40
Methoxychlor	0.1	10.0
Toxaphene	0.005	0.5
2,4,D	0.1	10.0
2,4,5-TP (Silvex)	0.1	1.0
Fluoride (Temp. dependent)	(1.4-2,4)	--
Combined Radium 226 and 228	5pCi/L	--
Gross Alpha particle activity	15pCi/L	--
Tritium	20,000 pCi/L	--
Strontium 90	8 pCi/L	--
Gross Beta particle activity	50 pCi/L	--

[a]EP = Extraction procedure.

Table 48. Free Oil and PAH in Oily Sludges

Source of Sludge	Toxicity EC_{50} (15 min)	Free Oil (%)	Correlation Free Oil to Toxicity	PAH (ppm)	Correlation PAH to Toxicity	% PAH in Free Oil
Oil recovery cookers	19	40.3	0.49	10,924	0.70	2.6
Oil waste barges	32	36.5	a	2,029	a	0.6
Gravity separator interface	35	18.5	negative	4,679	0.11	2.7
Fuel tanks	46	48.5	a	21,978	a	4.0
Dewatered sludge	46	10.8	negative	3,829	negative	3.6
Oil sumps	56	5.2	0.80	1,004	0.47	2.2
Gravity separator bottoms	62	23.6	0.77	7,823	0.75	2.8
Impounds of oily wastewaters	102	7.3	0.98	2,667	0.98	2.7
API - Coalescer separators	109	1.2	0.14	224	0.54	1.9
DAF separators	182	2.4	0.51	663	0.11	3.1
Average	69	19.4		5,582		2.6

[a]Not determined.

NOTE: The organization of sludge sources is in order of decreasing toxicity.

Table 49. Dissolved Oil and Phenol in Oily Sludges

Source of Sludge	Toxicity EC_{50} (15 min)	Dissolved Oil (%)	Correlation Dissolved Oil to Toxicity	Phenol (ppm)	Correlation Phenol to Toxicity	Phenol in Dissolved Oil
Oil recovery cookers	19	2.8	negative	563	0.12	8.5
Oil waste barges	32	2.0	--	1,719	--	7.3
Gravity separator interface	35	0.8	negative	575	0.16	8.2
Fuel tanks	46	1.3	--	1,098	--	16.2
Dewatered sludge	46	1.1	negative	9,255	negative	--
Oil sumps	56	1.0	0.17	423	0.10	--
Gravity separator bottoms	62	0.9	0.06	476	0.19	6.2
Impounds of oily wastewaters	109	1.0	negative	2,805	0.96	
API - Coalescer	109	0.5	0.17	211	0.55	5.8
DAF separators	182	0.6	negative	336	0.73	8.4
Average	69	1.0		1,746		8.6

NOTE: The organization of sludge sources is in order of decreasing toxicity.

Table 50. Solids in Oily Sludges

Source of Sludge	Toxicity EC_{50} (15 min)	Inorganic Solids (%)	Correlation Inorganic Solids to Toxicity	Organic Solids (%)	Correlation Organic Solids to Toxicity
Oil recovery cookers	19	1.3	0.08	2.9	0.09
Oil waste barges	32	3.6	--	2.1	--
Gravity separator interface	35	1.6	negative	2.9	0.22
Fuel tanks	46	0.5	--	10.7	--
Dewatered sludge	46	13.0	negative	10.2	negative
Oil sumps	56	7.1	0.09	4.8	0.07
Gravity separator bottoms	62	6.6	negative	2.1	negative
Impounds of oily wastewaters	102	8.6	negative	4.3	negative
API - Coalescer	109	2.5	0.64	2.6	0.26
DAF separators	182	2.0	0.59	4.9	0.90
Average	69	4.7		4.8	

NOTE: The organization of sludge sources is in order of decreasing toxicity.

Table 51. Heavy Metals in Oily Sludges

Source of Sludge	Toxicity EC_{50} (15 min)	Concentration (ppm)						Correlation Toxicity to Heavy Metals
		Cr	Cu	Pb	Ni	Zn	Total	
Oil recovery cookers	19	82	68	52	23	152	379	0.50
Oil waste barges	32	4	171	8	12	349	546	--
Gravity separator interface	35	46	107	52	16	180	402	0.12
Fuel tanks	46	0	3	4	0	2	9	--
Dewatered sludge	46	44	176	73	49	1,066	1,410	0.74
Oil sumps	56	28	285	299	41	418	1,072	0.12
Gravity separator bottoms	62	37	78	70	12	204	400	negative
Impounds of oily wastewaters	102	24	32	16	15	80	196	negative
API - Coalescer separators	109	5	34	18	5	83	146	0.61
DAF Separators	182	6	22	29	4	71	132	0.58
Average	69	28	98	62	18	260	470	

NOTE: The organization of sludge sources is in order of decreasing toxicity.

Table 52. Volatiles in Oily Sludges

Source of Sludge	Toxicity EC_{50} (15 min)	Volatiles (ppm)	Correlation Factor
Oil recovery cookers	20	49	0.32
Gravity separator interface	25	49	0.39
Fuel tanks	46	97	--
Dewatered sludge	40	6	negative
Oil sumps	49	29	negative
Gravity separator bottoms	38	42	0.51
Impounds of oily wastewaters	125	26	--
API - Coalescer separators	109	9	negative
DAF separators	219	5	0.31
Average	74	35	

NOTE: Smaller number of samples were analyzed for volatiles. Toxicity values refer to samples analyzed.

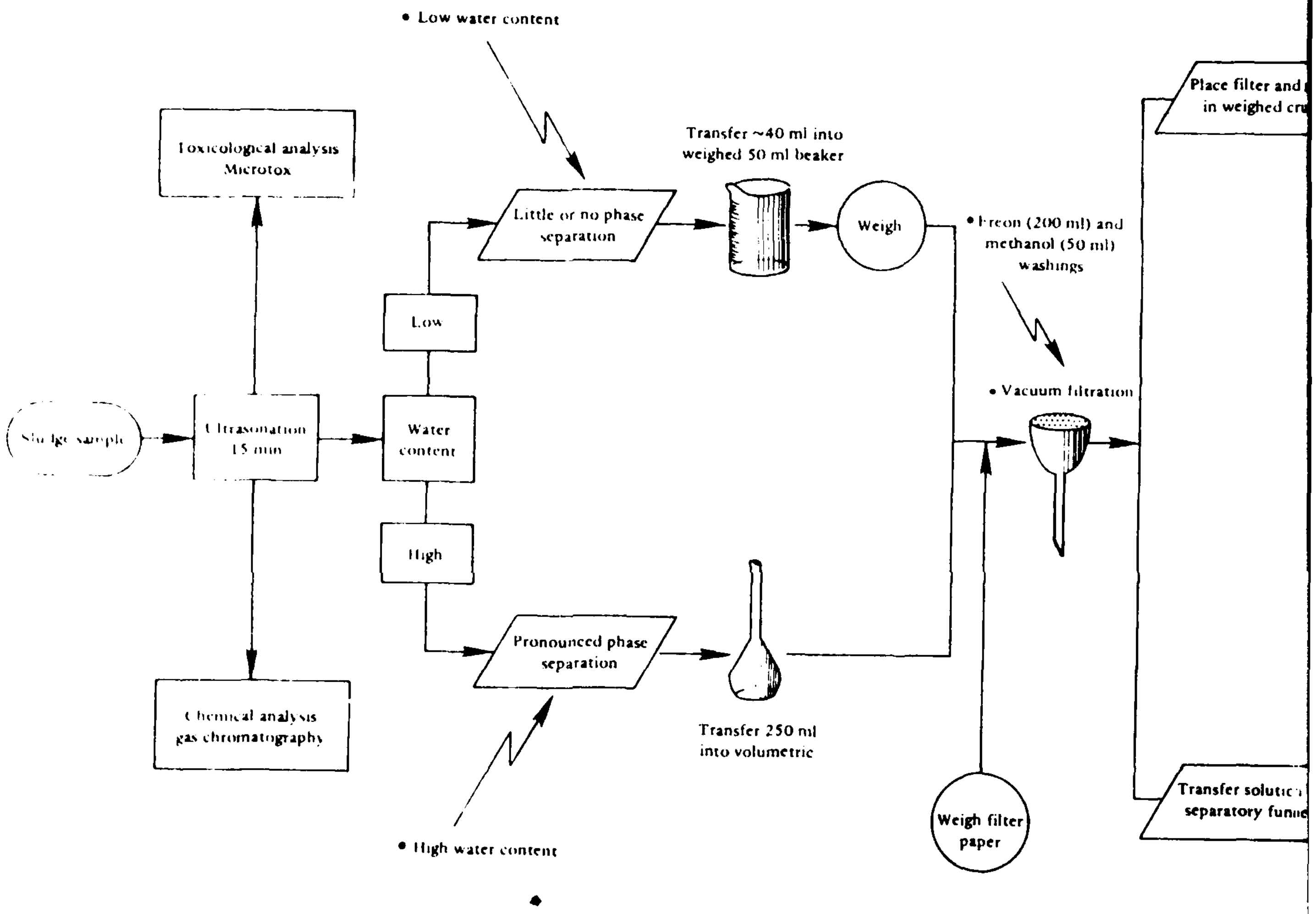
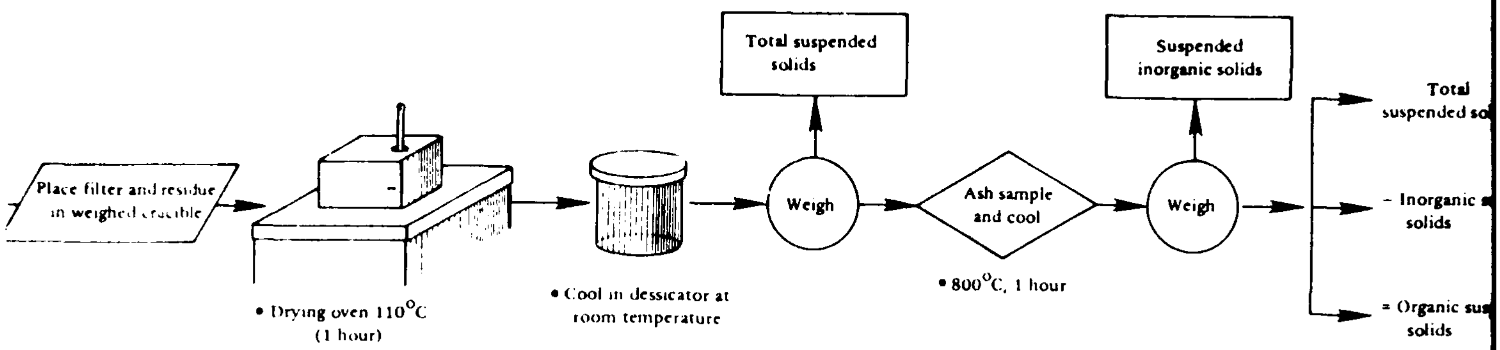
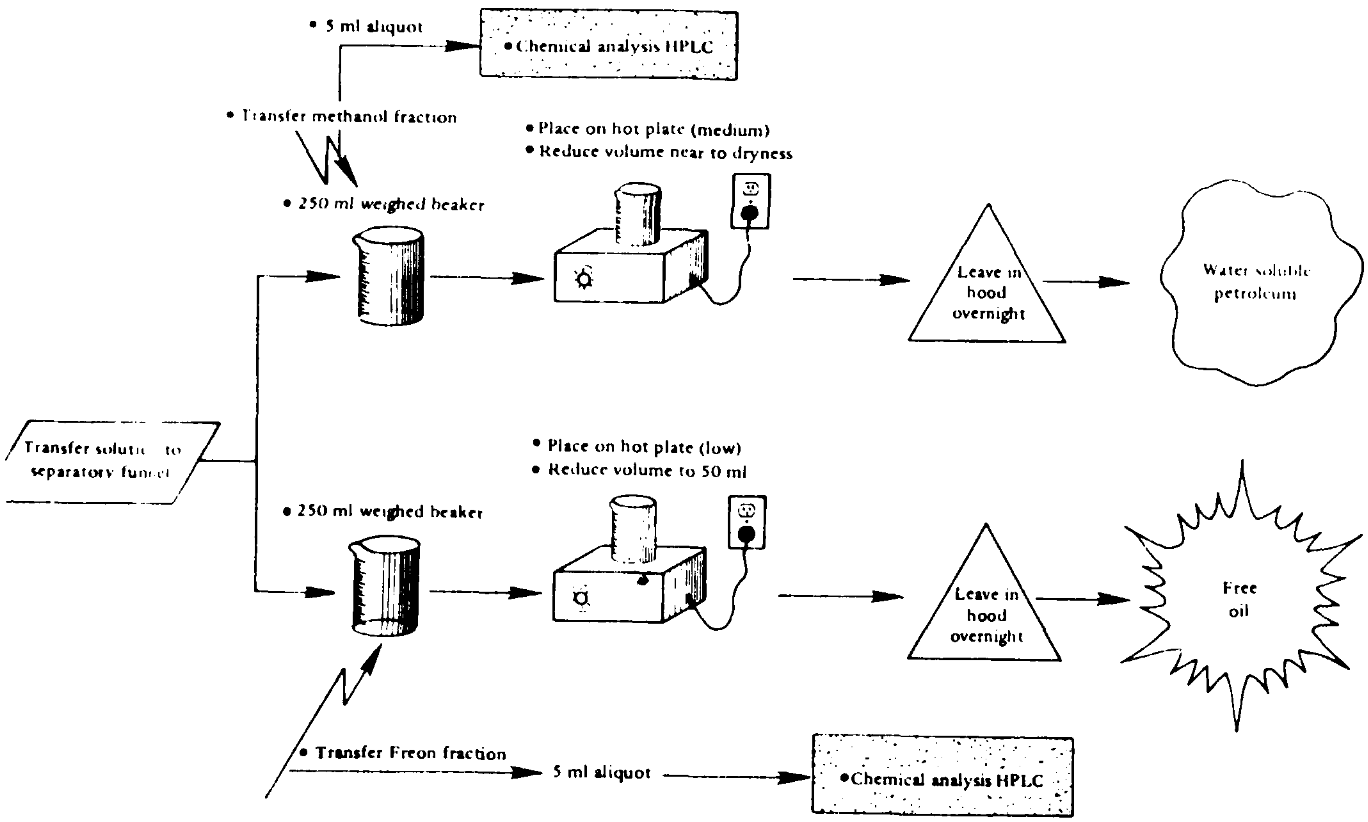
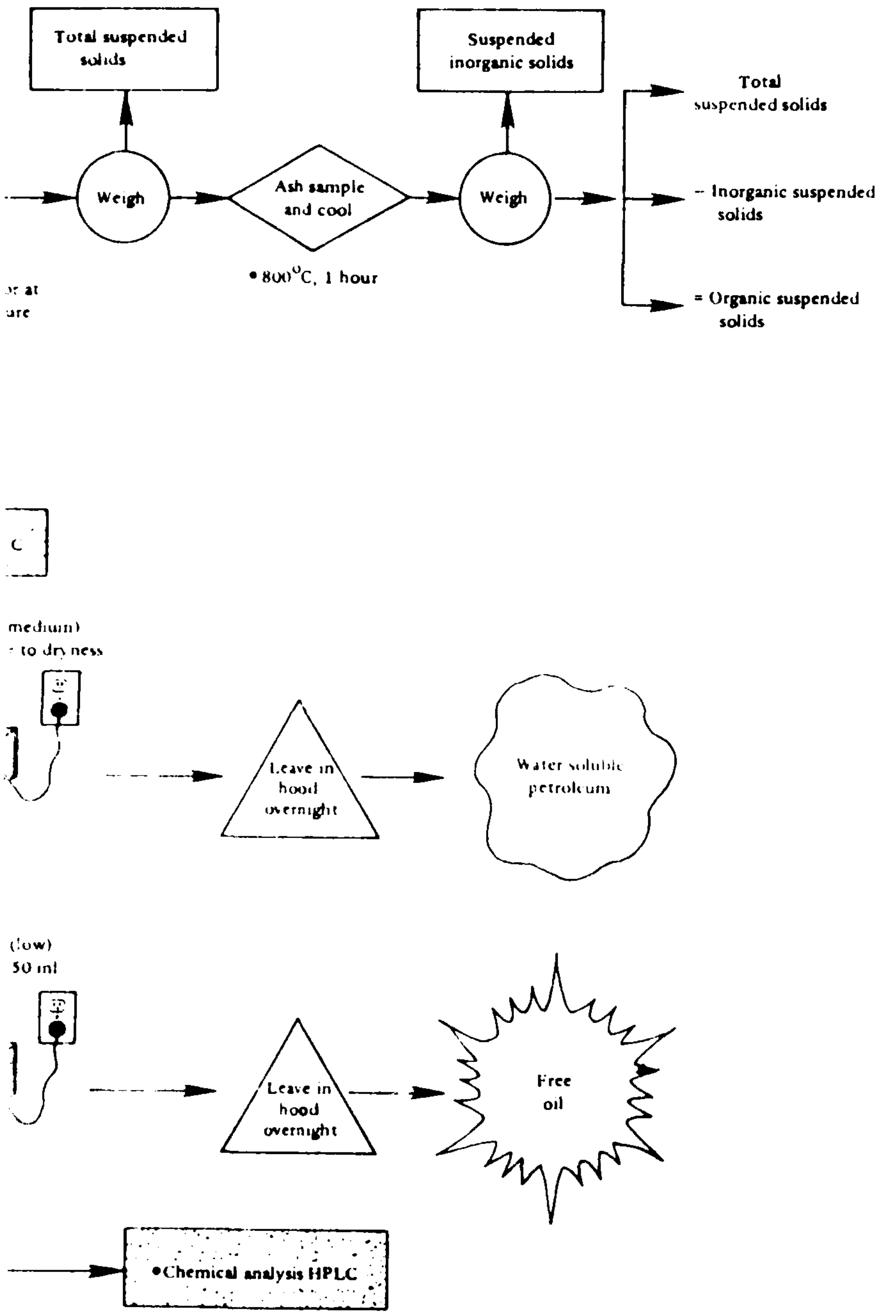


Figure 1. Flow diagram:





iiagram: A physical characterization.



Total suspended solids
Suspended inorganic solids
Weigh
Ash sample and cool
Weigh
• 800°C, 1 hour
Total suspended solids
– Inorganic suspended solids
= Organic suspended solids
medium)
to dryness
Leave in hood overnight
Water soluble petroleum
(low)
50 ml
Leave in hood overnight
Free oil
•Chemical analysis HPLC

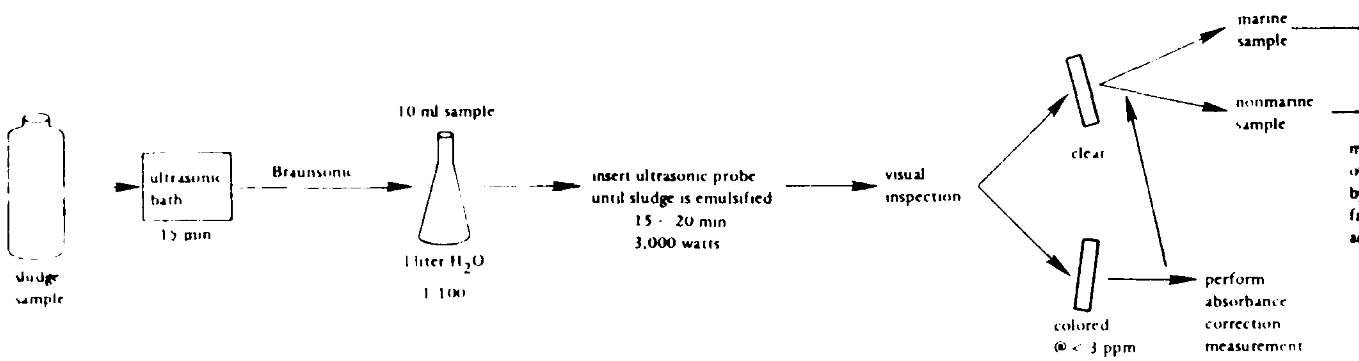
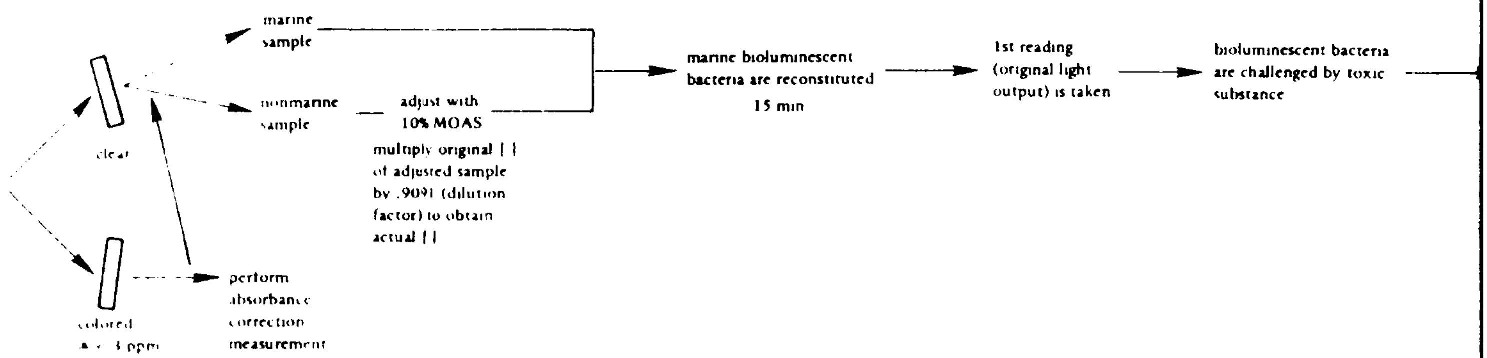


Figure 2. Flow diagram: A



ure 2. Flow diagram: A toxicological characterization.

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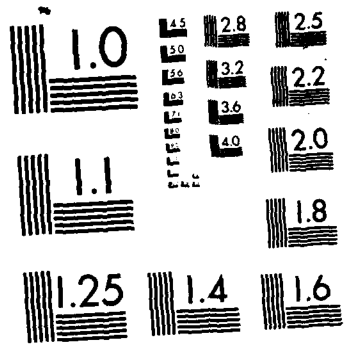


MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

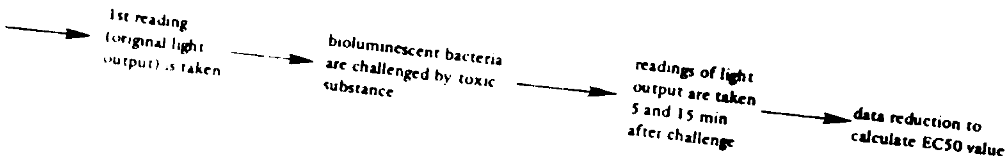

1st reading (original light output) is taken
bioluminescent bacteria are challenged by toxic substance
readings of light output are taken 5 and 15 min after challenge
data reduction to calculate EC50 value

Figure 3. Oily sludge sampling sites.

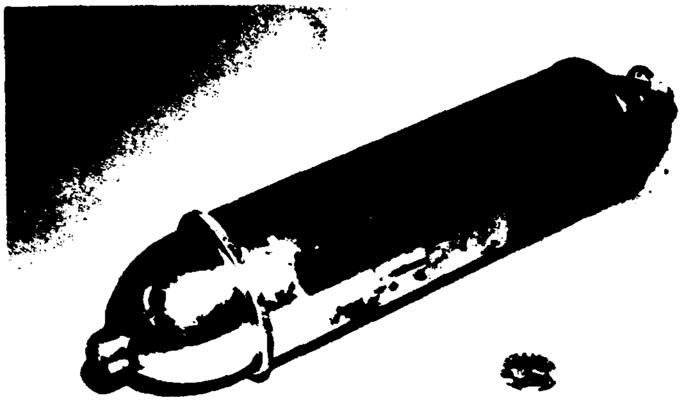


Figure 4. Bacon bomb sampler.

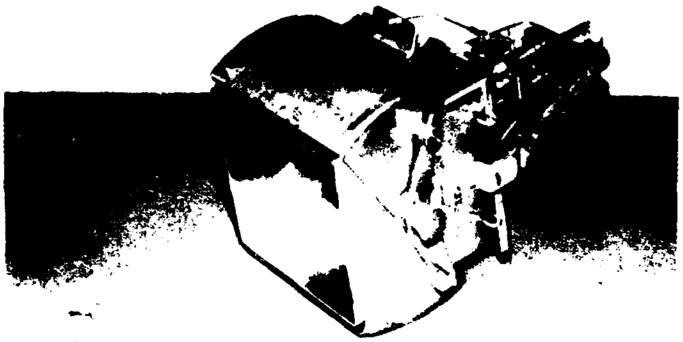


Figure 5. Sediment grab sampler.

Figure 6. Hand-operated bellows pump.

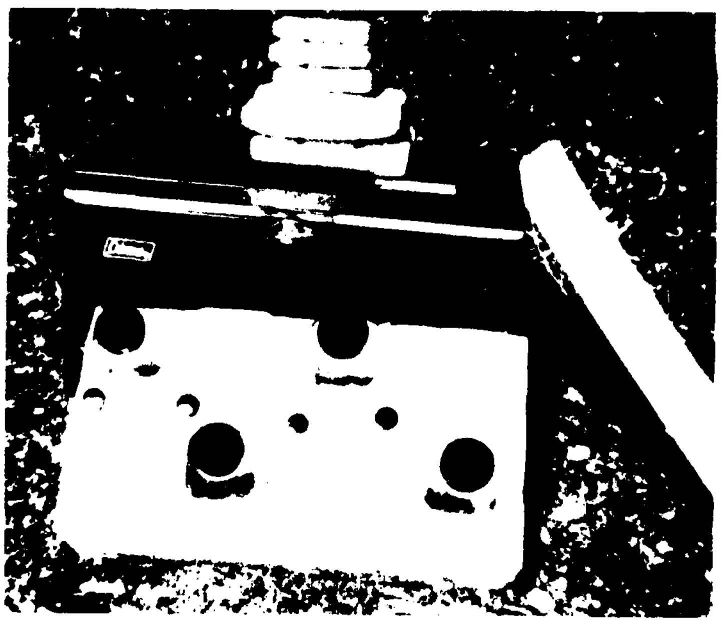
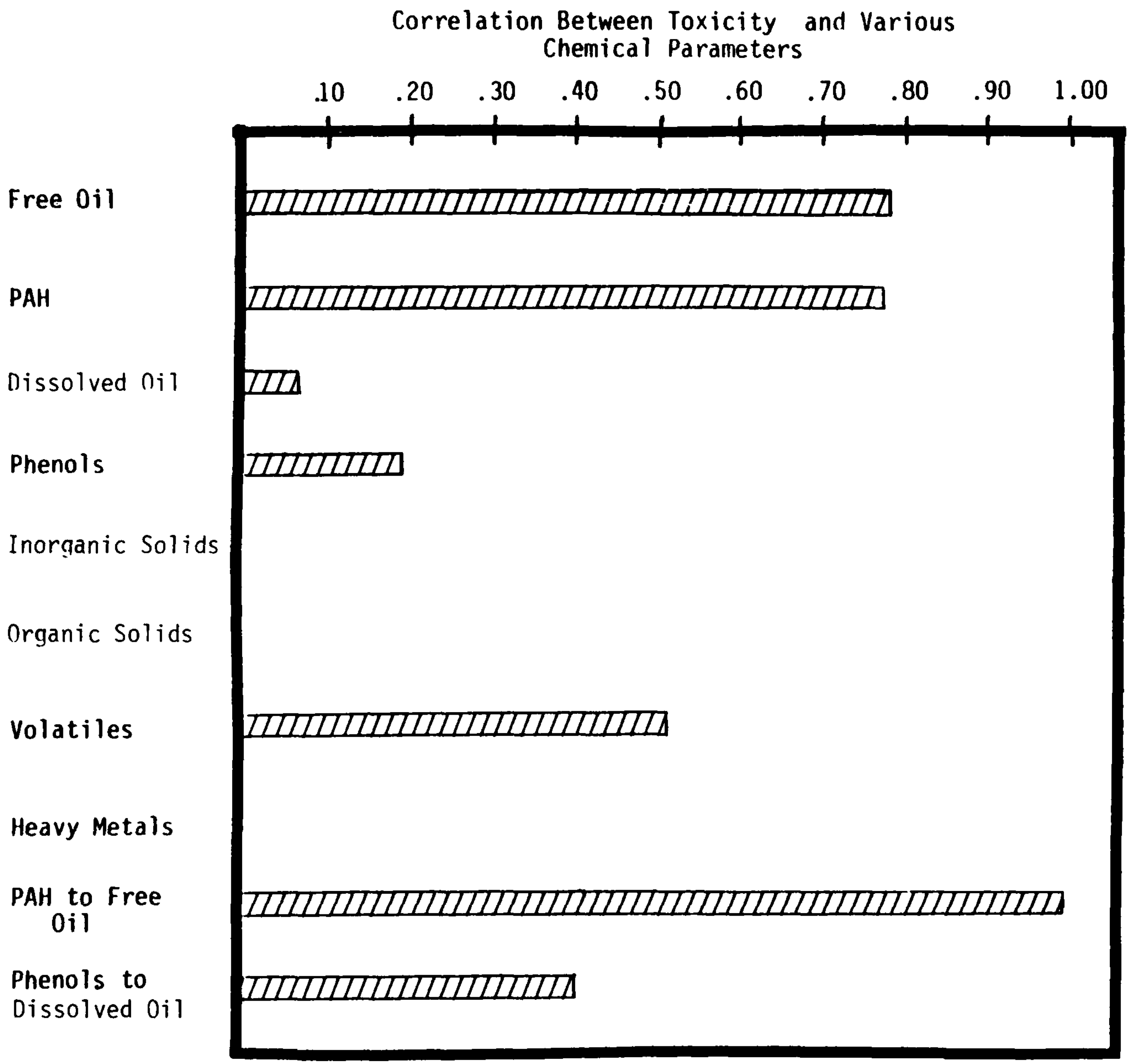


Figure 7. Sample shipping/preservation container.

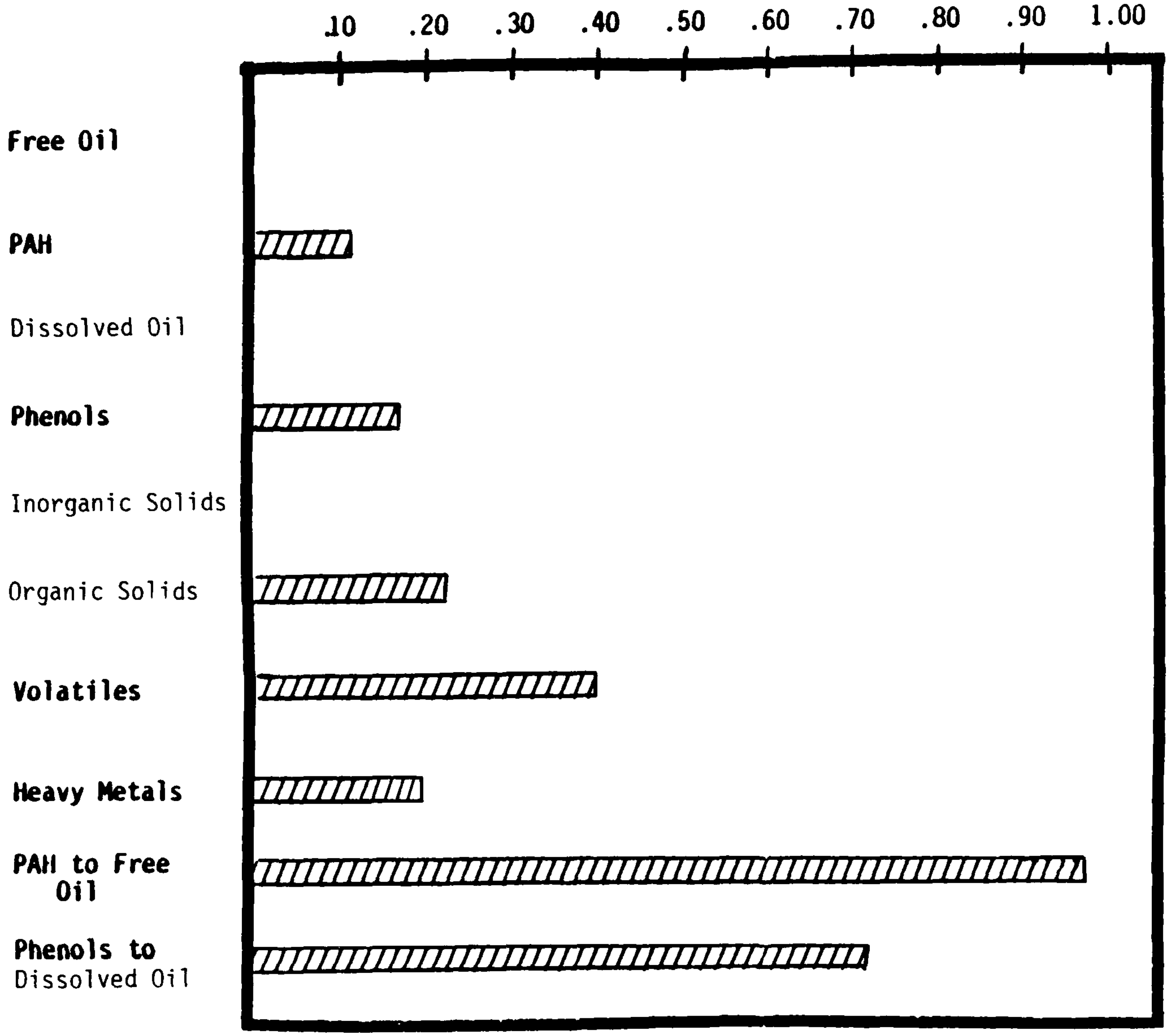


Chemical Composition	
Free Oil	23.6%
Dissolved Oil	0.9%
Inorganic Solids	6.6%
Organic Solids	2.1%
PAH	7,823ppm
Phenols	476ppm
Volatiles	42ppm
Heavy Metals	400ppm

Average Toxicity:
EC_{50}(15 min) 62

Figure 8. Relationship between toxicity and chemical composition of gravity separator bottom sludges.

Correlation Between Toxicity and Various Chemical Parameters

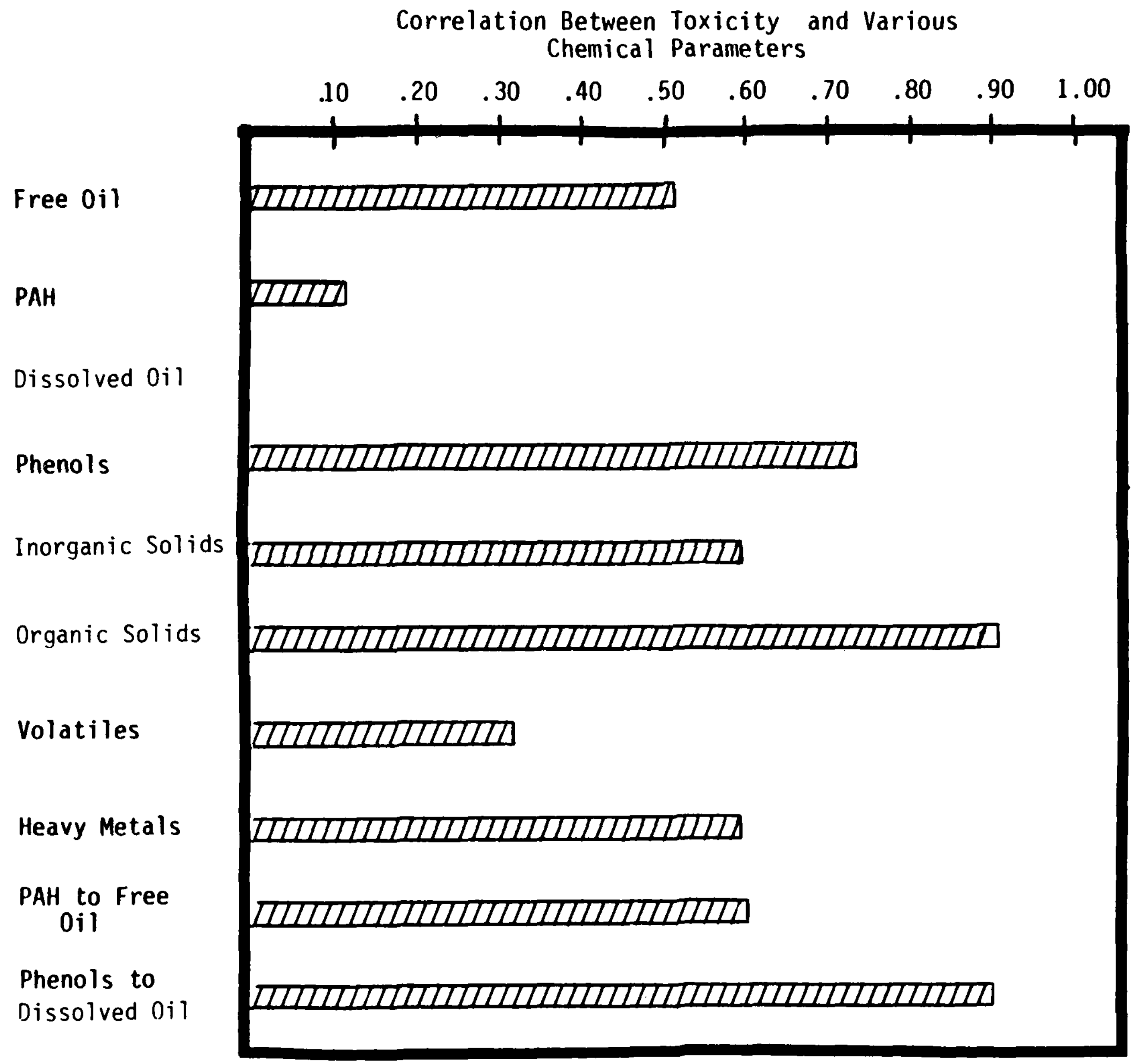


Chemical Composition

Free Oil	18.5%
Dissolved Oil	0.8%
Inorganic Solids	1.6%
Organic Solids	2.9%
PAH	4,679ppm
Phenols	575ppm
Volatiles	49ppm
Heavy Metals	402ppm

Average Toxicity:
EC_{50}(15 min) 35

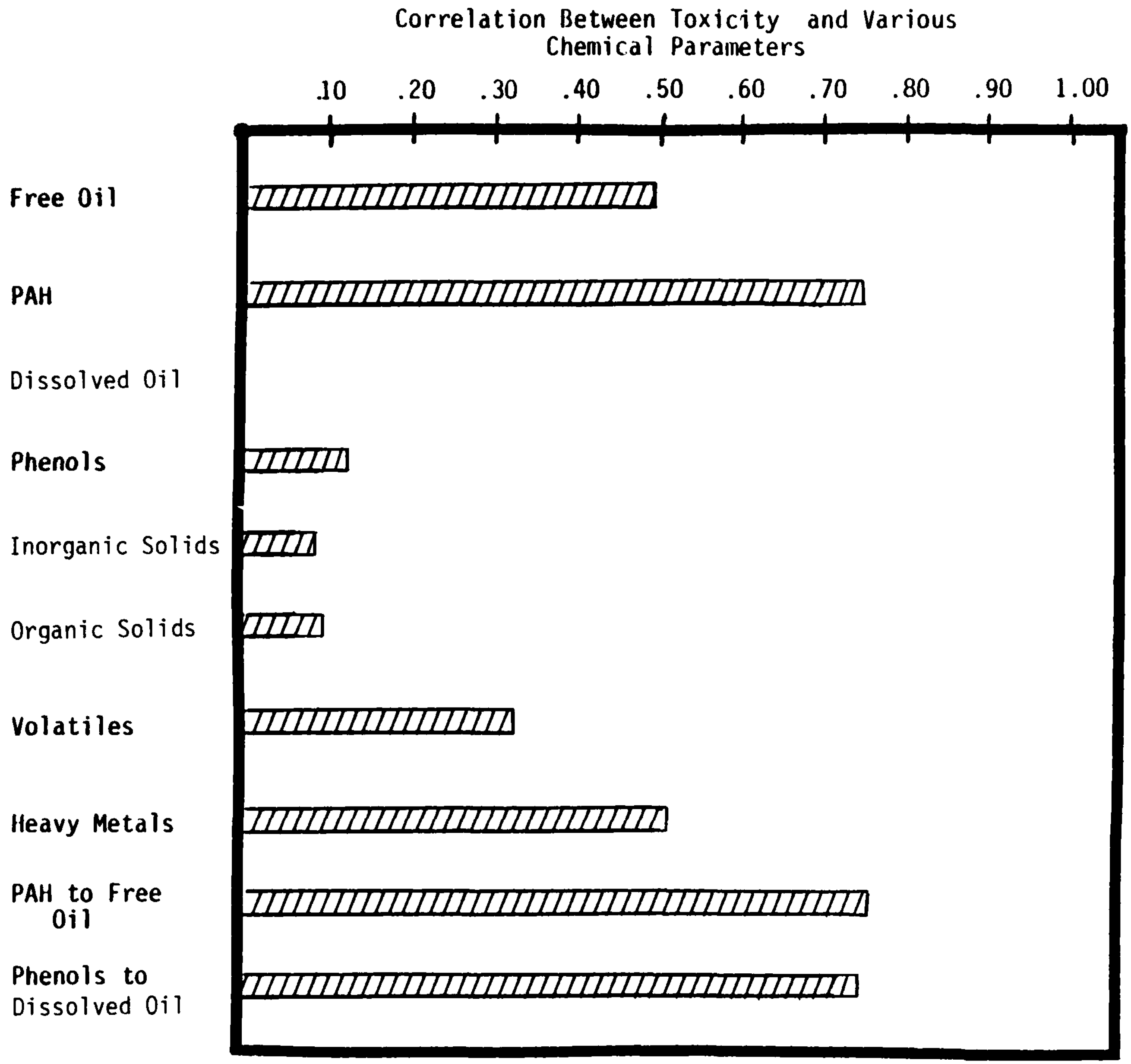
Figure 9. Relationship between toxicity and chemical composition of gravity separator interface sludges.



Chemical Composition	
Free Oil	2.4%
Dissolved Oil	0.6%
Inorganic Solids	2.0%
Organic Solids	4.9%
PAH	633ppm
Phenols	336ppm
Volatiles	5ppm
Heavy Metals	132ppm

Average Toxicity:
EC_{50}(15 min) 182

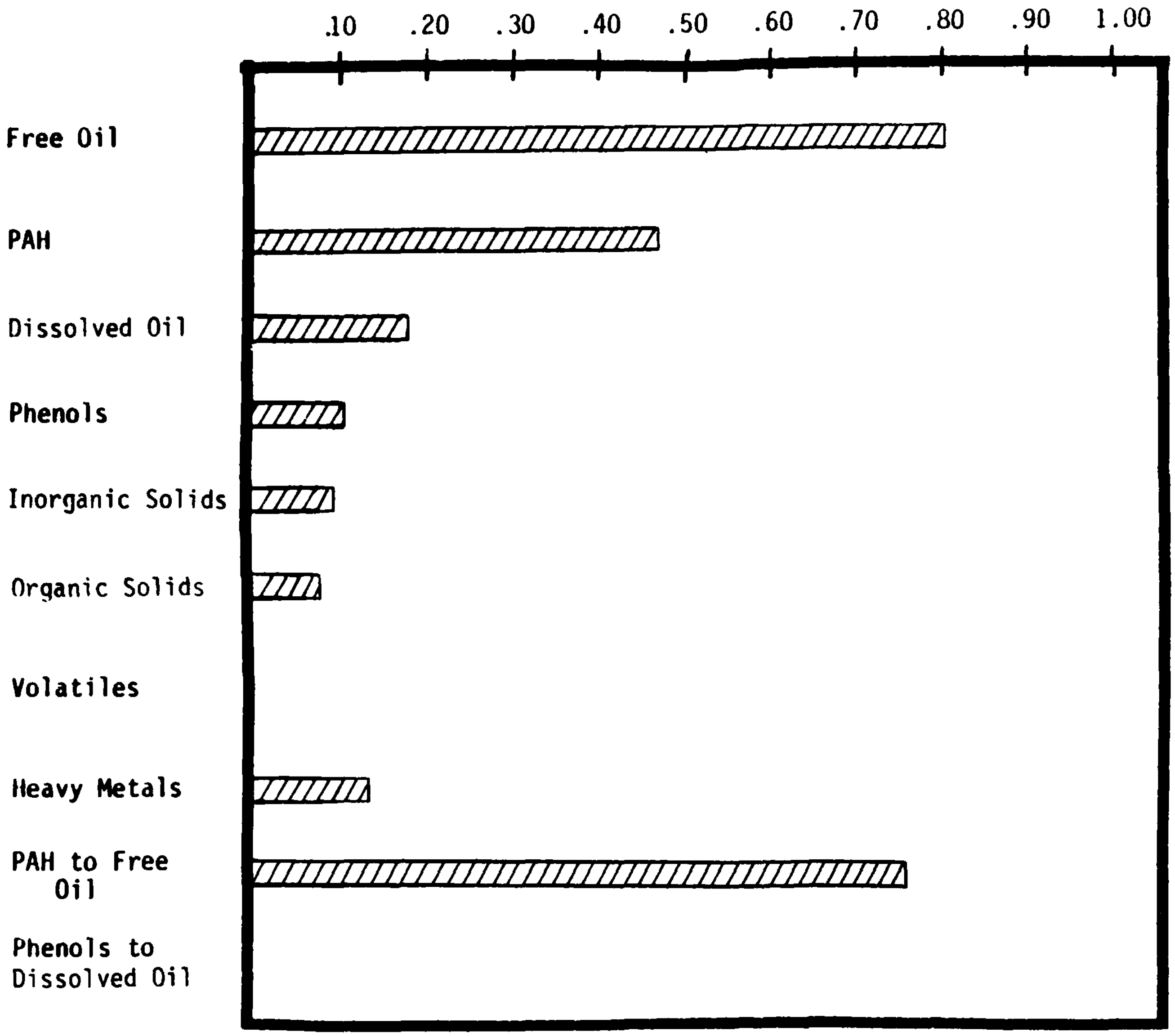
Figure 10. Relationship between toxicity and chemical composition of DAF sludges.



Chemical Composition	
Free Oil	40.3%
Dissolved Oil	2.8%
Inorganic Solids	1.3%
Organic Solids	2.9%
PAH	10,924ppm
Phenols	563ppm
Volatiles	49ppm
Heavy Metals	379ppm
Average Toxicity: EC_{50}(15 min)	19

Figure 11. Relationship between toxicity and chemical composition of oil recovery sludges.

Correlation Between Toxicity and Various Chemical Parameters



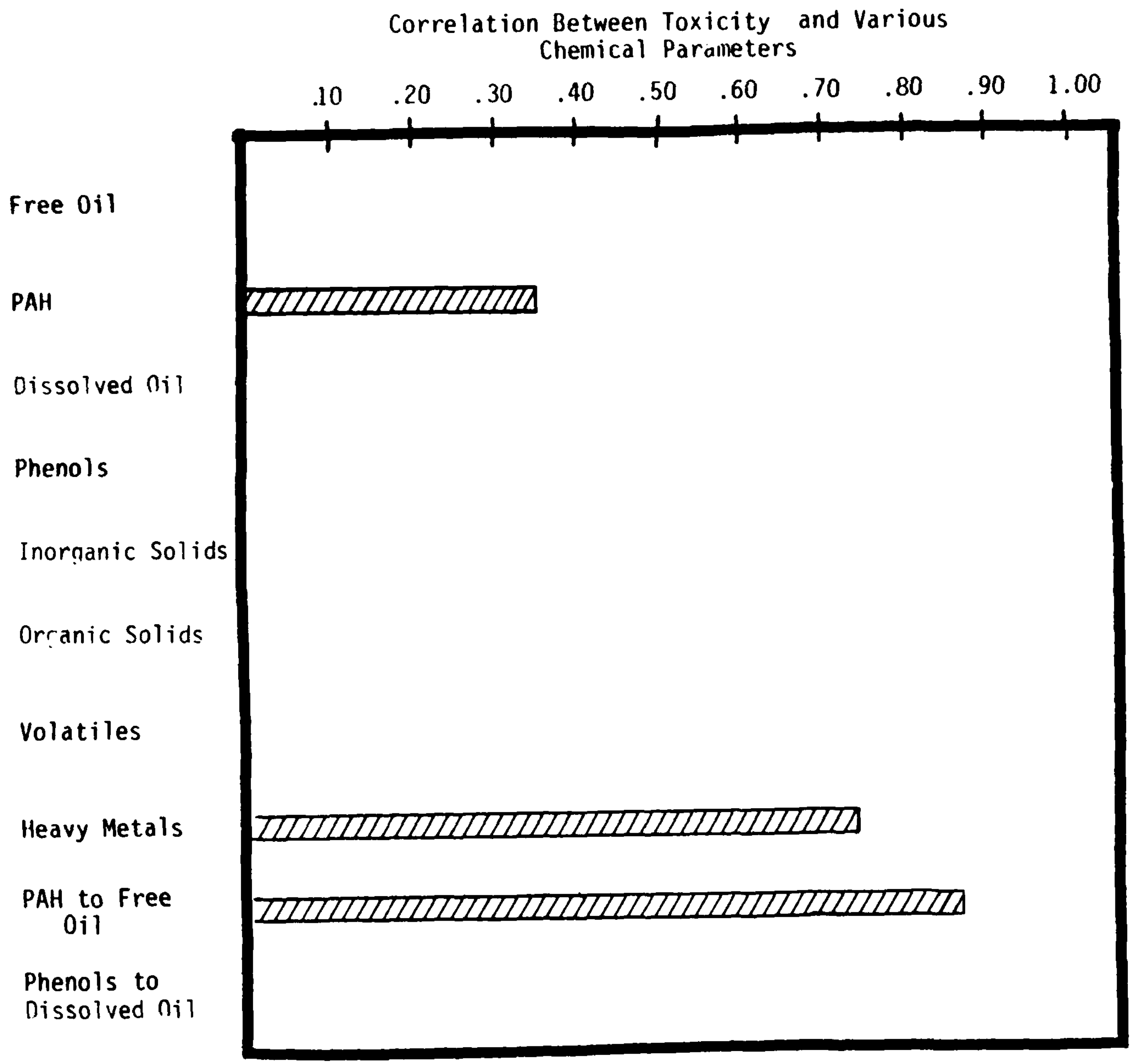
<u>Chemical Composition</u>

Free Oil	5.2%
Dissolved Oil	1.0%
Inorganic Solids	7.1%
Organic Solids	4.8%
PAH	1,004ppm
Phenols	423ppm
Volatiles	29ppm
Heavy Metals	1,072ppm

Average Toxicity:

EC_{50}(15 min) 56

Figure 12. Relationship between toxicity and chemical composition of oil sump sludges.

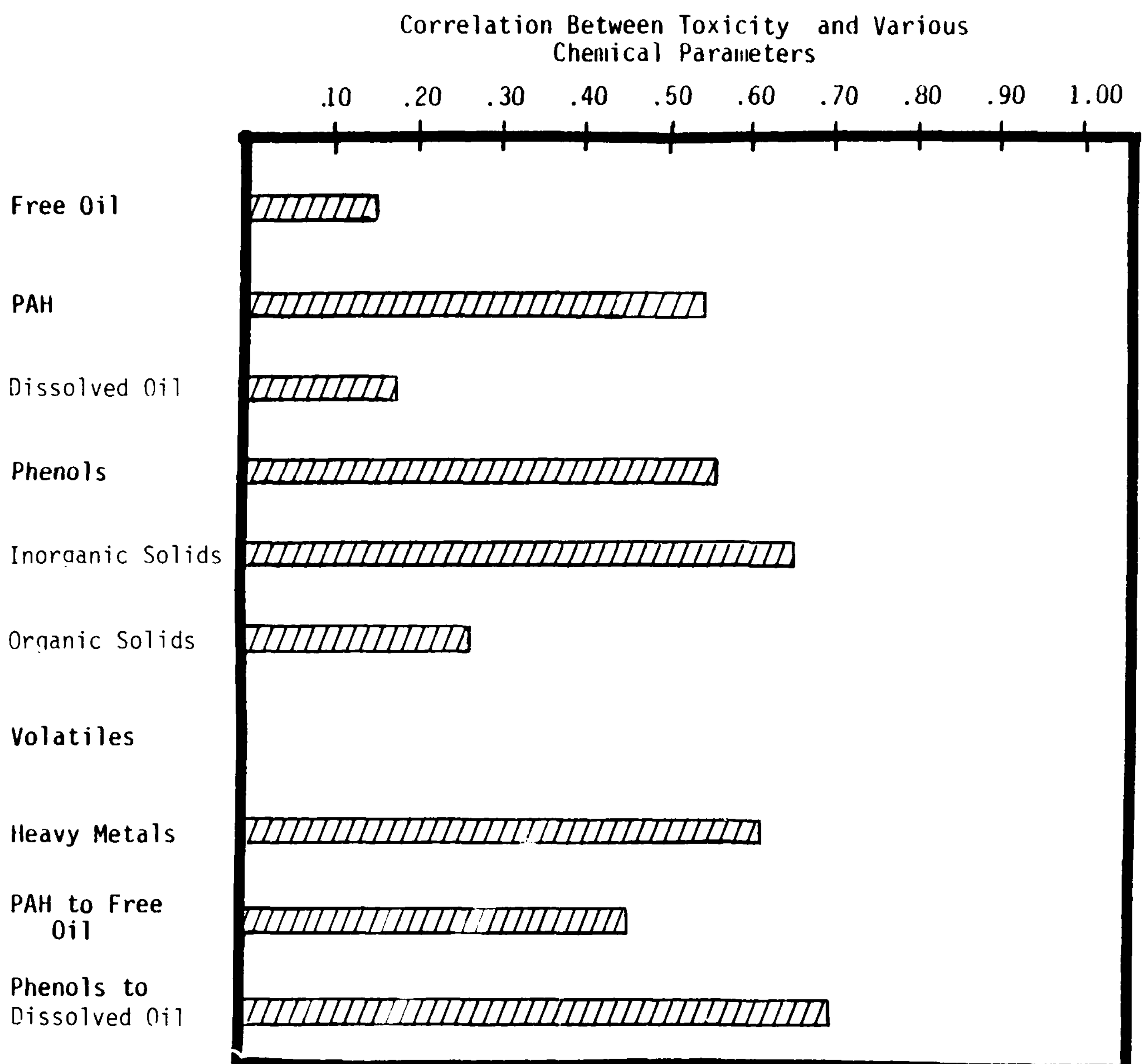


Chemical Composition

Free Oil	10.8%
Dissolved Oil	1.1%
Inorganic Solids	13.0%
Organic Solids	10.2%
PAH	3,829ppm
Phenols	9,255ppm
Volatiles	5.7%
Heavy Metals	1,626ppm

Average Toxicity:
EC_{50}(15 min)

Figure 13. Relationship between toxicity and chemical composition of dewatered sludges.

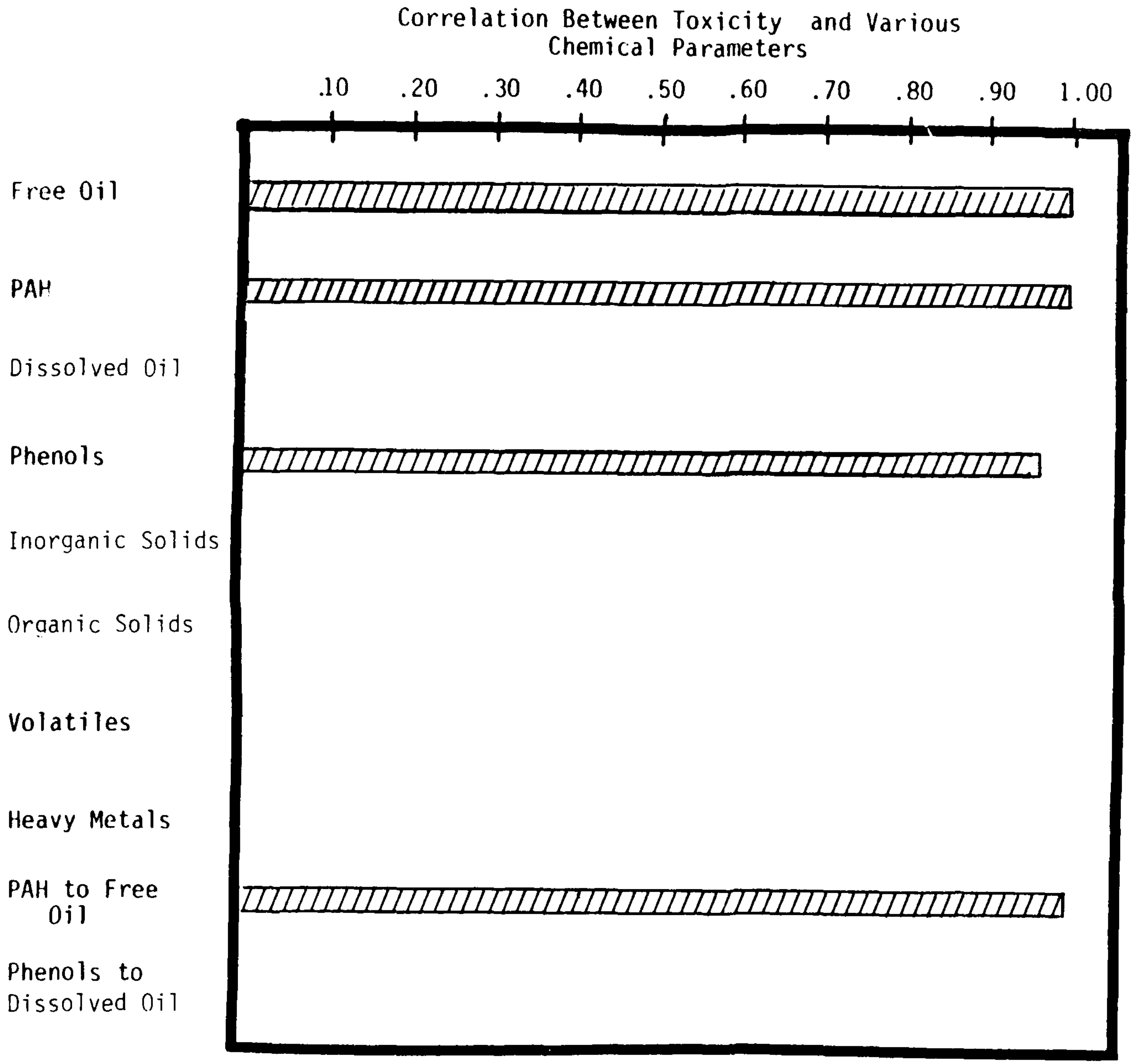


Chemical Composition	
Free Oil	1.2%
Dissolved Oil	0.5%
Inorganic Solids	2.5%
Organic Solids	2.6%
PAH	224ppm
Phenols	211ppm
Volatiles	9ppm
Heavy Metals	146ppm

Average Toxicity:

EC_{50}(15 min) 109

Figure 14. Relationship between toxicity and chemical composition of API and coalescer separators sludges.



Chemical Composition	
Free Oil	7.3%
Dissolved Oil	1.0%
Inorganic Solids	8.6%
Organic Solids	4.3%
PAH	2,667ppm
Phenols	2,805ppm
Volatiles	26ppm
Heavy Metals	196ppm

Average Toxicity:

EC_{50}(15 min) 102

Figure 15. Relationship between toxicity and chemical composition of impound sludges.

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