



# ANALYSIS AND REDUCTION OF TOXICITY IN BIOLOGICALLY TREATED PETROLEUM PRODUCT TERMINAL TANK BOTTOMS WATER

Health and Environmental Sciences Department Publication Number 4665 April 1998

Not for Resale





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# Analysis and Reduction of Toxicity in Biologically Treated Petroleum Product Terminal Tank Bottoms Water

#### Health and Environmental Sciences Department

#### **API PUBLICATION NUMBER 4665**

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#### PREFACE

The American Petroleum Institute (API), through its Marketing Terminal Effluent Task Force, conducted a multi-year research program to evaluate and identify practical and environmentally sound technology options for handling and treating waters generated at petroleum product distribution terminals. The results of this program are intended to provide industry and regulatory agencies with technical information to make informed decisions on appropriate alternatives for individual terminal facilities.

The Task Force has sponsored and published a significant amount of work in prior years on handling and treating terminal waters. The work contained in this report focuses on measuring the acute and chronic aquatic toxicity of tank bottom water sources at terminals and the effectiveness of conventional treatment methods to reduce this toxicity. Another purpose of this study was to test a wide variety of waters from different terminals to evaluate whether the results of a prior study (API Publication No. 4581) were representative. In that prior study, biological treatment was effective for removing contaminants and toxicity as measured by bioassay tests.

The results of this study showed that tank bottom waters at petroleum product terminals varied greatly in their toxicity—some being of a low toxicity, even before treatment, and other waters showing toxicity after extensive treatment. Hence, it points to the key conclusion found in prior studies that each situation at a particular terminal needs to be evaluated individually and even simple, standard treatment methods may need to be adjusted to meet local site effluent objectives.

Many petroleum companies have decided to extract the hydrocarbon value of tank bottom waters. Typically, these waters are not treated on site, but sent back to refineries or licensed oil recyclers to separate the oil from the waters, and to treat the residual waters. If onsite treatment is desired, this study as well as others documented in API publications will assist the environmental or facility engineer in deciding on approaches to define the preferred treatment option.

Prior studies sponsored by the Task Force have shown that operations and water characteristics at distribution terminals can vary significantly as do regulatory requirements in different geographical jurisdictions. Hence, it is recommended that terminal operators or engineers carefully review the terminal water characteristics and regulatory requirements for each facility before designing or installing treatment equipment. Also, other options such as pretreatment and discharge of waters to Publicly Owned Treatment Works (POTWs), use of packaged, mobile units for temporary treatment needs and integration of treatment with other existing petroleum or chemical facilities should be considered versus installation of equipment at the terminals.

The Task Force greatly acknowledges and appreciates the fine work performed by Texaco Research and Development Groups, based in Port Arthur and Bellaire, Texas, in conducting this comprehensive and challenging technical study.

R. R. Goodrich, for the Marketing Terminal Effluent Task Force, March 1998.

# TABLE OF CONTENTS

	EXECUTIVE SUMMARY
1.	INTRODUCTION
	OBJECTIVES 1-1
	BACKGROUND1-1
2.	GENERAL APPROACH
	OBJECTIVES
	Water Source2-1
	Normalization2-1
	Use of Biotreatment2-2
	Variety of Water Sources2-2
	TOXICITY IDENTIFICATION
	TOXICITY THRESHOLDS
	TREATMENT METHODS
	Selection of Treatments2-5
	Development of Treatments2-5
	Aerobic Biological Treatment
	Ammonia Removal
	Metals Removal2-6
	Arsenic Removal2-6
	Copper and Zinc Removal
	Removal of Residual Organics
	Oxidation of Residual Organics2-8
	Activated Carbon Adsorption of Residual Organics2-8
	Combined Treatment of Residual Organics2-8
	OVERALL TREATMENT SCHEME
	ANALYSIS OF RESIDUAL TOXICITY2-9
	Salinity Ionic Ratios2-9
	Other Known Toxicants2-9
	TOXICITY CORRELATIONS
3.	FEED WATERS
	Organic Constituents (COD, TOC, and BOD) 3-1
	Ammonia
	Conventional Metals
	Trace Toxic Metals
4.	EXPERIMENTAL EQUIPMENT AND PROCEDURES
	FEED PREPARATION AND SELECTION
	BIOLOGICAL TREATMENT
	AMMONIA REMOVAL
	ARSENIC REMOVAL
	COPPER AND ZINC REMOVAL
	UV-PEROXIDE OXIDATIVE REMOVAL OF RESIDUAL ORGANICS 4-3

# **TABLE OF CONTENTS**

ν,

4.	EXPERIMENTAL EQUIPMENT AND PROCEDURES Continued	
	POWDERED ACTIVATED CARBON REMOVAL	. 4-4
	OF RESIDUAL ORGANICS	
	COMBINED UV/PEROXIDE - POWDERED ACTIVATED	. 4-4
	CARBON TREATMENT	
	SAMPLING AND ANALYSIS	. 4-4
	TOXICITY TESTING	. 4-4
5.	RESULTS - INDIVIDUAL WASTEWATERS	
	WASTEWATER 1	. 5-1
	WASTEWATER 3	. 5-1
	WASTEWATER 4	. 5-1
	WASTEWATER 5	. 5-1
	WASTEWATER 6	. 5-1
	WASTEWATER 7	. 5-2
	WASTEWATER 8	. 5-2
	WASTEWATER 9	. 5-2
	WASTEWATER 11	. 5-2
	WASTEWATER 12	. 5-2
	WASTEWATER 15	. 5-2
6.	RESULTS - OVERALL	
	BIOLOGICAL REMOVAL OF CONVENTIONAL CONTAMINANTS	. 6-1
	Biochemical Oxygen Demand (BOD)	. 6-1
	Chemical Oxygen Demand (COD)	. 6-1
	Total Organic Carbon (TOC)	. 6-2
	Ammonia	. 6-2
	BIOLOGICAL REMOVAL OF TOXICANTS	. 6-3
	Low Level Metals (Cd, Cr, Ni, Pb, Hg)	. 6-3
	Bioeffluent Levels of Other Toxicants	. 6-3
	Metals	. 6-3
J	Surfactants (MBAS & CTAS)	. 6-3
5	PHYSICAL/CHEMICAL REMOVAL OF CONTAMINANTS	. 6-4
	Ammonia Removal by Alkaline Air Stripping	. 6-4
	Acute Toxicity and Metals Removal by Precipitation	. 6-4
	Acute Toxicity and Tertiary Treatment Removal of Residual Organics	. 6-6
	Chronic Toxicity and Tertiary Treatment Removal of Residual Organics	. 6-7
7.	INVESTIGATION OF RESIDUAL TOXICITY	
	TOXICITY FROM IONIC IMBALANCES	. 7-1
	OTHER POTENTIAL TOXICANTS	. 7-3
	Boron	. 7-4
	Barium	. 7-4
	Antimony	. 7-4

### TABLE OF CONTENTS

#### 7. INVESTIGATION OF RESIDUAL TOXICITY Continued

	Tin	7-4
	Vanadium	7-4
	Selenium	7-4
	Cyanides	7-4
	Priority Pollutant Metals (Be, Ag, Tl)	7-4
	Beryllium	7-4
	Silver	7-4
	Thallium	7-5
	Surfactants	7-5
	Naphthenic Acids	7-5
	Antifoam Agent	7-6
	Solid Phase (C18) Extraction	7-6
	Residual Organics	7-6
ļ	MATERIALS NOT ANALYZED	7-7
l.	Nitrate	7-7
	Phosphate	7-7
ł	Reduced Sulfur Species	7-8
	Overview	7-8
8.	TOXICITY CORRELATIONS	
	SCORING	8-1
	OVERALL SCORE	8-1
	REVISED SCORING	8-2
	PRODUCT TYPE	8-2
	GEOGRAPHICAL LOCATION	8-2
	BIOLOGICAL TREATMENT LEVELS	8-3
	Bioeffluent BOD	8-3
	Bioeffluent COD	8-3
	Bioeffluent TOC	8-4
	Bioeffluent Ammonia	8-4
	Bioeffluent Surfactants (MBAS and CTAS)	8-4
	FINAL EFFLUENT LEVELS OF KNOWN TOXICANTS	8-5
	Final Effluent Ammonia	8-5
	Final Effluent Metals - As, Cu, Zn	8-5
	Final Effluent Metals - Cr & Ni	8-6
	RESIDUAL TOC AFTER TERTIARY TREATMENTS	8-6
9.	SUMMARY OF RESULTS	9-1

#### BIBLIOGRAPHY

## LIST OF FIGURES

1	Flow Chart for Toxicity Reduction Testing	2-10
2	Sequencing Batch Reactor Time Sequence	4-1
3	Batch Alkaline Air Stripping of Ammonia	4-2
4	Batch Arsenic Co-Precipitation with Fe <sup>+++</sup>	4-2
5	Batch Copper & Zinc Precipitation with S=, Fe <sup>++</sup> , Air	4-3
6	Recirculating Batch UV-Hydrogen Peroxide Oxidation Reactor System for	
	Removing Residual Organics	4-3
7	Wastewater #1 Toxicity Reduction Testing Results	5-3
8	Wastewater #3 Toxicity Reduction Testing Results	5-4
9	Wastewater #4 Toxicity Reduction Testing Results	5-5
10	Wastewater #5 Toxicity Reduction Testing Results	5-6
11	Wastewater #6 Toxicity Reduction Testing Results	5-7
12	Wastewater #7 Toxicity Reduction Testing Results	5-8
13	Wastewater #8 Toxicity Reduction Testing Results	5-9
14	Wastewater #9 Toxicity Reduction Testing Results	5-10
15	Wastewater #11 Toxicity Reduction Testing Results	5-11
16	Wastewater #12 Toxicity Reduction Testing Results	5-12
17	Wastewater #15 Toxicity Reduction Testing Results	5-13
18	Biological Removal of Contaminants	6-2
19	Alkaline Air Stripping Removal of Ammonia	6-4
20	Precipitation Removal of Metals & Toxicity	6-6
21	Tertiary Treatment and TOC/Toxicity Removal	6-8
22	Acute Toxicity vs. Bioassay Sample TOC	7-6
23	Chronic Toxicity vs. Bioassay Sample TOC	7-7
24	Acute Toxicity vs. Nitrification	7-7
25	Toxicity Score vs. Bioeffluent BOD	8-3
26	Toxicity Score vs. Bioeffluent COD	8-3
27	Toxicity Score vs. Bioeffluent TOC	8-4
28	Toxicity Score vs. Bioeffluent Ammonia	8-4
29	Toxicity Score vs. Bioeffluent MBAS	8-4
30	Toxicity Score vs. Bioeffluent CTAS	8-4
31	Toxicity Score vs. Final Ammonia	8-5
32	Toxicity Score vs. Final Arsenic	8-5
33	Toxicity Score vs. Final Copper	8-5
34	Toxicity Score vs. Final Zinc	8-5
35	Toxicity Score vs. Final Chromium	8-6
36	Toxicity Score vs. Final Nickel	8-6
37	Toxicity Score vs. Oxidation Effluent TOC	. 8-6
38	Toxicity Score vs. PAC Effluent TOC	. 8-6
39	Toxicity Score vs. Ox/PAC Effluent TOC	. 8-6
40	Overall Removal of Toxicants and Toxicity	. 9-2

### LIST OF TABLES

1	Tank Bottoms Water Sources	2-3
2	Approaches to Toxicity Identification and Removal	2-4
3	Estimated Toxicity Thresholds for Ammonia and Metals	2-5
4	Tank Bottoms Waters Organic Ratios	3-1
5	As-Received Tank Bottoms Waters Conventional Contaminants	3-2
6	Cation Balance With Respect to Seawater Magnesium	3-3
7	As-Received Tank Bottoms Waters Metals and Conductivity	3-4
8	Percent Removal of Organics	5-1
9	Biological Removal of Conventional Contaminants	6-1
10	Biological Removal of Metals	6-3
11	Bioeffluent Contaminants	6-3
12	Ammonia Removal	6-4
13	Metals Removal by Precipitation	6-5
14	Tertiary Treatment of TOC and Acute & Chronic Toxicity	6-7
15	Concentrations of Major Ions in Bioassay Samples	7-2
16	Ionic Compositions of Real and Mock Effluents IDs 9 and 12	7-2
17	Results of Real/Mock Acute Toxicity Tests	7-3
18	Concentrations of Trace Metals and Cyanides Following Removal of Ammonia,	
	Metals, and Residual Organics	7-3
19	Concentrations of Priority Pollutant Metals Following Removal of Ammonia,	
	Metals, and Residual Organics	7-4
20	Concentrations of Surfactants After Tertiary Treatment	7-5
21	Concentrations of Naphthenic Acids After Tertiary Treatment	7-6
22	Materials Known Not to be Present at Toxic Levels in Acutely Toxic Effluents	7-9
23	Wastewater 100% Toxicity Scores	8-1
24	Wastewater 50% Toxicity Scores	8-2
25	Product Type and Toxicity	8-2
26	Location and Toxicity	8-2

#### **EXECUTIVE SUMMARY**

This study builds on previous studies sponsored by API on treating petroleum product terminal wastewaters. Previous work showed that terminal effluents could be treated successfully, but that some effluents were more difficult to treat than others. Also, the degree to which effluent toxicity was removed varied from wastewater to wastewater. This study examines the variability and treatability of tank water draws, one component of terminal wastewater.

An earlier study examined petroleum product effluent toxicity to selected vertebrate and invertebrate species, and reported 96-hour  $LC_{50}$  concentrations ranging from less than 3 percent effluent to more than 100 percent effluent. The toxicities observed in these samples could not be fully attributed to hardness or salinity, and so must be attributable to effluent contaminants which can be removed through treatment.

This study further addresses the treatability of toxicity in petroleum product terminal effluents, by examining the toxicity of terminal tank bottoms water, which is the major source of organic constituent toxicity in petroleum product terminal wastewaters. The objectives of the study are to measure toxicity in biologically treated petroleum product terminal tank bottoms waters, identify the chemical constituents causing that toxicity, identify treatment options, and measure the effectiveness of the treatment techniques in removing the constituents and reducing toxicity.

#### EXPERIMENTAL PROCEDURE

Nine gasoline and two diesel tank bottoms water samples were collected from petroleum product terminals at various geographical locations. To compare tank bottoms water toxicities and treatment efficiencies on the basis of equal strength, the samples were normalized by dilution to a common strength of 4000 mg/L chemical oxygen demand (COD). The samples were then subjected to biological treatment, and the effluents from biological treatment were analyzed for the known toxicants ammonia and metals.

If ammonia were present at concentrations exceeding reported toxic threshold concentrations for the toxicity test species (*Mysidopsis bahia*), the effluent was treated for ammonia by batch alkaline air stripping. Biological treatment (through sorption to biological sludge) was effective in removing the metals cadmium, chromium, nickel, lead, and mercury. Following biological treatment, if arsenic were present at concentrations exceeding its reported toxic threshold, arsenic was removed by iron(III) coprecipitation. Similarly, if copper and zinc were present at concentrations exceeding their toxic thresholds, they were removed by sulfide precipitation.

The treated samples were then tested for acute toxicity in 24-hour exposure tests using *Mysidopsis bahia*. Since *Mysidopsis bahia* is an estuarine organism, sufficient sea salt was added to each sample prior to testing in order to raise the salinity to 25,000 ppm, a concentration typical of seawater and tolerable to *Mysidopsis bahia*.

Samples failing the acute toxicity test were treated for residual organics by UV-peroxide oxidation and activated carbon adsorption, first separately and then in tandem. Samples passing the acute toxicity test were tested for chronic toxicity in 7-day static-renewal toxicity tests using

*Mysidopsis bahia*. Samples failing the chronic toxicity test were treated for residual organics in the same manner as those failing the acute toxicity test. Following organics treatment, samples were retested for acute and chronic toxicity.

Selected samples remaining acutely toxic after treatment for ammonia, metals, and residual organics were subjected to further examination for toxicity due to 1) salinity ion ratios; and 2) the toxicants boron, barium, antimony, tin, vanadium, selenium, cyanides, surfactants, naphthenic acids, and  $C_{18}$  adsorbable material.

Though the test organism, *Mysidopsis bahia*, is an estuarine organism tolerant of a wide range of salinities, it may not be capable of tolerating inorganic ion ratios which deviate markedly from those typical of seawater. To investigate this possibility, two acutely toxic samples were serially diluted with a mock wastewater. The mock wastewater for each sample consisted of distilled water into which was dissolved seawater ions at approximately the same concentrations as in the undiluted sample. Should ion ratios be responsible for sample toxicity, the toxicity measured in the serially diluted samples would be proportional to the mock wastewater content.

To assess the possibility of toxicity due to other toxicants, three samples were analyzed for boron, barium, antimony, tin, vanadium, selenium, cyanides, surfactants, naphthenic acids, and  $C_{18}$  adsorbable material. Concentrations of these consituents were compared with literature water quality and toxicity threshold data.

#### **RESULTS AND CONCLUSIONS**

Biological treatment was observed to effectively remove metals, but produced highly variable degrees of COD, total organic carbon (TOC), biochemical oxygen demand (BOD), and ammonia removal. Physical/chemical treatment for ammonia, copper and zinc was required for ten of the eleven samples, and for arsenic in five of the eleven samples.

Nine of the eleven samples contained residual acute toxicity ( $LC_{50}>100\%$  effluent) following biological treatment, metals precipitation and ammonia removal. Of the two samples not acutely toxic, one contained residual chronical toxicity (NOEC>100% effluent). Of the nine secondary effluent samples with residual acute toxicity, tertiary treatment for organics by oxidation and activated carbon was only moderately effective in reducing toxicity. Six of the samples remained acutely toxic following tertiary treatment. Tertiary treatment was also ineffective in reducing the chronic toxicity of the sample not acutely toxic following secondary treatment.

Two samples with residual acute toxicity following tertiary treatment for organics were examined for toxicity due to salinity ion ratios, as described above. Sample toxicity was not found to be due to salinity ion ratios. Three samples with residual acute toxicity following tertiary treatment were examined for toxicity due to the toxicants boron, barium, antimony, tin, vanadium, selenium, cyanides, surfactants, naphthenic acids, and  $C_{18}$  adsorbable material. Concentrations of these constituents were not found to exceed literature water quality criteria or toxic thresholds for *Mysidopsis bahia*. It was concluded that sample toxicity was not due to any of these constituents.

#### 1. INTRODUCTION

#### **OBJECTIVES**

The objectives of the study were to identify the degree and chemical nature of effluent toxicity in a variety of biologically treated petroleum product terminal tank bottoms water effluents and to explore techniques for cost-effectively removing the toxicity.

#### BACKGROUND

Current and anticipated regulations are placing stringent limitations on wastewater discharges from petroleum product terminals. Marketing terminal wastewater consisting of tank water bottoms and wash water from loading facilities is usually treated with an oil/water separator to remove free oil prior to discharge. This has been sufficient for most terminals since they have low flow rates and minimal amounts of contaminant discharge. However, additional treatment facilities may be needed for those marketing terminals whose effluents may have potential for environmental impact (1). In assessing that potential impact, regulatory bodies are now starting to add bioassay testing to ensure that the discharged water will not be toxic to aquatic life in the receiving waters.

A study of marketing terminal effluent toxicity to selected invertebrate and vertebrate test species reported 96-hour LC<sub>50</sub> values ranging from <3 percent effluent to >100 percent effluent among terminals. Invertebrates were more sensitive to the terminal effluents than vertebrate test species. Some fraction of the total observed toxicity may have been due to water quality parameters such as hardness and salinity. However, this cannot account for all of the effluent toxicity observed in this study. It is concluded that the observed mortality was a function of the concentration of pollutant(s) in the marketing terminal effluents.

A Texaco field and laboratory investigation of biological and chemical/physical wastewater treatment technologies showed that biological treatment followed by activated carbon polishing produced the least toxic marketing terminal effluent. However, after such treatment, effluents may still be acutely toxic at the "end of pipe." Based on these results, treated effluents would require dilution of twenty fold or more to be chronically non-toxic in receiving waters (1).

An extensive investigation comparing sequencing batch reactor (SBR) and rotating biological contactor (RBC) processes concluded that these biological treatments were capable of reducing acute and chronic toxicity in marketing terminal wastewaters (2). It was also determined that activated carbon treatment enhanced reduction of chronic toxicity but did not completely eliminate it. The chronic toxicity remaining after carbon treatment may have been due to the presence of ammonia, surfactants, metals and/or unmeasured biorefractory organic compounds.

This study examines wastewaters from a variety of source terminals to examine in detail the nature of any toxicity found in petroleum product terminal tank bottoms water, and to develop practical means for removing that toxicity.

#### 2. GENERAL APPROACH

As will be evident in the following discussion, this study involved the development of nonstandard approaches to obtaining meaningful data on the nature and removal of toxicity. This section provides an overview of what was done in the study, how it was done, and why the particular methods were chosen.

#### **OBJECTIVES**

The objectives of the study were to identify the degree and chemical nature of effluent toxicity in a variety of biologically treated petroleum product terminal tank bottoms water effluents and to explore techniques for cost-effectively removing the toxicity.

#### DISCUSSION

Water Source. Petroleum product terminal wastewaters can come from a variety of sources within the terminal (6), but the only source considered in this study was product tank bottoms water. That was done for the following reasons:

- Tank bottoms water is the major source of organic material in petroleum product terminal wastewaters, and is probably the major source of effluent toxicity.
- Tank bottoms water is the only petroleum product terminal wastewater stream inherent to the function of the facility (storage of petroleum products). Other wastewater streams are incidental.
- The flow of many other petroleum product terminal wastewater streams, particularly those derived from storm water (general runoff and loading rack water) are highly variable. Since toxicity is concentration-dependent, dilution by these variable flows will affect combined effluent toxicity. The study was limited to tank bottoms water to eliminate this source of variability.
- The other major source of organic material and toxicity in petroleum product terminals is detergents, which are commonly used on truck loading racks. Since detergent usage is not inherent to petroleum product terminals, it was decided to eliminate this stream from the water being tested. (It should be noted, however, that a facility which has effluent toxicity problems should examine its use of detergents.)

**Normalization.** All of the tank bottoms waters which were used in the final testing were normalized by diluting their COD levels to 4000 mg/L prior to treatment. The reasons for this are as follows:

• The various tank bottoms water samples varied considerably in strength and thus in their inherent toxicity (since toxicity is concentration-dependent). This fact, along with the fact that tank bottoms waters are normally diluted with other terminal waste streams, implies that comparison of the toxicity of various samples is best done on the common basis of wastewater strength. It should be noted that factors which affect tank bottoms water strength (dilution water from product shipment or from storm water bypassing floating roof seals) are not inherent to the product storage process.

- COD was chosen as the basis for normalization since the BOD test is more subject to variability unrelated to wastewater composition, and since the TOC test does not detect inorganic oxygen-demanding contaminants.
- 4000 mg/L COD was chosen as the normalization level based on previous testing (2) which showed this level to be typical in wastewaters from low-flow petroleum product terminals.

**Use of Biotreatment.** The reasons for subjecting all water samples to biotreatment before toxicity analysis or further treatment are as follows:

- Petroleum product terminal tank bottoms water generally has low flow, but quite high concentrations of organic contaminants expected to be toxic to aquatic life. Thus, it is assumed that any tank bottoms water which is discharged to the environment will receive biological treatment (or the equivalent) prior to discharge. There would be no point in testing the toxicity of untreated waters which would almost certainly fail the bioassay test.
- Biological treatment is the standard type of treatment utilized for almost all domestic, commercial, and industrial wastewaters bearing organic contaminants.

Variety of Water Sources. As shown on Table 1, tank bottoms water samples were obtained from nine member companies at terminals in various geographical locations, and from product tanks which contained a variety of products. These samples were assumed to cover the typical range of petroleum product terminal wastewater quality variability. Causes of such variability might include:

- Different companies may use different crudes and different refining processes to make the finished products.
- Different locations may be associated with different water qualities (for example, coastal terminals are more likely to receive products by ship, and thus more likely to have seawater contamination).
- Different petroleum products receive different refining processing (for example, gasolines require much different types of refining than diesel fuels).

As discussed in Section 4, not all collected samples were used throughout this study; samples were removed from consideration because of low COD concentration (samples 2, 10 and 13) and dilution by atmospheric condensate (sample 14).

ID	Product	Company	Region					
	Gasoline Tanks							
1	Gasoline Super Unleaded Reformulated (11% MTBE)	А	Gulf Coast					
3	Gasoline Regular Unleaded	В	Gulf Coast					
4	Gasoline Mid-grade Unleaded	С	Gulf Coast					
5	Gasoline Mid-grade Unleaded	С	Gulf Coast					
6	Gasoline Super Unleaded	D	Gulf Coast					
7	Gasoline Regular Unleaded	D	Gulf Coast					
9	Gasoline Regular Unleaded	F	East Coast					
12	Gasoline Regular Unleaded	G	East Coast					
15	Gasoline Super Unleaded	1	Midwest					
	Fuel Oil and Dies	el Tanks						
8	Fuel Oil #2	E	East Coast					
11	Diesel	G	East Coast					
Tank Bottoms Samples Not Used								
2	Gasoline Regular Unleaded	А	Gulf Coast					
10	Fuel Oil #2	F	East Coast					
13	Terminal Wastewater	Н	Gulf Coast					
14	Gasoline Super Unleaded with Vapor Recovery Water	н	Gulf Coast					

#### Table 1. Tank Bottoms Water Sources

#### TOXICITY IDENTIFICATION

The method used to identify the nature of the biologically treated effluent toxicity (for those bioeffluents which are toxic) is to analyze for known toxicants, and to apply various treatments and determine the degree of reduction of toxicity after the treatment. The treatments, although not commercial, were chosen to be at least potentially usable (effective, economical, and operable) for petroleum product terminals.

Toxicity was analyzed using 48-hour acute and 7-day chronic bioassays (survival endpoint) with a marine organism (*Mysidopsis bahia*). Acceptable levels of toxicity were considered to be, for acute testing, an LC50 value of 100 (survival of half the organisms in 100% effluent), and for chronic testing, an NOEC (no observable effect concentration) value of 100 (no observable effect on the organisms in 100% effluent).

#### DISCUSSION

The technique used in this study is a variation of the usual Toxicity Identification Evaluation (TIE) procedure, in which various laboratory techniques are used to treat water samples, and the toxicity determined before and after treatment. The same general approach was used in these studies, but the intent was not only to identify the nature of the toxicity, but also to find practical methods for removing it. Comparison of the methods is shown in Table 2. The basis for selecting the specific treatments is discussed below. Both acute and chronic bioassays were used since both are utilized in effluent discharge monitoring. Bioassays can use either freshwater or marine organisms, a choice usually based on the nature of the facility's receiving water for its effluent. For this study, there is no receiving water, and the choice was made to use marine organisms since the wastewaters were saline enough to affect freshwater organisms.

There are a number of endpoints for judging toxic effects, including survival, growth, and fecundity (number of offspring). In this study, only survival was used, since it is the most critical endpoint.

The bioassay levels of acceptable toxicity chosen for this study are quite stringent, being 48-hour survival of half the organisms in 100% effluent (acute), and no observed lethality in seven days of exposure of the organisms to 100% effluent (chronic). As noted above, petroleum product terminal tank bottoms water is unusually low-flow (total facility tank bottoms water flow of only 500 gallons/week is typical). As such, the treated wastewater could be combined with other facility wastewaters before discharge. In the receiving water mixing zone, the combined effluent would be further diluted and this would be reflected in the permitted bioassay for the facility. However, since this study was intended to be applicable to all petroleum product terminals, some of which discharge into low-flow receiving waters, 100% effluent was chosen as the acceptable toxicity.

Toxicant Standard TIE		This Study			
Ammonia	Adjust pH downward to convert ammonia to the less toxic ionized form	Analyze for ammonia. If excessive, remove ammonia by alkaline batch stripping			
Metals	Add EDTA to convert metals to less toxic chelated species	Analyze for metals. If excessive, remove metals by precipitation			
Toxic Organics	Remove organics with adsorbent C18 resin	Remove organics with activated carbon and/or UV-enhanced hydrogen peroxide			
Volatile Toxicants	Remove volatiles by batch air stripping	Remove volatiles by biodegradation and air stripping in aerated biotreatment			

Table 2.	Ap	proaches	to	Toxicity	Identification	and	Removal

#### **TOXICITY THRESHOLDS**

Since part of the study involved removing known toxicants down to non-toxic levels, it was necessary to determine what those levels are. Toxicity, of course, is not a fixed number, but varies by the species being used for the bioassays, and by the conditions of the tests. Since the overall objective was to achieve no detectable toxicity, the following table was developed from the technical literature to specify safe levels (i.e., the concentrations at which no adverse effects would be expected in 100% effluent in 7-day chronic bioassays on *Mysidopsis bahia*) for the various contaminants. Numerical water quality criteria as well as data from the respective criteria documents were used to determine acute toxicity thresholds for metals (8-11). The experience of the bioassay laboratory (12) as well as literature values (13) were used to develop the ammonia threshold for *Mysidopis bahia*.

 Table 3. Estimated Toxicity Thresholds for Ammonia and Metals

			Ali Vai	ues are pp					
Ammonia	Arsenic	Cadmium	Chromium	Copper	Mercury	Lead	Nickel	Zinc	
10,000	250	40	500	200	3	125	100	100	-

#### TREATMENT METHODS

The treatment methods chosen for the study were:

- Aerobic biological treatment by the sequencing batch reactor process.
- Ammonia removal by alkaline batch air stripping.
- Arsenic removal by ferric chloride precipitation.
- Copper and zinc removal by sulfide precipitation followed by ferrous sulfate treatment and aeration.
- Removal of residual organics by three techniques: powdered activated carbon, UV-light activated hydrogen peroxide oxidation, and a combination of the two.

#### DISCUSSION

Selection of Treatments. As noted in the Toxicity Identification discussion, the basis used for choosing toxicant-removal treatment methods in this study was that the method be at least potentially usable (effective, not excessively expensive, and operable by terminal personnel) in petroleum product terminals. That criterion was used in selecting among the options discussed below.

**Development of Treatments.** Aside from biological treatment, which was developed in previous studies (1, 2) for treatment of petroleum product terminal wastewaters, the other required treatments were either not commercial or not demonstrated for treating these types of wastewaters. Thus, in conjunction with (but not part of) this study, extensive method development work on removing ammonia, metals, and residual organics was done. Details on the final treatment methods chosen are given in Section 4.

Aerobic Biological Treatment. Aerobic biological treatment was chosen, as it is the standard type of biological treatment used for municipal and industrial wastewaters. Sequencing batch reactor treatment (a batch variation on the activated sludge process) was chosen because of its previously-demonstrated success in treating petroleum product terminal wastewaters (2) and because of its adaptability to relatively small laboratory treatment systems. Ammonia Removal. Ammonia was present in most of the biotreated tank bottoms waters at levels above the 10 ppm toxic threshold. There are a number of demonstrated methods for removing ammonia from wastewater, most of which were ruled out:

- Steam Stripping. Steam stripping is used in refineries for ammonia removal from sour water, but it is a very expensive process to build and operate, and requires steam, which is not available in most petroleum product terminals.
- Breakpoint Chlorination. Treatment with chlorine (or hypochlorite) is an established method for oxidizing residual levels of wastewater ammonia to nitrogen gas. However, the process uses large amounts of chlorine, and has the potential for converting residual organics into possibly more toxic chlorinated forms.
- Selective Ion Exchange. A natural mineral, clinoptilolite, has been used to selectively remove ammonia from wastewaters. In testing, excessively high dosages of clinoptilolite were found to be required to remove ammonia from tank bottoms water.
- Alkaline Air Stripping. At elevated pH, ammonia is converted to the nonionized volatile form, thus rendering it strippable at ambient temperatures. In testing, it was determined that batch stripping at pH 11 for 2-4 days was effective at removing ammonia from tank bottoms water to levels below the toxic threshold. In addition, batch stripping should also be practical for lowflow wastewater such as tank bottoms water.

Metals Removal. The only metals found in the tank bottoms water bioeffluents to be present at potentially toxic levels (see Table 2) were arsenic, copper, and zinc.

Arsenic Removal. Arsenic, a known petroleum industry contaminant from crude oils, is a difficult metal to remove because it is usually present as water-soluble anions (arsenite,  $AsO_2^{-}$ , and arsenate,  $AsO_4^{-3-}$ , ions). Arsenic was found in about half of the biotreated tank bottoms water effluents at levels above the 200 ppb toxic threshold.

- Ion exchange, a known technique for arsenic removal, was ruled out because effluent biological solids and oil would foul an ion exchange resin, and because competing anions present at high concentrations would make ion exchange inefficient.
- Adsorption onto activated alumina was found by testing to be effective, but was found to require excessive dosages of adsorbent, perhaps because of high levels of other anions.
- The method selected was batch coprecipitation with ferric chloride (to make an arsenated ferric hydroxide sludge), which was found by testing to be effective, and judged to be usable in petroleum product terminals.

**Copper and Zinc Removal.** Copper and zinc were found to be present at more than toxic levels (200 and 100 ppb, respectively) in many of the tank bottoms water bioeffluents. There are a variety of available methods for removing these toxic metals.

- Coprecipitation with ferric chloride and ferrous sulfate was tried, but was found to be inadequate for copper, and ineffective for zinc.
- Manganese dioxide adsorption, using both the reagent itself and material freshly precipitated from reduction of permanganate, was found in testing to provide inadequate removals of copper and zinc.
- Adsorption onto powdered activated carbon was found in testing to be effective at removing both metals, but at carbon dosages too high to be economical.
- The method chosen was a variation developed on the sulfide precipitation technique, in which sodium sulfide precipitates the very insoluble copper and zinc sulfides, ferrous sulfate is used to precipitate excess sulfide (itself a toxicant), and aeration is used to oxidize and precipitate excess ferrous ion (as ferric hydroxide). Although complex-sounding, the technique is both effective and simple, involving serial addition of two reagents to a mixed batch, followed by air sparging and settling, all in the same tank. Since many heavy metals have very insoluble sulfides, the method would also be expected to remove other metals if present at elevated levels.

**Removal of Residual Organics.** Residual organics are those organic materials which remain in bioeffluents. Although their chemical nature is complex and unknown, they are potential sources of effluent toxicity. Although commercial processes for this tertiary treatment exist, they are currently not much used because of their high cost and the ability of biological treatment to meet current discharge standards. Removal of residual organics is done by two general methods, adsorption and oxidation, both of which were subjected to method development by testing on the tank bottoms water bioeffluents. In the final treatments applied to the samples, both methods were used, singly and in tandem, since they potentially remove different organic species (those subject to adsorption and those subject to oxidation). As a rough rule, non-polar organics should be more adsorbable, while polar organics should be more oxidizable.

The degree of treatment by these tertiary treatment methods is dosage-dependent, i.e., more removal of organics can be done if the activated carbon dosage is increased, or if the dosage of hydrogen peroxide and/or UV light is increased. In order to provide a good basis for comparison, the approach taken in these studies was to apply the *same* dosages to all bioeffluent samples which were treated. Another approach would have been to increase the dosages for those samples which had higher levels of residual organics, but this was ruled out since it would have required predicting the performance of the tertiary treatment for each

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sample. As described below, it turned out that the dosages applied did achieve good removal of organics (as measured by TOC) for all the samples.

**Oxidation of Residual Organics.** Although there are number of oxidizing agents for organics in wastewater, this work was limited to use of hydrogen peroxide and ozone, both of which produce no byproduct sludge, and themselves decompose to harmless materials (water and oxygen).

- Catalyzed hydrogen peroxide was tested, but was found to give only limited removal of organics from these bioeffluents.
- Ozone was found to be somewhat more effective than hydrogen peroxide, but still only produced limited removal of organics from these bioeffluents.
- UV-light-enhanced oxidation with ozone was found to be effective at removing organics, but was not as cost-effective as with peroxide.
- UV-light-enhanced oxidation with hydrogen peroxide was found to be the optimum type of oxidative treatment with regard to cost-effectiveness.

Activated Carbon Adsorption of Residual Organics. Activated carbon can be used in two modes: granular carbon column treatment and powdered carbon mixed batch treatment. Although the former mode uses carbon more efficiently, it was decided to use powdered carbon in these studies since stirred batch carbon treatment gives more reproducible results (the effectiveness of column treatment varies with the amount of organics adsorbed on the carbon and with the shape of the breakthrough curve).

**Combined Treatment of Residual Organics**. In addition to the individual tertiary treatments with oxidation and with activated carbon, both treatments were also done in series, using half dosages of hydrogen peroxide, UV light, and powdered activated carbon.

#### **OVERALL TREATMENT SCHEME**

Figure 1 is a flow chart which shows the overall treatment scheme used for each tank bottoms water sample. As shown, the bioeffluent was analyzed for known toxicants (ammonia and metals). If excessive levels of ammonia or metals were present, then the bioeffluent was treated to remove them down to nontoxic levels. The ammonia- and metals-free sample was then tested for acute toxicity. If it passed the acute toxicity test (LC50 of 100%), it was tested for chronic toxicity. If it passed that test, no more was done to the sample. If it failed the chronic toxicity test, it was subjected to the three treatments for residual organics, and retested for chronic toxicity.

If the sample failed the acute toxicity test, it was subjected at that point to the three treatments for residual organics, and then retested for acute toxicity. If it passed that test, it was tested for chronic toxicity.

2-8

#### ANALYSIS OF RESIDUAL TOXICITY

Some samples, even after removal of known toxicants and after tertiary treatment removal of most of the residual organics, remained toxic. These were subjected to further examination for toxicity due to:

- Salinity ionic ratios. Marine animals are adapted to typical seawater ratios of common metal ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>) and anions (SO<sub>4</sub>=, Cl<sup>-</sup>), so the effect of these ratios on toxicity in the effluents was examined.
- Other known toxicants. The effluent concentrations of other known toxicants (B, Ba, Sb, Sn, V, Se, cyanides, surfactants, naphthenic acids, and C18 adsorbable material) were compared with expected toxic thresholds.

#### TOXICITY CORRELATIONS

The toxicities after treatment shown by the various tank bottoms water samples examined in this study were examined with regard to possible correlations with the following water properties:

- Tank product type
- Terminal location
- Bioeffluent BOD
- Bioeffluent COD
- Bioeffluent TOC
- Bioeffluent ammonia
- Final effluent ammonia
- Bioeffluent MBAS
- Bioeffluent CTAS
- Final effluent chromium
- Final effluent nickel
- Final effluent arsenic
- Final effluent copper
- Final effluent zinc
- Activated carbon effluent TOC
- UV/Peroxide effluent TOC
- Combined activated carbon UV/Peroxide effluent TOC





2-10

#### 3. FEED WATERS

Analysis of the feed waters prior to treatment can itself provide useful information, as described in this section.

Table 1 shows the sources of the feed waters used in the studies, and Tables 5 and 7 show the analyses of the waters. As can be seen, there was considerable variability in the quality of the waters. Factors which may affect the variation include the following:

**Organic constituents (COD, TOC, and BOD)** are water-soluble materials which are extracted from the petroleum products into the tank bottoms water. Since typically a large amount of product is associated with a small amount of water (i.e., most product tanks turn over large volumes of product for a given batch of tank bottoms water), the variation may represent the relative amounts of product and water which have been generated by a given tank at a given time. One of the factors which affects this is water input to the tank. Usually, tanks with fixed roofs produce much lower volumes of tank bottoms water than tanks with open floating roofs, in which some rainwater can run down the tank wall past the floating roof seals and enter the tank. Thus, tanks with fixed roofs (or with geodesic dome covers) tend to produce less, but more concentrated, tank bottoms water (6).

The ratios between the organics values are of interest, and are shown in Table 4. As can be seen, there is considerable variation between the TOC/COD and BOD/COD ratios in the samples. A

low TOC/COD ratio implies that the water contains high levels of inorganic oxygen demand (for example, from sulfur species). A low BOD/COD ratio implies (within the accuracy of the BOD test) that the organics in the sample are less biodegradable.

Ammonia in tank bottoms water is thought to come from refinery processing, in which naphtha streams (which are used to make gasoline and diesel) are typically separated from ammonialaden sour water. Various degrees of entrainment of this sour water in products delivered from the refineries could account for the variation in ammonia levels in the tank bottoms water.

It is worth noting that almost all of the samples contained ammonia at levels well above the 10 mg/L (Table 3) toxic limit.

# Table 4. Tank BottomsWaters Organic Ratios

ID	TOC/COD	BOD/COD
_1	0.13	0.11
3	0.26	0.24
4	0.20	0.15
5	0.29	0.36
6	0.22	0.10
7	0.19	0.09
9	0.34	0.41
12	0.27	0.29
15	0.22	0.12
8	0.15	0.20
11	0.26	0.11
2	0.21	. <u> </u>
10	0.27	
13	0.20	
14	0.11	
Avg.	0.22	0.23

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# Table 5 As-Received Tank Bottoms Waters Conventional Contaminants

	All values are mg/L								
ID	Product		COD	тос	Ammonia	BOD			
1	Gasoline Super Unlea Reformulated (11% M	aded ITBE)	42,850	5,595	16	4,510			
3	Gasoline Regular Unl	eaded	17,525	4,605	940	4,203			
4	Gasoline Mid-grade U	Inleaded	23,000	4,598	160	3,377			
5	Gasoline Mid-grade U	Inleaded	16,900	4,948	2,800	6,006			
6	Gasoline Super Unlea	aded	47,000	10,200	900	4,814			
7	Gasoline Regular Uni	eaded	22,825	4,251	560	1,961			
9	Gasoline Regular Unle	eaded	8,075	2,741	4,300	3,323			
12	Gasoline Regular Unl	13,825	3,723	2,600	3,951				
15	Gasoline Super Unlea	Ided	58,000	12,760	2,570	7,177			
		27,778	5,936	1,650	4,369				
	Gasoline	Maximum	58,000	12,760	4,300	7,177			
		Minimum	8,075	2,741	16	1,961			
8	Fuel Oil #2		8,200	1,191	2,500	1,617			
11	Diesel		9,175	2,381	770	992			
	<b>.</b>	Average	8,688	1,786	1,635	1,305			
	Diesel	Maximum	9,175	2,381	2,500	1,617			
		Minimum	8,200	1,191	770	992			
2	2 Gasoline Regular Unleaded			1,030	34				
10	Fuel Oil #2		3,268	875	280				
13	Terminal Wastewater	2,704	534	11					
14	Gasoline Super Unlea Vapor Recovery Wate	ded with r	12,850	1,350	130				

Conventional metals (sodium, calcium, magnesium, and potassium) are those metals commonly found at reasonably high concentration in natural waters. The most likely sources of these metals are residual salts from refinery processing (many transportation fuels are subjected to sodium hydroxide washing as part of the processing) and contamination with transport water, such as residual seawater ballast water in barge or tanker transport. One way to examine the likelihood of seawater contamination is to assume that all the magnesium comes from seawater, whose ionic composition, in mg/L, is Na=10,500, Mg=1,350, Ca=400, and K=380. Using this assumption, the excess ion percentages in Table 6 were calculated, the "excess percentage" being the percent of the sample metal which is not from seawater; if all the sample ions were derived from seawater, all the values on Table 6 would be zero.

#### Table 6 Cation Balance With Respect to Seawater Magnesium

Percent Excess Ion*								
_ םו	Na	Ca	Mg	К				
1	96	93	0	72				
3	82	74	0	62				
4	82	79	0	65				
5	88	65	0	34				
6	86	65	0	93				
7	80	60	0	95				
9	34	-57	0	18				
12	22	-38	0	-10				
15	77	56	0	37				
8	90	82	0	49				
11	95	53	0	72				
2	89	91	0	58				
10	54	-127	0	23				
14	75	85	0	79				

\*Calculated as

100\*[M-(sample M\*sample Mg/seawater Mg)]/M Where M is sample metal conc.

As can be seen, most of the samples contain ions in

excess of those expected from seawater. This may imply that the ions actually arise from freshwater (which has relatively less magnesium) and from refinery processing (to account for sodium enrichment). Negative values in Table 6 imply that the water contains magnesium from sources other than seawater; the nature of these sources is not known.

**Trace toxic metals** (Cd, Cr, Ni, Pb, Hg, As, Cu, Zn), as shown on Table 7, are mostly present at the sub-mg/L level.

Arsenic is a constituent of crude oil, and is probably derived from that source. The source, speciation, and fate of petroleum product arsenic have been investigated in a recent API report (3).

Cadmium, chromium, nickel, copper, and zinc may be derived from corrosion of various alloys since they are not (except for nickel) significant crude oil components or extensively used in refinery processing (nickel, copper, and chromium are used in small amounts in hydrotreating catalysts).

Lead was once very common in tank bottoms waters as a result of using tetra-ethyl lead as an octane enhancer. Since this practice has been discontinued in the US, tank bottoms water lead levels have fallen significantly, as shown by the mostly low levels in Table 7. The fact that some of the samples contained high lead (even though the products in the tanks were unleaded) may indicate that residual lead salts from previous handling of leaded products were present in the tank.

Table 7 shows the Table 3 toxic limits for the trace metals. As shown, the fractions of the samples which exceeded the limits prior to treatment were 1/11 for cadmium, 0/14 for chromium, 7/11 for nickel, 2/11 for lead, 1/11 for mercury, 12/15 for arsenic, 9/11 for copper, and 10/11 for zinc.

				mg	<u>/L</u>			μ <b>g/L</b>					μ <b>mho/cm</b>		
			٦	Γοχί	c Lin	nit:	40	500 100 125 3 250 200 100							
ID	Produc	t	Na	Ca	Mg	Κ	Cd	Cr	Ni	Pb	Hg	As	Cu	Zn	Conductivity
1	Gasoline Super Ur Reformulated (11%	nleaded % MTBE)	354	8	2	2	32	53	7 <del>9</del> 9	11	2.1	1978	179	1892	1050
3	Gasoline Regular	Unleaded	347	9	8	6	13	22	66	4	4.4	125	3477	497	1950
4	Gasoline Mid-grad Unleaded	le	215	7	5	4	17	138	287	1669	1.1	154	8028	3888	1400
5	Gasoline Mid-grad Unleaded	e	473	6	7	3	13	38	673	147	0.8	258	5258	601	473
6	Gasoline Super Ur	nleaded	386	6	7	28	35	59	177	12	2.4	441	3430	1289	386
7	Gasoline Regular	Unleaded	318	6	8	49	17	29	298	6	1.1	1037	2466	126	318
9	Gasoline Regular	Unleaded	1737	28	148	51	6	10	30	32	0.4	20794	4229	147	11,400
12	Gasoline Regular	Unleaded	1 <b>208</b>	26	121	31	10	17	338	108	0.7	550	2062	1237	7050
15	Gasoline Super Ur	nleaded	307	6	9	4	44	73	437	15	2.9	883	3057	9696	1920
		Average	594	11	35	20	23	94	321	213	2	2647	3238	1947	2883
	Gasoline	Maximum	1737	28	148	51	44	138	799	1669	4	20794	8028	9696	11,400
		Minimum	215	6	2	2	6	10	30	4	0	125	179	126	318
8	Fuel Oil #2		693	15	9	5	6	10	31	2	0.4	381	720	47	3620
11	Diesel		1331	5	8	8	7	11	100	2	0.5	3820	2235	445	6900
		Average	1012	10	9	7	7	11	66	2	0.4	2100	1478	246	5260
	Diesel	Maximum	1331	15	9	8	7	11	100	2	0.5	3820	2235	445	6900
		Minimum	693	5	8	5	6	10	31	2	0.4	381	720	47	3620
2	Gasoline Regular I	Unleaded	205	10	3	2						381		-	830
10	Fuel Oil #2		1958	15	115	42		5				12			11,250
13	13 Terminal Wastewater							16				445			700
14	14 Gasoline Super Unleaded with Vapor Recovery Water		92	6	3	4		5				229			420

#### Table 7. As-Received Tank Bottoms Waters Metals and Conductivity

#### 4. EXPERIMENTAL EQUIPMENT AND PROCEDURES

#### FEED PREPARATION AND SELECTION

As described above, preliminary analyses of the feeds indicated considerable variability in the strength of the tank bottom wastewaters provided by the member companies. COD levels ranged from less than 3000 mg/L to greater than 55,000 mg/L, TOC ranged from 500 mg/L to greater than 12,000 mg/L, and BOD ranged from 180 mg/L to 5000 mg/L.

All feeds were diluted to a nominal COD level of 4,000 mg/L in order to normalize for treatment and toxicity comparisons. This COD concentration was selected based on data reported as typical for wastewater from terminals with good stormwater segregation (2). Wastewaters with COD concentrations near or less than 4000 mg/L (IDs 2, 10 and 13) were excluded from further treatment and/or analyses. In addition, wastewater ID 14 was excluded because of being mixed with vapor recovery water (atmospheric moisture condensed in a cryogenic vapor recovery unit). From this point on, all treatments and analyses were limited to the eleven remaining wastewaters (IDs 1,3,4,5,6,7,9,11, 12,15).

#### **BIOLOGICAL TREATMENT**

As described above, biological treatment was done by the sequencing batch reactor process. Eleven 10-gallon sequencing batch reactors (SBRs) were used to biologically treat the terminal tank bottoms wastewaters.

Each SBR was constructed of high density polyethylene. Each was equipped with a stainless steel sparger for aeration purposes and a sidemounted spigot to allow for operation in a "fill and draw" mode as shown in Figure 2. The SBRs were operated on a fifty percent draw, 3-



REPEAT

SLUDGE

TREATED

WATER

Figure 2. Sequencing Batch Reactor Time Sequence

day/4-day cycle. Non-toxic (i.e., non-ammonia containing) nutrients were added as necessary. Mixed liquor suspended solids (MLSS) were allowed to accumulate and sludge was wasted only when it reached the fifty percent volume level. The SBRs were acclimated for four weeks until sample collection for testing was begun. A 4-week acclimation period was determined to be sufficient for adaptation of the microbial populations based on data generated previously for API (1). Biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and ammonia (NH<sub>3</sub>) were monitored during the acclimation period to confirm the acclimation. Biological treatment was continued for each wastewater until depletion of the feeds in order to ensure sufficient effluent volume for completion of the study.

FEED

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4-1

#### AMMONIA REMOVAL

Ten biologically treated final effluents contained ammonia in concentrations above their toxicity threshold. Alkaline air stripping was the treatment technique applied to all ten bioeffluents for ammonia removal. The equipment setup for the treatment, shown in Figure 3, consisted of a 55 gallon polyethylene drum equipped with four fritted glass fine bubble diffusers connected to the lab compressed air supply through a flowmeter and a pressure regulator. The treatment procedure consisted of filling the 55 gallon drum with about 15 gallons of wastewater, adding sodium hydroxide (NaOH) to increase the wastewater pH to above 11, and supplying the air at a rate of about 1 ft<sup>3</sup>/min. Thus every minute of aeration corresponded to a volumetric air:water ratio of 0.5, i.e., 3 hours of stripping would correspond to a volumetric air:water ratio of 90. All of the wastewaters had a very high foaming tendency, and to avoid wastewater loss due to foam overflowing, a slower air stripping rate was chosen. The wastewater pH was monitored from time to time and adjusted to above 11 when necessary. The wastewater was analyzed for ammonia periodically, and the stripping was stopped when the concentration fell below the target



value of 10 mg/L. The stripping time depended on the initial concentrations for the bioeffluents, and ranged from about 2 to 4 days, providing a volumetric air:water ratio range of 1380-3045. Following stripping, sulfuric acid was added to restore the pH to its original value.

#### **ARSENIC REMOVAL**

Five final effluents contained arsenic in concentrations above their toxicity threshold. The arsenic removal treatment was applied to the bioeffluents after the treatment for ammonia removal. The equipment setup for the treatment, shown in Figure 4, consisted of a 10 gallon polyethylene drum equipped with a mixer, a 1 L/min pump for filtration, and a 0.5  $\mu$ m cartridge filter. The treatment procedure consisted of filling the 10 gallon drum with about 10 gallons of the final effluent, adding about 76 g of FeCl<sub>3</sub>.6H<sub>2</sub>O (2 g/L dosage), turning on the mixer, adding concentrated hydrochloric acid (HCl) to adjust the pH to 5.5-6.0, rapidly mixing for 15 minutes to form ferric hydroxide, and then slowly mixing for 15 minutes to flocculate the precipitates. The pump was then turned on, and the water was recirculated through the filter for 30 minutes to form a ferric hydroxide coating on the filter surface. This was done to precoat the filter with the

precipitates to achieve complete removal of ferric hydroxide precipitates since the filter was only 80% efficient in removing particles of 0.5  $\mu$ m in size. After 30 minutes, the recirculation was discontinued, and the filtrate was collected by once-through filtration. This filtration technique is similar to the precoat filtration technique, with the only difference being that no filter aid was utilized for precoating the filter surface. Following filtration, the pH was restored to its original value with NaOH. Arsenic removal of greater than 90% was achieved on all the final effluents and was successful in removing arsenic to levels below its target value of 200  $\mu$ g/l.





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#### **COPPER AND ZINC REMOVAL**

All ten of the final effluents treated for ammonia also contained copper and zinc in concentrations above their toxicity threshold. The modified sulfide treatment was the treatment technique applied to the final effluents after ammonia and arsenic treatment. The equipment setup for the treatment, shown in Figure 5, consisted of a 10 gallon polyethylene drum equipped with a mixer, an air diffuser, a 1 L/min pump for filtration, and a 0.5  $\mu$ m cartridge filter. The treatment procedure consisted of filling the 10 gallon drum with about 10 gallons of final effluent, adding about 57 gm of Na<sub>2</sub>S.9H<sub>2</sub>O (1.5 g/L dosage), turning on the mixer, and slowly mixing for 15 minutes. After 15 minutes, about 98 gm of FeSO<sub>4</sub>.7H<sub>2</sub>O (2.6 g/L dosage) were added to precipitate the excess sulfide as ferrous sulfide, and the solution was mixed for 15 more minutes. Then, the wastewater was aerated for 30 minutes to oxidize ferrous iron to ferric iron. The pump was

t, 1. Mix, Na<sub>2</sub>S 1. Mix, Na<sub>2</sub>S 2. Mix, 4. Pump 8. Filter 8. Filter 1. Mix, Na<sub>2</sub>S 4. Pump 8. Filter

Figure 5. Batch

Copper & Zinc Precipitation with

S=, Fe++, Air

then turned on, and the water was recirculated through the filter for 30 minutes to form a coating of the precipitates on the filter surface. After 30 minutes, the recirculation was discontinued and the filtrate was collected by once-through filtration. The treatment was successful in removing copper and zinc to levels below their target values of 200 and 100  $\mu$ g/L, respectively.

#### UV-PEROXIDE OXIDATIVE REMOVAL OF RESIDUAL ORGANICS

As described above, UV-enhanced oxidation with hydrogen peroxide was used as one technique for removing toxic levels of residual organics. The system, shown in Figure 6, employed 14-watt germicidal 254 nm wavelength ultraviolet lamps in quartz sleeves immersed in Pyrex glass reactors surrounded by a reflective shield. These reactor systems were used in series, with two reactors used for the treatments preceding acute toxicity analysis, and with eight reactors in series for treatments preceding chronic toxicity analysis. As shown, water being treated was kept in a reservoir, from which it was circulated through the UV reactors.

For the acute testing treatment, the water liquid volume was 1.5 L, with each reactor holding 220 mL, and the remainder being in the reservoir. 30 mL of hydrogen peroxide were added to the system. For the chronic testing treatment, the water liquid volume was 6.4 L, and 128 mL of hydrogen peroxide were added; thus, in both cases,  $H_2O_2$  dosage was 20 mL/L. In both cases, the total run time was 20 hours at a UV "dosage" of about 18 watts/L, for a total UV "dosage" of about 360 watt-hours/L.

#### Figure 6. Recirculating Batch UV-Hydrogen Peroxide Oxidation Reactor System for Removing Residual Organics



4-3

As shown in the results section, the oxidative treatment was successful at removing organics (as shown by TOC analyses), but did not always remove toxicity.

#### POWDERED ACTIVATED CARBON REMOVAL OF RESIDUAL ORGANICS

As is inherent in the process, batch removal of residual organics with powdered activated carbon was very simple. Each sample was mixed with powdered carbon at a dosage of 49.5 g carbon per liter of water for 24 hours, and then filtered. As with oxidation, the carbon was effective at removing TOC, but did not consistently remove toxicity.

#### **COMBINED UV/PEROXIDE - POWDERED ACTIVATED CARBON TREATMENT**

The combined oxidative - carbon adsorption treatment for the wastewaters was simply both treatments as described above applied in series, with UV/peroxide treatment being done first. Dosages were reduced to half, with 10 mL  $H_2O_2/L$  of water and 5 hours of UV light at 37 watt/L of water, and with 25 g of carbon used per liter of water.

#### SAMPLING AND ANALYSIS

During the biotreatment acclimation period, samples were collected from each SBR at the end of every 3-day or 4-day cycle and analyzed for COD, TOC, and  $NH_3$  for a period of 4 weeks. During the biotreatment period, a similar sampling and analysis schedule was maintained for COD, TOC, and  $NH_3$  while collection and analysis of samples for metals (Cd, Cr, Cu, Ni, Pb, Zn, As, and Hg) were performed on a weekly basis. Sample collection and analysis were conducted by Texaco R&D personnel during the acclimation and biotreatment periods.

Sample analyses were conducted by Texaco R&D personnel and an independent contract laboratory during the ammonia and metals removal phase and during the acute toxicity testing phase of the investigation. Prior to acute toxicity testing, split samples were generated so that a paired data set containing both biological and chemical data was available for each effluent. Chemical parameters included in this paired data set were priority pollutant metals (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn), TOC, BOD, COD, NH<sub>3</sub>, surfactants (MBAS and CTAS), pH, dissolved oxygen, alkalinity, hardness, salinity, conductivity, and residual chlorine.

Following tertiary treatment, the samples were collected and analyzed for TOC by Texaco R&D personnel. Other analyses performed on effluents during the course of this investigation include cyanide, methyl tert-butyl ether (MTBE), naphthenic acids, and various metals (V, Sn, B, Ba, Sr).

All analyses except the special MTBE and naphthenic acids tests were done by standard methods.

#### **TOXICITY TESTING**

Initially all biologically treated samples were screened for acute toxicity using both *Daphnia pulex* (freshwater) and *Mysidopsis bahia* (marine) for 24-hour exposures. *Daphnia* was the organism of preference, but due to high conductivity and TDS in most samples, *Mysidopsis* was considered as an alternative. The results of the 24-hour screening toxicity tests indicated *Mysidopsis* was the more appropriate test organism for all the treated wastewater samples.

Definitive acute toxicity tests were conducted using effluent concentrations determined by 24-hour rangefinder tests. This allowed for a more accurate measurement of acute toxicity through estimation of LC50 concentrations. The definitive acute toxicity tests consisted of four replicates containing five mysids each, using five effluent concentrations and a reference control consisting of laboratory-prepared artificial seawater (Hawaiian Marine Mix) and five effluent concentrations determined by the results of the 24-hour screening tests. These testing procedures are consistent with USEPA methodology (4) for conducting acute toxicity tests with marine organisms.

The standard USEPA methodology (5) for estimating chronic toxicity of effluents to the mysid shrimp during a 7-day static-renewal exposure requires a sample volume of approximately 14 L. This provides sufficient sample volume for measurement of water quality parameters and daily renewals of test solutions. Chronic toxicity tests were conducted using mysid control water (laboratory-prepared artificial seawater) to determine the minimum sample volume per test vessel required to meet USEPA criteria for acceptability of test results. The minimum requirements for an acceptable test are eighty percent survival and an average weight of at least 0.20 mg/mysid in control water. Recommended test solution volume per test vessel is 150 mL. It was determined that sample volume could be reduced by fifty percent and still meet USEPA acceptance criteria. Adequate sample volume for chronic testing with mysids was reduced to 7 L (75 mL per test vessel) rather than 14 L. This test protocol modification decreased the probability that sample volume would become a limiting factor prior to completion of the study.

#### 5. RESULTS - INDIVIDUAL WASTEWATERS

The following eleven figures (Figures 7-17) show the step-by-step results of the treatment and testing for each individual wastewater, arranged in the schematic shown in Figure 1. The results are briefly discussed below, but most of the discussion on the results is given in the following section, in which each step of treatment and testing is examined for the group of wastewaters.

#### Wastewater 1

Wastewater 1, a tank bottoms water from super unleaded reformulated gasoline containing 11% MTBE, produced the best effluent of all the wastewater samples. As shown in Figure 7 and Table 8, biotreatment achieved very good removal of COD, and reduced an already low ammonia level to less than detectable. The only treatment required after biotreatment was arsenic removal, which was successful. At this point, the effluent passed both the acute and chronic toxicity tests without any need for further removal of residual organics.

Organics										
Percent Removal										
Eff #	BOD	COD	TOC							
1	86	90	89							
3	75	66	69							
4	49	50	43							
5	76	50	67							
6	95	50	-24							
7	89	70	11							
8	92	86	78							
9	79	40	57							
11	94	53	34							
12	97	80	77							
15	94	85	75							

Table 8. Percent Removal of

#### Wastewater 3

Wastewater 3, a tank bottoms water from regular unleaded gasoline, was moderately well treated biologically as shown

in Figure 8 and Table 8, and required removal of ammonia, copper, and zinc. The resulting effluent was acutely toxic (LC50 of 69%), and remained acutely toxic even after all three types of tertiary treatment for residual organics (adsorption, oxidation, and the combination of the two), and removal of almost all of the TOC.

#### Wastewater 4

Wastewater 4, a tank bottoms water from mid-grade unleaded gasoline, was not well treated biologically (only 50 percent COD removal) as shown on Figure 9 and Table 8. After removal of ammonia, copper, and zinc, the effluent was acutely toxic, and remained so after all three tertiary treatments. It is of interest that of the three treatments, UV/peroxide treatment removed the least amount of TOC and the most toxicity, perhaps implying that the toxicant is more oxidizable than adsorbable.

#### Wastewater 5

Wastewater 5, a tank bottoms water from mid-grade unleaded gasoline, had similar biotreatability and required removals similar to Wastewater 4, as shown in Figure 10 and Table 8. However, when the acutely toxic effluent was subjected to tertiary removal of residual organics, UV/peroxide treatment was able to remove all the acute toxicity. That treated sample, however, was chronically toxic, with an NOEC of 25%.

#### Wastewater 6

Wastewater 6, a tank bottoms water from super unleaded gasoline, was not well treated biologically as shown on Figure 11 and Table 8, and required removal of ammonia, arsenic, zinc,

and copper, as shown on Figure 11. The acutely toxic effluent from those treatments was quite amenable to tertiary treatment, with all acute toxicity removed by all three treatments. Those effluents, however, were chronically toxic, with NOECs of 50% for all.

#### Wastewater 7

Wastewater 7, a tank bottoms water from regular unleaded gasoline, was fairly well treated biologically as shown on Figure 12 and Table 8, with 70 percent COD removal and 89 percent BOD removal. In light of that, it is somewhat unusual that TOC removal was only 11 percent. Following removal of ammonia, arsenic, copper, and zinc, the effluent was still acutely toxic (LC<sub>50</sub> of 75%), but tertiary treatment by activated carbon or activated carbon with UV/peroxide removed the acute toxicity. The tertiary effluent, however, was chronically toxic.

#### Wastewater 8

Wastewater 8, a tank bottoms water from No. 2 fuel oil, was treated very well biologically as shown on Figure 13 and Table 8. After removal of ammonia, copper, and zinc, the effluent was not acutely toxic, but was chronically toxic, with an NOEC of 10%. Tertiary treatment by activated carbon or UV/peroxide removed some, but not all, of the chronic toxicity (final NOECs of 50%).

#### Wastewater 9

Wastewater 9, a tank bottoms water from regular unleaded gasoline, was only moderately well treated biologically as shown on Figure 14 and Table 8. After removal of ammonia, copper, and zinc, the effluent was acutely toxic, and remained so after application of all three tertiary treatments.

#### Wastewater 11

Wastewater 11, a tank bottoms water from diesel, was moderately well treated biologically, with poor TOC removal as shown on Figure 15 and Table 8. After removal of ammonia, copper, and zinc, the effluent was acutely toxic, and remained so after application of all three tertiary treatments.

#### Wastewater 12

Wastewater 12, a tank bottoms water from regular unleaded gasoline, was well treated biologically, as shown on Figure 16 and Table 8. However, after removal of ammonia, arsenic, copper, and zinc, the effluent was acutely toxic, and remained so after removal of residual organics with all three tertiary treatments.

#### Wastewater 15

Wastewater 15, a tank bottoms water from super unleaded gasoline, was well treated biologically, as shown on Figure 17 and Table 8. However, after removal of ammonia, arsenic, copper, and zinc, the effluent was acutely toxic, and remained so after removal of residual organics with all three tertiary treatments.






Figure 8. Wastewater #3 Toxicity Reduction Testing Results



Figure 9. Wastewater #4 Toxicity Reduction Testing Results



Figure 10. Wastewater #5 Toxicity Reduction Testing Results







Figure 12. Wastewater #7 Toxicity Reduction Testing Results

Not for Resale



Figure 13. Wastewater #8 Toxicity Reduction Testing Results

5-9













Not for Resale





#### 6. RESULTS - OVERALL

In this section, the overall results for all samples are discussed for each stage of treatment.

#### **BIOLOGICAL REMOVAL OF CONVENTIONAL CONTAMINANTS**

This section describes the removal of conventional contaminants encountered in biological treatment: BOD, COD, TOC, and ammonia. The overall results are tabulated in Table 9 and Figure 18, below.

[	В	OD, n	ng/L	С	OD, r	ng/L	Т	OC, r	ng/L	Am	monia	a, mg/L
1	Initial	Final	%									
ID	mg/L	mg/L	Removal									
1	429	60	86.0	4076	420	89.7	532	58	89.1	2	0.1	93.9
3	955	242	74.7	3982	1360	65.8	1046	328	68.6	214	42	80.4
4	589	303	48.6	4011	2000	50.1	802	456	43.1	28	27	3.6
5	1428	345	75.8	4018	2000	50.2	1177	388	67.0	666	70	89.5
6	407	20	95.1	3974	2000	49.7	862	1065	-23.5	76	21	72.4
7	342	36	89.5	3980	1200	69.8	741	660	10.9	98	37	62.2
8	786	61	92.2	3986	560	86.0	579	130	77.5	1215	351	71.1
9	1650	348	78.9	4010	2400	40.1	1361	582	57.2	2135	118	94.5
11	435	27	93.8	4023	1900	52.8	1044	694	33.5	337	44	86.9
12	1169	37	96.8	4090	800	80.4	1102	252	77.1	769	51	93.4
15	493	32	93.5	3984	600	84.9	877	222	74.7	176	33	81.3
Avg.	789	137	84.1	4012	1385	65.4	920	440	52.3	520	72.2	75.4

Table 9. Biological Removal of Conventional Contaminants

#### **Biochemical Oxygen Demand (BOD)**

BOD is, by definition, the biodegradable portion of oxygen demand in a wastewater. As a result, good removal of BOD in biological treatment is to be expected. As shown in Table 9 and Figure 18, although many tank bottoms waters had more than 85 percent BOD removal, there were several which were worse than that, and one (ID 4) which was much worse. Overall, these results showed much poorer BOD removal than the previous study (2), in which SBR treatment of four petroleum product terminal wastewaters was able to achieve an average BOD removal of 98 percent. The conclusion would be that not all such wastewaters can be thoroughly biotreated.

#### Chemical Oxygen Demand (COD)

COD was the parameter used to normalize the tank bottoms water samples — as shown on Table 9, all of the feed waters had essentially 4000 mg/L COD. COD removal percentage is usually less than BOD removal, since not all COD is biodegradable. This was borne out in this study, in which the average COD removal was 65 percent, while BOD removal was 84 percent. Previous SBR testing on four petroleum product terminal wastewaters (1) had average COD removals of 84 percent, considerably better than in this study.

Examining Table 11 shows that the average absolute removal of BOD was 652 mg/L, and for COD was 2627 mg/L. This is in accord with previous findings (2, 6), which showed that "biodegradable COD" considerably exceeds BOD removal, even though both have the same

units (mg/L of oxygen demand). The implication is that the BOD test is not very accurate at predicting overall oxygen demand for a wastewater, and that biotreatment COD removal is a better indicator of this.



#### Figure 18. Biological Removal of Contaminants All values are ma/L: White = Feed. Black = Effluent

#### **Total Organic Carbon (TOC)**

Total organic carbon is a direct indicator of organics in a wastewater. As shown in Table 9 and Figure 18, TOC removal for these wastewaters was extremely erratic, ranging from -23 to 89 percent removal. As with BOD and COD removal, previous SBR testing on four petroleum product terminal wastewaters (2) showed better TOC removal (83 percent) than the average removal found in this study (52 percent).

#### Ammonia

Ammonia is a toxic material which can be removed biologically by a process known as nitrification, in which the ammonia is converted to nitrate. Nitrifying bacteria are slow growing and susceptible to inhibition, so the process does not occur in all biotreatment systems. Since ammonia is toxic (threshold value of 10 mg/L) and present at high levels in these wastewaters (average value of 590 mg/L), it is important that it be removed. As shown on Table 9 and Figure 18, extensive nitrification did occur, with average biotreatment ammonia removals of 75 percent. However, almost all of the bioeffluents still contained ammonia at toxic levels, which meant that further ammonia removal was necessary, as described below.

#### **BIOLOGICAL REMOVAL OF TOXICANTS**

Specific toxicants (metals and surfactants) were known to be present in the tank bottoms waters, so their removal by biotreatment was of interest in this study.

#### Low Level Metals (Cd, Cr, Ni, Pb, Hg)

As shown in Table 10, below, these metals were removed by biotreatment to levels well below their toxic thresholds. The usual mechanism for removal is entrapment of the metals in the biological sludge.

	All values are µg/L													
	C	d	С	r	N	i	P	b	H	g				
ID	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final				
1	3	3	5	5	76	79	1	1.0	0.2	0.2				
3	3	3	5	5	15	15	1	1	0.2	0.2				
4	3	3	24	28	50	31	291	100	9	1				
5	3	3	62	33	160	23	35	1	0.2	0.2				
6	3	3	5	11	15	19	1	1	623	0.2				
7	3	3	5	5	52	15	1	1	0.2	0.2				
8	3	3	5	16	15	14	1	11	0.2	0.2				
9	3	3	5	13	15	18	16	1	64	0.2				
11	3	3	5	5	44	15	1	1	1417	0.2				
12	3	3	5	5	200	94	32	1	1083	0.2				
15	3	3	5	5	30	15	1	1	124	0.2				
Avg.	3.0	3.0	11.9	11.9	61.1	30.7	34.6	10.9	301.9	0.3				
Toxi	c Limit	40	Toxic Limit         40         500         100         125											

#### Table 10. Biological Removal of Metals

#### **Bioeffluent Levels of Other Toxicants**

Although feed values were not measured (and thus removals cannot be calculated), bioeffluent values of certain known toxicants were determined as shown in Table 11.

**Metals.** As can be seen, in most cases the metals shown (arsenic, copper, and zinc) exceeded their toxic thresholds, and thus required further removal, as discussed below.

Surfactants (MBAS & CTAS). Considerable foaming was observed in several of the SBRs during biotreatment of the tank bottom wastewaters (IDs 5, 6, 7, 9, 12, and 15) and during alkaline stripping for removal of ammonia

#### Table 11. Bioeffluent Contaminants

All values are  $\mu g/L$ 

ID	As	Cu	Zn	MBAS	CTAS
1	1978	17	180	193	1690
3	125	790	113	40	1690
4	154	1400	678	764	1690
5	258	1250	143	1560	1690
6	441	290	109	404	877
7	1037	430	22	404	1560
8	6	350	23	199	1690
9	189	2100	73	45	1690
11	195	980	195	3680	400
12	1130	610	366	1600	400
15	1098	210	666	3700	13600
Average	601	766	233	1144	2452
Tox Limit	250	200	100		

from the bioeffluents. Anti-foam agent was used to inhibit foaming and decrease loss of biosolids due to overflow from the SBRs during biotreatment. Table 11 shows surfactant levels in the

biotreated effluents measured as methylene blue-active substances (MBAS) and cobalt thiocyanateactive substances (CTAS). The MBAS technique measures anionic surfactants while the CTAS technique measures nonionic surfactants. MBAS levels ranged from 3.70 mg/L to 0.04 mg/L. CTAS levels ranged from 1.69 mg/L to 0.40 mg/L. Estimation of toxicity thresholds for surfactants was not attempted due to the wide range of toxicity values associated with nonionic and cationic surfactants in the open literature. In addition, the lack of specificity of the analytical techniques used to measure surfactants increases the probability that non-surfactant substances could be detected as methylene blue and/or cobalt thiocyanate-active detergents.

#### PHYSICAL/CHEMICAL REMOVAL OF CONTAMINANTS

Known toxicants (ammonia and certain metals) in bioeffluents at levels known to be toxic were subjected to further removal by physical/chemical treatment.

#### Ammonia Removal by Alkaline Air Stripping

As described above, alkaline air stripping was determined to be the optimum ammonia removal technique, and was applied to the ten bioeffluents with excessive ammonia levels. As shown in Table 12 and Figure 19, ammonia was successfully removed from all the bioeffluents to which this technology was applied.



# Table 12 Ammonia Removal All values are mg/L

ID	Feed	Effluent*
1	0.1	-
3	42	9
4	27	6
5	70	4
6	21	9/4
7	37	1/6
8	351	3
9	118	4
11	44	4
12	51	1/5
15	33	4
	<b>Toxic Limit</b>	10

\*Dual values indicates two treatment batches

#### Acute Toxicity and Metals Removal by Precipitation

Toxicity expressions involve an inverse relationship (i.e., the greater the toxicity, the lower the LC<sub>50</sub>). Therefore, it is sometimes more appropriate to translate concentration-based toxicity measurements into toxic units for comparison purposes. An acute toxic unit (atu, sometimes symbolized as  $tu_a$ ) is the reciprocal of the LC<sub>50</sub>, expressed as the percent effluent dilution which is lethal to fifty percent of the test organisms during the acute exposure period (atu = 100/LC<sub>50</sub>). The greater the toxicity, the higher the number of toxic units. For example, in the data presented here, an acceptable level of acute toxicity would have an atu  $\leq 1.0$  (LC<sub>50</sub>  $\geq 100\%$ ). A highly toxic effluent would have an atu > 3.0 (LC<sub>50</sub> < 33.33%).

Definitive acute toxicity tests were conducted on six bioeffluents. Five of the six bioeffluents were acutely toxic with atu ranging from 7.14 to 1.33. Corresponding analytical data for these effluents indicated toxic levels of Cu and Zn may have contributed to the observed toxicity.

These toxic levels of Cu and Zn were confirmed in the five effluents (IDs 3, 4, 5, 8, and 9). The presence of toxicity due to cationic metals can be tested through additions of ethylenediaminetetraacetic acid (EDTA), a strong chelating agent that produces non-toxic complexes with many metals. Because EDTA non-specifically binds mono-, di-, and trivalent metals, the appropriate EDTA concentration is highly dependent on calcium and magnesium concentration (i.e., hardness) and salinity. The toxicity of cationic metals (excluding mercury) can be determined by chelation of samples using EDTA and evaluating the change in toxicity. The success of EDTA in removing metal toxicity is a function of solution pH, the type and speciation of the metal, other ligands in the solution, and the binding affinity of EDTA for the metal versus the affinity of the metal for tissues of the test organism. Among the cations typically chelated by EDTA are aluminum, barium, cobalt, copper, iron, lead, manganese, nickel, strontium, and zinc. However, EDTA can be toxic at certain concentrations, depending on water hardness.

Copper was detected in effluent ID 9 at greater than 2000 ppb. Zinc levels were not elevated. Two aliquots of ID 9 were treated with EDTA concentrations of 37.0 and 75.0 mg/L. Acute toxicity screening tests were then conducted to determine the contribution of copper to the total observed toxicity. Acute toxicity was reduced by sixteen and forty-two percent following treatment with 37.0 and 75.0 mg/L EDTA, respectively. These results indicated that the bioavailability and, hence, the toxicity of copper were reduced through binding or complexation with EDTA. Elevated calcium and magnesium measured as hardness (2400 mg/L) and elevated salinity measured as conductivity (11,400  $\mu$ mhos/cm) probably prevented any further reduction in toxicity through competition with copper ions for EDTA at the two treatment concentrations.

	Ar	senic	Co	opper	2	Zinc	Ac	ute Toxi	city (atu)
ID	Feed	Effluent*	Feed	Effluent*	Feed	Effluent*	Feed	Effluent*	% Removal
1	1978	119	17	-	180	-			
3	125	-	790	20	113	14	3.11	1.46	53
4	154	-	1400	110	678	40	3.8	2.7	29
5	258	-	1250	90	143	35	2.3	1.8	22
6	441	27/70	290	130/20	109	36/26			
7	1037	73/87	430	90/20	22	13/24			
8	6	-	350	20	23	14	1.3	1.0	23
9	189	-	2100	70	73	26	7.0	2.7	61
11	195	-	980	50	195	60			
12	1130	102/232	610	40/90	366	28/70			
15	1098	77	210	20	666	37			
ох	ox Limit 250			200		100		1	

#### Table 13. Metals Removal by Precipitation

All values are  $\mu g/L$ , except toxicity, which is acute toxic units

\*Dual values indicate two treatment batches

As described previously, and as shown in Table 13, the bioeffluents contained excessive, and probably toxic, levels of arsenic, copper, and zinc. As described in the Experimental section, methods were developed for removing those three metals.

As shown in Table 13, elevated levels of arsenic (above 250  $\mu$ g/L) were detected in five of the biotreated effluents. Ferric chloride coprecipitation was used to successfully reduce arsenic levels to levels well below the estimated toxic threshold as shown in the table and in Figure 21.

As shown in Table 13 and Figure 20, copper and/or zinc levels in ten of the eleven bioeffluents exceeded the toxic thresholds of 200 and 100  $\mu$ g/L, respectively. As described in the Experimental section, those effluents were subjected to metals removal with sulfide precipitation followed by precipitation of excess sulfide with ferrous iron, and aeration precipitation of the excess iron. Table 13 and Figure 20 show that both copper and zinc were removed to levels well below the toxic threshold by this treatment.



Figure 20. Precipitation Removal of Metals & Toxicity

Values are ppb & Acute Toxic Units; White = Feed, Black = Effluent

Following removal of copper and zinc, effluent IDs 3, 4, 5, 8, and 9 were once again tested for acute toxicity. Toxicity reduction ranging from sixty-one to twenty-three percent was demonstrated in these effluents due to removal of these two metals (Table 13 and Figure 20). The remaining toxicity was apparently caused by other contaminants.

#### Acute Toxicity and Tertiary Treatment Removal of Residual Organics

As noted above, and shown on the "Feed" column of Table 14, below, nine out the eleven bioeffluents remained acutely toxic (atu >1, or LC<sub>50</sub> <100%) after removal down to non-toxic levels of the known inorganic toxicants (ammonia, arsenic, copper, and zinc). At this point, the most likely toxicants were unidentified organic species, which ought to be removable either by enhanced UV-peroxide treatment or by activated carbon adsorption. As described in the Experimental section, the nine effluents were thus subjected to the three (oxidation, carbon adsorption, and combined oxidation/carbon adsorption) tertiary treatments for removal of residual organics. As shown in Table 14, and in Figure 21, the tertiary treatments were quite successful at removing organic TOC, with 88-90 percent removal for the three types of treatment. Somewhat surprisingly, the removal of acute toxicity by tertiary treatment was much less successful, as shown by Table 14 and Figure 21. On the average, activated carbon treatment actually increased effluent acute toxicity, while the two treatments using oxidation only removed modest amounts of the acute toxicity. Of the nine effluents subjected to the tertiary treatments, only two were rendered nontoxic by each of the treatments. The other two effluents were already nontoxic without tertiary treatment.

		тос				Acute LC50 Toxic Units				Chronic NOEC Toxic Units			
			H <sub>2</sub> O	PAC+			H <sub>2</sub> O	PAC+			H <sub>2</sub> O	PAC+	
ID	Feed	PAC	2	H <sub>2</sub> O <sub>2</sub>	Feed	PAC	2	H <sub>2</sub> O <sub>2</sub>	Feed	PAC	2	H <sub>2</sub> O <sub>2</sub>	
1	67	-	-	-	1.00	-	-	-	1.00	-	-	-	
3	201	10	32	11	1.46	2.00	1.27	1.32					
4	320	10	58	16	2.75	3.25	1.44	1.22					
5	280	10	53	32	1.79	2.36	1.00	1.36			4.00		
6	590	143	10	34	1.98	1.00	1.00	1.00		2.00	2.00	2.50	
7	418	10	7	8	1.34	1.00	1.25	1.00		4.00		2.50	
8	18	-	-	-	1.00	-	-	-	4.00	2.00	2.00		
9	440	10	64	53	2.72	3.17	4.15	2.79					
11	638	77	83	67	3.24	2.30	1.23	2.97					
12	177	10	5	21	2.29	2.07	2.12	1.98					
15	120	10	9		1.53	1.22	1.21	1.12					
Avg.	297	32	36	30	1.92	2.04	1.63	1.64	2.50	2.67	2.67	2.50	
vg.% Re	vg.% Removal		88	90		-6	15	15		-7	-7	0	

Table 14. Tertiary Treatment of TOC and Acute & Chronic Toxicity

#### Chronic Toxicity and Tertiary Treatment Removal of Residual Organics

Out of necessity (since the chronic tests were prolonged versions of the acute tests), the only effluents submitted for chronic toxicity testing were those which passed (atu  $\leq 1.0$ ) the acute toxicity test.

Chronic toxicity is also presented as toxic units (ctu, sometimes shown as  $tu_c$ ) where a ctu = 100/NOEC. In the data presented here, an acceptable level of chronic toxicity would have a ctu  $\leq$  1.0 (NOEC  $\geq$  100%). The results of the chronic toxicity tests conducted on effluent IDs 1 and 8 are presented in Table 14, shown as "Feed." Effluent ID 1 was essentially nontoxic with a ctu = 1.0 (NOEC = 100%) while effluent ID 8 was very toxic with a ctu = 4.0 (NOEC = 25%). Effluent ID 8 was subjected to tertiary treatment followed by another round of chronic testing. Since it had demonstrated no toxicity, no further testing and/or treatment was performed on effluent ID 1.



### Figure 21. TERTIARY TREATMENT AND TOC / TOXICITY REMOVAL

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Not for Resale

The effects of tertiary treatment on chronic toxicity on the four effluents are shown in Table 14 and Figure 21. As shown, none of three effluents (IDs 5, 6 and 7) which were acutely nontoxic following tertiary treatment was chronically nontoxic. The only effluent whose tertiary treatment feed chronic toxicity was measured was ID 8. In its case, tertiary treatment reduced chronic toxicity by a factor of two, but did not eliminate the toxicity.

At this point in the testing, only one of the eleven effluents was completely nontoxic after 1) biotreatment, 2) removal down to nontoxic levels of known inorganic toxicants, and 3) about 90 percent removal of residual organics. This unexpected result led to a search for the cause of the residual toxicity.

6-9

#### 7. INVESTIGATION OF RESIDUAL TOXICITY

As described previously, only one of the eleven effluents after biotreatment, removal down to nontoxic levels of known inorganic toxicants, and about 90 percent removal of residual organics, was completely nontoxic. To attempt to determine the nature of the toxicity of the other effluents, other testing was done as described below.

#### TOXICITY FROM IONIC IMBALANCES

Aquatic animals are naturally strongly affected by the constituents of the water in which they live, even by the relative amounts of those dissolved inorganic ions which are not normally thought of as toxic.

Relatively little is known about the toxicity of individual major cationic (Na<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup>) and anionic (Cl<sup>-</sup>, SO<sub>4</sub>=) components of salinity. While not considered to be "traditional" toxicants, these inorganic ions have been shown to be toxic to organisms commonly used for biomonitoring purposes. Although the mysid shrimp used in these studies is an estuarine organism capable of tolerating a range of salinity, previous physiological investigations related to osmotic regulation in mysids suggest that this organism may not be capable of tolerating inorganic ion ratios and concentrations which deviate significantly from that of natural seawater.

As noted in Table 6 the feed waters as received contained ionic species in ratios atypical of seawater. Most of the feed waters were then subjected to various types of treatment which added ions (sodium sulfate from ammonia removal, sodium chloride from arsenic removal, and sodium sulfate from copper and zinc removal). Concentrations of sodium, calcium, magnesium, potassium, chloride, and sulfate were measured in six of the effluents following biotreatment and removal of ammonia and metals (Table 15A). As part of the standard test procedure for the marine test species, the bioassay laboratory first analyzed the salinity of each water sample, and then added sufficient sea salt to bring the salinity up to 25,000 ppm. Table 15B shows the calculated concentrations of the various ions resulting from this pretreatment. The ionic concentrations obtained after salting-up were compared to literature toxicity values (15) for the respective ions to determine if any ions were in excess at levels which would cause toxicity. All ions were in the acceptable range for mysids.

To provide a direct measure of possible ion imbalance toxicity, tests were done to isolate ionic composition as a variable. Two of the effluents (IDs 9 and 12) were selected for further study based on their residual toxicity following ammonia removal, metals removal, and tertiary treatment. The initial toxicity of effluent ID 9 was 2.72 atu. Following PAC, UV/H<sub>2</sub>O<sub>2</sub>, and combined PAC-UV/H<sub>2</sub>O<sub>2</sub> treatments, the toxicity was 3.17, 4.15, and 2.79 atu, respectively. The initial toxicity of effluent ID 12 was 2.29 atu. Following PAC, UV-H<sub>2</sub>O<sub>2</sub>, and combined PAC-UV/H<sub>2</sub>O<sub>2</sub> treatments, the toxicity was 2.07, 2.12, and 1.98 atu, respectively. Significant toxicity reduction was not observed following tertiary treatment of either of these two effluents, implying that the residual toxicity may not have been caused by organics. Therefore, these effluents were selected to determine if the observed residual toxicity was caused by the presence of ionic concentrations which were outside the range of environmental tolerance for mysids.

				ee ale mig									
A. Concenti	A. Concentration After Removal of Ammonia and Metals												
ID	Na	ĸ	Ca	Mg	SO4=	CI-	$\Sigma = TDS$						
3	2600	51	320	320	3198	1745	8234						
4	2000	41	109	270	2055	1375	5850						
5	3300	60	164	380	2385	1590	7879						
9	5900	154	340	700	4780	8000	19874						
11	4300	84	192	420	2560	5350	12906						
12	4800	109	247	540	1400	10520	17616						
Seawater	10500	378	399	1260	2657	19005	34199						

### Table 15. Concentrations of Major lons in Bioassay Samples All values are mg/l

B. Concen	tration in B	ioassay T	'est Samp	le*			
ID	Na	ĸ	Ca	Mg	SO₄=	CI-	$\Sigma$ =TDS
3	7748	236	516	938	4501	11062	25000
4	7880	253	332	976	3543	12017	25000
5	8557	249	364	1011	3715	11104	25000
9	7474	211	400	889	5178	10849	25000
11	8013	218	333	866	3500	12071	25000
12	7067	191	333	812	1974	14623	25000
*Calculated	by adding o	riginal ion	concentra	tion to the	amount of io	n in sea salt	
added to rai	ise the total	salinity to :	25,000 pp	m.			

To determine if	Tab	Table 16. Ionic Compositions of Real and Mock									
the toxicity in		Effluent IDs 9 and 12									
effluent IDs 9 and			All va	alues are r	na/L						
12 was caused by	ID	Na	к	Ca	Mg	SO₄=	CI-				
ionic imbalance,	Real 9	5900	154	340	700	4780	8000				
mock wastewaters	Mock 9	5150	174	655	350	7060	21840				
were made with	Real 12	4800	109	247	540	1400	10520				
ionic composition	Mock 12	4600	75	326	600	2025	10100				

similar to those two effluents, as shown in Table 16, but lacking any other wastewater contaminants. Thus, if the observed toxicity were due solely to the ionic balance, the mock waters should have the same toxicity as the corresponding effluents. On the other hand, if the real waters were more toxic than the mock waters, then the difference in toxicity would be caused by the other contaminants in the real waters.

To test the hypothesis that the toxicity was caused by ionic imbalance, a dilution series was prepared for toxicity testing with mysids using the real wastewater as the test solution and the mock wastewater as the diluent. Effluent concentrations tested were 100%, 75%, 50%, 25%, and 0%. The 100% test concentration contained only the real wastewater, while the 50% test concentration contained equal proportions of the real and mock wastewaters. The 0% test concentration contained only the mock wastewater. This experimental design permitted determination of acute toxicity due to ionic composition of the wastewaters. If no differences in toxicity were detected across the dilution series for wastewater IDs 9 and 12, then ionic

composition of the wastewaters would be implicated as the probable cause of the observed toxicity. If differences in toxicity were detected across the dilution series, then some component of the wastewater other than cations and/or anions, for example, metals or organics, would be implicated as the most probable source of the observed toxicity. The results of these tests are presented in Table 17. As can be seen, it appears that the toxicity is directly proportional to the fraction of real water in the sample, indicating that contaminants other than major ions are responsible for the toxicity.

Blend Percent	Percent Real	100	75	50	25	0
	Percent Mock	0	25	50	75	100
Percent	ID 9	0	0	20	85	100
Percent Survival	ID 12	0	10	30	55	95

#### Table 17. Results of Real/Mock Acute Toxicity Tests

These results indicate that although the ionic composition of the wastewaters (as delivered and as a result of treatments) deviated somewhat from that of natural seawater, these deviations do not account for the observed toxicity. In that both of these effluents had been treated for removal of ammonia and metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) to levels less than the estimated toxicity thresholds, it can be assumed that residual toxicity was caused by other unmeasured contaminants.

#### **OTHER POTENTIAL TOXICANTS**

In order to determine the causes of toxicity not related to ammonia, previously measured metals, or concentrations of major anions and cations, further analyses were conducted on tertiary effluent IDs 9, 11, and 12. These analyses included metals such as selenium (Se), vanadium (V), antimony (Sb), tin (Sn), boron (B), and barium (Ba). The effluents were also analyzed for naphthenic acids, cyanide and surfactants. The results of these analyses are presented below. The results of the tests for trace metals and for free and total cyanide are shown in Table 18.

ID	в	Ba	Sb	Sn	v	Se	Free Cyanide	Total Cyanide
9	200	500	34	300	53	5	13	49
11	100	500	6	400	49	7	1	10
12	200	500	44	200	32	6	6	11
Seawater	4600	30	0.33	3	2	0.09		

## Table 18. Concentrations of Trace Metals and Cyanides FollowingRemoval of Ammonia, Metals, and Residual Organics

All values are  $\mu g/L$ 

Secondary Acute Values (SAV) were used along with Water Quality Criteria (WAC) and other published data for determination of threshold values for cyanide and metals. Secondary Acute Values have been developed for use in ecological risk assessments based on methods described in EPA's Proposed Water Quality Guidance for the Great Lakes System. This method allows for the derivation of benchmarks with fewer data points than the number required for Water Quality Criteria. The SAVs are concentrations that would be expected to be higher than the WQC in no more that twenty percent of the cases (14).

**Boron.** The concentrations of boron detected in the effluents were much less than that found in natural seawater. Therefore, these levels would be assumed to be non-toxic.

**Barium.** The Secondary Acute Value for barium is 110  $\mu$ g/L. Effluent concentrations (IDs 9, 11, and 12) were in excess of the SAV, indicating that barium may have contributed to the observed acute toxicity. However, it is doubtful that the barium was actually present at the concentrations shown (which are near the detection limit for the analysis). Although toxic, barium is normally not considered by EPA (8) to be of concern for aquatic toxicity because of the extreme insolubility of barium sulfate (sulfate is typically a major ion in freshwater and seawater). Barium sulfate solubility is controlled by the solubility product constant, which is  $1.07 \times 10^{-10}$  at ambient temperature (16). At the lowest sulfate concentration in the three samples, 1400 mg/L, the maximum level of soluble barium would be 1.008  $\mu$ g/L, which is well below the analysis values and the SAV toxic threshold.

Antimony. The acute WQC for antimony is 200  $\mu$ g/L for marine life (most marine effects are in the 1-9  $\mu$ g/L range). The Secondary Acute Value for antimony is 180  $\mu$ g/L. The effluent concentrations were well below these values, implying that antimony toxicity would not be expected.

Tin. The SAV for tin is 2700  $\mu$ g/L. Effluent concentrations ranged from 200 to 400  $\mu$ g/L, indicating that tin would not be expected to have caused acute toxicity.

**Vanadium.** The SAV for vanadium is 280  $\mu$ g/L. Effluent concentrations ranged from 32 to 53  $\mu$ g/L, indicating that acute toxicity due to vanadium would not be expected.

**Selenium.** The acute WQC for selenium is 20  $\mu$ g/L. Effluent concentrations ranged from 5 to 7  $\mu$ g/L, indicating that acute toxicity due to selenium would not be expected.

**Cyanides**. A chronic threshold value of 69.71  $\mu$ g/L cyanide was determined in a life-cycle study using mysids (8). Cyanide would not have contributed to the observed acute toxicity in effluent IDs 9, 11, and 12, in which concentrations ranged from 10 to 49  $\mu$ g/L. Also, the levels of free cyanide (the toxic form) were even lower (1-13  $\mu$ g/L).

#### Priority Pollutant Metals (Be, Ag, Tl)

In addition to those already discussed, several other priority pollutant metals (beryllium, silver, and thallium) were also analyzed, and essentially not found, as shown on Table 19.

**Beryllium**. The SAV for beryllium is 35  $\mu$ g/L. Effluent concentrations were < 1  $\mu$ g/L, indicating that beryllium did not contribute to the observed acute toxicity.

Silver. The acute WQC for silver in marine systems is 2.3  $\mu$ g/L. All effluent concentrations were < 3  $\mu$ g/L, indicating

#### Table 19. Concentrations of Priority Pollutant Metals Following Removal of Ammonia, Metals, and Residual Organics

All values are  $\mu g/L$ ID Be Ag TI <2 6 <1 <2 7 <1 <2 7.5 11 <1 <3 <2 12 <1 <3 <2 15 <1 <3 <2 Seawater 0.0006 0.3 < 0.02 that silver cannot be ruled out definitively as a contributor to the observed acute toxicity. On the other hand, since there is no known source of silver in tank bottoms waters, it is unlikely that it is present even at low levels. Also, at the chloride levels in the samples (minimum 1375), and the ambient temperature solubility product value of  $1.77 \times 10^{-10}$  (16), the maximum level of soluble silver would have been 0.5 µg/L.

**Thallium.** The acute WQC for thallium in marine systems is 2130  $\mu$ g/L. All effluent concentrations were < 10  $\mu$ g/L, indicating that thallium did not contribute to the observed acute toxicity.

**Surfactants.** Surfactants are well known to be toxic, and are even used as toxicity standards in bioassays. Levels of surfactants in bioeffluent IDs 9, 11, and 12 were shown in Table 11 to be 45, 3680, and 1600  $\mu$ g/L, respectively, for MBAS, and 1690, 400, and 400  $\mu$ g/L, respectively, for CTAS. As shown in Table 20, tertiary treatment reduced surfactants levels considerably, to levels which are unlikely to be toxic.

	ID 9		ID 11				
Test	UV-H <sub>2</sub> O <sub>2</sub>	PAC	UV-H <sub>2</sub> O <sub>2</sub>	PAC + UV-H <sub>2</sub> O <sub>2</sub>	PAC	UV-H <sub>2</sub> O <sub>2</sub>	PAC + UV-H <sub>2</sub> O <sub>2</sub>
MBAS	<25	70	<25	<25	<25	<25	<25
CTAS	100	500	6	400	49	7	1

Table 20. Concentrations of Surfactants After Tertiary TreatmentAll values are  $\mu g/L$ 

To provide further indications as to whether surfactants were a source of toxicity, foam fractionation tests were done, in which the samples (IDs 3, 4, and 9) were aerated and half allowed to foam over into a foamate sample, whose toxicity was compared with the foam fractionation bottoms. Since the acute toxicity of both samples was the same, it was concluded that surfactants (which should have been concentrated in the foamate) were not a source of toxicity.

**Naphthenic Acids.** Naphthenic acids, derivatives of cycloparaffin carboxylic acids naturally found in many crude oils, are known to be difficult to degrade through biological treatment, are somewhat resistant to removal by oxidation and adsorption, and have also been determined to be toxic to marine vertebrates at concentrations ranging from 12 to 25 ppm. Acute toxicity tests were conducted with mysids and a stock solution made from commercial Eastman Chemicals refined naphthenic acids. The LC<sub>50</sub> values ranged from 2.5-4.2 ppm. Previous analyses of several effluents (IDs 1, 3, 4, and 9) following biological treatment detected naphthenic acids at concentrations ranging from 3 to 96 ppm. Although these concentrations probably contributed to the acute toxicity observed following biological treatment, the levels detected following tertiary treatments are less than the estimated LC<sub>50</sub> for mysids (2.5-4.2 ppm). As shown in Table 21, both PAC and UV/H<sub>2</sub>O<sub>2</sub> were capable of reducing naphthenic acids to less than toxic levels.

Antifoam Agent. Because of severe foaming found during SBR biotreatment aeration and alkaline air stripping of ammonia, an antifoam agent (Nalco 7452) was added to the water during those treatments. The additive, a mixture of glycol esters, fatty acids, and

# Table 21. Concentrations of Naphthenic Acids After Tertiary Treatment All values are undle

	Tertiary Effluent ID								
Treatment	1	3	4	5	6	7	11	12_	15
PAC	ND	ND	ND	ND	ND	120	ND	100	
UV-H <sub>2</sub> O <sub>2</sub>	ND	35	50	ND	100	ND	75	60	30

isopropanol, could potentially have been a source of toxicity. To test this, an alkaline air stripping treatment was conducted both with and without addition of antifoam agent, and showed equal acute toxicity in the effluent either way. Also, antifoam in bioassay dilution water (0.5 mL/L dosage) was directly determined to be nontoxic by bioassay testing.

Solid Phase (C18) Extraction. Solid phase extraction procedures with long chain C18 resin are used in toxicity identification evaluations for removal of sorptive, hydrophobic compounds, which sometimes enable identification of nonpolar organics as toxicants. In addition to sorptive removal of hydrophobic organics, the C18 resin has some physical filtration ability due to the small pore size of the resin. C18 solid phase extraction was conducted on tertiary effluents IDs 9, 11, and 12. However, no reduction in toxicity was observed in these three effluents following the C18 extraction procedure.

**Residual Organics.** The chemical nature of the organic material remaining after biotreatment and the various types of tertiary treatment is probably complex, and is not known. What is known is the total amount of organic carbon (TOC), which can be correlated with effluent toxicity as shown on Figures 22 and 23.

Figure 22 shows the correlation between acute toxicity (measured in acute toxicity units) and TOC in the bioassay sample for all the acute bioassays which were run. Also shown on Figure 22 is the "best fit" linear regression line. As can be seen by inspection, there was considerable scatter in the data, which is confirmed by the poor curve fitting statistics (R square value of 0.075). That fact, combined with the modest slope of the





line, implies little or no correlation between TOC and effluent acute toxicity, which in turn implies that the acute toxicity is not organic in nature.

Figure 23 shows the similar plot for the chronic toxicity data (for which there are much fewer data points, since only the acutely nontoxic effluents could be subjected to chronic bioassays). As can be seen, the scatter for those data is even worse, and the linear regression line implies a negative correlation between effluent TOC and chronic toxicity. Again, the implication is that the chronic toxicity is not organic in nature.



It is remarkable that organics were so thoroughly removed by tertiary treatment (over 90 percent average TOC removal from bioeffluent IDs 9, 11, and 12) with hardly any improvement in toxicity (average acute toxic units for IDs 9, 11, and 12 went from 2.75 to 2.53 following tertiary treatments), a fact which again implies either that the residual toxicants are not organic, or that they are a unique type of organic material which is not susceptible to biotreatment, carbon adsorption, and UV-enhanced oxidation.

#### MATERIALS NOT ANALYZED

Although the effluents were subjected to a multitude of analyses as described above, not every possible analysis was conducted, partially because of limitations in the amount of sample available for analysis. The "missing" contaminants, and discussion of their likely presence and toxicity, are discussed as follows.

Nitrate. The tank bottoms waters are unlikely to have contained much nitrate, but nitrate was probably generated by nitrification of ammonia in the biotreatment step. The toxicity of nitrate to marine organisms is not well defined. To provide an estimate of the potential nitrate toxic effects, the amount of biotreatment ammonia nitrogen removal for each sample (which should correspond with generation of nitrate nitrogen) was plotted against bioeffluent acute toxicity, as



shown in Figure 24. As can be seen, there is little correlation. The fact that one sample has high nitrification and no toxicity would appear to rule out nitrate as a source of toxicity in those effluents with less nitrification.

**Phosphate.** Although the tank bottoms waters are unlikely to have contained much phosphate, some was added as nutrient to the waters as they were biotreated. However, phosphate is not known to be toxic to marine animals.

**Reduced Sulfur Species.** The only sulfur ion analyzed was sulfate, which is naturally present in seawater and is nontoxic. Reduced sulfur species (sulfide, thiosulfate, and others), on the other hand, can be toxic. It is very unlikely that such species could have survived biotreatment (which oxidizes them to sulfate). Also, if reduced sulfur species were responsible for the observed toxicity, then UV/peroxide treatment should have greatly reduced toxicity, which did not occur.

#### **OVERVIEW**

At this point, some of the effluents (IDs 9, 11, and 12) remain acutely toxic despite either starting with levels of toxicants less than the toxic limits or having toxicants removed down to those levels. Table 22, following, summarizes all of the toxicants which have been ruled out as the source of the toxicity. Two metals (barium and silver) may have been present at toxic levels, but probably can be ruled out as explained above. Unfortunately, the list is fairly comprehensive, and does not appear to neglect any contaminants which would be expected to be in tank bottoms waters.

About the only candidate toxicants left are unidentified residual organics. Some organic species, although not analyzed, can be essentially ruled out because they are known to be well-removed by the types of treatment applied to the waters: biotreatment, enhanced oxidation, and carbon adsorption. Contaminants in this category include aromatics (BTEX), phenols, and alcohols.

Since no further chemical identification of residual toxicants was done, the next section examines possible correlations between characteristics of the tank bottoms waters and their toxicity.

#### Table 22

#### Materials Known Not to be Present at Toxic Levels in Acutely Toxic Effluents

Ammonia Free Cyanide Total Cyanide Nitrate Phosphate Reduced Sulfur Species

Naphthenic Acids MBAS Surfactants CTAS Surfactants Carbon Adsorbable Organics UV-H<sub>2</sub>O<sub>2</sub> Oxidizable Organics C18 Adsorbable Organics

Ionic Imbalance Between Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, Cl<sup>-</sup>, SO<sub>4</sub>=

> Antimony Arsenic Beryllium Boron Cadmium Chromium Copper Lead Mercury Nickel Selenium Thallium Vanadium Zinc

Materials Possibly, But Not Probably, Present at Toxic Levels in Acutely Toxic Effluents

> Barium Silver

#### 8. TOXICITY CORRELATIONS

As shown in the previous sections, there was considerable variability in the success of removing toxicity from the various tank bottoms wastewaters. Since all were normalized initially to the same COD level by dilution, the most obvious variable, concentration of contaminants, should have been eliminated.

#### SCORING

In order to examine other possible variables which affect toxicity, a scoring system was set up for each wastewater. This system assigns numbers to the following ratings, in order from least toxic to most toxic. The term secondary treatment refers to biotreatment and removal of ammonia, arsenic, copper, and zinc. The term tertiary treatment refers to removal of residual organics by UV/peroxide, activated carbon, and the combination of the two.

- 1. Not acutely or chronically toxic after secondary treatment
- 2. Not acutely toxic after secondary treatment and not chronically toxic after tertiary
- 3. Not acutely toxic after secondary treatment, but chronically toxic after tertiary
- 4. Acutely toxic after secondary treatment, but not acutely or chronically toxic after tertiary
- 5. Acutely toxic after secondary treatment, but not after tertiary; chronically toxic after tertiary
- 6. Acutely toxic after secondary and tertiary treatment

The scores for the various wastewaters are shown in Table 23.

In developing correlations, it should be kept in mind that a correlation can be coincidence rather than a cause-and-effect relationship, particularly for such a small sample size (11 wastewaters). It should also be kept in mind that this study employed stringent criteria for whether or not an effluent was toxic (LC<sub>50</sub> of 100%, and NOEC of 100%). If those criteria were relaxed to more typical levels, then the scoring would change considerably, as shown below.

#### **OVERALL SCORE**

The first fact to note from Table 23 is that the average overall score was not very good, being 5.0, or equivalent to the next to the worst rating. Looked at another way, only 2/11 effluents had scores of 3 or better. The uniformity of the scoring makes establishing correlations with this system impossible, so a revised scoring system with better discrimination among the effluents is needed.

Table 23. Wastewater 100% Toxicity Scores		
ID	Score	
1	1	
3	6	
4	6	
5	5	
6	5	
7	5	
8	3	
9	6	
11	6	
12	6	
15	6	
Avg.	5.0	

<b>REVISED SCORING</b> In order to provide a better basis for correlations, with more variability among the effluents, a revised scoring system was set up, with a 50%			Table 24. Wastewater 50% Toxicity Scores		
criterion for passing the acute and chronic bioassay tests instead of 100%.		<u>ID</u>	Score		
Th	he new numerical scores are as follows, from best to worst:		1		
	,	3	5		
1	Not acutely or chronically toxic after secondary treatment	4	6		
1. 2	Not acutely of chromeany toxic after secondary freatment	5	4		
2.	Not acutely toxic after secondary treatment, but chronically toxic;	6	4		
	after tertiary, not chronic	7	4		
3.	Not acutely toxic after secondary treatment, but chronically toxic after	8	2		
	tertiary	9	6		
4	Not acutely toxic after secondary and tertiary treatment chronic		6		
••	toxicity tested	12	6		
~		15	5		
э.	toxicity not tested		4.5		

6. Acutely toxic after secondary and tertiary treatment

The effluent scores for the revised system are shown in Table 24.

As can be seen, with the new criteria, there is a much more even distribution of scores, which will allow better development of correlations, and will be used in the following discussions.

#### PRODUCT TYPE

The first variable to be examined is the type of petroleum product from which the tank bottoms water was derived. Table 25 shows the five different types of products, and their average scores.

The higher grade gasoline with MTBE scored markedly better than the other fuels, although the explanation for

this result is not known. There is only a small difference among the other types of products, although it could be tentatively concluded that tank bottoms water from diesel / #2 fuel oil is less toxic than that from gasolines, and that tank bottoms water from higher grades of gasoline is less toxic than that from lower grades. These conclusions may in fact be true, since diesel generally receives less of the refinery processing which makes water-soluble organics, and since higher grades of gasoline may be subject to more stringent quality controls.

#### **GEOGRAPHICAL LOCATION**

Table 26 shows the relationship between the geographical locations of the terminals and the toxicity of their tank bottoms waters. Not surprisingly, there is no clear correlation between these.

#### Table 25. Product Type and Toxicity

		Avg.
Product	No.	Score
Super Unleaded with MTBE	1	1.0
Super Unleaded	2	4.5
Mid-grade Unleaded	2	5.0
Regular Unleaded	4	5.3
Diesel / #2 Fuel Oil	2	4.0

#### Table 26. Location and Toxicity

		Avg.
Location	No.	Score
Gulf Coast	6	4.0
East Coast	4	5.0
Midwest	1	5.0

#### **BIOLOGICAL TREATMENT LEVELS**

It is possible that toxicity may be related to the biological treatability of the wastewaters, as indicated by the level of various contaminants in the bioeffluents. Note that this is different from the absolute levels of contaminants, since the bioeffluents were subjected to removal of ammonia and metals prior to the bioassays, and, for most effluents, to removal of the residual organics prior to the second set of bioassays. Correlations with levels of contaminants in bioassay samples are considered in the next section.

#### **Bioeffluent BOD**

Bioeffluent BOD is an indicator of how well biotreatment could remove the supposedly biodegradable portion of the water. A high bioeffluent BOD could indicate the presence of materials inhibitory to the biotreatment bacteria, and thus perhaps toxic to bioassay animals. The correlation is shown in Figure 25. Although there are some points which support the hypothesis that high bioeffluent BODs correlate with toxicity, there is also a group of effluents

Figure 25. Toxicity Score vs. Bioeffluent BOD



which had very low bioeffluent BODs and high toxicity. Thus, if there is a correlation, it is not applicable to all tank bottoms waters.

#### **Bioeffluent COD**

Since all samples were normalized with respect to feed COD (at 4000 mg/L), bioeffluent COD is probably the best single indicator of how biotreatable the water was. As with BOD, a high value may indicate the presence of bacterial inhibitory substances. Even more likely, it may indicate the presence of high levels of materials resistant to biodegradation (biorefractory materials). Why such materials should be toxic is Figure 26. Toxicity Score vs. Bioeffluent COD



not known. The correlation, shown in Figure 26, seems to indicate at least a moderately strong relationship between bioeffluent COD and toxicity (although two effluents with low COD had high toxicity), so possibly the hypotheses above have merit.

#### **Bioeffluent TOC**

TOC is the most direct indicator of organic contaminants (BOD and COD may have inorganic components). As noted previously, biological TOC removal was quite erratic compared to BOD and COD removal. The correlation, shown on Figure 27, appears to show a fairly strong correlation between bioeffluent TOC and toxicity if two values with high TOC and moderate toxicity are ignored. Thus, there may be, for most waters, a relationship between TOC biodegradability and toxicity.

#### **Bioeffluent Ammonia**

Ammonia is a known toxicant, and was removed from bioeffluents prior to bioassay testing (i.e., the values shown in Figure 28 are well above those in the bioassay samples). This correlation, therefore, is mostly an attempted correlation between nitrification (biological ammonia removal) and toxicity. Inspection of Figure 28 shows that no correlation exists.

#### **Bioeffluent Surfactants (MBAS and CTAS)**

As discussed above, surfactants are known toxicants, and were *not* removed from bioeffluents prior to the initial acute bioassay testing. Figures 29 and 30 show the correlations of toxicity with MBAS (anionic surfactants) and CTAS (nonionic surfactants). There is, at best, a weak correlation of toxicity with MBAS levels, and no correlation with CTAS levels, which implies that surfactants were biologically removed down to nontoxic levels.







Figure 28. Toxicity Score vs. Bioeffluent Ammonia



Figure 30. Toxicity Score vs. Bioeffluent CTAS



Figure 27. Toxicity Score vs. Bioeffluent TOC

#### FINAL EFFLUENT LEVELS OF KNOWN TOXICANTS

In this section, the effluent levels of various contaminants are compared with the effluent toxicity scores. Since these levels are those actually in the bioassay waters, the results should directly show if toxic levels of the contaminants are present, and should provide confirmation or refutation of the threshold levels determined to be "safe" in Table 3.

#### **Final Effluent Ammonia**

The toxicity threshold for ammonia in this study was taken to be 10 mg/L. As shown in Figure 31, there does not appear to be any correlation between final effluent ammonia and toxicity, which confirms the threshold as chosen.











Figure 31. Toxicity Score vs. Final Ammonia



Final Effluent Metals - As, Cu, Zn

The toxicity thresholds for arsenic, copper, and zinc were taken to be 250, 200, and 100  $\mu$ g/L, respectively, and were used in applying precipitation removal processes for those metals.

The presence of relatively high levels of arsenic and zinc in samples with low toxicity as shown in Figures 32 and 34, respectively, is a strong indication that those levels are not toxic, and thus confirms the toxicity thresholds chosen.

Although hardly a definite pattern, the correlation between copper levels and toxicity on Figure 33 does appear to indicate a possible moderate correlation between those variables (implying that copper levels above 40  $\mu$ g/L would be toxic), although that would contradict the literature references to copper toxicity to mysids.

#### Final Effluent Metals - Cr & Ni

The toxicity thresholds for chromium and nickel were taken to be 500 and 100  $\mu$ g/L, respectively, and all of the bioeffluents had levels below those limits (i.e., no special removal processes were used for chromium and nickel). Figures 35 and 36 show the toxicity correlations for the two metals. The scatter in the data would appear to indicate a lack of relationship between toxicity and the levels of these metals.



#### **RESIDUAL TOC AFTER TERTIARY TREATMENTS**

As noted above, tertiary treatments (UV/peroxide oxidation, powdered activated carbon, and combined oxidation-carbon treatments) were successful at removing about 90 percent of the bioeffluent TOC, but much less successful at removing bioeffluent toxicity. This is confirmed in



the correlations shown in Figures 37, 38, and 39, in which the level of tertiary effluent TOC shows no correlation with effluent toxicity. This is a fairly strong argument against believing that the residual toxicant is organic in nature. Of course, this leaves the chemical identity of the residual toxicant as a mystery, since none of the extensive analyses of inorganic contaminants showed likely toxic levels of those materials.





#### 9. SUMMARY OF RESULTS

Eleven petroleum products terminal tank bottoms water samples were SBR-biotreated, subjected to ammonia and metals removal if needed, and subjected to tertiary treatment by carbon adsorption and/or UV- $H_2O_2$ . Figure 40 summarizes all the treatment results for the eleven tank bottoms waters. In this figure, at each stage of treatment, the results are ranked according to the quality of the effluent water with regard to the parameter being shown.

As can be seen, biotreatment produced highly variable degrees of COD, TOC, BOD and ammonia removal, and generally was able to remove heavy metals.

Physical/chemical treatment was able to remove toxic levels of ammonia, arsenic, copper, and zinc. Physical/chemical treatment was required for ammonia, copper, and zinc in ten of the eleven samples, and for arsenic in five of the eleven samples.

Only two of the eleven samples were not acutely toxic after secondary treatment, and only one of those was not chronically toxic.

For the nine secondary effluent samples which were acutely toxic, tertiary treatment by oxidation, activated carbon, and the combination of the two treatments was only able to achieve moderate reduction in acute toxicity.

#### PART A: FEED WATER QUALITY

(Note: all samples were diluted to the same COD level [4000 ppm] prior to analysis or treatment)

- 1. The TOC/COD ratios in the feed waters were highly variable.
- 2. The BOD/COD ratios in the feed waters were highly variable.
- 3. Some tank bottoms have extremely high ammonia levels, and almost all (10/11) samples contained toxic levels of ammonia.
- 4. Cadmium, chromium, and lead levels in all samples were low, and below toxic levels.
- 5. Mercury levels in 6 samples were high, and at toxic levels.
- 6. Nickel levels in 6 samples were high, and at toxic levels.

#### PART B: BIOTREATMENT

- 7. COD, TOC, and BOD removals during biotreatment were highly variable.
- 8. Biotreatment was not always effective at removing a substantial fraction of the feed COD and TOC.
- 9. Generally, biotreatment removed a substantial fraction (75%) of feed ammonia, probably by nitrification.
- 10. Even after ammonia removal by biotreatment, most (10/11) samples contained toxic levels of ammonia.
- 11. Toxic levels of mercury were completely removed by biological treatment.
- 12. Toxic levels of nickel were completely removed by biological treatment.
- 13. Copper levels in almost all (10/11) bioeffluents were above toxic levels, possibly as a result of complexation with ammonia.
- 14. Arsenic levels in about half (6/11) of the bioeffluents were above toxic levels.
- 15. Zinc levels in most (8/11) of the bioeffluents were above toxic levels.
- 16. Surfactants (MBAS and CTAS) concentrations in bioeffluents were generally moderate (less than 2 ppm) except for two samples; SBR aeration foaming was found in several samples.



Figure 40. Overall Removal of Toxicants and Toxicity
## PART C: AMMONIA REMOVAL

17. Ammonia removal by alkaline batch air stripping was completely effective at reducing levels to less than the toxic limit.

## PART D: METALS REMOVAL

- 18. Arsenic removal by ferric chloride precipitation was completely effective at reducing levels to less than the toxic limit.
- 19. Copper and zinc removal by sulfide precipitation followed by ferrous sulfate/air oxidation was completely effective at removing those metals down to less than toxic levels.

#### PART E: ACUTE TOXICITY AND TERTIARY TREATMENT

(Note: the "non-toxic" standard for acute toxicity is  $LC_{50} = 100\%$  [acute toxic unit = 1.0]; tertiary treatment comprised three treatments: powdered activated carbon treatment, UV-H<sub>2</sub>O<sub>2</sub> oxidation, and combined carbon/oxidation treatment.)

- 20. 9 out of 11 bioeffluents were acutely toxic.
- 21. Activated carbon treatment achieved very good (89% average) TOC removal.
- 22. Activated carbon was not very effective at removing acute toxicity: in 4 samples toxicity went up, in 4 samples toxicity was slightly reduced, and in 1 sample toxicity was substantially reduced; on average, acute toxicity rose 6 percent after carbon treatment.
- 23. UV-peroxide treatment achieved very good (88% average) TOC removal.
- 24. UV-peroxide treatment was moderately effective at removing acute toxicity: in 1 sample toxicity went up, in 4 samples toxicity was moderately reduced, and in 4 samples toxicity was substantially reduced; on average, acute toxicity was reduced 15 percent by oxidation.
- 25. Combined carbon/oxidation treatment achieved good (90% average) TOC removal.
- 26. Combined carbon/oxidation treatment achieved toxicity removal midway between the two individual treatments: in 1 sample toxicity went up, in 6 samples toxicity was moderately reduced, and in 2 samples toxicity was substantially reduced; on average, acute toxicity was reduced 15 percent by combined treatment.
- 27. Bioeffluent acute toxicity correlates poorly with bioeffluent TOC.
- 28. Acute toxicity remaining after biotreatment and physical/chemical treatments does not appear to be caused by organic contaminants.
- 29. Overall, out of 11 samples with non-toxic levels of ammonia and metals, 2 were acutely nontoxic without further treatment, 3 could be made acutely non-toxic by tertiary treatment, and 6 could not be made acutely non-toxic.

# PART F: CHRONIC TOXICITY AND TERTIARY TREATMENT

(Note: the "non-toxic" standard for acute toxicity is NOEC = 100% [chronic toxic unit = 1.0]; 5 samples [those which passed acute toxicity testing] were subjected to chronic bioassay testing.) 30, 1 out of 5 samples had no chronic toxicity even without tertiary treatment.

- 31. In 2 out of 5 samples, chronic toxicity was moderately reduced after tertiary treatment.
- 32. In 2 out of 5 samples, chronic toxicity could not be removed by tertiary treatment.
- 33. Both activated carbon and oxidation were able to achieve chronic toxicity reduction in at least one sample.
- 34. There is no apparent correlation between tertiary treatment effluent TOC and chronic toxicity.
- 35. Chronic toxicity remaining after biotreatment and physical/chemical treatments does not appear to be caused by organic contaminants.

# PART G: THE NATURE OF RESIDUAL TOXICITY

(Note: the following studies were done in an attempt to identify the toxicity remaining in 8 out of 11 samples after biotreatment, ammonia removal, metals removal, activated carbon treatment, and  $UV-H_2O_2$  treatment.)

- 36. As delivered, and as a result of treatments, the ionic balance of major cations (Na<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, K<sup>+</sup>) and anions (Cl<sup>-</sup> and SO<sub>4</sub>=) of the samples deviated somewhat from that of seawater; this deviation was shown not to account for sample toxicity.
- 37. Surfactants (MBAS and CTAS) in tertiary effluents are at sub-toxic levels.
- 38. Trace metals (Se, V, Sb, Sn, B, and Ba) and other priority pollutant metals (Be, Ag, and Tl) were analyzed in 3 toxic samples. Boron levels were below those of sea water, and thus non-toxic. Antimony, tin, vanadium, selenium, beryllium, and thallium were present at levels below expected toxic limits for marine animals. Barium and silver were possibly present at toxic levels, but their low solubilities (of their sulfate and chloride, respectively) make this unlikely.
- 39. Total and free cyanide were analyzed in 3 toxic samples; all contained less than toxic levels of cyanide.
- 40. Naphthenic acids were present at levels below their toxic threshold.
- 41. C18 absorbent treatment did not reduce toxicity in the three effluents tested.
- 42. Although not analyzed, it is likely that levels of nitrate, phosphate, and reduced sulfur anions were below their toxic thresholds.
- 43. Overall, it appears that the observed toxicity was *not* caused by ammonia, cyanides, nitrate, phosphate, reduced sulfur species, naphthenic acids, MBAS or CTAS surfactants, carbon adsorbable organics, UV-peroxidizable organics, C18 absorbable organics, or imbalances among the major ions, Sb, As, Ba, Be, B, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, V, or Zn.

#### PART H: TOXICITY CORRELATIONS

(Note: each effluent was given a toxicity score based on how well its toxicity was removed by the various treatments, and those scores were correlated with various variables.)

- 44. Effluent toxicity was *not correlated* with terminal geographical location; bioeffluent BOD; bioeffluent ammonia; bioeffluent surfactants (MBAS and CTAS); final effluent ammonia; final effluent chromium, nickel, arsenic and zinc; or TOC remaining after three types of tertiary treatments.
- 45. Effluent toxicity appeared to *moderately correlate* with bioeffluent TOC and final effluent copper.
- 46. Effluent toxicity appeared to *fairly strongly correlate* with bioeffluent COD (i.e., inversely with COD biodegradability).

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