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

Health and Environmental Sciences Department
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Analysis and Reduction of Toxicity in Biologically Treated Petroleum Product Terminal Tank Bottoms Water

Health and Environmental Sciences Department

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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
	BACKGROUND	1-1
2.	GENERAL APPROACH	
	OBJECTIVES	2-1
	Water Source	2-1
	Normalization	2-1
	Use of Biotreatment	2-2
	Variety of Water Sources	2-2
	TOXICITY IDENTIFICATION	2-3
	TOXICITY THRESHOLDS	2-4
	TREATMENT METHODS	2-5
	Selection of Treatments	2-5
	Development of Treatments	2-5
	Aerobic Biological Treatment	2-5
	Ammonia Removal	2-6
	Metals Removal	2-6
	Arsenic Removal	2-6
	Copper and Zinc Removal	2-7
	Removal of Residual Organics	2-7
	Oxidation of Residual Organics	2-8
	Activated Carbon Adsorption of Residual Organics	2-8
	Combined Treatment of Residual Organics	2-8
	OVERALL TREATMENT SCHEME	2-8
	ANALYSIS OF RESIDUAL TOXICITY	2-9
	Salinity Ionic Ratios	2-9
	Other Known Toxicants	2-9
	TOXICITY CORRELATIONS	2-9
3.	FEED WATERS	
	Organic Constituents (COD, TOC, and BOD)	3-1
	Ammonia	3-1
	Conventional Metals	3-3
	Trace Toxic Metals	3-3
4.	EXPERIMENTAL EQUIPMENT AND PROCEDURES	
	FEED PREPARATION AND SELECTION	4-1
	BIOLOGICAL TREATMENT	4-1
	AMMONIA REMOVAL	4-2
	ARSENIC REMOVAL	4-2
	COPPER AND ZINC REMOVAL	4-3
	UV-PEROXIDE OXIDATIVE REMOVAL OF RESIDUAL ORGANICS	4-3

TABLE OF CONTENTS

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
Surfactants (MBAS & CTAS)	6-3
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 (C ₁₈) Extraction	7-6
Residual Organics	7-6
MATERIALS NOT ANALYZED.....	7-7
Nitrate	7-7
Phosphate	7-7
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^{+++}	4-2
5	Batch Copper & Zinc Precipitation with $\text{S}^{=}$, Fe^{++} , 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 LC₅₀ 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 C₁₈ 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 C₁₈ adsorbable material. Concentrations of these constituents 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 (LC₅₀>100% effluent) following biological treatment, metals precipitation and ammonia removal. Of the two samples not acutely toxic, one contained residual chronic 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 C₁₈ 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 LC₅₀ 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 non-standard 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).

Table 1. Tank Bottoms Water Sources

ID	Product	Company	Region
<i>Gasoline Tanks</i>			
1	Gasoline Super Unleaded Reformulated (11% MTBE)	A	Gulf Coast
3	Gasoline Regular Unleaded	B	Gulf Coast
4	Gasoline Mid-grade Unleaded	C	Gulf Coast
5	Gasoline Mid-grade Unleaded	C	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	I	Midwest
<i>Fuel Oil and Diesel Tanks</i>			
8	Fuel Oil #2	E	East Coast
11	Diesel	G	East Coast
<i>Tank Bottoms Samples Not Used</i>			
2	Gasoline Regular Unleaded	A	Gulf Coast
10	Fuel Oil #2	F	East Coast
13	Terminal Wastewater	H	Gulf Coast
14	Gasoline Super Unleaded with Vapor Recovery Water	H	Gulf Coast

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.

Table 2. Approaches to Toxicity Identification and Removal

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

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 *Mysidopsis bahia*.

Table 3. Estimated Toxicity Thresholds for Ammonia and Metals

All values are ppb

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 terminal. 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 low-flow 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

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.