CHARACTERIZATION OF NON-POLAR ORGANIC COMPOUNDS IN PETROLEUM REFINERY WASTEWATERS

By

STACIE ANN SINGLETON

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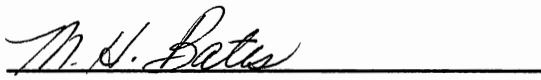

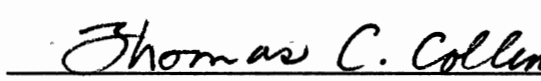

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CHAPTER I

INTRODUCTION

Petroleum refineries must meet certain guidelines established by the federal government when discharging wastewater into the environment. The discharging of toxic substances into American waters is governed by the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500). The goal of the CWA is to eventually prohibit the discharge of toxic pollutants in toxic amounts to the environment (PL 92-500). The CWA currently prohibits the discharge of pollutants to American navigable waters unless the discharger obtains a National Pollution Discharge Elimination System (NPDES) permit from the United States Environmental Protection Agency (EPA) or delegated state (PL 92-500). NPDES permits establish specific limitations for discharge levels of toxic pollutants in wastewater. If the industry exceeds toxic pollutant permit limitations, or is otherwise suspected or identified as a source of toxicity, enforcement actions will require that the industry begin a program to reduce the effluent toxicity. This program is called TRE or Toxicity Reduction Evaluation, part of the TRE/TIE (Toxicity Reduction Evaluation/Toxicity

Identification Evaluation) program. The object of TREs is to determine what measures are necessary to reduce the effluents' toxic effects to acceptable levels. The goals of this process may be set either by EPA or a state regulatory agency and are dependent on state standards (EPA, 1991).

This research investigated toxicity characterization of three process wastestreams from an area petroleum refinery. These process streams include water from the sour water stripper unit and the crude desalter unit. Previous research from the Oil Refiners Waste Control Council and the OSU WQRL found primary toxicants in the final effluent to be complex non-polar organic compounds (Burks, 1977). The Oklahoma State University Water Quality Research Laboratory (OSU WQRL) has investigated causes of petroleum refinery effluent toxicity in area refineries as well as the efficiency of activated carbon in reducing effluent toxicity (Burks, 1977; Burks, 1982; Johnson, 1990). The primary source of waste stream samples for this research, an area petroleum refinery, has consistently failed its required bioassays for the past year (Burks, 1991a).

The waste process streams from the oil refineries' contact units appear to be the sources of many of the non-polar organic contaminants. These contact units include the crude desalting unit, the coking unit, barometric condensers, and stripped waters from the sour water stripper unit (Burks, 1982). In most refineries, process waste streams are subjected to some type of biological treatment before being released to the environment as final effluent.

The biological processes most often used are biological ponds or bioditches and activated sludge units. In several area refineries, series of bioponds or activated sludge units appear to be the most effective method to reduce toxicity (Burks, 1982). A study by Burks (1977) indicated that contaminants may be of like polarity and low molecular weight, similar to molecules of naphthalene and toluene.

Research objectives were:

1. Gel fractionation of waste stream samples into discrete aliquots.
2. Determination of fractions' approximate molecular weights using gel chromatography.
3. Determination of fractional toxicity using acute bioassays.
4. Reduction of sample toxicity as measured with acute bioassays using activated carbon.

CHAPTER II

LITERATURE REVIEW

Petroleum Refinery Waste Origins

Petroleum refineries may produce gasoline, kerosine, diesel fuels, fuel oils, lubricants, gas oils and distillates, and grease (NPC, 1971; McManus, 1989). Refinery production waste was unregulated until 1972. Refineries were then required to obtain National Pollution Discharge Elimination System permits to discharge waste products directly into the aquatic environment.

Crude oil is refined by separation, conversion, treating, and blending processes. Separation is accomplished by fractional distillation which depends on the relative volatilities of hydrocarbons. Crude oil feed is heated and partially vaporized in a furnace before being taken to fractionating columns. Fractionation products are either treated and blended or fed to the conversion process (NPC, 1971).

The conversion process, or "cracking," changes the size or structure of hydrocarbons. By cracking the feed, heat-decomposition of larger molecules occurs. Small hydrocarbons are often polymerized to form larger hydrocarbons.

Hydrocracking, another type of cracking, uses a highly pressurized hydrogen atmosphere (NPC, 1971).

The treating process removes sulfur compounds for product quality and to prevent sulfur poisoning of certain catalysts. The sulfur is removed by either catalytic hydrotreating or sour water stripping (NPC, 1971). The waste stream from this process is referred to as sour water. Blending different base stocks produces final products (EPA, 1972; NPC, 1971). After extraction, crude oil is a mixture of hydrocarbons with small quantities of sulfur, oxygen, nitrogen, and trace elements, and water (EPA, 1972). Large quantities of salt water or brine may be combined with the crude oil mixture to enhance oil or gas recovery. The crude desalter waste stream is produced by separating the brine from crude oil and gas. Other wastes originate from cooling and condensing units and oil-contaminated water from inevitable small leaks as well as many other sources (NPC, 1971).

Contents of Waste Streams

Contents of the final waste streams are only partially known. Waste constituents often include aliphatic hydrocarbons such as n-alkanes, isoalkanes, resins, asphaltenes, low molecular olefins, low molecular cycloalkanes. Aromatics such as low molecular mononuclear aromatics are also present and often include benzene, alkylated benzene derivatives, naphthalene and derivatives, trinuclear aromatics (anthracene and phenanthrene) and

multinuclear aromatics (pyrene and C1- and C2-alkylpyrenes) (Kalbfus, 1986; Pearson and Gharfen, 1986; Sumskaya and Varfolomeyev, 1988). Sulfides are often present from the crude desalter process. Waste water containing ammonia and sulfides is steam-stripped in sour water strippers before biological treatment in most refineries (Esener et al., 1987). Heavy metals such as Cd, Cr, Cu, Pb, Ni, Zn, As, and Se also occur in petroleum refinery wastewaters (Burks, 1982). Phenols are usually produced both in gasoline washeries and in the cracking process (Rebhun and Galil, 1988).

Biological Treatment of Refinery Wastes

EPA (1972) suggested petroleum refinery waste water oxidation pond effluent have waste concentrations of <20 mg/l oil, 15 mg/l sulfide, and 7 mg/l phenol and a 60 day minimum retention time. Effluent of an aerated lagoon with a three month retention time showed a 94% phenol reduction to 0.4 mg/l, 96% sulfide reduction to 0.2 mg/l, 69% COD reduction to 146 mg/l, and a 76% BOD reduction to 42 mg/l. The refinery's treatment system had two aerated cells with three 60-hp mechanical aerators in the first lagoon and three 15-hp mechanical aerators in the second lagoon. The aerators were designed to transfer 13,000 pounds of oxygen per day (EPA, 1972).

Other biological treatments used on petroleum refinery wastes include trickling filters and activated sludge units (EPA, 1972). Trickling filters provide an oxygen source to

promote bacterial oxidation of oily wastewaters. The oxidation rate is determined by oil dispersion and temperature. Trickling filters have been used as primary treatment and with oxidation ponds and activated sludge units. They do not handle shock loading well and produce little sludge. Mediums used include rocks and plastic (EPA, 1972).

Activated sludge units (AS) mix wastewater, oxygen and bacteria. Complex mix systems may handle shock loads. Proper disposal of excess sludge is necessary. Disposal options for dewatered sludge include burning, burial, and use as soil conditioners. Separation of bacteria from treated waste is vital (EPA, 1972). Powdered activated carbon (PAC) can be added to AS systems to enhance adsorption of toxics and effluent quality. Cost effectiveness is reached by operating at a very high sludge age and a low carbon dose (EPA, 1978).

Fractionation Techniques

Molecular weight fractions were used to investigate unknown constituents of the final effluent, sour water and crude desalter waste streams. Fraction collection options included ultrafiltration and gel filtration chromatography, common methods in determining molecular weight distribution (Collins et al., 1986).

Ultrafiltration (UF) separates dissolved and colloidal organic matter into discrete molecular weight fractions (Reinhard, 1984). Ultrafiltration selectively rejects

solutes by convective flow, often in a pressurized, stirred cell, through a membrane (Amy et al., 1987). Molecules larger than the nominal molecular weight cutoff are retained while molecules smaller than the cutoff limit flow through the membrane as permeate (Amy et al., 1987). Sample aliquots can be passed through ranges of membranes in parallel succession. This creates a series of permeates (molecular weight fractions) just below the molecular weight cutoffs (Collins et al., 1986). Duration of sample storage, ionic strength, pH, flow rate, solute concentration, membrane type, and pressure can affect UF (Reinhard, 1984).

Gel filtration chromatography (gel permeation chromatography or size exclusion chromatography) separates higher molecular weights and is more significantly affected by pH conditions than ultrafiltration (Christian, 1980; Collins et al., 1986). Gel filtration involves a continuous flow of a mobile phase through a stationary phase. Solute fractionation is achieved by molecular diffusion (Amy et al., 1987). Smaller molecules enter gel pores easily while larger molecules pass through and are eluted off the column first. This leads to the elution of solute molecules in order of decreasing size (Pharmacia, 1976; Amy et al., 1987). Gels are characterized by molecular weight range fractionation. Biochemicals with known molecular weights are often used to calibrate the gel column (Amy et al., 1987). Many types of gels are available including silica, fused silica, micro styragel, and dextran gel. Sephadex is a bead-formed, dextran gel prepared by cross-linking

selected dextran fractions with epichlorohydrin. It has a high hydroxyl group content in its polysaccharide chains, making it strongly hydrophilic. Sephadex swells easily in water and electrolyte solutions (Pharmacia, 1976). Sephadex gels are characterized by their ability to retain or adsorb water (Christian, 1980). It is often used for fractionation of peptides, globular proteins, and dextrans (Pharmacia, 1976).

Microbial and Organismal Bioassays

Bioassays use living organisms to assess short term (acute) and long term (chronic) effects of a sample. Results are often reported as LC50, the concentration sample lethal to 50 percent of the test organisms. Bioassays may also be reported as EC50, the concentration of sample effecting 50 percent of the test organisms, such as the reduction in bacterial luminescence (Firth and Backman, 1990).

Chronic seven day growth and reproduction tests and acute 48 hour survival tests often use neonate cladocerans (*Ceriodaphnia* and *Daphnia* genus) and fathead minnow larvae (*Pimphales promelas*) (EPA, 1991). Early life stages (embryonic and larval) are most sensitive to toxicants (Norberg and Mount, 1985). Cladocerans occupy an important step in the food chain by converting phytoplankton and bacteria into nutritionally valuable animal protein (Mount and Norberg, 1984). They are small, easily maintained, and require small amounts of test sample. Cladocerans are often

more sensitive than other organisms to different types of toxicity (Mount and Norberg, 1984).

Fathead minnows are widely distributed and are important foragers in the food chain. They are easily obtained from commercial sources as well as bred and maintained in the laboratory (Norberg and Mount, 1985; Burks, 1982). Not only has a large toxicity database been established for acute and chronic tests using the fathead minnow (Norberg and Mount, 1985), but it has a median toxicity threshold relative to other fish species (Burks, 1982).

The Microtox bioassay (Microbics Corporation) utilizes the bioluminescent marine bacteria *P. phosphoreum* (Firth and Backman, 1990; Microbics, 1990). Chemical inhibition of any enzymes involved in the luminescence process will alter the bacterial rate of light production (De Zwart and Slooff, 1983). Bioassay results are based on sample light emission compared with a blank standard emission (De Zwart and Slooff, 1983).

Several studies compared the relative sensitivity between Microtox, cladocerans, and fish (Burks, 1983). One study showed *Daphnia* sp. to be more sensitive than Microtox to ammonia, cyanide, hexachloro-ethane, pentadione, and sodium lauryl sulphate (Munkittrick et al., 1991). No sensitivity differences were found to propanol, PCP, toluene, and some mono/di-chlorinated benzenes, phenols and ethanols. *Daphnia* sp. was reported to be less sensitive than Microtox to chloroform, styrene, and highly substituted

organics as multi-chlorinated benzenes, phenols, ethanols, and substituted pentadiones (Munkittrick et al., 1991). Firth and Backman (1990) reported that *Ceriodaphnia* sp. was more sensitive to bleach draft facility wastewater and pulp and paper mill final effluents than Microtox. De Zwart and Slooff (1983) showed that *D. magna* and *D. pulex* LC50s were 2.54 and 3.48, respectively, times more sensitive than Microtox EC10s after 48 hours exposure for each of fifteen chemicals.

Munkittrick et al. (1991) also showed fathead minnows were more sensitive than Microtox to cyanide, chloroethanol, hexachlorethane, benzene, pentadione, and acetone. Microtox was more sensitive to multichlorinated phenols, substituted pentadiones and sodium lauryl sulfate than the fathead minnows. Firth and Backman (1990) compared rainbow trout to Microtox using pulp- and paper-wastewater streams and sulfite mill wastewater. Microtox was a good predictor of the trout response. De Zwart and Slooff (1983) reported that *P. promelas* was 1.99 times more sensitive (48 hour LC10) than Microtox (EC10) for 15 chemicals.

Qureshi et al. (1982) compiled data from several studies. The Microtox 5 minute EC50s from two oil refinery effluents ranged from 6.5 % to over 50%. Microtox was more sensitive than rainbow trout and *Daphnia* sp. for the two effluents. Munkittrick et al. (1991) commented that Microtox highly correlated with rainbow trout assays and noted that Microtox results were less variable. This study also noted that Microtox would be good for monitoring

relative changes in petroleum refinery wastewaters. Chang et al. (1981) used several environmental samples with Microtox, including effluents from five oil refineries. Microtox EC50s ranged from 58% to 100% with one exception at 1.8%.

Physical-Chemical Analyses: SPE and HPLC

Solid phase extraction (SPE) or sorbant extraction retains solute molecules from a solvent onto a solid phase or sorbant by Van der Waals (dispersion) forces (Van Horne, 1990). The solid phase has non-polar surface functional groups with greater attraction for solute molecules than the solvent in which it is dissolved (Van Horne, 1990). Elution is facilitated by a mobile phase or solvent with sufficient non-polar character to disrupt the non-polar isolate/sorbant interactions (Van Horne, 1990). Bonded silica is often used as the solid phase. Different types of bonded silica exhibit specific properties, resulting from functional groups covalently bonded to the silica substrate (J. T. Baker, 1991).

Bonded silicas are produced by reacting organosilanes with activated silica. The resulting sorbant has organo-silane functional groups attached to the silica substrate with silyl ether linkages. The C18 type consists of octadecyl silane bonded to the silica substrate. This is the most widely used sorbant for non-polar interactions and tends to be a very non-selective sorbant (Van Horne, 1990).

High performance liquid chromatography or HPLC collects

separated components or isolates for alternative analyses (Cotterill and Byast, 1984). Because chromatography methods are separative, they cannot positively identify compounds. Through the use of different column packings, solvent systems, and a variety of detectors, HPLC can indicate characteristics of unknown compounds (Cotterill and Byast, 1984).

The separation efficiency of the column is inversely proportional to the packing particle size. The pressure drop in the system is proportional to the column length of a given packing material. Relatively short columns and fine packing materials are most often used. The stationary phase is chemically bonded to the supporting media to overcome column bleeding. One bonded phase, C18, is a versatile system and is used with a polar eluant (Cotterill and Byast, 1984).

HPLC fractionates compounds according to hydrophobicity or "water hating" properties. A more hydrophobic compound is recorded at the beginning of a chromatograph or at lesser retention times. A less hydrophobic compound is recorded at the end or greater retention times. For most relatively non-polar chemicals, this may show relative molecular weight (Yates, 1991). Generally, but not always, lower molecular weight compounds are recorded earlier and greater molecular weight compounds are recorded later (Yates, 1991).

Activated Carbon Treatment

Carbon adsorption effectiveness and efficiency are

influenced by organic matter concentration range, temperature, pH, and competing organics (Weber, 1984). Activated carbon capacities for organics adsorption vary. In general, polar, low molecular weight substances are not adsorbed well by carbon. Substances of medium to high molecular weight and low polarity are strongly adsorbed. Examples are aromatics, pesticides, polychlorinated biphenols (PCB's) and polynuclear aromatic hydrocarbons (PAH's) (Weber, 1984).

Oil refinery wastewaters can be treated with activated carbon (EPA, 1978). PAC (powdered activated carbon) is used as an additive and GAC (granular activated carbon) is used in large columns for wastewater treatment. The amount of carbon used can be varied.

Refinery effluent (EPA, 1978) averaged 82% BOD reduction and as PAC built up in the system, BOD removals reached 90-95%. Effluent COD was reduced from an average of 1180 ppm without carbon to 350 ppm with carbon. Average TOC decreased from 420 ppm to 100 ppm. Total carbon decreased from 520 ppm to 180 ppm. The treatment system used eight carbon columns with 0.03 m^3 activated carbon per column (EPA, 1978).

Effluent Characterization Studies

Few studies have investigated molecular weight fractionation of petroleum refinery wastewater and fractionation toxicity. Dorn et al. (1991) used TIE procedures to identify a chlorether fraction in petrochemical plant

effluent. The fraction was obtained by acid washing and vacuum distillation of a free organic phase separated from a continuous aqueous phase in an upstream process unit (Dorn et al., 1991).

Aquatic toxicity test results showed similar responses from sheepshead minnows and mysid shrimp to the whole effluent fraction. TIE studies indicated the toxic fraction was the total organic halide component with chloroethers. A secondary cause of toxicity appeared to be the cationic calcium species, affecting the mysid shrimp more than the minnows. The chloroether fraction was reported to be acutely and chronically toxic to the aquatic species. When diluted to receiving water concentrations of < 0.001%, no toxicity affected the test organisms. The same study reported that the chloroether fraction probably would not sorb to aquatic bottom sediments or bioconcentrate. The "safe" instream concentration for this mixture should be less than 1 mg/l (Dorn, et al. 1991).

Johnson (1990) used filtration, EDTA chelation, air stripping, and C18 solid phase extraction to fractionate domestic wastewater. A GC/MS was used for analytical analysis. Microtox and *C. dubia* bioassays were used to assess fraction toxicity.

Kalbfus (1986) analyzed hydrocarbons found in liquid process wastes and oil-polluted rainwater from three German oil refineries with catalytic cracking facilities. Samples were taken downstream of the oil separator. The two largest peak concentrations of aliphatic hydrocarbons with n-C_9H_{20}

and n-$C_{19}H_{40}$ had base molecular weights of 128.26 and 268.53, respectively. The proportional content of isoalkanes was low in comparison with n-alkanes and those that were present showed a low degree of isomerization. Additionly, large numbers of low-molecular weight olefins and cyclohexanes were present. Aliphatic concentrations in crude oil were higher than aromatic concentrations. Kalbfus (1986) found that untreated refinery wastes principly contained low molecular weight mononuclear aromatics, including benzene. Naphthalene, as well as C_1-, C_2-, and C_3-alkylnaphthalene derivatives (with more 1- and 2-methyl-naphthalene than unsubstituted naphthalene) were found in high concentrations (Kalbfus, 1986).

Sumskaya and Varfolomeyev (1988) investigated petroleum residues of biologically treated oil refinery wastewater. Infrared spectrophotometry (IR), mass spectrometry (MS), and gas liquid chromatography (GLC) identified fractions. Effluent was fractionated by distillation. Sumskaya and Varfolomeyev (1988) stated that distillation was a better process to fractionate wastewater. It leads to better separation of the petroleum products adsorbed on the surface of suspended particles.

A high content of binuclear aromatic structures was reported using IR spectral analysis. Biologically treated wastewater contained mono- and dimethylnaphthalenes, acenaphthalene, fluorene, dihydroanthracene, and phen-anthrene. Aromatic hydrocarbons accounted for 25-43% of the total content of neutral organic compounds (Sumskaya and

Varfolomeyev, 1988). They concluded that oxidation products (neutral and weakly acidic resinous substances) in biologically treated refinery effluent were 5-10 times greater than the petroleum products.

Other studies characterized crude oil, rather than the refinery waste streams (Schmitter et al., 1983; Kvalheim et al., 1985; Campbell and Lee, 1986; Grizzle and Sablotny, 1986; Larsen et al., 1986; and Pearson and Gharfeh, 1986). Wise et al. (1988) used separation techniques to analyze polycyclic aromatic hydrocarbons (PAHs) in complex mixtures. Most studies used GC or HPLC to identify constituents.

CHAPTER III

MATERIALS AND METHODS

Refinery Wastewater

Waste stream samples (final effluent (FE), sour water stripper water (SW), and crude desalter water (CD)) came from an area petroleum refinery, UPB. Area refineries are referred to by three letter codes. Samples were collected at the refinery in late July 1991 and early October 1991 and shipped to the OSU WQRL.

UPB refinery has an oil refining capacity of 65,000 barrels per day and discharges 396,000 to 468,000 gallons of wastewater per day (Marshall, 1991). The refinery wastewater treatment process consists of a stripping tower for ammonia and sulfide removal, an API gravity oil separator, a heat exchanger, and a system of 22 lagoons. Seven of the lagoons are aggressively aerated, utilizing one 7.5 hp pump per million gallons wastewater (Marshall, 1991). The remaining fifteen lagoons are bubble aerated using an octopus distribution system. The lagoon system retention time varies but is currently approximated at 12-18 days (Marshall, 1991). A clarifying pond is located at the end of the lagoon system. Two carbon filters were recently

installed but are not currently on line. Final effluent is discharged into a ditch that leads to a tributary of a nearby creek (Marshall, 1991).

Design Overview

Half of the three waste stream samples collected were treated with activated carbon and compared with untreated samples (Figure 1). Ammonia concentration, alkalinity, COD, TOC, pH, temperature, hardness, and conductivity were measured. Extractants from C18 columns were injected onto the HPLC. Peak areas from raw and carbon treated samples were compared. Molecular weight fractionation of C18 extractant was accomplished by Sephadex gel column chromatography.

Three bioassay methods used cladocerans (*Ceriodaphnia dubia*), fathead minnow larvae (*Pimephales promelas*), and marine bacteria (*Photobacterium phosphoreum*) as test organisms. Microtox, the bacterial assay, was used frequently. Fathead minnow and *C. dubia* 48 hour acute bioassays were also performed. Toxicity estimates were made by determining the percent mortality. LC50s were not calculated for organismal assays because multiple dilutions were not made.

Preliminary Physical-Chemical Analyses

A suitable buffering eluent or mobile phase for the Sephadex gel column was selected from very hard and moderately hard reconstituted water. The mobile phase

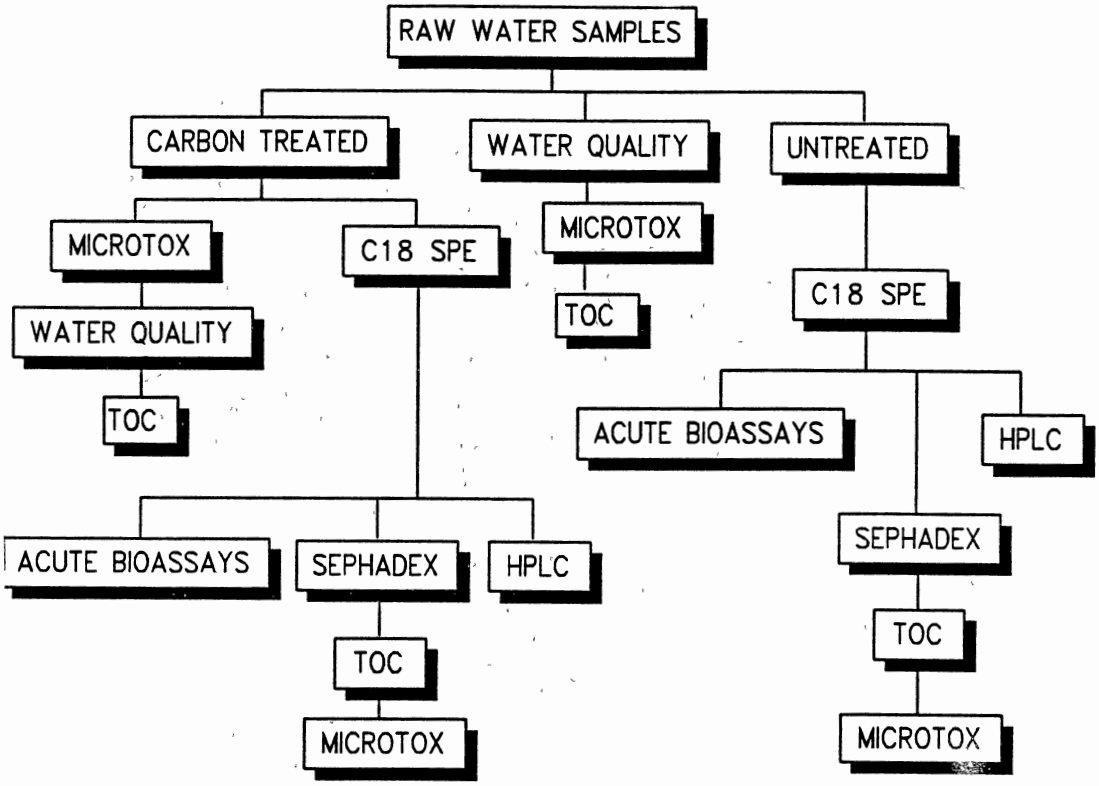

Figure 1. Project Design

conductivity, pH, and hardness were matched to the samples as closely as possible to prevent fractionation interferences. Conductivity (EPA, 1979), pH (EPA, 1979), and hardness (EPA, 1979) were performed on final effluent from two area refineries (DPQ and LNX) due to availability.

Gel Column Preparation

Sephadex G-15 gel was obtained from Pharmacia Fine Chemicals. The dry gel has a particle diameter of 40-120 u (microns) and a molecular weight fractionation range of 1500 and below. The gel has a water retaining value of 1.5 $\pm$ 0.2 ml/g dry gel (Christian, 1980). Pharmacia (1976) suggests using biocide in the buffer solution to decrease bacterial growth when the column is kept at room temperature. Because the biocide could interfere with organismal and Microtox bioassays, prospective biocide toxicity was determined. A 0.02% solution of sodium azide, one of the less toxic biocides Pharmacia suggests, was tested with Microtox and determined too toxic for use. Cold storage was chosen as an alternative. A temperature of 3° C appeared to prohibit bacterial growth for the duration of the project.

A pyrex Supelco column 50 cm X 2.5 cm with a bed volume of 4.91 ml/cm and a total capacity of 245.0 ml was used. Approximately 80 grams (dry) of the gel was soaked 12 to 24 hours in very hard reconstituted water (VH recon). After the column was poured (Figure 2), the void volume (one column volume) was determined to be approximately 100 mls. Blue dextran (Sigma) was dissolved in VH recon until the

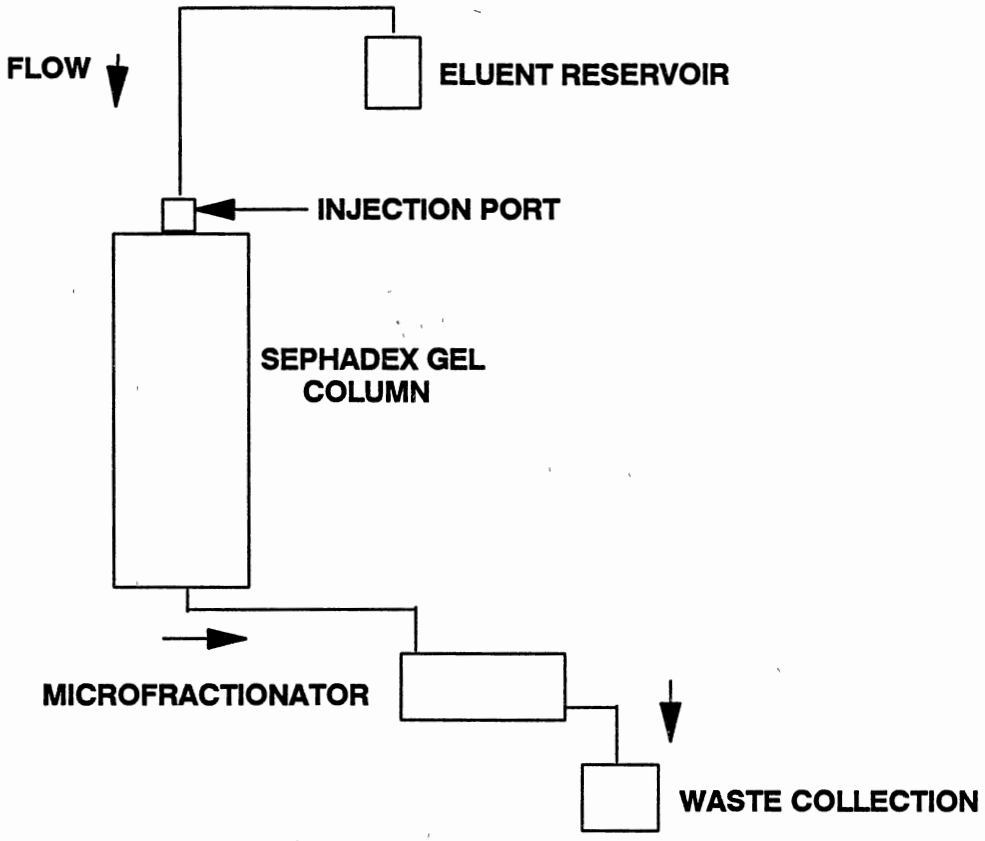

Figure 2. Sephadex System

solution was dark blue. One ml of blue dextran solution was injected onto the column and 1.5 ml or 31 drop fractions of eluent were collected by a Gilson FC-80 microfractionator operating in drop count mode. Eighty 13 mm X 100 mm pyrex test tubes were used for each collection. Blue dextran injections allowed visual observation of plug flow behavior. Blue dextran fractions were analyzed by a Secomam S. 1000 G UV-Vis Spectrophotometer. Six blue dextran injections were analyzed. Two wavelengths (610 nm and 380 nm) suggested by Sigma were used. Five of the runs were read at 610 nm and one was read at 380 nm, 610 nm being preferred. Absorbance and percent transmittance were recorded.

The column was marked for molecular weight elution using three substances: beta-NAD (1430 mw), bacitracin (724 mw), and raffinose (595 mw). Marker concentrations were 100 mg/l and 250 mg/l using VH recon water as solvent. Low range COD (EPA, 1979) results for 100 mg/l markers were too low for accurate readings. Injections were made using 250 mg/l concentrations and molecular weight elutions were determined. Bacitracin, beta-NAD, and raffinose data were linearly regressed to obtain a calibration curve from which corresponding volumes/molecular weights were found.

An eluent to extract compounds from C18 SPE columns was determined. Methanol (32.04 mw), hexane (86.18 mw), and decane (142.3 mw) were tested for toxicity using Microtox. Methanol is a commonly used eluent for C18 SPE. Hexane and decane were also examined, with the hope that higher molecular weight substances would decrease cell diffusion

and cause less damage to the test organisms, therefore increasing the EC50. Using Microtox bioassays, methanol was shown to be the least toxic of the three.

Physical-Chemical Analyses

A battery of physical-chemical tests were performed within approximately 72 hours of sample arrival. Samples were stored at 4° C. The analyses performed included pH, conductivity, hardness, and high-range COD. Alkalinity (EPA, 1979), temperature (EPA, 1979), TOC (EPA, 1979), and ammonia nitrogen (EPA, 1979) were also performed.

Total organic carbon (TOC) was determined with an O. I. Corporation Model 524 Carbon Analyzer. Ten microliter sample aliquots were injected into the DIM (direct injection module). A Hewlett Packard 3380 integrator determined peak areas. Raffinose standards in concentrations of 250, 500, 700, 1000, and 2500 mg/l as raffinose or 9.1, 18.2, 27.3, 36.4, and 91 mg/l carbon, respectively, were also analyzed. Standard peak areas were linearly regressed with the carbon content to develop a curve from which the carbon content of samples could be determined.

Microtox Bioassays

Acute laboratory bioassays determined the toxicity of raw and carbon treated waste streams. Microtox was used to determine the relative toxicity of molecular weight fractions from raw and treated samples.

A Microbics Microtox Model 500 with a 30-well incubator

block was used. Samples were prepared by two methods. The 100% assay required 2.5 mls of osmotically adjusted sample. Four 1 ml dilutions (1:2 sample:diluent) were made. The reagent (freeze-dried *P. phosphoreum*) was prepared by mixing powdered reagent with Microbics' reconstituting solution in the reagent well, maintained at 5° C. For each set of dilutions, a diluent blank was used. Samples were osmotically adjusted using MOAS (Microtox osmotic adjusting solution) for the 100% assay. Samples were osmotically adjusted with sodium chloride. This method was used when too little sample was collected to perform 100% assays. No dilutions were made when sodium chloride was used. Because no dilutions were made, EC50s could not be calculated and only rough estimates of toxicity could be made. This was used for the Sephadex fractionated samples due to sample size and to unknown amounts of methanol present in the fractions. Methanol, hexane, and decane were tested to determine the least toxic substance for solid phase extraction. Raw and treated effluent sample EC50s were determined.

C18 Solid Phase Extraction

J. T. Baker BAKERBOND C18 SPE octadecyl syringe columns were used for solid phase extraction. The column was conditioned by force pipetting 10-12 mls filtered HPLC grade methanol through each column followed by 10-12 mls filtered reagent grade water. Each waste stream was vacuum filtered using a Buchner funnel and Gelman glass fiber

filters (102 mm, Type A-E) to remove particulates before SPE. An air vacuum was used to pull one liter of sample through each C18 column. Eluent water was discarded and SPE columns were sealed in parafilm and aluminum foil, and refrigerated at 4° C until extraction. Three laboratory standard solutions (80%, 90%, 100%) of methanol:reagent grade water were used to extract compounds from each column. Two mls of each standard solution were sequentially passed through the column, beginning with the 80% solution. A total of 6 mls extracted sample for each raw and treated waste stream were sealed and refrigerated at 4° C.

HPLC Analysis

Compounds were also resolved and analyzed by HPLC. A Phenomenex Bondclone C18 column (3.6 mm X 300 mm) was used for reverse phase separation of non-polar organic compounds. A mobile phase of filtered reagent grade water and HPLC grade methanol was used. For each run, a gradient flow of 70% water/30% methanol to 100% methanol lasted approximately 45 minutes, followed by a constant flow of 100% methanol for 5 minutes. A gradient step back to 70% water/30% methanol lasted 5 minutes. A final 5 minute equilibrium flow of 70% water/30% methanol completed the run. Two Waters 501 Solvent Delivery System pumps delivered filtered water and HPLC grade methanol to the column. The column flow rate was kept to one ml/min. Daily start-up procedures required the pumps to be run manually. During sample runs pump control was integrated to the Maxima 820 computer control system

through the Waters System Interface Module (SIM box).

A Waters 484 Turnable Absorbance Detector was used. Wavelength was set at 278 nm for the C18 column, the sensitivity was kept at 0, and the sample injection volume was 10 μl. Additional methanol was run through the system to clean the lines and the column. A standard run using phenol, toluene, and fluoranthene was made. Analysis of the sample runs by the Maxima 820 computer program included peak integration and peak area calculations. Because compounds were not identified, retention times and peak areas were compared.

Activated Carbon Treatment

Each waste stream was run through carbon columns containing Westvaco Nuchar WV-B activated carbon (Table I). Glenco glass columns were used and measured 1.91 cm X 33.02 cm with an internal capacity of approximately 94.61 cm^3. Carbon was washed and dried to eliminate fines. Approximately 23-29 grams (60-70 mls) carbon were used per column with glass wool in both column ends. Reagent grade water was initially run to eliminate carbon fines. Approximately three liters of each waste stream were treated in an upflow mode. Loading rates were 2.13 gal/min ft^2 for final effluent, 1.93 gal/min ft^2 for sour water, and 2.19 gal/min ft^2 for crude desalter water. Empty bed contact times (EBCT) were 3.35 minutes for final effluent, 3.70 minutes for sour water, and 3.26 minutes for crude desalter water.

TABLE 1

NUCHAR WV-B ACTIVATED CARBON CHARACTERISTICS*

Molasses Decolorizing Index	14 (min)
Iodine Number (mg/g)	900 (min)
Butane Working Capacity (g/100 ml)	7 (min)
Moisture, as packed (%)	10 (max)
Particle Size (U.S. Sieve Series)	4 X 14
Oversize (%)	8 (max)
Undersize (%)	5 (max)
Apparent Density (lb/ft^3) or (kg/m^3)	14-18 or 224-289
Surface Area (Nitrogen BET Method) (m^2/g)	1400-1600

*from Westvaco Product Data Bulletin G-103

Sephadex Gel Fractionation

One ml aliquots of SPE extract from raw and treated waste streams were individually injected onto the Sephadex column. The flow rate was approximately one ml/min, averaging about 2-3 hours for completion of a run. Effluent was collected by a Gilson FC-80 microfractionator in aliquots of 2.5 mls. Two hundred milliliters were collected for each waste stream. Fractions were analyzed for total organic carbon. Fractions containing elevated levels of TOC were sequentially paired. Microtox bioassays were run on each paired sample.

Organismal Bioassays

Forty-eight hour acute bioassays using cladocerans (*C. dubia*) and fathead minnows (*P. promelas*) were performed on raw and carbon treated waste streams. For each raw and treated waste stream, toxicity test exposure units included eight sample cups, one blank cup, and one methanol standard cup. Each cup contained six *Ceriodaphnia* neonates or fathead minnow larvae < 24 hours old in 10 ml of VH recon water (blank). Methanol standards had 15 ul (1.5%) HPLC grade methanol added to the 10 mls of VH recon water. Sample cups were prepared by adding 15 ul (1.5%) waste stream C18 extract to the 10 mls of VH recon water. One dilution was used for all samples. Eight cups for each of three raw samples and three treated samples were made for each assay. A total of 360 larval minnows and 360 neonate

cladocerans were used. Cladocerans were fed 2 drops/cup suspended algae and 2 drops/cup digested trout chow, cerophyll, and yeast (TCY) twice during the assay. Organisms were visually monitored at 2, 4, 8, 24, and 48 hours for survival with a dissecting scope. Mortality for each cup was recorded. Estimates of sample toxicity were made using percent mortality. LC50s were not calculated.

Statistics

Student's T-test analysis was performed on data to compare treated and raw waste streams. The Systat statistical computer package (Wilkinson, 1990) was used to perform T-test analysis on water quality parameters and Microtox data. Sephadex fractions and TOC analyses did not result in enough sample to prepare 100% Microtox assays. In these cases, averages of data were compared.

Microbic's Microtox statistics package was used to calculate EC50 values. Average luminescence readings were used by the program to calculate gamma values. The software program calculates a calibration curve by performing a linear regression plot of dilution concentration versus gamma values. The curve slope and 95% confidence ranges were calculated.

CHAPTER IV

RESULTS AND DISCUSSION

Petroleum refinery waste streams were analyzed using TRE/TIE assessment techniques. Three waste streams were carbon treated: final effluent (FE), sour water stripper effluent (SW), and crude desalter effluent (CD). Microbial and organismal bioassays were used to assess waste stream toxicity before and after carbon treatment. C18 solid phase extraction was performed on raw and carbon treated waste streams. HPLC analysis and Sephadex gel fractionation used C18 extract. Fractions eluted from the Sephadex gel column were tested for TOC and microbial toxicity.

Preliminary Results

Preliminary conductivity, pH, and hardness assays (Table II) were conducted on waste streams from LNX and DPQ refineries. These assays indicated very hard reconstituted water (VH recon) would be compatible with waste stream samples. The conductivity (μs, microsiemens) of the VH recon was similar to sour water and final effluent conductivities. The pH of the samples (Table II) ranged from 6.6 to 8.4. Final effluent contained between 223-348

TABLE II

PRELIMINARY ELUENT TESTS

Water Sample (Raw)	Conductivity (μs)	pH	Hardness mg/l $CaCO_3$
DPQ Refinery:			
SW	598	6.6	---
CD	10700	7.6	---
LNX Refinery:			
FE	1420-2470	7.0-8.0	223-348
(2 samples)	1560-1790	7.0-8.0	264-314
V H RECON*	945	8.4	260-300
M H RECON**	250-300	---	70-80

*=very hard reconstituted water
**=moderately hard reconstituted water

mg/l $CaCO_3$ hardness while VH recon water showed 264-314 mg/l $CaCO_3$ hardness. Moderately hard recon water had 70-80 mg/l $CaCO_3$ hardness. The best choice for a column eluent was VH recon. Conductance, hardness, and pH appeared compatible between VH recon and waste streams.

A solid phase extraction carrier was determined from methanol, hexane, and decane by using Microtox bioassays (Table III). Methanol had the highest Microtox value and was the least toxic. Lower bacterial toxicity of hexane and decane from reduced biochemical disruption resulting from decreased membrane diffusion was anticipated because of their higher molecular weights (Burks, 1991b). Microtox disproved this and methanol was chosen. Methanol also flowed through the gel column more evenly. Hexane and decane did not appear miscible with the VH recon water and formed separate phases at the top of the column after injection. Methanol was also used as a mobile phase in HPLC analysis.

A Sephadex gel column molecular weight range was determined from linearly regressed marker data (Figure 3). Sephadex G-15 should theoretically fractionate from 1500 to 0 molecular weight. TOC analysis from practice fractions showed elevated TOC levels ending around 275 mls. From the calibration curve, TOC levels should end around 160 mls. The calibration curve is speculated to asymptote as it approaches 0 molecular weight. Thus the column would elute small molecules at large eluent volumes.

TABLE III

PERCENT LIGHT INHIBITION OF POTENTIAL CARRIERS

Carrier	Microtox Average Readings							EC50
				Dilutions				
	Blank	2.8%	5.6%	11%	22%	45%	90%	
Methanol	80.5	76.8	47.3	5.5	0.0	--	--	--*
Hexane	88.3	42.8	27.3	21.5	12.3	--	--	2.48
Decane (prelim. assay)	94.5	--	--	21.0	6.5	5.5	0.0	--

*=Insufficient data for calculation

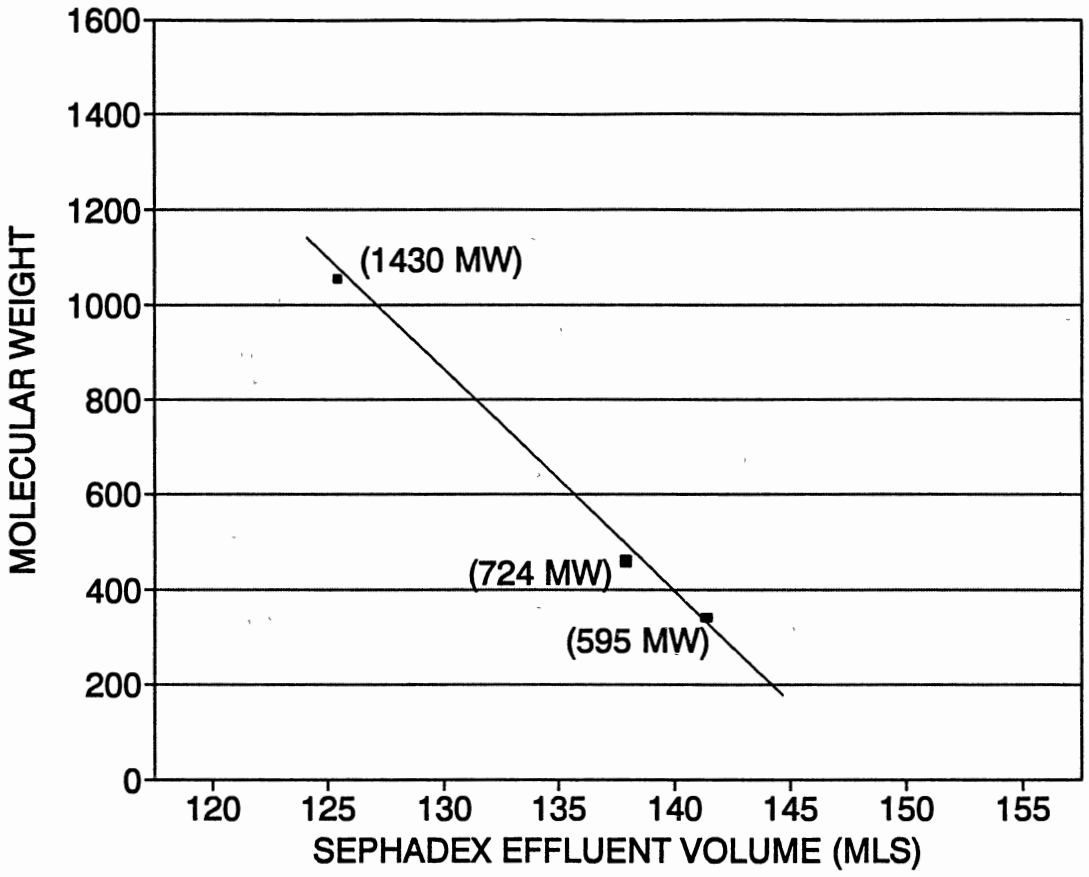

Figure 3. Molecular Weight Range of Sephadex Column

Raw and Carbon Treated Final Effluent Results

Raw final effluent means, ranges, and standard deviations are listed in Table IV. The pH for raw final effluent ranged from 6.9-7.2 to carbon treated values of 7.1 These were not significant as determined by Student's T-test. Carbon treated final effluent means, ranges and standard deviations are listed in Table V. The pH for all four replicates was 7.1. The raw sample temperature was 15° C, 4.5° C higher than the carbon treated replicates. Raw samples were inadvertently left at room temperature longer. The relatively small temperature change should have little or no effect on physical-chemical analyses or activated carbon adsorption (Weber, 1972).

The Student's T-test was used to compare water quality parameters between raw and carbon treated waste streams (Table VI). Raw and carbon treated final effluent values were significantly different for alkalinity, increasing from 64.5 mg/l $CaCO_3$ in raw samples to 77.0 mg/l $CaCO_3$ in treated samples. Ammonia nitrogen increased significantly in final effluent (Table VI) after carbon treatment from 11.8 ppm (parts per million) to 14.3 ppm. Activated carbon does not remove ammonia nitrogen. Carbon may remove organic nitrogen in domestic wastewaters with 50-90% removal efficiency (Metcalf and Eddy, 1972). These ammonia levels were higher than values from an EPA (1981) petroleum refinery study. Carbon treated, lagoon-aerated, and aquaculture treated

TABLE IV

RAW FINAL EFFLUENT RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	65 mg/l $CaCO_3$	64-66	0.9
Ammonia	11.8 ppm	10.7-13.2	1.1
COD	147 mg/l	141-153	6.9
Conductivity	6053 μs	6000-6080	33
Hardness	103 mg/l $CaCO_3$	98-106	3.0
pH	---	6.9-7.2	---
Temperature	15° C	none	0
TOC	36 mg/l	26-49	9.0

TABLE V

CARBON TREATED FINAL EFFLUENT RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	77 mg/l $CaCO_3$	76-80	1.7
Ammonia	14 ppm	13.9-14.4	0.3
COD	88 mg/l	85-97	6.00
Conductivity	6083 μs	6060-6090	13
Hardness	101.5 mg/l $CaCO_3$	96-104	3.3
pH	---	7.1**	---
Temperature	10.5° C	10-11	0.4
TOC	38.6* mg/l	29-50	8.6

*=3 replicates
**=all 4 values were 7.1

TABLE VI

T-TEST RESULTS OF WATER QUALITY ANALYSIS

Analysis	Type	Treatments	T	DF	PROB
Alkalinity	FE	Raw/Treated	9.934	3	0.002
	SW	Raw/Treated	8.660	3	0.003
	CD	Raw/Treated	1.555	2	0.260#
Ammonia	FE	Raw/Treated	4.313	3	0.023
	SW	Raw/Treated	14.897	3	0.001
	CD	Raw/Treated	14.177	3	0.001
COD	FE	Raw/Treated	-10.271	3	0.002
	SW	Raw/Treated	-20.859	3	0
	CD	Raw/Treated	-10.577	3	0.002
Conductivity	FE	Raw/Treated	2.449	3	0.092#
	SW	Raw/Treated	138.392	3	0
	CD	Raw/Treated	-8.198	3	0.004
Hardness	FE	Raw/Treated	-0.293	3	0.789#
	SW	Raw/Treated	0	0	1.000#
	CD	Raw/Treated	0	0	1.000#
pH	FE	Raw/Treated	0.676	3	0.547#
	SW	Raw/Treated	-5.960	3	0.009
	CD	Raw/Treated	15.588	3	0.001
TOC	FE	Raw/Treated	-0.256	2	0.822#
	SW	Raw/Treated	1.119	2	0.379#
	CD	Raw/Treated	-1.159	2	0.366#

#=Not significant at 0.05

final effluent averaged 1.0, 0.66, and 1.0 mg/l ammonia nitrogen, respectively. A study using three treatments (activated sludge, activated sludge-dual media filter, and activated sludge-dual media filter-activated carbon) showed ammonia levels were more consistent using activated carbon. All activated carbon values averaged from 14.6 to 17.7 mg/l (Burks, 1977). Similar responses were found at other petroleum refineries in the same study.

COD in raw final effluent was significantly reduced by activated carbon treatment (Table VI). Raw samples averaged 147 mg/l COD after UPB refinery biological treatment. Carbon treated samples averaged 88 mg/l COD, a difference of 59 mg/l COD. EPA (1971) gave typical COD refinery untreated waste values as 226-257 mg/l.

EPA (1981) obtained petroleum refinery effluent from the final discharge point. The effluent was treated by aerated lagoon, aquaculture, pilot-scale dual media filter (containing sand and anthracite coal), and activated carbon. The activated carbon treatment reduced COD concentrations (31.4 mg/l mean) to one-fourth the COD concentrations of the other two treatments (128.1 mg/l mean, aerated lagoon; 137.0 mg/l mean, aquaculture). Adding activated carbon treatment to activated sludge and dual media treated final effluent reduced COD concentrations from 200-300 mg/l to less than 50 mg/l. Similar responses were found at other petroleum refineries in the study.

No significant differences in conductivity were found

between raw and treated final effluent (Table VI). Only a slight increase was shown between raw and carbon treated final effluent, from 6052.5 to 6082.5 μs. No significant differences were found between raw and carbon treated final effluent for hardness analyses (Table VI). The hardness of all samples remained unchanged. Activated carbon does not remove divalent cations (calcium, magnesium, strontium, ferrous iron, and manganous) (Weber, 1984). Compounds of relatively small molecular weight and high polarity are poorly adsorbed by activated carbon (Sawyer and McCarty, 1978; Weber, 1984).

Total organic carbon analysis (TOC) (Tables IV, V) was performed on raw and carbon treated samples before C18 SPE. TOC values were expected to decrease after activated carbon treatment. However, TOC showed an insignificant increase in the final effluent (36 mg/l to 39 mg/l TOC). This may indicate that the activated carbon was overloaded. A decrease in TOC was reported by EPA (1981) for activated carbon treatment of petroleum refinery final effluent. The carbon treated effluent TOC was reduced to a mean of 11.2 mg/l. This compares with means of 45.1 mg/l and 46.9 mg/l for aerated lagoon and aquaculture treatments, respectively. Burks (1977) showed that, by adding activated carbon to treatments of activated sludge and dual media, average TOC concentrations were reduced in final effluent from 67.2 mg/l to about 6.7 mg/l. Similar responses were shown in other area refineries. The EPA (1971) study reported average TOC values (45-51 mg/l for raw wastewater) from various

petroleum refineries' final effluents.

Microtox bioassays were used on raw and carbon treated whole final effluent and on Sephadex column fractions. EC50s were calculated using Microbic's Microtox statistics package (Figure 4) and are reported in percent effluent. Activated carbon did not decrease Microtox toxicity for final effluent. The statistics program extrapolated an EC50 of 120.65% for raw final effluent. This effluent essentially showed no toxicity. The computer program simply stated "no toxicity" for carbon treated final effluent.

Symons and Sims (1988) reported Microtox bioassay results correlated with rainbow trout bioassay results and were more sensitive to inhibitory chemicals than activated sludge organisms. The complex wastes used by the study included a composite of American Petroleum Institute (API) separator sludge, dissolved air flotation float, and slop oil emulsion solids. These were mixed with two types of soil. Soil and leachate samples were then analyzed using Microtox bioassays. They concluded that Microtox provided a method for assessing the relative extent and rates of detoxification of complex petroleum wastes in soils.

Microtox bioassays were conducted on eluent fractions collected from the Sephadex gel column. Final effluent fraction toxicity between raw and carbon treated samples were significantly different (Table VII). A total volume of 27.5 mls was collected and were "located" from 172.5-200 mls eluent, corresponding to less than 500 mw (Figure 3). Microtox luminescence readings were compared (Table VIII).

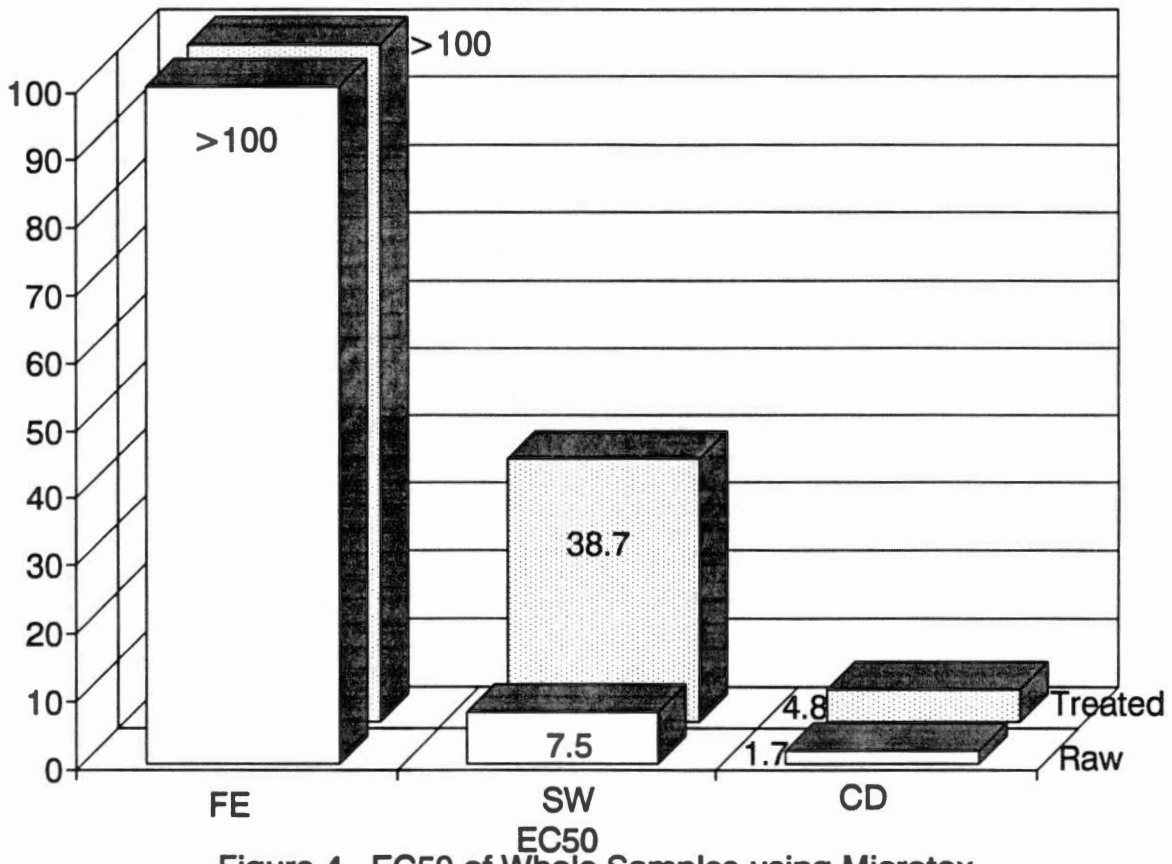

Figure 4. EC50 of Whole Samples using Microtox

TABLE VII

T-TEST RESULTS ON AVERAGE MICROTOX READINGS FROM SEPHADEX ELUENT FRACTIONS

Type	Treatment	T	DF	PROB
FE	Raw vs Treated	-11.549	4	0
SW	Raw vs Treated	-0.150	4	0.888#
CD	Raw vs Treated	-3.572	4	0.023

#=Not significantly different

TABLE VIII

AVERAGE MICROTOX READINGS* SEPHADEX ELUENT FRACTIONS

EFF	Treat-ment	Blank	Volume (mls)				
			177.5 to 180.0	182.5 to 185.0	187.5 to 190.0	192.5 to 195.0	197.5 to 200.0
FE	Raw	93.0	40.3	40.7	41.0	42.3	45.0
	Treated	103.7	70.7	68.7	70.7	70.3	62.7
SW	Raw	105.7	37.0	32.7	34.0	35.0	38.3
	Treated	92.0	31.7	34.3	38.0	38.3	36.0
CD	Raw	92.3	58.7	53.3	51.0	55.7	50.0
	Treated	95.3	61.0	64.3	62.7	58.3	61.7

*=lumninescence readings, not EC50s

EC50s were not calculated. Too little sample was collected to make dilutions. Occasionally, less than 2.5 mls per test tube was collected due to inconsistencies in the micro-fractionator. Had more sample per tube been collected, the molecular weight range captured per tube would have increased. Toxicity did not increase significantly as the eluting volume increased and the molecular weight decreased. Average Microtox luminescence readings between raw and treated final effluent decreased (Table VIII) showing reduced toxicity with activated carbon treatment.

Concentration and dilution factors were calculated for the C18 SPE and Sephadex column (Table IX). Whole effluent TOC mass was compared to mass recovered from the Sephadex gel column. The C18 concentration factor was calculated by dividing one liter (volume through the C18 column) by the whole effluent TOC mass. The dilution factor was calculated by dividing one ml (volume injected onto column) by the amount of eluent collected with elevated TOC levels (27.5 ml). This was constant for all waste streams. The C18 concentration factor (Table IX) was 29 for raw final effluent. The overall concentration factor was 1. The percent TOC recovered was 23% Carbon treated final effluent results showed 39 mg TOC injected and 6 mg TOC recovered from the Sephadex gel column. A C18 concentration factor of 26 was obtained with an overall concentration factor of 0.9.

Raw and treated final effluent C18 extract was run through the HPLC. Identification of peaks was not possible. Prominent peaks were sequentially numbered for untreated

TABLE IX

TOC CONCENTRATION AND DILUTION FACTORS

Effluent	Whole Effluent TOC (mg)	TOC Recovered From Gel Column (mg)	% TOC Recovered	C18 Concentration Factor	Overall Concentration Factor*
Raw FE	36	8	23	29	1
Treated FE	38	6	17	26	0.9
Raw SW	77	2	2	13	0.5
Treated SW	52	5	9	19	0.7
Raw CD	245	3	1	4	0.1
Treated CD	309	1	0.2	3	0.1

*=C18 conc. factor * dilution factor (1 ml/27.5 ml=0.036)

waste streams and compared to corresponding peaks of treated waste streams. Percent change of peak area was calculated between matched peaks.

Five final effluent peaks (Figures 5 and 6, Table X) were examined in the raw and carbon treated samples. The last four peak areas on the chromatogram decreased after carbon treatment. These decreased from 89.40% to 100% while the first peak increased by 236.56%. This first peak may be hydrophilic and may exhibit relatively low molecular weight.

TOC was determined in Sephadex gel fractions (Figure 7). Peak areas were converted to mg/l carbon. Background values were subtracted to calculate the actual carbon content. Trace amounts of carbon from reconstituted water accounted for much of the carbon background values. Background readings were determined on samples taken from just past the void volume, approximately tube 50 or 125 mls eluent. Raw and carbon treated final effluent background concentrations ranged from 125 mg/l to 160 mg/l TOC. Raw final effluent TOC values (Figure 7) ranged from about 125 mg/l to 370 mg/l, corresponding to molecular weights under 500 mw (Figure 3). Treated final effluent TOC values appeared reduced but may have been affected by concentration factors. More replications would give a more accurate value. TOC values for raw and treated fractions were higher than TOC found in whole raw and treated samples. High concentration factors may have affected the results (Table IX).

Two 48 hour organismal bioassays used neonate

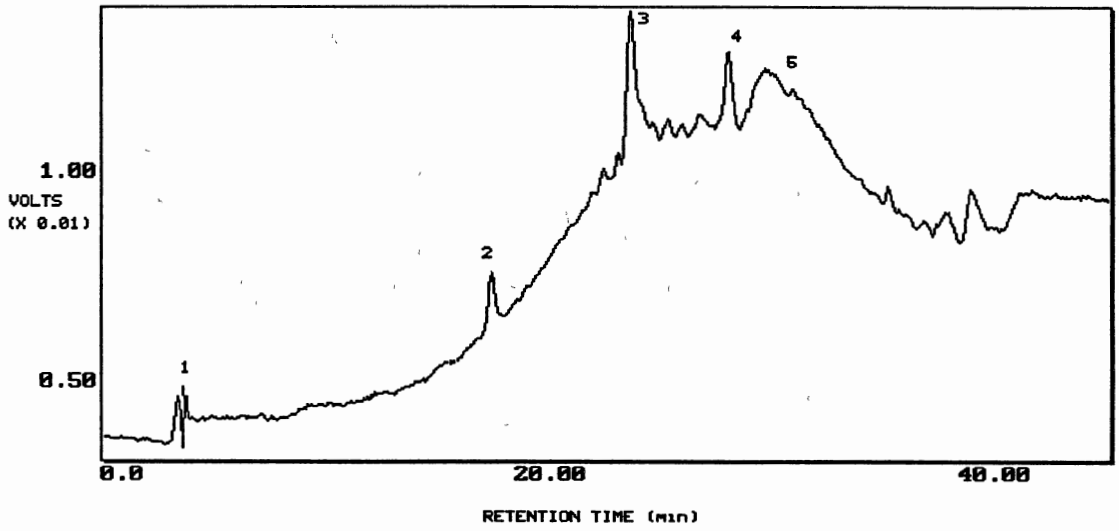

Figure 5. HPLC Analysis of Raw FE

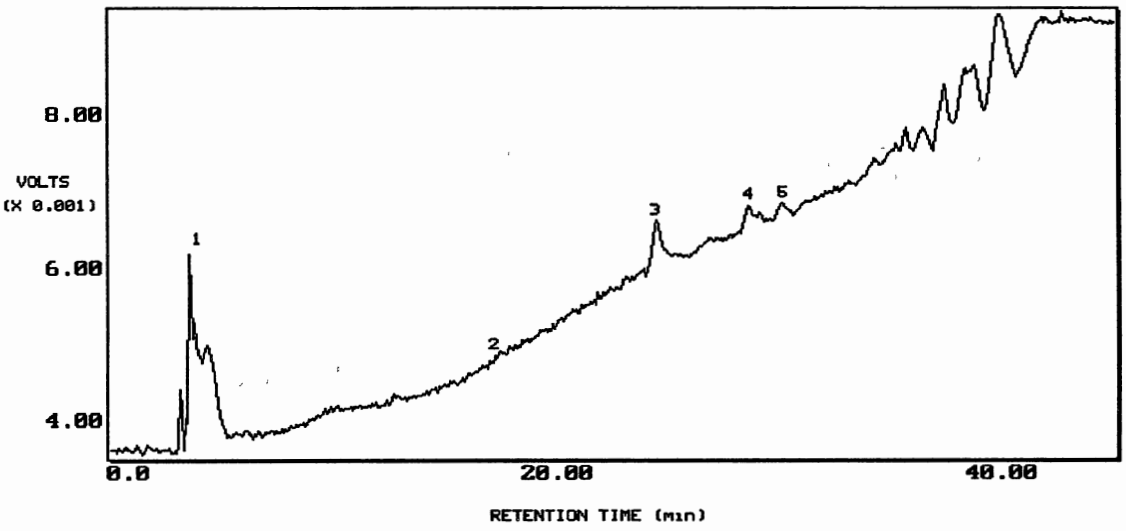

Figure 6. HPLC Analysis of Treated FE

TABLE X

% CHANGE IN FINAL EFFLUENT PEAK HEIGHT (HPLC)

Effluent	Peak #	Incr/Decr	%Change*
FE	1	Increase	236.6
(Raw vs Treated)	2	Decrease	100.0
	3	Decrease	89.4
	4	Decrease	93.4
	5	Decrease	92.2

*=(Raw-Treated/Raw)*100

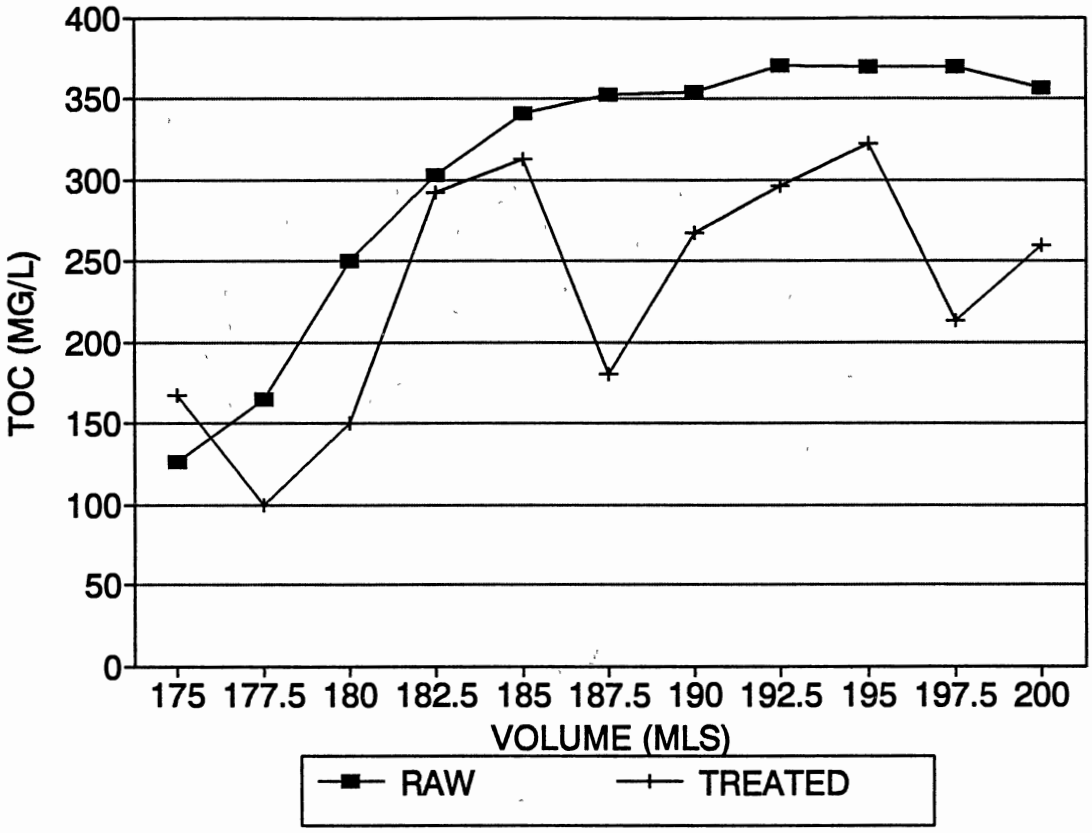

Figure 7. TOC of Final Effluent Fractions

cladocerans and larval fathead minnows (Tables XI and XII). Dilutions were not made and LC50s could not be calculated. Percent mortality of two *C. dubia* blank cups (carbon treated sour water, 33%, and carbon treated crude desalter water, 67%) exceeded the EPA (1991) recommended 20% mortality. These two assays may not be valid. Methanol standard mortalities ranged from 17% to 100% for all assays. Since the methanol standard was a 1.5% dilution. The *C. dubia* 48 hour final effluent bioassay (Table XI) showed increased mortality after carbon treatment. Raw effluent had 12.50% mortality and carbon treated effluent had 50% mortality. High C18 concentration factors may have affected mortality. Blank mortality for the raw sample was 0% and 17% for the carbon treated sample. Methanol standards were 17% and 33% for raw and treated samples, respectively.

Fathead minnows appeared less sensitive to final effluent than cladocerans. Both blanks and methanol standards (Table XII) showed no mortality. No mortality was recorded for either raw or carbon treated final effluent. Burks (1977) reported that by adding activated carbon treatment to activated sludge and dual media filter treatments of petroleum refinery final effluent, fathead minnow mortality was substantially decreased. Other treatments showed 100% minnow mortality. Minnow mortality was 0% except for an apparent activated carbon column breakthrough which resulted in 65% mortality (Burks, 1977). After carbon was replaced, mortality was once again 0%.

EPA (1982) investigated possible correlations between

TABLE XI

C. dubia 48 HR ACUTE BIOASSAY

Blank % Mortality	Methanol Standard % Mortality	Effluent	Treatment	%Mortality
0	17	FE	Raw	12.50
17	33		Treated	50.00
17	100	SW	Raw	87.50
33	50		Treated	91.38
17	83	CD	Raw	100.00
67	50		Treated	100.00

TABLE XII

FATHEAD MINNOW 48 HR ACUTE BIOASSAY

Blank %Mortality	Standard %Mortality	Effluent	Treatment	%Mortality
0	0	FE	Raw	0
0	0		Treated	0
0	0	SW	Raw	0
0	0		Treated	0
0	0	CD	Raw	39.63
0	0		Treated	6.38

fathead minnow and *Daphnia* sp. toxicity using oil refinery final effluent wastewater. Ninety-six hour acute bioassays were used and LC50s were recorded. Refineries LNX, DPQ, and UPB and other area refineries were included. Data was collected for approximately 1.5 years. Both LNX and DPQ showed >100% effluent LC50s for both bioassays in the first 6 months. UPB refinery fluctuated between 40% to >100% LC50 for cladoceran assays and 20% to >100% LC50 for fathead minnow assays. The following year, DPQ refinery wastewater LC50s were 65% for all organisms until summer, returning to 100% effluent. LNX refinery wastewater remained at 100% LC50. Until the summer months, refinery UPB LC50s remained the same. About half-way through the year LC50s increased to 80% to 100% effluent. EPA (1982) showed a correlation did exist between cladoceran and fathead minnow data. Cladacerans were more sensitive than the minnows.

Raw and Carbon Treated Sour Water Effluent Results

Raw sour water stripper effluent physical-chemical means, ranges, and standard deviations are in Table XIII. The raw sample pH for four replicates was 7.1. Carbon treated sour water stripper results are in Table XIV. The treated sample pH ranged from 6.9 to 7.0. Although this decrease was considered significant by T-test analysis, it does not appear significant. Temperature decreased from 17° C in raw samples to 11.4° C in carbon treated samples.

Alkalinity increased from an mean of 19.0 mg/l $CaCO_3$ to a mean of 34.0 mg/l $CaCO_3$. Ammonia levels for raw samples

TABLE XIII

RAW SOUR WATER STRIPPER WATER RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	19 mg/l $CaCO_3$	18-20	1.00
Ammonia	8.5 ppm	8.2-8.8	0.2
COD	428 mg/l	402-447	19
Conductivity	261 μs	260-262	0.8
Hardness	2.0 mg/l $CaCO_3$	none	0
pH	---	7.1*	---
Temperature	17° C	none	0
TOC	77*	65-91	11

*= 3 replicates
**=all 4 values were 7.1

TABLE XIV

CARBON TREATED SOUR WATER STRIPPER WATER RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	34 mg/l $CaCO_3$	30-36	2.5
Ammonia	11.1 ppm	10.8-11.3	0.2
COD	242 mg/l	226-264	16
Conductivity	327 μs	none	0
Hardness	2.0 mg/l $CaCO_3$	none	0
pH	---	6.9-7.0	---
Temperature	11.4° C	9-14	2.6
TOC	52 mg/l	33-89	21.7

averaged 8.5 ppm and carbon treated samples averaged 11.1 ppm. According to Snoeyink and Jenkins (1980) total alkalinity includes ammonia and, therefore, increased ammonia may result in increased alkalinity. Chemical oxygen demand (COD) in raw sample averaged 428 mg/l COD and the carbon treated COD averaged 242 mg/l. The COD removal efficiency was 43% for the carbon treated sample.

The difference in conductivity between carbon treated and raw sample was significant (Table VI). Conductance significantly increased in treated sour water, from an average of 260.8 to 327.0 μs.

No significant differences in hardness were found between the raw and carbon treated sour water waste streams (Table VI). All raw and carbon treated samples contained 2.0 mg/l $CaCO_3$. Hardness indicates calcium, magnesium, strontium, ferrous iron, and manganous cations (Sawyer and McCarty, 1978). A lack of these elements in the waste stream may cause relatively low conductance.

No significant differences in TOC (Table VI) were found between whole raw and carbon treated sour water samples. Sour water TOC decreased from 77 mg/l to 52 mg/l. Whole effluent TOC mass (Table IX) was 77 mg and 2 mg TOC was recovered from the gel column. The raw sample had a 2% recovery and the treated sample had a 9% recovery. The raw C18 concentration factor was 13 with an overall concentration factor of 0.5. The carbon treated C18 concentration factor was 19 and the overall concentration factor was 0.7.

The poor recovery may have been from low molecular weight compounds eluting past 200 mls or 80 test tubes. Additional carbon may have been lost in the C18 SPE process. A TOC decrease after activated carbon treatment was expected because COD levels were reduced.

Gardner et al. (1988) studied granular activated carbon in conjunction with anaerobic treatment of refinery sour water stripper bottoms. Dissolved organic carbon (DOC) was measured. Daily measurement of DOC ranged from 306 mg/l to 549 mg/l. COD values ranged from 937 mg/l to 1808 mg/l. These readings were much higher than the COD values in this study and DOC values were considerably higher than the TOC values obtained.

Carbon treated TOC values for sour water fractions (Figure 8) were higher than raw values. The fractionated, carbon treated sour water samples increased from 50 mg/l TOC to 260 mg/l TOC but overall TOC dropped between the raw and treated samples. The reason for the increase is unknown. All fractions were adjusted for background concentrations of 56 mg/l (raw samples) and 146 mg/l (treated samples).

Microtox bioassays (Figure 4) were performed on whole sour water samples. Raw samples had an EC50 of 7.5%. The carbon treated sample EC50 increased to 38.7%. The toxicity was decreased by carbon treatment. Microtox bioassays were conducted on Sephadex gel fractions. Elevated TOC levels were located from 177.5-200 mls, corresponding to molecular weights less than 500 (Figure 8). Microtox luminescence readings were compared before and after carbon treatment of

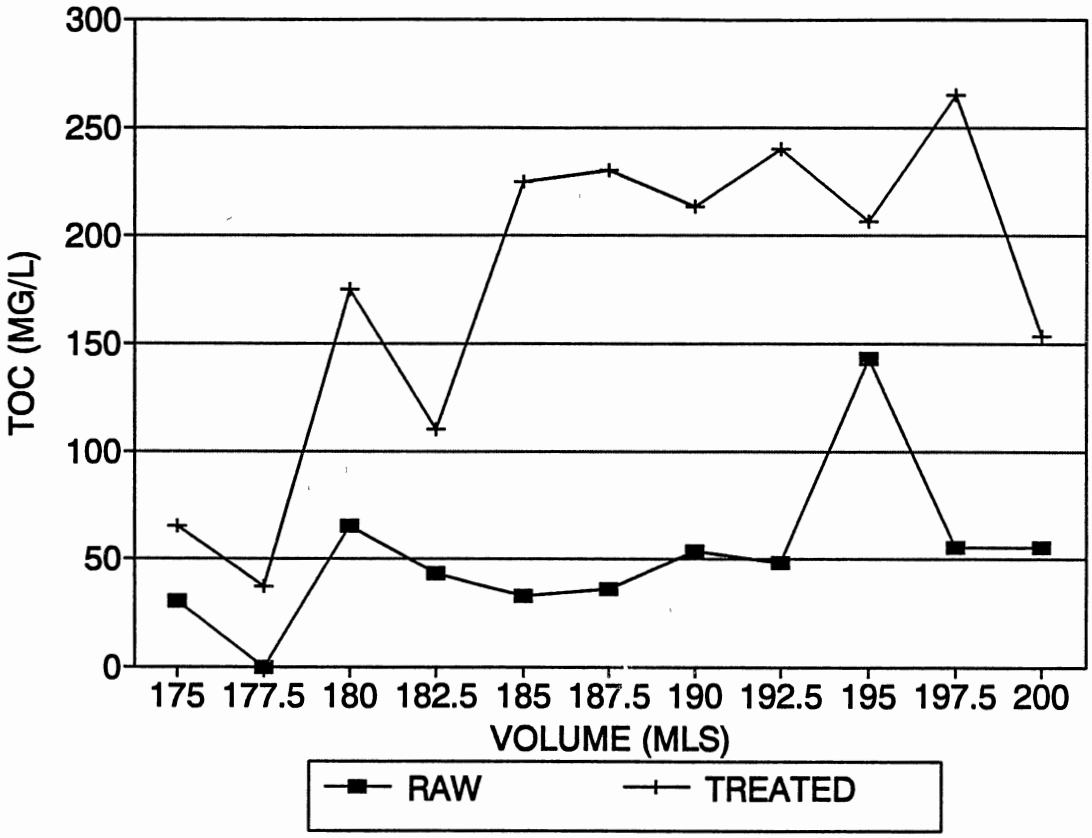

Figure 8. TOC of Sour Water Stripper Fractions

sour water samples (Tables VII, VIII). EC50s were not calculated. Toxicity did not increase as eluting volume increased and molecular weight decreased (Table VIII). Sour water toxicity between raw and carbon treated samples showed no significant differences at the 0.05 level (Table VII) even though TOC and COD were reduced by carbon treatment.

Sour water HPLC analysis produced (Figures 9 and 10, Table XV) four peaks, showing area decreases of 42.28% to 87.16% after carbon treatment. Longer retention times may indicate elution of smaller molecular weight over time. Some compounds, such as toluene, are retained longer than expected due to hydrophobicity (Yates, 1991).

Acute 48 hour organismal bioassays were performed on raw and carbon treated sour water samples (Tables XII, XIII). Raw sour water samples using *C. dubia* had 87.50% average mortality. Carbon treated samples' average mortality increased to 91.38%. Blank cups had 0% mortality for the raw samples. The carbon treated sour water blank had 33% mortality, possibly nullifying this assay. Methanol standards had 100% (raw) and 50% (carbon treated) mortality, possibly approaching the methanol LC50. Both blank and methanol standards for sour water samples (Table XIII) showed no mortality in the acute 48 hour fathead minnow assay. Sour water stripper effluent showed 0% mortality in the fathead minnow assay.

Qureshi et al. (1982) reported that Microtox was more sensitive to oil-refinery effluents than rainbow trout and daphnid bioassays. Dorn et al. (1991) used fathead and

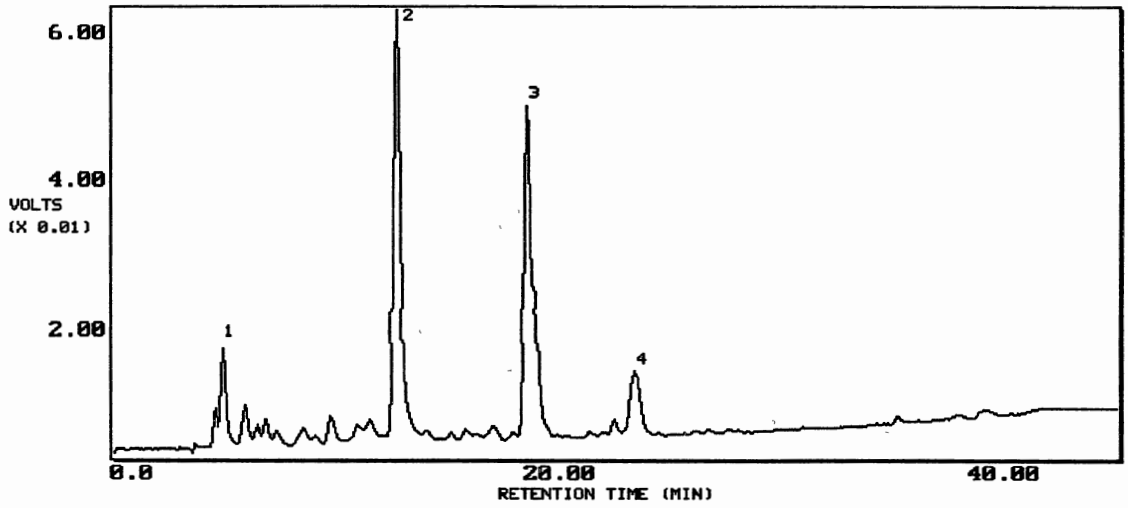

Figure 9. HPLC Analysis of Raw SW

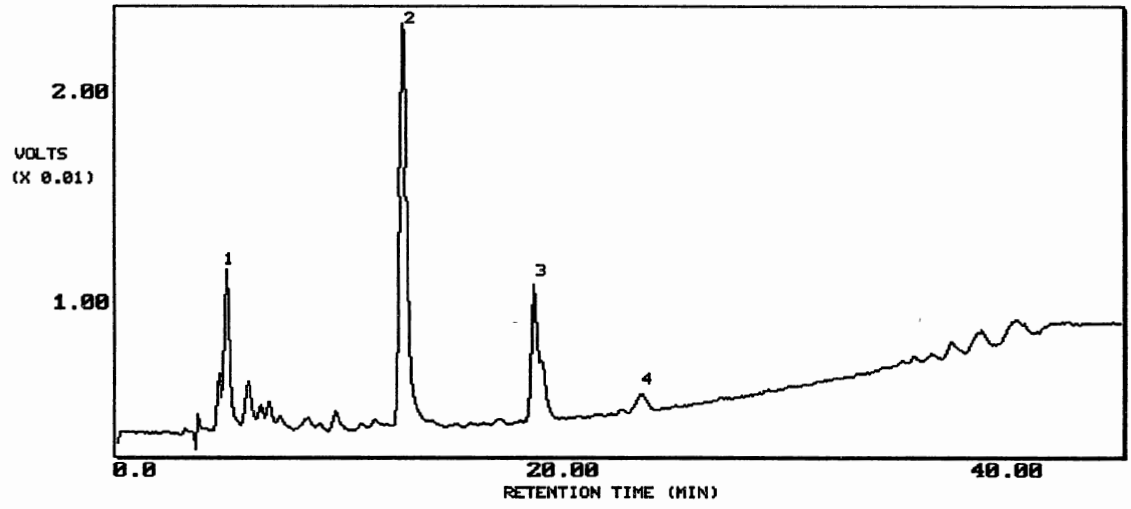

Figure 10. HPLC Analysis of Treated SW

TABLE XV

% CHANGE IN SOUR WATER PEAK HEIGHTS (HPLC)

Effluent	Peak #	Incr/Decr	%Change*
SW	1	Decrease	42.3
(Raw vs Treated)	2	Decrease	66.9
	3	Decrease	85.4
	4	Decrease	87.2

*=(Raw-Treated/Raw)*100

sheepshead minnows, *Daphnia* sp., mysid shrimp, and Microtox bioassays to assess a toxic fraction from petrochemical plant effluent. This study concluded that the fraction was acutely and chronicly toxic to aquatic species. From laboratory and stream toxicity tests, the chloroether fraction behavior was reasonably well predicted. From data given in this study, *Daphnia* sp. appear more sensitive to the toxic fraction than the fathead minnows.

Raw and Carbon Treated Crude Desalter Effluent Results

Raw crude desalter means, ranges, and standard deviations are given in Table XVI. The pH for raw samples was 5.8. The pH for carbon treated samples was 6.2-6.3. The difference between treatments was significant by Student's T-test. Carbon treated crude desalter means, ranges and standard deviations are listed in Table XVII. The temperature in raw samples was 19° C, 8.5° C higher than the carbon treated replicates, primarily from being at room temperature for a longer period of time.

At a 0.05 level, crude desalter effluent showed no significant differences between alkalinity of raw and carbon treated effluent. Crude desalter effluent had a low buffering capacity before and after activated carbon treatment. Raw crude desalter samples had 10.9 ppm ammonia nitrogen and carbon treated samples had 14.8 ppm ammonia nitrogen. This increase was considered significant by Student's T-test at the 0.05 level (Table VI).

Raw crude desalter COD averaged 910 mg/l and the COD of

TABLE XVI

RAW CRUDE DESALTER WATER RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	18* mg/l $CaCO_3$	16-20	1.6
Ammonia	10.9 ppm	10.7-11.3	0.3
COD	910 mg/l	867-992	59
Conductivity	9863 μs	9830-9920	34
Hardness	>1000 mg/l $CaCO_3$	none	0
pH	---	5.8**	---
Temperature	19° C	none	0
TOC	245 mg/l	200-287	35

*= 3 replicates
**=5.8 for all 4 replicates

TABLE XVII

CARBON TREATED CRUDE DESALTER WATER RESULTS

Analysis	Mean	Range	Standard Deviation
Alkalinity	28 mg/l $CaCO_3$	20-38	6.48
Ammonia	14.8 ppm	14.4-14.9	0.22
COD	641 mg/l	637-655	9.0
Conductivity	9583 μs	9500-9640	52.14
Hardness	>1000 mg/l $CaCO_3$	none	0
pH	---	6.2-6.3	---
Temperature	10.5° C	6-16	3.57
TOC	309* mg/l	230-398	68.99

*=3 replicates

carbon treated samples averaged 642 mg/l. The removal efficiency of the carbon treated crude desalter effluent was 29%, lower than values given by Metcalf and Eddy (1972) for domestic wastewater. Crude desalter conductance significantly decreased from an average of 9862.5 us to 9582.2 μs between raw and carbon treated samples (Tables XVI, XVII). The high conductivity likely resulted from its high salt content.

No significant differences for hardness analysis were found between raw and carbon treated samples (Table VI). All samples had over 1000 mg/l $CaCO_3$. The hardness remained unchanged since carbon does not remove divalent cations (Sawyer and McCarty, 1978; Weber, 1984).

TOC analysis was performed on raw and carbon treated samples before C18 SPE (Table IX). No significant differences at the 0.05 level were found between raw and carbon treated crude desalter samples (Table VI). TOC increased in crude desalter effluent from 245 mg/l raw TOC to 309 mg/l treated TOC. The percent TOC recovered from the Sephadex gel column was very low for both raw and treated. C18 concentration factors were 4 for raw and 3 for treated crude desalter samples. The overall concentration factor for both raw and treated samples was 0.1.

Microtox bioassays of whole, raw crude desalter effluent had an EC50 of 1.74%. Activated carbon treatment increased crude desalter EC50 to 4.81% effluent (Figure 4). As the COD increased, microtox toxicity increased. Linear regression analysis of all three carbon-treated waste stream

CODs and EC50s gave an R^2=0.78 (Figure 11). Linear regression for raw waste stream CODs and corresponding Microtox EC50s gave an R^2=0.63. A possible relationship may exist between treated COD and Microtox results. Raw and treated ammonia value versus corresponding Microtox EC50s showed little relationship (raw ammonia versus Microtox R^2=0.44 and treated ammonia versus Microtox R^2=0.001). Similarly, linear regression showed a limited relationship between raw TOC values and Microtox (R^2=0.47) and carbon treated TOC values versus Microtox (R^2=0.64). COD data correlated more with Microtox data than TOC data, indicating a reduction in oxygen demand more positively affects test organisms than reduced organic carbon.

Qureshi et al. (1982) suggested Microtox may be a poor indicator of ammonia toxicity. Rainbow trout were the most sensitive species to total ammonia with a 96 hour LC50 of 62%. Daphnids gave a 48 hour 129% LC50. Microtox was least sensitive to total ammonia (5 minute 3607% EC50).

Crude desalter fractions were analyzed for TOC (Figure 12). Except for one fraction, treated samples had lower TOC values than raw samples. Treated crude desalter TOC analysis showed several fractions below detectable limits and considered to be zero. Dilution factors may have distorted TOC results.

TOC concentration and dilution factors were determined for raw and carbon treated crude desalter effluents (Table X). The C18 concentration factor for the raw sample was 25 and the treated concentration factor was 19. These were

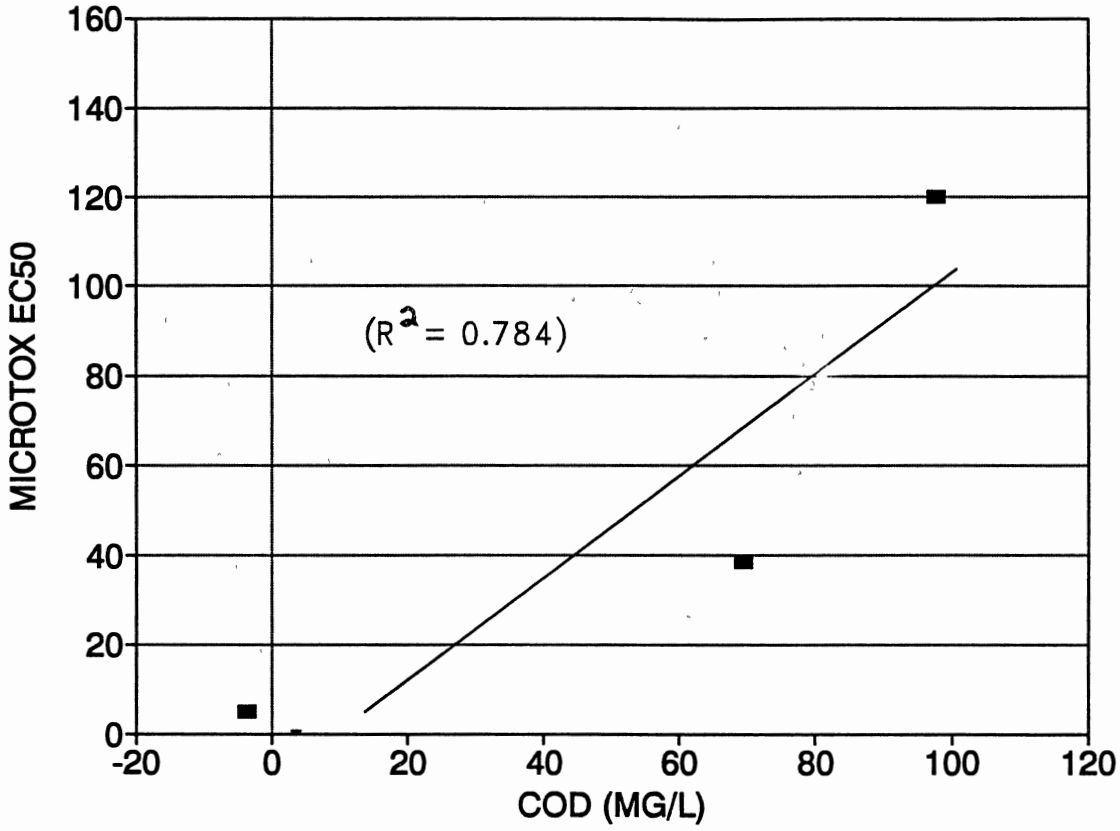

FIGURE 11. Treated effluent COD versus Microtox EC50

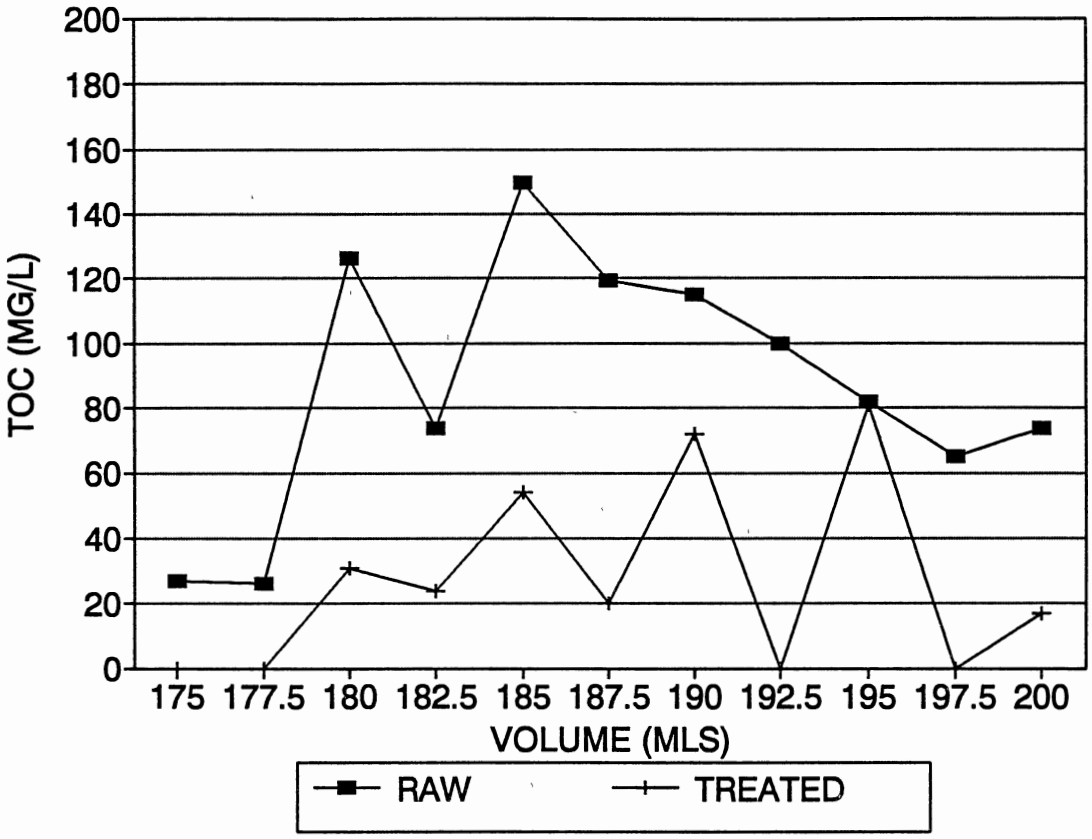

Figure 12. TOC of Crude Desalter Fractions

lower than the concentration factors for final effluent and sour water stripper effluent. Whole effluent TOC mass was 245 mg. Only 3 mg TOC from raw sample was recovered from the gel column while 1 mg was recovered from the treated sample. Carbon treated whole effluent TOC mass was 51 mg.

Microtox bioassays were conducted on eluent fractions. Raw and carbon treated samples did show significant differences in toxicity (Table VII). Microtox luminescence readings from crude desalter fractions were compared (Table VIII). EC50s were not calculated. The toxicity did not increase as the eluting volume increased and molecular weight decreased. From eluting locations, the toxic fractions' molecular weights were below 500. Activated carbon appeared to reduce fraction toxicity.

Fifteen crude desalter peaks were compared using HPLC analysis (Figures 13 and 14, Table XVIII). This was the most complex waste stream and the most toxic based on Microtox results. Of 15 peaks, the first 12 peak areas on the chromatograph decreased 24.15% to 96.63% with activated carbon treatment. The last three peaks increased from 184.78% to 382.18% with activated carbon treatment. The last three peaks are more hydrophobic than the other peaks and may have higher molecular weights, although compounds with greater hydrophobicity and lower molecular weights are possible (Yates, 1991). The reason for the peak area increase with activated carbon treatment remains unknown.

Acute 48 hour organismal bioassays were conducted using crude desalter effluent (Tables XI and XII). Cladoceran

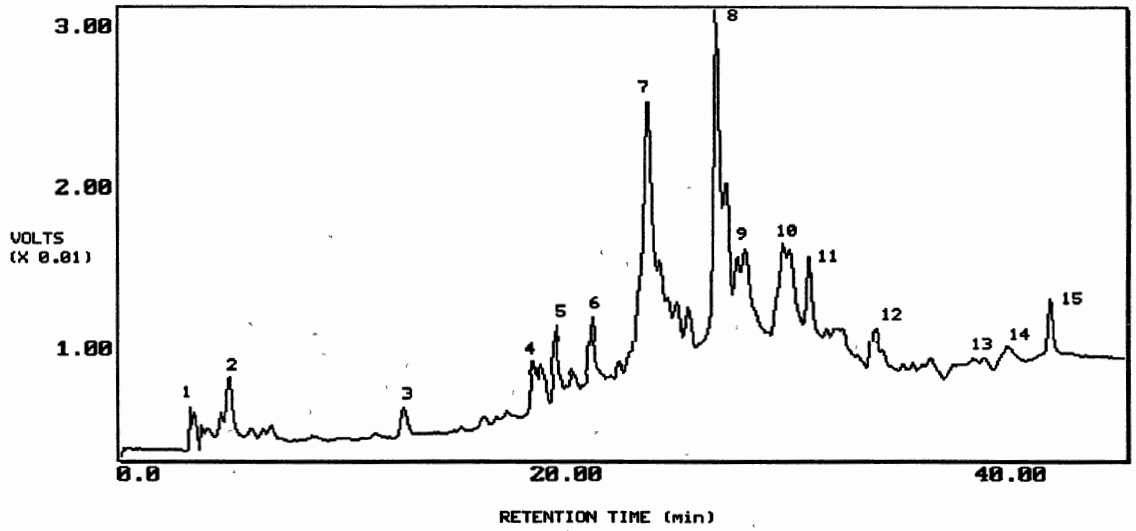

Figure 13. HPLC Analysis of Raw CD

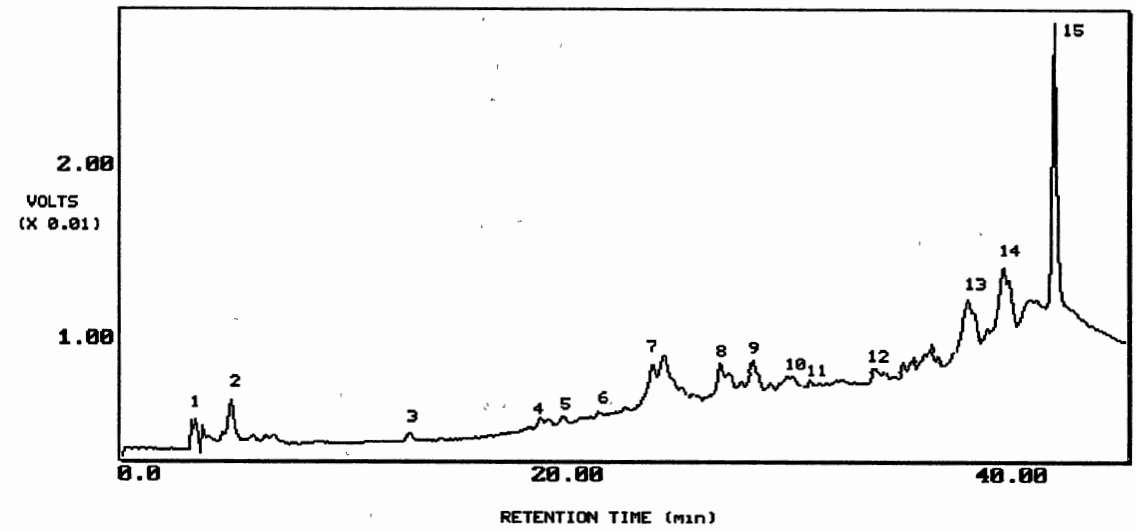

Figure 14. HPLC Analysis of Treated CD

TABLE XVIII

% CHANGE IN CRUDE DESALTER PEAK HEIGHTS (HPLC)

Effluent	PK #	Incr/Decr	%Change
CD	1	Decrease	24.2
(Raw vs Treated)	2	Decrease	48.1
	3	Decrease	73.3
	4	Decrease	85.1
	5	Decrease	88.4
	6	Decrease	96.6
	7	Decrease	78.7
	8	Decrease	89.8
	9	Decrease	61.3
	10	Decrease	93.4
	11	Decrease	95.0
	12	Decrease	37.1
	13	Increase	313.0
	14	Increase	185.0
	15	Increase	382.0

assay blanks showed 17% and 67% mortality for raw and treated samples, respectively. Because the treated sample blank was above the recommended 20% mortality, this assay may not be valid. Methanol standards showed 83% and 50% mortality for raw and treated samples, respectively. All *C. dubia* organisms for the raw and treated crude desalter sample died. Activated carbon treatment did not appear to increase effluent quality. Increased ammonia levels may have contributed to cladoceran toxicity.

Both fathead minnow blanks and methanol standards for crude desalter effluent (Table XIII) showed no mortality. Raw crude desalter effluent had 39.63% mortality. Activated carbon treatment reduced mortality to 6.38%. *C. dubia* appeared more sensitive than fathead minnows to methanol and to the three waste streams.

Carroll et al. (1990) performed 48 hour acute bio-assays, using *C. dubia* and fathead minnows, on influent and effluent from a bench-scale aerated submerged biological filter (ASBF). This treatment biologically reduced toxicity in a sour water stripper waste stream. The system used features of fixed film and completely mixed activated sludge units. Seven dilutions (from 1% to 100%) were made for both influent and effluent *C. dubia* and fathead minnow assays. The acutely lethal contaminants were either non-polar organics and/or weakly basic organics (Carroll et al., 1990).

Johnson (1990) evaluated toxicity of oil refinery effluents. *C. dubia* and fathead minnows were used in 48

hour acute bioassays. C18 SPE columns removed non-polar organic contaminants from refinery waste streams. Johnson (1990) showed sour water stripper effluent caused 100% mortality down to a 10% effluent concentration. A sample from the same refinery several months later caused 100% mortality to both *C. dubia* and fathead minnows. Effluent from several refineries all proved toxic to cladocerans but less toxic to fathead minnows. Johnson (1990) also showed crude desalter effluent was more toxic to cladocerans than fathead minnows. C18 treatment did decrease fathead minnow mortality.

Discussion

COD removal efficiencies were determined for treated final effluent. Carbon treated samples had an average removal efficiency of 40%. Activated carbon treatment should reduce COD in domestic wastewater with 60-75% removal efficiency (Metcalf and Eddy, 1972). These are higher efficiencies than obtained in this study.

Increased ammonia levels may have resulted from human error, instrument error, or from the breakdown of organic nitrogen from microbial deamination (Snoeyink and Jenkins, 1980). Microbial activity may not have completely subsided with cold storage at 4° C. Aerobic deamination of organic nitrogen by saprophytic bacteria may have occurred (Sawyer and McCarty, 1978), increasing waste stream ammonia levels. Under aerobic conditions, ammonia increases as organic nitrogen decreases overtime (Sawyer and McCarty, 1978).

Additionally, pH levels remained constant in final effluent and sour water but became more basic in crude desalter samples. Alkalinity and ammonia increased in all process streams, although the increases in ammonia did not appear to directly correspond with increases in alkalinity. The increase in pH and alkalinity accompanying the increase in ammonia agree with theoretical considerations given by Snoeyink and Jenkins (1980).

COD/TOC relationships from EPA (1971) ranged from 2.70 to 5.0 for petrochemical and refinery wastes, respectively. The stoichiometric COD/TOC ratio is the molecular weight ratio of oxygen to carbon (32/12 = 2.67) (EPA, 1971). COD/TOC ratios for raw and carbon treated final effluent were 4.08 and 2.26, respectively. The treated ratio is less than the stoichiometric relationship. Because TOC values were relatively constant, small oxidizable inorganic compounds such as hydrogen sulfide may have been removed, resulting in reduced COD values and stable TOC results. This is one of the considerations suggested by EPA (1971) that may discredit the COD/TOC relationship. COD tests do not include organic compounds which are partially or totally resistant to chemical oxidation. All organic carbon is theoretically recovered in TOC analysis (EPA, 1971).

The COD/TOC ratios were 5.56 and 4.65 for raw and carbon treated sour water samples, respectively. The COD/TOC ratios were 3.71 and 2.07 for raw and carbon treated final effluent, respectively. The carbon treated crude desalter ratio (2.07) was lower than the stoichiometric

ratio (2.67).

Compounds of low molecular weight and polar nature are not adsorbed well by activated carbon. Intermediate to high molecular weight and low polarity compounds are strongly adsorbed (Weber, 1984). Compounds' molecular weights may be so low that carbon adsorption would not adequately remove them. COD removal efficiencies appear low, especially the crude desalter water stream. Perhaps an additional or alternative treatment technology should be considered.

This research added to the petroleum refinery waste water knowledge base. Gel fractionation of final effluent, sour water stripper effluent and crude desalter effluent appeared somewhat successful. Fractional toxicity assessment was attempted with microbial bioassays. Procedural changes could make this more successful and practical. Activated carbon treatment of the waste streams reduced toxicity as measured by Microtox and fathead minnow bioassays. *C. dubia* toxicity was increased with carbon treatment. Although previous studies by the OSU WQRL indicated non-polar organics, some oxidizable inorganics might also cause toxicity in UPB refinery wastewater.

CHAPTER V

SUMMARY AND CONCLUSIONS

Using analyses techniques similar to those found in toxicity identification evaluations, such as initial toxicity, C18 SPE, and physical-chemical characterization, an attempt was made to characterize pollutants found in petroleum refinery waste streams. Three waste streams, final effluent, sour water stripper water, and crude desalter water, were tested for toxicity before and after activated carbon treatment. Bioassays used in toxicity testing included Microtox microbial bioassays and 48 hour survival bioassays using *C. dubia* and fathead minnows. Microtox was performed on raw and treated whole waste streams as well as all extracted samples from the C18 SPE column and the Sephadex gel column. The 48 hour organismal bioassays were performed only on raw and treated samples extracted from the C18 SPE column. C18 SPE was also performed on the three waste streams, both raw and carbon treated waste streams, to remove non- polar organic compounds.

Physical-chemical analyses indicated aerobic deamination may have occurred in the waste stream samples,

increasing ammonia and alkalinity. COD was significantly decreased by activated carbon treatment but removal efficiencies were slightly lower than those reported by Metcalf and Eddy (1972). Conductivity showed an increase in final effluent and sour water, although it decreased in crude desalter water. Hardness remained about the same in samples after activated carbon treatment since carbon has little effect on divalent cations (Veenstra, 1991). pH values both increased and decreased in treated samples. TOC values were not significantly changed with carbon treatment. However, elevated levels of TOC were found in gel column fractions roughly corresponding to molecular weights less than 500.

Microtox bioassays showed significant decreases in whole effluent toxicity after activated carbon treatment. In addition, raw Microtox data showed decreases in Sephadex gel fraction toxicity after activated carbon treatment. Organismal bioassays, 48 hour survival tests, were conducted on SPE extractants. *C. dubia* appeared more sensitive than fathead minnows to treated and untreated samples. Activated carbon treatment reduced minnow mortality for crude desalter water. A slight correlation was found between carbon treated waste stream COD values and carbon treated waste stream Microtox toxicity. Waste stream samples were fractionated at molecular weights less than 500. Microtox and fathead minnow assays showed activated carbon treatment decreased acute sample toxicity.

This project supports the findings of past research

conducted by the Oklahoma State University Water Quality Research Laboratory (Burks, 1977; EPA, 1981; Johnson, 1990). Pollutants characterized by physical-chemical means tended to be of low molecular weight. Microbial and vertebrate bioassays showed activated carbon treatment reduced toxicity of the waste stream samples.

CHAPTER VI

FUTURE RESEARCH SUGGESTIONS

1. Similar study with weekly or biweekly samples for several months to obtain a "profile" of the refinery.

2. Using TRE guidelines and incorporating gel chromatography or ultrafiltration for fractionation of non-polar organics.

3. Finding an alternative, non-toxic HPLC mobile phase and C18 SPE extractant other than methanol or alternative methods to accomplish solid phase extraction and liquid chromatography.

4. Using TRE procedures in addition to using alternative treatment methods such as ion exchange, reverse osmosis, or a biological reactor.

5. To determine if any physical-chemical changes were caused by activated carbon, VH recon water should have been run through the carbon columns prior to the waste streams.

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APPENDIX

RAW DATA

VERY HARD RECON WATER CONSTITUENTS
FOR 19 L

CONSTITUENT	AMOUNT
$CaSO_4$	4.560 G
$MgSO_4$	4.560 G
$NaHCO_3$ $4H_2O$	7.296 G
KCl	0.304 G

% TRANSMITTANCE (610 NM) OF BLUE DEXTRAN MARKER

TUBE #	% TRANSMITTANCE	TUBE #	% TRANSMITTANCE
41	105.6	55	83.5
42	59.4	56	89.5
43	105.6	57	92.6
44	106.1	58	95.9
45	106.1	59	97.9
46	105.6	60	97.7
47	101.1	61	25.0
48	85.9	62	90.1
49	98.2	63	100.6
50	80.1	64	101.7
51	58.7	65	102.0
52	62.2	66	102.0
53	69.3	67	102.6
54	74.3	68	102.8

% TRANSMITTANCE (380 NM) OF BLUE DEXTRAN MARKER

TUBE #	% TRANSMITTANCE	TUBE #	% TRANSMITTANCE
27	108.8	35	101.3
28	108.5	36	104.2
29	107.8	37	105.6
30	100.6	38	106.4
31	84.6	39	106.4
32	84.1	40	107.1
33	90.5	41	107.1
34	94.8	42	107.1

% TRANSMITTANCE (610 NM) OF BLUE DEXTRAN MARKER

TUBE #	% TRANSMITTANCE	TUBE #	% TRANSMITTANCE
44	105.7	55	93.8
45	105.4	56	95.2
46	99.0	57	96.6
47	79.6	58	97.2
48	51.1	59	97.2
49	48.0	60	98.6
50	58.7	61	99.0
51	68.9	62	99.3
52	76.7	63	100.0
53	85.1	64	100.0
54	89.5	65	100.6

5 MINUTE MICROTOX SCREEN
(LUMINESCENCE READINGS)

Dilution	Blank	SW 1.8%	CD 1.8%
A	94	73	42
B	90	67	38
C	94	72	38
D	91	73	38

5 MINUTE MICROTOX SCREEN
(LUMINESCENCE READINGS)

EFFLUENT	DILUTION	BLANK	45%	91%
SW	A	93	12	04
CD	B	97	03	02

5 MINUTE MICROTOX ASSAY USING UNTREATED FINAL EFFLUENT
(LUMINESCENCE READINGS)

Dilution	Blank	11%	22%	45%	91%
A	93	96	88	74	57
B	99	96	86	73	60
C	98	97	87	73	60
D	91	96	87	73	59

5 MINUTE MICROTOX ASSAY USING UNTREATED SOUR WATER
(LUMINESCENCE READINGS)

DILUTION	BLANK	1.375%	2.750%	5.500%	11.00%
A	107	81	68	55	41
B	93	78	69	58	41
C	91	79	64	53	39
D	95	78	67	52	38

5 MINUTE MICROTOX ASSAY USING UNTREATED CRUDE DESALTER
(LUMINESCENCE READINGS)

DILUTION	BLANK	0.687%	1.375%	2.750%	5.500%
A	93	62	50	38	28
B	90	60	47	32	38
C	91	64	45	34	24
D	91	66	50	33	25

5 MINUTE MICROTOX ASSAY USING CARBON TREATED FINAL EFFLUENT
(LUMINESCENCE READINGS)

DILUTION	BLANK	11%	22%	45%	91%
A	103	101	102	95	95
B	95	104	101	99	99
C	93	103	101	98	90
D	98	103	100	100	94

5 MINUTE MICROTOX ASSAY USING CARBON TREATED SOUR WATER
(LUMINESCENCE READINGS)

DILUTION	BLANK	11%	22%	45%	91%
A	95	71	59	44	29
B	95	74	60	44	28
C	97	75	60	41	28
D	93	73	61	41	31

5 MINUTE MICROTOX ASSAY USING CARBON TREATED CRUDE DESALTER
(LUMINESCENCE READINGS)

DILUTION	BLANK	1.375%	2.750%	5.500%	11.00%
A	99	77	60	45	35
B	99	71	58	42	29
C	101	73	57	44	37
D	93	78	60	45	35

% TRANSMITTANCE (610 NM) OF BLUE DEXTRAN MARKER

TUBE #	% TRANSMITTANCE	TUBE #	% TRANSMITTANCE
45	102.6	55	87.5
46	103.0	56	95.0
47	100.9	57	95.1
48	86.3	58	95.7
49	64.4	59	95.5
50	44.7	60	97.7
51	45.7	65	99.1
52	50.3	70	101.2
53	61.9	75	101.9
54	86.9	80	101.9

% TRANSMITTANCE OF BLUE DEXTRAN MARKER (610 nm)

TUBE #	% TRANSMITTANCE	TUBE #	% TRANSMITTANCE
40	106.4	52	91.9
42	106.2	53	98.0
43	106.4	54	101.2
44	106.0	55	102.1
45	100.7	56	102.1
46	79.1	58	103.5
47	49.3	60	104.0
48	38.4	65	104.3
49	44.2	70	104.3
50	56.2	75	104.2
51	73.8	80	102.1

100 MG/L BACITRACTIN MARKER COD RESULTS

TUBE	% TRANS.	COD mg/l	TUBE	% TRANS.	COD mg/l
blank	35	0	blank	35	0
standard	45	35.3	stan-dard	50	50.2
51,52	35	0	69,70	37	7.5
53,54	33	--	71,72	37	7.5
55,56	34	--	73.74	35	0
57,58	35	0	75.76	34	--
59.60	33	--	77,78	34	--
61,62	34	--	79,80	32	--
63,64	31	--			
65,66	34	--			
67,68	34	--			

250 MG/L BACITRACIN MARKER COD RESULTS

TUBE	% TRANS.	COD MG/L	TUBE	% TRANS.	COD MG/L
BLANK	35	0	56	32	--
STANDARD	42	25.6	57	36	3.7
50	32	--	58	32	--
51	32	--	59	36	3.7
52	32	--	60	33	--
53	35	--	61	36	3.7
54	37	7.5	62	35	0
55	32	--	63	33	--

250 MG/L BACITRACIN MARKER COD RUN

TUBE	% TRANS.	COD MG/L	TUBE	% TRANS.	COD MG/L
BLANK	35	0	BLANK	35	0
STAND.	44	32.1	STAND.	44	32.1
45	33	--	60	33	--
46	34	--	61	41	22.2
47	33	--	62	39	15.0
48	33	--	63	40	18.7
49	36	3.7	64	36	3.7
50	34	--	65	36	3.7
51	34	--	66	34	--
52	30	--	67	34	--
53	32	--	68	34	--
54	35	0	69	35	0
55	33	--	70	36	3.7
56	32	--	73	33	--
57	31	--	74	35	0
58	33	--	75	31	--
59	32	--			

250 MG/L RAFFINOSE MARKER COD RESULTS

TUBE	% TRANS.	COD MG/L	TUBE	% TRANS.	COD MG/L
BLANK	35	0	73	35	0
STAND.	45	35.3	74	35	0
67	36	3.7	75	35	0
68	35	0	76	35	0
69	37	7.5	77	32	--
70	36	3.7	78	33	--
71	40	18.7	79	39	15.0
72	37	7.5	80	36	3.7

250 MG/L BETA-NAD MARKER COD RESULTS

TUBE	% TRANS.	COD MG/L	TUBE	% TRANS.	COD MG/L
BLANK	35	0	73	34	--
STAND.	47	41.4	74	35	0
67	35	0	75	38	11.3
68	35	0	76	39	15.0
69	38	11.3	77	34	--
70	35	0	78	35	0
71	35	0	79	36	3.7
72	35	0	80	35	0

UNTREATED WHOLE WASTE STREAM COD RESULTS

TUBE #	% TRANSMITTANCE	COD MG/L
BLANK	100	0
STANDARD	83	188
STANDARD	83	188
FE 1	87	141
FE 2	86	153
FE 3	86	153
FE 4	87	141
SW 1	65	432
SW 2	67	402
SW 3	64	447
SW 4	65	432
CD 1	42	867
CD 2	42	867
CD 3	41	915
CD 4	37	992

CARBON TREATED WHOLE WASTE STREAM COD RESULTS

TUBE	% TRANSMITTANCE	COD MG/L
BLANK	100	0
STANDARD	61	496
FE 1	92	85
FE 2	92	85
FE 3	92	85
FE 4	91	97
SW 1	77	264
SW 2	80	226
SW 3	79	239
SW 4	79	239
CD 1	53	637
CD 2	53	637
CD 3	53	637
CD 4	52	655

UNTREATED WHOLE WASTE STREAM PHYSICAL-CHEMICAL ASSAY RESULTS

ASSAY/SAMPLE #	FE	SW	CD
pH 1	6.9	7.1	5.8
2	7.1	7.1	5.8
3	7.1	7.1	5.8
4	7.15	7.1	5.8
CONDUCTIVITY 1	6000 µs	260 µs	9850 µs
2	6050	260	9920
3	6080	261	9830
4	6080	262	9850
TEMPERATURE 1	15 C	17 C	19 C
2	15	17	19
3	15	17	19
4	15	17	19
ALKALINITY 1	66 mg/l $CaCO_3$	20 mg/l $CaCO_3$	18 mg/l $CaCO_3$
2	64	18	16
3	64	18	20
4	64	20	--
HARDNESS 1	106.0 mg/l $CaCO_3$	2.0 mg/l $CaCO_3$	>1000 mg/l $CaCO_3$
2	102.0	2.0	>1000
3	104.0	2.0	>1000
4	98.0	2.0	>1000

CARBON TREATED WHOLE EFFLUENT PHYSICAL-CHEMICAL ASSAY RESULTS

ASSAY/SAMPLE #	FE	SW	CD
pH 1	7.1	6.9	6.2
2	7.1	7.0	6.2
3	7.1	6.85	6.3
4	7.1	6.9	6.3
CONDUCTIVITY 1	6060 µs	327 µs	9580 µs
2	6090	327	9610
3	6090	327	9640
4	6090	327	9500
TEMPERATURE 1	11 C	9 C	10 C
2	10	14	16
3	10.5	8.5	10
4	10.5	14	6
ALKALINITY 1	76.0 mg/l $CaCO_3$	36.0 mg/l $CaCO_3$	26.0 mg/l $CaCO_3$
2	76.0	36.0	38.0
3	80.0	34.0	20.0
4	76.0	30.0	28.0
HARDNESS 1	96.0 mg/l $CaCO_3$	2.0 mg/l $CaCO_3$	>1000 mg/l $CaCO_3$
2	104.0	2.0	>1000
3	102.0	2.0	>1000
4	104.0	2.0	>1000

UNTREATED WHOLE WASTE STREAM AMMONIA ORION IONALYZER READINGS

STANDARD	FE	SW	CD
0.10 (0.5 PPM)	2.00	1.45	1.90
1.0 (5 PPM)	2.20	1.45	1.80
8 (50 PPM)	1.90	1.50	1.80
	1.80	1.40	1.85

CARBON TREATED WHOLE WASTE STREAM AMMONIA
ORION IONALYZER READINGS

STANDARD	FE	SW	CD
0.19 (0.2 PPM)	5.6	4.40	5.80
1.0 (2 PPM)	5.8	4.50	6.00
8.0 (20 PPM)	5.8	4.60	6.00
	5.8	4.60	6.00

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED FINAL EFFLUENT (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	1/6
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	0/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	0/6	0/6	0/6
7	0/6	0/6	0/6	1/6	2/5
8	0/6	0/6	0/6	0/6	3/6

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED SOUR WATER STRIPPER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	1/6
STANDARD	0/6	0/6	0/6	0/6	2/6
1	0/6	0/6	0/6	1/6	5/5
2	0/6	0/6	0/6	3/6	1/3
3	0/6	0/6	0/6	1/6	4/5
4	0/6	0/6	0/6	3/6	3/3
5	0/6	0/6	0/6	2/6	3/4
6	0/6	0/6	0/6	0/6	6/6
7	0/6	0/6	0/6	1/6	3/5
8	0/6	0/6	0/6	1/6	5/5

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED CRUDE DESALTER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	1/6
STANDARD	0/6	0/6	0/6	1/6	5/5
1	0/6	0/6	0/6	3/6	3/3
2	0/6	0/6	0/6	5/6	1/1
3	0/6	0/6	0/6	2/6	4/4
4	0/6	0/6	0/6	1/6	5/5
5	0/6	0/6	0/6	2/6	4/4
6	0/6	0/6	0/6	4/6	2/2
7	0/6	0/6	0/6	2/6	4/4
8	0/6	0/6	0/6	1/6	5/5

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED FINAL EFFLUENT (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	2/6
STANDARD	0/6	0/6	0/6	0/6	3/6
1	0/6	0/6	0/6	0/6	1/6
2	0/6	0/6	0/6	0/6	6/6
3	0/6	0/6	0/6	0/6	4/6
4	0/6	0/6	0/6	1/6	3/5
5	0/6	0/6	0/6	0/6	2/6
6	0/6	0/6	0/6	0/6	3/6
7	0/6	0/6	0/6	0/6	5/6
8	0/6	0/6	0/6	1/6	4/5

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED SOUR WATER STRIPPER WATER

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	1/6	0/5
STANDARD	0/6	0/6	0/6	1/6	4/5
1	0/6	0/6	0/6	0/6	6/6
2	0/6	0/6	0/6	0/6	5/6
3	0/7	0/7	0/7	2/7	5/5
4	0/6	0/6	0/6	1/6	3/5
5	0/6	0/6	0/6	1/6	4/5
6	0/8	0/8	0/8	3/8	5/5
7	0/6	0/6	0/6	1/6	5/5
8	0/6	0/6	0/6	1/6	5/5

C. dubia 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED CRUDE DESALTER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	1/6	3/5
STANDARD	0/6	0/6	0/6	0/6	3/6
1	0/6	0/6	3/6	3/3	--
2	0/6	0/6	0/6	6/6	--
3	0/6	0/6	1/6	5/5	--
4	0/6	0/6	0/6	6/6	--
5	0/6	0/6	1/6	5/5	--
6	0/6	0/6	2/6	4/4	--
7	0/6	0/6	0/6	6/6	--
8	0/6	0/6	1/6	5/5	--

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED FINAL EFFLUENT (DEAD/ALIVE)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/7	0/7	0/7	0/7	0/7
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	0/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	0/6	0/6	0/6
7	0/6	0/6	0/6	0/6	0/6
8	0/6	0/6	0/6	0/6	0/6

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED SOUR WATER STRIPPER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	0/6
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	0/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	0/6	0/6	0/6
7	0/6	0/6	0/6	0/6	0/6
8	0/6	0/6	0/6	0/6	0/6

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED UNTREATED CRUDE DESALTER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	0/6
1	0/6	0/6	0/6	0/6	3/6
2	0/6	0/6	0/6	0/6	2/6
3	0/6	0/6	0/6	0/6	4/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	1/6
6	0/6	0/6	0/6	0/6	3/6
7	0/6	0/6	0/6	0/6	4/6
8	0/6	0/6	0/6	0/6	2/6

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED FINAL EFFLUENT (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	0/6
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	0/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	0/6	0/6	0/6
7	0/6	0/6	0/6	0/6	0/6
8	0/6	0/6	0/6	0/6	0/6

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED SOUR WATER STRIPPER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	0/6
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	0/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	0/6	0/6	0/6
7	0/6	0/6	0/6	0/6	0/6
8	0/6	0/6	0/6	0/6	0/6

FATHEAD MINNOW 48 HOUR ACUTE BIOASSAY USING EXTRACTED CARBON TREATED CRUDE DESALTER WATER (DEAD/ALIVE RECORDED)

CUP	2 HOUR D/L	4 HOUR D/L	8 HOUR D/L	24 HOUR D/L	48 HOUR D/L
BLANK	0/6	0/6	0/6	0/6	0/6
STANDARD	0/6	0/6	0/6	0/6	0/6
1	0/6	0/6	0/6	0/6	0/6
2	0/6	0/6	0/6	0/6	0/6
3	0/6	0/6	0/6	0/6	1/6
4	0/6	0/6	0/6	0/6	0/6
5	0/6	0/6	0/6	0/6	0/6
6	0/6	0/6	1/6	0/5	0/5
7	0/6	0/6	0/6	1/6	0/5
8	0/6	0/6	0/6	0/6	0/6

TOC PEAK AREAS OF RAFFINOSE STANDARDS FOR OCT. 23, 1991

RAFFINOSE STANDARD	PEAK AREA	MG/L CARBON	RAFFINOSE STANDARD	PEAK AREA	MG/L CARBON
2500 MG/L	954769	952	750 MG/L	319069	243
	926546	921		328137	253
	836838	821		306282	229
	871712	859		318901	243
1000 MG/L	484645	428	500 MG/L	222039	135
	472019	414		214930	127
	437656	375		233329	147
	502522	448		215816	128
	480509	423			
	482994	426			
	485871	429			

RAW FINAL EFFLUENT TOC FRACTIONS OCT. 23, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR. TOC* MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	218364	131		75	514464	461	349
	196009	106		75	519930	467	355
	190881	100		74	507719	453	341
80	520944	468	356	73	459792	400	288
79	532214	481	369	73	486614	430	318
78	532271	481	369	72	426048	362	250
77	533365	482	370	71	349222	277	165
76	519030	466	354	70	314469	238	126

*=TOC CORRECTED FOR BACKGROUND LEVELS (AVE. OF TUBE 50 WAS SUBTRACTED)

RAW SOUR WATER STRIPPER EFFLUENT TOC FRACTIONS OCT. 23, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR.* TOC MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	160710	66		75	184373	93	36
	143230	47		74	180510	88	32
80	201206	111	55	73	190364	99	43
79	201207	111	55	72	210493	122	65
78	280029	199	143	71	144852	49	0
77	188207	97	40	70	179281	87	30
77	201086	111	55	69	182689	91	34
76	199367	109	53	69	184757	93	37

RAFFINOSE STANDARDS FOR OCT. 26, 1991

RAFFINOSE STANDARD	PEAK AREA	MG/L TOC
2500 MG/L	540862	816
	622557	956
	464757	686
	582371	887
	766570	1202
750 MG/L	221633	270
	223601	273
	220553	268
500 MG/L	174083	188
	176407	192
	163995	171

RAW CRUDE DESALTER EFFLUENT TOC FRACTIONS OCT. 26, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR.* TOC MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	105549	71		75	172428	185	95
	128097	109		74	205539	242	152
	116671	90		74	203663	239	149
80	160590	165	75	73	150497	148	58
80	160562	165	75	73	169788	181	91
79	154840	155	65	72	190587	216	126
78	164911	172	82	71	125666	105	15
77	175316	190	100	71	137906	126	36
76	183767	205	115	70	132624	117	27
75	199636	232	142				

CARBON TREATED FINAL EFFLUENT TOC FRACTIONS OCT. 26, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	150024	147		74	334746	463	320
	145948	140		73	318281	435	292
80	299457	403	259	72	235504	293	150
79	272545	357	213	71	206394	243	100
78	336272	466	322	70	260418	336	192
77	295179	395	252	70	230095	284	141
77	346659	484	340				
76	303732	410	267				
75	253091	323	180				
74	326434	449	305				

CARBON TREATED SOUR WATER STRIPPER EFFLUENT TOC FRACTIONS OCT. 26, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	142283	134		75	283777	376	230
	156762	158		74	280896	371	225
80	238757	299	153	73	213965	256	110
79	304410	411	265	72	251822	321	175
78	269672	352	206	71	171237	183	37
77	289860	386	240	70	187446	211	65
76	274142	359	213				

CARBON TREATED CRUDE DESALTER EFFLUENT TOC
FRACTIONS OCT. 26, 1991

TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L	TUBE #	PEAK AREA	MG/L TOC	CORR. TOC MG/L
50	161212	166		75	170120	181	20
	155826	157		74	189819	215	54
80	168281	178	17	73	172433	185	24
79	152618	151	0	72	176900	193	31
78	205879	243	81	71	149746	146	0
77	149041	145	0	70	147759	143	0
76	200817	234	72				

RAFFINOSE STANDARDS FOR OCT. 22, 1991

RAFFINOSE STANDARD	PEAK AREA	MG/L TOC	RAFFINOSE STANDARD	PEAK AREA	MG/L TOC
2500 MG/L	851908	963		336855	320
	820605	924		316053	294
	802646	902	500 MG/L	197163	145
	751257	838		220595	175
750 MG/L	308863	285		203462	153

WHOLE EFFLUENT TOC VALUES OCT. 22, 1991

EFFLUENT	PEAK AREA	MG/L TOC	EFFLUENT	PEAK AREA	MG/L TOC
RAW FE	105300	31	TREATED SW	114589	42
	119715	49		151866	89
	101383	26		107405	33
	111871	39		115036	43
TREATED FE	108882	35	RAW CD	258547	222
	104288	29		310626	287
	120663	50		240761	200
RAW SW	153532	91		296514	270
	139370	73	TREATED CD	264461	230
	132490	65		320667	300
				399101	398

VITA

Stacie A. Singleton

Candidate for the Degree of

Master of Science

Thesis: CHARACTERIZATION OF NON-POLAR ORGANIC COMPOUNDS IN PETROLEUM REFINERY WASTEWATERS

Major Field: Environmental Engineering

Biographical:

Personal Data: Born in Wichita, Kansas, November 19, 1966, the daughter of Dee A. Bohl Ford.

Education: Graduated from Jenks High School, Jenks, Oklahoma, in May, 1985; received Bachelor of Science Degree in Zoology from Oklahoma State University in May, 1989; completed requirements for the Master of Science degree at Oklahoma State University in July, 1992.

Professional Experience: Laboratory Technician, Oklahoma State University Water Quality Research Laboratory, May, 1990, to October, 1990. Research Assistant, Oklahoma State University Water Quality Research Laboratory, October, 1990, to February, 1992. Laboratory Technician, Stover Biometric Laboratory, February, 1992, to June, 1992.