THE REMOVAL OF ORGANIC CONTAMINANTS FROM GROUNDWATER BY REVERSE OSMOSIS

by

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(ABSTRACT)

The performance of a poly(ether/urea) membrane has been evaluated in a full scale reverse osmosis system. A series of experiments were conducted with six aromatic compounds - anthracene, pyrene, fluorene, 2-chlorobiphenyl, 2,4,6 trichlorophenol, and pentachlorophenol- and four volatile compounds - trichloromethane, bromodichloromethane, dibromochloromethane, and trichloroethene - as single and multi-solute contaminants. The objectives of the experiments were to determine if poly(ether/urea) membranes could produce a permeate that met maximum contaminant levels (MCL) set by the Safe Drinking Water Act (SDWA) and to correlate membrane performance with physical/chemical properties of the solute contaminants.

Aromatic contaminants were removed to concentrations below the current MCLs. However, volatile contaminants were not sufficiently rejected by the membrane to meet either the MCL for total trihalomethanes or trichloroethene.

Sorption onto the poly(ether/urea) was found to occur for several of the aromatic compounds tested in this research. This prevented developing any relationship between membrane performance and physical/chemical properties of the solute.

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CHAPTER 1
INTRODUCTION

Poly(ether/urea) membranes are used in U. S. Army reverse osmosis water purification units. Reverse osmosis was selected over other water treatment processes for its excellent desalination capabilities. Critical to the performance of the reverse osmosis process is the selection of the proper membrane. The poly(ether/urea) membrane is designated as a seawater membrane and as such has excellent rejection of inorganic salts. The poly(ether/urea) membrane has a performance standard, based on the removal of sodium chloride under standard conditions, that can be used for performance comparison between other membranes. Commercial use of reverse osmosis for removal of inorganic salts is well developed and in common use throughout the world.

The use of reverse osmosis membranes for the removal of organic compounds is a less developed process than reverse osmosis desalination. Performance is often stated in terms of molecular weight, i.e. 200 atomic mass units (amu) is a common lower limit for compounds removable by reverse osmosis (Dickson, 1988). However, organic water pollutants are such a diverse group of compounds in structure and properties that a removal standard based on molecular weight is ineffective. Removal is highly dependent on properties of the reverse osmosis membrane which makes comparison between membranes difficult.

The objectives of the research detailed in this thesis were to 1) determine if a poly(ether/urea) reverse osmosis membrane could produce, from a contaminated

water supply, a product water which met limits set by the Safe Drinking Water Act (SDWA) and 2) develop relationships between removal efficiency and a contaminant's physical and chemical properties. Attainment of these objectives would determine the performance of the poly(ether/urea) membrane and provide an understanding of what properties of a compound make it amenable to rejection by this specific poly(ether/urea) membrane.

CHAPTER 2
LITERATURE REVIEW

2.A HISTORICAL REVIEW

Consideration of reverse osmosis as a water treatment process began in the 1950's. In 1956, testing cellulose acetate and cellulose acetate-butyrate membranes for the separation of sodium chloride (NaCl) from water was conducted at the University of California at Los Angeles (Sourirajan, 1970). Sourirajan found that under static conditions cellulose acetate-butyrate membranes could achieve greater than 99.9 % NaCl removal over a thirty-day period. Researchers, working at the University of Florida under the sponsorship of the Office of Saline Water of the U.S. Department of Interior, found several materials capable of removing salts from water (Reid and Breton, 1959). Cellulose acetate was reported to have the highest removal efficiency. However, insufficient permeation rates prevented development as an economical commercial process.

In 1960, Loeb and Sourirajan developed a technique for producing cellulose acetate membranes which possessed both a high rejection of sodium chloride and a high water permeability (Sourirajan, 1970). This was a significant advancement in reverse osmosis membranes and stimulated increased research. In 1961, the Office of Saline Water began to vigorously sponsor research into reverse osmosis membranes and systems (Eisenberg and Middlebrooks,1986). New techniques for producing cellulose acetate and modified cellulose acetate membranes were widely

developed. In an effort to improve upon cellulose acetate membranes, polyamide membranes were first introduced by DuPont in 1968 (Hoornaert, 1984). These membranes, formed of hollow fibers, significantly increase the active membrane surface area permitting increased permeate flows.

In 1971, researchers at the North Star Research Institute were able to produce in situ a thin non-cellulosic film on a porous polysulfone structure (Riley et al., 1981). These membranes, known as composite membranes, were introduced commercially in 1977 by Universal Oil Products (UOP) (Gutman, 1987). Consisting of a polyamide surface layer atop a polysulfone supporting structural layer, these composite membranes maintained excellent salt rejection but also improved on the water permeability properties of membranes.

2.B TERMINOLOGY

The following terms will be consistently used throughout this paper and are defined here. Permeate refers to the purified product stream, while the term concentrate refers to the waste stream from a reverse osmosis membrane; rejection, removal, and separation are synonymous and refer to the inability of a compound to pass through a membrane. Percent rejection, removal, or separation define the difference between the feed concentration and the permeate concentration divided by the feed concentration. The terms element and membrane are often interchanged when discussing the reverse osmosis process. Membrane refers only to the sheets of membrane material performing the separation. Elements refer to the membrane and the supporting physical structure around the membrane.

2.C THEORY OF REVERSE OSMOSIS

Reverse osmosis is a pressure driven separation process utilizing a semipermeable membrane. It is often termed hyperfiltration. Related processes, such as ultrafiltration and microfiltration, rely solely on the size of the solute molecules and sieving action of the membrane for separation. Reverse osmosis relies on the difference in affinity between the solute molecules and the membrane and differences in diffusivity through the membrane (van den Berg and Smolders, 1988).

Osmosis, as shown in Figure 1, is the transport of water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. A semipermeable membrane, by definition, allows one component of a solution, typically water, to pass through but prevents the passage of other components, for example salt. Thermodynamically, the transfer of water is driven by a chemical potential gradient existing across the membrane. The pressure required to be exerted on the concentrated solution to prevent the transport of water through the membrane is referred to as osmotic pressure. If a pressure exceeding this osmotic pressure is applied, water will flow in reverse of its normal osmotic flow. Such a process is referred to as reverse osmosis.

2.D TRANSPORT THROUGH REVERSE OSMOSIS MEMBRANES

Many theories have been developed to explain the mechanism of solute and solvent transport through reverse osmosis membranes. Generally, these theories follow one of two models: nonporous transport or porous transport. These models differ principally in the interpretation of the surface layer of the membrane.

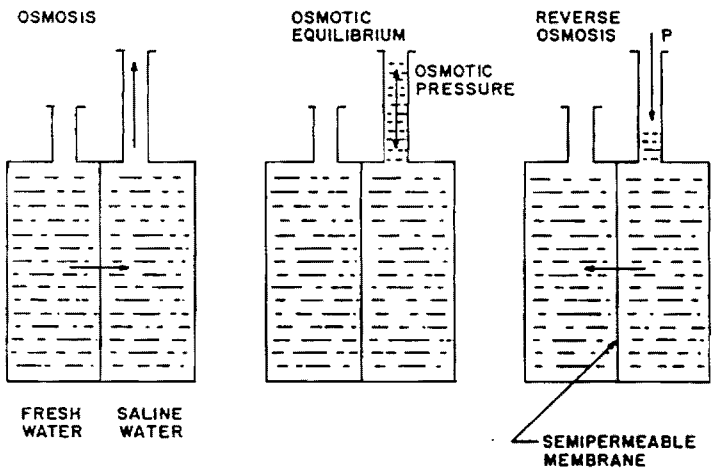

Figure 1. Principle of Water Purification by Reverse Osmosis.

The discussion of these models is strictly qualitative in nature.

2.D.1 SOLUTION DIFFUSION MODEL

Lonsdale, working with cellulose acetate membranes and NaCl solutions, developed a homogeneous diffusion model to describe the transport mechanism through the cellulose acetate membrane (Lonsdale *et al.*, 1965). In this nonporous transport model, ideal membranes are considered to have a nonporous surface layer. Solutes and solvents dissolve into the membrane and are transported through the membrane by molecular diffusion at rates dependent upon the diffusivity and solubility of the solvent and solute in the membrane. As indicated by another researcher (Dickson, 1985), this model fails to describe negative separations (separations in which the solute concentration is higher in the permeate than in the feed solution).

2.D.2 SOLUTION DIFFUSION IMPERFECTION MODEL

Since real membranes, in general, possess imperfections which may significantly increase the permeation of salt, the solution diffusion imperfection model was developed (Sherwood *et al.*, 1967). This model is a compromise between the porous and nonporous transport models. Transport of solutes and solvents occur by molecular diffusion. However, defects on the membrane surface may result in increased transport of solutes through the membrane.

2.D.3. PREFERENTIAL SORPTION-CAPILLARY FLOW MODEL

The preferential sorption-capillary flow model was developed by Sourirajan

to describe transport through porous reverse osmosis membranes (Sourirajan, 1970). In this porous transport model, transport through the membrane is a result of chemical interactions between the membrane, solvent, and solute at the membrane boundary. Sourirajan asserts that pores of a critical diameter exist at the surface layer of an ideal membrane. In this context, the term pore refers to any void space of any origin on the surface of the membrane. Pores increase in diameter with depth into the membrane. As a result, these membranes are called asymmetric membranes.

Several conditions can exist at the membrane boundary. First, the solvent is preferentially sorbed (and/or the solute is preferentially rejected). Second, the solute is preferentially sorbed. This results in a boundary layer of pure water, or for the latter, a boundary layer of pure solute. Under reverse osmosis pressure, the boundary layers pass through the surface pores into the membrane.

Another researcher, in support of Sourirajan's model, states that reverse osmosis separation is governed by the attractive and repulsive forces at the membrane interface, average pore size, and pore size distribution (Nguyen, 1987). The preferential-sorption capillary flow model has been the basis for additional investigations to develop an improved transport model. These efforts include the Kimura-Sourirajan analysis and the surface force-pore flow model (Dickson, 1985).

2.E PHYSICAL/CHEMICAL PARAMETERS RELATED TO SEPARATION

Based on the preferential sorption - capillary flow model, solutes must be sorbed at the membrane surface before passing through the membrane. Sorption of the solute is determined by the molecular properties of both membrane and

solute. However, molecular properties of membranes are not readily available; therefore, a correlation between molecular properties of the solute and membrane rejection would aid in the proper selection of reverse osmosis membranes.

2.E.1 MOLECULAR WEIGHT

As with normal filtration, a larger particle would be removed to a greater degree than a smaller particle. The same generally holds for reverse osmosis separation. A large molecule will be rejected by a membrane to a greater extent than a smaller molecule. Molecular weight is the simplest indication of molecular size. Thus, molecular weight can be useful in determining relative solute rejection.

Duvel and Helfgott (1975) performed a study to determine what solute characteristics could be used to predict the rejection of organic compounds with cellulose acetate membranes. In a homologous series of straight chain alcohols, solute rejection increased with increasing molecular weight.

Data from a study to evaluate reverse osmosis as a process to remove agricultural chemicals from groundwater indicated that higher molecular weight compounds are removed better than lower molecular weight compounds (Baier *et al.*, 1987).

2.E.2 MOLECULAR SIZE

Molecular size is not solely a function of molecular weight. Steric effects also determine molecular size. Duvel and Helfgott (1975) showed that steric configuration, branching, and spatial geometry play a large role in predicting solute rejection. Increased branching affected rejection greater than did molecular weight.

The increased cross section diameter of branched molecules prevents them from easily penetrating the membrane surface.

Chian and Fang (1976) demonstrated that steric effects influence solute rejection. The rejection of isomers of an amine, alcohol, and acid increased as the structure went from a normal to an iso- to a tertiary structure.

2.E.3 HYDROGEN BONDING

Hydrogen bonding between solute molecules and the membrane surface can create an attractive force that increases the permeability of the solute molecules. Organic molecules capable of strong hydrogen bonding with cellulose acetate membranes more readily passed through the membrane when compared to similar molecules not capable of hydrogen bonding (Duvel and Helfgott, 1975).

2.E.4 MEMBRANE SORPTION

Adsorption of solute molecules onto the membrane surface or into the membrane structure will initially improve rejection of solute. However, at equilibrium the solute may permeate the membrane. Sorption of solute molecules has been noted by several researchers. Abron and Osburn (1973) studied the transport mechanism of Aldrin and DDT through nylon hollow fiber membranes, and stated that both compounds were sorbed by the membrane and did not diffuse through the membrane. Nylon is an example of an aliphatic polyamide membrane.

Deinzer states that some aromatic compounds, including polynuclear aromatics, can adsorb to membranes. The report did not specify the types of membrane utilized (Deinzer *et al.*, 1975, citing Klein and Smith, 1972). Other

researchers, (Kinman *et al.*, 1987) found that chlorinated hydrocarbons do not sorb to a spiral wound thin film composite polyamide membrane.

2.E.5 SOLUTION pH

Feed solution pH will determine if a solute will exist as a molecule or as an ion. Several researchers have noted the relationship between a solute's ionic state and its degree of rejection. Chian and Fang (1976), in a study using crosslinked polyethyleninine membranes, state that the rejection of formic and acetic acids is a linear function of the degree of ionization of the solute molecule. When the solutes existed as molecules ($pH << pK_a$) the rejection was below 30%. However, when ionized ($pH >> pK_a$) the rejection increases to above 95%.

Similar results were obtained for phenol ($pK_a = 9.96$) using a poly(ether/amide) membrane (Riley *et al.*, 1976). At a pH of 4.9 ($pH < pK_a$), rejection was 93 %, but with a pH of 12.0 ($pH > pK_a$), rejection of greater than 99% was achieved.

2.F OPERATIONAL PARAMETERS RELATED TO SEPARATION

Solute rejection in a reverse osmosis system can be influenced by system operation. Pressure and temperature are variables which can be controlled by operators, while feed concentration is generally a fixed parameter in the operation of reverse osmosis systems.

2.F.1 FEED CONCENTRATION

Feed concentration does not play a large role in determining the separation

of organic compounds. The effect may be solute and/or membrane specific. For cellulose acetate membranes, solute separation decreased by less than 7 % with feed concentrations ranging from a 0.25 solute molality to a 1.50 solute molality for each of six organic compounds tested (Sourirajan, 1965). Rejections of benzene, cumene, and toluene by cellulose acetate membranes were independent of the solute feed concentration over the range of 5 to 260 mg/L (Dickson *et al.*, 1983).

Results from a pilot plant study using hollow-fiber polyamide membranes suggest that percent removal of aldicarb (sulfoxide and sulfone) decreases with increasing feed concentration (Baier *et al.*, 1987). A 94% removal was obtained with a feed concentration of 47 μg/L; however, when the feed concentration was lowered to 20 μg/L, complete removal was achieved. This contradicts data from a study on the rejection of chlorophenol by cellulose acetate membranes (Bennett *et al.*, 1968). When feed concentrations were increased from 9.5 mg/L to 106.0 mg/L and then to 1165 mg/L, the percent removal increased from 66.3% to 78.3% and finally to 87.0%.

2.F.2 OPERATING PRESSURE

The effect of operating pressure on solute removal has been studied and the results are ambiguous. Sourirajan (1965) found the removal of isopropanol to increase with increases in operating pressure, but he provided no explanation. In a study of cellulose acetate and aromatic polyamide membranes, solute rejection increased with increased operating pressure for a series 13 organic compounds (Chian and Fang, 1976). The compounds consisted mostly of low molecular weight polar compounds; such as methanol, ethanol, iso-propanol, acetic acid, acetone,

ethyl ether, phenol, urea, and aniline. In contrast, the rejection of benzene, toluene, and cumene decreased with increased pressure for six cellulose acetate membranes tested (Dickson *et al.*, 1983).

2.F.3 OPERATING TEMPERATURE

In a study evaluating temperature effects on the performance of polyamide membranes, researchers found separation of sodium chloride to be independent of temperature with the exception of low (150 psi) operating pressures (Mehdizadeh *et al.*, 1989). The test membranes included aromatic polyamide thin film composite membranes. Sourirajan (1965) found that solute separation decreased with increases in operating temperature for six organic compounds tested. Correspondingly, higher operating temperatures resulted in increased permeate flowrates. Separation of NaCl from water was found to be independent of temperature over a temperature range of 5°C to 35 °C (Dickson citing Yang and Dickson, 1988). While temperature has little effect on membrane rejection, increase in temperature resulted in increased permeate flux.

2.G REVERSE OSMOSIS MEMBRANES

Membranes are the essential element in reverse osmosis processes. The selection of the proper membrane is critical for achieving the desired separation. Rejection of organic compounds by reverse osmosis membranes is a function of both the physical and chemical properties of the membrane and the organic compound. Predictive models for determining separation performance have been developed. However, they generally tend to be complex when predicting rejection of multi-

contaminant solutions and have been developed based on cellulose acetate membranes. Testing is required for many new membrane materials to determine their adequacy to perform a desired separation.

Presented here is a brief overview of reverse osmosis membranes and configurations. A more detailed review can be found in Sourirajan 1977 and Eisenberg and Middlebrooks 1986.

2.G.1 MEMBRANE MATERIALS

Although a wide range of materials have been investigated for reverse osmosis membranes, very few have reached the point of widespread commercial use with the exception of cellulose acetate and polyamide membranes (Nielson, 1981).

2.G.1.1 CELLULOSE ACETATE

Cellulose acetate membranes were the first successful reverse osmosis membranes, and they still remain a standard commercial membrane (Lonsdale, 1982). The success of cellulose acetate membranes developed by Loeb and Sourirajan is due to the asymmetric structure of the membrane. Asymmetric membranes consist of a thin dense surface layer, a transition region and a spongy porous substructure (Eisenbrooks and Middlebrooks, 1986 citing Johnston and Lim 1973). Rejection is a function of the thin dense surface layer whereas the spongy porous substrate allows for the rapid movement of water once it penetrates the surface layer. This structure is a direct result of the casting process used to produce the membrane.

Cellulose acetate membranes exhibit poor chemical resistance, susceptibility

to biodegradation, and a tendency for membrane compaction (Gutman, 1987). Hydrolysis of the membrane polymer occurs when the feedwater pH is below 4 or above 8 and is enhanced at temperatures above 38 °C (Eisenberg and Middlebrooks, 1986 citing Porter, 1978).

2.G.1.2 POLYAMIDE

Polyamide membranes were developed to solve the limitations of cellulose acetate membranes. As a general classification, polyamide materials are polymers containing an amide group (Sourirajan, 1977). Polyamide materials are also described as "synthetic, organic nitrogen linked, aromatic, substantially linear condensation polymers" (Eisenberg and Middlebrooks, 1986 citing Burns and Roe, 1979). The term polyamides can constitute a wide assortment of membrane materials and includes poly(ether\urea) membranes.

In general, the transport, mechanical, thermal, biological, and chemical properties of polyamide membranes are superior to cellulose acetate (Riley *et al.*, 1976). These membranes can also be produced in a thin film composite configuration. Polyamide membranes were some of the first noncellulosic materials considered for desalination membranes (Breton and Reid, 1959).

2.G.2 MEMBRANE CONFIGURATIONS

Reverse osmosis membranes were first developed as flat sheets. New methods to configure the membrane inside the reverse osmosis element were developed. An increased membrane surface area per unit volume of element resulted in increased permeate production. Discussed will be several unique

designs that are currently common design configurations.

2.G.2.1 HOLLOW FIBER

Hollow fiber membranes were developed by DuPont in the late 1960's (Eisenberg and Middlebrooks, 1986). These membranes are constructed of hollow fibers connected between two nonporous plates. Feedwater passes over the outside of the fibers. Water molecules permeate into the fiber and are transported down the hollow center of the fiber and out of the pressure vessel. The outside/in flow of permeate prevents plugging of the hollow fibers and gives the membrane improved mechanical properties.

2.G.2.2 SPIRAL WOUND

Spiral-wound membranes are one of the most useful and unique membrane configurations developed to date (Riley *et al.*, 1977). As shown in Figure 2, two membranes and a porous support material are joined on three sides forming an envelope with the open side of this envelope being joined to a perforated hollow tube. This membrane envelope is then wound around the tube. In operation, feedwater passes over the outside of the membrane. Water penetrates into the membranes and travels spirally along the porous support material to the center collection tube.

The advantages of this configuration include a large membrane surface area per unit volume, ease of installation, handling, disposal and replacement, plus simple pressure vessel design (Riley *et al.*, 1977). The UOP Model 1501 membrane tested in this research is a spiral wound membrane.

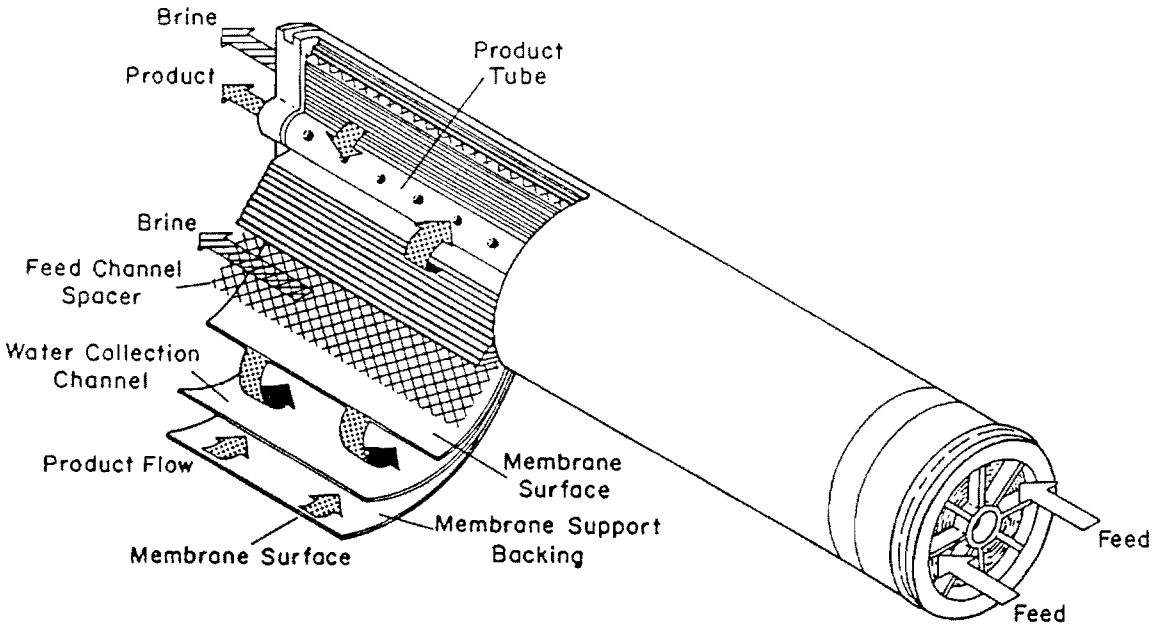

Figure 2. Internal Structure of a Spiral Wound Membrane.

2.G.2.3 THIN FILM COMPOSITE

Thin film composite membranes consist of three layers of different materials. These are 1) a backing of fabric or polyester, 2) an asymmetric porous support material, and 3) a thin, dense polymer surface layer (Belfort, 1981). Both cellulose acetate and polyamide materials have been used for this polymer coating. The surface layer of these membranes may be as thin as 500 Å (Lonsdale, 1982). Polysulfone is the most popular porous support material (Belfort, 1984).

The thin surface layer improves water permeability while maintaining high salt rejection. The transition region present in asymmetric cellulose acetatemembranes is avoided, thus improving the diffusion of water through the membrane.

2.H REMOVAL EFFICIENCY OF TEST AND RELATED COMPOUNDS

The rejection of organic compounds by reverse osmosis is a function of the specific membrane used. Therefore, relating the performance of other membranes to the membrane used in this research is difficult. However, such comparisons can provide some idea of membrane performance.

2.H.1 CELLULOSE ACETATE MEMBRANES

Chlorophenol is rejected an average of 77% for feed concentrations ranging from 9.5 milligrams per liter (mg/L) to 1165 mg/L. However, phenol is only rejected an average of 18% for feed concentrations ranging from 10.1 mg/L to 1031 mg/L (Bennett *et al.*, 1968). Feed solutions contained both phenol and chlorophenol and varied in pH from 7.5 to 9.0.

The difference in rejection of phenol and chlorophenol may have several explanations. The most obvious is molecular size. Chlorophenol has an additional chlorine atom and is a larger molecule than phenol. Solution pH may also help to explain the difference. Phenol with a pK_a of 9.96 exists as a molecule ($pH << pK_a$) under the test pH conditions and would be less effectively removed than if ionized. Chlorophenol has pK_a values of 8.11, 8.80, and 9.20 for its ortho, meta, and para structure respectively.

Trihalomethanes (THM's) were ineffectively removed by a reverse osmosis unit applied for point of use drinking water treatment. However, the concentration of chlorinated diphenyl was reduced by 95% (Regunathan et al.,1983). Cellulose triacetate hollow fiber membranes were found to ineffectively remove bromoform from seawater (Chang and Singer, 1981). Bromoform concentrations of 40 μg/L in the feed stream increased to 51 μg/L in the permeate. This is an example of negative separation where bromoform passes through the membrane easier than water.

2.H.2 POLYAMIDE MEMBRANES

The performance of a UOP PA-300 membrane was tested by Riley *et al.* (1976). This membrane is a spiral-wound poly (ether/amide) thin film composite membrane. Solute rejection exceeded 99% for ionized phenol (pH = 12.0), o-phenyl phenol, and trichlorobenzene but was only 93% for unionized phenol (pH = 4.9). These results show the significance of the ionic state of a compound in removal efficiency. The excellent removal of phenol at a pH of 4.9 contradicts the poor removal reported by Bennett for cellulose acetate membranes (Bennett et al., 1968).

This performance difference between polyamide membranes and cellulose acetate membranes shows the specificity of reverse osmosis membranes for the removal of certain organic compounds.

Mehta evaluated several membranes, including UOP-TFC membranes and UOP PA-300 membranes, in removing high concentrations of ethanol, 6% by weight, from water (Mehta, 1982). The UOP-TFC membrane reduced the ethanol concentration by 63 % while the UOP-PA-300 reduced the concentration by 44 %.

A pilot plant study at Water Factory 21 in Orange County, CA investigated the removal of trace organics from wastewater (Reinhard et al., 1986). Trihalomethanes were reduced by an average of 74 % while 1,1,1 TCE was removed in excess of 95%. Pentachlorophenol and 2,4,6-trichlorophenol were found to be completely removed (within the limits of detection for method of analysis).

A study on the removal of chlorinated hydrocarbons found that all ten compounds tested were completely rejected by the spiral wound thin film composite membrane (Kinman *et al.*,1987). Compounds tested included dichlorobenzenes, trichlorobenzenes, hexachlorobenzene, Heptachlor, and Endrin.

2.H.3 POLY(ETHER/UREA) MEMBRANES

A UOP poly(ether/urea) thin film membranes was found to effectively remove bromoform from seawater (Chang and Singer, 1981). Bromoform concentrations were reduced from 35 microgram per liter (μg/L) in the feed stream to a 5.0 μg/L in the permeate stream. Specific information regarding test conditions was not cited. Poly(ether/urea) membranes are capable of sodium chloride rejections in excess of 99% (Riley *et al.*, 1977).

2.I TEST COMPOUNDS

The test compounds are divided into two classes: aromatic organics and volatile organics. The aromatics consisted of three polyaromatics: anthracene, pyrene, and fluorene; two aromatic alcohols: pentachlorophenol and 2,4,6-trichlorophenol; and monochlorinated biphenyl: 2-chlorobiphenyl. The volatiles consisted of three trihalomethanes: trichloromethane, bromodichloromethane, and dibromochloromethane and one volatile organic: trichloroethene.

2.I.1 ENVIRONMENTAL SIGNIFICANCE

Tap water samples from homes located near a Norwegian alumina reduction plant had fluorene, anthracene, and pyrene concentrations of 0.72 ng/L, 0.35 ng/L, and 1.1 ng/L respectively (Olufsen, 1979). Concentrations of anthracene and pyrene in the wastewater from this same plant were 0.9 μg/L and 6.4 μg/L respectively.

A study tested 2,894 wells in eight states and found that 28 % of the wells were contaminated with trichloroethene (Hanson, 1985). The maximum concentration found was 35,000 μg/L. Contamination by trichloroethene has also been found in New Brighton, MN (70 - 290 μg/L); Rockaway, WI (90 - 240 μg/L); and in Silverdale, PA (20 - 100 μg/L) (Regunathhan, 1985). Trihalomethane concentrations ranging from 100 μg/L to 500 μg/L have been reported in several locations throughout the United States. A surface aquifer in West Jupiter, FL contained chloroform, dichlorobromomethane, chlorodibromomethane in concentrations of 222 μg/L, 142 μg/L and 60.3 μg/L respectively (Conlon and McClellan, 1989).

Groundwater at one site in Conroe, TX was contaminated with 2,4,6 - trichlorophenol at concentrations of 91.3 μg/L (Howard, 1983). Samples taken from a Washington lake were contaminated with 2,4,6 trichlorophenol ranging from 9.3 μg/L for surface samples to 2.2 μg/L for bottom samples (Howard, 1983).

2.I.2 PHYSICAL/CHEMICAL PROPERTIES:

Several properties of the contaminants are given in Table 2. Molar volume is calculated by the following equation:

$$Molar\ Volume = \frac{molecular\ weight}{(density) * (6.023 x 10^{23})} \qquad [Equ.\ 1]$$

Molar volume is a simple method to approximate molecular size. Numerically, the values are not accurate but do provide a scale for determining relative molecular size.

Table 1

Properties of Contaminants

COMPOUND	MOLECULAR WEIGHT	MOLAR VOLUME $Å^3$/molecule	pK_a
Anthracene	178.2	231	--
Pyrene	202.3	264	--
Fluorene	166.2	229	--
2-Chlorobiphenyl	188.7	272	--
2,4,6-Trichlorophenol	197.5	220	6.00
Pentachlorophenol	266.4	224	4.74
Trichloroethene	131.4	149	--
Trichloromethane	119.4	134	--
Bromodichloromethane	163.8	137	--
Dibromochloromethane	208.3	141N/A	

CHAPTER 3
METHODS AND MATERIALS

3.A OVERVIEW OF EXPERIMENTAL DESIGN

The experiments were designed to determine the short term efficiency of a reverse osmosis membrane to remove organic contaminants from groundwater. Feedwater was obtained from a well located at the site of the experiments. To minimize the volume of waste water generated the test unit was operated as a closed loop system. Various contaminants, either individually or as a group, were added to 300 gallons of groundwater. The water was cycled through the reverse osmosis unit for 12 hours, with samples taken at four locations every 1.5 hours. At the completion of a trial, the contaminated water was passed through an activated carbon column before discharge. Both new and used membranes were evaluated.

Heat generated by the high pressure pump in the closed loop system caused the temperature of the feed water increased significantly (60 °F temperature rise in 12 hours). This problem was solved by passing the concentrate stream through a heat exchanger before recycling back into a holding tank.

3.B REAGENTS

The following reagents were used in this research:

Aromatic Compounds

1. Anthracene ($C_{14}H_{10}$) 98+% Aldrich Chemical Co. (Milwaukee, WI)
2. Fluorene ($C_{13}H_{10}$) 98% Aldrich Chemical Co.

3. Pyrene ($C_{16}H_{10}$) 99+% Aldrich Chemical Co.
4. 2-Chlorobiphenyl ($C_{12}H_9Cl$) 99% Alpha Products (Danvers, MA)
5. Pentachlorophenol (C_6Cl_5H) Sigma Chemical Company (St. Louis, MO)
6. 2,4,6-Trichlorophenol ($C_6Cl_3H_3$) Sigma Chemical Company
7. Phenanthrene$_{d10}$ ($C_{14}D_{10}$) 98 % Cambridge Isotope Laboratories (Woburn, MA)
8. Acenaphthene ($C_{12}H_{10}$) Sigma Chemical Company

Volatile Compounds

1. Trichloromethane ($CHCl_3$) HPLC Grade Fisher Scientific (Columbia, MD)
2. Trichloroethene (C_2HCl_3) Mallinckrodt (Paris, Kentucky)
3. Bromodichloromethane ($CHCl_2Br$) 98 % Columbia Organic Chemical Company (Camden, SC)
4. Chlorodibromomethane ($CHClBr_2$) 98 % Columbia Organic Chemical Company

Solvents and Other Compounds

1. Methylene Chloride (CH_2Cl_2) Baxter Scientific (Columbia, MD)
2. Acetone (CH_3COCH_3) Optima Grade Fisher Scientific
3. Methanol (CH_3OH) Optima Grade Fisher Scientific
4. Sodium Sulfate (Na_2SO_4) Certified ACS Fisher Scientific
5. Hydrochloric Acid (HCl) Reagent ACS Fisher Scientific

3.C FIELD OPERATIONS

3.C.1 DESCRIPTION OF REVERSE OSMOSIS UNIT

The reverse osmosis unit used in this research was equipped with a single reverse osmosis membrane and configured according to the schematic diagram shown in Figure 3. The feed solution was drawn by a 1-hp centrifugal pump from a 300 gallon holding tank through six woven polypropylene cartridge filters having nominal openings of 5 μm. Prefiltration is necessary for removal of particles that could rapidly foul the reverse osmosis membrane. A high pressure positive displacement pump increased the feed water pressure to 325 pounds per square inch (psi) forcing the water through the membrane. Effluent from the membrane consisted of the permeate (treated) water and the concentrate (untreated) water both of which were recycled to the holding tank. To remove heat generated in the system the concentrate passed through a heat exchanger before returning to the holding tank.

The reverse osmosis membrane, manufactured by UOP Fluid Systems Division (San Diego, CA), is a seawater membrane designated as Model 1501. It is a spiral wound thin film composite poly(ether/urea) membrane having a length of 40 inches and a diameter of six inches. Each membrane has an output rate of 2200 gallons per day (gpd) or 1.53 gallons per minute (gpm). The membrane has a nominal surface area of 150 square feet and is considered to have a neutral charge. The UOP 1501 membranes are pretested by the manufacturer to meet minimum performance standards of 99.0% sodium chloride rejection of a 32,800 mg/L NaCl feed stream at an operating pressure of 800 psi (Allegrezza, 1988).

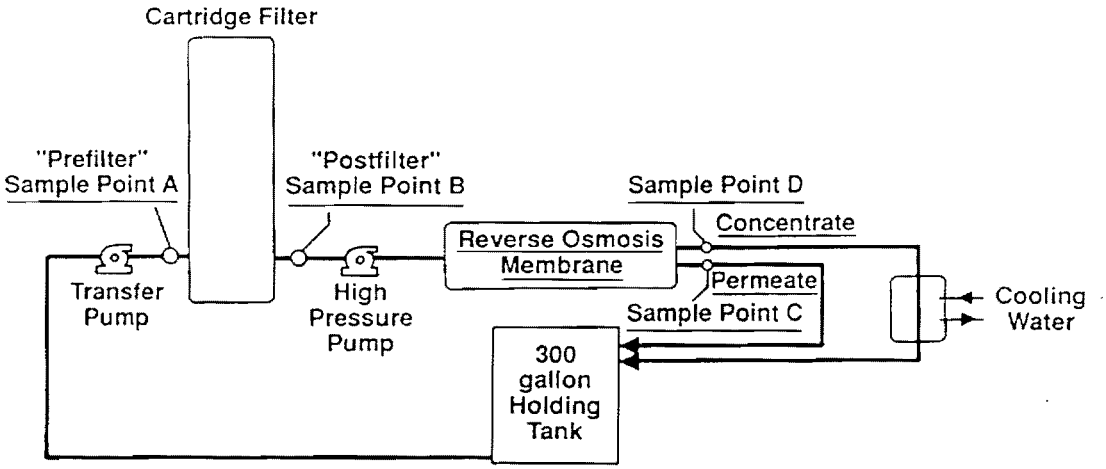

Figure 3. Schematic of Reverse Osmosis Field Unit.

Three hundred gallons of contaminated feed water solution were prepared on a batch basis from groundwater obtained at the site of the reverse osmosis experiments (Price's Fork Research Center). Analysis of the groundwater detected none of the aromatic and volatile compounds used in this research. An analysis of the groundwater is given in Table 2. All contaminants were dissolved in approximately 75 ml of acetone before being added to the water. To insure dissolution of the compounds, the acetone solution was added slowly to the tank and mixed.

After each test was completed, the contents of the holding tank were pumped through an activated carbon filter into a secondary holding tank. An analysis of the water in this tank was made. For the six trial runs using organic and volatile compounds, complete removal was achieved by the carbon filter. The water was discharged onto the ground.

During each trial run, feed water temperature, pressure, and flowrate were monitored. Operating pressure was held between 320 and 325 psi, while feed water flowrate was set between 22.0 - 23.0 gpm. Feed water temperature increased during each of the 12 hour tests but did not exceed 22 ° C.

3.C.2 SAMPLING STRATEGY

Membrane performance was tested in a series of three trials for each group of contaminants - aromatics and volatiles. In the first trial of the series, an unused membrane was evaluated with feed water containing only a single contaminant. For the second trial, an unused membrane was evaluated with the feed water

Table 2

Analysis of Groundwater Used in Reverse Osmosis Field Trials

Arsenic	< 1 µg/L
Copper	1 µg/L
Magnesium	36.5 mg/L
Nickel	1 µg/L
Lead	< 1 µg/L
Iron	0.03 mg/L
Manganese	0.01 mg/L
Calcium	75.5 mg/L
Sodium	10.3 mg/L
Potassium	2.4 mg/L
Fluoride	0.587 mg/L
Nitrate	14.858 mg/L
Potassium	10.014 mg/L
Lindane	None Detected
Heptachlor	None Detected
Methoxychlor	None Detected
Atrazine	None Detected
1,4-dichlorobenzene	None Detected
Total Organic Carbon	0.35 mg/L
Aromatic Compounds Used in This Research	None Detected
Volatile Compounds Used in This Research	None Detected

containing the entire group of contaminants. In the third trial, the same membrane used in the second trial was evaluated with feed water containing only the single contaminant used in the first trial. The membrane remained in the test unit for a 24-hour period between the two trials. This was done to determine if a performance difference existed between new and used membranes. The use of single and multiple contaminant trials would evaluate membrane performance for a compound that appeared both as a single contaminant and as one of a group of multiple contaminants.

Samples were collected at four locations in the system: (1) Sample point A - before the cartridge filters, (2) Sample Point B - after the cartridge filter, (3) Sample point C - the concentrate stream exiting the element, and (4) Sample point D - the permeate stream. Tests were scheduled for twelve hours with samples being collected at fifteen minutes after startup and every 90 minutes thereafter. The fifteen minute delay after startup provided time for the entire contents of the tank to theoretically pass through the system and to reach equilibrium. Duplicate samples were taken at each sampling point for the 3, 6, 9, and 12-hour sampling times.

3.C.3 CONTAMINANTS TESTED

The selection of contaminants was governed by criteria set by the U.S. Army and with respect to chemicals regulated under the Safe Drinking Water Act. Table 3 is a list of the contaminants tested in each trial for both aromatic and volatile compounds. Contamination of water sources by petroleum, oil, and

Table 3

Test Schedule of Aromatic and Volatile Compounds Tested

	AROMATICS	VOLATILES
TRIAL 1	Anthracene	Trichloroethene
TRIAL 2	Anthracene Pyrene Fluorene 2-Chlorobiphenyl 2,4,6-Trichlorophenol Pentachlorophenol	Trichloroethene Trichloromethane Bromodichloromethane Dibromochloromethane
TRIAL 3	Anthracene	Trichloroethene

lubricant products was a concern of the Army. For this reason, several polyaromatic hydrocarbons, namely anthracene, pyrene, and fluorene, were selected. These compounds are representative of products of combustion that are often found in water. Another group of compounds of interest were polychlorinated biphenyls (PCB's). Due to the toxicity of these compounds and the regulations and rigorous laboratory requirements necessary to handle PCB's, a monochlorobiphenyl was selected as an analog. The effectiveness of the reverse osmosis membrane in removing alcohol related compounds was evaluated with the inclusion of pentachlorophenol and trichlorophenol. Pentachlorophenol is a widely used wood preservative. Due to recent health concerns over volatile organic compounds, several volatile compounds were selected including trichloroethene and three compounds in the trihalomethane group. Trichloroethene is a common degreasing agent and groundwater contaminant, where as the THMs are byproducts of chlorination.

TEST CONCENTRATIONS

A concentration range was selected for each of the ten contaminants tested and is given in Table 4. The range for the volatiles was obtained by taking the maximum contaminant level (MCL) set by the Safe Drinking Water Act (SDWA) and multiplying by an appropriate factor. For those contaminants which are not covered under the SDWA or whose MCL's have yet to be specified, concentration ranges were set by best judgement.

Table 4

Target Concentration Range in Feed Water and MCLs Established by the SDWA

COMPOUNDS	FEED WATER CONCENTRATION	SDWA
AROMATICS		
Anthracene	0.050 - 0.50 mg/L	N/A
Pyrene	0.050 - 0.50 mg/L	N/A
Fluorene	0.050 - 0.50 mg/L	N/A
Pentachlorophenol	0.25 - 0.50 mg/L	0.2 mg/L
2,4,6 - Trichlorophenol	0.25 - 0.50 mg/L	N/A
2-Chlorobiphenyl	0.25 - 0.50 mg/L	0.0005 mg/L
VOLATILES		
Trichloroethene	0.05 - 0.50 mg/L	0.005 mg/L
Trichloromethane	0.20 - 0.50 mg/L	0.10 mg/L
Bromodichloromethane	0.20 - 0.50 mg/L	0.10 mg/L
Dibromochloromethane	0.20 - 0.50 mg/L	0.10 mg/L
N/A = Not regulated		

3.D METHODS OF ANALYSIS

3.D.1 AROMATIC COMPOUNDS

The six aromatic contaminants were analyzed using EPA Method 525 - Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (EPA Test Method 525 - Draft Method Revision 2.0 July 1988). This method is an alternate to EPA Method 625. A solid phase extraction procedure replaced the methylene chloride extraction procedure of Method 625.

3.D.1.1 SAMPLE COLLECTION AND PRESERVATION

The samples were collected in 1-L (one liter) amber glass bottles fitted with teflon lined screw tops. All sample bottles were cleaned with hot soapy water, rinsed with tapwater a minimum of three times, and rinsed with distilled water a minimum of three times before being used. Samples were preserved by adjusting the pH to 2.0 or less with 6 N hydrochloric acid. Samples were stored in ice from the time of collection until transported to the laboratory.

3.D.1.2 SOLID PHASE EXTRACTION

The extraction procedure used a C_{18} octadecyl solid phase cartridge. Analytichem International (Harbor City, CA) Bond Elut cartridges (500 mg of sorbent and a 10 ml capacity) were selected. The entire extraction procedure was done under a slight vacuum of 5 to 7 inches mercury with the sample at room temperature. The cartridge required conditioning prior to the extraction process. This was accomplished by successive flushes with two 10-ml aliquots of methylene

chloride, two 10-ml aliquots of methanol and one 10-ml aliquot of Milli-Q water.

A sample was placed in a 2-L separatory funnel. Internal standards, acenaphthene and/or phenanthrene$_{d10}$, were added and the funnel was vigorously shaken. The separatory funnel was attached to the extraction cartridge and the sample was passed through the column at a rate of approximately 15 ml/minute. If the sample did not pass through the cartridge within three hours, the extraction was stopped and the remaining sample volume was measured. Air was drawn through the cartridge for ten minutes to remove any traces of water. The cartridges were sealed in aluminum foil and were stored at 5°C for no longer than 48 hours before elution.

The cartridges were eluted, under no vacuum, with two successive 7.5 ml aliquots of methylene chloride. The 15 ml of sample was reduced to 5 ml under a gentle stream of nitrogen gas. The samples were air evaporated to between 1 to 2 ml. The samples were stored in glass vials fitted with teflon lined caps and were wrapped in aluminum foil and stored at 5 °C until analysis.

3.D.1.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The samples were analyzed on a Hewlett Packard (Avondale, PA) 5890 Gas Chromatograph connected to a Hewlett Packard 5970 Mass Spectrometer. The gas chromatograph was equipped with a J & W Scientific (Folsom, CA) 30 m x 0.25 mm DB-5 capillary column. A multi-ramp temperature program given in EPA Method 525 was utilized with one modification - injector temperature was increased from 45 °C to 200 °C. The temperature program was as follows: injector temperature 200 °C, initial oven temperature 45 °C, ramp ballistically to 130 °C, at 3 minutes ramp

12 °C/minute to 180 °C, ramp 7 °C/minute to 240 °C, ramp 12 °C/minute to 320 °C. A one minute purge and a 5 minute solvent delay were used. Helium was the carrier gas with a linear flowrate of approximately 33 cm/second.

A 1 or 2 μL sample volume was injected onto the column. Selected ion monitoring was utilized for mass spectrometer detection. The quantitation ion selected for each compound is shown in Table 5. Identification of peaks was accomplished through a computerized comparison of spectral data from Wiley Data Libraries. Verification was done by comparison of retention times for single compound injections.

Quantitative analysis was also performed on the GC/MS. Response factors for each compound were determined at concentration ratios of 20, 10, 5, 1, and 0.1. Operating conditions were identical to those used for analysis of the samples. Five replicate injections were made at each concentration ratio. The response factors in Table 6 were considered valid if the relative standard deviation was below 30%.

3.D.2 VOLATILE ORGANICS

The four volatile compounds were analyzed using EPA Test Method 502.1 - Volatile Halogenated Organic Compounds in Water by Purge and Trap Gas Chromatography. The sample was purged with an inert gas to extract the volatile compounds. The stripped volatile compounds were then sorbed to a solid matrix. After the purge is complete the solid matrix was heated and backflushed to desorb the volatile components onto a gas chromatography column. A halogen specific detector was used to detect volatile halogenated compounds.

Table 5

M/Z Values for SIM Analysis

COMPOUND	QUANTITATION ION (M/Z)
Anthracene	178
Pyrene	166
Fluorene	202
2-Chlorobiphenyl	188
2,4,6 -Trichlorophenol	196
Pentachlorophenol	266
INTERNAL STANDARDS	
Acenaphthene	154
$Phenanthrene_{d10}$	188

Table 6

Response Factors for Quantitative Analysis

COMPOUND	INTERNAL STANDARD	RESPONSE FACTOR
Anthracene	$Phenanthrene_{d10}$	1.09
Pyrene	$Phenanthrene_{d10}$	1.06
Fluorene	Acenaphthene	0.54
2 - Chlorobiphenyl	Acenaphthene	0.90
2,4,6 - Trichlorophenol	Acenaphthene	1.42
Pentachlorophenol	$Phenanthrene_{d10}$	1.60

3.D.2.1 SAMPLE COLLECTION AND PRESERVATION

The samples were collected in 20 ml amber vials fitted with teflon lined screw tops. All sample bottles were unused and initially rinsed with chromic acid to remove any organic contamination. Thereafter, all bottles were washed in hot soapy water, rinsed with tap water, and rinsed with distilled water. During sample collection head space in the sample bottles was minimized. Samples were stored in ice from time of collection until transported to the laboratory.

3.D.2.2 PURGE AND TRAP

A purge and trap procedure as given in EPA Method 502.1 was used for sample extraction. A 5-ml sample was injected into a Tracor LSC-2 sample concentrator and purged for 8 minutes with helium at a flowrate of 40 ml/minute. A four minute backflush with helium desorbed the volatiles from the Tenax sorbent.

3.D.2.3 GAS CHROMATOGRAPHY/HALL DETECTOR

A Tracor 560 gas chromatograph connected to a Tracor 1000 Hall Detector was used for the analysis. The gas chromatograph was equipped with a Supelco (Bellefonte, PA) 1% SP-1000 on 60/80 mesh Carbopack-B column (2.4 m x 2mm ID). The following gas chromatograph temperature program was used: initial oven temperature 100 °C, final oven temperature 220 °C, temperature ramp 10 °C/minute, initial hold time 0 minutes, and a final hold time 2 minutes. The gas chromatograph was connected to a Hall electrolytic conductivity detector configured to detect halogens. Calibration of the Hall detector was performed at the beginning

of each analysis period and checked every six samples.

3.E POST CHLORINATION

The potential for the formation of THMs was estimated by chlorination of permeate samples. Three permeate samples - 4 hour, 8 hour, and 12 hour - from each of the three trials using aromatic compounds were chlorinated. An approximate 40-ml sample was dosed with chlorine, as hypochlorous acid, to a concentration of 5 mg/L. A stock chlorine solution of 960 mg/L was used to chlorinate the samples. Chlorine concentrations were determined using a Fisher Scientific Model 900 titration burette attached to a Fisher Scientific computer aided titromoter. The sample were stored at room temperature in the dark for a 30 minute contact time. After the 30-minute contact time the samples were analyzed using EPA Method 502.1, as explained above.

3.F SORPTION EXPERIMENTS

Aliquots of 500 ml from a solution containing approximately 1.5 mg/L of anthracene, fluorene, 2,4,6 - trichlorophenol, and pentachlorophenol were placed in 1-L amber glass bottles. Approximately 20 grams of membrane were placed in each bottle and submerged in the solution. An additional 500 ml aliquot was placed in a 1-L amber glass bottle, with no membrane material, as a control. After 2, 20, and 52 hours the solutions were analyzed for the four contaminants using EPA Method 525 as described above.

CHAPTER 4
RESULTS

In this section, performance data for the reverse osmosis unit is presented in graphical form showing contaminant concentrations at the four sample locations - prefilter, postfilter, permeate, and concentrate (see Figure 3) - over the duration of the test. These graphs have been developed from laboratory analysis data tabulated in Appendix 2.

4.A REVERSE OSMOSIS CONTAMINANT REMOVAL

Figures 4 through 11 are the results of three trials involving the aromatic compounds used in this study. In each of these graphs contaminant concentration decreased in the prefilter, postfilter, and concentrate streams. Concentrations in the permeate stream decreased within the first 3 hours of each experiment until reaching a steady state concentration. Three exceptions were the permeate concentrations of 2,4,6-trichlorophenol (Figure 9), which increased for 6 hours before decreasing to near its original value, fluorene (Figure 6), which also increased for 6 hours before beginning an erratic decline, and anthracene (Figure 11), which began a steady increase at 4.5 hours into the experiment.

Figures 12 through 17 are the results of three trials involving the aromatic compounds used in this study. As was observed with the aromatic compounds, a decrease of contaminant concentration occurred in the prefilter, postfilter, and concentrate streams. However, the concentration of the permeate stream in all

three trials involving the volatiles increased during the experiment. In Figure 18, total THM concentrations (trihalomethane, bromodichloromethane, and dibromochloromethane) in the permeate is shown to increase with time. This data was accumulated from the multi-contaminant trial.

Figure 19 shows a comparison of anthracene concentrations in the permeate stream from a new membrane and from a used membrane. Figure 20 displays the results of tests to determine any difference in removal efficiency when a single feed water contaminant is present in comparison with the presence of additional contaminants. Anthracene removal was compared in these tests. Figures 21 and 22, respectively, show similiar comparisons for the volatile compounds using trichloroethene as the single contaminant.

4.B POST CHLORINATION

All chlorinated permeate samples from the three aromatic trials had total trihalomethane concentrations below 2 μg/L as shown in Table 7.

4.C SORPTION EXPERIMENTS

Results from the sorption experiments performed with the poly(ether/urea) membrane using anthracene, fluorene, trichlorophenol, and pentachlorophenol are given in Figure 23. A decrease in solute mass remaining in solution occurs for each of the four compounds tested.

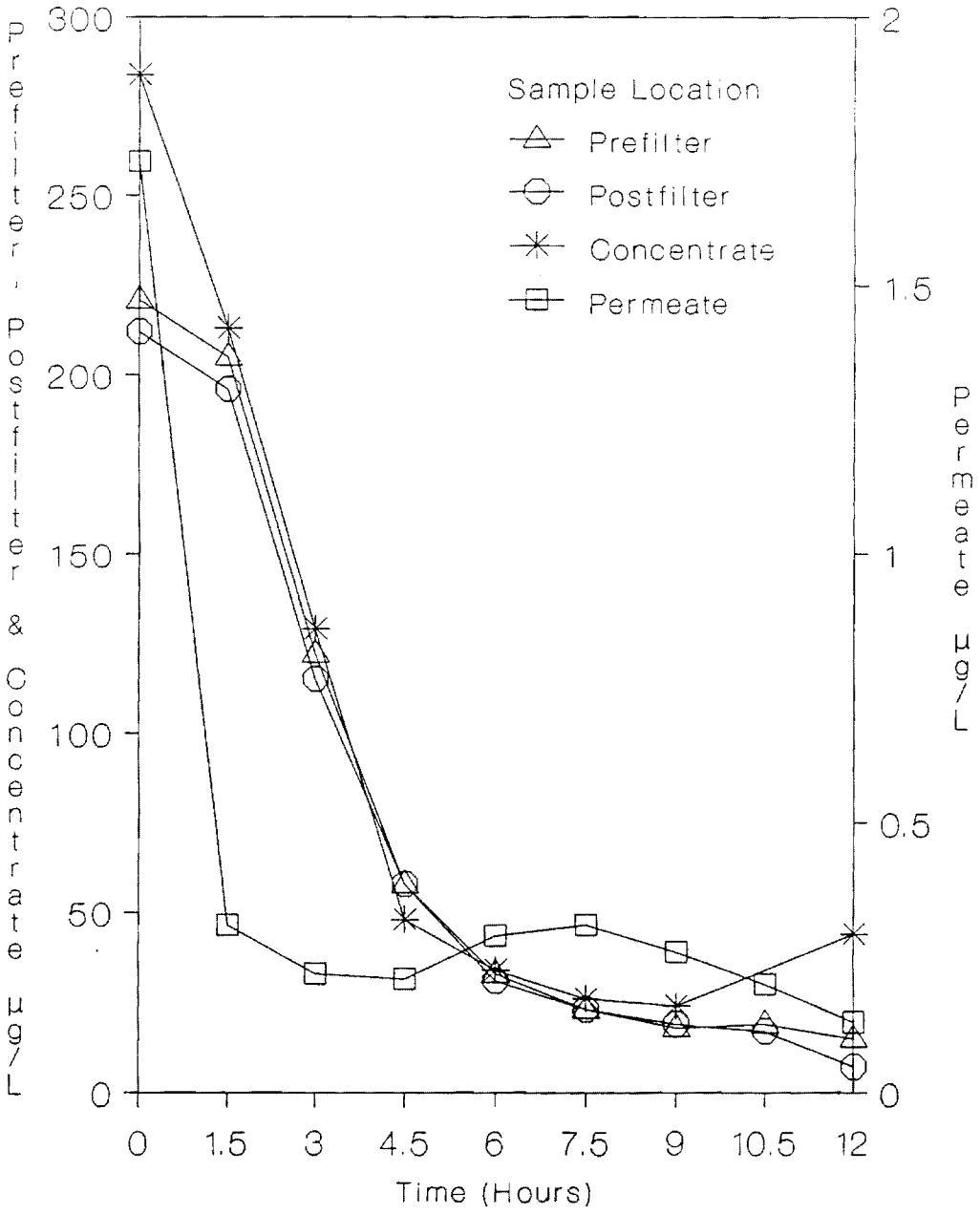

Figure 4. Concentrations of Anthracene at Four Sampling Points for a Single Contaminant Trial with a New Membrane.

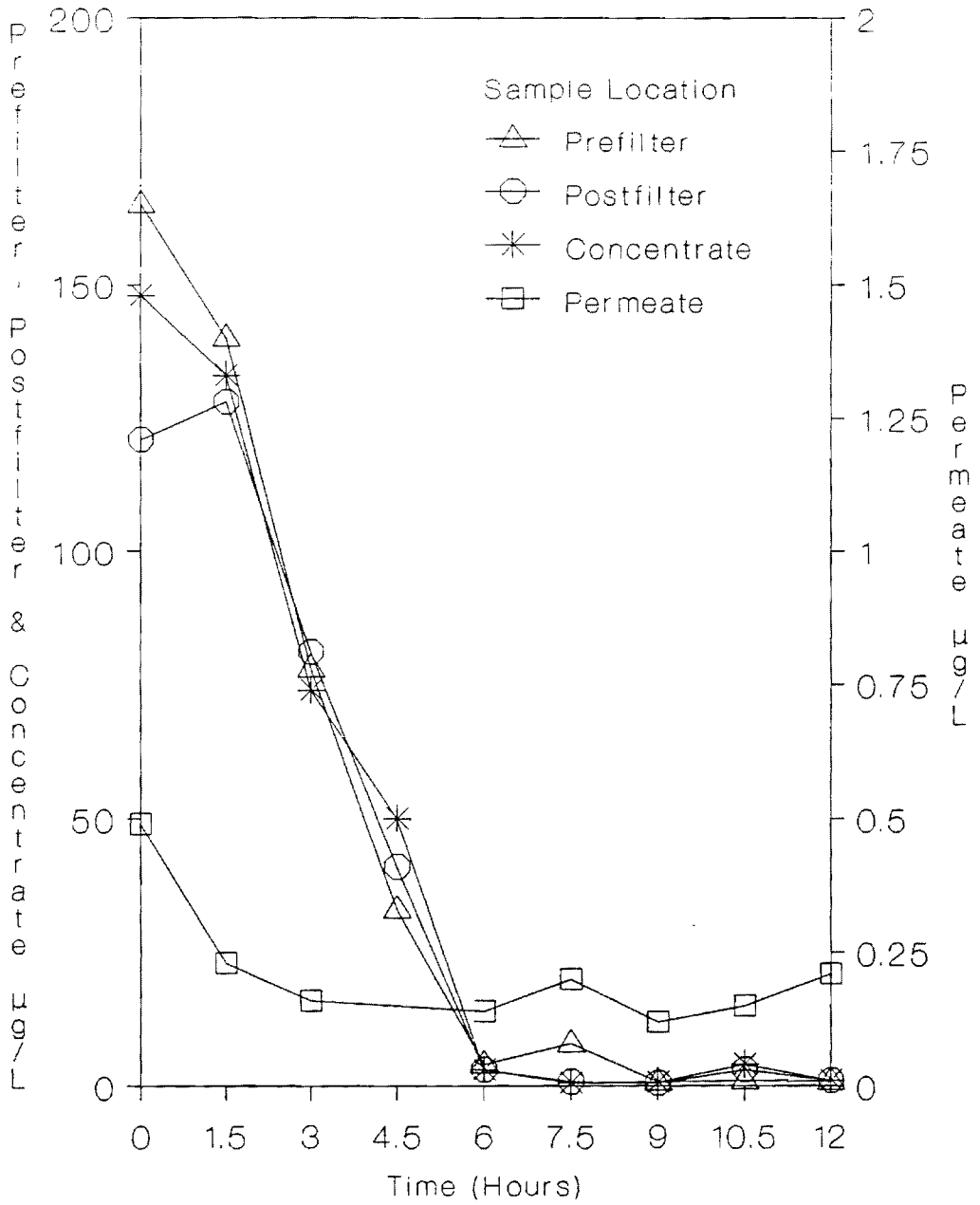

Figure 5. Concentrations of Anthracene at Four Sampling Points for a Multi-Contaminant Trial with a New Membrane.

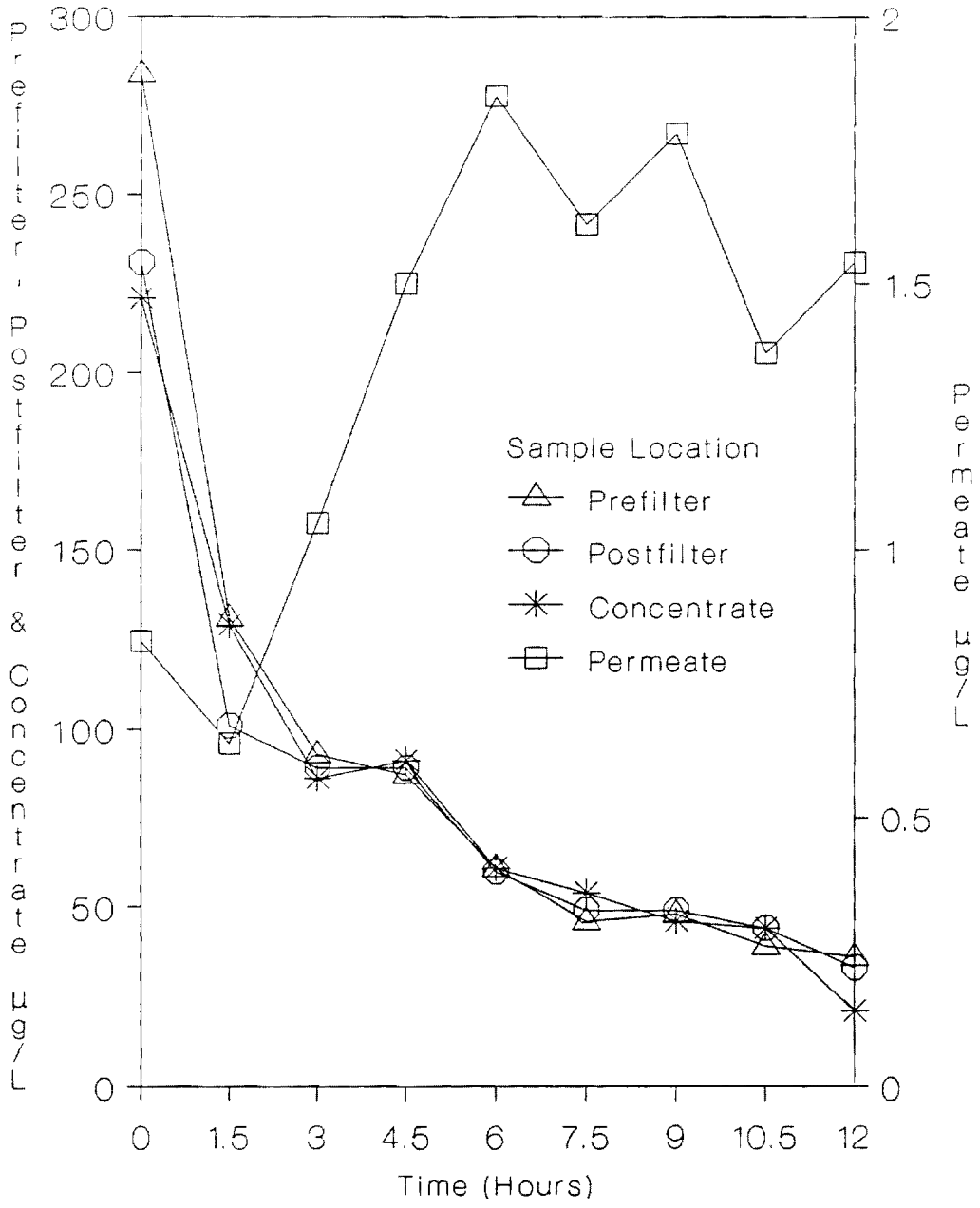

Figure 6. Concentrations of Fluorene at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

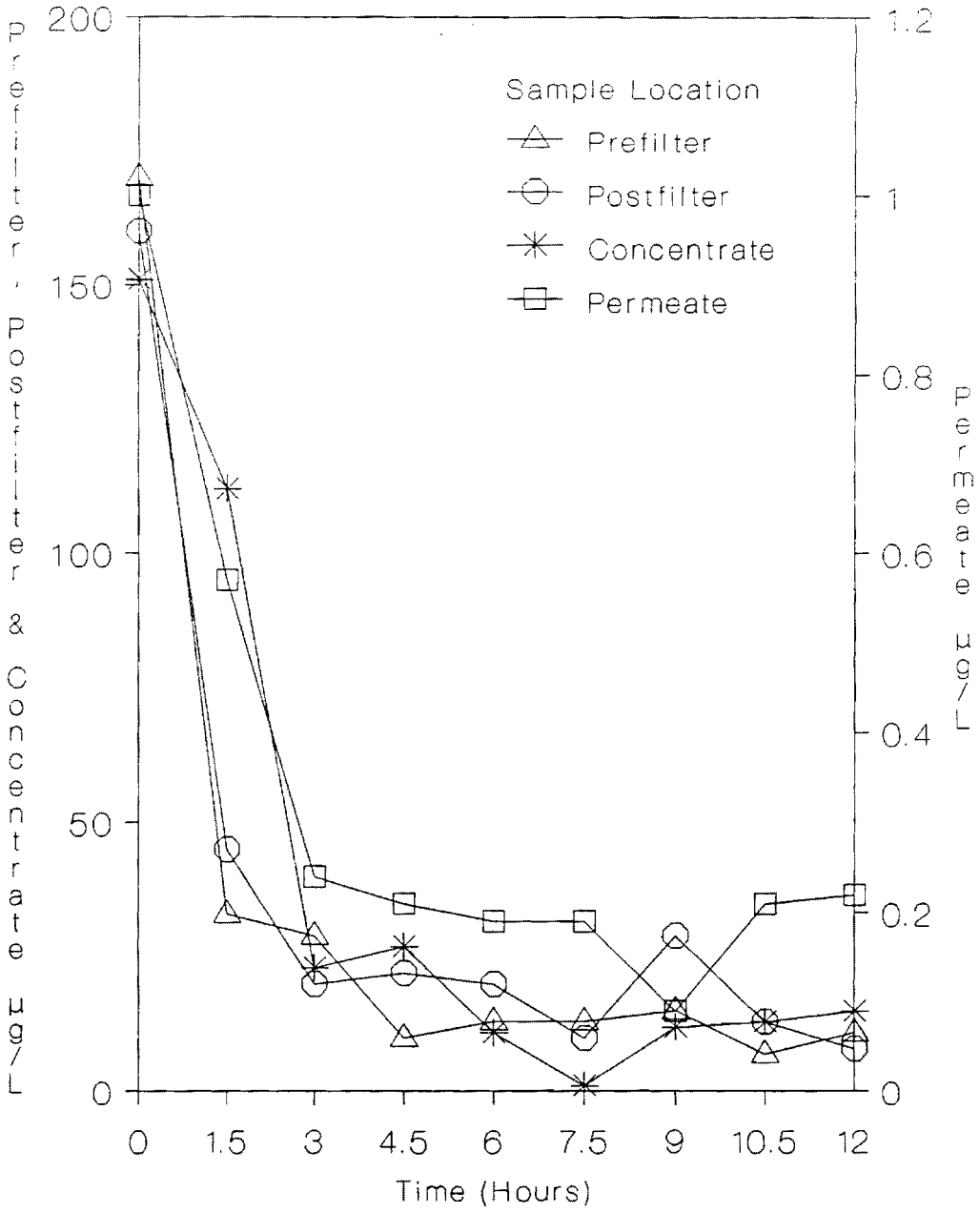

Figure 7. Concentrations of Pyrene at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

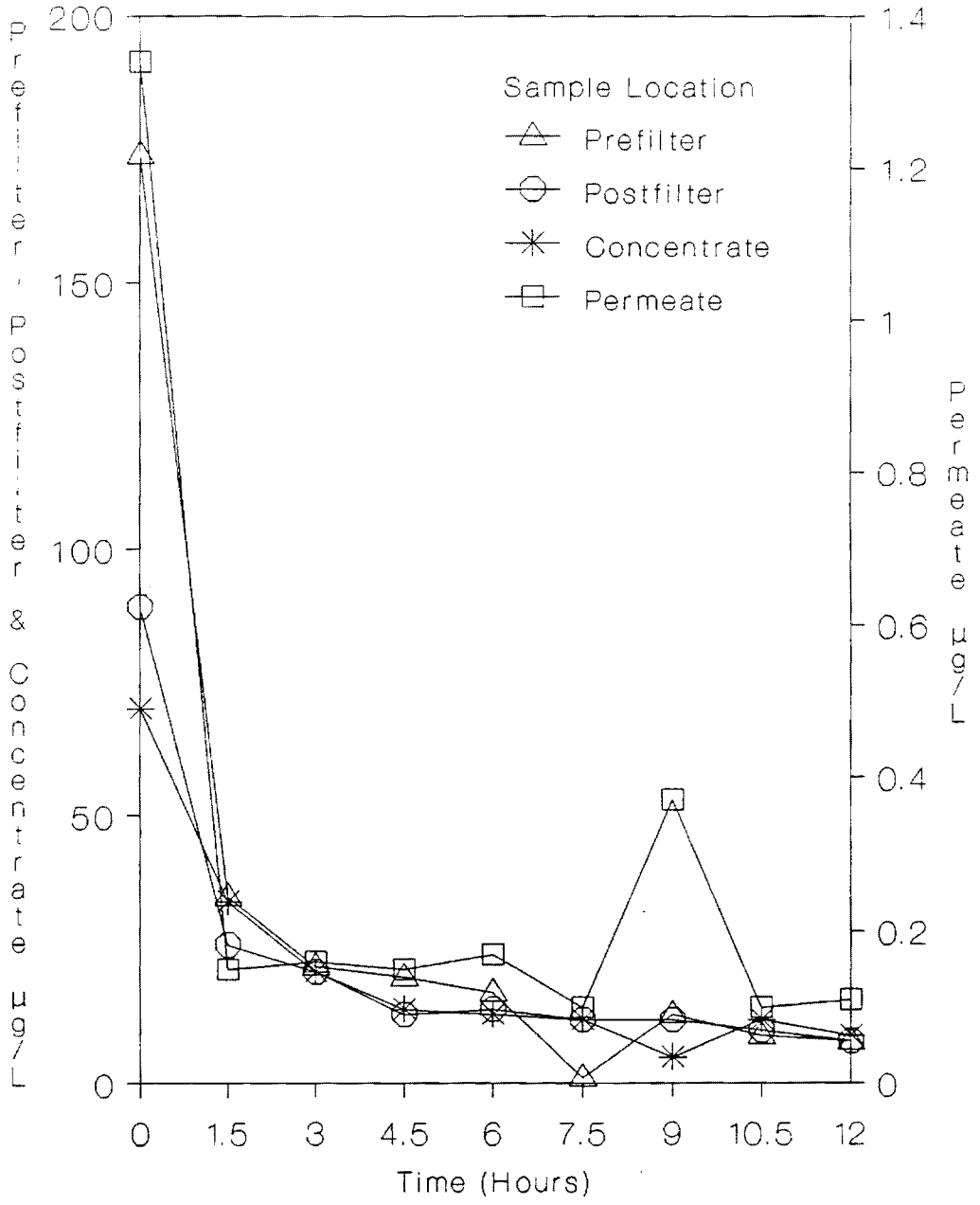

Figure 8. Concentrations of 2- Chlorobiphenyl at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

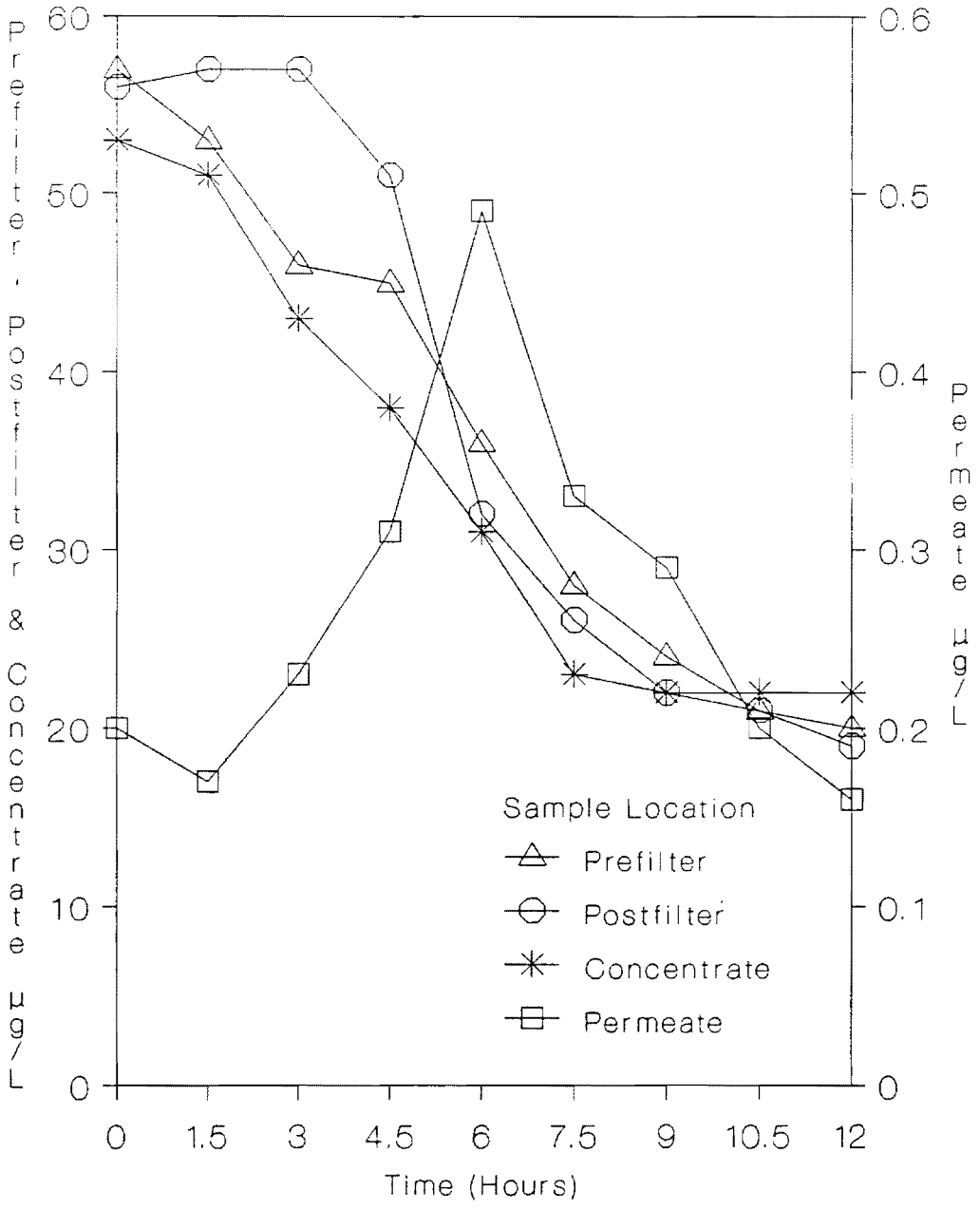

Figure 9. Concentrations of 2,4,6 - Trichlorophenol at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

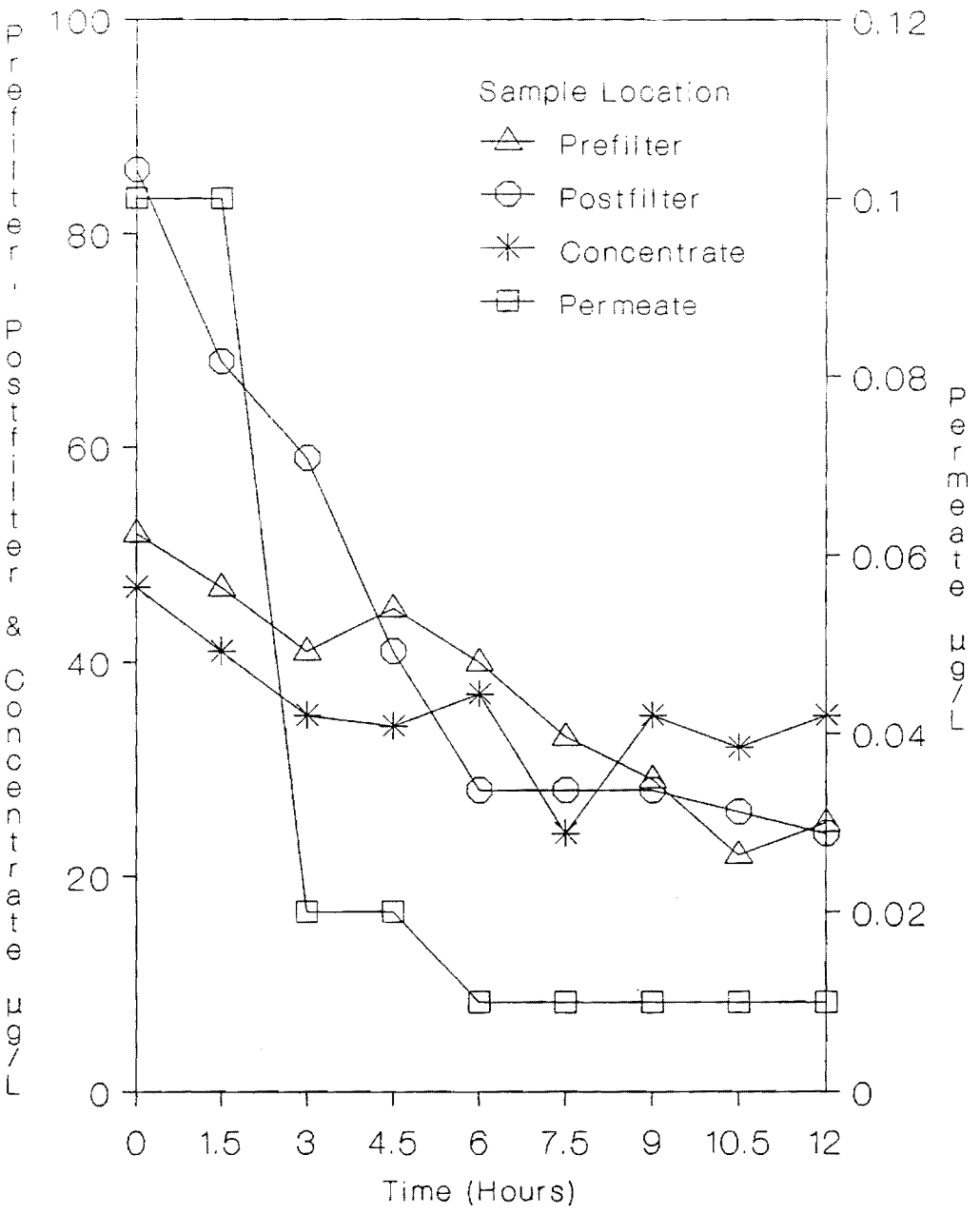

Figure 10. Concentrations of Pentachlorophenol at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

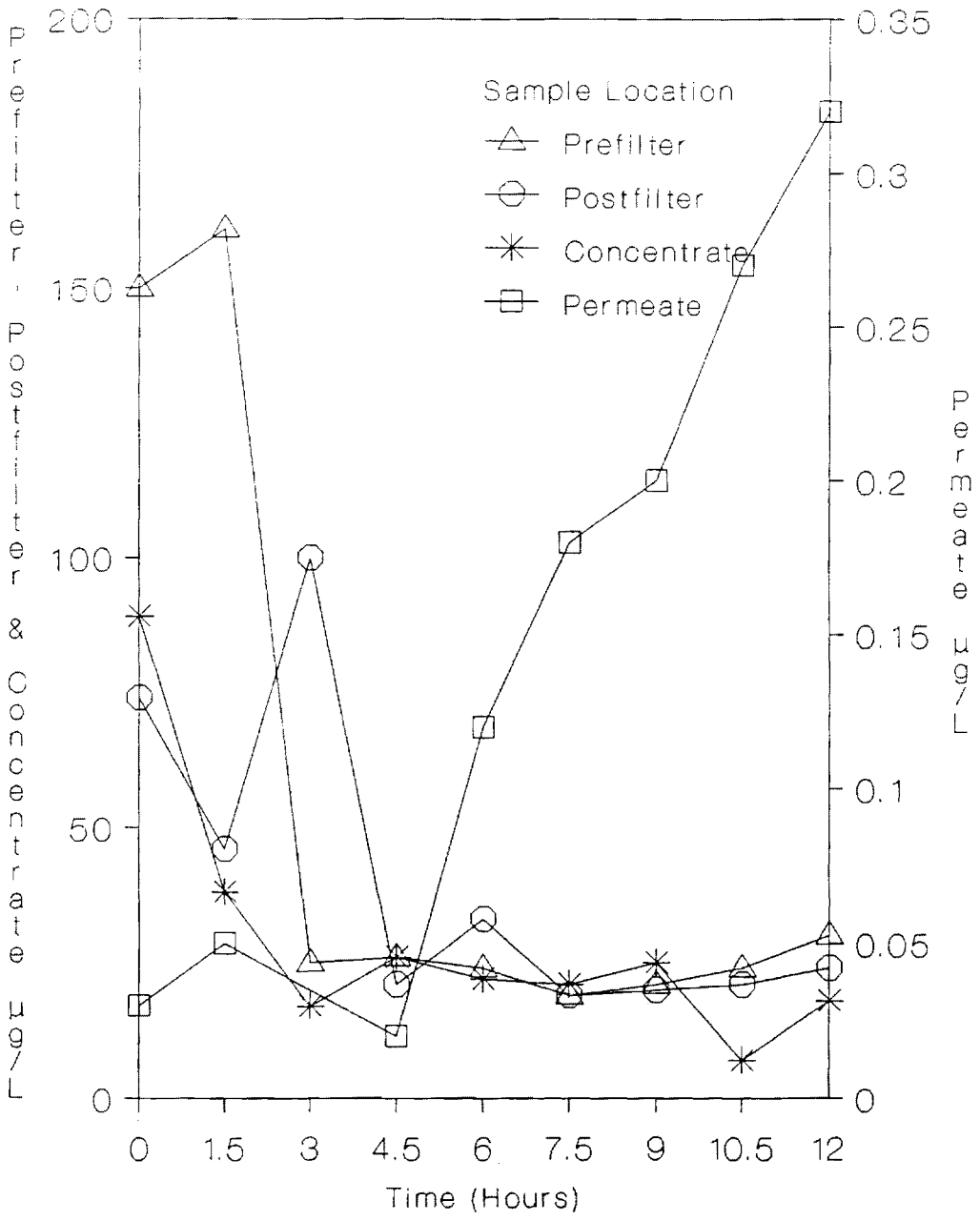

Figure 11. Concentrations of Anthracene at Four Sampling Points for a Single-Contaminant Trial With a Used Membrane from the Multi-Contaminant Trial.

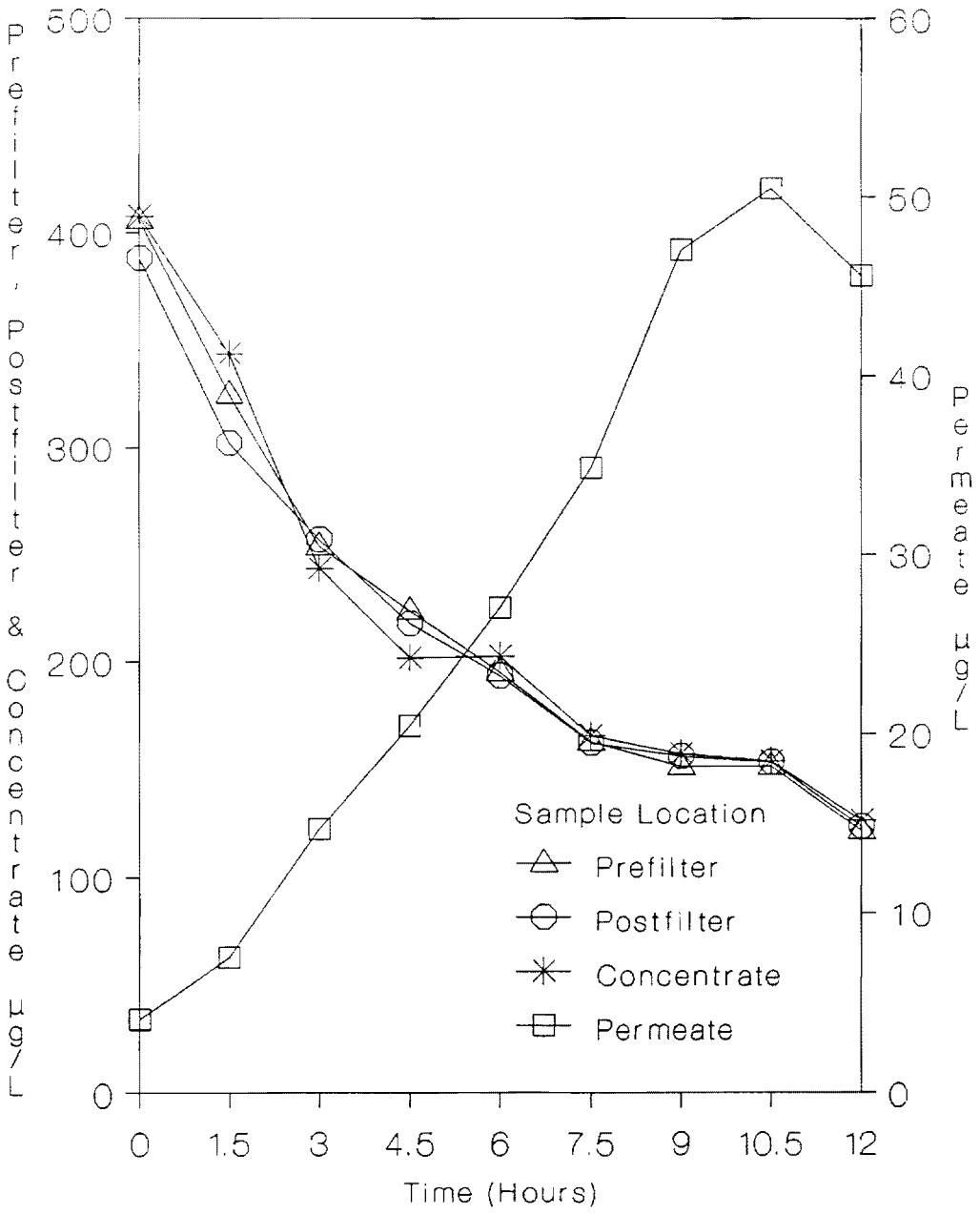

Figure 12. Concentrations of Trichloroethene at Four Sampling Points for a Single Contaminant Trial With a New Membrane.

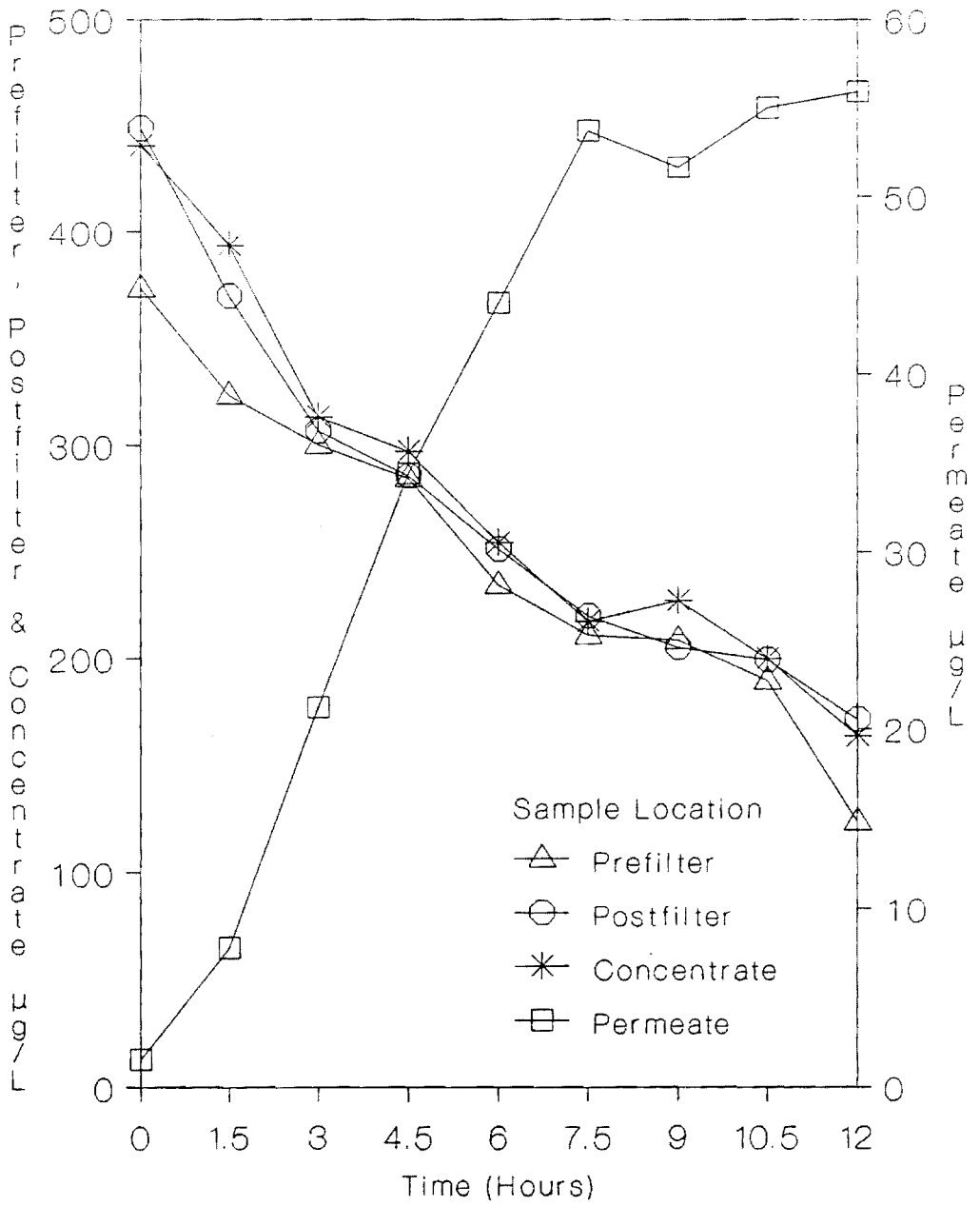

Figure 13. Concentrations of Trichloroethene at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

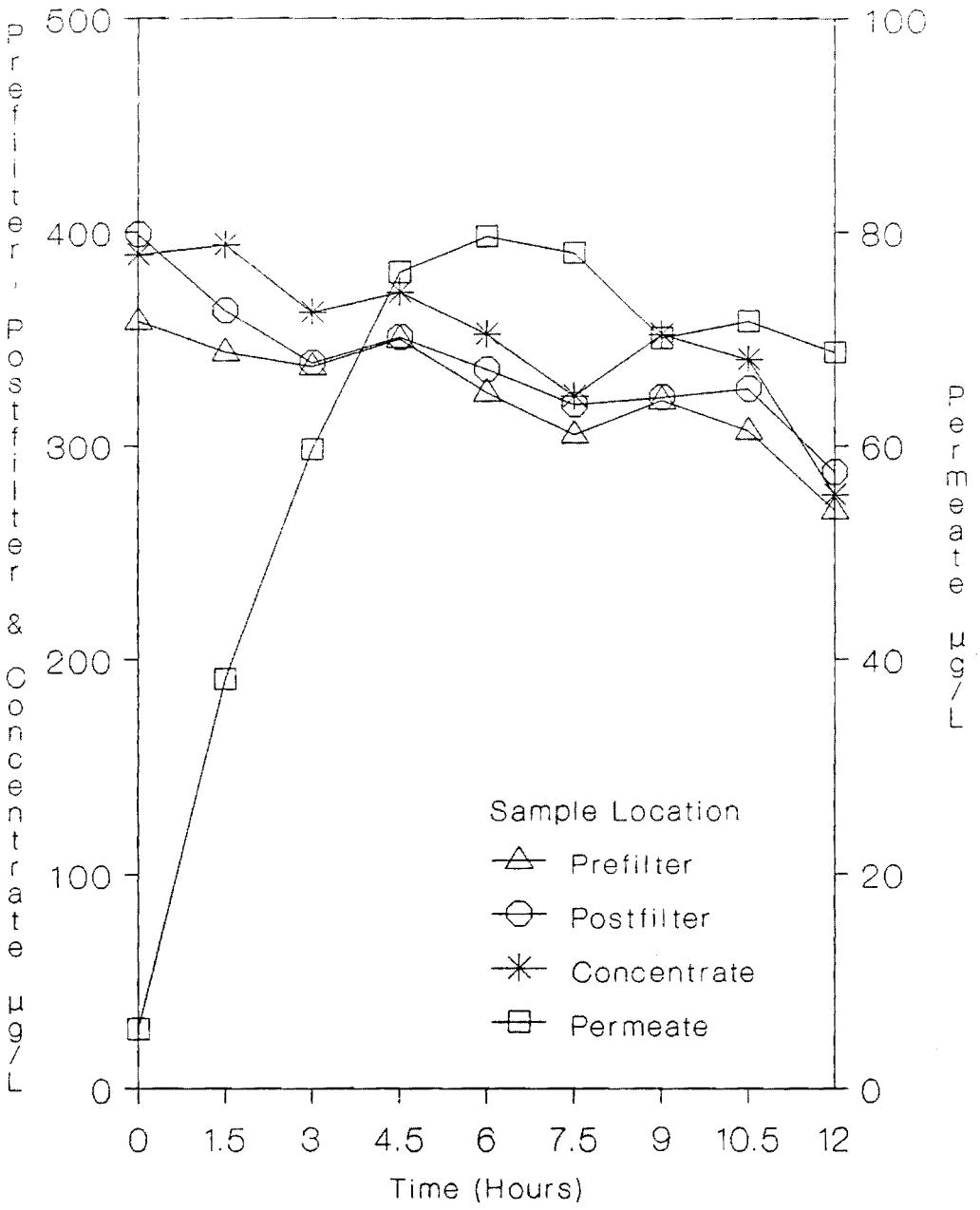

Figure 14. Concentrations of Trichloromethane at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

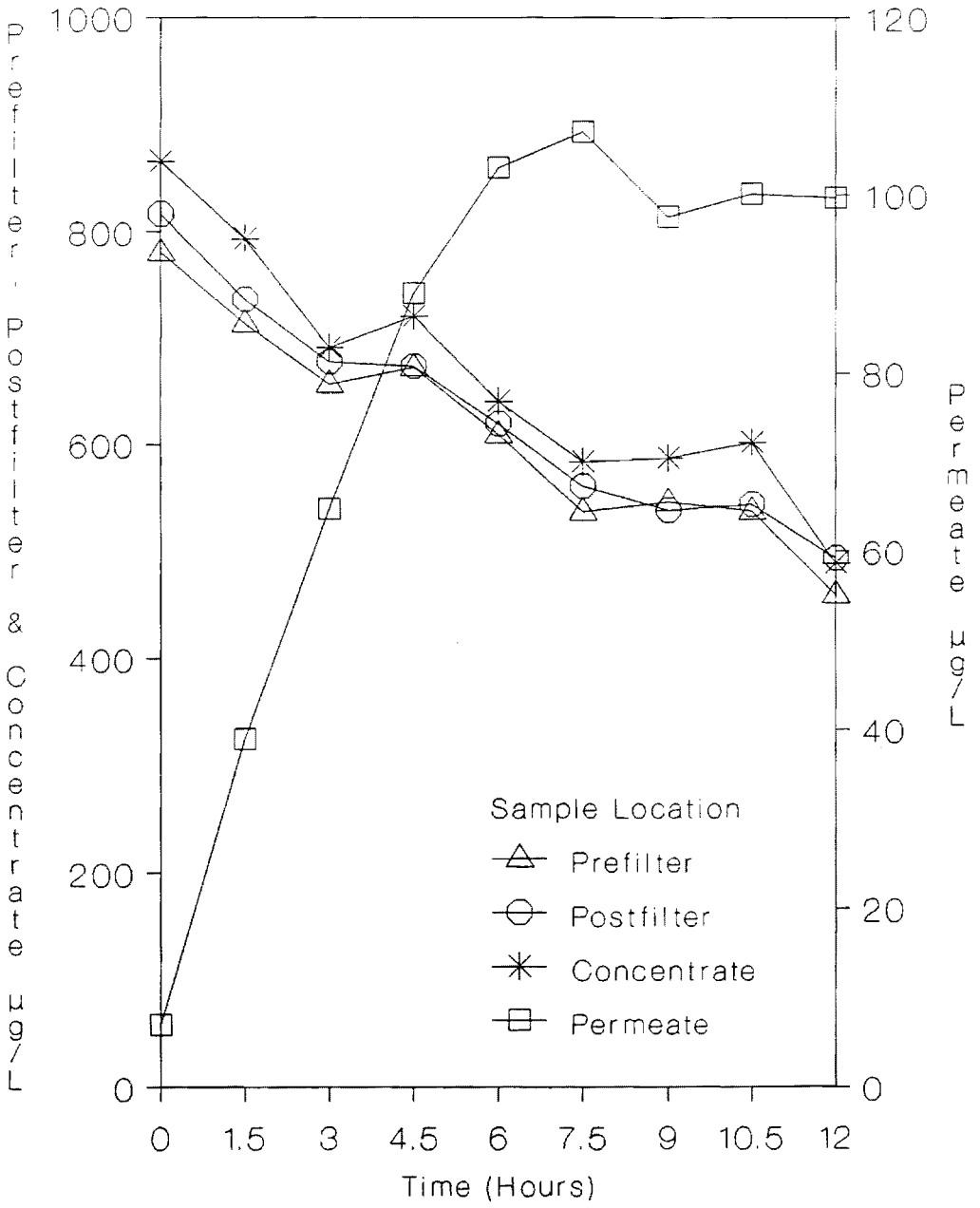

Figure 15. Concentrations of Dibromochloromethane at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

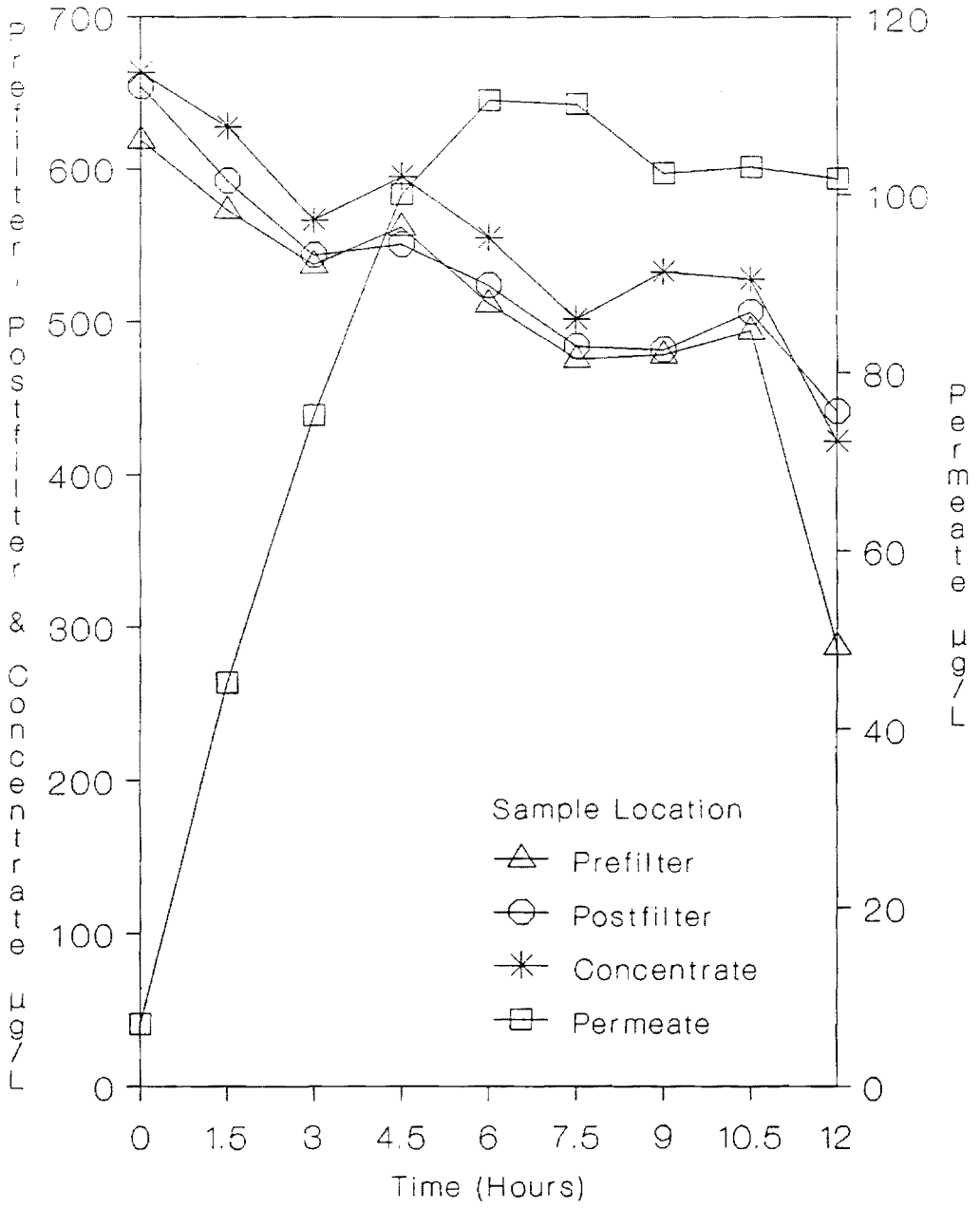

Figure 16. Concentrations of Bromodichloromethane at Four Sampling Points for a Multi-Contaminant Trial With a New Membrane.

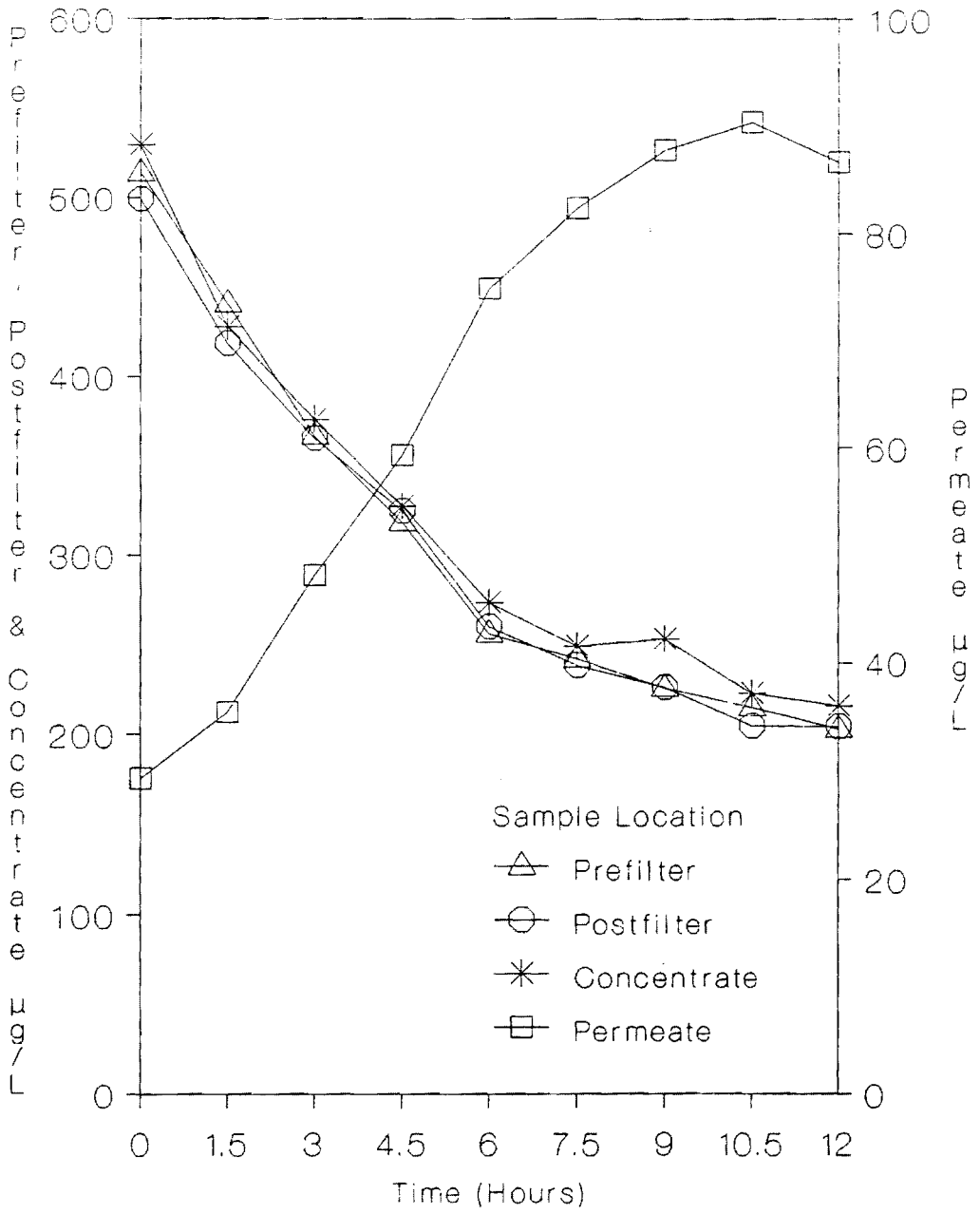

Figure 17. Concentrations of Trichloroethene at Four Sampling Points for a Single Contaminant Trial With a Used Membrane from the Multi-Contaminant Trial.

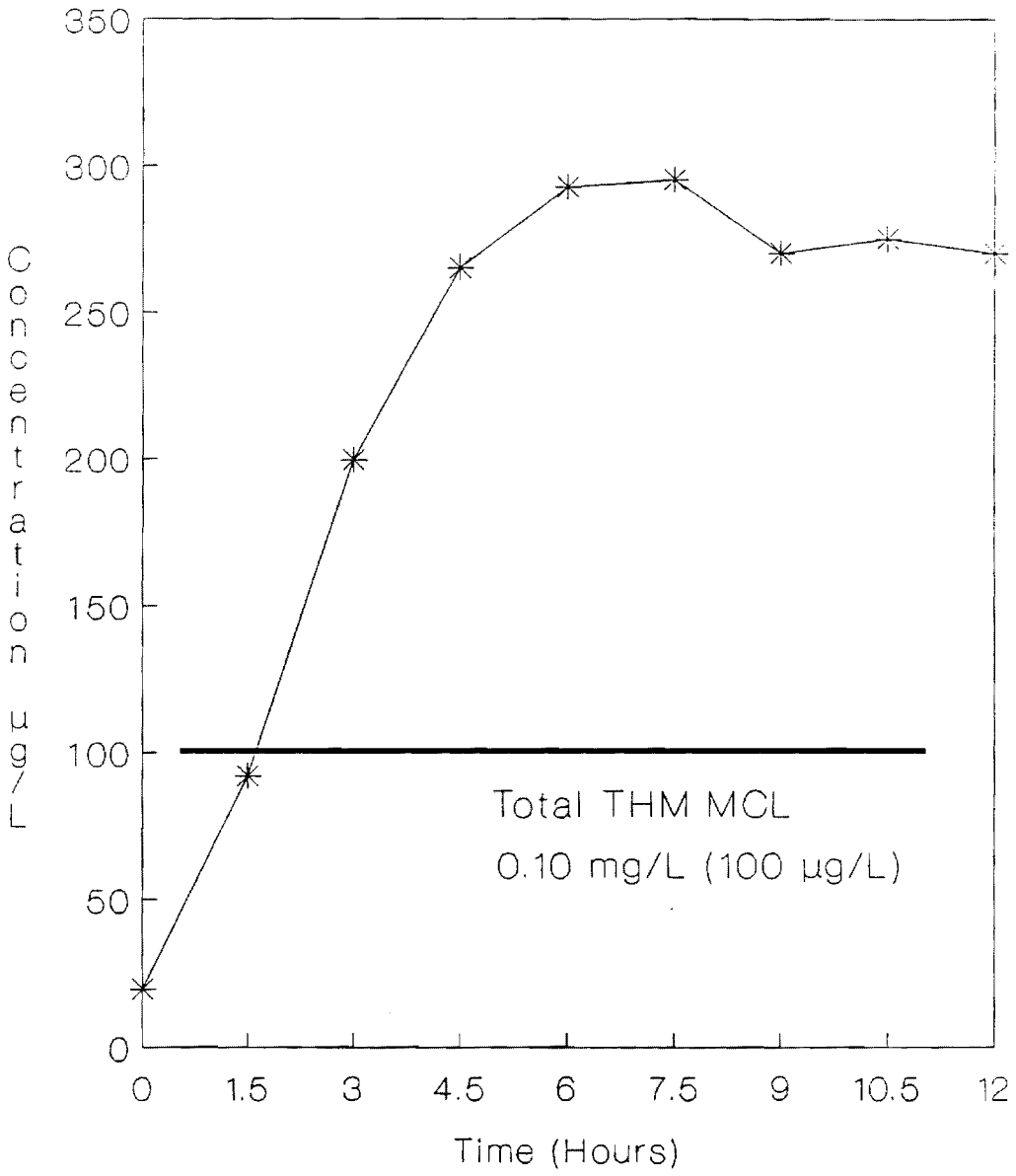

Figure 18. **Total Trihalomethane Concentration in Permeate Stream from the Multi-Contaminant Trial.**

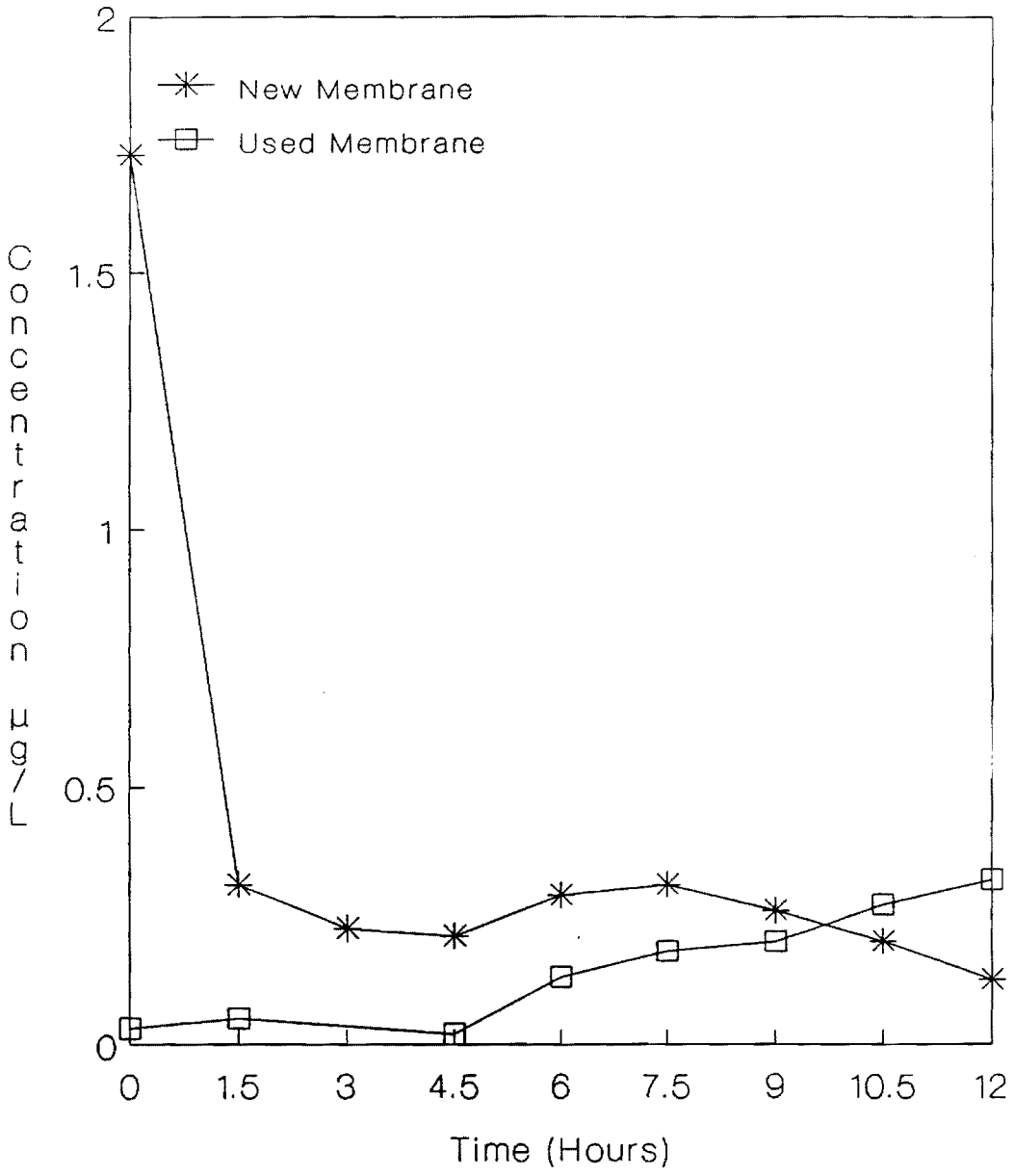

Figure 19. Comparison of Anthracene Concentrations in the Permeate Stream of New and Used Membranes with Anthracene as a Single Contaminant.

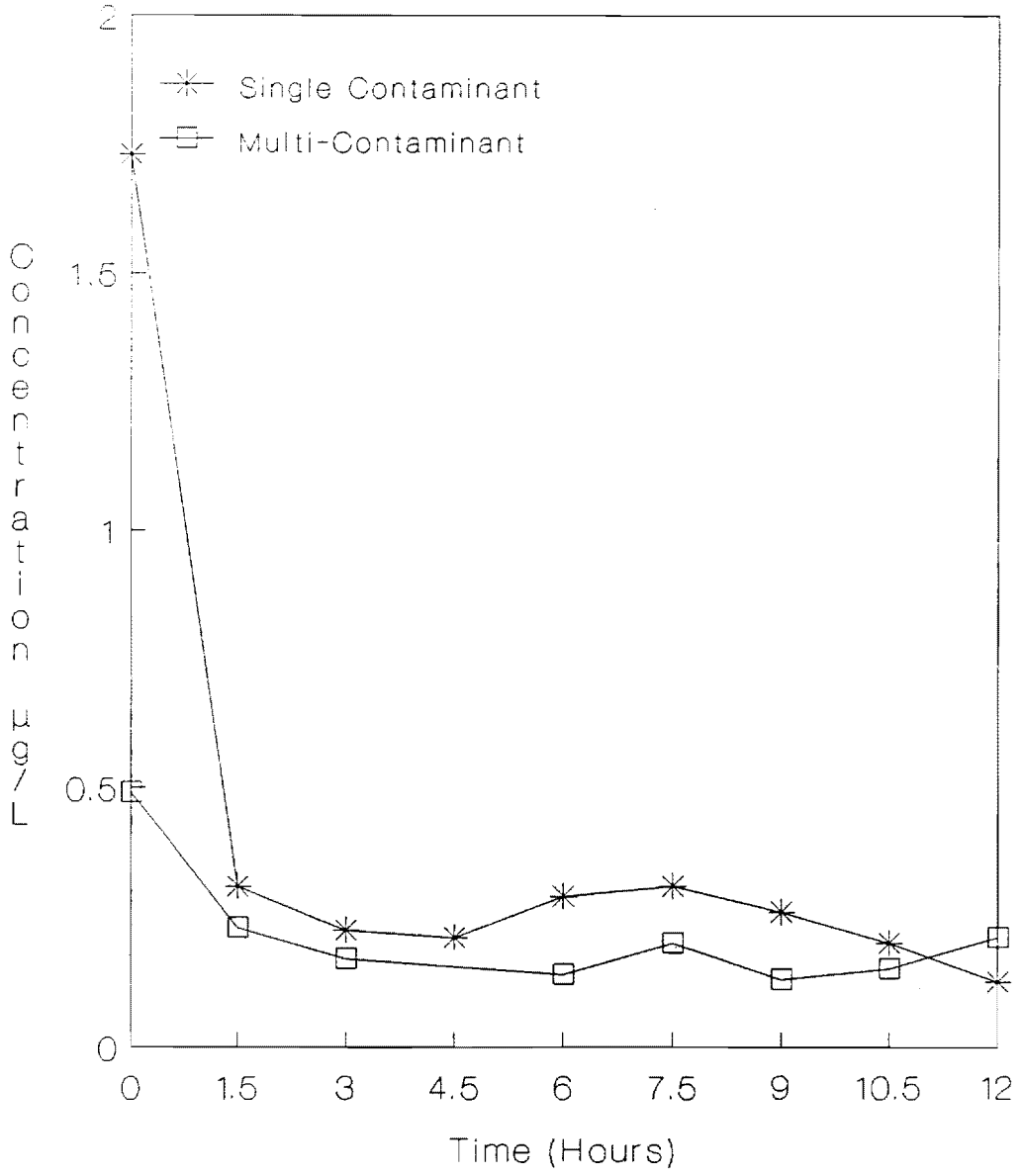

Figure 20. Comparison of Anthracene Concentrations in the Permeate Stream of New Membranes with Anthracene as a Single Contaminant and as a Multi-Contaminant.

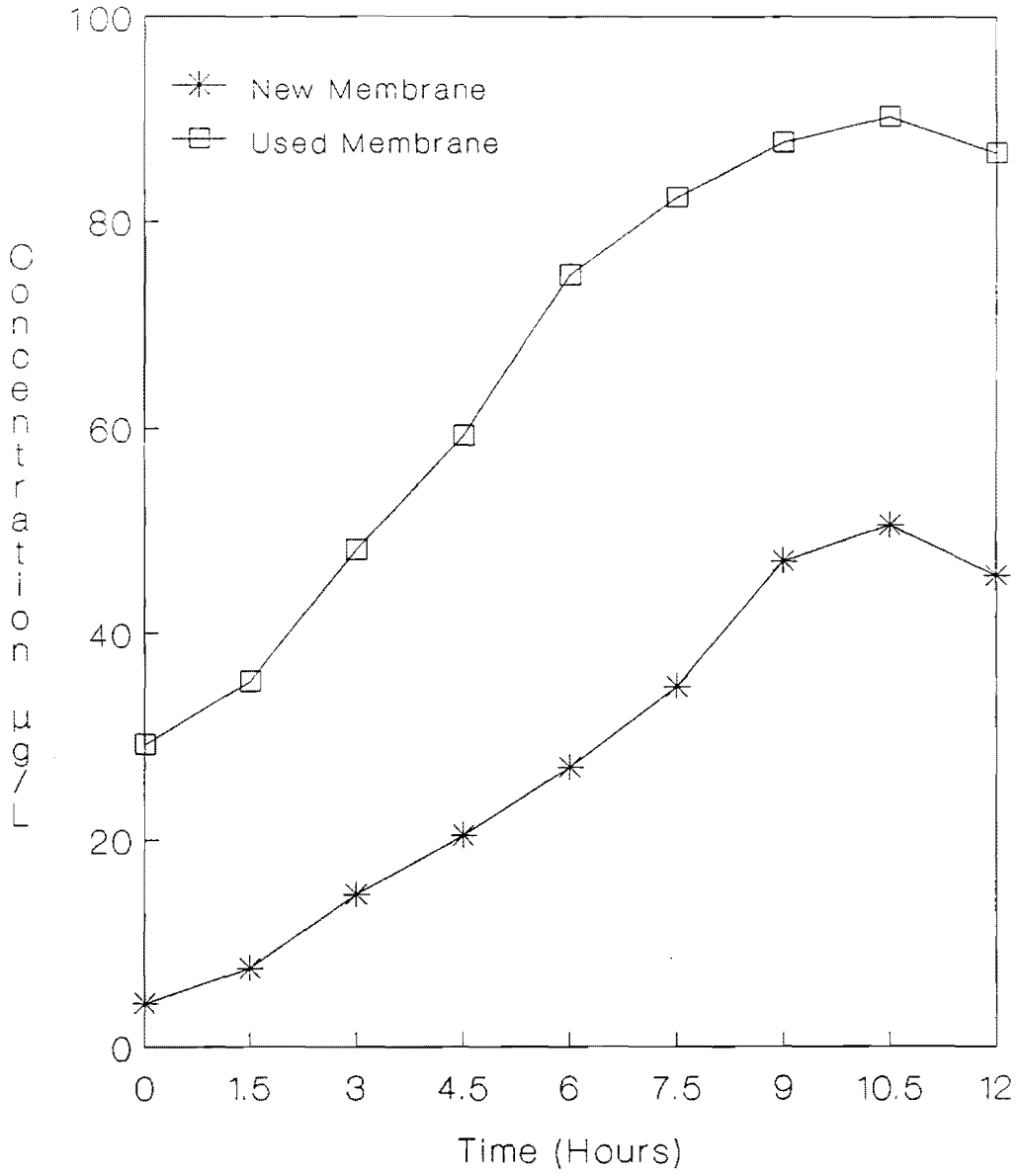

Figure 21. Comparison of Trichloroethene Concentrations in the Permeate Stream of New and Used Membranes with Trichloroethene as a Single Contaminant.

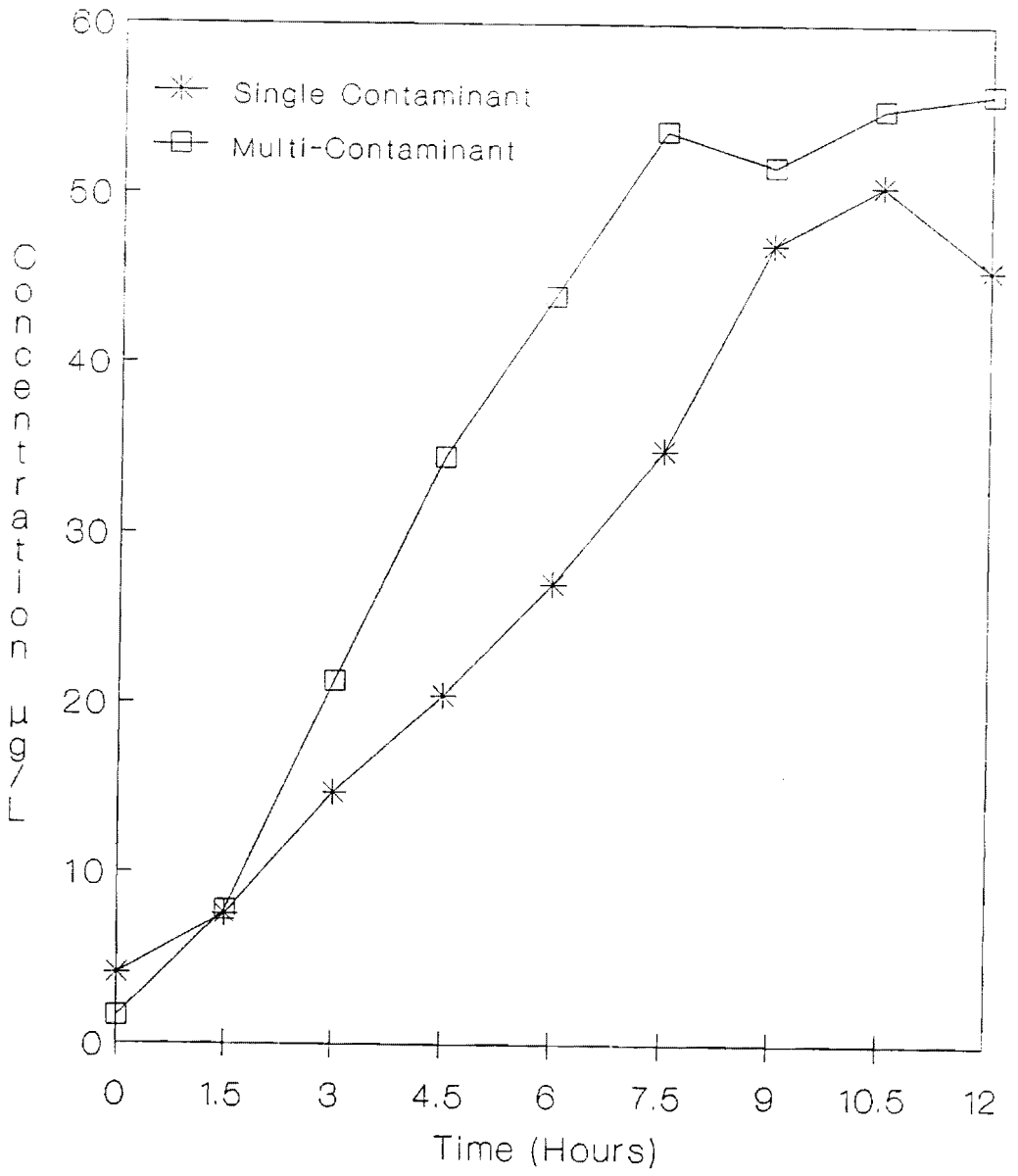

Figure 22. Comparison of Trichloroethene Concentrations in the Permeate Stream of New Membranes with Trichloroethene as a Single Contaminant and as a Multi-Contaminant.

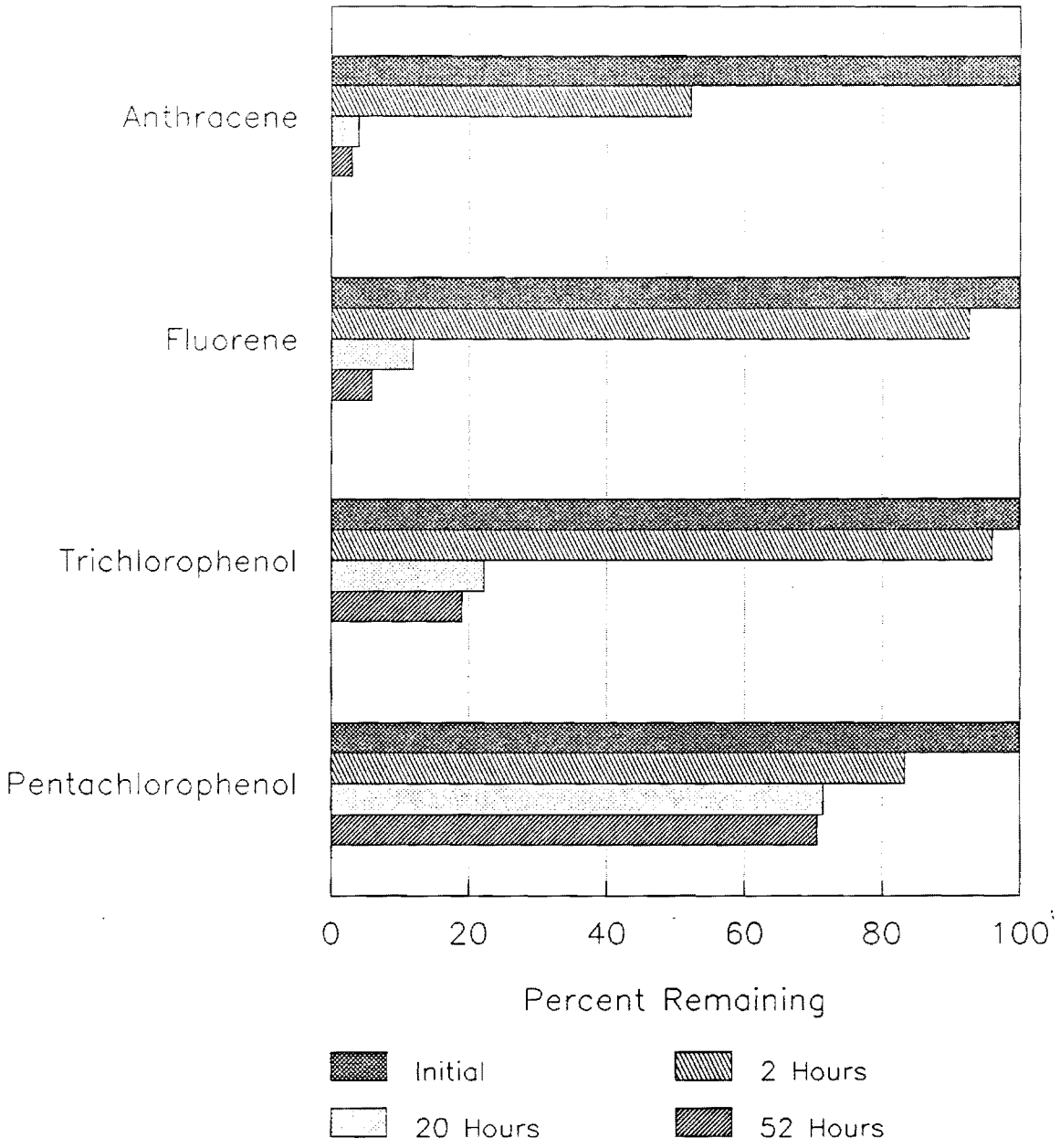

Figure 23. Percent Mass Remaining After Exposure to Membrane for Stated Time Interval.

Table 7

Total Trihalomethane Concentration in Chlorinated Permeate Samples

TRIAL	TIME	Total THM Concentration (μg/L)
1	4	1.7
	8	1.4
	12	1.0
2	4	1.2
	8	No Sample Available
	12	1.3
3	4	1.5
	8	1.0
	12	1.1

CHAPTER 5
DISCUSSION

The efficiency of a reverse osmosis membrane may be measured using two approaches. The first approach is to compare contaminant permeate concentration to an appropriate water quality standard. This provides an absolute quantification of membrane performance since the permeate either meets the standard or it does not. A second approach is to express efficiency in terms of percent removal of a contaminant. This method provides a relative measure of membrane performance and is often used in attempts to correlate membrane performance to physical and chemical properties of contaminants. Both methods are presented here.

When attempting to correlate membrane performance, sorption of organic compounds to the membrane needs to be considered. Tests performed for this research have shown that certain organic compounds are sorbed to the poly(ether/urea) membrane. Sorption and reverse osmosis occur simultaneously, and distinguishing between the two is difficult. Membrane performance may either be enhanced or degraded depending on the mobility of the organic compound once it is sorbed to the membrane. The average percent removals are given in Table 8 along with maximum and minimum values for each contaminant tested. Percent removal was calculated using contaminant concentrations in Equation 2.

$$Percent\ Removal = \frac{Postfilter - Permeate}{Postfilter} * 100\% \qquad [Equ.\ 2]$$

Table 8

Minimum, Maximum, and Average Percent Removal of Contaminants

COMPOUND	MINIMUM	MAXIMUM	AVERAGE	TREND
Anthracene (S,N)	98.03	99.84	99.03	D
Anthracene (M,N)	71.26	99.84	88.80	D
Pyrene (M,N)	95.34	99.72	98.68	C
Fluorene (M,N)	95.33	99.64	97.36	D
2-Chlorobiphenyl (M,N)	94.98	99.43	98.62	C
2,4,6 -Trichlorophenol (M,N)	98.46	99.70	99.12	E
Pentachlorophenol (M,N)	99.85	99.97	99.64	C
Anthracene (S,U)	98.36	100.00	99.37	D
Trichloroethene (S,N)	61.23	98.94	81.45	D
Trichloroethene (M,N)	63.29	99.65	82.17	D
Trichloromethane (M,N)	73.38	98.60	80.44	D
Bromodichloromethane (M,N)	73.84	98.93	82.36	D
Dibromochloromethane (M,N)	78.28	99.14	85.68	D
Trichloroethene (S,U)	55.85	94.14	72.50	D

S = Single Contaminant Trial
M = Multi-Contaminant Trial
N = New Membrane
U = Used Membrane

D = Decreasing
E = Erratic
C = Constant

The 'Trend' column is an indication of how percent removal varied during the trial; 'decreasing' indicates a continual decrease in percent removal with time, 'constant' indicates relatively no change in percent removal with time, and 'erratic' indicates variation in percent removal during the experiment.

5.A MASS BALANCES

Figures 4 - 17 indicated a loss of contaminant mass during each experiment, as the initial concentration in the 300-gallon holding tank can not be accounted for based on the concentration and flows at the four sampling locations. To determine if the loss occurred in the membrane, a mass balance was calculated for each contaminant. The mass balance, expressed as a mass fraction, was calculated around the membrane for each sampling interval using the following equation:

$$mass\ fraction = \frac{(pfc)*(conflo+permflo)}{(conco * conflo) + (permco + permflo)} \qquad [Equ.\ 3]$$

where:
pfc = postfilter concentration, mg/L
conco = concentrate concentration, mg/L
permco = permeate concentration, mg/L
conflo = concentrate flow, L/sec
permflo = permeate flow, L/sec

Mass fractions for each sampling time were averaged, and a confidence interval was calculated based upon the 95% confidence interval of the Student-t test as shown in Table 9. A margin of error of plus or minus 0.05 was assumed to exist in the mass balance calculations due to variability in the flow and concentration measurements.

Table 9

Results of Mass Balance Around Membrane Expressed as an Average Mass Fraction and Interval Based on the 95% Confidence interval of the Student-t Test.

COMPOUND	AVERAGE	INTERVAL
Anthracene	1.08	0.92 - 1.24
Pyrene	1.07	0.39 - 1.75
Fluorene	0.99	0.91 - 1.07
2-Chlorobiphenyl	1.04	0.92 - 1.16
2,4,6-Trichlorophenol	1.14	1.02 - 1.26
Pentachlorophenol	1.22	0.87 - 1.57
Bromodichloromethane	0.99	0.96 - 1.02
Dibromochloromethane	0.99	0.96 - 1.02
Trichloromethane	1.00	0.97 - 1.03
Trichloroethene	1.00	0.95 - 1.05

If the interval was between 0.95 and 1.05, the mass balances were considered closed (mass of contaminant entering the membrane essentially equals the mass of contaminant exiting the membrane). Mass fractions above 1.05 indicate a loss of mass, probably through sorption to the membrane. Mass fractions below 0.95 indicate a gain of mass, probably by desorption from the membrane. Sorption of aromatic compounds onto the membrane is indicated in view of the fact that mass fraction intervals tend to be greater than 1.0

5.B LOSS OF VOLATILE CONTAMINANTS

The mass fractions for the volatile contaminants were within the margin of error for a closed balance. This indicates either no mass was lost by sorption to the membrane or the loss was minimal compared to the error in the calculations. In either case, sorption is most likely not the reason for the loss.

Loss of contaminant from volatilization was expected to occur during the trials with the volatile compounds. The recycle holding tank was opened to the atmosphere and mixed by the concentrate stream entering below the water surface. The recycle line was the source of many small air bubbles. These bubbles rose to the surface resulting, most likely, in volatilization of the contaminants. The cause of these bubbles is unknown.

5.C LOSS OF AROMATIC COMPOUNDS

The mass fraction intervals for the aromatic compounds generally were above 1.0 indicating sorption to the membrane may be occurring. To confirm this possibility, simple sorption tests were performed. The results of these sorption

experiments, shown in Figure 23, indicate sorption of anthracene, fluorene, trichlorophenol, and pentachlorophenol by the poly(ether/urea) membrane. Concentration decreases of 4% to 48% occurred after two hours. Anthracene and fluorene concentrations were reduced by over 90% in 52 hours. Consideration must be given to the fact the sorption experiments were performed under static conditions at atmospheric pressure which are significantly different than actual membrane operation at 325 psi pressure. The duration of the sorption experiments was also longer than the 12-hour reverse osmosis trials.

The percent mass removed at 52 hours correlates well to the percent mass lost during the multi-contaminant trial as shown in Figure 24. Anthracene, with 97% removal in the sorption experiments had decrease of 99% in total mass during the reverse osmosis trial. Pentachlorophenol, with the lowest removal in the sorption experiments (29%), also had the lowest percent decrease in the trial. These data provide additional support of the view that sorption does occur and that sorption is responsible for the lost contaminant mass. Polar compounds, such as pentachlorophenol and trichlorophenol, are sorbed less by the poly(ether/urea) membrane than nonpolar compounds, such as anthracene and fluorene. This tendency was also exhibited with several pesticides (Chong, 1990).

5.D SAFE DRINKING WATER ACT - MAXIMUM CONTAMINANT LEVELS

A comparison of permeate contaminant concentrations with MCLs established by the SDWA provides a direct indication of membrane performance. An MCL, maximum contaminant level, is the maximum contaminant level allowable in a water which is delivered to any user of a public water system. An MCLG,

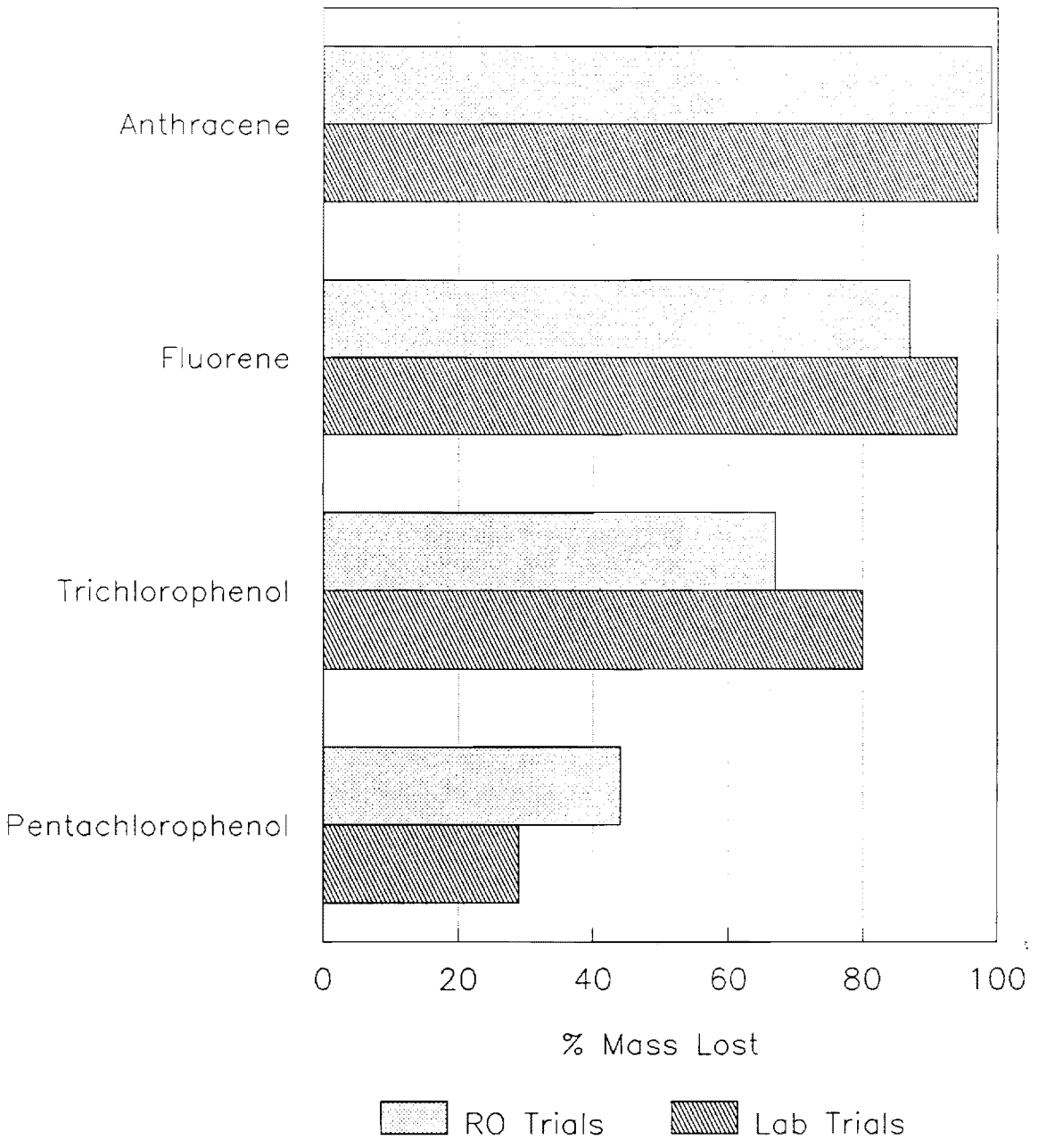

Figure 24. **Comparison of Percent Mass Lost After 52 Hour Interval of Sorption Experiments and Mass Lost During Reverse Osmosis Trials.**

maximum level contaminant level goal, is a non-enforceable concentration level which has no adverse human health effects. Polyaromatic hydrocarbons (PAHs) used in this research - anthracene, fluorene, and pyrene - are not currently regulated by the SDWA but are scheduled to be regulated at some future date. Currently, benzo(a)pyrene is the only PAH with an MCL and this is a tentative MCL of 0.002 mg/L. The other PAHs proposed for regulation include benz(a)anthracene, benz(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indenopyrene. These compounds are classified as probable human carcinogens, and as such have MCLGs of zero. The tentative MCL of 0.002 mg/L for benzo(a)pyrene will be used for comparison with the PAHs tested in this research.

Polychlorinated biphenyls (PCBs) have a proposed MCL of 0.0005 mg/L which will be used for comparison to the PCB analog compound 2-chlorobiphenyl. An MCL has not been proposed for regulating 2,4,6-trichlorophenol; therefore, the proposed MCL of 0.2 mg/L for pentachlorophenol will be used for comparison.

The current MCL for trihalomethanes is 0.10 mg/L for the total concentration of trichloromethane, tribromomethane, bromodichloromethane, and dibromochloromethane. Although only three THMs were tested (tribromomethane was omitted), the 0.10 mg/L MCL will be used for comparison of permeate concentrations. The current MCL for trichloroethene is 0.005 mg/L.

5.E COMPLIANCE WITH SDWA MCLs

Sorption of the aromatic test compounds onto the reverse osmosis membrane makes interpretation of membrane performance difficult, since removal

reflects both sorption and reverse osmosis rejection. Therefore, experimental results indicating compliance with the SDWA can only apply to short term conditions similar to the test conditions used in this research.

5.E.1 ORGANIC COMPOUNDS

Anthracene, tested as both a single contaminant and multi-contaminant, was lowered to less than 0.0005 mg/L with a new membrane. Pyrene averaged slightly above 0.0002 mg/L. Fluorene, with concentrations over the last six hours averaging 0.0016 mg/L, had the highest concentration of the three polyaromatic hydrocarbons. These values are all below the 0.002 mg/L MCL for benz(a)pyrene. If removal of the three PAH compounds was based strictly on reverse osmosis, i.e. sorption being ignored, removal of PAHs covered by the SDWA would be expected to be higher due to the postulated relationship between reverse osmosis rejection and molecular size (Chian and Fang, 1976).

Pentachlorophenol and trichlorophenol concentrations were both reduced to significantly below the MCL. Although the targeted feed water concentrations were 0.50 mg/L the actual feed water concentrations for both compounds were below the MCL due to sorption or other losses. The removal for pentachlorophenol was so significant, 0.00001 mg/L in the permeate stream, that the 0.2 mg/L MCL should be easily achieved at higher feed water concentrations. Pentachlorophenol, with the highest molecular weight of any compound tested (266.4 amu), had the lowest permeate concentration. The cause for the trichlorophenol permeate concentration to rise to maximum at six hours and then return to its initial value is unknown (see Figure 9).

The PCB analog, 2-chlorobiphenyl, was removed to below the PCB MCL of 0.0005 mg/L. PCBs (polychlorinated biphenyls) are larger molecules than 2-chlorobiphenyl (a monochlorinated biphenyl). Therefore, based on molecular size and steric effects, these results indicated that PCB removal would be more efficient than was achieved for 2-chlorobiphenyl , which had an average permeate concentration of 0.0001 mg/L from Figure 8.

5.E.2 VOLATILE COMPOUNDS

The three THMs tested had very poor removal. On an individual basis, both bromodichloromethane and dibromochloromethane exceeded the established MCL by the end of the 12-hour experiment. As exhibited in Figures 14 - 16, permeate concentration increased despite a decreasing feed concentration. After approximately six hours the rising permeate concentration reached a steady state. The 0.1 mg/L MCL for total THMs was exceeded after 1.5 hours as shown in Figure 18. For the final three hours the permeate concentration remained constant at 0.27 mg/L.

Trichloroethene removal followed a pattern similar to those of the THMs as shown in Figures 12, 13, and 17. The 0.005 mg/L MCL was exceeded within three hours for all three trials.

The volatile compounds were the smallest compounds tested based on the molar volume given in Table 1. The molecular weight of chlorodibromomethane, 208.3 amu, is greater than all the aromatic compounds tested except for pentachlorophenol. Based strictly on molecular weight, dibromochloromethane should have removal comparable to the aromatic compounds tested. Accordingly,

the poor rejection of dibromochloromethane must result from its smaller size. This fact emphasizes the importance of molecular size and steric effects, not just molecular weight, when evaluating contaminant rejection by reverse osmosis membranes. The planar molecular shape of aromatic compounds along with their larger size allows for better rejection by the membrane's porous surface than the spherical molecular shape of dibromochloromethane.

5.F REJECTION OF THMs

The critical role that molecular size can have in the rejection of a molecule by a reverse osmosis membrane is shown in Figure 25. A distinct performance difference, based on percent removal, is noted between dibromochloromethane, bromodichloromethane, and trichloromethane. The three molecules have the same molecular shape and differ only in the number of bromine and chlorine atoms attached to the central carbon atom. Dibromochloromethane, with one chlorine and two bromine atoms, has the highest molecular weight, 208.3 amu, and the highest rejection. Trichloromethane, with three chlorine atoms, has the lowest molecular weight, 119.4, and the lowest rejection. Bromodichloromethane, with two chlorine atoms and one bromine atom, is between the other two molecules in both molecular weight and performance. As bromine atoms are removed and replaced with chlorine atoms, the percent rejection of the compound decreases. The size difference between a bromine atom, covalent radius - 1.14 Å (Barrow, 1979), and a chlorine atom, covalent radius - 0.99 Å (Barrow, 1979), is large enough to alter the rejection of the compound.

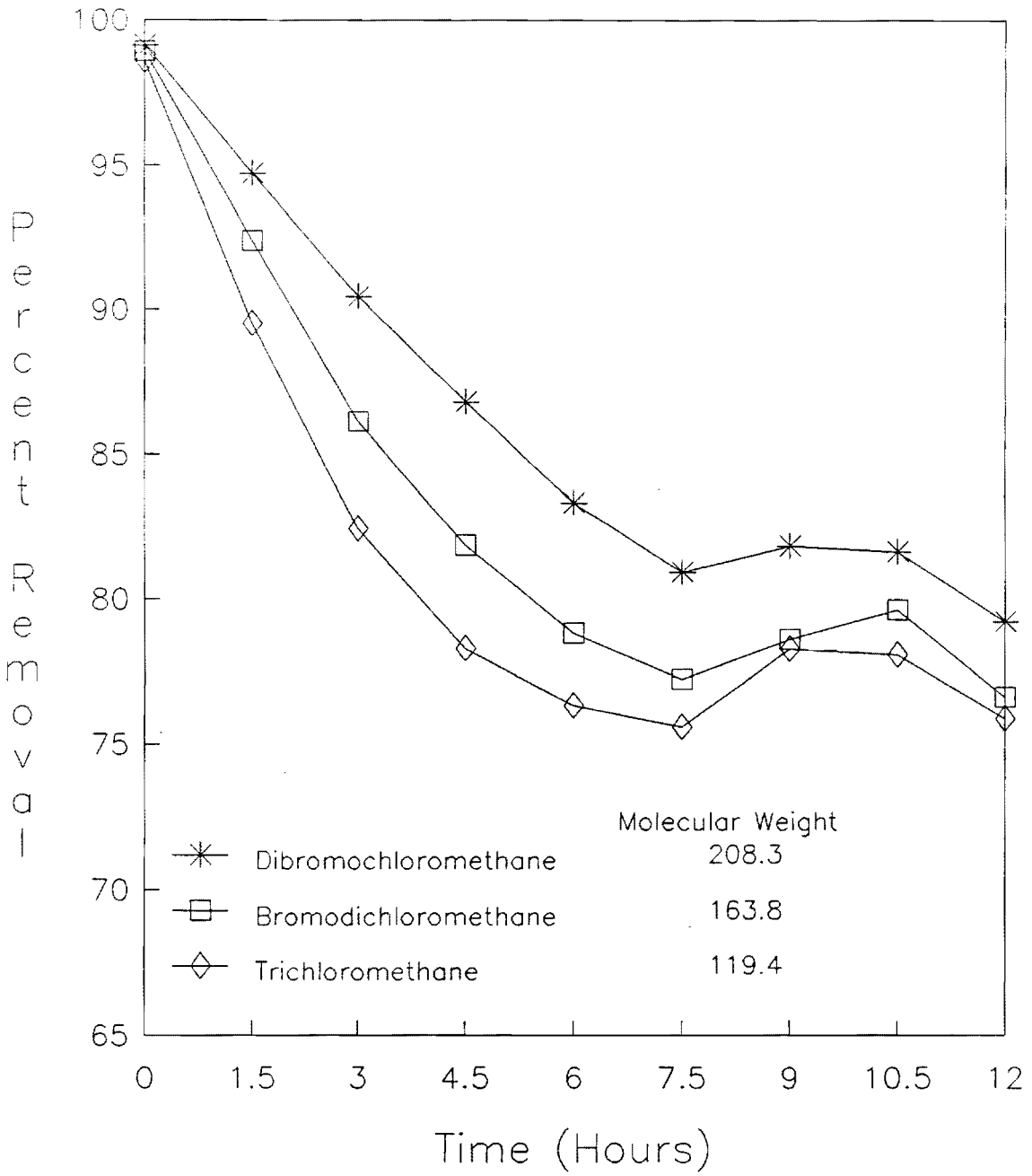

Figure 25. Comparison of Percent Removal of Individual THMs from Multi-Contaminant Trial.

5.G COMPARISON OF USED AND NEW MEMBRANE PERFORMANCE

Removal efficiency between new and used membranes was evaluated using anthracene and trichloroethene as single contaminants. Removal of trichloroethene by a new membrane was significantly better as shown in Figure 21. Permeate concentrations in the used membrane were a minimum of twice the permeate concentrations of the new membrane. These results would indicate possible degradation of the membrane by the test compounds.

Poly(ether/urea) membranes are generally resistant to chemical degradation except by acid/base hydrolysis and oxidation by chlorine or other oxidants (Eisenberg and Middlebrooks citing Kosarek, 1986). The water used for the experiments was neither chlorinated nor at a pH favorable for hydrolysis. Further, noncellulosic membranes are generally resistant to biodegradation. The time required for biodegradation to occur is much greater than the 24-hour period used in this research (Ridgeway, 1988). Therefore, the decreased performance of the used membrane is not likely the result of chemical and/or biological degradation of the membrane.

The performance difference between the new and used membranes is not likely due to membrane degradation. Permeate trichloroethene concentrations for both membranes used in the three volatile trials are shown in Figure 26. This is the same data as Figure 21 but plotted with the x-axis as hours of membrane use. The additional curve shown in Figure 26 is the initial 12 hours of use for the used membrane. Steady state membrane rejection of trichloroethene is not reached after 24 hours of operation. The difference shown in Figure 21 is not a difference between new and used membranes but shows performance at two time intervals

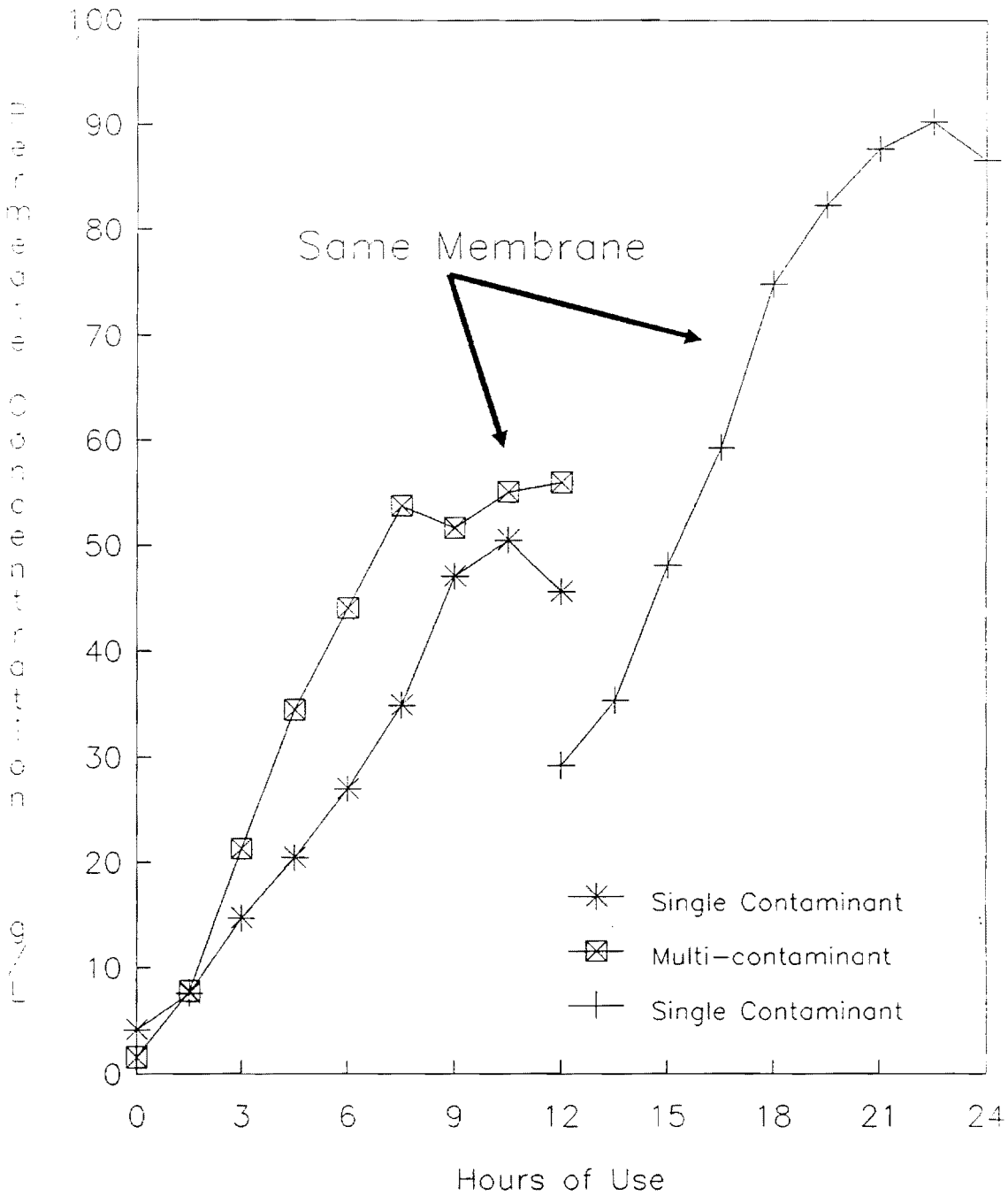

Figure 26. Permeate Concentrations of Trichloroethene from Three Trials as a Function of Hours of Membrane Use.

during which the membrane is approaching steady state conditions. The improved concentrations at the end of the trials may be the result of the feed concentration decreasing enough to affect membrane performance.

Comparison of anthracene removal between a used and new membrane is shown in Figure 19. The most significant finding from this test was the increases in permeate concentrations from the used membrane starting at 4.5 hours. This may be due to desorption of anthracene from the membrane. Desorption of sorbed organic compounds is critical when evaluating the long term use of the reverse osmosis membranes. An organic compound sorbed to a membrane during treatment of a contaminated water may desorb at a later time into noncontaminated water being treated by the membrane.

Another trait of Figure 19 is high initial concentration for the new membrane. The initial concentration is significantly higher than the 1.5 hour value and the initial value for the used membrane. Compression of the membrane by the high pressure feed water, hydraulic compaction, during startup of the system could decrease the porous membrane structure and improve rejection. This could result in improved Similar occurrences were also noted with metals and inorganic anions in other phases of this research (Chong, 1990).

5.H COMPARISON OF SINGLE AND MULITCONTAMINANT REMOVAL

Since contaminated water generally has more than a single contaminant, reverse osmosis membranes must be able to treat a multi-contaminant feed water as efficiently as a feedwater containing a single contaminant. Comparisons of membrane rejection of trichloroethene and anthracene as a single contaminant and

a multi-contaminant are shown in Figures 20 and 22. Rejection of trichloroethene a single contaminant was significantly greater than rejection as a multi-contaminant. A higher total molar concentration of solutes in the multi-contaminant trial may be the cause for this change in membrane performance. However, the exact cause for this change in membrane performance is not known.

In contrast to the removal of trichloroethene, anthracene was removed slightly better as a single contaminant. This demonstrates that reverse osmosis membrane separation is solute specific.

5.I CHLORINATION OF PERMEATE SAMPLES

The formation of trihalomethanes as a result of chlorination is important due to the suspected carcinogenicity of trichloromethane (chloroform) (Snoeyink and Jenkins, 1980). Three permeate samples from each trial with the aromatic contaminants were chlorinated and analyzed for the presence of trihalomethanes. Total trihalomethane concentrations were less than 2.0 μg/L for each permeate samples tested. The low levels probably are due to the low concentration of organic compounds in the permeate samples.

The major source of organics in natural waters is humic substances. Humics are a diverse group of compounds with molecular weights ranging from several hundred to several million atomic mass units (Snoeyink and Jenkins, 1980). Due to the large molecular size, these compounds are a major cause of membrane fouling (Lepore and Ahlert, 1988) and rejection by the poly(ether/urea) membrane should be excellent. Total organic carbon of the uncontaminated groundwater was 0.35 mg/L indicating a low level of humic material.

The major source of organic carbon in the feedwater was the acetone used to dissolve the aromatic contaminants in preparing the feed solution. Rejection of acetone by the membrane was not determined in this research but due to its low molecular weight and size, rejection could be poor. However, the reaction between acetone and chlorine is slow and would not occur during the 30 minute contact time (Snoeyink and Jenkins, 1980). Therefore, low organic concentrations resulted in the low formation of trihalomethanes.

CONCLUSIONS

The following conclusions are drawn from this research:

1. Aromatic compounds sorbed to the poly(ether/urea) membrane making extrapolation of the data to long term compliance with the SDWA unreliable.
2. The poly(ether/urea) membrane removed anthracene, pyrene, and fluorene sufficiently to meet the 0.002 mg/L SDWA MCL for benz(a)pyrene and would likely be able to meet that MCL for the other PAHs to be regulated by the SDWA.
3. The poly(ether/urea) membrane removed 2-chlorobiphenyl sufficiently to meet the 0.0005 mg/L SDWA MCL for PCBs.
4. The poly(ether/urea) membrane removed 2,4,6-trichlorophenol and pentachlorophenol sufficiently to meet the 0.20 mg/L SDWA MCL for pentachlorophenol.
5. The poly(ether/urea) membrane did not remove trihalomethanes effectively and permeate concentrations did not meet the 0.10 mg/L SDWA MCL.
6. The poly(ether/urea) membrane did not remove trichloroethene effectively and permeate concentrations did not meet the 0.005 mg/L SDWA MCL.
7. Rejection of trichloroethene was significantly decreased by the presence of additional contaminants in the feedwater.
8. Rejection of trihalomethane compounds by a poly(ether/urea) membrane improves as the molecular size of the compound increases.

9. Chlorination of permeate samples from three aromatic trials produced total trihalomethane concentrations below 2 μg/L.

RECOMMENDATIONS

Based on the results of this research the following recommendations are made:

1. Include long term tests, 24 hours or more, and a series of short term tests, three to six hours, in membrane evaluation. The short term tests should consist of a series of three to six hours trials separated by a 12 to 24 hour time interval. The short term tests will, perhaps, expose the membrane to more realistic operating conditions.
2. Perform specific membrane sorption/desorption tests for organic compounds.
3. Do not rely on poly(ether/urea) membranes to remove volatile organic compounds.
4. Evaluate activated carbon filters for the removal of volatile organic compounds from the permeate stream.

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APPENDIX A

FIELD DATA

Aromatic Compounds

Trial	Membrane	Time	Temperature (F)			Flowrate (gpm)	
			Tank	Inlet	Ambient	Permeate	Concentrate
1	205749	0	64	63	70	0.37	22.3
		1.5	68	64	73	0.43	22.1
		3	72	67	77	0.46	22
		3	72	67	77	0.46	22
		4.5	74	70	87	0.72	21.8
		6	76	72	92	0.68	21.7
		6	76	72	92	0.68	21.7
		7.5	77	73	93	0.93	21.7
		9	77	72	91	0.92	21.8
		9	77	72	91	0.92	21.8
		10.5	77	72	91	0.92	21.8
		12	77	71	88	0.91	21.8
		12	77	71	88	0.91	21.8
2	202173	0	75	69	72	0.52	21.9
		1.5	73	68	75	0.51	22
		3	73	68	82	0.8	22
		3	73	68	82	0.8	22
		4.5	73	69	88	0.8	21.9
		6	75	70	89	0.9	21.8
		6	75	70	89	0.9	21.8
		7.5	77	73	95	0.94	21.7
		9	79	74	91	0.98	21.7
		9	79	74	91	0.98	21.7
		10.5	79	74	87	0.99	21.8
		12	75	72	82	0.97	21.9
		12	75	72	82	0.97	21.9
3		0	61	63	70	0.67	22.1
		1.5	66	62	72	0.8	21.9
		3	70	64	73	0.92	21.8
		4.5	70	66	79	0.97	21.8
		6	72	67	79	0.98	21.8
		7.5	73	69	79	1.06	21.8
		9	75	71	81	1.09	21.7
		9	75	71	81	1.09	21.7
		10.5	77	72	79	1.09	21.6
		12	77	72	77	1.09	21.7
		12	77	72	77	1.09	21.7

Volatile Contaminants

Trial	Membrane	Time	Temperature (F)			Flowrate (gpm)	
			Tank	Inlet	Ambient	Permeate	Concentrate
1	202265	0	57	57	52	0.41	22.4
		1.5	63	59	61	0.48	22.3
		3	68	62	72	0.42	22.2
		3	68	62	72	0.42	22.2
		4.5	70	65	80	0.45	22.1
		6	72	67	85	0.45	22.2
		6	72	67	85	0.45	22.2
		7.5	76	72	88	0.48	22
		9	78	74	85	0.51	22
		9	78	74	85	0.51	22
		10.5	75	71	81	0.47	22.1
		12	75	72	77	0.48	22
		12	75	72	77	0.48	22
2	202232	0	55	56	58	0.8	22.1
		1.5	63	59	63	0.9	22.1
		3	67	63	68	1.02	21.9
		3	67	63	68	1.02	21.9
		4.5	72	67	73	1.13	21.8
		6	73	69	79	1.16	21.7
		6	73	69	79	1.16	21.7
		7.5	73	68	73	1.12	21.7
		9	72	66	70	0.78	21.8
		9	72	66	70	0.78	21.8
		10.5	70	65	66	1.06	21.8
		12	68	65	64	1.04	21.8
		12	68	65	64	1.04	21.8
3		0	54	46	43	0.88	22.3
		1.5	59	53	50	0.66	22.2
		3	64	59	52	0.89	22.1
		3	64	59	52	0.89	22.1
		4.5	67	62	53	1.03	21.9
		6	71	64	54	1.07	21.9
		6	71	64	54	1.07	21.9
		7.5	75	69	54	1.15	21.8
		9	72	66	52	1.07	21.8
		9	72	66	52	1.07	21.8
		10.5	68	63	52	1.03	21.8
		12	68	63	52	1.03	22

APPENDIX B

LABORATORY DATA

Aromatic Compounds

Trial	Contaminant	Time	Prefilter (mg/L)	Postfilter (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
1	Anthracene	0	0.22100	0.21200	0.28400	0.00173
1	Anthracene	1.5	0.20500	0.19600	0.21300	0.00031
1	Anthracene	3	0.12000	0.11300	0.14100	0.00022
1	Anthracene	3	0.12400	0.11700	0.11700	0.00023
1	Anthracene	4.5	0.05800	0.05800	0.04800	0.00021
1	Anthracene	6	0.03600	0.03200	0.03500	0.00049
1	Anthracene	6	0.03000	0.03000	0.03300	0.00009
1	Anthracene	7.5	0.02300	0.02300	0.02600	0.00031
1	Anthracene	9	0.01630	0.01900	0.02300	0.00025
1	Anthracene	9	0.01950	0.01800	0.02400	0.00027
1	Anthracene	10.5	0.01940	0.01680	0.68200	0.00020
1	Anthracene	12	0.01130	0.00700	0.04100	0.00012
1	Anthracene	12	0.01850	0.00660	0.04700	0.00013
2	Anthracene	0	0.16540	0.12090	0.14810	0.00049
2	Anthracene	1.5	0.13970	0.12840	0.13250	0.00023
2	Anthracene	3	0.07600	0.08870	0.07490	0.00014
2	Anthracene	3	0.07979	0.07286	0.07233	0.00019
2	Anthracene	4.5	0.03330	0.04050	0.05010	0.00354
2	Anthracene	6	0.00410	0.00233	0.00300	0.00016
2	Anthracene	6	0.00430	0.00280	0.00264	0.00012
2	Anthracene	7.5	0.00802	0.00088	0.00063	0.00020
2	Anthracene	9	0.00076	0.00065	0.00068	0.00014
2	Anthracene	9	0.00077	0.00062	0.00065	0.00009
2	Anthracene	10.5	0.00121	0.00052	0.00040	0.00015
2	Anthracene	12	0.00084	0.00086	0.00092	0.00019
2	Anthracene	12	0.00102	0.00150	0.00117	0.00023
2	Chlorobiphenyl	0	0.17350	0.08945	0.07040	0.00134
2	Chlorobiphenyl	1.5	0.03450	0.02620	0.03354	0.00015
2	Chlorobiphenyl	3	0.02244	0.02114	0.02112	0.00017
2	Chlorobiphenyl	3	0.02144	0.02117	0.02133	0.00016
2	Chlorobiphenyl	4.5	0.02000	0.01330	0.01420	0.00015
2	Chlorobiphenyl	6	0.01710	0.01374	0.01260	0.00023
2	Chlorobiphenyl	6	0.01660	0.01365	0.01290	0.00012
2	Chlorobiphenyl	7.5	0.01009	0.01189	0.01190	0.00010
2	Chlorobiphenyl	9	0.01245	0.01137	0.00976	0.00012
2	Chlorobiphenyl	9	0.01259	0.01250	0.00980	0.00063
2	Chlorobiphenyl	10.5	0.00874	0.01024	0.01155	0.00010
2	Chlorobiphenyl	12	0.00790	0.00789	0.00839	0.00008
2	Chlorobiphenyl	12	0.00765	0.00778	0.00937	0.00013

2	Flourene	0	0.28400	0.23070	0.22060	0.00083
2	Flourene	1.5	0.13068	0.10101	0.12920	0.00064
2	Flourene	3	0.09437	0.08851	0.08315	0.00099
2	Flourene	3	0.09131	0.08914	0.08933	0.00111
2	Flourene	4.5	0.08667	0.08947	0.09056	0.00150
2	Flourene	6	0.06102	0.05981	0.06142	0.00205
2	Flourene	6	0.06070	0.05951	0.06123	0.00165
2	Flourene	7.5	0.04587	0.04870	0.05358	0.00161
2	Flourene	9	0.04965	0.04883	0.04598	0.00170
2	Flourene	9	0.04720	0.04870	0.04609	0.00186
2	Flourene	10.5	0.03948	0.04373	0.04419	0.00137
2	Flourene	12	0.03666	0.03277	0.03828	0.00153
2	Flourene	12	0.03571	0.03334	0.04100	0.00154
2	Pentachlorophenol	0	0.05172	0.08601	0.04704	0.00010
2	Pentachlorophenol	1.5	0.04684	0.06775	0.04138	0.00010
2	Pentachlorophenol	3	0.04233	0.06015	0.03696	0.00003
2	Pentachlorophenol	3	0.04061	0.05753	0.03370	0.00001
2	Pentachlorophenol	4.5	0.04535	0.04128	0.03420	0.00002
2	Pentachlorophenol	6	0.04003	0.02801	0.03611	0.00001
2	Pentachlorophenol	6	0.03977	0.02800	0.03721	0.00001
2	Pentachlorophenol	7.5	0.03337	0.02806	0.02369	0.00001
2	Pentachlorophenol	9	0.02823	0.02818	0.03450	0.00002
2	Pentachlorophenol	9	0.02882	0.02799	0.03565	0.00001
2	Pentachlorophenol	10.5	0.02248	0.02644	0.03230	0.00001
2	Pentachlorophenol	12	0.02157	0.02209	0.03351	0.00001
2	Pentachlorophenol	12	0.02888	0.02569	0.03631	0.00001
2	Pyrene	0	0.17031	0.16025	0.15120	0.00140
2	Pyrene	1.5	0.03311	0.04492	0.11203	0.00057
2	Pyrene	3	0.02006	0.02012	0.03135	0.00020
2	Pyrene	3	0.03771	0.02035	0.01433	0.00029
2	Pyrene	4.5	0.01042	0.02200	0.02700	0.00021
2	Pyrene	6	0.01349	0.02050	0.01152	0.00020
2	Pyrene	6	0.01336	0.02018	0.01145	0.00018
2	Pyrene	7.5	0.01277	0.00954	0.00117	0.00019
2	Pyrene	9	0.01381	0.02895	0.01374	0.00008
2	Pyrene	9	0.01710	0.02980	0.01015	0.00010
2	Pyrene	10.5	0.00729	0.01302	0.13290	0.00021
2	Pyrene	12	0.01234	0.00800	0.01531	0.00007
2	Pyrene	12	0.00867	0.00815	0.01523	0.00038

2	Trichlorophenol	0	0.05708	0.05612	0.05321	0.00020
2	Trichlorophenol	1.5	0.05275	0.05743	0.05113	0.00017
2	Trichlorophenol	3	0.04718	0.05713	0.04443	0.00023
2	Trichlorophenol	3	0.04566	0.05685	0.04184	0.00023
2	Trichlorophenol	4.5	0.04506	0.05121	0.03751	0.00021
2	Trichlorophenol	6	0.03561	0.03285	0.03481	0.00050
2	Trichlorophenol	6	0.03550	0.03172	0.02789	0.00049
2	Trichlorophenol	7.5	0.02782	0.02555	0.02349	0.00033
2	Trichlorophenol	9	0.02297	0.02157	0.02157	0.00029
2	Trichlorophenol	9	0.02523	0.02188	0.02199	0.00030
2	Trichlorophenol	10.5	0.02100	0.02134	0.02151	0.00020
2	Trichlorophenol	12	0.01936	0.01935	0.02257	0.00016
2	Trichlorophenol	12	0.01964	0.01952	0.02134	0.00017
3	Anthracene	0	0.15774	0.07401	0.08946	0.00003
3	Anthracene	1.5	0.16123	0.04563	0.03844	0.00005
3	Anthracene	3	0.02267	0.02807	0.03135	0.00010
3	Anthracene	4.5	0.02618	0.02092	0.02626	0.00002
3	Anthracene	6	0.02599	0.03928	0.02223	0.00011
3	Anthracene	7.5	0.01938	0.01853	0.02136	0.00018
3	Anthracene	9	0.02008	0.01884	0.02435	0.00020
3	Anthracene	9	0.02236	0.02196	0.02635	
3	Anthracene	10.5	0.02448	0.02067	0.00682	0.00027
3	Anthracene	12	0.03024	0.02630	0.01866	0.00028
3	Anthracene	12	0.03066	0.02158	0.01651	0.00035

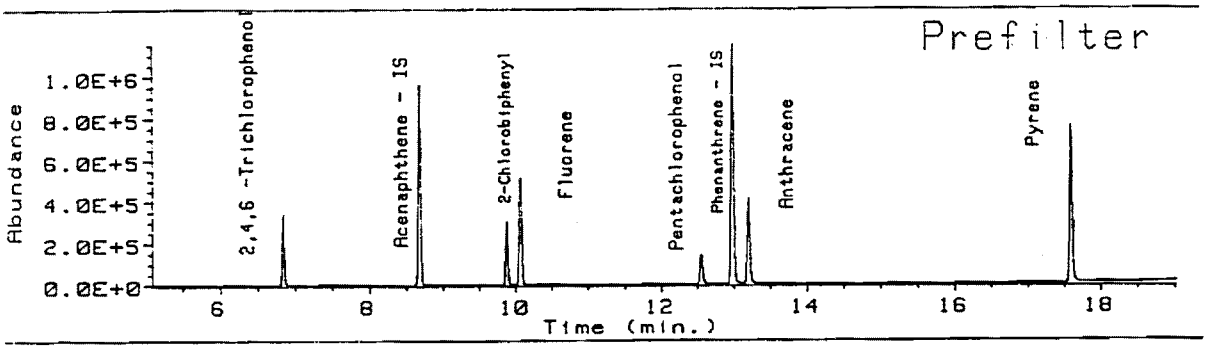
Volatile Compounds

Trial	Contaminant	Time	Prefilter (mg/L)	Postfilter (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
1	Trichloroethene	0	405.75	388.02	407.39	4.11
1	Trichloroethene	1.5	324.76	302.09	343.75	7.54
1	Trichloroethene	3	256.48	253.52	246.48	13.77
1	Trichloroethene	3	251.41	260.60	240.58	15.62
1	Trichloroethene	4.5	223.63	217.82	201.66	20.44
1	Trichloroethene	6	200.65	201.37	207.37	28.43
1	Trichloroethene	6	190.09	185.88	197.99	25.60
1	Trichloroethene	7.5	162.84	162.36	165.83	34.85
1	Trichloroethene	9	145.21	143.07	145.39	48.06
1	Trichloroethene	9	157.59	169.59	169.46	46.01
1	Trichloroethene	10.5	151.40	153.59	154.02	50.49
1	Trichloroethene	12	117.12	117.36	125.54	45.50
1	Trichloroethene	12	126.30	130.07	127.23	45.68
2	Bromodichlorometh	0	619.08	654.42	663.80	7.01
2	Bromodichlorometh	1.5	573.34	592.24	628.11	45.21
2	Bromodichlorometh	3	547.59	546.50	557.15	75.29
2	Bromodichlorometh	3	527.29	540.57	575.93	75.23
2	Bromodichlorometh	4.5	561.95	550.62	595.24	100.00
2	Bromodichlorometh	6	516.00	524.74	550.13	112.90
2	Bromodichlorometh	6	508.07	522.24	559.84	108.38
2	Bromodichlorometh	7.5	475.80	483.86	501.41	110.17
2	Bromodichlorometh	9	459.13	468.81	522.91	102.49
2	Bromodichlorometh	9	497.52	493.85	541.23	102.27
2	Bromodichlorometh	10.5	493.89	506.30	527.51	103.07
2	Bromodichlorometh	12	400.23	491.91	421.73	101.32
2	Bromodichlorometh	12	175.00	390.61	421.96	102.18
2	Chlorodibromometh	0	780.47	816.34	865.05	6.98
2	Chlorodibromometh	1.5	713.59	736.16	793.43	38.91
2	Chlorodibromometh	3	673.71	681.58	681.19	64.87
2	Chlorodibromometh	3	639.24	674.31	701.35	64.58
2	Chlorodibromometh	4.5	672.33	673.60	719.97	89.07
2	Chlorodibromometh	6	621.53	616.88	634.46	104.24
2	Chlorodibromometh	6	596.57	622.03	646.89	101.94
2	Chlorodibromometh	7.5	536.51	560.54	583.37	107.09
2	Chlorodibromometh	9	536.08	534.02	585.23	98.76
2	Chlorodibromometh	9	555.71	541.30	589.14	96.38
2	Chlorodibromometh	10.5	537.39	543.65	601.15	100.17
2	Chlorodibromometh	12	467.62	528.93	481.98	99.93
2	Chlorodibromometh	12	451.06	457.61	494.49	99.41

2	Trichloroethene	0	373.46	448.77	440.59	1.56
2	Trichloroethene	1.5	323.45	369.80	393.66	7.78
2	Trichloroethene	3	310.23	313.84	309.16	22.77
2	Trichloroethene	3	290.72	299.75	317.45	19.74
2	Trichloroethene	4.5	284.58	285.90	297.31	34.43
2	Trichloroethene	6	243.72	247.64	252.78	44.86
2	Trichloroethene	6	225.19	255.16	252.78	43.08
2	Trichloroethene	7.5	210.88	219.74	217.21	53.73
2	Trichloroethene	9	199.93	198.80	223.85	53.01
2	Trichloroethene	9	217.15	211.50	230.20	50.25
2	Trichloroethene	10.5	189.44	199.34	199.74	55.04
2	Trichloroethene	12	69.49	185.96	158.82	54.41
2	Trichloroethene	12	178.00	156.64	167.88	57.50
2	Trichloromethane	0	358.37	398.78	389.51	5.59
2	Trichloromethane	1.5	344.01	363.34	394.08	38.19
2	Trichloromethane	3	347.21	337.93	360.21	58.67
2	Trichloromethane	3	327.51	340.09	364.91	60.66
2	Trichloromethane	4.5	350.07	351.05	372.19	76.25
2	Trichloromethane	6	330.28	333.90	347.31	81.68
2	Trichloromethane	6	319.74	337.96	357.38	77.50
2	Trichloromethane	7.5	305.15	319.53	323.40	78.04
2	Trichloromethane	9	303.27	314.70	349.23	70.82
2	Trichloromethane	9	339.33	330.84	355.06	69.36
2	Trichloromethane	10.5	306.80	326.63	340.31	71.62
2	Trichloromethane	12	263.94	314.79	280.02	68.14
2	Trichloromethane	12	275.58	260.23	274.23	69.27
3	Trichloroethene	0	513.84	499.00	529.55	29.22
3	Trichloroethene	1.5	440.75	418.20	427.51	35.34
3	Trichloroethene	3	363.79	362.79	370.14	49.07
3	Trichloroethene	3	369.49	367.99	381.66	47.15
3	Trichloroethene	4.5	318.49	324.71	327.43	59.27
3	Trichloroethene	6	250.60	267.84	272.75	72.28
3	Trichloroethene	6	261.75	252.52	274.15	77.36
3	Trichloroethene	7.5	242.12	238.49	249.01	82.31
3	Trichloroethene	9	225.97	224.77	258.22	86.08
3	Trichloroethene	9	225.54	227.82	248.08	89.42
3	Trichloroethene	10.5	214.79	204.63	222.83	90.35
3	Trichloroethene	12	198.75	204.92	218.13	85.00
3	Trichloroethene	12	207.15	203.75	213.30	88.33

APPENDIX C

CHROMATOGRAMS


Prefilter
Abundance
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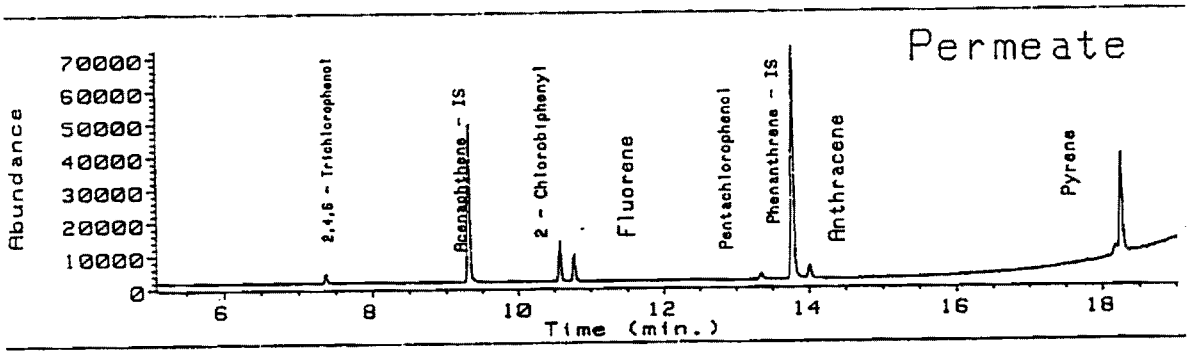
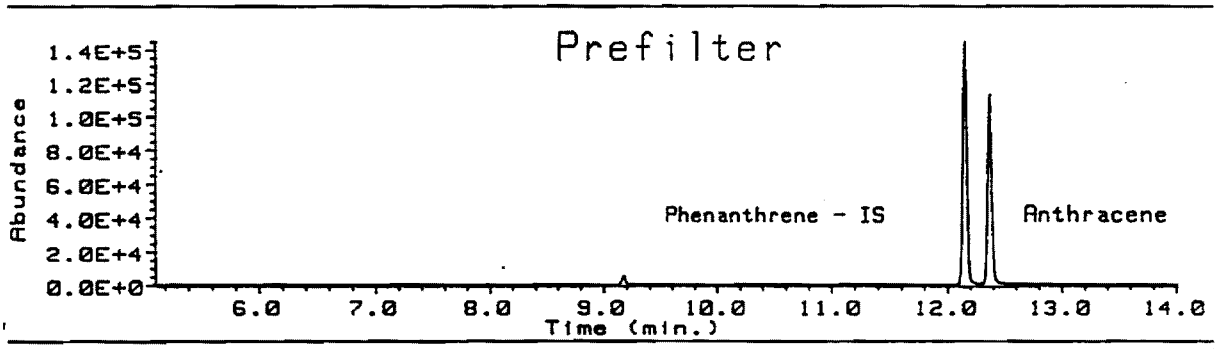
8.0E+5
6.0E+5
4.0E+5
2.0E+5
0.0E+0
2,4,6 -Trichlorophenol
Acenaphthene - IS
2-Chlorobiphenyl
Fluorene
Pentachlorophenol
Phenanthrene - IS
Anthracene
Pyrene
6
8
10
12
14
16
18
Time (min.)


Permeate
Abundance
70000
60000
50000
40000
30000
20000
10000
0
2,4,6 - Trichlorophenol
Acenaphthene - IS
2 - Chlorobiphenyl
Fluorene
Pentachlorophenol
Phenanthrene - IS
Anthracene
Pyrene
6
8
10
12
14
16
18
Time (min.)


Prefilter
Abundance
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1.2E+5
1.0E+5
8.0E+4
6.0E+4
4.0E+4
2.0E+4
0.0E+0
Phenanthrene - IS
Anthracene
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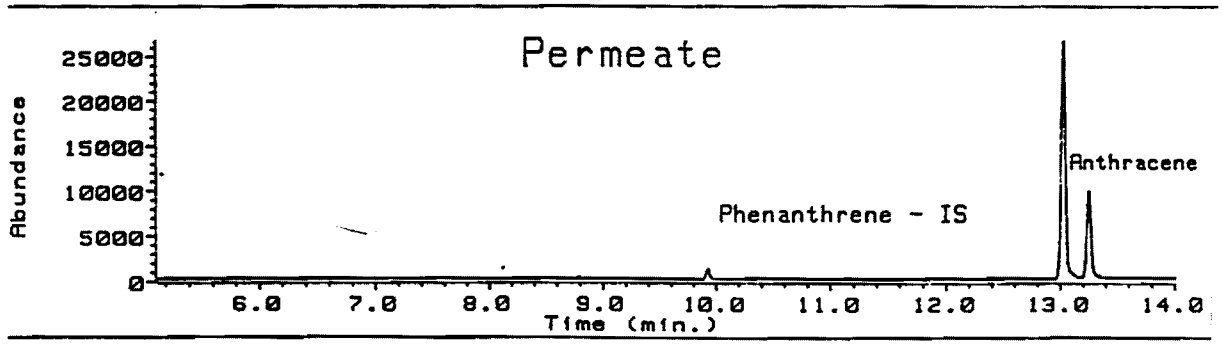
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
Time (min.)


Permeate
Abundance
25000
20000
15000
10000
5000
0
Anthracene
Phenanthrene - IS
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
Time (min.)

VITA

Michael Anthony Robinson was born on April 8, 1962, Weirton, WV. Upon graduation from Weir Senior High School in 1980, he attended West Virginia Institute of Technology. Graduating cum laude with a B.S. in chemical engineering in 1985, he was employed by Milliken and Company in LaGrange, GA for three months before accepting employment with Naval Surface Warfare Center in Dahlgren, VA. In January 1989 he began his graduate studies at Virginia Polytechnic Institute. Upon receiving a M.S. in Environmental Engineering in May 1990 he will continue his studies towards a Ph. D. in Civil Engineering at Virginia Polytechnic Institute.