

**THE REMOVAL OF PESTICIDES AND HEAVY METALS
BY REVERSE OSMOSIS**

by

Brian S.H. Chong

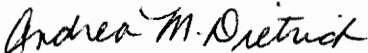
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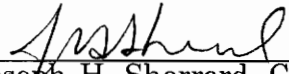
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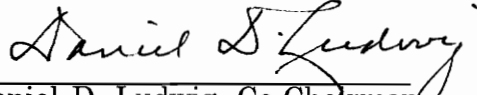
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(ABSTRACT)

In the past few years, the contamination by pesticides and heavy metals in surface water and groundwater has increased. Reverse osmosis is a unit process that has demonstrated capacity to remove dissolved pesticides and heavy metals from aqueous solution, and it is therefore worthwhile to consider this treatment process as a potential removal technique for hazardous constituents.

The purpose of this investigation was to determine the effectiveness of a field scale reverse osmosis unit, with a spiral wound poly(ether/urea) membrane, in removing pesticides and heavy metals from a contaminated source. The removal efficiency for a single contaminant alone and a part of a mixture was examined. The performance of new and used membranes over time was also investigated.

The average removal of pesticides was better than 99 percent. Reverse osmosis separation of pesticides was found to be dependent on the characteristics of the membrane and the physical/chemical properties of the pesticides. Pesticides in the mixed solution were found to behave independently. Sorption of the pesticides onto the reverse osmosis membrane was found to play a major role in the overall removal efficiency.

Better than 99 percent average removal was achieved for all the metals except arsenic. The importance of the physical/chemical properties of the metal ions such as solubility, ionic radius, and electronegativity were determined. In tests to compare removal efficiency between new membrane and membrane which had been used, virtually no differences occurred.

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INTRODUCTION

Reverse osmosis is a popular treatment process used worldwide to solve water treatment problems. While reverse osmosis is most commonly employed in the desalination of brackish waters, this process is also effective in removing dissolved organic and inorganic chemicals and softening of water. In view of higher costs to operate these systems in comparison with conventional water treatment processes, reverse osmosis is used to a much lesser extent. However, with the development of new membranes that require less feed pressure, system costs incurred will be considerably reduced, making the reverse osmosis process a more competitive water treatment process (AWWA Water Desalting and Reuse Committee, 1989).

Pesticides are chemicals used to control undesirable organisms including insects, weeds, fungi, bacteria, and animals. The increasing use of pesticides in the agricultural industry poses a serious threat to surface water and groundwater alike. The U.S. Geological Survey in 1984 reported that pesticides detected in groundwater has risen in the last decade (Revelle and Revelle, 1988). Due to their persistent and toxic nature, pesticides have emerged as a significant class of water pollutants (Eichelberger and Linchtenberg, 1971).

Heavy metal pollution is a major concern because metals cannot readily be reduced to harmless forms. Consequently, water systems contaminated with heavy metals will remain unsafe for many years. Not only are they hazardous, some of metals such as nickel and arsenic are carcinogenic as well (Morgan *et al.*,

1986). Mining wastewaters, domestic effluents, industrial effluents especially from the metal finishing industry, and the burning of fuels are common sources of heavy metal pollution to surface water and groundwater (Renberg, 1986).

The purpose of this research was to determine the effectiveness of reverse osmosis for removing pesticides and heavy metals from a contaminated water source. To evaluate reverse osmosis for water treatment, a field scale reverse osmosis water purification unit with a flow of 22 gpm and containing a spiral wound poly(ether/urea) membrane was used. Specifically, the objectives of this research were to evaluate the:

- i) effectiveness of reverse osmosis to produce potable water, as judged by the Safe Drinking Water Act of 1986;
- ii) effectiveness of the unit in removing single contaminants;
- iii) effectiveness of the unit in removing individual contaminants from a mixture or multicontaminant trial; and
- iv) removal efficiency of new membranes in comparison with that of used membranes.

Five pesticides and five heavy metals were used in these investigations:

- | | |
|-------------------------|---------------|
| i) Atrazine | i) Arsenic |
| ii) 1,4-Dichlorobenzene | ii) Copper |
| iii) Heptachlor | iii) Lead |
| iv) Lindane | iv) Magnesium |
| v) Methoxychlor | v) Nickel |

The strategy adopted for testing the reverse osmosis unit with these pesticides and heavy metals was to introduce the contaminants into a batch solution, pass the contaminated water through the reverse osmosis unit, taking samples before and after the reverse osmosis membrane every 90 minutes for 12 hours. Removal efficiencies were to be calculated after measuring the amount of the contaminant in the feedwater and permeate.

LITERATURE REVIEW

A. Theory

Reverse osmosis, also known as hyperfiltration, was first introduced in the mid-1960s, and since then it has become one of the most innovative water treatment techniques. Basically, reverse osmosis is a simple separation process. When a solution is pressurized against a membrane, the membrane allows certain chemical species to pass through and retains others. The liquid that passes through (permeate) is usually collected as product water. The rejected solution, which is known as the concentrate or the retentate, is discharged as waste. To operate reverse osmosis efficiently, the membrane employed must be permeable to water and significantly impermeable to solutes. Furthermore, reverse osmosis membranes must also be able to endure the pressure being applied without breaking down (Lonsdale and Podall, 1972).

When solutions of different soluble makeup exist at opposite sides of a semipermeable membrane, the less concentrated solute will diffuse through the membrane to the compartment with the higher solute concentration in order to achieve equilibrium (Figure 1a). At such time as the solvent in each compartment reaches equilibrium, the difference in pressure between the solutions is called the osmotic equilibrium (Figure 1b). If a pressure in excess of the osmotic pressure is applied on the more concentrated side of the membrane, solvent in the more concentrated side is forced to flow to the less concentrated side leaving a more concentrated solution behind. This process is called reverse

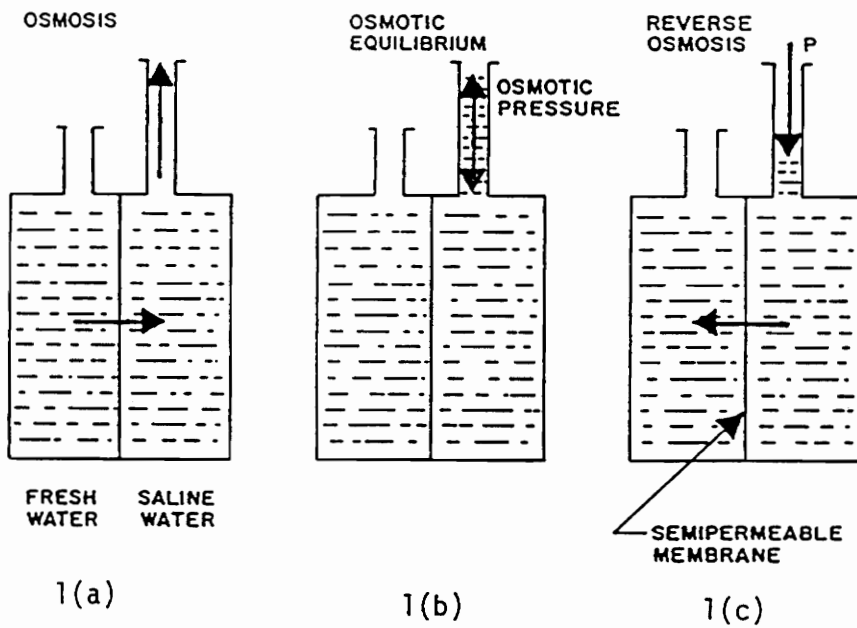


Figure 1. Simplified Concepts of Osmosis, Osmosis Equilibrium, and Reverse Osmosis

osmosis because it flows in a direction opposite to normal osmosis (Figure 1c) (AWWA Water Desalting and Reuse Committee, 1989; Eckenfelder, 1980).

B. Transport Mechanisms

According to Duvel and Helfgott (1975), solute (molecular and ionic species) transport through membranes is due to two factors:

- 1) Diffusion of molecules through the membrane under a concentration gradient when gaps of the appropriate sizes become available.
- 2) The extent of dissolution between the solute and the membrane. The degree of dissolution is dependent on the capability of the solute to form hydrogen bonds. When hydrogen bonding increases, more solute will "cling" onto the membrane, and therefore more solute is available for diffusion. The solute then diffuses through the membrane under a concentration gradient. This concept is known as the preferential sorption mechanism (Chian and Fang, 1975).

Duvel and Helfgott (1975), compendiously stated the following:

"Water passes through the membrane better than most other compounds for two reasons:

- 1) It can form strong hydrogen bonds and is therefore very highly sorbed in the membrane.
- 2) It is very small and can diffuse very rapidly."

C. Terminology

Permeate or product water refers to the purified water that permeates through the reverse osmosis membrane. Concentrate or retentate is the term

used for the portion of the feedwater that is rejected by the membrane. In this research, the words rejection and removal are used interchangeably. Percent removal and percent rejection indicate a measure of the overall amount of contaminant rejected in the feedwater.

D. Physical/Chemical Properties of Solutes Affecting Separation

Physical and chemical properties of a compound will influence the rate of passage of that compound through a membrane in reverse osmosis processes.

Understanding these properties will help to answer the following questions:

- 1) What features of a compound cause it to be rejected or pass through the membrane ?
- 2) Why are some solutes rejected better than others ?
- 3) By what mechanism do the solutes pass through the membrane ?

1. Physical Properties

A study by Duvel and Helfgott (1975) indicated that in a homologous series, solute rejection increases as molecular weight increases. Not only does the size of the molecule play an important role, the shape of the molecule is also critical. Highly branched molecules of the same weight will be rejected more readily than those which are less branched. To prove this point, the author performed a reverse osmosis rejection study on isomers of pentanol. A 90 percent rejection rate was observed with the extremely branched 2 methyl-2-butanol and 2,2-dimethyl-1-propanol. 3-methyl-1-butanol and the secondary

alcohol, 3-pentanol, showed a rejection between 60 - 70 percent whereas the linear 1-pentanol, which is least branched, showed only a rejection of about 40 percent. The authors learned that the increase in branching overshadowed the effect of molecular weight.

2. Chemical Properties

Ions are more effectively separated than molecules, and for this reason inorganic solutes are better separated than organic solutes. The ability of a solute to dissociate into its ionic form depends on the dissociation or equilibrium constant, pK_a , and the pH of the solution. The degree of ionization can be determined by the following equation :

$$\text{Degree of ionization} = \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH}} \times 100 \% \quad [1]$$

From equation [1], it can be deduced that in a basic solution, where the pH is very much greater than the pK_a , the degree of ionization will approach 100 percent. When this happens, the acid will be in the ionic form and thus better separation. The degree of ionization can be monitored by altering the pH (Chian & Fang, 1976).

An effective reverse osmosis membrane should have its polymer made from balanced hydrophobic and hydrophilic groups. The hydrophilic nature of the polymer allows better passage for solvent water, whereas the hydrophobic groups are needed for salts separation. The hydrophilic groups are the cause for

the poor rejection of polar molecules when a relatively more polar membrane is used (e.g. cellulose acetate). This is due to the poor affinity of the polar molecules towards the membrane. On the other hand, excellent rejection is obtained using relatively non-polar membrane like the aromatic polyamide membrane. The polar molecules are most probably adsorbed onto the hydrophobic region of the membrane. Therefore, through the mechanism of adsorption, depending on the polarity of the solutes, the membrane selected is very important (Chian *et al.*, 1975).

E. Operational Factors of a Reverse Osmosis System

1. Temperature

In general, increasing the temperature will significantly increase the permeate flux. Depending on the type of membrane that is being used, the recommended temperature range is generally 30-50 °C (AWWA Water Desalting and Reuse Committee, 1989). Temperatures in excess of 50 °C will affect the membrane life and cause membrane compaction. When a membrane undergoes compaction, the membrane surface structure is reversibly changed causing a reduction in permeability. Therefore, the higher the temperature, the lower the permeability (Mehdizadeh *et al.*, 1989).

An experiment on temperature effects on the performance of thin-film composite aromatic polyamide membranes was conducted by Mehdizadeh *et al.*, (1989). They found that separation of solute is unaffected by temperature.

However, at lower pressures, the separation of solutes first decreases, passes through a minimum and then increases with increasing temperature.

Chian *et al.*, (1975), observed that removal of chlorinated pesticides, which are rejected mostly through adsorption, improves with increasing temperature because the hydrophobic interactions that partially enhance the adsorption of the pesticides become stronger as temperature increases.

Leban and Wydeven, (1984), using poly (ether/urea) membrane discovered that permeate flux declined sharply at high temperatures.

2. Pressure

A high feed pressure is desirable because the higher the pressure, the greater the permeate flux. The applied pressure must also be high enough to ensure a turbulent flow of feed water through the membrane to reduce the chance of rejected salts being accumulated at the membrane surface (concentration polarization). Concentration polarization will impede the permeation of feed water through the membrane and may also cause precipitation of salts on the membrane surface (James M. Montgomery, 1985).

The applied pressure to use is dependent on the type and configuration of membrane. Generally, the maximum pressure allowed is 1000 psig. Through experience, pressures of 400 to 600 psig appear to be optimal (Eckenfelder, 1980).

3. pH

In actual practice, feed water and salt fluxes decline with time. The decrease in feed water flux is due to compaction of the membrane, while

membrane hydrolysis reduces salt flux. Membrane hydrolysis is a function of pH and temperature (Montgomery, 1985). To minimize the hydrolysis effect, polyamide and other composite membranes are best operated in the 4 - 10 pH range. Cellulosic membranes can tolerate pH range of 4 - 6.5 (AWWA Water Desalting and Reuse Committee, 1989).

F. Membrane Technology

An ideal membrane should possess the following features:

- i) transport mechanisms should be designed in such a way that the membrane offers the least resistance to water flow and at the same time perform as an impermeable barrier to contaminants,
- ii) membranes should be as thin as possible so that maximum flow across the membrane can be achieved,
- iii) membranes must also be able to withstand all applied pressures, and
- iv) membranes should have long service life, resistance to chemical and biological attack, and low cost. (James M. Montgomery, 1985)

Since 1970, significant growth in the development of membranes has occurred. Table 1 lists some of the major membrane producers. A description of some of the membranes follows.

TABLE 1

List of Major Membrane Producers*

Manufacturer	Configuration	Materials
DDS RO Division	Plate & frame	Cellulosic Polyamide thin film composite
DOW Chemical Co.	Hollow Fiber	Cellulosic
E.I. du Pont de Nemours & Co. (Inc.)	Hollow Fiber Spiral Wound	Cellulosic Polyaramid
Film Tec Corporation	Spiral Wound	Polyamide thin film composite
Hydranautics	Spiral Wound	Cellulosic Polyamide thin film composite
Millipore Corporation	Spiral Wound	Cellulosic Polyamide
Nitto Electric Industrial	Spiral Wound	Synthesis composites
Osmonics Inc.	Spiral Wound	Cellulosic
Toray Industries Inc.	Spiral Wound	Cellulosic Polyether composites
Toyobo Co. Ltd	Hollow Fiber	Cellulosic
United Oil Products (UOP)	Spiral Wound	Cellulosic Polyethyl urea

* After Lorch, 1987.

1. Cellulose Acetate Membrane

The modified cellulose acetate membrane by Leob and Sourirajan is the most commonly used membrane in the field of reverse osmosis. It has an asymmetric or "skinned" structure which is an extremely thin, but dense, surface layer or skin supported on a porous structure. This thin dense layer is approximately 2000 Å (0.2 µm) thick, and it can be made from different cellulose based polymers. The most common forms are cellulose diacetate, cellulose triacetate, or blended cellulose diacetate-triacetate (Sourirajan, 1977; Lonsdale and Pondall, 1972; James M. Montgomery, 1985).

Cellulose acetate membranes perform very effectively due to two reasons. First, the membrane is extremely thin and therefore very efficient. Secondly, the thin dense films are more permeable to water, by several orders of magnitude, than they are to salts (Lonsdale and Podall, 1972). According to James J. Montgomery (1985), for ultimate performance, the membrane should be operated at feed temperatures not exceeding 38°C (100°F) and at pH range of 3 to 7. When the feed is brackish, pressures of 400-500 psi should be used. Seawater feed is best operated at 800-1000 psi. Performance of cellulose acetate membranes in removing specific contaminants is shown in Table 2. Weber (1972) succinctly states the following conclusions concerning cellulose acetate membranes:

- " 1) multivalent ions are rejected more effectively than univalent ions;
- 2) undissociated or partially dissociated substances are poorly rejected;
- 3) acids and bases are rejected to a lesser extent than their salts;
- 4) co-ions affect the rejection of a particular ion (e.g., sodium is better rejected as sodium sulfate than as sodium

Table 2

**Typical Solute Rejection High-Selectivity
Cellulose Acetate Membrane***

Solute	Maximum Rejection (%)	Average Rejection (%)
Calcium, Ca ²⁺	99.7	>99
Magnesium, Mg ²⁺	99.9	>99
Sodium, Na ⁺	97.0	
Potassium, K ⁺	97.0	
Iron, Fe ²⁺ and Fe ³⁺	100**	100**
Manganese, Mn ²⁺	100**	100**
Aluminum, Al ³⁺	99.9	>99
Chromium, Cr ⁶⁺ pH 2.6		92.6
4.2		97.2
7.6		98.6
Ammonia, NH ₄ ⁺	95.0	
Bicarbonate, HCO ₃ ⁻		80-98
Sulfate, SO ₄ ²⁻	100	>99
Chloride, Cl ⁻	97.0	
Nitrate, NO ₃ ⁻	86.0	
Fluoride, F ⁻	98.0	

* After Weber, 1972

** approximate

- chloride);
- 5) in general, low molecular weight, water soluble organic molecules are poorly rejected;
 - 6) undissociated low molecular weight organic acids are poorly rejected, and their salts are well rejected; and
 - 7) trace quantities of univalent ions are in general poorly rejected."

2. *Polyamide Membranes*

In recent years, marked progress has been made in the development of new and better membranes. The family of polyamide membranes is typical of this growth. Polyamide membranes are characterized by high chemical and physical stability and therefore to longer lifetimes (Weber, 1972). This membrane is also not susceptible to chemical and biological attack making prechlorination of the feed water unnecessary. Conversely, polyamide membranes are very sensitive to chlorine and oxidants. Therefore, dechlorination is required if the source contains chlorine (Montgomery, 1985). Other advantages include versatility and reasonable cost (Lorch, 1987).

3. *Poly(ether/urea) Membranes*

Poly(ether/urea) membranes have very thin films with thickness ranging from 100 to 1000 Å. These thin films enable a reverse osmosis process to produce excellent flux (Pusch and Riley, 1977). The polyether composite (PEC-1000) membrane by Toray Industries, Inc. shows excellent solute rejection. Table 3 illustrates the performance of PEC-1000 membrane (Nakagawa *et al.*, 1985).

Table 3
Typical Performance of Polyether Composite (PEC-1000) Membrane*

Constituent	Feedwater (seawater)	Permeate	Removal ** (%)
TDS (ppm)	49,000	206	99.64
Ca ²⁺ (mg/l)	520	0.3	99.95
Mg ²⁺ (mg/l)	1,740	1.6	99.92
Na ⁺ (mg/l)	14,800	75	99.57
K ⁺ (mg/l)	568	3.7	99.44
SO ₄ ²⁻ (mg/l)	3,670	3.4	99.92
Cl ⁻ (mg/l)	26,300	109	99.64

**** Calculated at the base of average seawater ionic concentration**

*** Nakagawa et al., 1985**

This membrane is capable of an average of 99.85 percent salt rejection. It exhibits high permeate flow rate and has the ability to withstand high pressure operation (70 kg/cm² - 1000 psi) under high feedwater temperature. Experimental results also indicate that there is no effect of compaction on membrane performance (Itoh, *et al*, 1985). The poly(ether/urea) membrane (RC-100) from Universal Oil Products (UOP) is a thin film composite membrane supported on a fabric-reinforced porous structure. Besides showing high-water and low-salt permeability and wet-dry stability, it has proved also to be thermally and chemically stable. Poly(ether/urea) membranes have also been reported to be very resistant to biological fouling (Leban and Wydeven, 1984).

G. Membrane Configurations

Most reverse osmosis elements involve a modular form of membrane configurations. The four most common configurations are the plate system, the tubular, the spiral wound, and the hollow fine fiber. A comparison of these four reverse osmosis configurations is depicted in Table 4. Only the spiral wound and hollow fiber systems are discussed in this study. An effective configuration should have the following characteristics:

- 1) Support the membrane against the applied pressure of 14-82 bar (200-1200 lb/in²). The applied pressure is dependent on the TDS of the feed water
- 2) High productivity per unit volume (compactness)
- 3) Minimum concentration polarization
- 4) Easy to clean and not prone to fouling

Table 4
Comparison of Reverse Osmosis Configurations*

Module Type	Packing Density (ft²/ft³)	Water Output Per Unit Volume (gal/day/ft³)	Useful pH Range
Plate & Frame	150	1500	2-8
Large tubes	50	500	2-8
Spiral	250	2500	2-8
Polyamide hollow fine fibers	5000	5000	0-12
Cellulose acetate hollow fine fibers	2500	7500	3-7

* After Weber, 1972

5) The module must be effectively sealed

1. Spiral Wound Modules

A typical spiral wound module is shown in Figure 2. A flat membrane envelope (leaf) and a feed water spacer are rolled spirally around the product water collection tube. The spacer is usually made of plastic mesh to provide a passage for flow inside of the envelope. The open ends of the envelopes are then attached to the collection tube. Feed water enters the module through the feed water end of the element and permeates spirally towards the collection tube. The product water flows into the collection tube through holes on the tube and then out of the vessel. Typical length and diameter of a spiral wound module are 40 inches and 10 inches, respectively. Among the membranes that use spiral wound modules are the cellulose acetate, polyamide, and polyether amide-polysulphone composite membrane (James M. Montgomery, 1985; Lorch, 1987; U.S. Army, 1987).

2. Hollow Fiber Module

The module that gives the highest productivity per unit volume (compactness) is the hollow fiber module. The thickness of the fiber is approximately the thickness of the human hair (Lorch, 1987). These fibers are folded and arranged lengthwise along the module. Since they are folded, all the open ends are facing one end of the module. When feedwater enters the module, it permeates through the tiny spaces between the fibers. The fibers which are very dense at the surface obstruct the permeation of contaminants but

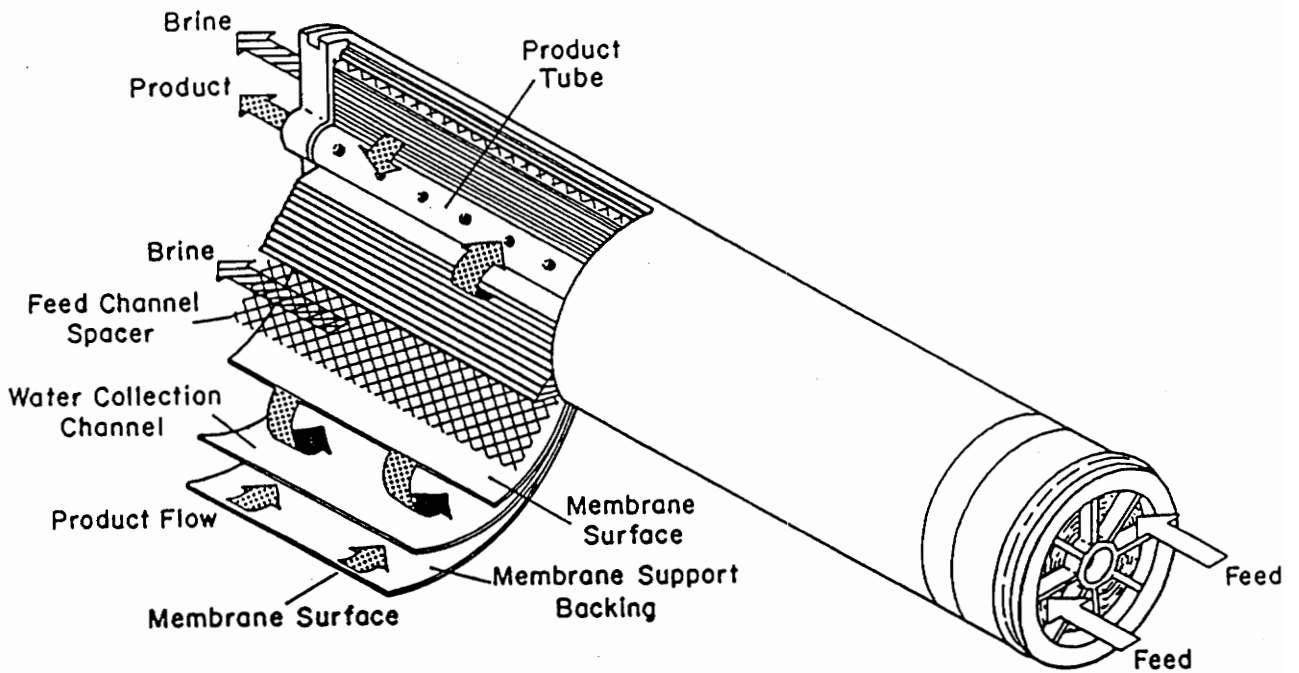


Figure 2. Internal Structure of A Spiral Wound Membrane

allow water to pass through. The purified water flows inside the hollow fiber to a collection header (Montgomery, 1985).

Du Pont Corporation's hollow fibers are made from aromatic polyamide, whereas those manufactured by Dow are hollow fibers made from cellulose triacetate (Lorch, 1987).

H. Removal of Pesticides by Reverse Osmosis

A study of pesticide removal by reverse osmosis was conducted by Chian et al., (1975) using cellulose acetate and aromatic polyamide membranes. Table 5 illustrates some of their findings. Chian *et al* found that most of the chlorinated pesticides, with the exception of Lindane, were very well rejected. Since most chlorinated pesticides tend to be non-polar, they were adsorbed onto the hydrophobic region of the membrane. The authors discovered that most of the pesticides were rejected by adsorption rather than reverse osmosis. This research concluded that the NS-100 (aromatic polyamide) membrane is more non-polar compared to CA (cellulose acetate) membrane because the NS-100 membrane has a higher percentage adsorption than the CA membrane. Using this reasoning, it was concluded that atrazine and radox are most likely to be polar pesticides because they are poorly adsorbed onto the membrane. Within the poorly rejected group (e.g. lindane, radox, atrazine), the differences in rejection is dependent upon the size and configuration of these pesticides. Lindane, being the heaviest molecule, is rejected the most.

Chian *et al* specified that membranes made from non-polar materials are

Table 5
Removal of Chlorinated Pesticides
by Reverse Osmosis*

Pesticides	Membranes	% Removal	% adsorbed
Lindane	NS-100	98.95	12.03
	CA	99.51	68.40
Heptachlor	NS-100	100	96.28
	CA	100	80.63
DDT	NS-100	100	94.29
	CA	100	100
Dieldrin	NS-100	100	95.36
	CA	99.88	76.31
Randox	NS-100	98.56	11.05
	CA	72.03	5.60
Atrazine	NS-100	97.82	11.00
	CA	84.02	6.74

* After Chian *et al.*,1975

NS-100 = polyamide membrane

CA = cellulose acetate membrane

better for pesticide removal but at the expense of reduced permeate flux. The solution for this drawback is to use a reverse osmosis configuration that gives a high productivity per unit volume (compactness) or to reduce the thickness of the skin to allow better permeate flow.

Abron (1972) evaluated the removal of DDT and Aldrin from aqueous solution using hollow nylon fiber membranes. The author found that 80 percent or more of the pesticides were adsorbed onto the membrane and that the pesticides are not moving once they are in the membrane. Abron concluded that much of the sorbed pesticides are still on the surface of the membrane as evident by the high reject concentrations.

Kinman *et al.*, (1986) studied the effectiveness of reverse osmosis in removing chlorinated hydrocarbons and pesticides from a hazardous waste leachate. Spiral wound cellulose acetate and polyamide thin film composite membranes were employed. Overall, the performance of the polyamide membrane was far better than that of the cellulose acetate membrane. Most of the pesticides were reported to be removed through adsorption onto the cellulose acetate membrane. Kinman also indicated that hydrocarbons of molecular weights more than 200 are rejected better than those that are below 200.

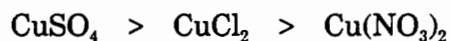
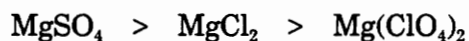
Edwards and Schubert (1973) found that pesticides with very low aqueous solubilities, such as DDT, are better separated than highly soluble molecules because they form colloidal particles or macro-molecules.

I. Removal of Heavy Metals by Reverse Osmosis

According to Johnston (1975) cellulose acetate membranes, in certain

aspects, act as ion exchange electrodes. Since the cellulosic films are slightly negatively charged, heavy metal ions, which are positively charged will be attracted to the membrane and then diffuse through it. The author cited Michaels *et al.* (1973), who claimed that heavy metal rejection increased with hydrated radius. Johnston also found that metal removal efficiencies were not affected by feed concentration. However, constant stirring over the membrane surface might have contributed to this steady performance.

The trend for metal cation separation was proposed by Sastri (1979). The order of separation affirmed was $M^{3+} > M^{2+} > M^+$ where M depicts a metal cation. This research also compared separation of salts of the same metal but with different anions. Some of the order of separation results and trends of interest he found were:



Sastri's works also established that the separation of manganous nitrate increased after the addition of sodium sulfate. This improved separation may be due to the formation of ion-paired species in solution ($M^{2+}SO_4^{2-}$). These ion-paired species are separated more effectively than metal ions formed with water (aquo metals). Accordingly, one can increase the separation of chlorine and nitrate anions by adding sodium sulfate to the solution.

Some metals exist in two different forms when they are in solution. A

good example is arsenic which exists as arsenite (Al^{3+}) and arsenate (Al^{+5}).

Arsenate was found to be considerably better removed than arsenite (Schneiter and Middlebrooks, 1983).

Table 6 illustrates some of the removal efficiencies of heavy metals found in the literature.

J. Test Compounds

1. Pesticides

The U.S. Environmental Protection Agency's (EPA) Office of Pesticide Programs estimated that 88 million pounds of atrazine was used annually from 1985 to 1987 making it one of the most heavily used pesticides in the United States. Atrazine is widely applied in corn and sorghum production, and it is one of the most commonly detected pesticides in groundwater (Barrett and Williams). A study by Baker and Richards (1989) revealed that concentrations of atrazine of 0.003 mg/l to 0.281 mg/l were found in various rivers and creeks in Northwestern Ohio.

Despite the fact that lindane production is generally on the decline, significant amounts of lindane are still found in marine animals. Average concentrations of 0.002 mg/l to 0.039 mg/l of lindane residue were found in brown shrimp from the North Sea. Lindane is highly carcinogenic with an acute oral LD_{50} of 88 - 91 mg/kg (rats).

Heptachlor is mainly used to control termites and for several agricultural crops (Farm Chemical Handbook, 1989). A study conducted by Cote *et al.*, (1985) on the Great Lakes showed that 0.001 ug/l of heptachlor was present in the

Table 6
Heavy Metals Removal by Reverse Osmosis

Metal	Counter ion	Membrane type	Average % removal	Source
As ³⁺	Aquo	Spiral wound cellulose acetate (Saltech)	58.0	Schneiter & Middlebrooks, 1983
As ⁵⁺	Aquo	Spiral wound cellulose acetate (Saltech)	91.0	Schneiter & Middlebrooks, 1983
Cu	SO ₄ ²⁻	Cellulose acetate (Osmonics Inc.)	95.3	Sastri, 1979
Mg	SO ₄ ²⁻	Cellulose acetate (Osmonics Inc.)	96.1	Sastri, 1979
Pb	Aquo	Hollow fiber (Dupont B-9-S)	64.3	Rosehart, 1973
Ni	Aquo	Hollow fiber (Dupont B-9-S)	82.4	Rosehart, 1973

water.

Methoxychlor is an insecticide and it is broadly used because of its durable action against many insects. Methoxychlor is replacing DDT because its residue is less toxic to humans and warm-blooded animals (Farm Chemicals Handbook, 1989). Concentrations of 0.04 ug/l have been detected in the waters of the Great Lakes (Cote *et al.*, 1985).

1,4 dichlorobenzene is a fumigant commonly applied to tobacco seeds to contain blue mold. It is also used to control mold on leather and clothes (Farm Chemical Handbook, 1989).

2. Heavy Metals

Arsenic is a naturally occurring element with applications in wood preservation, agriculture pesticides, and in the mining industry. Contamination of arsenic from rocks is also a problem (Revelle and Revelle, 1988). The two most common forms of arsenic in natural waters are As^{3+} and As^{5+} . An average arsenic concentration of 0.064 mg/l in U.S. rivers is not uncommon. Exposure to arsenic has been linked to skin and lung cancer (Buhler, 1972).

Neary, *et al.*, (1989) reported that the usual concentrations of copper in surface waters is less than 0.02 mg/l. Higher concentrations may be found when they are related to pipe corrosion, treatment plants effluents, leachates from mining operations, and aquatic pesticides. Copper is known for its ability to form complex formations, especially with humic substances. It also has strong affinity for clays, organic materials, and metal oxides (EPA, 1979).

In the past (1750 - 1940), the increase in lead concentration detected in

the environment was due to the lead smelting industry. Today, however, most lead pollution comes from gasoline containing lead additives. With increasing numbers of leaking gasoline underground storage tanks being reported, lead is, at an alarming rate, finding its way to the earth's groundwater. Concentrations of lead in this nation's waters ranges from a high of 0.14 mg/l to a low of 0.002 mg/l (Buhler, 1972).

James M. Montgomery (1985), revealed that concentrations of magnesium above 10 - 20 mg/l in surface waters and above 30 - 40 mg/l in groundwater are uncommon. Concentrations in a certain location can increase if significant weathering is taking place and if ion exchange is occurring between the soil and rock. The prevailing form of magnesium in natural waters is Mg^{2+} . Buhler (1972) stated that,

"About 400 million pounds of nickel are used annually in the U.S., primarily in stainless steel and various alloys, for nickel plating and as a catalyst."

Most nickel compounds are toxic, the most hazardous being nickel carbonyl which is a carcinogen known to cause lung cancer and cancer of the nose and sinus. The average nickel concentration in waters of the United States was reported to be 0.019 mg/l and can be as high as 0.13 mg/l (Buhler, 1972).

3. Physical/Chemical Properties

Some of the physical/chemical properties of pesticides and heavy metals tested are illustrated in Table 7 and 8, respectively.

K. Applications of Reverse Osmosis

1. Desalination

Desalination is the process whereby water is separated from dissolved salts in solution. California, Florida, Texas, and the Virgin Islands were pioneers in the U.S.A to use desalination to obtain freshwater. Different types of desalination technologies are currently being used in the United States and worldwide, the most successful being distillation, electro dialysis, and reverse osmosis. Table 9 shows that reverse osmosis was the preferred method used in the United States whereas distillation was most commonly chosen by the rest of the world.

One of the eminent applications of desalination is to eliminate the transportation of potable water over long distances. Southern California, New York City, and Key West are good illustrations where water is collected in a particular region and sent over long distances to areas of demand. Economically, transmission facilities are very costly to operate. Furthermore, moving water from one place to another is difficult especially when the activity involves crossing political jurisdictions. However, with desalination, the intricacy and expenditure of long distance transmission can be avoided (Buros, 1989).

Table 7

Physical/Chemical Properties of Pesticides Tested*

Pesticide	Molecular Weight	Solubility in Water	Octonal Water Coefficient, log P _{oct}
Atrazine	216	70 mg/l @ 25 °C	3.12 @ 25 °C
1,4 Dichlorobenzene	147	49 mg/l @ 22 °C	3.23 @ 22 °C
Heptachlor	373	**0.180 mg/l @ 25 °C	4.37 @ 25 °C
Lindane	291	17 mg/l @ 24 °C	3.72 @ 25 °C
Methoxychlor	346	0.04 mg/l @ 24 °C	4.47 @ 24 °C

* From Verschueren

** U.S. EPA

Table 8
Physical/Chemical Properties of Heavy Metals Tested*

Metal	Atomic Weight	Radius in A°	Specific Density (g/cm ³)	Electro-negativity
Arsenic	74.92	(3-) 2.22 (5+) 0.47	5.75	2.00
Nickel	58.71	(2+) 0.78 (3+) 0.62	8.90	1.80
Magnesium	24.31	(2+) 0.65	1.74	1.20
Lead	207.2	(2+) 1.20 (4+) 0.84	11.36	1.80
Copper	63.55	(1+) 0.96 (2+) 0.69	8.96	2.00

From Summers, 1970

TABLE 9

**Desalination Processes Employed by the United States
Versus the Rest of the World ***

Desalination Process	United States ** (%)	World- Wide (%)
Distillation	21	70
Electrodialysis	6	5
Reverse Osmosis	73	25

** US percentage include the Virgin Islands.

* Adapted from AWWA Water Desalting and Reuse Committee, 1989

2. *Water Softening*

Calcium and magnesium ions are primarily the cause of water hardness. Hardness in water induces scaling in heating pots and pipes and reduces the effectiveness of soap (Viessman and Hammer, 1985). Although lime-softening and ion-exchange are the two most commonly used methods to remove hardness, reverse osmosis is an appropriate process for removing water hardness (AWWA Water Desalting and Reuse Committee, 1989). Reverse osmosis is advantageous in comparison with conventional treatment techniques in that addition to removing hardness, reverse osmosis membranes serve as a barrier to reject bacteria and viruses and also remove color. Other apparent advantages of reverse osmosis for water softening include the following:-

- i) space needed is less (savings of 10 to 1) compared to conventional techniques;
- ii) easy to operate, thus minimizing operator attendance time;
- iii) disposal of sludge from the precipitation of lime and soda ash is eliminated;
- iv) more stringent maximum contaminant levels in the future could be met without adding treatment processes.

With the development of new and improved membranes, water softening by reverse osmosis is becoming more competitive but should be considered on a case by case basis (Conlon and McClellan, 1989).

3. Wastewater Treatment

Since the supply of natural fresh water is not sufficient to meet the ever-increasing demand for clean water, upgraded methods for treating wastewater are needed so that effluent reuse can be practiced (Smith *et al.*, 1970). According to Cruver and Nusbaum (1974), conventional wastewater treatment techniques remove most pollutant from wastewater, but the removal of dissolved organics and inorganics is not very satisfactory. As a result, conventional treatment techniques are generally not suitable for wastewater reclamation applications.

Reverse osmosis is one of the advanced wastewater treatment processes that have consistently shown excellent separation for dissolved organics and inorganics (Chian and Fang, 1976; Edwards and Schubert, 1974; Kinman *et al.*, 1987 and Smith *et al.*, 1970). Besides having the advantage of removing dissolved organics and inorganics, the reverse osmosis process also uses limited space while raising the temperature of the processed water only slightly, if at all (Curver and Nusbaum, 1974). A typical performance of reverse osmosis in treating municipal wastewaters is illustrated in Table 10. The greatest limitation of utilizing reverse osmosis to treat wastewater is that it requires a very high-quality feed so that membrane fouling and clogging from suspended matter in the wastewater on the concentrate side is kept to the minimum. Pretreatment of the effluent is therefore necessary. Filtration and carbon adsorption are the two most common pretreatment methods to ensure effective removal (Metcalf and Eddy, Inc., 1979; Smith *et al.*, 1970).

TABLE 10
Performance of Reverse Osmosis in the Treatment
of Municipal Wastewater *

Parameter	Treatment Efficiency (%)
TDS removal	78 - 92
Total Hardness removal	94 - 99
Turbidity	62 - 100
COD	89 - 98
Total Nitrogen	67 - 72
Ammonia	65 - 89
Nitrate	44 - 81
Phosphate	93 - 100
Sulfate	94 - 100

* After Eckenfelder, 1980

L. Summary

Reverse osmosis is one of the most encouraging techniques for the removal of pesticides and heavy metals from water. Reverse osmosis is a process that separates solute from the solvent. Reverse osmosis removal of pesticides is dependent on the polarity of the solute molecule in solution. Sorption of pesticides onto the membrane appears to play a significant role in the overall removal efficiency. Within the same homologous series, reverse osmosis removal of heavy metals increased with size, branching, valency of metal ions, and degree of ionization.

METHODS AND MATERIALS

A. Overview of Experiments

The reverse osmosis unit used in this experiment was a field scale reverse osmosis unit provided by the U.S. Army Research Center, Fort Belvoir, Virginia. This system was designed to be a closed looped system (see Figure 3) so that disposal of contaminated water can be minimized. Groundwater from a private well in Blacksburg, Virginia was used as feedwater. Characteristics of this water are shown Table 11. A cooling bath was needed to reduce the temperature of the effluent from the reverse osmosis element. Temperature of water in a closed loop of this nature can rise significantly due to heat generated by the pressurizing pump. The cooling bath maintained the water temperature at approximately 70 °F.

B. Reagents

1. Pesticides

The following pesticide grade reagents were purchased from Baxter Scientific: hexane, acetone and methylene chloride. Iso-Octane, acetone, sodium hydroxide, sulfuric acid and chromerge were obtained from Fisher Scientific. The following pesticides were purchased from Chem Services: atrazine (99.7 %), heptachlor, and D,D,D (99.0 %). Methoxychlor (98 %), lindane (97 %), and 1,4 Dichlorobenzene (99+ %) were obtained from Aldrich Chemical Company, Inc.

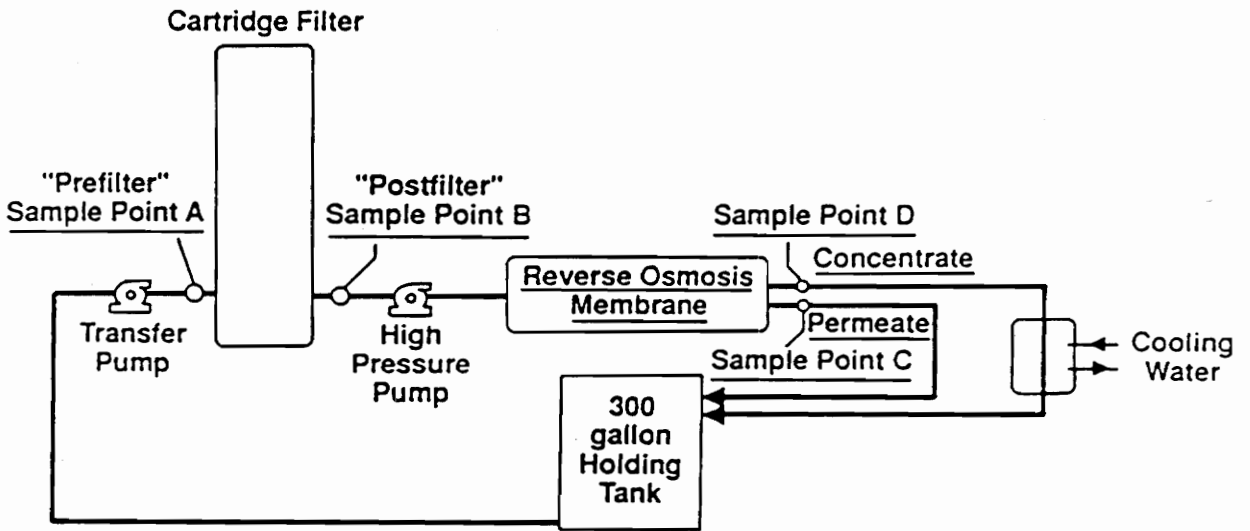


Figure 3. Schematic of the Reverse Osmosis Field Unit

Table 11

Well Water Characteristics

Heavy Metals

Arsenic	N.D.	LOD = 1 ug/l
Copper	1 ug/l	LOD = 1 ug/l
Magnesium	36.5 mg/l	
Nickel	1 ug/l	LOD = 1 ug/l
Lead	N.D.	LOD = 1 ug/l

Other Metals

Iron	0.03 mg/l	LOD = 0.03 mg/l
Manganese	0.01 mg/l	LOD = 0.01 mg/l
Calcium	75.5 mg/l	
Sodium	10.3 mg/l	
Potassium	2.4 mg/l	

Inorganic Ions

Fluoride	0.587 mg/l
Nitrate	14.858 mg/l
Sulfate	10.014 mg/l

Pesticides

All the pesticides investigated in this study were not detectable

N.D. = Non-Detectable LOD = Limit of Detection

Pesticide stock solutions were prepared with volumetric flasks, pipettes, and syringes. Iso-octane and acetone were used as solvents.

2. Heavy Metals

The following salts used in the experiment were purchased from Fisher Scientific: arsenic oxide (As_2O_3), copper sulfate (CuSO_4), lead sulfate (PbSO_4), magnesium nitrate (MgNO_3), and nickel nitrate (NiNO_3).

C. Field Operations

1. Description of Reverse Osmosis Unit

A schematic of the reverse osmosis unit is shown in Figure 3. The reverse osmosis unit used was equipped with a transfer pump, cartridge filter, high pressure pump, instrumentation panel, and a spiral wound poly(ether/urea) membrane. Table 12 illustrates the characteristics of the poly(ether/urea) membrane used in this investigation. The instrumentation panel shows permeate and concentrate flows, temperature, and the applied pressure. Below is a brief description on how the reverse osmosis system operates.

Pesticide and heavy metal stock solutions of desired concentrations were prepared and mixed with well water in a 300 - gallon holding tank. A transfer pump forced the feedwater mixture through the cartridge filter which protected the high pressure pump and the membrane from large particles. The high pressure pump provided the necessary pressure to force the feedwater across the

Table 12**Characteristics of the Poly(ether/urea) Membrane**

Manufacture : Universal Oil Products (UOP), Fluid Systems Division

Model Number : 1501

Membrane Material : Poly(ether/urea)

Membrane Configuration : Spiral wound thin film composite

Primary Use : Seawater membrane

Membrane Surface Area : 159 ft² nominal

Dimensions : 6 inch diameter x 40 inch length

Membrane Charge : Neutral surface

Output Rate : 2200 gpd (1.53 gpm)

Rejection Rate : 99.5 % Cl⁻

Test Conditions : 32,800 mg/l NaCl
800 psi
25 °C
pH = 5.7
7 % recovery

membrane and to overcome the osmotic pressure in the system. Figure 3 shows that there were two streams leaving the membrane vessel. The water that diffused through the membrane (permeate) leaves the vessel through the permeate tube at atmospheric pressure. The rejected water is emitted in the concentrate line under pressure. Both effluents returned, through the cooling bath, to the batch holding tank where they were remixed with the existing feedwater supply.

2. Sampling Strategy

Three different trials were conducted for both pesticides and heavy metals. They were:

<u>Pesticide</u>	<u>Heavy Metal</u>
Trial # 1 ---- Lindane only	Trial # 1 ---- Magnesium only
* Trial # 2 ---- Five pesticides	* Trial # 2 ---- Five Heavy Metals
* Trial # 3 ---- Lindane only	* Trial # 3 ---- Magnesium only
* same membrane	

Trials # 1 for both pesticide and heavy metal were single contaminant trials with new membranes. Trials # 2 were multicontaminant trials with five pesticides or heavy metals with a new membrane. Trials # 3 were also single contaminant trials with the same contaminant from Trials # 1 but using the same membrane as in Trials # 2. The time lapse between Trial # 2 and Trial # 3 was 24 hours.

The rationale for testing one contaminant using a new and used membrane was to determine whether the used membrane can performed as effectively as the new membrane. The logic behind doing multicontaminant trials was to find out whether the percent rejection in the mixed solutes solution is any different from the individual solute solution.

Samples were collected at sampling ports A, B, C, and D (A = prefilter, B = postfilter, C = concentrate, D = permeate). The first sample was collected after 15 minutes and the remaining of the samples were taken every 90 minutes for 12 consecutive hours. Thus, samples were taken at 15 minutes, 1.5 hours, 3 hours, etc. Duplicate samples were taken after three, six, nine, and twelve hours of operation.

3. Contaminants Tested

Tested contaminants and their respective initial concentrations are illustrated in Table 13 and 14.

Pesticides and heavy metals used in this investigation were chosen for the following reasons:

- (i) the U.S. Army is interested in their removal by reverse osmosis.
- (ii) they are environmentally significant.
- (iii) due to the sensitivity and accuracy of method of analysis.

Initial concentrations were set at two or three times the maximum contaminant level (MCL) or the maximum contaminant level goal (MCLG) as regulated by the Safe Drinking Water Act of 1986.

Figure 4 illustrates the molecular structures of the pesticides tested.

Table 13

Pesticides Tested Versus Initial Concentrations

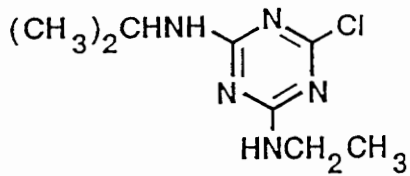
Pesticides tested	Starting conc. (mg/l)	MCLG (SDWA 1986) (mg/l)
Atrazine 99.7 %	0.05 - 0.15	0.003**
1,4 Dichloro- benzene 99+ %	0.01 - 0.10	0.075 (MCL)
Heptachlor (S.G.)	0.025 - 0.20	0.00
Lindane 97 %	0.02 - 0.20	0.0002
Methoxychlor 98 %	0.05 - 0.50	0.34

** 40 CFR (Federal Register)

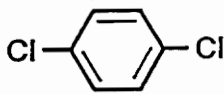
Table 14
Heavy Metals Tested Versus Initial Concentrations

Heavy Metal tested	Starting conc. (mg/l)	MCLG (mg/l)
Lead	0.05 - 0.25	0.02
Copper	2.0 - 5.0	1.3
Magnesium	150 - 500	---
Arsenic	0.2 - 1.0	0.05
Nickel	0.1 - 0.5	0.05**

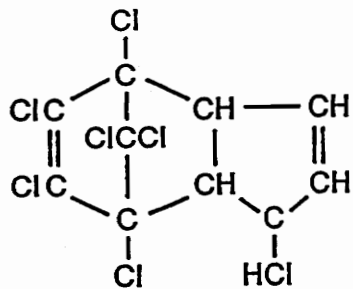
** European Standard



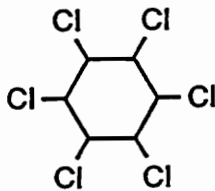
Atrazine



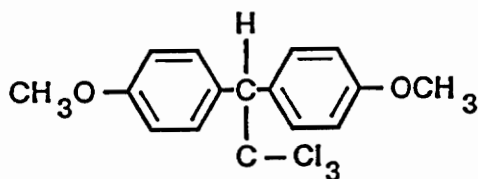
1,4 - Dichlorobenzene



Heptachlor



Lindane



Methoxychlor

Figure 4. Molecular Structure of Pesticides Tested

D. Methods of Analysis

1. Pesticides

Pesticide samples were collected in one liter amber glass bottles with screw caps lined with teflon. Samples collected were refrigerated at 4 °C if they were not analyzed immediately.

Clean glassware is essential to prevent cross-contamination of samples. Used glassware for pesticide analyzes was cleaned immediately in the following manner:

- 1) soaked in hot detergent water for 20 minutes
- 2) rinsed with tap water
- 3) rinsed with distilled water
- 4) rinsed thoroughly with pesticide-grade acetone

New glassware was first soaked in a chromic acid bath made from chromerge and sulfuric acid for 24 hours followed by the cleaning steps shown above. Clean glassware was stored in dust-free cabinets.

EPA Method 608 was used for pesticide analysis. This method is appropriate for the determination of chlorinated pesticides. A brief description of EPA Method 608 follows:

i. Extraction with Separatory Funnel

Since the concentration of the pesticides in the sample was too low for direct detection, it was necessary to extract the desired pesticides from the groundwater using liquid-liquid extraction. Each sample volume of 1000 mL was determined by using a graduated cylinder. The sample was then transferred into a 2 - liter separatory funnel, and the appropriate internal standard (D,D,D) was added. One mL of 0.1 mg/l internal standard was added to the prefilter, postfilter, and concentrate samples whereas 1 mL of a 0.001 mg/l internal standard was added to the permeate. Sixty mL of methylene chloride was divided equally to rinse the sample bottle and the graduated cylinder. This volume was then added to the separatory funnel and shaken thoroughly for two minutes. The mixed solvent was allowed to separate from the water phase by sitting the funnel for approximately ten minutes. Finally, the methylene chloride extract was collected in a 250 - mL sample bottle. The above procedure was performed three times after which the methylene chloride extract was collected for concentration using a Kuderna-Danish evaporator.

ii. Concentration by Kuderna-Danish (KD)

Before starting the KD concentration, the methylene chloride extract was passed through an anhydrous sodium sulfate column to remove any water that might be present in the extract. The 250 - mL sample bottle was rinsed with 20 mL of methylene chloride to ensure complete quantitative transfer. Another 5 mL of methylene chloride was poured through the sodium sulfate to rinse down any pesticides adhering to the drying column. Boiling chips were added to the

methylene chloride extract prior to KD concentration. The methylene chloride extract was concentrated down in the KD apparatus which was partially submerged in a hot water bath (60-65 C). When the volume of the methylene chloride reached approximately 15 mL, the KD apparatus was removed from the hot water bath and allowed to drain and cool for ten minutes. The temperature of the bath was increased to 90 - 95 °C and 50 mL of hexane and a new boiling chip was added to the KD apparatus. When adding hexane, the wall of the evaporative flask was flushed with hexane to ensure that no pesticides adhered to it. Aluminum foil was used to insulate the evaporative flask. This was necessary to keep the flask sufficiently hot so that evaporation of hexane could be achieved in a reasonable amount of time. When the volume reached two mL, the KD apparatus was removed from the hot bath and once again allowed to drain and cool for ten minutes. Two to three mL of hexane were then used to rinse the evaporative flask and its lower joint. The concentrated extract in the concentrator tube was next transferred to a 12 - mL vial with a Pasteur pipette. After proper labeling, the vial was then allowed to air evaporate until a final volume of 1 mL was attained. The vial was then be refrigerated at 4 °C until gas chromatographic analysis.

iii. Response Factor

Response factors enabled the calculation of the quantity of pesticide present. Three different concentration levels of a mixture of the five pesticides to the internal standard, D,D,D, were prepared. They were 0.1:1, 1:1, and 9:1, in which the amount of internal standard was kept constant and the amount of

analyte varied. Each dilution was injected six times. Response were calculated using the following equation:

$$\text{Response Factor} = (A_s \times C_{is}) / (A_{is} \times C_s) \quad [2]$$

where

A_s = peak area of the compound of interest

A_{is} = peak area of internal standard

C_{is} = concentration of internal standard

C_s = concentration of the compound of interest

The response factor for each compound for each injection was calculated. A simple linear regression was performed on all the response factors obtained for each individual pesticides as a function of relative amounts of analyte and internal standard. The results attained were:

$$\text{Lindane} \quad \text{RF} = 0.042 \times (A_s/A_{is}) + 2.15 \quad [3]$$

$$\text{Heptachlor} \quad \text{RF} = -0.04 \times (A_s/A_{is}) + 2.109 \quad [4]$$

$$\text{Methoxychlor} \quad \text{RF} = -0.013 \times (A_s/A_{is}) + 0.521 \quad [5]$$

$$\text{Atrazine} \quad \text{RF} = -0.112 \times (A_s/A_{is}) + 0.035 \quad [6]$$

$$\text{1,4-Dichlorobenzene} \quad \text{RF} = -0.092 \times (A_s/A_{is}) + 0.04 \quad [7]$$

where RF = Response Factor

The response factor calculated was used to quantify the actual concentration of pesticide in each sample using the formula:

$$\text{Conc pesticide} = \frac{\text{RR} * \text{conc. of internal standard added to each sample prior to injection}}{\text{RF}} \quad [8]$$

RR = (Peak area of the compound of interest)/(peak area of internal standard)

iv. Gas Chromatography (GC) Analysis

The pesticide extracts were analyzed using a Hewlett-Packard 5890 Gas Chromatograph equipped with a capillary column and a electron capture detector (ECD). Excellent peak separation was obtained using the following GC double ramped temperature program. The injector temperature was set at 200 °C and the ECD was maintained at 310 °C while the helium flow rate was set at 24 cm/sec. The temperature program was as follows: 180 °C hold for 6 minutes, ramp # 1 - 3 °C/minute to 220 °C, hold 2 minutes, ramp # 2 - 12 °C/minute to 300 °C, hold six minutes for a total trial time of 34 minutes. The program was trial with a split injection of 20:1.

Several different concentrations of pesticides were injected to determine the detection limit of the GC. The concentration that gave the smallest measurable amount was taken as the detection limit. The results obtained were:

Atrazine	0.001 ng/ul
1,4 Dichlorobenzene	0.0001 ng/ul
Lindane	0.00001 ng/ul
Heptachlor	0.00001 ng/ul
Methoxychlor	0.00001 ng/ul

v. Post Chlorination

The permeate for all the pesticide trials was chlorinated with a dose of 5 mg/l of free chlorine at a contact time of 30 minutes to determine the presence of trihalomethane precursors. The chlorinated samples were analyzed using EPA method 502.1 which utilizes Purge and Trap of 5 - mL sample of water, followed by GC/FID. A packed column was employed with helium as the carrier gas. Below are some of the chromatographic conditions for the GC:

Initial Temperature	=	100 °C
Final Temperature	=	220 °C
Program Rate	=	10 °C/min
Initial Hold	=	0 min
Final Hold	=	2 min
Detector Temperature	=	225 °C

vi. Sorption Experiment

To confirm the sorption of pesticides onto the reverse osmosis membrane, a simple sorption experiment was conducted. Approximately 20 grams of new membrane was soaked in 500 mL of Milli-Q water containing all the five pesticides. Five different sets were prepared. The membranes were soaked for 0, 2, 11, 36, and 73 hour. Quantitative analyses of pesticides were performed using solid-phase extraction (Baker Chemicals EPA approved method) and GC-MS. Hewlett Packard 5890 Gas Chromatograph connected to a Hewlett Packard 5970 Mass Spectrometer was used. A DB-5 capillary column was used in the gas chromatograph. Helium was the carrier gas with a flowrate of 33 cm/second.

The temperature program used 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, and ramp 12 °C/minute to 320 °C. Peak areas were used to determine the loss of pesticides.

Heavy Metals

i. Analytical Procedure

The 100 - mL plastic bottles used for sample collection were first soaked in a 10 percent nitric acid bath for four hours. They were then rinsed with tap water followed by distilled water. Magnesium and the heavy metal samples were collected in 100 - mL plastic bottles and refrigerated if they were not being analyzed immediately. Samples collected were first treated with nitric acid to reduce interference by organic matter before refrigeration (Standard Method, 1989).

Two instruments were used for heavy metal analysis. They were the Perkin Elmer Zeeman 5100 PC graphite furnace and the Perkin Elmer 703 flame atomic absorption spectrophotometer. All arsenic and lead samples were analyzed using the graphite furnace. All magnesium samples were analyzed using the flame atomic absorption spectrophotometer. For nickel and copper, the graphite furnace was used for trace samples (permeate), whereas the flame method was used to analyze samples of higher concentration (prefilter, postfilter and concentrate).

For quality control (Q.C.), EPA water supply Q.C. samples WS 378 - concentration 5 were used for arsenic and lead to confirm recovery. No water

supply Q.C. samples were available for nickel, copper and magnesium. Therefore, known concentration of the three heavy metals were prepared and analyzed for recovery. Operating conditions for the graphite furnace were set according to the recommended conditions: standard temperature platform format (STPF)/Zeeman (refer to Perkin Elmer 1). On the other hand, operating conditions for the atomic absorption spectrophotometer were set according to the standard conditions in the Perkin Elmer Manual (Perkin Elmer 2).

ii. Detection Limit

The detection limits of the graphite furnace are as follow:

Arsenic	1 ug/l
Lead	1 ug/l
Copper	1 ug/l
Nickel	1 ug/l

The detection limits for the atomic adsorption spectrophotometer are:

Nickel	0.04 mg/l
Magnesium	0.001 mg/l
Copper	0.02 mg/l

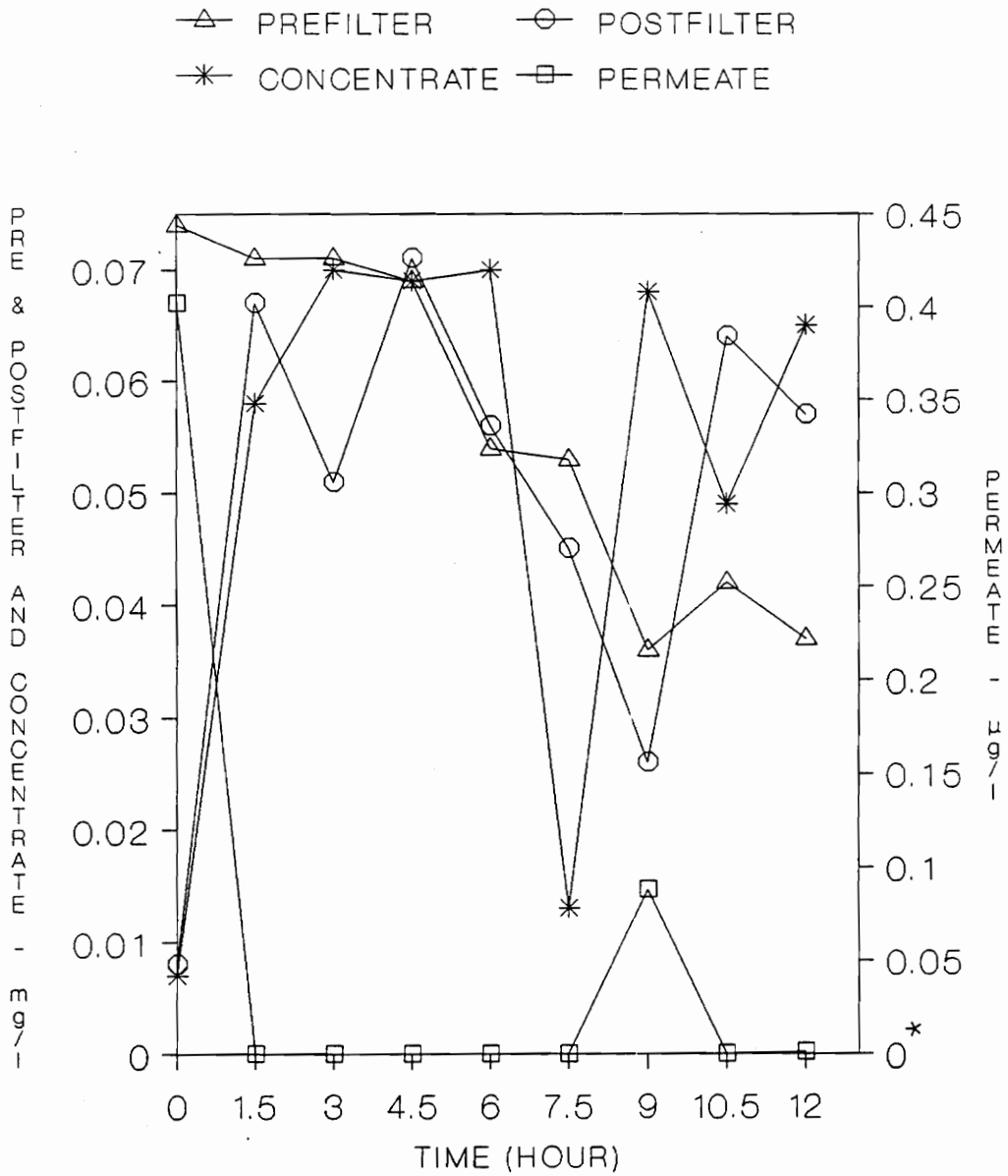
RESULTS

In this section, data for each pesticide and heavy metal are presented graphically to illustrate the removal efficiencies for each contaminant with respect to time. Tables are also constructed to show the percent removal of each contaminant during the three trials.

A. Pesticides Results

Figure 5 illustrates the single contaminant trial with lindane utilizing a new membrane. A continuous but rather erratic decrease in the prefilter, postfilter, and concentrate concentrations with time was observed. The concentration of the permeate reached a concentration that was below the detection limit after two hours.

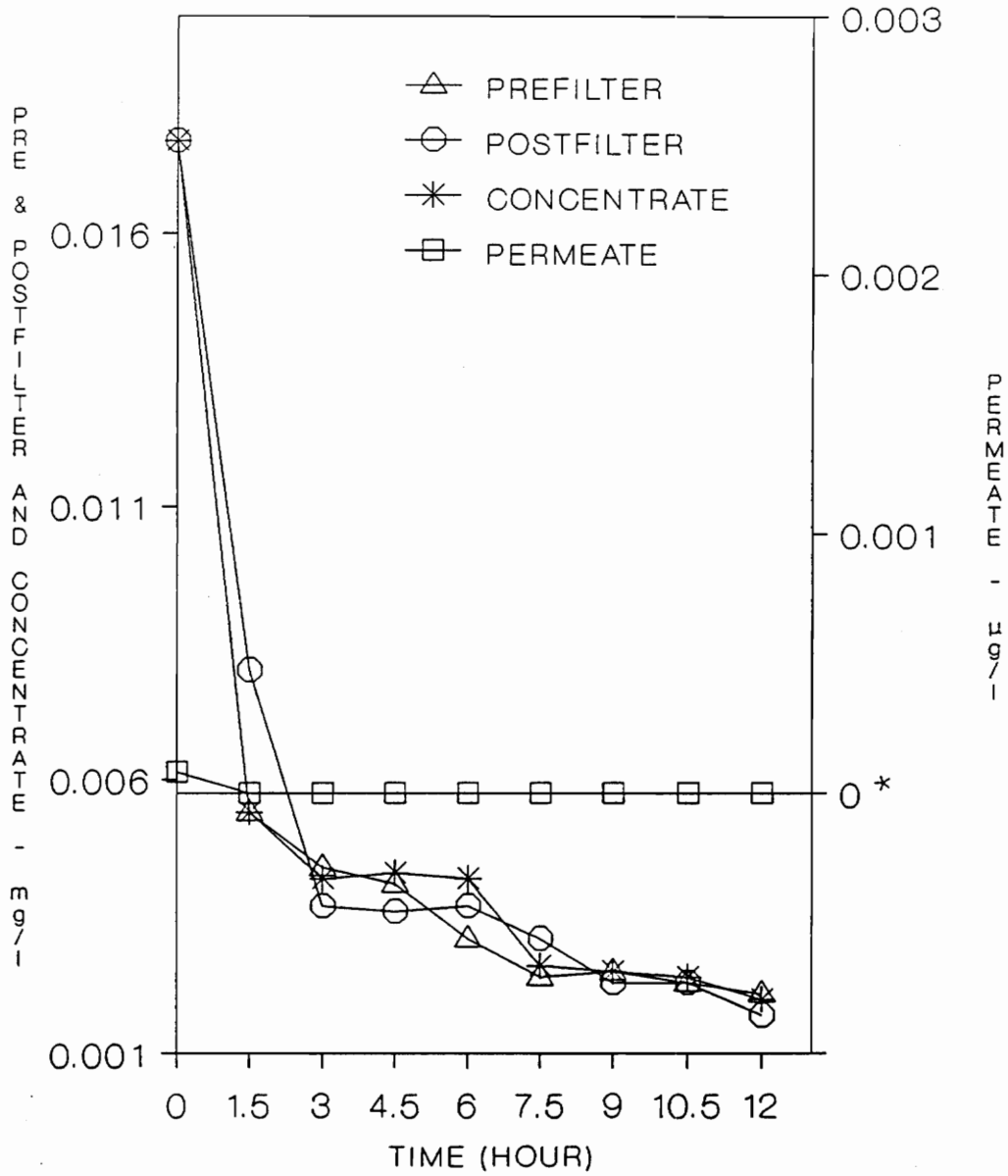
Figures 6 - 10 depict removal efficiency data for the multicontaminant (mixed-solute) trial in which heptachlor, methoxychlor, 1,4 - dichlorobenzene, atrazine, and lindane were evaluated. In general, concentrations of the prefilter, postfilter, and concentrate decreased with time except for atrazine. Figure 9 shows that the concentrations for the prefilter, postfilter, and concentrate for atrazine actually increased with time. Concentrations of the permeate for all pesticides were essentially below the detection limit except for methoxychlor and lindane. Very inconsistent permeate concentrations were observed for the methoxychlor plot (Figure 7). For Figure 7 concentration of methoxychlor at time zero was 0.5 ug/l and went up to 2 ug/l by the fourth hour and then



MCLG = 0.0002 mg/l (SDWA, 1986)

* Below detection limit

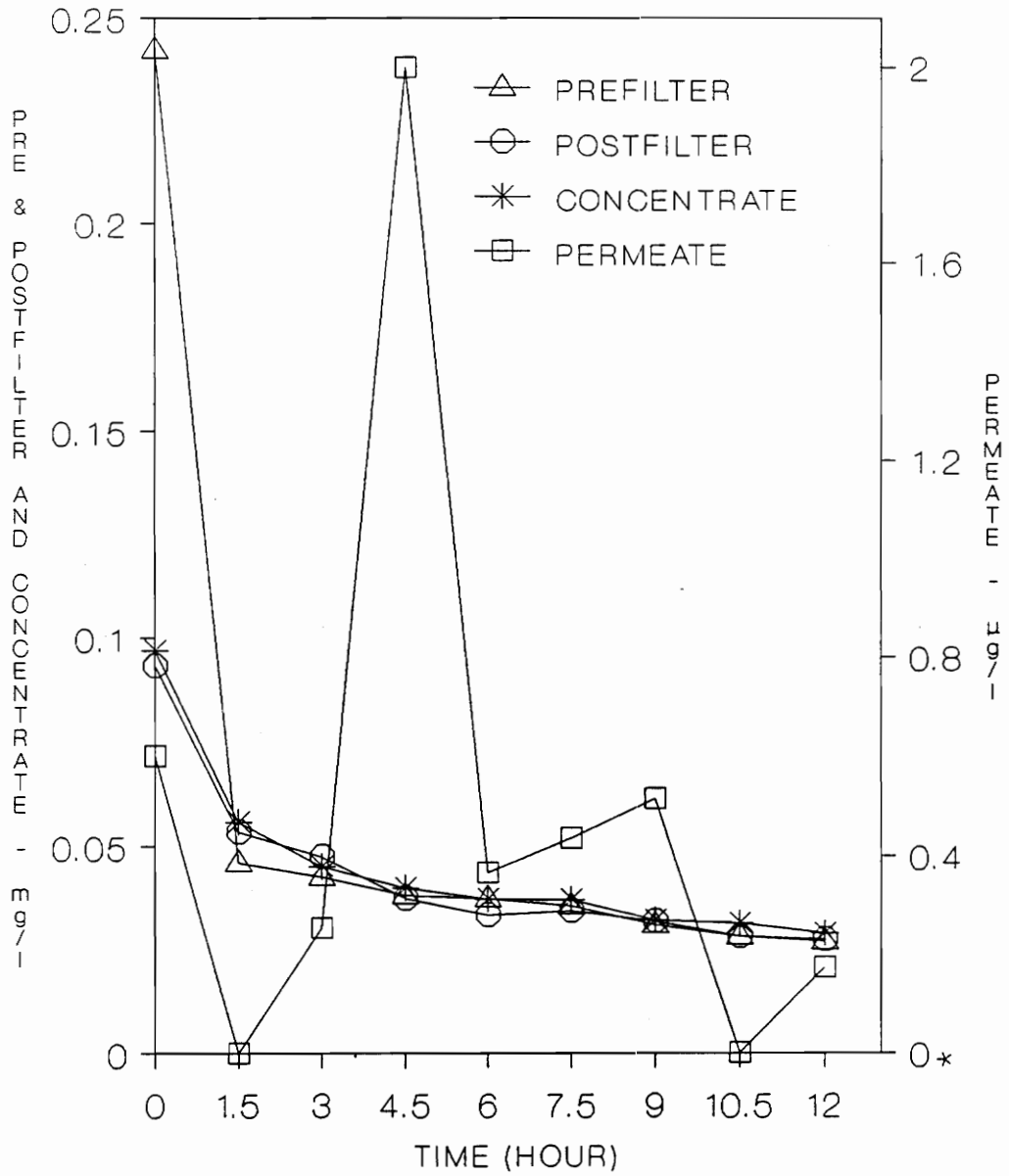
Figure 5. Removal of Lindane for a Single Contaminant Trial with a New Membrane



MCLG = 0.00 mg/l (SDWA, 1986)

* Below detection limit

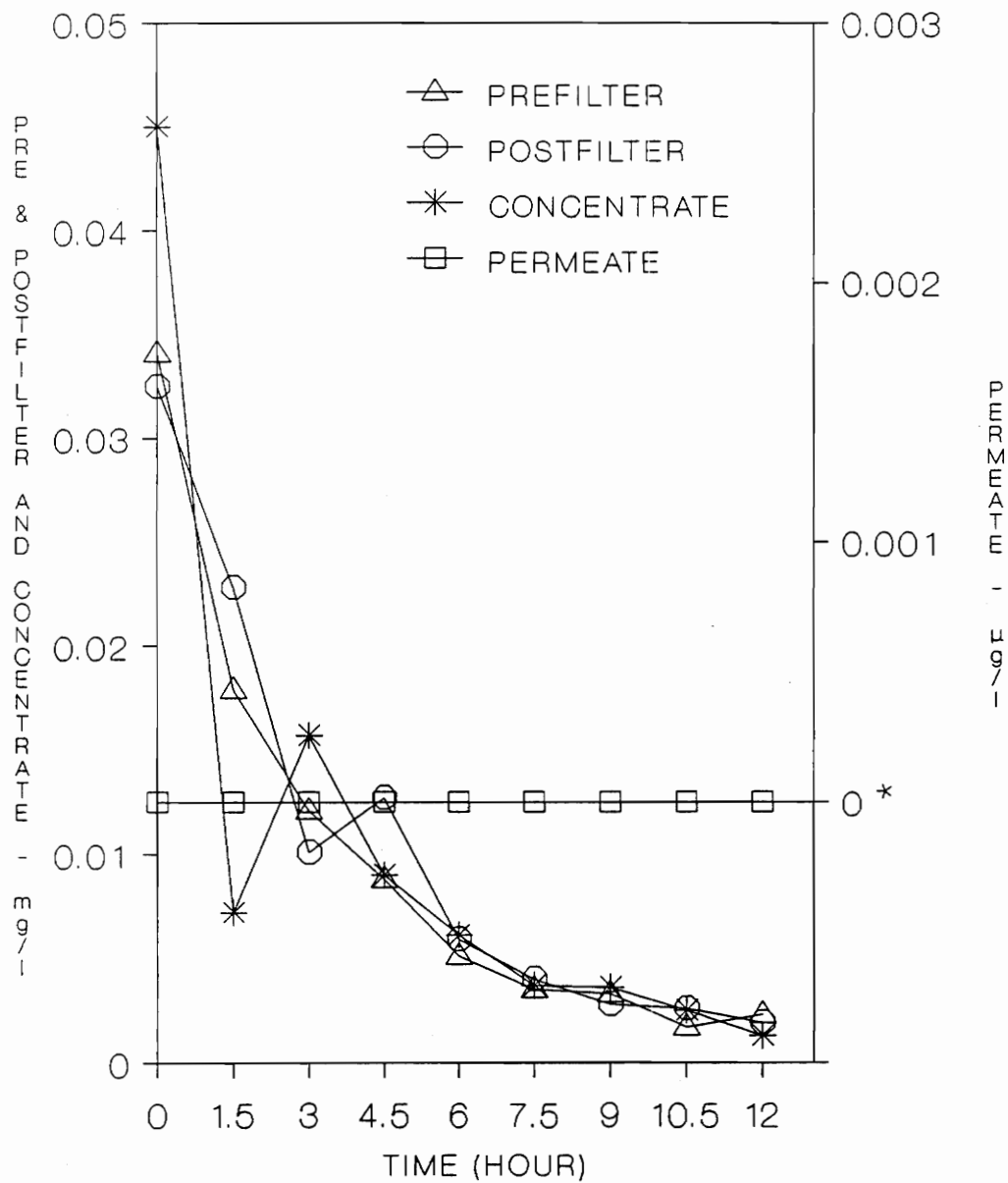
Figure 6. Removal of Heptachlor for a Multicontaminant Trial with a New Membrane



MCLG = 0.34 mg/l (SDWA, 1986)

* Below detection limit

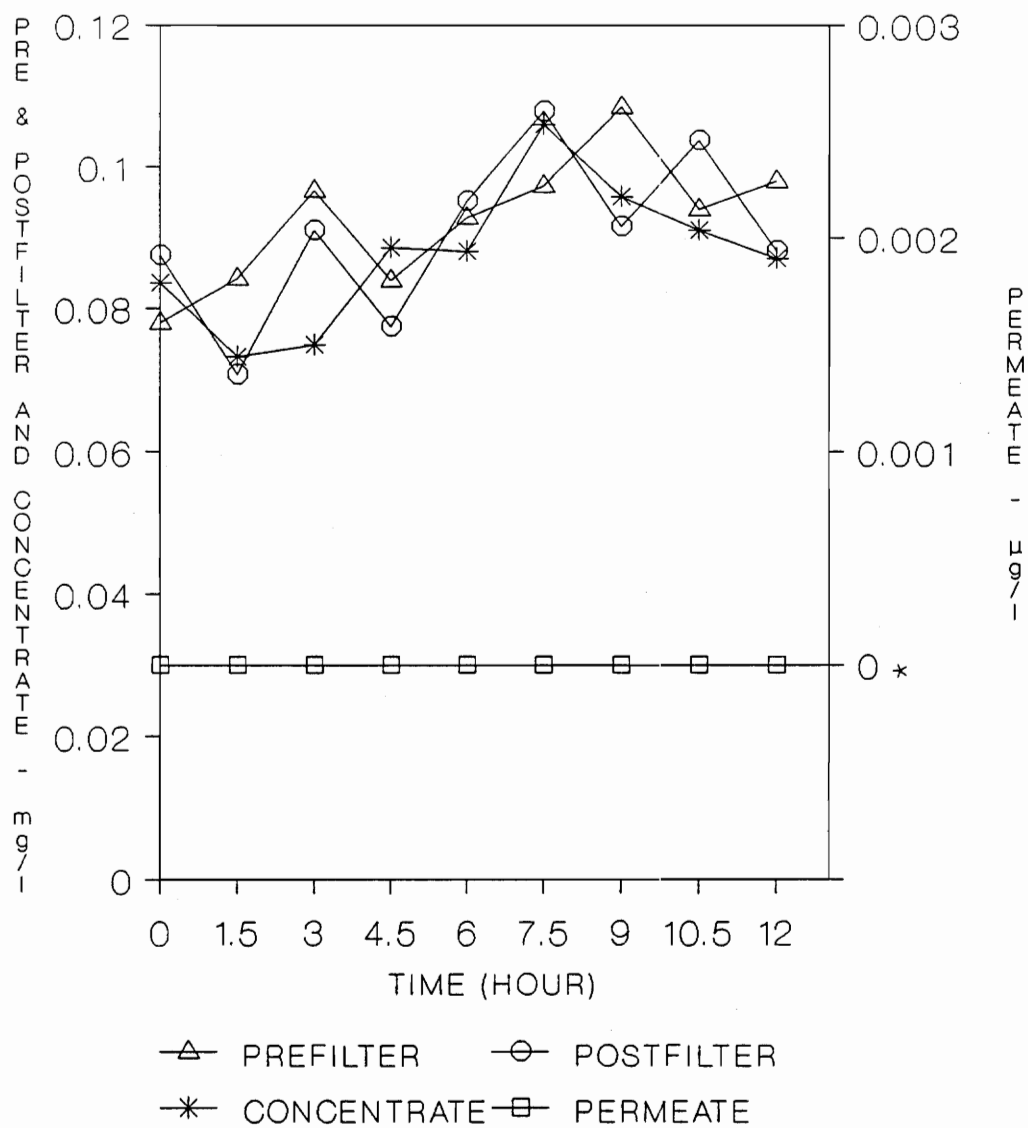
Figure 7. Removal of Methoxychlor for a Multicontaminant Trial with a New Membrane



MCL = 0.075 mg/l (SDWA, 1986)

* Below detection limit

Figure 8. Removal of 1,4 Dichlorobenzene for a Multicontaminant Trial with a New Membrane



MCLG = 0.003 mg/l (40 CFR)

* Below detection limit

Figure 9. Removal of Atrazine for a Multicontaminant Trial with a New Membrane

decreased irregularly. The permeate for the lindane trial declined rather steadily as time increased (Figure 10).

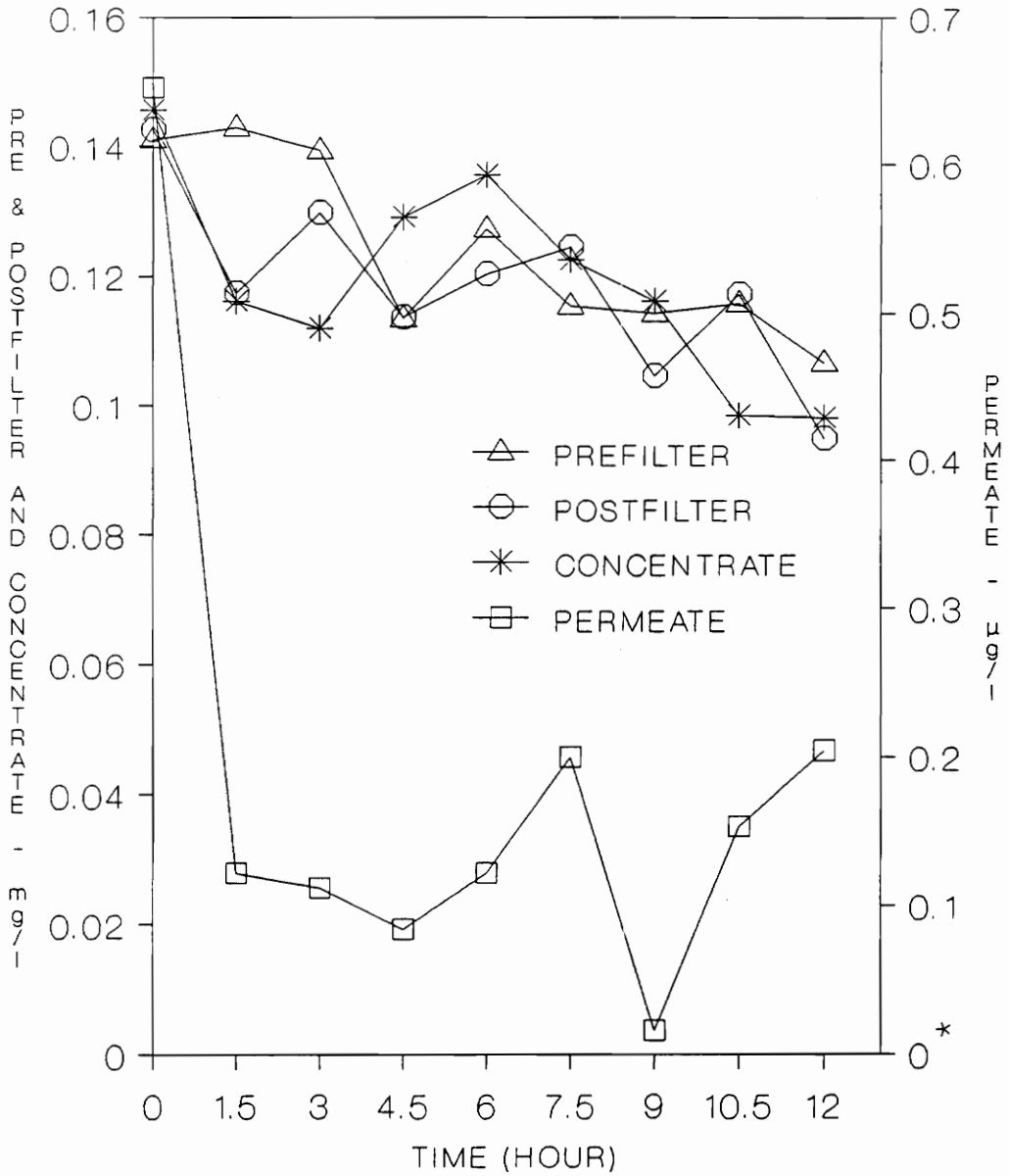
Very erratic concentrations were again observed for the prefilter, postfilter, concentrate and permeate for the lindane trial using a used membrane (Figure 11).

Figure 12 illustrates the permeate concentration over time from the three different trials. The single contaminant trial using the used membrane appeared to have the highest permeate concentration followed by the multicontaminant trial and then the single contaminant trial that utilized a new membrane. In each of these trials, initial concentrations were approximately identical.

Figure 13 shows the plot of temperature versus permeate flow during the multicontaminant trial. The plot clearly illustrates that permeate flow increased as the feedwater temperature rose.

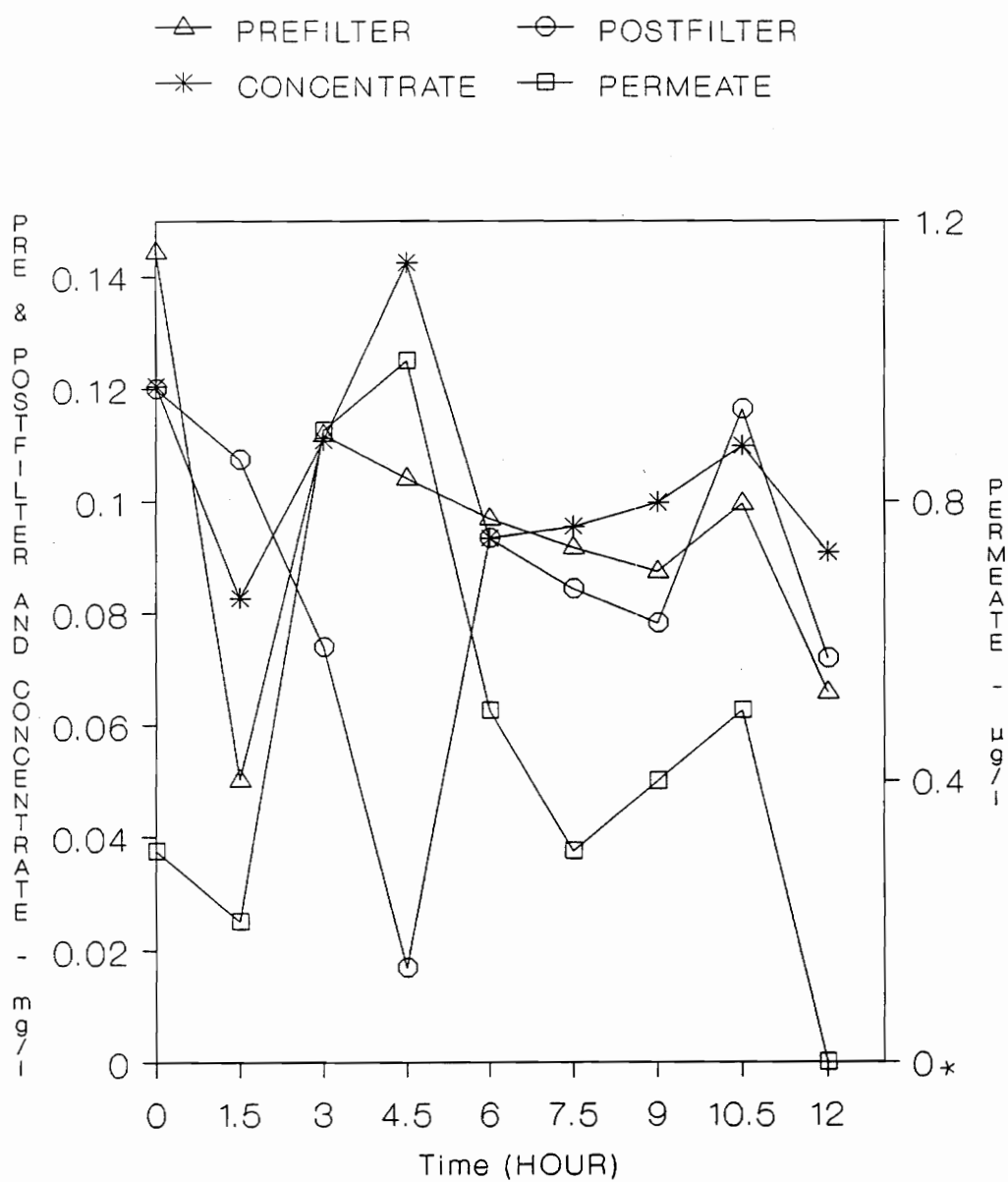
Figure 14 illustrates the result of the sorption experiment performed on the pesticides. Only three of the five pesticides were recovered. The percentage of mass remaining over the 73 hours experimentation time is presented.

Chromatograms for all five pesticides tested are shown in Appendix C. Due to significant difference in concentration, permeate samples had to be analyzed separately from the prefilter, postfilter, and concentrate samples. Appendix C (i) shows the chromatogram for the prefilter, postfilter and concentrate samples while Appendix C (ii) illustrates the chromatogram for the permeate samples. Both chromatograms show that excellent peak separation was achieved.



MCLG = 0.0002 mg/l (SDWA 1986)
 * Below detection limit

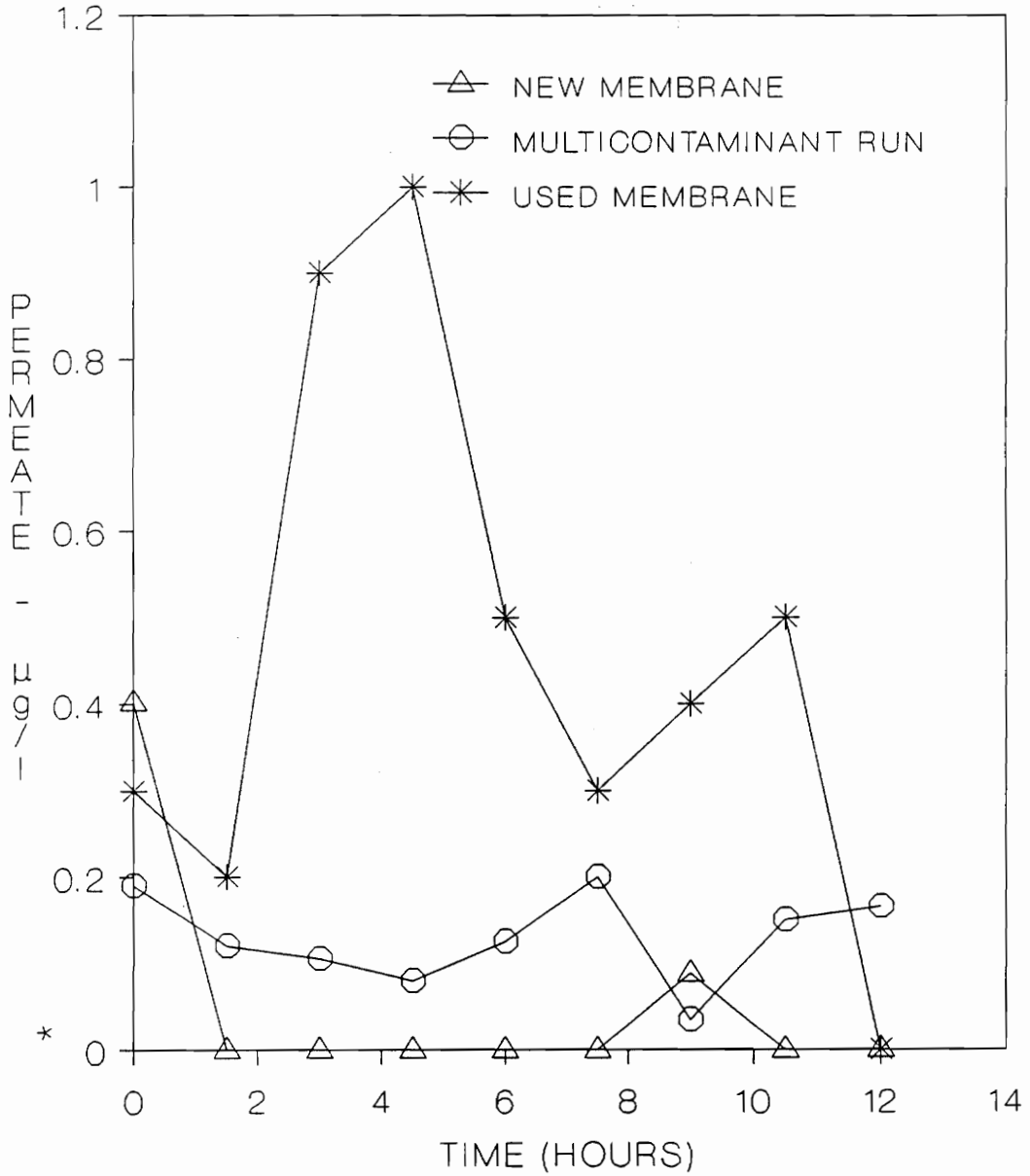
Figure 10. Removal of Lindane for a Multicontaminant Trial with a New Membrane



MCLG = 0.0002 mg/l (SDWA, 1986)

* Below detection limit

Figure 11. Removal of Lindane for a Single Contaminant Trial with a Used Membrane



MCLG = 0.0002 MG/L (SDWA 1986)

* Below detection limit

Figure 12. Comparison of the Permeate Concentrations of Lindane for All Three Trials

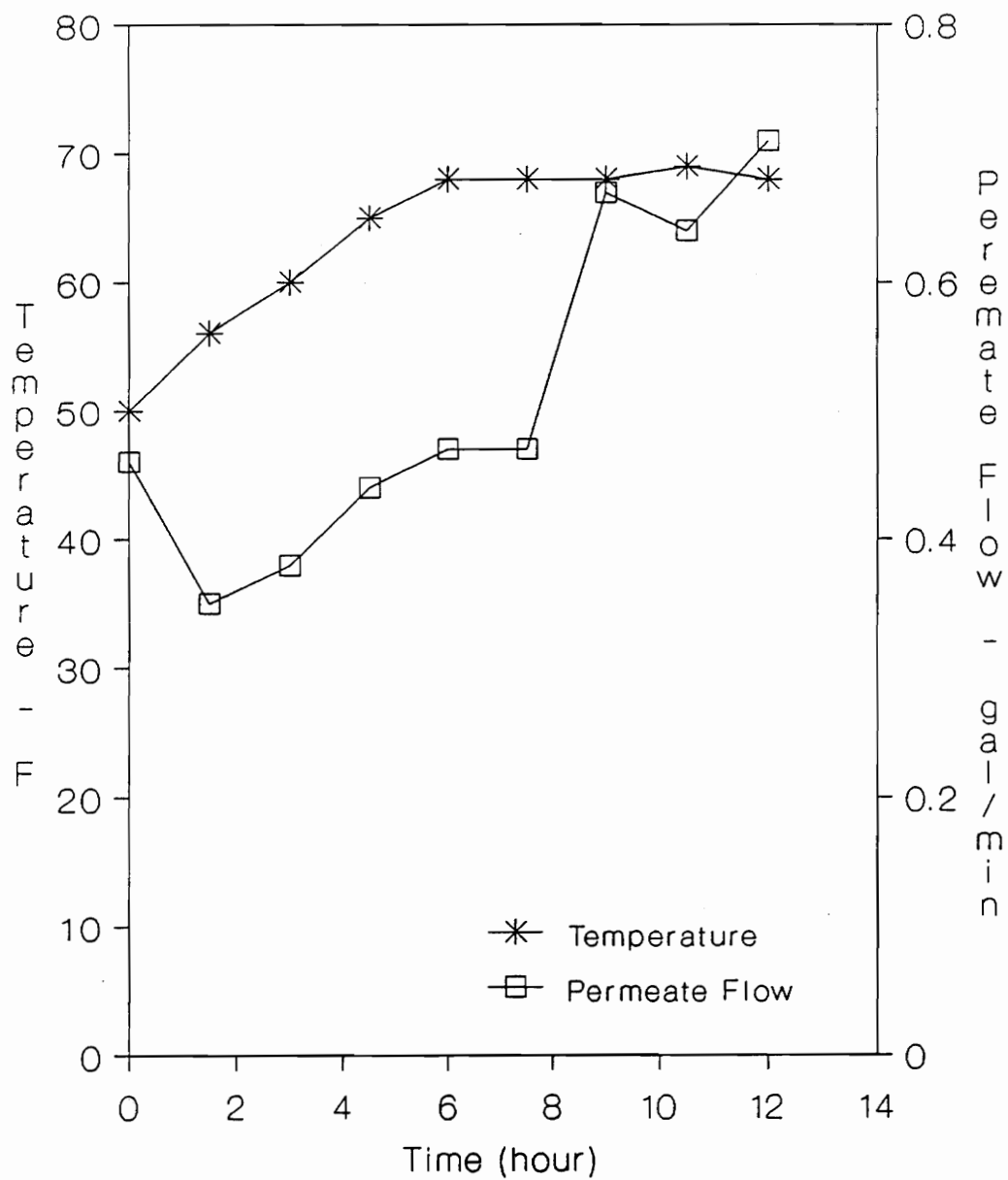


Figure 13. Comparison of Temperature and Permeate Flow During the Multicontaminant Trial

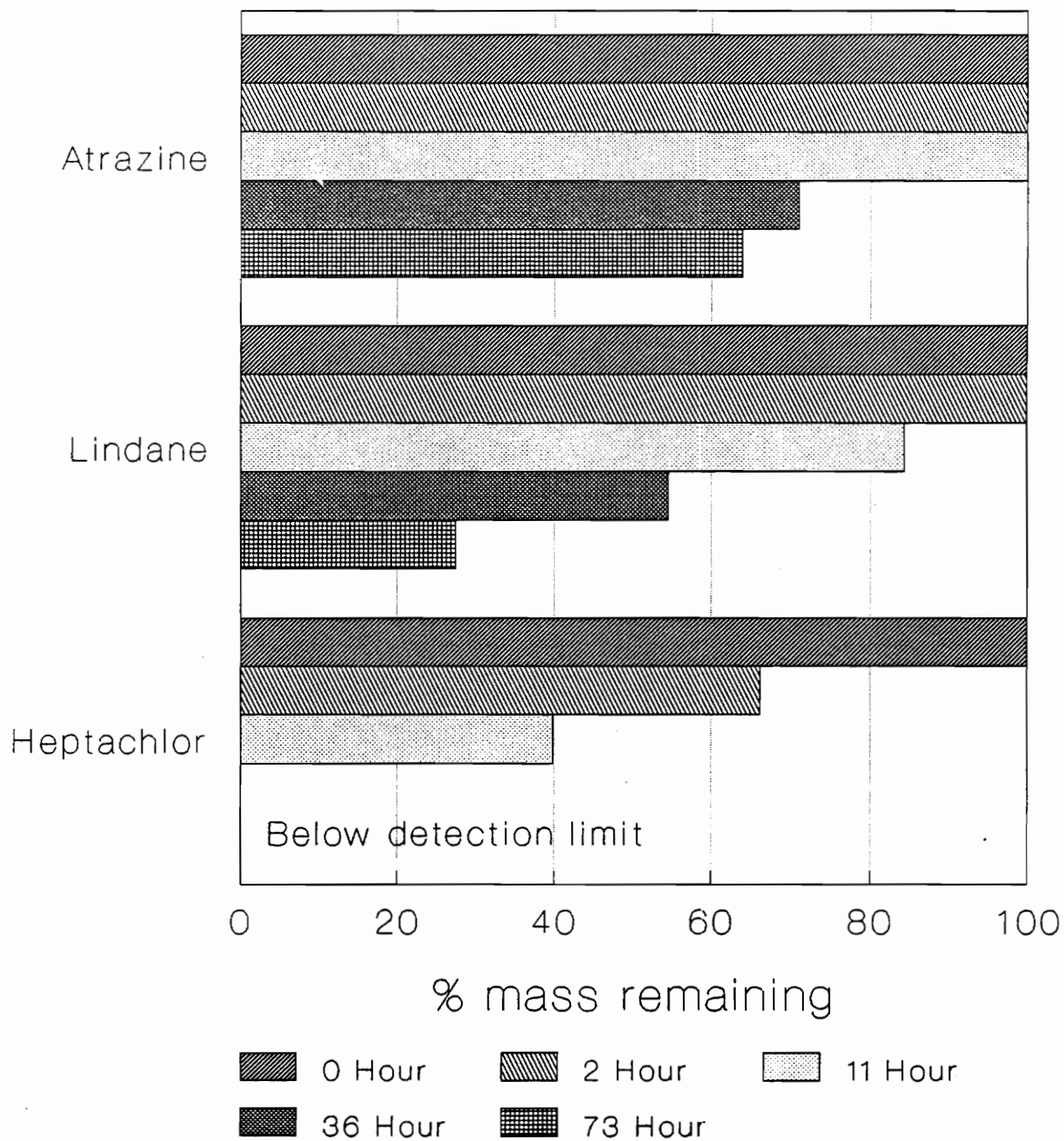


Figure 14. Percent Mass Remaining After Exposure to Membrane for the Contact Time Stated

B. Heavy Metals Results

Figure 15 represents the removal efficiency data for the magnesium single contaminant trial employing a new membrane. Concentrations of the prefilter, postfilter, and concentrate decreased and then rose slightly but continuously after the second hour. The permeate concentration decreased steadily from 2.4 mg/l to 1.2 mg/l.

Figures 16 - 20 illustrate the results of the multicontaminant trial with arsenic, copper, lead, nickel and magnesium in the feedwater. The prefilter, postfilter and concentrate concentrations remained fairly constant with time for all metals except copper and lead. As time progressed, the concentrations of the prefilter, postfilter, and concentrate for both of these heavy metals decreased as time progressed. All permeate concentrations decreased with time except for lead where the permeate concentrations were below the detection limit. Concentrations of the concentrate in all cases were higher than the prefilter and postfilter except for lead. In the lead trial, postfilter concentrations were much higher than the concentrate.

Figure 21 depicts the single contaminant trial with magnesium for a used membrane. Again, the concentrations of the prefilter, postfilter, and concentrate stayed remained very constant with the concentrate concentrations being the highest throughout the trial. The concentration of the permeate gradually decreased with time.

Figure 22 portrays the permeate concentrations for the three different trials of magnesium. It is very clear from the graph that the trial using the new membrane has the highest permeate concentrations. The trial with the used

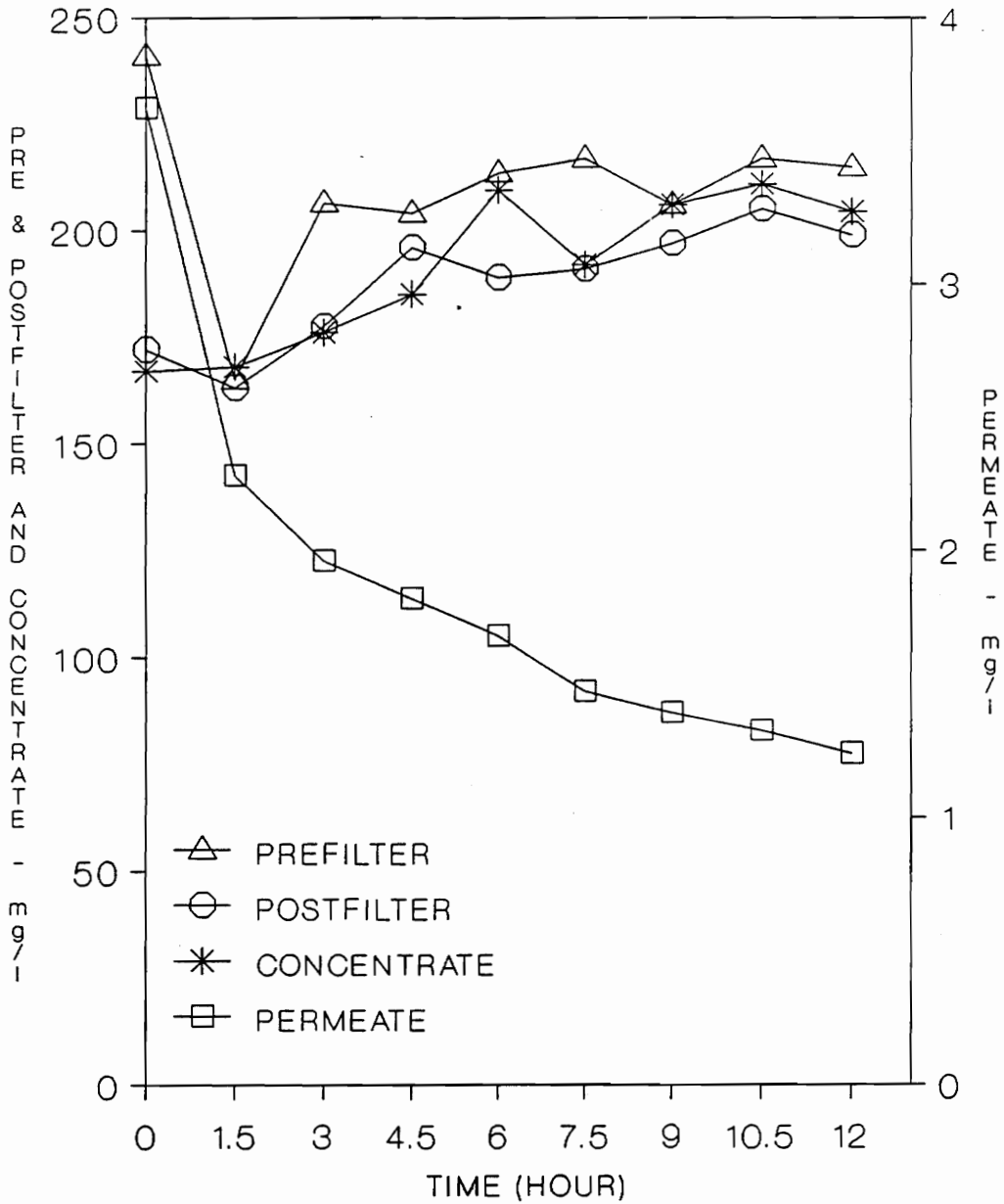
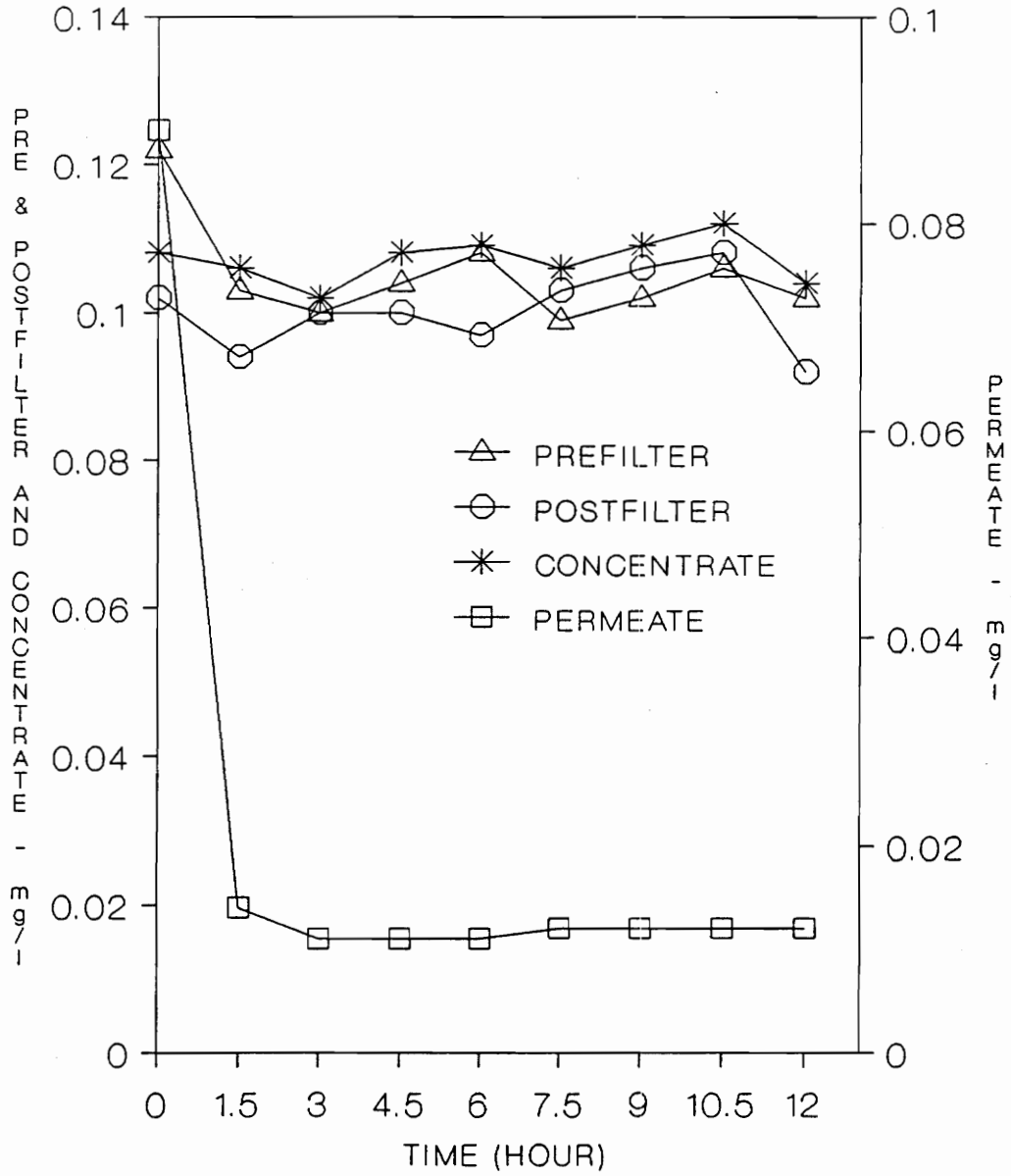
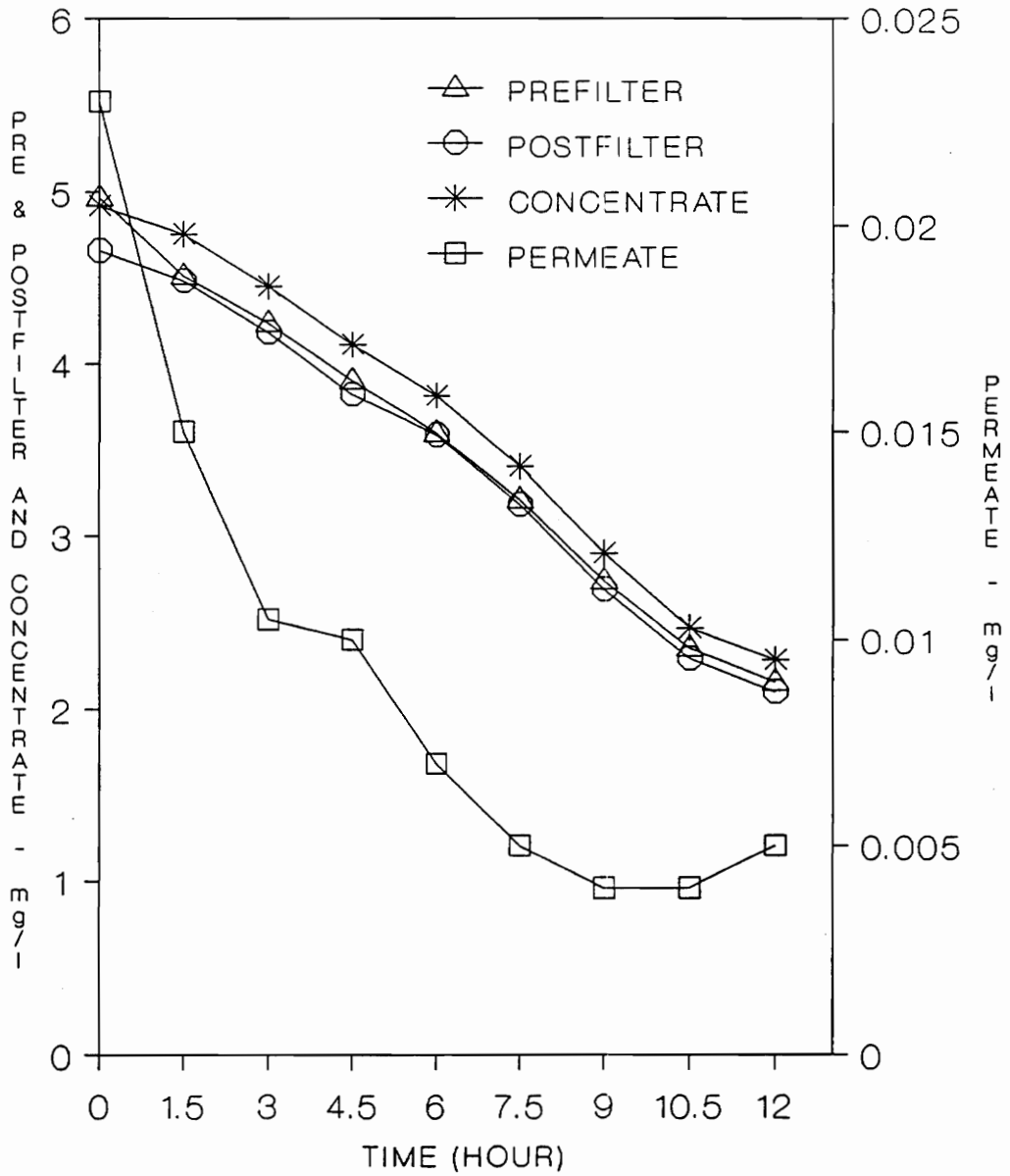


Figure 15. Removal of Magnesium for a Single Contaminant Trial with a New Membrane



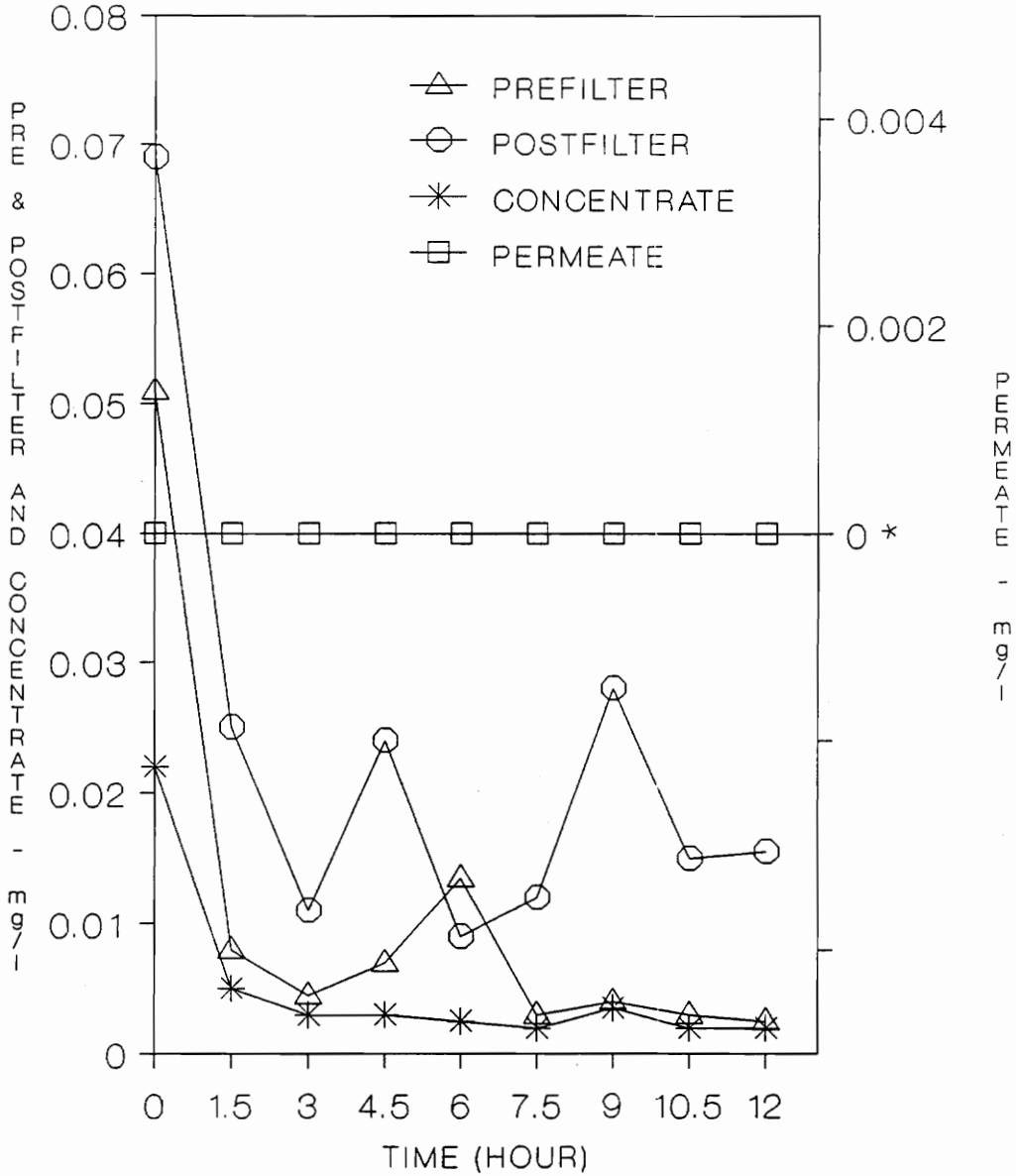
MCLG = 0.05 mg/l
(SDWA, 1986)

Figure 16. Removal of Arsenic for a Multicontaminant Trial with a New Membrane



MCLG = 1.3 mg/l
(SDWA, 1986)

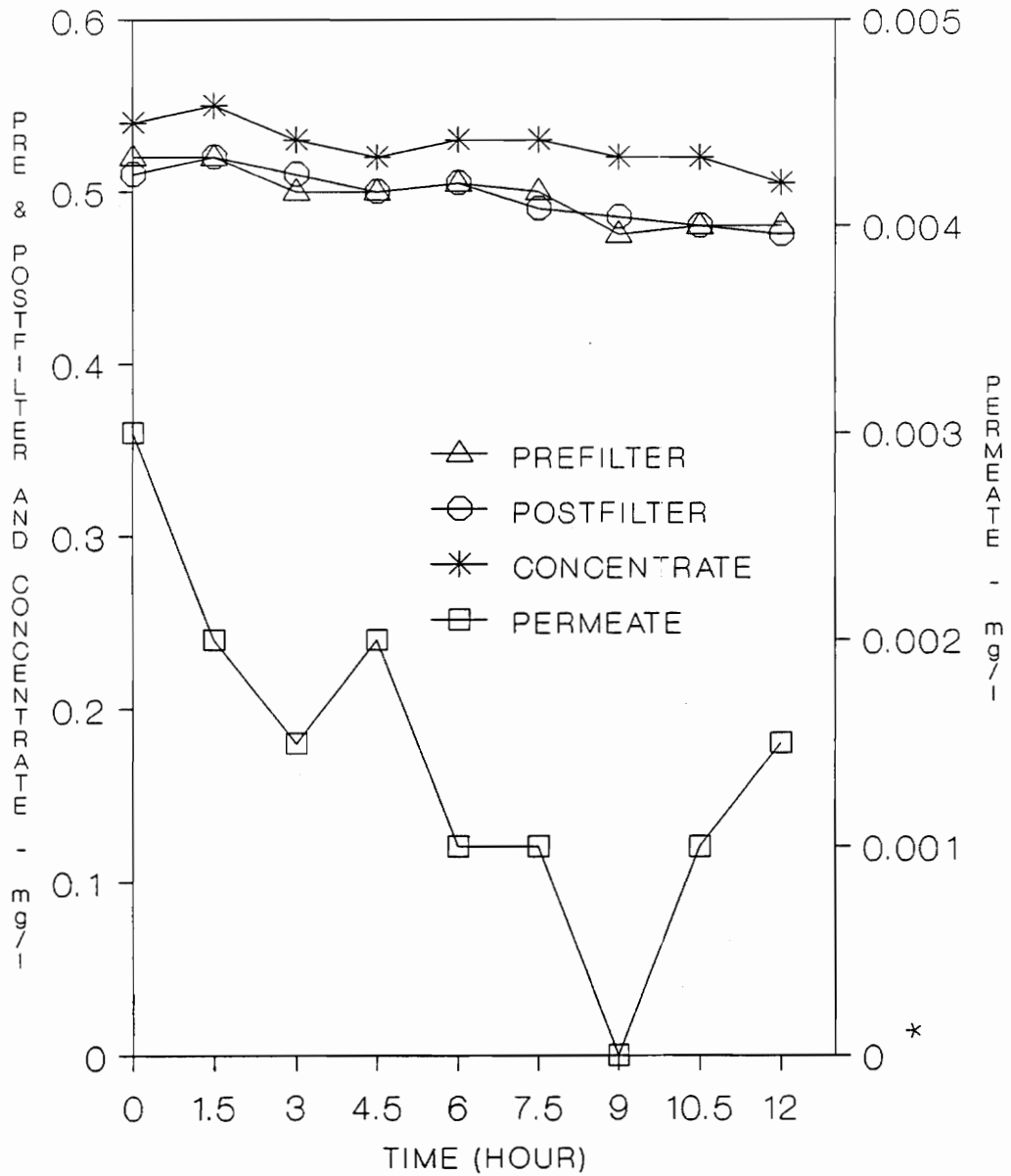
Figure 17. Removal of Copper for a Multicontaminant Trial with a New Membrane



MCLG = 0.02 mg/l (SDWA, 1986)

* Below detection limit

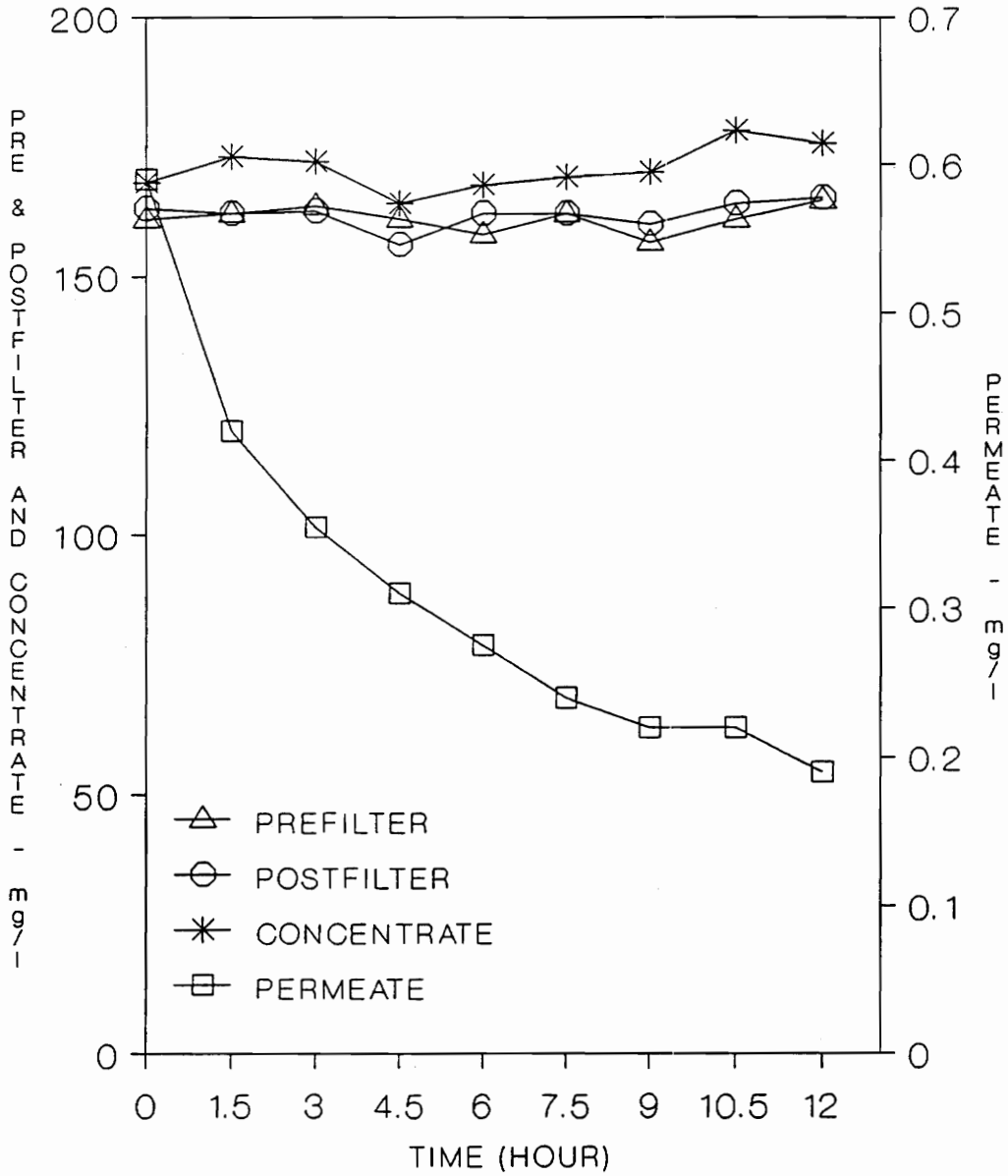
Figure 18. Removal of Lead for a Multicontaminant Trial with a New Membrane



MCL = 0.05 mg/l (European Standard)

* Below detection limit

Figure 19. Removal of Nickel for a Multicontaminant Trial with a New Membrane



MCL = 50 mg/l
(EEC DRINKING WATER STD)

Figure 20. Removal of Magnesium for a Multicontaminant Trial with a New Membrane

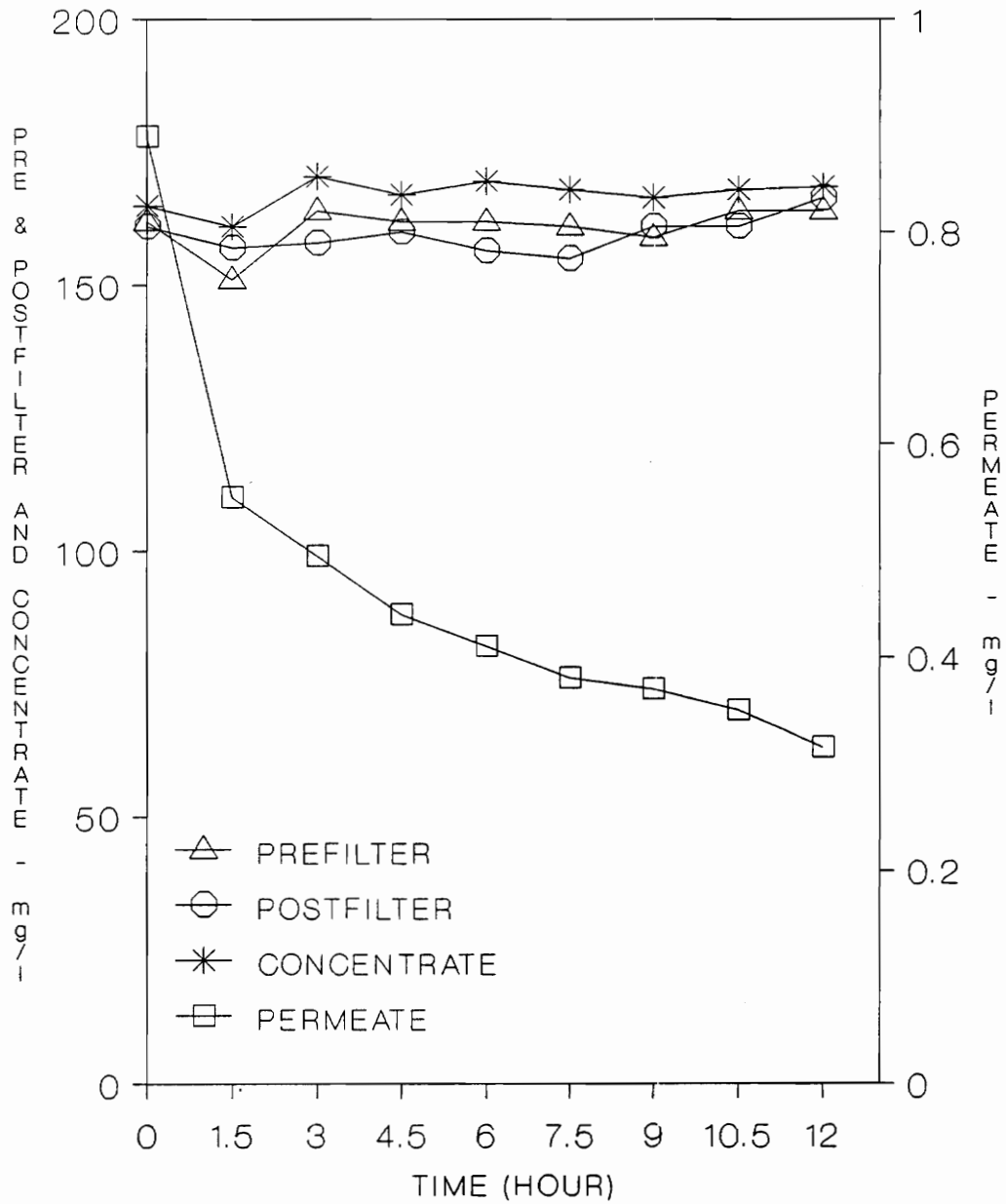


Figure 21. Removal of Magnesium for a Single Contaminant Trial with a Used Membrane

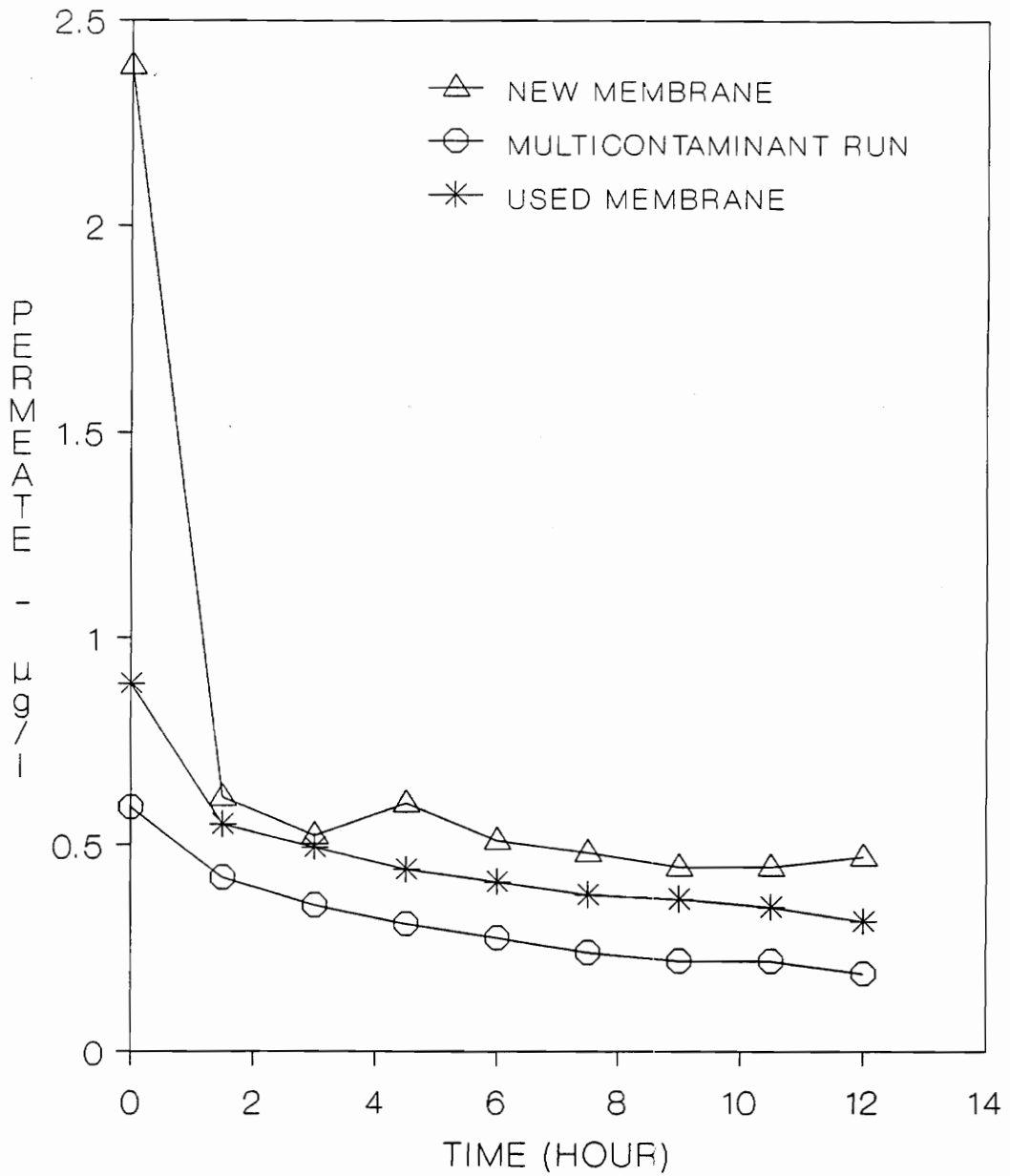


Figure 22. Comparison of the Permeate Concentrations of Magnesium for All Three Trials

membrane has lower permeate concentrations whereas the multicontaminant trial has the lowest permeate concentrations.

A plot of temperature versus permeate flow is shown in Figure 23. The graph demonstrates that the permeate flow increases with increasing temperature. When the temperature declined at 10.5 hours, where the cooling system was activated, the permeate flow also decreased.

C. Percent Removal

Table 15 and 16 contain percent removal data for all pesticides and heavy metals obtained from all trials conducted. The rejection (percent removal) of the chlorinated pesticides and heavy metals were determined using the following equation :

$$\text{Percent Removal} = \frac{C_{\text{post}} - C_{\text{per}}}{C_{\text{post}}} \quad [9]$$

where

C_{post} = Concentration of solute before the membrane

C_{per} = Concentration of solute in permeate stream

Maximum, minimum as well as the average rejections of pesticides are listed in Table 15. The average rejection was calculated by taking the average of all the samples in a particular trial. Percent removal for atrazine, 1,4-dichlorobenzene, lindane, and heptachlor was constant throughout the 12 hour trial. Percent

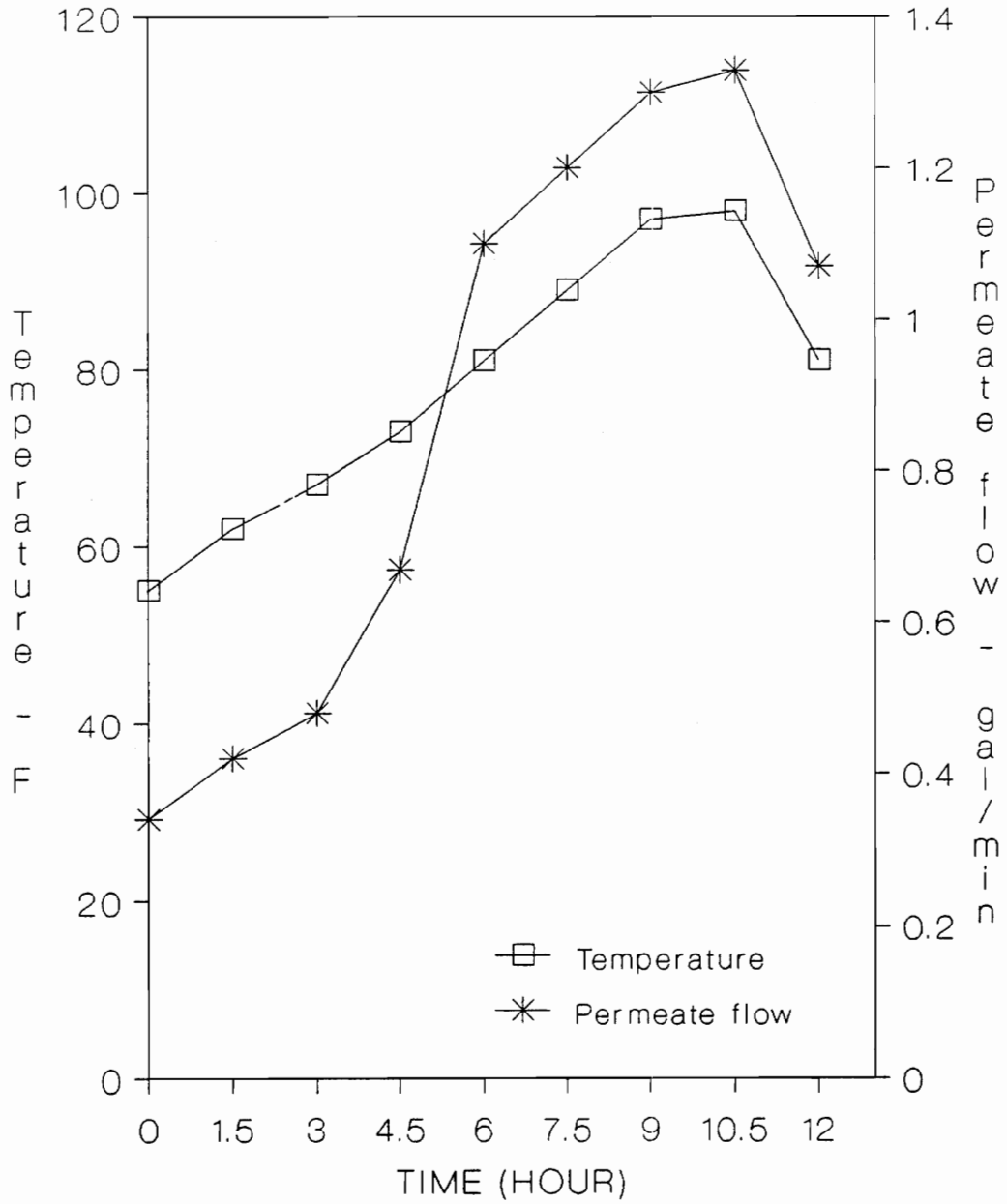


Figure 23. Comparison of Temperature and Permeate Flow During the Multicontaminant Trial

Table 15

Percent Removal for Pesticides

	Maximum Rejection (%)	Minimum Rejection (%)	Average Rejection (%)	Trend
Atrazine	100	100	100	Constant
1,4 Dichloro-benzene	100	100	100	Constant
Lindane	99.98	99.54	99.84	Constant
Heptachlor	100	95.62	99.52	Constant
Methoxychlor	100	94.80	98.27	Increase
Lindane (used)	100	81.50	97.54	Increase
Lindane (new)	100	94.80	99.32	Increase

Table 16

Percent Removal for Heavy Metals

	Maximum Rejection (%)	Minimum Rejection (%)	Average Rejection (%)	Trend
Arsenic	89.00	12.75	79.20	Increase
Lead	100	100	100	Constant
Nickel	100	99.41	99.74	Constant
Magnesium	99.89	99.64	99.82	Constant
Copper	99.85	99.51	99.76	Increase
Magnesium (used)	99.82	99.45	99.72	Increase
Magnesium (new)	99.78	98.58	99.65	Increase

removal for methoxychlor, however, increased as the trial progressed. The rejection of the single contaminant (lindane) with a used membrane ranged from 81 percent to 100 percent. A range from 95 percent to 100 percent was obtained for the single contaminant trial with the new membrane. In the multicontaminant trial, better than 94 percent removals were achieved for all the pesticides. The efficiency of rejection of the heavy metals during the three trials is presented in Table 16. All the heavy metals and magnesium have an average rejection of better than 99 percent except arsenic. Arsenic has a maximum rejection of 89 percent and an unsatisfactory minimum rejection of only 12.75 percent.

D. Percent Water Recovery

Water recovery is the percentage of the feedwater recovered as useful (product) water. Percent water recovery was calculated using the following equation:

$$\text{Percent recovery} = \frac{\text{Permeate flow}}{\text{Feedwater flow}} \times 100\% \quad [10]$$

Only an average of 2.5 percent recovery was obtained for pesticides and 4 percent for heavy metals. This low recovery rate would not be representative of typical industrial systems operating with multiple elements and at higher pressures.

DISCUSSION

The objective of this study was to determine if the pesticides and heavy metals investigated could be removed from contaminated feedwater using a poly(ether/urea) membrane to produce potable water.

A. Interpretation of Pesticide Results

Interpretation of pesticide removal data was difficult since solubility effects strongly influence the data. Table 13 shows that the poly(ether/urea) membrane used was very effective in removing pesticides from feedwater, as evidenced by the rejection range of 97.54 percent to 100 percent that was achieved for all the pesticides. From Figures 5 through 11, it is clear that concentrations of the prefilter, postfilter, and concentrate decreased, at times abruptly, as a trial progressed. This suggests that a significant quantity of pesticides was lost within the system. Since none of the pesticides were volatile, decline of the feed concentration throughout the trial was probably not due to volatilization. The decomposition of pesticides during the trial was not ruled out but seems rather improbable due to the short time involved and stability of these compounds. Several physicochemical criteria can be used to explain why such excellent removals were obtained with this membrane and why an appreciable amount of pesticides was lost in the system.

1. Sorption of Pesticides

Within the reverse osmosis test system, pesticides might be lost at several locations. Since PVC pipe was used throughout, it is very possible that some of the pesticides might have been sorbed onto the tubing.

The pesticides may also have been trapped within the cartridge filters. This is very likely to happen especially for those pesticides that are not very soluble in water. Table 7 shows the solubility of the pesticides used in this study. Atrazine is the most soluble whereas methoxychlor is the least soluble. Pesticides are known for their ability to form complex formations with clays and humic acid that might be present in the groundwater. When this happens, the pesticides will "cling" onto the much larger and bulkier clay or humic acid. The cartridge filter, which acted as a barrier to large particulates, prevented clay and humic acids from passing through and consequently the pesticides as well.

Lastly, the pesticides might have been sorbed onto the reverse osmosis membrane itself. To find determine whether this was true, a simple mass balance was performed on the pesticides present in the postfilter, concentrate, and permeate. Mass ratios were calculated using equation [12]

$$\text{mass ratio} = \frac{(\text{PF}) * (\text{PC})}{[(\text{CF}) * (\text{CC}) + (\text{PeF})(\text{PeC})]} \quad [12]$$

where

PF = postfilter flow, where $\text{PF} = \text{CF} + \text{PeF}$
 PC = postfilter concentration
 CF = concentrate flow
 CC = concentrate concentration
 PeF = permeate flow
 PeC = permeate concentration

A mean mass ratio value was then calculated for all the pesticides. The 95 % confidence interval for the mean was calculated using the t-test (Table 17). There is no mass gained or lost if the mass ratio equals one. A range of plus and minus 0.05 was consider acceptable, i.e 0.95-1.05. Mass ratios greater than 1.05 suggest that some pesticides was absorbed by the membrane. Mass ratios less than 1.05 imply desorption of pesticides from the membrane. From Table 18 1,4 Dichlorobenzene is the only pesticide that shows sign of sorption onto the membrane. The lindane trial with a new membrane also indicates that some of lindane was sorbed onto the membrane. The lindane trial using a used membrane has a mean mass ratio of 0.886. This might suggests that some desorption of lindane had ocured.

The polarity of an organic compound is related upon its octanol/water partition coefficient ($\log P_{\text{oct}}$). For the pesticides used in this investigation, $\log P_{\text{oct}}$ was calculated using the following equation:

$$\log P_{\text{oct}} = 4.5 - 0.75 \log S \quad (\text{Source: Vershueren}) \quad [11]$$

where S is the solubility of the compound in water in mg/l. Therefore, the larger the octanol/water partition coefficient, the less polar the molecule. Table 18 illustrates the octanol/water partition coefficient, the polarity ranking, and the average percent removal for each of the tested pesticides.

In the sorption experiment, heptachlor was found to be sorbed the most followed by lindane and then atrazine. The most polar of these three pesticides was atrazine whereas the least polar was heptachlor. Therefore, it can be

Table 17

Mass Balance Of Pesticides Around The Membrane

Pesticides	Mean Mass Ratio	Interval
Atrazine	1.06	0.818 - 1.302
1,4-Dichloro Benzene	1.28	-0.584 - 3.14
Lindane	1.02	0.757 - 1.283
Heptachlor	1.02	0.533 - 1.511
Methoxychlor	0.974	0.861 - 1.087
Lindane (new)	1.154	-1.23 - 3.54
Lindane (used)	0.886	0.026 - 1.750

Table 18

Polarity Ranking of Pesticides

Pesticides	Log P _{oct}	* Polarity Ranking	% Removal
Atrazine	3.12 @ 25 °C	1	100
1,4-Dichloro benzene	3.39 @ 20 °C	2	100
Heptachlor	4.37 @ 25 °C	4	99.52
Lindane	3.57 @ 24 °C	3	99.84
Methoxychlor	4.47 @ 24 °C	5	98.27

* 1 = most polar

5 = least polar

(based on water solubility)

concluded that the more the polar the pesticide, the less it is sorbed by the poly(ether/urea) membrane. Since atrazine was completely removed by the membrane and there appeared to be little sorption of atrazine onto the membrane, it was felt that most of the atrazine was removed by reverse osmosis. In the sorption experiment, most of the heptachlor was sorbed onto the membrane. Therefore, it was concluded that heptachlor in this investigation was removed by sorption and reverse osmosis.

2. Temperature

The average permeate and concentrate flows during all the three trials were 0.776 gallons/min and 22 gallons/min, respectively. A constant pressure of 325 psi was used for all the trials. The range of the inlet temperature encountered during all the trials was from 50 °F to 76 °F (see Appendix A). As the temperature increased, the permeate flow also increased. This phenomena had also been reported by other researchers.

According to Chian and Fang (1975), increasing the temperature tends to improve rejection of solutes. In this study, no apparent increase in removal efficiency of the pesticides was observed as a result of temperature rise because all the pesticides were very well rejected in the first place, i.e. an average removal efficiency of better than 95 percent. The temperature effect will, however, play a larger role in rejecting non-polar pesticides because increasing the temperature will enhance the sorption of the non-polar pesticides onto the membrane.

3. Post Chlorination

The chlorinated samples showed no detectable concentration of trihalomethanes. Most of the trihalomethane precursors (e.g. humic acid) present in groundwater was probably removed by the membrane due to their huge size.

4. Single Contaminant Trial Versus Multicontaminant Trial

Average percent removal of lindane in both the multicontaminant trial and the single contaminant trial a new membrane exceeded 99 percent. Permeate concentrations of lindane for both of these trials were below the MCLG/MCL (maximum contaminant level goal)/(maximum contaminant level) of 0.0002 mg/l. Based upon that comparison and other data in this study, pesticides in a mixed solute system performed independently in reverse osmosis.

5. New Membrane Versus Used Membrane

Average lindane removal with the used membrane was relatively lower than the average removal in the multicontaminant trial and the single contaminant trial with the new membrane. This can be attributed to the exhaustion of the sorption capacity of the membrane. When the maximum sorption capacity is reached, it can be expected that some leakage of pesticides occurs and eventually ends up in the permeate stream (Chian and Fang, 1975). Permeate concentrations of lindane for the used membrane trial were not below the MCLG/MCL of 0.0002 mg/l.

6. Permeate Concentrations for the Three Different Trials

Permeate concentrations of lindane for the three different trials were compared in Figure 12. The trial with the used membrane has the highest permeate concentration of lindane. This may be attributed to partial breakdown of the membrane. Reverse osmosis membranes have small spaces or gaps within the polymer matrix. After withstanding high pressure over an extended period of time, the small gaps will become larger thus making permeation of solutes easier. The used membrane described above was used in two different trials. Under high pressure, the membrane may have lost some of its compactness and allowed more lindane to permeate.

Figure 5 and Figure 11 show very erratic prefilter, postfilter, concentrate and permeate concentrations. It was felt that steady-state was never attained for these two systems.

Figure 9 shows that concentrations of the prefilter, postfilter and concentrate for Atrazine increased with time. A possible explanation may be that since atrazine was not very soluble in water, it might be trapped by the cartridge filter and as time progressed and temperature increased, some of the atrazine might start to dissolve in water.

Since the pesticides tested were not in the same homologous series, it was very difficult to conclude whether steric effects played a significant role in the overall rejection of the pesticides. However, if the pesticides were in the same homolog, the shape and size of the molecules will be a determining factor.

B. Interpretation of the Heavy Metals Result

Table 15 reveals that all the heavy metals in the multicontaminant trial were very efficiently rejected by the poly(ether/urea) membrane except for arsenic. Greater than 99.74 percent average rejection was attained for lead, nickel, magnesium, and copper, while 79.20 percent average rejection was achieved for arsenic. Average rejections of magnesium with the new and used membrane were 99.65 percent and 99.72 percent, respectively. Permeate concentrations of all the heavy metals and magnesium were below the MCLG.

Figure 15 shows that the concentrations of the prefilter, postfilter, and concentrate decreased with time for copper and lead. This was attributed to the precipitation of copper and lead onto the side of the 300 gallon feed tank. To confirm this, deposits attached to the side of the tank were scraped off and tested on the atomic adsorption spectrophotometer. The material was identified as copper and lead.

The capability of the poly(ether/urea) membrane to remove heavy metals from contaminated feedwater is dependent on the physical and chemical characteristics of the elements. However, to compare and explain the criteria for rejection in this investigation proved difficult because most of the heavy metals tested were not in the same homologous series. Arsenic belongs to Group VA elements, magnesium to Group IIA elements and copper to Group IB elements. Nickel and lead, however, correspond to the same homolog, i.e. Group VIII elements.

1. Solubility

Table 14 illustrates the solutes used in this study. All sulfate (SO_4^{2-}) salts were generally very soluble except lead sulfate (PbSO_4), which is insoluble in water. Nickel nitrate (NiNO_3) is also very soluble in water, whereas arsenous oxide (As_2O_3) is much less soluble. Comparing the solubility products, K_{sp} , PbSO_4 is more insoluble in water than As_2O_3 . Since PbSO_4 is practically insoluble in water, this contaminant was likely trapped by the cartridge filter. Consequently, by the time lead ions reached the reverse osmosis membrane, their concentrations were very low and therefore 100 percent removal was achieved.

2. Ionic Radius

Table 8 shows the ionic radius of the heavy metals in angstroms. Johnson (1975) reported that rejection increased with increasing ionic radius. Lead which has the largest ionic radius, 1.20 Å, was the most efficiently removed. Only minor differences are noted in the ionic radii of nickel, magnesium, and copper; therefore, it can be expected that the percent removal for these heavy metals is very similar. Arsenic has the smallest ionic radius and hence has the poorest rejection. The small radius enables arsenic ions to fit into gaps present in the polymer and then to diffuse through the matrix by passing from one opening to the next. Ions with larger radii do not diffuse as readily as those with smaller radii because of their larger cross-sections.

3. Valency of Metal Ions

According to Sastri (1979) the order of separation of metal salts is $M^{3+} > M^{2+} > M^+$ where M represents a metal ion. In this investigation, valency of the metal ion is not relevant because all the metal ions tested are divalent except for arsenic. Arsenic ions are trivalent but they have poorer rejection in comparison with other divalent ions. However, in this case, it was felt that the ionic radius effect overshadowed the effect of valency.

4. Electronegativity of Metal Ion

Abron (1972) proposed that reverse osmosis membrane has preference for water because water is able to form covalent bonds with the membrane and permeate it. She reported that the membrane allegedly has preference for any material capable of forming covalent bonds with the membrane. Formation of covalent bonds between solute ions and the membrane is a function of the electronegativity of the ion. The larger the electronegativity value, the greater the probability of forming covalent bonding with the membrane, and thus greater permeability. Table 8 lists the electronegativity value for the heavy metals investigated in this study. Arsenic and copper, having the largest electronegativity values, would be expected to have lower rejection. As shown, arsenic and copper displayed an average rejection of 79.20 percent and 99.76 percent, respectively. A possible explanation of why copper was better rejected than arsenic, since both of them have the same electronegativity value, may be due to the fact that copper has a larger ionic radius in comparison with arsenic. Copper, having a larger ionic radius, was more sterically hindered while diffusing

through the membrane matrix, and hence separated more effectively from water. On the other hand, arsenic experienced less difficulty in diffusing through the matrix and thus was rejected less.

Magnesium having the smallest electronegativity value was very effectively removed, i.e. an average removal of 99.82 percent. Among the heavy metals, lead was very effectively removed despite its high electronegativity value of 1.80. This effect may be explained by the fact that lead has the largest radius of all the metals and therefore had difficulty diffusing through the membrane matrix.

5. Temperature

Figure 22 shows the plot of the permeate flow versus temperature. The increased in permeate flow was proportional to the increased in temperature as temperature increased from 55 °F to 98 °F. At 10.5 hours, a cooling bath was installed to lower the temperature of the concentrate and permeate streams as they flowed back to the feed tank. As the cooling bath lowered the effluent temperatures from 98 °F to 81 °F, the permeate flow likewise decreased from a maximum of 1.33 gal/min to 1.07 gal/min. This phenomena is consistent with the reports of other researchers in the literature.

6. Permeate Concentrations for the Three Different Trials

The comparison of the permeate concentration of magnesium for all the three trials is shown in Figure 21. The permeate concentration was the highest in the trial using the new membrane following by the trial with the used membrane. The multicontaminant trial exhibited the lowest permeate

concentration. The low permeate concentration in the multicontaminant trial may be attributed to the interactions between the different solutes in the solution. Soluble species in the feedwater might react with other species in the mixture to form insoluble species. These reactions might occur in the reverse osmosis system ahead of the membrane. The insoluble species formed can then be precipitated onto the membrane which in turn increased the compactness of the membrane. Some of this rejuvenation might be carried over to the trial with the used membrane. This is probably the reason that the permeate concentrations in the used membrane trial were lower than the trial with the new membrane.

7. Mass Balance

A simple mass balance was performed on the mass going into the reverse osmosis membrane and the mass leaving the membrane (Table 19). Mass was conserved for arsenic, copper, magnesium, and nickel. A significant amount of lead was lost as the feedwater permeated through the membrane.

C. Summary

The poly(ether/urea) membrane demonstrated better than 97 percent removal for all pesticides. Permeate concentrations for all the pesticides were below the Safe Drinking Water Act (1986) standards except for the lindane trial using the used membrane. A considerable amount of pesticide was found to be sorbed onto the membrane. Excellent removal efficiencies were achieved for all heavy metals except for arsenic. The permeate concentrations, however, were

Table 19

Mass Balance of Heavy Metals Around The Membrane

Heavy Metals	Mean mass ratio	Interval
Arsenic	0.969	0.858 - 1.08
Copper	0.971	0.931 - 1.01
Magnesium	0.990	0.939 - 1.11
Nickel	0.981	0.941 - 1.02
Lead	7.33	-2.79 - 1.75

below the Safe Drinking Water Act (1986) standard. The removal efficiency increases with ionic radius of the metal ion. The removal efficiency, however, is inversely proportional to the electronegativity value of the metal.

CONCLUSIONS

The results of this study substantiate the following conclusions:

Pesticides:

1. Within the limits of this investigation, conclusions concerning the permeate produced by the poly(ether/urea) membrane can be summarized as follows:
 - permeate concentration of methoxychlor was below the MCLG of 0.34 mg/l (SDWA, 1986)
 - permeate concentration of 1,4 Dichlorobenzene was below the MCL of 0.075 mg/l (SDWA, 1986)
 - permeate concentration of atrazine was below the MCLG of 0.003 mg/l (40CFR)
 - permeate concentration of heptachlor was below the detection limit (0.00001 mg/l). The MCL for heptachlor is and the MCLG is 0.00 mg/l (SDWA, 1986)
 - permeate concentration of lindane was below the MCLG of 0.0002 mg/l for the trial with the new membrane and the multicontaminant trial. However, the permeate concentration was above the MCLG for the used membrane trial
2. It was found that pesticides in a mixed solute behaved independently

3. Temperature affects the permeate flow. The greater the temperature, the greater the permeate flow.
4. The poly(ether/urea) membrane demonstrated the ability to remove pesticides by sorption and by reverse osmosis.

Heavy Metals:

1. All the heavy metals and magnesium investigated exhibited excellent removal efficiencies (> 99 percent) except arsenic (79 percent). In spite of the relatively poor removal, the permeate concentration for arsenic was below the MCLG of 0.05 mg/l
2. The average removal efficiency of the new and used membrane were approximately the same. Therefore, it was felt that the new and used membrane behaved in the same manner. However, the 24 hour lapse time between trials might not be long enough for fouling of membrane to occur.
3. The concentrations of metal in the permeate were very low. All the concentrations were below the MCL/MCLG (SDWA 1986).
4. Increasing temperature increases the permeate flow.
5. Heavy metal removal increases with ionic radius of the metal ion.
6. Heavy metal removal efficiencies were dependent on the capability of the metal ions to form covalent bonds with the membrane. The greater the electronegativity value of the metal, the greater the probability of forming covalent bonding with the membrane and hence the lesser the removal.

SUGGESTIONS FOR FUTURE STUDIES

1. Further studies should be conducted to determine to what extent pesticides removed from the feedwater are removed by sorption rather than by reverse osmosis
2. The membrane employed can be tested with different feed pressures to determine the effect of pressure on removal efficiency and permeate flow
3. Longer than 12-hour experiment time should be evaluated

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APPENDIX A. FIELD DATA

PESTICIDES

Trial	Time (hrs)	Permeate Flow (gal/min)	Concentrate Flow (gal/min)	Tank Temp (°F)	Inlet Temp (°F)	Ambient Temp (°F)
1	0	0.57	22.1	59	54	64
1	1.5	0.99	22	66	61	70
1	3	1.02	21.9	70	65	77
1	3	1.02	21.9	70	65	77
1	4.5	1.04	21.7	73	69	82
1	6	1.13	21.6	77	75	84
1	6	1.13	21.6	77	75	84
1	7.5	1.12	21.5	80	75	88
1	9	1.19	21.5	81	76	84
1	9	1.19	21.5	81	76	84
1	10.5	1.19	21.5	81	76	81
1	12	1.19	21.4	81	76	81
1	12	1.19	21.4	81	76	81
2	0	0.46	22.5	57	50	48
2	1.5	0.35	22.3	62	56	55
2	3	0.38	22.2	66	60	57
2	3	0.38	22.2	66	60	57
2	4.5	0.44	22.1	68	65	70
2	6	0.47	22.1	72	68	75
2	6	0.47	22.1	72	68	75
2	7.5	0.47	22	72	68	79
2	9	0.67	22	72	68	77
2	9	0.67	22	72	68	77
2	10.5	0.64	22.1	73	69	81
2	12	0.71	22	73	68	80
2	12	0.71	22	73	68	80
3	0	0.3	22.3	64	58	63
3	1.5	0.65	22.1	70	65	68
3	3	0.74	22	73	66	72
3	3	0.74	22	73	66	72
3	4.5	0.76	21.9	75	70	74
3	6	0.75	22	74	69	79
3	6	0.75	22	74	69	79
3	7.5	0.91	21.9	77	72	79
3	9	0.93	21.8	79	74	77
3	9	0.93	21.8	79	74	77
3	10.5	0.94	21.9	79	74	75
3	12	0.95	21.8	79	75	75
3	12	0.95	21.8	79	75	75

APPENDIX A. CONTINUED

HEAVY METALS

Trial	Time (hrs)	Permeate Flow (gal/min)	Concentrate Flow (gal/min)	Tank Temp (°F)	Inlet Temp (°F)	Ambient Temp (°F)
1	0	0.73	21.9	64	50	66
1	1.5	1.14	21.7	72	68	66
1	3	1.24	21.4	79	77	68
1	3	1.24	21.4	79	77	68
1	4.5	1.47	21.1	88	84	70
1	6	1.59	20.8	95	90	70
1	6	1.59	20.8	95	90	70
1	7.5	1.71	20.7	100	96	72
1	9	1.85	20.4	106	101	75
1	9	1.85	20.4	106	101	75
1	10.5	1.93	20.4	111	107	73
1	12	1.97	20.3	115	110	73
1	12	1.97	20.3	115	110	73
2	0	0.34	22.3	57	55	66
2	1.5	0.42	22.1	64	62	73
2	3	0.48	21.9	70	67	73
2	3	0.48	21.9	70	67	73
2	4.5	0.67	21.7	77	73	77
2	6	1.1	21.4	86	81	88
2	6	1.1	21.4	86	81	88
2	7.5	1.2	21.2	95	89	91
2	9	1.31	21	102	97	93
2	9	1.31	21	102	97	93
2	10.5	1.33	21	100	98	93
2	12	1.07	21.5	82	81	81
2	12	1.07	21.5	82	81	81
3	0	0.39	22.3	61	57	68
3	1.5	0.45	22.1	67	63	70
3	3	0.52	21.8		69	
3	3	0.52	21.8		69	
3	4.5	0.68	21.8	75	71	81
3	6	0.97	21.7	77	73	86
3	6	0.97	21.7	77	73	86
3	7.5	1.01	21.6	81	75	88
3	9	1.04	21.6	82	77	91
3	9	1.04	21.6	82	77	91
3	10.5	1.06	21.5	82	78	92
3	12	1.07	21.5	82	79	91
3	12	1.07	21.5	82	79	91

APPENDIX B. LABORATORY DATA

PESTICIDES

Trial	Contaminant	Time	Prefilter (mg/L)	Postfilter (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
1	Lindane	0	0.07	0.01	0.01	0.00
1	Lindane	1.5	0.07	0.07	0.06	0.00
1	Lindane	3	0.07	0.05	0.07	0.00
1	Lindane	3	0.07	0.03	0.07	0.00
1	Lindane	4.5	0.07	0.07	0.07	0.00
1	Lindane	6	0.01	0.06	0.04	0.00
1	Lindane	6	0.05	0.02	0.07	0.00
1	Lindane	7.5	0.05	0.05	0.01	0.00
1	Lindane	9	0.01	0.01	0.04	0.00
1	Lindane	9	0.04	0.03	0.07	0.00
1	Lindane	10.5	0.04	0.06	0.04	0.00
1	Lindane	12	0.66	0.02	0.07	0.00
1	Lindane	12	0.04	0.06	0.00	0.00
2	Atrazine	0	0.08	0.09	0.08	0.00
2	Atrazine	1.5	0.08	0.07	0.07	0.00
2	Atrazine	3	0.10	0.09	0.06	0.00
2	Atrazine	3	0.07	0.09	0.07	0.00
2	Atrazine	4.5	0.08	0.08	0.09	0.00
2	Atrazine	6	0.09	0.10	0.09	0.00
2	Atrazine	6	0.10	0.10	0.11	0.00
2	Atrazine	7.5	0.10	0.11	0.11	0.00
2	Atrazine	9	0.11	0.09	0.10	0.00
2	Atrazine	9	0.09	0.10	0.10	0.00
2	Atrazine	10.5	0.09	0.10	0.09	0.00
2	Atrazine	12	0.11	0.09	0.09	0.00
2	Atrazine	12	0.10	0.10	0.08	0.00
2	Heptachlor	0	0.07	0.02	0.02	0.00
2	Heptachlor	1	0.01	0.01	0.01	0.00
2	Heptachlor	3	0.00	0.00	0.01	0.00
2	Heptachlor	3	0.00	0.00	0.00	0.00
2	Heptachlor	4.5	0.00	0.00	0.00	0.00
2	Heptachlor	6	0.00	0.00	0.00	0.00
2	Heptachlor	6	0.00	0.00	0.00	0.00
2	Heptachlor	7.5	0.00	0.00	0.00	0.00
2	Heptachlor	9	0.00	0.00	0.00	0.00
2	Heptachlor	9	0.00	0.00	0.00	0.00
2	Heptachlor	10.5	0.00	0.00	0.00	0.00
2	Heptachlor	12	0.00	0.00	0.00	0.00

APPENDIX B. CONTINUED

2	Heptachlor	12	0.00	0.00	0.00	0.00
2	Lindane	0	0.14	0.14	0.15	0.00
2	Lindane	1.5	0.14	0.12	0.12	0.00
2	Lindane	3	0.14	0.13	0.11	0.00
2	Lindane	3	0.12	0.13	0.12	0.00
2	Lindane	4.5	0.11	0.11	0.13	0.00
2	Lindane	6	0.13	0.12	0.14	0.00
2	Lindane	6	0.14	0.14	0.15	0.00
2	Lindane	7.5	0.12	0.12	0.12	0.00
2	Lindane	9	0.11	0.10	0.12	0.00
2	Lindane	9	0.10	0.11	0.11	0.00
2	Lindane	10.5	0.12	0.12	0.10	0.00
2	Lindane	12	0.11	0.09	0.10	0.00
2	Lindane	12	0.10	0.10	0.10	0.00
2	Methoxychlor	0	0.24	0.13	0.12	0.00
2	Methoxychlor	1.5	0.05	0.05	0.06	0.00
2	Methoxychlor	3	0.05	0.05	0.04	0.00
2	Methoxychlor	3	0.04	0.05	0.05	0.00
2	Methoxychlor	4.5	0.04	0.04	0.04	0.00
2	Methoxychlor	6	0.04	0.04	0.03	0.00
2	Methoxychlor	6	0.04	0.03	0.04	0.00
2	Methoxychlor	7.5	0.04	0.03	0.04	0.00
2	Methoxychlor	9	0.03	0.03	0.03	0.00
2	Methoxychlor	9	0.03	0.03	0.03	0.00
2	Methoxychlor	10.5	0.03	0.03	0.03	0.00
2	Methoxychlor	12	0.03	0.03	0.03	0.00
2	Methoxychlor	12	0.03	0.03	0.03	0.00
2	p - Dichlorobenze	0	0.03	0.03	0.04	0.00
2	p - Dichlorobenze	1.5	0.02	0.02	0.01	0.00
2	p - Dichlorobenze	3	0.01	0.01	0.02	0.00
2	p - Dichlorobenze	3	0.01	0.02	0.02	0.00
2	p - Dichlorobenze	4.5	0.01	0.01	0.01	0.00
2	p - Dichlorobenze	6	0.01	0.01	0.01	0.00
2	p - Dichlorobenze	6	0.01	0.01	0.01	0.00
2	p - Dichlorobenze	7.5	0.00	0.00	0.00	0.00
2	p - Dichlorobenze	9	0.00	0.00	0.00	0.00
2	p - Dichlorobenze	9	0.00	0.00	0.00	0.00
2	p - Dichlorobenze	10.5	0.00	0.00	0.00	0.00
2	p - Dichlorobenze	12	0.00	0.00	0.00	0.00
2	p - Dichlorobenze	12	0.00	0.00	0.00	0.00

APPENDIX B. CONTINUED

3	Lindane	0	0.14	0.12	0.12	0.00
3	Lindane	1.5	0.05	0.11	0.08	0.00
3	Lindane	3	0.11	0.07	0.11	0.00
3	Lindane	3	0.10	0.06	0.11	0.01
3	Lindane	4.5	0.10	0.02	0.14	0.00
3	Lindane	6	0.08	0.09	0.07	0.00
3	Lindane	6	0.10	0.12	0.09	0.00
3	Lindane	7.5	0.09	0.08	0.10	0.00
3	Lindane	9	0.09	0.08	0.10	0.00
3	Lindane	9	0.09	0.08		0.00
3	Lindane	10.5	0.10	0.12	0.11	0.01
3	Lindane	12	0.07	0.07	0.07	0.00
3	Lindane	12	0.06	0.06	0.09	0.00

APPENDIX B. LABORATORY DATA

Trial	Contaminant	Time	HEAVY METALS			
			Prefilter (mg/L)	Postfilter (mg/L)	Concentrate (mg/L)	Permeate (mg/L)
1	Mg	0	241.00	172.00	167.00	3.66
1	Mg	1.5	165.00	163.00	168.00	2.28
1	Mg	3	214.00	173.00	185.00	1.95
1	Mg	3	199.00	182.00	167.00	1.97
1	Mg	4.5	204.00	196.00	185.00	1.82
1	Mg	6	213.00	183.00	218.00	1.72
1	Mg	6	214.00	195.00	201.00	1.64
1	Mg	7.5	217.00	191.00	192.00	1.47
1	Mg	9	194.00	192.00	207.00	1.38
1	Mg	9	218.00	202.00	205.00	1.40
1	Mg	10.5	217.00	205.00	211.00	1.32
1	Mg	12	213.00	211.00	209.00	1.24
1	Mg	12	217.00	187.00	200.00	1.23
2	As	0	0.11	0.11	0.01	0.10
2	As	0	0.11	0.12	0.09	0.10
2	As	1.5	0.11	0.10	0.01	0.09
2	As	3	0.11	0.10	0.01	0.10
2	As	3	0.10	0.10	0.01	0.10
2	As	4.5	0.11	0.10	0.01	0.10
2	As	6	0.10	0.10	0.01	0.10
2	As	7.5	0.11	0.10	0.01	0.10
2	As	9	0.10	0.09	0.01	0.09
2	As	9	0.11	0.10	0.01	0.11
2	As	10.5	0.11	0.11	0.01	0.11
2	As	12	0.11	0.09	0.01	0.10
2	As	12	0.10	0.10	0.01	0.01
2	Cu	0	4.97	4.66	4.92	0.02
2	Cu	1.5	4.51	4.48	4.75	0.01
2	Cu	3	4.26	4.19	4.43	0.01
2	Cu	3	4.21	4.17	4.47	0.01
2	Cu	4.5	3.90	3.82	4.11	0.01
2	Cu	6	3.55	3.59	3.80	0.01
2	Cu	6	3.64	3.58	3.82	0.01
2	Cu	7.5	3.21	3.18	3.40	0.01
2	Cu	9	2.72	2.70	2.91	0.00
2	Cu	9	2.76	2.68	2.89	0.00
2	Cu	10.5	2.35	2.29	2.47	0.00
2	Cu	12	2.15	2.05	2.28	0.00

APPENDIX B. CONTINUED

2	Cu	12	2.16	2.15	2.29	0.01
2	Mg	0	161.00	163.00	168.00	0.59
2	Mg	1.5	162.00	162.00	173.00	0.42
2	Mg	3	166.00	164.00	172.00	0.35
2	Mg	3	161.00	161.00	172.00	0.36
2	Mg	4.5	161.00	156.00	164.00	0.31
2	Mg	6	160.00	162.00	167.00	0.28
2	Mg	6	156.00	162.00	168.00	0.27
2	Mg	7.5	162.00	162.00	169.00	0.24
2	Mg	9	160.00	160.00	167.00	0.22
2	Mg	9	153.00	160.00	173.00	0.22
2	Mg	10.5	161.00	164.00	178.00	0.22
2	Mg	12	164.00	167.00	177.00	0.19
2	Mg	12	165.00	163.00	174.00	0.19
2	Ni	0	0.52	0.51	0.54	0.00
2	Ni	1.5	0.52	0.52	0.55	0.00
2	Ni	3	0.50	0.51	0.53	0.00
2	Ni	3	0.50	0.51	0.53	0.00
2	Ni	4.5	0.50	0.50	0.52	0.00
2	Ni	6	0.50	0.51	0.53	0.00
2	Ni	6	0.51	0.50	0.53	0.00
2	Ni	7.5	0.50	0.49	0.53	0.00
2	Ni	9	0.47	0.49	0.52	0.00
2	Ni	9	0.48	0.48	0.52	0.00
2	Ni	10.5	0.48	0.48	0.52	0.00
2	Ni	12	0.48	0.47	0.51	0.00
2	Ni	12	0.48	0.48	0.50	0.00
2	Pb	0	0.05	0.07	0.02	0.00
2	Pb	1.5	0.01	0.03	0.01	0.00
2	Pb	3	0.01	0.01	0.00	0.00
2	Pb	3	0.00	0.01	0.00	0.00
2	Pb	4.5	0.01	0.02	0.00	0.00
2	Pb	6	0.02	0.01	0.00	0.00
2	Pb	6	0.00	0.01	0.00	0.00
2	Pb	7.5	0.00	0.01	0.00	0.00
2	Pb	9	0.00	0.04	0.00	0.00
2	Pb	9	0.00	0.01	0.00	0.00
2	Pb	10.5	0.00	0.01	0.00	0.00
2	Pb	12	0.00	0.03	0.00	0.00
2	Pb	12	0.00	0.01	0.00	0.00

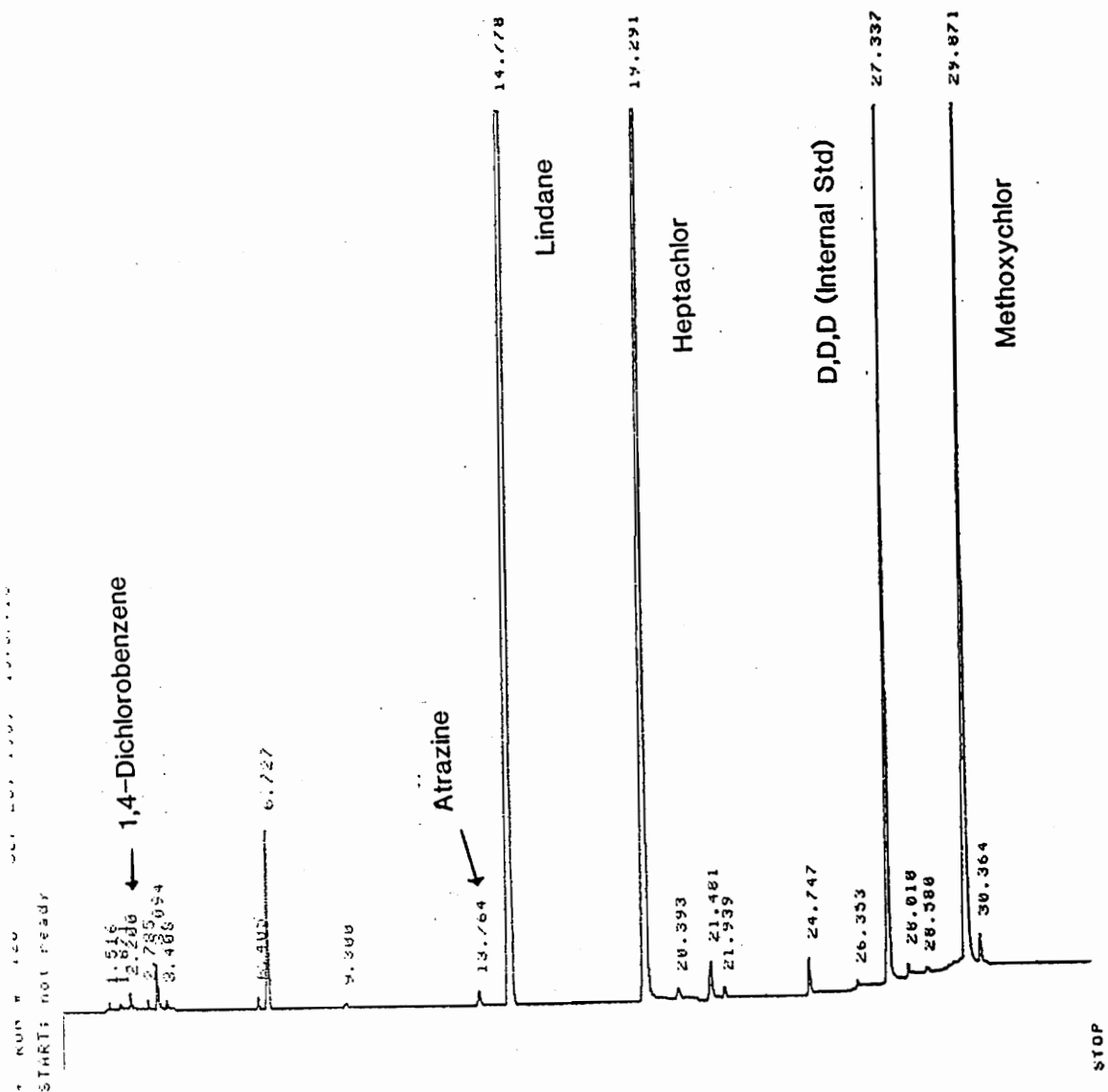
APPENDIX B. CONTINUED

3	Mg	0	162.00	161.00	165.00	0.89
3	Mg	1.5	151.00	157.00	161.00	0.55
3	Mg	3	163.00	161.00	175.00	0.48
3	Mg	3	165.00	155.00	166.00	0.51
3	Mg	4.5	162.00	160.00	167.00	0.44
3	Mg	6	162.00	156.00	167.00	0.41
3	Mg	6	162.00	157.00	172.00	0.41
3	Mg	7.5	161.00	155.00	168.00	0.38
3	Mg	9	153.00	162.00	169.00	0.37
3	Mg	9	165.00	160.00	164.00	0.37
3	Mg	10.5	164.00	161.00	168.00	0.35
3	Mg	12	162.00	164.00	174.00	0.32
3	Mg	12	166.00	169.00	163.00	0.31

As = Arsenic
Cu = Copper
Mg = Magnesium
Ni = Nickel
Pb = Lead

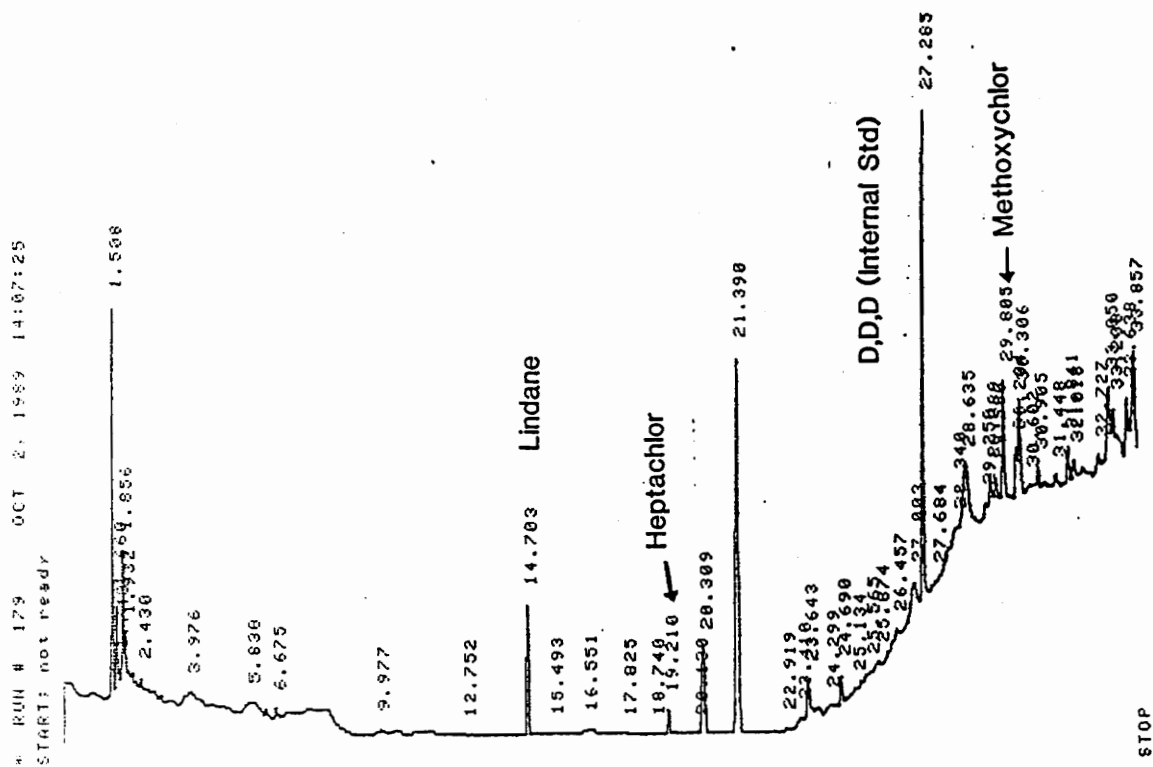
APPENDIX C. CHROMATOGRAMS

Chromatogram for the Prefilter, Postfilter, and Concentrate Samples



APPENDIX C. CONTINUED

Chromatogram for the Permeate Samples



* Concentration of 1,4-dichlorobenzene and atrazine below the detection limit

VITA

Brian S.H. Chong was born in Malaysia on July 9, 1966 and lived there throughout his primary and secondary education. Mr. Chong received his Bachelor of Science degree in Civil Engineering from the University of Southwestern Louisiana in December of 1987. He successfully completed his Master of Science degree in Environmental Engineering at Virginia Polytechnic Institute and State University in March of 1990.

A handwritten signature in black ink, appearing to read 'B.S.H. Chong', with a large, stylized flourish above the name.