REMOVAL OF VOCS FROM GROUNDWATER USING MEMBRANE-ASSISTED SOLVENT EXTRACTION*

Joseph C. Hutter, George F. Vandegrift, Luis Nunez, and David H. Redfield

Argonne National Laboratory Chemical Technology Division

MASTER

Removal of VOCs from Groundwater Using Membrane-Assisted Solvent Extraction

Joe C. Hutter, David H. Redfield,
Luis Nuñez, and George F. Vandegrift

Chemical Technology Division
Argonne National Laboratory
9700 S. Cass Avenue
Argonne IL, 60439

ABSTRACT

A membrane-assisted solvent extraction (MASX) system coupled to a membrane-assisted distillation stripping (MADS) system for use in decontaminating groundwater is discussed. Volatile organic compounds (VOCs) are extracted in the MASX using a sunflower oil solvent. In the MADS, VOCs are stripped from the sunflower oil, and the oil is recycled to the MASX. Thermodynamic data for the sunflower oil-water-VOCs system were experimentally collected. Published membrane-mass transfer results along with these data were used to design the MASX and MADS modules.

Introduction

Membrane-assisted solvent extraction is an emerging new technology in the chemical industry with many potential applications. Prasad and Sirkar [PRASAD and SIRKAR-1987, -1988, -1990] have demonstrated solvent extraction using this technology on several liquid-liquid systems. They have worked out the details for a resistance in series mass transfer model to evaluate the film resistances and membrane resistances for these types of systems. Yang and Cussler [YANG and CUSSLER-1986] evaluated and correlated the mass transfer resistances of the liquid films for these types of modules. Their work was primarily with mass transfer of oxygen from air into water; some work was also done on the mass transfer of carbon dioxide into water. These systems are well known liquid-phase-controlled mass transfer processes. Yang and Cussler evaluated a standard lab-scale shell-and-tube

configuration module, and a pure cross-flow lab-scale module. Their dimensionless analysis results were consistent with established heat transfer results for analogous geometries.

Membrane-assisted solvent extraction has several advantages over conventional solvent extraction. The microporous membranes are used to separate the liquid phases, so that extraction can occur without the conventional mixing followed by phase separation. In the membrane extraction modules the two liquid phases are contacted with the interface immobilized by the microporous membrane. No phase separation is required because the two liquid phases are never mixed. This allows independent variation of the two liquid flow rates without the problems of flooding, stable emulsion formation, or poor contacting resulting in a low stage efficiency. The surface area per unit volume of contacting module is higher than in conventional packed or agitated columns, so that mass transfer is enhanced due to the larger interfacial area. The interfacial area in these modules can be accurately determined from the fiber dimensions and characteristics; thus the equipment is easily characterized for pilot plant tests and scale-up.

The high surface area enhances the mass transfer in these modules and makes them ideal candidates for applications of solvent extraction to dilute systems. Groundwater remediation and some process water applications require the recovery of dilute VOCs in the ppm-ppb range. Dilute concentrations of VOCs (ppb) are commonly found large distances from the immediate contamination source, and recovery of these dilute VOCs from the aquifer is a very difficult remediation problem. The most widely used technology to remove dilute VOCs from water is air stripping [BROWN-1991]. Membrane extraction technology is effective in the same concentration range of VOCs as air stripping.

Zander and Semmens et al., first demonstrated this technology for recovering dilute VOCs from water using sunflower oil as the solvent [ZANDER-1989A, SEMMENS-1990]. They used a composite microporous polypropylene membrane coated with a disiloxane polymer in their studies. This unique design allowed the pores to remain gas filled, thus they claimed that the mass transfer resistance of the membrane was considerably reduced. Our work shows that oil-filled pores in a microporous membrane extraction gives a comparable overall resistance to the gas-phase dense-phase composite membrane extraction used by Semmens. Thus, overall mass transfer coefficients are about the same in both extraction configurations. This results from the favorable equilibrium partitioning of the VOCs between the water and the oil phases. Zander demonstrated that the extraction of the VOCs worked; the

regeneration of the solvent was much more difficult. A previous paper describes the MASX/MADS system and data needed to design one [HUTTER]. Since that time, we have collected the required thermodynamic data to evaluate this new membrane technology for both the extraction step and the regeneration of the solvent. A preliminary design of a pilot -scale membrane-assisted solvent extraction (MASX) system coupled to a membrane-assisted distillation stripping (MADS) system is discussed.

Process Description

The MASX/MADS system [HUTTER] consists of two types of hollow fiber units (Fig. 1). A nonvolatile organic solvent is used to extract the VOCs from the water in the MASX unit. In the MASX, the organic phase and aqueous phase flow counter-currently and are separated by the walls of membrane hollow fibers. The aqueous phase runs through the lumen; the solvent is on the shell side.

The VOC-contaminated water is contacted with the nonvolatile organic solvent and exits the MASX unit decontaminated of VOCs. The nonvolatile organic solvent containing the VOCs exits the MASX unit and is heated to 70°-90°C then sent to the MADS unit to remove the VOCs from the nonvolatile solvent. In the MADS unit the nonvolatile organic solvent is stripped of VOCs by a gas phase. The VOCs, water which is extracted by the nonvolatile solvent, and a trace amount of solvent are vaporized into the stripping gas. The VOCs, water, and a trace amount of nonvolatile solvent is recovered from the stripping gas by a condenser. The stripping gas is recycled to the MADS to recover more VOCs from the nonvolatile solvent. The nonvolatile solvent is recycled to the MASX unit to recover more VOCs from the aqueous feed. Overall, this process has one feed, VOC contaminated water, and two products: decontaminated water and a concentrated solution of VOCs in water containing a trace amount of the nonvolatile solvent. A flow diagram of the process is shown in Fig. 1.

Experimental

In order to design the MASX/MADS system, various fundamental experimental data about each VOC, water, and sunflower oil are needed. The experimental procedures used to obtain these data are discussed here.

Quantitative Analysis of VOCs. A Varian 3400 gas chromatograph equipped with photoionization and electrolytic conductivity detectors was used to measure VOC concentrations in water and sunflower-oil samples. A Tekmar LSC-2000 purge-and-trap concentrator was used to recover the VOCs from the samples. Water samples were evaluated using a method identical to EPA Method 502.2. Sunflower oil samples were heated to 90°C in a 5mL fritless purge cell to recover the VOCs from the samples for adsorption onto the trap. The GC was equipped with a 30m x 0.53mm ID Supelco VOCOL column with a 3μm film. Helium carrier gas was used at a flow rate of 6 mL/min. The GC oven was temperature programmed for 5°C for 35 min, then ramped to 150°C at 10°/min. Data were collected using a 2-channel Spectra-Physics Model SP4290 integrator and Winner386 software package.

Distribution Ratio Measurements. Equilibrium distribution ratios for each VOC between oil and water (D-values) were experimentally measured by contacting sunflower oil, water, and each VOC in a centrifuge tube submerged in a temperature-controlled bath. Samples were mixed, then separated in a centrifuge; the temperature was maintained by subsequent immersion in a controlled temperature bath before samples of both the aqueous and organic phases were analyzed for each VOCs concentration. Care was taken to avoid any head space in sample vials since VOCs were found to be rapidly lost from liquids exposed to an open headspace.

Henry's Law Constant Measurements. Henry's Law Constants were measured in a sparged gas reactor similar to the one used by MacKay [MACKAY-1979]. The reactor, which is shown in Fig. 2, is made out of glass and is 6.35 cm ID and 63.5 cm long. The reactor holds 1.70 L of liquid when full. This reactor is longer than the one used by MacKay. Nitrogen gas was sparged into the reactor by a sintered glass diffuser. The gas flowrate was measured by factory calibrated Cole-Palmer rotameter Model N112-02. Gas flows were varied from 0.5 mL/s to 3.5 mL/s. Temperature was controlled by circulating water through a external heating jacket. The heat transfer water was circulated to a temperature controlled bath. The reactor temperature itself

was monitored by a thermocouple. Samples of the liquid were withdrawn from the reactor using a syringe with an extended needle. A mixer (not shown) with three 2.54 cm marine impellers equally spaced on a 45 cm shaft was installed to improve the mixing of the high viscosity oil and insure a completely mixed liquid phase. The entire reactor was placed inside a fume hood.

The mass transfer of a sparingly soluble component in a liquid phase to gas phase is a liquid phase controlled process. For a fine bubble diffuser system, it has been observed that fine bubbles rapidly approach equilibrium with a sparingly soluble substance in the liquid phase within the first 15 cm of the disengagement of the bubbles from the diffusers. This phenomena has been successfully applied to measure the Henry's Law Constants for various VOCs in water [MACKAY-1979]. The technique requires accurate concentration vs. time data for desorption of a VOC from a sparged reactor. A material balance on the reactor allows one to calculate the Henry's Law Constant from the concentration vs. time data.

The material balance must include subsurface mass transfer between the dispersed gas and the bulk liquid as well as mass transfer at the liquid surface in contact with an infinite sink of gas [MCWHIRTER and HUTTER-1989]. The Henry's Law Constant is determined from the portion of the mass transfer due to the subsurface effects. The subsurface gas dispersion exits the reactor in equilibrium with the completely mixed liquid phase. A material balance for each VOC component is given by Eq. 1.

$$V_L \frac{dC_{oi}}{dt} = -G \frac{H_i RT C_{oi}}{P} - K_{LS} a_S (C_{oi} - C_{oi}^*) \tag{1}$$

Because the reactor was installed in a fume hood which is continuously purged with clean air, as the sparge gas exits the reactor, it is rapidly entrained by the large fume hood gas flow. Due to the high volumetric flow of the fume hood gas, the gas above the reactors turbulent liquid surface does not contain any VOCs, and C_{oi}^* is zero. Equation 1 can be integrated with the initial condition, $C_{oi} = C_{oi}^o$ at t = 0.

$$\ln \frac{C_{oi}}{C_{oi}^o} = -\left(\frac{GH_i RT}{P} + K_{LS} a_S\right) \frac{t}{V_L} \tag{2}$$

The sparged reactor was initially filled with a 1000 ppb of each of the VOCs listed in Table 1. Grab samples were taken from the reactor, and the concentration vs. time

results were collected for each VOC. Experiments in the sparged reactor were evaluated using Eq. 2. From the zero gas rate test, G=0 in Eq. 2, $K_{LS}a_S$ could be determined. This value of $K_{LS}a_S$ was used in the experiments with the gas flow in the calculation of the Henry's Law Constants using Eq. 2. A plot of typical experimental data is shown in Fig. 3. As predicted by Eq. 2, a plot of ln C_{oi}/C_{oi}^o vs. t is a straight line. The least squares fit of the slope was used in the analysis.

The zero gas flow rate line shown in Fig. 3 is for the component methylene chloride. Since all the components were desorbed at almost the same rate, the zero gas rate values of $K_{LS}a_S$ were all within about 10% of each other for all the components. This would be expected since all the components have about the same diffusivity in the sunflower oil, and the mass transfer coefficient is directly proportional to the diffusivity according to the standard theoretical arguments of the film theory [BIRD-1960]. Methylene chloride had the highest estimated diffusivity in sunflower oil and thus it showed the most rapid loss from the sparged reactor in the zero gas tests.

Viscosity Measurement. The viscosity of sunflower oil was measured using a Brookfield Viscometer Model LVF. The liquid was contained in a temperature controlled cylindrical test cell. A cylindrical spindle was used on the viscometer.

Water Solubility Measurements. The water concentration in sunflower oil in equilibrium with pure water at 20°C was measured using a Karl Fischer Coulometer, Model KF652. The coulometer was calibrated with hydranal standard methanol (Riedel-de Haen AG, Switzerland) which contained 5.00 +/- 0.02 mg water/mL. Sample sizes of 5-25 µL of sunflower oil equilibrated with water were introduced into the Karl Fisher Coulometer titration system.

Reagent Chemicals. The analytical reagent quality VOCs used in this study were purchased from Aldrich Chemical Co., Milwaukee WI, and Fisher Scientific Co., Pittsburgh PA. Sunflower oil was a commercial edible grade manufactured by Hunt-Wesson, Inc., Fullerton CA that was purchased locally. Water was obtained from the laboratory deionized and distilled water system. In addition, all the water was heated to 70°C and sparged with nitrogen for at least 4 hr prior to use. This procedure insured that no VOCs could be detected in the water using our analytical equipment.

Measured Thermodynamic and Physical Properties

The important properties required to design the MADS/MASX are reported below.

Distribution Ratios. The partitioning of the VOCs between the feed water and the nonvolatile solvent is an important parameter in designing the MASX unit. D-values between water and sunflower oil at 20°C are shown in Table 1. As shown in the table, VOCs that can hydrogen bond with water (e.g., chloroform) have consistently smaller D-values then those components which do not hydrogen bond, (e.g., carbon tetrachloride). Components such as carbon tetrachloride, or weakly hydrogen bonding components such as trichloroethylene, tend to break-up the hydrogen bonding structure in water and thus are energetically favored to partition to the oil phase. This effect is also observed in a homologous series of alcohols, i.e., decreasing solubilties in water as chain lenght increases (methanol is miscible with water, n-butanol is not). Intermediate D-value components such as benzene do not hydrogen bond with water, but can interact with water by induced polarization effects, which tend to lower the D-values compared to the components like carbon tetrachloride [KING-1982, -1984].

Table 1. D-values for 8 Candidate VOCs between
Water and Sunflower Oil at 20°C

Component	$D=\dfrac{C_{oi}}{C_i}$
Methylene Chloride	47
Trans-1,2-Dichloroethylene	130
Cis-1,2-Dichloroethylene	120
Chloroform	91
1,1,1-Trichloroethane	340
Carbon Tetrachloride	770
Benzene	210
Trichloroethylene	340

Henry's Law Constants in Sunflower Oil. The Henry's Law Constants for the VOCs in sunflower oil are summarized in Table 2. As shown in the table, the Henry's Law Constants in sunflower oil can be correlated with the pure component boiling points of each VOC. Components are in vapor-liquid equilibrium in a capillary column GC. Therefore, the retention time is directly related to the partial pressures of the components above the stationary phase. Also as shown in the table, the components are listed in the order that they elute from the GC.

Table 2. Pure Component Boiling Points and Henry's Law Constants in Sunflower Oil

Component	Boiling Pt. °C, 1 atm	Retention Time, min	50°C	70°C	90°C
Methylene Chloride	40.0	10.5	0.021	0.029	0.071
Trans-1,2-Dichloroethylene	47.0	12.0	0.018	0.025	0.071
Cis-1,2-Dichloroethylene	60.0	21.9	0.012	0.020	0.036
Chloroform	61.7	24.0	0.0099	0.015	0.037
1,1,1-Trichloroethane	74.1	28.8	0.010	0.015	0.034
Carbon Tetrachloride	76.6	32.0	0.0099	0.017	0.031
Benzene	80.0	35.6	0.010	0.017	0.028
Trichloroethylene	87.0	39.1	0.0062	0.011	0.019

The Henry's Law Constants can also be correlated by Eq. 3.

$$\ln H_i = -\frac{\Delta H_{i\ diss}}{RT} + \frac{\Delta S_{i\ diss}}{R} \tag{3}$$

Figure 4 shows a plot of $\ln H_i$ vs. $1/T$ typical for the VOCs we studied. The thermodynamic quantities obtained from these plots are listed in Table 3. The values of $\Delta H_{i,diss}$ agree well with the published values of ΔH_{vap} for the pure components at their boiling points [LIDE-1991]. As shown in the table, the pure component enthalpies are smaller than the enthalpies of dissolution from sunflower oil. This indicates that it takes more energy to vaporize the VOCs from the sunflower oil as compared to the pure components, thus indicating the high affinity of the sunflower oil for the VOCs.

Using these data, it is possible to extrapolate our experimental Henry's Law constant data over a wide range of temperatures, which will be useful in optimizing the MADS unit.

Table 3. Thermodynamic Quantities of Various VOCs in Sunflower Oil

Component	$\Delta H_{i,vap}$ (kJ/moL)	$\Delta H_{i,diss}$ (kJ/moL)	$\Delta S_{i,diss}$ (J/moL-K)
Methylene Chloride	28.1	43	96
Trans-1,2-Dichloroethylene	-	42	94
Cis-1,2-Dichloroethylene	-	34	65
Chloroform	29.2	41	86
1,1,1-Trichloroethane	29.9	38	78
Carbon Tetrachloride	29.8	40	83
Benzene	30.8	39	79
Trichloroethylene	31.4	38	71

Viscosity of Sunflower Oil. The viscosity measurement results are shown in Fig. 5. At all temperatures tested except 10°C, the sunflower oil was Newtonian; its viscosity was independent of shear rate. Even at 10°C, the sunflower oil was close to Newtonian. Viscosity was found to decrease with temperature as expected.

MASX Unit Design.

Design Basis for the MASX/MADS. To evaluate the performance of the MASX/MADS process, an aqueous flow rate of 378.5 L/min was chosen. The inlet concentration was set at 10 ppm, which is high compared to most groundwater remediation problems. The MASX was designed to remove VOCs to at least 10 ppb, the drinking water standard typical for common VOCs. This is a decontamination factor of 1000, which is beyond the performance of most conventional remediation equipment. An O/A of 0.1 was chosen to conserve the sunflower oil flow.

The mass transfer of the VOCs between the water and oil phases in a counter-current flow shell-and-tube module can be modeled by the following equations. These equations assume that the mass transfer of the VOC components are independent of

each other, there are no interaction effects. This assumption works best in dilute solutions, which is the case for the application being considered. For the water inside the fibers, the following equation applies.

$$v \frac{dC_i}{dz} = - K_L a \, (C_i - C_i^*)$$ (4)

Membranes are a unique system since the interfacial area for mass transfer can be calculated from the geometry of the membranes. For the case here, the water-oil interface is immobilized at the inside wall of the hollow fibers. Thus the area is based on the inside diameter of the fibers. The area per unit volume of fiber is simply $4/d_{ID}$.

If the oil is assumed to enter the module clean, containing no VOCs, the following material balance will apply at any cross section in the module.

$$C_{oi} = \frac{L}{V} \, (C_{i\text{-}in} - C_i)$$ (5)

By using the definition of a D-value, Eq. 5 can be rewritten as,

$$C_i^* = \frac{L}{VD_i} \, (C_{i\text{-}in} - C_i)$$ (6)

Equation 6 can be substituted into Eq. 4 for C_i^* and integrated with the boundary condition $C_i = C_{i\text{-}in}$ at z=0.

$$\frac{C_i}{C_{i\text{-}in}} = \frac{R_i \, EXP \left(\frac{K_L a}{v} z \, \frac{(R_i - 1)}{R_i} \right) - 1}{R_i - 1}$$ (7)

Solution of Eq. 7 will give the concentration of VOC_i for any fiber length z in a counter-current shell and tube module, provided the overall mass transfer coefficient K_L is known.

The overall mass transfer resistance can be considered the sum of three resistances in series: tube-side resistance, membrane resistance, and shell-side resistance. Yang and Cussler [YANG and CUSSLER-1986] developed a correlation to estimate k_{Lt} from tube- and shell-side resistances. For the tube-side the following equation applies for the hollow fibers:

$$\frac{k_{Lt}d_{ID}}{D_{AB}} = 1.64 \left(\frac{d_{ID}^{2} v}{D_{AB} z}\right)^{0.33} \tag{8}$$

For the shell-side the following equation can be used to estimate the local mass-transfer coefficient. This equation applies for fibers in a close-packed geometry, the situation in the shell-and-tube hollow fiber modules.

$$\frac{k_{Ls}d_{e}}{D_{AB}} = 24 \tag{9}$$

The equivalent diameter is defined similarly to the hydraulic radius, four times the cross-sectional area divided [PERRY-1984]. The membrane resistance can be calculated by Eq. 10, developed by Prasad and Sirkar [PRASAD and SIRKAR-1988].

$$k_{m} = \frac{D_{AB} \varepsilon_{m}}{\left(\tau (d_{OD} - d_{ID})/2\right)} \tag{10}$$

The resistances are additive, using Eq. 11 developed by Prasad and Sirkar [PRASAD and SIRKAR-1988] for a hydrophibic, microporous hollow fiber with water in the lumen and the oil phase in the shell.

$$R_{overall} = R_{tube} + R_{membrane} + R_{shell} \tag{11a}$$

$$\frac{1}{K_{L}d_{ID}} = \frac{1}{k_{Lt}d_{ID}} + \frac{1}{D_{i}k_{m}d_{LM}} + \frac{1}{D_{i}k_{Ls}d_{OD}} \tag{11b}$$

The logarithmic mean diameter is calculated by Eq. 12.

$$d_{LM} = \frac{d_{OD} - d_{ID}}{\ln\frac{d_{OD}}{d_{ID}}} \tag{12}$$

The diffusivities of each of the VOCs in water can be estimated by the Hayduk and Laudie modified equation of Wilke-Chang below. These data originally correlated

dilute organic components in water, the system of interest on the tube-side in the MASX [PERRY-1984]. The diffusivities of several VOCs in water at 20°C are reported in Table 4.

$$D_{AB} = 7.4 \times 10^{-8} \frac{(2.26 \, M_w)^{0.5} T}{\mu_W \, V_i^{0.6}} \qquad (13)$$

The diffusivities of the VOCs in sunflower oil can be estimated from the water data using the dependences in the Stokes-Einstein Equation [PERRY-1984]. From this equation, the diffusivity is inversely proportion to the viscosity, thus the ratios of the viscosities of water to sunflower oil at 20°C can be used to estimate the diffusivities in sunflower oil. The diffusivities for sunflower oil are also shown in Table 4.

Table 4. Diffusivities of VOCs in Water and Sunflower Oil at 20°C

Component	Diffusivity in Water $(10^{-5} \, cm^2/s)$	Diffusivity in Sunflower Oil $(10^{-7} \, cm^2/s)$
Methylene Chloride	1.14	1.90
Trans-1,2-Dichloroethylene	1.02	1.70
Cis-1,2-Dichloroethylene	1.03	1.72
Chloroform	0.99	1.65
1,1,1-Trichloroethane	0.88	1.45
Carbon Tetrachloride	0.89	1.49
Benzene	0.94	1.56
Trichloroethylene	0.93	1.55

Using the results of Eqs. 8 through 12 and the appropriate physical property data, the mass transfer coefficients for a MASX can be estimated. The estimated mass transfer coefficients are shown in Table 5. As shown in the table, the smallest individual mass transfer coefficients result inside the membrane. Using the dependencies in Eq. 11, these membrane coefficients would be multiplied by the D-values in Table 1 (47-770). Even with including the D-values, the membrane resistance is the largest resistance and controls the overall mass transfer resistance.

The D-values are also used to multiply the values of k_{Ls} as shown in Eq. 11. Thus the shell-side oil resistance is the smallest contributor to the overall resistance. The tube-side resistance, although more important then the shell-side resistance, is typically about 10-100 times smaller than the membrane resistance. The overall mass transfer coefficients range from 0.4-4.6 x 10^{-3} cm/s, which is about the same range as those found by Zander, et al., [ZANDER-1989A] at similar operating conditions.

A prototypical shell-and-tube configuration pilot scale membrane module would have the characteristics listed in Table 6. The fibers in the module are made out of microporous polypropylene. This type of equipment is commercially available on a lab-scale and is under development on a pilot scale. The fiber characteristics are those of Hoechst Celanese X-10 hollow fibers, and they are marketed under the trade name Celgard. The Celgard fibers have been used in the work of Zander, et al. [ZANDER-1989A, -1989B], Sirkar, et al. [SIRKAR-1986], and Yang, et al.,[YANG-1986], and others.

Table 5. Mass Transfer Coefficients in the MASX

Components	k_{Lt} (10^{-2} cm/s)	k_m (10^{-6} cm/s)	k_{Ls} (10^{-3} cm/s)	K_L (10^{-3}cm/s)
Methylene Chloride	4.49	7.92	6.84	0.40
Trans-1,2-Dichloroethylene	4.17	7.08	6.12	0.98
Cis-1,2-Dichloroethylene	4.20	7.15	6.18	0.91
Chloroform	4.10	6.91	5.97	0.67
1,1,1-Trichloroethane	3.76	6.08	5.25	2.11
Carbon Tetrachloride	3.81	6.19	5.35	4.56
Benzene	3.94	6.51	5.62	1.43
Trichloroethylene	3.93	6.47	5.59	2.25

Table 6. Membrane Module Characteristics

Module Diameter (cm)	20
Void Fraction	0.65
Number Fibers	110,000
Fiber Length(cm)	100
Fiber ID (cm)	0.034
Fiber OD (cm)	0.04
Fiber Porosity (%)	30
Pore Size (μm)	0.05
Area/Volume (cm^2/cm^3)	37.4
No. Fibers/Area (No./cm^2)	350
Liquid Velocity in Fibers (cm/s)	0-10

Using Eq. 8 through 12, and the membrane module characteristics in Table 5, the mass transfer coefficients for a 387.5 L/min pilot scale MASX can be calculated. For this design, the water is pumped through the lumen. Oil flows in the shell at a flowrate of 38.75 L/min so that the MASX operates at an O/A of 0.1. The velocity of water in the fibers controls the capacity of each module. For a velocity of 5.25 cm/s in the fibers, each module with the characteristics in table 5 will have an aqueous flow of 31.5 L/min. Thus, 12 modules in parallel will be required to handle the 378.5 L/min feed. The calculated individual mass transfer coefficients and the overall mass transfer coefficient are listed in Table 6. A tortuosity of 2.5 was used for this calculation.

The results of the design calculations are displayed in Figure 6. As shown, carbon tetrachloride is the easiest component to extract since it has the highest D-value (770 at 20°C) and the highest relative mass transfer coefficient. The VOC most difficult to extract is methylene chloride, it has the smallest D-value and the smallest relative mass transfer coefficient. The percentage removal of each VOC for 2 m of fiber length is given in Table 7. Also shown in the table are the overall values of $K_L a$ for each component. All of the components except methylene chloride are removed by more than 97% after only 2 m of fiber length. About 8 m of fiber length would be required to remove 97% of the methylene chloride. Increases in fiber length can be achieved by putting the modules with the characteristics in Table 5 in series.

The mass transfer coefficients were estimated from sparingly-soluble-gas absorption data, for gases such as oxygen. The dimensionless forms used to estimate

the mass transfer coefficients should correlate well with similar characteristic systems, i.e., sparingly soluble substances with high D-values (or Henry's Law Constants). Sparingly soluble systems of gas such as nitrogen, oxygen, carbon dioxide and argon in water all have been experimentally observed to have about the same mass transfer coefficient as the correlated results for oxygen [MCWHIRTER-1978]. For mass transfer of volatile organic compounds, the alpha factor, the ratio of the VOC mass transfer coefficient to the mass transfer coefficient of oxygen has been reported in the range of 0.5-0.7 [ROBERTS-1984, SMITH-1979], even for components with high solubilities in water such as acetone or chloroform. For these conditions, the mass transfer coefficients are very close to the values reported by Zander et al. [ZANDER-1989] in their gas-filled microporous composite membrane extraction module (0.6-2.5 x 10^{-3}cm/s). Therefore, the alpha factor for extraction in this system approaches unity based on these data because the oxygen-water correlations agree so well with Zander's results. All the diffusivities are within 15% of each other, so it should be expected that the individual film mass transfer coefficients should all fall within about the same range. As seen in Table 6, the individual film coefficients for the tube-side, membrane, and shell-side all do fall within the same range. The overall coefficients, however, vary by more than an order of magnitude due to the variation in the D-values. If this were not the case, the mass transfer coefficient for methylene chloride should be similar to the mass transfer coefficient of carbon tetrachloride instead of an order of magnitude smaller, as predicted by Eq. 11.

Table 7. Overall Mass Transfer Coefficients in the MASX, and the Percentage Removal for a 2 m Fiber

Component	$K_L a$ (HR^{-1})	% Removal 2 m Fiber
Methylene Chloride	169.4	79.8
Trans-1,2-Dichloroethylene	412.9	98.4
Cis-1,2-Dichloroethylene	385.8	97.8
Chloroform	284.2	93.8
1,1,1-Trichloroethane	893.6	>99.9
Carbon Tetrachloride	1931.3	>99.9
Benzene	605.6	99.8
Trichloroethylene	952.9	>99.9

MADS Unit Design

The MADS unit is unique because it operates at a relatively high temperature 70-90°C. If a MADS were coupled to the MASX previously described, and the MASX were made long enough so that the VOCs in the aqueous stream exited at a concentration near the drinking water standards (10 ppb for each component), a stream of oil at a flowrate of 37.85 L/min with about 100 ppm of each VOC would leave the MASX unit and need to be regenerated in the MADS unit. This assumes a concentration of 10 ppm for all VOCs in the groundwater feed.

The mass transfer in the MADS unit can be modeled in the same way as the MASX unit. For the oil flowing through the fibers the following equation applies.

$$v\frac{dC_{oi}}{dz} = -K_L a\,(C_{oi} - C_{oi}^*) \tag{14}$$

As in the case of the MASX unit, the interfacial area can be calculated from the geometry of the membranes. In this case the oil gas interface is immobilized at the outside wall of the fibers so that the interfacial area per unit fiber volume is simply $4/d_{OD}$.

If the stripping gas is assumed to enter the module clean, containing no VOCs, the following material balance will apply at any cross section in the module.

$$C_{gi} = \frac{V}{G}\,(C_{oi-in} - C_{oi}) \tag{15}$$

By using the definition of Henry's Law Constant, Eq. 15 can be rewritten as,

$$C_{oi}^* = \frac{V}{GH_i}\,(C_{oi-in} - C_{oi}) \tag{16}$$

Equation 16 can be substituted into Eq. 14 for C_{oi}^* and integrated with the boundary condition $C_{oi} = C_{oi-in}$ at z=0.

$$\frac{C_{oi}}{C_{oi\text{-}in}} = \frac{R_i \, EXP\left(\frac{K_La}{v} z \frac{(R_i - 1)}{R_i}\right) - 1}{R_i - 1} \tag{17}$$

R_i is equal to GH_i/V in Eq. 17. Solution of Eq. 17 will give the concentration of VOC_i for any fiber length z in a counter-current shell and tube module, providing the overall mass transfer coefficient K_La is known, just like the case for the MASX. Equation 17 is similar to the well known published equations to design an air stripping column [OKONIEWSKI-1992].

As with modeling the MASX, an estimate of the mass transfer coefficient is needed for the MADS unit. In the MADS, oil will be in the lumen and a strip gas will be in the shell. The strip gas pressure must exceed the oil pressure so that the oil is contained in the pores. The oil could also be contained in the pores by using a coated membrane fiber; however, this solid film would significantly increase the resistance to mass transfer.

Since oil is in both the tube and the fiber pores, Eq. 11 does not apply. An alternative form of Eq. 11 for this situation derived by Prasad and Sirkar [PRASAD and SIRKAR-1988] is given below. If a composite membrane with a dense phase coated fiber is used, an additional term including the resistance of the dense phase would need to be included in Eq. 18.

$$\frac{1}{K_L d_{OD}} = \frac{1}{k_{Lt} d_{OD}} + \frac{1}{k_m d_{LM}} + \frac{H_i}{k_{Ls} d_{OD}} \tag{18}$$

The gas-phase mass transfer can be neglected since H_i is a small number for the sunflower oil system as shown previously in Table 2. An estimate of both the tube side mass transfer coefficient and the membrane mass transfer coefficient was obtained for sunflower oil at 90°C, then the overall mass transfer coefficient was calculated using Eq. 18.

The membrane resistance can be estimated using the diffusivity of the VOCs in sunflower oil and the membrane properties reported in Table 6. The diffusivity of the VOCs in sunflower oil was adjusted for temperature using the Stokes-Einstein dependencies as shown by Eq. 13. The viscosity of sunflower oil at both 20°C and 90°C as shown in Fig. 5 was used in this calculation. This procedure is discussed in the Chemical Engineer's Handbook for adjusting diffusivity for temperature [Perry-1984]; it is empirical and it is inadequate compared to experimental data. It was

used since no data are currently available for the sunflower oil system at the conditions in the MADS. Once the diffusivity was estimated, Eq. 10 was used to calculate k_m, and the results are shown in Table 8. Based on this diffusivity estimate, the values of k_m are small, and thus the membrane resistance is the major factor in the overall mass transfer resistance.

There are no available correlations for the tube-side resistances for sunflower oil at 90°C. As an estimate, the surface mass transfer coefficients from the zero gas rate experiments in the sparged reactor at 90°C were used. These numbers are shown in Table 8. The values of k_{Lt} from this estimate ranged from 4.0×10^{-4} to 1.0×10^{-3} cm/s, about 1-2 orders of magnitude larger than the estimated values of k_m for oil at 90°C in the MADS membrane as well as the values of k_{Lt} predicted for the water in the tube-side of the MASX (Table 5). Thus, the tube-side resistance in the MADS is small, and the overall mass transfer resistance is dominated by the membrane resistance. The overall mass transfer coefficients in the MADS are summarized in Table 8.

Table 8. Mass Transfer Coefficients in MADS

Component	Diffusivity 90°C (10^{-6} cm^2/s)	k_{Lt} (10^{-4} cm/s)	k_m (10^{-5} cm/s)	K_L (10^{-5} cm/s)
Methylene Chloride	1.53	9.61	6.11	5.32
Trans-1,2-Dichloroethylene	1.37	11.9	5.46	4.84
Cis-1,2-Dichloroethylene	1.38	6.47	5.52	4.72
Chloroform	1.33	6.89	5.33	4.59
1,1,1-Trichloroethane	1.17	5.70	4.69	4.02
Carbon Tetrachloride	1.19	6.27	4.78	4.12
Benzene	1.25	4.69	5.02	4.22
Trichloroethylene	1.25	4.70	4.99	4.20

The overall mass transfer coefficients in the MADS are predicted in the range of $4.0\text{-}5.5 \times 10^{-3}$ S^{-1}. These estimates will have to be verified in a pilot study. The results of the design calculations for the MADS are shown in Fig. 7, the stripping gas flow was chosen to be 50 L/min for these calculations.

As shown in the figure, methylene chloride is the easiest component to strip, this should be no surprise since it was the most difficult to extract. 1,1,1-Trichloroethane is the most difficult component to strip since it has the smallest mass transfer coefficient due its small diffusivity. Methylene chloride has the largest diffusivity. All the other VOCs are intermediate between these two cases and are not shown on the figure. The VOC components were removed from the oil at rates directly proportional to their diffusivities. A MADS about 10-11 m fiber length is adequate to reduce the VOCs concentration in the oil phase by a factor of 10. Another factor of 10 would require the same length of fiber. Fiber length could be increased by putting modules in series or parallel. A parallel configuration would be effective at increasing the fiber length until the flow rate though the fiber would be cut to the point that it increased tube side resistance. In order for the oil to be recycled to the MASX unit, it must be decontaminated to a level good enough so that the MASX unit meets its performance requirements. The oil fed back to the MASX must be low enough in VOCs so that groundwater does not strip VOCs from the oil and make the aqueous contamination worse. The oil purity criteria is easily calculated using the extraction factor and the minimum length of the MADS fiber can be calculated once this target concentration is known. For MASX concentrations of groundwater approaching 10 ppb, the minimum purity of the oil and the length of the required fiber is listed in Table 9.

Table 9. Minimum Oil Purity Required for Recycle Back to MASX and the Required Fiber Length in the MADS

Component	Minimum Oil Concentration (ppb)	Length of Fiber Required[a] (m)
Methylene Chloride	47	28.9
Trans-1,2-Dichloroethylene	130	28.3
Cis-1,2-Dichloroethylene	120	28.7
Chloroform	91	30.2
1,1,1-Trichloroethane	340	28.4
Carbon Tetrachloride	770	23.8
Benzene	220	29.2
Trichloroethylene	340	27.2

[a]Series joining of modules.

As shown in Table 9, chloroform controls the design of the MADS when the concentration of all components are equaldue to a combination of high required purity in the oil and its difficulty to strip from the oil. The component that controls the design must be evaluated on a case to case basis. It is determined by a combination of factors such as the purity required in the decontaminated water, its D-value in the extraction step, its oil-phase Henry's Law constant, and its oil phase diffusivity.

Since diffusion in the pores of the membrane dominates the mass transfer resistance in the MADS, this design calculation was largely based on a diffusivity estimate from the empirical form of the Stokes-Einstein Equation. Other forms to adjust diffusivity have been proposed which give significantly different results from the Stokes-Einstein result. Compared to water, sunflower oil should have a much smaller diffusivity for each of the VOCs. It is also expected that diffusivity should increase with temperature. The trend in the Stokes-Einstein predicted result is in the right direction, but it is likely that it is not very accurate. Thus, the large size of the MADS required for this process may be an overly conservative design. Pilot studies are planned to verify the mass transfer in the MADS and obtain accurate measurements of local mass transfer coefficients.

Condenser Performance Estimate

The strip gas exiting the MADS will contain a trace of vaporized sunflower oil, but will contain mostly water vapor and VOCs. Water will be extracted into the sunflower oil in the MASX. Karl Fisher Titration results indicate that 1.98 g/L sunflower oil will be extracted in the MASX at 20°C. If all this water is assumed to vaporize in the MADS along with the VOCs, and this gas is passed through an equilibrium condenser at 10°C, the condenser performance in Table 10 is expected. In this calculation, none of the sunflower oil is assumed to vaporize. Natural oils like sunflower oil, all triglycerides with C_{18} fatty acid chain length, have very low vapor pressures (1.3×10^{-5} atm at 254°C) [SWERN-1979]. This low vapor pressure results in an insignificant amount of sunflower oil vaporization in the MADS. The Henry's Law constants published for water at 10°C were used in the condenser performance calculation. Some of the Henry's Law Constants for VOCs in water at 10°C were not published so they were estimated from data in the 20-25°C range [YAWS-1991, MUNZ-1987,

KAVANAUGH-1980]. There is a large variation in published values of the Henry's Law constants for the VOCs in water, and these numbers will have to be verified experimentally.

As shown in the table, recovery of the VOCs from the strip gas is poor and this recovery is not high enough to recycle this gas back to the MADS. Although the concentration of VOCs in the product liquid is high, approaching 1 % for each VOC, the flow rate of this water is small (75 cm^3/min) and most VOCs remain in the gas phase. In order to improve the performance of this condenser a lower temperature can be used. Another way to improve this design is to stage the condensers, but this improvement is not that significant, especially for components with large Henry's Law Constants in water such as carbon tetrachloride or 1,1,1-trichloroethane. In order to recycle the strip gas back to the MADS the gas must be cleaned much better. An adsorbent in the gas line would be required to recover enough VOCs to recycle the gas. Activated carbon could be used, but also it is possible to use sunflower oil at a low temperature (20°C), with very small Henry's Law Constants, to recover the VOCs. The flow rate of this sunflower oil strip solution would be significantly lower than the flow in the MADS (<0.01%) . Experimental determination of this effect is currently planned.

Table 10. Performance of MADS Condenser at 10°C

	Inlet Flows moL/min	Henry's constant 10°C	Exit Liquid Conc. ppm	Exit Vapor Flows moL/min	Percent Removal from Strip Gas
Strip Gas	1.6777	-	-	1.6777	-
Water	4.1607	-	-	0.0203	99.5
Methylene Chloride	0.0446	0.040	10500	0.0353	20.7
Trans-1,2- Dichloroethylene	0.0390	0.133	11600	0.0301	22.9
Cis-1,2- Dichloroethylene	0.0390	0.147	11600	0.0301	22.9
Chloroform	0.0317	0.076	13600	0.0232	26.8
1,1,1- Trichloroethane	0.0284	0.352	14700	0.0201	29.1
Benzene	0.0485	0.102	9800	0.0391	19.3
Carbon Tetrachloride	0.0246	0.606	16300	0.0167	32.1
Trichloroethylene	0.0288	0.191	14600	0.0205	28.7

Conclusions

Based on experimental equilibrium data for the sunflower oil-water-VOCs system and previous work evaluating mass transfer coefficients, the MASX/MADS concept is functional. High D-values significantly improve the MASX performance. The MADS performance is about the same for each VOC since all the diffusivities are about the same. The controlling feature in designing the MADS is the minimum oil concentration required for recycle, which depends on the D-value in the MASX. Thus, low D-value components, which require a high oil purity for recycle, or very low diffusivity components in the MADS, will determine the critical species in designing this device. Condenser performance after the MADS is calculated to be ineffective alone and only 20-30 % of the VOCs are recovered from the gas phase in this condenser. Staging the condensers does not significantly improve its performance. In order to recycle the gas to the MADS, the VOCs must be removed by sunflower oil at

~20°C. Experimental pilot data (Water flow 40 L/min) is required to verify the mass transfer coefficients in both the MASX and especially the MADS to verify the design formulated here which was based on lab-scale experiments (Water flow 400 cm^3/min). Pilot mass transfer data to design the MADS is not yet available.

The design basis for the MASX/MADS requires a very high level of performance for this equipment, a decontamination factor of 1000 for the aqueous side. This factor is significantly larger than what is typical for competitive remediation equipment. If the system were operated at a larger O/A, the performance of the MASX would be improved. Also, the performance of the MADS would be improved due to the higher carry-over of water into the condenser. The design of the MASX/MADS will have to be optimized to determine its complete capabilities.

Nomenclature

a_s = Turbulent liquid surface area per unit bulk liquid volume, cm^2/cm^3

a = Interfacial area per unit fiber volume, cm^2/cm^3

C_{oi} = VOC component i concentration in the oil phase, mol/cm^3 or mg/L

C_i = VOC component i concentration in the aqueous phase, mol/cm^3 or mg/L

C_{oi}^* = VOC component i concentration in the oil phase that is in equilibrium with the VOC$_i$ in the gas phase adjacent in the shell or at the turbulent liquid surface in the sparged gas reactor, mol/cm^3 or mg/L

C_i^* = VOC component i concentration in the aqueous phase that is in equilibrium with the VOC$_i$ in the oil phase adjacent in the shell, mol/cm^3 or mg/L

$C_{i\text{-in}}$ = Aqueous concentration of VOC$_i$ entering the module, mol/cm^3 or mg/L

$C_{oi\text{-in}}$ = Oil concentration of VOC$_i$ entering the module, mol/cm^3 or mg/L

C_{gi} = Gas concentration of VOC$_i$ entering the module, mol/cm^3

D_i = D-value$_i$, organic concentration/aqueous concentration, dimensionless

D_{AB} = Diffusivity of VOC$_i$, cm^2/s

d_{ID} = Fiber ID, cm

d_{OD} = Fiber OD, cm

d_e = Fiber equivalent diameter, cm

d_{LM} = Fiber log-mean diameter, cm

G = Gas rate, moL/s or cm^3/s

H_i= Dimensionless Henry's Law Constant for VOC$_i$

$\Delta H_{i,diss}$ = Enthalpy of dissolution of component i, J/moL

ΔH_{vap} = Enthalpy of vaporization of pure component i, J/moL

K_{LS} = Overall turbulent liquid mass transfer coefficient, cm/s

K_L = Overall laminar liquid mass transfer coefficient, cm/s

k_{Lt} = Tube-side mass transfer coefficient, cm/s

k_m = Membrane mass transfer coefficient, cm/s

k_{Ls} = Shell-side mass transfer coefficient, cm/s

R= Universal gas constant, cm^3-atm/moL-K

R_i = VD$_i$/L, dimensionless

$\Delta S_{i,diss}$ = Entropy of dissolution of J/moL-K

L = Aqueous flowrate in module, cm^3/s

M_w = Molecular weight of water, g/moL

P = Pressure of the gas in the sparged reactor, atm

t= time, s

T= Absolute temperature, K

v = Liquid velocity in fibers, cm/s

V_L = Reactor liquid volume, cm^3

V_i = Molar volume of VOC$_i$ solute, cm^3/moL

V = Oil flowrate in module, cm^3/s

z = Fiber length, cm

Greek Letters

ε = Porosity of membrane, dimensionless

μ_W = Viscosity of water, cp

τ = Tortuosity of the membrane, dimensionless

References

BIRD-1960
> Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, J. Wiley & Sons, NY, 1960, 658-661.

BROWN and SULLIVAN-1991
> Brown, R. A., and K. Sullivan, "Integrating Technologies Enhances Remediation," *Poll. Eng.*, 1991 23, 62-68.

HUTTER
> Hutter, J. C. and G. F. Vandegrift, "Decontamination of Groundwater by Using Membrane Assisted Solvent Extraction," *ACS Symp. Ser.*, No. 509, 47-60, 1992.

KAVANAUGH
> Kavanaugh, M. C., and R. R. Trussel, Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water, *J. AWWA*, Dec. 1980, 684-692.

KING-1982
> King, C. J., et al., "Equilibrium Distribution Coefficients for Extraction of Chlorinated Hydrocarbons and Aromatics from Water into Undecane," *Env. Sci. Tech.* 16(9) 624-627, 1982.

KING-1984
> King, C. J., et al., "Solvnet Extraction for Removal of Polar Organic Pollutants from Water," *Ind. Eng. Chem., Pro. Des. Dev.* 23(4) 748-754, 1984.

LIDE
> Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*, 72 ed., CRC Press, Inc., Boca Raton FL, 1991.

MACKAY-1979
> MacKay, D., W. Y. Shiu, and R. P. Sutherland, "Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants," *Env. Sci. Tech.*, 1979 13(3), 333-337.

METCALF & EDDY
> Metcalf & Eddy, Inc., *Wastewater Engineering: Treatment, Disposal, Reuse,* McGraw-Hill Book Co., Inc. 1979.

MCWHIRTER
> McWhirter, J. R., ed., *The Use of High Purity Oxygen in the Activated Sludge Process*, CRC Press, Boca Raton FL, 1978.

MCWHIRTER and HUTTER, 1989
> McWhirter, J. R., and J. C. Hutter, "Improved Oxygen Mass Transfer Modeling for Diffused/Subsurface Aeration Systems," *AIChE J.*, 1989 35(9), 1527-1534.

MUNZ
 Munz, C., and P. V. Roberts, "Air-Water Phase Equilibria of Volatile Organic Solutes," *J. AWWA*, May 1987, 62-69.

OKONIEWSKI
 Okoniewski, B. A., "Remove VOCs from Wastewater by Air Stripping,", *CEP*, Feb. 1992, 89-93.

PERRY
 Perry, R. H., ed., *Perry's Chemical Engineer's Handbook*, 6 th ed., McGraw-Hill Book Co., 1984.

PRASAD AND SIRKAR-1987
 Prasad, R., and K. K. Sirkar, "Solvent Extraction with Microporous Hydrophilic and Composite Membranes," *AIChE J.*, 1987 33(7), 1057-1066.

PRASAD and SIRKAR-1988
 Prasad, R., and K. K. Sirkar, "Dispersion-Free Solvent Extraction with Microporous Hollow-Fiber Modules," *AIChE J.*, 1988 34(2), 177-188.

PRASAD and SIRKAR-1990
 Prasad, R., and K. K. Sirkar, "Hollow Fiber Solvent Extraction: Performances and Design," *J. Mem. Sci.*, 1990 50, 153-175.

ROBERTS
 Roberts, P. V., C. Munz, and P. Dandliker, "Modeling Volatile Organic Solute Removal by Surface and Bubble Aeration," *J. WPCF*, 56(2), 1984.

SEMMENS
 Semmens, M. J., "Method of Removing Organic Volatile and Semivolatile Contaminants from Water," U. S. Patent No. 4960520, 1990.

SMITH and BOMBERGER-1978
 Smith, J. H., D. C. Bomberger, "Prediction of Volatitization of Chemicals in Water", *AIChE Sym. Ser.*, 75(190), 1978, 375-381.

SWERN
 Swern, D., ed., *Bailey's Industrial Oil and Fat Products*, 4th ed., John Wiley & Sons, Inc., 1979.

WISE and HOUGHTON
 Wise, D. L., and G. Houghton, "The Diffusion Coefficients of 10 Slightly Soluble Gases in Water at 10-60°C," *Chem. Eng. Sci.*, 21, 1966, 999.

YANG and CUSSLER-1986
 Yang, M.-C., and E. L. Cussler, "Designing Hollow-Fiber Contactors," *AIChE J.*, 1986 32(11), 1910-1916.

YAWS
    Yaws, C., H. C. Yang, and X. Pan, "Henry's Law Constants for 362 Compounds in Water," *Chem. Eng.*, Nov. 1991, 179-185.

ZANDER-1989A
    Zander, A. K., R. Qin, and M. J. Semmens, "Membrane/Oil Stripping of VOCs from Water in a Hollow Fiber Contactor," *J. Env. Eng.*, 1989 115, 768-784.

ZANDER-1989B
    Zander, A. K., M. J. Semmens, and R. M. Narbaitz, "Removing VOCs by Membrane Stripping," *J. AWWA*, Nov. 1989, 76-80.
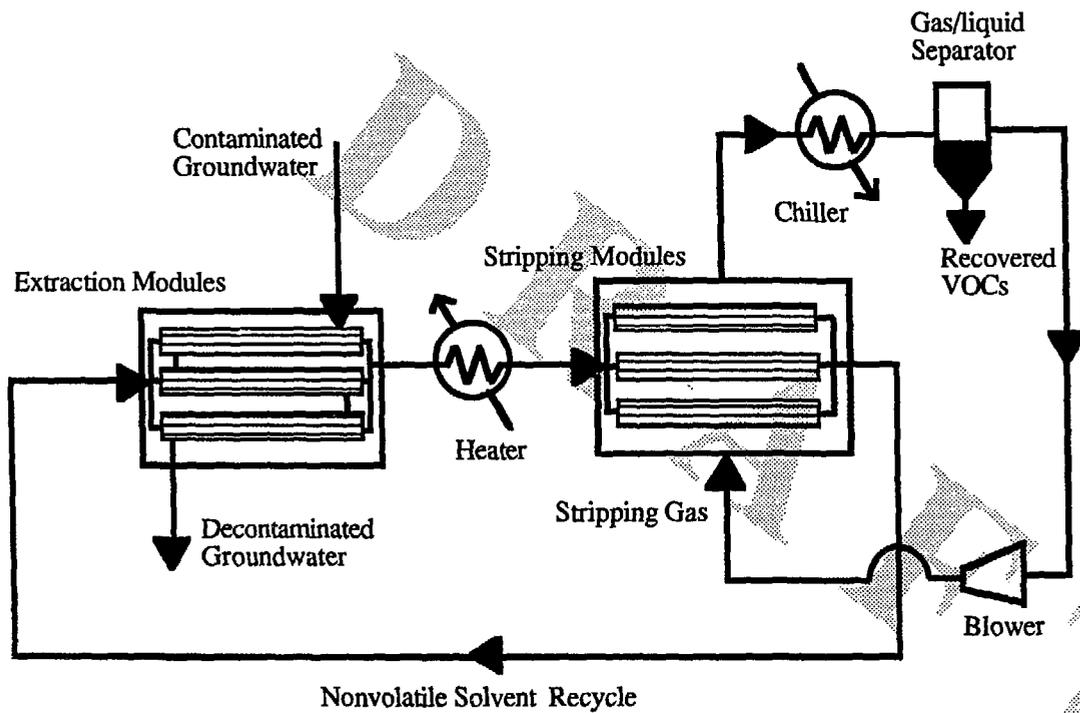
Gas/liquid
Separator

Contaminated
Groundwater

Chiller

Stripping Modules

Extraction Modules

Recovered
VOCs

Heater

Decontaminated
Groundwater

Stripping Gas

Blower

Nonvolatile Solvent Recycle

Figure 1. Flow Diagram of MASX/MADS Process
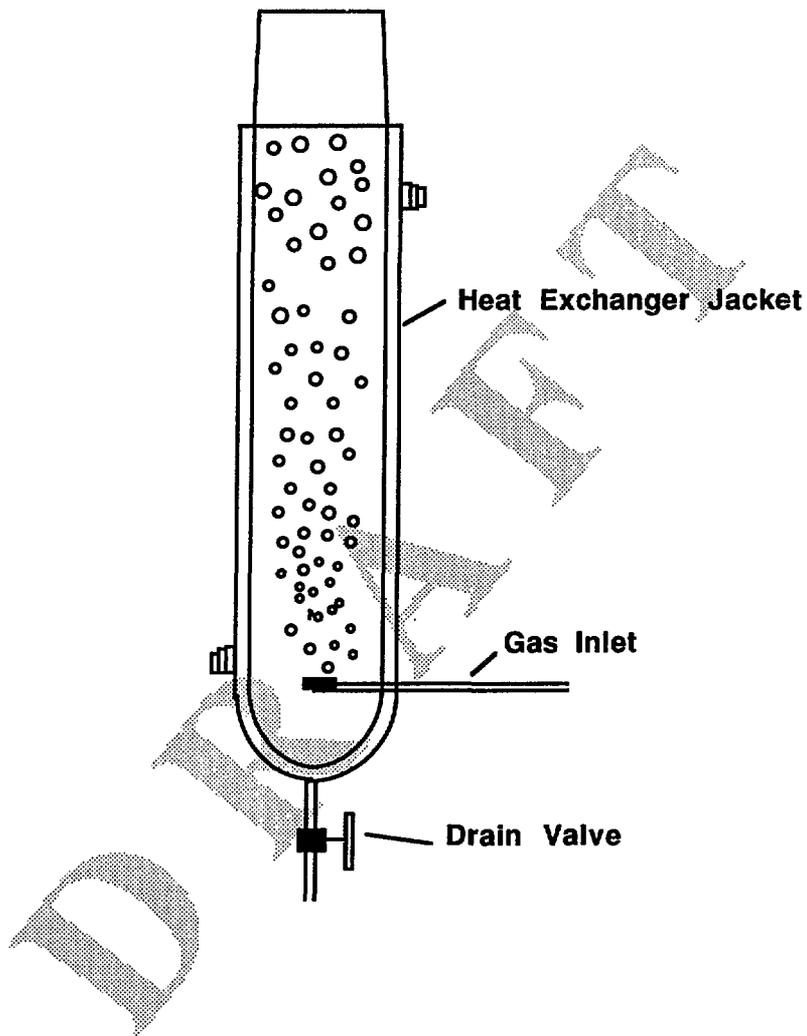
Figure 2. Sparged Reactor Used to Evaluate Henry's Law Constants of VOCs in Sunflower Oil
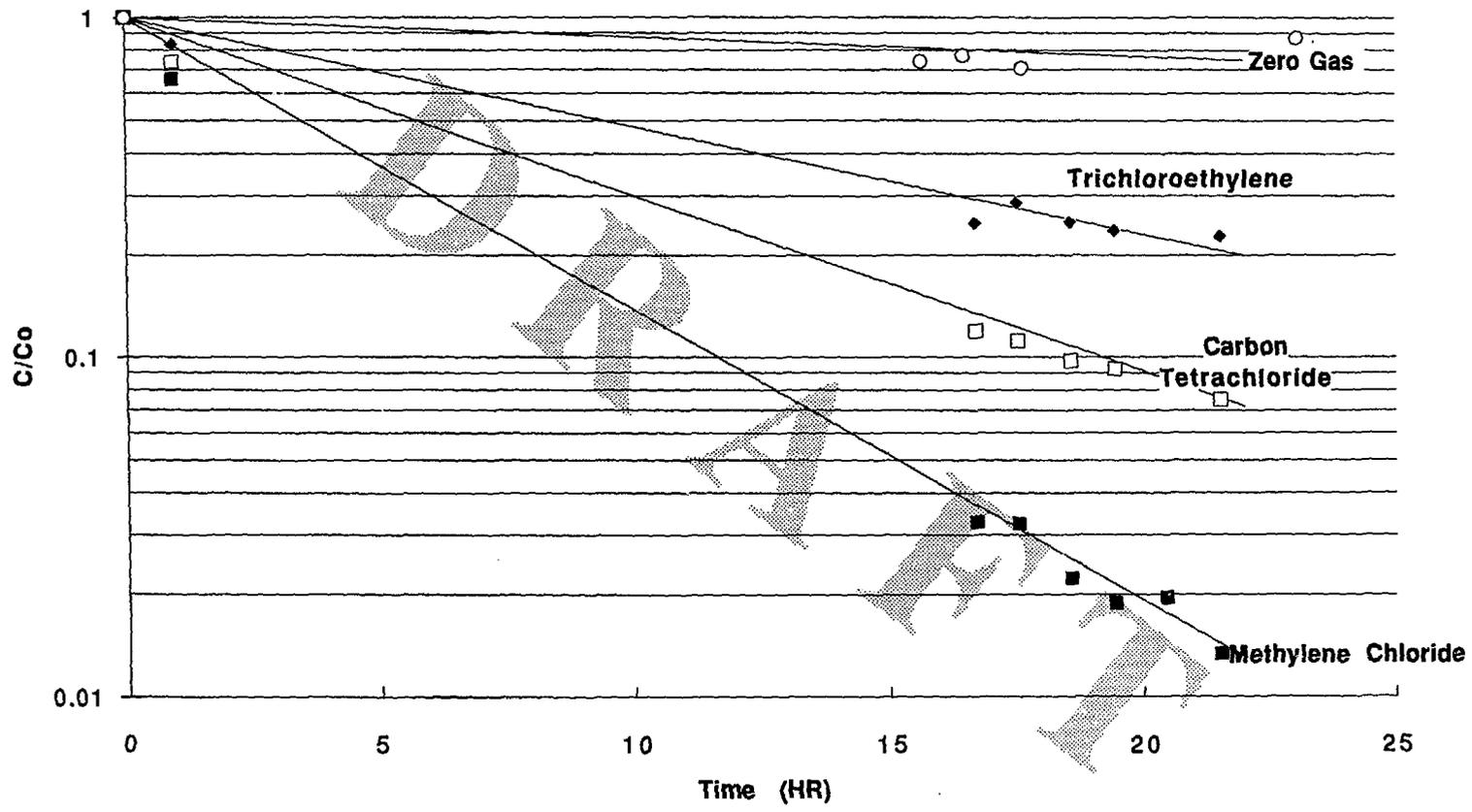
Figure 3. Plot of Experimental Data Obtained from the Sparged Gas Reactor at 70°C, with a Gas Rate of 2.71 mL/s
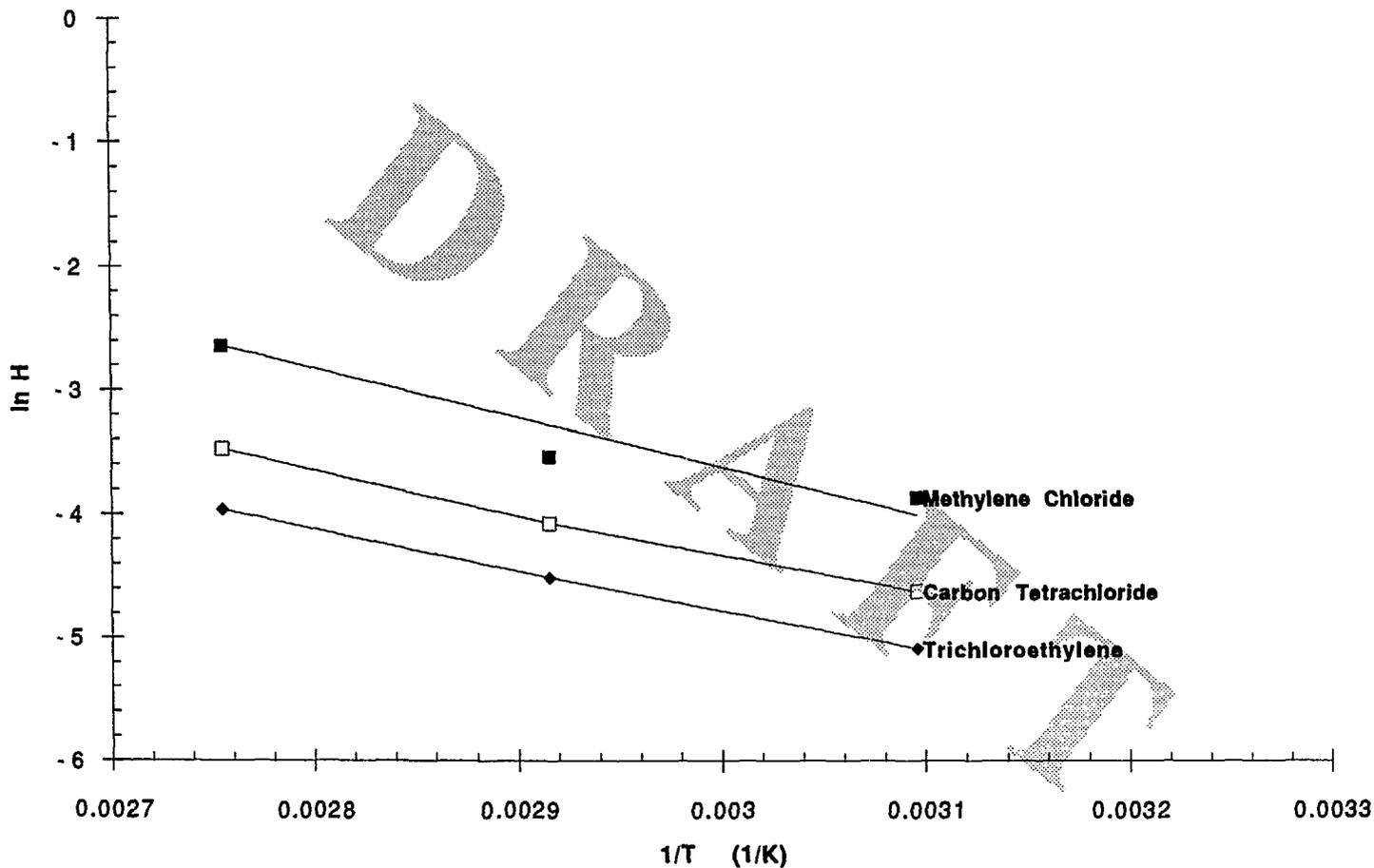
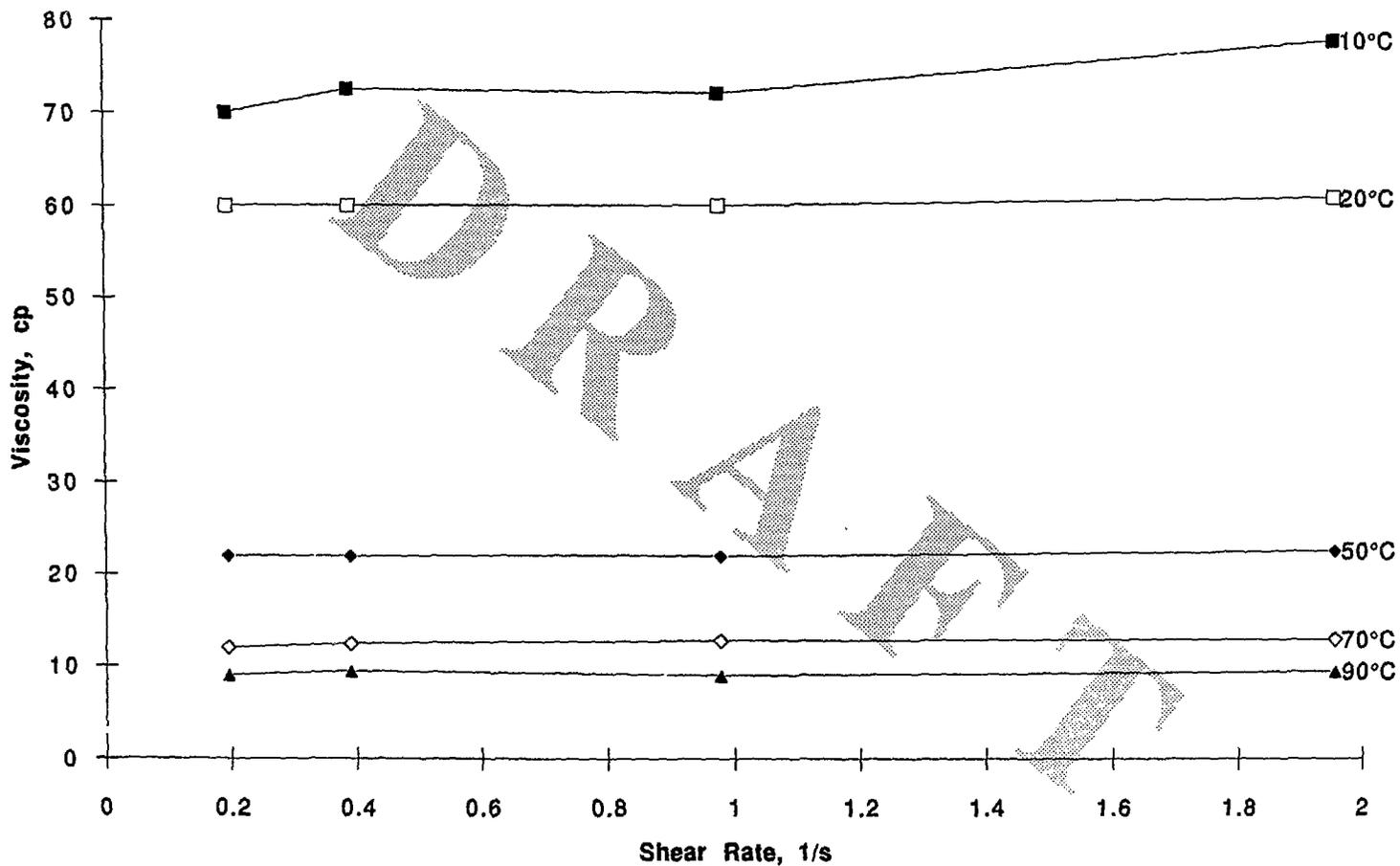Figure 4. Plot of Ln H_i vs. 1/T of Various VOCs in Sunflower Oil
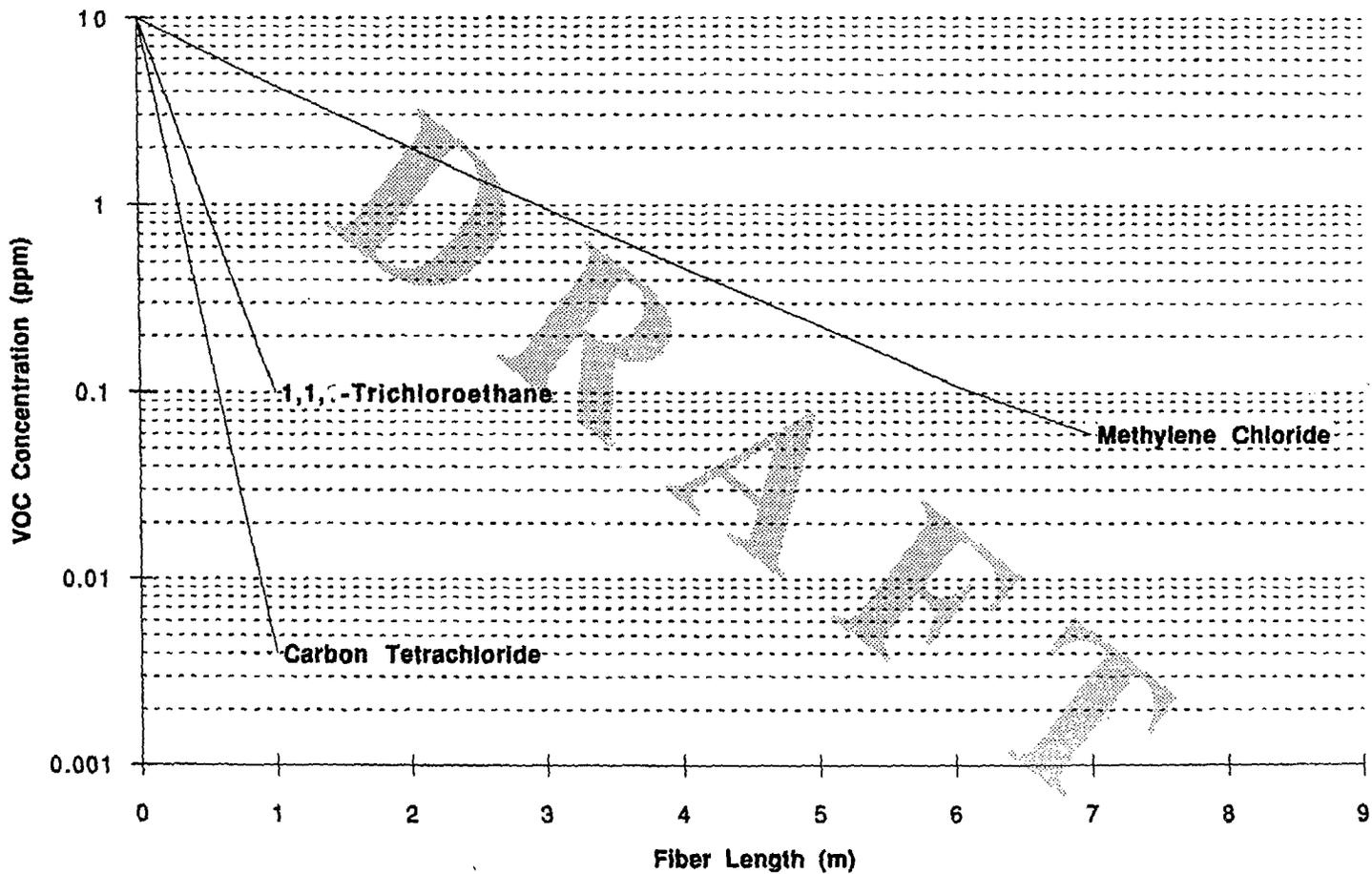
Figure 5. Viscosity vs. Shear Rate for Sunflower Oil

Figure 6. Concentration vs. Fiber Length in the MASX Using the Mass Transfer Coefficients in Table 6.
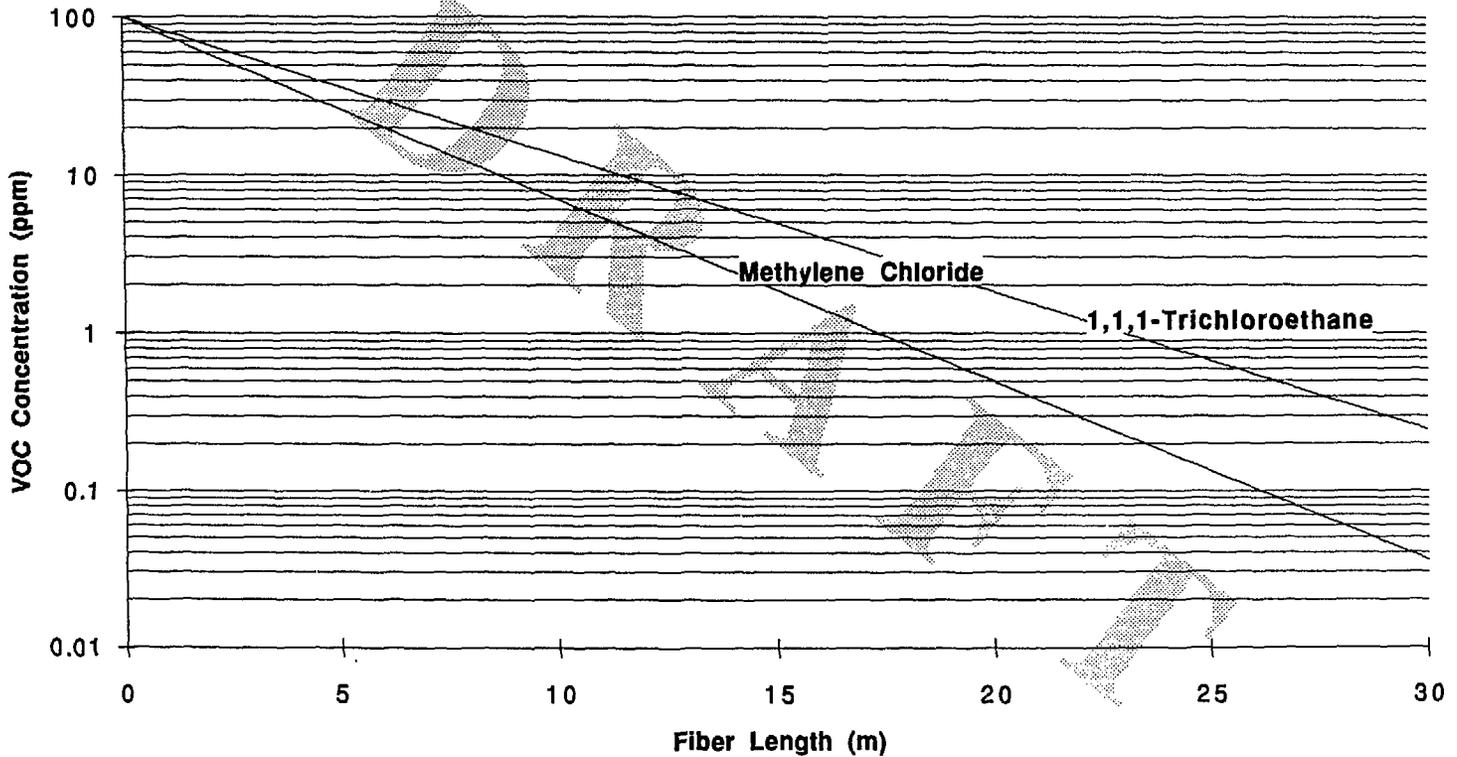
MADS Unit Design

Figure 7. Concentration vs. Fiber Length in MADS Using Mass Transfer Coefficients at 90°C in Table 8.