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Mass separation techniques for the design of fixed film bioreactors

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MASS SEPARATION TECHNIQUES

FOR THE DESIGN OF FIXED FILM BIOREACTORS

by

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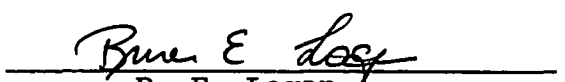
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ABSTRACT

Dissolved organics in wastewater samples were separated into three size fractions (0 - 1,000 amu, 1,000 - 10,000 amu, and 10,000 amu - 0.22 m) using ultrafiltration (UF) membranes. The mass distribution within each fraction was adjusted by using a new permeation coefficient model to account for membrane rejection.

Dissolved organic and soluble BOD (sBOD) removals in a trickling filter were studied for the different size fractions. The Logan trickling filter model was recalibrated and used to generate predicted removals by size fraction of sBOD, dissolved organic carbon (DOC), and biodegradable DOC (bDOC) for a given influent. Although there was moderate agreement between observed and predicted removals, more investigation is needed to explain shifts in material between different size fractions. Of the three parameters, bDOC may offer a better parameter for modelling trickling filter performance than sBOD.

MASS SEPARATION TECHNIQUES FOR THE DESIGN OF FIXED FILM BIOREACTORS

1. INTRODUCTION

Biological treatment of municipal wastewaters using trickling filters has proven in practice to be very cost-effective. Municipal wastewater varies widely in its content, but includes soluble greases, proteins, and carbohydrates, the nature of which affects the mechanisms and kinetics of the removal process. A better understanding of the mechanisms involved in the biodegradation of pollutants in fixed-film bioreactors will enhance the design and operation of trickling filters, and may extend their use into areas of toxic waste treatment (Hannah, 1988) which are of monumental concern.

Currently, the most commonly used design equation for describing trickling filter performance is the modified Velz equation. A basic assumption of this equation is that soluble biochemical oxygen demand (sBOD) removal follows a first order kinetic model. A careful examination of sBOD removals in trickling filters shows that the first order rate coefficients for the modified Velz representation vary with differing media and wastewater composition (Parker and Merrill, 1984). These variations require lengthy pilot plant studies to determine the Velz constants for a given media and wastewater.

A trickling filter model developed by Logan *et al.*, (1987a) better approximates the performance of trickling filters. The model predicts sBOD removal based on the diffusivities of soluble organic molecular weight fractions and accounts for some variations in performance based on the following synthetic filter media characteristics:

surface angles	-	affect flow velocity and liquid film thickness.
continuous surface length	-	related to the amount of mixing resulting from discontinuities between plates.
specific surface area	-	related to the hydraulic loading rate (wastewater applied per unit area) based on a unit flow rate.

Logan's model establishes a basis for extending pilot study results from one kind of synthetic media to any of the other plastic media types, potentially reducing the costs of the pilot studies, (Logan *et al.*, 1987b). At present, a pilot study is still necessary in order to calibrate the Logan model to the specific wastewater to be treated.

This study was undertaken to further clarify the mechanisms of sBOD and dissolved organic carbon (DOC) removal as a function of the specific characteristics of a wastewater. The research examined the relationship of the molecular size distribution of a wastewater to substrate removal in trickling filters. The primary question to be answered is: "Can the removal of the sBOD in a trickling filter be predicted based on the apparent molecular weights

of the soluble constituents in the feed stream?" This study should provide the basis for further calibrating the Logan model for direct application to any wastewater. Eventually, this would allow a laboratory analysis of the wastewater to supercede pilot studies for trickling filter design, resulting in tremendous savings in cost and time when designing a trickling filter.

Secondary objectives deal with improving molecular weight separation techniques; exploring specific techniques for generating the necessary information to apply the Logan model. Size exclusion techniques investigated include liquid chromatography and ultrafiltration with emphasis on the development of a convenient method for determining ultrafiltration membrane permeation characteristics. To quantify the residual soluble organics, the biochemical oxygen demand of the various size fractions of wastewater constituents is determined using standard bottle and respirometer techniques. These BOD measurements are compared to dissolved organic carbon (DOC) concentrations for the various molecular weight fractions. Based on these investigations, recommendations are made for methods to determine the wastewater characteristics necessary for application of the Logan model.

2. LITERATURE REVIEW

The literature reviewed for this study covers the major developments of trickling filter models, with a special emphasis on the model developed by Logan, *et al.* (1987a,b). That model leads logically into the investigations presented in this work, and so deserves special treatment in order to understand the full implications of the research.

A second area covered by the literature deals with advances in ultrafiltration theory and related techniques. The theory of ultrafiltration and membrane technology has generated a good deal of interest in recent years. The work of other researchers in this advancing field will be examined, especially where their work relates to characterizing molecular size distributions of organics in wastewaters. Existing methods for categorizing size distributions will also be reviewed.

2.1. Review of Existing Models

2.1.1. The NRC Model

The National Research Council developed a model in 1946, (see Baker and Graves, 1968), which is based on an empirical correlation of results from similar trickling filters. A form of the model is:

$$E = \frac{1}{1 + 0.0561(w/(V_m R_f))^{\frac{1}{2}}} \qquad (2.1)$$

E : the fraction of BOD removed : $\frac{BOD_{in} - BOD_{out}}{BOD_{in}}$

w : the loading rate : [lb-BOD/day]

V_m : Volume of media in 1000 ft^2

R_f : Recycle factor : $\frac{1 + R_r}{(1 + (1-p)R_r)^2}$ (2.2)

p : weighting factor ~ .9

R_r : recycle ratio : $\frac{\text{recycle flow}}{\text{inflow}}$: $\frac{(Q_r)}{(Q_i)}$

There are several limitations to the NRC model. There are no allowances for differences in temperature although temperature can significantly affect the fluid viscosities and thus the fluid detention times and liquid film thicknesses within the trickling filter. In addition, temperature affects the diffusivities of substrates, a factor to be discussed later in this work. Finally, temperature also affects the kinetics of the biological process and the viability of organisms in the biofilm (Metcalf & Eddy, 1972, pp. 400-418).

The NRC model does not specifically address variations in media and configuration. Although generally used in early attempts to correlate results from stone media trickling filters, equation 2.1 does not make allowances for variation in media size or angularity, including

specific surface area and porosity, which should affect BOD removal.

Finally, no attempt is made to tailor this equation to specific wastewater characteristics, beyond total BOD loading. As shall be seen, certain characteristics of a wastewater can have fundamental effects on removal mechanisms and efficiencies.

2.1.2. The Modified Velz Equation

W.E. Howland (1958) developed an equation which takes into account the average hydraulic residence time on an inclined plate, which is related to the contact time of a substrate with a biofilm. The theory takes into account the fluid viscosity, (including temperature affects), as well as the plate characteristics. Howland assumed that removal is a function of contact time, thus paving the way for a more robust trickling filter model.

Howland's equation was eventually modified to produce the modified Velz equation. One form of the modified Velz equation follows (Parker and Merrill, 1984):

$$\frac{S_1}{S_2} = [R + 1] \exp\left[\frac{k_{20} A_s D \Theta^{(T-20)}}{[Q_i (R + 1)]^n}\right] - R \qquad (2.3)$$

S_1 : dissolved BOD_5 concentration in the trickling filter influent before recycle flow is added. [mg/l]

S_2 : dissolved BOD_5 concentration in the trickling filter underflow. [mg/l]

R : recycle ratio : $\frac{\text{recycle flow rate}}{\text{effluent flow rate}} : \frac{(Q_r)}{(Q_e)}$

k_{20}: first order reaction rate coefficient @ 20°C. $[\frac{L}{m^2 sec}]^n$

A_s : media specific surface area. [m^2/m^3]

D : media depth. [m]

Θ : temperature correction coefficient. [dimensionless]

T : wastewater temperature. [°C]

Q_i : trickling filter feed flux : $\frac{\text{effluent flow}}{\text{x-sectional area}} : [\frac{L}{m^2 sec}]$

n : dimensionless flow exponent ~ .5

The Velz equation is essentially a two-dimensional empirical model of trickling filter performance. Some of the assumptions of the Velz relationships are:

1) The k_{20} reaction rate coefficient is constant for a given wastewater and filter configuration.

2) The removal is governed by biological kinetics rather than oxygen transfer or substrate diffusion limitations.

The modified Velz equation is widely used for the design of trickling filters but requires a pilot study to determine k_{20} and n for each media, wastewater, and filter geometry since these constants vary with the characteristics of plastic media (Parker and Merrill, 1984). Parker and Merrill also reported significant

changes in k_{20} values as the initial sBOD concentrations or other characteristics of the wastewater changed due to annual cycles.

The k_{20} factor, which is a kinetic coefficient, varies with differing media geometries even when run with the same wastewater (Richards and Reinhard, 1984). Logically, biofilm microbial kinetics should be roughly equivalent when based on the same wastewater regardless of media geometry. Thus, it would be more accurate to attribute the differences in removals to media geometry rather than biological kinetics.

2.1.3. The Logan Model

The Logan model (Logan, 1986; Logan, *et al.* 1987a,b) builds on the assumptions inherent to other trickling filter models by adding the provisions for media and wastewater characteristics. The additional assumptions set forth by Logan are:

1) The removal of sBOD in trickling filters is related to the diffusivities of the wastewater constituents. ie: the mass transfer of constituents in the fluid film is important as well as the biological kinetics.

2) The hydraulic regime is of the thin fluid film is assumed to be laminar rather than completely mixed.

The Logan model takes into account the theory of substrate uptake by attached biofilms on inclined plates, as developed by Howland (1958) and others (Atkinson *et al.*, 1967; Maier *et al.*, 1967). BOD removal is related to diffusivity via coupling of a model of substrate flux through the thin fluid film to the hydraulics of flow through plastic media in trickling filters.

The Logan model consists of three major components. The first building block is a calculation of the substrate flux into a deep (mature) biofilm based on a first order kinetic model (Logan, *et al.*, 1987a):

$$J_b = C_s D \left[\frac{3E_B(1-\epsilon)}{a_c^2}\right]^{\frac{1}{2}} \qquad (2.4)$$

J_b : substrate flux in the biofilm [mg-BOD_5/cm^2-s]

C_s : surface substrate concentration [mg-BOD_5/cm^3]

D : molecular diffusivity [cm^2/s]

E_B : collision efficiency or flux constant. (includes a factor for reduction of diffusivity in the film and reduced cell viability.) [dimensionless]

ϵ : biofilm porosity [dimensionless]

a_c : cell radius [cm]

Therefore, the flux J_b is a function of cell size, substrate diffusivity, biofilm porosity, and the collision efficiency (via Brownian motion), of substrate molecules with cells in the biofilm.

Second, the flow over the trickling filter media is assumed to be laminar rather than completely mixed. This results from calculations of the flow velocity due to gravity, slope, and roughness, resulting in Reynold's numbers generally between 1 and 10 (Logan, *et al.*, 1986). The flow velocity profile used by Logan is a uniform, parabolic approximation of flow down an inclined flat plate, as given by Bird *et al.*, (1960), where the average velocity $\bar{v}$ is given as follows:

$$\bar{v} = \frac{\rho g \delta^2 \cos\beta}{3\mu} \qquad (2.5)$$

ρ : liquid density [mass/vol.] : .9982 g/cm^2 @ 20°C.

g : accel. due to gravity : 980.7 cm/sec^2

δ : film thickness [length in cm]

β : Angle of plate from vertical

μ : liquid viscosity ~ 0.01002 g/cm-sec

The Reynold's number (Re) can be calculated as follows:

$$\mathrm{Re} = \frac{\delta \bar{v} \rho}{\mu} \qquad (2.6)$$

For a typical measured fluid thickness of 100 μm and a plate angle of 30° from the vertical, the average fluid velocity is 8.5 cm/sec. This results in a Reynold's number of 8.5, which indicates some rippling may occur in the fluid flow, although the flow regime is much less than the region of

flow classified as turbulent. Reynold's numbers below 6 describe clearly laminar flow while above 250, the flow is characterized by turbulence (Bird *et al.*, 1960, p. 41). For Reynold's numbers greater than 6, the flow may be somewhat wavy or transitional, but in general, laminar flow can be assumed in a trickling filter. Surface roughness is damped out under these conditions rather than creating turbulent flow.

The most important hydraulic considerations are the discontinuities at the end of every module and the fluid mixing which takes place at flow intersections. Fluid mixing is assumed to occur at any place where the fluid separates from the media, and at any place within media where fluid streams intersect. Fluid applied to plastic trickling filter media forms a thin fluid film which separates from the media at the end of every module, either as droplets or as free jets, (Logan *et al.*, 1987a). Cross-flow media has a configuration in which fluid flowing down one inclined surface periodically meets the flow on the opposing surface. The mixing from this interaction can occur several times over the length of a module.

The thickness of the thin film is a function of plate angle, specific hydraulic loading, and viscosity. Logan modeled the hydraulics of the trickling filter using these factors, which control the advective movement of the substrate through the filter.

The third component consists of a model of substrate diffusion across the fluid film into the biofilm at the same time as substrate is transported by advection in the direction of hydraulic flow. The Logan model therefore requires an estimate of the diffusivity of each substrate component.

The diffusivities used by Logan are based on molecular weight distributions reported by Levine *et al.*, (1985), correlated to diffusivities via the Polson relationship (Polson, 1950):

$$D = 2.74 \times 10^{-5} \ (MW)^{-1/3} \qquad (2.7)$$

where MW is the molecular weight in atomic mass units (amu). The diffusivities used by Logan are:

Molecular Weight (10^3 amu)	Diffusivity (10^8 cm^2/s)
3-30	112
30-50	85
50-100	65
100-500	50
500-1000	30

The diffusivities of the substrate molecules are affected by temperature, and can be corrected as follows, (Welty *et al.*, 1976):

$$D_T = D_{293} \frac{T_k}{293} \frac{\mu_{293}}{\mu_T} \qquad (2.8)$$

D_T : diffusivity at temperature T.

D_{293} : diffusivity at 293°K (20°C).

T_k : temperature in degrees Kelvin.

μ_{293} : standard viscosity at 293°K.

μ_T : viscosity at temperature T.

The previous three components of the model are combined and used to calculate the concentration of substrate within the fluid film as a function of fluid depth (x), and distance along the biofilm (z), using the explicit forward-finite difference equation (Logan *et al.*, 1986):

$$\frac{\Delta C}{\Delta t} = \frac{D}{\Delta x^2} \{C_{x-1,z} + C_{x+1,z} - 2C_{x,z}\} - \frac{v_x}{\Delta z} \{C_{x,z} - C_{x,z-1}\} \qquad (2.9)$$

C : concentration of sBOD component.

D : diffusivity of sBOD component.

v_x : velocity of the fluid at the node.

The subscripts x and z indicate node locations for the numerical solution. Boundary conditions used to solve equation 2.9 are:

1) At the plate entrance, the liquid film is completely mixed and of concentration C_o.

2) There is no sBOD flux into the air.

3) The flux of substrate out of the fluid is determined by biofilm kinetics described by equation 2.4 where $\epsilon \sim 0.8$ and $a_c \sim 1$ μm.

Equation 2.9 is iteratively solved until the average concentration of substrate leaving a plate on successive iterations differs by less than 0.01%.

Logan *et al.*, (1987b) found good correlation between the model predictions and the reported results from 10 actual trickling filters, ranging from pilot scale to full size. Discrepancies between the model and the actual data sets were attributed to differences in wastewater composition.

2.2. Molecular Weight Separations

The molecular size distribution of soluble organics in wastewater is an important factor for modelling the biological treatment process. Several investigators have noted that the biodegradation rate of organics in domestic wastewater, as measured by a BOD test, increases with decreasing size for different size fractions (Rudolfs and Gehm, 1939; Heukelekian and Balmat, 1959; Levine *et al.*, 1985). The size characteristics of dissolved organics are also an important factor in the fate of toxic pollutants in natural and engineered systems. For example, the partitioning of heavy metals and many hydrophobic toxic chemicals, such as lindane and DDT, has been shown to be related to the dissolved organic molecular weight (Chiou *et al.*, 1986). A better model of trickling filter performance

requires consideration of the diffusivities as well as the biological degradation kinetics of the substrate components. The following sections consist of a review of methods for determining the necessary molecular size distributions in wastewater.

Size distributions of dissolved organics in wastewater are determined as either a continuous distribution, using size exclusion chromatography (SEC) or as a discrete distribution, using ultrafiltration (UF). The sizes of dissolved organics are referred to as apparent molecular weights (AMW), usually in atomic mass units (amu), since separations are calibrated with compounds of known molecular weight, and not size. Both size exclusion chromatography and ultrafiltration techniques have several disadvantages.

Size exclusion chromatography techniques include both high performance liquid chromatography (HPLC) and low pressure column techniques, generally referred to as gel permeation chromatography (GPC). GPC has been used to make molecular weight determinations on wastewater by several researchers (Amy *et al.*, 1987a,b; Millot *et al.* 1987). High performance liquid chromatography has been explored as a possible method for size characterization by some other researchers (R. Gloor *et al.*, 1981).

Permeation or size exclusion chromatography is based on allowing smaller molecules to diffuse further into a

matrix gel in the column; larger molecules are not as deeply admitted, and are purged more quickly from the column by the carrier fluid. Successful separation is based on the absence of chemical interaction between the column packing, the solvent, and the organic components. However, some components may pass through the column more rapidly than calibration standards due to ion-exclusion or complex formation resulting in an overestimation of the component molecular weights. Other components may be delayed by adsorption or electrostatic interaction with column packing. Such chemical interaction would cause the size of these molecules to be underestimated. Also, sample concentration by evaporation, (Hart, 1980; van Steenderen and Malherbe, 1982), or freeze drying (Sachdev *et al.*, 1976), is often employed in order to achieve concentrations high enough to employ the SEC techniques, and may alter the sizes of dissolved components.

The alternative to SEC for determining size distributions in wastewater is separation of the material into distinct size fractions using ultrafiltration membranes. UF is better adapted to collecting large volumes of material, allowing the determination of the size distribution of dissolved components, while simultaneously separating material of a specified size fraction for additional study. The UF process uses stirred pressure vessels to drive a sample through a membrane which has a

specified nominal size cutoff, usually in angstroms. UF membranes typically have molecular weight cutoffs between 500 and 100,000 amu.

The major experimental obstacle in developing a consistent procedure to determine size distributions using UF is lack of a rapid method to quantify membrane rejection. Experiments by B. Alleman (Alleman, 1986) on paper mill wastewaters, using methods discussed below, show mass fractions able to pass the membrane can be underestimated by up to 70 percent if membrane rejection is not determined. Existing methods to account for membrane rejection are time consuming, and this may explain why many researchers do not account for membrane rejection (e.g. Grady, *et al.*, 1984; Amy, *et al.*, 1986; Namkung and Rittman, 1986; and Wheeler, 1976). Size distributions as determined by ultrafiltration for a wastewater in Tucson, Arizona are reported by Amy *et al.*, (Table 1) and show 60 percent of the organics occur in the low molecular weight (less than 500 amu) fractions. In contrast, chromatography results reported by Levine *et al.*, (1985), for primary effluents in San Diego, CA, South Lake Tahoe, CA, and Davis, CA demonstrate a "significant peak" in the size range from 5,000 amu to 20,000 amu.

TABLE 1 : Molecular size distribution of Tucson, Arizona primary effluent wastewater (Amy, *et al.*, 1986).

Size (1000 amu)	Percent of NPOC*
< 0.5	60
.5 - 5	16
5 - 10	6
10 - 30	7
30 - 100	4
> 100	7

* Given as a percent of 53.9 mg/L total NPOC.

3. METHODS

The methods described below were used to determine the molecular size distributions of sBOD and dissolved organics in wastewaters. Wastewater was fractionated using ultrafiltration (UF) membranes and then subjected to 10-day BOD tests. For each molecular weight fraction, changes in DOC were examined as well as kinetic constants and ultimate oxygen demands.

3.1. Molecular Size Distributions

Two methods were used to characterize molecular size distributions of soluble substrates in wastewater: ultrafiltration and high performance liquid chromatography (HPLC). Both methods achieve separations based on the sizes, and therefore the apparent relative diffusivities of the molecules.

3.1.1. Ultrafiltration Methods

Size distributions of organics using UF membranes were determined by parallel processing of samples through an array of membranes with different molecular weight cut-offs in stirred cells, with a measurement of the material (DOC) in each permeate. Size distributions were calculated by

subtraction of the mass in the permeate of a smaller sized membrane from the mass in the permeate from UF separation using the next incremental molecular weight cut-off membrane.

The pressure vessels used for the ultrafiltrations were obtained from Amicon division of W.R. Grace & Co. The cells had a maximum capacity of 180 mL and were 62 mm in diameter. The following Amicon Diaflo ultrafiltration membranes were used: YC05 (lot #AL25260RAR), YM2 (lot #AS3171AEAR), YM5 (lot #AN3191EFAA), YM10 (lot #A002536D), YM30 (lot #AP3120ATAR), and YM100 (lot #AL28920RAR). The Amicon diaflo membranes are constructed of unspecified inert synthetic materials. The YC05 has a nominal molecular size cutoff of 500 amu and is described by Amicon as a "low-adsorption membrane with moderate flow rates" (Amicon, 1982). The YM membranes have size cutoffs of 1,000 amu (YM2), 5,000 amu (YM5), 10,000 amu (YM10), 30,000 amu (YM30), and 100,000 amu (YM100) and are described by Amicon as "advanced hydrophilic membranes... for low non-specific protein binding properties..." (Amicon 1982).

Several methods were evaluated for determining the membrane rejection characteristics: Refiltration and the Incremental techniques based on a new permeation coefficient model, and the Dilution method developed by Alleman (1986). The molecular weight fractions determined in this study are adjusted using either the Refiltration

method for determining permeation coefficients or the earlier Dilution method, for samples taken in 1987.

For ultrafiltration membranes, the mass carried with the permeate is less than the actual material which could theoretically pass the membrane. Molecules in solution are sometimes rejected at the membrane surface for reasons distinct from size, including chemical interaction with the membrane or with other molecules on or near the surface. It is therefore important to correct the mass fraction measured, otherwise the material in the low weight fraction of the original sample will be underestimated. Corrections are typically made using a rejection coefficient as defined below.

The rejection coefficient, R, was originally developed for applications where concentration of macromolecules in a retentate is desired, and is defined as (Amicon Corp., 1982):

$$R = \frac{\ln (C_r / C'_o)}{\ln (V_o / V_f)} \qquad (3.1)$$

where V_o is the initial volume of fluid with a concentration C'_o, and V_r is the final volume of retentate after ultrafiltration of concentration C_r. For 100% rejection by the membrane, the rejection coefficient is unity; for material unhindered in passage through the membrane, the rejection coefficient is zero. Both

molecules larger than the membrane cut-off, and smaller molecules remaining in solution are measured as C_r. The concentration of organics in the original sample with a size allowing passage through the membrane, C_o, not the total concentration of organics, C'_o, is required to determine the size distribution of dissolved organics. C_o is not obtainable from the rejection coefficient as defined in equation 3.2. Furthermore, C_r is not a useful quantity in determining size distributions, and is not typically measured.

Dilution technique: A method was proposed by Alleman (1986), hereafter called the Dilution technique, to correct the molecular weight distributions of organics in pulp and paper mill wastewaters for membrane rejection. In this method, a 45 mL sample is placed into a UF cell and pressurized to 50 psi. The first 5 mL of filtrate (11%) are discarded, and the next 20 mL collected. The retentate volume is then diluted to 40 mL using ultrapure water, and 20 mL again pushed through the membrane. The dilution is repeated three more times until 80 mL are collected and combined. Assuming 50% of the organics capable of passing through the membrane are transported with 50% of the solvent, only 3.125% of the organics capable of passing through the filter are assumed to remain (0.5^5). From a mass balance, the concentration of organics less than the membrane pore size are calculated from:

$$C_o = \frac{20\ C_{f20} + 80\ C_{f80}}{38.75} \qquad (3.2)$$

where C_{f20} is the concentration of organics from the first 20 mL sample, and C_{f80} is the concentration of organics in the 80 mL sample.

Permeation coefficient model: In order to determine the true concentration (C_o) of material in a sample with a molecular size less than the membrane pore size, a new separation model was developed. The size distributions of dissolved organics are determined in pressurized UF cells initially at a volume V_o. In each UF cell, the filtrate that is pushed through the membrane is assumed to contain only those molecules smaller than the membrane pores. The volume of retentate at any time above the membrane, V, may contain both large and small molecules. From a mass balance, the change of the mass of organics with sufficient size to pass through the membrane is:

$$\frac{d(Vc)}{dt} = -pcQ \qquad (3.3)$$

where c is the instantaneous concentration of organics in the retentate with a size less than the pore size of the membrane, Q is the filtration flow rate, t is time, and p is a permeation coefficient defined by:

$$p = \frac{c_f}{c} \qquad (3.4)$$

where c_f is the instantaneous concentration of organics in the filtrate. Expanding the differential in equation 3.3, and assuming constant flow, or $dV/dt = -Q$, equation 3.4 can be written as:

$$\frac{dc}{dt} = (1-p)\ \frac{cQ}{V} \qquad (3.5)$$

Integrating from $c(0)=C_o$, and $c(t)=C_r$, an expression is obtained for the concentration of retentate:

$$C_r = C_o \left[\frac{V_r}{V_o}\right]^{(p-1)} \qquad (3.6)$$

The result can be written in a condensed expression as:

$$C_r = C_o F^{(p-1)} \qquad (3.7)$$

where $F = V_r / V_o$ is the fractional reduction in volume above the membrane during the ultrafiltration procedure. Comparison of equation 3.7 with equation 3.1 shows that $R = 1-p$ if and only if $C_o = C'_o$.

The concentration of organics in a filtrate sample, C_f of volume $V_f = V_o - V_r$, is:

$$C_f = \frac{C_o - C_r F}{1-F} \qquad (3.8)$$

The size distribution of organics is determined by calculating the concentration of organics in the original sample, C_o, that should have been able to pass through the membrane, from experimental measurements of C_f and F.

Combining equations 3.7 and 3.8 results in the following:

$$C_o = C_f \frac{(1-F)}{(1-F^p)} \qquad (3.9)$$

According to equation 3.9, the concentration of organics in a filtrate sample increases as the volume filtered increases. Therefore, while the permeation coefficient specified in equation 3.4 is constant, different filtrate volumes can result in different apparent permeation coefficients. An operationally defined permeation coefficient, obtained with a standard after having collected some defined volume of filtrate, can be defined as:

$$p_{app} = \frac{C_f}{C_o} \qquad (3.10)$$

where p_{app} is the apparent permeation coefficient based on collection of a volume V_f with concentration C_f. Unless researchers all collect the same filtration volume, different apparent permeation coefficients and rejection coefficients can be determined even if the actual membrane rejection is constant.

The permeation coefficient model was examined using samples of known molecular weight by two methods: Incremental filtrate collection, and Refiltration. For the Incremental filtration method, a 180 mL stirred cell ultrafiltration device (Amicon Corp.) containing a 62 cm diameter UF membrane was filled with 100 mL of a sample and

pressurized to 50 psi. 10 mL filtrate samples were then successively collected until only 10 mL of retentate remained in the cell. The dissolved organic concentration (DOC) in all samples was determined using a Dohrman DC-80 total organic carbon analyzer. All samples were acidified and purged of dissolved CO_2 gas immediately before analysis. Observed filtrate concentrations were compared to model predictions. Experimental errors are reported for two standard deviations on replicates, which span a 95% confidence interval.

The predictions of the permeation coefficient model were also examined using an alternative procedure called the Refiltration method, based on equation 3.9. The basis of this approach is that the membrane permeation coefficient is constant for refiltration of a former UF filtrate. In this method, a 120 mL sample is placed in the ultrafiltration cell, and the cell pressurized to 50 psi. 2 mL (1.6% of V_o) of permeate is discarded to avoid dilution from ultrapure filter washwater, after which 40 mL of filtrate are collected. Thirty of the 40 mL are poured back into a the same cell containing the same membrane which has been rinsed in distilled water, retaining 10 mL for subsequent analysis. The cell is again pressurized and another 10 mL of filtrate are collected. By this method, F is nearly equal to 2/3 for both ultrafiltration steps. By assuming the permeation coefficient is constant, according

to equation 3.9, the ratio C_o/C_f is a constant for the two successive filtrations. The concentration in the original sample can therefore be determined using:

$$C_o = \frac{C_{1f}^2}{C_{2f}} \qquad (3.11)$$

where C_{1f} is the concentration of organics in the first filtrate sample withdrawn, and C_{2f} is the concentration of organics in the second filtrate sample withdrawn.

Experimental tests of the permeation coefficient model: Ultrafiltration experiments were conducted with a known substance (inulin), as well as unknowns (yeast extract and a municipal wastewater). Inulin, obtained from Sigma Chemical (lot #124F-7295), has an apparent molecular weight of approximately 5,000 amu. Amicon YM10 and YM5 membranes, with molecular weight cut-offs of 10,000 amu, and 5000 amu, respectively, were used to separate inulin samples. Yeast extract, which is thought to be a complex mixture of relatively small molecular weight compounds, is frequently added to microbial cultures. Yeast extract was fractionated using an Amicon YM2 membrane, with a molecular weight cutoff of 1000 amu. Wastewater samples were obtained from the Roger Road Wastewater Treatment Plant in Tucson, AZ, (see section 3.1.3).

3.1.2. Size Exclusion Chromatography Methods

Continuous size distributions were prepared using a Beckman high performance liquid chromatography (HPLC) system. Separation was accomplished by isocratic pumping of the sample in a solvent stream through a Beckman Spherogel™ 2000 SW HPLC 300 mm × 7.5 mm column (TSK, Toyo Soda, Japan), with a guard column (75 mm × 7.5 mm) of the same material. According to the manufacturer's specifications, this column can distinguish molecular weights in a range from 2000 amu to about 30,000 amu. Therefore, all material above 30,000 amu will come out in a peak along with the solvent front, not being retarded by the column matrix while material below 2,000 amu will all come out at the longest solvent retention time, passing through the entire column pore structure. For material between 2,000 and 30,000 amu, the retention time in the column is variously proportional to the molecular size; relationships can be determined by calibration with materials of known molecular weights.

The in-line detector used for the analysis was a Beckman model 163 variable wavelength spectrophotometer, set at 254 nm (unless otherwise indicated). The use of the spectrophotometer is based on an assumption that all of the organic carbon in the sample absorbs light equally and presumes a constant relationship between light adsorption

and DOC content as suggested by Amy *et al.*, (1986). However, spectrophotometry measures all of the material in the sample, both biodegradable and nonbiodegradable, as well as organics and inorganics. A wavelength scan was run on a wastewater sample to determine an appropriate wavelength for characterizing the organic content of a sample. Then, to determine if there was a simple conversion from U.V. absorption to organic carbon content regardless of molecular size, samples were separated using ultrafiltration, and analyzed using both a spectrophotometer (Perkin-Elmer/Hitachi model 200) and a total organic carbon analyzer (Dohrmann DC-80). The DOC results were then plotted against the U.V. absorbance in order to determine a possible relationship.

The following materials were use to calibrate the HPLC system: ovalbumin (egg, grade III, Sigma Chemical lot #125F-0364, AMW 45,000 amu), blue dextran (Sigma Chemical lot #127C-0016, AMW 1×10^6 amu), laboratory humic acid (Aldrich lot #121137, AMW ~13,000 amu), trypsin 1:250 (Difco lot # 0152-13, AMW 24,000 amu), and glucose (Mallinckrodt lot #KEYA, AMW 180 amu). Glucose was used to observe the breakthrough of small molecules, and ovalbumin and blue dextran standards were used to observe the elution time of large molecular weight material. Standards were prepared at a concentration of 50 mg/l in ultrapure water to roughly compare with the levels which might be expected

of certain constituents in wastewater. Samples were injected via a 20 μL loop using an Altex injection port intercepting the carrier stream, which was maintained at 1 mL / minute using a Beckman 110B constant flow delivery module. Output from the inline spectrophotometric detector was sent to a Hewlett Packard model 3390A integrator.

3.1.3. Wastewater Sampling Techniques and Preparation

Roger Road WWTP: The Roger Road municipal wastewater treatment plant is located in Tucson, Arizona, and was adapted with high rate trickling filters in 1960. Figure 1 shows a stylized schematic of the treatment plant and indicates the various wastewater sampling points used during this study. Currently the treatment plant is rated for 30 mgd, although experience has shown the plant capable of handling higher periodic flows. (Pima County Wastewater Management Department Annual Report, 1984-1985).

Upon discharge from the collection system, the wastewater is sent through a pair of primary circular clarifiers with a total volume of 1940 m^3 (68,500 ft^3) and a surface are of 2900 m^2 (31,200 ft^2). At a typical flow of 32 mgd, this produces and an overflow rate of 41.8 m^3/m^2d (1026 gpd/ft^2) and a detention time of 105 minutes. Samples taken from the primary clarifier overflow are referred to as 'influent' samples.

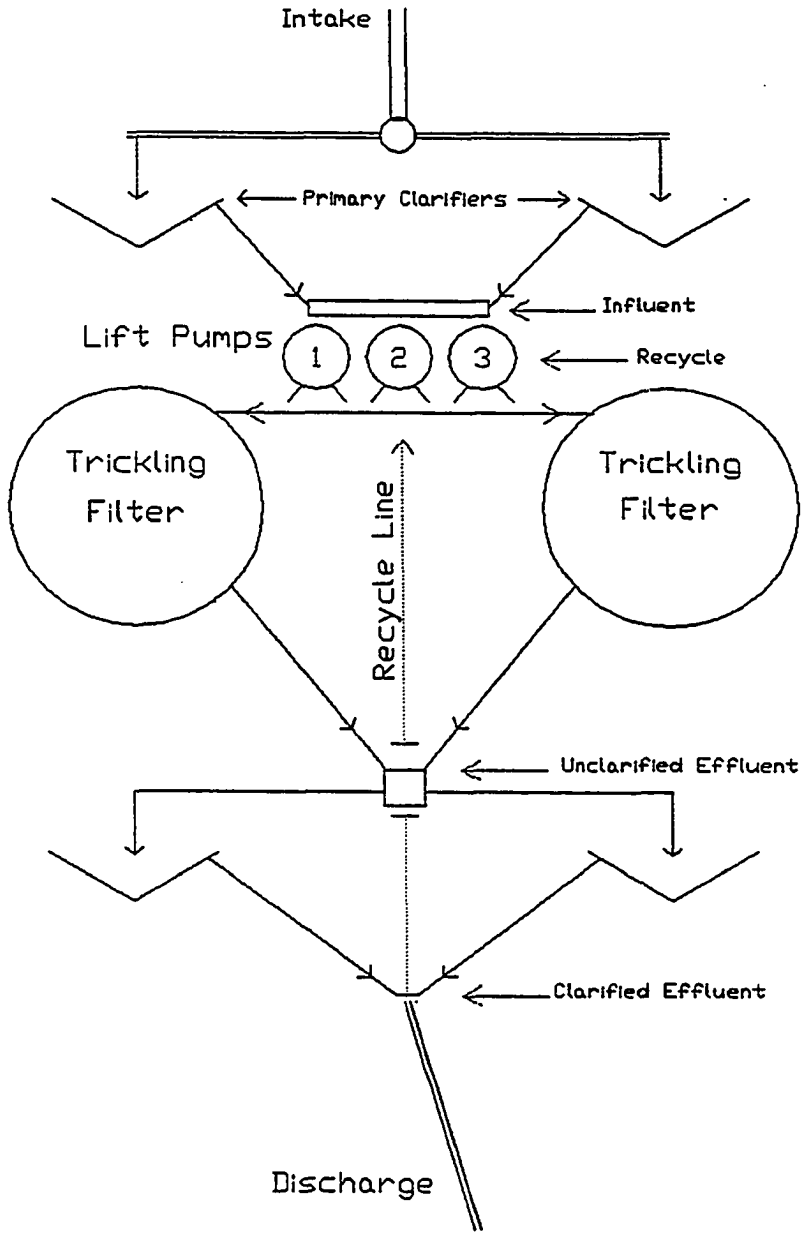


FIGURE 1 : Roger Road Wastewater Treatment Plant.

The treatment system consists of two filter towers containing 28 ft. (14 modules = 8.54 m) of G.F. Goodrich vertical flow media with a specific surface area of 101 m^2/m^3 (30.8 ft^2/ft^3). The cross-sectional area of each tower is 1,986 m^2 (21,382 ft^2). Lift pumps feeding the filter towers are designed to operate in stepped manner: one pump when the plant inflow is less than 15 mgd, two pumps when the inflow is between 15 and 30 mgd, and three pumps when the intake surpasses 30 mgd. Although the plant inflow varied from 15 to 45 mgd at various sampling times, only two lift pumps were observed to be operating whenever the flow was greater than 20 mgd. Each lift pump has a rated output of 35 mgd, the difference between the pump flow rate and the influent flow rate being made up with recycled flow from the trickling filter effluent.

The recycle rate at Roger Road can be calculated as follows:

$$R = 1 - \frac{Q_i}{35 \times n_{pumps}} \qquad (3.12)$$

Where Q_i is the inflow to the plant in millions of gallons per day [mgd], n_{pumps} is the number of pumps in operation, and 35 mgd is the output from each pump. At a typical flow of 32 mgd, using two pumps, the recycle rate can be calculated to be 0.543. The hydraulic loading on the trickling filters is a constant for a given number of operating pumps:

One pump	==>	0.386 l/s-m^2	(0.57 gpm/ft^2)
Two pumps	==>	0.772 l/s-m^2	(1.14 gpm/ft^2)
Three pumps	==>	1.157 l/s-m^2	(1.70 gpm/ft^2)

Samples taken from the lift pumps are referred to in this work as 'recycle' samples since they consist of a blend of recycle and new influent. This material is what directly passes through the trickling filters.

The trickling filter underflow, referred to as 'unclarified effluent', subsequently passes through a pair of secondary circular clarifiers equivalent in configuration to the primary clarifiers. Overflow from these clarifiers is tapped to provide the recycled portion of the flow, and will be referred to in this work as 'clarified effluent' or simply 'effluent'.

The number of lift pumps in operation at the time of each sampling was noted in order to allow calculation of the recycle ratio. The temperature of the wastewater for each sample was extrapolated from information available in the plant operator's log book in which wastewater temperatures are recorded every six hours, and show variations reflecting atmospheric temperatures. Finally, the new plant inflow rate at the time of sampling was noted from flow measurement instruments.

Atlanta WWTP: Wastewater was also obtained from the Utoy Creek wastewater treatment plant of the City of Atlanta in Georgia. At the time of the sampling, there was

a pilot trickling filter with the following characteristics:

media	- Münters cross-flow, specific surface area 30 ft^2/ft^3.
flow rate	- 1.5 gpm/ft^2.
height	- 20 ft.
x-section area	- 16 ft^2.

Samples were taken from the feed at the top of the tower (influent) and from the effluent immediately after the tower (effluent). The pilot plant had no provision for recycle.

Prefiltration procedure: Before UF or HPLC processing, and within 30 minutes of being drawn, all samples were vacuum filtered to remove suspended material. The sample was first filtered through a Whatman GF/D filter with a nominal pore size of 2.7 μm. Next, the material was filtered through a Whatman GF/C filter (pore size 1.2 μm), followed by a Millipore 0.45 μm filter (type GS, Millipore Corporation). Finally, the material was filtered through a Millipore 0.22 μm filter (type GS, Millipore Corporation). All filters for this step were prewashed with 50 mL of ultrapure water (Millipore Milli-Q system). The four part prefiltration process was chosen to reduce the time between sampling and removal of suspended microorganisms. Filters were replaced immediately upon clogging (as evidenced by reduced throughput), to prevent microstraining due to filter compaction and surface buildup. Filters were operated under a 15-18 psi vacuum. Upon completion of the

prefiltration step, the wastewater was either processed immediately, or, when necessary, refrigerated at 0-5°C for not more than 48 hours. If refrigerated, samples were equilibrated with ambient temperatures during a 30 minute period before further processing.

3.2. BOD Tests

Ultimate sBODs were determined for separated weight fractions of wastewater using bottle BOD methods and respirator (HACH) methods. For both methods, distilled dilution water was aerated to saturation and critical nutrients supplied via BOD buffer pillows (Hach Chemical Co., 1 pillow added per 6 liters of dilution water). 2 mL (unless otherwise specified) of seed material drawn from the same wastewater after a short settling time was added to each liter of dilution water to provide a heterogenous population similar to that present under actual treatment conditions. Blanks of seeded dilution water were run to determine the BOD of the seed. A nitrification inhibitor (Hach Chemical Co., lot #06AT) as reccommended by Standard Methods... (APHA, 1980) was applied at 0.16 g / 300 mL of diluted sample, which resulted in an increase in DOC of 2.2 mg/l. The tests were run in an incubator at 20° ± 1°C.

Bottle BOD: Procedures for determining biochemical oxygen demand were taken from Standard Methods... (1980,

pp. 483-489). To reduce the necessary sample volume, vials of 20 mL capacity, and later, Wheaton BOD bottles of 60 mL capacity were used rather than standard 300 mL bottles. To adjust for the sample dilution, the sample uBOD was calculated as follows:

$$uBOD = \frac{DO_i - (DO_f + (1-F_s) * BOD_s)}{F_s} \qquad (3.13)$$

uBOD : the ultimate soluble BOD fraction of the sample.

DO_i : initial dissolved oxygen of sample in mg/L.

DO_f : final dissolved oxygen of sample in mg/L.

BOD_s : BOD of the seeded dilution water in mg/L.

F_s : Fraction of sample [dimensionless]: V_s / V_b where V_s is the volume of the sample and V_b is the volume of the bottle or reactor.

Oxygen levels were measured with a YSI model 57 portable oxygen meter, calibrated and checked frequently with a Winkler dissolved oxygen test (Standard Methods... 1980, pp. 390-393) using the azide modification to avoid measuring dissolved nitrates. The oxygen probe served to indicate reproducibility of data, and allowed samples to be subsequently tested for DOC. The Winkler test was run on a representative replicate to get a more exact value for dissolved oxygen but destroyed the sample by the addition of reagents. The rest of the samples were then physically averaged (ie: mixed in equal volumes) through a 0.22 μm filter (as in prefiltration) for DOC analysis.

HACH procedures: An alternate procedure utilizing a Hach 2173B Manometric BOD apparatus was used to determine kinetic uptake constants. The Hach test is a variation of a device called a Warburg Respirator found in the literature (Metcalf & Eddy, 1979) and consists of a stirred, sealed reactor with known volumes of air and aqueous sample. Oxygen is continuously transferred from the air reservoir to the sample in order to replenish that used by the biodegradation. The CO_2 produced by the microorganisms is removed via contact with lithium hydroxide in the air space. The transfer of O_2 to sample and the removal of CO_2 produces a pressure drop proportional to the oxygen usage. The pressure drop is read on a manometer connected to the air space, where the units have been calibrated to correspond to sample BOD in mg/l.

To calculate the BOD of the sample, the following relationship was used:

$$BOD = \frac{BOD_f - BOD_b(1-F_s)}{F_s} \qquad (3.14)$$

BOD_f : The BOD of the reactor as reported by the Hach apparatus in mg/L.

BOD_b : The BOD of the seeded blank. (mg/L)

F_s : Fraction of sample [dimensionless]: V_s / V_b where V_s is the volume of the sample and V_b is the volume of the bottle or reactor.

3.2.1. BOD/DOC relationships

To support the prediction of sBOD removals from DOC measurements, the relationship between sBOD and DOC was examined using the following procedures. Wastewater samples were collected and prefiltered according to the methods in section 3.1.3. After ultrafiltration (section 3.1.1), the starting DOC (DOC_i) was determined for each weight fraction using the Dohrman DC-80 analyzer. Thereafter the BOD test was run as outlined in section 3.2. After a determination of the ultimate BOD (uBOD), either using the standard BOD or the Hach test, the residual sample was again measured for DOC, giving a final DOC. The bDOC is the difference between the DOC of a fresh sample and the DOC of the same sample after an ultimate BOD test:

$$bDOC = DOC_i - rDOC \qquad (3.15)$$

The refractory DOC (rDOC), by definition, does not change during treatment or during a BOD test, and is the DOC remaining after complete biodegradation.

The uBOD test assumes that all the organic carbon in the sample that can biologically degrade has done so during the course of the test, ie: the carbon is limiting to the further growth of the microorganisms. This process usually takes approximately ten days to reach a point within 90% of

the ultimate BOD value; the BOD curve is expected to be asymptotic to the uBOD.

Correction for sample volumes after BOD tests: Since the wastewater samples must be diluted to assure adequate oxygen during the BOD tests, the final DOC of the sample must be calculated based on the dilution volumes, as well as adjusted for the inert organic carbon added via the nitrification inhibitor. The following adjustment of the reactor DOC was used:

$$DOC = \frac{DOC_f - DOC_b(1-F_s) - DOC_{ni}}{F_s} \qquad (3.16)$$

DOC_f : The final DOC of the sample in mg/L.

DOC_b : The DOC of the seeded blank after the BOD test. (mg/L)

DOC_{ni}: The excess DOC of the reactor attributable to the nitrification inhibitor. (mg/l)

F_s : Fraction of sample [dimensionless]: V_s / V_b where V_s is the volume of the sample and V_b is the volume of the bottle or reactor.

3.3. Model Calibration

The computer program designed by Logan *et al.*, (1986), was altered to use size distribution data from changes in BOD and DOC and is shown in Appendix A. Once the diffusivities of wastewater size fractions are defined, model calibration requires adjusting the collision

efficiency (E_B), which requires only one data point. The Atlanta pilot plant was used to calibrate the model by adjusting E_B to match the results for the data in terms of sBOD, DOC, and bDOC removals for each molecular size in the wastewater. After calibration based on the wastewater in Atlanta, the model was used to predict removals by size for each of the subsequent BOD and DOC examinations of wastewater from the Roger Road wastewater treatment plant in Tucson.

4. RESULTS

Wastewater molecular weight distributions were examined using ultrafiltration (UF) techniques and high performance liquid chromatography. UF determinations were corrected for membrane rejections using a new method which proved to be accurate and convenient based on successful determination of filtrable fractions of test compounds as well as comparison with other methods when using wastewater. Size fractionated wastewater samples were then subjected to tests to determine their biodegradation characteristics. HPLC investigations were not fruitful due to detector and column deficiencies as well as the nature of the wastewater under study.

A representative diffusivity was defined for each size fraction for subsequent use in the trickling filter model. Based on the diffusivities, the Logan trickling filter model was recalibrated to improve predictive capabilities, and the removals of organics and sBOD by size fraction in a trickling filter were compared to predictions generated using the model. Inconsistencies arose due to unexplained shifts in molecular size fractions during treatment that require further investigation before the model can be fully generalized.

4.1. Molecular Size Distributions

4.1.1. Ultrafiltration Results

Tests on Inulin: Inulin, (mol. wt. ~ 5,000), was used to compare the permeation coefficient model with two other methods for determining membrane rejections: Dilution and Refiltration. For a defined removal fraction, F, the permeation model contains two adjustable parameters, C_o and p. These values were obtained from successive filtration data by minimizing the least squares errors between model predictions and experimental data. The effect of membrane rejection by a 10,000 amu cut-off membrane (YM10) on DOC measurements of inulin (5,000 amu) in successively collected 10 mL filtrate samples is shown in Figure 2, for an applied DOC of 55 ± 2 mg/L. Without accounting for membrane rejection, the first 10 mL sample would have indicated that 49.7 mg-DOC/L, or 90% of the initial DOC applied to the ultrafiltration cell would have an AMW less than 10,000 amu. Within the 95% confidence interval of DOC measurements (2 standard deviations), the concentration of DOC in the filtrate remained unchanged for the first 4 filtrate samples. The DOC in successive filtrate samples contained increasingly larger amounts of DOC, until finally, the ninth sample contained 65.4 mg-DOC/L, a DOC significantly in excess of the original DOC applied to the ultrafiltration cell. The best-fit model result for the

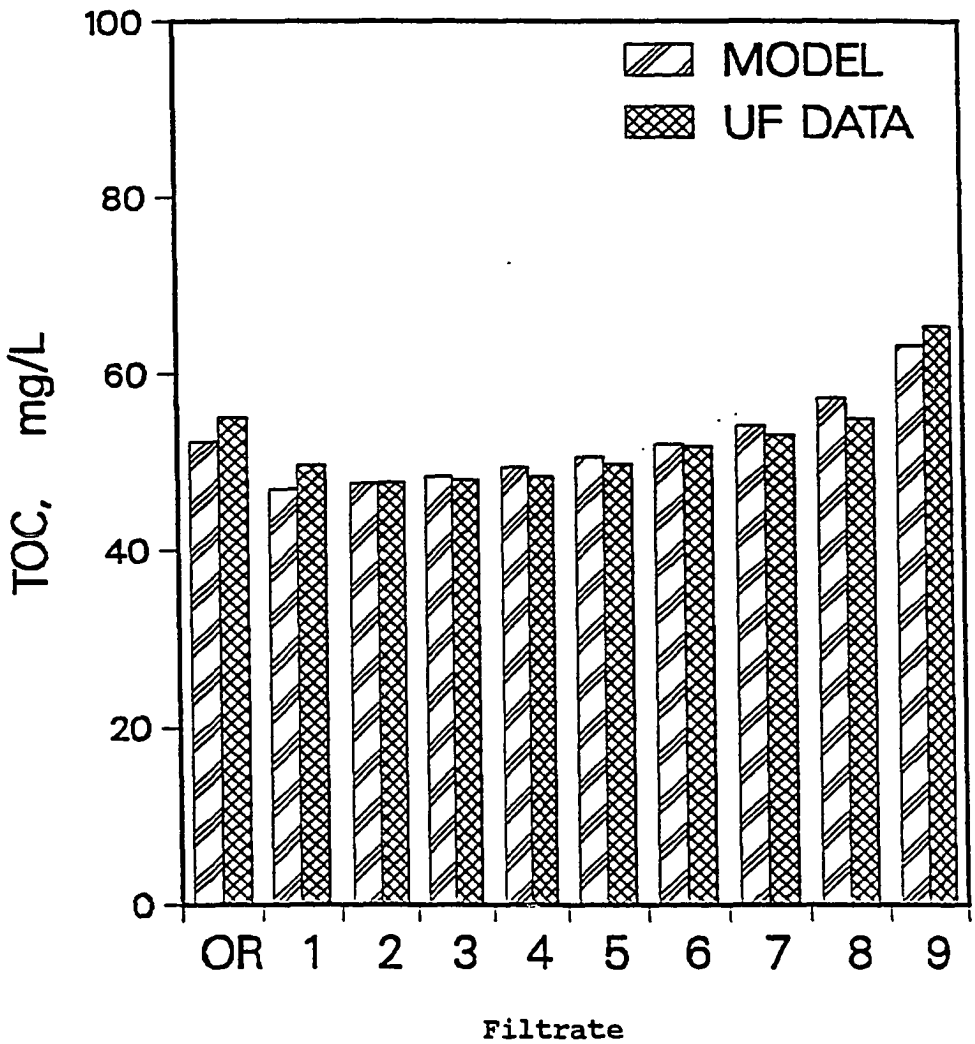


FIGURE 2 : Measured and predicted DOC concentrations in successive 10 mL filtrates of Inulin. (AMW 5,000 amu, UF filter cutoff : 10,000 amu, p=0.37, OR=original 0.22μm filtered sample)

inulin separation, also shown in Figure 2, occurs for an initial concentration of 52.4 mg-DOC/L with an AMW <10,000 amu, and a permeation coefficient of 0.88. This initial DOC is equal to the applied DOC within the 95% confidence interval for the DOC measurements. In general, there is excellent agreement between model predictions and measurements.

The percent material calculated to be less than the manufacturers specified molecular weight cut-off for this membrane of 10,000 amu was calculated using the Alleman Dilution method (eq. 3.2) and the Refiltration method (eq. 3.11). Filtrations based on the Dilution method resulted in a calculated recovery of 106% of the original DOC added. As shown in Table 2, 98% of inulin (molecular weight 5,000 amu) was calculated to be less than 10,000 amu using equation 3.11, which was within the 95% confidence interval for DOC measurements used to predict the initial DOC.

Tests on Yeast Extract (low mol. wt.): The exact size distribution of Yeast Extract is unknown. Both the Refiltration and Dilution methods predicted that 67% of the yeast extract tested was less than 1000 amu (Table 2). However, the Refiltration method requires only two filtration steps to complete, while the Dilution method requires four filtration steps. In addition, the Dilution procedure requires the addition of ultrapure water, and is

TABLE 2 : Percent material calculated to be less than the nominal membrane molecular weight cut-off by determination method.

Substance	Cut-off (amu)	*P_{app}	Percent Material Refiltration	Dilution
Inulin	10,000	0.81	98	106
Inulin	5,000	0.54	41	55
Yeast Extract	1,000	0.78	67	67

* P_{app} is the apparent permeation coefficient calculated from equation 3.10.

a potential source of sample contamination, particularly at low organic concentrations.

Wastewater Samples: The size distribution of dissolved organics present in untreated wastewater obtained from the Roger Road Treatment Plant was determined according to the Dilution and Refiltration methods, as summarized in Table 3. Also shown are the uncorrected results (without adjusting for rejection) based on only the first filtrate during the Refiltration procedure. All methods indicated that the size fraction with an AMW less than 1,000 amu consistently contained the largest fraction of DOC in the wastewater. The Dilution method and proposed method indicated 71% and 68%, respectively, of the DOC fraction had an apparent molecular weight less than 1,000 amu. Only 59% of DOC would have been calculated to be contained within this size fraction without correction for membrane rejection.

The Dilution procedure over-estimates the concentration of dissolved organics in the fraction below 10,000 amu, with a calculation result of 112% of the applied DOC, while the proposed calculations indicate 83% of the DOC fall within this size category. Without correction for membrane rejection, 77% of the mass would have been calculated to be <10,000 amu. As shown in Table 4, subtraction of the mass determined to fall in the <1,000 amu fraction results in a calculation of 16% of mass in the

TABLE 3 : Comparison of correction methods for ultrafiltration determinations on untreated wastewater.

	% of total DOC	
Method	< 10,000 amu	< 1,000 amu
Refiltration		
(Uncorrected)	77	59
Corrected	83	68
Dilution	112	71

TABLE 4 : Discrete* size fractions of untreated wastewater.

	DOC [mg/L] (% of total mass)		
Method	< 1,000 amu	1,000 - 10,000 amu	> 10,000 amu
Refiltration			
(Uncorrected)	7.9 (23)	5.8 (17)	20.1 (60)
Corrected	5.6 (16)	5.3 (16)	22.9 (68)
Dilution	-----	-----	24.0 (71)

* Exclusive of smaller fractions.

10,000 amu to 0.22 μm fraction for corrected samples, while 23% of the DOC would have been calculated without correction for membrane rejection.

The concentration of dissolved organic carbon in wastewater with an AMW less than 1,000 amu was also determined by collecting sequential 10 ml filtrate samples. Results for the wastewaters entering and leaving a trickling filter are shown in Figures 3 and 4, respectively. For the wastewater entering the trickling filter, which includes recycled effluent, the original DOC of the sample was 21.8 mg/L, of which 74% (16.2 mg-DOC/L) was determined by best fit of the model to have a molecular weight less than 1,000 amu. The membrane permeation coefficient (p, eq. 3.4) was determined to be 0.9 after adjusting the model to the best fit. The relatively slow increase in the observed DOC of successive wastewater filtrate samples shown in Figure 3 indicates a rejection coefficient near unity. The trickling filter effluent contained a total of 11.5 mg/L of dissolved DOC, of which 60% (6.9 mg/L) is estimated to be less than 1,000 amu. This indicates that small molecular weight organics were removed more efficiently than larger organics.

For the YM2 UF membrane, the uncorrected DOC value for the wastewater is 88% of the corrected value in Table 3. For the YM10 UF membrane the uncorrected DOC value for the wastewater is 95% of the corrected value. This indicates

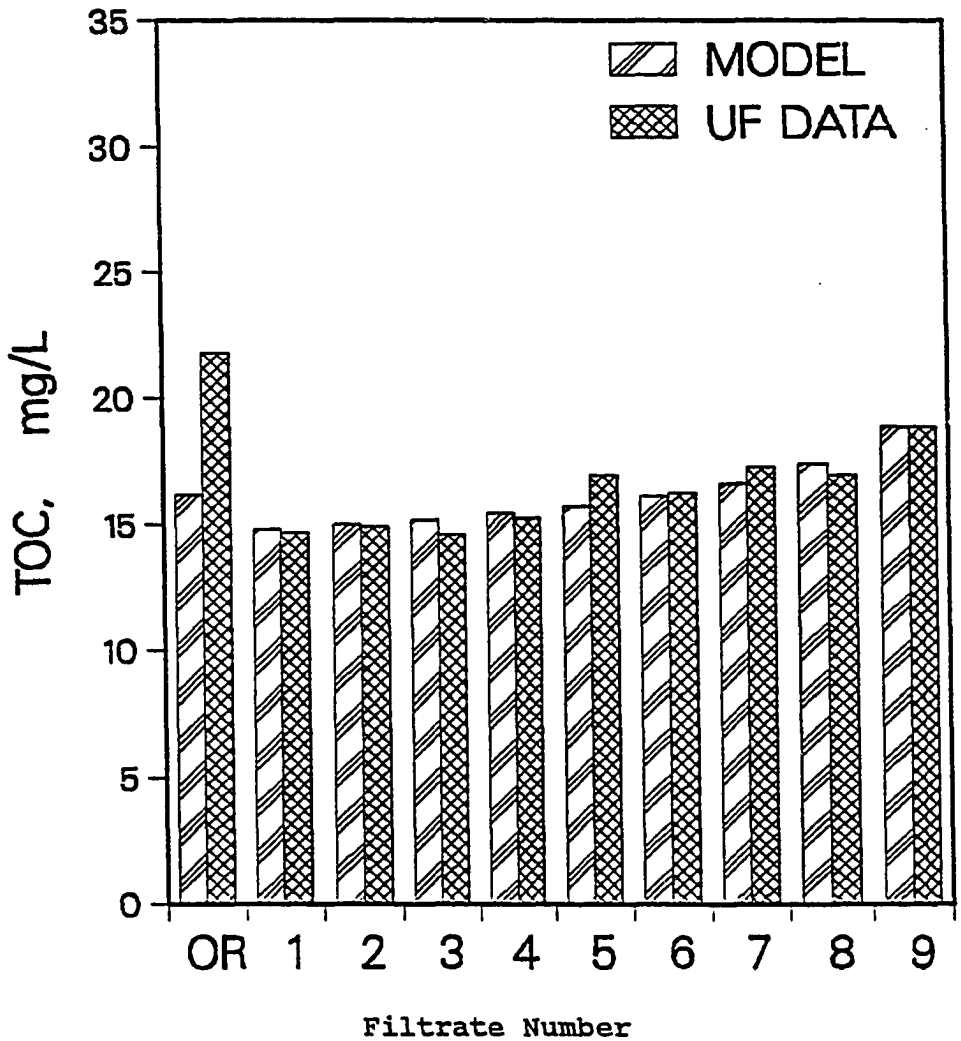


FIGURE 3 : Measured and predicted DOC concentrations in successive 10 mL filtrates of a trickling filter influent + recycle. (p = 0.90)
OR = original 0.22 μm filtered sample
Mol. Wt. cutoff of filter = 1,000 amu.

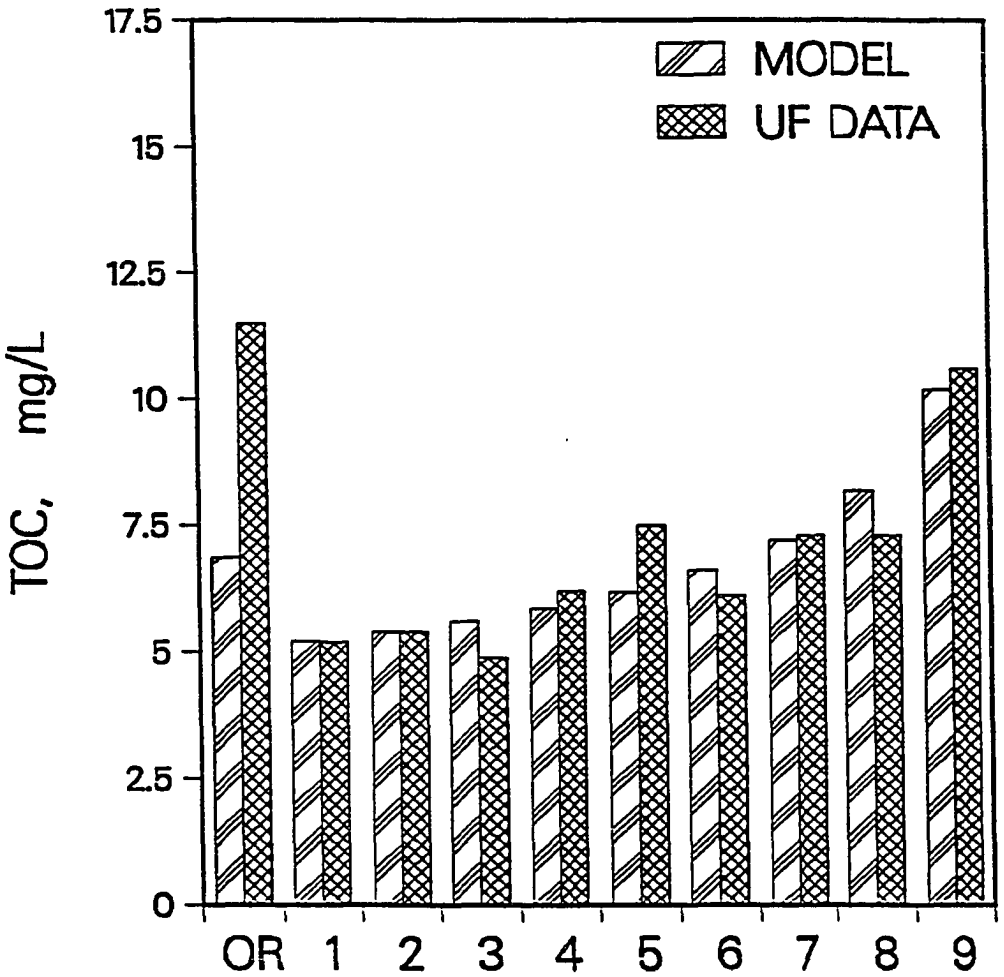


FIGURE 4 : Measured and predicted DOC concentrations in successive 10 mL filtrates of trickling filter effluent. ($p = 0.72$)
OR = original 0.22 μm filtered sample
Mol. Wt. cutoff of filter = 1,000 amu.

that membrane rejection is more pronounced for smaller molecular weight membranes.

The repeatability of the BOD tests was generally only 90%, and the repeatability of DOC and other tests was up to 95%, thus corrections are only necessary for separations with UF membranes having cut-offs lower than 10,000 amu; corrections for the larger size cut-off membranes are unnecessary within the experimental limits of error. Reported values are corrected for YM2 membranes (unless otherwise indicated), while the YM10 values are given uncorrected in the following sections.

Membranes used for wastewater analysis: The resolution of the size distribution using UF membranes depends on the number of different size cut-offs used. The membranes used for the earliest UF separations of wastewater taken from Roger Road treatment plant included YC05, YM2, YM5, YM10, YM30, and YM100 (see section 3.1.1). The fraction separated with the YC05 membrane often resulted in greater mass than fractions separated by membranes with higher nominal cutoffs. Figure 5 shows a case where the observed DOC of the YC05 filtrate was 3.5 mg/L higher than even the 0.22 μm filtrate, and was 24 mg/L higher than the YM2 filtrate. This indicates that some of the additional material in the fraction below 500 amu must have been produced by contamination, probably from the membrane itself; some additional discrepancy was attributed

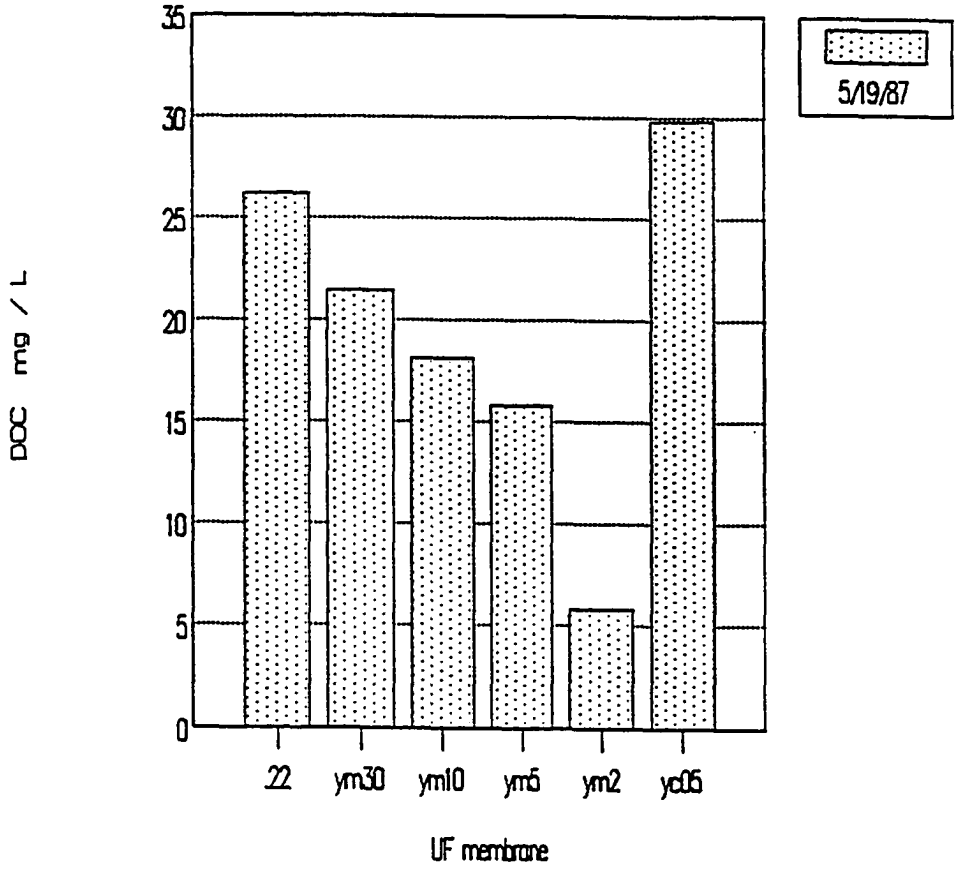


FIGURE 5 : Molecular weight distribution using 6 UF membranes.

Sample: Roger Road unclarified effluent
Date: 5/19/87

to differences in membrane construction material, surface characteristics and perhaps inaccuracies in the pore sizes as well. Based on these results, use of the YC series membrane was discontinued for the remaining investigations.

The wastewater from Roger Road treatment plant normally has a high percentage of material in the lowest size fractions, and additional resolution in the larger size fractions has little significance in terms of the overall distribution. Figure 6 shows that the amount of organic carbon in each discrete size fraction, (ie: exclusive of the smaller material), can become very small when all the membranes are used. This causes the inaccuracies in measurements and statistical errors to take on increased significance. It was therefore decided to limit the investigation primarily to three size ranges: 0 to 1,000 amu, 1,000 to 10,000 amu, and 10,000 amu to 0.22μm using 2 UF membranes: YM2 and YM10, as well as the prefiltration membrane with pore size 0.22μm.

Annual trends at Roger Road: The three size distributions of wastewater components were examined over the course of a year and showed notable changes in total and fractional (by apparent molecular weight) amounts of dissolved organics at the Roger Road wastewater treatment plant. These variations are mitigated by the addition of recirculated (treated) wastewater into the influent stream. Figure 7 shows the molecular weight distributions in

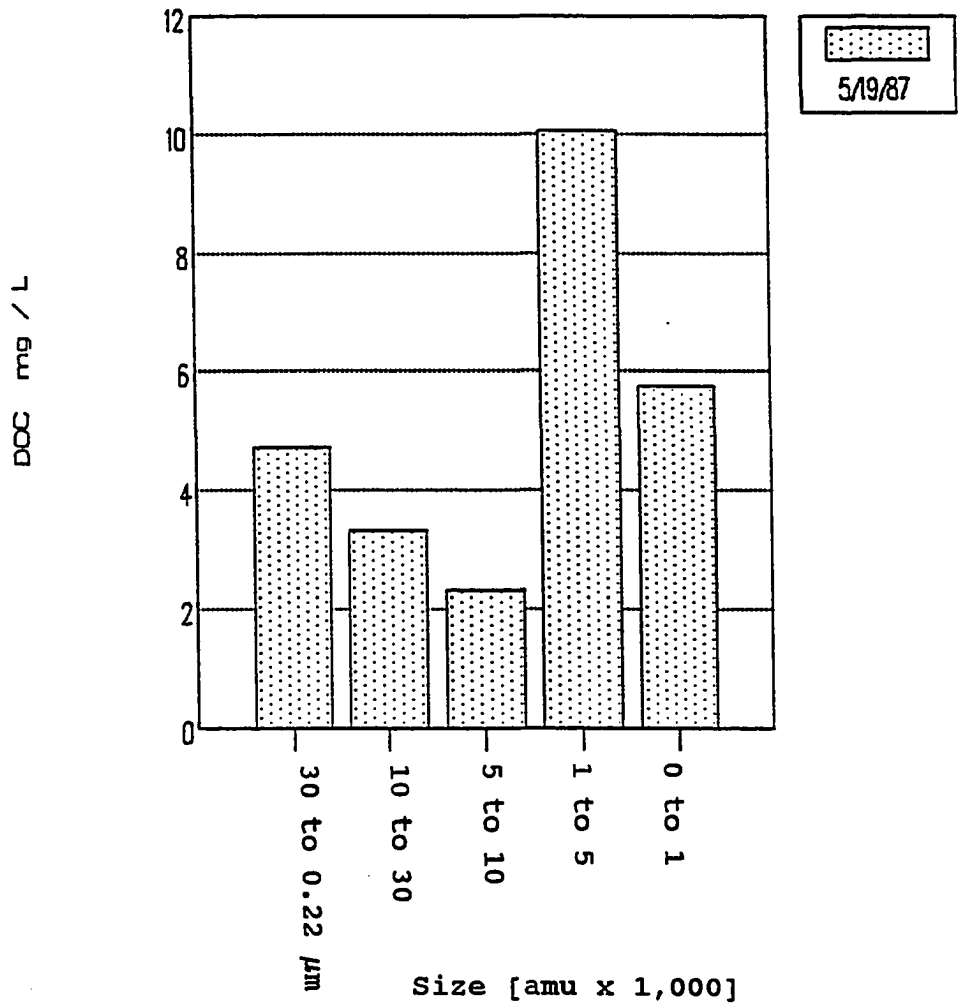
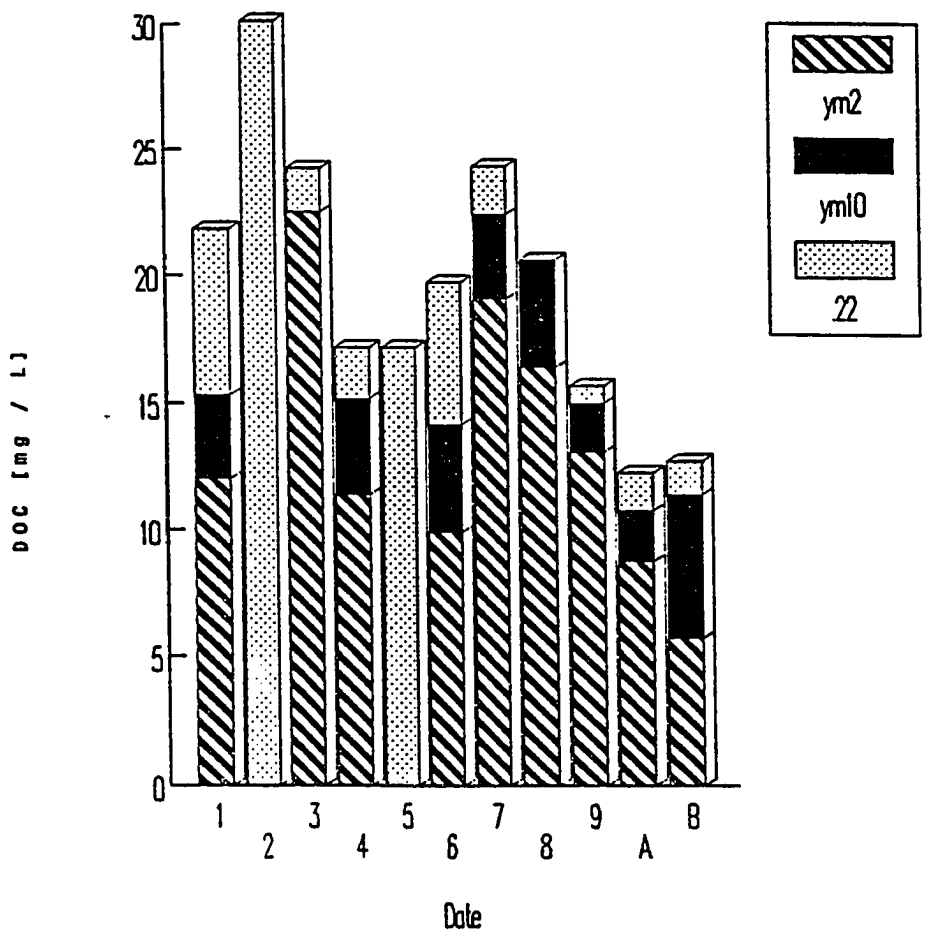


FIGURE 6 : Discrete molecular weight fractions from separations using 5 UF membranes. Bars show only the material actually in the indicated molecular weight range.

Sample: Roger Road unclarified effluent
Date: 5/19/87



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 7 : Annual trends in molecular weight distributions at Roger Road. Blended recycle flow measured as DOC in mg/L.

Chart for conversion of code numbers to date of sampling:

1 - 3/31/87	4 - 1/07/88	7 - 2/19/88	A - 5/09/88
2 - 5/19/87	5 - 1/18/88	8 - 3/11/88	B - 5/20/88
3 - 12/21/87	6 - 1/27/88	9 - 3/31/88	

recycled wastewater at different sampling times. Dissolved organic carbon ranges from a high of 50 mg/L to a low of 13 mg/L, while the small size fraction varies from 23 mg/L to 6 mg/L. The midrange fraction (1,000 - 10,000 amu) is consistent when measured (not determined in samples 2 and 5) at 3 to 7 mg/L. Similar data representing the influent, unclarified effluents, and clarified effluents over the course of the research are shown in Appendix B.

When the DOCs of recycle flow molecular weight fractions are shown as percentages of total DOC (Figure 8), no clear trend appears in the distribution pattern over the data sets available. For Roger Road recycle flow, the small size fraction, (0 - 1,000 amu), makes up from 48 to 92 percent of the total DOC.

Clarified vs. Unclarified effluents: The removal of solids by clarification greatly aided the subsequent filtrations carried out for this study, but it was necessary to investigate the effect of clarification to assure that the results would not be affected. The soluble organics in the unclarified and clarified effluents are nearly identical in distribution, as evidenced in Figure 9. The differences in DOC for the three dates shown represent 0.5%, 10.0%, and -9.0% all of which are within the range of accuracy for the BOD tests. Thus, clarified rather than unclarified effluent was chosen for most subsequent experiments.

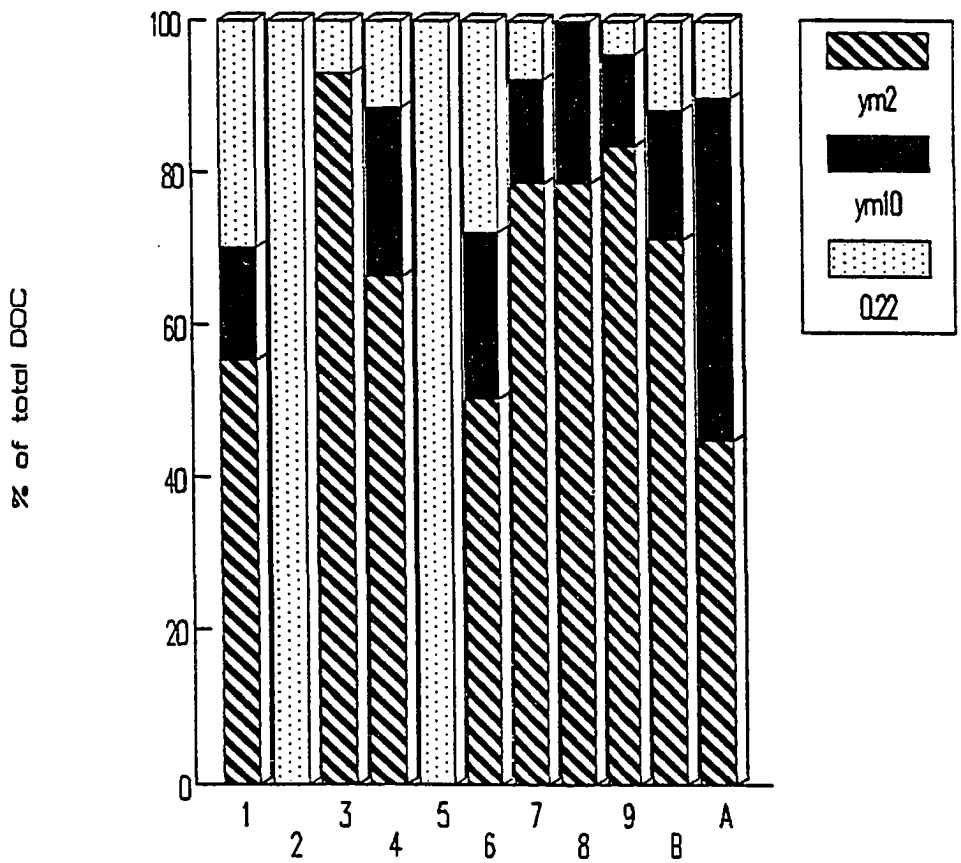
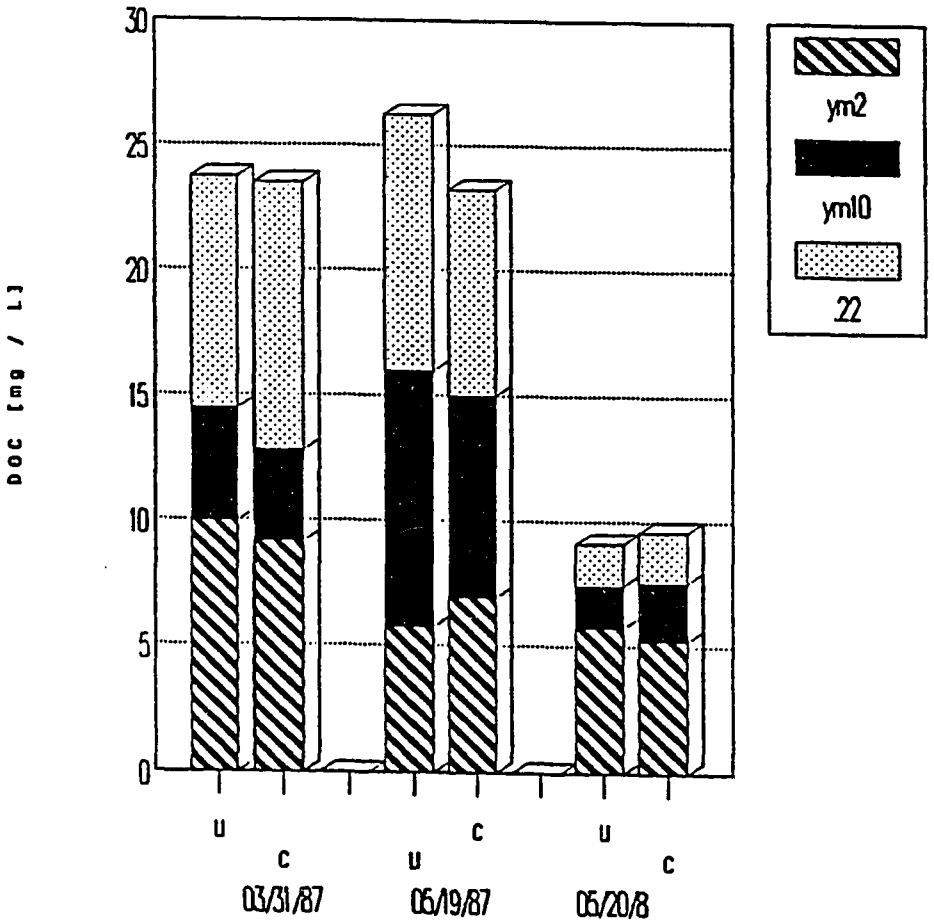


FIGURE 8 : Molecular weight distributions at Roger Road. Blended recycle flow shown as percentages of total DOC.

Chart for conversion of code numbers to date of sampling:

1 - 3/31/87	4 - 1/07/88	7 - 2/19/88	A - 5/09/88
2 - 5/19/87	5 - 1/18/88	8 - 3/11/88	B - 5/20/88
3 - 12/21/87	6 - 1/27/88	9 - 3/31/88	



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 9 : Comparison of unclarified and clarified molecular weight distributions of trickling filter effluent at Roger Road.

u = unclarified c = clarified

DOC removal in trickling filters: Total DOC was reliably reduced in the wastewater by the trickling filter treatment, but it was necessary to investigate the removals by molecular weight fraction to test the model. According to equation 2.4, the low molecular weight material will be removed fastest in a trickling filter. Figure 10 shows a case where the reductions in DOC generally followed the theory, the smallest substrate molecules being removed best (from 10 to 6 mg/L; 40%), followed by the material in the 1,000-10,000 amu range (4 to 3 mg/L; 25%), and finally the larger material (6 to 4 mg/L; 33%), resulting in a total DOC removal of 40%. Given the 10% range of error for the measurements the 25% and 33% removals are essentially the same. Predicted effluent distributions (eff. pred.) will be discussed in section 4.3.

Two variants from the "theory" appeared. First, Figure 11 shows a small size fraction increase from 2 to 3 mg/L of DOC (50%) while the overall DOC is reduced by 20%, which suggests that larger substrate molecules are broken down into smaller sizes and are incompletely removed from the fluid. Microorganisms must break larger molecules into smaller compounds for intracellular use, and this data set may indicate incomplete oxidation.

Second, new material is sometimes produced in the larger size range in the effluent. This was also reported by Namkung and Rittman (1986) investigating phenol

ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

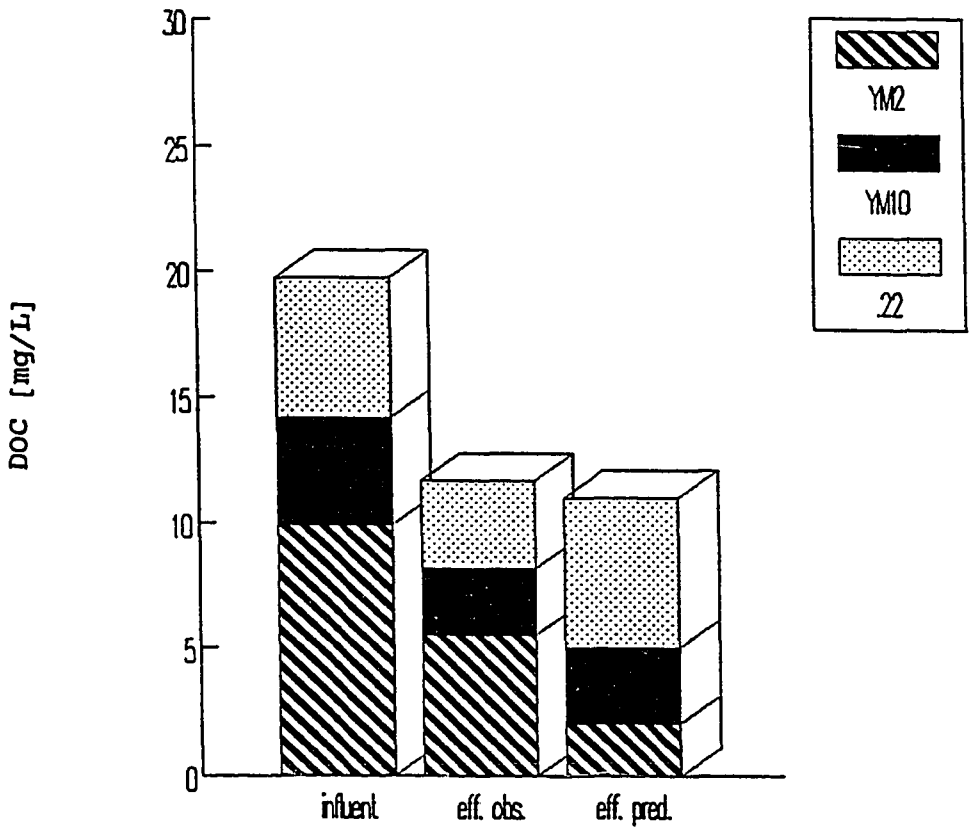
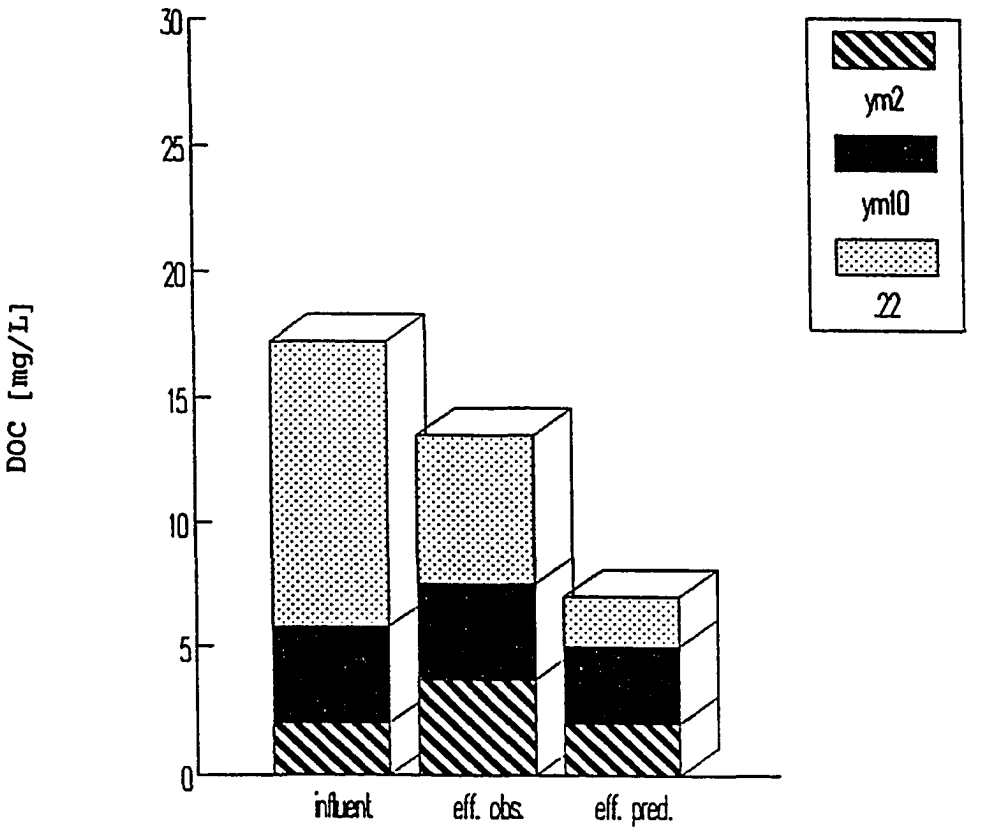


FIGURE 10 : Trickling filter recycle, effluent and predicted effluent molecular weight distributions based on DOC measurements.

Roger Road 1/27/88
Normal Removal E_B = 0.00002



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

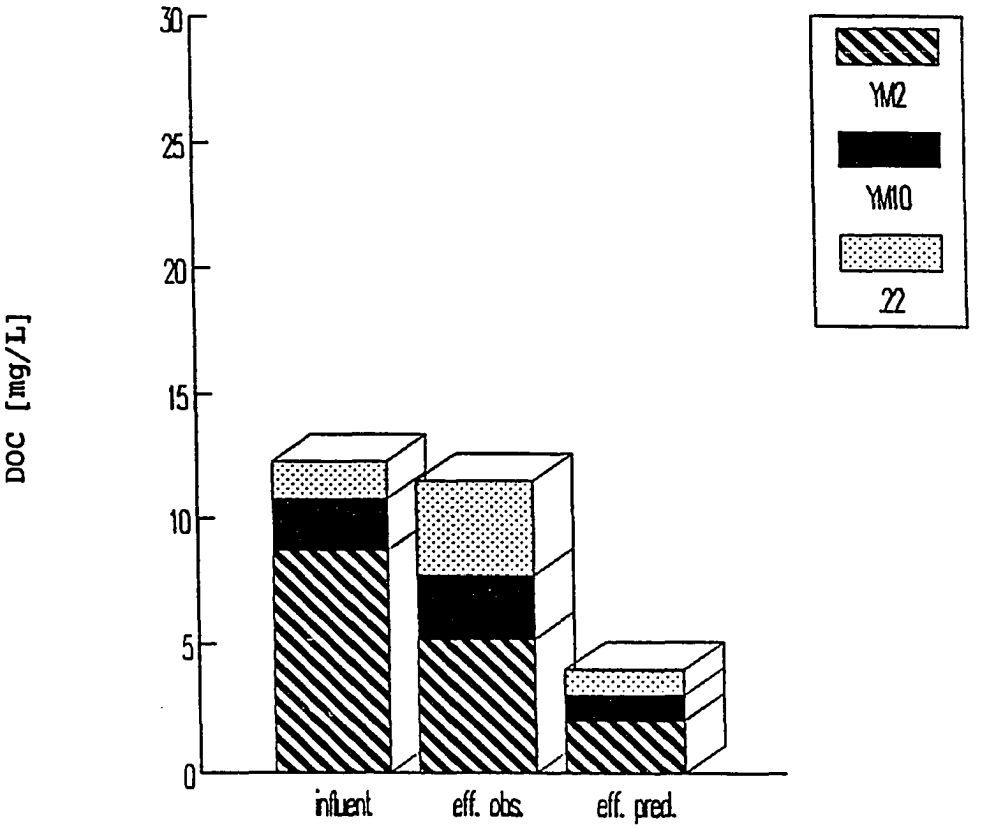
FIGURE 11 : Trickling filter influent, effluent and predicted effluent molecular weight distributions based on DOC measurements.

Roger Road 1/7/88 E_B = 0.00002
Unexplained increase in low molecular weight fraction.

degradation in biofilms. As shown in Figure 12, the DOC concentration in the large size range, (10,000 amu to 0.22 μm), more than doubles during passage through the filter. This could result from either the production of high molecular weight byproducts in this size range, (from smaller molecules), or a solubilization of suspended material larger than 0.22 μm which is not included in the mass balance for determining the DOC. Results from other data sets are presented in Appendix C. Saunders and Dick (1981) reported increases in high molecular weight organic fractions during activated sludge treatment for solids retention times up to 5 days. Both Saunders (1981) and Namkung (1986) attributed the increases to high molecular weight soluble microbial products.

bDOC removals: When the refractory DOC (rDOC) is subtracted from the DOC for each size fraction, the result is the biodegradable DOC (bDOC) by molecular size. The smaller size fraction of bDOC is generally removed faster than large size fractions. Figure 13 shows the bDOC of the small size fraction (0 to 1,000 amu) is 89% removed while the midrange material (1,000 to 10,000 amu) is 75% removed and the large molecular weight material (10,000 to 0.22 μm) is only 50% removed during treatment.

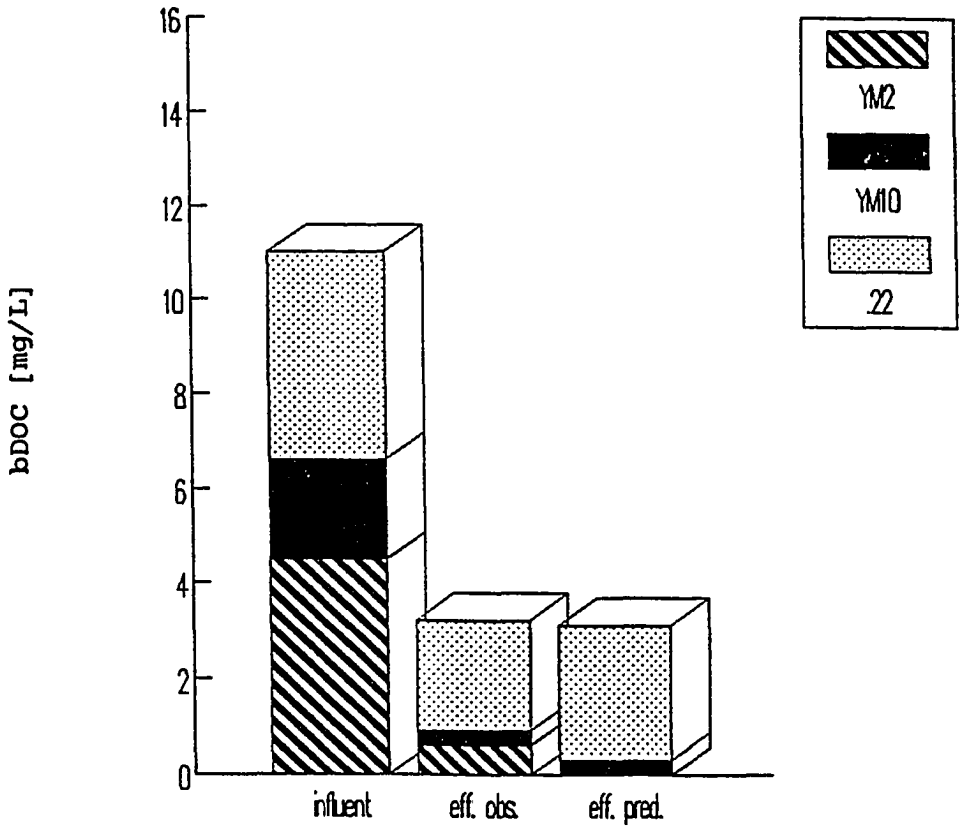
Similar problems noted for DOC removal also occur for bDOC removals, however. Figure 14 shows a creation of 3 mg/L of larger molecular weight bDOC during treatment



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 12 : Trickling filter recycle, effluent and predicted effluent molecular weight distributions based on DOC measurements.

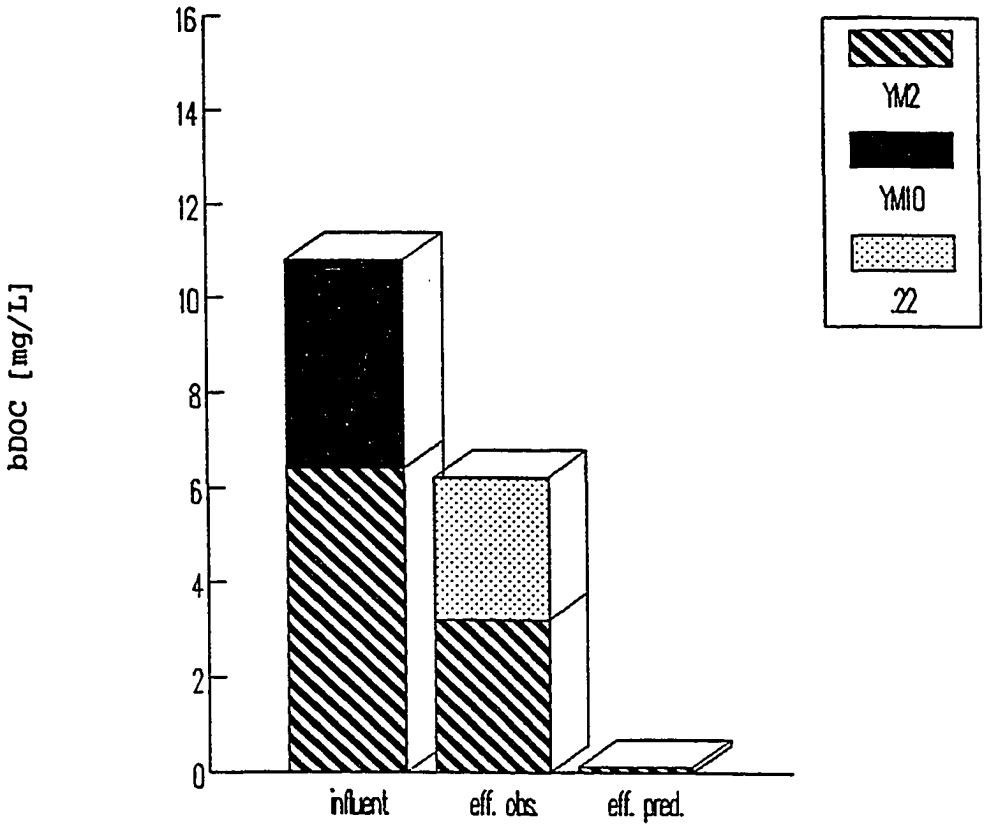
Roger Road 5/9/88 E_B = 0.00002
Shows an unexplained increase in high molecular weight material during treatment.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 13 : Trickling filter influent, effluent and predicted effluent molecular weight distributions based on bDOC measurements.

Atlanta 8/29/88 E_B = 0.001
Normal bDOC removal.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 14 : Trickling filter influent, effluent and predicted effluent molecular weight distributions based on bDOC measurements.

Roger Road 5/9/88 E_B = 0.001
Shows unexplained appearance of high molecular weight material during treatment.

although none was initially measured. The discrepancy here may be due to a change in biodegradability as measured in the BOD test as well as the factors mentioned for Figure 12, above.

4.1.2. Chromatography Results

An attempt was made to predict soluble organics removal in wastewater based on changes in molecular size distributions using high performance liquid chromatography. This required that a relationship be found to relate UV absorption reported by the HPLC detector to the DOC of a given size fraction of wastewater. The technique requires that all materials in the wastewater elute in the HPLC column according to size with no interaction with the column packing.

UV absorption: A wavelength scan was run on a sample to determine the U.V. adsorption profile. The results are presented in Figure 15. It was found that light at 254 nm, a standard wavelength for laboratory analyses, was not highly absorbed by the wastewater from Roger Road treatment plant. A peak above the detection limit of 12 absorbance units was found at 228 nm, however, the slope of the absorption profile is too steep to yield reliable results below a wavelength of 242 nm. A ratio of the UV absorption on fractionated Roger Road wastewater versus the DOC is

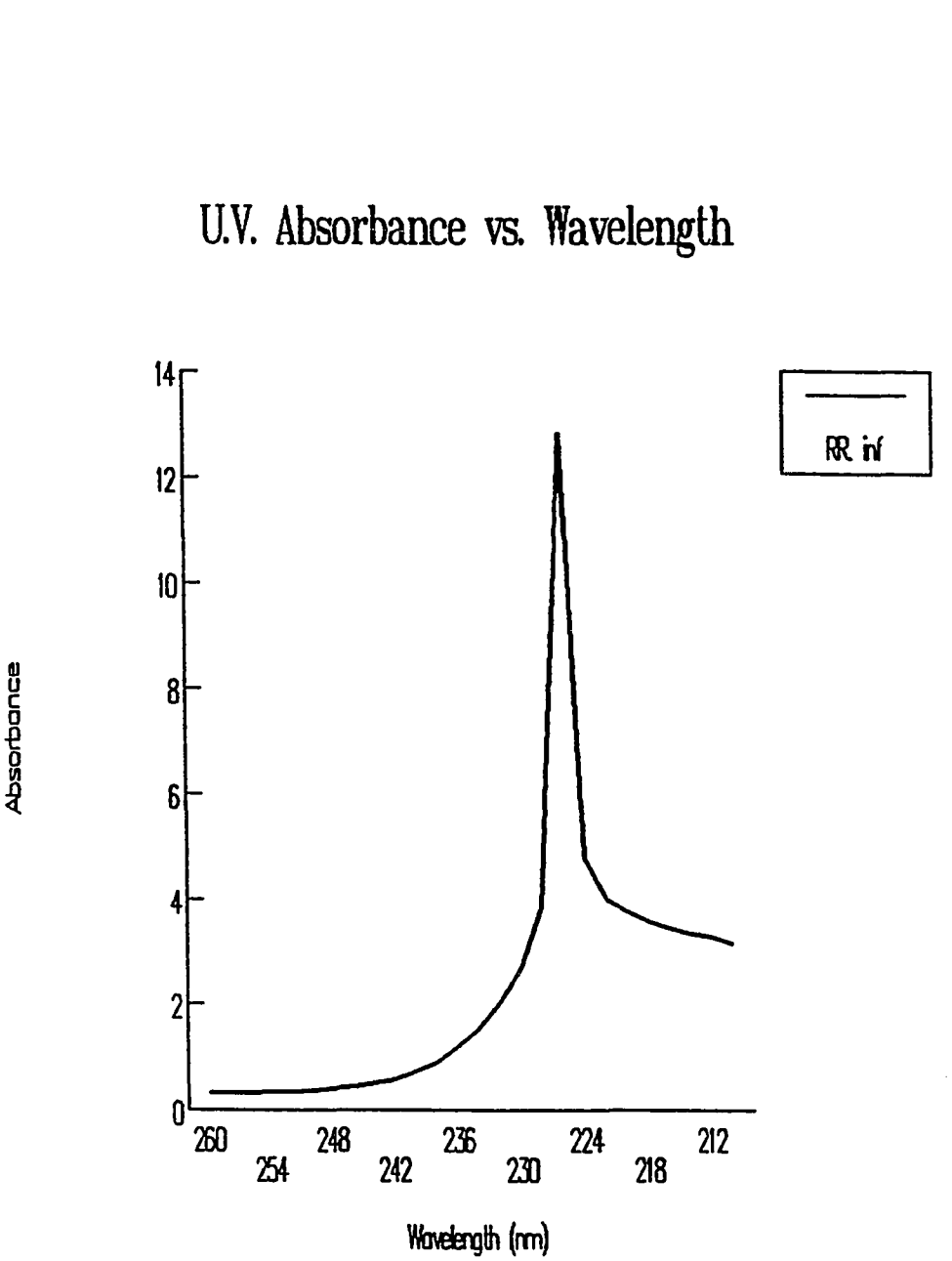


FIGURE 15 : UV Wavelength Scan on Roger Road Trickling Filter influent.

5/18/87

presented in Figure 16 which indicates there is no clear relationship between DOC and UV absorbance at 254 nm. A useful relationship would result in a single line or at least a statistically defined mathematical curve. The two distinct lines (different slopes and intercepts) shown in Figure 16 for influent and effluent indicate that there is no constant correlation between the DOC and UV absorbance. This may explain discrepancies found by Amy (1986) when correlating UV absorbance and DOC measurements on some wastewater treatment effluents resulting from different treatment processes.

Calibration Results: The HPLC column was calibrated with glucose, trypsin, humic acid, ovalbumin, and blue dextran (Figure 17). The low molecular weight standard (glucose) produced a chart peak at 13.4 minutes, which was combined with the absorption variation due to the solvent front reaching the detector at that time. Large molecular weight materials, (greater than 30,000 amu, blue dextran and ovalbumin) appeared reliably at 5.05 to 5.10 minutes, which corresponded to the direct passage of those molecules with no interaction with the column.

Calibration runs with trypsin (mol. wt. 24,000) did not reliably appear on the detector output, and a subsequent examination of the material by UV spectrophotometer indicated that at a concentration of 50 mg/L, the UV absorbance of the material was below the detection

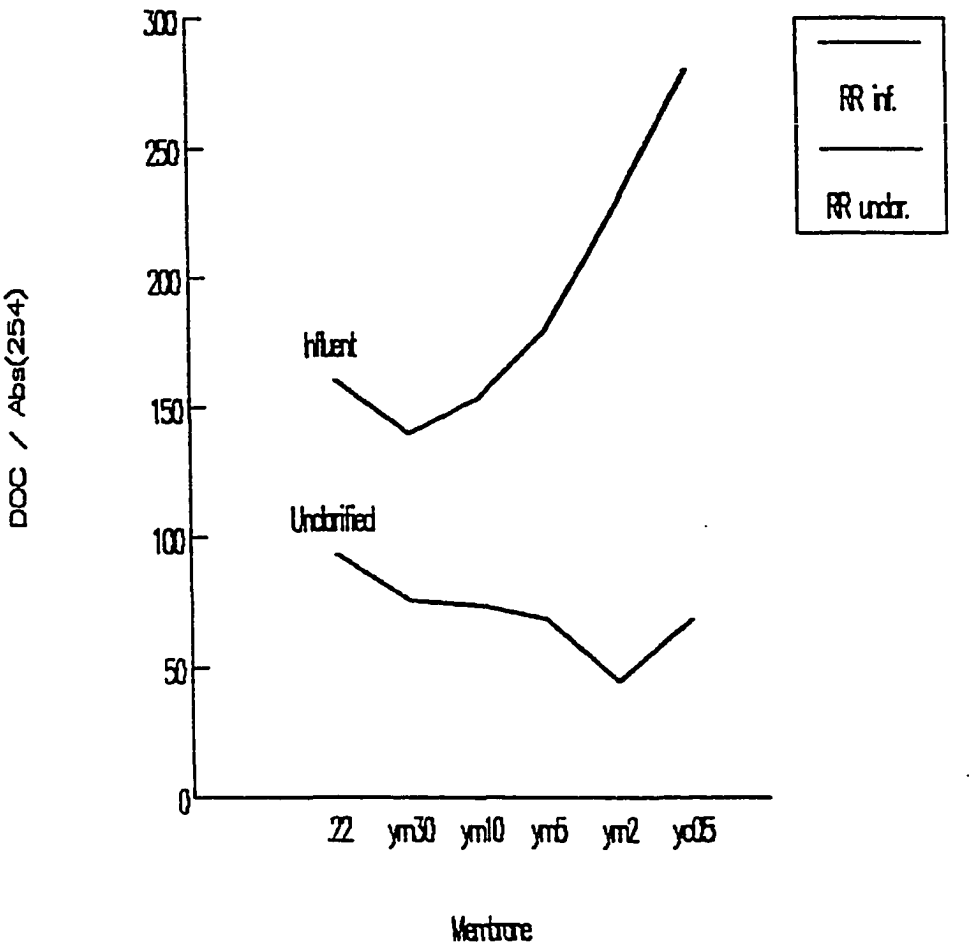


FIGURE 16 : Relationship between DOC and UV absorbance for Roger Road trickling filter influent and effluent.

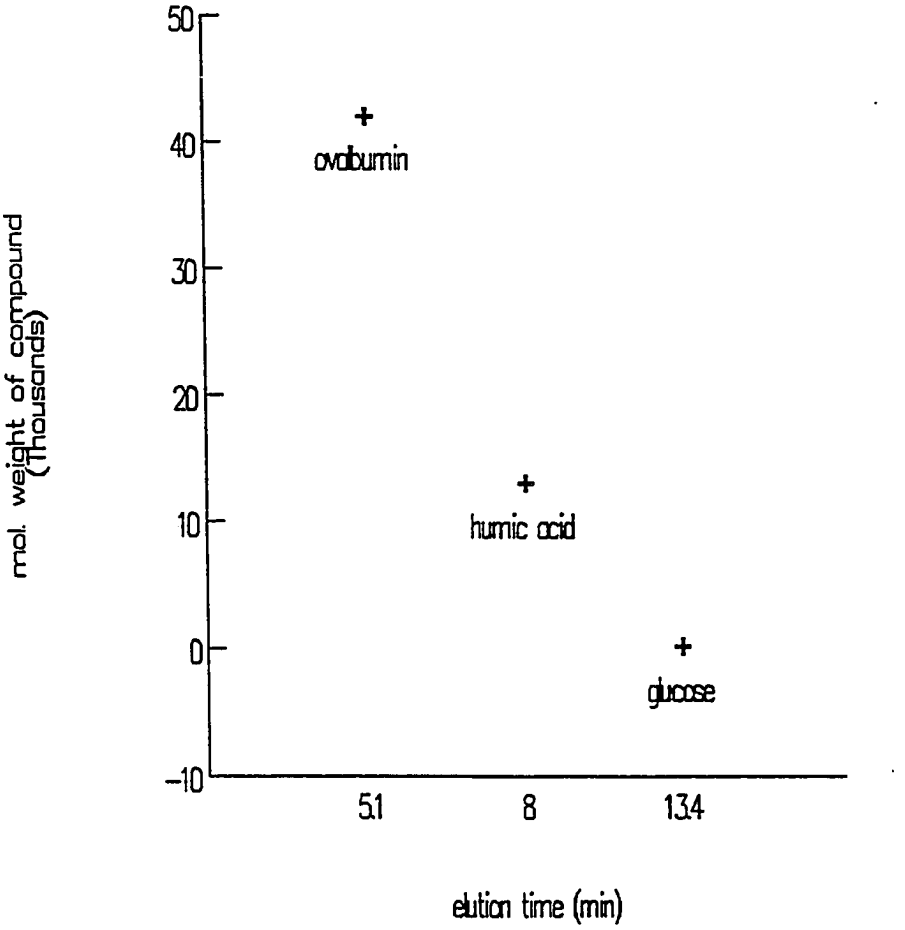


FIGURE 17 : Calibration of HPLC.

limit of the instrument, being masked by the absorbance of the buffer solution.

Calibration runs with laboratory humic acid (mol. wt. ~13,000) at a nonstandard concentration of 80 mg/l resulted in detection at roughly eight minutes, but chart peaks appeared randomly even after the full elution time of 13.4 minutes, and for several hours thereafter. Material appearing after the full elution time for the column must necessarily have been retained by chemical interaction with the resin rather than pure size exclusion. This contributed to the abandonment of the technique for this investigation since it is known that wastewater samples also contain significant amounts of humic acids.

Wastewater Results: Most of the detectable mass in the samples seemed to appear with the solvent molecules, indicating a large fraction of low molecular weight material. However, the data were not reproducible with the techniques used for this analysis.

4.2. BOD Results

Size distribution of sBOD: Soluble organics in wastewater samples were separated into three size fractions using previously described ultrafiltration methods (section 3.1.1), and then used in the BOD tests. The BOD in each UF size fraction was determined by subtraction of the BOD of

the smaller molecular weight material, as was done for the determination of DOC in the fractions. Both standard and Hach BOD tests were done to determine uBODs for the three molecular weight fractions of 0-1,000 amu, 1,000-10,000 amu, and 10,000 amu to 0.22 μm.

Bottle BOD tests: Ultimate soluble biochemical oxygen demands based on the 10 day BOD test for 4 sampling dates are shown in Table 5. The ultimate sBOD of the recycle material varied from 20 to 38 mg/L, while the small material (<1,000 amu) accounted for 11 to 30 mg/L of that total. Subtracting off the BOD accounted for by the small material, the discrete BOD for the mid-range material (1,000 to 10,000 amu) accounted for 0 to 7 mg/L of the total, and the large size fraction (>10,000 amu) accounted for between 1 and 12 mg/L of the total. These results indicate an overwhelming portion of the oxygen demand is generated by the low molecular weight material.

Ultimate sBODs for the trickling filter effluent show that the total sBOD varies from 3 to 23 mg/L. The small material exerts an oxygen demand of 1 and 10 mg/L, while the mid-range size fraction exerts a demand between 0 and 1. The large molecular size material is responsible for between 0 and 13 mg/L of oxygen demand. These results indicate that after treatment, the larger material may comprise a greater part of the remaining oxygen demand.

TABLE 5 : Results from the bottle BOD tests.

Sample	sBOD	discrete* sBOD	Sample	sBOD	discrete sBOD
RR 3/11/88			RR 3/31/88		
Recycle 0.22	38	1	Recycle 0.22	28	12
YM10	37	7	YM10	16	0
YM2	30	30	YM2	16	16
Effluent .22	23	13	Effluent 0.22	3	1
YM10	10	0	YM10	2	1
YM2	10	10	YM2	1	1
RR 5/9/88			RR 5/20/88		
Recycle 0.22	26	1	Recycle 0.22	20	5
YM10	25	0	YM10	15	4
YM2	25	25	YM2	11	11
Effluent .22	8	2	Effluent 0.22	5	0
YM10	6	0	YM10	5	1
YM2	6	6	YM2	4	4

* exclusive of smaller weight fractions.

Hach BOD tests: Results from the Hach test runs on 4 sampling dates show the ultimate sBOD for each sample as well as the estimated kinetic growth coefficients (k) based on the Thomas-Slope method for best data fit, (see Table 6). Ultimate BODs for the complete soluble wastewater after mixing with the recycle flow varied from 33 to 45 mg/L. BOD tests on fractionated wastewater samples showed the low molecular weight material produced an oxygen demand between 18 and 36 mg/L, while the mid-range material accounted for between 0 and 12 mg/L. The large molecular weight material produced an oxygen demand varying from 1 to 14 mg/L. A BOD curve is shown in Figure 18 to illustrate the nature of the data produced by the Hach BOD test.

For the trickling filter effluent, the total sBOD ranged from 4 to 20 mg/L. Of this total, 1 to 8 was the range for the low molecular weight range; 0 to 3 was the range for the mid-range material; and the range for the high molecular weight material was 2 to 10. Again, less oxygen demand was exerted proportionally by the low molecular weight material after treatment.

Rate constants (k values) were erratic for the Hach BOD tests, and it is difficult to draw conclusions useful for the trickling filter model from these. Soluble recycle (blended) kinetic rates varied from 0.28 to 0.65 /day. The effluent samples generated lower kinetic rates between 0.16 and 0.55 /day. According to the theory, larger molecular

TABLE 6 : Results from the Hach BOD tests.

Sample	sBOD	discrete* sBOD	k	Sample	sBOD	discrete sBOD	k
Atlanta 8/22/87				Atlanta 8/29/87			
Recycle 0.22	45	1	0.65	0.22	37	14	0.56
YM10	44	8	0.84	YM10	23	1	0.48
YM2	36	36	0.70	YM2	22	22	0.25
Effluent .22	20	10	0.55	0.22	10	5	0.17
YM10	10	2	0.67	YM10	5	3	0.30
YM2	8	8	0.54	YM2	2	2	0.23
Roger Road 1/27/88				Roger Road 2/19/88			
Recycle .22	34	14	0.35	0.22	35	5	0.28
YM10	16	--	0.34	YM10	30	12	0.20
YM2	20	20	0.40	YM2	18	18	0.28
Effluent .22	10	4	0.39	.22	4	2	0.16
YM10	3	--	0.28	YM10	2	1	0.14
YM2	5	5	0.36	YM2	1	1	0.06

* exclusive of smaller weight fractions.

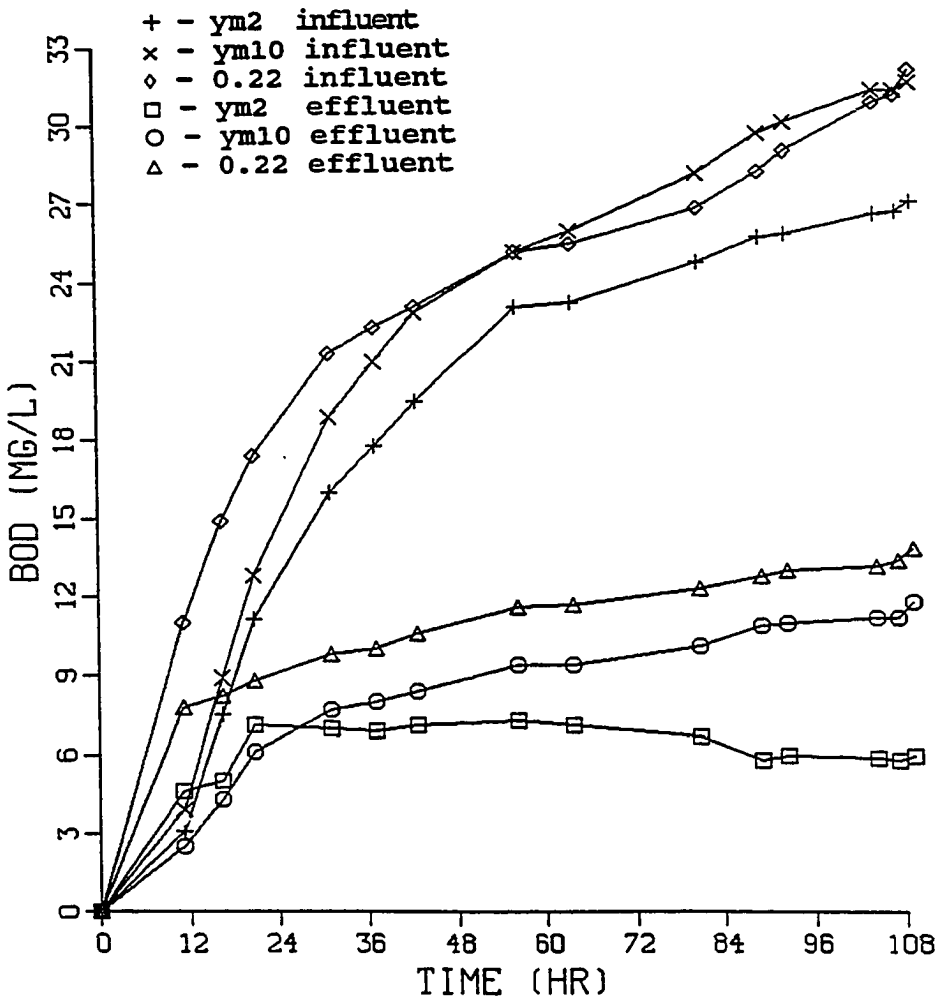


FIGURE 18 : BOD curves produced using the Hach respirometer method.

Atlanta data from 8/22/87

weight material should result in slower kinetics, however, it is difficult to see this trend in the data. In some cases, the presence of larger molecular weight material in a sample seems to enhance the kinetics of degradation, indicating a need for further investigation of the kinetics of size fractionated samples.

4.2.1. BOD/bDOC ratios

A relationship between BOD and bDOC (biodegradable DOC) would offer a convenient alternative to BOD for measuring treatment performance. The biodegradable organic carbon is directly responsible for the biochemical oxygen demand, thus it is logical to look for a relationship between the two.

Figure 19 shows the uBOD/bDOC ratios for Roger Road blended recycle. The average ratio for the low molecular weight material was 2.7 with a standard deviation of 0.6. For the medium molecular weight material, the average was 2.1 with a standard deviation of 0.4. The large molecular weight substrate showed a ratio of 2.5 ± 1.0. Finally, if all the ratios are combined, the average is 2.4 with a standard deviation of 0.7.

Figure 20 shows the uBOD/bDOC ratios for Atlanta influent and effluent. The ratios for influent are higher than those for Roger Road although there are no replicates.

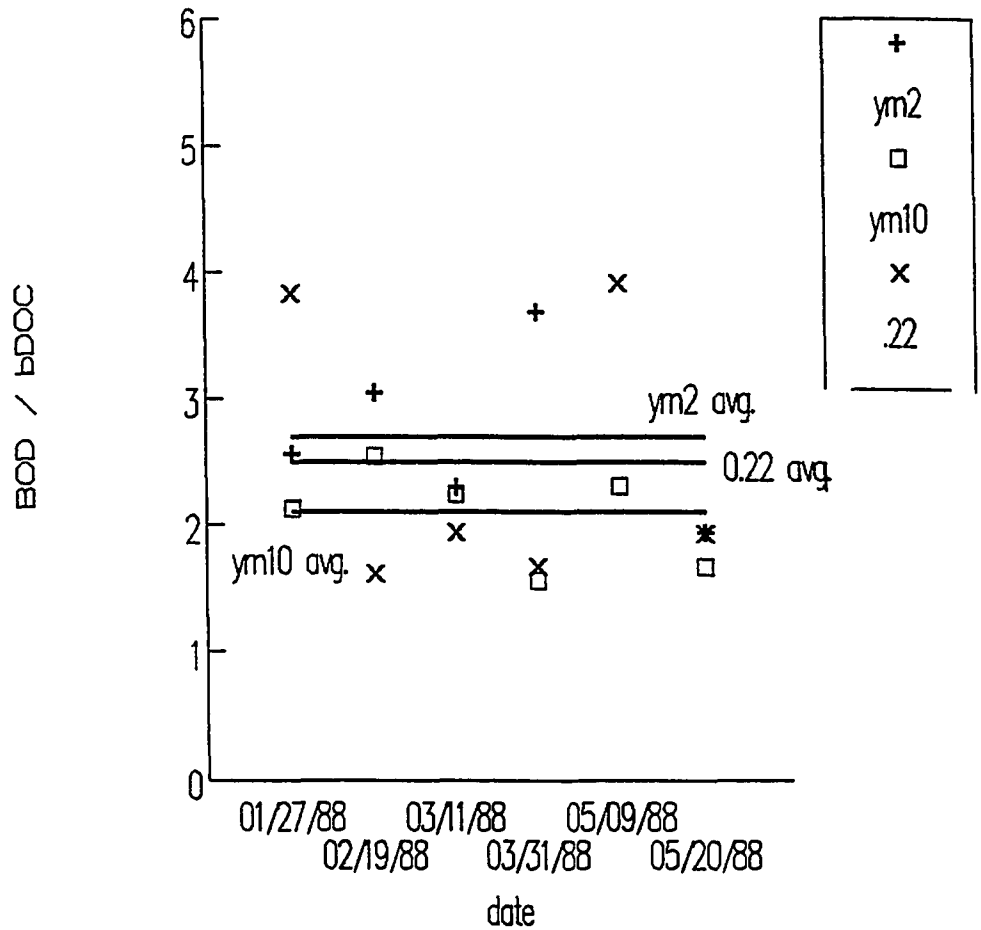


FIGURE 19 : uBOD/bDOC ratio of Roger Road recycle blend.

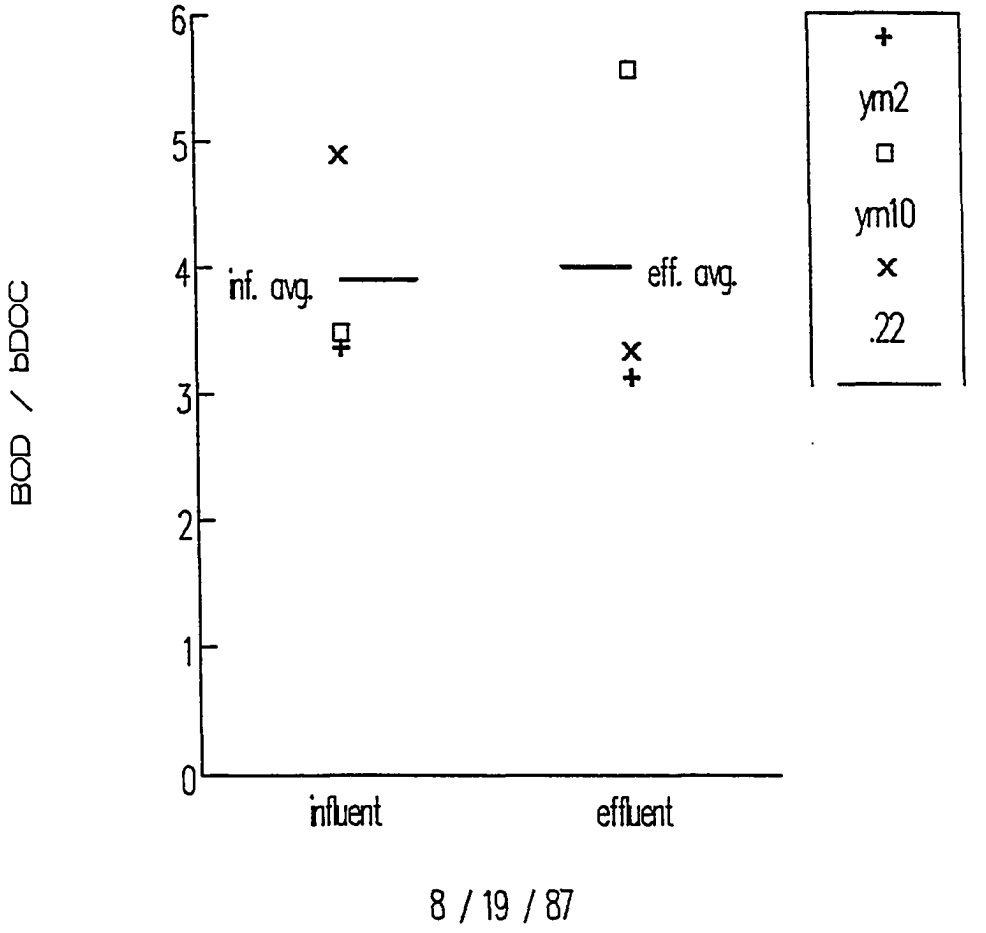


FIGURE 20 : uBOD/bDOC ratios of Atlanta influent and effluent. 8/29/87

The ratio for small material is 3.4, for medium material, 3.5, and for large molecular weight material, 4.9. The overall average for these three values is 3.9 with a standard deviation of 0.8.

For Atlanta trickling filter effluent, the small material produced a ratio of 3.1, the medium 5.6, and the large material 3.3. The overall ratio for effluent data was 4.0 ± 1.4. Combination of influent and effluent ratios for Atlanta yield an average of 4.0 with a standard deviation of 1.0.

The average uBOD/bDOC ratios for Roger Road effluent (Figure 21) for all three size ranges fall within a very narrow band at 1.9 with an overall standard deviation of 0.7. However, the individual standard deviations of each size range are 0.7, 0.5, and 1.0. If all the ratios generated from Roger Road data are considered, both recycle and effluent, the average is 2.2 with a deviation of 0.7

Although the variations in uBOD/bDOC ratios are quite significant, much of this variation can be traced to the variability of the BOD results. The close agreement of the average ratios for Roger Road effluent, and the consistency of Roger Road ratios and Atlanta ratios indicate a great deal of potential for the use of bDOC data to model wastewater treatment performance.

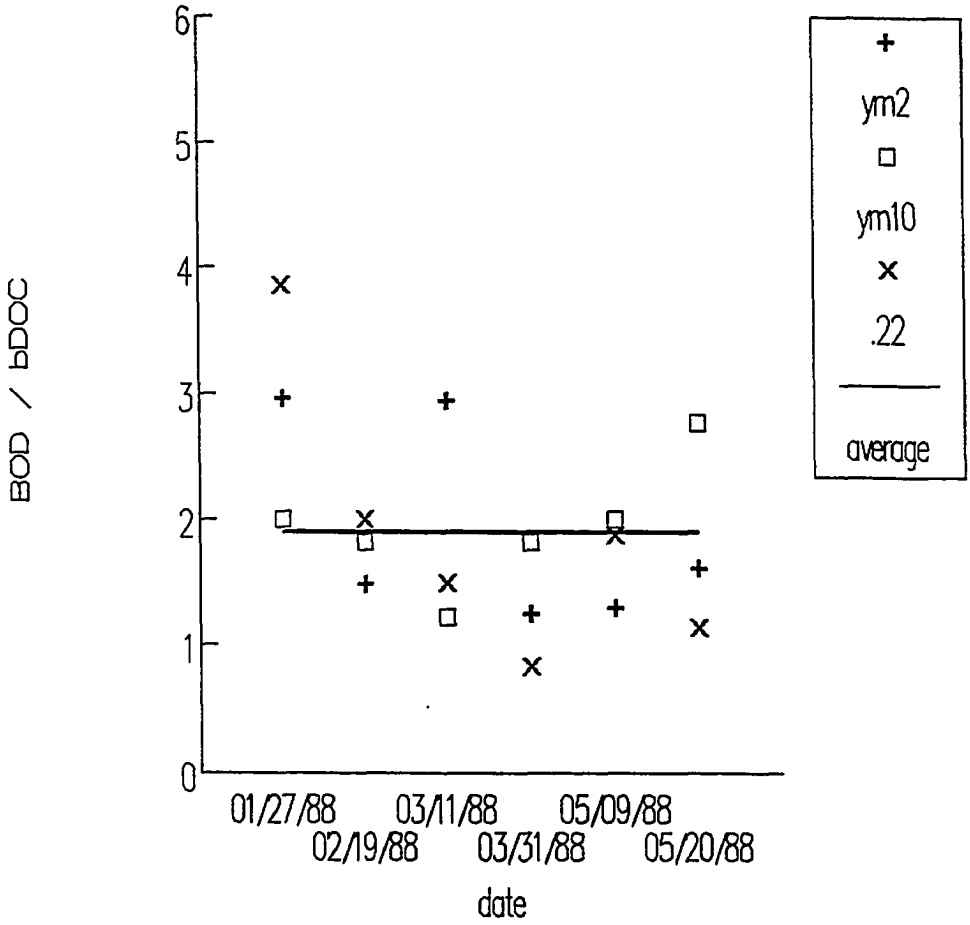


FIGURE 21 : uBOD/bDOC ratios of Roger Road effluent.

4.2.2. Low vs High Molecular Weights : Dextran Test

As previously noted, (section 4.2) there were unexplained shifts in molecular weight distributions during treatment of the wastewater. A special test was run on wastewater having passed a 1,000 amu nominal cutoff ultrafilter membrane in combination with an easily biodegradable dextran having a molecular weight of 42,000. The objective of this test was to note the inter-relationship of the two extremes in molecular weight during biodegradation and to track the products' size distribution. It was hoped that this would clarify transitions between molecular weight fractions such as those noted in section 4.2.

Hach BOD test reactors were loaded with ultrafiltered wastewater (molecular weight less than 1,000 amu), with a combination of ultrafiltered wastewater and the dextran, and with a dextran solution only. After a 10-day Hach BOD test, the product water was fractionated using the standard ultrafiltration technique to see the resulting molecular weight distribution.

In the Dextran-only samples, very little organic carbon was detected at all after the Hach run, and no material was detected above 1000 amu, despite an initial DOC of 21.9 mg/L of larger molecular weight material. In contrast, the wastewater-only samples, which initially had

a DOC of 9.8 mg/L of material less than 1,000 amu, produced a product having 53% material larger than 1,000 amu. Finally, the combined wastewater and dextran, with a starting DOC distribution of 84% ~ 42,000 amu and 16% < 1,000 amu, ended with a distribution of 55% > 1,000 amu and 45% < 1,000 amu.

The addition of a large molecular weight dextran did not significantly change the degradation characteristics of the small molecular weight fraction of a wastewater. Regardless of the presence of the dextran, which was always degraded, the small material from the wastewater had a tendency to form larger molecular weight products during the BOD tests.

4.3. Computer predictions of trickling filter performance.

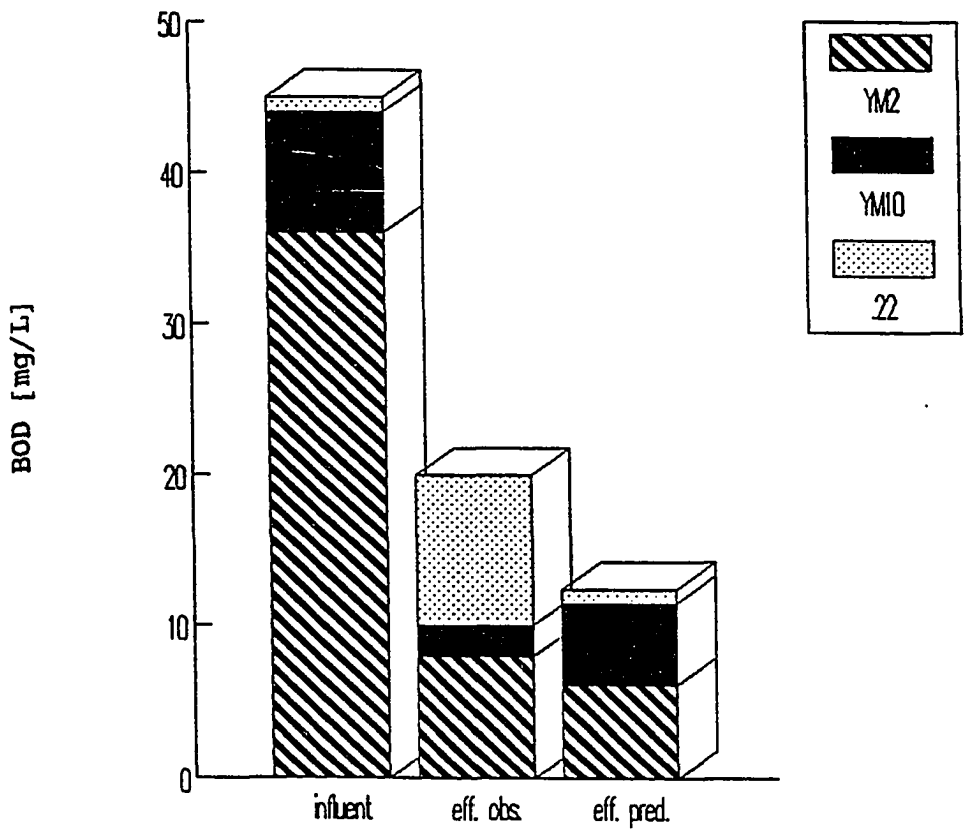
The first step in calibrating the Logan model is to determine the appropriate diffusivities of the molecular weight fractions of the wastewater. Based on the Polson correlation (eq. 2.8), the following diffusivities were determined to be representative of the three size fractions used in this study:

Size	Diffusivity (10^8 cm^2/s)
0 - 1,000 amu	500
1,000 - 10,000 amu	100
10,000 amu - 0.22 m	10

Model Calibrations using Atlanta data: The trickling filter model (Appendix A) can be calibrated by adjusting the collision efficiency (E_B). E_B was determined for three types of data: DOC, sBOD, and bDOC. The two replicates for tests on Atlanta wastewater were averaged to yield a best estimate for the collision efficiency (E_B) to be integrated into the model based on uBOD removal. Because the two replicates did not agree very well for BOD data, the model overshoots one data set (Figure 22) by 80% and undershoots the other (Figure 23) by 40%. The value for E_B based on sBOD removal in Atlanta was determined to be 0.0001.

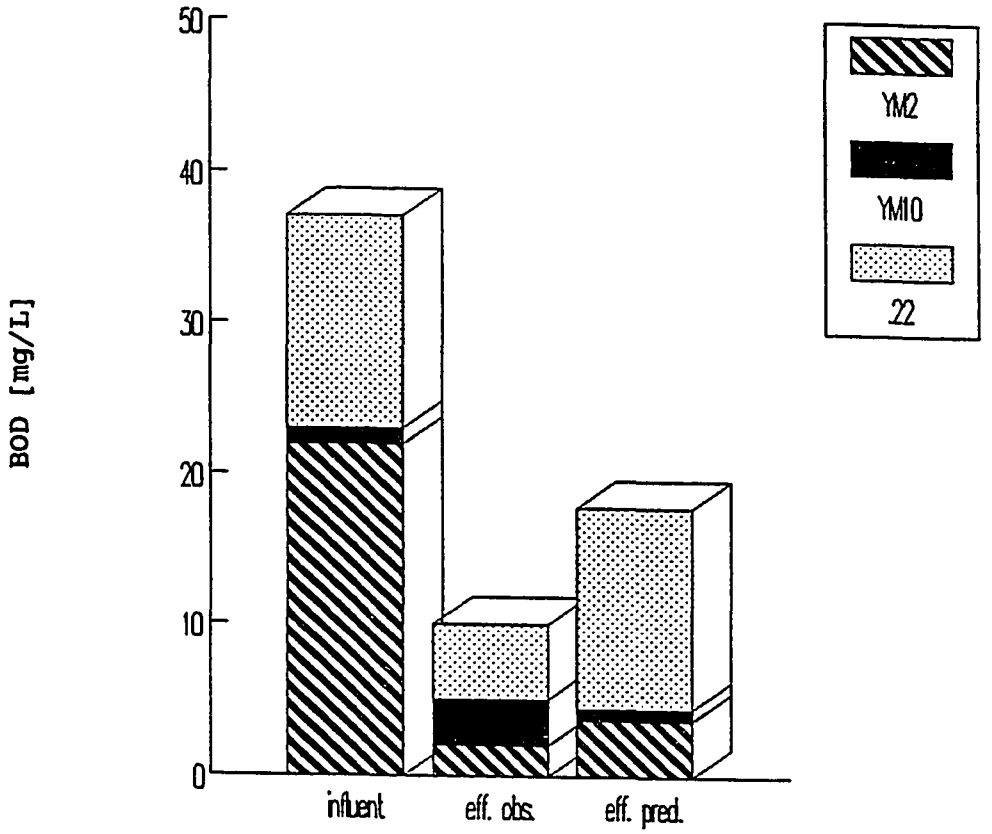
The first DOC data from Atlanta were used to determine an E_B of 0.00002 for DOC removal. The observed DOC removal versus the predicted DOC removal for the Atlanta data is shown in Figure 24. The observed removal of DOC agrees within 10% of the predicted overall removal, however, the predicted removal of low molecular weight material is overestimated (~ 66%) while the predicted removal of the high molecular weight substrate is underestimated (~ 100%). The midrange DOC removal is underestimated, but within 30% of the observed removal.

The Atlanta bDOC data produced an E_B of 0.001, which generated a predicted overall bDOC removal within 5% of the observed bDOC removal (Figure 13). The residual bDOC in the effluent was not predicted, while large molecular weight material removal was underpredicted by 14%. Medium



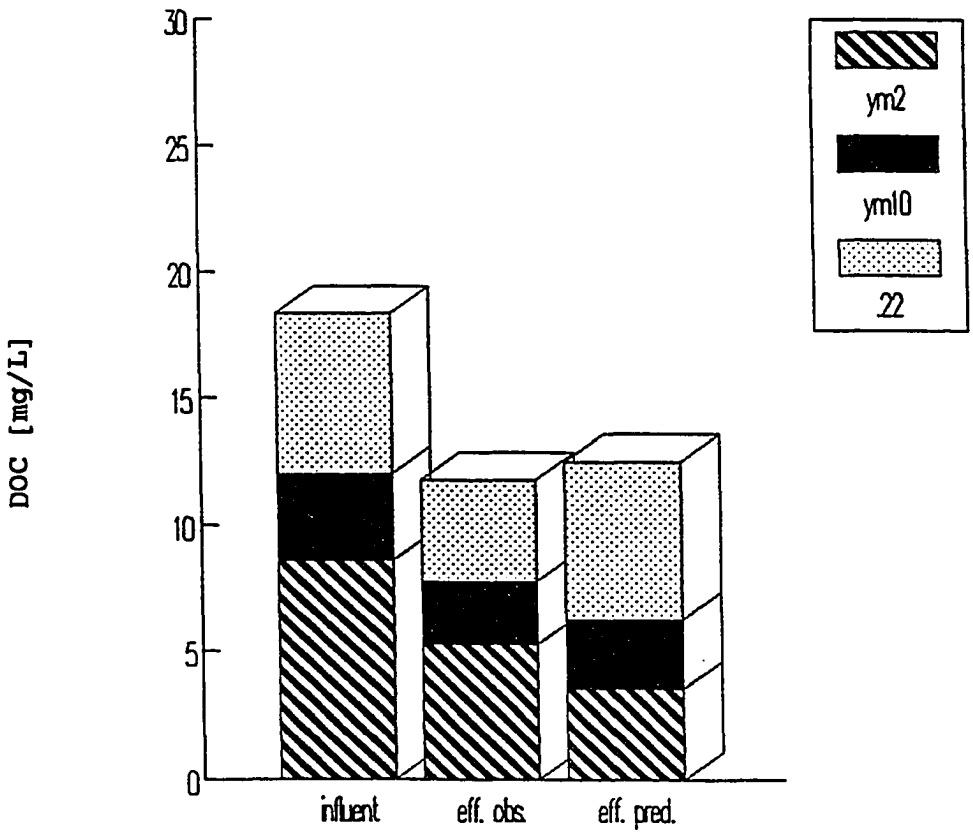
ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 22 : Observed versus predicted removals based on BOD measurements. Atlanta 8/22/87.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 23 : Observed versus predicted removals based on BOD measurements. Atlanta 8/29/87.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 24 : Observed versus predicted removals based on DOC measurements. Atlanta 8/29/87.

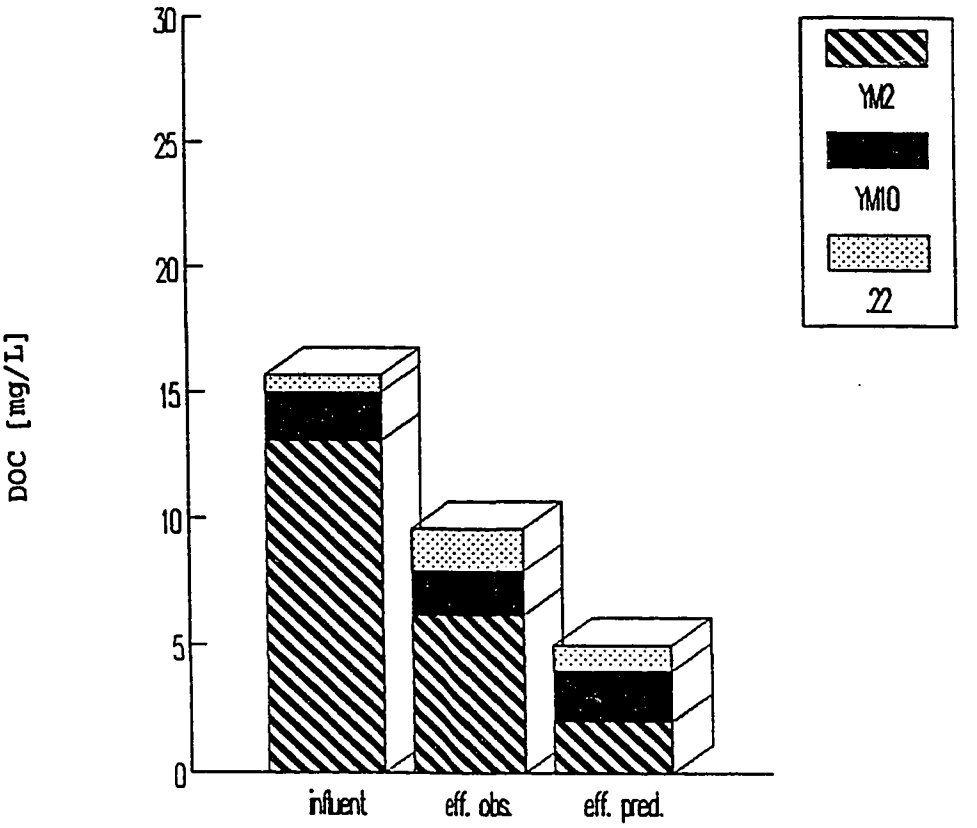
size bDOC removal was predicted within 5%. The values for E_B are summarized in Table 7.

Roger Road (predictions vs. observed): After calibration of the model based on observed removals in Atlanta, predictions were made for the removals in Tucson. Figure 25 shows a plot of influent DOC distribution, compared with the observed effluent, along with the predicted effluent as calculated by the model. The observed DOC removals for small, intermediate, and large size fractions are 6, 0.5, and -1 mg DOC/L respectively, while the corresponding predicted removals are 10, 2, and 1.

Figure 26 is similar but uses BOD as a measurement basis. The observed BOD removals for small, intermediate, and large size fractions are 18, --, and -2, while the corresponding predicted removals are 23, --, and 0 mg BOD/L, where there was no intermediate size material originally present in the sample. The observed bDOC (Figure 27) removals for small, intermediate, and large size fractions are 3.5, 2.3, and 4.5, while the corresponding predicted removals are 5, 2.4, and 3 mg bDOC/L. Plots for other available data sets are included in Appendix C.

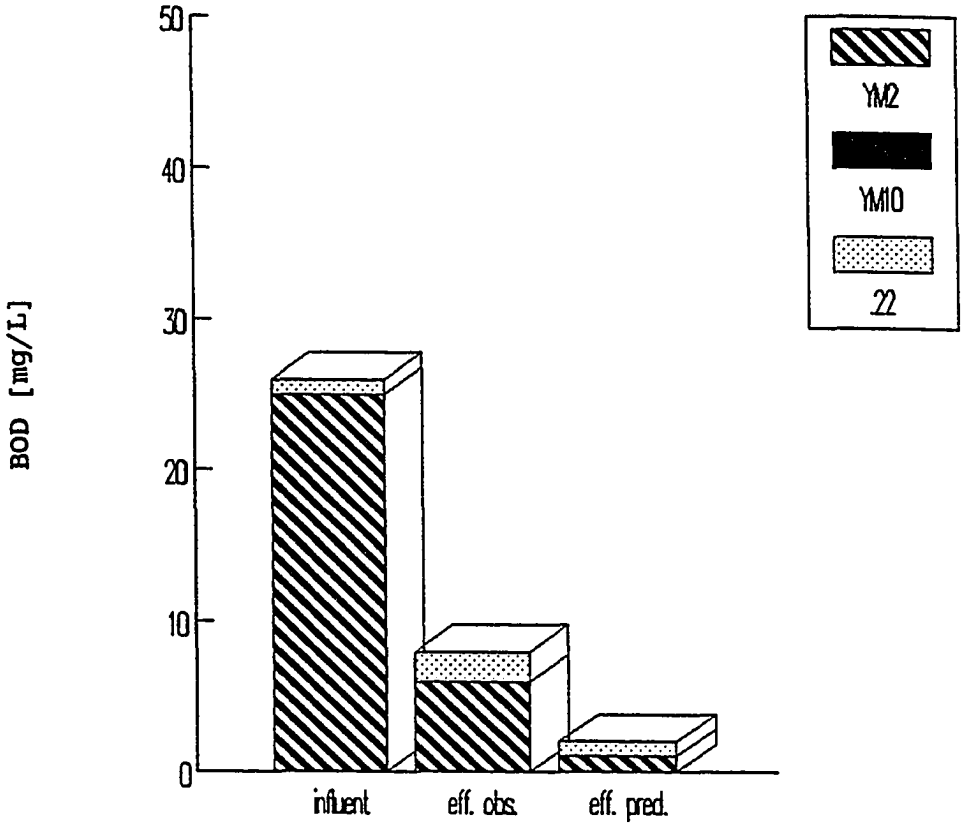
TABLE 7 : Values determined for collision efficiency (E_B)

Parameter	E_B
sBOD	0.0001
DOC	0.00002
bDOC	0.001



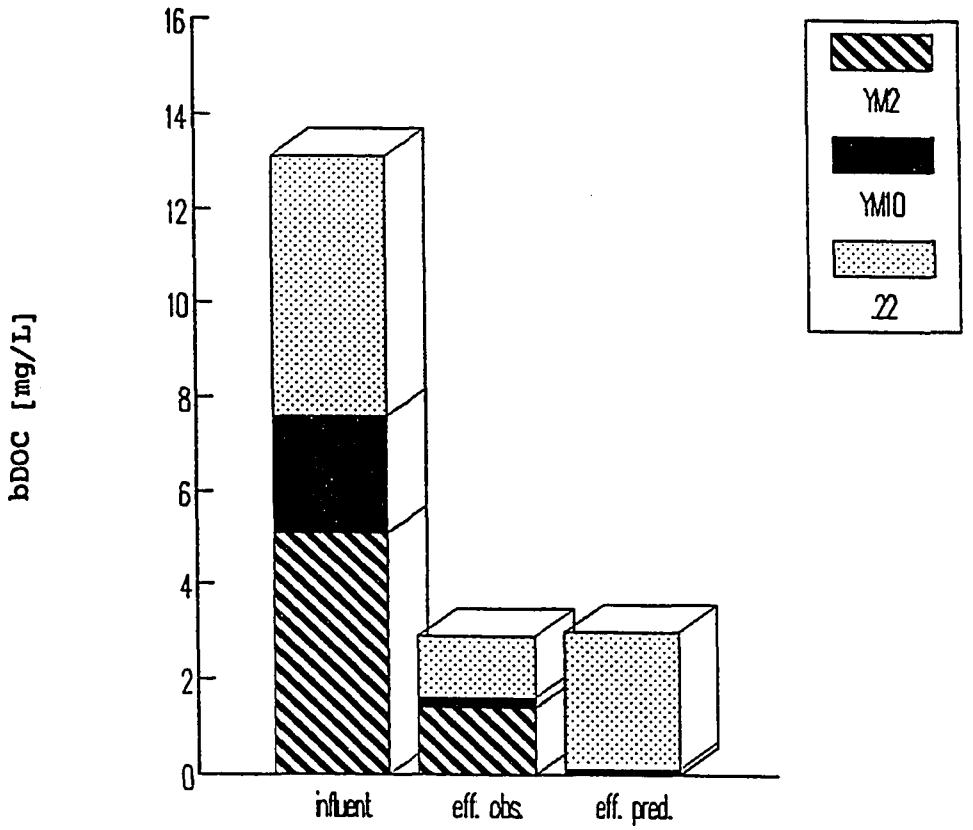
ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 25 : Observed versus predicted removals based on DOC measurements. Roger Road 3/31/88.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 26 : Observed versus predicted removals based on BOD measurements. Roger Road 5/9/88.



ym2 ==> 0 to 1,000 amu, ym10 ==> 1,000 to 10,000 amu, and 0.22 ==> 10,000 amu to 0.22μm.

FIGURE 27 : Observed versus predicted removals based on bDOC measurements. Roger Road 1/27/88.

5. DISCUSSION

The Refiltration method for determining UF membrane rejections based on the permeation coefficient model proved to be effective and economical. It permitted correction of the UF separations for membrane rejection which might otherwise have been neglected--improving the accuracy of all the UF molecular size determinations and subsequent size fractionated BOD tests. HPLC did not prove to be a viable alternative for the wastewater characterization studies.

There are numerous problems with the use of sBOD as a treatment performance parameter. bDOC may offer an attractive alternative parameter based on preliminary studies of the relationship between sBOD and bDOC. The Logan model was recalibrated based on size fractionated sBOD, DOC, and bDOC data, and predictions were examined for a series of data sets. The predictions of the model improved only slightly compared to the results obtained with the previous arrangement of the Logan model based on total BOD removals. Future investigations should clarify the remaining questions to allow the realization of the full benefit of the model, eliminating the need for trickling filter pilot studies.

5.1. Molecular Size Distributions

A new technique was developed for correcting apparent molecular weights of wastewater as fractionated using UF, and the UF methods were compared to HPLC determinations. The improved UF methods proved to be useful for the determination of wastewater molecular size distributions.

5.1.1. Ultrafiltration

Three methods, Refiltration, Incremental filtrate collection, and Dilution were compared to determine size distributions of dissolved organics using specific compounds and 0.22 μm filtered wastewater samples. Of these three methods, the Refiltration method was found to be fast and accurate. For example, an apparent permeation coefficient of 0.81 was determined for inulin separations using a 10,000 amu cut-off (YM10) membrane for the Refiltration procedures. Only 79% of the original DOC concentration was recovered in filtrate samples without correction; unrecovered organics would be assumed to have an AMW greater than 10,000 amu. With correction for membrane rejection, 98% of the actual DOC was calculated to be less than 10,000 amu in the original sample.

The Incremental filtration method accounted for 95% of the mass that should have been able to pass through the

membrane. However, this method required 10 collection steps and several DOC measurements per sample, as well as a statistical analysis to find the best-fit for estimation of the permeation coefficient and DOC able to pass through the membrane.

Dilution method calculations of the mass able to pass the membrane frequently resulted in a greater mass than was initially present in the sample. For inulin, the material less than 10,000 amu was calculated to account for 106% of the applied DOC, and for wastewater, this fraction was calculated at 112% of the applied DOC. These large values are unreasonable and make it difficult to determine mass fractions within larger size categories. The probable cause of the discrepancies is contamination, either from the handling of the sample, or from the membrane itself.

The Refiltration method assumes that the permeation coefficient remains unchanged during successive filtrations of the sample. This will be true if components within the original retentate that are unable to pass through the membrane do not significantly influence the passage of the remaining filtrable components. Shown in Table 8 are DOC data on wastewater samples prepared by three filtrations of a 0.22 μm prefiltered sample. During each ultrafiltration step through the indicated membrane, one-third of the sample was collected in the filtrate, and the top two-thirds of the retentate discarded. The filtrate was

TABLE 8 : DOC of three successive ultrafiltrations on a wastewater sample.

	DOC [mg/L]	
Sample	10,000 amu	1,000 amu
Total Soluble	33.8 ± 1.3	33.8 ± 1.3
Filtrates		
First	26.9 ± 0.5	20.1 ± 0.4
Second	25.4 ± 0.7	17.7 ± 0.3
Third	25.8 ± 0.2	15.5 ± 0.1

then placed above the membrane and this process repeated. The DOC listed for the original sample contains components both larger and smaller than the membrane cut-off. However, all filtrates contain only material that has successfully passed through the membrane. Using filtrates 2 and 3, obtained with the YM10 membrane, the Refiltration method (eq. 3.11) results in a predicted DOC of 25.1 ± 1.6 mg/L for the first filtrate, versus the actual DOC of 26.9 ± 0.5 mg/L. These numbers are equal within the reported errors in DOC within two standard deviations, or the 95% confidence interval. A similar calculation for the YM2 membrane suggests a DOC of 20.2 ± 0.4 mg/L based on filtrates 2 and 3, versus the first filtrate DOC of 20.1 ± 0.4 mg/L. These calculations support the model assumption that the permeation coefficient is relatively unchanged during successive filtration steps. The generality of this assumption should be examined for a wider range of water and wastewater samples.

The use of the proposed permeation coefficient based on equation 3.4, and not an apparent rejection coefficient, could provide a common basis for ultrafiltration experiments. Most investigators that have incorporated membrane rejection coefficients (e.g. Wheeler, 1976; Adachi *et al.*, 1986) have used:

$$R^* = \frac{C_f}{C_r} \qquad (4.1)$$

Comparison with equation 3.11 shows that this rejection coefficient, R^*, actually an apparent rejection coefficient, must be dependent on the volume of filtrate relative to the original sample volume. Since the volumes of filtrate are rarely reported, results from different studies cannot be compared on a common basis. The first step in resolving variations in size distributions in the literature on ultrafiltration separations requires that investigators report both apparent rejection coefficients and absolute permeation coefficients.

Shown in Figure 28 are ultrafiltration data reported by Wheeler (1976). In this experiment, successive 50 ml ultrafiltrate samples of inulin from a 400 ml stirred ultrafiltration vessel were collected using a 10,000 amu membrane, and samples analyzed for dissolved organic carbon. Wheeler recognized that inulin concentrated above the membrane and accumulated in the retentate. However, he attributed increased concentrations found in the latter filtrate samples to leakage through the membrane when retentate was reduced by more than 50%. His recommendation was to discard the first 50 mL, and collect and analyze the next 150 ml. Also shown in Figure 28 are the predicted DOC's of 50 mL withdrawals assuming a permeation coefficient model with p=0.9. Wheeler did not report the initial DOC, but if an initial DOC of 3.2 mg/L is assumed, the model results are very similar to the data presented by

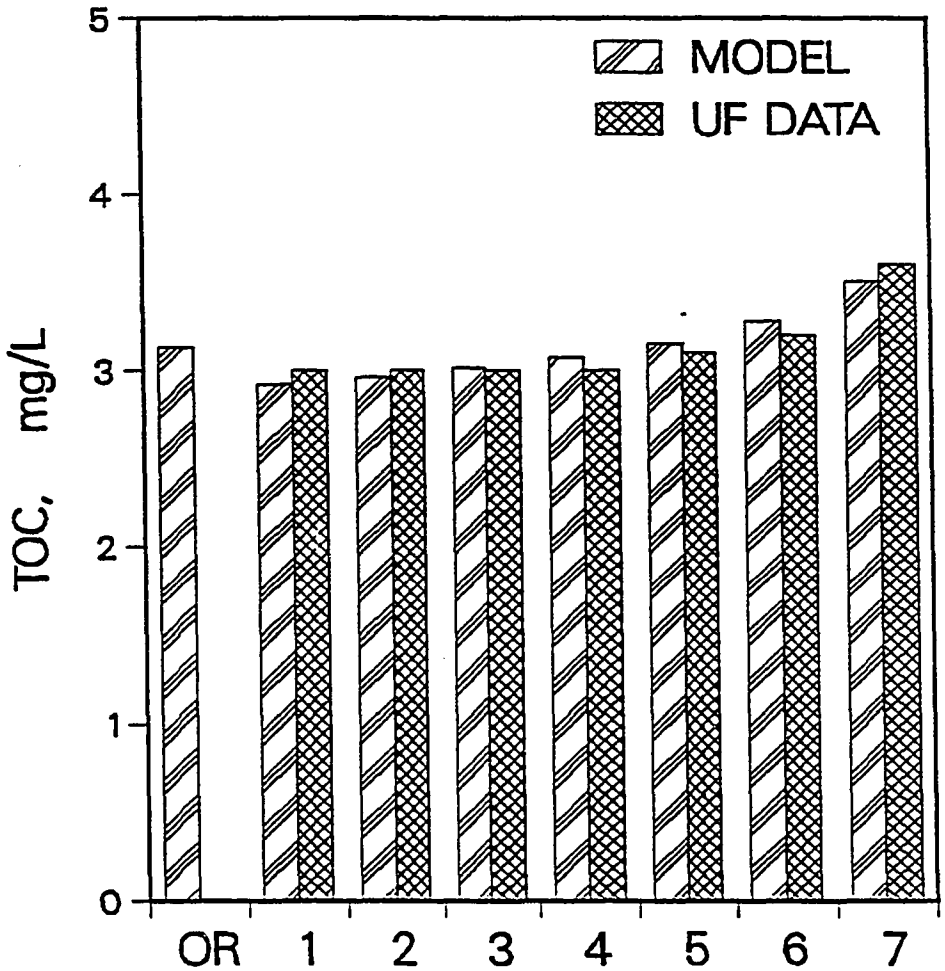


FIGURE 28 : Measured DOC as reported by Wheeler (1976) versus permeation coefficient model predictions using p = 0.9.
OR = original 0.22 μm filtered sample.

Wheeler. If we assume a 5% error in DOC measurements, model predictions agree with Wheeler's data within a 95% confidence interval. In this investigation, the first four sequential inulin filtrates, (Figure 2), were not significantly different.

Size distributions of wastewaters were also determined with UF membrane cut-offs of 500, 1000, 5000, 10,000, 30,000, and 100,000 amu. In general, the permeation coefficient approaches unity for wastewater samples as the pore size of the UF membrane increases. For the 100,000 amu membrane, the permeation coefficient is not significantly different from unity. This results in more accurate identification of dissolved organics in larger size fractions, with increasing underestimation of mass in smaller size fractions. The precision of the Refiltration method is limited by variability in DOC measurements, and reproducibility of ultrafiltration separations. Experience indicates that for wastewater separations, ~1 mg-DOC/L is the limit of precision for routine analysis by the Refiltration procedure, since errors in DOC measurements are doubled by squaring the first filtrate measurement (eq. 3.11) to obtain the initial DOC. Although this error can be reduced by increasing the number of DOC measurements, parallel sample ultrafiltrations are not sufficiently reproducible to support more significant estimation of organic size fractions.

This study (section 4.1.1) demonstrates that the use of uncorrected UF separation filtrates can result in an underestimation of smaller size fractions due to membrane rejection. The proposed model, however, based on a permeation coefficient, can successfully account for membrane rejection during organic compound separations. The Refiltration procedure is a quick and accurate method for determining the portion of dissolved organics able to pass through an ultrafiltration membrane, and can be used to characterize size distributions of dissolved organics in wastewaters.

5.1.2. Chromatography Separations

The use of HPLC appears to be inferior to UF for determining the size distribution of soluble organics in wastewater. No clear relationship was found between DOC concentrations and UV absorbance (section 4.1.2.) Because of the high absorptivity of certain substances (ie: humic and fulvic acids), small amounts of these materials would override the sensitivity of any spectrophotometric technique for judging substrate removals. Comparison of inulin and fulvic acid, which have roughly comparable molecular weights (~ 5,000 amu) and organic carbon contents (0.382 mg DOC/mg inulin, 0.485 mg DOC/mg fulvic acid, Collins, 1985), show two orders of magnitude difference in

UV absorbance. For inulin, abs_{254} is 0.026 @ 100 mg/L while fulvic acid produces an abs_{254} of 0.212 @ 10 mg/L, (Collins, 1985), demonstrating that the individual light absorbing qualities of a molecule do not directly reflect the organic carbon content of a molecule.

Based on these observations, it is not recommended that a spectrophotometric detector be used for determining size exclusion data on heterogenous wastewaters. The examination of any wastewater containing even small amounts of humic or fulvic acids would report erroneously large values for fractions containing these materials. For size characterization work on wastewaters, a much better and more direct parameter would be organic carbon measurements, even though the resolution of the chromatogram would suffer since organic carbon analyzers are generally batch operated rather than continuous.

One of the main assumptions of the HPLC technique is that the interaction between molecules and matrix is based strictly on size exclusion rather than surface chemistry. A problem occurred when water samples containing humic acids were introduced to a size exclusion chromatography column. Laboratory grade humic acid (section 3.1.2.) was introduced into the column. Instead of observing one clean peak from the spectrophotometer output, a series of peaks were observed which lasted nearly six hours until the column was washed with HPLC grade water and 0.4 *M* NaCl. It

appears that under the elution conditions chosen, the humic acid molecules were able to chemically bond with the column packing material. Were such an occurrence to happen even to a small degree when examining an actual wastewater sample, the size distribution would be greatly skewed since the humic acid would come out substantially retarded and not correspond in the chromatogram to its actual molecular size. If this consideration applies to humic acid, then it is likely that other compounds found in wastewater samples also would interact with the column packing. Many size exclusion tests have been done using carefully crafted synthetic materials (ie: polymers) or specifically chosen single substrates such as vitamin B12 or special dextrans. A wastewater has a mixture of well-behaved materials, as well as materials with strong surface interactive tendencies, and some molecules may behave in a hydrophobic manner. Given these considerations, certain precautions should be taken when using size exclusion chromatography, such as routine correlation of size exclusion results with another method, perhaps ultrafiltration.

Lower and upper limits to HPLC resolution: When molecules having a size smaller than 2000 amu are introduced into the column, they are able to freely diffuse into the pore structure of the matrix. These molecules are retained by the column pores until the column is completely

flushed out, essentially acting the same as molecules of carrier fluid.

A calibration curve for the column which was provided by the manufacturer (Figure 29) shows the expected loss in resolution for very small molecules. Unfortunately, the wastewater to be examined from the Tucson area has a large fraction of soluble organics below 2000 amu, and the resolution of the column does not extend to this range. Ultrafiltrations using a membrane with a 1000 amu nominal pore size showed this small size fraction accounted for as much as 90% of the dissolved organic material in the influent (Figure 30) and blended recycle (Figure 8). Ultrafiltrations of the wastewater from the Roger Road trickling filter also showed that only a small fraction of the organic carbon was normally found between 1,000 amu and 30,000 amu, (also in Figures 30 and 8).

The most important reason for finally abandoning the size exclusion approach in this research was the finding that large percentages of the dissolved organics in the wastewater under study proved to have molecular weights under 2000 amu. Considering the expense in time and resources of HPLC work, and the problems encountered in implementation, it is not considered a good choice at this time for routine characterization of molecular size distributions for the purposes of applying the trickling filter model.

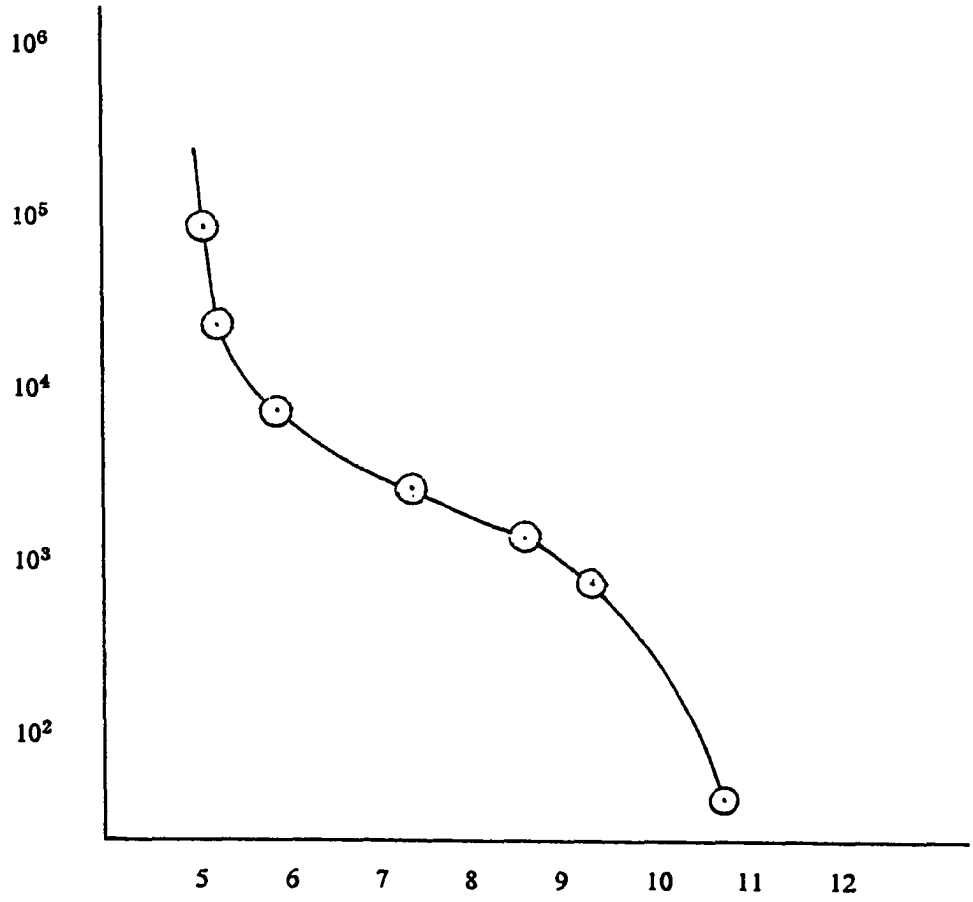


FIGURE 29 : Calibration curve as provided by manufacturer for the Sperogel™ 2000 sw column.

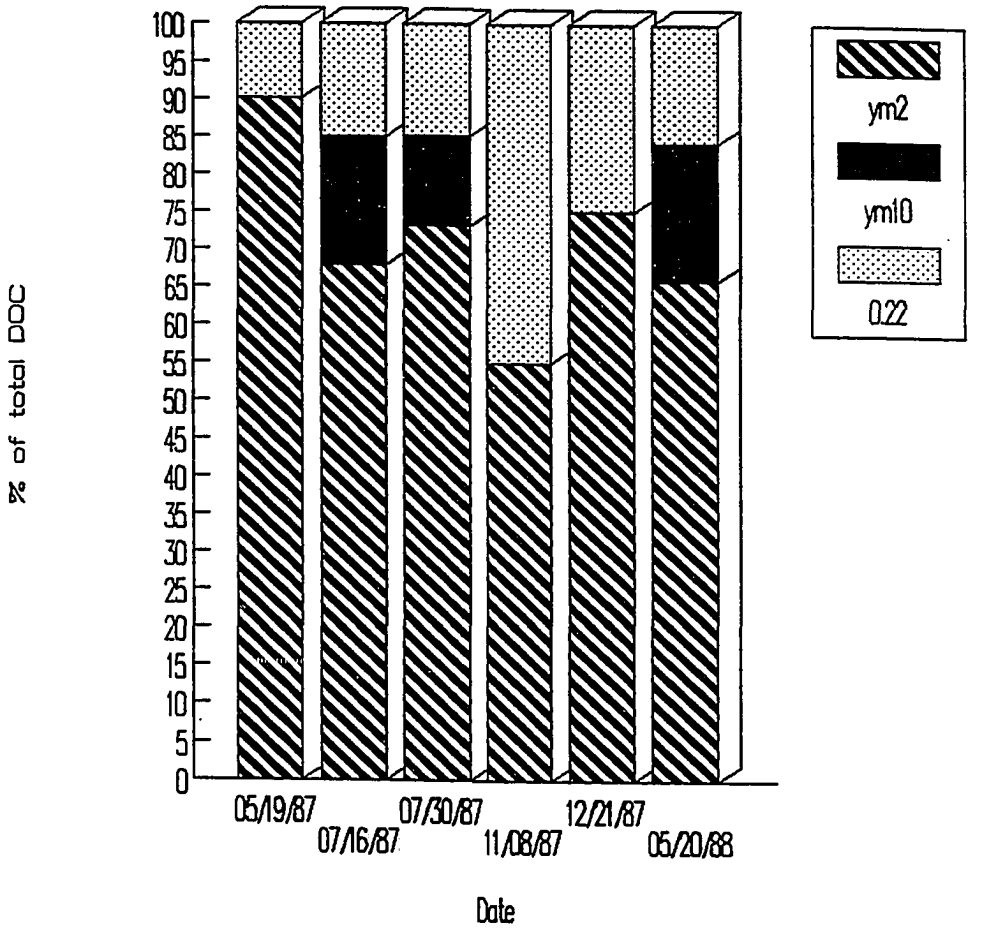


FIGURE 30 : Molecular weight distribution of Roger Road Influent shown as a percentage of the total DOC. Shows that the low molecular weight material (ym2: < 1,000 amu) accounts for up to 90% of the DOC.

5.2. sBOD Implications

SBOD removal is often used as a gauge of wastewater treatment efficiency, however, there are various problems with the sBOD test, which is often run for a 5 day period, with the assumption that 65% of the total biochemical oxygen demand for wastewaters is exerted in that period. First, the standard BOD test has limited reproducibility in comparison to machine measurements such as DOC; average coefficients of variation replicates on all the BOD tests were 10 to 15%. Second, some difficulties arise in stocking a well-acclimated seed material without adding a significant amount of substrate to the dilution water as well. Third, the standard BOD test is quiescent and may not accurately reflect the hydrodynamic environment of a trickling filter. It is suspected that increased mixing will increase microbial degradation rates (Logan 1986) thus the reported biological kinetic constants from bottle tests may not be directly applicable to biofilm kinetics in thin fluid film reactors.

Under stirred conditions with essentially unrestricted oxygen availability as in the Hach tests, the biological reaction very rapidly approached completion, suggesting that such an environment might make the measurement of ultimate BOD viable in a shorter time frame. The stirring

supplied to the samples during the Hach test may be a better approximation of conditions in a trickling filter than a quiescent standard BOD test.

Fourth, the suspended organisms used for a BOD test might not have the same kinetic responses as the attached microorganisms of interest in a trickling filter. Finally, as was shown in Figure 18, there is little basis for using a five-day sBOD test as a standard criteria for trickling filter performance. Since the rates of reaction appeared to vary considerably, (from 60% to 98% complete at five days) the state of completion at five days under quiescent conditions may not adequately reflect variation in wastewater strength.

A measurement of biodegradable DOC (bDOC) offers some advantages over the sBOD test. A measurement of DOC does not require careful incubation and airtight reactors. The amount of DOC used by the microorganisms should correspond to the BOD exerted; certainly the maximum DOC used (the bDOC), corresponds to the uBOD, by definition. Instead of determining the bDOC under quiescent conditions, the sample might be stirred to speed the reaction. In the case of trickling filters, the tests could perhaps even be adapted to attached growth organisms rather than suspended organisms. Certainly organic carbon removal is appropriate data for tracking trickling filter performance, and bDOC could perhaps replace sBOD as a performance parameter.

5.2.1. sBOD/bDOC ratios

It was anticipated that there would be a correlation between the dissolved carbon in a wastewater and the ultimate sBOD. This would allow an approximation for the removal of sBOD based on DOC measurements. An article by Pierre Servais *et al.* (1987) explores the relationship of biodegradable DOC usage (ΔbDOC) to cell growth, and reports a good correlation. However, Servais *et al.* noted significant variations in the bDOC during different times of the year. These variations would reflect variations in the amount of refractory materials, like humics and fulvics, present in the waste stream as well as total organics loadings and could cause DOC measurements to be an unreliable predictor of sBOD. Monitoring ΔbDOC, however, would give needed insight into the removal of sBOD since the bDOC is directly responsible for exertion of oxygen demand. The bDOC removed should be roughly proportional to the BOD exerted. The use of bDOC as a treatment performance parameter should be investigated further.

5.3. Implications for predicting the performance of trickling filters.

Molecular weight distributions appear very promising for characterizing wastewater, and ultimately predicting its treatability in trickling filters. The size distribution of the soluble substrates bears on the fundamental mechanisms of removal and mass transfer in the trickling filter. The basis of departure for the Logan model from previous approaches is the reliance on mass transfer limited substrate removal. Smaller molecular weight materials appear to be removed faster in trickling filters than larger substrates. This is complicated by shifts in size distributions during treatment that are not yet fully understood and need more investigation before successful predictions can be made for trickling filter performance based on the size distribution of the feed wastewater.

The original model developed by Logan considered five wastewater molecular size fractions. Based on the results of this study (section 4.1.1), it was seen that three UF size fractions provided sufficient resolution for the wastewaters investigated.

The main parameter to be determined within the Logan model is the collision efficiency (E_B). E_B equal to .001 means that 1 in 1,000 collisions between a substrate

molecule and an uptake cell are successful. E_B is between 0 and 1, where a value near to 1 indicates a mass transfer limitation and a value near to 0 indicates the removal is limited by biofilm uptake kinetics. For bDOC, the E_B was determined to be 0.001, which indicates mass transfer limitations on bDOC removals predominate rather than kinetic limitations (Logan *et al.*, 1987a). A large proportion of the soluble organics were found to be less than 1,000 amu, however, and for these compounds with their high diffusivities, kinetic factors are probably important as well.

The model seems to predict higher removals for low molecular weight materials than is observed, while underpredicting removal of low molecular weight materials. This may indicate that a single E_B for a wastewater may be an oversimplification and may need to be adjusted for different molecular weight sizes independently.

Using the mass transfer relationships already presented, Logan's model predicts sBOD profiles throughout a trickling filter, based on the assumption that the diffusion of soluble organics through the liquid towards the biofilm is largely what limits the removal. However, the collision efficiencies found in this study for sBOD indicated that sBOD removal may have been kinetically limited. bDOC is easier to measure, offering a better

alternative for tracking the treatment of wastewater and was more clearly mass transfer limited.

Since the microorganisms of interest in a biological treatment process use organic carbon as the primary substrate, a measurement of the total carbon provides a reliable gauge of relative level of treatment. However, the regulatory parameter for the wastewater treatment is BOD_5 (<30 mg/L in the effluent). There is usually a refractory carbon component present in the wastewater, and the bDOC measurement makes the necessary distinction between refractory and non-refractory carbonaceous material.

The advantages of DOC over sBOD measurements include greater reproducibility and significantly faster response time. Tracking the carbon utilization in biological systems gives a good approximation of relative sBOD removals since the non-refractory carbon removal is directly responsible for the BOD exerted.

5.4. Directions for future investigations

In order to further develop the trickling filter model, DOC, BOD, and bDOC data should be generated from additional trickling filter locations. Further investigations on the shifts in size distribution during wastewater treatment and during BOD tests are also

necessary. These investigations might consist of examining the effect of a BOD test on size distributions in cultures of different materials including size fractionated wastewater.

More research should be done to determine if the collision efficiency (E_B) for substrate removal in a trickling film varies according to the molecular size of the wastewater constituent. If this proves true, then the trickling filter model may need to be recalibrated with an E_B for each molecular weight fraction.

Another area of potential for characterizing wastewater and biological treatability is to further define the relationship between removal of bDOC and BOD exertion, allowing future performance determinations to be based on bDOC removal instead of BOD removal. Such a test might consist of a simple stirred reactor containing sample, trace nutrients, nitrification inhibitor, and an acclimated seed population. Instead of measuring oxygen depletion, periodic measurement of the DOC would indicate the progress of the biodegradation; when the DOC no longer is reduced during a measurement interval, the remaining DOC is refractory and the maximum carbon uptake has been achieved. From periodic data, a growth rate (k) could be determined based on carbon uptake rather than oxygen uptake. The reactors could be open to the atmosphere and would allow

sampling without destroying the integrity of the reactor as is the case with bottle BOD tests.

6. CONCLUSIONS

Steps were taken to generalize a model for trickling filter performance based on size distributions of wastewaters. Explorations were made into BOD and organic carbon removal by size fraction, and methods were improved for determining permeations during ultrafiltration.

From these investigations, it can be seen that further clarification of molecular weight shifts during biological treatment is necessary before the trickling filter model can supercede the use of pilot plants. It was seen that size exclusion chromatograph use is limited for this application both because of equipment constraints, (resolution limits, detector requirements, and wastewater/-resin interactions), and because it is difficult to isolate material for further investigations such as BOD tests. The removal of sBOD in trickling filters, based on the molecular weights of the wastewater constituents, is at present difficult to predict and warrants further investigation. Biodegradable DOC may eventually replace sBOD as a performance parameter for predicting trickling filter removals.

APPENDIX A : Computer Application of the Logan Model for Trickling Filter Performance.

```
********** TRICKLING FILTER PROGRAM *******B.E. LOGAN*** 1-MAR-88********
C
C**********MAIN PROGRAM*************************************************
C       INLEV=INPUT LEVEL FOR DATA INPUT (SEE SUBROUTINE DATSEL)
C       NQAPP=TOTAL NUMBER OF HYDRAULIC LOADINGS (NO. OF QAPP)
C       NDAT=TOTAL NUMBER OF SBOD INPUT PER HYDRAULIC LOADING
C       IXIT=COUNTER FOR PROGRAM EXIT
      COMMON/DATIN/TCSFO,ETCSFO,CSFO(5),XKS,DIFS(5),RCYC,NR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,TMP,IB,IQ,IDAT,IXIT
      COMMON/DATMED/MEDTYP,PWID,PLEN,PANGLE,XPM,PPMOD,SSA
C       IF IB=0, PROGRAM IS RUN BATCH.  IF IB=1, PROGRAM IS INTERACTIVE.
      OPEN (7,FILE='TRIFIL.OUT',STATUS='OLD')
      IB=1
      INLEV=1
      NQAPP=10
      CALL DATSEL (INLEV)
      CALL MEDSEL
      DO 10 IQ=1,NQAPP
      NDAT=10
      IXIT=0
      CALL DATINP
      CALL SSREM
      DO 20 IDAT=1,NDAT
      CALL FILTER
      IF (IXIT.EQ.1) GO TO 10
   20 CONTINUE
   10 CONTINUE
      STOP
      END
C**********SUBROUTINE DATSEL*************************************************
C       NM=NUMBER OF PLASTIC MODULES IN TRICKLING FILTER TOWER
C       NS=NUMBER OF COMPONENTS IN DIFFUSION SPECTRUM
C       DFS20=DIFFUSIVITIES OF SUB. COMPONENTS AT 20C (MAX OF 5)
C       MEDTYP=MEDIA TYPE CODE (SEE SUBROUTINE MEDSEL)
C       PWID=PLATE WIDTH (UM)
C       PLEN=PLATE LENGTH (UM)
C       PANGLE=PLATE ANGLE FROM HORIZONTAL IN DEGREES
C       XPM=INTERRUPTIONS PER MODULE DEPTH
C       PPMOD=PLATES PER SQUARE FOOT OF MODULE
C       SSA=MEDIA SPECIFIC SURFACE AREA (FT2)
C       TMP=TEMPERATURE OF WASTEWATER IN DEGREES CELCIUS
C       DEPB=BIOFILM THICKNESS
C       EB=COLLISION EFFICIENCY (0<= EB <= 1)
C       QGPMSF=HYDRAULIC LOADING (Q) IN GAL PER MIN PER FT2
C       RCYC=RECYCLE RATIO DEFINED AS THE FRACTION OF INFLUENT THAT IS
C            RECYCLED EFFLUENT
C       TCSFO=TOTAL CONCENTRATION OF SUBSTRATE IN THE FLUID ENTERING
C             THE TRICKLING FILTER
C       CSFO=CONC. OF SUBSTRATE IN FLUID OF EACH DIFFUSIVITY COMPONENT
C       THIS SUBROUTINE IS USED TO INPUT ALL DESIGN INFORMATION
      SUBROUTINE DATSEL (INLEV)
      COMMON/DATIN/TCSFO,ETCSFO,CSFO(5),XKS,DIFS(5),RCYC,NR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,TMP,IB,IQ,IDAT,IXIT
      COMMON/DATMED/MEDTYP,PWID,PLEN,PANGLE,XPM,PPMOD,SSA
      CHARACTER IREPLY*2,ICH*2
      DATA IREPLY /'YE'/
      IF (IB) 5,5,40
    5 READ (8,10) T1,T2,T3,T4
   10 FORMAT (4A4)
      WRITE (7,15)T1,T2,T3,T4
   15 FORMAT (//' RESULTS OF TRICKLING FILTER DESIGN PROGRAM USING: ',
     *4A4)
      READ (8,20)MEDTYP,NM,NS,(DFS20(IS),IS=1,NS)
   20 FORMAT (I2/I2/I1/5F5.0)
      READ (8,25) NQAPP
   25 FORMAT (I2)
      RETURN
   40 GO TO (1,2,3) INLEV
    1 WRITE (*,50)
   50 FORMAT (' TRICKLING FILTER DESIGN PROGRAM'/
     *' PLEASE ENTER UP TO 16-LETTER OUTPUT FILE TITLE'/)
      READ (*,10) T1,T2,T3,T4
      WRITE (7,15) T1,T2,T3,T4
      WRITE (*,55)
   55 FORMAT (//' SELECT A MEDIA OR DEFINE YOUR OWN MEDIA GEOMETRY'/
     *'    (ENTER ONLY A SINGLE NUMBER FROM 1-9):'/
     *' XFA-27=1          VFC-28=6'/
     *' XFA-30=2          VFD-28=7'/
     *' XFA-42=3          TBE-66=8'/
     *' VFB-27=4          YOUR OWN=9'/
     *' VFB-30=5'/)
      READ (*,60) MEDTYP
   60 FORMAT (I1)
      IF (MEDTYP.NE.9) GO TO 70
      WRITE (*,65)
   65 FORMAT (' ENTER THE FOLLOWING (USING A DECIMAL POINT)'/
     *' (ONE VALUE PER LINE)'/
     *' PLATE WIDTH (CM)'/
     *' PLATE LENGTH (CM)'/
     *' PLATE ANGLE (DEGREES FROM HORIZONTAL)'/
     *' INTERRUPTIONS PER MODULE'/
     *' NUMBER OF PLATES (PER SQUARE FOOT OF X-SECTIONAL AREA)'/
     *' MEDIA SPECIFIC SURFACE AREA (FT2/FT3)')
      READ (*,66)PWID,PLEN,PANGLE,XPM,PPMOD,SSA
   66 FORMAT (F10.2)
      PWID=PWID*1E04
      PLEN=PLEN*1E04
   70 WRITE (*,72)
   72 FORMAT (' INPUT THE NUMBER OF MODULES IN THE TOWER (I2):'/)
      READ (*,25) NM
      NS=5
      DFS20(1)=112.
      DFS20(2)=80.
      DFS20(3)=65.
      DFS20(4)=50.
      DFS20(5)=30.
      WRITE (*,78)
   78 FORMAT (' DO YOU WANT TO SPECIFY YOUR OWN DIFFUSIVITY SPECTRUM'/
     *' OF SBOD COMPONENTS?  (YES OR NO):'/)
      READ (*,80) ICH
   80 FORMAT (A2)
      IF (ICH.NE.IREPLY) RETURN
      WRITE (*,82)
   82 FORMAT (' ENTER IN NUMBER OF COMPONENTS (UP TO 5):'/)
      READ (*,25) NS
      DO 85 IS=1,NS
```

```
      WRITE (*,86) IS
   86 FORMAT (' ENTER DIFFUSIVITY OF COMPONENT ',I2,':'/)
      READ (*,66) DFS20(IS)
   85 CONTINUE
      RETURN
    2 IF (IQ.EQ.1) GO TO 92
      WRITE (*,79) QGPMSF,TMP
   79 FORMAT (' WOULD YOU LIKE TO RUN ANOTHER HYDRAULIC LOADING OR'/
     *' WASTEWATER TEMPERATURE (YES OR NO)?'/
     *' (Q=',F5.2,' (GPM/FT2)     TEMP=',F5.1,' C)'/)
      READ (*,80) ICH
      IF (ICH.EQ.IREPLY) GO TO 92
      STOP
   92 WRITE (*,94)
   94 FORMAT (' ENTER TOTAL APPLIED HYDRAULIC LOAD ON FILTER (GPM/FT2):'
     *)
      READ (*,66) QGPMSF
      WRITE (*,95)
   95 FORMAT (' ENTER IN WASTEWATER TEMPERATURE (DEGREES CELCIUS)'/)
      READ (*,66) TMP
      WRITE (*,170)
  170 FORMAT (' DO YOU WANT TO CHANGE THE VALUE OF EB OR'/
     *' BIOFILM THICKNESS?'/)
      READ (*,80) ICH
      IF (ICH.NE.IREPLY) RETURN
      WRITE (*,175)
  175 FORMAT (' ENTER IN NEW COLLISON EFFICIENCY (0<EB<1)'/)
      READ (*,66) EB
      WRITE (*,180)
  180 FORMAT (' ENTER IN NEW BIOFILM THICKNESS (UM)'/)
      READ (*,66) DEPB
      RETURN
    3 IF (IDAT.EQ.1) GO TO 104
      WRITE (*,100) ETCSFO,RCYC
  100 FORMAT (' WOULD YOU LIKE TO ENTER ANOTHER SBOD OR '/
     *' RECYCLE RATIO (YES OR NO)?'/
     *' (SBOD=',F5.0,' (MG/L)     R=',F4.2,')'/)
      READ (*,80) ICH
      IF (ICH.EQ.IREPLY) GO TO 104
      IXIT=1
      RETURN
  104 WRITE (*,105)
  105 FORMAT (' ENTER IN TOTAL SOLUBLE BOD (MG/L):'/)
      READ (*,111) TCSFO
  111 FORMAT (F10.2)
      WRITE (5,115)
  115 FORMAT (' ENTER IN SBOD (MG/L) FOR EACH DIFFUSIVITY COMPONENT:'/
     *' (IF UNKNOWN, ENTER IN EQUAL FRACTIONS PER DIFFUSIVITY,'/
     *' I.E. FOR  100 MG/L, USE 20. FOR EACH DIFFUSIVITY'/)
      DO 130 IS=1,NS
      WRITE (*,140) IS,DFS20(IS)
  140 FORMAT (' DIFFUSIVITY ',I2,' (',F5.0,' UM2/S)')
      READ (*,111) CSFO(IS)
  130 CONTINUE
      WRITE (*,150)
  150 FORMAT (' INPUT RECYCLE RATIO:'/
     *' (FRACTION OF HYDRAULIC LOAD THAT IS RECYCLE)'/)
      READ (*,160) RCYC
  160 FORMAT (F5.2)
      RETURN
      END
C**********SUBROUTINE MEDSEL*********************FROM MAIN***************
      SUBROUTINE MEDSEL
C       THIS SUBROUTINE DEFINES MEDIA CHARACTERISTICS
      COMMON/DATMED/MEDTYP,PWID,PLEN,PANGLE,XPM,PPMOD,SSA
      GO TO (1,2,3,4,5,6,7,8,9) MEDTYP
    1 WRITE (7,51)
   51 FORMAT (' XFA-27 MEDIA')
      PWID=5.0E04
      PLEN=8.6E04
      PANGLE=60.
      XPM=8.
      PPMOD=144.
      SSA=27.
      RETURN
    2 WRITE (7,52)
   52 FORMAT (' XFA-30 MEDIA')
      PWID=4.3E04
      PLEN=7.5E04
      PANGLE=60.
      XPM=9.
      PPMOD=182.
      SSA=30.
      RETURN
    3 WRITE (7,53)
   53 FORMAT (' XFA-42 MEDIA')
      PWID=2.8E04
      PLEN=5.0E04
      PANGLE=60.
      XPM=14.
      PPMOD=403.
      SSA=42.
      RETURN
    4 WRITE (7,54)
   54 FORMAT (' VFB-27 MEDIA')
      PWID=6.1E04
      PLEN=62.0E04
      PANGLE=90.
      XPM=1.
      PPMOD=131.
      SSA=27.
      RETURN
    5 WRITE (7,55)
   55 FORMAT (' VFB-30.8 MEDIA')
      PWID=7.0E04
      PLEN=62.0E04
      PANGLE=90.
      XPM=1.
      PPMOD=130.
      SSA=30.8
      RETURN
    6 WRITE (7,56)
   56 FORMAT (' VFC-28 MEDIA')
      PWID=10.E04
      PLEN=66.E04
      PANGLE=60.
      XPM=1.
      PPMOD=62.
      SSA=28.
      RETURN
```

```
      7 WRITE (7,57)
     57 FORMAT (' VFD-28 MEDIA')
        PWID=4.8E04
        PLEN=69.E04
        PANGLE=60.
        XPM=1.
        PPMOD=155.
        SSA=28.
        RETURN
      8 WRITE (7,58)
     58 FORMAT (' TBE-66 MEDIA')
        PWID=0.92E04
C       PWID=0.47E04
        PLEN=220.E04
        PANGLE=90.
        XPM=1.
        PPMOD=2170.
        SSA=66.
        RETURN
      9 WRITE (7,59)
     59 FORMAT (' USER DEFINED MEDIA')
        RETURN
        END
C**********SUBROUTINE DATINP ********************FROM MAIN****************
C       NF=NUMBER OF NODES OF FLUID THICKNESS
C       NP=NUMBER OF NODES ALONG PLATE LENGTH
C       IEND=COUNTER OF MAXIMUM NUMBER OF NUMERICAL ITERATIONS FOR STEADY
C            STATE SOLUTION TO BE ACHIEVED BY
C       STAB=STABILITY CRITERIA TO ASSURE MASS IS CONSERVED
C       GRAV=ACCELERATION DUE TO GRAVITY (CM/S2)
C       EP=POROSITY OF THE BIOFILM
C       A0=RADIUS OF CELLS IN THE BIOFILM
C       NR=MAXIMUM NUMBER OF ITERATIONS FOR RECYCLE STEADY-STATE
C       THPK=TMP IN DEGREES KELVIN
C       VISC=FLUID VISCOSITY
C       VISC20=FLUID VISCOSITY AT 20C
C       VBAR=AVERAGE VELOCITY OF FLUID MOVING DOWN THE PLATE (UM/S)
C       VBARCM=VBAR IN CM/S
C       PWIDCM=PLATE WIDTH IN CM
C       PLENCM=PLATE LENGTH IN CM
C       PANGRD=PLATE ANGLE FROM HORIZONTAL IN RADIANS
C       TBAR=AVERAGE RESIDENCE TIME OF FLUID ON PLATE
C       DXF=THICKNESS OF FLUID ELEMENT (DELTA X IN FLUID)
C       DT=INCREMENT OF TIME (DELTA T)
C       XKS=KINETIC CONSTANT BASED ON COLLISION FRACTION
C       XKDS=SQUARE ROOT OF RATIO OF XKS TO SUBSTRATE DIFFUSIVITY
C       NT=NUMBER OF INCREMENTS IN ITERATION CYCLE
C       THIS SUBROUTINE DEFINES ALL DATA FOR MODEL CALCULATIONS
      SUBROUTINE DATINP
      COMMON/DATIN/TCSFO,ETCSFO,CSFO(5),XKS,DIFS(5),RCYC,NR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,TMP,IB,IQ,IDAT,IXIT
      COMMON/DATMED/MEDTYP,PWID,PLEN,PANGLE,XPM,PPMOD,SSA
      NF=10
      NP=10
      IEND=20
      ERROR=0.00001
      STAB=0.5
      GRAV=980.
      EP=0.80
      A0=1.0
      NR=20
      EB=0.0035
      DEPB=1000.
      IF (IB.EQ.1) GO TO 11
      READ (8,10) NDAT,QGPMSF,TMP
     10 FORMAT (I2/2F10.2)
      GO TO 12
     11 INLEV=2
      CALL DATSEL (INLEV)
      IF (IQ.EQ.10) RETURN
C      CONVERT QGPMSF TO QAPP (CM3/S)
     12 QAPP=(QGPMSF/PPMOD)*3.7854*1000./60.
      NFM1=NF-1
      NPM1=NP-1
      THPK=TMP+273.15
      TMP20=20.
      THPK20=TMP20+273.
      VISC20=0.01
C      INCORPORATE CHANGES IN CONSTANTS THAT ARE A FUNCTION OF TEMP.
C
C     CALCULATE THE FLUID VISCOSITY
     67 IF (TMP.GT.5.) GO TO 70
      VISC=0.01787-TMP*0.000536
      GO TO 80
     70 IF (TMP.GT.10.) GO TO 71
      VISC=0.01731-TMP*0.000424
      GO TO 80
     71 IF(TMP.GT.15.) GO TO 72
      VISC=0.01641-TMP*0.000334
      GO TO 80
     72 IF (TMP.GT.20.) GO TO 73
      VISC=0.01548-TMP*0.000272
      GO TO 80
     73 IF (TMP.GT.25.) GO TO 74
      VISC=0.01448-TMP*0.000222
      GO TO 80
     74 IF (TMP.GT.30.) GO TO 75
      VISC=0.01353-TMP*0.000184
      GO TO 80
     75 IF (TMP.GT.35.) GO TO 76
      VISC=0.01263-TMP*0.000154
      GO TO 80
     76 VISC=0.01186-TMP*0.000132
C      CORRECT THE DIFFUSIVITIES FOR THE INPUT TEMPERATURE
     80 DO 85 IS=1,NS
      DIFS(IS)=DFS20(IS)*(VISC20/VISC)*(THPK/THPK20)
     85 CONTINUE
      PANGRD=(3.14159/2.)*(PANGLE/90.)
      DEPF=(((3.*QAPP*VISC)/(GRAV*(PWID/10000.)*SIN(PANGRD)))**0.333)*
     *10000.
      VBAR=(GRAV*((DEPF*1.0E-4)**2.)*SIN(PANGRD)/(3.0*VISC))*10000.
      VBARCM=VBAR/10000.
      PWIDCM=PWID*1.E-4
      PLENCM=PLEN*1.E-4
      TBAR=PLEN/VBAR
      DXF=DEPF/FLOAT (NF)
      DZ=PLEN/FLOAT(NP)
C      CALCULATE VELOCITY AT EACH NODE, OR V(IX)
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      DXFS=DXF/2.
      VSUM=0.
      DO 99 IX=1,NF
      V(IX)=1.5*VBAR*(1.0-(DXFS/DEPF)**2.)
      VSUM=VSUM+V(IX)
      DXFS=DXFS+DXF
   99 CONTINUE
C      CALUCLATE REACTION CONSTANTS, TIME STEPS
      XKS=(3.*(1.-EP)/A0**2.)*EB
      XKDS=XKS**0.5
      STAB1= (2.*DIFS(I)/(DXF**2.))+(2.*V(1)/DZ)+XKS*DIFS(1)
      DT=STAB/STAB1
      NT=IFIX(TBAR/DT)
C      DETERMINE IF BIOFILM IS A DEEP BIOFILM
C      THIS OCCURS FOR STAB2 OF UNITY, OR HERE ASSUMED OKAY IF >0.99
      STAB2=TANH(DEPB*XKDS)
      IF (STAB2.GE.0.99) GO TO 30
      PSTAB2=STAB2*100.
      WRITE (7,20) PSTAB2,DEPB
      WRITE (*,20) PSTAB2,DEPB
   20 FORMAT (//' STABILITY CRITERIA NOT MET--LOOKOUT!!!!'/
     *' ONLY',F8.2,' PERCENT SUBSTRATE UTILIZATION VERSUS THE ASSUMED'/
     *' 100 PERCENT.  RE-RUN PROGRAM WITH NEW BIOFILM THICKNESS.'/
     *' CURRENT THICKNESS = ',F10.0,'(UM)'/)
      STOP
   30 WRITE (7,40) EB,TBAR,VBARCH,PANGLE,PWIDCH,PLENCH,XPH,QGPMSF,
     *QAPP,DEPF,VISC,TMP
   40 FORMAT (//' DATA SUMMARY:'/
     *' SUBSTRATE LIMITED MASS TRANSFER ONLY'/
     *' COLLECTOR EFFICIENCY (EB) =',F8.5,/
     *' AVERAGE CONTACT TIME=',F8.2,'(S)'/
     *' AVERAGE FLUID VELOCITY=',F8.3,' (CM/S)'/
     *' PLATE ANGLE (DEGREES FROM HORIZONTAL)=',F4.1/
     *' PLATE WIDTH=',F8.2,'(CM)'/
     *' PLATE LENGTH=',F8.2,'(CM)'/
     *' INTERRUPTIONS PER MODULE LENGTH=',F8.1/
     *' APPLICATION RATE=',F8.3,' (GPM/FT2)'/
     *'                  ',F8.3,' (CM3/S-PLATE)'/
     *' FLUID DEPTH=',F6.0,'(UM)'/
     *' FLUID VISCOSITY=',F8.5,' (CM2/S)'/
     *' TEMPERATURE=',F6.1,' (C)'/)
      RETURN
      END
C**********SUBROUTINE SSREM********************FROM MAIN******************
C      TIME=ACCUMULATE SUM OF RESIDENCE TIMES
C      RSA=SUBSTRATE ACCUMULATOR OF REACTED MASS IN BIOFILM
C      TCSF0=TOTAL CONC. OF SUBSTRATE--IN MG/UM3 IN THIS SUBROUTINE
C      ERR=RELATIVE CHANGE OF AVERAGE SUBSTRATE CONCENTRATION IN FLUID
C           LEAVING THE PLATE SINCE LAST RESIDENCE TIME
C      FSRM=FRACTION OF SUBSTRATE REMOVED FOR DIFFUSION COMPONENT
C      TCSEND=TOTAL AVERAGE CONCENTRATION OF SUBSTRATE AT THE PLATE END
C      REMOV=FRACTION OF TOTAL SUBSTRATE REMOVED RELATIVE TO THE LAST
C            RESIDENCE TIME
C      CS(IS,IX,IZ)=CONC. OF SUBSTRATE DIFFUSION COMPONENT IS, AT NODE
C                   LOCATION IX,IP, WHERE NODE 1 IS AT THE FLUID ENTRY
C                   AND THE AIR-LIQUID INTERFACE
C      THIS SUBROUTINE CALCULATES THE FRACTION OF BOD REMOVAL FOR A
C           THEORETICAL PLATE FOR EACH SUBSTRATE COMPONENT
      SUBROUTINE SSREM
      COMMON/DATIN/TCSF0,ETCSF0,CSF0(5),XKS,DIFS(5),RCYC,HR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,TMP,IB,IQ,IDAT,IXIT
      COMMON/CONC/CS(5,10,10),RSA
      COMMON/FDIFF/CSN(5,10,10),CSSUR(5),RS(5),CSEND(5)
      TIME=0.0
      RSA=0.0
      TCSF0=100.E-15
      WRITE (*,5)
    5 FORMAT (///' BIOFILM NUMERICAL PROGRAM BEGINS EXECUTION'/
     *' (CONVERGENCE COMPLETE WHEN FRACTION IS LESS THAN 0.00001)'//)
C      INITIALIZE SUBSTRATE CONCENTRATIONS FOR EACH OF NS COMPONENTS
      DO 10 IS=1,NS
   10 CSF0(IS)=TCSF0/FLOAT(NS)
C      INITIALIZE NODES AT TIME=0
      DO 15 IX=1,NF
      DO 15 IZ=1,NP
      DO 15 IS=1,NS
   15 CS(IS,IX,IZ)=CSF0(IS)
C      BEGIN ITERATIONS FOR EACH RESIDANCE TIME TBAR OF NT INTERVALS
      DO 20 IAP=1,IEND
      TIME=TIME+TBAR
C      CALL SUBROUTINE WETPLT TO CALCUATE SUBSTRATE PROFILES IN FLUID
      CALL WETPLT (IAP,TCSEND)
      REMOV(IAP)=((TCSF0-TCSEND)/TCSF0)*100.
      IF (IAP.EQ.1) GO TO 20
C      CALCULATE IF AVERAGE SUB CONC. LEAVING PLATE IS UNCHANGED
C      SINCE LAST RESIDENCE TIME CALCULATION
      ERR=REMOV(IAP)-REMOV(IAP-1)
      ERR=ABS(ERR)
      WRITE (*,7) ERR
    7 FORMAT (' CONVERGENCE FRACTION=',F10.5)
      IF (ERR.LT.ERROR) GO TO 30
   20 CONTINUE
C      PRINT OUT NODE SUMMARY FOR NODES 1,2,3,9,10
   30 WRITE (7,35)
   35 FORMAT (//'FRACTION REMAINING AFTER ONE THEORETICAL PLATE')
      DO 40 IS=1,NS
      FSRM(IS)=CSEND(IS)/CSF0(IS)
      WRITE (7,42)IS,DIFS(IS),FSRM(IS)
   42 FORMAT (' DIFS(',I2,')=',F8.0,10X,'FRACTION REMAINING=',F10.4)
   40 CONTINUE
      WRITE (7,110) NPM1,NP
  110 FORMAT (//' NODAL CONCENTRATIONS'/'   SUBSTRATE'/
     *' X-NODE',3X,'CS(Z=1)',8X,'CS(Z=2)',8X,'CS(Z=3)',8X,'CS(Z=',I3,')'
     *,6X,'CS(Z=',I3,')')
      DO 112 IX=1,10
      WRITE (7,120)IX,CS(1,IX,1),CS(1,IX,2),CS(1,IX,3),CS(1,IX,NPM1),
     *CS(1,IX,NP)
  120 FORMAT (I5,5(3X,E12.4))
  112 CONTINUE
      RETURN
      END
C**********SUBROUTINE WETPLT********************FROM MAIN***********
C      CSSUR=CONC. OF SUBSTRATE AT THE BIOFILM-LIQUID INTERFACE
C      RS=RATE OF SUBSTRATE REMOVAL FOR A SURFACE CONC. CSSUR
C      CSEND=CONC. OF SUBSTRATE COMPONENTS AT PLATE END
C      THE NODE LOCATIONS ARE AS FOLLOWS:  1,2,3 ARE THE ENTRY NODES
C          (X=1), 4,5,6 ARE THE NODES FOR OTHER X LOCATIONS.  NODES 1,4
C          ARE AT Z=1, 3,6 ARE AT NEAR THE LIQUID-BIOFILM SURFACE, AND
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C         2,5 ARE NODES FOR ANY OTHER Z LOCATION.
C       CSN=CS AT NEXT TIME INTERVAL
C       THIS SUBROUTINE DETERMINES THE SUBSTRATE PROFILES IN THE FLUID
C       FILM AND CALCUATES THE AVERAGE SUSTRATE CONC. LEAVING THE PLATE
      SUBROUTINE WETPLT (IAP,TCSEND)
      COMMON/DATIN/TCSFO,ETCSFO,CSFO(5),XKS,DIFS(5),RCYC,NR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,THP,IB,IQ,IDAT,IXIT
      COMMON/CONC/CS(5,10,10),RSA
      COMMON/FDIFF/CSN(5,10,10),CSSUR(5),RS(5),CSEND(5)
      DO 50 IT=1,NT
      DO 55 IZ=1,NP
      DO 15 IS=1,NS
      CSSUR(IS)=0.5*(3.*CS(IS,NF,IZ)-CS(IS,NFM1,IZ))
   15 RS(IS)=(DIFS(IS)/DXF)*XKDS*CSSUR(IS)
      DO 54 IS=1,NS
      IF (IZ.EQ.1) GO TO 3
    6 CSN(IS,NF,IZ)=CS(IS,NF,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,NFM1,IZ)
     *-CS(IS,NF,IZ))-RS(IS)-(V(NF)/DZ)*(CS(IS,NF,IZ)-CS(IS,NF,IZ-1)))
      GO TO 53
    3 CSN(IS,NF,IZ)=CS(IS,NF,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,NFM1,IZ)
     *-CS(IS,NF,IZ))-RS(IS)-(V(NF)/DZ)*(CS(IS,NF,IZ)-CSFO(IS)))
   53 RSA=RSA+RS(IS)
   54 CONTINUE
   55 CONTINUE
      DO 60 IZ=1,NP
      DO 60 IX=1,NFM1
      DO 60 IS=1,NS
      IF (IZ.NE.1) GO TO 5
      IF (IX.EQ.1) GO TO 1
    2 CSN(IS,IX,IZ)=CS(IS,IX,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,IX+1,IZ)
     *+CS(IS,IX-1,IZ)-2.*CS(IS,IX,IZ))-(V(IX)/DZ)*(CS(IS,IX,IZ)-
     *CSFO(IS)))
      GO TO 60
    1 CSN(IS,IX,IZ)=CS(IS,IX,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,IX+1,IZ)
     *-CS(IS,IX,IZ))-(V(IX)/DZ)*(CS(IS,IX,IZ)-CSFO(IS)))
      GO TO 60
    5 IF (IX.EQ.1) GO TO 4
      CSN(IS,IX,IZ)=CS(IS,IX,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,IX-1,IZ)
     *+CS(IS,IX+1,IZ)-2.*CS(IS,IX,IZ))-(V(IX)/DZ)*(CS(IS,IX,IZ)-
     *CS(IS,IX,IZ-1)))
      GO TO 60
    4 CSN(IS,IX,IZ)=CS(IS,IX,IZ)+DT*((DIFS(IS)/DXF**2.)*(CS(IS,IX+1,IZ)
     *-CS(IS,IX,IZ))-(V(IX)/DZ)*(CS(IS,IX,IZ)-CS(IS,IX,IZ-1)))
   60 CONTINUE
      DO 90 IZ=1,NP
      DO 90 IX=1,NF
      DO 90 IS=1,NS
   90 CS(IS,IX,IZ)=CSN(IS,IX,IZ)
   50 CONTINUE
      DO 92 IS=1,NS
   92 CSEND(IS)=0.0
      DO 80 IX=1,NF
      DO 80 IS=1,NS
   80 CSEND(IS)=CSEND(IS)+CS(IS,IX,NP)*V(IX)
      DO 83 IS=1,NS
   83 CSEND(IS)= CSEND(IS)/VSUM
      TCSEND=0.0
      DO 84 IS=1,NS
   84 TCSEND=TCSEND+CSEND(IS)
      RETURN
      END
C**********SUBROUTINE FILTER******************FROM MAIN*****************
C       ECSFO=ENTERING SUBSTRATE COMPONENT CONCENTRATION TO TOWER
C       ETCSFO=ENTERING TOTAL CONCENTRATION OF SUBSTRATE TO TOWER
C       TCSFO=TOTAL CONC. OF SUBSTRATE WITH RECYCLE INCLUDED ENTERING
C       TCSEND=TOTAL CONC. OF SUBSTRATE EXITING THE TOWER
C       TCSNDM=TOTAL CONC. OF SUB. REMOVED AT EACH SUCCESIVE MODULE
C       PCREM=PERCENT OF SUBSTRATE CONC. REMOVED
C       TREM=TOTAL SUBSTRATE PERCENTS REMOVED
C       THIS SUBROUTINE CALCS THE SBOD LEAVING THE FILTER AT ANY RECYCLE
C            RATIO FOR A GIVEN HYDRAULIC LOAD AND TEMPERATURE
      SUBROUTINE FILTER
      COMMON/DATIN/TCSFO,ETCSFO,CSFO(5),XKS,DIFS(5),RCYC,NR,FSRM(5),EB,
     *DXF,DT,TBAR,DZ,QAPP,DEPF,V(10),VBAR,VSUM,NF,NFM1,NP,NPM1,NT,VISC,
     *GRAV,TIME,IEND,XKDS,DEPB,NS,ERROR,REMOV(20),NM,NQAPP,NDAT,DFS20(5)
     *,QGPMSF,THP,IB,IQ,IDAT,IXIT
      COMMON/DATMED/MEDTYP,PWID,PLEN,PANGLE,XPM,PPMOD,SSA
      COMMON/CONC/CS(5,10,10),RSA
      COMMON/FDIFF/CSN(5,10,10),CSSUR(5),RS(5),CSEND(5)
      DIMENSION ECSFO(5),TCSNDM(15),CSENDN(15,5)
C       READ IN INFLUENT SBOD AND RECYCLE RATIO
      IF (IB.EQ.1) GO TO 10
      READ (8,11) TCSFO,(CSFO(IS),IS=1,NS)
   11 FORMAT (6F5.0)
      READ (8,12) RCYC
   12 FORMAT (F5.2)
      GO TO 14
   10 INLEV=3
      CALL DATSEL (INLEV)
      IF (IXIT.EQ.1) RETURN
   14 DO 15 IS=1,NS
   15 ECSFO(IS)=CSFO(IS)
      ETCSFO=TCSFO
      WRITE (7,20)IDAT
   20 FORMAT (//' APPLICATION SUMMARY: ',I3/
     *' MODULE',5X,' BOD(MG/L)',5X,'CS(1)',5X,'CS(2)',5X,'CS(3)',
     *5X,'CS(4)',5X,'CS(5)')
      WRITE (7,25)TCSFO,(CSFO(IS),IS=1,NS)
   25 FORMAT ('  PRI',5X,F12.2,5F10.2)
C       THIS LOOP ITERATES UNTIL A STEADY STATE CONCENTRATION OF EACH
C       SBOD COMPONENT IS REACHED FOR THE RECYCLE RATIO
      DO 100 IR=1,100
      DO 50 IM=1,NM
      TCSEND=0.0
      DO 40 IS=1,NS
C       AT THE TOWER EXIT (NM MODULES), THE REMOVAL IS EQUAL TO THE
C       FRACTIONAL REMOVAL TIMES THE NUMBER OF PLATES FOR THE TOWER DEPTH
      CSEND(IS)=CSFO(IS)*(FSRM(IS)**(FLOAT(IM)*XPM))
      TCSEND=TCSEND+CSEND(IS)
      TCSNDM(IM)=TCSEND
   40 CSENDM(IM,IS)=CSEND(IS)
   50 CONTINUE
      TREM=((TCSFO-TCSEND)/TCSFO)*100.
      PCREM=((ETCSFO-TCSEND)/ETCSFO)*100.
      IF (IR.EQ.1) GO TO 70
      ERR=ABS(XCSF-TCSEND)
      IF (ERR.LT.ERROR) GO TO 80
   70 XCSF=TCSEND
```

```
      TCSFO=0.0
      DO 60 IS=1,NS
      CSFO(IS)=RCYC*CSEND(IS)+(1.-RCYC)*ECSFO(IS)
   60 TCSFO=TCSFO+CSFO(IS)
  100 CONTINUE
C      WRITE OUT RESULTS
   80 IM=0
      WRITE (7,85)IM,TCSFO,(CSFO(IS),IS=1,NS)
   85 FORMAT (3X,I2,5X,F12.2,5F10.2)
      DO 90 IM=1,NM
      WRITE (7,86) IM,TCSNDM(IM),(CSENDM(IM,IS),IS=1,NS)
   86 FORMAT (F5.0,F5.2)
   90 CONTINUE
      WRITE (7,95)ETCSFO,TCSFO,RCYC,TCSEND,PCREM,TREM
   95 FORMAT (//' FINAL SIMULATION RESULTS'/
     *' PRIMARY CLARIFIER BOD=',F8.2,' (MG/L)'/
     *' TRICKLING FILTER COMBINED INFLUENT BOD=',F8.2,' (MG/L)'/
     *' RECYCLE RATIO=',F8.4/
     *' TRICKLING FILTER EFFLUENT BOD=',F8.2,' (MG/L)'/
     *' REMOVAL BASED ON PRIMARY CLARIFIER=',F8.2,'%'/
     *' REMOVAL BASED ON INFLUENT TO TF=',F8.2,'%'///)
      WRITE (*,111) TCSFO,TCSEND,PCREM
  111 FORMAT ('  BODIN=',F5.0,'   BODOUT=',F5.0,F10.0,'% REM')
      RETURN
      END
```

APPENDIX B : Molecular Weight Distributions Determined by Ultrafiltration using DOC measurements.

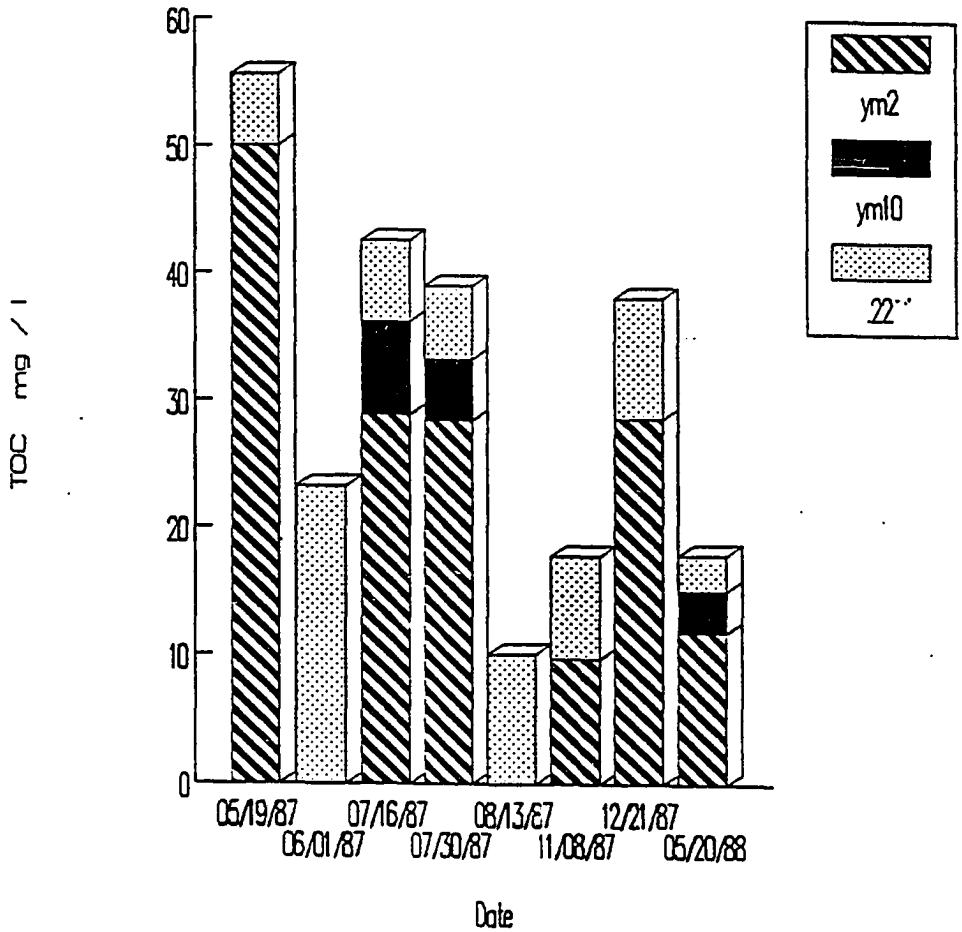

Figure B.1 Molecular weight distributions of Roger Road influent over time.

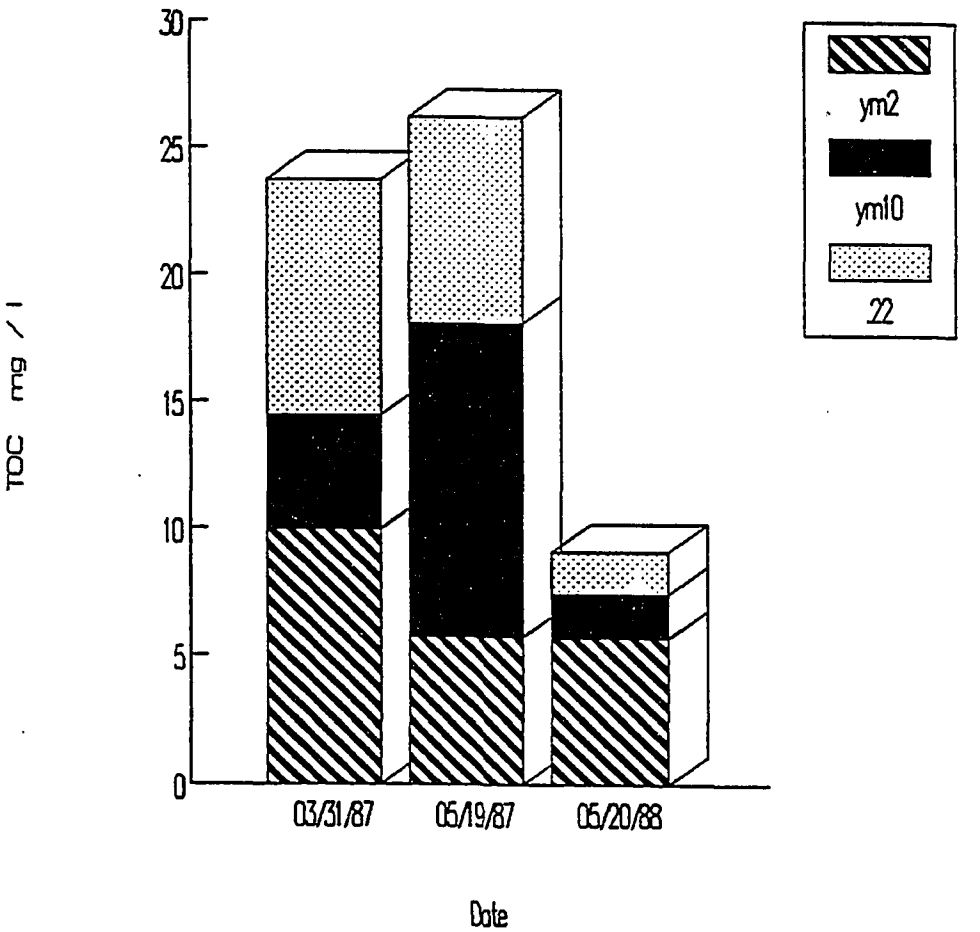

Figure B.2 Molecular weight distributions of Roger Road unclarified effluent over time.

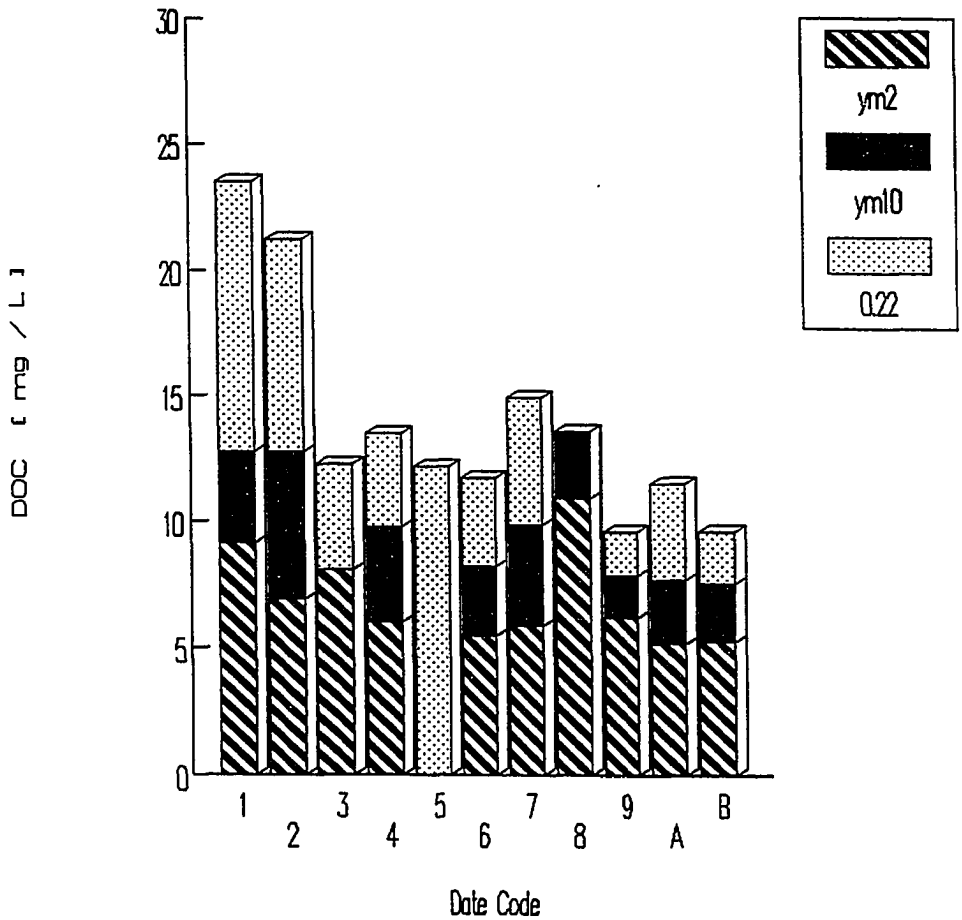

Figure B.3 Molecular weight distributions of Roger Road clarified effluent over time.

Chart for conversion of code numbers to date of sampling:

1 - 3/31/87	4 - 1/07/88	7 - 2/19/88	A - 5/09/88
2 - 5/19/87	5 - 1/18/88	8 - 3/11/88	B - 5/20/88
3 - 12/21/87	6 - 1/27/88	9 - 3/31/88	

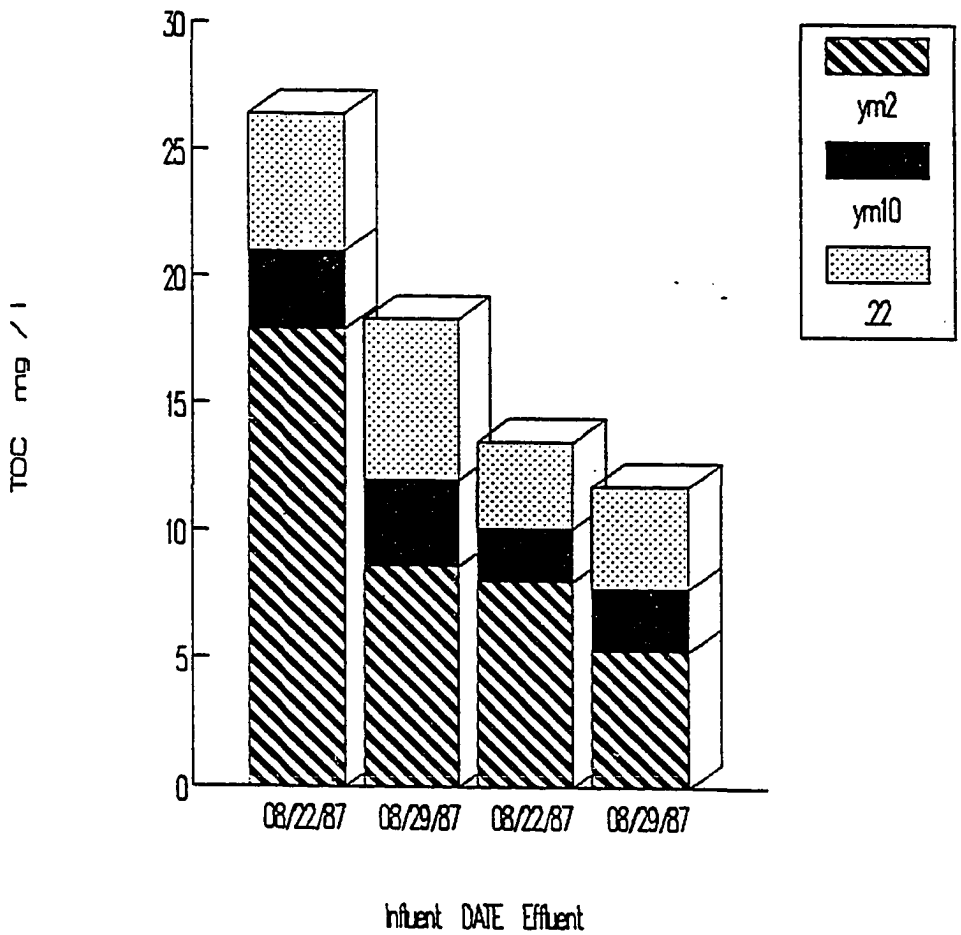

Figure B.4 Molecular weight distributions of Atlanta wastewater. Utoy Creek WWTP.

APPENDIX C : Predicted Versus Observed Removals for Trickling Filter Performance.

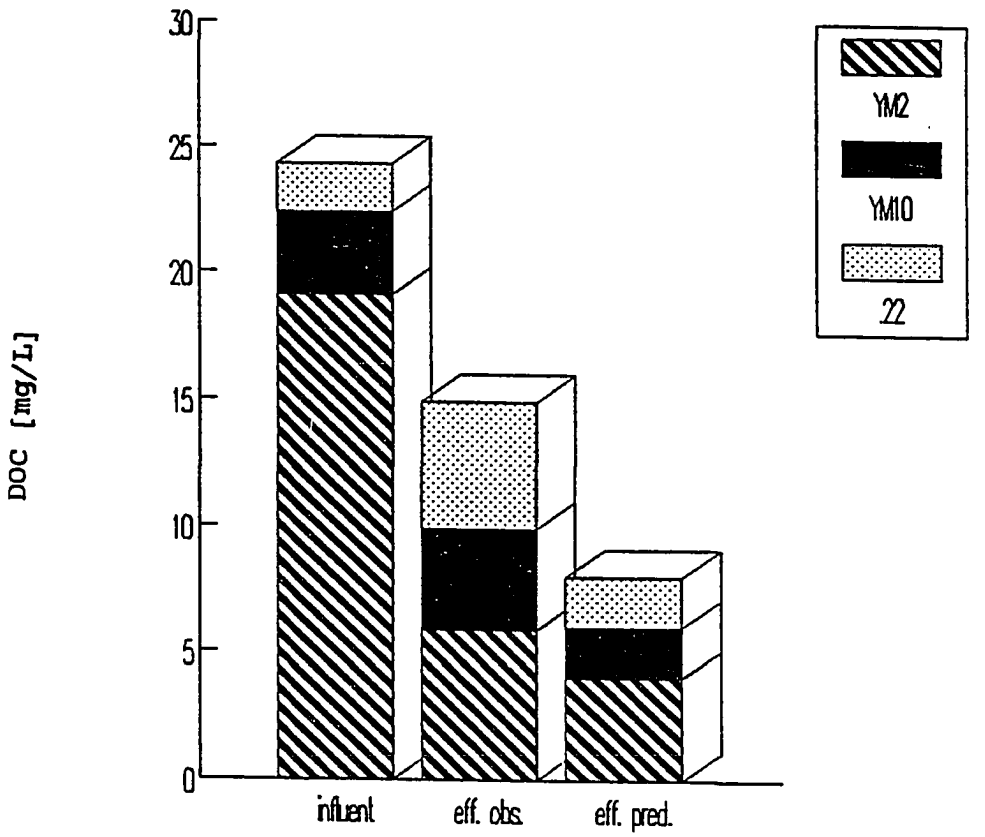

Figure C.1 : Predicted vs. Observed DOC removals for Roger Road. 2/19/88

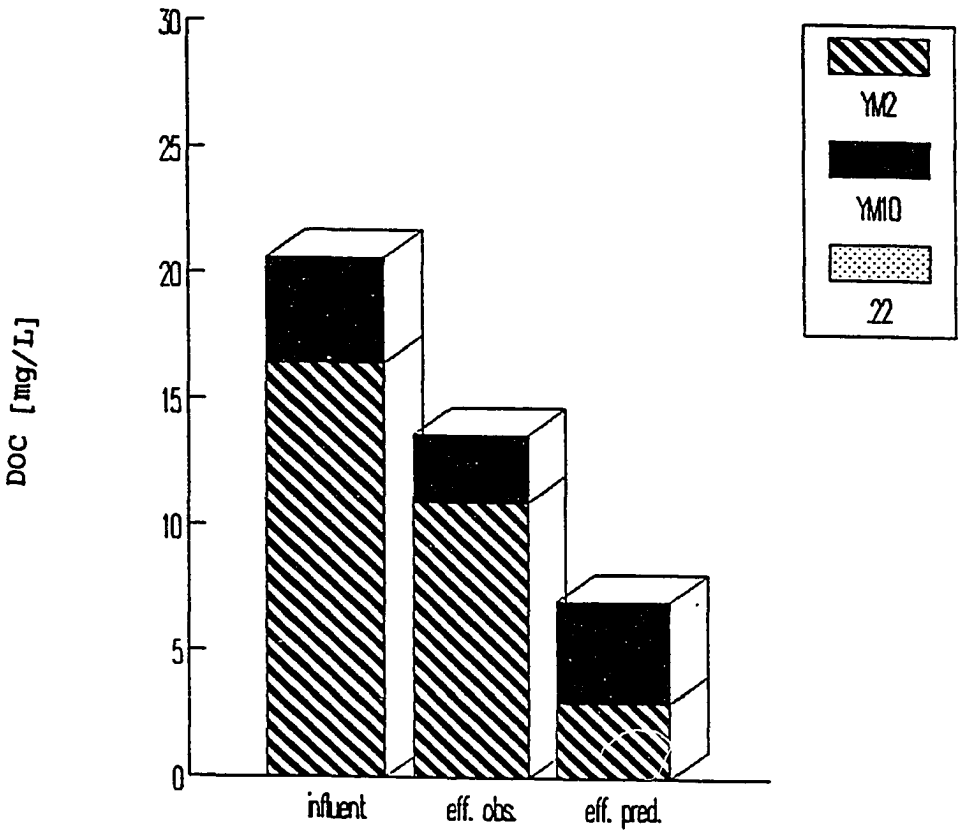

Figure C.2 : Predicted vs. Observed DOC removals for Roger Road. 3/11/88

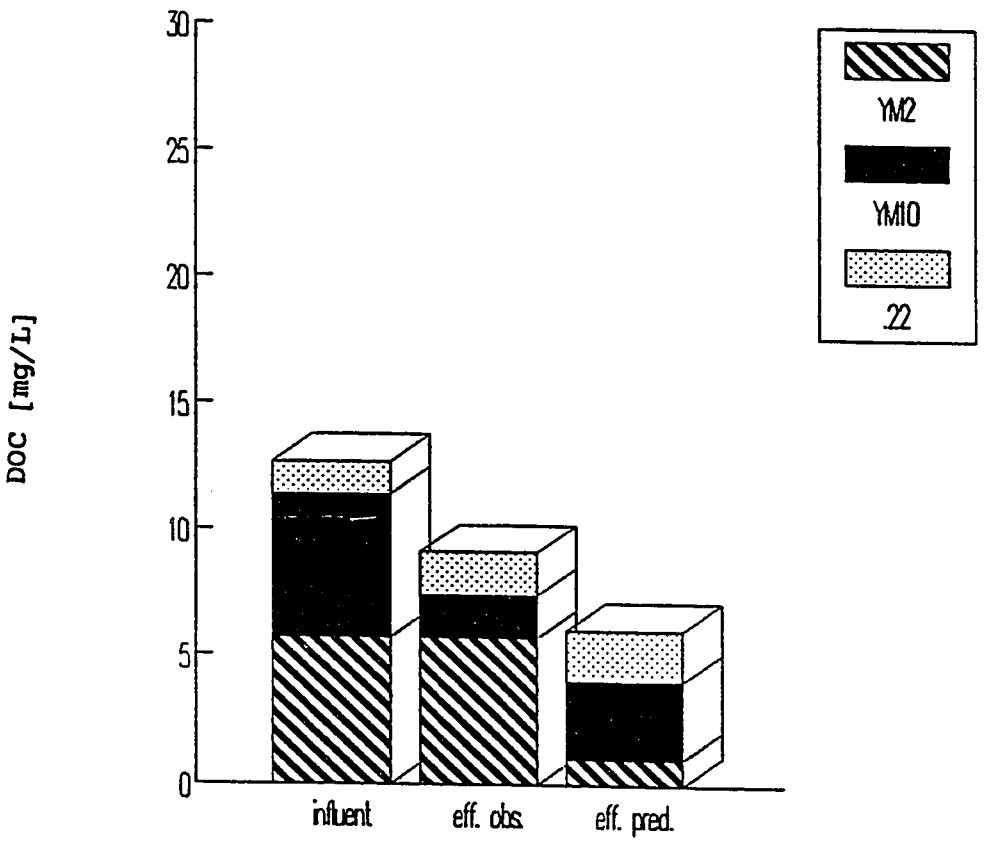

Figure C.3 : Predicted vs. Observed DOC removals for Roger Road. 5/20/88

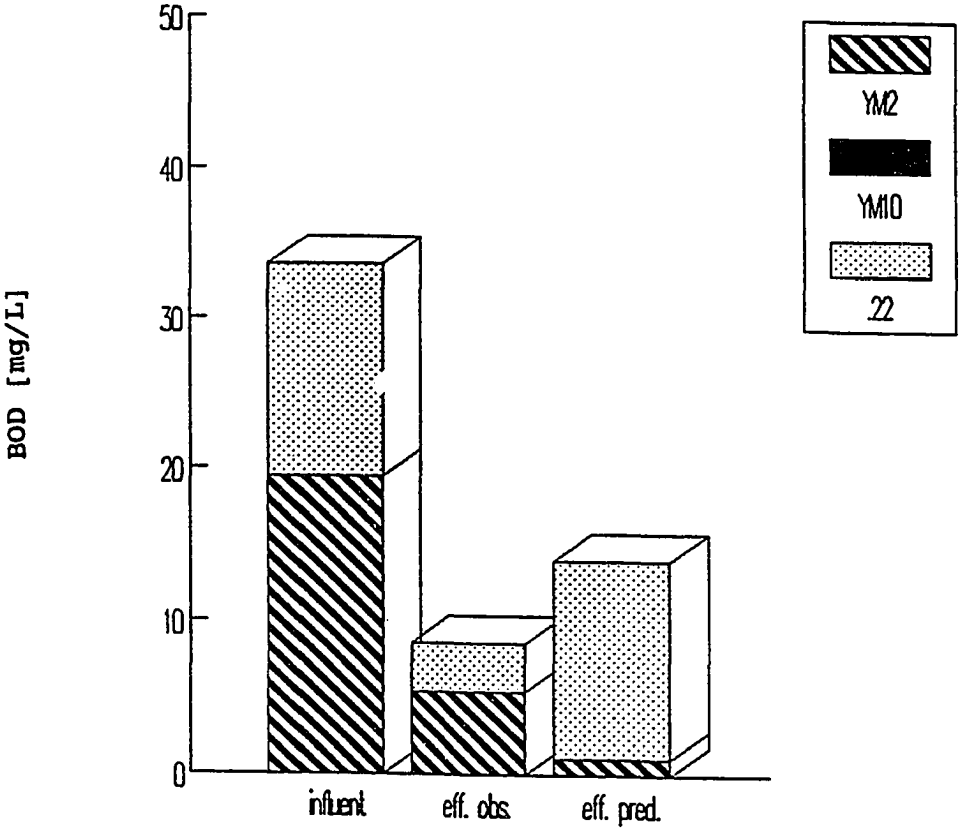

Figure C.4 : Predicted vs. Observed sBOD removals for Roger Road. 1/27/88

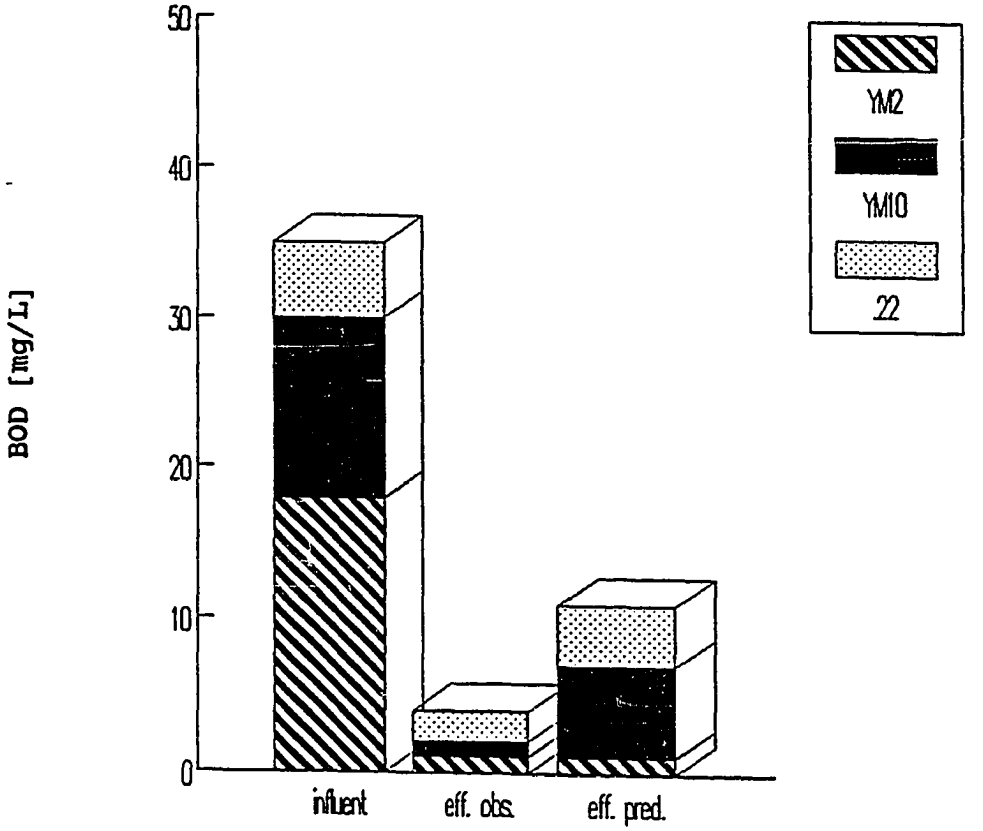

Figure C.5 : Predicted vs. Observed sBOD removals for Roger Road. 2/19/88

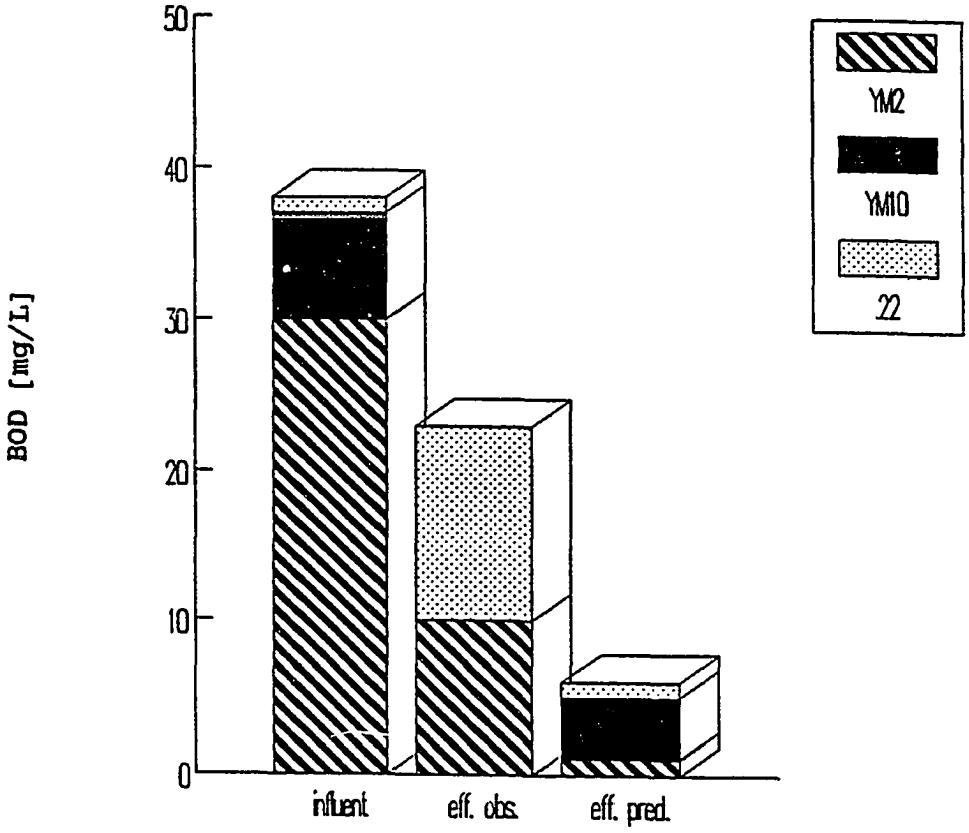

Figure C.6 : Predicted vs. Observed sBOD removals for Roger Road. 3/11/88

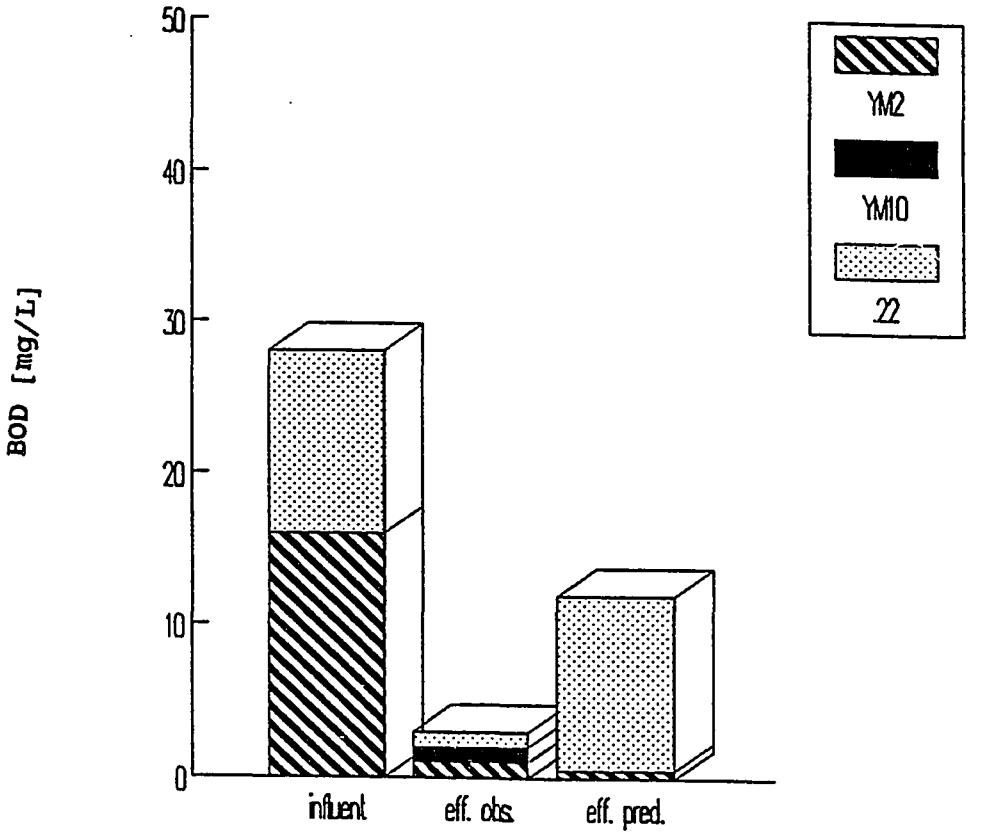

Figure C.7 : Predicted vs. Observed sBOD removals for Roger Road. 3/31/88

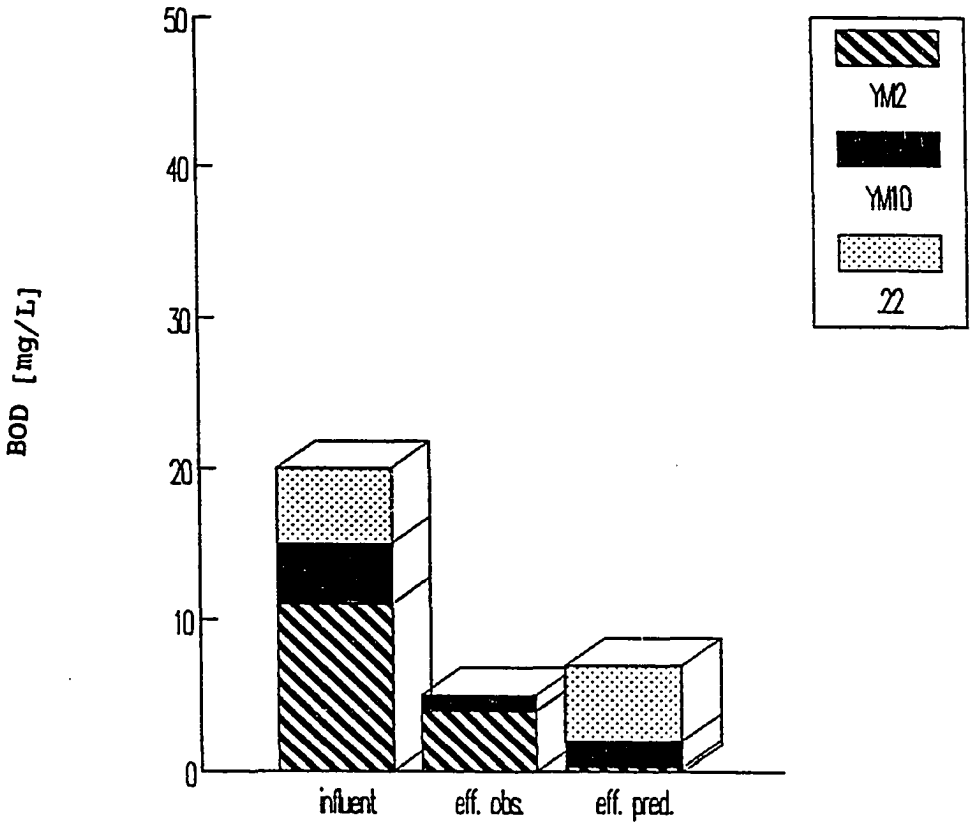

Figure C.8 : Predicted vs. Observed sBOD removals for Roger Road. 5/20/88

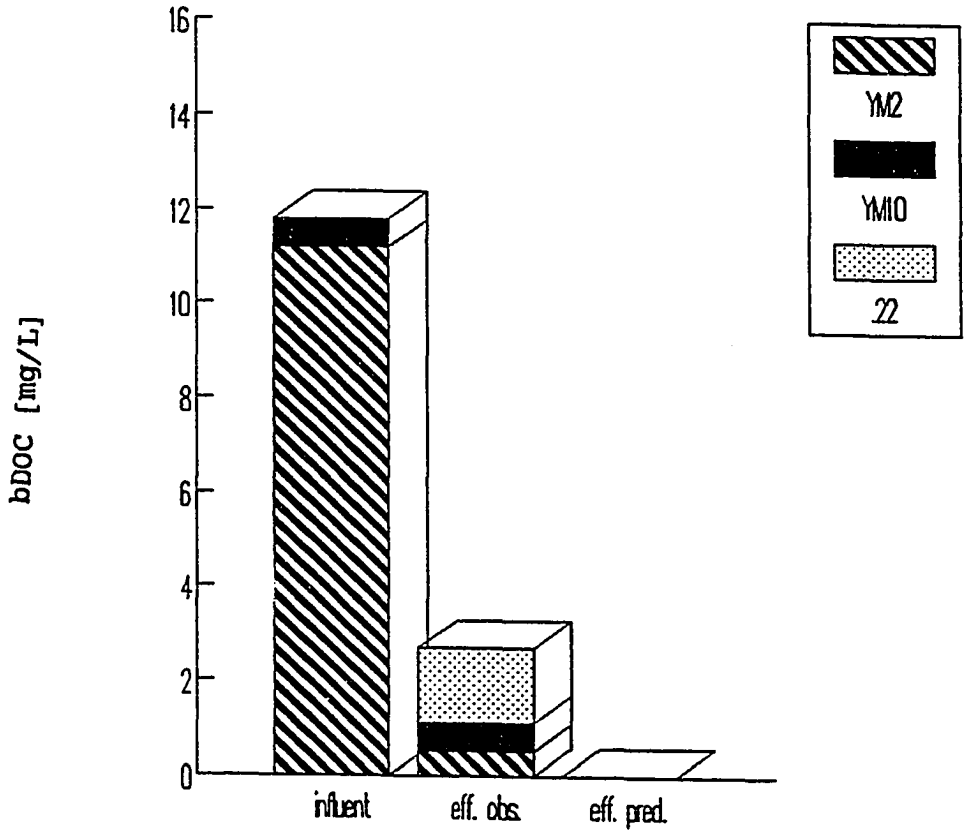

Figure C.9 : Predicted vs. Observed bDOC removals for Roger Road. 2/19/88

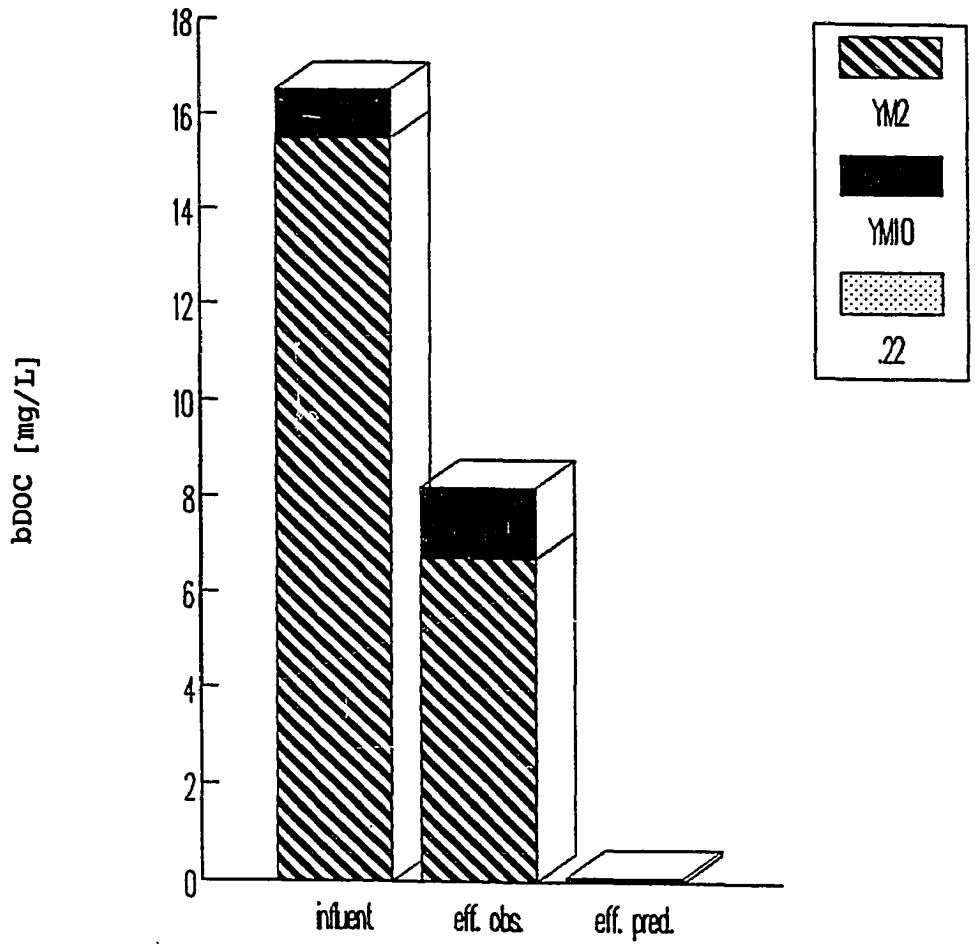

Figure C.10 : Predicted vs. Observed bDOC removals for Roger Road. 3/11/88

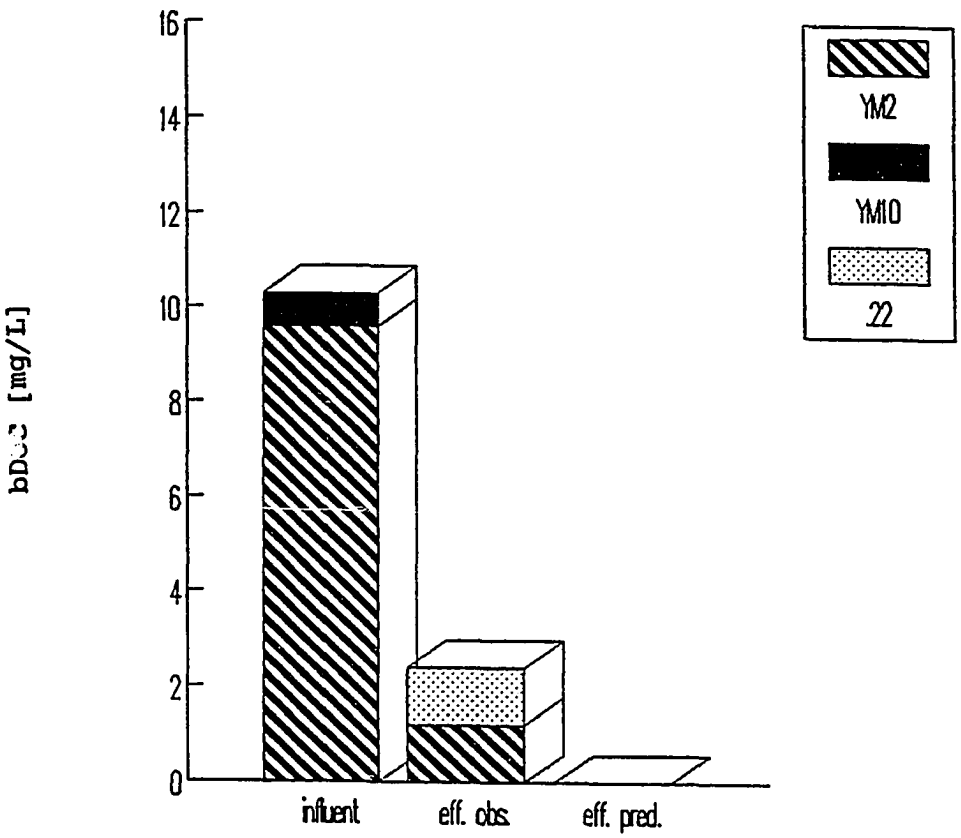

Figure C.11 : Predicted vs. Observed bDOC removals for Roger Road. 3/31/88

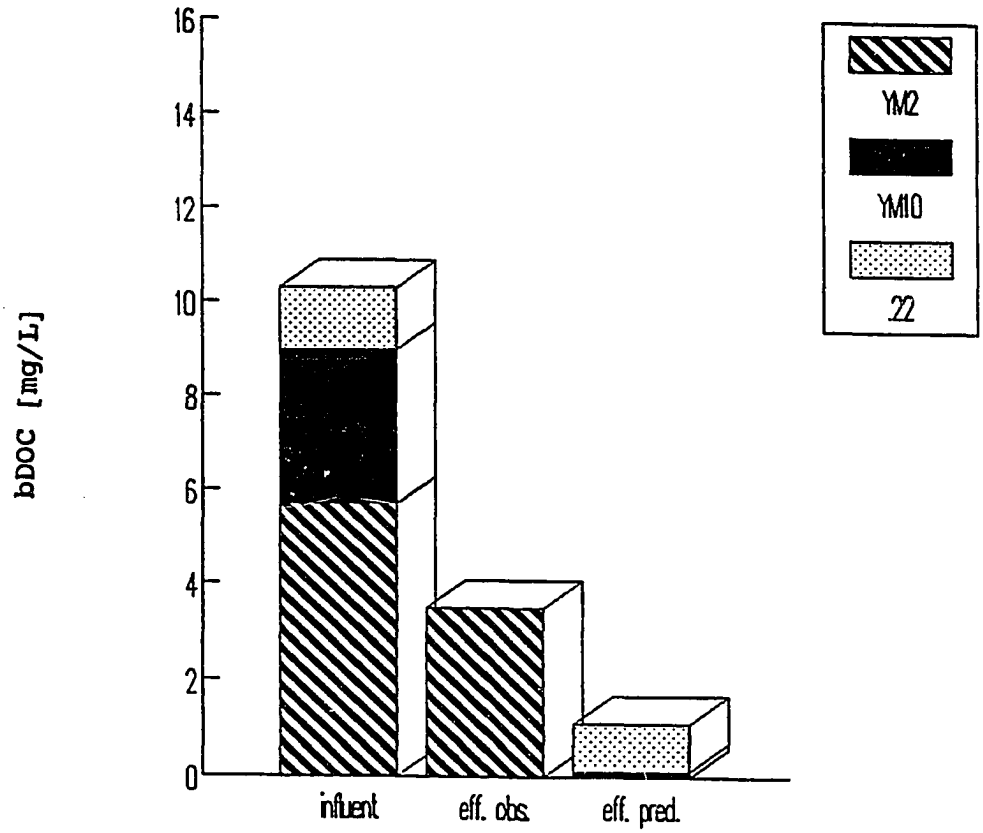

Figure C.12 : Predicted vs. Observed bDOC removals for Roger Road. 5/20/88

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