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THE ROLE OF STREAMBED BIOFILMS IN THE REMOVAL OF BIODEGRADABLE CONTAMINANTS FROM SHALLOW STREAMS

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ABSTRACT

Biological activity in shallow streams is dominated by biofilms which are attached to the surfaces of the streambed. Although biofilm kinetic models are well developed and are successfully applied to biological treatment process, they cannot be applied directly to predict water quality in shallow streams, because the area and mass-transport aspects of streambed biofilms are complicated and not defined. Therefore, the main purpose of this study was to develop area and mass-transport functions for cobble-and gravel-lined streambeds. An artificial stream was used to grow biofilms and conduct kinetic experiments on the biofilm utilization of an easily degraded sugar. Media size (i.e., cobble or gravel) and flow velocity were varied over a wide range of values typical to shallow streams. Water velocity had short-term and long-term effects on the rate of contaminant removal. The short-term effects were related to increased mass-transport kinetics for higher flow velocities, while the long-term effects also included increased surface colonization by biofilm. The cobble streambed was more sensitive to short-term changes in water velocity than was the gravel bed, and it gave faster removal kinetics. Equations to predict the mass transfer coefficients were appropriate for more than one biofilm community, as long as the same medium size was used. The simulations from the water quality models containing the biofilm reaction term were markedly different from the simulations from traditional water-quality models that use only suspended-organism kinetics.

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INTRODUCTION

Advantage of Being Attached in Streams

The relative importance of streambed biofilms compared to suspended microorganisms in removing contaminants from a shallow stream's water column is largely a function of biomass. For unpolluted streams less then 1.5 meters deep, Wuhrmann (1972) estimated that 90 to 99.9 percent of the heterotrophic biomass beneath a square meter of water surface area is attached to the streambed. This predominance of attached biomass in shallow streams can be related to residence time, which can be defined as the amount of time a microorganism stays in a 1-meter long segment of the stream. The residence time for a suspended organism in a shallow stream is short, i.e., inversely proportional to the average stream velocity. The suspended residence time is usually less then the doubling time for the suspended microorganisms (Hynes, 1970). Because the suspended residence times do not allow significant microbial growth, the amount of suspended biomass at a point in a stream is primarily determined by the amount of biomass drifting from upstream (Wuhrmann, 1972). In contrast, the residence time for an attached microorganism is much longer than the microorganism's doubling time (Hynes, 1970) and is inversely proportional to the rate at which the biofilms are scoured from the streambed. Because the attached residence times are long enough to allow microbial growth, the amount of attached biomass at any point in a stream is primarily determined by the substrate concentration at that point.

The importance of residence time in developing microbial biomass and in influencing contaminant removal rates can be illustrated by examining what regions of a river system have faster rates of nitrification. Because of

the relatively slow growth of nitrifying bacteria, high rates of nitrification are limited to river habitats that have residence times sufficient to develop substantial populations of nitrifying bacteria. Except for estuaries, the short residence times characteristic of flowing waters does not allow the development of significant populations of suspended nitrifying bacteria. Conversely, due to the long residences times associated with being attached to the streambed, large populations of attached nitrifying bacteria can be found on the bottom of all sizes of streams. However, due to surface-to-volume ratios, the rapid reduction of ammonia concentration by streambed nitrifiers is observed only in shallow streams. Therefore, due to residence time and stream channel geometry considerations, high rates of ammonia removal are only observed in estuaries and shallow streams (Tuffey, et. al., 1974).

The above example indicates that while the high residence times associated with being attached to the streambed can allow sizeable populations of microorganisms to develop, the importance of attached biomass in reducing water column concentrations of pollutants is dependent on the surface area to volume ratio for the stream channel (Wuhrmann, 1972). Therefore, the streambed biofilms will be most important in determining contaminant removal rates in streams with high surface area to volume ratios, i.e., shallow streams.

In addition to stream morphology, the importance of streambed biofilms in removing water column contaminants is also a function of the stream velocity. A cobble streambed acclimated to a stream velocity of 24 cm/sec was 22 times more effective in removing low concentration of glucose than a similar cobble streambed acclimated to a stream velocity of 4 cm/sec

(Wuhrmann, et. al., 1975). This sensitivity to stream velocity was probably due to the changes in the mass transport regime to which biofilms were exposed and to differences in biofilm biomass.

When stream velocities become too great, significant portions of the biofilm community can be scoured from the streambed. For example, immediately after a severe rain storm, nitrification rates in a shallow stream were reduced by 50 percent, due to the scouring and sloughing of nitrifying bacteria from the streambed surfaces by the increased stream velocities. Recovery to pre-storm nitrification rate required over 14 days (Williamson and Cooke, 1985).

The concept of residence time is particularly important in explaining contaminant removal rate in a shallow stream just below a point source. The suspended stream biomass drifting into the point source's plume and the organisms found in the discharge that survived chlorination will be exposed to organic substrates or environmental conditions to which they are not acclimated. Acclimation periods of 20 hours can be required before the suspended microorganisms start to utilize the new organic substrates at appreciable rates (Apoteker and Thevenot, 1983). Even more time may be required before the suspended microorganisms develop enough biomass to affect substrate concentrations. Due to acclimation time requirements and to a lack of biomass, suspended microorganisms may not be important in removing discharged contaminant until several hours downstream of the point source. However, the streambed biofilms that are attached in the point source's plume have an immediate effect on contaminant concentrations, because they are already acclimated to the discharged substrates and represent a large amount of biomass. Thus, in shallow streams, the

reduction in contaminant concentrations immediately below a point source will be determined predominantly by the streambed biofilms.

While the principal reason for the predominance of attached microbial biomass in shallow streams is residence time, there are also several nutritional advantages associated with being attached, especially in streams with low substrate concentrations. First, the mass transfer rates associated with being attached to the stream bottom can be greater than the mass transfer rates associated with being suspended in the stream water column. Thus, the flux of substrate in attached microorganisms can be greater than the flux in suspended microorganisms when both are exposed to the same bulk substrate concentration, allowing biofilms to have faster growth rates than suspended organisms at low substrate concentrations (Paerl, 1980). In shallow, clear streams, the algae attached to the streambed surfaces have greater primary production rates and faster growth rates than the algae drifting in the stream's water column (Hynes, 1970; Wetzel, 1975).

The second nutritional advantage of being attached is that the substratum to which the biofilm is attached and the biofilm's slime matrix can adsorb organic compounds. In water having low nutrient concentrations, the extent of microbial growth is related to the available solid-liquid interfacial area, suggesting that nutrients are concentrated at the substratum's surface (Marshall, 1978) or adsorbed to biofilm slime (Characklis, 1973a). ZoBell (1943) noted that in carboys having low organic concentrations, bacterial concentrations increased with increased surface area. Kirchman and Mitchell (1982) reported that in lenthic systems, the uptake per cell of dissolved organic compounds is higher for bacteria

attached to suspended particles than for free-floating bacteria, suggesting that adsorption plays an important role in the survival of attached microorganisms in low nutrient environments.

The third nutritional advantage is that the biofilm's slime matrix retards the diffusion of exoenzymes and metabolic products away from the microorganisms. Since it is generally believed that large organic molecules and organic particulates must be hydrolyzed by exoenzymes before the organic material can be utilized by bacteria, in dilute solutions the bacteria that prevent the diffusive loss of these exoenzymes, and the products of their action, are utilizing the available substrate more efficiently (ZoBell, 1943). Ladd, et. al, (1979) have shown that biofilm slime slows the diffusion of simple organic compounds to the biofilm cells, implying that the slime layer could also be slowing the diffusive loss of hydrolyzates. Thus, biofilms can allocate less energy into the production of exoenzymes and potentially degrade organic compounds further than suspended microorganisms. This observation has implications in determining the fate of organic compounds that are slightly hydrophobic and recalcitrant to biodegradation.

Functional Dominance of Streambed Biofilms

Streambed biofilms account for most of the microbial biomass found in shallow streams, due primarily to residence time and mass transfer considerations. Consequently, because of the high surface area to volume ratios characteristic of shallow streams, streambed biofilms are predominantly responsible for the removal of biodegradable compounds from the water column. Tuffey, et. al., (1974) observed that most of the ammonia

removal in shallow streams was due to nitrifiers attached to the stream bottom. Lock and Hynes (1976) concluded that benthic microorganisms were the cause of most of the degradation of dissolved organic material (leaf leachates) in several unpolluted Canadian streams. Ladd, et. al., (1979) demonstrated that streambed bacteria were at least 8 times more effective at removing organic substances from the water column of a shallow unpolluted stream than were planktonic bacteria. Therefore, streambed biofilms account for most of the removal of naturally occurring organic compounds from shallow streams.

Several researchers have observed that streambed biofilms immediately below point sources in shallow streams are predominantly responsible for the removal of discharged biological oxygen demand (BOD). Kittrell and Kochtitzky (1947) compared the BOD removal rates observed in BOD bottles filled with undiluted stream water. Since most the BOD discharged into the stream was considered soluble, the difference between the two rates (stream BOD minus bottle deoxygenation) was indicative of the rate at which the streambed biofilms removed BOD from the water column. For the first 1.5 hour (0.7 miles) below a point source, the rate of BOD removal was 2.26 day^{-1} and the bottle deoxygenation rate was 0.35 day^{-1}, both values reported at 20°C. Therefore, the calculated rate at which streambed biofilms removed BOD was 1.91 day^{-1} or about 85 percent of the total BOD removal rate.

Velz and Gannon (1964) also approximated the rate at which streambed biofilms removed BOD as the difference between the observed BOD removal rate and the deoxygenation rate observed in a BOD bottle containing a stream water sample. Based on 13 sets of data collected at various locations on the Jackson River in Michigan, total BOD removal rates ranged from 0.39 to

1.11 day^{-1} with an average value of 0.70 ± 0.25 day^{-1}. Deoxygenation rates ranged from 0.07 to 0.134 day^{-1} with an average of 0.11 ± 0.03 day^{-1}. The calculated rates at which streambed biofilms removed BOD ranged from 0.26 to 1.0 day^{-1} with an average of 0.60 ± 0.24 day^{-1}. On the average, streambed biofilms accounted for 83.7 ± 7.4 percent of the total BOD removal rate.

For the first 5 hours (7 miles) below the outfall of a municipal wastewater treatment plant in a shallow cobble-lined stream, the removal rate of total organic carbon (TOC) was approximately 1.6 day^{-1} (Srinanthakumar and Amirtharajah, 1983). Based on a site-specific streambed-biofilm-kinetic model, they concluded that the streambed biofilms were predominantly responsible for the removal of the TOC, while the contribution of suspended biomass was negligible.

In a shallow stream 400 meters below a papermill outfall, total deoxygenation rates averaged about 3.7 day^{-1}. Based on comparative respirometry experiments, about 90 percent of the total deoxygenation rate was caused by streambed biofilms (Boyle and Scott , 1984).

Harremoës (1982) investigated the discharge of a partly treated waste into a shallow stream. The stream was 20 cm deep with an average velocity of 20 cm/sec. Over the first 4.3 hours (3.1 km) below the outfall, the total non-settlable BOD removal rate was 3.6 day^{-1}. The suspended microorganisms removed non-settlable BOD at 0.27 day^{-1}. Therefore, the rate at which streambed biofilms removed non-settlable BOD was 3.3 day^{-1}, or 92 percent of the total removal rate.

Lack of Predictive Capacity

The above examples indicate that suspended organisms play a minor role in determining contaminant removal rates in shallow streams. Consequently, attempts to predict removal rates in shallow streams based on suspended-growth kinetics have proven unsatisfactory. Thomann (1982) reported that suspended-growth water quality models provided poor predictions of dissolved oxygen concentrations in small streams. While the models predicted dissolved oxygen concentrations in large rivers, such as the Ohio and Upper Mississippi, with a mean relative error of less than 10 percent, the mean relative error for small, shallow streams was 60 percent. This inability to predict streambed biofilm removal rates is not limited to BOD and dissolved oxygen. Games (1982) observed that suspended-growth models were inappropriate in predicting the rate at which trace concentrations of organic compounds were removed from shallow streams.

Although the concepts of cell residence time and surface to volume ratios provide a theoretical basis for explaining the functional dominance of streambed biofilms in shallow streams, heretofore models that can predict the rates at which streambed biofilms remove biodegradable materials from the water column have not existed. The present study examines using mechanistic biofilm kinetics models to predict streambed biofilm activity.

Objective

The objective of the present study is to define--in forms suitable for use in a water quality model based on biofilm kinetics--the mass transfer and surface area parameters for gravel and cobble streambeds. A water quality model based on an existing biofilm kinetics model, the first-order

flux model, is developed first. Then, the first-order flux model is used to determine the mass transfer rates and active biofilm surface area found in gravel and cobble streambeds. Finally, the results of incorporating mass transfer and surface area relationships into the water quality model are discussed.

DEVELOPMENT OF STREAM WATER QUALITY MODEL

Introduction

The mathematical representation of the role that streambed biofilms play in determining contaminant concentrations in shallow streams has typically been limited to site-specific descriptions. Site-specific models, while providing information about an existing situation, may not be appropriate for use in predicting contaminant removal rates under different biological, chemical, or hydraulic situations, much less so for predicting removal rates in other streams (Branson, 1978). For example, assume a water quality model described the rate at which streambed biofilms removed COD from a stream with an average velocity of 20 cm/sec. The ability of this model to predict COD removal rates in the same stream, but at a velocity of 45 cm/sec, probably would be poor--unless the model accounted for the mechanisms that make streambed biofilm activity sensitive to changes in hydraulic conditions.

The first objective of this chapter is to present a water quality model which incorporates the mechanisms that are responsible for determining the rate at which streambed biofilms remove contaminants from a stream's water column. The sink term in the water quality model is based on existing mechanistic biofilm kinetics models, so that the flux of contaminants into a

streambed biofilm is a function of intrinsic kinetics, mass transport, and the physical characteristics of the biofilm. Because the model mathematically accounts for the major mechanisms that determine contaminant removal rates, it should be applicable to any stream system in which streambed biofilms are predominantly responsible for the removal of contaminants.

Stream Water Quality Model

The mass balance equation for a one-dimensional, steady-state water quality model has the following form (Thomann, 1972):

$$E \frac{d^2C}{dx^2} - V \frac{dC}{dX} - RATE = 0 \qquad (1)$$

in which E is the longitudinal dispersion coefficient (cm^2/hr), C is the water column concentration of the contaminant (mg/cm^3), x is longitudinal distance down the stream channel (cm), V is the average stream velocity (cm/hr), and RATE is the rate at which the contaminant concentrations are being reduced due to microbial activity ($mg\ cm^{-3}\ hr^{-1}$). In this chapter, the RATE term will include only the removal of water column contaminants by streambed biofilms. Equation 1 assumes that variations in C across the cross-section of the stream are small and not of interest, i.e., a uniform value of C is assumed in the vertical (depth) and horizontal (width) directions. The variations in water velocity across the stream's cross-section will cause a diffusion-like mixing in the x direction, which is accounted for by the first term in the above equation. The steady-state

condition assumes that C is not changing with time at any point in the stream.

Rittmann (1982b) defined the RATE term for biofilm reactions by

$$RATE = J\ a \tag{2}$$

in which J is the flux of substrate into a biofilm (mg cm^{-2} hr^{-1}), and a is the specific biofilm surface area, or biofilm-covered surface area per total reactor volume (cm^{-1}). When specific biofilm surface area is defined in terms of unit length of reactor or streambed, Equation 2 can be rewritten as

$$RATE = J\ \frac{\text{biofilm surface area per length}}{\text{FLOWAREA}} \tag{3}$$

in which FLOWAREA is the cross-sectional area available for flow (cm^2). For a stream, Equation 3 would take this form,

$$RATE = J\ \frac{P}{\text{FLOWAREA}} \tag{4}$$

in which P is the amount of biofilm-covered surface area per unit stream length, or the amount of wetted perimeter covered with biofilms per unit stream length (cm). The value of P includes external and interstitial surface area of the streambed, as long as it's covered by biofilms.

For wide streams, FLOWAREA can be approximated by

$$FLOWAREA = H\ W \tag{5}$$

in which H is stream depth (cm) and W is the width of the stream channel (cm). Substituting Equation 5 into 4 and dividing both the numerator and denominator by W gives the following equation:

$$RATE = J \frac{P/W}{H} \cdot \tag{6}$$

P/W is a useful dimensionless parameter that accounts for the amount of wetted perimeter covered by biofilms per unit channel width (unitless). Equation 6 illustrates that the rate at which streambed biofilms remove contaminants from the water column is greatest in shallow streams (small H) with high P/W values. If a stream is lined with a flat, smooth surface, such as bedrock, which is entirely covered with biofilms, then P/W = 1. However, for gravel and cobble-lined streambeds whose interstitial voids are free of sand and silt, P/W values can be substantially greater than 1, because biofilms can be on the interstitial areas, as well as the exposed surfaces of the streambed (Novotny, 1969).

Substituting Equation 6 into Equation 1 produces the following equation:

$$E \frac{d^2C}{dx^2} + V \frac{dC}{dx} + J \frac{P/W}{H} = 0 \tag{7}$$

which can be used to describe contaminant concentrations as a function of distance down the stream channel.

First-Order Biofilm Kinetics

The biofilm kinetics model developed in this section is designed to predict the flux (J) of microbial substrates into the biofilm based on the

bulk concentration of the substrate and on certain quantifiable characteristics of the biofilm. The derivation of the model assumes an idealized biofilm, which is characterized as having a uniform biomass density, Xf (mg VSS/cm^3), and a locally uniform thickness of Lf (cm). Concentration of the substrate varies only in the z direction, i.e., normal to the surface of the biofilm. The modeled substrate is assumed to be the rate-limiting compound. Figure 1 depicts an idealized biofilm.

The biofilm model assumes that the flux of substrate into a biofilm is a function of three mechanisms: 1) mass-transport from the bulk liquid to the biofilm surface, 2) mass-transport within the biofilm, and 3) microbial transformation of the substrate within the biofilm (Williamson and McCarty, 1976a). The two mass-transport mechanisms are represented mathematically as diffusion processes; consequently, they are sensitive to the substrate concentration gradient within the biofilm. The rate at which biofilm microorganisms transform the substrate is the driving force in the formation of the concentration gradient.

The rate at which the modeled substrate is degraded or transformed at any point within the biofilm can be represented generally by Monod kinetics (Williamson and McCarty, 1976a; Rittmann and McCarty, 1980),

$$\frac{dCf}{dt} = - \frac{k\ Xf\ Cf}{Ks + Cf} \tag{8}$$

in which Cf is substrate concentration at a point within the biofilm (mg/cm^3), t is time (hr), k is the maximum specific rate of substrate transformation (mg substrate mg VSS^{-1} hr^{-1}), and Ks is the half-maximum-rate concentration (mg substrate/cm^3). However, for many potential stream contaminants, Ks can be assumed to be much greater than the expected

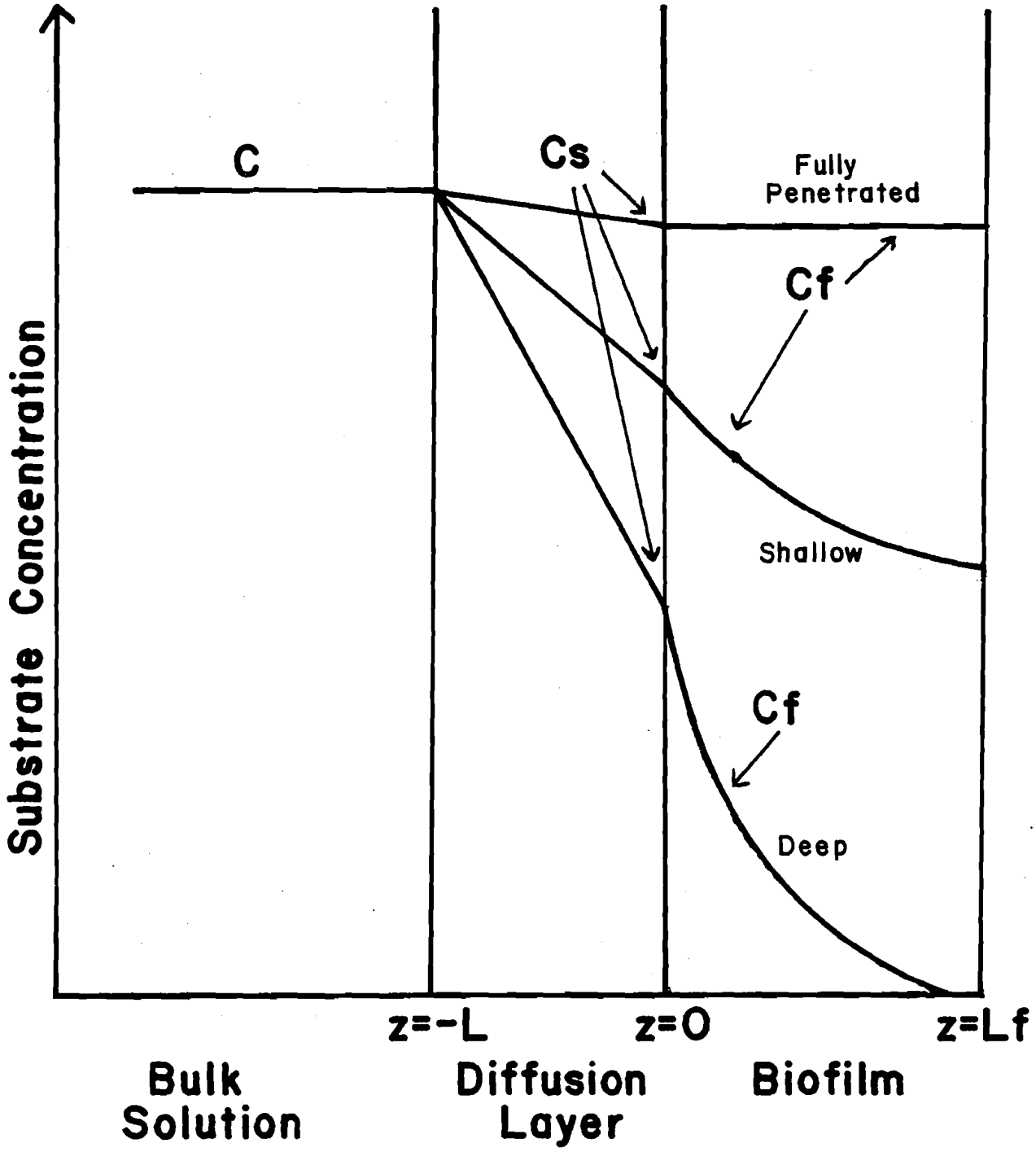

Figure 1. Schematic of an Ideal Biofilm

environmental concentration of the contaminant (Baughman, et. al., 1980). Because concentrations of such contaminants within the biofilm also are much less than Ks, Equation 8 can be reduced to the following mixed second-order rate equation:

$$\frac{dCf}{dt} = - K\ Xf\ Cf \tag{9}$$

in which K is the mixed second-order rate constant (cm^3 mg VSS^{-1} hr^{-1}) and is equal to k/Ks.

The only means of mass transport within the idealized biofilm is by molecular diffusion, which is related to substrate concentration by Fick's second law of diffusion (Williamson and McCarty, 1976a; Rittmann and McCarty, 1980),

$$\frac{dCf}{dt} = Df\ \frac{d^2Cf}{dz^2} \tag{10}$$

in which Df is the diffusion coefficient of the substrate within the biofilm (cm^2/hr).

Because the processes of molecular diffusion and microbial transformation simultaneously affect substrate concentrations, the rate of substrate concentration change at any point within the biofilm is defined by

$$\frac{dCf}{dt} = Df\ \frac{d^2Cf}{dz^2} - K\ Xf\ Cf \tag{11}$$

Assuming steady-state conditions (i.e., dCf/dt = 0) at all points within the biofilm converts Equation 11 to the following differential equation for substrate concentrations within the biofilm (Williamson and McCarty (1976a):

$$0 = Df \frac{d^2Cf}{dz^2} - K\ Xf\ Cf \tag{12}$$

Equation 12 is subject to the following two boundary conditions: the substrate concentration at the outer surface of the biofilm (z = 0) equals Cs (mg/cm^3), and the substrate concentration gradient at the inner biofilm surface (z = Lf) is zero (dCf/dz = 0), i.e., the surface to which the biofilm is attached is impermeable and does not adsorb the modeled substrate. Integration of Equation 12 produces the following equation (Williamson and McCarty, 1976a):

$$Cf(z) = Cs \frac{\cosh[PHI\ (Lf-z)]}{\cosh[PHI\ Lf]} \tag{13}$$

in which Cf(z) is the substrate concentration (mg/cm^3) at z cm in from the outer surface of the biofilm, and PHI is a characteristic biofilm kinetic parameter (cm^{-1}) that is defined by

$$PHI = [\frac{K\ Xf}{Df}]^{1/2} \tag{14}$$

The flux of substrate into the outer layer of the biofilm is described by Fick's first law (Rittmann and McCarty, 1978),

$$J = - Df \frac{dCf}{dz} \tag{15}$$

in which dCf/dz is the concentration gradient at z = 0. Substituting the first derivative with respect to z of Equation 13 into Equation 15 and solving for z = 0 yields

$$J = Cs\ Df\ PHI\ \tanh(PHI\ Lf) \tag{16}$$

Equation 16 gives J, a parameter needed in Equation 7, as a function of the substrate concentration at the outer surface of the biofilm, Cs.

Because the water quality model (Equation 7) keeps account of the bulk liquid concentration, C, the objective of biofilm kinetics models must be to predict the flux into the biofilm based on the substrate concentration in bulk solution and not on substrate concentrations at the biofilm surface. Cs can be defined as a function of bulk substrate concentration by considering the mass-transport of materials moving from bulk solution to the outer surface of the biofilm. The flux of substrate from bulk solution to the surface of the biofilm can be defined by (Frank-Kamenetskii, 1969)

$$J = Km\ (C - Cs) \tag{17}$$

in which Km is the mass transfer coefficient (cm/hr) and C is the substrate concentration in bulk solution (mg/cm^3). Km can be expressed in terms of the substrate's diffusivity in water (Frank-Kamenetskii, 1969),

$$Km = \frac{D}{L} \tag{18}$$

in which D is the diffusion coefficient for the substrate in water (cm^2/hr) and L is the thickness of the effective diffusion layer (cm). In biofilm kinetics models, mass-transport resistance has traditionally been defined in terms of L instead of Km. By substituting Equation 18 into Equation 17, Cs can be determined from the following equation:

$$Cs = C - \frac{J\ L}{D} \tag{19}$$

in which J is the flux of substrate across the effective diffusion layer (mg cm^{-2} hr^{-1}).

Because the flux of substrate across the effective diffusion layer is equal to the flux of substrate into the outer layer of the biofilm, substitution of Equation 19 into Equation 18 produces

$$J = \frac{D\ Df\ PHI\ \tanh(PHI\ Lf)}{D + L\ Df\ PHI\ \tanh(PHI\ Lf)}\ C \tag{20}$$

which defines substrate flux into the biofilm as a function of substrate concentration in bulk solution. Therefore, for a constant value of Lf, the removal of substrate from bulk solution by biofilms is first-order with respect to C,

$$J = Kf\ C \tag{21}$$

in which Kf is the first-order flux constant (cm/hr) and is defined by

$$Kf = \frac{D\ Df\ PHI\ \tanh(PHI\ Lf)}{D + L\ Df\ PHI\ \tanh(PHI\ Lf)} \tag{22}$$

Stream Water Quality Model Based on Biofilm Kinetics

Substituting the first-order flux model (Equation 21) into the mass balance equation for the stream water quality model (Equation 7) yields

$$E\frac{d^2C}{dx^2} + V\frac{dC}{dx} + \frac{P/W}{H}Kf(x)\ C = 0 \tag{23}$$

which can be used to predict substrate concentrations when streambed biofilms are responsible for their removal. The first-order flux constant

is written as the function Kf(x), because the value of Kf decreases as biofilm biomass decreases in response to the lower substrate levels further downstream.

DETERMINATION OF MASS TRANSFER AND SURFACE AREA RELATIONSHIPS IN GRAVEL AND COBBLE STREAMBEDS

Controlling Influence of Stream Velocity

The problem with applying biofilm kinetics models to stream water quality modeling is that the local mass transfer coefficients and the amount of biofilm surface area presented by natural streambeds are not known. For three reasons, the problem is especially acute for shallow streams that are lined with gravel or cobble. First, biofilms located on the interstitial surfaces of the streambed may significantly contribute to the removal of biodegradable contaminants from the stream's water column. Thus, potential biofilm surface area will be greater than the vertically projected surface area. Second, the actual amount of the potential surface area colonized by biological films varies with streambed particle size. Larger streambed particles, such as cobble, tend to have a greater portion of their surface area covered by biological growths than smaller streambed particles, such as gravel and sand (Novotny, 1969). Third, equations have not been developed to describe the mass transport of dissolved compounds from the water column to these interstitially located biofilms. The mass transport phenomenon would simultaneously resemble that of flow through porous media and of open channel flow, which implies that the mass transport of contaminants from the water column to the interstitial biofilms would be difficult to model *a priori*.

The obstacle to applying biofilm kinetics to stream water quality modeling stems not only from the paucity of information about biofilm surface area and local mass transfer coefficients, but also involves a lack of information on how mass transfer rates and biofilm surface area are interrelated in gravel and cobble streambeds. Stream flow--as advection eddies, vortices, and other forms of turbulence--penetrates the entire depth of the porous layer of rocky streambeds. However, within this porous layer, interstitial water velocities sharply decrease with increasing depth into the streambed. Because local mass transport rates are a function of the local water velocities, the biofilms attached to rock surfaces found in the upper portion of a streambed are more active in removing substrates than those biofilms found at the bottom of the streambed.

While the upper streambed biofilms may always have greater activities than the lower streambed biofilms, the ratio between biofilm activities at different depths in the streambed can change with steam velocity. At slower stream velocities, the upper portion of a streambed accounts for the almost all of the substrate removal from the water column. As stream velocities increase, the interstitial water velocites will also increase throughout the entire depth of the streambed. The incremental increases in interstitial velocities will have a greater effect on substrate flux into the lower streambed biofilms (previously exposed to very low mass transfer rates) than on substrate flux into the biofilms located in the upper layers of the streambed (previously exposed to high mass transfer rates). This differential response to increases in stream velocity is due to the relationship between the local mass transfer coefficient (Km) and substrate flux into a biofilm (J). As illustrated by Figure 2, beyond a certain mass

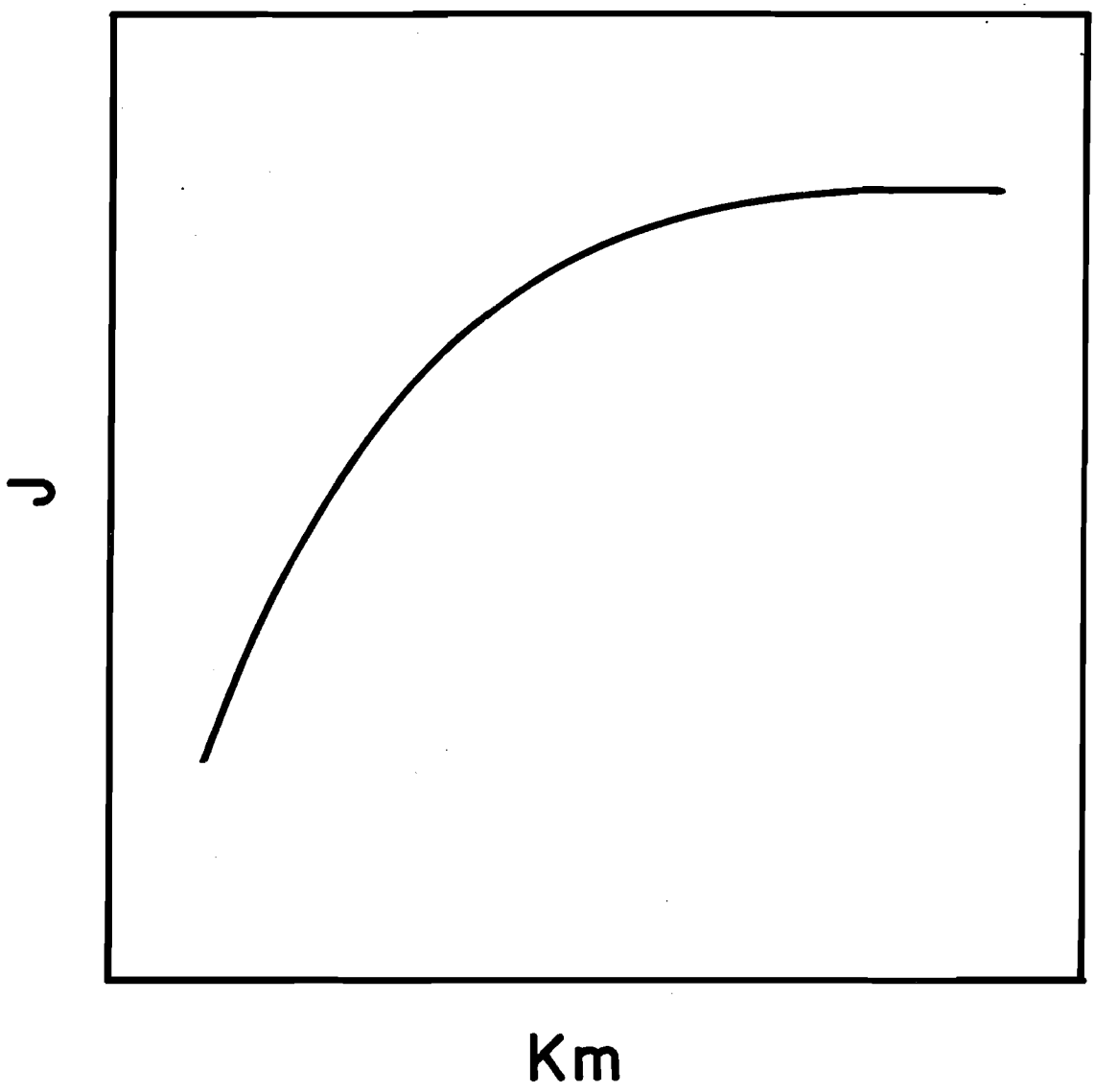

Figure 2. Relationship Between Flux (J) and the Local Mass Transport Rate Coefficient (Km) as Defined by Equations 18 and 20.

transport regime, further increases in Km have a negligible effect on J. Thus, as stream velocity increases, an increasing depth of the streambed becomes important in determining the rate in which streambed biofilms remove contaminants from the water column.

A simplification of the above discussion is presented by Figure 3. At low stream velocities, only the biofilms located above the upper portion of the streambed are active in removing water column contaminants, due to the decrease in interstitial mass transfer coefficients with depth into the streambed. As stream velocities increase, the biofilms located in the lower regions of the streambed become increasingly important in removing water column contaminants, i.e., substrate flux into the deeper biofilms increases more rapidly than into the upper biofilms with incremental increases in stream velocity. This differential response to increases in stream velocity is due to the shape of the flux versus mass transfer rate curve shown in Figure 2. Therefore, changes in stream velocity not only affect mass transport, but also affect the amount of biofilm surface area active in contaminant removal.

At least two types of variations in the physical characteristics of the interstitial biofilms should occur with increasing depth into the streambed. First, the amount of active biofilm biomass per unit surface area ($Xf^{*}Lf$ or B) should decrease with depth into the streambed. Rittmann and McCarty (1980) stated that biofilm biomass under dynamic steady-state conditions would be directly proportional to the flux of substrate into the biofilm. Because the flux of substrate should decrease with decreasing local mass transfer rates, biofilm biomass per unit surface are (B) is expected to decrease with increasing depth into the streambed. Second,

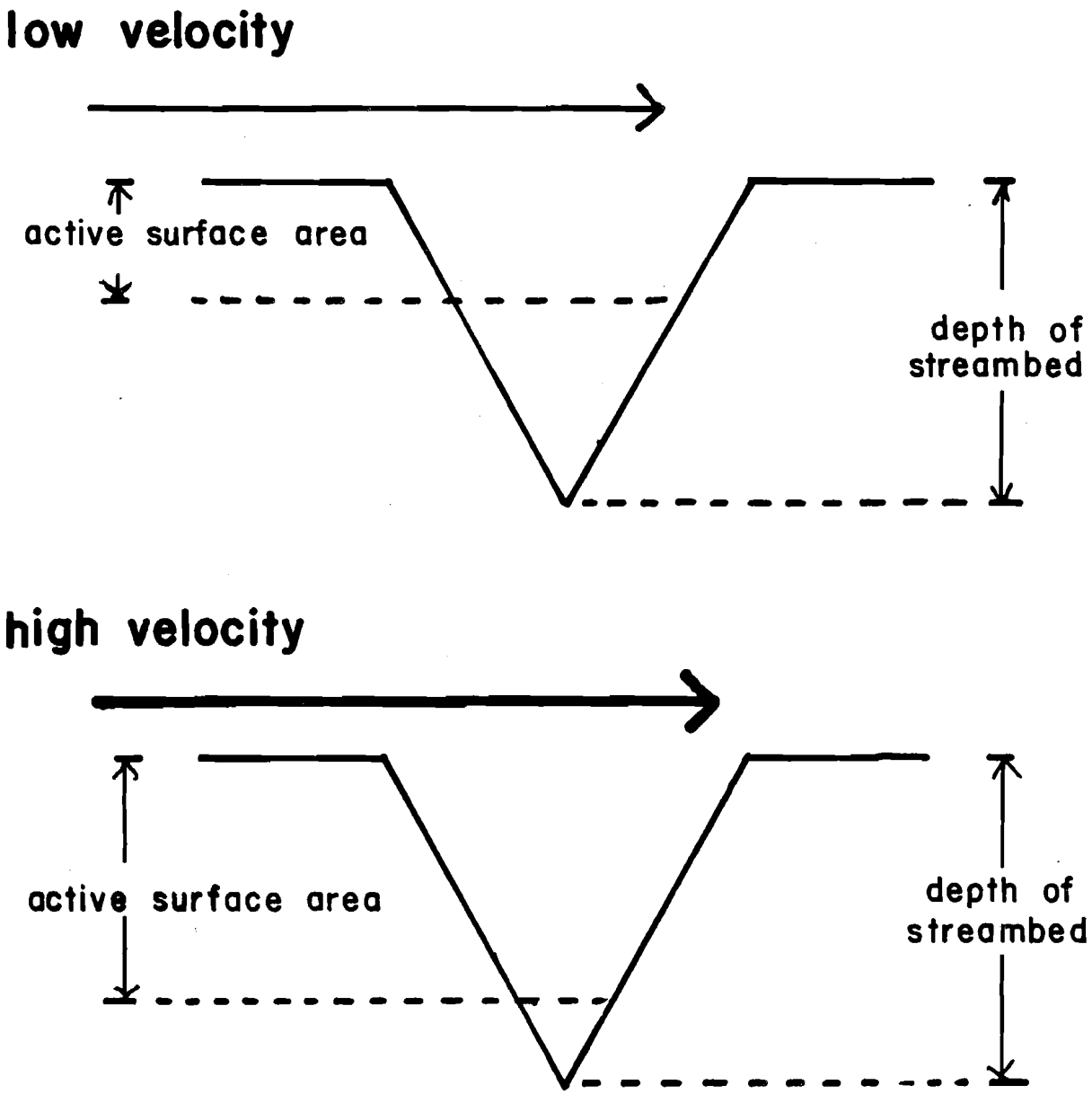

Figure 3. Amount of Active Interstitial Streambed Surface Area at Low and High Stream Velocities. In both situations, the region of active streambed surface area is predominantly responsible for the removal of contaminants from the water column.

biofilm density (Xf) may also vary with depth into the streambed in direct response to the decrease in eddy velocities. This is significant because rates of substrate removal by deep biofilms is more sensitive to changes in Xf than to changes in biofilm thickness (Lf).

Because biofilm biomass is directly related to local interstitial mass transfer rates and because the local interstitial mass transfer rates are a function of stream velocity, the amount and distribution of interstitial biofilm biomass will be determined by a long-term, average stream velocity. A rocky streambed acclimated to faster stream velocities should support more biofilm biomass than a similar stream acclimated to a slower velocity. Therefore, the rate at which interstitial biofilms can remove contaminants from a stream's water column is not only a function of the velocity at which the streambed is presently being exposed, but also is a function of the stream velocity to which the biofilm community was acclimated. For example, assume that stream velocity VEL-B is greater than stream velocity VEL-A. A streambed biofilm community acclimated to VEL-B and presently exposed to VEL-B should remove contaminants at a faster rate than if the streambed community was acclimated to VEL-A and exposed to VEL-B, assuming constant primary substrate loading during acclimation. Although both biofilm communities are exposed to the same mass transfer regime, the community acclimated to the higher velocity should have more biofilm biomass than the community acclimated to the slower VEL-A.

In summary, stream velocity controls the rate at which streambed biofilms remove contaminants from the water column. In the short-term, stream velocity controls contaminant removal rates by determining the distribution of local mass transfer coefficients within the streambed.

Faster stream velocities mean high interstitial mass transfer rates for a greater proportion of the streambed, which translates into a greater amount of streambed surface area active in contaminant removal. Long-term exposure to faster stream velocities allows a streambed to support greater biofilm biomass. Thus, stream velocity controls contaminant removal rates by determining the magnitude of local mass transfer coefficients, the distribution of the local mass transfer coefficients (amount of active surface area), and streambed biofilm biomass. Therefore, the rate at which biofilms living on and within rock-lined streambeds remove biodegradable contaminants from the water column will be more sensitive to changes in velocity than would be predicted based on changes in mass transfer alone.

Representative Mass Transfer Equations

In rock-lined streams, a major portion of stream flow travels over the top of the streambed, while some fraction of stream flow penetrates into the interstitial voids of the streambed. In either case, the local mass transfer can be described in a manner similar to other external mass transfer regimes. Frank-Kamenetskii (1969) reported that mass transfer coefficients for most external mass transfer regimes can be described an equation of the following form:

$$Km = \text{Constant } Re^{m} Sc^{n} \frac{D}{Lc} \tag{24}$$

in which Km is the mass transfer coefficient, Lc is the characteristic length, the Reynolds number (Re) is calculated based on Lc, m ranges in value from 0.4 to 0.67, and D is diffusivity. In most applications, the Schmidt number (Sc) is raised to the one-third power (n = 1/3).

The purpose of this section is to demonstrate that local mass transfer coefficients can be calculated from an equation of the same form as Equation 24, whether water is flowing over, around, or between the streambed particles. When particle diameter (Dp) represents Lc and n = 1/3,

$$Km = \text{Constant } Re^{m}\ Sc^{1/3}\ \frac{D}{Dp} \tag{25}$$

in which Km is the mass transfer coefficient (cm/hr),

$$Re = \frac{3600\ Vx\ Dp}{KVIS} \tag{26}$$

Sc = KVIS/D, Vx is either average stream velocity (V) or shear velocity (U) with units of cm/sec, Dp is streambed particle diameter (cm), D is the diffusivity of the contaminant in water (cm^2/hr), and KVIS is the kinematic viscosity of water (cm^2/hr).

The mass transfer to biofilms located on the upper surfaces of a streambed can be approximated by equations that define the mass transport of material to the surface of a sphere. Bird, et. al., (1960) reported that the mass transfer coefficient for flow around a single sphere can be calculated from

$$Km = (2.0 + 0.6\ Re^{1/2}\ Sc^{1/3})\ \frac{D}{Dp} \tag{27}$$

For large Re values, the 2.0 term becomes insignificant, and Equation 27 is of the same form as Equation 25, i.e.,

$$Km = 0.6\ Re^{1/2}\ Sc^{1/3}\ \frac{D}{Dp} \tag{28}$$

The local mass transfer coefficients for the biofilms deeper within the streambed can be approximated by equations developed for flow through porous spherical media. The McCune-Wilhelm equation has been used to describe the mass transfer rates in fixed-bed biological reactors (Rovita and Kittrell, 1973; Traber and Kittrell, 1974) and has the following form:

$$Km = 1.625\ Re^{1/2}\ Sc^{1/3}\ \frac{D}{DP} \tag{29}$$

in which

$$Re = \frac{3600\ Vs\ Dp}{KVIS} \tag{30}$$

and Vs is the superficial (empty bed) velocity (cm/sec). Equation 29 is valid for Reynolds numbers ranging from 0.2 to 100. Except that Re in Equation 29 is based on Vs instead of Vx, Equation 29 is of a form similar to Equation 25.

Another equation used to calculate the local mass transfer coefficient for flow through porous media was used by Jennings (1975),

$$Km = 5.7\ Vs\ Rem^{-3/4} Sc^{-2/3} \tag{31}$$

in which Rem is a modified Reynolds number,

$$Rem = \frac{2\ Vs\ Dp}{KVIS\ (1-Ep)} \tag{32}$$

and Ep is the porosity of the media. Equation 31 is valid between Rem values of 1 and 30. Rearranging Equation 31 produces the following equation:

$$Km = 3.39\ (1-Ep)^{3/4}\ Re^{1/4}\ Sc^{1/3}\ \frac{D}{Dp} \tag{33}$$

in which Re is defined by Equation 30. Once again, Equation 33 has a form similar to Equation 25.

The hydraulic regime experienced by biofilms attached to the external and interstitial surfaces of a streambed is a combination of flow around streambed particles and flow through porous media. The local mass transfer coefficients can not be described only as flow around an object or as flow through porous media, because of vertical velocity gradients within a streambed. Fortunately, the mass transfer equations useful for flow around spheres, and flow through porous media have a common form, namely

$$Km = \text{Constant } Re^{m} \, Sc^{1/3} \, \frac{D}{Dp} \qquad (25)$$

The above examples indicate that typical values of m range from 1/4 to 1/2. However, the above examples assume that the reactive surface area remains constant with changing water column velocities. As illustrated before, in shallow rock-lined streams, the amount of streambed surface area actively involved in contaminant removal is related to the velocity of water flowing over its upper surfaces; more precisely, the distribution of active biofilm surface area depends on the distribution of the local mass transfer coefficients within the streambed. Lower velocities give lower mass transfer coefficients within the streambed and allow less biofilm accumulation. Therefore, the apparent, overall mass transfer coefficient representative of the entire streambed is more sensitive to variations in water velocity (Reynolds number) than is the mass transfer coefficient at any one point within the streambed. Consequently, the value of m in Equation 25 is expected to be larger than 1/2 for gravel and cobble lined streambeds when biofilm utilization is the reaction term.

As discussed earlier, the velocity at which stream water flows over the upper surfaces of a rocky streambed determines the apparent, overall mass transfer coefficient for the streambed biofilms. Because of the logarithmic vertical velocity profile in streams, a problem arises as to what is the best way to define water velocity at the streambed surface. Railsback (1981) noted that streambed surface velocities could not be described as a direct function of the average stream velocity. Therefore, if the Reynolds number in Equation 25 were based on average stream velocities, then the values of Constant and m determined for a stream system probably would be site and flow specific. A mass transport model that is flow specific would defeat the purpose of model development.

However, the site and flow specificity of models used to describe phenomena controlled by the magnitude of water velocities at streambed surfaces can be reduced by describing the phenomena in terms of the shear stress exerted on the streambed surfaces by the flowing water. Streambed shear stress is often quantified not as an absolute value with units of force per unit surface area, but as a dimensionless ratio of shear stress to viscous stress known as the shear Reynolds number. For a streambed particle, the shear Reynolds number is defined as (Henderson, 1966)

$$Re = \frac{3600\ U\ Dp}{KVIS} \tag{34}$$

in which U is the shear velocity (cm/sec), Dp is streambed particle diameter, and KVIS is the kinematic viscosity of water (cm^2/hr). Shear velocity is related to shear stress by the following equation:

$$U = \left[\frac{TAU}{RHO}\right]^{1/2} \tag{35}$$

in which TAU is the shear stress to which the upper streambed surfaces are exposed (dyne/cm^2), and RHO is the density of water (1 gram/cm^3). However, in practice, U is often calculated as (Chow, 1959).

$$U = (g\ R\ S)^{1/2} \tag{36}$$

in which g is the gravitational constant (980 cm/sec^2), R is the hydraulic radius (cm) of the stream channel, and S is the slope of the energy grade line. For wide channels, R can be approximated by stream depth. For steady uniform flow, S can be approximated by the slope of the water surface elevation or of the channel bottom. For gravel and cobble streambeds, U can be approximated by the Keulegan equation (Bray, 1979):

$$U = \frac{V}{6.25 + 5.75 \log (R/Dp)} \tag{37}$$

in which V is the average stream velocity (cm/sec) and log is the base 10 logarithm. Equation 37 assumes steady, uniform flow.

Railsback (1981) found that water velocities at 0.09 cm above gravel and cobble streambed surfaces could be described as a power function of the shear Reynolds number (Equation 34), regardless of average stream water column velocity or stream depth. Water column velocity and stream depth showed little correlation with streambed water velocities. Similarly, researchers in sediment transport found that describing the beginning of bed material motion in terms of shear Reynolds number allowed the application of experimental results to a wider range of stream conditions than when bed motion was defined in terms of water column velocity (Simons and Senturk, 1977). Therefore, modeling streambed velocity phenomenon in terms of shear

stress, instead of water column velocity and water depth, removes the problem of site and flow specificity.

As with the above streambed velocity phenomena, the mass transfer coefficients that describe the transport of material to stream channel surfaces can be expressed as a function of shear stress the flowing water exerts on the streambed surface. Novotny (1969) derived the following mass transfer equation:

$$Km = c\ D\ \frac{3600\ U}{KVIS}^{1/2}\ Sc^{1/3}\ kr^{-1/2} \tag{38}$$

in which c is a constant and kr is the roughness height of the streambed projections (cm). In gravel and cobble lined stream channels, kr can be approximated by streambed particle diameter, Dp (Bray, 1979). Substituting Dp into Equation 38 and rearranging the result yields an equation of the same form as Equation 25, i.e.,

$$Km = c\ Re^{1/2}\ Sc^{1/3}\ \frac{D}{Dp} \tag{39}$$

in which Re is the shear Reynolds number (Equation 34).

As with the other mass transfer equations, Equation 39 assumes that reactive surface area remains constant with changing water column velocities and the corresponding changes in shear stress. Because the amount of streambed biofilm surface area active in substrate removal is a function of the water velocity at the streambed surface, the Reynolds number in Equation 39 is expected to be raised to a higher power than 1/2 for gravel and cobble streambeds.

Scope of Artificial Stream Experiments

The goal of the artificial stream experiments is to determine the values of Constant and m in Equation 25,

$$Km = \text{Constant } Re^{m} \, Sc^{1/3} \, \frac{D}{Dp} \tag{25}$$

in which Re is the shear Reynolds number, that enables Equation 25 to describe the apparent, overall mass transfer coefficients for gravel and cobble streambeds. Since the overall mass transfer coefficients will be defined in terms of shear Reynolds number, the resulting equations should be applicable to wide range of natural streams that have gravel and cobble streambeds similar to those found in the artificial stream.

Specifically, experiments were performed in an artificial stream reactor to assess the short- and long-term effects of stream velocity on contaminant removal rates by streambed biofilms. Heterotrophic biofilms were grown on either cobble (mean diameter of 6.0 cm) or gravel (mean diameter of 1.6 cm) streambeds. The rate at which streambed biofilms removed chemical oxygen demand (COD) from the artificial stream was determined under batch conditions. The source of the COD was a glucose solution. The short-term mass-transport-related effects of stream velocity on contaminant removal rates were assessed by acclimating the biofilm community to a specific stream velocity and observing how contaminant removal rates varied as the stream velocity was altered, i.e., the stream velocity at which the batch tests were conducted. Because the batch tests were of short duration, streambed biofilm biomass did not change from the amount accumulated during streambed acclimation. Therefore, the sensitivity of COD removal rates to changes in stream velocity was attributed solely to

changes in the overall mass transfer coefficient. When the amount of streambed surface area available for biofilm colonization was set equal to the geometric surface area, the values of Constant and m in Equation 25 were calculated. The resulting equations described the overall mass transfer coefficients for the gravel and cobble streambeds as a function of shear velocity.

Experiments also were performed on the cobble streambed to observe how the long-term exposure of a streambed biofilm community to a new stream velocity altered biofilm biomass. For this purpose, batch tests were conducted at different acclimation velocities. The sensitivity of COD removal rates to changes in the acclimation velocity were a function of the overall mass transfer coefficient and streambed biofilm biomass. Because the variation in the overall mass transfer coefficient with stream velocity was defined by the short-term experiments (i.e., Equation 25), the long-term effect of stream velocity on biofilm biomass could be determined. Changes in cobble streambed biofilm biomass with acclimation velocity were expressed in terms of surface area available for colonization, such that the deviation of available surface area from the geometric value -- the value at which Equation 25 was defined -- indicated an increase or decrease in streambed biofilm biomass.

An accidental desiccation of the cobble streambed presented the opportunity to test the predictive capacity of the equations that define the short- and long-term effects of stream velocity on contaminant removal rates. The recovering cobble streambed was exposed to a previously untested acclimation velocity. Upon reaching steady-state conditions, a series of short term batch tests were conducted on the resulting biofilm community to

assess the sensitivity of COD removal rates to changes in stream velocity. A comparison was made between the experimentally observed removal rates and the removal rates predicted by the previously developed equations that described changes in the overall mass transfer coefficient and changes in biofilm biomass with stream velocity. Close agreement between the observed and predicted removal rates was considered to indicate that the equations successfully captured the phenomena which control the rate of contaminant removal by cobble streambed biofilms.

Materials and Methods

Description of Artificial Stream

The experimental determination of mass transfer coefficients for gravel and cobble streambeds was performed in a 10-meter long Frigid-Units (TM) fish raceway. The fish raceway was modified such that water was recycled through a system of centrifugal pumps and pipes. The use of return pipes and associated pumps allowed water velocities to be much higher in the artificial stream than would have been allowed with the traditional false bottom recycle. A schematic of the flow chart for the artificial stream is shown on Figure 4.

Velocities in the artificial stream were controlled by varying stream discharge either by altering the number of recycle pumps in operation or by adjusting discharge for individual pumps via valves on each pump's discharge pipe. There were four separate recycle pumps: one 1-HP Gorman-Rupp centrifugal pump with a 5.1 cm (2 inch) I.D. recycle pipe, two 1/3-HP Cole-Palmer high capacity centrifugal pumps with 2.5 cm (1 inch) I. D.

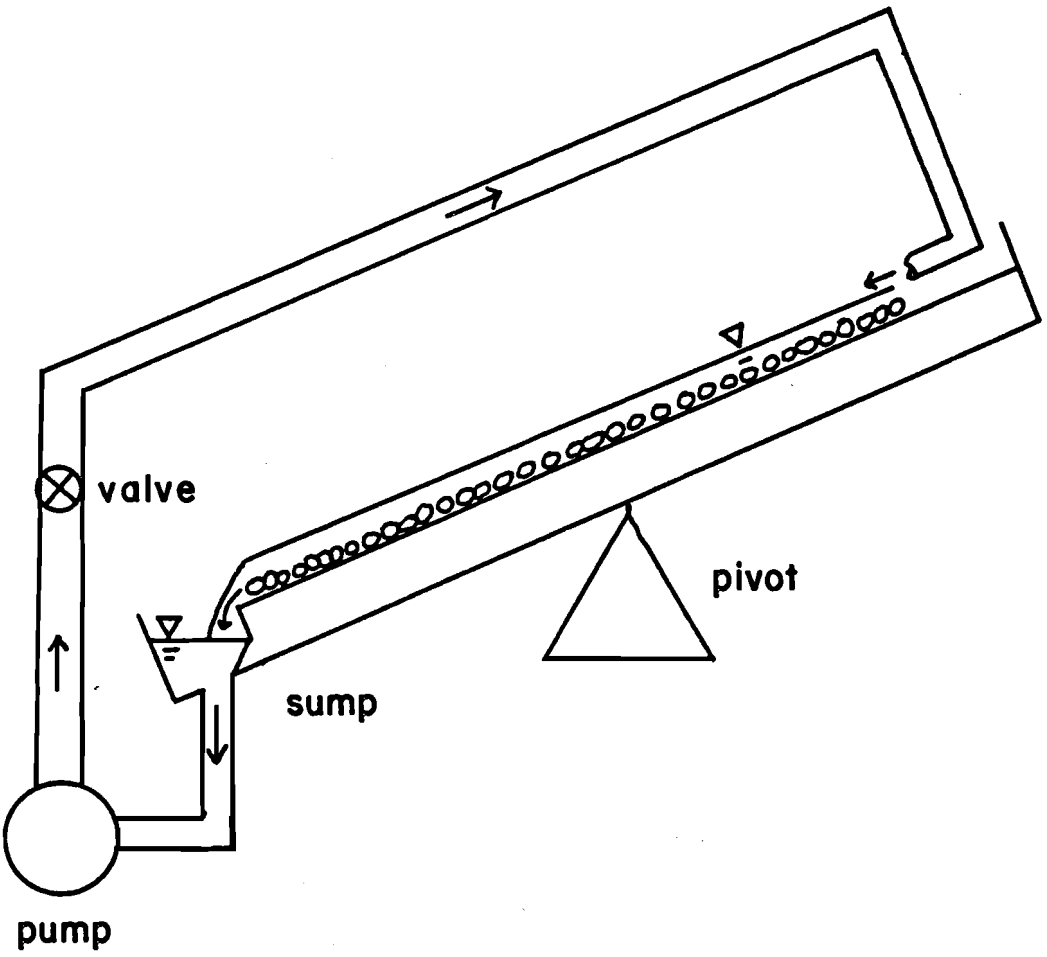

Figure 4. Schematic of Artificial Stream

recycle pipes, and one 1/3-HP Cole-Palmer high capacity centrifugal pump which recycled water through a 3.8 cm (1.5 inch) I.D. pipe.

Two different sizes of sieved calcareous rock were used to represent two types of natural streambeds. Gravel and cobble streambeds were represented by rocks with a mean diameter of 1.6 cm and of 6.0 cm, respectively. The rocks were placed in a lined rectangular channel that was 27.5 cm wide and between 690 and 760 cm long. Streambed slope was 2.9 percent. Both the gravel and cobble streambeds were 1.5 to 2 layers of rock thick. Sufficient water flowed over the gravel and cobble streambeds to completely cover all of the rocks.

Velocity Determinations

Average stream velocities in the artificial stream were determined from visually observed dye travel time, i.e. time needed for a slug of potassium permanganate to travel the length of the streambed. The length of the streambed divided by the dye travel time was equal to the average stream velocity. The principal advantage of the dye method was that the impact of lateral and vertical velocity profiles on average stream velocity was incorporated into the dye velocity measurement. Therefore, for each determination of average stream velocity, only one dye velocity measurement was required, compared to the several velocity probe measurements required to integrate stream profiles into an average velocity.

The ability of the dye travel time method to determine average stream velocities was tested by comparing its results to those obtained by a NaCl tracer method at several different pump settings. Sample gravel and cobble stream velocities were determined by step-feed adding NaCl to the head of

the artificial stream and observing NaCl travel time with a conductivity meter at the end of the streambed. Procedures for the NaCl tracer studies are presented in the next section.

Shear velocities were calculated from that form of the Keulegan equation suitable for use with rough channels (Chow, 1959),

$$U = \frac{V}{6.25 + 5.75 \log(R/kr)} \tag{40}$$

in which U is the shear velocity (cm/sec), V is the average stream velocity (cm/sec), R is the hydraulic radius of the channel (cm), and kr is the roughness height (cm). Bray (1979, 1982) examined high in-bank flows in 67 gravel-lined river reaches and found that when kr was approximated either by the D_{50}, D_{65}, or D_{90} for the streambed particles there was no significant difference in the ability of Equation 40 to describe the relationship between V and U. Thus, in the present study, kr was set equal to Dp and

$$R = \frac{H\ W}{2H + W} \tag{41}$$

in which H is the depth of flowing water in the artificial stream channel (cm) and W was channel width (27.5 cm). For the gravel streambed, H was the depth of water above the gravel bed. While for the cobble streambed, H was the depth of water above the channel bottom.

Chow (1959) considered a channel to be rough when the velocity distribution depended on the form and size of the streambed projections. A rough channel surface had roughness elements that were of sufficient magnitude to extend their effects beyond the laminar sublayer and thus

disturbed the water flow in the channel. Mathematically, Chow (1959) defined a surface as being rough when the following is true:

$$kr > \frac{100\ KVIS}{3600\ V} \qquad (42)$$

in which KVIS is the kinematic viscosity of water (cm^2/hr), and V is average stream velocity (cm/sec).

In a strict sense, the artificial stream channel conformed to Chow's definitions of a rough channel. Because of the shallowness of the artificial stream, both the gravel and cobble streambeds determined stream velocity distribution. This was evident by the formation of standing waves even at the slowest of stream velocities. When Dp was substituted into Equation 42 for kr, the relationship was determined to be true for both the gravel and cobble streambeds, i.e., both the gravel and cobble streambeds met the mathematical criterion for a channel being rough. However, the Keulegan equation (Equation 40) and the roughness relationship (Equation 42) were developed from stream channels in which the depth of the flowing water was much greater than streambed particle size. The gravel and cobble artificial streams had water depths only a few times greater than streambed particle diameter, i.e., the artificial stream was much shallower than the streams for which Equations 40 and 42 were originally developed. Thus, the mass transfer equations determined in the artificial stream, which are based on the shear velocity calculated by the Keulegan equation, may not be applicable to every stream channel.

Stream discharges were approximated by constricting the channel width at the end of the streambed and measuring stream velocity in the constriction. The product of the cross-sectional area available for flow at

the constriction and the measured velocity was the stream discharge. Water velocities within the constriction were measured with a Kent Miniflo velocity meter with a 1 cm impeller. Because the water surface elevations were not uniform throughout the length of the constriction, the reported discharges should be viewed only as an index of the actual flow rates within the artificial stream.

Mid-channel vertical stream velocity profiles for the cobble streambed at different stream velocities were developed based on the curve fitting procedure of Debevoise and Fernandez (1984). Data was collected at points in the cobble streambed where interstitial voids allowed the 1 cm diameter velocity probe of a Kent Miniflo velocity meter to be positioned anywhere on a vertical line stretching from the channel bottom to the water surface. The following equation was used to describe the profile data collected at several stream velocities as a continuous curve (Debevoise and Fernandez, 1984):

$$V = Y'^{\,b*Y'+c}\ \ell n(Y') \tag{43}$$

in which a, b, and c are empirically determined constants for each stream velocity, and V is the water velocity at the dimensionless depth Y'. The Y' parameter was defined by

$$Y' = 1 - \frac{Y}{H} \tag{44}$$

in which Y is distance above the channel bottom (cm) and H is the total water depth (cm). The values of a, b, and c for each set of profile data were obtained from a multiple regression performed on a linearized form of

Equation 43. The matrix formed by the multiple regression was solved by the Crout algorithm outlined in Pinder and Gray (1977).

Tracer Studies

Tracer studies were performed on the gravel and cobble streambeds at specific stream velocities to determine the time required for batch additions of dissolved chemicals to be uniformly distributed throughout the artificial stream. Such tests were important because the ability of streambed biofilms to remove glucose-derived COD was determined under batch conditions, and the analysis of the COD batch experiments assumed that COD was uniformly mixed.

The tracer studies were conducted under the same time and physical constraints as were the COD batch tests. The tracer (200 grams of NaCl in 9 liters of water) was added at the rates at which the glucose-derived COD was added to the stream during the COD batch tests, i.e., 30 to 120 seconds to add the 9 liters of solution. NaCl concentrations were monitored by a Yellow Springs conductivity probe located at the end of the streambed just before the stream water fell into the sump. This location was comparable to where the water samples for the COD batch tests were collected.

Tracer studies were also conducted to see if any vertical concentration gradients existed in the cobble streambed. These studies were conducted as above, but with two conductivity probes. One probe was located at the end of the streambed, as above, while the second probe was buried at the bottom of the cobble streambed midway down the streambed. The conductivity peaks for the two probes should be out of phase by the time required for stream water to travel one-half of length of the streambed. However, if the

magnitude to the two peaks should be comparable, then such data would suggest that despite the vertical velocity profile there is no vertical concentration gradient within the cobble streambed.

Growth of Streambed Biofilm Community

The artificial stream was initially inoculated with microorganisms found in well water that was pumped from a 46-meter deep well in Urbana. The well water also functioned as the nutrient media for the streambed biofilms. The well water was characterized as being moderately hard with 3.5 to 4.0 mg/ℓ of total organic carbon (TOC) (Randtke and Jepson, 1981). The other major constituents of the well water are presented on Table 1.

The artificial stream was covered and kept in a dark room to prevent the growth of phototrophic microorganisms. When streambed biofilms were being acclimated to a specific stream velocity, each day 50 liters of the existing artificial stream water was replaced with fresh well water to maintain nutrient concentrations and to reduce any existing suspended populations of microorganisms. The volume of water being recycled in the stream ranged from 90 to 200 liters. An acidified (pH=3) glucose solution of 75 gm COD/1 was added to the artificial stream at the rate of 0.75 liters per hour -- a rate that was approximately equal to the rate of water lost due to evaporation -- to be used as a carbon source by the streambed biofilms. With stream water being recycled at flows of at least 3050 liters per hour, recycle ratios during biofilm acclimation exceeded 4000. Therefore, during biofilm growth, the artificial stream approximated a completely-mixed reactor, which meant that physical biofilm characteristics could be assumed to be uniform over the length of the streambed.

Table 1

Major Inorganic Constituents of Well Water
(from Randtke and Jepsen, 1981)

Constituent	Concentration (mg/ℓ)
iron	1.1
manganese	0
calcium	59.6
magnesium	23.7
ammonium	1.1
silica	19.6
fluoride	0.3
boron	1.0
chloride	0
nitrate	1.5
sulfate	1.2
alkalinity (as $CaCO_3$)	324.0
sodium	37.0
phosphate	0.03
potassium	1.0

Streambed biofilm communities were acclimated to stream velocities that had sufficient flow to completely cover all rock surfaces. Most of the research effort involved the cobble streambed, with some experiments being performed on the gravel streambed for comparative purposes. The cobble streambed biofilm community was acclimated to stream velocities of 9.5, 10.9, 13.2, 16.2, 16.6, 17.8, and 18.7 cm/sec. For the gravel streambed, the biofilm community was acclimated to a single stream velocity of 17.7 cm/sec. The biofilm community was considered to be acclimated to a stream velocity when the ability of the streambed to remove COD was constant over a two week period.

Determining COD Removal Ability of Streambed Biofilms

The rate at which a streambed biofilm community removed contaminants from the stream's water column was determined by means of batch tests. A batch test consisted of three steps. First, the streambed biofilms were starved for 12 hours by stopping the addition of the 75-mg COD/1 feed solution. This was done to reduce background COD concentrations in the stream. Second, the COD concentration in the artificial stream was rapidly increased to between 30 and 45 mg COD/1 by adding 9 liters of concentrated glucose solution; the actual concentration of this feed solution varied with the volume of water being recycled in the artificial stream. The nine liters of glucose solution was added at a uniform rate for 30 to 120 seconds. The time at which the entire 9 liters of the feed solution had been added to the artificial stream corresponded to $t = 0$. Third, the rate of COD removal from the waters of the artificial stream was determined by measuring COD concentrations in stream water samples that were collected at

regular time intervals. The stream water samples were collected as the stream water fell into the artificial stream's sump and not from the sump itself (Figure 4). The first stream water sample was collected after the time required for the COD concentrations to become uniform throughout the artificial stream--as determined from the tracer studies. The water samples were filtered through a 0.45-μm membrane filter. COD analysis of the water samples followed the low-level procedure described in Standard Methods (APHS, 1978).

The initial rate at which streambed biofilms removed COD from the artificial stream followed first-order kinetics with respect to COD concentrations, namely

$$\frac{dC}{dt} = - \frac{Kf\ P\ Ls}{VOL} C \qquad (45)$$

in which C is COD concentration (mg/ℓ) in the stream water, t is time (hr), Kf is the first-order flux constant (cm/hr), P is the amount of active biofilm surface area per unit streambed length (cm), Ls is the length of the streambed (cm), and VOL is the volume of water being recycled in the artificial stream during the batch test (cm^3). The natural logarithm of C was plotted versus time, giving a straight line with a negative slope of M (hr^{-1}). The absolute value of the slope equalled

$$M = \frac{Kf\ P\ Ls}{VOL} \qquad (46)$$

The specific goal of the batch tests was to determine the value of KfP for each tested stream velocity. By rearranging Equation 46, KfP was calculated from

$$KfP = \frac{M\ VOL}{Ls} \tag{47}$$

The volume of water being recycled in the artificial stream was obtained from the following equation:

$$VOL = \frac{Qf\ Cfd}{M\ C(o)} [1-e^{-Mtf}] \tag{48}$$

in which VOL is the volume of water being recycled (cm^3), Qf is the volumetric rate at which the COD feed is added to the artificial stream (9000 cm^3/tf), tf is the length of time over which the COD feed was added to the stream (hr), Cfd is the COD concentration of the feed (mg/ℓ), M is the observed degradation slope (hr^{-1}), and C(o) is the calculated stream COD concentration (mg/ℓ) when COD addition to the stream had just stopped, which corresponds to t = 0 for batch test. C(o) is defined by the following equation:

$$C(o) = e^{Y\text{-inter}} \tag{49}$$

in which Y-inter is the Y-intercept of the straight line produced on a ln C versus t plot of the decay of stream COD concentrations during the batch test. Therefore, Equation 48 assumed that the COD feed was added to a completely mixed reactor at a uniform rate (Qf) for a known length of time (tf) and that some stream COD was removed by the streambed biofilms during feed additions to the stream.

The value of KfP calculated by Equation 47 included, in some cases, contributions from biofilms located on the inner walls of the recycle pipes. During biofilm acclimation to a stream velocity, biofilms colonized the recycle pipes. Fortunately, the recycle pump and pipe that were used to

acclimate the gravel streambed biofilms were not needed to supply flow for the gravel batch tests. Therefore, the determination of the KfP values for the gravel streambed needed no corrections for biofilms in the pipes. However, the recycle pumps and pipes used to acclimate the cobble streambed biofilms to specific average stream velocities had to be operated during the batch tests. Thus, the observed removal slopes for cobble batch tests were corrected by subtracting the removal slope due to biofilms located in the pipes,

$$M(s) = M - M(p) \tag{50}$$

in which M(s) is the removal slope due only to the streambed biofilms (hr^{-1}), M is the experimentally observed removal slope (hr^{-1}) due to both streambed and pipe biofilms, and M(p) is the removal slope due to biofilms located within the recycle pipes (hr^{-1}). Assuming that the pipe biofilms were deep with respect to glucose (Rittmann and McCarty, 1978), the value of M(p) was estimated by

$$M(p) = \frac{D\ Df\ PHI}{D + Lp\ Df\ PHI}\ \frac{Ap}{VOL} \tag{51}$$

in which Ap is the total amount of pipe surface area that can be colonized by biofilms (cm^2) and Lp is the thickness of the effective diffusion layer surrounding the pipe biofilms (cm). The value of Lp was determined by equations described in the next section. Thus, for the cobble streambed batch tests, M(s) instead of M was used to calculate KfP in Equation 47.

Determination of Biofilm Kinetics Parameters

The diffusion coefficient of glucose in water was determined from the Wilke-Chang expression (Perry and Green, 1984) and was estimated to be 0.025 cm^2/hr at 20°C. Because water temperatures within the artificial stream were seldom 20 degrees, COD diffusivities were corrected for temperature by the following equation (Rittmann, et. al., 1983):

$$D = 0.025 * 1.043^{(T-20)} \tag{52}$$

in which D is the diffusivity of glucose in water (cm^2/hr) at temperature of T (C) (Rittmann, et. al., 1983). The diffusivity of the glucose within the biofilm (Df) was assumed to be 0.8 times D (Williamson and McCarty, 1976b).

Based on data presented in Streeter and Wylie (1975), the variation in the kinematic viscosity of water with temperature (between 15 to 30°C) was described by

$$KVIS = 36.25 * 0.977^{(T-20)} \tag{53}$$

in which KVIS is the kinematic viscosity of water (cm^2/hr) at the water temperature T, and 36.25 cm^2/hr is the kinematic viscosity of water at 20°C.

The value of the characteristic biofilm kinetic parameter also changed with temperature,

$$PHI = \left[\frac{K\ Xf}{Df}\right]^{1/2} \tag{54}$$

in which PHI is the characteristic biofilm kinetic parameter (cm^{-1}). The value of K was assumed to double for every 10°C increase in temperature; thus (Rittmann, et. al., 1983)

$$K = K(20) * 1.072^{(T-20)} \quad (55)$$

in which K is the mixed second-order rate constant at a water temperature of T, and K(20) is the mixed second-order rate constant at 20°C. Xf was considered insensitive to changes in temperature. Based on the above equations, the value of PHI at the water temperature T was obtained from

$$PHI = PHI(20)\ sqrt[1.0278^{(T-20)}] \quad (56)$$

in which PHI(20) is the value of the characteristic biofilm kinetic parameter at 20°C.

PHI(20) was obtained from the removal slope due to pipe biofilms [M(p)], because the surface area and mass transfer coefficient were calculable for the recycle pipe. During gravel streambed acclimations, the recycle pipe became covered with biofilm. The pipe biofilm was assumed to have the same bacterial composition and the same PHI value as the streambed biofilm community.

The removal slopes of two batch tests were needed to calculate M(p). The first batch test determined M by routing water over the gravel streambed and through biofilm-colonized recycle pipes. The second batch test determined M(s) by recycling water through clean pipes after the water flowed over the gravel streambed. M(p) was calculated from

$$M(p) = M - M(s). \quad (52)$$

After M(p) was calculated, the value of PHI was obtained from

$$PHI = \frac{D\ M(p)\ VOL}{D\ Df\ Ap - Lp\ Df\ M(p)\ VOL} \quad (58)$$

in which Ap is total amount of pipe surface area that can be colonized by biofilms (cm^2) and Lp is the thickness of the effective diffusion layer surrounding the pipe biofilms (cm). Equation 56 was used to calculate PHI(20) from PHI. Ap was equal to the wetted perimeter of the recycle pipe times its length. Lp was calculated from (Bird, et. al., 1960)

$$Lp = \frac{2\ D\ Sc^{2/3}}{f\ Vp} \tag{59}$$

in which f is the friction factor for flow paste the wall of the pipe, Vp is the average water velocity in the pipe (cm/hr) and is equal to stream flow divided by the cross-sectional area of the recycle pipe, and Sc is the Schmidt number. The friction factor was calculated by the Blasius formula (Chow, 1959),

$$f = 0.316\ Re^{-1/4} \tag{60}$$

in which Re is the Reynolds number (Vp DM/KVIS) and DM is the diameter of the pipe. The Blasius formula is considered valid in smooth pipes up to Re values of 100,000 (Bird, et. al., 1960).

However, the presence of biofilms inside of a pipe can increase the pipe's friction factor to values much greater than those predicted by the Blasius formula. Characklis (1973b) reported that the result of biofilms colonizing the inner surface of a 36-inch diameter pipe was a decrease the capacity of the pipe by 23 percent, which corresponded to a 73 percent increase in the friction factor (f).

Because the Blasius formula probably underestimated the value of f for the recycle pipe, the determination of PHI based on Blasius value of f

probably overestimated the value of PHI for the pipe biofilms. The sensitivity of PHI to changes in f was determined with parameters representive of the artificial stream system, (Figure 5). The Blasius value of f for the recycle pipe was approximately 0.025. If the value of f were to increase by 75 percent, due to biofilm growth on the recycle pipe surfaces, the value of PHI determined by the above method (f = 0.025) would overestimate the actual PHI (f = 0.044) by only 5 percent. Therefore, while biofilm growth in the recycle pipe probably significantly increased f above the Blasius value, the effect on the calculated value of PHI was minimal.

Determination of Mass Transfer Coefficients for Streambeds

By assuming a deep biofilm, the KfP term calculated from the removal slope obtained from each batch test was defined by

$$KfP = \frac{D\ Df\ PHI\ P}{D + L\ Df\ PHI} \tag{61}$$

or, since L = D/KM,

$$KfP = \frac{Km\ D\ Df\ PHI\ P}{Km\ D + D\ Df\ PHI} \tag{62}$$

in which Km is defined as the overall mass transfer coefficient representative of the entire streambed (cm/hr). The response of KfP to changes in Km is shown of Figure 6. At low Km values, there is a linear response between an increase in Km and the resulting increase in KfP. At higher Km values, KfP becomes incresingly insensitive to changes in Km. No matter how great Km, the maximum obtainable value of KfP is DfPHIP. Therefore, better information is obtained about Km from batch tests

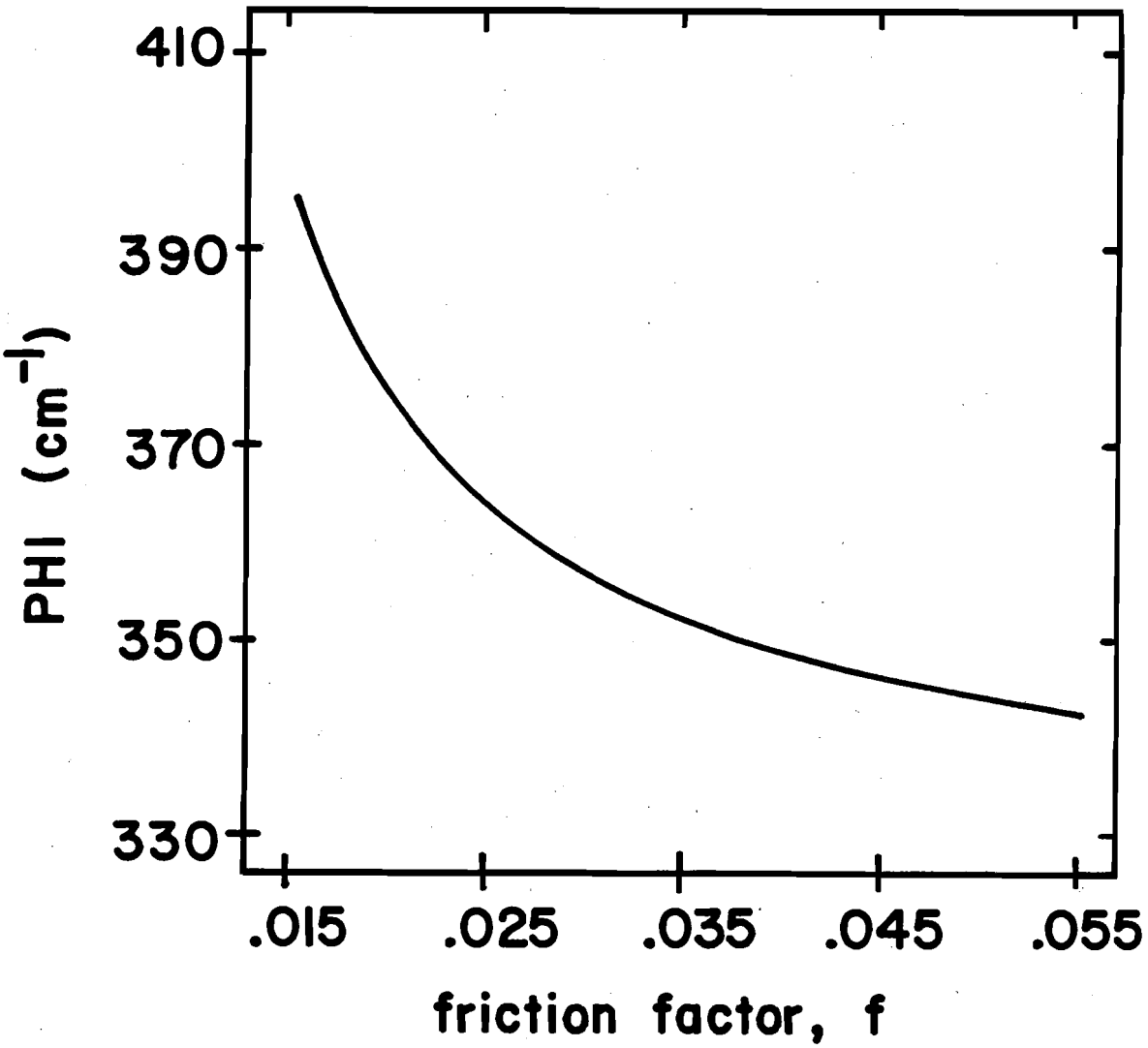

Figure 5. Sensitivity of Calculated PHI Values to Changes in the Pipe Friction Factor (f). The following parameters were assumed in the development of the graph: T = 20°C, M(p) = 0.8 hr^{-1}, Ap = 123000 cm^2, Vp = 220 cm/sec, and VOL = 100 liters.

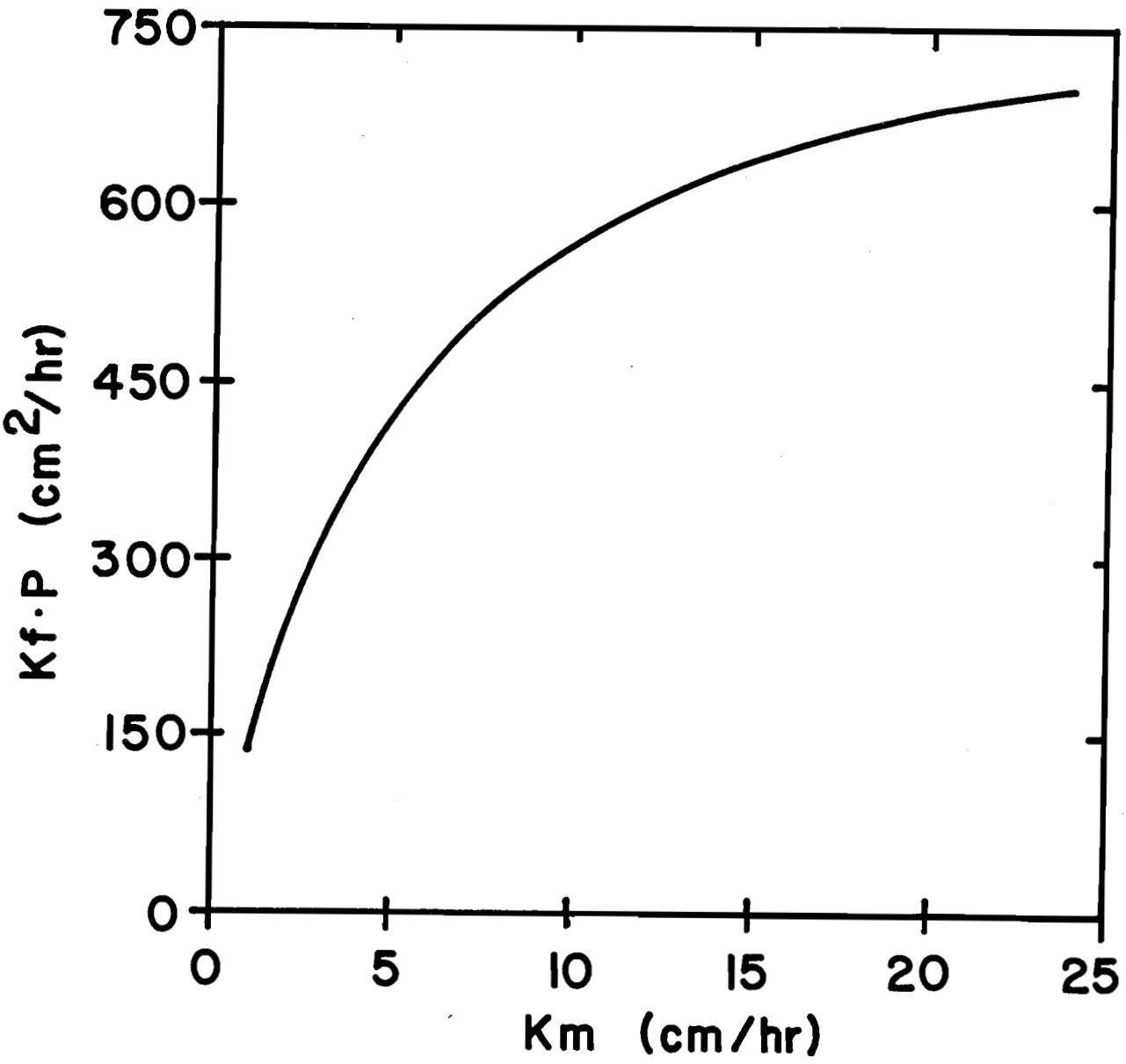

Figure 6. Response of KfP to Changes in Km. The following parameters were assumed in the development of the graph: T = 20°C, PHI = 250 cm^{-1}, P/W = 6.2, W = 27.5, and D = 0,025 cm^2/hr.

conducted under low mass transport regimes (slow stream velocities) than under high mass transport regimes (fast stream velocities).

Unfortunately, there is no unique set of Km and P values that satisfies Equation 62 for each experimentally determined value of KfP. This problem was solved by fixing the value of P for each streambed equal to the geometric surface area available for biofilm colonization within the stream channel. The cobble streambed had geometric P/W value--P divided by the width of the stream channel (W = 27.5 cm)--of 6.2, which included the surface area of the plastic liner that was wet during biofilm acclimation. The gravel streambed's geometric P/W was 7.0, which also included the wetted surface area of the plastic liner. Once P had been set at the geometrically available surface area (P equals geometric P/W times channel width), Km for each experimentally determined value of KfP could be calculated from

$$Km = \frac{Kf\ D\ Df\ PHI}{D\ Df\ PHI - Kf\ D} \tag{63}$$

in which Kf is first-order flux constant representative of the entire streambed (cm/hr) and is equal to the experimentally determined value of KfP (Equation 47) divided by P.

A question arises as the whether the geometric P value is an appropriate measure of actual biofilm surface area in the gravel and cobble streambeds. While the actual amount of active biofilm surface would be impossible to determine, a range of feasible P/W values can be calculated for each batch test and for each series of batch test performed on a streambed acclimated to a constant velocity. The smallest value of P/W that could possibly explain the results of a single COD batch test would be equal to KfP divided by the maximum possible value of Kf. Since the

maximum possible value of Kf for a deep biofilm is equal to DfPHI (kinetic-limited biofilm), the minimum value of P/W can be calculated from

$$P/W(min) = \frac{KfP}{Df\ PHI\ W} \tag{64}$$

in which P/W(min) is the minimum value of P/W that could explain the value of KfP for a single batch test. Likewise, the largest P/W that could possibly explain the results of a batch test would be equal to KfP divided by the smallest possible value of Kf. As Km approaches zero in Equation 62, the value of Kf approaches it minimum value, Km (mass-transport-limited biofilm). Therefore, the maximum possible P/W value that can explain the results of a batch test is

$$P/W(max) = \frac{KfP}{Km\ W} \tag{65}$$

in which P/W(max) is the largest possible value of P/W can explain the KfP value obtained from a single COD batch test. If the slowest rate of mass transfer found in the artificial stream corresponds to Km = 1.0 cm/hr (L = 250 microns at 20°C), the value of P/W(max) can be determined from

$$P/W(max) = \frac{KfP}{W} \tag{66}$$

Because P/W(min) and P/W(max) represent the extreme possible values of active biofilm surface area, actual P/W values probably lie between the two values. Therefore, if the assumed geometric value of P/W lies within the feasible range of P/W(min) to P/W(max) for a batch test (or a series of batch tests), then the geometric P/W value can be considered an appropriate representation of the amount of biofilm surface area active in COD removal

and can be used in determining the overall stream mass transfer coefficient, Km.

Once Km was determined for each stream velocity in a series of batch COD tests, an equation was developed to describe the streambed mass transfer coefficient as a function of the stream shear velocity. A power regression analysis was performed between stream Reynolds number (Re) and the right-hand side of this equation

$$\text{Constant } Re^{m} = \frac{Km\ Dp}{D\ Sc^{1/3}} \tag{66}$$

to determine the values of Constant and m. The above equation is a rearrangement of Equation 25.

$$Km = \text{Constant } Re^{m\ 1/3}\ \frac{D}{Dp} \tag{25}$$

in which Re is shear Reynolds number and is defined as

$$Re = \frac{3600\ U\ Dp}{KVIS} \tag{34}$$

U is the shear velocity (cm/sec) obtained from the Keulegan equation (Equation 40), and Dp is the mean diameter of streambed particles (cm). Values of Constant and m were determined from series of batch tests performed on a gravel streambed acclimated to an average stream velocity of 17.7 cm/sec and a cobble streambed acclimated to 13.2 cm/sec.

Streambed Biofilm Biomass versus Acclimation Velocity

A long-term change in the average stream velocity can be expected to alter the distribution and amount of streambed biofilm biomass. Faster

stream velocities should support more biofilm biomass, at least up to the point where scour effects become overwhelming (Rittmann, 1982a). In this study, changes in the amount of cobble streambed biofilm biomass with acclimation velocity were quantified by back-calculating values of P/W at six different acclimation velocities, i.e., 9.5, 10.9, 13.2, 16.2, 17.8, and 18.7 cm/sec. The P/W value indicative of streambed biofilm biomass at each acclimation velocity was obtained from

$$P/W(acc) = \frac{M(s)\ Ls\ (Km\ D + D\ Df\ PHI)}{W\ VOL\ Km\ D\ Df\ PHI} \qquad (67)$$

in which P/W(acc) is the calculated amount of biofilm surface area per unit channel width active in COD removal at a specific acclimation velocity (dimensionless) and Km is the overall mass transfer coefficient (cm/hr) obtained from Equation 25 with the appropriate values of Constant and m for a cobble streambed.

Thus, the back-calculated P/W values were indices of how streambed biofilm biomass changed with acclimation velocities. For example, a value of P/W(acc) greater than 6.2 for a specific acclimation velocity would indicate that more biofilm biomass was present within the streambed than at an acclimation velocity of 13.2 cm/sec. Conversely, a P/W(acc) value less than 6.2 would indicate less biomass was present at the tested acclimation velocity than at 13.2 cm/sec.

Testing of the Mass Transfer Equation

After the above experiments were performed, a pump failure caused the desiccation of existing cobble streambed biofilms. The system was repaired and the streambed was acclimated to an average stream velocity of 16.6

cm/sec. A series of batch tests was performed on the acclimated streambed to test the ability of the mass transfer equation derived from a cobble streambed acclimated to 13.2 cm/sec to predict the observed KfP values. For this test, the value of P/W used in the prediction of KfP was consistent with the results of the experiments outlined in the previous section. The results of comparing predicted KfP values versus observed KfP values were reported as relative error,

$$\text{Relative Error } (\%) = \frac{100\,[KfP(pred) - KfP(obs)]}{KfP(obs)} \tag{68}$$

in which KfP (pred) is the value of KfP (cm^2/hr) predicted by the mass transfer equation, and KfP(obs) is the experimentally observed value of KfP (cm^2/hr) for the cobble streambed. Small relative errors would indicate that the mass transfer equation and the P/W relationship captured both the short- and long-term impacts stream velocity has on the rates at which cobble streambed biofilm communities remove stream contaminants.

Results of Artificial Stream Experiments

Hydraulic Characteristics of Gravel and Cobble Streambeds

A comparison between stream velocities determined by the dye method and the NaCl step-feed method for the gravel and cobble streambeds is shown on Figure 7. The good agreement between the stream velocities obtained from the two methods indicated that the dye method was a valid way of determining stream velocities in the artificial stream.

For predicting shear velocities at various average stream velocities, it was desired to describe the depth of flowing water as a function of average stream velocity. In the gravel streambed, the relationship

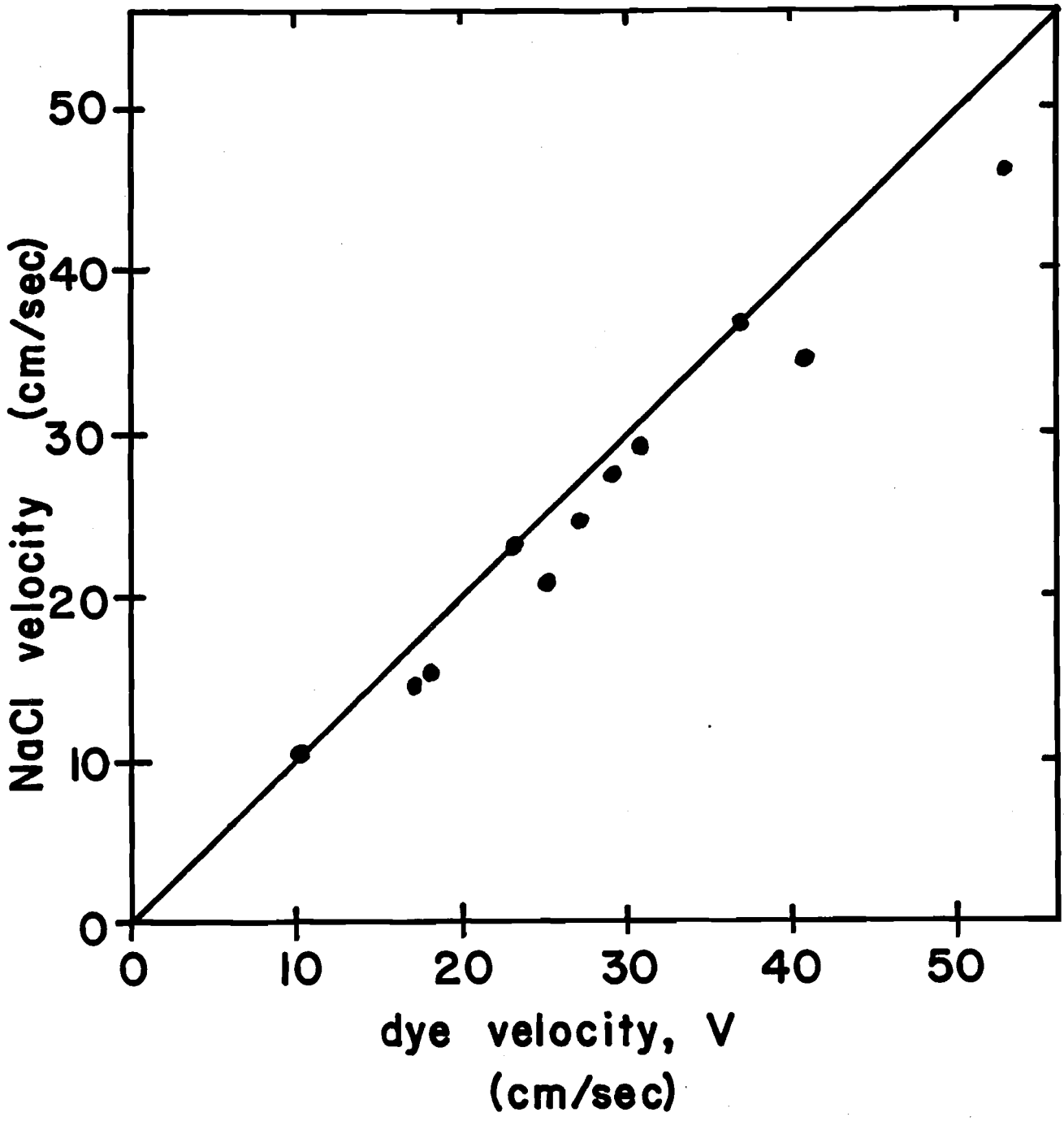

Figure 7. Comparison of the Stream Velocities Determined by the Dye Method and the NaCl Step-Feed Method for the Gravel and Cobble Streambeds.

between stream depth and average stream velocity (shown on Figure 8) was defined by

$$H = 0.43\ V^{0.65} \tag{69}$$

in which H is the water depth above the gravel streambed (cm) and V is the average stream velocity (cm/sec). In the cobble streambed, the relationship between depth of flowing water and stream velocity (shown on Figure 9) was defined by

$$H = 4.0\ V^{0.30} \tag{70}$$

in which H is the depth of water above the channel bottom (cm).

The method of Debevoise and Fernandex (1984) was used to generate continuous vertical velocity profiles in the cobble streambed. The empirical constants a, b, and c, listed on Table 2, were used to develop vertical velocity profiles found in the cobble streambed for different average stream velocities. Representative velocity profiles are shown on Figures 10-13. The mathematically generated velocity profiles accurately portrayed the velocity measurements taken in the upper portions of the streambed. Because the water velocities deep within the cobble streambed--less than 3.5 cm above the channel bottom--were usually less than the detection limit for the Kent Miniflo velocity meter (about 5 cm/sec), the shape of the generated velocity measurements taken at 3.6 cm and above.

Because the Kent Miniflo velocity probe only measured velocities perpendicular to the plane of its impeller, the probe--due to its position--was only measuring that component of water velocity traveling down and parallel to the stream channel slope. Due to the orientation of the

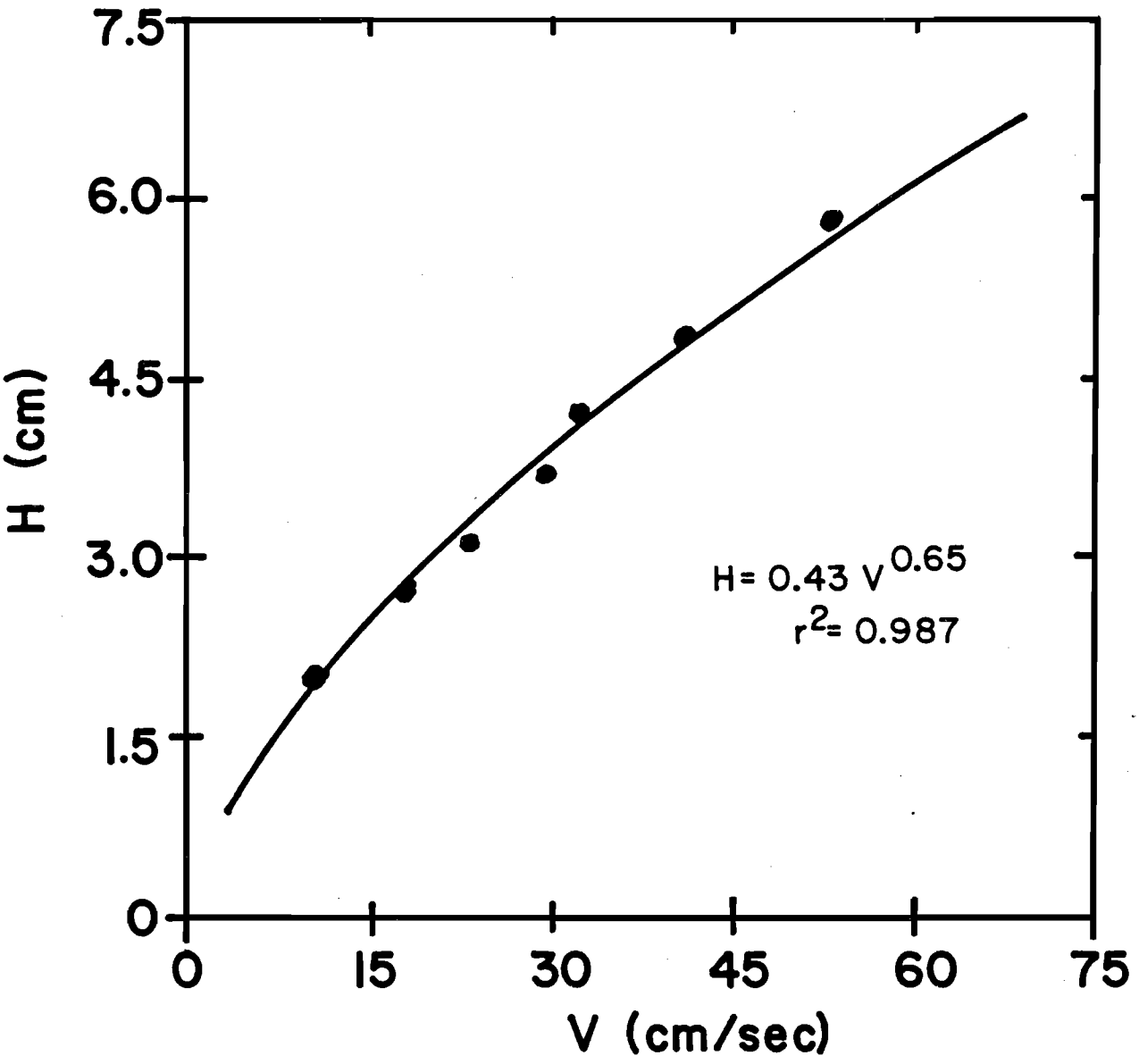

Figure 8. Depth of Flowing Water (H) versus Stream Velocity (V) in the Gravel Streambed.

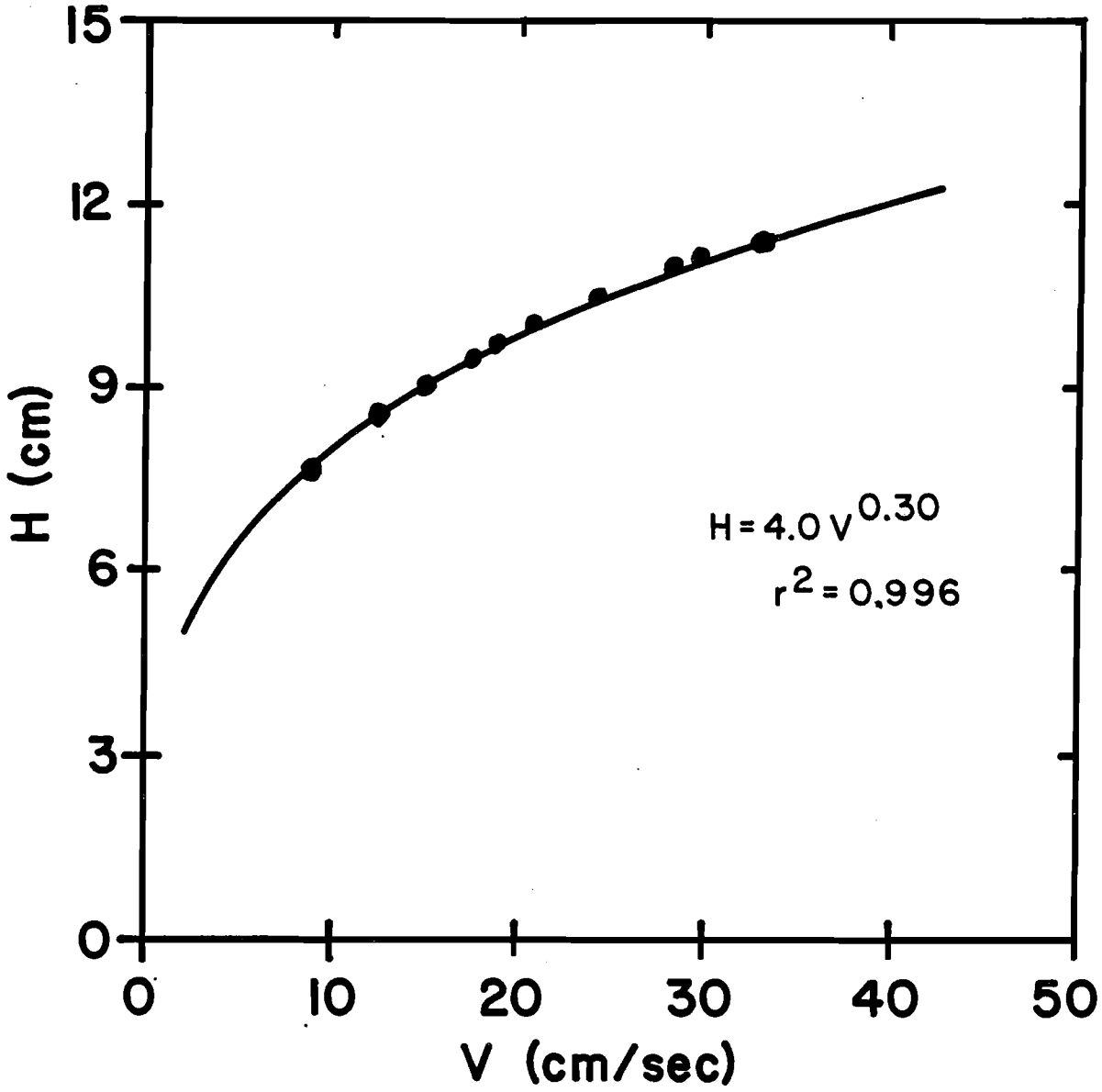

Figure 9. Depth of Flowing Water (H) versus Stream Velocity (V) in the Cobble Streambed.

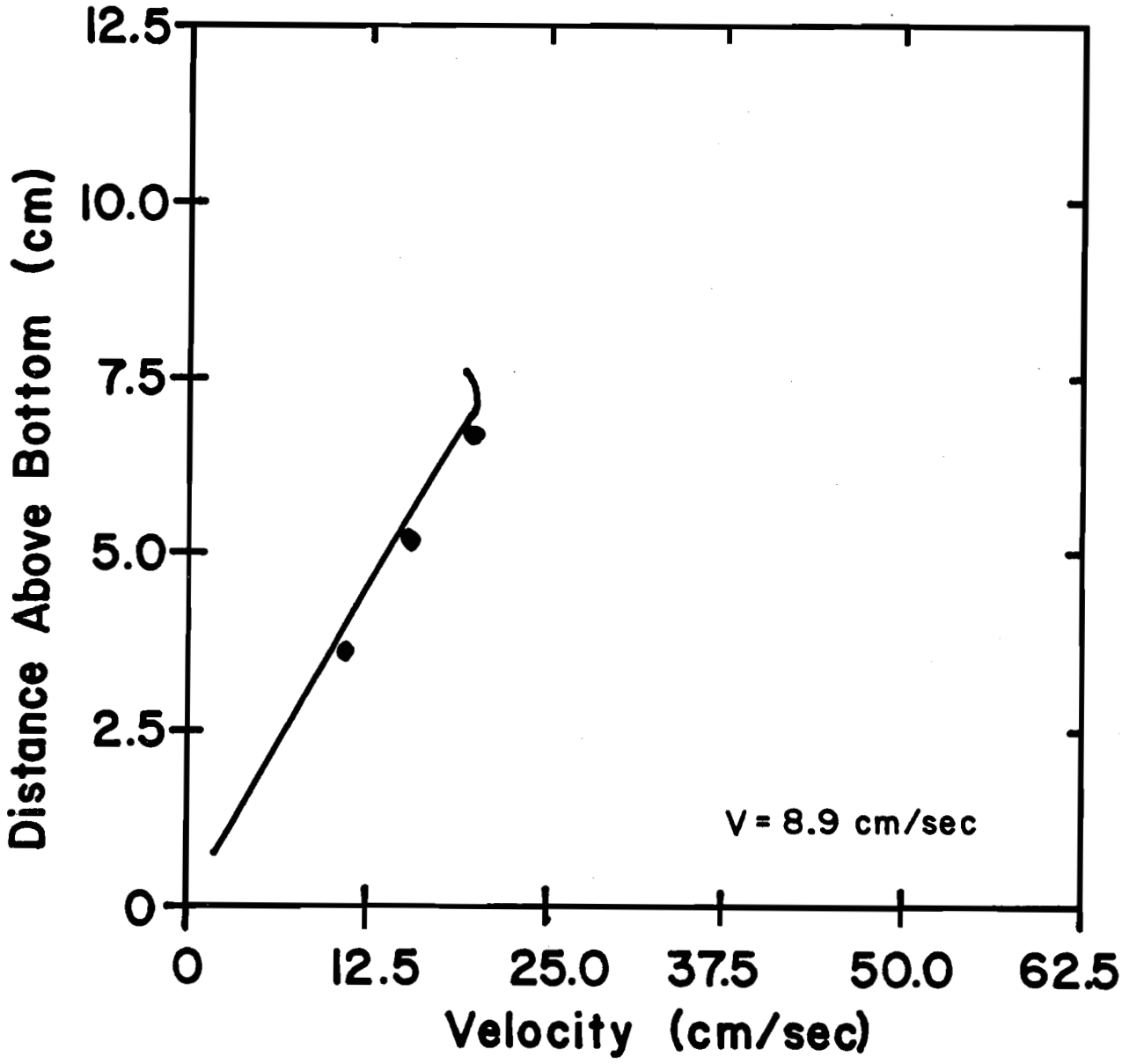

Figure 10. Velocity Profile in the Cobble Streambed at a Stream Velocity of 8.9 cm/sec.

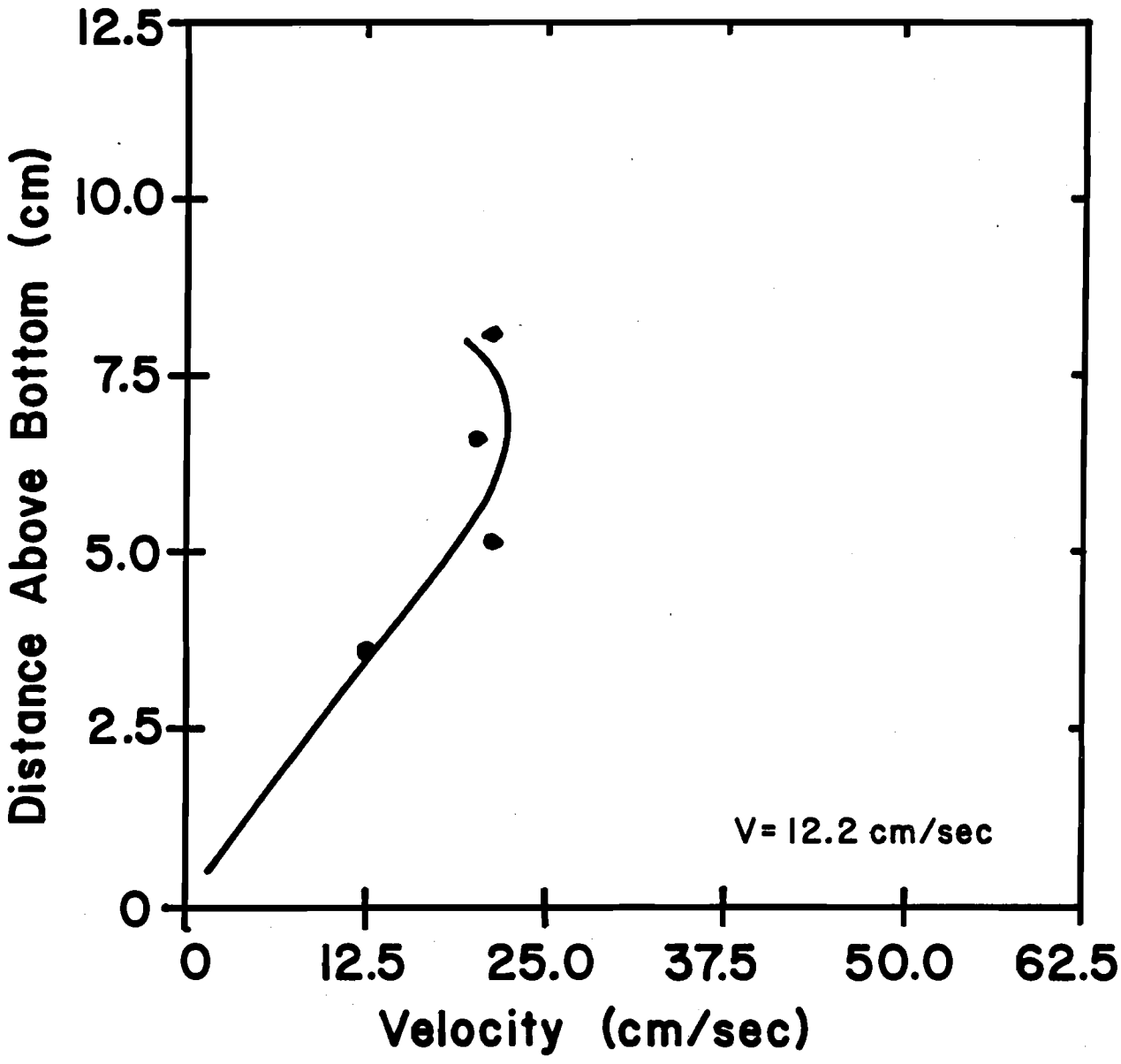

Figure 11. Velocity Profile in the Cobble Streambed at a Stream Velocity of 12.2 cm/sec.

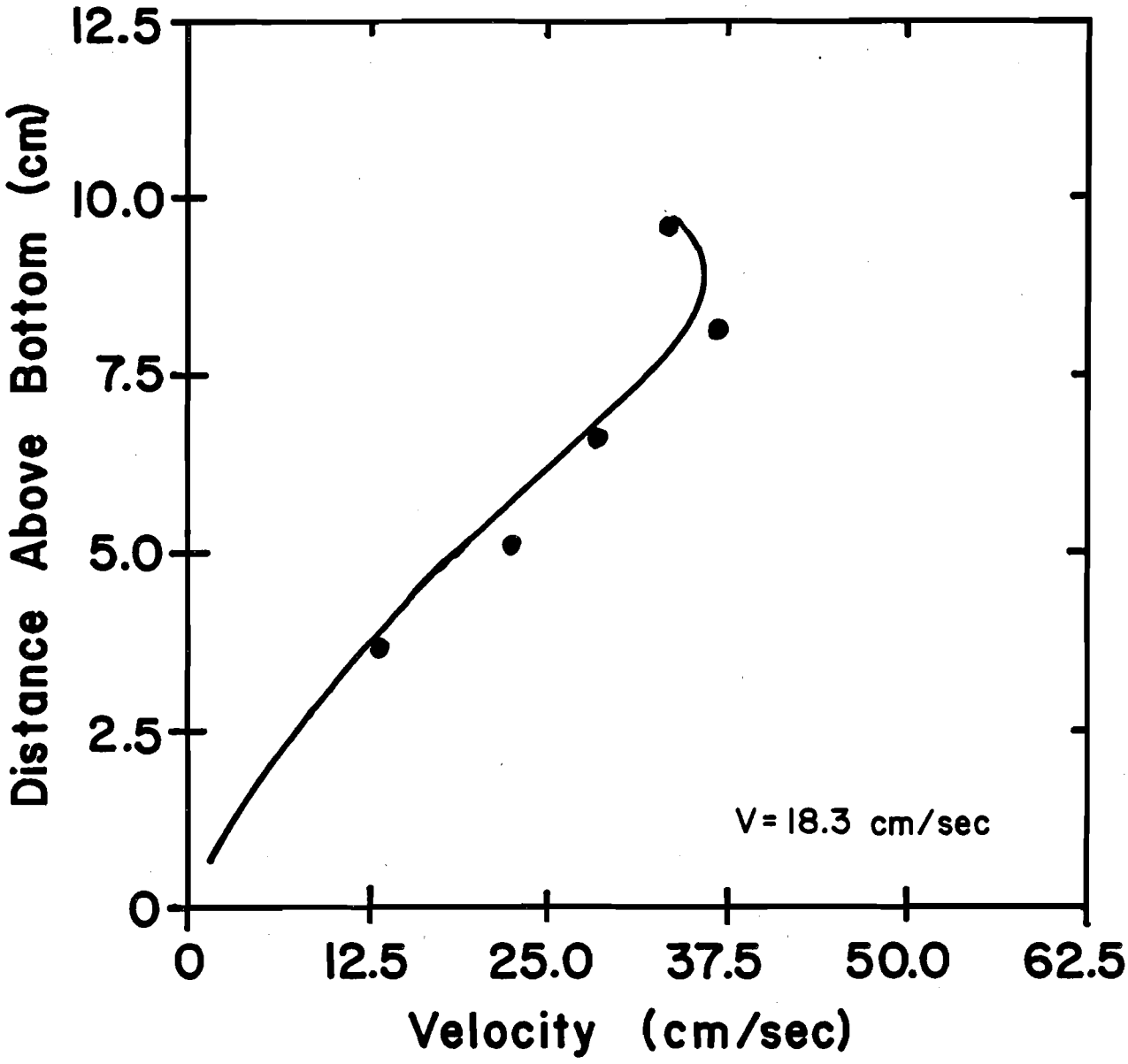

Figure 12. Velocity Profile in the Cobble Streambed at a Stream Velocity of 18.3 cm/sec.

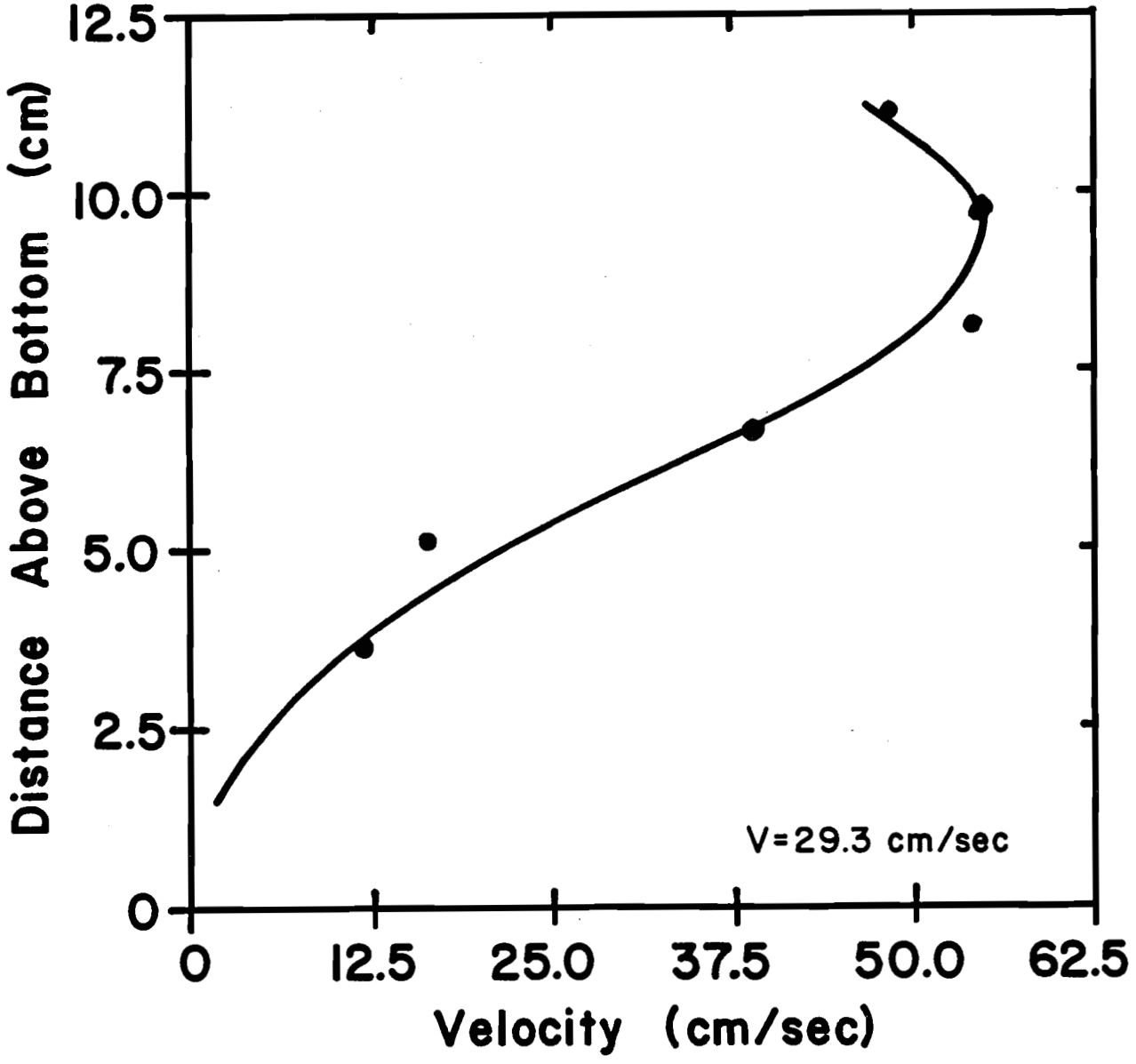

Figure 13. Velocity Profile in the Cobble Streambed at a Stream Velocity of 29.3 cm/sec.

Table 2

Empirical Constants for the Generation of Vertical Velocity Profiles by the Debevoise-Fernandez Method

Stream Velocity (cm/sec)	Constant a	Constant b	Constant c
8.9	23.911	0.4158	0.4040
12.2	24.853	-0.7097	0.4933
18.3	24.434	-0.8786	0.2837
29.3	10.468	-3.8063	0.0374

interstitial voids within the streambed, significant portions of interstitial flow could have been travelling in a direction different from the one the probe was best able to measure. Thus, the interstitial water velocities within the cobble streambed--the water velocities to which the streambed biofilms were exposed--could have been substantially greater than those indicated by the mathematically generated velocity profiles.

When several velocity profiles obtained from the cobble streambed are plotted on the same graph (Figure 14), the effect of average stream velocity on the vertical stream profile is clear. At low stream discharges, a slight increase in discharge (average stream velocities increased from 8.9 to 12.2 cm/sec) tended to increase water velocity throughout the entire depth of the cobble streambed. Above this range, increases in average stream velocity tended to sharply increase the velocities of water located above the streambed and only slightly increased velocities in the upper layers of the streambed. However, velocities deep within the streambed remained relatively constant.

Figure 14 also indicates that as stream flow increased over the cobble streambed, the velocity gradient (change in velocity with increased distance into the streambed) across the upper layers of the cobble streambed increased. The increased level of turbulence associated with the increased velocity gradient at higher stream flows probably increased the rate at which material was transported from the water column to the interstitial voids found in the cobble streambed. Therefore, despite a greater fraction of flow traveling over the top of the cobble streambed at higher stream discharges, the difference in contaminant concentrations between the water column and the interstitial voids may not be greater at high flow, because

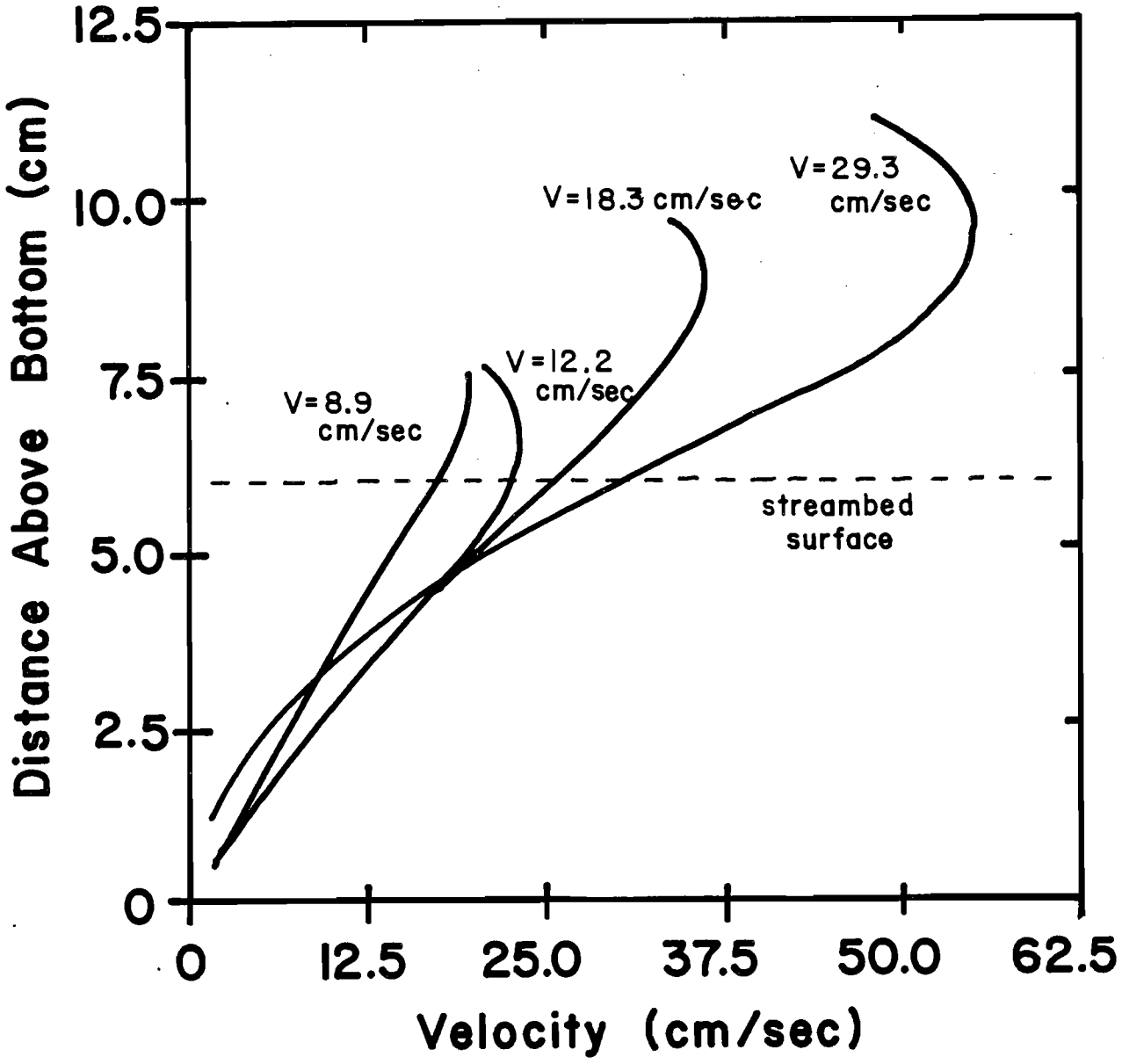

Figure 14. Composite of Four Velocity Profiles.

of the high mass transfer rates into the upper streambed boundary.

The NaCl tracer studies performed on the cobble stream suggest that there was no difference in bulk concentrations between the water column and the interstitial voids for a conservative material. Figure 15 shows the results of the NaCl tracer studies for the cobble streambed subjected to an average stream velocity of 30.5 cm/sec. The graph displays the conductivities obtained from two probes; the first probe was positioned at the end of the streambed prior to the sump and the second probe was buried in the cobble streambed at a point slightly less than one-half the distance down the stream channel. Thus, the first probe measured conductivities for the water column and the second probe measured conductivities 1 cm above the bottom of the stream channel. The degree that the two types of NaCl tracer curves were out of phase equalled the time required for a parcel of water to travel half the length of the streambed. Because the magnitude of the conductivity peaks for the water column and streambed probes were the same, the bulk concentrations of NaCl at the two locations were the same regardless of average stream velocities. Therefore, the rate of mixing of water from the water column to the streambed voids was rapid.

The NaCl tracer experiments for the cobble streambed and for the gravel streambed (Figure 16) indicated that NaCl was uniformly mixed over the length of the artificial streambed by the time a parcel of water had recycled three times after the NaCl feed had stopped. Thus, COD samples collected during a batch test were collected later than the time required for water to recycle three times in the artificial stream.

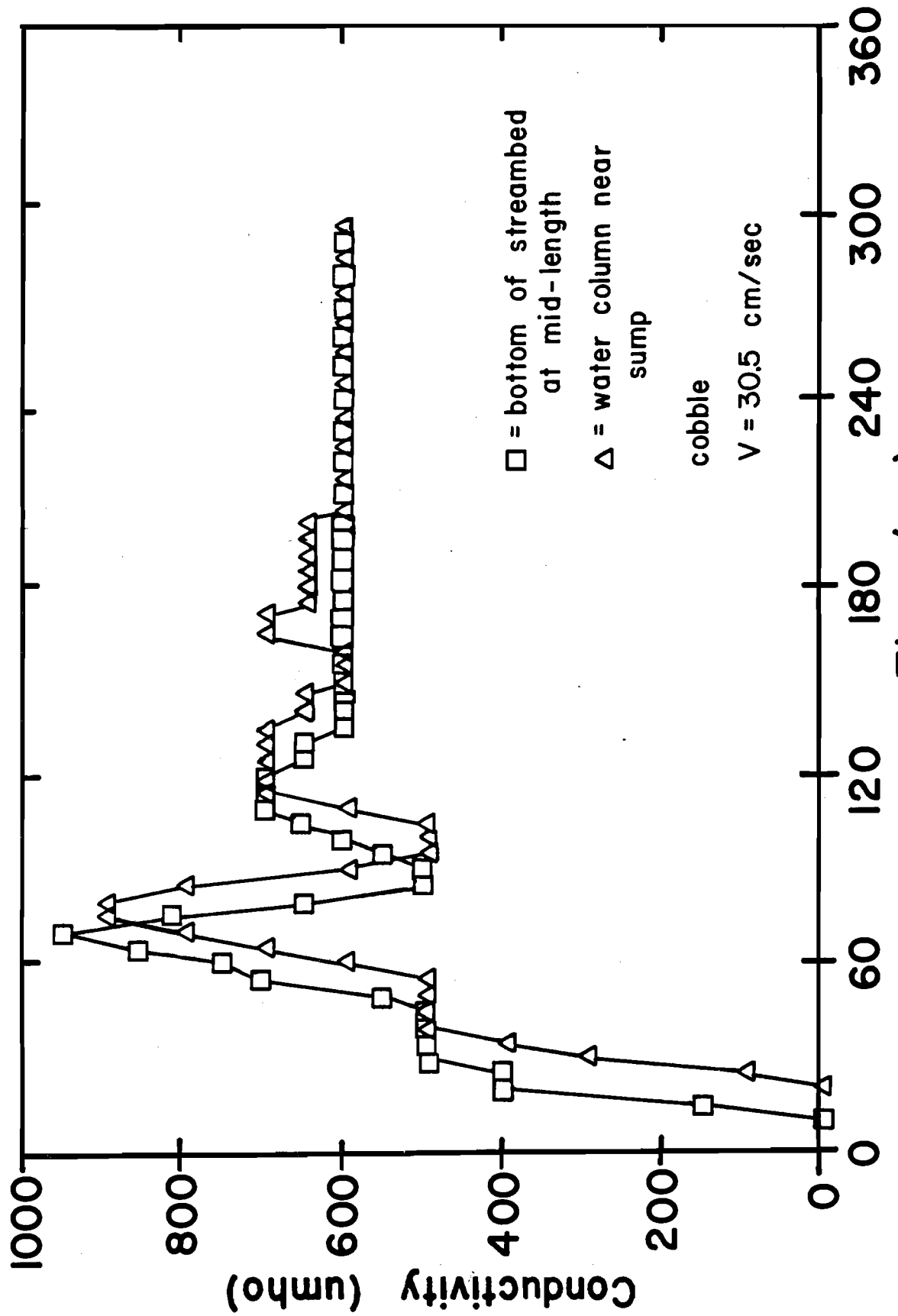

Figure 15. NaCl Tracer Study in the Cobble Streambed at a Stream Velocity of 30.5 cm/sec. NaCl solution was added during the first 35 seconds.

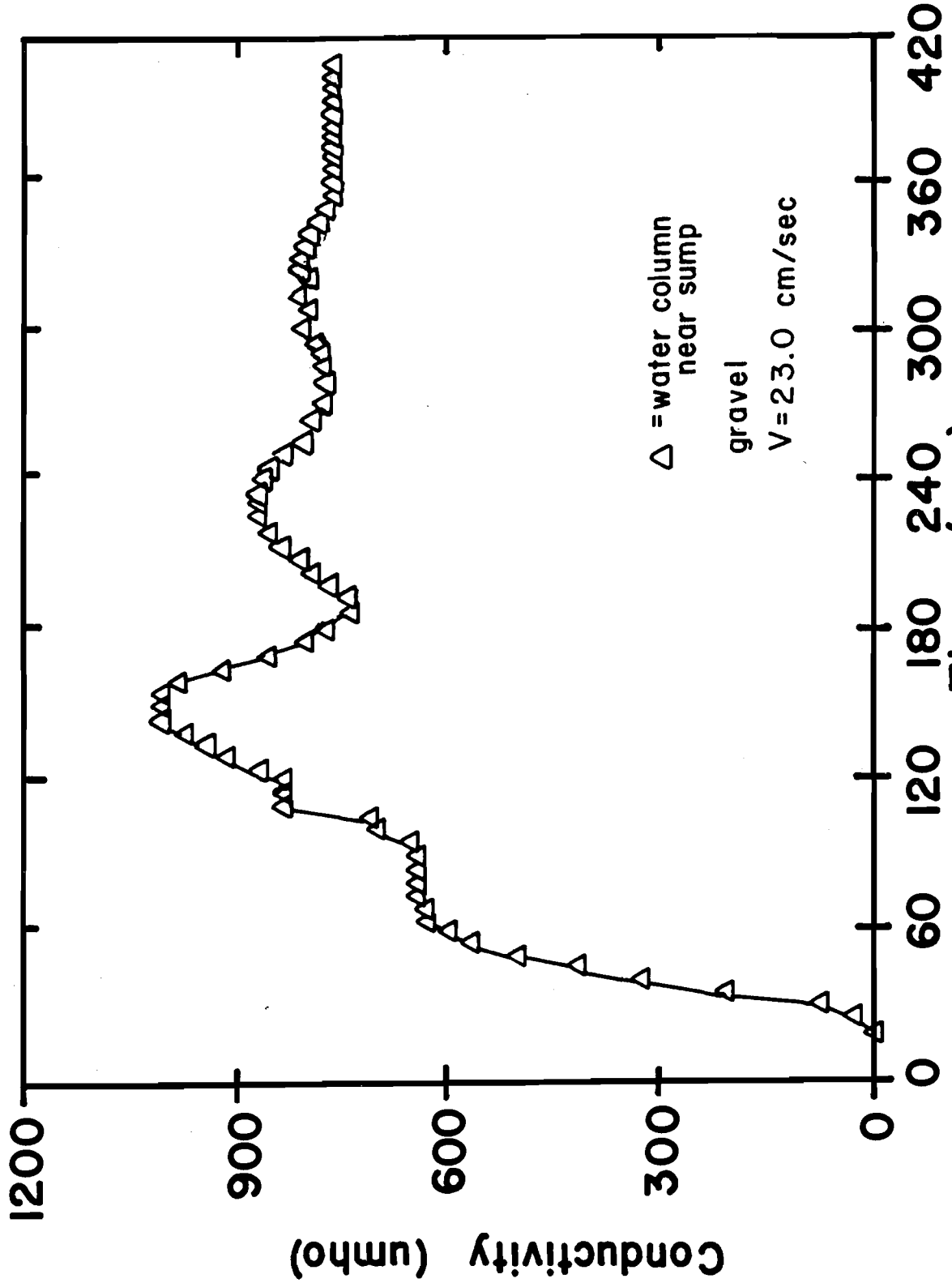

Figure 16. NaCl Tracer Study for the Gravel Streambed at a Stream Velocity of 23.0 cm/sec. NaCl solution was added during the first 125 seconds.

Value of PHI

The average value of PHI at 20°C, based on three pipe experiments, was 253 ± 29 cm^{-1} (Table 3). In all three experiments, the removal of glucose-derived COD followed first-order kinetics with respect to COD concentration. This average value of PHI(20) was used in the calculation of the contribution pipes made in removal of COD from the cobble streambed reactor and ultimately in the calculation of mass transfer coefficients for the gravel and cobble streambeds.

KfP Values for the Gravel and Cobble Streambeds

Typical COD-removal curve for the gravel and cobble streambeds are shown on Figures 17 and 18, respectively. Because straight lines were produced when the natural logarithm of stream COD concentrations were plotted against time, COD removal in the artificial stream followed first-order kinetics. Batch tests conducted at higher stream velocities had steeper removal slopes than batch tests conducted at slower velocities. Thus, as stream velocities increased, the values of KfP increased.

A series of batch tests was performed on a gravel streambed that had been acclimated to a stream velocity of 17.7 cm/sec. The extent to which the upper surfaces of the gravel streambed had been colonized by biofilms could be approximated visually, due to the dark brown coloration of the thicker biofilms and the light color of the gravel. Based on a visual inspection of the gravel streambed after the biofilm community was given an acclimation period of four months, thick biofilms were evident only as patches on the uppermost surfaces of the gravel. They appeared to be most prevalent immediately behind the ridges found on the surfaces of

Table 3

Parameters Used in the Calculation of PHI(20)

Parameters	Trial Number		
	1	2	3
M(p), hr^{-1}	0.73	0.87	0.65
VOL, liters	99	95	107
T, C	24.1	24.8	25.5
Ap, cm^2	12310	12310	12310
Vp, cm/sec	219	219	219
PHI, cm^{-1}	268	301	242
PHI(20), cm^{-1}	254	282	224

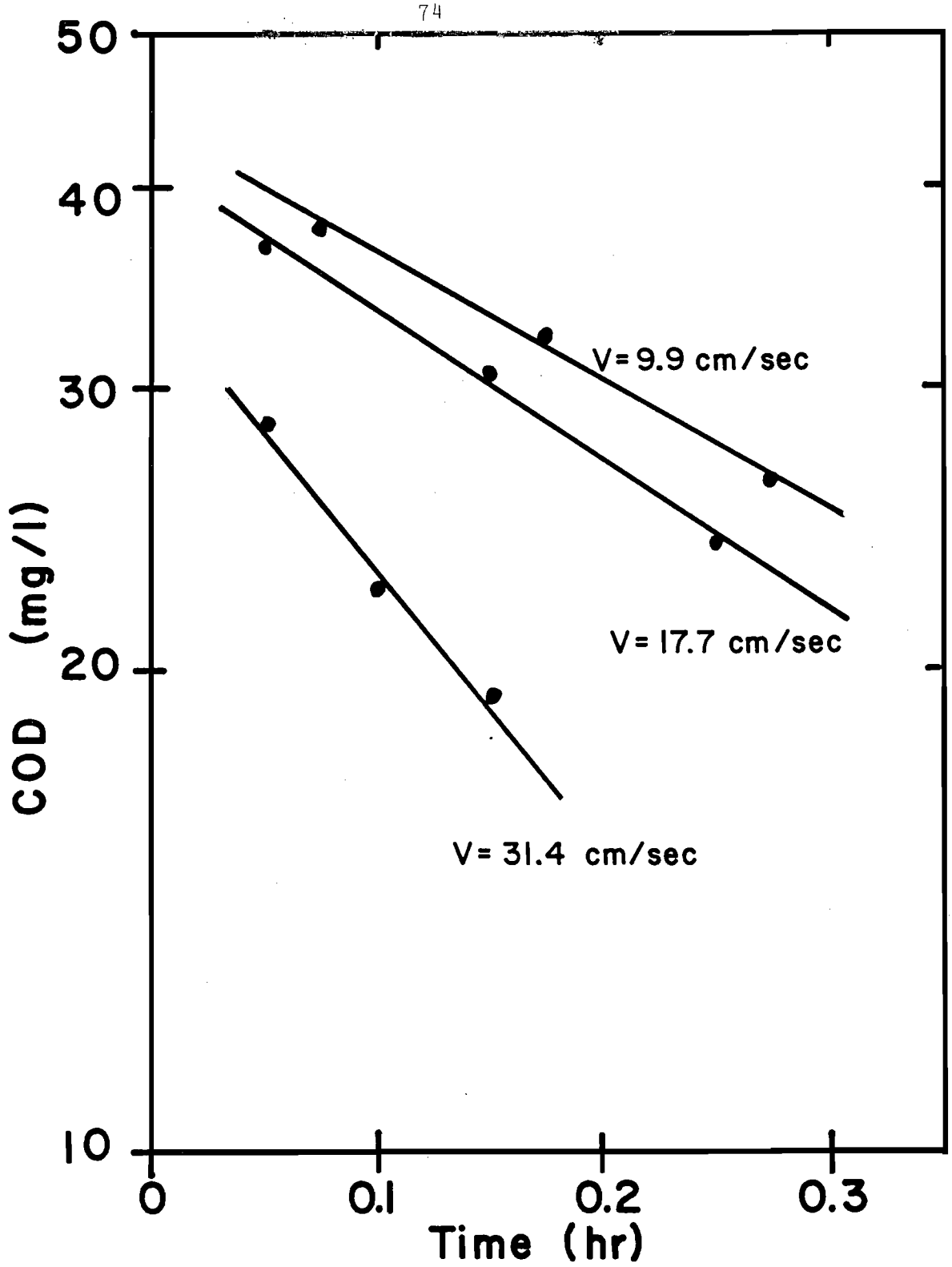

Figure 17. COD Removal by the Gravel Streambed at Three Different Stream Velocities.

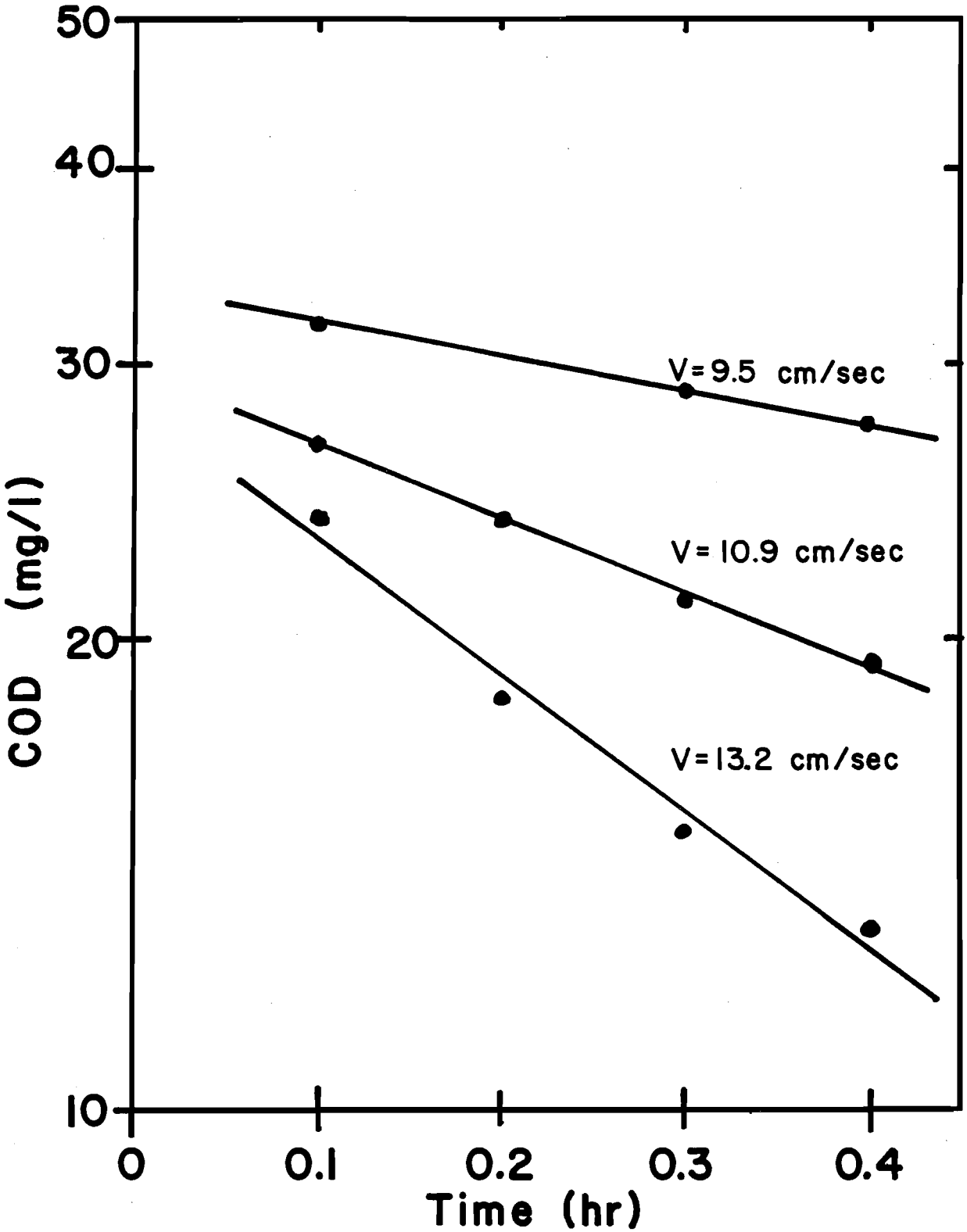

Figure 18. COD Removal by the Cobble Streambed at Three Different Stream Velocities.

individual pieces of gravel. The surface area covered by these patches of macroscopic biofilm colonies represented less than 50 percent of the projected surface area of the gravel streambed. However, thinner biofilms could have existed elsewhere in the gravel streambed.

The data used in the calculation of KfP values for seven gravel batch tests are shown on Table 4. The KfP values ranged from 254 cm^2/hr at a stream velocity of 9.9 cm/sec to 729 cm^2/hr at 40.6 cm/sec. When the calculated KfP values were plotted versus stream velocity (Figure 19), the following linear relationship was observed:

$$KfP = 17.3\ V - 21 \tag{71}$$

with squared linear regression coefficient of 0.939, in which KfP is in units cm^2/hr and V is the average stream velocity (cm/sec). Because streambed biofilm biomass was virtually constant throughout this series of batch tests, the increase in KfP values with increases in stream velocity was caused by increases in the overall mass transfer rates to the biofilm covered surfaces.

Three series of COD batch tests were conducted on the cobble streambed. The first series of batch tests determined KfP values for the cobble streambed that had been acclimated to a stream velocity of 13.2 cm/sec. During the second series, batch tests were conducted only at the stream velocities to which the cobble biofilm community had become acclimated. Thus, the first series of batch tests evaluated changes in KfP values due only to mass transfer effects, while the second series

Table 4

KfP Values for the Gravel Streambed
For each of the listed batch tests, Ls = 690 cm

Average Velocity, V (cm/sec)	Observed Slope, M (hr^{-1})	VOL (liter)	T (°C)	KfP (cm^2/hr)
9.9	1.81	97	24.5	254
17.7	1.80	110	25.0	287
17.7	2.11	102	24.5	312
23.0	1.94	128	24.0	360
28.8	1.95	178	25.0	503
31.4	1.96	219	25.7	622
40.6	2.78	181	25.0	729

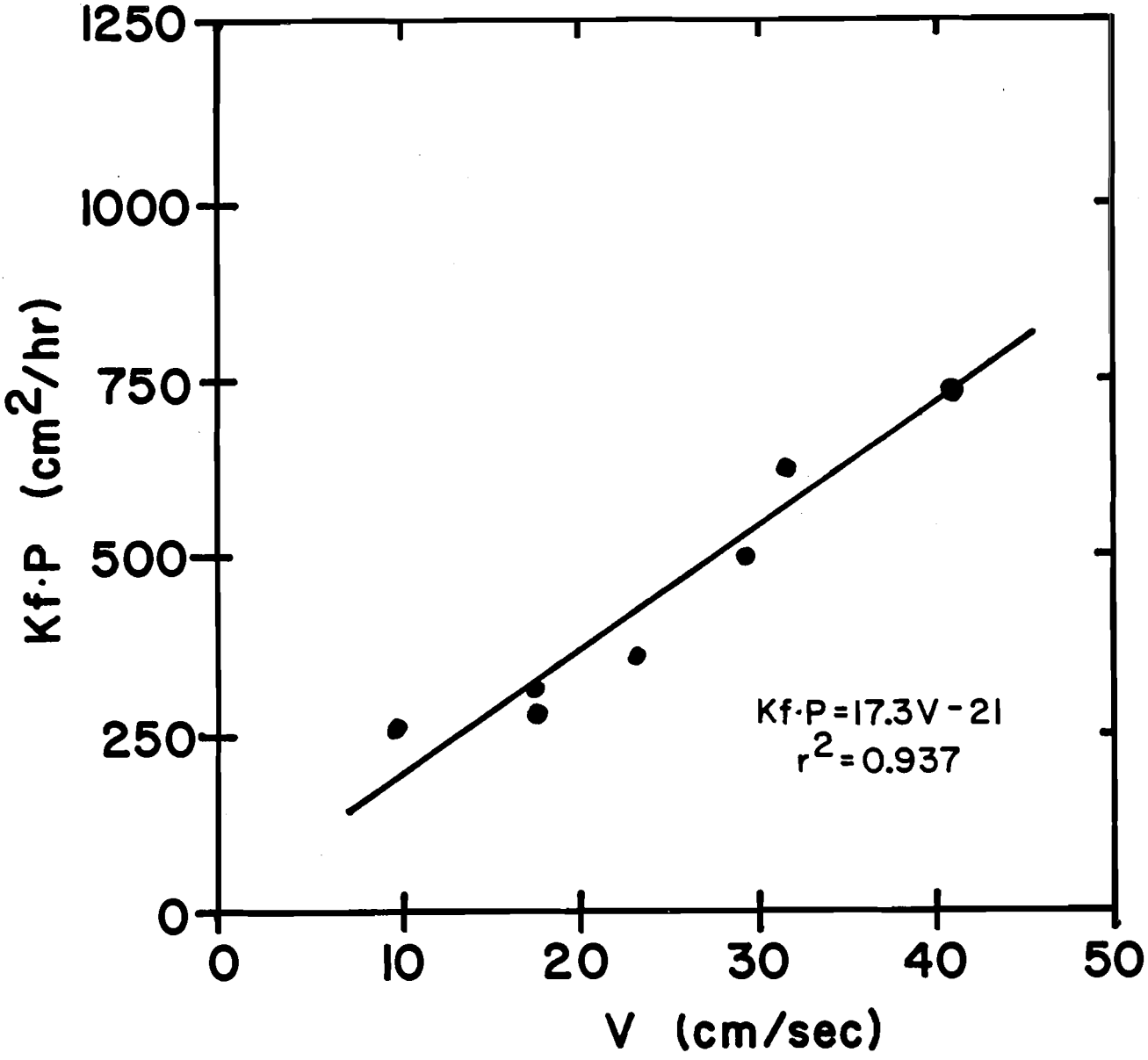

Figure 19. KfP versus V for the Gravel Streambed

demonstrated variation in KfP values due to both mass transfer and biomass effects.

The third series of COD batch tests was performed following the first two series and after the stream's biofilm community had recovered from an accidental desiccation. In this series of batch tests the biofilm community was acclimated to an average stream velocity of 16.6 cm/sec. The KfP values obtained from the third series of batch tests will be discussed in a later section and were used to test the findings of the first two series.

As with the gravel streambed, macroscopic biofilm colonies appeared dark brown against the cobble streambed particles. Unlike the patchy macroscopic biofilm distribution noted in the gravel streambed, all cobble surfaces were covered with macroscopic biofilms. Therefore, the geometrically available surface area (P/W = 6.2) was a good measure of biofilm surface area found in the cobble streambed.

The values of KfP calculated for the cobble biofilm community acclimated to an average stream velocity of 13.2 cm/sec are shown on Table 5. As with the other series of batch tests performed on the cobble streambed, the calculation of streambed KfP values included the correction for pipe biofilms. The KfP values ranged from 71 cm^2/hr at an average stream velocity of 4.6 cm/sec to 857 cm^2/hr at 25.2 cm/sec (Figure 20). At stream velocities of 4.6 and 6.9 cm/sec, the upper surfaces of the cobble streambed were not covered with water. Because their KfP values reflected a change in physical surface are, they were not used in the development of a mass transfer equation for the cobble streambed.

Since biofilm biomass was virtually constant throughout the first series of batch tests, the increase in KfP values with increases in stream

Table 5

KfP Values for the Cobble Streambed When Acclimated to a Stream velocity of 13.2 cm/sec. For the listed batch tests, Ls = 730 cm

Average Velocity, V (cm/sec)	Slope, M (hr^{-1})	VOL (liter)	T (°C)	KfP (cm^2/hr)
4.6	0.55	93	21.0	71
6.9	0.51	141	19.5	97
8.8	0.45	161	21.0	100
9.9	0.86	167	23.0	195
10.2	1.08	153	22.0	227
11.6	1.74	132	21.5	314
13.2	2.45	121	22.0	406
16.6	2.44	205	22.0	683
25.2	2.58	243	22.0	857

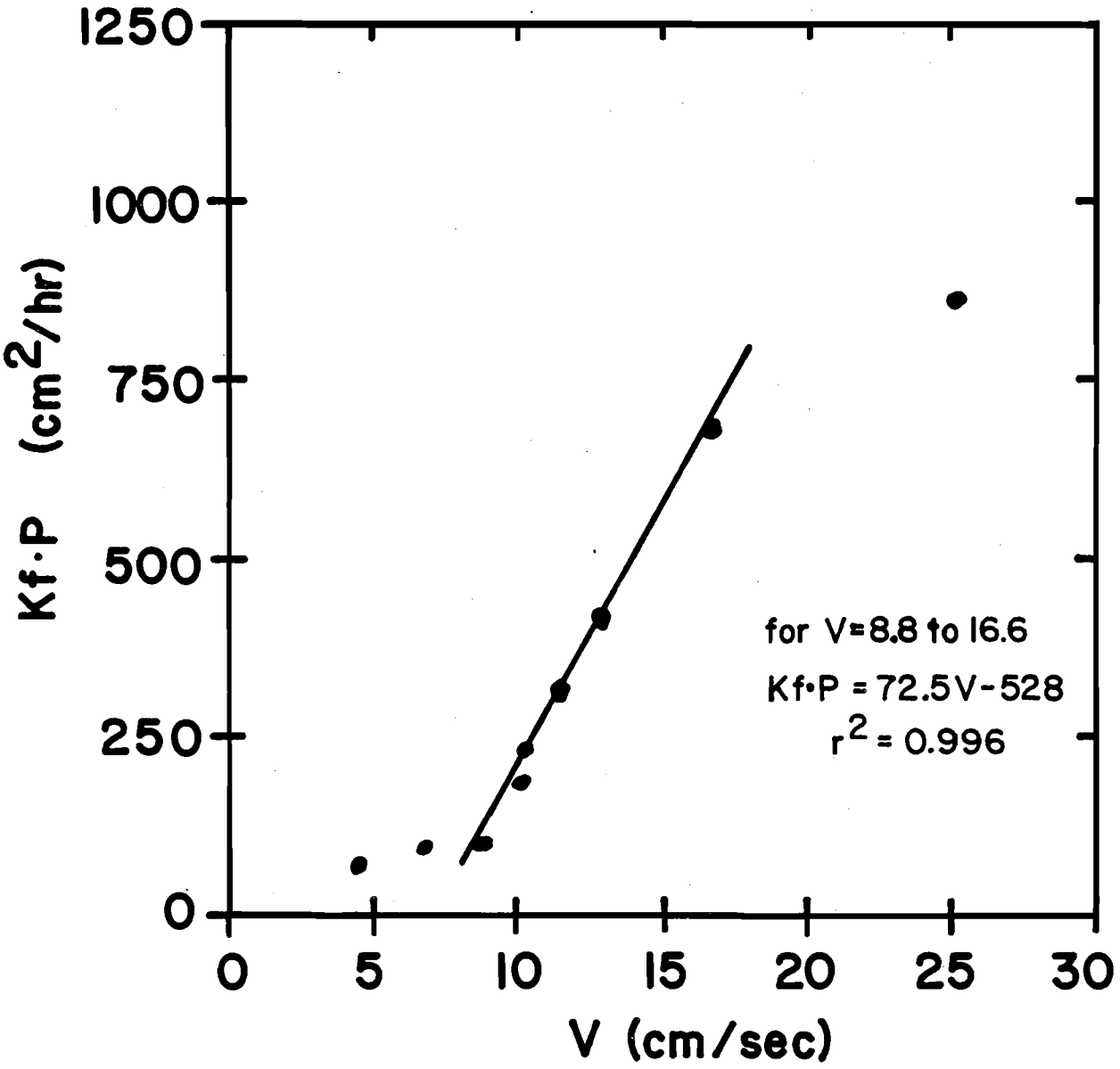

Figure 20. KfP versus V for the Cobble Streambed When Acclimated to V = 13.2 cm/sec.

velocity--between V = 8.8 cm/sec and V = 25.2 cm/sec--was due to increases in the overall mass transfer rate of COD to the cobble biofilms. As illustrated on Figure 20, KfP values increased linearly with increases in stream velocity between velocities of 8.8 and 16.6 cm/sec; the increase can be described by the following equation:

$$KfP = 72.5\ V - 528 \qquad (72)$$

$$r^2 = 0.996$$

in which KfP is in units of cm^2/hr, V is in cm/sec, and r^2 is the square of the linear regression coefficient. The flattening of the curve in Figure 20 at V = 25.2 cm/sec implies that Kf P was approaching DfPHI, such that further increases in Km would not significantly increases the value of KfP.

The second set of batch tests were performed at each of the six acclimation velocities shown on Table 6. The KfP values ranged from 32 cm^2/hr at an acclimation velocity of 9.5 cm/sec to a KfP of 1225 cm^2/hr when the streambed was acclimated to V = 18.7 cm/sec. The KfP values are plotted versus stream velocity on Figure 21. The relationship between KfP and stream velocity can be described by

$$KfP = 138.4\ V - 1313 \qquad (73)$$

$$r^2 = 0.993$$

Table 6

KfP Values for the Cobble Streambed When Acclimated to the Listed Stream Velocities
Except for batch test conducted at V = 9.5 cm/sec (Ls = 760), the length of the streambed for the listed batch tests was 730 cm (Ls = 730cm).

Average Velocity, V (cm/sec)	Slope, M(s) (hr^{-1})	VOL (liter)	T (°C)	KfP (cm^2/hr)
9.5	0.16	151	22.0	32
10.9	0.83	175	20.1	199
13.2	2.45	121	22.0	406
16.2	3.47	187	27.0	888
17.8	4.31	188	29.0	1108
18.7	3.96	226	28.0	1225

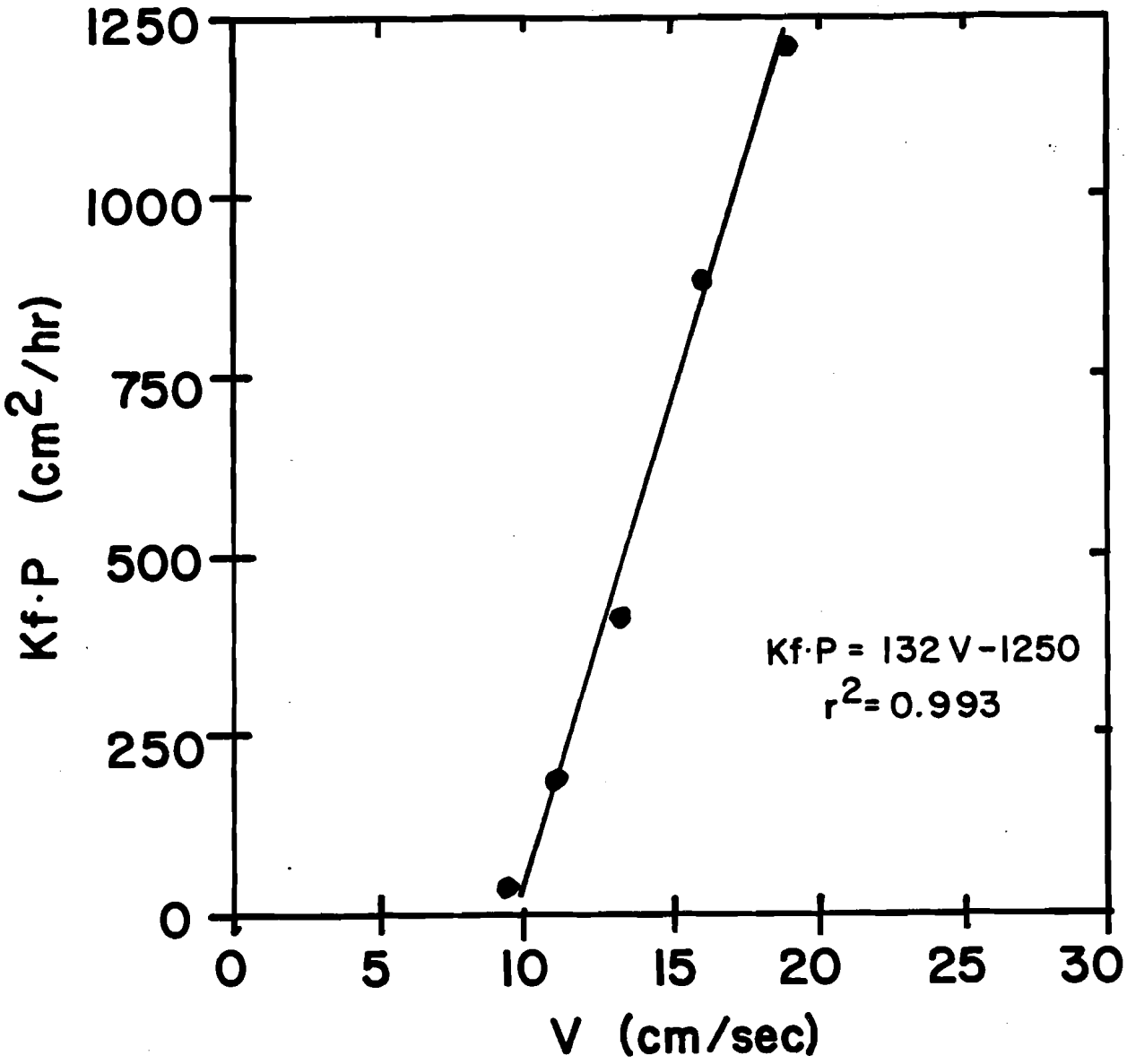

Figure 21. KfP versus Acclimated Velocity for the Cobble Streambed

in which V is the average stream velocity (cm/sec) to which the cobble streambed had become acclimated. As expected, when both biomass and mass transfer varied with stream velocity, KfP was more sensitive to velocity changes (Equation 73) than when only mass transfer varied with velocity (Equation 72).

The lines defined by Equations 72 and 73 are plotted on Figure 22. The crossing of the two lines supports the argument that faster stream velocities support the accumulation of more biofilm biomass. For example, if batch tests were performed at V = 10 cm/sec for a biofilm community acclimated to V = 10 (Equation 73) and for a biofilm community acclimated to V = 13.2 (Equation 72), the difference between the KfP values produced by the two batch tests would be due to biofilm biomass, because both tests were conducted under the same mass transfer regime. Since the KfP value at V = 10 for the biofilm community acclimated to V = 10 is less than KfP value at V = 10 for the biofilm community acclimated to V = 13.2, a cobble streambed biofilm community acclimated to V = 10 has less biomass than a community acclimated to V = 13.2. Therefore, the vertical distance between the Equation 72 line and the Equation 73 line on Figure 22 is mainly a function of streambed biofilm biomass. However, some of the vertical distance between the two lines at points above the intersection is due to the differences in water temperature. These temperature differences will be accounted for and a simple relationship will be developed between acclimation velocity and streambed biofilm biomass in a later section.

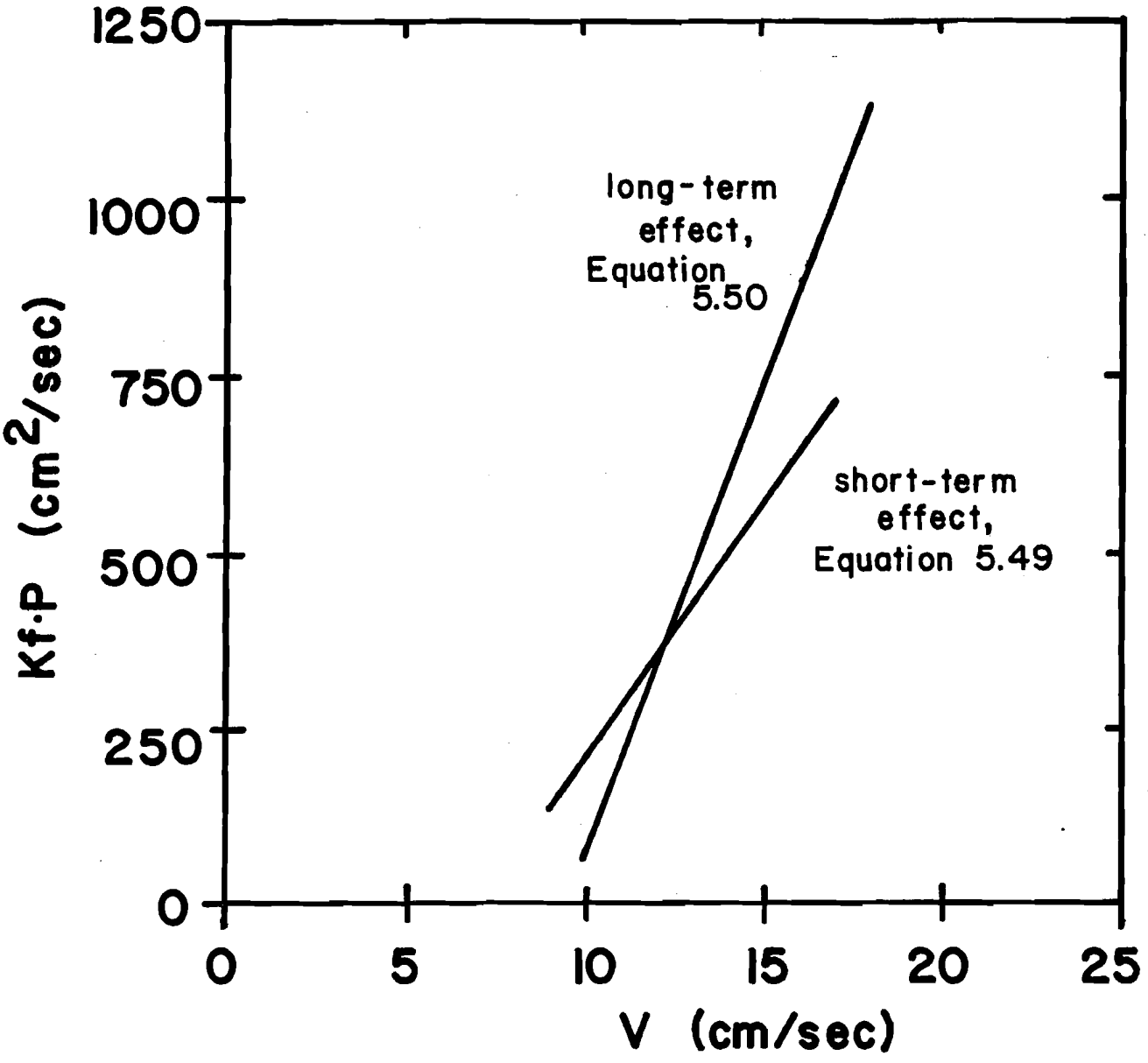

Figure 22. Graphical Comparison of the Short-Term and Long-Term Effects Stream Velocity had on KfP Values for the Cobble Streambed.

Calculation of Mass Transfer Equations

Determination of the mass transfer coefficient for each batch test was sensitive to the value of P/W assigned to the gravel or cobble streambed. For the artificial stream experiments, P/W was set equal to the geometric surface area presented by the gravel (P/W = 7.0) and the cobble (P/W = 6.2). The appropriateness of equating the geometric P/W value to actual biofilm surface area was assessed by observing if the geometric P/W value was between the calculated values of P/W(min) and P/W(max) for each batch test. The P/W(min) and P/W(max) for batch tests performed on the gravel streambed acclimated to V = 17.7 cm/sec and on the cobble streambed acclimated to V = 13.2 cm/sec are listed on Table 7. Since the geometric P/W was between the P/W(min) and P/W(max) determined for each batch test, the use of the geometric P/W was appropriate in the determination of the mass transfer coefficient for each batch test performed on the gravel and cobble streambeds.

A more stringent test of geometric P/W appropriateness was observing if the geometric P/W value was within the feasible range of P/W values determined for a series of batch tests. If the geometric P/W was between the maximum P/W(min) and the minimum P/W(max) for a series of batch tests, then the geometric P/W value was appropriate for use in determining the values of Constant and m in Equation 25. The feasible range of P/W values for the gravel streambed was from 4.0 to 9.2 (Table 7). The geometric P/W value of 7.0 for the gravel streambed was within this range. The accepted range of P/W values for the cobble streambed acclimated to V = 13.2 cm/sec was from 5.5 to 9.2 (Table 7). The cobble streambed's geometric P/W value was 6.2, which was within the feasible range. Therefore, the geometric P/W

Table 7

Values of P/W(min) and P/W(max) for the Gravel and Cobble Streambeds

Gravel Streambed (acclimated to V = 17.7 cm/sec)

Stream Velocity, V (cm/sec)	P/W (min)	P/W (max)	
9.9	1.4	9.2	
17.7	1.6	10.4	
17.7	1.7	11.3	feasible range for series
23.0	2.1	13.1	4.0 to 9.2
28.8	3.3	22.6	
31.4	3.3	22.6	
40.6	4.0	26.5	

Cobble Streambed (acclimated to V = 13.2 cm/sec)

Stream Velocity, V (cm/sec)	P/W (min)	P/W (max)	
9.9	1.2	7.1	
10.2	1.5	8.3	
11.6	2.1	11.4	feasible range for series
13.2	2.6	14.8	5.5 to 7.1
16.6	4.4	24.8	
25.2	5.5	31.2	

values for the gravel and cobble streambeds were considered suitable for use in the development of mass transfer equations for the two streambeds.

The shear velocities (U), shear Reynolds numbers (Re), and the apparent, overall mass transfer coefficients (Km) associated with each COD batch tested performed on the gravel streambed are listed on Table 8. The listed Km values, calculated by Equation 63, were based on the KfP values determined from each COD batch test. Based on the power regression defined by Equation 67, the apparent, overall mass transfer coefficients for the gravel streambed are described by the following equation:

$$Km = 0.00229\ Re^{1.42}\ Sc^{1/3}\ \frac{D}{Dp} \qquad (74)$$

$$r^2 = 0.846$$

for Re values between 260 and 881, in which

$$Re = \frac{3600\ U\ Dp}{KVIS} \qquad (34)$$

U is the shear velocity (cm/sec), Dp is the mean diameter of the gravel (1.6 cm), KVIS is the kinematic viscosity of water (cm^2/hr), D is the diffusivity of glucose in water (cm^2/hr), Sc is the Schmidt number and is defined as KVIS/D. As expected, Re in Equation 74 is raised to power greater than 1/2.

A comparison between the experimentally observed values of KfP for the gravel streambed (listed on Table 4) and the KfP values calculated by Equation 62 when Km was obtained from Equation 74 is shown on Figure 23. Equations 62 and 74 produced good descriptions of the COD removal rates in the gravel streambed over the whole range of tested stream velocities.

The values U, Re, and Km used to develop the mass transfer equation for the cobble streambed are listed on Table 9. The Km are calculated by

Table 8

Values of Km Calculated by Equation 63 for the Gravel Streambed (P/W = 7.0)

Stream Velocity, V (cm/sec)	Shear Velocity, U (cm/sec)	Shear Reynolds Number, Re (unitless)	Overall Mass Transfer Coefficient, Km (cm/hr)
9.9	1.5	260	1.7
17.7	2.5	440	1.9
17.7	2.5	440	2.1
23.0	3.1	543	2.7
28.8	3.7	667	4.3
31.4	3.9	716	6.0
40.6	4.9	881	8.7

Table 9

Values of Km Calculated by Equation 63 for the Cobble Streambed When Acclimated to V = 13.2 cm/sec.

Stream Velocity, V (cm/sec)	Shear Velocity, U (cm/sec)	Shear Reynolds Number, Re (unitless)	Overall Mass Transfer Coefficient, Km (cm/hr)
8.8	1.5	932	0.7
9.9	1.7	1088	1.4
10.2	1.8	1091	1.7
11.6	2.0	1214	2.8
13.2	2.2	1385	4.1
16.6	2.7	1709	13.7
25.2	4.0	2517	45.1

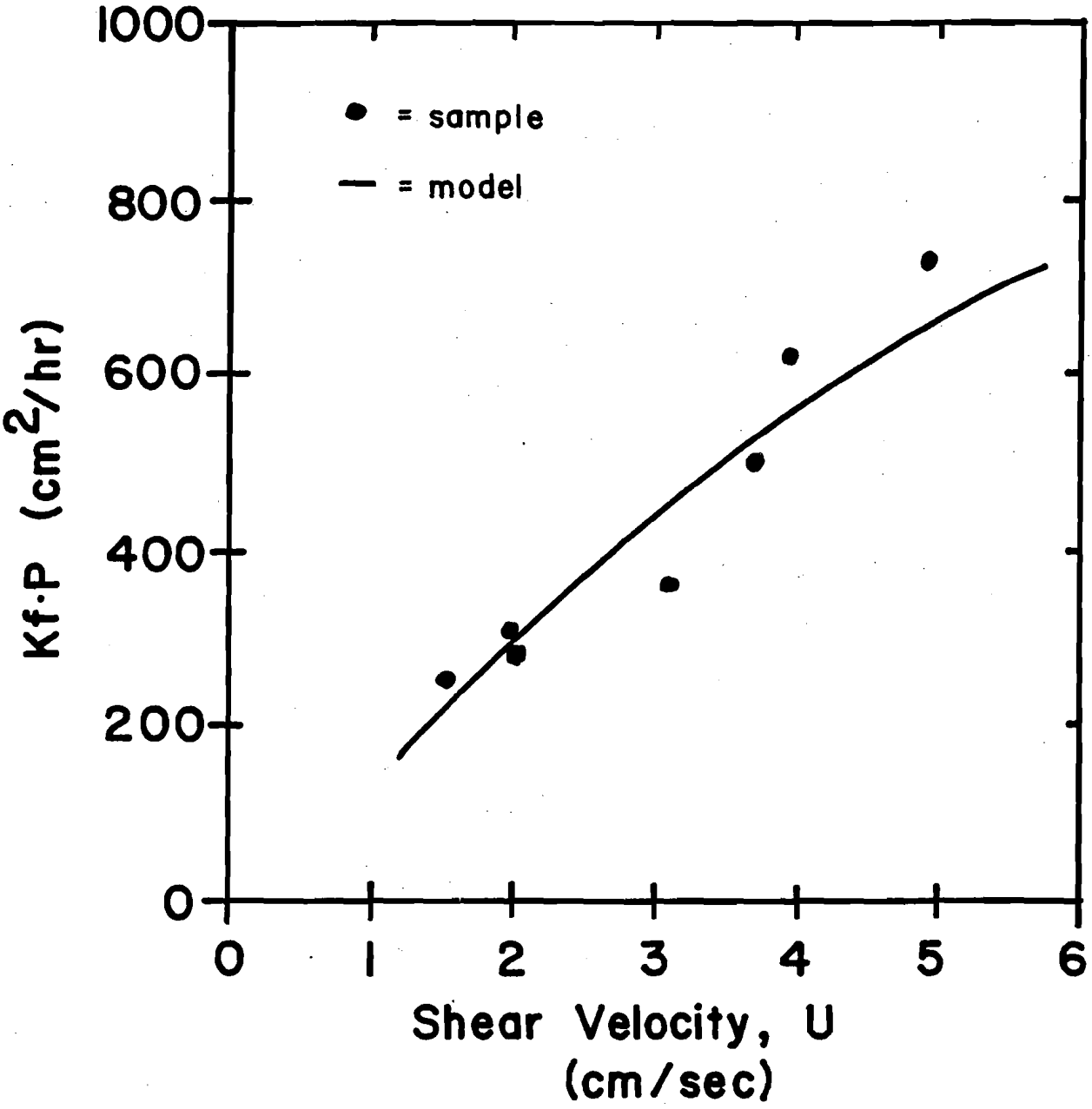

Figure 23. KfP versus U for the Gravel Streambed. Temperatures for the samples ranged from 24.5 to 25.7 C. The model assumed T = 25°C.

Equation 63 from data obtained from COD batch tests performed on the cobble streambed acclimated to V = 13.2 cm/sec. Based on the power regression defined by Equation 67, the apparent, overall mass transfer coefficients for the cobble streambed can be described by

$$Km = 4.17\ 10^{-12}\ Re^{4.24}\ Sc^{1/3}\ \frac{D}{Dp} \qquad (75)$$

$$r^2 = 0.986$$

for Re values between 932 to 2517, in which Re, the shear Reynolds number, is defined by Equation 34 and Dp is the mean diameter of the cobble (6.0 cm). As with the gravel mass transfer equations, Re in the cobble mass transfer equation (Equation 75) is raised to a power greater than 1/2--the expected result.

The experimentally observed values of KfP for the cobble streambed acclimated to V = 13.2 cm/sec and the KfP values predicted by Equations 62 and 75 are shown on Figure 26. The cobble mass transfer equation (Equation 75) and Equation 62 produced good descriptions of the COD removal rates for over the entire range of velocities at which COD batch tests were performed on the cobble streambed acclimated to v = 13.2 cm/sec.

Acclimation Velocity on Cobble Streambed Biofilm Biomass

Interpretation of Figure 22 suggested that cobble streambed biofilm biomass was a function of acclimation velocity. However, this interpretation was biased by differences in batch test temperatures. In this section, changes in cobble streambed biofilm biomass with acclimation velocity are indexed by a back-calculated value of P/W, termed P/W(acc). For each acclimation velocity (listed on Table 6) a value of P/W was

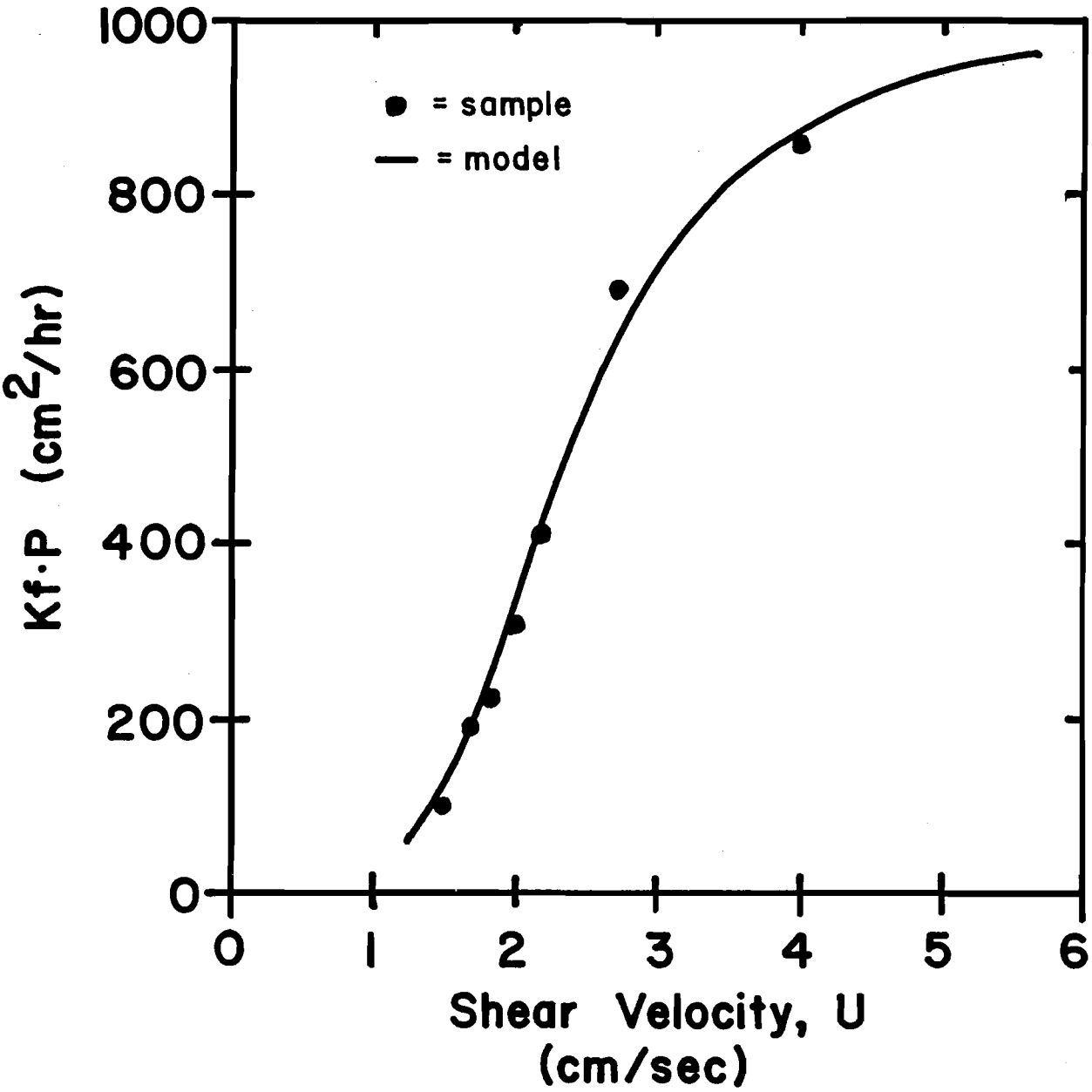

Figure 24. KfP versus U for the Cobble Streambed When Acclimated to V = 13.2 cm/sec (U = 2.2 cm/sec). Temperatures for the samples ranged from 21.0 to 22.0 C. The model assumed T = 22 C°.

calculated via Equation 66. A larger value of P/W(acc) meant a greater amount of biofilm biomass within the cobble streambed. However, values of P/W(acc) should not be assumed to be directly proportional to biomass levels. Therefore, the P/W(acc) values provided a temperature independent correction factor for use in Equation 62 and accounted for changes in streambed biofilm biomass--in terms of P [P = W*P/W(acc)]--associated with changes in acclimation velocity.

The P/W(acc) values calculated for each acclimation velocity by Equation 66 when Km was obtained from Equation 75 are listed in Table 10 and are plotted on Figure 25. P/W(acc) increased sharply between acclimation shear velocities of U = 1.64 cm/sec (V = 9.5) and U = 1.86 cm/sec (V = 10.9). Between acclimation shear velocities of U = 1.86 cm/sec (V = 10.9) and U = 3.06 cm/sec (V = 18.7) the calculated value of P/W appeared to gradually increase and could be described by the following equation:

$$P/W(acc) = 5.21\ U^{0.2} \qquad (76)$$

in which P/W(acc) is the calculated amount of active biofilm surface area per unit channel width (unitless) and U is the shear velocity (cm/sec) to which the biofilm community was acclimated. Because P/W(acc) increased with acclimation velocity, cobble streambed biofilm biomass also increased with acclimation velocity.

Testing Predictive Capacity of Cobble Streambed Models

A third series of COD batch tests were performed on the cobble streambed after an accidental desiccation of the biofilm community. The acclimation velocity for this series was V = 16.6 cm/sec, which corresponded to a shear velocity of U = 2.73 cm/sec. The biofilm community required over

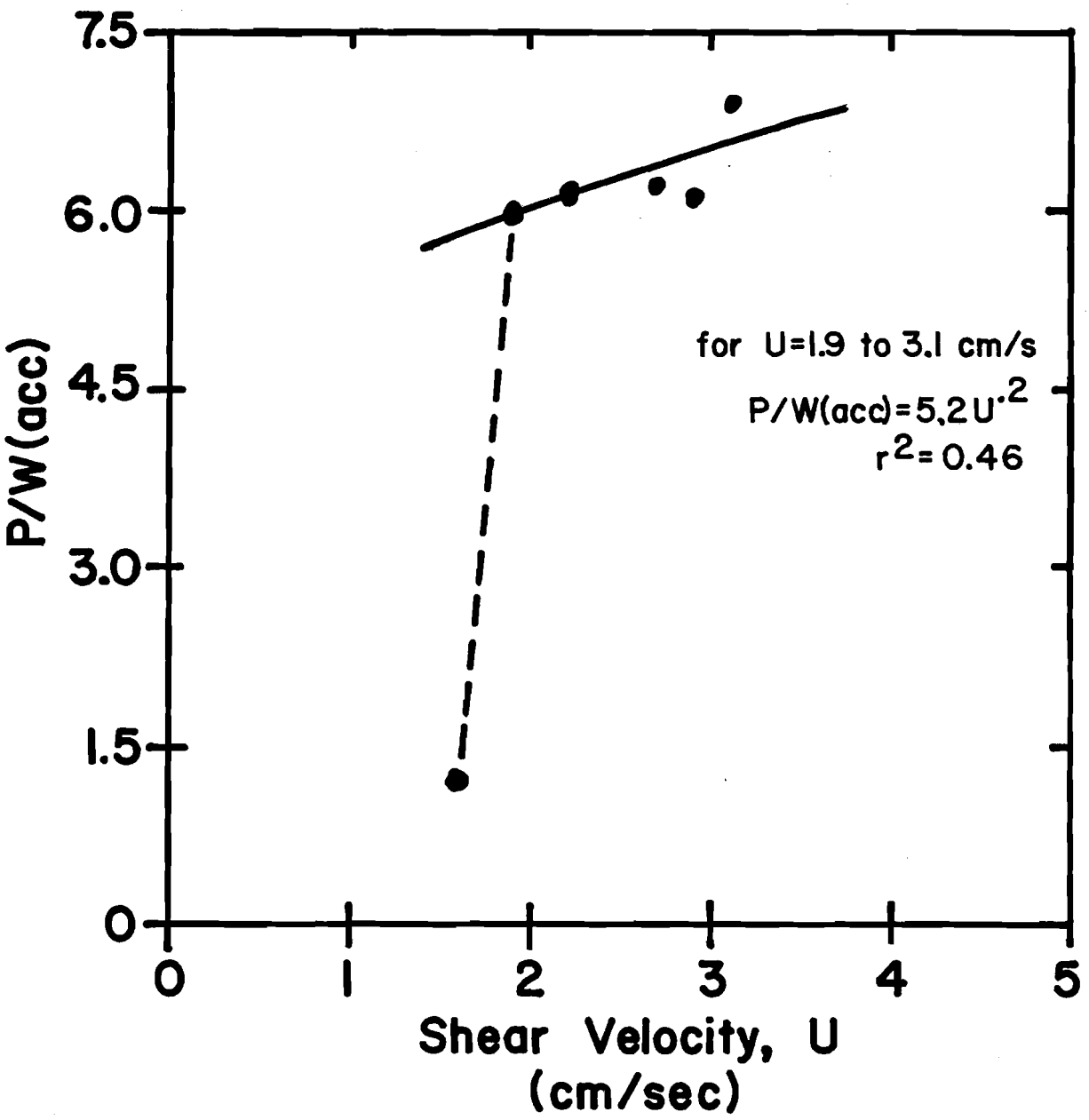

Figure 25. P/W(acc) versus Acclimation Shear Velocity for the Cobble Streambed.

Table 10

P/W(acc) Values for the Cobble Streambed When Acclimated to the Listed Stream Velocities

Stream Velocity, V (cm/sec)	Shear Velocity, U (cm/sec)	P/W(acc) (unitless)
9.5	1.6	1.2
10.9	1.9	6.0
13.2	2.2	6.1
16.2	2.7	6.2
17.8	2.9	6.1
18.7	3.1	6.9

two months to become acclimated, which suggested that a significant portion of the original community was lost as a result of desiccation. The results of the batch tests performed after the biofilm community was acclimated to U = 2.73 cm/sec are shown on Table 11.

The combined ability of the previously developed models to predict values of COD removal rates were tested by observing how well they predicted the KfP values listed on Table 11. Equation 76 determined a value of P/W = 6.4 for a cobble streambed acclimated to U = 2.73 cm/sec. Km for each of the shear velocities at which a batch test was conducted were obtained from Equation 75. Equation 62 was then used to predict the value of KfP for each batch test.

The observed and predicted values of KfP are listed on Table 12 and plotted on Figure 26. The combination of Equations 62, 75, and 76 predicted KfP values that were within 7 percent of the observed KfP values. Therefore, the combination of Equations 75 (Km) and 76 [P/W(acc)] successfully captured the short- and long-term effects stream velocity had on the rate of COD removal by the artificial stream's cobble biofilm community.

Comparison of Gravel and Cobble Streambeds

Mass Transfer Equations

The artificial stream experiments developed equations that described the apparent, overall mass transfer coefficients for gravel (Dp = 1.6 cm) and cobble (Dp = 6.0 cm) streambeds in terms of the shear Reynolds number. Both streambeds were between 1.5 and 2 layers of rock thick, and their interstitial voids were free of sand or silt. In the determination of the

Table 11

KfP Values for the Cobble Streambed When Acclimated to a Stream Velocity of 16.6 cm/sec. For the listed batch tests, Ls = 730 cm

Average velocity, V (cm/sec)	Slope, M(s) (hr^{-1})	VOL (liter)	T (°C)	KfP (cm^2/hr)
16.6	4.28	192	29.0	1125
20.3	5.73	166	28.5	1301
24.4	5.71	168	28.5	1313
26.1	6.29	171	29.5	1472
30.5	5.35	220	30.0	1611

Table 12

Observed and Predicted KfP values for the Cobble Streambed When Acclimated to V = 16.6 cm/sec

Stream Velocity, V (cm/sec)	Shear Velocity, U (cm/sec)	Observed KfP (cm^2/hr)	Predicted KfP (cm^2/hr)	Relative Error (%)
16.6	2.7	1125	1090	-3.1
20.3	3.3	1301	1230	-5.5
24.4	3.9	1313	1326	1.0
26.1	4.2	1472	1432	-2.7
30.5	4.8	1611	1511	-6.2

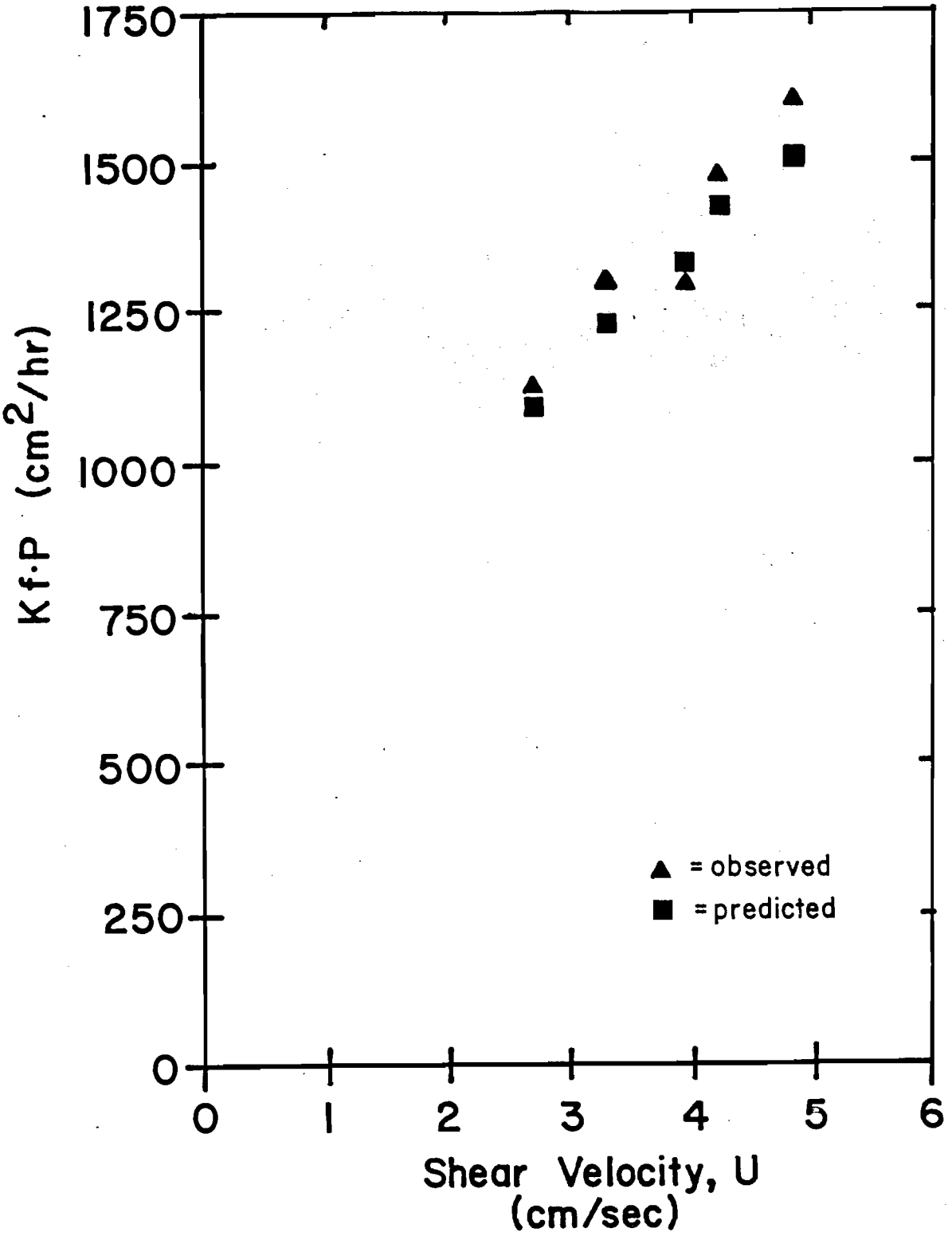

Figure 26. Observed and Predicted KfP Values for the Cobble Streamed Acclimated to a Stream Velocity of 16.6 cm/sec (U = 2.7)

transfer equations, the amount of biofilm film surface active in COD removal (P/W) was set equal to the geometrically available surface area. The apparent, overall mass transfer coefficient for the gravel streambed (P/W = 7) was described by

$$Km = 0.00229\ Re^{1.42}\ Sc^{1/3}\ \frac{D}{DP} \tag{74}$$

The apparent, overall mass transfer coefficient for the cobble streambed (P/W = 6.2) was described by

$$Km = 4.17\ 10^{-12}\ Re^{4.24}\ Sc^{1/3}\ \frac{D}{DP} \tag{75}$$

In both equations, Km is the apparent, overall mass transfer coefficient (cm/hr), Re is the shear Reynolds number defined by

$$Re = \frac{3600\ U\ DP}{KVIS} \tag{34}$$

U is the shear velocity (cm/sec), Dp is the mean diameter of the streambed particles (cm), D is the diffusivity of modeled substrate in water (cm^2/hr), KVIS is the kinematic viscosity of water (cm^2/hr), and Sc is the Schmidt number (KVIS/D).

The shear Reynolds number was raised to a greater power in the cobble mass transfer equation than in the gravel mass transfer equation. Therefore, Km values and, consequently, COD removal rates were more sensitive to changes in shear velocity in the cobble streambed than in the gravel streambed.

Unfortunately, the two mass transfer equations are not interchangeable. For example, merely substituting the Dp value for cobble

into the gravel mass transfer equation (Equation 74) will not produce accurate values of Km for the cobble streambed. Streambed factors such as porosity and the physical size of the interstitial voids probably played an important role in determining the response of Km to changes in shear velocity and, thus, prevent the interchangeable application of the gravel and cobble mass transport equations. Therefore, the development of a mass transport equation applicable to a wide range of streambed types probably should involve the characterization of the streambed in terms of porosity and void size, instead of just mean streambed particle diameter.

Streambed Activities

Previously, a direct comparison of the ability of the gravel and cobble streambeds to remove COD from the artificial stream was difficult, because of differences in experimental temperatures, acclimation velocities, and the shear velocities at which the individual batch tests were run. In this section, corrections will be made for differences in experimental variables, allowing the direct comparison of KfP values for the gravel and cobble streambeds. The comparison will involve calculation of KfP values for the two streambeds assuming that they were acclimated to the same shear velocity.

Since the gravel streambed was acclimated to shear velocity of 2.5 cm/sec, an appropriate value of P/W(acc) was used in the calculation of KfP values for the cobble streambed. From Equation 76, P/W(acc) for the cobble streambed was set equal to 6.3. The KfP values for both the gravel and cobble streambeds were determined for shear velocities ranging from 1.5 to 4.8 cm/sec, i.e., the range over which the two mass transfer equations were

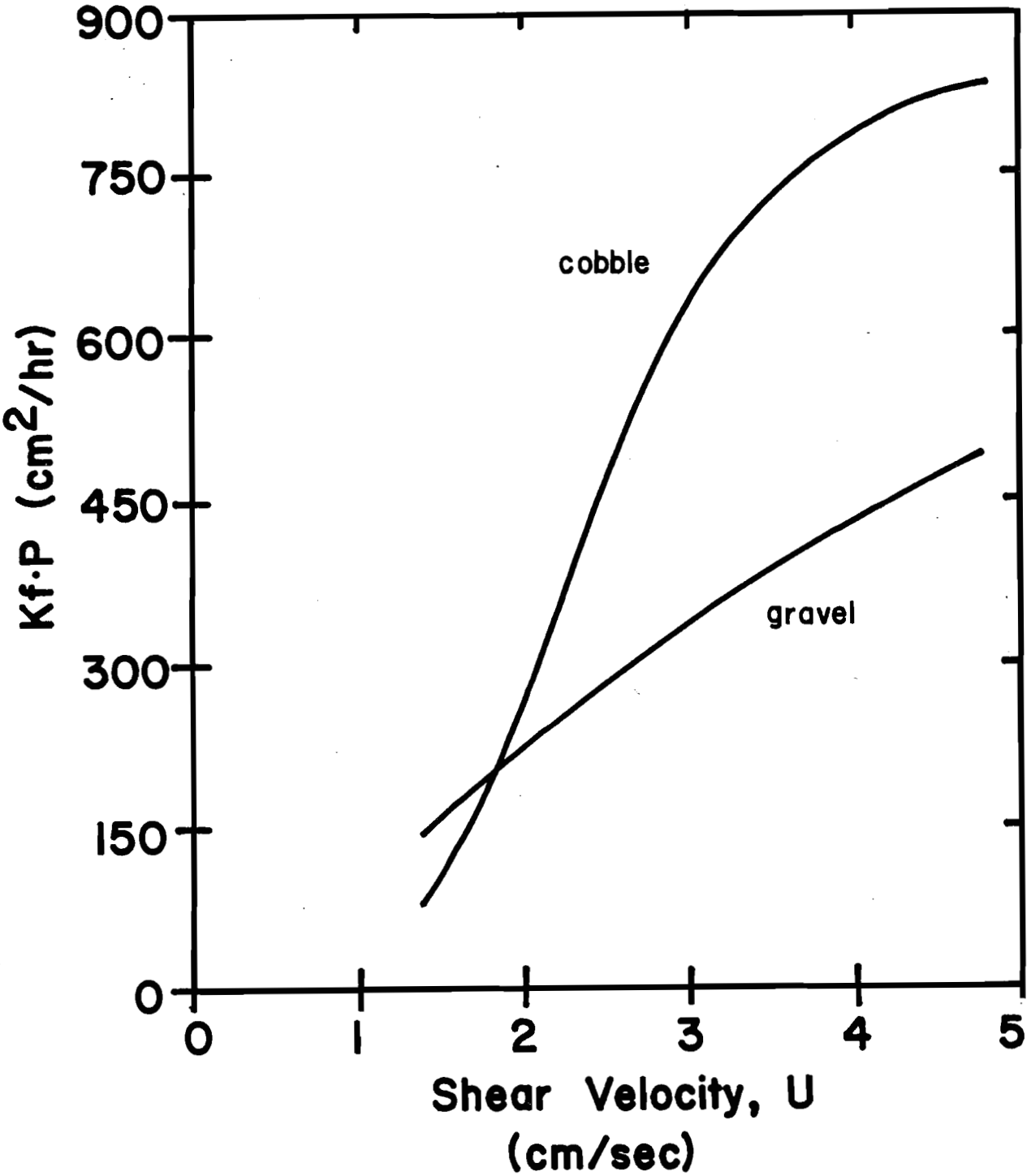

Figure 27. Comparison of Gravel and Cobble KfP Values When Both Streambeds are Acclimated to U = 2.5 cm/sec. The graph assumes that T = 20°C, PHI = 253 cm^{-1}, and D = 0.025 cm^2/hr.

developed or tested. KfP values were calculated by Equation 62 with Km values determined from the respective mass transfer equations. Water temperatures were assumed to be 20°C, and thus PHI was set to 253 cm^{-1}.

A comparison of the calculated KfP values for gravel and cobble streambeds is shown on Figure 27. Except for shear velocities less than 1.8 cm/sec, the cobble streambed removed COD at faster rates than did the gravel streambed, despite the gravel streambed having a greater geometric surface area. As expected from the respective mass transfer equations, the rate at which cobble streambed removed COD from the artificial stream was more sensitive to changes in shear velocity than was the gravel streambed.

The lower and less sensitive KfP values for the gravel streambed were probably caused by two factors. First, the physically smaller interstitial voids of the gravel streambed, compared to those of the cobble streambed, limited the mass transport of COD to the deeper biofilms, which made the amount of active surface area in the gravel streambed a smaller percentage of the geometrically available area than in the cobble streambed. In addition, by limiting the extent to which turbulence could penetrate into the streambed, the smaller interstitial voids of the gravel streambed were responsible for decreasing the sensitivity of removal rates to changes in shear velocity.

Second, the upper surfaces of the gravel streambed were, at most, 50 percent covered with macroscopically visible biofilms, while the upper surfaces of the cobble streambed were completely covered. Novotny (1969) also noted that gravel streambed particles had only a fraction of their exposed surface area colonized by biofilms, while the exposed surfaces of cobble streambed particles tended to be completely covered with biofilms.

Thus, despite having a greater geometric surface area, the gravel streambed may have had less biofilm-covered area than did the cobble streambed.

In summary, streambed particle size and the corresponding size of the interstitial voids influenced both the magnitude of the COD removal rates and sensitivity of COD removal rates to changes in stream velocity.

Conclusions

The artificial stream experiments demonstrated that water velocity had both short-term and long-term effects on the rate at which streambed biofilms removed contaminants from the water column. Streambed biofilm activity was defined by

$$KfP = \frac{Km\ Df\ PHI\ P/W\ W}{Km + Df\ PHI} \tag{77}$$

in which KfP is a measure of streambed biofilm activity per unit stream length (cm^2/hr), Kf is the first-order flux constant (cm/hr), P is the amount of active biofilm surface area per unit streambed length (cm), Km is the apparent, overall mass transfer coefficient (cm/hr), Df is the diffusivity of COD in the streambed biofilms (cm^2/hr), PHI is a characteristic biofilm kinetic parameter (cm^{-1}), and W is the width of the artificial stream channel (cm). For the short-term experiments, P/W was set equal to the available geometric surface area per unit stream channel width. In assessing the long-term effects of stream velocity, P/W was replaced by P/W(acc), which was used to account for changes in streambed biofilm biomass at different acclimation velocities.

The short-term effects were observed by noting the changes in streambed removal rates when stream velocities differed from the acclimation velocity

for brief periods of time. From these observations, overall mass transfer equations were developed. The overall mass transfer equation for the gravel streambed (DP = 1.6 cm) was

$$Km = 2.29\ 10^{-3}\ Re^{1.42}\ Sc^{1/3}\ \frac{D}{Dp} \tag{74}$$

and the overall mass transfer equation for the cobble streambed (Dp = 6.0 cm) was

$$Km = 4.17\ 10^{-12}\ Re^{4.24}\ Sc^{1/3}\ \frac{D}{DP} \tag{75}$$

in which Re is the shear Reynolds number (dimensionless),

$$Re = \frac{3600\ U\ Dp}{KVIS} \tag{34}$$

U is the shear velocity (cm/sec) to which the streambed is exposed, Dp is the mean diameter of the streambed particles (cm), KVIS is the kinematic viscosity of water (cm^2/hr), D is the diffusivity of COD in water (cm^2/hr), and Sc is the Schmidt number (KVIS/D).

Becasue the Reynolds numbers in both overall mass transfer equations were raised to powers significantly greater than 1/2, streambed removal rates by biofilms were more sensitive to short-term changes in water velocity than would be predicted by existing mass transfer equations, which assume that reactive surface area remain constant with changes in mass transport rates. Because open channel flow created vertical gradients of local mass transfer rates within a streambed, changes in stream velocity altered the distribution of mass transfer coefficients within the streambed, the net result being that the amount of active surface area within a

streambed was a function of mass transfer rates. Therefore, the sensitivity of COD removal rates in the gravel and cobble artificial streams to short term changes in stream velocity demonstrated that velocity influenced contaminant removal rates by not only affecting the magnitude of mass transfer rates, but also by determining the amount of streambed surface area active in contaminant removal.

The long term effects of stream velocity on substrate removal rates were assessed by acclimating a cobble streambed to several different stream velocities. The rate of COD removal by the cobble streambed increased with acclimation velocity at a rate faster than due to an increase in the overall mass transfer coefficient alone. This additional increase in the rate of COd removal with acclimation velocity was caused by an increase in biofilm biomass. For the cobble streambed, the relationship between acclimation velocity and biofilm biomass--indexed by the P/W(acc) parameter-- was described by the following equation:

$$P/W(acc) = 5.21\ U^{0.2} \qquad (76)$$

for acclimation shear velocities (U) between 1.9 and 3.1 cm/sec. Therefore, the long term exposure to the more favorable mass transfer regime associated with faster stream velocities allowed the streambed biofilm community to accumulate more biomass.

The gravel and cobble overall mass transfer equations can not be applied to the other streambed, apparently because streambed porosity and interstitial void size influence overall mass transfer rates. Although porosity and void size are directly related to streambed particle size, the shape of the streambed particles and particle packing are also determining

factors. Since the developed mass transfer equations appear to be streambed-particle-size specific, mass transfer equations need to be developed for other types of streambeds.

Application of Results

Gantzer (1986) utilized the mass-transport equations developed in this chapter for modeling water quality in cobble-and gravel-lined streams. The simulations using biofilm activity predicted significantly faster rates of contaminant removal that did conventional water-quality models that employed only suspended reactions. The simulations suggested that when water quality models based only on a suspended kinetics are applied to shallow rock-lined streams, they probably underestimate contaminant removal and misrepresent the mechanisms by which contaminant - removal kinetics are controlled. This misrepresentation can invalidate existing models.

The simulations also suggested that streambed biofilms contributed a major portion of the suspended biomass through streambed scour.

The simulations suggested that the continued application of suspended-kinetics-based water quality models to shallow rock-lined streams could be a mixed blessing in terms of environmental protection. First, since the suspended kinetics simulations predicted slower substrate removal rates than did the simulations that included biofilm kinetics, management schemes based on the results of suspended kinetics models would "over protect" the stream's biota from individual contaminants what might be toxic. By "over protecting" the stream, dischargers of the contaminants would have greater treatment costs.

Second, in terms of managing dissolved oxygen concentrations in shallow rock-lined streams, the application of suspended kinetics could "under protect" the stream's biota. The simulations suggested that water quality models based on biofilm kinetics would predict faster rates of BOD removal by oxidation than would models based on suspended kinetics. In shallow streams with high reaeration rates, the difference between the two predicted deoxygenation rate constants would only slightly affect dissolved oxygen concentrations and probably would not significantly alter management schemes. However, for shallow streams with low reaeration rates, the simulations suggest that management decisions based on suspended kinetics may not adequately protect stream dissolved oxygen concentrations. Therefore, depending on stream reaeration rates, the determination of allowable stream BOD loading by models based on suspended kinetics could be detrimental to the stream's biota.

The cobble and gravel simulations indicated that when streambed biofilms are largely responsible for initial contaminant removal, stream water quality models should include biofilm kinetics or else poor predictions may result. However, the a priori determination of streambed biofilm importance, i.e., should biofilm kinetics be included in a stream water quality model, depends on the interactions between several kinetic and stream channel parameters. The relative importance of streambed biofilms in contaminant removal can be estimated by the following equation,

$$\text{RATIO} = \frac{H\ K\ Xs}{Kf\ P/W} \tag{78}$$

When RATIO is greater than 1, biofilm kinetics are more important than suspended kinetics. Increases in stream depth (H) or suspended microbial

biomass concentrations (Xs) decreases the importance of streambed biofilms. If sand were to fill in the interstitial voids of a cobble streambed, then the resulting decrease in P/W would decrease the importance of streambed biofilms in determining contaminant removal rates. If the suspended microorganisms were not acclimated to the contaminant (low K) and the streambed biofilms were acclimated (high K used in calculation on Kf), then the importance of streambed biofilms would be increased.

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