THE EFFECTS OF CORAL-ROUGHNESS ON MASS TRANSFER

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Abstract

The uptake of nutrients (nitrogen and phosphorus compounds) into coral reef communities is proposed to be limited by diffusion through a depleted boundary layer between the water and the organisms, or what is termed "mass transfer limitation". Theory from the engineering literature indicates that increased surface roughness should increase mass transfer; thus in this project the effects of coral-roughness on mass transfer were investigated experimentally using the dissolution of gypsum (plaster-of-paris) in fresh water from coral-shaped surfaces. The dissolution rate was measured as an increasing concentration of calcium ions over time in a flume of constant volume. The technique was first applied to a flat, smooth surface of gypsum over a wide range of temperatures and ionic strength. Stanton numbers (Stm, a dimensionless number giving the ratio of uptake rate per unit area to the rate of advection of the substance past the uptake surface) of experimental smooth surfaces ranged from 2.6-3.5 x10^{-5} and were within 15% of engineering literature values. Stanton numbers for coral-shaped surfaces ranged from 70 x 10^{-5} at 0.03 m s^{-1} to 17 x 10^{-5} at velocities up to 0.50 m s^{-1}, and were in general 9 ± 1 times that of smooth surfaces. The results are compared (using Stm) with flume studies on experimental coral communities, and engineering literature. The relationship between mass transfer, friction and roughness of coral-shaped gypsum surfaces can be predicted from correlations of heat transfer from sand-roughened pipes. Results presented provide confirmation of Bilger and Atkinson's (1992) model of nutrient uptake being mass-transfer limited and can be used to predict nutrient-uptake into living coral reef communities.
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<tr>
<td>A</td>
<td>projected area $[m^2]$</td>
<td>$k_\sigma$ standard deviation of roughness</td>
</tr>
<tr>
<td>$A_c$</td>
<td>cross sectional area $[m^2]$</td>
<td>element height $[m]$</td>
</tr>
<tr>
<td>a</td>
<td>activity</td>
<td>$k_{1,2,\ldots}$ other roughness scales $[m]$</td>
</tr>
<tr>
<td>C</td>
<td>concentration $[mol \cdot m^{-3}]$</td>
<td>$L$ length $[m]$</td>
</tr>
<tr>
<td>$c_f$</td>
<td>friction coefficient</td>
<td>$m_s$ flux from surface $[mol \cdot m^{-2} \cdot s^{-1}]$</td>
</tr>
<tr>
<td>D</td>
<td>diffusivity $[m^2 \cdot s^{-1}]$</td>
<td>$m$ molality of chemical species</td>
</tr>
<tr>
<td>$D_h$</td>
<td>hydraulic diameter $[m^2]$</td>
<td>$n$ quantity of chemical species</td>
</tr>
<tr>
<td>F</td>
<td>thermodynamic force</td>
<td>$n$ Manning roughness parameter $[m^{1/6}]$</td>
</tr>
<tr>
<td>G</td>
<td>Gibb's free energy</td>
<td>$P$ perimeter $[m]$</td>
</tr>
<tr>
<td>$GPE$</td>
<td>gravitational potential energy $[J]$</td>
<td>$p$ pressure $[Pa]$</td>
</tr>
<tr>
<td>g</td>
<td>gravity $[m \cdot s^{-2}]$</td>
<td>$Pr$ Prandtl number</td>
</tr>
<tr>
<td>H</td>
<td>head $[m]$</td>
<td>$R$ universal gas constant $[J \cdot K^{-1} \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>h</td>
<td>height $[m]$</td>
<td>$Re$ Reynolds number</td>
</tr>
<tr>
<td>I</td>
<td>ionic strength</td>
<td>$Re_k$ Reynolds roughness number</td>
</tr>
<tr>
<td>J</td>
<td>flux $[mol \cdot m^{-2} \cdot s^{-1}]$</td>
<td>$s$ slope $[m \cdot m^{-1}]$</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium constant</td>
<td>$s_d$ drift speed $[m \cdot s^{-1}]$</td>
</tr>
<tr>
<td>KE</td>
<td>kinetic energy $[J]$</td>
<td>$Sc$ Schmidt number</td>
</tr>
<tr>
<td>K</td>
<td>constant</td>
<td>$Sc_t$ turbulent Schmidt number</td>
</tr>
<tr>
<td>k</td>
<td>constant</td>
<td>$Sh$ Sherwood number</td>
</tr>
<tr>
<td>k'</td>
<td>roughness element height $[m]$</td>
<td>$St_k$ roughness Stanton number</td>
</tr>
<tr>
<td>$k_s$</td>
<td>equivalent sand-grain roughness $[m]$</td>
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</table>
\( \text{St}_m \) Stanton number for mass transfer

\( T \) temperature [K]

\( U \) velocity [m s\(^{-1}\)]

\( u^* \) friction velocity [m s\(^{-1}\)]

\( V \) volume of flume [m\(^3\)]

\( W \) width [m]

\( x \) thickness of diffusive boundary layer [m]

\( z \) valence

\( \alpha \) angle of slope with horizontal wetted area / projected area ratio

\( \gamma \) activity coefficient

\( \mu \) chemical potential [J mol\(^{-1}\)]

\( \nu \) kinematic viscosity [m\(^2\) s\(^{-1}\)]

\( \rho \) density [kg m\(^{-3}\)]

\( \tau_w \) wall shear stress [N m\(^{-1}\)]

\textbf{Subscripts / Superscripts}

\( b \) bulk

\( w \) wall

\( \emptyset \) standard state

1,2,3.. chemical species

1 upstream of sample

2 downstream of sample
It seems appropriate, before so mechanically discussing the workings of coral reef ecosystems, to dwell briefly on the words of one of the first to marvel at the simple existence of coral reefs:

"The organic forces separate the atoms of carbonate of lime, one by one, from the foaming breakers, and unite them into a symmetrical structure. Let the hurricane tear up its thousand huge fragments; yet what will that tell against the accumulated labour of myriads of architects at work night and day, month after month? Thus do we see the soft gelatinous body of a polypus, through the agency of the vitals laws, conquering the great mechanical power of the waves of an ocean which neither the art of man nor the inanimate works of nature could successfully resist".

Charles Darwin, Voyage of the Beagle (1836)
Introduction

The transfer of dissolved compounds to and from a solid surface is fundamental to many processes in engineering, biology, chemistry and geology. Examples in these disciplines include industrial electrochemical processes, the growth and metabolism of organisms, the dissolution and precipitation of minerals, and the formation and destruction of geological features.

In a turbulent flow, when the reaction rate at the surface is fast compared to diffusion through the fluid, transfer rate between the fluid and the surface becomes dependent on the velocity of the fluid. This velocity dependence has been observed in natural environments (Atkinson and Bilger, 1992; Jumars and Nowell, 1984) and laboratory setups (Selman and Tobias, 1978; Grifoll et al., 1986). Under the condition of velocity dependence, transfer rate is generally considered to be mass-transfer limited.

Roughness of the surface can influence the turbulence and velocity of the fluid near the surface. Roughness is ubiquitous in natural environments, occurring on both organic and inorganic surfaces. The investigation of the transfer of chemical species to and from a rough living surface has been conducted in terrestrial environments (Raupach and Thom, 1981), and marine systems (Boudreau and Guinasso, Jr., 1978; Atkinson and Bilger, 1992; Bilger and Atkinson, 1995; Thomas and Atkinson, 1996). A strong correlation between flow characteristics such as bulk velocity and turbulence with metabolic rate has been a theme of the above cited studies.

A characteristic common to most of the laboratory studies in engineering literature is an ordered rough surface, with only one scale of relatively small roughness element heights (Dawson and Trass, 1972; Tantirige and Trass, 1984; Reynolds, 1975;
Lee and Soliman, 1977; Weber, 1979; Steward 1987; Grifoll et al., 1986; Herrero et al., 1991, 1994). Naturally rough surfaces, such as those studied in biology (Atkinson, 1992) and geology (Boudreau and Guinasso, Jr., 1978), are typically disorderly, often with large variation in roughness scales, and large surface area to projected area ratios.

Bilger and Atkinson (1992) attempted to use the engineering literature to explain field measurements for the uptake of phosphate and ammonia on coral reef flats. They concluded that "regardless of the mechanism, it has been shown that P [phosphate] uptake on a large coral reef flat is anomalously fast when compared with existing engineering literature on mass transfer." The velocity dependence of mass transfer (Atkinson and Bilger, 1992) indicates that the rate limiting step is diffusion through the boundary layer. In other words, the nutrient uptake is mass-transfer limited. The "anomalously fast" transfer rate suggests a difference in the boundary layer structure between the ordered rough laboratory environments and rough field environments.

Atkinson (1992) applied mass-transfer limited relationships from Bilger and Atkinson (1992) and Atkinson and Bilger (1992), to obtain good agreement between predicted and measured productivity of Enewetak Atoll reef flats. Furthermore, Thomas and Atkinson (1996) experimentally showed a strong correlation between uptake-rates of ammonia, energy dissipated and roughness of four different reef communities, confirming ammonium-uptake is mass transfer limited.

The higher rates of mass transfer observed in natural environments compared to engineering experiments could be geometric in origin, such as: different scales of roughness (Atkinson, 1992); the proposed fractal nature of the surface (Bilger and Atkinson, 1992); a different surface area to projected area ratio; or a preference for more
effective shapes. These geometric phenomena would also be present on an inorganic surface of the same shape with a dissolution rate which is mass-transfer limited. Alternatively, the enhancement could be due to uniquely biological structures such as: "surface slimes" or the "action of cilia and flagella of microscopic organisms" (Bilger and Atkinson, 1992); the elastic properties of the surface (Peskin and McQueen, 1995); or a non-Newtonian mucus layer. An enhancement due to biological structures in the boundary layer, however, would not be observed on an inorganic mineral surface.

The commercial grade of gypsum, plaster-of-paris, can be molded into coral shapes, and the dissolution rate of gypsum in water is mass-transfer limited (Barton and Wilde, 1971). Thus the goal of this research is to use an analog, the dissolution of gypsum, to investigate the effects of coral-roughness on mass transfer, and to compare these results with measurements of nutrient-uptake on experimental and field coral communities. The results may also indicate the feasibility of similar mass transfer studies on disordered rough surfaces throughout the natural sciences.

The fluxes of different chemical species in varying mediums and concentrations can be compared using a set of non-dimensional parameters common to engineering literature. Fluxes are described by a rate coefficient called the Stanton number, and are compared at similar flow conditions, as measured by the friction factor, Reynolds roughness number and Schmidt number. The engineering methods provide a direct comparison of the fluxes on a living coral community to an inorganic coral-shaped surface.
The experimental flume used in this study was geometrically similar to the flume used for the Atkinson and Bilger experiments of 1992-1995, and those used in many engineering studies.
Background

As fluid flows past a stationary wall a gradient in velocity is observed from the wall to the center of the flow. The region of the flow where the velocity changes from that at the wall to 99% of the freestream flow is called the momentum boundary layer. Natural fluid flows are often turbulent. In turbulent flows, the velocity gradients are steep at the wall, and the momentum boundary layer is thin (John and Haberman, 1988). Turbulence is responsible for convective transport of momentum (and, as shall been seen later, heat and mass) which is orders of magnitude quicker than diffusive transport. The transport of momentum by turbulence quickly homogenizes the fluid away from the wall. As a result, there are only small velocity gradients within the bulk flow where turbulence proliferates, but steep gradients close to the wall, where momentum is transported by diffusion.

Turbulence is also responsible for convective transport of heat and mass transfer, which is orders of magnitude faster than diffusive mass and heat transfer. In a turbulent flow, dissolved compounds in the bulk fluid move equally in all directions, resulting in a well-mixed volume, with no chemical potential gradient. Close to the wall, however, velocity decreases, and all transport is by diffusion. Thus, a fast rate of input or removal of dissolved compounds at the wall creates a chemical potential gradient. For a chemical flux to occur from the bulk volume to the surface, it must be transported by diffusion down the chemical potential gradient.

The diffusive sublayer is a thin region close to the wall where transport is down chemical potential gradients towards the wall. The outer extension of the diffusive sublayer is set by the point at which the fluid velocity perpendicular to the wall
approaches zero. As water velocity across a surface is increased, the flow becomes more turbulent, the diffusive sublayer becomes thinner, and the chemical potential gradient is increased.

The diffusive sublayer thickness is therefore set by the physical - not chemical - characteristics of the flow. Mass transport to the wall in the diffusive sublayer can only occur by diffusion, which is orders of magnitude slower than convective transport within the bulk fluid. The transport of dissolved compounds to and away from the surface is determined by the slowest or rate limiting step: diffusion through the diffusive sublayer.

The chemical potential, \( \mu \), in a one-chemical system is defined (Atkins, 1994) as:

\[
\mu = \mu^0 + RT \ln \left( \frac{p}{\bar{\varnothing}} \right)
\]

where \( R = 8.315 \text{ [J K}^{-1} \text{ mol}^{-1}] \) is the universal gas constant, \( T \) is temperature [K], \( p \) is pressure, and \( \bar{\varnothing} \) signifies a property at a standard state. In a multi-component system, the chemical potential of one species is a function of changing chemical potential of other components as well. The chemical potential of a chemical species in an infinite species system is most generally defined as:

\[
\mu_1 = \left( \frac{\partial G}{\partial n_1} \right)_{p,T,n_2,n_3,...}
\]

where \( G \) is total Gibb's free energy, and \( n_1 \) is the quantity of species 1 in solution.

Diffusion is the movement of a chemical species from one energy level to another energy level a distance away, and will be considered as a thermodynamic force per mole, \( F \) [J m\(^{-1}\) mol\(^{-1}\), kg m s\(^{-1}\) mol\(^{-1}\), or N mol\(^{-1}\)]. We can now write the force \( F \) as a change in chemical potential per unit length, \( \partial x \):

\[
F = -\left( \frac{\partial \mu}{\partial x} \right)_{p,T,n_1,n_2,...}
\]
Another force that can exist in a chemical potential gradient is due to an electric field. In the case of charge separation of ion species without an external electric field being applied, such as found in this study, the force will be relatively small, and will not be included in the analysis. To work towards a more familiar relationship for diffusion, we return to a single component system, without an electric field, and we obtain from Eq. 1:

$$\mu = \mu^\circ + RT \ln a$$  \hspace{1cm} (4)

where the activity, $a$, of the one species is defined as the 'effective' mole fraction or pressure, relative to that a standard state. i.e., $a = \left( p / p^\circ \right)$.

The thermodynamic force is the gradient in chemical potential. Substituting Eq. 4 into Eq. 3 gives:

$$F = -(d / dx)\left\{ \mu^\circ + RT \ln a \right\} = RT(\partial \ln a / \partial \chi)_{p,T}$$  \hspace{1cm} (5)

The activity is given by: $a = \gamma C$ where $\gamma$ is the activity coefficient. In an ideal solution, or when the dissolved chemical species is infinitely dilute, $\gamma = 1$, and $a = C \text{ [mol m}^{-3}\text{]}. Since (d/dx)ln C = (1/C)(dC/dx), (5) becomes:

$$F = -\left( RT/C \right)(\partial c / \partial \chi)_{p,T}$$  \hspace{1cm} (6)

In the presence of a chemical potential gradient, the thermodynamic force, $F$, results in the relative motion of the chemical species. A force balance may be constructed by balancing the thermodynamic force (Eq. 6) moving Gibb's free energy down the chemical potential gradient, with the viscous drag that opposes the motion. The viscous drag will be proportional to the viscosity of the solvent and the atomic radius of the solute. The balance is achieved at a drift speed, $s_d$, proportional to $F$. A drift speed, $s_d \text{ [m}$
relative to a volume of solution \([m^3]\), gives rise to a flux, \(J = s_d C = kFC\) (where \(J\) is a flux \([mol \, m^{-2} \, s^{-1}]\), and \(k\) is a constant \([m^2 \, mol^{-1} \, s^{-1}]\)). Solving for the flux, \(J\), gives:

\[
J = -(kRT)(\partial C/\partial x)_{p,T}
\]  

Eq. 7 has the form of Fick's 1st law, where \(D_{12} = kRT \, [m^2 \, s^{-1}]\), the diffusion coefficient of species 1 through species 2, is a constant. Fick's 1st law is often a good approximation of the diffusion of chemical species down chemical potential gradients.

The dissolution of gypsum in a fluid of changing ionic strength, \(I\), and temperature, however, departs significantly from ideal Fick's law behavior with constant \(D_{12}\). The methodology to quantify the non-ideal behavior of the mass transfer of a chemical species to and from a rough surface in a turbulent flow is the focus of the rest of this section, and lays the foundation for using the dissolution of gypsum as an experimental analogue for nutrient uptake on coral reefs.

Non-dimensionless Analysis

Quantities that influence the transport-rate of chemical species\(^1\) (\(J\) in the previous sections, but from now on referred to as \(m_s\)) to and from a surface include:

1. Kinematic viscosity of the fluid, \(\nu \, [m^2 \, s^{-1}]\).
2. Density of the fluid, \(\rho \, [kg \, m^{-3}]\)
3. Ratio of the volume of the flume to the projected area of the sample, \(V/A \, [m]\).
4. Diffusivity of the chemical species 1 through species 2, \(D_{12} \, [m^2 \, s^{-1}]\).
5. Chemical potential gradient, \(\mu_w - \mu_b\), or more simply the concentration

\(^1\) The effects of temperature and ionic strength on mass transfer can be measured indirectly as a change in the viscosity, density and diffusivity of the fluid.
gradient, $C_w - C_b$ [mol m$^{-3}$].

6. Bulk velocity of fluid, $U_b$ [m s$^{-1}$].

7. Roughness height, $k$ [m].

To compare the dissolution of gypsum to nutrient uptake on coral reefs we must take into account the seven above-listed variables ($v$, $\rho$, $V/A$, $D$, $C_w - C_b$, $U_b$ and $k$). To experimentally investigate the effect of each variable would be a very lengthy and expensive process. For example, to take 10 measured points for each variable while holding the other variables constant would require $10^7$ measurements. Furthermore, a correlation with seven variables would be overly complex and prone to error propagation.

Fundamental fluid dynamics texts (John and Haberman, 1988) detail a method (Buckingham-Pi theorem$^2$) of reducing the number of physical variables required to describe a mass transfer on a rough surface. The above seven quantities contain only three fundamental units: mass, length, and time. It is therefore predicted by the Buckingham-Pi theorem that $7 - 3 = 4$ dimensionless groups of variables will describe the mass-transfer rates. Dipprey and Sabersky (1963) use the Stanton number, $St_m$, the friction coefficient $c_f$, the Schmidt number, $Sc$, and the Reynolds roughness number, $Re_k$. This leaves us with only four dimensionless groups which influence mass transfer.

The following theoretical development will derive these dimensionless groups, and how they can be calculated from measurable quantities. With this achieved, we will be able to compare the dissolution of gypsum from coral-shapes to nutrient uptake on coral reefs.

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$^2$ The description and justification of this method are well detailed in most fundamental fluid dynamics texts.
Momentum Transport

Moving water in a recirculating flume must maintain a balance of the kinetic energy (KE), gravitational potential energy (GPE) and energy dissipation by friction. In the absence of an acceleration of the volume of water, and in order to conserve mass, the KE of the fluid will not change over time. The friction dissipation must therefore be balanced by a loss in GPE. The loss in GPE over a distance results in a slope on the surface of the water (Fig. 1). The rougher the surface, the larger the friction dissipation by the surface, and therefore the greater the loss in GPE required to balance the loss of energy due to friction. The greater change in GPE is observed as a steeper slope (Fig. 2).

For steadily flowing water in the empty flume (Fig. 1), a force balance on a volume of fluid in a flume with friction on the bottom and sides is summarized as:

\[
\rho g L W h s = \tau_w (L W + 2 L h) = \left(\frac{c_f}{2}\right) \rho U_b^2 (L W + 2 L h)
\]

where \(\rho\) is density \([\text{kg m}^{-3}]\); \(g\) is acceleration due to gravity \([\text{m s}^{-2}]\); \(L, W, h\) are the length, width and height \([\text{m}]\) of the volume of water; \(s\) is the slope of the water \([\text{m m}^{-1}]\); and \(\tau_w\) is the wall shear stress \([\text{N m}^{-1}]\). \(c_f\) is the dimensionless friction coefficient, defined as:

\[
c_f \equiv \frac{\tau_w}{\rho U_b^2 / 2}
\]

The friction coefficient, \(c_f\), is a dimensionless measure of the shear stress arising from both skin friction and form drag. The experimental flume is filled to \(W \approx 2h\), and solving for \(c_f\) from Eqs. 8 & 9:
\[ c_f = \frac{2gWh_s}{U_b^2(W + 2h)} \approx \frac{gW_s}{2U_b^2} \]  

From readily measurable variables, the friction coefficient can now be obtained.

The friction coefficient, along with other dimensionless parameters, has been used in empirical correlations for estimating other property transport phenomena such as heat transfer in roughened pipes (Dippery and Sabersky, 1963), mass transfer on grooved surfaces (Dawson and Trass, 1972), and nutrient-uptake on coral reefs (Bilger and Atkinson, 1992).

For flow in the flume, the Reynolds number, the ratio of inertia forces to viscous forces, is defined as:

\[ \text{Re} \equiv \frac{U_b D_h}{\nu} \]  

where \( U_b \) [m s\(^{-1}\)] is the bulk velocity of the fluid over the surface, \( D_h \) [m] is the hydraulic diameter, and \( \nu \) [m\(^2\) s\(^{-1}\)] is the kinematic viscosity. The hydraulic diameter of the flume is given as (Kays and Crawford, 1993):

\[ D_h = \frac{4 A_c}{P} \quad D_{h,\text{smooth}} = \frac{4 \times 0.4 \times 0.2}{0.4 + 0.2 + 0.2} = 0.4 \]  

where \( A_c \) [m\(^2\)] is the cross-sectional area of the flow, and \( P \) [m] the perimeter of the flow experiencing a shear-stress. For the empty flume, the friction coefficient of the air-water interface, \( c_{f,\text{air}} \), will be small compared to the sides, \( c_{f,\text{side}} \), and the bottom, \( c_{f,\text{bottom}} \). The hydraulic diameter for this smooth flow is \( D_h = 0.4 \). The Reynolds number can now be calculated, given \( D_h, U_b, \rho, \) and \( \mu \).

The Manning formula [John and Haberman, 1988] is an experimentally derived relationship for the slope of the water surface as a function of velocity:
\[ U_b = \frac{0.820}{n} \left( \frac{A_c}{P} \right)^{2/3} \sqrt{\sin \alpha} \]  

(13)

where the Manning roughness parameter is \( n = 0.01 \text{ m}^{1/6} \) for a smooth surface, and \( \alpha \) is the angle of the slope with the horizontal.

When rough objects are placed in the bottom of the flume (Fig. 2), the friction due to the side walls becomes small compared with the bottom. The flow acts as though the walls were not there because the presence of the walls has only a small effect on flow compared to the bottom. This is a similar condition to an open channel, such as a reef flat. A similar equation development as above for an open channel - describing the flume with a rough bottom - is given by Bilger and Atkinson (1992), with Eqs. 8, 10, & 12 becoming:

\[ \rho g L W s = \tau_w L W = \left( \frac{c_f}{2} \right) \rho U_b^2 L W \]  

(14)

\[ c_f = \frac{2ghs}{U_b^2} \]  

(15)

\[ D_{h, \text{rough}} = 4h = 0.8m \]  

(16)

Bilger and Atkinson (1992) choose Haaland's (1983) relationship, modified for an open channel, to describe the friction coefficient in terms of roughness heights, height of the water, and the Reynolds number. Haaland's relationship gives a similar result to the Manning equation, but is specific to open channel type flows:

\[ \left( \frac{c_f}{2} \right)^{-1/2} = -5.1 \log_{10} \left[ \frac{6.9}{\text{Re}} + \left( \frac{k_s}{14.8h} \right)^{1.17} \right] \]  

(17)

where \( k_s \) is the equivalent sand-grain roughness, as defined by Schlichting (1955). Both the Manning and Haaland relationships provide useful comparisons between the performance of the flume used in this study and those of previous investigators.
Mass Transport

The primary aim of this study is to investigate the mass transfer characteristics of an inorganic coral-shaped surface in characterized laboratory flows. As shown in Fig. 3, conservation of mass of a chemical species, given no sources or sinks within the fluid, requires that:

$$\text{Flux}_{\text{out, bottom}} = \text{Flux}_{\text{in}} - \text{Flux}_{\text{out, front}} \quad (18)$$

Using the notation in Fig. 3, Eq. 18 requires:

$$-mWdx = U_h h W dC_b \quad (19)$$

where $C_b \ [\text{mol m}^{-3}]$ is the average bulk concentration, $C_w$ is the concentration at the wall, and $dx$ is an elemental length of the fluid volume. To compare the flux of different chemicals over different concentration gradients, a non-dimensional flux, the Stanton number ($St_m$) is introduced (Eq. 20).
Figure 1. Illustration of the flume during a smooth surface experiment. The velocity is measured by timing a drogue placed in the flow. The slope is measured by a pressure drop across the reactive surface. The slope balances the friction dissipation with a loss in gravitational potential energy.
Figure 2. Illustration of flume during coral-rough surface experiments. The slope of the water is greater than that over a smooth surface, due to a higher frictional resistance of the coral. Roughness is measured at 1 cm intervals along the sample.
The Stanton number is defined as the advection of a substance past the surface divided by the uptake of that substance on the reacting surface (Eq. 20).

\[
St_m = \frac{m_s}{U_b (C_b - C_w)}
\]  

(20)

The St_m can be thought of as the ratio of the uptake rate, \( (m_s, \text{mol m}^{-2} \text{s}^{-1}) \) to the rate of a the substance that is carried, or advected, past the uptake surface \( (U_b(C_b - C_w)) \). Using the conservation of mass (Eq. 19), and our newly defined St_m (Eq. 20), we obtain:

\[
dC_b = -\frac{m_s}{U_b} \left( \frac{dx}{h} \right) = -St_m (C_b - C_w) \frac{dx}{h}
\]  

(21)

Experimentally, a strong correlation between momentum transport and mass transport is observed (Kays and Crawford, 1993). Thus, the Schmidt number (Sc), a non-dimensional ratio of the diffusivity of momentum and mass is used in equations to predict St_m:

\[
Sc = \frac{\nu}{D_{12}}
\]  

(22)

Sc is therefore the ratio of molecular diffusivity of momentum, \( \nu \text{ m}^2 \text{s}^{-1} \), to molecular diffusivity of mass, \( D_{12} \text{ m}^2 \text{s}^{-1} \). Diffusivity is a function of ionic strength, \( I \), and temperature, \( T \text{ K} \). Ionic strength is defined (Atkins, 1994) as:
\[ I = \frac{1}{2} \sum_j \left( \frac{m_j}{m^\ominus} \right)^2 z_j^2 \]  

where \( m_j = \) molality species \( j \), \( m^\ominus = \) molality of solute, and \( z_j^2 = \) valence of species \( j \).

To compare measured \( St_m \) from different experiments and to other studies, \( Sc \) of the chemical species at the time of measurement must be determined. \( Sc \) is strongly a function of temperature and ionic strength, and both must therefore be measured throughout experimentation.

Given identical flow conditions (and therefore friction factor \( c_f \)), it should be expected that \( St_m \) will be a function of \( Sc \) only. Therefore, we can study the fluxes of one chemical species by substituting a different chemical of measurable \( Sc \) under the same flow conditions. A comparison of \( St_m \) for a smooth surface has been made by Steward (1987) fitting data of Shaw and Hanratty (1977) of \( 1730 < Sc < 37200 \), and infinite dilution to formulate:

\[ St_{m,\text{smooth}} = \sqrt{c_f/2} \left( 0.0575Sc^{-2/3} + 0.1184Sc^{-1} \right) \]  

As suggested above, for identical \( c_f \), \( St_m \) is a function of \( Sc \) only. It should be noted that the use of Eq. 24 required extrapolation to \( Sc = 1250 \).

The non-ideal effects of ionic strength and temperature variation on diffusion (Eq. 1-7) in general have not been applied in mass transfer studies. Thus using a changing diffusivity in the \( Sc \) (Eq. 22) is unique. This combination of physical chemistry and engineering mass-transfer formulations provides the basis for experimentation on naturally rough surfaces using the dissolution of gypsum.

Stanton numbers calculated from the dissolution of coral-shaped gypsum can now be compared to the flux of nutrients to a live coral community. This fulfills the goal of
the experimentation: to determine if the origin of the mass transfer enhancement is geometric or biological. We need to calculate the Sc number of gypsum in fresh water of changing temperature and ionic strength. We must also learn to quantify flow conditions over a coral-rough surface in terms of Reₖ and cₙ.

**Mass Transfer of Gypsum**

As outlined in the introduction, the dissolution of coral-shaped gypsum will be compared to the uptake of nutrients on living coral. The dissolution of a mineral, forming two or more ions, differs from the uptake of a single compound, such as ammonia. These differences are discussed and corrected for in the following section.

When gypsum (CaSO₄•2H₂O) dissolves from a surface, Ca²⁺ and SO₄²⁻ ions are released in equal quantities into solution. With an equal flux of both ions, the bulk concentrations will be approximately equal:

\[
[\text{Ca}^{2+}]_b = [\text{SO}_4^{2-}]_b \quad (25)
\]

However, the rate of diffusion of the two species through water is different, Ca²⁺ being the slower of the two (Li and Gregory, 1974). The thickness of the diffusive sublayer, \(x\), is set by the point of no vertical motion of fluid in the momentum boundary layer, and applies equally to both chemical constituents. As a result, to maintain the same flux, bulk concentration and diffusive sublayer thickness, the chemical potential gradient of Ca²⁺ must be greater than SO₄²⁻.

From Eq. 20, we can derive an equal flux of Ca²⁺ and SO₄²⁻ over a chemical potential gradient as:

\[
m = St_{m,\text{Ca}} U_b ([\text{Ca}^{2+}]_w - [\text{Ca}^{2+}]_b) = St_{m,\text{SO}_4^{2-}} U_b ([\text{SO}_4^{2-}]_w - [\text{SO}_4^{2-}]_b) \quad (26)
\]
where the effects of changing ionic strength and temperature (making concentration gradient ≠ chemical potential gradient) are contained within the calculation of Sc (Eq. 22), St_m being a function of Sc (Eq. 24).

Dawson and Trass (1972) experimentally show for a chemical species with high Schmidt numbers that:

\[ \text{Sh} = 0.0153 \text{Re}^{0.88} \text{Sc}^{0.32} \quad (27) \]

where Sh = Sherwood number. The Sherwood number is the dimensionless concentration gradient at the surface, and provides a measure of the convective mass transfer occurring from the surface (Incropera and de Witt, 1990). Since St_m = Sh / ReSc, the ratio of Stanton numbers for Ca\(^{2+}\) and SO\(_{4}^{2-}\) is given by:

\[
\frac{St_{m, Ca^{2+}}}{St_{m, SO_{4}^{2-}}} = \frac{0.0153 \text{Re}^{-0.12} \text{Sc}^{-0.68}}{0.0153 \text{Re}^{-0.12} \text{Sc}^{-0.68}} \frac{\nu / D_{Ca^{2+}}}{\nu / D_{SO_{4}^{2-}}} = \frac{D_{Ca^{2+}}^{0.68}}{D_{SO_{4}^{2-}}^{0.68}} = \left( \frac{7.93 \times 10^{-10}}{10.7 \times 10^{-10}} \right)^{0.68} = 0.816
\]

(28)

where the diffusivity of Ca\(^{2+}\) and SO\(_{4}^{2-}\) at infinite dilution and at 25°C are given by Li and Gregory (1974). Now, for the equal flux condition to be met, using Eq. (26), canceling the bulk velocity U_b, and using the ratio of Stanton numbers in terms of diffusivity obtained from (28), we arrive at:

\[
\frac{D_{Ca^{2+}}^{0.68}}{D_{SO_{4}^{2-}}^{0.68}} = \frac{[SO_{4}^{2-}]_{w} - [SO_{4}^{2-}]_{b}}{[Ca^{2+}]_{w} - [Ca^{2+}]_{b}}
\]

(29)

Substituting the equal bulk concentration condition (Eq. 25) and solving for [Ca\(^{2+}\)]_b reveals:
\[
\left(1 - \frac{D_{Ca^{2+}}^{0.68}}{D_{SO_4^{2-}}^{0.68}}\right)[Ca^{2+}]_b = \left[SO_4^{2-}\right]_w - \frac{D_{Ca^{2+}}^{0.68}}{D_{SO_4^{2-}}^{0.68}}[Ca^{2+}]_w
\]  

(30)

The equilibrium constant at saturation, $K(T)$, of gypsum in fresh water, atmospheric pressure and varying temperatures is reasonably well known (Hardie, 1967). Since the wall is assumed to be at saturation:

\[K(T) = [SO_4^{2-}]_w[Ca^{2+}]_w\]  

(31)

Substituting Eq. 31 into Eq. 30 gives the quadratic equation:

\[
\frac{D_{Ca^{2+}}^{0.68}}{D_{SO_4^{2-}}^{0.68}}[Ca^{2+}]_b^2 + \left(1 - \frac{D_{Ca^{2+}}^{0.68}}{D_{SO_4^{2-}}^{0.68}}\right)[Ca^{2+}]_b[Ca^{2+}]_w - K(T) = 0
\]  

(32)

Since $[Ca^{2+}]_b$ and $K(T)$ are measured and calculated respectively, the positive root of Eq. 32 gives the value for $[Ca^{2+}]_w$. With this we can then calculate the concentration gradient using $[Ca^{2+}]_b$. By measuring velocity, $U_b$, and changes in $[Ca^{2+}]_b$ over time per unit area to obtain a flux, the Stanton number, $St_m$, can be calculated. As the ratio of diffusivity changes with temperature and ionic strength, and as $K(T)$ is also a function of temperature, it is necessary to solve Eq. 32 at each time interval throughout the experiment. So to obtain the $St_m$ and Sc numbers as derived above, we require the equilibrium constant, temperature, bulk velocity, kinematic viscosity, density, and $Ca^{2+}$ concentration in solution.

**Mass Transfer on Rough Surfaces**

The quantification of roughness is difficult. Surface area estimation is dependent on the resolution of measurement (i.e., the area of the smallest surface feature which can be measured). For example, a fractal is an object of infinite surface area, because an infinitely fine resolution is defined. The choice of a roughness scale is also confusing.
because the very nature of the disordered roughness is to have many different scales of roughness. I will choose between two of the most commonly used roughness measures, and discuss the limitations of my choice later.

The major two non-dimensional parameters that have been used to describe surface geometry in engineering literature are wetted area to projected area ratio, \( \alpha \), and the Reynolds roughness number, \( \text{Re}_k \):

\[
\alpha = \frac{\text{wetted surface area}}{\text{projected wall area}} \quad (33)
\]

\[
\text{Re}_k \equiv \frac{u_* k}{\nu} \quad (34)
\]

where the friction velocity, \( u_* \), is defined by:

\[
u_* = \sqrt{\frac{\tau_w}{\rho}} = U_b \sqrt{c_f/2} \quad (35)
\]

and \( k \) is a roughness scale such as average roughness element height (\( k' \)) or sand-grain roughness (\( k_s \)). While \( \alpha \) is perhaps the most appealing to use, Dawson and Trass (1972) have shown that for geometrically similar surfaces (i.e., equal \( \alpha \)) in the same flow regime, \( \text{St}_m \) numbers differ. As a result, \( \text{Re}_k \) has been more successfully employed, and will be the used as the roughness measure in this paper.

This study will use the standard deviation of average roughness element height, \( k_\sigma \), as it is the best measure of the changing height of coral heads, especially when the heads are packed together. The difference between using \( k_\sigma \) and \( k' \) (Fig. 4) can only be a maximum of 3% of the \( \text{St}_m \). To be consistent, I have used \( k_\sigma \) on the data sets of Thomas and Atkinson (1996), Larned and Atkinson (1996) and this study (Fig. 17).
Dipprey and Sabersky (1963) developed correlations for heat and momentum transfer in sand-roughened tubes. The geometric similarity between tubes and the experimental flume is shown by Bilger and Atkinson (1992). When the rate limiting step of transfer is known to be diffusion, heat transfer and mass transfer are analogous. The dimensionless group, Pr, is the ratio of diffusive momentum transfer to diffusive heat transfer (just as the Sc number is momentum transfer to mass transfer), and can be used interchangeably with the Sc number. Bilger and Atkinson (1992) summarize the Dipprey and Sabersky (1963) correlation as:

\[
St_{m,rough} = \frac{c_f}{2} \left[ Sc_t + \sqrt{c_f/2} / St_k \right]
\]

where \( Sc_t \) = turbulent Sc number in the outer boundary layer and is approximated as 0.9, and \( St_k \), the roughness Stanton number, is defined for \( 70 \leq Re_k \leq 2,400 \) as:

\[
St_k^{-1} = 5.19 \ Re_k^{0.2} \ Sc^{0.44} - 8.48
\]

Eq. 36 now gives the \( St_{m,rough} \) as a function of the Sc, and geometric parameters \( Re_k \) and \( c_f \). To calculate \( Sc \), \( Re_k \), and \( c_f \) we need to measure bulk velocity, \( U_b \), hydraulic diameter, \( D_h \), roughness height, \( k \), the slope of the water surface, \( s \), temperature, \( T \), concentration of calcium ions, \( [Ca^{2+}]_b \), water height, \( h \), and the volume to surface area ratio of the flume. With the measurement of these variables over time, we can compare the dissolution of a coral-shaped gypsum surface to the uptake of nutrients on coral communities.
Figure 4. Illustration of roughness scales. This study uses $k_\sigma$ as a roughness scale, as it provides the best measure of the changing height of the roughness elements.
Methods

A recirculating flume (Fig. 1-2) with a volume of 2.3 m$^3$ and channel dimensions 0.4 m x 0.2 m x 24 m was used for all experiments. Fresh water was recirculated using a variable speed pump. The projected planar surface area of smooth (and flat) and coral-rough surfaces varied from 0.8-3.2 m$^2$, giving a volume to projected surface area ratio of 0.72-2.9 m. The bulk water velocity ($U_b$) of the flume was calculated from the mean of 10 measurements of the time for a drogue to travel over 1 or 2 m of sample. The flume contained flow straighteners to dampen production of turbulence through the motor and turning sections. For further flume design considerations, see Atkinson and Bilger (1992).

Measurement of Momentum Transport

The slope, $s$ [m m$^{-1}$], of the water was determined by measuring the relative height difference over 9 m. Two 1.6 mm holes were drilled in the base of the flume 9 m apart. 'Tygon' tubing ran from each hole to a central point, where the water height difference was measured on a vernier scale to the nearest 0.1 mm (Figs. 1 & 2). The height of the water at the vernier scale will be exactly the same as that at the holes, provided that the water in the tubes is of identical density. The tubing was flushed before reading, to avoid gas build up or thermal gradients, either of which changes the average density of the fluid within the tube. The measured water height difference for 2 m samples of coral-rough surface included a height drop over 7 m of empty flume. Eq. (38) was used to calculate the equivalent head difference ($\Delta H$) over 9 m of coral-rough surface.
Three measurements of height difference were averaged to obtain the slope at each velocity for every experiment. Measured head difference can then be compared to predicted head difference (Fig. 5) using the Manning formula (John and Haberman, 1988).

\[
\Delta H_{\text{rough,9m}} = \frac{9}{2}\left(\Delta H_{\text{measured,9m}} - \Delta H_{\text{smooth,7m}}\right)
\]  

Figure 5. Measured and predicted head differences vs. velocity (Exp. 14A) for 9 meters of the empty flume.

**Measurement of Mass Transport**

The gypsum surfaces were prepared using US Gypsum No. 1 Pottery Plaster, a high quality plaster-of-paris used in the ceramics industry. The manufacturer gives typical chemical analysis (% by weight) of the plaster-of-paris powder as: 96.2% Beta-
Hemihydrate $[\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}]$, 0.5% Calcium Sulfate $[\text{CaSO}_4]$, 2.4% Dolomite $[\text{CaMg(CO}_3)_2]$, 0.4% Oxides, 0.5% Acid Insolubles. Analysis by Inductively-Coupled Plasma / Optical Emission Spectroscopy (ICP/OES) of a single sample of highly diluted US Gypsum No. 1 Pottery Plaster, dissolved in nitric acid, gave cation ratios for Ca:Mg:Na of 532:5.6:8. This is consistent with the manufacturer's analysis.

The plaster powder was hydrated using tap water in a 6:5 powder to water ratio by volume. The resulting reaction is:

$$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (39)$$

The plaster was then mixed vigorously for approximately 2.5 minutes, and applied to the surface. The plaster was allowed to set overnight, before the experiment began.

The rates of dissolution of a variety of surfaces of different geometries were investigated. Smooth surfaces were prepared by pouring the plaster directly into the flume, and allowing it to set inside the flume. For the coral-rough surfaces, (Exp. 11 onwards) the coral skeletons were coated in plaster and allowed to set outside the flume (Fig. 6) before being placed in the flume at the beginning of each experiment. Coral reef skeletons were collected from the shoreline of Coconut Island, Kane'ohe Bay, Oahu, Hawaii, and soaked in tap water overnight before being coated with gypsum. The coral skeletons included Porities compressa, Monitpora verrucosa and Fungia sp. Soaking the coral skeletons in tap water reduced the possibility of seawater ions being released during the experiment, which would increase the conductivity of the water, causing error in calculation of calcium concentrations.
The roughness of the assemblage was determined by measuring the height of the skeletons above the flume bottom at 1 cm intervals along transects parallel to the flow (Fig. 3 & 7). Three, 200 cm transects (600 points) were measured. The height of the water column from the bottom, minus the average roughness height, k', was used to determine the average height of the water over the sample. The standard deviation of the roughness height was used as an estimate of the roughness height (kσ). The same coral skeletons were used for Exps. 11-19. A different set of coral skeletons were used for Exps. 20-21.

Time, temperature and conductivity were measured by a SEABIRD, Seacat 19 Profiler CTD. The CTD uses a Wein bridge-type oscillator to measure the conductivity of ions in solution at high frequencies. The high frequencies minimize the effects that ion-ion interactions have on conductivity measurement. This results in the near-linear relationship experimentally found between conductivity and calcium concentrations (Fig. 8). The SEABIRD software calculates specific conductance [μS cm⁻¹], which is the raw conductivity measurement, normalized to obtain the conductivity value that the same composition solution would measure at 25°C. It is important to note that the CTD measures at one position in the flume over time. Later in this section spatial variability will be inferred from a point measurement over time.
Figure 6. Coral-rough surfaces were made by plastering coral skeletons. The surfaces were allowed to dry overnight before placement in the flume.

Figure 7. Measurement of roughness height for coral-rough surface. The parallel rods 1 cm apart duplicate the surface profile, and facilitate easy measurement of roughness height.
Water samples were routinely taken at the beginning and end of the each experiment, as well as a number of times during the experiment. Samples were filtered using a GF/C glass-fiber filter, with a nominal pore size of 0.7 μm, and then refrigerated until analyzed. Samples were analyzed for calcium and other ions concentrations using a ICP/OES, and by potentiometric ion-selective electrode titrated with EGTA (Grasshoff et al., 1983).

![Calcium Concentration vs Specific Conductance](image)

Figure 8. Calcium concentration measured by titration vs. specific conductance calculated from CTD measurement of conductivity [μS cm⁻¹] and temperature [K].

Samples were analyzed between a week and a few months after sampling. In all cases, the only cation to vary significantly in concentration over time was calcium, and was tightly correlated to the specific conductance measured at the time of sampling (Fig. 8). From the measured points a quadratic regression was developed, with 95% confidence levels shown. The points on this curve were taken from experiments over a six month
period; there were no significant changes in the CTD calibration or the quality of the plaster.

For each experiment, a curve of specific conductance vs. time was plotted (Fig. 9). This formed a logarithmic curve, as the conductance asymptotically approaches the saturation value. For low velocities, it is evident that there was considerable mixing time of the flume water before there was no spatial variability in concentration in the flume. The peaks in conductance are due to the higher concentration of ions in the volume of water which were exposed to plaster before circulation began. The peaks recur periodically as the volume of water initially exposed to the plaster passes the conductivity sensor. A polynomial fit is used to obtain the average concentration for the whole volume required.

Figure 9. Specific conductance vs. time for Exp. 16. The corals were placed in the flume at time = 25 minutes. The initial peak is the first time the recirculating water that has been
exposed to the gypsum surface passes the sensor. The peak reoccurs about every 5 minutes, the time for one pass around the flume. Within 5 cycles, the flume is well mixed.

in Stanton number calculations.

An example of calculated Stanton numbers (Eq. 20) throughout a gypsum dissolution experiment for a smooth surface (Exp. 4) are shown in Fig. 10. Due to a changing ionic strength and temperature, both predicted and measured Stanton numbers change throughout an experiment. The reported Stanton numbers are an average of the 390 points shown in Fig. 10. The typical 95% confidence limit for a mean Stanton number is 1%. The largest error is due to a 5% error in the measurement of \( U_b \) and flume volume.

![Stanton Number for Experiment 4](image)

Figure 10. Stanton number for a smooth surfaces vs. time (Exp. 4). The prediction by Stewart (1987), Eq. 24 has been extrapolated to the lower \( Sc \) numbers of this experiment. After 15 hours the concentration gradient between the saturated wall and the near saturated water
approaches zero, resulting in the Stanton number (Eq. 20) becoming heading towards infinity. The reported results from all experiments will be within the first 5 hours.

The equipment, methods and calculations are now in accordance with the extensive engineering literature for both momentum and mass transfer characteristics for a smooth surface, and can therefore be confidently applied to coral rough surfaces (Dipprey and Sabersky, 1963).

**Measurement of Mass Transport on Coral-rough Surfaces**

The calculated rough $St_m$ decreased because of a increase of bear surfaces as the gypsum dissolved. (Fig. 11; also Fig. 14 in results). Thus the reported $St_m$ for each coral-rough gypsum surface was corrected to the initial measured value, when the surface was

![Stanton Number for Experiment 14](image)

Figure 11. Measured Stanton numbers for a coral-rough surface (Exp. 14). $U_b = 0.32 \, \text{m s}^{-1}$ for first 54 minutes. For the rest of the experiment, $U_b = 0.24 \, \text{m s}^{-1}$. 

33
fully coated. For example, when the velocity was changed in Exp. 14 at 54 minutes\(^3\), no step change occurred in \(S_{tm}\). For both velocities, \(S_{tm}\) was taken to be 25 x 10\(^{-5}\), the value recorded initially before the loss of surface area caused the slow decay from the initial value of 25 x 10\(^{-5}\).

**Experimental Outline**

A few preliminary experiments were conducted (Exp. 1-3) to test the experimental equipment. Three smooth surface experiments (Exp. 4-6, Table 2) were then conducted to test the performance of gypsum dissolution against other mass-transfer limited chemical systems. Exp. 4 was conducted over a large temperature range, and therefore resulted in a large change in diffusivity. Exp. 5 used the same surface as Exp. 4, conducted eight days later, and at a variety of velocities. Exp. 6 involved the sandpapering of the new surface to create small roughness elements.

A variety of methods of creating rough surfaces were then tested (Exp. 7-10, 12). These surfaces resembled coral surfaces to varying degrees, notably a plaster smothered assemblage of coral skeletons (Exp. 9, Table 2), and a collection of randomly orientated triangular shapes (Exp. 12). Although the results or these experiments were representative of the surfaces themselves, the surfaces tested were not particularly good analogues for nutrient-uptake on coral reefs and thus are not included in the results.

The most successful replication of coral-rough surfaces was achieved by submerging coral skeletons in plaster-of-paris as the water-plaster mixture was hydrating.

\(^3\) There is a step change in flux, but this is canceled out in the \(S_{tm}\) calculation (Eq. 20) by the change in \(U_b\).
(Exps. 11,13,14-17,19, 20F, 21A-B, Table 2). The setting speed of a six parts plaster, five parts water mixture allowed an approximately 2 minute "window" in which quickly submerged coral skeletons would be almost completely covered with an even, 0.5-2 mm thick of gypsum coat (Appendix D). These surfaces, with at least 95% of the surface coated, have been termed coral-rough gypsum surfaces. The gypsum was completely dissolved from each skeleton after experimentation, and the skeletons reused. The roughness of the two different assemblages was carefully analyzed during Exps. 15 and 16 (Fig. 12, Table 1) and Exp. 20.

At low velocities (Exp. 17), the pump's speed was not as consistent as at velocities above 0.05 m s\(^{-1}\), and in fact the motor stalled on two occasions, but was immediately restarted. Pump reliability at low velocities was fixed for experiment 21A-B. Exp. 19 involved roughening the coral surfaces by the addition of plaster particles into the setting plaster mix, and further roughening with 60 grit sandpaper. Further roughening of the coral-rough gypsum surface was used to investigate whether small-scale roughness on the coral-rough gypsum surface enhances mass transfer.

Two experiments (Exp. 14A, 18, Table 2) were performed to determine the momentum characteristics of the empty flume (Exp. 14A) and the flume filled with coral skeletons (Exp. 18). By only measuring the momentum characteristics (velocity, head difference and height of flume), and not being concerned with dissolution characteristics, better precision was obtained.

Exp. 20 involved the direct comparison of ammonia uptake on a living coral community followed by the dissolution of gypsum from the same coral skeletons, placed in the same arrangement in the flume. Exps. 20A-D were ammonia-uptake experiments
from a coral assemblage in recirculated seawater, using the same procedures as Thomas and Atkinson (1996). The flume walls were scrubbed before each experiment, and the dirty seawater drained. The flume was refilled with Kane'ohe Bay seawater, and the corals left for 30 minutes in recirculating water. A 200 ml spike of 26 mM N as (NH₄)₂SO₄ was then administered evenly throughout the flume. The flume water continued to recirculate for a further 20 minutes, and then sampling begun. The water velocity was kept constant throughout the experiment. Eight to ten samples were taken over an eight hour period. Samples were siphoned from downstream of the community into a bucket for 25 minutes, to obtain an integrated concentration over the time period. The bucket was then sub-sampled using a 150 mL syringe, then filtered through a GF/C glass-fiber in-line filter and the sub-sample placed in a Nalgene bottle in a freezer within 5 minutes. NH₄ was measured using a Technicon II Autoanalyzer with modified standard Technicon industrial methods (Walsh, 1989). Exp. 20F was a control run, using the same methods as Exp. 20A-D, but without the coral community, to account for ammonia uptake by plankton and from the walls.

Exp. 20E used the same coral assemblage arranged identically, but the Stanton number was measured by gypsum dissolution using the techniques described for Exps.11-19. Finally Exps. 21A and 21B, using gypsum dissolution of the assemblage of Exp. 20, involved a comparison of coral-rough and roughened coral-rough surfaces at low velocities.
Results

Momentum Transport on Coral-rough Surfaces

An example of coral-roughness is shown in Fig. 12 (Exp. 16). For the coral assemblage of Exps. 11-19, the mean height, $k'$, is 8.22 cm, and the standard deviation of the mean height, $k_\sigma$, is 4.8 cm (Table 1). For Exps. 20-21, $k' = 7.41$ cm, and $k_\sigma = 4.05$ cm.

Table 1. Topographical profile of the coral-rough assemblages used in Exp. 11-19, measured during Exps. 15 and 16. Transect positions were at 10, 20, and 30 cm from the left side of the flume if looking downstream.

<table>
<thead>
<tr>
<th>Transect position</th>
<th>Experiment #15</th>
<th>Experiment #16</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k'$ Mean Height [m]</td>
<td>$k_\sigma$ Standard Deviation</td>
</tr>
<tr>
<td>Left - 10 cm</td>
<td>0.0843</td>
<td>0.0504</td>
</tr>
<tr>
<td>Center - 20 cm</td>
<td>0.0782</td>
<td>0.0498</td>
</tr>
<tr>
<td>Right - 30 cm</td>
<td>0.0820</td>
<td>0.0478</td>
</tr>
<tr>
<td>TOTAL</td>
<td>0.0815</td>
<td>0.0493</td>
</tr>
</tbody>
</table>

Measured by volumetric displacement in a tank of known dimensions, the volume of the coral skeletons used for Exps. 11-19 was $27.0 \pm 0.3$ liters.

On surfaces with high roughness, Eq. 17 (Haaland, 1983) does not predict the friction coefficient measured in the flume (Fig. 13). This contrasts with smooth surfaces, for which the measured and predicted are similar (Fig. 5), indicating that engineering literature will not predict momentum transport at the high roughness of coral surfaces. However, the Haaland relation was developed from experiments at much smaller roughness height to water column height ratios than found in the flume (see Appendix B). The measured points in Fig. 13 are fitted to a cubic polynomial.
Figure 12. Roughness profile for Exp. 16. The mean height, $k'$, and standard deviation of the mean height $k$, for the left, center and right (facing downstream) transects are listed in Table 1.

Mass Transport on Coral-rough Gypsum Surfaces

The plaster surfaces placed in the flume dissolved, releasing calcium and sulfate ions into solution, as expected. Fig. 14 shows the dissolution of the plaster from coral skeletons during Exp. 14 ($U_b \sim 0.3 \text{ m s}^{-1}$). The photographs are taken at the time the flow was started, 25 minutes, 45 minutes, and 17 hours later. The progressive photos of Fig. 14 show that the dissolution of plaster was not even on all surfaces, but instead tended to be removed more quickly at the tips of the corals (see Appendix D). During high flow rate conditions (above 0.1 m s$^{-1}$), the surface was visibly removed within an hour, and results obtained thereafter are from dissolution of a smaller surface area, as discussed in methods (Fig. 11).
St_m for smooth gypsum surfaces ranged between 2.6 - 3.5 x 10^{-5} for varying temperature, ionic strength and bulk velocities above 0.1 m s^{-1} (Exps. 4-6, Table 2, Fig. 15). St_m for coral-rough gypsum surfaces ranged from 22 - 31 x 10^{-5} at velocities greater than 0.1 m s^{-1}, an enhancement of 9 \pm 1 over a smooth gypsum surface (Exps. 11,13-16, Table 2, Fig. 15). Much higher St_m numbers were measured for low water velocities (Exp. 17, Table 2, Fig. 15). Fine-scale roughening of a coral-rough gypsum surface does not increase mass transfer (Exp. 19 & 21, Table 2, Fig. 15). The St_m for coral-rough gypsum

Figure 13. Predicted head difference over 9 m vs. head differences over 9 m calculated from the measured head differences over 2 m (Eq. 38).
(i) Experiment 14, $t=0$, when water is just beginning to be recirculated.

(ii) Experiment 14, $t=25$ minutes.
(iii) Experiment 14, t=110 minutes.

(iv) Experiment 14, t=17 hours.
surface of Exps. 20-21 ranged from $17 - 19 \times 10^{-5}$, an enhancement of $6 \pm 0.3$. The same enhancement was found from ammonia uptake experiments on the living coral community (Exp. 20B-D) over a theoretical smooth surface value. Exp. 20-21 had a 10% lower $k_\sigma$ than Exp. 11-19.

Figure 15. Stanton number, $St_m$ vs. bulk velocity, $U_b$ for gypsum dissolution Exps. 4-6, 11,13-16, 17 and 19-21. Confidence intervals ($\pm 10\%$ of $St_m$) are based on the variation in measured bulk velocity ($\pm 5\%$) and height of the water ($\pm 5\%$) affecting $St_m$ in Eq. 20. Exp. 11-19 are from one set of coral skeletons, and Exp. 20-21 from another, less rough (smaller $k_\sigma$) assemblage.
Table 2. Summary of experimental results. The same coral skeletons were used for Exps. 11-19. The living corals from Exp. 20B-D were used for Exps. 20E, 21A-B. Stm and Sc are for gypsum dissolution unless stated. Coral skeletons evenly coated with gypsum are referred to as coral-rough. The roughened coral-rough surfaces (Exps. 19 & 21B) refer to coral-rough surfaces further roughened with sandpaper to create randomly-orientated 1 mm grooves on coral-rough surface. Smothered coral rubble of Exp. 9 referred to coral-rubble coated with plaster in the flume. The reported results of Exp. 20B-D include correction for uptake on flume surfaces measured by Exp. 20F.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Roughness</th>
<th>$U_b$ [m/s]</th>
<th>$c_f$ ($10^{-3}$)</th>
<th>$Sc^*$</th>
<th>$St_m$ ($10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Smooth</td>
<td>0.20</td>
<td>7.95</td>
<td>1360</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.24</td>
<td>7.61</td>
<td>1360</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.26</td>
<td>7.45</td>
<td>1370</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.29</td>
<td>7.31</td>
<td>1370</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.37</td>
<td>7.10</td>
<td>1380</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>Smooth</td>
<td>0.35</td>
<td>see Exp. 14A</td>
<td>1360</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.84</td>
<td></td>
<td>1410</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.69</td>
<td></td>
<td>1440</td>
<td>2.6</td>
</tr>
<tr>
<td>6</td>
<td>Sandpaper 1500 and 60 grit</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.84</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>0.69</td>
<td></td>
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</tr>
<tr>
<td>9</td>
<td>Smothered coral rubble</td>
<td>0.19</td>
<td>140</td>
<td>1300-2000</td>
<td>20</td>
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<td>11</td>
<td>Coral-rough</td>
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<td>see Exp. 18</td>
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<td></td>
<td></td>
<td>0.38</td>
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<tr>
<td>12</td>
<td>Coral-rough</td>
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<td>see Exp. 18</td>
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<td>24</td>
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<tr>
<td></td>
<td></td>
<td>0.47</td>
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<td></td>
<td>25</td>
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<td></td>
<td></td>
<td>0.31</td>
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<tr>
<td>13</td>
<td>Coral-rough</td>
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<td>see Exp. 18</td>
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<td></td>
<td>0.24</td>
<td></td>
<td>1340</td>
<td>25</td>
</tr>
<tr>
<td>14</td>
<td>Coral-rough</td>
<td>0.21</td>
<td>0.0084</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28</td>
<td>0.0080</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14A</td>
<td>Smooth</td>
<td>0.30</td>
<td>0.0068</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(velocity and $c_f$ measurements only)</td>
<td>0.36</td>
<td>0.0067</td>
<td>-</td>
<td>-</td>
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<td></td>
<td></td>
<td>0.41</td>
<td>0.0070</td>
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<td></td>
<td></td>
<td>0.50</td>
<td>0.0068</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Coral-rough</td>
<td>0.13</td>
<td>see Exp. 18</td>
<td>1260</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
<td></td>
<td>1270</td>
<td>28</td>
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<tr>
<td></td>
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<td>0.15</td>
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<td>1280</td>
<td>29</td>
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<tr>
<td>16</td>
<td>Coral-rough</td>
<td>0.19</td>
<td>see Exp. 18</td>
<td>1320</td>
<td>25</td>
</tr>
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<td></td>
<td></td>
<td>0.26</td>
<td></td>
<td>1340</td>
<td>22</td>
</tr>
<tr>
<td>17</td>
<td>Coral-rough</td>
<td>0.030</td>
<td>see Exp. 18</td>
<td>1260</td>
<td>70</td>
</tr>
<tr>
<td>18</td>
<td>Coral-rough</td>
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<td>0.1065</td>
<td>-</td>
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<tr>
<td></td>
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<td>0.29</td>
<td>0.1003</td>
<td>-</td>
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<td></td>
<td>(velocity and $c_f$ measurements only)</td>
<td></td>
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<tr>
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</tr>
<tr>
<td></td>
<td>0.36</td>
<td>0.0886</td>
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<td></td>
<td>0.38</td>
<td>0.1046</td>
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<td></td>
<td>0.44</td>
<td>0.1085</td>
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</tr>
<tr>
<td></td>
<td>0.48</td>
<td>0.1182</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Roughened coral-rough</td>
<td>0.48</td>
<td>see Exp. 18</td>
<td>1260</td>
<td>23</td>
</tr>
<tr>
<td>20B - D</td>
<td>Ammonia uptake by living corals</td>
<td>0.24</td>
<td>0.041</td>
<td>475</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>0.042</td>
<td>475</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>0.040</td>
<td>475</td>
<td>39</td>
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<tr>
<td>20E</td>
<td>Coral-rough</td>
<td>0.26</td>
<td>0.050</td>
<td>1300</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.043</td>
<td>1350</td>
<td>17</td>
</tr>
<tr>
<td>20F</td>
<td>Ammonia uptake by empty flume</td>
<td>0.20</td>
<td>see Exp. 14A</td>
<td>475</td>
<td>34</td>
</tr>
<tr>
<td>21A</td>
<td>Coral-rough</td>
<td>0.045</td>
<td>0.233</td>
<td>1230</td>
<td>52</td>
</tr>
<tr>
<td>21B</td>
<td>Roughened coral-rough</td>
<td>0.043</td>
<td>0.207</td>
<td>1240</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 2 (cont.).
Discussion

Momentum Transport

The largest random error in all measurements in this study was due to the turbulent nature of the flow. An average water velocity, $U_b$, was calculated from 10 drogue measurements. While individual measurements were accurate, in a randomly fluctuating medium a finite sampling provides only an approximation of the true average. This error was greater on rough surfaces, where turbulence was greater and velocity gradients steeper. A comparison with the literature values (Fig 5, John and Haberman, 1988) for smooth surfaces, and the repeatability of measurements on rough surfaces (Table 2), show the errors were on the order of $\pm 5\%$ or less, as would be indicated by the variability in the measurement of velocity.

The measurement of the height of volume of water in the flume was made difficult by evaporation during an experiment, the slope on the flume bottom (up to 15 mm difference in height), as well as the slope created by friction. The height measurement was also important for friction coefficient, $c_f$, calculations. An error of up to $\pm 5\%$ is estimated due to miscalculation of volume.

The variability seen in the experimental curve fitting of velocity to head difference (Fig. 13) was of the same magnitude as would be expect from the error in the measurement of bulk velocity and volume. The measured values do not vary by more than $\pm 10\%$ from the plotted cubic fit. Considering the strong correlation between friction coefficient and mass transfer, the same variability is to be expected in mass transfer results as well.
As stated in the introduction, Bilger and Atkinson (1992) suggest that corals may possess an enhancement mechanism unexplained in engineering literature. As pointed out by Thomas and Atkinson (1996), and illustrated in Fig. 13, the calculated friction factors, $c_f$, from Haaland (1983) and used by Bilger and Atkinson, are low. The higher friction factor measured on coral skeletons must be due to geometric differences between engineering surfaces and coral-rough surfaces. Thus it should be expected that in a turbulent flow, for a mass-transfer limited chemical, enhanced $c_f$ will result in an enhanced $St_m$.

**Mass Transport**

The photographs in Fig. 14 show the plaster being removed from the coral skeleton surface. The dissolution of gypsum, as described in the background section, experimentally showed a velocity dependence. It also had Stanton numbers of the same magnitude, and temperature and ionic strength dependence, of other chemicals for smooth surfaces found in the literature (Steward, 1987). Furthermore, in an independent study of gypsum dissolution on a smooth, rotating disk, Barton and Wilde (1971) conclude that the dissolution of gypsum is mass transfer limited. Therefore, as the dissolution of gypsum is mass transfer limited, it is a good experimental analogue for the flux of chemical species to and from a coral-rough object. Thus the $St_m$ from the dissolution of gypsum from a coral-rough surface can be compared to the $St_m$ for the uptake of ammonia and phosphorus to live coral reef communities.

Fig. 14 illustrates some qualitative aspects of the flux of chemical species to and from a coral-shaped object. The transport rate is not even on the surface, but is greater
at points of faster local velocity, such as on the tips (see Appendix D). A greater removal rate is also observable from delicately branched coral skeletons, which probably induce more turbulence.

**Other Mass Transfer Studies on Coral-rough Surfaces**

Table 3 lists a number of mass transfer studies on coral-rough surfaces. The studies of Thomas and Atkinson (1996) and Larned and Atkinson (1996) provide the basis for comparison of coral-rough gypsum surfaces to live coral communities.

The measured $St_m$ of different chemical species is a function of $Sc$ of the species, $Re_k$ and $c_r$. (Dipprey and Sabersky, 1963). To compare $St_m$ of gypsum to the $St_m$ of ammonia from geometrically similar surfaces (and therefore $Re_k$ and $c_r$), $St_m$ can be scaled according to the ratio obtained from Eq. 24 (Bilger and Atkinson, 1995). For the same $Re_k$ and $c_r$:

$$\frac{St_{m,ammonia}}{St_{m,gypsum}} = \frac{0.0575Sc_{ammonia}^{-2/3} + 0.1184 / Sc_{ammonia}}{0.0575Sc_{gypsum}^{-2/3} + 0.1184 / Sc_{gypsum}} \approx 2 \quad (40)$$
Table 3. Data analysis of experiments undertaken on coral-rough surfaces for a variety of chemical species and flow conditions. Atkinson and Bilger (1992) gave $c_f$ values, but they were calculated, not measured, and have since been questioned by Thomas and Atkinson (1996).

<table>
<thead>
<tr>
<th>Environment</th>
<th>Chemical (Sc number$^*$)</th>
<th>$U_b$ [m/s]</th>
<th>$Re_k$</th>
<th>$c_f$</th>
<th>$Re$ ($\times 10^3$)</th>
<th>$St_m$ ($\times 10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kane'ohi Bay barrier reef (Bilger and Atkinson, 1992)</td>
<td>phosphate (~1340)</td>
<td>0.1</td>
<td>230 - 2000</td>
<td>0.010 - 0.026</td>
<td>425</td>
<td>4,250</td>
</tr>
<tr>
<td>Uniform flow experimental coral community (Atkinson and Bilger, 1992)</td>
<td>phosphate (~1340)</td>
<td>0.0229 - 0.581</td>
<td>313 - 7900</td>
<td>not measured</td>
<td>15.9 - 403</td>
<td>13.8 - 106</td>
</tr>
<tr>
<td>Enewetak Atoll reef flats (Atkinson, 1992)</td>
<td>phosphate (~1340)</td>
<td>not given</td>
<td>not measured</td>
<td>not measured</td>
<td>not given</td>
<td>not given</td>
</tr>
<tr>
<td>Uniform flow experimental Porites compressa (Thomas and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.48 - 0.57</td>
<td>not given</td>
<td>not given</td>
<td>43.6 - 185</td>
<td>38.4 - 38.4</td>
</tr>
<tr>
<td>Uniform flow experimental. (PC) (Thomas and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.039 - 0.375</td>
<td>853 - 5208</td>
<td>0.264 - 0.109</td>
<td>43.6 - 185</td>
<td>38.4 - 38.4</td>
</tr>
<tr>
<td>Uniform flow experimental. (PD) (Thomas and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.036 - 0.296</td>
<td>501 - 2986</td>
<td>0.126 - 0.063</td>
<td>39.9 - 108</td>
<td>58.3 - 54.1</td>
</tr>
<tr>
<td>Uniform flow experimental. (HR) (Thomas and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.09 - 0.277</td>
<td>1015 - 3262</td>
<td>0.101 - 0.111</td>
<td>100 - 54.4</td>
<td>37.4 - 41.5</td>
</tr>
<tr>
<td>Uniform flow experimental. (LR) (Thomas and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.033 - 0.308</td>
<td>107 - 935</td>
<td>0.052 - 0.045</td>
<td>36.2 - 36.0</td>
<td>48.4 - 36.7</td>
</tr>
</tbody>
</table>
Table 3 (cont.). Data analysis of experiments undertaken on coral-rough surfaces for a variety of chemical species and flow conditions.

<table>
<thead>
<tr>
<th>Uniform flow gypsum coral shapes</th>
<th>gypsum (1200-1400)</th>
<th>0.03 - 0.506</th>
<th>700 - 5400</th>
<th>0.06 - 0.5</th>
<th>-</th>
<th>22-70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dictyosphaeria (Larned and Atkinson, 1996)</td>
<td>ammonium (~475)</td>
<td>0.02 - 0.12</td>
<td>700 - 1200</td>
<td>0.03 - 0.45</td>
<td>-</td>
<td>45 - 170</td>
</tr>
</tbody>
</table>

Eq. 40 is used to scale the \( St_{m,gypsum} \) to \( St_{m,ammonia} \) (Fig. 16), the result being that measured \( St_{m,gypsum} \) is multiplied by two to account for the slower diffusion of gypsum relative to ammonia. Now a direct comparison of \( St_m \) for ammonia uptake on a coral community and coral-rough gypsum surface can be made (Fig. 16).

The similar magnitude of the \( St_m \) of a live coral community and a coral-rough gypsum surface is proof that the mechanism of mass transfer enhancement is geometric rather than biological. Furthermore, since the coral-rough surfaces did not possess the fine scale roughness of living coral, and yet had the same magnitude of \( St_m \), the geometric features responsible for enhancement are all large scale. The similar dissolution rate of the roughened coral-rough gypsum surface (Exp. 19 & 21) to unroughened coral-rough gypsum surfaces also illustrates this point. Small-scale phenomena (Fig. 4, \( k_1 - k_4 \)) such as a fractal surface, are not responsible for the enhancement of mass transfer on coral-rough surfaces.
Figure 16. A comparison of mass transfer on coral-rough surfaces. Shaded symbols are measured values; outlined symbols are predicted values using Dipprey and Sabersky, 1963 with $C = 5.19$, and using the standard deviation of the roughness height, $k_\sigma$, as the roughness height. *Porites compressa* (PC), *Pocillopora damicornis* (PD), and HR (high relief rubble) (Thomas and Atkinson, 1996), Dictyosphaeria (Larned and Atkinson, 1996) and Exp. 20B-D were measured using the uptake of ammonia. Exp. 11-19 and Exp. 20E, 21A-B were measured from gypsum dissolution from coral-rough surfaces.
As pointed out earlier in the discussion, Bilger and Atkinson (1992) cited the work of Dipprey and Sabersky (1963), but incorrectly calculated the mass transfer because they underestimated the friction coefficient (Thomas and Atkinson, 1996). Fig. 13 shows the measured head difference over a coral surface compared to the predicted value used by Bilger and Atkinson for their mass transfer calculations. The Dipprey and Sabersky (1963) study involved the investigation of heat transfer from sand-roughened pipes. The geometric similarity between pipes and channels has already been shown, as well as the fact that both heat and mass transfer are examples of diffusion along chemical potential gradients.

Dipprey and Sabersky chose sand-grain roughness to "simulate natural roughness" because of its "three-dimensional nature and the random shape of the roughness elements." Dipprey and Sabersky's correlation Eq. 36-37 uses a coefficient of 5.19 for $St_c^{-1}$. Fig. 16 is a graph of the predicted Stanton numbers (Eq. 36-37) for the data of this study, Thomas and Atkinson (1996), and Larned and Atkinson (1996), plotted with the measured values for these respective studies.

Dipprey and Sabersky point out that the coefficient of 5.19 (Eq. 37) is a function of the type of roughness. Replacing 5.19 with 7.0 for coral-roughness (Fig. 17) provides an excellent agreement between predicted values and the measured values of Thomas and Atkinson (1996), this study, and from Dictyosphaeria (Larned and Atkinson, 1996). The fact that changing the Dipprey and Sabersky coefficient to 7.0 improves both the prediction of living coral surfaces and coral-rough gypsum surfaces is further evidence that the format
Figure 17. A comparison of mass transfer on coral-rough surfaces. Shaded symbols are measured values; outlined symbols are predicted values using Dipprey and Sabersky, 1963 with $C = 7.0$, and using the standard deviation of the roughness height, $k_n$, as the roughness height. Porites compressa (PC), Pocillopora damicornis (PD), and HR (high relief rubble) (Thomas and Atkinson, 1996), Dictyosphaeria (Larned and Atkinson, 1996) and Exp. 20B-D were measured using the uptake of ammonia. Exp. 11-19 and Exp. 20E, 21A-B were measured from gypsum dissolution from coral-rough surfaces.
of Dipprey and Sabersky's heat transfer correlation is valid for coral-rough surfaces. Since Dipprey and Sabersky's correlation uses only geometric parameters (and not biological ones), this is further grounds for quantifying mass transfer rates in terms of geometric and not biological variables.

The predicted $St_m$ of Dipprey and Sabersky's (1963) correlation modified for coral-roughness does not correlate well below 0.1 m s$^{-1}$. However, the correlation is empirically determined from rough surfaces in which $c_f$ does not change with Re: a phenomena described in engineering literature as the momentum boundary layer being fully rough. Below 0.1 m s$^{-1}$, $c_f$ increases with Re on coral-rough surfaces (Thomas and Atkinson, 1996), and the boundary layer is considered transitional (Kays and Crawford, 1993). Therefore, Dipprey and Sabersky's modified relationship is only useful on coral-roughness for velocities above 0.1 m s$^{-1}$. Further study may determine why flow over coral-roughness is transitional at $Re_k$ of up to 1000 ($U_b \sim 0.1$ m s$^{-1}$), an order of magnitude higher than on sand-grain roughness and other engineering surfaces.

**Implications for Coral Reef Ecology**

The results of this thesis support Atkinson and Bilger's (1992) assertion that the diffusion of nutrients to coral reefs is mass transfer limited, the mechanism of limitation being diffusion through the diffusive sublayer. Bilger and Atkinson's (1992) field observations yield a Stanton number for phosphate of at least 1.7x10$^{-3}$. To compare the Stanton number from a uniform flow to an oscillatory flow such as seen in a wave-driven environment, a correction factor must be included (Appendix A). For the field conditions
Figure 18. A comparison of mass transfer on coral-rough surfaces to a common relation of St_m vs. U_b for smooth and grooved surfaces. Measured points as per Fig. 17-18. The constant, k = 1/2800, has been chosen so St_m has the same magnitude as coral-rough surfaces.

\[ \text{St}_m = \frac{1}{2800} U_b^{-0.2} \]
described by Bilger and Atkinson (1992), this factor is 3.2. Therefore using the uniform flow, coral-rough results obtained in this study, we can say that $2.5 \times 10^{-4} \times 3.2 = 0.8 \times 10^{-3}$ can be accounted for by geometric enhancement of mass transfer in a oscillatory flow. A factor of two remains unaccounted.

The results of this study show that corals have a morphology that is highly effective at extracting nutrients from the water column. Fig. 18 presents the measured results of Fig. 17, along with a curve fitting the data of the form $St_m = kU_b^{-0.2}$, where $k$ is a constant. This form of relationship is observed on smooth and ordered-rough surfaces such as grooves. Note the enhancement of coral-rough surfaces at low velocities above that of engineering surfaces. This enhancement may be explained by the following ecological arguments.

Competition will be strongest when resources are scarce. Under these conditions, adaptations are expected to be more refined by natural selection. For nutrient uptake, the scarce availability of nutrients occurs at low velocities, and it is at low velocities we see the strongest trend away from ordered rough surfaces (Fig. 18). Therefore, it is reasonable to argue that coral morphology is highly adapted for the uptake of nutrients at low velocities.

A counter argument, however, would suggest that the coral morphology is highly adapted to survival in a wave swept environment, where structural integrity is of the utmost importance. As we have already learned, the friction factor, $c_f$, is a measure of the shear stress (and hence force) exerted by the water on the coral, and $c_f$ and $St_m$ are strongly correlated. So to protect themselves from injury, the corals must reduce $c_f$, thereby reducing $St_m$, effectively trading off between survival and nutrient uptake.
Or has natural selection sidestepped this "trade off?" Survival in a wave swept environment need only be considered at high velocities, and nutrient uptake becomes increasingly important at low velocities. It is my hypothesis, therefore, that coral-rough shapes are highly adapted to both nutrient uptake at low velocities, and survival in a wave-swept environment at high velocities.

My argument is further strengthened by considering the importance of roughness on an individual organism, as opposed to the whole community. At low velocities the flow is less turbulent. The presence of a particular roughness element results in significantly more turbulence (and therefore higher $c_f$) in the vicinity of the element. At high velocities, the flow is much more turbulent, and there is only a small increase in turbulence about the vicinity of a particular roughness element. A coral that increases $c_f$ at low velocities will therefore primarily affect its own uptake rate. A high velocities, however, turbulence created by the whole community tends to dominate, as flow over one organism is highly altered by its neighbors. A type of roughness that results in a higher $c_f$ at high velocities will have little additional benefit to the individual in nutrient uptake. As a result, we see the high velocity $St_m$ following the trend (although not magnitude) of regular engineering surfaces.

A corollary to the above arguments must be provided to explain the variety of different coral-rough morphologies that thrive in coral reefs. Thomas and Atkinson (1996), along with Larned and Atkinson (1996), show that a variety of different species, with different rough morphologies, follow the same $St_m$ vs. $U_b$ curve (Fig. 18). A wide range of coral-rough morphologies appear capable of obtaining the highly adapted
performance exhibited in Fig. 18. This is one factor in allowing the diversity of rough morphologies for which coral reefs are cherished.

A particular coral species can also exhibit more than one morphology, depending on the environment in which it grows. To what extent are coral morphologies controlled by environmental factors? The evidence of faster dissolution rates from the tips of coral-rough gypsum surfaces (Appendix D) raises the possibility that a branching structure could develop as a result of the tips receiving more nutrients, and therefore the length of the branch grows faster than the diameter.

A Changing Boundary Layer

Diffusive fluxes, such as those of nutrients and other chemicals beneficial or harmful to corals, are strongly dependent on water velocity and temperature. Sea surface temperature and local weather patterns are predicted to vary with global climate change (Steering Committee of the Climate Change Study, 1995). For example, a change from 22°C to 25°C in sea surface temperature will decrease kinematic viscosity by ~6% and increase diffusivity of NH$_4^+$ by ~7%, resulting in a decrease in Sc number of 12%. Using Eq. 24, this results in an increase in Stanton number of NH$_4^+$ of 8%. To assess the effects of increased uptake of nutrients on coral communities, growth rates of different species at elevated nutrient uptake rates must be assessed. It may well be found that an algae such as Dictyosphaeria fares better with higher uptake rates than historically more established species.

As introduced earlier, naturally rough surfaces are ubiquitous in nature. Throughout the oceans, and other ecosystems, many chemical systems appear never to
reach equilibrium, but are instead kinetically controlled. The results from this study may be applicable to other naturally rough surfaces that are mass transfer limited. Naturally rough inorganic surfaces are capable of at least 9 ± 1 times the flux of a smooth surface, and may be subject to significant variations with changing global climate patterns.

Industry efficiency relies heavily on transport phenomena, particularly heat exchange and heat recovery. The usefulness of a heat exchange surface is often assessed by plotting the ratio of heat transfer to friction dissipated (St/cf) against Reynolds number. This gives an indication, at a specified Re, whether the addition of roughness to a smooth surface "costs" more in friction dissipated than the gain in heat transfer. The same analysis can be done for mass transfer to coral-rough surfaces (Fig. 19). At 2 x 10^5 < Re < 5 x 10^5 (U_b = 0.2-0.5 m s^{-1}), there is a marginal gain in mass transfer over friction loss, compared to a smooth surface. Similar size gains are of great interest to engineers (Dipprey and Sabersky, 1963).

Fouling, however, is a problem that must be overcome before the application of coral-rough surfaces in industrial processes becomes a possibility. Fouling occurs when a surface becomes coated by constituents of the flow that stick to the heat transfer surface, reducing heat transfer and often increasing pressure drop through constriction of flow. Living coral communities, incidentally, overcome the problem of fouling through the action of grazers on the coral surface.
Returning briefly to coral ecology, Fig. 19 quantifies the ecological arguments given earlier in the discussion. The most "cost-effective" mass transfer on coral-rough surfaces occurs at between 0.20-0.50 m s\(^{-1}\). In this range, nutrient uptake is required, but risk of injury introduces a "cost" for the corals. Below 0.20 m s\(^{-1}\), the "cost" diminishes, as the ocean provides the energy, and there is little risk of injury. As a result, coral-rough surfaces are designed for maximum efficiency at velocities above 0.20 m s\(^{-1}\), and, at low velocities, maximum mass transfer at any "cost."
Conclusions

1. The dissolution of coral-rough gypsum surfaces proved to be an effective experimental analogue for investigating chemical fluxes to and from live coral communities.

2. Coral-rough gypsum surfaces had fluxes (as measured by the Stanton number) of between $17 - 70 \times 10^{-5}$, depending on the water velocity, friction factor and roughness height of the assemblage. The enhancement of mass transfer over that of a smooth surface is up to $9 \pm 1$ times, and is similar to that observed for phosphate and ammonia uptake on a variety of experimental coral communities.

3. The similar mass transfer characteristics of coral-rough gypsum surfaces and a living coral community is due to similar large scale geometric features such as branching. Neither active biological mechanisms nor small scale phenomena such as fractal geometry affect mass transfer rates on living coral communities.

4. The Atkinson and Bilger (1992) model of nutrient uptake, using the rate limiting step of fluxes resulting from diffusion through the boundary layers, is valid. Such models may be useful tools for understanding chemical fluxes on reef systems in future environments of altered sea surface temperature and weather patterns.

5. Coral-roughness has probably arisen through natural selection to maximize the uptake of nutrients at low velocities, and to increase survival at high velocities in a wave swept environment.
References


Other Sources

Plasters and Gypsum Cements for the Ceramic Industry. United States Gypsum Company.
Glossary

**Activity (a):** An experimental measure to represent the 'effective' mole fraction of chemical. Activity corrects for the non-ideal behavior of ions, due to phenomena such as ion-ion interactions.

**Bulk velocity (U_b):** The velocity measured by a neutrally buoyant drogue traveling over the sample area. U_b will be the integrated velocity of the fluid in contact with all of the drogue's surfaces over the measurement time interval.

**Chemical potential of i (µ_i):** The rate of change in total Gibb's free energy with respect to the change in quantity of chemical species i, while keeping pressure, temperature and the ratio of the quantity of other chemical species constant.

**Coral-rough:** Phase termed for this study to refer to surfaces of similar roughness to coral communities.

**Diffusive sublayer:** The inner portion of the momentum boundary layer where the transport of a chemical species is by diffusion down chemical potential gradients.

**Friction coefficient (c_f):** Dimensionless measure of shear stress exerted on a fluid by a surface, arising from both form drag and skin friction.

**Friction (or shear) velocity (u_*):** A characteristic velocity used to represent the velocity within the momentum boundary layer.

**Form drag:** A stress exerted on a fluid by a protruding shape interrupting the flow, including effects such as the stress created by the wake of a protruding shape.

**Fully rough:** A condition of a flow where, due to surface roughness, the friction coefficient becomes independent of Reynolds number. Generally occurs at Re_k > 70,
although on a coral-rough surface transition to fully rough behavior does occur until a much higher Reₖ.

**Head:** Pressure measured as the equivalent height of water at the prevailing hydrodynamic conditions (salinity, temperature, atmospheric pressure).

**Hydraulic diameter (Dₜ):** A calculated dimension shown to correlate the momentum transport behavior of different flow geometries, such as an open channel and a pipe.

**Hydraulically smooth:** A surface whose cₜ and Stₘ are those of a smooth surface. Generally observed on surfaces at Reₖ < 5, but not investigated for coral-rough surfaces.

**Mass-transfer limited:** The rate limiting step for transport of a chemical species from a fluid to a surface is diffusion through the diffusive sublayer.

**Momentum boundary layer:** The region of flow where velocity changes from the wall velocity to 99% of the free stream velocity.

**Plaster-of-paris:** Commercial name for the mined gypsum (CaSO₄•2H₂O). Also known as alabaster.

**Prandtl number (Pr):** Ratio of molecular diffusivity of momentum to the molecular diffusivity of heat.

**Reynolds number (Re):** Ratio of viscous forces to inertial forces. It is a measure of the likelihood of a fluid to be laminar or turbulent.

**Reynolds roughness number (Reₖ):** Nondimensional measure of the surface roughness, based on either the average roughness height, k', the standard deviation of roughness height, k₊, or the equivalent sand-grain roughness height, kₕ.

**Sand-grain roughness height (kₕ):** The mesh dimension of a sieve used to sort sand-grains by Nikuradse (1933) for friction dissipation experiments. An equivalent sand-grain
roughness (also $k_s$) has since been defined (Schlichting, 1955) to give a roughness dimension to other shapes observed to have the same friction characteristics as the sand-grains of Nikuradse of dimension $k_s$.

**Schmidt number (Sc):** Ratio of molecular diffusivity of momentum to molecular diffusivity of a chemical species.

**Sherwood number (Sh):** Dimensionless flux of a chemical species.

**Skin friction:** A shear stress exerted on a fluid by a surface parallel to the flow.

**Specific Conductance:** The calculated conductance for a solution, as would be measured at 25°C. The units of $\mu$S/cm or $\mu$mhos/cm are equivalent to $\mu\Omega^{-1}$cm$^{-1}$.

**Stanton number ($St_m$):** Ratio of the uptake of a substance to the advection of that substance past the uptake surface.

**Thermodynamic Force (F):** A theoretical force (per mole) defined so as to oppose the work per unit distance done by random molecular motion in a chemical potential gradient.

**Transitional roughness:** Flow behavior intermediate between hydraulically smooth and fully rough. Generally occurs at $5 < Re_k < 70$, although seen at much higher $Re_k$ on coral-rough surfaces.

**Turbulent Schmidt number (Sc$_t$):** The ratio of eddy diffusivity of momentum to the eddy diffusivity of a chemical species, and approximately equal to one.