Colloid Retention Behavior in Environmental Porous Media Challenges Existing Theory

PAGES 179–180

Chances are the quality of your drinking water was improved by filtration through porous media at some point before it reached your tap, perhaps naturally by transport through the subsurface, or purposefully by passage through an engineered sand filter.

Engineered filtration processes have been utilized for decades, and these processes are monitored to ensure the removal of a required degree of particles, e.g., colloids (biological and non-biological particles ranging between a few tens of nanometers to ten microns), from water. Filtration is manifest in both natural and engineered contexts, e.g., by the relatively high quality of spring water, and by the difficulty of targeting the delivery of microbes, zero-valent iron, and other colloids with novel properties to contaminated locales in the subsurface for the purpose of remediation.

Physicochemical filtration is a process distinct from physical straining. The latter process concerns colloid capture in pore throats (spaces between porous media grains) too small to pass. Physicochemical filtration entails colloid removal by association with porous media surfaces under conditions where colloids are sufficiently small to pass through pore throats.

Despite the prevalence of filtration in environmental media, the physicochemical processes governing filtration under environmental conditions are not well understood. This article demonstrates important deviations from existing theory regarding colloid deposition in porous media, and highlights the need to develop colloid transport theories to account for the behavior described below.

Existing Models

Existing theories describing colloid filtration in porous media represent physicochemical filtration as being dependent on the colloid trajectory relative to the porous media grain surface, where deposition occurs only for colloids moving along streamlines that intercept the grain surface, and where diffusion and sedimentation cause colloids to cross streamlines [e.g., *Rajagopalan and Tien,* 1976]. The rate coefficient for colloid deposition (k_f) under favorable deposition conditions is dependent on the probability of colloid collision with the grain surface (η), the porosity of the porous media (θ), the porous media grain diameter (d_c), and the fluid velocity (v):

$$k_f = \frac{3}{2}\frac{(1-\theta)}{d_c}v\eta \quad .$$

By W. P. Johnson, X. Li, and M. Tong

Colloid filtration models assume that the rate coefficient for deposition onto porous media is spatially invariant, and that the rate of colloid re-entrainment into solution is negligible. Both assumptions have been demonstrated applicable under conditions where the colloid and grain surfaces are of opposite charge (absent electrostatic repulsion), and filtration models yield accurate predictions of deposition rate coefficients under such conditions.

Environmental porous media and environmental colloids carry overall negative surface charges, yielding significant electrostatic repulsion between colloids and porous media grain surfaces in environmental systems. The fact that filtration is prevalent under environmental conditions, i.e., conditions where an energy barrier to deposition (electrostatic repulsion) is present, runs counter to expectations from theory, which dictates that significant electrostatic repulsion should disallow colloid deposition.

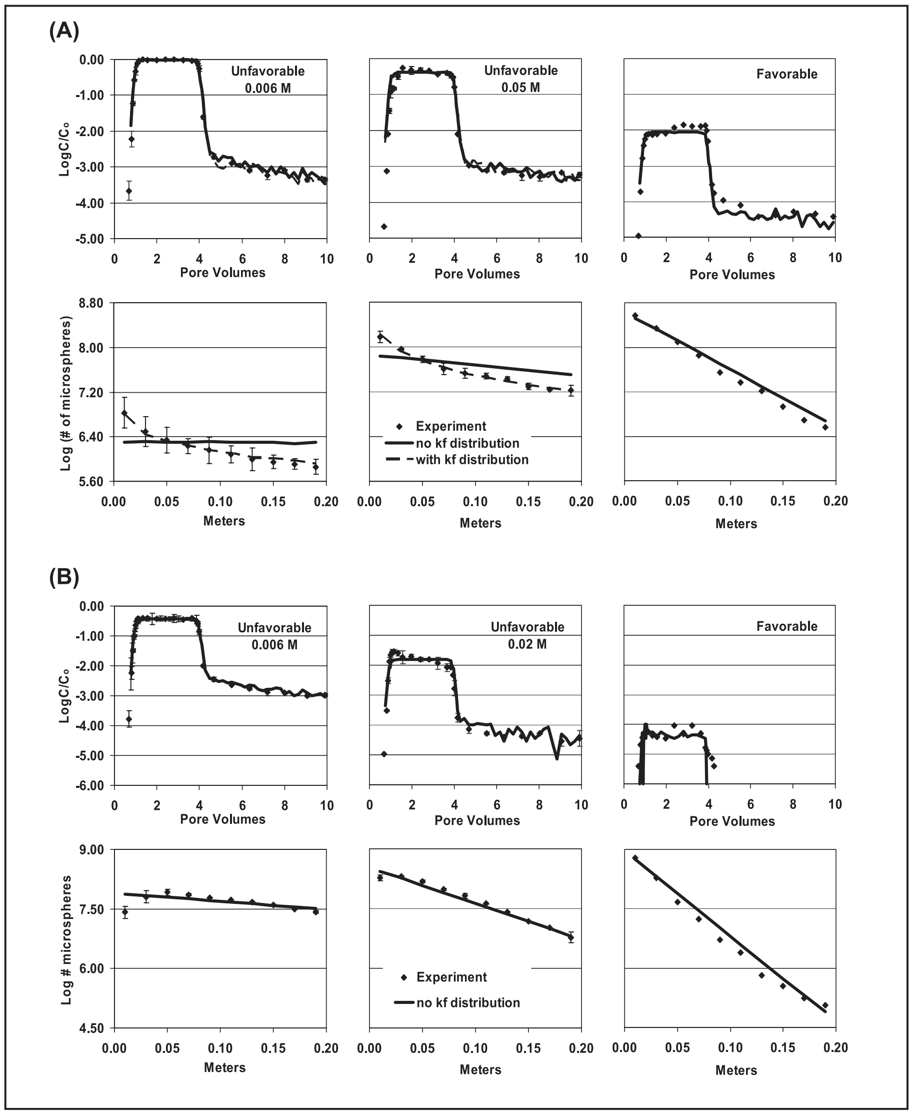

Fig. 1. Experimental results for microspheres in (a) glass beads and (b) quartz sand at average pore water velocity of 4 m d^{-1}. Effluent breakthrough-elution curves (top rows of Figures 1a and 1b) and retained profiles (bottom rows) are shown for the 1.1-µm carboxylate-modified microspheres in the presence of an energy barrier (unfavorable conditions) with 0.006 and 0.05 M NaCl (left and middle colu mns) and in the absence of an energy barrier (favorable conditions, using 0.93-µm amine-modified microspheres in 0.001 M NaCl, right column). Error bars represent standard deviations in results from replicate experiments (n ≥ 2). Simulations using the particle transport model with a single deposition rate coefficient (single k_f, solid curves) are contrasted against those using a deposition rate coefficient distribution (distributed k_f, dashed curves). In contrast to those of the carboxylate-modified microspheres (left and middle columns), effluent curves and retained profiles of the amine-modified microspheres (right column) could be simulated simultaneously using a single deposition rate coefficient. The influent concentration of amine-modified microspheres (1.35 × 10^{7} particles mL^{-1}) was normalized to the average influent concentration of carboxylate-modified microspheres (3.5 × 10^{6} particles mL^{-1}).

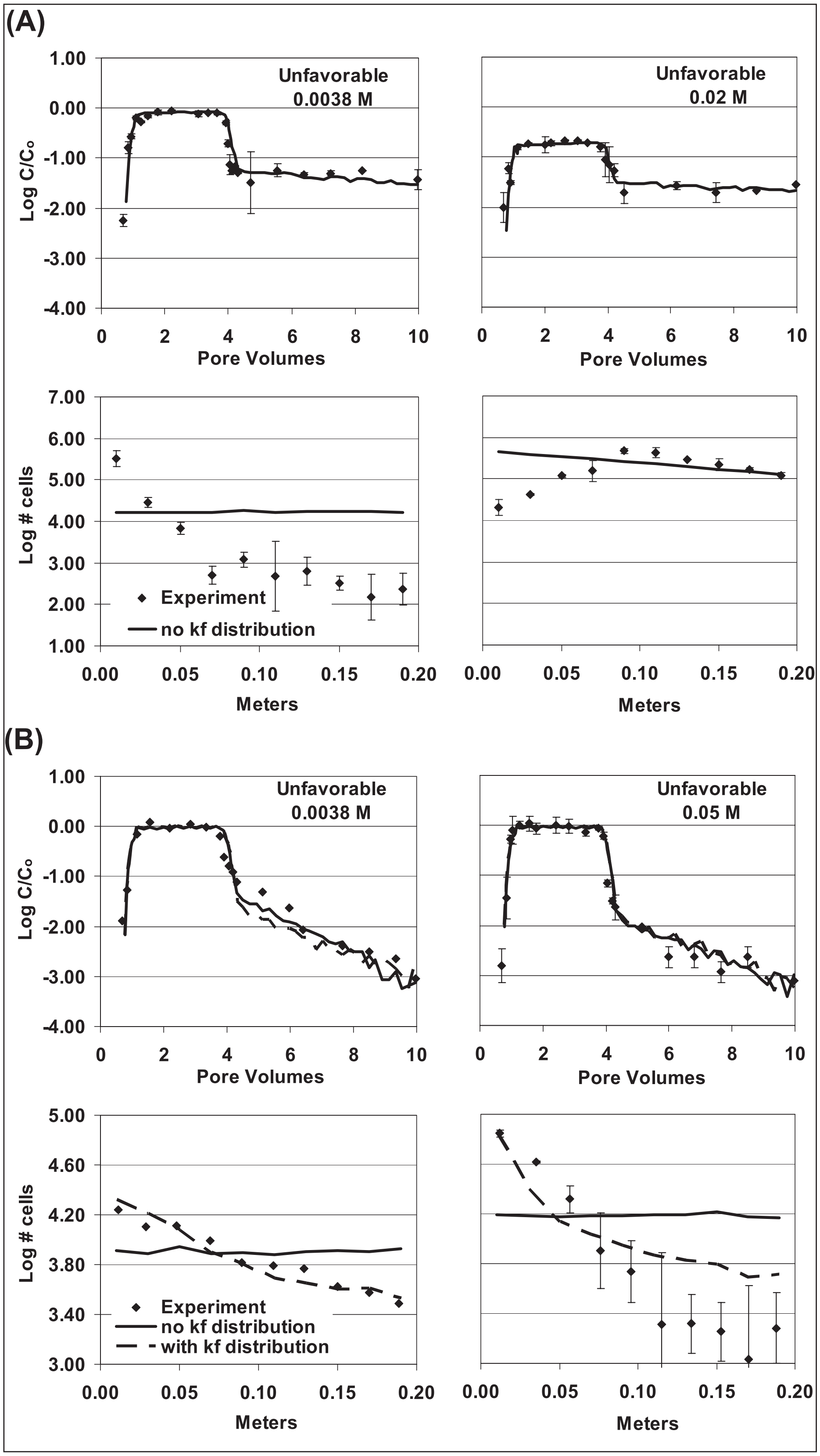

Fig. 2. Experimental results for DA001 (bacteria) in (a) glass beads and (b) quartz sand in the presence of an energy barrier (unfavorable conditions) with average pore water velocity of 4 m d^{-1}. Effluent breakthrough-elution curves (top rows of Figures 2a and 2b) and retained profiles (bottom rows) are shown for DA001 in glass beads at various ionic strengths. Error bars represent standard deviations in results from replicate experiments ($n \geq 2$). Simulations are shown from the particle transport model using a single deposition rate coefficient (k_f) (solid curves) and a deposition rate coefficient distribution (dashed curves). The influent concentration ($2.0 \times 10^4 \pm$ 50% cells mL^{-1}) was normalized to 1.0×10^4 cells mL^{-1} for comparison between experiments.

This discrepancy with theory has tentatively been ascribed to surface charge heterogeneity and surface roughness within environmental porous media, which serve to locally eliminate electrostatic repulsion [e.g., *Elimelech and O'Melia*, 990]. Alternatively, it has been proposed that colloid deposition in the presence of a repulsive energy barrier occurs outboard (more distant from the grain surface) of the energy barrier, where electrostatic repulsion becomes negligible but where van der Waals attraction (emanating from fleeting and/or permanent dipoles in molecular bonds) remains significant. This slightly attractive region is called the secondary energy minimum, and there has been a recent surge of papers corroborating the possibility of colloid deposition in this region [e.g., *Hahn et al.*, 2004].

Colloid filtration models have been adapted to reflect the presence of an energy barrier by introducing an additional parameter, α, which represents the probability of deposition upon collision in the presence of an energy barrier (α< 1). The product of α with η yields a reduced deposition rate coefficient in the presence of an energy barrier relative to the absence of an energy barrier for a given physical system. The above equation, with α included, has been widely utilized to describe colloid filtration under environmental conditions. The parameter α can be rationalized as representing the impedance of deposition by the energy barrier or, alternatively, limited retention capacity of the secondary energy minimum.

The assumption of a spatially invariant colloid deposition rate coefficient yields the expectation of log linear decreases in colloid concentrations (suspended and retained) with distance (x) from the source, as shown below:

$$Ln\frac{C}{C_0} = -\frac{k_f}{v}x \, .$$

This log linear dependency of colloid concentration on distance from the source has long served as the basis for estimating the transport distance of colloids in porous media prior to reduction to a given normalized concentration (C/C_0), where C_0 is the concentration at the source.

Discrepancies with Existing Models

A deviation from log linear distributions of colloid concentrations with distance from the source in porous media has recently been recognized for microbes, and was first reported for bacteria about a decade ago [*Albinger et al.*, 1994]. The concentration of retained bacteria decreased with distance from the source at a rate that was greater than that expected from log linear behavior. These hyper-exponential decreases in retained concentrations with distance from the source indicated that the deposition rate coefficient was not spatially invariant, but rather decreased with distance of transport.

It was hypothesized that spatial decreases in deposition rate coefficients are driven by the presence of a distribution of bacteria-sediment interaction energies among the bacterial population, such that "stickier" (i.e., having a greater tendency to deposit) bacteria are retained up-gradient of less sticky bacteria [*Albinger et al.,* 1994]. This implies that the bacterial population becomes progressively less sticky with increasing distance of transport. The observed deviation has since been extended to other bacteria, viruses and protozoa [e.g., *Redman et al.,* 2001]. Recent investigations demonstrate that hyper-exponential and other forms of deviation from filtration theory (log linearity) are not simply a peculiarity of microbes, but instead are fundamental aspects of colloid filtration in the presence of an energy barrier [*Li et al.,* 2004; *Li and Johnson,* 2005; *Tong et al.,* 2005a, 2005b].

The corresponding experiments involve introducing a suspension of colloids to a packed glass bead or quartz sand column, and monitoring the column effluent during injection for three pore volumes (of solution containing colloids) and elution (injection of colloid-free solution) for an additional seven pore volumes. The concentrations of retained colloids on sediment were determined at the end of the experiment by sectioning the columns into segments and desorbing the retained microspheres into pure water.

In the examples given below, carboxylate-modified latex microspheres (1.1 μm) (Molecular Probes, Inc., Eugene, Oregon) and an adhesion-deficient bacterial strain, DA001 (1.1 by 0.3 μm) were used to represent non-biological and biological colloids, respectively, during transport in porous media columns (20-cm length, 3.81-cm diameter) at an average pore water velocity of 4 m d^{-1}.

The glass beads and quartz sand (417–600 μm) and the carboxylate-modified microspheres carried negative surface charge under the conditions of the experiments; pH 6.92 (MOPS or $NaHCO_3$ buffer) and various ionic strengths (NaCl), thereby creating electrostatically repulsive deposition conditions with energy barriers of varying magnitudes. The surface charge of DA001 was only slightly negative (zeta potential ranged from -3 mV to less than -1 mV), and was hydrophilic under these conditions.

Microsphere concentrations were determined using flow cytometry (rapid cell counting technology) [*Li et al.,* 2004], whereas suspended DA001 concentrations were determined using ferrographic capture, a high-resolution modified form of immunomagnetic analysis [*Tong et al.,* 2005a]. Mass balances were mostly very good. For the microspheres, mass balances were between 86% and 107%, with the vast majority ranging between 95 and 100%. For bacteria, mass balances were between 70% and 105%, with the vast majority ranging between 81 and 100% [*Li et al.,* 2004; *Tong et al.,* 2005a; *Li and Johnson,* 2005; *Tong et al.,* 2005b].

Breakthrough-elution curves for colloidal transport in porous media in the presence of an energy barrier typically display increasing retention (decreasing steady state breakthrough concentration) with increased ionic strength. This expected behavior is demonstrated in Figures 1 and 2, and is consistent with expected compression of the electric double layer and decreased distance of significant electrostatic repulsion with increasing ionic strength.

Unexpected are the shapes of the profiles of retained colloids obtained in the presence of an energy barrier (unfavorable deposition conditions). In Figure 1a, the solid curves represent simulations using a spatially invariant deposition rate coefficient consistent with the mass balance. The experimental retained microsphere concentrations decreased faster than the simulated (no k_f distribution) concentrations (solid curves), indicating that the deposition rate coefficient effectively decreased with increasing distance of transport, i.e., hyper-exponential deviation from theory. Results such as these demonstrate that retained profiles of non-biological colloids also deviate from filtration theory, and that deviation from filtration theory is not a peculiarity of microbial populations.

Simulations using a log normal distribution of deposition rate constants (with k_f distribution, dashed curves) produced excellent fits to the data, reinforcing the hypothesis that distributed interaction potentials among the population generated the observed hyper-exponential deviation (Figure 1a) [*Li et al.,* 2004].

Deviation from log linear retained profiles decreased with increasing ionic strength, and was eliminated in the absence of an energy barrier (where the microspheres were positively charged 0.93-μm-diameter amine-modified polystyrene latex microspheres) (Figure 1a). This indicates that deviations were produced as a result of mechanisms operating in the presence of an energy barrier.

It has been well demonstrated in the literature that profiles of retained bacteria yield hyper-exponential deviation from filtration theory. However, more dramatic forms of deviation of bacterial retained profiles have been observed. For example, profiles of retained DA001 at various ionic strengths (flow rate of 4 m d^{-1}) in glass beads showed a dramatic shift in form from hyper-exponential to non-monotonic form as ionic strength increased (Figure 2a). Furthermore, the center of mass of the retained bacteria shifted increasingly down-gradient with increasing elution (not shown), demonstrating that under some conditions detachment can significantly increase the distance of microbial transport [*Tong et al.,* 2005a].

Non-monotonic retained profiles have also been obtained for non-biological colloids, e.g., microspheres in quartz sand (Figure 1b), which demonstrates that the form of deviation of retained microsphere profiles from log linearity (hyper-exponential in glass beads and non-monotonic in quartz sand) is highly sensitive to the system conditions [*Li and Johnson,* 2005]. Experiments in these systems also show that the extent of non-monotonic deviation from log linear behavior decreases with increasing ionic strength, and is eliminated under favorable deposition conditions (positively charged microspheres, 0.93-μm-diameter amine-modified) (Figure 1a). This result demonstrates that the non-monotonic form of deviation is also driven by processes operating in the presence of an energy barrier.

That the form of deviation from filtration theory can be highly sensitive to the system conditions is also demonstrated by the observation that retained profiles of DA001 cells in quartz sand were hyper-exponential (Figure 2b), in contrast to the non-monotonic retained profiles of DA001 in the glass beads [*Tong et al.,* 2005b]. Electrostatic repulsion is not the only means of generating an energy barrier to attachment. For example, DA001 is near neutral in its negative surface charge under the conditions examined, which results in calculated interaction energy profiles that are attractive (electrostatic energy barrier is absent). The observed adhesion deficiency (low deposition) of DA001 is not due to an electrostatic energy barrier; rather, it is likely driven by steric (structural) interactions with extracellular polymers on the cell surface [*Tong et al.,* 2005b].

Implications of Colloid Deposition-Reentrainment Dynamics

The profiles of retained biological and non-biological colloids examined here demonstrate that colloid deposition under unfavorable conditions is not governed by a spatially invariant deposition rate coefficient as has been traditionally assumed. Rather, the deposition rate constants vary spatially for biological and non-biological colloids under conditions where an energy barrier to deposition is present, and yield different forms depending upon system conditions.

The retained colloid profile shapes cannot be explained by sediment characteristics that would be evenly distributed across a packed porous media column, i.e., surface charge heterogeneity and surface roughness, since the deposition rate coefficient would necessarily be constant with distance. The retained colloid profiles provide a window into the mechanisms governing colloid deposition processes in the presence of an energy barrier, and their mutability suggests that the processes of colloid deposition and reentrainment in porous media are more dynamic than has been traditionally assumed.

The profiles demonstrated here also carry practical implications. For example, colloid deposition rate coefficients are traditionally utilized for log linear extrapolation of the transport distance that would be achieved prior to reduction to a given concentration. This practice must be reexamined under environmental conditions (unfavorable for deposition), since deviation from log linear retained profiles would yield inaccurate predictions; e.g., hyper-exponential deviations would result in greater transport distances relative to expectations from log linear extrapolation (the colloidal population effectively becomes less sticky during transport). Reentrainment (detachment) (shown here for DA001 in glass beads) presents another mechanism by which colloidal transport can be enhanced relative to expectations based on log linear extrapolation, since the practice of log linear extrapolation also assumes that reentrainment is negligible.

The examples shown here demonstrate that the process of colloid filtration during transport through environmental porous media is surprisingly complex, requiring direct visualization, measurement, and simulation techniques to investigate pore-scale processes governing filtration under environmental conditions.

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MEETINGS

Objectives for a Cabled Observatory in Alaska's Beaufort Sea

PAGES 177, 182

Study of the Arctic Ocean is limited by the sea ice and harsh weather that prevent access through much of the year. These constraints have restricted data acquisition in the past and obscured understanding of events, processes, and variability of the environment of the Arctic Ocean. Breaching this isolation can be achieved through the use of new technologies and the adaptation of existing instrumentation to monitor the shelf and basin independent of surface conditions.

Through much of its history, Arctic oceanography has been dedicated to the study of large-scale seafloor structure, ocean circulation, and hydrographic structure. Recently, expedition-based observations have been augmented by moored or ice-tethered instruments that provide year-round observations during the span of their deployment. With increased knowledge collected over an extended period, variability has become apparent but is not well understood. Permanent seafloor instrumentation is the only way to understand this variability (seasonal and annual) in the context of what may be rapid climate change (annual to decadal).

The scientific potential of a cabled seafloor observatory in the Arctic was explored by participants of a U.S. National Science Foundation (NSF)-funded open workshop, "Science and Education Objectives for a Seafloor Cabled Observatory on the Beaufort Shelf, Alaska," held early this year. Thirty-two people representing academia, government, private industry, and citizens of Barrow, Alaska, participated.

Discussions of what permanently installed seafloor instrumentation could accomplish for science and for Barrow ranged widely across the broad spectrum of disciplines including chemical, biological, and physical oceanography; geology and geophysics; and marine mammal and ice canopy studies. The key questions and problems addressed included, How would a cabled observatory for Arctic studies be designed? Where and how it should operate? What are the current engineering and science constraints for this facility in the Arctic? What are the science and education objectives for such a project?

The Beaufort Sea Shelf is a Key Location

Barrow, Alaska, which is located at the juxtaposition of the Chukchi and Beaufort seas, is ideal for investigating oceanographic processes pertinent to basin-scale and regional processes. The Beaufort and Chukchi shelve are heterogeneous environments, characterized by complex oceanography that dramatically affects the local ecosystem. Because this region is particularly sensitive to climatically driven environmental changes, understanding the variability and the linkages between and within the atmosphere and the ocean are necessary to constrain change, to predict how it will evolve over time, and to develop plans to mitigate the consequences to local communities.

The regional oceanography sets the stage for this facility. The shelf environment is heterogeneous and highly variable, dictated by the interaction between shelf, slope, and basin currents. These currents include flow through Barrow Canyon, complex and poorly understood boundary flows along the continental slope, and the Beaufort Gyre, which dominates circulation in the Canada Basin.

The connections among these current systems result in mixing and exchanges between the shelf and the basin. This complex interaction is influenced by water mass modification processes associated with the annual freeze/melt cycle, by winds, and by the steep and complicated bathymetry. The various currents transport organic material and nutrients between regions, which affects ecosystem structure, function, and chemical cycling. Very little is known about these ecosystems, particularly with respect to seasonal variation. Observing these changes beneath the ice, and through the fall and spring seasons, is not now possible. Permanent installation of oceanographic sensors on the seafloor would make study of these complex processes possible.

From the science and instrumentation talks at the workshop, three scientific foci emerged as priorities for the cabled observatory location:

• Barrow Canyon is a conduit for water and marine mammals into the deep Arctic Ocean. Monitoring of the transport of water and sediment, and of animal migration, through the canyon was seen as necessary to understanding the regional shelf-slope transfer.

• Hanna Shoal, east of Barrow Canyon and north of Point Barrow on the Beaufort Shelf, is a relatively shallow portion of the seafloor. Flow separation between the eastwardly flowing Pacific Ocean water and the much larger Beaufort gyre shifts across the shoal. Sea ice also advances and retreats across the shoal. Both of these complex events can be difficult or dangerous to observe from the surface.

• Canada Basin, the deep water north of the Beaufort Shelf, would make it possible to monitor the Beaufort Gyre and provide a quiet location for seismometers and cross-basin acoustic tomography.

A suite of oceanographic instrumentation was proposed that would provide valuable insights into a wide range of physical, biological, chemical, and geological properties, and that would take advantage of the infrastructure capabilities of a cabled observatory (kilowatts of power and gigabit-rate data transmission).

For example, passive acoustic monitoring would support comprehensive and continuous