# In Situ Sediment Remediation Through Capping: Status and Research Needs

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## I. Introduction and Background

Most sediment contaminants are strongly sorbed to the solid phase. To a first approximation, containment of the solid phase leads to containment of the contaminants. Thus significant natural recovery of a body of water can occur simply by deposition of clean sediment over the contaminated layers. Similarly, artificial placement of a clean sediment layer by in-situ capping can provide significant reductions in exposure and risk.

In-situ capping can be conducted by placement of almost any type of clean layer although sand or other coarse media is normally used due to its availability, low cost and ease of placement. More recently, additives to encourage degradation or sequestration of contaminants have been proposed as cap material. Geomembrane material may be used beneath a cap in soft sediments to aid in the support of the cap and stones or other large material may be employed as armoring on top of the cap to reduce cap resuspension and erosion. Surficial cap layers may also be designed to improve habitat values of the substrate.

The design objectives of a cap are normally one or more of the following:

- Physical containment of the underlying contaminated sediment
- Separation of the contaminants from biota at the sediment-water interfce
- Isolation of the chemical contaminants from the overlying water
- Encouragment of habitat values of the surficial sediments

Because containment of the solid phase largely contains the strongly sorbed sediment contaminants, one goal of a cap is to ensure that hydraulic forces do not erode and resuspend the underlying contaminated sediment. Since contaminated sediment sites often represent areas of deposition of even fine grained sediments, sand can often provide adequate stability. When the material employed as cap material is insufficient to provide adequate protection, cobble or stone may be added to the top of a cap to provide further armoring against erosion. This may be especially important in near shore areas where wave action or navigational stresses may be significant. Armoring may add considerable thickness to a cap and may also require additional filtering layers to control fines movement through the coarse armor material. Dredging prior to capping may sometimes be proposed to allow cap placement at depth where it will be subject to reduced hydraulic forces or to avoid significant reductions in water depth.

Separation of the contaminated sediment from benthic organisms that live near the sediment-water interface is one of the most important factors in reducing exposure and risk to those sediments. If adequate separation is provided, direct contact between the sediment contaminants and the organisms can be avoided, reducing the potential for contaminant accumulation in the organisms and reducing chemical release due to the physical and chemical changes introduced by those organisms.

Isolation of the chemical contaminants by a cap is also linked to the separation of the biota from the contaminated sediments. Bioturbation, the mixing associated with the normal activities of the benthic organisms, continuously reworks the surficial sediments and the contaminants associated with those sediments. This activity can maintain contaminant profiles relative uniform in the upper 5-10 cm due to effective particle reworking rates of a cm/year or higher in this region (Reible et al., 1996). The presence of a cap of sufficient thickness means that this reworking occurs in the clean cap material rather than in the contaminated sediment. Since the zone subject to the greatest organism activity is typically 5-10 cm, even a relatively thin capping layer can effectively eliminate bioturbation. Some organisms can penetrate more deeply but these are rarely population level effects. Thoms et al. (1995) summarized 240 observations of bioturbation mixing depths in fresh and salt water involving a wide variety of sediment dwelling organisms and found that more than 90% were 15 cm or less, and more than 80% were 10 cm or less. The elimination of particle movement by either erosion or bioturbation means that contaminant migration within a stable cap is limited to porewater processes of advection and diffusion. Since typical sediment contaminants are hydrophobic, these processes are strongly retarded by sorption onto the immobile solid phase. This elimination of active movement of sediment and the comparatively large contaminant burden the sediment contains is the primary reason that a conventional sand cap is effective.

The effective layer of a cap, $h_{cap}$, is depicted in Figure 1. After placement of a cap, consolidation of both the underlying sediment and the cap layer will occur. The consolidation of the cap layer, $\Delta h_{cap}$, directly reduces the effective cap thickness but has no other effect and is typically small. The consolidation of the underlying sediment, $\Delta h_{sed}$, does not directly influence cap thickness but expresses porewater from the contaminated layer up into the cap. This introduces contaminants into the cap but due to their hydrophobic nature, the chemical migration is retarded by sorption. The average penetration depth of the chemical contaminants is given by

$$\Delta h_{cont} = \frac{\Delta h_{sed}}{R_f} = \frac{\Delta h_{sed}}{\varepsilon + \rho_b K_d^{cap}}$$

Where ε is the void fraction in the cap, $\rho_b$ is the bulk density of the cap and $K_d^{cap}$ is the contaminant partition coefficient between the cap and the adjacent porewater. $K_d^{cap}$ is typically large ($10^2 – 10^6$) for the strongly sorbed sediment contaminants. $R_f$ is the retardation factor, whose magnitude is typically controlled by $K_d^{cap}$, is here defined as the ratio of the total mass per unit volume of sediment to the concentration in the porewater alone. Note that retardation associated with sorption is a transient phenomena and is not relevant to steady conditions when no net accumulation is occurring in the solid phase. Thus definition of a layer influenced by consolidation of the underlying sediment is also only relevant to transient calculations. Note that the existence of a steady state implies that there exists an infinite mass of contaminants in the underlying sediment at a concentration that is maintained constant. This is a common, although conservative, assumption. The bioturbation layer, $h_{bio}$, is also shown in Figure 1. Due to the high rate of contaminant movement as a result of organism-induced sediment reworking in the bioturbation layer, this is often considered to pose little or no resistance to mass transfer through the cap. Thus the effective cap thickness for chemical isolation under transient conditions is given by

$$h_{cap} = h_0 - \frac{\Delta h_{sed}}{R_f} - \Delta h_{cap} - h_{bio}$$

Where $h_0$ is the initially placed thickness. Under steady conditions, the second term is not applicable since it represents only the transient effect of consolidation of the underlying sediment. A separate armoring layer is generally assumed to pose no resistance to mass transfer and its thickness is in addition to the cap layer shown here.

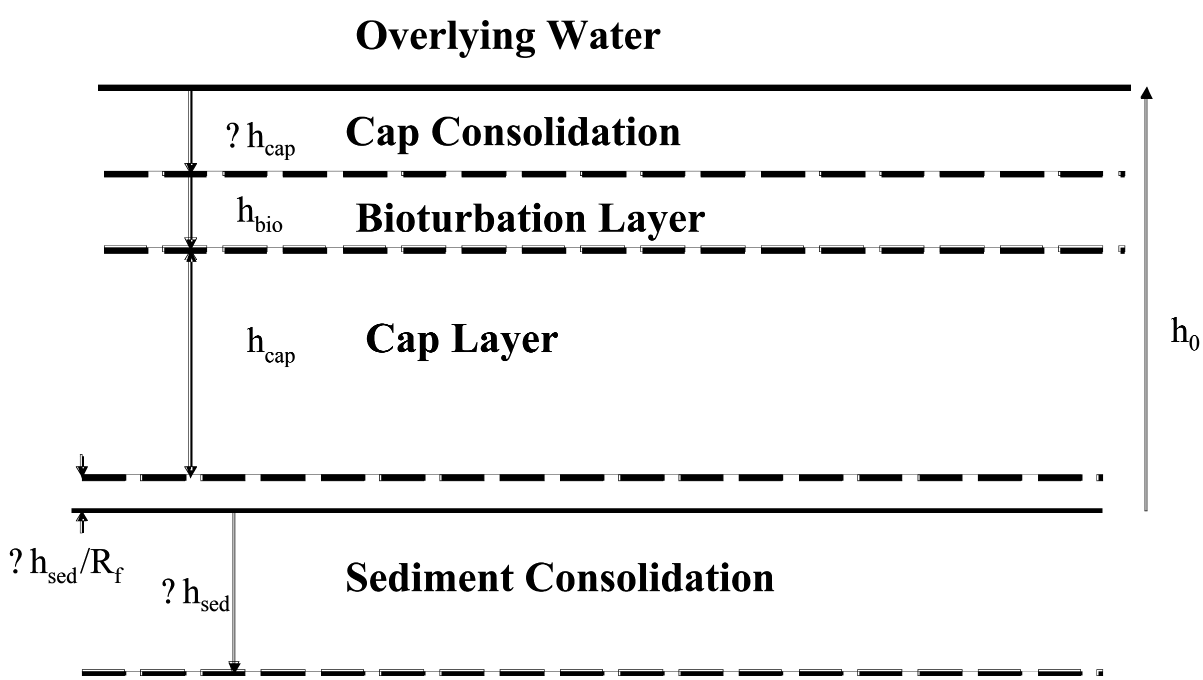


Figure 1 – Schematic Representation of the Various Cap Components

Assessment of transient cap performance is often accomplished with analytical semi-infinite advection-diffusion models (Palermo et al. 1998). The semi-infinite models are accurate predictions of contaminant migration and resulting concentrations only until the influence of the conditions at the upper boundary can no longer be ignored, i.e. when contaminants have begun to penetrate the entire chemical isolation layer. The time required to penetrate the chemical isolation layer under advectively dominated transport and diffusion dominated transport can be estimated by the relationships (Wang et al., 1991, Thoma et al., 1993)

$$\tau_{ss,adv} = \frac{R_f \; h_{cap}}{U}$$

$$\tau_{ss,diff} = 3.69 \frac{h_{cap}^2 R_f}{\pi^2 D}$$

Where U is the Darcy seepage velocity through the cap and D is the diffusivity of the contaminant in the pore space of the cap. For times approaching or exceeding these times under either advectively-dominated or diffusion dominated conditions, a more complete model that includes the transport processes at the upper boundary is necessary to accurately predict fluxes and contaminant concentrations. These simple models, however, indicate that a cap can be very effective for long periods of times for sorbing contaminants for which $K_d^{cap}$, and therefore $R_f$, are large. For example, even seepage velocities that suggest complete penetration of a cap in a year suggests that the contaminant may require of order $R_f$ years (i.e. $10^2$-$10^6$ years) to penetrate a cap.

Encouragement of habitat values may also be a design objective of capping but it is rarely the primary goal. The effect of a cap to reduce contaminant flux to the overlying water and reduce direct exposure to benthic organisms, however, produces an environment that can be beneficial to habitat values. In addition, the surficial characteristics of a cap can be modified to create any type of habitat, encouraging specific desirable species or discouraging undesirable species. In contaminated waterways, deposition over time often has left a relatively homogeneous fine grained substrate that does not support historical habitat uses. Waterway regulation may have reduced the flow variability and reduced the diversity of the bottom sediments. The addition of sand or more coarse material from the cap or armoring layer can restore diversity and habitat. Alternative substrate material that differs from the composition of the capping or armoring layer may also be placed if desired.

## II. Summary of Technical Findings and Issues

As indicated above, conventional sediment capping with sand or similar material can be extremely effective over long times with strongly sorbing contaminants. Retention of contaminants for decades, centuries, or longer may be expected if the cap can be properly placed and retained over these time periods and as long as facilitated transport mechanisms do not compromise their effectiveness. In some cases, however, proper placement or long term cap stability are difficult to ensure and transport mechanisms may exist that cause more rapid reductions in effectiveness. In this section the key issues and current technical approaches to evaluating capping at a site will be summarized. Key issues to address in design, evaluation and implementation of caps include

- Determination of appropriate performance criteria
- Evaluation of mechanisms compromising cap or chemical containment effectiveness
- Evaluation of required armoring layer characteristics
- Identification of appropriate cap material including potential amendments to encourage fate processes

- Evaluation of appropriate cap placement approaches

In addition, monitoring of the implementation and long-term cap performance is critical to the evaluation of success of a capping operation and to provide information on the appropriateness of in-situ capping as a remedy. Rarely is monitoring a high priority in remedial programs. Further complicating monitoring of in-situ capping is the long design lifetime of a cap. It is possible to conduct monitoring and identify failure due to poor placement or inadequate containment, but demonstration of a successful capping operation may require monitoring for decades or centuries. Long term monitoring concerns and issues are common to other in-situ remedial approaches and will not be discussed further herein.

**Cap performance criteria**

Selection of appropriate performance criteria is critical to the design of the cap and long-term monitoring programs to evaluate cap effectiveness. Lu et al. (2003, 2004a) and Kraaij (2003) have both identified porewater concentration as a good indicator of risk to contaminants exhibiting limited bioavailability and, as shown by Lu et al. (2004b), regardless of route of exposure in organisms. Contaminant flux is directly related to water column concentrations and therefore also a good indicator of risk to organisms in that medium. Chemical flux to the overlying water and mobile phase (i.e. porewater) concentrations may be good indicators of exposure and risk but these are difficult to measure and only a limited database is available to help define quantitative performance criteria.

Traditionally, cap performance criteria have been based upon sediment concentrations. Such criteria can be determined from site specific bioassays but can rarely be extrapolated to other sites or even to areas within a site exhibiting different sediment characteristics that can influence bioavailability (e.g. organic carbon content for hydrophobic organic contaminants). Sediment quality criteria using equilibrium partitioning theory for organic contaminants or indicators such as simultaneously extractable metals vs acid volatile sulfides for certain metals, are good screening tools for sediments but oversimplify the actual physical and chemical processes, limiting their accuracy as cap performance criteria.

The importance of the performance criteria can be illustrated by examining their influence on cap isolation layer design. Contaminant flux is largely controlled by the cap isolation layer, while surficial sediment concentrations are largely controlled by the flushing action of bioturbation and the sorption characteristics of the layer influenced by benthic organisms. Porewater concentrations are continuous across layer interfaces while sediment concentrations can change dramatically as sediment properties (and sorption characteristics) change. A sediment concentration criteria to define cap performance encourages the use of low sorptivity caps such as sand which may exhibit low solid phase concentrations while not having a significant influence on the porewater concentrations or risk. Performance criteria focused on porewater concentrations or flux do not artificial encourage low sorptivity caps but, as indicated previously, there are few absolute guidelines on acceptable levels of these quantities as is the case with sediment concentrations.

**Contaminant migration mechanisms in a cap**

Conventional approaches to predict contaminant migration in a cap assume only advection and diffusion of dissolved contaminants. Palermo et al. (1998) provides a simple analytical model of transient chemical migration through such a layer and this model is often used as the basis for design of the chemical isolation layer thickness. This model does not allow for variations in sediment or transport properties, for example in the surficial sediments where bioturbation is important and where organic carbon content can be significantly higher than in the underlying cap material. Reible et al. (2004) has proposed a simple analytical model to predict flux and concentration in the surficial sediments under steady state conditions that relaxes these assumptions. This model is useful in predicting the potential surficial sediment concentrations for comparison to typical cap performance criteria. For conditions that neither analytical model can address, numerical models have been developed, e.g. the Recovery model of the US Army Corps of Engineers and the model developed by Reible referenced in Palermo et al. (1998).

Key parameters in addressing chemical migration rates through a cap are cap partition coefficients, effective diffusivities in the cap media and the seepage rate through the cap. Cap partition coefficients define the sorption-related retardation factor through the cap layer and therefore directly relate to transient behavior in the cap. At steady state, however, the partition coefficient only defines the potential solids concentration and does not influence porewater concentrations that may be a better indicator of exposure and risk. Effective diffusivities in the cap media are a function of a chemical-specific property, the diffusivity in water, and media-specific properties, the porosity and tortuosity. Although diffusion rates are sensitive to these values, it is possible to make a priori estimates that are well within an order of magnitude based upon tabulated and easily measurable physical properties of the cap media.

More difficult to assess is the significance of seepage through the cap layer. Of primary concern is seepage into the body of water that might transport contaminants out of the cap. Over time, a seepage dominated system will contaminate a cap and ultimately achieve a flux to the overlying water identical to pre-cap conditions if a large inventory of contamination maintains sediment concentrations effectively constant. The surficial sediment concentrations, however, may still be lower than pre-cap conditions due to bioturbation of the surficial sediments if a viable benthic community is maintained. Seepage meters have been employed for direct measurements and recent improvements in such systems have improved their accuracy and sensitivity (Petrocelli, 2003). They remain point measurements, however, and it is sometimes difficult to extrapolate such measurements over the entire area of interest. Seepage is normally a strong function of distance from shore with higher seepage rates along a shoreline or along river banks and much lower rates further from shore. Local geology, however, can alter this considerably. Piezometers can provide more detailed coverage of an area and directly indicate driving forces for seepage and locations of outflow versus inflow. They do not, however, directly indicate seepage rates. Often large head gradients can be measured across low permeability aquitards without indicating a significant flow. Large head gradients across a low permeability or impermeable cap, however, have been identified as a concern for possible uplift of a cap (Mutch, 2003) and this concept is being testing in a field demonstration innovative capping technologies conducted by the author on the Anacostia River in Washington DC (www.hsrc-ssw.org/anacostia/).

Also difficult to assess is the importance to contaminant migration of other phases in the sediment. Gases are often generated in sediments due to the degradation of organic matter. These gases can transport volatile contaminants through partitioning into the gas phase and transport low volatility, hydrophobic contaminants through accumulation at the gas-water interface. The gas may also physically disrupt the sediment or cap layer, creating secondary porosity and increasing seepage and/or surface water flushing of the sediments or cap layer. Nonaqueous phase liquids (NAPL) exhibit even more potential to enhance contaminant release through a cap. NAPLs would generally contain the bulk of any hydrophobic organic contaminants and any NAPL migration would result in significant contaminant migration. Seepage forces during consolidation or the physical disturbance of placing a cap may encourage movement in a NAPL that was previously stable. The influence of NAPL and gas transport on cap effectiveness is an important area of future research and is discussed in more detail below.

**Cap armoring requirements**

Long-term cap effectiveness depends upon stability of the cap layer. Hydraulic forces that could work to destabilize and erode a cap can be the result of

- High flow events in a river
- Waves in the surf zone or due to winds in lakes
- Ice breakup and damming
- Propeller wash or other navigation related influences

In general, each of these must be assessed and the controlling forces used to design an armoring layer for a cap. Three basic approaches may be used to control hydraulic forces and ensure long-term cap stability

1. Armor the cap layer sufficiently to sustain the hydraulic forces
2. Dredge and cap at a deeper layer recognizing that the influence of hydraulic forces typically decreases significantly with depth
3. Provide controls of the hydraulic forces (breakwaters, dams, navigation controls) to limit their effect on the cap layer

Typically, technical guidance for shore and bank protection is applied to the design for a cap. Palermo et al. (1998) provides design approaches for assessing armoring necessary to sustain high flow events and propeller wash. The USACE also provides guidance that can be used to establish necessary armoring due to waves in the surf zone and wind driven waves through the Automated Coastal Engineering System (ACES) program. The influence of ice on cap structures had not received significant attention until an ice jam resulted in significant erosion on a pilot cap placed in the Grasse River in New York in 2003. Investigation of that event has led to improved approaches for assessing and managing the effects of ice in those areas where it may be important. Ice jams during breakup appear to have the greatest potential for cap destabilization and either increased armoring of the cap or the use of dams to control the location of jamming may be successful for control.

In any effort to design armoring requirements, the design life and potential exposure of the cap must be assessed. It is likely feasible to design a cap to be stable under almost any hydraulic forces but it is necessary to specify an appropriate design event. A "100 year" storm or flood is often used as a design basis for low probability natural events but higher or lower probability events may be appropriate depending upon the degree of confidence required and the lifetime of the contaminants.

Traditional approaches to selection of armoring for a cap focus on defining the threshold of erosion. This is a conservative approach and does not attempt to address the commonly observed behavior of erosion to a finite depth in a particular erosive event with deposition occurring at other times. In such a situation, it may be possible to have more modest armoring requirements as long as the armoring layer was sufficiently thick to avoid complete loss during erosive events.

**Selection of cap material**

Sand has normally been used as cap material because it is readily available, relatively inexpensive, and easy to place. Although sand provides many of the basic protective features of a cap, additional cap effectiveness could be achieved through the use of alternative materials to achieve specific objectives. Alternative materials that have been suggested for use in caps include

- Organic rich soil or organically amended sand to increase the retardation of hydrophobic organic contaminants through the cap or to encourage degradation
- Organoclays to control NAPL migration through caps
- Swelling clay formulations such as bentonite or Aquablok®, a clay mineral-based capping material, to control permeability
- Coke or activated carbon to sequester organic contaminants
- Apatite to sequester metal contaminants
- Zero valent iron to encourage dechlorination

Most of these materials have been evaluated in the laboratory and demonstrated some effectiveness in particular situations. Their feasibility, cost and effectiveness in the field is largely unknown. The author is leading a demonstration in the Anacostia River in Washington DC designed to help answer these questions (www.hsrc-ssw.org/anacostia). A wide variety of materials, including those listed above, were considered for inclusion in the program. Due to a variety of considerations including cost, placement or effectiveness concerns, and site characteristics, the materials tested in the field program are

- Aquablok®, in cooperation with the EPA SITE program
- Coke
- Apatite

In addition, the coke is placed in a laminated mat developed in to control placement and reduce fines loss. Coke exhibits a sorption capacity analogous to that of a high organic carbon sediment such that placement in a thin (1" thick) mat will provide only small benefits in sequestration of organic contaminants. Due to its low cost, coke was originally selected for bulk placement where its sorption capacity would be much more significant. Potential concerns about loss of the near neutrally buoyant material during placement, however, and the desire to test a means of controlled placement of high value materials led to the use of the laminated mat technology. Activated carbon and supported or nanoscale zero valent iron are materials that might be cost-effectively placed with the laminated mat approach. Activated carbon has been shown to be effective at sorption and reduction of bioavailability of organic contaminants (Luthy et al. 2002) and supported and nanoscale iron have been shown to be effective at reductive dechlorination of chlorinated benzenes and PCBs (Lowry, 2003, Gardner, 2003). Cost and placement concerns normally preclude the use of conventional broadcasting techniques for these materials.

Cap amendments are designed to retard contaminant migration, encourage degradation within the cap or to provide finite sequestration capacity. Because they have only limited impact on the contaminants in the underlying sediment, cap amendments should normally be considered a means of delaying, but not eliminating, the ultimate migration of contaminants through the cap. They are perhaps best used as a secondary barrier to improve confidence in a cap that is expected to reach risk reduction goals.

**Cap Placement Approaches**

The cap placement technique can have dramatic consequences for the success or failure of a cap. Many contaminated sediment sites exhibit exceedingly soft sediments that can be easily disturbed, may be dislocated or destabilized by uneven placement, and may have insufficient load bearing capacity to support some cap materials. Palermo et al. (1998) provides approaches to assess the geotechnical characteristics of the sediments as well as design estimates for load bearing capacity. These methods normally require reconstituting collected sediment samples in the laboratory, raising concerns about the representativeness of the data generated. Collection of undisturbed cores is preferred with consolidation and cap placement experiments being conducted directly on the candidate sediments. These data can be supplemented with in situ measurements such as vane shear tests to determine surficial sediment strength. Large diameter vanes, such as those used in wastewater treatment ponds, may be necessary to get measurable strengths in some soft sediments.

Field efforts have shown, however, that it is possible to place caps over exceedingly soft sediments although special care may be required. Uniform placement in very thin lifts may be required to allow strengthening of the underlying sediment (e.g. Thompson et al., 2003). In general, uniform placement by releasing at the top of the water column and allowing gravity settling of cap material is an excellent means of placing material without disturbance and in such a manner that the ability to support the cap layer is maximized. As indicated above, however, cap amendments often do not have the favorable settling characteristics of sand, and cap placement is an especially important consideration for such materials.

A conventional clamshell bucket can be used to place a cap layer uniformly in thin (~6")
lifts using a digital GPS for bucket location and with controlled opening of the bucket with an experienced operator. This method was employed to place sand, apatite soil and Aquablok® in the Anacostia capping demonstration project. Using this method a 6 inch cap layer was placed with a standard deviation of approximately 2 inches. In shallow waters, it is likely possible to replace even thinner lifts uniformly with a conveyor or broadcast system.

## III. Future Research Issues

Advancement of in-situ capping as a remedial approach for contaminated sediments requires improvements in several areas. Regulatory and implementation issues are critical to the success of in-situ capping but are not significantly influenced by capping research. Research into the appropriate indicators of sediment quality, whether solid concentration, porewater concentration, or flux, is important to the assessment of all remedial approaches. A variety of implementation issues were identified above but these are often better addressed by field demonstrations and pilot studies as opposed to research efforts. Research developing better methods of geotechnical characteristics of in-situ sediment may be beneficial, however, if coupled with field demonstrations.

Research into the processes controlling cap effectiveness and how to control and enhance cap effectiveness, is most likely to enhance the feasibility and applicability of capping. Research needs include

- research into the fate and transport behavior of specific contaminants that do not behave in the simple manner assumed in current cap evaluation approaches (e.g. mercury)
- research into the fate processes associated with physical, chemical and biological gradients within a cap (i.e. the potential for even a conventional cap as a permeable reactive barrier)
- research into the influence of transport processes facilitated by NAPL or gas migration
- research into cap amendments that may encourage sequestration or degradation fate processes

The cap-sediment interface is a unique environment that encourages fate processes. Anaerobic conditions typically develop at depth in a cap while near the surface, the activity of benthic organisms may maintain aerobic conditions. The benthic community controls the movement of oxygen and organic matter into the cap and sediments. For some contaminants this complex environment may significantly influence fate and transport behavior. Methylation of mercury, for example, may occur in surficial sediments immediate after capping due to the development of anaerobic conditions. Over time, however, the ability of a cap to reduce organic matter loading to the underlying sediment may eliminate significant methylation. For chlorinated organics, the bottom layers of a cap may provide an anerobic dechlorinating environment while the more aerobic conditions at the surface may provide a polishing environment for the degradation of the dechlorinated contaminants. The addition of amendments appropriate to a particular contaminant to either provide sorption and retardation or to actively encourage degradation may significantly enhance the ability of a cap to control these contaminants.

Capping is not normally considered to be an aid in controlling a contaminated groundwater plume that is entering a water body. A cap, however, provides a means to control oxygen conditions within the groundwater plume. Thus the application of a sediment cap can provide a relatively simple means of engineering a reactive permeable barrier as has been developed for subsurface treatment of groundwater (e.g. NRC, 2003). Specifically, a cap can behave like a two step reactive treatment barrier in that anaerobic conditions are normally maintained at depth in a cap while aerobic conditions can be maintained near the surface by either diffusion or bioturbation from the water body. The cap can potentially provide the residence time necessary to achieve the degradation of halogenated compounds, such as chlorinated solvents, that are common groundwater contaminants. These processes are illustrated in Figure 2 for chlorinated ethenes that are common groundwater contaminants. Other chlorinated compounds and even PAHs that predominantly but not exclusively degrade aerobically, will also be

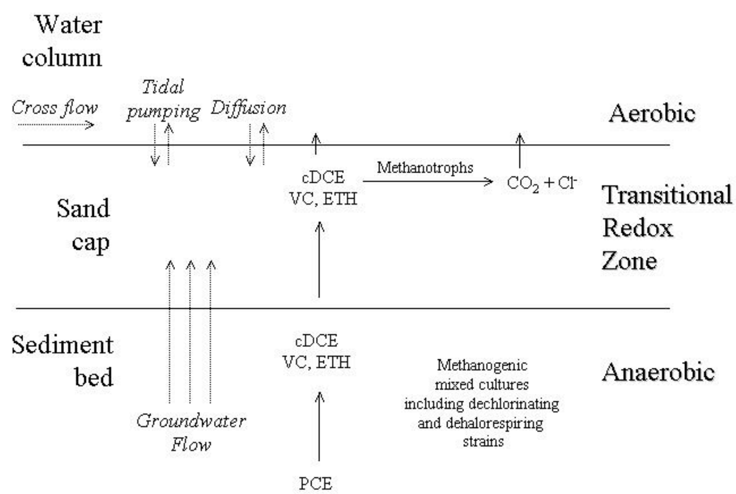


Figure 2 –Flux and transformation processes of chlorinated ethenes in a capped sediment system (Hughes, 2004)

Fate processes such as those depicted in Figure 2 may also be encouraged artificially by addition of cap amendments. Zero valent iron has been demonstrated to be an effective reduction tool in groundwaters but their behavior, especially over long periods of time, in surface waters and surficial cap layers is unknown. Finely divided iron, such as supported iron or microscale iron, appear to show greater reduction potential but are expensive to apply over large areas (Lowry, 2003; Gardner, 2003). The use of a laminated mat or similar technology to control placement and reduce reagent loss may be in order.

Degradation of both organic matter and contaminants in a cap are controlled by the nature of the microbial community. In a stable environment such as a cap, the physical conditions in the sediment and the density and diversity of the microbial community are significantly influenced by the macrobenthic community, a diverse group of organisms that populate the biologically active zone in the upper layers of sediment (Reible et al., 1991, Reible et al., 1996). This community introduces contaminants into the food chain via accumulation and subsequent predation by higher organisms, and encourages release and exposure in the overlying water through bioturbation, the reworking and mixing processes associated with the benthic organisms. This community also encourages degradation of contaminants, however, both directly through the ability of some organisms to metabolize selected contaminants, and more commonly through the microbial population that develops in response to the environmental conditions in the biologically active zone. The ability to fully exploit the potential of this community to control or limit exposure and risk to the sediment contaminants is dependent upon developing a better understanding of the structural and functional diversity of the microbial populations and their response to the macrobenthic community. To-date there have been few evaluations of the relationships between the microbial and macrobenthic community of sediments (Gillan et al., 1998, Chung and King, 2001). A better understanding of the relationships between these communities opens the potential for manipulation of the microbial consortia and optimization of the cap as a remedial measure.

Figure 3 illustrates the potential for the upper sediment layers to serve as an effective degrader of PAH contaminants and the importance of the macrobenthos on that degradation. This figure shows the residual pyrene concentrations as a function of depth after a several month microcosm experiment with an oligochaete. Although this organism shows little potential to directly degrade pyrene, the presence of the oligochaete significantly increases the depletion of the pyrene. This is expected to be largely due to the increased mixing of relatively oxygen rich overlying water deeper into the sediments by burrowing and porewater flushing activities, but may also be due to direct enhancements of the microbial community by the organism, for example due to the presence of surfactants, microbes, and partially decomposed organic matter in the fecal matter of the organism. It is understanding the underlying reasons for such dramatic increases in degradation effectiveness as well identification of means to manipulate this effectiveness that would be a worthy goal of research in this area.

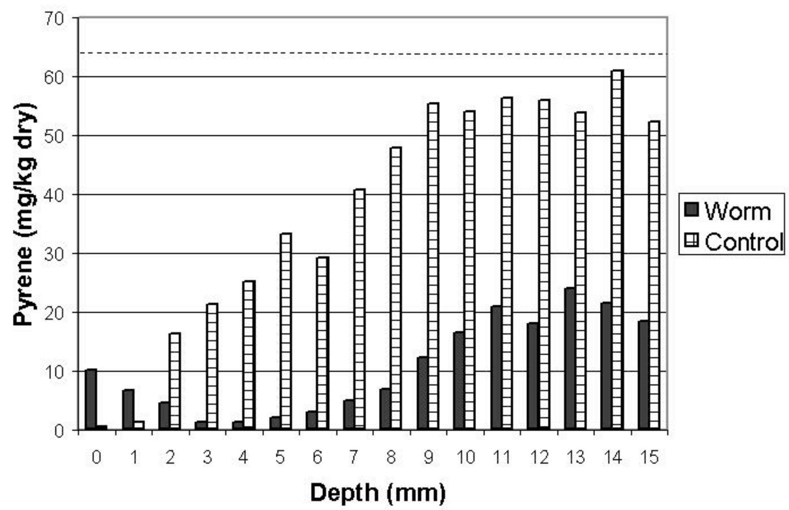


Figure 3 – Pyrene depletion with and without a macrobenthic community in the upper 15 mm of sediment in a laboratory microcosm

NAPL or gas generation and migration may facilitate transport of contaminants through a cap. The concerns about facilitated transport in contaminated sediments can best be illustrated by example. Figure 4 shows a conceptual model of the Thea Foss Waterway in Tacoma, WA which has been prepared by Foster Wheeler, Inc. A zone of dense nonaqueous phase liquid (DNAPL) that extends to near the sediment-water interface and is mobile is complicating the desired application of a cap in this area. How can a cap be designed to control the DNAPL? How can placement be implemented to ensure that it the DNAPL is not further mobilized. What are the key characteristics of the sediment that can mitigate destabilizing factors leading to DNAPL migration? These are questions that are critical to the successful implementation of any remedial strategy in this waterway but certainly to an in situ capping based strategy. Historically an area with this complicated of a conceptual model and contaminant fate processes might not be considered for conventional capping but closer examination of the DNAPL and geological heterogeneity of the system indicates that no conventional remedial approach other than capping is likely to be successful. Similar complications have been observed by the principal investigator at other sites contaminated with a NAPL including the Pine Street Canal in Burlington VT.

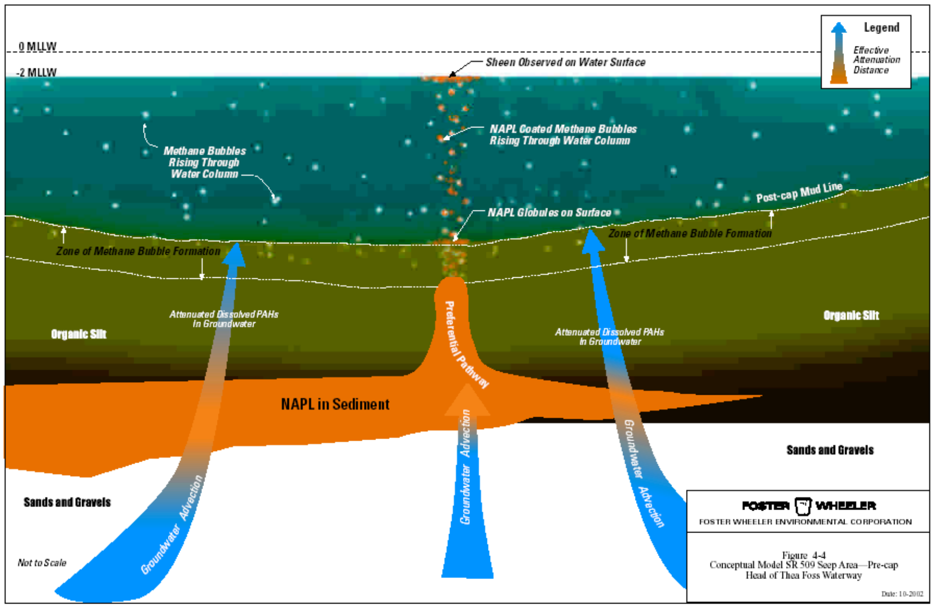


**Figure 4 - Conceptual Model of NAPL Seep in Thea Foss Waterway, Tacoma, WA**

The mobility of a NAPL at the sediment-water interface is controlled by capillary effects in the pore structure of the sediment. This retarding force is offset by the destabilizing influences of groundwater seepage flow due to either regional groundwater gradients or tidal fluctuations, physical disruption associated with cap placement and consolidation, and gas generation and migration. In a stable sediment environment, the Capillary number ($N_c$) , which relates viscous forces to capillary forces, and the Bond number ($N_B$) , which relates gravitational forces to capillary forces, are indicators of the mobility of NAPL (Reible and Illangasekare, 1989; Wilson et al., 1990).

$$N_c = \frac{U_w \mu_w}{\sigma_{ow}} \qquad N_B = \frac{kg\Delta\rho}{\sigma_{ow}}$$

Numerical criteria based upon these dimensional groupings can be developed which should provide guidance on NAPL mobility or entrapment (e.g. Chatzis et al., 1983).

Capping also introduces unique influences on NAPL stability. The contrast in physical properties of the sediment and capping layer provides an opportunity for development of either a capillary barrier or a preferential migration zone similar to that described by Illangasekare et al. (1995). During cap placement, the force of the cap settling to the sediment surface will potentially destabilize the NAPL. This may be parameterized by the ratio of the drag force on settling particles to capillary forces since the drag force defines the settling velocity of the cap materials. Generally cap placement by gravity settling is preferred to ensure uniformity of the completed cap. Subsequent consolidation of the underlying sediment after cap placement also provides a destabilizing factor for NAPL migration. The same processes describing dewatering and consolidation of sediments can (e.g. Poindexter-Rollins, 1990) can, in principle, be applied to NAPL migration and subsequent sediment consolidation but this approach is unproven.

A better understanding of NAPL behavior in sediments may help to assess if capping will cause unacceptable release or migration of NAPL. Even if mobile, however, or to improve confidence in a capping solution in the presence of apparently stable NAPL, capping may still be implemented with the addition of amendments specifical designed to control the mobilized NAPL. Organo-modified clays show considerable promise in this regard but not enough is known about commercially available formulations to predict NAPL performance. Research is recommended to better understand the process of NAPL retention of organo-modified clays and to help optimize their use in caps.

Another destabilizing factor in the DNAPL plume shown in Figure 4 is the gas generated by organic degradation processes in the sediment. Mineralization of sedimentary organic matter by bacteria generates gases such as $CH_4$, $N_2$, $CO_2$ and other trace gases. Denitrifying bacteria produce $N_2$, methanogenesis results in $CH_4$ and, $CO_2$ results from fermentation and sulfate reduction processes in sediments. These gases tend to migrate out of sediments into overlying water and are vented to the atmosphere. The gas ultimately migrates to the surface, encouraging migration of separate phase material as well as contaminant to the sediment-water interface. This facilitated transport process is of concern at a number of other sites as well. For example, the principal investigator is leading a reactive capping demonstration project at the Anacostia River in Washington DC. A recent sediment imaging camera assessment of the subsurface sediments showed a number of locations influenced by gas generation and migration. Figure 5 shows sediments in the vicinity of the Anacostia active capping demonstration.

**Figure 5 -Image of gas voids and gas bubble exiting sediments west of Washington Navy Yard on the Anacostia River**

The migration of gases depends upon the requirement that the sum of the partial pressures of gases in the bubbles exceed the sum of the atmospheric and hydrostatic pressures above the sediment (Heslein, 1976; Fendinger, 1981). Gas bubble ebullition rates of 224 to 2640 mL.m-2.d-1 have been reported for several sediments (Ward and Frea, 1979; Chau et al, 1977; Howard et al, 1971). Such gas migration and ebullition can significantly affect the integrity of sediment and can facilitate transport or organic contaminants by gas bubbles (Johnson et al, 2002; Adams et al, 1997). Bubble entrapment and mobilization in a porous media are governed by the same forces as control NAPL migration. Buoyancy driven migration of the gas opens channels through a cap or, if contained by an impermeable layer, may accumulate potentially causing greater damage when ultimately released. Gas bubbles are inherently hydrophobic and therefore also tend to accumulate both hydrophobic organic contaminants and colloids from porewaters and therefore their migration can have significant impact on the transport of contaminants through the cap. A key parameter in describing contaminant transport by bubbles is the bubble-water partition coefficient, $K_{bw}$, which tends to significantly exceed the conventional air-water Henry's constant due to the accumulation of hydrophobics at the interface. This interface is highly conducive to the adsorption and uptake of dissolved hydrophobic contaminants (example, polycyclic aromatic hydrocarbons, PAHs) (Raja et al, 2002; Smith and Valsaraj, 1997; Sojitra et al, 1996).

Understanding this effect is important in engineering the desired cap material and structure. The processes of gas bubble generation and migration, and associated contaminant transport are shown in Figure 6. As the gas bubbles exit the cap material, they also will change the integrity of the cap opening up macropores and providing additional pathways for exchange of porewater with the underlying contaminated sediment. As the enriched gas bubbles exit the clean cap it carries with it any volatile materials that can subsequently desorb into the water column above or be transported directly to the atmosphere as the gas bubbles break the water surface.

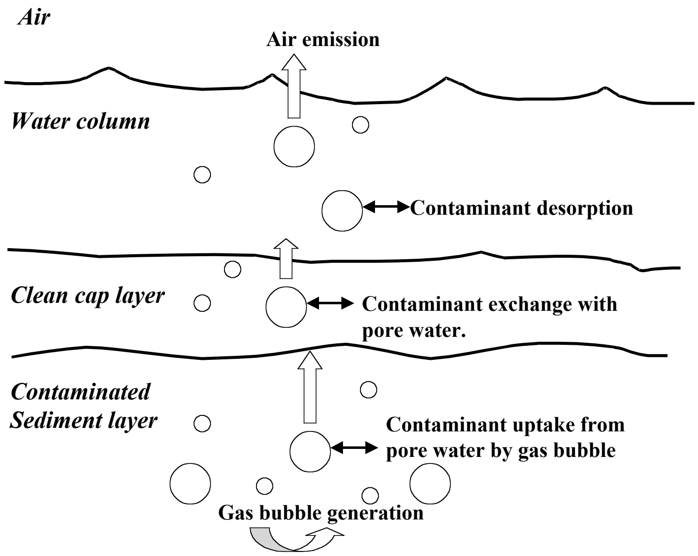


**Figure 6 - Depiction of gas bubble generation and migration through a cap**

Mitigation of facilitated chemical transport by groundwater seepage, NAPL migration and gas generation and migration may be enhanced by the use of amended sediment caps. In addition to those amendments described above to enhance reactivity, sequestration or groundwater control agents can be of benefit. Aquablok® has been used to control permeability and is being demonstrated in the Anacostia capping demonstration. Permeability control may be of limited benefit if the groundwater is contaminated since the Aquablok or a similar cap would simply divert the groundwater to another location. If the goal is to divert the groundwater before coming in contact with the contaminated sediment, however, this approach may be useful. Research investigating the effects of permeability controls on surface water – groundwater interactions and the ability to control accumulating gas or tidal fluctuations in pressure with an impermeable cap should be conducted.

Sequestration agents that are currently under investigation include activated carbon (Luthy et al., 2002), coke (Lowry, 2003) for organic controls and apatite for metals control. Activated carbon is an especially promising material if a placement technology like the laminated mat employed in the Anacostia capping demonstration can control placement and improve long-term retention of the activated carbon. Other sequestration agents should be investigated and considered for incorporation into a cap although it is critical that feasible placement in the field be an early consideration in any cap amendment research effort.

## IV. Conclusions

In-situ capping has proven to be a very effective means of reducing risks associated with contaminated sediments in some situations. Conventional sand capping has been employed at a variety of sites and has demonstrated the potential of the approach. There are sites, however, where capping by conventional means may provide insufficient risk reduction or where ambiguities in cap performance goals or implementation feasibility have not provided sufficient confidence in a capping solution. Setting appropriate performance goals is a problem common to all sediment remediation approaches and capping specific research is unlikely to resolve the problem. Improving the implementation of in-situ capping is perhaps best addressed by field demonstration and pilot scale work combined when combined with sufficient monitoring to understand and generalize the results. Fundamental research likely to significantly expand the applicability of capping, however, should be directed toward understanding and mitigating facilitated transport and encouraging fate processes in cap materials.

Several basic directions of research are likely to prove fruitful:

- research into the fate and transport behavior of specific contaminants that exhibit complex biogeochemistry
- research into the physical, chemical and biological processes that control the biogeochemical gradients within a cap
- research into the influence of transport processes facilitated by NAPL or gas migration
- research into cap amendments that may encourage sequestration or degradation fate processes

Specific issues of concern and research directions were included above. Research into understanding multiphase movement (NAPL and gas) and the resulting contaminant migration in sediment was recommended. A better understanding of fate processes in conventional caps and the interactions of the complex biological, chemical and physical processes affecting the caps and individual contaminants and the effectiveness of manipulating those fate processes through cap amendments or otherwise was also recommended.

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