

Effectively Managing Risks of Contaminated Sediments – 8309

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ABSTRACT

Various research undertaken over the past decade has improved our ability to assess and effectively manage contaminated sediments. Key to this improvement is a better understanding of the risks, both in time and space. Sediments can pose risks if contaminants are present in the biologically active zone of a water body or if transport processes can move contaminants into that zone. Conversely, effective management of contaminants can be accomplished by physically separating contaminants from the biologically active zone or hindering the transport processes that can result in contaminant migration. Both of these are accomplished by sediment capping, either conventional capping with a passive barrier such as sand, or, when greater control over mobile contaminants is required, by active capping in which amendments are used to retard any applicable transport processes. In this paper, the key transport and exposure processes are assessed and the ability to manage these risks with both passive and active capping evaluated.

INTRODUCTION

Contaminated sediments pose some of the most difficult problems for site remediation and risk management. Sites typically have large sediment volumes with relatively low contaminant levels. Because of the extent and difficulties of managing these sediments, literally billions of dollars often depend upon the selection and implementation of appropriate remedial decisions. As highlighted by a recent National Research Council study [1], traditional approaches calling for the removal of sediments for subsequent treatment or disposal often leave significant residual contamination and generate large amounts of water that must be treated. Thus invasive removal options are often less protective of the environment in addition to being more costly than other approaches. As a result, efficient and effective management of contaminated sediments has often been a contradiction in terms.

Various research undertaken over the past decade has improved our ability to assess and effectively manage contaminated sediments. Key to this improvement is a better understanding of the risks, both in time and space. These risk assessments address three basic requirements. The first is accessibility; strongly sorbed contaminants suggest that only the actively eroded or biologically active zone is relevant. The second is availability and assimilative capacity, which considers whether contaminants can desorb to water or be directly absorbed by benthic organisms. Normally, however, benthic organisms are not the focus of risk assessments and the third requirement is accumulation, which considers whether contaminants can accumulate to toxic levels or be biomagnified as they pass to higher organisms of more relevance to assessing ecological or human health risk.

In-situ containment (i.e. sediment capping) is designed to intervene in one or more of these components of risk and thus effectively manage contaminated sediments. The purpose of this paper is to identify the effectiveness of in-situ capping at managing risks and identify situations where conventional capping with passive media (i.e. sand) is sufficient and when amendments are necessary to more effectively reduce contaminant exposure and risks.

CONTAMINANT EXPOSURE

Routes of exposure include (1) direct flux to water (via sediment erosion, bioturbation and surface release, or physicochemical processes), (2) accumulation in benthic organisms and food chain transfer, and (3) direct exposure within the biologically active zone. Each of these is largely controlled by the life cycle activities of organisms at the sediment-water interface. Erosion of sediment can rapidly cause movement of sediment and associated contaminants but erosion is rarely the most important process in the depositional environment where contaminated sediments have accumulated. Physicochemical processes such as advection and diffusion can be important but in the near surface environment they are often overshadowed by bioturbation. Bioturbation is the mixing and sediment reworking processes as a result of the normal life-cycle activities of benthic organisms. Bioturbation also controls the depth of sediments that can contribute to contaminant exposure, as well as the rate of sediment reworking, redox conditions, and pore water release of contaminants. Bioturbation is dominated by deposit feeders that ingest sediment, such as freshwater oligochaetes, which can bring contaminants at depth to the surface in a single feeding cycle. Thus the zone which is populated and continuously reworked by benthic organisms largely defines all exposure pathways and risks of contaminated sediment.

If the zone that defines risk is the surficial sediments in which the benthic community lives, the next question is what defines the magnitude of that risk. Sediment quality is normally defined by the concentration of contaminants and typically the bulk sediment concentration is commonly used to indicate risk. The extent of release and physicochemical availability of hydrophobic organic contaminants, however, is often controlled by desorption resistance phenomena which complicates the relationship between bulk sediment concentration and organism response. Contaminant bioavailability is largely defined by what can be moved, metabolized by, or accumulated in benthic organisms and recent research has focused on porewater concentrations as an indication of bioavailability for hydrophobic organic compounds [2,3,4,5]. Models for assessing contaminant availability are largely empirical and difficult to relate to measured uptakes. Porewater concentration, however, can be considered an integrative measure of the effects of desorption resistance. Effectively, the portion of the contamination by hydrophobic organics that is available for migration and uptake into benthic organisms is indicated by porewater concentration. This conclusion was also reached by Kraaij et al. [6].

The primary difficulty with the porewater paradigm for defining exposure and risks to hydrophobic organics in the biologically active zone of contaminated sediments is the ability to measure the low concentrations normally observed. PAH and PCB porewater concentrations in moderately contaminated sites will typically be ng/L or less, concentrations that are detectable by conventional techniques only with water volumes of hundreds of mL or more. Conventional approaches to measuring porewater concentrations require the collection of hundreds of g of sediment and centrifugation or filtration to generate sufficient porewater for analysis. This

processing of samples can lead to significant loss of contaminants and will limit the spatial precision of the analysis.

As an alternative approach, an innovative field tool and technique using solid phase microextraction (SPME) was developed allowing the measurement of truly dissolved organic contaminant concentrations with cm or less spatial resolution [7]. SPME employs fibers 100-250 microns in diameter with a thin annulus of sorbent material (typically polydimethylsiloxane, PDMS). SPME has traditionally been used for the determination of aqueous phase concentrations but work in the laboratory has shown that it can be used for in situ determination of pore water concentrations if appropriately armored and strengthened and if sufficient time is provided for equilibration. The field deployable SPME system was developed with a protective sheath over a slotted rod containing the fiber (see Figure 1). The rod and sheath can be inserted into the sediments or cap layer, allowed to equilibrate with local porewater over a 2-4 week period, and then retrieved for sectioning. An individual section will contain contaminants in proportion to the local dissolved phase contaminant concentration. The resolution of the migration assessment is dependent upon the length of the individual segments cut from the fiber. The contaminants in each section can be extracted with a solvent and injected into a gas or liquid chromatograph for analysis.

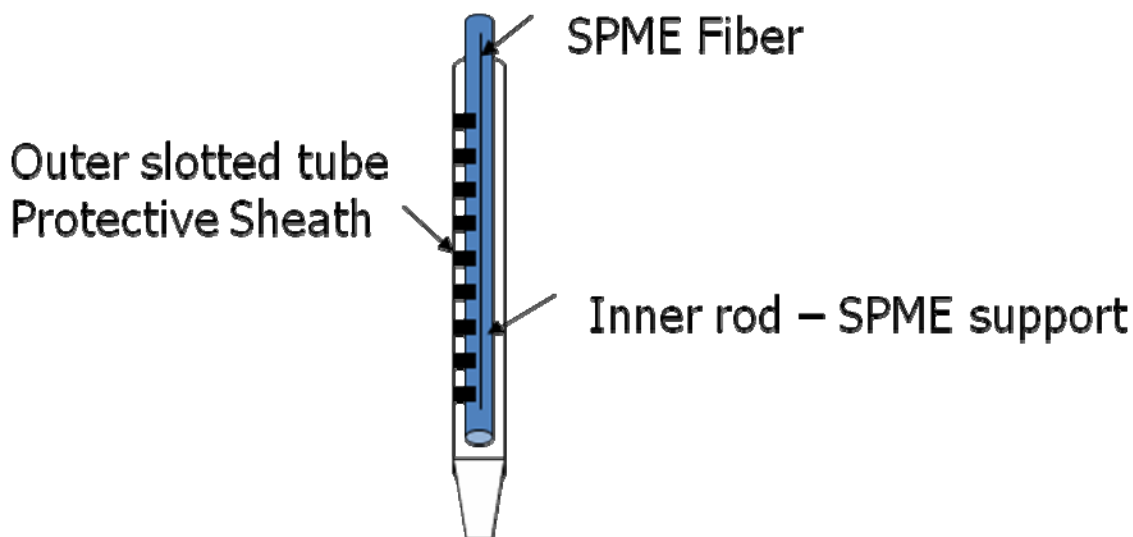


Figure 1 - Field Deployable SPME

Figure 2 shows the detection limits observed for a variety of PAH and PCB compounds for a 1 cm length of 170 micron diameter fiber. The correlation with hydrophobicity (as measured by Log octanol-water partition coefficient) is also shown. The lower detection limits with highly hydrophobic compounds is the result of their greater tendency to sorb to the SPME fiber.

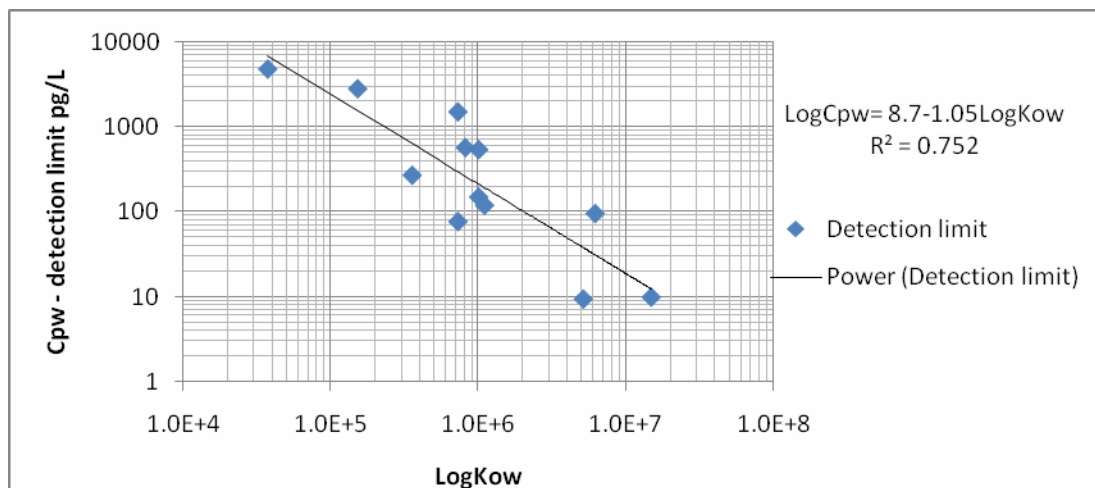


Figure 2 - Detection limits of sample SPME fiber

More importantly, the concentration of contaminants absorbed to the fibers (which relates directly to the porewater concentration) also correlates with steady state accumulation in benthic organisms. In Figure 3, the correlation of fiber concentration to lipid normalized PCB concentration in a tubificid oligochaete is shown

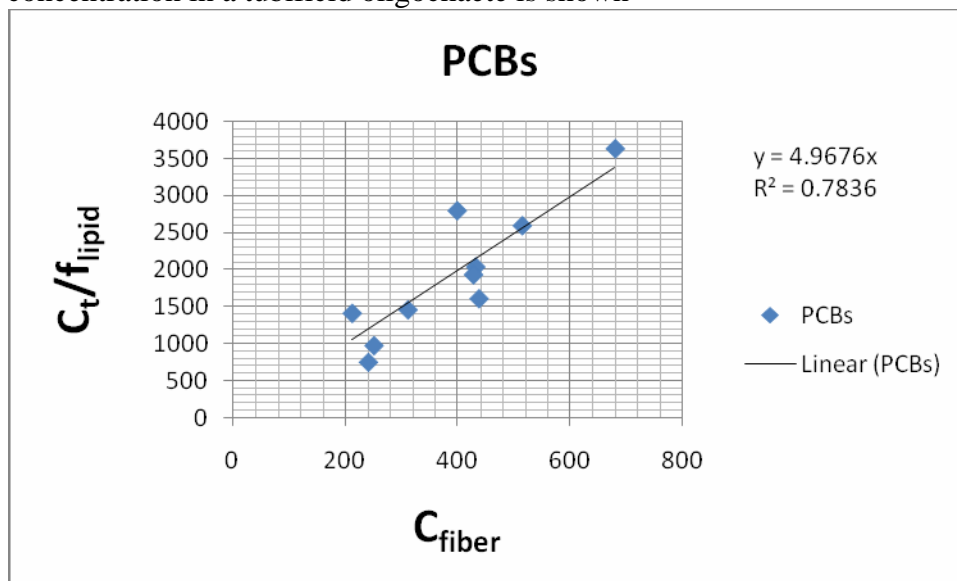


Figure 3 - Lipid Normalized PCB Concentration in a Tubificid Oligochaete Compared to Sorbed Fiber Concentration

Steady state accumulations of contaminant in the benthic organisms represents directly,

1. The potential body burden transferred during predation by higher level organisms, and,
2. Availability to the benthic organism and potential availability to higher level organisms

Thus pore water concentrations, or its surrogate, fiber concentrations, provide directly an indication of bioavailability and potential exposure and risks in the biological active layer of sediments.

Equilibrium partitioning theory has been used to link bulk sediment concentration to toxicity and other endpoints in benthic organisms [8]. It has been faulted for producing overly conservative

conclusions about sediment toxicity since it does not account for desorption resistance and limited bioavailability. The ability to measure porewater concentrations directly provides a potentially powerful alternative approach. By measuring the porewater concentrations, the effects of desorption resistance and limited bioavailability are incorporated explicitly and the porewater concentrations can be directly compared to water toxicity or other measures of environmental impacts. This represents a significantly more powerful physicochemical indicator of sediment toxicity or negative endpoints without the use of biological assays, which can be expensive to implement, complicated to interpret, and provide ambiguous results.

EFFECTIVE MANAGEMENT OF EXPOSURE

Given that porewater concentrations may provide an effective means of assessing the potential risks of contaminated sediment, effective management approaches are those approaches that directly address porewater concentrations in the biologically active zone. Dredging is a viable option where removal can be accomplished with limited post-remedial exposure and without significant negative consequences during implementation. When conditions are such that dredging may not be effective, e.g. with significant debris, bedrock or barriers to effective removal may exist [1], in-situ management options such as in-situ treatment or containment are likely to be preferred. Options for treating sediments in place are limited, and their effectiveness is largely unproven. Most contaminants of interest (including polycyclic aromatic hydrocarbons and polychlorinated biphenyls) are strongly sorbed and undergo minimal to partial degradation, even with amendments to enhance degradation. Furthermore, few amendment delivery methods exist that can avoid compromising the basic advantage of in-situ approaches, namely minimal disturbance.

In-situ containment, or capping, however, does not directly disturb the contaminated sediment and can

1. Physically isolate and stabilize contaminated sediment
2. Separate benthic organisms from contaminated sediment buried beneath the cap and beneath the biologically active zone in the cap
3. Reduce contaminant flux to the overlying water by slowing or eliminating advection, diffusion and bioturbation from the contaminated sediments

In-situ capping includes the placement of thin layers of sand as backfill (often employed as a residual control approach with dredging), as well as engineered capping using sand or other isolation layers with armoring and/or habitat layers, and active capping that includes an active control agent to enhance degradation and/or containment beyond sand alone. Capping has the immediate effect of eliminating erosion of the contaminated sediment (as long as the cap is in place) and moving bioturbation from the upper 10-15 cm of contaminated sediment to the upper 10-15 cm of clean cap material. As a result, particle associated transport processes (erosion and bioturbation) are replaced by porewater transport processes (typically advection and diffusion). Because diffusion is an exceedingly slow process, capping is generally very effective as a contaminant containment process as long as the advective transport can be controlled.

In large open lakes and in the center of large rivers, advection as a result of groundwater upwelling is likely small. Upwelling velocities of the order of cm/yr are expected. Near banks,

however, upwelling can be far greater. Upwelling of the order of cm/day was measured in portions of the Anacostia River as part of the Anacostia active capping demonstration [9]. The influence of upwelling rates can be seen in Figures 4 and 5 which compares the steady state porewater concentration profile of phenanthrene in a cap with an upwelling rate of 1 cm/yr (4) with an upwelling rate of 1 cm/day (5). At the higher upwelling rate, the “effective” cap layer contains porewater concentrations effectively identical to that of the underlying sediment.

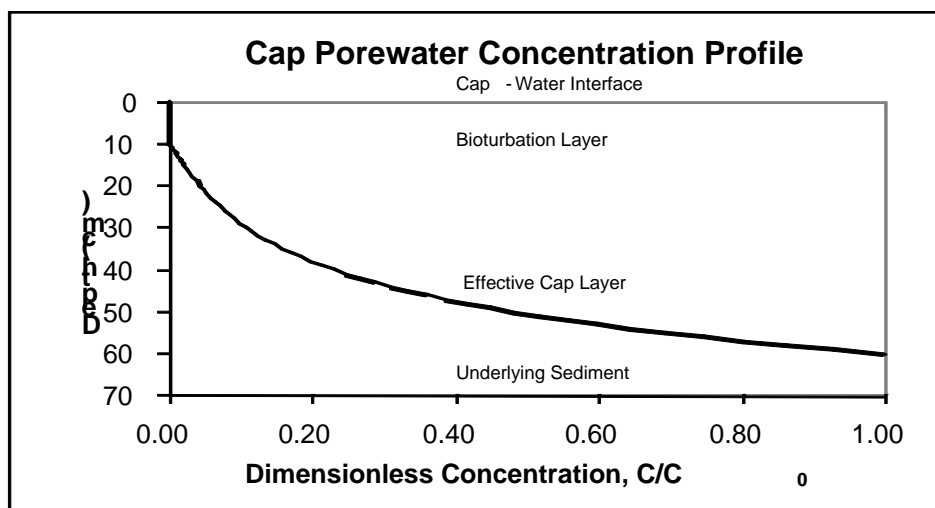


Figure 4 - Steady State Phenanthrene Concentrations in a 60 cm Sand Cap with 1 cm/yr Upwelling

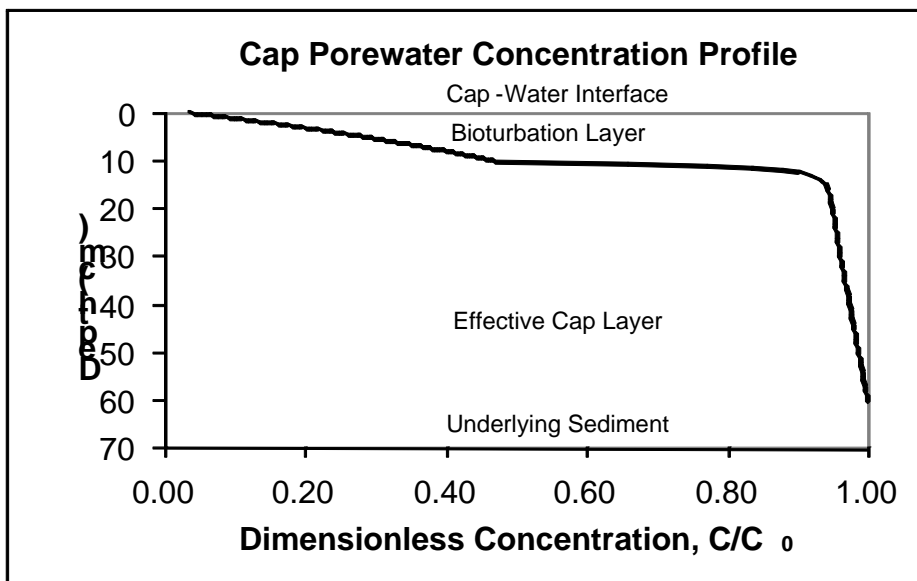


Figure 5 - Steady State Phenanthrene Concentration in a 60 cm Sand Cap with Upwelling of 1 cm/day

When high upwelling rates will ultimately compromise the effectiveness of a cap, active caps are often considered which can further retard a contaminant. The retardation agent can be directed toward the upwelling, through amendments that reduce permeability such as AquaBlok [9], or toward the contaminant transport by the upwelling. If the contaminant in the underlying sediment contains a nonaqueous phase liquid (NAPL), organoclay layers in the cap will absorb the NAPL and slow contaminant migration [10]. Organoclay can absorb its own weight in NAPL. If the contaminant in the underlying sediment is solely in dissolved form, activated

carbon has been placed in a layer of the cap [11]. Activated carbon can absorb of the order of 10% dissolved contaminant by weight. The effectiveness of activated carbon, other carbon amendments are evaluated in [12, 13]. A summary of the effectiveness of various organic sorbents is shown below

Contaminant: NAPL

Organoclays can absorb 1-4 g NAPL/g organoclay although in place capacity is typically 0.5-1.5 g/g

Contaminant: Dissolved Hydrophobic organics (high K_{oc} , 10^3 - 10^7 L/kg)

Activated Carbon (Retardation ~ 10-100 K_{oc})

Organoclays (Retardation ~ 0.5-5 K_{oc})

Organic rich soil (Retardation ~ K_{oc})

Nonporous Carbons (Coke, Coal) (Retardation ~ 0.05 K_{oc})

Although these sorbents have a large sorption capacity for hydrophobic organic contaminants, they will ultimately become saturated if there is not adequate control over the source of contamination. Active adsorptive layers buy time and slow contaminant migration. They work best when managing a residual source that cannot be controlled or completely controlled by other means. Ultimately, however, the concentration profiles observed in Figures 4 and 5 will be observed unless the additional time afforded by the active cap provides additional degradation or if the source is finite and is exhausted prior to complete breakthrough. If the source is infinite, however, and degradation is not enhanced, the profiles in Figures 4 and 5 will be observed because sorption related retardation is a transient phenomena and steady state behavior is unchanged.

SUMMARY

In summary, conventional sand capping can be effective in reducing exposures, while active capping can provide greater control; options include activated carbon/coke (to sequester organic compounds), organoclays (to control nonaqueous phase and dissolved liquids), and clay polymers (to control permeability). Field demonstrations are underway on both coasts (including Portland, Oregon[10], and the Anacostia [9]) to assess the effectiveness of various in-situ options, including organoclay mats and other active caps. In addition, a unique in-situ sampling approach is demonstrating that pore water concentrations can be determined and employed to assess baseline or post-remedial risks due to contaminated sediments. Additional capping research is addressing issues such as gas release, treatment for other contaminants, and geotechnical tests to evaluate mobility of nonaqueous phase liquids due to cap loading and consolidation. Science and technology are combining to support more realistic risk assessments and practical management measures for contaminated sediments, with particular emphasis on in-situ approaches.

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