CONTAINMENT FACILITIES TO PROMOTE CONTAMINANT SEPARATION AND DEGRADATION

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ABSTRACT

Due to their relatively lower cost, sediment containment technologies are currently favored over treatment processes to manage large quantities of polychlorinated biphenyl (PCB) contaminated sediments. However, since containment does not reduce the PCB concentration in the sediments, it should be considered a temporary remedial measure that will require perpetual monitoring and maintenance. By designing, operating, and managing containment facilities to promote organochloride separation and destruction, they can be used as treatment facilities. The physicochemical properties of PCBs in many anaerobic sediments will facilitate separation and treatment. It is difficult to inexpensively treat PCB-contaminated sediments due to the strong sorption of the contaminant to organic and inorganic particulate matter. Once separated from the particulates, however, volatile and aqueous contaminants can be more easily destroyed by existing treatment technologies. A conceptual model for containment cell management includes multi-phased treatment processes incorporating 1) anaerobic dechlorination, 2) aerobic degradation, 3) enhanced desorption processes, 4) leachate and vapor treatment, and 5) passive *in situ* residual treatment. The ultimate objective is to produce a residual contaminant fraction with significantly reduced mobility and bioavailability.

Key words: *PCBs, containment, degradation, dredging, sediment*

INTRODUCTION

There is extensive, worldwide contamination of riverine and harbor sediments by polychlorinated biphenyls (PCBs) and other semi-volatile compounds. Millions of cubic yards of PCB-contaminated sediments will require management as rivers and harbors are dredged for navigational and/or remedial purposes. Confined disposal facilities (CDFs) or secured containment landfills are the method of choice (Tuchman et al., 1997) and are favored over treatment technologies that employ contaminant destruction primarily due to their lower costs. The National Research Council Marine Board Committee on Contaminated Marine sediments in 1997 examined different remedial technologies for contaminated sediments (Pavlou and Thibodeaux, 1997). They stated that "capping, containment and natural recovery are effective management methods for most contaminated sediments" and that "treatment is usually justified for only relatively small volumes of highly contaminated sediments" (Pavlou and Thibodeaux, 1997).

In New York State alone, dredging is ongoing, completed, planned, or proposed for the St. Lawrence, Grasse, Raquette, and Upper Hudson Rivers and for the New York/New Jersey Harbor. Recent policy decisions suggest that much of the contaminated sediment produced by dredging will be placed in CDFs. For example, the amended Superfund Post Decision Proposed Plan for the General Motors Superfund site, Massena, New York, will place approximately 18,000 cubic yards of dredged sediment and on-site soils containing greater than 10 ppm of PCBs in off-site landfills or other secure facilities with no treatment (US EPA, 1998b). The Reynolds' Metals, Massena, New

York, EPA Superfund Post Decision Proposed Plan calls for the on- and off-site landfilling of approximately 73,000 cubic yards of St. Lawrence River sediment containing less than 500 ppm of PCBs (US EPA, 1998a). Dredging has also been proposed for PCB hot spots in the Upper Hudson River, but controversy remains concerning what to do with the dredged sediments. There is continuing public opposition to the siting of CDFs in host communities.

CDFs can be used to store sediment before treatment or as a final disposal facility. Examples of CDFs include engineered upland disposal facilities, excavated pits, subaqueous pits, fill sites, and islands. Conventional CDFs were designed to contain sediments within a dike system; however, chemical contaminants can escape through runoff, dike seepage, effluent flow through weirs and filters, foundation seepage of leachate, uptake by plants and animals, and volatilization (Richardson et al., 1995). CDFs, therefore, must be designed to isolate contaminants to prevent off-site migration. A facility designed with impermeable barriers can prevent contaminant loss and minimize the production of leachate. If the system within the facility is kept dry and the integrity maintained, chemical and microbial processes will be inhibited and contaminants can remain relatively unchanged for decades (Rhee, personal communication, 1998). Soil profiles of sterile foundry waste contaminated with Aroclor 1248 at a New York State Superfund site demonstrated that while the top layers showed enrichment of the heavier congeners, which suggests volatilization, the deeper soils and dirt recovered from the floor were essentially unchanged almost 20 years after placement (Chiarenzelli et al., 1998b). Containment facilities as currently designed and operated, may therefore serve as tombs with little or no changes in the concentration or character of the contaminants. Failure of any part of the containment facility can lead to the off-site migration of contaminants.

Conventional CDF design permits the release of volatile contaminants. This can occur during the placement of the contaminated sediment, as a result of sediment drying, and through the evaporative loss of water when the sediment is submerged or exposed to the atmosphere. Research at the laboratory scale on anaerobically degraded St. Lawrence River sediments demonstrated that PCBs readily volatilize and losses were directly related to original water content; maximum losses occur from completely saturated sediments and essentially no losses from dry sediments (Figure 1; Chiarenzelli et al., 1997). Incremental losses of PCBs can also occur as sediments are rewet and dried as shown in Figure 2 (Chiarenzelli et al., 1998a; Bushart et al., 1998). These observations are supported by the worldwide distribution of persistent organic contaminants. There is considerable evidence to confirm that considerable amounts of PCBs have been deposited in the Arctic and Antarctic via atmospheric transport (Wania and Mackay, 1993; Simonich and Hites, 1995; Tenenbaum, 1998).

Modeling was performed on dredged materials at Indiana Harbor, Indiana, to predict if a significant mass of PCBs would volatilize from an in-lake CDF and an upland CDF. These models, which examined volatilization from submerged and exposed unvegetated sediment, indicated that volatilization was a significant pathway for off-site PCB transfer (Semmler, 1990). This work did not consider volatilization during placement, exposure to rain, or from vegetated sediments (Semmler, 1990). Covering or submerging dredged sediments has been recommended to prevent volatilization (Semmler, 1990; Richardson et al., 1995). However, research suggests that the maximum rate of volatilization can occur when sediments are submerged. As much as 75 percent of the total PCBs in an subaqueous, anaerobically dechlorinated sediment were lost as water was evaporated at ambient temperatures (Chiarenzelli et al., 1997).

The EPA considers CDFs as having a "lesser degree of permanence" than treatment technologies (US EPA, 1998a). There are no long-term examples to show the effectiveness of containment facilities, and they will therefore need perpetual maintenance and monitoring. Containment strategies transfer liability to the future, and CDFs should, therefore, be considered temporary remedial measures. CDFs should be used to store PCBs until cost-competitive destructive processes become feasible.

By designing, operating, and managing containment facilities to promote organochloride separation and destruction, CDFs can be used as treatment facilities. The physical properties and the actual composition of the PCBs in many anaerobic sediments facilitates this separation and with the use of conventional technologies, degradation may be more effectively accomplished.

PROPOSED CONCEPT

PCBs are a class of compounds, each comprised of a biphenyl ring with one to ten chlorines attached at the *ortho*-, *meta*-, or *para*- positions on the ring. There are 209 theoretical compounds, known as congeners, but fewer are found in the environment. Each congener has unique physicochemical properties, but in general, these compounds have low water solubility and low vapor pressure. The solubility of individual congeners varies depending on the chlorine content of the congener and can vary from several ppm for the lower chlorinated congeners to sub ppb for the more chlorinated congeners (Ruell et al., 1993). The low solubility and strong partitioning of the more chlorinated congeners result in bottom sediments serving as vast repositories for PCBs.

PCB-contaminated sediments are difficult to treat inexpensively and efficiently for a variety of reasons. Oxidative treatment technologies can be limited by scavenging by non-target compounds and it can be difficult producing short-lived radicals in proximity to target compounds (Chiarenzelli et al., 1995). Organic-rich sediments usually require large quantities of reagent to offset the quenching effects of the non-target species. Sequestering of PCBs can limit the effectiveness of oxidation and enhance the residual concentration sorbed to the sediment (Hatzinger and Alexander, 1995). The sediment can physically inhibit mixing and thereby reduce forms of energy transmission. High concentrations of contaminants may require large quantities of reagents, which lowers the efficiency as reactive species interact. Finally, the physical properties of the sediment, including porosity and permeability, limit handling, reagent or energy introduction, transfer, and treatment efficiencies.

TREATMENT PROCESSES

PCBs are more readily degraded when desorbed from the sediment. There are technologies that can destroy or remove aqueous and gaseous PCBs including activated carbon or resin sorption, biofiltration, and advanced oxidative technologies. Due to the challenges inherent in treating PCB-contaminated sediment, most of the technologies utilized are a combination of extraction followed by treatment or disposal. Technologies developed to extract PCBs from sediment involve physical, thermal, and/or chemical partitioning. These include soil washing, surfactant addition, organic or inorganic solvent extraction, and low temperature thermal extraction.

Indigenous anaerobic and aerobic microbial degradation of PCBs have been described in the literature and research continues on these processes (Abramowicz, 1995; Spain, 1997). Anaerobic bacteria can dechlorinate PCBs in sediment if the total concentration is above a threshold level. This level varies depending on the sediment, the congener patterns, and the availability of the PCBs to microbes (Sokol et al., 1998). Anaerobic dechlorination occurs until the PCB concentration reaches a plateau, with little dechlorination occurring thereafter. The extent of dechlorination depends on many factors including initial PCB concentration (Sokol et al., 1998).

The anaerobes remove the *meta*- and *para*-positioned chlorines of the PCBs, resulting in lower *ortho*-substituted PCB congeners. These PCBs are more soluble, volatile, and mobile than the original PCB mixture (Chiarenzelli et al., 1998a), and are more likely to partition into the aqueous and gaseous phases. These lower *ortho*-chlorinated PCBs dominate the PCB fraction in water, biota, and air near anaerobically dechlorinated sediment. For example, approximately 65 percent of the PCBs recovered from Hudson River water consisted of three completely *ortho*-chlorinated congeners (Bush et al., 1985).

Aerobic dechlorination complements anaerobic degradation by mineralizing the lower chlorinated *ortho*-substituted congeners that accumulate.

DISCUSSION

As an alternative to current practices, CDFs can be designed, operated, and managed to enhance degradation and promote desorption. Aqueous and volatile phase PCBs released can be destroyed using existing advanced oxidative technologies. A conceptual model would include a multi-phased, *in situ* treatment process within a containment structure. The sediment would be degraded in treatment cells that would be manipulated through a series of microbial and physico-chemical phases to enhance contaminant degradation, desorption, and destruction. The material would be regulated at all times in a controlled system, with all vapors and aqueous phases collected, treated and/or recycled. Effective means for recirculating and collecting gases and fluids would be integrated into the CDF. Instead of serving as tombs, CDFs could be used as dynamic systems designed and managed to actively degrade organic compounds.

The process would include a series of steps such as anaerobic dechlorination, aerobic degradation, enhanced desorption processes, leachate and vapor capture, and decontamination followed by additional treatment. The first phase would optimize anaerobic microbial dechlorination by managing cell conditions. The transformed PCB congeners are more volatile, soluble, mobile, and more likely to move into the gaseous and aqueous phases. Recirculation would be utilized to remove and collect leachate and released gases, which then could be degraded through conventional treatment technologies. Anaerobic dechlorination can be enhanced by a variety of processes including, but not limited to, addition of ferrous sulfate (Zwiernik et al., 1998), bacteria inocula, nutrients, moisture, substrates, surfactants, and others. If the dredged sediment has been extensively degraded by anaerobic processes prior to transfer to the CDF or if the sediment is lightly chlorinated to begin with, this anaerobic phase would not be necessary.

The next phase would enhance desorption and degradation through aerobic processes. Aerobic degradation processes can be used to degrade the lower *ortho*-chlorinated congeners that remain after anaerobic degradation plateaus have been achieved. Aerobic degradation can be enhanced by the addition of inorganic nutrients, biphenyl, and oxygen (Harkness et al., 1993). Aeration, landfarming, composting, solar heating, bioventing, and other enhancements to the aerobic degradation can be used to allow PCBs to partition to the gaseous and aqueous phases. Fluid recirculation would again be promoted to remove and collect leachate and gases for treatment.

The goal of the previous phases is to destroy as much of the sorbed PCBs as allowed by efficiency and economic constraints, as well as to separate the target contaminants into gaseous and liquid phases for collection and destruction. Depending on the residual left after the anaerobic dechlorination, enhanced desorption, and aerobic degradation, additional *in situ* treatment may be necessary to reach an immobile residual concentration of contaminants. These treatments could include additional physicochemical or passive processes such as phytoremedation. If further treatment was not required, reclamation and final closure could occur.

SUMMARY

CDFs are the likely choice for managing the millions of cubic yards of PCB-contaminated sediments produced by dredging or excavation. However, CDFs should be regarded as temporary storage facilities for PCB-contaminated sediments since they limit chemical and microbial degradation, essentially entombing PCBs. Since there is no data on the long-term effectiveness of CDFs to maintain contaminants, off-site migration is possible. Through design, monitoring, and maintenance, CDFs can be utilized as dynamic treatment facilities that protect the surrounding environment and actively promote degradation of organic contaminants. By enhancing natural processes, contaminated sediment can be degraded to a level that does not pose a threat to the environment.

CDFs can be designed and managed as multi-phased treatment systems that enhance degradation, desorption, and destruction processes. A conceptual process includes anaerobic degradation, aerobic degradation, enhanced desorption, leachate and vapor treatment, and additional treatment. In all phases, the system would be managed to reduce the potential for off-site releases. The ultimate goal of the CDF should be to create a residual with greatly decreased mobility and bioavailability in a cost-effective manner.

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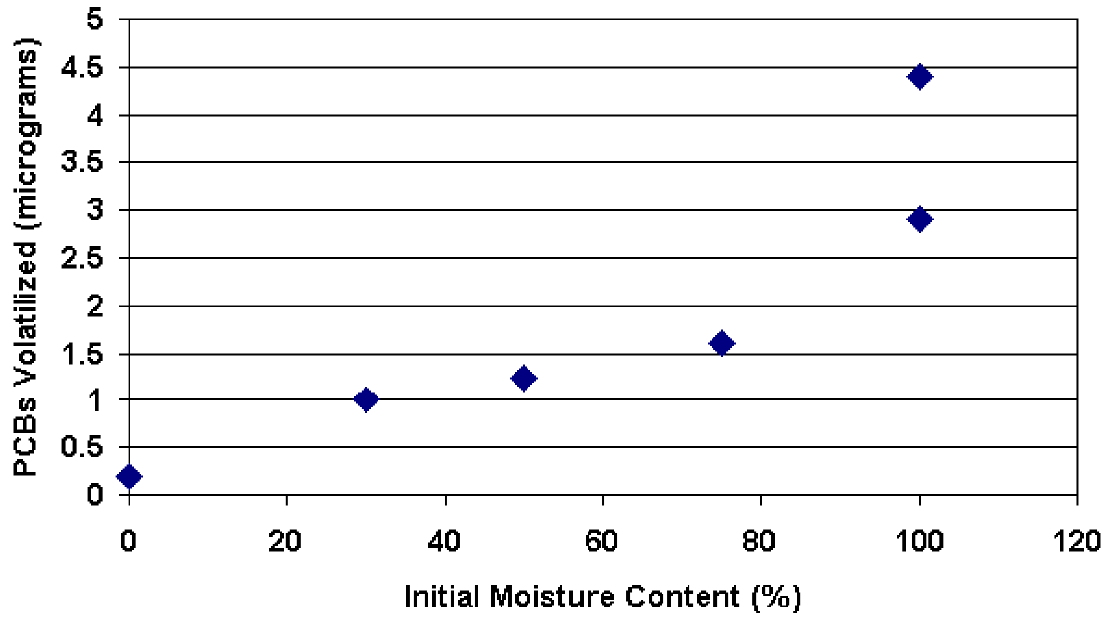

Figure 1. Evaporative loss of PCBs from contaminated sediments at various initial moisture contents; note that PCBs readily volatilized when the sediment was completely saturated (Chiarenzelli et al., 1997).

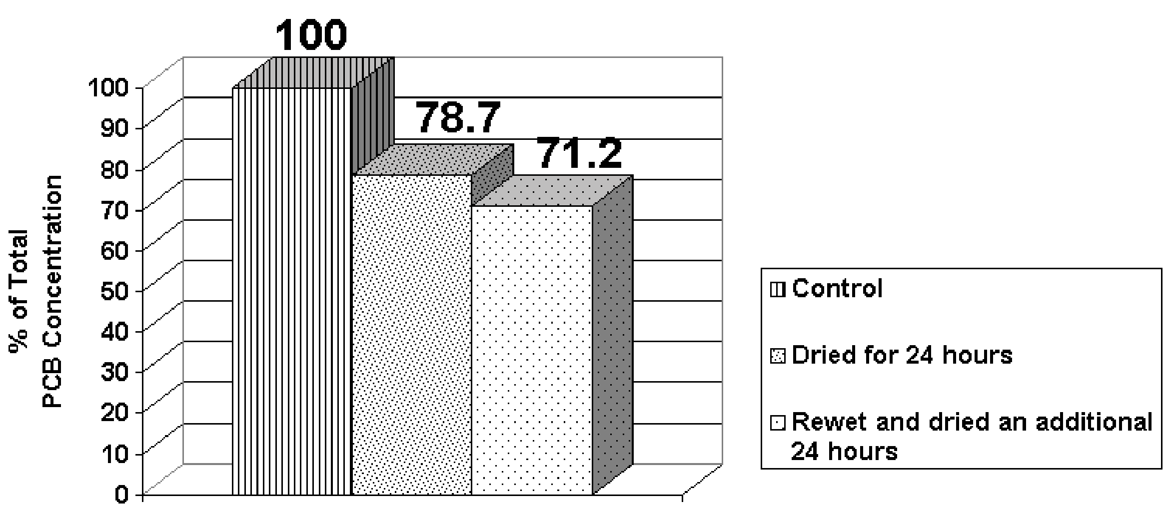

Figure 2. PCBs lost by air drying wet St. Lawrence River sediment for 24 hours; rewetting and drying an additional 24 hours (Chiarenzelli et al., 1997).