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Environmental Effects of Dredging Technical Notes

Natural Processes for Contaminant Treatment and Control at Dredged Material Confined Disposal Facilities

Purpose

This note examines the potential for natural processes to treat contaminants and maximize contaminant containment at dredged material confined disposal facilities (CDFs).

Background

CDFs are used by the Corps of Engineers to dispose contaminated dredged material from shipping channels and harbors in the Great Lakes, along the Atlantic and Gulf coasts, and to a limited extent along the Pacific coast. The nature and level of contamination in dredged materials disposed in CDFs vary widely on a project-to-project basis. Application of CDF technology has focused on containment effectiveness, and this focus will probably continue to be appropriate for many navigation maintenance projects. However, increasing attention is being directed to the containment effectiveness of CDFs for dredged materials that are viewed by resource agencies as highly contaminated (Petrovski 1995). One major criticism of CDFs is that they were not designed, nor are they managed, to treat the pollutants placed inside, but merely function as repositories from which there may be slow but long-term release of contaminants. In addition, many CDFs are now nearing or exceeding design capacity, and the Corps is in the process of developing new disposal options and evaluating closure requirements for existing CDFs.

Numerous phenomena affect contaminant containment efficiencies at CDFs and, in some cases, degrade contaminants or retard contaminant migration. Some of these phenomena occur without intervention by humans and are referred to as natural processes. The effects that natural processes have on contaminant containment and the potential for enhanced effects, however, are

rarely considered during design, construction, operation, and management of CDFs. With increasing concerns about the effectiveness of contaminant containment at CDFs, the need for improved CDF technology also increases (Petrovski 1995). Better understanding of natural processes could provide a basis for developing improved CDF technology.

Additional Information

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Natural Process Overview

Treatment by natural processes is defined as the in situ biological transformation of contaminants to less harmful forms by microorganisms and the in situ physicochemical alteration of contaminants to less mobile forms. Processes such as biodegradation and photolysis reduce organic contaminant concentrations through chemical transformation reactions.

Figure 1 is a schematic showing some of the natural processes that alter contaminant concentrations and mobility in CDFs. Some natural phenomena tend to clean the site by moving contaminants offsite. Processes such as leaching, volatilization, and runoff reduce contaminant concentrations by removing pollutant mass from the CDF. Still other natural phenomena tend to reduce contaminant migration. For example, desiccation reduces volatilization by increasing tortuosity, and self-weight consolidation minimizes leaching by reducing hydraulic conductivity. Other natural processes not shown in Figure 1 include sorption, hydrolysis, microbially mediated oxidation-reduction reactions, and abiotic reactions. Of these various processes, in situ natural biodegradation is the process with most promise for treating organic contaminants in CDFs.

Biodegradation

Application Potential

Natural biodegradation (aerobic and anaerobic) uses in situ, naturally occurring microorganisms to degrade contaminants (Norris and others 1994). The microorganisms are mainly bacteria but can be fungi. The ability of indigenous microorganisms in fresh and salt water, soils, and groundwater to chemically transform a wide variety of organic contaminants is well known (Wise 1988; Ehrlich and others 1992; King, Long, and Sheldon 1992; National Research Council 1993; Norris and others 1994). These same microorganisms may also be capable of transforming contaminants in CDFs, aerobically in the vadose zone and in the capillary fringe where oxygen is not limiting and anaerobically in the saturated zone (Figure 1).

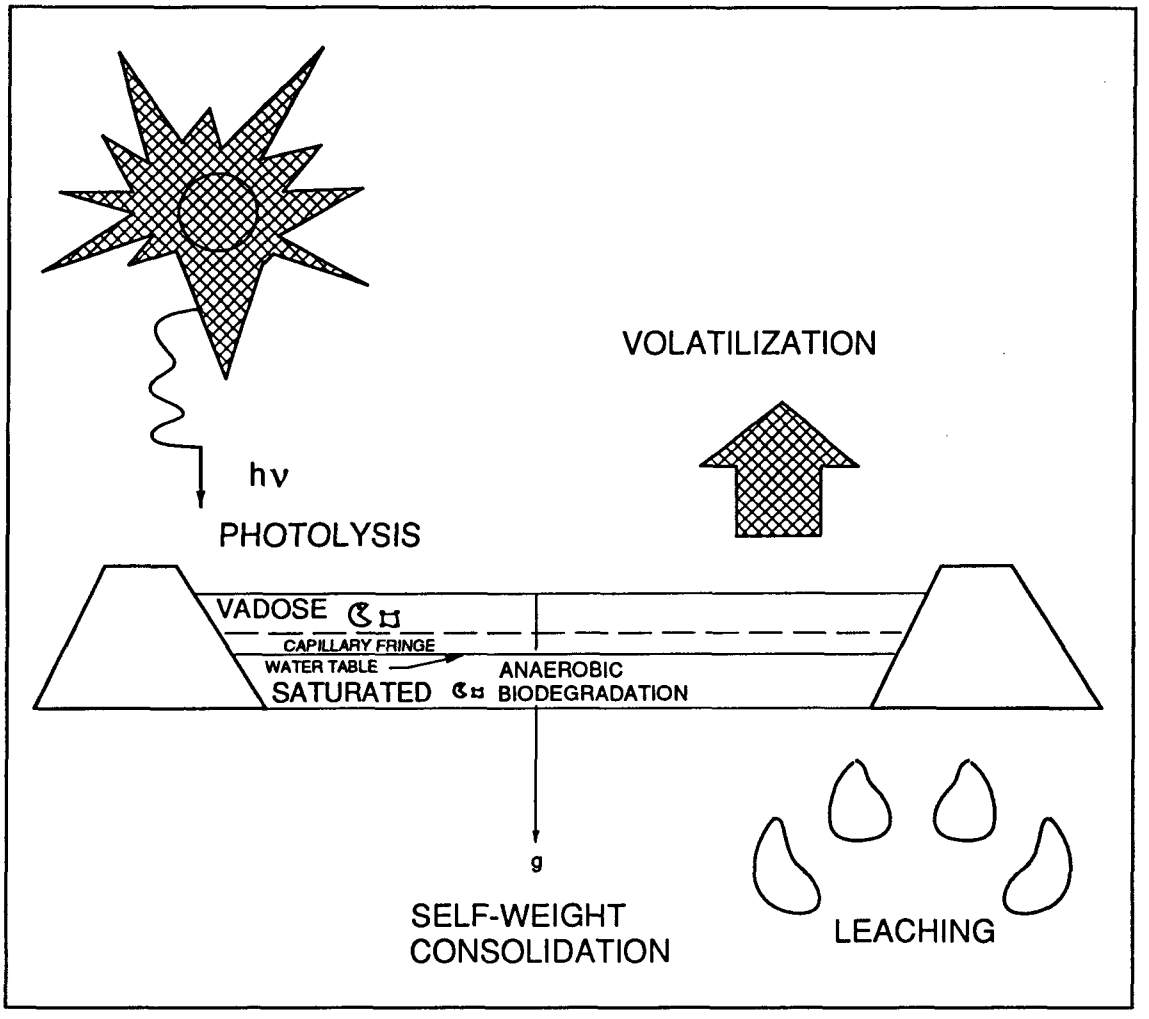

Figure 1. Natural processes affecting contaminants in CDFs

Organic chemicals can be classified into two groups: halogenated and nonhalogenated. Chlorine and bromine are halogens. Thus, halogenated organics are organic chemicals with either chlorine or bromine in their molecular structure. As a general rule, organic molecules containing halogens are more difficult to biodegrade than the same molecules without halogens present.

Petroleum hydrocarbons and nonhalogenated solvents such as alcohols, ketones, ethers, carboxylic acids, and esters are readily biodegraded (National Research Council 1993, Norris and others 1994). Monoaromatic compounds such as benzene, toluene ethylbenzene, and xylenes (BTEX compounds) are more rapidly degraded than the two-ring compounds such as naphthalene, which are in turn more easily degraded than the three-, four-, and five-ring polycyclic aromatic hydrocarbons (PAHs). Dredged material contaminated with creosote, coal tar, and heavier petroleum products often contains higher molecular weight PAHs (fluorene, phenanthrene, chrysene, etc.). These chemicals have limited solubility in water, adsorb strongly, and degrade at rates much slower than other hydrocarbons.

For years it was thought that halogenated organics, such as dichlorodiphenyl-trichloroethane (DDT) and polychlorinated biphenyls (PCBs), were persistent and did not biodegrade. However, laboratory and field studies have shown that biodegradation of these contaminants occurs and that degradation is affected by environmental conditions, such as pH and oxidation-reduction potential. For example, DDT degrades more rapidly under anaerobic conditions typical of saturated dredged material than under aerobic conditions (Guenzi and Bread 1967, Gambrell and others 1984). Anaerobic dechlorination of PCBs in sediments has also been reported (Brown and others 1987); however, PCB mineralization rates are higher under aerobic than anaerobic conditions (Pardue, Delaune, and Patrick 1988).

Metals do not biodegrade, but biological processes may incidentally mobilize mercury, arsenic, and selenium or immobilize other metals through oxidation-reduction reactions. Generally, the presence of metals has little direct effect on bioremediation rates. While some metals such as mercury can be toxic, microbial populations frequently adapt to the concentrations present (Ahring and Wastermann 1988).

Performance Evaluation

Questions concerning treatment effectiveness remain. There is very little operating history to judge the effectiveness of natural bioremediation for CDFs. It is therefore necessary to develop a performance track record before the potential of natural bioremediation can be realized as a component of an improved CDF technology. Development of such a track record requires an evaluation framework to quantify when natural biodegradation processes are working or have worked.

The National Research Council Committee on In Situ Bioremediation recommends an evaluation strategy that builds a consistent, logical case based on converging lines of independent evidence (National Research Council 1993). The strategy includes three types of information: documented loss of contaminants from the site, laboratory assays showing that microorganisms from site samples have the potential to transform contaminants under site conditions, and one or more pieces of information showing that the biodegradation potential is actually realized in the field. A critical factor in deciding whether bioremediation is working or has worked is whether the contaminants are susceptible to biodegradation by the organisms at the site. This must be demonstrated in either laboratory or field tests performed on site-specific samples and may require continual monitoring of contaminants and transformation products indicative of bioremediation.

For natural bioremediation to be effective, biodegradation must proceed faster than contaminant migration processes such as leaching and volatilization. These processes are discussed below.

Leaching

Leaching is a contaminant migration pathway that lowers contaminant concentrations in CDFs. The process is usually very slow in CDFs containing fine-grain dredged material because the hydraulic conductivity of fine-grain dredged material is low (10^{-5} to 10^{-9} cm/sec) and hydraulic gradients are low (near 1) after filling. Organic carbon contents of polluted dredged materials are usually high ($f_{oc} > 0.01$) so that sorption coefficients and retardation factors are large.

Dredged material specific tests (Brannon, Myers, and Tardy 1994) have been developed for obtaining site-specific sorption coefficients. These tests can be used in lieu of estimation techniques to obtain retardation factors.

Seepage rates can be estimated using minimal site-specific information and the Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder and others 1994a, 1994b), or more accurate estimates can be obtained using site-specific piezometer data and a groundwater model. First-cut seepage velocities can be obtained using Darcy's law, typical dredged material hydraulic conductivities of 10^{-5} to 10^{-9} cm/sec, and a hydraulic gradient of 1 (Figure 2). This simple approach usually overestimates seepage because hydraulic gradients in CDFs can be less than 1.

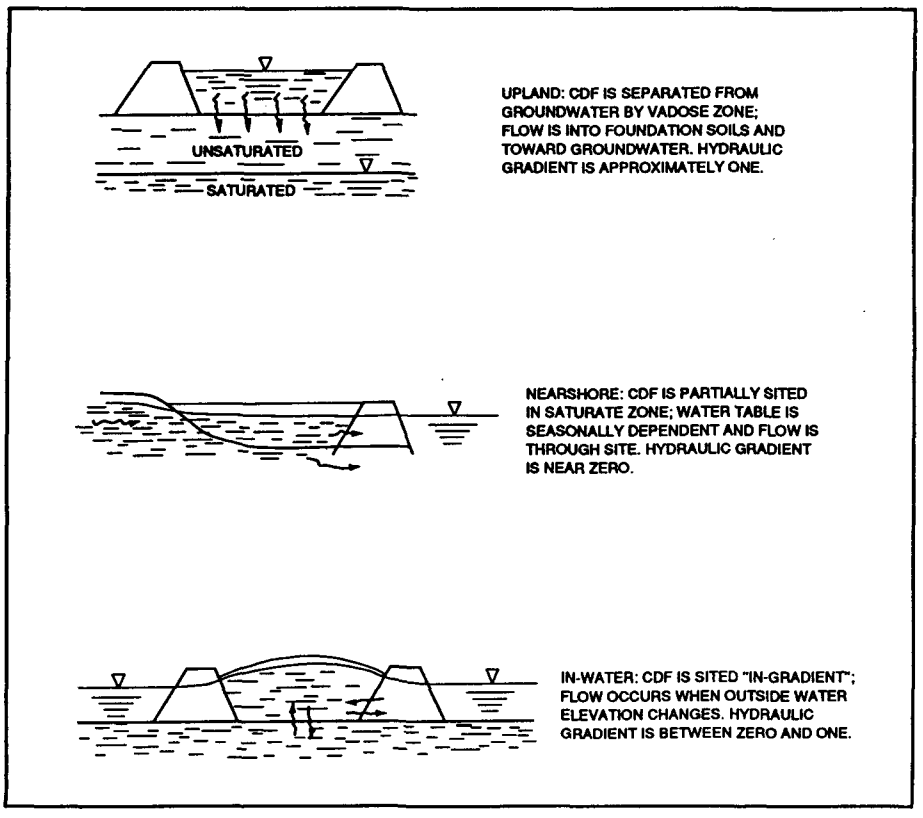

Figure 2. Long-term average hydraulic gradients in CDFs

Contaminant losses by leaching are usually of minor significance relative to effluent losses during filling operations and volatile losses from exposed, fresh dredged material. In spite of the low loss potential relative to other contaminant loss mechanisms, leaching can adversely impact groundwater, depending on site geohydrological conditions. For example, if the CDF foundation soils are sandy or there is a sand wedge in the CDF as a consequence of long-term hydraulic placement of sandy dredged material at one location, contaminants originally in the dredged material may eventually appear in the water table aquifer beneath the CDF.

Volatilization

Many organic chemicals will vaporize from the surface of freshly exposed dredged material. This natural process is often referred to as volatilization. Unless a cap is placed on freshly exposed dredged material, organic chemicals will volatilize. A common misconception is that the tendency for organic chemicals to volatilize from dredged material is indicated by vapor pressure. The tendency for chemicals to volatilize from dredged material depends on the Henry constant (Thibodeaux 1989), which is a function of water solubility and vapor pressure. Thus, organic chemicals with low vapor pressures and low water solubilities can have sufficiently high Henry constants for volatilization to be significant.

Simmler (1990) evaluated the tendency for PCBs to volatilize from dredged material in a CDF and suggested that PCB losses via volatilization could exceed PCB losses by other contaminant migration pathways. Myers and others (1993) estimated PAH losses for a CDF and suggested that volatilization was a major contaminant migration pathway. Both Simmler's work and the estimates made by Myers and others (1993) were based on theoretical models developed by Thibodeaux (1989). There are no field data available to verify the estimated tendency of these chemicals to volatilize from dredged material.

Volatile losses can be estimated using theoretical models, but the reliability of such estimates is unclear. Model uncertainty is high. In addition, the estimates are large, suggesting that the first millimeter of aged dredged material (1 year exposure to the atmosphere) should be substantially reduced in organic chemical contamination via volatilization alone. Unfortunately, there are no published reports that confirm or refute this prediction.

Photolysis

Photolysis refers to molecular chemical change due to absorption of light energy. Laboratory studies of photolysis in aqueous solutions have led to increasing attention to photolysis as an important process in determining the fate of many organic chemicals. For example, surface water half-lives of 21 to 118 hr have been estimated for photolysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (Podoll, Jaber, and Mill 1986). In a CDF, photolysis would be expected to be of little significance since light cannot penetrate dredged material.

Exceptions may be photochemical reactions in ponded water and on frequently tilled dredged material. (Dredged material tilling is not a common practice in the United States.) Photolysis in the vapor state, that is after volatilization, is potentially more significant than photolysis in the aqueous phase. The half-life of TCDD in the vapor state has been estimated to be as low as 58 min (Podoll, Jaber, and Mill 1986).

Self-Weight Consolidation/Desiccation

Self-weight consolidation is compression of dredged material under its own weight. During self-weight consolidation, bulk density increases and the void ratio and hydraulic conductivity decrease. Since the solid particles do not compress, reduction in void ratio involves release of water from the pores in the dredged material. The direction of water movement is governed by pore pressure gradients as influenced by hydraulic conductivities. Water usually moves upward into the negative pore pressure zone of the desiccated crust, if present. If the pressure is lower in the underlying materials than in the consolidating layer due to the presence of drainage material such as sand, water will tend to move down.

During desiccation of the surface layer, negative pore pressures develop which cause fine-grain dredged material to shrink. A hard crust can form that has low hydraulic conductivity, low evaporative rates for water, and low volatilization rates for organic chemicals. The crust also acts as overburden and generates excess pore pressures in the lower saturated material, increasing hydraulic gradients. When new dredged material is placed on top of previously desiccated material, an overconsolidated interior sublayer remains which does not behave as the normally consolidating material above and below. The desiccated and overconsolidated material will initially behave as a semipermeable drainage boundary that resists downward movement of water.

The bottom boundary of consolidating dredged material in a CDF can sometimes be compressed to the point that the layer is an effective liner. Figure 3 shows the relationships between void ratio and effective stress and hydraulic conductivity and void ratio for three dredged materials. At the minimum void ratio (about 2) achieved at about 95 percent of ultimate consolidation, hydraulic conductivities are on the order of 10^{-8} cm/sec for clay material. The time needed to achieve 95 percent of ultimate consolidation is about 1 year for a drainage length up to 1 meter (Cargill 1985). For CDFs that are permanently maintained, self-weight consolidation can be very effective in controlling leaching losses.

Relative Significance of Biodegradation

When the naturally occurring rate of contaminant biodegradation is faster than the rate of contaminant migration, natural bioremediation can provide significant treatment. The relative rates of natural bioremediation and contaminant migration depend on types and concentrations of contaminants, the

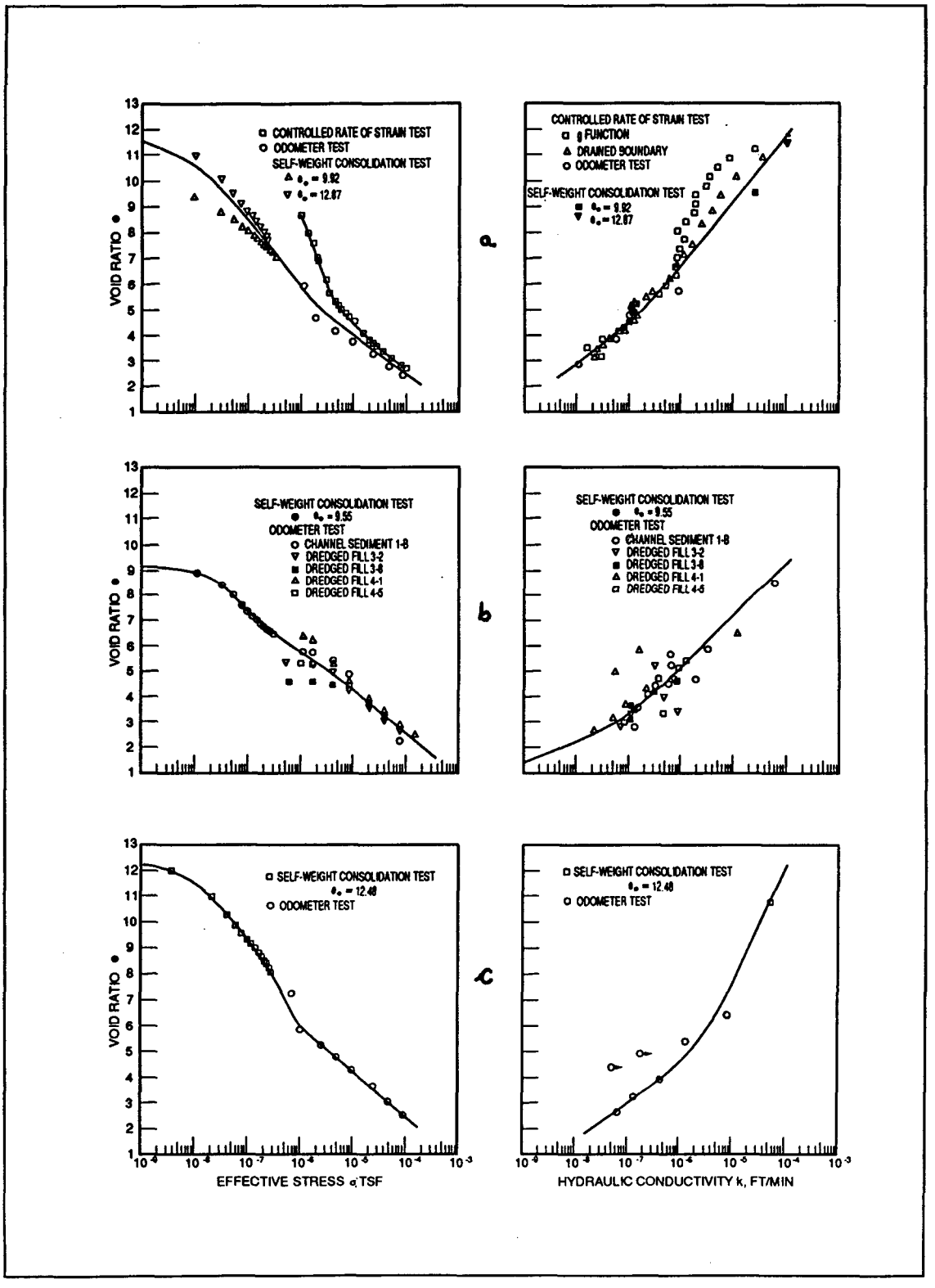

Figure 3. Stress, void ratio, and hydraulic conductivity relationships in three dredged materials: (a) Canaveral Harbor, Florida, (b) Craney Island, Virginia, and (c) Drum Island, South Carolina (from Cargill 1985)

microbial community, CDF design and operation, and various other site-specific conditions.

To illustrate the potential for natural bioremediation, a simple analysis of the contaminant loss due to biodegradation and leaching is provided as follows:

$$F_L = 1 - e^{\left(\frac{-vt}{LR}\right)}$$

$$F_B = 1 - e^{(-K_b t)}$$

where

F_L = fraction of initial contaminant mass lost due to leaching
v = average seepage velocity, m/day
t = time, day
L = dredged material thickness, m
R = retardation coefficient, dimensionless
= $\rho_b K_d / n$
ρ_b = bulk density, kg/L
K_d = equilibrium distribution coefficient, L/kg
= 0.411 $f_{oc} K_{ow}$ (Karickhoff, Brown, and Scott 1979)
n = porosity, dimensionless
f_{oc} = fraction organic carbon, dimensionless
K_{ow} = octanol-water partitioning coefficient, L/kg
F_B = fraction of initial contaminant mass lost due to biodegradation
K_b = overall first-order biodegradation constant, day^{-1}

The above process relationships are not coupled, that is, the expression for F_L assumes leaching to be the only removal process, and similarly the expression for F_B assumes biodegradation to be the only removal process. From these relationships, times required for half of the initial contaminant mass to be removed either by leaching or biodegradation (but not both) can be estimated as follows:

$$t_{\frac{1}{2},L} = \frac{0.69\, L\, R}{v}$$

$$t_{\frac{1}{2},B} = \frac{0.69}{K_b}$$

where

$t_{1/2,L}$ = time required for leaching to remove one-half of the contaminant mass initially present

$t_{1/2,B}$ = time required for biodegradation to remove one-half of the contaminant mass initially present

Table 1 shows times required for half of the initial mass of fluoranthene (a PAH), TCDD, and hexachlorobiphenyl to disappear by leaching only and anaerobic biodegradation only. The calculations were made for L = 10 m, three seepage velocities, and a range of octanol-water partitioning coefficients. Anaerobic biodegradation half-lives in Table 1 are suggested values based on scientific judgment (Howard and others 1991). Data on anaerobic biodegradation of many toxic organics are so sparse that biokinetic constants and half-lives are not usually available. Table 1 shows that for even very slow anaerobic degradation rates, biodegradation can be significant for CDFs that must be maintained into perpetuity. As shown in Table 1, the potential significance of anaerobic biodegradation versus leaching is substantial. Anaerobic biodegradation could be 1,000 to 100,000 times faster than leaching, depending on the chemical considered and seepage velocity.

Table 1. Leaching Versus Anaerobic Degradation

Chemical	Anaerobic Biodegradation Half-Life[1] (thousands of years)	Octanol-Water Partioning Coefficient,[2] log K_{ow} (L/kg)	Retardation Factor,[3] *R*, dimensionless	Seepage Velocity, *v* (cm/sec)	Half-Life for Leaching (thousands of years)
Fluoranthene	0.005 - 0.48	4.70 - 650	648 - 41,000	10^{-5}	1.4 - 89
				10^{-6}	14 - 890
				10^{-7}	142 - 8,900
TCDD	0.01 - 1	5.38 - 7.70	3,100 - 647,000	10^{-5}	6.8 - 1,400
				10^{-6}	68 - 14,000
				10^{-7}	678 - 140,000
PCB (Hexachlorobiphenyl)		6.70 - 6.80	64,000 - 81,000	10^{-5}	142 - 180
				10^{-6}	1,420 - 1,800
				10^{-7}	14,200 - 18,000

[1] Minimum biodegradation half-lives for fluoranthene and TCDD are best-judgment estimates suggested by Howard and others (1991) for anaerobic biodegradation of these chemicals. Maximum values were obtained by multiplying the minimum values by 100. Anaerobic biodegradation half-lives for hexachlorobiphenyl are not available.
[2] Mackay, Shiu, and Ma (1992a, 1992b).
[3] Retardation factors were calculated using bulk density = 1.1 kg/L, fraction organic carbon = 0.02, and porosity = 0.7.

The simple half-life comparison method discussed above is useful for generating planning-level approximations, but is a gross simplification of the complex phenomena affecting leaching and biodegradation. Site-specific factors, such as heterogeneities in dredged material properties and inhibitory conditions such as low pH, could reduce the relative significance of anaerobic biodegradation. Though many site-specific factors potentially alter the relative

significance of biodegradation, factors of 1,000 to 100,000 are large enough to indicate significant potential for field biodegradation rates to exceed leaching rates.

In Situ Natural Treatment Engineering

Districts choosing to approach CDF design, operation, and management as natural process treatment facilities will have to use sound scientific and engineering judgment since specific guidelines are not available. The potential exists, however, to design, operate, and manage CDFs to achieve the following:

- Self-cleaning on the surface.
- Self-sealing on the bottom.

It may also be possible to recover storage capacity through reclamation of cleaned dredged material.

Fully meeting these objectives may require operation and management of CDFs to enhance natural treatment processing of dredged material. Some of the techniques used in land treatment of wastes may be applicable to enhancing natural process rates in CDFs (Ferdinandy-van Vierken 1995). Land treatment techniques include tilling (reduces mass transfer limitations on oxygen availability and volatile emissions), liming for pH adjustment, nutrient and alternative electron acceptor addition, and water budget management (control of oxidation-reduction potential and volatile emissions). The unique nature of CDFs, for which in situ natural treatment may be particularly applicable, makes consideration of land treatment techniques warranted.

Summary

A myriad of natural processes that deplete organic contaminants are potentially active in CDFs. Natural surface-cleaning processes include aerobic biodegradation, volatilization, runoff, and photolysis. Anaerobic biodegradation and leaching are solids-cleaning processes that may be important in the saturated zone of CDFs. Self-weight consolidation is an important process that reduces leaching potential.

Engineering of CDFs (design, construction, operation, and management) to achieve in situ natural processing of contaminants is a promising concept. However, before full-scale, natural processes remediation of contaminated dredged material in CDFs can become engineering practice, a number of hurdles must be overcome. Some of the major hurdles include:

- Demonstrated effectiveness in spite of significant chemical heterogeneity in contaminated sediments.
- Development of design, operation, and management guidelines.
- Development of beneficial uses for decontaminated dredged material.

- Acceptance by regulatory agencies and the public.

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