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THEORETICAL MODELS FOR EVALUATION OF VOLATILE EMISSIONS TO AIR DURING DREDGED MATERIAL DISPOSAL WITH APPLICATIONS TO NEW BEDFORD HARBOR, MASSACHUSETTS

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Some bottom sediments in both fresh and marine waters are contaminated with hazardous organic chemicals that are classified as volatile and semivolatile. An example is the New Bedford Harbor and Acushnet River Estuary sediment, which contains quantities of the polychlorinated biphenyls Aroclors 1242, 1248, and 1254. Dredged material contaminated with these and other volatile organic chemicals (VOCs) can release these contaminants to the atmosphere during and after disposal by volatilization. Methods to predict these volatilization losses are needed to develop design, operation, and management guidelines for controlling VOC emissions. Volatilization rates for hydrophobic organic compounds from a confined disposal facility (CDF) containing contaminated dredged material are presently unknown. The primary purpose of this study was to assess the availability of theoretical models for the evaluation of volatile emissions to air during the process of dredged material disposal in a CDF. The (Continued)					
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first objective was to identify the primary vapor phase transport mechanism for various CDF designs and stages of filling. This provided the theoretical basis for assessing relative volatilization rates. The second objective was to review available laboratory and field procedures for obtaining the information needed to measure volatile losses.

Four VOC emission locales were identified: the sediment (dredged material) relocation locale, the exposed sediment locale, the ponded sediment locale, and the vegetation-covered sediment locale. These were specific locations within a CDF that exhibited common behavioral or operational characteristics that resulted in the release/generation of VOCs to air.

Following a section that considers the thermodynamic basis of chemical vapor equilibrium and contaminated sediment, rate equations are presented and reviewed. These equations represent the quantitative results of the models of emission mechanisms from each of the four locales. Computations using these equations yield the chemical flux rate in mass per unit time. The rate equations are based on transport phenomena fundamentals and have the further advantage of inputs that require concentrations and surface areas of the contaminated sources.

Emission rates, in the mass of specific or total VOCs per unit time, are primarily dependent on the chemical concentration at the source, the surface area of the source, and the degree to which the dredged material is in direct contact with the air. The relative magnitude of these three parameters provides a basis upon which a tentative ranking of emission rates from the various locales can be given. On this basis, the exposed sediment locale ranks first. The ponded sediment locale with a high suspended solids concentration in surface waters ranks second. Low in the rankings are the bed sediment below a relatively quiet water column, such as exists in some ponded sediment locales, and the vegetation-covered sediment locale.

The report also contains preliminary calculations of the emission rates of Aroclors 1242 and 1254 from a hypothetical CDF operation in the Upper Acushnet River Estuary (Appendix A). Appendix B presents a detailed derivation of the rivulet and ponded VOC emission model.

PREFACE

This study was conducted as part of the Acushnet River Estuary Engineering Feasibility Study (EFS) of Dredging and Dredged Material Disposal Alternatives. The US Army Corps of Engineers (USACE) performed the EFS for the US Environmental Protection Agency (USEPA), Region 1, as a component of the comprehensive USEPA Feasibility Study for the New Bedford Harbor Superfund Site, New Bedford, MA. This report was prepared by the US Army Engineer Waterways Experiment Station (WES) in cooperation with the New England Division (NED), USACE. Coordination and management support was provided by the Omaha District, USACE, and dredging program coordination was provided by the Dredging Division, USACE.

Project manager for the USEPA was Mr. Frank Ciavattieri. The NED project managers were Messrs. Mark J. Otis and Alan Randall. Omaha District project managers were Messrs. Kevin Mayberry and William Bonneau. Project managers for the WES were Messrs. Norman R. Francingues, Jr., and Daniel E. Averett.

The study was conducted during the period July 1987 to June 1988 by Dr. Louis J. Thibodeaux, Baton Rouge, LA. The work was performed for the WES under Contract No. DACW39-87-M-2487. Mr. Tommy E. Myers, Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), Environmental Laboratory (EL), was the WES technical monitor. General supervision was provided by Mr. Norman R. Francingues, Jr., Chief, WSWTG; Dr. Raymond L. Montgomery, Chief, EED; and Dr. John Harrison, Chief, EL. The report was edited by Ms. Jessica S. Ruff of the WES Information Technology Laboratory.

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DURING DREDGED MATERIAL DISPOSAL WITH APPLICATIONS
TO NEW BEDFORD HARBOR, MASSACHUSETTS

PART I: INTRODUCTION

Background

1. In August 1984, the US Environmental Protection Agency (USEPA) reported on the Feasibility Study of Remedial Action Alternatives for the Upper Acushnet River Estuary above the Coggeshall Street Bridge, New Bedford, MA (NUS Corporation 1984). The USEPA received extensive comments on the proposed remedial action alternatives from other Federal, state, and local officials, potentially responsible parties, and individuals. Responding to these comments, the USEPA chose to conduct additional studies to better define available cleanup methods. Because dredging was associated with all of the removal alternatives, the USEPA requested the US Army Corps of Engineers to conduct an Engineering Feasibility Study (EFS) of dredging and disposal alternatives. A major emphasis of the EFS was placed on evaluating the potential for contaminant releases from both dredging and disposal operations.

2. A confined disposal facility (CDF) is a diked area for gravity separation and storage of dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals (VOCs) associated with the solid fraction of the sediment to be released to the air during and after disposal. The process is termed volatilization and under certain conditions may involve release of significant quantities of hydrophobic compounds such as polychlorinated biphenyls (PCBs) (Thomas, Mt. Pleasant, and Maslansky 1979). The emission rates of PCBs and other more volatile organic compounds due to volatilization processes associated with operating a CDF are presently unknown. Methods for predicting these losses are needed to fully evaluate the confined disposal alternatives for dredged material from Superfund sites such as New Bedford Harbor.

Objectives

3. The primary objective of this investigation was to present a general theoretical framework for the development of methods, mathematical and experimental, for predicting volatile chemical emissions to air from a CDF and its associated operations. An additional objective was to apply the methods to a CDF containing New Bedford Harbor dredged material. The emphasis here is on the development of methods that address the VOC source generation terms in the water and dredged material compartments of the CDF. The information on source strength must be coupled with the appropriate air dispersion model to determine such factors as downwind concentration levels and contaminated air plume sizes. These aspects of air modeling are not within the scope of this report.

Project Tasks

4. The scope of the project involved the following four tasks:
- a. Identify the primary volatile chemical generating processes for various CDF designs and operating modes. (Knowledge of the details of filling, operating, and managing typical CDFs was obtained by visiting sites, consulting with knowledgeable individuals, and studying selected reports on the design, operation, and management of CDFs.)
 - b. Review and/or develop appropriate theoretical chemodynamic models capable of making quantitative predictions of volatile chemical emissions to air.
 - c. Review appropriate laboratory procedures and field protocols for obtaining data that will allow the most accurate prediction, simulation, and verification of volatile chemical emissions processes.
 - d. Prepare a final report giving relevant and practical details on the models, experimental methods, and calculations done for the proposed New Bedford Harbor pilot CDF.

Scope of Report

5. This report presents the results and findings as a consequence of completing the above tasks. No attempt was made to review or present all the information in the open literature on the subject of volatiles from water, dredged material, or soils. The subject area is very mature and the information extensive, and that body of knowledge provided the technical foundation

for this report. Relevant portions of that body of knowledge, as it was perceived to apply to CDFs, were either selected whole or modified for presentation in this report. Other portions had to be developed from first principles.

6. The theoretical chemodynamic models presented in this report reflect the need for mathematical algorithms that are practical but nevertheless contain sound scientific underpinnings. In many cases, the result is a set of vignette models. These models are sophisticated in the sense that they contain all the complexities of the physiochemical phenomena, but some license is taken in assigning gradients, source terms, geometric dimensions, etc., with simple approximations. This trade-off results in mathematical forms that are concise and explicit but allow the incorporation of all the known and relevant chemical behavior characteristics that are inherently difficult to model otherwise.

7. One or more partial differential equations can be presented to describe the minutia of chemical behavior in the various locales of a CDF. The result is mathematical overkill in the face of the degree of randomness and uncertainty that exists from site to site and time to time in nature. Development of this type of theoretical model framework was not within the scope of this study. In this light, the degree of compromise provided for by vignette models is justified.

8. The report begins with a review of equilibrium concepts. These concepts provide a basis for quantifying the proper solubility and vapor concentration for VOCs in the CDF locales. This in turn establishes the high end of the concentration gradient for the chemical transport process, which terminates in emission to air.

9. The section that describes the chemical transport process is built around VOC generating locales. Emission locales are defined as specific locations within the CDF that contain common behavioral or operational characteristics that result in the release/generation of volatile organic chemicals to air. Four are identified: sediment relocation locales, exposed sediment locales, ponded sediment locales, and vegetation-covered sediment locales. Most of the locales are further divided into subsections to account for significantly different operational characteristics.

10. In some, if not most cases, it will be necessary to perform limited laboratory and/or field experiments. For example, this will need to be done to test the significance of a particular VOC source term to verify some hypothesized VOC generation process or to obtain critical adjustable parameters in the final mathematical algorithm of the model. In this regard, a section of the report is devoted to reviewing existing laboratory and field test procedures for the technical information they can provide in support of the modeling objectives.

11. The final section of the main text presents the study conclusions and recommendations. This includes conclusions as to the existence of appropriate theoretical frameworks for the various emission locales and recommendations for obtaining the missing pieces of the VOC emission processes as they apply to CDFs. Appendix A discusses the derivation of the rivulet and ponded VOC emission model. Appendix B presents the VOC emission calculations for the proposed New Bedford Harbor pilot CDF.

PART II: EQUILIBRIUM PROCESSES

12. All waterways contain particles, and sedimentation is a natural process resulting in deposition on the bottom. Particles enter urban waterways with water runoff and from controlled and uncontrolled water discharges. Chemical pollutants enter waterways by the same routes. The particles are predominantly soil solids. Fine-grained soils, such as silts and clays, have a high affinity for many pollutants. Volatile organic chemicals comprise a general class of pollutants with finite vapor pressures and water solubilities that are known to be associated with waterborne soil particles. These VOCs include hydrophobic contaminants, such as PCBs, which have an especially high affinity for sediments containing organic matter (both natural and anthropogenic). As a result, deposited sediments have been a significant sink for pollutants discharged to waterways.

13. Cleanups that involve dredging result in the removal and relocation of in-place polluted sediments. The process of sediment removal and relocation creates conditions that enhance the release of VOCs to air. The VOCs enter the air primarily as individual molecular species in the gaseous state from water or sediment surfaces. The entry of VOCs to air from droplets created by bursting bubbles and wind-blown sediment dust or other means of particle generation will not be considered in this work.

14. Chemical equilibrium between the various phases is a branch of the science of thermodynamics. The general criteria for chemical equilibrium as it applies to pollutants in the natural environment are presented elsewhere (Thibodeaux 1979). In the case of VOCs associated with sediment, three phases of matter are involved. The first consists of the solid particles that constitute the sediment, including the subphases of organic matter and mineral matter. The organic matter can be both natural and anthropogenic in origin. The mineral matter is inorganic and includes the sand, silt, and clay fractions. The two other primary phases are the fluids--air and water. In general, these are less complex in physical makeup than is the solid phase.

15. The emission of VOCs to air must commence with the proper theoretical chemical equilibrium laws between the three primary phases. A complete description in the case of the locales within a CDF will by necessity involve three binary-phase chemical equilibrium conditions. These are air-water, water-sediment, and sediment-air. The following sections give the details of

each and present the appropriate theoretical framework for deriving equations to relate the chemical concentrations of VOCs in the air, water, and sediment.

Chemical Equilibrium Between Air and Water

Henry's Law

16. The distribution of a volatile chemical between air and water can be represented by a simple ratio of concentrations if true solutions exist in both phases. Historically, the ratio has become known as Henry's constant, and the equilibrium condition for volatile chemical A is represented as

$$\rho_{A1} = H_{\rho} \rho_{A2} \quad (1)$$

where

$$\begin{aligned} \rho_{A1} &= \text{concentration in air, g A/cm}^3 \text{ air} \\ H_{\rho} &= \text{Henry's constant, cm}^3 \text{ water/cm}^3 \text{ air} \\ \rho_{A2} &= \text{concentration in water, g A/cm}^3 \text{ water} \end{aligned}$$

The literature is rich with data and computational methods for obtaining this constant. A general source is the work of Lyman, Reehl, and Rosenblatt (1982).

Oil-type film on water

17. It has been observed both in the field and in the laboratory that an oil-type film can develop on the surface of water as contaminated sediments are agitated or otherwise violently disturbed. Apparently, the natural process of depositing sediment on the bottom is a more gentle process, and the free-phase oil attached to individual soil particles remains. It is also possible that once deposited on the bottom, the contaminated sediment undergoes some diagenetic processes whereby the adsorbed oil migrates under interfacial tension forces and coalesces. This results in the formation of oil microdroplets within the sediment. Agitation of this sediment with water during dredging can create conditions for the formation of an oil film.

18. This oil-type film floats on the water, and its juxtaposition between the phases gives rise to a third fluid phase that separates the air from direct contact with the water. This film appears to be a few monomolecular layers in thickness and exists in patches so that complete coverage of the

water surface does not occur. Nevertheless, its presence may complicate the normal treatment according to Henry's Law.

19. The equilibrium relationship for organic chemical A between air and an oil phase is (Thibodeaux 1979, p 196)

$$p_A = x_{A4} \delta_{A4} p_A^* \quad (2)$$

where

p_A = partial pressure in the air, atm

x_{A4} = mole fraction A in the oil phase

δ_{A4} = activity coefficient of A in the oil phase

p_A^* = pure component vapor pressure, atm

20. The equilibrium relationship between the oil and the underlying water is (Thibodeaux 1979, p 196)

$$\rho_{A2} = \rho_{A2}^* x_{A4} \delta_{A4} \quad (3)$$

where ρ_{A2}^* is the solubility of A in water, g A/cm³. If the oil film is thin so that it responds quickly and is in equilibrium with both air and water simultaneously, the product $x_{A4} \delta_{A4}$ may be eliminated and Equations 2 and 3 combined to give Henry's constant.

21. Using the ideal gas law, $\rho_{A1} = p_A M_A / RT$ completes the transformation so that the result is identical to Equation 1 where the constant is

$$H_\rho = \frac{M_A p_A^*}{RT \rho_{A2}^*} \quad (4)$$

and

M_A = molecular weight of A, g/mol

R = gas constant, 82.1 atm · cm³/mol K

T = absolute temperature, K

22. If the oil film is thick, it cannot be assumed to be in equilibrium with both phases simultaneously. In this case, it provides an additional resistance to the VOCs' movement from water to air, and the partition

coefficient of the VOC between oil and water is needed (Springer, Valsaraj, and Thibodeaux 1985). Since very thin oil films appear to be the norm at CDF operations, the above exception will not be considered further in this report.

Chemical Equilibrium Between Water and Sediment

Distribution coefficient

23. The equilibrium distribution of a volatile chemical between water and sediment is typically represented by a constant, which is the ratio of the concentration in (or on) the sediment to the concentration in water:

$$K_d = \frac{\omega_A}{\rho_{A2}} \quad (5)$$

where

K_d = distribution coefficient, cm^3 water/g sediment (or ℓ/kg)

ω_A = concentration in sediment, g A/g sediment

24. The work of Huang et al. (1987) was concerned with VOCs on soils and contained limited desorption data. This is a much studied parameter, particularly for adsorption in the laboratory, and enjoys a voluminous literature heritage beyond the point of realistic applications to the natural environment in many cases. Hill, Myers, and Brannon (1988) presented the essential aspects of the theory of these distribution coefficients as they apply to CDFs. Pavlou and Kadeg (1987) demonstrated that several published correlations are adequate for predicting the range of the field-observed partition coefficients. These field values were derived from analysis of pore water and sediment samples from contaminated sites.

25. For the purposes of this work, it will be assumed that K_d can be adequately estimated by the most appropriate (i.e., chemical matchup) literature correlation or can be measured in the laboratory under desorption conditions. It will be assumed that, in the case of dilute solutions up to the solubility limit, the organic matter content of the sediment is the primary independent variable. This quantity along with a relationship between K_{oc}

and the solubility of the VOC in water will yield K_d . The relation between the coefficients is

$$K_d = K_{oc} \omega_c \quad (6)$$

where

K_{oc} = chemical partition coefficient normalized to the mass organic content in the sediment, l/kg organic matter

ω_c = mass fraction organic content of the sediment, kg organic matter/kg

The specific correlation for K_{oc} is the choice of the user. The compilation in Lyman, Reehl, and Rosenblatt (1982) is a readily available source of current correlations.

Solubility limit

26. Extremely high concentrations of PCBs have been measured in the New Bedford Harbor sediment. Weaver (1982) reported concentrations from a few parts per million to over 100,000 mg/kg. If 0.13 mg/l is accepted as the solubility of Aroclor 1242 in freshwater at 11° C (Dexter and Pavlou 1978), then reasonable values of K_{oc} range from 10,000 to 100,000 l/kg (see Lyman, Reehl, and Rosenblatt 1982). For a sediment containing 5 percent organic matter, with 70 percent of the total PCBs being 1242 and a sediment total PCB concentration of 36,000 ppm, Equations 5 and 6 yield an equilibrium Aroclor 1242 concentration in water of 2.5 and 0.25 mg/l, respectively. Each, based on a different K_{oc} value, exceeds the solubility of 0.13 mg/l. This is thermodynamically impossible for a pure aqueous phase.

27. The use of distribution coefficients to compute equilibrium concentrations in water, based on concentrations in sediment, has its limits. Beyond that critical chemical concentration in sediment,

$$\omega_A^c = K_d^* \rho_{A2} \quad (7)$$

such that the distribution coefficient model is inappropriate. Beyond this limit, the concentration in water is constant and equals the solubility. Figure 1 illustrates the solubility limit concept. However, batch leach data have been found to exceed such theoretical limits for "operationally defined" concentrations in water. Aroclor 1242 and 1254 concentrations in whole and centrifuged water samples in the Standard and Modified Elutriate Tests

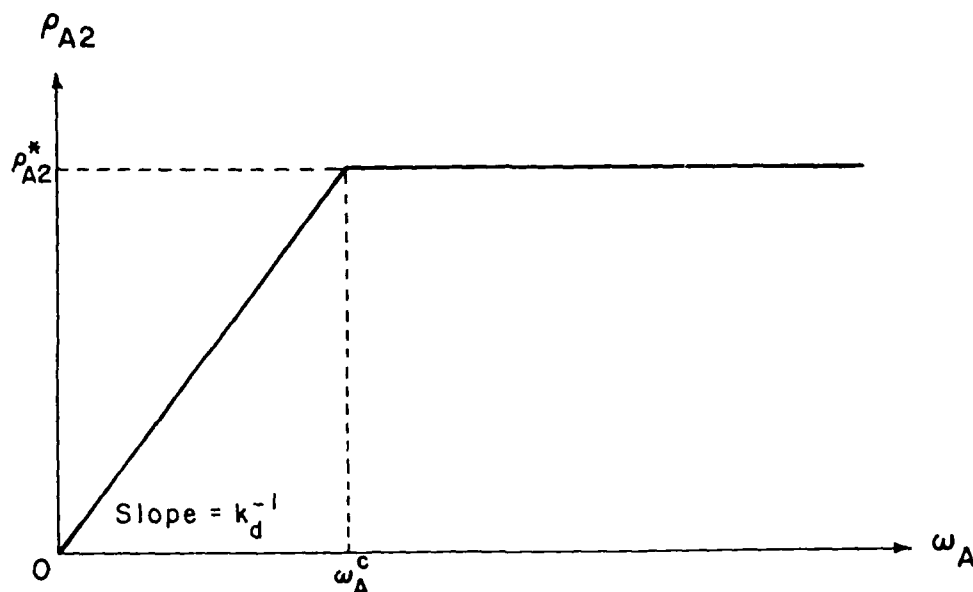


Figure 1. Limits of applicability of distribution coefficient law and the solubility limit

exceeded the solubility limit (Otis 1987). This effect is likely due to microparticulates in water and is therefore not a true solution.

28. In this work, the ultimate source of all VOCs will be the solid particles either suspended in the water column or as bottom sediment. In the region of chemical concentrations at and beyond ω_A^c , evaporation, under equilibrium conditions, occurs at a constant rate. The concentration in air is the pure component vapor pressure. Substituting ρ_{A2}^* into Equation 1 and using Equation 4 for H_ρ reveals this fact. As the concentration in sediment falls below ω_A^c , the equilibrium concentration in water falls below the solubility. The evaporation process is said to be in the falling rate period. The equilibrium concentration in air is below the pure component vapor pressure. The chemical concentrations in all three phases approach zero as the equilibrium evaporation process continues.

Chemical Equilibrium Between Sediment and Air

Adsorption on dry sediment

29. The adsorption of VOCs from the air onto dry sediment apparently obeys the characteristics of the Brauner, Emmett, and Teller (BET) isotherm (Chiou and Shoup 1985; Poe, Valsaraj, and Thibodeaux 1988). Dry refers to a

water content on the sediment of less than 5 percent of that needed to form a complete monolayer on the surface of the sediment. In most cases, the Langmuir modification is appropriate for the levels of chemical concentration observed on most sediment. The Langmuir isotherm is

$$p_A = \frac{p_A^*}{B_1} \left(\frac{\omega_A / \omega_A^*}{1 - \omega_A / \omega_A^*} \right) \quad (8)$$

where

ω_A^* = quantity of the VOC required to form one monolayer on the sediment surface adsorption sites, g A/g sediment

B_1 = BET isotherm constant, dimensionless

30. In the case of a dilute loading of A on the soil, the isotherm is linear and of the form

$$p_A = K_a \omega_A \quad (9)$$

where $K_a \equiv p_A^* / B_1 \omega_A^*$ is the dry sediment air-solids partition coefficient.

Adsorption on damp sediment

31. Damp sediments are those that contain water to the extent that it occupies 5 to 95 percent of that required for a single monolayer of coverage. Within this range, the water molecules occupy significant quantities of the adsorption sites so that water effectively competes with the VOC. Valsaraj and Thibodeaux (1987) employed the competitive multicomponent version of the BET and obtained an expression for VOC adsorption on damp sediment. The working form of the equation is

$$p_A = \frac{p_A^*}{B_1} \left(\frac{\omega_A / \omega_A^*}{1 - \omega_A / \omega_A^* - \omega_B / \omega_B^*} \right) \quad (10)$$

where

ω_B = moisture content of the sediment

ω_B^* = moisture needed to form one monolayer on the sediment surface adsorption sites, g H₂O/g sediment

32. For dilute loading levels of A on the sediment, Equation 10 becomes

$$P_A = K'_a \omega_A \quad (11)$$

where $K'_a = K_a / (1 - \omega_B / \omega_B^*)$ is the damp sediment air-solids partition coefficient. Methodologies for estimating ω_A^* , ω_B^* , and B_1 are given by Valsaraj and Thibodeaux (1987). It is apparent from Equation 11 that as the sediment moisture level increases, so does the equilibrium partial pressure of the VOC for a fixed soil loading level.

Adsorption onto wet sediment

33. A wet sediment is one that contains at least a monolayer of water molecules on the active adsorption sites. Due to its small thickness, the water film on the sediment particles is simultaneously in equilibrium with the solid surface and with the pore gas. In the region of soil loadings below the solubility limit, Henry's Law applies for the air-water equilibrium, and the distribution coefficient model applies for the water-sediment equilibrium. Eliminating the chemical concentration in water by solving and equating it in Equations 1 and 5 yields

$$\rho_{Al} = \frac{H}{K_d} \omega_A \quad (12)$$

34. The ideal gas law can be used to express the left-hand side as a partial pressure to yield

$$P_A = K''_a \omega_A \quad (13)$$

where $K''_a = RTH_\rho / M_A K_d$ is the wet sediment air-solids partition coefficient.

Vapor pressure limit

35. Just as in the case of the solubility limit, it is thermodynamically impossible to increase the VOC content within the sediment above a level (ω_A^p) that the partial pressure in the air- (or gas-) filled pore spaces exceeds the pure component vapor pressure at the system temperature. This pressure is an upper bound and limits the applicabilities of Equations 8 through 13 to a

range of ω_A values. Figure 2 illustrates the vapor pressure limit concept and gives general regions of applicability of the dry, damp, and wet sediment-air VOC adsorption models.

36. The VOC evaporation from exposed sediment to air is a very complex process. The water content of the sediment is the primary factor. Its competition with the VOC for adsorption sites plus the coevaporation with the VOC under low-humidity air and moderate temperature conditions is the root of the problem. As an example, consider a wet sediment-air equilibrium condition represented by the point A in Figure 2. This point may be representative of the recently deposited and exposed surface of dredged sediment in the delta zone near the slurry discharge pipe within a CDF. This is a wet sediment case. The VOC content is high and above the solubility limit so that the pure component vapor pressure is exerted in the air layers immediately above the

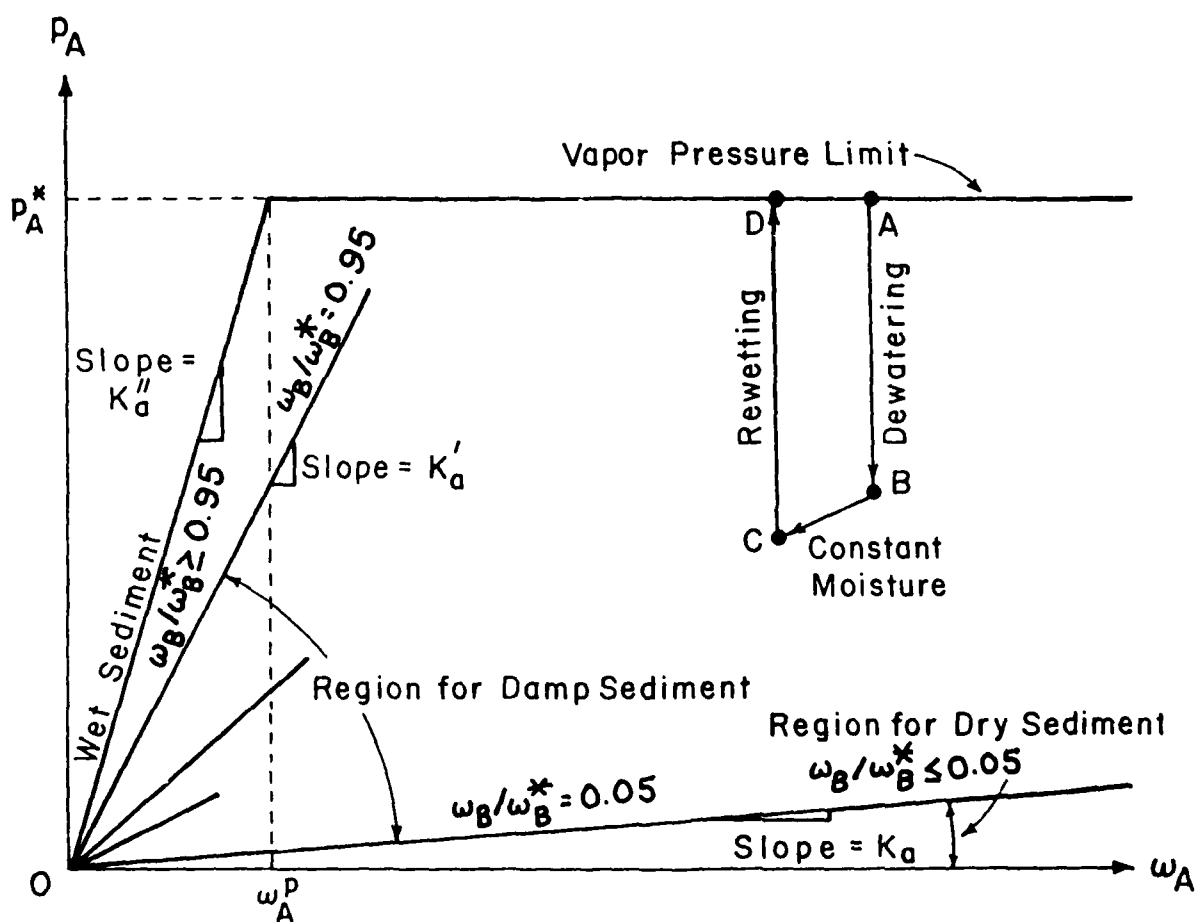


Figure 2. Vapor pressure limit and regions of applicability of sediment-air absorption models

wet sediment bed. Due to downward percolation of water and low air humidity, the water content in the upper sediment layer drops rapidly. This is now a damp sediment case. The loss of water exposes active adsorption sites on the solid surface, which can now be occupied by the VOC molecules, and this effectively lowers the partial pressure in the air. The value is lower than p_A^* and is represented by point B. The surface sediment remains at this water content, somehow, for a period, and the VOC content is reduced by evaporation to air. The equilibrium partial pressure decreases linearly with ω_A to a value represented by point C. Upon reaching point C, a rain event wets the soil, and the VOC pressure returns to its full saturation value (point D). This is once again a wet sediment case. The net effect has been that ω_A is reduced due to the vaporization to air. However, the vapor pressure above the sediment remains high at p_A^* because the sediment is wet and contains the VOC at a concentration above ω_A^P .

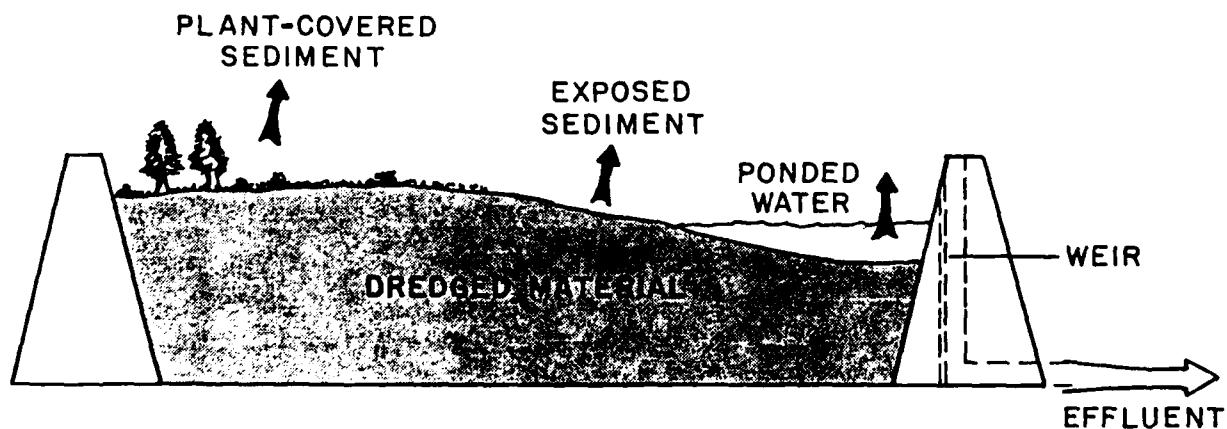
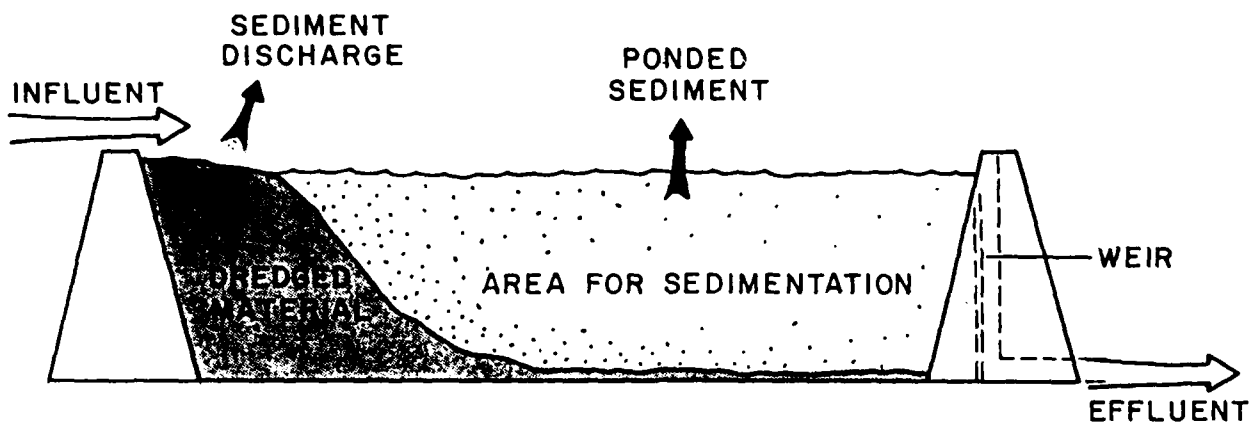
PART III: TRANSPORT PROCESSES

Volatile Organic Chemical Emission Locales

37. A CDF and its associated operations is a fairly complex unit from the standpoint of VOC generation and emission to air. The procedure for developing a proper conceptual model, with the goal of providing realistic algorithms that will quantify emission rates, must address specific physicochemical mechanisms within the CDF with regard to how they control chemical transport to air. In this light, it is necessary to divide a CDF and its associated operations into four general VOC emission locales. As defined in the introduction, an emission locale is a specific location that contains common behavioral or operational characteristics that result in the release/generation of VOCs to air. Figure 3 illustrates the general locations of each major emission locale in a CDF.

38. Four locales have been identified. One involves those CDF operations that are concerned with sediment relocation. Specifically, they are dredging, transporting, discharging, and other related sediment handling operations. The second emission locale is exposed and drying sediment beds void of vegetation. Typically, this may be the delta region formed from sediment laid down as the slurry emerges from a discharge pipe. This locale occupies the region from the water's edge to the dike or to the vegetation line that commences the marsh or upland region of the CDF. The third emission locale is that portion that contains water. This includes the area of sedimentation during disposal. The fourth emission locale is that portion of the CDF that is covered with vegetation. This may range from grasses near the water's edge to trees in the older parts of the CDF.

39. The VOCs emerging from the various locales described above do so through specific areas of the CDF surface. Plane surface areas need to be associated with each locale. As will be developed in the next part, the individual locales will be characterized by a VOC emission flux rate that has dimensions of chemical mass rate per unit plant area. Fairly precise areas will be required to yield the total chemical mass rates emitted.



↑ Denotes VOC emission locale

Figure 3. Major VOC emission locales: sediment relocation (discharge), ponded, exposed, and plant-covered

Locale 1 - Sediment Relocation Devices

Sediment resuspension due to dredging

40. During operation, all dredge plants, to differing degrees, disturb bottom sediment, creating a plume of suspended solids in the surrounding waters. The suspended solids plume can form relatively low concentrations in

the upper water column, high concentrations near the bottom, or both, depending on the type of sediment and the amount of energy introduced by the dredge.

41. Resuspension can be viewed as the difference between the amount of sediment loosened or disturbed from the bottom and the amount actually entrained and removed by the dredge. Therefore, the more efficient the dredging process is, the less resuspension is likely to occur.

42. Dredges are of two basic types: hydraulic and mechanical. Hydraulic dredges remove and transport sediment in slurry form. They are usually barge mounted and carry diesel- or electric-powered centrifugal pumps with discharge pipes. Cutterhead, suction, dustpan, hopper, and special-purpose dredges are types of hydraulic dredges. Mechanical dredges remove bottom sediment through the direct application of mechanical force to dislodge and excavate the material at most in situ densities. Clamshell, dipper, dragline, and ladder dredges are types of mechanical dredges.

43. Volatile organic chemical emissions may be enhanced due to the increase in suspended solids in the water column and the energy imparted, which increases water turbulence. Contaminated sediment may release some constituents into the water column through resuspension of the sediment solids, dispersal of interstitial water, or desorption from the resuspended solids. Once resuspended, fine-grained sediments (clay and silt) tend to remain in the water column longer than sandy sediments due to slower settling velocities.

44. Undoubtedly, VOCs are being emitted to air prior to the arrival and operation of the dredge. The contaminated sediment bed is a source of organic chemicals to the water column, and these eventually move through the water surface to the air. The resuspension of bottom sediment by the dredge enhances the emission process. Contaminated sediment is brought into the water column near the air-water interface. Desorption of the contaminants from the suspended particles places them in solution from which evaporation to air occurs. Desorption from suspended particles short-circuits the original pathway from the bottom and increases the concentration and emission rate.

45. Enhanced VOC emission will be assumed to be occurring from an area of the water surface, $A \text{ (cm}^2\text{)}$, that encompasses the suspended sediment plume generated in the waterway by the dredging operation. The concentration of suspended solid in the plume is $\rho_{32} \text{ (kg/l)}$. If the rate of chemical vaporization is small relative to the mass of chemical associated with suspended solids, then an equilibrium model can be used to estimate the VOC

concentration in solution. The concentration in solution, ρ_{A2} (mg/l) is

$$\rho_{A2} = \frac{\omega_A \rho_{32}}{K_d \rho_{32} + 1} \quad (14)$$

where ω_A is the concentration of the VOC on the original bed sediment, g/g. This equation applies, provided $\rho_{A2} < \rho_{A2}^*$.

46. It is convenient to use chemical equilibrium models such as the above to arrive at concentrations in sediment pore water or the water column. Their use implies some assumptions that may not always be met in the particular locale. In this case, the critical assumption is that the water and solids are in contact a sufficient length of time so that equilibrium between the phases has been achieved. In the case of large particles or large K_d values, the release of the chemical is slow so that large times are needed for equilibrium to be achieved. The process is particle diffusion controlled and therefore not at equilibrium. The assumption of equilibrium yields an elevated estimate of the VOC in solution and also an elevated emission rate.

47. The VOC flux rate through the air-water interface (n_A) (expressed in g A/cm² · sec) is

$$n_A = {}^1K'_{A2} (\rho_{A2} - \rho_{A2}^{**}) \quad (15)$$

where

${}^1K'_{A2}$ = overall liquid phase mass-transfer coefficient, cm/sec

ρ_{A2}^{**} = hypothetical concentration in water for a VOC concentration in air of ρ_{A1} , g A/cm³

This coefficient is computed from the two-resistance theory (Thibodeaux 1979). The product of the flux rate and the sediment plume surface area yields the VOC emission rate, W_A , in grams per second.

Dredge machinery water disturbances

48. The presence of dredging machinery (i.e., barge) will likely enhance ${}^1K'_{A2}$ above its background value as water turbulence is increased due to the operation. The degree of enhancement is unknown but likely to be no more than a few percent to a factor of two. The increased VOC emissions directly attributed to the operation of the dredge in the case of hydraulic devices are possibly small. On the other hand, the operation of mechanical dredges will likely cause significant point sources of VOC emissions.

49. Mechanical dredges cause significant water turbulence at the point where the bucket, shovel, etc., breaks through the water surface in the process of being hoisted or lowered. This creates intense turbulence in the surface water and enhances VOC emissions. The surface of the bucket or shovel is coated with sediment, and this is a very direct pathway for VOC emission. The surface area is small, which makes the total emission rate small but creates an intense "point" source each time it is raised above the water surface. The discharge of the bucket contents into a scow or hopper barge creates another intense point source, as does the exposed surface of the sediment in the receiving vessel.

50. Mechanical dredging thus involves three VOC point sources: the water surface under the bucket, the surface of the bucket with sediment heap, and the surface of the receiving vessel. Two are intermittent and depend upon the cycle time and exposure time to air of the bucket, while the third is continuous. Emission rates from each can be quantified with rate equations such as those used above.

51. The energy imparted into the water surface (i.e., horsepower or watts) each time the bucket is raised or lowered can be easily estimated from the mass, velocity of the mechanical device, and event time. This, coupled with information on the water surface area disturbed and an estimate of the transport coefficient due to mechanical surface agitation (Equation 4.1-13, p 146, Thibodeaux 1979, is suggested), will yield the product $^1k'_{A2}A$, cm^3/sec . The number of events is double the 20 to 30 per hour, which would be a typical bucket cycle time. The concentration driving force is that given in Equations 14 and 15.

52. As the bucket is lifted through the surface, swings upward and over the scow, deposits its load, swings back, and finally plunges through the water surface again, it is for all practical purposes a contaminated sphere bobbing about in the air. The surface area of this almost spherically shaped object is known. Air-side transport coefficients, $^2k'_{A1}$, cm/sec , for such objects can be estimated from correlations involving the object Reynolds number (Bird, Stewart, and Lightfoot 1960, p 647). The VOC emission rate equation is

$$n_A = ^2k'_{A1} \left(\rho_{A1}^* - \rho_{A1} \right) \quad (16)$$

where ρ_{Al}^* is the effective VOC concentration in air originating from the sediment clinging to the bucket, which is dependent on the concentration in the sediment. Equation 12 is the appropriate equilibrium expression for this so that $\rho_{Al}^* = \omega_A H_p / K_d$ in Equation 16.

Receiving vessel source

53. The receiving vessel (scow or barge) is an open-top vessel and a continuous VOC source either full or empty as long as it is mud splattered. Reible* has developed a modification of the conventional turbulent boundary layer theory expression for the $^2k'_{Al}$ of flat surfaces. The term is the modification that accounts for the evaporating surface being a distance Z (feet) below the top of the vessel with diameter D (feet). The expression for the air-side transport coefficient is

$$Nu_{AB} = 0.036 \left(\frac{2D - Z}{2D} \right) R_e^{0.8} S_c^{0.33} \quad (17)$$

where

$$Nu_{AB} \equiv ^2k'_{Al} D / \mathcal{D}_{Al}$$

$$\mathcal{D}_{Al} = \text{molecular diffusivity of the VOC in air, cm}^2/\text{sec}$$

$$R_e \equiv DV_\infty / \nu_1$$

$$V_\infty = \text{background windspeed, cm/sec}$$

$$\nu_1 = \text{kinematic viscosity of air, cm}^2/\text{sec}$$

$$S_c \equiv \nu_1 / \mathcal{D}_{Al}$$

54. The above development demonstrates the mechanisms by which VOC emission in a waterway can be enhanced by the presence of a dredging operation. It was assumed at the onset that the enhancement created by hydraulic dredging was due only to the generation of a suspended sediment plume. This plume was also present in the case of mechanical dredging but, in addition, there were three more point sources. Rate equations and specific methodologies were suggested for each source of the dredging locale.

Sediment discharge emission models

55. Most hydraulic dredges such as the cutterhead, suction, and dustpan are also equipped to pump all types of alluvial materials and compacted deposits, such as clay and hardpan, to CDFs. The sediment and water slurry is

* Personal Communication, 1987, D. D. Reible, Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA.

discharged from the end of a pipe either into the water or onto the sediment delta of the receiving CDF.

56. The discharge of a slurry from pipe is not unlike the natural process of water flowing over a dam. Reaeration occurs as the water flows over the dam, and empirical relationships for this have been developed and verified by field data. Among the empirical relationships available, the equation commonly referred to as the British formula seems particularly well suited because it was calibrated with 54 small-stream head loss structures (Tetra Tech 1978). Since oxygen transport into water is liquid phase-controlled and most VOCs are desorbed by the same liquid phase mechanism, the fraction volatilized across the discharge (F) can be estimated by

$$F = \frac{0.11ab(1 + 0.046T)H_d(D_{A2}/D_{B2})^{1/2}}{1 + 0.11ab(1 + 0.046T)H_d(D_{A2}/D_{B2})^{1/2}} \quad (18)$$

where

a = water quality factor; equal to 1.00 in polluted water

b = 0.60 for a round broad-crested curved face spillway

T = water temperature (°C)

H_d = height through which the water falls, ft

D_{A2} , D_{B2} = molecular diffusivities of the VOC and oxygen in water, respectively, cm^2/sec

The half power of the diffusivity ratio converts the correlation from an oxygen data base to that for the VOC of interest.

57. The quantity of the VOC approaching the discharge point that is volatilized is

$$W_A = Q\rho_{A2}F \quad (19)$$

where Q is the volumetric rate of water (solids-free) flow in the pipeline, cm^3/sec . The use of Equation 14 to estimate the concentration is an excellent choice since the residence time and high turbulence levels in the pipe will ensure near-equilibrium conditions at the exit. The value of ρ_{32} is that of the pipeline sediment slurry.

58. The use of oxygen transfer coefficients as the data for a dredge slurry, as proposed above, will likely result in an overestimate of the actual VOC emission rate. The recommended water quality factor α for clean water is 1.25. The recommended value of $\alpha = 1.00$ for polluted water is a reasonably conservative choice for a sediment slurry. Because effective viscosity of the slurry is much greater than that of water and the transport coefficient is typically a function of viscosity to the negative 2/3 power, Equation 18 will overpredict actual VOC emission rates. The magnitude of the error cannot be estimated with available information.

59. If the discharge is submerged, Equation 18 is inappropriate for estimation of VOC emission because there is no contact between air and the dredged material slurry. For submerged discharge, VOC emission is hindered by the overlying water. The VOC emission models for ponded sediment, discussed later in this report, are applicable to submerged discharge. The discharge of dredged sediment into the CDF may also be by bucket or shovel. In this case, the appropriate methodology recommended above for VOC emission estimates during bucket or shovel dredging should be used (see paragraphs 50-52).

60. It is possible that significant overland flow of water and sediment may occur from the discharge point to the water's edge of the CDF. Sediment deposition occurs along the entire stretch of the rivulet's flow path, providing a constant supply onto the bottom. This redeposited material will be considered to be a VOC source of constant concentration ω_A . Shallow rapid streams are known to be good VOC strippers (Thibodeaux 1979, p 156). In the following paragraphs a vignette model is developed that accounts for these and other major sediment and chemical transport processes within the rivulet. A detailed derivation appears in Appendix A. The development is general enough that it can also be applied to the ponded locale of a CDF.

61. A sketch of a section of a rivulet stream is shown in Figure 4. As indicated, the VOC evaporation occurs across the air-water interface. Other transport processes affecting the VOC within the differential element are advection by water flow, advection by suspended particle flow, deposition (net) of particles onto the bed, dissolution from the bed surface, and dynamic equilibrium between suspended particles in the water column. This vignette model is steady state, with uniform concentration in the vertical and lateral directions.

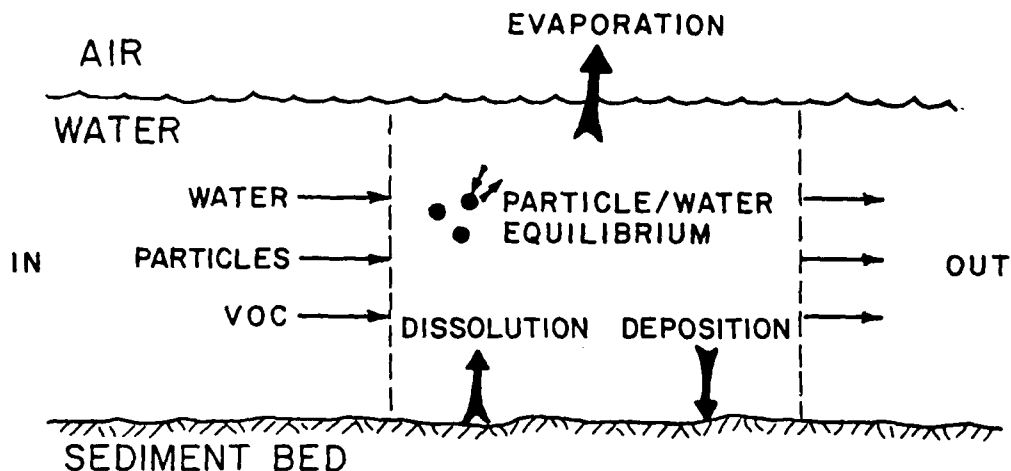


Figure 4. Major VOC transport pathways in a rivulet

62. A simple net deposition particle transport and exchange model is used to describe the suspended solids concentration:

$$\rho_{32} = \rho_{32}^0 \exp \left(\frac{-v_d x w}{Q} \right) \quad (20)$$

where

ρ_{32}^0 = concentration of particles at the head of the rivulet stream, g/cm³

v_d = net velocity of particle deposition, cm/sec

x = distance from the rivulet head, cm

w = rivulet width, cm

This is one case of several particle transport and exchange models proposed in the USEPA Technical Guidance Manual, Book II, Streams and Rivers, Chap. 3, Toxic Substances (Delos et al. 1984).

63. A mass balance on the VOC yields the following equation for the concentration ρ_{A2} , with reach x :

$$\rho_{A2} = \frac{3k'_{A2}\omega_A^*/K_d + 1K'_{A2}\rho_{A2}^*}{3k'_{A2} + 1K'_{A2}} + \left(\rho_{A2}^o + \frac{3k'_{A2}\omega_A^*/K_d + 3k'_{A2}\rho_{A2}^*}{3k'_{A2} + 1K'_{A2}} \right) \exp \left\{ - \left(3k'_{A2} + 1K'_{A2} \right) xw/Q + \left(\frac{3k'_{A2} + 1K'_{A2}}{v_d} \right) \ln \left[\frac{1 + K_d\rho_{32}^o}{1 + K_d\rho_{32}^o \exp(-v_dxw/Q)} \right] \right\} \quad (21)$$

where

$3k'_{A2}$ = water-side transport coefficient above the bed, cm/sec

ρ_{A2}^o = initial VOC concentration at $x = 0$, g/cm³

Appendix A contains the derivation of Equation 21.

64. The relative importance of the various transport parameters in Equation 21 is unknown. For example, if large particles fall out quickly and $v_d = 0$ for the remainder of the length plus $3k'_{A2} \gg 1K'_{A2}$, then $\rho_{A2} = \omega_A H_\rho / K_d$. These conditions force the evaporation to be much slower than dissolution, resulting in a VOC concentration in water at equilibrium with the concentration in the bed. Nevertheless, it will be necessary to integrate ρ_{A2} over the length of the rivulet to obtain the average, in order to use Equation 15 for the flux rate. (Consult Delos et al. (1984) for means of estimating v_d and Thibodeaux, Chang, and Lewis (1980) for calculating $3k'_{A2}$ based on stream and chemical properties.)

Summary

65. This concludes the section on models for VOC emissions resulting from the discharge of sediment into the CDF. As in the previous section on dredging operations, the mechanisms that drive the VOC emission process are fairly energy intensive. Although the sources are intense in a comparative sense, the areas are small, and only by calculation can the quantitative significance be determined. This is the case for the waterfall from the discharge pipe, the bucket/shovel discharge, and the rivulet for water that runs down the face of the sediment pile. Models for submerged discharge are considered in the section on ponded sediment (see paragraph 83). The remaining emission locales are influenced by natural processes to a greater extent. The energy sources are subtle. However, the emission areas are large, and the net effect could

be the generation of a significant quantity of VOCs to the surrounding air boundary layer.

Locale 2 - Exposed Sediment

66. This VOC emission locale is characterized by sediment that is exposed directly to air and void of any vegetation cover. It is the delta region formed by sediment discharged from a pipeline or from the bucket/shovel placement of sediment within the CDF and generally occupies the region from the water's edge to the vegetation line. Figure 3 illustrates this locale both in the early stages of filling and at the time the CDF is full. With regard to chemical transport, this is the most complex of the four VOC emission locales. The complexity is caused primarily by the presence of water. Attempts at complete mathematical descriptions of the coupled diffusion of thermal energy, with a phase change due to the evaporation of water, VOC, water vapor, and liquid water in the three phases of a porous media with realistic closure and equilibrium formulations, have been proposed (Linstrom and Piver 1985). The data input for such models is enormous, and the output, without site-to-site calibration, is more doubtful than a series of vignette models where the inputs are few. The following development is such a set of vignette models that describe the major aspects of the VOC emissions from the exposed sediment locale.

Water transport in upper soil layers

67. The VOC emission rate from the upper soil layers is dependent on both the moisture content and the water transport rate. The dredged material in this locale will also be termed soil. The theoretical aspects of the role of water on the equilibrium partitioning of VOCs between soil particles and the vapor phase were presented in Part II. Water transport in the upper soil layers is driven by advection processes. It percolates downward and moves upward by capillary forces as liquid, and evaporates and diffuses as vapor. In the case of soils that were once sediment contaminated with VOCs, it can be assumed that the VOCs are transported in the upper layers at much slower rates than water. This is true primarily for three reasons. The VOCs are strongly sorbed onto/into the soil particles, they enjoy less direct transport pathways, and their vapor pressures are, in general orders of magnitude, lower than that of water. In the case of less direct transport pathways, it must be

realized that liquid water can move as an essentially pure phase, whereas the VOC must move with it and then only in solution. It will also be assumed that the upper soil layers in a CDF will exist in a predominantly unsaturated state with respect to water. Water that arrives at the exposed sediment locale, either by rain or runoff, is assumed to evaporate upward and/or percolate downward rapidly so that, during the majority of the year, the upper soil layers are unsaturated.

68. Since water is so mobile, its evaporation from the surface or from within soil enhances the transport of the VOC in the vapor state. The coupled process for transport through the soil-air interface is described by the following two equations (Thibodeaux 1979, p 79)

$$N_A = {}^3k_{Al}(y_{Ai} - y_A) + y_{Ai}(N_A + N_B) \quad (22)$$

and

$$N_B = {}^3k_{Bl}(y_{Bi} - y_B) + y_{Bi}(N_B + N_A) \quad (23)$$

where

N_A, N_B = molar flux rates of VOC ($\equiv A$) and water ($\equiv B$) vapor, respectively, $\text{mol/sec}\cdot\text{cm}^2$

${}^3k_{Al}, {}^3k_{Bl}$ = respective mass transfer coefficients on air side of soil surface, $\text{mol/sec}\cdot\text{cm}^2$

y_{Ai}, y_{Bi} = mole fraction concentrations at a surface

y_A, y_B = concentrations far from the surface

It is argued above that $N_B \gg N_A$.

69. If the air is dry, contains none of the VOC, and the mass-transport coefficients are inversely proportional to the square root of molecular weight, then the equations can be combined to yield

$$N_A = \left\{ \frac{[y_{Bi}(M_A/M_B)^{1/2} - 1] + 1}{y_{Bi} - 1} \right\} {}^3k_{Al}y_{Ai} \quad (24)$$

where M_A and M_B are the molecular weights of the VOC and water, respectively. The expression within braces is the enhancement factor that the water vapor transport imparts to the VOC transport. For example, at 40° C, the vapor pressure of water is 0.0732 atm (7.4 kPa), so that for a VOC of $M_A = 300$, the enhancement factor is 1.32. This is not insignificant.

Vapor phase VOC
transport in upper soil layers

70. Contaminated sediment that is wet and exposed directly to the atmosphere is the case that results in the highest instantaneous VOC emission rates; however, the process is short lived. Volatile organics sorbed onto/into particles at the soil surface have a very short pathway to the air. The mechanism of evaporation includes:

- a. Desorption from the particle surface (or pore) into the water film.
- b. Diffusion through the water film.
- c. Desorption from the water film into the air boundary layer.
- d. Vapor phase diffusion.

This is a series of four resistances. The water film is very thin and usually provides minimum resistance. If it is assumed, as before, that chemical equilibrium exists between the particle and the water film, and since this interface and the water-air interface present no resistance, then Equation 16 can be used. The assumption of particle-water chemical equilibrium is very weak in this case because, at some point in this rapid surface evaporation process, chemical diffusion within the particle phase will become the controlling factor. Nevertheless, Equation 16 will yield an upper-bound VOC emission rate. Algorithms based on pesticide flux rate data above surface soils are available for estimating the air-side mass transfer coefficient (Thibodeaux and Scott 1985). This coefficient needs to be corrected by the water vapor transport enhancement factor in Equation 24.

71. At the above VOC loss rate from the soil surface, the top layers will quickly become depleted of the chemical. Continuing losses will come from within the soil pore spaces. At this point, the process of evaporation is transient and changes from being air-side resistance controlled to soil-side vapor phase diffusion controlled. This occurs when the effective plane of VOC evaporation recedes to a depth h :

$$h = \frac{192 \rho_{Al} \epsilon_1^{10/3}}{3 k'_{Al} \epsilon^2} \quad (25)$$

where

ϵ_1 = air-filled porosity, cm^3/cm^3

ϵ = total soil porosity

Typically h is a few millimetres.

72. A model has been developed for the case of volatile chemical losses from soils that receive petroleum waste in the so-called landfarming treatment process (Thibodeaux and Hwang 1982). This model has been verified in a laboratory microcosm (Dupont 1986). This investigator reported that the model "consistently overestimated flux rates for the pure constituents by only a factor of approximately 2 to 10, and consequently appears quite effective for the estimation of volatile organic emissions from complex waste/soil systems." Since soil formed from dredged material is very similar, this model will be used as the basis for the case of VOCs originating from within the soil.

73. The emission pathway for VOC originating from particles positioned below the soil-air interface has an additional resistance to the four mechanisms detailed in paragraph 70. The vapor phase molecules must diffuse through the air- (or gas-) filled soil for spaces prior to emerging into the air boundary layer. This is the fifth step in the overall evaporation process and is apparently the rate limiting step (Dupont 1986). The soil zone containing VOCs in the landfarm situation was a finite depth of 10 to 15 cm whereas that for dredged material in a CDF is infinite for all practical purposes. Fick's second law with an effective diffusivity that reflects the so-called retardation factor is appropriate. Due to the flat nature of the surface and the depth of the dredged material, the semi-infinite solution is appropriate. In this case the instantaneous flux is

$$n_A = \left[\frac{D_{A3} \left(\frac{\epsilon_1 H_\rho + K_d \rho_B}{H_\rho} \right)}{\pi t} \right]^{1/2} \left[\frac{\omega_A H_\rho}{K_d} - \rho_{A1f} \right] \quad (26)$$

where

D_{A3} = effective diffusivity (i.e., $D_{A1} \epsilon_1^{10/3} / \epsilon^2$)

ρ_B = bulk density, g/cm³

t = time the soil system has been in place, sec

ρ_{A1i} = VOC concentration at the soil surface, g A/km³

Equation B4 in Appendix B combines the air- and soil-side resistances into one relationship.

74. It is convenient to define the phrase "age of a sediment-soil." First, the term "sediment-soil" will be used to denote the dredged material in the CDF that is exposed directly to the air so that with time it becomes a true soil. The age of a sediment-soil is the time it has been in place in the CDF. In general, the soil near the water's edge of a CDF is younger than that at the vegetation line. This occurs mainly because of the delta-forming process in which dredged sediment may be placed within a CDF. Therefore, the variable t in Equation 26 is the age of the sediment-soil and appears in the denominator.

75. As a sediment-soil ages, the VOC emission rate decreases (see Equation 26). If a simple moving boundary evaporation plane and pore diffusion model is assumed (Thibodeaux 1979, p 337), the VOC lost from the soil surface creates a "dried-out" zone. This term is meant to denote that the VOC content of the sediment-soil has been depleted, and does not refer to moisture. The depth-time relationship for creating this dried-out zone is approximately

$$t \approx \frac{h^2 \left(\frac{\epsilon_1 H_\rho + K_d \rho_B}{H_\rho} \right)}{2D_{A3}} \quad (27)$$

where h is the depth of the zone in centimetres. Considering the aging process as described in this and the previous two paragraphs, it is obvious that a realistic quantification of the VOC emission rate from the exposed sediment locale at any particular time will require a knowledge of the age of the sediment-soil in addition to the surface area. The total emission rate is the sum of the products of flux rate and surface area for the number of age categories chosen.

Caveats of the VOC transport model

76. The basic assumptions in the above VOC transport model are that the process is rate limited by the molecular diffusion of chemical species through the open vapor pores within the soil and that the particles, with their moisture covering, are the chemical mass source, always maintaining an equilibrium concentration in the pore gas. A simple calculation with Equation 27, for Aroclor 1242 using the average solubility and vapor pressure, shows that approximately 50 years is required to create a 30-cm-deep dried-out zone if vapor phase diffusion is assumed and 50,000 years if liquid phase chemical diffusion is assumed. Some laboratory data suggest the vapor phase process is more realistic. It has been observed in the laboratory that for an 8-cm layer of Indiana Harbor sediment exposed to air, an 83-percent decrease in total Aroclor 1248 congener concentration occurred in 6 months (Palermo and Miller 1987).

77. The mechanisms that dominate the VOC emission process over the long term are likely to be as demonstrated above. Water movement due to wet/dry cycles will likely have a secondary effect on the VOC loss rate from the upper soil layers. In general, the effect will be to enhance the rate. Wet and dry cycles will cause the VOC to move upward in clay and low-permeability soils. Water evaporation at the surface and its capillary rise transport the soluble chemical upward. Here it readsorbs onto the cleaner surface soil and awaits dry-out so it can reevaporize. In sandy, low-permeability soils, downward leaching is more likely to occur.

78. Soil surface cracking will likely enhance the VOC loss rate. Cracking increases the overall sediment-soil porosity and also shortens the diffusion pathway to the surface. As a first approximation, the solid geometric shapes that make up the cracked soil surface can be modeled as vertical spines with cross section area A_c , cm^2 , and perimeter P_c , cm. Heat transfer flux expressions for such shapes have been developed (Welty, Wicks, and Wilson 1984). By use of analogy theories, these expressions can be transformed to mass-transfer flux expressions and used for estimating VOC emission rates to air. Evaluation of this and other secondary effects on the VOC emission process in the upper soil layers, such as capillary water movement, awaits vignette model development.

Summary

79. The exposed sediment locale is likely to be a significant source of VOCs from the CDF to the surrounding air. In general, the pathway is short and the surface area is extensive, so one would expect a relatively large quantitative rate. Tofflemire, Shen, and Buckley (1981) give both laboratory and field data as evidence that PCBs volatilize from exposed sediment.

Locale 3 - Ponded Sediment

80. This VOC emission locale is characterized by a water body that contains contaminated sediment in suspension and on bottom. The emissions occur through the water surface. Figure 3 illustrates the ponded sediment locale during the time dredged material is being placed into the CDF and when disposal has been completed. Each of these modes must be considered separately.

Filling phase

81. In paragraphs 60-64, a generalized model for VOC emissions from the overland flow of a rivulet was developed. This development was generalized so that it would apply to the filling phase of a CDF and reflect all the relevant transport and aspects of the particle sedimentation process that are occurring during this period. The primary model equations are Equations 15, 20, and 21. A less general model for estimating the PCB flux to the atmosphere has been developed.*

82. The significant differences in the VOC emission rates between lake and rivulet are due to the relative magnitudes of the transport coefficients, the surface area of the water body, and the volumetric flow rate. In general, both mass-transfer coefficients, k'_{A2} and k'_{A2} , will be smaller for the lake than for the rivulet. In addition, the overall particle deposition velocity, v_d , will depend on the settling characteristics of the dredged material. The removal of solids in a CDF is by either flocculent or zone settling of the dredged material slurry and is a function of many variables (Montgomery 1978; Palermo, Montgomery, and Poindexter 1978). Laboratory procedures developed by Montgomery (1978) should be used to determine settling

* D. M. DiToro and D. J. O'Connor. 1981. "Estimate of Maximum Probable PCB Flux to the Atmosphere from the Hudson River Sediment Disposal Basin," Hydro Qual, Inc., Mahwah, NJ.

velocities. The product of the length x and the width w of the surface will be larger for the lake. The volumetric flow rate for both will be comparable. For calculating the transport coefficients, the appropriate correlations that represent lake conditions should be used. In the case of unstratified water bodies, the $^3k'_{A2}$ correlation developed by Thibodeaux and Becker (1982) is recommended. For the case of a stratified water column, an overall coefficient (i.e., $^1k'_{A2}$) must be chosen that represents the three or so layers of relatively unmixed water (see Thibodeaux 1979, p 402).

83. The amount of water column turbidity generated by an open-water pipeline disposal operation or barge pumpout into a CDF can probably be minimized most effectively by using a submerged diffuser system. This system is designed to eliminate all interaction between the slurry and the upper water column by radially discharging the slurry parallel to and just above the bottom at a low velocity. Some degree of sediment entrainment in the water column will occur. The degree likely falls somewhere on a scale between the sediment resuspension due to hydraulic dredging and that due to mechanical dredging. It is also likely that a higher suspended solids concentration will occur near the air-water interface in shallow water than in deep water. From a mechanistic point of view, the chemical transport processes up the water column and the VOC emission process through the air-water interface is similar to dredging operations. The procedures outlined in paragraphs 45-47 are appropriate for estimating flux rates of submerged discharges.

Bed-sediment source

84. When the discharge of dredged material into the CDF is terminated, for a period thereafter the bed-sediment surface is the VOC source. The chemical pathway steps are:

- a. Desorption from the bed surface particles.
- b. Molecular diffusion through the benthic boundary layer.
- c. Movement up the water column to the interface.
- d. Volatilization through the air-boundary layer into the atmosphere.

85. From the steady-state mass balance, the following expression results for the VOC concentration in water:

$$\rho_{A2} = \frac{\left(\frac{\omega_A^3 k'_{A2} + {}^1K'_{A2} \rho_{A2}^* K_d}{K_d} \right)}{{}^3k'_{A2} + {}^1K'_{A2}} \quad (28)$$

Equation 15 is then used to arrive at the flux rate. If the water in the CDF is stratified, then ${}^1K'_{A2}$ must be appropriately modified as indicated in paragraph 82.

86. As the sediment bed surface ages and gradually loses its VOC content, a natural chemical leaching process occurs from the particles within the bed. The process of VOC emission is now controlled primarily by the very slow process of desorption and diffusion, in the water-filled pores, to the sediment surface. The leaching is transient at this point and behaves similarly to the vapor phase transport model presented in paragraphs 70-75. This type of transient leaching model has been developed for solid particles in bed-sediment form discharged at sea during offshore drilling for oil (Thibodeaux, Reible, and Fang 1986). Selected portions of this model along with Equation 15 will yield the VOC emission flux rate for this aging period of the ponded locale in a CDF.

87. Hwang (1987) has developed a similar transient approach for estimating air emissions for estuaries during high tide and low tide and for the exposed sediment. He also presents a steady-state emission rate equation for bed sediment. These models are based on knowing the average diffusion path length for a contaminant in sediment. This parameter can be estimated from concentration versus depth measurements. He notes that the models need to be validated.

Summary

88. The ponded sediment locale is likely to be significant VOC source only near the point where a sediment/water slurry enters. At this point the VOC concentration in solution is high and is maintained by a relatively high suspended sediment concentration in the region. As the water moves along, the particles settle, and vaporization lowers the concentration. On the discharge end of the ponded locale, the VOC emissions are likely low. As the CDF fills the ponded locale surface area diminishes, and so do the emissions from this source. Remnant water bodies containing clear water that cover aged bottom sediment are likely to be very low VOC emission locales.

89. There is both laboratory and field evidence that VOCs contained in bottom sediment are released to the air. Laboratory experiments that simulate vaporization of VOCs from bed-sediment covered with water were performed to demonstrate the release of PCBs (Tofflemire, Shen, and Buckley 1981) and two chlorinated benzenes (Karickhoff and Morris 1985). Studies with PCBs in two artificial outdoor ponds demonstrate that the same process occurs in the field (Larsson 1985). Clophen A 50, a PCB, was blended into sediment and observed both in air (20 cm above the surface) and in water for a 2-year period. The results led Larsson to conclude that contaminated sediment may act as a source of chlorinated hydrocarbons released to the environment.

Locale 4 - Vegetation-Covered Sediment

90. The fourth emission locale is that portion of the CDF that is covered with vegetation. It occupies the region that commences with the line of grasses at the edge of the exposed sediment locale and extends into that region of the CDF containing older sediment. It can be characterized in general as the region of the CDF with a vegetation cover.

91. The existence of a vegetation cover on this locale causes significant changes in the soil environment, as compared with the exposed sediment locale, which affects the VOC emission rate. The presence of vegetation usually renders the upper soil layers more porous. This and other bioturbation processes in the zone would tend to increase ϵ_1 , and ϵ , which in turn increases the effective diffusivity of the VOC in soil (see paragraph 70). With time, the natural organic matter content of the soil will slowly increase. The source of this organic matter is decayed vegetation, micro-organism remains, etc. Its presence will tend to retard the VOC transport by providing additional adsorption sites near the soil surface. The protrusion of plants into the air boundary layer increases the resistance of this chemical transport pathway. The net effect is a decrease in $^3k'_{Al}$. This reduces the water vapor and VOC transport rates directly but also reduces these rates indirectly by maintaining a cooler (i.e., lower temperature) soil surface thermal environment. A reduction in the moisture evaporation rates has a secondary effect; it maintains the soil water content high, thereby reducing ϵ_1 . As indicated in paragraph 73, this decreases the effective diffusivity of the VOC through the soil and should reduce the emission rate.

92. It appears from the above that the presence of vegetation compounds the process of modeling the VOC emission process from this locale. The net effect of the above factors is a reduction in the VOC emission rates when compared with a similar exposed sediment locale that has the same age and depth to the sediment-soil contaminated zone. Nevertheless, the models developed for the exposed sediment locale generally apply. Equation 16 applies for the air side; however, a factor to account for extent of vegetation cover in reducing the $^3k'_{A1}$ mass-transfer coefficient must be incorporated. An equation similar to Equation 26 applies on the soil side. It is likely more appropriate to restart the time (i.e., soil age) to zero and assume that a clean soil cover of depth h exists above the remaining contaminated sediment-soil. A model for the analogous problem of subsurface injection of liquid waste has been developed (Thibodeaux and Hwang 1982) and verified in the laboratory (Dupont 1986).

93. Since this locale likely has the lowest VOC emission rates, existing vignette models may be appropriate until such time that field data indicate otherwise. Theoretically, the other locales should have higher emission rates and therefore deserve closer attention.

PART IV: LABORATORY AND FIELD EXPERIMENTS

94. Theoretical models must be tested against and adjusted to both laboratory and field data prior to their acceptance and use as predictive tools. In some, if not most, cases it is necessary to perform limited laboratory and/or field experiments. For example, this will need be done in order to test the significance of a particular VOC source term, to verify some hypothesized VOC generation process, or to obtain critical adjustable parameters in the final mathematical algorithm of the model. In this regard, this part of the report is devoted to a brief review of existing laboratory and field test procedures for the technical information they can provide in support of the modeling objectives.

95. Three levels of experimental protocols are necessary to arrive at a complete understanding of VOC emission processes. Equilibrium experiments to quantify the partitioning of VOCs between sediment and air are necessary. Some protocols have been developed. The techniques developed by Spencer and coworkers (Spencer, Farmer, and Jury 1982) for quantifying the relative vapor pressures of pesticides that have been incorporated into soil are directly applicable. The above literature citation is a review article that includes the investigators' work in this area for the last 20 years. The recent works of Chiou and Shoup (1985) and of Poe, Valsaraj, and Thibodeaux (1988) are also relevant to the subject.

96. Critical laboratory experiments simulating the transport of VOCs from water surfaces and exposed sediment surfaces will be necessary. Tofflemire, Shen, and Buckley (1981) developed an apparatus and appropriate experimental procedures to measure VOC emission rates from water-covered bottom sediment. The adaptation and modification of this apparatus and procedure should lead to a more realistic laboratory simulation of the ponded sediment VOC emission locale. In the case of simulating the transport of VOCs from exposed sediment, the techniques developed by Farmer et al. (1980) are most appropriate. The device was more recently applied by Karimi (1983) to measure VOCs from contaminated soils.

97. Field measurement techniques that allow the direct quantification of VOC emission rates from the exposed sediment and ponded locales are needed. Similar techniques for measuring volatiles from surface impoundments (Thibodeaux, Parker, and Heck 1984), landfills (Eklund, Balfour, and Schmidt

1985), and land treatment facilities (Eklund, Nelson, and Wetherold 1987) have been developed and tested. The application of these apparatuses and procedures to the CDF emission locales should be direct. Emissions from the sediment relocation devices are, in effect, point sources. Techniques for quantifying emissions from such sources are available. That developed by Kolnsberg (1976) seems most appropriate for the sediment relocation operations associated with a CDF.

PART V: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

98. Much general information is available in the technical literature on the subject of volatile chemicals in water and on solids relative to contact with the gas phase. The basic theory of chemical volatilization from such sources is in place. With a few minor exceptions, this theory has been developed such that equations have been formulated to quantify the various rates. Specifically, on the subject of VOCs from CDF sources, little of the above is directly applicable.

99. This document contains an assemblage of vignette models and associated equations plus guidance for their use. The models are general so that they can be applied to any CDF; however, features of the proposed dredging and disposal operations at New Bedford Harbor were used as the specific application. Four principal VOC emission locales were identified to exist in any CDF: sediment relocation devices (dredging-associated activities), exposed sediment, ponded sediment, and vegetation-covered sediment. Although it is theoretically possible for VOCs to be emitted from each locale, it is very likely that some are more significant sources than others.

100. Emission rates, in mass of specific or total VOCs per unit time, are primarily dependent on the chemical concentration at the source, the surface area of the source, and the degree to which the dredged material is in direct contact with the air. The relative magnitude of these three parameters provides a basis upon which a tentative ranking of emission rates from the various locales can be given. On this basis, the exposed sediment locale ranks first. The ponded sediment locale with a high suspended solids concentration in surface waters ranks second. Low in the rankings is bed-sediment below a relatively quiet water column, such as exists in some ponded sediment locales. Emissions from the vegetation-covered sediment locale are also expected to be low.

Recommendations

101. The following are recommendations derived from the information generated in preparing this report. Preliminary model calculations can be made for

the locales at this time. However, some aspects are based on very crude equations, and further development is needed. The recommendations regarding model development address these specific deficiencies. The recommendations on laboratory and field testing reflect general research activities that must be performed to build a higher degree of confidence in the predictive capability of the current generation of VOC emission models.

Preliminary model calculations

102. Recommendations are to:

- a. Perform detailed model calculations for all locales with quantitative information for New Bedford Harbor sediment. Appendix B contains two such detailed calculations.
- b. Fine-tune the tentative rankings of sources by performing a sensitivity analysis of critical model input parameters using the New Bedford Harbor information.

Model development

103. Recommendations are to:

- a. Develop a vignette model and associated equations for the surface cracking/water evaporation coupled phenomena observed with much dredged material undergoing drying.
- b. Develop an appropriate VOC emission model that accommodates the cracking/evaporation model.

Laboratory testing

104. Recommendations are to:

- a. Develop laboratory test procedures to measure selected sediment/air chemical partition coefficients and related vapor pressure/adsorption parameters.
- b. Simulate the VOC emission process from exposed sediment and ponded sediment locales for selected chemicals in a pilot-scale wind tunnel apparatus.

Field tests:

105. Recommendations are to:

- a. Perform field tests at the New Bedford Harbor Superfund site to measure VOC emission rates and concentrations in air.
- b. Use these and other measured rates and concentrations in air for preliminary model verification, validation, and calibration exercises.

REFERENCES

- Bird, R. B., Stewart, W. E., and Lightfoot, E. N. 1960. Transport Phenomena, John Wiley and Sons, New York.
- Chiou, C. T., and Shoup, T. D. 1985. Environmental Science and Technology, Vol 19, p 1196.
- Delos, C. G., DePinto, J. V., Richardson, W. L., Rodgers, P. W., and Rygwelski, K. 1984. "Appendix B: Estimation and Use of Parameters in Modeling Toxics, Section 3.0, EPA Technical Guidance Manual, Book II, Streams and Rivers, Chap. 3, Toxic Substances," US Environmental Protection Agency, Washington, DC.
- Dexter, R. N., and Pavlou, S. P. 1978. "Mass Solubility and Aqueous Activity Coefficients of Stable Organic Chemicals in the Marine Environment: Polychlorinated Biphenyls," Marine Chemistry, Vol 6, pp 41-53.
- Dupont, R. R. 1986. "Evaluation of Air Emission Release Rate Model Predictions of Hazardous Organics from Land Treatment Facilities," Environmental Progress, Vol 5, No. 3, p 197.
- Eklund, B. M., Balfour, W. D., and Schmidt, C. E. 1985. "Measurement of Fugitive Volatile Chemical Emission Rates," Environmental Progress, Vol 4, No. 3, pp 199-202.
- Eklund, B. M., Nelson, T. P., and Wetherold, R. G. 1987. "Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility," EPA/600/2-87/086a, Hazardous Waste Engineering Research Laboratory, US Environmental Protection Agency, Cincinnati, OH.
- Farmer, W. J., Yang, M., Letey, J., and Spencer, W. G. 1980. "Land Disposal of Hexachlorobenzene Waste: Controlling Vapor Movement in Soil," EPA-600/12-80-11, Office of Research and Development, US Environmental Protection Agency.
- Hill, D. O., Myers, T. E., and Brannon, J. M. 1988. "Development and Application of Techniques for Predicting Leachate Quality in Confined Disposal Facilities; Part I: Background and Theory," Miscellaneous Paper D-88-1, US Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Huang, J. C., Dempsey, B. A., Chang, S. V., and Ganjidoost, H. 1987. "Effects of Solid Concentration on the Partition Coefficient of Volatile Organic Compounds with Soils," paper presented at AIChE National Meeting, Houston, TX.
- Hwang, S. T. 1987 (Nov). "Multimedia Approach to Risk Assessment for Contaminated Sediment in a Marine Environment," Proceedings, Superfund Conference, Washington, DC.
- Karickhoff, S. W., and Morris, K. R. 1985. "Impact of Tubificid Oligochaetes in Pollutant Transport in Bottom Sediment," Environmental Science and Technology, Vol 19, No. 1, pp 51-56.
- Karimi, A. A. 1983. "Studies of the Emission and Control of Volatile Organics in Hazardous Waste Landfills," Dissertation, University of Southern California, Los Angeles, CA.

- Kolnsberg, H. J. 1976. "Technical Manual for Measurement of Fugitive Emissions: Upwind/Downwind Sampling Methods for Industrial Emissions," EPA/600/2-76/089a, Industrial Environmental Research Laboratory, US Environmental Protection Agency.
- Larson, P. 1985. "Contaminated Sediments of Lakes and Oceans Act as Sources of Chlorinated Hydrocarbons for Release to Water and Atmosphere," Nature, Vol 317, No. 6035, pp 347-349.
- Linstrom, F. T., and Piver, W. T. 1985. "A Mathematical Model for the Transport and Fate of Organic Chemicals in Unsaturated/Saturated Soils," Environmental Health Perspectives, Vol 60, pp 11-18.
- Lunney, P., Springer, C., and Thibodeaux, L. J. 1985. Environmental Progress, Vol 4, No. 3, p 203.
- Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H. 1982. Handbook of Chemical Property Estimation Methods: Chemical Behavior of Organic Compounds, McGraw-Hill, New York.
- Montgomery, R. L. 1978. "Methodology for Design of Fine-Grained Dredged Material Containment Areas for Solids Retention," Technical Report D-78-56, US Army Engineer Waterways Experiment Station, Vicksburg, MS.
- NUS Corporation. 1984. "Draft Feasibility Study of Remedial Action Alternatives, Acushnet River Estuary Above Coggeshall Street Bridge, New Bedford Site, Bristol County, Massachusetts," Pittsburgh, PA.
- Otis, M. J. 1987. "Pilot Study of Dredging and Dredged Material Disposal Alternatives - Superfund Site, New Bedford Harbor, Massachusetts," US Army Engineer Division, New England, Waltham, MA.
- Palermo, M. R., and Miller, J. 1987. "Disposal Alternatives for PCB-Contaminated Sediments from Indiana Harbor, Indiana," Miscellaneous Paper EL-87-9, Vol I, US Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Palermo, M. R., Montgomery, R. L., and Poindexter, M. E. 1978. "Guidelines for Designing, Operating, and Managing Dredged Material Containment Areas," Technical Report D-78-10, US Army Engineer Waterways Experiment Station, Vicksburg, MS.
- Pavlou, S. P., and Kadeg, R. D. 1987 (Nov). "Preliminary Field Verification of the Equilibrium Partition Approach to Sediment Criteria Development," Paper No. 289, 8th Annual Meeting, Society of Environmental Toxicologists and Chemists, Pensacola, FL.
- Poe, S. H., Valsaraj, K. T., and Thibodeaux, L. J. 1988. "Equilibrium Vapor Phase Adsorption of Volatile Organic Chemicals on Dry Soils," Journal of Hazardous Materials.
- Spencer, W. F., Farmer, W. F., and Jury, W. A. 1982. "Review: Behavior of Organic Chemicals at Soil, Air, Water Interfaces as Related to Predicting the Transport and Volatilization of Organic Pollutants," Environmental Toxicology and Chemistry, Vol 1, pp 17-26.
- Springer, C., Valsaraj, K. T., and Thibodeaux, L. J. 1985. "The Use of Floating Oil Covers to Control Volatile Chemical Emissions from Surface Impoundments: Laboratory Investigations," Hazardous Waste and Hazardous Materials, Vol 2, No. 4, pp 487-501.

- Tetra Tech. 1978. "Rate Constants and Kinetic Formulations in Surface Water Quality Modeling," prepared for the US Environmental Protection Agency.
- Thibodeaux, L. J. 1979. Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil, John Wiley and Sons, New York.
- _____. 1981. "Estimating the Air Emissions of Chemicals from Hazardous Waste Landfills," Journal of Hazardous Materials, Vol 4, pp 235-244.
- Thibodeaux, L. J., and Becker, B. 1982. "Chemical Transport Rates near the Sediment in Wastewater Impoundments," Environmental Progress, Vol 1, No. 4, pp 296.
- Thibodeaux, L. J., Chang, L. K., and Lewis, D. J. 1980. "Dissolution Rates of Organic Contaminants Located at the Sediment Interface of Rivers, Streams and Tidal Zones," Contaminants and Sediments, Vol 1, R. A. Baker, ed., Ann Arbor Science Publishers, Ann Arbor, MI, p 349.
- Thibodeaux, L. J. and Hwang, S. T. 1982. "Landfarming of Petroleum Waste - Modeling the Air Emission Problem," Environmental Progress, Vol 1, No. 1, p 42.
- Thibodeaux, L. J., Parker, D. G., and Heck, H. H. 1984. "Chemical Emissions from Surface Impoundments," Environmental Progress, Vol 3, No. 2, pp 73-78.
- Thibodeaux, L. J., Reible, D. D., and Fang, C. S. 1986. "Transport of Chemical Contaminants in the Marine Environment Originating from Offshore Drilling of Bottom Sediment," Pollutants in a Multimedia Environment, Y. Cohen, ed., Plenum Press, New York, pp 49-64.
- Thibodeaux, L. J., and Scott, H. D. 1985. "Air/Soil Exchange Coefficients," Environmental Exposure from Chemicals, Vol 1, W. Brock Neely and G. E. Blau, eds., CRC Press, Inc., Boca Raton, FL, pp 65-89.
- Thomas, R. F., Mt. Pleasant, R. C., and Maslansky, S. P. 1979. "Removal and Disposal of PCB-Contaminated River Bed Materials," paper presented at the 1979 National Conference on Hazardous Material Risk Assessment, Disposal and Management, 25-27 April 1979, Miami Beach, FL.
- Tofflemire, T. J., Shen, T. T., and Buckley, E. H. 1981. "Volatilization of PCB from Sediment and Water: Experimental and Field Data," Technical Paper No. 63, PCB Workshop, Toronto, Ontario, Canada.
- Valsaraj, K. T., and Thibodeaux, L. J. 1987 (Nov). "Role of Physical Adsorption in Determining the Vapor Pressure of Volatile Organic Chemicals Above Landfills and Landfarms," Paper No. 105, 8th Annual Meeting, Society of Environmental Toxicologists and Chemists, Pensacola, FL.
- Weaver, G. 1982. "PCB Pollution in the New Bedford, Massachusetts, Area: A Status Report," Massachusetts Coastal Zone Management, Boston, MA.
- Welty, J. R., Wicks, C. E., and Wilson, R. E. 1984. Fundamentals of Momentum, Heat and Mass Transfer, John Wiley and Sons, New York, p 266.

APPENDIX A: DERIVATION OF RIVULET AND PONDED VOC EMISSION MODEL

1. The major volatile chemical transport pathways for the rivulet and ponded sublocales within a CDF are illustrated in Figure 4 of the main text. The following assumptions are involved in the model development for particle behavior:

- a. Plug flow of water and particles in the direction of flow.
- b. Unstratified and isothermal water column.
- c. Particle scour and resuspension from the sediment bed characterized by net deposition velocity.
- d. Steady-state flow process.

2. A particle mass balance on the volume element Δxhw in grams per second is

$$whv_x \rho_{32} \Big|_x - whv \rho_{32} \Big|_{x+\Delta x} - v_d \rho_{32} \Delta xw = 0 \quad (A1)$$

where the respective pathways are in by advection, out by advection, and out by deposition. Dividing by Δx and taking the limit as $\Delta x \rightarrow 0$ yields

$$\frac{d}{dx} (Q \rho_{32}) + wv_d \rho_{32} = 0 \quad (A2)$$

where $Q \equiv whv_x$. For constant flow, separation of variables and integration between $(x = 0)$ inlet solids of ρ_{32}^0 to ρ_{32} at x yields (see Equation 20, main text)

$$\rho_{32} = \rho_{32}^0 \exp \left(\frac{-v_d xw}{Q} \right) \quad (A3)$$

The result is a simple exponential decrease of suspended solids concentration from the entrance with distance down the rivulet.

3. A portion of the volatile chemical is sorbed onto particles and behaves like the particles. However, it enjoys several other transport pathways. The following additional assumptions apply:

- a. Volatilization occurs across the air-water interface from solution only.
- b. Dissolution occurs from the bottom sediment to the water column.
- c. Advection of both soluble and sorbed fractions.
- d. Bottom sediment of constant concentration.
- e. VOC equilibrium between particle and solution phase in the water column.

4. A VOC mass balance on the volume element shown in Figure 4 (main text) in grams per second is

$$\begin{aligned} & (Q\rho_{A2} + Q\rho_{32}\omega_A) \Big|_x + 3k'_{A2} \left(\frac{\omega_A - \rho_{A2}K_d}{K_d} \right) w\Delta x \\ & - (Q\rho_{A2} + Q\rho_{32}\omega_A) \Big|_{x+\Delta x} - v_d\rho_{32}\omega_A w\Delta x - k'_{A2}(\rho_{A2} - \rho_{A2}^*)w\Delta x = 0 \end{aligned} \quad (A4)$$

where the respective terms are in by particle plus solution advection, in by dissolution from the sediment bed, out by particle plus solution advection, out by net particle deposition, and out by evaporation. The limiting process is repeated and the following equation results:

$$\begin{aligned} & \frac{d}{dx}(Q\rho_{A2} + Q\rho_{32}\omega_A) + 3k'_{A2} \left(\frac{\omega_A - \rho_{A2}K_d}{K_d} \right) w \\ & - v_d\rho_{32}\omega_A w - k'_{A2}(\rho_{A2} - \rho_{A2}^*)w = 0 \end{aligned} \quad (A5)$$

Equation A5 is used to eliminate ω_A , and Equation A3 is used to eliminate ρ_{32} in Equation A5.

5. Performing the indicated differentiation yields to some simplifications. The following differential equation results:

$$\begin{aligned} & -\frac{Q}{w} \left[1 + K_d\rho_{32}^o \exp \left(\frac{-v_d x w}{Q} \right) \right] \frac{d\rho_{A2}}{dx} = \left(3k'_{A2} + k'_{A2} \right) \rho_{A2} \\ & - \left(\frac{3k'_{A2}\omega_A + k'_{A2}\rho_{A2}^*K_d}{K_d} \right) \end{aligned} \quad (A6)$$

Separation of variables and integration of ρ_{A2} from its inlet $x = 0$ value of ρ_{A2}^0 to ρ_{A2} at x yields Equation 21 (see main text).

APPENDIX B: PCB VAPORIZATION ESTIMATES FOR NEW BEDFORD HARBOR
DREDGING AND DREDGED MATERIAL DISPOSAL PILOT STUDY

1. To demonstrate the application of the theoretical models for evaluating volatile emissions to air during dredged material disposal operations, calculations were made based on the conditions of the pilot-scale confined disposal facility (CDF) alternative proposed for New Bedford Harbor (NBH). Detailed operational, physical, and chemical aspects of the site were obtained from Otis (1987).^{*} Three calculations were performed that represented possible operational stages of the pilot CDF.

2. The primary cell has a capacity to hold approximately 25,000 yd³ (19,000 m³) of slurry. The surface area of the slurry is to be approximately 250 by 250 ft (76 by 76 m), and this is the surface area of the PCB emissions. Aroclor 1242 (A-1242) and 1254 (A-1254) and total PCB are the volatile chemicals of concern. Table B1 summarizes the physicochemical properties of the Aroclors. The partition coefficients were estimated from the results reported on the Standard Elutriate Test with NBH sediment (Otis 1987) and therefore represent a desorption process. Solubility in water, pure component vapor pressure, and molecular weight are from a USEPA priority pollutant data list. Henry's constant (ℓ H₂O/ ℓ air) was computed from the ratio of pure vapor density in air (mg/ ℓ air) to solubility in water (mg/ ℓ H₂O) as in Equation 4 of the main text. The molecular diffusivities were estimated using the appropriate inverse molecular weight corrections (Thibodeaux 1979) as a first approximation. Phenol in water was used as the D_{A2} basis, and benzene in air was used as the D_{A1} basis. Table B2 contains site-specific information. The PCB and suspended solids concentrations are based on the test results reported by Otis (1987). Except for the density and porosities, which are estimates, the other data have the same source.

Emissions During Filling

3. Filling is assumed to occur by discharging the slurry into the CDF through a submerged diffuser. Due to the shallow depth of water, the suspended solids concentration reported from the Standard Elutriate Test was

* See References at the end of the main text.

used. The appropriate model for this case is that discussed for the ponded sediment locale. (See paragraphs 80-83 of the main text.) Equations 14 and 15 apply. Combining these yields:

$$n_A = l_{k'_{A2}} \left[\left(\frac{\omega_A}{K_d + \frac{1}{\rho_{32}}} \right) + \rho_{A2}^{**} \right] \quad (B1)$$

4. Since PCB emission from water is water-side resistance controlled and the fetch/depth ratio is $250/4 = 62.5$, the following correlation from Lunney, Springer, and Thibodeaux (1985) was appropriate:

$$l_{k'_{A2}} = 19.6 V_x^{2.23} \rho_{A2}^{2/3} \quad (B2)$$

5. With $V_x = 25$ mph (40 km/hr) and $A_2 = 0.45 \text{ E-05 cm}^2/\text{sec}$ for A-1242, $l_{k'_{A2}} = 7.0$ cm/hr. Assuming no PCBs exist in the air above the CDF makes $\rho_{A2}^{**} = 0$. The effective concentration in water ρ_{A2} is

$$\rho_{A2} = \left(\frac{\omega_A}{K_d + \frac{1}{\rho_{32}}} \right) \quad (B3)$$

6. For A-1242, this is

$$\rho_{A2} = \frac{0.48(432)}{1.88 \text{ E+05} + \frac{1}{490 \text{ E-06}}} = 0.00109 \text{ mg/l}$$

This is less than the solubility of A-1242 in water. Substituting the effective concentration and the transport coefficient values into Equation B1 yields

$$n_A = 7 \text{ cm/hr } (0.00109 - 0 \text{ mg/l}) \frac{1}{1,000 \text{ cm}^3} = 7.63 \text{ E-06 mg/cm}^2 \cdot \text{hr}$$

For $A = 5.8 \text{ E-07 cm}^2$, this gives the emission rate of

$$W_A = n_A A = 443 \text{ mg/hr}$$

7. The calculation for A-1254 is 311 mg/hr for a total PCB rate of 754 mg/hr.

Exposed Sediment

8. Once the CDF is filled and the water removed, the solid dredged material will be exposed directly to the atmosphere. The section of the main report on the exposed sediment locale applies (specifically, paragraphs 70-75). Early in the process, the air-side resistance dominates. Later, the soil-side processes dominate. Using the resistance-in-series concept yields

$$n_A = \frac{\left(\frac{\omega_A H \rho}{K_d} - \rho_{A1} \right)}{\left\{ \left[\frac{\pi t}{D_{A3} \left(\frac{\epsilon_1 H \rho + K_d \rho_B}{H \rho} \right)} \right]^{1/2} + \frac{1}{3 k'_{A1}} \right\}} \quad (\text{B4})$$

Equation 26 of the main text, the soil-side vaporization equation, is a part of Equation B4. Time appears explicitly and accounts for the transient nature of the evaporation process. Not included in this equation are enhancements due to water evaporation and soil surface cracking. Both are likely to increase the rate significantly.

9. The effective concentration of A-1242 in the soil pore air (ρ_{A1}^*) is

$$\rho_{A1}^* = \frac{\omega_A H \rho}{K_d} = 0.48 \times 432 \text{ mg/kg} \left| \frac{0.0249 \text{ l H}_2\text{O}}{\text{l air}} \right| \frac{\text{kg}}{188,000 \text{ l H}_2\text{O}} = 2.75 \text{ E-05 mg/l}$$

This is less than the pure vapor density of A-1242, which is ($\rho_{A1}^* = p_A^0 M_A / RT$) 0.058 mg/l air (see paragraph 21 of main text). As in the previous calculation, $\rho_{A1} = 0$. The group of terms $\epsilon_1 + K_d \rho_B / H \rho$ is 9.06 E+06. From the relationship in paragraph 71:

$$D_{A3} = \frac{D_{A1} \epsilon_1^{10/3}}{\epsilon^2} = \frac{0.036(0.3)^{10/3}}{(0.7)^2} = 0.00133 \text{ cm}^2/\text{sec}$$

10. For the air-side mass-transfer coefficient, the equation recommended by Thibodeaux and Scott (1985) is used

$$^3k'_{A1} = 0.036 R_e^{4/5} S_c^{1/3} D_{A1} \quad (B5)$$

where $R_e = V_\infty / \nu_1$, $S_c = \nu_1 / D_{A1}$, and $L = \text{fetch}$. For 25-mph (40-km/hr) wind (V_∞) and 250-ft (76-m) fetch, R_e (dimensionless number) = 5.68 E-07 and $S_c = 4.17$ for $\nu_1 = 0.15 \text{ cm}^2/\text{sec}$. This yields, from Equation A5,

$$^3k'_{A1} = 0.036(5.68 \text{ E-}07)^{4/5}(4.17)^{1/3}(0.036 \text{ cm}^2/\text{sec})/(7,620 \text{ cm})3,600 \text{ sec/hr}$$

and

$$^3k'_{A1} = 1,580 \text{ cm/hr}$$

11. Substituting into Equation B4 yields

$$n_A = \frac{(2.75 \text{ E-}08 \text{ mg/cm}^3 - 0)}{(0.00132\sqrt{t} + 1/1,580)} \text{ in mg/cm}^2 \cdot \text{hr}$$

and

$$W_A = \frac{2,520}{(2.08\sqrt{t} + 1)} \text{ in mg/hr, with } t \text{ in days}$$

where $W_A = n_A A$ as before. Table B3 contains the calculated A-1242 emission rates at selected days during the first 2 years for the uncapped, exposed sediment operation of the pilot CDF. The calculation is repeated using the A-1254 properties in Table B1. The final flux equation is $W_A = 2,357 / (1.08\sqrt{t} + 1)$, mg/hr with t in days. Calculated results appear in Table B3. The total emission rate is the sum of the individual Aroclors rounded to three significant figures.

12. If the average emission rate for the first 2 years is 1,000 g/hr, then 0.9 percent of the PCBs in the 5,000 yd³ (3,820 m³) of dredged material placed in the CDF evaporates. Capping with clean (i.e, nearly PCB-free) sediment will reduce the emissions.

Capped PCB-Contaminated Dredged Material

13. The emission rate theory for this particular case was not considered in the body of the report. If a 6.5-in. (16.5-cm) cap consisting of similar material is placed over the contaminated sediment, the models used for steady-state emission from soil-covered landfills apply (Thibodeaux 1981). The same basic theory applies; however, the pure component vapor density, used in landfill flux calculations, is replaced with $\omega_A H_p / K_d$. The appropriate flux equation is

$$n_A = \frac{D_{A3}}{h} \left(\frac{\omega_A H_p}{K_d} - \rho_{A1} \right) \quad (B6)$$

where h is the cap thickness. As before, $\rho_{A1} = 0$. For A-1242, the calculations are

$$n_A = \frac{0.00133 \text{ cm}^2}{\text{sec}} \left| \frac{1}{16.5 \text{ cm}} \left[2.75 \text{ E-05} - 0 \text{ mg/l} \right] \frac{1}{1,000 \text{ cm}^3} \right| \frac{3,600 \text{ sec}}{\text{hr}} = 8.0 \text{ E-09 mg/cm}^2 \cdot \text{hr}$$

and $W_A = 0.46 \text{ mg/hr}$. For A-1254, $W_A = 0.44 \text{ mg/hr}$. The total PCB flux is 0.9 mg/hr. As time progresses, if the cap does not crack but retains its original seal, the rate will fall with the inverse of $\sqrt{t}$ just as with the exposed sediment case.

Summary

14. The preceding set of calculations are illustrative examples of how emission estimates can be performed. To the degree possible, parameterization of conditions for the proposed New Bedford Harbor pilot study dredging operation was used. Except for the exposed sediment case, the numerical values

represent initial emission rates and are only approximate. This fact reflects the relative crude state-of-knowledge of the sediment-bound volatile chemical desorption/evaporation process. However, the relative ratios of the predicted rates for each case are likely realistic. The exposed sediment rate is ~5,000 mg/hr, ponded sediment is ~800 mg/hr, and capped sediment is 1 mg/hr. These are relative ratios with the capped case as the base. Obviously, capping will be effective control methodology. Reducing the suspended solids level in the CDF during filling will reduce the emission rate during this period of operation.

Table B1
Aroclor Physicochemical Properties at 25° C

Aroclor	K_d l/kg	H_o l/l	Solubility ppm	Vapor. Pressure mm Hg	Mol. Weight g/mol	D_{A2} cm ² /sec	D_{A1} cm ² /sec
1242	188,000	0.0249	0.24	4.06 E-04	267	0.45 E-05	0.036
1254	304,000	0.0337	0.030	7.71 E-05	238	0.48 E-05	0.038

Table B2
NBH Site-Specific Information and Data

Total PCB concentration in bed sediment: 432 mg/kg
Aroclor ratios: 48% (wt) (A-1242) and 52% (A-1254)
CDF suspended solids concentration: 490 ppm
Temperature 25° C; wind 25 mph (40 km/hr)
Dredged material: air porosity (ϵ_1 =) 0.3, total porosity (ϵ =) 0.7, and bulk density (ρ_B =) 1.2 kg/l
Water: depth 4 ft (1.2 m), surface area 250 by 250 ft (76 by 76 m)

Table B3
PCB Emission Rates from Exposed Sediment Versus Time

Time days	Aroclor 1242 mg/hr	Aroclor 1254 mg/hr	Total mg/hr
0	2,520	2,360	4,880
0.25	1,240	1,530	2,770
0.5	1,020	1,340	2,360
1	818	1,130	1,948
3	548	820	1,368
10	333	534	867
100	116	200	316
730	44	78	122