

VOLATILIZATION RATES FROM DREDGED MATERIAL AND SOILS  
- A LITERATURE REVIEW

With Application to Indiana Harbor and Canal

by

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## EXECUTIVE SUMMARY

One means of storing or disposing of contaminated sediment extracted from water bodies is to place the dredged material onshore. Such repositories designed to receive this material are termed confined disposal facilities (CDFs). Typically they are constructed of earthen material and occupy large areas hundreds of acres in size. During the filling of these diked enclosures the top surface of the dredged material mass is exposed to the atmosphere. This direct contact with air encourages the loss of volatile and semi-volatile chemicals from the upper surface layers. This report was the result of a study of published literature on the subject of data and theoretical models that address the evaporative losses of these chemicals. The focus is on gathering the best available information in order to provide a basis of making quantitative projections of evaporative fluxes to air for estimating human exposures to these chemicals. Although the data and models are generally applicable, to any CDF of similar design, the flux projections are specific to the Indiana Harbor Canal (IHC) sediment and its chemical characteristics.

A literature search was conducted for information concerning the theory, models and data on the general subject of chemical volatilization from soils, soil-like solid materials, and sediment-derived dredged material surfaces. In addition to dredged materials, the search focused on pesticide vaporization from agricultural soils and hazardous substances vaporized from “land farming” and land filling treatment and disposal operations. In principle all involve the same basic chemodynamic processes which govern the behavior of chemicals in similar porous media.

Chemodynamics process models are in an advance state of development with regard to chemical desorption, transport in porous media, and movement across the air-soil interface. Models are capable of quantifying many second generation processes, such as loosely and tightly bound fractions, humidity/moisture desorption enhancements, and air thermal stability in the atmospheric boundary layer (ABL) that are supported by theoretical arguments and observations. Two deterministic chemical release and transport models have been developed independently starting in the 1970s. The Jury et al model was developed based on forecasting pesticide evaporation from applications to agricultural soils. The Thibodeaux et al model evolved simultaneously and was initially focused on forecasting the volatilization of hazardous substances from solid waste. Both efforts are founded on well established physical chemical principles quantifying processes through the use of the Lavoisier’s species mass balance on the soil column. Although the final algorithms are slightly different, the model foundations and results are nearly identical; both have undergone significant and repeated peer review and testing by other investigators. Without sacrificing accuracy the Thibodeaux et al model is algebraically simpler and allows easy incorporation of additional transport resistances. Its use is recommended for the IHC CDF application. A single statistics-based volatilization model was found; the model of Woodrow et al obtained by correlating fifteen measured chemical fluxes to air with four independent variables reflecting species characteristics of the soil source was shown to be consistent with the theory-based model of Thibodeaux et al.

Chemical specific flux data to air was located for 21 of the 24 volatile compounds identified as substances of concern in the proposed IHC CDF. A total of 232 flux values were located representing laboratory measurements, pilot-scale simulations, and field data. The data from these

measurements was summarized by using the six chemical categories: polyaromatic hydrocarbons; pesticides; the benzene, toluene, xylene(BTX) group; metals; polychlorinated biphenyls (PCBs); and the dioxin/furans. The report contains a discussion of the measurements found in each category, the experimental techniques employed, and focuses on the quality of the measurements and applicability to the IHC CDF situation. Summary flux tables representing each of the six chemical categories are presented in the body of the report.

The third section of the report addresses the application of the Thibodeaux et al model to the IHC CDF. Algorithms reflecting instantaneous and time-average volatile fluxes are presented so as to project emissions throughout the approximate thirty year lifetime of the CDF. Graphical line projections are presented of the model flux estimates based on the thermodynamic and transport parameters specific to the average chemical composition expected in the dredged material. Appropriate times for use in assigning average flux estimates needed for risk assessments are shown on the graphs as well. Only four graphs appear in the body of the report; they are for benzo(a)pyrene, dieldrin, Aroclor 1248, and benzene. The others appear in the appendix. Superimposed on the graphical model flux projections are the reported flux measurements. These graphs are to be used by the reader so as to appreciate the ranges of the numerical variations of the fluxes, model vs. data, that results between chemical types. The reader should not use the information presented on each chemical to make judgments about model vs. data congruence. The model projections reflect conditions of the IHC CDF; the data, although based on average dredged material concentrations, reflect soils of different organic matter content and other characteristics, different air or gas velocities, and temperatures in the experimental apparatus, differing vessel shapes, operations protocols, differing chemical analytical protocols, etc. Modeling each set of flux measurements was not within the scope of this project plus it was impossible to normalize all these variations to the IHC CDF projected conditions. Never-the-less viewed in a scaling context based on chemical species, the trend of model vs. data give a generally congruent behavior pattern. Those for dieldrin, naphthalene, phenanthrene, toluene, the xylenes, and dibenzo-furans are in notable agreement. Not surprisingly, flux measurements reflect the early period (i.e., days only) of the evaporative lifetime of these chemical/soil mixtures.

In summary, it appears that much knowledge is available about the process of volatile chemical emissions from soils. The basic processes are well understood and models are available that can mimic the observed behavior. The quantity of measured data is relatively rich for short-term fluxes in laboratory scale equipment, but there is less for the field and for the long-term. Despite these shortcomings, the proposed modeling algorithm may be used with confidence to make realistic time-averaged flux predictions. Averages must be used since real time predictions for a system as complex as the surface of the proposed IHC CDF are beyond the knowledge base of the science at this time. In light of the processes that are known to attenuate the chemical flux such as a snow cover, and slow chemical desorption of the tightly bound fraction etc., the selection of average model input parameters will generally result in conservatively high emission predictions. Whereas, a selection of alternative input parameters can result in even higher chemical fluxes.

## INTRODUCTION

### GENERAL

The U. S. Army Corps of Engineers, Chicago District (Corps) plans to dredge the federal channel in the Indiana Harbor Canal(IHC) starting in 2005. Due to past industrial activities within the watershed, the sediments in the canal are considered unsuitable for open water disposal. The Corps plans to construct a confined disposal facility(CDF) on a former petroleum refinery site owned by Energy Cooperative, Inc. (ECI).

As part of the Environmental Impact Statement (EIS) for the proposed IHC dredging activities, the U. S. Environmental Protection Agency, Region V(USEPA), performed an inhalation risk assessment (USACE 1999) associated with the CDF. It involved comparing particulate and volatile toxic loadings to the atmospheric boundary layer (ABL) and assessing human health risk posed by inhalation of these airborne contaminants. The Corp and USEPA are considering additional risk analysis work. To this end research is needed to incorporate new data and project design information into the risk analysis. One key aspect of this activity is to determine the most scientifically valid chemical volatilization rates from the proposed CDF.

### REPORT AUTHORITY AND SCOPE

This report summarizes the results of a research effort proposed under the U.S. Army Engineer Waterways Experiment Station Broad Agency Announcement(BAA) in the program on Sediment Water Interactions. Contract for the service (No. DACW42-01-P-0165) was awarded to Louisiana State University March 15, 2001. The scope of the project was to perform all work necessary for research and development efforts to conduct a critical literature review of volatilization rates for selected volatile, semi-volatile and metals.

## DESCRIPTION

### INDIANA HARBOR CANAL

The IHC is located in East Chicago, Lake County, Indiana. It is on the southwest shore of Lake Michigan approximately four miles east of the Indiana-Illinois State line and seventeen miles south of downtown Chicago. The Harbor has an entrance channel and outer harbor protected by breakwaters, and an inner harbor. The inner harbor consists of the IHC and its two branches. The main channel extends inward from a railway bridge to the Forks, a distance of 7,400 ft (2.3 Km). From here the Lake George Branch extends west for a distance of 6,800 ft (2.1 Km) and the Calumet River Branch extends south for about two miles (3.2 Km). Dredging to maintain adequate depth has not been conducted in this harbor since 1972 due to the lack of an approved economically feasible and environmental acceptable disposal facility for the dredged material.

## SEDIMENT AND CONTAMINATION

There are three major sources which account for the sediment entering the IHC and Grand Calumet River. They are municipal and industrial discharges, combined sewer overflows, and urban runoff which contribute an estimated 152,000 CY (116,000 m<sup>3</sup>) of sediment each year. Most of the system hydraulics has reached a steady state condition, meaning there is a balance of sediment deposition and scour/transport. The result of this condition is a loading of 100,000 (76,500) to 200,000 CY (153,000 m<sup>3</sup>) of sediment to Lake Michigan from the mouth of the Indiana Harbor each year.

The USEPA Great Lakes National Program Office (GLNOP) under the Assessment and Remediation of Contaminated Sediments (ARCS) Programs conducted two sediment sampling surveys of the IHC. Survey 1 was performed in August 1989 and consisted of grab samples taken at seven Master Stations and Survey 2, sampled in November 1990, consisted of core samples taken at 37 locations. A summary and analysis report of the data from the two sampling surveys has been issued (USEPA, 1996). Not surprising, the analytical chemistry portion of the study revealed the sediment of IHC contained the usual suspects of both metals and organics typically found in these types of contaminated aquatic environments. Table 1 contains a listing of those substances of concern in this project and their concentrations. The results of sediment testings on the potential for contaminants to cause adverse impacts to aquatic life or to users of the IHC systems were reported as well. Metals that exceeded some or all of the benchmark criteria or guidelines used to examine the sediment included: arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, silver and zinc. The organics with unusual exceedences of criteria and guidelines included: total PCB's, the PAH's anthracene and phenanthrene, flourene and flouranthene.

## THE ECI SITE CONFINED DISPOSAL FACILITY

The dredged material formed from the above, described contaminated sediment in IHC will be placed in a nearby CDF. The CDF site consist of about 164 acres (68.0 ha) of land formerly occupied by an oil refinery owned by Atlantic Richfield Company and subsequently by ECI which went bankrupt in 1981. The plan view of the CDF is shown in Figure 1. It will consist of three cells as indicated in the figure. The total area occupied by the cells will be approximately 131 acres (53 ha) after the railroad tracks are removed. As shown in the figure the west cell in the southern portion of the site would be divided to create and isolated sub cell for the disposal of TSCA level PCB contaminated sediments.

Dredging would be performed using a closed bucket mechanical dredge. The dredged material would be loaded onto barges or scows which would then be moved to the disposal area. Next, the dredged material would be loaded into trucks at the CDF rehandling area (Figure 1). The trucks would then transport the dredged material to the CDF by the use of haul roads placed around the site and on top of the dikes. Alternate methods of transport, such as the use of a conveyor system or pumping through pipes, may be considered at a later date.

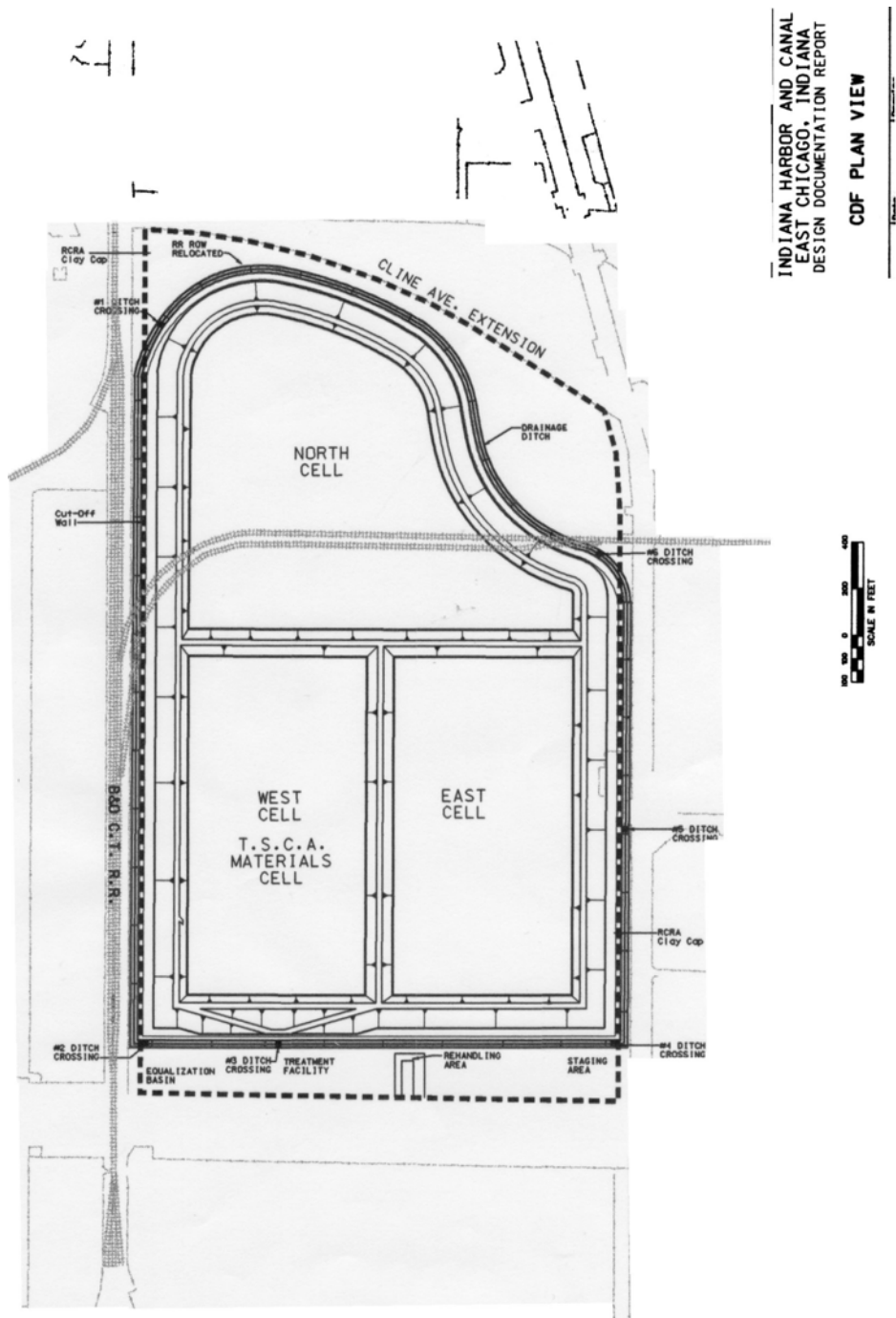


Figure 1. Schematic plan of the Indiana Harbor Canal CDF

Table 1 Selected Chemical Concentrations in IHC Sediments

| Chemical(unit)                     | Median         | Maximum        |
|------------------------------------|----------------|----------------|
| Arsenic(ug/g)                      | 56             | 93             |
| Mercury(ug/g)                      | 1.77           | 2.06           |
| Zinc(ug/g)                         | 3540           | 10,000         |
| Benzene (ug/g)                     | 7.2            | 28             |
| Toluene (ug/g)                     | 8.4            | 55             |
| Ethyl benzene (ug/g)               | 1.3            | 3.4            |
| Xylenes total (ug/g)               | 15             | 77             |
| Anthracene(ng/g)                   | 3450           | 300,000        |
| Benz(a)anthracene(ng/g)            | 11,650         | 39,000         |
| Benzo(a) pyrene(ng/g)              | 15,500         | 41,000         |
| Benzo(k) flouranthene(ug/g)        | 131            | 230            |
| 2-Methylnaphthalene(ng/g)          | 2,600          | 42,000         |
| Naphthalene(ng/g)                  | 6,200          | 24,000         |
| Phenanthrene(ng/g)                 | 11,400         | 270,000        |
| Pyrene(ng/g)                       | 27,000         | 55,000         |
| Total PCBs (ng/g)                  | 12,000         | 43,000         |
| Aroclor 1248(ng/g)                 | - <sup>^</sup> | - <sup>^</sup> |
| Aroclor 1254(ng/g)                 | 2100           | 3400           |
| Dibenzofuran(pg/g)                 | 2,300          | 53,000         |
| 2378tetrachlorodibenzofuran(pg/g)  | 310            | 740            |
| 2378tetrachlorodibenzodioxin(pg/g) | <110           | 130            |
| Chlordane(ng/g)                    | 86             | 170            |
| 4,4DDT(ng/g)                       | 79             | 100            |
| Dieldrin(ng/g)                     | 280            | 343            |
| Heptachlor(ng/g)                   | 200            | 320            |

Source (USEPA. 1996) \*ug= micrograms, ng= nanograms and pg= picograms.

<sup>^</sup> US ACE (1997) document provides a value of 4.1 mg/Kg.

Table 2. Estimated Dredged Material Quantities by Channel Reach (1000CY)

| No.           | Channel Reach<br>Description                  | Years         |               | Total        |
|---------------|---|---------------|---------------|--------------|
|               |   | 2005-<br>2015 | 2016-<br>2035 |              |
| 1             | Outer Harbor Approach Channel                 | 49            | 370           | 419          |
| 2             | Outer Harbor Approach Channel                 | 377           | 387           | 764          |
| 3             | Anchorage & Maneuver Basin                    | 102           | 223           | 325          |
| 4             | Anchorage & Maneuver Basin                    | 505           | 380           | 885          |
| 5             | Canal Entrance Channel                        | 9             | 149           | 158          |
| 6             | Inner Harbor Channel                          | 0             | 16            | 16           |
| 7             | Inner Harbor Channel                          | 5             | 22            | 27           |
| 8             | Inner Harbor Channel                          | 117           | 111           | 228          |
| 9             | Inner Harbor Channel                          | 115           | 82            | 197          |
| 10            | Lake George Branch                            | 10            | 20            | 30           |
| 11            | Lake George Branch                            | 46            | 47            | 93           |
| 12            | Lake George Branch                            | 74            | 35            | 109          |
| 13            | Calumet River Branch, Lower Reach             | 180           | 42            | 222          |
| R03           | Inland Steel Hooper & Stone Docks             | 57            | 117           | 174          |
| R04           | Inland Steel Dock No.4 & Adjacent<br>Dockface | 417           | 105           | 522          |
| R05           | Inland Steel Dock No. 2                       | 11            | 15            | 26           |
| L05           | LTV Steel Ore Dock                            | 26            | 24            | 50           |
| R06           | Inland Steel Consent Decree Dockface          | 7             | 3             | 10           |
| L06           | PCB Hot Spot                                  | 14            | 5             | 19           |
| R07           | Inland Steel Dock No.3                        | 8             | 7             | 15           |
| R08           | Inland Steel Consent Decree Dockface          | 139           | 20            | 159          |
| L11           | Amoco Oil Company Dock                        | 5             | 2             | 7            |
| U13           | Calumet River Branch, PCB Hot Spot            | 172           | 48            | 220          |
| <b>Totals</b> |   | <b>2,445</b>  | <b>2,230</b>  | <b>4,675</b> |

Source Appendix Q of (USACE 1999).

Dredged material would be placed in the CDF in lifts of approximately 3 feet. Such limited lifts would promote greater efficiency of the natural drying processes and greatly enhance the potential gains in CDF capacity. To allow for natural drying, not more than one 3-foot lift would be placed on top of the previous lift in each cell. Lifts would continue to be placed until 3 to 4 feet of freeboard remained, at which time the containment dikes would be raised. An estimate of anticipated dredging requirements for the thirty year period of operation is given in Table 2.

Each cell would be graded towards a dewatering sump to avoid ponding of water. Placement would begin at the high end of each cell and continue towards the sump. The first placement of dredging material is expected to be “windrowed” on the bottom of the CDF. Windrows are long parallel piles with space in between for vehicle access. Dump trucks would drive into the CDF and place the dredge materials on the bottom in rows 3 to 4 feet high. Subsequent lifts would be windrowed if possible or dumped from the edge and then mechanically distributed.

During the first year of CDF construction, the southwest cell dikes would be completed. In the second year, the dredged material would be placed in the southwest cell while the dikes were being constructed in the southeast and north cells. Dredged materials would be placed in the southeast and north cells during the third year, while the existing dredged material in the southwest cell was managed in order to promote drying and consolidation. Placement of the dredged material would then be alternated between the southwest cell one year and the southeast and north cells the following year over the next 7 years. No dredging would be undertaken in the following year. Dredging and disposal would be subsequently completed on a 4-year cycle until the three cells were filled to capacity, which would occur about year 2035, and then capped with clay. This cycle would consist of rotating the disposal on an annual basis between the three cells followed by 1 year of no dredging in the fourth year. The cell set aside for the TSCA materials would be constructed prior to the year 2010, and filled with PCB contaminated dredged materials from Reaches 6 and 13.

## PROBLEMS AND ISSUES

### ENVIRONMENTAL IMPACT STATEMENT OBJECTIVES

As part of the Environmental Impact Statement (EIS) for the proposed Indiana Harbor Canal dredging activities, the U.S. Environmental Protection Agency, Region V (USEPA), performed an inhalation risk analysis. The objectives of this study were: 1) to compare the proposed CDF particulate and volatile toxic loadings to those reported in the Toxic Release Inventory; 2) to compare the expected particulate and volatile loadings from the CDF to the expected loadings from the site without the CDF; and 3) to assess the human health risks posed by the inhalation of potential airborne contaminants released from the CDF. Compounds which were considered in the risk analysis are compounds which are present in the Indiana Harbor Canal sediment, and for which health effects information exists. The compounds were: acenaphthylene, acenaphthene, arsenic, benzene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chromium(VI), chrysene, dibenzo(a,h)anthracene, ethylbenzene, fluorene, fluoranthene, naphthalene, phenanthrene, polychlorinated biphenyls (Arochlor 1248), toluene and xylene (all isomers).

## ADDITIONAL RISK ANALYSIS AND TASKS

At this time, the Corps and USEPA are considering additional risk analysis work, to incorporate new data and project design information into a risk analysis. A critical literature review of volatilization rates for the compounds listed above would give a basis for determining the most scientifically valid volatilization rates. In addition, volatilization rates for mercury, anthracene, 2-methylnaphthalene, pyrene, <sub>m</sub>chlordane, dieldrin, total DDT, heptachlor epoxide, dioxins, and furans should be added. Lead and zinc are a possible concern due to air particulate transport but are not considered volatile. These substances represent all of the compounds of concern that have been measured in the sediment at Indiana Harbor. This information could then be evaluated and incorporated into any future risk analysis work, as appropriate. The specific task performed included the following:

- 1) Conduct a review of sediment quality data from Indiana Harbor, as a basis for a literature review,
- 2) Conduct a thorough search of data, reported rates, and modeling of volatilization from sediments and soils reported in the scientific and technical literature, for the compounds listed above,
- 3) Provide a critical review of the information, to evaluate the literature volatilization rate(s) for application to conditions similar to the proposed Indiana Harbor Canal Confined Disposal Facility,
- 4) Write a final report which summarizes the information from the literature review, and which recommends the most valid volatilization rate(s) to use in a risk assessment, based on the critical review of information found in the literature,

## LITERATURE REVIEW

A literature search was conducted for information concerning theory, models and data on the general subject of chemical vaporization from soil or sediment surfaces. Based on the design and operating conditions projected for the IHC CDF, the search was restricted to chemicals originating from a porous solid medium. These included natural soil surfaces, such as encountered in agricultural plots where pesticides are applied to the surface, modified soil surfaces used in the "land farming" or land treatment of oily waste, and CDF soils made of sediment material dredged from water bodies. Typically this solid surface material may contain much moisture and water in the pore spaces of the solid mass, however literature that represented processes of vaporization from aqueous solutions or those containing suspensions of soil or sediment were not considered. Pondered areas formed in the CDF during rain storms are projected to cover limited surface areas and to be transient and short lived so that evaporative losses will be negligible compared to the exposed solid surfaces. However, the wetting-drying cycles known to enhance vaporization from solid surfaces was reviewed thoroughly. The search revealed an array of theoretical models and data. The first section to follow contains the findings concerned with the theory of chemical vaporization from soil surfaces and models based on this theory. Numerous reported rates of evaporation for the chemicals of interest in this study were located as well. The second section contains a tabulation of this data by chemical species. The final section is a critical evaluation of the theoretical models and data for application to the chemical volatilization problem at a CDF such as proposed for the IHC dredged material.

## THEORY AND PROCESS MODELS FOR CHEMICAL VAPORIZATION FROM SOIL-LIKE SURFACES

Drying commonly refers to the removal of a relatively small amounts of a liquid from a solid, the liquid most frequently being water. Because of the relatively great importance of the practice of air drying, i.e., vaporization of the water into air or other carrier gases, the theoretical mechanism were discovered and quantified beginning in the 1920's (Perry, 1941). It was found that during the initial stages of the drying process of a very wet solid that the evaporation rate was constant and not a function of the changing water content of the solid. However, at some definite lower water content the rate of drying begins to decrease and the process from there to the dry product is called the falling rate period. The water content separating the constant and falling rate periods is termed the critical water content. The final water content of the dried solid depends entirely on the relative humidity of the air and is termed the equilibrium water content. This historical description of the drying process is very relevant to chemical vaporization from soil surfaces. Essentially the same mechanisms apply to chemicals on and in soil-like media. In addition the water evaporation process influences the chemical vaporization process.

The most important variable driving the release of chemicals including water is its partial pressure either at the soil surface or within the gas filled pore spaces of the solid media. Depending on the contaminant and its availability on the soil surface, the partial pressure must be greater than that in the overlying air mass for evaporation to occur. In the absence of appreciable mass transfer due to water movement, pesticide chemists found that the diffusion processes within the soil accounts for the movement of pesticides to the soil surface to replace that lost by vaporization and that a pesticide concentration gradient across an assumed non-moving air layer may also influence the rate (Mayer et al. 1974). The air-side process was assumed to be controlled by a thin layer of stagnant air. Its numerical value was used as a calibration parameter in the model developed for testing laboratory experiments. Provisions for estimating its value under field conditions were not given. Dieldrin and lindane evaporative behavior with time was well captured by the process model; it used an apparent diffusion coefficient in the soil coupled with diffusion through a thin air layer on the soil surface.

In a series of papers this group of workers at Riverside California established that although the pesticides may exist sorbed to soil solids primarily and in solution with the pore water and in the soil pore gas phase as well it was the gas-phase molecular diffusion process that delivered quantities to the surface that were eventually vaporized (Jury et al., 1980; Jury et al., 1983; Jury et al., 1984(a); Jury et al., 1984(b); Jury et al., 1984(c)). Although initiated by Mayer, the model is now known as Jury et al. and has been validated and used by others. Lindhardt et al. (1996) studied the volatilization of aromatic hydrocarbons from coal tar contaminated surface soils using a form of the Jury et al. model. Used without the air-side boundary layer resistance term the model could not capture the volatilization flux of phenanthrene with time but performed well with o-xylene, naphthalene, and 1-methylnaphthalene. Eduljee (1987) modeled the volatilization of 2,3,7,8-tetrachlorodibenzodioxin and Aroclors 1242, 1254 and 1260 from soil using the Jury et al. model and found that the trends observed were in qualitative agreement with field and laboratory studies.

Cohen et al. (1988) developed a diffusion based volatilization model that includes additional transport processes. It includes non-isothermal conditions and the effect of natural convection

within the soil. Important conclusions were that natural convection is not an important process and that "... a simple linear isothermal diffusion model may be adequate for describing chemical concentration profiles at times that are sufficiently long past the initial soil contamination event".

Chemical vaporization modeling was occurring simultaneously and independent to the above described pesticide studies and aimed at quantifying the flux of volatile liquids spilled on soils related to hazardous waste material placed on and in the soil surface. Chemical evaporation and diffusion within pore spaces was modeled by Thibodeaux (1979) employing a moving dried-out zone in the upper soil layer. This model yielded a surface evaporation flux equation which was subsequently validated with two sets of data with dieldrin (Thibodeaux and Hwang, 1982). In addition, its other quantitative attributes were verified with measured emission kinetic data on petroleum hydrocarbon. This model became known as the Thibodeaux-Hwang air emission release rate (AERR) model and underwent further testing. Dupont (1986) performed an extensive evaluation of the AERR model on benzene, toluene, the xylenes and naphthalene. Using measured vs model fluxes they concluded that it "consistently overestimated flux rates for the pure constituents by only a factor of 2 to 10, and consequently appears quite effective for the estimation of volatile organic emissions from complex waste/soil systems". For the types of volatile compounds studied in oily waste and liquid spills, the air-side resistance contribution can be neglected. Due to the low level of adsorption on soil solids these chemicals are gone from the surface very quickly (i.e. within minutes) and the soil side processes become dominant to the emission release process. The model equations and theoretical concepts are well established for the evaporation process of chemicals resting directly on the surface of soils as well.

Mass-transfer processes in the atmospheric boundary layer (ABL) have been studied extensively and algorithms are available for estimating the air-side mass-transfer coefficient under both forced (i.e., wind) and natural convection (i.e., no wind) conditions. (Thibodeaux, 1979; Thibodeaux and Scott, 1985). Effective air-side coefficients for dieldrin, Heptachlor and DDT extracted from flux measurements in the lab and in the field were shown to be a function of the wind velocity and fetch. Pilot scale experiments using acetaldehyde, acetone, isopropanol and methanol evaporating from flat surfaces were used to develop algorithms in the absence of wind (Hedden et al., 1990). Appropriate equations that include these key variables are given for use in estimating the air-side mass-transfer coefficient in the ABL above soil surfaces.

A recent literature review performed by Cousins et al. (1999) covers the volatilization of semi-volatile chemicals from soil. It contains much of the information covered in the previous paragraphs. In addition it reviews the influence of various factors on the volatilization process ; these include the co-evaporation of water, soil air-filled porosity, molecular diffusivities in air and water filled pore spaces, physical-chemical properties, temperature, wind speed, humidity, soil properties, and vegetation cover. Basically, the Cousins et al. review supports ours in that two independent theory-based deterministic models exist to quantify emissions to air. The models developed by Jury et.al. for the semi-volatile chemicals and that by Thibodeaux-Hwang et al. for both the volatile and semi-volatile are complimentary. Besides having the correct theoretical approaches they have undergone rigorous testing primarily in the laboratory. Both models have undergone additional commissioned reviews and are being recommended for use in regulatory guidance aimed at estimating emission from soil-like surfaces to air (U.S. EPA, 1988; U.S. EPA,

1992; U.S. EPA, 1987).

## SUMMARY

The Jury et al. model consists of a classical solution of Ficks second law for chemical transport in the soil column. At the soil surface the air-side resistance to transport is quantified by specifying a thin layer thickness for molecular diffusion. So structured as a flux it provides a concentration gradient boundary condition for the analytical solution. A closed form analytical solution results. The flux expression contains the key parameter: chemical concentration on soil, soil water content, soil porosity, solute convection velocity in soil, molecular diffusivity in both air and liquid water, an air-side boundary layer thickness, and a finite depth of soil below the surface containing the chemical mass. Emission time is the independent variable and the flux to air is the dependent variable. The close-form solution is given as equation 25 in Jury et al. (1983).

The Thibodeaux-Hwang model is also based on Ficks second law for chemical transport in the soil column. The depth of the contaminated sediment column is assumed to be infinite. The air-side resistance is quantified by accepted and published mass-transfer coefficient relationship. Although the closed form analytical solution for the flux exists for the soil/sediment system (Thibodeaux, 1996), an exact but simpler form has evolved (USACE, 1990). A similar equation was developed for the flux of chemical contaminants to air from the land treatment of hazardous waste (USEPA, 1987). This flux algorithm contains the key parameters: chemical concentration on sediment, soil-to-water partition coefficient, Henrys constant, soil water content, soil porosity, molecular diffusivity in air, and the air-side mass-transfer coefficient. Emission time is the only independent variable and the flux to air is the dependent variable. The algorithm appears as Eq. 5 in USACE (1990).

Both the models presented above are deterministic models based on the current state of knowledge and using established and verified chemodynamics processes operative in both the soil column and associated air boundary layer. Only one statistical model was found. It was based on a compilation of flux data “accurately measured under field conditions for which physicochemical property information was available”; a statistical correlation was obtained (Woodrow et al., 1997). The fluxes of fifteen chemicals were determined immediately after soil treatment (within 12~24 hours) when volatility was greatest so as to represent the worst case scenario for vaporization. The correlation of the data is represented by:

$$\ln(n_e) = 19.35 + 1.0355 \cdot \ln(VP \cdot AR / K_D \cdot S_w) \quad (1)$$

with  $R^2 = 0.93$ . The flux  $n_e$  is in :  $g/m^2 \cdot hr$ . The independent variables are: VP is vapor pressure in Pa,  $K_D$  is the soil-to-water partition coefficient in mL/g,  $S_w$  is chemical solubility in water, mg/L and AR is the chemical application rate to soil in kg/ha.

## REPORTED RATES FOR COMPOUNDS OF CONCERN

A key aspect of the literature review was the search for measured evaporation rates. Although flux measurements from field sites were first priority, those from pilot-scale simulations and laboratory apparatus were acceptable. The laboratory measurements were the more numerous. They contained one or more measurements on the chemical of interest. The data located are in Tables 3 - 8 according to the class of contaminants. Each table lists fluxes that were either directly reported in the cited source or calculated from other reported data such as loss rates and other details of flux measurement. A number of studies reported the air concentrations of some of the target chemicals around contaminated soil sources and these could not be used to extract emission fluxes. In some cases, where enough experimental details are provided, the emission fluxes were calculated based on the geometry and the maximum surface area of the experimental apparatus (such as Erlenmeyer flasks or round bottom flasks). The data tables also contain the conditions (where reported) during data collection such as contaminant concentration in the soil (Cs), temperature of air (T), air flow rate above the soil, organic carbon content, apparatus type (L for laboratory, F for field measurements or PS for pilot-scale studies), measurement method, nature of surface or contaminant source, and any other specific information that might be important for the evaluation of the data. The two basic experimental techniques that were used to measure emission fluxes from soil-like surfaces are as follows:

*a) Flux Chamber/Box or Enclosed surface method:* In this method, the emissions from an enclosed area of contaminated surface are captured using an adsorbent and quantified. This is called a direct method and is the most commonly used technique to obtain the reported fluxes in this document. The various designs that were used differ primarily in terms of the volume of head space above the soil/sediment surface and the flow of air. This method does not take into account the natural aerodynamics that might exist above a soil surface since it creates a new externally forced flow field inside the enclosed air space. Therefore, appropriate corrections must be made, wherever necessary, to the air-side mass transfer resistances in order to extrapolate the experimental results to conditions pertaining to an open natural surface. Such corrections were not attempted for this literature review.

*b) Aerodynamic method:* The flux is calculated from the measured concentration, temperature and air humidity gradient in the atmospheric boundary layer above the soil surface. This method has been a widely used indirect method to measure contaminant fluxes and requires extensive meteorological data. As the name suggests, this method takes into account the aerodynamics above the soil surface.

The terms direct and indirect used to describe the flux chamber/box method and the aerodynamic method is somewhat unfortunate. Although termed direct, the enclosure placed on the soil is an intrusive object that alters the natural chemical emission processes. It reduces the air turbulence above the soil thus reducing the evaporative flux of those chemicals that are controlled by the air-side mass transfer resistance. In addition it isolates the soil from a thermal perspective. Often, shading of the soil from the sun results in a cooler soil surface and reduced flux. However, the control of the micro-environment within the enclosure allows uniform air samples for analytical chemistry measurements in and out of the box; this provides reproducible protocols for the chemical mass balance over a well-defined area. In other words, flux measurements are obtained with

laboratory like controls. The inherent problem that the flux chamber has of yielding incorrect measurements can be overcome by using the aerodynamic method. Theoretically if degradation in air is absent, the chemical concentration gradients in the atmospheric boundary layer are a direct result of the emissions occurring from the surface. However, a transport model must be used to convert these to appropriate fluxes from the surface. To do this correctly, numerous other simultaneous measurements of wind, temperature and humidity are needed to provide closure of the transport model. Fluctuations in wind direction and magnitude severely reduce the time periods in which measurements can be taken that match the theoretical constraints of the transport model. The sampling and equipment requirements of the aerodynamic method are much more burdensome. Although the fluxes obtained from the so-called indirect aerodynamic method are likely to be the more realistic ones, the method is not very cost-effective for routine flux measurements. Although the “direct” flux-chamber method does alter the process controlling the flux while it is being used, it is nevertheless easy to use, cost-effective, and gives reproducible results that may or may not be the actual emission rate.

The remainder of this section is a presentation of the data by chemical compound categories. Six categories were chosen: the polyaromatic hydrocarbons, pesticides, the BTX category, metals, PCBs and finally dioxins and furans.

#### POLYAROMATIC HYDROCARBONS (PAHs)

Table 3 lists the emission data for some of the polyaromatic hydrocarbons (PAHs) listed in Table 1. Hawthorne and Grabanski (2000) estimated the volatilization of a number of PAHs from contaminated manufacturing plant site sediment. The studies were performed in 500 mL Erlenmeyer flasks, but fluxes were not directly reported. The reported change in soil concentration were combined with reported volatile percentage to obtain emission fluxes; the area of the emission surface was estimated based on the diameter of the flask. Dupont (1986) measured the emission fluxes of naphthalene along with a number of volatile organic compounds (VOCs) from oily waste mixed with soil and sand. The experiments were conducted in cylindrical vessels by capturing and analyzing the vapor phase emissions. Under the LEDO (Long term Effects of Dredging Operations) program of the US ACE, several studies were conducted at the Engineering Research and Development Center (ERDC), Waterways Experiment Station and at Louisiana State University. Emission of several PAHs, from dredged material from contaminated sites (Indiana Harbor Canal, Grand Calumet River, Rouge River) and laboratory inoculated sediments (University Lake, Baton Rouge, LA), were measured in a flux chamber that allows a thin sheet of air to flow over the sediment surface (Valsaraj et al., 1997; Ravikrishna et al., 1998; US ACE, 1997, 1999b). Emissions of PAHs were also measured from a pilot scale CDF at US Army Engineers, Waterways Experiment Station, Vicksburg (US ACE, 1999c; Ravikrishna et al., 2001). Flux measurements were obtained at various times under different conditions of air relative humidity and also after “reworking” of the dredged materials. All the fluxes displayed high values initially and then lower ones as chemical depletion occurred from the top layers of the exposed material. It was also observed that “re-wetting” a dry sediment surface and “reworking” (or mixing the sediment to expose lower layers) after a few days increased the fluxes, demonstrating that the emission will respond to similar events that might occur in a CDF.

Lindhardt et al.(1996) measured time-series flux measurements of selected PAHs from coal tar contaminated sediment using a flux chamber. Park et al (1990) measured the volatilization rates of several PAHs during a biodegradation experiment in a glass container. No external mixing was provided to the microbe amended soil. In all the above studies the soil/sediment surface was relatively undisturbed, representative of a situation in a CDF after the dredged material is placed in its intended location. Lewis (1993) conducted a study of biodegradation of a highly contaminated slurry (30% solids content) in a slurry bioreactor equipped with mixing impellers. There was a very high degree of mixing and consequently enhanced mass transfer; during the first day and half, total hydrocarbon emission rates reached 0.14 lb/hour. This impeller mixing process is normally not present in a CDF in its natural state. The data is presented here as an illustration of the possibility of higher emissions in the presence of mixing.

The fluxes listed in Table 3 were, in most cases, the highest fluxes reported within 24 hours after exposing the soil surface to air. These flux values may be used as target chemical emission rates that may be supplied to an air dispersion model used to estimate downwind air concentrations. The flux values listed in the tables correspond to different soil concentration levels, organic carbon and moisture content and velocities of air in contact with the soil surface. There may be some correlation between the flux data and the different parameters within a data set (i.e. reported in a single data source). However, due to project time constraints and insufficient experimental details in some cases, a rigorous normalization procedure was not applied to the data that may otherwise have resulted in a better correspondence between data from two different sources.

## PESTICIDES

Table 4 lists the reported emission rates of selected pesticides. Only those applicable to the IHC dredged material appear. For most of the studies conducted to measure pesticide emission from soil, it was applied to the surface. In such cases, the soil concentration was expressed in per-soil mass basis by assuming a certain penetration depth of the pesticides on surface application. Farmer et al. (1972) studied the volatility of dieldrin and p,p-DDT under various conditions. The contaminated soil used was uniformly mixed with the chemical of interest before its use in the experiment. The experiments were performed in one of the earliest versions of flux chambers and the flux measurements were obtained as a time series. Nash (1983) performed emission experiments in micro-agrosystems measuring the flux of a number of pesticides of interest . Willis et al (1972) obtained emission fluxes from a field soil using the aerodynamic method. The flux shown in the table was the highest in long time-series study. Guenzi and Beard (1970) measured pesticide loss rates from contaminated soils in Erlenmeyer flasks by measuring the change in the mass of the contents of the flask.

There are strong correlations between the critical parameters, such as wind speed and concentration, affecting emissions and the fluxes within a particular data set. The differences between the fluxes reported from various sources is attributed to the lack of concentration normalization of the flux values in the listing. However, a significant observation can be made in the comparison of the emission fluxes of dieldrin as reported by Farmer (1972) and Willis (1972) using different methods and consequently different windspeeds. The aerodynamic method uses natural windspeeds which are much larger than those used in the laboratory and therefore the fluxes are orders of magnitude higher.

## BTX COMPOUNDS

Table 5 lists the emission flux of the BTX compounds found in the IHC. Dupont (1986) reported the flux of several from soils and sand amended with oily waste. There is a definite correlation between the fluxes within a data set and the soil concentration. Eklund et al.(1991) reported benzene flux from a number of field sites using a high head space flux chamber and found a 0.98 correlation coefficient between benzene flux and its concentration. Millison (1991) reported the fluxes of benzene, ethylbenzene, xylene, and toluene from a waste seep under the ground.

## METALS

The metals of concern at IHC are mercury, arsenic, lead and zinc. Table 6 lists the volatile metal fluxes from soils. Mercury is the most studied species with respect to the volatilization from soil like surfaces. Xinbin et al (1996) measured emission of mercury from various sites. Schroeder et al. (1989) measured volatile mercury fluxes from open fields. Lindberg et al. (1979, 1999) and Carpi et al.(1998) measured volatile mercury emissions from soils using teflon flux chambers. In these studies a significant correlation with soil concentration and temperature was observed. No direct data for arsenic evaporation from soils was found. Arsenic in soil is converted to the volatile species arsines, under special conditions. There is very little data measuring direct arsenic fluxes. Woolson et al. (1973) report that 30-70% of the arsenic in aerobic soils were volatilized as alkyl arsine (As-R) species in tracer experiments with <sup>14</sup>C-cacodylic acid. No arsenic emissions data are included in Table 6. No volatile zinc or lead reports were found in literature. Most of the air pollution concerns from these metals were associated with the entrainment of metal zinc and lead with particulate transport from soil-like surfaces (i.e., dust generation).

## POLYCHLORINATED BIPHENYLS (PCBs)

PCBs constitute a high percentage of many industrially contaminated soils and sediments, since PCBs are man made pollutants. Aroclor 1248 (a PCB mixture) was one of the priority pollutants in the IHC sediment listed in Table 1. Table 7 lists PCB fluxes reported in several sources as individual congeners, as mixtures (such as Aroclors) or as total PCB concentrations. To best deal with this non-uniformity in reporting in all the data sources, Table 7 is arranged according to the various data sources and not by compound name.

Indiana Harbor canal sediment contains a number of PCB congeners. In laboratory experiments performed at the U.S. Army Engineers Waterways experiment station, Vicksburg, PCB fluxes were measured at different times and at different conditions of air relative humidity and after reworking of the sediment (US ACE , 1997). The fluxes for Aroclor 1248 and two congeners PCB-8 and PCB-18 are shown in Table 7. The PCB fluxes showed a decline after the first 6 hours and then increased to initial rates when the dry dredged material surface was exposed to humid air. Bushart et al. (1998) reported PCBs emissions from drying sediments from St. Lawrence river sediment with high levels of Aroclor 1248 contamination as fluxes of individual congeners. Their experiments were performed with 25 g of wet sediment in 500 ml round bottom flasks with varying amounts of water (0-25 ml) added to the drying sediments every 24 hours for 4 days. This represented a wet-dry cycling condition that exposed sediment dredged material in a CDF might undergo. The highest flux

**Table 3. Listing of available reported PAH fluxes from sediment/soil surfaces**

| Compound                    | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site   | Measurement<br>Type/Surface   | Special Notes   | Reference              |
|-----------------------------|----------------------------------|--------------|-----------|---|------|--|---|---|------------------------|
| <b>Naphthalene</b>          | 761.4                            | 2470         | 33        | 50  | -na- | L  | Sediment from former gas plant site. Flow over soil in Erlenmeyer flasks  | Flux estimated from reported soil concentration change and volatile fraction capture percentage                       | Hawthorne et al.(2000) |
|                             | 43.7                             | 443          | 33        | 50  | -na- | L  |   |   |                        |
|                             | 202.3                            | 64           | 15        | 350                                       | 2.1  | L  | Slop oil - surface soil   | Air flow over soil in special chambers  | Dupont (1986)          |
|                             | 745.8                            | 64           | 15        | 350                                       | 1.5  | L  | -surface sand   | Air flow rate: 300-400 ml/min   |                        |
|                             | 680.1                            | 81           | 15        | 350                                       | 2.1  | L  | Separator Sludge - surface soil   | Reported flux at 1 hr   |                        |
|                             | 784.8                            | 83           | 15        | 350                                       | 1.5  | L  | - surface sand  | %OC includes oil-grease   |                        |
|                             | 1730                             | 101          | 25        | 200                                       | 0.5  | L  | Inoculated Loamy soil Experiments in a Flask. (2 hr average)  | Flux estimated from reported percent volatilization in a biodegradation control cell                                  | Park et al. (1990)     |
|                             | 2.5                              | 0.4          | 10        | 900                                       | 0.2  | L  | Coal tar contaminated surface soils   | Flux reported as a function of time.  | Lindhart et al.(1996)  |
|                             | 3200                             | 3120         | 10        | 900                                       | 1.7  | L  | Laboratory Flux Chamber   | Shown flux is the highest value measured<br>Calculated air velocity: 7.5 cm/s   |                        |
|                             | 50                               | 38           | 23        | 1700                                      | 3.6  | L  | Indiana Harbor Canal dredged material in laboratory flux chamber  | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s | US ACE (1997)          |
| 7                           | 4.1                              | 30           | 11000     | 6   | PS   | Indiana Harbor Canal dredged mat in pilot scale CDF. Flux Chamber.               | Flux reported as a function of time.<br>Shown flux is the highest value measured at 6hrs. Calculated air velocity: 4.9 cm/s | US ACE (1999c)<br>Ravikrishna et al. (2001)   |                        |
| 1000                        | 586                              | 23           | 1700      | 6.8                                       | L    | Grand calumet river dredged material in laboratory flux chamber                  | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s       | US ACE (1999b)<br>Valsaraj (1999),  |                        |
| 3.6e5 (ng/hr)               | 2143                             | -na-         | -na-      | -na-                                      | PS   | Bioreactor Slurry: 30 % wt/vol Creosote contaminated soil from a Superfund site. | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day                             | Lewis (1993)  |                        |
| <b>2-methyl-naphthalene</b> | 433                              | 1970         | 33        | 50  | -na- | L  | Sediment from former gas plant sit  | Flux estimated from reported soil concentration change and volatile fraction capture percentage                       | Hawthorne et al.(2000) |
|                             | 68.4                             | 563          | 33        | 50  | -na- | L  | plant site. Flow over soil in Erlenmeyer flasks   |   |                        |
|                             | 6.4e4 (ng/hr)                    | -na-         | -na-      | -na-                                      | PS   | PS   | Bioreactor Slurry: 30 % wt/vol Creosote contaminated soil from a Superfund site.  | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day                       | Lewis (1993)           |

**Table 3. Listing of available reported PAH fluxes from sediment/soil surfaces (contd.)**

| Compound                    | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC          | Site   | Measurement<br>Type/Surface  | Special Notes  | Reference                                   |
|-----------------------------|----------------------------------|--------------|-----------|---|--------------|--------|--|--|---|
| <b>2-methyl-naphthalene</b> | 12                               | 11.4         | 23        | 1700                                      | 3.6          | L      | Indiana Harbor Canal dredged material in laboratory flux chamber                         | Flux reported as a function of time. Shown flux is the highest value measured at 12 hrs  | US ACE (1997)                               |
|                             | 286.6<br>71.3                    | 1250<br>458  | 33<br>33  | 50<br>50                                  | -na-<br>-na- | L<br>L | Sediment from former gas plant sit<br>plant site. Flow over soil in<br>Erlenmeyer flasks | Flux estimated from reported soil<br>concentration change and volatile<br>fraction capture percentage                          | Hawthorne et al.(2000)                      |
| <b>1-methyl-naphthalene</b> | 25                               | 1.4          | 10        | 900                                       | 0.2          | L      | Coaltar contaminated surface soils   | Flux reported as a function of time.   | Lindhart et al.(1996)                       |
|                             | 1600                             | 41.3         | 10        | 900                                       | 1.7          | L      | Laboratory Flux Chamber  | Shown flux is the highest value measured<br>Calculated air velocity: 7.5 cm/s  |   |
|                             | 795                              | 102          | 25        | 200                                       | 0.5          | L      | Inoculated Loamy soil<br>Experiments in a Flask.<br>(2 hr average)                       | Flux estimated from reported<br>percent volatilization in a<br>biodegradation control cell                                     | Park et al. (1990)                          |
| <b>Fluorene</b>             | 34.6<br>7                        | 438<br>282   | 33<br>33  | 50<br>50                                  | -na-<br>-na- | L<br>L | Sediment from former gas plant sit<br>plant site. Flow over soil in<br>Erlenmeyer flasks | Flux estimated from reported soil<br>concentration change and volatile<br>fraction capture percentage                          | Hawthorne et al.(2000)                      |
|                             | 2.5                              | 18           | 23        | 1700                                      | 3.6          | L      | Indiana Harbor Canal dredged material in laboratory flux chamber                         | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>at 6 hrs                                   | US ACE (1997)                               |
| <b>Phenanthrene</b>         | 19.6<br>0.82                     | 1590<br>784  | 33<br>33  | 50<br>50                                  | -na-<br>-na- | L<br>L | Sediment from former gas plant sit<br>plant site. Flow over soil in<br>Erlenmeyer flasks | Flux estimated from reported soil<br>concentration change and volatile<br>fraction capture percentage                          | Hawthorne et al.(2000)                      |
|                             | 12                               | 22.3         | 30        | 11000                                     | 6            | PS     | Indiana Harbor Canal dredged mat<br>in pilot scale CDF: Flux Chamber.                    | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>at 6hrs. Calculated air velocity: 4.9 cm/s | US ACE (1999c)<br>Ravikrishna et al. (2001) |
|                             | 5<br>20                          | 4.4<br>318   | 10<br>10  | 900<br>900                                | 0.2<br>1.7   | L<br>L | Coaltar contaminated surface soils<br>Laboratory Flux Chamber                            | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>Calculated air velocity: 7.5 cm/s          | Lindhart et al.(1996)                       |
|                             | 1.3e3 (ng/hr)                    | 518          | -na-      | -na-                                      | -na-         | PS     | Bioreactor Slurry: 30 % wt/vol<br>Creosote contaminated soil<br>from a Superfund site.   | Reported Rate (ng/hr) from measured<br>cumulative fugitive emissions from a<br>bioreactor after 1 day                          | Lewis (1993)                                |

**Table 3. Listing of available reported PAH fluxes from sediment/soil surfaces (contd.)**

| Compound            | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site | Measurement<br>Type/Surface  | Special Notes   | Reference                                   |
|---------------------|----------------------------------|--------------|-----------|---|------|------|--|---|---|
| <b>Phenanthrene</b> | 1.9                              | 51           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
|                     | 20                               | 97           | 24        | 1700                                      | 2.6  | L    | Clean sediment inoculated with Phenanthrene, pyrene and Dibenzofuran.<br>Laboratory Flux chamber | Flux reported as a function of time. Shown flux is the highest value measured<br>Drying sediment with initial moisture:26%<br>Calculated air velocity: 5.67cm/s | Ravikrishna et al., (1991)                  |
|                     | 8                                | 65           | 24        | 1700                                      | 2.6  | L    | Clean sediment inoculated with Phenanthrene, pyrene and Dibenzofuran.<br>Laboratory Flux chamber | Flux reported as a function of time. Shown flux is the highest value measured<br>Drying sediment with initial moisture:48%<br>Calculated air velocity: 5.67cm/s | Ravikrishna et al., (1991)                  |
|                     | 10                               | 21           | 23        | 100                                       | 1.2  | L    | Rouge River dredged material in laboratory flux chamber<br>Drying of thin sediment layers        | Flux reported as a function of time. Shown flux is the highest value measured<br>at 2 hrs. Calculated air velocity: 2.8 cm/s                                    | Valsaraj et al., (1997),                    |
| <b>Fluoranthene</b> | 0.48                             | 416          | 33        | 50  | -na- | L    | Sediment from former gas plant sit plant site. Flow over soil in Erlennmeyer flasks              | Flux estimated from reported soil concentration change and volatile fraction capture percentage   | Hawthorne et al.(2000)                      |
|                     | 2.5                              | 51           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
|                     | 20                               | 21           | 30        | 11000                                     | 6    | PS   | Indiana Harbor Canal dredged mat in pilot scale CDF. Flux Chamber.                               | Flux reported as a function of time. Shown flux is the highest value measured<br>at 6hrs. Calculated air velocity: 4.9 cm/s                                     | US ACE (1999c)<br>Ravikrishna et al. (2001) |
| <b>Pyrene</b>       | 0.66                             | 790          | 33        | 50  | -na- | L    | Sediment from former gas plant sit plant site. Flow over soil in Erlennmeyer flasks              | Flux estimated from reported soil concentration change and volatile fraction capture percentage   | Hawthorne et al.(2000)                      |
|                     | 0.104                            | 59           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
|                     | 7                                | 23.8         | 30        | 11000                                     | 6    | PS   | Indiana Harbor Canal dredged mat in pilot scale CDF. Flux Chamber.                               | Flux reported as a function of time. Shown flux is the highest value measured<br>at 6hrs. Calculated air velocity: 4.9 cm/s                                     | US ACE (1999c)<br>Ravikrishna et al. (2001) |

**Table 3. Listing of available reported PAH fluxes from sediment/soil surfaces (contd.)**

| Compound                  | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site | Measurement<br>Type/Surface  | Special Notes   | Reference                                   |
|---------------------------|----------------------------------|--------------|-----------|---|------|------|--|---|---|
| <b>Pyrene</b>             | 2                                | 94           | 24        | 1700                                      | 3    | L    | Clean sediment inoculated with Phenanthrene, pyrene and Dibenzofuran.<br>Laboratory Flux chamber | Flux reported as a function of time. Shown flux is the highest value measured<br>Drying sediment with initial moisture:26%<br>Calculated air velocity: 5.67cm/s | Ravikrishna et al., (1991)                  |
|                           | 0.7                              | 36           | 23        | 100                                       | 1.2  | L    | Rouge River dredged material in laboratory flux chamber<br>Drying of thin sediment layers        | Flux reported as a function of time. Shown flux is the highest value measured at 2 hrs. Calculated air velocity: 2.8 cm/s                                       | Valsaraj et al., (1997),                    |
| <b>Benzo(a)anthracene</b> | 0.27                             | 240          | 33        | 50  | -na- | L    | Sediment from former gas plant sit plant site. Flow over soil in Erlenmeyer flasks               | Flux estimated from reported soil concentration change and volatile fraction capture percentage   | Hawthorne et al.(2000)                      |
|                           | 0.018                            | 27           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
| <b>Chrysene</b>           | 4                                | 10.5         | 30        | 11000                                     | 6    | PS   | Indiana Harbor Canal dredged mat in pilot scale CDF. Flux Chamber.                               | Flux reported as a function of time. Shown flux is the highest value measured at 6hrs. Calculated air velocity: 4.9 cm/s  | US ACE (1999c)<br>Ravikrishna et al. (2001) |
|                           | 0.04                             | 222          | 33        | 50  | -na- | L    | Sediment from former gas plant sit plant site. Flow over soil in Erlenmeyer flasks               | Flux estimated from reported soil concentration change and volatile fraction capture percentage   | Hawthorne et al.(2000)                      |
| <b>Acenaphthene</b>       | 0.01                             | 40           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
|                           | 1.5e4 (ng/hr)                    | 1937         | -na-      | -na-                                      | -na- | PS   | Bioreactor Slurry: 30 % wt/vol Creosote contaminated soil from a Superfund site.                 | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day   | Lewis (1993)                                |
| <b>Acenaphthylene</b>     | 7.1                              | 27           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |
|                           | 3.1e3 (ng/hr)                    | 17           | -na-      | -na-                                      | -na- | PS   | Bioreactor Slurry: 30 % wt/vol Creosote contaminated soil from a Superfund site.                 | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day   | Lewis (1993)                                |
|                           | 0.41                             | 1.54         | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s  | US ACE (1997)                               |

**Table 3. Listing of available reported PAH fluxes from sediment/soil surfaces (contd.)**

| Compound                          | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site | Measurement<br>Type/Surface  | Special Notes  | Reference                                   |
|-----------------------------------|----------------------------------|--------------|-----------|---|------|------|--|--|---|
| <b>Anthracene</b>                 | 2.9e2                            | 307          | -na-      | -na-                                      | -na- | PS   | Bioreactor Slurry; 30 % wt/vol Creosote contaminated soil from a Superfund site. | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day                          | Lewis (1993)                                |
|                                   | 0.19                             | 11           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s       | US ACE (1997)                               |
| <b>Benzo(b)-<br/>fluoranthene</b> | 2                                | 9.17         | 30        | 11000                                     | 6    | PS   | Indiana Harbor Canal dredged mat in pilot scale CDF. Flux Chamber.               | Flux reported as a function of time. Shown flux is the highest value measured at 6hrs. Calculated air velocity: 4.9 cm/s | US ACE (1999c)<br>Ravikrishna et al. (2001) |
|                                   | 0.028                            | 19           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                 | Flux reported as a function of time. Shown flux is the highest value measured<br>Calculated air velocity: 5.67cm/s       | US ACE (1997)                               |
|                                   | 0.033                            | 14           | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                 | Flux reported as a function of time. Shown flux is the highest value measured at 7 days                                  | US ACE (1997)                               |
| <b>Benzo(a)pyrene</b>             | 0.27                             | 294          | 33        | 50  | -na- | L    | Sediment from former gas plant sit   | Flux estimated from reported soil concentration change and volatile fraction capture percentage                          | Hawthorne et al.(2000)                      |
|                                   | 0.026                            | 21.7         | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                 | Flux reported as a function of time. Shown flux is the highest value measured at 7 days                                  | US ACE (1997)                               |
| <b>Perylene</b>                   | 0.11                             | 38           | 33        | 50  | -na- | L    | Sediment from former gas plant sit   | Flux estimated from reported soil concentration change and volatile fraction capture percentage                          | Hawthorne et al.(2000)                      |
|                                   | 0.009                            | 15.7         | 23        | 1700                                      | 3.6  | L    | Indiana Harbor Canal dredged material in laboratory flux chamber                 | Flux reported as a function of time. Shown flux is the highest value measured at 7 days                                  | US ACE (1997)                               |

**Table 4. Listing of available reported Pesticide fluxes from sediment/soil surfaces**

| Compound        | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site | Measurement<br>Type/Surface                  | Special Notes  | Reference            |
|-----------------|----------------------------------|--------------|-----------|---|------|------|--|--|----------------------|
| <b>Dieldrin</b> | 4.2 (4d)                         | 50           | 20        | 120                                       | 0.58 | L    | Silt loam                                    | Parenthesis in flux column represents time interval of the average flux<br>Air velocity for 120 ml/min : 0.2 cm/s<br>Air velocity for 480ml/min : 0.8 cm/s | Farmer et al. (1972) |
|                 | 2.9 (4d)                         | 10           | 20        | 120                                       | 0.58 | L    | Flux Chamber                                 |  |                      |
|                 | 1.7 (4d)                         | 5            | 20        | 120                                       | 0.58 | L    |  |  |                      |
|                 | 0.3 (4d)                         | 1            | 20        | 120                                       | 0.58 | L    |  |  |                      |
|                 | 8.3 (4d)                         | 50           | 20        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 4.6 (4d)                         | 10           | 20        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 2.5 (4d)                         | 5            | 20        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 0.4 (4d)                         | 1            | 20        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 16.7 (1d)                        | 50           | 30        | 120                                       | 0.58 | L    |  |  |                      |
|                 | 10 (1d)                          | 10           | 30        | 120                                       | 0.58 | L    |  |  |                      |
|                 | 4.2 (1d)                         | 5            | 30        | 120                                       | 0.58 | L    |  |  |                      |
|                 | 33 (1d)                          | 50           | 30        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 16.7 (1d)                        | 10           | 30        | 480                                       | 0.58 | L    |  |  |                      |
|                 | 8.4 (1d)                         | 5            | 30        | 480                                       | 0.58 | L    |  |  |                      |
| <b>p,p- DDT</b> | 91                               | 10           | 30        | 45.8 cm/s                                 | 0.83 | F    | Field Soil<br>Aerodynamic method             | Highest flux in a long series of measurements  | Willis et al. (1972) |
|                 | 32                               | 2 kg/ha      | 27        | 8.3 cm/s                                  | -na- | L    | Field Soil - sandy loam<br>Micro-agro system | Soil concentration expressed in terms of application rate per hectare.<br>Calculated loading on the basis of 1 cm depth coverage : 7 ug/g                  | Nash (1983)          |
| <b>p,p- DDT</b> | 0.32                             | 5            | 30        | 480                                       | 0.58 | L    | Silt loam                                    | Parenthesis in flux column represents time interval of the average flux  | Farmer et al. (1972) |
|                 | 3.6                              | 10           | 30        | 480                                       | 0.58 | L    | Flux Chamber                                 |  |                      |
|                 | 0.043                            | 10           | 30        | 20  | 0.6  | L    | loamy sand                                   |  |                      |
|                 | 0.05                             | 10           | 30        | 20  | 1.6  | L    | loam   |  |                      |
|                 | 0.038                            | 10           | 30        | 20  | 3.1  | L    | clay loam                                    |  |                      |
|                 | 0.042                            | 10           | 30        | 20  | 3.6  | L    | clay   |  |                      |
|                 | 0.13                             | 10           | 55        | 5   | 0.63 | L    | loamy sand                                   |  |                      |
|                 | 0.2                              | 10           | 55        | 5   | 1.6  | L    | loam   |  |                      |
|                 | 0.137                            | 10           | 55        | 5   | 3.06 | L    | clay loam                                    |  |                      |
|                 | 0.103                            | 10           | 55        | 5   | 3.57 | L    | clay   |  |                      |
|                 | 4.5                              | 2 kg/ha      | 27        | 8.3 cm/s                                  |      | L    | Field Soil - sandy loam<br>Micro-agro system |  |                      |

**Table 4. Listing of available reported Pesticide fluxes from sediment/soil surfaces (contd.)**

| Compound           | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site | Measurement<br>Type/Surface | Special Notes   | Reference   |
|--------------------|----------------------------------|--------------|-----------|---|-----|------|-----------------------------|---|-------------|
| trans-chlordane    | 83                               | 2 kg/ha      | 27        | 8.3 cm/s                                  |     | L    | Field Soil - sandy loam     | Soil concentration expressed in terms<br>of application rate per hectare. | Nash (1983) |
| cis- chlordane     | 54                               | 2 kg/ha      | 27        | 8.3 cm/s                                  |     |      | Micro-agro system           | Calculated loading on the basis of 1 cm<br>depth coverage : 7 ug/g        |             |
| heptachlor epoxide | 58                               | 2 kg/ha      | 27        | 8.3 cm/s                                  |     |      |                             |   |             |

**Table 5. Listing of available reported VOC fluxes from sediment/soil surfaces**

| Compound       | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site                                       | Measurement<br>Type/Surface                 | Special Notes  | Reference        |                           |
|----------------|----------------------------------|--------------|-----------|---|-----|--|---|--|------------------|---------------------------|
| <b>Benzene</b> | 112320 (1hr)                     | 216          | 15        | 300-400                                   | 2.1 | L  | Slop Oil<br>surface soil                    | Air flow over soil in special chambers   | R. Dupont (1986) |                           |
|                | 18972 (20hr)                     | 216          | 15        | 300-400                                   | 2.1 | L  | surface soil                                | Parenthesis in Flux column indicates<br>time at end of flux measurement interval |                  |                           |
|                | 108360 (1hr)                     | 216          | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 18324 (20hr)                     | 216          | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 52560 (1 hr)                     | 82           | 15        | 300-400                                   | 2.1 | L  | Separator Sludge<br>surface soil            |  |                  |                           |
|                | 13608 (20 hr)                    | 82           | 15        | 300-400                                   | 2.1 | L  | surface soil                                |  |                  |                           |
|                | 25092 (1 hr)                     | 84           | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 1396.8 (20 hr)                   | 84           | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 0.9                              | -na-         |           | 5000                                      |     | F  | Controlled RCRA Landfill                    | Flux chamber designed by<br>Bart Eklund used for flux measurement                |                  | Bart Eklund et al. (1991) |
|                | 4.5                              | 13.7         |           | 5000                                      |     | F  | Controlled RCRA Landfill                    |  |                  |                           |
|                | 3.84                             | 0.028        |           | 5000                                      |     | F  | Controlled RCRA Landfill                    | Shown fluxes are average over<br>several measurements and time<br>intervals      |                  |                           |
|                | 13.56                            | -na-         |           | 5000                                      |     | F  | Uncontrolled Landfill                       |  |                  |                           |
|                | 342                              | -na-         |           | 5000                                      |     | F  | Uncontrolled Landfill                       |  |                  |                           |
|                | 3.78                             | 0.006        |           | 5000                                      |     | F  | Uncontrolled Landfill                       |  |                  |                           |
|                | 216                              | 0.36         |           | 5000                                      |     | F  | Uncontrolled Landfill                       |  |                  |                           |
| 6              | -na-                             |              | 5000      |   | F   | Uncontrolled Landfill                      |   |  |                  |                           |
| 15600          | 39                               |              | 5000      |   | PS  | Test Soil Pile                             |   |  |                  |                           |
| 57780          | 341                              |              | 5000      |   | PS  | Test Soil Pile                             |   |  |                  |                           |
| 6960           | 42.2                             |              | 5000      |   | PS  | Test Soil Pile                             |   |  |                  |                           |
| 597            | 0.05                             |              | 5000      |   | F   | Landtreatment Unit                         |   |  |                  |                           |
| 2124           | -na-                             | 27           | 4000      |   | F   | Waste Seep<br>Soil with pure phase benzene | Bart Eklund's Flux chamber                  | Millison et al. (1991)   |                  |                           |
| <b>Toluene</b> | 252720 (1 hr)                    | 307          | 15        | 300-400                                   | 2.1 | L  | Slop Oil<br>surface soil                    | Air flow over soil in special chambers   | R. Dupont (1986) |                           |
|                | 4140 (20 hr)                     | 307          | 15        | 300-400                                   | 2.1 | L  | surface soil                                | Parenthesis in Flux column indicates<br>time at end of flux measurement interval |                  |                           |
|                | 191880 (1 hr)                    | 307          | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 24732 (20 hr)                    | 307          | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 54360 (1 hr)                     | 87           | 15        | 300-400                                   | 2.1 | L  | Separator Sludge<br>surface soil            |  |                  |                           |
|                | 11304 (20 hr)                    | 87           | 15        | 300-400                                   | 2.1 | L  | surface soil                                |  |                  |                           |
|                | 20484 (1 hr)                     | 90           | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 221.76 (20 hr)                   | 90           | 15        | 300-400                                   | 1.5 | L  | surface sand                                |  |                  |                           |
|                | 6054                             | -na-         | 27        | 4000                                      |     | F  | Waste Seep<br>Soil with pure phase compound | Bart Eklund's Flux chamber   |                  |                           |
|                |                                  |              |           |   |     |  |   |  |                  | Millison et al. (1991)    |

**Table 5. Listing of available reported VOC fluxes from sediment/soil surfaces (contd.)**

| Compound        | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g)  | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC     | Site | Measurement<br>Type/Surface                | Special Notes  | Reference                              |
|-----------------|----------------------------------|---------------|-----------|---|---------|------|--|--|--|
| <b>o-xylene</b> | 34488 (1 hr)                     | 135           | 15        | 300-400                                   | 2.1     | L    | Slop Oil<br>surface soil                   | Air flow over soil in special chambers   | R. Dupont (1986)                       |
|                 | 9792 (20 hr)                     | 135           | 15        | 300-400                                   | 2.1     | L    | surface soil                               | Parenthesis in Flux column indicates<br>time at end of flux measurement interval |  |
|                 | 33372 (1 hr)                     | 135           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 5940 (20 hr)                     | 135           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 15480 (1 hr)                     | 77            | 15        | 300-400                                   | 2.1     | L    | Separator Sludge<br>surface soil           |  |  |
|                 | 5472 (20 hr)                     | 77            | 15        | 300-400                                   | 2.1     | L    | surface soil                               |  |  |
|                 | 11880 (1 hr)                     | 79            | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 756 (20 hr)                      | 79            | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 714                              | -na-          | 27        | 4000                                      |         | F    | Waste Seep                                 | Bart Eklund's Flux chamber   | Millison et al. (1991)                 |
|                 | -na-                             |               |           |   |         |      |  |  |  |
| <b>p-xylene</b> | 10116 (20 hr)                    | 136           | 15        | 300-400                                   | 2.1     | L    | Slop Oil<br>surface soil                   | Air flow over soil in special chambers   | R. Dupont (1986)                       |
|                 | 28872 (1 hr)                     | 136           | 15        | 300-400                                   | 2.1     | L    | surface soil                               | Parenthesis in Flux column indicates<br>time at end of flux measurement interval |  |
|                 | 5868 (20 hr)                     | 136           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 12744 (1 hr)                     | 59            | 15        | 300-400                                   | 2.1     | L    | Separator Sludge<br>surface soil           |  |  |
|                 | 2772 (20 hr)                     | 59            | 15        | 300-400                                   | 2.1     | L    | surface soil                               |  |  |
|                 | 7848 (1 hr)                      | 61            | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 7.128 (20 hr)                    | 61            | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
|                 | 2964                             | -na-          | 27        | 4000                                      |         | F    | Waste Seep<br>Soil with pure phase benzene | Bart Eklund's Flux chamber   | Millison et al. (1991)                 |
|                 |                                  |               |           |   |         |      |  |  |  |
|                 | <b>m-xylene</b>                  | 137160 (1 hr) | 340       | 15  | 300-400 | 2.1  | L  | Slop Oil<br>surface soil   | Air flow over soil in special chambers |
| 33264 (20 hr)   |                                  | 340           | 15        | 300-400                                   | 2.1     | L    | surface soil                               | Parenthesis in Flux column indicates<br>time at end of flux measurement interval |  |
| 97560 (1 hr)    |                                  | 340           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
| 18936 (20 hr)   |                                  | 340           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
| 51840 (1 hr)    |                                  | 127           | 15        | 300-400                                   | 2.1     | L    | Separator Sludge<br>surface soil           |  |  |
| 14940 (20 hr)   |                                  | 127           | 15        | 300-400                                   | 2.1     | L    | surface soil                               |  |  |
| 36720 (1 hr)    |                                  | 131           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
| 957.6 (20 hr)   |                                  | 131           | 15        | 300-400                                   | 1.5     | L    | surface sand                               |  |  |
| 2964            |                                  | -na-          | 27        | 4000                                      |         | F    | Waste Seep<br>Soil with pure phase benzene | Bart Eklund's Flux chamber   | Millison et al. (1991)                 |

**Table 5. Listing of available reported VOC fluxes from sediment/soil surfaces (contd.)**

| Compound            | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site | Measurement<br>Type/Surface                | Special Notes  | Reference        |                            |                        |
|---------------------|----------------------------------|--------------|-----------|---|-----|------|--|--|------------------|----------------------------|------------------------|
| <b>Ethylbenzene</b> | 76680 (1 hr)                     | 66           | 15        | 300-400                                   | 2.1 | L    | Slop Oil<br>surface soil                   | Air flow over soil in special chambers<br>Parenthesis in Flux column indicates<br>time at end of flux measurement interval | R. Dupont (1986) |                            |                        |
|                     | 28908 (20 hr)                    | 66           | 15        | 300-400                                   | 2.1 | L    | surface soil                               |  |                  |                            |                        |
|                     | 74880 (1 hr)                     | 66           | 15        | 300-400                                   | 1.5 | L    | surface sand                               |  |                  |                            |                        |
|                     | 17712 (20 hr)                    | 66           | 15        | 300-400                                   | 1.5 | L    | surface sand                               |  |                  |                            |                        |
|                     | 38520 (1 hr)                     | 21           | 15        | 300-400                                   | 2.1 | L    | Separator Sludge<br>surface soil           |  |                  |                            |                        |
|                     | 10008 (20 hr)                    | 21           | 15        | 300-400                                   | 2.1 | L    | surface soil                               |  |                  |                            |                        |
|                     | 2782 (1 hr)                      | 22           | 15        | 300-400                                   | 1.5 | L    | surface sand                               |  |                  |                            |                        |
|                     | 97.9 (20 hr)                     | 22           | 15        | 300-400                                   | 1.5 | L    | surface sand                               |  |                  |                            |                        |
|                     | 243                              | -na-         | 27        | 4000                                      |     | F    | Waste Seep<br>Soil with pure phase benzene |  |                  | Bart Eklund's Flux chamber | Millison et al. (1991) |

**Note:** -na- not available  
L Laboratory  
PS Pilot Scale  
F Field  
Cs Soil/sediment concentration  
T Temperature

**Table 6. Listing of available reported Metal fluxes from sediment/soil surfaces**

| Compound       | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site                | Measurement<br>Type/Surface     | Special Notes         | Reference            |                         |
|----------------|----------------------------------|--------------|-----------|---|------|---------------------|---------------------------------|-----------------------|----------------------|-------------------------|
| <b>Mercury</b> | 0.0145                           | 19.73        | 27.3      | 1000                                      | -na- | F                   | Contaminated soil               |                       | Xinbin et al. (1996) |                         |
|                | 0.003                            | 19.73        | 17        | 1000                                      | -na- | F                   | at a plant                      |                       |                      |                         |
|                | 0.002                            | 19.73        | 16.4      | 1000                                      | -na- | F                   | Flux box method                 |                       |                      |                         |
|                | 0.0092                           | 10.3         | 26.2      | 1000                                      | -na- | F                   |                                 |                       |                      |                         |
|                | 0.0083                           | 10.3         | 23.8      | 1000                                      | -na- | F                   |                                 |                       |                      |                         |
|                | 0.001                            | 10.3         | 21.2      | 1000                                      | -na- | F                   |                                 |                       |                      |                         |
|                | 0.0029                           | 0.931        | 29.5      | 1000                                      | -na- | F                   |                                 |                       |                      |                         |
|                | 0.0012                           | 0.931        | 26.7      | 1000                                      | -na- | F                   |                                 |                       |                      |                         |
|                | 0.0026                           | 1.92         | 23.4      | 1000                                      | -na- | L                   |                                 |                       |                      |                         |
|                | 0.00024                          | 1.92         | 14.7      | 1000                                      | -na- | L                   |                                 |                       |                      |                         |
|                | 0.00014                          | -na-         | 17        | 2000                                      | -na- | F                   | Open field                      |                       |                      | Schroeder et al. (1989) |
|                | 0.00009                          | -na-         | 17        | 2000                                      | -na- | F                   | Flux box method                 |                       |                      |                         |
|                | 0.012-0.014                      | 97           | 6 - 35    | na  | na   | F                   | chamber                         | Soils near a mine     |                      | Lindberg et al. (1979)  |
|                | 0.032-0.034                      |              | 6 - 35    | na  | na   | F                   | chamber                         | Soils near a mine     |                      | Lindberg et al. (1979)  |
| 0.001-0.002    | 63                               | 26           | 400       | na  | F    | Teflon flux chamber | Control soil at a landfill site | Lindberg et al.(1999) |                      |                         |
| 0.0003         | 0.5                              | 15-40        | 5000      | 8.7                                       | F    | Teflon flux chamber | USDA silty clay loam site       | Carpi et al. (1998)   |                      |                         |
| 0.001          | 0.06                             | 15-40        | 5000      | 6.2                                       | F    |                     | USDA shaly silt loam site       |                       |                      |                         |
| 0.004          | 0.1                              | 15-40        | 5000      | 6.6                                       | F    |                     | Silt load                       |                       |                      |                         |

**Table 7. Listing of available reported PCB fluxes from sediment/soil surfaces**

| Compound            | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site | Measurement<br>Type/Surface  | Special Notes   | Reference             |
|---------------------|----------------------------------|--------------|-----------|---|-----|------|--|---|-----------------------|
| <b>Aroclor 1248</b> | 0.23                             | 4.1          | 23        | 1700                                      | 3.6 | L    | Indiana Harbor Canal dredi<br>material in laboratory flux chambers | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>at 6 hrs                    | US ACE (1997)         |
|                     | 0.32                             | 4.1          | 23        | 1700                                      | 3.6 | L    | Indiana Harbor Canal dredi<br>material in laboratory flux chambers | Flux reported as a function of time.<br>Shown flux is the value measured<br>at 800 hrs after sediment rewetting | US ACE (1997)         |
| <b>PCB-8</b>        | 0.02                             | 0.032        | 23        | 1700                                      | 3.6 | L    | Indiana Harbor Canal dredi<br>material in laboratory flux chambers | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>at 6 hrs                    | US ACE (1997)         |
|                     | 0.025                            | 0.032        | 23        | 1700                                      | 3.6 | L    | Indiana Harbor Canal dredi<br>material in laboratory flux chambers | Flux reported as a function of time.<br>Shown flux is the value measured<br>at 800 hrs after sediment rewetting | US ACE (1997)         |
| <b>PCB-18</b>       | 0.11                             | 0.129        | 23        | 1700                                      | 3.6 | L    | Indiana Harbor Canal dredi<br>material in laboratory flux chambers | Flux reported as a function of time.<br>Shown flux is the highest value measured<br>at 6 hrs                    | US ACE (1997)         |
| <b>PCB Congener</b> |                                  |              |           |   |     |      |  |   |                       |
| 2,                  | 1.61                             | PCBs         | 23        | 1000                                      |     | L    | St. Lawrence River   | Flux values shown in table were the   | Bushart et al. (1998) |
| 4,                  | 1.33                             | Total        | 23        | 1000                                      |     | L    | Sediment contaminated  | average values after 1 day of drying  |                       |
| 2,2'                | 11.78                            | 660          | 23        | 1000                                      |     | L    | with Aroclor 1248  | Flux calculated from mass loss and  |                       |
| 2,6                 | 4.82                             |              | 23        | 1000                                      |     | L    | Experiments performed  | assuming diameter of flask = 10 cm  |                       |
| 2,3'                | 3.21                             |              | 23        | 1000                                      |     | L    | in a 500 ml round  | Initial moisture content in sediment: 70%   |                       |
| 2,4'                | 5.35                             |              | 23        | 1000                                      |     | L    | bottom flask   | Mass of sediment used : 25 g  |                       |
| 2,6,2'              | 8.56                             |              | 23        | 1000                                      |     | L    | Fluxes of PCB from   |   |                       |
| 4,4'                | 1.61                             |              | 23        | 1000                                      |     | L    | drying sediment  |   |                       |
| 2,4,2'              | 1.61                             |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,3,6 + 2,6,3'      | 6.42                             |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,6,4'              | 8.03                             |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,5,3'              | 0.535                            |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,5,4'              | 0.803                            |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,4,4'              | 1.07                             |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,5,2',6'           | 1.07                             |              | 23        | 1000                                      |     | L    |  |   |                       |
| 2,4,2',6'           | 0.535                            |              | 23        | 1000                                      |     | L    |  |   |                       |

**Table 7. Listing of available reported PCB fluxes from sediment/soil surfaces (contd.)**

| Compound             | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site | Measurement<br>Type/Surface                        | Special Notes  | Reference                     |
|----------------------|----------------------------------|--------------|-----------|---|-----|------|--|--|-------------------------------|
|                      |                                  |              |           |   |     |      |  |  |                               |
| Total PCBs           | 1.35                             | 65           | 25        | 1200                                      |     | L    | St. Lawrence River                                 | Flux average over 24 hour period   | J. Chiarenzelli et al. (1997) |
|                      | 1.38                             | 65           | 25        | 1200                                      |     | L    | Sediment contaminated with Aroclor 1248            | Initial Sed. moisture content for the flux values are 99%, 99%, 99%, 76%, 50%, 30% and 0% respectively in the order shown  |                               |
|                      | 0.94                             | 65           | 25        | 1200                                      |     | L    | Experiments performed in a 2 L jar                 | Flux calculated from mass loss rate assuming jar diameter = 15 cm.   |                               |
|                      | 0.52                             | 65           | 25        | 1200                                      |     | L    | Fluxes of PCB from drying sediment                 | Sediment mass used = 0.25 g  |                               |
|                      | 0.39                             | 65           | 25        | 1200                                      |     | L    |  |  |                               |
|                      | 0.32                             | 65           | 25        | 1200                                      |     | L    |  |  |                               |
|                      | 0.015                            | 65           | 25        | 1200                                      |     | L    |  |  |                               |
|                      | 0.0487                           | total        | 25        | 1200                                      |     | L    | St. Lawrence River                                 | Flux average over 24 hour period   |                               |
|                      | 0.0156                           | PCB          | 25        | 1200                                      |     | L    | Sediment contaminated with Aroclor 1248            | Flux averaged from 4 sets of experiments of drying sediment with starting moisture ranging from 63% to 84% and averaging 70%. Flux calculated from mass loss rate assuming jar diameter = 15 cm. |                               |
|                      | 0.37                             | average      | 25        | 1200                                      |     | L    | Experiments performed in a 2 L jar                 | Sediment mass used = 0.25 g  |                               |
|                      | 0.0084                           | 13.3 ppm     | 25        | 1200                                      |     | L    |  |  |                               |
|                      | 0.025                            |              | 25        | 1200                                      |     | L    |  |  |                               |
|                      | 0.07                             |              | 25        | 1200                                      |     | L    |  |  |                               |
| 0.047                |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.058                |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.03                 |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.012                |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.012                |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.01                 |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 0.016                |                                  | 25           | 1200      |   | L   |      |  |  |                               |
| 2,4,2',4' + 2,4,5,2' |                                  |              |           |   |     |      |  |  | J. Chiarenzelli et al. (1997) |
| Aroclor 1242         | 18.29                            | 83.9         | 20        | 1200                                      |     | L    | Soils spiked                                       | Flux values shown are the first hour averages in a time series drying  | J. Chiarenzelli et al. (1997) |
| Aroclor 1248         | 15                               | 100          | 20        | 1200                                      |     | L    | with mixture of Aroclors 1242, 1248, 1254 and 126  | drying experiments. 0.25 g sediment/soil used with 25 ml water. Represents a   |                               |
| Aroclor 1254         | 3.2                              | 78.3         | 20        | 1200                                      |     | L    | PCB contaminated                                   |  |                               |
| Aroclor 1260         | 1.15                             | 74.8         | 20        | 1200                                      |     | L    | St. Lawrence River Sedir ponded sediment in a CDF. |  |                               |
| Total PCBs           | 2.34                             | 65.3         | 20        | 1200                                      |     | L    |  |  |                               |
| PCB-18               | 7.10E-03                         | 0.33         | 16.2      | 4000                                      | 4.4 | L    | Sandy loam soils                                   | Flux values shown are the average values for 8 days. Clean soil was mixed with   | Ian Cousins et al. (1997)     |
| PCB-33               | 3.80E-03                         | 0.087        | 16.2      | 4000                                      | 4.4 | L    | amended with PCB                                   | 250 mg of sludge to prepare the  |                               |
| PCB-47               | 2.90E-03                         | 0.039        | 16.2      | 4000                                      | 4.4 | L    | contaminated sludge                                | surface. Calculated mean air velocity  |                               |
| PCB-52               | 0.027                            | 0.087        | 16.2      | 4000                                      | 4.4 | L    | Flux chamber                                       | in flux chamber : 3.2 cm/s   |                               |
| PCB-87               | 2.40E-04                         | 0.047        | 16.2      | 4000                                      | 4.4 | L    | measurements                                       |  |                               |
| PCB-101              | 2.80E-04                         | 0.016        | 16.2      | 4000                                      | 4.4 | L    |  |  |                               |
| PCB -8               | 1.94                             | -na-         |           | 5000                                      |     | PS   | Dredged sediment                                   | Flux measurements are an average over  |                               |
| PCB-18               | 2.1                              | -na-         |           | 5000                                      |     | PS   | from New Bedford                                   | an unspecified period of time typically  |                               |
| PCB-28               | 0.468                            | -na-         |           | 5000                                      |     | PS   | harbor Superfund                                   | a few hours. The dredged material was  |                               |
| PCB-44               | 0.227333                         | -na-         |           | 5000                                      |     | PS   | site. Bart Eklund's                                | in the form of a slurry.   |                               |
| PCB-52               | 0.438667                         | -na-         |           | 5000                                      |     | PS   | flux chamber used.                                 |  |                               |
| PCB-66               | 0.008215                         | -na-         |           | 5000                                      |     | PS   |  |  |                               |
| PCB-90/101           | 0.022067                         | -na-         |           | 5000                                      |     | PS   |  |  |                               |

**Table 7. Listing of available reported PCB fluxes from sediment/soil surfaces (contd.)**

| Compound              | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC | Site | Measurement<br>Type/Surface  | Special Notes  | Reference             |
|-----------------------|----------------------------------|--------------|-----------|---|-----|------|--|--|-----------------------|
| <b>PCB-151</b>        | 0.0015                           | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Mono CB</b>  | 0.201                            | -na-         | -na-      | 5000                                      |     | PS   |  |  | Bart Eklund (2001)    |
| <b>Total Di-CB</b>    | 6.06                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Tri-CB</b>   | 6.44                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Tetra-CB</b> | 1.926667                         | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Penta-CB</b> | 0.148                            | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Hexa-CB</b>  | 0.008767                         | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>PCB - 8</b>        | 0.84                             | -na-         | -na-      | 5000                                      |     | PS   | Dredged sediment   | Flux measurements are an average over an unspecified period of time typically a few hours. The dredged material contained a layer of water on top of the dredged solids representing a ponding situation in a CDF. | Bart Eklund (2001)    |
| <b>PCB-18</b>         | 1.23                             | -na-         | -na-      | 5000                                      |     | PS   | from New Bedford harbor Superfund site. Bart Eklund's flux chamber used. |  |                       |
| <b>PCB-28</b>         | 0.36                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>PCB-44</b>         | 0.165                            | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>PCB-52</b>         | 0.28                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>PCB-66</b>         | 0.0087                           | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>PCB-90/101</b>     | 0.0205                           | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Mono CB</b>  | 0.085                            | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Di-CB</b>    | 2.7                              | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Tri-CB</b>   | 3.93                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Tetra-CB</b> | 1.23                             | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Penta-CB</b> | 0.183                            | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Total Hexa-CB</b>  | 0.0042                           | -na-         | -na-      | 5000                                      |     | PS   |  |  |                       |
| <b>Aroclor 1254</b>   | 1.51                             | 10           | -na-      | -na-                                      |     | L    | Natural Evaporation of Aroclor 1254 from a spiked sand in a petri-dish   | Flux values calculated from reported mass loss rates of individual chlorinated groups using average composition of Aroclor 1254. Assumed the diameter of petri dish : 15 cm  | Rizwanul Haque (1974) |

**Table 8. Listing of available reported Furans/Dioxins fluxes from sediment/soil surfaces**

| Compound      | Flux<br>(ng/cm <sup>2</sup> /hr) | Cs<br>(ug/g) | T<br>(°C) | Air<br>Flowrate<br>(cm <sup>3</sup> /min) | %OC  | Site | Measurement<br>Type/Surface   | Special Notes   | Reference                   |
|---------------|----------------------------------|--------------|-----------|---|------|------|---|---|-----------------------------|
| Dibenzofuran  | 60                               | 40           | 23        | 100                                       | 1.2  | L    | Rouge River dredged material in laboratory flux chamb. Drying of thin sediment layers         | Flux reported as a function of time. Shown flux is the highest value measured at 2 hrs. Calculated air velocity: 2.8 cm/s                                 | Valsaraj et al., (1997),    |
|               | 100                              | 108          | 24        | 1700                                      | 2.6  | L    | Clean sediment inoculated with Phenanthrene, pyrene and Dibenzofuran. Laboratory Flux chamber | Flux reported as a function of time. Shown flux is the highest value measured Drying sediment with initial moisture:26% Calculated air velocity: 5.67cm/s | Ravikrishna et al., (1998); |
|               | 32                               | 66           | 24        | 1700                                      | 2.6  | L    | Clean sediment inoculated with Phenanthrene, pyrene and Dibenzofuran. Laboratory Flux chamber | Flux reported as a function of time. Shown flux is the highest value measured Drying sediment with initial moisture:48% Calculated air velocity: 5.67cm/s | Ravikrishna et al., (1998); |
| 7.3e3 (ng/hr) | -na-                             | -na-         | -na-      | -na-                                      | -na- | PS   | Bioreactor Slurry: 30 % wt/vol Creosote contaminated soil from a Superfund site.              | Reported Rate (ng/hr) from measured cumulative fugitive emissions from a bioreactor after 1 day   | R.F. Lewis, (1993)          |

was observed in the case where no water is added to the sediment after the start of the experiment. The fluxes of various congeners dropped to about 10-30 percent of the initial values in four days. For the other cases with the increase in the amount of water added, the fluxes were lower, but the decrease was also small (40-60%). Chiarenzelli et al. (1996, 1997(I)) studied the same system with a very small amount of sediment (0.25g) and thus all the sediment is in contact with the water. Chiarenzelli et al. (1997(II)) also measured PCB fluxes from subaqueous sand that was inoculated with Aroclor 1242, 1248, 1254 and 1260. The fluxes from these are compared with those from St. Lawrence River sediment. The total emissions from the individually inoculated sediments are reported as total PCBs. Cousins et al. (1997) reported flux from soil amended with PCB contaminated sludge as individual PCB congeners. Those experiments were conducted in a flux chamber. Eklund (2001) measured PCB emissions from a CDF with dredged material from New Bedford harbor. The fluxes were obtained from fresh dredged solid slurry and also with a layer of water on top of it.

## DIOXINS/FURANS

The only compound for which flux data was available was dibenzofuran. This is listed in Table 8. The reported fluxes were obtained in laboratory microcosms (US ACE, 1999b; Ravikrishna et al., 1998) using sediment from Indiana Harbor Canal and an inoculated sediment.

## SUMMARY

Chemical specific flux data was located for 21 of the 25 compounds in the IHC sediments identified as being substances of concern as air pollution risk. Data for volatile arsenic, zinc, 2,3,7,8 TCDF and 2,3,7,8 TCDD were not located. A total of 259 flux values are contained in this report. Reported flux measurements that did not match the vaporization processes that occur in a CDF were not included in this review. For example, emissions to air from aqueous solutions sparged or originating from water surfaces more characteristic of river, lakes etc. were excluded. Submerged sediments were also not included. At the CDF the dredged material arrives containing solids primarily and some amount of water. The soil is placed in layers and provisions made for the water to drain away, so that after a short period of time (i.e. a few days), the surface material is basically mud undergoing drying, consolidation and de-watering. Standing water in small pools may be present, but as time progresses, what remains is a soil-like solid material on the surface of the CDF. The flux data reflects the various soil-like materials, water or moisture contents, concentration levels and experimental apparatus types and operating procedures. Layered on top of this are the uncertainties of the analytical protocols used to isolate identify and quantify the various chemical species. A herculean effort may not put all these flux values on a common basis. The only attempt in this regard was to normalize the measured flux values to the concentration levels of the specific chemicals found in the IHC.

## MODELING CHEMICAL VOLATILIZATION FROM THE IHC CDF

The previous section was used to assemble general information about the theoretical process of chemical vaporization from soil-like surfaces and experimental data that closely mimics conditions of a CDF and its operation. A key outcome of the literature review was the selection of

the most appropriate model for use at CDF's. In this section the selected volatilization model will be applied specifically to the conditions and operation parameters forecast for the IHC CDF. In the first subsection the model will be given, along with modifications. It will then be extended and used to arrive at some general results about the volatilization fates of the chemicals of interest in the IHC CDF. The second subsection will be a comparison of chemical fluxes using the selected model and measurements based on the appropriate laboratory and/or field data.

## MODEL FORMULATION

The model selected has appeared previously in USACE and USEPA publications. The algorithms shown below appeared as Equation 39 in the ARCS Program report for estimating contaminant losses in remediation alternatives for contaminated sediments (USEPA, 1996). Development of the model commences with a Lavosier species mass balance in a dredged material column assumed infinite depth with the top surface adjoining the air. The transient mass balance quantifies the mass of A in the combined solid-water-air phases resulting in a partial differential equation resembling Fick's second law. A uniform chemical concentration,  $C_s$ , throughout the column is assumed. Using the "semi-infinite slab" boundary condition for unchanged concentration at great depth and a constant surface concentration,  $C_{si}$ , allows the conventional "semi-infinite slab" solution to be used. The flux expression obtained from the solution is equated to another one for the transport of A across the air-side boundary layer; this eliminates  $C_{si}$ ; and replaces it with  $C_{ai}$ . The instantaneous flux for chemical species i is :

$$n_e = \frac{\left( \frac{C_s H}{1000 K_d} - C_{ai} \right)}{\sqrt{D_{a3} \left( \epsilon_1 + \frac{K_d \rho_b}{H} \right) + \frac{1}{K_G}}} \quad (2)$$

where

$n_e$  = instantaneous flux of chemical A through the dredged material-air interface at time  $t$ , mg/cm<sup>2</sup> sec

$C_s$  = average concentration of chemical A in the dredged material, mg/kg

$H$  = Henry's constant, dimensionless

$K_d$  = contaminant specific equilibrium distribution coefficient, cm<sup>3</sup>/g

$C_{ai}$  = background concentration of chemical A in air at dredged material-air interface, mg/cm<sup>3</sup>

$B = 3.14159 \dots$

$t$  = time since initial exposure, sec

$D_{A3}$  = effective vapor diffusivity of chemical A in the dredged material pores, cm<sup>2</sup>/sec

$\epsilon_1$  = air-filled porosity, dimensionless

$\rho_b$  = bulk density, g/cm<sup>3</sup>

$K_G$  = gas side mass transfer coefficient, cm/sec

Equation 2 is an idealized transport model that describes chemical movement in the

unsaturated zone near the air-dredged material interface and finally into the bulk air above. The chemical emission pathways modeled include surface depletion, desorption from the particle surfaces into a surrounding water film (hence, the appearance of  $K_d$ ), desorption from the water film into the pore gas (hence, the appearance of  $H$ ), and vapor phase diffusion in the dredged material pore spaces (hence, the appearance of  $D_{A3}$ ,  $D_a$ , and  $D_b$ ). It appears at the solid-air interface. Once here it must finally move through the air-side boundary layer (hence, the appearance of  $K_G$ ). At this point it arrives in the bulk air mass that is moving across the surface of the CDF.

An algebraic modification of the instantaneous flux equation aids in its interpretations. Multiplying the top and bottom of Eq. 2 by  $K_G$  yields

$$n_e = \frac{K_G \left( \frac{C_s H}{1000 K_d} - C_{ai} \right)}{\sqrt{\frac{\pi K_G^2 t}{D_{A3} \left( \varepsilon_1 + \frac{K_d \rho_b}{H} \right)} + 1}} \quad (3)$$

In this form the numerator is the maximum flux,  $n_e$  (MAX), which occurs at time  $t=0$ . The coefficient  $K_G$  times the bracketed concentrations is that flux which results if the chemical always remains available on the surface layer of the dredged material in the CDF. In reality this does not occur. As time progresses the surface layer becomes depleted of its load of chemical mass available for volatilization. In other words the surface layer becomes “weathered”. The group of terms in the denominator accounts for this weathering-away of the volatile and semi-volatile chemicals, it is defined as the “weathering factor”,  $W_f$ :

$$W_f = \left( \sqrt{\frac{\pi K_G^2 t}{D_{A3} \left( \varepsilon_1 + \frac{K_d \rho_b}{H} \right)} + 1} \right)^{-1} \quad (4)$$

Initially  $W_f = 1$  but as time progresses it becomes small; much smaller than unity. These small values acknowledge mathematically the realities of the process of chemical vapor production and release which occurs within the dredged material soil-like porous matrix. Clearly, in simple terms the instantaneous flux given by equation Eq. 3, can be written  $n_e = n_e(\text{MAX})Q(W_f)$ . Viewed in this context,  $W_f$  is the factor by which the maximum flux must be adjusted downward to produce the actual instantaneous flux. It is NOT the fraction of volatile chemical mass remaining in the dredged

**Table 9. Thermodynamic and Transport Parameters  
Specific to Chemicals in IHC CDF**

| Chemical             | H<br>(-) | K <sub>d</sub><br>(L/kg) | K <sub>gf</sub> - (day)<br>(cm/h) | K <sub>gn</sub> - (day)<br>(cm/h) | D <sub>a3</sub><br>(cm <sup>2</sup> /h) | k <sub>s</sub><br>(h <sup>-1</sup> ) | t <sub>99</sub><br>(days) |
|----------------------|----------|--------------------------|-----------------------------------|-----------------------------------|---|--------------------------------------|---------------------------|
| Naphthalene          | 0.01828  | 1.80E+02                 | 777.0                             | 2438.1                            | 9.12                                    | 3.01E+02                             | 1.36E+00                  |
| 2-Methyl Naphthalene | 0.01775  | 1.19E+03                 | 667.3                             | 2097.3                            | 7.26                                    | 5.55E+01                             | 7.36E+00                  |
| Anthracene           | 0.01331  | 3.36E+03                 | 696.0                             | 2186.7                            | 7.73                                    | 1.39E+01                             | 2.94E+01                  |
| Phenanthrene         | 0.00170  | 2.86E+03                 | 695.8                             | 2185.9                            | 7.73                                    | 2.09E+00                             | 1.96E+02                  |
| Pyrene               | 0.00109  | 1.34E+04                 | 667.3                             | 2097.3                            | 7.26                                    | 3.05E-01                             | 1.34E+03                  |
| Benzo(a)anthracene   | 0.00013  | 2.07E+04                 | 640.6                             | 2014.3                            | 6.83                                    | 2.44E-02                             | 1.67E+04                  |
| Benzo(k)fluoranthene | 0.00158  | 1.06E+05                 | 619.6                             | 1948.9                            | 6.50                                    | 6.21E-02                             | 6.58E+03                  |
| Benzo(a)pyrene       | 0.00014  | 2.70E+05                 | 619.6                             | 1948.9                            | 6.50                                    | 2.12E-03                             | 1.93E+05                  |
| Dieldrin             | 0.00097  | 2.02E+03                 | 540.1                             | 1701.2                            | 5.29                                    | 1.19E+00                             | 3.42E+02                  |
| Chlordane            | 0.00248  | 1.02E+04                 | 667.3                             | 2097.3                            | 7.26                                    | 4.41E-01                             | 9.26E+02                  |
| p,p-DDT              | 0.00124  | 3.21E+04                 | 553.2                             | 1742.0                            | 5.48                                    | 9.24E-02                             | 4.42E+03                  |
| Heptachlor           | 0.06450  | 3.73E+03                 | 527.1                             | 1660.7                            | 5.10                                    | 4.46E+01                             | 9.16E+00                  |
| Aroclor 1248         | 0.08573  | 1.72E+04                 | 588.8                             | 1853.0                            | 6.02                                    | 1.09E+01                             | 3.75E+01                  |
| Aroclor 1254         | 0.03701  | 6.70E+04                 | 567.9                             | 1787.8                            | 5.70                                    | 1.27E+00                             | 3.20E+02                  |
| Benzene              | 0.22500  | 4.85E+01                 | 916.5                             | 2871.0                            | 11.68                                   | 1.48E+04                             | 2.75E-02                  |
| Ethylbenzene         | 0.37600  | 1.72E+02                 | 827.4                             | 2594.6                            | 10.02                                   | 8.16E+03                             | 5.00E-02                  |
| Toluene              | 0.28900  | 9.69E+01                 | 867.0                             | 2717.3                            | 10.75                                   | 1.04E+04                             | 3.93E-02                  |
| Xylenes              | 0.45600  | 1.72E+02                 | 827.0                             | 2593.3                            | 10.02                                   | 9.90E+03                             | 4.12E-02                  |
| Dibenzofuran         | 0.00300  | 1.40E+03                 | 709.6                             | 2228.8                            | 7.96                                    | 1.01E+01                             | 4.04E+01                  |
| 2,3,7,8,TCDD         | 0.00061  | 3.13E+05                 | 581.0                             | 1828.7                            | 5.90                                    | 1.23E-02                             | 3.32E+04                  |
| 2,3,7,8 TCDF         | 0.00056  | 2.32E+05                 | 571.2                             | 1798.2                            | 5.75                                    | 1.58E-02                             | 2.59E+04                  |

material mass. It more appropriately applies for millimeter to a few centimeter thick layers on the surface since the vaporization losses typically accounts for only a fraction of 1% of the initial quantity of each chemical in the deep soil layers.

For risk assessment purposes the average chemical flux over a defined period of exposure time,  $t_e$ , is a more useful result. Integrating Eq. 2 from  $t=0$  to  $t=t_e$  yields the average flux  $\bar{n}_e$ .

$$\bar{n}_e = 2K_G \left( \frac{C_s H}{1000K_d} - C_{ai} \right) \left( \frac{1}{\sqrt{k_s t_e}} + \frac{1}{k_s t_e} \ln \left( \frac{1}{\sqrt{k_s t_e} + 1} \right) \right) \quad (5)$$

where  $k_s / B K_G^2 / D_{A3} (1 + K_d D_B / H)$  is the soil weathering decay constant with units of  $s^{-1}$ . This constant is very chemical specific and plays a key role in regulating the flux.

The chemodynamic parameters in the sediment volatilization decay constant are of two general types. These are the thermodynamic ones and the transport ones. Algorithms are needed in order to provide numerical values for each. The thermodynamic parameters are the Henry's

constant,  $H$ , and the equilibrium distribution coefficient,  $K_d$ . Much information exist by which to estimate both these thermodynamic parameters. Table 9 contains both  $H$  and  $K_d$  for the substances of interest in the IHC dredged material. The transport parameters are:  $D_{A3}$ , the effective chemical vapor phase diffusion coefficient in the soil pore spaces and  $K_G$  is air-side mass-transfer coefficient. These in turn depend upon various soil and boundary layer characteristics. Algorithms for these are as follows:

$$D_{a3} = D_{A1} \cdot \tau^{10/3} / \tau_a^2 \quad (6)$$

where  $D_{A1}$  is the molecular diffusivity of the chemical species in air,  $\text{cm}^2/\text{s}$ .  $\tau$  is the air filled soil porosity and  $\tau_a$  is the total soil porosity; both have dimensions of  $\text{cm}^3/\text{cm}^3$ .

$$K_G = K_{Gf} + K_{Gn} \quad (7)$$

where  $K_G$  is the forced convection air-side coefficient. It consist of the one for forced convection,  $K_{Gf}$ , and that for natural convection,  $K_{Gn}$ . The algorithms for these are:

$$K_{Gf} = 0.036 \frac{D_{A1}}{F} \left( \frac{FV_z}{\nu_a} \right)^{4/5} \left( \frac{\nu_a}{D_{A1}} \right)^{1/3} \quad (8)$$

and

$$K_{Gn} = 0.5 \left( \frac{D_{A1}^2 g}{\nu_a} \right)^{1/3} \left\{ \left[ \frac{T_s - T_a}{T_s} \right]^{1/3} + 0.724 \left[ \frac{P_s - P_a}{P_T} \right]^{1/3} \right\} \quad (9)$$

where

$F$  = the average fetch of the dredged material pile, cm

$V_z$  = the average wind speed, cm/s

$\nu_a$  = the viscosity of air at the average air temperature  $T_a$  (K/),  $\text{cm}^2/\text{s}$

$g$  = the gravitational constant ( $980.7 \text{ cm/s}^2$ )

$T_s$  = the average soil surface temperature, K/.

$T_a$  = air temperature, K/.

$P_s$  = the water vapor pressure at the average soil surface temperature

$P_a$  = the product of the water vapor pressure at the average air temperature, ( $P_s, P_a$ ) times the respective fractional relative humidity.

$P_t$  = is the total atmospheric pressure,  $1.01\text{E}5 \text{ Pa}$ .

In both cases  $K_G$  is in cm/s. Both the forced convection (Eq. 8) and the natural convection correlations (Eq. 9) are based on turbulent conditions in the atmospheric boundary layer. The use of these will produce the highest flux estimates.

Because of the vast difference in meteorological conditions between day and night it is appropriate for the transport coefficient to reflect this occurrence. At night time the winds are calm and the boundary layer is stable (i.e.  $K_{Gf} \cdot 0$ ). Typically in the daylight hours the surface winds are significant and the boundary layer is unstable. A warm or hot soil temperature enhances the transport significantly. The use of average night vs day wind speed and soil surface temperature will capture this difference. Table 9 contains a listing of the transport coefficients for average daytime environmental conditions expected at the IHC CDF and Table A1 in the Appendix A contains the environmental variables used.

## THE EVAPORATIVE FATE OF CHEMICALS ON SOIL SURFACES - SOME GENERAL ASPECTS

In this section some general aspects of the evaporative fate of chemicals on soil surfaces will be presented. The numerical results presented will reflect the proposed IHC CDF operation in general and day-time environmental characteristics specifically.

In a previous section the weathering factor,  $W_f$ , was defined by Eq. 4. Expressed in terms of the soil weathering decay constant, which was defined along with Eq. 5, it becomes:

$$W_f = \frac{1}{\sqrt{k_s t + 1}} \quad (10)$$

As the group  $\sqrt{k_s t}$  increases with time,  $W_f$  decreases and so does the flux by equivalent amount. If  $C_{ai} = 0$  or is much smaller than  $C_s H / 1000 K_d$ , then  $W_f$  also tracks the behavior of the soil surface particles chemical concentration. This decay of the soil surface concentration is important with regard to the risk posed by dust originating from the surface of the dredged material in the CDF. Obviously  $k_s$ , the soil weathering decay constant for each substance is an important term. Table 9 contains a listing of values for average daytime conditions.

### EVAPORATIVE HALF-LIFE

Clearly if  $W_f = 0.5$  in Eq. 10, the effective concentration on the soil surface is half the original. In this case  $t = J_{1/2}$  and from Eq (10) the evaporative half life can be obtained as:

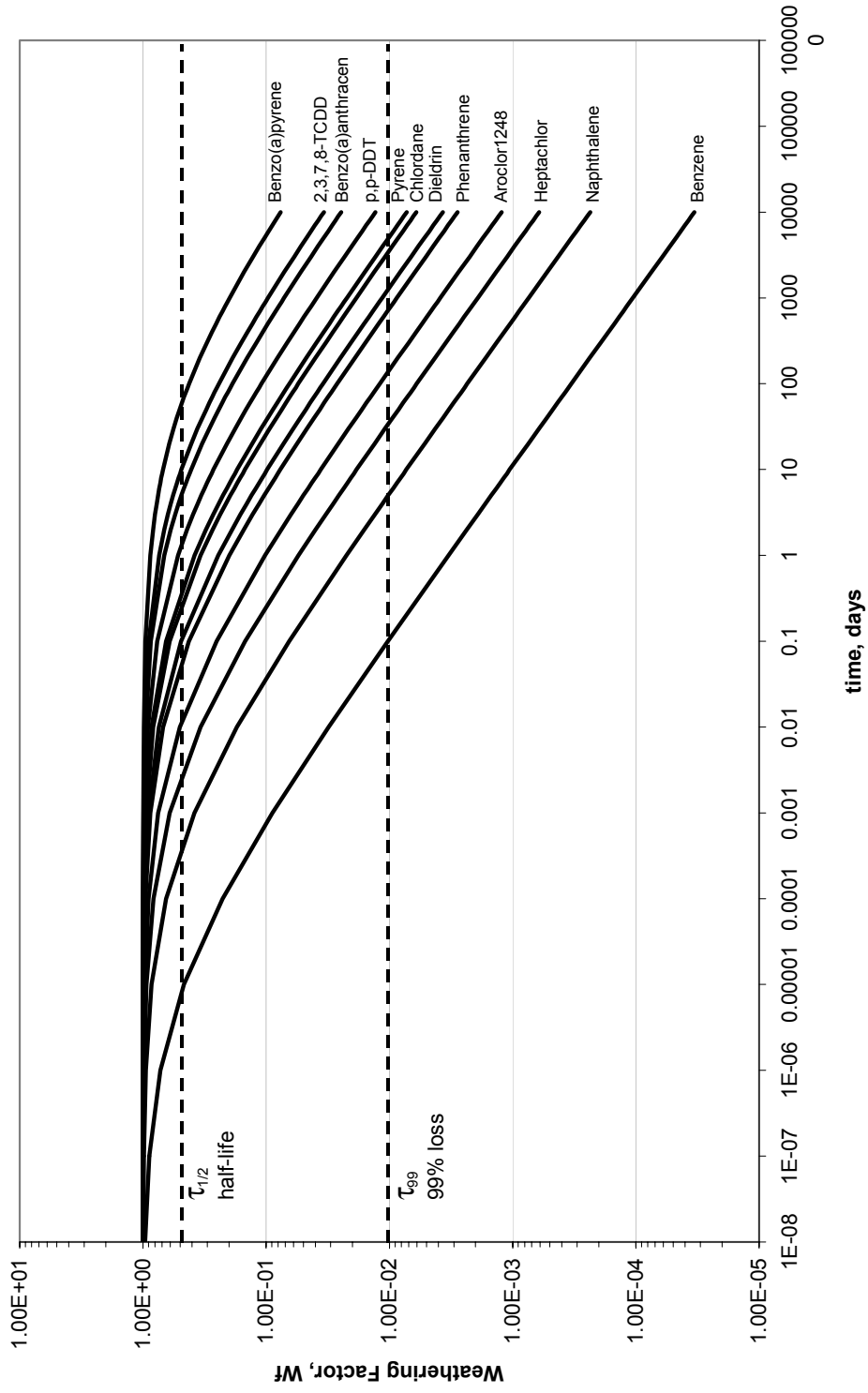
$$J_{1/2} = 1/k_s \quad (11)$$

In a similar fashion if 99% loss is considered the evaporative life-time then  $W_f = 0.01$  and  $t = J_{99}$  to yield

$$\tau_{99} = 9801/k_s \quad (12)$$

Numerical values of the evaporative lifetimes for each chemical on the surface layer appears in Table 9.

Figure 2. Theoretical Behavior Surface Layer Flux Evaporative Weathering Factor



A graphical illustration of the theoretical behavior of the weathering factor for twelve of the chemicals appears in Figure 2. Logarithmic axes are used for the  $W_f$  and the time variables so as to capture the ranges of variation. Horizontal lines representing half-life and 99% loss are shown. All  $W_f$  curves are arbitrarily terminated at 10,000 days (27 years) evaporation time. The message in this exercise is that due to the mix of very volatile and semi-volatile chemicals in the IHC dredged material there are extremely large variations in the evaporative potential of the chemicals present. For example benzene is essentially gone from the surface in a day while pyrene persist on the surface for a much longer time and benzo(a)pyrene is very resilient to evaporation and remains in high concentrations for most of the operating life-time of the IHC CDF.

## CONGRUENCE OF MODEL PREDICTED AND MEASURED EVAPORATIVE FLUXES

At the onset it should be realized that any attempt at trying to compare the results of a theoretical model with reported measurements is an activity performed on an “uneven playing field” so to speak. The broad outline of this attempt is to scale numerous sets of laboratory measurements, primarily, to the volatile emissions modeled on the field-scale. No attempt was made to model the emission process of the individual laboratory experiments for which data was obtained other than the specific experiments with the IHC sediments. These will be discussed separately. The other measurements reflect the apparatus designs of the various investigators conducting emission flux measurements. However, both the experimentalists and the modelers will agree that the flux is proportional to the chemical concentration on the soil. Therefore, the reported experimental chemical fluxes were adjusted to that projected for the IHC dredged material by the ratio of concentrations. Otherwise, no adjustments were made to the reported laboratory flux data. Depending upon the aggressive nature of the gas (i.e., air,  $N_2$ , etc.) to solid particle (i.e., bed of soil or sediment) interaction and the size of the apparatus etc., a large range of measured flux are possible. And indeed a large range of flux measurements were located (see Tables 4-8). The variation was reduced however when the fluxes were concentration normalized.

The study reported by Woodrow et al. (1997) produced an algorithm for estimating the maximum flux from a soil-like surface to air; see Eq.1 above. The numerator of the theoretical emission model is this maximum flux (see Eq. 2 above). Using the average parameters reflective of the IHC CDF (mol.wt 300 g/mol, air-side coefficient 6.23 m/h, temperature 25°C and soil bulk density 1.2 Kg/L) yields the following equation:

$$n_A = (6.28 \text{ e7 / } ) (VP \cdot AR / K_{OC} \cdot S_w) \quad (13)$$

where  $\delta$  mm is the effective depth of soil penetration of the applied chemical. Using a value of 0.25 mm followed by natural logarithm transformation yields

$$\ln(n_e) = 19.34 + 1.00 \ln (VP \cdot AR / K_d \cdot S_w) \quad (14)$$

This theoretical equation can be compared to the one based on laboratory measurements, Eq. 1; they are practically identical. Therefore, the theoretical model supports the maximum flux measurements

derived regression equation both in algebraic form and in the numerical constants reported. The maximum flux is controlled by the mass-transfer resistance that exist within the atmospheric boundary layer (ABL) very near the soil surface. The chemical in volatile form is readily available at the surface so that its rate of evaporation is controlled by the  $K_G$  only.

Theoretically and practically, this maximum flux cannot continue indefinitely. A time period of evaporation will occur when the surface quantity is depleted and additional release must come from chemical quantities within the soil column. Equation 3 contains the theoretically correct algebraic function reflective of the process chemistry that causes the reduction in the instantaneous flux with increasing time. Figures 3 through 6 display the flux vs. time behavior of benzo(a)pyrene, dieldrin, Aroclor 1248 and benzene. Although good for model and data comparisons the log-log flux vs. time graphical behaviors do not capture the real-time flux function. In reality, after a very short time interval, of minutes to hours, the chemical flux falls dramatically and continues to decrease with increasing time. Theoretically a zero flux is never achieved but it nevertheless falls to very low values due to smallness of the  $1/t$  function at large  $t$  values. These four chemicals were chosen to reflect varying emission flux attenuation rates depending on their chemical properties and also to represent four categories of organic chemicals in the IHC sediments. Similar graphical presentations for other chemicals listed in Table 1 appear in Appendix A (figures A.1 through A.19). In all these figures, the model predicted fluxes were obtained using average dredged material properties (i.e., bulk density of  $1.2 \text{ g/cm}^3$ , organic carbon fraction of 0.14, air-filled porosity of 0.3 and total porosity of 0.7) and median sediment concentrations listed in Table 1. The other relevant thermodynamic and transport parameters used in the model are shown in Table 9. These model predicted fluxes are compared with reported measured fluxes normalized to the median chemical concentrations expected in the IHC dredged materials.

The log-log graphical presentation of the flux for each chemical as a function of time allows the reader to appreciate several facts about the model, the available data and the operation of the CDF all on a single page. First the solid and dashed lines represent the time averaged and the instantaneous fluxes respectively. For early times, the average flux is equal to the instantaneous, but they diverge as time becomes large. The average is always larger than the instantaneous. Also the flux for average day time conditions (i.e. 10 mph wind,  $35^\circ\text{C}$  soil surface,  $30^\circ\text{C}$  air and 50% soil vapor and 27% air relative humidity) and average night time conditions (i.e. 3 mph wind,  $15^\circ\text{C}$  soil surface,  $15^\circ\text{C}$  air and 100% soil vapor and 100% air relative humidity) appear on the graphs. Both the increased wind speed and high soil surface temperature result in the day time instantaneous flux being approximately ten times higher than the night time flux early on. See the benzo(a)pyrene flux for the first 100 days shown in Figure 3 for example. As evaporation time gets larger, the day time and the night time fluxes converge. This occurs because at large times the evaporation is controlled by conditions of release deep within the soil column so that meteorological variation in the ABL are of no consequence. Benzo(a)pyrene is very resilient to evaporation. Its 99% evaporation time (i.e.,  $J_{99}$ ) from the surface is projected to be 328 years; see Table 9. This results in a flux vs. time behavior that is constant for an extended time period. Only two measured fluxes were located and they fall with the average day to night time model predicted fluxes. The 10,000 days (27 years) time axis maximum roughly represent the thirty year life-time projected for the IHC CDF. The other two vertical time lines represent convenient average times that can be used in estimating average fluxes for the purposes of exposure. The 400 day time line represents the number of days, at an average

Figure 3. Benzo(a)Pyrene - Comparison of Model Predicted and Reported Fluxes

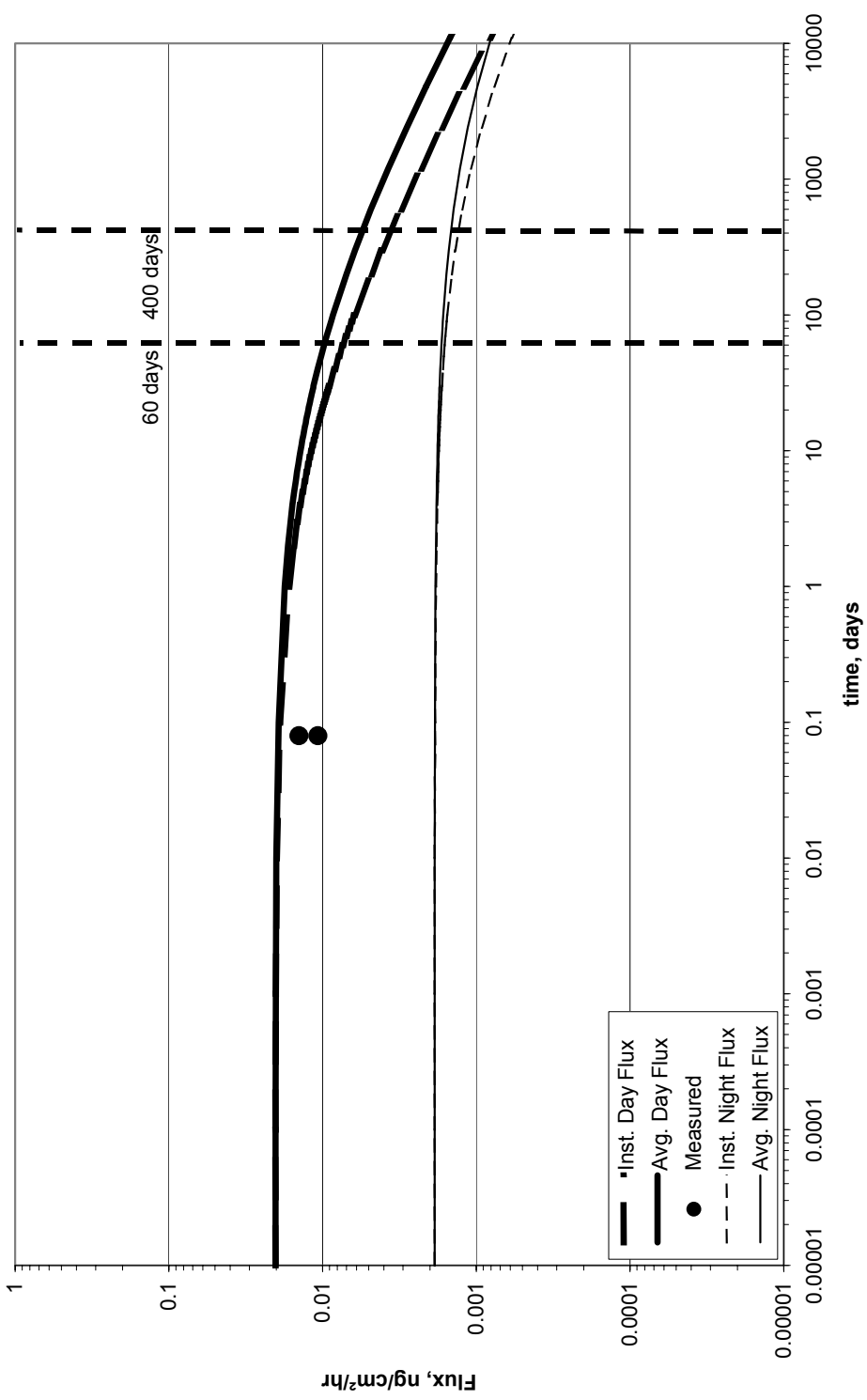


Figure 4. Dieldrin - Comparison of Model Predicted and Reported Fluxes

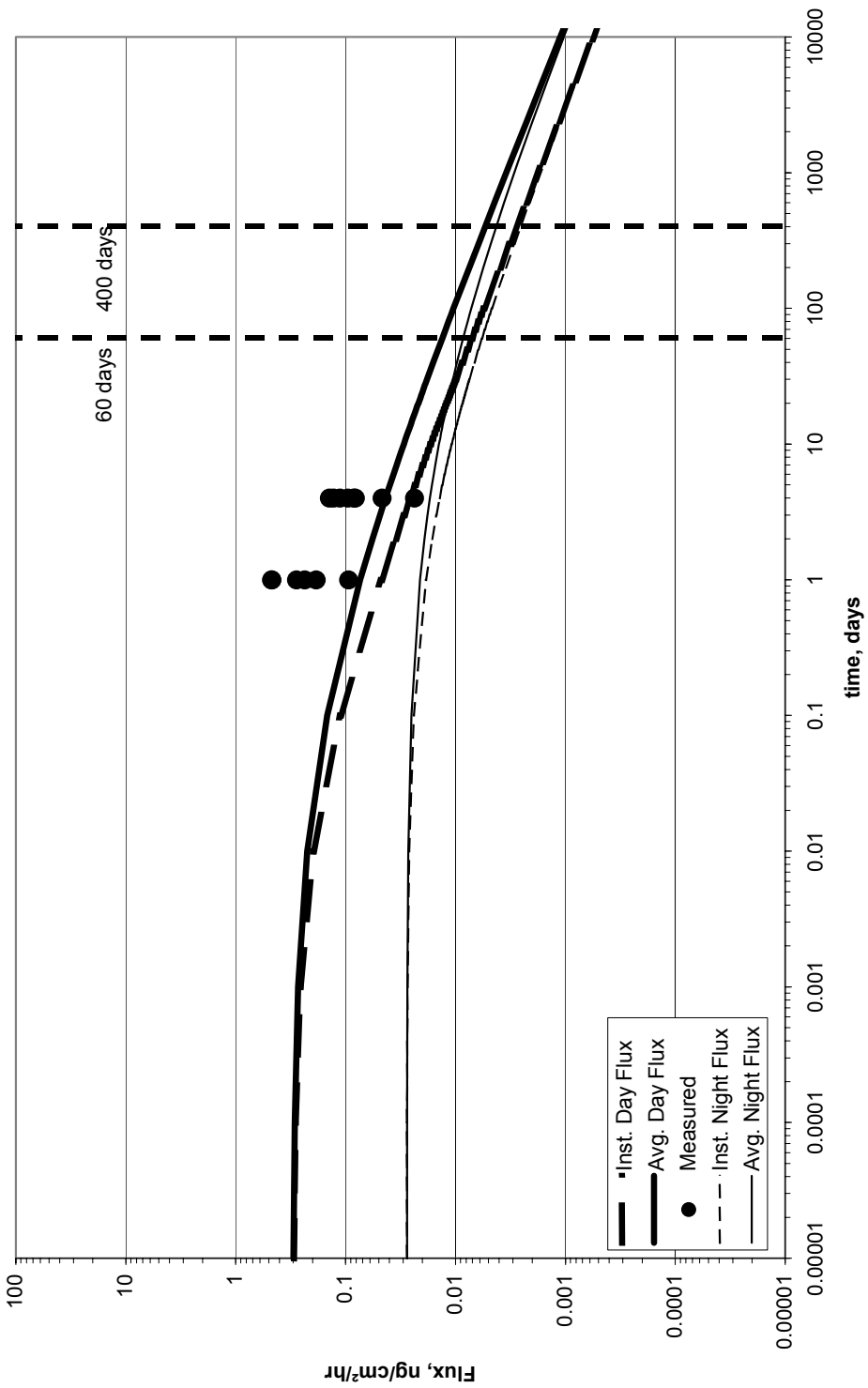


Figure 5. Aroclor 1248 - Comparison of Model Predicted and Reported Fluxes

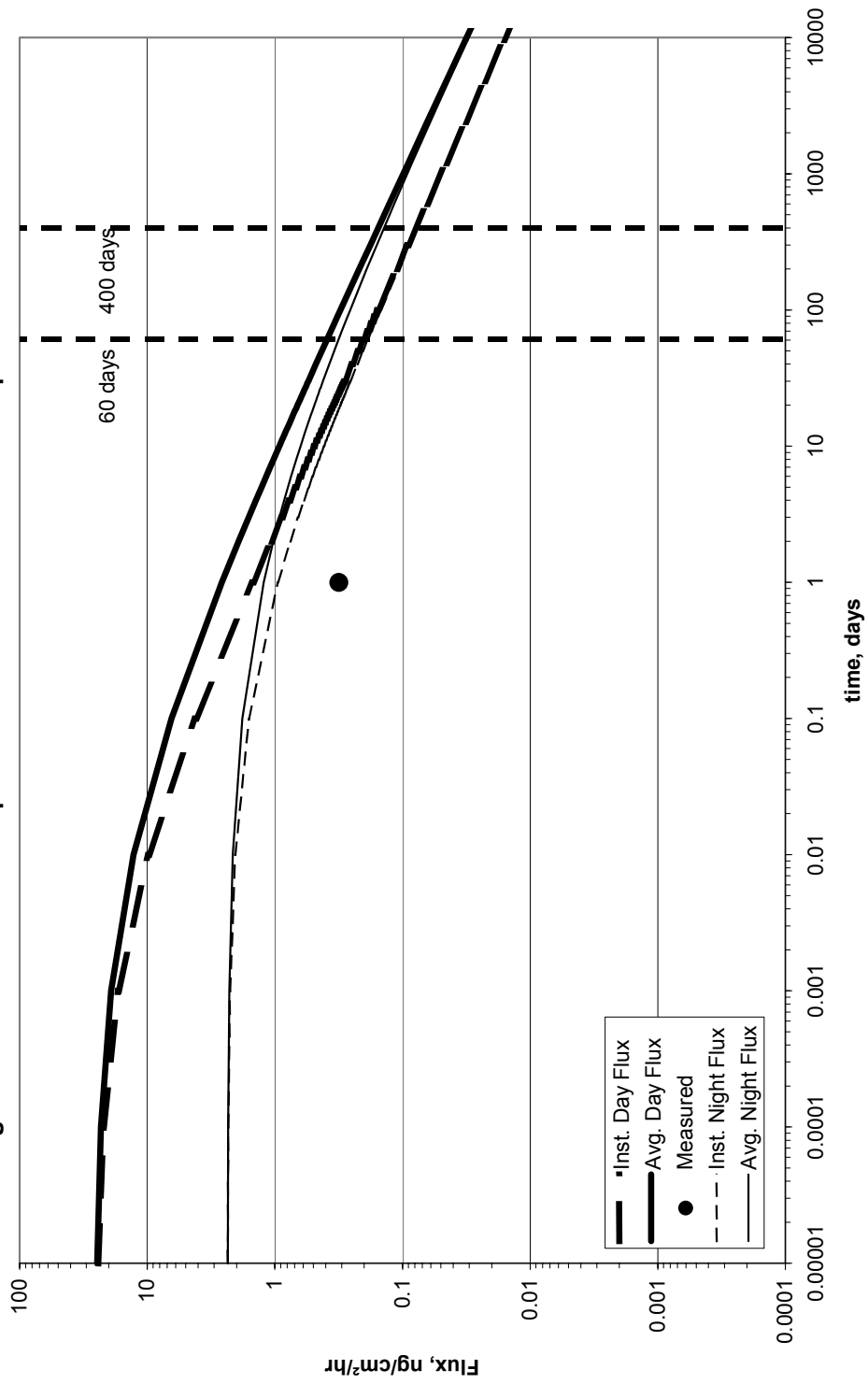
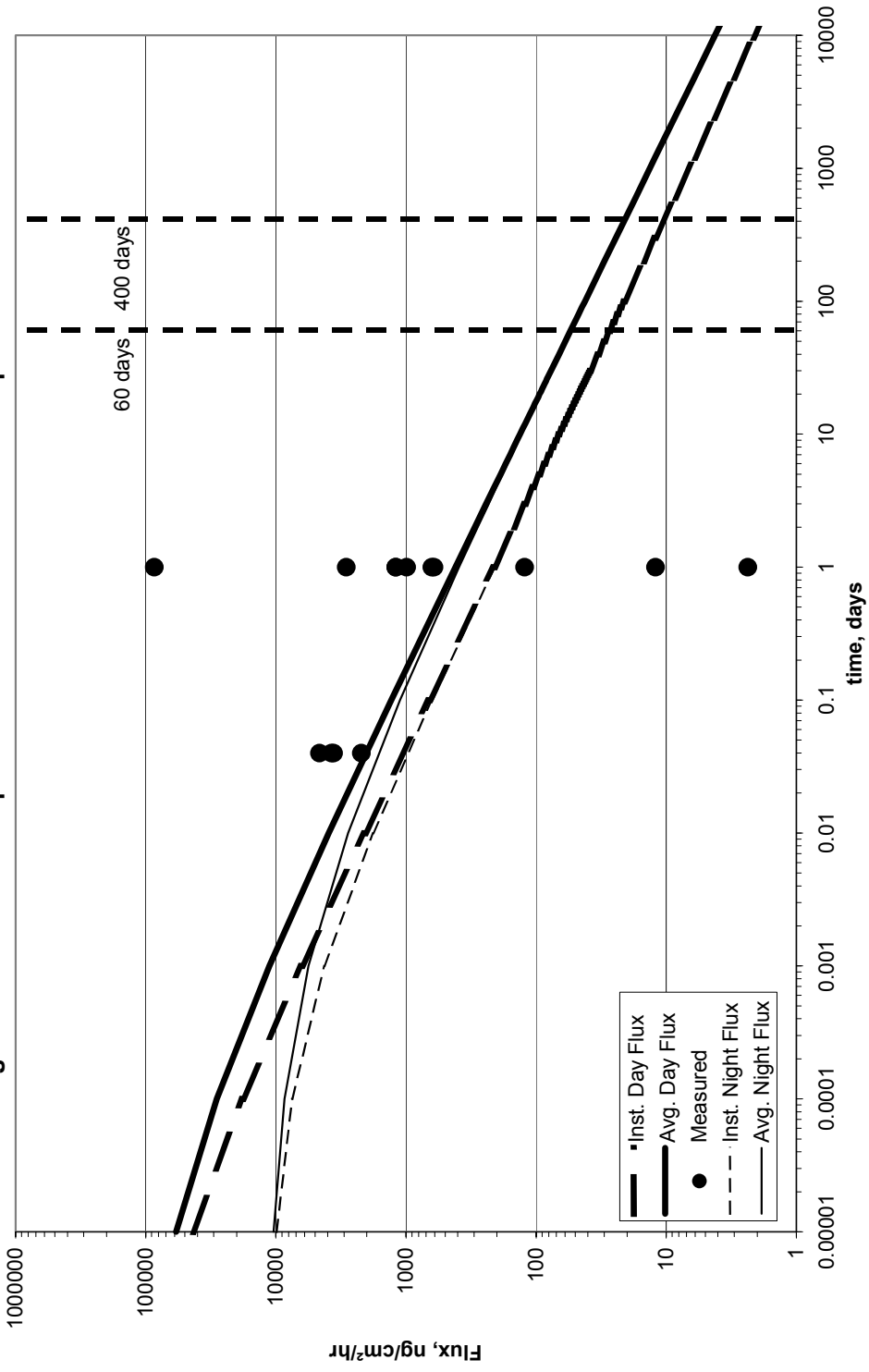


Figure 6. Benzene - Comparison of Model Predicted and Reported Fluxes



filling rate of 511 CY per day, place one layer of dredged material over the entire 131 acres of the CDF. This calculation assumes each cubic yard yields 27 square feet of exposed area. The 60 day time line is a slightly more conservative average time that represents realistic CDF operational events that may cause enhanced flux to air. Such operational events include wind-rowing the dredged material and rain storms that may re-wet the surface. In the laboratory, both surface sediment reworking and re-wetting of certain sediments have been demonstrated to cause the flux to increase to maximum or near maximum values. Using a 60-day averaging time in effect restarts the weathering process by placing fresh material with corresponding initial concentration directly on the surface every 60 days. These lines appear on the graphical presentations for each chemical.

Figure 4 is for dieldrin, a pesticide. It is not as persistent in the dredged material as benzo(a)pyrene; its  $J_{99}$  is 340 days. Significant flux reductions occur in the 60 to 400 day evaporative time periods. Several flux measurements representing two laboratory studies are shown in the figure. They are slightly higher than the model projected ones but nonetheless show a decrease with increasing time in parallel with the model projections. The difference in fluxes can possibly be explained by the difference in the organic carbons contents of the IHC sediment (0.14) shown in the simulation and the soils used in the study reporting the dieldrin flux (0.0058). It must be further noted that all the organic carbon contents, where reported along with the flux values, were lower than 14% used in the simulations. Higher organic carbon content implies a higher  $K_d$  value and correspondingly lower vapor phase chemical concentration available for transport. The model uses a higher organic carbon content and hence predicts much lower vapor phase concentration than what might have been the case. The model therefore under-predicts the fluxes since the reported fluxes were not normalized to a common organic carbon content. Using an organic carbon content of 0.0058, the model projected curves match or slightly over predict the reported dieldrin fluxes.

Figure 5 shows the comparison for Aroclor 1248, a commercial PCB mixture. Only one data point is reported on this figure. From Table 9, the  $J_{99}$  of 37.5 days indicates that this is far less persistent in the CDF than dieldrin or benzo(a)pyrene. The model projected curves slightly over-predict the reported flux. Further analysis of the performance of the model with respect to Aroclor 1248 is not appropriate until further experimental fluxes are obtained.

Figure 6 shows the comparison for benzene, a volatile organic compound (VOC). The projected and reported fluxes are very high but not controlled by the air side mass transfer coefficient. In Table 9, benzene shows a  $J_{99}$  of 0.0275 days (or about 40 minutes). Benzene has a very high vapor pressure and Henry's constant that explain the volatility of the compound. The evaporation of benzene is controlled almost entirely by the sediment-side mass transfer resistance represented by the soil-air partition constant and the effective diffusivity. The reported fluxes shown in the figure are derived from two sources. The first set represent laboratory data from Dupont (1986) and are close to the projected fluxes. The second set of fluxes were the field studies of Eklund et al.(1991) and represent a number of different sources. The concentration normalized fluxes are spread across the model projected fluxes over several orders of magnitude. In the absence of any extra information that could help in critiquing this data with the appropriate qualifiers, further analysis is not possible.

Figures A.1-A.7 show the comparison for other PAHs listed in Table 1 in the increasing order or persistence in the CDF. The  $J_{99}$  values for all these compounds are listed in Table 9. The comparison of model projections and reported flux is close for naphthalene, 2-methyl naphthalene, phenanthrene and pyrene which have a  $J_{99}$  of 1.36, 7.36, 196 and 1340 days respectively. As the  $K_d$  values of these compounds increase there is a very significant increase in their persistence levels in the CDF. There are few reported flux data for the remaining compounds, anthracene, benzo(a)anthracene and benzo(k)fluoranthene with one or two fluxes and the comparison is not as close. Figures A.8 - A.10 show the comparison for the remaining pesticides listed in Table 1. The reported fluxes of p,p-DDT fall within and slightly above the predicted flux zone. Reported values of chlordane and heptachlor fall above the predicted fluxes. Figure A.11 shows the comparison for Aroclor 1254 and the two reported flux values fall within the predicted flux curves. Figures A.12 through A.16 show the comparison for the remaining VOCs (ethylbenzene, toluene and three xylene isomers). Several of the reported flux values fall very close to the predicted curves. These compounds have very short persistence times similar to that of benzene. Figures A.17, A.18 and A.19 show the predicted fluxes for the dibenzofuran, 2,3,7,8 TCDF and 2,3,7,8 TCDD respectively. Only dibenzofuran has any reported flux values and they fall close to the predicted fluxes. The projected fluxes for TCDF and TCDD show very long  $J_{99}$  values of the order of 3300 and 2590 days.

Although the projected fluxes displayed in Figures 3 through 6 decreased by factors of ten, one hundred and even more in the case of benzene, significant mass of each substance remains in the CDF dredged material. A ten or hundred fold reduction in flux does not equate to a 90% and 99% reduction in chemical mass in the soil column. Only a thin layer of the surface soil experiences any depletion of chemical mass. This partially depleted layer is very thin in the case of Benzo(a)pyrene, being less than 1 mm. In the case of Benzene, which is the most volatile substance under consideration, the partially depleted layer may be a few centimeters thick. Ravikrishna et al. (1997) report that for a 10 cm deep laboratory column of dredged material 0.84 mg of the initial 125 mg of phenanthrene was lost in 28 days. This is a depletion of 0.67% and 99.33% remained. In another experiment with phenanthrene in IHC dredged material a 61 cm deep field scale test, ~73 mg of the initial 9390 mg was vaporized over 70 days. This is 0.77% vaporized and 99.2% remaining (Ravikrishna et al., 2001). Chiarenzelli et al. (1996) performed laboratory test that reflected the volatilization that does occur in thin surface layers. Using a layer ~0.002 cm in thickness, it was observed that 26 to 27% of the substance of the St. Lawrence River Sediment PCB was vaporized in 24 hours. This result is generally consistent with the soil surface weathering factor for Aroclor 1248 shown in Figure 2. This figure shows the Aroclor 1248 flux decreasing ~90% in the first day.

Some of the compounds shown in Figures 3 through 6 and in Appendix A do not show very close comparison between the model projections and reported values. There might be several reasons and explanations for that. In cases such as chlordane and anthracene, the reported values of Henry's constant, which is critical to the calculation of the soil-air partition constant, vary widely across several orders of magnitude (Mackay et al., 1992). This imparts significant uncertainty to the predicted flux values. Furthermore, the lack of a statistically significant number of reported flux values is not available to quantify the closeness of match between the experimental and predicted fluxes. On a more realistic point of view, the projected fluxes are a result of analytical solutions easily performed on a hand calculator and therefore use average properties that represent a long

period of time. Significant local variations with respect to time and space might occur that may fall outside the confidence limits of the projected curves. It is often difficult to accurately place or correlate a reported data point to the average conditions used in the model simulations without adequate information regarding the experimental conditions.

A close study of the 97 data points used in Figures 3 through 6 and the remainder in the appendix suggest that the model predicted instantaneous fluxes generally tend to be higher than the measured values. For 10% of the measured values the model predictions are nearly identical. For 51% the measured fluxes are below the model values. So, for 61% of the time the model predicts or over-predicts the measured fluxes. The measured fluxes exceed the modeled ones in 5% of the cases by more than a factor of 10. Somewhat better model vs. data congruence occurs with test using IHC sediments. As part of the Design Documentation Report (DDR) the Chicago District of the US ACE did an independent analysis of the measured values found in the US ACE (1997) report. This report consists of laboratory studies performed at the Corps' Waterways Experiment Station (WES), Vicksburg and consist of five flux tests with IHC sediments. A summary given by the reviewer is presented in the following paragraph.

“For the experiment a total of 2,184 analyses were completed (91 compounds at 24 separate time intervals). From the total number of analyses completed there were 266 (12%) that were detectable and 226 (10%) estimated but below the detection limit (J-values). The J-values were treated as actual values, however, because using the estimated values in this manner the actual flux from the experiment could be over estimated. In most cases the modeled fluxes exceeded the measured fluxes confirming the conservative nature of the model used in the CMP (US ACE 1999a-Appendix V). Modeled fluxes exceeded measured fluxes on average by 16 times for PCB congeners, and 30 times for PAHs. However, a total of 25 (5.1%) of the 492 detectable and estimated values produced measured fluxes which exceeded calculated fluxes for some of the time steps for PCBs (54, 114, 121, 159), Benzo(a)pyrene, Benzo(ghi)perylene, Benzo(k)Fluoranthene, Chrysene, Naphthalene and Pyrene. The range for cases where measured flux exceeded calculated flux was from 1.2-5.5 times for the PCBs and 1.4-38 times for the PAHs. In summary, the comparison of measured flux to modeled flux indicates that the model is conservative in that it overestimates the actual flux. On average, these results showed an exceedence of at least 1 order of magnitude (10x). For a few compounds, at low flux rates the model under predicted volatilization. However, given that these differences, either occurred at low rates or were only slightly lower, and that the experimental design was setup to maximize flux, the model functioned well for a screening level estimate.”

## CHEMICAL EMISSIONS ATTENUATION AND ENHANCEMENT FACTORS

The instantaneous flux equation, Eq. 2, provides the theoretical basis for quantifying the emission to air. As has been demonstrated above, it gives realistic numerical estimates. Further, it has undergone both laboratory and field testing. When used for estimating emissions, a fairly rigorous simulation regime must be followed. Time  $t$ , is the only independent variable and the flux to air,  $n_e$ , the only dependent variable. The algorithm also contains eight parameters. None of these eight parameters can be adjusted or changed during any flux vs time calculation. Time, as the average exposure time however, can be selected and used in the models so as to achieve realistic

conditions that reflect CDF operations or other environmental factors that occur periodically. The parameters in Eq. 2 that must be specified are two chemical concentrations, two thermodynamic coefficients, two transport properties and two physical properties of the dredged material. Typically average or other representative values of these will be selected for performing a specific emission simulation. Once chosen the flux vs time behavior is fixed. It is important that the model user understands the cause-and-effect characteristics of some key parameters. The real world processes operating on and in the CDF are very dynamic and do not always adhere to the strict regime of applying Eq. 2. The model user should be aware of these operational and environmental factors that influence model parameters so as to take some accounting of them in a qualitative sense. In the following section, the factors affecting key model parameters will be reviewed in order to give the model user some sense of the role they play in the simulation outcome. Both the flux attenuating and enhancing factors will be considered.

*Equilibrium Partition Coefficients:* Typically soil-to-water partition coefficients ( $K_d$ ) are based on equilibrium chemical adsorption. Compilations or published correlations of  $K_{OC}$  or  $K_{OW}$  for chemicals used to estimate  $K_D$  are similarly constrained. The process of vaporization is a desorption process. Recent advances suggest that only the loosely bound fraction tracks the adsorption isotherm and the tightly bound chemical fraction displays a much larger soil-to-water partition coefficient (Kan et al., 1994). A larger  $K_D$  in Eq. 2 equates to lower expected flux. The use of measured IHC sediment desorption partition coefficients would reduce the uncertainty in estimating this key parameter. Oil and grease in the sediment has the same effect of increasing  $K_D$ . Its presence in the sediment will lower the model expected flux. It plays the equivalent role of increasing the organic matter content in the sediment (Ravikrishna et al., 2001b).

*Surface Drying:* Soil moisture has a very strong influence on the solid-to-water partition coefficient. Laboratory and field evidence abound to show that as moisture content decreases and approaches the 2-5% level the  $K_D$  increases significantly for hydrophobic organic chemicals (HOC) (Valsaraj and Thibodeaux, 1988). This increase in the  $K_D$  lowers the expected flux. Apparently water competes for chemical adsorption sites on the soil solids; when absent the HOCs are more strongly bound.

*Surface Re-wetting:* Increases in soil moisture by rain showers, increases in air humidity, etc. has the opposite effect. When the soil moisture rises above 5% and remains unsaturated with water, the  $K_D$  typically decreases. When this occurs, increased fluxes are expected.

*Rainfall:* Deluges will saturate the soil and close the air-filled pore spaces effectively blocking the vapor release process. The effective diffusivity becomes that of the HOC in water solution. It is approximately 10,000 times smaller than that in the air-filled pore spaces. Theoretically the fluxes are reduced by a factor of  $(10000)^{-1/2} = 100$  by this event alone.

*Consolidation:* As the dredged material ages in the CDF, the solid particles move closer together. This results in water being expelled. As this occurs in the surface layers, where the volatiles originate, the air-filled and bulk porosity decreases. This lowers the effective diffusion coefficient; see Eqn. 6. The expected flux to air is reduced.

*Cracking*: Water lost from the surface of a dredged material with high clay content produces cracking. Numerous large open fissures appear on the surface of the dredged material and extend downward for several centimeters. A larger evaporative surface is produced. However, the simultaneous processes of soil drying and consolidation occurs on the surface. The net effect is that the appearance of cracks and increased vaporization area is offset by higher  $K_D$  and lower  $D_{A3}$  values due to water losses. In the laboratory, enhanced volatilization was not observed with soil cracking (Ravikrishna, 2000).

*Surface Reworking or "Windrowing"*: The process of HOC vaporization produces a "weathered" layer that effectively retards further evaporation. Chemicals at depth encounter a lengthening and tortuous diffusion path. To a degree a natural cap develops on the surface; its depth increases as  $t^{1/2}$  increases according to Eq. 2. The process of mixing solids at depth upward in the soil column places fresh, unweathered dredged material directly on the surface. This effectively restarts the evaporation process (Valsaraj et al., 1999). The flux increases to values at or near the original high flux ones. In effect the soil column mixing restarts the weathering process time clock. Time,  $t$ , in the model must be set to zero to allow the algorithm to capture the surface reworking event.

*The vaporization particle resuspension connection - wind / particles*: Entrained dust originating from soil-like surface of the CDF is another process for chemical expose. Emissions to air by this process are based on the chemical concentration in the surface layer of the CDF. As shown in Figure 2, the concentration levels weather away as this layer is exposed to air. Basing particle emission rates on the initial chemical concentration of the dredged material solids in the CDF will result in "double counting". The exposure occurs once by the evaporation emission process which lowers the surface concentration. Using the initial surface concentration in the particle resuspension model without correcting for the evaporative weathering that has occurred results in a second exposure which is not appropriate. Figure 2 contains two vertical time lines at 60 days and 400 days that can be used in estimating reduction in the surface layer particle concentrations for entrainment emission calculations.

*Snow Cover*: The placement of a layer of a porous material such as sand or soil upon the surface of dredged material containing volatile or semi-volatile chemicals will reduce the flux to air (Ravikrishna et al., 2000). Laboratory test with a 1 cm soil layer over dredged material resulted in a flux reduction of dibenzofuran, phenanthrene and pyrene by 90%, 94% and 95% respectively. The flux retarding mechanism was the creation of a slow chemical vapor molecular diffusion process through the air-filled pore space of the capping soil. Layers of snow will act as a temporary cap in an analogous fashion. Carbon-dioxide diffusion measurements in snow under isothermal conditions have been reported for samples 10 to 40 cm in length (Sokratov and Maeno, 2000). Experimentally measured effective  $CO_2$  diffusion coefficients ranged from 0.0072 to 0.014 m/h for snow porosities of 0.89 to 0.67. With this data it is possible to estimate the flux retarding effect the snow cover will provide for the IHC CDF. Environmental chemodynamic algorithms developed for the steady state process of volatile chemicals originating in landfill cells and moving through the porous caps are directly applicable (Thibodeaux, 1996; Ch. 6) for a snow cap. Theoretically, the modification involves  $K_G$  in Eq. 3 above. It appears both in the maximum flux and in the weathering factor portions of the equation. The snow cover layer provides an additional mass transfer resistance. The

snow corrected,  $K_{GS}$ , replaces  $K_G$  in Eq. 3. The relationship between the two coefficients is

$$\frac{1}{K_{GS}} = \frac{1}{K_G} + \frac{h}{D_{AS}} \quad (15)$$

where  $h$  is the thickness of the snow layer (m) and  $D_{AS}$  is the effective vapor diffusivity of A in the porous snow. Equation 15 is the usual resistance-in-series algorithm used for landfill vapors emission. With this modification to the basic emission model, it is possible to make theoretical estimates of the flux retarding effect snow will have on reducing the volatile emissions from the surface of the IHC CDF. For the purposes of this estimate the average parameters reflective of the IHC CDF used previously in developing Eqns 13 and 14 apply. Grahams' Law of inverse square root of molecular weight will be used to transform the effective diffusivity of  $CO_2$  to the typical IHC volatile chemical. In addition, two snow cover thicknesses of 1 cm (0.01m) and 3 cm (0.03m) will be assumed. Using the high  $CO_2$  effective diffusivity as a basis these cover thicknesses yield  $K_{GS}$  values of 0.62 and 0.22 m/h for the 1 and 3 cm snow layers. Compared to the  $K_G = 6.23$ m/h, these therefore result in flux reductions of 90 and 96% respectively for the two layers. A 11cm (0.11m) snow layer will result in 99% emission reduction.

In summary, it appears that a few centimeters of snow on the surface of the IHC CDF will have a significant effect in reducing the emissions of volatile chemicals. Reduction of 90% or greater can be expected. In effect the volatile chemical cannot effectively evaporate from the soil-like surface of the dredged material. This occurs because the surface winds cannot make direct contact with the soil interface due to the presence of the snow. If evaporation reduction occurs then chemical weathering of the soil surface layer ceases as well. So, what snow covers does in effect is essentially stop the evaporation process while it is present. Once it melts away the process restarts where it left off. From a human exposure perspective the yearly exposure time period is reduced by the fraction of days an effective snow cover exist on the CDF.

*The Average Chemical Flux:* Mass emissions to air are based on a flux and area product. It may be reasonable to use the entire CDF surface area of 131 acres as the emission source area for risk modeling purposes. Then the question is what average flux to use? As noted earlier, based on daily dredging and spreading in approximately 400 days, the CDF has received one 3 foot layer of material. The appropriate flux is the average for 400 days (i.e.  $n [400]$ ). However, this approach assumes that once each day's material is placed in the CDF and it is not disturbed again for 400 days. Such an assumption is unrealistic. Clearly operational events of earth moving for whatever reason: windowing, rain storms, drying cycles, etc. will cause the surface layer to be "refreshed" periodically. So the choice of the average flux should be done using an averaging time less than 400 days. Local information about the frequency of rain storm events, windowing time intervals and other on-site surface earth disturbance activities will aid in estimating this average time. It should represent the average time the surface of the entire 131 acres is so disturbed. For example the 60 day, the time mentioned in page 43, is based on the assumption that the entire site gets a rainstorm once every two months. In effect the choice of average flux can be used to attenuate or enhance what is expected to be the real flux.

*Measured vs. Modeled Flux:* It seems reasonable to consider a methodology that uses actual (i.e. measured) fluxes instead of a model for predicting the fluxes. Many problems and limitations are involved in this approach. First the field or laboratory measurements will represent a small subset of operating conditions on the CDF. The decision must be made as to the measurement time period. Once done, how do you extrapolate the measurements to the actual times of the various surface areas of the CDF? How does one extend the measured values to account for differences in wind and temperature? Does the measurement include a snow event; a rain event? In desperation, the experimentalist realizes that the measurement approach cries out for a theoretically sound model to use for extending the data to a variety of real-world conditions.

## SUMMARY AND RECOMMENDATION

The primary objective of this project was a literature review of the volatilization of chemicals from the soil-like surfaces of dredged materials. The report commences with a brief description of the Indiana harbor sediment quality and the planned dredging activities and physical structure of the confined disposal facility. While this site provides the *raison d'être* the results of the literature and the recommended model are generally applicable to any site receiving dredged materials containing volatile and semi-volatile chemical quantities. The report starts with a description of the theory of the vaporization process from soil-like surfaces that identifies the key elements of the mobilization process. The review identifies two diffusion-based models (the Jury et al. model and the Thibodeaux-Hwang model) that have appeared in the peer-reviewed literature and have since undergone extensive evaluation.

A significant quantity of high quality laboratory and field flux measurements on twenty chemicals were located in the open literature. The report provides a thorough review of volatilization of the chemicals found in Indiana harbor plus detailed summary tables of measured volatilization rates for PAHs, pesticides, petroleum hydrocarbons, metals, PCBs and furans/dioxin from surface soil sources. Theory and data suggest that the volatile chemicals placed in a CDF such as the one proposed for Indiana Harbor follow a pattern of constant rate followed by a falling rate. The falling rate reflects the relative rapid loss of ~1% of the chemicals from a thin surface layer which then provides a natural cap for the remaining ~99% of the chemical in the dredged material mass. The measured falling rate is consistent with the theoretical projections of the diffusion-controlled models. Predictions from the instantaneous flux model are compared to measured flux for benzo(a)pyrene, dieldrin, Aroclor 1248 and benzene. These compounds were selected to represent the four categories of organic chemicals in the Indiana Harbor sediments. A graphical comparison of these and the others contained in the appendix show the general good agreement between modeled and measured volatilization rates.

Based on the review, a diffusion-controlled model (Thibodeaux-Hwang) is proposed as the best available approach to estimating the volatilization of contaminants from a CDF containing dredged material and specifically one that contains the Indiana Harbor sediments. A new time-averaged flux expression is developed for use in estimating emission rates for making inhalation risk assessments. Under assumed operating conditions for the Indiana Harbor CDF day-time and night-time fluxes for both 60 and 400 day averaging-times are projected. The final section of the report covers real-world operational and environmental factors at a CDF that will attenuate or enhance the

model predicted flux. Based on these and a comparison of the model vs measured fluxes the diffusion controlled algorithm tends to generally over-predict the measurements.

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