Contaminant Pathways Evaluations: Leachate, Volatilization and Plant & Animal Uptake

Tab U3

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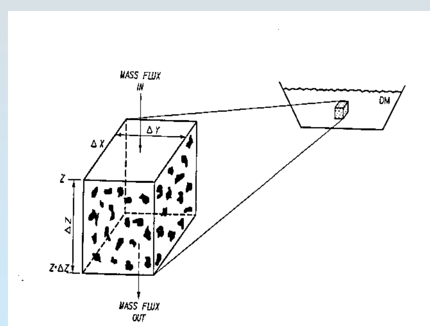
Keywords: CDFs, Contaminant Pathways, Testing

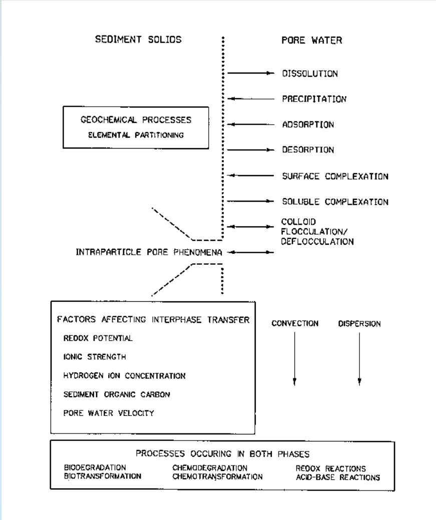
Mathematical Visualization of Dredged Material Leaching

- Porous-medium contaminant transport problem
- Inter-phase transfer of contaminants from dredged material solids to pore water surrounding the solids
- Subsequent transport of these contaminants by pore water seepage
- Complex interaction of many processes



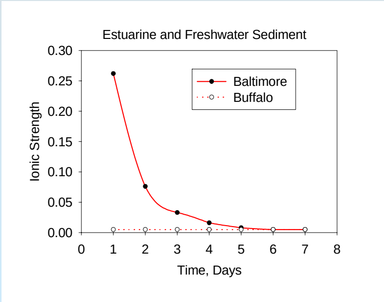
Interphase Transfer Processes and Factors Affecting Interphase Transfer Processes

- Processes control the rate at which steady-state conditions between dredged material and pore water are reached
- The factors affecting inter-phase transfer are particularly important



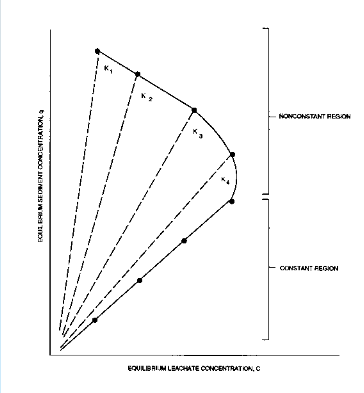
Changes in Ionic Strength (Sediment Salinity)

- Estuarine sediments lose salts when fresh water leaches through the material
- Loss of salinity can change the leaching characteristics of the sediment
- Salt washout is a fundamental difference between freshwater and saline sediment leaching



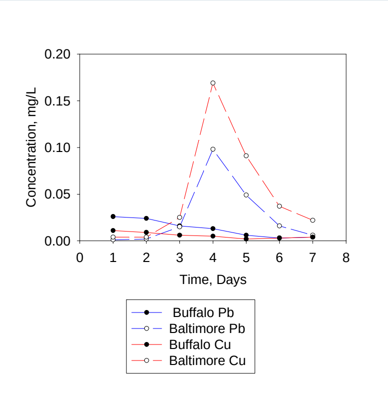
Non-Constant Distribution of Contaminants in Leachate

- Commonly observed during leaching of estuarine sediments
- Non-constant distribution related to elution of salt
- Loss of salt results in deflocculation of colloidal matter
- Colloid deflocculation results in DOC-facilitated transport in leachate



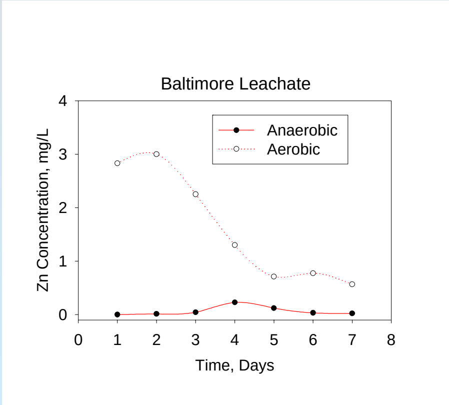
Effects of Salt Washout on Contaminant Leaching

- Results in increased concentrations of metals and organic contaminants
- Peak leachate concentrations will occur after salts have washed out of the sediment
- Batch tests cannot accurately predict the magnitude of contaminant releases from estuarine sediments



Zinc Concentrations in Leachate Under Aerobic and Anaerobic Conditions

- If the pH drops substantially during aerobic conditions, some metals may be mobilized
- If the CDF is not oxidized throughout, leachate passing through the anaerobic sediment zone will be reduced to that of anaerobic leachate



Selection of Test Procedure

- **Freshwater Dredged Material: Batch Testing**

  Generally yields well-behaved contaminant desorption isotherm or single point K_D if clustered concentration data result

- **Saline Dredged Material: Column Testing**

  Salt elution from saline dredged materials results in colloid release to leachate that cannot be quantitatively described by batch test results because of the effects of leachate shear velocity

Sequential Batch Leach Test (SBLT)

“Pancake” Column Leach Test (PCLT)

Batch Test Procedures

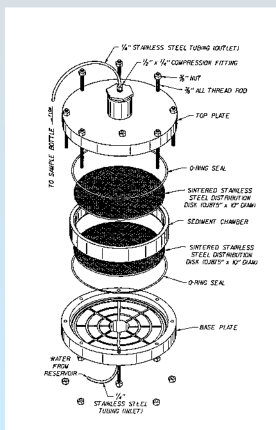
- Load sediment in a 4:1 water-to- sediment ratio under anaerobic (nitrogen atmosphere) conditions
- Shake for 24 hours, centrifuge, and filter leachate
- Add water to sediment to make up that removed. Repeat steps 1 and 2
- Repeat procedure for at least four cycles

Column Test Procedures

- Laboratory-scale physical model of contaminant elution from dredged material
- Testing conducted in up-flow mode
- Elution of 30 pore volumes recommended

Column Test Apparatus

- Thin layer column for maximizing number of pore volumes eluted
- Improved flow control and delivery
- Column is 25.4 cm in diameter
- Details on column design and operation available in guidance documents



Leachate Pathway Assessment

- Quality
  - Partitioning
  - Leachable Fraction
- Quantity
- Dilution Attenuation Factor
  - Diffusion
  - Degradation
  - Volatilization
  - Irreversible exchange with solids
- Receptor
- Transport
- Groundwater Modeling
  - Vadose Zone
  - Saturated Zone

Vadose Zone Transport Considerations

- **Vadose Zone Properties**
  - Quantity of fine-grained materials, oxides, sulfides, and organic matter
  - Thickness
  - Porosity
  - Partitioning relationship
- **CDF Design and Location**
  - Thickness
  - Permeability
  - Climate
  - Dredged material characteristics

Vadose Zone Screening

- Peak Contaminant Concentration
- Travel Time for Breakthrough of 0.1%, 1%, 10%, and 50% of Initial Leachate Concentration as well as Peak Concentration

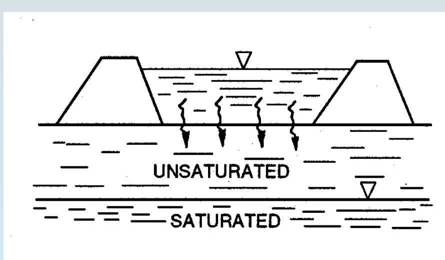
Saturated Zone Transport Considerations

- **Groundwater velocity**
  - increases diffusion and dilution
  - decreases the time to reach receptor
- **Receptor locations**
  - Upgradient or off-center limits exposure
  - Distance increases diffusion
- **Aquifer thickness increases diffusion**
- **Aquifer heterogeneity**
  - increases short-circuiting
  - decreases diffusion and dilution
- **Retardation capacity**
  - function of the quantity of fine-grained materials, oxides, sulfides, and organic matter in the aquifer
  - reduces the long-term exposure

Saturated Zone Screening

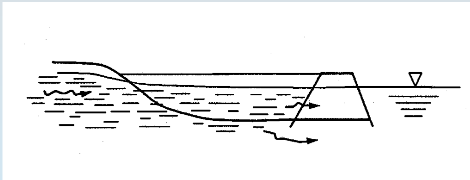
- Dilution of Peak Concentration Passing through the Vadose Zone
- Function of Length and Width of CDF, Net Infiltration Rate, Groundwater Velocity, Aquifer Thickness, and Distance to Receptor

Upland CDF



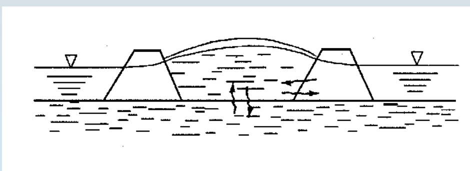
The CDF is separated from groundwater by the vadose zone; flow is into foundation soils and toward groundwater. Hydraulic gradient is approximately one.

Nearshore CDF



The CDF is partially sited in the saturated zone; water table is seasonally dependent and flow is through site. Hydraulic gradient is between zero and one (typically near zero).

In-Water CDF



The CDF is sited “in-gradient”; flow occurs when outside water elevation changes. Hydraulic gradient is between zero and one (typically near zero).

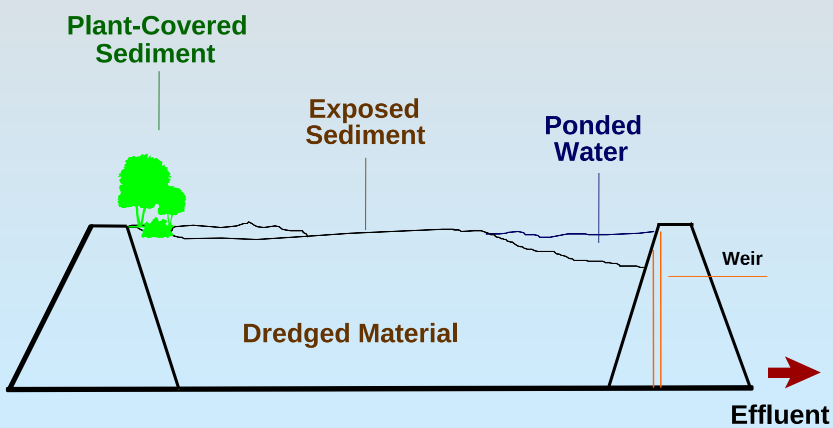
Site-Specific Modeling

- Regional groundwater modeling using Groundwater Modeling System
- Consolidation testing to predict hydraulic conductivity of dredged material and net infiltration

Leachate Guidance Available

- http://el.erdc.usace.army.mil/el/dots/
- Documents available at Web site
  - USACE Implementation Memorandum
  - Technical Framework
  - Leachate Testing and Evaluation for Freshwater Sediments
  - Leachate Testing and Evaluation for Estuarine Sediments
  - Technical Note - Technical Considerations for Applications of Leach Tests of Sediments and Dredged Material
  - Technical Note - Leachate Screening Considerations
  - Technical Note - Effects of CDF and Vadose Zone on Leachate
  - Technical Note - Dispersion of Leachate in Aquifers
  - Technical Note - ADDAMS Application: Hydrologic Evaluation of Leachate Production and Quality (HELPQ) Module in CDFs
  - Technical Note - Documentation of the Hydrologic Evaluation of Leachate Production and Quality (HELPQ) Module

Volatile Emissions from Dredged Material



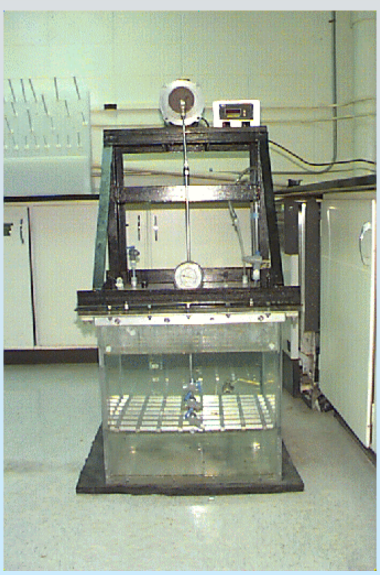
Volatilization Considerations

- Sediment Physical Characteristics
  - Moisture content, porosity, aging, oil and grease concentration
- Contaminant Chemical Properties
  - Henry's Law Constant, vapor pressure, sediment contaminant concentrations
- Environmental Variables
  - Relative air humidity, temperature
  - Mechanical movement (mixing) of the sediment

Evaluation of Volatile Losses

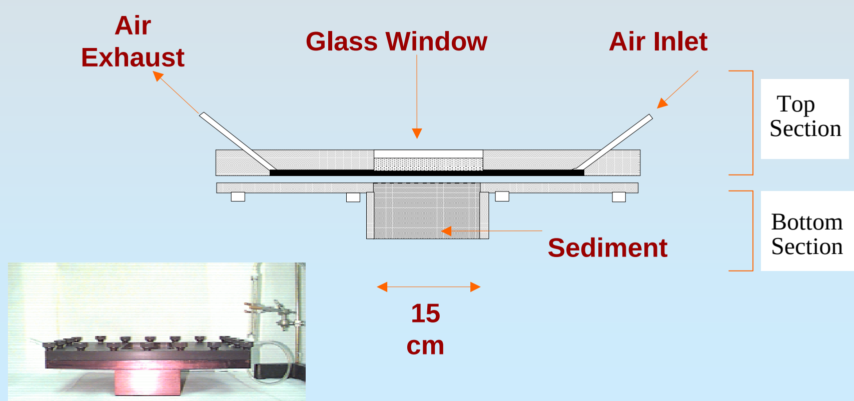
- Laboratory procedures to quantify volatile losses in the field
- Predictive models to describe the loss of volatile organic compounds from DM disposal sites
- Initial processes describing volatile losses during dredging operations

Sediment Resuspension Chamber



Provide information on the emission of VOCs from contaminated sediments when they are resuspended in the water column

Flux Chamber for Quantifying Volatile Emissions in a Laboratory Setting



VOC Flux Chamber

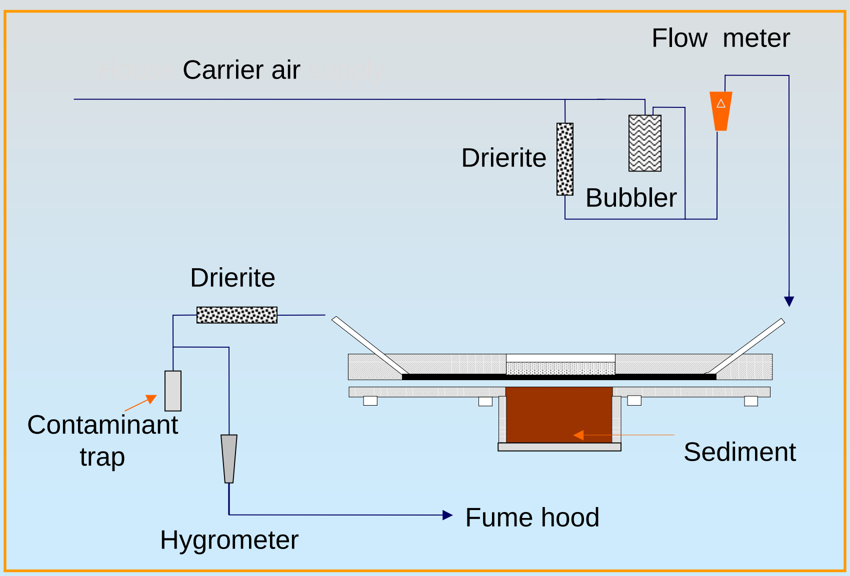
- Two-piece construction of anodized aluminum
- Bottom section
  – Sediment chamber-25 cm x 15 cm x 10 cm deep
- Top portion
  – Designed with channels to distribute airflow uniformly across sediment surface
  – Fitted with glass window to allow visual monitoring of sediment surface
- Chamber is sealed with an O-ring and threaded fasteners to produce an airtight fit

Components

- Air Supply – laboratory "house" air or compressed gas cylinder; vacuum pump
- Sampling Traps - contaminant-specific air sampling tubes (Supelco, Inc.)
- Flow Meter (able to handle flows > 1 L/min
- Tygon tubing
- *Humidity Meter (for in-line monitoring)
- *Water Bubbler (air humidity adjustment)

* optional (dependent upon sampling conditions)

Laboratory Experimental Design



Test Protocol (Laboratory)

- Carrier Air – “house” air; compressed gas of sufficient purity, or vacuum pump
- Flow rate - 1.7 L/min
- Trapping Material - dependent upon contaminants of interest
- Humidity - controlled via water bubbler
- Sampling Regime - dependant upon: contaminant concentrations, trapping material and retention capacity, experimental conditions (i.e., soil moisture)

Sediment Preparation

- Core or grab samples should completely fill storage containers (cores not removed need to be immediately sealed)
  - Volume of sample is dependent upon compounds of interest
- Refrigerate samples
- Thoroughly homogenize samples prior to sediment analysis and volatile emissions testing

Example Sampling Protocol

- Sampling times / intervals:
  - 6, 24, 48, 72 hours, 5, 7, 10, and 14 days
    - Sample continuously (replace trap at each sample interval making sample intervals anywhere from 6 to 96 hours each)
    - Sampling length dependent on contaminant concentrations and analytical detection limits
- Experimental conditions:
  - Initiate experiment with field moist sediment and apply dry air over sediment surface (14-day experiment)
  - Apply humid air over sediment surface for 7 days
  - Rework sediment and repeat with dry air

Test Protocol (Field)

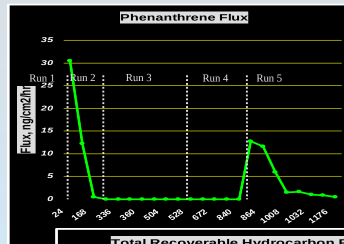
- Field Apparatus - constructed of top portion identical to that of laboratory chamber; bottom portion has central opening for sediment surface and is surrounded by 2-inch-long side plates to seal the apparatus from the surrounding air
- Carrier Air - “outside” air is pulled through a trap (to assure uncontaminated air) across sediment surface with battery-operated vacuum pump
- All other materials and sampling procedures identical to those in the laboratory

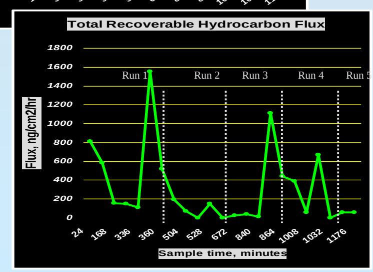
Field Apparatus

Field Measurements

Phenanthrene Flux from Aged Field Sediment*

- Run 1 – Dry air for 14 days
- Run 2 – Humid air for 7 days
- Run 3 – Sediment saturated followed by dry air for 14 days
- Run 4 – Sediment reworked followed by dry air for 7 days
- Run 5 – Sediment saturated followed by dry air for 7 days





***Sediment contains 1% oil and grease**

Flux Calculations

- Contaminant flux is calculated by determining the total mass of material captured in a given time interval using the equation:

$$N_A(t) = \frac{\Delta m}{\Delta t A_c}$$

Δm = mass (ng) of compound collected on the trap in time Δt(hr)

A_c = area the sediment-air interface, cm^2 (375)

$N_A(t)$ is expressed in $ng/cm^2/hr$

Example of Available Models for Prediction of Volatile Emissions

Model Simulation of Phenanthrene Flux from Indiana Harbor Sediment

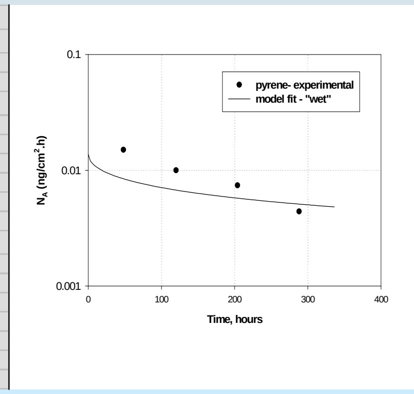
Flux1	Model flux with no surface mass transfer resistance
Flux2	Model flux with surface mass transfer resistance

Flux 1 - Model

$$Flux(t) = C_0 \cdot \sqrt{\frac{D_{eff} \cdot R_f}{\pi \cdot t}}$$

Flux 2 - Model

$$Flux(t) = k_a \cdot C_0 \cdot \exp(\frac{k_a^2 t}{D_{eff} R_f}) \cdot erfc(k_a \sqrt{\frac{t}{D_{eff} R_f}})$$



Gaussian Dispersion Air Quality Model

- Steady-state, area source, Gaussian models for simple terrains
- SCREEN3
- ISC3 (Industrial Source Complex Model)
- Other complex models available for Tier IV
- http://www.epa.gov/scram001/tt22.htm#isc

Volatile Emissions Results

- Highest contaminant fluxes from sediments occurred during initial sediment exposure (after placement)
- In sediments containing high concentrations of oil and grease (~1%), reworking of the sediment (exposing new material to the air) caused equally high contaminant fluxes

Volatile Emissions Results

- Increases in relative humidity of the air passed over the sediment surface resulted in increased fluxes in laboratory and field sediments containing no oil and grease; in those with oil and grease, fluxes did not increase (with the exception of lower chlorinated PCB congeners)
- Higher sediment moisture content (>6.5%) resulted in lower long-term flux of contaminants than from low moisture sediment (<6.5%)

Volatilization Controls

- Submerged Discharges
- Reduced Areas
- Films/Covers
- Activated Carbon
- Capping
- Vegetation
- Ponding

References

- “Development of Laboratory Procedures to Predict Volatile Losses from Contaminated Sediments,” Technical Note EEDP-02-23, August 1997.
- “Volatile Losses From Exposed Sediment,” Technical Note EEDP-02-24, May 1998.
- “ Volatile Emissions from Aged Field Sediments,” Technical Note EEDP-02-26, January 1999.
- “Prediction of Volatile Losses from Exposed Sediment,” Technical Note, EEDP-02-28.
- “Volatile Losses from Resuspended Dredged Material,” Technical Note, EEDP-02-30.

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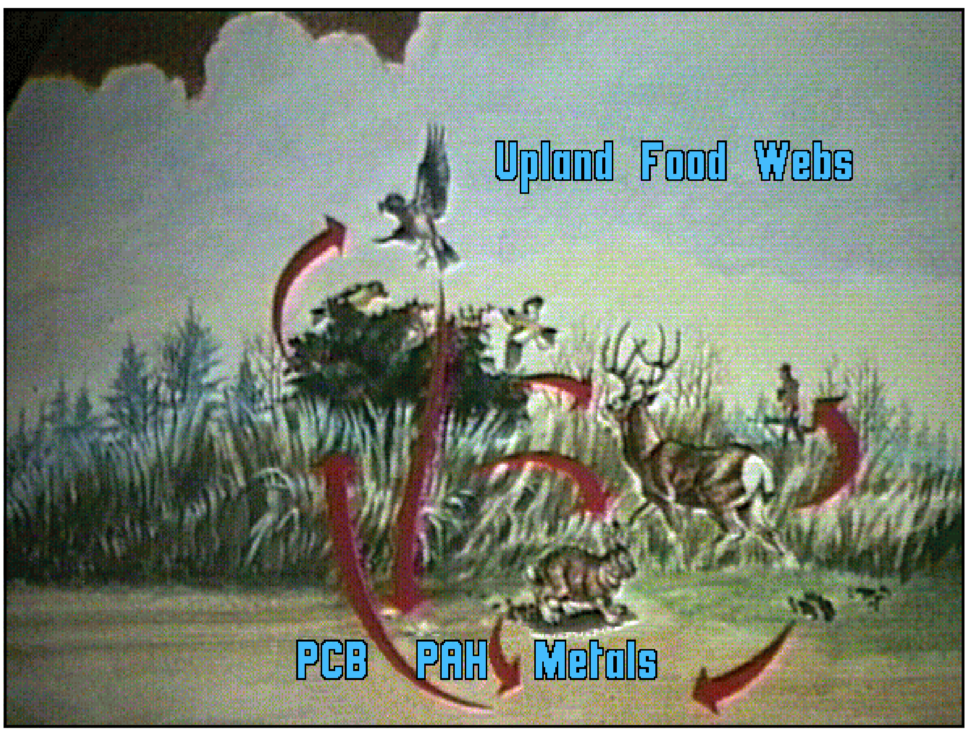
Dense Vegetation Used by Many Species of Animals for Food & Shelter

- Many of the plant species are used for food by insects, birds, and mammals



Regulatory Considerations

- No specific standards for plant tissue contaminant concentrations in general
- Evaluating potential effects of plant uptake may be required under NEPA to allow regional or local authorities to reach agreement on dredged material disposal alternatives

Plant Uptake Evaluation

- Determine potential for contaminant migration into plants colonizing dredged material
- DTPA extraction of metals
- Plant Uptake Program (PUP)
- Plant Bioassay Test
- More applicable to freshwater sediments

DTPA Extraction Test

- Chemical characterization of sediment
  - Acid-digest metals, pH, organic matter
- DTPA extraction of wet and dry sediment to predict predict plant extractable metals
- Results are input into the Plant Uptake Program (PUP)

PUP Prediction Tool

- Generates predicted concentrations based on entered data and a database of sediment and plant tissue metals
- Estimates total plant uptake of metals
  - (tissue concentration x plant biomass)
- Compares predicted results of test sediment to reference sediment

Typical Upland Plant Bioassay

Plant Uptake

Index Plant – Cyperus

Plant Uptake Bioassay

Effects Levels

- FDA Action Levels for foodstuffs
- European/WHO recommended limitations in foodstuffs on animal feeds, leafy vegetables
- USDA demonstrated effects levels - plant toxicity
- Reference Soil results

Plant Uptake Summary

- DTPA extraction/PUP for metal uptake
- Plant bioassay to determine plant toxicity, uptake of inorganic and organic contaminants
- Compare to reference and to FDA type limitations
- Control measures are available

Plant Uptake Control Measures

- No plants - herbicide
- Selected plants - plants that minimize uptake
- Soil amendments to reduce availability of contaminants - lime, phosphorus, etc.
- Cap with clean material, shallow rooted plants

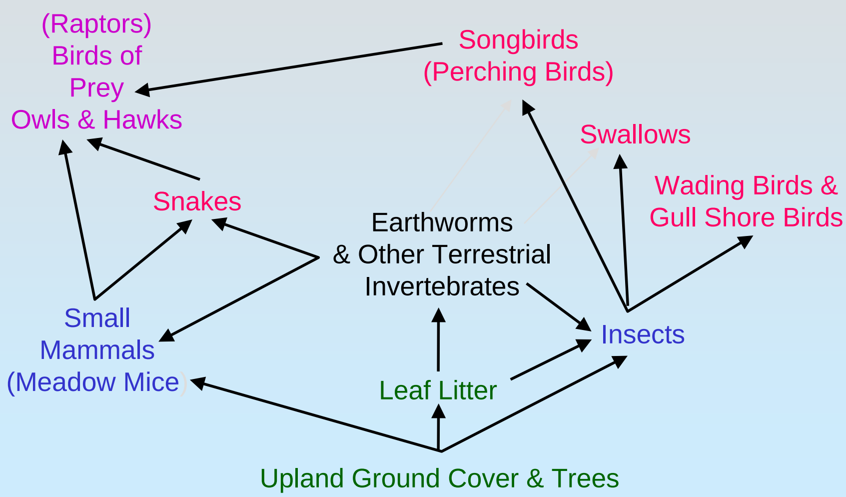
Animal Uptake Evaluation

Earthworm bioassay test for toxicity and bioaccumulation

Regulatory Considerations

- No specific standards for earthworm contaminant concentrations in general
- Evaluating potential toxicity and bioaccumulation through food webs may be required under NEPA to allow regional or local authorities to reach agreement on dredged material disposal alternatives

Upland Site - Generalized Food Web



Earthworm Bioassay Test

- Salinity of dredged material (<10 ppt)
- Earthworm bioassay for toxicity (7 days)
- Bioaccumulation (28 days)
- Analyze for metals, PAHs, PCBs, etc.
- Compare to reference & controls

Animal Uptake Summary

- Earthworm bioassay determines potential for toxicity and bioaccumulation of contaminants in dredged material
- Comparisons to reference soils and FDA-type action levels help determine need for restrictions/management
- Control measures are available

Other Animal Uptake Tests

- Other test procedures to evaluate contaminant effects on animals in transitional saltwater wetlands are available but are more site-specific
- Water column bioassays are suitable for permanent to semi-permanent wetlands

Management and Controls

- Manage vegetative cover
- Amendments/treatments to reduce bioavailability
- Cap to reduce exposure
- Others more site specific depending on target species

Guidance Documents for CDFs

- USACE/EPA Technical Framework
  - http://www.epa.gov/OWOW/oceans/framework/
- Engineer Manual 1110-2-5027 Confined Disposal of Dredged Material
  - http://www.usace.army.mil/inet/usace-docs/eng-manuals/em1110-2-5027/toc.htm
- **Upland Testing Manual**
  - **http://el.erdc.usace.army.mil/dots/pdfs/trel03-1.pdf**
- DOTS Website
  - http://el.erdc.usace.army.mil/dots/guidance.htm

The High Points

- CDFs are containment options
- Contaminant pathways must be appropriately evaluated
- UTM provides a tiered approach for evaluations
- Testing/ evaluation procedures are available for all pathways
- Pathway controls are available