Sampling and Analysis Relevant to Air-Based Remediation Technologies

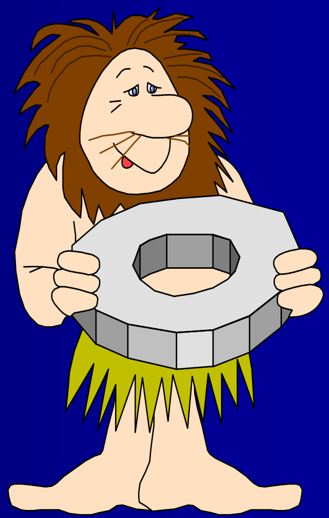
Chung-Rei Mao
Chemist
USACE EM CX

Overview and Objectives

- Describe general technical project planning approach for site characterization and remediation
- Describe the benefits of proper project planning and how planning supports site closeout
- Describe sampling strategies and technologies for soils, ground water, soil gas, air, and process controls
- Introduce analytical methods and strategies for chemical testing

Technical Project Planning in Support of Air-Based Remediation

- **Needs a multi-disciplinary approach**
- **Focuses on site closeout**
- **Defines project objectives**
- **Defines constraints and dependencies**
- **Determines data needs based on project objectives**
- **Promotes documentation**
  - **Planning Worksheets**
  - **Data Quality Objectives (DQOs)**
- **Follows USEPA Guidance QA/G-4 on Systematic Planning Using DQO Process or USACE EM 200-1-2 Technical Project Planning (TPP) Process**



What are DQOs?

- Data Quality Objectives (DQOs) are quantitative and qualitative criteria that:
  - Clarify study objectives
  - Define appropriate types of data to collect
  - Specify the tolerable levels of potential decision errors

The 7 Steps of DQO Process

- Step 1 – State the problem
- Step 2 – Identify the decision
- Step 3 – Identify the inputs to the decision
- Step 4 – Define the boundaries of the studies
- Step 5 – Develop a decision rule
- Step 6 – Specify tolerable limits on decision errors
- Step 7 – Optimize the design

Stating the Problem

- What is the problem?
- What resources are available?
- What time is available?
- What important social / political issues have an impact on the decision?

Identifying the Decision

- **Identify the principal study question**
  - ***Clarify the main issue to be resolved***
- **Specify the alternative actions that would result from each resolution**
  - ***Associate a course of action with each possible answer***
- **Define the decision statement that must be resolved to address the problem**
  - ***Combine the principal study question and the alternative actions into a specific decision statement***

Identifying Inputs for the Decision

- Focus on what information is needed for the decision
- Identify the variables / characteristics to be measured
- Identify the information needed to establish the action level

Defining the Boundaries

- Define the spatial boundary for the decision
  - Define the geographical area within which decisions apply
  - Define the media of concern
  - Divide each medium into homogeneous strata
- Define the temporal boundary of the decision
  - Determine the time frame to which the study results apply
  - Determine when to study
- Define a scale of decision making
- Identify practical constraints on data collection

Develop a Decision Rule

- **Develop an "If…, then…" statement that incorporates:**
  - **The population parameter of interest (e.g., mean, maximum, percentile)**
  - **The scale of decision making (e.g., residential lot size)**
  - **The action-triggering value**
  - **The alternative actions**

Specify Limits on Decision Errors

- Determine the possible range of the parameter of interest
- Determine baseline condition (null hypothesis)
- Determine consequences of each decision error. Consequences may include:
  - Health risks
  - Ecological risks
  - Political risks
  - Social risks
  - Resource risks

Optimize the Design

- Develop general data collection design alternatives
  - Simple random sampling
  - Simple random sampling with compositing
  - Stratified random sampling
- For each design, develop cost formula, select a proposed method of data analysis, develop method for estimating sample size to correspond to method for data analysis
- Select the most resource-effective design
  - Consider cost, human resources, other constraints
  - Consider performance of design

DQO Process Output

- Qualitative and quantitative framework for a study
- Feeds directly into the Quality Assurance Project Plan (QAPP) which is mandatory for USEPA environmental data collection activities

Develop Conceptual Model

- **Develop a mental picture of the site and how it interacts in the environment (sources, hydrogeology)**
  - **Review site information and data to identify preliminary Conceptual Site Model (CSM)**
  - **Concept of CSM may be different for different team members**
- **CSM helps identify data gaps**
- **Data collected should be focused on adding certainty to CSM**
- **CSM leads to common understanding of where the site is today**

Conceptual Site Model

- **Minimum components:**
  - Source
  - Environmental setting
    - Topography, surface water hydrology, geology, hydrogeology, land use
  - Release mechanism
  - Migration pathways
  - Exposure routes
  - Receptors
- **USACE EM 1110-1-1200, CSM for OE/HTRW Projects, ASTM D5979 and E1689**

Identify Data Needs

- **Data Types – examples for air based technologies**
  - Locations of municipal wells
  - Stratigraphy
  - Depth to water
  - Soil permeability
  - Location of waste
  - Ground water concentrations
- **Data Amount**
  - Function of uncertainty, resources
  - Statistical analysis may be appropriate
- **Data Location**
- **Data Quality – screening vs. definitive**

Summary on Project Planning

- Project planning involves all team members, including stakeholders and regulators
- Agreement on conceptual site model and site closeout statement is critical
- Data needs are governed by project objectives and conceptual site model
- Sampling program is designed to obtain data by most efficient means and is well documented

Sampling Selection Criteria

- **Method Selection**
  - Sample matrices
  - Contaminant type
  - Sample representativeness
  - Practicality / simplicity
  - Cost
  - Safety
- **Layout Selection**
  - Judgmental / Biased (soil gas, GW)
  - Random
  - Stratified random
  - Systematic (soil)
- **Location Selection**
  - Objectives
  - Site history and disposal practices
  - Hydrogeology
  - Contaminant behavior
  - Receptor location
  - Statistical significance
  - Safety

Visual Sample Plan (VSP)

- VSP is a tool that helps gather the right type, quality, and quantity of data to support confident decisions
- Helps answer following questions:
  - How many samples do I need?
  - Where should I take samples?
  - What decisions do my data support?
  - How confident am I in those decisions?
- Covers many sampling designs: random, systematic, stratified, multi-increment, combined judgment/probabilistic, etc.
- VSP: http://vsp.pnl.gov/

Soil Sampling Objectives

- Assessment and remediation
  - Determine levels of contamination
  - Compare with numeric standards
  - Calculate site-specific risk
  - Verify cleanup
- Sample for chemical and geotechnical testing
- Method should yield most representative sample that meets DQOs

Soil Sampling Equipment

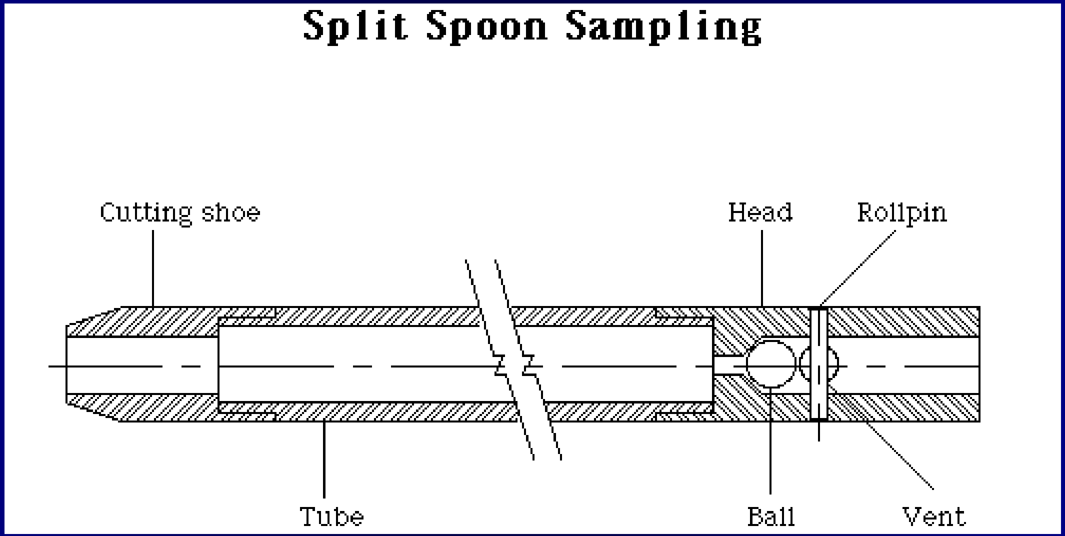
- Select equipment based on:
  - Depth of sample
  - Type of sample
    - Disturbed vs. Undisturbed
  - Type of soil
  - Type of contaminants

Sampling Tools

- **Soil**
  - Hand auger
  - Split spoon
  - Thin-walled sampler
  - California modified split spoon
  - Continuous sampler
  - Cone penetrometer

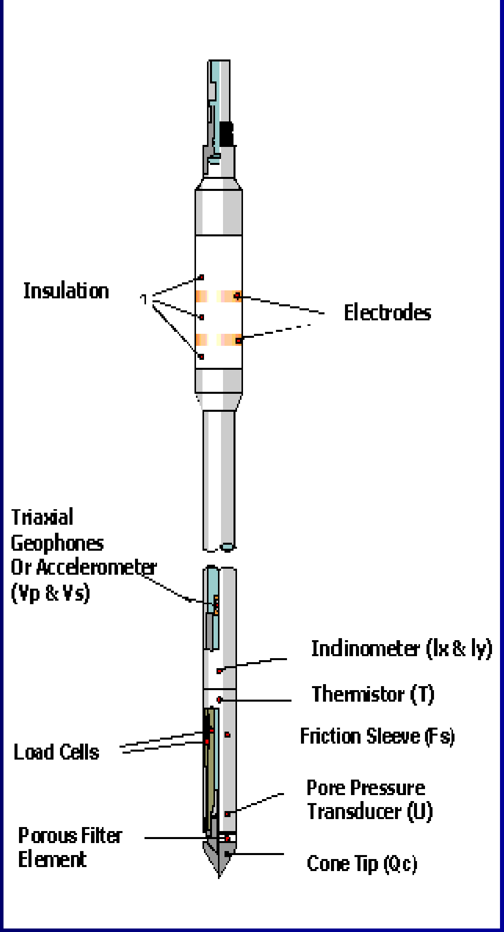
Split Spoon

- Most common sampling method
- Used extensively in different soil types
- Driven with weighted hammer
- Disturbed sample



Cone Penetrometer

- Cone Penetrometer (Geoprobe) provides “real-time” data for subsurface characterization
  - Hydraulically push a steel cone into ground at up to 40K pounds of pressure to 150 feet depth typically
  - Limited sample volume, no cuttings to deal with
  - Difficult to penetrate sites with large boulders or rock
  - Sensors on the cone classify soil type
  - Chemical sensors available for organic compounds, metals, radioactivity, explosives, soil moisture, etc.



Sampling Procedures

- **Discrete Sampling**
  - **Taken from one relatively small depth interval in one borehole or at one sample location**
- **Composite Sampling**
  - **Mixture of discrete samples taken at a certain depth from a number of locations or from a number of depths in a single borehole; "physical averaging"**

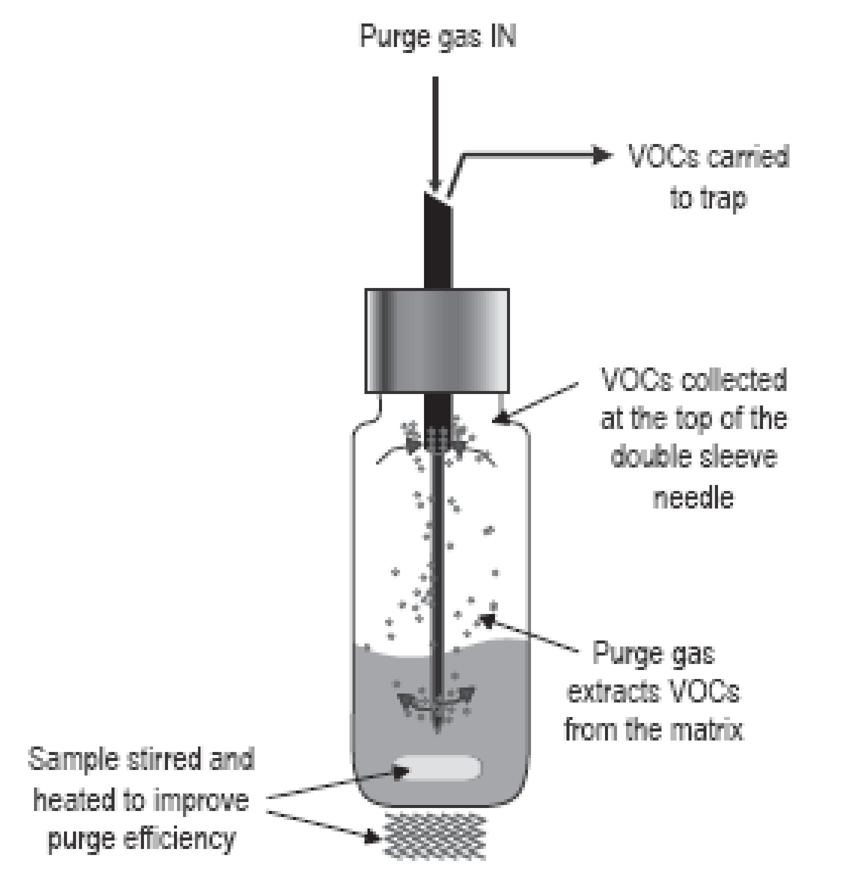
SW-846 Method 5035

- Over half of total volatile organics lost within 10 min of sampling by conventional means (jars, cores with Teflon liners)
- Samples must be either sealed immediately (10 seconds) and not opened again <u>or</u> placed in extraction solvent (water or methanol)
- Low-level vs. high-level sample collection
- Screen sample, check for carbonates
- EnCore Sampler, sodium bisulfate, or methanol preservation
- Refer USACE EM 200-1-3, App E.4 or ASTM D6418 for more detail

Soil Sampling for VOCs

USEPA SW-846 Method 5035A:

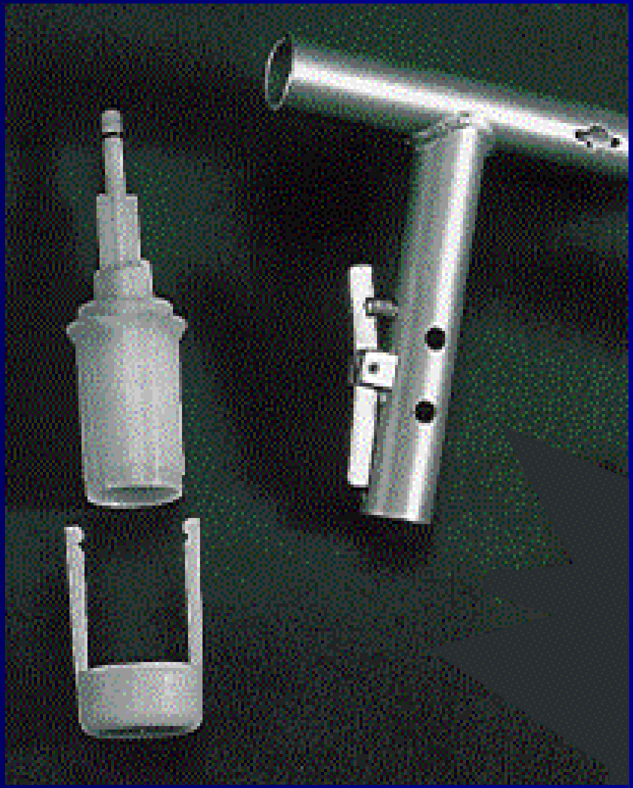
Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples



Sample Purging: Soil Mode

EnCore Samplers

- Disposable core type sampler
- Approved for sampling by USEPA for Method 5035A
- Advantages:
  - Disposable
  - Easy to use
- Disadvantages:
  - Expense ~$8 each
  - Not effective in some soils
  - Short field holding time

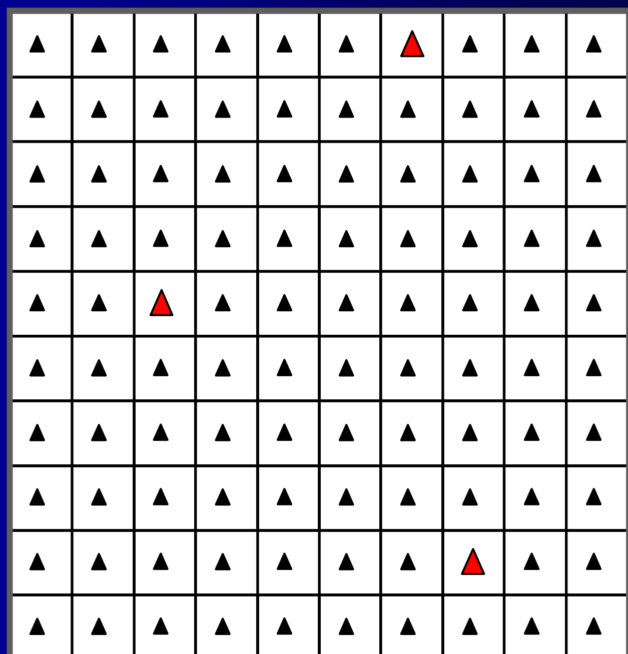


Multi-Increment Sampling (MIS)

- Composite sampling protocol for a single analytical sub-sample having all constituents in exactly the same proportion as a specifically defined volume of soil in the field (a sampling unit / decision unit)
  - Representative estimate of mean analyte concentration
  - Highly reproducible / scientifically defensible (RSD <15%)
- All soil constituents are heterogeneously distributed
  - Compositional (micro-scale, particulate)
  - Distributional (macro-scale, non-uniform distribution)
  - Every point in the field Sampling Unit has equal probability of being included in analyzed aliquot
- Most often applied to surface soil, but can be used for subsurface. Requires multiple borings
- Confirmation after treatment

Discrete vs. MIS Sampling

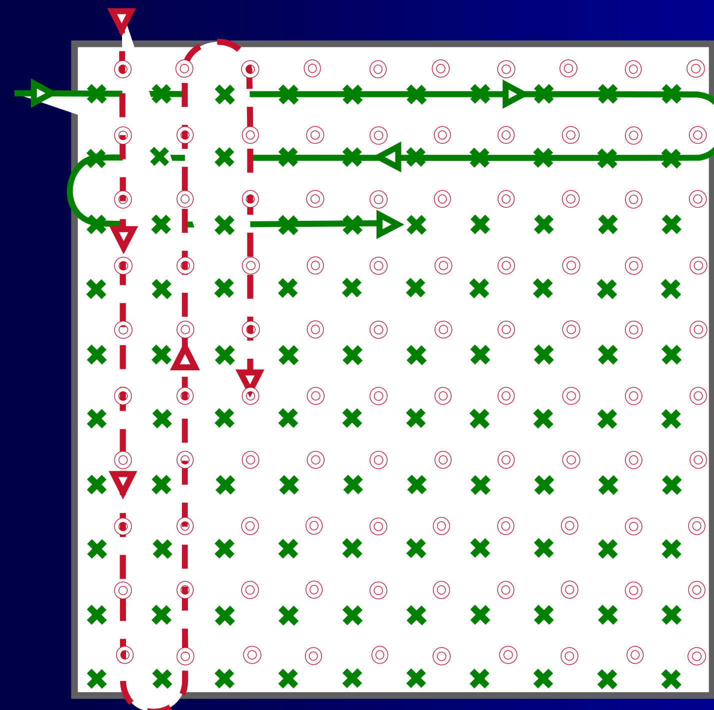
Discrete Sampling



▲ Collection points for 100 discrete samples

▲ Typically only a few discrete samples are collected

Multi-Increment Sampling



o ✖ Increment collection points for two replicate MI samples (100 increments each)

MIS is a 2-Part Process

- Controls error due to heterogeneity
- Field sample collection:
  - Collect multiple (30 - 100) increments (discrete)
  - Of uniform size
  - In an unbiased manner
  - From the entire volume of soil to be represented (Sampling Unit)
  - Combine increments into a single sample (1 – 2 kg dry weight)
- Laboratory processing and sub-sampling:
  - Particle size reduction (drying / sieving / possibly grinding)
  - Representative sub-sampling (multi-increment or rotary sectorial splitter)

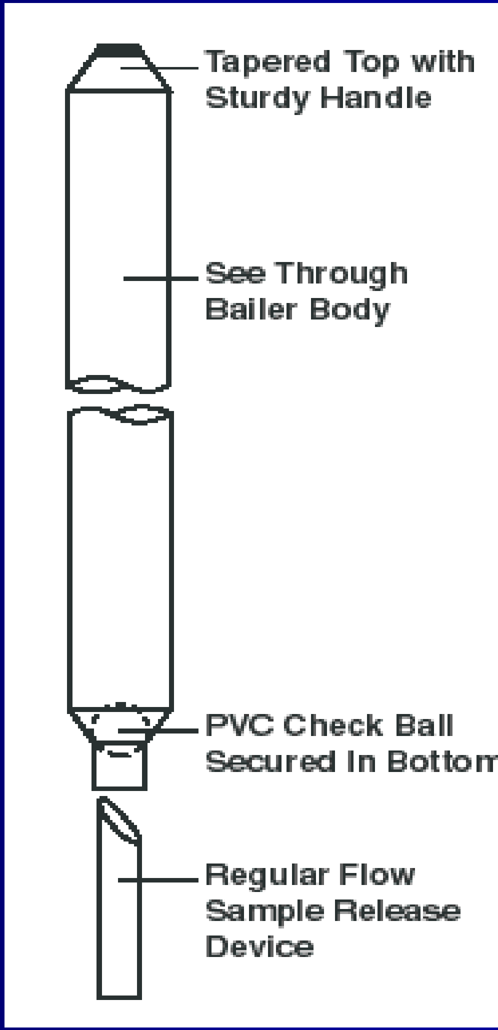
Sampling Procedures

Ground Water Sampling

- Ground Water and product sampling
  - Equipment
    - Bailers
    - Pumps
  - Procedures
    - Purge and low-flow sampling
    - No-purge sampling

Bailers

- Readily available
- Inexpensive
- Time consuming
- Physically demanding
- Aeration of sample (not recommended for VOCs)
- Dedicated use



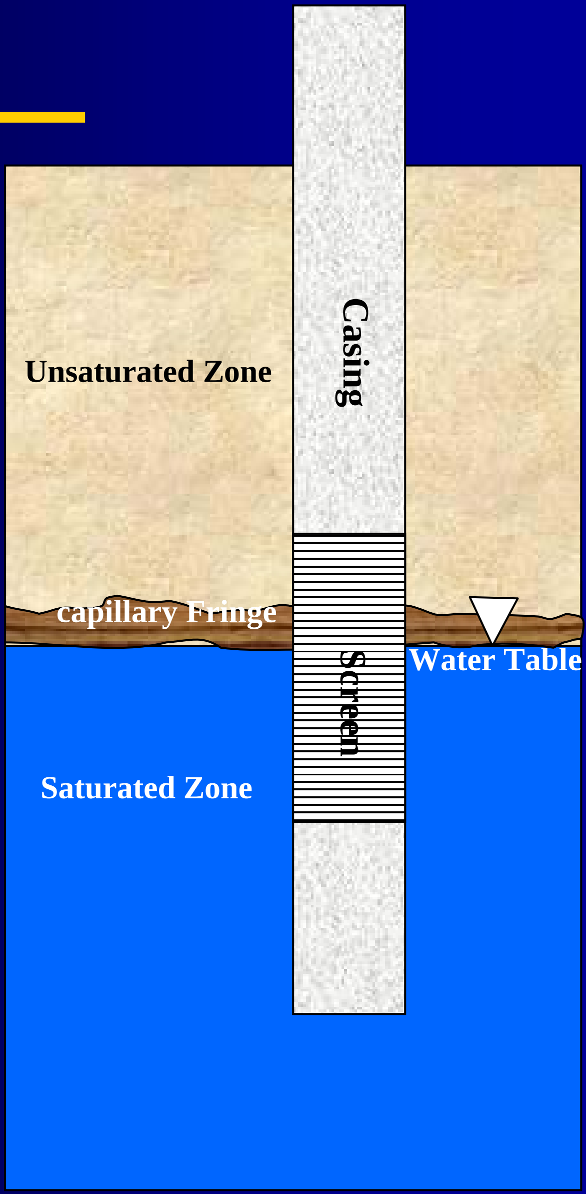
Sampling Procedures (cont.)

Ground Water Sampling

- **Pumps**
  - Bladder pumps
  - Suction-lift pumps (peristaltic pump)
  - Submersible pumps
  - Inertial pumps (direct push)

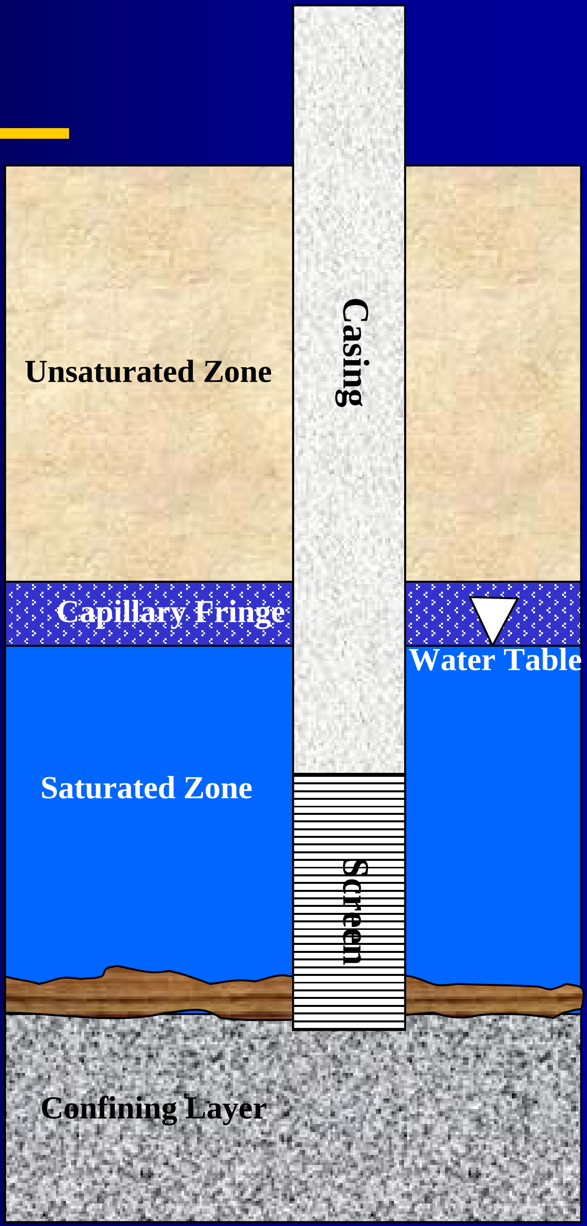
Sampling for LNAPLS

- Low density & solubility
- Occupies capillary fringe
- Well must be screened across water table
- Sample / measure LNAPL
  - Tape, interface probe, clear Teflon bailer



Sampling for DNAPLS

- High density - sinks
- Low solubility
- Screened down to confining layer
- Measure DNAPL layer prior to purging well
  - Interface probe
- Sample with dual check valve bailer
- Use weighted sampler or pump



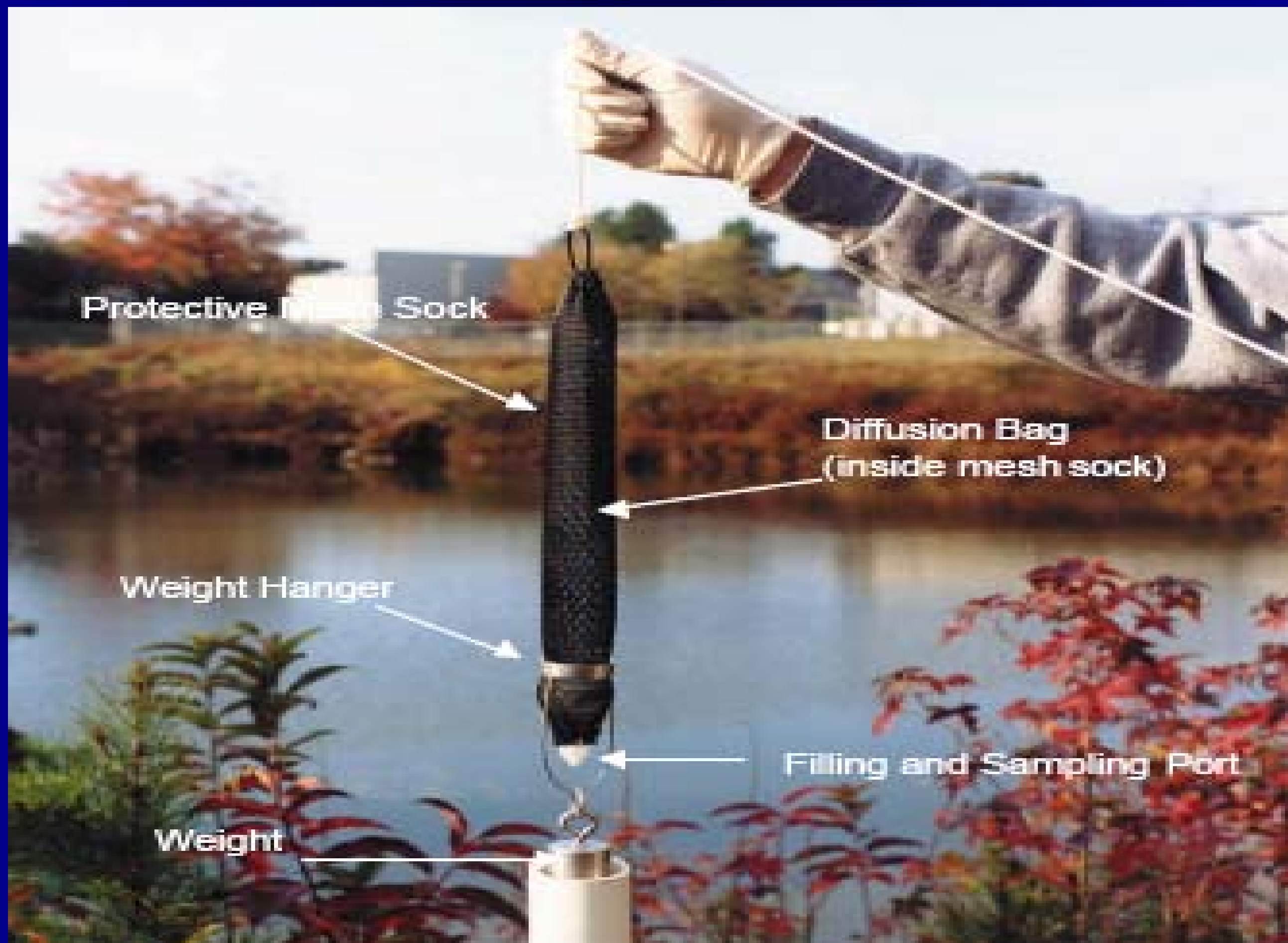
Low-Flow Sampling Procedures

- Minimize disturbance to well and ground water
- Sound water level
- Set pump slowly to point midway in screened interval
- Pump at rate that results in minimal drawdown, laminar flow from formation to pump (Target < 4 inch, 100 – 500 ml/min, but this is only guide)
- Monitor pH, conductivity, temperature, redox, DO, turbidity in flow-through cell
- When parameters stable, take sample, not based on purge volume. DO and turbidity often last to stabilize

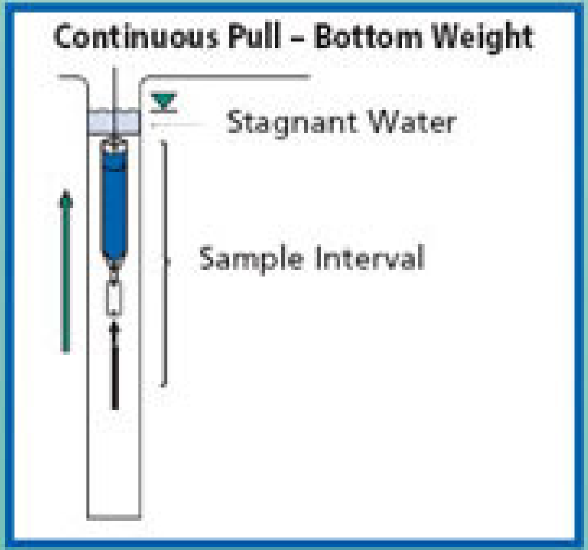
No-Purge Samplers

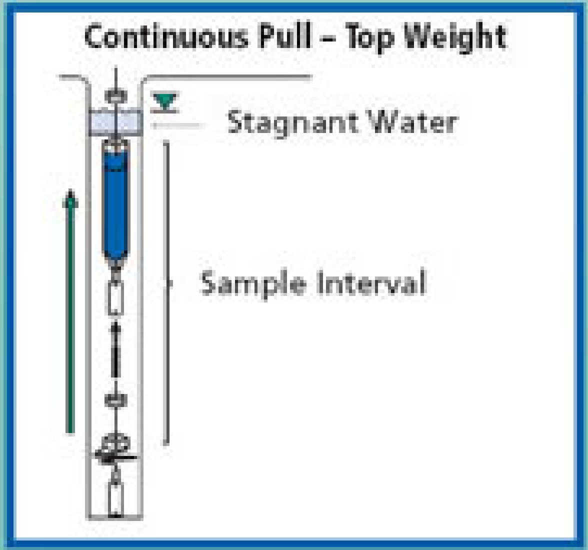
- **Passive Diffusion Bag Samplers (PDBs)**
  - Low density polyethylene (LDPE) bags filled with lab grade water
  - Bags set in screened interval for period of time
  - Contaminants of right molecular size diffuse into bag and reach equilibrium
  - Retrieve bag, analyze
  - Less waste, less labor, better recovery
  - Comparability issues, consider vertical stratification
- **Hydrasleeve, Snap sampler**
- **ITRC Guidance**

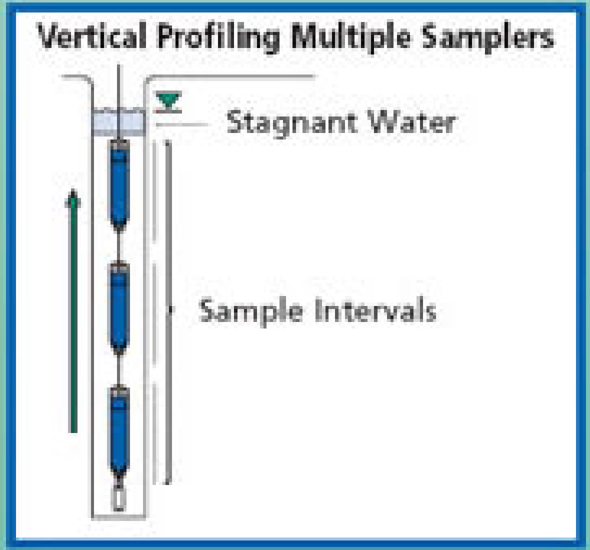
Passive Samplers (cont.)



Hydrasleeve, Snap Samplers







Soil Gas Sampling
Applications

- Locate source(s)
- Design air-based remediation
- Track performance of air-based technologies

Soil Gas Sampling
Uncertainty and Limitations

- Lateral transport of vapors
- Subsurface stratification
  - Unsaturated zone
  - Ground water plume
- Surface coverings
- Precipitation / atmospheric conditions
- Other sources
- Analytical uncertainties

Passive Soil Gas Sampling

- Sorbent material allowed to equilibrate with soil gas (days, weeks)
- Retrieve and desorb mass, quantify
- Qualitative evaluation of mass – correlate with hot spots. Grid for characterizing large areas
- Takes time
- Relatively inexpensive

Active Soil Gas Sampling

- Drive probe or drill borehole
- Seal to prevent atmospheric air entry
  - Probe seal, grout seal, packer
  - Check for leaks, ambient air interferences
- Draw vacuum, purge air from hole
  - Look at concentrations as f(purge volume)
- Take sample, analyze on- or off-site
- Rapid results possible
- Areal survey – shallow depths, vertical profiling
- Partitioning of vapors, correlation with soil samples, and interpretation
- Sampling of SVE systems – wells under vacuum


6 12 '94


TE
5 12 '93

Air Sampling Techniques

- **Ambient air sampling**
  - **USACE EP 1110-1-21 (Air Pathway Analysis)**
  - **USACE EM 200-1-5 (Fixed-Fenceline)**
  - **USEPA TO-Methods**
    - **EPA/600/4-84/041**
    - **EPA/625/R-96/010b)**
- **Point source emission / remedial process sampling**
  - **40 CFR 60, 61, 266**
  - **USEPA SW-846 Chapter 10**
- **Surface area emission flux**
  - **ASTM D 5314**

Air Sampling

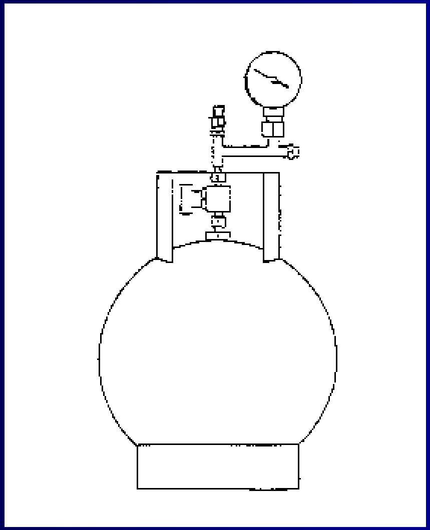
- Direct measurement with on-site instruments
  - NO_x, SO_2, O_3, NH_3, H_2S, CO, VOCs, PM, etc.

Air Sampling
Sampling Techniques

- Whole Air Samples
  - Plastic bags (Tedlar)
  - Metal canisters (Summa)
  - Glass globes
- Component Samples
  - Filtered sample media
  - Solid sorbent media (resin)
  - Trapping liquid (acid impingers, solvents)

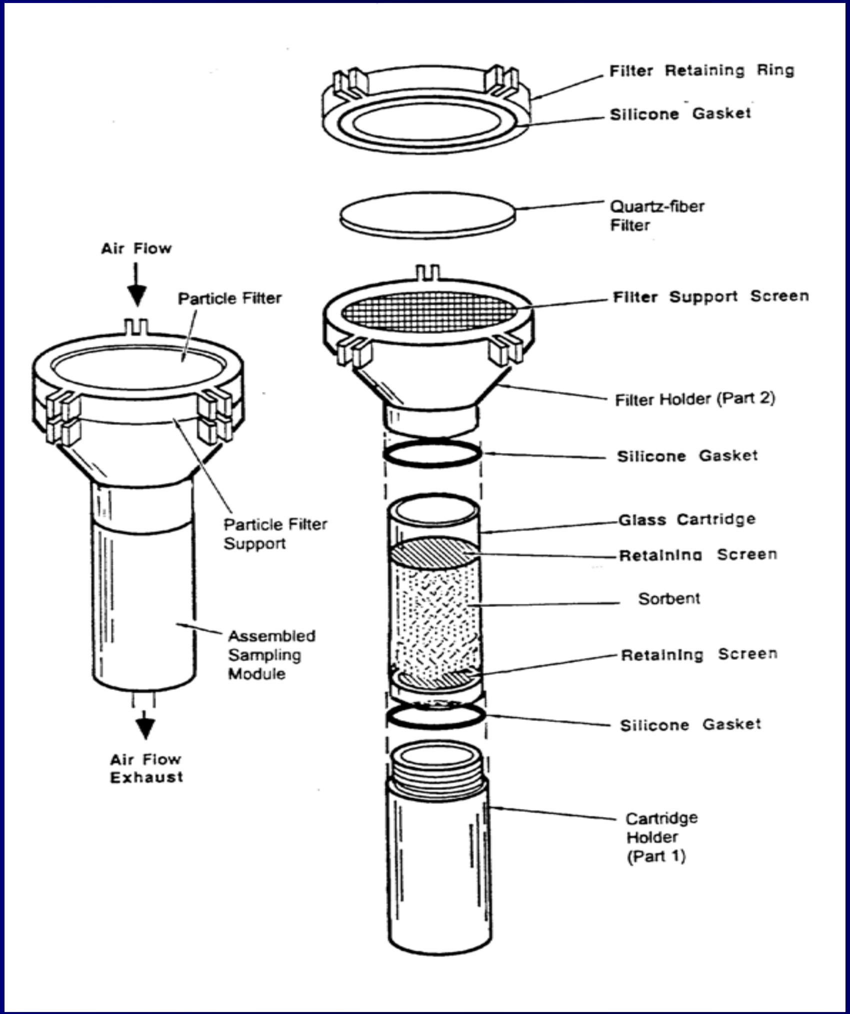
Tedlar Bags

Metal "Summa" Canisters



Air-Based Remediation Technologies

Solid Sorbent Media Cartridge



Point Source Emission / Remedial Process' Sampling

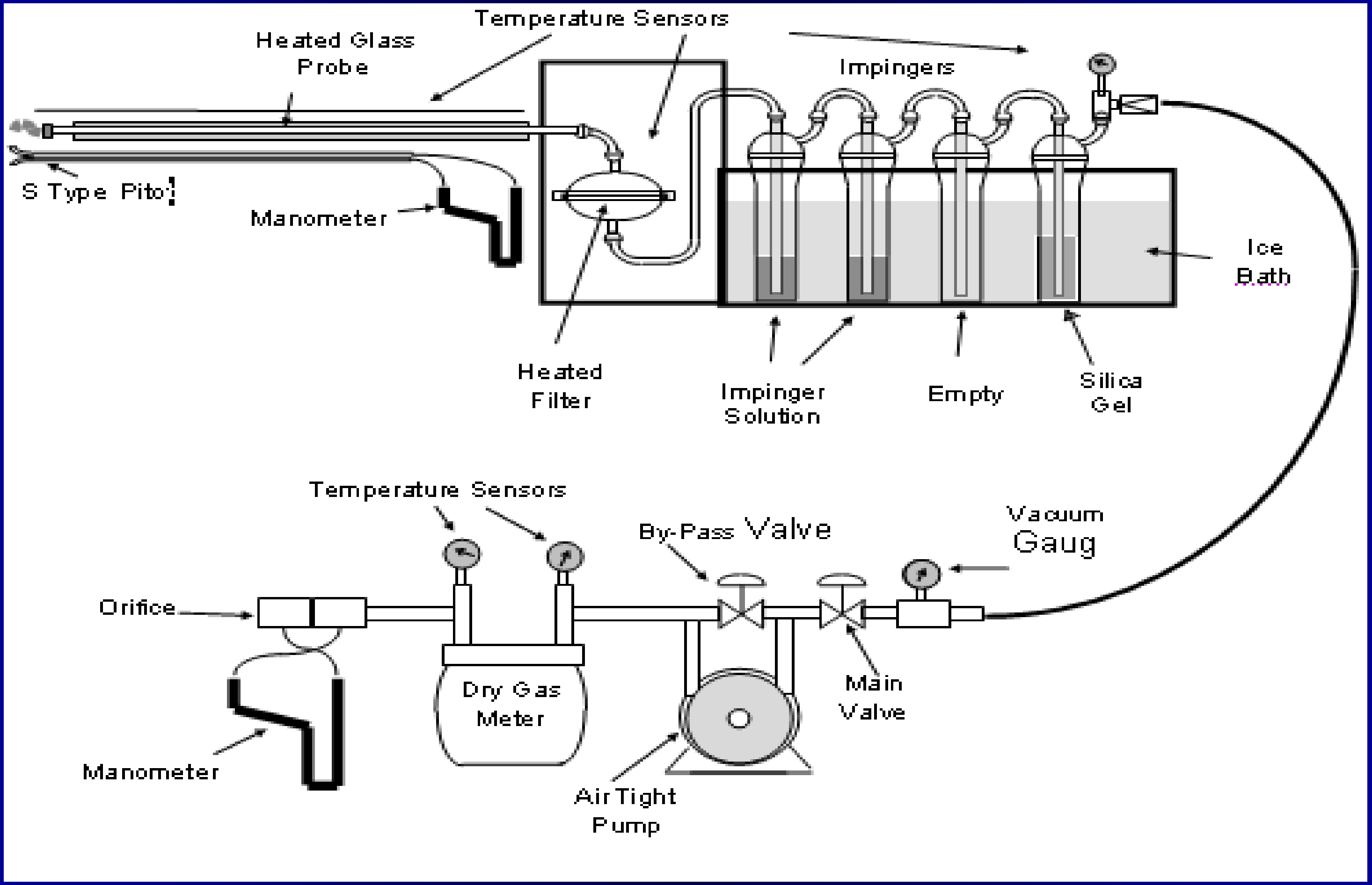
Scope / Application Scenarios

- Regulatory emission compliance
- System process'
  - Optimize operating parameters at start-up
  - Evaluate efficiency / performance
- Air pollution control system performance verification

Point Source Sampling
Sampling Techniques

- **Continuous Emission Monitors (CEMs)**
- **Extractive Sample Collection Analysis**
  - **Sample is extracted from source (i.e., stack) with a vacuum pump through a <u>Sampling Train</u> designed to capture project-specific contaminants**

Stack Sampling Train Schematic



Analytical Methods and Strategies

Chung-Rei Mao

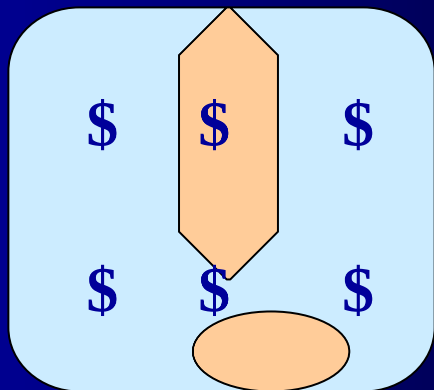
Chemist

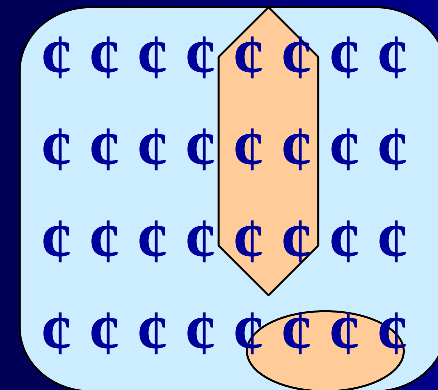
USACE EM CX

Selection of Analytical Techniques / Methods

- Review candidate analytical technologies for measuring project COCs
- Consider strengths and limitations of analytical options against critical decision elements
- Consider site conditions / constraints
- Potential method modifications to accommodate project analytical needs

Data Quality vs. Information Value





Fewer "higher quality" data points ⇒ Lower information value of the data set

Many "lower quality" data **points** ⇒ **Higher** information value of the data **set**

Less likely

More likely

Goal: A defensible site decision that reflects the "true" site condition

Analytical Strategy

- **Establish an analytical strategy that <u>integrates a variety of analytical techniques</u> to help**
  - **Direct fieldwork real-time to areas requiring evaluation**
  - **Focus $$$ analysis to provide the most benefit**
  - **Provide more <u>site information value:</u> Greater sample density results in a larger data-set and improves overall characterization of the site and media**
  - **Implements a standard of checks / balances based on data comparability that can provide the extra assurance in ALL the data supporting project decisions**

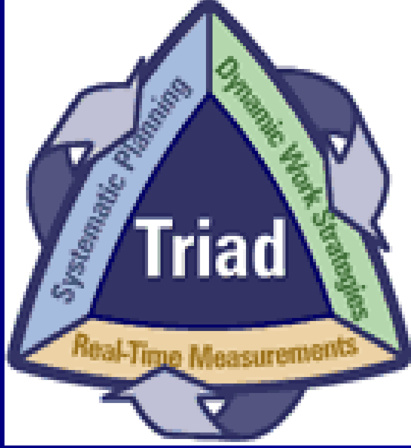
Screening Data

- Screening Data are generated by rapid, less precise methods of analysis with less rigorous sample preparation
- Provide analyte identification and quantification, although quantification may be relatively imprecise
- Require 10% of the screening data be confirmed using analytical methods, QA/QC procedures, and criteria associated with Definitive Data to be considered “data of known quality”
- May be generated on-site or at an off-site location
- Often used for process control

Definitive Data

- Generated using rigorous analytical methods, such as approved USEPA reference methods
- Provide data that are analyte-specific, with confirmation of analyte identity and concentration
- Produce tangible raw data output in the form of paper printouts or electronic files
- Must determine either analytical or total measurement error in order to be considered definitive data
- May be generated on-site or at an off-site location, as long as additional QA/QC requirements are satisfied
- Often used to demonstrate compliance with regulatory requirements

Triad



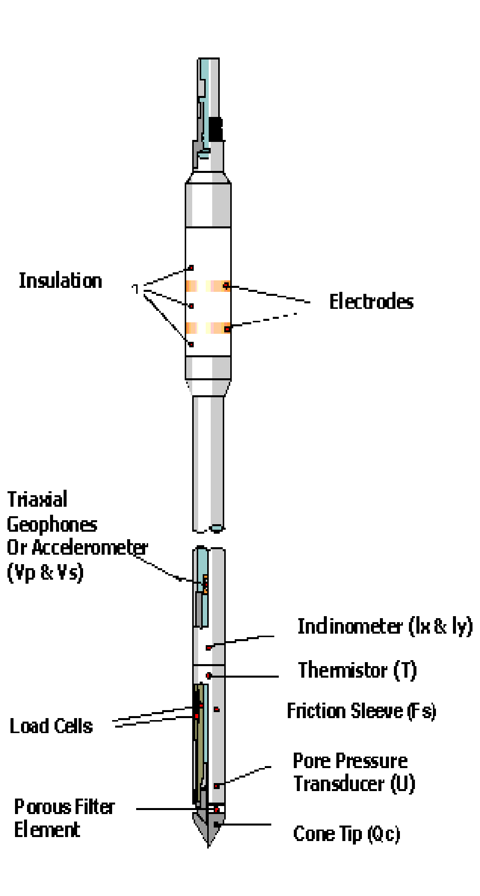
- **Three components:**
  1. **<u>Systematic Planning</u>**
     - **Scientifically defensible**
     - **Identification of decisions to be made**
     - **Development of a Conceptual Site Model (CSM)**
     - **Evaluation of decision uncertainty**
  2. **<u>Dynamic Work Strategies</u>**
     - **Flexible to adapt information generated by real-time measurement technologies**
     - **As information gathered, make decisions on subsequent activities to meet cleanup goals**
  3. **<u>Real-Time Measurement Technologies</u>**
     - **Any data generation mechanism that supports real-time decision-making, including:**
       - **Field-based measurement technologies**
       - **Rapid turn-around lab analysis**

Organic Chemical Characterization Techniques

- **Screening**
  - Hand-held survey instruments (PID / FID)
  - Colorimetric tests / indicators
  - Immunoassay
  - SCAPS – Laser-Induced Fluorescence (LIF) probe and other sensors
- **Definitive**
  - Gas Chromatograph (GC)
  - Gas Chromatograph / Mass Spectrometer (GC/MS)
  - High Performance Liquid Chromatograph (HPLC)
  - Fourier Transform Infrared Spectrometer (FTIR)

Direct Push Technology
Sensors

- Electrical Resistivity
- Membrane Interface Probe
- Laser-Induced Fluorescence (Petroleum, Oil, & Lubricant)
- Thermal Desorption VOC
- Hydrosparge VOC Sensing
- Multiport Sampler



Sampling and Analysis

Summary

- Describe general technical project planning approach for site characterization and remediation
- Describe the benefits of proper project planning and how planning supports site closeout
- Describe sampling strategies and technologies for soils, ground water, soil gas, air, and process controls
- Introduce analytical methods and strategies for chemical testing

References

- DQO – USEPA QA/G-4 http://www.epa.gov/QUALITY/qs-docs/g4-final.pdf
- TPP – USACE EM 200-1-2 http://140.194.76.129/publications/eng-manuals/em200-1-2/entire.pdf
- Low Flow – USEPA/540/S-95/504 http://www.epa.gov/swertio1/tsp/issue.htm
- USEPA Chemical Testing – SW-846 http://www.epa.gov/osw/hazard/testmethods/sw846/online/index.htm
- USEPA Air Toxic Methods – TO http://www.epa.gov/ttnamti1/airtox.html
- DoD Quality Systems Manual: http://www.navylabs.navy.mil/QSM%20Version%204.1.pdf
- USACE Engineer Manuals http://140.194.76.129/publications//eng-manuals/

QUESTIONS?

Chung-Rei Mao
Chemist
USACE EM CX