Sampling, Analysis, and Monitoring to Evaluate Monitored Natural Attenuation

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Site Characterization

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Monitoring the Effectiveness of Natural Attenuation

U.S. Geological Survey
and
Barbara H. Wilson

Methods for Monitoring Contaminants

Analysis	Method/Reference	Comments
Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds)	SW8020 (sites with petroleum hydrocarbons only) SW8260A (sites with chlorinated solvents or mixed solvents/petroleum hydrocarbons)	Handbook method; analysis may be extended to higher molecular weight alkyl benzenes

Monitoring for Geochemical Conditions

Analytical Parameter	Field or laboratory parameter	Method of analysis
Dissolved oxygen (DO)	field	meter, field kit titration
Nitrate (NO_3)	laboratory	Ion Chromatography
Nitrite (NO_2)	laboratory	Ion Chromatography
Dissolved ferrous iron (Fe^{2+})	field	Field kit spectrophotometer
Sulfate (SO_4)	laboratory	Ion Chromatography
Hydrogen sulfide (H_2S)	field	Field kit spectrophotometer
Dissolved Methane (CH_4)	laboratory	GC FID[1]
pH (units)	field	meter
Eh (redox potential)	field	meter
Dissolved Hydrogen (H_2)	field	gas chromatography[2]

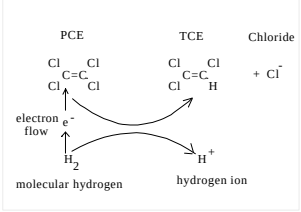
When Hydrogen Analyses are Useful

Some chlorinated solvents plumes exhibit attenuation of solvents without significant accumulation of transformation products.

If hydrogen concentrations range from 1 nannomolar to 4 nannomolar, reductive dechlorination will occur.

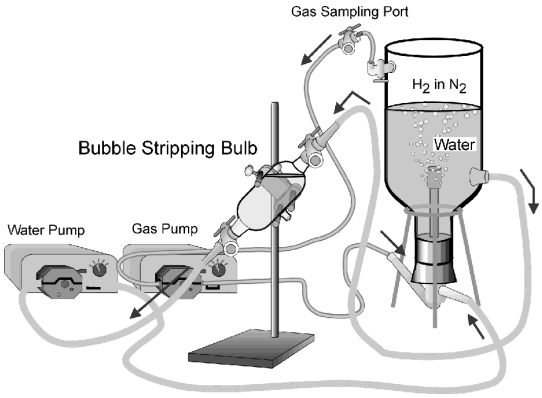
Molecular Hydrogen (H_2)drives Reductive Dechlorination

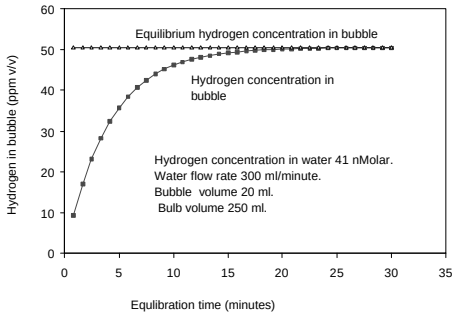
(Gosset and Zinder, 1996)



Steady-State Hydrogen Concentrations Reflect Redox Processes

Terminal Electron-Accepting Process	Characteristic Hydrogen Concentration (nM)
Denitrification	0.1
Fe(III) Reduction	0.2-0.8
Sulfate Reduction	1.0-4.0
Methanogenesis	>5.0





Monitoring Strategies

There are three kinds of monitoring.

1) Site characterization to describe disposition of contamination and forecast its future behavior.
2) Validation monitoring to determine whether the predictions of site characterizations are accurate.
3) Long-term monitoring to ensure that the behavior of the contaminant plume does not change.

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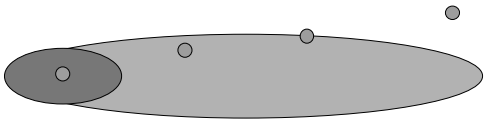
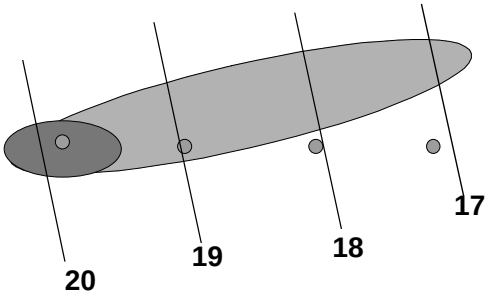
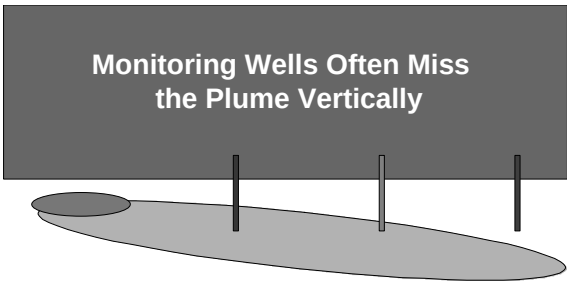
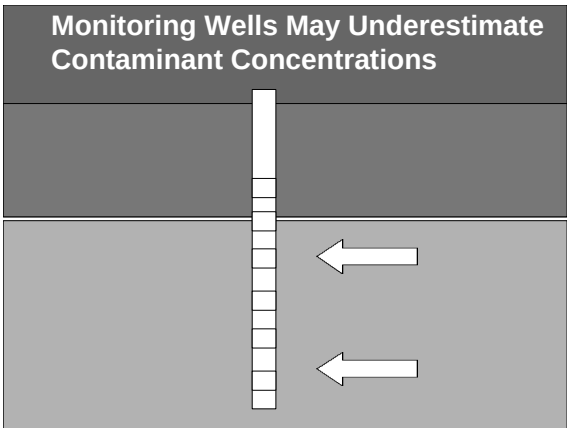
Monitoring Wells Often Miss the Plume (Plan View)



Until you have wells, you don't know the direction of ground-water flow







Example of Characterization Monitoring

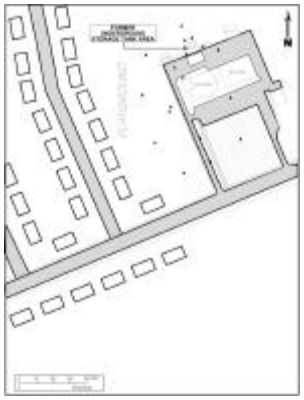
It's not nice to fool Mother Nature,
but she doesn't mind fooling you

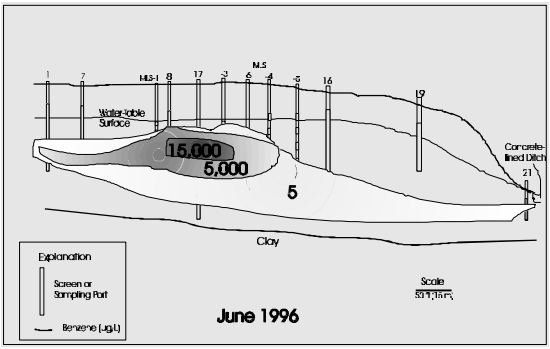
Fate of MTBE relative to benzene at a gasoline spill site (1993-98)

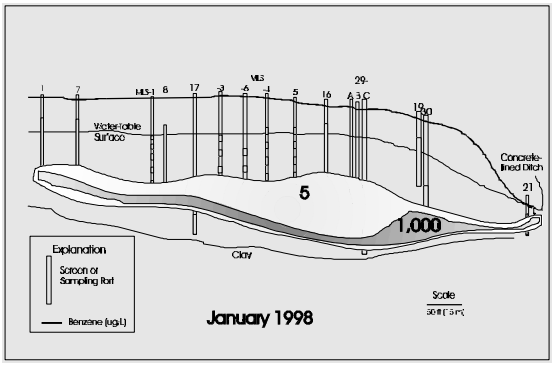
By

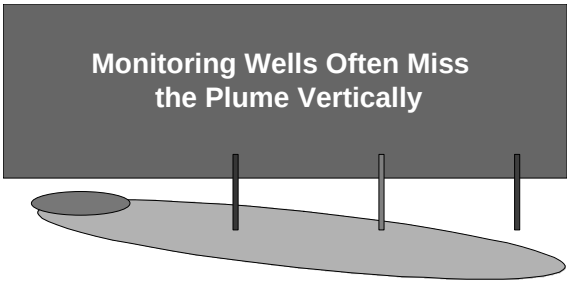
James E. Landmeyer
U.S. Geological Survey

Battelle Conference, May 1998









Site Characterization

- **Distribution of contamination can be mapped using:**
- **Geoprobe samples**
- **The Waterloo sampler**
- **Hydropunch samples**
- **other water sampling through a cone penetrometer**
- **extraction of core samples**
- **soil gas sampling**

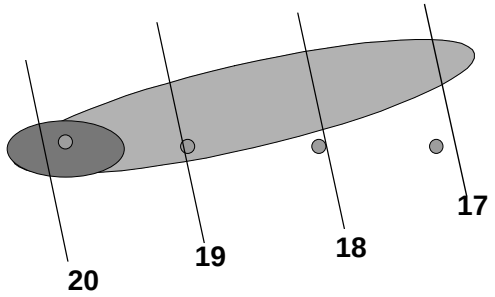
Example: Characterization Monitoring: Kings Bay, GA

- Monitoring Wells
- Geoprobe Source area delineation
- Redox parameters
- Chlorinated ethenes

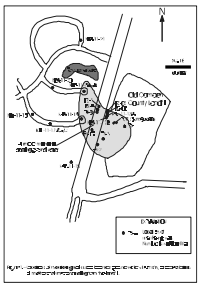
Site Characterization

- **Each potentially transmissive interval should be sampled**
- **YOU OUGHT TO KNOW WHERE THE WATER'S GOING TO GO *BEFORE* YOU PUT IN YOUR WELLS!!**

Until you have wells, you don't know the direction of ground-water flow



Old Camden County Landfill, Kings Bay, GA

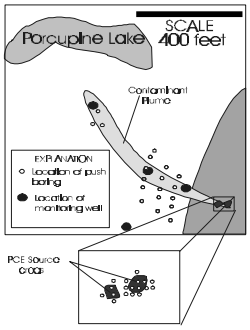


Site Characterization

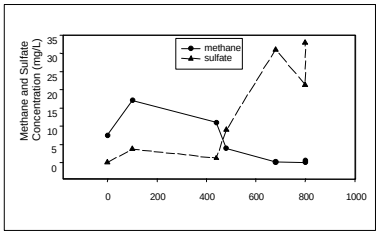
- **The density of sampling during the site characterization must be related to:**

  The geological complexity of the site

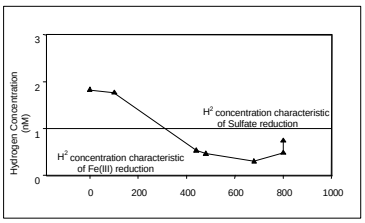
Location of Source Areas and Contamination Plume



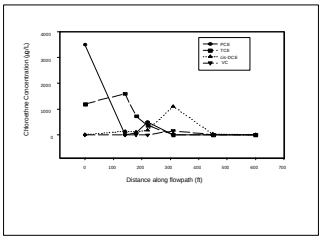
Redox Zonation of Kings Bay Site



Redox Zonation of Kings Bay Site (Cont'd)



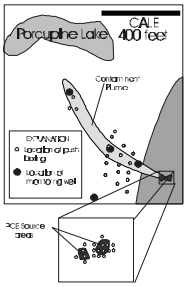
Concentrations of Changes of Chlorinated Ethenes



Natural Attenuation of Chlorinated Solvents, Old Camden County Landfill

- Is relatively efficient.
- Nevertheless, it is not efficient enough to meet remediation goal.
- NA was combined with source removal.

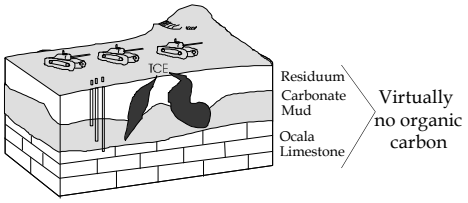
CAP Specifies Source Area removal, Plume is treated with Natural Attenuation.



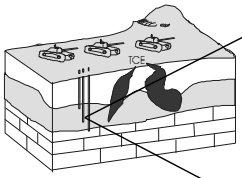
Example: Characterization Monitoring: Albany, GA

- Monitoring Wells
- Redox parameters
- Chlorinated ethenes

Marine Corps Logistics Base, Albany, Georgia

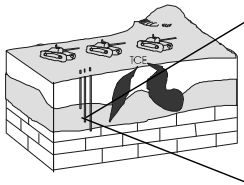


Well ALB 12-1B--Redox Conditions not favorable for Reductive Dehalogenation



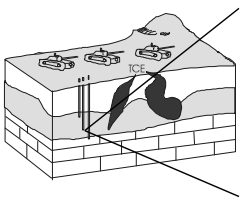
- DO = 7.5 mg/L
- H_2 = 0.05nM
- CH_4 < 0.02 mg/L
- Benzene < 0.2 µg/L
- TCE = 2,202 µg/L
- cis DCE < 0.2 µg/L
- VC < 0.2 µg/L

Well 2218-MW2--Presence of BTEX drives Reductive Dehalogenation



- DO = 2.0 mg/L
- H_2 = 7.3 mg/L
- CH_4 = 0.7 mg/L
- Benzene = 151 µg/L
- TCE = 168 µg/L
- cis DCE = 568 µg/L
- VC = 236 µg/L

Well 2218-MW-1-- Water Chemistry Records Past Reductive Dehalogenation



- DO = 5.0 mg/L
- H_2 = 0.59 nM
- CH_4 < 0.02 mg/L
- Benzene < 0.2 µg/L
- TCE = 201 µg/L
- cis DCE = 71 µg/L
- VC = 2.7 µg/L

Redox Chemistry gives a Snapshot in Time.

- It may not reflect the historical behavior of the contamination.
- It may not predict future behavior of the contamination.

Kings Bay is an Example of Efficient NA--Albany is an example of Inefficient NA

- This illustrates why characterization monitoring is so important for assessing natural attenuation.
- EVERY SITE IS DIFFERENT!!!

Site Characterization Monitoring Should Consider Multiple Lines of Evidence

- Redox Conditions
  - Presently observed conditions
- Distribution of Daughter Products
  - Record of past conditions
- Hydrologic Framework
  - Prediction of future conditions

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Verification and Long-term Monitoring

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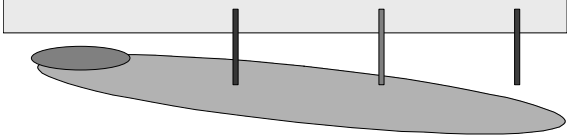
Validation Monitoring

- **Once a conceptual model has been accepted, a period of monitoring is required to verify that the forecast of the conceptual model is adequate**

Monitoring Wells Often Miss the Plume Vertically



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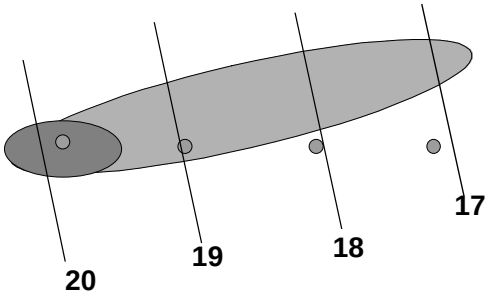
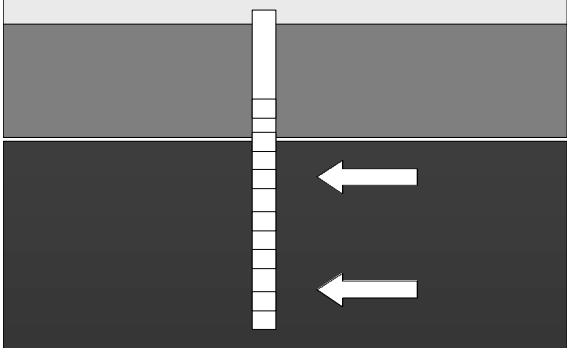


Monitoring Wells May Underestimate Contaminant Concentrations



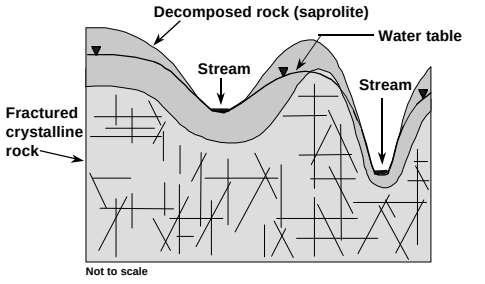
The frequency of validation monitoring should be related to:

- The natural variability in contaminant concentrations
- The distance and time of travel from the source to the location where the acceptance criteria are applied
- The reduction in contaminant concentration required to meet the acceptance criteria

Example: Woodlawn NPL Site Cecil County, Maryland

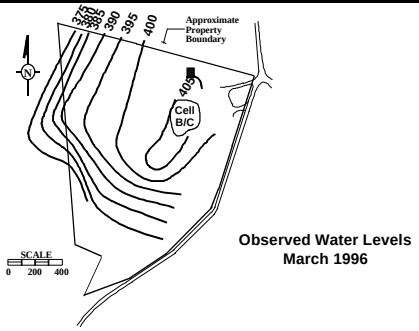
Vinyl Chloride Plume in Decomposed Rock (Saprolite) and Fractured Bedrock. VC at this site is from an industrial source.

Woodlawn NPL Site Cecil County, Maryland



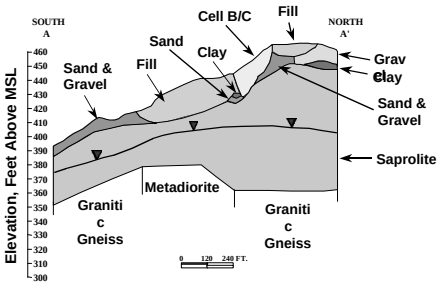
Occurrence of ground water in the Piedmont

Woodlawn NPL Site Cecil County, Maryland



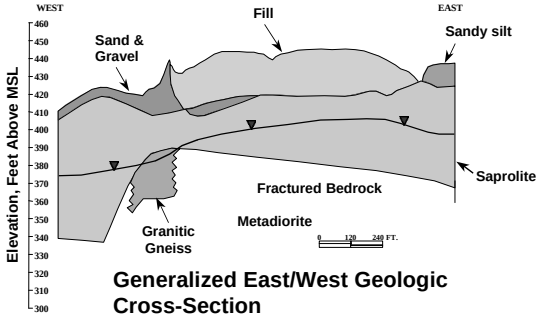
Observed Water Levels March 1996

Woodlawn NPL Site Cecil County, Maryland



Generalized North/South Geologic Cross-Section

Woodlawn NPL Site Cecil County, Maryland



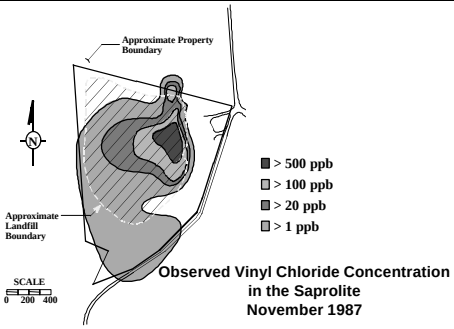
Generalized East/West Geologic Cross-Section

Woodlawn NPL Site
Cecil County, Maryland

Saprolite

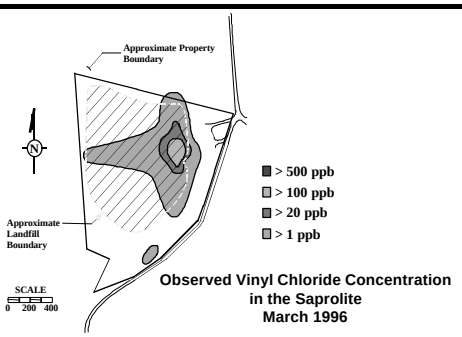
Hydraulic Conductivity	**0.24 to 0.79 ft/d**
Hydraulic Gradient	**0.06**
Seepage Velocity	**87 ft/year**
Plume Length	**1,000 feet**
Half Life total plume	**-0.3 years**

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride Concentration
in the Saprolite
November 1987

Woodlawn NPL Site
Cecil County, Maryland



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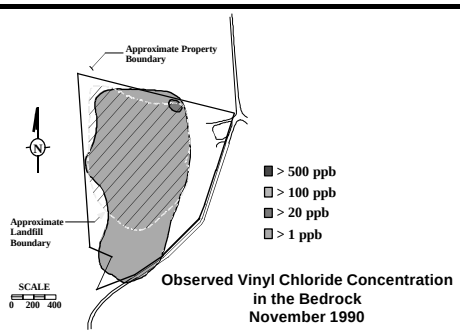
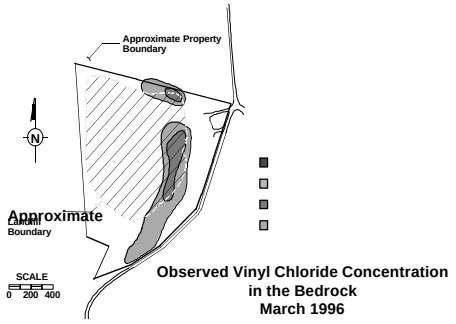


Observed Vinyl Chloride Concentration
in the Bedrock
November 1990

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride Concentration
in the Bedrock
March 1996

Contaminant Transport

- **Contaminant plume appears to be moving through fractured portions of the bedrock.**

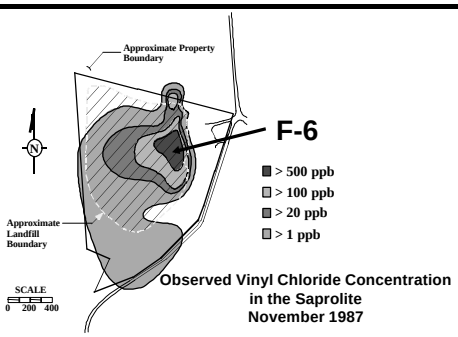
Woodlawn NPL Site
Cecil County, Maryland

VC degradation: WHY IS IT HAPPENING?

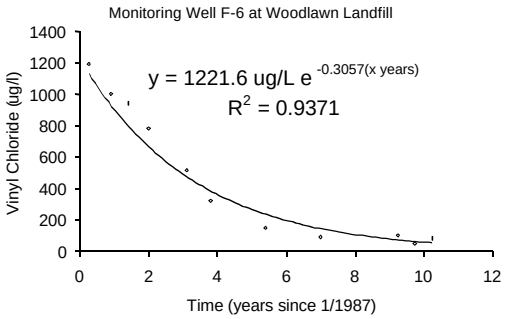
- **Aerobic Oxidation (most rapid)**
  » $2O_2$ + $CH_2 = CHCl$ >> $2CO_2$ + $3H^+$ + Cl
- **Anoxic Oxidation**
  $10Fe_3^+$ + $CH_2 = CHCl$ + $4H_2O$ --> $2CO_2$ + $11H^+$ + Cl + $10Fe_2^+$
- **Volatilization**
- **Sorption (very low for vinyl chloride)**

Location of Well F-6

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride Concentration in the Saprolite November 1987



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2) **Validation monitoring to determine whether the predictions of site characterizations are accurate.**
3) **Long-term monitoring to ensure that the behavior of the contaminant plume does not change.**

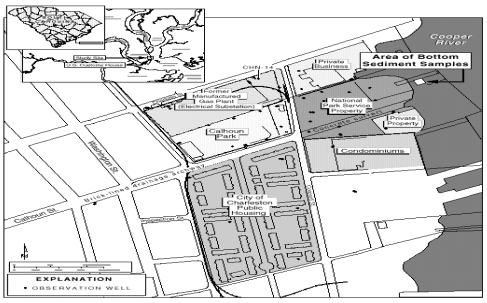
Long-term Monitoring

- **If validation monitoring documents that natural attenuation will meet the acceptance criteria, then a program of long-term monitoring should be implemented.**

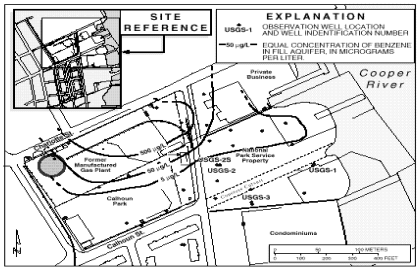
Long-term Monitoring

- **The interval of sampling should be related to the expected time of travel of the contaminant along the flow path from one monitoring well to the next.**

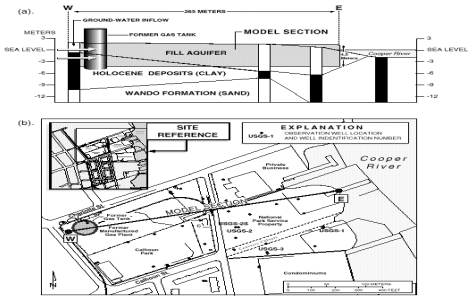
Example of Validation & Long-Term Monitoring:Charleston MGP Site



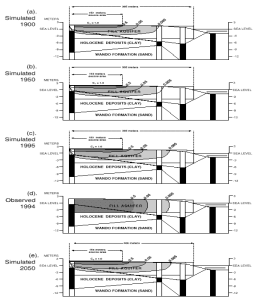
Contaminants in Ground Water



Hydrogeology of MGP Site



Simulation of Plume Migration



See following page for an enlarged version of this slide.

Long-Term Monitoring Plan for the MGP Site

- Model indicates plume is stationary. Long Term Monitoring designed to evaluate changes in plume size.
- GW time of travel is relatively slow (~40 ft/yr). Quarterly sampling is probably too frequent; annual or biannual sampling is more appropriate.