VI: Chlorinated vs Petroleum Hydrocarbons

Key topics

- Differing characteristics between petroleum and chlorinated solvents
- Petroleum chemistry and biodegradation
- Multiple lines of evidence
- Conceptual Site Model

Morning

Welcome

↓

ITRC Introduction

↓

General VI Overview

↓

VI: Chlorinated vs Petroleum Hydrocarbons

↓

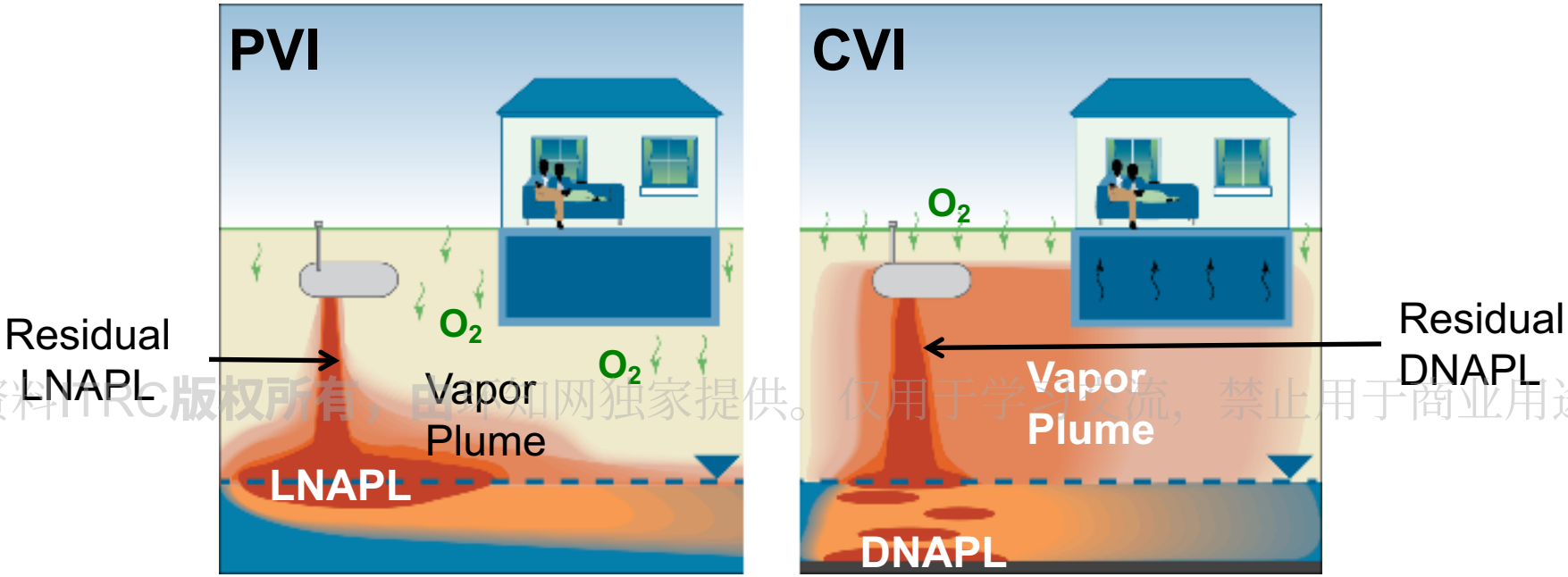
Lunch

Learning Objectives

At the end of this module, the learner should be able to:

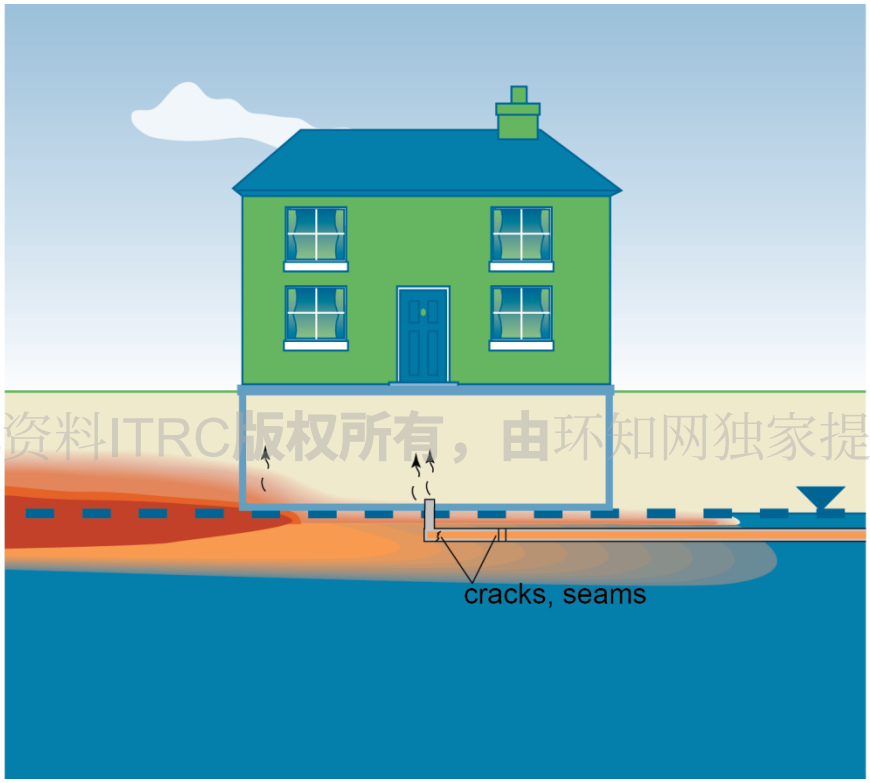
- Understand the differences between PVI and CVI
- Understand the basic principles of vapor movement
- Understand the basics of a conceptual site model (CSM) for the PVI pathway
- Recognize the significant role aerobic biodegradation plays in limiting the PVI pathway potential

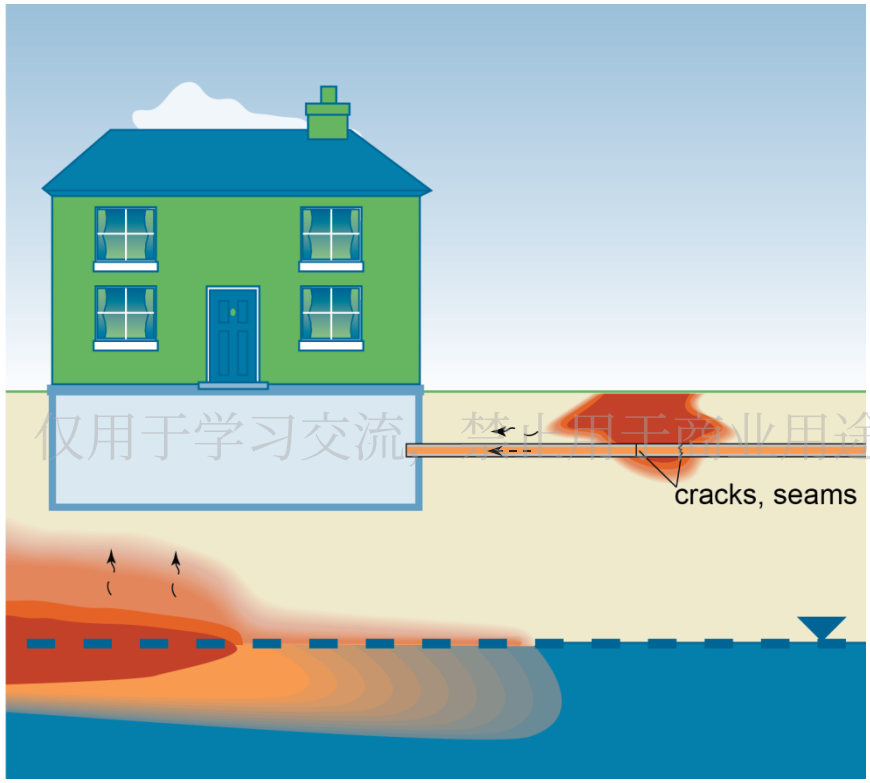
Differences Between PVI and CVI



Variable	PVI	CVI
Type of chemical	petroleum hydrocarbon	chlorinated hydrocarbon
Example	benzene	tetrachloroethene (PCE)
Source Type	LNAPL	DNAPL
Aerobic biodegradation	**Consistently very rapid**	consistently very limited
Vapor intrusion potential	low	high
Degradation products	CO_2, H_2O	intermediates

PVI: Experience from PVI Investigations

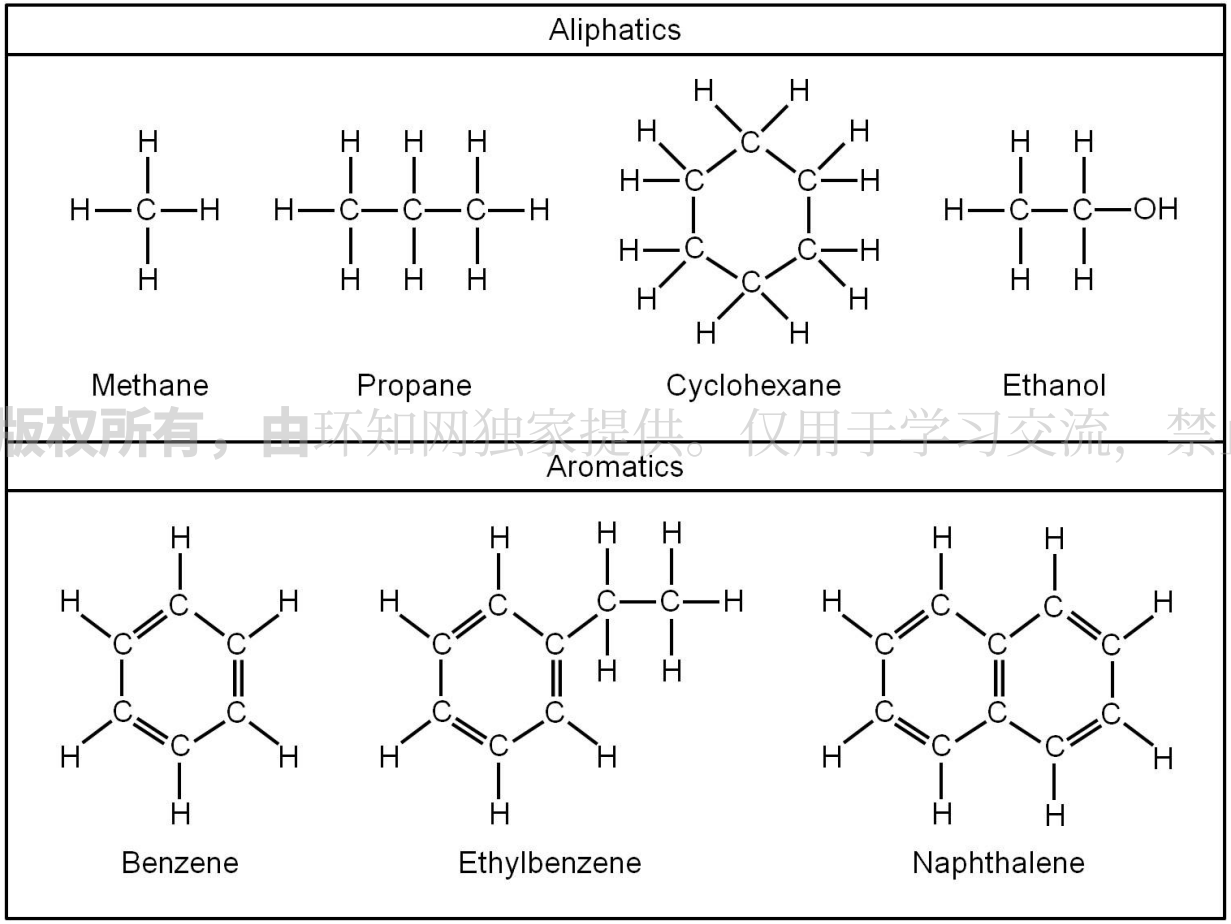




KEY POINT:

- **For petroleum sites, vapor intrusion is generally associated with i) direct impacts or ii) LNAPL sources, but not diffusion of vapors from dissolved plumes.**
- **Delineation of vapor sources is important for screening**

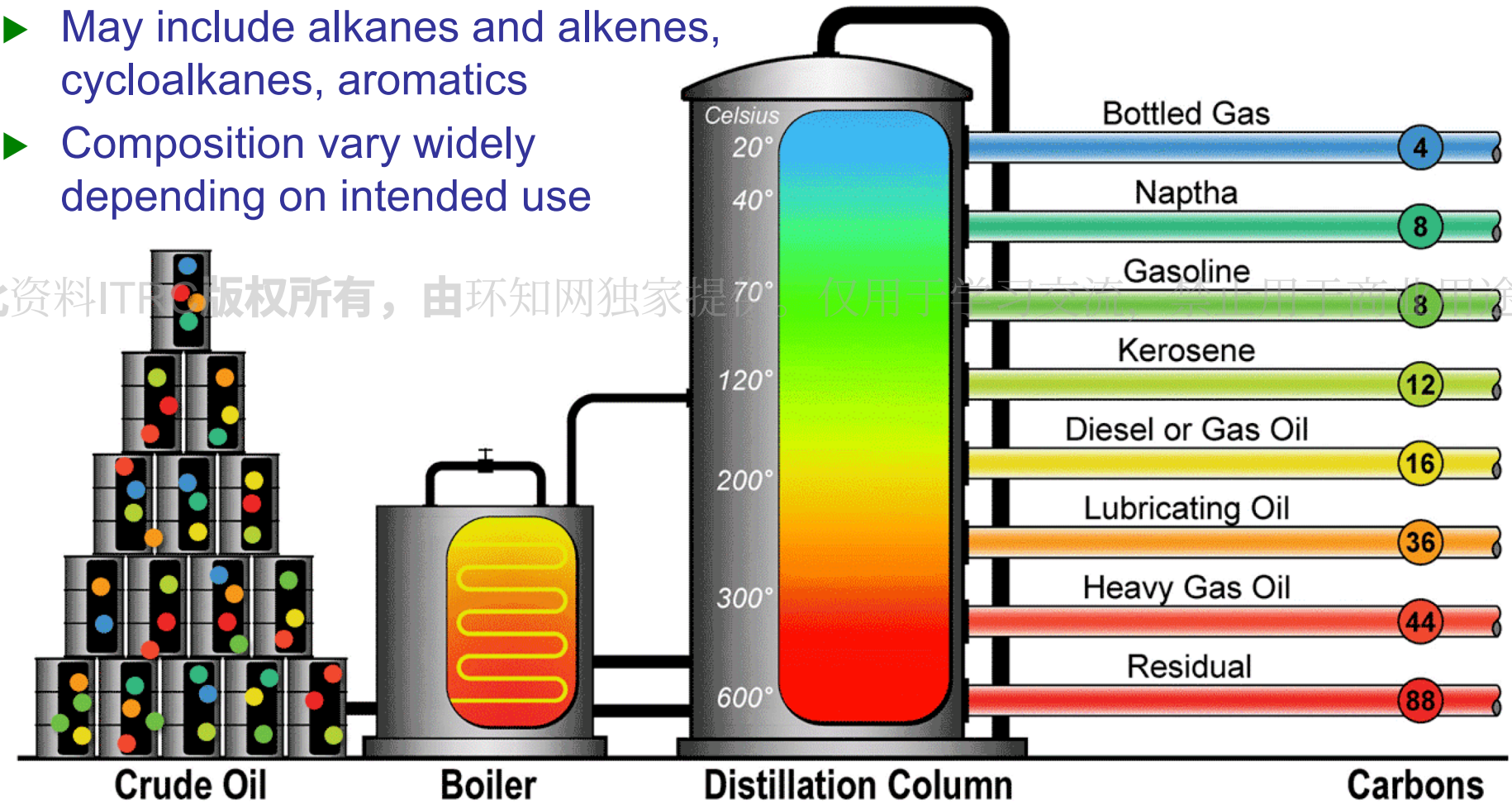
Aliphatic and Aromatic Compounds



Crude oil contains many types of hydrocarbons, including paraffins, isoparaffins, aromatics, naphthenes, and olefins.

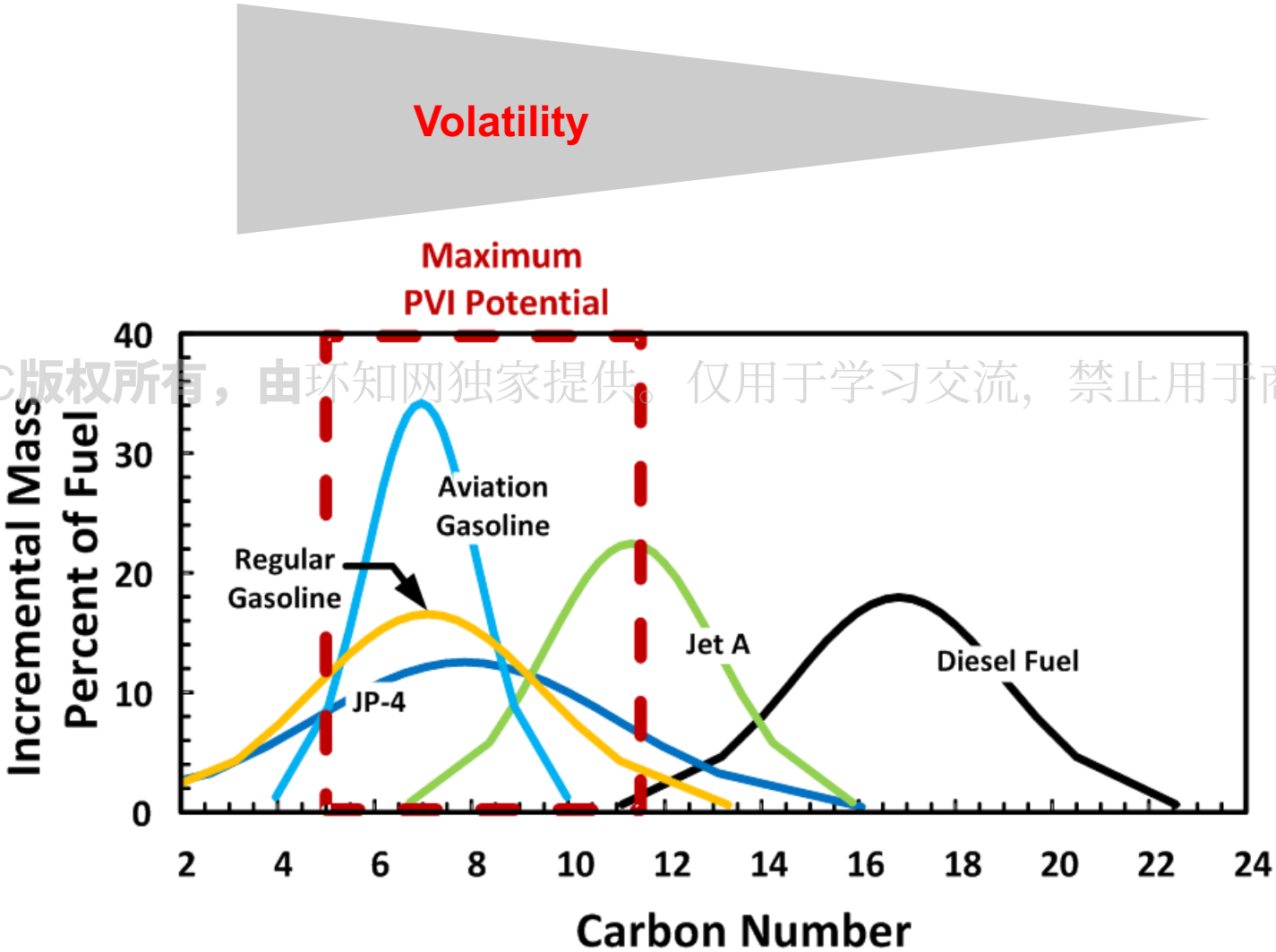
Understanding the Chemistry of Petroleum

- Mixtures of hydrocarbons
- May include alkanes and alkenes, cycloalkanes, aromatics
- Composition vary widely depending on intended use



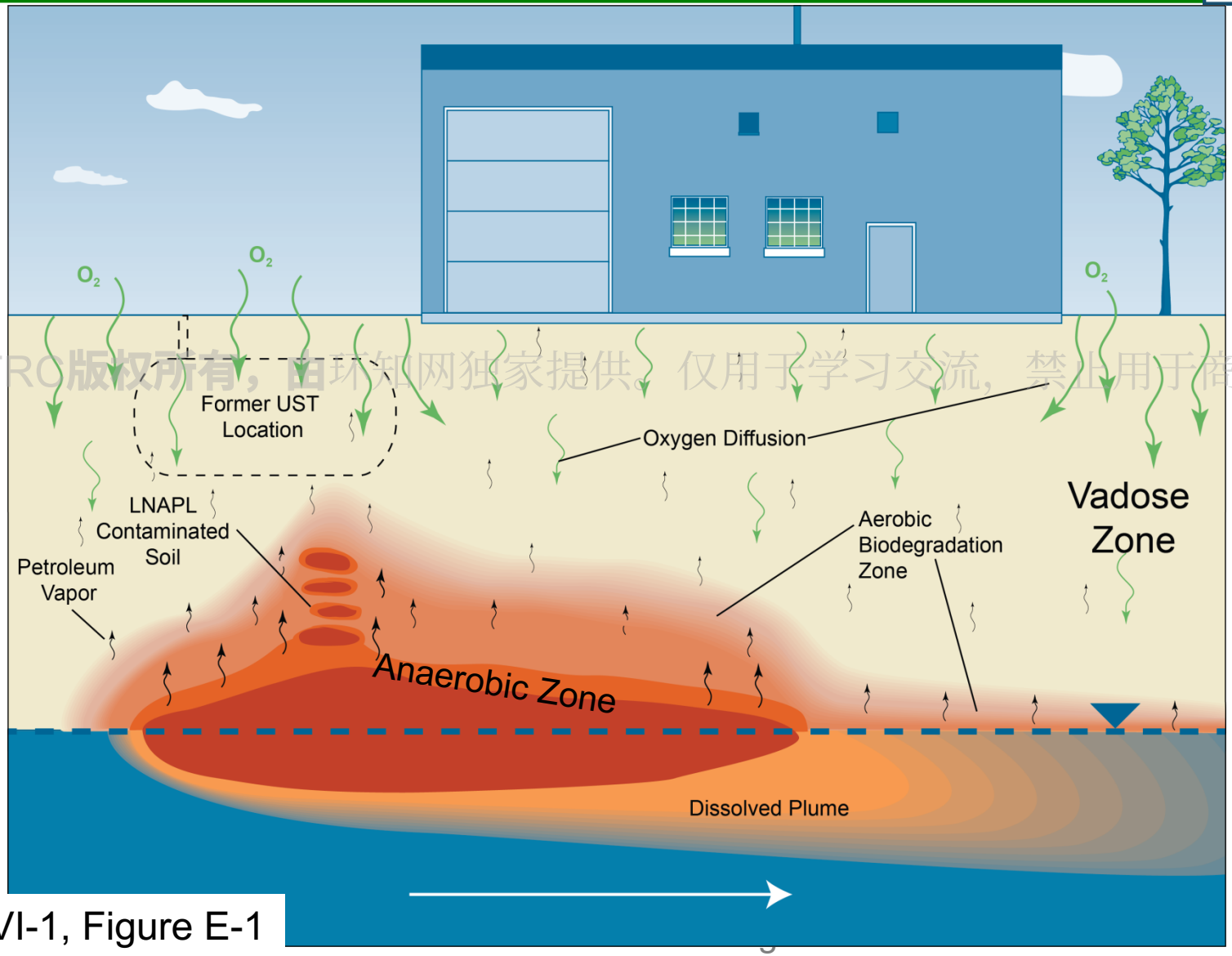
Source: Haley & Aldrich

Which Petroleum Fuels have the Greatest PVI Potential?



ITRC PVI-1, Figure 2-3

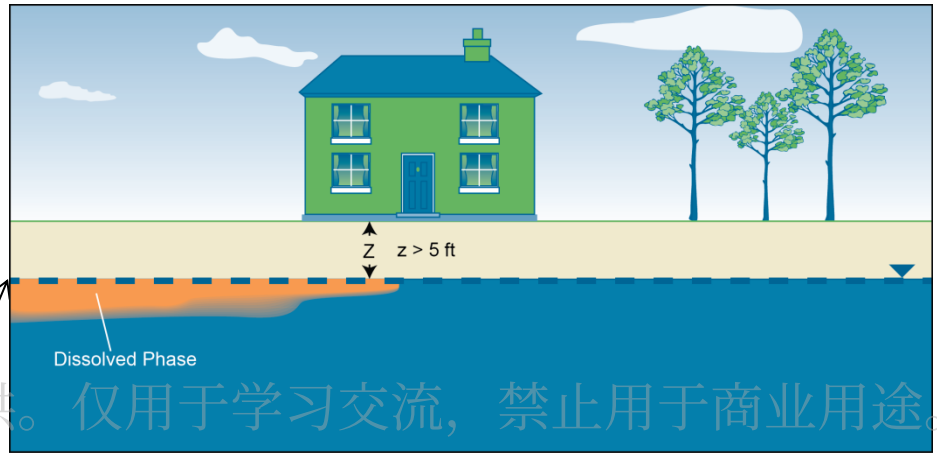
Typical PVI Conceptual Site Model



ITRC PVI-1, Figure E-1

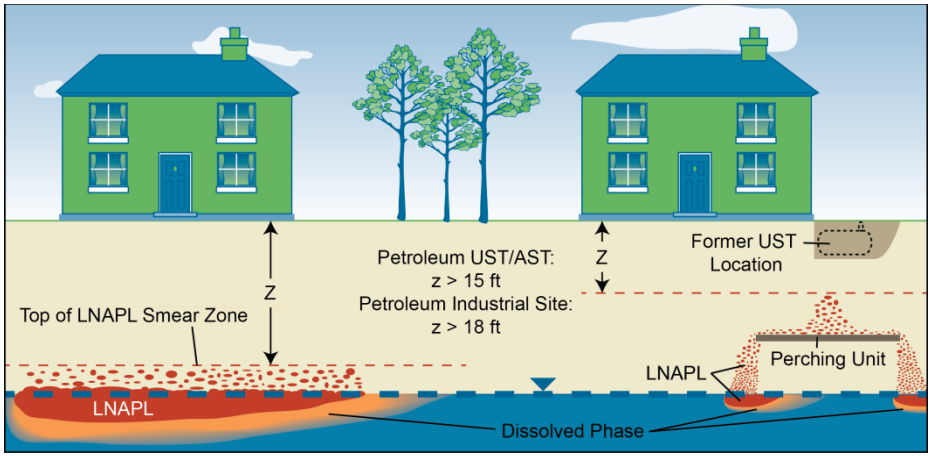
Conceptual Site Model and Vertical Separation Distance

- Vertical screening distances can be used when biodegradation interface occurs at a distance away from the receptor

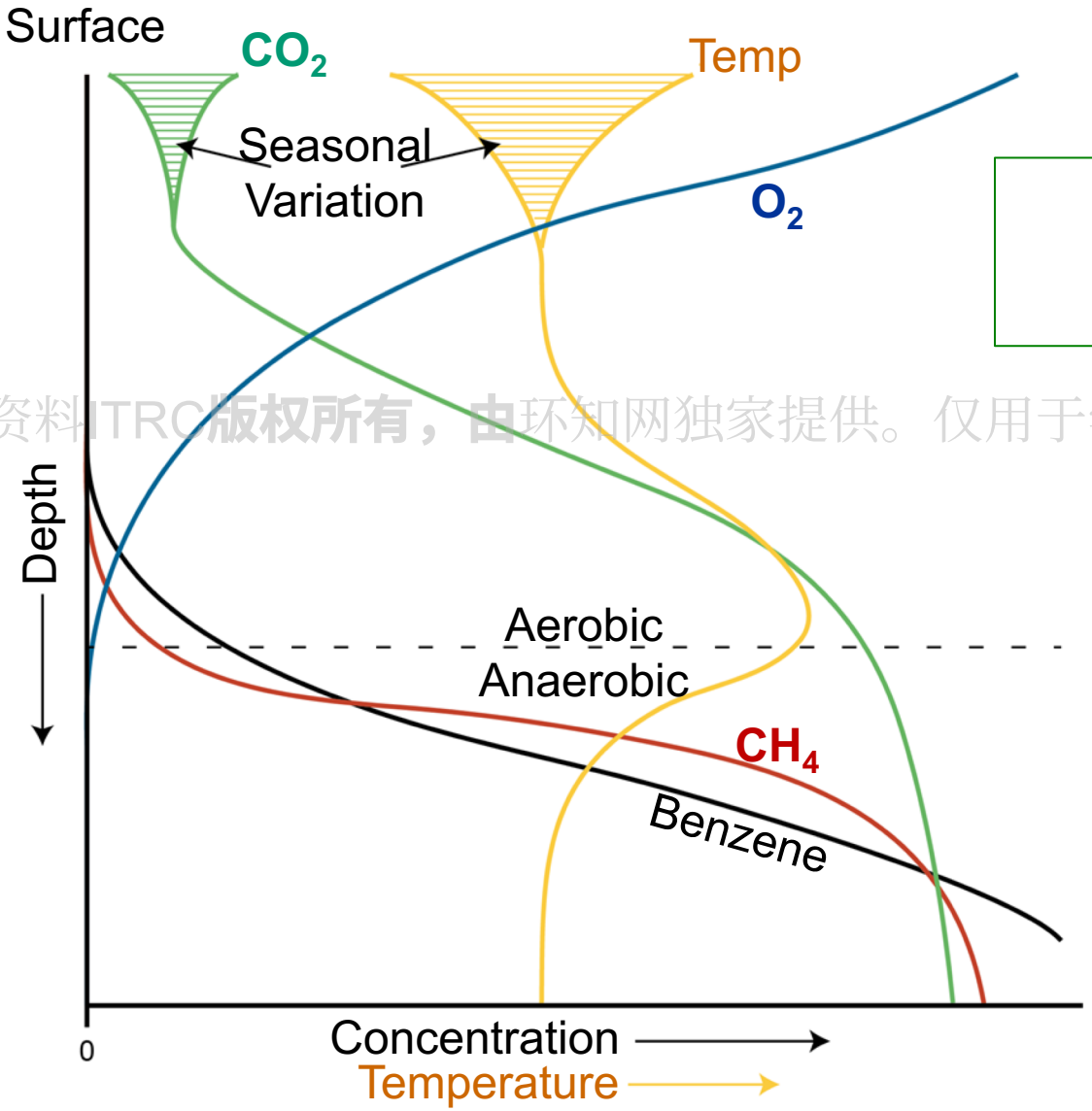


- If soil above a vapor source is ‘clean’ then building may be screened out

- If soil above the vapor source is ‘dirty’ then additional investigation may be necessary to determine if PVI pathway is complete



PVI Conceptual Site Model – Surrounding Soils are Clean



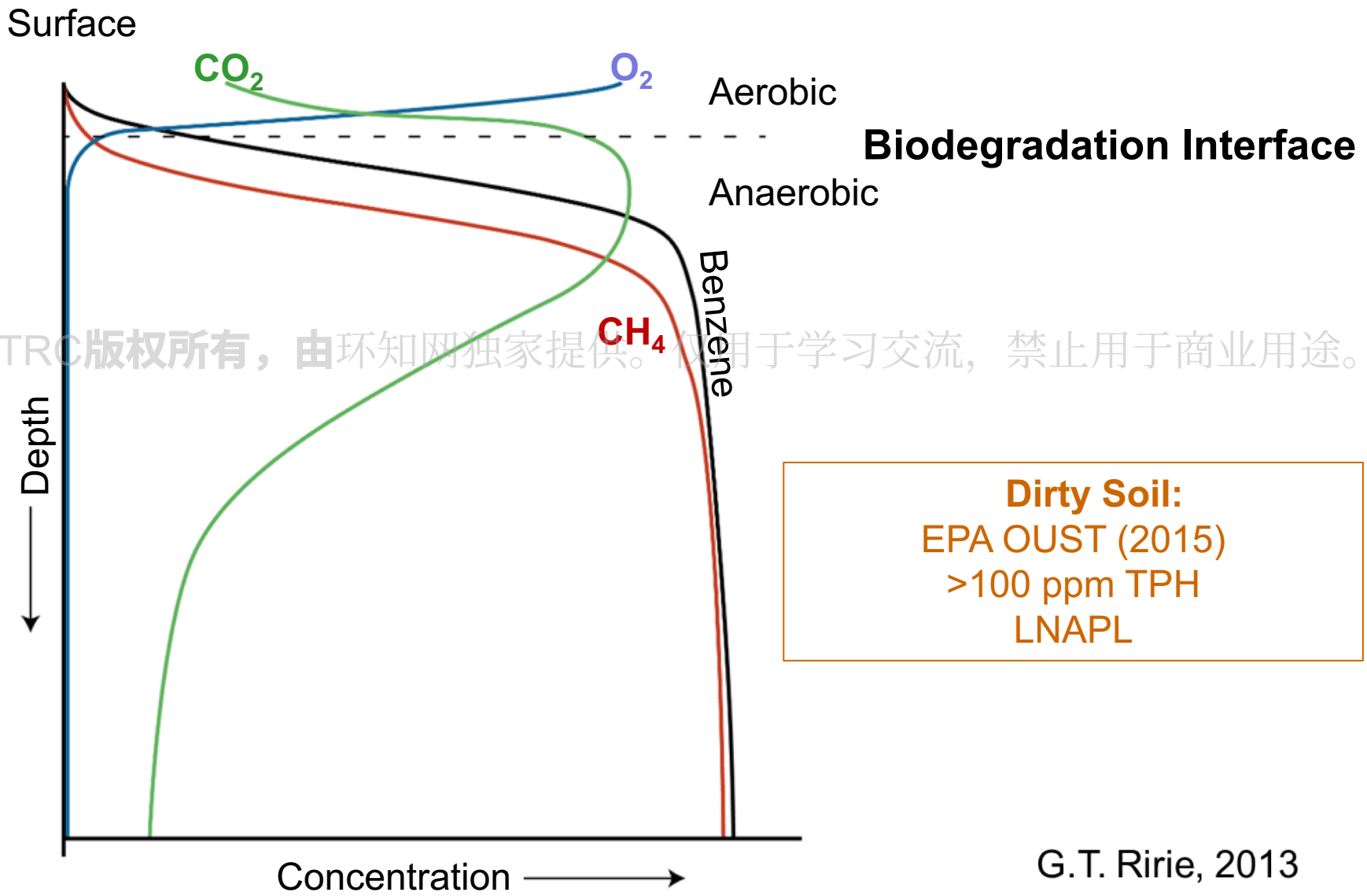
Clean Soil:
EPA OUST (2015)
<100 ppm TPH

$$HC + O_2 \longrightarrow CO_2 + H_2O$$

Biodegradation Interface

G.T. Ririe, 2013

PVI Conceptual Site Model – Surrounding Soils are Dirty



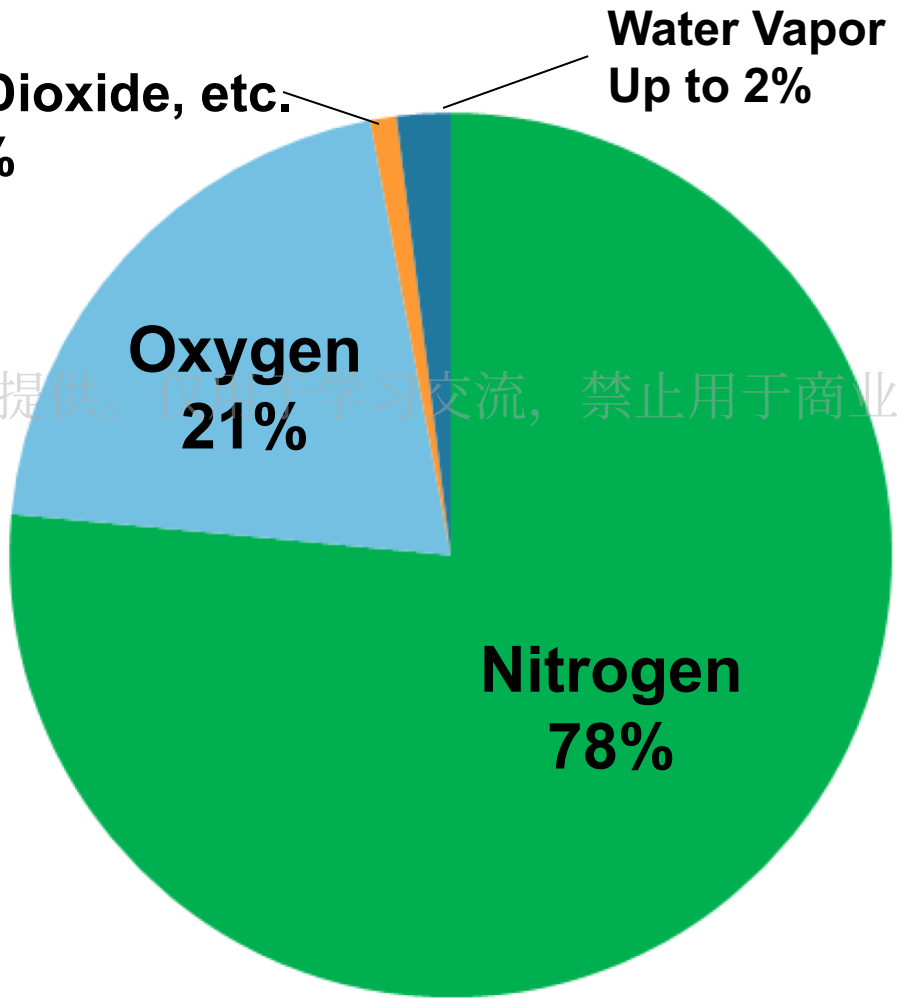
Dirty Soil:
EPA OUST (2015)
>100 ppm TPH
LNAPL

G.T. Ririe, 2013

Fixed Air Gases

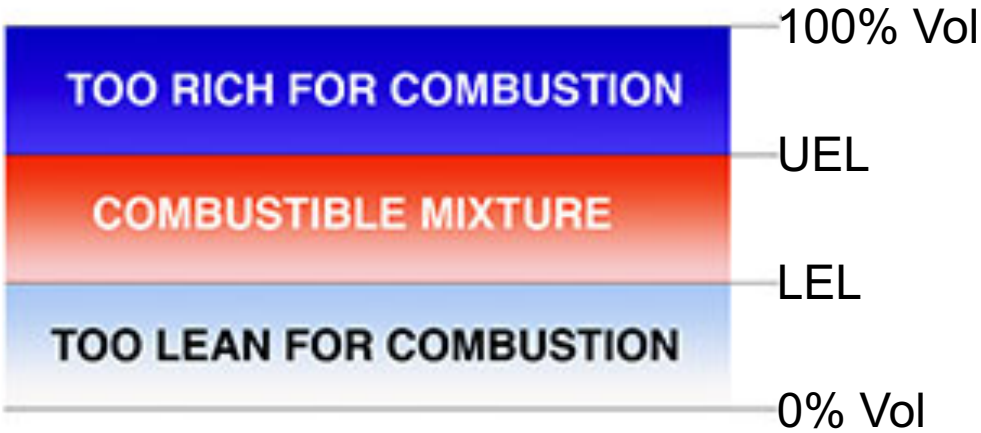
Argon, Carbon Dioxide, etc.
0.98%

Carbon Dioxide 0.03%
Methane 0.00018% (1.8 ppmv)

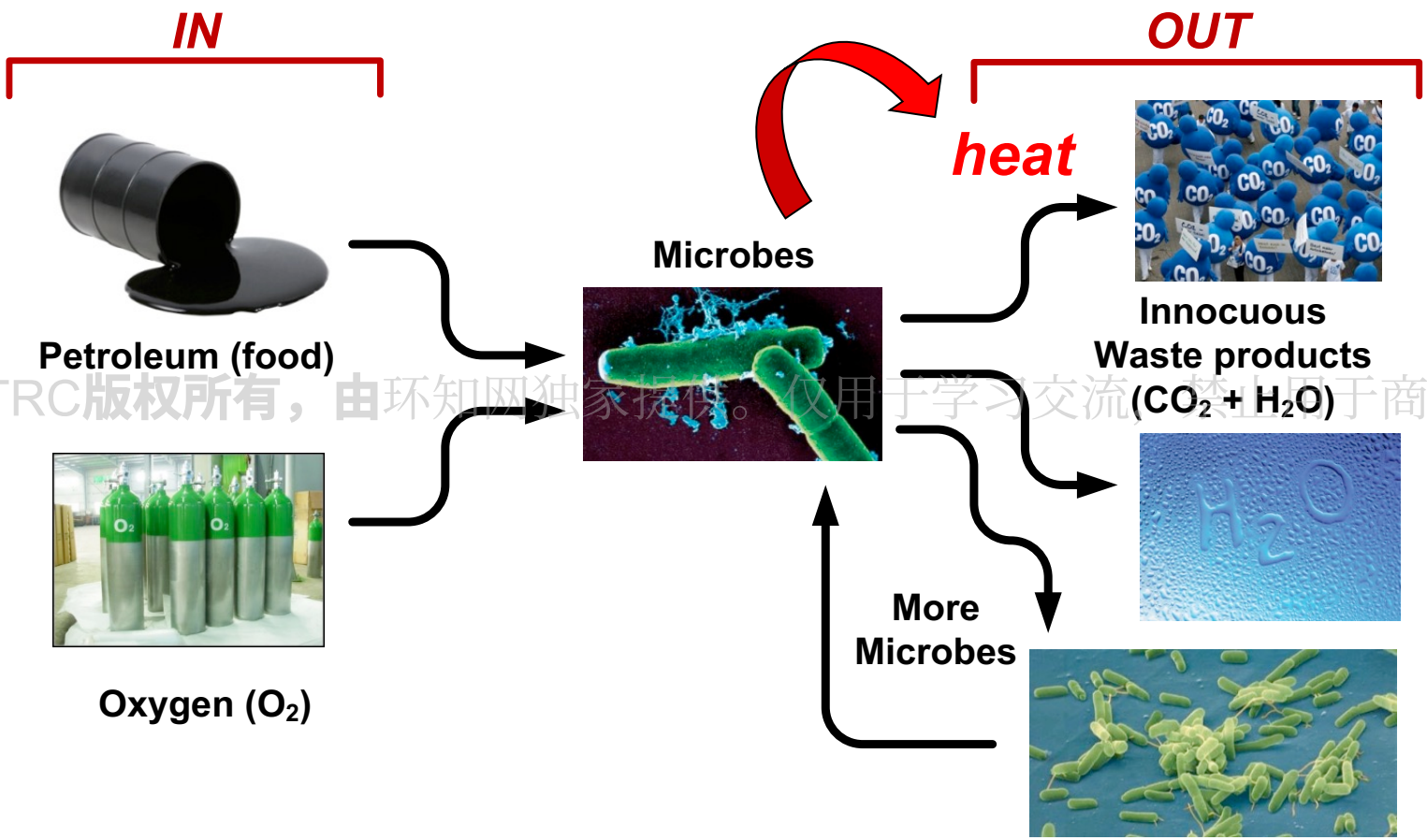


Methane Considerations

- Colorless, odorless gas, 1.8 ppmv (1260 μg/m^3) in the atmosphere (most abundant organic compound on Earth)
- Main component of natural gas (odorant added)
- Methane also present at virtually all hydrocarbon spills
- Potential safety hazard (**in air**)
  - Upper Explosive Limit (UEL) = 15%
  - Lower Explosive Limit (LEL) = 5% (35 x 10^6 μg/m^3)



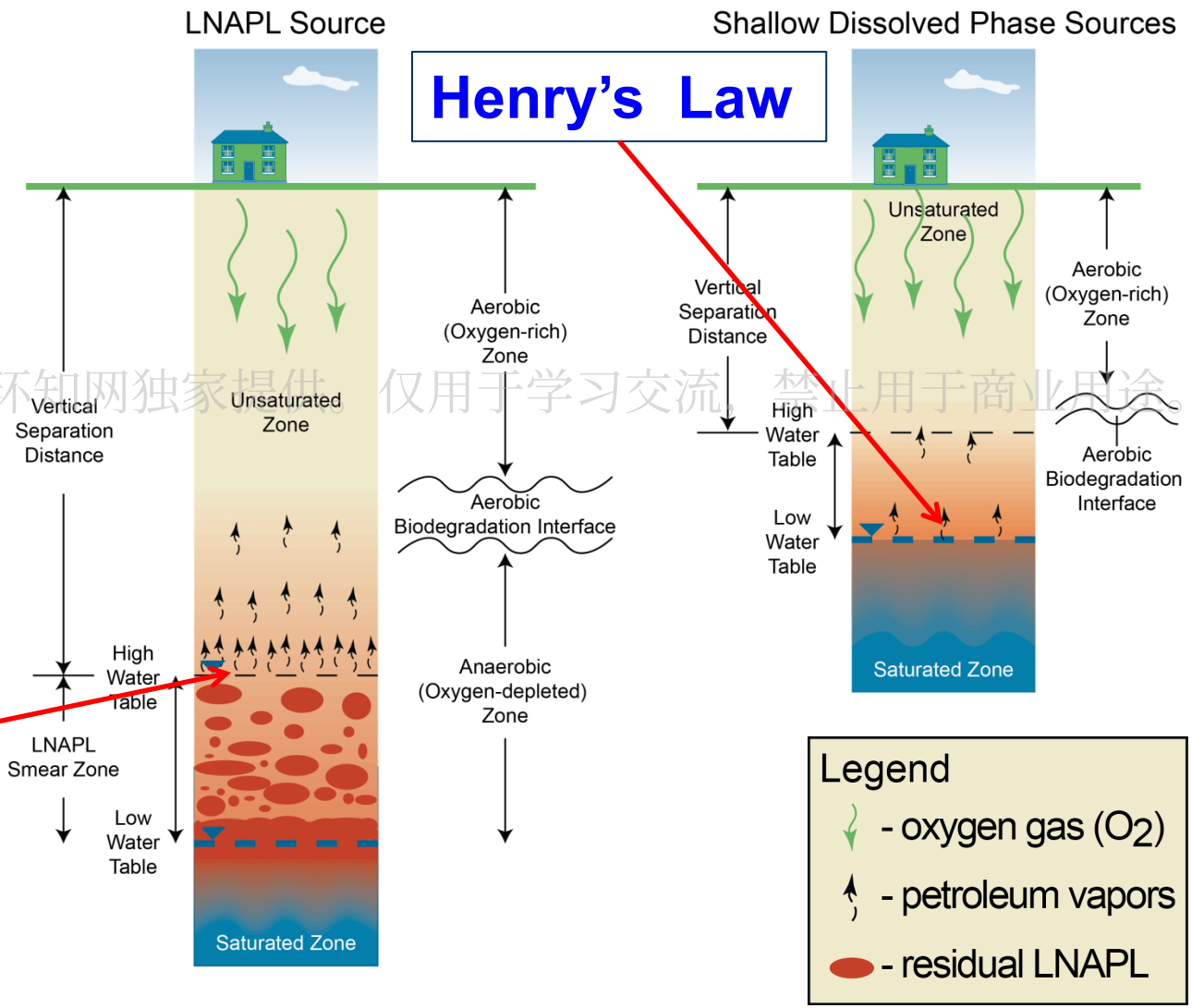
Aerobic Biodegradation Basics



KEY POINT: Aerobic biodegradation can limit transport of PHC vapors and preclude VI.

Aerobic Biodegradation – Limiting Potential for PVI

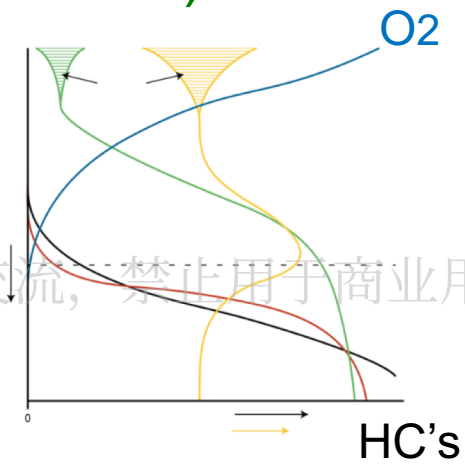
PHC-degrading bacteria found in all environments & can consume hydrocarbons rapidly in the presence of O_2



ITRC PVI-1, Figure 3-1

Petroleum Vapors Biodegrade Rapidly

- Petroleum biodegradation
  - Occurs reliably (even in hot and cold climates)
    - Microorganisms are ubiquitous
  - Starts rapidly
    - Short acclimation time
  - Occurs rapidly – "Instantaneously"

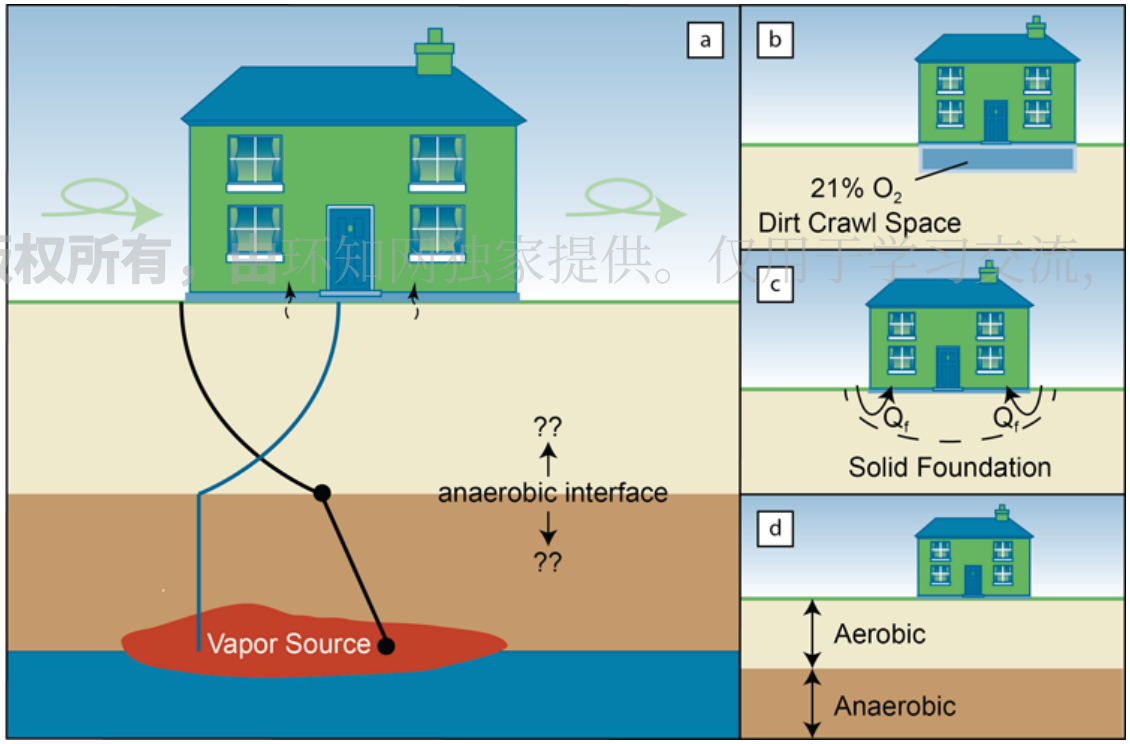


  - Atmospheric air (21% Oxygen; 275 g/m^3 oxygen) provides the capacity to degrade 92 g/m^3 hydrocarbon vapors (92,000,000 µg/m^3)

Why is this significant? **In the presence of O_2, aerobic degradation rate <u>overtakes</u> migration rate.**

Is There Enough O_2 under Buildings to Support Biodegradation?

ANSWER: Generally, **Yes**, even modest O_2 transport yields sufficient aerobic biodegradation in most cases



KEY POINT:

Two key factors – both needed – to run out of oxygen:

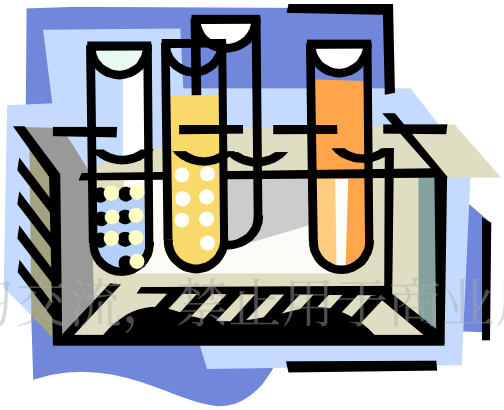
- Limited oxygen transport below the foundation
- High oxygen demand

Site-Specific Features

- Source
  - Degradable vs. non-degradable
  - VOCs vs. SVOCs
  - Vadose zone vs. groundwater
  - NAPL or not
- Pathway
  - Diffusion vs. advection dominated
  - Barriers: wet clay-rich layers, freshwater lens
  - Preferential pathways: high-K fill, openings in building envelope
- Receptor
  - Building pressure/vacuum, ventilation rates
  - Interior sources (background)
  - Sensitive populations
- Emerging concept – “Taxonomy” of VI sites (Johnson, 2008)

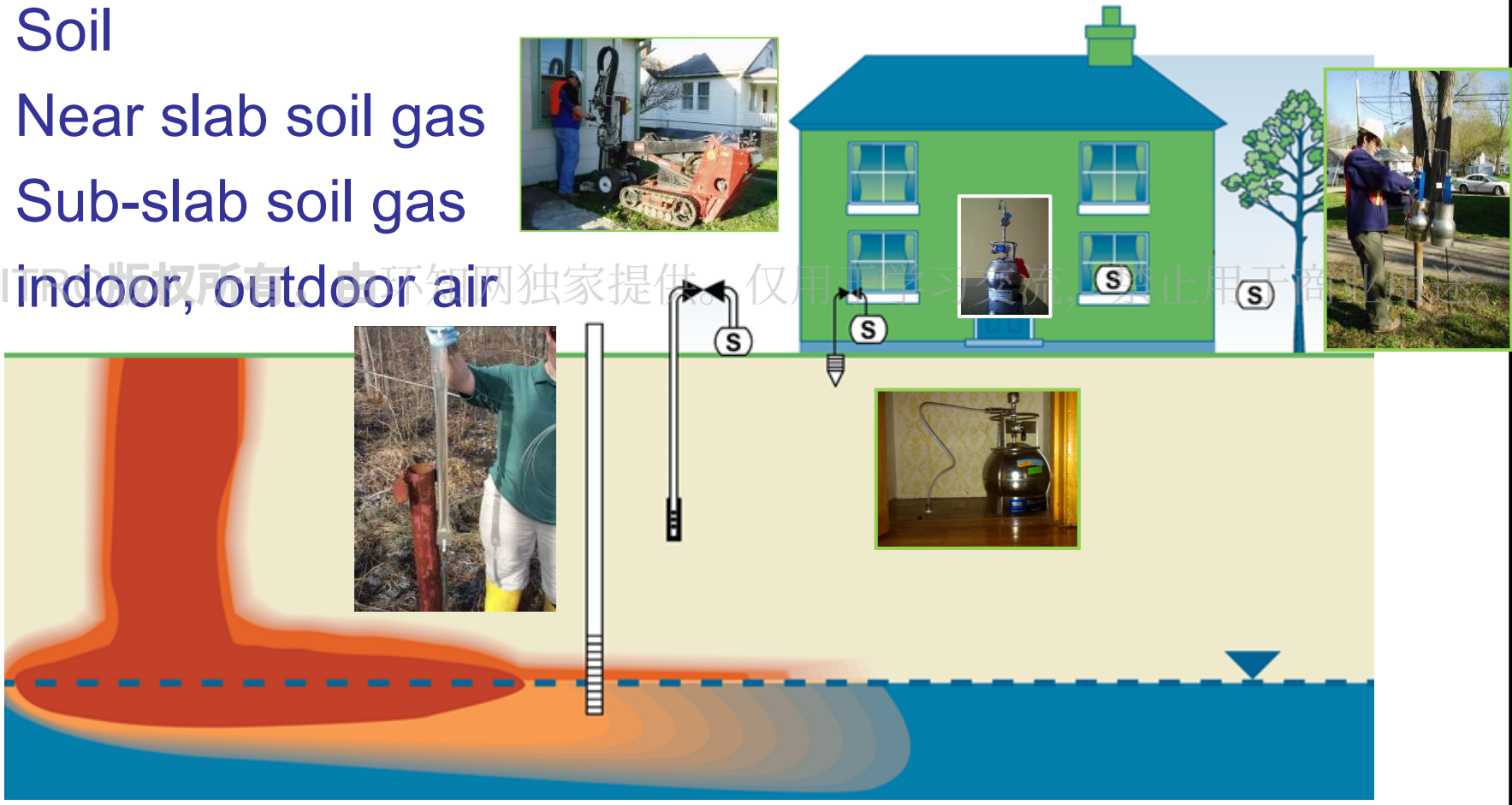
Multiple Lines of Evidence (MLE)

- Chemistry
- Soil properties
- Weather data
- Gas pump tests
- HVAC monitoring
- Building pressure manipulation
- Degradation
- Modeling



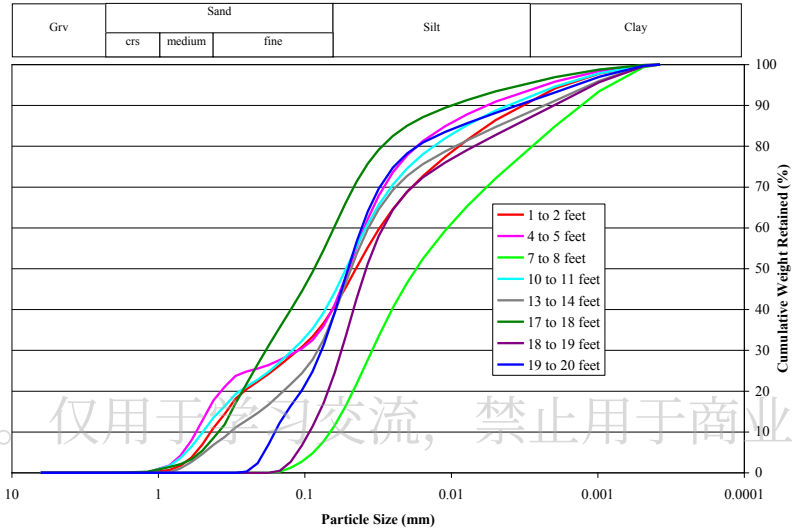
MLE: Chemistry

- Groundwater
- Soil
- Near slab soil gas
- Sub-slab soil gas
- indoor, outdoor air

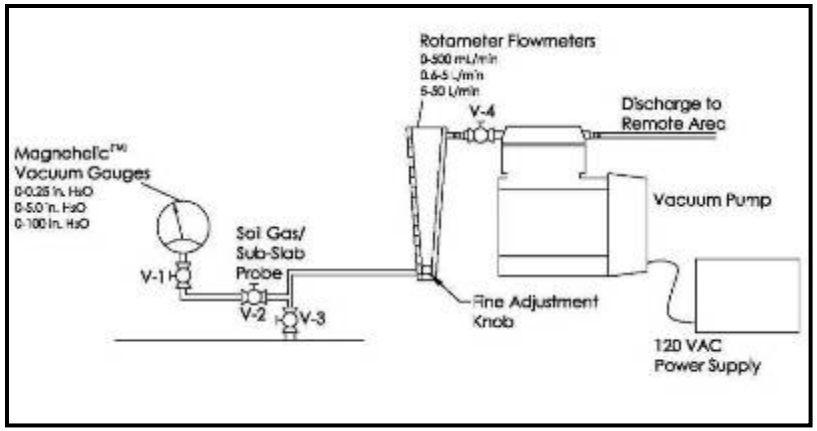


MLE: Soil Properties

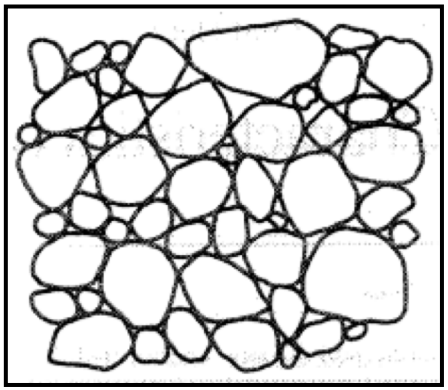
Coring and Visual Inspection



Particle Size Distribution



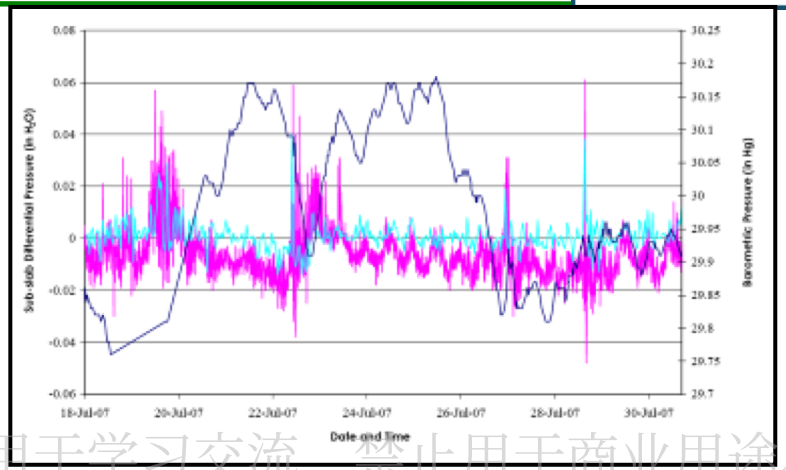
Flow, Vacuum, and Permeability



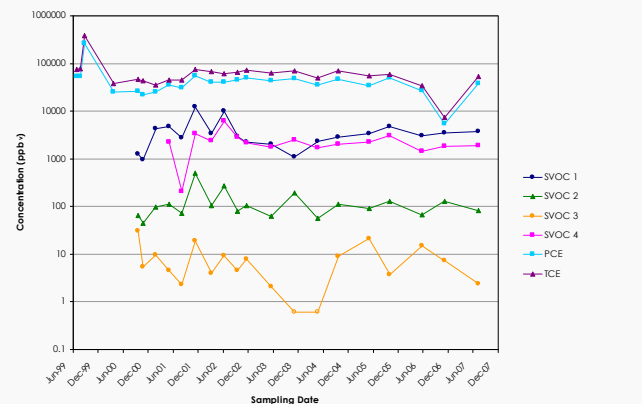
Porosity and Moisture Content

MLE: Weather Data

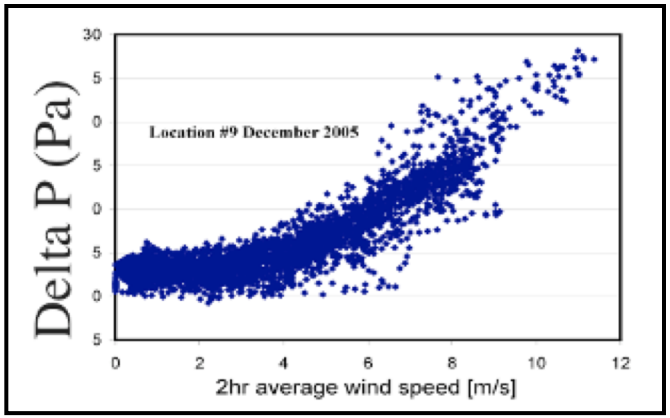
Barometric and Differential Pressure



Soil Gas Pressure over Time



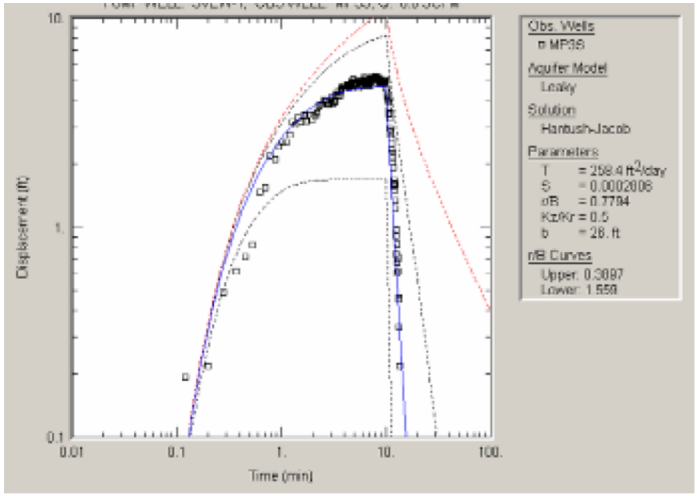
Seasonal Trends from Weather Effects



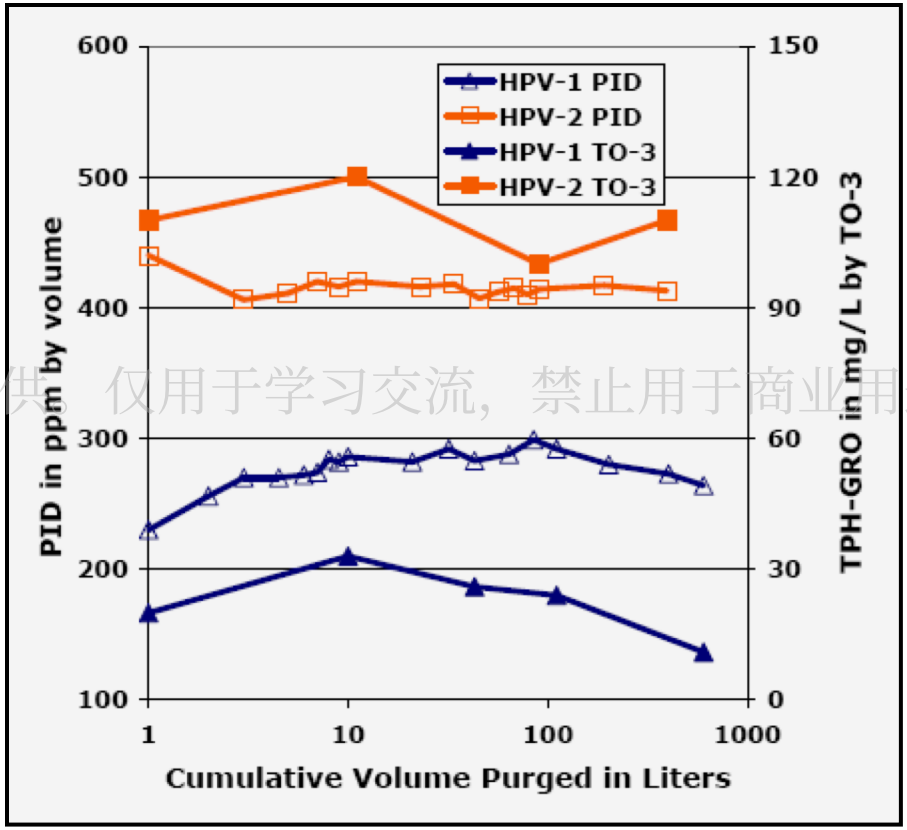
Wind Speed vs. Building Vacuum

MLE: Gas Pump Tests

Gas Pumping Tests



Analysis of Pneumatic Properties



Concentration vs. Volume Purged

MLE: HVAC Monitoring

Pressure/Ventilation Testing

Electromagnetic Flow Meters

Smoke Pen

Test and Balance Reports

Building Ventilation Rates

ANSI / ASHRAE Standard 62.1 – 2004
Ventilation for Acceptable Indoor Air Quality

Building Type	Air Exchange Rate (# / day)
USEPA Default (Residential)	6
Office Space	12
Supermarket	17
Classroom	68
Restaurant	102

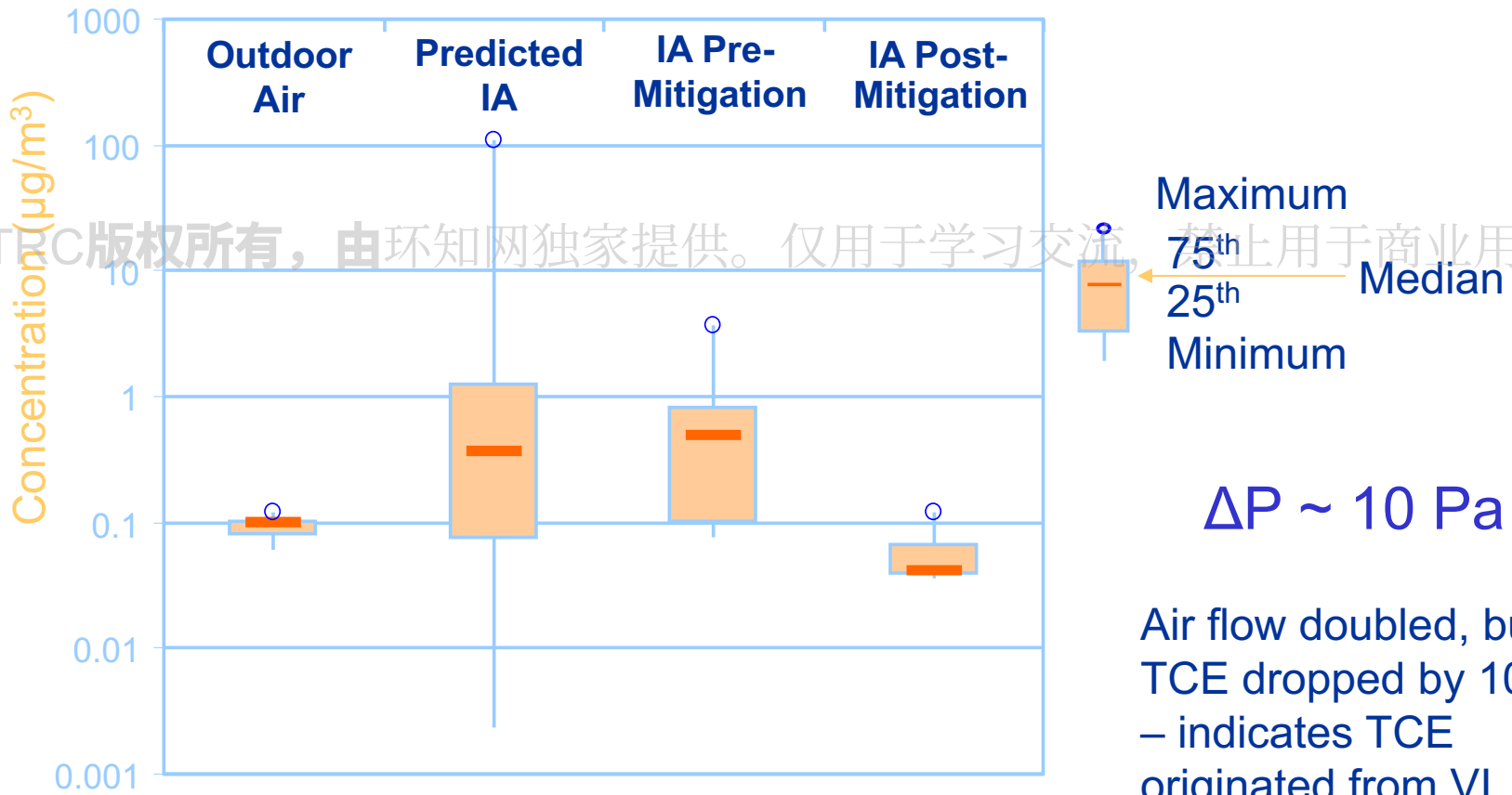
High Building Ventilation

Key Point: Buildings designed for high density use will have high air exchange rates

Courtesy: Tom McHugh, GSI

MLE: Building Pressure Manipulation

Adjust HVAC to pressurize building – do $[VOCs]_{IA}$ drop?
IA = Indoor Air



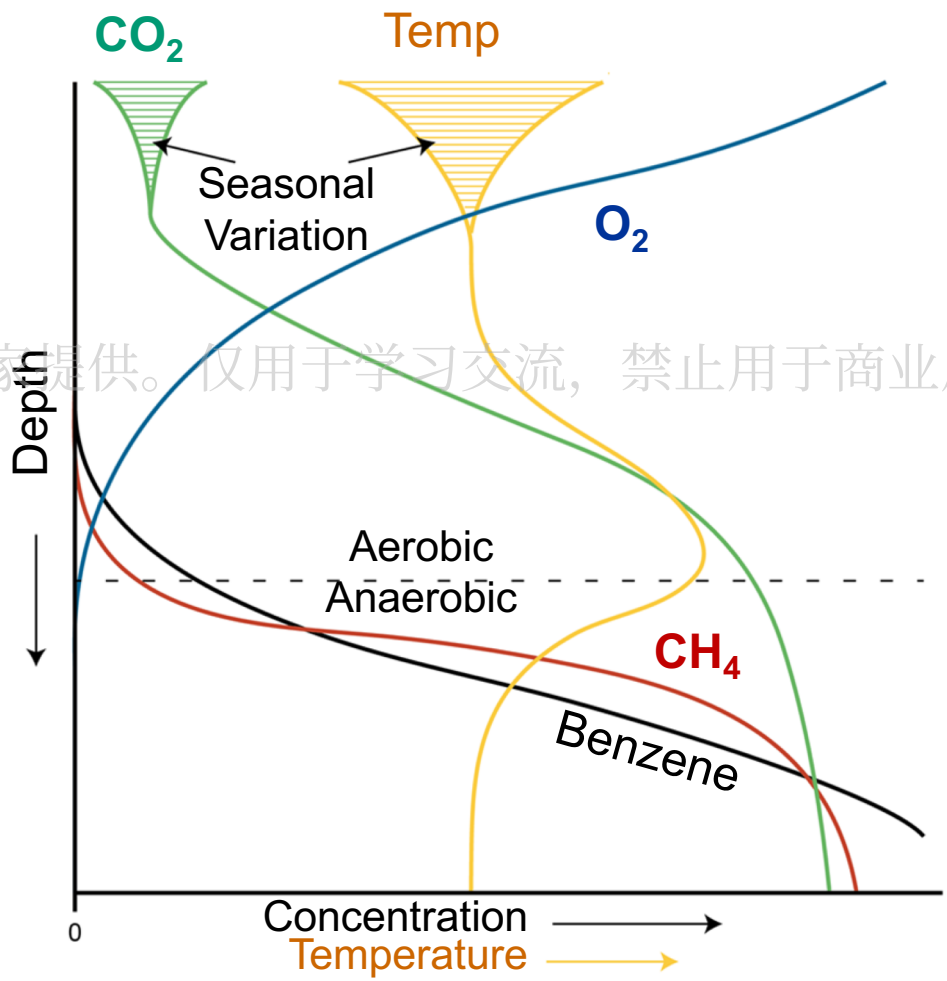
Berry-Spark et. al., 2005

$\Delta P \sim 10$ Pa

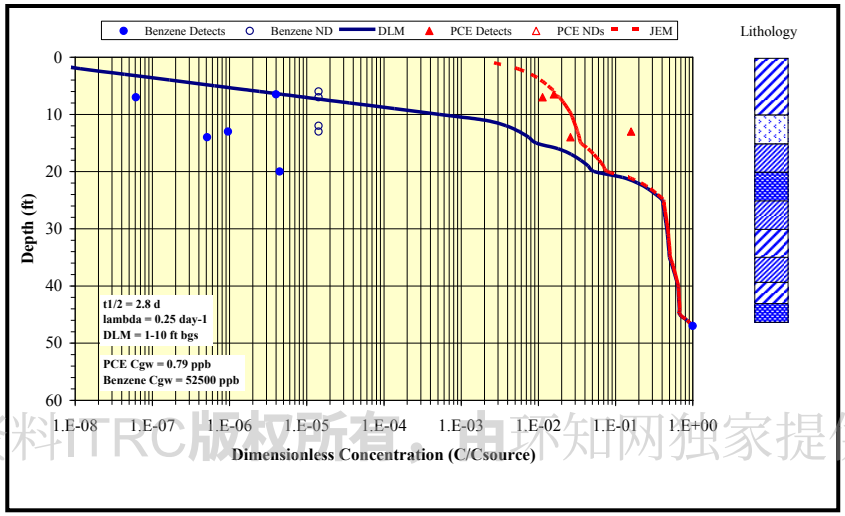
Air flow doubled, but TCE dropped by 10x – indicates TCE originated from VI

MLE: Degradation

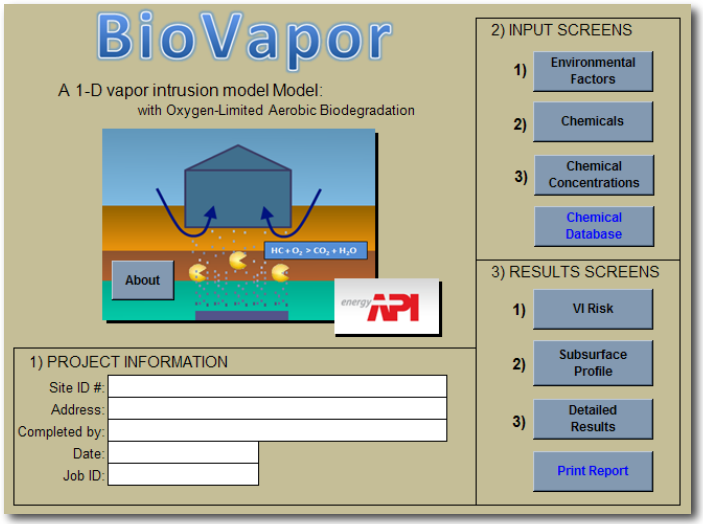
Field Screening for O_2 and CO_2

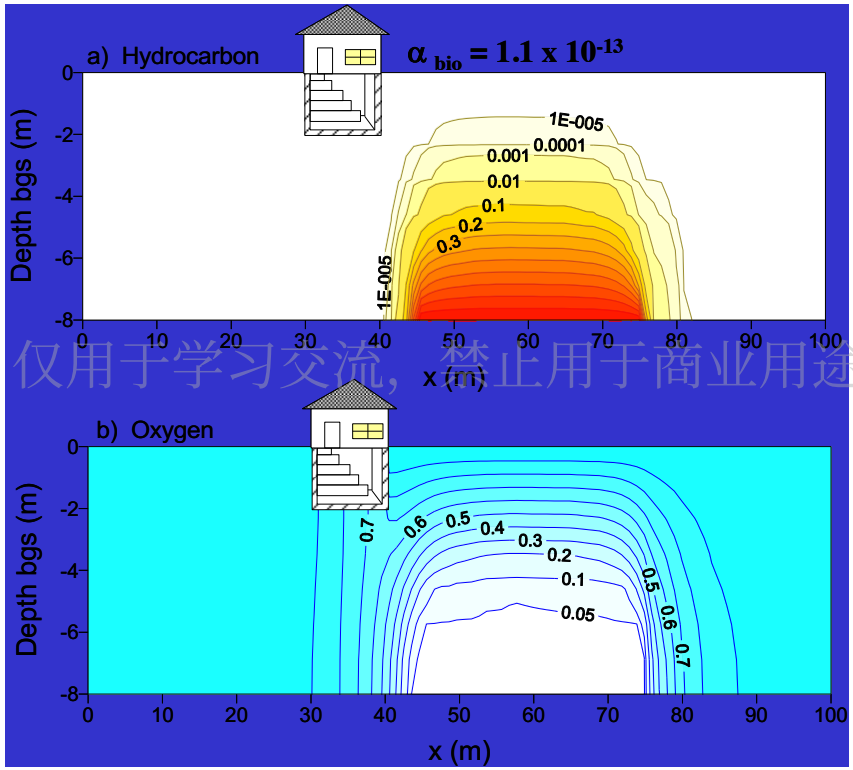


MLE: Modeling



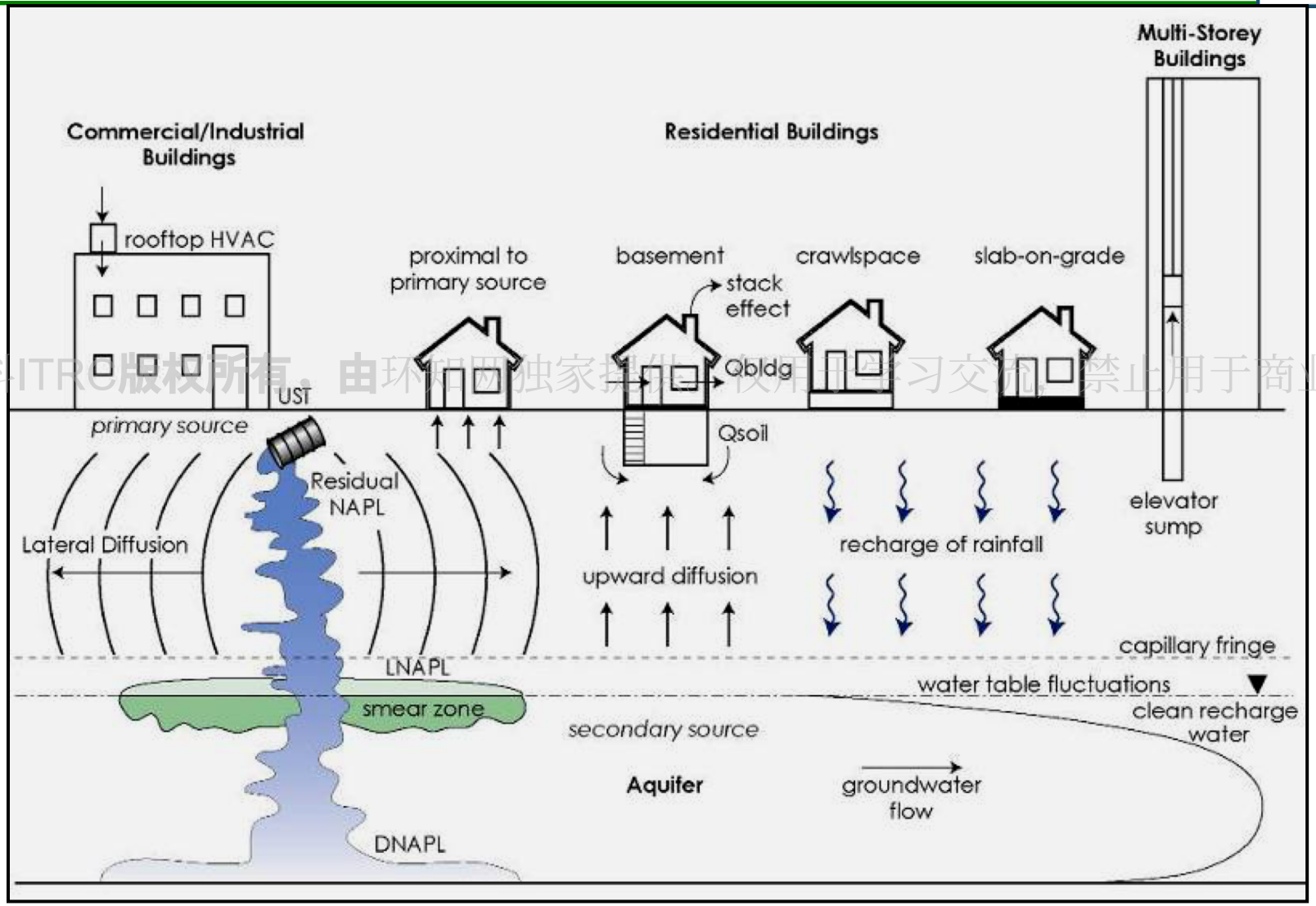
1-D J&E Model with Biodegradation





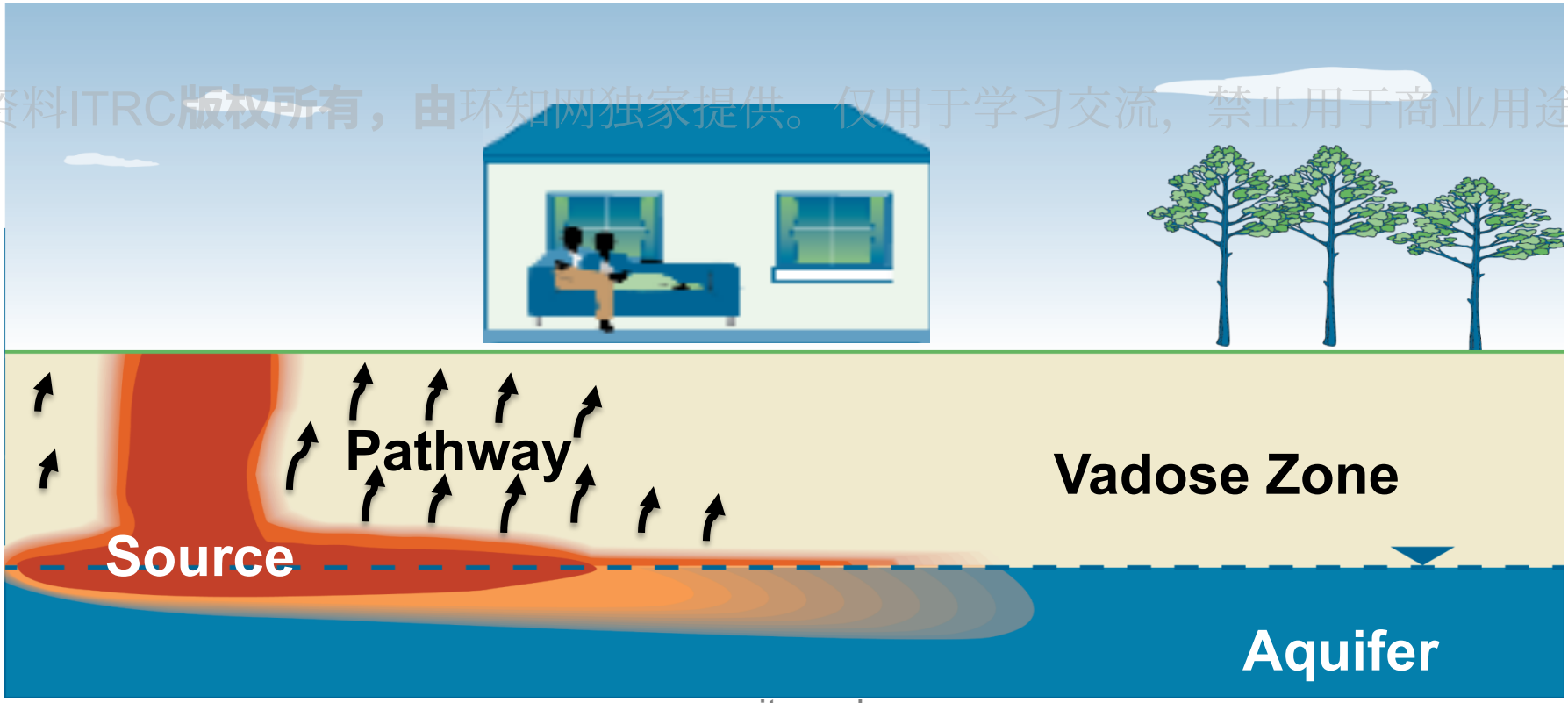
3-D Abreu and Johnson Model

Is This Your Site?



Conceptual Site Model (CSM)

- Simplified version (pictures and/or descriptions) of a complex real-world system that approximates its relationships

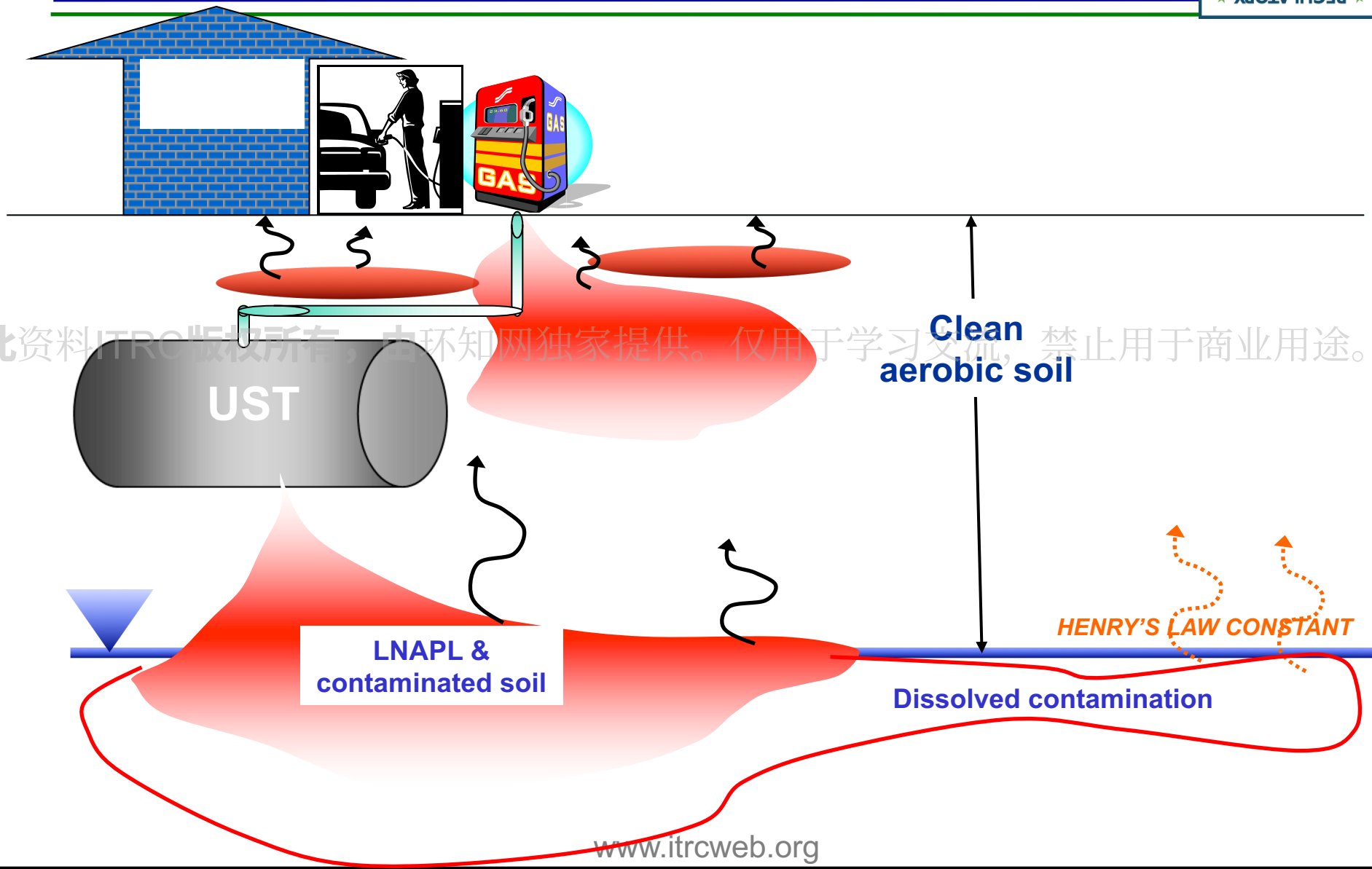


Components of a CSM

- Underground utilities and pipes
- Existing and potential future buildings
- Construction of buildings
- Type of HVAC system
- Soil stratigraphy
- Hydrogeology and depth to water table
- Receptors present (sensitive?)
- Nature of vapor source
- Vadose zone characteristics
- Limits of source area and contaminants of concern
- Surface cover description in source and surrounding area

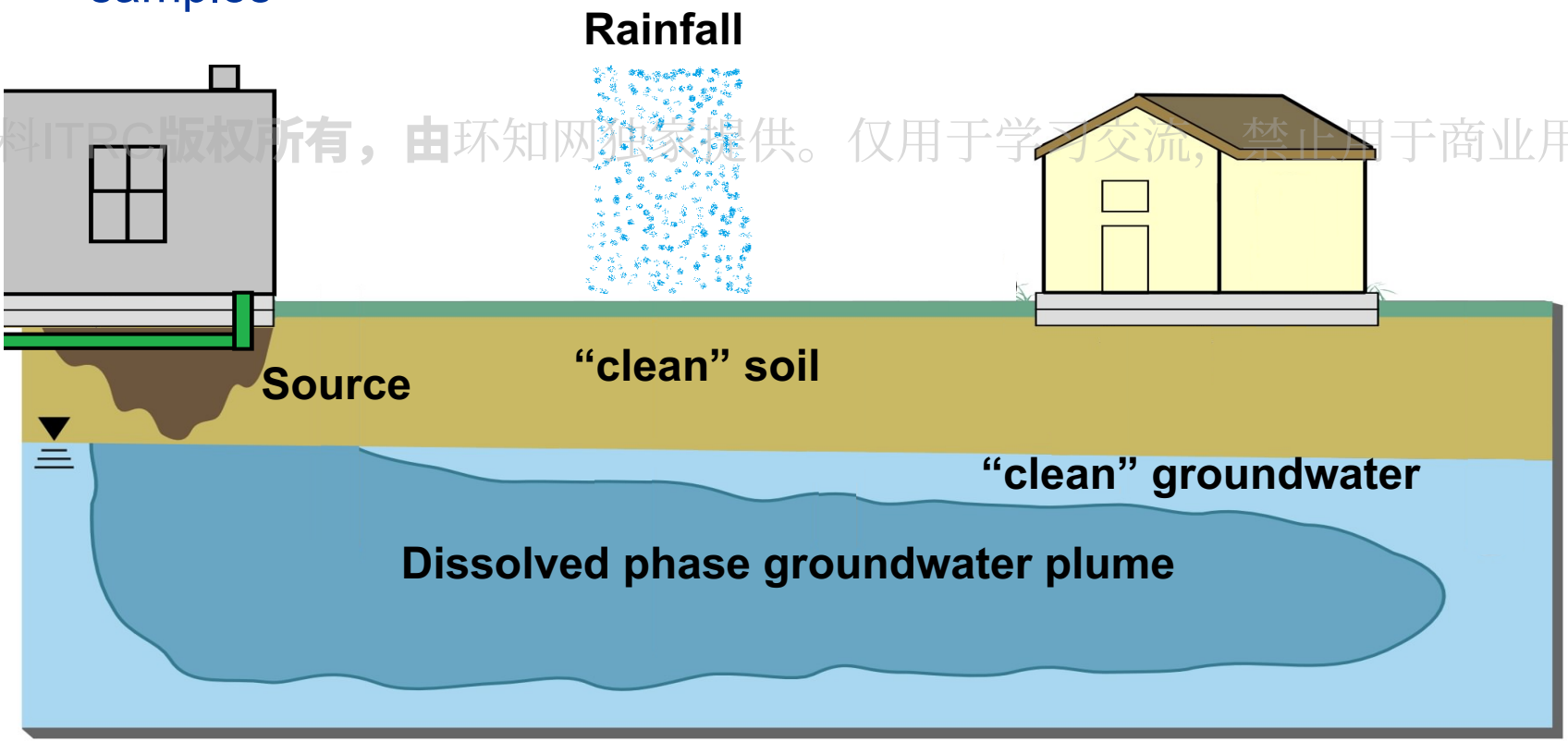
VI Guideline Appendix B

CSM for Petroleum Vapors



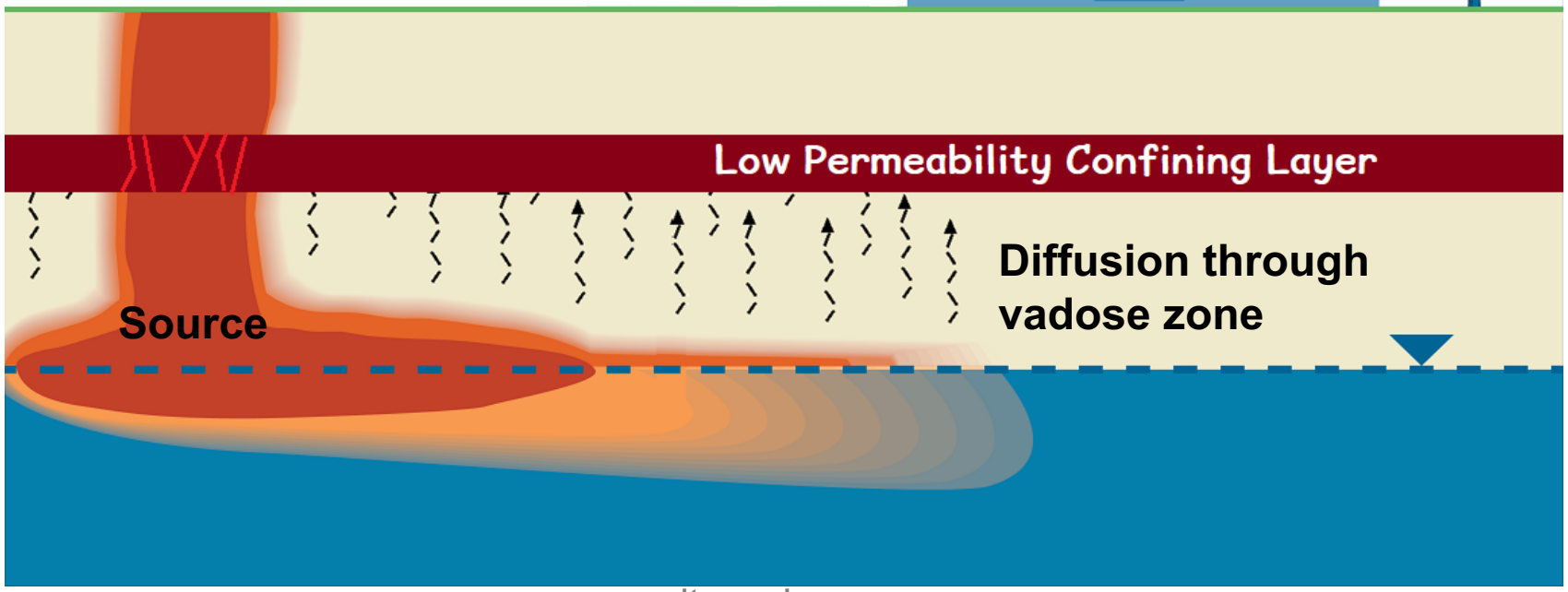
Conceptual Site Model
Other Factors - Fresh-Water Lens

- Assess off-gassing with combined shallow GW and deep soil gas samples
- Map “extent” in soil gas before selecting buildings for intrusive samples



Conceptual Site Model
Other Factors – Geologic Barrier

- Soil cores to assess stratigraphy, soil texture, porosity, and moisture content
- Measure flow and vacuum in soil gas probes during purging and sampling
- Monitor ambient pressure/vacuum in soil gas probes = f (barometric pressure)
- Vertical profiles of soil gas concentrations in select locations



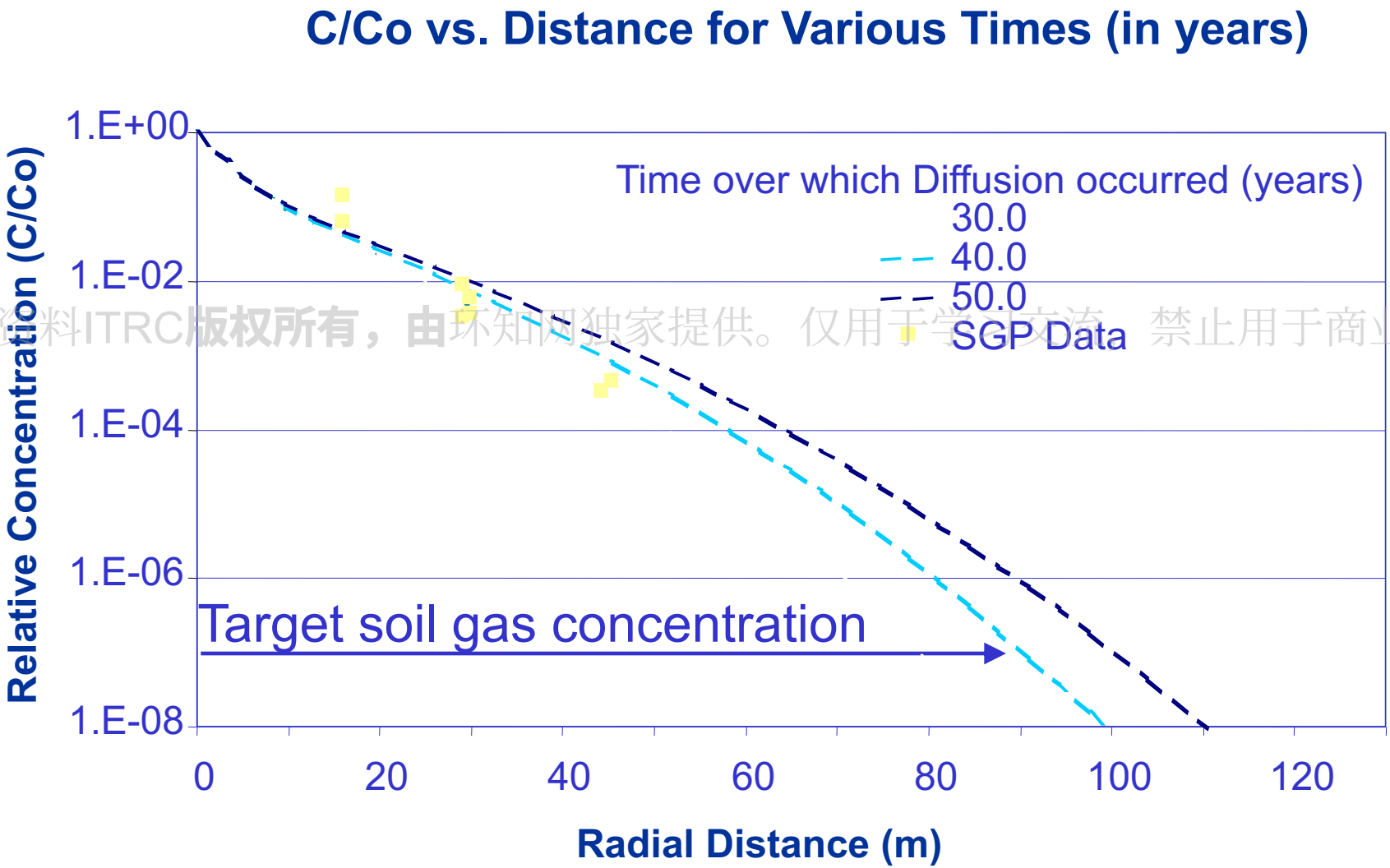
CVOC in Vadose Zone – Strategy

- Diffusion is a relatively predictable process

$$\frac{C}{Co} = \frac{a}{r}\, erfc\left[\frac{r - a}{\sqrt{4D_{eff}t}}\right]$$

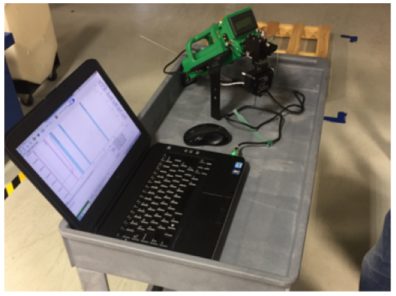
- Semi-infinite uniform half-space with point-source
  - C/Co is the relative concentration at a specified time and distance
  - a is the radius of the source [m]
  - r is the radius at which C/Co is to be calculated [m]
  - D_{eff} is the effective overall vapor-phase diffusion coefficient [m^2/s],
  - t is time since diffusion began [s]

CVOC in Vadose Zone – Strategy (continued)



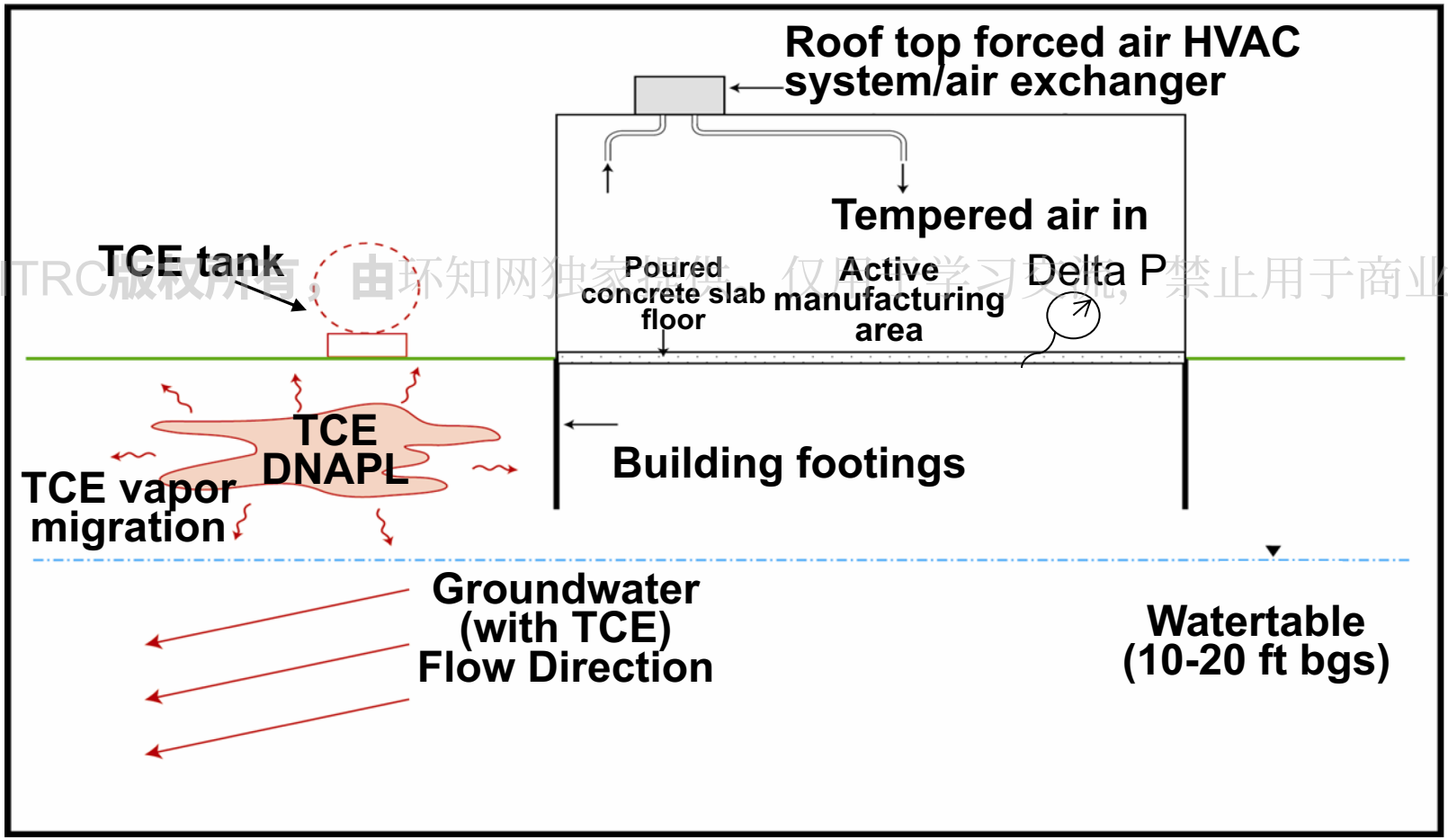
Conceptual Site Model
Other Factors – Large Buildings

- Talk with Facilities Engineer – review Test and Balance Report
- Monitor sub-slab to building pressure differential over time
- Review historic VOC use, storage, handling locations
- PID (photoionization detector) screening at select locations (floor drains, sumps, etc.)



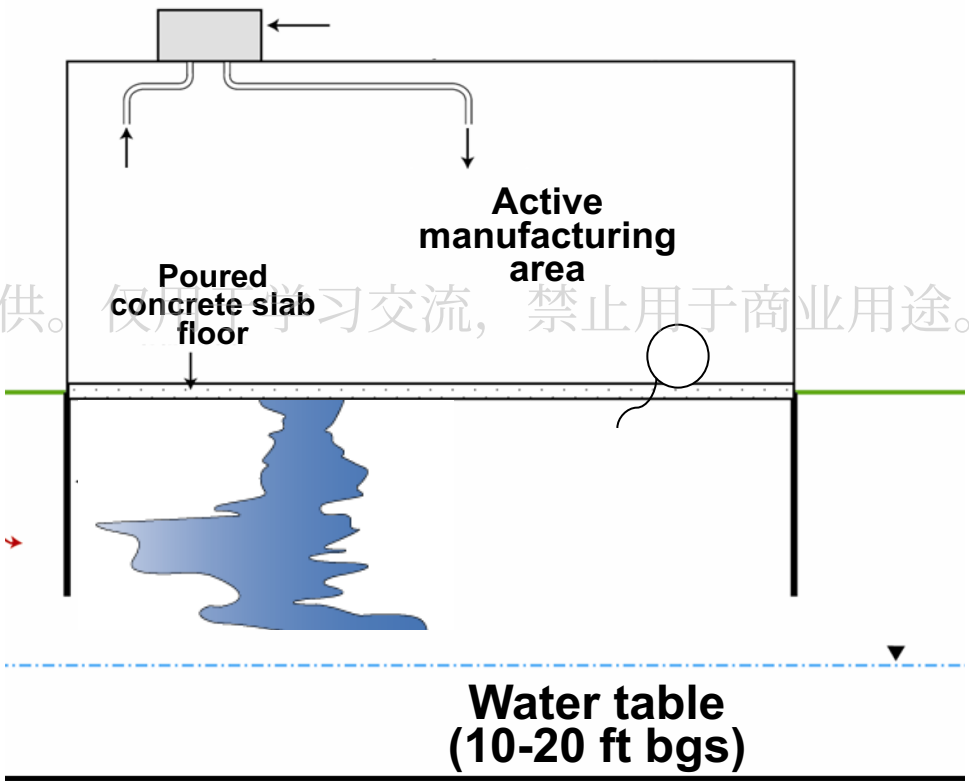
Conceptual Site Model
Other Factors – Source Outside Building

- Review depth of footings vs. water table (barrier?)
- Soil gas and sub-slab samples and pressure differential



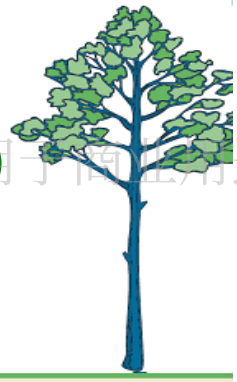
Conceptual Site Model
Other Factors – Source Beneath Building

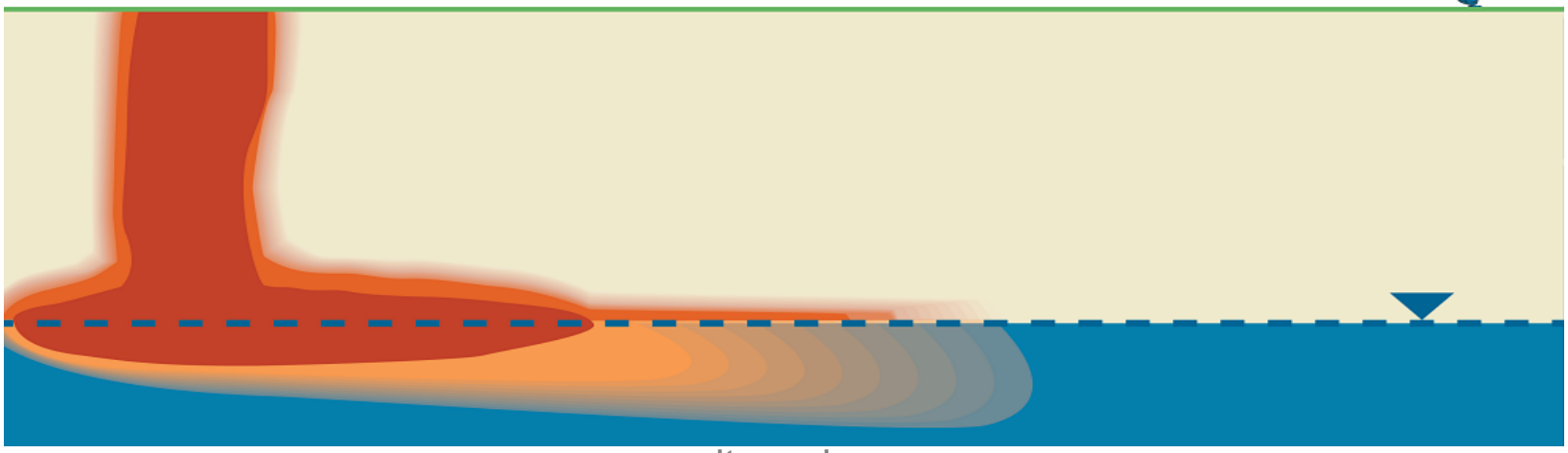
- External data not as useful
- May want to consider SVE if concentrations are >> screening levels
- Assess spatial distribution in sub-slab concentrations
- Consider indoor air data with changes in HVAC operation



Conceptual Site Model
Other Factors – Vacant Lot

- Start with a cost-benefit analysis for soil gas monitoring program vs. proactive mitigation
  - Avoidance: build away from areas of suspected VOCs
  - Passive barrier (visqueen, HDPE, spray tars)
  - Passive venting (gravel layer and wind-turbines)
  - Intrinsically safe design (podium construction)





Complicating Factors for VI Assessments

- Ultra low screening levels
  - Increases chances for false positives
- Inconsistent screening levels
- Allowed assessment methods
  - Vary among agencies
- Chlorinated vs. petroleum hydrocarbons
  - Treat same way?
  - Allow for bioattenuation – how?