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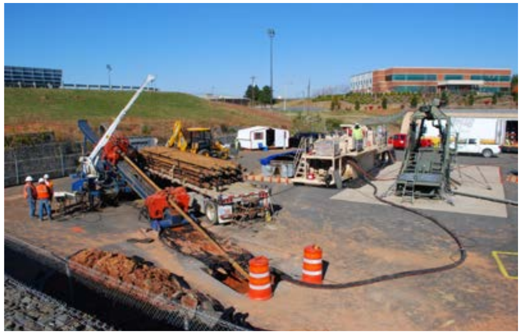
New Methods to Assess and Support Monitoring Natural Source Zone Depletion



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Innovation that Solves Complex Local Challenges, Worldwide

Presentation Agenda

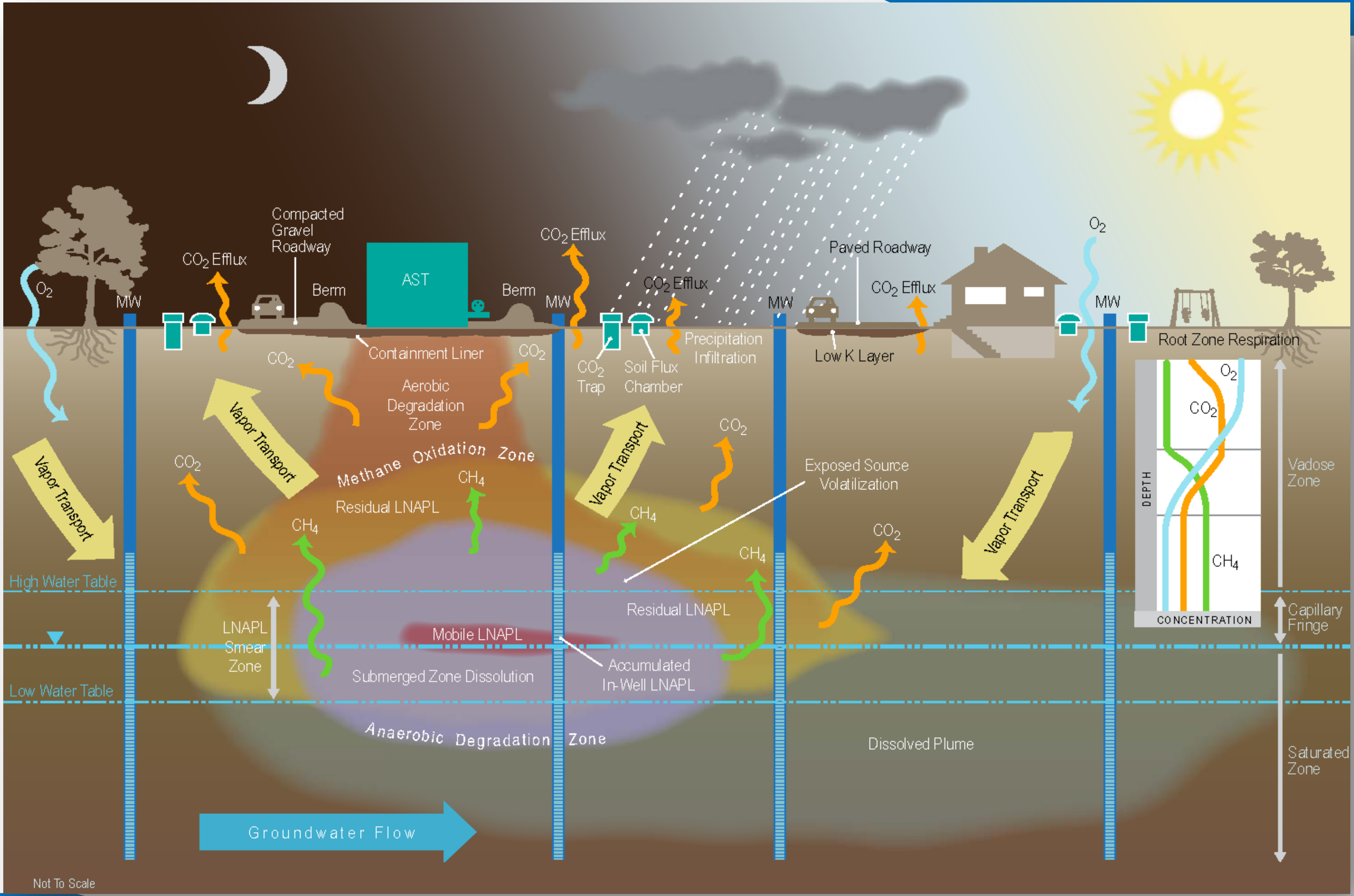


- Introduction to Natural Source Zone Depletion (NSZD) and Carbon Dioxide (CO_2) Efflux
- New NSZD Monitoring Methods
  - Soil flux system (LI-COR, Inc.)
  - CO_2 Traps (E-Flux, LLC)
- Case Study 1 – Large Diesel Release, Colorado
- Case Study 2 – Natural Gas Well Site, Alberta
- Conclusions



Introduction

Visual Representation of NSZD and CO_2 Efflux



How has CO_2 efflux traditionally been monitored?



- CO_2 efflux has not been part of the routine of monitored natural attenuation (MNA)
- Typical focus has been on groundwater - electron acceptors, redox parameters, microbiological evidence, and contaminant concentrations
- Theoretical analysis (P.Johnson, ASU, 2009) and LNAPL stability efforts (T.Sale, CSU, 2012) indicate that more degradation is occurring than conventional mass budgeting techniques are accounting for

Why is CO_2 efflux monitoring important?

- Current practice does not account for all natural losses and is significantly under-estimating them
- CO_2 measurement at ground surface can be a very cost-effective alternative to groundwater monitoring

How does CO_2 efflux apply to my remedial efforts?

- Can be used at remediation sites to:
  - Delineate subsurface NAPL footprint
  - Monitor natural attenuation processes and estimate contaminant destruction rates
  - Better understand source zone longevity
  - Benchmark remedies and establish endpoints

How can CO_2 efflux be measured?



- CO_2 efflux can be directly measured at ground surface using:
  - Flux Chamber Method (LI-COR, Inc.)
  - CO_2 Trap Method (E-Flux, LLC)
- CO_2 is created by both petroleum- (deep) and ecosystem-related (shallow) decomposition sources
  - Requires quantitative separation technique to isolate NAPL-related loss rates
  - Techniques are available to “correct” the total measured CO_2 efflux values

What influences it?



- CO_2 efflux varies with temperature (seasonal), wind, and spatially due to changes in ground cover (i.e., grass, gravel)

CO_2 efflux monitoring requires a carefully designed and technically sound approach to accurately estimate annual NAPL loss rates across large diverse areas

Industry Acceptance for NSZD and CO_2 Efflux

- Advocates include:
  - ITRC 2009 guidance published to assess NSZD
  - British Columbia (U.Mayer and N.Sihota) and Arizona (P.Johnson and P.Lundegard) continue to publish peer-reviewed literature in support of the methods
  - Colorado State (T.Sale and J.Zimbron) commercialized the CO_2 Trap technology (E-Flux, LLC)
  - Various site owners and consultants are pushing acceptance
    - 11 abstracts submitted on NSZD to Battelle 2014 conference
- Provinces/States with known applications
    - Yukon, Alberta, Colorado, Illinois, Wyoming, Missouri, Hawaii, Minnesota, and Michigan

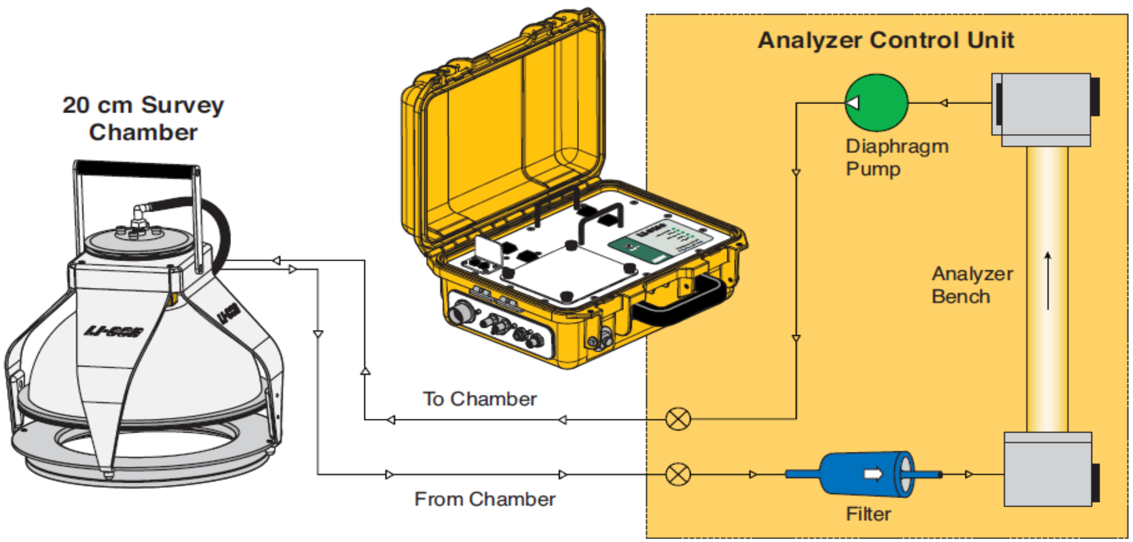
New NSZD Monitoring Methods

Soil Flux System (LI-COR, Inc.)



NSZD CO_2 Flux = Total CO_2 Flux - Background CO_2 Flux

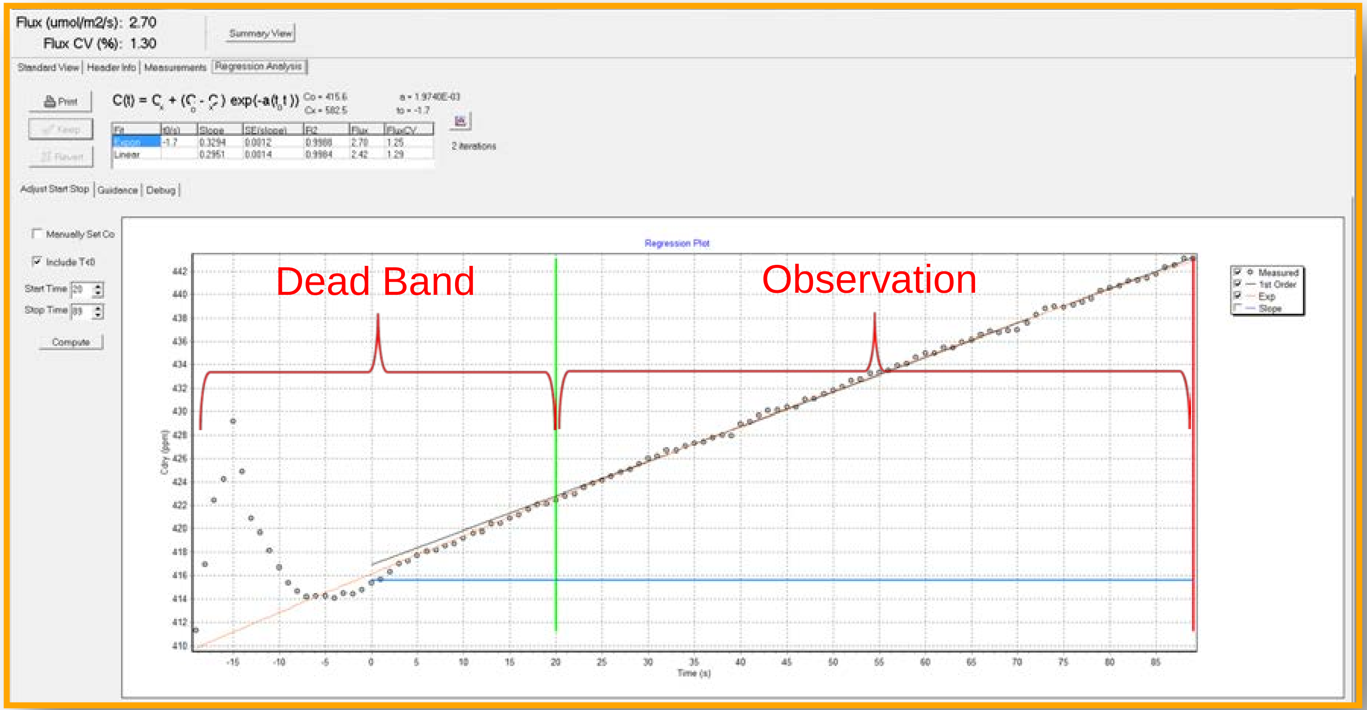
- Theory
  - Total CO_2 flux measured over the NAPL footprint
  - Background CO_2 flux measured outside the NAPL footprint
  - Instantaneous measure
- Equipment
  - Collar (thick-walled 8" diameter PVC with a beveled edge)
  - Vented bellows-controlled flux chamber
  - Analyzer control unit (including infrared gas analyzer and pump)
  - Application software



http://licor.com/env/products/soil_flux/

Soil Flux System - Data Analysis

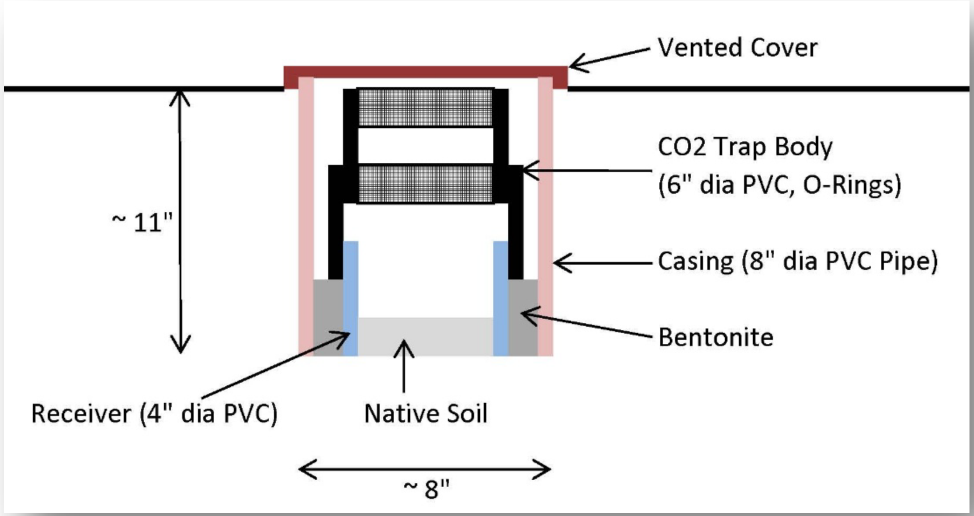
- Real-time data collection and analysis
  - CO_2 concentration measured in return air over preset time period
  - Efflux = slope of CO_2 concentration versus time



CO_2 Trap (E-Flux, LLC)



- Theory
  - Flow-through sorbent trap method
  - Time-averaged CO_2 flux



- Equipment
  - Receiver pipe
  - CO_2 Trap with dual sorbent pucks
  - Vented protective cover



CO_2 Trap – Data Analysis



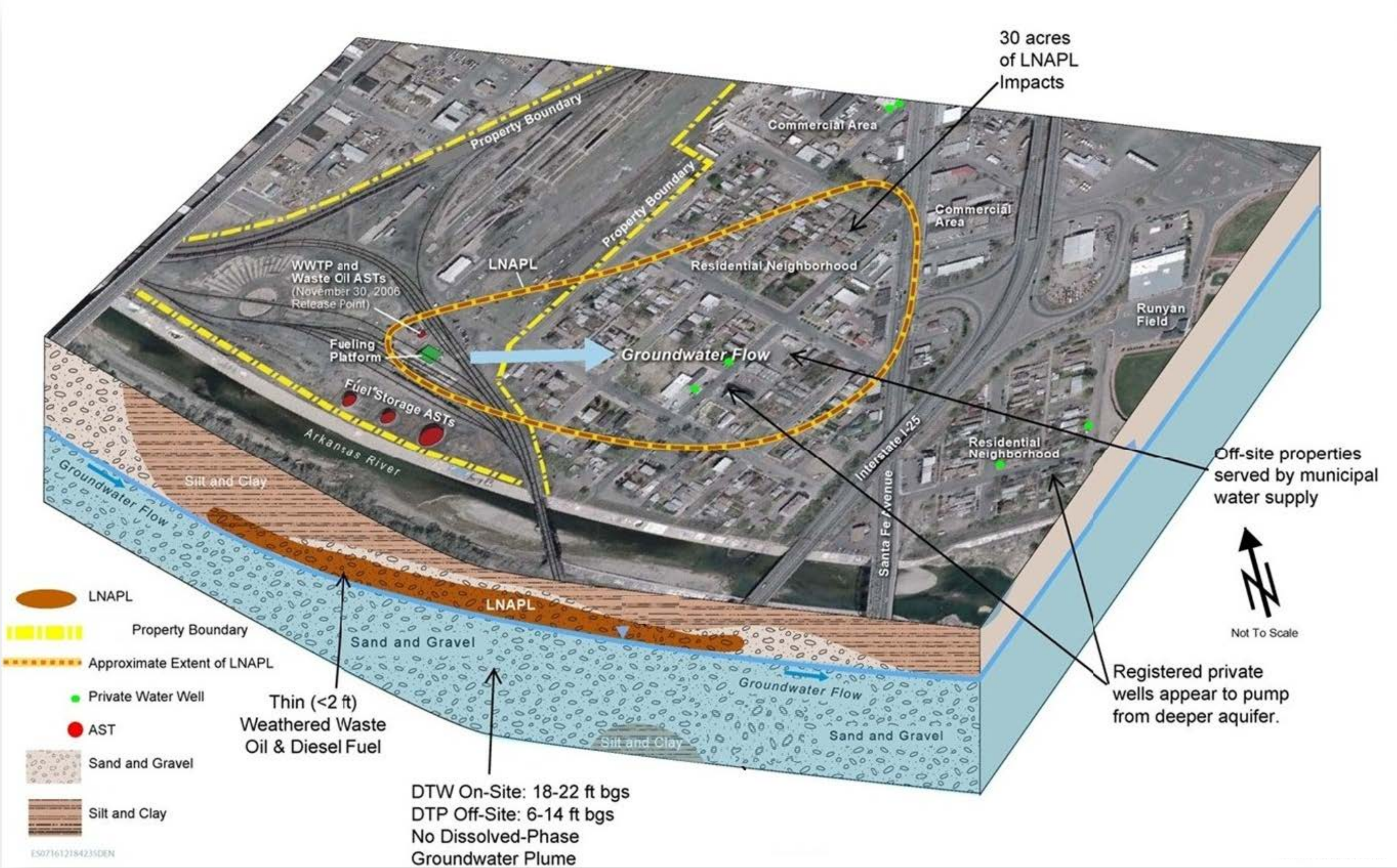
- Raw Data:
  - Step 1: Measure sorbed CO_2 by acidifying sorbent and measuring the volume of evolved CO_2 gas
  - Step 2: Subtract CO_2 due to travel and background
  - Step 3: Divide the mass of CO_2 by the cross-sectional area of the column and the period of time the trap was deployed to calculate CO_2 efflux
  - Step 4: Convert CO_2 efflux to hydrocarbon loss by selecting appropriate stoichiometric ratio between CO_2 and LNAPL petroleum hydrocarbons
    - $2\ C_6H_6 + 15\ O_2 \rightarrow 12\ CO_2 + 6\ H_2O$ (benzene example)



Case Study 1:
Large Diesel Release, Colorado

Conceptual Site Model

Large Diesel Release, Colorado



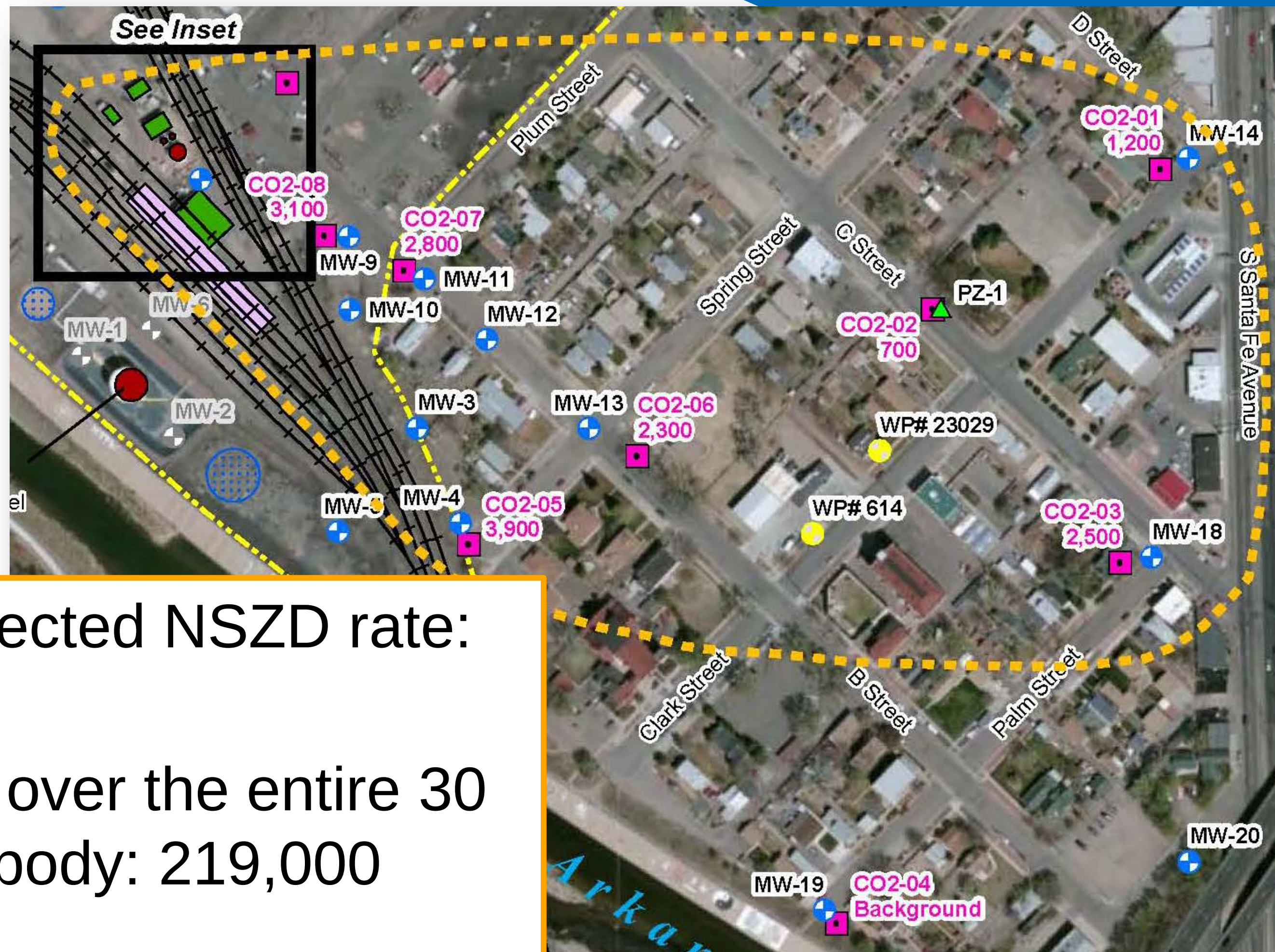
Corrected CO_2 Efflux and Loss Rate Estimates



CO_2 Trap	Travel Adjusted Total CO_2 Mass (g)	CO_2 Efflux (µmol/m²/sec)	Background Adjusted CO_2 Efflux (µmol/m²/sec)	Background Adjusted LNAPL Loss Rate (g/m2/d)
BACKGROUND TRAPS				
PUEB-CO2-04	1.4	2.4	- -	- -
PUEB-CO2-10	1.1	1.9	- -	- -
LNAPL LOCATIONS TRAPS				
PUEB-CO2-01	2.5	4.2	2.1	472
PUEB-CO2-02	2.0	3.4	1.2	273
PUEB-CO2-03	3.6	6.2	4.0	917
PUEB-CO2-05	5.0	8.5	6.3	1,444
PUEB-CO2-06	3.4	5.8	3.7	842
PUEB-CO2-07	4.0	6.8	4.6	1058
PUEB-CO2-08	4.2	7.2	5.1	1160
PUEB-CO2-09	0.4	*	*	*

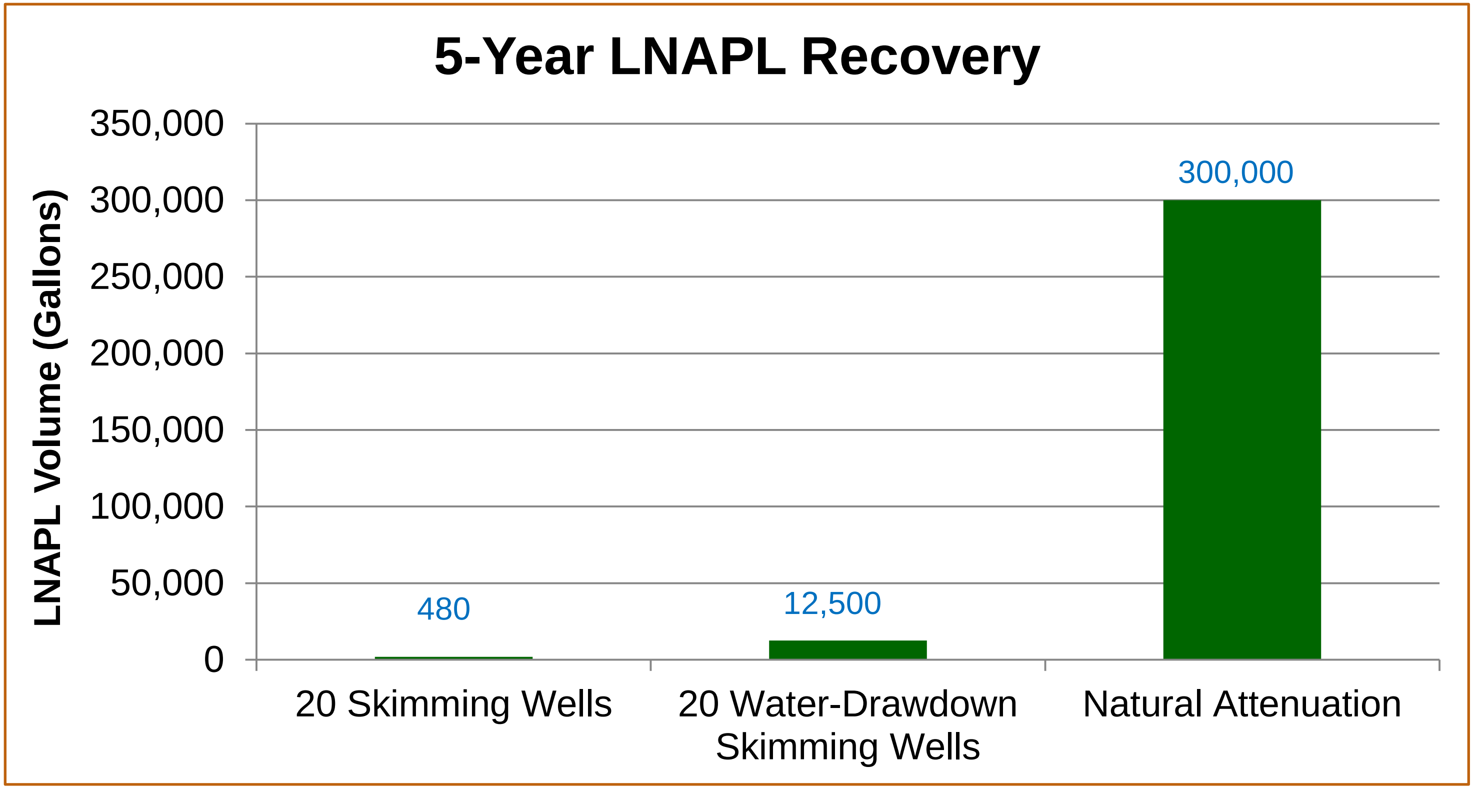
Summary of NAPL Loss Rates

Large Diesel Release, Colorado



- Average corrected NSZD rate: 766 $g/m^2/d$
- Extrapolated over the entire 30 acre LNAPL body: 219,000 kg/yr

Conclusions and Ultimate Data Use



- Used CO_2 Trap data in conjunction with in-well LNAPL flux data from dye tracer testing to demonstrate LNAPL plume stability
- MNA selected as the sole remedy

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Case Study 2:
Natural Gas Well Site, Alberta

Site Conditions
Natural Gas Well Site, Alberta

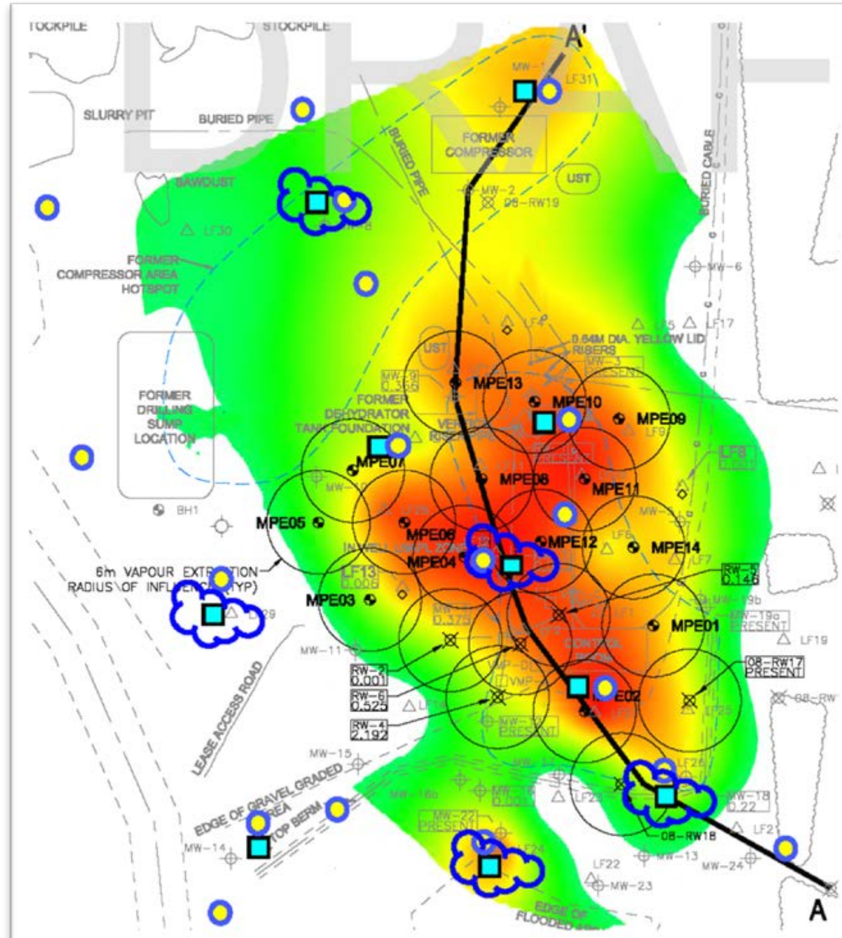


- Natural gas well and compressor station installed on gravel pad in 1996 within a forested and marshy area
- Releases of natural gas liquids/condensate (C6-16) and drilling fluids (C16-50)
- Areas of granular fill underlain by medium-grained sand and inter-bedded clay and organic materials
- Laser-induced fluorescence survey
  - LNAPL delineated over 1.2 acre
- Focused active remedy over 0.4 acre and natural attenuation for fringe


Project Objectives and CO_2 Survey Scope



- Compare natural losses to active removal using multiphase extraction
- Field Program
  - 20 locations – LI-COR 20cm chamber
  - 10 locations – E-Flux 10cm CO_2 traps



Field Methods

Natural Gas Well Site, Alberta



- MPE system shut down for several days prior to start of CO_2 survey for re-equilibration of subsurface
- LI-COR collars set ~5-8cm depth with hand tools



- E-Flux CO_2 Traps set ~18cm depth

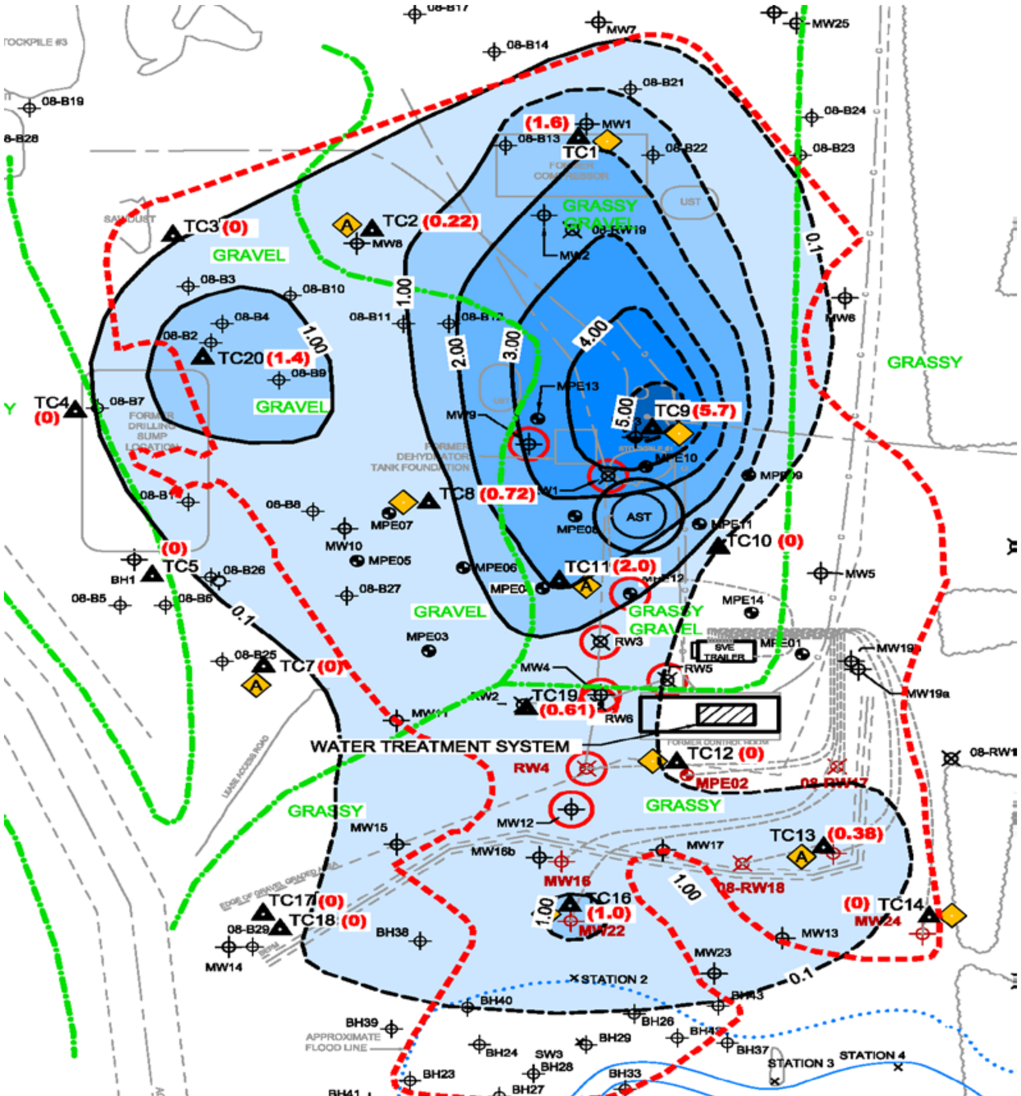



Comparison of CO_2 Efflux Method Results - Natural Gas Well Site, Alberta

- Decent correlation between LI-COR and E-Flux in grassy areas with loose ground surface soil
- Poor correlation between LI-COR and E-Flux in gravelly areas with dense ground surface soil
  - Factor of installation depth – deeper ground surface penetration of Traps broke through semi-confining gravel-hard pan and opened a chimney for CO_2 escape that was not "naturally" occurring

Results – What did that mean?

Natural Gas Well Site, Alberta



- Segregate data sets into grassy and gravelly areas
- CO_2 efflux:
  - Low in MPE areas
  - Highest in LNAPL core outside MPE influence
- NAPL loss rates up to 5.7 g/m^2/d

Ultimate Data Use

Natural Gas Well Site, Alberta



- LI-COR measurements used in gravel and E-Flux ^{14}C corrected results used in grassy areas
- Geospatially-weighted average mass loss rate estimated to be 1,900 kg/year across LNAPL footprint
- Establishes a good basis for an endpoint to MPE operation
- Follow-on efforts to ascertain long-term monitoring protocol and better refine estimates of NSZD

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Conclusions

Approximate Deployment Costs (Alberta example)



- LI-COR soil flux system
  - Rental ~$1,700/month
  - 20 beveled 8” PVC collars ~$300
  - Five site visits over 2 weeks (1 hr drive time each way, 8 hrs onsite/visit, 2 field technicians, $75/hr) – install collars and perform four rounds of daily measurements
  - $9,500 ($500/location)
- E-Flux CO_2 traps
  - Supply and CO_2 and ^{14}C analysis of 10 traps ~$18,000
  - Two site visits, start and end of 2 week deployment period (install and retrieve/ship traps, 1 hr drive time each way, 4 hrs onsite, 1 field technician)
  - $18,900 ($1,900/location)

Role of CO_2 Monitoring at Your Site



- CSM development
  - Estimate amount of NSZD currently occurring
  - Delineate LNAPL footprint
- Line of evidence
  - Use estimate to compare NSZD to active treatment remedies (e.g., Colorado example)
  - Evaluate the value of active remediation
  - Credible active remedy showing substantive NSZD is at work
    - active remedy is in place with minimal remediation costs
- Compare efficacy of remedial actions
  - Compare pre- and post-site conditions to evaluate efficacy of installed remedies (e.g., biosparging)

Applicability of CO_2 Efflux Monitoring



- Most suitable for petroleum sites with:
  - Identified NAPL within unconsolidated geology
  - Predominantly pervious ground cover and effective atmospheric exchange
  - Planned or existing MNA remedy component
  - Active remedies approaching/at asymptotic recovery limit
  - Enhanced bioremediation remedies looking for cost-effective monitoring technology
- Useful to projects in all stages of remediation from initial characterization to remedy optimization

CO_2 Efflux Monitoring Method Comparison



Method	Advantages	Disadvantages
Soil Flux System (LI-COR)	• Less susceptible to soil cover density • Quick measurements – can do more of them • Real-time data	• Snap shot in time only - need for repeat measurements • Measurement variability and need for background correction
CO_2 Trap Method (E-Flux)	• Time averaged CO_2 flux • Less labor intensive • Ability to use ^{14}C radio isotope to correct for background • Simpler math to get results	• More affected by soil cover density • Analytical cost

Conclusions

- CO_2 efflux monitoring technologies offer a less invasive and less labor intensive alternative to traditional methods
- More accurately account natural losses, improve understanding, and provide a more technical sound benchmark for remedy evaluation

Conclusions



- These methods provide data to more accurately quantify NSZD and are gaining ground toward regulatory acceptance
- Technology selection and the field program require careful consideration of data objectives, logistics, site conditions, and ultimate data use

These CO_2 efflux methods are a significant improvement in source zone monitoring. Their technical-defensibility, application ease, and cost-effectiveness could lead to replacing traditional methods and gaining a broad industry acceptance as a best practice.

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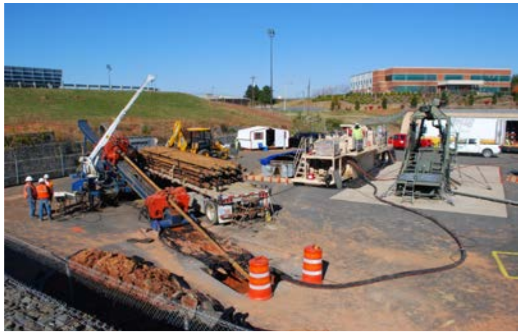

Questions?

Thank You For Your Time



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