A-027, in K.A. Fields and G.B. Wickramanayake (Chairs), *Remediation of Chlorinated and Recalcitrant Compounds—2010.* Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2010). ISBN 978-0-9819730-2-9, Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Two-Dimensional Compound-Specific Isotope Analysis to Assess Remediation System Effectiveness

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Compound-specific isotope analysis (CSIA) is a method to measure stable isotope ratios for a compound of concern to evaluate the occurrence of biodegradation. Carbon isotope ratios can change as a result of biological and chemical degradation processes, referred to as isotope fractionation. Some physical processes can result in measurable changes in carbon isotope ratios, however the magnitude of such changes is insignificant compared to the signatures of biodegradation. Therefore, CSIA can distinguish contaminant mass loss due to transformation versus loss due to physical processes.

CSIA can serve as an additional line of evidence in a multi-tiered assessment of monitored natural attenuation (MNA). In addition to supporting MNA, stable isotope ratios can also be used to evaluate the effectiveness of engineered remediation technologies such as bioremediation and in situ chemical oxidation (Hunkeler et al., 2003). CSIA may also be useful to distinguish between biological and physical remediation removal processes.

CSIA has been applied to sites with petroleum hydrocarbons, specifically those with benzene plumes. The proportion of carbon and hydrogen isotopic enrichment factors calculated at several field sites from two-dimensional CSIA (i.e., using carbon and hydrogen isotopes) are consistent with published results obtained from laboratory experiments. Results from sites have also varied as some have demonstrated significant isotopic enrichment and others show less enrichment, indicating in the latter cases the larger relative contribution of physical processes to natural attenuation.

Two-dimensional CSIA was applied at a California remediation site that utilizes air sparging and soil vapor extraction. Carbon and hydrogen CSIA was conducted for benzene in five monitoring wells. Sampling and CSIA was conducted three times. Modest carbon fractionation occurred, suggesting limited biodegradation. Inverse hydrogen fractionation was observed; enrichment of the light isotope and depletion of the heavy isotope. A similar pattern of isotope fractionation was observed after repeated sampling. Depletion of the heavy hydrogen isotope resulting from volatilization is consistent with column studies of isotope effects in volatilization of NAPL (Kuder, 2008). The signature for volatilization was strongest in a monitoring well in close proximity to a soil vapor extraction well.

CSIA can potentially distinguish between biological and physical remediation removal processes, and should be useful to: (1) monitor remediation progress, (2) optimize remediation system performance, and (3) recommend the timing to terminate remediation and/or select an alternative remediation strategy.

Two-Dimensional Compound Specific Isotope Analysis to Assess Remediation System Effectiveness

Battelle Remediation of Chlorinated and Recalcitrant Compounds

Session A3: Application of Compound Specific Isotope Analysis In Forensic Analysis

May 24-27, 2010

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Leslie Klinchuch (Chevron Environmental Management Company)
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Abstract

- 2D-CSIA was applied at an air sparging(AS)/soil vapor extraction (SVE) site.
- Carbon and hydrogen CSIA was conducted for dissolved benzene in four or more monitoring wells over three sampling events.
- Inverse hydrogen fractionation was observed, i.e., depletion of the heavy isotope associated with decreasing benzene concentration.
- Depletion of the heavy hydrogen isotope is consistent with isotope effects in volatilization of benzene and MTBE nonaqueous phase liquid (NAPL) (Wang and Huang, 2003; Kuder et al., 2009).

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Outline

- Isotope Fractionation
- Effects of Volatilization on Carbon and Hydrogen Isotope Ratios
- 2D Carbon and Hydrogen CSIA
- Remediation Site Description
- Preliminary Evidence for AS/SVE-Induced Volatilization
- Discrimination of Volatilization and Biodegradation
- Conclusions

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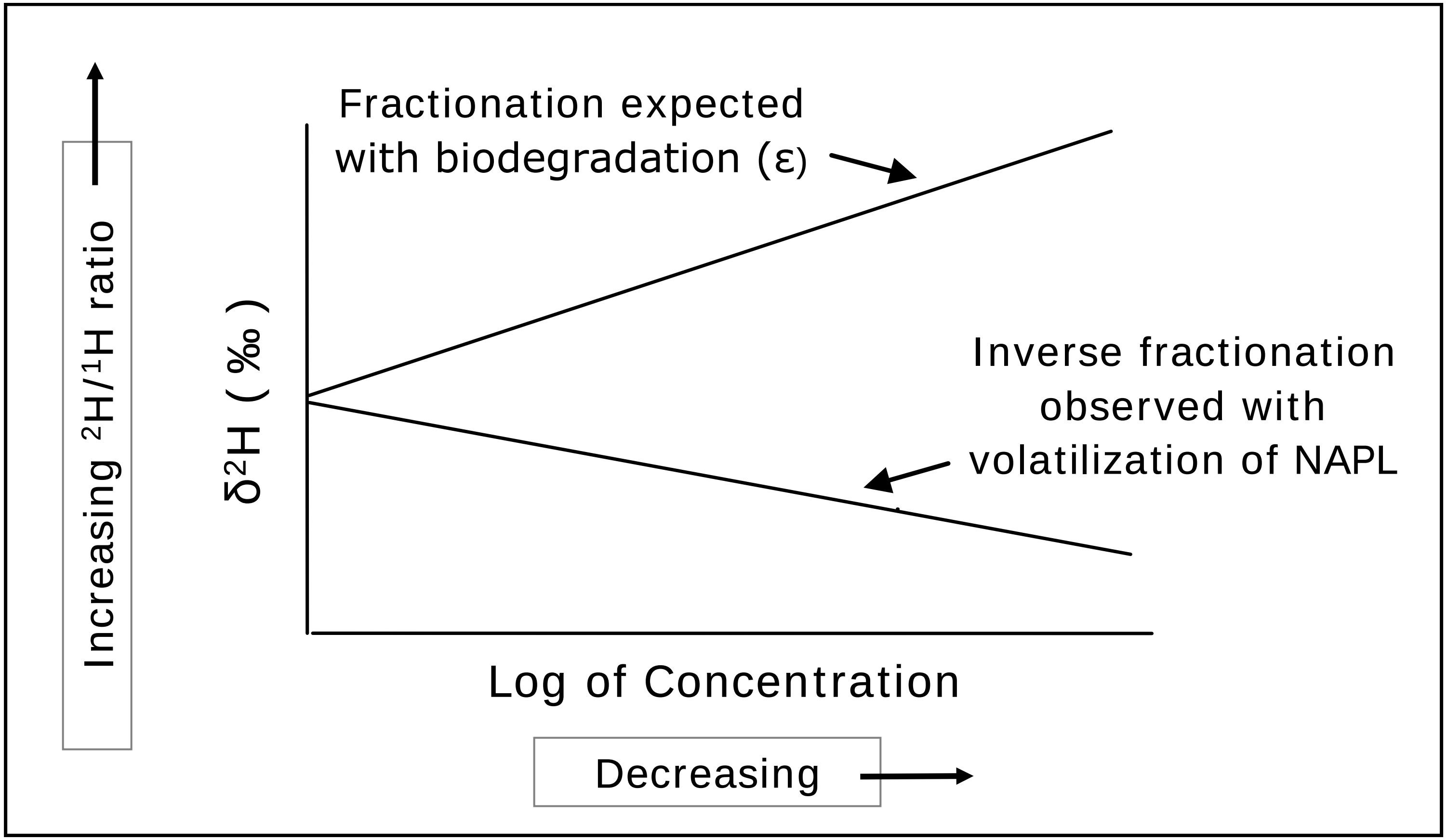
Isotope Fractionation for Petroleum Hydrocarbons



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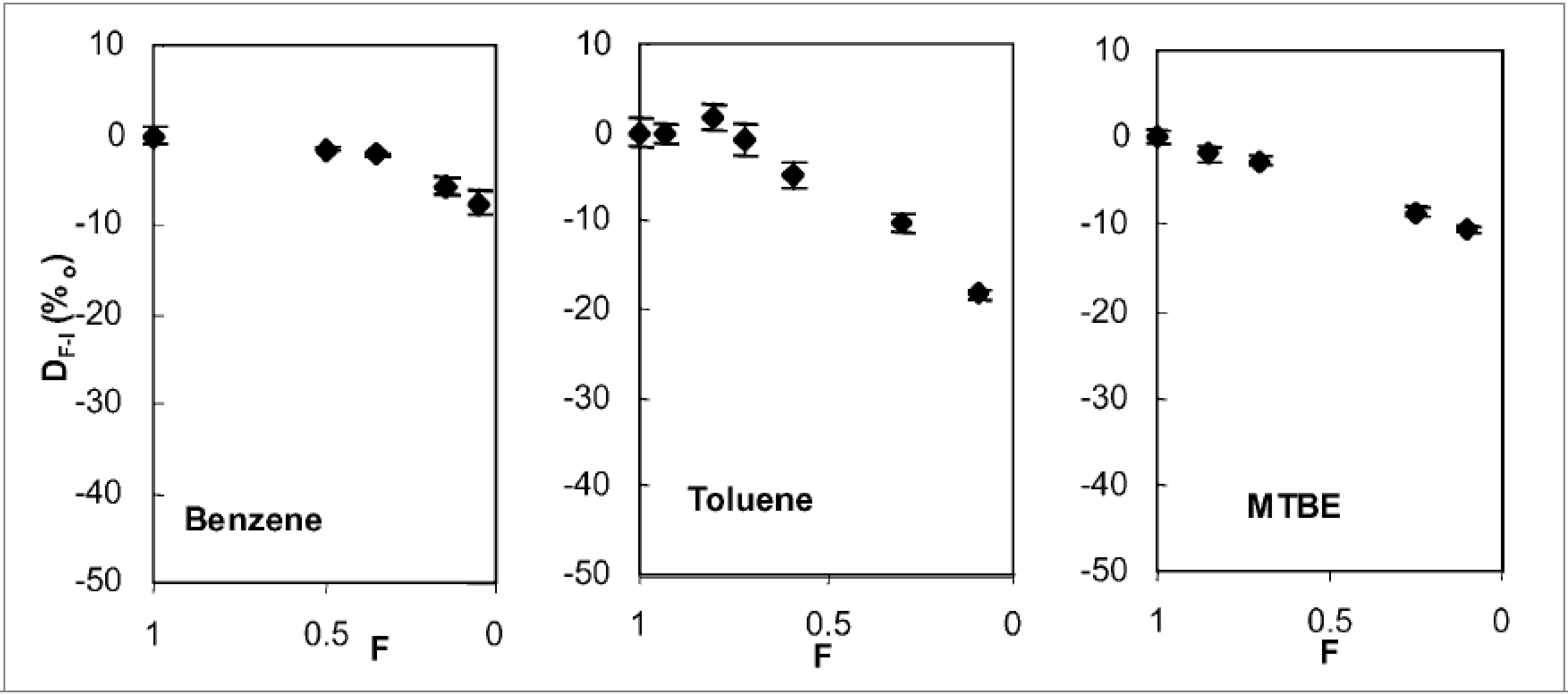
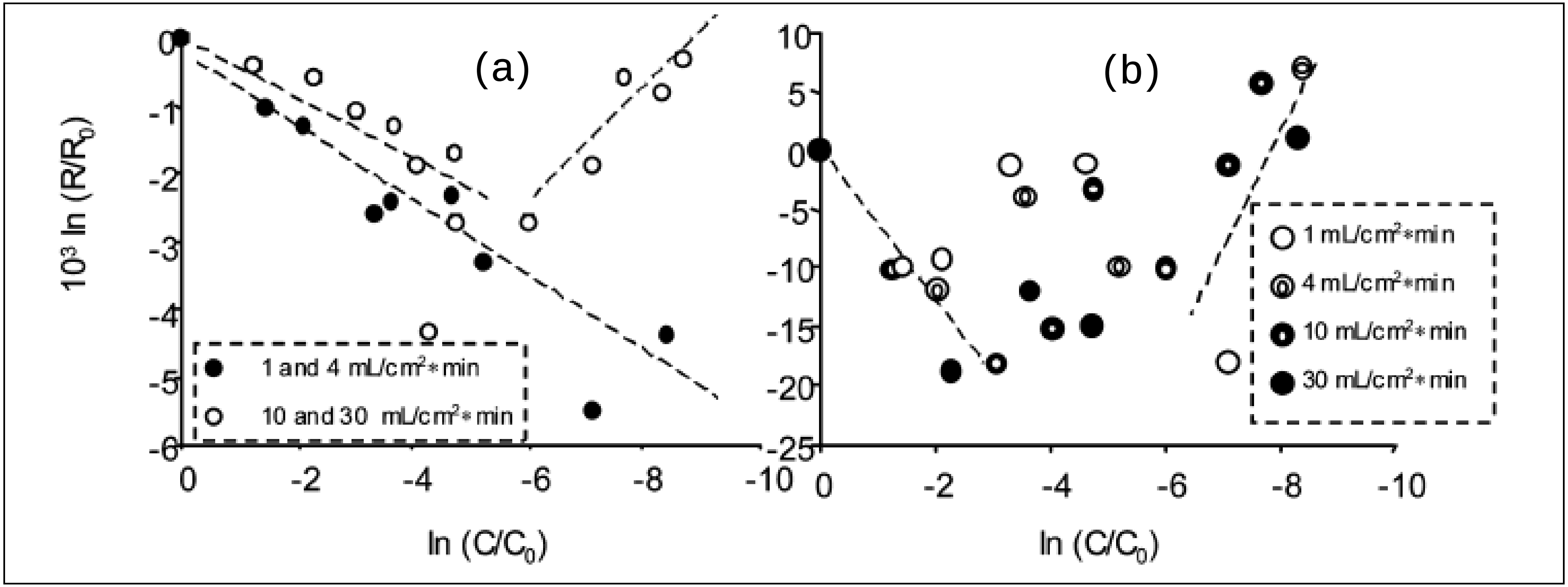
Hydrogen Isotopic Fractionation for Petroleum Hydrocarbons During Vaporization

(Wang and Huang, 2003)



- Heavy isotopes have higher vapor pressures, attributed to the smaller intermolecular binding energies in the liquid phase.
- Effect of binding energy difference is dominant over the effect of mass difference.
- The net result: the heavy isotope, D (^{2}H), is enriched in the vapor phase and depleted in the liquid phase.

MTBE Volatilization and Biodegradation Laboratory Experiments (Kuder et al., 2009)

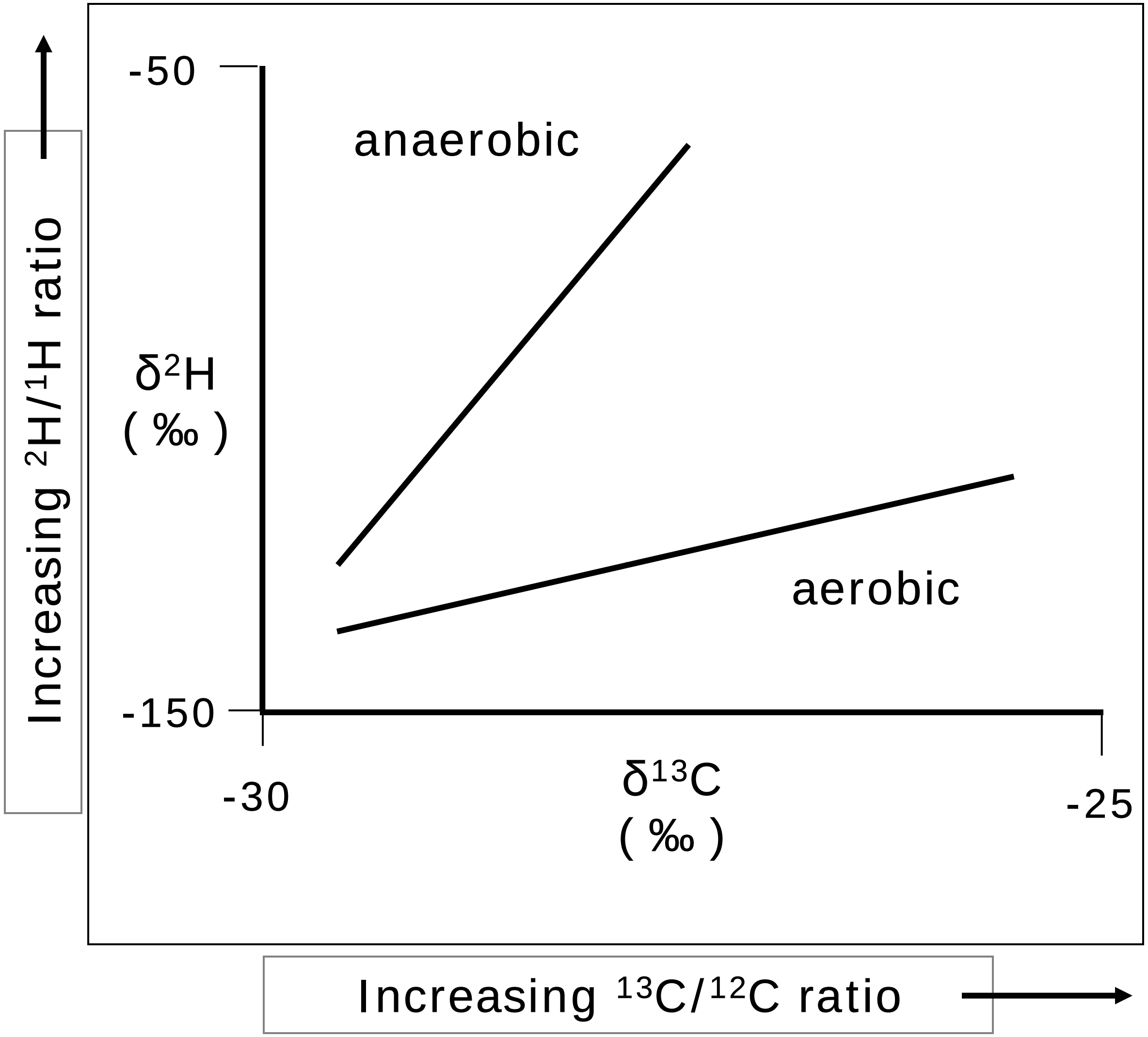


(a) Carbon

(b) Hydrogen

- Higher concentrations – inverse isotope effect associated with volatilization
- Lower concentrations – fractionation characteristic of biodegradation
- Benzene hydrogen isotope effects likely follow a similar pattern

2D-CSIA for Benzene Biodegradation



Hydrogen enrichment is greater than carbon enrichment due to the larger relative mass differences

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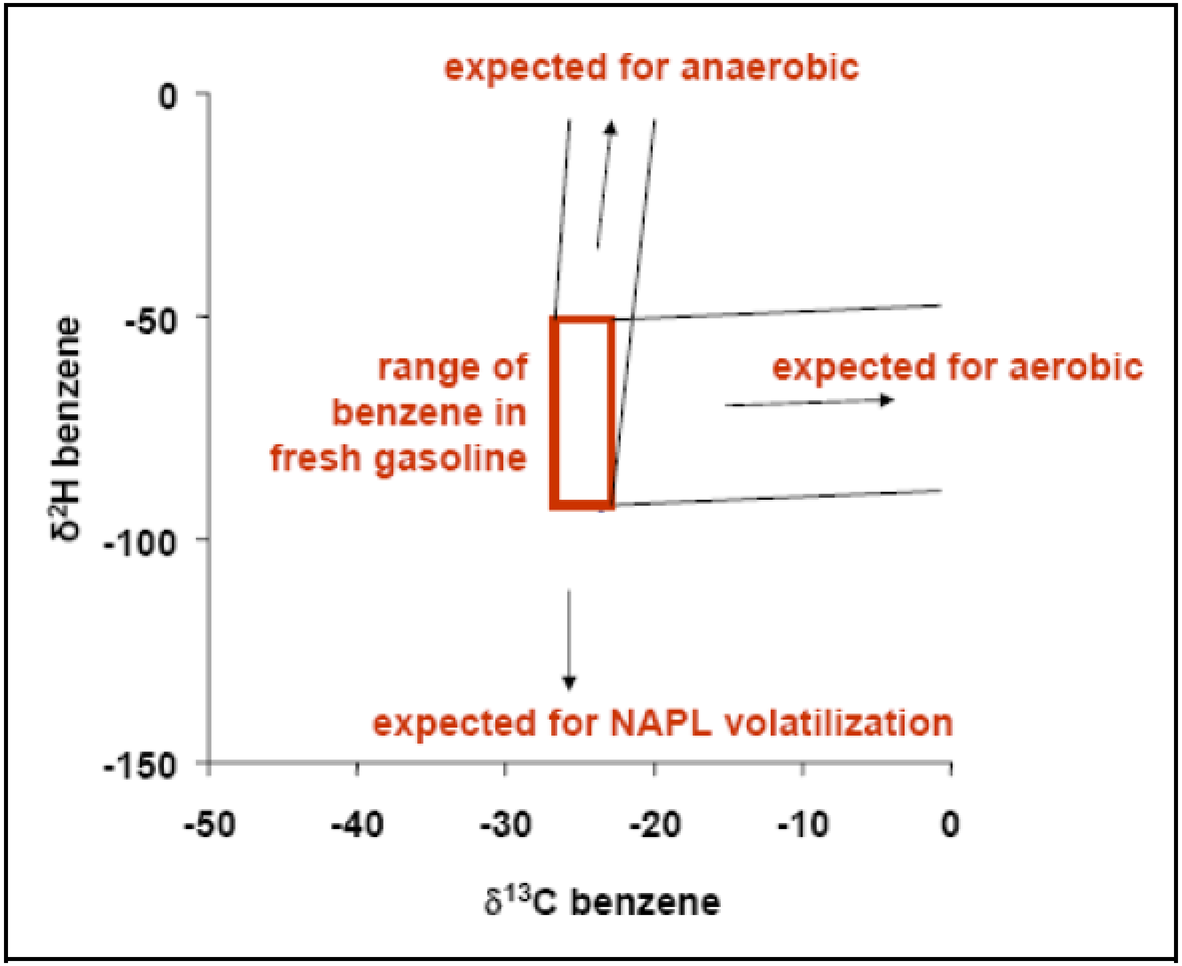
2D-CSIA for Benzene Biodegradation and Volatilization



Kuder, 2008

Volatilization signature is different than anaerobic and aerobic biodegradation

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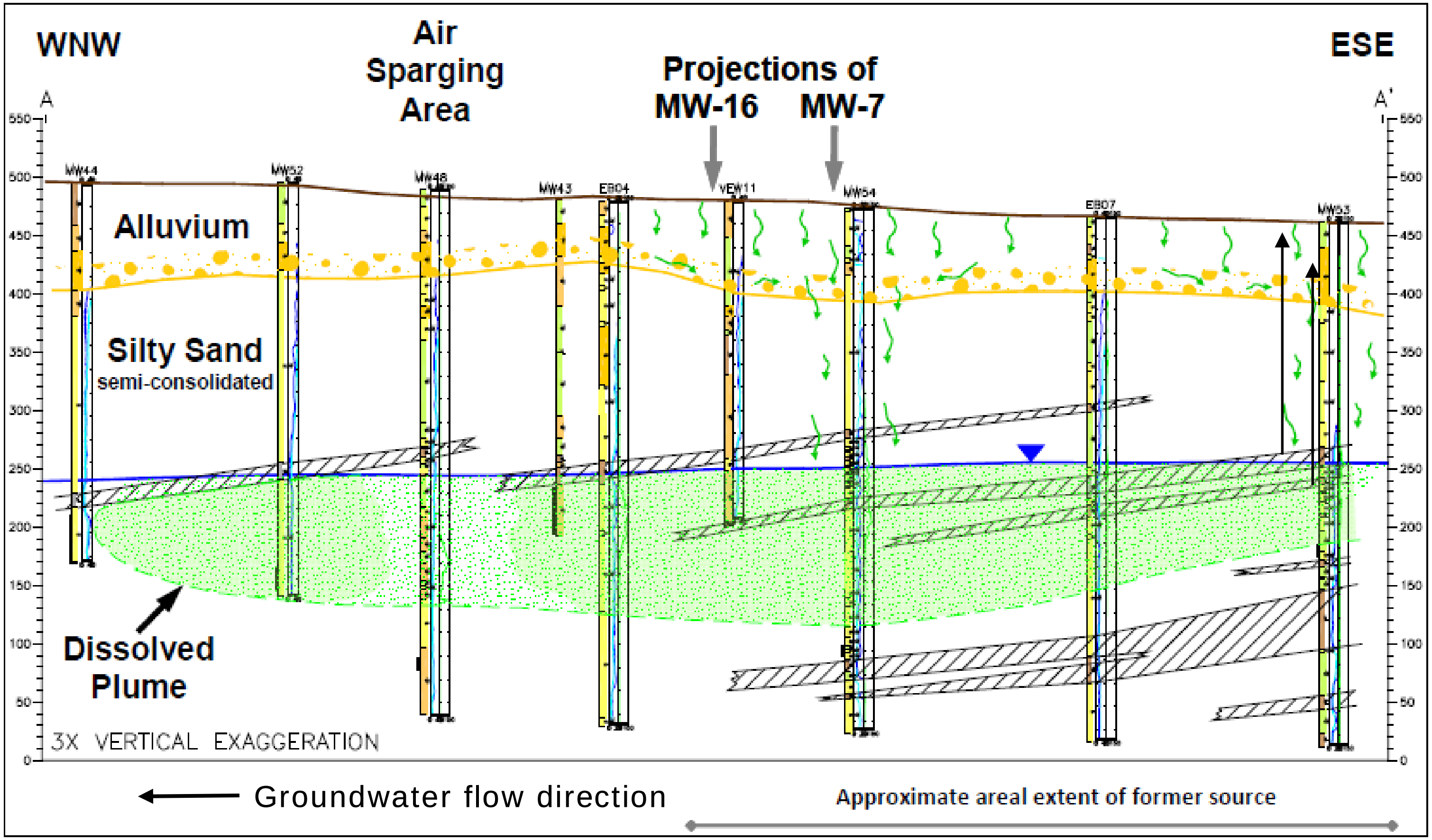
California Remediation Site Conceptual Model (Klinchuch et al., 2007)



- Groundwater velocity 115 ft/yr.
- Depth to groundwater in CSIA wells 215 to 255 ft.
- Highest BTEX concentrations in upper 100 ft of the saturated zone.

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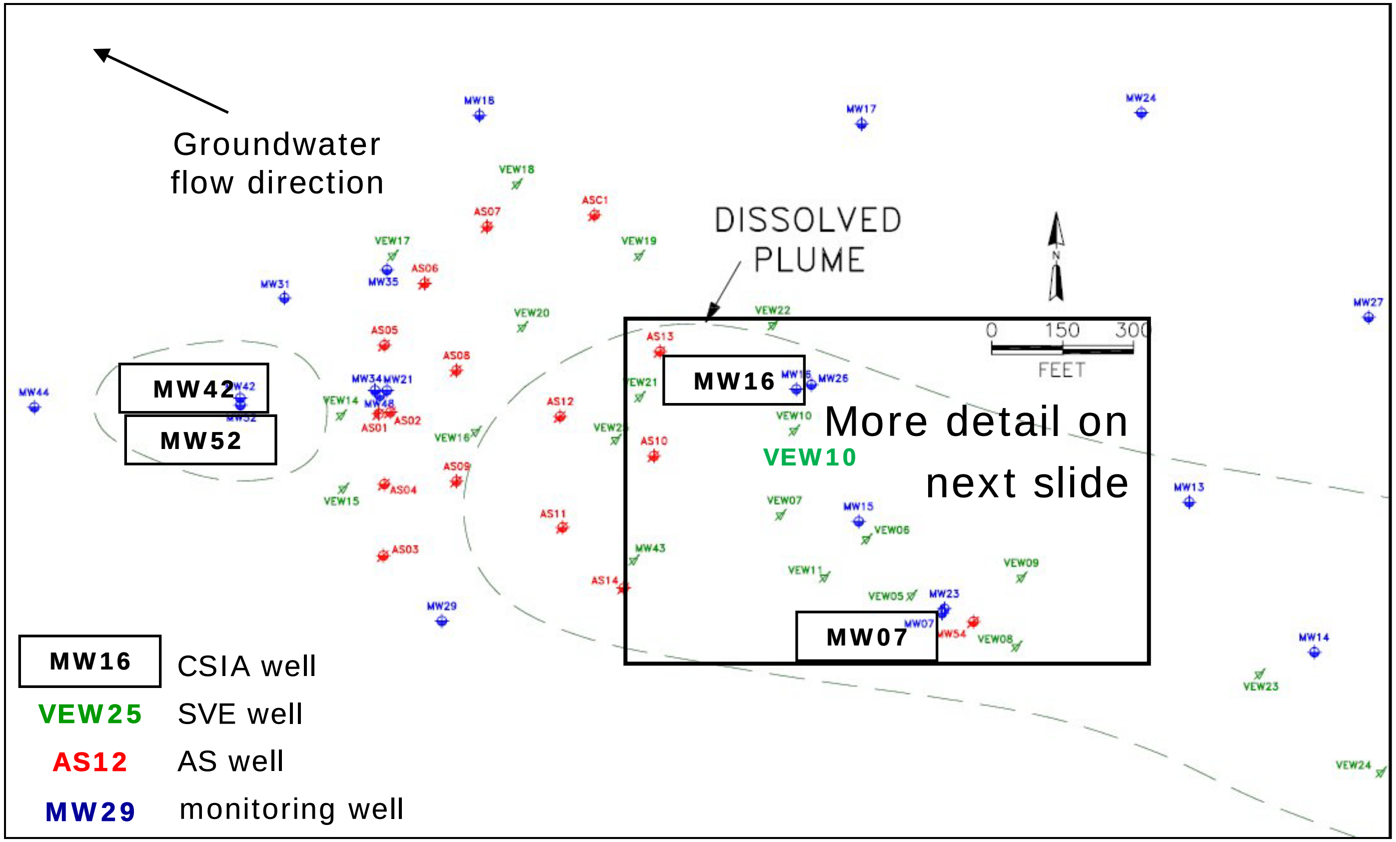
Site Map with Well Locations



- Zone of influence (ZOI)
- ZOI for AS wells = 80 to 100 ft
- ZOI for vapor extraction wells (VEW) <200 ft.
- Sparge air flows preferentially up stratigraphic dip (northerly)

Klinchuch et al., 2007

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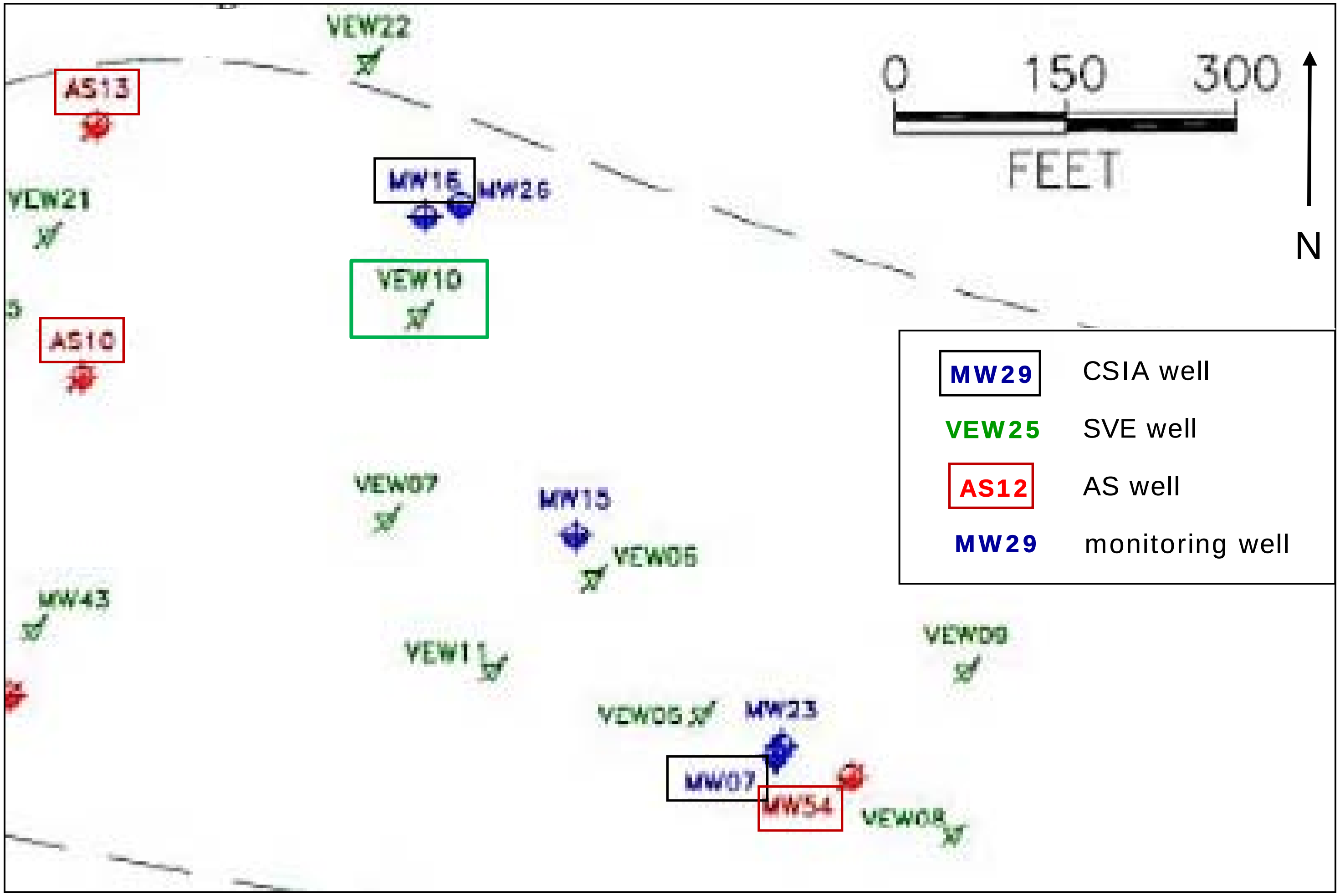
CSIA Wells within ROI for SVE and AS



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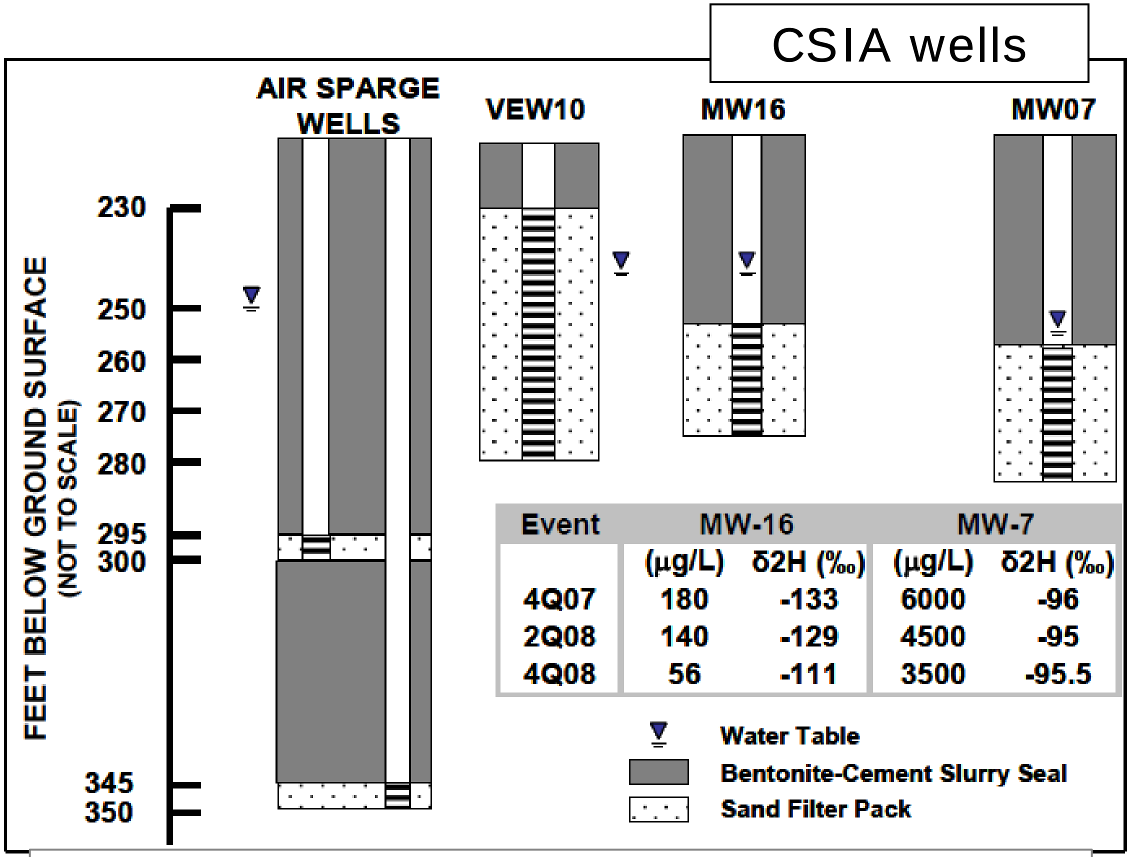
Preliminary Evidence for AS/SVE-Induced Volatilization



CSIA wells

Event	MW-16		MW-7	
	(µg/L)	δ2H (‰)	(µg/L)	δ2H (‰)
4Q07	180	-133	6000	-96
2Q08	140	-129	4500	-95
4Q08	56	-111	3500	-95.5

Well Construction and Water Table Details for AS, SVE (VEW), and CSIA Wells

- Deep AS at 50 and 100 ft beneath the water table
- δ^2H values (very negative) provide good evidence for volatilization in MW16
- Less negative δ^2H values in MW07 suggest volatilization is not prominent

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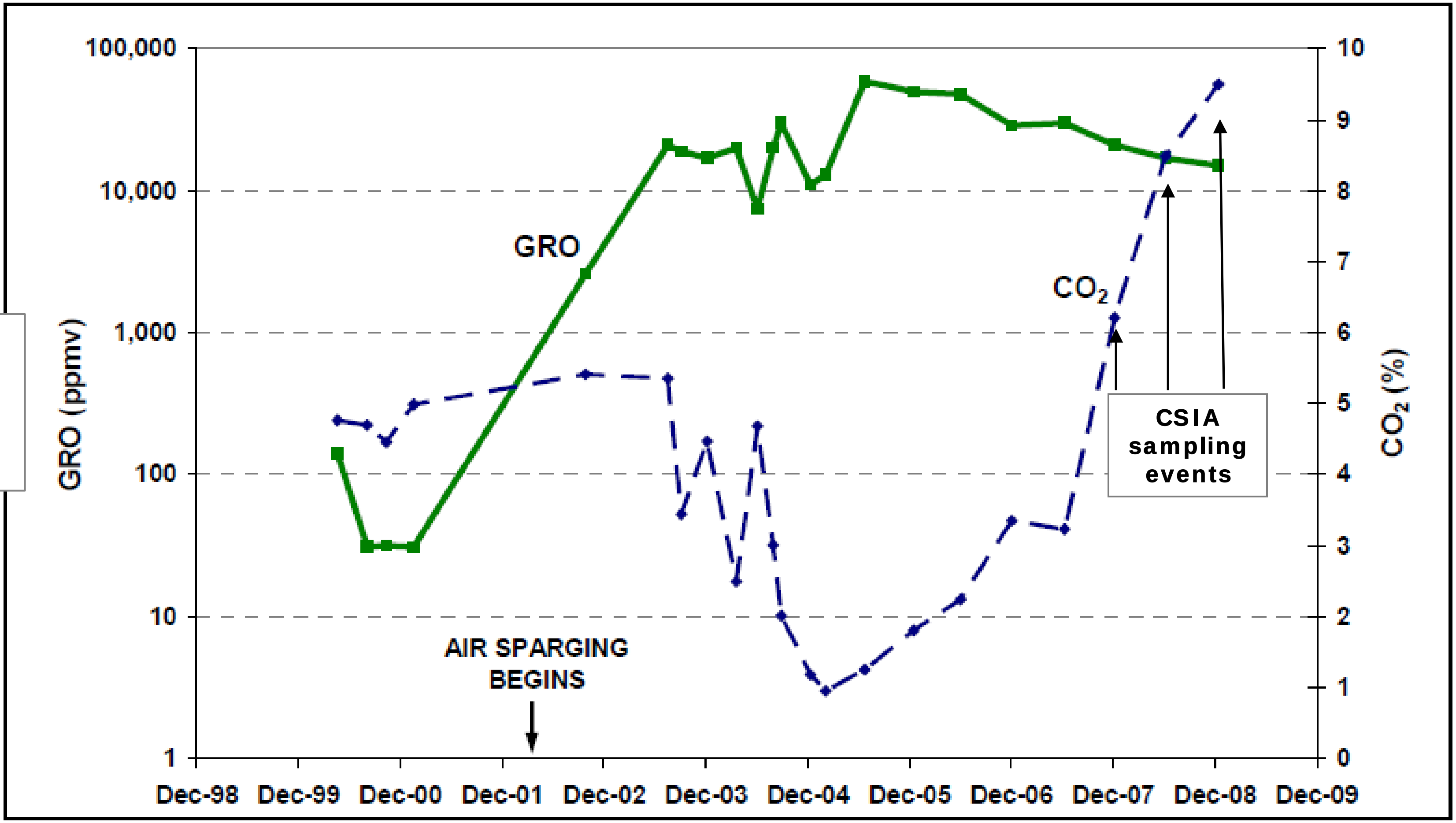
VEW10 Vapor Concentrations during AS / SVE

GRO:
Gasoline Range Organics



VEW10 is located 90 ft south of MW16

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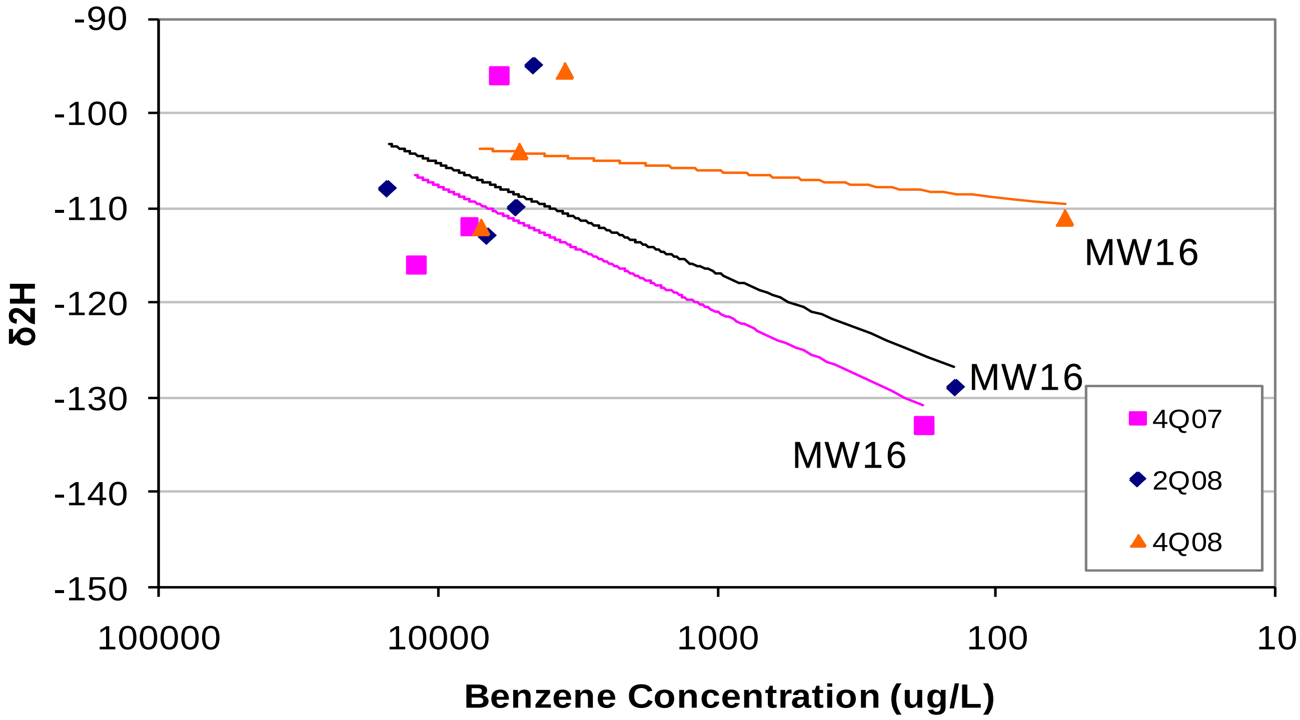
Hydrogen Fractionation for Benzene



- Inverse fractionation shows evidence for volatilization
- Volatilization effect is apparent in the reduction of δ^{2}H
- In 4Q08 there is a dampening of the inverse fractionation with lower concentrations

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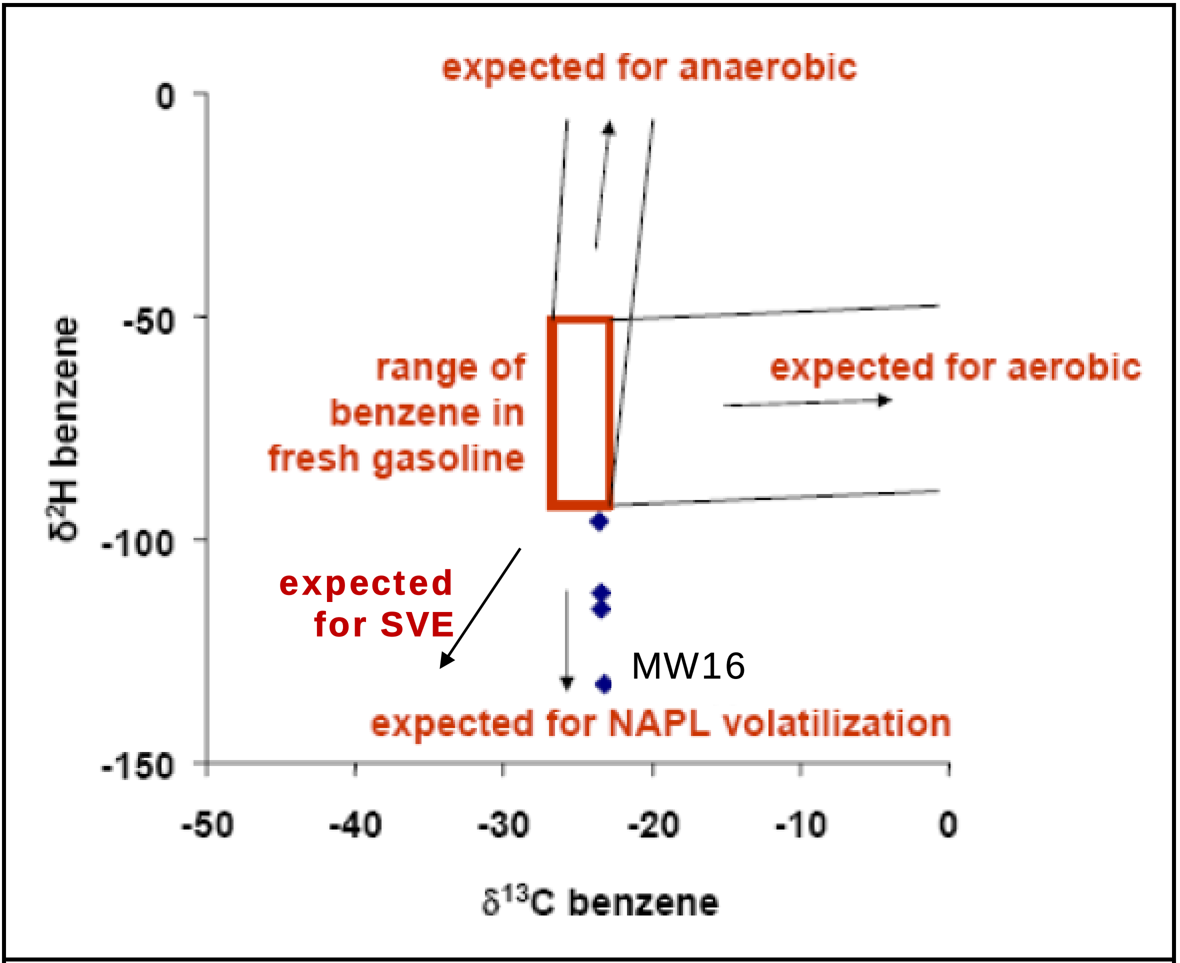
Discrimination of Volatilization and Biodegradation by 2D-CSIA



- MW16 plots beyond the range for the SVE scenario, potentially the cumulative effect of volatilization and biodegradation
- Depletion of δ^2H can also result from natural volatilization, but larger carbon fractionation would be expected

Modified after Kuder, 2008.

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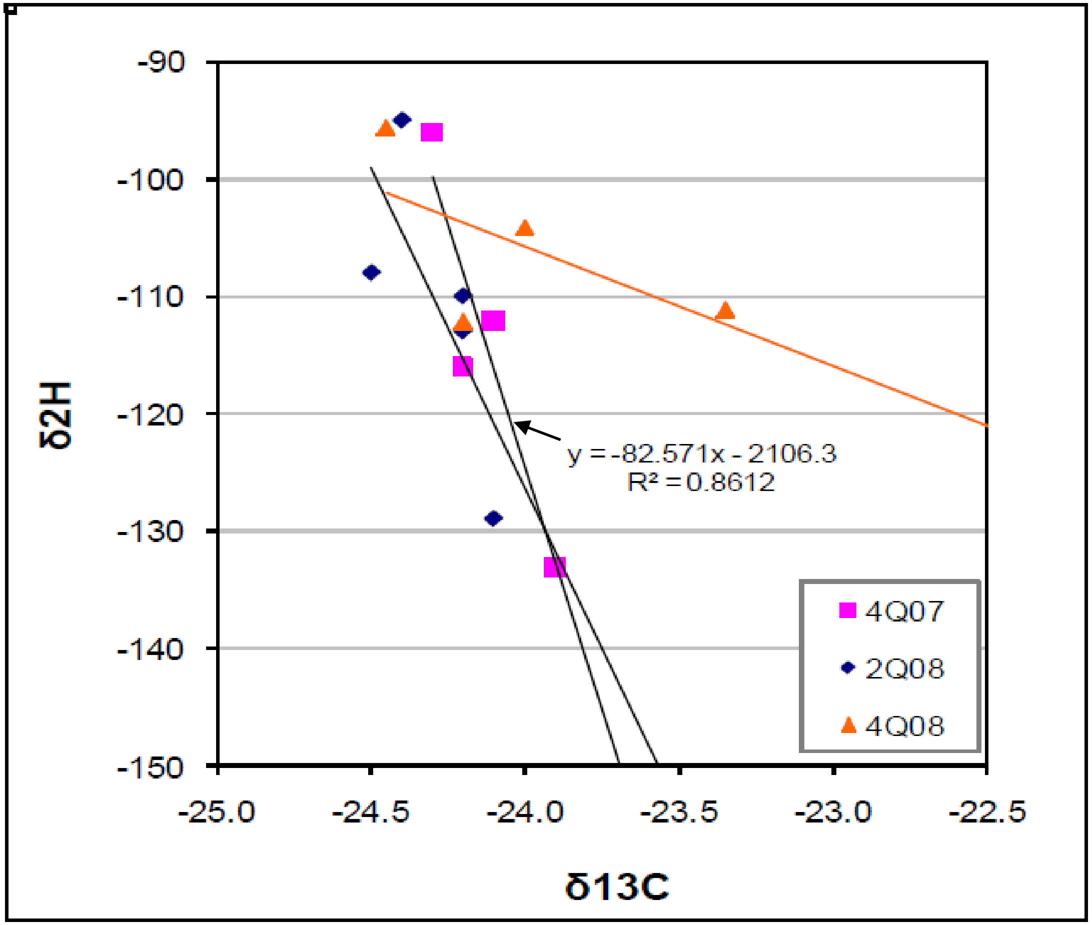
2D-CSIA: $\delta^{13}C$ versus $\delta^{2}H$



- The inverse isotope effect in 4Q07 is statistically significant
- The inverse isotope effect is repeated in 2Q08
- In 4Q08, the relative contribution of volatilization is less pronounced possibly because:
  - larger impact of biodegradation and/or
  - dampening of inverse fractionation at low concentrations

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Remediation Decision Making

- CSIA results ratios can be compared to effluent concentrations and used to assess remediation system effectiveness
  - Enrichment in the heavy isotope suggests biodegradation is the primary process
  - Depletion in the heavy hydrogen isotope suggests volatilization is the primary process
- CSIA results can be used to optimize the system; it may be appropriate to cease or increase extraction in remediation wells, depending on isotope ratios

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Conclusions

- Carbon and hydrogen CSIA conducted at this remediation site provides preliminary evidence for the contribution of volatilization from AS/SVE.
- Inverse hydrogen fractionation for benzene observed at this site is consistent with column studies for volatilization of MTBE NAPL in a degradation-free environment (Kuder et al., 2009) and volatilization experiments of benzene NAPL (Wang and Huang, 2003).
- At a remediation site the effects of volatilization and biodegradation can both contribute to isotopic fractionation.

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Potential CSIA Applications for Remediation

- Isotope data are potentially informative for assessment of physical attenuation progress in SVE and/or AS (Kuder et al., 2009)
- CSIA can be used to:
  - monitor remediation progress
  - optimize remediation system performance
  - recommend the timing to terminate remediation and/or select an alternative remediation strategy

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