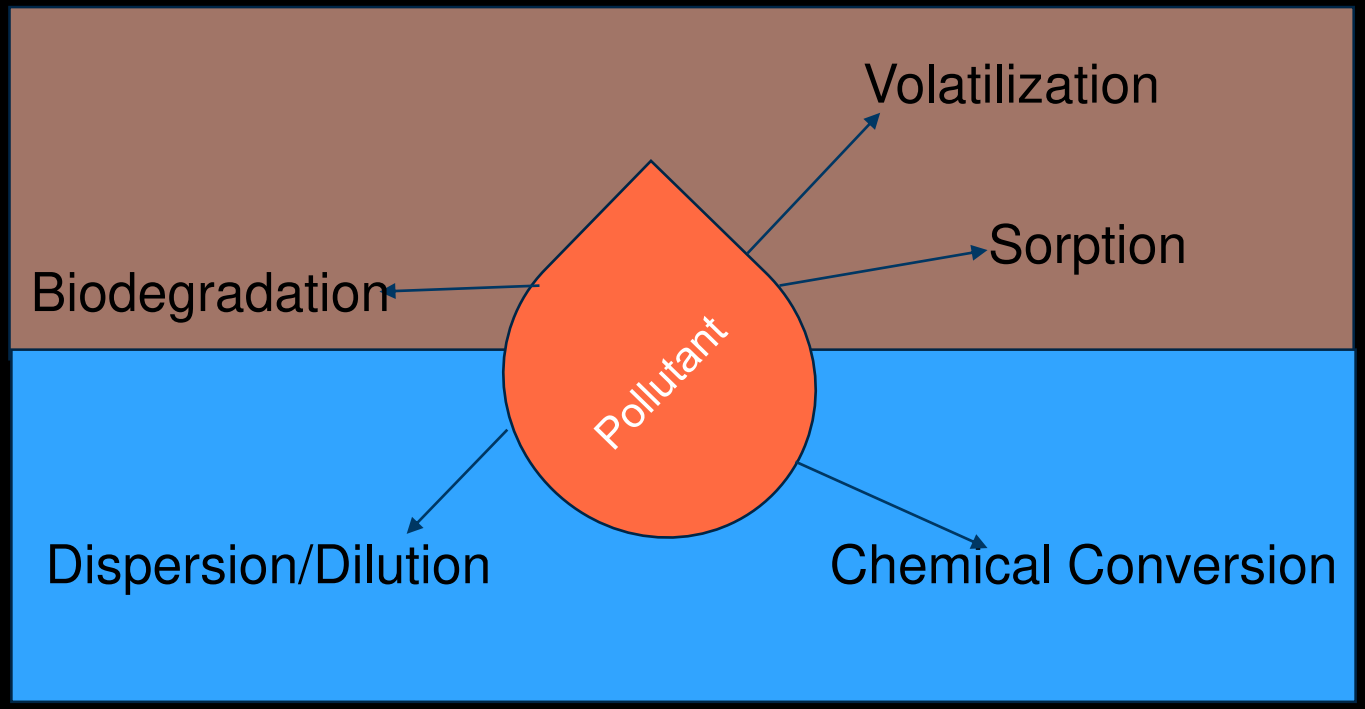
Sophia Dore
GHD

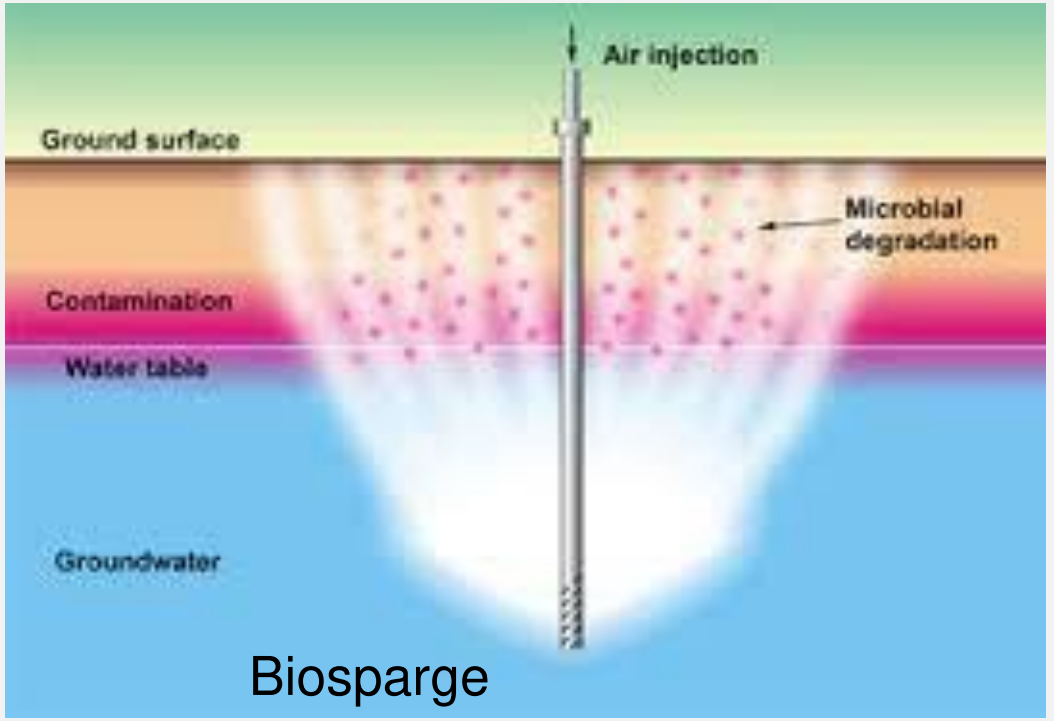
Soil Respiration Rates Under Natural Attenuation versus Enhanced Biodegradation

Welcome

Natural Attenuation



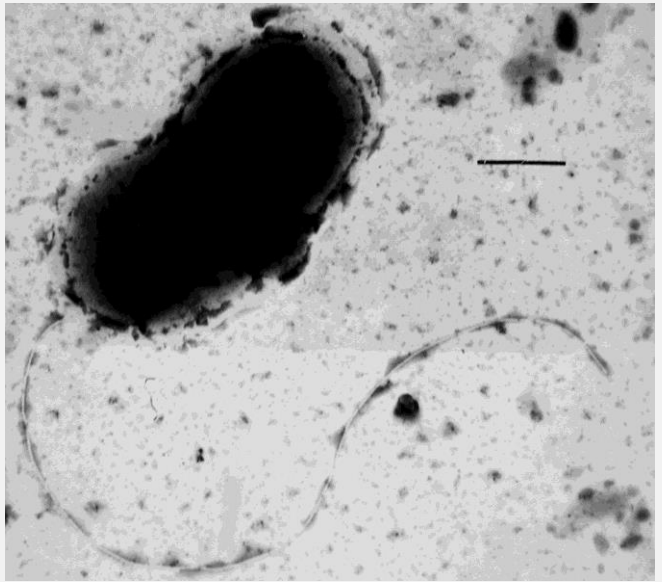
→ Enhanced Biodegradation



Biosparge

Sulfate Reduction

$SO_4^{2-} \rightarrow S^{2-}$



GHD

→ Site

- Groundwater at a petroleum industry site contains benzene, toluene, gasoline range hydrocarbons
- Laboratory study was performed to evaluate intrinsic and enhanced biodegradation using soil and groundwater from the site
- Study Objectives
  - Determine the effectiveness of natural attenuation and enhanced biodegradation for the treatment of benzene and petroleum hydrocarbon in Site groundwater and soil
  - Determine whether enhanced biodegradation provides a significant advantage over natural attenuation
  - Determine whether natural attenuation could already be occurring at the site
- Microcosm tests were performed

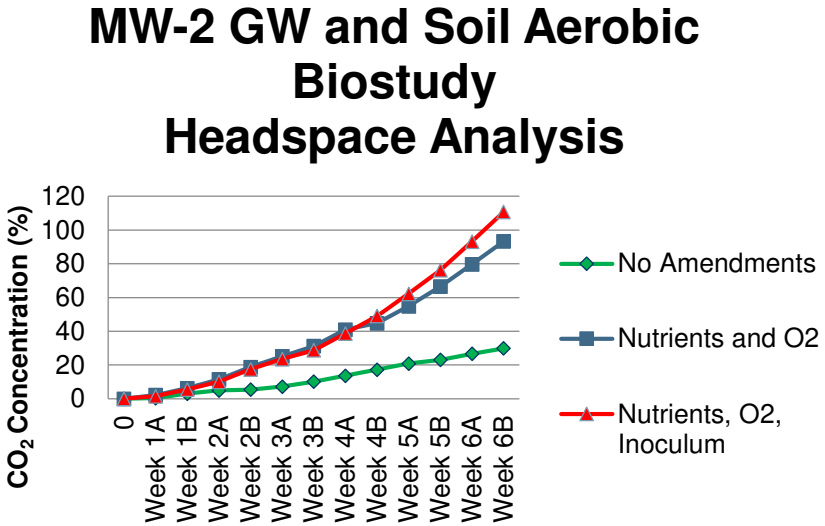
Groundwater Samples

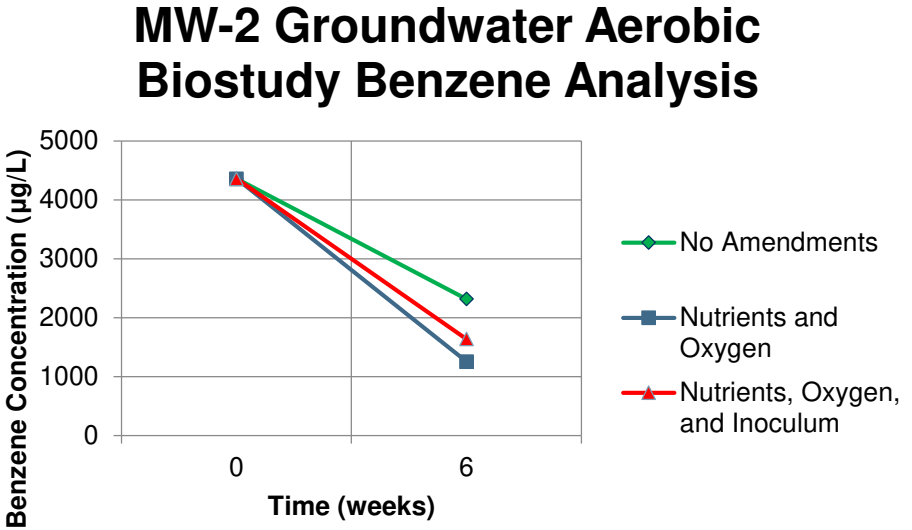
Parameters	Units	MW-1	MW-2
Microbiology			
Total Aerobic Microbial Population	CFU/L	1.11E+04	1.79E+04
Total Anaerobic Microbial Population	CFU/L	2.18E+04	1.42E+04
Volatile Organic Compounds			
Benzene	µg/L	147	4840
Ethylbenzene	µg/L	3.75	436
Toluene	µg/L	103	9010
Total Xylenes	µg/L	26.2	2330
TPH(C_5-C_{12})	mg/L	2.8	97

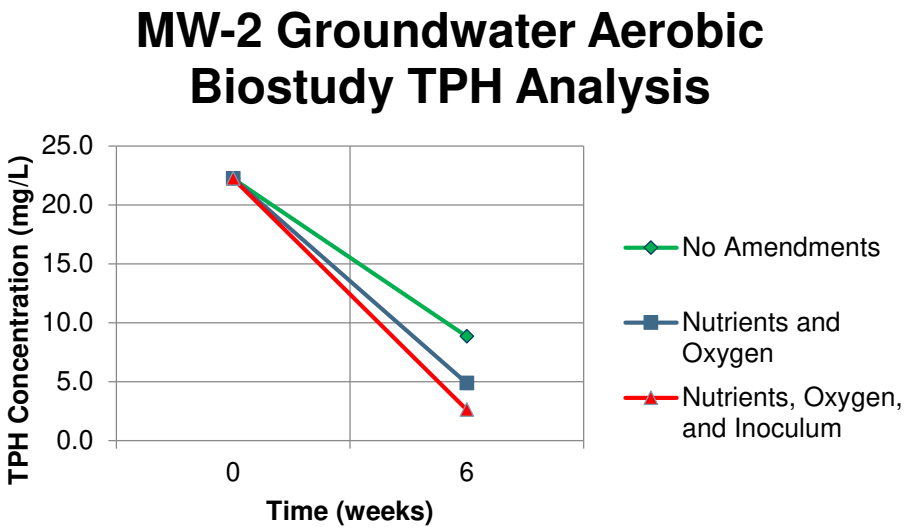
Soil Samples

Parameters	Units	MW-1	MW-2
Microbiology			
Total Aerobic Microbial Population	CFU/kg	2.50E+02	1.00E+02
Total Anaerobic Microbial Population	CFU/kg	0.00E+00	0.00E+00
Volatile Organic Compounds			
Benzene	µg/kg	ND (50)	443
Ethylbenzene	µg/kg	ND (50)	6010
Toluene	µg/kg	ND (50)	5800
m/p-Xylene	µg/kg	49.4 J	25000
o-Xylene	µg/kg	ND (50)	9530
Total Petroleum Hydrocarbons			
TPH(C_5-C_{12})	mg/kg	211	2340

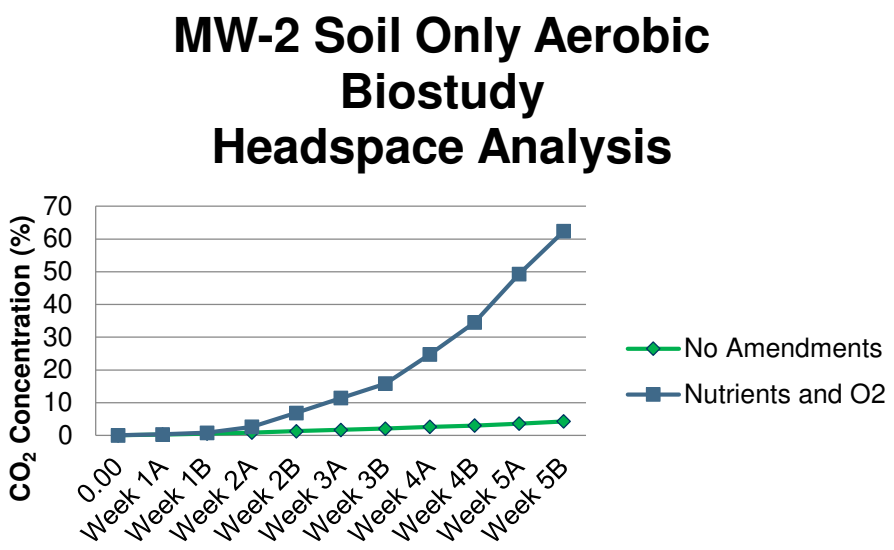
MW-2 Groundwater Aerobic Conditions

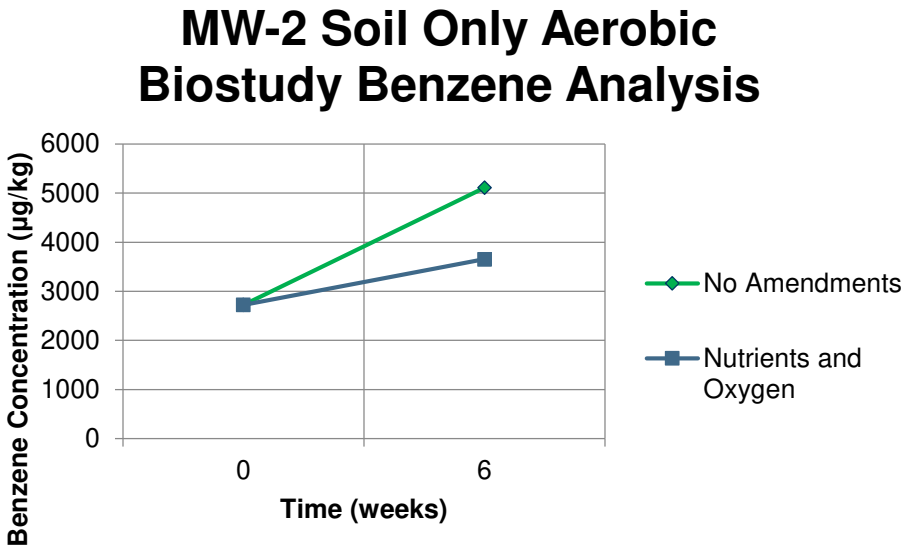


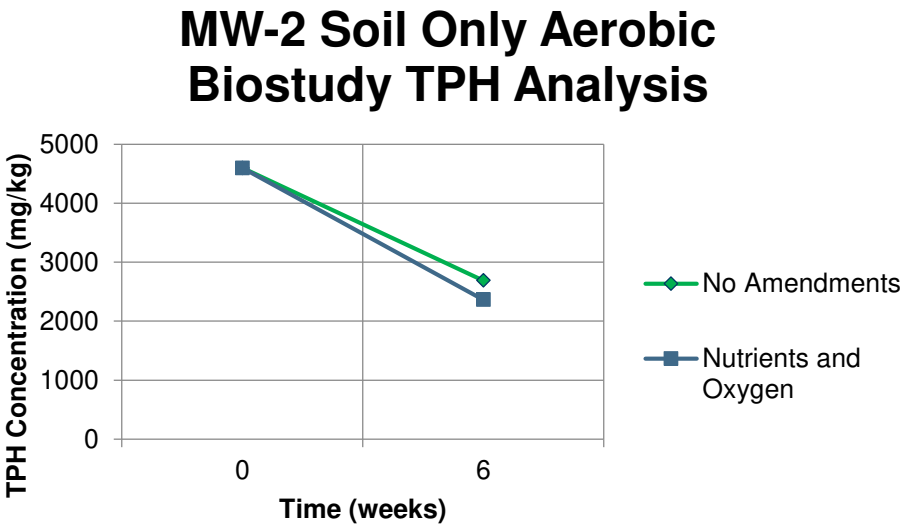




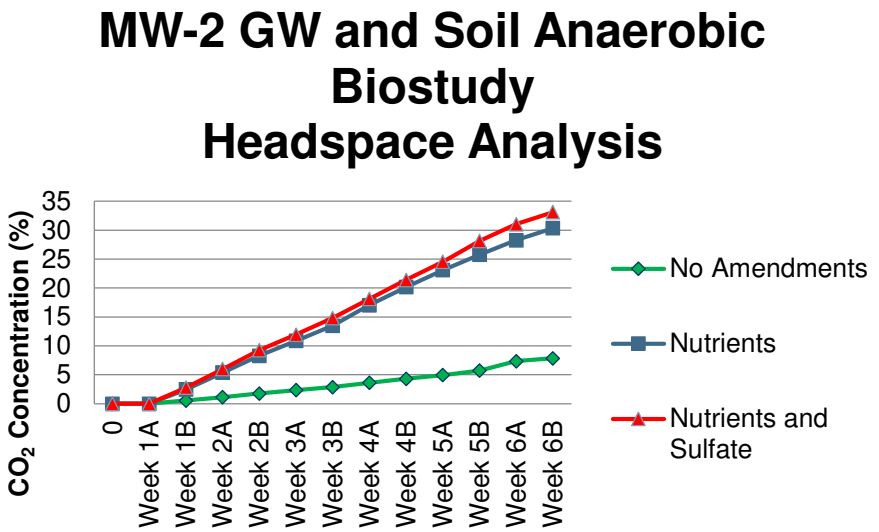
MW-2 Soil
Aerobic Conditions

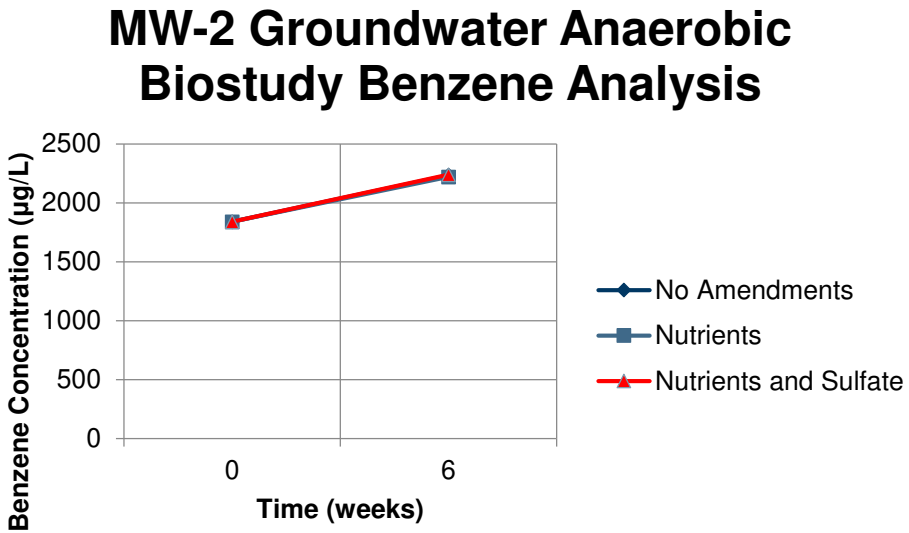


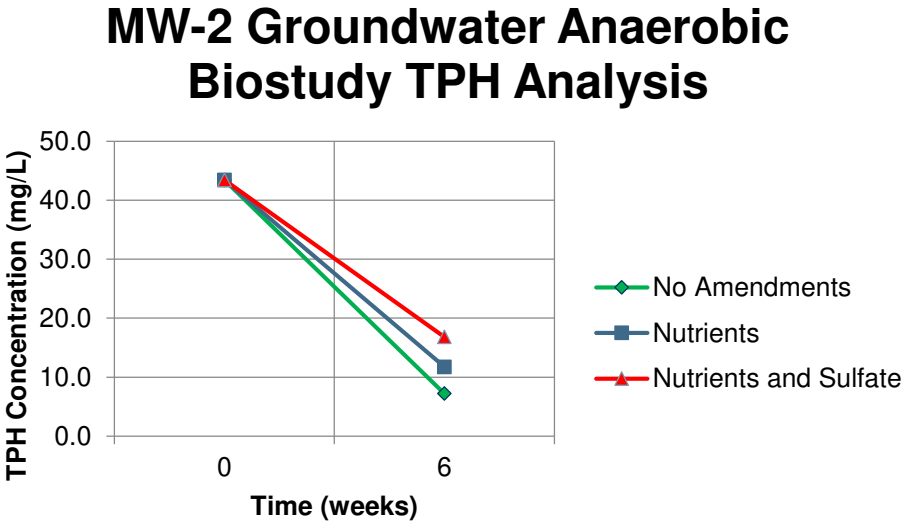




MW-2 Groundwater Anaerobic Conditions

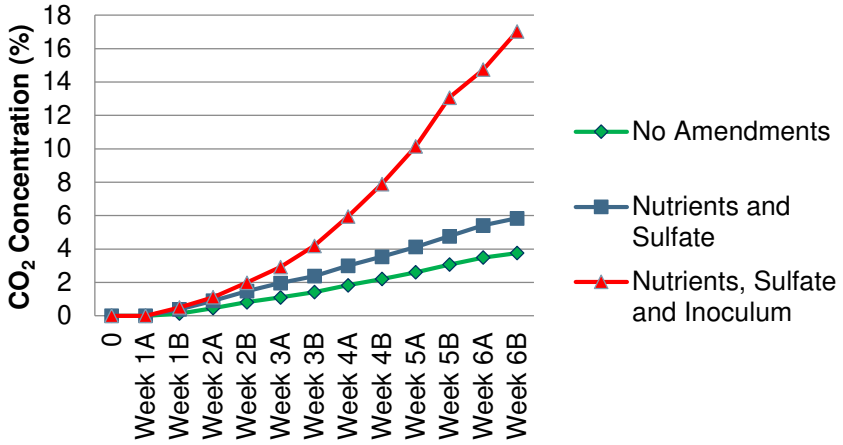




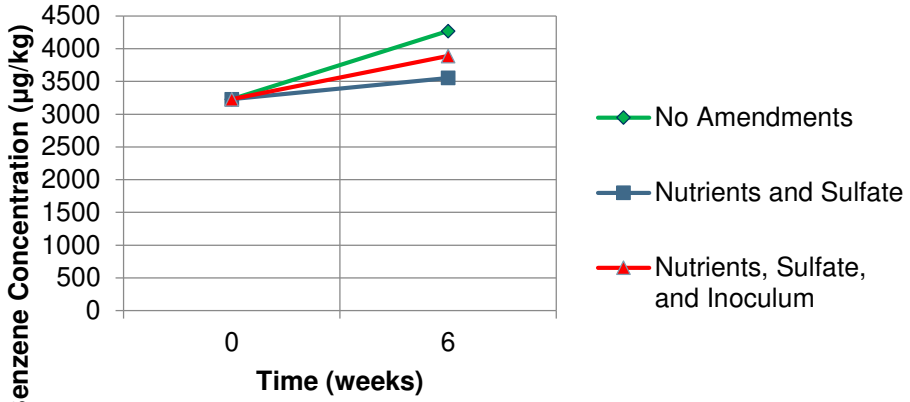


MW-2 Soil Anaerobic Conditions

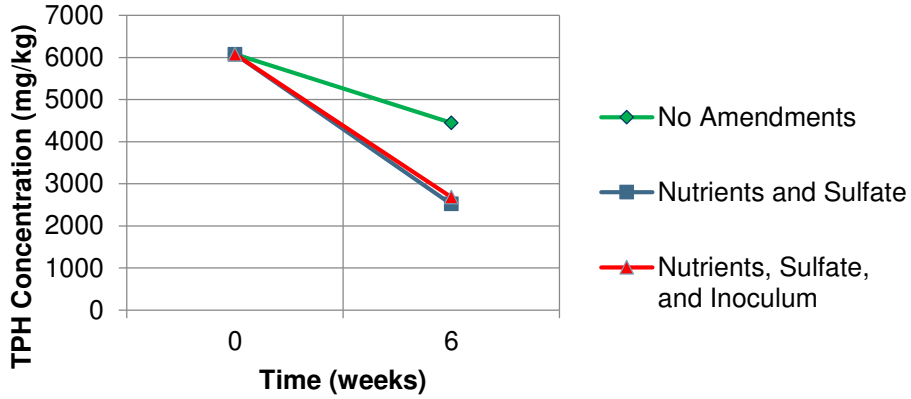
MW-2 Soil only Anaerobic Biostudy Headspace Analysis



MW-2 Soil Only Anaerobic Biostudy Benzene Analysis

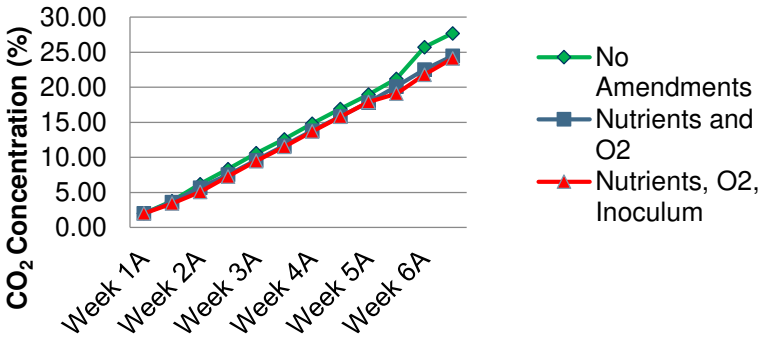


MW-2 Soil Only Anaerobic Biostudy TPH Analysis

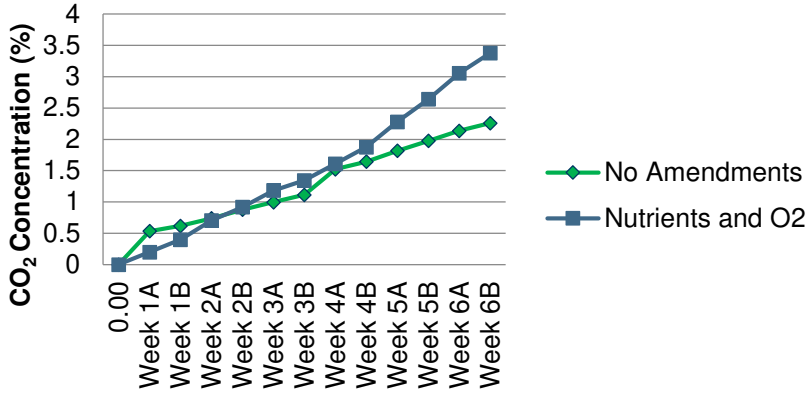


MW-1 Respirometry

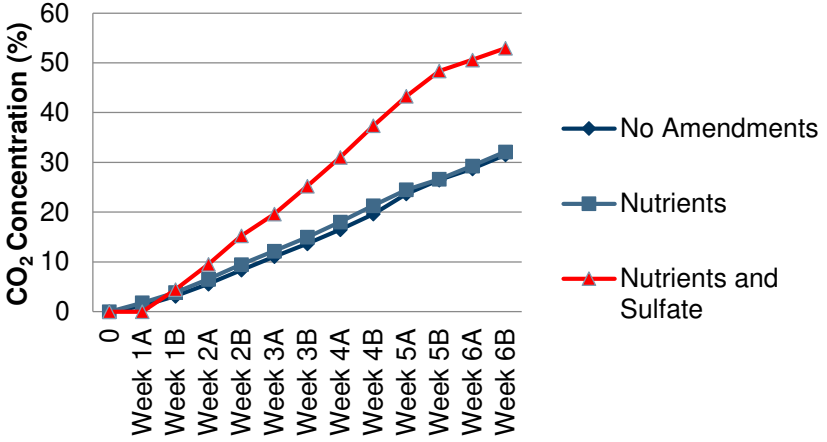
MW-1 GW and Soil Aerobic Biostudy Headspace Analysis



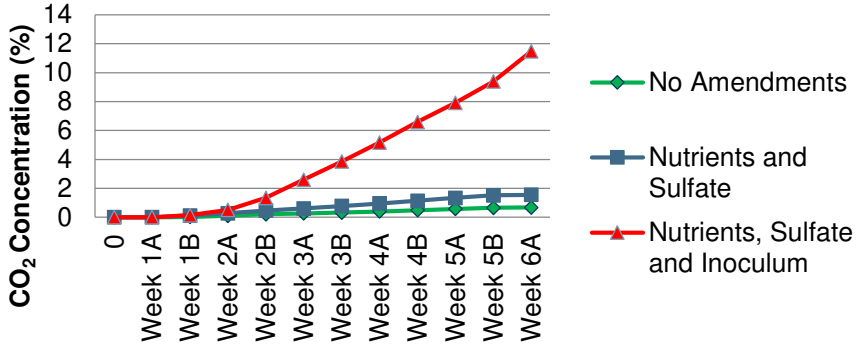
MW-1 Soil Only Aerobic Biostudy Headspace Analysis



MW-1 GW and Soil Anaerobic Biostudy Headspace Analysis



MW-1 Soil Only Anaerobic Biotudy Headspace Analysis



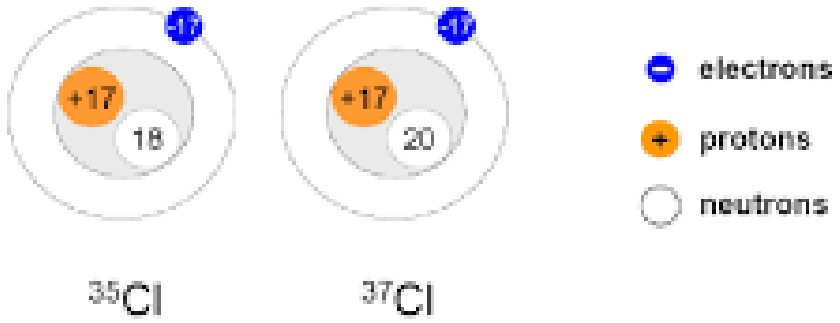
Preliminary Conclusions from Laboratory Tests

- Natural attenuation is occurring in the microcosms
- Rate of biodegradation can be enhanced by the addition of amendments
- Enhanced aerobic biodegradation was an effective treatment for stimulating the biodegradation of benzene and TPH in the microcosm tests
- The natural microbial population is capable of significant degradation with oxygen is added
- Biodegradation of benzene was not observed under enhanced anaerobic conditions but biodegradation of TPH was observed
- The addition of sulfate raised soil respiration rates

Compound Specific Isotope Analysis

Stable isotope = not radio active

Number of electrons	→ same
Number of protons	→ same
Number of neutrons	→ different
Mass	→ different



- Many elements have naturally occurring stable isotopes
- Examples of these include ^{13}C, ^{18}O, ^{37}Cl, ^{2}H, and ^{15}N.
- The ratio between the different isotopes can differ depending on the source of the material.
- In biological systems the lighter isotope is used preferentially to the heavier isotope therefore where biodegradation is occurring, undegraded materials have a higher concentration of the heavier isotope since the lighter isotopes have been degraded.
- The ratio between the heavier and lighter isotope is expressed as a delta value (δ).
- The δ value is calculated according to the following equation:

$$\delta(‰) = (R(sample)/R(standard)-1)X1000$$

R= ratio of heavy to light isotope

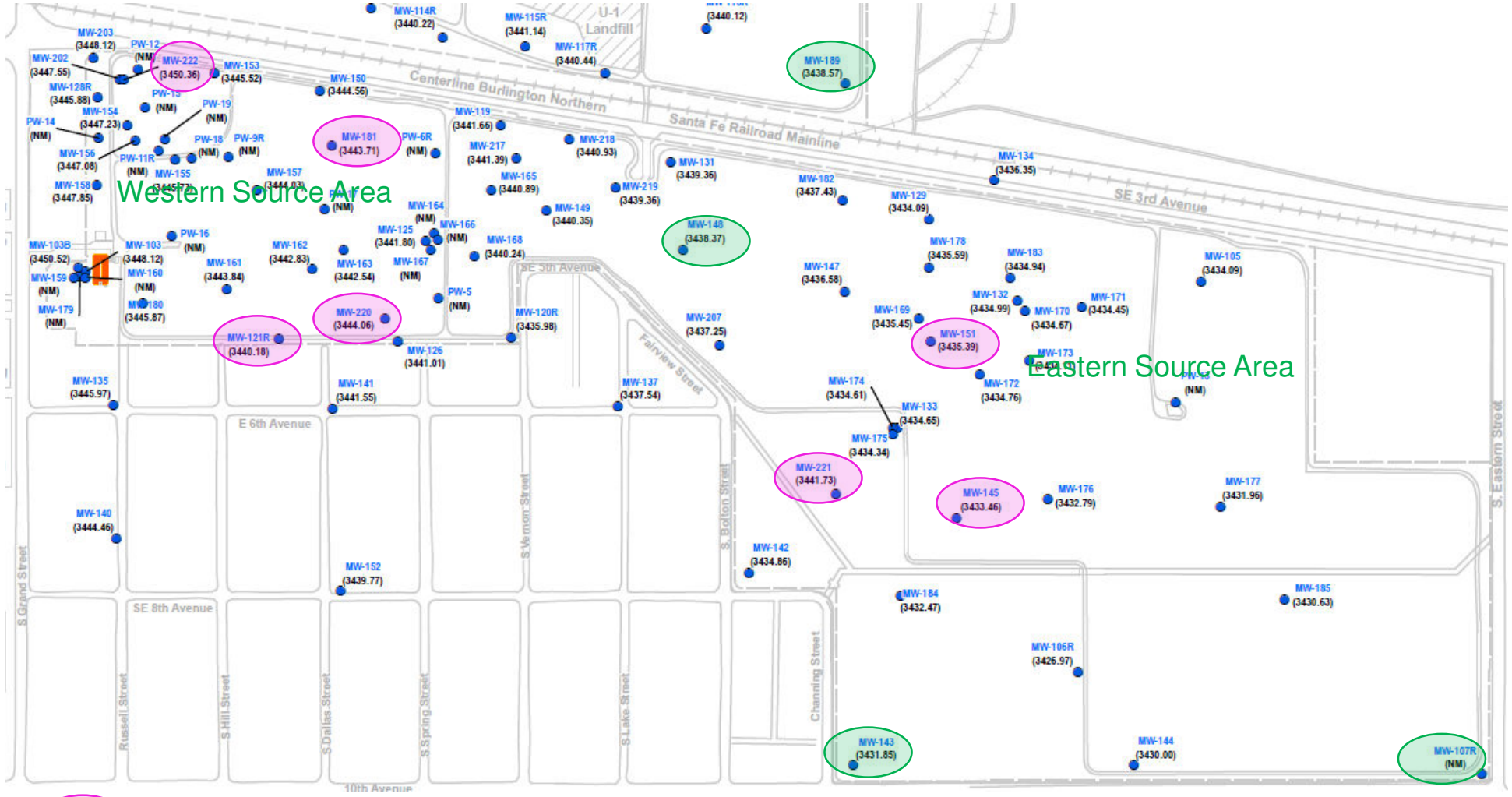
- Carbon has two naturally occurring stable isotopes: ^{12}C and ^{13}C.
- Hydrogen also has two naturally occurring stable isotopes: ^{1}H and ^{2}H.

Samples for CSIA

Well	Location
MW-121R	~500 feet south of Western Source Area
MW-145	~800 feet south of Eastern Source Area
MW-151	In Eastern Source Area
MW-181	In Western Source Area
MW-107R*	Outside the dissolved plume at the southeastern Site boundary
MW-143*	Outside the dissolved plume south of the Eastern Source Area
MW-148*	Between the two source areas
MW-189*	Outside the dissolved plume northwest of the Eastern Source Area
MW-220	~100 feet south of the Western Source Area
MW-221	~200 feet southwest of the Eastern Source Area
MW-222	In Western Source Area

*CSIA analysis not performed because of low benzene concentration

CSIA Well Locations



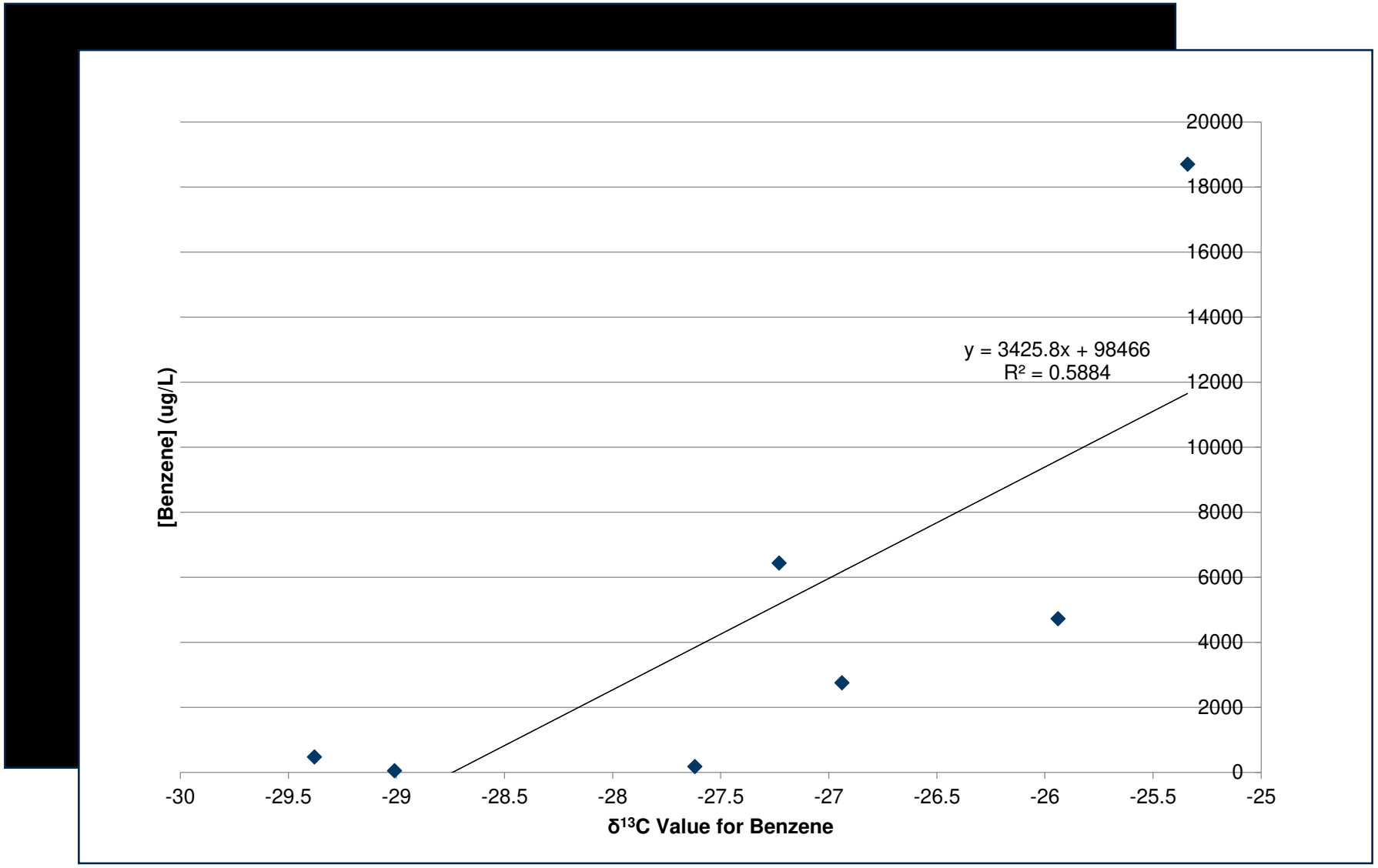
Location with sufficient benzene for CSIA

Location with insufficient benzene for CSIA

Samples for CSIA

Parameter	Units	Standard	MW-145	MW-121R	MW-181	MW-151	MW-220	MW-221	MW-222
Benzene	µg/L		2760	56.1	4730	18700	483	188	6440
$\delta^{13}C$ values	‰	−26.6‰	-26.94	-29.01	-25.94	-25.34	-29.38	-27.62	-27.23
$\delta^{2}H$ values	‰	−77‰	-108.43	-171.34	-118.70	-121.27	-120.94	-170.72	-96.42

Benzene $\delta^{13}C$ Values Versus Benzene Concentration

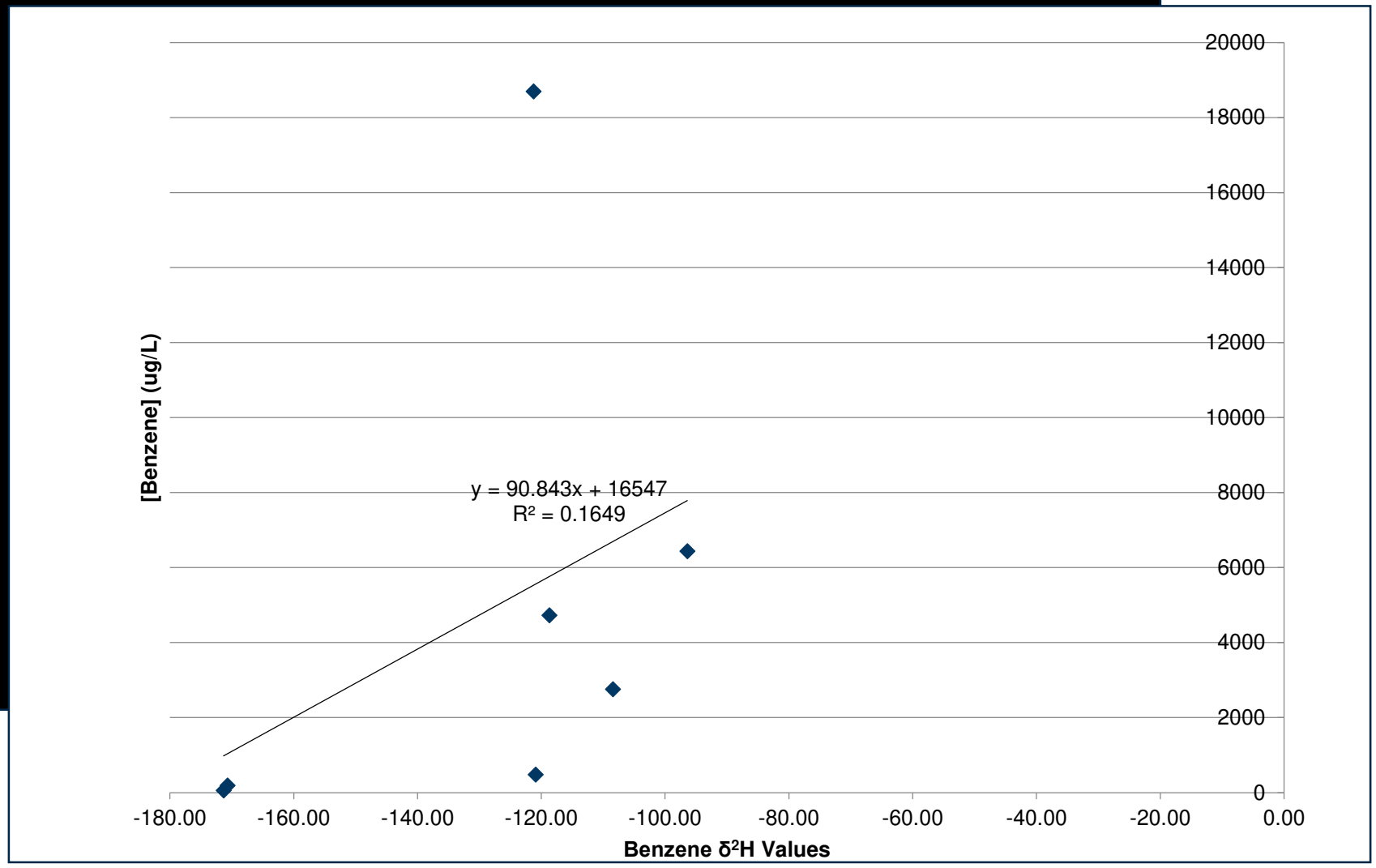


Relationship Statistically Significant $p<0.05$

Statistically Significant Relationship Between Benzene Concentration and $\delta^{13}C$

- Regression analysis showed that source area wells were slightly enriched in the heavier isotope compared to the downgradient wells
- Suggests that some biodegradation of benzene has occurred in the source area
- Little evidence of biodegradation in the downgradient wells suggests that lower concentrations of benzene in downgradient wells is due to dilution rather than biodegradation

Benzene δ^2H Values Versus Benzene Concentration

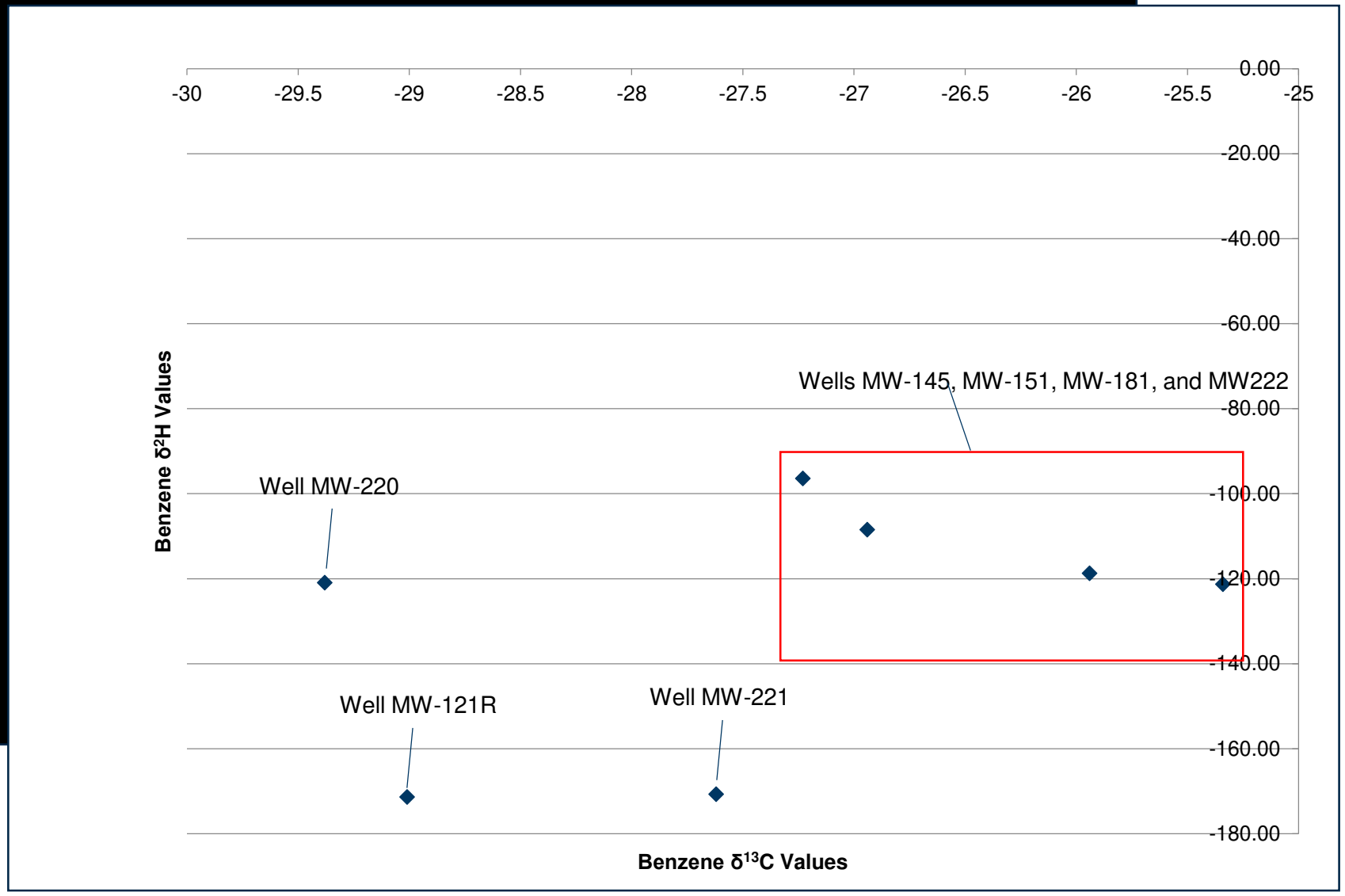


Relationship Not Statistically Significant

No Statistically Significant Relationship Between Benzene Concentration and δ^2H

- The observation that the hydrogen isotope data did not show a pattern consistent with the carbon isotope data suggests that biodegradation is primarily occurring through the breakage of carbon-carbon bonds rather than carbon-hydrogen bonds.
- This is consistent with the known benzene biodegradation pathway.

Benzene $\delta^{13}C$ Values Versus Benzene $\delta^{2}H$ Values



Benzene $\delta^{13}C$ Values Versus Benzene $\delta^{2}H$ Values

- The ratios for the samples from wells MW-145, MW-181 MW-151, and MW-222 appear to cluster together, while the sample from wells MW-121R, MW-221, and MW-220 do not occur within this cluster.
- The benzene concentration in these samples is at least an order of magnitude lower than the other samples, which may affect the isotope ratios.

Summary from CSIA Testing

- Samples with the higher benzene concentrations had higher $\delta^{13}C$ values suggesting that some biodegradation is occurring at a low rate in the source areas but that there is little biodegradation occurring outside the source areas.
- No relationship between $\delta^{2}H$ values and benzene concentration was observed, suggesting that biodegradation is primarily occurring through the breakage of carbon-carbon bonds rather than carbon-hydrogen bonds.
- When $\delta^{13}C$ were plotted versus $\delta^{2}H$, the ratios for the samples from the wells with higher concentrations of benzene in the groundwater clustered together, while wells with lower benzene concentrations are located outside the cluster.

→ Conclusions

- The data suggests that natural attenuation would occur at the site over time however rates would be slow and an extended time period would be required for treatment by natural attenuation
- Enhanced biodegradation of benzene and TPH was observed in the microcosms under both aerobic and anaerobic conditions
- More biodegradation of benzene and TPH was observed under aerobic conditions
- The data from the CSIA analysis and the microcosms shows that it is likely that natural attenuation is occurring at the site