

Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA): Example and Planned Development

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Natural Attenuation Methods

- Current ASTM and AFCEE protocols measure only dissolved phase electron acceptors
 - Can identify certain microbial redox processes
 - Difficult to quantitatively estimate biodegradation
- Site is then “modeled” to estimate contaminant fate (questionable accuracy)
- A long-term monitoring program is instigated
- Contaminant decay is determined in monitoring phase
 - Why do the attenuation study?

AMIBA

- Aqueous and Mineral Intrinsic Bioremediation Assessment is more accurate
 - mineral (sediment) **and** groundwater is analyzed
- A single assessment can:
 - Accurately determine redox zones
 - Estimate natural attenuation efficiency
 - Demonstrate plume retreat (plume footprint)
 - Estimate total contaminant decay rate
 - Provide more accurate data for modeling
 - Give important complimentary data for RBCA and remediation design

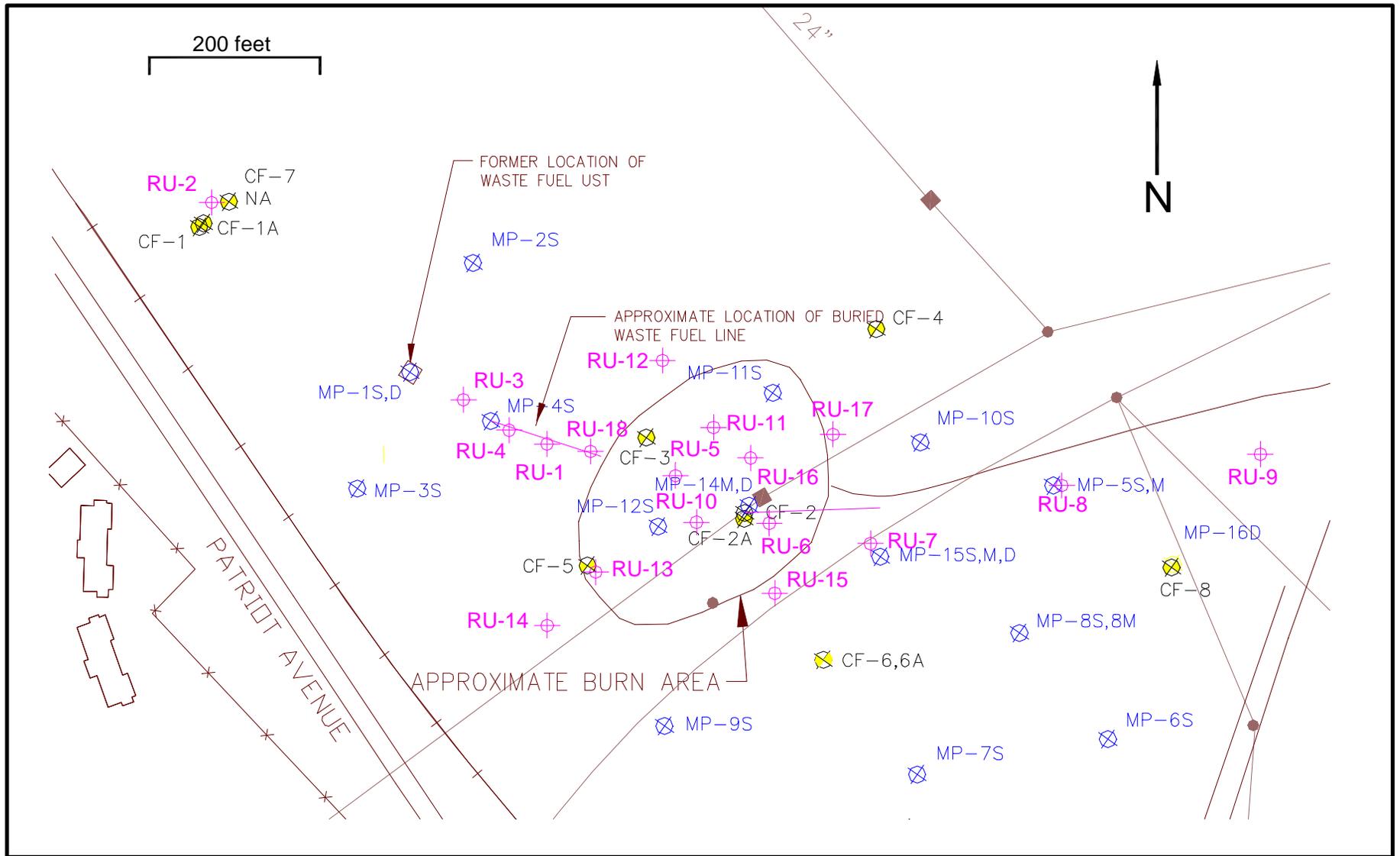
Why AMIBA Works

- In most cases, Fe^{3+} and SO_4^{2-} constitute the largest electron acceptor pool
 - 10 to 1000 times more than O_2 or NO_3^-
- Fe^{3+} and SO_4^{2-} reduction makes reduced **mineral** species (FeCO_3 , FeS , FeS_2, \dots)
 - in stoichiometric proportion to organic contaminant destroyed
- O_2 and NO_3^- expressed capacity can be estimated by “Sulfate Indexing”
 - Uses S expressed capacity and background $\text{O}_2:\text{SO}_4^{2-}$ and $\text{NO}_3^-:\text{SO}_4^{2-}$ ratios

Westover Air Reserve Base, MA

Fire Training Site: Fuel + Chlorinated Solvents





UST, burn pit, and soil boring/monitoring well locations.
 Current set of soil borings shown in red with the designation RU.
 Considerable effort expended at site prior to this investigation.

Conclusions from Aqueous-only Study

- All redox processes operational, fuel is degrading
- Most oxidation is from SO_4 , O_2 , and NO_3^- microbial reduction (incorrect)
- Fe contribution is slight and not important (incorrect)

AMIBA Sampling

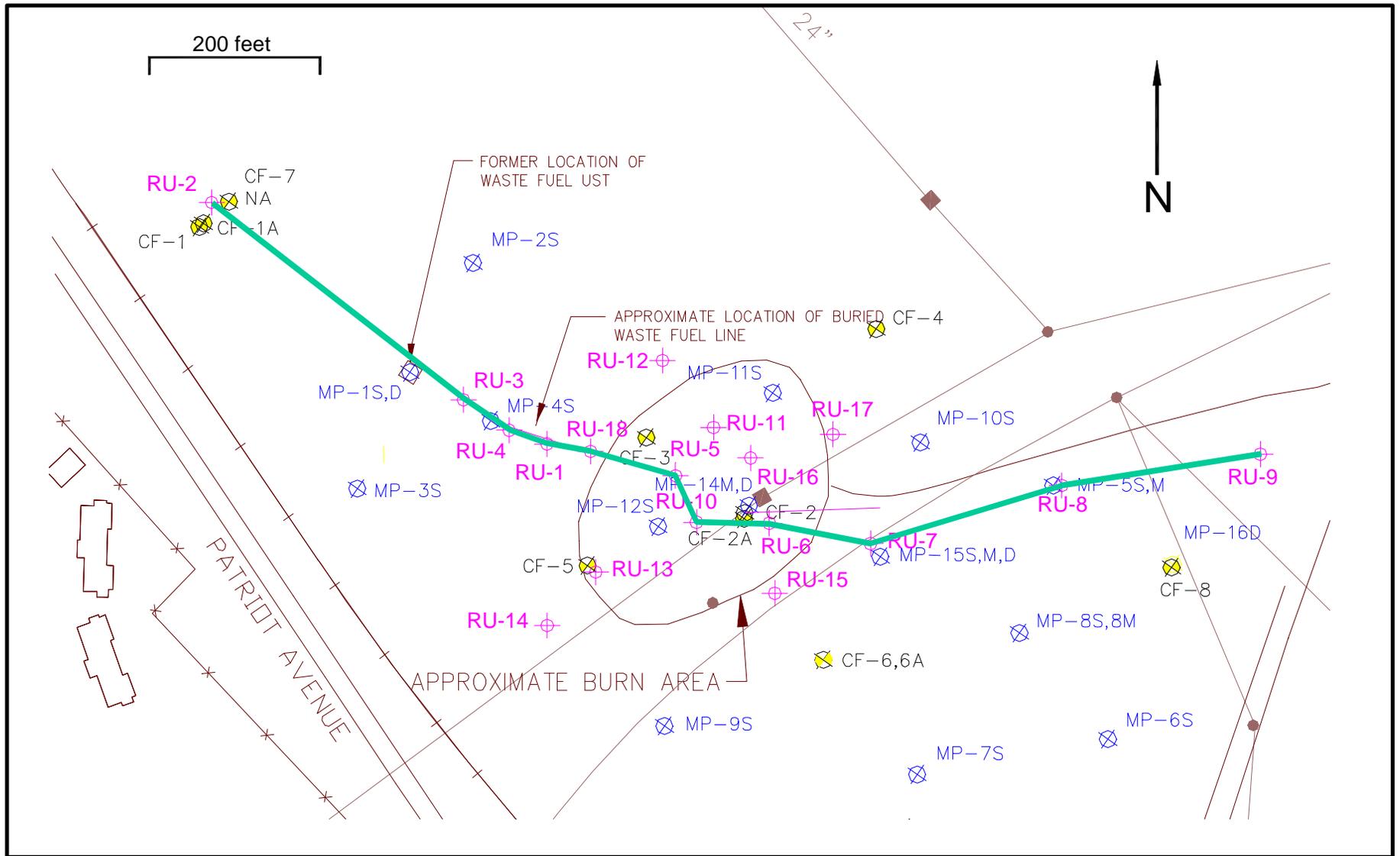
- 200 Soil samples
 - Pore water anions/ Fe^{2+}
 - Reactive mineral Fe^{2+}
 - Reactive mineral Fe Total
 - Sulfides (FeS & FeS_2)
- 130 Soil
 - EPA 8260 - fuels, chlorinated solvents,...
- 11 Groundwater
 - EPA 8260



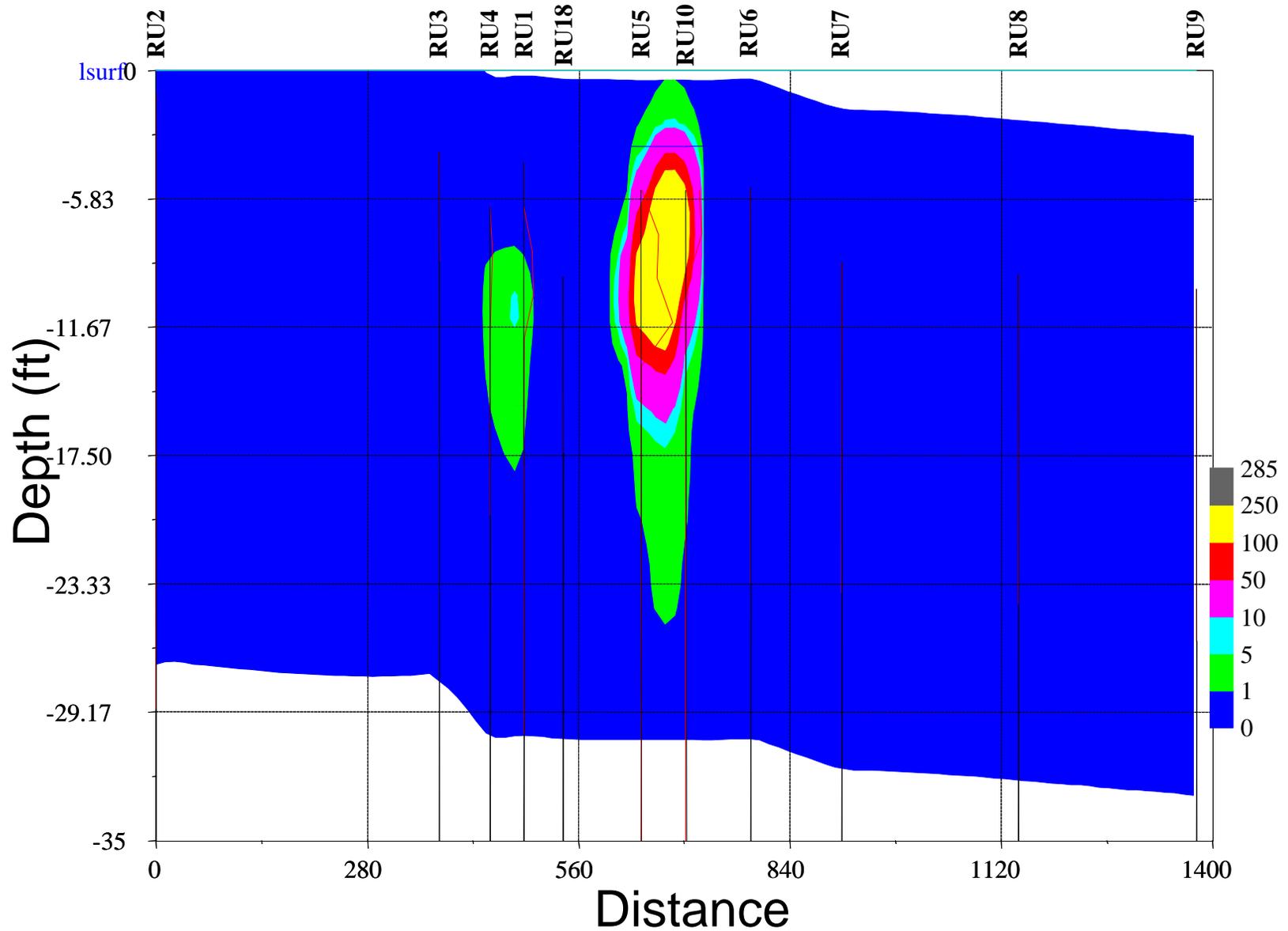
AMIBA METHODS

- Sediment samples collected / preserved in the field using simple, rapid, inexpensive method
- O_2 measured in monitoring wells
- Aqueous SO_4^{2-} , NO_3^- , Fe^{2+} measured from sediment pore water (not monitoring wells)
- Reactive Mineral Fe^{2+} and Fe total, S from FeS and FeS_2 measured using simple HCl and Cr^{2+} extractions

AMIBA Observed Data Analysis



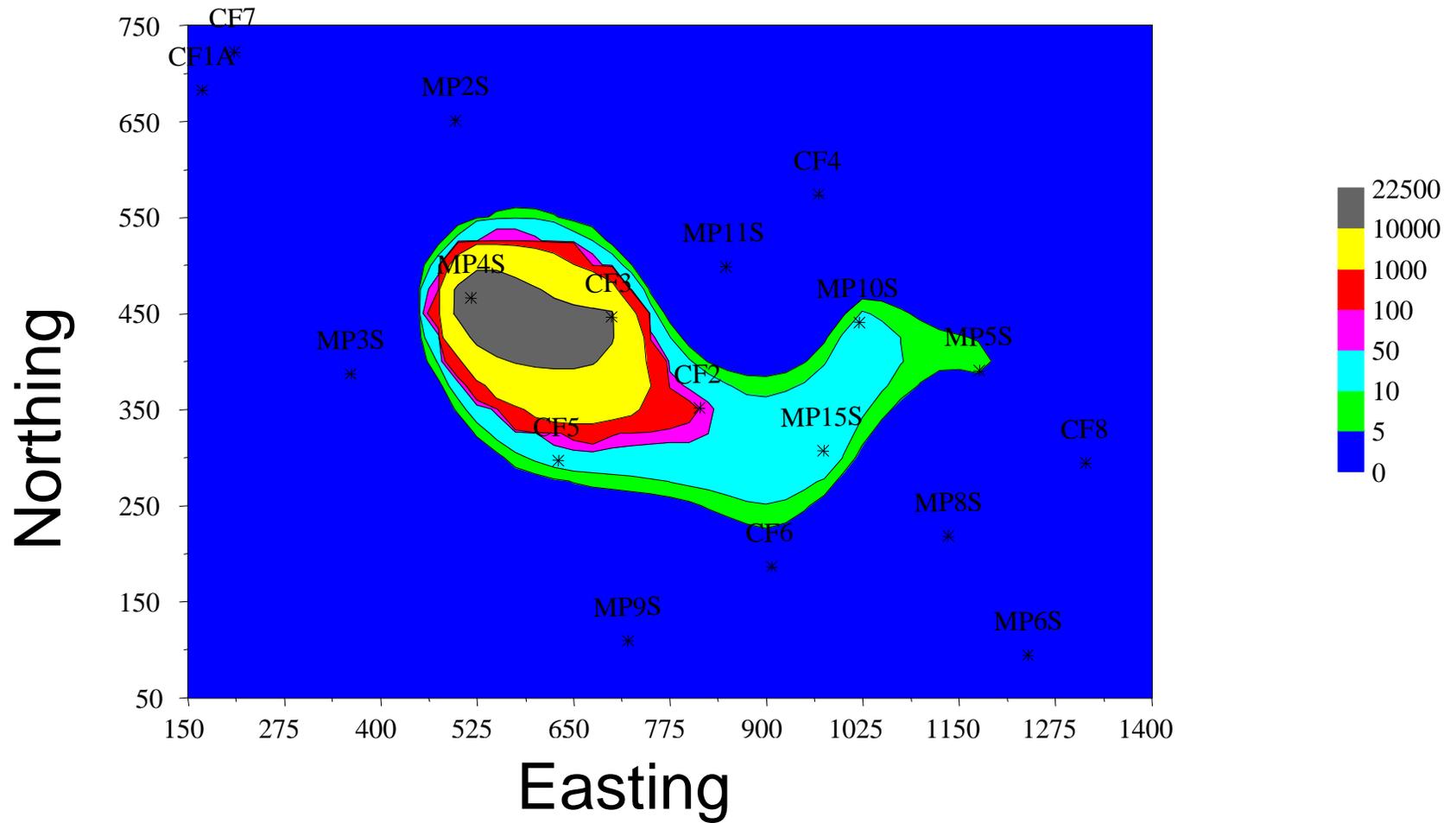
Line shows cross-sections used in many of the subsequent figures.



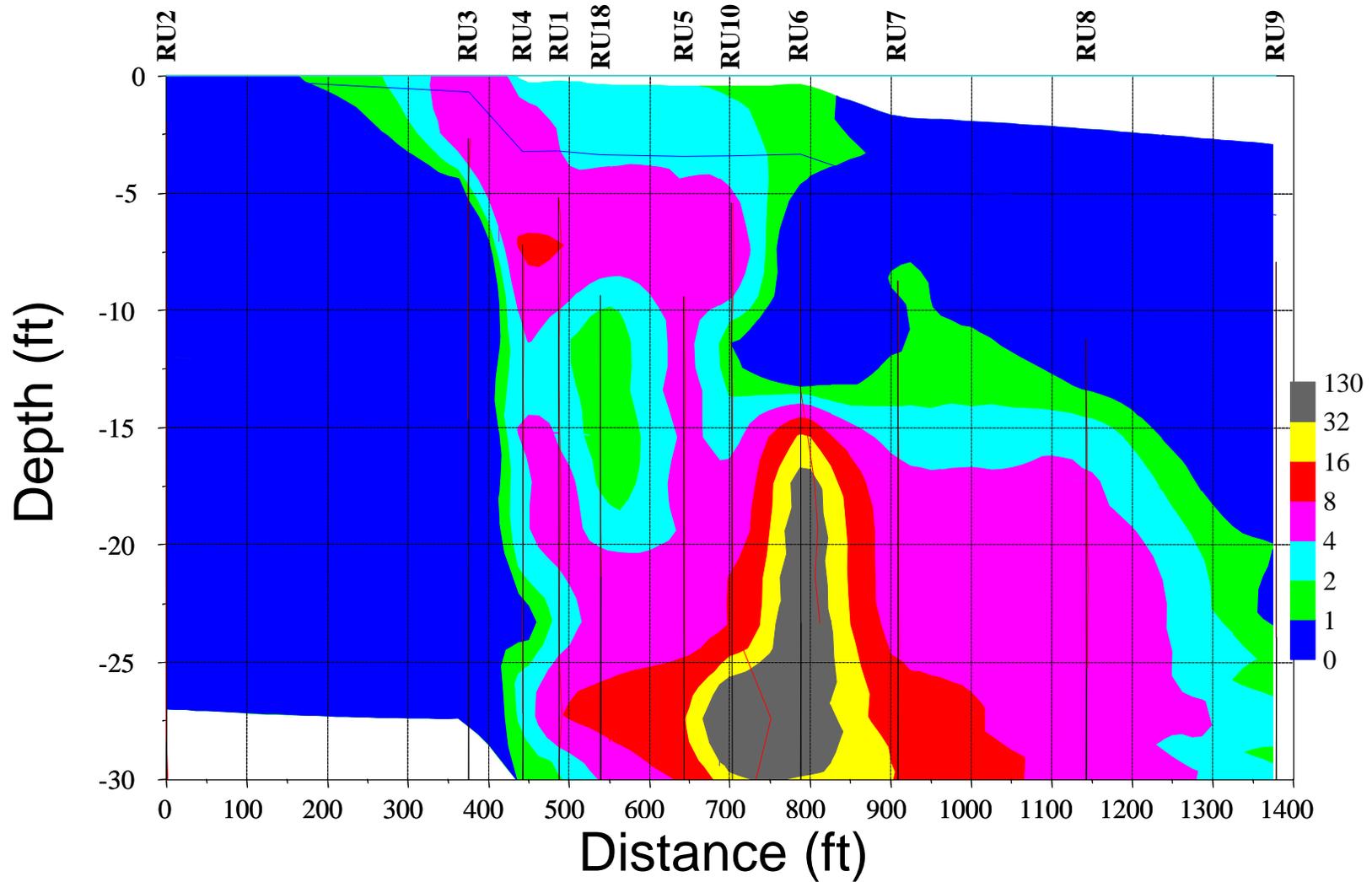
Soil BTEX (mg/Kg): Source of BTEX located around the UST and burn pit.

See 3D

Dissolved BTEX (ug/L)

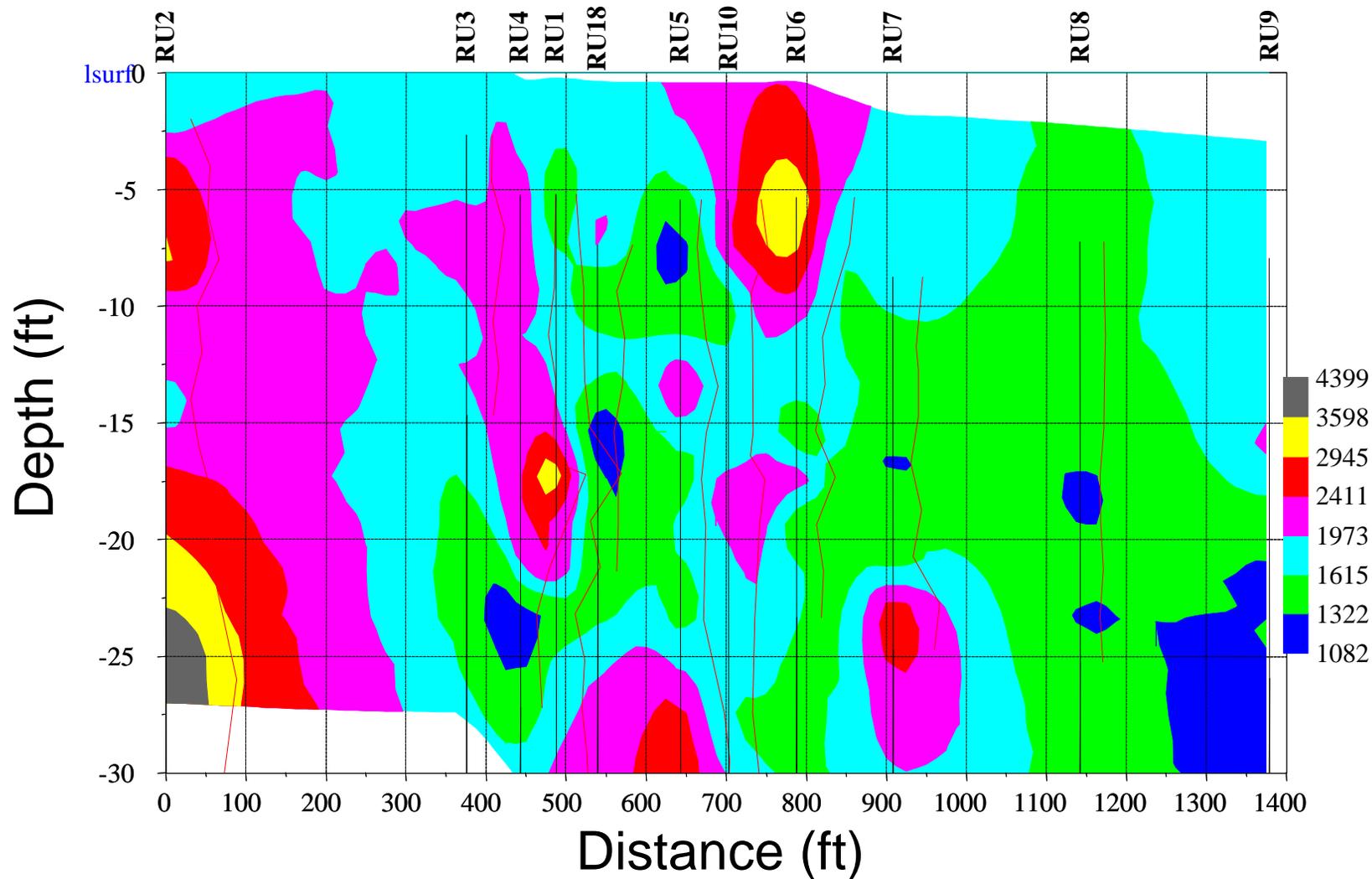


Dissolved BTEX plume extends far down-gradient from the source area .



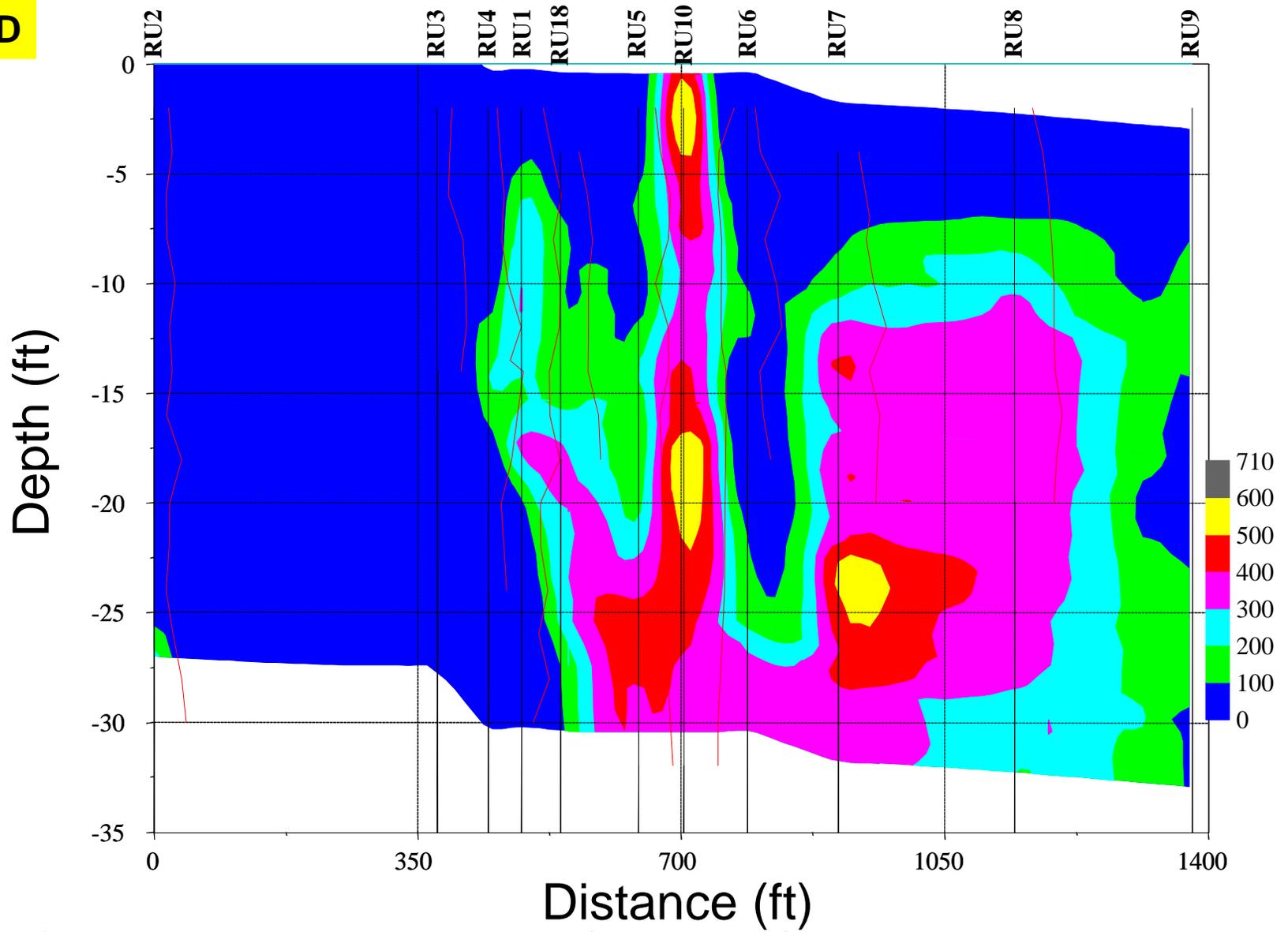
Pore Water Fe^{2+} (mg/L): Shows downward contaminant migration. Demonstrates Fe^{3+} reduction is ongoing but can't quantify amount.

See 3D

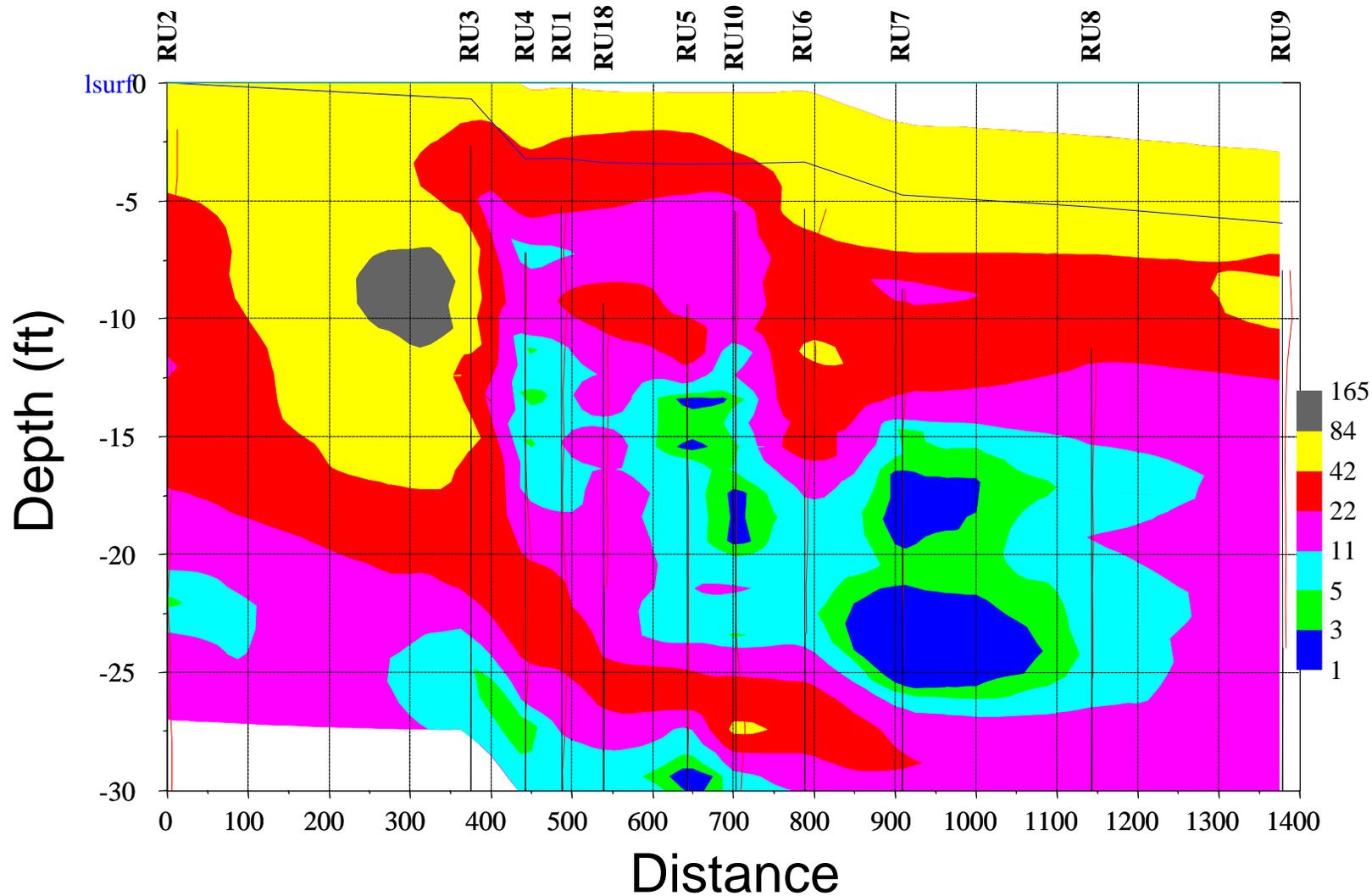


Reactive Mineral Fe Total (mg/Kg): Shows depositional pattern, little influence by contaminant/microbial processes.

See 3D

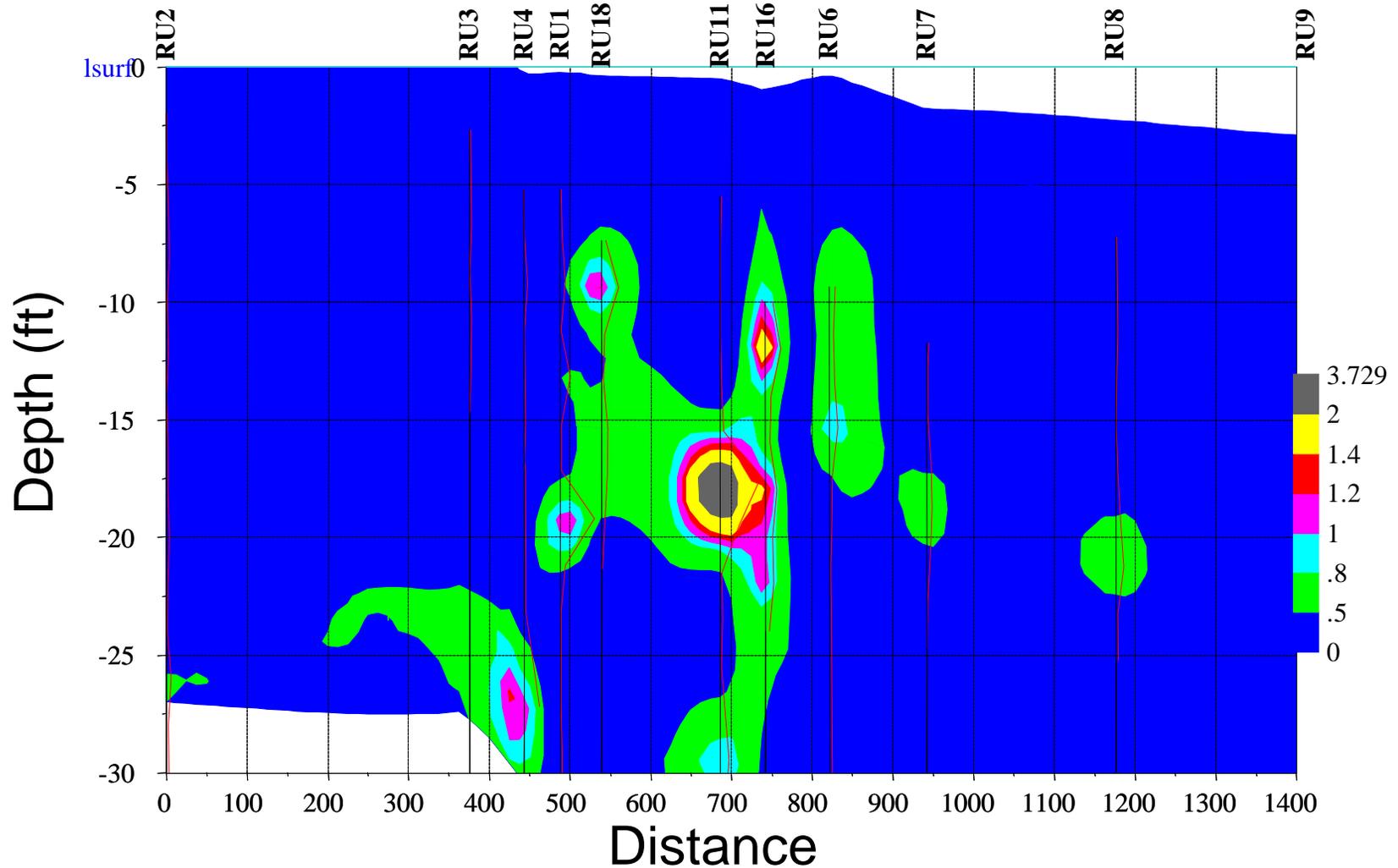


Bio Fe²⁺ (mg/Kg): Reactive Mineral Fe²⁺ where Fe²⁺ is > 50% of Fe Total.
Identifies Fe²⁺ from primary biological / secondary abiotic processes.

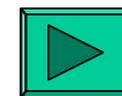


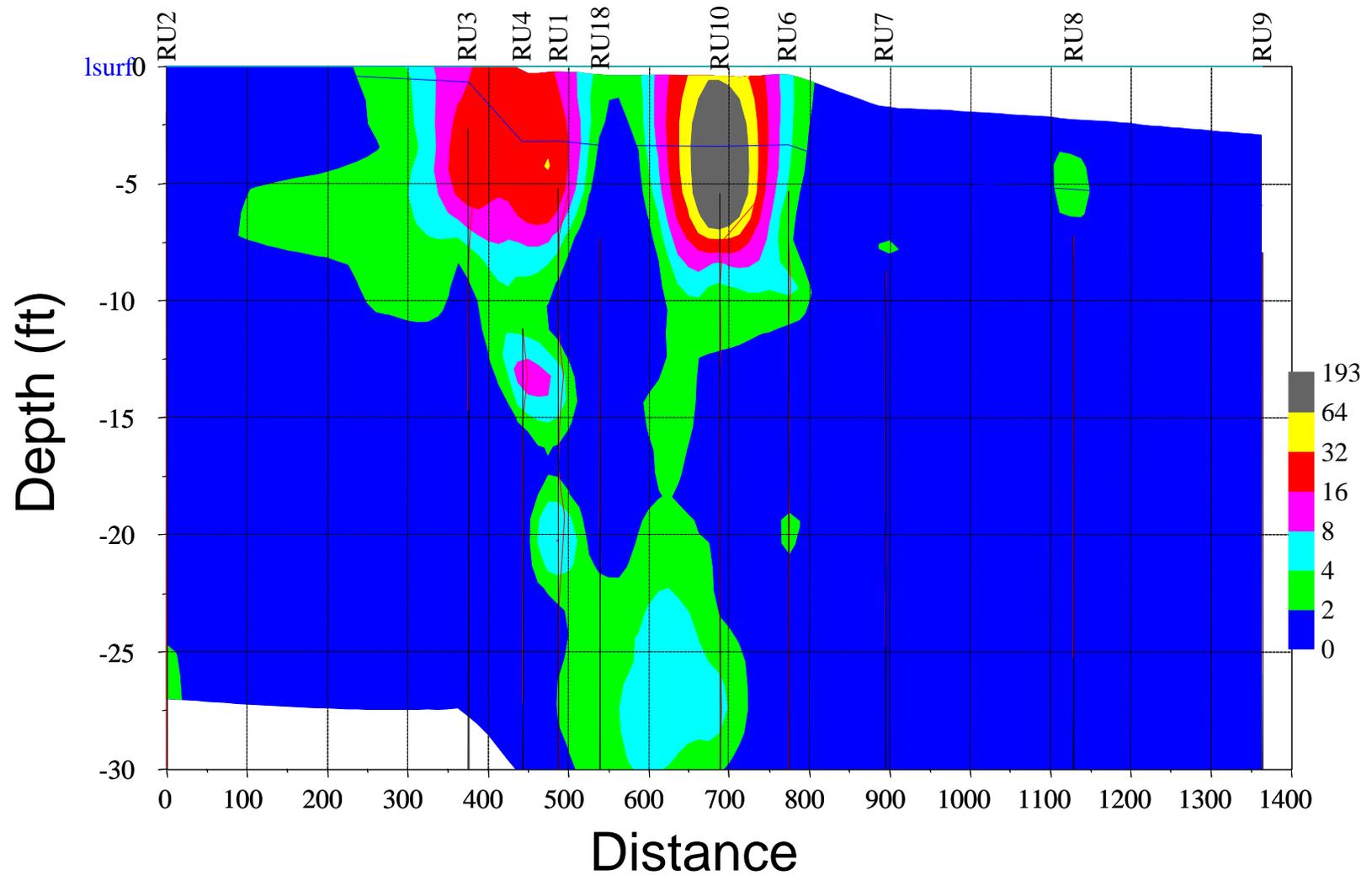
Pore Water Sulfate (mg/L): Shows significant depletion of SO_4^{2-} in the plume area.

Go to Slice



Mineral S from FeS (mg/Kg): FeS concentrations are slight indicating a relatively old plume where most iron sulfides are expressed as FeS₂.





Mineral S from FeS_2 (mg/Kg): FeS_2 concentrations are greater than FeS and distributed near the up gradient edge of the plume.



Natural Attenuation Analysis

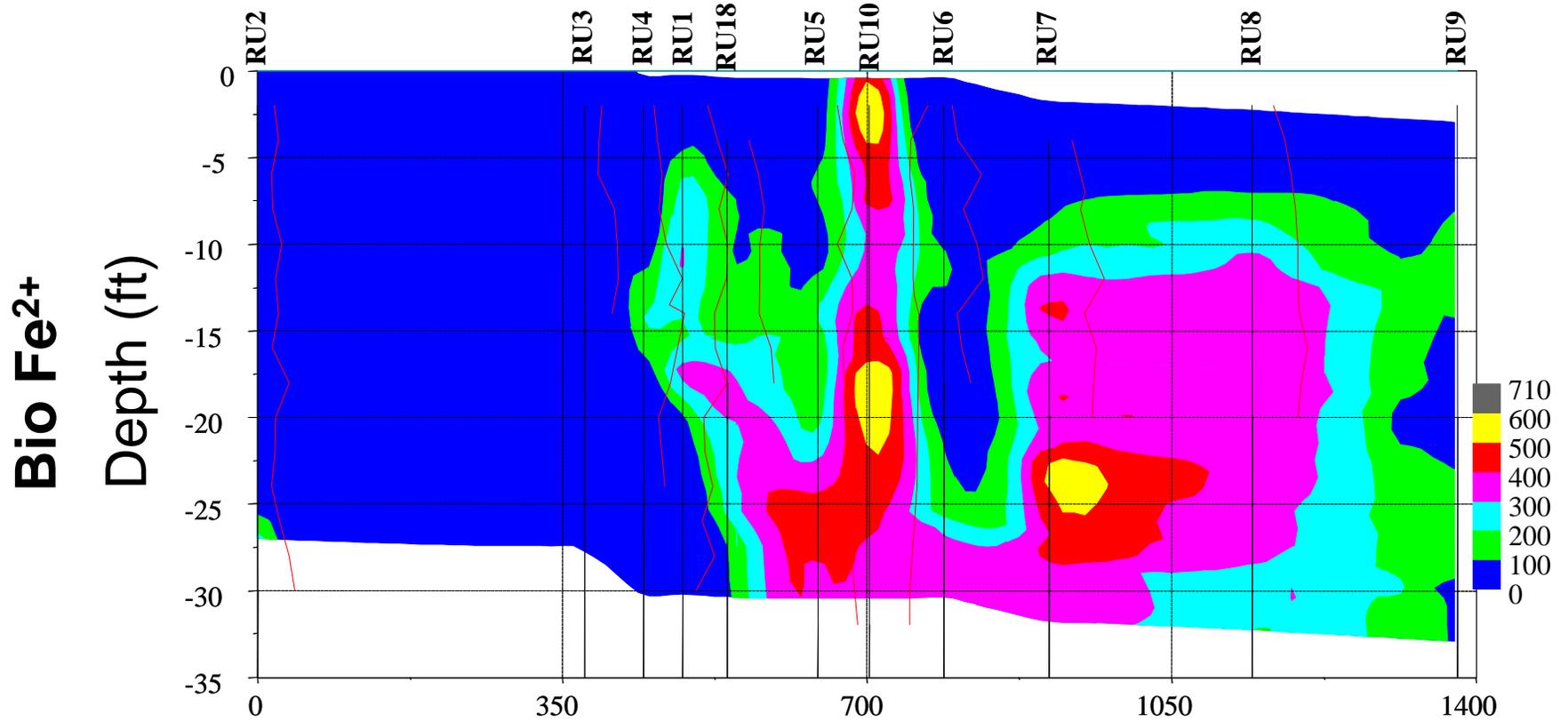
Natural Attenuation Analysis

***Iron Footprint**

Is plume retreating?

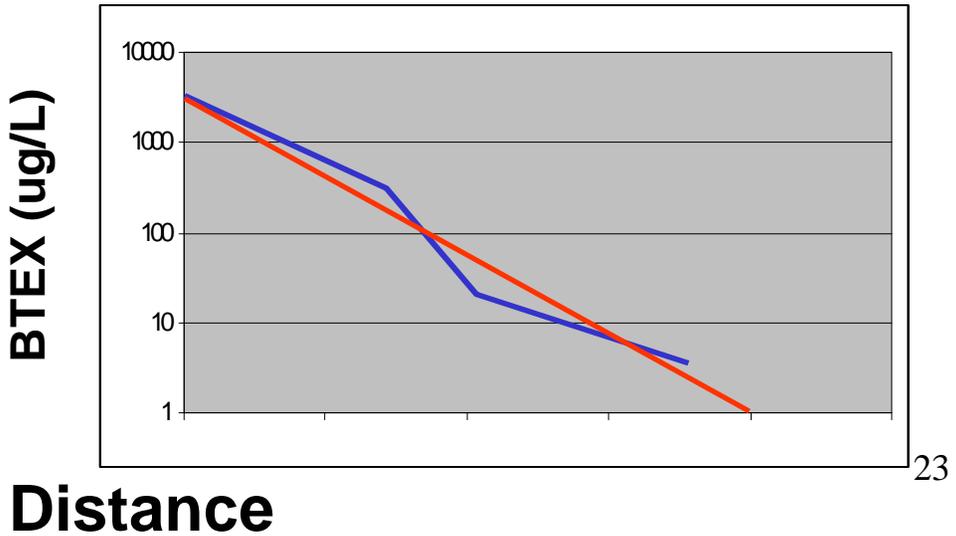
Iron footprint

- Qualitatively evaluates past plume position
 - compare spatial distribution of elevated reactive mineral Fe^{2+} and current hydrocarbon plume.
- Plume retreat indicated if Fe^{2+} distribution is much greater than hydrocarbon area.



— Measured
BTEX

— BTEX
Trend



Natural Attenuation Analysis

*Iron Footprint

***Expressed Capacity**

**How much contaminant has
been degraded?**

Expressed Capacity: ASTM / AFCEE

- Measure aqueous electron acceptors consumed (O_2 , NO_3 , SO_4) and aqueous Fe^{2+} produced. Compare background to plume concentrations. Relate stoichiometrically to contaminant.
- Problem: Only a small fraction of expressed capacity can be measured in ground water alone.

Expressed Capacity: AMIBA

- Measure deposition of S and Fe^{2+} and background concentrations of dissolved O_2 , NO_3 , SO_4
- Use sulfate indexing to estimate expressed capacity associated with O_2 and NO_3 .
- Advantage: more expressed capacity is measured (but still conservative).

Fuel Mass Analysis

Analyte	Moles Fuel Present
Soil BTEX	2,050
Water BTEX	345
Total BTEX	2395

Total Current Fuel Onsite Approximately = 72.7 gallons

Ratio of Dissolved BTEX to Soil BTEX = 1.7%

Fe Observations

- Mass Bio Fe²⁺ = 1,584,916 Mol
 - Moles from FeS = 567 Mol
 - Net Fe²⁺ after FeS = 1,584,348 Mol
 - Aqueous Fe²⁺ = 5,271 Mol
- Ratio of aqueous to mineral Fe²⁺:
 - $5,270 / 1,584,348 = 0.003$
 - Less than 1% Fe expressed capacity found in aqueous phase or **333 times more Fe in mineral than aqueous.**

S Observations

- S from FeS = 568 Mol
 - S from FeS₂ = 18,537 Mol
 - S from SO₄ = 8,060 Mol
- Percent FeS to FeS₂ = 3.0%. SO₄ reduction sites may be old and iron deficient.
 - Percent S from SO₄ to mineral S = 40%
 - 2.5 times as much expressed S in mineral form as aqueous.

Stoichiometry (Toluene)

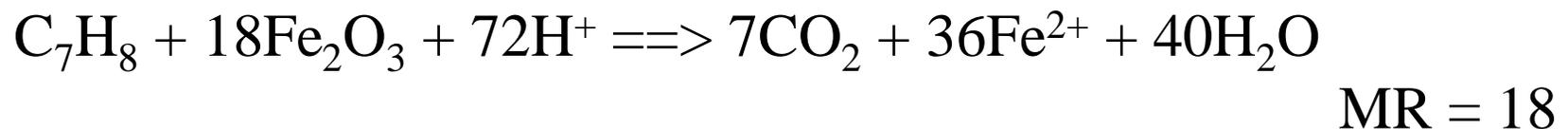
Oxygen:



Nitrate Reduction:



Iron Reduction (Hematite)



Sulfate Reduction:

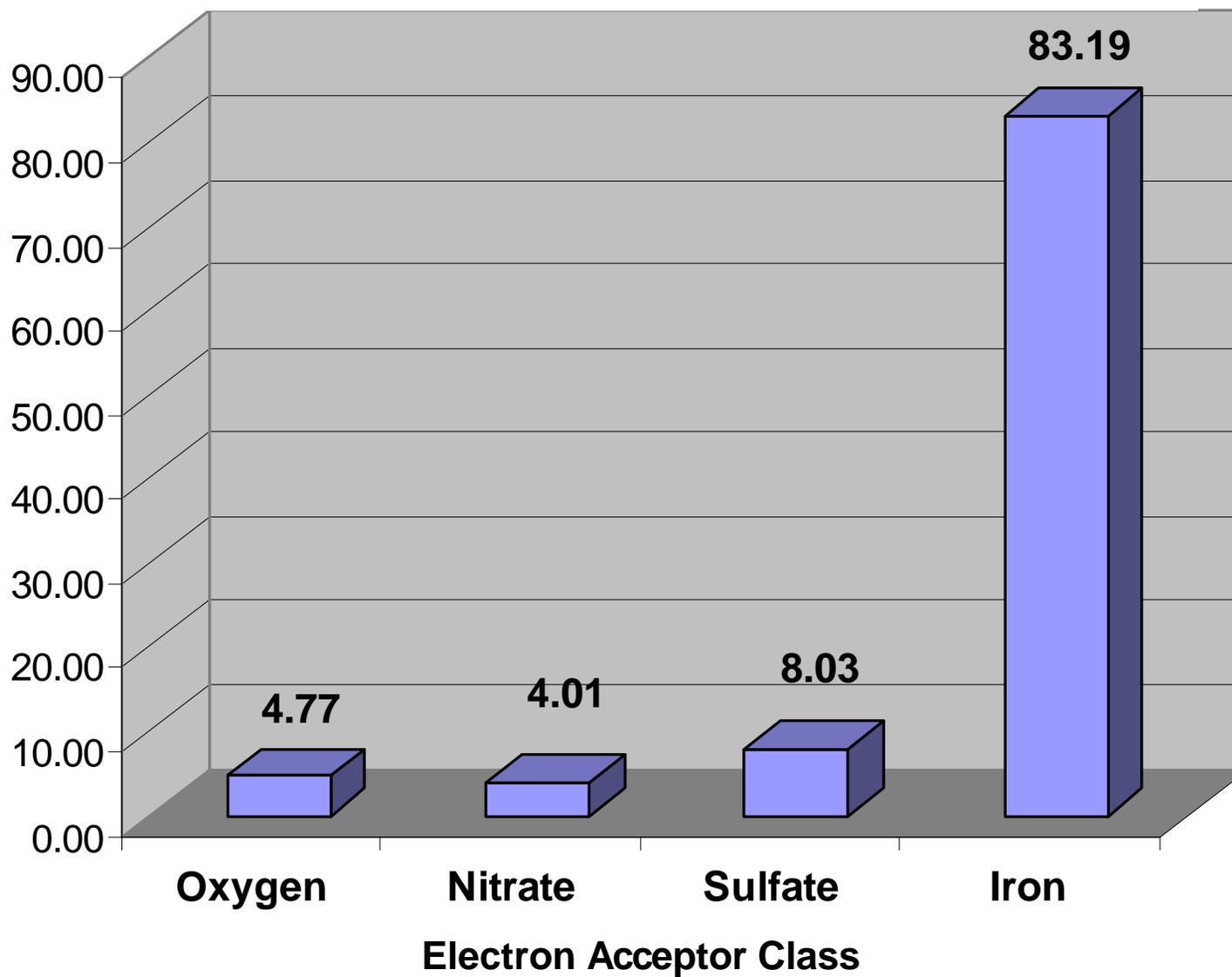


Expressed Capacity: AMIBA

Analyte	Moles Measured	Moles Fuel Oxidized
Net Fe ²⁺ (after AVS)	1,584,348	44,010
AVS	568	126
CrES	18,537	4,119
Sulfate Indexed Oxygen	22,735	2,526
Sulfate Indexed Nitrate	15,284	2,123
Total Fuel Attenuated		52,904

Percent Fuel Degradation by electron Acceptor Class

AMIBA



Expressed Capacity Index (ECI)

- Total expressed mass fuel = 52,904 Mol (1,607 gal)
- Current fuel mass = 2,084 Mol (73 gal)
- Total fuel mass = 54,988 Mol (1,680 gal)
- Contaminants at least **96% remediated** by intrinsic bioremediation

Natural Attenuation Analysis

*Iron Footprint

*Expressed Capacity

***Predictive Modeling**
Bioplume simulation

Modeling Results

- Time for natural attenuation alone:
 - 30 - 50 years
 - model results similar to simple first-order equation estimation
- Conclusion: site will naturally cleanup but may take too long.
- It is observed that:
 - Dissolved phase decays quickly
 - Source phase decays more slowly
- Examine source removal combined with natural attenuation of the dissolved phase as treatment option
 - With source removal, the site will be clean in 15 years

Conclusions

Intrinsic Bioremediation Assessment Using Mineral Fe and S Analysis:

- Improved estimate of expressed capacity by 13 times over aqueous only method.
 - Improved SO_4 analyses by factor of 2.5 and Fe analysis by 333 times.
- Demonstrated site 96% remediated by intrinsic bioremediation alone.
- Accurately determined redox zonation.

Intrinsic Bioremediation Assessment Using Mineral Fe and S Analysis:

- Fe footprint technique demonstrates that plume is retreating which:
 - - Defines compliance point boundaries
 - - Simplifies modeling to a retreating plume
 - - Automatically assures source decay is occurring
- Estimated source decay constant for computer or simple predictive analysis using ECI
- With modeling it is shown that the site will naturally attenuate in 30 to 50 years

Intrinsic Bioremediation Assessment Using Mineral Fe and S Analysis:

- Although cleanup can be assured the time duration may be too long
- Based on AMIBA, source removal is recommended
- Standard in-situ techniques of source treatment will be difficult due to reduced mineral mass
- Direct excavation is recommended with natural attenuation of dissolved phase in 15 years.

The Future: AMIBA-CAH

- AMIBA-CAH demonstration - 2001
- It has been demonstrated that elimination of VC is due predominantly to Fe^{3+} reducing bacteria
- Labile Fe^{3+} distribution will be evaluated to determine if VC will buildup in the environment during PCE/TCE degradation