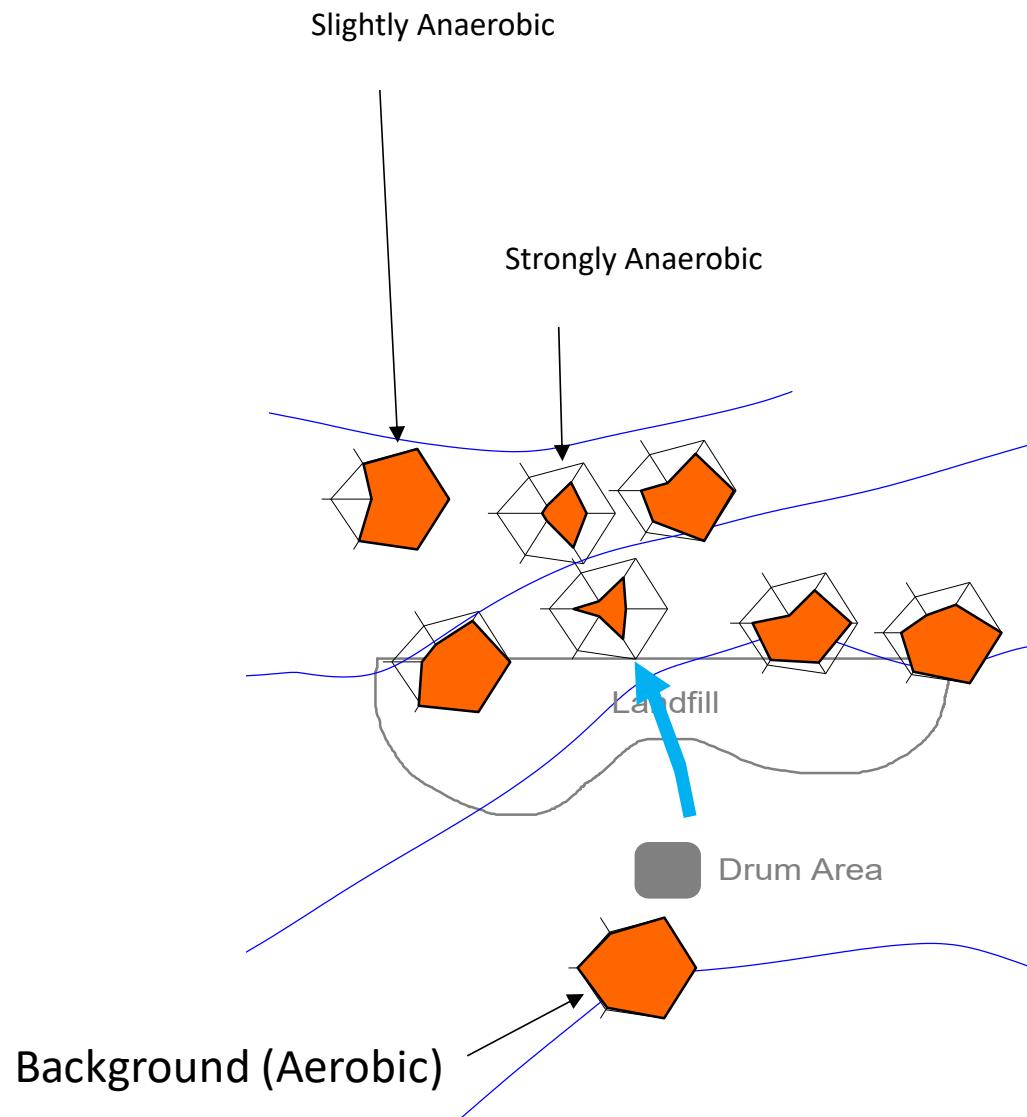


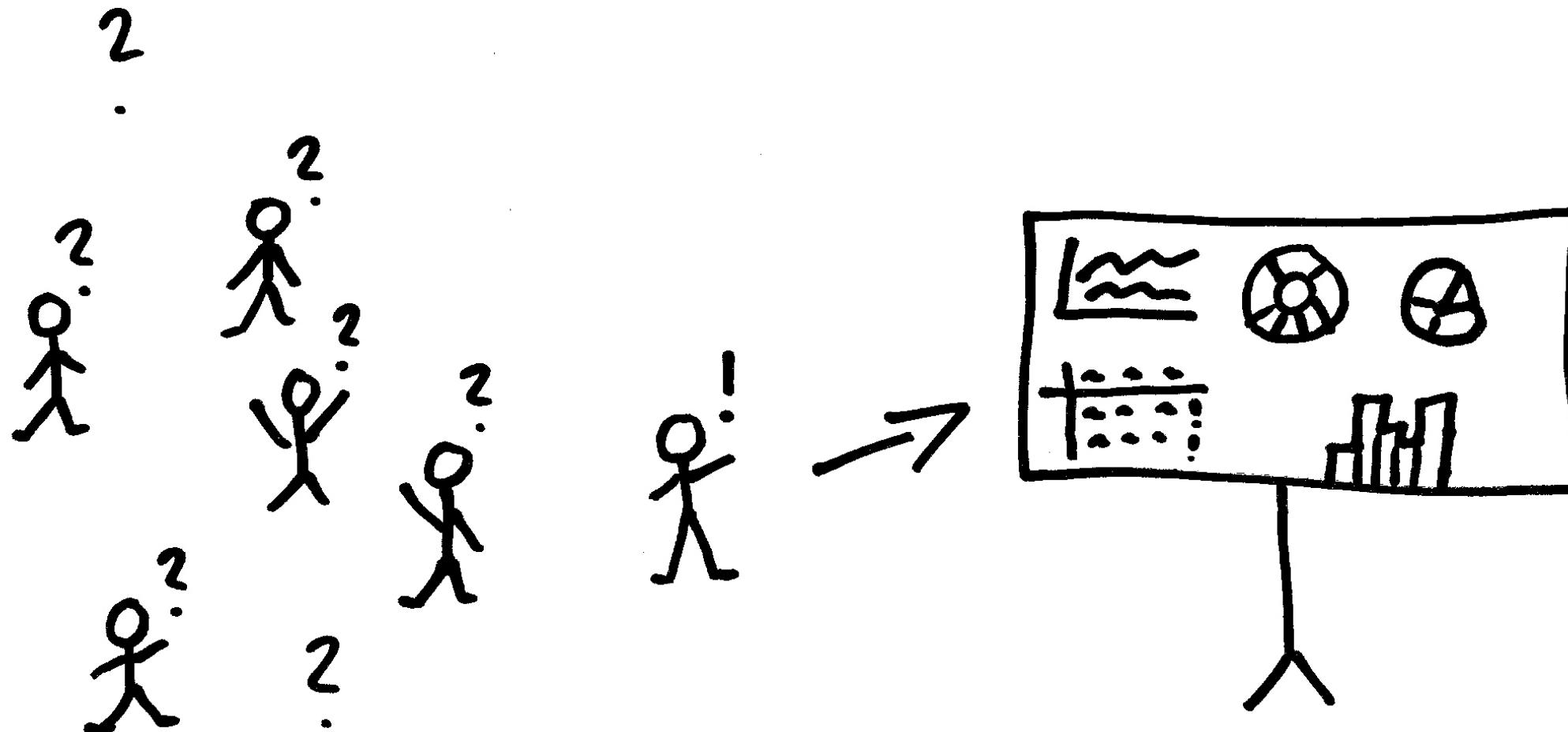
Visualizing Biodegradation Zones

By Grant R. Carey, Ph.D.

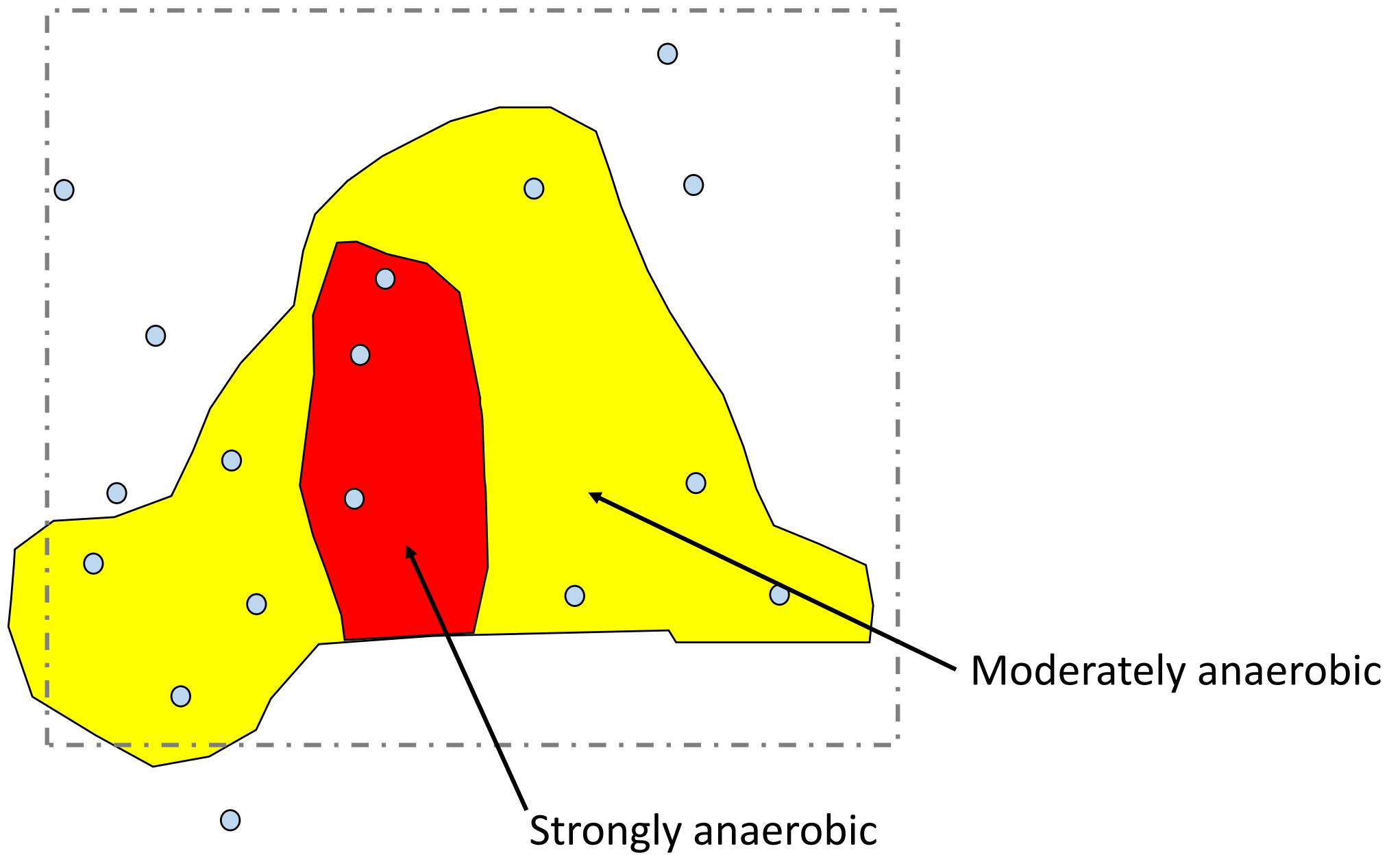


Main Challenge with MNA and EISB, or PFAS

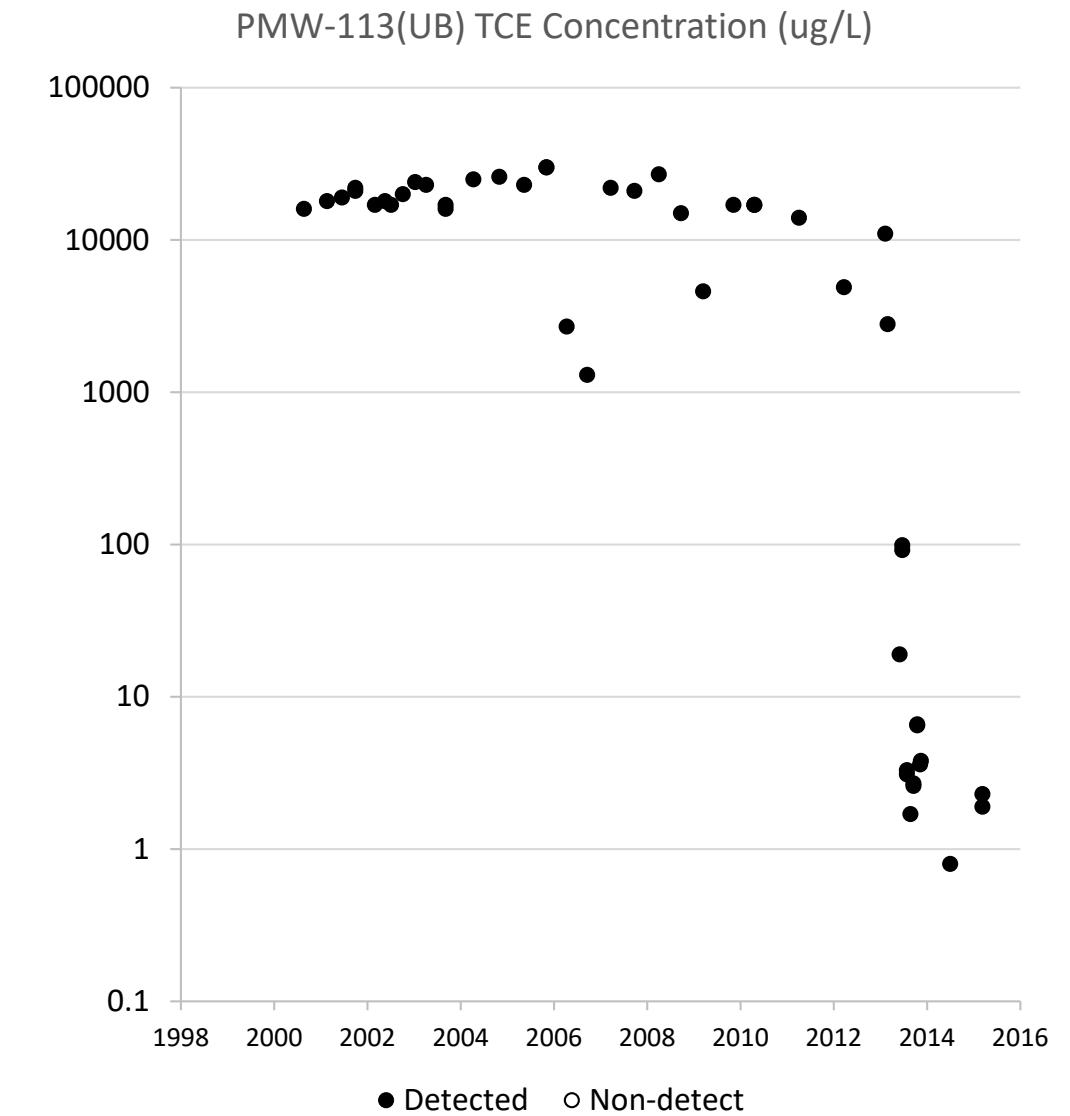
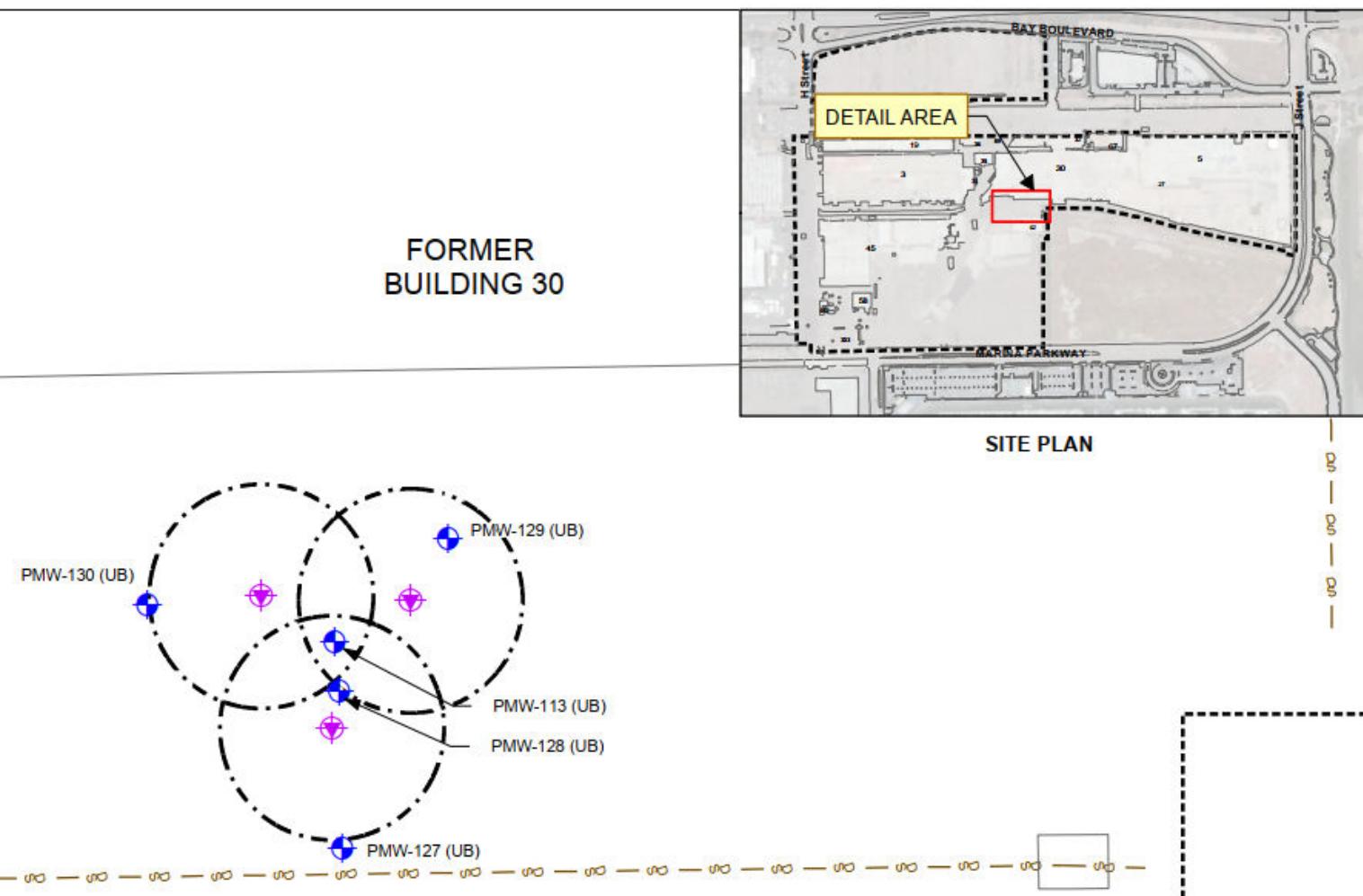
How do we communicate results??



Example of Redox Zone Delineation



Enhanced In-Situ Bioremediation (EISB) Pilot Test



Full-Scale Design



Attenuation Concepts

Section 1.1

Source Attenuation: $C \downarrow$ over *time*

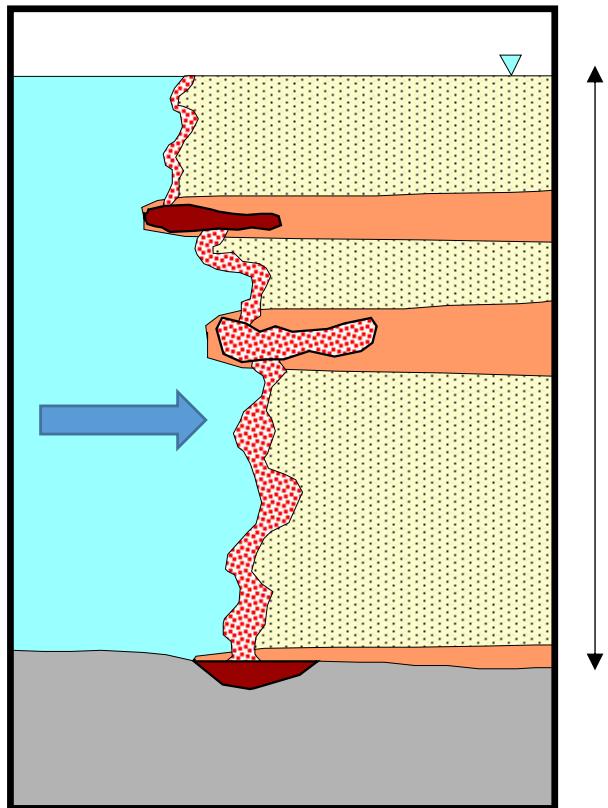
Plume Attenuation: $C \downarrow$ over *distance*

Natural Attenuation Mechanisms

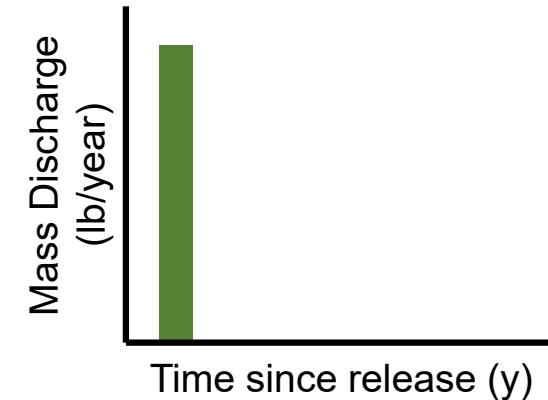
- There are two main processes by which natural attenuation may be protective at a site:
 1. Source depletion – concentrations decline with time;
 2. Plume attenuation – concentrations decline along the flow path downgradient from the source zone.
- Plume attenuation is most significant when biodegradation is occurring along the flow path. Other processes which influence plume attenuation include dispersion, abiotic degradation, and sorption when the plume is still advancing.

Mass Discharge (Source Strength) Trends

Fresh Source



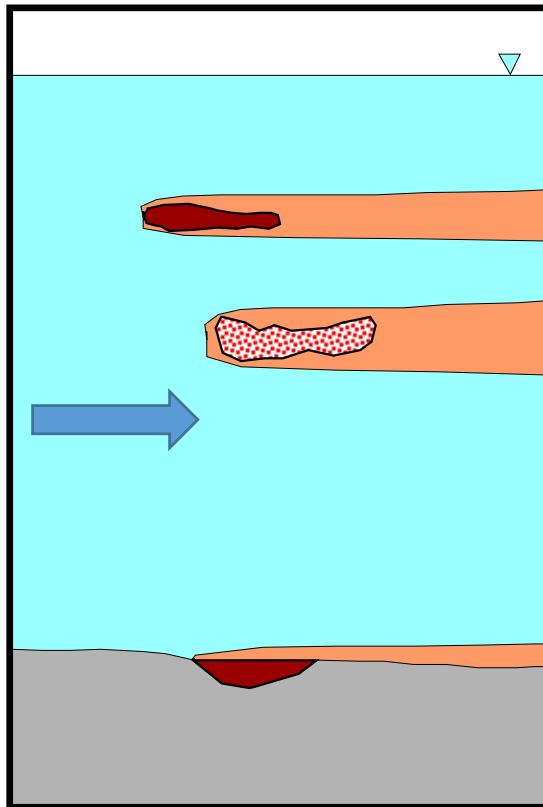
**Mass discharge
from source zone
(kg/y)**



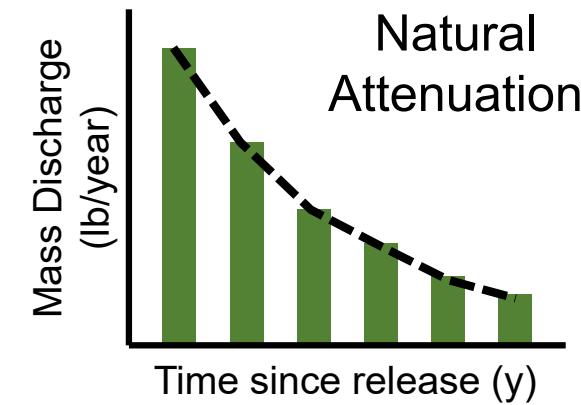
Modified from Parker et al., 2003

Mass Discharge (Source Strength) Trends

Aged Source



Typical source zone mass discharge = 1 to 100 kg/year



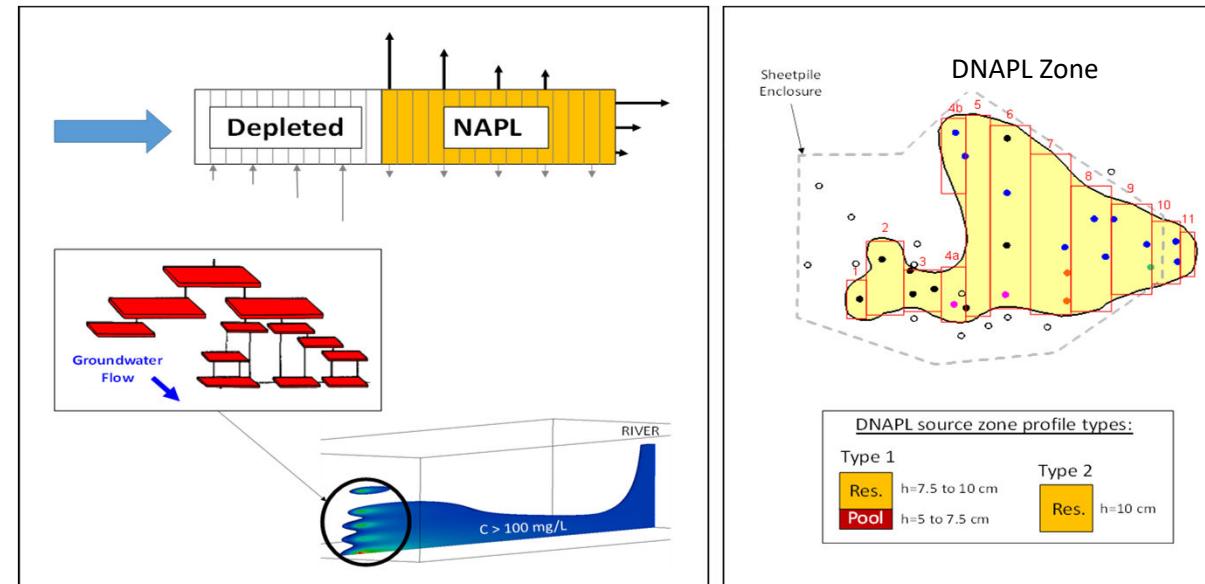
Newell et al., 2006:
Median TCE DNAPL half-life of 6 years

Mass discharge reduction 30x in 30 years

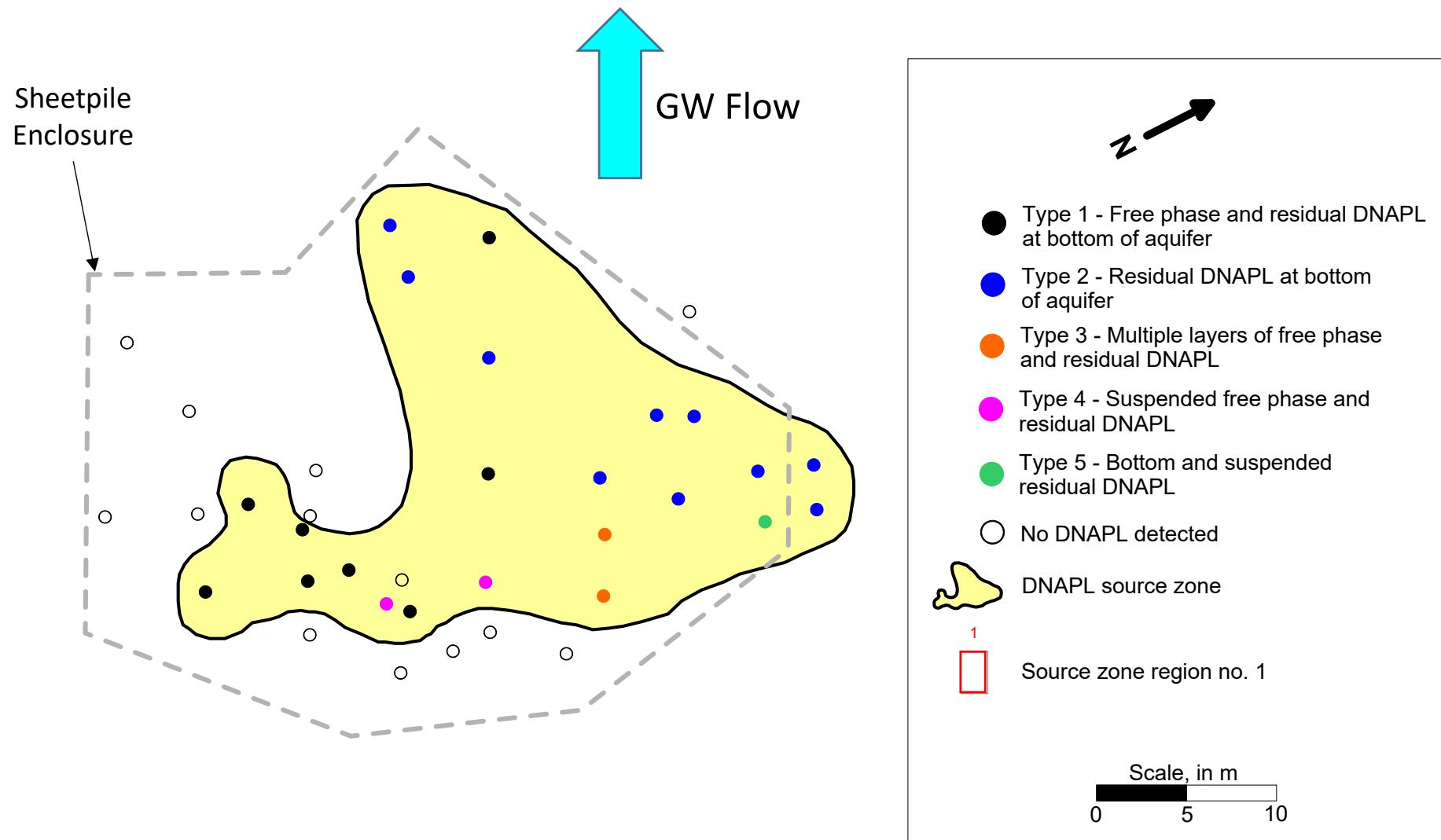
NAPL Depletion Model (NDM)

Estimating Timeframes for Natural and Enhanced NAPL Depletion

Free software and 4-hour short course download: www.porewater.com

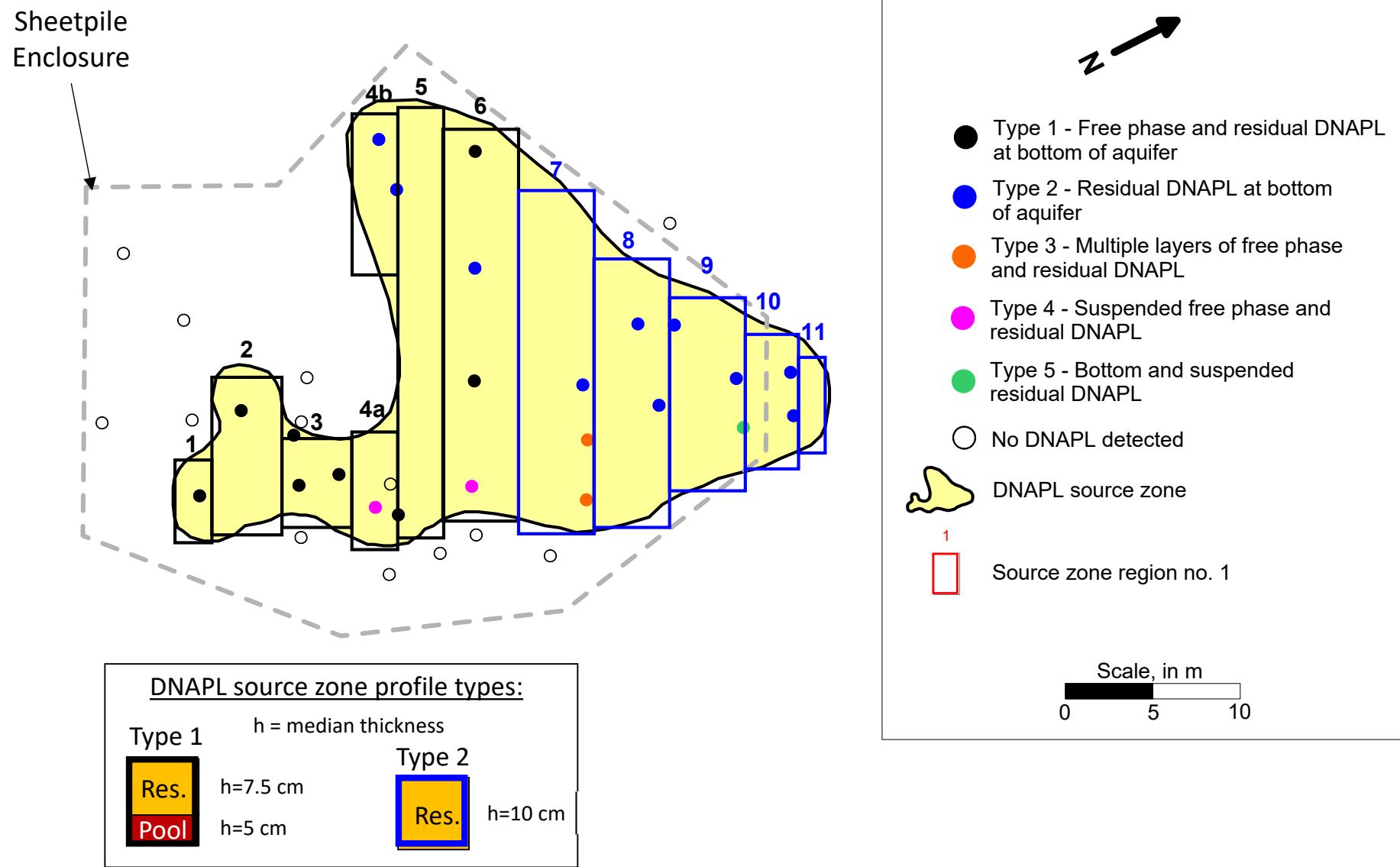


Case Study: Beth Parker et al. (2003) CT Site

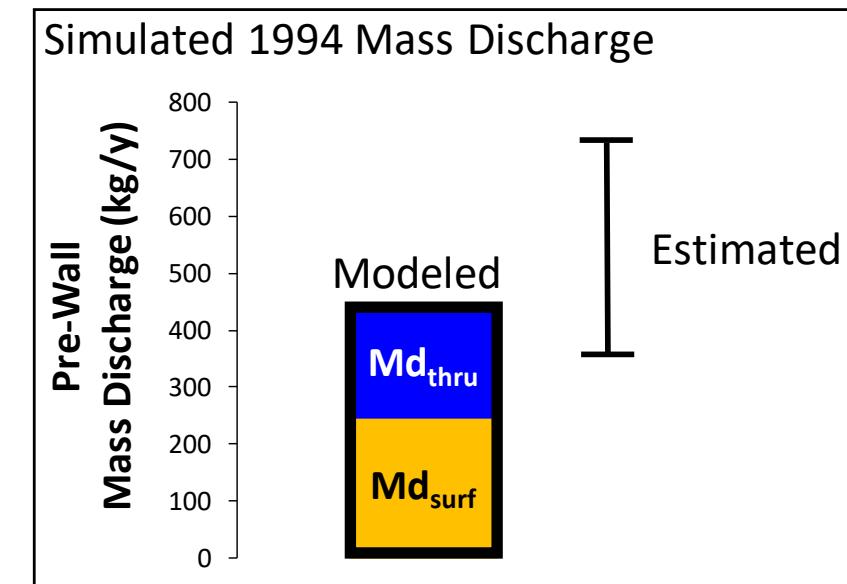
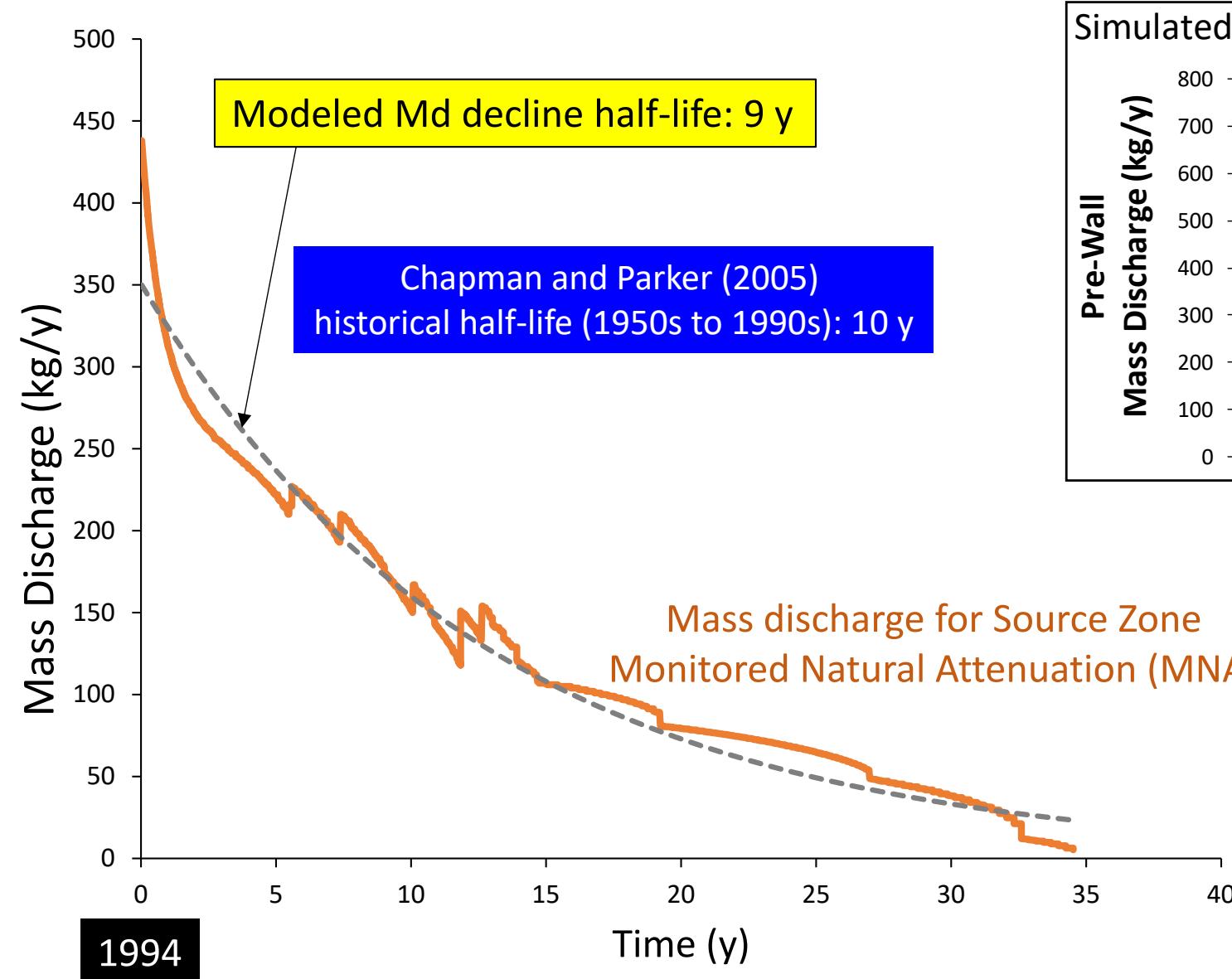


Data summarized in Stewart (2002) and Parker et al. (2003)

DNAPL Sub-Zones

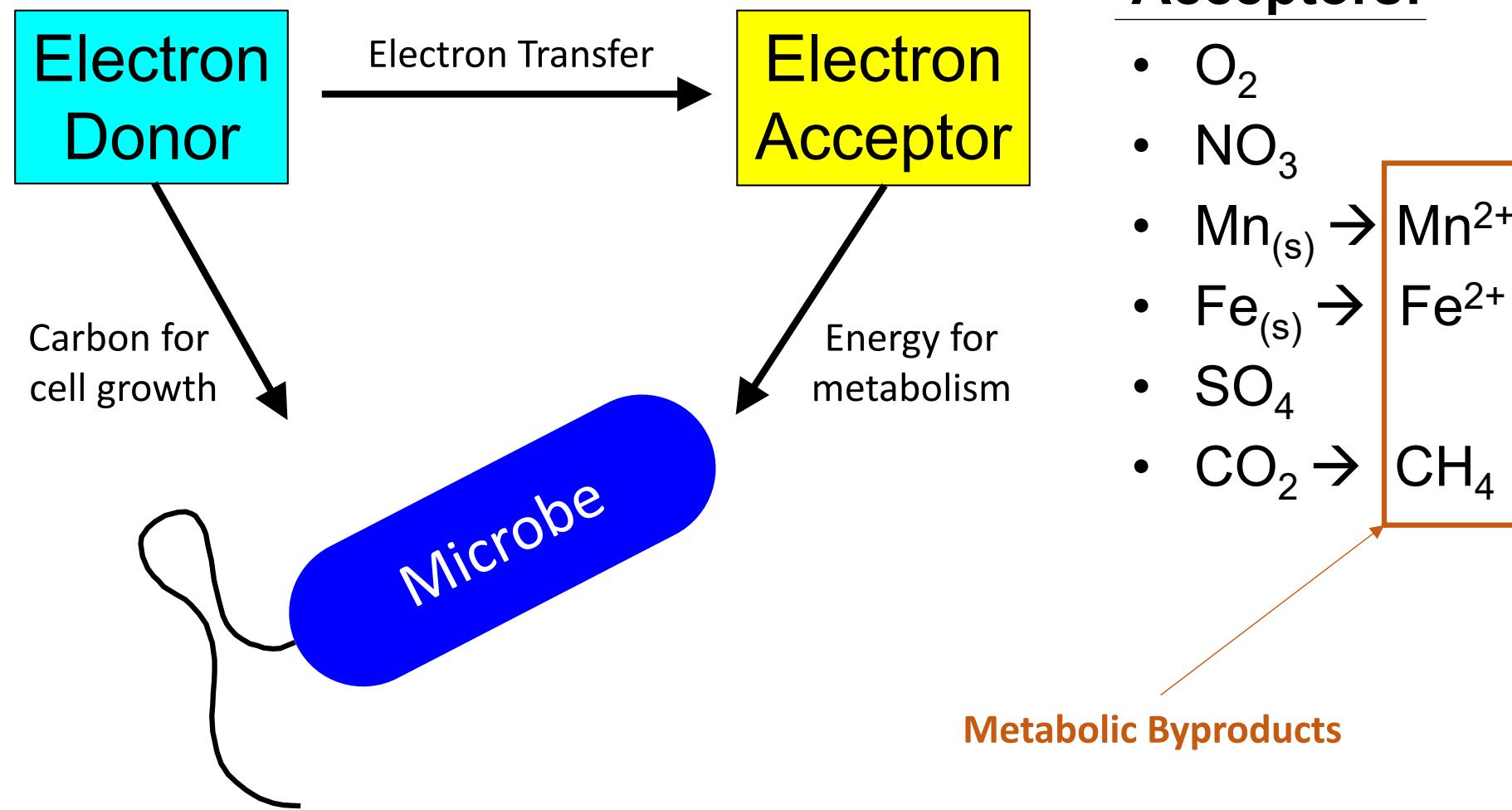


Source Depletion: Modeled vs. Estimated Half-Life



Md = Mass discharge

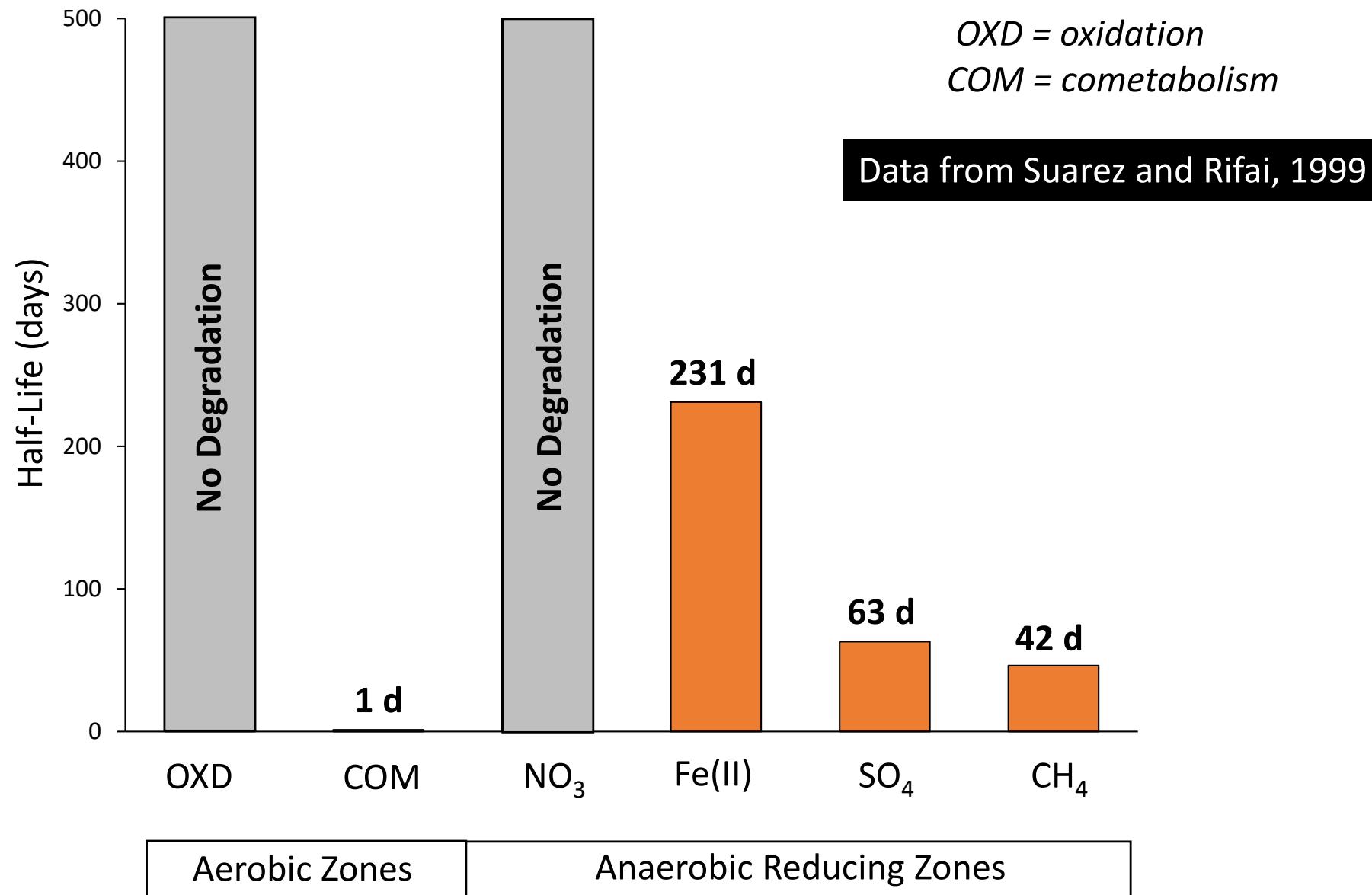
Biogeochemical Processes



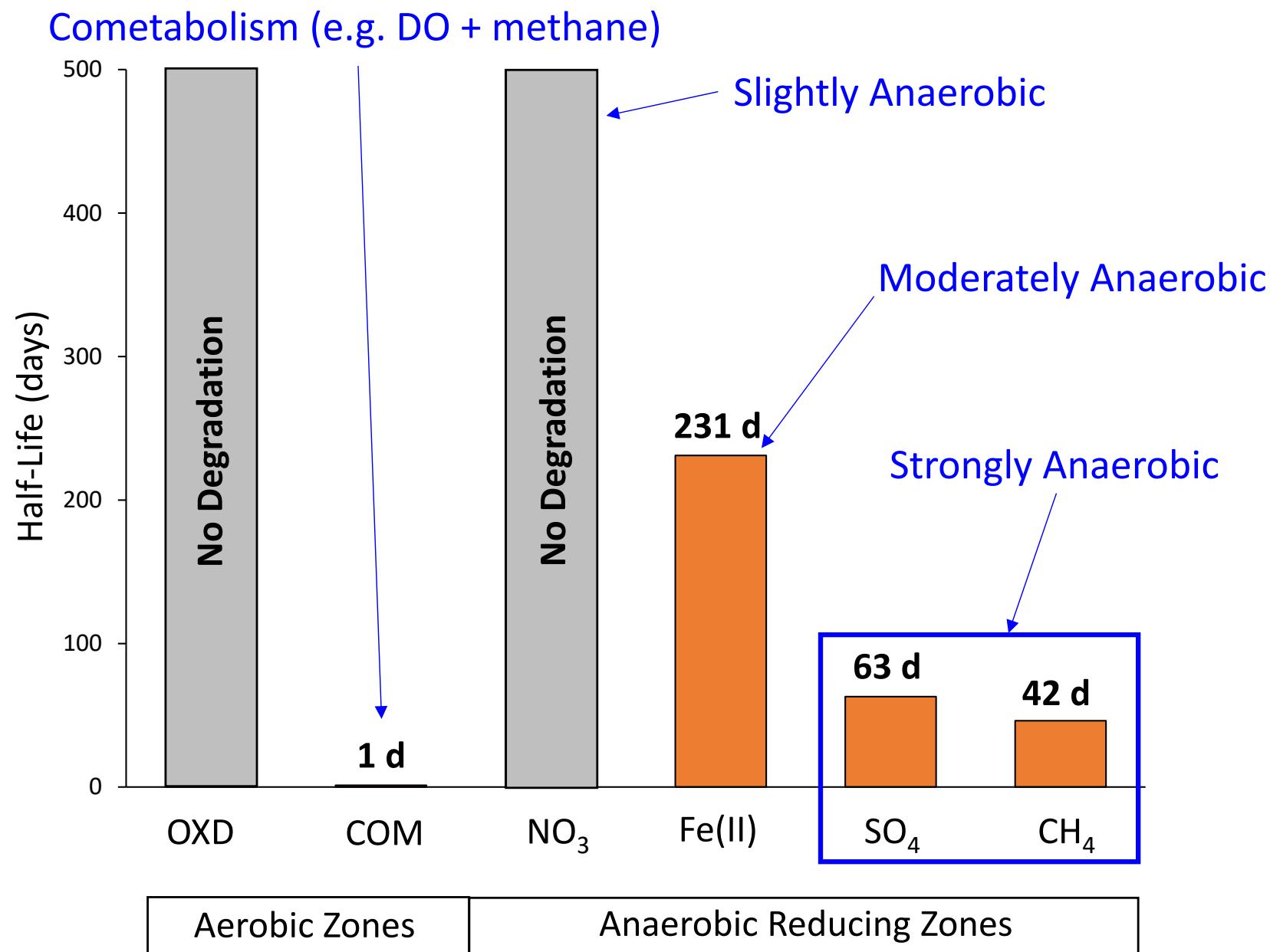
Plume Biogeochemical Processes

- Typical concentration trends during biodegradation
 - Electron acceptors (oxygen, nitrate, sulfate) decline
 - At some sites, sulfate may increase due to dissolution of sulfate-bearing minerals during geochemical changes associated with biodegradation. Sulfate reduction is typically still occurring, even with an increase in sulfate concentrations.
 - Metabolic byproducts (manganese, iron, methane) increase
 - Naturally-occurring arsenic may be temporarily co-dissolved into groundwater with iron. (This arsenic is typically sorbed into iron coatings on sand grains in aerobic aquifers.) Arsenic will later co-precipitate with iron when mixed with oxygen.

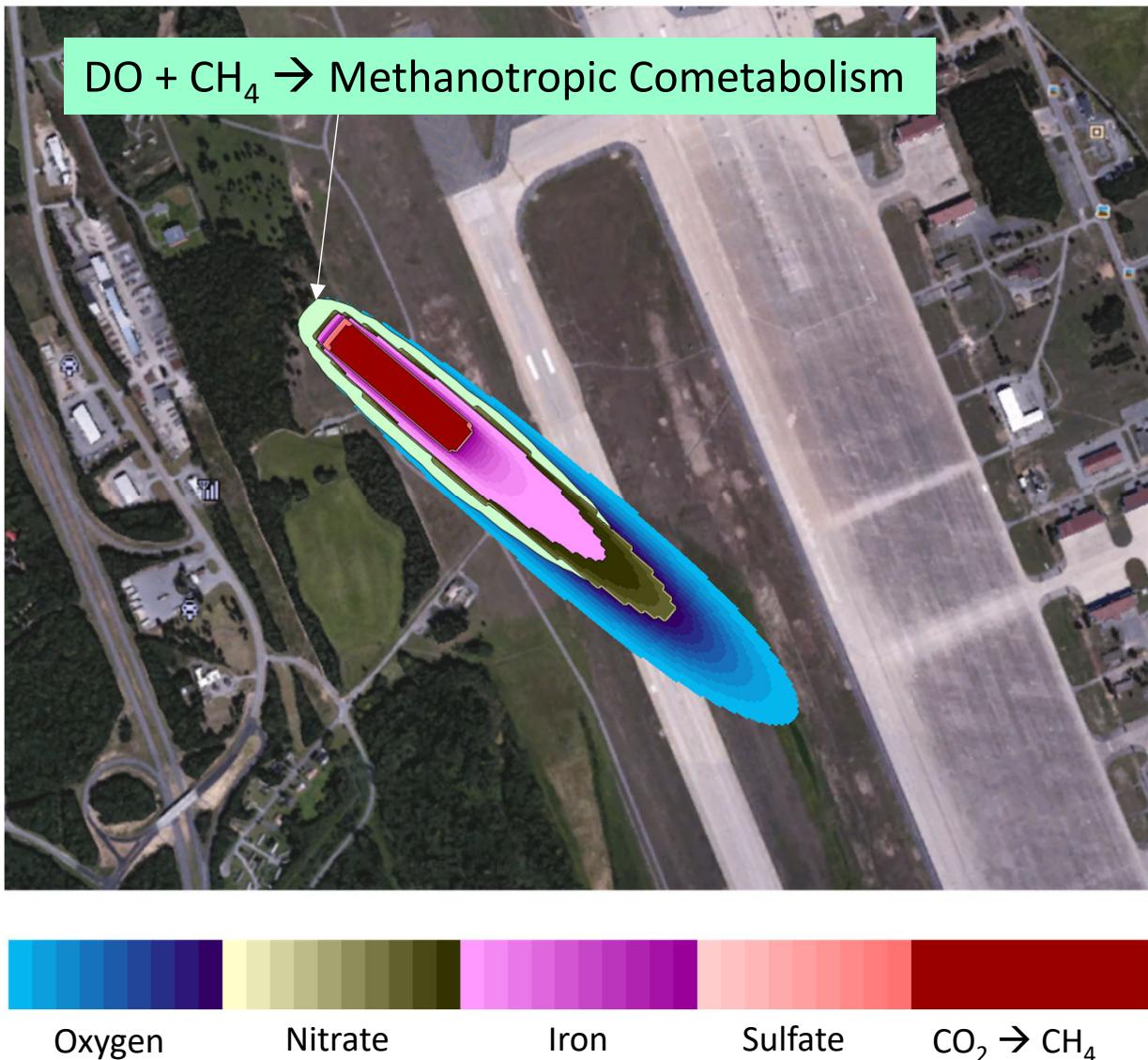
TCE Mean Degradation Half-Life by Redox Zone



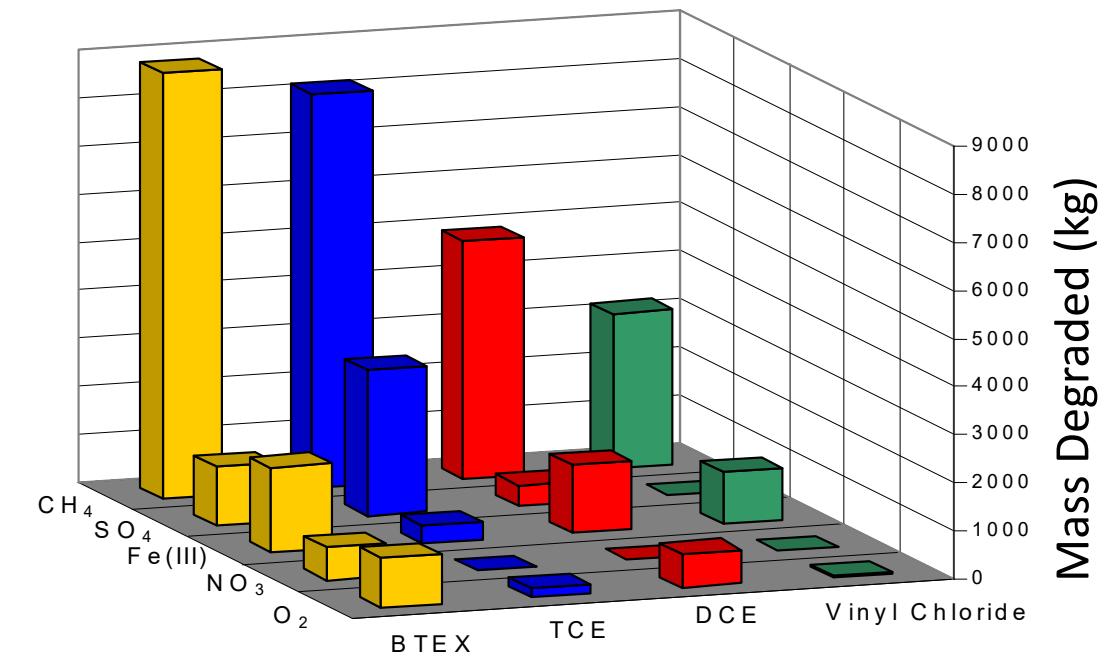
TCE Degradation Half-Life by Redox Zone



Redox Zone Mass Balance at Plattsburgh Air Force Base



Modeled Mass Balance by Redox Zone (t = 40 years)



	CH ₄	SO ₄	Fe/Mn	NO ₃	O ₂
PCE	Green	Green	Light Green		
TCE	Green	Green	Light Green		Orange
cis-DCE	Green	Green	Blue		Blue
Vinyl Chloride	Light Green		Blue		Blue

- Blue: Oxidation (rapid, NO Daughters)
- Green: Reductive Dechlorination (moderate, Daughters, need ED)
- Light Green: Reductive Dechlorination (slow, Daughters, need ED)
- Orange: Cometabolism (rapid if substrate present, NO Daughters)

Modeled using In-Situ Remediation (ISR-MT3DMS)

Redox-Dependent Biodegradability

- Parent VOCs (PCE, TCE, 111-TCA)
 - Aerobic cometabolism – when chemicals like methane or toluene are present to stimulate rapid degradation
 - Otherwise need moderately or strongly anaerobic conditions
- VOC Daughter products (e.g. 12-DCE, VC, 11-DCA, 11-DCE)
 - May undergo oxidation (without daughters) under aerobic or moderately anaerobic conditions
 - Undergo reductive dichlorination under moderate to strongly anaerobic conditions
- PFAS precursors degrade to PFCAs and PFSAs mainly under aerobic conditions

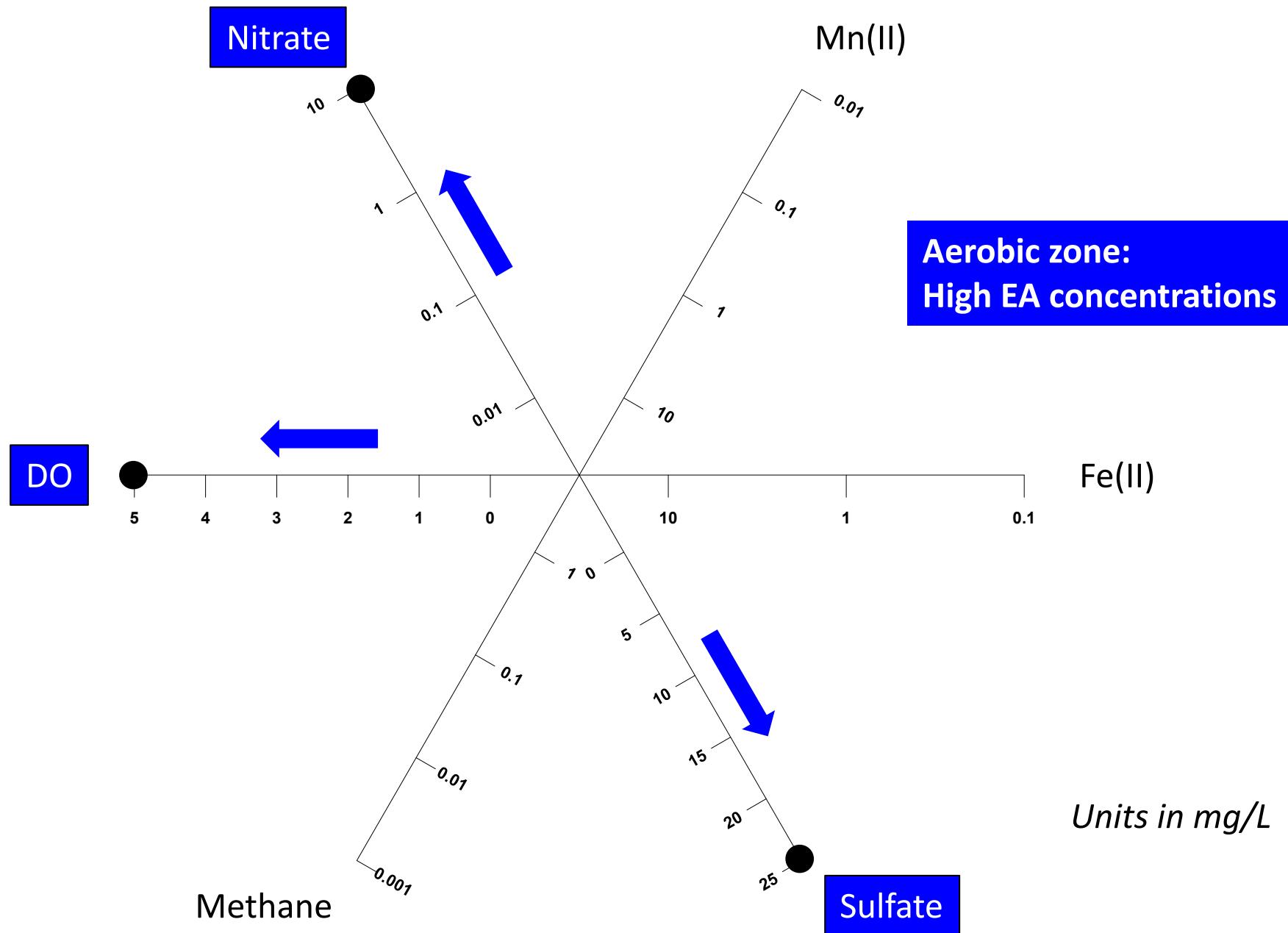
Natural and Enhanced Degradation

- Analysis requires:
 - Delineation of major redox zones
 - Illustration of parent to daughter product ratios at wells
 - Illustration of trends along flowpath
 - Decreasing parent and increasing daughter products?
 - Illustration of trends over time across the entire site
- Applicable to natural and enhanced attenuation

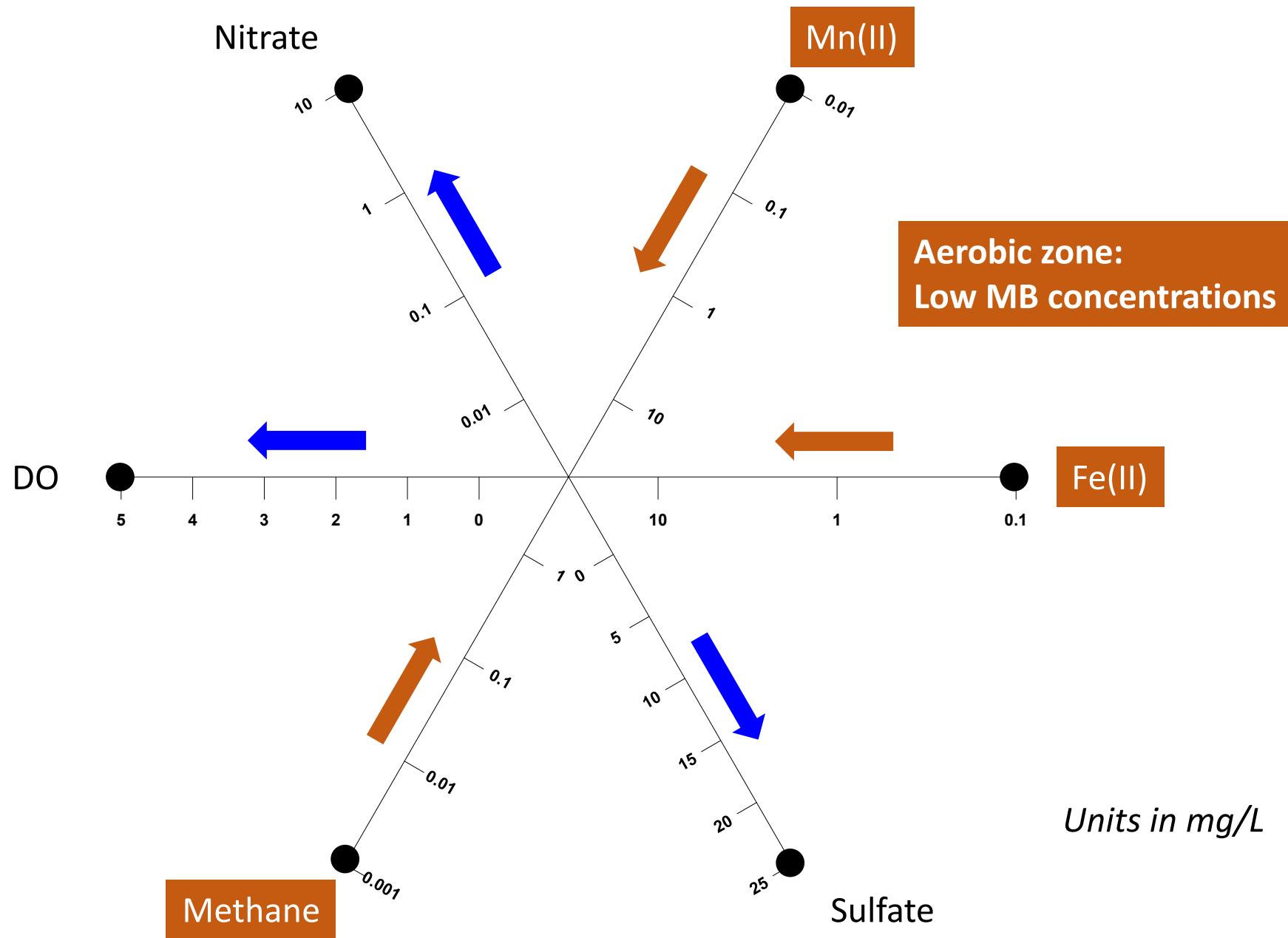
Redox Radial Diagrams

Section 1.2

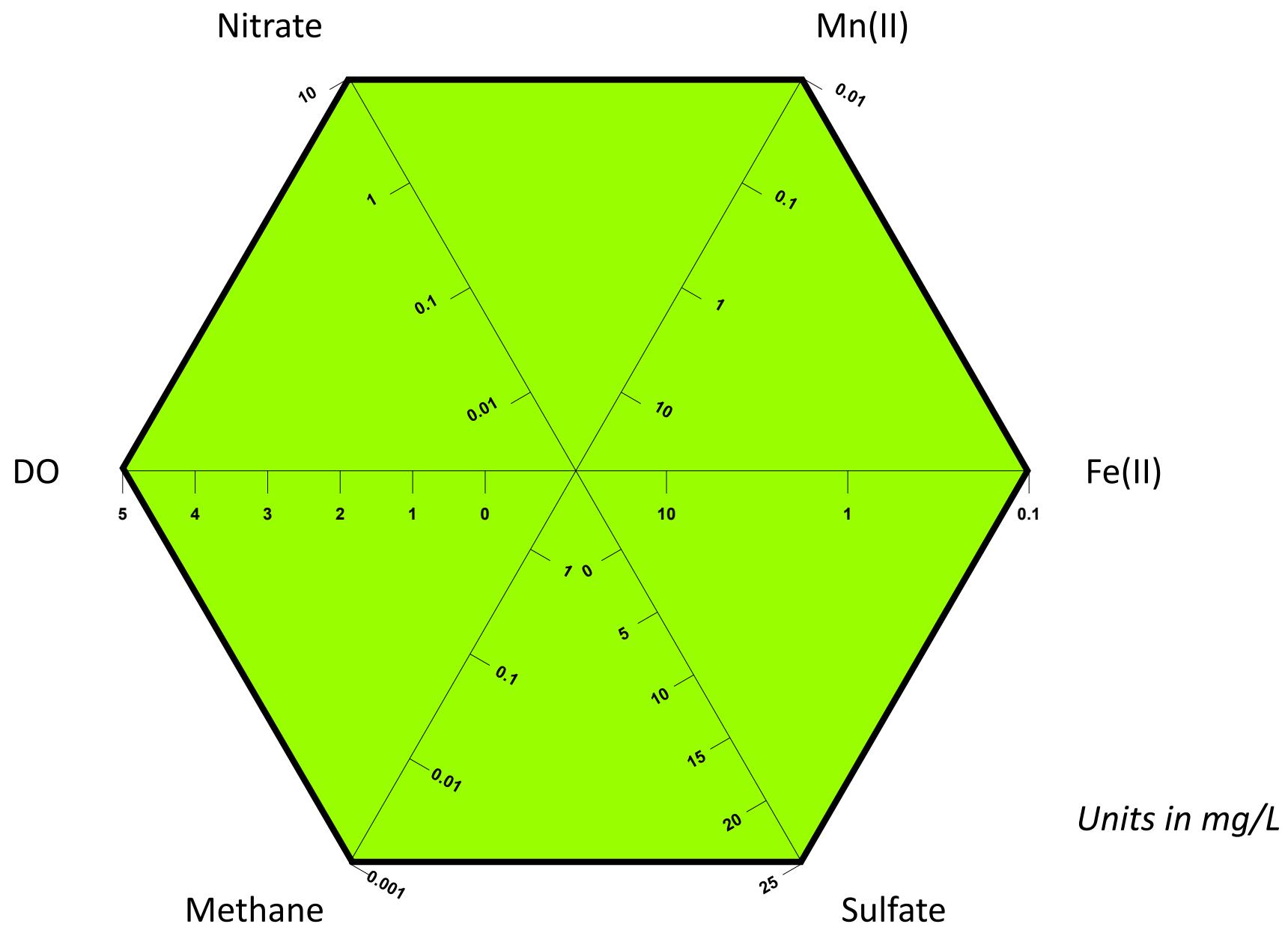
Redox Diagram: Electron Acceptors (EA)



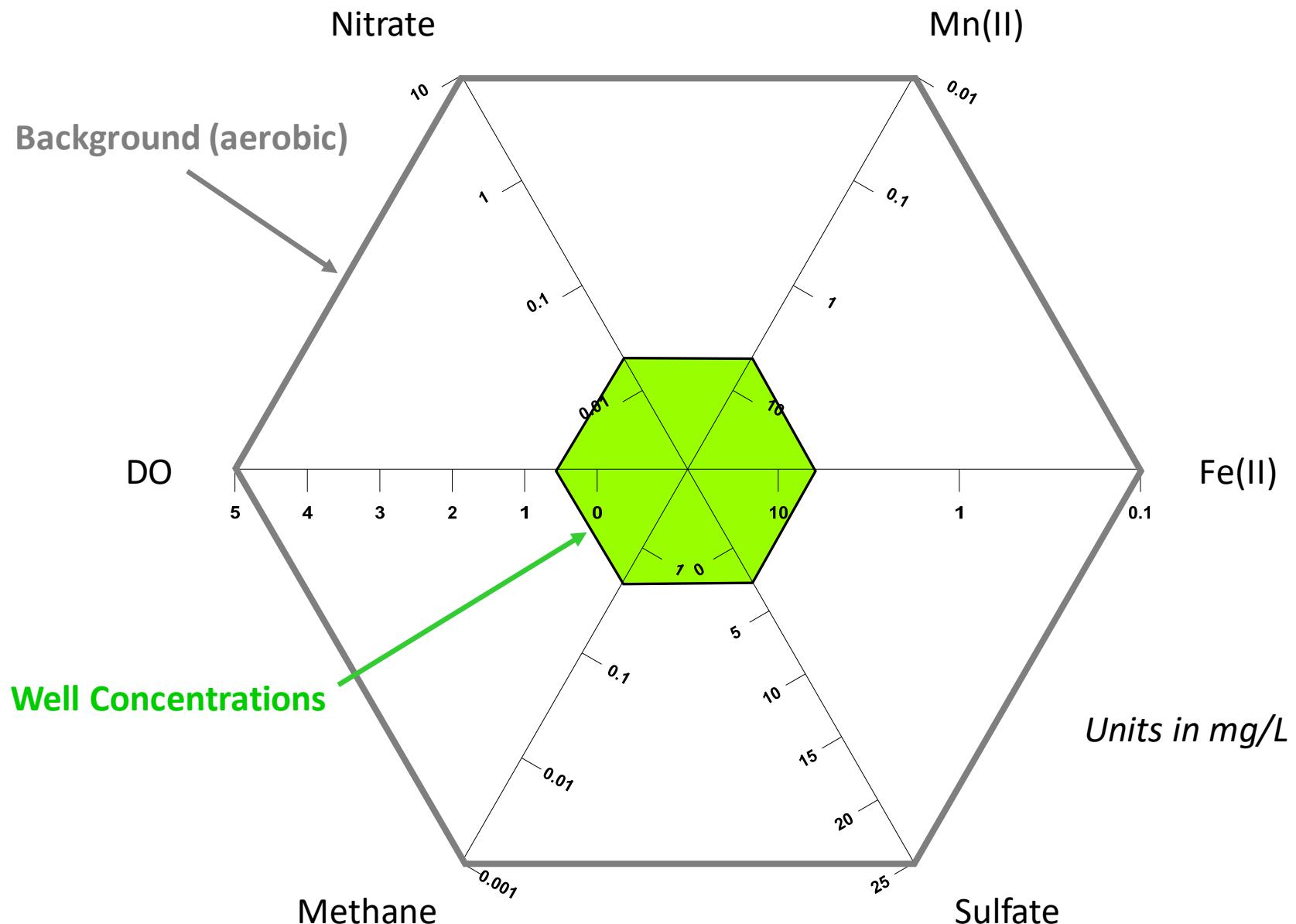
Redox Diagram: Metabolic By-Products (MB)



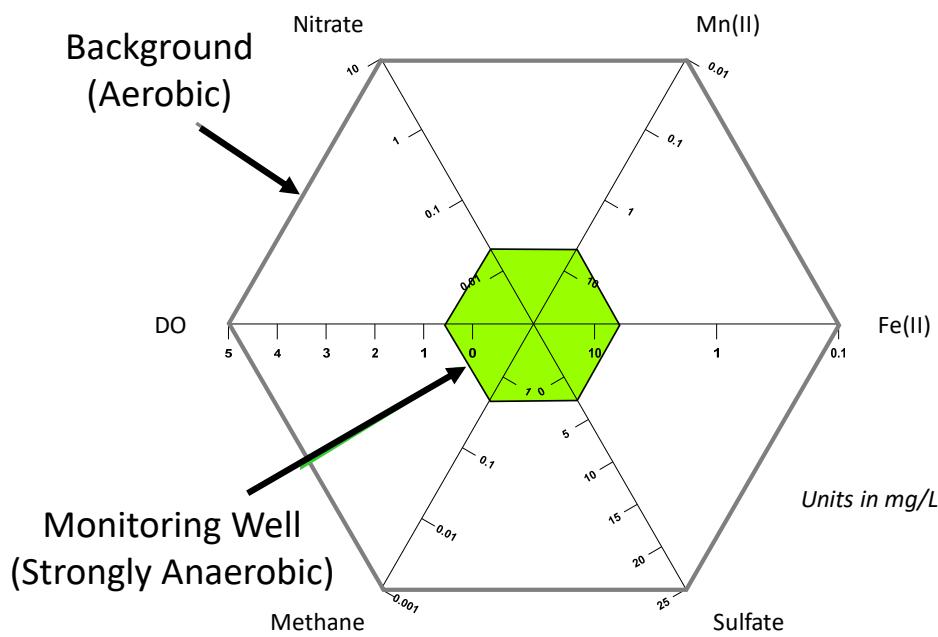
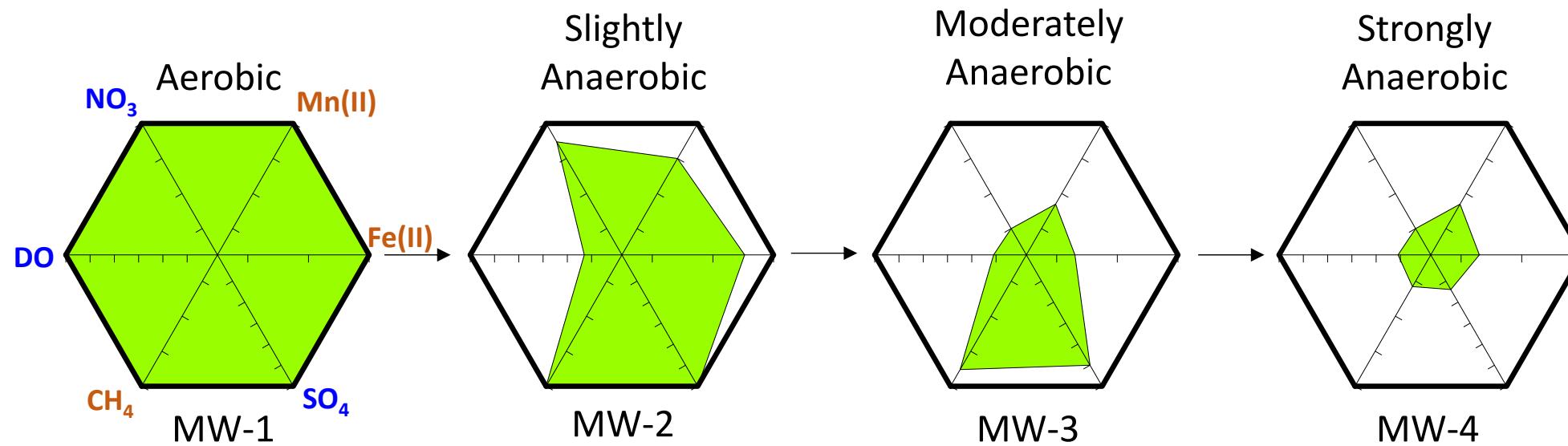
Redox Diagram: Aerobic (Background)



Redox Diagram: Strongly Anaerobic at Well



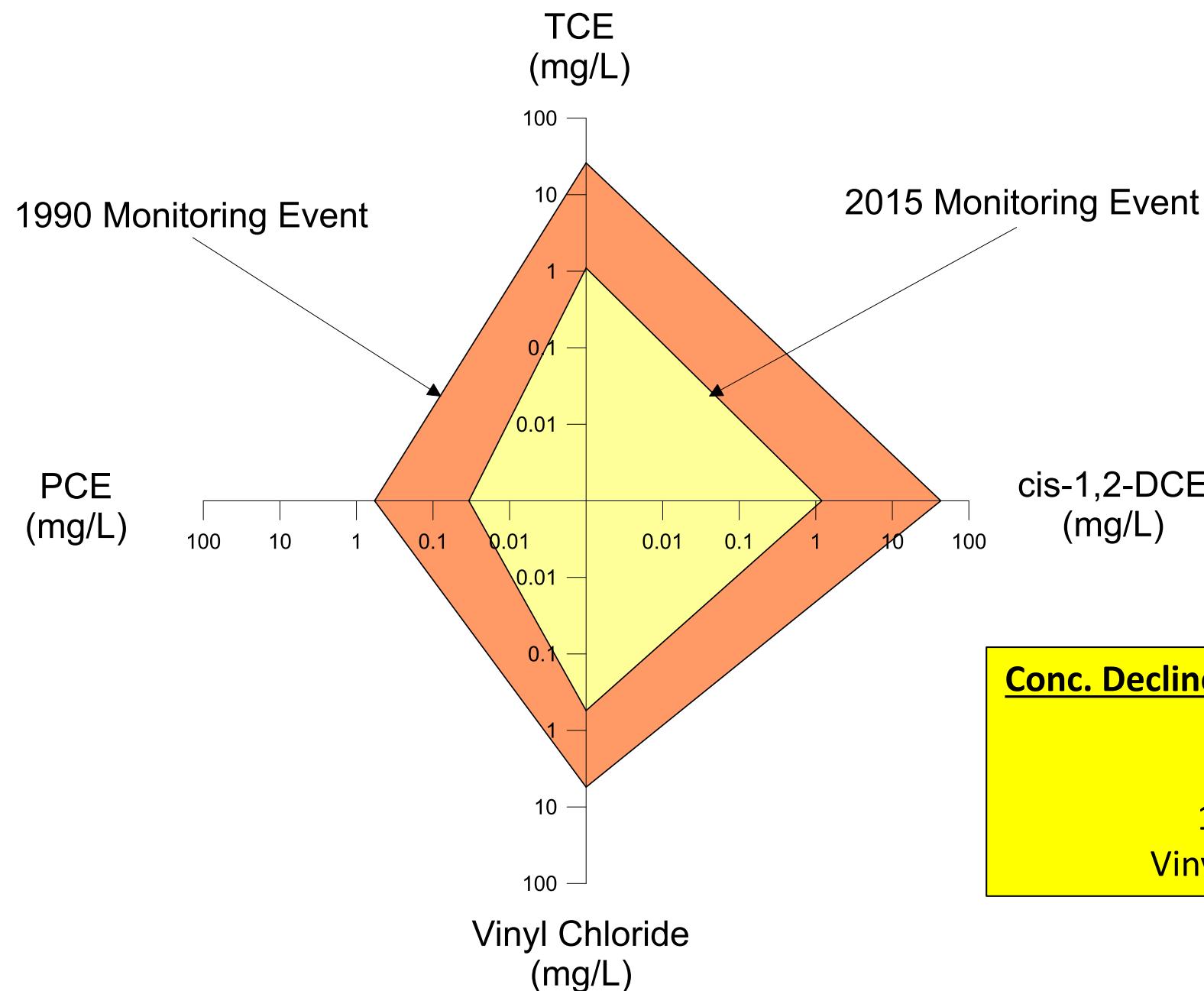
Redox Zone Transition



VOC Radial Diagrams

Section 1.3

VOC Radial Diagram: Source Depletion

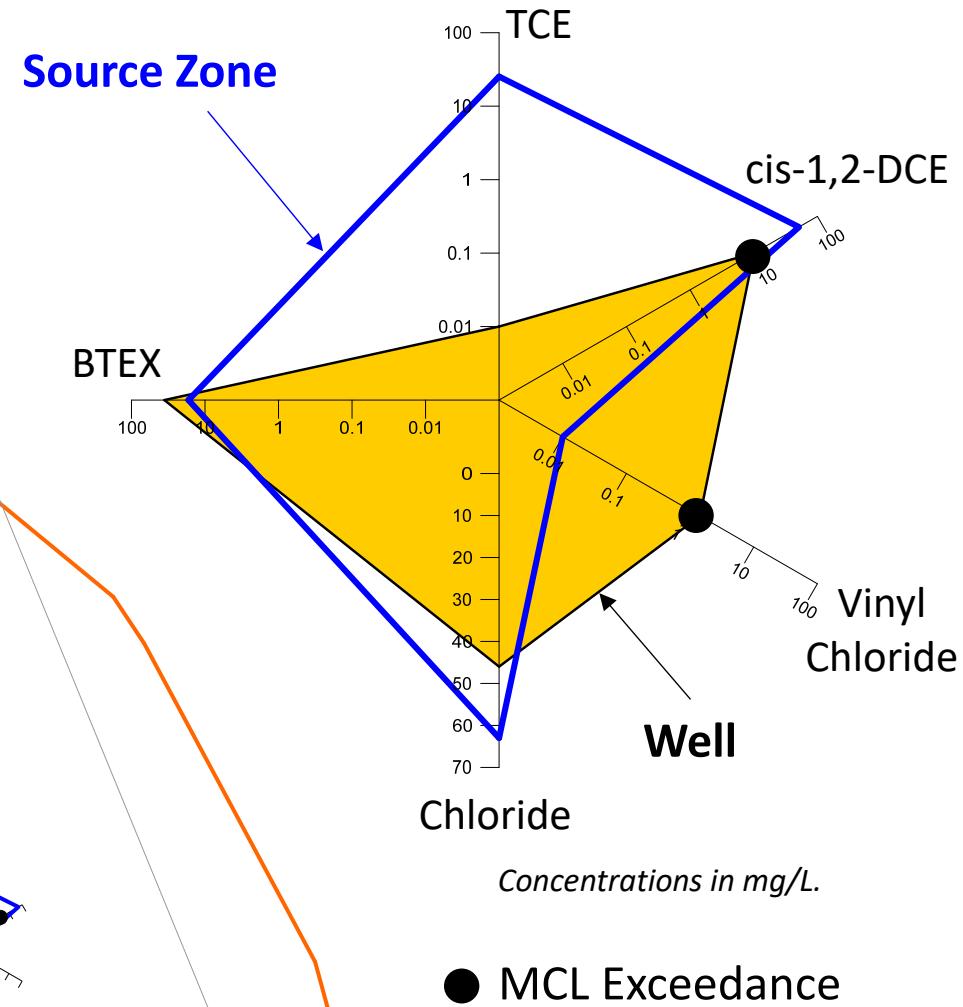
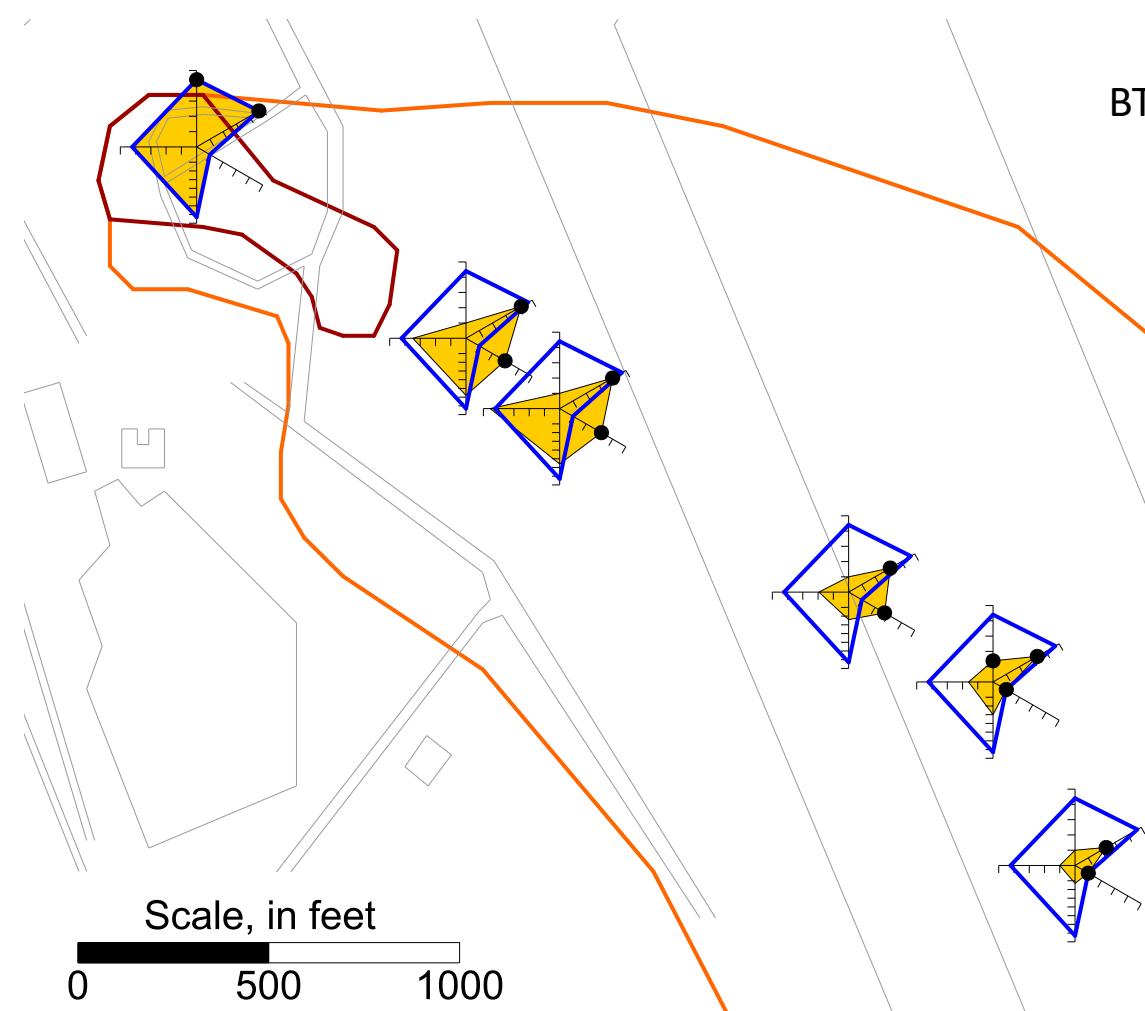


Conc. Declines at Well (1990 to 2015)

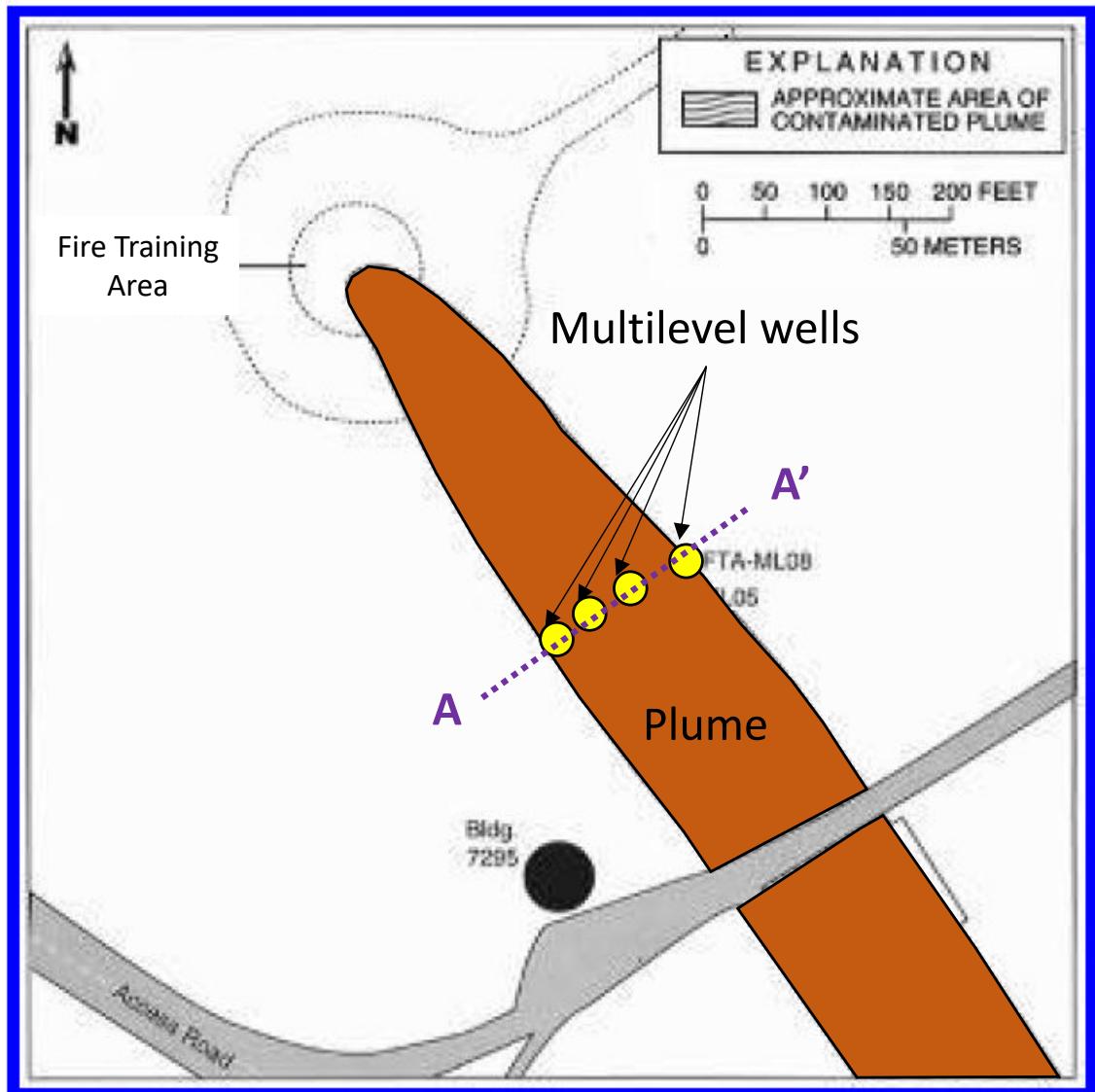
PCE: 10x
TCE: 30x
1,2-DCE: 30x
Vinyl Chloride: 10x

Plattsburgh Air Force Base: Plume Attenuation

Carey et al. (2003)



Wurtsmith Air Force Base, Michigan



Redox Indicators

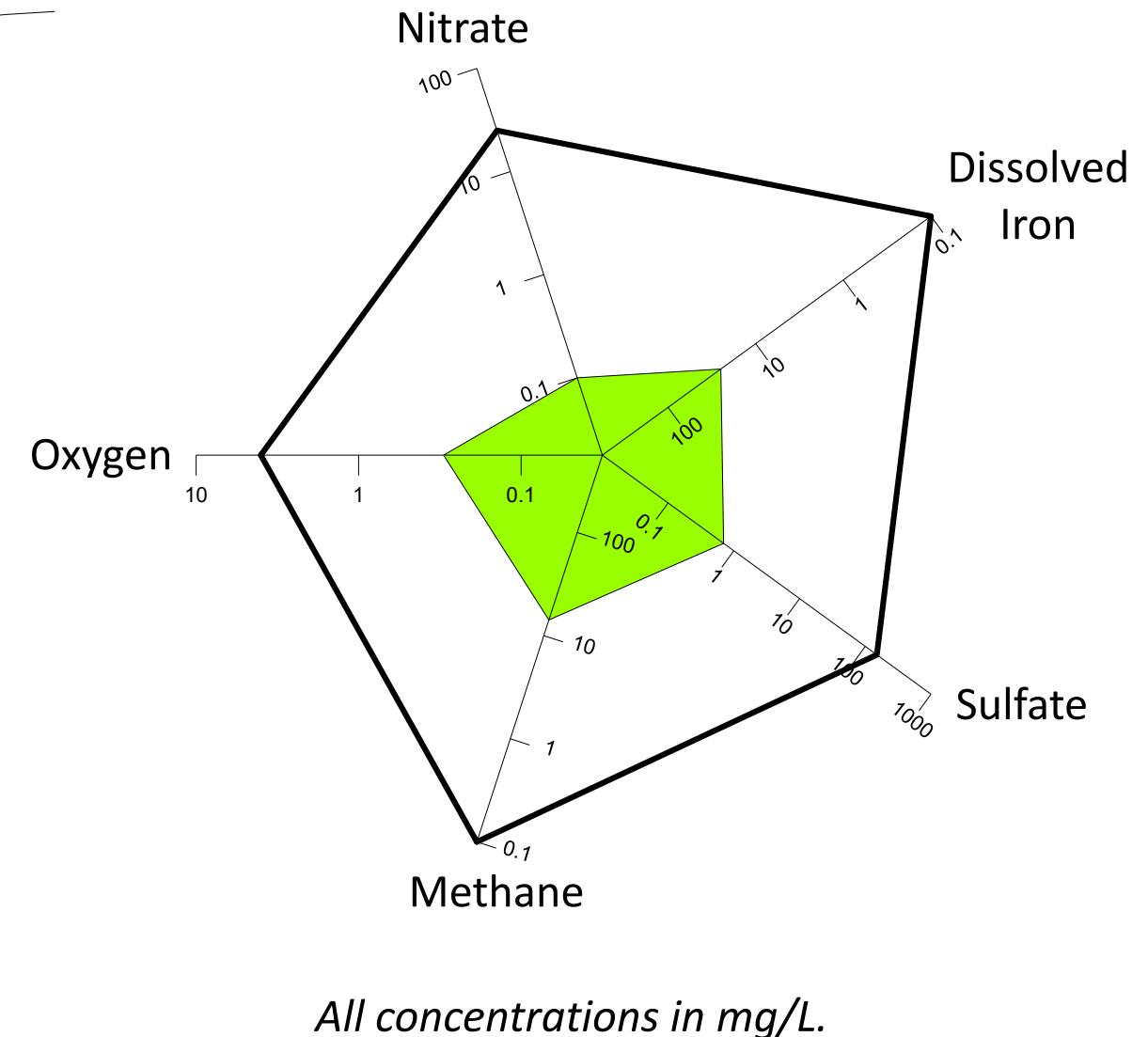
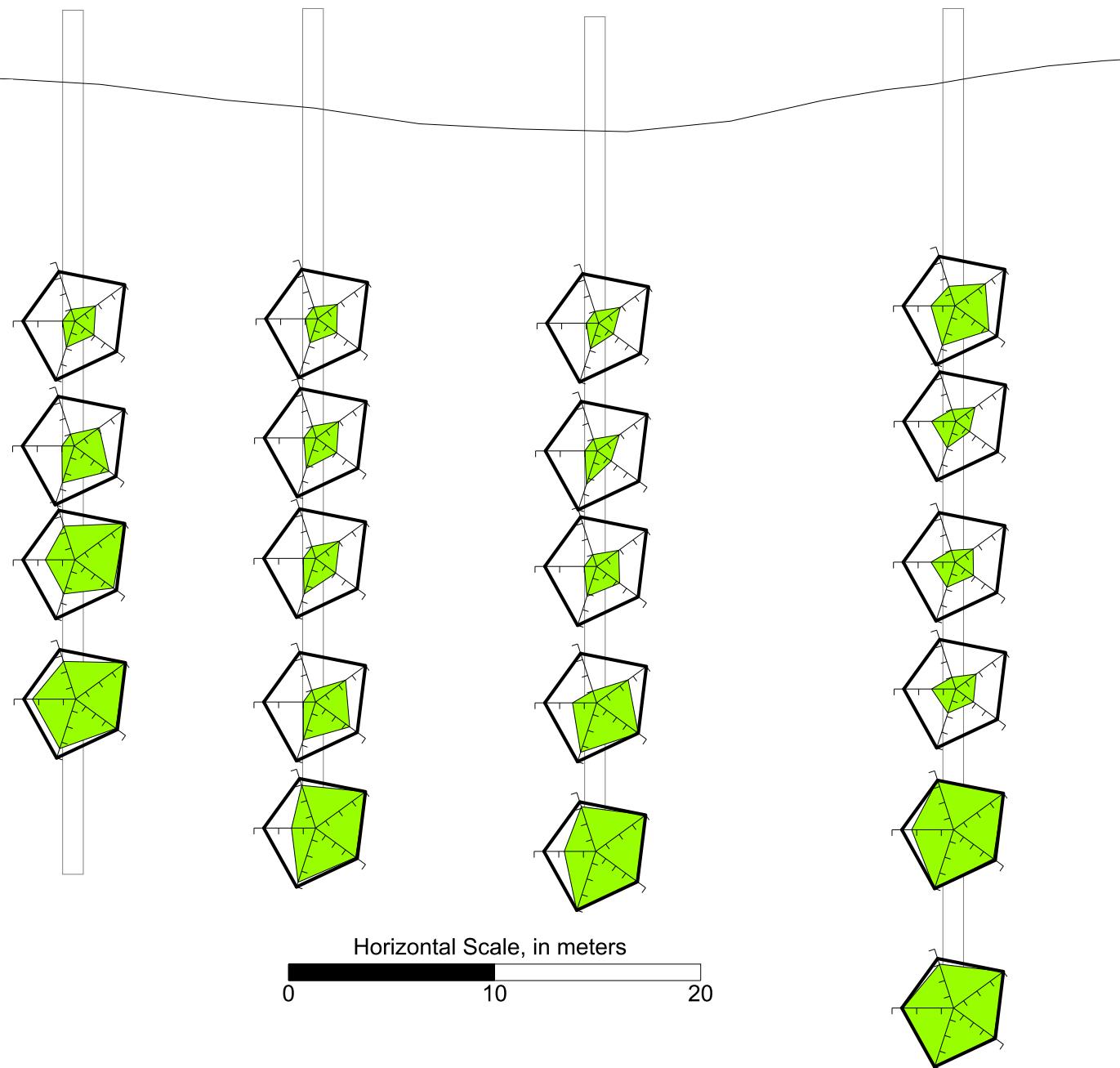
- 20 wells
 - 5 indicators
- 100 data points

ES&T, 1996, 30: 3565-3569

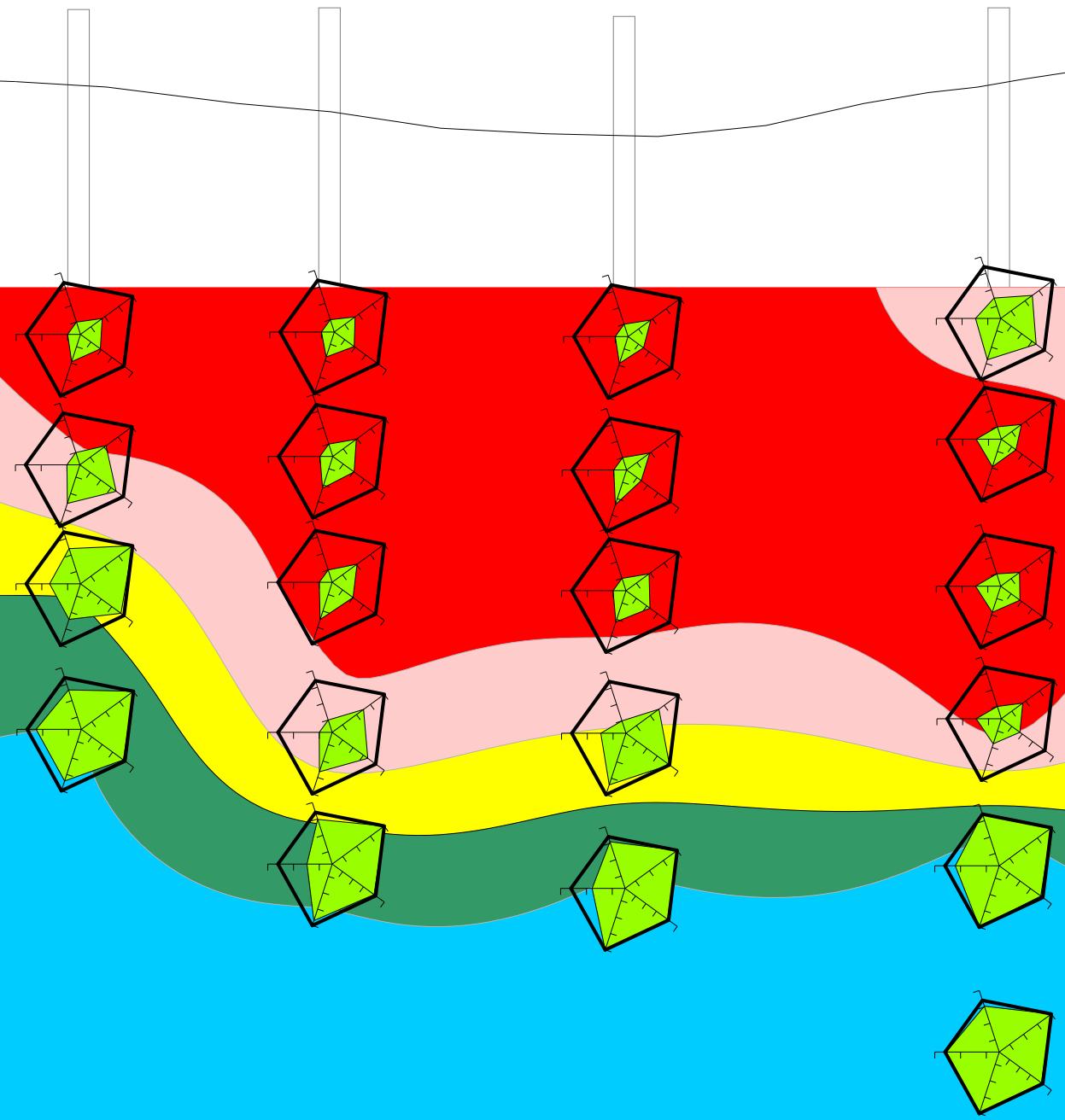
Comparison of E_h and H_2 Measurements for Delineating Redox Processes in a Contaminated Aquifer

FRANCIS H. CHAPELLE,^{*,†}
SHERIDAN K. HAACK,[‡]
PETER ADRIAENS,[§]
MARK A. HENRY,^{||} AND
PAUL M. BRADLEY[†]
*U.S. Geological Survey, 720 Gracern Road, Suite 129,
Columbia, South Carolina 29210-7651; U.S. Geological Survey,
6520 Mercantile Way, Suite 5, Lansing, Michigan 48911,
Department of Civil & Environmental Engineering,
University of Michigan, 181 EWRE Building,
Ann Arbor, Michigan 48109-2125, and National Center for
Integrated Bioremediation Research,
4140 East California Street, Oscoda, Michigan 48750*

Redox Radial Diagrams



Relative Redox Area Contours

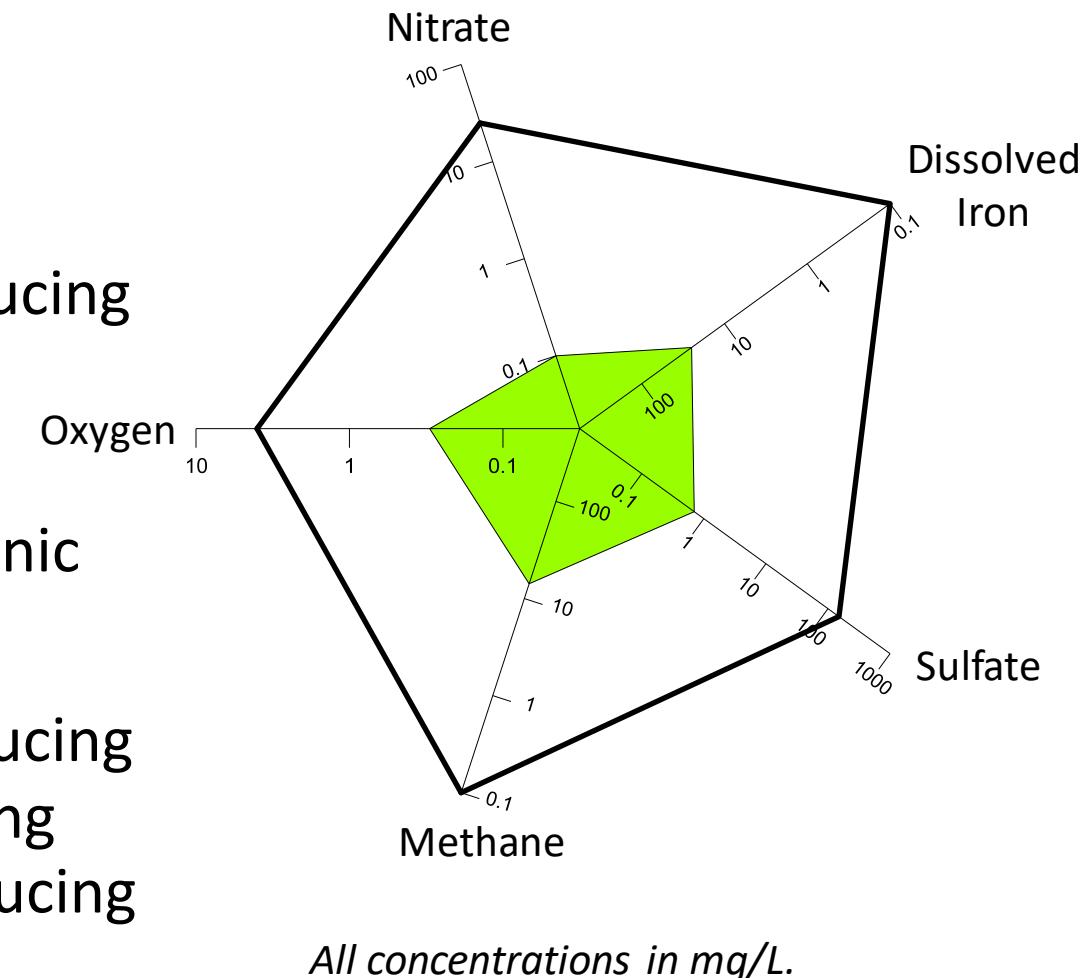


Sulfate-reducing

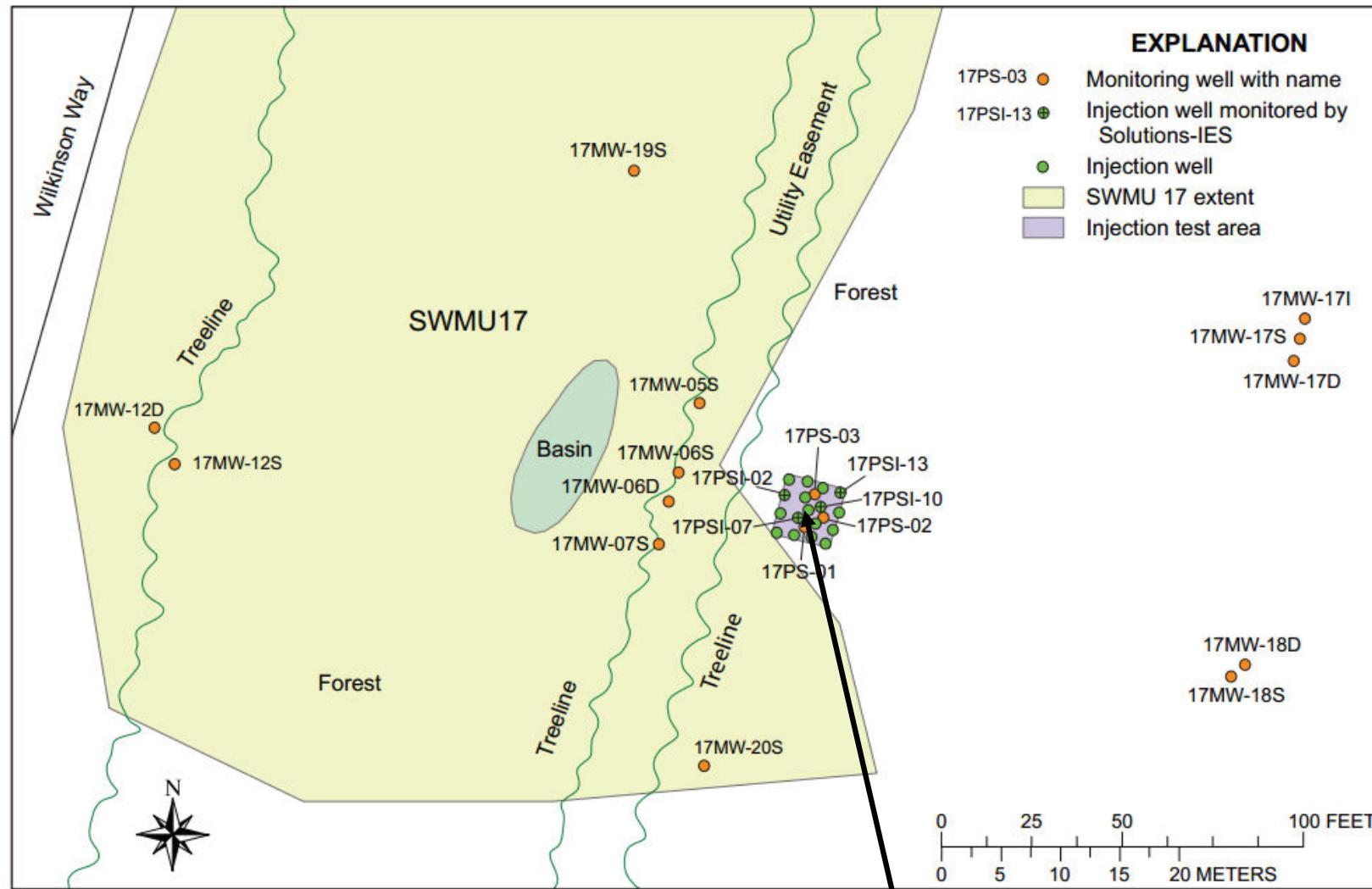
Methanogenic

Sulfate-reducing
Iron-reducing
Nitrate-reducing

Aerobic



Charleston Naval Weapons Station, South Carolina



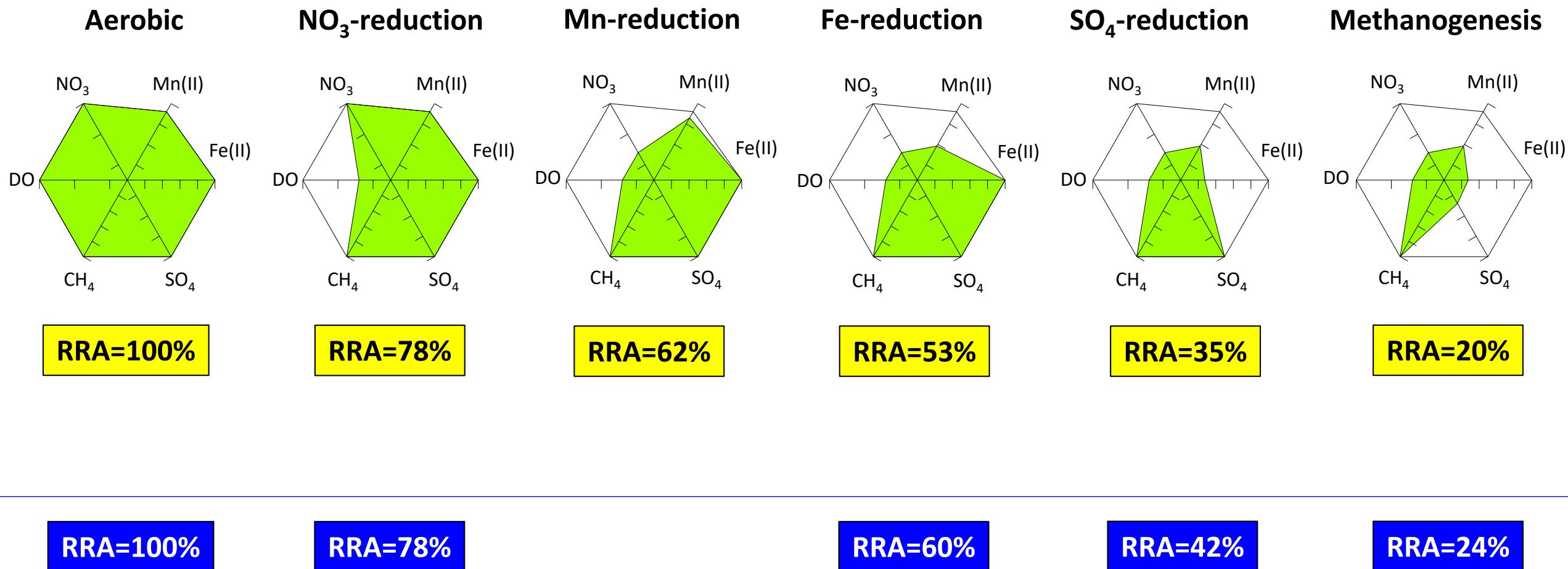
USGS, 2009

Emulsified Oil
Pilot Test Area

Redox Indicators

- 7 wells
 - 6 redox indicators
 - 12 events
- 500 data points

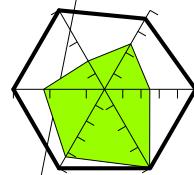
Charleston NWS Relative Redox Area by Zone



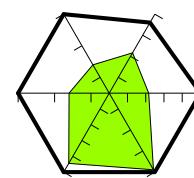
Wurtsmith AFB redox zone thresholds (p. 1.57):

Redox Indicator Event 1: 2004-04-01 (Pre-Injection)

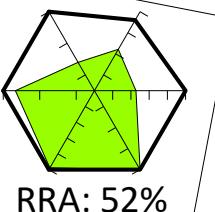
RRA: 46%



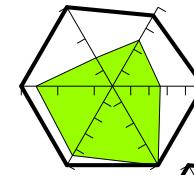
RRA: 39%



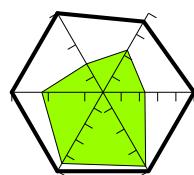
RRA: 52%



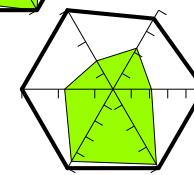
RRA: 51%



RRA: 44%



RRA: 41%

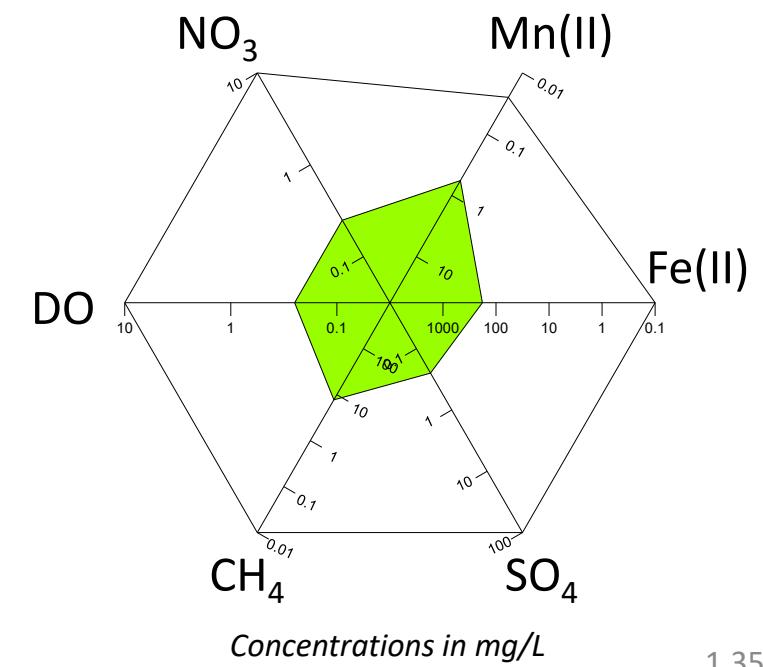


Days after start of Phase I injection: -42

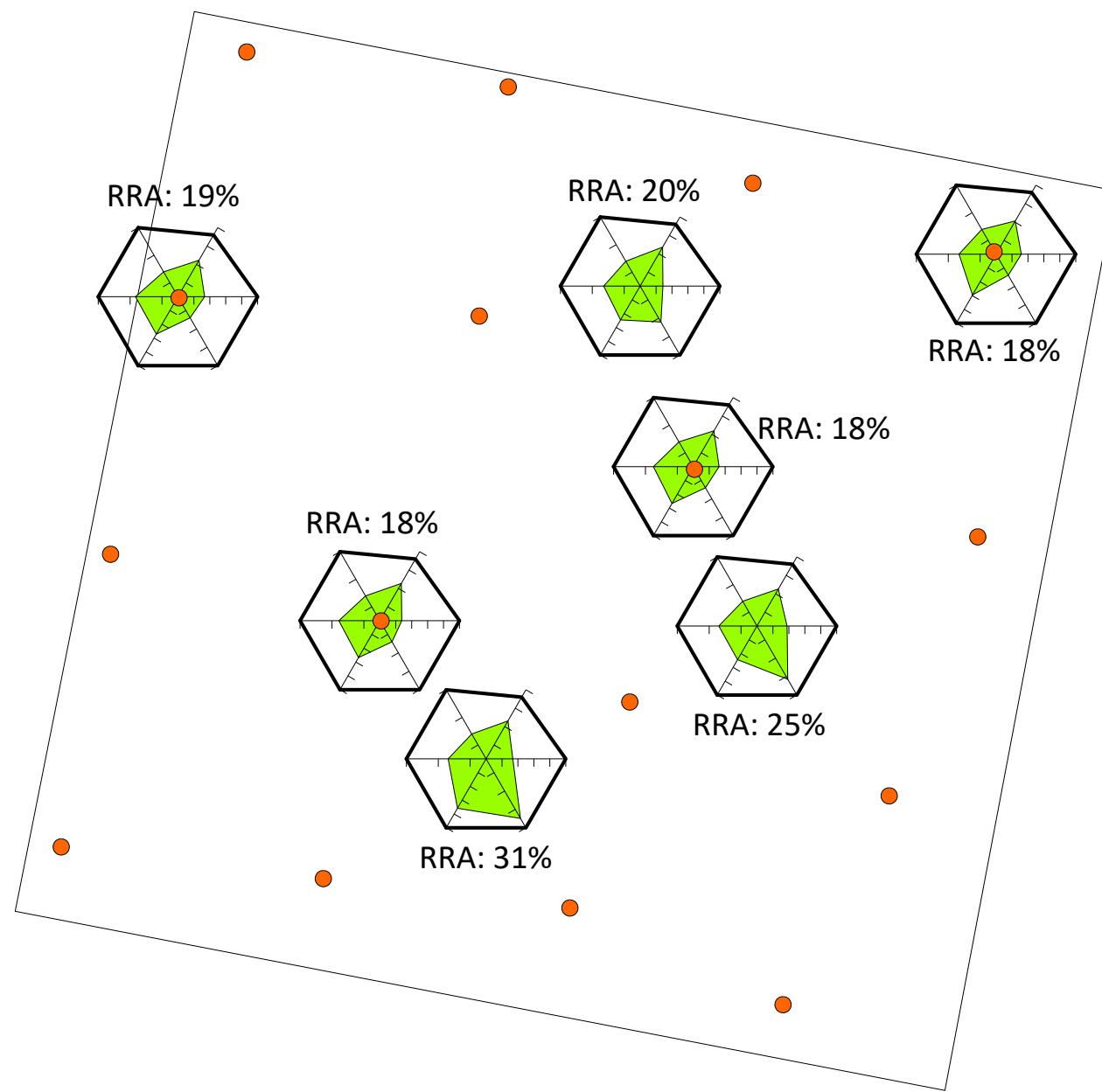
Days after start of Phase II injection: -

Phase I injection well

Redox Zone	RRA (%)
Aerobic	78-100
NO_3^-	62-78
Mn(II)	53-62
Fe(II)	35-53
SO_4^{2-}	20-35
CH_4	≤ 20



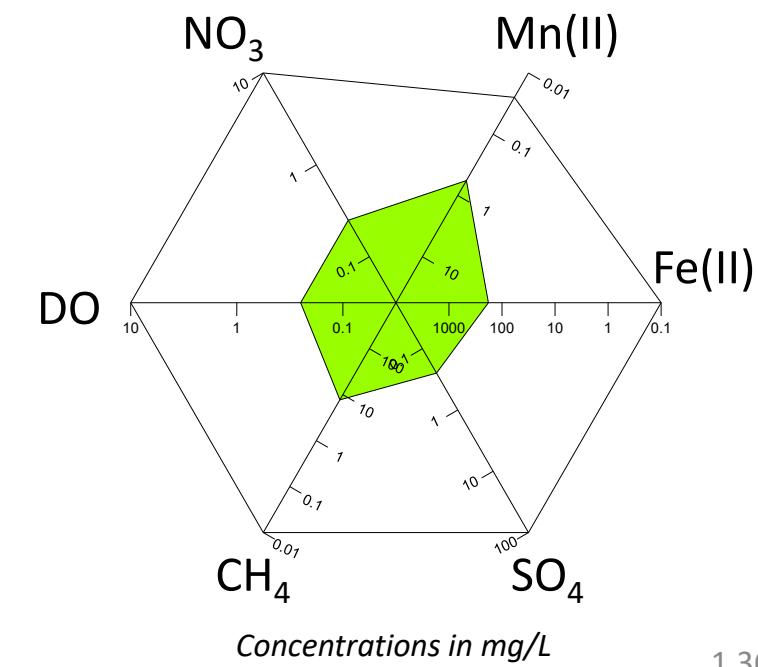
Redox Indicators Event 8: 2006-03-29



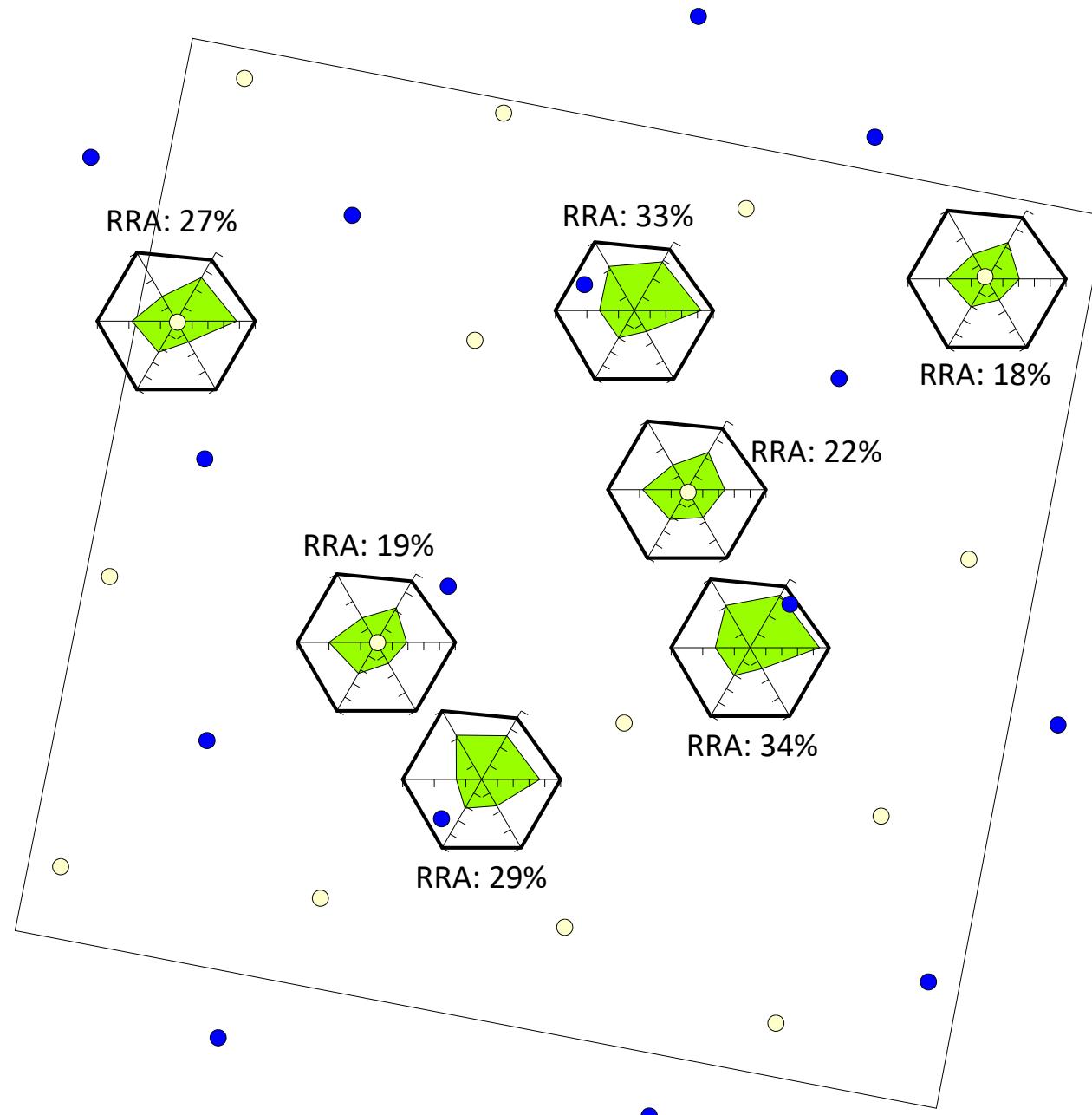
Redox Zone	RRA (%)
Aerobic	78-100
NO_3^-	62-78
Mn(II)	53-62
Fe(II)	35-53
SO_4^{2-}	20-35
CH_4	≤ 20

Days after start of Phase I injection: 685
Days after start of Phase II injection: -

Phase I injection well

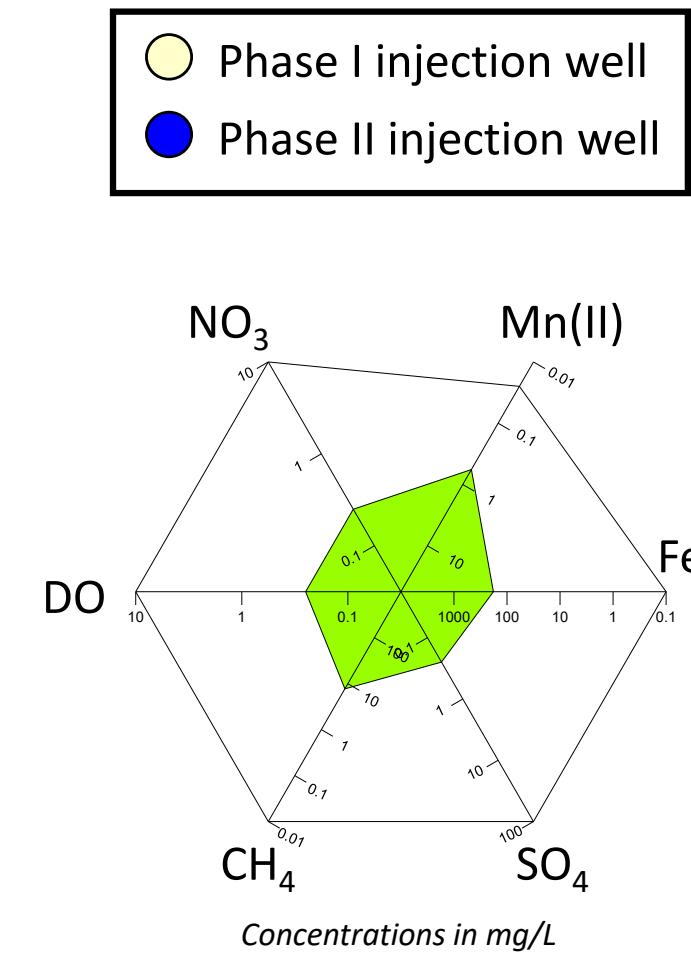


Redox Indicators Event 12: 2007-10-17

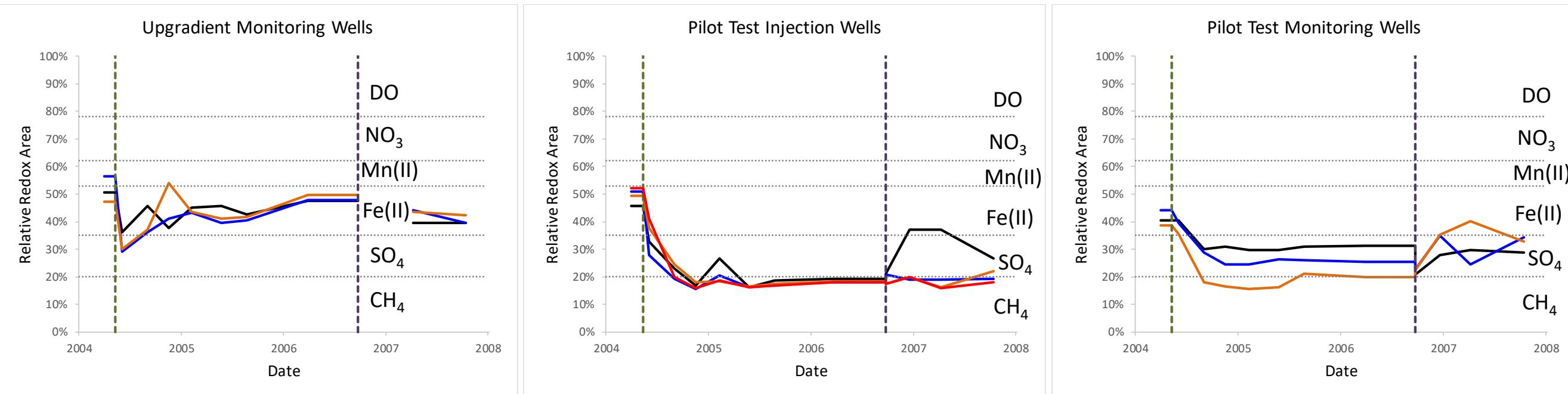


Days after start of Phase I injection: 1252
Days after start of Phase II injection: 386

Redox Zone	RRA (%)
Aerobic	78-100
NO_3^-	62-78
Mn(II)	53-62
Fe(II)	35-53
SO_4^{2-}	20-35
CH_4	≤ 20



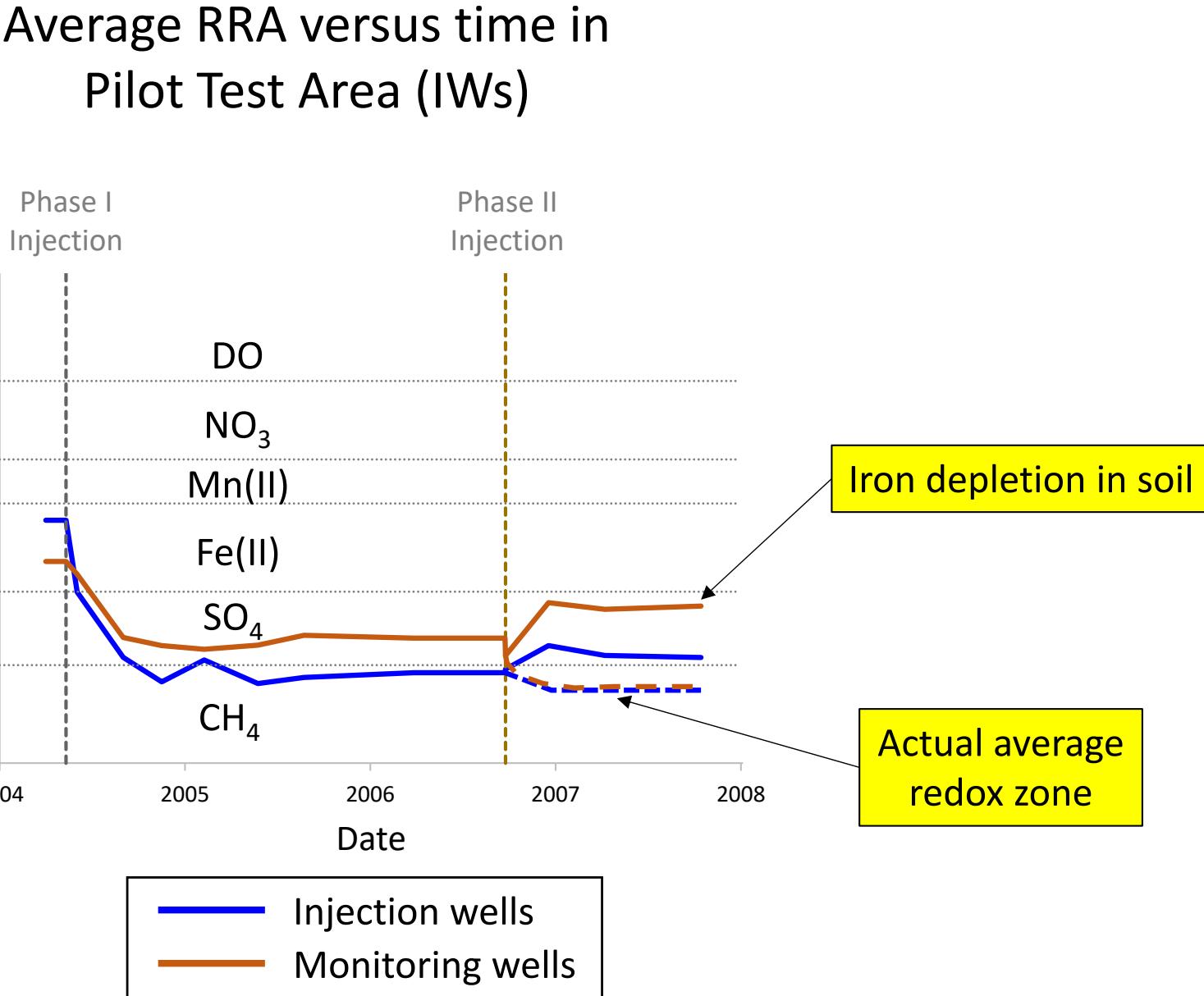
Relative Redox Area versus Time



Redox Zone	RRA (%)
Aerobic	78-100
NO ₃	62-78
Mn(II)	53-62
Fe(II)	35-53
SO ₄	20-35
CH ₄	≤20

Charleston Naval Weapons Station

Location	Days Since Injection 5/13/2004	Sample Date	Dissolved Oxygen (mg/L)	Nitrate (mg/L)	Manganese (mg/L)	Dissolved Iron (mg/L)	Sulfate (mg/L)	Methane (µg/L)
17PSI-02	-43	3/31/04	1.48	<0.5	0.390	33	91.5	53.2
17PSI-02	20	6/2/04	0.39	<0.5	0.570	150	18.0	47.4
17PSI-02	111	9/1/04	0.42	<0.5	0.510	130	<0.5	42.6
17PSI-02	188	11/17/04	0.14	<0.5	0.530	210	<0.5	256.3
17PSI-02	271	2/8/05	0.44	1.0/1.0	0.550	210	0.95	429.6
17PSI-02	377	5/25/05	0.19	<0.5	0.660	210	<0.5	1135
17PSI-02	468	8/24/05	0.35	<0.5	0.630	180	<0.5	812.8
17PSI-02	684	3/28/06	0.68	<0.5	0.590	210	<0.5	1933.2
17PSI-02	865	9/25/06	0.62	<0.5	0.530	60	<0.5	1366.9
17PSI-02	951	12/20/06	NM	<0.5	0.100	6.9	28.3	2135.8
17PSI-02	1062	4/10/07	0.36	<0.5	0.300	6.6	32.8/35.8	9433.9
17PSI-02	1252	10/17/07	0.80	<0.5	0.230	1.5	<0.5	5269.8
17PSI-07	-43	3/31/04	3.93	<0.5	0.370	24	102.5	40.7
17PSI-07	20	6/2/04	0.60	<0.5	0.710	180	1.8	53.7
17PSI-07	111	9/1/04	0.13	<0.5	0.820	300	0.5	26.6
17PSI-07	188	11/17/04	0.09	<0.5	0.740	240	<0.5	156.3
17PSI-07	271	2/8/05	0.48	<0.5	0.790	320	<0.5	151.7
17PSI-07	377	5/25/05	0.26	<0.5	0.810	310	<0.5	1469.4
17PSI-07	468	8/24/05	0.39	<0.5	0.710	260	<0.5	1816.0
17PSI-07	684	3/28/06	0.61	<0.5	0.530	420	<0.5	2121.1
17PSI-07	865	9/25/06	1.81	<0.5	0.620	320	<0.5	2684.9
17PSI-07	951	12/20/06	0.62	<0.5	0.750	220	<0.5/0.7	5509.0
17PSI-07	1062	4/10/07	0.98	<0.5	0.700	250	<0.5	4086.0
17PSI-07	1252	10/17/07	1.00	<0.5	0.720	120	<0.5	5377.2
17PSI-10	-43	3/31/04	4.05	<0.5	0.400	29	58.7	35.5
17PSI-10	20	6/2/04	0.47	<0.5	0.320	150	53.5/52.6	16.9
17PSI-10	111	9/1/04	0.26	<0.5	0.700	130	0.5	20.1
17PSI-10	188	11/17/04	0.14	<0.5	0.940	190	<0.5	27.2
17PSI-10	271	2/8/05	0.41	<0.5	0.630	220	<0.5	851.9
17PSI-10	377	5/25/05	0.32	<0.5	0.800	220	<0.5	2626.4
17PSI-10	468	8/24/05	0.45	<0.5	1.200	190	<0.5	1884.3
17PSI-10	684	3/28/06	0.56	<0.5	0.640	240	<0.5	2152.8
17PSI-10	866	9/26/06	0.52	<0.5	0.720	210	<0.5	4147.0
17PSI-10	951	12/20/06	0.74	<0.5	0.590	170	0.7	5972.8
17PSI-10	1062	4/10/07	0.51	<0.5	0.750	200	<0.5	9999.4
17PSI-10	1252	10/17/07	0.80	<0.5	0.510	40	<0.5/0.6	6651.4
17PSI-13	-43	3/31/04	4.66	<0.5	0.610	53	102.6	13.4
17PSI-13	20	6/2/04	0.74	<0.5	0.920	120	82.6	17.5
17PSI-13	111	9/1/04	0.19	<0.5	0.840	200	<0.5	14.3
17PSI-13	187	11/16/04	0.10	<0.5/0.5	0.920	210	<0.5/0.5	78.7
17PSI-13	271	2/8/05	0.39	<0.5	0.880	190	<0.5	534.5
17PSI-13	376	5/24/05	0.29	<0.5/0.5	0.800	160	<0.5/0.5	3441.6
17PSI-13	468	8/24/05	0.35	<0.5	0.990	160	<0.5	2550.7
17PSI-13	684	3/28/06	NA	<0.5	0.880	260	<0.5	1105.7
17PSI-13	866	9/26/06	0.56	<0.5	0.830	180	<0.5	5069.7
17PSI-13	951	12/20/06	0.81	<0.5	0.850	260	1.1	5540.8
17PSI-13	1062	4/10/07	0.46	<0.5	0.840	280	<0.5	7879.1
17PSI-13	1252	10/17/07	0.60	<0.5	0.570	90	<0.5	9099.5
17PS-01	-42	4/1/04	0.67	<0.5	0.630	78	65.5	27.2
17PS-01	20	6/2/04	1.14	<0.5	0.720	120	44.1/44.6	25.8
17PS-01	111	9/1/04	0.15	<0.5	0.540	110	15.3	37.7
17PS-01	187	11/16/04	0.17	<0.5	0.780	130	23.4	33.1
17PS-01	271	2/8/05	0.23	<0.5	0.680	150	27.9	145.0
17PS-01	377	5/25/05	0.34	<0.5	0.690	130	20.3	231.9
17PS-01	468	8/24/05	0.33	<0.5	0.570	190	21.6	92.2
17PS-01	685	3/29/06	0.49	<0.5	0.490	210	30.9	261.2
17PS-01	866	9/26/06	0.81	<0.5	0.690	110	<0.5	1232.6
17PS-01	951	12/20/06	NA	<0.5	0.190	7.2	1.4	7415.3
17PS-01	1062	4/10/07	0.72	<0.5	0.050	1.0	<0.5	11308.5
17PS-01	1252	10/17/07	0.20	1.3	0.230	2.1	0.5	7759.2
17PS-02	-42	4/1/04	1.50	<0.5	0.560	50	58	30.8
17PS-02	20	6/2/04	3.36	<0.5	0.740	81	5.4	30.6
17PS-02	111	9/1/04	0.14	<0.5	0.570	170	15.0	36.7
17PS-02	187	11/16/04	0.16	<0.5	0.590	150	2.8	66.0
17PS-02	271	2/8/05	0.20	<0.5/0.5	0.520	120	10.0	1144.8
17PS-02	377	5/25/05	0.47	<0.5	0.660	92	6.7	1176.5
17PS-02	468	8/24/05	0.32	<0.5	0.540	150	20.8	1681.8
17PS-02	685	3/29/06	0.50	<0.5	0.550	130	14	3639.3
17PS-02	866	9/26/06	0.48	<0.5	0.620	170	2.8	2133.3
17PS-02	951	12/20/06	NA	<0.5	0.180	1.10	9.6	9880.6
17PS-02	1062	4/10/07	0.75	<0.5	0.260	12.0	<0.5/0.57	8896.9
17PS-02	1252	10/17/07	0.40	1.1	0.075	0.41	<0.5	9148.4
17PS-03	-42	4/1/04	0.40	<0.5	0.680	69	77.5	36.0
17PS-03	20	6/2/04	1.22	<0.5	0.810	110	10.0	50.7
17PS-03	111	9/1/04	0.14	<0.5	0.460	130	<0.5	173.3
17PS-03	187	11/16/04	0.18	<0.5/0.5	0.800	200	0.5/0.5	2062.5
17PS-03	271	2/8/05	0.25	<0.5	0.570	180	<0.5	7737.5
17PS-03	377	5/25/05	0.31	<0.5	0.700	180	<0.5	4428.3
17PS-03	468	8/24/05	0.37	<0.5	0.470	190	2.10	3136.5
17PS-03	685	3/29/06	0.44	<0.5	0.430	370	1.8	3522.2
17PS-03	866	9/26/06	0.57	<0.5	0.580	96	1.9	4852.4
17PS-03	951	12/20/06	NA	<0.5	0.170	1.1	9.6/9.5	9639.1
17PS-03	1062	4/10/07	0.68	<0.5	0.055	0.38	5.0	4281.3
17PS-03	1252	10/17/07	0.40	1.3	0.120	0.58	<0.5	10127.1



Relative Redox Area Findings

- CHECK RRA RESULTS – Do they make sense?
- Single metric that integrates trends for 5-6 redox indicators, relative to aerobic conditions
- Good predictor of dominant redox processes
- Useful for contouring key redox zones (e.g. aerobic, moderately anaerobic, and strongly anaerobic)
- Higher uncertainty at RRA transition points
- RRA limitations:
 - Downgradient transport of indicators (e.g. methane)
 - Concomitant redox processes

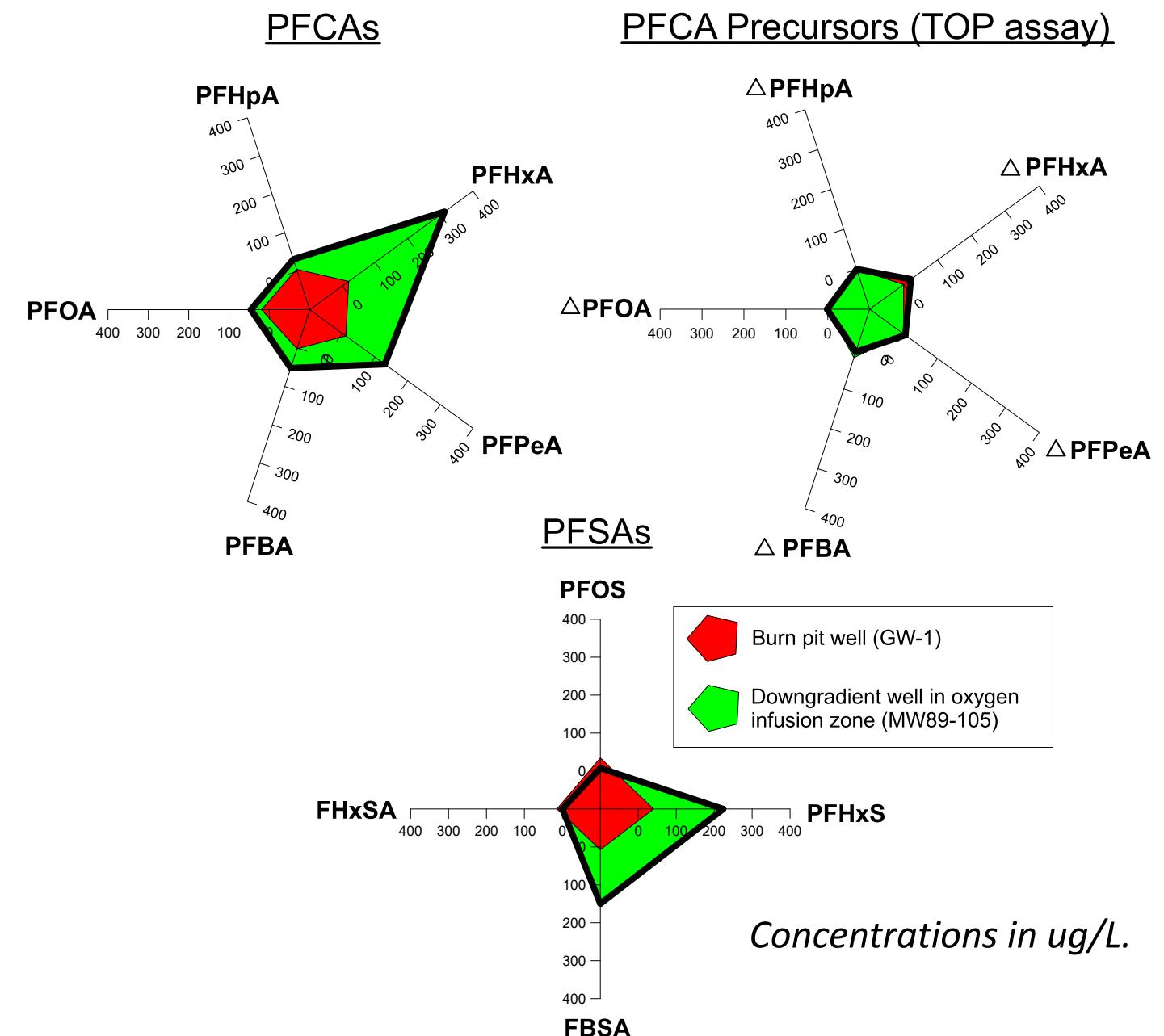
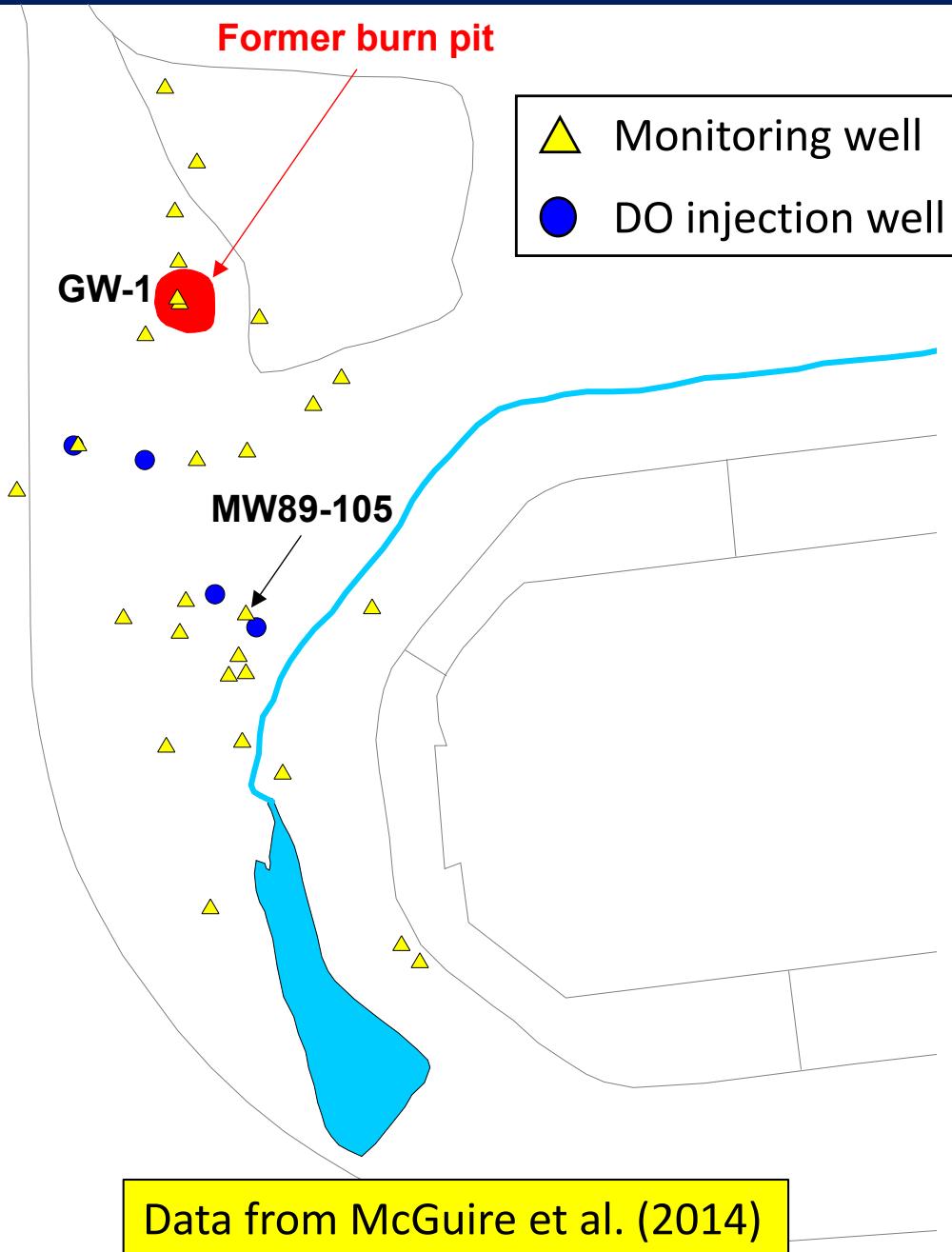
Potential RRA Zones for delineation:

1. Aerobic
2. Nitrate-reducing
3. Manganese / Iron-reducing
4. Sulfate-reducing / Methanogenesis

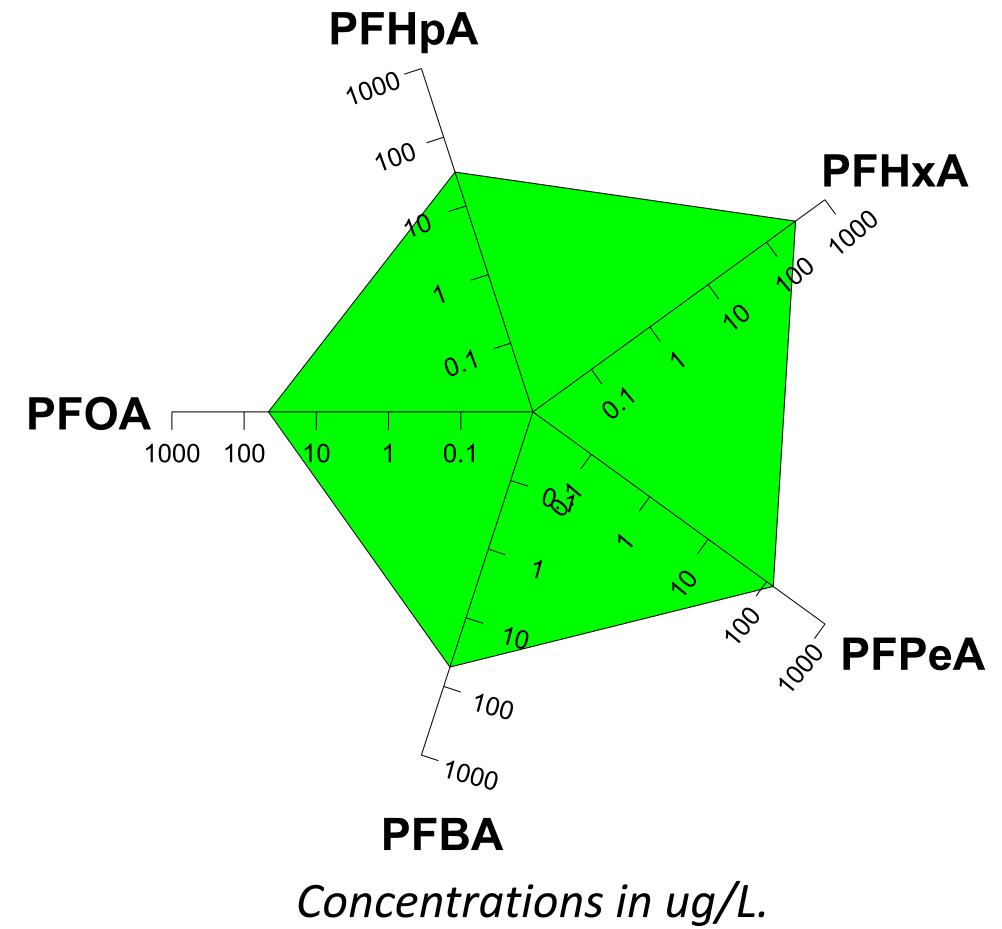
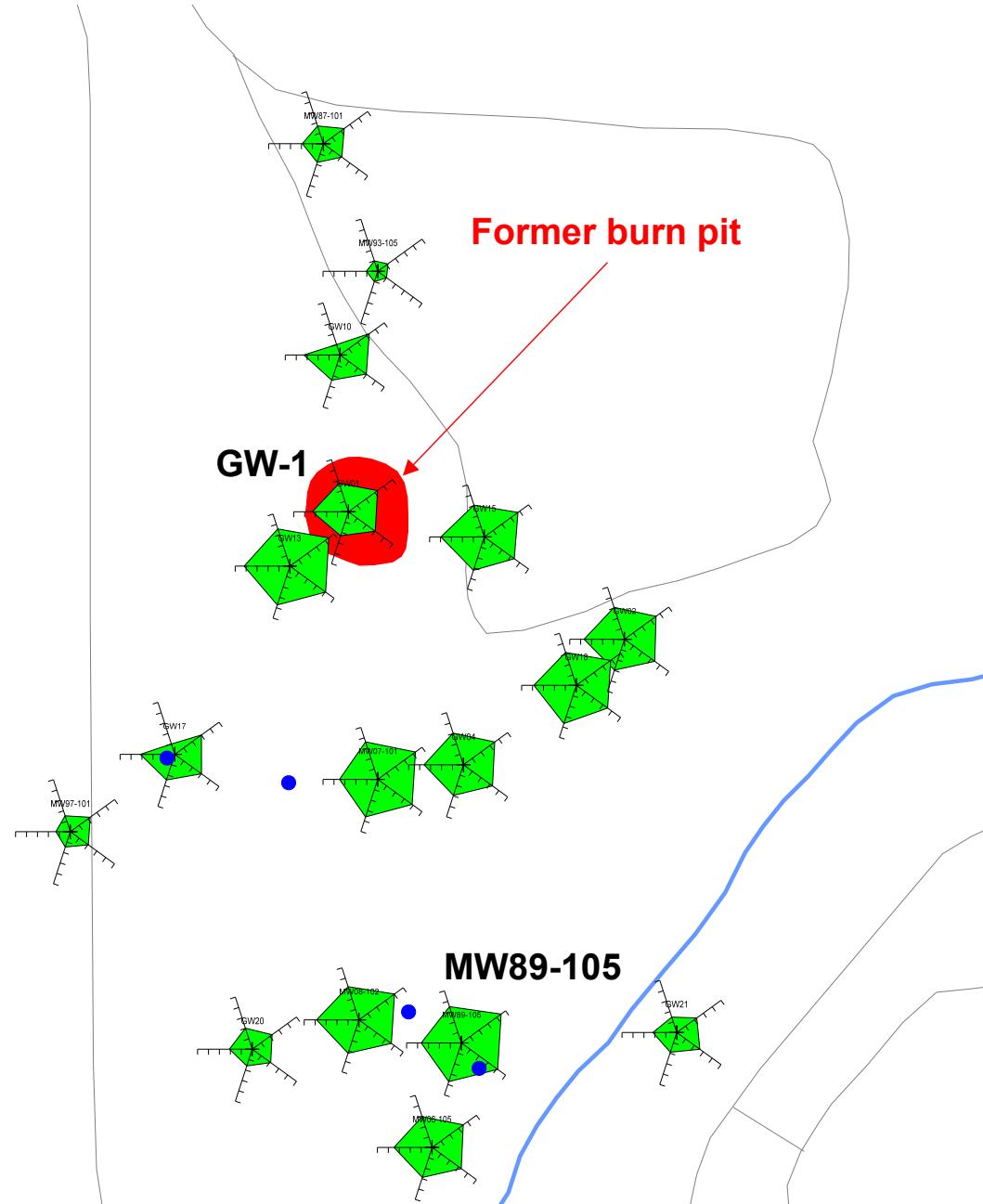
PFAS Radial Diagrams

Section 1.4

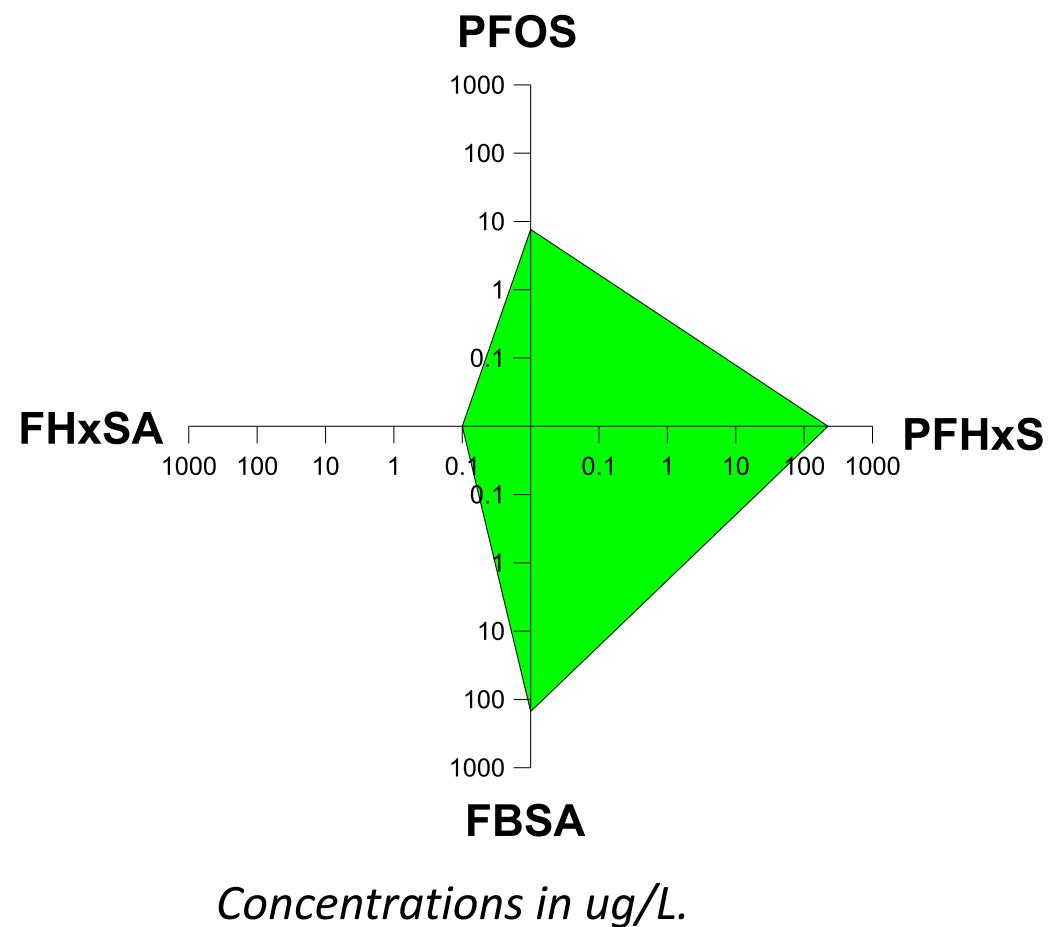
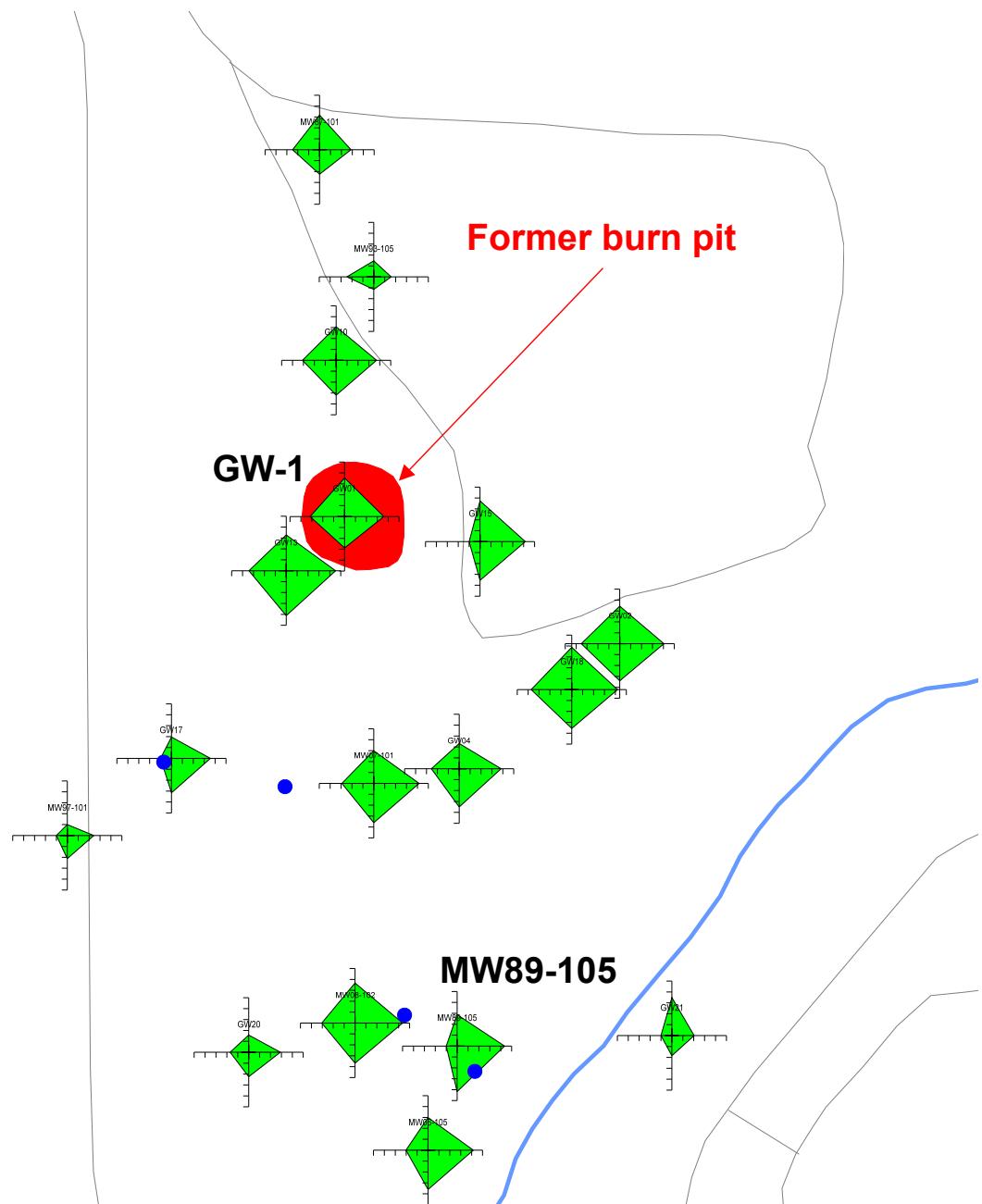
PFAS at Ellsworth Air Force Base



PFCAs



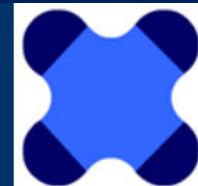
PFSAs



Key Functionality for Radial Diagrams

- Axes can increase in concentration away from, or towards the origin of the radial diagram
- Each axis has option of log or arithmetic scale
- Multiple events and reference data series
 - e.g. background redox indicators, or source zone VOCs
- Option to shade in one or more data series, different line colors
- Symbols to represent non-detects, and/or MCL exceedances

FREE Visual Bio Software



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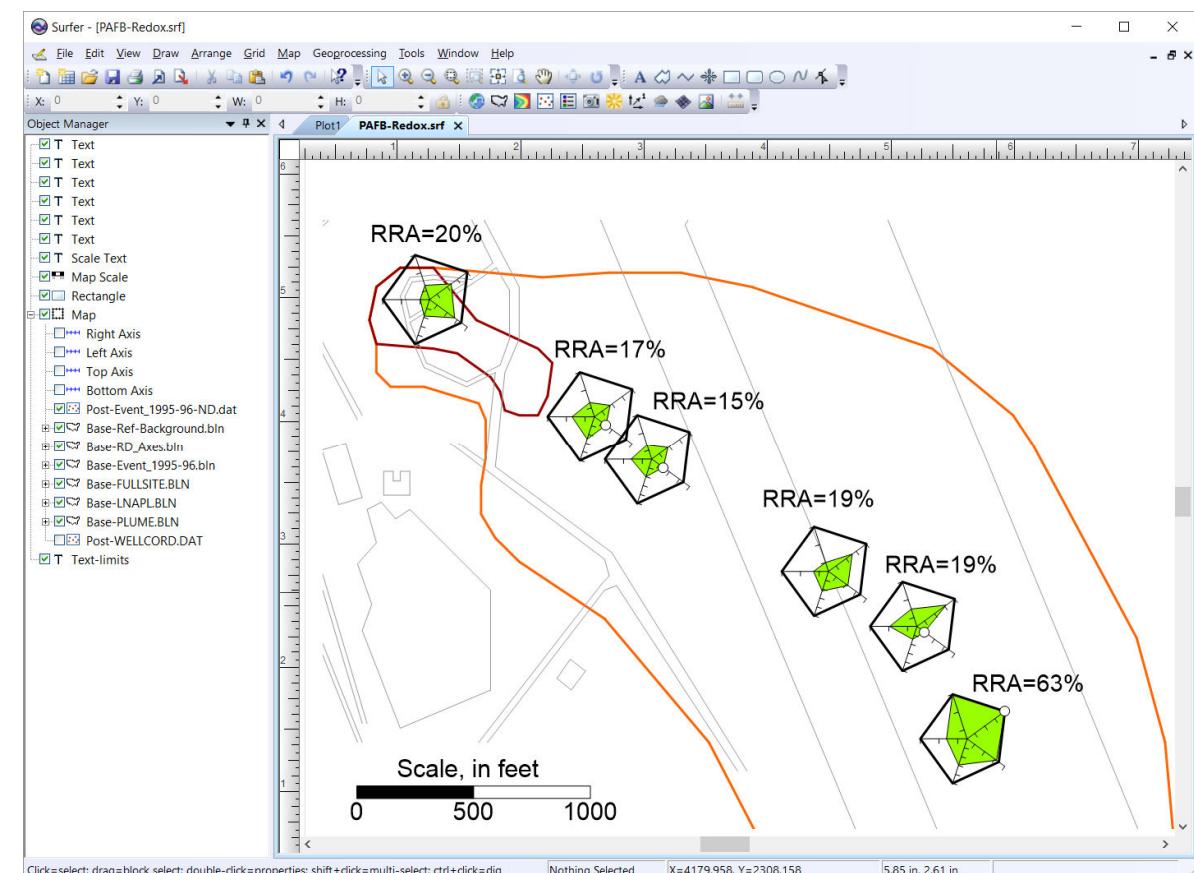
Visual Bio Software

Text Input Files

RD_Properties.dat - Notepad

```
File Edit Format View Help
PAFB - Redox
 5
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2 108 151 2 0.1 10. 1 3 -1. 'Line 3.2: NO3 ScaleFlag, angle, chemID, unitID, Min, Max, Direction, nMajorTicks, MCL
2 36 173 2 0.1 100. -1 4 -1. 'Line 3.3: Fe2+ ScaleFlag, angle, chemID, unitID, Min, Max, Direction, nMajorTicks, MCL
2 324 160 2 0.1 100. 1 4 -1. 'Line 3.4: SO4 ScaleFlag, angle, chemID, unitID, Min, Max, Direction, nMajorTicks, MCL
2 252 175 2 0.001 10. -1 5 -1. 'Line 3.5: CH4 ScaleFlag, angle, chemID, unitID, Min, Max, Direction, nMajorTicks, MCL
6
1 A
2 B
3 C
4 D
5 E
6 F
1
1 Event_1995-96
1 2
Ref-Background
10. 10. -0.05 25. -0.001
2
200.
0
0.1
1
0
'Line 2: nRD_Axes
'Line 4: nRD_well
'Line 5.1: well ID
'Line 5.2: well ID
'Line 5.3: well ID
'Line 5.4: well ID
'Line 5.5: well ID
'Line 5.6: well ID
'Line 6: nRD_EventSeries
'Line 7.1: Event ID, Filename
'Line 8: nRD_Refseries, input unitsID
'Line 9.1: Ref Series filename
'Line 10: Background redox reference concentrations
'Line 11: NDflag (1=DL, 2=0.5*DL, 3=axis minimum)
'Line 12: axis length (map units)
'Line 13: Calculate ratio of detected parent to daughter products? (0=no, 1=yes)
'Line 15: TickLengthMajorP
'Line 16: Output symbols for Event series? (0=no, 1=yes)
'Line 17: Output symbols for Reference series? (0=no, 1=yes)
```

Golden Surfer® for Making Figures



Questions



Grant Carey, Ph.D.
Porewater Solutions

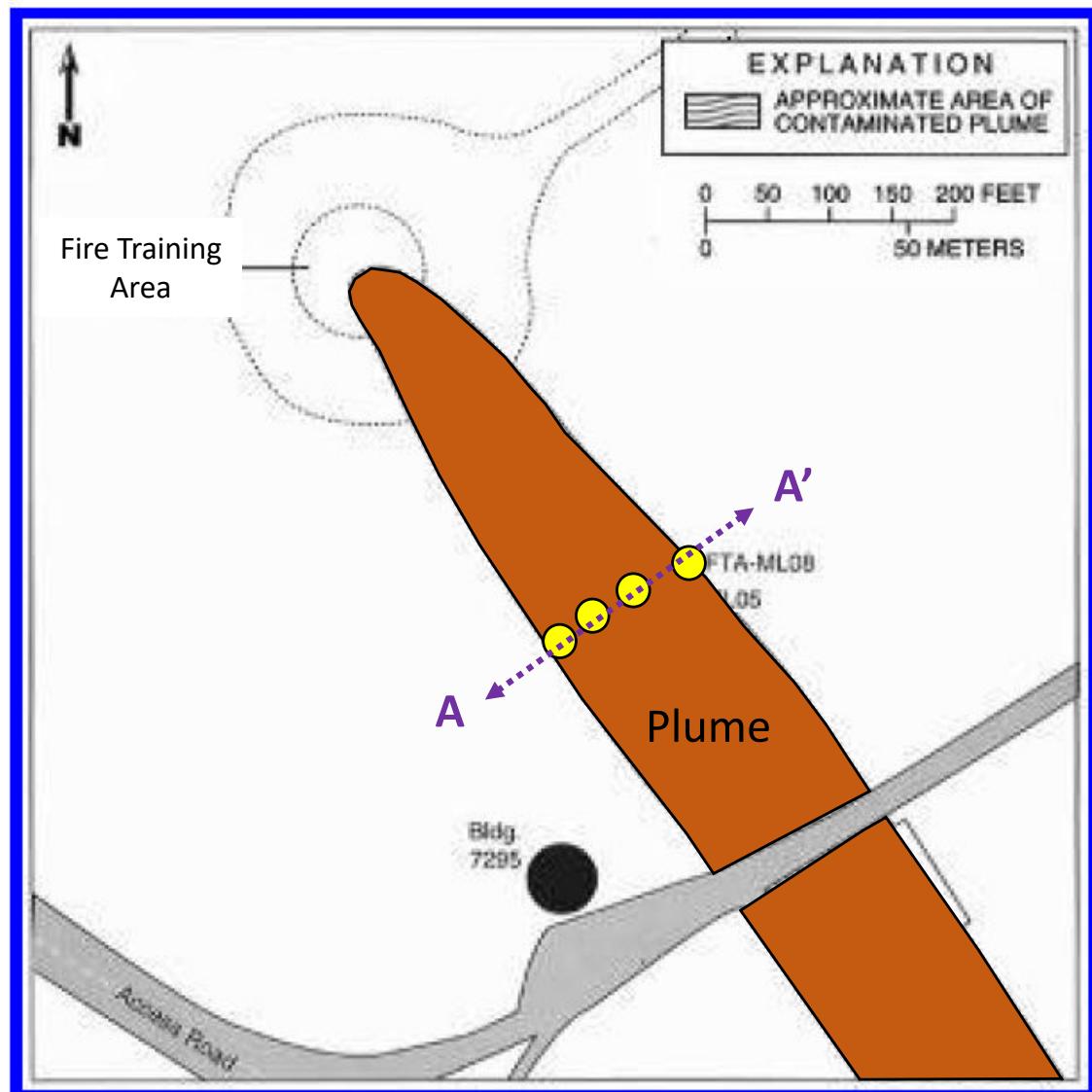
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Supplemental Slides

Wurtsmith Air Force Base Case Study

Section 3.3

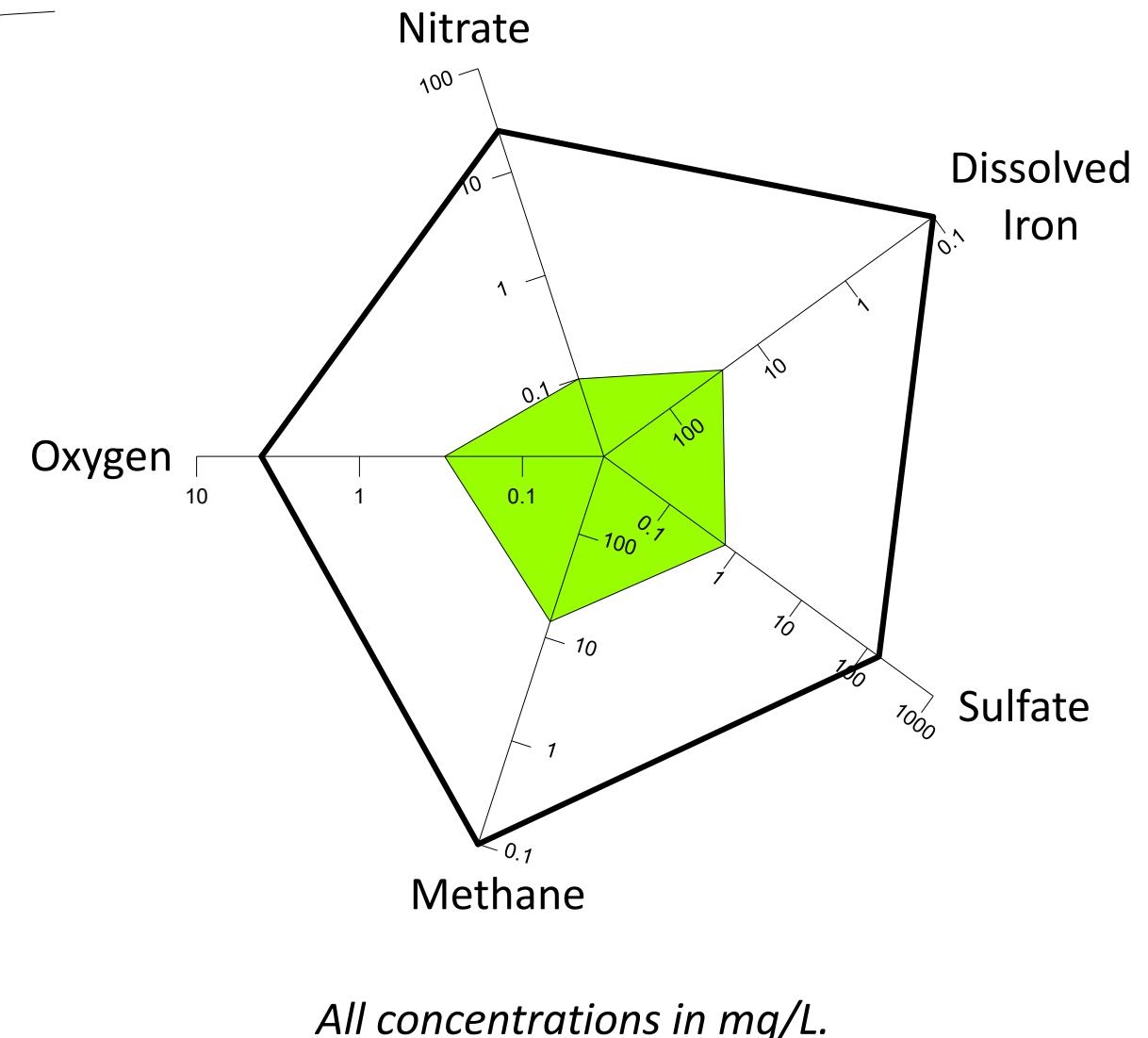
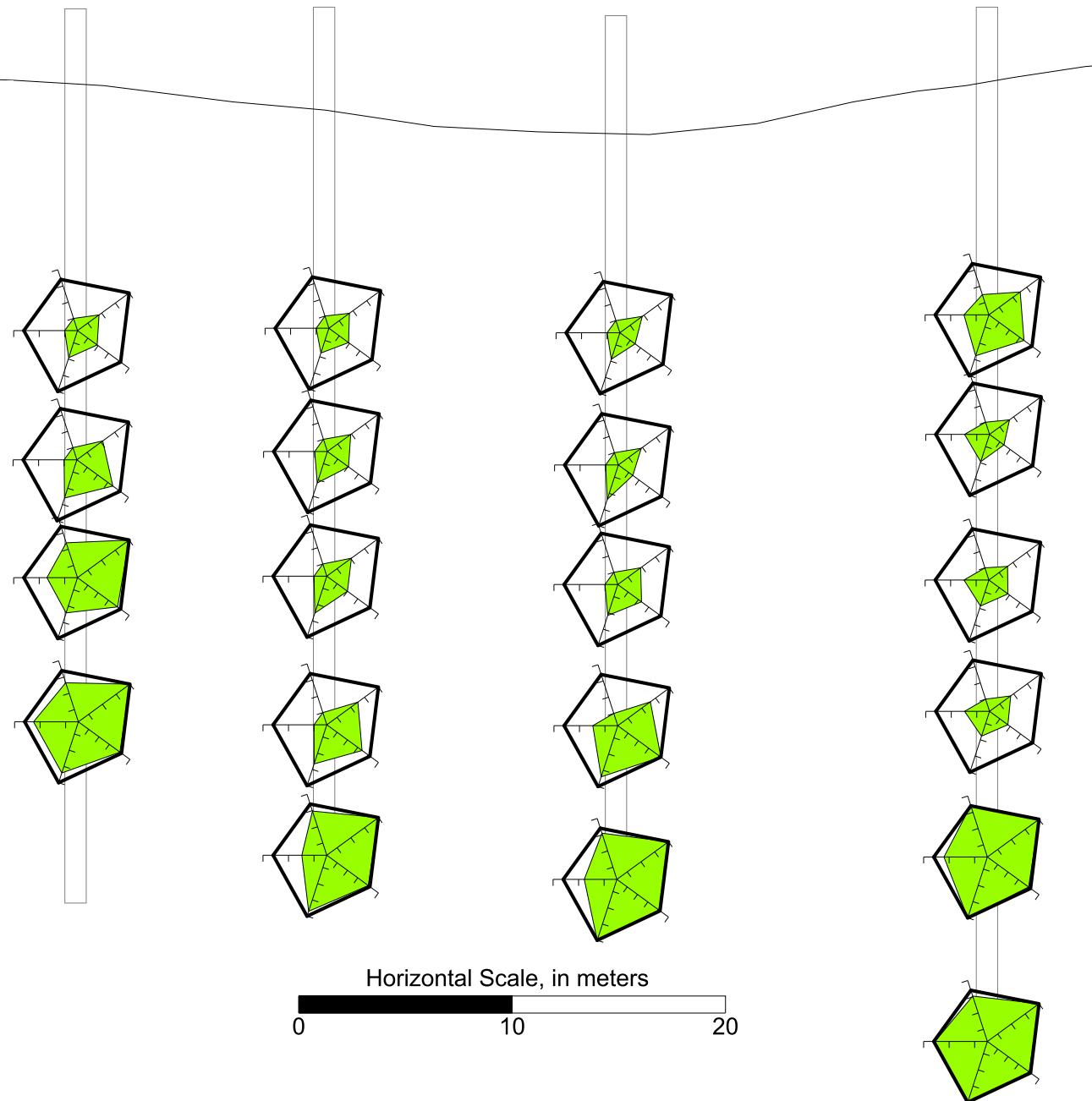
Wurtsmith Air Force Base, Michigan



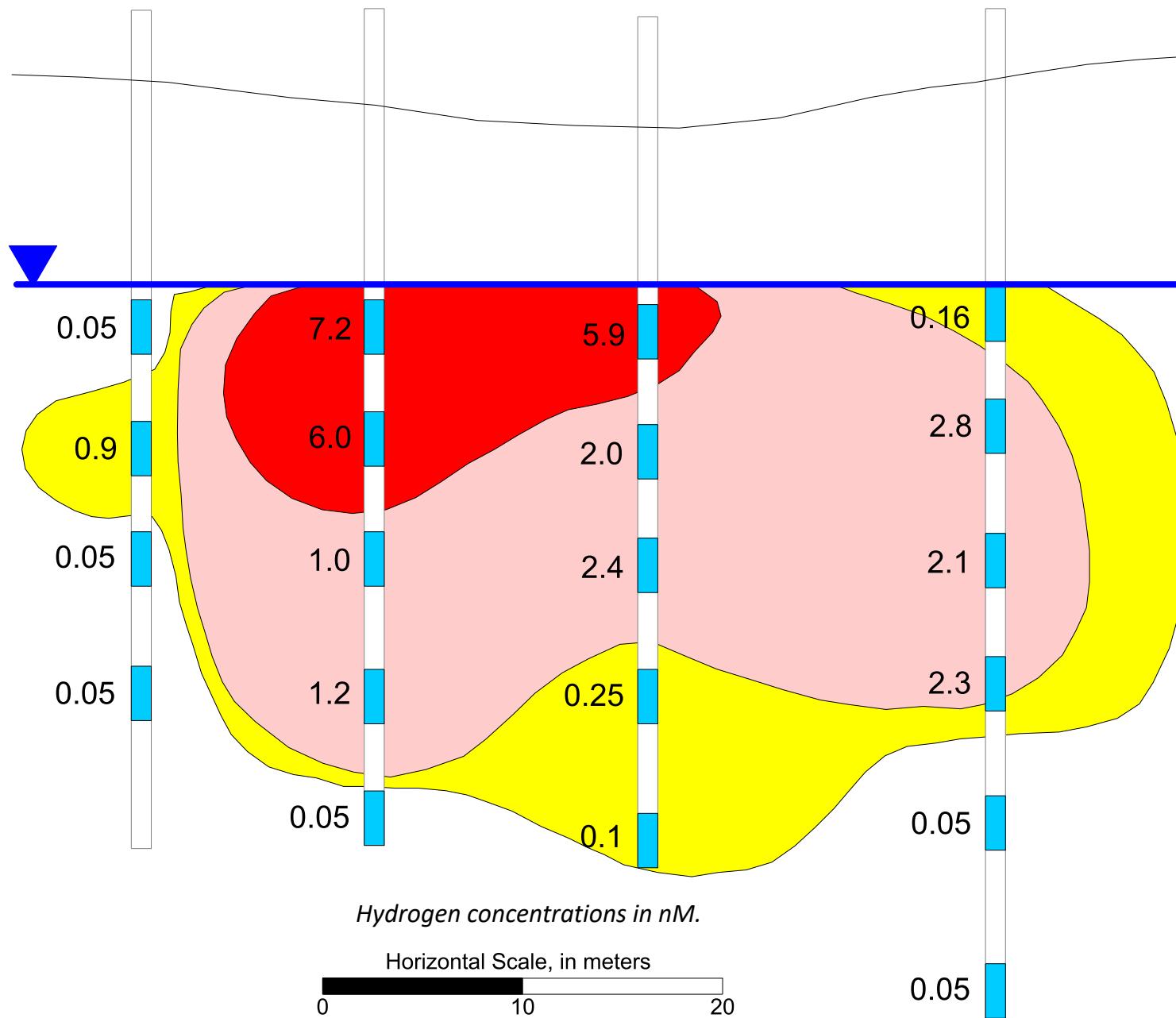
- Chlorinated solvents and petroleum hydrocarbons used to start fires (1952-86)
- Contaminants seeped to underlying water table (5-8 m bgs)
- Permeable sands and gravels
- Four multilevel wells
 - 1" diameter
 - 0.3 m screens, separated by 0.2 to 0.5 m

Chapelle et al. (Env. Sci. & Tech., 1996)

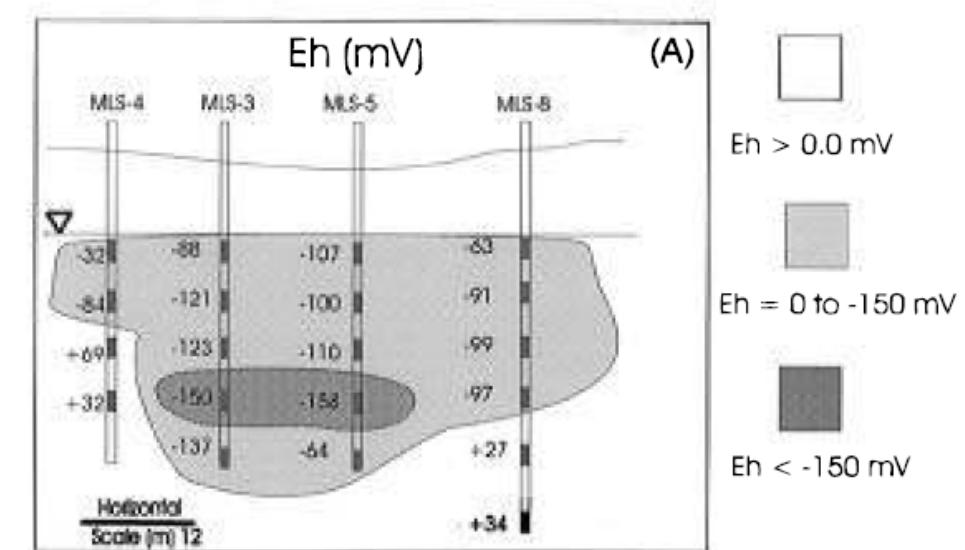
Redox Radial Diagrams



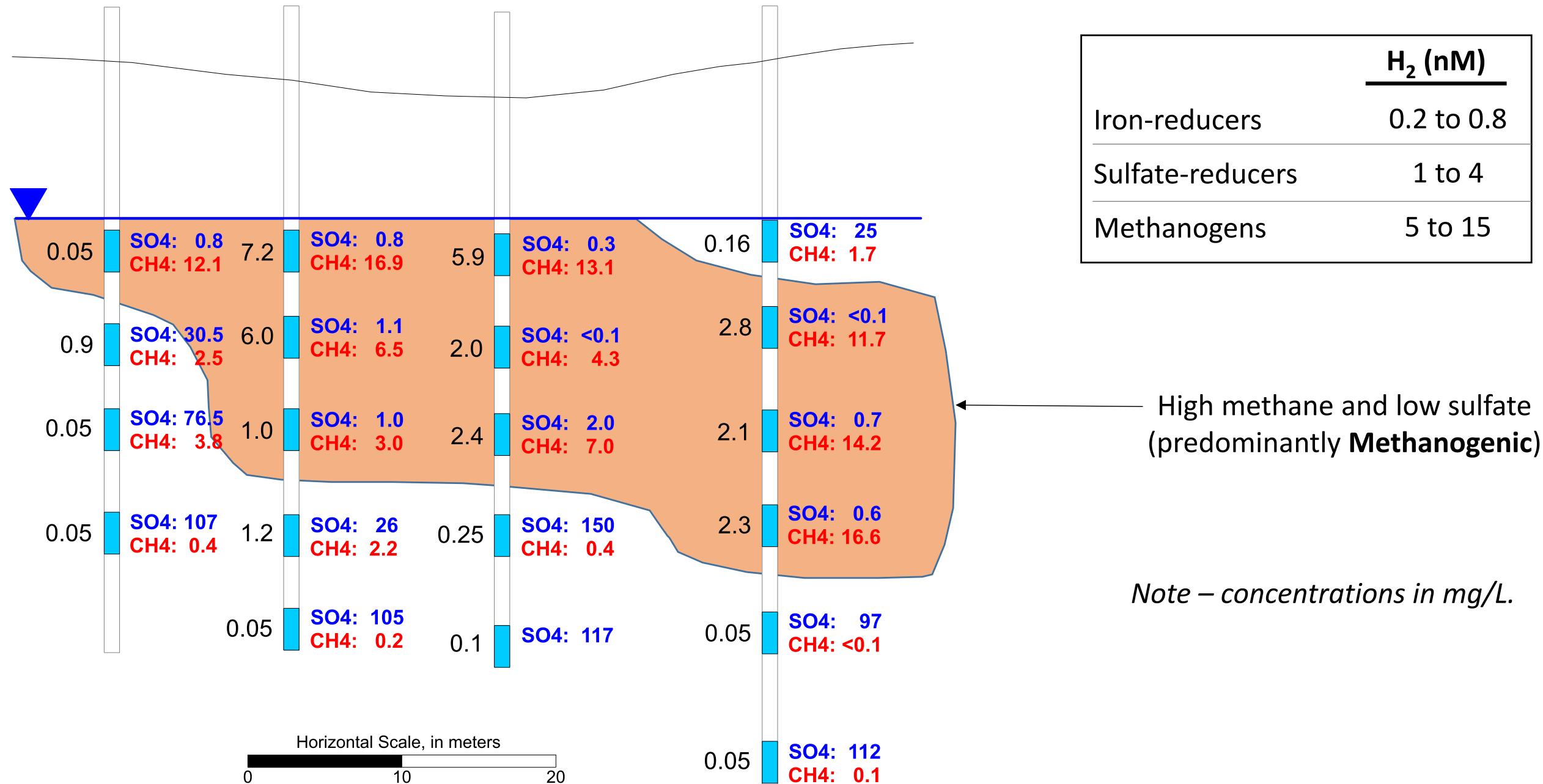
Hydrogen Concentrations (Chapelle et al., 1996)



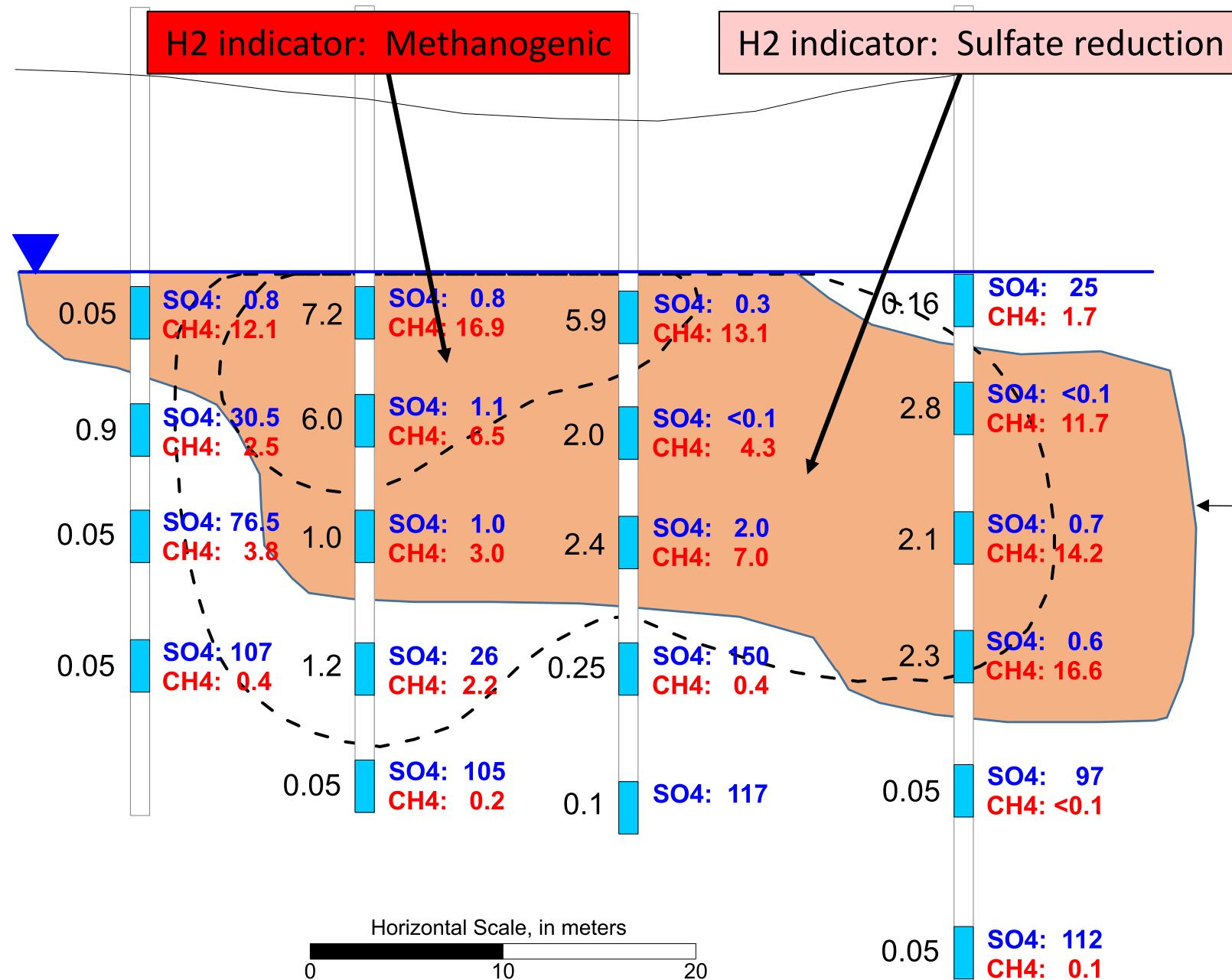
H_2 (nM)	
Iron-reducers	0.2 to 0.8
Sulfate-reducers	1 to 4
Methanogens	5 to 15



Hydrogen Concentrations (Chapelle et al., 1996)



Hydrogen Concentrations (Chapelle et al., 1996)



Chapelle et al. (1996):
“Because of these complexities,
using H₂ measurements as a
sole indicator of redox
processes is not appropriate.”

Delineating Redox Zones Based on Indicator Concentrations

Redox Processes and Water Quality of Selected Principal Aquifer Systems

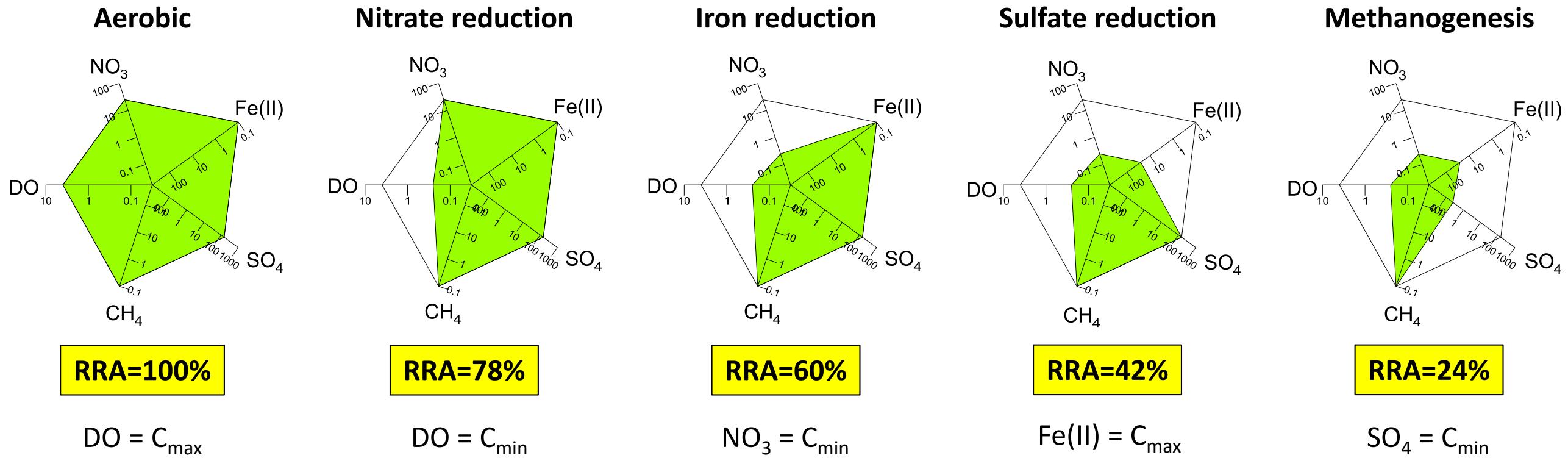
by P.B. McMahon¹ and F.H. Chapelle²

Ground Water, 2008, 46(2): 259-271

Redox Zone	Oxygen	Nitrate	Mn(II)	Fe(II)	SO4	Methane
Aerobic	≥0.5	--	<0.05	<0.1	--	--
Nitrate reduction	<0.5	≥0.5	<0.05	<0.1	--	--
Manganese reduction	<0.5	<0.5	≥0.5	<0.1	--	--
Iron / Sulfate reduction	<0.5	<0.5	<0.5	≥0.1	≥0.5	--
Methanogenesis	<0.5	<0.5	--	≥0.1	<0.5	--

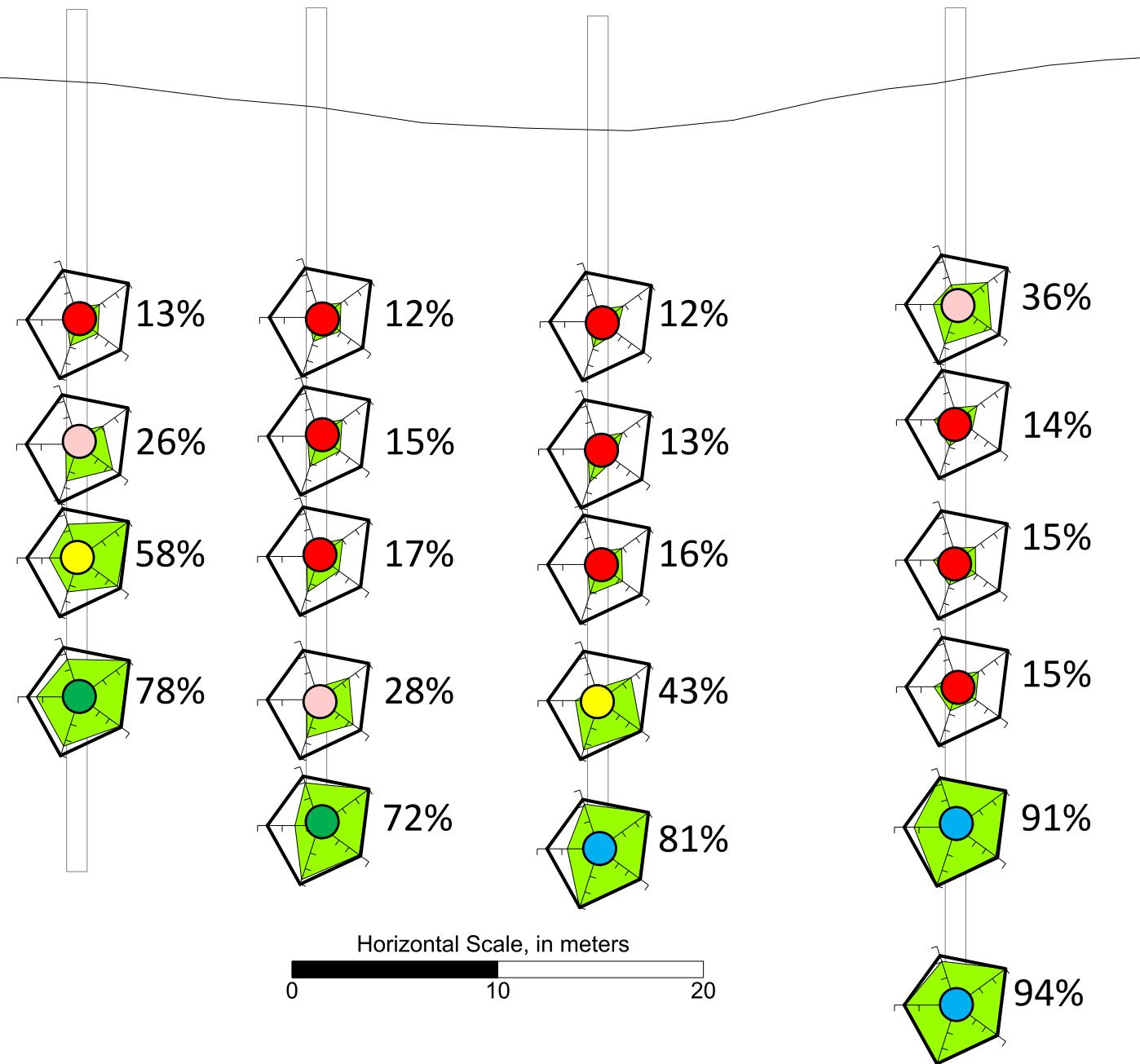
Wurtsmith Relative Redox Area by Zone

- Threshold Areas in Visual Bio – define RRA for the initial transition to each redox zone.

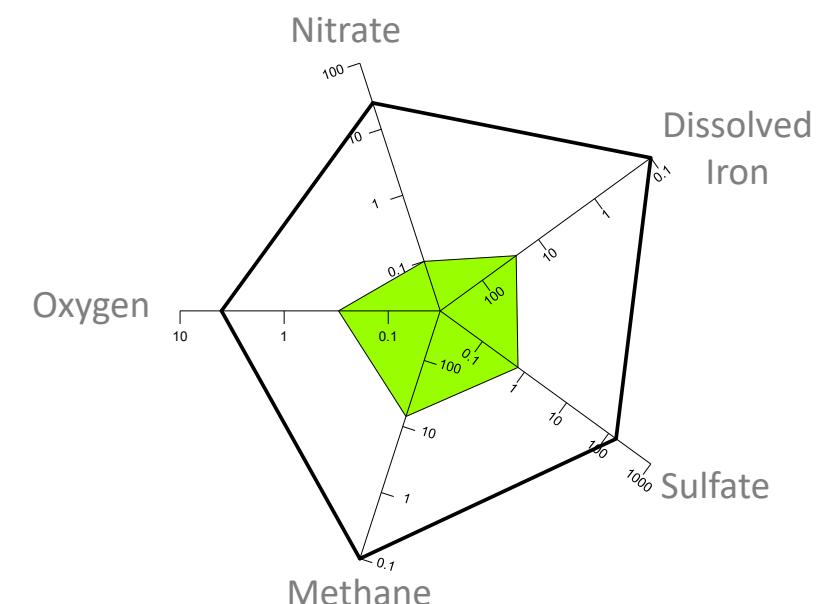


$$\text{Relative Redox Area (RRA)} = \frac{\text{Area of monitoring well polygon}}{\text{Area of reference polygon (Aerobic)}}$$

Relative Redox Area

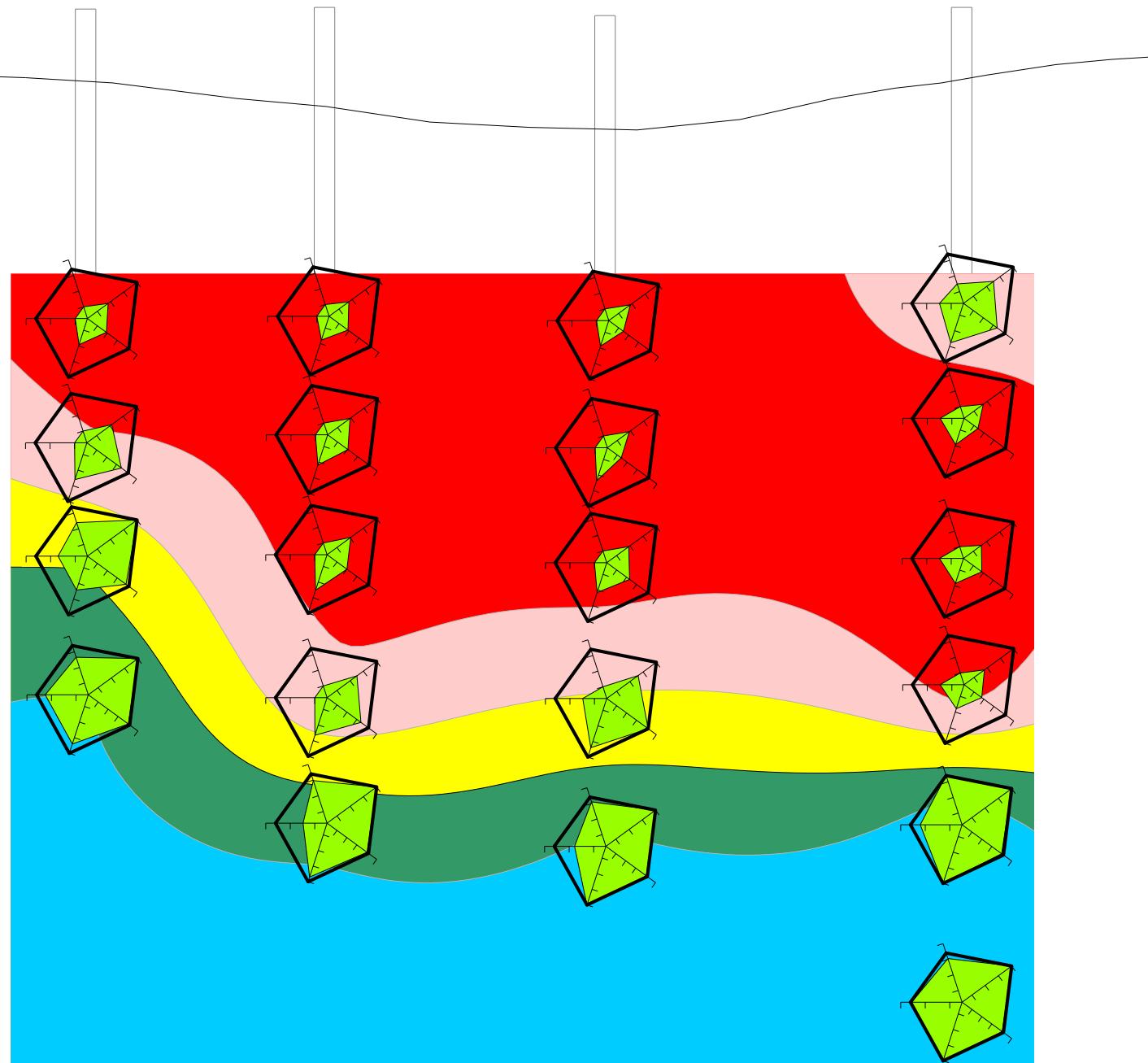


Aerobic:	78 to 100%	(Blue circle)
Nitrate-reducing:	60 to 78%	(Green circle)
Iron-reducing:	42 to 60%	(Yellow circle)
Sulfate-reducing:	24 to 42%	(Pink circle)
Methanogenic:	$\leq 24\%$	(Red circle)

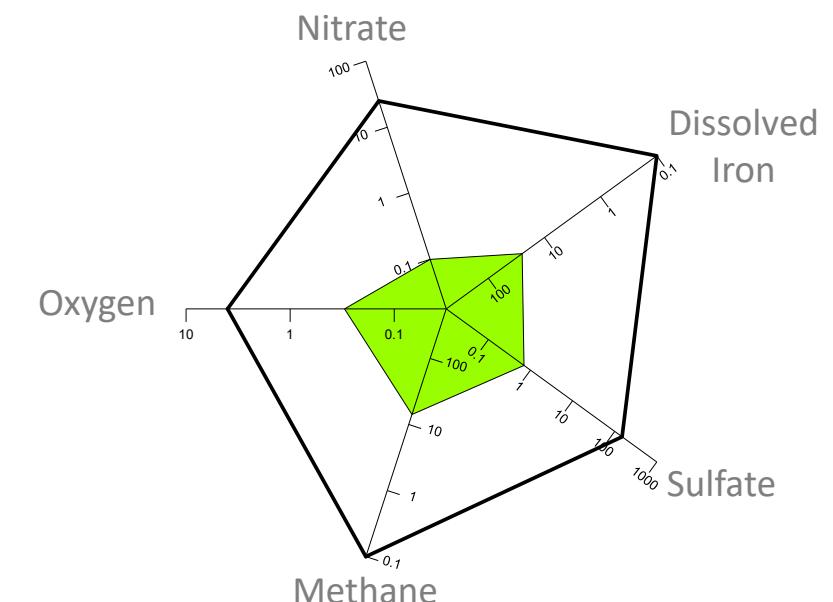


All concentrations in mg/L.

Relative Redox Area Contours

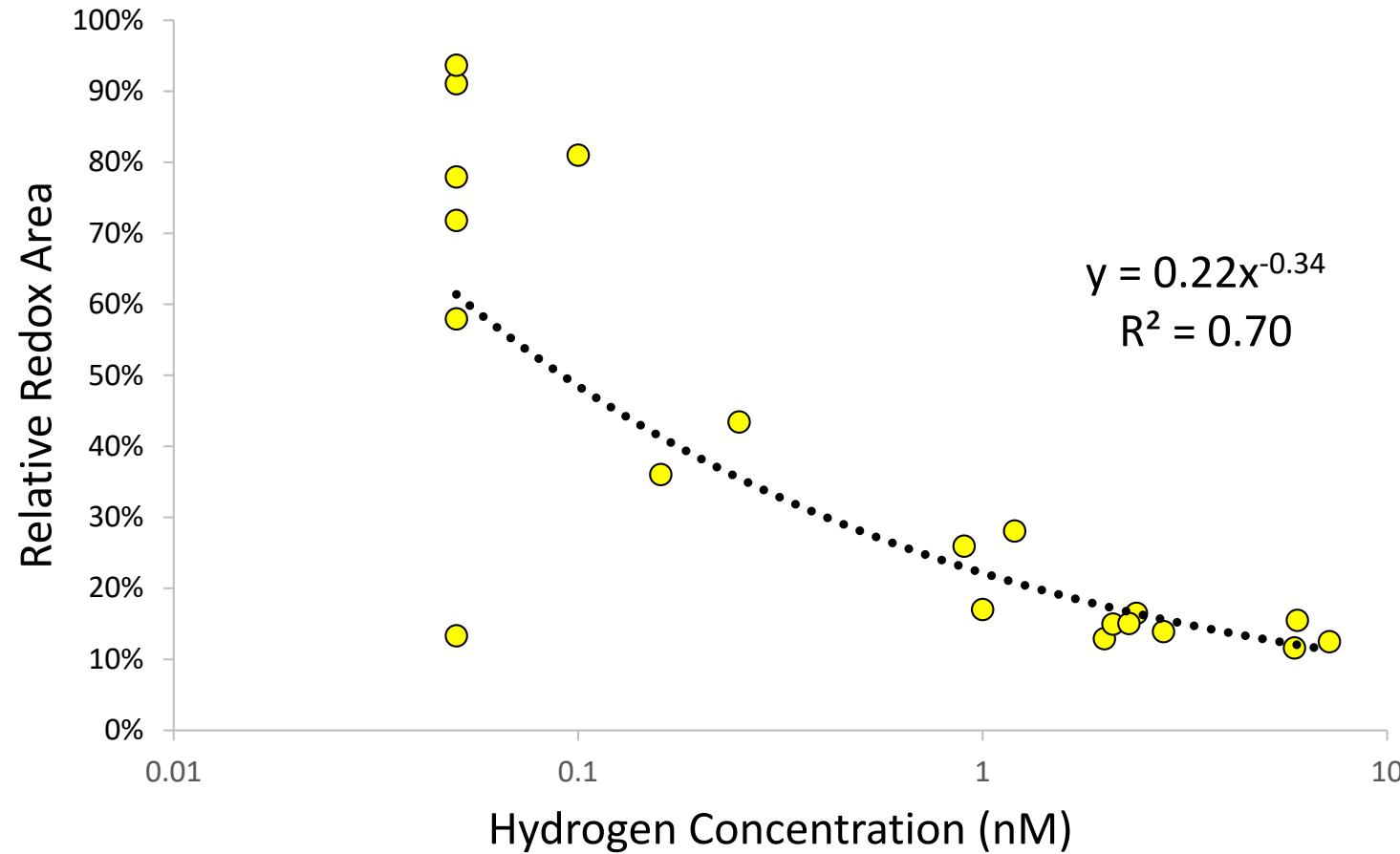


Aerobic:	78 to 100%	(Blue circle)
Nitrate-reducing:	60 to 78%	(Green circle)
Iron-reducing:	42 to 60%	(Yellow circle)
Sulfate-reducing:	24 to 42%	(Pink circle)
Methanogenic:	$\leq 24\%$	(Red circle)

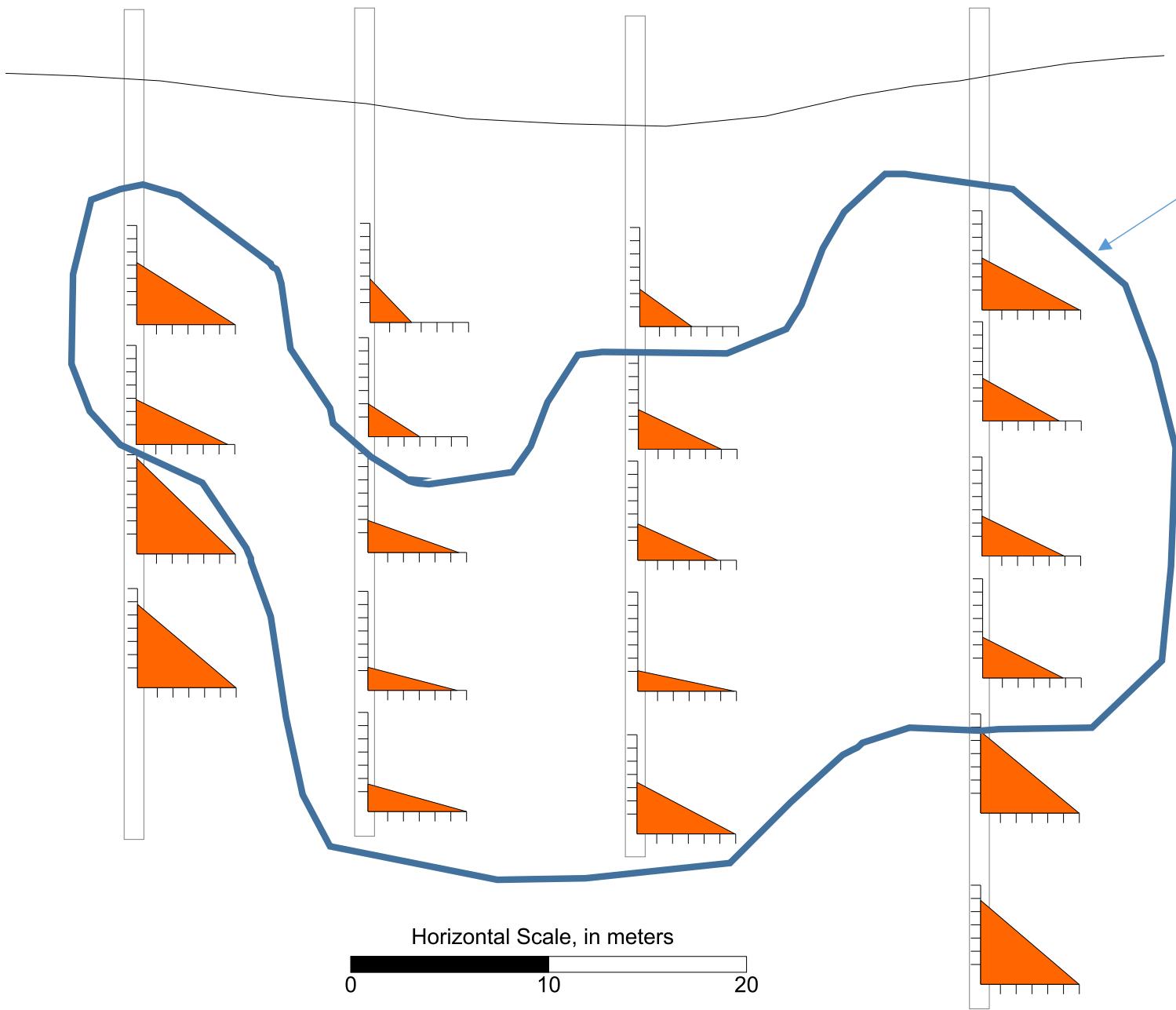


All concentrations in mg/L.

RRA versus Hydrogen Concentration



Eh vs. Hydrogen Concentrations



Low Eh and low Hydrogen

