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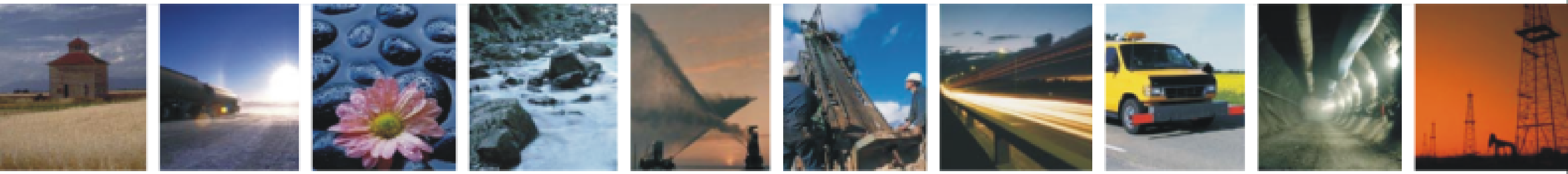

Characterization of Redox Conditions and the Implications for Fate and Transport of Hydrocarbons

CREATING AND DELIVERING BETTER SOLUTIONS

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October 2007

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Contents

- Hydrochemistry and redox reactions
- Simplified redox levels
- Mapping redox conditions
- Plume stability
- Attenuation rates

Hydrochemistry

"Tales sunt aquae quales terrae per quas fluunt"

(Plinius, 74 AD)

Translation:

"the composition of water reflects the material it contacted"

But also:

"a good set of groundwater quality data gives valuable information about subsurface conditions"

Redox

"The mobility, dissolution, degradation, toxicity of inorganic and organic substances in or in contact with the water phase strongly depends on the redox potential of the system"

(Stumm & Morgan, 1981).

Example benzene degradation (Howard et al., 1991):

- Half-life aerobic: 10 days
- Half-life anaerobic: 24 months

Redox Measurements

"Direct measurements of redox potential (using redox electrodes) should be conducted as sloppy as possible to deter scientists from using the data… "

(Anonymous)

Redox reactions

Typical sequence of biodegradation reactions for benzene (after Armstrong et al., 1999 and Borden et al., 1995)

Aerobic Respiration:

$C_6H_6 + 7.5\ O_2 \text{->} 6\ CO_2 + 3\ H_20$ (1)

Denitrification (when oxygen is depleted):

$C_6H_6 + 6\ H^+ + 6\ NO_3^- \text{->} 6\ CO_2 + 6\ H_20 + 3\ N_2$ (2)

Manganese Reduction:

$C_6H_6 + 15\ MnO_2 + 30\ H^+ \text{->} 6\ CO_2 + 15\ Mn^{2+} + 18\ H_20$ (3)

Iron Reduction:

$C_6H_6 + 30\ Fe(OH)_3 + 60\ H^+ \text{->} 6\ CO_2 + 30\ Fe^{2+} + 78\ H_20$ (4)

Sulphate Reduction:

$C_6H_6 + 3.75\ SO_4^{2-} + 7.5\ H_20 \text{->} 6\ CO_2 + 3.75\ H_2S + 3\ H_2O$ (5)

Methanogenesis:

$C_6H_6 + 4.5\ H_2O \text{->} 3.75\ CH_4 + 2.25\ CO_2$ (6)

Reaction sequence (Stuyfzand, 1993)

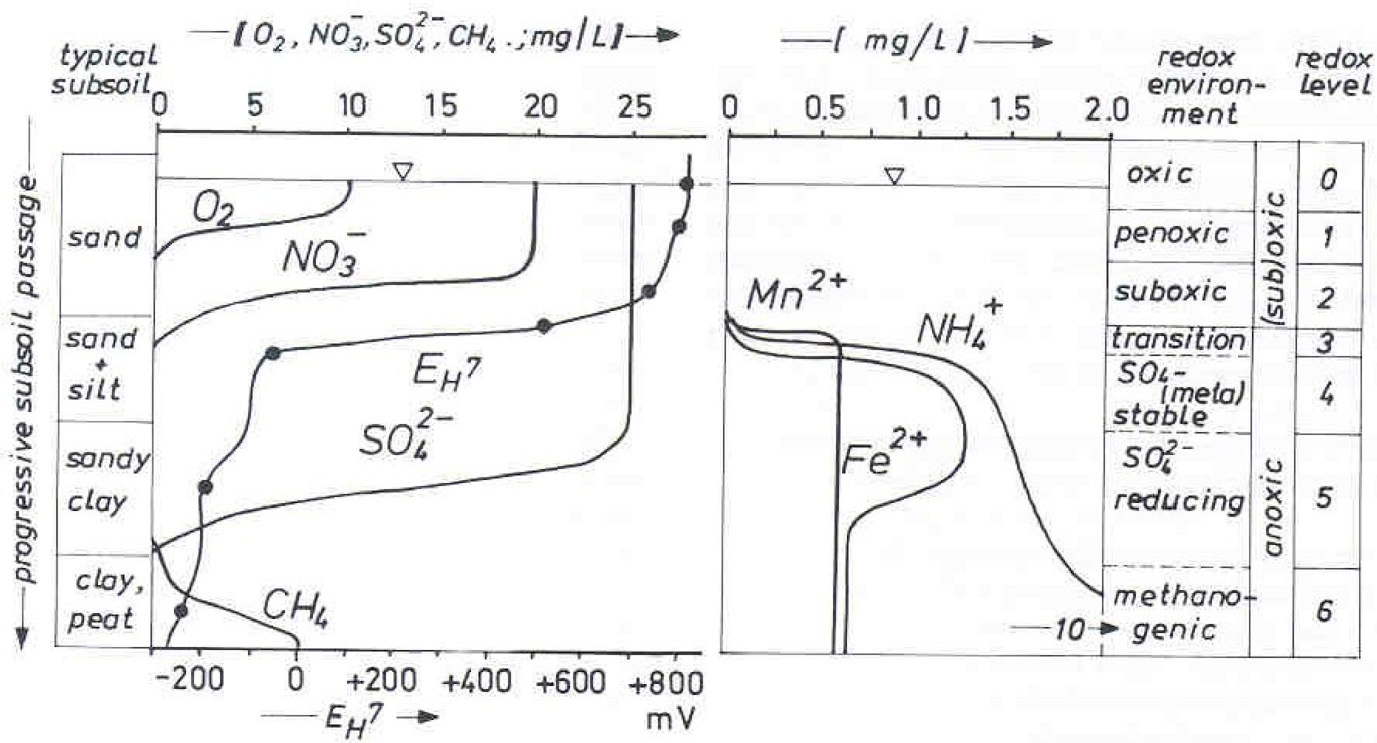
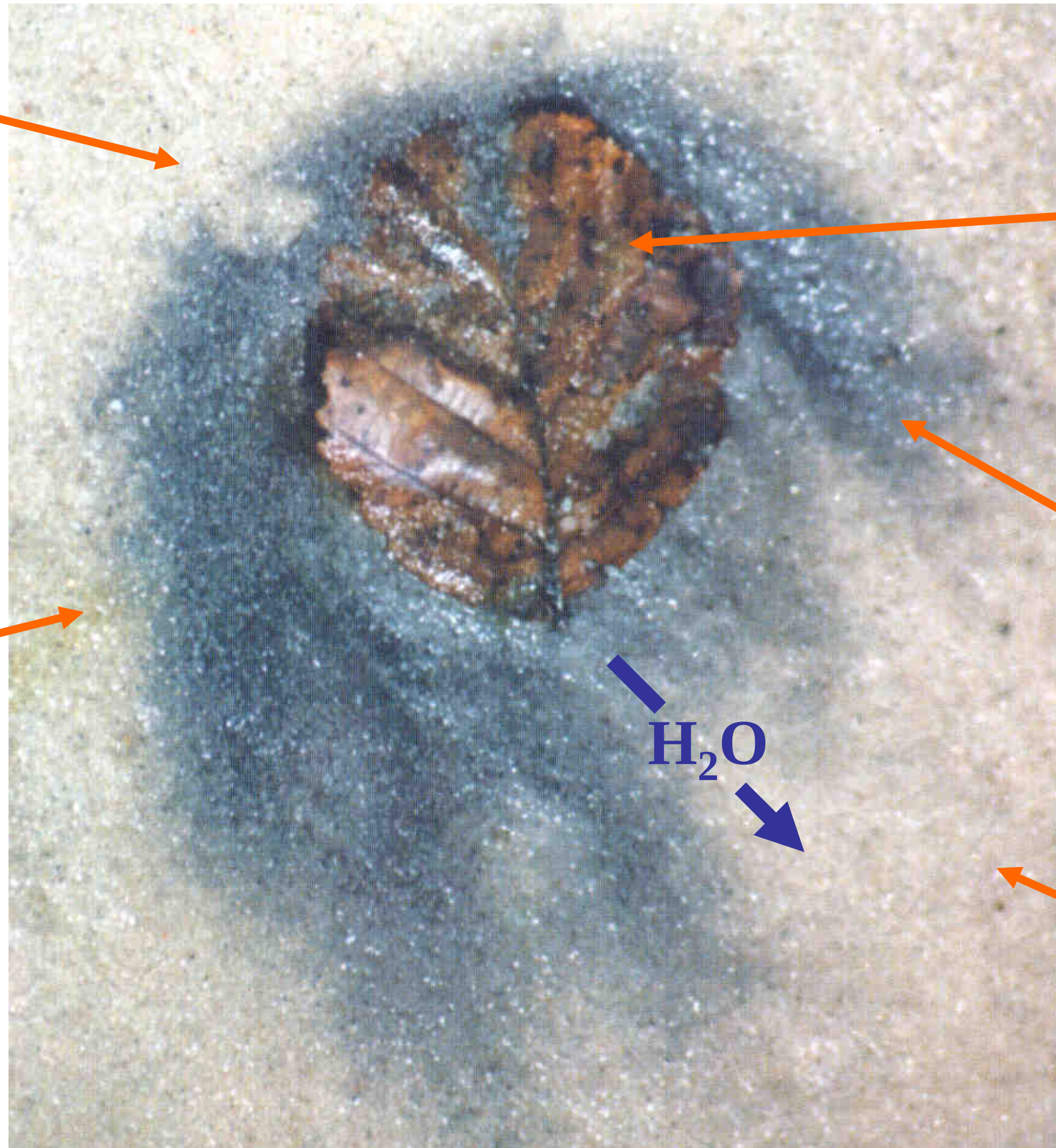


FIG. 2.11 General classification of the natural redox environment, based on the presence or absence of the main redox components of water : O_2, NO_3^-, SO_4^{2-}, Fe, Mn and CH_4. Subsoil passage is assumed as piston flow in a system, which is closed from the atmosphere and progressively richer in organic carbon. The initial O_2, NO_3^- and SO_4^{2-} concentrations (at the water table) are set at 10, 20 and 25 mg/l, respectively. The indicative redox potentials at pH = 7 (E_H7) are derived from Stumm & Morgan (1981).

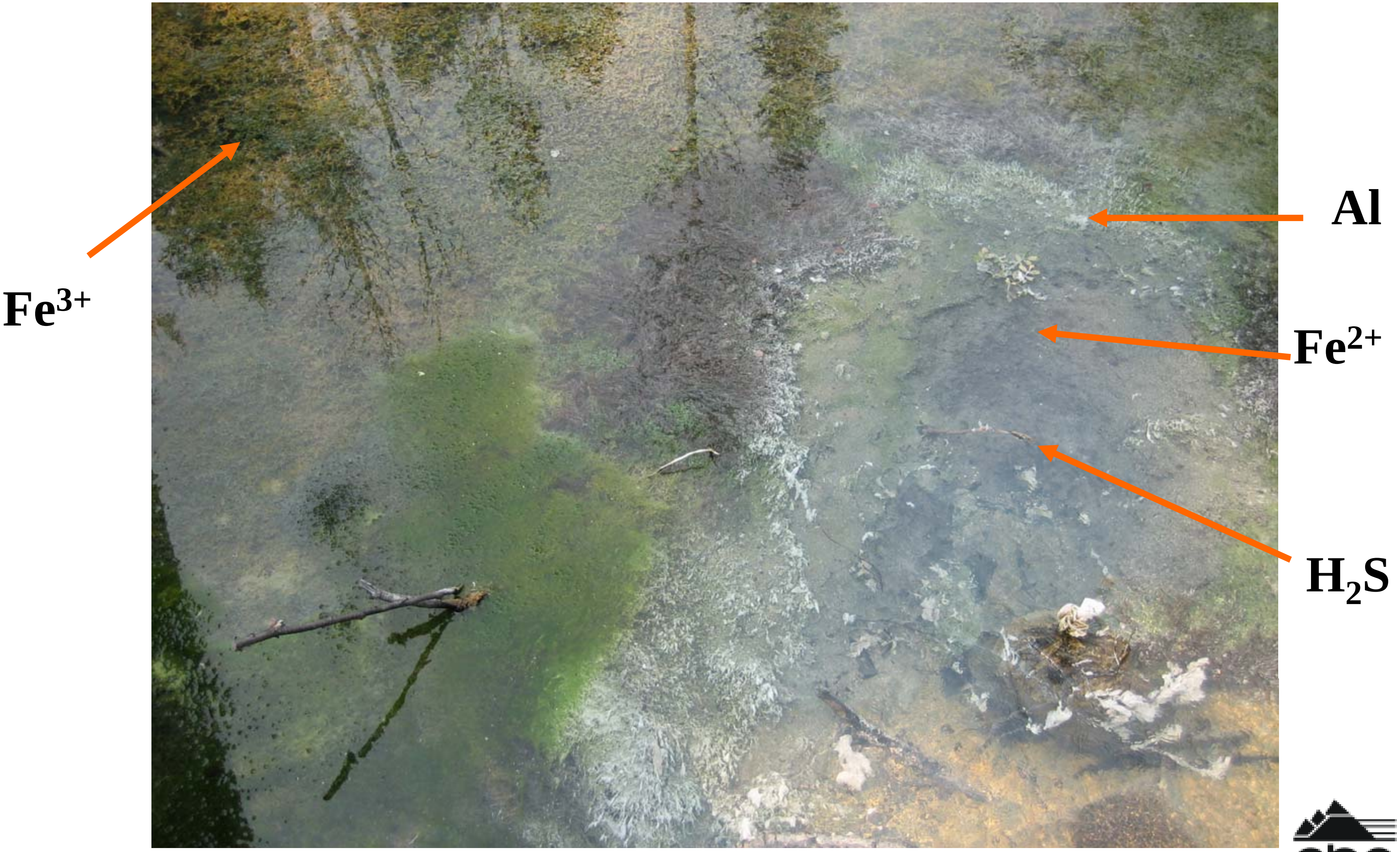
Redox indicators



Redox indicators

Staining

Banff Springs



Drain from old tank farm

Al

Sheen (iron bacteria)

$Fe(OH)_3$

Simplified redox levels

Oxic zone (ox): Dissolved oxygen is between 1 mg/L and near-saturation, nitrate is stable but dissolved iron and manganese are not present in appreciable concentrations.

Suboxic zone (so): In this redox situation nitrate is nearly completely reduced (less than 1 mg/L), dissolved manganese is present in concentrations greater 0.1 mg/L without accompanying dissolved iron increase.

Anoxic zone (ao): nitrate has been reduced, iron and manganese occur in concentrations greater than 0.1 mg/L, also evidence that sulphate reduction is occurring.

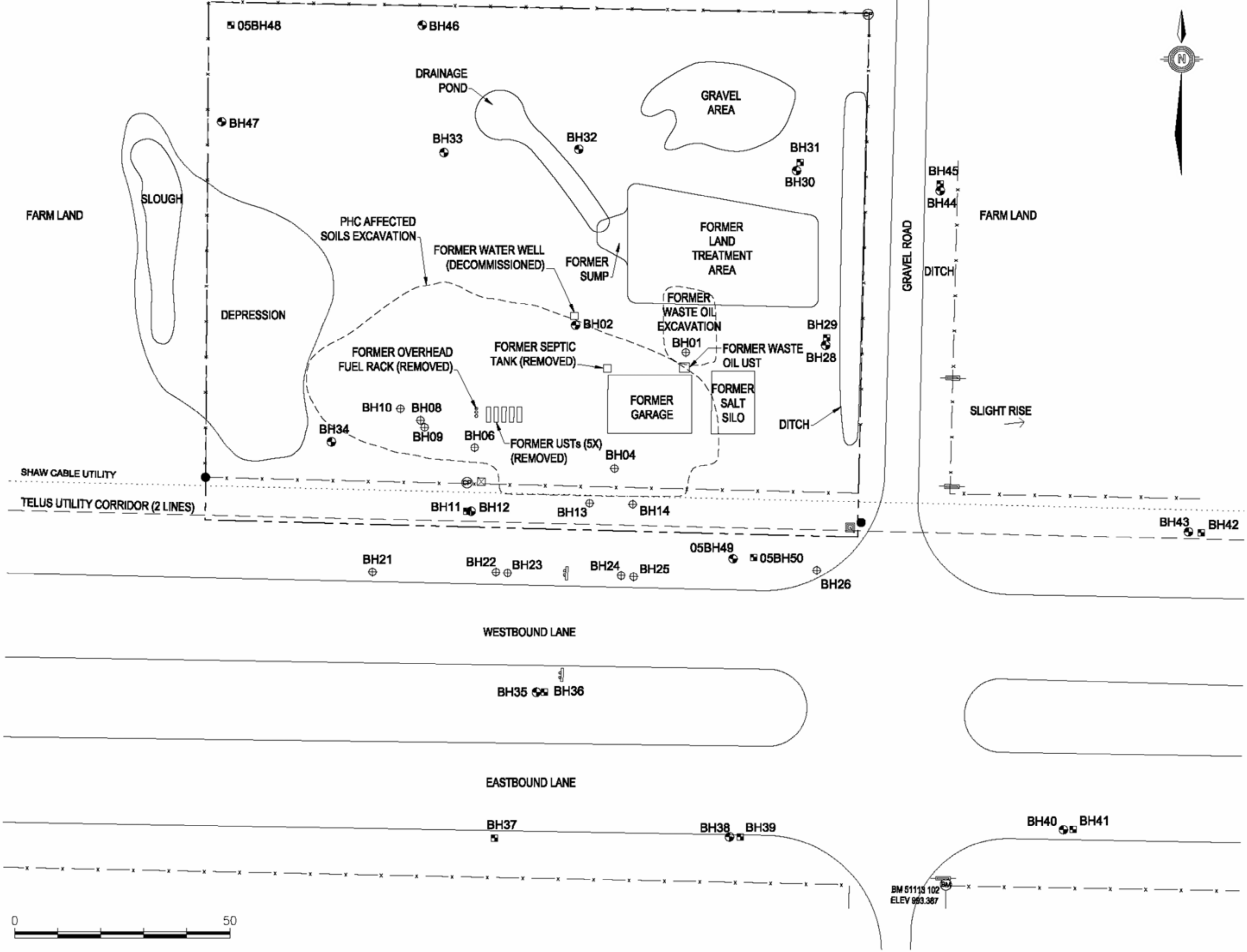
Inferred redox levels

Other important information:

- Site history, contaminant sources
- Mechanism of impact
- Contaminant characteristics; mobility, breakdown products
- Borehole logs (stratigraphy, soil colour, vapour readings)
- Well completion including screen length
- Groundwater and sediment colour
- Odours (e.g H_2S), gas bubbles, stained bailers

Case History – Highway Maintenance Yard

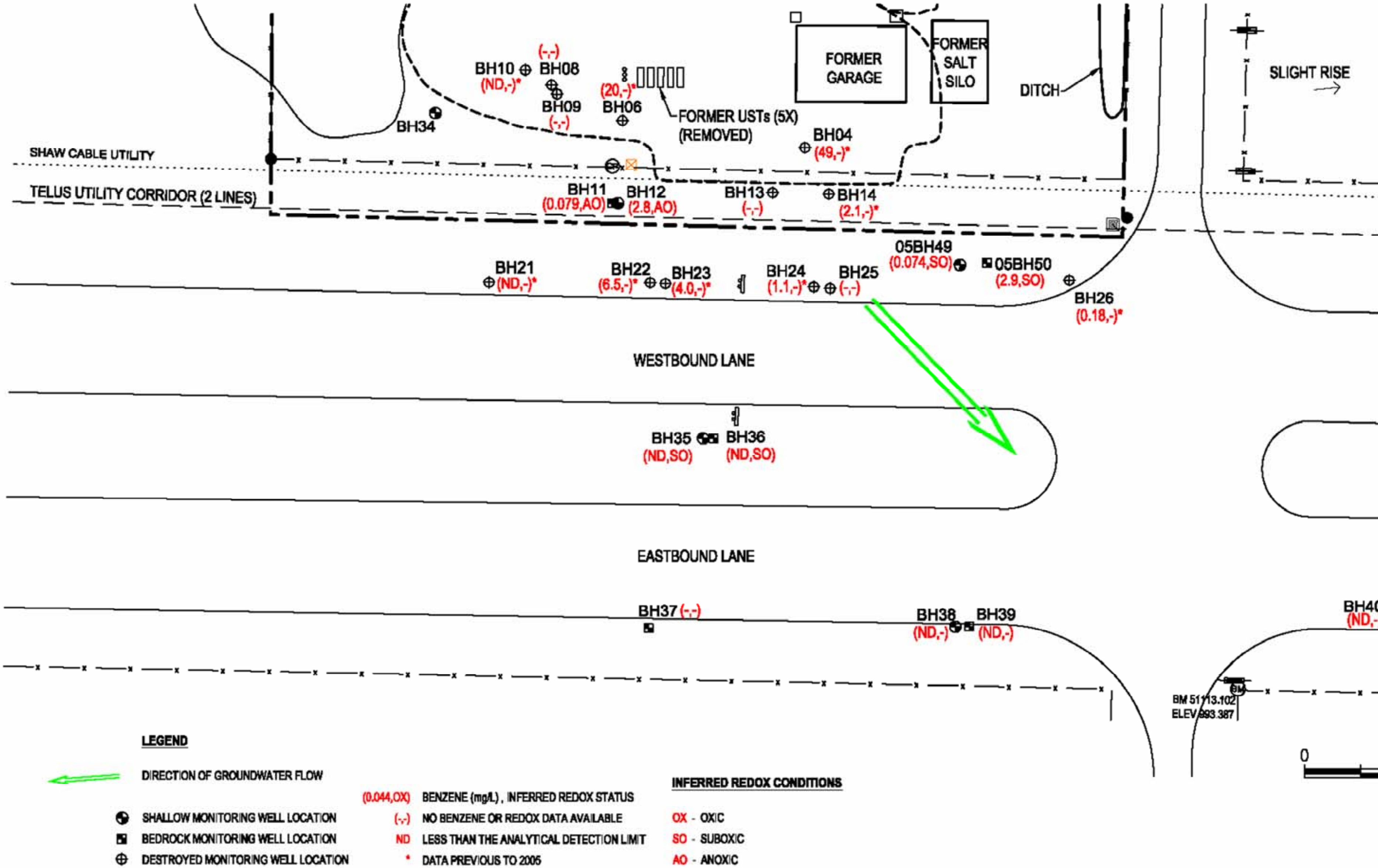
- Former service station and bulk fuel plant
- Salt storage between mid 1980s and 1997
- Hydrocarbon impact near highway
- Full remediation not feasible; source removal conducted in 2004
- Monitored natural attenuation of residual impact



05BH48
BH46
DRAINAGE POND
GRAVEL AREA
BH47
BH33
BH32
BH31
BH30
BH45
BH44
SLOUGH
FARM LAND
PHC AFFECTED SOILS EXCAVATION
FORMER WATER WELL (DECOMMISSIONED)
FORMER SUMP
FORMER LAND TREATMENT AREA
GRAVEL ROAD
DITCH
FARM LAND
DEPRESSION
BH02
FORMER WASTE OIL EXCAVATION
BH01
FORMER WASTE OIL UST
BH29
BH28
FORMER SEPTIC TANK (REMOVED)
FORMER OVERHEAD FUEL RACK (REMOVED)
FORMER GARAGE
FORMER SALT SILO
BH10
BH08
BH09
BH34
BH06
FORMER USTs (5X) (REMOVED)
DITCH
SLIGHT RISE
BH04
SHAW CABLE UTILITY
TELUS UTILITY CORRIDOR (2 LINES)
BH11
BH12
BH13
BH14
BH43
BH42
05BH49
05BH50
BH21
BH22
BH23
BH24
BH25
BH26
WESTBOUND LANE
BH35
BH36
EASTBOUND LANE
BH37
BH38
BH39
BH40
BH41
BM 51113 102
ELEV 993.387
0
50

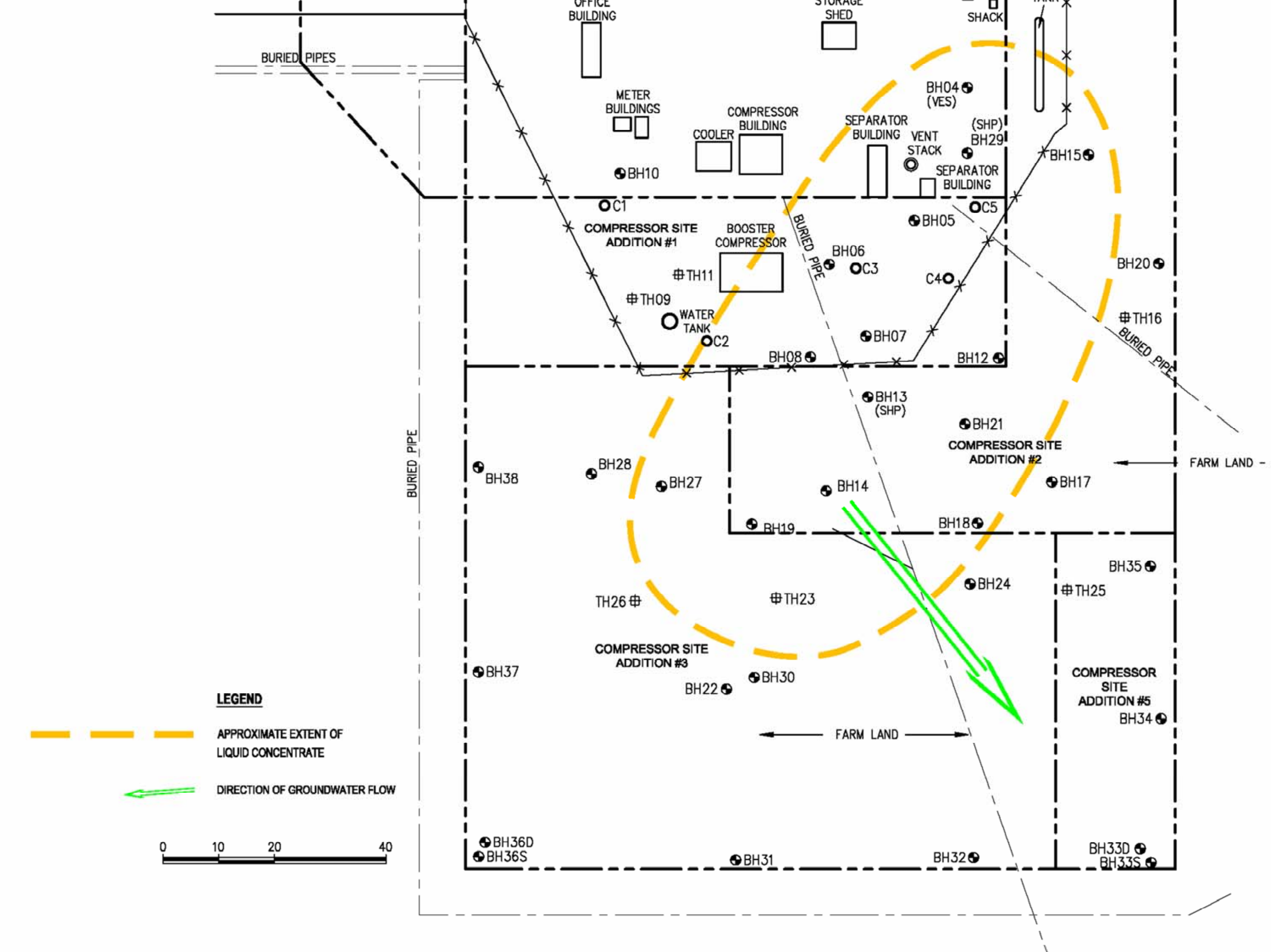
Case History: Highway Maintenance Yard

Parameter	Monitoring Well Location							
	Till				Bedrock			
	BH12		BH35		BH11		BH36	
	Nov-04	Nov-05	Nov-04	Nov-05	Nov-04	Nov-05	Nov-04	Nov-05
pH (lab)	7.0	6.3	7.0	7.6	6.9	7.1	7.5	7.0
pH (field)	6.95	6.98	7.49	7.54	7.00	6.64	7.49	6.88
Dissolved Oxygen (field)	2.78	1.12	0.87	2.10	0.78	9.90	0.90	1.20
Temperature (field)	8.2	6.8	8.3	8.6	8.4	6.4	8.26	8.2
Total Dissolved Solids (TD	**1,450**	**6,570**	**1,260**	**536**	**2,850**	**2,660**	**1,130**	**1,110**
Hardness	480	3,810	500	135	1,630	1,450	241	536
Chloride (Cl)	**321**	**3,810**	**421**	46.9	**1,200**	**1,110**	176	**408**
Sulphate (SO_4)	14.0	9.9	18.4	45.1	362	375	221	16.7
Bicarbonate (HCO_3)	1,080	1,020	671	474	606	638	626	548
Nitrate/Nitrite - as N	0.08	0.94	0.72	<0.05	0.16	0.13	<0.05	0.61
Iron (Fe)	<0.01	**4.06**	<0.01	0.05	**1.00**	**0.64**	<0.01	0.03
Manganese (Mn)	**1.61**	**13.30**	<0.01	**0.21**	**1.27**	**0.96**	**0.10**	**6.20**
Benzene	**1.5**	**2.8**	<0.005	<0.005	**0.014**	**0.079**	<0.005	<0.005
Inferred redox condition:	**SO**	**AO**	**OX**	**SO**	**AO**	**AO**	**OX/SO**	**SO**


FORMER GARAGE
FORMER SALT SILO
DITCH
SLIGHT RISE
BH10 (ND,-)*
BH08 (-,-)
BH09 (-,-)
BH06 (20,-)*
FORMER USTs (5X) (REMOVED)
BH04 (49,-)*
BH34
SHAW CABLE UTILITY
TELUS UTILITY CORRIDOR (2 LINES)
BH11 (0.079,AO)
BH12 (2.8,AO)
BH13 (-,-)
BH14 (2.1,-)*
05BH49 (0.074,SO)
05BH50 (2.9,SO)
BH21 (ND,-)*
BH22 (6.5,-)*
BH23 (4.0,-)*
BH24 (1.1,-)*
BH25 (-,-)
BH26 (0.18,-)*
WESTBOUND LANE
BH35 (ND,SO)
BH36 (ND,SO)
EASTBOUND LANE
BH37 (-,-)
BH38 (ND,-)
BH39 (ND,-)
BM 51113.102
ELEV 993.387
LEGEND
DIRECTION OF GROUNDWATER FLOW
SHALLOW MONITORING WELL LOCATION
BEDROCK MONITORING WELL LOCATION
DESTROYED MONITORING WELL LOCATION
(0.044,OX) BENZENE (mg/L), INFERRED REDOX STATUS
(-,-) NO BENZENE OR REDOX DATA AVAILABLE
ND LESS THAN THE ANALYTICAL DETECTION LIMIT
* DATA PREVIOUS TO 2005
INFERRED REDOX CONDITIONS
OX - OXIC
SO - SUBOXIC
AO - ANOXIC

Case History: Gas Plant

- Natural gas processing plant
- Sandy soils
- Subsurface disposal of condensate in 1980s
- Liquid condensate plume ~1,500 m^3
- Only redox conditions assessed and contaminant distribution monitored prior to 2006
- Source removal initiated in 2006



OFFICE BUILDING
STORAGE SHED
SHACK
TANK
BURIED PIPES
METER BUILDINGS
COMPRESSOR BUILDING
COOLER
SEPARATOR BUILDING
VENT STACK
SEPARATOR BUILDING
BH04 (VES)
(SHP) BH29
BH15
BH10
C1
C5
BH05
COMPRESSOR SITE ADDITION #1
BOOSTER COMPRESSOR
BURIED PIPE
BH06
C3
C4
BH20
TH11
TH09
WATER TANK
C2
TH16
BURIED PIPE
BH07
BH08
BH12
BH13 (SHP)
BH21
COMPRESSOR SITE ADDITION #2
FARM LAND
BURIED PIPE
BH38
BH28
BH27
BH14
BH17
BH19
BH18
BH35
BH24
TH25
TH26
TH23
COMPRESSOR SITE ADDITION #3
BH37
BH30
BH22
COMPRESSOR SITE ADDITION #5
BH34
FARM LAND
LEGEND
APPROXIMATE EXTENT OF LIQUID CONCENTRATE
DIRECTION OF GROUNDWATER FLOW
0
10
20
40
BH36D
BH36S
BH31
BH32
BH33D
BH33S

Case History: Gas Plant

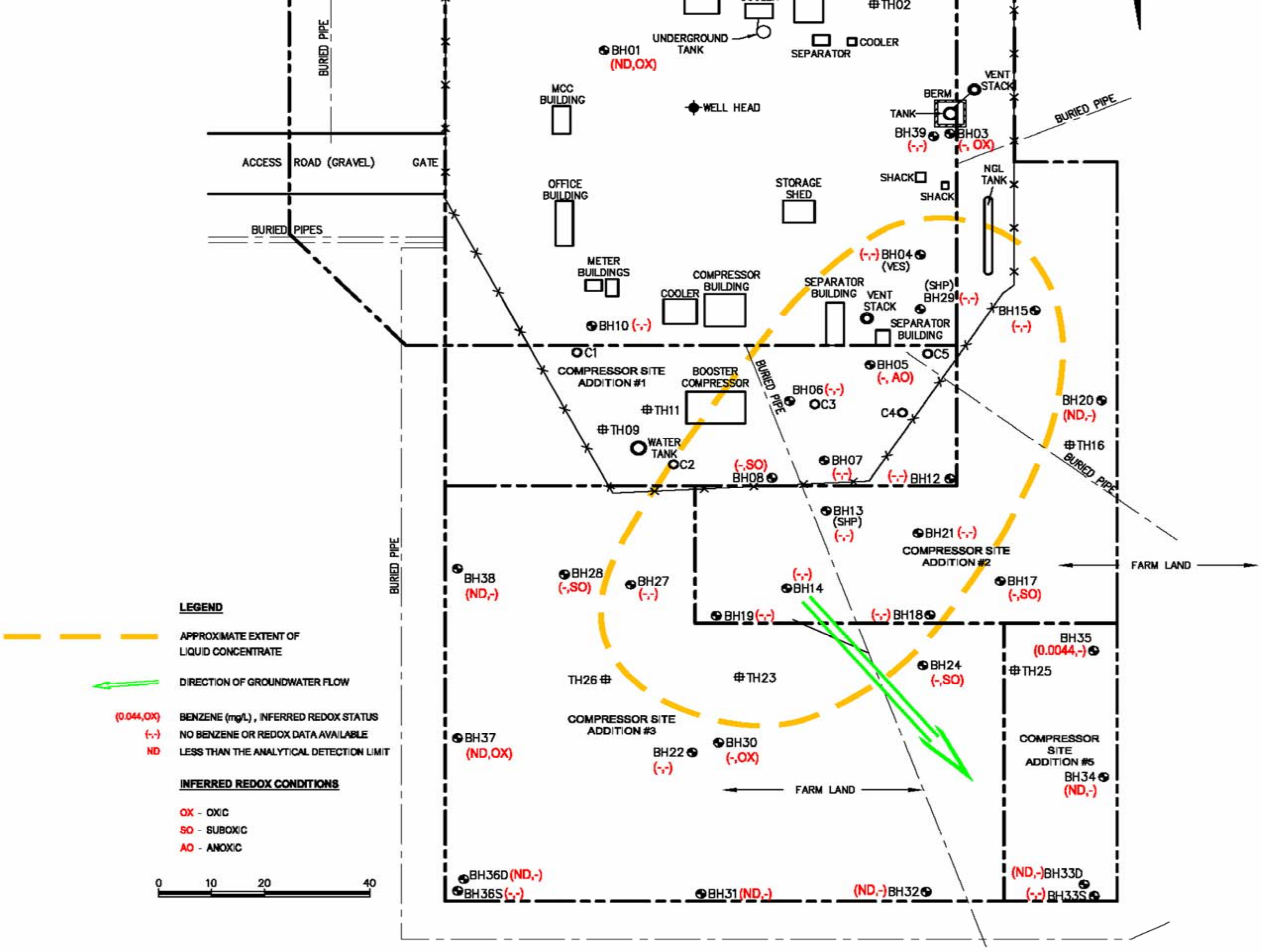
BTEX

Parameter	BH35 (Downgradient)									
	13-Aug-99	7-Dec-99	18-Jul-00	8-Dec-00	18-Jul-01	19-Dec-01	6-Dec-02	14-Nov-03	14-Dec-04	27-Oct-05
Petroleum Hydrocarbons										
Benzene	0.34	0.098	0.072	0.014	0.052	0.027	<0.0005	<0.0005	0.0009	0.0044
Toluene	<0.0005	< 0.0005	< 0.0005	0.012	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ethylbenzen	0.001	< 0.0005	< 0.0005	0.003	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Xylenes	0.0027	0.003	0.002	0.073	0.0023	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Total Volatile	0.34		<0.1							
Total Extract	<0.05		0.07							
Total Petrole	0.34		0.07							
F1(C_6 to C_{10})								<0.1	<0.1	<0.1
F2 (>C_{10} to C_{16})								<0.05	<0.05	<0.05
F1-BTEX								<0.1	<0.1	<0.1

Case History : Gas Plant

Redox Sensitive Parameters

Parameter	BH03	BH05*	BH08*	BH17**	BH24**	BH30				
	27-Oct-05	6-Dec-02	6-Dec-02	6-Dec-02	6-Dec-02	8-Dec-00	19-Dec-01	6-Dec-02	14-Nov-03	14-Dec-04
General Parameters	Upgradient									
pH (Lab. measurement)	7.9	6.8	6.9	7.4	7.6	7.1	7.5	7.5	7.2	7.9
Total Dissolved Solids (TDS)	905	847	823	807	640	538	419	441	423	425
Hardness	794	695	793	755	520	477	399	394	373	363
Chloride (Cl)	10	25.7	23.4	6.5	3.5	4.4	4	4.7	3.3	4
Sulphate (SO_4)	91.5	1.4	24.4	35.8	89.7	36.9	48.2	37.5	42.2	38.6
Nitrate-N	40.7	<0.05	0.32	8.26	4.90	0.05	0.2	2.18	3.82	4.2
Ammonia-N	<0.05	9.44	0.43	<0.05	<0.05	0.1	<0.05	<0.05	<0.05	<0.05
Iron (Fe)-Dissolved	<0.06	53.5	12.3	<0.005	<0.005	0.029	0.008	<0.005	<0.01	<0.06
Manganese (Mn)-Dissolved	<0.01	0.434	2.93	0.545	0.446	1.71	0.793	0.307	0.08	<0.01
Total Kjeldahl Nitrogen	<0.2	26.4	4.5	0.7	1.3	1.9	3.2	9.3	0.7	0.5
Dissolved Organic Carbon	5			5	6	12	6	3	4	9
Inferred Redox Condition:	Oxic	Anoxic	Anoxic	Suboxic	Suboxic	Suboxic	Suboxic	Suboxic	Oxic	Oxic
* - Within LPH plume										
** - Downgradient of LPH plume										



TH02
UNDERGROUND TANK
SEPARATOR
COOLER
BH01 (ND,OX)
BURIED PIPE
MCC BUILDING
WELL HEAD
VENT STACK
BERM
TANK
BH39 (-,-)
BH03 (-, OX)
BURIED PIPE
ACCESS ROAD (GRAVEL)
GATE
OFFICE BUILDING
STORAGE SHED
SHACK
SHACK
NGL TANK
BURIED PIPES
METER BUILDINGS
COMPRESSOR BUILDING
COOLER
SEPARATOR BUILDING
VENT STACK
(-,-) BH04 (VES)
(SHP) BH29 (-,-)
BH15 (-,-)
SEPARATOR BUILDING
BH10 (-,-)
C1
C5
COMPRESSOR SITE ADDITION #1
BOOSTER COMPRESSOR
BURIED PIPE
BH05 (-, AO)
BH06 (-,-)
C3
BH20 (ND,-)
TH11
C4
TH09
WATER TANK
C2
(-,SO) BH08
BH07 (-,-)
(-,-) BH12
TH16
BURIED PIPE
BH13 (SHP) (-,-)
BH21 (-,-)
COMPRESSOR SITE ADDITION #2
FARM LAND
BURIED PIPE
BH38 (ND,-)
BH28 (-,SO)
BH27 (-,-)
(-,-) BH14
BH17 (-,SO)
LEGEND
BH19 (-,-)
(-,-) BH18
APPROXIMATE EXTENT OF LIQUID CONCENTRATE
BH35 (0.0044,-)
BH24 (-,SO)
TH25
DIRECTION OF GROUNDWATER FLOW
TH26
TH23
(0.044,OX) BENZENE (mg/L), INFERRED REDOX STATUS
(-,-) NO BENZENE OR REDOX DATA AVAILABLE
ND LESS THAN THE ANALYTICAL DETECTION LIMIT
COMPRESSOR SITE ADDITION #3
BH37 (ND,OX)
BH22 (-,-)
BH30 (-,OX)
COMPRESSOR SITE ADDITION #5
BH34 (ND,-)
INFERRED REDOX CONDITIONS
FARM LAND
OX - OXIC
SO - SUBOXIC
AO - ANOXIC
BH36D (ND,-)
BH36S (-,-)
BH31 (ND,-)
(ND,-) BH32
(ND,-) BH33D
(-,-) BH33S
0 10 20 40

Stability of redox conditions

Use redox conditions to determine if a zone of affected groundwater will:

- Increase in size
- Remain the same
- Shrink

Increasing plume or affected zone

- Concentrations increase between monitoring events
- Continued leaching from soil exceeds the natural attenuation capacity
- May suggest source control needed

Stable plume

- Concentrations are the same between successive monitoring events
- Leaching from the soil is balanced by natural attenuation capacity
- No source control needed - may need to management of affected groundwater - receptor sensitivity

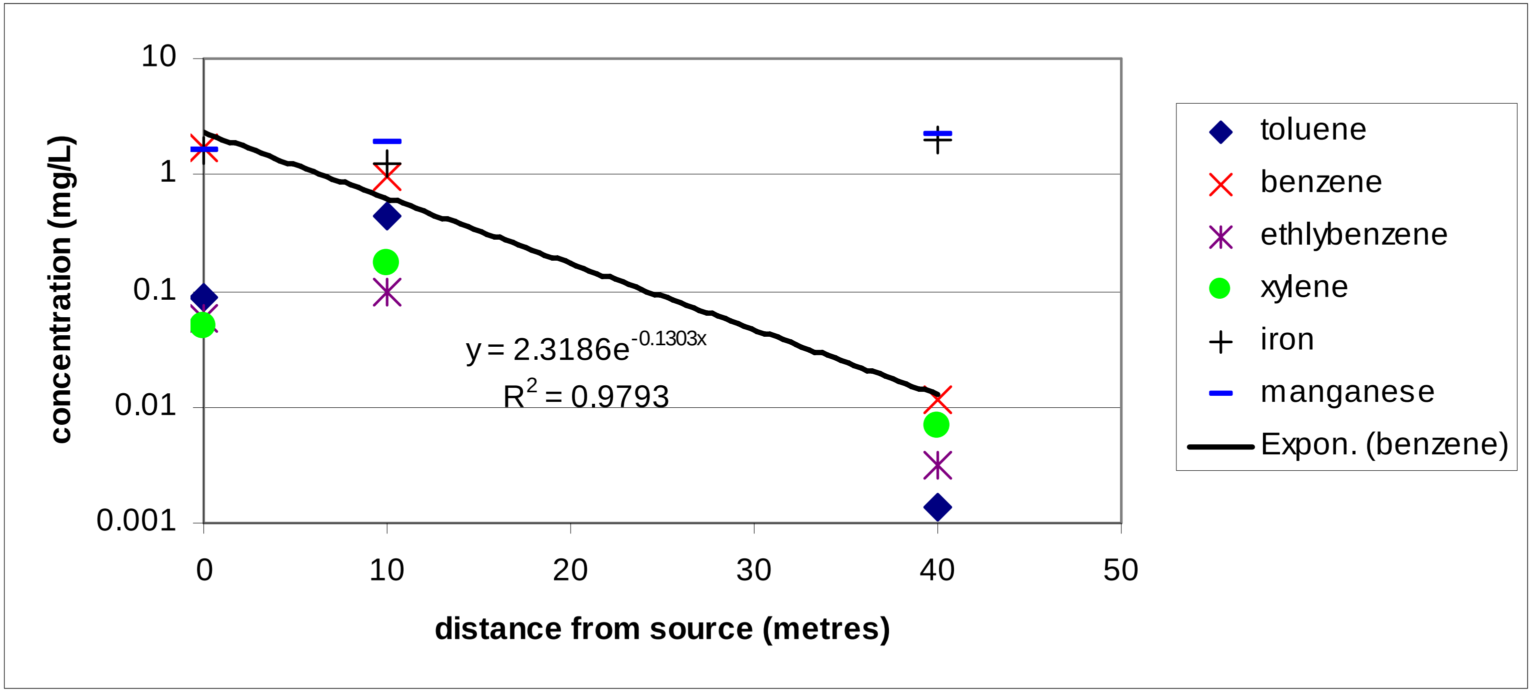
Shrinking plume

- Concentrations at monitoring points decrease with time (allowing for seasonal variations)
- Leaching from soil less than attenuation capacity
- No source control needed - a reliable means of assessing the performance of remedial action

Tools for predicting plume stability

- Concentration vs distance plots for three or more monitoring points
- Concentration vs time plots for individual monitoring points

Concentration vs distance

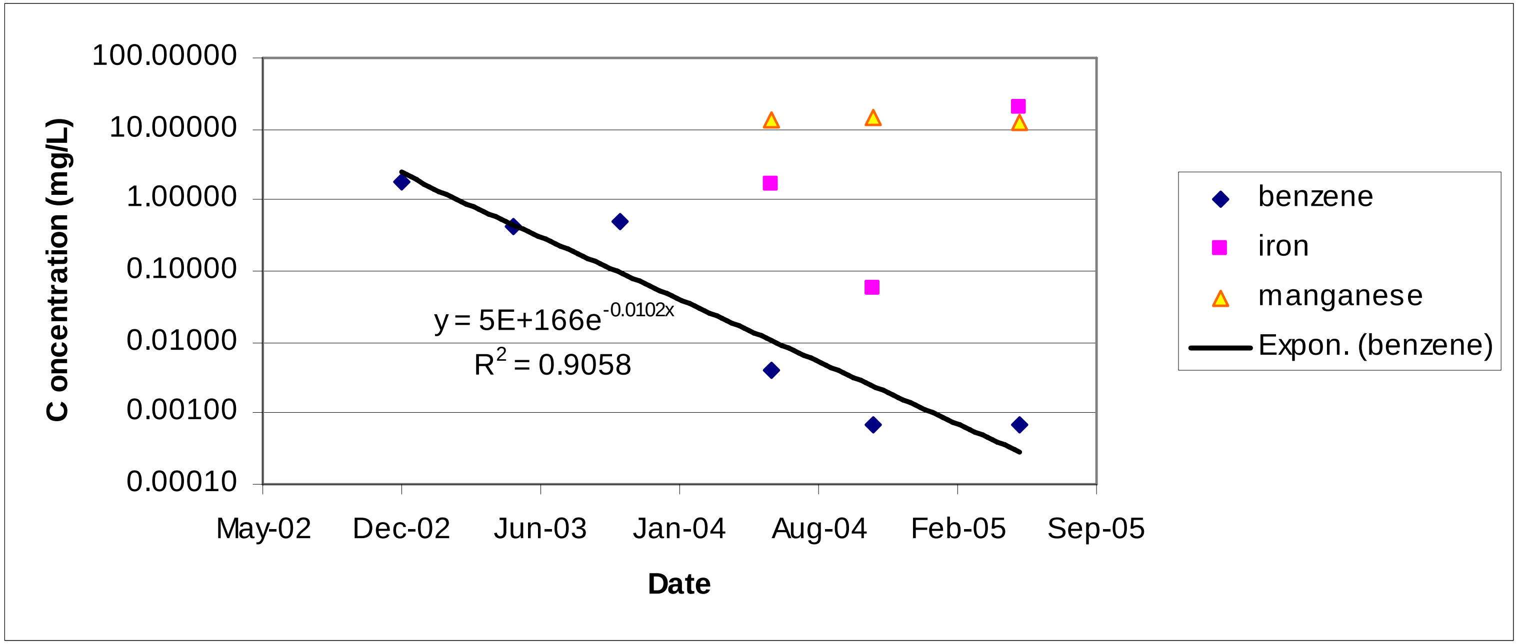


Three monitoring wells

Concentration vs distance

- Plot shows that Mn and Fe stable throughout the plume - lots of biological degradation occurring to support attenuation - not just dilution and dispersion
- First order degradation rate
- Slope of line for benzene ~ 0.13 mg/L/m

Concentration vs time



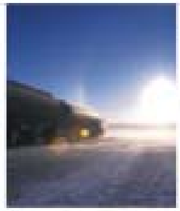
Single Monitoring well

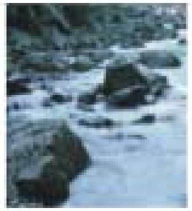
Concentration vs time

- Rate of decline predictable
- Slope of line ~0.01 mg/L/month (~ 0.12 mg/L/year)

Conclusions

- Redox indexing method useful for mapping contaminant distribution
- Redox zones help determining whether plumes are increasing, stable or shrinking
- Change of contaminant concentration with distance and time allow calculation of attenuation rates







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