In-Situ Chemical Oxidation: ISCO

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Today's talk

- Overview of ISCO
- Discuss individual oxidants
- Look at applicability for Gasoline sites
- Review Case Histories
- I like Ozone

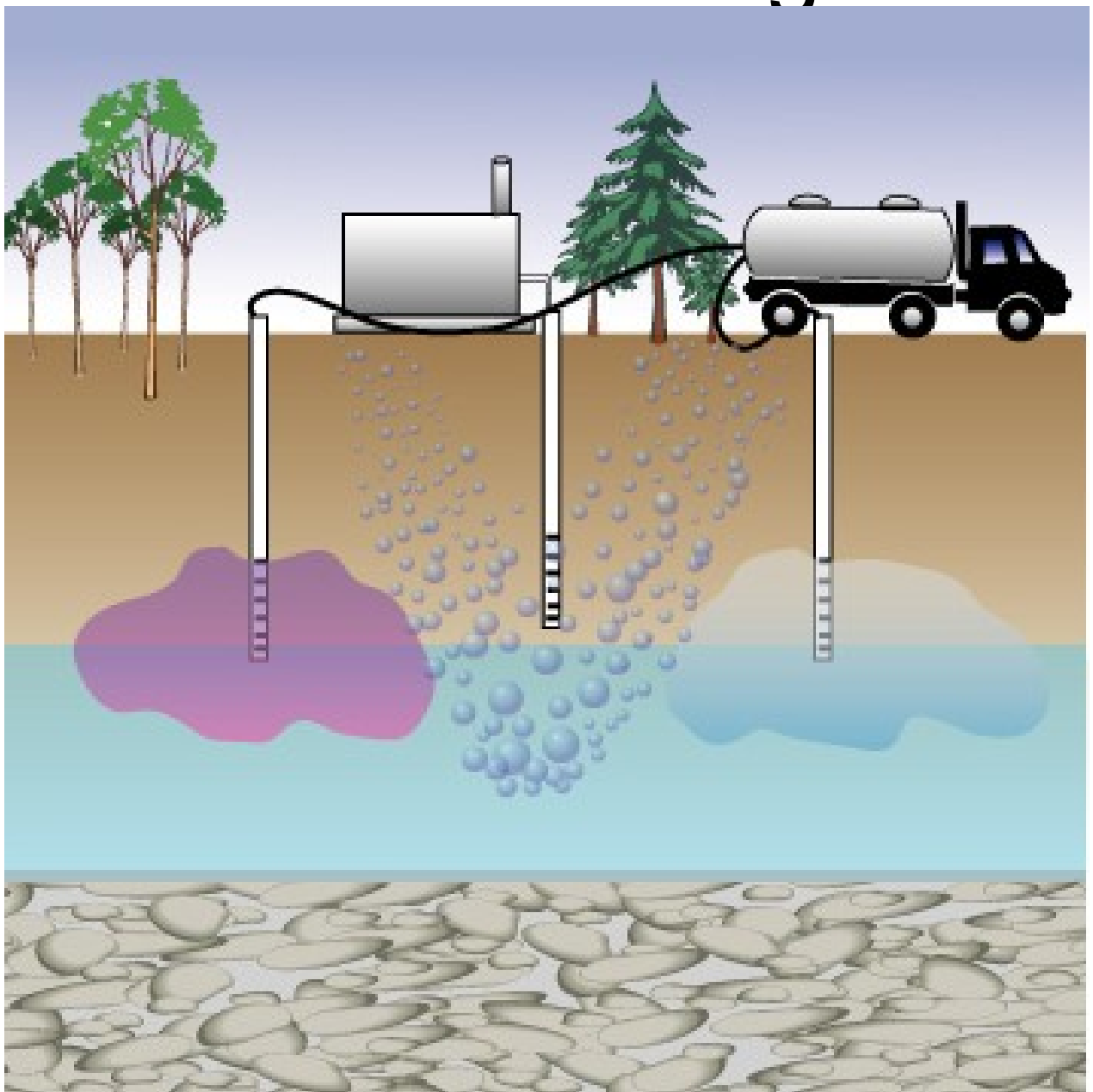
What is ISCO?

- Taking electrons away from a molecule oxidizes it.
- This oxidation may make the molecule more stable or less stable and susceptible to further oxidation.
- Radicals – $OH^{\bullet}$ $SO4_2^{\bullet}$
- an oxygen molecule that has lost an electron is looking to rip one off somebody else

Types of In Situ Oxidants

Features	Fenton's Reagent	Ozone	Persulfate	Permanganate
Physical State as Injected	Liquid	Gas	Liquid	Liquid
Key Oxidant	OH^-	O_3 and OH^-	SO_4^{2-}	MnO_4^-
Oxidation Potential	2.8V	2.07V and 2.8V	2.5 V	1.7V
By Products	Fe(III), O_2, and H_2O	Oxygen	Sulfate	Mn(VI)
Subsurface Fouling	Possible	None	None	Yes, due to Mn (VI) formation
Oxygenate Effectiveness	Yes	Yes	Yes	No – MTBE Benzene
Relative Costs	Moderate	Moderate	Moderate	Moderate $KMnO_4$ – High $NaMnO_4$

ITRC ISCO Tech Reg. Jan 2005



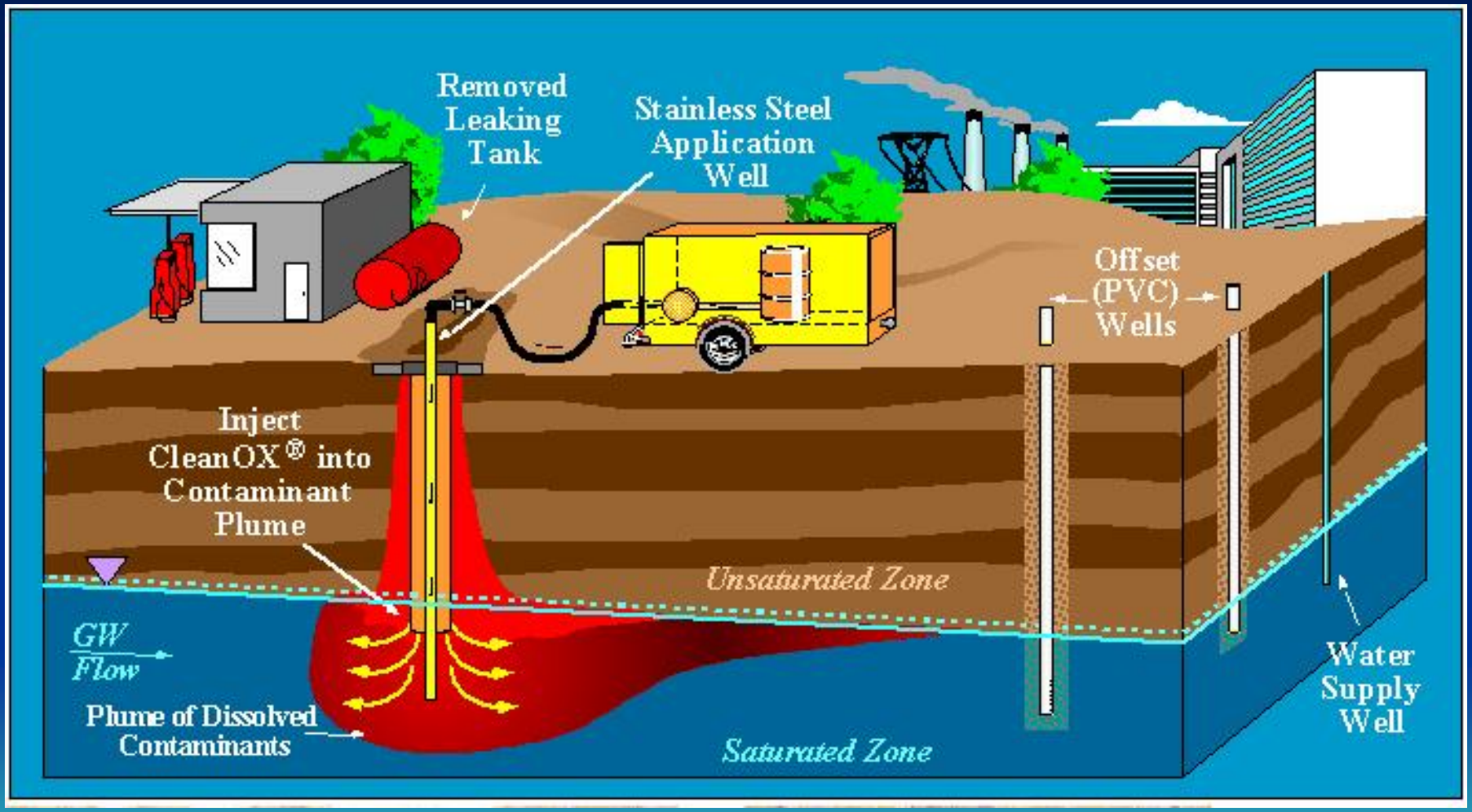
Fenton's and MTBE

First reported in 1894 by H.J.H. Fenton

- $H_2O_2 + Fe^{+2} \rightarrow OH\bullet + OH^- + Fe^{+3}$
- $OH\bullet \rightarrow$ Free Radical
  - ❖(Second Most Powerful Oxidizer)
- $OH\bullet$ + Organic Contaminant $\rightarrow CO_2 + H_2O$
  - (Complete oxidation to carbon dioxide and water)

Chemical oxidation of MTBE (C5H120)

$$C_5H_{12}0 + 15H_2O_2 \xrightarrow{(Fe)} 5CO_2 + 21H_2O$$



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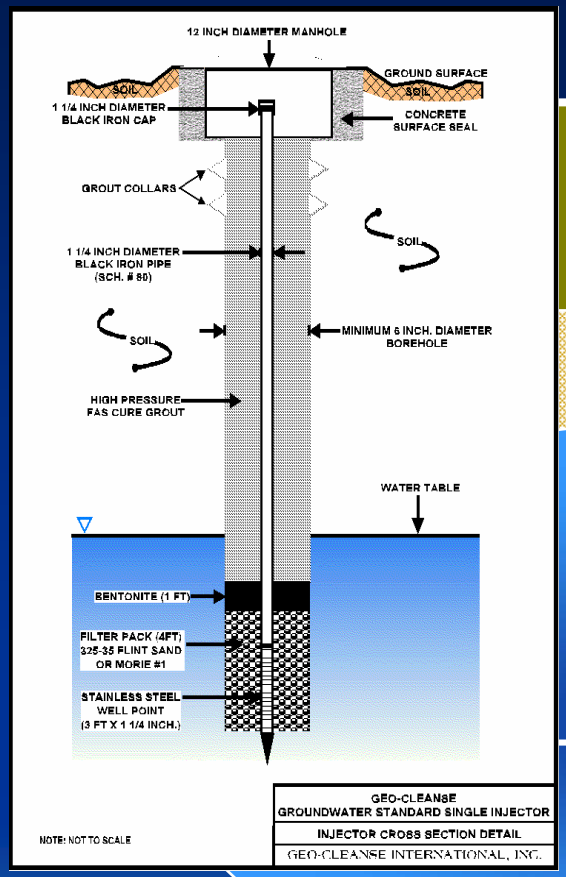
Cross Section View of Injection



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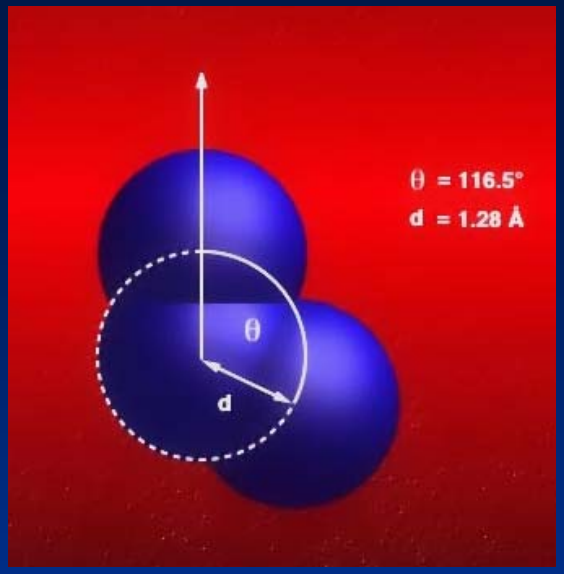
Ozone: Chemical Specifications



Ozone is strong oxidant

- Tri-atomic form of oxygen **O_3**
- Molecular Weight : **48 g/mol**
- Formed by corona discharge
- Unstable Molecule : **Half-life ~ 2 minutes in air**
  Half-life ~ 20 minutes dissolved
- High oxidation potential: **2.07 V**
- Solubility: **600 mg/l at 20 deg. C**
  (12.5 x more soluble than oxygen)

Ozone gas is generated on site from only air and electricity

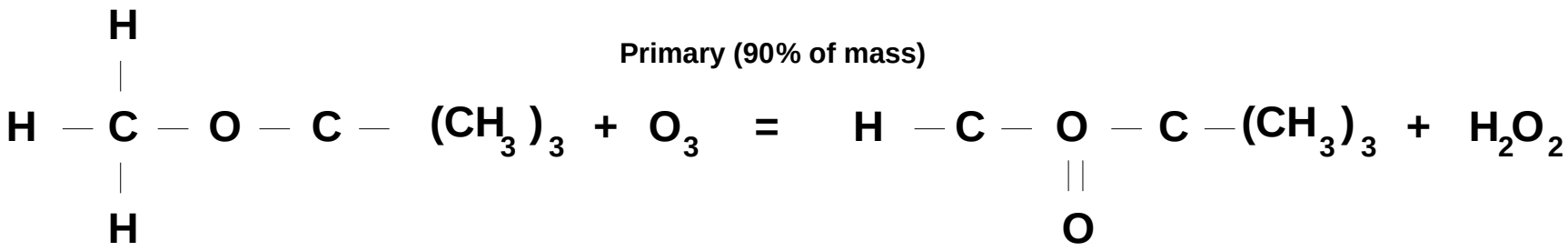
Ozone

- Ozone has been demonstrated to remediate BTEX, Napthalene, MTBE ETBE, TAME, DIPE, TBA and other gasoline COCs.
- Ozone and peroxide can be highly effective in combination (Perozone™)
  - Usually not necessary to treat gasoline COCs
  - Could aid with distribution in certain geologic settings

Ozone MTBE Oxidation Reaction

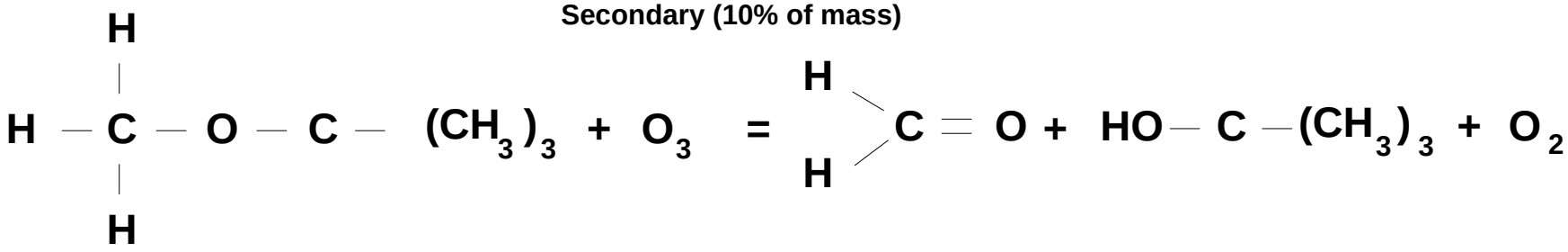
MtBE **Ozone** **Tert-butyl formate (TBF)** **Hydrogen peroxide**

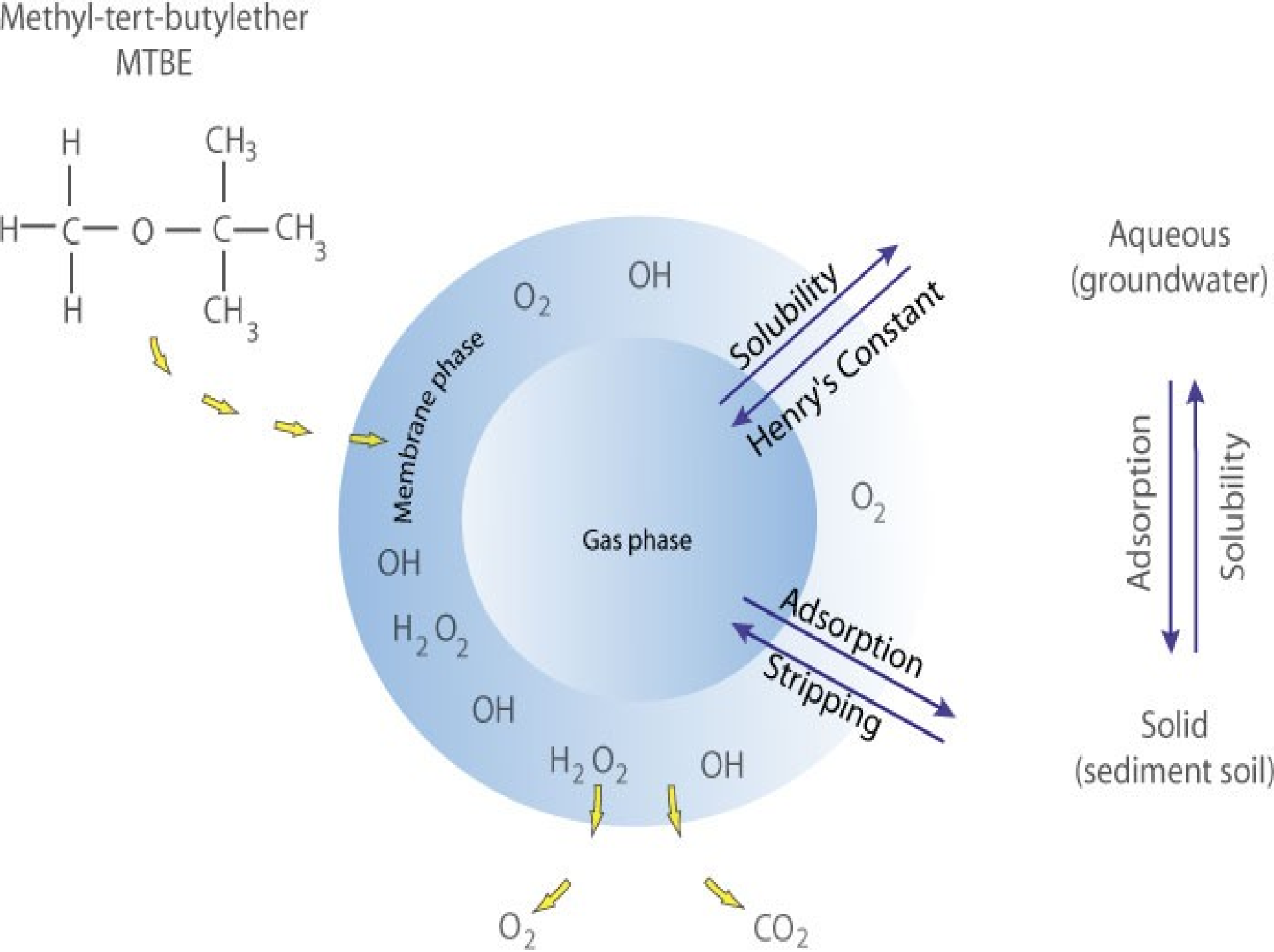
Primary (90% of mass)



MtBE **Ozone** **Formaldehyde** **Tert-butyl alcohol** **Oxygen**

Secondary (10% of mass)




Methyl-tert-butylether
MTBE
H
CH3
H—C—O—C—CH3
H
CH3
Membrane phase
O2
OH
OH
H2O2
OH
H2O2
OH
Gas phase
Solubility
Henry's Constant
O2
Adsorption
Stripping
Aqueous
(groundwater)
Adsorption
Solubility
Solid
(sediment soil)
O2
CO2

Sodium Persulfate $Na_2S_2O_8$

- Persulfate anion =
  - $S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO4\text{-}2$
- Sulfate Radical =
  - $S_2O_8^{-2} \rightarrow$ activation $\rightarrow$ $2SO_4^{-\bullet}$
- Radical degrades BTEX, MTBE and other oxygenates
- Emerging technology – but very promising

Permanganate

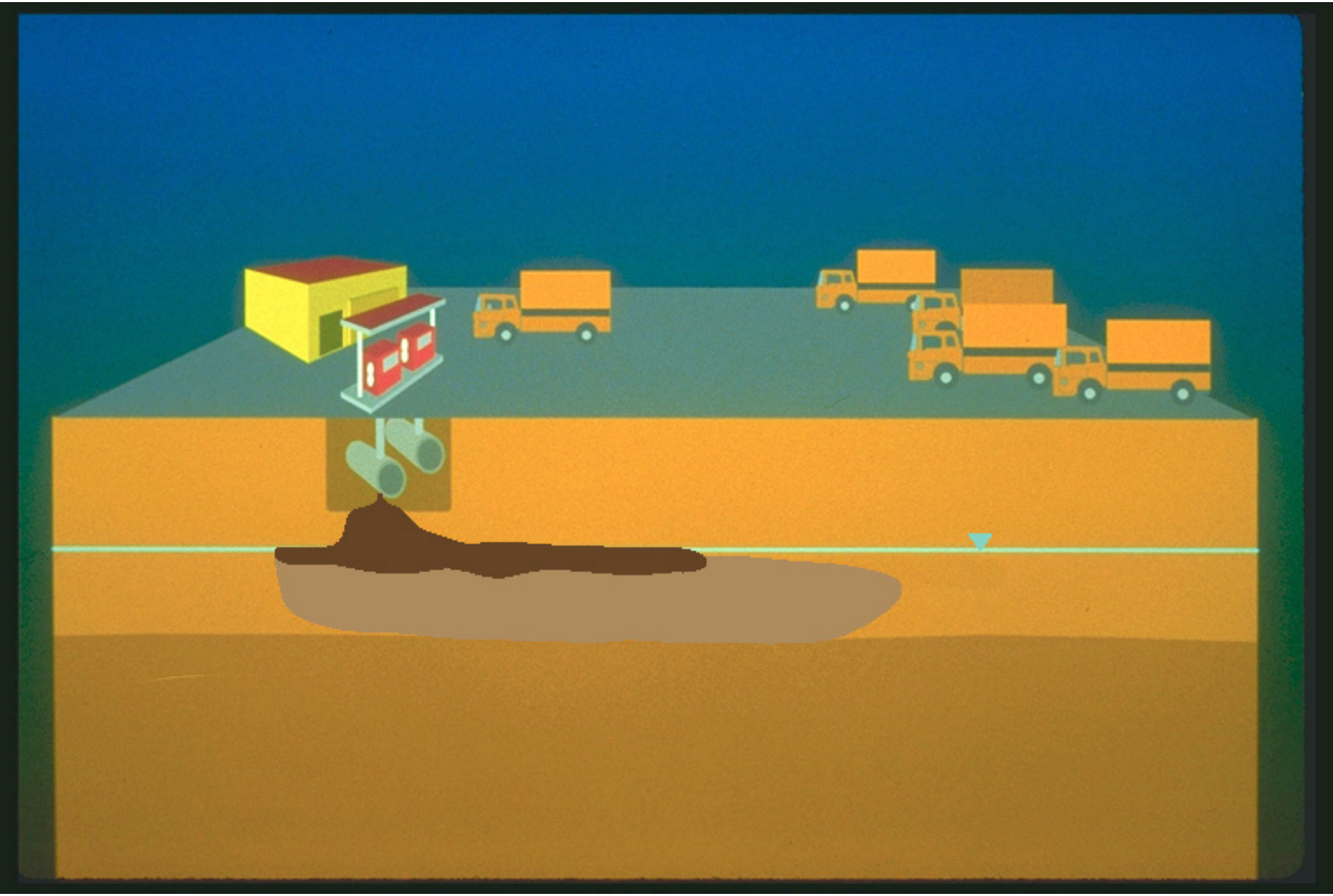
- Permanganate does not oxidize Benzene effectively
- MTBE mineralization may not be complete
- Don’t try this at home!

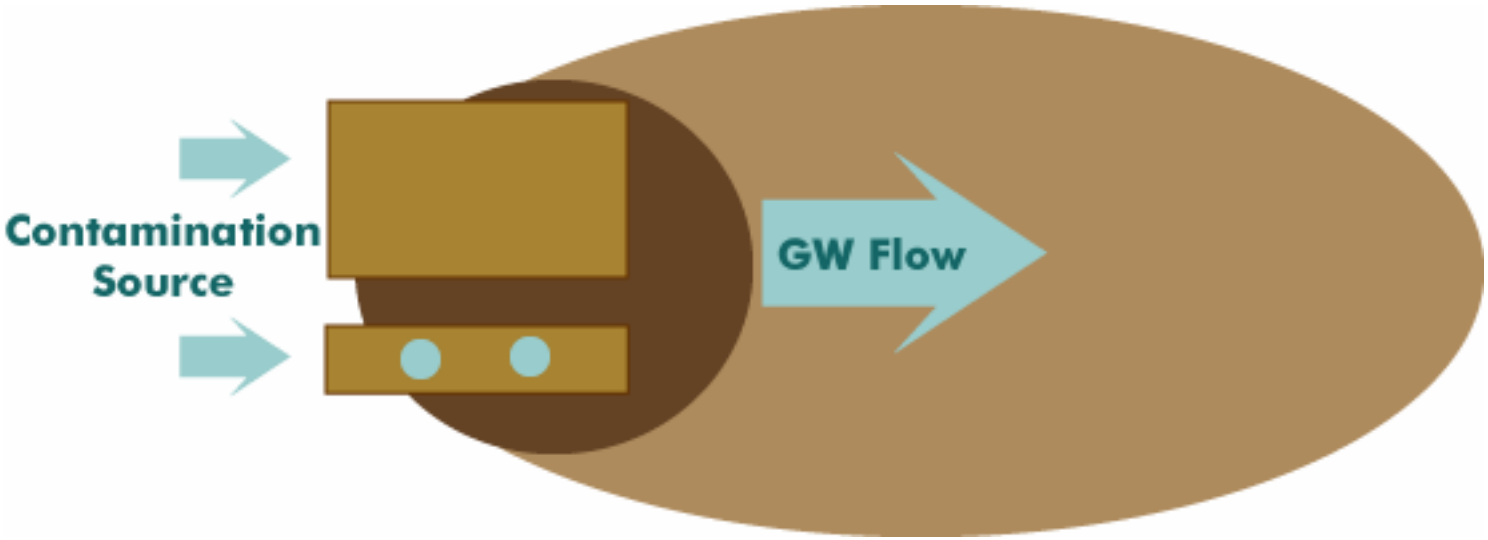
ISCO Site Characterization

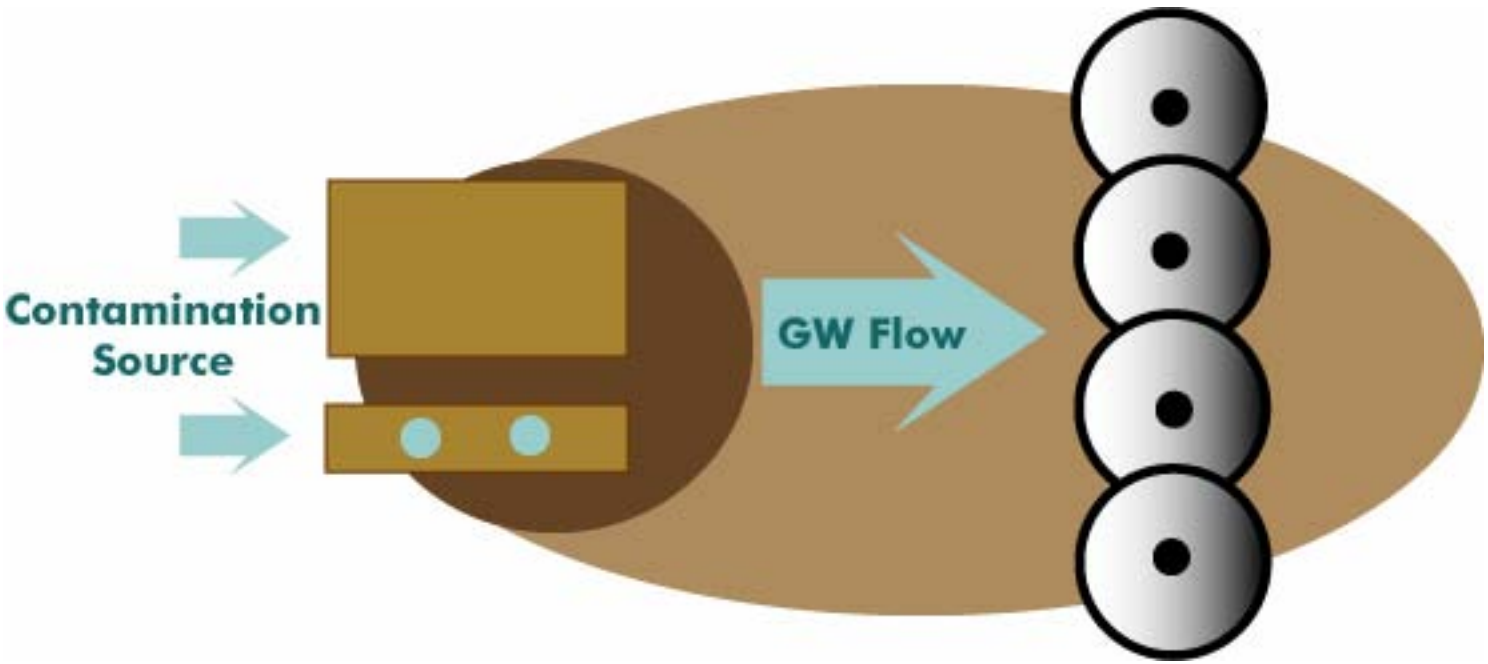
- In addition to the standard characterization (hydrogeology, mass balance, geochemistry) we need to assess the oxygen flux and oxidant demand at each site
- COCOD – Constituent of Concern Oxygen Demand
- NOD – Natural Oxygen Demand
  - SOD – Soil Oxygen Demand
  - DOD – Dissolved Oxygen Demand

Applicability of Oxidants

- Source Area
  - Applicable to address source areas
    - Based on mass present
  - If significant free-product is present, ISCO is generally not the best value approach
  - Be aware of tanks and product lines
- Near Source
  - Mass flux barrier
- Downgradient – Mass Flux Barrier
  - Oxidant injection array as barrier




Contamination
Source
GW Flow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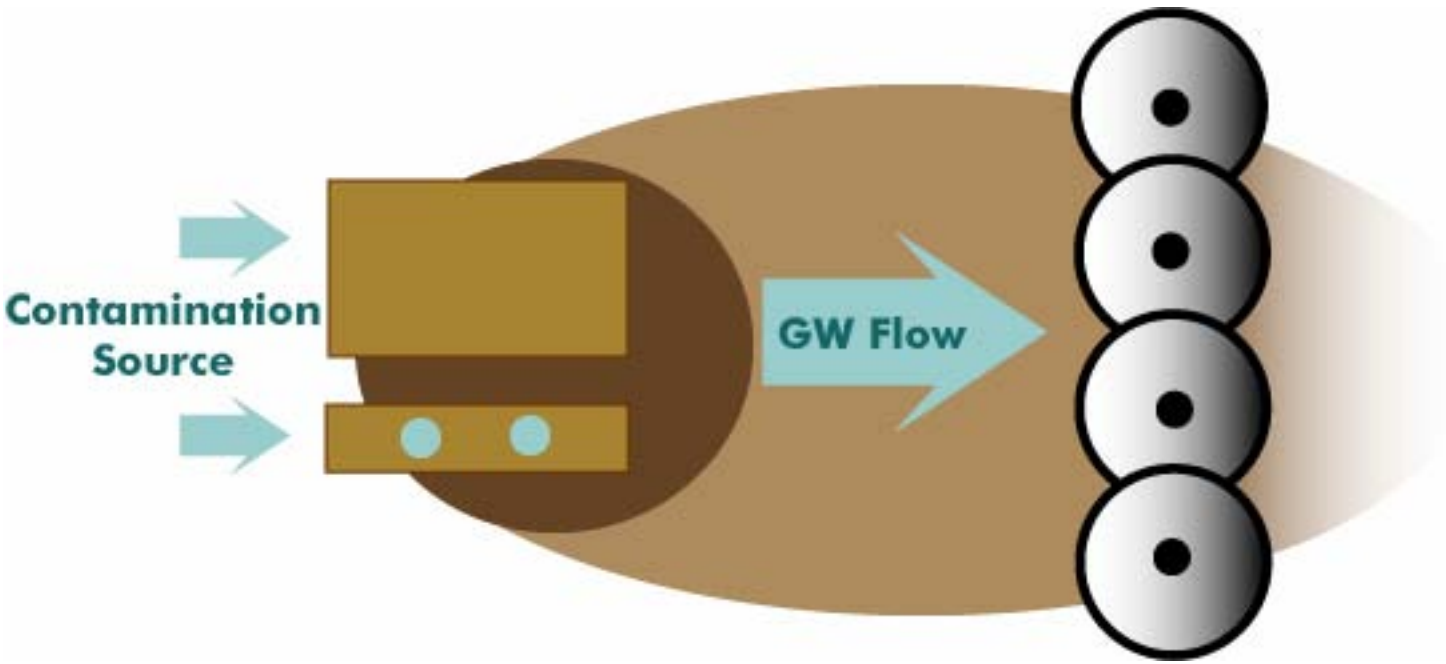
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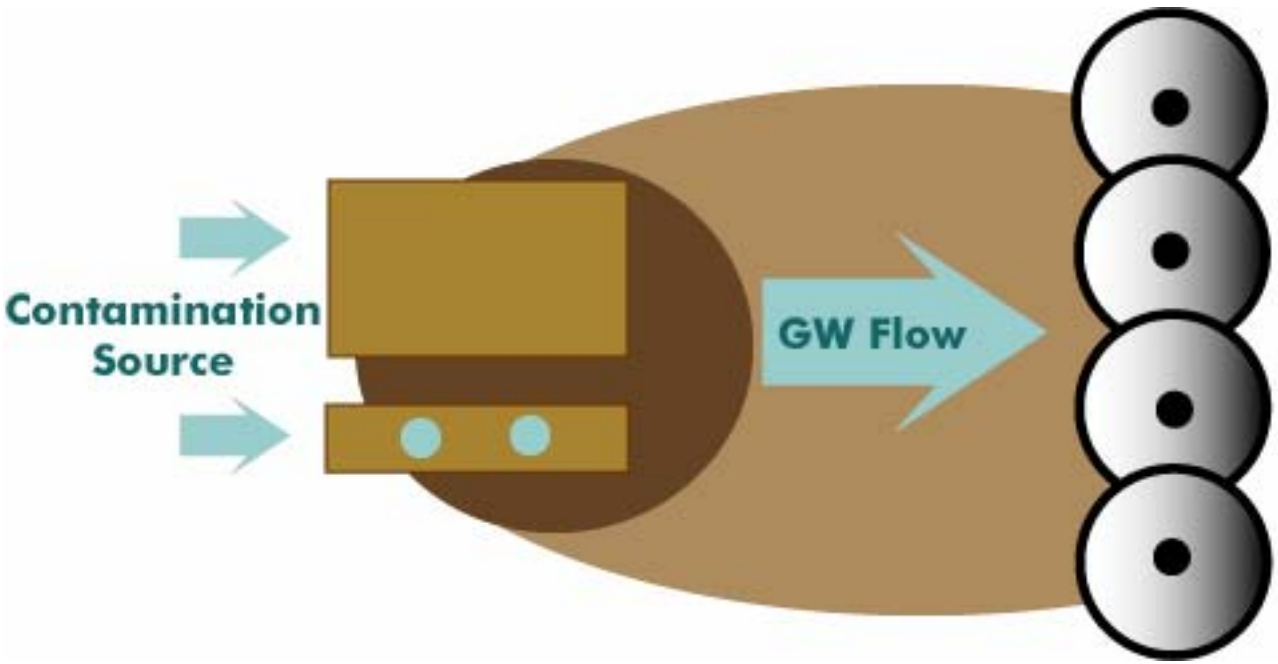
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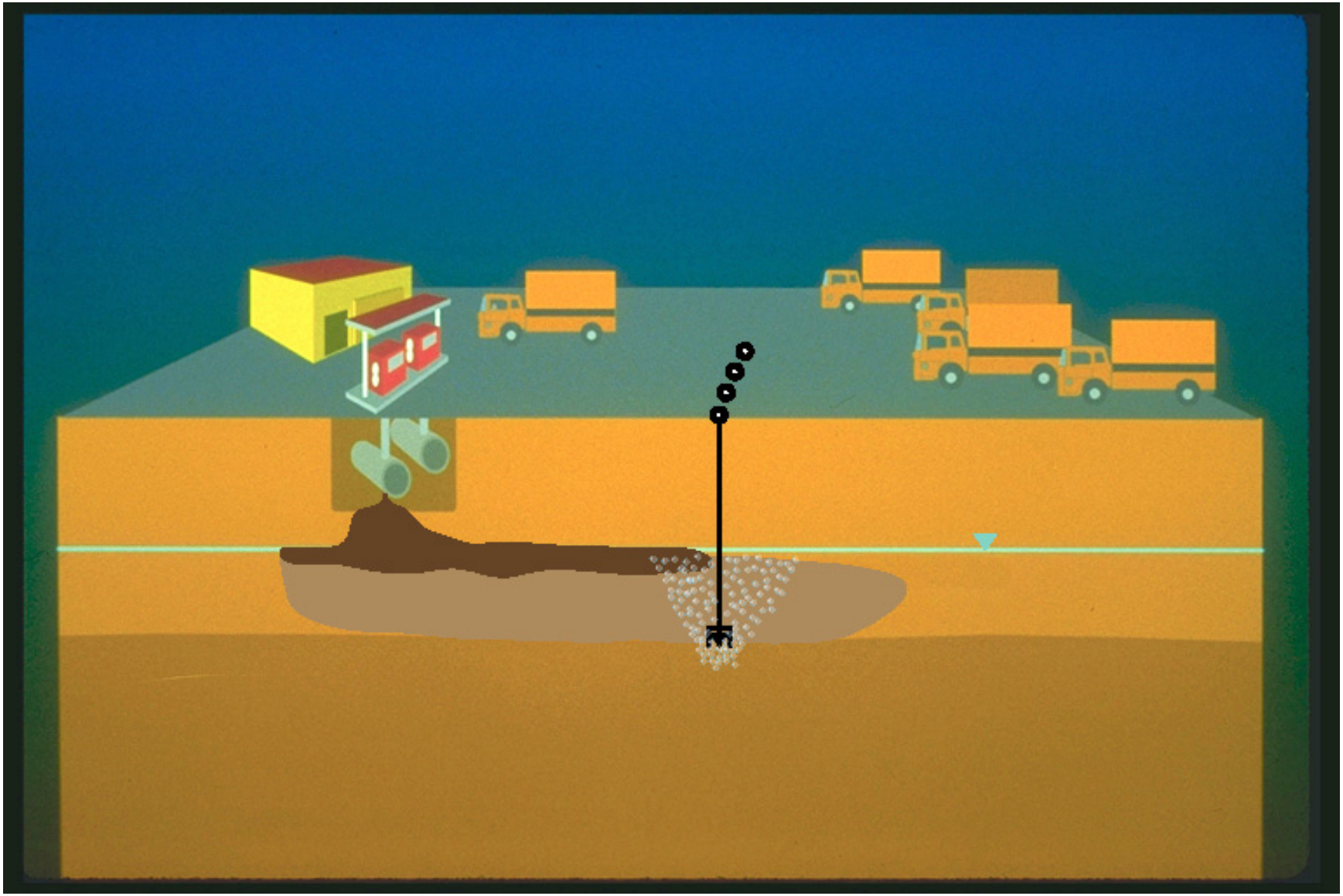

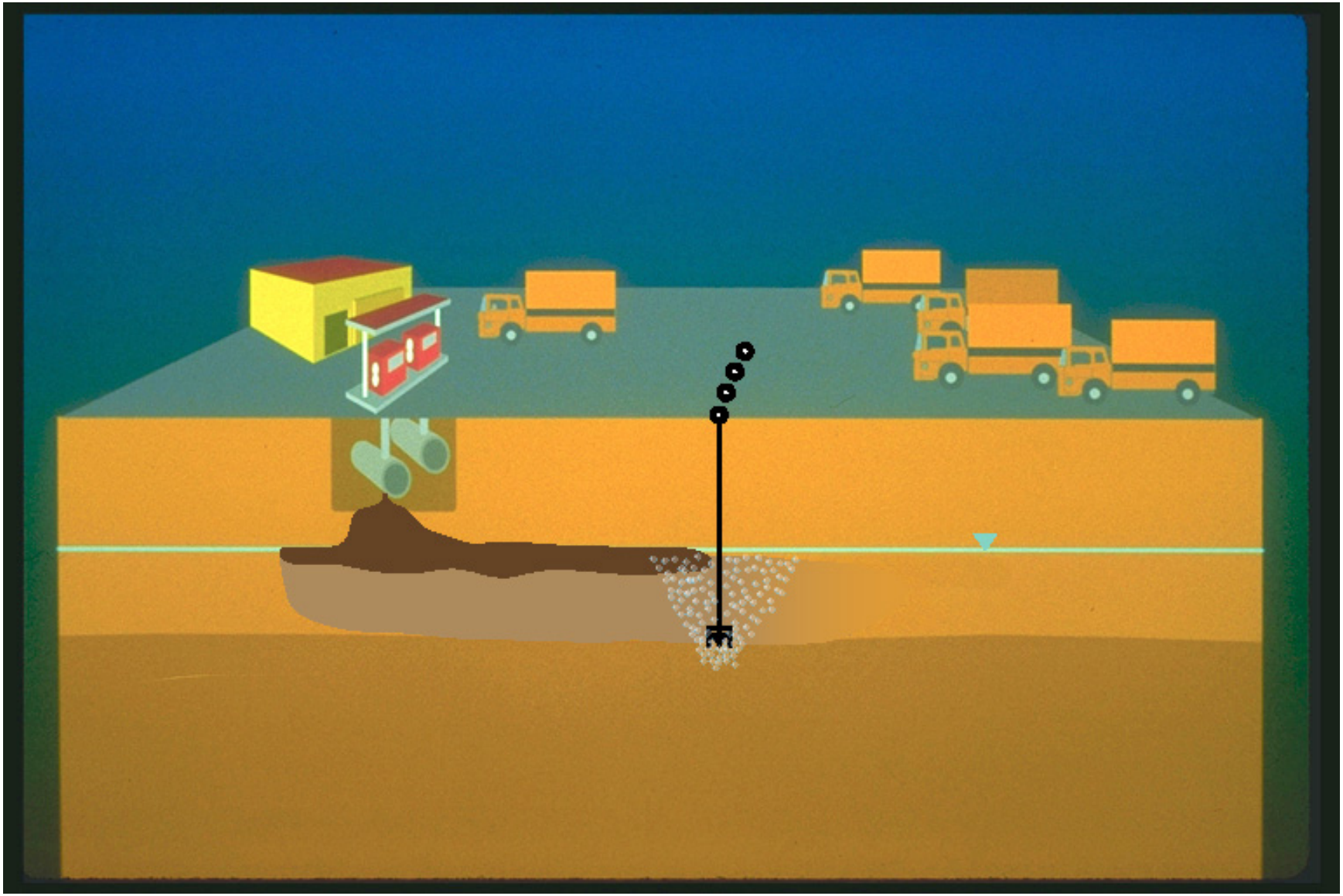

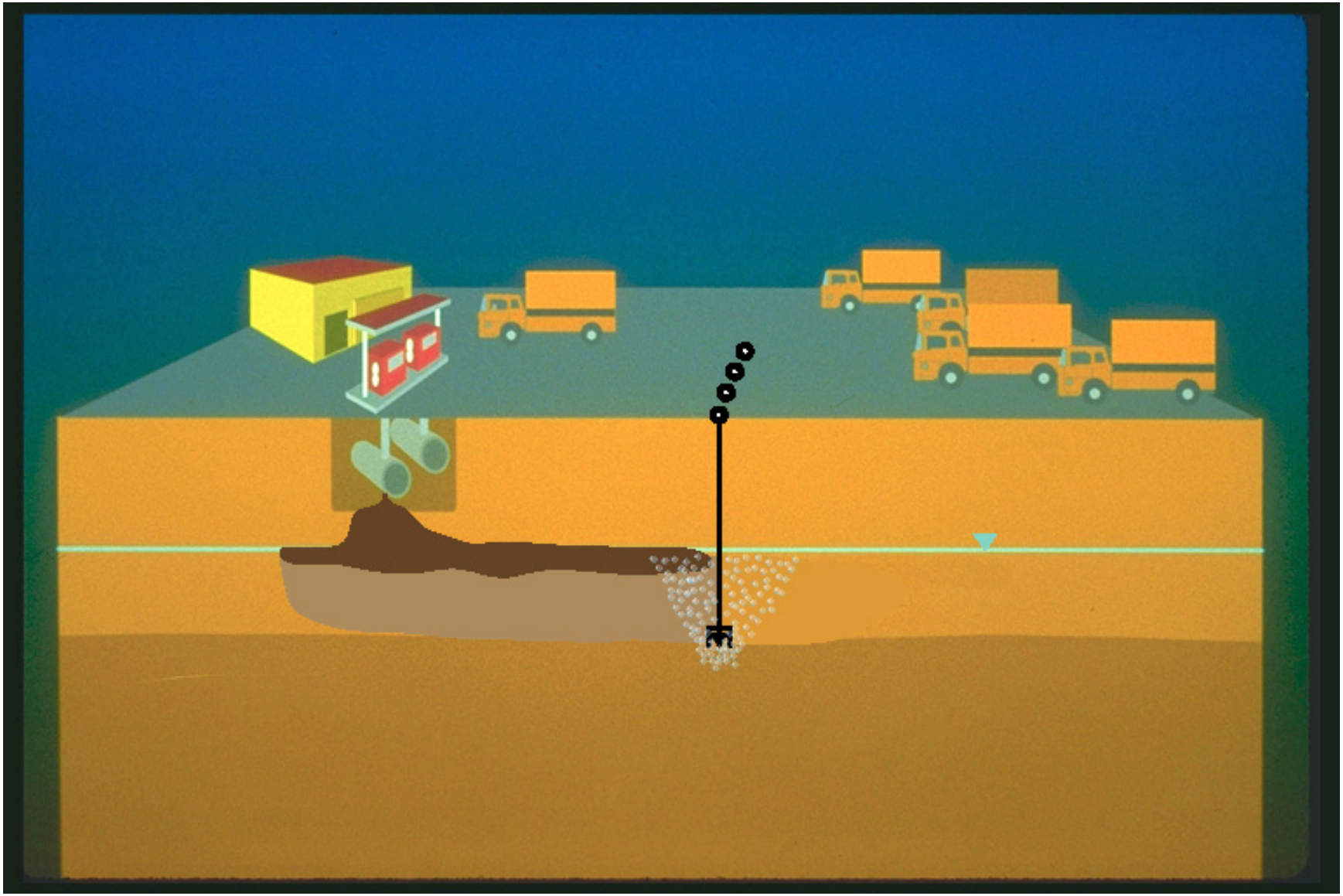

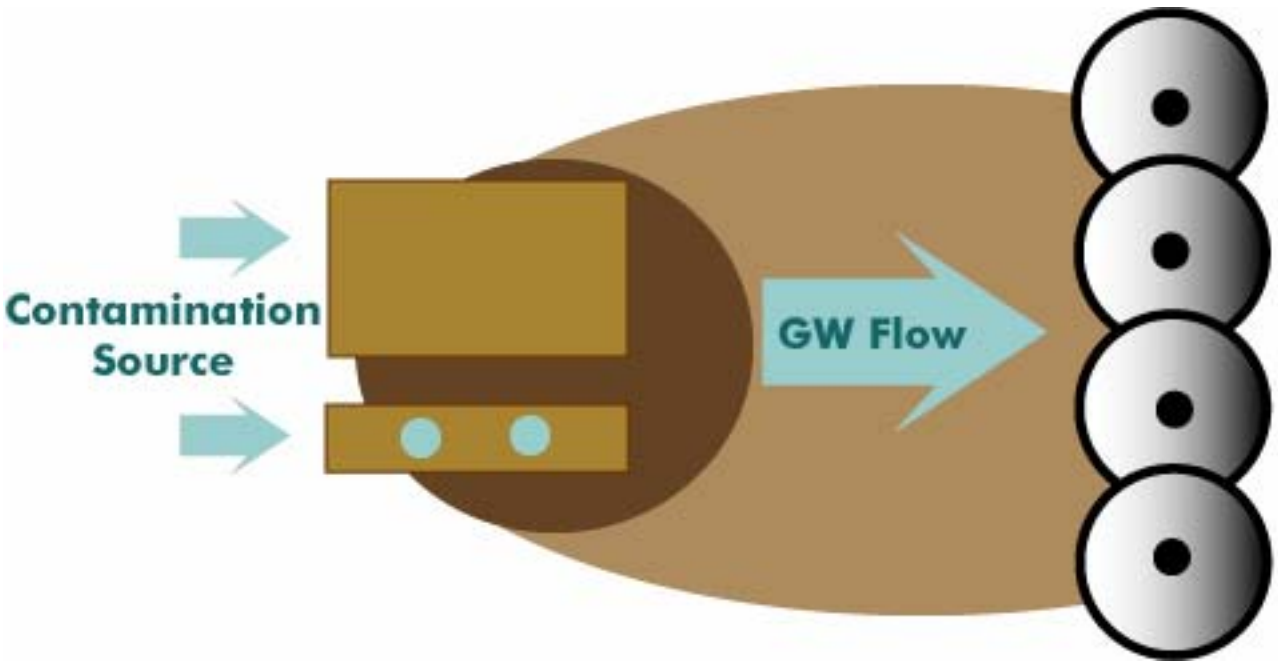
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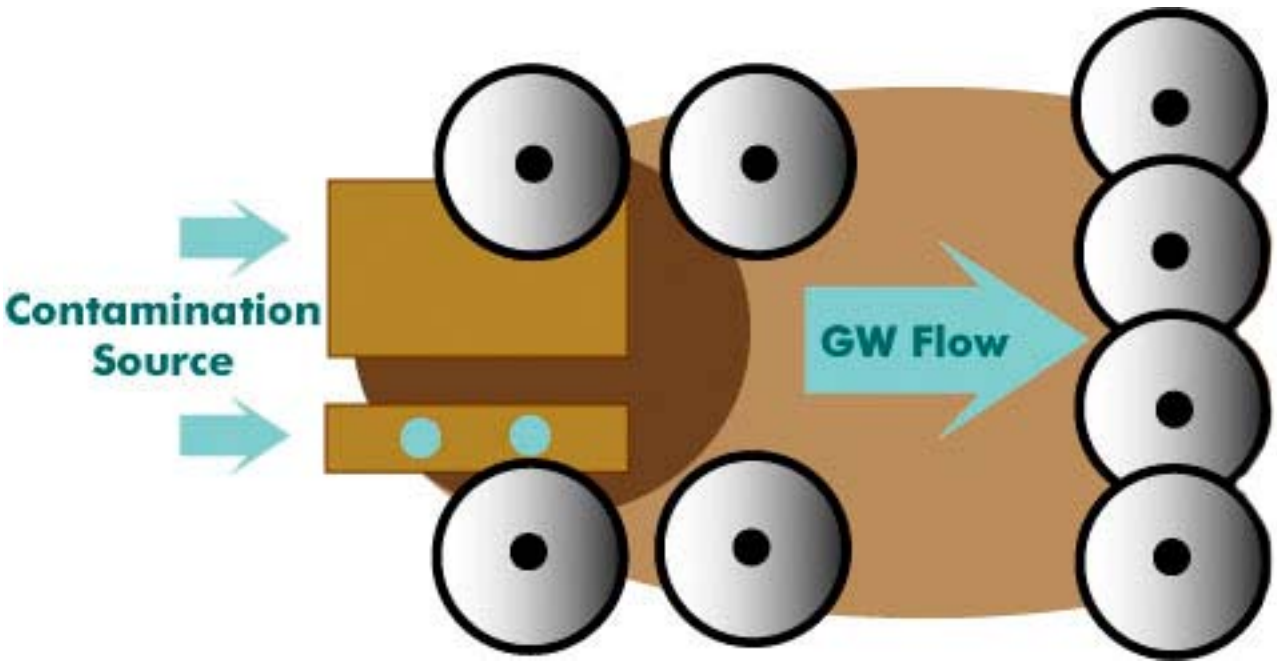
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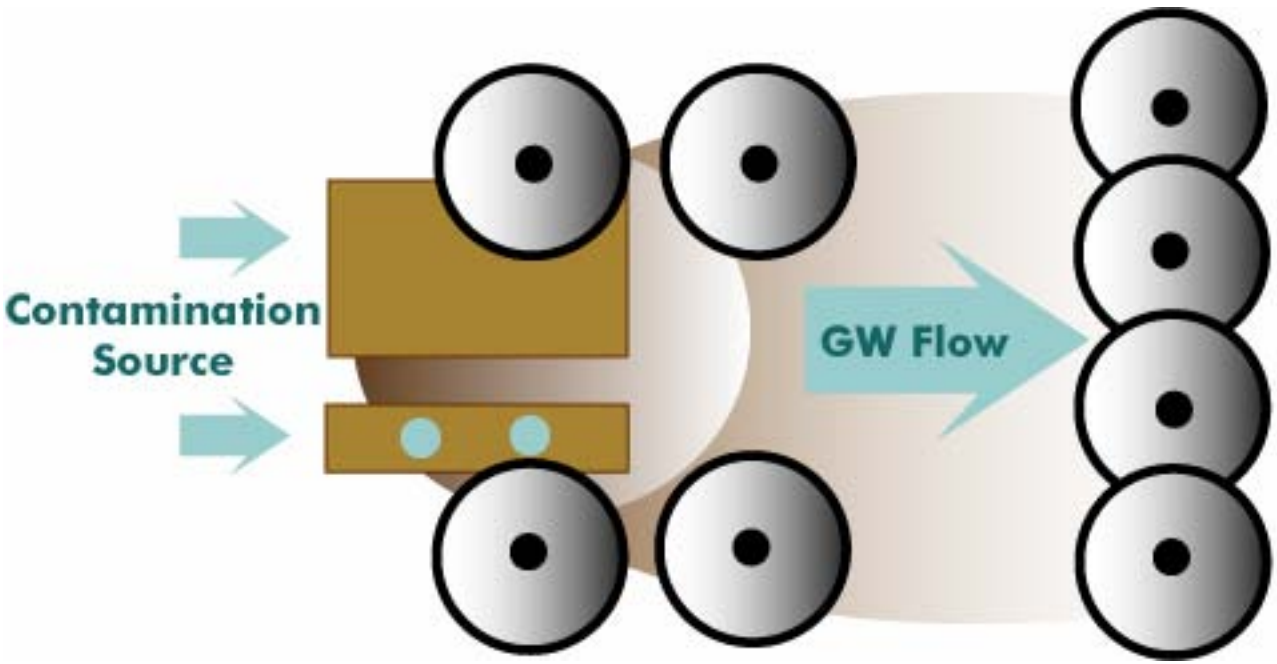
GW Flow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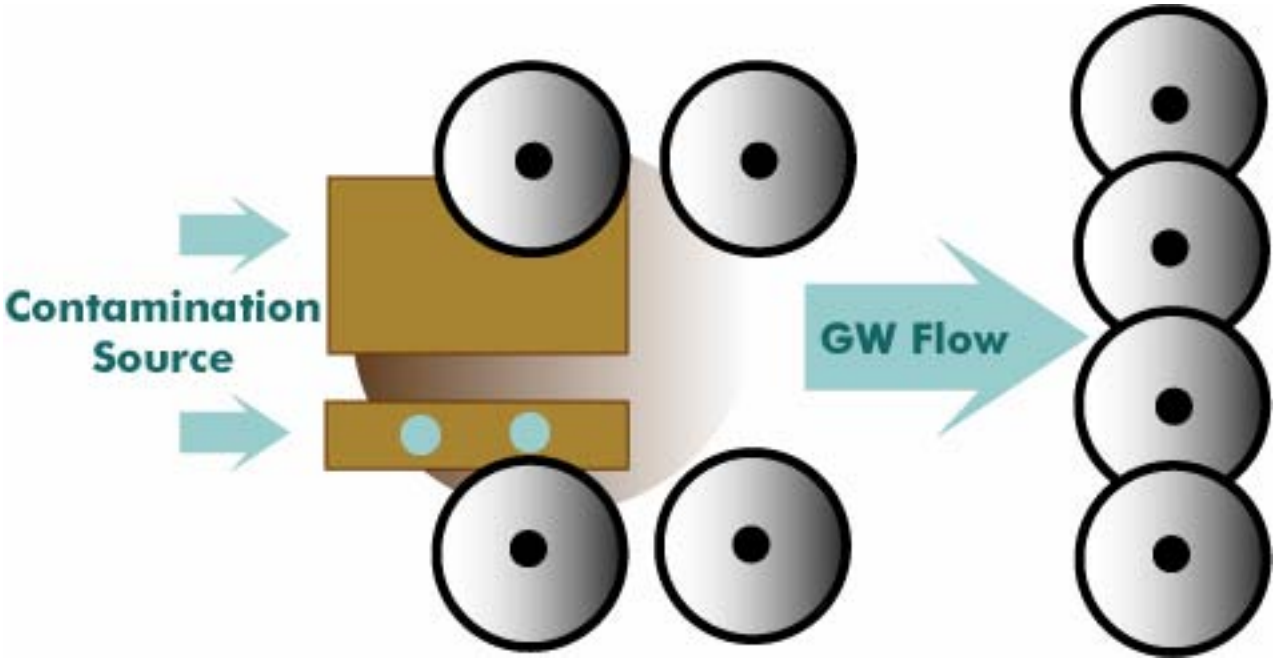
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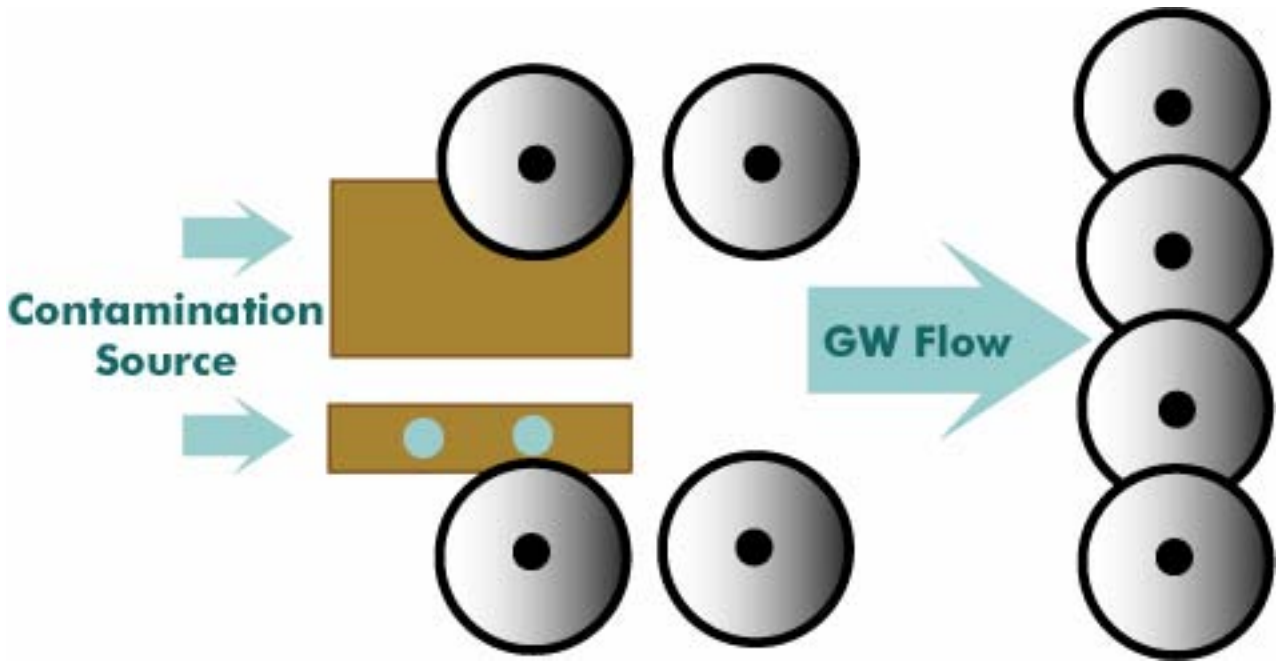
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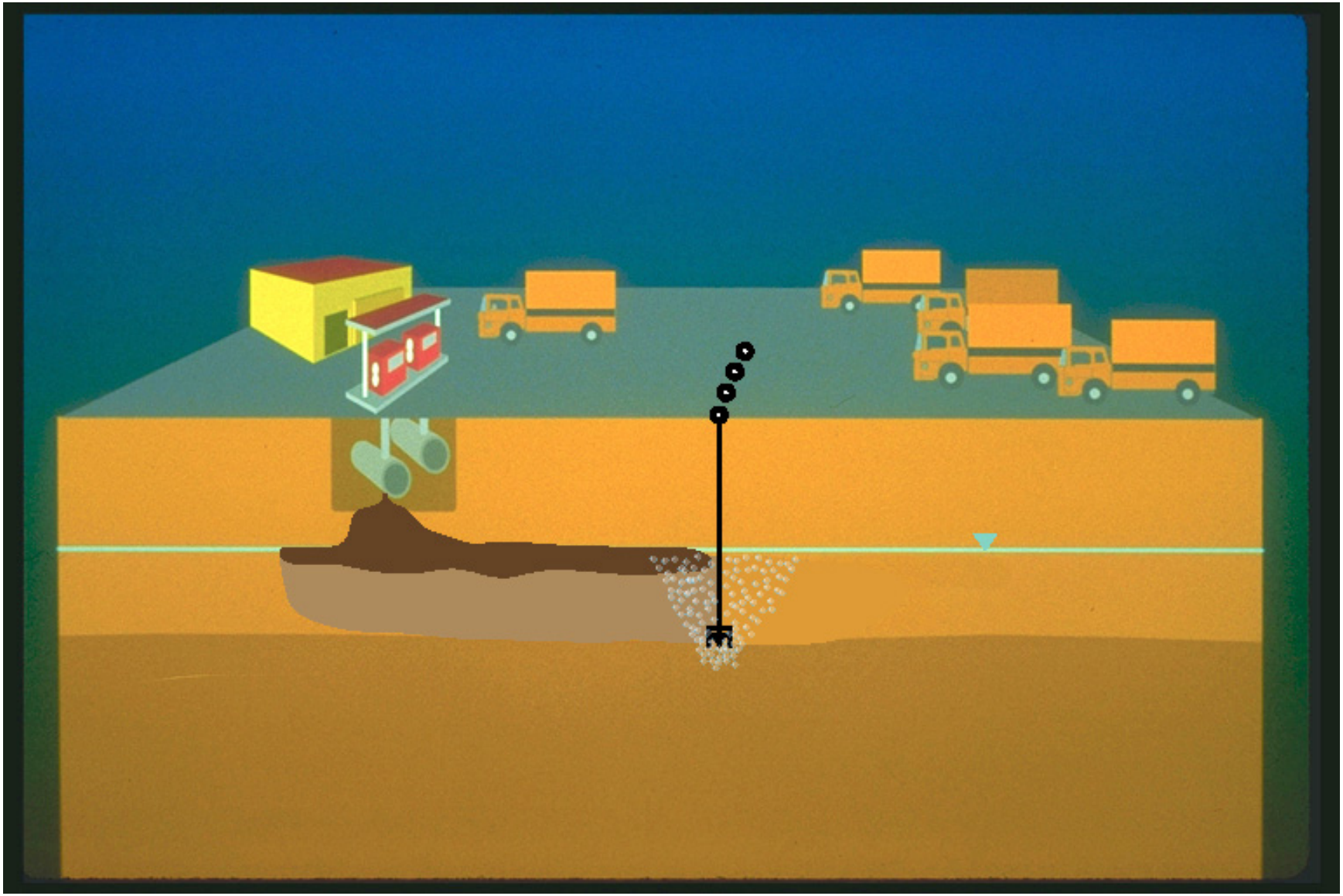

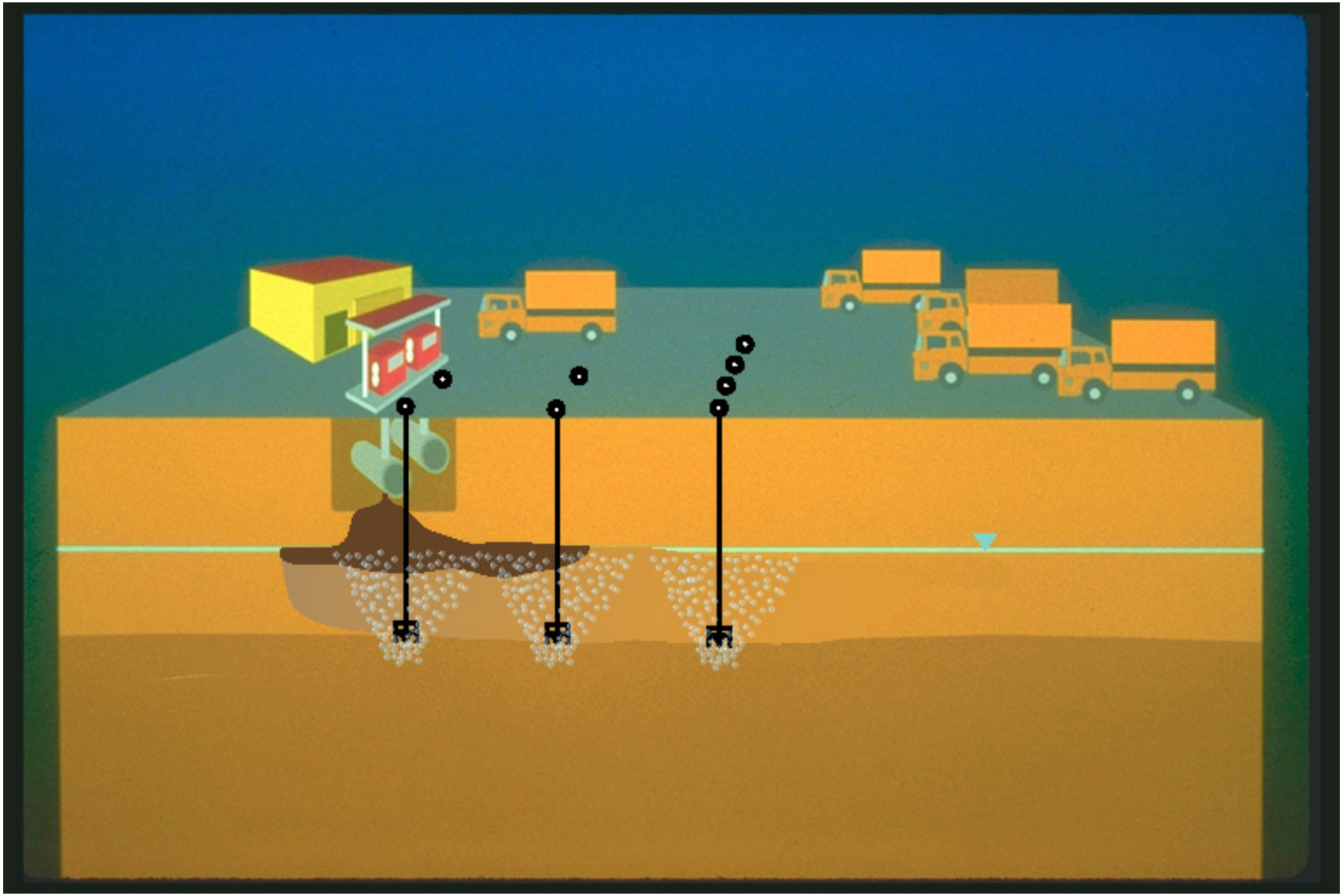

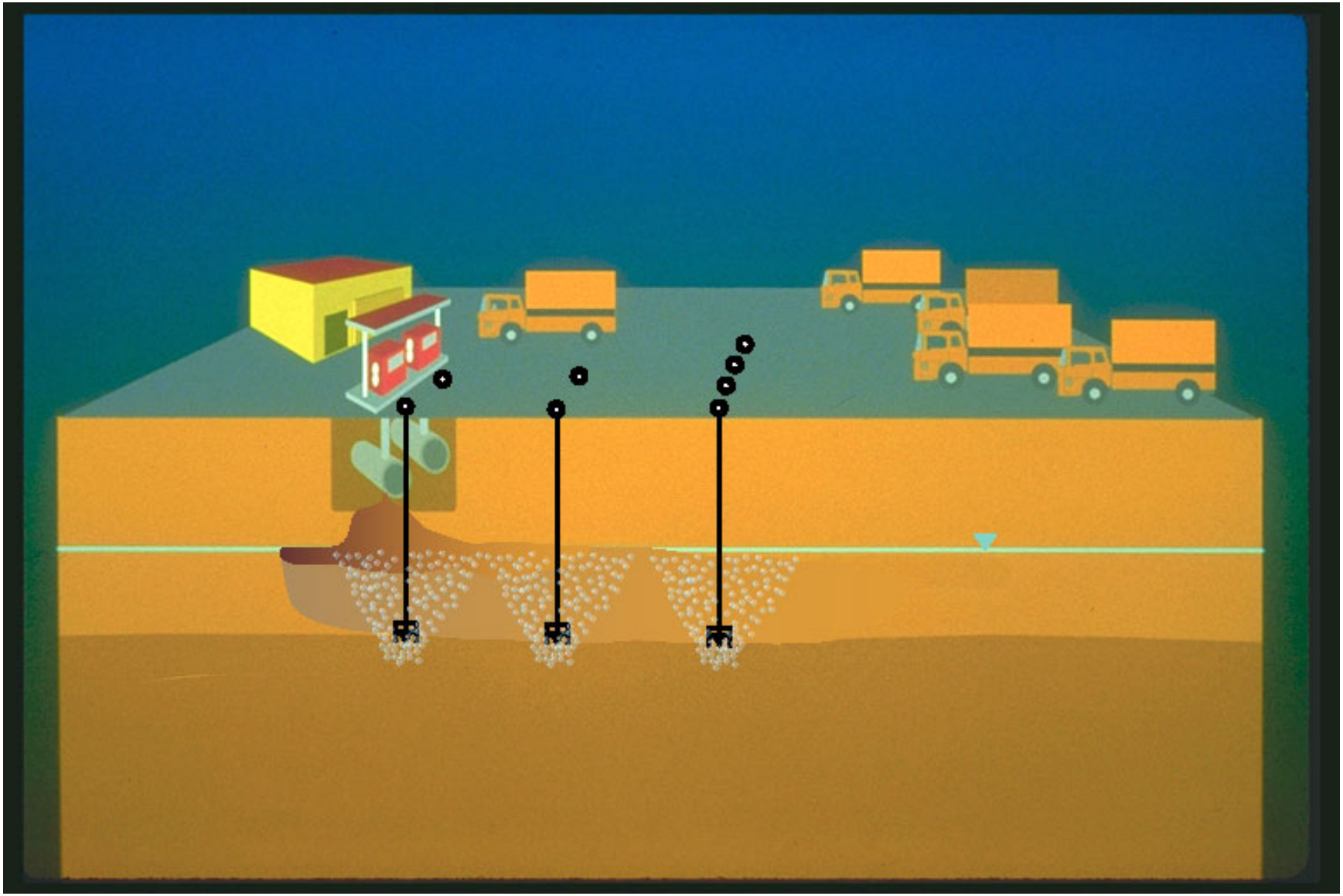

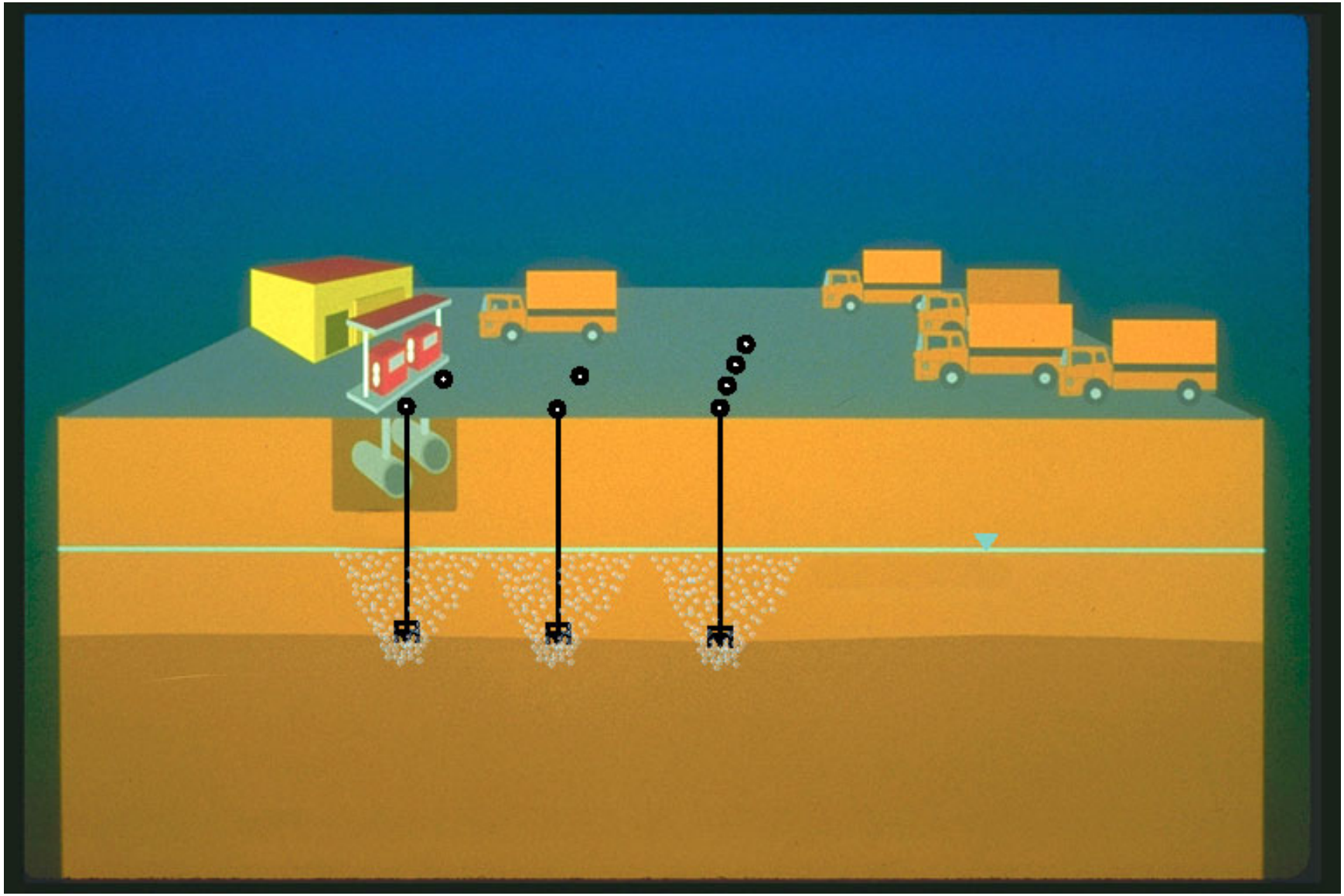

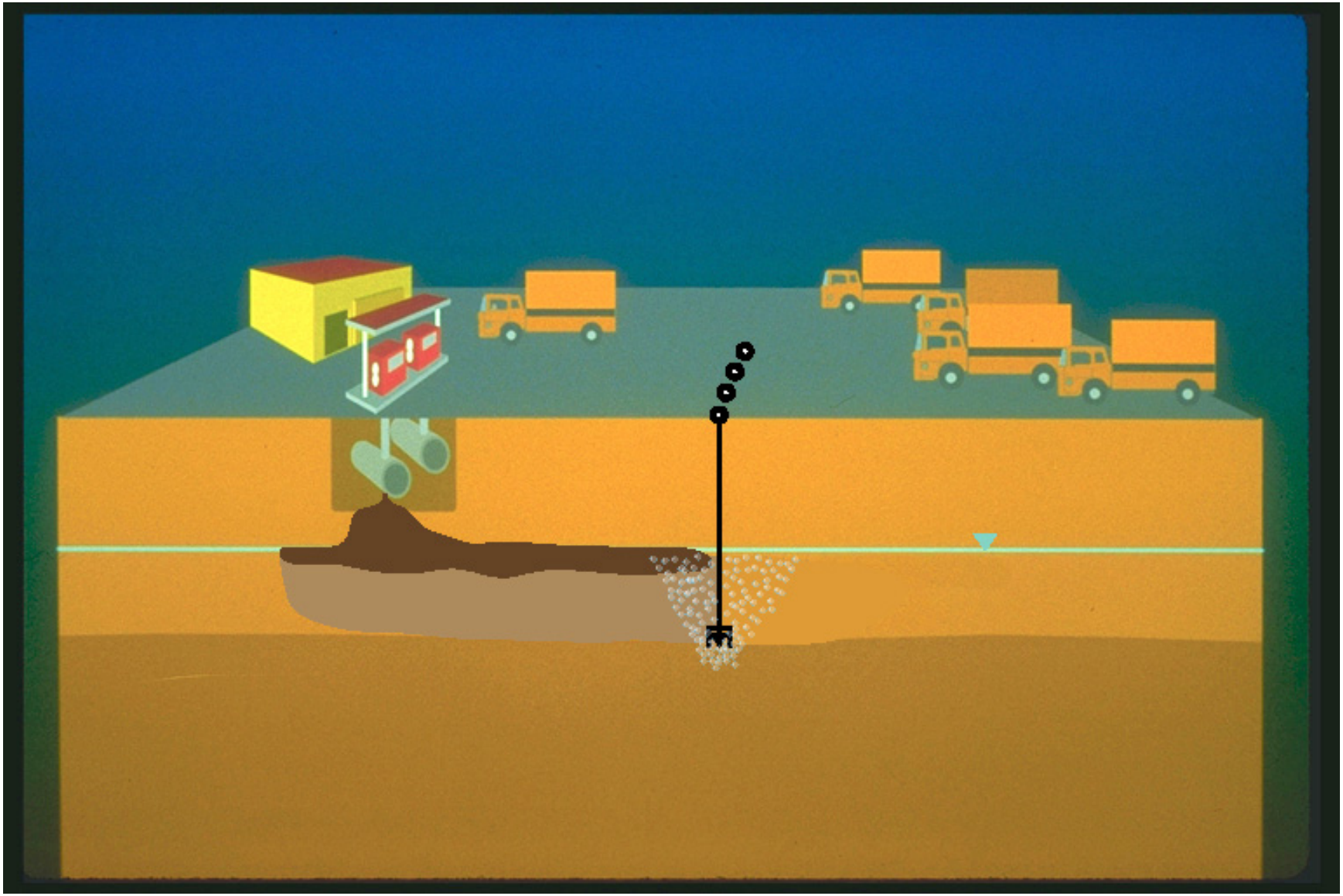

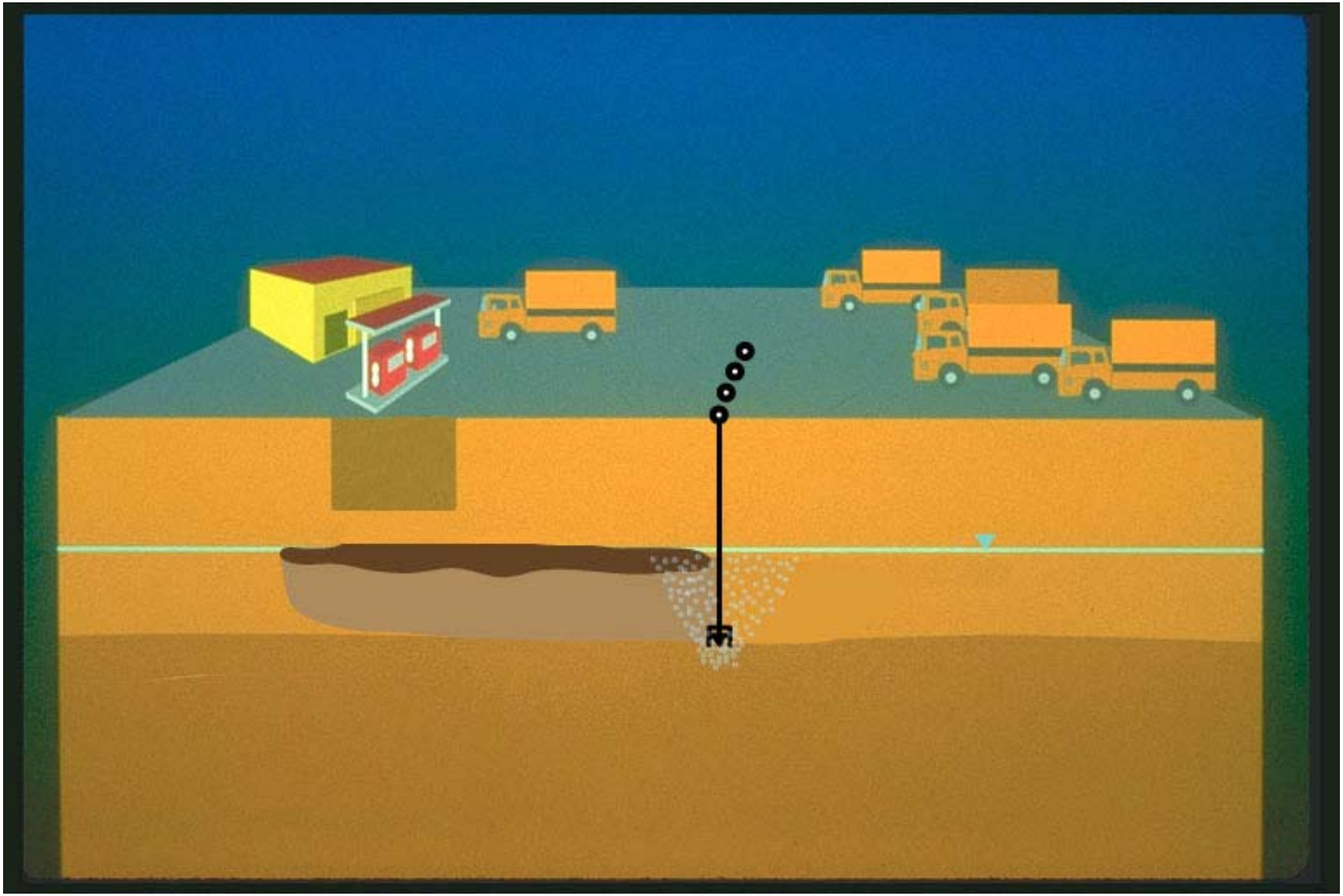

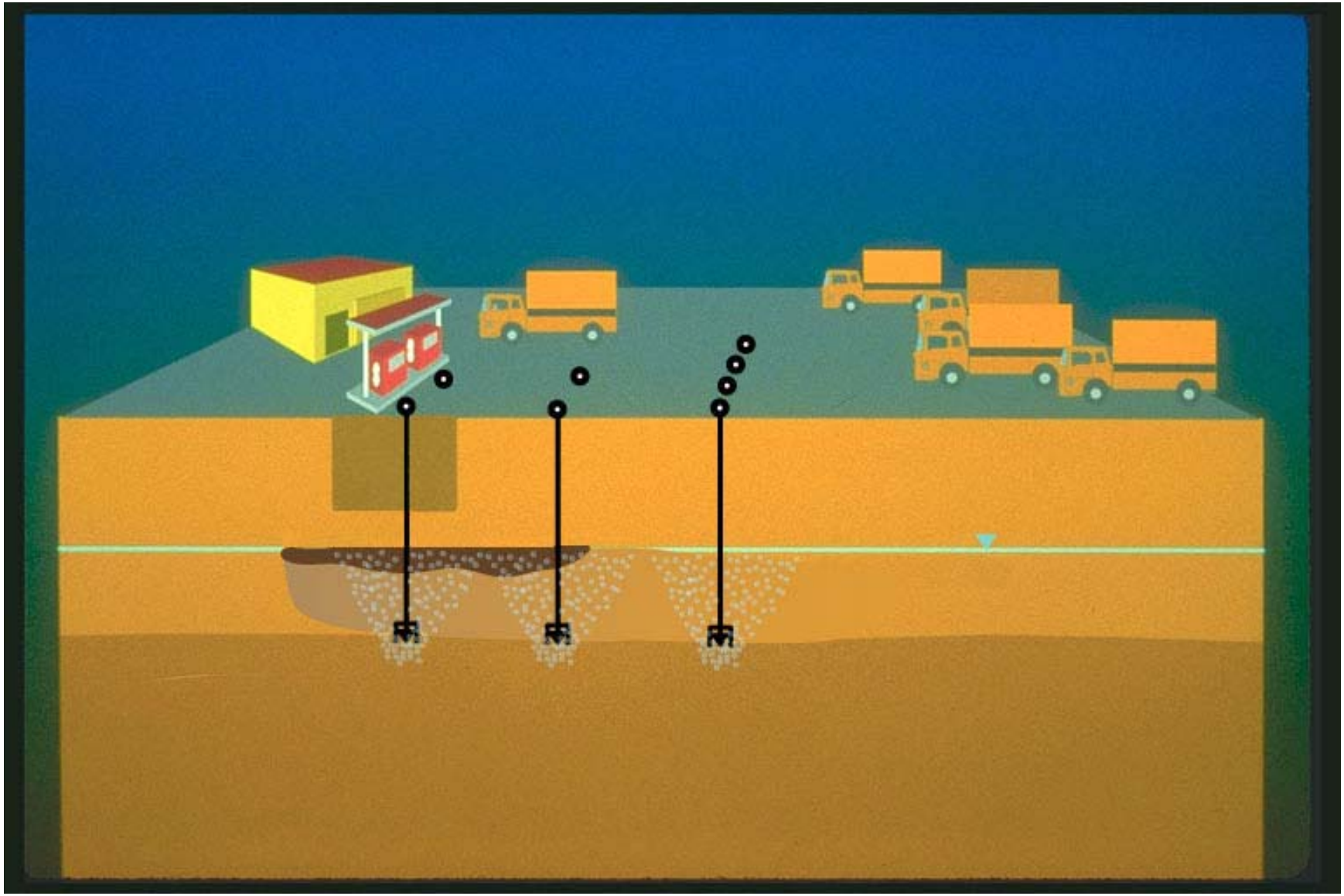

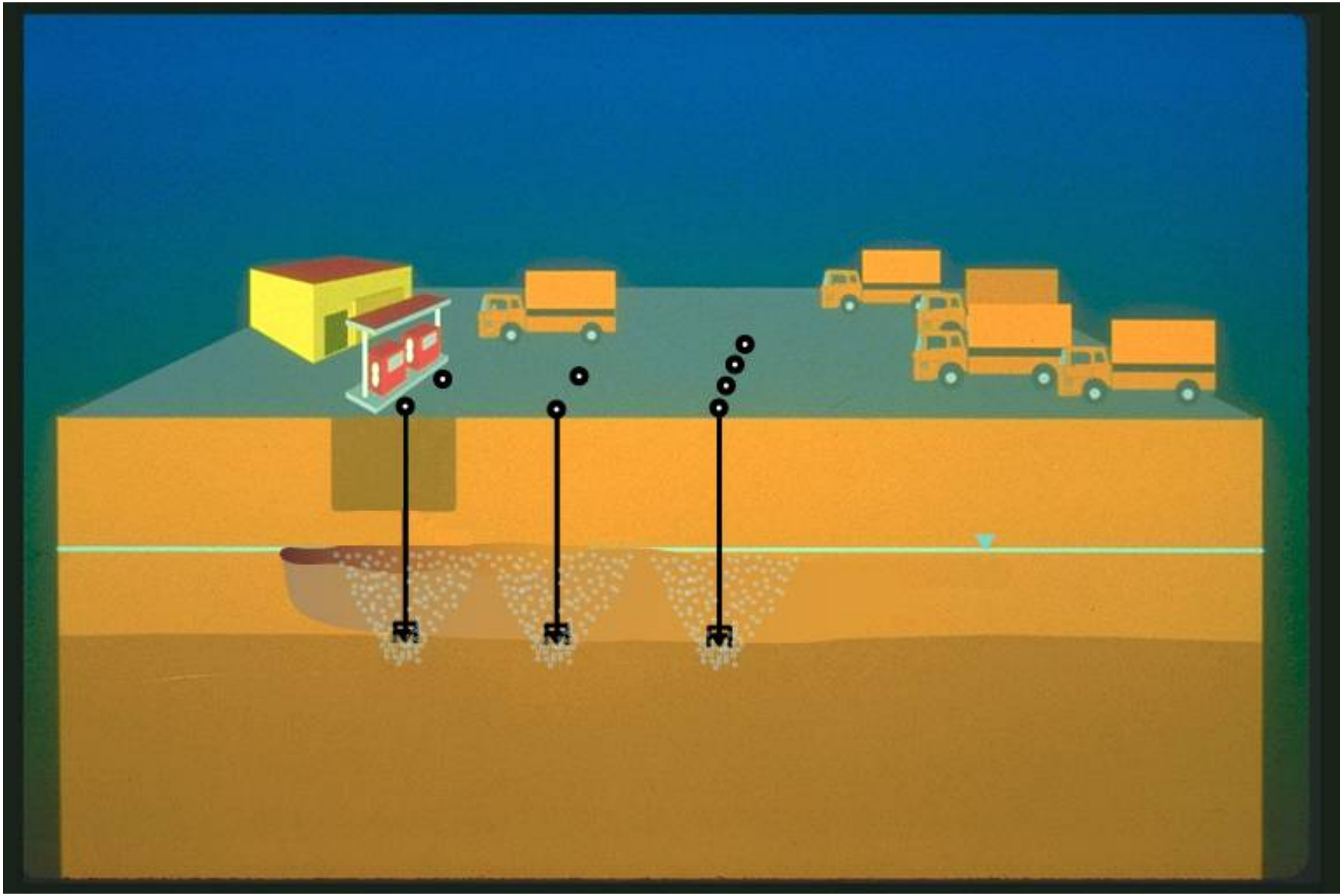

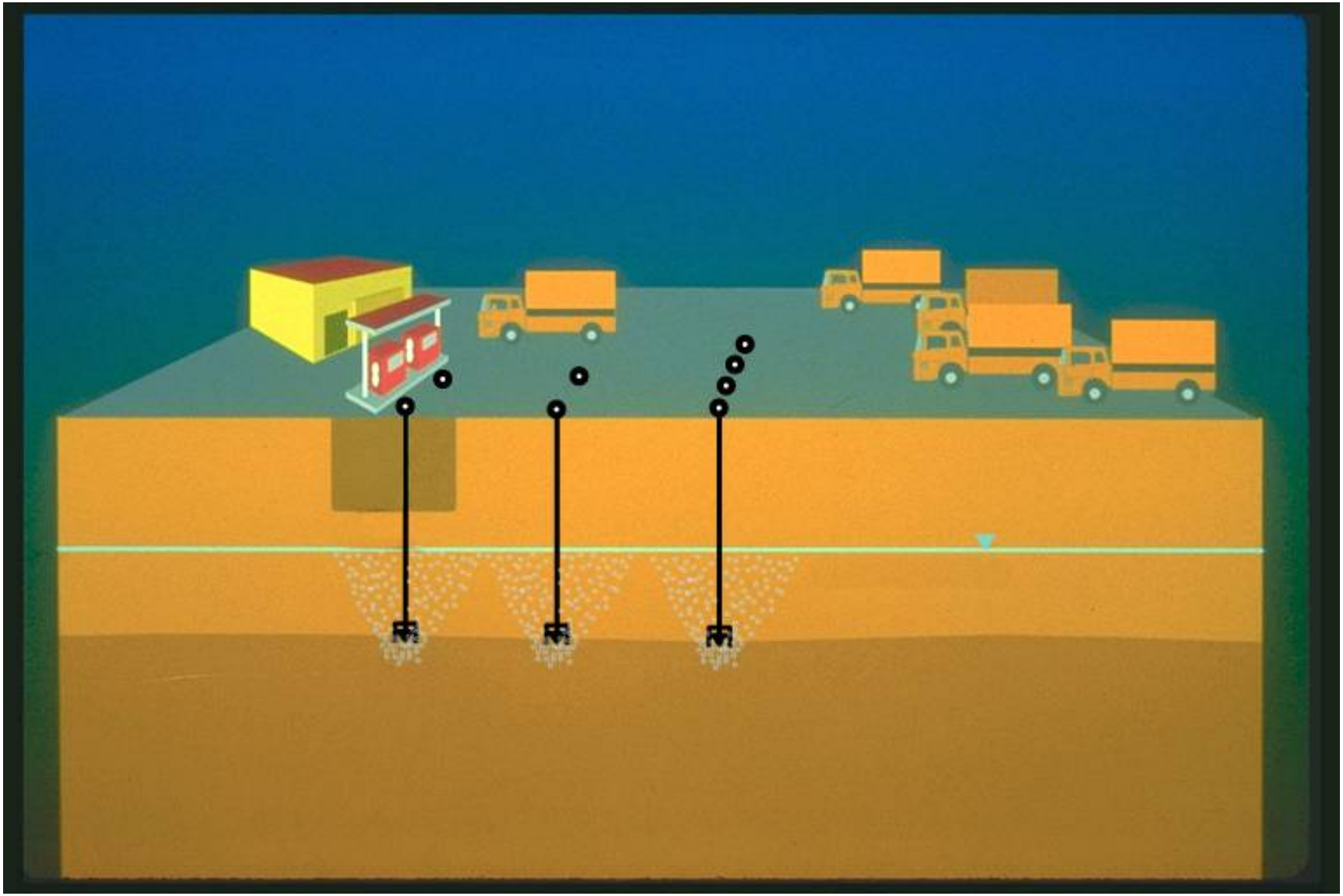

ISCO Application Summary

- ISCO can be applied safely and effectively
- Experience is a factor in success
- Source area or source mass flux barrier can be good applications for ISCO
- Has been applied for plume treatment
- Site characterization data is critical

ISCO
Case Histories

- Fenton's
- Persulfate
- Ozone

Select CleanOX® MTBE Site

- Active Gasoline Service Station - NJ
  - Product Sheen in all wells
  - 1-2 feet of smear zone
  - two well two cycle application, initial cycle stripped adsorbed contamination into dissolved
  - second round consumed dissolved only
  - 97% reduction in BETX constituents
  - 75% reduction in MTBE

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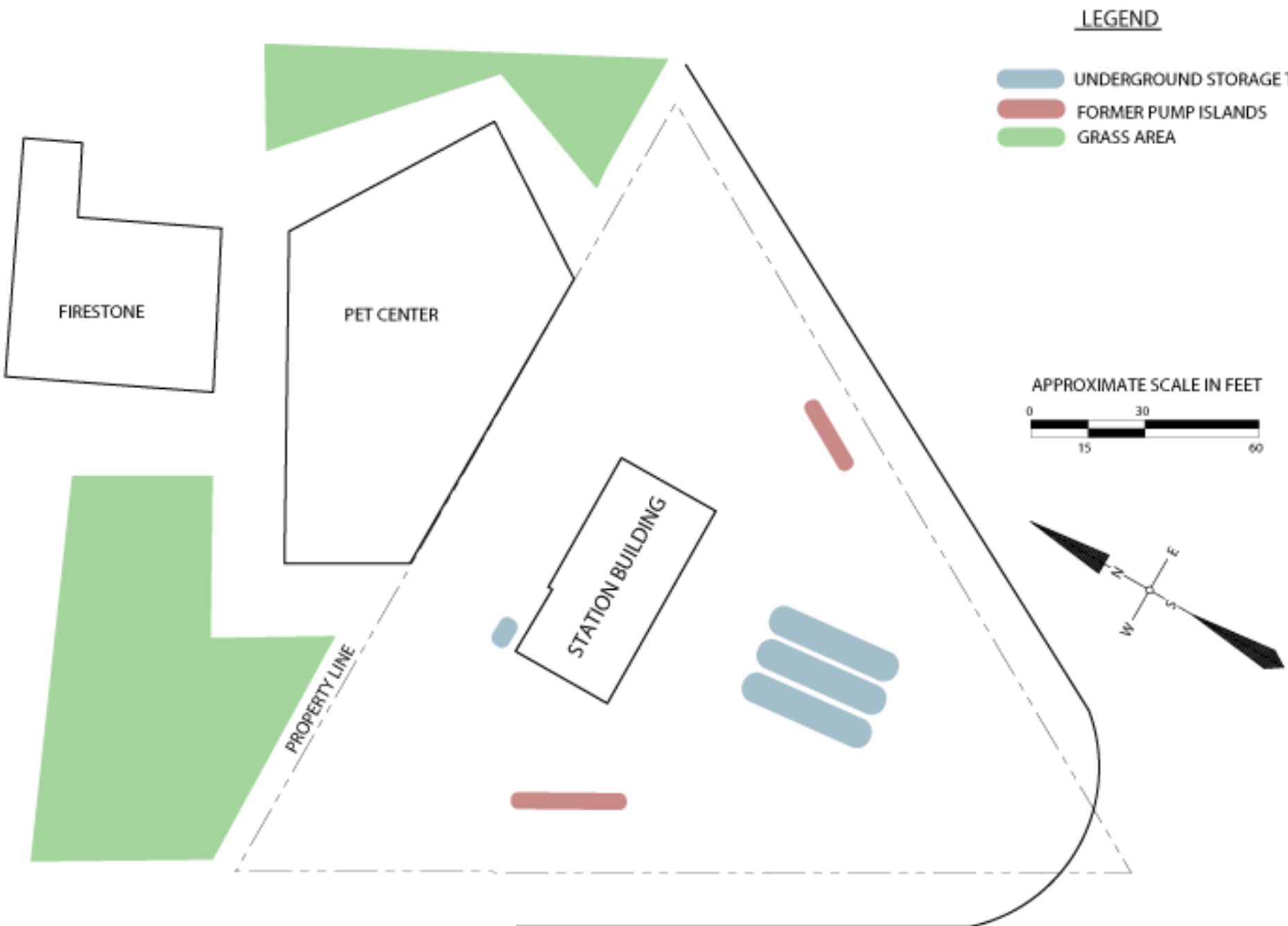
Petroleum

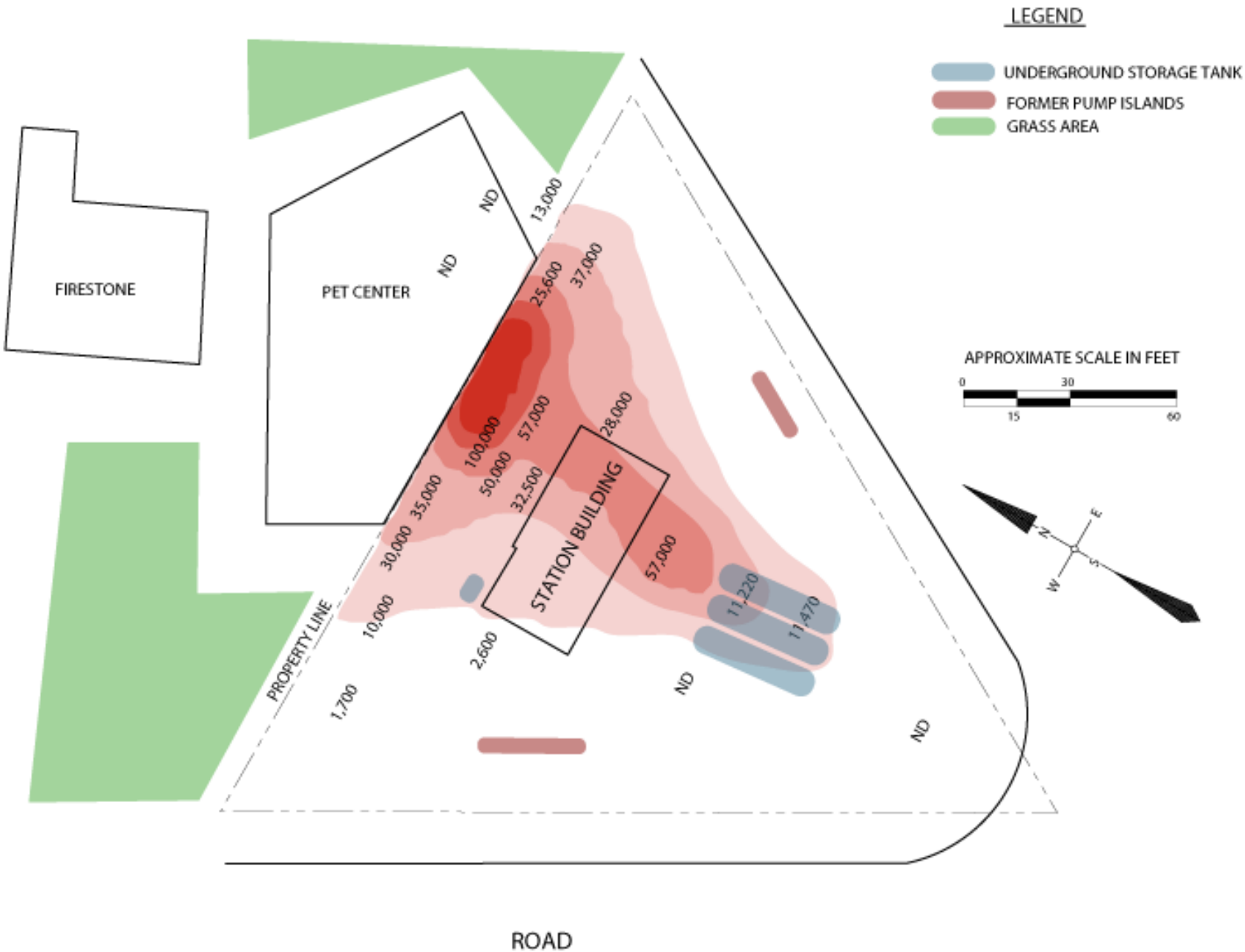
Location	benzene (ug/l)	MTBE (ug/l)
Blackstone, VA	1600/78	1300/360
Clayton, DE	519/7.4	16,100/233

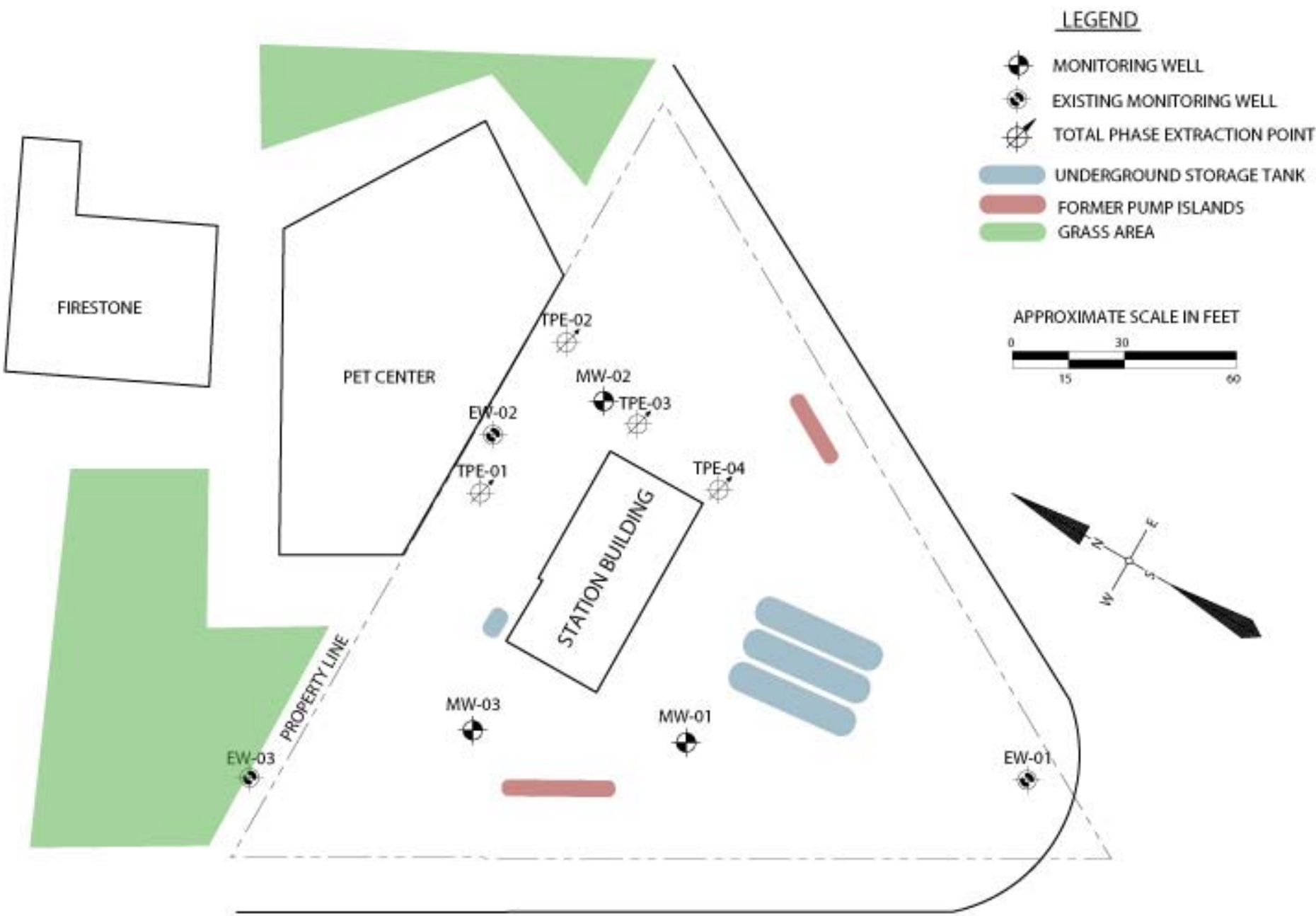
Location	xylene (ug/l)	naphthalene (ug/l)
Hagaman, NY	2,778/22	
Lexington, NC		>1,000,000/<1,000

Site Number	Site Description	Initial MtBE concentration	Lithology	Ozone Application	Duration (months)	MTBE Reduction
1	Former Retail Service Station	17,000 ppb	Saprolite	2.5 lbs per day	4	> 90% Sitewide. Below Standards
2	Toll Road Service Plaza	100,000 ppb	Clean Sand	2.5 lbs per day	12+	> 95% Reduction
3	Former Retail Service Station	1,800 ppb	Sandy Silt	4 lbs per day	3	75-90% Reductions Below SSTLS.
4	Active Retail Service Station	510 ppb	Weathered Schist	2 lbs per day	3	75-90% Reductions Below Standards.
5	Former Retail Service Station	6,500 ppb	Saprolite	5 lbs per day	2	> 90% Reductions Below SSTLS

SSTL – Site-specific target levels of concentrations of contaminants

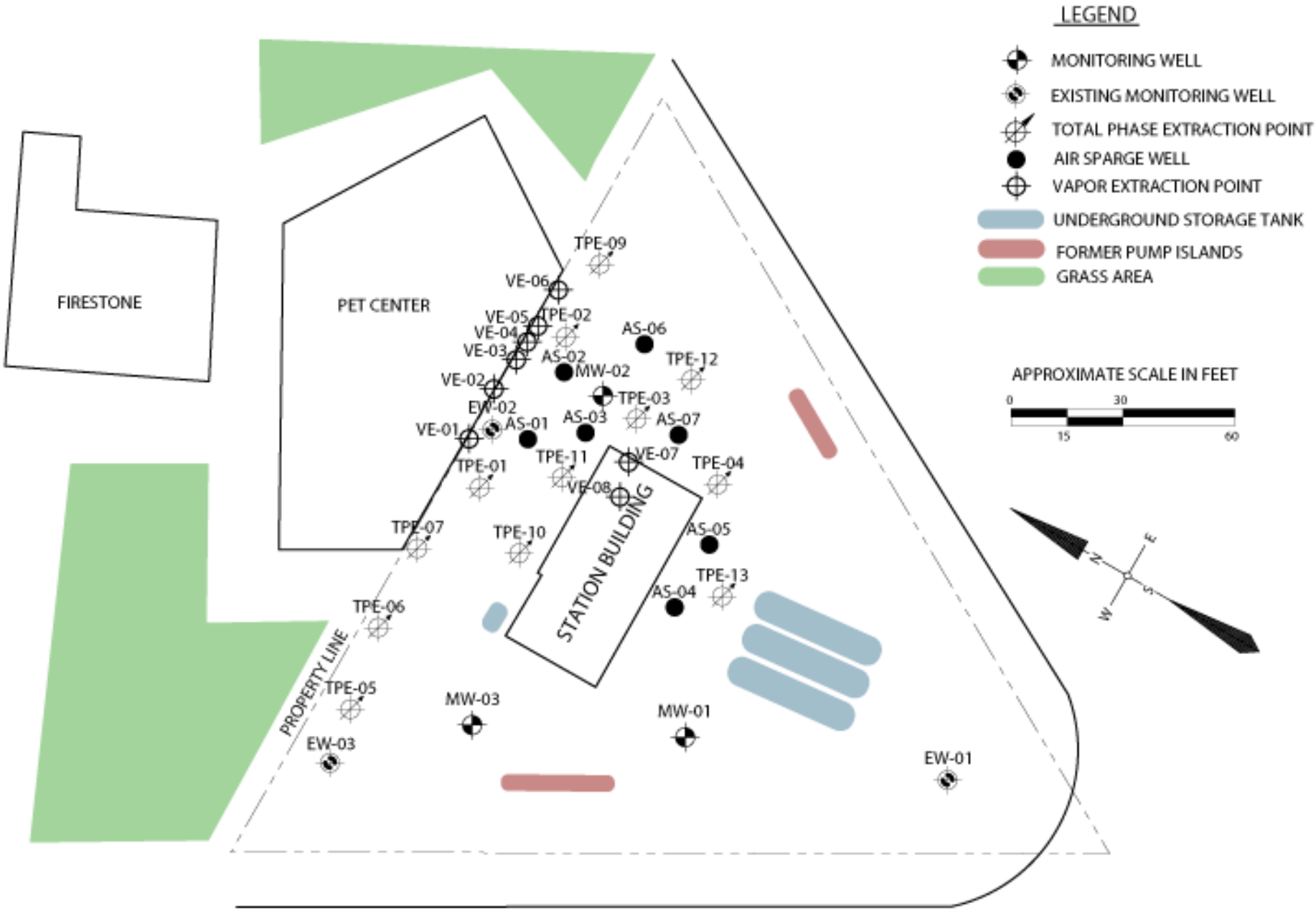

LEGEND
UNDERGROUND STORAGE T
FORMER PUMP ISLANDS
GRASS AREA
FIRESTONE
PET CENTER
STATION BUILDING
PROPERTY LINE
APPROXIMATE SCALE IN FEET
0
30
15
60
N
E
S
W


LEGEND
UNDERGROUND STORAGE TANK
FORMER PUMP ISLANDS
GRASS AREA
APPROXIMATE SCALE IN FEET
0
30
15
60
N
E
S
W
FIRESTONE
PET CENTER
ND
ND
13,000
25,600
37,000
100,000
57,000
28,000
50,000
32,500
35,000
30,000
STATION BUILDING
57,000
11,220
11,470
10,000
2,600
1,700
PROPERTY LINE
ND
ND
ROAD


LEGEND
MONITORING WELL
EXISTING MONITORING WELL
TOTAL PHASE EXTRACTION POINT
UNDERGROUND STORAGE TANK
FORMER PUMP ISLANDS
GRASS AREA
APPROXIMATE SCALE IN FEET
0
30
15
60
FIRESTONE
PET CENTER
TPE-02
MW-02
TPE-03
EW-02
TPE-01
TPE-04
STATION BUILDING
PROPERTY LINE
MW-03
MW-01
EW-03
EW-01
N
E
S
W

Total VOCs in Wells

mw-1	16
mw-2	29600
mw-3	1451
ew-2	50000
ew-3	387
tpe-1	5830
tpe-2	14140
tpe-3	6200
tpe-4	3660
tpe-5	10410
tpe-6	51400
tpe-7	8340
tpe-8	12430
tpe-9	3510
tpe-10	10360
tpe-11	21490


LEGEND
MONITORING WELL
EXISTING MONITORING WELL
TOTAL PHASE EXTRACTION POINT
AIR SPARGE WELL
VAPOR EXTRACTION POINT
UNDERGROUND STORAGE TANK
FORMER PUMP ISLANDS
GRASS AREA
APPROXIMATE SCALE IN FEET
0
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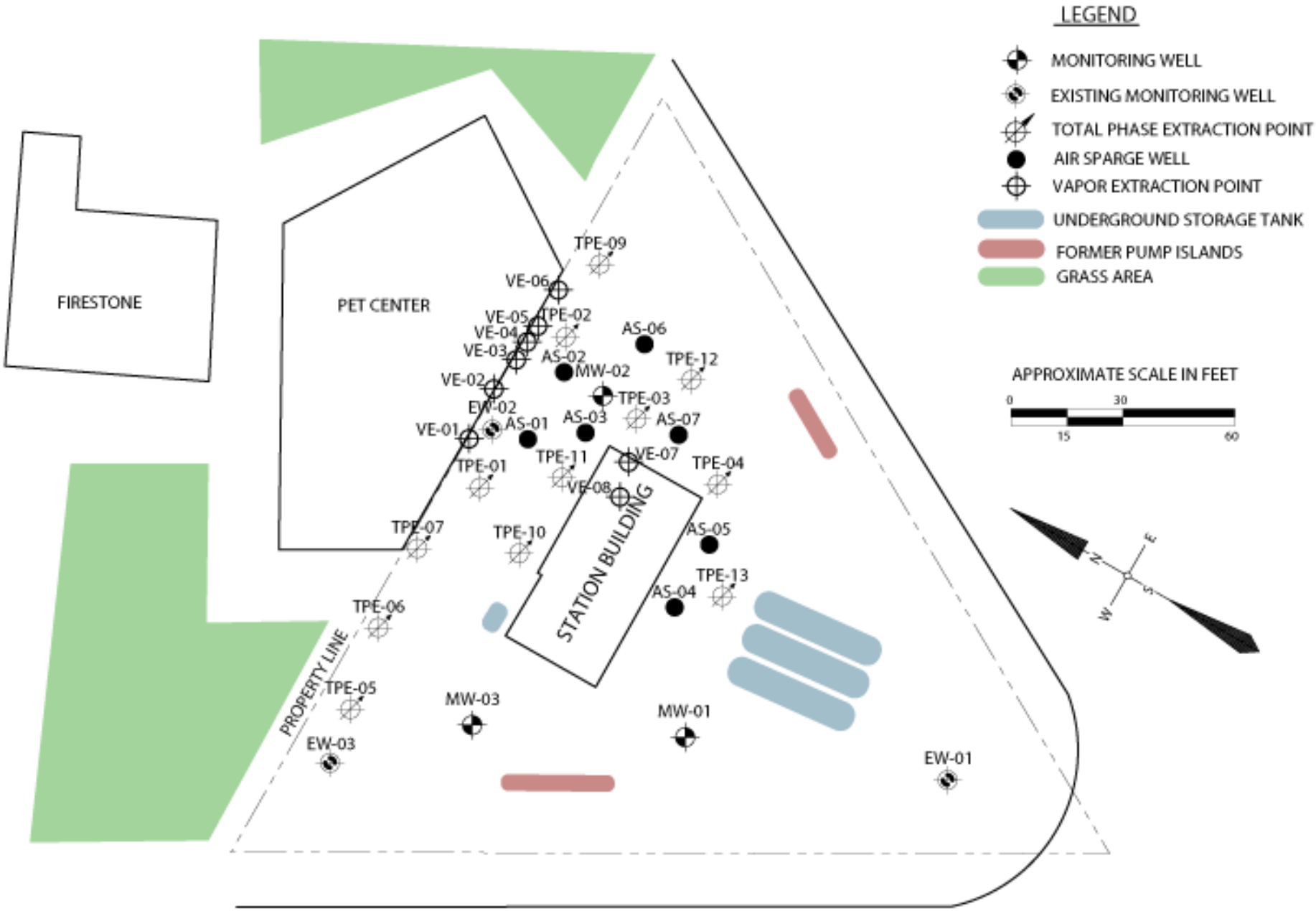
FIRESTONE
PET CENTER
STATION BUILDING
PROPERTY LINE
TPE-09
VE-06
VE-05
TPE-02
VE-04
VE-03
AS-02
MW-02
AS-06
TPE-12
VE-02
EW-02
TPE-03
VE-01
AS-01
AS-03
AS-07
TPE-11
VE-07
TPE-01
TPE-04
VE-08
TPE-07
TPE-10
AS-05
TPE-13
AS-04
TPE-06
TPE-05
MW-03
MW-01
EW-03
EW-01
N
E
S
W

Second Post Remedial Sampling Event

- Comparing pre-remedial groundwater analyses from 17 wells to the data from this sampling event from the same wells, reductions across the site are noted as follows:
- 98.83% site-wide reduction of BTEX,
- 90.05% site-wide reduction of MTBE
- 68.02% site-wide reduction of Naphthalene


LEGEND
MONITORING WELL
EXISTING MONITORING WELL
TOTAL PHASE EXTRACTION POINT
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VAPOR EXTRACTION POINT
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APPROXIMATE SCALE IN FEET
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STATION BUILDING
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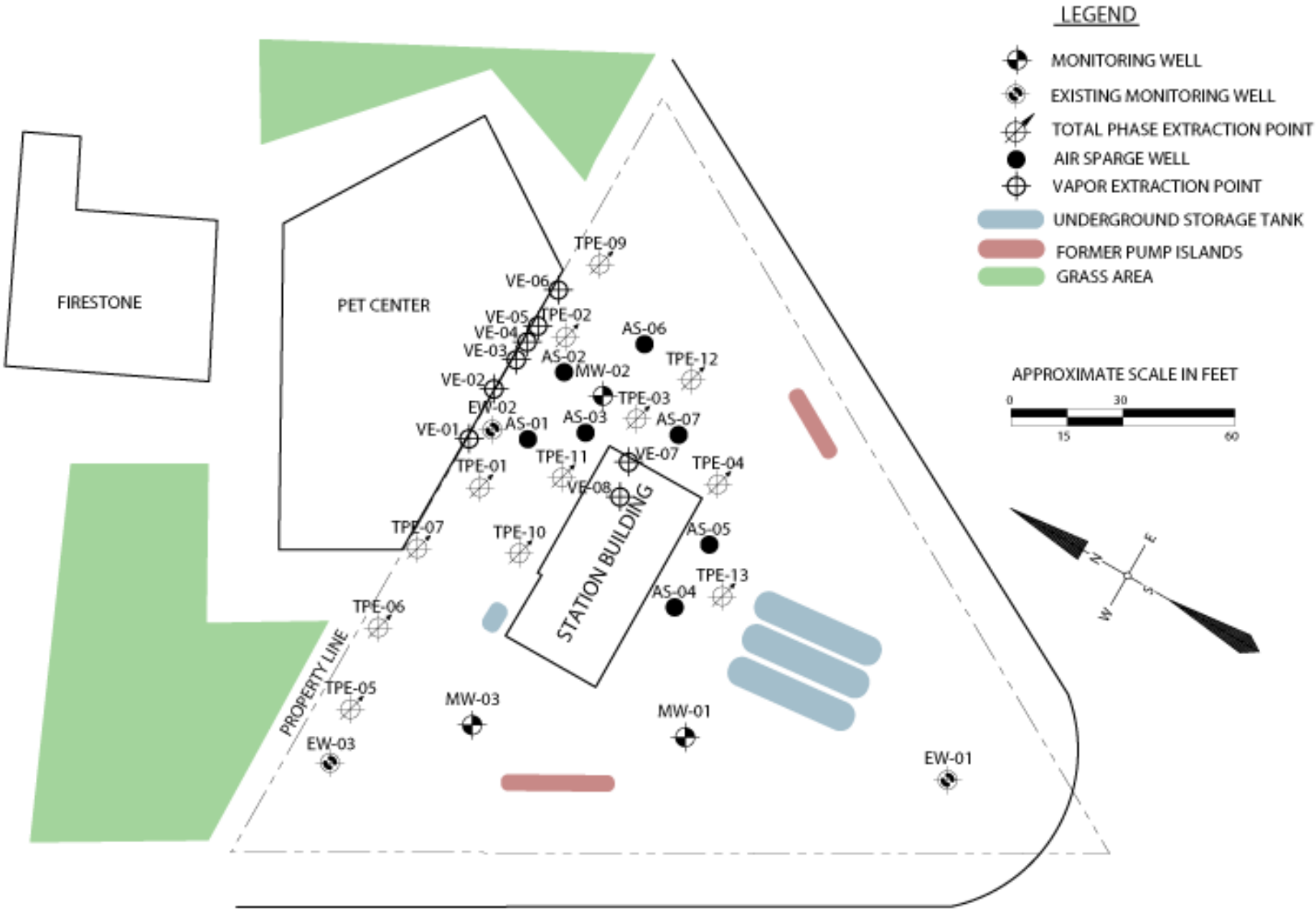
TPE-09
VE-06
VE-05
TPE-02
VE-04
VE-03
AS-02
MW-02
AS-06
TPE-12
VE-02
EW-02
TPE-03
VE-01
AS-01
AS-03
AS-07
TPE-11
VE-07
TPE-01
TPE-04
VE-08
TPE-07
TPE-10
AS-05
TPE-13
AS-04
TPE-06
TPE-05
MW-03
MW-01
EW-03
EW-01
N
E
S
W

Third Post Remedial Temp Wells

- BTEX has been reduced by 85.94% in the source area
- MTBE has been reduced by 96.92% in the source area
- Naphthalene has been reduced by 51.64 % in the source area


LEGEND
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0
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STATION BUILDING
PROPERTY LINE
TPE-09
VE-06
VE-05
TPE-02
VE-04
VE-03
AS-02
MW-02
AS-06
TPE-12
VE-02
EW-02
TPE-03
VE-01
AS-01
AS-03
AS-07
TPE-11
VE-07
TPE-01
TPE-04
VE-08
TPE-07
TPE-10
AS-05
TPE-13
AS-04
TPE-06
TPE-05
MW-03
MW-01
EW-03
EW-01
N
E
S
W

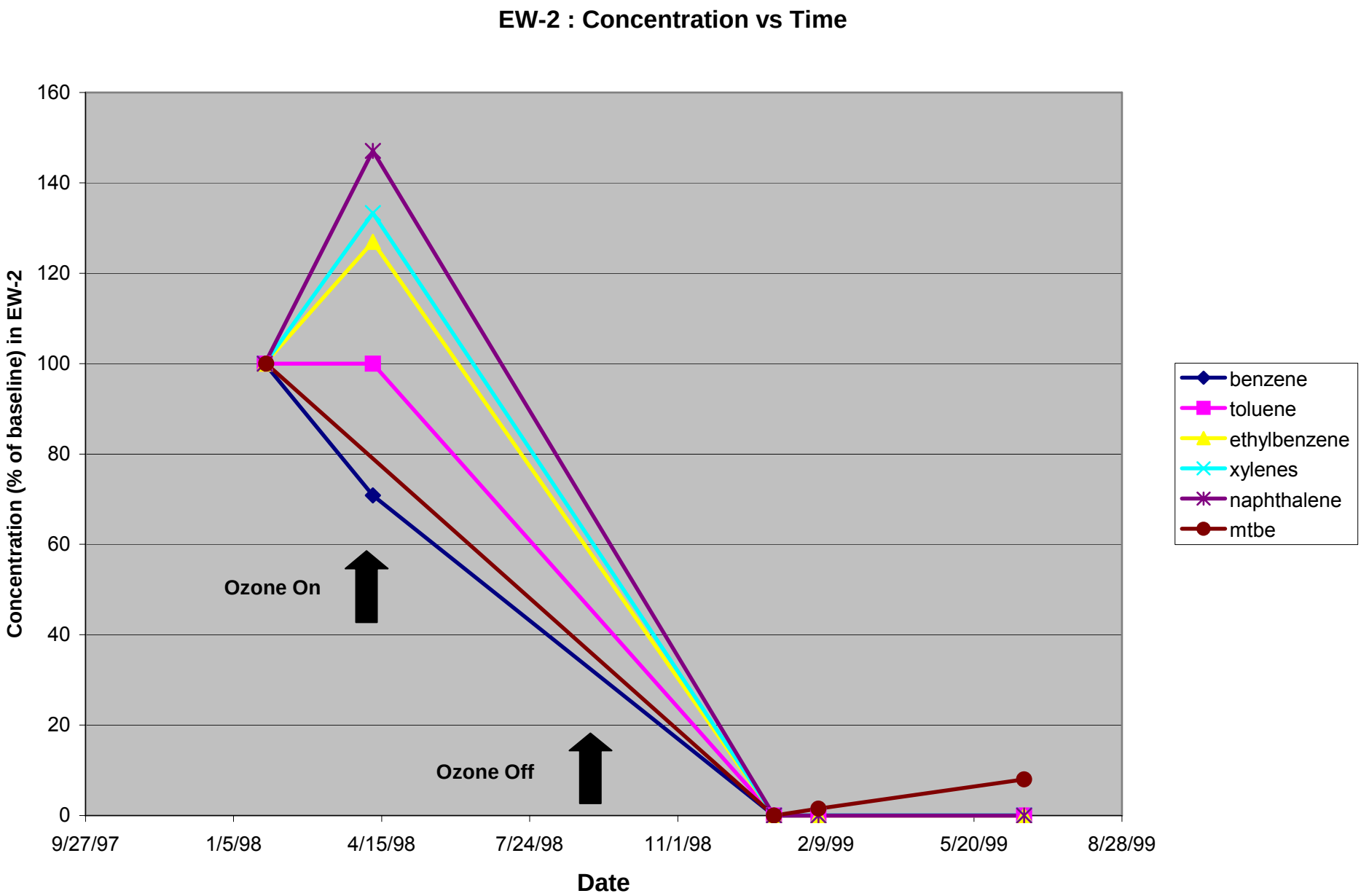
Post Remedial Results (ug/L)

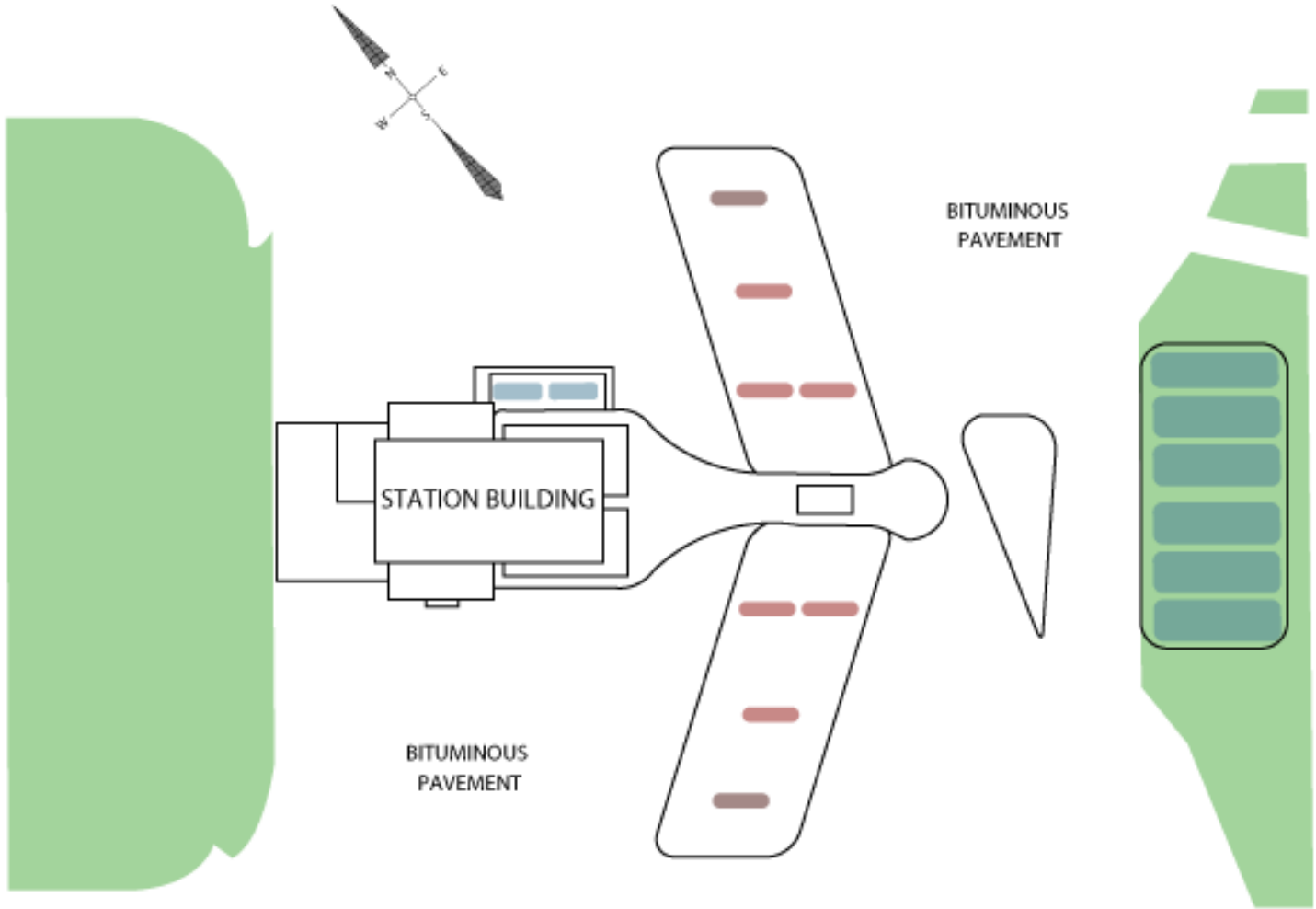
mw-1	16	9.3
mw-2	29600	59.7
mw-3	1451	468.4
ew-2	50000	11.8
ew-3	387	12
tpe-1	5830	24
tpe-2	14140	33.9
tpe-3	6200	0
tpe-4	3660	273.1
tpe-5	10410	124
tpe-6	51400	53.7
tpe-7	8340	12
tpe-8	12430	11
tpe-9	3510	540
tpe-10	10360	37
tpe-11	21490	79

4th Post Remedial Key Wells

- Hydrocarbon rebound is not occurring. Comparing Key Wells MW-2, EW-2, TPE-2 and TPE-6 to the last sampling event for these permanent wells (February 1999 – 2nd post remedial) has indicated the following:

- BTEX has decreased an additional 79%
- MTBE has decreased and additional 82%
- Naphthalene has decreased an additional 91%


EW-2 : Concentration vs Time
Concentration (% of baseline) in EW-2
160
140
120
100
80
60
40
20
0
9/27/97
1/5/98
4/15/98
7/24/98
11/1/98
2/9/99
5/20/99
8/28/99
Date
Ozone On
Ozone Off
benzene
toluene
ethylbenzene
xylenes
naphthalene
mtbe

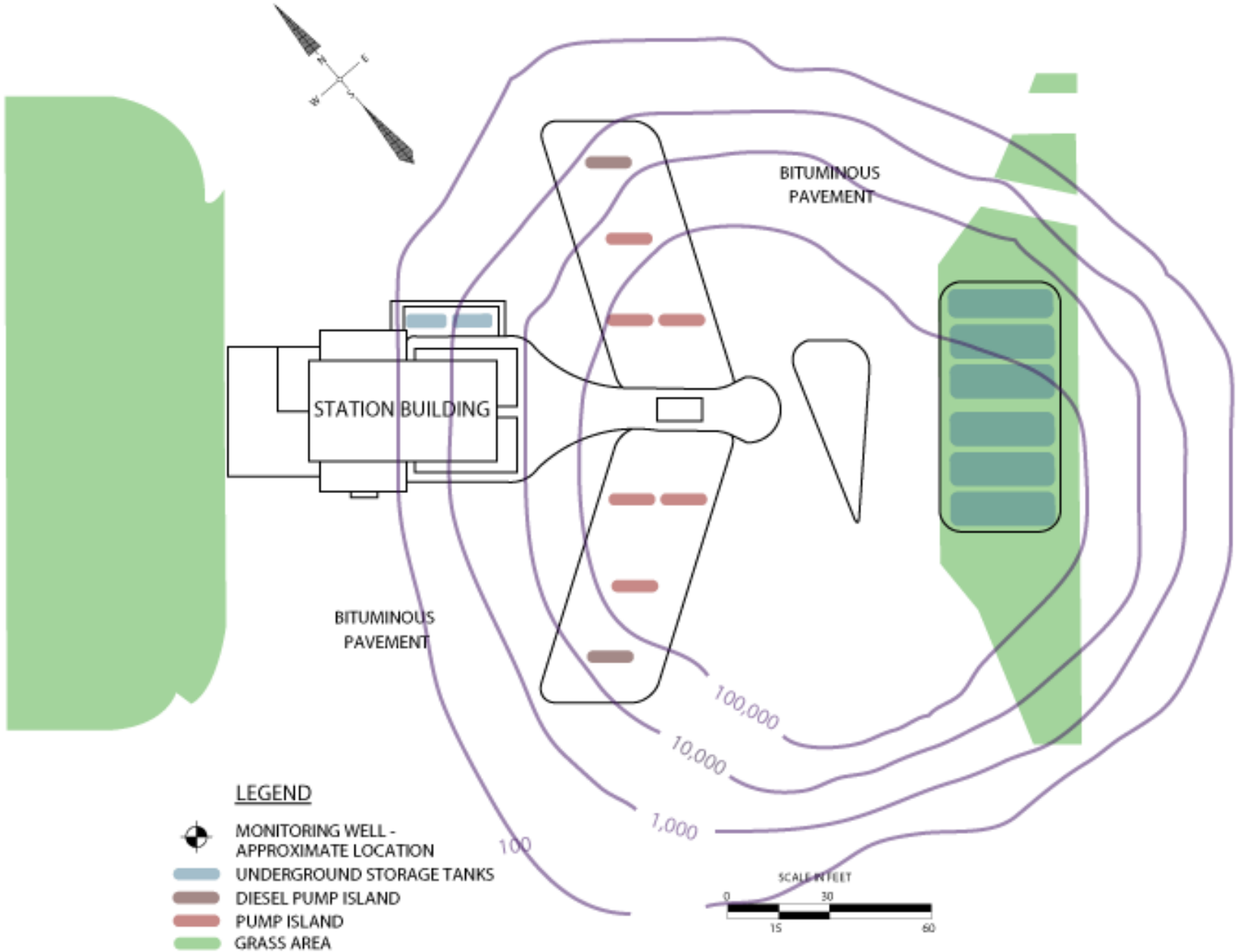


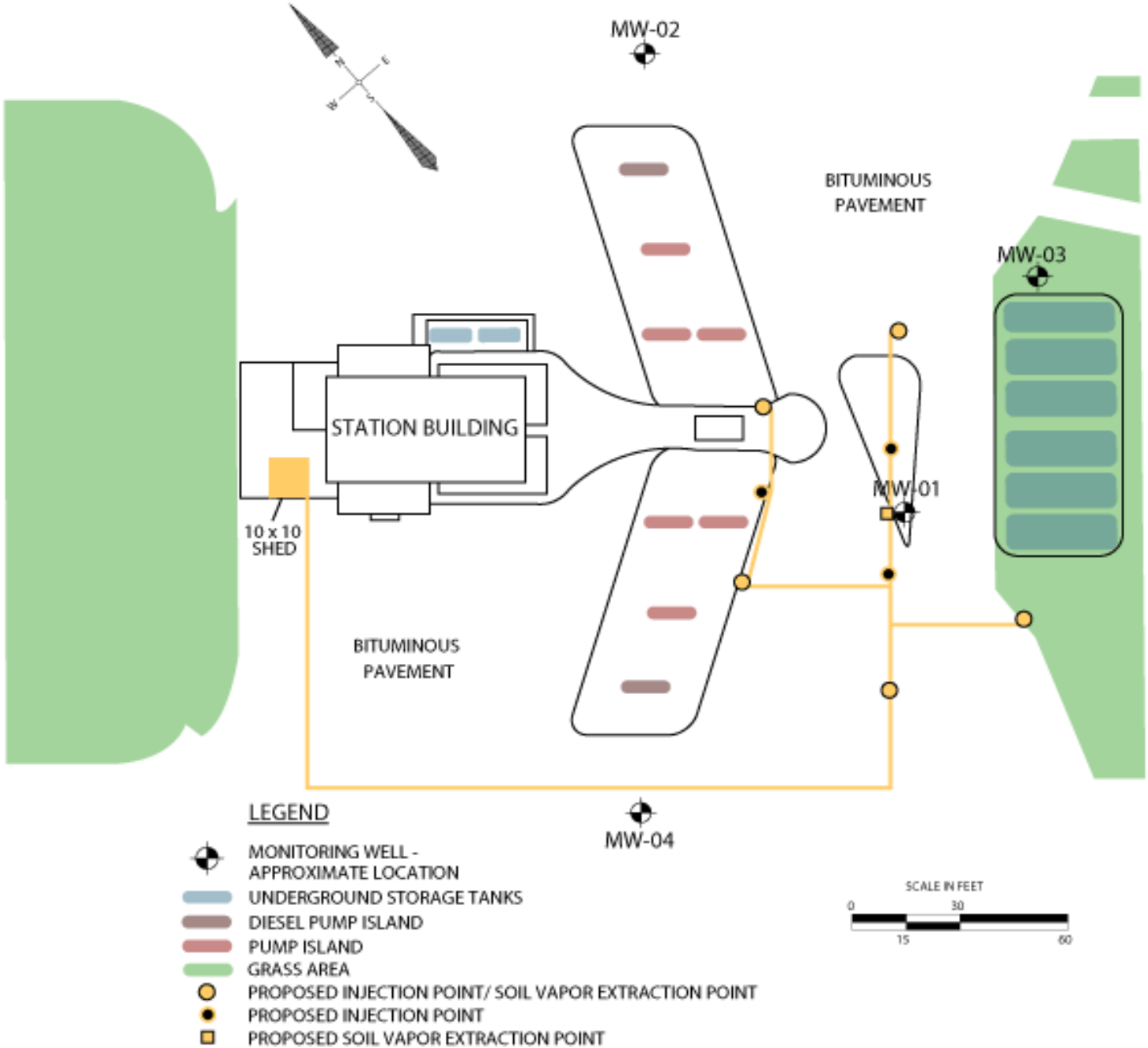
LEGEND

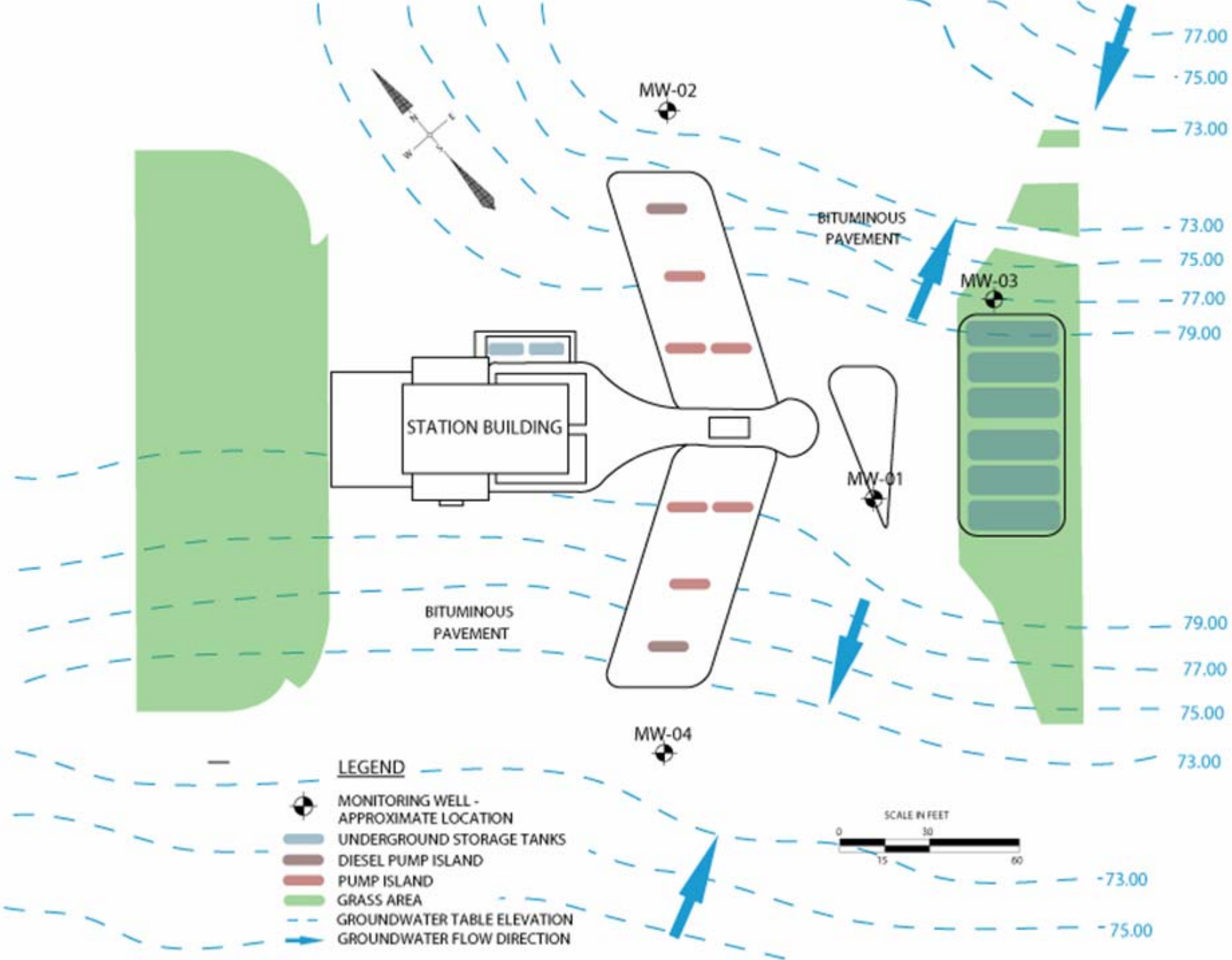
- MONITORING WELL - APPROXIMATE LOCATION
- UNDERGROUND STORAGE TANKS
- DIESEL PUMP ISLAND
- PUMP ISLAND
- GRASS AREA

SCALE IN FEET

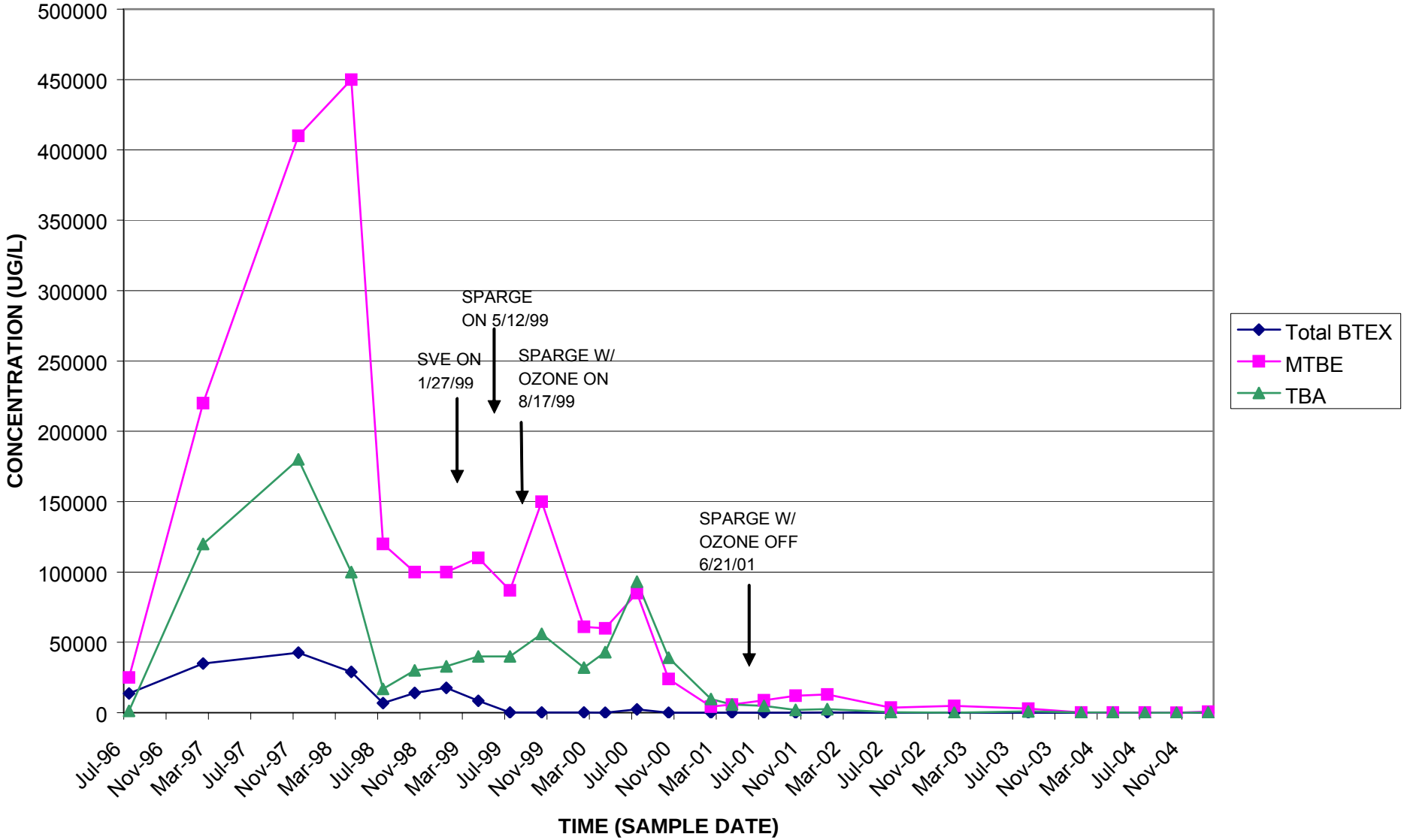
0 30 15 60

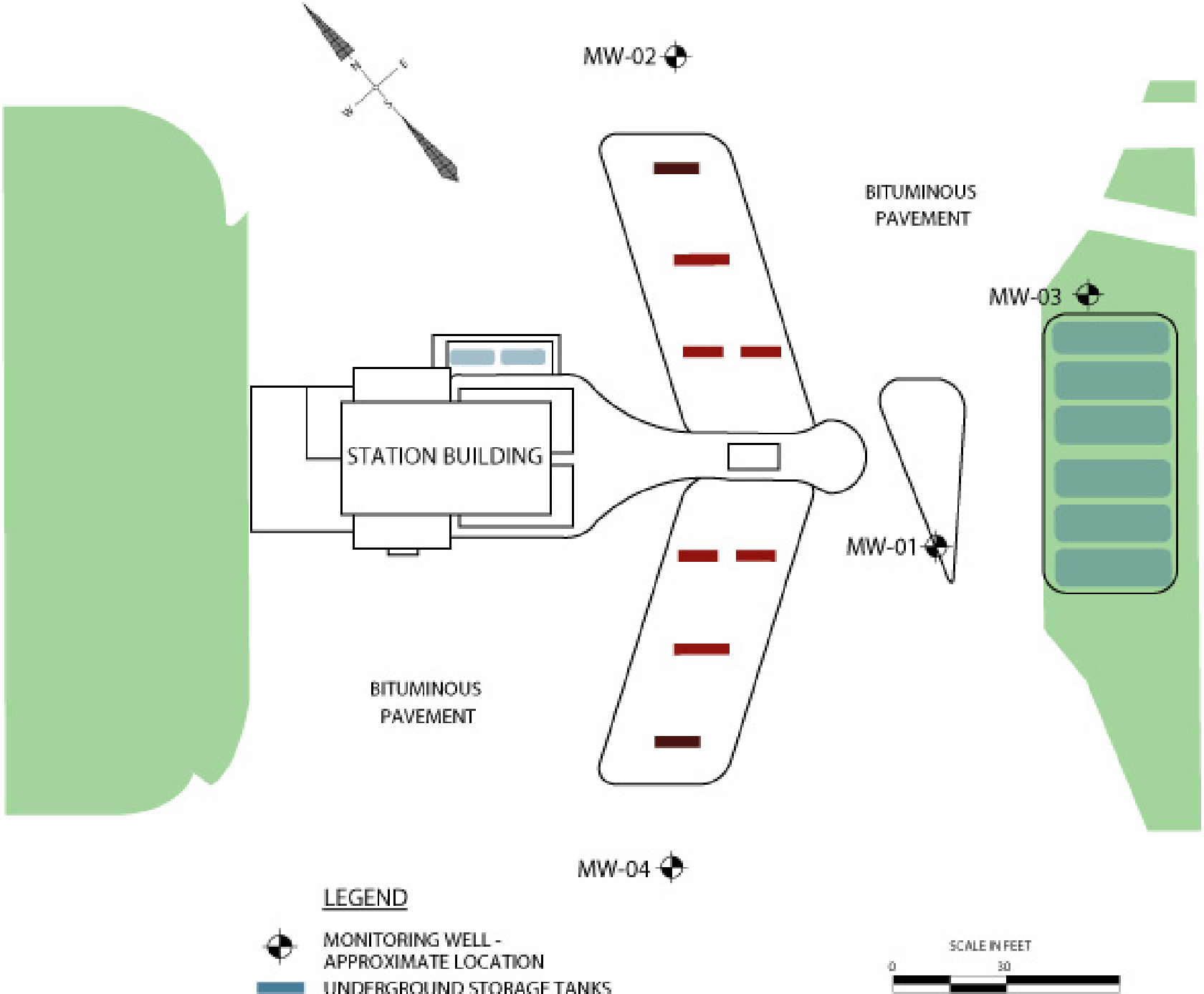

BITUMINOUS PAVEMENT
STATION BUILDING
BITUMINOUS PAVEMENT
100,000
10,000
1,000
100
LEGEND
MONITORING WELL - APPROXIMATE LOCATION
UNDERGROUND STORAGE TANKS
DIESEL PUMP ISLAND
PUMP ISLAND
GRASS AREA
SCALE IN FEET
0
30
15
60

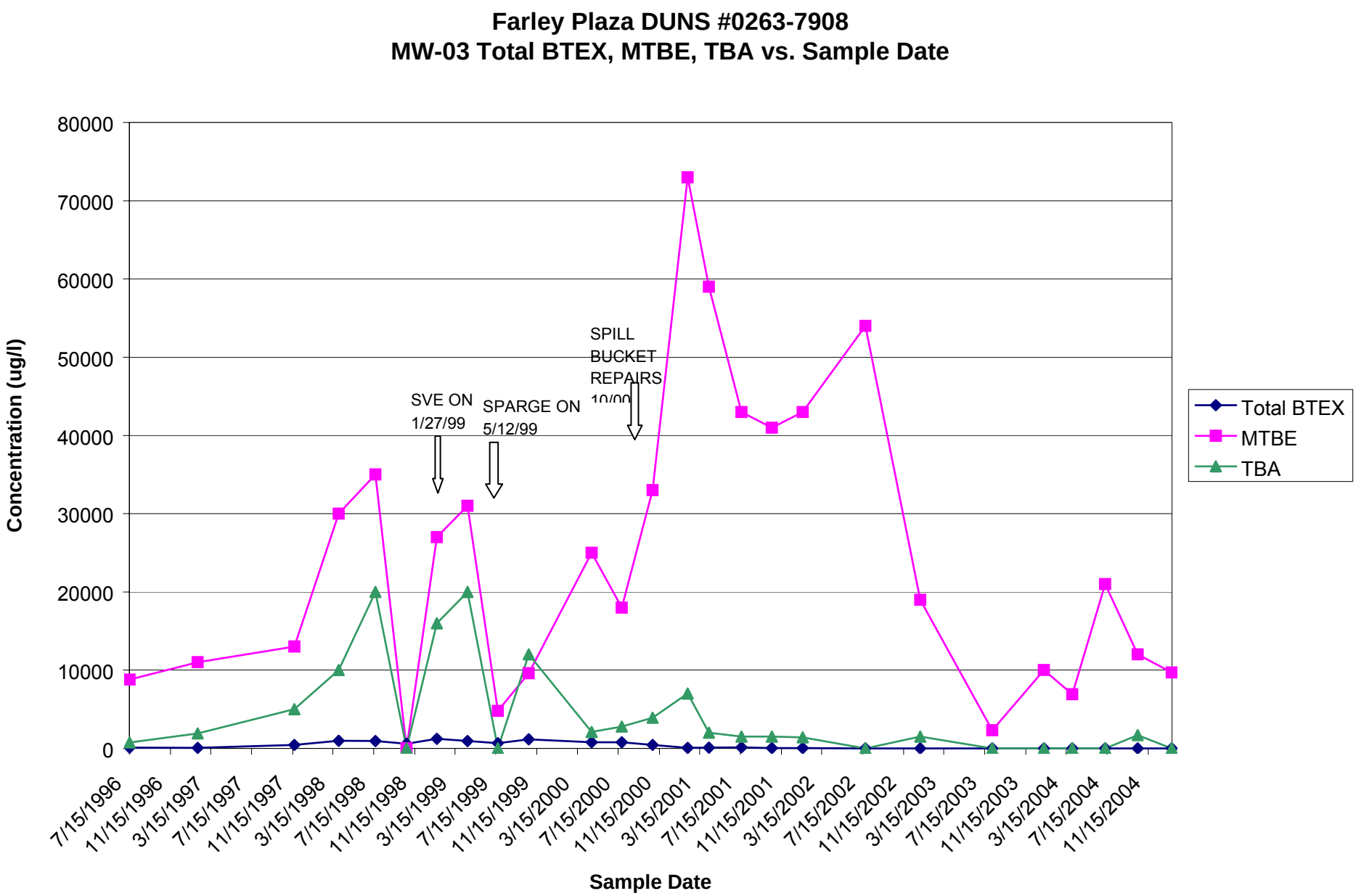

MW-02
BITUMINOUS PAVEMENT
MW-03
STATION BUILDING
MW-01
10 x 10 SHED
BITUMINOUS PAVEMENT
MW-04
LEGEND
MONITORING WELL - APPROXIMATE LOCATION
UNDERGROUND STORAGE TANKS
DIESEL PUMP ISLAND
PUMP ISLAND
GRASS AREA
PROPOSED INJECTION POINT/ SOIL VAPOR EXTRACTION POINT
PROPOSED INJECTION POINT
PROPOSED SOIL VAPOR EXTRACTION POINT
SCALE IN FEET
0
30
15
60

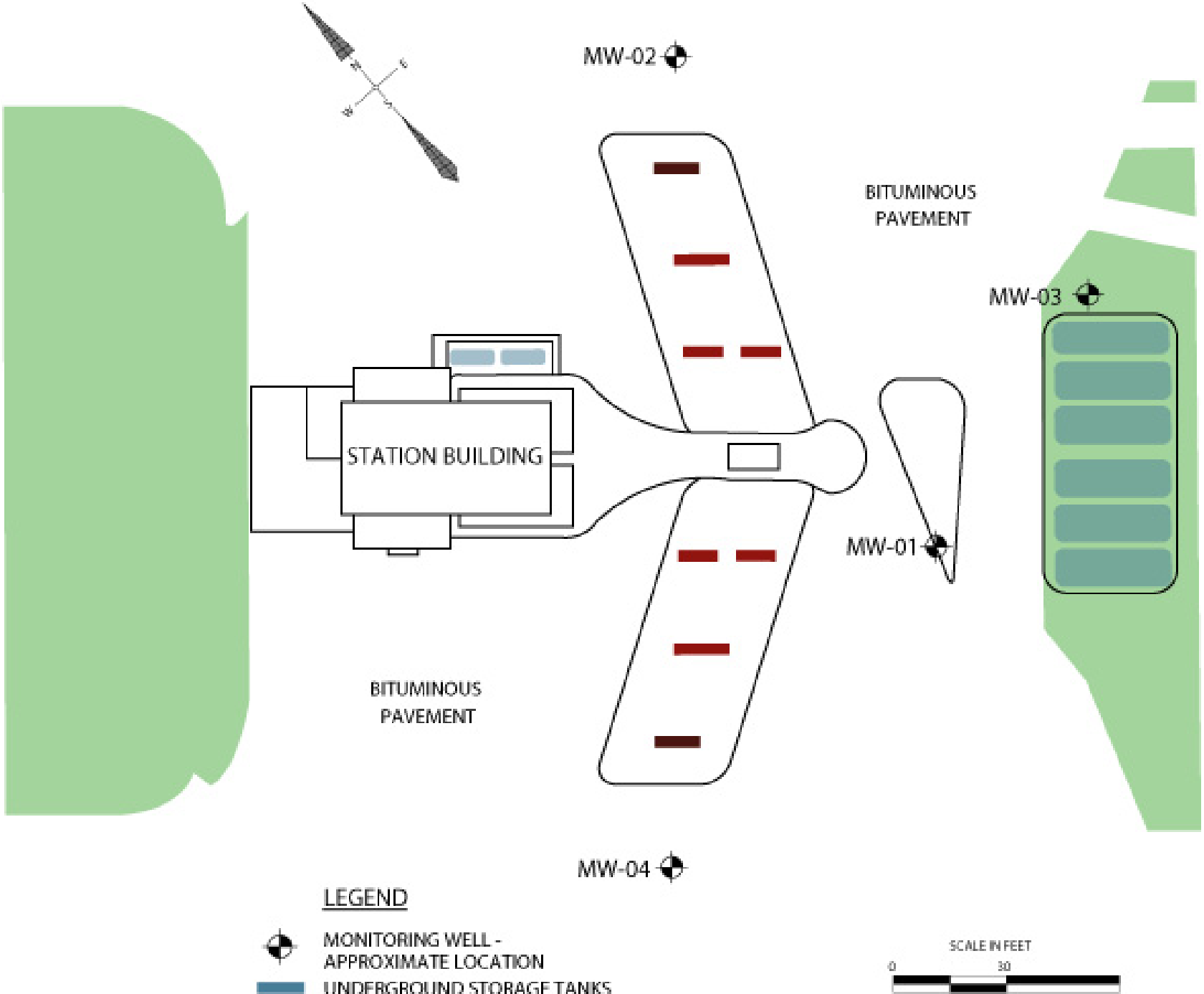

MW-02
MW-03
MW-01
MW-04
STATION BUILDING
BITUMINOUS PAVEMENT
BITUMINOUS PAVEMENT
77.00
75.00
73.00
73.00
75.00
77.00
79.00
79.00
77.00
75.00
73.00
73.00
75.00
LEGEND
MONITORING WELL - APPROXIMATE LOCATION
UNDERGROUND STORAGE TANKS
DIESEL PUMP ISLAND
PUMP ISLAND
GRASS AREA
GROUNDWATER TABLE ELEVATION
GROUNDWATER FLOW DIRECTION
SCALE IN FEET
0
30
15
60

MW-1 TOTAL BTEX & MTBE & TBA CONCENTRATIONS OVER TIME




MW-02
BITUMINOUS
PAVEMENT
MW-03
STATION BUILDING
MW-01
BITUMINOUS
PAVEMENT
MW-04
LEGEND
MONITORING WELL -
APPROXIMATE LOCATION
UNDERGROUND STORAGE TANKS
SCALE IN FEET
0
30


Farley Plaza DUNS #0263-7908
MW-03 Total BTEX, MTBE, TBA vs. Sample Date
Concentration (ug/l)
80000
70000
60000
50000
40000
30000
20000
10000
0
SVE ON
1/27/99
SPARGE ON
5/12/99
SPILL
BUCKET
REPAIRS
10/00
Total BTEX
MTBE
TBA
7/15/1996
11/15/1996
3/15/1997
7/15/1997
11/15/1997
3/15/1998
7/15/1998
11/15/1998
3/15/1999
7/15/1999
11/15/1999
3/15/2000
7/15/2000
11/15/2000
3/15/2001
7/15/2001
11/15/2001
3/15/2002
7/15/2002
11/15/2002
3/15/2003
7/15/2003
11/15/2003
3/15/2004
7/15/2004
11/15/2004
Sample Date


MW-02
BITUMINOUS
PAVEMENT
MW-03
STATION BUILDING
MW-01
BITUMINOUS
PAVEMENT
MW-04
LEGEND
MONITORING WELL -
APPROXIMATE LOCATION
UNDERGROUND STORAGE TANKS
SCALE IN FEET
0
30