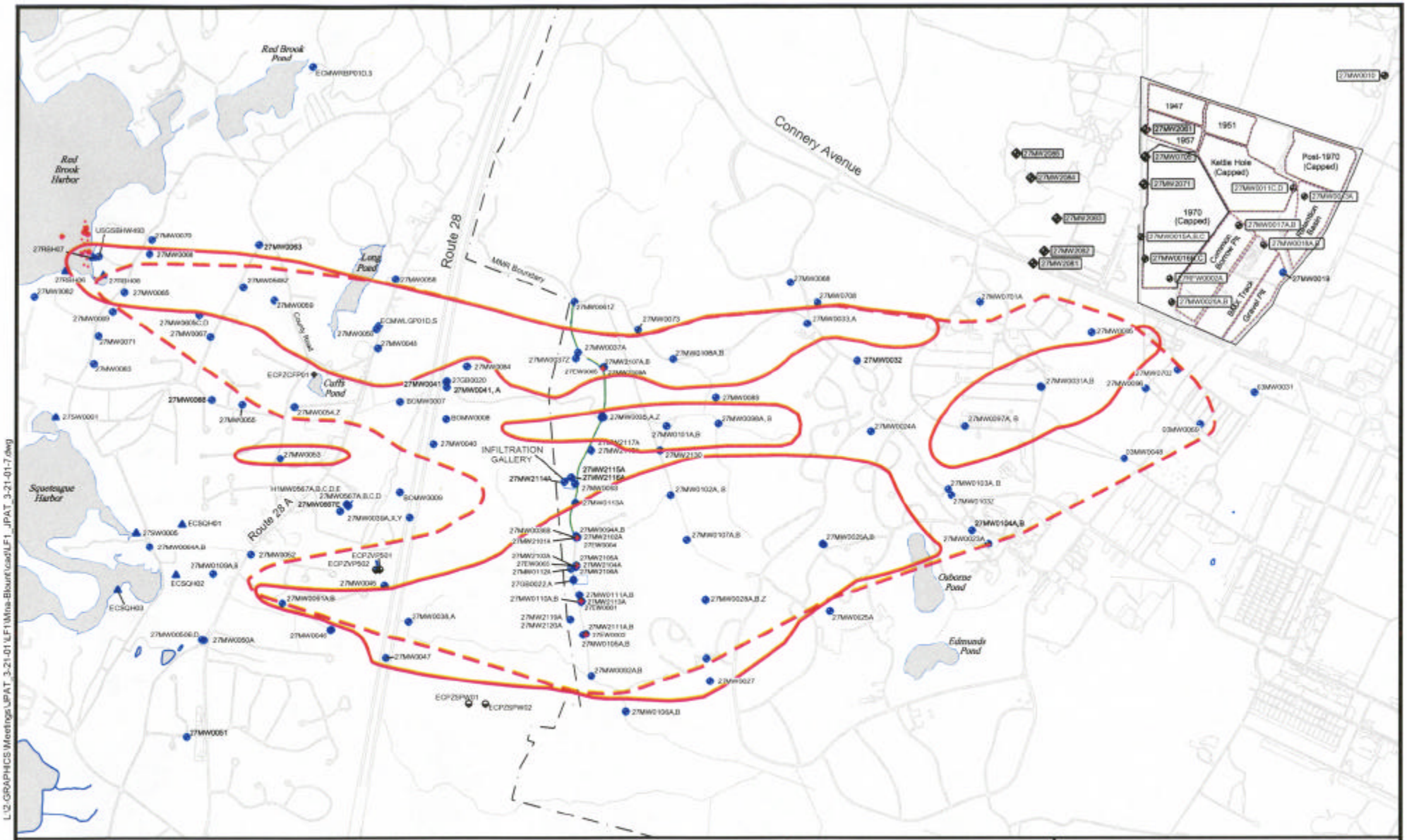
The Air Force Center for Environmental Excellence
Brooks AFB, San Antonio, Texas

MASSACHUSETTS MILITARY RESERVATION

NATURAL ATTENUATION AT LANDFILL-1 (LF-1)

USEPA Technical Support Project Meeting

07 Nov 01



Legend

Data Source: Jacobs Engineering Group Inc., November 2000. Site Environmental Evaluation (SEE) Database.

- Extraction well
- Monitoring well
- Shallow Piezometer
- MCL Exceedance Plume Outline Based on 2001 Data (TCE, PCE, CCl_4 MCL = 5.0 µg/L)
- MMR Boundary
- USGSBHW493 — USGS Monitoring Well
- 27MW2061 — NWOU Well
- 27MW0010 — Post-Closure Well
- MCL Exceedance Plume Outline Based on Historic Data (TCE, PCE, CCl_4 MCL = 5.0 µg/L)
- USGS Drive Point Sampling Location
- USGS Drive Point VOC Detection
- Groundwater Seep Sampling Point

N

0 2100

Scale in Feet

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2000 LF-1 Composite MCL Exceedance Map for PCE, TCE, and CCl_4

Massachusetts Military Reservation
Cape Cod, Massachusetts

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Some History

- Source (5 landfill cells and a kettle hole) used for waste disposal:
  - 1947, 1951, 1957 (NWOU – 40 acres)
  - 1970, post-1970, kettle hole (50 acres)
- Waste disposal practices at landfill ceased in 1989
- Landfill closed in 1993
- 1970 cell, post-1970 cell, and kettle hole capped in 1995

LF-1 Plume

- Groundwater plume ~ 17,300 ft long, 5,500 ft wide, and averages 35 feet thick with a max thickness of 125 feet.
- The plume is ~150-300 ft below ground and 50-200 ft below the water table along most of its length

Remedial Design

- Treat areas of higher contaminant concentration in the northern and southern lobes of the plume while relying on natural attenuation to reduce contaminant mass and concentrations in the central part of the plume
  - extraction, treatment, and infiltration (ETI) system
  - monitored natural attenuation (MNA)
- Design to remove 75 to 80% of the COC mass crossing the base boundary

LF-1 Treatment System

Primary Contaminants:
TCE, PCE, CCl_4

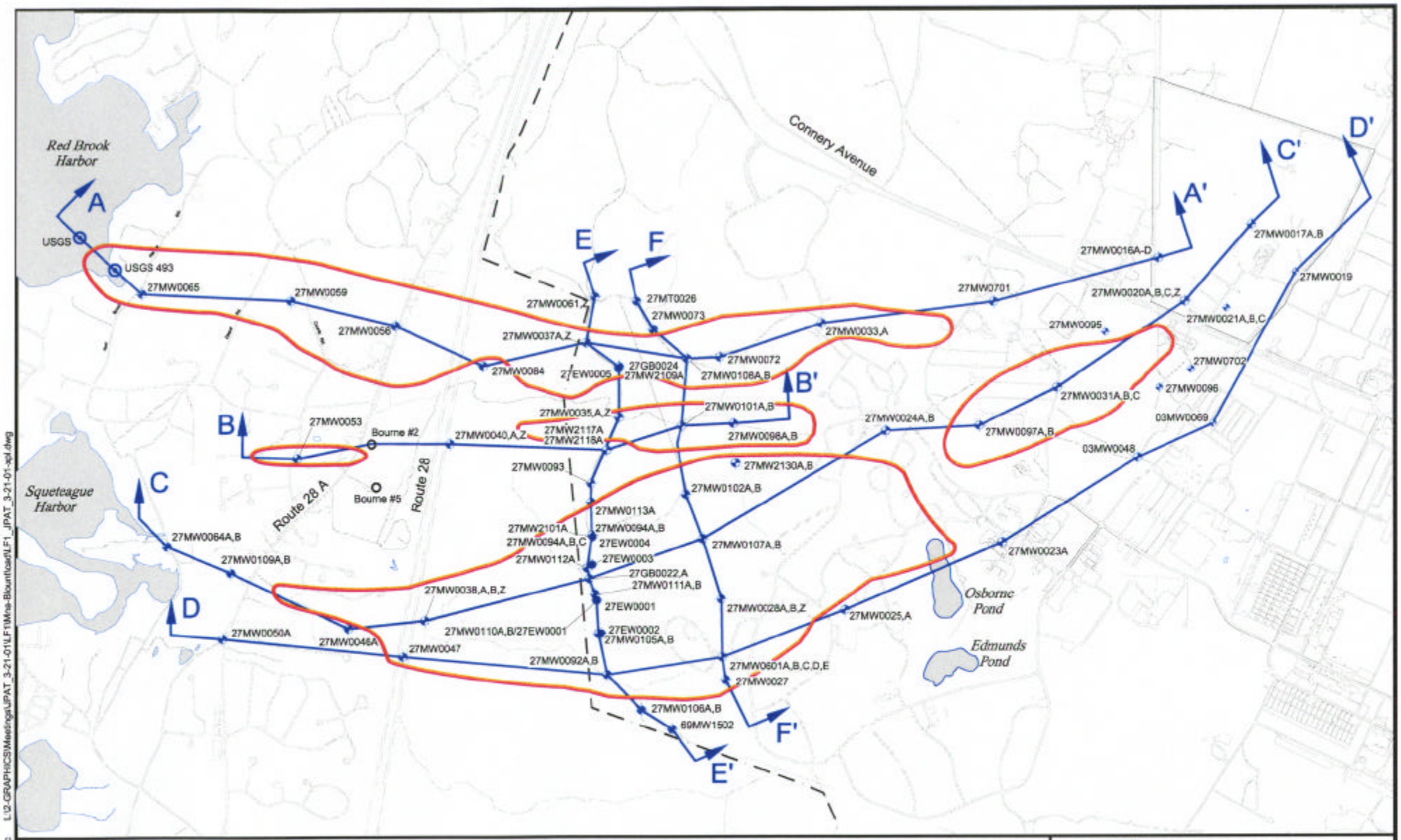
Date In Operation: August 1999

# of Extraction Wells: 5

Type of System: ETI

Treatment Rate:
Million gallons per day: 1.01

Volume Treated, through Dec. 2000
Million gallons: 456



Legend

- Monitoring wells
- MMR boundary
- Extraction wells
- A - A' Cross-sectional plume slice
- USGS borehole or drivepoint
- Plume Contour (TCE, PCE, CCl_4 MCL = 5.0 µg/L) Based on data from 6/97 to 11/98

0 2100

Scale in Feet

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Selected Wells and Cross-Sections at the LF-1 Plume Area

Massachusetts Military Reservation
Cape Cod, Massachusetts

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Figure

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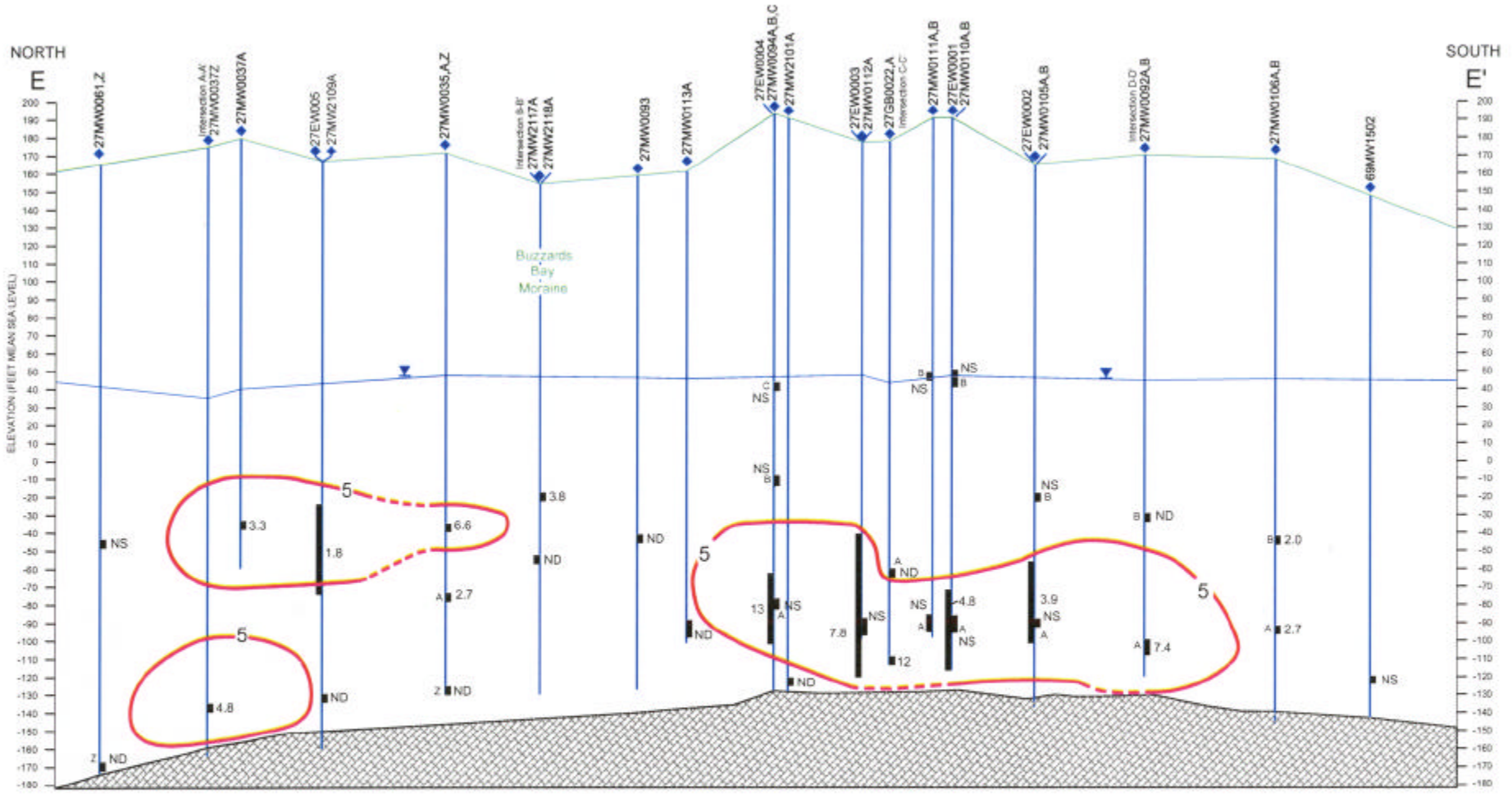

Legend

- Water table
- Monitoring well
- Lithologic boring
- ND — Not detected
- NS — Not sampled
- A — Well Screen ID
- 5 — Plume Contour (MCL = 5 µg/L)
- 2.7 — July 2000 PCE data, except where noted
- BR BEDROCK

0 — Scale in Feet — 90 Vert. 750 Horiz.

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LF-1 Plume Cross-Section E-E' July 2000 MCL Exceedance Isoconcentration Contours

Massachusetts Military Reservation
Cape Cod, Massachusetts

03/20/01 SR LF1_JPAT_3-21-01-ee.dwg

Figure 4-10

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LF-1 (Hydro)Geology

- Sediments/soils are primarily fine- to coarse-grained sands and silts, till overlying bedrock
- Single source aquifer
- Groundwater flows mainly west from source area to Buzzards Bay (Red Brook and Squeteague Harbors)
- Horizontal flow gradient: 0.001 to 0.007 ft/ft (steeper gradients observed in moraine area)
- Hydraulic conductivity varies from 13 to 350 ft/day (depending on moraine or outwash)
- Horizontal flow velocities range from 0.1 to 3 ft/day (depending on moraine or outwash)

LF-1 COCs

- Carbon Tetrachloride (CCl_4)
  - Conc Range: ND – 42 ug/L (Aug 99, 27MW0023A)
  - Apr 01 – 27MW0023A @ 0.09 ug/L
  - 2001 Highest Conc: 10 ug/L (Apr 01, 27MW0092A)
- Trichloroethylene (TCE)
  - Conc Range: ND – 150 ug/L (Aug 99, 27MW0031A)
  - Apr 01 - 27MW0031A @ 84 ug/L
  - 2001 Highest Conc: 100 ug/L (Jan 01, 27MW0031A)
- Perchloroethylene (PCE)
  - Conc Range: ND – 67 ug/L (Dec 98, 27MW0102A)
  - Apr 01 – 27MW0102A @ 27 ug/L
  - 2001 Highest Conc: 30 ug/L (Apr 01, 27MW0035)

MNA

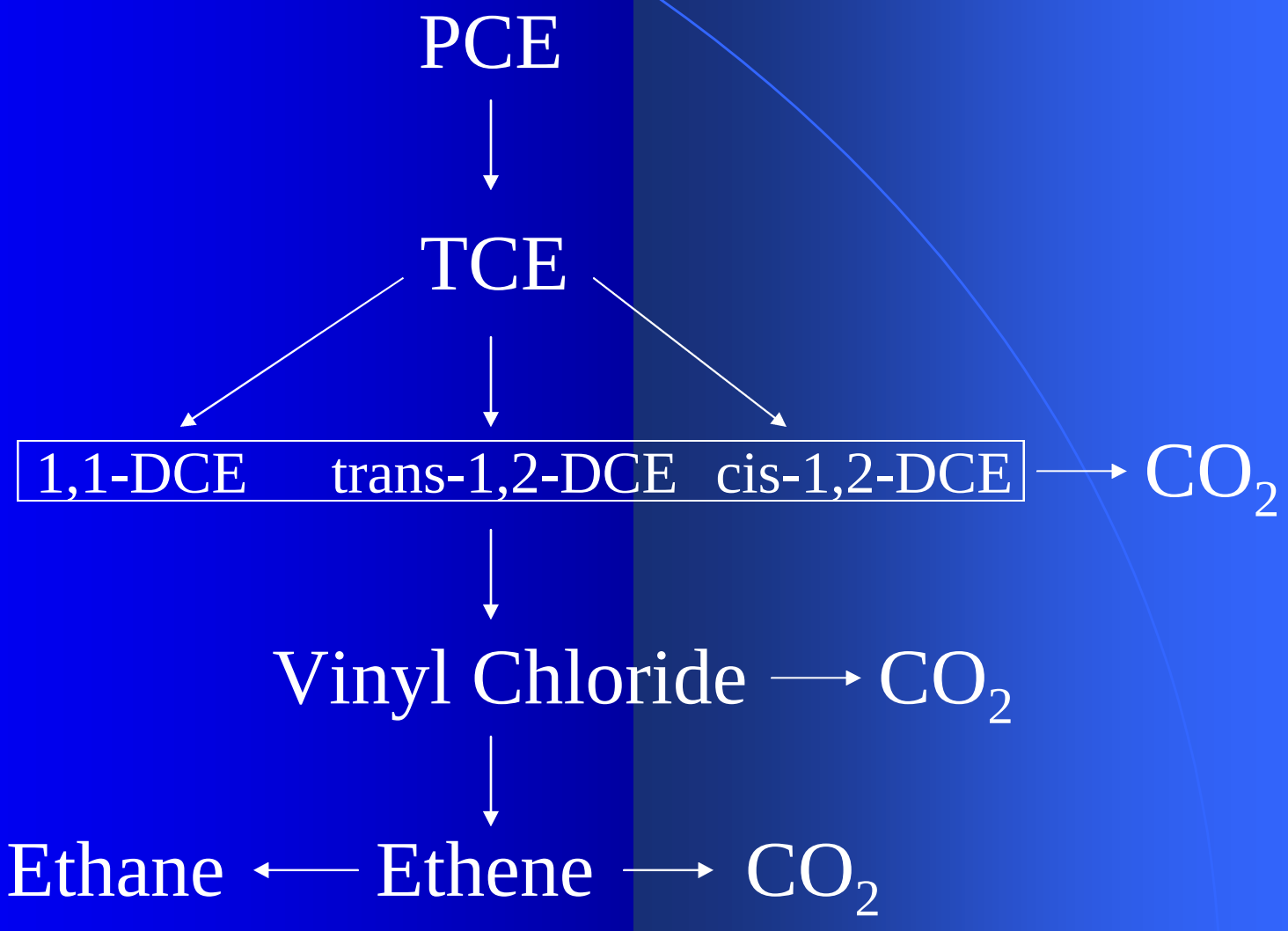
The use of naturally occurring attenuation processes* combined with environmental monitoring to remediate contaminated groundwater.

* Attenuation processes include: biodegradation, hydrolysis, dispersion, dilution, sorption, volatilization

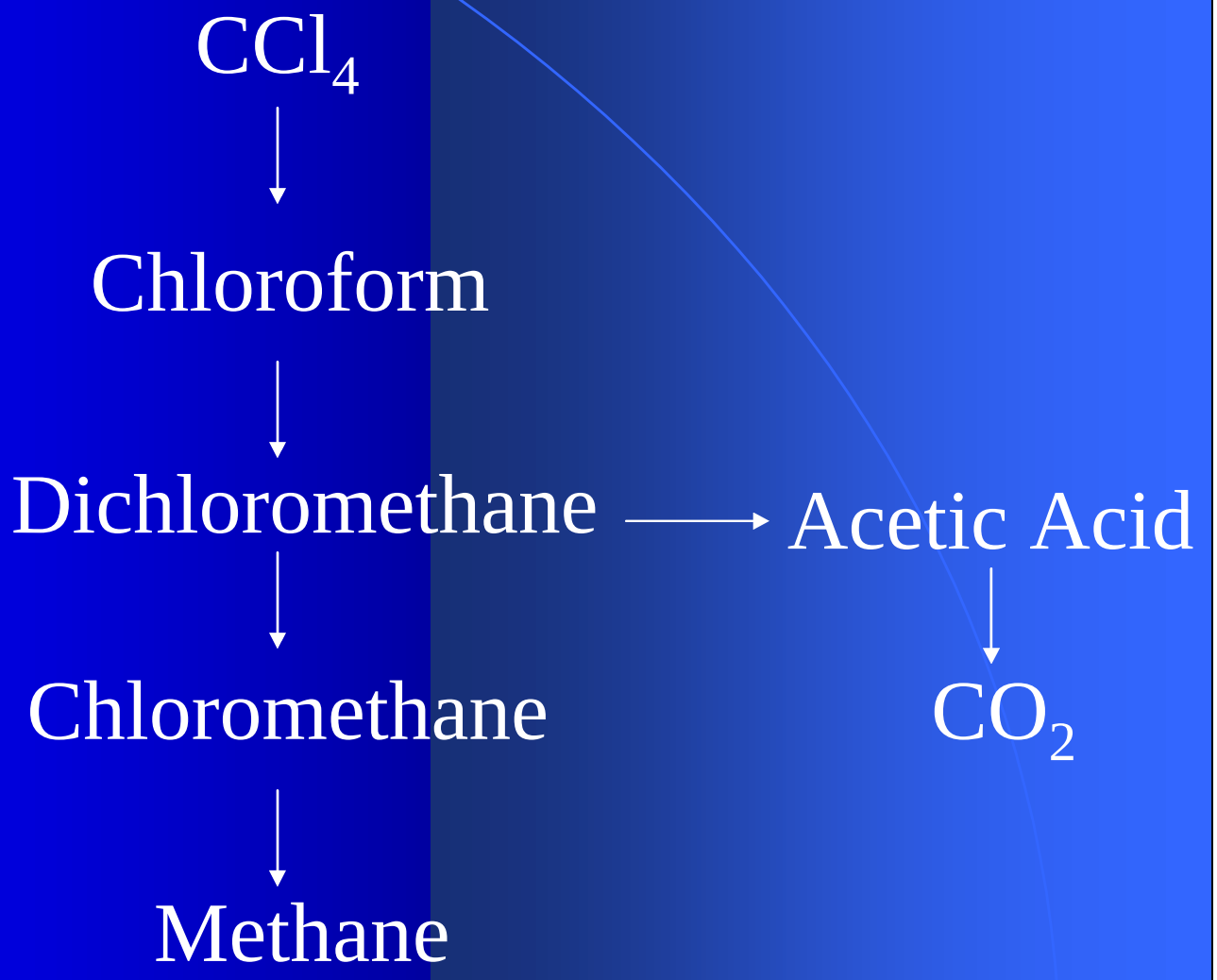
Lines of Evidence for Natural Attenuation

- Plume is shrinking, stable, or growth is slower than expected
- Time vs. contaminant concentration trends at source area and along flowpaths
- Presence and distribution of geochemical and biochemical indicator parameters (e.g., oxygen, nitrate, sulfate, iron II, methane) and “daughter products”
- Correlation of indicator parameters with areas of contaminant mass loss
- Direct microbiological evidence (e.g., microcosm studies)
- Indirect microbiological evidence (PLFA analysis to show that appropriate bacteria are present in the aquifer)

Breakdown Products



Breakdown Products



Focused Feasibility Study

- Focused feasibility study (FSS) initiated in 1998
- Groundwater samples analyzed for VOCs, TOC, Methane, Ethane, Ethene, Nitrate, Sulfate, Chloride, DO, ORP
- Soil samples analyzed for VOCs and TOC

FFS (cont)

- Landfill cap appears to have reduced leaching of contamination
  - 27MW0016: total VOC concentration at 315 ug/L (1989-1990) reduced to 3.9 ug/L (1997)
  - 27MW0031: highest total VOC concentration of 211 ug/L detected since 1998
- Landfill leachate (elevated TOC), present in groundwater plume, serves as electron donors

FFS (cont)

- Electron acceptors such as DO and sulfate are depleted
- Elevated concentrations of metabolic byproducts present in plume – i.e. methane, ethene, Fe (II), carbon dioxide, alkalinity, and chloride
- Degradation products also present in the plume – i.e. cis-1,2-DCE and vinyl chloride
- ORP of impacted groundwater is lower than background

Biodegradation Rates

- Biodegradation rate constants were approximated for total VOCs across three flow paths
- Determined that rates in center of the plume were higher than the rest of the plume
  - Used as an explanation for the observed bifurcation of the northern and southern lobes
- Biodegradation rates ranged from 0.00015 to 0.0004 $days^{-1}$, corresponding to half lives of 4.9 to 12.8 years

FFS Conclusions

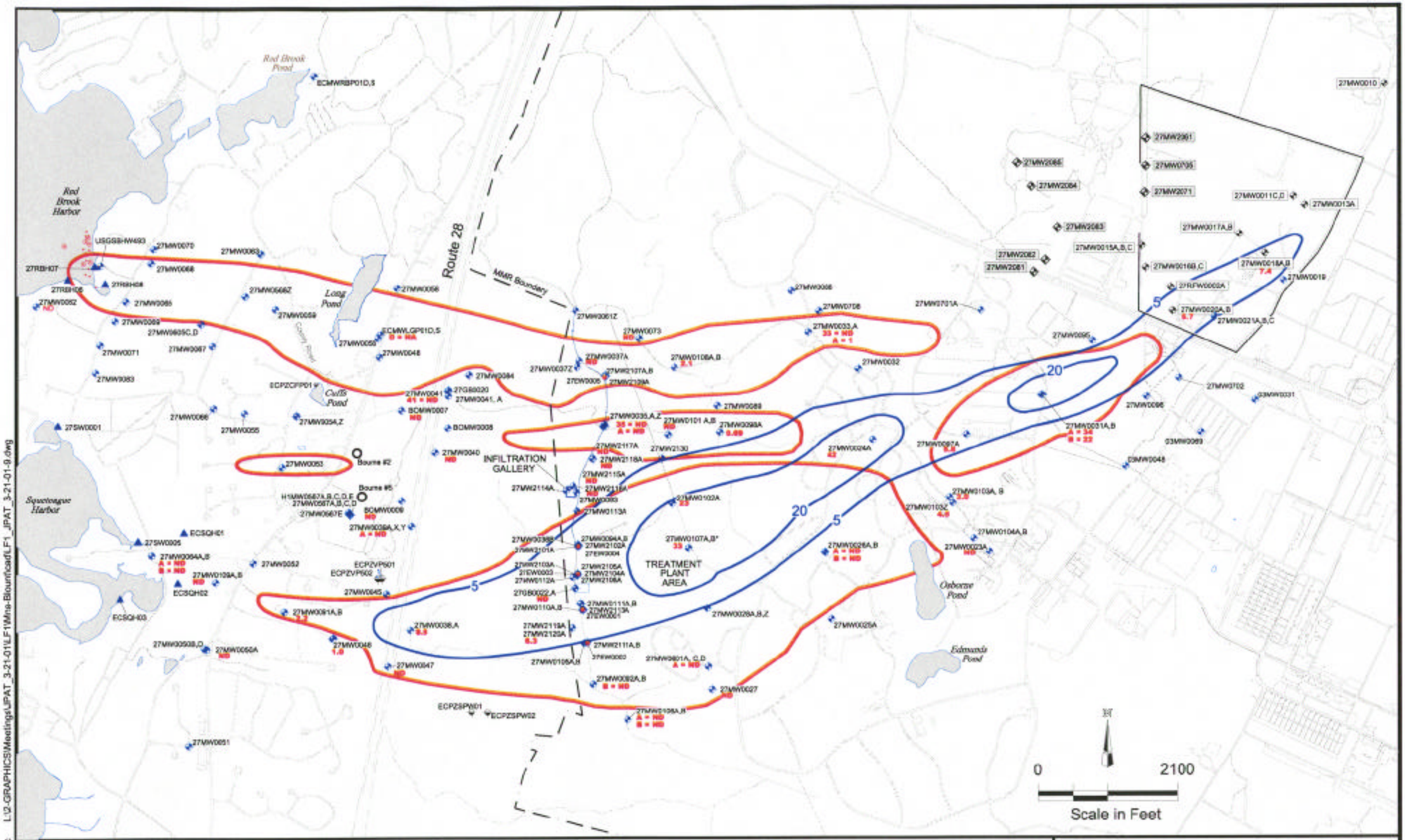
- There is strong evidence for reductive dechlorination of chlorinated organics in the plume
- Natural attenuation alone could treat the plume and that no significant benefit would be gained by installation of an active treatment system

Long Term Monitoring

- Continued collecting chemical and hydraulic data through a long term monitoring (LTM) program
- Refined flow paths through additional modeling
- Suggested different contributing source areas and/or release events
- Refined contaminant zones

LTM - MNA

- 26 wells sampled quarterly for evaluating MNA in the central portion of the plume
- Wells sampled for VOCs, MNA parameters, and field parameters



Legend

- Extraction well
- Monitoring Well
- Shallow piezometer
- Groundwater seep sampling point
- A = 13 Data 0 to -200 ft msl
- MMR boundary
- USGS drive point sampling location
- USGS drive point VOC detection
- cis-1,2-DCE plume contour based on 7/2000 data (cis-1,2-DCE MCL= 70 µg/L)
- Plume Contour (TCE, PCE, CCl_4 MCL = 5.0 µg/L)
- 27MW2081 NWOU well
- 27MW0010 Post-closure well

Data source: Jacobs Engineering Group Inc., 11/00, Site Environmental Evaluation (SEE) Database except where otherwise noted.

* = 1998 screening data used because 27MW107A is too deep and 27MW107B is too shallow to show plume appropriately

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LF-1 cis-1,2,-DCE Isopleth Map for 0 to -200 ft msl (July 2000 Data)

Massachusetts Military Reservation
Cape Cod, Massachusetts

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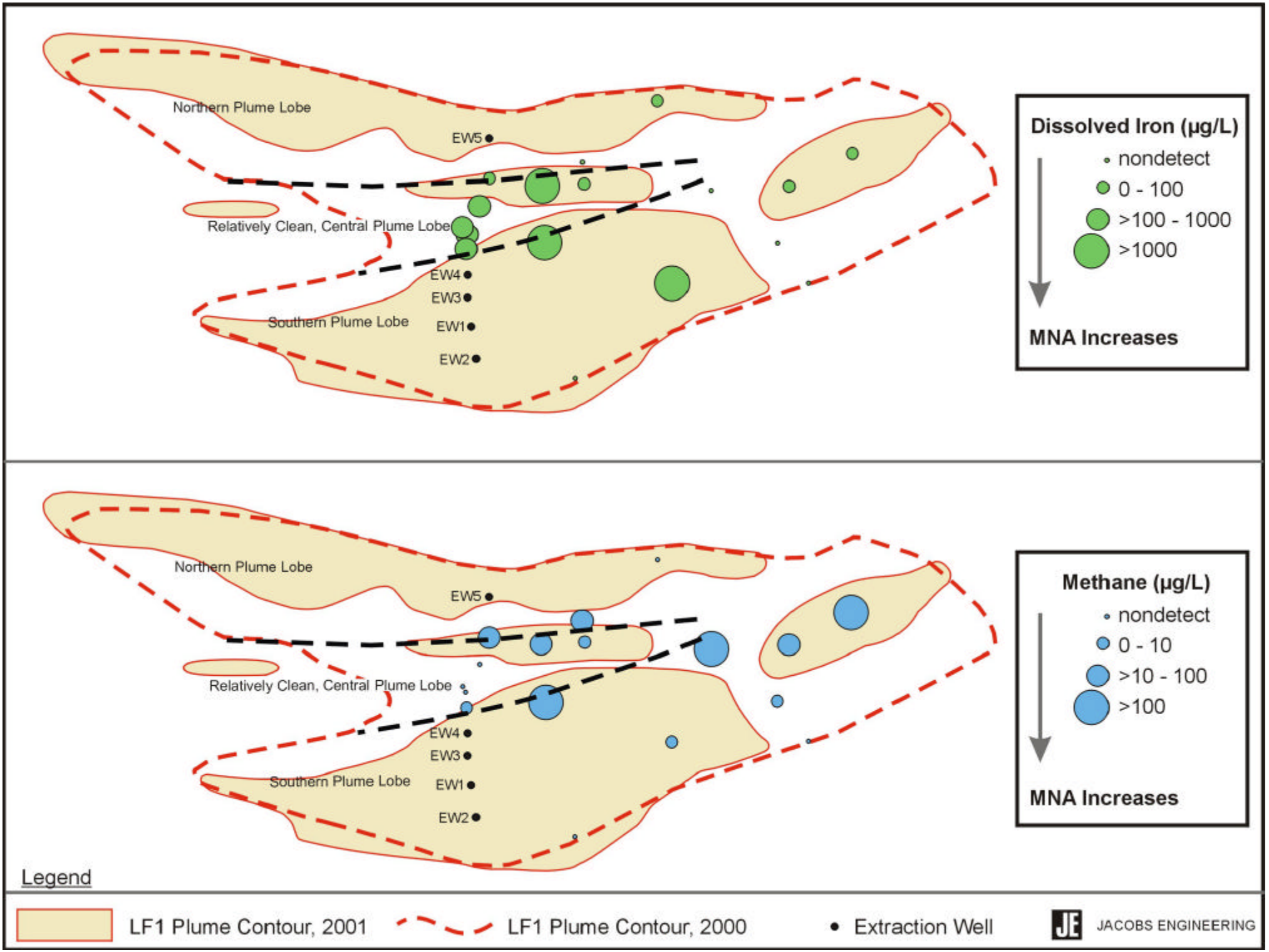
Northern Plume Lobe
EW5
Relatively Clean, Central Plume Lobe
EW4
EW3
Southern Plume Lobe
EW1
EW2
Dissolved Iron (µg/L)
nondetect
0 - 100
>100 - 1000
>1000
MNA Increases
Northern Plume Lobe
EW5
Relatively Clean, Central Plume Lobe
EW4
EW3
Southern Plume Lobe
EW1
EW2
Methane (µg/L)
nondetect
0 - 10
>10 - 100
>100
MNA Increases
Legend
LF1 Plume Contour, 2001
LF1 Plume Contour, 2000
Extraction Well
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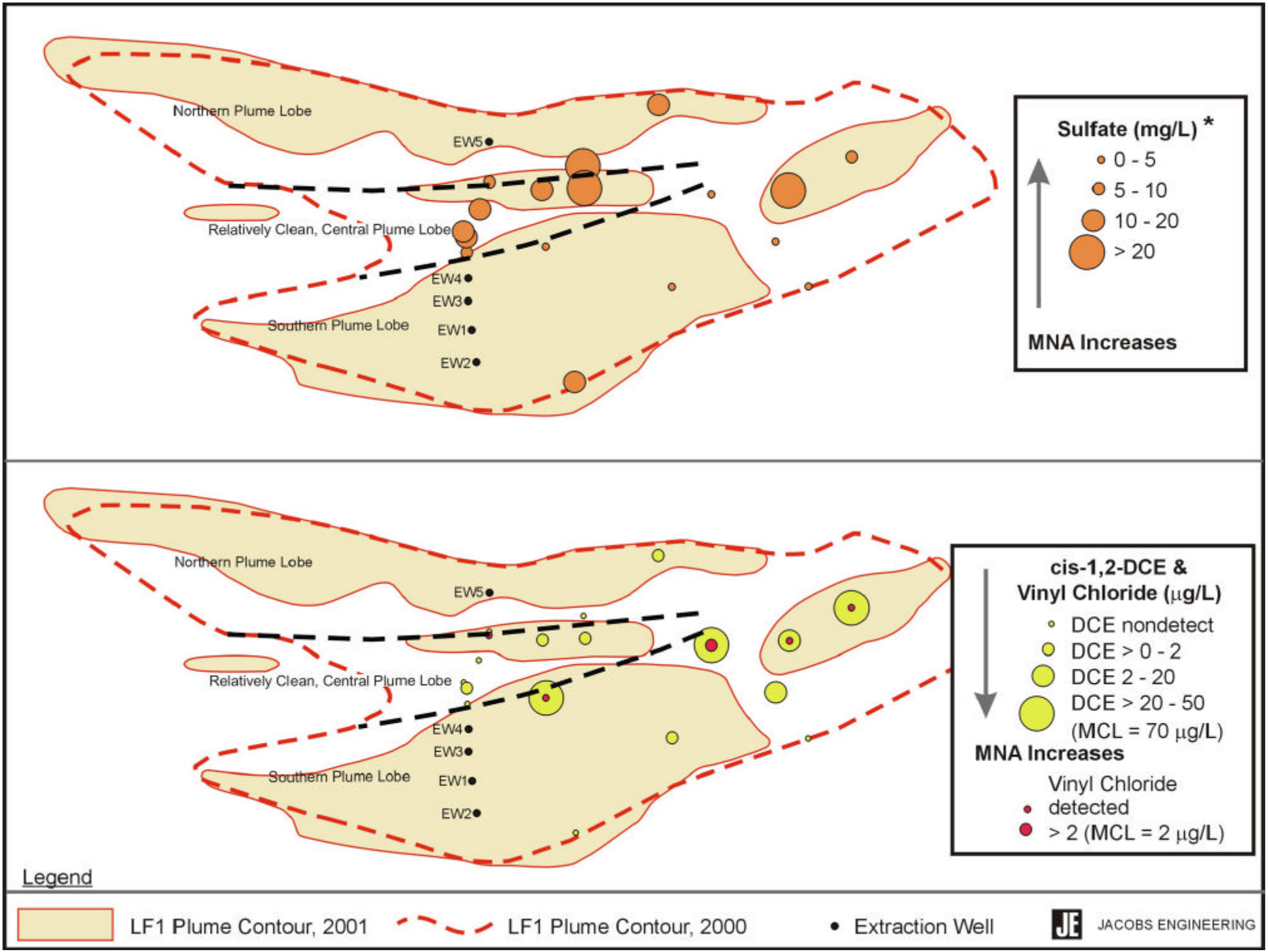
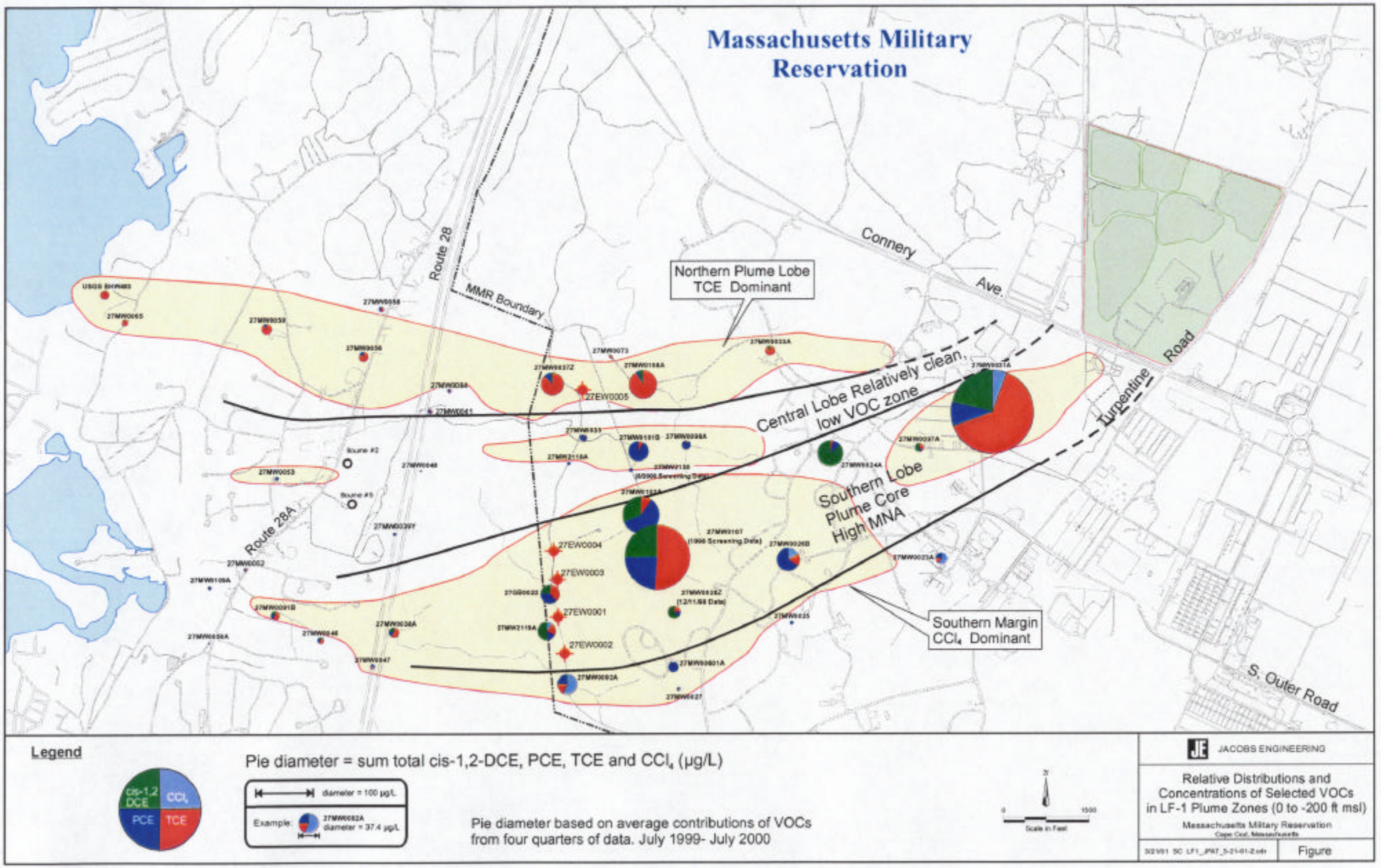

Northern Plume Lobe
EW5
Relatively Clean, Central Plume Lobe
EW4
EW3
Southern Plume Lobe
EW1
EW2
Sulfate (mg/L) *
0 - 5
5 - 10
10 - 20
> 20
MNA Increases
Northern Plume Lobe
EW5
Relatively Clean, Central Plume Lobe
EW4
EW3
Southern Plume Lobe
EW1
EW2
cis-1,2-DCE &
Vinyl Chloride (µg/L)
DCE nondetect
DCE > 0 - 2
DCE 2 - 20
DCE > 20 - 50
(MCL = 70 µg/L)
MNA Increases
Vinyl Chloride
detected
> 2 (MCL = 2 µg/L)
Legend
LF1 Plume Contour, 2001
LF1 Plume Contour, 2000
Extraction Well
JE
JACOBS ENGINEERING


Massachusetts Military Reservation
Route 28
MMR Boundary
Connery Ave.
Turpentine Road
S. Outer Road
Route 28A
Northern Plume Lobe
TCE Dominant
Central Lobe Relatively clean,
low VOC zone
Southern Lobe
Plume Core
High MNA
Southern Margin
CCl_4 Dominant
27EW0005
27EW0004
27EW0003
27EW0001
27EW0002
Boune #2
Boune #5
Legend
Pie diameter = sum total cis-1,2-DCE, PCE, TCE and CCl_4 (µg/L)
cis-1,2 DCE
CCl_4
PCE
TCE
diameter = 100 µg/L
Example:
27MW0082A
diameter = 37.4 µg/L
Pie diameter based on average contributions of VOCs
from four quarters of data. July 1999- July 2000
Scale in Feet
JACOBS ENGINEERING
Relative Distributions and
Concentrations of Selected VOCs
in LF-1 Plume Zones (0 to -200 ft msl)
Massachusetts Military Reservation
Cape Cod, Massachusetts
Figure

LTM - MNA Conclusions*

- Biodegradation generally appears to be more significant in the southern plume lobe than in the northern or central lobes based on:
  - Higher methane concentrations
  - Lower sulfate concentrations
  - More strongly reducing conditions
  - Higher cis-1,2-DCE (a degradation product) concentrations
- Central lobe contains smaller areas of PCE which appear to be related to a small or declining source term rather than to biodegradation

* Year 2000 Annual Report

LTM - MNA Conclusions*

- Northern lobe contains elevated levels of TCE and demonstrates little evidence that microbially- driven attenuation is significant
- Bifurcation of northern and southern lobes due to geology and different contributing source areas

* Year 2000 Annual Report

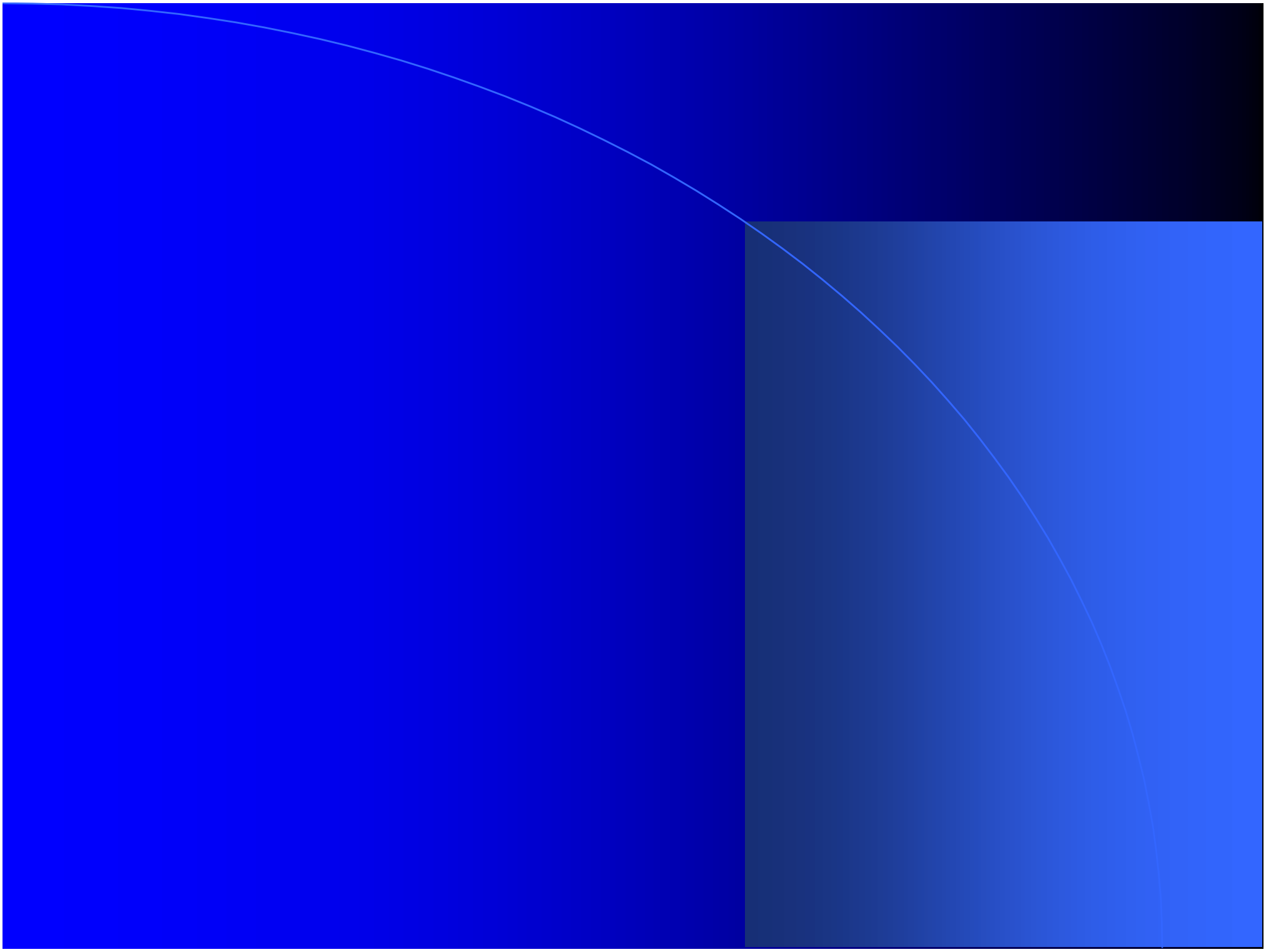
MNA Recommendations*

- Install additional monitoring wells along the extraction fence to supplement the existing monitoring network

- Refocus the LTM-MNA monitoring well network for chemical sampling on the plume areas where MNA and concentration changes are occurring more rapidly

- Continue LTM/LTO

* Year 2000 Annual Report



MNA (cont)

- A remedial strategy that incorporates the fact that contaminants will naturally attenuate through physical, chemical, and especially biological processes.
  - Different from “no action” alternative
  - Is only appropriate at sites where the rate of natural attenuation is sufficient to meet remedial objective
  - Depends on extensive monitoring and institutional controls to ensure protection of human health and the environment
  - Management of a known condition of contamination

Natural Attenuation under Sequential Anaerobic-Aerobic Conditions

- Most common at sites with regional aerobic groundwater and anthropogenic carbon source present
- Highly chlorinated VOC concentrations declining near source area under anaerobic conditions, replaced by breakdown products
- Breakdown products decline downgradient under more aerobic conditions
- Depletion of oxygen and nitrate in source area
- Appearance of methane and Fe II in source area, disappearing downgradient

- Chlorinated solvents can be transformed by:
  - Use of the solvent as an electron acceptor – appears to be the most important mechanism in LF-1
  - Use of the solvent as an electron donor
  - Cometabolism – degradation resulting from exposure to a catalytic enzyme fortuitously produced during and unrelated process

Reductive Dechlorination

- Chlorinated hydrocarbons act as electron acceptors – the chlorine atom is replaced by a hydrogen atom
  - The hydrogen atom comes from fermentation of other substrates (electron donors)
- Evidence of occurrence includes production of degradation products and metabolic byproducts

e^- Donors and Acceptors

- Driving force behind biodegradation is electron transfer from donors to acceptors
- Results in oxidation of electron donors and reduction of electron acceptors
  - Donors: natural organic carbon, petroleum hydrocarbons, light chlorinated hydrocarbons (i.e. VC and DCE or DCA), landfill leachate
  - Acceptors: oxygen, nitrate, Fe(III), sulfate, carbon dioxide, heavy chlorinated hydrocarbons (PCE, TCE, TCA, PCBs, etc)

FFS (cont)

- Oxygen
  - Areas of low DO (<0.5 mg/L) in LF-1 plume
  - Background DO at 11 mg/L
- Nitrate
  - Nitrate concentrations primarily nondetect in plume; highest concentration was 0.68 mg/L
  - Background concentrations low or nondetect
  - Denitrification not occurring to any measurable extent in LF-1
  - Not competing with reductive dechlorination

FFS (cont)

- Fe (III) –
  - Reduced to Fe (II)
  - Elevated concentrations (up to 18 mg/L) of Fe (II) relative to background present in plume
- Sulfate
  - Sulfate reduction not occurring to any measurable extent in LF-1

FFS (cont)

- Methane
  - Organic carbon is being degraded via methanogenesis
  - Concentrations up to 4.4 mg/L in plume: suggests strongly reducing conditions favorable to support reductive dechlorination in plume
- Carbon dioxide
  - Concentrations up to 190 mg/L in plume: suggests microbial activity is occurring
  - Supported by elevated alkalinity concentrations
- Degradation Products:
  - Cis-1,2-DCE, vinyl chloride, chloride, ethene and ethane are present in LF-1

- Anaerobic biodegradation can occur by denitrification, manganese reduction, Fe(III) reduction, sulfate reduction, methanogenesis
- Reductive dechlorination may dominate if subsurface conditions favor the use of electron acceptors
- Rate decreases as degree of chlorination decreases

Reductive Dechlorination Half Reactions

$$C_2Cl_4 + H_2 \rightarrow C_2HCl_3 + H^+ + Cl^-$$
$$C_2HCl_3 + H_2 \rightarrow C_2H_2Cl_2 + H^+ + Cl^-$$
$$C_2H_2Cl_2 + H_2 \rightarrow C_2H_3Cl + H^+ + Cl^-$$

$$C_2Cl_4 + 3H_2 \rightarrow C_2H_3Cl + 3H^+ + 3Cl^-$$

166 g/mol 62.5 g/mol

$$100 \frac{ug}{L} \text{ PCE} * \frac{\text{mol PCE}}{166 \text{ g PCE}} * \frac{1 \text{ mol VC}}{1 \text{ mol PCE}} * \frac{62.5 \text{ g VC}}{\text{mol VC}} = 37.7 \frac{ug}{L} \text{ VC}$$