

Fingerprinting and Forensic Techniques for Landfill Gas Geochemical Assessment

LEA/CIWMB Partnership Conference
Monterey, CA - August 2, 2006



Orange County LEA

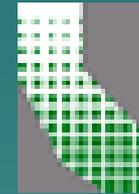
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Session Agenda

Theory of Gas Geochemistry

- I. Introduction – Stating the Problem
- II. Identification of Methane Sources
- III. Analytical Procedures/Methods
- IV. Data Interpretation Techniques

Case Studies in Orange County

Case I (Newport Terrace Landfill – Newport Beach, CA)

Case II (Cannery Street Landfill – Huntington Beach, CA)

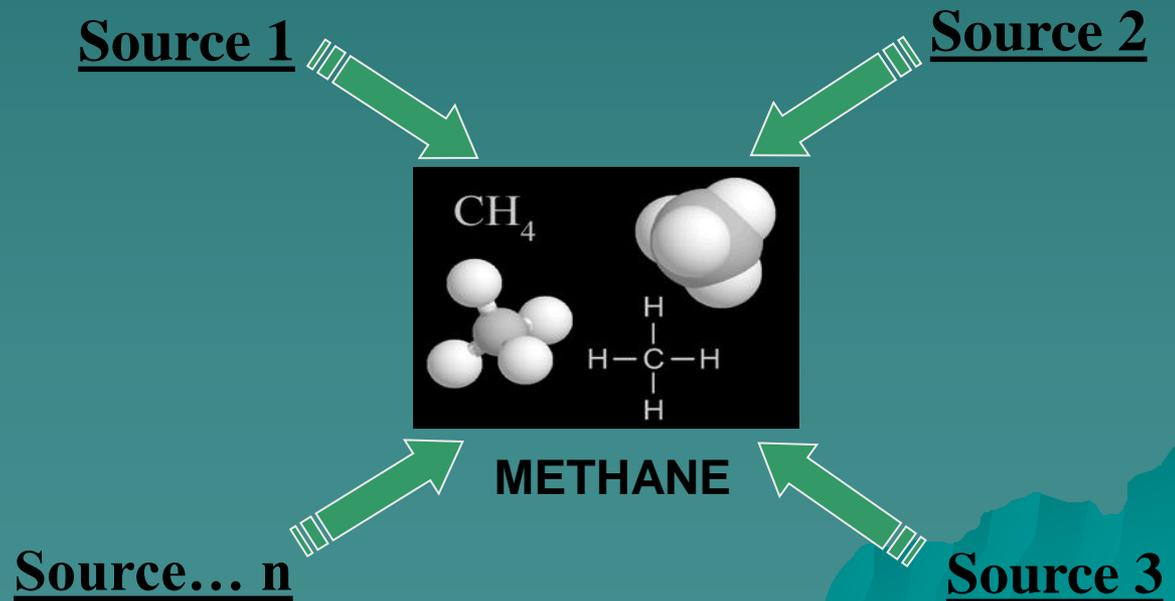
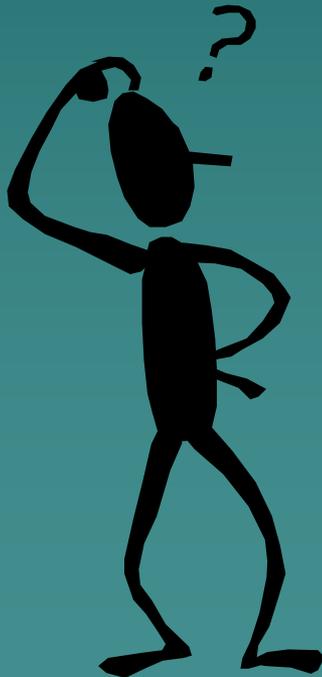
- V. Background/Description of Case Studies
- VI. Workplan Implementation and Procedures
- VII. Results and Interpretation
- VIII. Conclusions

Questions

I

Introduction

Stating the Problem



Problem Setting

- ◆ Methane as greenhouse & explosive gas
- ◆ CH₄ Migration/Accumulation = Hazards
- ◆ LEA/CIWMB task = Gas Monitoring and Control (27 CCR, Section 20919)

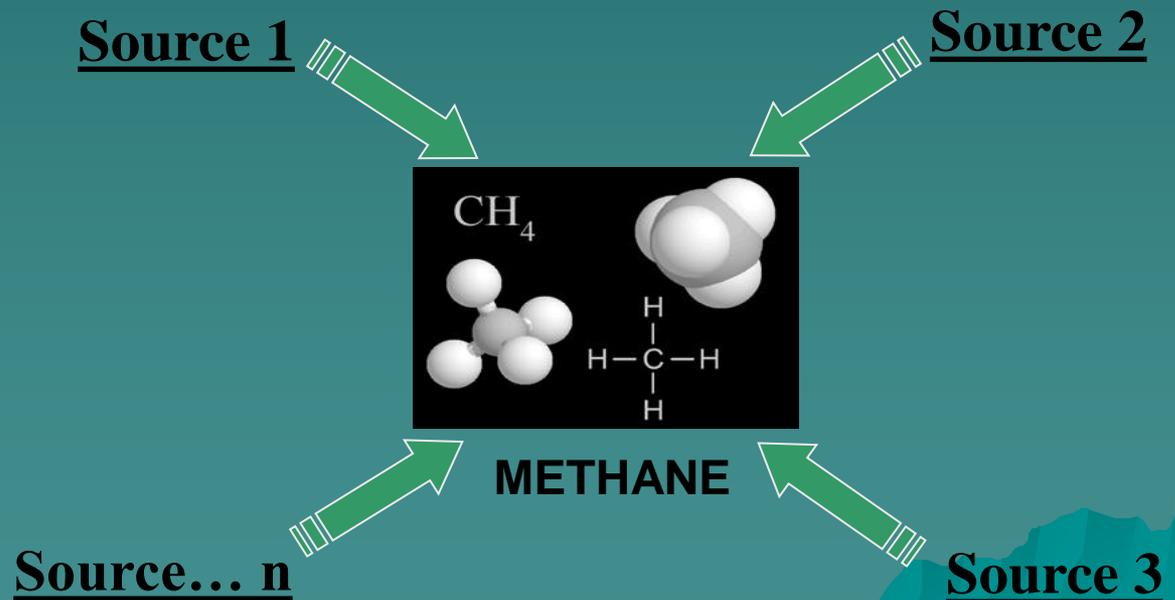
Fugitive methane from **OTHER SOURCES**

Problem Setting (contd.)

Identification and correlation of methane releases to their source

Why?

Scenarios/
Sources?



Why?

- ◆ To determine Responsible Parties
- ◆ To determine LEA involvement
- ◆ Adequate remediation design and implementation



“define the problem before the solution”

II

Identification of Methane Sources

What types of scenarios would the LEA encounter?



LANDFILL

+

**Common
(Most Likely)**

**Rare
(Not Likely)**

Most Common Sources

Sources that generate CH_4 in high enough volumes and pressures to generate a migrating plume through soils

{FUGITIVE METHANE}

(Gas that you would see in your probes)

Natural Gas Leaks (Pipeline Gas)

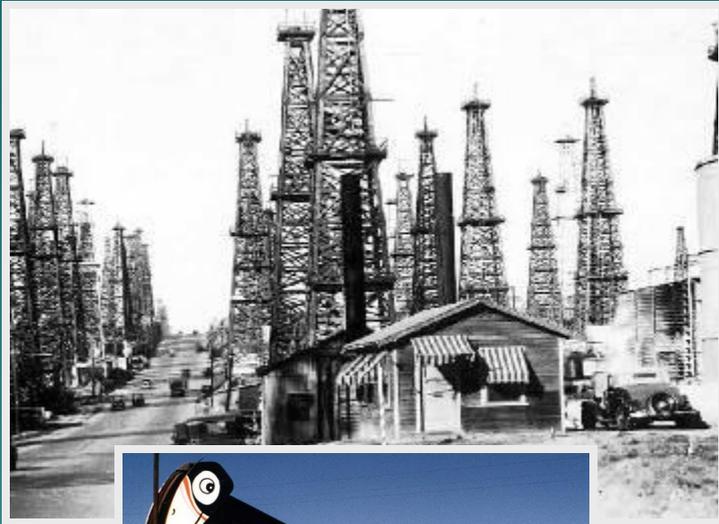


Transportation Lines

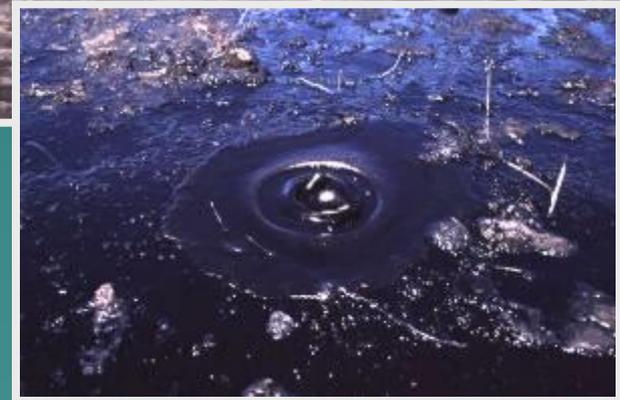


**Residential/Commercial
Supply Lines**

Naturally Occurring Methane (Thermogenic/Petrogenic Gas)



**Active/Abandoned
Well Leaks**



**Natural Seepage
(Underground Sources/Reservoirs)**

Other Biogas (Swamp/Marsh Gas)



**Decay of Organic Matter
(CH₄ Formation)
&
Seepage
Through Soil**



Other Sources

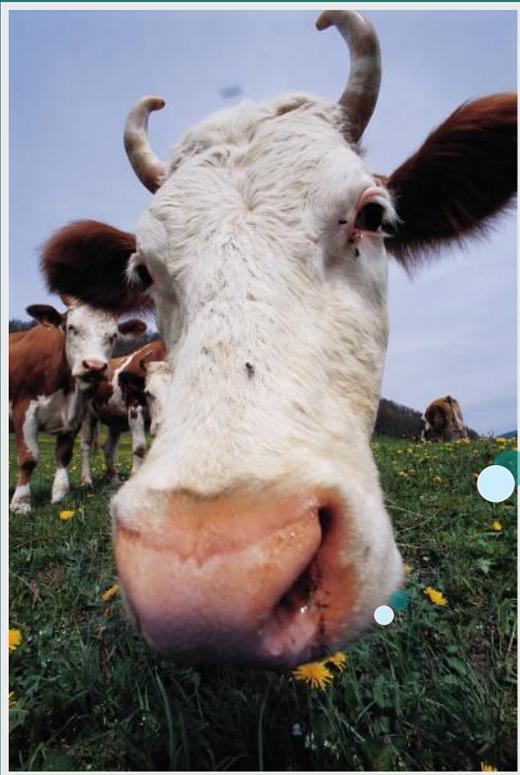
(Less Common/Not Likely)

- ◆ Low Potential – Underground Migrating Plumes
- ◆ Not Enough Documented Data (CH₄ Migrating-Problems)

(Gas that you wouldn't likely see in your probes)

- ◆ **Sewer Lines/Systems** (accumulation @ enclosed spaces)
- ◆ **Coal Mines**
- ◆ **Rice Fields**
- ◆ **Termites**
- ◆ **Oceans**
- ◆ **Livestock**

Factoid Livestock



Got Gas?

A cow can
belch up to
 $\frac{1}{2}$ lb of
 CH_4 /Day

+

Sheep
Goats
Buffalo
Camels

Can Do It Too

Factoid Livestock

97.1 Million Cattle in the US

DO THE MATH!

48.5 Million lb CH₄/Day



Got Gas?

**An untapped
source of energy**

Not For Every Landfill in CA

Common Scenario for the LFA

LANDFILL VS THERMOGENIC SOURCE

➤ **Be Informed**

➤ **Do your Homework**

DESPITE

- ◆ CA ranked 4th oil producing state in the US
 - ◆ 100's of oil/gas seeps found in 28 counties in CA (Marathon San Diego)
- There are tools available!**



Oil & Gas Fields in CA

- ◆ Are the maps (Map)
- ◆ Are we (Data)
- Res
- http

The screenshot shows a Microsoft Internet Explorer browser window with the address bar displaying <http://www.consrv.ca.gov>. The page content includes a 'California Home' banner, a 'Department of Conservation' logo, and a 'Division of Oil, Gas & Geothermal Resources' header. A search bar is present on the right. The main content area is titled 'Digital Well Locations' and contains the following text:

Digital well locations are available in a database file that contains the latitude and longitude for each well in the state. These database files can be downloaded as a statewide file (with approximately 195,000 wells listed) or by district office.

Each database file is a compressed EXE file that can be downloaded (saved) to your computer. To use the database file after you have saved it to your computer, it must be uncompressed (by double clicking on it, or use Start, Run process).

The compressed file will extract into a DBF file that can be imported into your mapping software. Mapping software used by the Division to prepare maps is MapInfo, but other mapping software should be able to import the DBF files. The information contained in the file includes API number; operator; well name and number; section, township, and range; and the latitude and longitude (the map projection used is Latitude:Longitude-NAD27 for the Continental United States).

Note: The [well status codes](#) contained within the database files are listed near the bottom of this page.

Click on the links below to download (save) the well location database(s) to your computer:

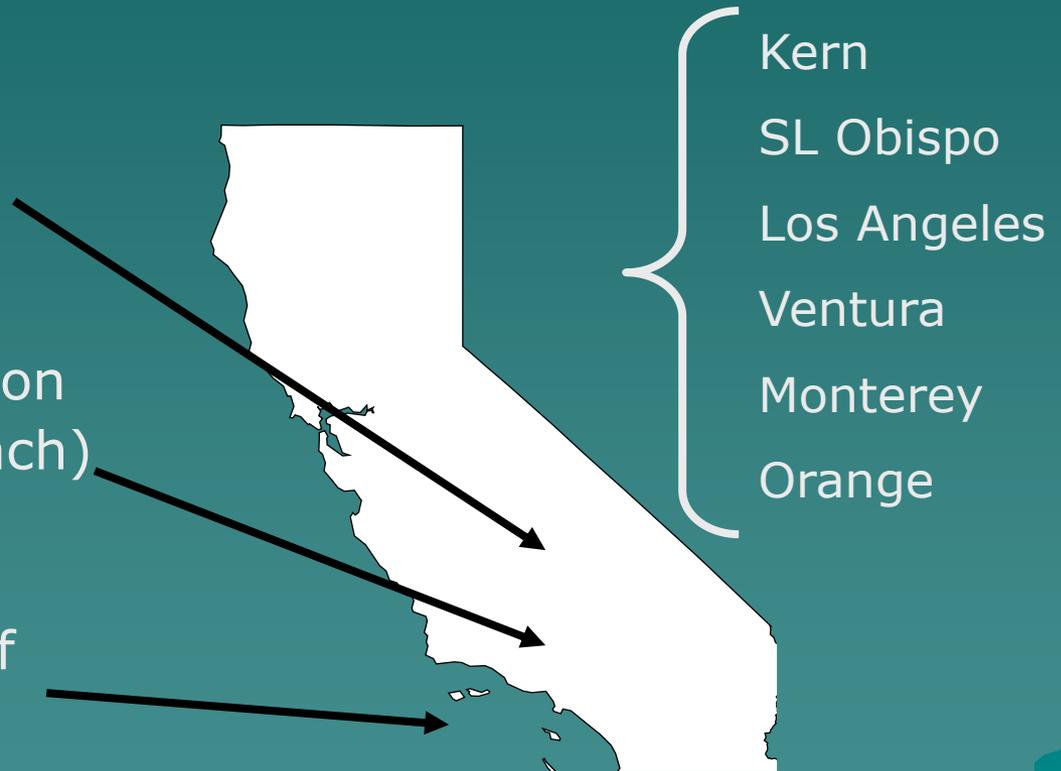
- [Statewide database](#)

The Windows taskbar at the bottom shows the Start button, several application icons, and the system tray with the time 2:49 PM on Thursday, 7/6/2006.

Oil Production in CA

3 Major Regions

- Kern County Region (69%)
- Los Angeles Basin Region (Central LA – Long Beach) (~10%)
- Outer Continental Shelf (Offshore 10.2%)



Forensics

Correlating CH₄ Releases to their Source

III

Analytical Procedures/Methods

Analytical Procedures/Methods

Fingerprinting Gas Releases (Gas Geochemistry)

Groups:

1. Looking at the Various Constituents

- BTEX
- H₂S
- C₂+
- Fixed Gases
- Chlorinated Hydrocarbons/VOCs
- Mercaptans

2. Stable Isotope Composition

- Hydrogen Isotopic Ratio ($^2\text{H}/^1\text{H}$)
- Carbon Isotopic Ratio ($^{13}\text{C}/^{12}\text{C}$)

3. Radio Isotope Composition

- ^{14}C Concentration (Carbon Dating)
- ^3H Concentration

4. Measuring the Caloric Values

- CH_4 BTU value

Not an Easy Task!

Screening Process

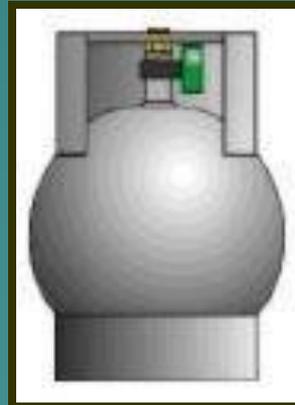
Source x



Gas Probe



Landfill



Screening Process (contd.)

Formation Process

- LFG
 - Swamp/Marsh Gas
 - Naturally Occurring
 - Pipeline Gas
- Biogenic
Shallow depths/low temps
Anaerobic bacterial decomp
New Gas (0-100 years)
- Thermogenic
High temps/depth/pressure
Thermal crack org. matter
Old Gas (Millions of years)

Elements for the ID of Sources

LFG

- ◆ $\text{CO}_2 + \text{CH}_4$ almost equal proportions
- ◆ VOCs/BTEX (trace)
- ◆ Low Oxygen
- ◆ H_2S (0-100 ppm) Note: 3-5% (US EPA)
- ◆ $\text{C}_2\text{-C}_5$ (trace)
- ◆ Unique Isotopic Fingerprinting ($^{13}\text{C}/^{12}\text{C}$ and $^2\text{H}/^1\text{H}$)
- ◆ ^{14}C Detected (Modern/New Gas)

Elements for the ID of Sources (contd.)

SWAMP/MARSH GAS

- ◆ Easily mistaken with LFG
- ◆ Same formation process (biogenic/anaerobic)
- ◆ No VOCs/BTEX
- ◆ No H₂S
- ◆ Unique Isotopic Fingerprinting (¹³C/¹²C and ²H/¹H)

Elements for the ID of Sources (contd.)

NATURALLY OCCURRING GAS

- ◆ BTEX (trace)
- ◆ No VOCs
- ◆ H₂S Low–High (0.1 – 2.5%)/(0-98%)
- ◆ C₂-C₅ (up to 20%)
- ◆ Unique Isotopic Fingerprinting (¹³C/¹²C and ²H/¹H)
- ◆ ¹⁴C (Not Detected/Old Gas)

Elements for the ID of Sources (contd.)

PIPELINE GAS

- ◆ Almost Pure CH₄ (80-90%)
- ◆ Some C₂-C₅ (%)
- ◆ Unique ID Element: Tracers (25-100 ppm)
Mercaptans/Thiophene other Odorants

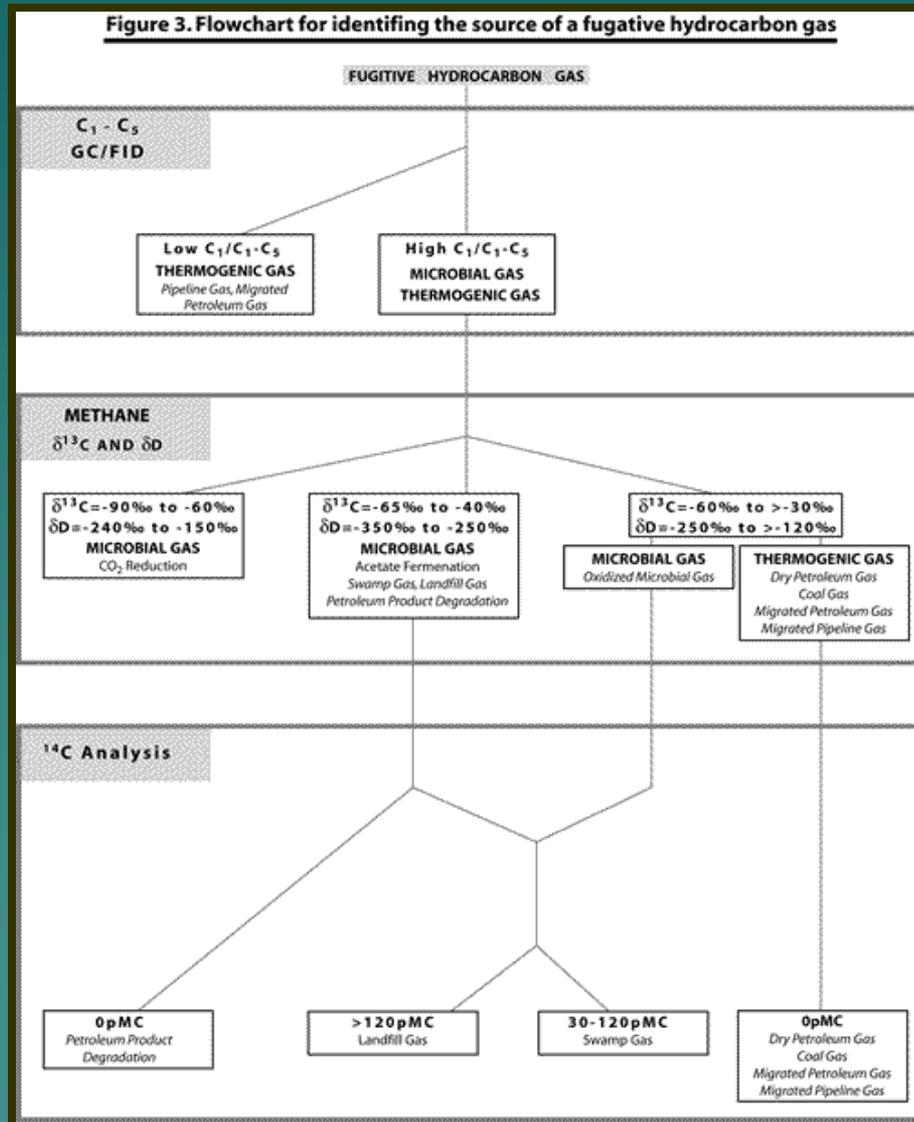
Forensics

Correlating CH₄ Releases to their Source

IV

Data Interpretation Techniques

Data Interpretation

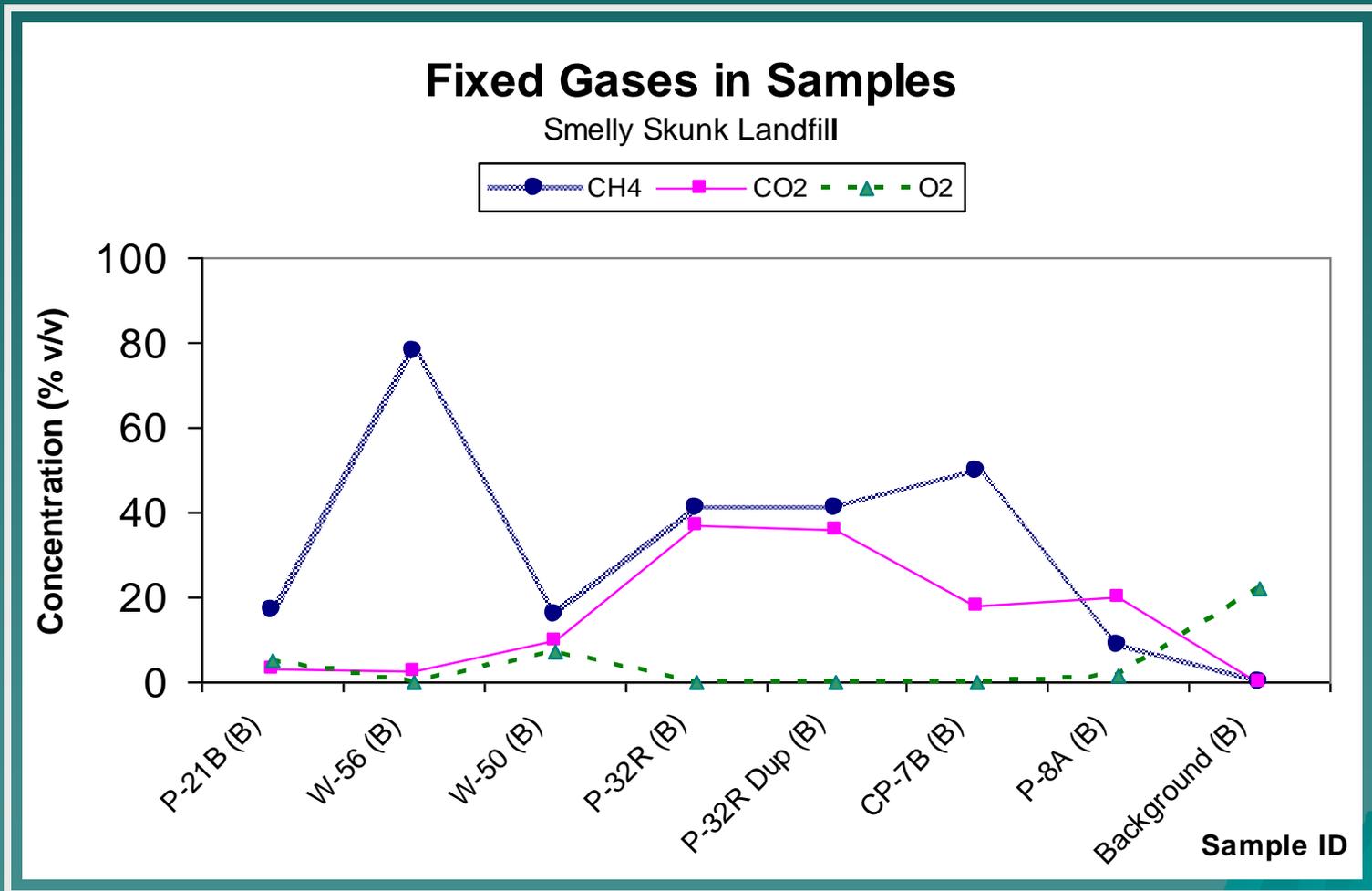


Tier Evaluation Process

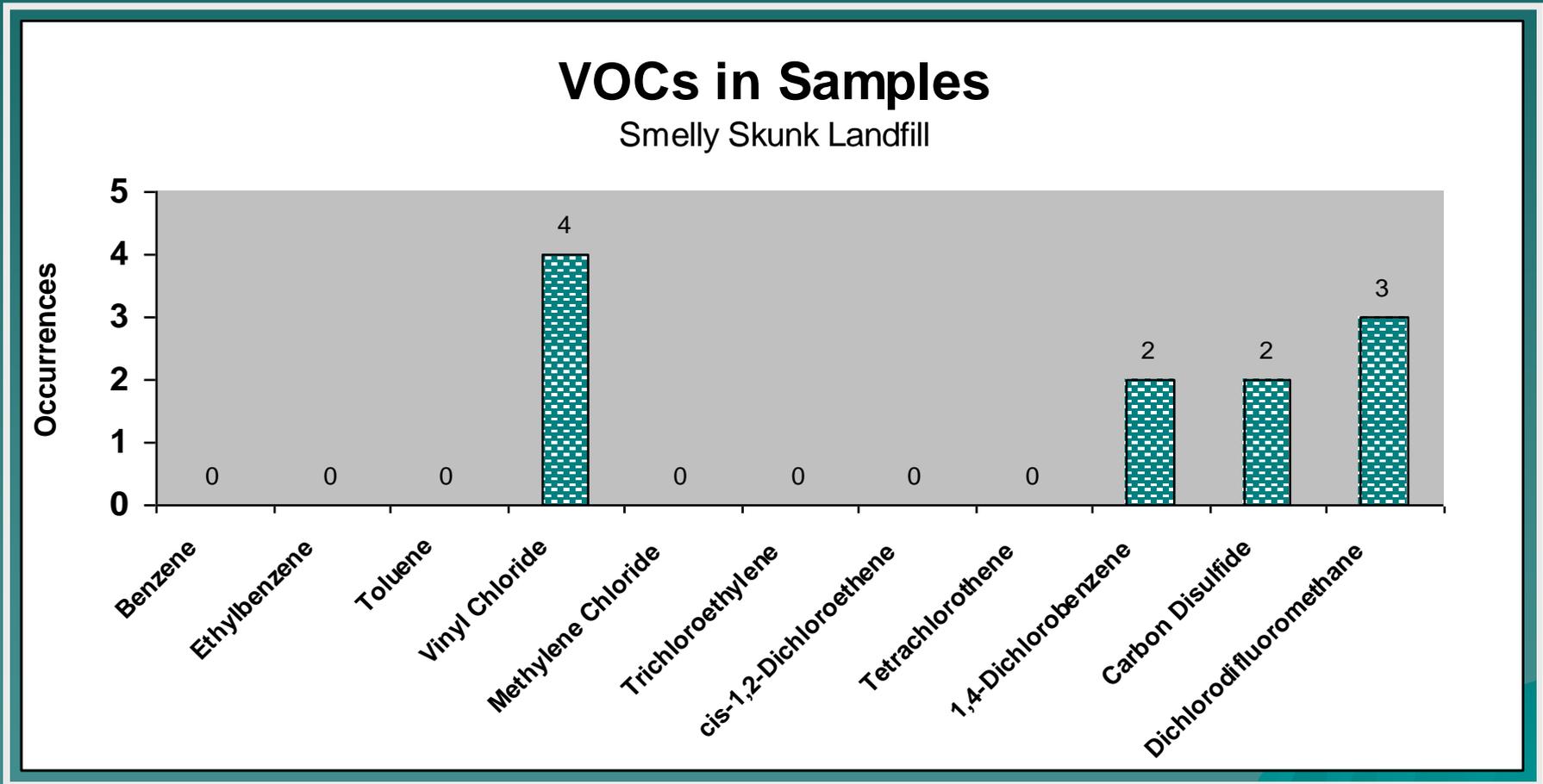
Source's Unique ID ELEMENTS



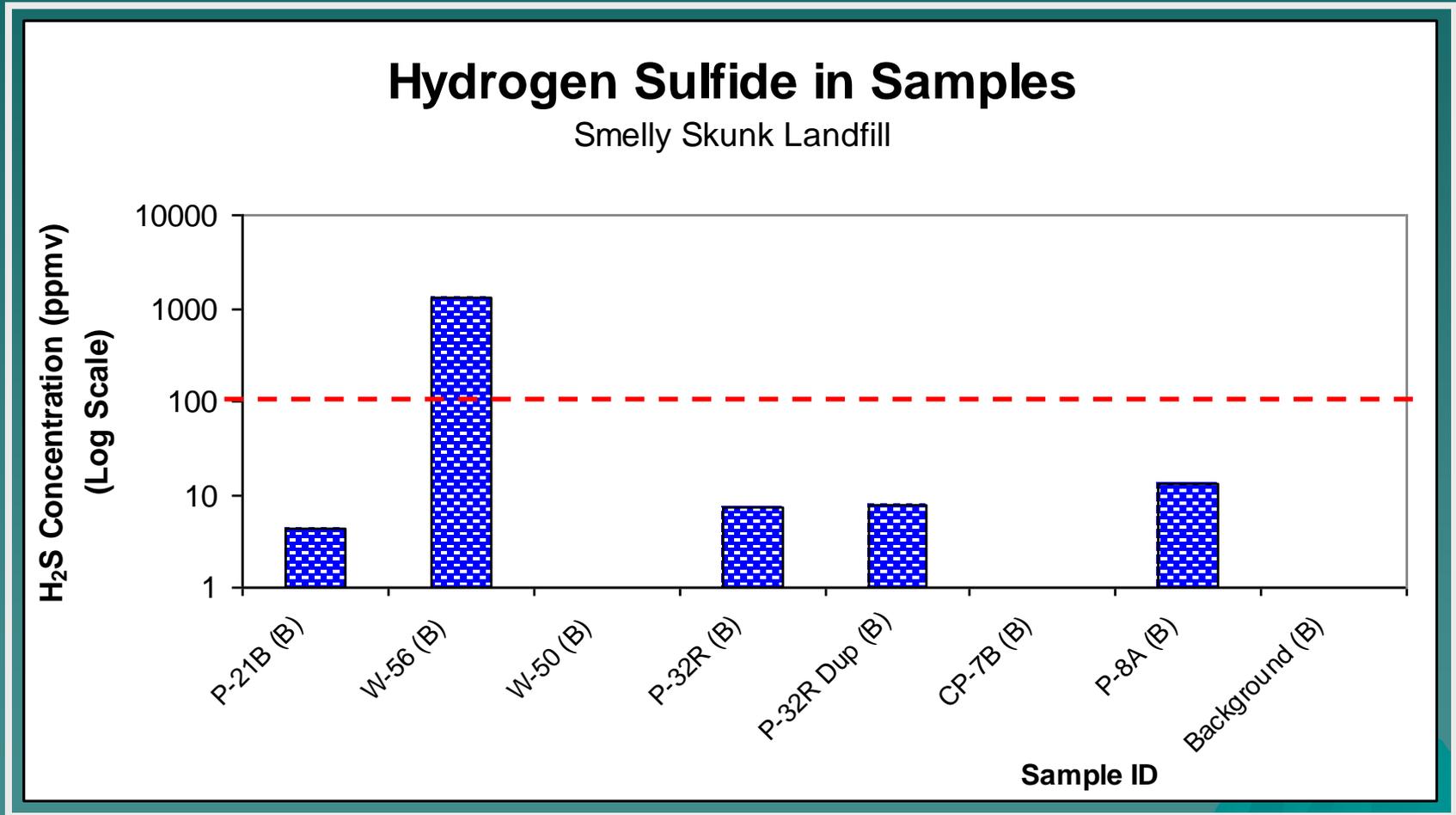
Unique ID Elements



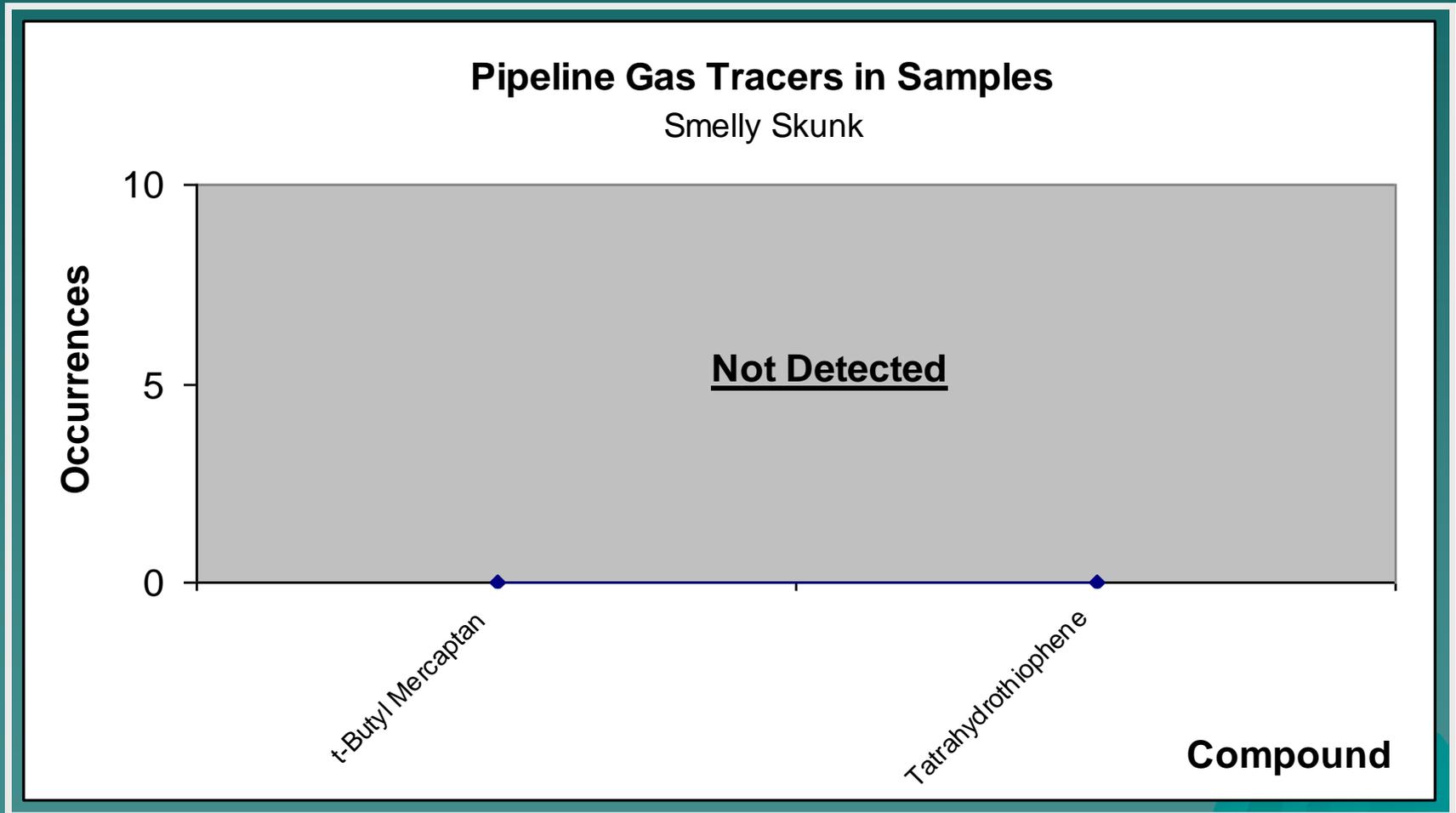
Unique ID Elements (contd.)



Unique ID Elements (contd.)

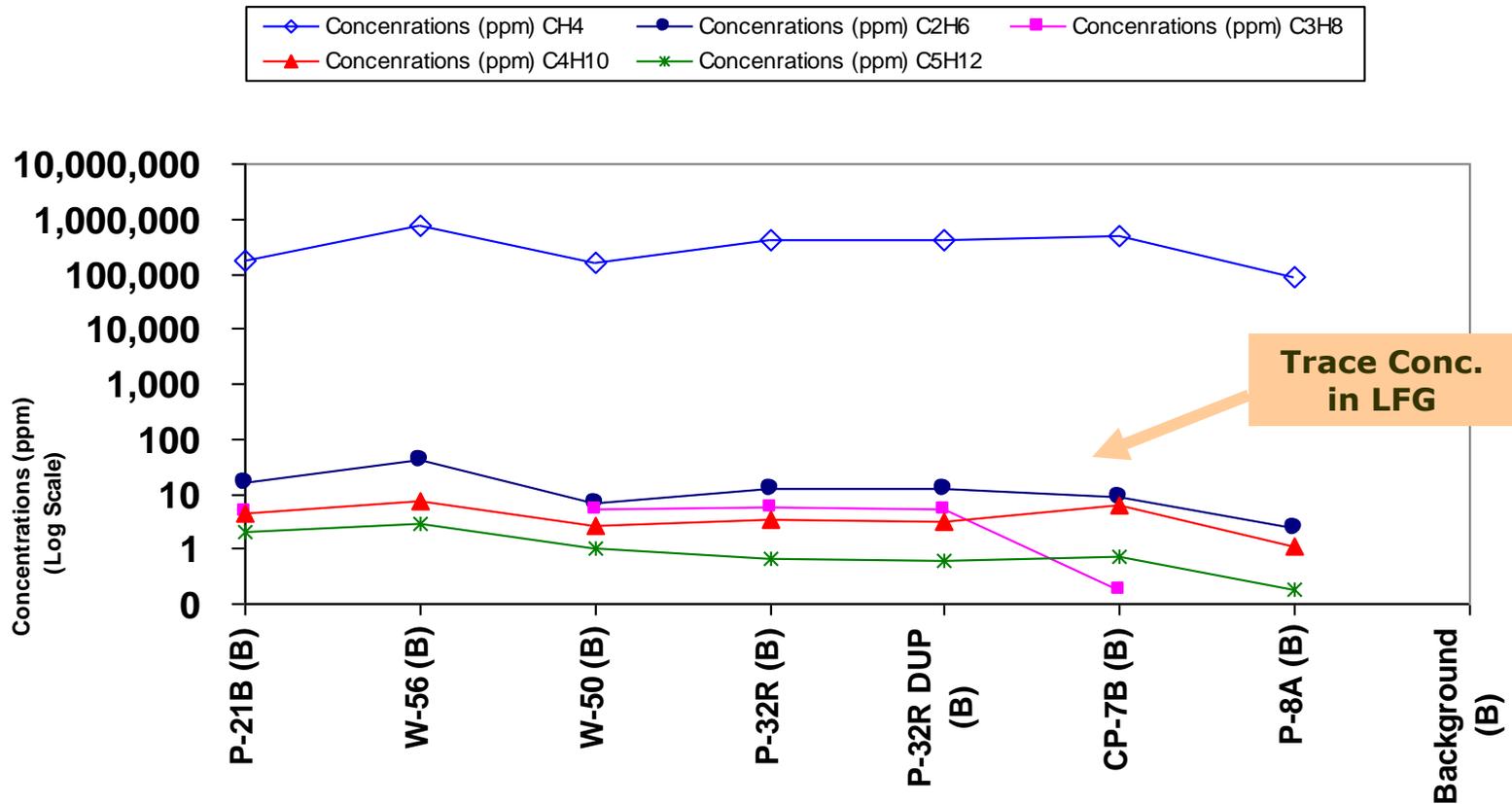


Unique ID Elements (contd.)



Unique ID Elements (contd.)

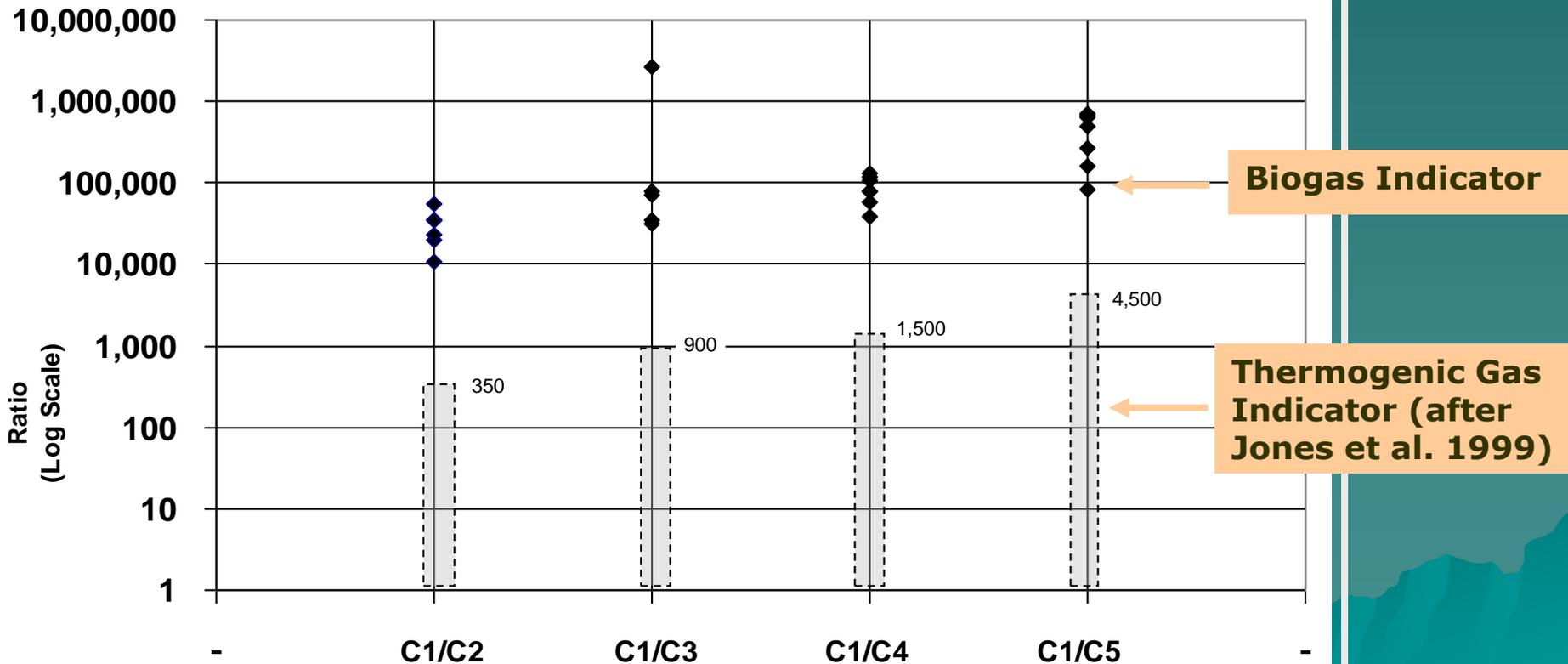
Hydrocarbons/Alkanes (C2-C5) & Methane Smelly Skunk Landfill



Unique ID Elements (contd.)

Hydrocarbon Ratios (C1/C2-C5)

Smelly Skunk Landfill



Sophisticated Geochemistry to ID Sources

Stable Isotope Composition (Isotope Chemistry 101)

Naturally Occurring Isotopes:

^{12}C 98.89%

^{13}C 1.11%

} Same Element
Different Atomic Weight

^1H ~99.98%

^2H 0.0184%

} Same Element
Different Atomic Weight

The Principle of Employing Isotopes

Distribution of Isotopes



Biogenic Methane Formation

¹²
C
¹³
C
C



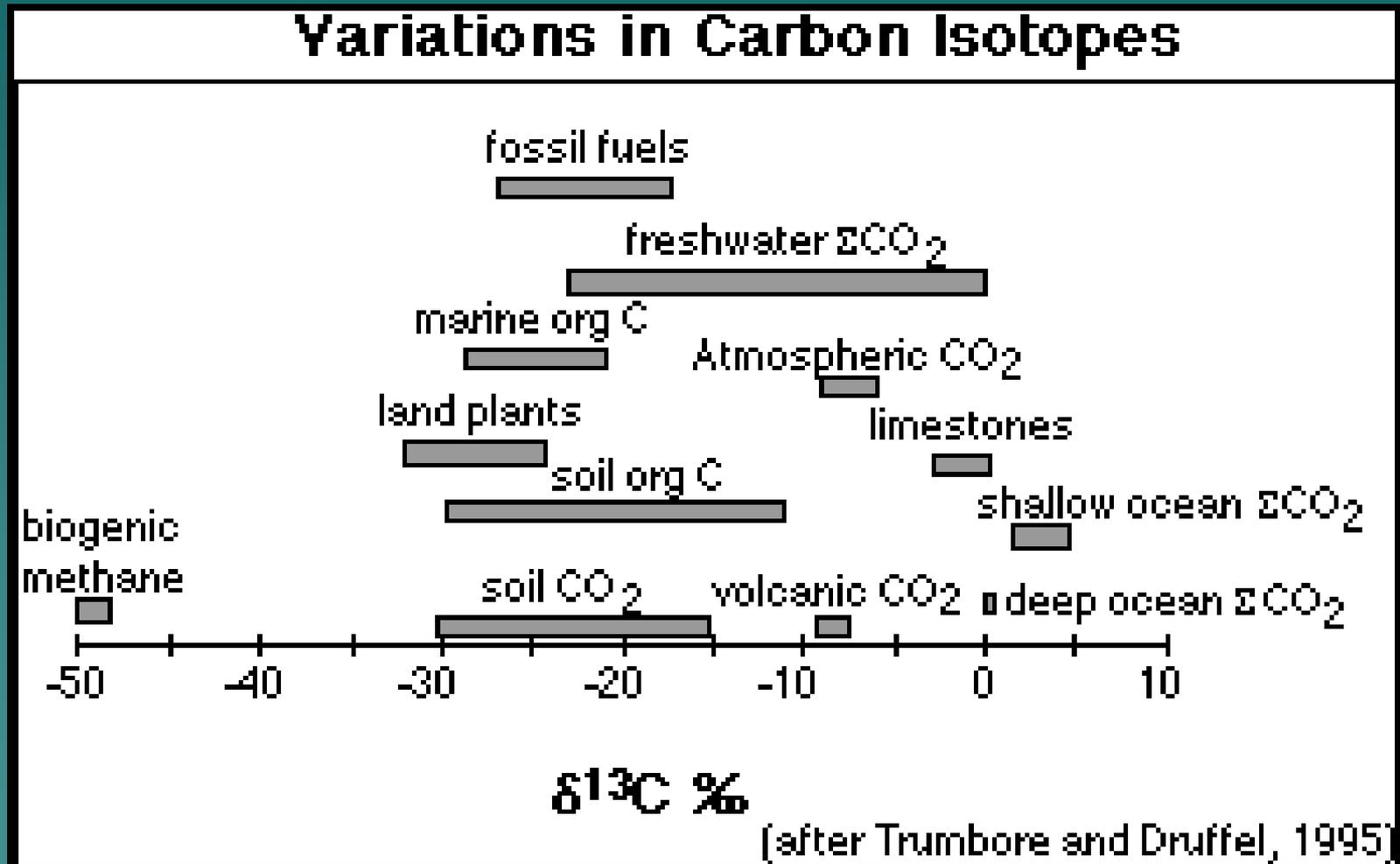
Bacterial Decomposition
Light Isotopes ¹²C & ¹H
Preferentially Selected



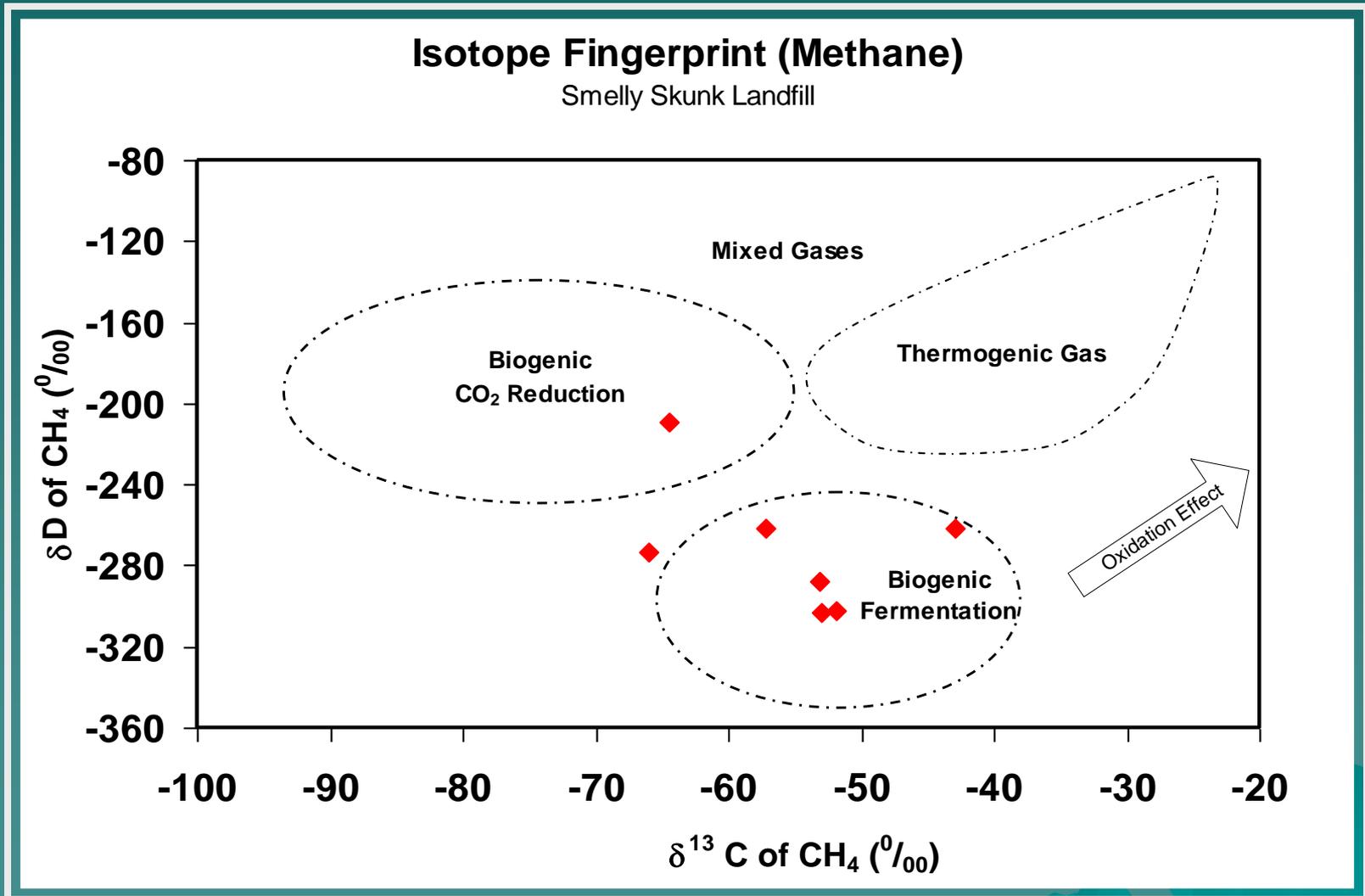
¹³C/¹²C Ratio: Unique to the source

²H/¹H Ratio: Unique to the source

The Principle of Employing Isotopes



The Principle of Employing Isotopes



Radioisotope Composition

^{14}C Concentration – Carbon Dating

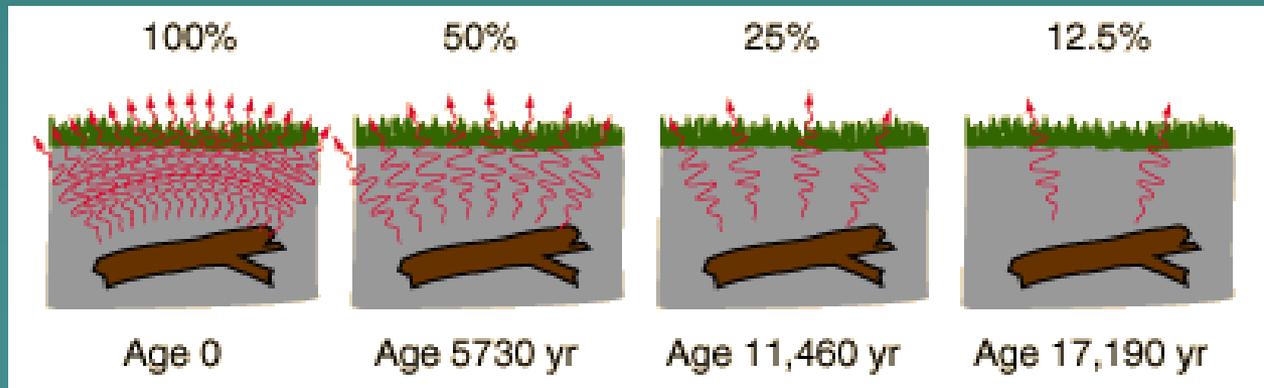
Naturally Occurring Isotopes:

^{12}C 98.89%

^{13}C 1.11%

^{14}C 0.0000000001% (Radioactive)

^{14}C Decays = Half-life 5730 yrs



How much ^{14}C is remaining in the CH_4 ?

^{14}C Concentration – Carbon Dating

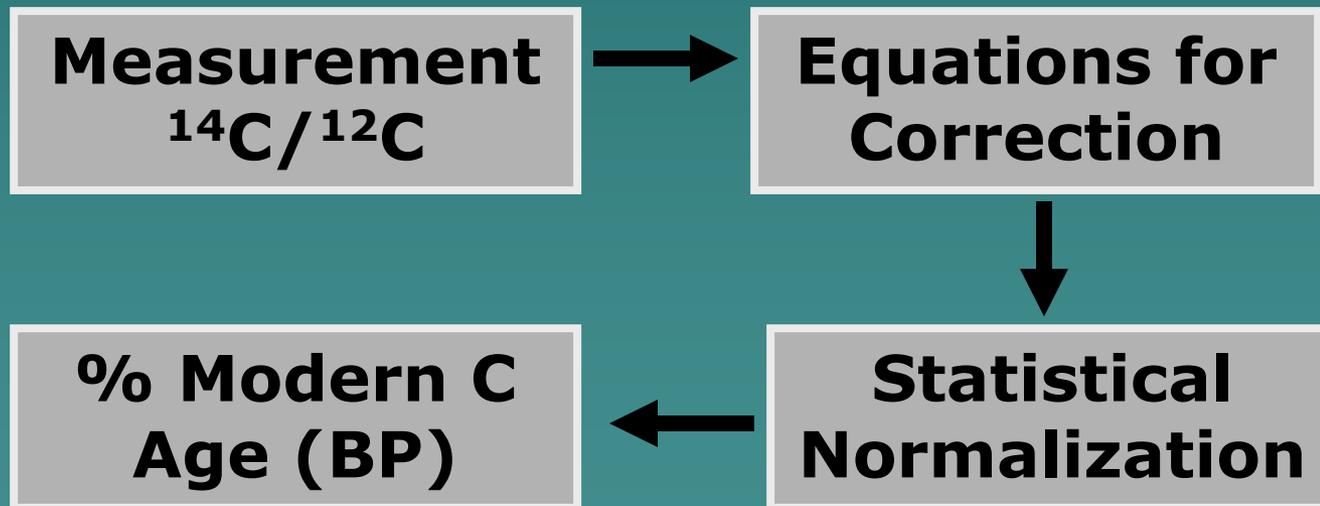
- ◆ Anything older than 60,000 years should have no detectable ^{14}C (thermogenic gas)
- ◆ If we detect ^{14}C , it is good evidence that gas was generated less than 60,000 years (landfill gas)

1. LFG **should** contain ^{14}C

2. Thermogenic gas **should not** contain ^{14}C

How is ^{14}C Measured

- ◆ Counting atoms/Accelerator MS
- ◆ AMS sophisticated - (UCI & Livermore)

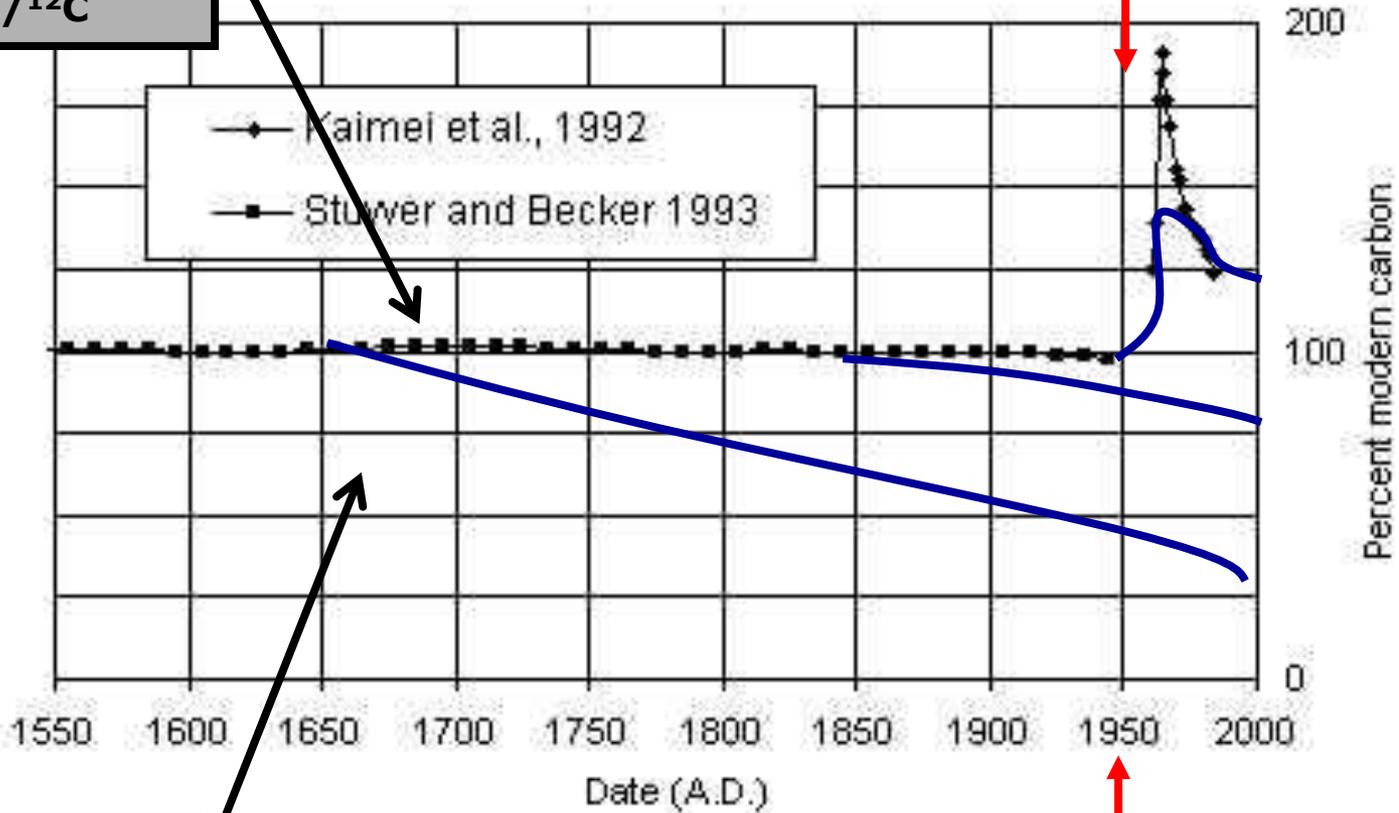


How is ^{14}C Measured

Atmospheric
 $^{14}\text{C}/^{12}\text{C}$

0-100 pMC

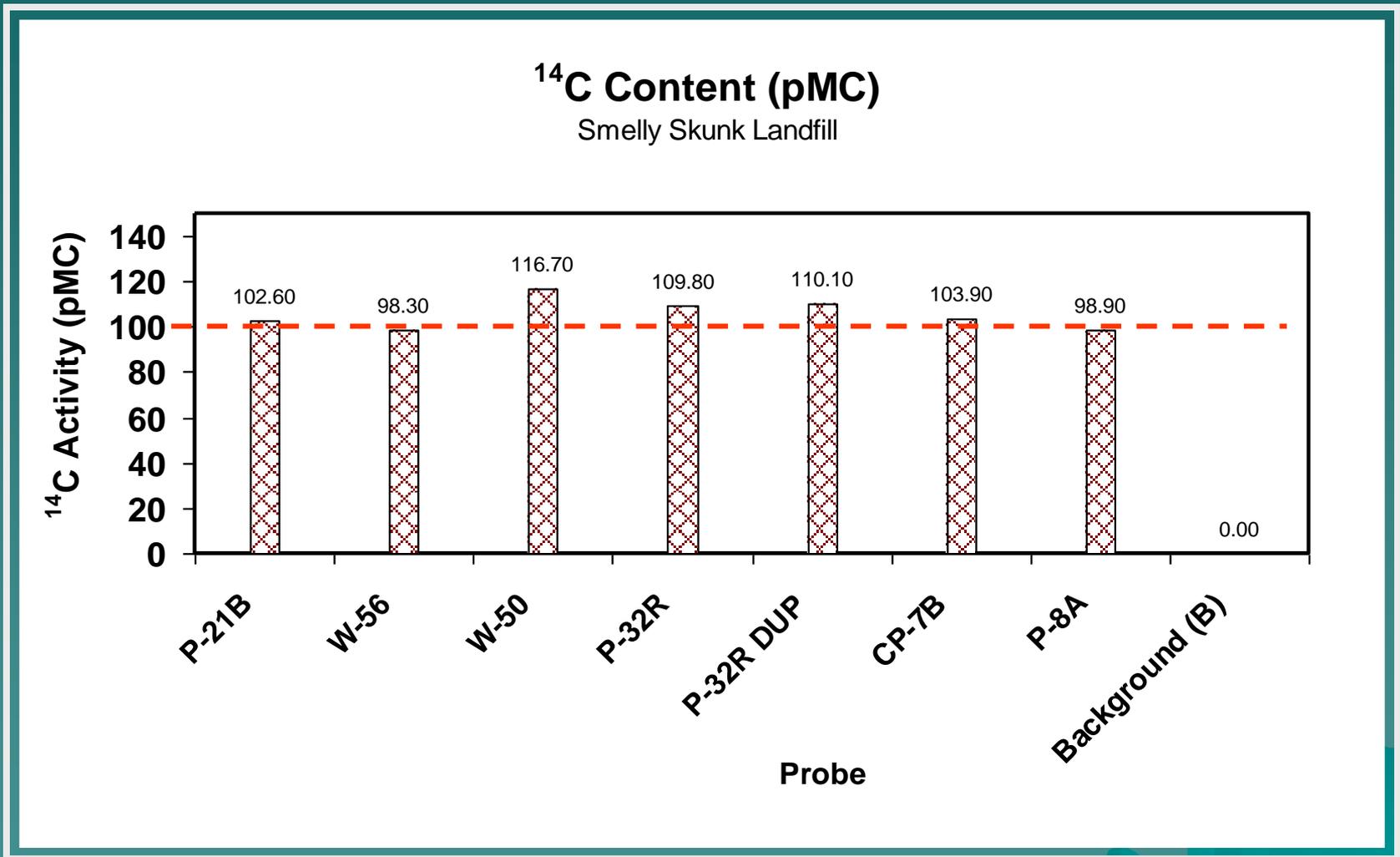
100-120 pMC



$^{14}\text{C}/^{12}\text{C}$
Decaying Matter

1950 is year 0 BP

Reporting ^{14}C Results





Case Studies in Orange County

Case I

(Newport Terrace Landfill)

Newport Beach, CA

V

Case Background

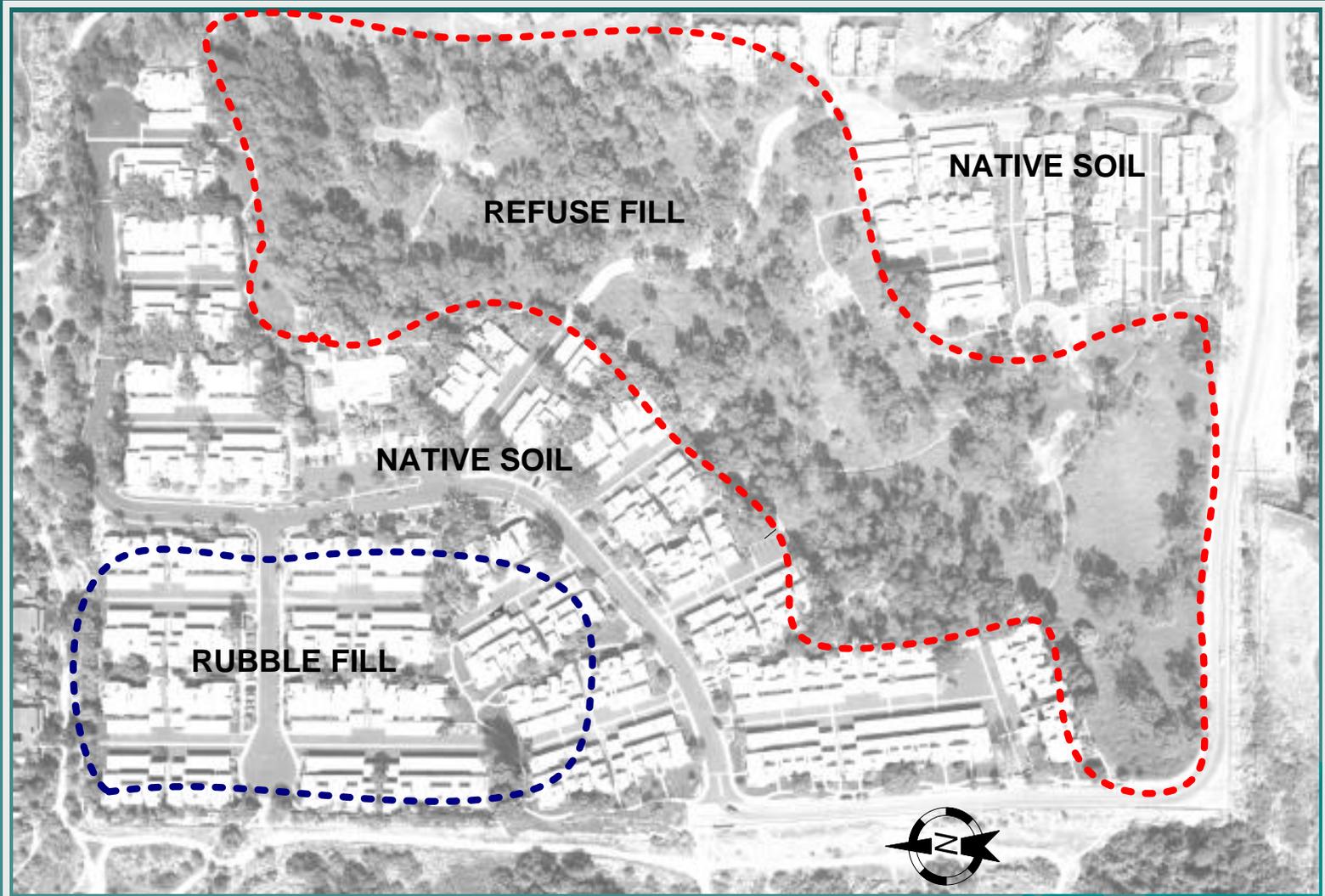
&

Description

Background

- Originally a gravel mining pit
- Owned and operated as a disposal site by City of Newport Beach between 1953 – 1967
- Located near wetlands and encompasses 41 acres including 17 acres of Refuse Fill and Rubble Fill areas
- Accepted C&D, plastic, paper, cardboard, metals, glass and yard wastes

Site Fill Areas



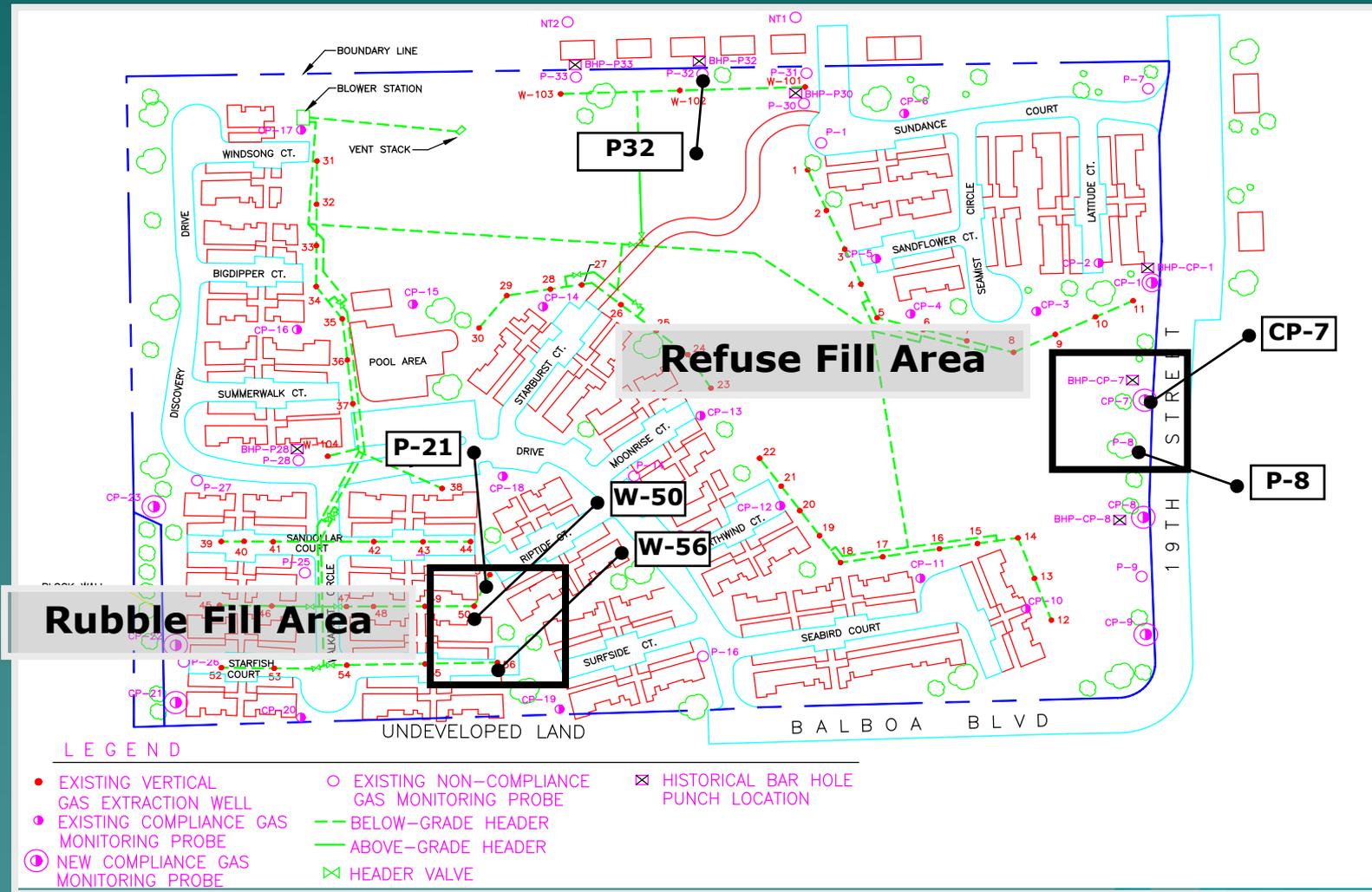
Background (contd.)

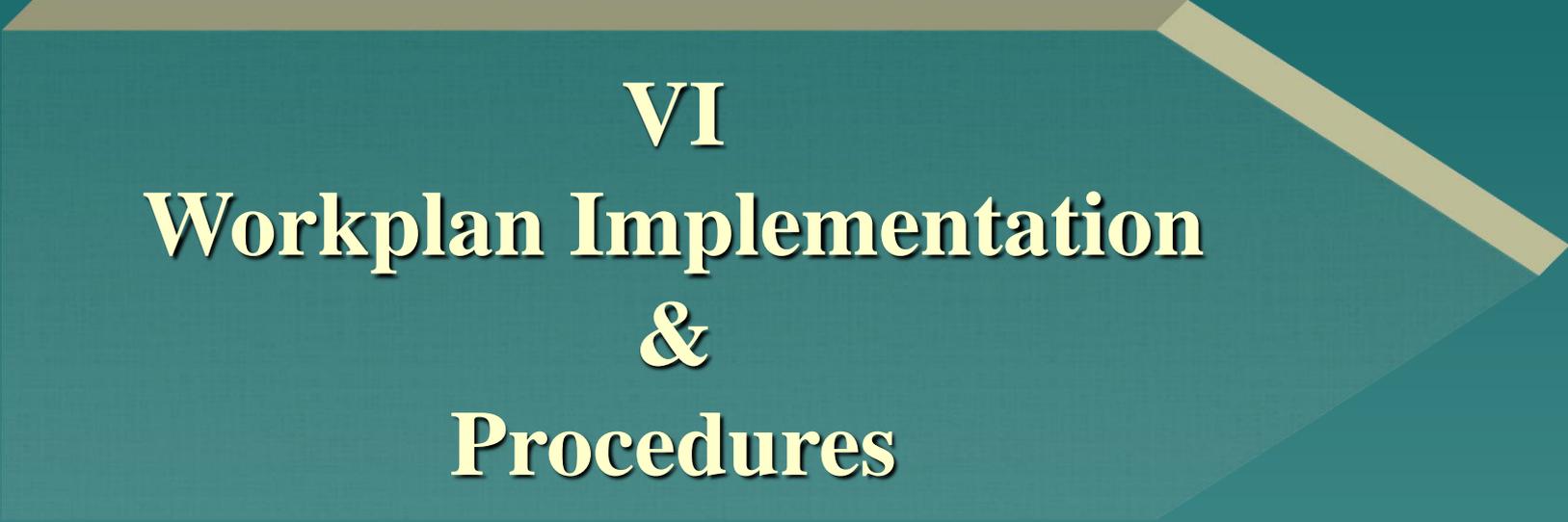
- Sold to a developer who, in 1974, built condominiums on-site
- 1974-1975 LFG control system was installed (archaic by today's standards)
- The LEA notified HOA on numerous occasions of the Site's violation of SMS for LFG
- 1998 HOA's consultant concluded that repairs to LFG control system were impractical and uneconomical

Background (contd.)

- 2001, CIWMB detected $\text{CH}_4 > 5\%$ in Rubble Fill and Refuse Fill's eastern and southern boundaries ($\text{H}_2\text{S} > 1,000$ ppm in Rubble Fill)
- In 2002, the LEA issued N&O to control LFG
- Based on high H_2S levels, City argued the source of CH_4 in Rubble Fill is not buried waste

Site Probes





VI
Workplan Implementation
&
Procedures

Investigation Workplan

- Focused on Rubble Fill area, southern and eastern boundaries of Refuse Fill area
- Screening of sampling locations for CO₂, O₂, N₂, CH₄ and H₂S
- If CH₄ > 1% collect samples for lab analysis
- Background and duplicate samples (QA/QC)

Investigation Workplan (contd.)

- Lab analysis:
 - CO₂, O₂ and Balance (mostly N₂)
 - Hydrocarbons C₁ – C₅
 - Pipeline gas tracers
 - VOCs (including BTEX)
 - (¹³C/¹²C) + (²H/¹H)
 - ¹⁴C
 - H₂S

Workplan Implementation

- June 2005
- Sample locations were 1st purged and screened for CH₄, fixed gases, H₂S
- Field measurements logging
- Lab samples were collected from:
 - Rubble Fill (P-21, W-50 and W-56)
 - Refuse Fill (P-32, CP-7 and P-8)
 - Background

Field Logbook



California Integrated Waste Management Board

1001 I Street - Sacramento, CA 95814

Permitting & Enforcement

(Closed Illegal & Abandoned Site Investigation Unit)

Landfill Gas Monitoring Log

Location: Newport Beach

Instrument: GEM-2000

Date: 6/22/2005

Project: Newport Terrace Landfill

Field Staff: AMC + DO

Weather Condition: Sunny and Clear

Bar. Pressure: 29.8" Hg

Comments: Samples taken for lab analysis.

ID	Probe Depth (feet)	Purge Time (sec)	Time	Static Pressure	Temperature (°F)	Monitoring Data					Field Observations
						CH4 (%)	CO ₂ (%)	O ₂ (%)	Balance (%)	H ₂ S (ppm)	
P21-B	Deep	Reading Stable	8:08	n/a	70	10	3.9	1.6	84.5	0	Samples Taken: 2 Summa Canisters + 1 Tedlar Bag H2S reading using GMI-442.
P21-R	Shallow	Reading Stable	8:17	n/a	70	0	9	4.4	86.8	n/a	Samples Taken: None
W-56	n/a	Reading Stable	8:25	n/a	70	64.7	2.9	0.7	31.5	above scale	Samples Taken: 2 Summa Canister + 1 Tedlar Bag (H2S reading using GMI-442 above the instrument's scale/1000 ppm)
W-50	n/a	Reading Stable	8:40	n/a	70	12.5	9.2	6.9	71.7	n/a	Sample Taken: 2 Summa Canisters + 1 Tedlar Bag
P-32 R	Deep	Reading Stable	9:00	n/a	74	31	31.2	3.2	34.2	11	Samples Taken: 2 Summa Canisters + 1 Tedlar Bag Duplicates Taken: 2 Summa Canisters + 1 Tedlar Bag
P-32 B	Shallow	Reading Stable	9:04	n/a	74	28.5	32.5	2	37.1	18	Samples Taken: None
CP-7B	n/a	Reading Stable	9:25	n/a	74	45.1	17.7	1.4	35.4	3	Samples Taken: 2 Summa Canisters + 1 Tedlar Bag
CP-7A	n/a	Reading Stable	9:31	n/a	74	0	8.3	14.4	77.3	n/a	Samples Taken: None
CP-7C	n/a	Reading Stable	9:34	n/a	74	11.9	7.9	9.8	70.1	n/a	Samples Taken: None
P-8B	n/a	Reading Stable	9:39	n/a	74	0	8	13.3	78.7	n/a	Samples Taken: None
P-8A	n/a	Reading Stable	9:42	n/a	74	7.7	22.1	1.9	69.8	n/a	Samples Taken: 2 Summa Canisters + 1 Tedlar Bag
Background	-	-	9:58	-	74	-	-	-	-	-	Samples Taken: 2 Summa Canisters + 1 Tedlar Bag

Field Logbook

ID	Probe Depth (feet)	Purge Time (sec)	Time	Static Pressure	Temperature (°F)	Monitoring Data				
						CH ₄ (%)	CO ₂ (%)	O ₂ (%)	Balance (%)	H ₂ S (ppm)
P21-B	Deep	Reading Stable	8:08	n/a	70	10	3.9	1.6	84.5	0
P21-R	Shallow	Reading Stable	8:17	n/a	70	0	9	4.4	86.8	n/a
W-56	n/a	Reading Stable	8:25	n/a	70	64.7	2.9	0.7	31.5	above scale
W-50	n/a	Reading Stable	8:40	n/a	70	12.5	9.2	6.9	71.7	n/a
P-32 R	Deep	Reading Stable	9:00	n/a	74	31	31.2	3.2	34.2	11
P-32 B	Shallow	Reading Stable	9:04	n/a	74	28.5	32.5	2	37.1	18

Field Sampling



Field Sampling



Workplan Implementation (contd.)

- Samples for H₂S and pipeline gas tracers lab analysis were collected last
- Lab samples labeling, logging in COCs, packing and shipping
- 3 different analytical labs



VII

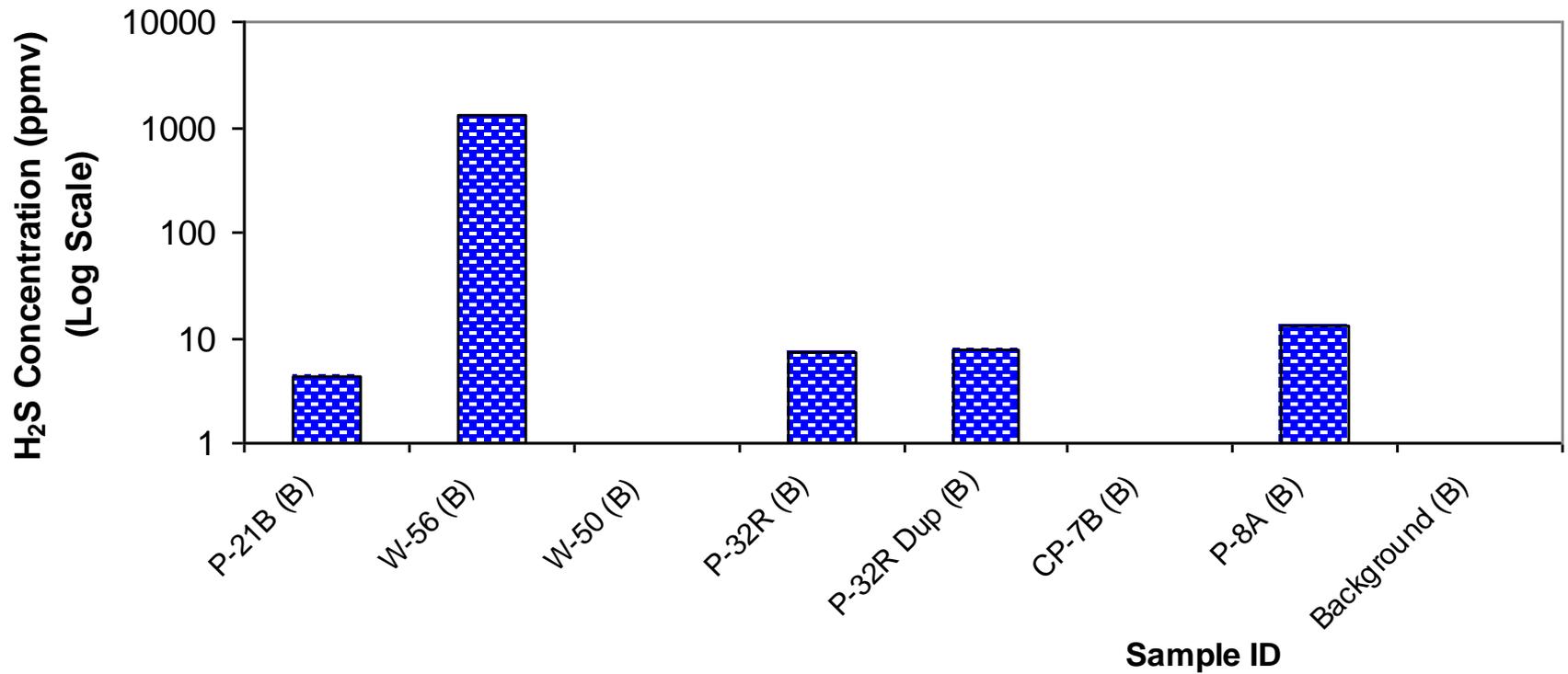
Results and Interpretation

Results and Interpretation

- Since no tracers were detected in any collected sample, leaking gas pipeline was ruled out as a source
- Consistent Hydrocarbons $C_1 - C_5$ concentrations in all lab samples
- Only one sample from Rubble Fill had very high H_2S level – outside the typical range for LFG

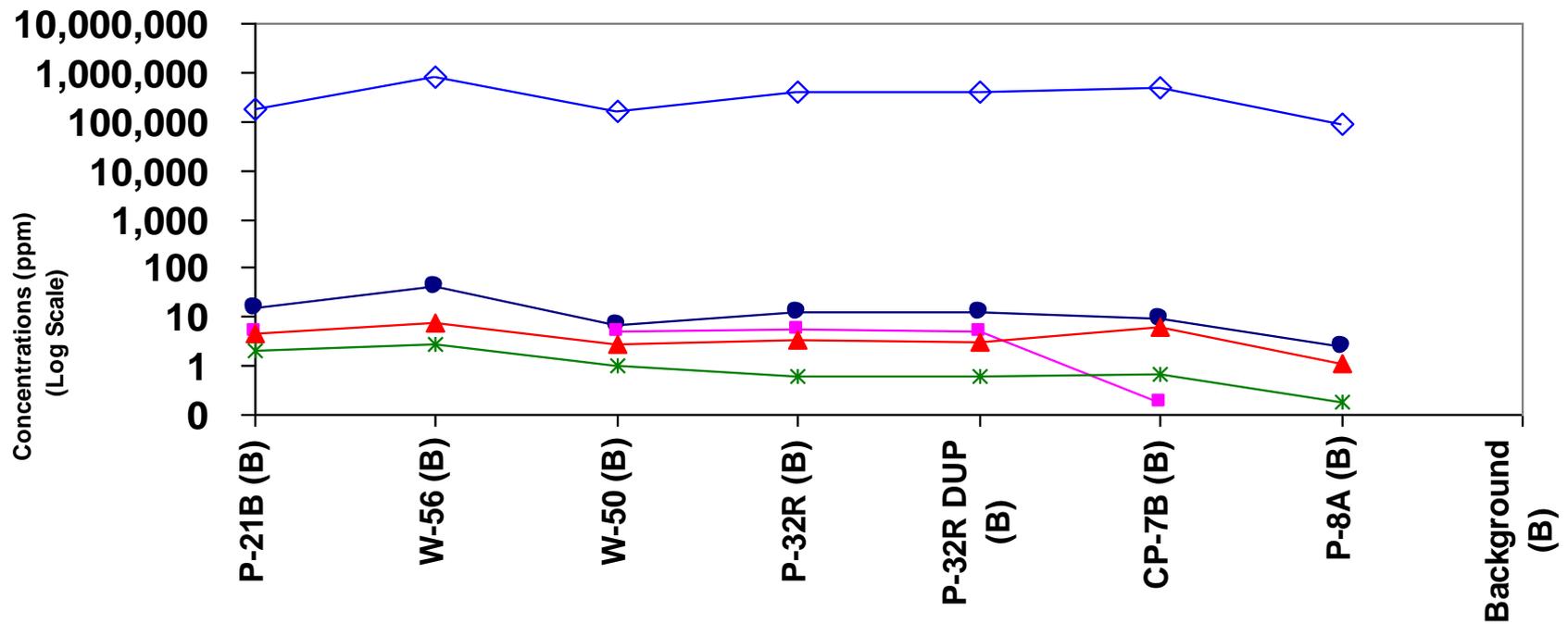
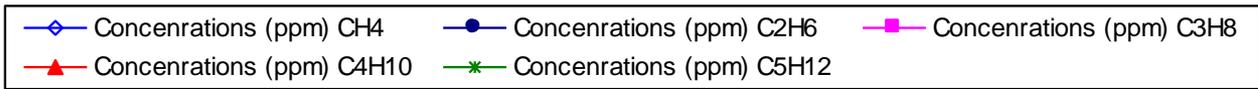
Hydrogen Sulfide in Samples

Newport Terrace Landfill



Hydrocarbons/Alkanes (C2-C5) & Methane

Newport Terrace Landfill

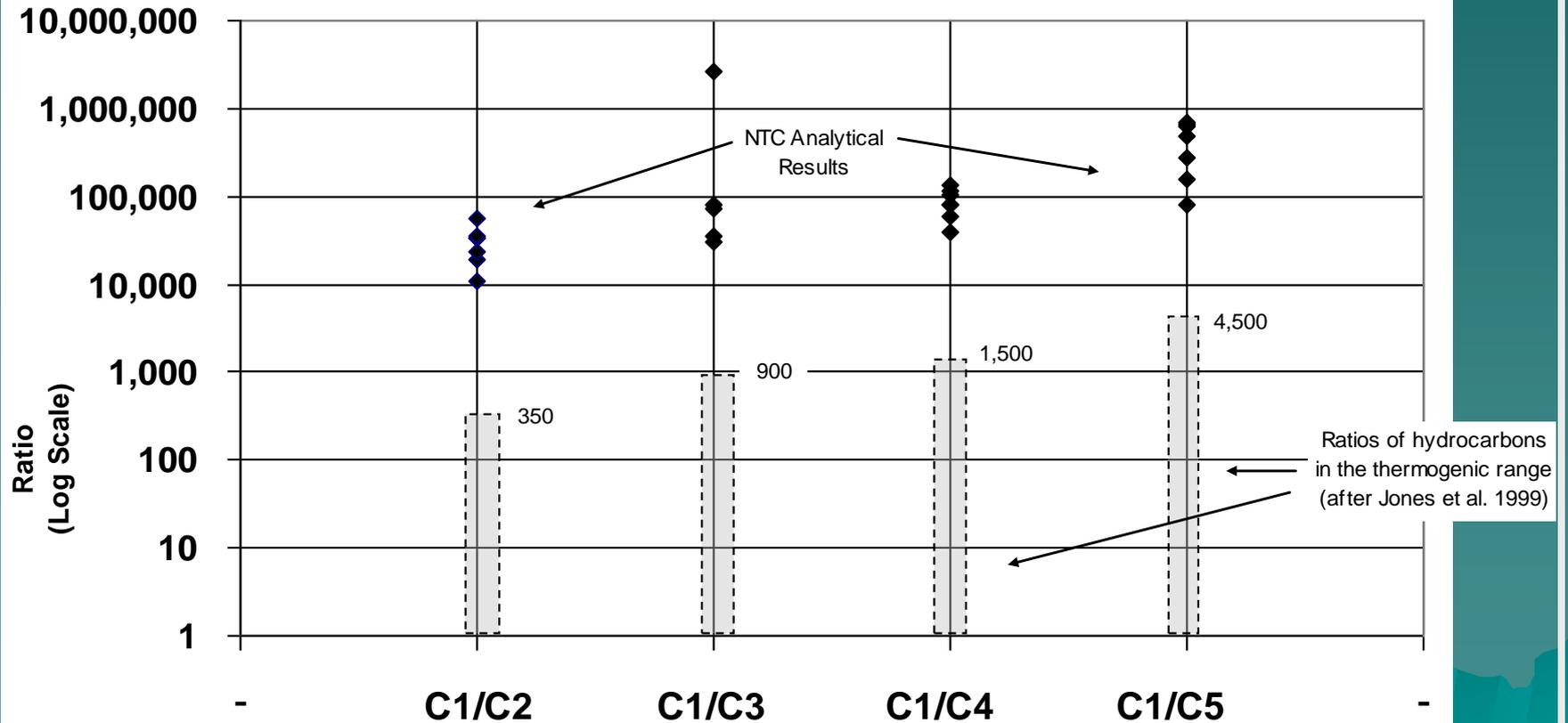


Results and Interpretation (contd.)

- Hydrocarbon ratios (C_1/C_2-C_5) were outside the thermogenic range
- ($^{13}C/^{12}C$) values were consistent and within range of biogenic gas
- (^{14}C) content was consistent and very close to the biogenic gas range

Hydrocarbon Ratios (C1/C2-C5)

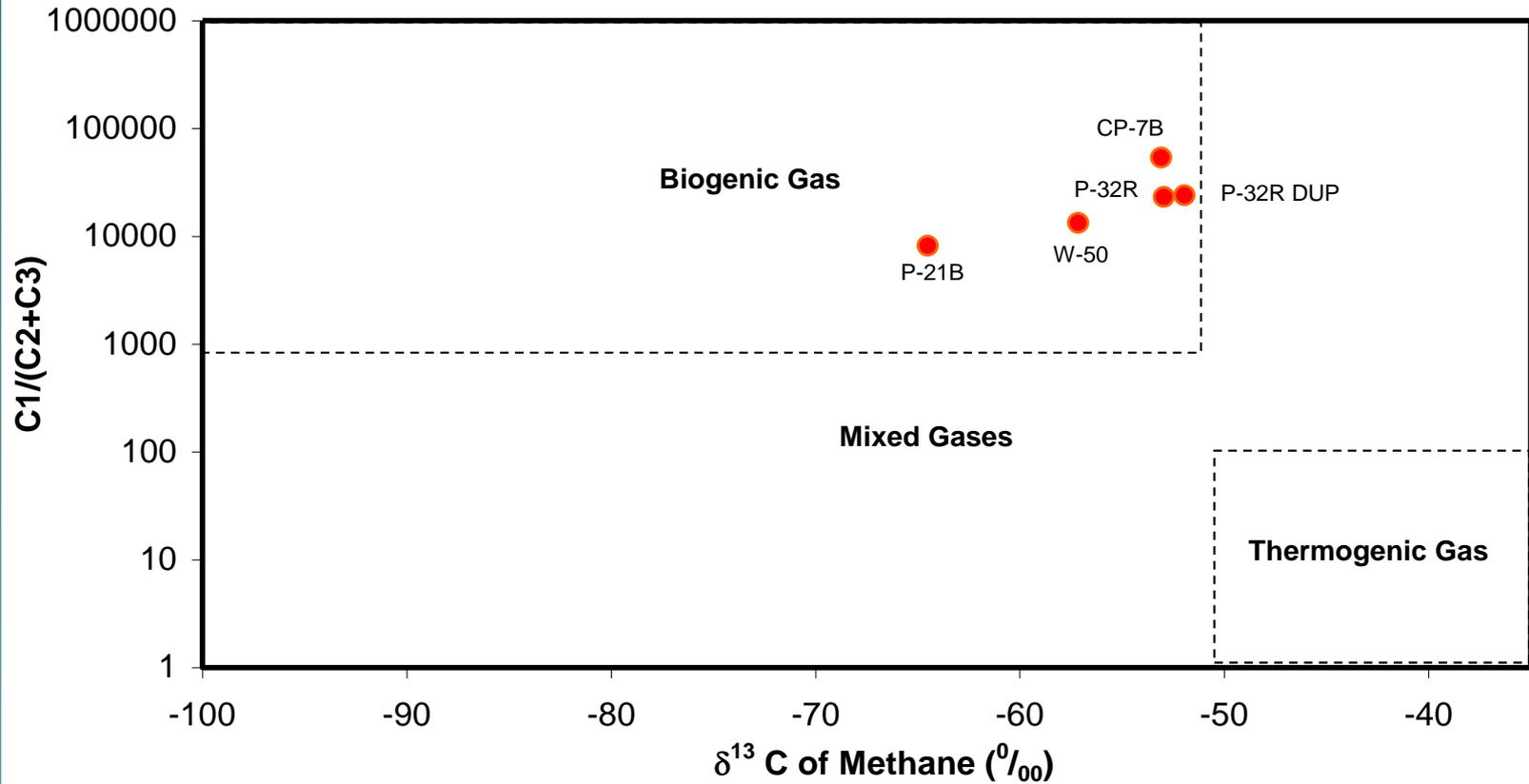
Newport Terrace Landfill



Isotope Fingerprint (Methane)

Plot of $\delta^{13}\text{C}$ of CH_4 vs $\text{C1}/(\text{C2}+\text{C3})$

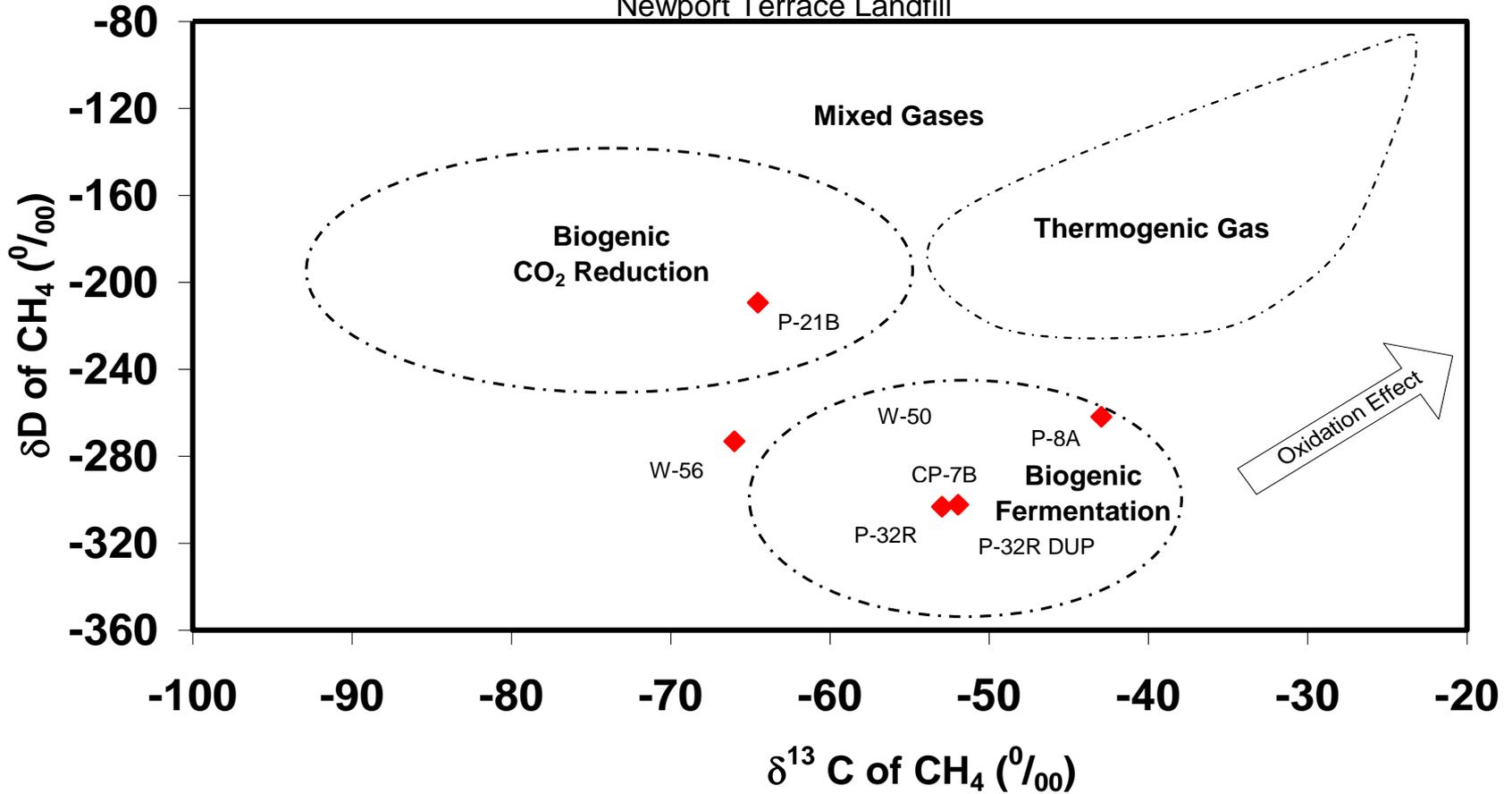
Newport Terrace Landfill



Isotope Fingerprint (Methane)

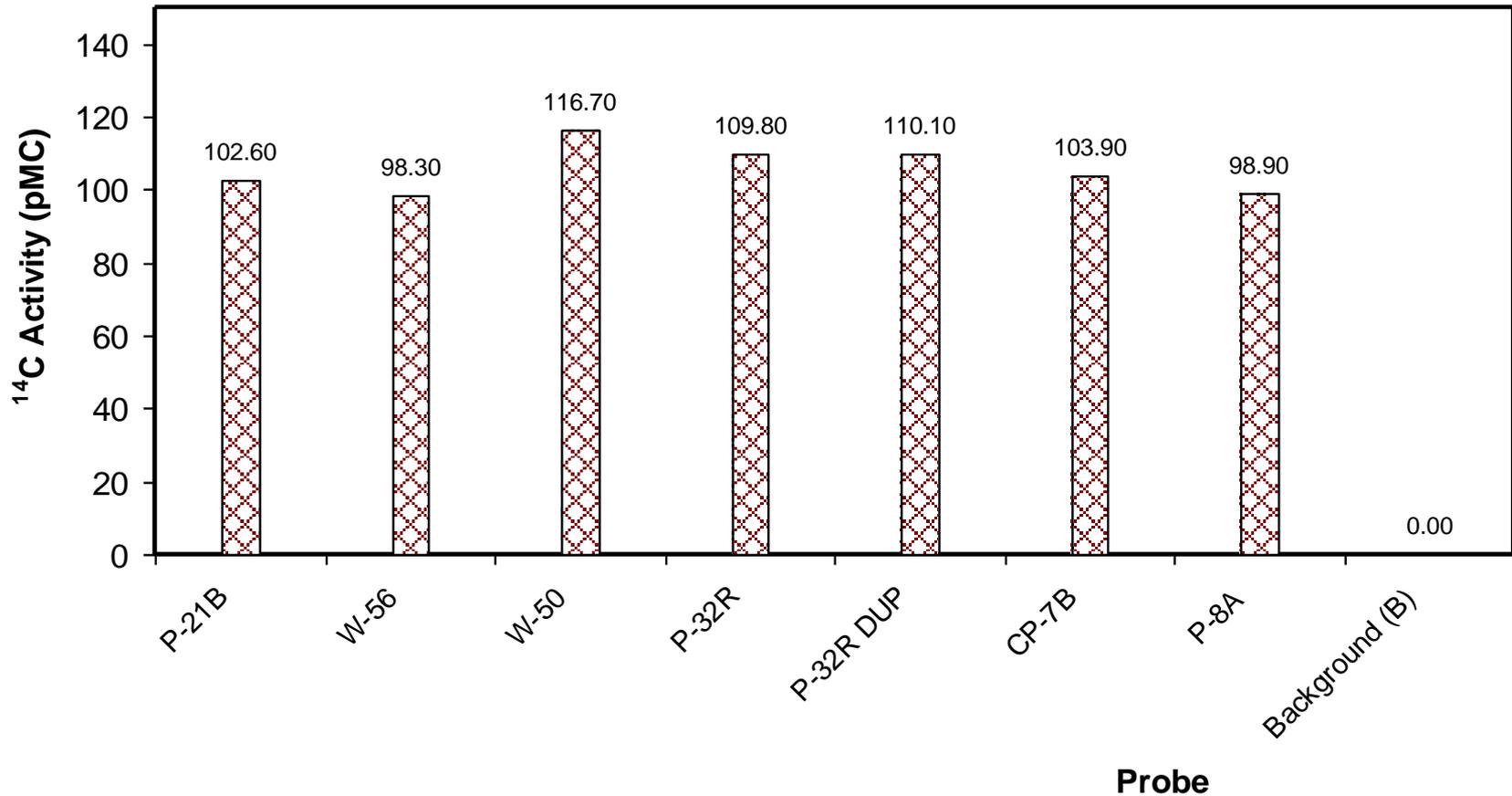
Plot of $\delta^{13}\text{C}$ of CH_4 vs δD of CH_4

Newport Terrace Landfill



^{14}C Content of the Methane (pMC)

Newport Terrace Landfill





VIII
Conclusions

Conclusions

- CH₄ detected in the Rubble Fill area is of a biogenic source.
- Since Rubble Fill gas samples had similar levels of C₁ – C₅ to that of Refuse Fill (reference samples), CH₄ detected in Rubble Fill is more likely to be from biodegradation of buried waste.

Conclusions (contd.)

- High levels of H_2S in some Rubble Fill samples are possibly due to:
 1. Reduction of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in discarded dry wall (C&D waste)
 2. Drill cuttings from oil well explorations disposed of in Rubble Fill area
 3. Others (sewage sludge, local soil type, etc.)

Case Studies in Orange County

Case II

(Cannery Street Landfill)

Huntington Beach, CA

V

Case Background

&

Description

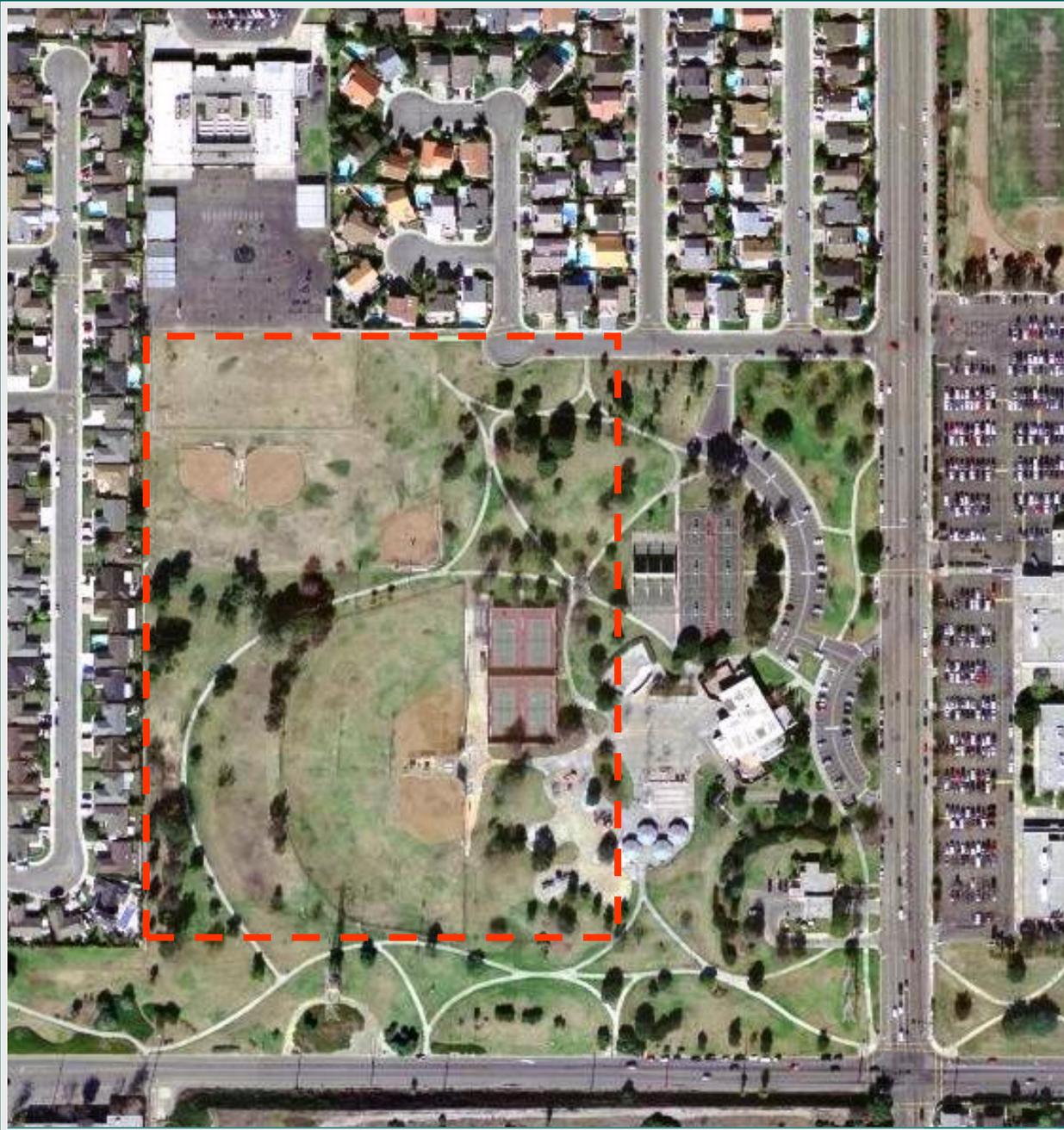
Background

- Located in City of Huntington Beach (approx. 1 mile from the ocean)
- Originally owned by SCE
- 1957 purchased by the County of Orange
- 1957–1969 County-operated disposal site

Background (contd.)

- Total 27.7 acres (20.5 acres waste-fill)
- Accepted mainly inert waste (C&D, logs, stumps, timber, etc.)
- 1970 County deeded Site to City for use as a public park
- 1971 City deeded NW 5 acres to School District for elementary school playground

Site Layout



Background (contd.)

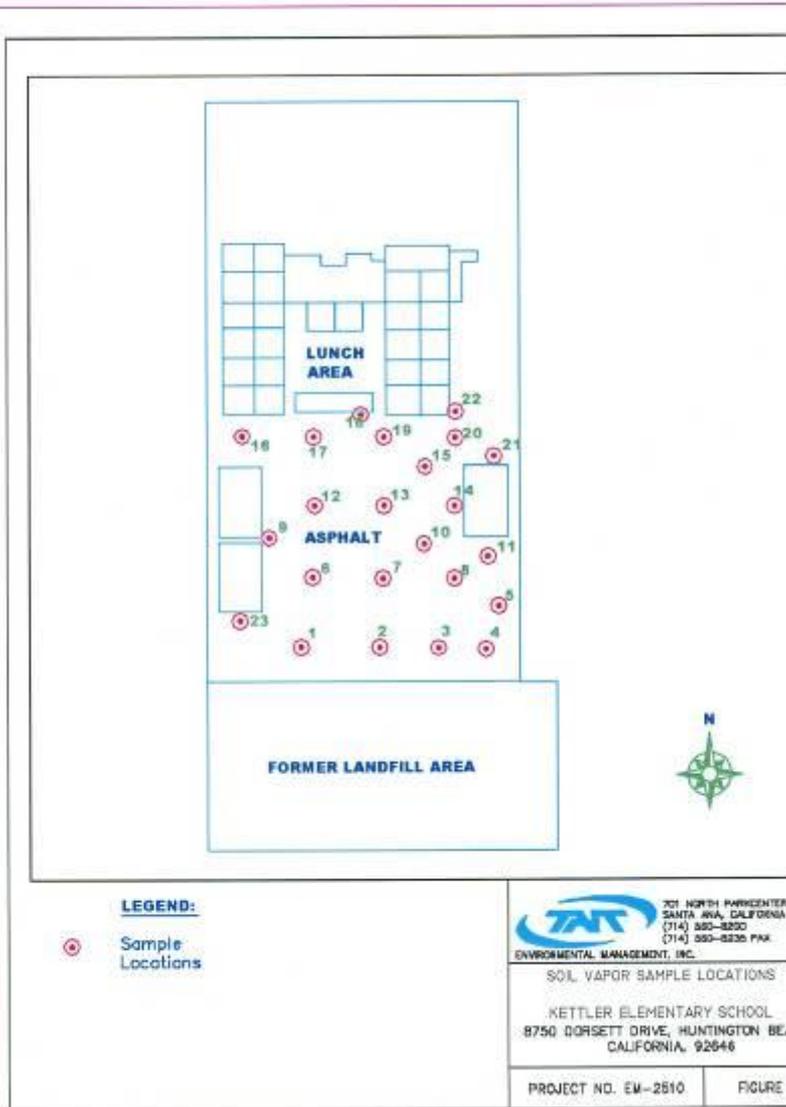
- 1996-2000 Several Site Assessments confirmed $\text{CH}_4 > 5\%$ along northern and western boundaries
- 2000 The LEA issued N&O to the City and School District
- 2001 City installed 5 vertical passive vents (ineffective)

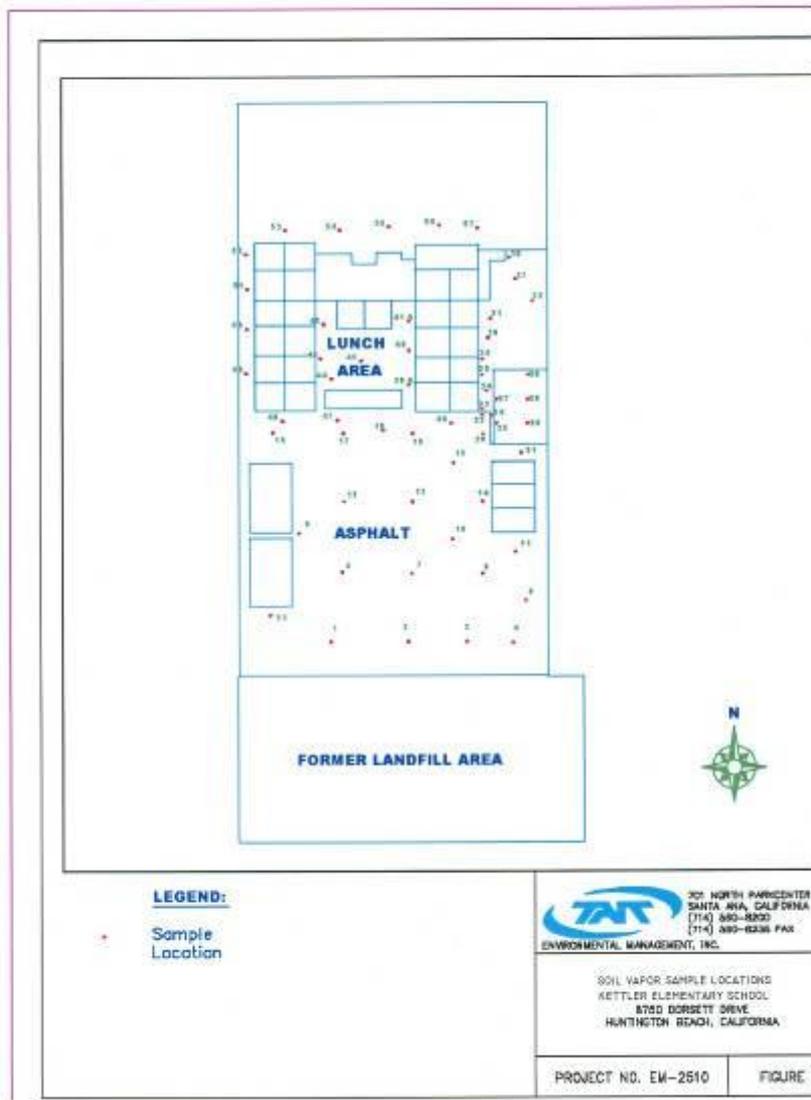


Background (contd.)

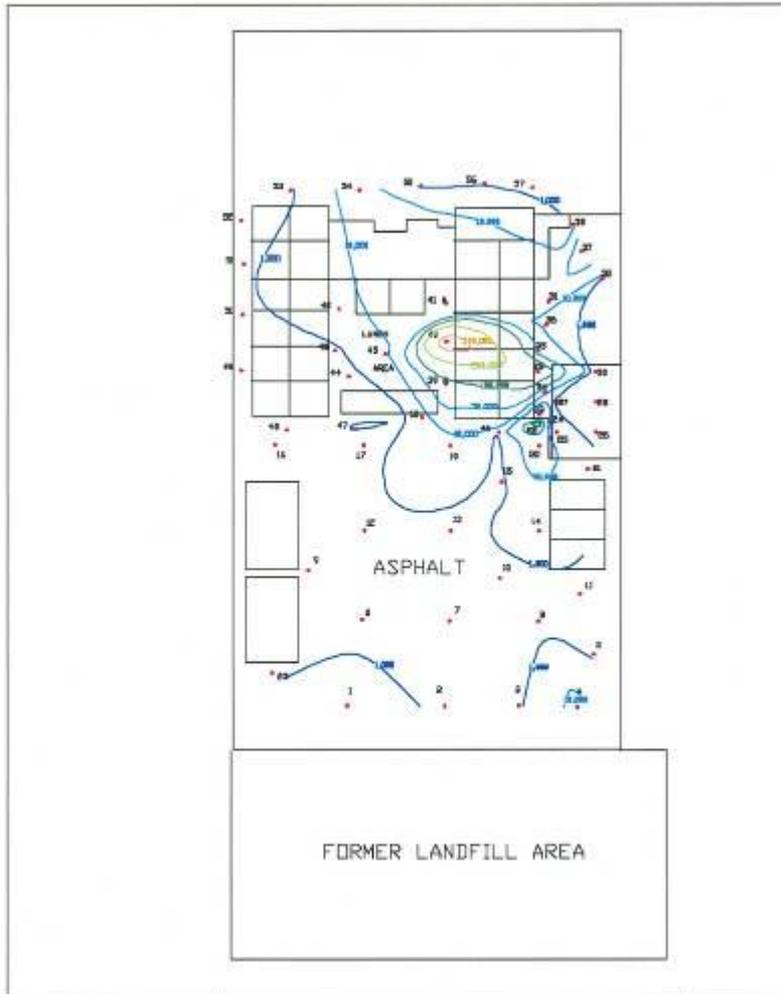
- 2002 LEA issued a new N&O (Compliance Order)
- 2003 Soil gas survey by School District (w/o LEA's knowledge) in asphalted playgrounds showed $\text{CH}_4 = 13\%$ adjacent to School's east wing
- 2004 Additional soil gas surveys confirmed elevated levels of CH_4

Soil Gas Survey Exhibit 1





Soil Gas Survey Exhibit 2



CLIENT:	HUNTINGTON BEACH SCHOOL DISTRICT	DATE:	
PROJECT/SITE:	KETTLER ELEMENTARY SCHOOL 8758 BORDITT DR. HUNTINGTON BEACH, CA	PROJECT No.:	C
TITLE:	METHANE CONCENTRATION CONTOURS IN	P/S No.:	3

Soil Gas Survey Exhibit 3

Background (contd.)

- School District's consultant explained that high CH₄ levels detected:
 1. Around the east wing *"probably are related to gas migration from a source area at the east wing"*
 2. Along the south end of the asphalted playgrounds *"probably are related to gas migration from former Cannery Street Landfill area"*

Background (contd.)

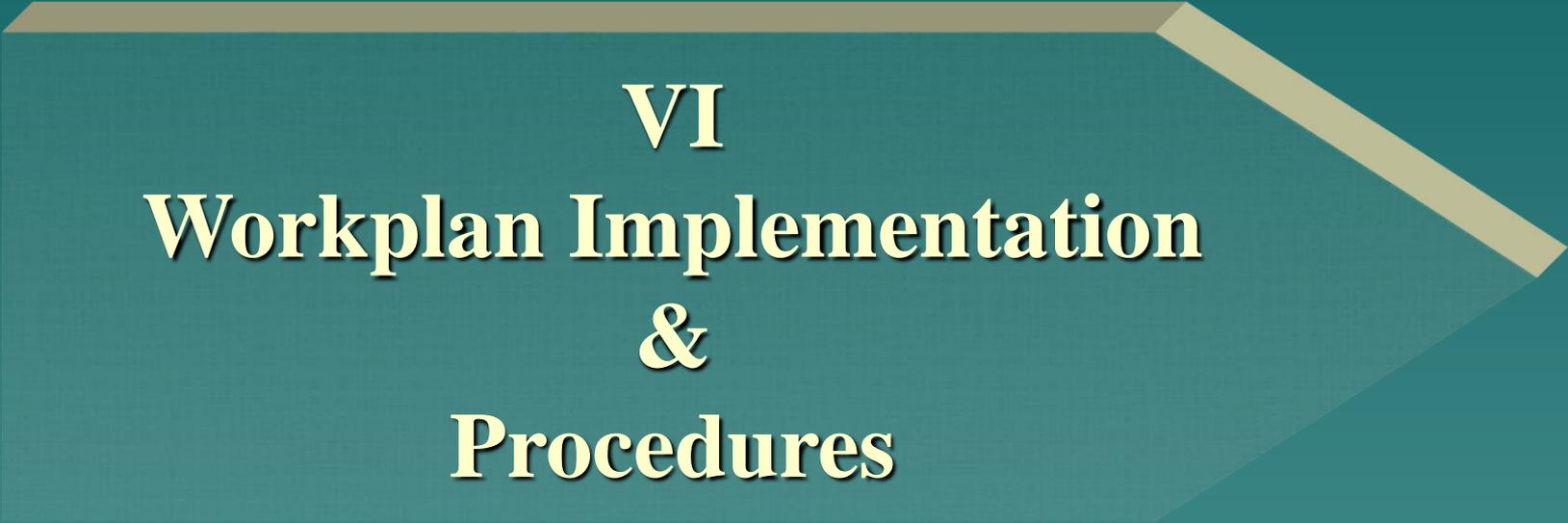
- School District tried to keep field results a secret, but.....
- The genie was out of the bottle



Background (contd.)

- After field results were leaked out, the School District:
 1. Promptly installed CH₄ sensor/alarm in every class room
 2. Maintained that the disposal site was the source of all CH₄ detected throughout the elementary school

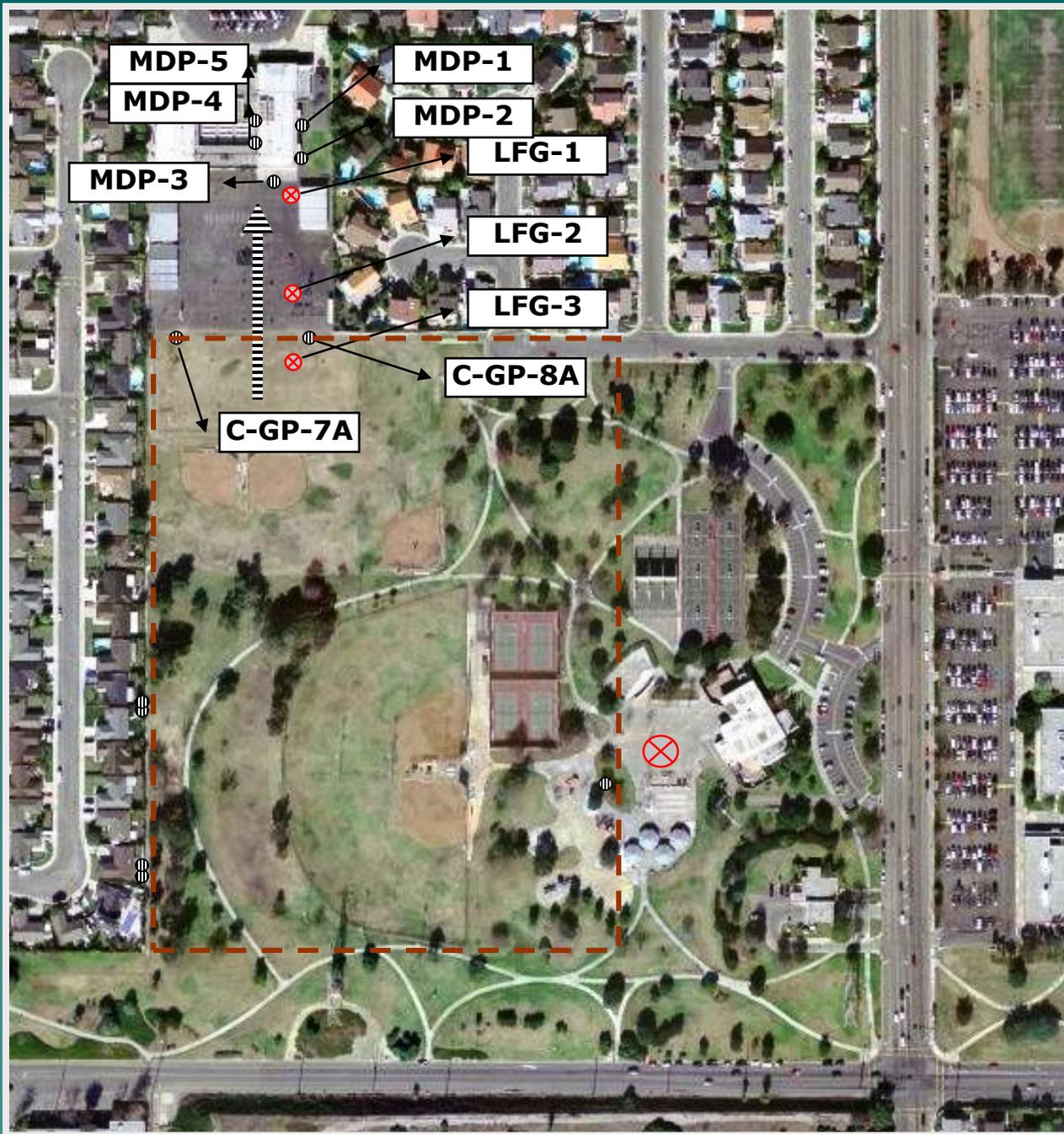
- The LEA wanted to confirm that migrating LFG plume has reached the school's east wing



VI
Workplan Implementation
&
Procedures

Investigation Workplan

- To determine if the disposal site is (or isn't) the source of CH₄ detected at all locations of the school facility
- Installation of 3 dual completion probes along the potential migration pathway (1 in refuse and 2 in asphalt)
- Sampling probe locations:
 - 5 exist. near east wing (MDP series)
 - 3 newly-installed (LFG series)
 - 2 exist. along N side of Cannery St. (C-GP series)



Investigation Workplan

- Screen sampling locations for CO₂, O₂, N₂, CH₄ and H₂S
- If CH₄ > 1% collect samples for lab analysis
- Background and duplicate samples (QA/QC)

Investigation Workplan (contd.)

- Lab analysis:
 - CO₂, O₂ and Balance (mostly N₂)
 - Hydrocarbons C₁ – C₅
 - Pipeline gas tracers
 - VOCs (including BTEX)
 - (¹³C/¹²C)
 - ¹⁴C
 - H₂S

Workplan Implementation

- June 2005
- 3 Proposed probes (LFG-1, -2 and -3) were installed
- Sample locations were 1st purged and screened for CH₄, fixed gases, H₂S
- Field measurements logging

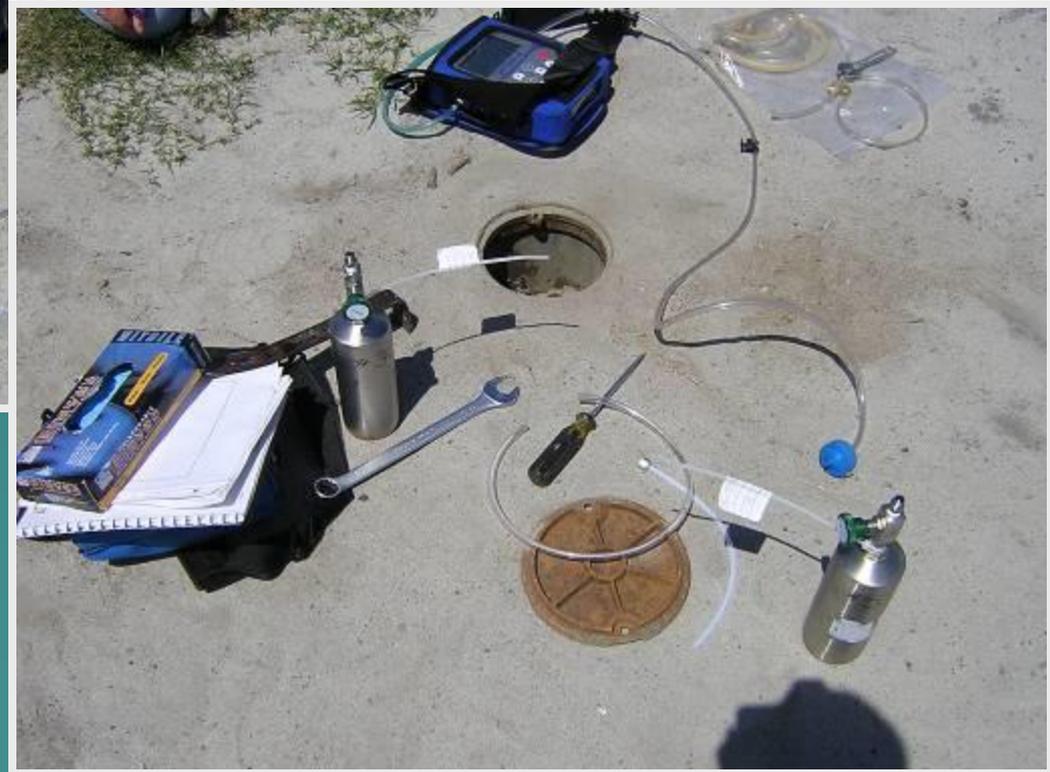
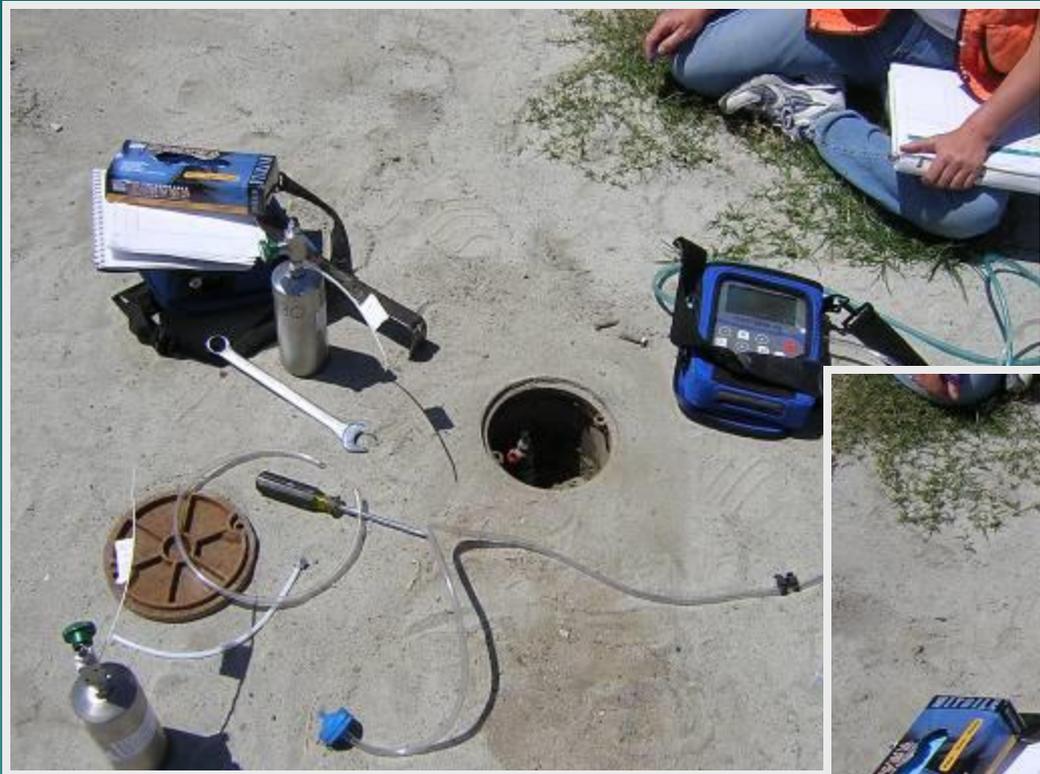
Workplan Implementation (contd.)

- Collected samples if $\text{CH}_4 > 0.1\%$
- Added hydrogen isotope ratio ($^2\text{H}/^1\text{H}$) of CH_4 to the lab analysis
- Collected samples from probes:
 - 3 exist. near east wing (MDP-2, -3, & -4)
 - 3 newly-installed (LFG-1, -2 & -3)
 - 1 exist. probe along N side of Cannery St. Landfill (C-GP-7)

Workplan Implementation (contd.)

- Samples for H₂S and pipeline gas tracers lab analysis were collected last
- Lab samples labeling, logging in COCs, packing and shipping
- 3 Different analytical labs

Field Sampling





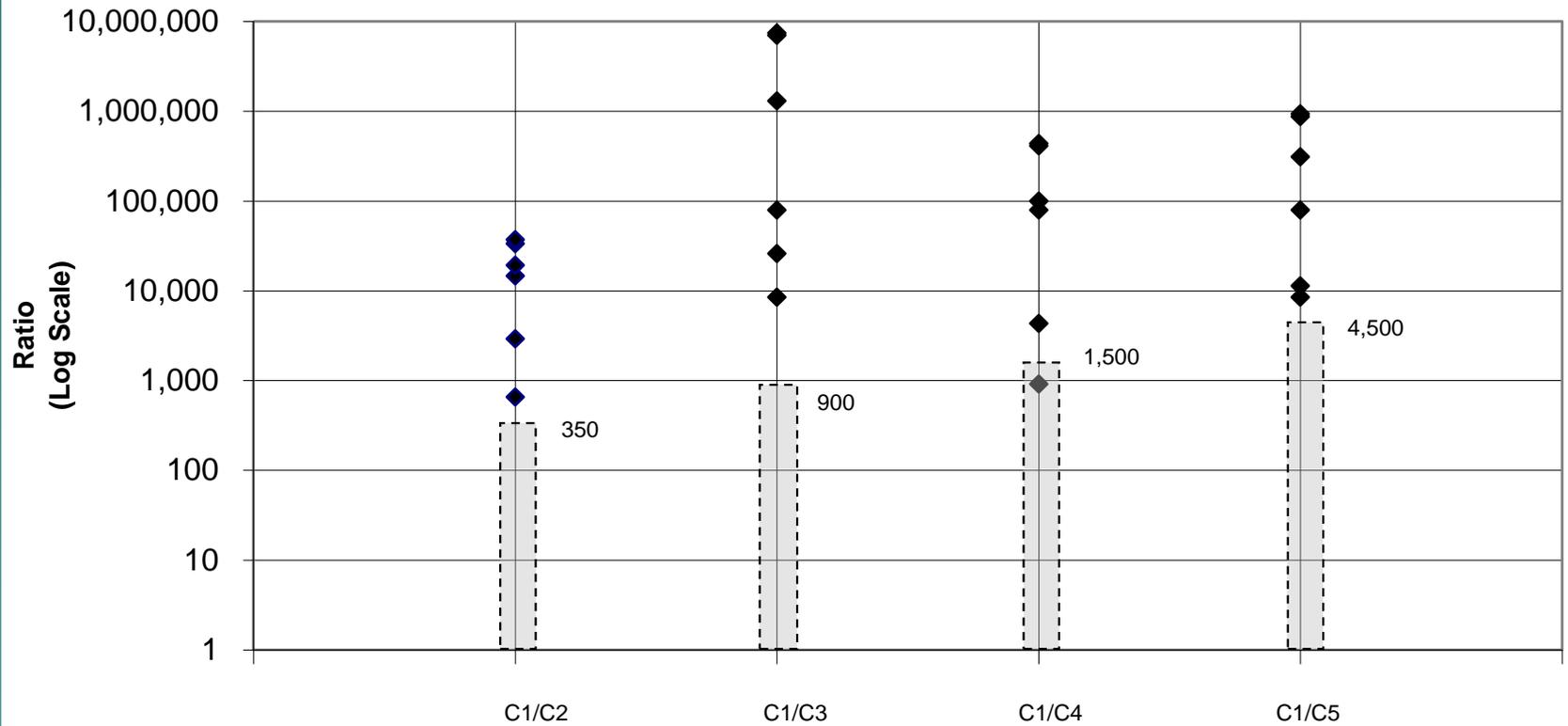
VII
Results and Interpretation

Results and Interpretation

- Since no tracers were detected in any collected sample, leaking gas pipeline was ruled out as a source
- Except for LFG-1, ($^{13}\text{C}/^{12}\text{C}$) for CH_4 fell within range of biogenic gases
- Except for MDP-4, (^{14}C) content was consistent and very close to biogenic gas range

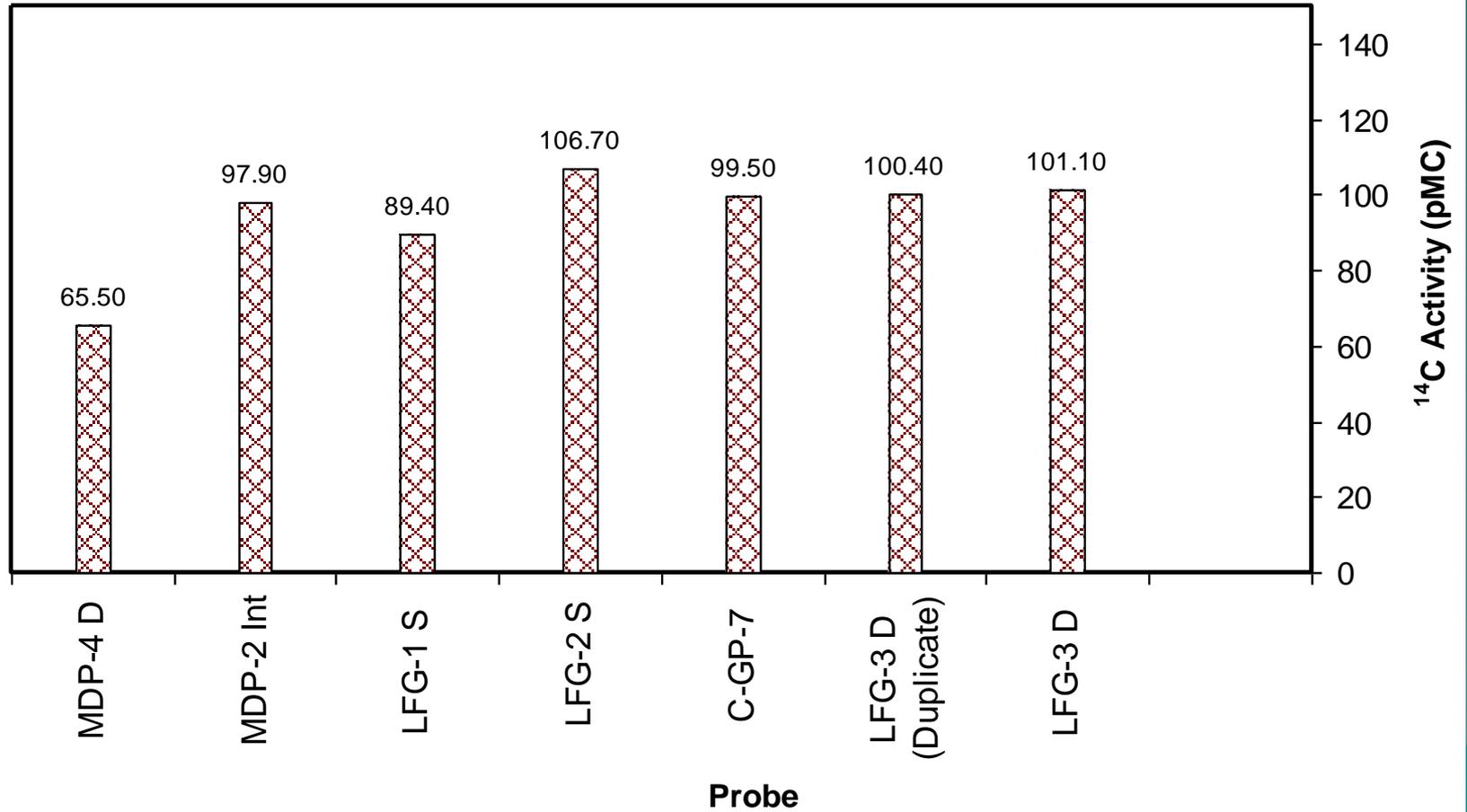
Hydrocarbon Ratios (C1/C2-C5)

Kettler Elementary School & Cannery St. Landfill



¹⁴C Content of the Methane (pMC)

Kettler Elementary School & Cannery St. Landfill



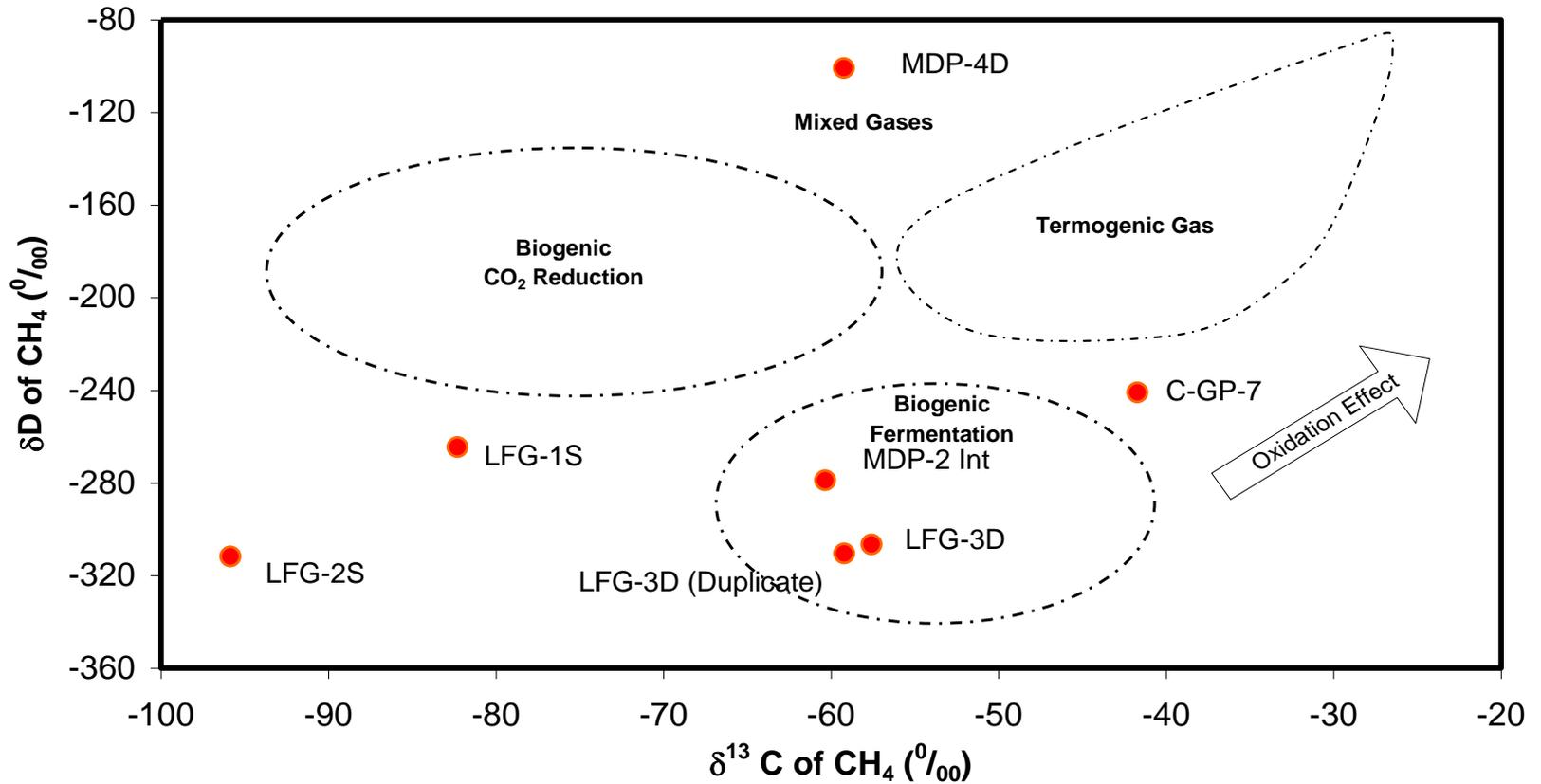
Results and Interpretation (contd.)

- C-GP-7, LFG-2 and LFG-3 had (^{14}C) and ($^2\text{H}/^1\text{H}$) values within the ranges of LFG
- MDP-4 had (^{14}C) and ($^2\text{H}/^1\text{H}$) values that clearly suggest commingling of both landfill gas and thermogenic (older gas source)

Formation of Detected Methane

Plot of $\delta^{13}\text{C}$ of CH_4 vs δD of CH_4 (‰)

Kettler Elementary School & Cannery St. Landfill





VIII

Conclusions

Conclusions

- LFG plume has migrated off-site under the school's asphalted playgrounds.
- Cannery St. Landfill is one source of CH₄ detected around the school's east wing, there is-are other older source (s) for CH₄ detected



Questions?