



The Los Angeles City Oil Field, circa 1900





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Background: Field survey point based GIS interpolation of particulate matter pollution in Beijing, Image provided by Dr. Tao Tang, see related article on page 1. Top and Bottom Insets: The Los Angeles City Oil Field, circa 1900. Permission to use the image granted by Seaver Center for Western History Research, Los Angeles County Museum of Natural History (www.nhm.org), see related article on page 45. Middle Inset: Savannah plain (c.1881): the birthplace of chaotic megacity (Kinshasa). Image is property of the Rayal Museum for Central Africa (HP.1957.80.38-1, collection RMCA Tervuren). Permission to use the image has been granted by the Contemporary History Department of the Rayal Museum for Central Africa, see related article on page 1.

ERRATUM

Environmental Geosciences, v.16, n.4 (December 2009), "Characterization of the Helderberg Group as a geologic seal for CO₂ sequestration," by J. Eric Lewis, Ronald R. McDowell, Katharine Lee Avary, and Kristin M. Carter, p. 201, Acknowledgements should read: Project supported by U.S. Department of Energy cooperative agreement DE-FC26-05NT42589, under

Project supported by U.S. Department of Energy cooperative agreement DE-FC26-05NT42589, under supervision of the Midwest Regional Carbon Sequestration Project (MRCSP). Thanks to Richard Smosna for granting permission to modify one of his published figures for use in the paper. The authors wish to thank the reviewers Timothy R. Carr, Janet S. Roemmel and Erik Venteris for their constructive suggestions that helped improve the quality of the paper. Geochemical characterization, source, and fate of methane and hydrogen sulfide at the Belmont Learning Center, Los Angeles

Isaac R. Kaplan and John E. Sepich

ABSTRACT

This article examines environmental concerns at the site of a Los Angeles, California, high school known as Belmont Learning Center (BLC) during its construction. A part of the site on which the school was to be built is a largely depleted oil field in the center of Los Angeles, close to a heavily populated area. Located nearby are another high school and an elementary school, each constructed more than 70 yr ago atop the same oil field. Prior to and during construction at the BLC site, which began in 1990, methane (CH₄) and hydrogen sulfide (H₂S) were detected in deep soil borings and monitoring wells. After the building construction began, a stratigraphic offset was also detected and interpreted as a fault line, which could be traced beneath one of the nearly completed buildings. This resulted in a decision to demolish that building and an adjacent one and to temporarily suspend all construction activity. Additional analytical measurements showed that the highest concentrations of both CH₄ (>5% atmospheric concentration) and H₂S (>100 ppmv) occurred only in the deeper samples, and that only traces of these environmentally hazardous gases were present at or near the soil surface. In this article, we use carbon, hydrogen, and sulfur stable isotope data, as well as ¹⁴C measurements to describe the sources and natural processes of CH₄ and H₂S removal.

The interpretations offered in this article will hopefully be useful in assisting environmental professionals and government officials who evaluate hazardous soil gas concentrations to make decisions during the process of issuing or denying construction permits.

INTRODUCTION

In 1988, to address extreme overcrowding and a rapidly growing population in central Los Angeles, the Los Angeles Unified School District

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(LAUSD) decided on an ambitious program to build a new downtown high school facility capable of accommodating 5300 students. The original estimate for building this facility was \$45 million. In the early 1990s, 35 ac of land in two parcels was purchased, and planning for the building began. By 1997, the cost had escalated to \$175 million. The purchased land is on top of the Los Angeles City Oil Field (LACOF, Figure 1), a mostly depleted field, which at the turn of the 20th century had over 1000 oil rigs on it. Some, but not all, the oil wells on the Belmont Learning Center (BLC) site (Figure 2) were abandoned under the oversight of the California Department of Oil, Gas, and Geothermal Resources (DOGGR). One production well, Suplin 1, renamed LAUSD 1A (Figure 2), which is situated in the northern part of Area 1 near soil vapor probe ESV-55 (Figure 3), was abandoned in October, 1997. It was replaced with a new well named LAUSD 1B (Figure 2), installed to the east of monitoring well EMW-15 (Figure 3), for the purpose of monitoring the pressure in the LACOF (Schlumberger, 2000a). Some production wells still operate commercially near the purchased property. The DOGGR maps (DOGGR, 2009a) show that the school site had 15 oil wells on it at one time, with other production wells adjacent to the property lines, such as LAUSD 1, 2, 3, and 4 (formerly Toluca 1, 2, 3, and 4) (Figure 2). The wells are generally at atmospheric pressure, and the area has produced very little gas in the past 70 yr. Hydrocarbon well abandonments in California are conducted to DOGGR standards since 1975, but prior to that time, many production wells in California may have been inadequately plugged and abandoned.

Directly west of the northern BLC property is the location of the Belmont High School (BHS) built in 1923 and a short distance west of BHS is the Union Elementary School (UES) built in 1923 (Figure 1). Whereas the BLC and BHS properties are only partially situated on the LACOF. UES sits entirely on the LACOF (Figure 1). The BHS property is known to have had three oil wells on the site and one immediately off the southeast border (DOGGR, 2009a) for which DOGGR has no records of abandonment. The UES property had 17 wells on the site and one immediately offsite on the northwest corner. The DOGGR records show that two of the wells onsite were abandoned in 1941, and the one offsite was abandoned in 2003. The DOGGR has no records of abandonment for the remainder of the UES wells. When the DOGGR has no abandonment records, the wells may have been abandoned prior to

1915, when records began to be kept, or they may not have been abandoned at all (DOGGR, 2009b).

Environmental studies performed in the early and mid 1990s showed the BLC property to have mild contamination from lubricating oil, automobile fuels, some heavy metals, and acetone (which was pervasive). The cleanup of these substances was considered to be in the scope of the budget. However, the testing also disclosed that methane (CH_4) was present in soil, but the concentration became a matter of dispute among the companies performing the analyses. To expedite the program, the LAUSD decided in 1997 to proceed with the construction of buildings. During land excavation and grading, CH₄ was detected in several locations, as was hydrogen sulfide (H₂S). Construction was stopped while additional investigation was conducted that confirmed the presence of high concentrations of CH₄ (>5%) exceeding the lower explosion concentration of CH_4 in air. This resulted in a work stoppage for several months. Following further design implementation to prevent migration of these gases into buildings, construction resumed in 2000.

In 2002, during excavation of the land nearby, in one of the nearly completed school buildings, a stratigraphic offset in the largely Miocene sandstone was identified and interpreted by seismologists (Sieh and Gonzalez, 2003) as a blind north–south–trending thrust fault that could be traced beneath one of the school buildings. Construction was immediately terminated, and the LAUSD decided to demolish the two buildings closest to the fault line, although no evidence was observed that the fault had displayed any recent motion (Sieh and Gonzalez, 2003). Several seismologists in Southern California opined that buildings are constructed over minor faults throughout the Los Angeles Basin (McFarling, 2002).

The decision to demolish the buildings, combined with concern over toxic and potentially explosive gases, caused significant turmoil among citizens (Endres, 2001; Barrett, 2005), contractors, and city officials (Anderson, 2000), which included legal suits among consultants, contractors, and even the law firm representing the LAUSD for failure of contractual commitments, embezzlement, and conflict of interest, as well as an investigation by the Los Angeles District Attorney's Office (Cooley, 2003).

In October 2001, the California Legislature enacted Assembly Bill (AB) 1301 requiring the LAUSD to prepare a Remedial Investigation/Feasibility Study (RI/FS) and appointed the State of California Department of Toxic Substances Control (DTSC) to oversee the construction project as the lead environmental agency.



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Figure 1. Map of central Los Angeles showing the locations of the Los Angeles City Oil Field, Belmont Learning Center, Union Elementary School, and old Belmont High School. DOGGR = California Department of Oil, Gas, and Geothermal Resources.



Figure 2. Map of the BLC site, showing oil production wells that were located on the site. The Los Angeles Unified School District (LAUSD) 1A (formerly Suplin 1 well) and the new pressure monitoring well, LAUSD 1B, which replaced it, are also shown, as well as LAUSD 1, 2, 3, and 4 (formerly Toluca 1, 2, 3, and 4) wells adjacent to the westernmost part of the site.

The RI/FS on the entire site was completed in November 2003 based on analytical results for hazardous chemicals and gases from 670 soil samples and 80 groundwater samples. The DTSC approved the FS and released it to the public in April 2004. The FS document described several options to reduce risks from the presence of CH₄ and H₂S below ground surface (Meredith and Associates, 2004). The draft Remedial Action Plan (RAP) included (1) a passive venting system with air sweep under paved areas more than 5000 continuous square feet; (2) gas vents and barrier membranes using thick flexible plastic liners placed underneath building slabs; (3) gas barrier dams in trenches around electrical, gas, water, and sewer lines; (4) conduit seals at terminations of dry utility electrical and cable lines; (5) gas dispersion layers of sand used below site softscape soil and vegetation; and (6) gas electronic monitoring inside school buildings and elsewhere (Geosyntec Consultants, 2008).

Proposals to the RAP were solicited, and upon approval in January 2005, fieldwork and environmental testing were performed, after which a completion report was submitted to DTSC in March 2005, and construction began again in early 2006.

Eighteen years after the initial environmental investigations, the project was finally completed and opened for the school term beginning September 2008 at a cost of \$400 million. The original name for the school project was Belmont Learning Center; however, after the initiation of construction in 2005, its name was changed to Vista Hermosa (PCR Services Corp., 2004), and finally in the last year of construction, it was renamed Edward R. Roybal Learning Center in honor of the congressman who championed the concept and construction efforts (Blume, 2008).

Given the wide range of opinions regarding the safety of the site, we have compiled the various analytical data about the chemical and isotopic composition of CH_4 and H_2S from reports submitted to the DTSC by LAUSD contractors in an attempt to determine the origin of these hazardous gases and to discuss how serious a problem, if any, they actually posed to the safety of the buildings, the students, and the teaching and maintenance staffs.

Description of the Belmont Learning Center Campus Property

The BLC property, composed of two parcels, is shaped like a reclining L that has the long vertical arm lying in a

northwest-southeast direction and the short arm lying approximately northeast-southwest (Figure 2). This article continues to use names that, during the life of the project, designated various parcels and areas of the site (Figure 3). Parcel 1 is 11 ac in area, extends northward from Colton Street to Temple Street, and it is bounded on the east side by Beaudry Avenue and on the west side by Boylston Street. Parcel 2 (also termed the Southern Parcel) is approximately 24 a in area and is bounded to the west by Toluca Street, to the south by 1st Street, to the north by Colton Avenue, and to east by Beaudry Avenue. The northern area of Parcel 1, where most of the athletic fields are situated, is referred to as Area 1; the school campus in the south of both parcels is referred to as Area 2, and the northwest park area is Area 3.

Brief Geologic Description

Area 1 (Figure 3) of the site straddles the southerly limits of the old east–west–trending LACOF, which is 4.8 km (3 mi) long and 0.4 km (0.2 mi) wide (Figure 1). Area 1 is located along the south side of a narrow zone of folding and faulting, south of the Elysian Park Anticline (Soper, 1943), within the upper Miocene Puente Formation. Three primary oil production zones are recognized in fine sand zones. These are the following.

- First zone: average depth of 900 ft below ground surface (bgs) (274 m bgs) and average thickness of 125 ft (38 m)
- Second zone: average depth of 1100 ft bgs (335 m bgs) and average thickness of 30 ft (9 m)
- Third zone: average depth of 1500 ft bgs (457 m bgs) and average thickness of 30 ft (9 m)

The four offsite Toluca wells in the northwest of Area 3 (abandoned to DOGGR standards after completion of sampling by Environmental Strategies Corp. [ESC] in 2003 and renamed LAUSD 1, 2, 3, and 4) have been recognized as terminating in the second zone at an estimated depth of 1024 ft (312 m). The stratigraphy beneath the site is composed of interlayered Tertiary and Miocene siltstones, clays, fine-grained sandstones, and shales (reported by Schlumberger, 2000b; see also Diblee, 1991).

The following is a summary of 14 producing oil wells (in addition to Suplin 1), which are on the BLC site (District 1 Map 116, insert map D, DOGGR, 2009a),





identifying known and unknown abandonment dates (DOGGR, 2009b).

- Tierra Oil Co. 1: no abandonment records found in DOGGR files
- Tierra Oil Co. 2: no abandonment records found in DOGGR files
- M. Frazier 1: no abandonment records found in DOGGR files
- Young & Johnson 1: no abandonment records found in DOGGR files
- Dividend Oil Co. 1: surface plugging 11-20-97
- Dividend Oil Co. 2: surface plugging 3-6-98
- Dividend Oil Co. 3 no abandonment records found in DOGGR files
- Combine Oil Co. 1: no abandonment records found in DOGGR files
- Combine Oil Co. 2 no abandonment records found in DOGGR files
- Los Angeles Unified School District 1B (Schlumberger monitoring well)
- L.A.R.R. Co. 1: no abandonment records found in DOGGR files
- L.A.R.R. Co. 2: no abandonment records found in DOGGR files
- L.A.R.R. Co. 3: no abandonment records found in DOGGR files
- Kenneth and Katherine Manley Beaudry Plaza Co. 1: surface plugging 4-30-97

Summary of Environmental Testing

Field Qualitative Testing

The first recorded environmental studies on the two parcels at the site, which began in 1988, were geophysical and chemical testing of the soils. The first geochemical testing, specifically for CH₄ and H₂S, was undertaken in October 1990 by Geoscience Analytical Inc. (GAI, 1990). Phase II site investigation and other soil testing were continued by several consultants until 2003. During this period, 670 soil matrix samples, 530 soil vapor samples, and 80 groundwater samples were tested (Meredith and Associates, 2004).

The results showed the presence of low levels of California Assessment Manual (CAM) elements, i.e., arsenic and lead, low concentrations of benzene, and polynuclear aromatic hydrocarbons (PAH) compounds, all at approximately regional background levels, but higher concentrations of the nontoxic acetone ($\sim 100 \text{ ppmv}$).

- In Area 1, 14 soil borings, 17 soil vapor probes, and 10 monitoring wells were installed (Figures 3, 4).
- In Area 2, 30 soil borings, 42 soil vapor probes, and 15 monitoring wells were installed (Figure 3).
- In Area 3, 20 soil borings, 25 soil vapor probes, and 4 monitoring wells were installed (Figure 3).

During the 1999 soil boring and vapor probe installation, ESC detected a strong petroleum odor on 21 occasions, a moderate odor on 32 occasions, and a slight odor on 18 occasions (ESC, 1999). Petroleum (crude oil) was detected visually as a sheen, droplets, or soil coating in 6 borings, 11 vapor probes, and 5 monitoring wells. The odor of H_2S was detected (from slight to strong) in 12 borings, 26 soil vapor probes, and 11 monitoring wells.

Field Quantitative Testing

Field instrumental measurements by ESC (Meredith and Associates, 2004) display a different distribution of H_2S than is apparent from the odor tests. Only two soil vapor probe locations (ESV-45 and ESV-51), both in the north-northeast of Area 1 (Figure 3), contained significantly high concentrations (>1000 ppmv) of H_2S (Table 1). Of the remaining 82 soil vapor probe samples, only eight samples contained a detectable H_2S concentration distribution ranging from 0.05 to 20 ppmv.

Tables 1 and 2 display CH_4 and H_2S concentration data for sampling points in Areas 1 and 2, respectively, that contained greater than 1000 ppmv CH_4 and/or greater than 50 ppmv H_2S . Many of the measurements for any particular well were taken at different depths and at different time intervals between April 1999 and August 2003. Only 17 soil vapor probes out of 68 contained greater than 1000 ppmv CH_4 and only 3 probes contained greater than 50 ppmv H_2S . Although some high concentrations of CH_4 were detected in Area 2, most of the very high concentrations of CH_4 occur in the northern part of Area 1. High concentrations of H_2S only occur in the northwestern part of Area 1, i.e., at ESV-47 and ESV-55, within the boundaries of the LACOF (Figures 1, 2, 4).

Most of the vapor borings in Area 2 occurred in the southeast of that area, in the proximity of the school buildings (Table 2). The highest CH_4 concentration detected was in soil vapor boring ESV-13 (Figure 3),



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Figure 4. Map showing the sampling locations of soil borings and monitoring wells in Area 1 of the BLC site placed by GAI (1990). Highlighted numbers in black represent monitoring wells. Numbers in circles represent soil borings having CH₄ concentrations greater than 10,000 ppmv. Numbers in bold squares represent near-surface soil probes referenced in the report. Select producing well locations are also shown.

Probe	Date	Depth (ft hos)	CH ₄	H ₂ S
11000		(11 0 65)	(ppint)	
V-39	Aprii–May 1999	5	920	ND
		12	4300	
	h.h. 20, 1000	20	15,000	
	July 20, 1999	5		
	Contombor 1 1000	12	56	
	September 1, 1999	5	160	
		12	140	
	Cantanih an 2002	20	14,000	
	September 2002	5	ND	ND
		12	ND	ND
		20	ND	ND
V-40	April–May 1999	8	2.1 J	ND
		20.5	250	ND
		27	410,000	ND
	July 20, 1999	8	810	ND
		20.5	240,000	ND
		27	460,000	ND
	September 1, 1999	8	98,000	ND
		20.5	500,000	ND
		27	530,000	ND
	September 2002	8	45,100 Q	ND
		20.5	526,000 Q	ND
		27	421,000 Q	ND
V-42	April–May 1999	5	130	ND
		14	120,000	ND
		48.5	770,000	ND
		48.5 (dup)	490,000	ND
	July 20, 1999	5	2200	ND
		14	120,000	ND
	September 1, 1999	5	100	ND
		14	100,000	ND
		14 (dup)	110,000	ND
	September 2002	5	320 Q	ND
		14	24,300 Q	ND
		48.5	NS(o)	ND
SV-43	April–May 1999	5	560,000	ND
		63	660,000	ND
	July 20, 1999	5	210,000	ND
	September 2002	5	5210 Q	ND
		36	NS(w)	ND
		63	NS(o)	ND(o)
SV-44	April–May 1999	5	70	ND
		18	1100	ND
	July 20, 1999	5	27	ND
		18	1800	ND
	September 1, 1999	5	85	ND
	,			

Table 1. Belmont Learning Center: Area 1 Soil Vapor Sampling
Results: Methane and Hydrogen Sulfide*

Table 1. Continued

		Depth	CH ₄	H ₂ S
Probe	Date	(ft bgs)	(ppmv)	(ppmv)
		18	2100	ND
	September 2002	5	ND	ND
		18	-	ND
ESV-45	April–May 1999	5	58	ND
		16	100,000	ND
		28	400,000	3300
	July 20, 1999	5	52	ND
		16	92,000	ND
		28	390,000	1500
		28 (dup)	390,000	8600
	August 30, 1999	5	2.2 J, MRE	1.4
		16	19,000	0.13
		28	390,000	2700
		28 (dup)	400,000	2800
	September 2002	5	110 Q	ND
		16	14,700 Q	8 Q
		28	162,000 Q	6300 Q
	August 23, 2003	5	ND	ND
	August 21, 2003	16	190,000	47
		28	600,000	2600
ESV-47	April–May 1999	5	810,000	ND
		53	650,000	ND
	July 20, 1999	5	76	ND
		53	210,000	ND
	August 31, 1999	5	1300	ND
	September 2002	5	4220 Q	ND
		40	NS(o)	ND(o)
		53	NS(o)	ND(o)
ESV-48	April–May 1999	5	1600	ND
		39	330,000	ND
		39 (dup)	360,000	ND
	July 20, 1999	5	140	ND
		39	600,000	ND
	September 1, 1999	5	150	ND
		39	710,000	0.19
	September 2002	5	ND	ND
		24	ND(W)	NS(W)
501/ 10		39	ND(0)	NS(0)
ESV-49	April–May 1999	5	70	ND
		40.5	/80,000	ND
		40.5 (dup)	780,000	ND
	July 20, 1999	5	120	ND
	A	40.5	/40,000	ND
	August 31, 1999	5	49	ND
		40.5	820,000	0.13
		40.5 (dup)	/00,000	20

Table 1. Continued

		Depth	CH ₄	H ₂ S
Probe	Date	(ft bgs)	(ppmv)	(ppmv)
	September 2002	5	ND	ND
		17	NS(w)	NS(w)
		40.5	NS(o)	NS(o)
ESV-50	April–May 1999	5.5	51	ND
		18.5	36,000	ND
		40	280,000	ND
	July 21, 1999	5.5	110	ND
		18.5	36,000	ND
		40	160,000	ND
	August 31, 1999	5.5	4	ND
		18.5	46,000	ND
	September 2002	5.5	64.5 Q	ND
		18.5	91 Q	ND
		40	NS(o)	NS(o)
ESV-51	April–May 1999	5	90	ND
		17.5	260	ND
		33.5	130,000	3000
	July 21, 1999	5	6.4	ND
		17.5	35	ND
		17.5 (dup)	51	ND
		33.5	130,000	13,000
	August 30, 1999	5	3.7 MBE	0.44
		17.5	20 MBE	0.18
		33.5	120,000	33,000
		33.5 (dup)	120,000	18,000
	September 2002	5	602 Q	ND
		17.5	134 Q	ND
		33.5	87,500 Q	7700 Q
	August 21, 2003	5	ND	ND
		17.5	ND	12
		17.5 (dup)	ND	12
	Annii 1000	55.5	160,000	9000
ESV-54	April–May 1999	5	1.1	6.3
		10 71 F	6600 12,000	
	huhu 20, 1000	51.5	12,000	
	July 20, 1999	2 10	0.2	
		10 16 (dup)	12,000 00	
		16 (uup)	02	
	August 70, 1000	5	13,000 17 MDE	
	August 50, 1999	16	3800	0.00
		715	13 000	0.05 J
	Sentember 2002	5	13,000 mc	
	September 2002	16	12 800 U	
		315	62 100 Q	8 0
ESV-55	April-May 1999	5.5	37 000	ND
LJV-JJ	April May 1999	5.5	51,000	

 Table 1. Continued

Probe	Date	Depth (ft bgs)	CH ₄ (ppmv)	H ₂ S (ppmv)
		40	900,000	ND
		40 (dup)	740,000	ND
	July 20, 1999	5.5	410	ND
	August 31, 1999	5.5	7.3	ND
		15.5	110	ND
	September 2002	5	ND	ND
		15.5	ND	ND

*G = elevated reporting limit due to matrix interference; J = estimated value; JA = analyte was positively identified, but quantization is an estimate; MBE = analyte was present in the associated method bank; Q = data qualified due to sampling and/or analytical problems; NA = not analyzed; ND = not detected; NS = not sampled; NS(o) = not sampled, oil; NS(w) = not sampled, water; bgs = below ground surface; dup = duplicate.

during April–May 1999, when 56,000 ppmv was measured at 17 ft bgs (5.1 m bgs). With the possible exception of ESV-08, where an uncertain value of 132 ppmv H_2S was determined, all other samples in this area contained very small concentrations of H_2S .

In most of the soil vapor probe samples, the concentration of CH_4 was found to decrease between the time of initial sampling in spring 1999 and resampling in autumn 2003. However, this was not the case in vapor probes ESV-40, -45, -51, and -54. ESC had installed very few soil vapor probes or borings in western Area 3, and none of the gas analyzed from these probes contained CH_4 concentrations greater than 1000 ppmv or H_2S concentrations greater than 10 ppmv.

However, Sepich (1998), acting as a subcontractor through his company, Methane Specialists, to the BLC School primary building contractor, Kajima International, detected both CH_4 and H_2S in the southwestern part of Area 3, south of the Toluca wells. Twelve soil vapor probes, extending from 5 to 42 ft bgs (1.5 to 12.8 m bgs), detected CH_4 concentrations as high as 30,000 ppmv and H_2S concentrations as high as 190 ppmv.

In groundwater at the site, traces of dissolved sulfide (<1.0 mg/L) were detected in 7 of 25 monitoring wells sampled by ESC in September 2002. Only five monitoring wells contained greater than 10 mg/L: EMW-10 at 14 mg/L, EMW-5 at 39.4 mg/L, EMW-4 at 40 mg/L, EMW-1 at 144 mg/L, and EMW-17 at 162 mg/L. With the exception of EMW-17, which is in Area 1, all the other identified monitoring wells are in Area 2.

Prohe	Date	Depth (ft hos)	CH ₄	H ₂ S (ppmv)
		(11 Dg3)	(ppint)	
E2A-01	Aprii–May 1999	б 20	6500	
	luby 10, 1000	20	150,000	
	August 31 1000	6	10	
	September 2002	6	ND	ND
	September 2002	20	263,000,0	7.0
		35	NS(w)	NS(w)
	August 23 2003	6	ND	ND
	14645(25) 2005	20	35.000	ND
		35	NS(w)	NS(w)
ESV-08	April–May 1999	4.5	160	ND
	July 19, 1999	4.5	180	ND
	August 31, 1999	4.5	5100	ND
	September 2002	4.5	2600 O	ND
		26	2370 Q	132 Q
		47	NS(w)	NS(w)
	August 23, 2003	4.5	ND	ND
	3 . ,	26	NS(w)	ND
		47	NS(w)	ND
ESV-09	April–May 1999	5	20,000	ND
	1 /	26	3300	ND
	July 19, 1999	5	21	ND
		26	81,000	ND
	August 30, 1999	5	62	ND
	-	26	18,000	0.028 J
	September 2002	5	53 Q	ND
		26	11,000 Q	1.0 Q
		37	NS(w)	NS(w)
	August 22, 2003	5	ND	ND
		26	38,000	0.74
		37	NS(w)	NS(w)
ESV-10	April–May 1999	4.5	510	ND
		18	1400	ND
	July 19, 1999	4.5	62	ND
		18	1100	ND
	August 30, 1999	4.5	170	ND
		18	1100	ND
		37	32	ND
	September 2002	4.5	95 Q	ND
		18	62 Q	ND
		37	144 Q	12 Q
ESV-11	April–May 1999	5.5	8.6	ND
		20.5	1100	ND
	July 22, 1999	5.5	2.2 J	ND
		20.5	4.9 J	ND
	September 2, 1999	5.5	3.9	ND

Table 2. Belmont Learning Center: Area 2 Soil Vapor Sampling

 Results: Methane and Hydrogen Sulfide*

Table 2. Continued

Probe	Date	Depth (ft bgs)	CH ₄ (ppmv)	H ₂ S (ppmv)
		20.5	3.3 J	ND
	September 2002	5.5	ND	ND
		20.5	ND	ND
		40	NS(w)	NS(w)
ESV-13	April–May 1999	5	3100	ND
		17	56,000	ND
	July 22, 1999	5	16	ND
		17	39,000	ND
		17 (dup)	28,000	ND
	September 2, 1999	5	11	ND
		17	40,000	ND
	September 2002	5	ND	ND
		17	9620 Q	ND
		44	ND	ND
	August 22, 2003	5	ND	ND
		17	25,000	8.2
		44	NS(w)	NS(w)
ESV-15	April–May 1999	4.5	21,000	ND
		11.5	27,000	0.14 J
	July 20, 1999	4.5	720	ND
		11.5	5400	4.9
		11.5 (dup)	5400	4.9
	August 30, 1999	4.5	58	0.05
		11.5	11,000	28
		11.5 (dup)	11,000	ND
	September 2002	4.5	ND	ND
		11.5	23,000 Q	9 Q
		16.5	NS(w)	NS(w)
	August 22, 2003	4.5	ND	ND
		11.5	ND	ND
		16.5	NS(w)	NS(w)

*G = elevated reporting limit due to matrix interference; J = estimated value; JA = analyte was positively identified, but quantitation is an estimate; MBE = analyte was present in the associated method bank; Q = data qualified due to sampling and/or analytical problems; NA = not analyzed; ND = not detected; NS = not sampled; NS(o) = not sampled, oil; NS(w) = not sampled, water; bgs = below ground surface; dup = duplicate.

Because the aqueous solubility of CH_4 is low in comparison to H_2S , the highest concentration of CH_4 measured was 72 mg/L in EMW-10, and the next highest was 4.2 mg/L in EMW-17. With the exception of EMW-6, which contained 2.2 mg/L dissolved H_2S , all remaining wells contained either less than 1.0 mg/L CH_4 or no detectable value.

Monitoring Wells			Soil Borings			
Sample**	CH ₄ (ppmv)	C ₁ /CO ₂	Sample**	CH ₄ (ppmv)	C ₁ /CO ₂	
3a	181,820	0.33	6	30,533	1.00	
5a	4834	0.05	7	4702	0.55	
7a	2518	0.11	10	15,901	0.20	
7b	179	<0.01	14	121	0.01	
9a	137,710	2.70	15	209	< 0.01	
9b	236,319	4.15	17	1664	0.08	
11a	40	0.01	23	23,799	1.26	
11b	62	<0.01	24	5318	0.43	
13a	28	<0.01	25	63,795	3.07	
13b	319	0.05	28	18,429	1.02	
14a	2079	0.03	30	239	< 0.01	
15a	100	<0.01	38	342	0.02	
15b	238	<0.01	39	10,935	0.72	
Suplin 1, gas	562,917	8.41	40	2159	0.32	
			42	945	0.04	
			43	763	0.05	
			44	7525	0.63	
			53	1188	0.04	
			56	722	0.04	
			57	28,932	1.89	
			58	4730	0.31	
(a) Shallow (10 ft); (b) deep (20 ft)			60	323	0.02	

Table 3. Belmont Learning Center: Soil Gas Data Monitoring Wells and Soil Borings*

*GAI (1990).

**Samples 1, 2, 4, 6, 8, 10, and 12 had no methane.

GEOCHEMISTRY OF NEAR-SURFACE HAZARDOUS GASES IN AREA 1

One of the first comprehensive geochemical studies of the distribution of near-surface hazardous gases was conducted jointly in 1990 by GAI, and A.B. Environmental Services Inc. (ABE) on the initial 11 ac (Parcel 1) soon after its purchase by the LAUSD (GAI, 1990). At that time, Area 1 was divided into three packages of land, with approximately 50% of the land vacant and the rest occupied by residential and some commercial properties, such as an automobile dismantling operation as well as one production oil well, Suplin 1, now renamed LAUSD 1A (Figure 4).

To perform their studies, GAI and ABE analyzed gas from Suplin 1 and developed on Parcel 1 a series of the following.

• 15 monitoring wells (MWs), to a depth of about 30 ft bgs (9.1 m bgs); samples were collected from

9 to 18 ft bgs (2.7 to 5.5 m bgs) and from 18 to 28 ft bgs (5 to 8 m bgs)

- 45 soil borings (SBs) at 28 ft bgs (8 m bgs)
- 57 borehole type soil probes (SPs), near surface (3 to 4 ft bgs [1 to 1.2 m bgs])

The gases analyzed for were (1) C_1 – C_4 hydrocarbons; (2) C_5 – C_7 hydrocarbons; (3) H_2S ; and (4) CO_2 , N_2 , and O_2 (Tables 3, 4). The objective of the monitoring grid was to determine if the gases identified originated from leakage in improperly plugged oil wells at the site or from soil in the immediate vicinity of the wells.

Suplin 1 (LAUSD 1A) Former Production Well

A gas sampled from this well contained 26.7% N_2 , 6.75% O_2 , and 6.7% CO_2 . Suplin 1 contained 562,917 ppmv CH_4 , 4825 ppmv ethane, 290 ppmv C_3 – C_4 , and

Well	N ₂ (%)	02 (%)	N ₂ /O ₂
3a	73.70	1.25	58.96
5a	82.08	2.06	39.84
7a	75.73	16.91	4.48
7b	76.80	11.29	6.80
9a	80.87	1.21	66.83
9b	65.68	1.05	62.55
11a	74.78	19.07	3.92
11b	78.27	11.85	6.61
13a	76.19	20.11	3.79
13b	76.70	15.62	4.91
14a	86.55	3.40	25.46
15a	79.49	14.13	5.63
15b	79.22	14.36	5.52
Suplin 1	2.68	0.67	4.00

Table 4. Belmont Learning Center: N₂/O₂ Ratios from

 Monitoring Wells*

*GAI (1990).

245 ppmv C_5 - C_7 hydrocarbons. When corrected for air and CO_2 , the CH_4 content would be about 96.5%, defining it as a dry gas.

GAI Monitoring Wells

If widespread leakage from production wells was occurring at the site or in adjacent locations, hydrocarbon enrichment in the groundwater and overlying soil should be expected. However, as shown in Table 3, only two monitoring wells contained CH₄ at concentrations of greater than 5%(1% = 10,000 ppmv; 0.1% =1000 ppmv): MW-3 (18.18% at 10 ft bgs [3 m bgs]) and MW-9 ($CH_4 = 13.35\%$ at 10 ft bgs [3 m bgs] and 23.61% at 20 ft bgs [6 m bgs]). In all three samples, ethane was the dominant wet gas, containing less than 300 ppmv with only traces of C_3 – C_7 hydrocarbons. Only three other wells contained CH₄ at levels of 0.1 to 0.5% (wells 5a, 7a, and 14a). The CH_4 concentration measured at the remaining monitoring wells was less than 0.1%. There appears to be no leakage from the Suplin 1 abandoned production well to the adjacent MW-4 and MW-7 wells, or from the Tierra 2 abandoned production well to adjacent MW-5, at the corner of Temple and Boylston Streets (Figures 2, 4).

No measurable amounts of H_2S greater than 100 ppmv were analytically detected in any of the MW samples, but trace odors were detected in cuttings from MW-2 and MW-3.

GAI Soil Borings

Of the 45 Area 1 soil borings analyzed, one sample displayed a CH₄ concentration greater than 5% (sample 25, CH₄ = 6.38%), six had concentrations between 1 and 5%, and all others had concentrations less than 0.5% (Table 3). The highest ethane concentration was 56.8 ppmv in sample 25, six samples contained from 10 to 50 ppmv, and all other samples contained 10 ppmv or less (ethane data not included on Table 3). No measurable H₂S was detected in any of these soil borings. The location of the individual soil boring samples is shown in Figure 4.

GAI Soil Probes

The highest Area 1 CH₄ concentration (327 ppmv) was detected in one soil probe, sample 45. Another soil probe, sample 31, contained 85 ppmv CH₄ and sample 41 contained 22 ppmv, whereas the remaining 48 soil probes had CH₄ concentrations of less than 10 ppmv. The locations of sample 45 just north of Colton Street and soil probe sample 31 adjacent to the abandoned oil well Tierra 2A are shown in Figure 4.

GAI Stable Carbon Isotope Analyses of Subsurface CH₄ and CO₂ The stable isotopes carbon 13 (¹³C) and deuterium (D) were analyzed for variations in their concentrations (δ). These variations are reported as a ratio to an international standard for each element, as δ^{13} C and δ D, in parts per thousand (‰). The δ^{13} C isotope ratios of CH₄ and CO₂ from Suplin 1 oil well; MW-3, MW-5,

Table 5. Belmont Learning Center: Carbon Isotope Ratios of CH₄ and CO₂ from Monitoring Wells and Soil Borings*

Well	Depth (ft)	δ ¹³ C (‰) (CH ₄)	δ ¹³ C (‰) (CO ₂)
MW-3	10	-42.3	-25.6
MW-5	10	-44.2	-26.5
MW-9	10	-42.1	-25.1
MW-9	20	-45.1	-23.3
SB-6	20	-37.6	-28.2
SB-10	20	-33.9	-29.1
SB-23	20	-36.2	-25.8
SB-25	20	-36.4	-27.2
SB-28	20	-35.1	-28.0
SB-39	20	-38.3	-27.9
SB-44	20	-35.7	-29.8
SB-57	20	-38.9	-29.1
Suplin 1	Тор	-40.7	-3.2

*GAI (1990).

Table 6. Belmont Learning Center: Soil Gas Concentrations and Ratios

Sample ID, ESV-	*GGC ID 4898-	0 ₂ + Ar (%)	N ₂ (%)	CH ₄ (%)	N ₂ /O ₂ **	CO ₂ (%)	C ₁ /CO ₂
51 at 5 ft [†]	-1	18.2	81.0	<0.01	4.71	1.7	_
51 at 17 ft	-2	3.6	88.6	<0.01	34.08	8.9	-
51 at 33 ft	-3	1.8	70.9	11.9	88.63	16.0	0.74
45 at 5 ft	-4	5.0	82.2	1.2	20.55	11.8	0.10
45 at 16 ft	-5	1.8	71.8	12.0	89.75	16.3	0.73
45 at 28 ft	-6	1.8	47.8	39.7	59.75	13.1	3.03
15 at 4.5 ft	-7	3.2	92.2	0.1	41.09	6.3	-
15 at 4.5 ft	-7D	3.3	92.8	0.1	40.35	6.3	0.02
15 at 11.5 ft	-8	2.3	88.3	0.9	67.92	7.3	0.12
15 at 16.5 ft	-9	21.7	77.0	<0.01	3.72	0.1	-
47 at 53 ft	-18	18.4	74.1	3.0	4.26	4.9	0.61
47 at 5 ft	-20	6.9	78.6	3.2	13.32	12.7	0.25
49 at 40 ft	-21	10.1	36.2	48.8	3.98	5.7	8.56
49 at 5 ft	-22	19.0	79.2	<0.01	4.40	2.6	-
42 at 14 ft	-23	1.7	65.2	15.1	93.14	19.0	0.79
42 at 5 ft	-24	14.9	80.0	0.6	5.76	6.0	0.10
40 at 47 ft	-25	1.5	35.8	46.7	71.60	16.3	2.87
40 at 21 ft	-26	1.5	45.5	40.0	91.00	13.5	2.96
40 at 8 ft	-27	12.6	79.1	1.4	6.82	6.3	0.22
7 at 5.5 ft	-28	20.6	76.9	<0.01	3.92	3.0	-
24 at 14 ft	-29	4.1	94.3	<0.01	30.42	3.2	-
24 at 14 ft	-29D	4.0	93.5	<0.01	31.17	3.3	-
24 at 5 ft	-30	22.0	79.5	<0.01	3.79	0.2	-
13 at 17 ft	-31	1.9	79.5	4.7	88.33	15.7	0.30
13 at 5 ft	-32	18.8	79.5	<0.01	4.47	4.8	-
Detection levels		0.05	0.05	10 ⁻³		0.05	

*GGC/Zymax (1999).

** O_2 concentration calculated by subtracting 1% equivalent to Ar atmospheric concentration.

[†]Depth in feet below ground surface.

and MW-9 at 10 ft bgs (3 m bgs); and MW-9 at 20 ft bgs (6 m bgs), all in Area 1, are shown in Table 5. Additionally, δ^{13} C values for the eight soil boring samples containing the highest CH₄ concentrations are also displayed.

The δ^{13} C value for the Suplin 1 headspace CH₄ is -40.7‰, the range of values for the four monitoring well samples is -45.1 to -42.1‰, and a mean of -43.4‰ (Table 5). For eight soil boring samples, the δ^{13} C range is -38.9‰ to -33.9‰, and a mean of -36.6‰. By contrast, the δ^{13} C of CO₂ has a value of -3.2‰ for the Suplin 1 well samples; a range of δ^{13} C from -26.5 to -23.2‰ and a mean of -25.2‰ for the MW samples; and a range of -29.8 to -25.8‰ and a mean of -28.2‰ for δ^{13} C in the soil boring samples.

SECOND ROUND OF GEOCHEMICAL INVESTIGATIONS: AREAS 1, 2, AND 3

In 1999, Global Geochemistry Corp. and Zymax Forensics (GGC/Zymax, San Luis Obispo, California) was a subcontractor to ESC and undertook studies on the atmospheric, hydrocarbon, and H_2S gases at the enlarged BLC site. Ten soil borings were installed, with samples ranging from 4.5 to 53 ft bgs (1.4 to 16.2 m bgs) for a total of 23 individual samples (Table 6). In addition, five water monitoring wells (Table 7) (EMW-20, -21, and -22, and MW-4 and MW-20), one soil boring (ESB-48C), which contained crude oil, and one production well, Toluca 4 (LAUSD 4), were sampled (see Figure 3 for the locations).

Sample ID	GGC ID	0 ₂ + Ar (%)	N ₂ (%)	CH ₄ (%)	N ₂ /O ₂ **	CO ₂ (%)	C ₁ /CO ₂
MW-4 top	4898-34	22.6	80.3	<0.01	3.72	0.4	-
MW-4 bottom	4898-35	20.4	80.7	0.1	4.16	1.9	-
MW-20	4898-37	8.7	30.6	53.3	3.97	6.7	7.96
Toluca 4	4898-39	4.7	17.5	54.3	4.73	21.2	2.56
Toluca 4	4898 39D	4.9	18.0	53.9	4.62	20.8	2.59
Detection levels		0.05	0.05	10 ⁻³	0.05		

Table 7. Belmont Learning Center: Gas Data from Monitoring Wells and Toluca 4 Producing Well*

*GAI (1990).

**O2 concentration calculated by subtracting 1% equivalent to Ar atmospheric concentration.

In addition to composition and concentration, δ^{13} C was measured on CH₄ and CO₂ samples, and where enough volume was available, δ^{34} S was also measured on H₂S, dissolved sulfate, and sulfide and total sulfur in crude oil.

Atmospheric Fixed Gases and CH₄ Concentrations

Methane, nitrogen, oxygen (plus argon), and CO_2 concentrations were measured in each of the soil boring samples, in two of the monitoring wells, and in the Toluca 4 (LAUSD 4) production well (Table 6).

It is evident from the data that N_2 and O_2 + Ar content dominate in all boring samples with the exception of four deep samples, i.e., ESV-45 at 28 ft (8.5 m), ESV-49 at 40 ft (12 m), ESV-40 at 47 ft (14.3 m), and ESV-40 at 21 ft (6.4 m). The data further show that with the exception of seven samples (ESV-51 at 5 ft [1.5 m], ESV-15 at 16.5 ft [5 m], ESV-47 at 53 ft [16 m], ESV-49 at 5 ft [1.5 m], ESV-7 at 5.5 ft [1.7 m], ESV-24 at 5 ft [1.5 m], and ESV-13 at 5 ft [1.5 m]), the ratio of N_2/O_2 is significantly higher (5.76 to 91.00) than the atmospheric mean ratio (3.8) for the remaining 12 samples (Table 6). These results indicate that (1) samples with high CH₄ content have the lowest oxygen content and (2) deeper samples, irrespective of the CH_4 content, have lower O₂ concentrations, the exception being sample ESV-47 at 53 ft (16 m). This oxygen depletion is strongly suggestive of biogenic (the term biogenic, used in this article, is related to gas genesis from bacterial and other microbial activities) respiration, through the oxidation of either CH₄, H₂S, or petroleum hydrocarbons (Lundegard et al., 2000).

The inverse relationship between O_2 and CH_4 in the subsurface, i.e., O_2 depletion accompanied by high (>10,000 ppmv) subsurface CH_4 concentrations, is also evident from the soil boring data set analyzed by GAI (Tables 3, 4).

Elevated subsurface CO₂ concentrations are another indicator of respiratory oxidation. Table 6 shows that the highest CO₂ concentrations (samples ESV-51 at 33 ft [10 m], ESV-45 at 16 ft [4.9 m], ESV-45 at 28 ft [8.5 m], ESV-42 at 14 ft [4.2 m], ESV-40 at 21 ft [6.4 m], ESV-40 at 47 ft [14.3 m], and ESV-13 at 17 ft [5.2 m], all have concentrations of O_2 + Ar less than 2% and CO₂ greater than 10%, which is greater than $300 \times$ atmospheric concentration of CO₂ (atmospheric CO₂ in the past 10–20 yr was about 380 ppmv, and atmospheric O_2 at 21% by volume). The CO_2/O_2 ratio for these samples ranges from 16.37 to 32.60 (atmospheric CO_2/O_2 ratio is 0.018). These ratios represent samples highly affected by microbial respiration. Concentrations of CO₂ relative to CH₄ are also presented for two well gas analyses (MW-4 and MW-20), as well as for the production well Toluca 4 (Table 7). Only a trace of CH_4 was detected in MW-4, and the N_2/O_2 ratio is typical of atmospheric content accompanied with a low CO₂ concentration (0.4 to 1.9%). By contrast, MW-20 contains 53.3% CH₄, 6.7% CO₂, and $N_2/O_2 = 8.7$, whereas the headspace in Toluca 4 contains about the same concentration of CH₄ as MW-20, has a CO₂ concentration of 21%, and the $N_2/O_2 = 3.97$. In a headspace sample such as this, the excess CO_2 is assumed to be generated in the well and not from respiratory microbial activity.

ESC (1999) measured H_2S at a concentration of 3300 ppmv at a depth of 30 ft bgs (9.1 m bgs) at the baseball field in the northern parcel of land. This high value, if reliable, may be related to the nearby, newly abandoned (1997) Suplin 1 production well, or one of the other nearby wells (Figure 2).

Isotopic Ratios of CH_4 , CO_2 , H_2S , $SO_4^=$, and Hydrocarbons

Table 8 displays concentrations and isotopic data for gas, water, and oil samples from borings, monitoring wells,

Sample ID	GGC ID 4898-	CH ₄ , δ ¹³ C (‰)	CO ₂ δ ¹³ C (‰)	CH ₄ , δD (‰)	Crude Oil, δ^{13} C (‰)	Crude Oil, δ^{34} S (‰)	H ₂ S/SO ₄ , δ ₃₄ S (‰)	H ₂ S, Crude Oil, S, SO ₄ , S ⁼ (ppm)
ESV-51 at 5 ft	1	nd**	-31.11	nd				
ESV-51 at 17 ft	2	nd	-23.68	nd				
ESV-51 at 33 ft	3	-26.30	-28.14	-81			-19.5 [†]	3300 [†]
ESV-45 at 5 ft	4	-12.17	-25.86	-84				
		-12.3D	_					
ESV-45 at 16 ft	5	-23.24	-26.60	-75				
ESV-45 at 28 ft	6	-29.05	-25.66	-134			-15.7 [†]	3300 [†]
ESV-15 at 4.5 ft	7	-23.24	-23.42	nd				
ESV-15 at 11.5 ft	8	-20.30	-30.55	-109				
ESV-15 at 16.5 ft	9	nd	-25.91	nd				
ESV-47 at 53 ft	18	-35.19	-5.93	-146				
ESV-47 at 5 ft	20	-27.31	-	-111				
ESV-49 at 40 ft	21	-39.02	+28.82	-176				
			+29.07D					
ESV-49 at 5 ft	22	nd	-21.76	nd				
ESV-42 at 47 ft	23	-25.26	-30.16	-50				
ESV-42 at 5 ft	24	–0.67, –0.51D	-28.16	-49				
ESV-40 at 47 ft	25	-34.09	- -29.04	-72				
ESV-40 at 21 ft	26	-31.65	-28.38	-68				
ESV-40 at 8 ft	27	-15.22	-28.93	-39				
ESV-7 at 5.5 ft	28	nd	-24.60	nd				
ESV-24 at 14 ft	29	nd	-29.75	nd				
ESV-24 at 5 ft	30	nd	-26.93	nd				
ESV-13 at 17 ft	31	-21.09	-31.25	-94				
ESV-13 at 5 ft	32	nd	-21.24	nd				
EMW-20, oil	10	-	-	-	-23.29	+7.9		5437 ^{††}
EMW-22, oil	11	-	-	-	-22.92	nd		9595 ^{††}
EMW-22, water	15	-	-	-			-4.5 [‡]	475 [‡]
EMW-9, water	16	_	-	-			-8.3 [‡]	418 [‡]
EMW-21, water	33	_	-	-			+26.2 [‡]	215 ^{‡‡}
MW-4 top, gas	34	_	-	-				
MW-4 bottom, gas	35	nd	-	-				
MW-4, water	36	_	-	-			-9.1 [‡]	195 ^{‡‡}
MW-4, gas	37	-38.39	-	-182				
ESB-48c, oil	12	-	-	-	-22.85	+6.7		5063 ^{††}
Toluca 4, oil	13	-	-	-	-23.41	+8.5		7438 ^{††}
Tolca 1, oil	14	-	-	-	-23.20	+7.4		
Toluca 4, water	38	-	-	-			+51.9 [‡]	70 ^{‡‡}
Toluca 4, gas	39	-43.32	-31.11	-181			+14.1 [†]	250 [†]

Table 8. Belmont Learning Center: Concentration and Isotopic Data for Gas, Water, and Oil Samples from Borings, Monitoring Wells, and Oil Producing Wells*

*GGC/Zymax data.

**nd = insufficient sample for analysis.

 $^{\dagger}H_{2}S$ by volume.

^{††}Total sulfur in oil samples.

[‡]Dissolved SO₄.

^{‡‡}Dissolved sulfide.

and oil production wells, including the vapor phase $\delta^{13}C$ and δD isotope ratios of CH_4 and the $\delta^{13}C$ of CO_2 ; the crude oil concentrations of dissolved H_2S , dissolved total sulfide, dissolved total sulfate, and organic phase sulfur; their $\delta^{34}S$ ratios; and vapor phase $\delta^{34}S$ measured by GGC/Zymax.

Data in Table 8 show that the CH₄ having the most isotopically depleted ¹³C is in the Toluca 4 production well (δ^{13} C = -43.32‰, δ D= -181‰). Only four other boring samples (ESV-47 at 53 ft [16.2 m], ESV-49 at 40 ft [12.2 m], ESV-40 at 47 ft [14.3 m], and ESV-40 at 21 ft [6.4 m]) and MW-20 gas have δ^{13} C values less than -30‰. However, only samples MW-4 gas and ESV-49 at 40 ft (12 m) have δ D less than -176‰. In samples EMW-20, EMW-22, ESB-48C, EMW-9, and Toluca 1, no headspace gas was collected.

With the exception of samples ESV-47 at 53 ft (16 m) and ESV-49 at 40 ft (12 m), the δ^{13} C of CO₂ gas ranges over a range of -21.24 (ESV-13 at 5 ft [1.5 m]) to -31.25‰ (ESV-13 at 17 ft [5.1 m]). The two samples where δ^{13} C for CO₂ differed significantly from other samples are ESV-49 at 40 ft (12 m) (+29.0‰) and ESV-47 at 53 ft (16 m) (-5.93‰). With the exception of these two samples, the other 20 gas samples indicate that CO₂ originates from microbial respiratory metabolism in the soil.

The distribution of δD ranged from -39 to -182%. Thirteen boring samples display δD values greater than -150%. These δD values most probably represent different degrees of bioxidation of the CH₄ in the samples. Three gas samples, i.e., ESV-40 at 8 ft, ESV-42 at 5 ft (1.5 m), and ESV-42 at 47 ft (14 m) display very high enrichment of deuterium (Table 8).

The δ^{13} C of the whole (crude) oil and the paraffinic and aromatic hydrocarbon fractions is typical of Monterey Formation crude oil present in the LACOF and many other reservoirs in Central and Southern California.

Only two samples from the borings contained enough $\rm H_2S$ for isotope analysis. These are ESV-51a at 31 ft

 $(9.5 \text{ m}) (\delta^{34}\text{S} = -19.5\%)$ and ESV-45 at 28 ft (8.5 m) $(\delta^{34}S = -15.7\%)$. Both of these gas samples are from the deepest part of the boring, and each contained 3300 ppmv H₂S. Hydrogen sulfide was also detected in the headspace of Toluca 4 production well (Table 8). The δ^{34} S value (+14.1‰) of this H₂S is enriched in 34 S. Dissolved sulfide from this well displays a δ^{34} S of +15.1‰, whereas dissolved sulfate from the same water sample has a δ^{34} S value = +51.9‰, suggesting that the dissolved S^{2-} and gaseous H₂S are the result of bacterial sulfate reduction. Dissolved sulfide from EMW-21 and MW-4 also appears to originate from bacterial sulfate reduction, where previous reports (Kaplan and Rittenberg, 1964) have shown the fractionation factor to be greater than 40‰. Dissolved sulfate in two wells, EMW-22 and EMW-9, has δ^{34} S values of -4.5 and -8.3‰, respectively. Therefore, EMW-9 is most similar to the value for δ^{34} S in sulfate from MW-4. However, no sulfide was detected in the two EMW water samples.

Methane Specialists Isotope Analyses

Methane Specialists had one sample, Probe 12, in which CO₂ was analyzed for δ^{13} C and CH₄ analyzed for δ^{13} C and δ D. The following were the concentrations of fixed air gases plus hydrocarbon gas: N₂ = 67.48%, O₂ = 0.65%, CO₂ = 29.86%, CH₄ = 21.16%, and Ar = 0.84%; δ^{13} C_{CO₂} = -29.32‰, δ^{13} C_{CH₄} = -24.07‰, and δ D = -154.4‰. The CH₄ in this sample is obviously highly biodegraded and is consistent with the data obtained by GGC/Zymax.

CARBON 14 AGE DATING OF COEXISTING CH₄ AND CO₂

In an attempt to determine if the CH_4 in the borings is ancient or recent, four gas samples were selected from four different borings at different depths for analysis of

Table 9. Carbon 14 Age Dating of CH₄ and CO₂ from Soil Borings (GGC/Zymax, 1999)

Sample ID, ESV-	GGC ID	CH4 (%)	δ ¹³ C (‱) (CH ₄)	Fraction Modern Carbon in CH₄	∆ ¹⁴ C (ybp)* (CH₄)	CO ₂ (%)	δ ¹³ C (CO ₂)	Fraction Modern Carbon in CO ₂	∆ ¹⁴ C (ybp)* CO ₂
45 at 16 ft	4948-5	12.5	-23.2	0.0326	27,510	16.3	-26.6	0.2939	9,835
47 at 53 ft	4948-18	3.0	-35.2	<0.0069	>40,000	4.9	-5.9	0.1141	17,440
49 at 40 ft	4948-21	42.2	-39.0	<0.0045	>44,700	5.7	-29.0	0.0079	38,800
13 at 17 ft	4948-31	4.8	-21.1	0.0074	39,400	16.7	-31.3	0.2290	11,845

*ybp = years before present.

CH₄ and CO₂ by the Nuclear Analytical Laboratory at the University of Arizona, Tucson, Arizona. The samples chosen were ESV-45 at 16 ft (4.9 m), ESV-47 at 53 ft (16.2 m), ESV-49 at 40 ft (12.2 m), and ESV-13 at 17 ft (5.1 m) (Table 9). The data show that all of the samples analyzed are older than 20,000 yr. The two deepest samples, ESV-47 at 53 ft (16.2 m) and ESV-49 at 40 ft (12.2 m), are outside the range of ¹⁴C detection (>40,000 ybp [years before present]), and sample ESV-13 at 17 ft (5.1 m) (39,400 ybp) is at the extreme limit for the method employed. Only the shallowest sample displayed an age of 27,510 ybp, which is indicative of probable mixing of very old CH₄ with a small amount of modern (biogenic) carbon.

The coexisting CO_2 have ¹⁴C age dates ranging from 9835 ybp for sample ESV-45 at 16 ft (4.9 m) to 38,800 ybp for sample ESV-49 at 40 ft (12 m). The younger ages could result from mixing of modern biogenic CO_2 with old CO_2 .

INTERPRETATION OF BELMONT LEARNING CENTER DATA

Questions to Answer from the Investigations Conducted

- 1. Does CH₄ concentration exceed the DTSC guidelines for hazard at levels greater than 5% concentration and atmospheric pressure (DTSC, 2005), especially at the soil surface?
- 2. What is the source of CH_4 and H_2S ?
- 3. What is the distribution of CH_4 and H_2S on the BLC property?
- 4. Can the buildings and open spaces on the BLC property be protected from both CH_4 and H_2S migration?

Borehole Data from Initial (1990) Investigation on Area 1

The analyses performed by GAI show that of 48 borehole samples analyzed (Figure 4), only 8 samples (Table 1) contained CH₄ at concentrations greater than 0.5%, and only one of these samples (no. 25) contained CH₄ at the level (>5%) considered combustible in the atmosphere. Seven of these samples contained ethane at concentrations greater than 15 ppmv, suggesting a probable petrogenic origin for the hydrocarbon gases. By contrast, in the 57 shallow probe samples, GAI only measured one sample of soil gas having a CH₄ concentration greater than 100 ppmv and two others having concentrations between 10 and 50 ppmv (Figure 4).

These differences in concentration between deep and shallow samples are strong evidence for the removal of CH_4 during its ascent to the surface.

Soil Boring Data from Environmental Strategies, 1998–2003

ESC set down a series of 59 soil borings (Figure 3) over a nearly 5-yr period at depths range from 4.5 to 63.5 ft bgs (1.3 to 19.3 m bgs). During that period, 520 samples were collected, but 45 samples could not be analyzed because of the presence of liquid petroleum in 9 samples and water in 36 others. Approximately 140 samples tested below the level of detection (n.d.) for CH₄ concentration. In Area 1, 130 contained less than 10 ppmv, 26 contained between 10 and 100 ppmv, 28 contained between 100 and 1000 ppmv, 20 contained between 1000 and 10,000 ppmv, 28 contained between 10,000 and 50,000 ppmv, 27contained between 50,000 and 500,000 ppmv, and 12 samples contained greater than 500,000 ppmv CH4; the highest concentration, 900,000 ppmv, was measured in ESV-55 at 40 ft bgs (12 m bgs) on April and May 1999 (Table 1, Figure 5). The highest concentrations occurred at the maximum depth of sampling, and the concentration of CH₄ generally decreased with time (although not in every boring), indicating that the rate of CH₄ removal was faster than the rate of regeneration. In Area 2 (Table 2), no samples exceeded a concentration of 500,000 ppmv, two samples at different depth in ESV-07 measured greater than 100,000 ppmv, and the remainder was in the range of n.d.-81,000 ppmv.

Borehole Data from GGC/Zymax Investigations

The declining CH_4 concentration in near-surface soil is also observed in the GGC/Zymax data collected and analyzed in 1999 on both parcels of land (Table 6). The highest CH_4 concentrations (39.7 to 48.8%) occur at depths greater than 20 ft bgs (6 m bgs), and the two highest values (48.8 and 46.7%) were detected at 40 and 47 ft bgs (12.2 and 14.3 m bgs), respectively. The concentration decreased at intermediate depths and was either n.d. or less than 4.0% in 10 samples from surface to 10 ft bgs (3 m bgs). In samples from ESV-47, the CH_4 concentration (3.0%) at 53 ft bgs (16 m bgs), suggesting that CH_4 was not generated at that location but probably



Figure 5. Bar diagrams showing the number of samples with different CH_4 concentrations for (a) GAI monitoring wells (Table 4), (b) GAI soil borings (Table 3), and (c) ESC soil borings (Tables 1, 2).







Figure 6. Crossplot showing the variation in CH₄ concentration in ESC soil borings (Table 1) as a function of depth.

migrated into the soil. These data further support the conclusion reached from the GAI data set that CH_4 removal occurs during its vertical migration to the surface.

Monitoring Well CH₄ Concentration

Fifteen monitoring wells were sampled (GAI, 1990) for gas phase concentrations from 7 to 28 ft bgs (2.1 to 8.5 m bgs) in depth. Methane in measurable quantities was found in 8 of the 15 wells. Methane in excess of 500 ppmv was only found in five monitoring wells in addition to Suplin 1 (Table 3). These monitoring wells also contained ethane and other wet gases, but none exceeded a concentration of 250 ppmv. Only three monitoring wells (MW-3 shallow and MW-9 shallow and deep) contained CH₄ greater than 10%. MW-3 contained 18.18% at 10 ft bgs (3 m bgs), whereas MW-9 contained an average of 23.63% at 20 ft bgs (6 m bgs) and 13.77% at 10 ft bgs (3 m bgs). These data also display the loss of CH₄ during upward migration. GGC/ Zymax collected headspace gas from MW-4 and MW-20 (Table 7). Only traces of CH₄ were detected in MW-4, whereas MW-20 contained 53.3% CH₄. ESC (1999)

measured 29 monitoring wells for dissolved CH_4 . Only 12 detections were recorded above 3 ppbv, and only 4 contained greater than 1 ppmv CH_4 , the highest being 10.8 ppmv.

Relationship Between CH₄, CO₂, N₂, and O₂

In general, CH₄ in the soil on the BLC property is present in low concentrations (<0.1%), characteristic of soil profiles in semiarid zones. In some locations, CH₄ concentrations exceed 1.0% (Tables 1–3, 6), and in a smaller number of samples, it exceeds 5.0%. However, these high concentrations were mainly found to occur at depths greater than 20 ft (6 m) (Figure 6).

Based on these data, it is apparent that CH_4 generation is not pervasive throughout the entire site, but occurs at specific locations only. The following could be the source of the higher CH_4 concentrations.

- 1. seepage from improperly abandoned oil wells
- 2. vertical seepage from migration paths in the LACOF reservoir beds and source rocks
- 3. biogenic genesis in the soil profile

4. horizontal migration along permeable stratified sediments.

Characteristics of gas concentration data displayed in Tables 1–3, 6, and 8 illustrate the following.

- 1. Where the greatest concentration of CH_4 was measured, CO_2 concentration was relatively low.
- 2. With decreasing depth below surface, CH_4 concentration decreases, but CO_2 displays variable concentrations.
- 3. The O_2 and N_2 concentrations are variable and depend on depth as well as the concentration of CH_4 and CO_2 .
- 4. At soil depths where CH_4 concentration is greatest, O₂ is depleted relative to N₂, indicating that O₂ is being consumed by CH_4 (and/or H₂S) oxidation. The exception is sample ESV-49 at 40 ft bgs (12 m bgs) (Table 6), where the CH_4 concentration of the soil gas is 48.8% and the N₂/O₂ ratio is 3.98, almost identical with that in air. In the data from the GAI monitoring wells (Tables 3, 4), four of eight wells sampled displayed significant O₂ depletion in the presence of high CH_4 contents, whereas in the other four wells, air contamination during sampling may have been partially responsible for the low CH_4 concentration measured.
- 5. Production wells Suplin 1 and Toluca 4 have high C_1/CO_2 ratios and N_2/O_2 ratios close to those of air, indicating that, at the wellhead of a production well, where the escape of CH_4 is relatively rapid, the rate of CH_4 introduction into the soil is more rapid than the rate of its oxidation.

These data are strongly suggestive that, in the soil profile where an improperly plugged and abandoned oil well is present, CH_4 may escape rapidly to the surface with little biogenic oxidation because the gas flow is pressure motivated. However, in soil profiles where the seepage or generation of CH_4 is slow and gas movement in the soil is probably diffusive, most of the CH_4 is oxidized microbially prior to it reaching the surface. This conclusion is important because it provides the reason why near-surface CH_4 concentrations are very low.

Carbon 13 and Deuterium Isotope Analyses of CH_4 and CO_2

The δ^{13} C and δ D of CH₄ in the headspace gas of Toluca 4 (Table 8) production well are -43.32 and -181‰, respectively, and for the Suplin 1 well (Table 5), δ^{13} C is -40.7‰ (δ D was not measured). In four monitoring wells (MW-3 at 10 ft [3 m], MW-5 at 10 ft [3 m], MW-9 at 10 ft [3 m], and MW-9 at 20 ft [6 m]), δ^{13} C of CH₄ is in the range of -42.3 to -45.1‰ (Table 5). In the GGC/Zymax measurement on MW-4, gas is δ^{13} C = -38.39‰ and δ D = -182‰ (Table 8). By comparison, CH₄ from 14 actively producing wells in Southern California (Jenden, 1985) yielded the following range of δ^{13} C values: -35.0 to -51.4‰, mean = -45.2‰; and δ D values: -165 to -260‰, mean = -200.9‰.

If it can be assumed that these ranges of values represent the isotopic range of associated gas in the oil wells for the LACOF, then a comparison of the soil CH₄ δ^{13} C and δ D with the same isotope ratios in CH₄ from monitoring wells can be made to interpret similarities and deviations. When comparing the GAI δ^{13} C values of soil CH₄ with both the monitoring and production well CH₄, the soil gas is evidently more enriched in ¹³C. Furthermore, ¹³C of the coexisting CO₂ gas in the soil boring samples is consistently enriched in ¹²C relative to both the monitoring wells and Suplin 1 samples. This latter sample does not display evidence for the oxidation of the CH₄ (Table 5), which is consistent with the C₁/CO₂ and N₂/O₂ ratios presented previously.

The GGC/Zymax data displayed in Table 8 show that δ^{13} C of CH₄ from soil borings is enriched in ¹³C relative to Toluca 4 and Suplin 1 well headspace gas (Figure 7). This divergence in the soil gas relative to the production and monitoring well data is pronounced in the shallower samples and is characteristic of bacterial CH₄ oxidation (Coleman et al., 1981; Schoell, 1983; Kaplan, 1994; Lundegard,2006). Additionally, two samples, ESV-45 at 5 ft (1.5 m) and ESV-42 at 5 ft (1.5 m), display high enrichment of both ¹³C and deuterium relative to other gas samples (Figure 8, Table 8), a feature characteristic of horizontal migration away from the source (Coleman et al., 1981).

Sample ESV-49 at 40 ft (12.2 m) is different from all other soil samples measured, in that the δ^{13} C of the coexisting CO₂ in the sample is +29.07‰ (Table 8). This suggests that some part of the CH₄ has formed from the bacterial reduction of CO₂ with hydrogen, whereas all other soil CH₄ samples originate from slow seepage from the LACOF. This conclusion is reached from the δ^{13} C and δ D patterns of CH₄ generated from different sources (Figure 9) as shown by Schoell (1983), Kaplan (1994), and Lundegard (2006).



Figure 7. Crossplot showing variation of δ^{13} C of CH₄ as a function of depth (Table 8). The enrichment of 13 C with decreasing depth from the soil surface and farther away from the source is interpreted as resulting from microbial oxidation.

Hydrogen Sulfide

The 1990 GAI study did not detect H_2S in the soil borings or in the headspace gas of monitoring wells (i.e., no results above laboratory method detection limits). However, they detected an odor of H_2S at the corner of Boylston and Temple streets, at the extreme northeast boundary of the BLC property, presumably coming from the abandoned Tierra 2 well, but they did not detect H_2S in the Suplin 1 well (before abandonment).

ESC detected H_2S greater than 10 ppmv in only two borings (ESV-45 and ESV-51) in Area 1 at a maximum depth of sampling; ESV-51 at 33.5 ft (10.2 m) reaching a maximum of 33,000 ppmv on August 30, 1999 (Table 1). In both borings, the concentration decreased with time. ESC also measured dissolved sulfide in 4 of 29 wells at levels of 1.61 to 7.21 ppmv.

The GGC/Zymax investigation detected H_2S in two deep borings, ESV-51 at 33.5 ft (10.2 m) and ESV-45 at 28 ft (8.5 m) (Table 8), and the concentration for each of the samples is 3300 ppmv. Their location (Figure 3) is in the vicinity of the Suplin 1 well and other adjacent producing wells. Their δ^{34} S isotope ratios (-19.5 and -15.7‰, respectively) suggest that the gas originated from biogenic sulfate reduction in an oxygen-depleted environment. The H₂S was also detected in the headspace gas of Toluca 4 well at a measured concentration of 250 ppmv and a δ^{34} S²⁻ value of +14.1‰ (Table 8). The water in this well contained dissolved sulfide at a concentration of 5.0 ppm, but it was insufficient for a δ^{34} S measurement. This well water also contained a small amount of dissolved sulfate (70.0 ppm) having a high δ^{34} S value of +51‰. The large difference in δ^{34} S between the sulfate and H₂S or dissolved S²⁻ again indicates a biological mass fractionation resulting from bacterial sulfate reduction.

This process is also responsible for the production of sulfide in the water of two monitoring wells, EMW-21 and MW-4. Their respective $\delta^{34}S_{SO_4}$ was measured as +26.2 and -9.1‰, respectively (Table 8). For the dissolved S^{2–} in the water, $\delta^{34}S$ was measured as -13.7 and -23.2‰, respectively, at the two monitoring wells. Well EMW-21 contained 71 ppm SO₄ and well MW-4 contained 714 ppm SO₄. This concentration difference



Figure 8. Relationship between δ^{13} C and δ D in CH₄ samples (Table 8), displaying both bioxidation and diffusion away from the thermogenic source.

suggests greater loss of SO4 in EMW-21 than EMW-4, which is commensurate with the $\delta^{34}S$ ratios of the two samples.

The difference in concentrations may explain the large difference in the $\delta^{34}S$ of the two dissolved sulfate samples.



Figure 9. Approximate regions of δ^{13} C and δ D, where CH₄ formed by different processes occurs (Coleman et al., 1981; Schoell, 1983; Kaplan, 1994).

Age of Methane Production

The measured age of CH_4 using ${}^{14}C$ (Table 9) indicates that two of the four samples measured were older than the limit of detection, 40,000 ybp, and another was at the limit of detection, indicative of an oil well origin. Only one sample (ESV-45 at 16 ft [4.9 m]) had a measured carbon 14 age of 27,500 ybp. This last date represents a mixing of a minor amount of modern CH₄ with a majority of old CH₄. The age of CO₂ generation ranged from 9800 to 38,800 ybp. Measured carbon 14 ages of CH₄ less than approximately 40,000 yr could be indicative of either old biogenic CH₄ or mixing of petrogenic oil field CH₄ with young biogenic CH₄. Because we have shown here that it is unlikely that CH₄ can persist in the soil environment for long periods without being oxidized, we conclude the mixing of mostly old (petrogenic) CH₄ with minor amounts of young (bacterial) CH₄ to display the ages measured. For example, it requires only 3.5% modern (pre nuclear bomb) CH₄ mixed with 96.5 petrogenic CH₄ to give an assumed 27,500 ybp for sample ESV-45 at 16 ft (4.9 m).

DID ENVIRONMENTAL CONDITIONS REQUIRE HIGHLY CONSERVATIVE METHANE MITIGATION MEASURES AT BELMONT LEARNING CENTER?

It has been well established (Sepich, 1998, 2008) that CH₄ will not accumulate at the soil surface unless the pressure at which it enters the soil profile is higher than the ambient atmospheric pressure. Petrogenic CH₄ can be generated in the sedimentary layers at depths of several thousand meters below ground surface, resulting in gas pressures many orders of magnitude above atmospheric pressure. When gas from a deep undepleted reservoir rises to the surface, as in a production well, the pressure forces the gas rapidly to the surface. When a reservoir is mostly depleted, the pressure drops and hydrocarbon gases emerge slowly or not at all. Under these conditions, CH₄ (and H₂S if present) when entering the soil profile will mix with air and become sufficiently diluted that is it no longer dangerous. For CH₄, this is less than 5% of the atmospheric concentration.

The LACOF is a shallow oil field, with production zones found from 900 to 1500 ft bgs (274–457 m bgs). Pressures in oil fields are a function of the geologic overburden. The LACOF never exhibited the pressures found in deep production zones of some oil fields.

A monitoring well, LAUSD 1B (Figure 1), installed on the site in Area 1 for continuous pressure measurement (Schlumberger, 2000a) showed that the pressure in the well was at equilibrium with atmospheric pressure at the depth of measurement, indicating no excess gas present in the well above atmospheric pressure. Furthermore, as shown by the data in this study, the emerging CH4 and H2S decrease to either a trace or nondetect level at the soil surface. This effect is due, in addition to dilution with air, to the microbial oxidation of CH_4 to CO_2 and of H_2S to SO_4 . Under these circumstances, the gases are no longer hazardous. When the rate of CH₄ or H₂S introduction to the soil profile is significantly faster than the rate of bacterial oxidation, high concentrations of these gases can migrate vertically and horizontally near the soil surface. This does not occur at the BLC site.

CONCLUSIONS

The CH₄ and minor amounts of H_2S were detected in a small number of locations on the site but particularly in the areas where previous production oil wells were located. Elsewhere on the site, CH₄ could have migrated along fissures and minor faults to the surface from underlying source or reservoir rocks. Carbon and deuterium stable isotope ratios of CH₄ produced results that matched those of petrogenic CH₄. Hydrogen sulfide most probably was derived from release of oil well formation water containing sulfate, which was reduced in deep oxygen-depleted soil by bacteria to H₂S.

Analytical results show, however, that both the CH₄ and H₂S were diluted with air as they migrated to the surface and were oxidized by methanotrophes and sulfur-oxidizing bacteria. As a result, only trace amounts of these hazardous gases reached the surface. Furthermore, the production wells in this mostly depleted oil field were not under excessive pressure. Hence, the rate of release of CH₄ and H₂S was in equilibrium with the atmospheric pressure, and because of their dilution and oxidation during migration, they would not present a danger to surface structures or to humans. It is important to consider the old BHS and UES (Figure 1), which were constructed many decades previously over soil gas conditions very similar to those at BLC and which have operated continuously without any history of soil gas problems, complaints, or incidents. The BLC soil gas conditions posed little or no risk to the safety of the structures, students, teachers,

and maintenance personnel, even without the code mitigation system, which had been approved prior to the negative publicity that nearly ended the project. Routine engineering mitigation practices, as suggested by competent engineers working on the project and accepted by regulatory agencies, will protect both people and property from accidental inhalation or explosions.

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