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To:	Brown, Kevin@Waterboards; Hill, Stephen@Waterboards; Headlee, Chuck@Waterboards
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Subject:	1705/1709 Contra Costa Blvd., Pleasant Hill
Date:	Wednesday, October 30, 2013 4:39:26 PM
Attachments:	Notes to CSM Slides_1705_1709_Contra_Costa_Blvd.pdf 42461_Forensics Report.pdf

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Gentlemen:

Following up on Kevin Brown's request after our meeting on October 2, I am sending you the attached memorandum dated October 30, 2013, and conceptual site model presentation slides. I am also sending you the "Forensic Report for Groundwater Samples Collected in Pleasant Hill, California," dated October 9, 213, prepared by Zymax Forensics. Please contact me if you have any questions. Thank you.

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MEMO

To:
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Kevin Brown

Copies:
Catalina Espino Divine, Chevron
Brian Waite, Chevron

From:
Scott Seyfried, P.G., CH.G.
P.G. #7374, CH.G. #764

Date:
October 30, 2013

ARCADIS Project No.:
B0047469.0000

Subject:
Notes to Accompany Conceptual Site Model Presentation Slides, 1705/1709 Contra Costa Boulevard Properties, Pleasant Hill, California

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Representatives from Chevron Environmental Management Company (CEMC), Arcadis-US, Inc. (Arcadis), and Conestoga-Rovers and Associates (CRA) met with the San Francisco Regional Water Quality Control Board (SFRWQCB) staff on October 2, 2013, to discuss the results of recent investigations conducted at the 1705 and 1709 Contra Costa Boulevard Properties in Pleasant Hill, California (site). During that meeting, Arcadis presented a conceptual site model for soil and groundwater conditions beneath and downgradient from subject properties using Power Point slides. After the meeting, the SFRWQCB requested a copy of the slides.

The following sections of this memorandum provide a written summary of the key technical points that were discussed with each slide

Slide 1

This slide presents groundwater elevation data collected on June 6 and December 18, 1990, in routine quarterly monitoring reports prepared by EA Engineering, Science and Technology, Inc. (EA).

- Multiple rounds of groundwater elevation data demonstrate that the direction of shallow groundwater flow beneath the site is toward the northeast. Four groundwater elevation gauging events were selected for illustration for the presentation to represent the consistently northeast flow direction measured at the site.

- A rose diagram prepared by Terradex that compiles historical data also shows that the orientation of the gradient to be northeast. (Terradex, September 14, 2004 “Closure Request, Chevron Service Station 9-6817.”)

    a. The layout of the wells is appropriate to characterize flow direction (i.e., they are sufficiently spread out to allow for triangulation, and are all screened across the water table and completed to similar depths to allow for comparison of groundwater level data).

    b. Nine rounds of complete groundwater elevation measurements were collected from the properties over a period of approximately 2 years prior to startup of the remediation system at the Chevron-branded service station site in August 1991. A northeast flow direction was indicated in each of these nine monitoring events.

    c. Because groundwater flow from the site is generally to the northeast, the September 13, 2004, Site Management Plan appropriately designated EA-5 as the downgradient sentinel well. (The Site Management Plan was approved by the SFRWQCB on January 14, 2005).

- The data do not support the assertion in the May 28, 2013, letter from PES Environmental, Inc. (PES) that groundwater flow from the site is to the northwest.

    a. In its evaluation of groundwater flow beneath the site, PES stated “because groundwater elevation data were affected by the operation of a groundwater extraction and treatment system at 1705 Contra Costa Boulevard, water level elevation data from a nearby site were used to assess groundwater flow directions in this area. Evaluation of groundwater data form 1996 to 2010 for the former Unocal 76 Station at 1690 Contra Costa Boulevard (i.e., just east of 1705 Contra Costa Boulevard) shows that shallow groundwater gradients in this area generally are oriented to the northwest.”[1]

    As presented above, groundwater elevation historical data collected before startup of the extraction system consistently showed a northeast gradient at the site. This northeast gradient continued to be measured in monitoring wells surrounding the two extraction wells after startup of the extraction system.

[1] The PES letter does not provide data to support the statement that shallow groundwater gradients at the 1609 Contra Costa Boulevard site "generally are oriented to the northwest." The statement that 1609 Contra Costa Boulevard is "just east" of the 1705 Contra Costa property is not accurate; 1609 Contra Costa Boulevard is more than 250 feet northeast of the 1705 Contra Costa Boulevard property.

Slide 2

This slide shows groundwater elevation data collected on March 31, 1991, and August 24, 1994. These figures were originally submitted in routine quarterly monitoring reports prepared by EA.

- March 1991 groundwater elevations demonstrate northeast direction of flow.
- Groundwater elevation data collected after startup of the extraction system at the site in August 1991 also show northeast groundwater flow, based on monitoring wells located upgradient and downgradient of on-site extraction wells.

Slide 3

The base map for this slide is a plot of concentrations of PCE detected in soil gas during an investigation conducted by EA in May 1988, along with its interpreted iso-concentration contours based on that data. This figure was submitted as Figure 12 of the "Report of Investigation, Chevron SS 9-6817, 1705 Contra Costa Boulevard, Pleasant Hill, California," prepared by EA, dated February 3, 1989. Overlain on those contours are iso-concentration contours for PCE detected in groundwater in June 1989 developed by EA using groundwater quality data collected from monitoring wells installed after the 1998 soil gas investigation. (Figure 8 of the "Report of Investigation, Soil Vapor Contaminant Assessment, Chevron SS 9-6817, 1705 Contra Costa Boulevard, Pleasant Hill, California," prepared by EA, dated August 9, 1989.) Other features shown on this Slide include the interpreted >1 µg/L contour for benzene (also based on groundwater data collected during June 1989, Figure 6 of the August 1989 EA report), the approximate locations of a former dry cleaner facility, the sewer line along Linda Avenue, and recent soil boring CPT-14.

Evaluation of these data indicates the following:

- Soil, groundwater, soil gas, and compound-specific isotope data for groundwater all indicate the presence of a source of PCE associated with the location of a dry cleaner formerly located on the southern portion of what is now known as 1705 Contra Costa Boulevard.
- There is no evidence that the former 1986 or 1988 used oil USTs located at the service station property contained PCE or TCE.
- There is no indication that the former 1986 or 1988 used oil USTs located at the service station property contributed to the presence of PCE or TCE beneath the site, or downgradient of the site, for the following reasons:

Soil Gas Data

- The distribution of PCE and TCE detected in soil gas during the 1988 investigation is consistent with and reflects the distribution of PCE- and TCE-affected groundwater.

  a. The iso-concentration contours for soil gas shown on Slide 3 were developed based on the results of the 1998 soil gas survey, which did not include locations near or around the apparent source area(s) for the former dry cleaner. In its report presenting the results of the 1988 soil gas survey, EA notes: "it is believed that if the dry cleaner had underground tanks they would have been in the area of the car wash. This area could not be explored with the SCVA (soil vapor contaminant assessment), so the interpolations of concentrations in this area must be considered more uncertain than for other areas of the site." As a result, potential contribution of the actual former dry cleaner source area to concentrations of PCE in soil gas was not evaluated in the 1988 assessment.

Soil Data

- The concentration of PCE detected in soil samples collected from the location of the former dry cleaning facility during the 2011 investigation indicates the presence of a residual source area for PCE in the vicinity of the former dry cleaner operation.

  a. The highest concentration of PCE in soil during the recent investigation in 2011 was detected in soil samples collected from location CPT-14 (location shown on Slide 3). PCE was detected at that location at concentrations up to 20 mg/kg, which was an order-of-magnitude higher than any other concentration detected during that investigation in any other location at the site. CPT-14 is located near the back of the former dry cleaning business, and to the south and west (i.e., upgradient) from the former used oil tank. The predominance of the parent product (PCE) used in dry cleaning, without a substantial amount of the daughter product (TCE), suggests that CPT-14 is in close proximity to the residual source of the CVOCs.

  b. Boring CPT-13 is located along the southern wall of the former used oil UST (as confirmed by the lithologic log for the CPT-13 boring) and contained 0.34 mg/kg PCE and 0.21 mg/kg TCE at 9.5 feet below grade (fbg) in soil. These PCE and TCE concentrations do not indicate a source of DNAPL in the close vicinity of the used oil UST.

- Soil data collected from beneath the former used oil tank also does not indicate that the used oil tank represents a source for VOCs.

  a. Two rounds of soil sampling beneath the used oil tank revealed concentrations of petroleum hydrocarbons that are not indicative of the presence of non-aqueous phase hydrocarbons, or other indication of a significant release of hydrocarbons from the used oil tank into the underlying soil.

  b. PCE and TCE were detected in a soil sample collected from beneath the used oil tank in 1988 at concentrations of 0.200 mg/Kg and 0.035 mg/Kg, respectively. Based on the magnitude of the 1988 and 2011 concentration data, and the fact that the soil samples were collected from the approximate zone of fluctuation of the water table (approximately 10 feet bgs), the source of these VOCs is most likely sorption from PCE- and TCE-affected groundwater migrating from the upgradient dry cleaner source, as explained below.

<u>Groundwater Data</u>

- Based on data from the former Chevron well network, the depth to groundwater has ranged from approximately 5 to 20 fbg with an average depth of approximately 9.5 fbg and was calculated to flow consistently toward the northeast. The depth to groundwater in destroyed well EA-2, located adjacent to the former used-oil UST, ranged between 8.82 and 11.29 fbg, and during the operation of the groundwater extraction system from August 1991 to July 1996 ranged between 9.90 and 19.94 fbg.

- The highest concentration of PCE in groundwater (maximum detection of 5,000 µg/L) was detected at well EA-3 in January, 1989, slightly more than two years after the dry cleaner reportedly ceased operations. EA-3 is located adjacent to the sewer line in Linda Avenue. This location is upgradient from the location of the former dry cleaner when considering groundwater flow direction and indicates potential migration via a preferential pathway associated with the sewer piping and/or backfill associated with that piping from the former dry cleaning facility to the sewer line, and/or a potential upgradient source, and subsequent release to groundwater.

  a. Based on the northeast groundwater gradient measured at the site, it is expected that PCE-affected groundwater from the former dry cleaner and/or sewer source migrated to the northeast. Some of this PCE encountered petroleum-affected sediment and groundwater associated with the former petroleum USTs (area indicated in brown on Slide #3).

  b. PCE transformed via reductive dechlorination (weathered) as it migrated through the petroleum area, forming TCE and DCE, which are breakdown products of PCE.

Isotope Data

- Zymax performed an isotope analysis of the hydrogen, chloride, and carbon in the PCE, TCE, and DCE detected in several groundwater samples collected from the site. Results of that study indicate that the source of TCE detected in groundwater beneath the site is breakdown from PCE. This independent line of evidence is consistent with the site conceptual model described above.

Based on the fate and transport characteristics of PCE, the fact that the 1988 soil sample (#1) from the former used-oil UST was collected within the zone of fluctuation of the water table, compound specific isotope data that demonstrated that TCE at the site is a daughter product of PCE degradation, and the magnitude and vertical distribution of PCE concentrations detected at CPT 14 compared to the concentrations detected near the former used oil UST, it is our opinion that the former dry cleaner and/or an unknown upgradient source are the source(s) of PCE at the site.

Slide 4

The base map for this slide was taken from Figure 4 of the report: “Quarterly Groundwater Monitoring Report, Fourth Quarter 2009,” prepared by Erler & Kalinowski, Inc., dated February 16, 2010. On that figure, concentrations of VOCs collected from monitoring wells in the vicinity of the 1705/1709 properties from 2003 and 2004 (most recent data available at that time) are plotted along with VOC results for grab groundwater samples collected from the north of those properties during an groundwater investigation conducted in December 2009. Overlain on that base map figure is an arrow depicting a northeast groundwater gradient. Also, PCE to DCE ratios calculated from the concentrations shown on that figure are indicated in italics and circles next to the well or grab groundwater sample locations.

- Circled numbers in italics on Slide 4 are the calculated concentration ratios of [PCE] to [DCE]. Larger numbers indicate high [PCE] relative to [DCE], indicating that the PCE is relatively unweathered. Lower numbers indicate higher [DCE] relative to [PCE], which indicates potentially more weathered PCE.

- The [PCE] to [DCE] ratio, and the concentration of PCE, are higher at ECP-2 than at locations that are downgradient of the site. This indicates that the source or pathway for the PCE at EPC-2 may differ from the PCE detected at locations that are downgradient of the site.

Slide 5

The base map for this figure was taken from Figure 2 of the report “Additional Site Investigation Report, Chevron Service Station 96817, 1705 Contra Costa Boulevard, Pleasant Hill, California,” prepared by CRA, dated March 2, 2012. Overlain on that base map are: the ratio of the concentrations of PCE to DCE reported for shallow and deep grab groundwater samples collected during December 2011, and for water samples collected from monitoring wells during September 2011.

- Results from CRA's 2011 investigation confirm the distribution of apparently weathered versus unweathered PCE noted on Slide 4. PCE detected north and northeast of the Linda Avenue sewer line (e.g., locations CPT-8 and CPT-7) is less weathered (higher [PCE] to [DCE] ratios, shown in circles) than the PCE detected in groundwater located northeast of the former dry cleaner PCE source area on site.

- These results are consistent with the northeast migration of PCE-affected groundwater beneath the 1705 property. The PCE in that groundwater undergoes weathering due to the presence of petroleum hydrocarbons in saturated soil and groundwater, resulting in a weathered signature in groundwater downgradient from the 1705 property, in the eastern portion of the parking lot. As a result, PCE is apparently more weathered toward the east beneath the shopping center parking lot.

- In contrast, the presence of a relatively unweathered PCE signature toward the western portion of the parking lot (e.g. CPT-7 and CPT-8) indicates a different migration pathway for PCE that did not include as much weathering. Also, these locations are not directly downgradient from the 1709 Property source area. Based on these observations, it appears that PCE detected at CPT-8 and CPT-7 may have migrated via the sewer line, or the backfill of the sewer line, along Linda Avenue, and continued that north/northeasterly migration where the sewer line makes a 90 degree turn to the west. PCE potentially released from this location may have originated at the former dry cleaner at the 1709 Property or other upgradient locations.

- Groundwater with the relatively unweathered PCE signature appears to migrate primarily to the north/northeast from the CPT-7/CPT-8 area. The amount of weathering increases along this flow path, as evidenced by decreasing [PCE]:[DCE] ratios toward the north and northeast.

- These data do not indicate migration from the shopping center parking lot to the west, toward the P&K Cleaners site, or to areas to the northwest of the shopping center.

    a. Groundwater beneath the P&K site has a distinctly different [PCE]:[DCE] ratio that reflects a relatively unweathered PCE source. This unweathered signature is consistent with the presence of a separate source at that location.

- Also, these data also do not indicate migration of PCE from the parking lot to the vicinity of MW-8.

    a. The [PCE]:[DCE] signature at MW-8 is consistent with the signature found at the upgradient P&K cleaner site, and is distinct from the PCE:DCE signature found in the shopping center parking lot.

Slides 6 – 9

Slide 6 shows groundwater elevation data collected from the P&K site during September 5, 2012 (Figure 2 of the "Quarterly Groundwater Monitoring Report, Third Quarter 2012," prepared by Erler & Kalinowski, Inc. (E&K) and data October 31, 2012).

The base map for Slide 7 is a plot of groundwater analytical data from the October 2012 report. Overlain on that base map are groundwater elevation contours from Slide 6, and [PCE] to [DCE] ratios calculated from the data posted on the base map.

Slide 8 shows groundwater elevation data collected from the P&K site during March 2013 (Figure 2 of the "Semi-Annual Groundwater Monitoring Report, First Half 2013," prepared by Erler & Kalinowski, Inc. and data April 22, 2013).

The base map for Slide 9 is a plot of groundwater analytical data from the April 2013 report. Overlain on that base map are groundwater elevation contours from Slide 8, and [PCE] to [DCE] ratios calculated from the data posted on the base map.

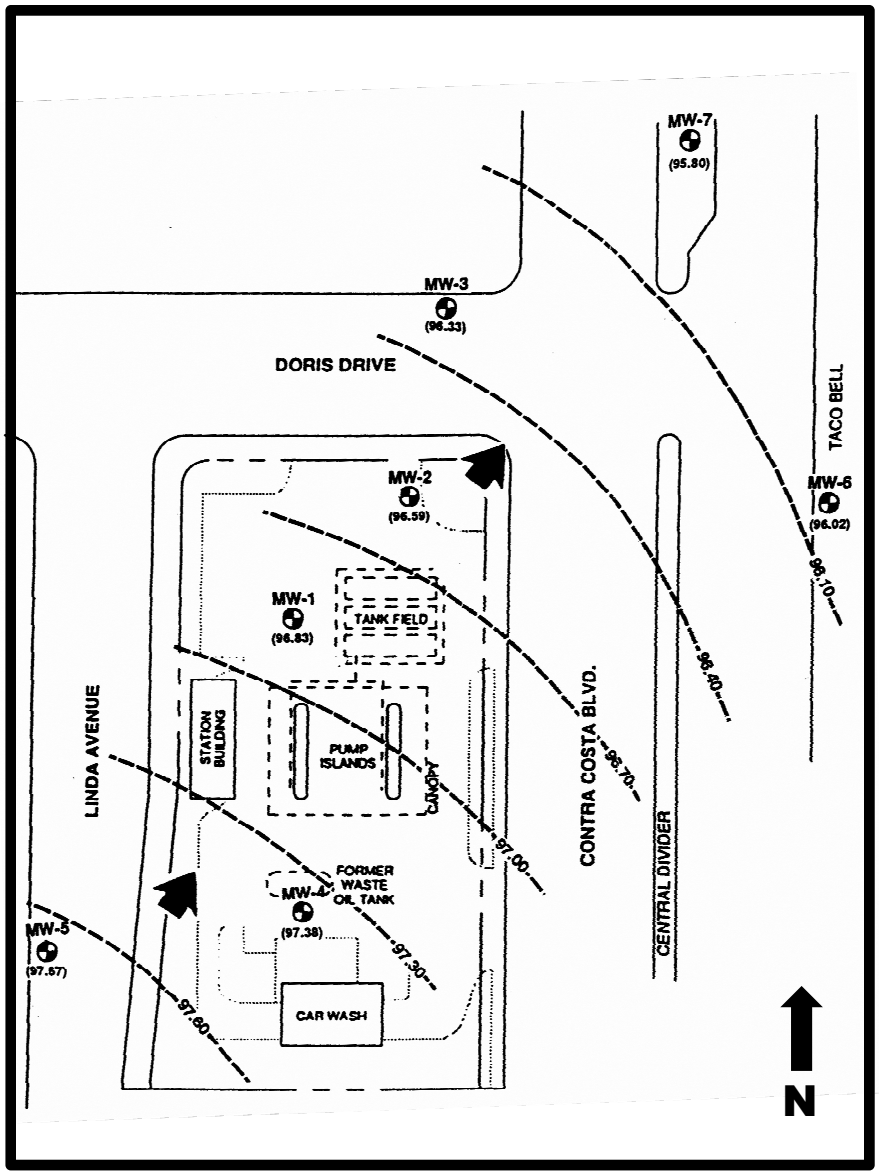
- Groundwater flow in the vicinity of the P&K site is predominantly to the north in this area.

- Groundwater analytical data collected from monitoring wells in the vicinity of the P&K site are consistent with a predominantly northerly migration of PCE-affected groundwater in the shopping center parking lot, and northerly migration away from the former P&K cleaners site.

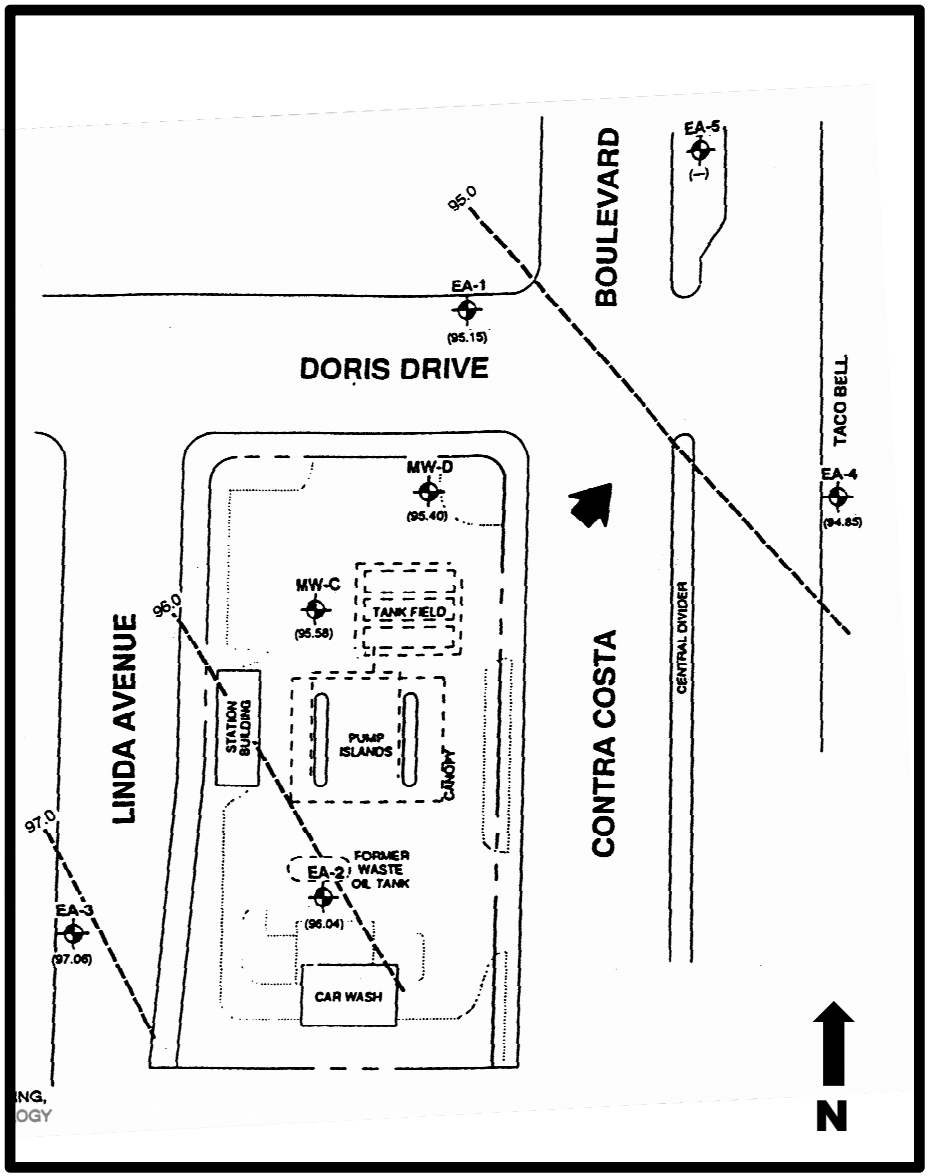
    a. Groundwater quality at MW-7 is consistent with continued northerly migration from the shopping center parking lot. DCE is detected at MW-7 at concentrations that are consistent with northerly migration of DCE from the parking lot.

    b. [PCE] to [DCE] ratios also are consistent with a primarily northerly migration of groundwater in this area. The relatively unweathered signature (higher [PCE] to [DCE] ratios) appear to propagate north away and downgradient from the former P&K source, resulting in the relatively unweathered PCE signature in MW-8. Similarly, the weathered signature characteristic of groundwater beneath the shopping center parking lot propagates to the north, in the direction of monitoring well MW-7, where elevated concentrations of DCE from the shopping center parking lot are detected.

Slide #1



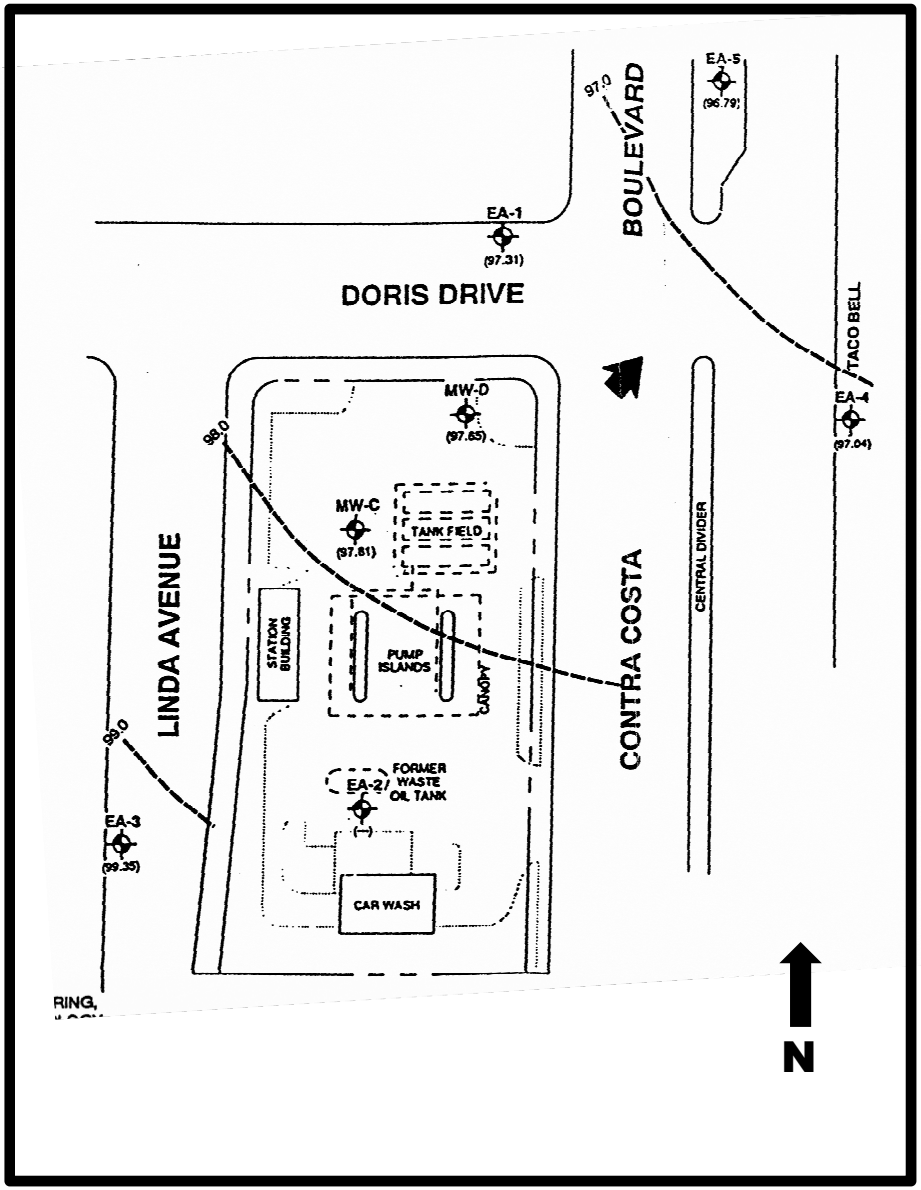
6/6/1990



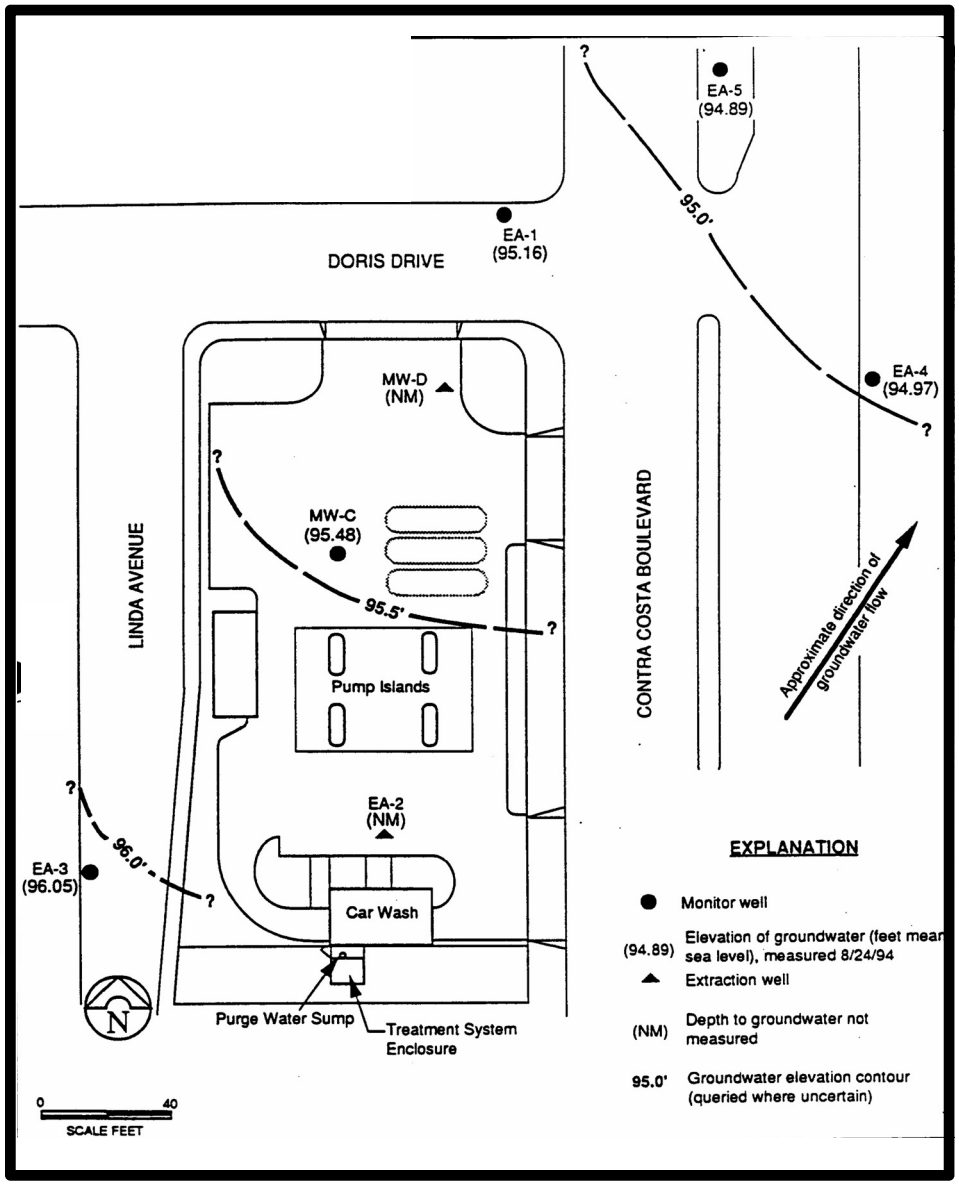
12/18/1990

ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.

Slide #2



03/31/1991



08/24/1994

ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.

Slide #3

Groundwater Flow

Sewer Line

Iso-concentration – PCE Groundwater

Source: EA Engineering August 1989. Data collected June 1989.

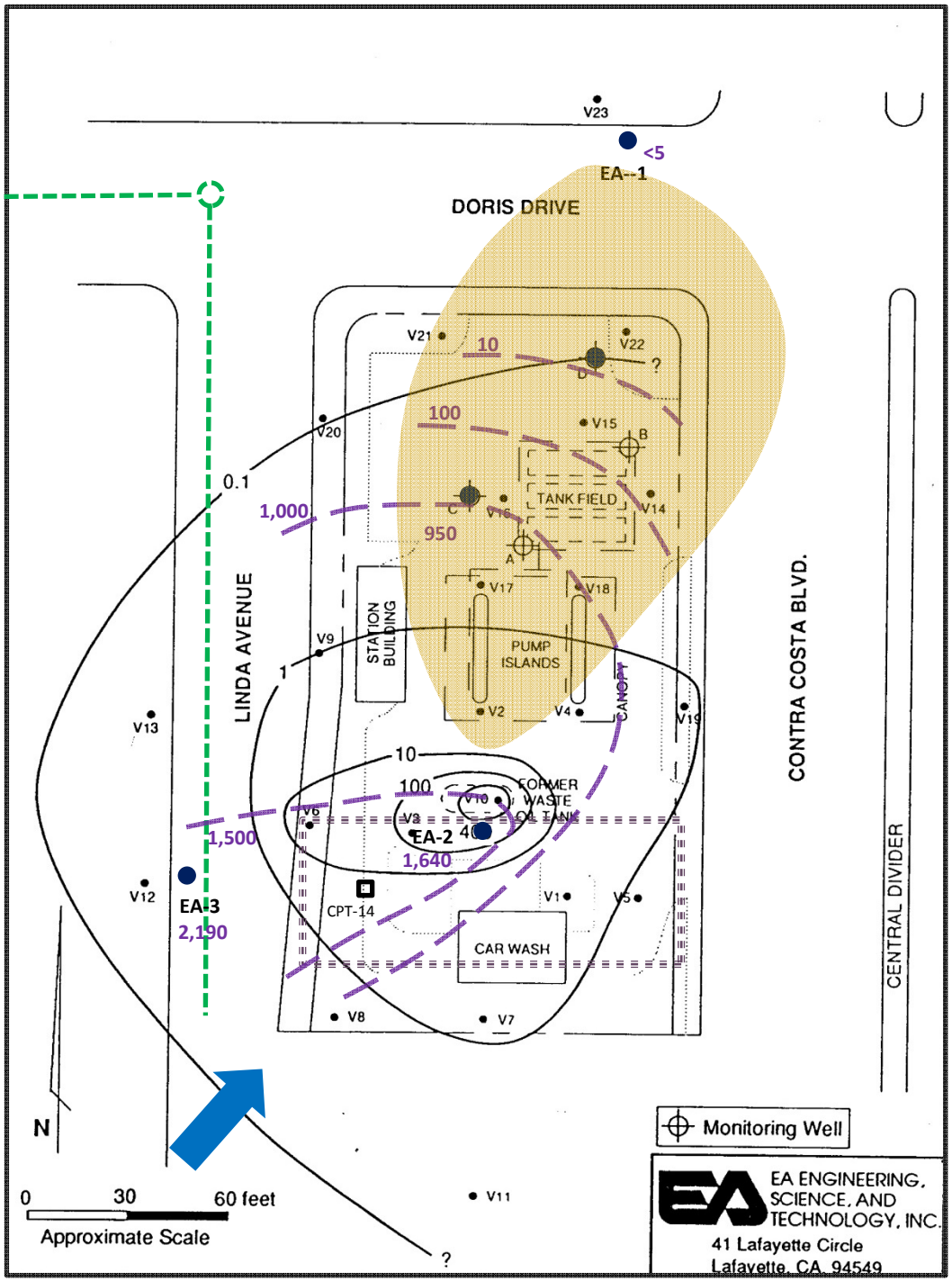
Elevated Petroleum Hydrocarbons

Source: EA Engineering August 1989. >1 ppb benzene. Data collected June 1989.

PCE in Soil Gas (ppmv)

Source: EA Engineering February 1989. Data collected May 1988.

Outline of former One Hour Martinizing Facility



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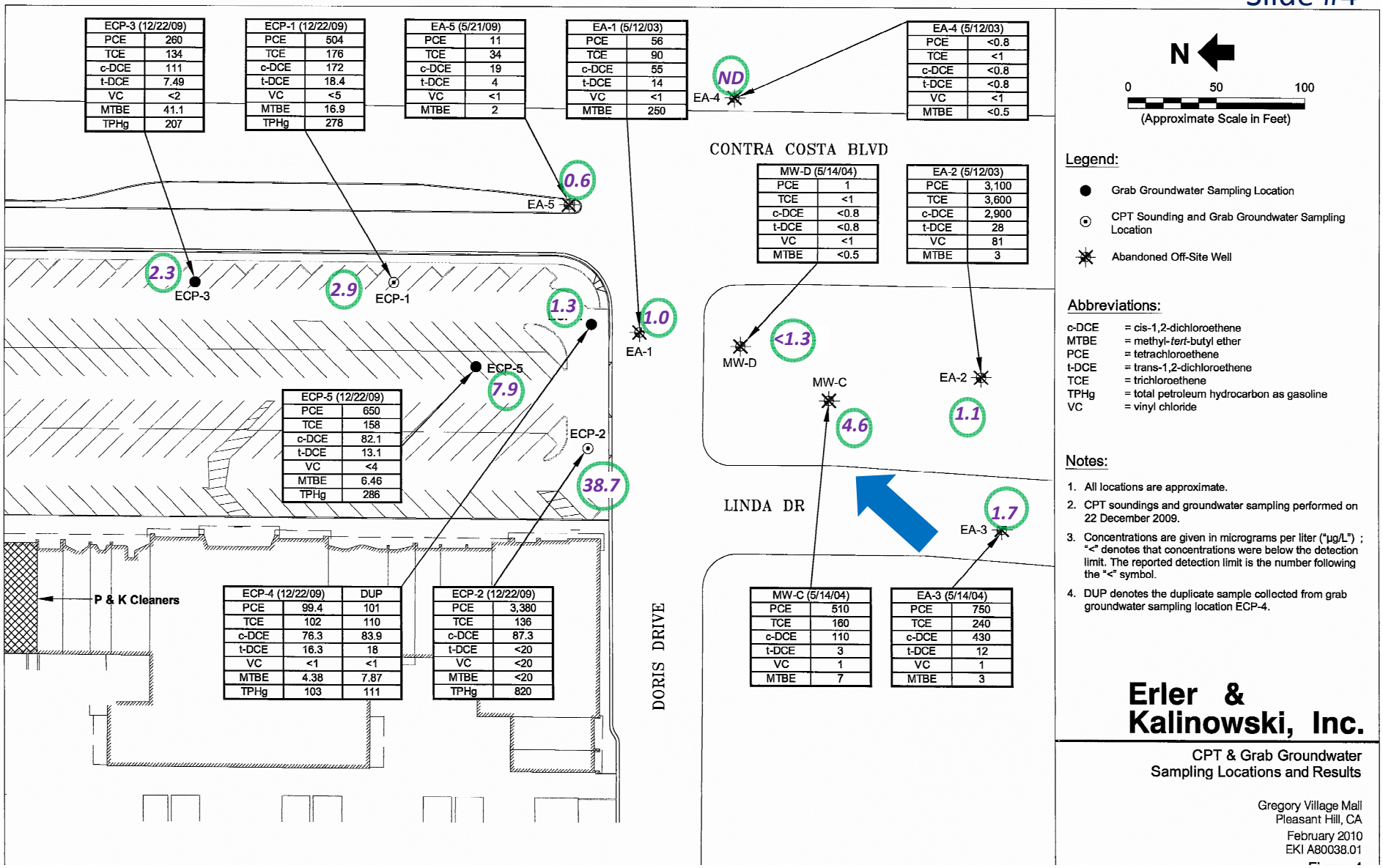
Slide #4



ECP-3 (12/22/09)	
PCE	260
TCE	134
c-DCE	111
t-DCE	7.49
VC	<2
MTBE	41.1
TPHg	207

ECP-1 (12/22/09)	
PCE	504
TCE	176
c-DCE	172
t-DCE	18.4
VC	<5
MTBE	16.9
TPHg	278

EA-5 (5/21/09)	
PCE	11
TCE	34
c-DCE	19
t-DCE	4
VC	<1
MTBE	2

EA-1 (5/12/03)	
PCE	56
TCE	90
c-DCE	55
t-DCE	14
VC	<1
MTBE	250

EA-4 (5/12/03)	
PCE	<0.8
TCE	<1
c-DCE	<0.8
t-DCE	<0.8
VC	<1
MTBE	<0.5

MW-D (5/14/04)	
PCE	1
TCE	<1
c-DCE	<0.8
t-DCE	<0.8
VC	<1
MTBE	<0.5

EA-2 (5/12/03)	
PCE	3,100
TCE	3,600
c-DCE	2,900
t-DCE	28
VC	81
MTBE	3

ECP-5 (12/22/09)	
PCE	650
TCE	158
c-DCE	82.1
t-DCE	13.1
VC	<4
MTBE	6.46
TPHg	286

ECP-4 (12/22/09)		DUP
PCE	99.4	101
TCE	102	110
c-DCE	76.3	83.9
t-DCE	16.3	18
VC	<1	<1
MTBE	4.38	7.87
TPHg	103	111

ECP-2 (12/22/09)	
PCE	3,380
TCE	136
c-DCE	87.3
t-DCE	<20
VC	<20
MTBE	<20
TPHg	820

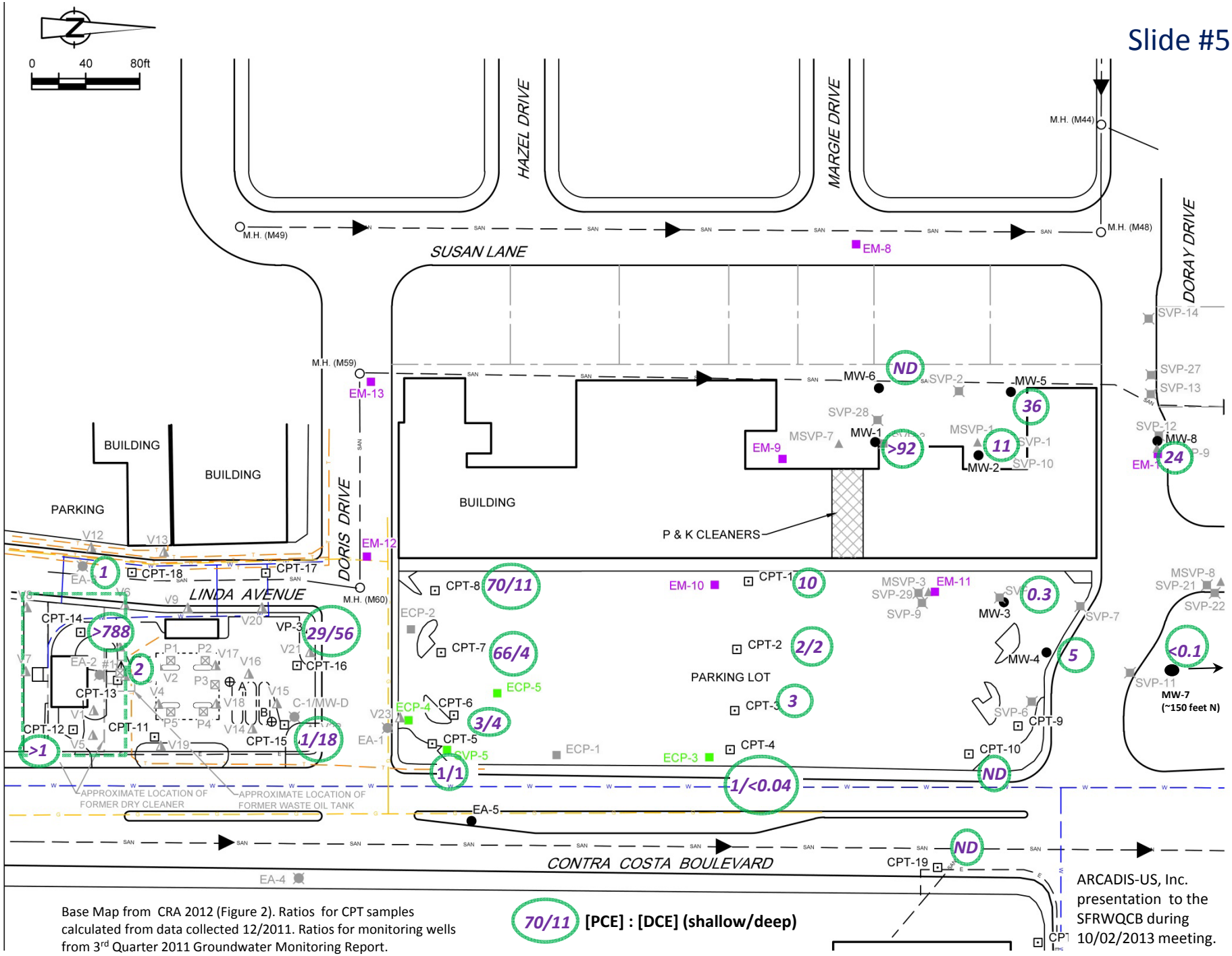
MW-C (5/14/04)	
PCE	510
TCE	160
c-DCE	110
t-DCE	3
VC	1
MTBE	7

EA-3 (5/14/04)	
PCE	750
TCE	240
c-DCE	430
t-DCE	12
VC	1
MTBE	3

Source: EKI , Inc., February 2010.

38.7 **PCE : DCE**

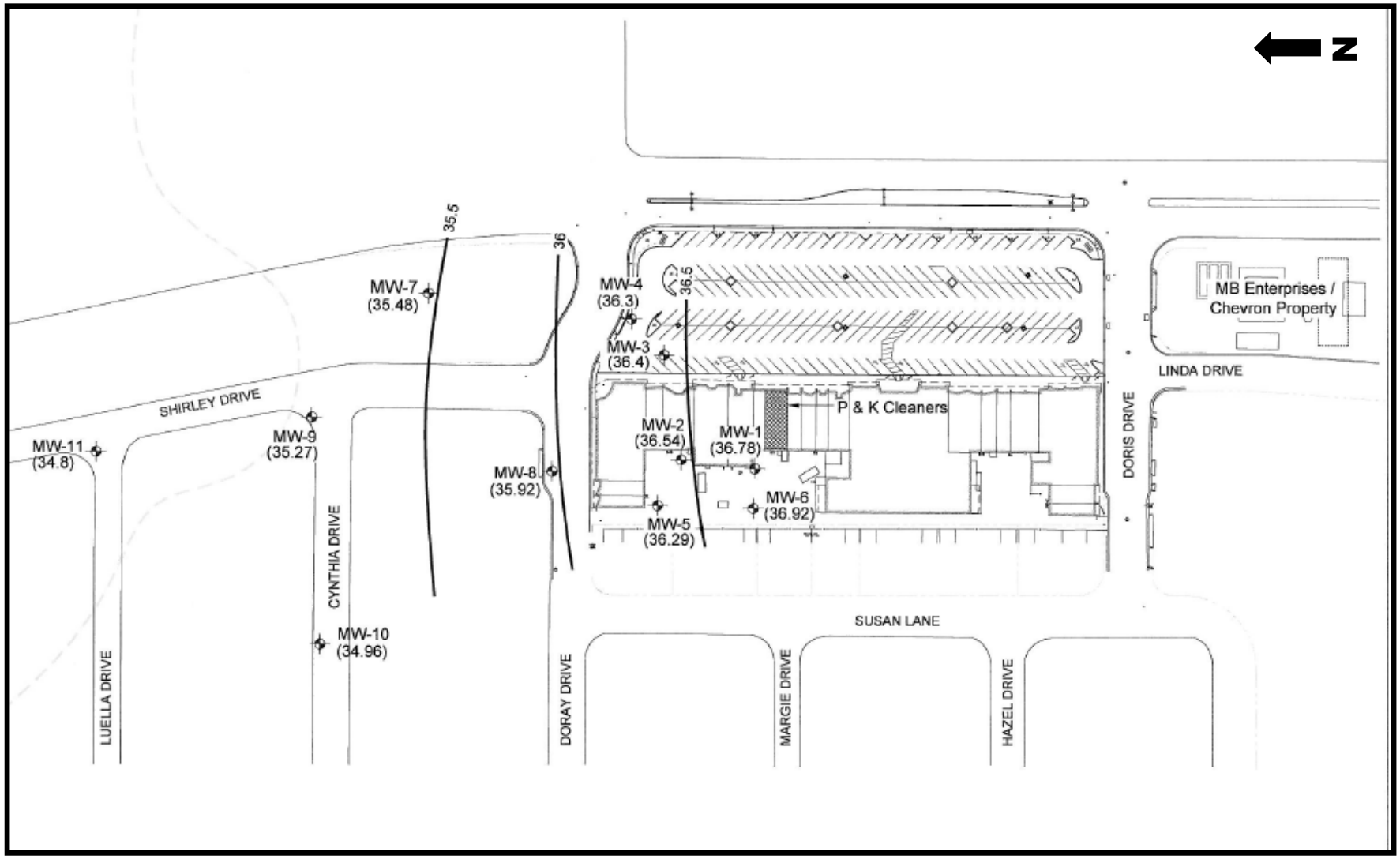
ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.



Base Map from CRA 2012 (Figure 2). Ratios for CPT samples calculated from data collected 12/2011. Ratios for monitoring wells from 3rd Quarter 2011 Groundwater Monitoring Report.

70/11 [PCE] : [DCE] (shallow/deep)

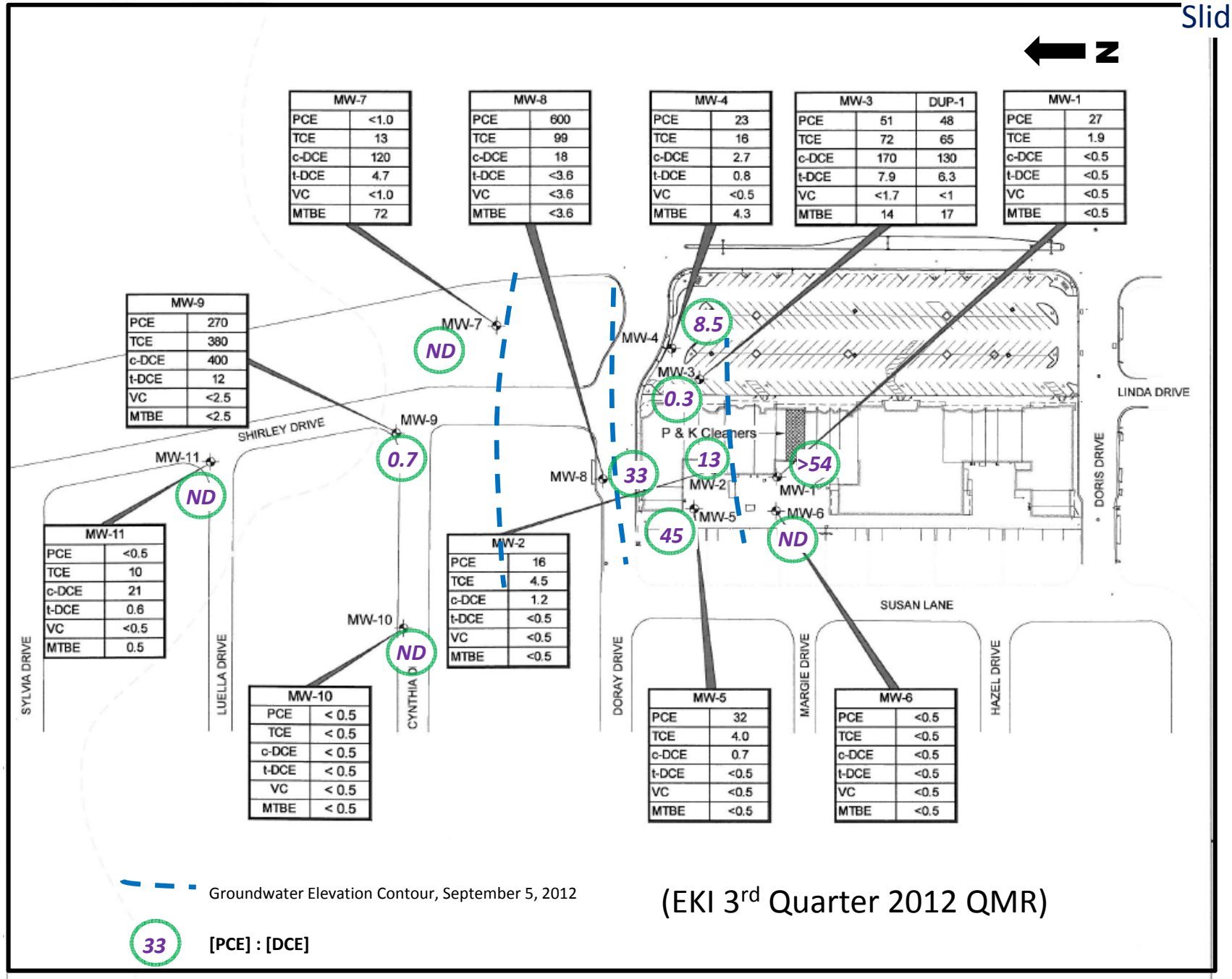
ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.



Groundwater Elevations September 5, 2012

(EKI 3rd Quarter 2012 QMR)

ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.



(EKI 3rd Quarter 2012 QMR)

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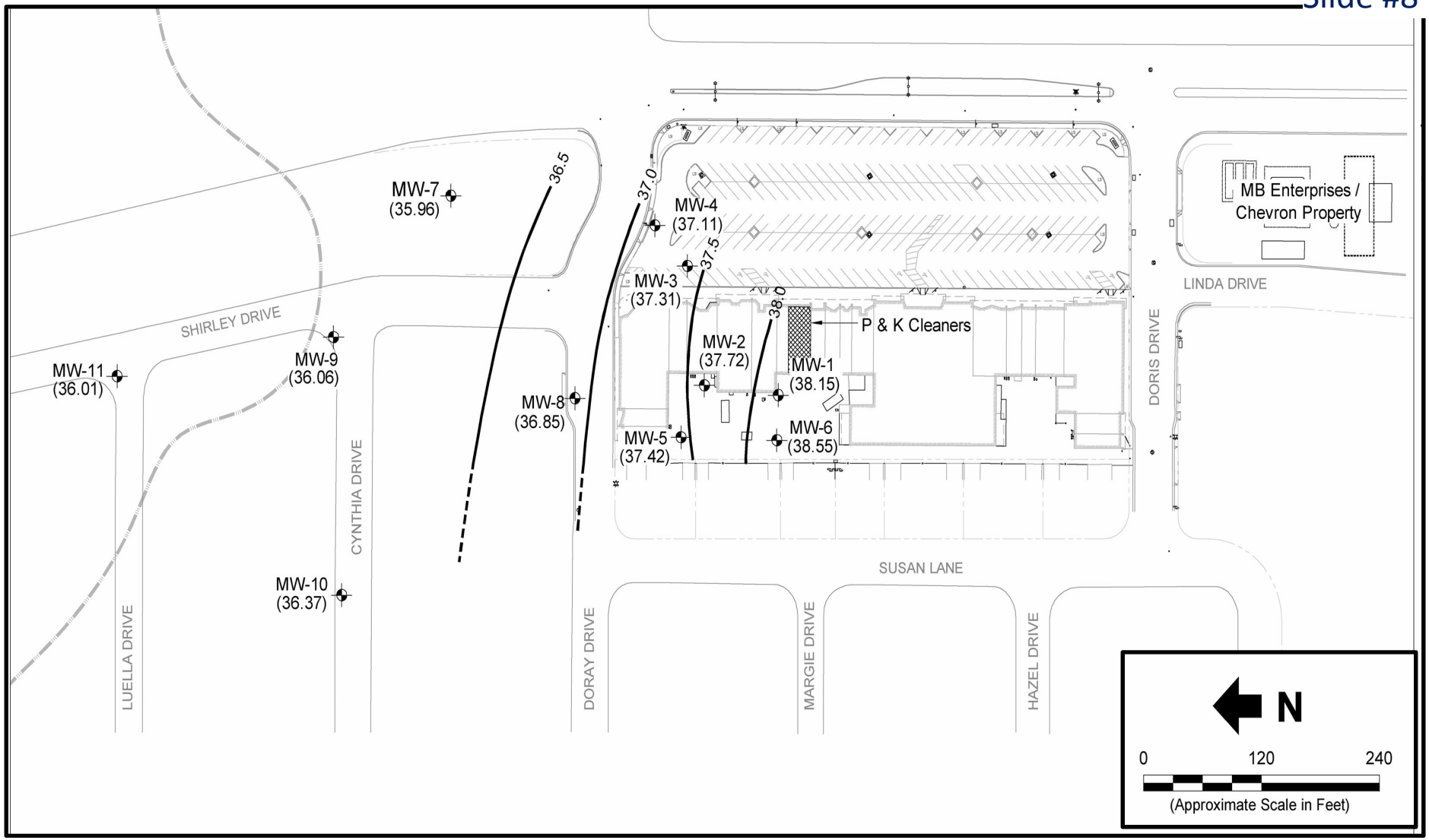
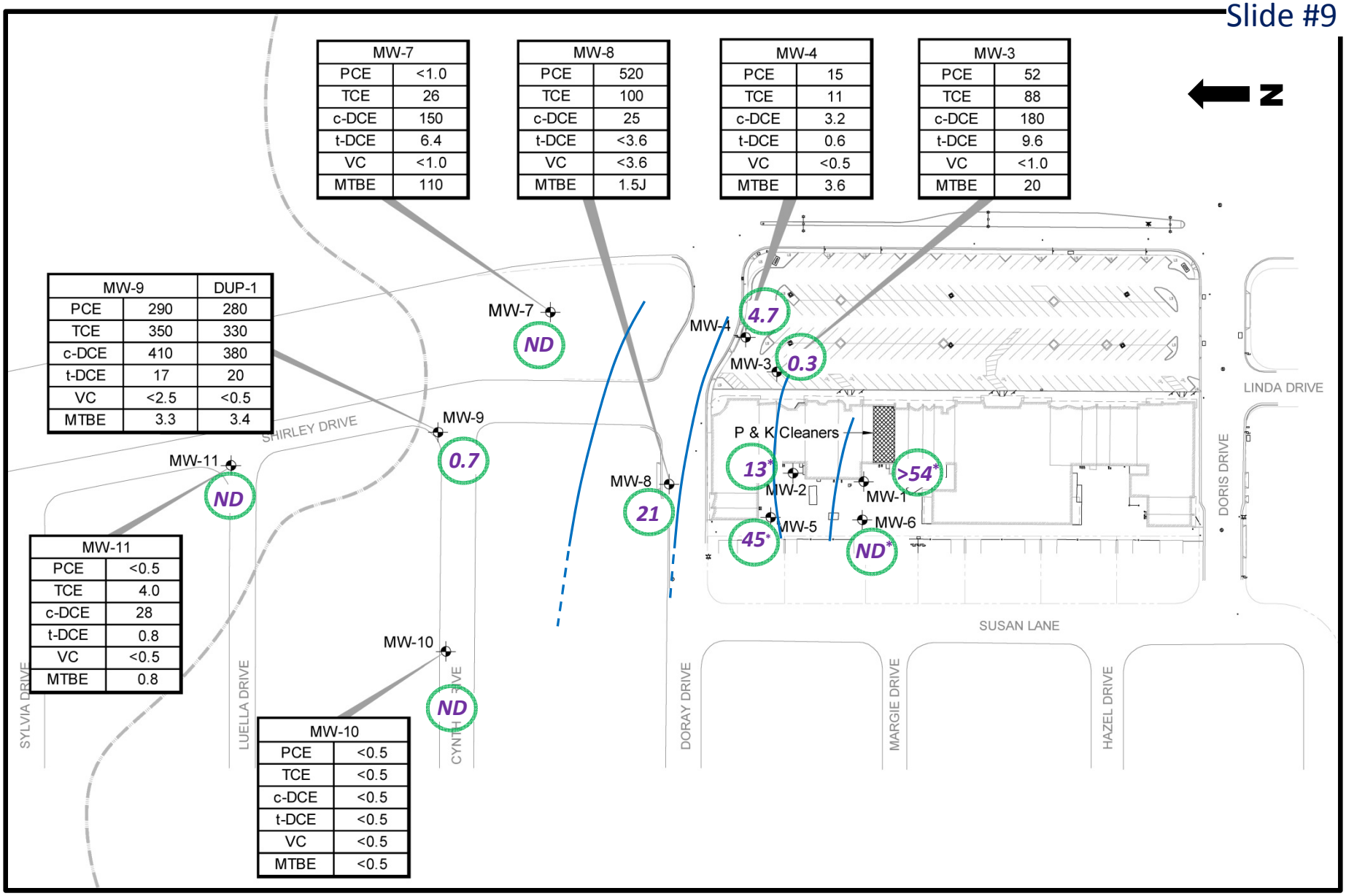


Groundwater Elevations, March 2013

(Source: EKI 1st Quarter 2013 QMR)

ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.

Slide #9



MW-7	
PCE	<1.0
TCE	26
c-DCE	150
t-DCE	6.4
VC	<1.0
MTBE	110

MW-8	
PCE	520
TCE	100
c-DCE	25
t-DCE	<3.6
VC	<3.6
MTBE	1.5J

MW-4	
PCE	15
TCE	11
c-DCE	3.2
t-DCE	0.6
VC	<0.5
MTBE	3.6

MW-3	
PCE	52
TCE	88
c-DCE	180
t-DCE	9.6
VC	<1.0
MTBE	20

MW-9		DUP-1
PCE	290	280
TCE	350	330
c-DCE	410	380
t-DCE	17	20
VC	<2.5	<0.5
MTBE	3.3	3.4

MW-11	
PCE	<0.5
TCE	4.0
c-DCE	28
t-DCE	0.8
VC	<0.5
MTBE	0.8

MW-10	
PCE	<0.5
TCE	<0.5
c-DCE	<0.5
t-DCE	<0.5
VC	<0.5
MTBE	<0.5

24 **[PCE] : [DCE]**

Groundwater iso-elevation contour (March 2013)

* Data from 3rd Quarter 2012 (most recent available)

(Source: EKI 1st Quarter 2013 QMR)

ARCADIS-US, Inc. presentation to the SFRWQCB during 10/02/2013 meeting.

Forensic Report for Groundwater Samples Collected in Pleasant Hill, California

Isotope Project #42461

Report Prepared for:

ARCADIS US, Inc.

Report Prepared by:

Yi Wang, PhD

Director, ZymaX Forensics Isotope

600 S. Andreasen Drive, Suite B

Escondido, CA 92029-1917

October 9, 2013

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INTRODUCTION

Ten groundwater samples and four trip blank samples were received at the ZymaX Forensics Isotope Laboratory on December 6th, 9th, 16th, and 22nd, 2011 for volatile organic compounds (VOCs) composition test and stable isotope analyses (Three Dimensional-Compound Specific Isotope Analysis, 3D-CSIA for carbon, chlorine, and hydrogen isotopes). The samples were logged in as, ZymaX Forensics Isotope Project #42461. The groundwater samples were collected from the vicinity of two former dry cleaner locations: one located at 1601-1609 Contra Costa Blvd., and the other located at 1705 to 1709 Contra Costa Blvd, both in Pleasant Hill, California (**Figure 1**). The goal of this study was to assess whether compound specific isotope fingerprinting tools could be used to assess the potential source(s) for volatile organic compounds (VOCs) that have been detected in the vicinity of these two properties.

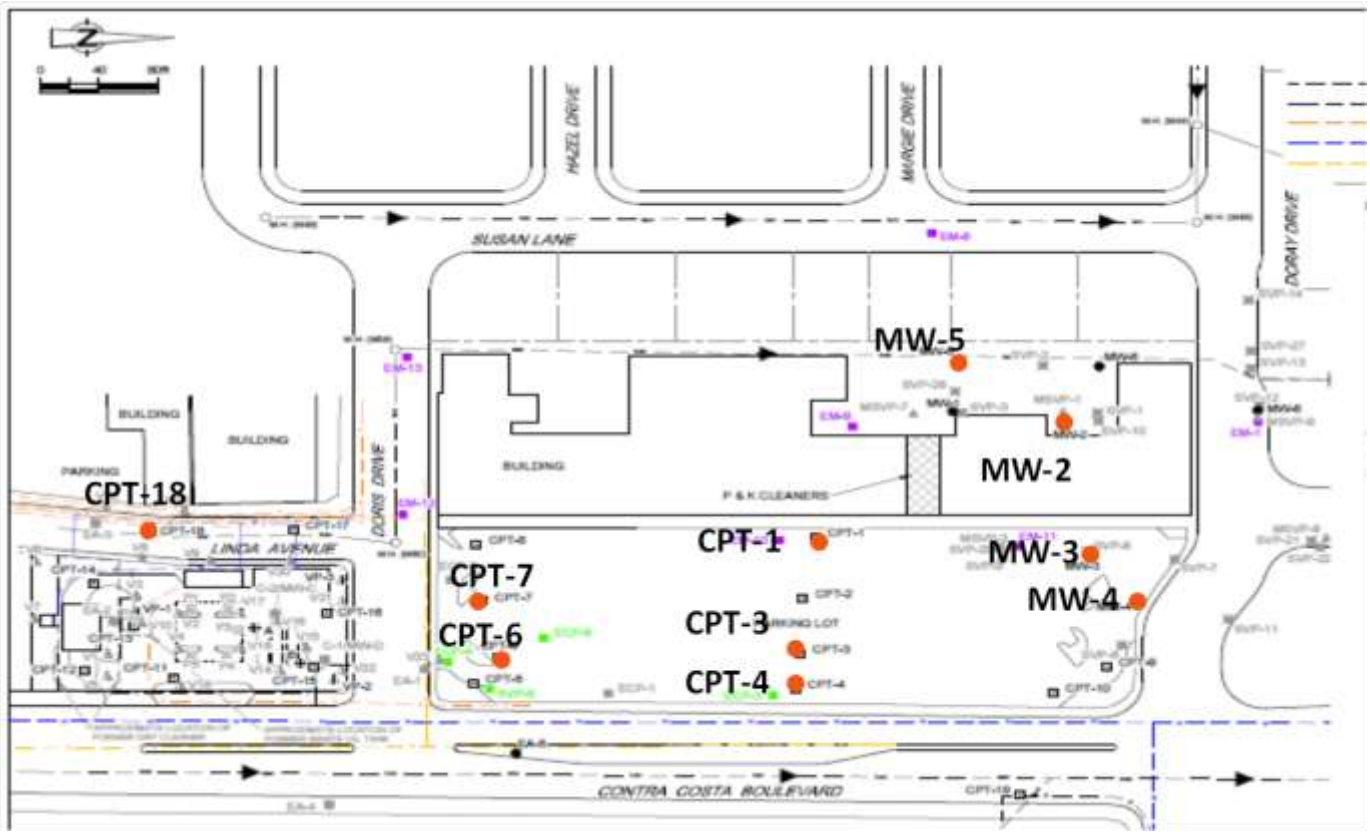

Figure 1 Site plan for 10 groundwater samples collected in Pleasant Hill, California.

METHODOLOGY

Traditional analytical methods for VOCs and molecular fingerprinting analysis, such as gas chromatograph-mass spectrometry (GC-MS), are unable to differentiate chlorinated solvents, such as PCE and TCE, from different releases (sources), because: (1) unlike petroleum hydrocarbon products which are mixture of hydrocarbons with useful biomarkers and also abundance ratio tools, chlorinated solvents are often used as a single compound, e.g. PCE as a popular dry cleaning reagent; and (2) any chlorinated solvent of different sources are chemically identical on any traditional analytical instruments, such as GC-MS, etc.

Chemically identical PCE or TCE from different sources, however, may have an isotopic difference. If used wisely with caution, compound specific isotope analysis (CSIA) of individual compounds in a sample mixture may help identify chlorinated solvents of the same source, or distinguish between chlorinated solvents from different sources. New lines of evidence provided by the isotope analysis, however, must be consistent with any known site hydrogeology information so that reasonable and defendable conclusions can be made.

The basis of the stable isotope analytical method is that many elements exist in nature in more than one isotopic form (Clark, I. and Fritz, P. 1997). For example, carbon exists in two stable isotopic forms: ^{12}C, with 6 protons and 6 neutrons, accounts for about 99% of carbon; ^{13}C, with also 6 protons while 7 neutrons, accounts for about 1% of carbon. The ratio of the isotopes of an element is not the same in all naturally occurring compounds. There are small variations caused by the different atomic weights of the isotopes. Thus, ^{13}C react the same as ^{12}C in chemical transformations, but the heavier ^{13}C can be discriminated against in processes where weight is important, such as evaporation and diffusion.

The heavier isotope also forms a slightly stronger bond with other atoms (X), and when such bonds are broken in chemical or enzymatic reactions, slightly less of the ^{13}C-X bonds are broken. If all the C-X bonds are broken, the ratio of $^{13}C/^{12}C$ in the starting material is the same as in the product. But if the reaction does not go to completion, the product may be enriched in ^{12}C, and the starting material enriched in ^{13}C.

This isotope fractionation (changes in the isotope ratios) can occur when carbon-containing compounds are biodegraded in the environment.

In the industrial manufacturing of chemicals, including chlorinated solvents, stable isotope ratios of the final product depends on the stable isotope ratios of the feedstock and the manufacturing processes used to convert the feedstock into the final product. For example, many investigations have documented that differences exist in the stable isotope ratios of PCE and TCE produced by various manufacturers (van Warmerdam et al., 1995; Ertl et al., 1998; Shouakar-Stash et al., 2003). Therefore stable isotope ratios determined by CSIA provide a method for potentially discriminating between contaminants such as PCE or TCE from different releases (sources) and as a method for identifying contaminants potentially from the same release (source) at complex sites. This knowledge can be used to identify the parties that were responsible for the contamination (Hunkeler et al., 2004; Stark et al., 2003; Walker, et al., 2005) and CSIA has been accepted as one line of evidence in litigation (U.S. EPA Guidance on CSIA, 2008).

Stable isotope analysis has been recognized by the U.S. Environmental Protection Agency (EPA) as an advanced site diagnostic tool, which has an array of applications for organic pollutants, contaminated site investigation, and remediation. Carbon, chlorine, and hydrogen isotope ratios determined by 3D-CSIA provide a method for potentially discriminating between chlorinated solvents such as PCE and TCE from different releases (sources) or a method for identifying solvents potentially from the same release (source) at complex sites.

Dr. John Wilson from the U.S. EPA has given four webinars featuring the use of stable isotope analyses:

1. June 16, 2010 - Stable Isotopes Analyses to Understand the Degradation of Organic Contaminants in Ground Water (Summary)
2. Sept 9, 2010 - Stable Isotopes Analyses to Understand the Degradation of Organic Contaminants in Ground Water (Part 1)
3. Sept 16, 2010 - Stable Isotopes Analyses to Understand the Degradation of Organic Contaminants in Ground Water (Part 2)
4. Oct 27, 2010 - Applications of Stable Isotopes Analyses to Environmental Forensics (Part 3) and to Understand the Degradation of Chlorinated Organic Contaminants (Part 4)

The U.S. EPA's Report (A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis, December 2008) describes the benefits and value of data provided by CSIA, and contrasts the information provided by CSIA to information provided by long-term monitoring of concentrations of contaminants, or information provided from techniques where specific stable isotopes are added to environmental samples.

Stable Isotope Ratios

Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element. For carbon it is the ratio of ^{13}C, with a terrestrial abundance of 1.11%, to common ^{12}C which represents 98.89% of terrestrial carbon. Thus the $^{13}C/^{12}C$ ratio is about 0.011.

Measuring an absolute isotope ratio requires rather sophisticated mass spectrometers. Rather than measuring a "true ratio", its "apparent ratio" can be easily measured by gas source mass spectrometry. To cancel the instrumental error due to operational variations in different laboratories and instruments, etc., a known reference can be measured on the same instrument at the same time (Clark and Fritz, 1997). The difference between the measured ratios of the sample and reference is expressed by the delta (δ) notation. Further, δ values are expressed as parts per thousand or per mil (‰) difference from the reference, for carbon:

$$\delta^{13}C = [(^{13}C/^{12}C_{sample}) / (^{13}C/^{12}C_{standard}) - 1] \times 1000‰ \text{ PDB}$$

where PDB is the name of the reference used, in this case Pee Dee Belemnite, a belemnite rostrum from the Cretaceous Peedee formation of South Carolina. The standard, by definition, has a δ value of 0‰, and samples may have positive or negative δ values depending on whether the sample is enriched or depleted in the heavier isotope relative to the international standard. Positive δ values are commonly referred to as being isotopic heavier and negative δ values are referred to as isotopic lighter. The sedimentary carbonate PDB lies at the heavy end of the naturally occurring carbon range, so most terrestrial materials on earth have negative δ values. For example, a δ-‰ value that has a positive value

of +5‰, signifies that the sample has 0.5% more ^{13}C than the reference, or is enriched by 5‰. Similarly, a sample that is depleted from the reference by this amount would be expressed as $\delta^{13}C$ = -5‰ PDB.

The ratios for the other elements, such as hydrogen, chlorine, oxygen, sulfur, or nitrogen, are expressed in the same way relative to their specific standards. For oxygen or hydrogen isotopes, the accepted reference is Standard Mean Ocean Water (SMOW); for the chlorine isotope, it is Standard Mean Ocean Chloride (SMOC); for the sulfur isotope, it is the troilite (FeS) phase of the Canon Diablo meteorite (CDT); for the nitrogen isotope, it is atmospheric nitrogen (Air).

Stable Isotope Fractionation

The isotopic ratio of an element is not the same in all naturally occurring compounds. There are small variations caused by the different atomic weights of the isotopes. When one of the above heavy isotopes is a part of a compound, its bond to adjacent atoms is slightly stronger than the equivalent bond of the lighter isotope when it is in the same position in another molecule of the same compound. When molecules of this compound enter into chemical or biologically mediated reactions, the molecules with the lighter isotopes react slightly faster than the ones with the equivalent heavier isotopes. Thus, for example, a ^{13}C atom can act the same as ^{12}C in chemical transformations, but the heavier ^{13}C can be discriminated against in such processes. The heavier isotope ^{13}C forms a slightly stronger bond with other atoms (e.g., chlorine), and when such bonds are broken in chemical or enzymatic reactions, slightly less of the ^{13}C-Cl bonds are broken. If all the C-Cl bonds are broken, the ratio of $^{13}C/^{12}C$ in the starting material is the same as in the product. But if the reaction does not go to completion, the product may be enriched in ^{12}C, and the starting material enriched in ^{13}C. This means that, as the reaction proceeds, the reactant that remains has a progressively higher content of the heavy isotope since the molecules containing light isotopes have reacted to form product faster than those containing heavier isotopes. Such process, i.e., change in the stable isotope ratios, is called “stable isotope fractionation”. Fractionation processes will slightly modify the stable isotope ratio for any compounds containing a target isotope, such as carbon.

CSIA for Carbon and Hydrogen Isotopes

Under constant operating conditions, the standard deviation of the mean of the replicate measurements for chlorinated solvents is typically <0.5‰ for $\delta^{13}C$ values, and <5‰ for $\delta^{2}H$ values.

CSIA for carbon isotopes involves a three step process using GC-IRMS: (1) separation of individual carbon-bearing compounds on a gas chromatograph (GC from Agilent, USA), (2) quantitative conversion of each compound to CO_2 in a high temperature combustion oven with CuO at 850°C, and (3) removal of H_2O produced in combustion, and introduction of the CO_2 derived from each compound into the isotope ratio mass spectrometer (IRMS from Micromass Isoprime, UK) for isotope analysis (as shown in **Figure 2**).

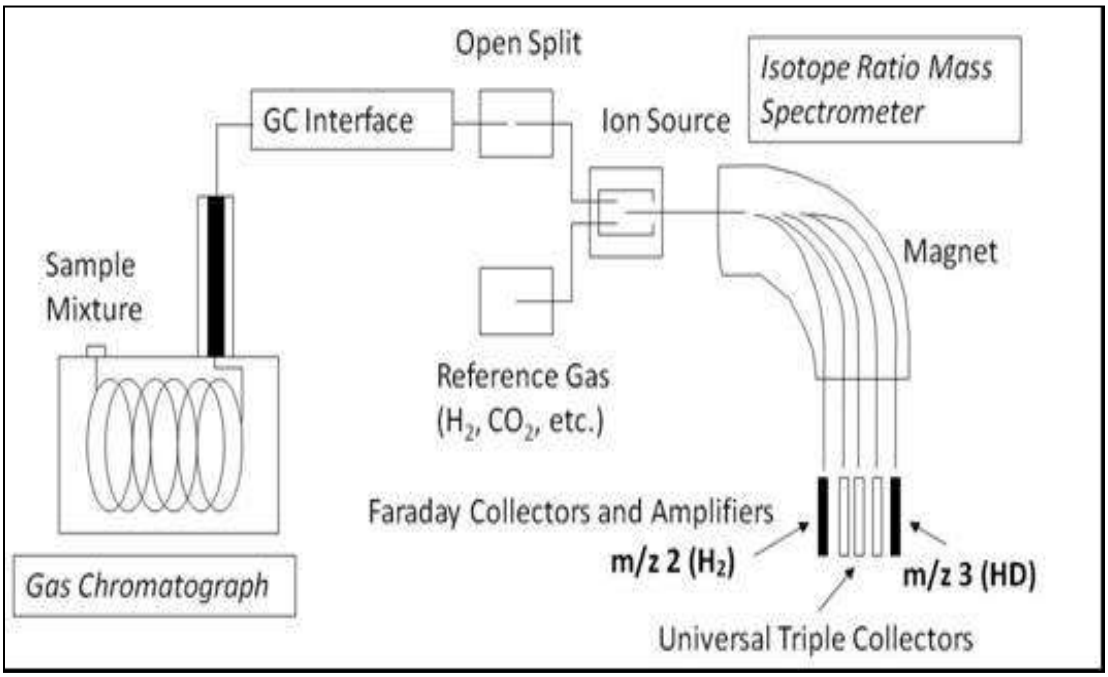

Figure 2 Schematic of the GC-IRMS and general procedure used in carbon and hydrogen CSIA

After ionization of CO_2, the mass spectrometer separates ions with different mass-to-charge ratios in space, allowing the simultaneous measurement of the ions with fixed Faraday cups. The high precision required in CSIA at the natural abundance level of stable isotopes can be achieved only with this simultaneous ion measurement. A typical GC-IRMS chromatogram by carbon CSIA of chlorinated solvents is shown in **Figures 3**.

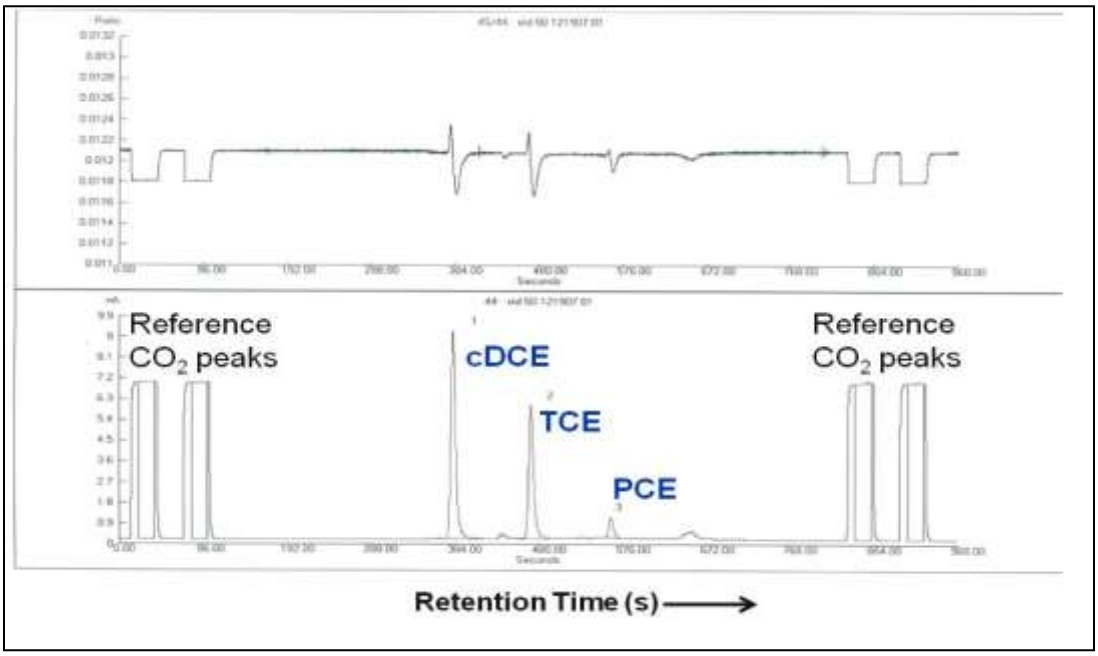

Figure 3 A GC-IRMS Chromatogram by Carbon-CSIA for cDCE, TCE, and PCE

For hydrogen isotopes, the same three-step process applies except for the conversion of each compound to H_2 and C in a higher temperature oven with chromium (Cr) at 1050°C, and introduction of the H_2 derived from each compound into the mass spectrometer for hydrogen isotope analysis.

CSIA for Chlorine Isotopes of CVOCs

Unlike carbon and hydrogen isotope CSIA which have become available for decades, until recently, chlorine isotope analysis by traditional methods could not be carried out without lab-intensive, offline pretreatments to convert chlorinated compounds into a molecule containing a single chlorine atom, such as methyl chloride (CH_3Cl). After such conversion, the chlorine isotope ratio is determined using a dual-inlet isotope ratio mass spectrometer. The complex sample preparation process is the main disadvantage of conventional chlorine isotope analysis. However, high-precision isotopic analysis (±0.1‰) is achievable with these techniques.

Since 2009, chlorine isotopes of CVOCs, including PCE and TCE, have been analyzed using a modified method originally based on work of Sakaguchi-Söder et al. (2007) and later optimized based on work of Jin et al. (2011). This is a simple, quick, and sensitive CSIA method for chlorine isotope of CVOCs by using gas chromatography coupled to a quadrupole mass spectrometer (GC-qMS, Agilent, USA). In contrast to carbon and hydrogen, the two stable isotopes of chlorine are two-mass units apart and both occur at relatively similar abundances (^{35}Cl at 75.78% and ^{37}Cl at 24.22%). These characteristics enable a scanning quadrupole MS to record mass spectral data precisely to calculate isotope ratios. However, unlike an IRMS, which allows detecting several masses simultaneously, a GC-qMS has only one detector, which records selected masses consecutively. Therefore, instrument parameters of a quadrupole MS including dwell time, number of selected masses, etc., are crucial factors for the reproducibility and precision of chlorine CSIA using GC-qMS.

The chlorine isotopes by GC-qMS technique does not require off-line sample pretreatments, but requires complicated mathematical data analysis to derive chlorine isotope ratios from mass spectra. The chlorine isotope ratios of target compounds, such as PCE, are calculated from the peak areas of selected molecular ions and fragment ions of the substances (as shown in **Figure 4**), using a set of unique mathematic equations.

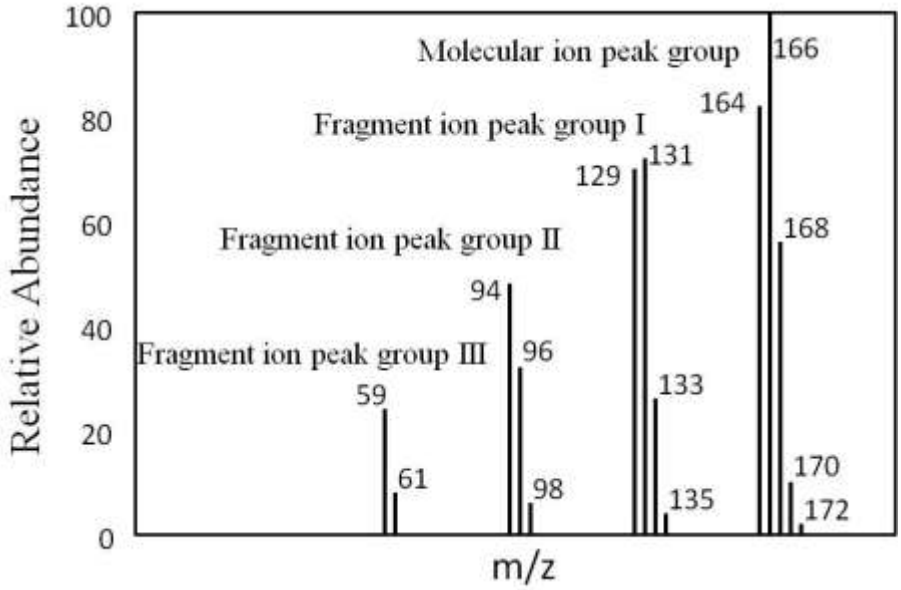

Figure 4 Molecular and Three Fragment Ion Peak Groups of PCE Obtained from a GC-qMS

Besides the evaluable schemes used to calculate chlorine isotope ratios, instrumental settings including split ratio, ionization energy, and dwell times are also evaluated to optimize the chlorine isotope measurement of chlorinated solvents. With the established SPME sample preparation protocols, samples of PCE and TCE at aqueous concentrations in the range of 10-500 µg/L, precisions with relative standard deviations typically are within ±1‰.

Sample preparation

All groundwater samples collected were preserved with HCl during sample collection in the field. Up to eight VOA vials (40mL) were collected for each sample, so both VOCs and CSIA tests could be performed. Trip blanks filled with pure water were used for each batch of sample collection and submission. All samples received for CSIA were checked for any headspace and noted on the chain of custody forms. All samples were kept in dark in a refrigerator below 4°C while waiting for their VOCs results to become available.

When CSIA is performed on a sample, VOCs are extracted from water samples on a Solid Phase Micro-Extraction (SPME) fiber (U.S. EPA 2008). In a temperature-controlled room at 25°C, the SPME fiber is placed in the headspace of a vial above 35mL of the water sample, which has been allowed to stir for 60 minutes to achieve equilibrium of the volatile compounds between water and headspace. After another 30 minutes, the SPME fiber is inserted into the GC injection port.

VOCs are desorbed from the SPME fiber at a high temperature (300°C) in the GC injection port and into a helium carrier gas flow. *c*DCE, TCE, and PCE, etc., if present are separated on the GC column, flushed in the carrier gas through the furnace to convert the carbon or hydrogen in each compound to CO_2 or H_2 and the isotope ratios are measured in the IRMS. Three pulses of reference gas are injected during each sample run to calibrate CO_2 or H_2 signals from the sample peaks. For chlorine isotope analysis, separated CVOCs enter the ion source of mass spectrometer detector directly for analysis.

RESULTS AND DISCUSSION

Six "CPT" wells and four "MW" wells were chosen for groundwater sample collection in December 2011. Well location for 3D-CSIA forensics is displayed in **Figure 1**. The concentrations of VOCs were measured by Method EPA 8260B in December 2011, and shown in **Table 1**.

Table 1 VOCs Result in 14 Samples collected for 3D-CSIA forensics

ZymaX	Sample	Concentrations of VOCs in µg/L						
Lab ID	Well ID	PCE	TCE	*c*DCE	*t*DCE	VC	*c*DCE%	MTBE
42461-1	MW-2-W-111202	15	7.2	2.3	<1.0	<0.5	13.3	<1.0
42461-2	MW-3-W-111202	61	82	160	8.7	<0.5	60.5	33
42461-3	MW-4-W-111202	28	22	5.9	1.2	<0.5	14.9	15
42461-4	MW-5-W-111202	40	5	<1.0	<1.0	<0.5	3.4	<1.0
42461-6	CPT-7-W-18'-22'	1200	44	<10	<10	<5.0	1.3	<10
42461-8	CPT-1-W-15'-20'	560	250	57	<1.0	<2.5	10.0	1.0
42461-9	CPT-4-W-15'-20'	5.2	14	6.3	<1.0	<0.5	30.5	13
42461-10	CPT-3-W-15'-20'	30	43	15	2.4	<0.5	22.5	28
42461-11	CPT-6-W-16'-20'	200	130	100	14	<0.5	30.6	6.7
42461-13	CPT-18-W-20'-25'	3.2	3.0	2.5	<1.0	<0.5	33.0	<1.0
42461-5	TB-111202	<1.0	<1.0	<1.0	<1.0	<0.5	0	<1.0
42461-7	TB-20111207	<1.0	<1.0	<1.0	<1.0	<0.5	0	<1.0
42461-12	TB-20111215	<1.0	<1.0	<1.0	<1.0	<0.5	0	<1.0
42461-14	TB-20111221	<1.0	<1.0	<1.0	<1.0	<0.5	0	<1.0

PCE: Tetrachloroethylene
TCE: Trichloroethylene
*c*DCE: *cis*-1,2-Dichloroethylene
*t*DCE: trans-1,2-Dichloroethylene
VC: Vinyl Chloride
MTBE: Methyl-t-Butyl Ether
*c*DCE%: Molar percentage of cDCE among all chlorinated components detected

Molecular Fingerprinting Evidence

A series of QA/QC samples were used for this study. Four samples #42461-5, #42461-7, #42461-12, and #42461-14 were used as trip blanks for each batch of sample collection and shipment. Target compounds for this study, PCE, TCE, *c*DCE, MTBE, and BTEX compounds were absent in these trip blank samples, indicating other samples were collected without secondary contamination either in the field or during the sample shipment.

As seen in **Table 1**, PCE and TCE are the most commonly detected VOCs at the site. The highest PCE concentrations were observed in the samples from three "CPT" monitoring wells, CPT-7 (1200µg/L), CPT-1 (560µg/L), CPT-6 (200µg/L), and one "MW" well, MW-3 (61µg/L). The highest TCE concentrations were observed in the samples from the same four well locations (**Figure 1**) but in different order: CPT-1 (250µg/L), CPT-6 (130µg/L), MW-3 (82µg/L), and CPT-7 (44µg/L).

MTBE, a gasoline additive, was observed in most of groundwater samples except in two of the "MW" wells located to the north-northwest (MW-2 and MW-5).

As a predominant biodegradation product of TCE, the significant amount of cDCE among all chlorinated hydrocarbons in most of groundwater samples indicate active in situ degradation of TCE in the plume, which could have altered isotope signatures of released PCE and/or TCE.

In order to determine whether the detected TCE is a degradation product of PCE, or is manufactured TCE from a separate TCE release it is necessary to analyze the samples using the new 3D-CSIA fingerprinting approach.

3D-CSIA Isotope Fingerprinting Evidence

Carbon, hydrogen, and chlorine isotope ratios of chlorinated solvent compounds in 10 groundwater samples were obtained at ZymaX Forensics Isotope Laboratory in December 2011 and are illustrated in **Table 2**.

Isotope ratios for certain samples were not determined (ND) due to either: (1) concentration of target compound was too low to ensure reliable isotopic results; (2) matrix interference, i.e., baseline co-elution affecting the generation of isotopic results.

Table 2 3D-CSIA Results of Chlorinated Solvents in 10 Samples

ZymaX Lab ID	Sample Well ID	$\delta^{13}C$ PCE	$\delta^{13}C$ TCE	$\delta^{13}C$ cDCE	$\delta^{37}Cl$ PCE	$\delta^{37}Cl$ TCE	$\delta^{2}H$ TCE
42461-1	MW-2-W-111202	-25.4	[a]-25.9	ND	2.1	ND	N/A
42461-2	MW-3-W-111202	-24.6	-24.8	-28.1	2.0	1.9	-142
42461-3	MW-4-W-111202	-23.8	-30.1	[a]-39.3	2.0	1.8	N/A
42461-4	MW-5-W-111202	-28.2	ND	ND	1.9	ND	N/A
42461-6	CPT-7-W-18'-22'	-27.5	-33.7	ND	2.0	1.7	[a]-125
42461-8	CPT-1-W-15'-20'	-24.7	-36.0	ND	1.9	1.7	-129
42461-9	CPT-4-W-15'-20'	[a]-16.7	-27.9	[a]-37.6	ND	1.8	N/A
42461-10	CPT-3-W-15'-20'	-23.8	-28.1	-24.6	2.1	1.9	[a]-142
42461-11	CPT-6-W-16'-20'	-27.2	-30.9	-28.1	2.0	1.8	-133
42461-13	CPT-18-W-20'-25'	[a]-28.3	ND	ND	ND	ND	N/A

ND: Ratio Not Determined due to low concentration and/or matrix interference
[a]: Estimate. Isotope ratio obtained at low concentration. Enhanced sensitivity on GC-IRMS
N/A: Certain samples were not analyzed for hydrogen CSIA upon client's request
PCE: Tetrachloroethylene
TCE: Trichloroethylene
*c*DCE: *cis*-1,2-Dichloroethylene

Use of CSIA Data for Site Investigation

The use of stable isotopes to differentiate manufacturers of chlorinated solvents has been proposed as a means to distinguish sources contributing to a co-mingled groundwater plume (Morrison, 1999). CSIA may also provide evidence of the time sequence of multiple releases at a site. The principle behind this is

that in older releases biodegradation may have altered the isotope ratio of the target component so the oldest release may be the most altered compared to the most recent one.

The low abundance of ^{37}Cl isotope fraction in chlorinated solvents is bound more tightly to carbon than are ^{35}Cl atoms (Bartholomew et al., 1954). The difference in bond strength results in chlorine isotope fractionation due to temperature and pressure differences during the manufacturing of the chlorinated solvents (Tanaka and Rye, 1991). For example, the isotopic range of TCE (>99.5% TCE) from multiple manufacturers has been reported to be: $\delta^{13}C$= -48.0 to -27.8‰, $\delta^{37}Cl$= -2.54 to +4.08‰, $\delta^{2}H$= -30 to +530‰ (Poulson and Drever, 1999).

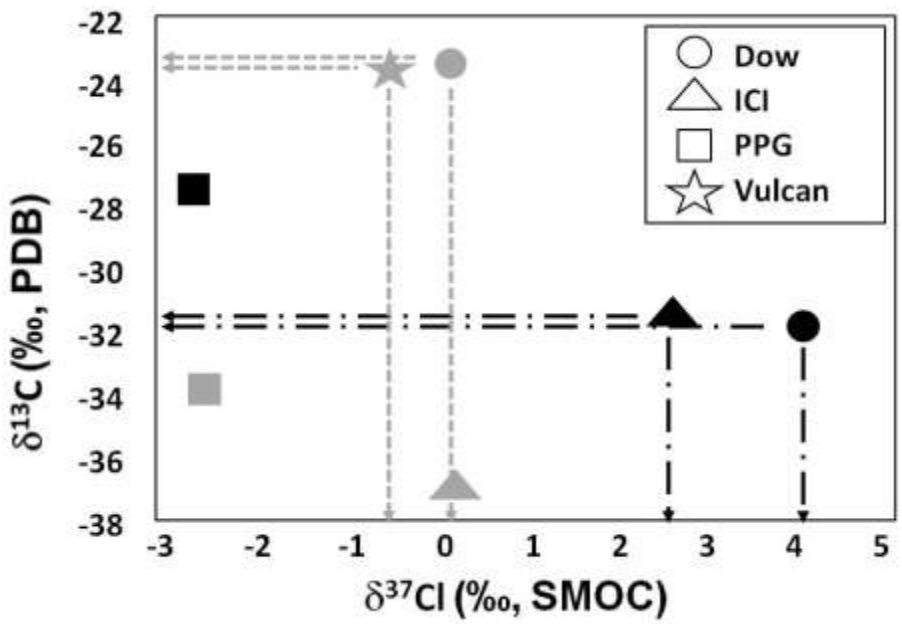

Figure 5 CSIA of PCE (grey) and TCE (black) of 4 manufacturers for $\delta^{13}C$ and $\delta^{37}Cl$ ratios

Figure 5 shows different $\delta^{13}C$ and/or $\delta^{37}Cl$ values of PCE and TCE from four manufacturers (modified from multiple sources). In one case, the isotopic ratios for $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ were used to distinguish among three chlorinated solvent manufacturers (van Warmerdam et al., 1995). In a similar application,

^{13}C and ^{37}Cl were used to discriminate between two different pure phase chlorinated solvent batches obtained from various manufacturers using CSIA (Beneteau et al., 1996).

Many studies have characterized selected chlorinated solvents in terms of their hydrogen, carbon and chlorine isotopic composition. Shouakar-Stash et al. (2003) noted that δ^2H for certain manufactured TCE varied between +466.9‰ and +681.9‰ due to the dehydrochlorination reactions used in the industrial production of TCE, whereas TCE generated as a dechlorination (a degradation pathways) product of PCE was significantly depleted (negative δ^2H), a result of H atom incorporation from the environmental water. This suggests that δ^2H of certain chlorinated solvents such as TCE may be a powerful means of distinguishing between degradation products and manufactured solvents, especially when TCE tested at the site has a fairly high δ^2H values.

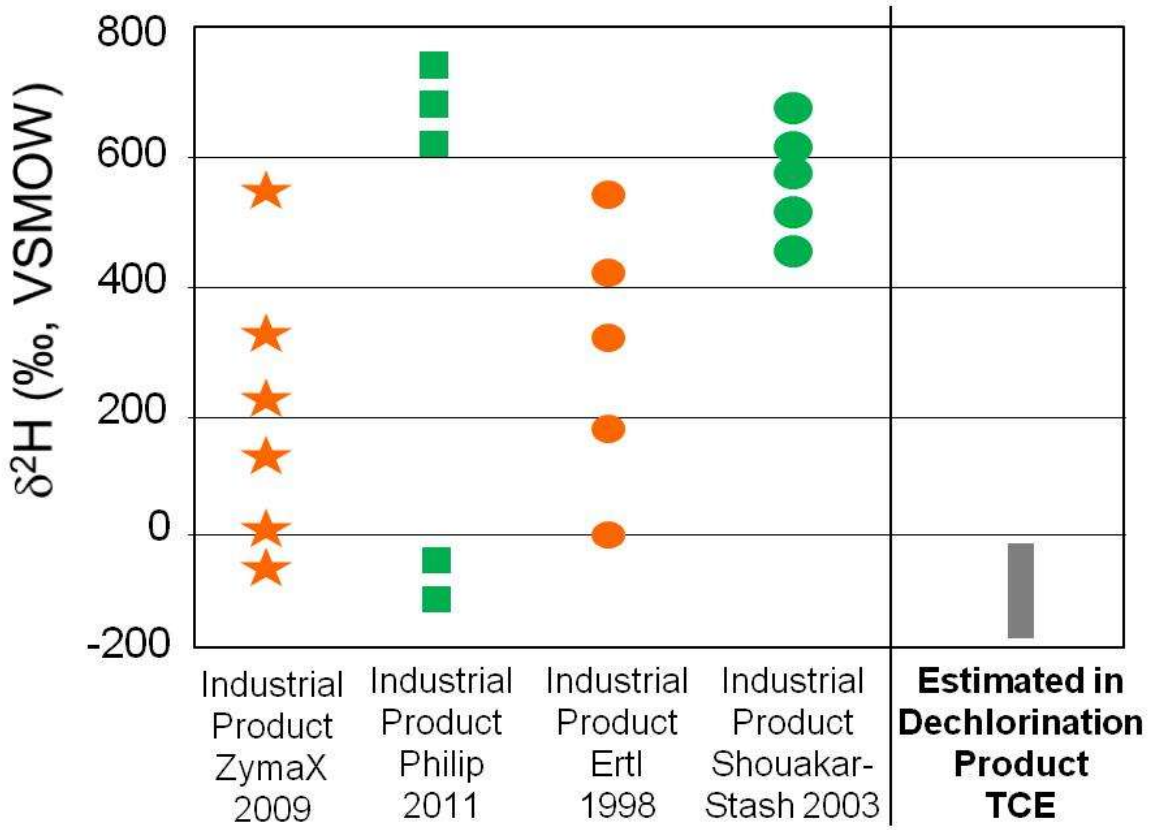

Figure 6 Summary of δ^2H ratios of industrial product TCE and dechlorination product TCE

Dechlorination Evidence from CSIA Forensics

In **Table 2**, hydrogen isotope analysis of TCE in five groundwater samples from the site showed strong evidence on TCE's origin at the site as a degradation product: δ^2H of TCE were between -142‰ and -125‰, which was within the estimated δ^2H ratio range in dechlorination product TCE of PCE as shown in **Figure 6**.

In addition, all TCE detected in the 10 groundwater samples have δ^{13}C and δ^{37}Cl ratios lighter than those of PCE by less than a few per mil. Such a trend in isotope ratios of PCE and TCE, demonstrated the fractionation occurring in carbon and chlorine isotopes during the in situ dechlorination process. Comparable isotope ratios for TCE to those PCE, along with even lighter isotope ratios for cDCE, further indicated the occurrence of TCE's degradation into cDCE at the site.

Therefore, based on carbon, chlorine, and hydrogen isotope ratios of chlorinated solvents detected in the samples, one conclusion made from this CSIA study is that the chlorinated compounds TCE and cDCE, originated during the dechlorination of released PCE.

CONCLUSIONS

By integrating molecular and CSIA isotope fingerprinting evidence obtained in this study, together with the known hydrologic and geologic information on the solvent plumes in Pleasant Hill, California, we have concluded that:

Hydrogen, carbon, and chlorine isotope ratios of TCE demonstrated TCE's origin as a daughter product of the released PCE, same for the other contaminants, such as cis-1,2-DCE.

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