## RECEIVED

By Alameda County Environmental Health at 3:50 pm, Mar 05, 2014



Mr. Jerry Wickham Alameda County Environmental Health 1131 Harbor Bay Parkway, Suite 250 Alameda, California 94502-6577 Shell Oil Products US

Soil and Groundwater Focus Delivery Group 20945 S. Wilmington Avenue Carson, CA 90810 Tel [425] 413 1164 Fax [425] 413 0988 Email perry.pineda@shell.com Internet http://www.shell.com

Re:

8999 San Ramon Road Dublin, California SAP Code 135244 Incident No. 97565995 Agency No. RO0002744

Dear Mr. Wickham:

The attached document is provided for your review and comment. Upon information and belief, I declare, under penalty of perjury, that the information contained in the attached document is true and correct.

As always, please feel free to contact me directly at (425) 413-1164 with any questions or concerns.

Sincerely, Shell Oil Products US

0

Perry Pineda Senior Environmental Program Manager



5900 Hollis Street, Suite A Emeryville, California 94608 (510) 420-0700

Telephone:

Fax: (510) 420-9170

www.CRAworld.com

				TR	ANS	MITT	AL					iller Grade
DATE:	Marc	h 4, 2014			Refe	RENCE N	O.:	240724				
-						ECT NAM			n Ram	on Road, Di	 thl <del>i</del> n	
То:	Terrv	Wickham	ı		1110)	LCI I TIM		- 0777 841	it Ruiti	on Road, Di	Ш	
-			nty Environ	mental H	ealth		_					
-			ay Parkway				_					
_	•	100	ornia 94502	****	0		<del></del>					
_	Mani	eua, Cam	011IIa 94302	2-0377								
				,,	*****							
Please find	enclos	ed:	Draft Originals Prints			Final Other						
Sent via:			Mail Overnight	Courier		Same Da Other			l Alam	eda County F	TP	
QUANT	ITY		· · · · · · · · · · · · · · · · · · ·			DESC	RIPTI	ON				
1		Update	Updated Well Survey and Groundwater Modeling Report									
	questeo our Use		] ] ]	For F	Review	and Com	ment					
COMMEN If you have Peter Schae	any q	uestions 1 (510) 420-	egarding t	he conten Shell pro	t of thi	s docum	ent, pl	ease call t Pineda at	he CR (425)	A project m 413-1164	anager	
									(120)	110 1101.		
Copy to:			eda, Shell (			-	-					
			Viney, Zon								_	
		CATI Cox	588	ox Corpor	ation (	property	owne	r), 4431 St	tonerio	dge Drive, P	leasantc	on,
Completed	by: _	Peter Sch	aefer			Signed	: <u> </u>	la Solut	Ja.			
Filing: Co	rrespo	ndence Fi	le									



# UPDATED WELL SURVEY AND GROUNDWATER MODELING REPORT

SHELL-BRANDED SERVICE STATION 8999 SAN RAMON ROAD DUBLIN, CALIFORNIA

SAP CODE 135244 INCIDENT NO. 97565995 AGENCY NO. RO0002744

> Prepared by: Conestoga-Rovers & Associates

5900 Hollis Street, Suite A Emeryville, California U.S.A. 94608

Office: (510) 420-0700 Fax: (510) 420-9170

web: http:\\www,CRAworld.com

MARCH 4, 2014 REF. NO. 240724 (14) This report is printed on recycled paper.

## TABLE OF CONTENTS

		<u>Page</u>
EXE	CUTIVE SUMMARY	I
1.0	INTRODUCTION	1
2.0	WELL SURVEY	1
3.0	GROUNDWATER MODEL	1
4.0	CONCLUSIONS AND RECOMMENDATIONS	2

## LIST OF FIGURES (Following Text)

FIGURE 1

VICINITY MAP

LIST OF TABLES (Following Text)

TABLE 1

WELL SURVEY RESULTS

### LIST OF APPENDICES

APPENDIX A

2-DIMENSIONAL CROSS-SECTIONAL MODELING OF MTBE MIGRATION

#### **EXECUTIVE SUMMARY**

- CRA's updated well survey identified a domestic well 2,000 feet down gradient south of the site and an irrigation well 2,700 feet down gradient south of the site.
- CRA used a groundwater transport model to evaluate whether the two
  water-producing wells down gradient from the site could potentially be impacted by
  residual soil and groundwater impacts at the site, principally by MTBE detected in
  groundwater samples collected from deeper wells.
- Based on CRA's groundwater transport model, it appears unlikely that groundwater pumped from these wells would be affected by residual MTBE in soil and groundwater at the subject site; and therefore, there is no human health risk due to human consumption of groundwater pumped from known water-producing wells located down gradient from the site.

#### 1.0 INTRODUCTION

Conestoga-Rovers & Associates (CRA) prepared this report on behalf of Equilon Enterprises LLC dba Shell Oil Products US (Shell) summarizing well survey and groundwater modeling results as proposed in CRA's September 26, 2013 *Updated Site Conceptual Model* which was approved in Alameda County Environmental Health's (ACEH's) November 19, 2013 letter.

The site is an operating Shell-branded service station located at the southeast corner of San Ramon Road and Alcosta Boulevard in Dublin, California (Figure 1). The site layout includes a kiosk, store, a car wash, three dispenser islands, and four fuel underground storage tanks.

A summary of previous work performed at the site and additional background information is presented in CRA's September 26, 2013 *Updated Site Conceptual Model* and is not repeated herein.

#### 2.0 WELL SURVEY

CRA obtained well records from the California Department of Water Resources and the Zone 7 Water Agency.

CRA found records for two water-supply wells within approximately one-half mile of the site. The wells are an active domestic well (2S1W 35L1, Via Zapata Well) and an active irrigation well (2S1W 35K1, Shannon Park Well) located approximately 2,000 and 2,700 feet south of the site, respectively.

These wells are listed in Table 1, and the locations are shown on Figure 1. Available well logs will be maintained in CRA's files and will be made available for review upon request.

#### 3.0 GROUNDWATER MODEL

Based on groundwater monitoring data, methyl-tertiary butyl ether (MTBE) concentrations in the deeper down-gradient wells are the primary remaining concern for evaluating potential human health risk due to residual soil and groundwater impacts at this site. CRA used available hydrogeologic data to evaluate the distance needed for the MTBE plume to stabilize to below San Francisco Bay Regional Water Quality Control

Board environmental screening levels (ESLs)<sup>1</sup> for groundwater (5 micrograms per liter  $[\mu g/L]$ ) where groundwater is a potential source of drinking water.

CRA developed a conceptual hydrogeologic model as the basis for the construction of the two-dimensional (2D) cross-sectional groundwater flow and MTBE transport model. The screening-level 2D cross-section model of MTBE migration was constructed using the finite-difference method, with a flow regime estimated using MODFLOW-2005.

Based on transport simulations using very conservative input parameters, concentrations of MTBE in groundwater do not reach the Via Zapata Well at levels above the ESL following 100 years of migration from a continuous source. CRA's simulation results are presented in Appendix A.

### 4.0 CONCLUSIONS AND RECOMMENDATIONS

CRA identified two water-producing wells down gradient from the site that could potentially be impacted by residual soil and groundwater impacts at the site, principally by MTBE detected in groundwater samples collected from deeper wells.

Based on CRA's groundwater transport model, it appears unlikely that groundwater pumped from these wells would be affected by residual MTBE in soil and groundwater at the subject site; and therefore, there is no human health risk due to human consumption of groundwater pumped from known water-producing wells located down gradient from the site.

Screening for Environmental Concerns at Site With Contaminated Soil and Groundwater, California Regional Water Quality Control Board, Interim Final – November 2007 [Revised May 2008] – Updated May 2013

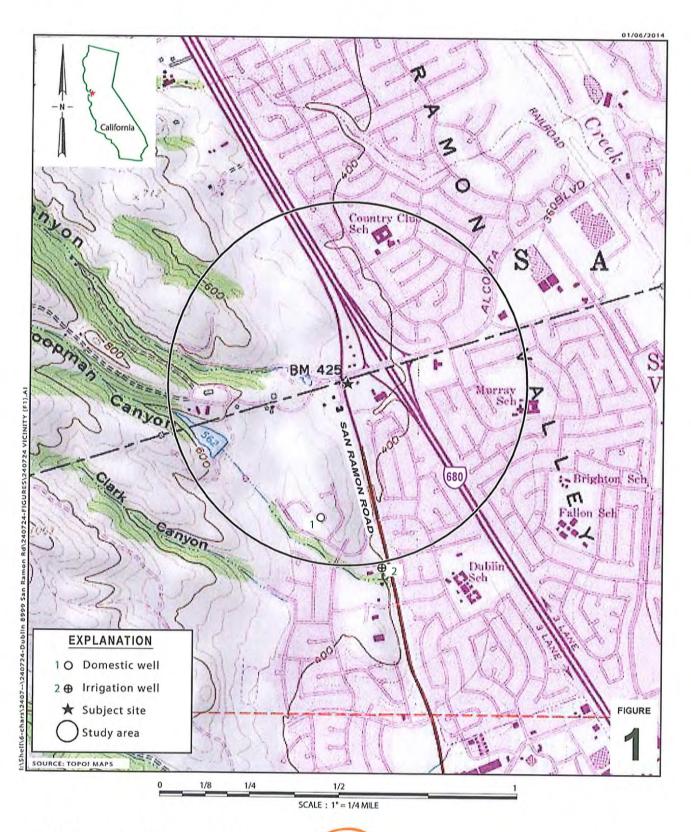
## All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES

Peter Schaefer, CEG, CHG



Dan Puddephatt, M. Sc.

**FIGURE** 



**Shell-branded Service Station** 

8999 San Ramon Road Dublin, California



**Vicinity Map** 

TABLE

#### TABLE 1

## WELL SURVEY RESULTS SHELL-BRANDED SERVICE STATION 8999 SAN RAMON ROAD, DUBLIN, CALIFORNIA

Map ID	State Well ID	Approximate Distance from Site (feet)	Direction from Site	Use	Well Status	Depth (fbg)	Diameter (inches)	Top of Screen (fbg)	Bottom of Screen (fbg)
1	2S/1W-35L1	2,000	S	DOM	active	307	8	222	282
2	2S/1W-35K1	2,700	S	IRR	active	390	5	100	280

#### Notes:

State Well ID = California State well identification number as provided by California Department of Water Resources (DWR) and/or Zone 7 Water Agency (Zone 7).

fbg = feet below grade

DOM = Domestic

IRR = Irrigation

Map ID number refers to map location on Figure 1.

Well information provided by the DWR and/or Zone 7.

Well locations are approximate and have not been field verified. The well locations are plotted on

Figure 1 are based on the information provided by DWR and/or Zone 7.

Monitoring wells and destroyed wells were not included in the table or mapped.

#### APPENDIX A

2-DIMENSIONAL CROSS-SECTIONAL MODELING OF MTBE MIGRATION



651 Colby Drive, Waterloo, Ontario, Canada N2V 1C2 Telephone: (519) 884-0510 Fax: (519) 884-0525

www.CRAworld.com

### **MEMORANDUM**

To:

Peter Schaefer

REF. No.:

240724

FROM:

Dan Puddephat/Hongze Gao/kf/2

DATE:

February 19, 2014

RE:

2-Dimensional Cross-Sectional Modeling of MTBE Migration

Shell-Branded Service Station 8999 San Ramon Road, Dublin, CA

#### 1.0 Introduction

This memorandum presents the results of the screening-level groundwater flow and methyl tertiary-butyl ether (MTBE) transport modeling evaluation conducted by Conestoga-Rovers & Associates (CRA) to evaluate contaminant migration in groundwater from the Shell-branded service station located at 8999 San Ramon Road, Dublin, California. CRA conducted the modeling evaluation on behalf of Equilon Enterprises LLC dba Shell Oil Products US (Shell). Figure 1 illustrates the site location, and a site plan is presented on Figure 2.

#### 2.0 Purpose and Objectives

The purpose of this modeling evaluation is to provide a screening-level assessment of the potential MTBE migration down gradient from the site to a residential well labeled Well ID 2S1W 35L1 (Via Zapata Well) nearby, which is located approximately 2,000 feet to the south, and an irrigation well labeled Well ID 2S1W 35K1 (Shannon Park Well), located approximately 2,700 feet to the south.

The Via Zapata Well is a residential well installed near the base of Wiedemann Hill, a 1,844-foot mountain. This well was drilled into 10 feet of clay loam and 380 feet of underlying bedrock. The Via Zapata Well was selected as the potential down-gradient receptor for assessing MTBE migration because of its relative proximity to the site. The MTBE migration evaluation was developed using a screening-level 2-dimensional (2D) cross-sectional groundwater flow and MTBE transport model. As described below in Section 3.0, there is little hydraulic connection between the shallow overburden and the underlying bedrock formation; therefore, using this well as the closest potential receptor provides a very conservative evaluation of potential MTBE migration to water-producing wells.

The Shannon Park Well is screened in gravels and clay at a depth interval ranging from 222 feet below ground surface (bgs) to 282 feet bgs. The stratigraphy near this consists of clays with some gravel from ground surface to a depth of 175 feet bgs. From 175 feet bgs to 290 feet bgs layers of gravel and clay alternate with the thickest of the gravel units (50 feet) being located at a depth of 205 feet bgs. This well is screened in the unconsolidated overburden in the same geological unit as the impacted groundwater at the site.



CRA MEMORANDUM Page 2

CRA evaluated the distance needed for the MTBE plume to stabilize to below San Francisco Bay Regional Water Quality Control Board (RWQCB) environmental screening levels (ESLs) in groundwater (5 micrograms per liter [µg/L]) based on groundwater use as a drinking water resource<sup>1</sup> and using available hydrogeologic data.

#### 3.0 Background Information

Site history and other background information was presented in CRAs September 26, 2013 *Updated Site Conceptual Model* and is not repeated herein.

The regional groundwater flow from the site is anticipated to be south-southeast toward the South San Ramon Creek as presented on Figure 3. Figure 3 shows that the potential receptors are located cross gradient from the site. The site is situated in the northwestern edge of the Dublin Sub-basin of the Livermore Valley Groundwater Basin. Topographically, the site is situated on the western margin of Livermore Valley between the Dublin Upland area to the west and the Tassajara Upland area to the east2. Ground surface at the site is at an elevation of approximately 425 feet above mean sea level (AMSL) and slopes eastward and southeastward away from the Dublin Upland area towards South San Ramon Creek as presented on Figure 4. Vertical profile sections have also been prepared depicting the topography between the site and Via Zapata Well (i.e., vertical profile A-A') and between the site and the Shannon Park Well (i.e., vertical profile B-B') and are presented on Figure 5. Between the site and the Via Zapata Well, a topographic ridge formed between two parallel canyons, Big Canyon and Koopman Canyon, and rises to approximately 530 feet AMSL, which is approximately 105 feet above the site elevation. The ridge is demarked in Figure 5 by highlighting of the 500 feet AMSL contour. The ridge drops in elevation towards the east between Via Zapata Well and the Shannon Park Well such that near Shannon Park Well the ridge rises to approximately 435 feet AMSL (i.e., approximately 10 feet above the site elevation). Since groundwater typically follows ground surface topography, it is anticipated that regional groundwater flow originating from the site will be to the east of the potential receptors, away from Wiedemann Hill and towards South San Ramon Creek.

The site is underlain by Quaternary alluvium deposits of upper Pleistocene age to recent aged deposits. The alluvium consists of alluvial fan deposits of alternating clay and gravel facies<sup>2</sup>. The shallowest alluvium deposit in the Dublin Sub-basin consists of thick clay beds, which in the site area can range from 60 feet to 108 feet thick and regionally from 0 feet to 150 feet. Stratigraphy across the site is presented in cross-sections on Figures 6 and 7 for cross-sections C-C' and D-D', respectively. West and southwest of the site, the geology is characterized by bedded deposits of Pliocene-aged tuff, shale, sandstone, and tuffaceous sandstone, collectively identified as the Tassajara Formation<sup>2</sup>. The Tassajara Formation dips sharply to the east, plunging below the quaternary deposits in the Livermore Valley. The Via Zapata Well is screened in the sandstones of the Tassajara Formation, which because of the fine-grained materials of the overlying tuff and shale, has little hydraulic communication with overlying quaternary deposits<sup>2</sup>.

Groundwater in the area of the site primarily receives recharge from: 1) precipitation at a reported total annual rate of 15.7 inches per year (in/yr) based on 1981-2010 climatic norms<sup>3</sup>; and 2) lateral groundwater flow from up-gradient

RWQCB, 2013. Environmental Screening Levels (Interim Final - December 2013), Summary Table C, Environmental Screening Levels (ESLs), Deep Soil (>3m bgs), Groundwater Is A Current or Potential Source of Drinking Water.

Department of Water Resources, 1974. Livermore and Sunol Valleys Evaluation of Ground Water Resources, Bulletin No. 118-2, June.

National Climatic Data Center, 2013. Climate Data Online: Dataset Discovery, Livermore Municipal Airport CA US. Viewed February 7, 2014. http://www.ncdc.noaa.gov/cdo-web/.

areas. The amount of precipitation reaching the groundwater table is typically anticipated to range from approximately 10 to 40 percent of the average annual precipitation<sup>4</sup>.

#### 4.0 Site Conceptual Model

A conceptual hydrogeologic model was developed for the site to convey the understanding of the stratigraphic, groundwater flow, and groundwater quality conditions observed at the site. The conceptual hydrogeologic model forms the basis for the construction of the 2D cross-sectional groundwater flow and MTBE transport model.

The site is situated at an elevation of approximately 425 feet AMSL near the mouth of Big Canyon. The overburden consists of interlayered beds of silt and clay with sands and gravel. Soils beneath the site consist primarily of silts and clays with interbedded layers of sands and gravel to the maximum explored depth of 111.5 feet bgs. The transport of MTBE will occur predominantly through the sand and gravel fraction of the overburden. As of the January 17, 2013 groundwater quality monitoring event, the highest concentrations of MTBE were collected from wells screened between 85 feet bgs and 110 feet bgs (i.e., the deep water-bearing unit). At these depths, MTBE concentrations in groundwater ranged from 31  $\mu$ g/L at MW-14C to 140  $\mu$ g/L at MW-13C. Figure 8 presents groundwater concentrations of MTBE collected from deep monitoring wells on January 17, 2013.

Based on groundwater elevation contours illustrated on Figure 8, there is a 0.02 feet per foot south and southeastward hydraulic gradient in the deep water-bearing unit across the site. The site-specific hydraulic gradient is likely the result of head loss across low permeability units. Regional groundwater elevation contours in the upper aquifer presented on Figure 3 have a southeasterly gradient of approximately 0.003 feet per foot near the site area<sup>5</sup>. The regional hydraulic gradient values were applied in the groundwater flow and MTBE transport model to represent the regional flow system.

Hydraulic testing has not been performed at the site, so a literature value of  $1 \times 10^{-2}$  centimeters per second (cm/s) (28.3 feet per day) was estimated for the permeable sand and gravel<sup>5</sup>. A literature value of 27 percent was estimated for the specific yield/effective porosity of the sand and gravel unit<sup>7</sup>. For the purpose of the highly conservative conceptual model and subsequent screening-level cross-section 2D groundwater flow and MTBE transport numerical model, the aquifer was assumed to be continuous and groundwater was assumed to flow in a straight line between the site and the Shannon Park Well, when in reality regional flow is to the east of the well towards the South San Ramon Creek. The resulting model is a highly conservative estimate of MTBE migration.

#### 5.0 Simulation Program Selection

MODFLOW-2005<sup>8</sup>, developed by the USGS, is capable of simulating steady-state or transient groundwater flow in two or three dimensions. MODFLOW-2005 uses the finite-difference method leading to a numerical approximation that allows for a description and solution of complex groundwater flow problems. A rectangular grid of 5-foot-wide model cells was extended across a cross-section through the study area. The finite-difference grid originates up

Rushton, K.R. and C. Ward, 1979. The Estimation of Groundwater Recharge. Journal of Hydrology, 41, pp. 345-361.

Ferriz, H., 2001. Groundwater Resources of Northern California: An Overview.

Bear, J, D. Zaslavsky, and S. Irmay, 1968. Physical Principles of Water Percolation and Seepage. UNESCO, pp 465.

Johnson, A.I., 1967. Comparison of Specific Yields for Various Materials, Geological Survey Water-Supply Paper 1962-D.

Harbaugh, A.W., 2005. MODFLOW-2005, The U.S. Geological Survey Modular Ground-Water Model-The Ground-Water Flow Process, U.S. Geological Survey Techniques and Methods 6-A16.

CRA MEMORANDUM
Page 4

gradient from the approximate source location by 500 feet and extends down gradient from the approximate source location by a distance of 3,400 feet, corresponding with a model domain that extends 1,400 feet down gradient from the approximate distance to the Via Zapata Well (i.e., 2,000 feet). The distance to the down-gradient edge of the model domain was assigned to ensure that the model domain does not interfere with the transport simulations by accumulating mass at the model boundary. Model observation wells were assigned 2,000 feet and 2,700 feet down gradient from the approximate source location to record MTBE concentrations reaching an equivalent distance to the Via Zapata Well. It should be noted that both potential receptor wells are somewhat cross gradient from the site based on the regional gradients presented on Figure 3. Layers were used to subdivide the study area vertically into 60 layers with uniform thicknesses of 5 feet each. The groundwater flow equation was formulated as a differential water balance for every model cell. MODFLOW-2005 allows for the specification of flows associated with wells, area-averaged groundwater recharge, rivers, drains, streams, and other groundwater sources/sinks.

MODFLOW-2005 was selected to simulate groundwater flow for this modeling study. MODFLOW-2005 is an update to the original MODFLOW<sup>9</sup>. MODFLOW has been extensively verified and readily accepted by many regulatory agencies throughout North America and Europe. MODFLOW-2005 is capable of representing the hydrogeologic components included in the conceptual hydrogeologic model for the site and surrounding area.

To obtain a simulated groundwater flow field within the model domain, the solution to the groundwater flow equation was obtained using a numerical solver with specified convergence criteria. The Preconditioned Conjugate Gradient (PCG2) algorithm <sup>10</sup> has been developed for solving systems of equations resulting from applying the cell-centered finite-difference algorithm to flow in porous media. The PCG2 solver has been adapted by the USGS into MODFLOW-2005 and was employed to solve the groundwater flow equation. For convergence, the PCG2 solution technique requires satisfaction of both hydraulic head-change and flow residual criteria providing a rigorous and reliably simulated water balance throughout the model domain. Closure criteria of 0.001 feet and 0.01 cubic feet per day were assigned to the groundwater flow model for the head-change and flow residual closure criteria, respectively.

Contaminant Transport was simulated using MT3DMS<sup>11</sup>. MT3DMS is a reactive transport model that, when integrated with MODFLOW-2005, can simulate multispecies chemical transport in one, two, or three dimensions and is able to simulate all the transport processes in the groundwater flow system that are applicable to the MTBE transport modeling study including advection, dispersion, and degradation. MT3DMS is commonly used by the industry and accepted by the regulatory agencies, and therefore was selected for this study to evaluate MTBE migration.

The graphical user interface (GUI) Groundwater Vistas<sup>12</sup> was employed as the interface between the assembled hydrogeologic data and the required MODFLOW-2005/MT3DMS input files. The GUI also provides pre-processing and post-processing of MODFLOW/MT3DMS input/output files.

McDonald, M.G. and A.W. Harbaugh, 1988. A Modular Three Dimensional Finite Difference Ground Water Flow Model, United States Geological Survey Techniques of Water Resources Investigations, Book 6, Chapter A1.

Hill, M.C., 1990. Preconditioned Conjugate Gradient 2 (PCG2), A Computer Program for Solving Ground-Water Flow Equations, Water-Resources Investigation Report 90-4048.

Zheng, C., and P.P. Wang, 1999. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide, U.S. Army Corps of Engineers Contract Report Number SERDP-99-1, December.

Rumbaugh, J.O., 2011. Guide to Using Groundwater Vistas, Version 6, Environmental Simulations Inc., Herndon, Virginia.

#### 6.0 MTBE Transport Model Construction

The MTBE transport model was applied to conduct highly conservative simulations of uninhibited MTBE plume migration and attenuation in groundwater beneath the site and site vicinity. The transport model was developed to provide screening-level predictive analyses of the potential MTBE migration from the site to a distance down gradient that corresponds to the distance to the Via Zapata Well. The predictive model was developed for a 100-year time-frame (i.e., from the January 17, 2013 to January 17, 2113). The 100-year time-frame was selected to provide sufficient time for the simulated plume to reach steady-state (i.e., the rate of transport equals the rate of attenuation such that the plume front ceases to advance).

The MTBE transport model inputs are described below in terms of aquifer physical properties, initial concentrations, dispersivity values, retardation, and biodegradation rates. The model inputs described below correspond to the base-case conditions applied in the modeling evaluation. Sensitivity analysis to source concentration was performed and is described in Section 6.1.

#### Advection

Advection (the bulk movement of a fluid through a geologic medium) is the primary transport mechanism of the dissolved phase through the porous media at the site. The advection mechanism is governed by Darcy's Law, which determines the groundwater flow velocity, accounting for hydrogeologic characteristics (hydraulic gradient, hydraulic conductivity, permeability, and porosity) of the water-bearing unit.

Hydrogeologic properties applied for the MTBE transport simulation are listed below based on generalized hydrogeologic conditions summarized in Section 4.0.

Parameter	Property Value		
Aquifer Material	Interbedded clay and grave		
Hydraulic Conductivity (ft/day)	28		
Hydraulic Gradient (ft/ft)	0.003		
Porosity	0.27		
Recharge (ft/day)	0.001		
Distance to Potential Receptor (ft)	2.000		
Via Zapata Well (2S1W 35L1)	2,000		

#### Initial Groundwater Concentrations

Initial concentrations for MTBE were implemented based on maximum concentrations measured in the deep monitoring wells during the January 17, 2013 monitoring event (i.e., 140  $\mu$ g/L). The initial concentrations were assigned at a depth 80 feet bgs to correspond with the approximate depth of the deep water-bearing unit. The initial concentrations were extended a distance of 270 feet from the dispenser islands to MW-13C and were held at a constant concentration for the duration of the model simulation (i.e., 100 years).

#### Dispersion

Dispersion is a transport mechanism by which dissolved compounds spread along the groundwater flow path. Dispersion results from two basic processes: molecular diffusion and mechanical mixing. Molecular diffusion is a process where solutes move from zones of higher concentrations to zones of lower concentrations. The driving force of this movement is kinetic activity at the molecular level. Mechanical dispersion is derived from the variability

CRA MEMORANDUM

(heterogeneity) of the microscopic velocities in groundwater that act to spread or mix a solute in an aquifer. The primary aquifer characteristics that cause this mixing are variable frictional forces in pore channels, variations in pore channel geometry, and pore channel branching.

Dispersion/spreading of MTBE during groundwater flow results in dilution of solute pulses and attenuation of concentration peaks. This dilution/attenuation affect is taken into account in the transport equation by applying longitudinal and vertical dispersion coefficients in the cross-sectional domain.

Selection of dispersivity values is a difficult process, given the impracticability of measuring dispersion in the field. However, simple estimation techniques, based on the length of the plume or distance to the measured point ("scale"), are available by compiling field test data. It is noted that researchers indicate that dispersivity values can range over 2 to 3 orders of magnitude for a given value of plume length or distance to a measurement point<sup>13</sup>. Typical relationships of dispersivity and plume length ( $L_P$ ), are provided by a few researchers<sup>14</sup> as described in the following equation:

$$\alpha_L = 0.83 \times [log_{10}(L_P)]^{2.414}$$

Equation 1

Where:

 $\alpha_{L}$  = the longitudinal dispersivity [meters (m)]

 $L_P$  = the estimated plume length (m)

The plume length was assumed to be the distance between the middle dispenser island (i.e., the approximate source location) and MW-13C of 235 feet. The horizontal dispersivity was calculated to be 4 m (12 feet). The vertical dispersivity was assumed to be 1/10 of the longitudinal dispersivity<sup>15</sup>. Transverse dispersion was not included in the 2D cross-section MTBE transport model. Omission of transverse dispersion term will result in an overestimate of the peak MTBE concentration along the flow line.

#### Sorption/Retardation

Sorption describes the interaction of contaminants with a solid through partitioning between the solution and the solid phase. Sorption causes the contaminant to move at a velocity ( $V_c$ ) that is slower than the mean pore water velocity ( $V_g$ ) by a factor  $R_d$  (known as the retardation factor) expressed as:

$$R_d = 1 + \frac{\rho K_d}{\eta_e}$$

**Equation 2** 

Gelhar, L.W., C. Welty, and K.R. Rehfeldt, 1992. A Critical Review of Data on Field Scale Dispersion in Aquifers. Water Resources Research, 28(7), pp. 1955 1974.

Xu, M. and Y. Eckstein, 1995. Use of Weighted Least Squares Method in Evaluation of the Relationship Between Dispersivity and Scale, Groundwater, 33(6), pp. 905 908.

U.S. EPA, 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water: Appendix B, Important Processes Affecting the Fate and Transport of Organic Compounds in the Subsurface, EPA/600/R-98/128, September.

Thus,

$$V_c = \frac{V_g}{R_d}$$

**Equation 3** 

Where:

 $\rho$  = is the dry bulk density of the soil [kilograms per liter (kg/L)]

 $K_a$  = is the distribution coefficient [liters per kilogram (L/kg)]

Linear isotherms describe hydrophobic adsorption of organic COCs to soil organic matter. A linear isotherm is expressed as:

$$S = K_d c$$

Equation 4

Where:

S = is the organic MTBE concentration adsorbed to the soil matrix [micrograms per kilogram ( $\mu g/kg$ )]

c = is the dissolved phase MTBE concentration ( $\mu g/L$ )

 $K_a$  is related to the organic carbon content of soil by:

$$K_d = K_{oc} f_{oc}$$

**Equation 5** 

Where:

 $K_{oc}$  = is the organic carbon partition coefficient of MTBE (L/kg)

 $f_{\infty}$  = is the fraction of organic carbon in the soil by weight (percent)

For this modeling study, the following parameter values were used for the estimation of retardation factors:

- ullet A dry bulk density ( ho ) of 1.7 kg/L for the sand and gravel fraction of the deep water-bearing unit was applied
- An effective porosity of 27 percent was applied based on literature values for specific yield?
- The  $K_{\infty}$  value for MTBE of 11.56 was selected based on the value presented in the United States Environmental Protection Agency (U.S. EPA) Regional Screening Level Tables<sup>16</sup>.
- An average  $f_{oc}$  value of 0.2 percent was used to provide an estimate of retardation and is based on the default value presented in the U.S. EPA Soil Screening Guidance<sup>17</sup>.

The values listed above provide a retardation factor value of 1.15.

U.S. EPA, 2013. Regional Screening Levels (Formerly PRGs), Screening Levels for Chemical Contaminants, RSL Tables, Chemical Specific Parameters, November.

U.S. EPA, 1996. Soil Screening Guidance: User's Guide, EPA/540/R-96/018, July.

**CRA MEMORANDUM** 

#### Degradation Rate

Degradation describes the process of organic breakdown by biomass naturally present in the water-bearing unit. Microorganisms present in the soil and groundwater utilize organic compounds such as those in MTBE as electron donors for cell metabolism, resulting in a degradation of the organic compounds.

It is difficult to describe the rate of degradation in a rigorous mathematical manner; however, by simplification and approximation, a rate of degradation can be employed to describe this process using a first-order degradation rate (decay constant), expressed as:

$$\frac{\partial c}{\partial t} = -\lambda c$$

Equation 6

Where:

t = the time in years

 $\lambda$  = is the first-order degradation rate (1/years)

The degradation rate is related to the MTBE half-life by:

$$t_{1/2} = \frac{\ln(2)}{\lambda} = \frac{0.693}{\lambda}$$

Equation 7

Where:

 $t_{1/2}$  = the half-life (years)

The site-specific degradation rates in the vicinity of the plume were estimated based on the attenuation half-life documented for MTBE in well MW-5B of 0.95 years<sup>18</sup>. The remaining wells for which half-life values were calculated: MW-2RC, MW-5C, MW-13B, MW-13C, and MW-14C exhibited stable concentration trends over time. The stable trends were represented in the transport model using a constant concentration boundary condition.

CRA, 2013. Updated Site Conceptual Model, Shell-Branded Service Station, 8999 San Ramon Road, Dublin, California. September, 26.

#### 6.1 Sensitivity Analysis

Development of any numerical model to represent physical systems will be based on a series of simplifying assumptions that can influence the interpretation of contaminant transport. The sensitivity analysis was performed to address uncertainties associated with the source concentration. The initial mass specified in the model is based on concentrations measured in groundwater from MW-13C during the January 17, 2013 groundwater monitoring event. The geological heterogeneity can lead to zones with potentially higher concentrations than have been collected from MW-13C. Thus the groundwater MTBE concentration measured at the MW-13C monitoring well may underestimate the actual mass present in the aquifer. To address this uncertainty, the constant concentration assigned to the base-case between the location of the dispenser islands and the down-gradient MW-13C location was assigned a value that is double the initial concentration assigned to the base-case model (i.e., 280 µg/L). The initial concentration assigned in this sensitivity model was held fixed for the duration of the 100-year model simulation which is considered to be very conservative.

The change to the initial concentration was for the base-case MTBE transport simulation. Although the base-case applied conservative estimates for the source concentration, uncertainties could still exist and are addressed by the sensitivity analysis simulation presented herein.

#### 7.0 MTBE Transport Model Results

#### 7.1 Base Case

For the MTBE migration simulations, the predicted concentrations are illustrated through profiles of concentration versus distance from the approximate source area (i.e., the dispenser island area) and are presented on Figure 9. At steady-state, groundwater MTBE concentrations drop to concentrations below the ESL of 5  $\mu$ g/L a distance of approximately 660 feet from the source area. Based on the conservative transport simulations, MTBE is not expected to reach the Via Zapata Well at concentrations above detectable levels (i.e., simulated concentrations are below 0.01  $\mu$ g/L).

#### 7.2 Sensitivity Analysis: Influence of Source Concentration

By doubling the source concentration from a value of 140  $\mu$ g/L based on observed groundwater MTBE concentrations collected from MW-13C on January 17, 2013 to a value of 280  $\mu$ g/L, simulated groundwater MTBE concentrations extend at levels above 5  $\mu$ g/L over a distance approximately 765 feet from the approximate source location. The profiles of concentration versus lateral distance from the approximate source area for the Sensitivity Analysis are presented on Figure 10. Based on the conservative condition applied to this sensitivity analysis MTBE is not expected to reach the Via Zapata Well at concentrations above detectable levels (i.e., simulated concentrations are below 0.01  $\mu$ g/L).

#### 8.0 Summary and Conclusions

The screening-level 2D cross-section model of MTBE migration was constructed using the finite-difference method implemented in MT3DMS, which itself was integrated with a flow regime estimated using MODFLOW-2005. CRA used the 2D cross-section model to estimate the uninhibited MTBE transport over a length corresponding to the distance to the Via Zapata Well, approximately 2,000 feet down-gradient from the dispenser islands (i.e., the approximate source location).

The source concentration was assigned based on MTBE concentrations measured in groundwater collected from MW-13C and was held fixed for a simulation period of 100 years. The source concentration was assigned as a constant concentration from the approximate location of the dispenser islands to MW-13C. The simulations considered the solute transport processes of groundwater advection, dispersion, adsorption, and degradation. The transport simulation was constructed based on a set of very conservative assumptions. These assumptions include the following:

- The source concentrations were held fixed for the duration of the transport simulation when in reality natural attenuation processes would be anticipated over the 100-year time period of the transport simulation.
- 2. The transport model assumes that the Via Zapata Well is along the direct groundwater flow path. Based on regional groundwater elevation contours presented on Figure 3, the Via Zapata Well is located somewhat side gradient from the site and is not situated along the direct groundwater flow path.
- 3. The transport model assumes that the flow path is continuous and uninterrupted. The geology at the site includes interlayered sands and clays as presented on Figures 6 and 7. The physical reality likely includes tortuous and discontinuous MTBE transport pathways.
- 4. Transverse dispersion was not included in the 2D cross-section MTBE transport model. The influence of transverse dispersion is to lower the peak concentrations along the flow path. By omitting the transport parameter, the transport model over-predicts the concentration reaching the Via Zapata Well.

Based on the simulation results, predicted steady-state concentrations for MTBE do not reach the Via Zapata Well distance of 2,000 feet at levels above the ESL of 5  $\mu$ g/L. A Sensitivity Analysis was performed to investigate the effect of doubling the source concentration of 140  $\mu$ g/L to a conservative value of 280  $\mu$ g/L. Under this conservative sensitivity analysis, concentrations of MTBE at the Via Zapata Well distance of 2,000 feet remain below the 5  $\mu$ g/L ESL value. The simulation results indicate that the residual MTBE concentrations currently detected in groundwater at the site are not expected to impact the Via Zapata Well potential down-gradient receptor in the future.

