The ART In-Well Technology Test at a Chlorinated Solvent Site in Central Iowa

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An Accelerated Remediation Technologies (ART) In-Well Technology pilot test was performed to evaluate the removal of chlorinated volatile organic compounds (VOCs) from groundwater. The ART In-Well Technology was installed in one well located in the source area where dense nonaqueous-phase liquid has been identified and VOC concentrations exceed 140,000 μg/L. Monitoring wells at the site were positioned between 10 and 170 feet from the ART test well. Overall, VOC concentrations from samples collected from the groundwater monitoring wells and in the vapors extracted for discharge from the ART treatment well were analyzed over the testing period. Monitoring results showed that concentrations of perchloroethylene were reduced in the closest monitoring well to nondetectable concentrations within 90 days. The cumulative removal of chlorinated VOCs from the ART test well over the six-month pilot test period exceeded 9,500 pounds based on air monitoring data. The ART technology proved effective and cost-efficient in reducing contaminant concentrations and removing a large mass of contamination from the subsurface in a short period of time. The radius of influence of the ART technology at the site was estimated to range between 65 and 170 feet. © 2007 Wiley Periodicals, Inc.

INTRODUCTION

Halogenated hydrocarbons (chlorinated solvents) have many different industrial and commercial uses as cleaning and degreasing agents. Some halogenated solvents, such as trichloroethylene (TCE), perchloroethylene (PCE) and 1,1,1-trichloroethane (TCA), were widely used in dry cleaning, in the cleaning and degreasing of metal parts, and in the electronics industry. The pure compounds are denser than water, tend to migrate to substantial depths below the water table, and are only slightly soluble in water; therefore, they may persist for many decades in subsurface soil and deep pools, known as dense nonaqueous-phase liquid (DNAPL). The area where DNAPL contamination is present typically has two primary components: the source zone, which usually contains most of the contaminant mass, and a dissolved groundwater plume, which occupies a greater volume of the aquifer downgradient of the source zone. At sites where DNAPL has been detected, many methods have been attempted to contain and/or remediate the contamination. However, due to the nature of the chemicals, relatively few technologies have provided effective treatment, and the plume of contamination is most often contained rather than remediated.

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An Accelerated Remediation Technologies (ART) In-Well Technology pilot test was performed by CH2M HILL at a site in Pleasant Hill, Iowa, in 2005. Bulk chemical handling of solvents had been conducted for many years at the facility. The pilot test was designed to evaluate the removal of chlorinated volatile organic compounds (VOCs) from groundwater. The ART In-Well Technology was installed in one well located in the source area near the former bulk chemical storage tanks where DNAPL has been identified and VOC concentrations exceed 140,000 μg/L.

Monitoring wells at the site were positioned between 10 and 170 feet from the ART test well. Overall, VOC concentrations from samples collected from the groundwater monitoring wells and in the vapors extracted for discharge from the ART treatment well were analyzed over the testing period. Monitoring results showed that the PCE concentrations were reduced in the nearest monitoring well to nondetectable concentrations within 90 days. The cumulative removal of chlorinated VOCs from the ART test well over the six-month pilot-test period exceeded 9,500 pounds based on air monitoring data. The ART technology proved effective and cost-efficient in reducing contaminant concentrations and removing a large mass of contamination from the subsurface in a short period of time. The radius of influence of the ART technology at the site was estimated to range between 65 and 170 feet.

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SITE HISTORY

The site is situated in an industrial and agricultural area southeast of Des Moines, Iowa. The site has been used for industrial purposes since 1944. A chemical company leased the property in the 1970s for a period of six years. During this time, it was used to store and distribute agricultural, industrial, laundry, and dry cleaning chemicals, and to store spent solvents generated offsite by customers. Once collected, the spent solvents were shipped offsite to a reclaimer (CH2M HILL, 2003).

The main exterior storage area for chemicals was located on the northeastern portion of the site. Drums containing spent solvent were stored in the east building on the site (the "container storage" building) and outside of the northeast corner of the main building. The facility submitted a Resource Conservation and Recovery Act (RCRA) Part A application to store hazardous waste at the facility. The facility operated the container storage building under interim status as a hazardous waste management facility.

Pursuant to an Administrative Order on Consent (AOC) issued for the site in 1991, a remedial investigation and corrective measures study were conducted. Dissolved-phase VOCs (primarily chlorinated compounds) were detected in groundwater along with DNAPL. Dense nonaqueous-phase liquid was detected in the area of the former tank storage area (Exhibit 1). The DNAPL consists of a mixture of 40 percent xylene, 40 percent PCE, and 20 percent mineral spirits (CH2M HILL, 2003). This former tank storage area, along with the remainder of the five-acre facility, was surrounded in 1995 with a soil-bentonite containment wall (SBCW) that was keyed into the bedrock and/or clay till surface approximately 45 feet beneath grade. The presence of the SBCW contains the DNAPL zone and the highest dissolved groundwater concentrations identified at the site. To contain the contamination, a gradient control treatment system (GCTS) is used to remove and treat the volume of groundwater required to obtain an inward hydraulic

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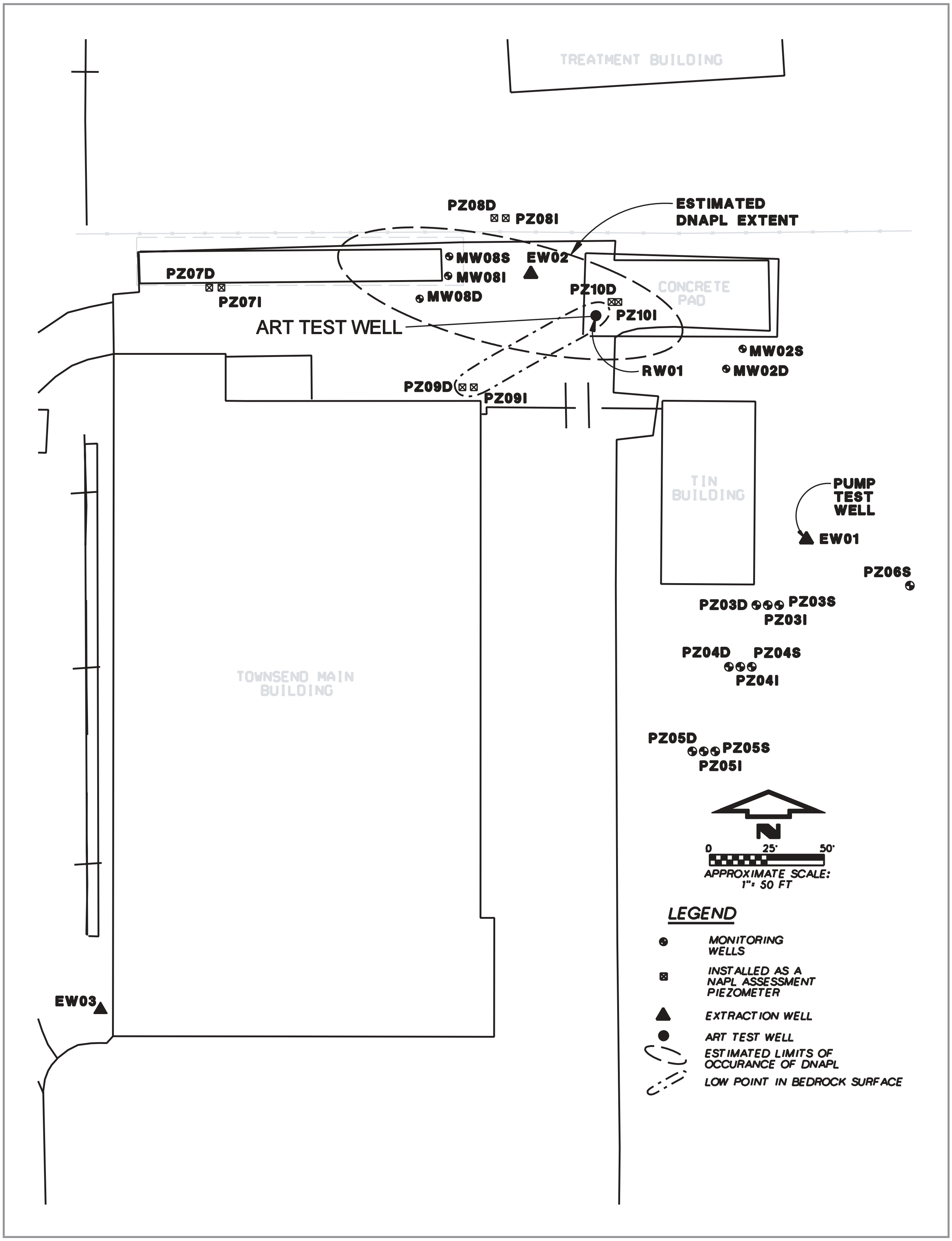

Exhibit 1. ART remediation well and monitoring well locations

gradient across the SBCW. Primary treatment for the GCTS consists of an ultraviolet (UV)-oxidation treatment system.

Low-flow pulse pumping techniques have been used to remove DNAPL from the subsurface. A total of 100 gallons of DNAPL have been removed over a ten-year period (CH2M HILL, 2003).

OBJECTIVES OF THE ART TEST

The ART process was considered for a pilot test as a means to accelerate mass removal at the site and thus reduce the project life-cycle costs.

The ART process was considered for a pilot test as a means to accelerate mass removal at the site and thus reduce the project life-cycle costs. The objectives of the ART pilot test were to:

1. Evaluate and optimize the performance of each system component for possible full-scale implementation or treatment of specific areas at the site;
2. Determine the radius of influence of the system by monitoring surrounding groundwater monitoring wells;
3. Determine the efficiency at which VOCs are removed from groundwater;
4. Determine if the system can enhance the removal of DNAPL; and
5. Evaluate the effect of iron or other minerals on the ART technology.

TECHNOLOGY DESCRIPTION

The ART technology combines *in situ* air stripping, air sparging, soil vapor extraction, and enhanced bioremediation/oxidation into one wellhead system (Exhibit 2) (www.ARTinwell.com). The VOCs are stripped from water as a result of the combined effects of in-well air stripping and in-well air sparging. The air-sparging component lifts the water table in the vicinity of the well. The vacuum pressure from the soil vapor extraction component is applied to the well to extract vapor from the subsurface. The negative pressure from vacuum extraction results in water suction that creates additional water mounding near the well.

A submersible pump is placed at the bottom of the well to pump water to the top of the well for downward discharge through a spray head. The water cascades down the interior of the well and system piping, providing multiple wetted surfaces for mass transfer. In addition to the air stripping resulting from the pumping/cascading, the pumped, stripped, and highly oxygenated water will flow down the well annulus and over the mounded water back into the aquifer and vadose zone—hydraulically enhancing the radius of influence. These combined technology effects will set up a circulation zone surrounding the well, with the objective of enhancing cleanup.

DESCRIPTION OF TEST

Remediation Well Installation

The remediation well was installed in the northern portion of the property beneath a former bulk chemical storage tank area where chlorinated solvents and other solvents were handled (Exhibit 1) and was constructed as shown in Exhibit 3 (CH2M HILL, 2005).

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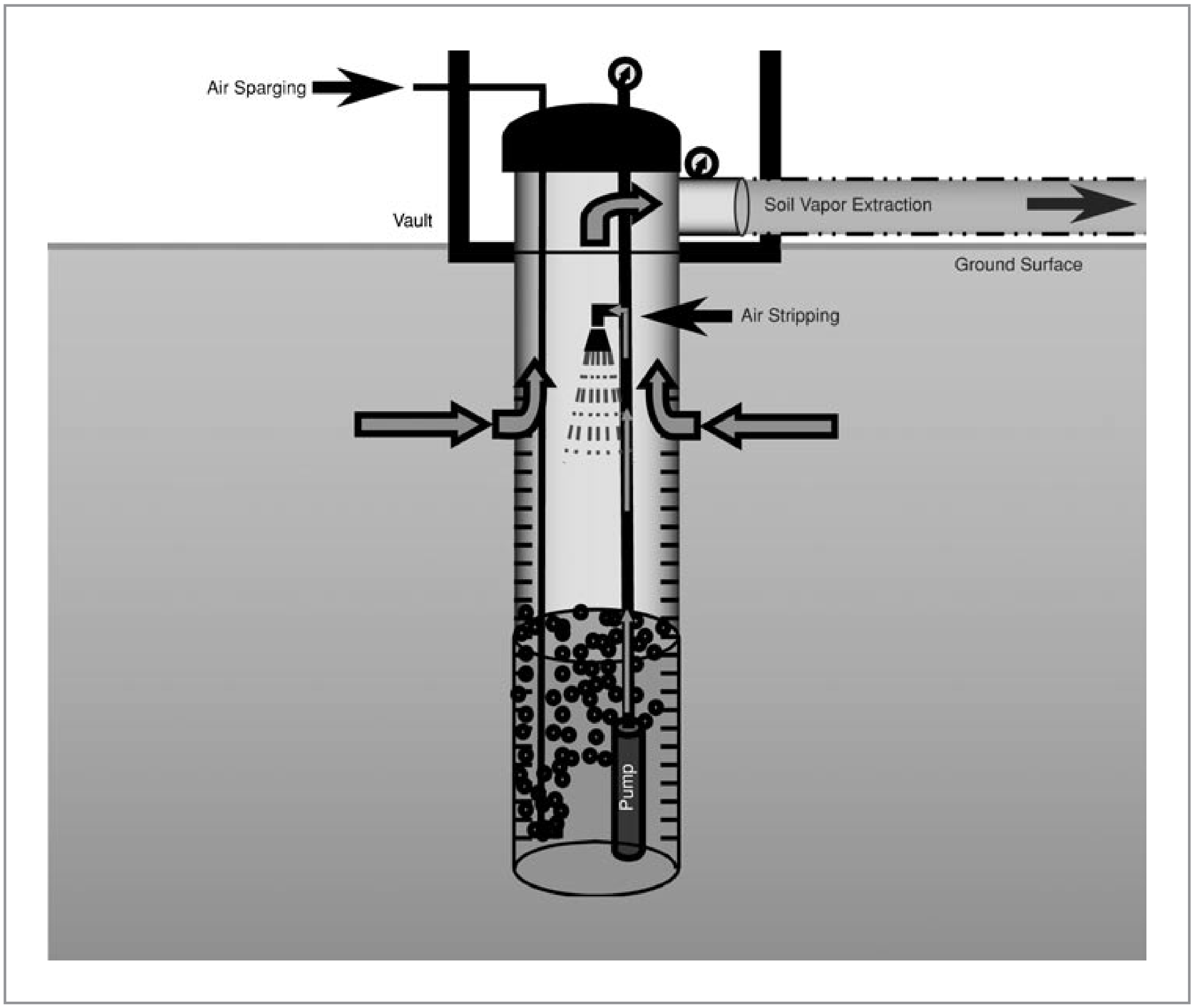

Exhibit 2. Conceptual depiction of combined technologies in ART remediation well

The well was constructed to be screened from approximately 5 feet below ground to approximately 45 feet below ground, immediately above the bedrock surface. The screen is situated to cross the water table, which occurs at an approximate depth averaging from 7 to 11 feet below ground. The geological profile at the site consists of a layer of silty clay from 4 to 7 feet thick underlain by approximately 30 to 35 feet of poorly graded sand and gravel with a cobble zone up to 6 feet thick commonly encountered approximately 24 to 30 feet deep.

The well was developed by setting the pump intake at a given screened interval and oscillating flow rates between 5 and 60 gallons per minute (gpm), then moving the pump intake down 5 feet and repeating the process. Approximately 10,000 gallons of groundwater were removed during development (CH2M HILL, 2005). ART personnel installed the well sparging and in-well apparatus.

Air Sparging and Soil Vapor Extraction System Connections

The air sparging and soil vapor extraction (SVE) connections to required pipes and blowers was completed after the well installation and development. The air sparging line

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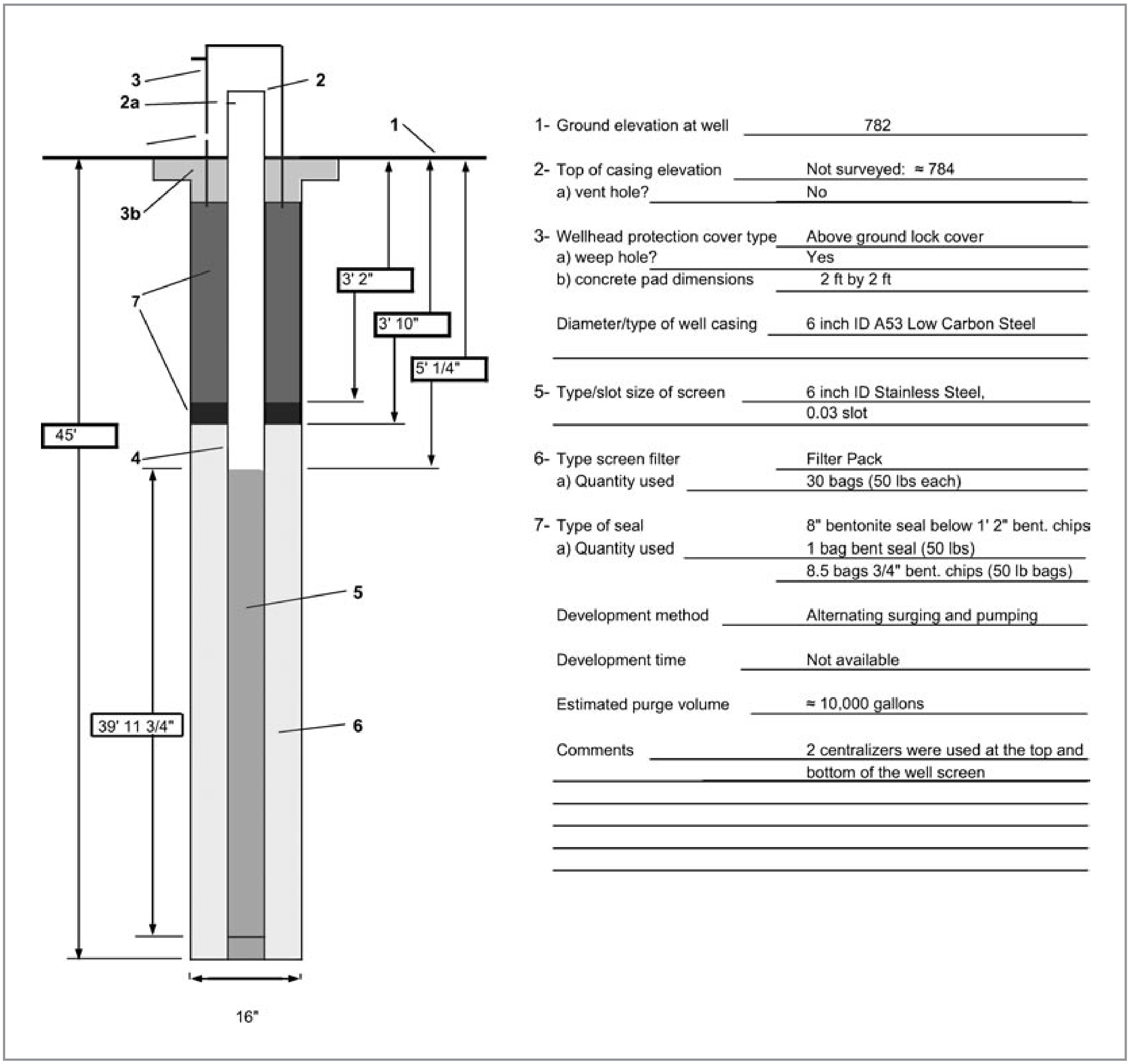

Exhibit 3. RW01 well construction diagram

for the ART system was connected to the existing, onsite UV system compressor. The SVE discharge system was constructed such that air samples could be collected immediately downstream of the remediation well and from the air stack (Exhibit 4).

TEST DURATION AND SAMPLING

The ART air sparging and SVE system was operated from September 24, 2004, until March 21, 2005, with the following exceptions (CH2M HILL, 2005):

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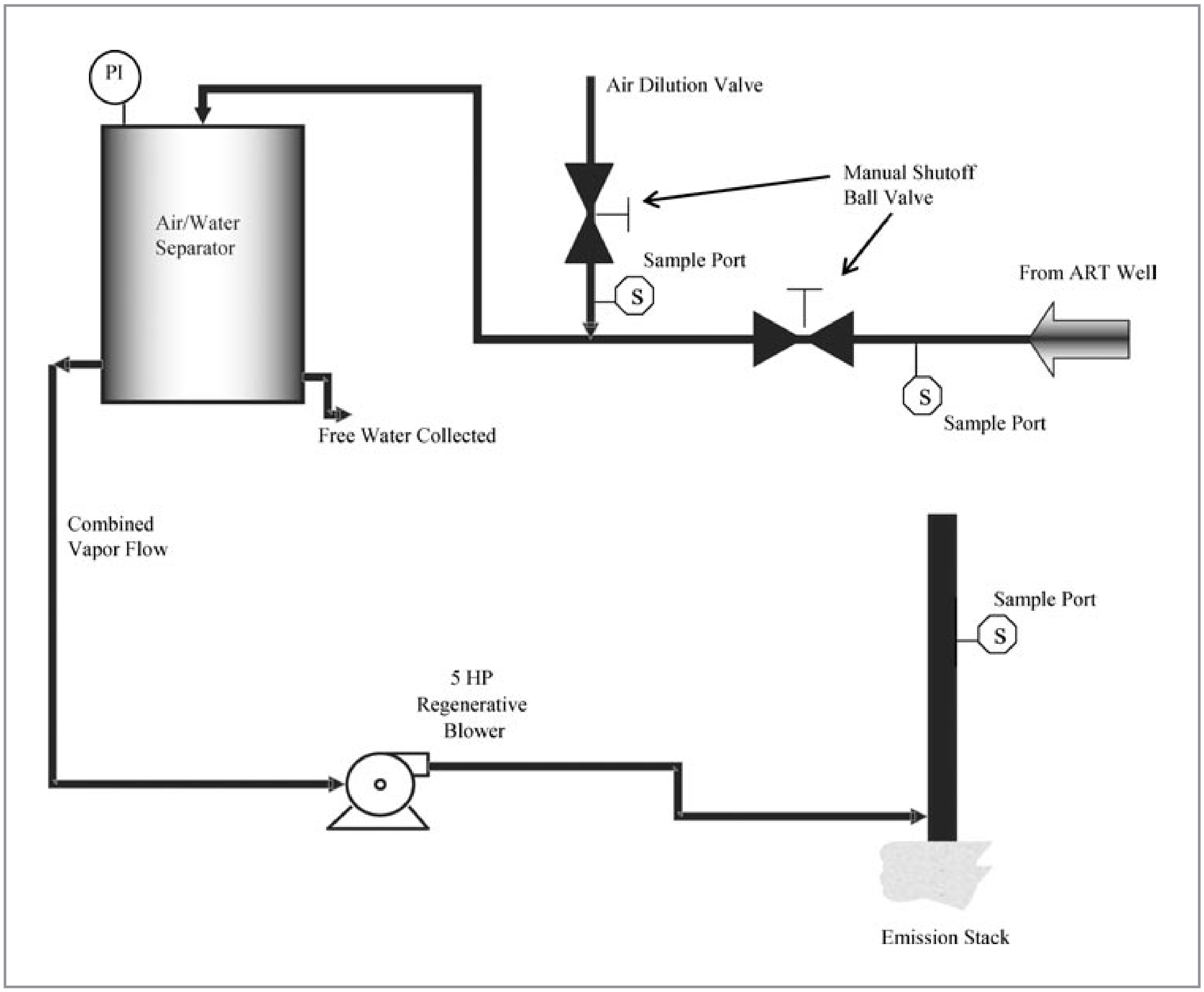

Exhibit 4. Schematic drawing of aboveground vapor stream line

- The ART well injection system was shut off between October 19 and 22, 2004. The air injection component for ART is tied into the UV system. A power failure caused the UV system and the ART air injection to shut down. A vacuum was still present for the SVE portion of the system, but *in situ* air stripping was not occurring. The system was restarted on October 22, 2004.
- The ART SVE system was down between December 27, 2004, and January 17, 2005, because the lines were frozen.

In addition, the existing GCTS was in operation during the ART pilot test on the following dates:

- September 24–25, 2004
- September 27, 2004
- October 2, 2004
- October 15–17, 2004
- December 3, 2004

- December 6–15, 2004
- December 23–25, 2004
- December 30–31, 2004
- January 3–8, 2005
- February 2–4, 2005

The GCTS consists of an extraction well system that pumps an approximate total of 40 gpm from wells EW-02 (15 gpm) and EW-03 (25 gpm) to obtain an inward gradient between the regional groundwater elevation and the groundwater elevation inside the site's soil-bentonite containment wall (CH2M HILL, 2003). When pressure transducer data indicate that an average inward gradient of approximately 1.5 feet has been obtained, the system shuts off and is not reactivated until water levels at monitoring location PZ-13 within the SBCW start to decrease (i.e., when the gradient shifts from inward to outward through the SBCW).

According to the calculations completed using the pilot test data, the ART In-Well Technology was successful in removing more than 9,000 pounds of VOC mass during the pilot tests based on air sampling data.

Pilot-test monitoring and sampling were performed during the ART system operation. Field meters were used to record measurements for soil vapor and groundwater parameters in the monitoring wells near the ART well, including dissolved oxygen, pH, oxidation-reduction potential (ORP), temperature, and water levels (CH2M HILL, 2004). Air samples were collected from the ART well sampling port and from the air stack during the test. Groundwater samples were also collected from 12 wells on three occasions: September 10, 2004 (baseline conditions prior to system start-up); December 19, 2004; and March 19, 2005.

DATA RESULTS AND DISCUSSION

Air Samples—ART Wellhead and Stack

Exhibit 5 summarizes the well data for the air samples collected from the wellhead and from the stack (CH2M HILL, 2005). Air samples from the wellhead were collected throughout the duration of the pilot test, and stack samples were initiated in November 2004. Exhibit 6 is a summary of the monthly stack and wellhead estimates using the VOC and velocity information collected during the test (CH2M HILL, 2005).

The sample results for those dates when both wellhead and stack samples were collected appear to be directly comparable. Because the wellhead has more sample data than the stack, Exhibit 6 includes a monthly estimate of total VOCs extracted from the subsurface using the wellhead data. According to the calculations completed using the pilot test data, the ART In-Well Technology was successful in removing more than 9,000 pounds of VOC mass during the pilot tests based on air sampling data (CH2M HILL, 2005). Overall, the VOC mass removal rate decreased throughout the period of the pilot test. For example, using the wellhead data, results from the September sampling event indicated a total removal of 269 pounds per day of VOCs, while results from the March sampling event indicated a reduced amount of 20 pounds per day. The high initial VOC removal rate is likely due to the removal of readily available VOCs in the groundwater and soil vapor within the radius of influence of the test. After the initial removal, the ART system was likely only removing mass as it entered the radius of influence of the well. Alternatively, some of the reduction in mass removal rates may be

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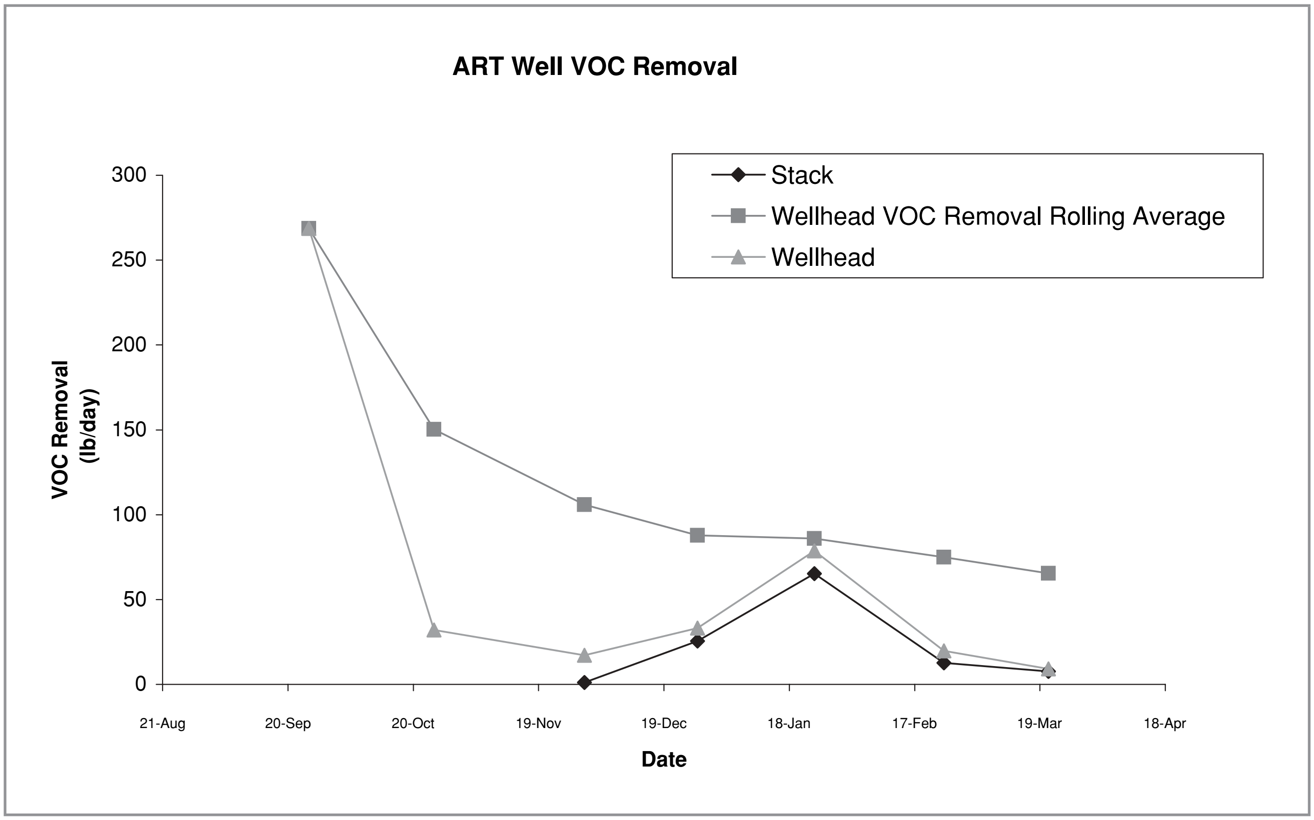

Exhibit 5. ART well VOC removal

due to mineralization within the ART well and/or on its components (see the "Mineralization in the ART Well Screen" section later in this article).

Exhibit 7 is a summary, by individual VOC, of estimated constituent removal using monthly wellhead data. The last column in Exhibit 7 is the average for each VOC that is detected using all the time periods' data. Based upon the data collected over the six-month duration of the pilot test, an average estimated total of 12 tons per year of VOCs would be removed using this well (CH2M HILL, 2005).

It should be noted that the threshold for requirement of a US EPA Title V air permit, given the constituents present in the air data, is 25 tons per year (TPY) for total VOCs, or 10 TPY for any individual hazardous air pollutant (HAP). Polk County is authorized by the State of Iowa to permit air emissions for sites within the county. All results of the air sampling performed during the pilot test were submitted to Polk County. Based on all the pilot-test data collected the threshold limits for VOCs would not be exceeded for a 12-month period of operation.

GROUNDWATER MONITORING WELLS AND PIEZOMETERS

Air Monitoring

Air meter readings were taken from the monitoring well casings during the ART pilot testing. Photoionization detector (PID), oxygen, and carbon dioxide readings were

Exhibit 6. Monthly summary—Total VOCs removal estimates*

Date	Stack (TPY)	Stack (lb/day)	Wellhead (TPY)	Wellhead (lb/day)	Wellhead VOC Removal Rolling Average (lb/day)	Period (days)	lbs/period	Cumulative VOCs (lbs)	Time Interval
25-Sep-04			49.0	268.7	268.7				
25-Oct-04			5.8	32.0	150.4	30	4511	4511	Sep 25–Oct 25, 2004
30-Nov-04	0.2	1.0	3.1	17.1	105.9	36	885	5396	Oct 26–Nov 30, 2004
27-Dec-04	4.7	25.5	6.1	33.3	87.8	27	680	6076	Dec 1–Dec 27, 2004
24-Jan-05	11.9	65.3	14.4	78.7	86.0	28	1568	7644	Dec 28, 2004–Jan 24, 2005
24-Feb-05	2.3	12.8	3.6	19.7	74.9	31	1526	9170	Jan 25–Feb 24, 2005
21-Mar-05	1.4	7.7	1.7	9.1	65.5	25	360	9530	Feb 25–Mar 21, 2005

*Estimates were calculated using monthly VOC sample data for wellhead and stack samples.

TPY = tons per year.

Exhibit 7. Estimated average VOC removal—Individual VOCs*

	Annual VOC Removal Projections using Monthly Data (TPY)							
Parameter	**Sep-04**	**Oct-04**	**Nov-04**	**Dec-04**	**Jan-05**	**Feb-05**	**Mar-05**	**Average**
carbon tetrachloride	0.001	0	0	0	0	0	0	0.000
chloroform	0.001	0	0	0	0	0	0	0.000
1,1-dichloroethane	0.060	0.010	0.068	0.009	0.028	0.008	0.003	0.026
cis-1,2-dichloroethene	0.487	0.156	0.753	0.092	0.447	0.126	0.045	0.301
ethylbenzene	0.108	0.090	0.062	0.072	0.088	0.028	0.011	0.066
methylene chloride	0.515	0.024	0.003	0.022	0.055	0.017	0.007	0.092
tetrachloroethene	34.909	4.449	1.141	4.546	10.057	2.235	1.180	8.359
toluene	0.300	0.111	0.132	0.110	0.340	0.118	0.041	0.165
1,1,1-trichloroethane	10.730	0.833	0.377	0.847	2.773	0.913	0.306	2.397
trichloroethene	1.147	0.109	0.029	0.090	0.287	0.061	0.024	0.250
vinyl chloride	0.080	0.002	0.399	0.003	0.008	0.002	0.001	0.071
xylenes (total)	0.694	0.065	0.160	0.279	0.288	0.092	0.041	0.231
							Total	11.958

*For each sampling month's VOC data, projected annual VOC removal rates were estimated. These monthly projections were then averaged to provide an overall yearly projection representative of all VOC data collected during the ART pilot test.
TPY = Tons per Year.

recorded (Exhibit 8). Carbon dioxide was generally not detected at the limits of the field equipment. A summary of data results for oxygen and PID readings is discussed below.

Oxygen

The overall site trend appears to consist of an initial increase in oxygen with an anomalous high reading in December and a general declining trend in March. This appears to correlate to operating the GCTS for 16 days during December—as such groundwater levels may have been depressed, allowing more oxygen in the well screens and at the well heads (CH2M HILL, 2005). The GCTS was not operated between February 5, 2005, and the end of the ART remediation well test in March. Groundwater levels may have stabilized at slightly higher elevations during this time, allowing for lower oxygen levels in air meter readings at the wellheads.

PID

Photoionization readings in the monitored wells generally showed no trends.

Groundwater Monitoring

Water-level measurements and field parameter measurements were taken at the monitoring wells and piezometers shown in Exhibit 1 during the ART pilot testing. Water-level measurements were made using an interface probe before three well volumes

Exhibit 8. Groundwater field and laboratory data-site trends and observations

				Field Parameter						Laboratory Data		
Well	**Unit**	**VOC Conc**	**Approx. Distance from ART well (ft)**	**O2 (air)**	**PID (air)**	**DO**	**pH**	**ORP**	**Temp**	**PCE**	**cis-1,2-DCE**	**Other VOC Trends**
PZ-10I	I	H	11	Increase in beginning, high reading in late Dec, declining in March	Flat until mid-Dec, followed by an exponential increase, spike and decrease in March	Increase after each startup	Downward	Increase	Downward	Decrease by 7.5x	No trend	VC increase 5.6x
PZ-08I	I	L	58	Increase in beginning, high reading in late Dec, declining in March	Flat until Jan, increase until mid-Jan, followed by decrease, spike in March followed by decrease	Decreasing	Downward	Downward	Downward	Decrease by 1.9x	No trend	
MW-02D	D	M	60	High reading in late Dec, declining in March	Downward, increasing in March	No trend	Downward, inflection in late Dec	Increasing, inflection in late Dec	Downward	No trend	No trend	
MW-081	I	H	60	Increase in beginning, high reading in late Dec, declining in March	Inflection after shutdown in Jan	Decreasing	Downward, inflection in late Dec	Increasing, flat in Nov/Dec	Downward	Decrease by 20x	Decrease 1.7x	1,1,1-TCA decrease by 1.7x, 1,1-DCA decrease by 1600X to ND; 1,1-DCE decrease 800X to ND; 2-butanone decrease 16000x to ND; decrease acetone 2.4x; increase VC 1.8x; decrease 1,4-dioxane 1.9x
PZ-08D	D	L	62	Increase in beginning, high reading in late Dec, declining in March	Flat until increase in Jan after shutdown, decrease in March, multiple inflections	Flat, spike in Nov	Downward	Increase	Downward	ND	Increase 5.8x	1,4-dioxane decrease 10x
PZ-9I	I	H	62	Stable with a low in beginning of Dec	Flat until mid December followed by an exponential increase	No trend	Downward	Increase	Downward	ND	Decrease by 25x	
MW-02S	S	M	65	Increase in beginning, high reading in late Dec, declining in March	Decrease in beginning. Flat, increase March	Slight increase to flat	Downward, Inflection in late Dec	Increasing after shutdown in Jan	Downward	Decrease by 4x	Increase 1.5x	1,1,1-TCA decrease by 4x, 1,1-DCA increase 3.8X, 1,1-DCE decrease 2.3X, increase VC 4.5x
PZ-09D	D	H	65	Increase in beginning, high reading in late Dec, declining in March	Flat until increase beginning in Jan	Decreasing	Downward	Increase in beginning, flat later	Downward	Overall decrease by 1.7x	Decrease by 1.3x	1,1,1-TCA decrease by 2400x to ND, 1,1-DCA decrease to 4500x to ND, 1,1-DCE increase 3.2X, decrease acetone 30000x to ND.
MW-08S	S	H	68	Increase in beginning, high reading in late Dec, declining in March	Flat, spike late Feb	No trend	Downward	Flat	Downward	Decrease by 2.5x	No trend	1,1,1-TCA decrease by 1.8x, 1,1-DCA decrease by 1100x to ND; 1,1-DCE decrease 1.6x; 2-butanone decrease 62x; decrease 4-methyl-2-pentanone 7900x to ND; decrease acetone 7.5x; decrease TCE 2200x to ND; decrease 1,4-dioxane 7x

Exhibit 8. Groundwater field and laboratory data-site trends and observations (continued)

				Field Parameter						Laboratory Data		
Well	**Unit**	**VOC Conc**	**Approx. Distance from ART well (ft)**	**O2 (air)**	**PID (air)**	**DO**	**pH**	**ORP**	**Temp**	**PCE**	**cis-1,2-DCE**	**Other VOC Trends**
PZ-7I	I	L	165	Increase in beginning, high reading in late Dec, declining in March	Flat, spike following shutdown in Jan	Increase after each startup	Downward	Increase	Downward	ND	No trend during ART test; however, large increase from previous conc observed at well	Increases in other parameters also apparent
PZ-7D	D	L	170	Increase in beginning, high reading in late Dec, declining in March	Flat, increase in beginning of Dec, increase and spikes following shutdown in Jan, decrease in March	Slight increase after each startup	Flat	No trend	Flat	ND	No trend during ART test; however, large increase from previous conc observed at well	Increases in other parameters also apparent
Overall Observations:				Overall trend appears to be an initial increase, an anomalous high reading in late Dec (corresponds to low water elevations) and a decline in March	No overall trends	No overall trends	Overwhelmingly downward, may be a result of CO2 productlon from natural attenuation. CO2 dissolves in water reducing pH	In general increasing, becoming more oxidized; anomalies at MW-08S (flat), PZ-08I (downward). and PZ-7D (no trend)	Downward at all locations except PZ-7D; downward is likely related to seasonal variations and may usually be more apparent in shallow wells; however, with the "circulation" induced from the ART well, all zones reacting to seasonal variation. If this is true, it would suggest that the radius of influence does not extend to PZ-7D (170 ft) because there is no temperature decease there	Decreases the greatest amount at wells with highest "starting" concentrations and at shallow/intermediate locations	Decreases observed at intermediate and deep wells with the highest "starting" concentrations. Large increases at PZ-07 nest vs. background concentration. suggesting radius of influence does reach the nest	Some significant decreases in some compound concentrations (generally parent chlorinated compounds or other compounds—such as 2-butanone and acetone). Some increases in degradation product concentrations

Notes:

S = Shallow well screen (typically situated across the groundwater table).

D = Deep well screen (typically situated at the bottom of the aquifers 45 feet deep).

I = Intermediate well screen (between shallow and deep).

ND = Not detected.

111-TCA = 1,1,1-Trichloroethane.

PCE = Tetrachloroethene.

Cis-12-DCE = cis-1,2-Dichloroethene.

1,1-DCE = 1,1-Dichloroethene.

1,1-DCA = 1,1-Dichloroethane.

TCE = Trichloroethene.

VC = Vinyl chloride.

Exhibit 9. Data from CMS pilot studies, August and September 1996

		Parameter		
Date	**GCTS Well**	**Iron (mg/L)**	**Calcium (mg/L)**	**Magnesium (mg/L)**
08/21/1996	EW-02	4.5	107	38.9
09/06/1996	EW-02	4.4	NR	NR
08/21/1996	EW-03	3.4	99.5	36.3
09/06/1996	EW-03	3.2	NR	NR

had been purged from each monitoring point. Field parameters were taken from each well using a flow-through cell attached to Waterra tubing.

Water-Level and DNAPL Measurements

Water-level elevations were calculated from measurements for each well. The trend from well to well is identical, starting with an overall high in September and November, decreasing steadily until mid-February, then increasing again in March. These declines in water elevations correspond directly to GCTS operation, which was for 16 days during December, 5 days in January, 3 days in February, then no more GCTS operation until the end of the ART remediation well test on March 21, 2005 (CH2M HILL, 2005).

The influence of the ART system could not be directly measured at wells that have historically shown the presence of DNAPL, MW-08D and PZ-10D. Due to the instrumentation present in these wells for DNAPL collection as part of the GCTS system, measurement of DNAPL thickness using an interface probe was impeded. However, it was noted that there was not a measurable increase in the volume of DNAPL collection from these wells during the ART pilot test. DNAPL was not identified at any of the other monitoring points during the ART pilot test measurements.

Field Parameters

Dissolved oxygen, pH, ORP, and temperature were measured using flow-through cell analysis and field meters attached to the Waterra well purge system. Dissolved oxygen concentrations showed no discernible trends based on the site data.

pH

The pH trend throughout the site was downward. This may be a result of biological degradation processes releasing carbon dioxide, which in turn dissolves in groundwater and decreases the pH (CH2M HILL, 2005).

ORP

The ORP trend increased during the ART system operation, indicating that subsurface conditions were becoming more oxidized (CH2M HILL, 2005). At the monitoring location closest to the remediation well, PZ-10I, the ORP value increased from –100 mV

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Exhibit 10. VOC removal estimate using GCTS (EW-02) data*

Parameter	Conc. (ug/L)	Discharge (ug/min)	Discharge (lb/min)	Hourly Discharge (lb/hr)	Daily Discharge (lb/day)	Annual Discharge (lb/yr)	Annual Discharge (TPY)
carbon tetrachloride	ND						
chloroform	—						
1,1-dichloroethane	1930	292,234	0.0006	0.039	0.926	337.92	0.169
cis-1,2-dichloroethene	27700	4,194,234	0.0092	0.554	13.287	4849.88	2.425
ethylbenzene	1360	205,926	0.0005	0.027	0.652	238.12	0.119
methylene chloride	ND						
tetrachloroethene	106	16,050	0.0000	0.002	0.051	18.56	0.009
toluene	1320	199,870	0.0004	0.026	0.633	231.11	0.116
1,1,1-trichloroethane	1570	237,724	0.0005	0.031	0.753	274.88	0.137
trichloroethene	ND						
vinyl chloride	7400	1,120,481	0.0025	0.148	3.550	1295.64	0.648
xylenes (total)	4520	684,402	0.0015	0.090	2.168	791.39	0.396
1,1-dichloroethene	300	45,425	0.0001	0.006	0.144	52.53	0.026
acetone	4450	673,803	0.0015	0.089	2.135	779.13	0.390
trans-1,2-Dichloroethene	182	27,558	0.0001	0.004	0.087	31.87	0.016
2-butanone (MEK)	1350	204,412	0.0004	0.027	0.648	236.37	0.118
				Total:	25.034	9137.378	4.569

*Calculations were performed using one set of groundwater sample results for EW-02, the GCTS extraction well situated in the immediate vicinity of ART remediation well RW-01 and assuming a pumping rate of 40 gpm.

TPY = Tons per Year.

Example Calculation for vinyl chloride:

Column C: 7400 ug/L × 3.7854 L/gal × 15 gpm = 420,181 ug/min.

Column D: 420,181 ug/min × 2.20 × 10^{-9} Ib/ug = 0.0009 Ib/min.

Column E: 0.0009 Ib/min × 60 min/hr = 0.055 Ib/hr.

Column F: 0.055 Ib/hr × 24 hr/day = 1.33 Ib/day.

Column G: 1.33 Ib/day × 365 day/yr = 485.86 Ib/yr.

Column H: 485.86 Ib/yr × 0.0005 ton/Ib = 0.243 tons/yr.

to –14 mV over the test duration, with the increase most obvious starting in mid-December. Locations MW-08S and MW-08I are a little further from the remediation well than PZ-10I, and these locations experienced an ORP increase from –100 mV to –40 mV starting near the end of December. The location furthest from the remediation well is the PZ-07 nest. ORP at PZ-07I was mostly stable, with an ORP of –100 mV, but experienced an increase starting in mid-February to –55 mV.

Anomalies to the increasing ORP trend were at MW-08S and PZ-7D where no trend was observed, and PZ-08I where a downward trend was observed. MW-08S and PZ-08I are relatively close to the location of the ART well, and mixing due to ART well groundwater circulation may have voided any upward ORP trend at these points. The ORP data suggest that changes to water quality can take several months (three months) to occur near the ART well, and even longer (five months) further from the ART well. Furthermore, the magnitude of water quality changes is highest near the well and decreases with distance from the well. The ORP data suggest that the radius of influence of the ART well reaches to at least 165 feet in the intermediate zone at the site.

The overall increasing ORP trend is independent of the groundwater level trend with a low ORP reading in mid-December, increasing ORP through the end of the test in

March. In other words, the increasing ORP trend is not due to additional oxygen in the aquifer matrix from a depressed water table due to GCTS operation. The ORP trend is due to other factors, including the effect of the ART well operation.

Temperature

The temperature trend was downward at all locations except PZ-7D. The downward temperature trend is likely related to seasonal variations (the system was started in the fall of the year and continued through the winter months) (CH2M HILL, 2005). It is expected that the shallow wells of each nest may be more susceptible to air temperature changes. However, a temperature difference was not seen between shallow and deep well sets that are near the ART well during this pilot test, possibly due to the circulation of water induced by the operation of the remediation well system. PZ-7D, located approximately 170 feet from the ART well, showed no trend in temperature, similar to the ORP data for this well, suggesting that the radius of influence from the ART well may not reach 170 feet in the deep interval.

Overall, the greatest decreases in concentration were noted at those wells with the highest "starting" concentrations and at shallow or intermediate screened wells as opposed to deep screened wells.

Laboratory Analytical Results

Analytical results are presented in Exhibit 8.

Overall trends by parameter, both "parent" and "daughter" parameters in terms of natural attenuation processes, are discussed herein.

Tetrachloroethene

PCE is considered a "parent" constituent in regard to the presence of chlorinated constituents and their potential degradation at the site. Parent constituents degrade to "daughter" constituents. The PCE concentration decreased at every well where it was detected during the study, with the exception of MW-02D, where there was no discernible trend (CH2M HILL, 2005). The amount of concentration decrease ranged from 1.7 to 20 times between the initial and final groundwater data sets. MW-08I, which is nearest to the ART well and screened at the optimum depth at which ART well influence should be seen, had a decrease from 390 μg/L to not detected over the duration of the test. Overall, the greatest decreases in concentration were noted at those wells with the highest "starting" concentrations and at shallow or intermediate screened wells as opposed to deep screened wells.

Cis-1,2-dichloroethene (*cis*-1,2-DCE)

Cis-1,2-DCE is a "daughter" constituent that results from biological processes of parent constituents such as PCE and TCE. Decreases in *cis*-1,2-DCE concentrations were observed at intermediate and deep wells that had the highest "starting" concentrations at the beginning of the test (CH2M HILL, 2005). An example is PZ-09I, where concentrations decreased from 450,000 μg/L to 18,000 μg/L. A relatively large increase is evident at the PZ-07 nest versus historical background concentrations, which suggests the radius of influence does reach this location. The increased *cis*-1,2-DCE concentration

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at PZ-07 may have been caused by the operation of the GCTS, since pumping occurs at EW-02, which is in the vicinity of PZ-07.

Other VOC Trends

Trends for some of the other VOC constituents were evaluated through time for the test duration. There were significant decreases in some of these compounds during the test as noted in Exhibit 8—generally parent chlorinated compounds (TCE) or other compounds, such as 2-butanone and acetone. There were also some increases noted in common degradation products such as vinyl chloride in PZ-10I near the remediation well and 1,1-DCE in PZ-09D approximately 65 feet away from the remediation well.

GROUNDWATER DATA DISCUSSION

The field parameters of ORP, temperature, and pH provided some insight into estimation of a radius of influence (ROI) for the ART well, as well as support for the premise that natural attenuation of chlorinated constituents is ongoing in the vicinity of the well. The ORP generally increases at all locations, becoming more oxidized through time. The increase in ORP also appears to be dependent upon how close the monitoring point is situated to the remediation well: the closer to the remediation well, the earlier the ORP increase is noted, and the greater the increased oxidation.

The variability in the groundwater data is likely due to the many factors at work in response to the multiple technologies being implemented inside the remediation well. Some of these potential factors include:

- NAPL being mobilized within the aquifer matrix;
- NAPL dissolving in groundwater;
- NAPL evaporating to the air phase;
- dissolved constituents in groundwater concentrations being stripped into the vapor phase; and
- dissolved constituents in groundwater moving nearer and/or farther from the remediation well depending where the circulation cycle is situated.

The variability in the groundwater data is likely due to the many factors at work in response to the multiple technologies being implemented inside the remediation well.

In addition, the extraction wells for the GCTS were operated several times during the ART pilot test. The operation of these wells (most notably, EW-02) may have moved groundwater and impacted the groundwater elevation in the vicinity of the ART monitoring points.

Another factor potentially influencing the data collected was winter weather. The SVE system froze in January for 1–2 weeks so SVE operation was suspended during this time, although the sparging was apparently still operating. Several other observations relevant to the evaluation of groundwater data collected during the pilot test can be made including: (1) a determination of the radius of influence for the remediation well, (2) a determination that there is an overall reduction in constituent concentration (and therefore mass) in groundwater, and (3) a determination that natural attenuation is ongoing in this region, possibly due to or enhanced by operation of the ART.

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RADIUS OF INFLUENCE

The monitoring well nest located farthest from the remediation well, at approximately 170 feet, is the PZ-07 nest, for which there is conflicting data. The ORP and temperature data for PZ-7D appear to indicate there is no influence of the remediation well out this far/this deep. However, large increases of *cis*-1,2 DCE at both PZ-07 wells versus background concentrations suggest that the ROI does reach the nest (i.e., that concentrations from farther east beneath the former tank farm area have been pushed westward toward the PZ-07 nest). These conflicting data may indicate that the PZ-07 nest is on the fringe of the radius of influence provided by the remediation well. The remainder of the monitoring points are all well within the 170-foot radius (PZ-10I is very close at 11 feet away; the remainder of the locations are all between 60 and 65 feet away from the remediation well), and data available for these points do not appear to indicate a specific radius of influence. Even with an ROI of 100 feet, the area where DNAPL has been identified is covered by the one remediation well.

Subsurface data collection starting in the early 1990s has indicated reducing conditions and ongoing natural attenuation, both beneath the former storage tank area and downgradient of the site.

CONCENTRATION/MASS REDUCTION

Laboratory analytical data for groundwater indicate significant decreases in the concentrations of some of the parent, chlorinated compounds and for other compounds. such as 2-butanone and acetone. Some increases in chlorinated degradation product concentrations are also indicated. These effects are probably due to the combined effect of ART processes (stripping, sparging, vacuum extraction, etc.) and due to natural attenuation processes.

EVIDENCE OF NATURAL ATTENUATION

Subsurface data collection starting in the early 1990s has indicated reducing conditions and ongoing natural attenuation, both beneath the former storage tank area and downgradient of the site. Pilot-test data also indicate ongoing natural attenuation processes are evident in the vicinity of the remediation well and its monitoring points based upon a reduction of pH in the groundwater, an increase in *cis*-1,2-DCE in some wells, and an increase in vinyl chloride at some locations. Degradation products identified during pilot testing could be from previous conditions but may have been enhanced by the remediation well processes to some degree.

MINERALIZATION IN THE ART WELL SCREEN

The reduced VOC removal efficiency through the duration of the ART pilot test (Exhibit 5) may be due to mineralization from dissolved groundwater constituents such as on the well screen and/or on ART components such as the sparging head. A downhole camera was utilized to observe the screen condition. Mineralization was evident within the screen based on the downhole photography. In addition, the wellhead cover was dismantled, and a visual inspection of the well sparging apparatus noted the presence of mineralization on the outside of the air sparging casings.

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Iron, calcium, and magnesium data are available for pumped samples from EW-02 and EW-03, collected during CMS pilot studies completed for this site. These studies were completed in August and September 1996, and the results are shown in Exhibit 9.

Based upon these data, it is anticipated that dissolved minerals may precipitate over time with continued addition of air to the subsurface during the ART operation. Continued precipitation will result in encrustation of the well screen, for which rejuvenation (typically consisting of acidification and surging of the well screen) needs to be periodically performed.

VOC REMOVAL EFFICIENCIES

Estimated VOC removal for the ART system, using the ART pilot-test data, indicates that an average of 12 TPY of total VOCs can be removed using ART. To evaluate "removal efficiency" of this technology at this site, the total ART removal estimate was compared to an estimate of VOCs removed using the GCTS groundwater pumping system. Note that the objective of current GCTS operation is not mass removal. Extraction well EW-02 is situated in the same immediate vicinity of the ART remediation well. The most recent groundwater sample collected from EW-02 was collected in March 2004. Exhibit 10 includes a mass removal estimate, using the concentrations detected in groundwater in 2004 and assuming a flow rate of 40 gpm, which is the maximum throughput of the treatment system. Using the GCTS, and pumping only from EW-02 at 40 gpm, it is estimated that approximately 4.6 TPY of total VOCs could be removed. Note that this assumes continuous operation of EW-02 at a rate of 40 gpm. These assumptions produce a high estimate of what could be removed from groundwater at EW-02 using the 40-gpm-flow rate. Actual mass removal using the existing GCTS would be lower because the GCTS is not operated continuously—it is activated based upon the difference between groundwater levels inside and outside of the SBCW.

The treatment cost for the extracted water produced from the pumping varies with the concentrations of the influent but falls within the range of \$8 to \$10 per thousand gallons when the treated effluent is discharged to the publicly owned treatment works. This results in an annual cost for treatment and discharge of approximately \$167,000 to \$210,000 if continuous pumping is assumed. These costs to operate the GCTS far exceed the annual projected cost to maintain the ART well of less than \$50,000 per year.

The comparison of 12 TPY ART versus the estimated 4.6 TPY using GCTS/EW-02 indicates that ART operation provides a relatively efficient way to remove VOC mass.

It is anticipated that dissolved minerals may precipitate over time with continued addition of air to the subsurface during the ART operation.

CONCLUSIONS

Conclusions from the ART system pilot test are as follows:

- The ART remediation well can remove contaminant mass from the subsurface, including the aquifer system, based upon remediation well and well stack air data.
- There is no direct evidence that operation of the ART remediation well enhances the current system of DNAPL collection at the site.
- The radius of influence of the ART well with respect to groundwater remediation appears to be between 65 and 170 feet.

- Natural attenuation of chlorinated constituents has been ongoing in the groundwater in the vicinity of the remediation well for many years. The rate of natural attenuation in this vicinity may decrease with increasing ART remediation well operation as the aquifer becomes more oxygenated and as easily available carbon sources (i.e., acetone, 2-butanone, benzene, toluene, ethylbenzene, and xylene) are degraded. However, the potentially reduced rate of degradation in groundwater would be offset by the mass removed from the subsurface by the ART system.
- The comparison of 12 TPY ART versus the estimated 4.6 TPY using GCTS/EW-02 indicates that ART operation provides a more cost-effective way to remove VOC mass.
- Mineralization effects on the ART system components and on the well screen were evident based on visual observation of ART components and downhole photography. Based upon the site's existing data for dissolved iron, calcium, and magnesium, it is anticipated that these concentrations of dissolved minerals may continue to precipitate on the well screen and/or other ART components over time with continued addition of air to the subsurface during ART operation. Rejuvenation of the well screen can be periodically accomplished as necessary using acidification and surging methods.

FUTURE PLANS

The existing ART well will be restarted. With the renewed operation of this well, Polk County may require an air construction permit. Groundwater field parameters will continue to be monitored upon well start-up. Monitoring points farther out than 160 feet may be included to confirm the radius of influence in more than one direction within the SBCW. A baseline conditions set of data will be collected, including a full round of VOC data and field parameters prior to ART well start-up. Well-screen rejuvenation will be incorporated in future operation and maintenance activities one to two times per year.

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