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Implementation of Passive Samplers for Monitoring Volatile Organic Compounds in Ground Water at the Kansas City Plant

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**Implementation of Passive Samplers
for Monitoring Volatile Organic Compounds
in Ground Water at the Kansas City Plant**

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For Environmental Restoration Program
at the
Kansas City Plant
U.S. Department of Energy
Kansas City, Missouri

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ACRONYMS AND ABBREVIATIONS

AlliedSignal FM&T	AlliedSignal Federal Manufacturing & Technologies
bgs	below ground surface
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,2-DCE	1,2-dichloroethene
DI	deionized
ft	feet
g	gram(s)
KCP	Kansas City Plant
µg/L	micrograms per liter
µL	microns per liter
mL	milliliter
MS/MSD	matrix spike/matrix spike duplicate
ND	non-detectable
QA	quality assurance
QC	quality control
TCE	trichloroethene
VC	vinyl chloride
VOCs	volatile organic compounds

EXECUTIVE SUMMARY

Passive sampling for monitoring volatile organic compounds (VOCs) has been suggested as a possible replacement to the traditional bailer method used at the Department of Energy Kansas City Plant (KCP) for routine groundwater monitoring. To compare methods, groundwater samples were collected from 19 KCP wells with VOC concentrations ranging from non-detectable to >100,000 µg/L.

Analysis of the data was conducted using means and medians of multiple measurements of TCE, 1,2-DCE, 1,1-DCE and VC. All 95% confidence intervals of these VOCs overlap, providing evidence that the two methods are similar.

The study also suggests that elimination of purging and decontamination of sampling equipment reduces the labor required to sample by approximately 32%. Also, because the passive method generates no waste water, there are no associated disposal costs. The results suggest evidence to continue studies and efforts to replace traditional bailer methods with passive sampling at KCP based on cost and the similarity of the methods.

1.0 INTRODUCTION

AlliedSignal Federal Manufacturing & Technologies (AlliedSignal FM&T) and Oak Ridge National Laboratory/ Environmental Technology Section conducted field scale tests of passive samplers capable of producing representative water samples for volatile organic compounds (VOCs). The objective of the demonstration was to compare the passive sampling method with the standard bailer method typically used at the Kansas City Plant (KCP) for routine monitoring. The passive samplers consisted of polyethylene bags containing deionized (DI) water. Sampling relies on diffusion of VOCs through the polyethylene membrane. The passive sampling approach was tested and evaluated at the KCP using a population of 19 wells with VOC concentrations ranging from non-detectable to >100,000 µg/L. The tests were based on the successful application of the method at a site in South Carolina (Vroblesky and Hyde 1997) where the primary VOCs include trichloroethene (TCE), *trans* and *cis* 1,2-dichloroethene (1,2-DCE), 1,1-dichloroethane (1,1-DCA), and vinyl chloride (VC).

2.0 SAMPLING AND ANALYSIS

2.1 Well Selection

The wells were selected from the KCP groundwater monitoring data base. The selection process began with development of five categories or ranges to address the cumulative concentration of four chlorinated VOCs: TCE, 1,2-DCE; 1,1-dichloroethene (1,1-DCE) and VC hence forth referred to as total VOCs. The total VOC ranges in µg/L were non-detectable (ND), ND to 20, 20 to 100, 100 to 500, and >500. Wells with highly variable trends in total VOC and/or individual VOC concentrations were eliminated to reduce bias. Three to four wells were selected in each range to comprise the study population. Logistics, such as location and whether the well had a dedicated pump, also contributed to the selection. The list of wells sampled, respective VOC ranges, and other pertinent sampling information is presented in Table 1.

2.2 Sampler Deployment

The passive samplers, consisting of 2 mL polyethylene bags measuring 2 × 8 inches with zipper closures, were installed in the selected wells on May 28 through 29, 1997. Each bag was filled with approximately 130 mL of DI water and then sealed. A perforation through the top of the bag closure was fit with a length of nylon twine used to suspend the bag in the well. The perforation was placed below a reinforced strip in the bag to prevent any ripping and potential loss of the bag in the well. To overcome the buoyancy of the bag, approximately 20 g of pre-cleaned fishing weight was enclosed in the bag. The water-filled bag was lowered into each well to a predetermined depth adjacent to the screened

Table 1. Database sampling data

Well number and Sample ID	Total VOC range, ug/L	Screened interval, ft/bgs	Sampler depth, ft/bgs	1 st event collection date	1 st event residence time, days	2 nd event collection date	2 nd event residence time, days	QA/QC sample type
KC85-030	ND	22 to 26	25.0	06/12/97	14	07/09/97	26	
KC88-079	ND	15.9 to 25.9	28.0	06/12/97	14	07/09/97	26	
KC89-104L	ND	32.3 to 37.3	36.0	06/12/97	14	07/09/97	26	Duplicate
KC87-074L	ND	40.9 to 45.9	45.0	06/12/97	14	07/10/97	24	
KC85-040M	ND to 20	23 to 27	29.0	06/12/97	14	07/09/97	26	
KC86-047L	ND to 20	38 to 42	41.0	06/12/97	14	07/10/97	24	
KC91-183L	ND to 20	35.5 to 40.5	39.5	06/12/97	14	07/09/97	26	
KC84-006L	20 to 100	34.5 to 38.5	37.5	06/12/97	14	07/10/97	24	
KC89-125U	20 to 100	15 to 25	24.0	06/13/97	14	07/10/97	27	
KC91-155L	20 to 100	34 to 39	38.0	06/13/97	14	07/10/97	24	Duplicate
KC94-191U	20 to 100	2 to 22	21.0	06/12/97	14	07/10/97	24	
KC85-045U	100 to 500	11.5 to 15	14.5	06/12/97	14	07/09/97	26	
KC85-045L	100 to 500	23.5 to 27.5	26.5	06/12/97	14	07/09/97	26	Duplicate
KC87-070L	100 to 500	2.4 to 36.4	35.5	06/12/97	14	07/10/97	24	
KC87-070U	100 to 500	10 to 18	17.0	06/12/97	14	07/10/97	24	
KC84-018L	>500	39.5 to 43.5	42.5	06/12/97	14	07/09/97	26	
KC85-039L	>500	37.5 to 41.5	43.0	06/12/97	13	07/09/97	26	Duplicate
KC92-184L	>500	35 to 40	39.0	06/13/97	14	07/10/97	27	MS/MSD
KC94-192L	>500	36.5 to 41.5	40.5	06/13/97	15	07/10/97	24	
Field Blank 1	NA	NA	NA	06/13/97	15	NA	NA	DI water
Field Blank 2	NA	NA	NA	06/13/97	15	NA	NA	DI water

QA/QC = quality assurance/quality control
MS/MSD = matrix spike/matrix spike duplicate

NA = not applicable
DI = deionized (water)

portion of the well, and the nylon twine was secured to the top of well casing. The bags were left in place a minimum of 13 days during the first sampling event, and then the bags were hoisted to the surface and sampled. The second set of passive samplers were deployed on June 12 through 13, 1997 and remained in place 24 days. The second sampling event was completed on July 10 through 11, 1997.

2.3 Sample Collection and Analysis

The passive samples were collected by carefully retrieving the bag from the well and slowly pouring the contents of the bag into two 15 mL vials. Immediately following each passive sampling event, personnel with Pace Analytical Services used routine purging and sampling collection techniques (i.e., three well volumes evacuated with a bailer) to collect VOC samples in 40 mL VOA vials. Although smaller vials (15 mL) were used for the passive method due to volume limitations associated with the size of the bag, this did not affect the analytical process as sufficient volume was provided to perform the analysis as many as three times if required. This approach also permitted the collection of duplicate samples from a single bag. The samples were transported by Pace Analytical Services personnel to their laboratory. VOC analysis were performed using SW-846 Method 8021 (Gas Chromatography) with confirmatory analysis using Method 8240 (Gas Chromatography/Mass Spectroscopy).

3.0 QUALITY ASSURANCE (QA)/QUALITY CONTROL (QC)

The following elements comprised the QA program:

3.1 Blanks

At the beginning of the field effort, two polyethylene bags were filled with DI water from the same source used to fill the bags deployed in the wells and then sealed in pre-cleaned polyethylene containers filled with DI water to serve as field blanks. The two field blanks were sampled during the first sampling event and were submitted for VOC analysis. Pace Analytical Services collected and analyzed one equipment rinseate during each sampling event to measure the effectiveness of sampling equipment decontamination measures. Trip blanks provided by Pace Analytical Services consisted of three 40-mL VOA vials filled with DI water, which accompanied each cooler of groundwater samples. The trip blank was placed in the cooler before the collection of samples.

No significant data were reported in any of the blank results, suggesting that there were no contamination problems with the DI water, effective decontamination procedures were used, and no cross contamination occurred during sample collection and transportation to the laboratory.

3.2 Field Duplicates

Duplicate samples for each sampling method were collected from four wells during the first round and from three wells during the second round. Duplicate samples were collected from the same bailer and the same polyethylene bag at each location to eliminate additional variability.

3.3 Sample Preservation

All of the samples, duplicates, and blanks were maintained at 4° C and preserved with the appropriate amount of hydrochloric acid to reduce the pH to ≤ 2 .


3.4 Laboratory QC

Pace Analytical Services followed the QA/QC requirements stipulated by the laboratory contract scope of work in place with AlliedSignal FM&T (Pace 1996).

4.0 RESULTS AND DISCUSSION

Passive and bailed samples were collected from 19 wells on two separate occasions as previously described. Six wells produced non-detectable results. This was expected since four of the wells were in the ND range and the other two ranged from ND to 20 $\mu\text{g/L}$ (Table 1). VOCs detected from both sampling events are presented in Table 2 and allow a comparison of the sampling methods. The chart at the top of Table 2 compares total VOC results resulting from each method and sampling event. The data are presented so that the concentration of individual VOCs (TCE, 1,2-DCE, 1,1-DCE, and VC) resulting from both methods and sampling events can be correlated. The data at the bottom of Table 2 presents the total VOCs for each sampling method and sampling event (i.e., Total VOC Passive 1st).

Table 2. Total VOC results: Method comparison

				
Well No. (Sample ID)	Passive 1st TCE	Bailed 1st TCE	Passive 2nd TCE	Bailed 2nd TCE
1 (KC91-183L)	<1	3.90	<1	3.40
2 (KC91-155L)	16.00	11.00	11.00	8.10
3 (KC91-155L duplicate)	16.00	12.00	11.00	8.00
4 (KC94-191U)	5.40	1.40	2.60	<1
5 (KC85-045U)	17.00	16.00	20.00	12.00
6 (KC85-045L)	24.00	10.00	35.00	13.00
7 (KC85-045L duplicate)	20.00	18.00	39.00	13.00
8 (KC87-070L)	100.00	50.00	38.00	45.00
9 (KC87-070U)	<1	1.40	<1	<1
10 (KC84-018L)	32.00	35.00	2.10	12.00
11 (KC85-039L)	<1	96.00	<1	210.00
12 (KC85-039L duplicate)	140.00	120.00	Not collected	Not collected
13 (KC92-184L)	8700.00	7400.00	6500.00	6700.00
14 (KC94-192L)	290000.00	120000.00	130000.00	320000.00
Total TCE	299070.40	127774.70	136658.70	327024.50
Well No. (Sample ID)	1,2-DCE	1,2-DCE	1,2-DCE	1,2-DCE
1 (KC91-183L)	<1	5.90	<1	<1
2 (KC84-006L)	27.00	43.00	<1	20.00
3 (KC91-155L)	12.00	7.70	6.20	<1
4 (KC91-155L duplicate)	13.00	8.20	6.30	<1
5 (KC94-191U)	19.00	65.00	30.00	60.00
6 (KC85-045U)	270.00	290.00	210.00	290.00
7 (KC85-045L)	250.00	190.00	240.00	310.00
8 (KC85-045L duplicate)	160.00	370.00	240.00	350.00
9 (KC87-070L)	910.00	450.00	540.00	430.00
10 (KC87-070U)	130.00	160.00	170.00	300.00
11 (KC85-039L)	1100.00	1100.00	1100.00	1500.00
12 (KC85-039L duplicate)	1200.00	1100.00	Not collected	Not collected
13 (KC92-184L)	500.00	560.00	540.00	510.00
14 (KC84-018L)	12000.00	11000.00	13000.00	12000.00
15 (KC94-192L)	83000.00	35000.00	36000.00	100000.00
Total 1,2-DCE	99591.00	50349.80	52082.50	115770.00
Well No. (Sample ID)	1,1-DCE	1,1-DCE	1,1-DCE	1,1-DCE
1 (KC85-045U)	<1	2.40	1.50	<1
2 (KC85-045L)	<1	<1	<1	2.10
3 (KC85-045L duplicate)	<1	1.70	1.70	2.30
4 (KC87-070L)	3.50	150.00	69.00	74.00
5 (KC87-070U)	3.20	<1	2.50	4.20
6 (KC84-018L)	24.00	24.00	26.00	29.00
7 (KC85-039L)	3.50	3.20	5.00	5.00
8 (KC85-039L duplicate)	5.10	3.20	Not collected	Not collected
9 (KC92-184L)	8.50	8.20	9.70	7.30
10 (KC94-192L)	180.00	190.00	210.00	200.00
Total 1,1-DCE	227.80	382.70	325.40	323.90
Well No. (Sample ID)	VC	VC	VC	VC
1 (KC94-191U)	<1	3.60	<1	2.20
2 (KC89-125U)	84.00	83.00	61.00	52.00
3 (KC87-070L)	43.00	64.00	44.00	27.00
4 (KC87-070U)	17.00	40.00	31.00	54.00
5 (KC85-039L)	66.00	39.00	55.00	44.00
6 (KC85-039L duplicate)	68.00	38.00	Not collected	Not collected
7 (KC94-192L)	58.00	65.00	52.00	180.00
8 (KC84-018L)	810.00	950.00	720.00	890.00
Total VC	1146.00	1282.60	963.00	1249.20
Total VOC	Total VOC	Total VOC	Total VOC	Total VOC
Total VOCs	400035.20	179789.80	190029.60	444367.60
Adjusted Total VOCs *	27035.00	24790.00	24029.00	24367.00

* Excludes TCE and 1,2-DCE measured in well KC94-192L.

Review of the compound-specific data indicate the bulk of the total VOC values stems from the gross levels of TCE and 1,2-DCE in well KC94-192L that comprise 84 to 94% of the total VOCs measured in all of the wells. Because the TCE and 1,2-DCE results from this well are significantly higher than those from the other wells measured, they bias the statistical analysis and wash out the data from other wells. Therefore, the TCE and 1,2-DCE values from well KC94-192L are excluded from the results labeled as “adjusted total VOCs” presented at the bottom of Table 2. Although the analytical data packages are not included with this report, they are available on request from AlliedSignal FM&T.

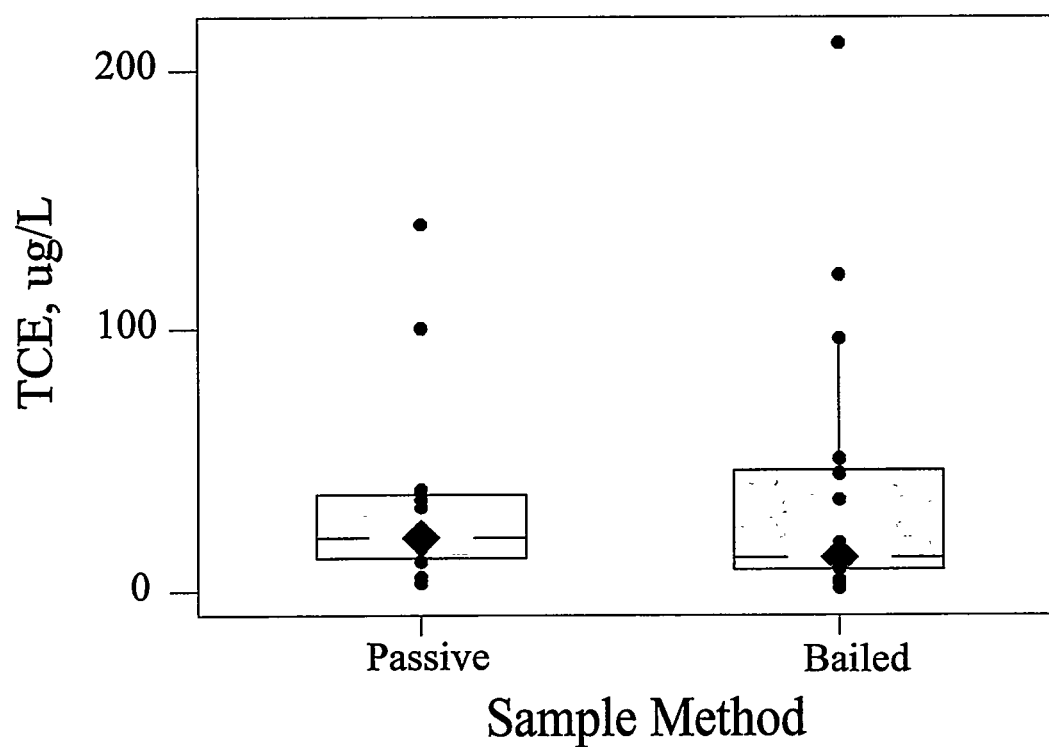
It is common practice to dilute the sample aliquot by a high factor (up to 2500 \times 's) in performing analysis of grossly contaminated samples in order to keep the instrument response within the calibration range. Thus, when a typical sample aliquot of 5 μ L is diluted by a factor of 2500, the resulting sample volume is very small (0.002 μ L) and difficult to handle and measure accurately. The variability introduced by this analytical practice is reflected in the range of TCE and 1,2-DCE concentrations observed between sampling events and methods for well KC94-192L. For example, results from the first sampling event delivered concentration ranges of 120,000 to 290,000 μ g/L of TCE and 35,000 to 83,000 μ g/L of 1,2-DCE with the higher concentrations resulting from the passive method. Results from the second sampling event produced concentration ranges of 130,000 to 320,000 μ g/L of TCE and 36,000 to 100,000 μ g/L of 1,2-DCE with the higher concentrations resulting from the bailed method. Although temporal distribution of contaminants may account for some of variability between sampling events, it is reasonable to attribute most of the variability to the sample dilution practices and not the sample collection methods.

In order to determine the variability between sampling methods and sampling events, the data were treated in two ways. To illustrate the variability between sampling methods, the first approach averaged the adjusted VOC results for both passive sampling events. A mean of 25,532 μ g/L with a standard deviation of 2,125 μ g/L was calculated. In comparison, the adjusted total VOC results for both sets of bailed samples yielded a mean of 24,579 μ g/L with a standard deviation of 299 μ g/L. The method-comparison approach suggests that the passive method has a higher degree of variability. To illustrate the variability between sampling events, the second approach averaged results of the first sampling event yielding a mean of 25,913 μ g/L with a standard deviation of 1,587 μ g/L. The average of the second sampling event was calculated to be 24,198 μ g/L with a standard deviation of 239 μ g/L. The event-comparison approach suggests that the second sampling event experienced less variability than the first. However, both comparisons suggest that the variability between sampling methods and sampling events is approximately the same.

The medians were compared graphically with box plots in Figs. 1 through 3. To keep the data within a few orders of magnitude and make the graphs reasonable, a few highest values were removed in each case: note that all the box plots also excluded NDs from the analysis.

Passive vs Bailed for TCE

n = 16 for Passive, n = 22 for Bailed
All NDs and values > 210 filtered out



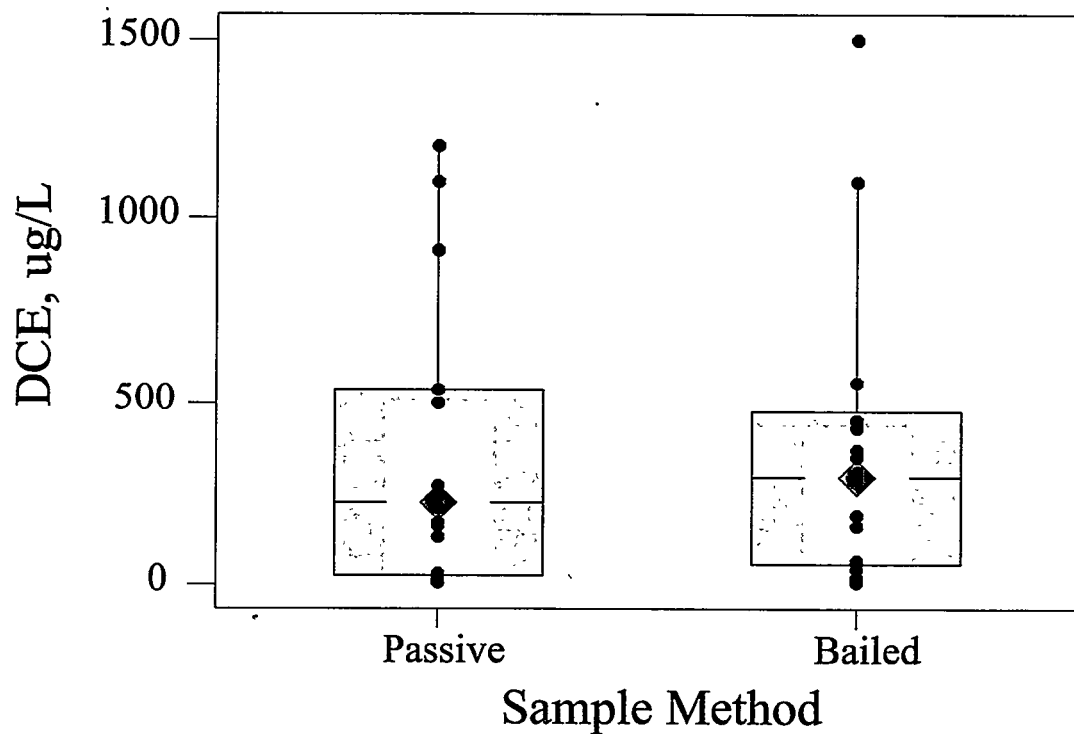
Yellow box is 95% confidence interval around red median.

Fig. 1. Passive versus bailed method for TCE.

Passive vs Bailed for 1,2-DCE

n = 22 for Passive, n = 22 for Bailed

All NDs and values > 1500 filtered out



Yellow box is 95% confidence interval around red median.

Fig. 2. Passive versus bailed method for 1,2-DCE.

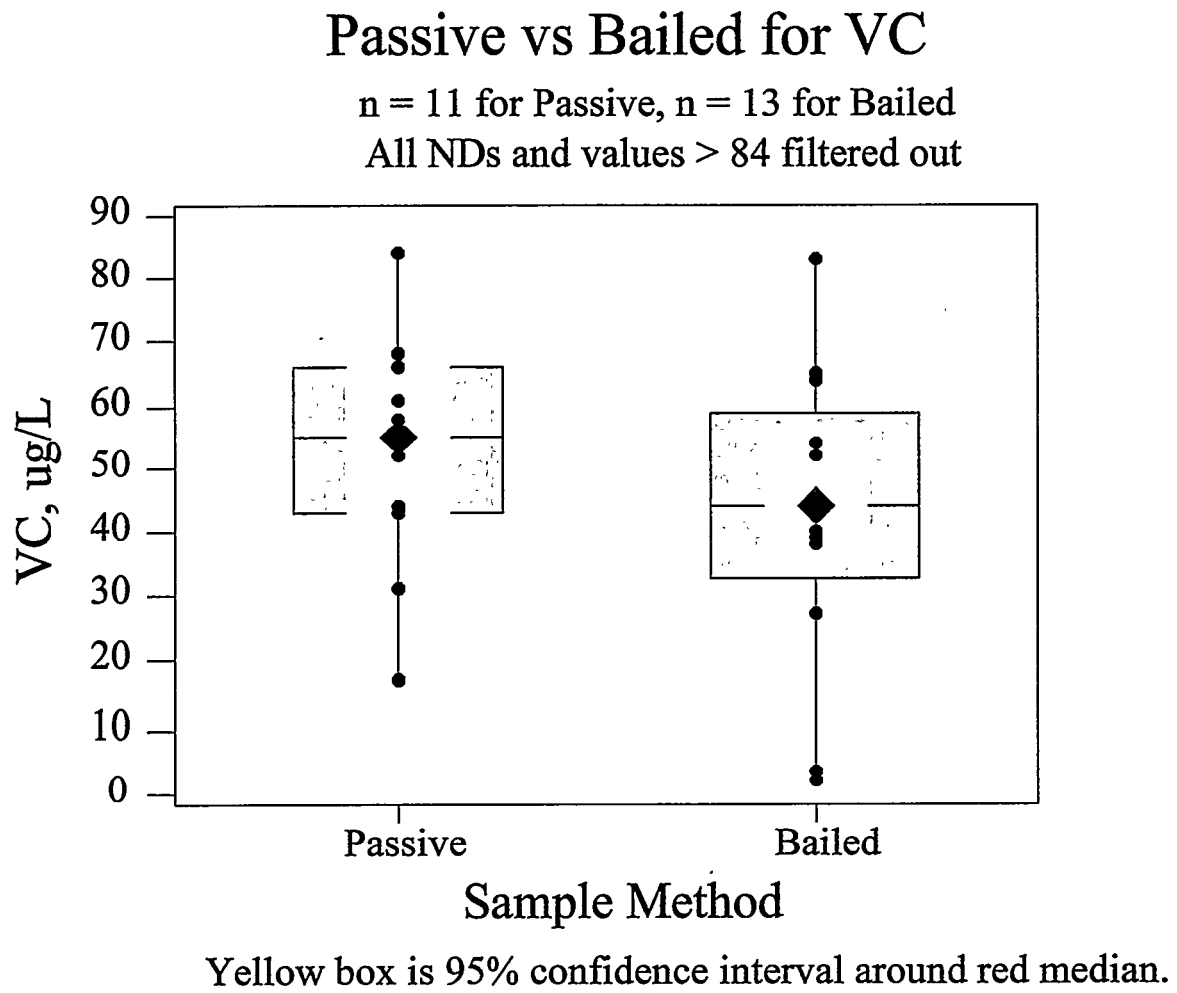


Fig. 3. Passive versus bailed method for VC.

The result of the statistical analysis shows that all 95% confidence intervals about the medians for the data sets overlap. This provides evidence that the results from the passive method are comparable to the results from the bailed method and, therefore, evidence to support the hypothesis that the medians for the two methods are equivalent.

Further graphic analysis of the data was achieved by plotting the individual VOC compounds of interest: TCE, 1,2-DCE, 1,1-DCE, and VC presented in Tables 3 through 6, respectively. The data are presented without the exclusions or filtering used for the statistical analysis. A data gap in all of the tables results from the omission of a duplicate sample intended for collection from well KC85-039L during the second sampling event. Review of Tables 3 through 6 suggests that results obtained with the passive sampling method are comparable to those obtained with the bailer method. The graphic representations illustrate that the variability between sampling methods is not any greater than variability between sampling events.

Although the discussion has focused on total VOCs as previously defined, the demonstration was useful in showing that other VOC compounds can be monitored effectively using the passive method. Review of the data presented in Table 7 indicates that six other constituents were detected. Of these, only benzene was consistently detected between sampling events and sampling methods. The other compounds were typically detected by both sampling methods, but only in the second sampling event. The variability in sample results between the sampling events suggests that factors associated with sample collection and analysis as well as temporal distribution of contaminants, may be attributable. However, due to the relatively sparse data population, statistical treatment of these data is not realistic. Regardless, the data are useful to show that other constituents may be monitored using the passive method.

The other factor involved in the comparison of the sampling methods is one of cost. The level of effort to complete the passive sampling required approximately 32% less labor than the bailed method. The estimate of labor is based on the time required to complete each of the sampling approaches. The elimination of purging and decontamination of sampling equipment are the principle factors that make the passive sampling approach less labor intensive. This is a direct result of the simplicity of the passive method that with additional streamlining, could leverage further reductions in labor costs. An additional cost savings advantage of the passive method is the lack of purge water disposal associated with the bailer method. Because the passive method generates no waste water, there are no associated disposal costs. The savings realized in reduced labor and the elimination of purge water, support the implementation of the passive sampling method.

Table 3 Comprehensive Results for TCE

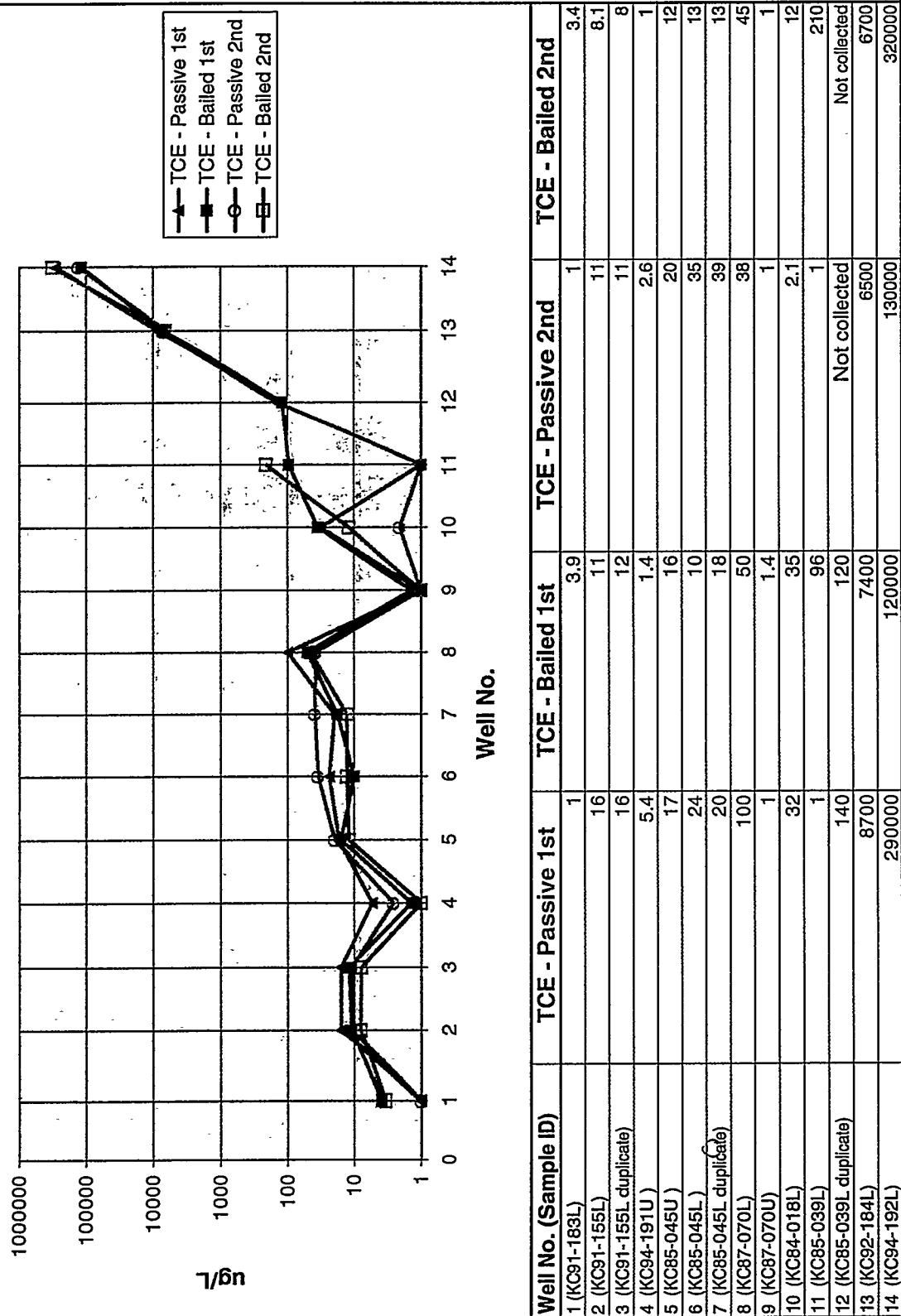
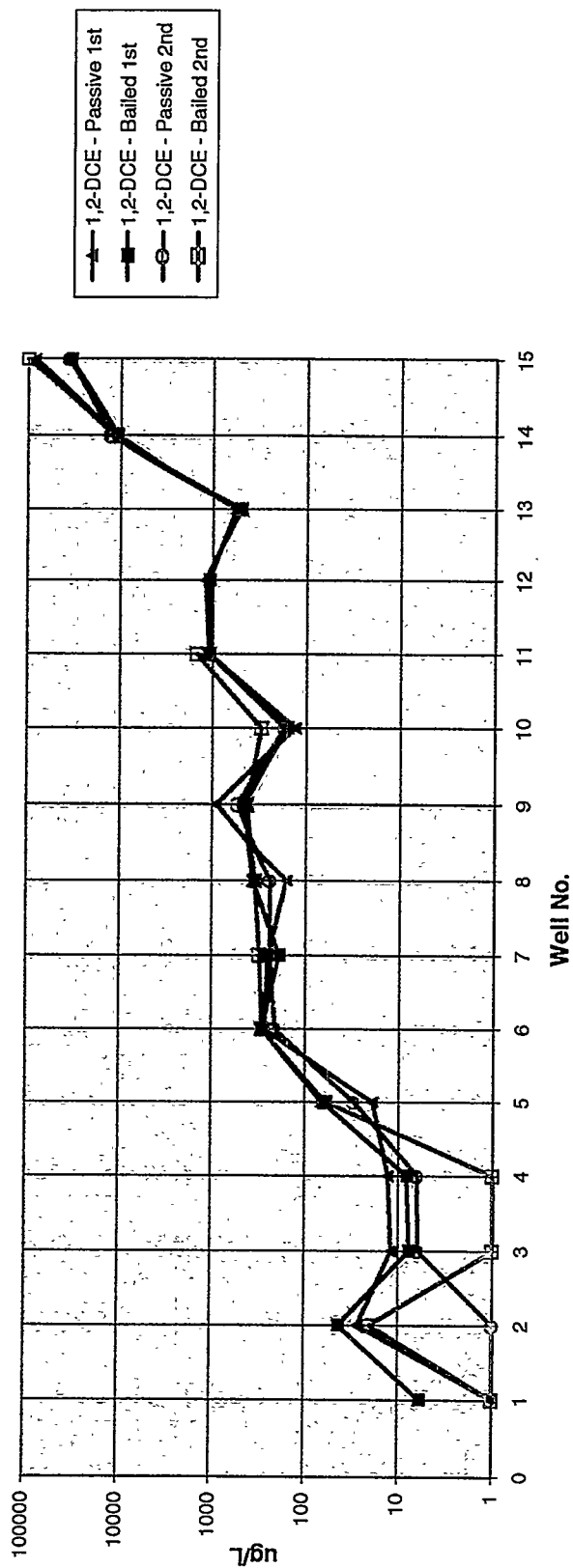


Table 4. Comprehensive Results for 1,2-DCE



Well No. (Sample ID)	1,2-DCE - Passive 1st	1,2-DCE - Bailed 1st	1,2-DCE - Passive 2nd	1,2-DCE - Bailed 2nd
1 (KC91-183L)	1	5.9	1	1
2 (KC84-006L)	27	43	1	20
3 (KC91-155L)	12	7.7	6.2	1
4 (KC91-155L duplicate)	13	8.2	6.3	1
5 (KC94-191U)	19	65	30	60
6 (KC85-045U)	270	290	210	290
7 (KC85-045L)	250	190	240	310
8 (KC85045L duplicate)	160	370	240	350
9 (KC87-070L)	910	450	540	430
10 (KC87-070U)	130	160	170	300
11 (KC85-039L)	1100	1100	1100	1500
12 (KC85-039L duplicate)	1200	1100	Not collected	Not collected
13 (KC92-184L)	500	560	540	510
14 (KC84-018L)	12000	11000	13000	12000
15 (KC94-192L)	83000	35000	36000	100000

Table 5. Comprehensive Results for 1,1-DCE

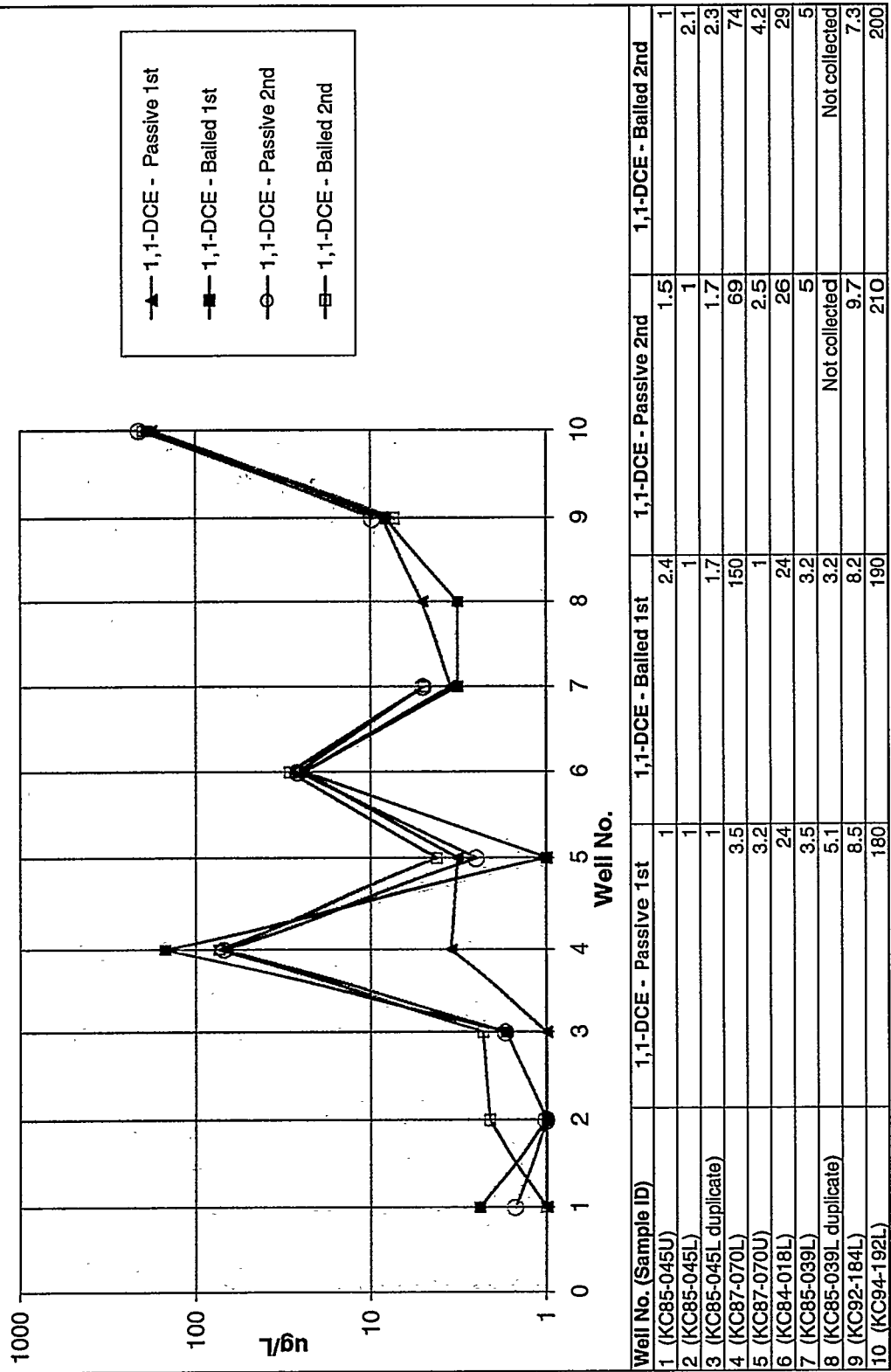


Table 6. Comprehensive Results for VC

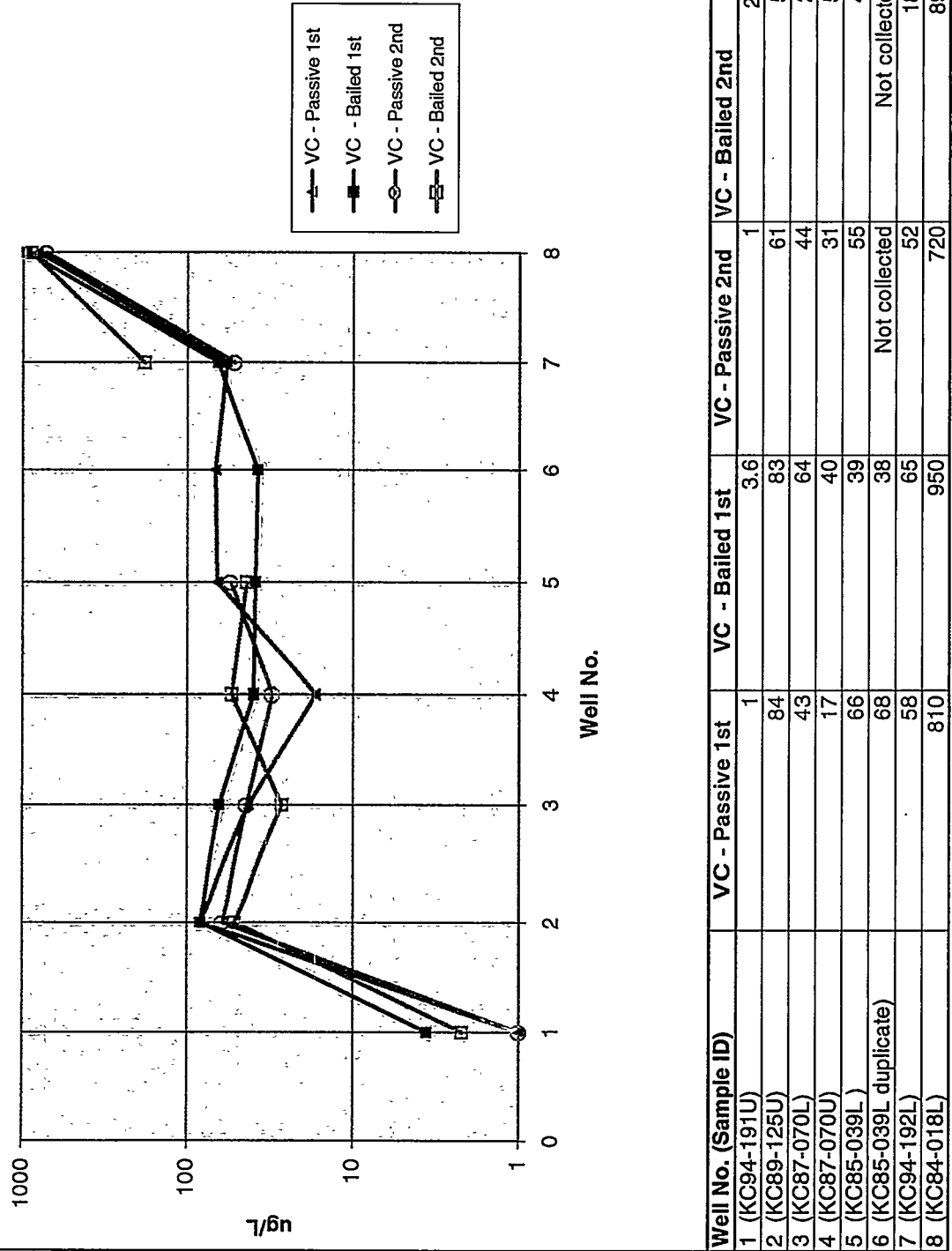


Table 7. Other VOC compounds detected, µg/L

Well ID	Sample type	Sample date	Benzene	Toluene	Chlorobenzene	1,2-Dichlorobenzene	1,3-Dichlorobenzene	1,1,2-Trichloroethane
KC87-070L	Passive	06/12/97						
KC87-070L	Bailed	06/13/97						
KC87-070L	Passive	07/10/97			9.5		5.3	
KC87-070L	Bailed	07/10/97			4.5		2.6	
KC87-070U	Passive	06/12/97						
KC87-070U	Bailed	06/13/97						
KC87-070U	Passive	07/10/97			19	2	22	
KC87-070U	Bailed	07/10/97			30	2.4	30	
KC84-018L	Passive	06/12/97	26					
KC84-018L	Bailed	06/12/97	25					
KC84-018L	Passive	07/09/97	21					2
KC84-018L	Bailed	07/10/97	23					
KC94-192L	Passive	06/13/97		2				
KC94-192L	Bailed	06/13/97		2.3				
KC94-192L	Passive	07/10/97	2.2	2.8				9.2
KC94-192L	Bailed	07/11/97						9.2

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on the analytical results and statistical analysis of the data, the comparison of the passive and bailer sampling methods indicate that both methods produce similar results. However, the potential savings in labor (32%) and purge water disposal costs (100%) delivered by the passive method, favor implementation of this method at the KCP for routine monitoring of groundwater VOCs.

6.0 REFERENCES

- Pace Analytical Services, Inc. 1996. Health and Safety Plan for Contract 052G38055.
- Vroblesky, Don A., and W. Thomas Hyde. 1997. Diffusion samplers as an inexpensive approach to monitoring VOCs in ground water. *Ground Water Monitoring and Review*, Summer, pp 177-184.

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