

LOW LEVEL DETECTION OF PCE IN MONITORING WELL SAMPLES USING A TOTAL ORGANIC CHLORINE BASED FIELD METHOD

Theodore B. Lynn, Ph.D., Director of Research, Dexsil Corporation, One Hamden Park Drive, Hamden, Connecticut 06517; Keith A. Wright, Consulting Soil Scientist, Camino, California 95709

Presented at the Waste Testing and Quality Assurance Symposium 2001, August 13-16, 2001, Arlington, VA

ABSTRACT

Using the newly developed liquid-liquid extraction procedure for the L2000DX Chlorine Analyzer, Dexsil Corporation, in conjunction with Levine Fricke Recon (LFR) conducted a series of field trials at a Tetrachloroethylene (PCE) contaminated site. The site chosen for the demonstration consisted of a network of monitoring and extraction wells located in a PCE plume impacting ground water.

The new procedure is an addition to the existing methods for the L2000DX Chloride Analyzer which is the basis for SW-846 Method 9078 "Screening Test Method for Polychlorinated Biphenyls in Soil." Using the same reaction and quantification steps as the established L2000DX methods, the new method uses a liquid-liquid extraction step to achieve method detection limits (MDLs) in the 15-30 ppb range for most chlorinated solvents. The MDL for PCE using this method is 22 ppb. This new method will allow nearly real time data to be collected from ground water monitoring wells at a fraction of the cost of laboratory analysis.

The field trial was conducted in two phases. Each phase was planned to coincide with the normal monitoring activities at this site. During the sampling operations, split samples were taken to be analyzed by the L2000DX at the field location. The laboratory samples were sent off to the state certified lab, as usual, for analysis by SW-846 Method 8260A. A total of 17 monitoring wells were sampled for a total of 26 samples and 12 duplicates. The L2000DX results were available the same day as the sampling event. The PCE concentration in the samples ranged from non-detect to greater than 20 ppm, providing a good sample set to test the comparability over a large concentration range.

A regression analysis of the data set indicates that the L2000DX results compare very well with the lab results over the full range. The excellent correlation between the L2000DX results and the lab results, ($R^2 = 0.99$) indicates that the field method provides data comparable to the laboratory in practically real time. This field trial demonstrated the utility of a total halogen based field method for ground water monitoring of PCE contamination.

INTRODUCTION

Regulatory driven quarterly monitoring is a common event at sites where groundwater is contaminated by chlorinated organic compounds. The objective of quarterly monitoring is to determine the concentration of a contaminant in the water from established monitoring wells over time. The data are then examined and seasonal changes and overall plume trends can be evaluated quarterly.

The conventional protocol for quarterly monitoring consists of collecting water samples from monitoring wells and sending them to a certified analytical laboratory for analysis. This conventional "sample and send" method may not be justified when the purpose is to monitor the clean-up of known contaminants over decades. A low cost accurate field analytical test kit is essential for sites like these that require long term monitoring. A sample for laboratory analysis can be collected when contaminant concentrations indicated by the field test data are at or near actual clean-up concentrations, when an anomaly is detected by the field analysis, or as a quality assurance step for a field test.

If extraction wells and a remediation system are added to the site, the quarterly monitoring data is also studied to determine changes in plume dynamics as well as expected changes in contaminant concentrations at each monitoring well over time. At sites where a remediation system is in place, a low cost field analytical test kit should be

considered as an alternative to the conventional "sample and send" to the laboratory protocol.

Sites contaminated with a dense non-aqueous phase liquid (DNAPL) in either the vadose zone, or groundwater, are difficult to assess due to the fact that DNAPLs react differently than light non-aqueous phase liquids (LNAPLs) do in the subsurface. Both will move through the vadose zone and can dissolve into groundwater forming a contamination plume that will move and expand in the direction of groundwater flow, but DNAPLs will continue to move down through groundwater and form pools of DNAPL that can then be a continuous source of groundwater contamination or continue to move downward eventually contaminating deeper aquifers. These DNAPL pools are difficult to locate using conventional methods and are often the reason these types of sites may require long-term quarterly monitoring and long-term remedial efforts. The use of a field analytical test kit at long term monitoring sites provides better site control, while saving time and financial resources.

In response to the demand for a field test kit for water, Dexsil has developed a new extraction method for use with the L2000DX Chlorine Analyzer. The new procedure uses a liquid/liquid extraction to concentrate organo-chlorine contaminants into an organic layer for introduction into the L2000DX system. The L2000DX chemistry then uses metallic sodium to convert all of the organic chlorine into chloride for quantification by chloride ion specific electrode. The L2000DX system has been shown to be a reliable platform for chloride analysis through the USEPA SITE and ETV programs.^{1,2} The new procedure and the laboratory development of the extraction step is detailed in a concurrent paper.³

After laboratory testing of the new method, Dexsil teamed up with Levine-Fricke-Recon (LFR) to conduct field trials at a real world site. LFR, a leader in the use of innovative environmental technology, was aware of the need for an accurate, low cost, quantitative field test kit for use at sites where chlorinated compounds, are contaminating groundwater. Also interested in the potential for saving its client's long-term costs at DNAPL sites, LFR suggested a site where they had been implementing a system of monitoring wells for a quarterly monitoring program. Previous monitoring activity had documented the presence of tetrachloroethylene (PCE) at concentrations of up to 30 ppm in some wells.

This paper describes the field testing activities, conducted jointly by LFR and Dexsil personnel, comparing the L2000DX Analyzer to laboratory analysis. The sampling was conducted in two separate three-day events, the first in November of 1998 and the second in February of 1999.

SAMPLING AND ANALYSIS

The site chosen for the field trials encompasses a large downtown retail area with a network of monitoring wells and extraction wells located throughout. The sampling activities planned for this study were scheduled to coincide with the scheduled quarterly sampling of the monitoring wells and were performed by LFR personnel. Most of the sampling was performed after 8:00pm to avoid a conflict with active businesses located on or in the vicinity of the site. All water samples, upon collection, were immediately stored in coolers containing crushed ice. The samples that were collected for laboratory analysis were placed into a separate cooler from those collected for field analysis and a courier for the laboratory picked them up each morning. Dexsil also picked up the corresponding field test samples each morning. Each water sample was collected using accepted EPA methods. The laboratory samples were collected in 40mL VOA vials preserved with HCl and collected to zero headspace. The samples for field analysis, requiring a liter of sample with no preservative were also collected to zero headspace. Dexsil personnel analyzed each sample and duplicate samples the day they were collected. The analysis time per sample using Dexsil's L2000DX analyzer was approximately 10 minutes per sample. Dexsil requested that duplicate samples be collected whenever possible. Dexsil personnel had ample time to analyze trip blanks, spikes and duplicate samples each day. Dexsil analyzed a total of 50 samples, 12 of them were duplicates, eight were spikes and four were trip blanks.

The L2000DX analysis procedure used for this study consisted of a liquid/liquid extraction using 10 mL of 2,2,4 trimethylpentane (isooctane) followed by the standard L2000DX analysis procedure. To begin the analysis, 40 mL of

water was removed from the cooled, zero headspace sample. This left 960 mL in the sample jar with enough headspace for extraction. 10 mL of isooctane was added and the sample was shaken by hand for 2 minutes. After extraction, sufficient deionized water was added to the sample jar to bring the organic layer up into the neck of the jar. The sample was allowed to sit capped for three minutes. 5 mL of the organic layer was then removed and introduced into the standard L2000DX sample tube. The standard procedure was then followed according to the instruction manual.⁴

RESULTS AND DISCUSSION

All of the water samples collected during this comparative study were sent to a certified laboratory and were analyzed using EPA SW-846 Method 8260A. The laboratory results were available four (4) weeks after the samples were sent in. In contrast, the analytical results for each of the corresponding water samples analyzed using the L2000DX analyzer were available the same day and in some cases, hours after they were received. At the conclusion of each three-day round of field testing, Dexsil faxed the analytical results from the on-site L2000DX testing to LFR.

Initial analysis of phase I data resulted in a correlation coefficient of 0.982 but a regression slope of only 0.6. This would indicate only a 60% recovery. This would be unlikely because the L2000DX software has a correction for extraction efficiency built into each method. Further investigation indicated that the regression was strongly influenced by sample MW-006A. The laboratory result for this point was 39 ppm whereas the L2000DX result was only 23.4 ppm. Subsequent laboratory experiments revealed that the linear range for the extraction procedure extends only to approximately 20 ppm, after which the solvent becomes saturated. Removing point MW-006A from the analysis results in an R^2 of 0.989 which is not much different but the slope becomes 1.1 indicating the L2000DX results correlate well with the lab and the slope is not statistically different from 1 (See Figure 1).

Analysis of the duplicate sample results indicates that the L2000DX produces very consistent results with an average RPD of 7.1% for the five duplicates for which valid results were obtained. NOTE: Results for samples MW-002A, MW-009A and MW-104A and their duplicates were non-detect (ND) and, therefore, could not be used to calculate an RPD. In addition, during the processing of sample MW-010A-D, some of the extraction solvent was lost after the chloride conversion, possibly lowering the result. This point was not used to calculate the average RPD (See Table 1).

Between phase I and phase II, the analysis protocol was modified to include a re-analysis of high samples using a reduced sample size. This was easily accomplished by using the 40 mL removed from the sample at the start of the analysis as a laboratory split sample and extracting this sample for later analysis, if the initial analysis is high. Samples MW-006A, MW-006A-D and MW-101A from the second round of sampling were analyzed and reported using this method.

The analysis of phase II data resulted in an R^2 of 0.991 and a slope of 1.24 indicating a slightly elevated recovery (See Figure 2). Again, the regression is influenced by the one high data point, elevating the slope. An analysis of all the data (excluding MW-006A) results in an R^2 of 0.990 and a slope of 1.23 (See Figure 3). Excluding points greater than 10 ppm results in a slope of 0.996 and an R^2 of 0.977 (See Figure 4).

As part of the field QA/QC program, Dexsil also analyzed 8 spiked samples and 4 trip blanks. The spikes were made in chilled water at 1657 ppb. The results shown in Table 1 indicate a good spike recovery ranging from 89% to 117% with an average recovery of 102%. All four trip blanks tested ND.

SUMMARY

During this comparative study, a total of 17 monitoring wells were sampled. This resulted in a total of 31 water samples being sent to a laboratory for analysis by US EPA SW-846 Method 8260A, and 38 samples were analyzed using Dexsil Corporations' L2000DX Analyzer Field Test Kit method. The analytical results of both the field test and the Laboratory analysis were compared directly. The correlation was excellent ($R^2 = 0.990$) when all the data were compared. Dexsil's L2000DX Analyzer proved to be an easy to use, low cost and accurate field analytical test

method. In addition to the excellent correlation with lab samples, the low cost of the test (less than \$10 per test versus \$200 for an 8260A) coupled with near real time results makes the L2000DX an excellent alternative to laboratory analysis at sites where water is contaminated with PCE or other DNAPLs. The L2000DX can replace the conventional method of "sample and send" with an on-site field analytical test kit. At the beginning of a project, a few samples must be sent to a laboratory for characterization. Once sample characterization is complete, the L2000DX Analyzer is easily programmed for the site-specific contaminant. After this initial characterization is complete, the L2000DX should be used exclusively to analyze water samples at the site. Prudence dictates that an occasional random sample should be sent to a laboratory for analysis by the appropriate method to confirm correlation with the field method.

Quarterly monitoring and site investigations are expensive, and using the conventional "sample and send" protocol does not make economic sense based upon the benefit derived versus the cost of the lab data. New strategies for site assessments, long-term monitoring and site remediation need to be considered for DNAPL sites due to the problems they present when discovered. Dexsil's L2000DX is an important and significant new field test kit that environmental professionals can use to improve site assessments. The use of the L2000DX Analyzer at a wide variety of DNAPL sites, will aid in facilitating and directing site assessment strategies, save time and money, and save long-term costs and overall project costs significantly.

ACKNOWLEDGMENTS

Dexsil would like to thank Dan J. Foster, Kimberly A. Brandt and Sarah L. Raker of Levine-Fricke-Recon for their enthusiastic support of this project.

REFERENCES

1. Dindal, A.B., Billetts, S. (1998) Electrochemical Technique/Ion Specific Electrode Dexsil Corporation L2000 PCB/Chloride Analyzer, Environmental Technology Verification Report, US-EPA, Office of Research and Development, Washington, D.C., EPA/600/R-98/109, August
2. Dindal, A.B., Bayne, C.K., Koglin, E.N., (2000) PCB Detection Technology Dexsil Corporation L2000DX Analyzer, Draft Environmental Technology Verification Report, US-EPA Office of Research and Development, Washington, D.C. Report (in Press)
3. Lynn, T. B., Boggiano, M. K., Sacramone, L. M., Balog, D. L., Lynn, A. C., (2001) Analysis of Water for PPB Range Chlorinated Organics Using a Total Organic Chlorine Analyzer, Proceedings of the Waste Testing and Quality Assurance Symposium 2001, Arlington, VA, (Manuscript Submitted)
4. Dexsil Corporation (2000) L2000DX Users Manual, Hamden, CT

Table 1: Comparison Data for Phase I and Phase II Testing

| Sample ID | Phase I | | | Phase II | |
|------------|---------------------------|----------------------|-----------|---------------------------|----------------------|
| | Method 8260A Result (ppb) | L2000DX Result (ppb) | L2000 RPD | Method 8260A Result (ppb) | L2000DX Result (ppb) |
| MW-001A | ND (7.2) | ND (9.8) | | | |
| MW-002A | ND (7.9) | ND (7.4) | | 7.19 | ND (12.3) |
| MW-002A-D | ND (8.3) | ND (9.7) | | | |
| MW-003A | 350 | 339 | 6.39 | 1400 | 2104 |
| MW-003A-D | | 318 | | | |
| MW-004A | 1100 | 1168 | | 1130 | 1262 |
| MW-005A | 17 | 40.5 | 14.3 | | |
| MW-005A-D | | 35.1 | | | |
| MW-006A | 39000 | 23445 | 4.20 | 21196 | 26880* |
| MW-006A-D | | 22481 | | | 29920* |
| MW-007A | 480 | 608 | 8.20 | 445 | 468 |
| MW-007A-D | | 660 | | | |
| MW-009A | 11 | ND (18.8) | | 9.3 | ND (11.2) |
| MW-009A-D | 14 | ND (20.8) | | | |
| MW-010A | 360 | 407 | | 8.9 | 30.3 |
| MW-010A-D | | 327 [†] | | | |
| MW-101A | 6100 | 6484 | | 6831 | 6150* |
| MW-101A-D | | 6329 | | | |
| MW-104A | ND (12.8) | ND (13.4) | 2.42 | | |
| MW-104A-D | ND (12.5) | ND (14.8) | | | |
| MW-108A | 2360 | 3254 | | 2051 | |
| MW-109A | 307 | 309 | | 58.8 | 143 |
| MW-113A | | | | 7 | ND (11.2) |
| MW-113A-D | | | | | ND (4.1) |
| MW-205B | 691 | 742 | | 735 | |
| MW-209B | 5.6 | 12.7 | | | |
| MW-210B | | | | 4 | ND (0) |
| MW-210B-D | | | | 4.9 | ND(4.7) |
| SPIKE | | 1601 | | | 1494 |
| SPIKE | | 1739 | | | 1519 |
| SPIKE | | 1701 | | | 1851 |
| SPIKE | | 1419 | | | 1935 |
| TRIP BLANK | | ND (0.8) | | | ND (7.9) |
| TRIP BLANK | | ND (0.8) | | | ND (1.1) |

* High range procedure used

Figure 1: L2000DX vs Lab for PCE Analysis of Water Phase I (outlier removed)

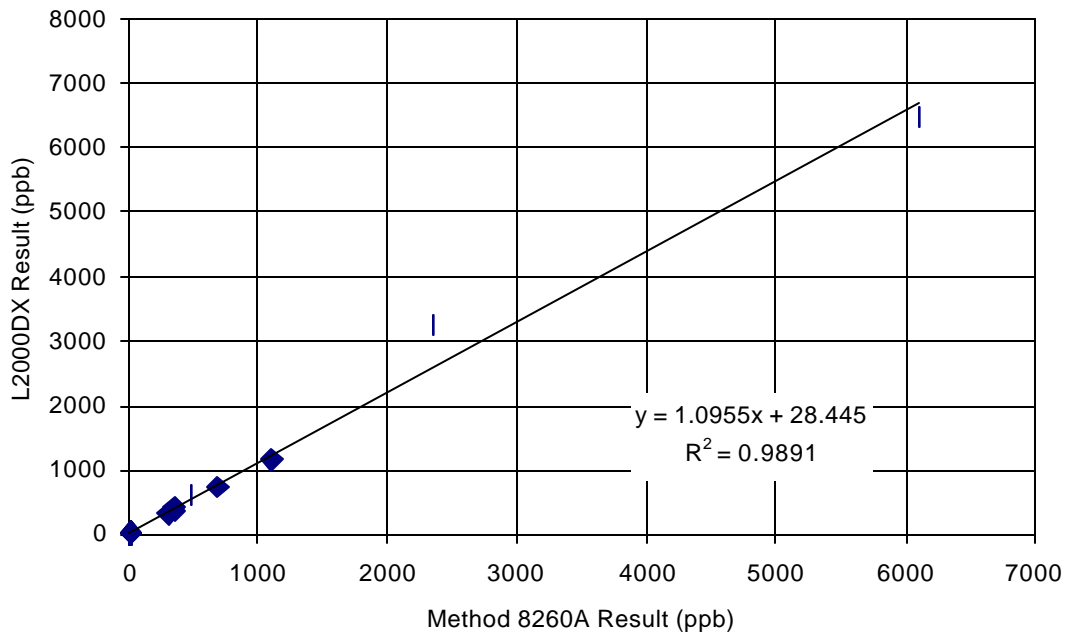


Figure 2: L2000 vs. Lab for PCE in Water (Phase II)

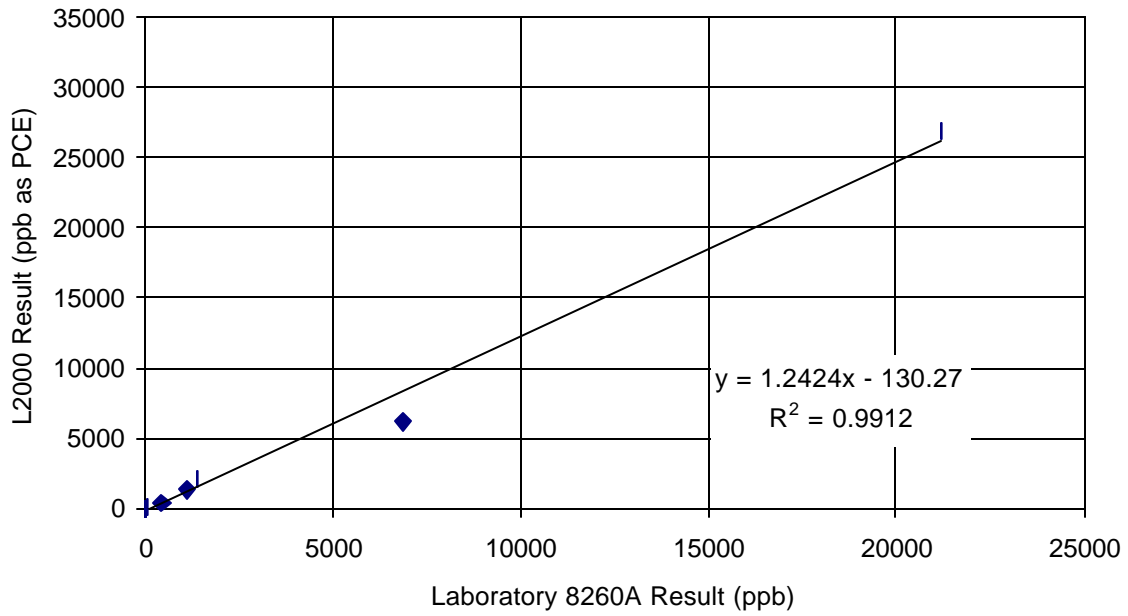


Figure 3: Comparison Data PCE in Water (All Data except MW-006A Phase I)

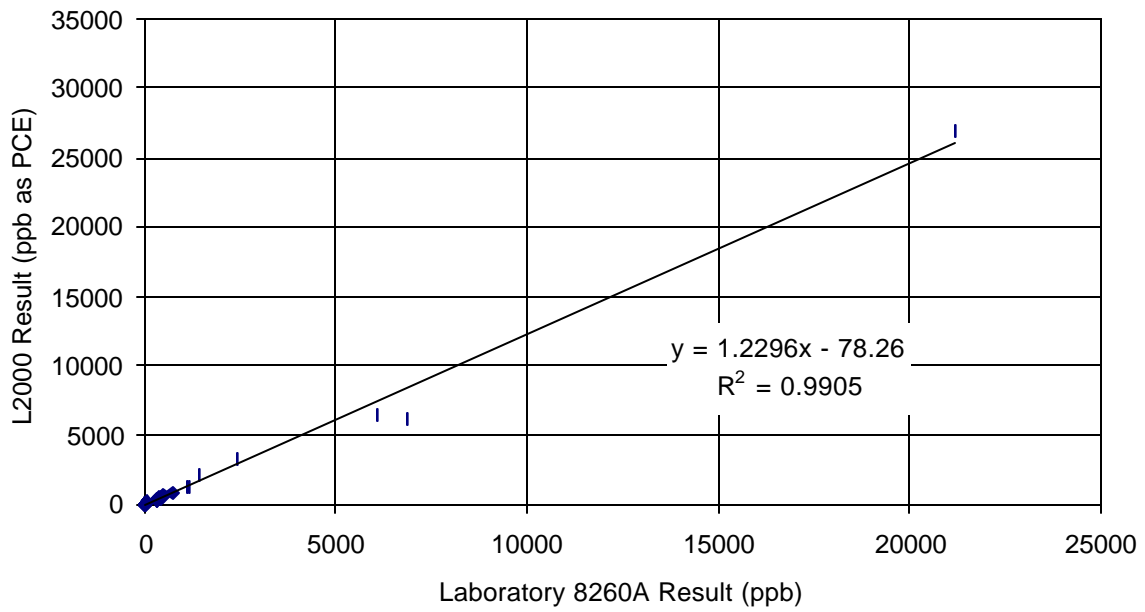


Figure 4: Comparison Data for PCE in Water (All data points less than 10 ppm)

