

## DETERMINATION OF CHLORINATED HYDROCARBON CONCENTRATIONS IN SOIL USING A TOTAL ORGANIC HALOGEN METHOD

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### ABSTRACT

Total organic halogen screening has been used extensively to quantify chlorinated organic compounds in soil and is the basis for a new EPA method — SW-846 Draft Method 9078 “Screening Test Method for Polychlorinated Biphenyls (PCB) in Soil”. This method uses an organic solvent to extract the chlorinated organics from the soil and a Florisil column to remove any inorganic chloride from the extract. The extracted chlorinated organics are then reacted with metallic sodium and the resulting chloride ions are quantified using a chloride specific electrode. Using a commercially available field test kit (the L-2000 PCB/Chloride Analyzer™), the ability of this technology to measure concentrations of chlorinated pesticides and chlorinated solvents in soil was determined. The compounds investigated were: DDT, pentachlorophenol (PCP), toxaphene, chlordane, trichloroethylene, tetrachloroethylene. The L2000 response was found to be linear over the range 0-100 ppm for all analytes and the method detection limits for these analytes ranged from a low of 2.7 ppm for Chlordane to a high of 4.8 ppm for Trichloroethylene. The average extraction efficiency varied from 39% for PCP to greater than 90% for the chlorinated solvents.

### INTRODUCTION

The procedure for total organic chloride analysis was originally developed for use on PCB contaminated soils and the L2000 has been used extensively since 1990 for this purpose. There is a fairly large body of data amassed demonstrating the effectiveness of the L2000 at quantifying PCB in soil.<sup>1-7</sup> The underlying principals, however, are equally applicable to other chlorinated organic compounds such as chlorinated solvents and chlorinated pesticides, most of which are regulated in some way.

The L2000 has, in fact, been used to measure other chlorinated compounds in soil. In the majority of these cases the end user has undertaken to validate the feasibility of the technology for their particular use. This validation information is usually site specific and not available to the general public. With the growing interest in the remediation of other chlorinated compounds in soil and the increase in information requests for L2000 chlorinated organics applications, we have undertaken a validation program for these applications of the L2000.

The first and most important step in a total organic halogen analysis, or any chemical analysis, is the extraction of the chlorinated compounds, quantitatively, from the soil matrix. Performing this step in the field, quickly and reproducibly, on the broad range of soil matrices typically encountered is not a simple task. The solvent system must be designed to handle everything from wet clay to bone dry organic material. Unlike other field analytical methods, the organic chlorine is converted to inorganic chloride in a non aqueous solvent. (The chloride ions are then extracted for quantification using a chloride specific electrode.) The solvent can, therefore, be easily tailored and optimized for a particular application.

The standard L2000 procedure uses a proprietary organic solvent that is polar enough to penetrate a wet clay matrix to solvate the PCB, but is itself not soluble in water. Water is added to the system to help partition the inorganic chloride into the water layer and away from the solvent layer. A Florisil column is used to remove any residual water and inorganic chloride from the extract.

This solvent/clean-up procedure has been shown to be effective at extracting PCB from most types of soils.<sup>1-7</sup> In some types of heavy clay soils with high water content, the extraction efficiency may be lowered and some of the more polar chlorinated organic

compounds are removed by the Florisil column. Dexsil has developed an improved alternative two-step extraction procedure that has been shown to efficiently extract PCB from wet clay soils and can also be used on polar compounds such as PCP.<sup>8</sup> This system uses both a polar and a non-polar organic solvent combination and an aqueous / organic solvent partition step. An optional Florisil clean-up step can be added if the analyte is not one of the polar chlorinated organics such as PCP or if PCP is considered an interfering compound.

In this study all of the non-polar compounds were analyzed using the standard solvent system and the alternative system was used to analyze the PCP contaminated soils. PCP was analyzed in this study using the alternative solvent system to demonstrate the flexibility of the L2000 solvent system.

Following the solvent extraction and clean-up (if necessary), the extract is reacted with metallic sodium in the presence of a catalyst. This removes the covalently bonded chlorine from the organic backbone producing chloride ions. The chloride is then extracted into an aqueous buffer and then quantified using a chloride specific electrode. The user can select a standard conversion factor for one of the typical PCB Aroclors to quantify the chloride ions as "equivalent Aroclor". The actual chlorine content of the original sample can be also be displayed. Using the chlorine content of the specific analyte, the equivalent concentration of the specific contaminant can be determined. Because the response of the instrument follows the standard Nernst equation and the quantified result is the chlorine content of the sample, any chlorinated organic compound can be quantified knowing only the percent chlorine in the compound. If the contaminant is unknown at the time of measurement, the results can later be converted using a simple linear transform, once the contaminant has been identified.

This study is the first in a series documenting the performance of the L2000 in new applications. Starting with the fundamental information required to determine if the L2000 technology is suitable for a particular application we have limited the scope of this investigation to determining: the method MDL, the

range of linearity, and the extraction efficiency for a few of the most commonly encountered, regulated, chlorinated compounds. We have used laboratory spiked soils to simplify the experimental considerations.

## EXPERIMENTAL

### Preparation of Spiked Soil Samples

To ensure a consistent soil matrix throughout the spiking experiments, a large batch of composite soil was prepared prior to beginning. To simulate soils found in uncontrolled waste contaminated environments, the soil composite was prepared by mixing two types of clay and one type of sand. Each of the three soils were sifted through an 0.850  $\mu\text{m}$  sieve, and then combined in a 1:1:2 ratio to form the composite.

The method of spiking depended on the particular analyte characteristics. For the non polar, semi-volatile compounds, DDT, toxaphene, and chlordane, a 1% stock solution in chlorine free mineral oil was prepared. PCP, being more polar, is not soluble in mineral oil; therefore, methanol was used to make up the 1% stock solution. The soils were spiked at 100 ppm by adding 5 grams of the 1% stock solutions to 500 gram aliquots in aluminum pans. The spiked soil aliquots were then slurried with hexane (or, in the case of PCP, methanol) and allowed to evaporate overnight in a hood space. The soils were then transferred to 16 oz glass jars and tumbled for one hour. The jars were then stored at room temperature for later use.

For each experiment, soils were prepared with the desired contaminant concentration by mixing together the correct proportions of the 100 ppm spiked soil and clean composite soil. The mixture was then tumbled for an hour prior to use.

Spiking soils with volatile solvents, uniformly and reproducibly, presented a formidable challenge. In previous work, all attempts to produce a quantity of soil, uniformly spiked, without loss of the analyte proved to be ineffective. Therefore, for the volatile solvents, trichloroethylene and tetrachloroethylene, each 10 gram soil sample was spiked, using a microliter-syringe, just prior to analysis.

### Method Detection Limit Determination

The L2000 method detection limits for each of the chlorinated compounds were determined from replicate analysis using the method prescribed by the EPA<sup>9</sup>. An estimate of each of the detection limits was made using the concentration equivalent of three times the standard deviation of replicate measurements of the analytes in the composite soils. Soil was then spiked at the estimated detection limit. The spiking concentration for each of the chlorinated compounds are listed in Table 1 below:

**Table 1: MDL Soil Spiking Concentrations**

Analyte	Spiked Level	Percent Chlorine	Soil Chlorine Content
DDT	5 ppm	50.0	2.5 ppm
PCP	30 ppm	66.6	20 ppm
Toxaphene	5 ppm	~68	3.4 ppm
Chlordane	5 ppm	69.2	3.5 ppm
Trichloroethylene	16 ppm	81	13 ppm
Tetrachloroethylene	24 ppm	85.5	20.5 ppm

Each of the spiked soils were analyzed seven times using the standard extraction method, or the alternative solvent method in the case of the PCP contaminated soils. Seven matrix blanks were also analyzed using each method. The average blank measurements were subtracted from the respective sample measurements. The MDL was then computed using the following formula:

$$MDL = t_{(n-1, 1-\alpha=0.99)} * S$$

where: t = the students t value

S = the standard deviation of the replicate analyses

The student's t value for 6 degrees of freedom at a 99% confidence interval used was 3.143. The mean recovery for each analyte was calculated by dividing the measured concentration by the theoretical concentration of analyte.

### Response Curve Determination

In addition to the stock soil spiked at 100 ppm, standards were prepared in the composite soil at 2, 5, 10, 20, and 50 ppm of each of the chlorinated solvents and pesticides. Standards were analyzed on the L2000 using the standard extraction method, except for PCP which was analyzed using the alternative extraction method. A reagent blank was run with each analyte. These data were then compared to analysis by gas chromatography. The extraction for the DDT, PCP, chlordane and toxaphene samples to be measured by gas chromatography at the following concentrations: 2, 5, 10, 20, 50, and 100 ppm was performed by adding three 10 mL aliquots of 1:1 acetone-hexane solvent to 5 gram aliquots of each of the spiked semi-volatile soils while rinsing each soil with each addition. The solvent was then removed from the soil and run through a polypropylene filter into a 25 mL volumetric flask. The volume was filled to the mark with excess 1:1 acetone-hexane. The solvent was then transferred to another 25 mL glass test tube and capped with a teflon cap, then centrifuged to remove remaining soil particles, and prepared for gas chromatography analysis. The extraction method used for the soils spiked with volatile analytes, trichloroethylene and tetrachloroethylene, utilized 10 mL methanol mixed with 5 grams of soil at each of the concentrations 2, 5, 10, 20, 50 and 100 ppm. The methanol was then removed from the soil and the samples were then prepared for gas chromatography. The results were then analyzed and compared to the results obtained from the L-2000 analysis.

## RESULTS AND DISCUSSION

### Method Detection Limits

The MDLs calculated from the replicate analysis of spiked soils were within the recommended range for all analytes. (See Table 2 on page 4). The MDLs calculated for the non-polar compounds using the standard analysis method ranged from a low of 2.7 ppm for Chlordane to a high of 4.8 ppm for Trichloroethylene and 4.4 ppm for Tetrachloroethylene. The semi-volatile MDLs being all lower than the MDLs for the volatile compounds. A contributing factor to the higher

**Table 2: MDL Results**

Analyte	Spiked Level	Mean Recovery	Replicate Standard Deviation	Calculated MDL
DDT	5 ppm	54%	1.15 ppm	3.6 ppm
PCP	30 ppm	56%	2.8 ppm	8.7 ppm*
Toxaphene	5 ppm	37%	0.91 ppm	2.8 ppm
Chlordane	5 ppm	57%	0.85 ppm	2.7 ppm
Trichloroethylene	21 ppm	102%	1.54 ppm	4.8 ppm†
Tetrachloroethylene	23 ppm	110%	1.3 ppm	4.4 ppm†

\*Determined using the alternative extraction method.  
 †Determined using a direct spiking method.

MDLs for the two volatile compounds was the difficulty in preparing the spiked soils. This was not unexpected, given the difficulty of working with volatile compounds in the field.

The MDL of 8.7 ppm calculated for the analysis of PCP was higher than expected. This may have been due to low extraction efficiency of the new solvent system on polar compounds. A low extraction efficiency indicates that the combination solvent was not able to penetrate the soil matrix to completely solvate the more polar PCP. In this type of a situation the analyte recovery is very sensitive to the exact handling of each sample replicate. Small changes in the shaking of the extraction tube or the length of extraction will have a larger effect on the recovery than is acceptable.

While the new solvent system facilitated the analysis of polar compounds, this sensitivity to extraction conditions is not a desirable characteristic. It produces variable results in the field and it indicates that the extraction efficiency will vary excessively with soil matrix. A second generation two-step alternative solvent system has been developed<sup>8</sup> and will be the subject of the next phase of this project.

**Response Linearity**

For each of the analytes investigated, the response of the L2000 using either solvent system was found to

be linear over the range of concentrations studied. The resulting R<sup>2</sup> was greater than 0.96 for all analytes. (See Figures 1- 6). This indicates that the extraction efficiency is consistent over this analyte range. The results from the L2000 can, therefore, be corrected using the known recovery. There is no indication from this data that the range of linearity is limited to 100 ppm.

**Extraction Efficiency**

Data on the extraction efficiency of both solvent systems were obtained from the MDL determinations at a single point and from the response curve determination. The single point and the response curve determination of average extraction efficiency correlated well over the range 0-100 ppm.

**Table 3: Extraction Efficiency**

Analyte	MDL Mean Recovery	Average Recovery (from slope)
DDT	54%	52%
PCP	56%	39%
Toxaphene	37%	65%
Chlordane	57%	70%
Trichloroethylene	102%	112%
Tetrachloroethylene	110%	112%

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## Summary

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In this study it has been shown that the L2000 can be used effectively to analyze soil for chlorinated volatiles and semi-volatiles. The method detection limits were shown to be in the low ppm range. This should be adequate for most contaminated sites. The response has been shown to be linear over the range of concentrations studied and a good correlation with lab methods demonstrated. A new solvent system suitable for polar organic compounds was shown to be promising.

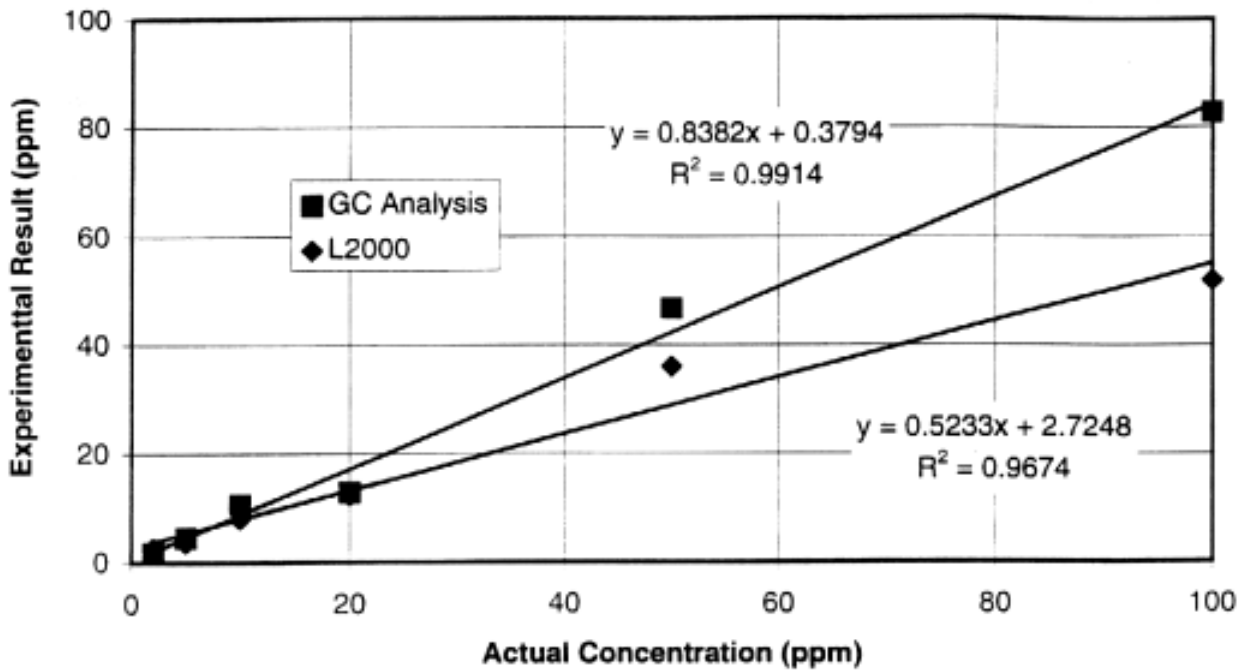
The effectiveness of a second generation two-step solvent system, demonstrated in a separate study, will be the subject of phase two of this project. Furthermore, the list of suitable chlorinated compounds will be expanded and the effectiveness of the new alternative solvent system on other chlorinated compounds will be investigated. The analyte concentration range will also be extended to 2000 ppm, the upper limit on the L2000's quantification range.

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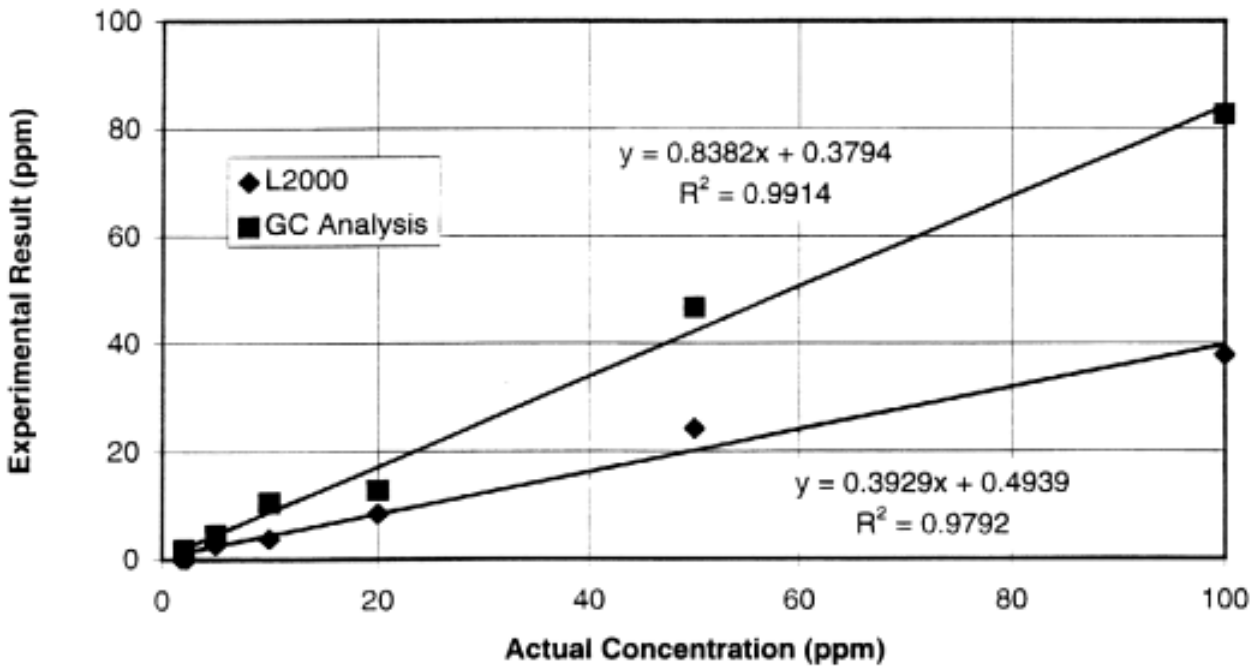
## REFERENCES

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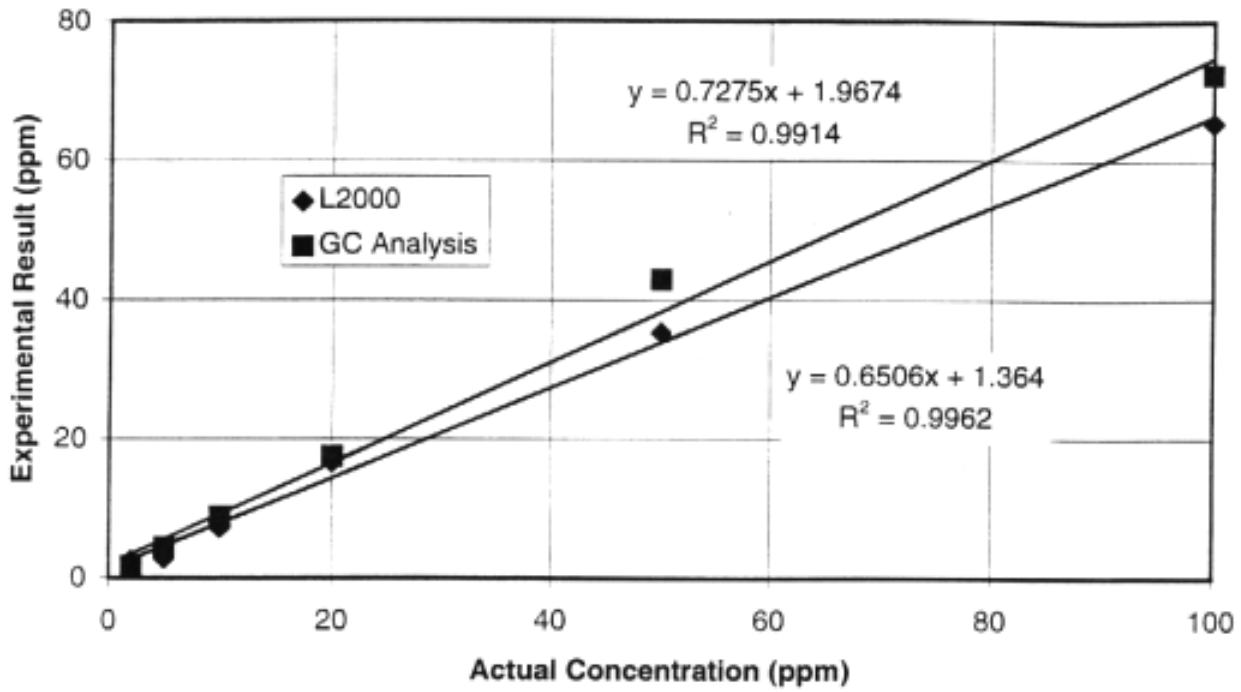
- 1 "Case Study of a New Field Screening Tool for Delineating Soil PCB Contamination", Mark B. Williams, PE and John S. Flickinger-Dames & Moore (Madison, WI), Joseph E. Shefchek, CHMM-Wisconsin Power & Light (Madison, WI), E. Jonathan Jackson, CHMM-Haliburton NUS Environmental Corp. (Aiken, SC); Proceedings: 1991 EPRI PCB Seminar.
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- 9 *Definition and Procedure for the Determination of the Method Detection Limit*, Environmental Protection Agency Publication, 40 CFR Ch.1 (7-1-89 Edition), Appendix B, part 136, 525-527.



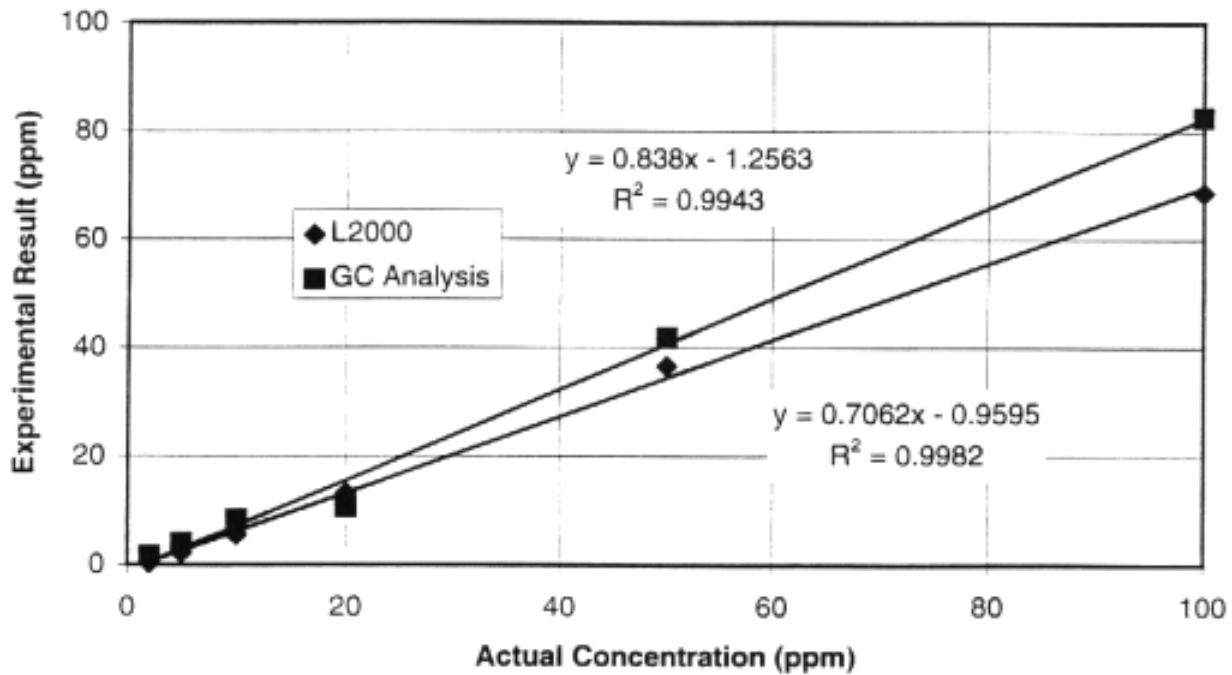
**Figure 1: Response Curve for DDT**



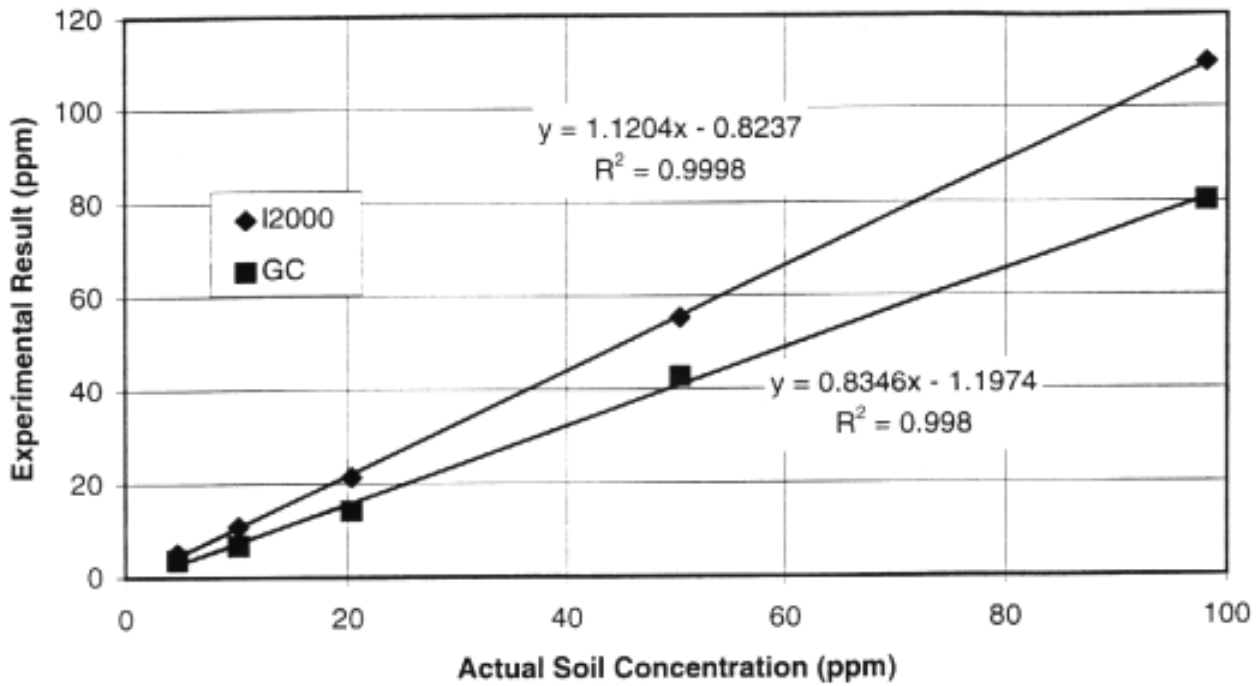
**Figure 2: Response Curve for PCP**



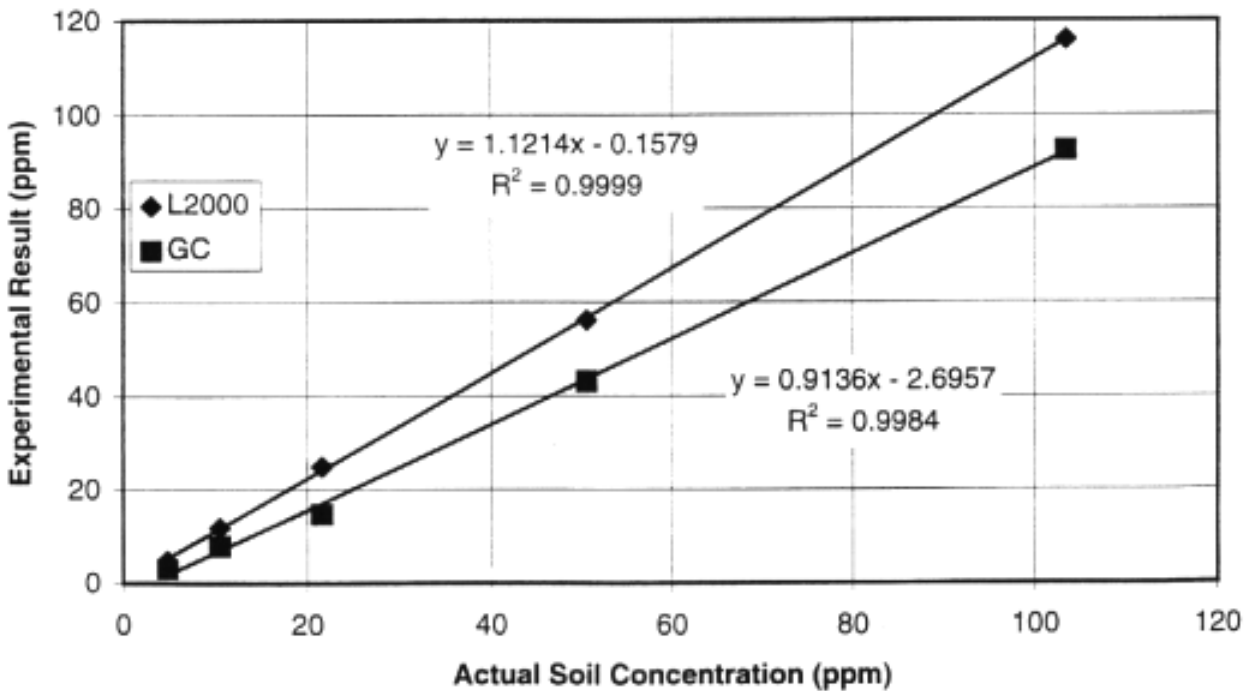
**Figure 3: Response Curve for Toxaphene**



**Figure 4: Response Curve for Chlordane**



**Figure 5: Response Curve for Trichloroethylene**



**Figure 6: Response Curve for Tetrachloroethylene**