Applications of a New PCB Field Analysis Technique For Site Assessment

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INTRODUCTION

The Toxic Substance Act as well as state and local regulations require the cleanup of PCB contaminated soils to levels less than 50 ppm. PCBs are a family of polychlorinated biphenyl compounds with widely varying physical and chemical properties. PCBs are also highly regulated substances associated with cancer in animals.

One of the key tasks in remediating contaminated property is to define the vertical and horizontal extent of contamination of that property. Once the depth and lateral extent of PCB contamination are known, it is possible to lay out a cost effective strategy for remediating the site. Rapid turnaround of analytical results at a reasonable cost is a benefit to all parties in the site assessment and mediation process.

In this assessment, approximately 200 contaminated soil samples were analyzed with the results available the same day. The samples were analyzed using a prepackaged test kit which reacted the PCBs in the soil with metallic sodium followed by extraction and analysis of the resulting chloride concentration. The chloride is proportional to the original PCBs in the individual soil samples.

On the property in question, a release of PCBs occurred a number of years ago which required cleanup. Of particular concern was the need for a complete delineation of the soil PCB concentrations. Figure 1 shows the levels of regulatory concern for PCBs in soils and the final cleanup level determined by the local agency for this site.

The site soils consist of dark silty sands. Laboratory testing of a soil sample obtained within the area of concern suggests a local surface permeability of 1.3 x 10^{-4} cm/sec, based on Hazen's formula.

PCB ANALYSIS OPTIONS

A review of the literature indicates that PCBs, while being highly regulated, have a range of interesting physical and chemical properties which lend themselves to certain techniques of assessment. The PCB grouping called Aroclor 1260 were the only PCBs found on the property. Aroclor 1260 is a mixture of hexa- and hepta-chlorinated biphenyls with an average chlorine content by weight of 60%.

Project Objective and Alternate Methods

For both spill cleanup and remediation, as well as selection of personal protective equipment, three tools are currently available for PCB concentrations in soils. Those include soil sampling with lab analysis at another location, or a screening level technique which gives onsite data via secondary measurements. These latter include 1) immuno-assay techniques and, 2) reaction of the PCB molecule to a free chloride condition using metallic sodium followed by measurement of the chloride concentration.

Ideally, whatever method is used to meet the objectives of either site assessment, personal protective equipment selection, or monitoring during remediation, the technique should be fast, relatively inexpensive, selective to PCBs, insensitive to interferences, and cover a wide range of concentration from less than 10 ppm to over 1,000 ppm.

Lab analyses (EPA method 8080) of soil samples are important as the reference method and provide quantification and specific identification of the PCB. The negative aspects, however, are that these methods tend to be expensive with fees ranging from $150 to $175 per sample. Also, a two-week turnaround time is "industry standard." If there are unexpected values or questions on the data, additional sampling efforts are required by field crews which greatly slows down the assessment and/or remediation. In addition, hazards and liability may be high for personnel with inadequate protective equipment.

Immuno-assay techniques are relatively new in the field and show promise for being able to identify PCBs and other chlorinated aromatic compounds in soils. There appear to be concerns, however, regarding the ability to analyze a wide range of concentrations with one set of reagents where the existing levels are unknown.

The field instrument technique uses a prepackaged test tube reaction. The governing reaction is given below.

PCB/Soil water solvent PCB . Na NaCl + Biphenyl water Cl_
(Eq. 1)
wash extraction reaction extraction

This technique involves weighing out a ten-gram sample of the contaminated soil, extracting it with a small quantity of solvent, and reacting it with a metallic sodium dispersion. This converts the PCBs into ionic chloride, which is then extracted into a water solution. Prepackaged ingredients eliminate any weighing after the initial sample.

The field instrument measures the equivalent PCB concentration using an ion-specific electrode. This technique was found to be highly correlated with EPA Method 8080. It operates on two ranges: a 0-100 ppm scale and a 100-2000 ppm scale. This was found to be an excellent survey tool for evaluating PCBs in soils down to approximately 4-8 ppm. Ion-specific analysis appeared to be the more appropriate choice for field assessment on this particular site.

FIELD TESTING PROGRAM

Following discovery of soil contamination at the site, the local regulatory agency required a characterization of the property. Grab samples indicated that the contaminants previously released at the site included lube oil, grease, and polychlorinated-biphenyls (PCBs). Interviews with the owner indicated that the lube oil and grease spills probably occurred within the past ten years when tractors, agricultural and road equipment were temporarily stored on the parcel. The visual surface contamination of oil and grease was removed by excavation and transport to a licensed TSDF early in the assessment process. The vertical and horizontal extent of PCB contamination was the final requirement. There were no visual indications, however, of PCB concentrations in the soils.

Sampling

Following acceptance of the site sampling plan, Griffin Environmental sampled for PCBs on a grid pattern with ten-foot by ten-foot cells covering the southeastern area of the parcel. EPA Method 8080 samples were taken at the center of each of the ten-foot by ten-foot cells for the agency's files. All EPA Method 8080 samples were labeled, sealed, placed in an ice chest and transferred to the analytical laboratory along with the chain of custody documentation. When arrival was too late in the day, the samples were stored in a refrigerator at 40 degrees Fahrenheit overnight. All of the laboratories were certified by the State of California Department of Health Services.

In addition to lab testing for PCBs using EPA Method 8080, this effort included the field sampling technique used by Griffin Environmental in which PCB concentrations were evaluated in the field by means of a field instrument, field extraction and analysis

In general, soil sampling methods consist of boring to depth by stainless steel hand auger, or taking a surface sample by scraping soil from a 4-inch by 3-inch area directly into the glass sampling jar. The jar was then sealed with a Teflon capped lid. The 10-gram field samples were transferred directly into the test tube using stainless steel scoops for analysis. The augers were decontaminated between samples and air dried.

Field samples were taken at five-foot intervals on the original grid spacing (assigned by columns running north to south, and rows running from west to east). This gives a better definition of the PCB concentrations at the surface. In addition, samples outside the grid were taken on ten-foot centers to give additional information regarding possible hot spots outside of the contamination zone.

Two of the sample cells, where elevated EPA Method 8080 concentrations were found, were re-analyzed. These analyses are shown in Table 2 as the second reading for cell 6 and cell 10 by both methods. This indicates the variability of the method for the same sample with analyses on different days. Cell 2 was also re-analyzed using just the field method.

Of particular concern was the vertical distribution of PCBs in the soil. Accordingly, PCB field analyses vs. depth were performed.

Method Assessment and Correlation

Since the field method is non-specific for organic chlorides, it is necessary that the background soil matrix be previously screened for the existence of other organic chlorine compounds. An analysis of the cell 6 and 10 sample extracts was performed for trichlorobenzene (TCB), a common contaminant associated with certain PCB spills. Lab analysis via EPA methods indicated that TCB was non-detectable in these high-concentration Aroclor 1260 samples. The other EPA Method 8080 analytes were non-detectable.

To correlate the field method with the standard EPA Method 8080 for PCBs, the cell soil samples were analyzed by both methods in order to increase the confidence in the field method. The manufacturer of the field instrument indicates that the lower limit of accuracy is in the 4-8 ppm range. The manufacturer of the field analysis kits was Dexsil Corporation.

Portions of soil from the same glass jar were taken for analysis by both methods. These data were subjected to a statistical analysis in order to evaluate the degree of correlation between the two methods on the same soil sample. The intent of this correlation was to be able to use a field method with a high degree of correlation to the EPA standard method for field assessment purposes. Final compliance with clean-up levels, of course, is found by using EPA Method 8080.

Checks for instrument linearity across the concentration range were performed and found valid. These included a millevolt vs. concentration static check and a dynamic serial dilution check.

A plot of the PCB concentrations above 5 ppm (manufacturer's lower operating range) by both analysis methods is seen in Figure 2. Where multiple analyses were performed on the same sample, an "error bar" is seen over the range of values. From the linear relationship seen, a standard "least squares" regression analysis was performed on the data set.

For repeat analyses of the same sample (i.e., Cell 6 at 300 and 375 ppm--EPA 8080) the values were arithmetically averaged to a maximum of three significant figures prior to the regression analysis. The relative percent differences (RPD) for each of the data points used prior to regression analysis are:

I.D.	Method	Analysis Values	Average	RPD %
Cell 6	EPA	300/375	338	12.7/12.7
	Field	357/326/327	337	5.9/3.3/3.0
Cell 10	EPA	106/134	120	11.7/11.7
	Field	116/117	116	0/0.9
Cell 2	Field	79/76	78	1.3/2.6

These were within the acceptable 30% relative percent difference ranges.

The correlation via least squares regression was found to be:

$$\text{EPA 8080 ppm} = 1.048 \text{ (field data)} - 1.48 \text{ ppm}$$

with the coefficient of correlation, r = 0.995 and standard error of the estimate, S = 8.43.

The high correlation between these methods indicated that the field test method is an excellent tool to use for onsite PCB data at the site.

RESULTS OF THE TESTING

Following the on-site sampling and analysis, Figure 3 was prepared, which shows the surface contours of PCB concentrations. For better definition 10, 50 and 500 ppm isopleths are shown. This would more closely approximate the potential remediation area in the contamination zone. For a 5 ppm contour at the surface, the area is extended by only two to three feet.

Soil borings to 24 inches were performed across an E/W and N/S axis over the contamination zone. From those borings and analyses, the PCB concentration is plotted in Figure 4 versus the depth in inches. This shows an exponential decay which is indicative of a soil adsorption phenomenon. This would be responsible for the apparent lack of mobility of PCBs in soil and the decrease of concentration by more than an order of magnitude (10x) in less than a foot of soil depth.

Based on soil sorption coefficients (K_{oc}) and octanol/water coefficients (K_{ow}), Chan and Griffin[1] classify soil mobility for PCBs as "immobile" if the KOC exceeds 5,000 and the

[1]Waid, *PCBs and the Environment, Vol1*, CRC Press, Boca Raton, Florida, 1986; pg. 115.

exceeds 6,000. The K_{OW} for Aroclor 1260 exceeds 349,000 and the K_{OW} exceeds 4,000,000. These data support that assessment.

The immobility of PCBs and the lack of water solubility is one positive benefit of dealing with PCBs in soils: that is, they are relatively immobile even after years of exposure to the environment

Contaminant Volume and Mass

The volumes of contaminated soil and the PCB mass were calculated from the isopleths of surface contamination and the diminishment of PCB concentration vs. depth.

The “hot spot” (> 500 ppm) and fringe soils down to 10 ppm consist of 3.1 pounds of PCBs in a volume of approximately 16 yd^3 (or 35,000 lbs.) of soil. To reach the final 5 ppm level, the field method was used to guide the remediation. Approximately 26 yd^3 of contaminated soil were ultimately removed.

CONCLUSIONS

Based upon this work in which over 40 EPA soil analyses were performed in conjunction with approximately 200 field measurements of PCBS, the following conclusions were drawn:

1. The PCB/sodium reaction/chloride analysis (the field method) is a fast technique for measuring PCB concentrations in soil down to approximately 5 ppm.
2. The method covers a linear range from approximately 5 ppm to over 400 ppm without change in test kits or sample sizes.
3. Using prepackaged ingredients, the field test method allows one to calculate the approximate PCB soil concentration in less than 15 minutes.
4. The field method allows an investigator to evaluate soil concentrations in order to determine personal protective equipment, and compliance with soil cleanup levels as well as delineating areas of very high (potentially incineratable) PCB concentration.
5. The cost per analysis is less than 25% of the reference laboratory analysis cost.
6. Provided that the type of PCB has been identified via EPA Method 8080 and other interfering chlorinated aromatic compounds are not present, the field method can be ideally suited for assessment and remediation efforts during actual cleanup operations.
7. The field method shows a very high correlation to the EPA Method 8080 analyses.

REFERENCES

1. Site Assessment and Mitigation Manual, County of San Diego HMMD, January 1991.

2. Finch, S.R., Lavigne, D.A.; and R.P.W. Scott, One Example Where Chromatography May Not Necessarily Be The Best Analytical Method, *The Journal of Chromatographic Science,*Volume 28, July 1990.

3. Lavigne, D.A., Accurate, Onsite Analysis of PCBs in Soil, A Low Cost Approach, Proceedings of the Superfund, '90 Conference, November 1990, Washington, D.C., pages 273-276.

4. Dexsil Corporation, L 2,000 PCB/Chloride Analyzer, Operating Instructions for the L 2000 PCB/Chloride Analyzer, Hamden, Connecticut, January 1991.

5. Personal communication with D.A. Lavigne, August 7, 1991.

Table 1
PCB - Aroclor 1260 Physical Data

Form	Light yellow, soft sticky resin
Specific Gravity	1.56 to 1.62
Distillation Range, ^{O}C	385 to 420
Average molecular weight	375.7
Water solubility, _g/L	2.7 to 25 (ppb)
Soil Sorption Constant, K_{OC}	349,462
Octanol/Water Coefficient, K_{OW}	4,073,800
Surface Vaporization Rate, gm/cm^{2}/hr (non-sorbed)	0.000009 (at 100^{0}C)

Table 3
PCB Analysis Methods Comparison EPA 8080 vs. Field Instrument*

Sample I.D./Cell No.	ppm, as Aroclor 1260 in Soil**	
	Lab Analyses	Field Analyses
Cell 2	83	79/76
Cell 4	21	22
Cell 5	12	14
Cell 6	300/375	357/326/327
Cell 7	29	27
Cell 10	106/134	116/117
Cell 12	3	7.6
Cell 14	9.3	7.2
Cell 15	1.5	5.2
Cell 2R	99	93
C3c	7/9	13
C7a	3.6	12
D8	4.2/6.2	2.9
L2	290	254/265

*For concentrations above 5 ppm.
**Second and subsequent numbers are repeat analyses of the same sample or solution.